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Statistical Physics of Fluids

Basic Concepts and Applications

With 52 Figures and 5 Tables



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To the memory of my mother

Preface

This book grew out of the senior level lecture course I teach at Delft University and which I have taught in recent years at Eindhoven University and the University of Utrecht. Numerous discussions with students and colleagues led me to the conclusion that in spite of the existence of excellent books on the statistical theory of fluids, there is a gap between the fundamental theory and application of its concepts and techniques to practical problems. This book is an attempt to at least partially fill it.

It is not intended to be a thorough and comprehensive review of liquid state theory, which would inevitably require invoking a large number of results without actual derivation. Rather I prefer to focus on the main physical ideas and mathematical methods of fluid theory, starting with the basic principles of statistical mechanics, and present a detailed derivation of results accompanied by an explanation of their physical meaning. The same approach applies to several specialized topics of the liquid state, most of which are recent developments and belong to the areas of my own activities and thus reflect my personal taste. Wherever possible, theoretical predictions are compared with available experimental and simulation data.

So, what you are holding in your hands is neither a textbook nor a monograph, but rather a combination of both. It can be classified as an advanced text for graduate students in physics and chemistry with research interests in the statistical physics of fluids, and as a monograph for a professional audience in various areas of soft condensed matter. It can also be used by industrial scientists for background information, and as an advanced text for self-study.

I gratefully acknowledge the assistance of my colleagues and friends at various stages of the work. Chap. 7 on Monte Carlo methods was written together with Iosif Dyadkin; his vision of the subject and extraordinary general physical intuition guided me for many years. Carlo Luijten placed at my disposal his computer programs for the density functional calculations of surface tension in one-component systems (Sect. 9.3) and binary mixtures (Sect. 13.4.1). I would like to express my gratitude to Jos Thijssen for his careful reading of the manuscript and for a number of very constructive criticisms.

VIII Preface

In creating the book I benefited greatly from discussions with a number of colleagues. In particular, Rini van Dongen, Bob Evans, Vladimir Filinov, Daan Frenkel, Ken Hamilton, Gert-Jan van Heijst, Jouke Heringa, Geert Hofmans, Simon de Leeuw, Henk Lekkerkerker, Christopher Lowe, Carlo Luijten, Thijs Michels, Bela Mulder, Piet Schram, Berend Smit, Vladimir Vorobiev, and Ben Widom made many helpful comments and suggestions.

Delft, April 2001

Vitaly Kalikmanov

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1. Ensembles in statistical mechanics

1.1 Notion of a phase space

The main aim of statistical physics is to establish the laws governing the behavior of macroscopic systems – i.e. systems containing a large number of particles – given the laws of behavior of individual particles. If a macroscopic system has s degrees of freedom, its state at each moment of time can be characterized by s generalized coordinates $q_1, \dots, q_s$ and s generalized momenta $p_1, \dots, p_s$ (in statistical physics p_i is used instead of velocities $\dot{q}_i$). For example, for a system containing N spherical particles in a 3-dimensional space, $s = 3N$. In principle, in order to study the behavior of this system, one could write down the mechanical equations of motion for each degree of freedom. We then would face the problem of solving $2s$ coupled differential equations. In Hamiltonian form they read

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}, \quad \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}, \quad i = 1, 2, \dots, s \quad (1.1)$$

where upper dot denotes time differentiation and $\mathcal{H}$ is the total energy (Hamiltonian) of the system:

$$\mathcal{H}(p, q) = \sum_{i=1}^s \frac{p_i^2}{2m} + U(q) \quad (1.2)$$

Here the first term is the kinetic energy of point-like particles of mass m , and $U(q)$ is the total interaction energy. To understand how large s can be, let us recall that one mole of gas contains $N_A = 6.02 \times 10^{23}$ molecules (N_A is Avogadro's number), so $s = 3N_A \sim 10^{24}$. Solving the system of 10^{24} equations is, of course, all but impossible. However, this unavoidable (at first sight) difficulty, resulting from the presence of an extremely large number of particles, gives rise to some special features of the behavior described by *statistical* laws. These cannot be reduced to pure mechanical ones. In other words, although the microscopic entities (particles) follow the usual mechanical laws, the presence of an extremely large number of them yields new qualitative features which disappear when the number of degrees of freedom becomes small. The principal features of these laws are to a large extent common to systems

obeying classical or quantum mechanics, but their derivation requires separate considerations for each of these cases; we shall focus on classical systems.

Each state of a system with s degrees of freedom can be characterized by a point in a *phase space* of dimensionality $2s$ with coordinates $p_1, \dots, p_s, q_1, \dots, q_s$; we shall denote it by (p, q) . As time goes on, the point in phase space forms a line called a *phase trajectory*. Let us assume that our system is closed, i.e. it does not interact with any other system. We can single out a small part (i.e. we choose a certain number of degrees of freedom out of s and the corresponding number of momenta) which still contains a large number of particles. This subsystem is no longer closed: it interacts with all other parts of the entire system. In view of the large number of degrees of freedom, these interactions will be rather complicated.

Let us look at what will happen to a small volume $\Delta p \Delta q$ of the phase space of the subsystem in the course of time. Due to the complex nature of interactions with the "external world," each such volume will be visited many times during a sufficiently large time interval t . If Δt is time the subsystem spends in the given volume $\Delta p \Delta q$, the quantity

$$\Delta w = \lim_{t \rightarrow \infty} \frac{\Delta t}{t}$$

characterizes the probability of finding the subsystem in a given part of the phase space at an arbitrary moment of time. At the same time a probability of finding the system in a small element of phase space

$$dp dq \equiv dp_1 \dots dp_s dq_1 \dots dq_s$$

around the point (p, q) can be written

$$dw = \rho(p, q) dp dq$$

where $\rho(p, q)$ is called a distribution function. It is normalized by requiring that

$$\int' \rho(p, q) dp dq = 1 \quad (1.3)$$

where the integral is taken over the phase space and the prime indicates that integration only involves physically different states (we shall clarify this point later).

These considerations reveal that the mathematical basis of statistical mechanics is probability theory. The latter, however, must be combined with the requirements of fundamental physical laws. An important question is: how small can an element $dp dq$ of the phase space be? The answer can be found by considering the semiclassical limit of quantum mechanics. According to the uncertainty principle, for each degree of freedom i

$$\Delta p_i \Delta q_i \sim 2\pi\hbar$$

where $\hbar = 1.05 \times 10^{-27}$ erg s is Planck's constant. It means that a cell in the phase space with the volume $(2\pi\hbar)^s$ corresponds to each quantum state¹ and therefore the partitioning of the phase space into small elements must satisfy $dpdq \geq (2\pi\hbar)^s$. The dimensionless quantity

$$d\Gamma = \frac{dpdq}{(2\pi\hbar)^s} \geq 1 \quad (1.4)$$

is the number of quantum states inside the domain $dpdq$ (see Fig. 1.1).

An important feature of $\rho(p, q)$ is that for a given subsystem it does not depend on the initial state of any other subsystem, or even on its own initial state in view of the large number of degrees of freedom. This means that it has no memory. Hence we can find the distribution function of a (macroscopically) small subsystem (which is at the same time microscopically large) without solving the mechanical problem for the whole system. If $\rho(p, q)$ is known, the average value of an arbitrary physical quantity $X(p, q)$ is

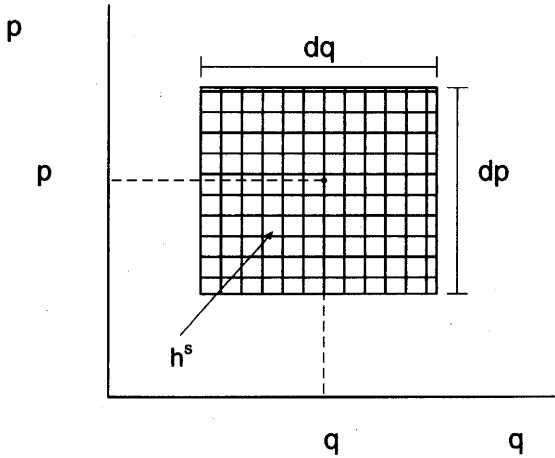


Fig. 1.1. Phase space of a system with s degrees of freedom. The volume of an elementary cell is $h^s = (2\pi\hbar)^s$. The number of quantum states inside the domain $dpdq$ about a point (p, q) is $dpdq/(2\pi\hbar)^s$

$$\overline{X} = \int' X(p, q) \rho(p, q) dp dq$$

According to our considerations, statistical averaging is equivalent to temporal averaging, i.e. we can also write

¹ In other words, states within a cell of volume $(2\pi\hbar)^s$ cannot be distinguished quantum mechanically.

$$\bar{X} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t X(t') dt'$$

This statement constitutes the so called ergodicity hypothesis. The equivalence of temporal averaging and phase space averaging, while sounding reasonable, is not trivial. Although in the general case it is difficult to establish rigorously whether a given system is ergodic or not, it is believed that ergodicity holds for all many-body systems encountered in nature.

It is important to understand that the probabilistic nature of the results of classical statistical mechanics does not reflect the nature of the physical systems under study (as opposed to quantum mechanical systems), but is a consequence of the fact that they are obtained from a very small subset of the data required for a full mechanical description. This probabilistic feature does not yield serious difficulties: if we observe a system for a long enough period of time (longer than its relaxation time), we will find that macroscopic physical quantities are essentially equal to their average values. This situation corresponds to *statistical* (or *thermodynamic*) *equilibrium*. Thus, an arbitrary physical quantity $X(p, q)$ will almost always be equal to $\bar{X}$ to within some small deviation. In terms of probability distributions this means that the probability distribution of X is sharply peaked at $X = \bar{X}$, and differs from zero only in a small neighborhood of $\bar{X}$. In this book we will be interested in equilibrium. Processes of relaxation to equilibrium are studied in physical kinetics (see e.g. [93]).

The subsystem that we have singled out is not closed; it interacts with the rest of the system. However, taking into account that the subsystem contains a very large number of particles, the effect of these interactions in terms of energy will be small compared to the bulk internal energy. In other words, they produce surface effects that vanish at large system sizes. That is why we can consider the subsystem to be quasi-closed for moderate periods of time (i.e. less than the relaxation time). For long times this concept is not valid: interactions between subsystems become important and actually drive the entire system to the equilibrium state. The fact that parts of the entire system interact weakly with one another means that the state of a given subsystem has no influence on the states of others, i.e. we can speak of a statistical independence. In the language of probability theory this statement can be written in terms of probability distributions:

$$\rho_{ab}(q_a, q_b, p_a, p_b) = \rho_a(q_a, p_a) \cdot \rho_b(q_b, p_b)$$

where the density distribution ρ_{ab} refers to the system composed of subsystems a and b , their distribution functions being ρ_a and ρ_b , respectively. This statement can be also presented as

$$\ln \rho_{ab} = \ln \rho_a + \ln \rho_b \quad (1.5)$$

showing that $\ln \rho$ is an additive quantity.

1.2 Statistical ensemble and Liouville's theorem

Having studied some general properties of subsystems, let us return to the entire closed system and assume that we observe it over a long period of time which we can divide into small (in fact, infinitely small) intervals given by $t_1, t_2, \dots$. Then the system will evolve to form a trajectory in phase space passing through some points $A_1, A_2, \dots$ (see Fig 1.2). Some of the domains in phase space will be visited more frequently and others less.

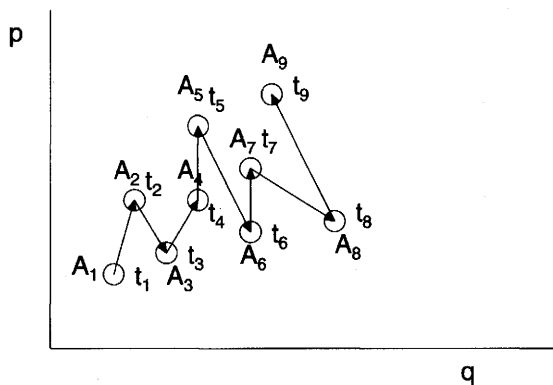


Fig. 1.2. Phase trajectory of a subsystem

This set of points is distributed with density proportional to $\rho(p, q)$. Instead of following in phase space the position of the *given* system at various moments of time, we can consider a large (in fact, infinitely large) number of totally identical copies of the system characterized by $A_1, A_2, \dots$ at some given moment of time (say, $t = 0$). This imaginary set of identical systems is called a *statistical ensemble*. Since the system (and each of its identical copies) is closed, the movement of points in phase space is governed by mechanical equations of motion containing only its own coordinates and momenta. Therefore the movement of points corresponding to the statistical ensemble in phase space can be viewed as the flow of a “gas” with density ρ in a 2s-dimensional space (see Fig. 1.3). The continuity equation (conservation of mass) for this gas reads

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \mathbf{v}) = 0$$

and for a stationary flow ($\partial \rho / \partial t = 0$)

$$\text{div}(\rho \mathbf{v}) = 0$$

Here the velocity $\mathbf{v}$ is the 2s-dimensional vector $\mathbf{v} = (\dot{p}_1, \dots, \dot{p}_s, \dot{q}_1, \dots, \dot{q}_s)$. Using the identity $\text{div}(\rho \mathbf{v}) = \rho \text{div} \mathbf{v} + \mathbf{v} \nabla \rho$ we obtain

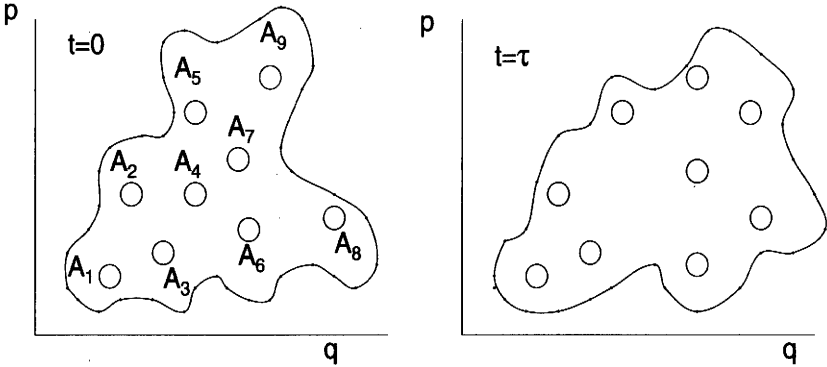


Fig. 1.3. Statistical ensemble

$$\rho \sum_{i=1}^s \left\{ \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right\} + \sum_{i=1}^s \left[\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right] = 0 \quad (1.6)$$

Hamilton's equations (1.1) yield

$$\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0$$

implying that each term in curly brackets in (1.6) vanishes, resulting in

$$\sum_{i=1}^s \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i = 0 \quad (1.7)$$

The left-hand side is the total time derivative of ρ . We have derived Liouville's theorem, stating that the distribution function is constant along the phase trajectories of the system:

$$\frac{d\rho}{dt} = 0 \quad (1.8)$$

One can also formulate it in terms of conservation of phase-space volume. Note that Liouville's theorem is also valid for a subsystem over not very long periods of time, during which it can be considered closed.

1.3 Microcanonical ensemble

From the additivity of the logarithm of the distribution function and Liouville's theorem, we can conclude that $\ln \rho$ is an additive integral (constant) of motion. As known from classical mechanics [79], there are only seven independent additive integrals of motion, originating from three fundamental laws of nature:

- homogeneity of time, yielding conservation of energy E
- homogeneity of space, yielding conservation of the three components of the total momentum $\mathbf{P}$
- isotropy of space, yielding conservation of the three components of the total angular momentum $\mathbf{M}$

Any other additive integral of motion must therefore be an additive combination of these quantities. Applying these considerations to a subsystem a with total energy E_a , total momentum $\mathbf{P}_a$, and total angular momentum $\mathbf{M}_a$, we state that $\ln \rho_a$ can be written

$$\ln \rho_a = \alpha_a + \lambda E_a(p, q) + \gamma \mathbf{P}_a + \delta \mathbf{M}_a \quad (1.9)$$

with some constant coefficients α_a , λ , γ , δ . The coefficient α_a can be found from the normalization of ρ_a :

$$\int' \rho_a dp^{(a)} dq^{(a)} = 1$$

The remaining seven coefficients λ , γ , δ are the same for every subsystem. We conclude, and this is the key feature of statistical mechanics, that a knowledge of additive integrals of motion makes it possible to calculate the distribution function of any subsystem and therefore the average values of any physical quantity. These seven integrals of motion replace an enormous amount of information (initial conditions) required for the solution of the full mechanical problem.

Now one can propose the simplest form of the distribution function satisfying the Liouville theorem: it must be constant for all phase points with given values of energy E_0 , momentum $\mathbf{P}_0$, and angular momentum $\mathbf{M}_0$, and must be normalized:

$$\rho = \text{const } \delta(E - E_0) \delta(\mathbf{P} - \mathbf{P}_0) \delta(\mathbf{M} - \mathbf{M}_0) \quad (1.10)$$

This is the so-called microcanonical distribution. Momentum and angular momentum describe the translational and rotational motion of the system as a whole. The state of a system in motion with some $\mathbf{P}$ and $\mathbf{M}$ is thus determined solely by its total energy. This is why energy plays the most important role in statistical physics.

We can exclude $\mathbf{P}$ and $\mathbf{M}$ from consideration if we imagine that the system is located in a box inside which there is no macroscopic motion. If we use a coordinate system rigidly attached to the box, then the only remaining additive integral of motion will be the total energy, and (1.10) takes a simple form:

$$\rho = \text{const } \delta(E(p, q) - E_0) \quad (1.11)$$

The microcanonical distribution requires that for an isolated system with a fixed total energy E_0 and size (characterized by the number of particles N_0

and volume V_0), all microscopic states with total energy E_0 are equally likely. Using the same considerations, the logarithm of a distribution function of a subsystem (1.9) can be rewritten in a simpler form:

$$\ln \rho_a = \alpha_a + \lambda E_a(p^{(a)}, q^{(a)}) \quad (1.12)$$

1.3.1 Entropy

Let us consider a subsystem a and denote its distribution function by $\rho_a(p_a, q_a)$. The subsystem has its own phase space with s degrees of freedom (we retain the same notation for this quantity as for the entire system). Since each point of phase space corresponds to a certain energy E_a , we can consider ρ_a to be a function of E_a and write the normalization condition (1.3) as

$$\int' (2\pi\hbar)^s \rho_a(E_a) d\Gamma_a = 1 \quad (1.13)$$

If we consider Γ_a to be equal to the number of microscopic states with energies less than E_a , then²

$$d\Gamma_a = \frac{d\Gamma_a}{dE_a} dE_a$$

is the number of states with energies between E_a and $E_a + dE_a$. Then the normalization condition (1.13) reads

$$\int' \left[(2\pi\hbar)^s \rho_a(E_a) \frac{d\Gamma_a}{dE_a} dE_a \right] dE_a = 1 \quad (1.14)$$

Since ρ_a is sharply peaked at $E_a = \overline{E}_a$, we replace the integrand by its value at $\overline{E}_a$, thereby defining the quantity ΔE_a :

$$\Delta E_a(\overline{E}_a) \equiv \frac{1}{(2\pi\hbar)^s \rho_a(\overline{E}_a) \left. \frac{d\Gamma_a}{dE_a} \right|_{\overline{E}_a}} \quad (1.15)$$

which characterizes the mean energy fluctuation (Fig. 1.4). The quantity

$$\Delta\Gamma_a(\overline{E}_a) \equiv \left. \frac{d\Gamma_a}{dE_a} \right|_{\overline{E}_a} \Delta E_a(\overline{E}_a) = \frac{1}{(2\pi\hbar)^s \rho_a(\overline{E}_a)} \quad (1.16)$$

describes the degree of smearing of the given macroscopic state. In other words, $\Delta\Gamma_a$, which is called the statistical weight of the macroscopic state of the system, gives the number of ways (microscopic states) to “create” the

² Note that while $\rho(E)$ is δ -function of energy (i.e. fluctuations of the total energy of an isolated system are prohibited), $\rho_a(E_a)$ is not: the energy of a subsystem fluctuates about the average value $\overline{E}_a$.

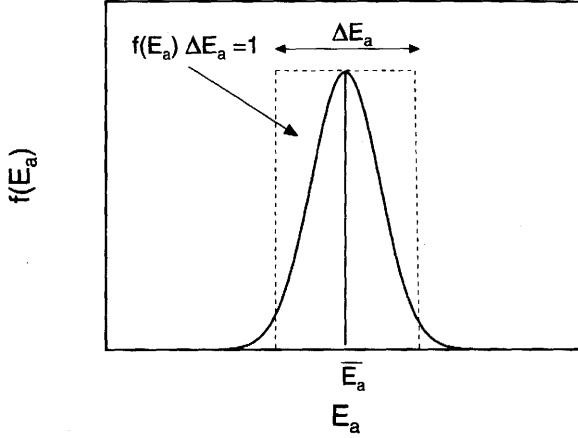


Fig. 1.4. Definition of the mean energy fluctuation ΔE_a ; here $f(E_a) = (2\pi\hbar)^s \rho_a(E_a) \frac{d\Gamma_a}{dE_a}$

given macroscopic state with energy $\overline{E_a}$. One can also say that $\Delta p \Delta q = \Delta \Gamma_a (2\pi\hbar)^s$ is the volume of phase space in which the subsystem a spends most of its time. The quantity proportional to the logarithm of $\Delta \Gamma_a$ is called the *entropy* of the subsystem:

$$S_a = k_B \ln \Delta \Gamma_a \quad (1.17)$$

where

$$k_B = 1.38 \times 10^{-16} \text{ erg/K}$$

is the Boltzmann constant.

Entropy is the second key quantity in statistical mechanics. We stress that S_a is a state parameter, i.e. it is determined by the state $\overline{E_a}$ of the subsystem. Since the number of states $\Delta \Gamma \geq 1$, the entropy is nonnegative. Combining (1.16) and (1.17) we find

$$S_a = -k_B \ln [(2\pi\hbar)^s \rho_a(\overline{E_a})]$$

Let us express S_a in terms of the distribution function using the linear dependence of $\ln \rho_a$ on E_a . Substituting the mean energy into (1.12), we have

$$\ln \rho_a(\overline{E_a}) = \alpha_a + \lambda \overline{E_a} = \overline{\ln \rho_a(E_a)}$$

which yields for the entropy

$$S_a = -k_B \overline{\ln [(2\pi\hbar)^s \rho_a]} = -k_B \int' \rho_a \ln [(2\pi\hbar)^s \rho_a] dp_a dq_a \quad (1.18)$$

Since each subsystem can be in one of its $\Delta\Gamma_a$ microscopic states, for the entire system, which can be represented as a collection of subsystems, the total number of microscopic states is

$$\Delta\Gamma = \prod_a \Delta\Gamma_a$$

and the entropy reads

$$S = \sum_a S_a \quad (1.19)$$

S is thus an extensive property: the entropy of the entire system is a sum of entropies of its subsystems.

To study the properties of the entropy let us return to the microcanonical distribution (1.11):

$$dw = \rho dp dq = \text{const } \delta(E - E_0) \prod_a d\Gamma_a \quad (1.20)$$

Treating as previously $d\Gamma_a$ as a differential of the function $\Gamma_a(E_a)$, we can write

$$dw = \text{const } \delta(E - E_0) \prod_a \frac{d\Gamma_a}{dE_a} dE_a$$

We defined in (1.16) the statistical weight $\Delta\Gamma_a$ as a function of the mean energy $\overline{E}_a$. Let us formally extend this definition and consider $\Delta\Gamma_a$ and S_a as functions of the actual value of the energy E_a (so we assume the same functional form to be valid for all E_a , not just for the mean value). Then using (1.16) we write

$$\frac{d\Gamma_a}{dE_a} = \frac{\Delta\Gamma_a}{\Delta E_a} \quad (1.21)$$

and using the definition of entropy we obtain

$$dw = \text{const } \delta(E - E_0) e^{S/k_B} \prod_a \frac{1}{\Delta E_a} dE_a \quad (1.22)$$

where

$$S = \sum_a S_a(E_a)$$

is the entropy of the entire closed system treated as a function of the actual values (not necessarily averages!) of the subsystems' energies. The strong dependence of e^S on the energies E_a makes it possible to neglect the variation of $\prod_a \Delta E_a$ with E_a , so to high accuracy we can absorb it into the constant factor and write (1.22) as

$$dw = \text{const } \delta(E - E_0) e^{S/k_B} \prod_a dE_a \quad (1.23)$$

Equation (1.23) describes the probability of subsystems having energies in the interval $(E_a, E_a + dE_a)$. It is fully determined by the total entropy, while the δ -function ensures total energy conservation.

The main postulate of statistical physics states that the most probable statistical distribution corresponds to the state of thermodynamic equilibrium. The most probable values of E_a are their mean values $\overline{E_a}$. Hence for $E_a = \overline{E_a}$ the function $S(E_1, E_2, \dots)$ should have its maximum (at the given $\sum_a E_a = E_0$). At the same time the latter situation corresponds to statistical equilibrium. Thus, the entropy of a closed system at equilibrium attains its maximal value (for the given total energy E_0). We can formulate this statement in another way: during the evolution of a closed system its entropy increases monotonically, reaching maximum at equilibrium. This is one of the possible formulations of the *second law of thermodynamics*, discovered by Clausius and developed by Boltzmann in his famous *H*-theorem.

The total entropy is an additive quantity. Moreover if we partition the system into small subsystems, the entropy of any subsystem a depends on its own energy E_a and not on the energies of other parts of the system. Maximizing

$$S = \sum_a S_a(E_a)$$

under the condition that $\sum_a E_a = E_0$ (using Lagrange multipliers) we obtain

$$\frac{dS_1}{dE_1} = \frac{dS_2}{dE_2} = \dots$$

In equilibrium the derivative of entropy with respect to energy is thus equal for all parts of the system. Its reciprocal is called the *absolute temperature* T :

$$\frac{dS}{dE} \equiv \frac{1}{T} \quad (1.24)$$

Thus, in equilibrium the absolute temperature is constant throughout the system.

1.4 Canonical ensemble

The microcanonical distribution describes a system that is completely isolated from the environment. In the majority of experimental situations we are dealing with small (but macroscopic) parts of a closed system in thermal contact with the environment, with the possibility of exchange of energy and/or particles. Our aim in this and the next section will be to derive a

distribution function for this small subsystem (which we will also call a *body*. The canonical, or NVT , ensemble is a collection of N identical particles contained in a volume V at a temperature T in thermal contact with the environment providing the constant temperature T . In general, an external field U_{ext} (gravitational, electromagnetic, etc.) can be also present.

We begin with some simple illustrations. Each particle is characterized by a 6-dimensional vector $(\mathbf{r}_i, \mathbf{p}_i)$, where $\mathbf{r}_i$ is the radius vector of its center of mass and $\mathbf{p}_i$ is its momentum; the number of degrees of freedom is therefore $s = 3N$. The state of the body is characterized by a point $(\mathbf{r}^N, \mathbf{p}^N)$ in the $6N$ -dimensional phase space, where $\mathbf{r}^N \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N)$, $\mathbf{p}^N \equiv (\mathbf{p}_1, \dots, \mathbf{p}_N)$. The total energy of the body

$$E = \mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + U_N(\mathbf{r}_1, \dots, \mathbf{r}_N) + U_{N,\text{ext}}(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (1.25)$$

The first term is the kinetic energy of the pointlike particles of mass m . The second term is the total interaction energy

$$U_N(\mathbf{r}^N) = \sum_{i < j} u(\mathbf{r}_i, \mathbf{r}_j) + \left[\sum_{i < j < k} u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \right] \quad (1.26)$$

which involves pairwise interactions, and probably triplet or higher-order interactions. The last contribution in (1.25)

$$U_{N,\text{ext}} = \sum_{i=1}^N u_{\text{ext}}(\mathbf{r}_i)$$

is the energy of the system in an external field with a one-body external potential $u_{\text{ext}}(\mathbf{r}_i)$. Simple examples of a *pairwise* interaction energy $u(\mathbf{r}_i, \mathbf{r}_j)$ are

- the Lennard–Jones (LJ) potential (see Fig. 1.5)

$$u_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1.27)$$

Here r is the separation between two particles, ϵ is the depth of the interaction, and σ is the molecular diameter. The first term represents a short-range repulsion while the second describes long-range van der Waals attractions due to dispersion forces. The spatial dependence $\sim 1/r^6$ of the attractive tail originates from the interaction between induced dipoles and results from second-order quantum mechanical perturbation theory [21]. The power $\sim 1/r^{12}$ of the repulsive term is to a large extent arbitrary. The intermolecular distance corresponding to the depth (minimum) of the

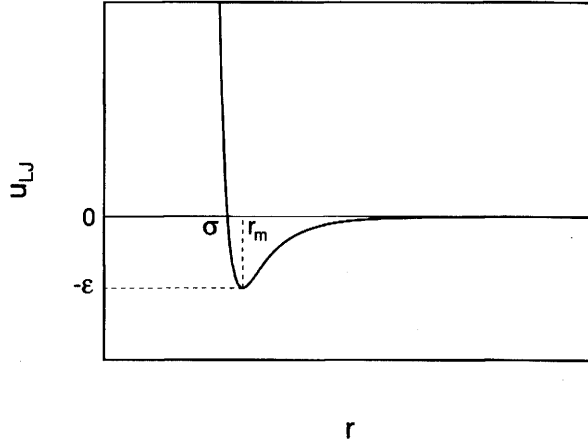


Fig. 1.5. Lennard-Jones potential; ϵ is the depth of the interaction and σ the molecular diameter

potential is $r_m = 2^{1/6}\sigma$. The Lennard-Jones potential describes interactions in simple fluids, e.g. rare gases or small nonpolar molecules like the noble gases argon, krypton, xenon. Typical values of the Lennard-Jones parameters are:

$$\sigma_{Ar} = 3.405 \text{ \AA}, \epsilon_{Ar}/k_B = 119.8 \text{ K},$$

$$\sigma_{Kr} = 3.630 \text{ \AA}, \epsilon_{Kr}/k_B = 163.1 \text{ K}.$$

- EXP-6 potential

$$u_{\text{EXP-6}}(r) = \frac{\epsilon}{\alpha - 6} \left\{ 6 \exp \left[\alpha \left(1 - \frac{r}{r_m} \right) \right] - \alpha \left(\frac{r_m}{r} \right)^6 \right\}$$

is an example of a three-parameter (ϵ, r_m, α) pairwise potential. Here the repulsive term contains a stiffness parameter α ; at r_m the potential attains its minimum value: $u_{\text{EXP-6}}(r_m) = -\epsilon$.

An example of a three-particle interaction energy is the Axilrod-Teller potential [6]–[7]:

$$u_3 = \nu \frac{1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3}{r_{13}^3 r_{12}^3 r_{23}^3},$$

where r_{ij} is separation between particles i and j ($i, j = 1, 2, 3$), and ν characterizes the strength of the interaction (and depends on the dipole oscillator strength); θ_i are the angles of the triangle formed by the three particles. It is obvious that only compact triplets contribute to u_3 .³

³ More complex interactions can include anisotropic terms, e.g. dipole-dipole interactions. In this case the N -particle subsystem will have more than $3N$ degrees of freedom. But the general form of distribution functions remains the same.

To derive the distribution function for the body, which contains N particles, we will consider it to be a (macroscopically) small part of the closed system with energy

$$E_{\text{tot}} = E + E'$$

where E is the energy of the body and E' is the energy of the environment (heat bath); the latter is much larger than the body. The microcanonical distribution for the closed system body + heat bath reads

$$dw_{\text{tot}} = \text{const } \delta(E + E' - E_0) d\Gamma d\Gamma'$$

The desired distribution for the body can be found if we integrate this expression over the phase space of the heat bath:

$$dw = \int_{\Gamma'} dw_{\text{tot}} \equiv \rho d\Gamma$$

with

$$\rho(\mathbf{r}^N, \mathbf{p}^N) = \text{const} \int \delta(E + E' - E_0) d\Gamma'$$

Introducing the entropy of the heat bath $S' = S'(E')$ and using (1.17) and (1.21), we replace $d\Gamma'$ with

$$\frac{e^{S'/k_B}}{\Delta E'} dE'$$

to obtain

$$\rho = \text{const} \int \frac{e^{S'/k_B}}{\Delta E'} \delta[E' - (E_0 - E)] dE'$$

The presence of the δ -function implies that in the integrand one must replace E' with $E_0 - E$:

$$\rho = \text{const} \left(\frac{e^{S'/k_B}}{\Delta E'} \right)_{E'=E_0-E} \quad (1.28)$$

Since the body is small compared to the entire system, $\Delta E'$ varies slowly with E , so that it can be absorbed into the unknown constant in front of this expression:

$$\rho = \text{const} \left(e^{S'/k_B} \right)_{E'=E_0-E} \quad (1.29)$$

For the entropy term (since it is in the exponential) we expand in powers of E ($E \ll E_0$):

$$S'(E_0 - E) = S'(E_0) - E \left. \frac{\partial S'}{\partial E'} \right|_{E'=E_0} + \text{h.o.t.}$$

where “h.o.t.” stands for higher-order terms. Using the definition of temperature (1.24) and the fact that T is the same for the body and the environment we rewrite this as

$$S'(E_0 - E) = S'(E_0) - \frac{E}{T} \quad (1.30)$$

Here we keep the term linear in E ; the second-order term of the expansion is

$$\frac{1}{2} E^2 \left. \frac{\partial^2 S'}{\partial E'^2} \right|_{E'=E_0} = \frac{1}{2} E^2 \frac{\partial}{\partial E'} \left(\frac{1}{T} \right) = -\frac{1}{2T^2} E^2 \frac{\partial T}{\partial E'} \quad (1.31)$$

The ratio of the two successive terms is

$$\frac{E}{2T} \frac{\partial T}{\partial E'} = \frac{\frac{E}{2T}}{\frac{\partial E'}{\partial T}}$$

The quantity $\frac{\partial E'}{\partial T}$ tends to infinity as the heat bath grows, implying that (1.31) tends to zero and supporting the neglect of h.o.t. in (1.30). Combining (1.29) and (1.30) we obtain the Gibbs (canonical) distribution function:

$$\rho = A e^{-\frac{E}{k_B T}} \equiv A e^{-\beta \mathcal{H}} \quad (1.32)$$

where

$$\beta = \frac{1}{k_B T}$$

and A is a constant to be determined. The Hamiltonian is a sum of the momentum part, which depends only on $\mathbf{p}^N$, and the potential part, which depends only on positions $\mathbf{r}^N$. Therefore ρ is a product of two distribution functions

$$\rho(\mathbf{r}^N, \mathbf{p}^N) = a e^{-\beta K(\mathbf{p}^N)} \cdot b e^{-\beta U(\mathbf{r}^N)}$$

with normalization constants a and b .

The kinetic energy of the whole body is a sum of the kinetic energies of its particles. According to the Gibbs formula, the momentum of one particle has no influence on the momenta of others, and we can write the momentum distribution for a single particle:

$$dw_p = a_0 e^{-\frac{p^2}{2mk_B T}} d\mathbf{p}$$

The normalization constant satisfies

$$a_0 \int e^{-\frac{p^2}{2mk_B T}} d\mathbf{p} = a_0 \left[\int_{-\infty}^{+\infty} e^{-\frac{p^2}{2mk_B T}} dp \right]^3 = 1$$

The integral is of the Gaussian type, and using the identity

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}, \quad \alpha > 0 \quad (1.33)$$

we obtain: $a_0 = (2\pi m k_B T)^{-3/2}$. The final result is

$$dw_p = \frac{1}{(2\pi m k_B T)^{3/2}} e^{-\frac{p_x^2 + p_y^2 + p_z^2}{2m k_B T}} dp_x dp_y dp_z \quad (1.34)$$

This in turn is a product of distribution functions for p_x, p_y, p_z . In terms of velocities this function is called the Maxwell velocity distribution:

$$dw_v = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}} dv_x dv_y dv_z \quad (1.35)$$

Thus, the velocity along each of the directions has the Gaussian form

$$dw_{v_x} = \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{m v_x^2}{2k_B T}} dv_x$$

with zero mean and standard deviation

$$\overline{v_x^2} = \frac{k_B T}{m}$$

Hence, each degree of freedom contributes $k_B T/2$ to the total kinetic energy of the body; this statement is known as the equipartition theorem.

Let us now return to the general form of the Gibbs distribution and find the physical meaning of the normalization constant A . Substituting the Gibbs distribution into Eq. (1.18) for the entropy of the body we obtain

$$S = -k_B \overline{\ln[(2\pi\hbar)^s \rho]} = -k_B \ln[(2\pi\hbar)^s A] + \frac{\overline{E}}{T}$$

where $\overline{E}$ is the mean energy, the quantity we are dealing with in thermodynamics. Then

$$k_B T \ln[(2\pi\hbar)^s A] = \overline{E} - TS \equiv \mathcal{F}$$

where $\mathcal{F}$ is the Helmholtz free energy. Hence,

$$A = (2\pi\hbar)^{-s} e^{\beta \mathcal{F}} \quad (1.36)$$

and the Gibbs distribution becomes

$$\rho = (2\pi\hbar)^{-s} e^{\beta \mathcal{F}} e^{-\beta \mathcal{H}} \quad (1.37)$$

Our last step is the normalization condition for ρ :

$$\int' \rho d\mathbf{r}^N d\mathbf{p}^N = 1 \quad (1.38)$$

As stated earlier, $\int'$ denotes integration over all physically different states. In other words we have to count each microstate only once. One has to take into account that particles are indistinguishable and therefore a change in their labels does not result in a physically different state. The number of permutations of N particles is $N!$. The prime on the integral can be thus omitted and integration can be performed over the full phase space of the body if we introduce the multiplier $\frac{1}{N!}$.

From (1.37)–(1.38) we obtain

$$\mathcal{F}(N, V, T) = -k_B T \ln Z_N \quad (1.39)$$

where

$$Z_N(N, V, T) = \frac{1}{N!} \int e^{-\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)} d\Gamma_N \quad (1.40)$$

is called the *canonical partition function*. A simple observation shows that the right-hand side is a sum of the Boltzmann factors $e^{-\beta \mathcal{H}}$ over all possible microscopic states.⁴ These two expressions form the basis for derivation of various thermodynamic properties. The probability for a body to stay in phase-space element $d\mathbf{r}^N d\mathbf{p}^N$ about the point $(\mathbf{r}^N, \mathbf{p}^N)$ is

$$dw = \frac{1}{Z_N} e^{-\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)} d\Gamma_N \quad (1.41)$$

We can single out the momentum and configurational contribution to Z_N . Integration over momenta in (1.40) results in $3N$ Gaussian integrals (cf. Maxwell distribution):

$$Z_N = \frac{1}{N! \Lambda^{3N}} Q_N, \quad (1.42)$$

where

$$\Lambda = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2} \quad (1.43)$$

is the thermal de Broglie wavelength of a particle and

$$Q_N = \int \exp[-\beta(U_N + U_{N,\text{ext}})] d\mathbf{r}^N \quad (1.44)$$

⁴ In quantum statistical mechanics, in view of the uncertainty principle, it is not possible to follow the trajectory of every identical particle and therefore to distinguish (enumerate) them. In other words, identical particles totally lose their individuality. Therefore, the partition function of a quantum system contains no prefactor: $Z = \sum_n e^{-\beta E_n}$, where summation is over all different quantum states n with the energy E_n .

is called a *configuration integral* since integration in (1.44) is over the configuration space of dimensionality $3N$. Using Stirling's formula

$$\ln N! = \ln 1 + \ln 2 + \dots + \ln N \simeq \int_1^N \ln x \, dx = N \ln(N/e), \quad N \gg 1 \quad (1.45)$$

we rewrite the free energy as

$$\mathcal{F} = -k_B T \ln Q_N + N k_B T \ln(N \Lambda^3/e) \quad (1.46)$$

The first term gives a configurational contribution, whereas the second is the momentum part. Once $\mathcal{F}$ is known, various thermodynamic properties can be found by straightforward differentiation using the thermodynamic relationship (note that $\mathcal{F} = E - TS$ is an example of the Legendre transformation discussed in Sect. 1.4.1)

$$d\mathcal{F} = -S \, dT - p \, dV + \mu \, dN \quad (1.47)$$

where p is the pressure⁵ and μ the chemical potential. Recall some results:

- pressure

$$p = - \left(\frac{\partial \mathcal{F}}{\partial V} \right)_{T,N} \quad (1.48)$$

- entropy

$$S = - \left(\frac{\partial \mathcal{F}}{\partial T} \right)_{V,N} \quad (1.49)$$

- chemical potential

$$\mu = \left(\frac{\partial \mathcal{F}}{\partial N} \right)_{V,T} \quad (1.50)$$

For the vast majority of realistic problems calculation of the configuration integral meets with serious difficulties and cannot be done exactly due to interparticle interactions. In the absence of interactions we have ideal gas. In the absence of external fields its configuration integral is simply $Q_{N,\text{ideal}} = V^N$ and the free energy is

$$\mathcal{F}_{\text{ideal}} = N k_B T \ln(\rho^{(1)} \Lambda^3/e) \quad (1.51)$$

where $\rho^{(1)} = N/V$ is the number density. From this expression, using (1.48), we deduce the pressure

$$p_{\text{ideal}} = \rho^{(1)} k_B T \quad (1.52)$$

⁵ We use for the pressure the same notation as for the momentum; this must not cause confusion, since momenta enter thermodynamics only via the de Broglie wavelength Λ .

This expression is the equation of state of an ideal gas. Separation of the momentum and configurational part in the Gibbs distribution results in the configurational probability

$$dw_r(\mathbf{r}^N) = D_N(\mathbf{r}^N) d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (1.53)$$

where

$$D_N(\mathbf{r}^N) = \frac{1}{Q_N} e^{-\beta U(\mathbf{r}^N)} \quad (1.54)$$

is the configurational Gibbs distribution function with the normalization

$$\int D_N(\mathbf{r}^N) d\mathbf{r}^N = 1$$

The average value of an arbitrary physical quantity that depends only on particle coordinates, $X(\mathbf{r}^N)$, can be obtained by integration over the configuration space:

$$\langle X(\mathbf{r}^N) \rangle = \int X(\mathbf{r}^N) D_N(\mathbf{r}^N) d\mathbf{r}^N \quad (1.55)$$

To distinguish between different ensembles we denote canonical averages by means of angular brackets and grand canonical averages, discussed in the next section, by an overbar).

1.4.1 Legendre transformations

According to the first law of thermodynamics,

$$dE = T dS - p dV + \mu dN \quad (1.56)$$

which means that the internal energy E is a function of its natural variables N, V, S . Other thermodynamic functions depend on their own natural variables. What are the relationships between these functions? This knowledge can be useful for analyzing experimental data presented in a form most appropriate for particular conditions. These relationships can be obtained using a simple mathematical method called Legendre transformation. Let $f(x_1, \dots, x_n)$ be a natural function of $x_1, \dots, x_n$. Then

$$df = \sum_{i=1}^n u_i dx_i, \quad \text{where } u_i \equiv \frac{\partial f}{\partial x_i} \quad (1.57)$$

The quantity u_i is called conjugate to the variable x_i . Let us introduce a function

$$g = f - \sum_{i=r+1}^n u_i x_i \quad (1.58)$$

and take its total differential:

$$dg = df - \sum_{i=r+1}^n (u_i dx_i + x_i du_i)$$

Using (1.57) we have

$$dg = \sum_{i=1}^r u_i dx_i + \sum_{i=r+1}^n (-x_i) du_i \quad (1.59)$$

Thus, g is a natural function of $x_1, \dots, x_r$ and the variables conjugate to $x_{r+1}, \dots, x_n$:

$$g = g(x_1, \dots, x_r, u_{r+1}, \dots, u_n)$$

The function g is called a *Legendre transform* of f . It replaces a group of natural arguments of f by their conjugate variables. Let us discuss several examples. The Helmholtz free energy $\mathcal{F}(N, V, T)$ is the Legendre transform of the internal energy $E(N, V, S)$; it substitutes the conjugate variables $S \rightarrow T$. According to (1.58) the function of natural variables N, V, T is $E - TS$, which is just $\mathcal{F}$. Other possible Legendre transforms are

$$G(N, p, T) = E - TS - (-pV) = E - TS + pV \quad (1.60)$$

which is the *Gibbs energy*, and is most useful in studies of phase transitions (see Sect. 6),

$$H(N, p, S) = E - (-pV) = E + pV \quad (1.61)$$

which is the *enthalpy*, and

$$\Omega(\mu, V, T) = \mathcal{F} - \mu N \quad (1.62)$$

which is the *grand potential*. Their differentials are

$$dG = -S dT + V dp + \mu dN \quad (1.63)$$

$$dH = T dS + V dp + \mu dN \quad (1.64)$$

$$d\Omega = -S dT - p dV - \bar{N} d\mu \quad (1.65)$$

where $\bar{N}$ is the average number of particles.

The Legendre transformation allows us to interchange a thermodynamic variable *only* with its conjugate. Exchanges between nonconjugate pairs are prohibited. Thermodynamic quantities $\mathcal{F}$, E , S , G are extensive quantities, which implies that they are homogeneous functions of the first order with respect to the additive (extensive) variables. By definition, a function f is homogeneous of order l in variables $x_1, \dots, x_n$ if for all α

$$f(\alpha x_1, \dots, \alpha x_n) = \alpha^l f(x_1, \dots, x_n)$$

It is straightforward to verify Euler's theorem for homogeneous functions: if f is a homogeneous function of order l , then

$$\sum_{i=1}^n x_i \frac{\partial f}{\partial x_i} = l f(x_1, \dots, x_n) \quad (1.66)$$

The Gibbs energy depends on only one extensive variable, N , and two intensive variables p and T ; Euler's theorem combined with (1.63) yields

$$G = \mu N \quad (1.67)$$

Taking the differential $dG = \mu dN + N d\mu$ and comparing it with (1.63), we obtain the Gibbs–Duhem equation

$$S dT - V dp + N d\mu = 0 \quad (1.68)$$

The grand potential depends on only one extensive variable V , and Euler's theorem yields

$$\Omega = -pV \quad (1.69)$$

1.5 Grand canonical ensemble

A physical body described by the canonical ensemble does not have a fixed energy – it can exchange energy with the environment – but it does have a fixed number of particles. In a number of physical problems one has to deal with a body which can exchange both energy and particles with the environment. In this case the description based on the canonical ensemble becomes less useful. The grand canonical ensemble describes such an open subsystem specified by the fixed values of the chemical potential μ , volume V , and temperature T ; the number of particles and the energy are allowed to fluctuate.

To obtain a corresponding distribution function we take an approach similar to that for the canonical distribution; additionally we have to take variations of N into account. Starting with the microcanonical distribution for the entire closed system consisting of our body, which contains N particles and has energy E_N , and the environment (heat bath) with $N_0 - N$ particles and energy $E_0 - E_N$, we obtain according to (1.28)

$$\rho^{(N)} = \text{const} \cdot \exp [S'(E_0 - E_N, N_0 - N)/k_B] \quad (1.70)$$

but now with the entropy of the environment S' , which depends not only on the energy E' but also on the number of particles $N' = N_0 - N$ in it. By writing the superscript (N) in the notation for the distribution function

we emphasize that each value of N corresponds to its own phase space, with dimensionality $2s = 6N$.

Expanding the entropy in powers of E_N and N and keeping linear terms only, we have

$$S'(E_0 - E_N, N_0 - N) = S'(E_0, N_0) - E_N \left. \frac{\partial S'}{\partial E'} \right|_{E'=E_0} - N \left. \frac{\partial S'}{\partial N'} \right|_{N'=N_0}$$

Equation (1.56) can be represented as a total differential of the entropy:

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN \quad (1.71)$$

The temperature and chemical potential are the same for the body and the environment in equilibrium conditions (see Sect. 6). We identify

$$\left. \frac{\partial S}{\partial E} \right|_{V,N} = \frac{1}{T}, \quad \left. \frac{\partial S}{\partial N} \right|_{E,V} = -\frac{\mu}{T}$$

For the distribution function we obtain

$$\rho^{(N)} = A e^{\beta(\mu N - E_N)} \quad (1.72)$$

To determine A we calculate the entropy from (1.18):

$$S = -k_B \overline{\ln[(2\pi\hbar)^s \rho^{(N)}]} = -k_B \overline{\ln[(2\pi\hbar)^s A]} - \frac{\mu \overline{N}}{T} + \frac{\overline{E}}{T}$$

which yields

$$k_B T \overline{\ln[(2\pi\hbar)^s A]} = \overline{E} - TS - \mu \overline{N}$$

The expression on the right-hand side is the grand potential of the body, Ω . Thus,

$$A = (2\pi\hbar)^{-s} e^{\beta\Omega} \quad (1.73)$$

while the distribution becomes

$$\rho^{(N)} = (2\pi\hbar)^{-s} e^{\beta\Omega} \lambda^N e^{-\beta E_N} \quad (1.74)$$

where we have introduced the *activity*

$$\lambda = e^{\beta\mu} \quad (1.75)$$

The final step is the normalization condition for $\rho^{(N)}$. Since N can vary, normalization includes not only integration over the phase space of the N -particle system, but also summation over all possible N , i.e.

$$\sum_{N \geq 0} \int' \rho^{(N)} d\mathbf{r}^N d\mathbf{p}^N = 1 \quad (1.76)$$

Substituting (1.74) into (1.76), we obtain

$$\Omega(\mu, V, T) = -k_B T \ln \Xi \quad (1.77)$$

where

$$\Xi = \sum_{N \geq 0} \lambda^N Z_N \quad (1.78)$$

is called the *grand partition function*. Here Z_N is the canonical partition function for the system of N particles. The grand potential is thus related to the grand partition function in the same way as the Helmholtz free energy is related to the canonical partition function. Thermodynamics in the grand ensemble follows from the relationship

$$\Omega = -pV = -k_B T \ln \Xi \quad (1.79)$$

Once Ω is known, one can find various thermodynamic properties using the expression for its total differential (1.65):

- pressure

$$p = - \left(\frac{\partial \Omega}{\partial V} \right)_{T, \mu} \quad (1.80)$$

- entropy

$$S = - \left(\frac{\partial \Omega}{\partial T} \right)_{V, \mu} \quad (1.81)$$

- average number of particles

$$\bar{N} = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{V, T} \quad (1.82)$$

Equation (1.78) means that the probability that the body contains exactly N particles is

$$P_N = \frac{1}{\Xi} \lambda^N Z_N, \quad \sum_{N \geq 0} P_N = 1 \quad (1.83)$$

It is easy to see how to calculate the average of an arbitrary quantity $X(\mathbf{r}^N)$ in the grand ensemble. First, for arbitrary N the canonical average in the (N, V, T) ensemble should be found:

$$\langle X \rangle_N = \int X(\mathbf{r}^N) D_N d\mathbf{r}^N$$

This then should be averaged over N using the probability distribution P_N :

$$\bar{X} = \sum_{N \geq 0} \langle X \rangle_N P_N \quad (1.84)$$

Using (1.83) and (1.42) we can express it as:

$$\bar{X} = \sum_{N \geq 0} \frac{(\lambda/\Lambda^3)^N}{N!} \int d\mathbf{r}^N X(\mathbf{r}^N) \frac{e^{-\beta(U_N + U_{N,\text{ext}})}}{\Xi} \quad (1.85)$$

Let us use these results to derive some important thermodynamic properties. For the average number of particles we have

$$\bar{N} = \sum_{N \geq 0} N \frac{\lambda^N Z_N}{\Xi} = \left(\frac{\partial \ln \Xi}{\partial \ln \lambda} \right)_{V,T} \quad (1.86)$$

which can be easily checked by differentiation of (1.78). It is not surprising that the final result coincides with the thermodynamic relationship (1.82). Using the same technique one can obtain the variation of $\bar{N}$ with respect to a change in chemical potential:

$$k_B T \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{V,T} = \overline{N^2} - (\bar{N})^2 \quad (1.87)$$

It is worth noting (and we shall make use of it later on) that this variation gives the mean square fluctuation of the number of particles. Note also that the choice of a particular statistical ensemble for a given problem is a matter of mathematical convenience. In most cases the microcanonical distribution is difficult to use. The canonical and grand canonical distributions prove to be much more convenient. The latter is especially preferred when the system under study is inhomogeneous.

1.5.1 Barometric formula

An example of a simple inhomogeneous system for which calculations in the grand ensemble prove to be most convenient is the ideal gas in an external field: $U_N \equiv 0$, $U_{N,\text{ext}} = \sum_{i=1}^N u_{\text{ext}}(\mathbf{r}_i)$. Particles are independent and the configuration integral can be written in product form:

$$Z_N = \frac{1}{\Lambda^{3N} N!} \left[\int e^{-\beta u_{\text{ext}}(\mathbf{r})} d\mathbf{r} \right]^N = \frac{1}{N!} \left[\frac{1}{\Lambda^3} \int e^{-\beta u_{\text{ext}}(\mathbf{r})} d\mathbf{r} \right]^N$$

The grand partition function then reads:

$$\Xi = \sum_{N \geq 0} \frac{a^N}{N!} \equiv e^a, \quad \text{with } a = \frac{\lambda}{\Lambda^3} \int e^{-\beta u_{\text{ext}}(\mathbf{r})} d\mathbf{r}$$

For the average number of particles we obtain from (1.86)

$$\bar{N} = \frac{\partial a}{\partial(\ln \lambda)} = \int \frac{\lambda}{\Lambda^3} e^{-\beta u_{\text{ext}}(\mathbf{r})} d\mathbf{r}$$

On the other hand, by the very definition of the number density, its integral over the physical volume gives the number of particles:

$$\bar{N} = \int d\mathbf{r} \rho^{(1)}(\mathbf{r})$$

Comparing these two expressions we obtain the Boltzmann barometric formula

$$\rho^{(1)}(\mathbf{r}) = \rho_0 e^{-\beta u_{\text{ext}}(\mathbf{r})} \quad (1.88)$$

with $\rho_0 = \frac{\lambda}{\Lambda^3} = \rho^{(1)}(u_{\text{ext}} = 0)$. For an ideal gas the density is proportional to the pressure, so we can write it as

$$p = p_0 e^{-\beta u_{\text{ext}}(\mathbf{r})} \quad (1.89)$$

The origin of u_{ext} can be quite arbitrary, so the result we have obtained is of quite general validity. Let us discuss the case when u_{ext} is the gravitational field. Near the Earth's surface the potential energy of a molecule with mass m at height z is $u_{\text{ext}} = mgz$, where $g = 9.8 \times 10^2 \text{ cm/s}^2$ is the acceleration of gravity. If the temperature is considered to be constant (independent of z) then the pressure at height z will be related to the pressure at the Earth's surface p_0 by

$$p(z) = p_0 e^{-mgz/k_B T} \quad (1.90)$$

The same formula can be applied to a mixture of ideal gases for the partial pressure of each species. The higher the molecular weight of a gas, the faster the exponential decay of its partial pressure with altitude. One can see it by studying the function

$$\frac{\rho^{(1)}(z)}{\rho_0} = e^{-mgz/k_B T}$$

for different gases. It is convenient to introduce the molecular weight M of a species by multiplying the numerator and denominator of the exponent by Avogadro's number:

$$\frac{\rho^{(1)}(z)}{\rho_0} = e^{-z/z^*}$$

Here

$$z^* = \frac{RT}{Mg}$$

is a characteristic altitude for density decay, $R = k_B N_A = 8.3 \times 10^7$ erg/K/mole is the gas constant. For $T = 273$ K the characteristic decay length for oxygen is (see Fig. 1.6)

$$z_{O_2}^* = \frac{RT}{M_{O_2}g} \approx 7.2 \text{ km}$$

(that is why it is difficult to breath high in the mountains) whereas the same quantity for hydrogen is more than an order of magnitude larger

$$z_{H_2}^* = \frac{RT}{M_{H_2}g} \approx 115 \text{ km}$$

As a result, at large z the atmosphere is enriched in light gases.

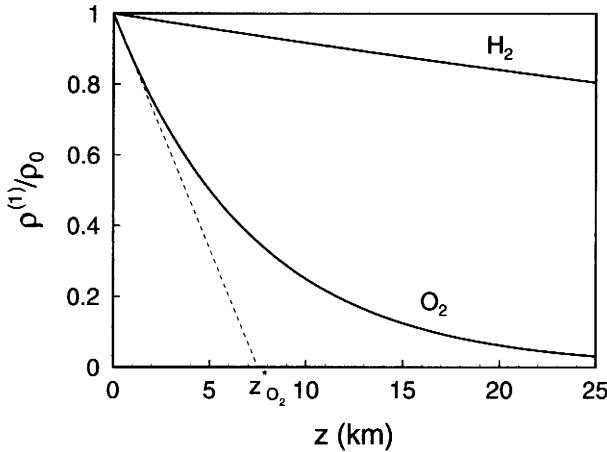


Fig. 1.6. Illustration of the barometric formula. Characteristic decay length for oxygen is $z_{O_2}^* \approx 7.2$ km, and for hydrogen $z_{H_2}^* \approx 115$ km

However, the applicability of the barometric formula to the atmosphere is rather limited because the latter in fact is *not* an isothermal system: its temperature changes (decreases) with altitude. Let us consider predictions of the barometric formula for the atmosphere at an arbitrary distance from Earth. The simple expression $u_{\text{ext}} = mgz$ must be replaced by the general form of Newton's gravitational law:

$$u_{\text{ext}}(r) = -G \frac{M_E m}{r}$$

where $M_E = 5.98 \times 10^{27}$ g is the mass of the Earth, $G = 6.67 \times 10^{-8}$ cm³/g/s² the gravitational constant, and r the distance from the center of the Earth. Then the gas density becomes

$$\rho^{(1)} = \rho_{\infty} e^{GM_E m / k_B T r}$$

where ρ_{∞} is the density at infinity (where $u_{\text{ext}} = 0$). From this formula we can find the relationship between ρ_{∞} and the density at the surface of the Earth ($R_E = 6.37 \times 10^8$ cm is its radius):

$$\rho_{\infty} = \rho^{(1)}(R_E) e^{-GM_E m / k_B T R_E} \quad (1.91)$$

According to (1.91) the density of the atmosphere infinitely far from Earth must be finite. This is of course impossible, since the finite amount of gas cannot be distributed inside the infinitely large volume with a nonvanishing density. We obtained this erroneous result because the atmosphere was considered to be in thermal equilibrium, which is not true. However, this result shows that the gravitational field is not able to keep the gas in thermal equilibrium, and the atmosphere should ultimately diffuse into space. For Earth this process is extremely slow, and during its lifetime Earth has not lost an appreciable amount of its atmosphere. For the Moon the process is significantly faster because its gravitational field is many times weaker, so the Moon now has no atmosphere. One can reach the same conclusions by recalling the Maxwell distribution, according to which there is always a nonzero probability that molecules attain velocities higher than the escape velocity $v_e = \sqrt{2gR_E}$ which is necessary to leave the atmosphere; for Earth $v_e = 11.2$ km/s.

Finally, we point out that the barometric formula has a spectrum of other applications, e.g. it describes the sedimentation profile of colloidal particles dispersed in a solvent contained in a closed domain.

2. Method of correlation functions

In Chap. 1 we derived the distribution function for a closed system (micro-canonical ensemble), which is very rarely used in practical calculations but is of great fundamental importance, serving as a starting point for derivation of distribution functions of small (but macroscopic) subsystems corresponding to the canonical and grand canonical ensemble. But the latter are still difficult (in fact virtually impossible) to calculate for realistic interactions. In this chapter we study an effective approximate technique that makes it feasible to describe distribution functions of small groups containing n particles ($n = 1, 2, 3, \dots$), the so called *n-particle distribution functions* and *n-particle correlation functions*. With the help of this technique we will be able to construct the route from a statistical mechanical description to thermodynamics. For most problems the knowledge of just the first two distribution functions (i.e. $n = 1$ and $n = 2$) is sufficient; sometimes (albeit rarely) it is necessary to also know the ternary ($n = 3$) distribution function. In Chap. 8 we present an efficient approximate technique to derive n -particle distribution functions. Here we introduce definitions and obtain some important general results. Since the momentum and configurational parts of the partition function are separable, we focus on distribution functions in configuration space (the momentum part is given by the Maxwell distribution). We present derivations in the canonical ensemble; similar results can be obtained for the grand ensemble.

2.1 n -particle distribution function

The configurational probability resulting from the Gibbs distribution

$$dw_r(\mathbf{r}^N) = D_N(\mathbf{r}^N) d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad D_N(\mathbf{r}^N) \equiv \frac{1}{Q_N} e^{-\beta U(\mathbf{r}^N)} \quad (2.1)$$

describes the distribution of *all* particles of the body in configuration space. Let us select a group of n particles out of N (n can be any integer between 1 and N), denoting their positions by $\mathbf{r}_1, \dots, \mathbf{r}_n$. By integrating $dw_r(\mathbf{r}^N)$ over the positions of the remaining $N - n$ particles we find the probability for

the particles $1, \dots, n$ to be near $\mathbf{r}_1, \dots, \mathbf{r}_n$ irrespective of positions of the remaining particles:

$$dw_r^{(n)}(\mathbf{r}^n) = d\mathbf{r}_1 \dots d\mathbf{r}_n \left[\int D_N(\mathbf{r}^N) d\mathbf{r}_{n+1} \dots d\mathbf{r}_N \right]$$

The function $dw_r^{(n)}(\mathbf{r}^n)$ describes the probability of finding “labeled” particles. If we are interested in the presence of one particle, *regardless* of its label at position $\mathbf{r}_1$ (there are N such particles to choose from), another at $\mathbf{r}_2$ (there are $N - 1$ such particles), and so on up to n , then this probability, denoted by

$$\rho^{(n)}(\mathbf{r}^n) d\mathbf{r}^n$$

will be $N(N - 1) \dots (N - n + 1)$ times the value of $dw_r^{(n)}$:

$$\rho^{(n)}(\mathbf{r}^n) d\mathbf{r}^n = N(N - 1) \dots (N - n + 1) dw_r^{(n)}$$

Using (2.1) we obtain

$$\rho^{(n)}(\mathbf{r}^n) = \frac{N!}{(N - n)!} \int D_N(\mathbf{r}^N) d\mathbf{r}_{n+1} \dots d\mathbf{r}_N \quad (2.2)$$

A function $\rho^{(n)}(\mathbf{r}^n)$ is called an *n-particle distribution function*. Its normalization condition is

$$\int \rho^{(n)}(\mathbf{r}^n) d\mathbf{r}^n = \frac{N!}{(N - n)!} \quad (2.3)$$

It is important to point out that there is an implicit dependence of $\rho^{(n)}$ on density and temperature. One can say that $\rho^{(n)}$ are generalized densities with dimensionalities of V^{-n} . A singlet (one-particle) distribution function represents the number density. From (2.3)

$$\int \rho^{(1)}(\mathbf{r}) d\mathbf{r} = N \quad (2.4)$$

(for a homogeneous system $\rho^{(1)}$ is simply N/V). For $n = N$ we obtain

$$\rho^{(N)} = D_N N!$$

where $N!$ is the number of ways to label N particles.

2.2 Calculation of thermal averages

A knowledge of $\rho^{(n)}$ permits the calculation of average values of quantities of the type

$$X_n(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{1 \leq i_1 < i_2 < \dots < i_n \leq N} f(\mathbf{r}_{i_1}, \dots, \mathbf{r}_{i_n}) \quad (2.5)$$

(where the summation is over all ordered permutations of n particles) without reverting to the Gibbs distribution. We have

$$\langle X_n \rangle = \sum_{1 \leq i_1 < \dots < i_n \leq N} \langle f(\mathbf{r}_{i_1}, \dots, \mathbf{r}_{i_n}) \rangle = \frac{N!}{n!(N-n)!} \langle f(\mathbf{r}_1, \dots, \mathbf{r}_n) \rangle$$

Using the averaging procedure we can rewrite this as

$$\langle X_n \rangle = \frac{N!}{n!(N-n)!} \int f(\mathbf{r}_1, \dots, \mathbf{r}_n) D_N d\mathbf{r}_1 \dots d\mathbf{r}_N$$

Integration over particles $n+1, n+2, \dots, N$ and using (2.2), we obtain

$$\langle X_n \rangle = \frac{1}{n!} \int f(\mathbf{r}^n) \rho^{(n)}(\mathbf{r}^n) d\mathbf{r}^n \quad (2.6)$$

This result will be referred to as the *theorem of averaging*. Many of the most important quantities in statistical physics are additive functions of a single particle coordinate, X_1 , or functions of the coordinates of two particles, X_2 . The total external field energy

$$U_{N,\text{ext}}(\mathbf{r}^N) = \sum_{i=1}^N u_{\text{ext}}(\mathbf{r}_i)$$

is an example of X_1 . The total energy of pairwise interactions

$$U_N(\mathbf{r}^N) = \sum_{1 \leq i < j \leq N} u(\mathbf{r}_i, \mathbf{r}_j)$$

is an example of X_2 . For $n=1$ and $n=2$ the theorem of averaging reduces to

$$\langle X_1 \rangle = \int f(\mathbf{r}) \rho^{(1)}(\mathbf{r}) d\mathbf{r} \quad (2.7)$$

$$\langle X_2 \rangle = \frac{1}{2} \int f(\mathbf{r}_1, \mathbf{r}_2) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.8)$$

2.3 n -particle correlation function

A useful quantity in statistical mechanics (especially for homogeneous systems) is the n -particle correlation function defined by

$$g_n(\mathbf{r}^n) = \frac{\rho^{(n)}(\mathbf{r}^n)}{\rho^{(1)}(\mathbf{r}_1) \cdots \rho^{(1)}(\mathbf{r}_n)} \quad (2.9)$$

g_n are dimensionless functions that remain finite when $V \rightarrow \infty$. For all n , they are symmetric functions of their arguments, e.g. $g_2(\mathbf{r}_1, \mathbf{r}_2) = g_2(\mathbf{r}_2, \mathbf{r}_1)$. Obviously that $g_1 \equiv 1$; for noninteracting particles this identity holds for all n . The implicit dependence of g_n on density and temperature is very important, especially for liquids and solids.

For homogeneous systems the relationship between $\rho^{(n)}$ and g_n becomes particularly simple:

$$\rho^{(n)}(\mathbf{r}^n) = \rho^n g_n(\mathbf{r}^n) \quad (2.10)$$

where $\rho \equiv \rho^{(1)} = N/V$. A pair correlation function, usually denoted simply as g , depends in this case only on the separation between molecules (and not on the positions themselves):

$$g(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|) \equiv g(r_{12})$$

An important observation is that

$$\begin{aligned} \rho g(r) &= \text{average density of particles at } r, \\ &\text{given that a tagged particle is at the origin} \end{aligned} \quad (2.11)$$

Let us illustrate these properties. A typical behavior of $g(r)$ is shown in Fig. 2.1. It demonstrates essential structural differences between the gaseous, liquid, and solid states.

An ideal gas has no structure, since the pair potential is zero everywhere; this implies $g(r) \equiv 1$. For a dilute gas $g(r)$ has one peak at r_m corresponding to the minimum of the pair potential. Well beyond r_m , the likelihood of finding another molecule is no greater than that given by the bulk density ρ . Thus, in a real gas there exists a shell of nearest neighbors.

The liquid state corresponds to the intermediate situation between the crystalline solid and the gas. Liquid possesses short-range order which means that $g(r)$ has several peaks, indicating the presence of first-, second-, and probably third neighbor shells, but for large separations $g(r) \rightarrow 1$. In speaking of a fluid, one is dealing with a *relative* arrangements of atoms and molecules, rather than absolute arrangements like those found in solids. Typical liquid densities (far from the critical point) are $\rho\sigma^3 \sim 1$, where σ is a molecular diameter. Since a liquid is dense, there is a high probability that a first-neighbor shell is located at $r \approx \sigma$ (see Fig. 2.2). A second shell is located around $r \approx 2\sigma$. This short-range order derives from the corpuscular nature of the liquid. Due to excluded volume effects in the regions between consecutive neighbor shells, the presence of molecules there is unlikely (e.g. around $r = 3/2\sigma$), so $g(r)$ there is less than unity. Oscillations in $g(r)$ persist until

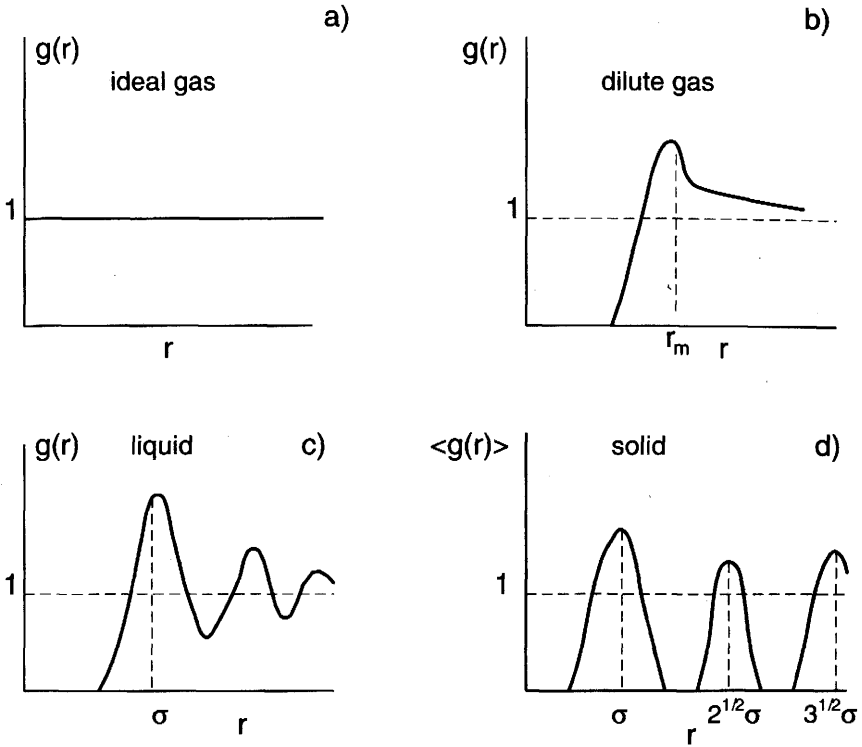


Fig. 2.1. Pair correlation function for various systems (qualitative behavior): (a), ideal gas, (b) dilute gas, (c), liquid, (d), solid (angle-averaged $g(r)$)

r exceeds the so-called correlation length which in a dense liquid is about several molecular diameters. In a dilute gas the correlation length is just the range of the potential (r_m), and there is no layering. It is important to stress that although interaction potentials in dilute gases and liquids can be the same, their correlation functions appear to be significantly different. The reason for this is the density dependence of g .

In a *crystalline solid*, molecules are oscillating in the vicinity of the lattice sites and large-scale translational motion is very rare; the density has sharp (Gaussian-like) peaks at the lattice sites and is almost zero for other values of r . A solid is thus an inhomogeneous, anisotropic system characterized by long-range order. Therefore the correlation function of a solid is long-ranged. In view of this anisotropy one can speak of the angle-averaged g , which is shown in Fig. 2.1d. In a solid, ordering occurs in shells (contrary to the situation in fluids), which makes it possible to place neighboring particles closer to the tagged one (situated in the origin). For a 3-dimensional face-centered cubic (fcc) or body-centered cubic (bcc) solid at low temperatures the second peak

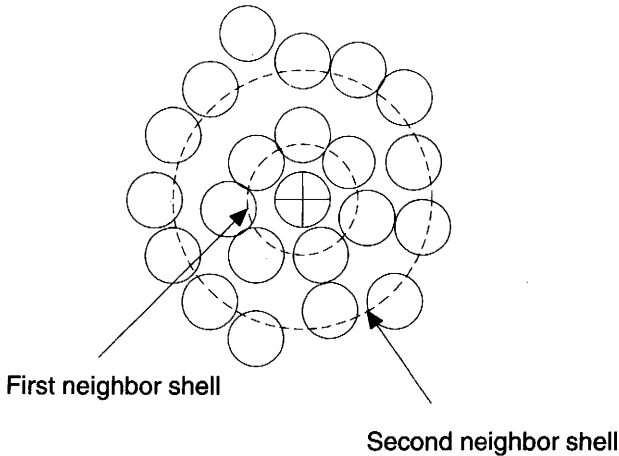


Fig. 2.2. Structure of a simple liquid

is at $r = \sqrt{2}\sigma$, and the third at $r = \sqrt{3}\sigma$. The number of neighboring particles situated within a distance r of the origin is

$$n(r) = 4\pi\rho \int_0^r r'^2 g(r') dr' \quad (2.12)$$

Thus, the number of molecules inside the first neighbor shell for a dense liquid or solid (with $\rho\sigma^3 \approx 1$) is

$$n_1 \approx 12 \quad (2.13)$$

We see that the molecular structure is in many respects determined by the function $g(r; \rho, T)$. It therefore appears that the pair correlation function plays an exceptionally important role. It is convenient to introduce a *total pair correlation function* $h(\mathbf{r}_1, \mathbf{r}_2)$:

$$h(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} = g(\mathbf{r}_1, \mathbf{r}_2) - 1 \quad (2.14)$$

which tends to zero when the particle separation tends to infinity, i.e. when particles become uncorrelated.

2.4 The structure factor

Experimentally the fluid structure can be determined by means of X-ray or neutron scattering. X-rays are scattered mainly by electrons; the scattering intensity on a nucleus is m_e/M_{nuc} times less than that on an electron (m_e and M_{nuc} are the masses of the electron and nucleus, respectively). Thus, in

order to calculate the scattering intensity one has to know the electron density distribution in an atom of the given substance. The Fourier transform of this quantity is called the atomic form factor f_e . The intensity of X rays scattered at an angle θ is given by [99]

$$I(\mathbf{k}) = N|f_e(\mathbf{k})|^2 S(\mathbf{k}) \quad (2.15)$$

Here N is the number of atoms and the $\mathbf{k}$ is the difference between the wave vectors of the scattered and incident beams (see Fig. 2.3):

$$\mathbf{k} = \mathbf{k}_{\text{scatt}} - \mathbf{k}_{\text{incid}}$$

Since scattering of photons is almost elastic $|\mathbf{k}_{\text{scatt}}| \approx |\mathbf{k}_{\text{incid}}|$ and $\mathbf{k}$ is related to the incident wave length λ_{incid} and the scattering angle as

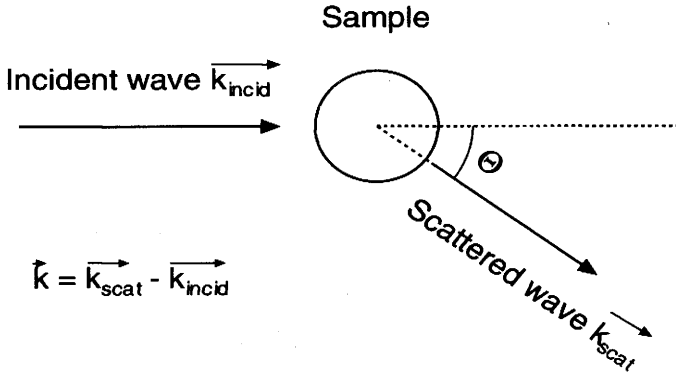


Fig. 2.3. X-ray scattering

$$k = |\mathbf{k}| = \frac{4\pi \sin(\theta/2)}{\lambda_{\text{incid}}}, \quad (2.16)$$

The quantity $S(\mathbf{k})$ in (2.15) is called the static structure factor, and is a Fourier transform of the total correlation function:

$$S(\mathbf{k}) = 1 + \rho \int h(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r} \quad (2.17)$$

Neutrons, in view of their large mass, are scattered mainly by nuclei, so information about correlations of nuclei can be obtained in a more natural way by means of neutron scattering, for which proportionality of the scattering intensity to the structure factor $I(\mathbf{k}) \sim S(\mathbf{k})$ also holds. Thus, by measuring the scattering intensity one can experimentally find $h(\mathbf{r})$ by taking the inverse Fourier transform of $S(\mathbf{k})$. The structure factor therefore represents a direct link between theory and experiment.

Keeping λ_{incid} constant, one can study $S(k)$ for small k by varying the scattering angle. This domain is particularly interesting, since the value of $S(k)$ as $k \rightarrow 0$ is closely related to the phase behavior of the system; experimentally it can be obtained by using small-angle scattering,¹ for which (2.16) reads

$$k \simeq \frac{2\pi}{\lambda_{\text{incid}}} \theta \simeq k_{\text{incid}} \theta, \quad \theta/2 \ll 1 \quad (2.18)$$

In the limit $k \rightarrow 0$ (which is also called the long wave-length limit, referring to the wave length $\lambda = 2\pi/k$) we have

$$S(0) = 1 + \rho \int h(\mathbf{r}) \, d\mathbf{r} \quad (2.19)$$

For a homogeneous system $h(\mathbf{r}) = h(r)$. Rewriting (2.17) in spherical coordinates we obtain

$$S(k) = 1 + 4\pi\rho \int_0^\infty dr \, r^2 h(r) \frac{\sin(kr)}{kr} \quad (2.20)$$

Finally, we present several numerical estimates for $S(0)$:

- for an ideal gas $h(r) \equiv 0$ and therefore $S(0)_{\text{ideal}} = 1$
- for argon at its triple point $S(0) \approx 0.06$ [23]
- for liquid metals near the melting point, $S(0)$ is between 0.01 and 0.03 [23].

¹ This technique is called SAXS (small angle X-ray scattering) in the case of X rays and SANS in the case of neutron scattering.

3. Equations of state

Having introduced the necessary statistical technique, we are now in a position to establish routes from statistical mechanics to thermodynamics, i.e. to observable macroscopic properties. There are three such routes, provided by

- energy
- pressure (virial)
- compressibility

equations of state. This brings us to a problem of thermodynamic consistency. As we will see later, all these equations require a knowledge of correlation functions. Since exact correlation functions for realistic potentials are not known and one has to use approximate models for them, an arbitrary thermodynamic property calculated on the basis of one equation of state will not in general be the same if calculated on the basis of another one. For example, the pressure calculated from the virial equation will differ from the pressure found by means of the compressibility equation.

3.1 Energy equation

The macroscopic total energy can be obtained by averaging the Hamiltonian

$$E = \langle K \rangle + \langle U_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \rangle + \langle U_{N,\text{ext}}(\mathbf{r}_1, \dots, \mathbf{r}_N) \rangle$$

A simple way to derive the momentum part $\langle K \rangle$ without performing any calculations is to recall that each degree of freedom contributes $k_B T/2$ to the kinetic energy, so

$$\langle K \rangle = \frac{3}{2} N k_B T \quad (3.1)$$

Assuming the interaction energy to be pairwise additive and translationally invariant

$$U_N = \sum_{1 \leq i < j \leq N} u(\mathbf{r}_i, \mathbf{r}_j) = \sum_{1 \leq i < j \leq N} u(r_{ij}) \quad (3.2)$$

we use the theorem of averaging to obtain

$$E = \frac{3}{2}Nk_B T + \frac{1}{2} \int u(\mathbf{r}_1, \mathbf{r}_2) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + \int u_{\text{ext}}(\mathbf{r}) \rho^{(1)}(\mathbf{r}) d\mathbf{r} \quad (3.3)$$

The second term is the average interaction energy, and the third the contribution of the external field. For a system in the absence of external fields $u_{\text{ext}} = 0$. Then

$$\rho^{(1)}(\mathbf{r}) = \rho = \frac{N}{V}, \quad \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(r_{12})$$

Since U_N is translationally invariant we can transform to new coordinates by moving the origin from 0 to $\mathbf{r}_1$, i.e. $\mathbf{r}'_1 = \mathbf{r}_1$, $\mathbf{r}'_2 \equiv \mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ which yields the final result

$$E = N \left[\frac{3}{2}k_B T + 2\pi\rho \int_0^\infty u(r_{12})g(r_{12}; \rho, T)r_{12}^2 dr_{12} \right] \quad (3.4)$$

It is important to bear in mind that there is not only an explicit dependence of energy on temperature and density, but also an implicit dependence on ρ and T contained in the pair correlation function. Knowing $E(N, \rho, T)$ one can calculate other thermodynamic functions by means of standard thermodynamic relationships. We will see that some of these functions can be calculated directly from $u(r)$ and $g(r)$ without reference to the internal energy.

3.2 Pressure (virial) equation

We now discuss how the pressure in the bulk system can be calculated directly from an assumed intermolecular potential and a pair correlation function. We again assume that U_N is pairwise additive and the system is uniform, hence $\rho^{(1)} = \rho$, $g(\mathbf{r}_1, \mathbf{r}_2) = g(r_{12})$. The thermodynamic relationship $p = -(\partial \mathcal{F} / \partial V)_{N, T}$ can be expressed in terms of the configuration integral

$$\stackrel{\uparrow}{(A.46)} \quad p = \frac{k_B T}{Q_N} \left(\frac{\partial Q_N}{\partial V} \right)_{N, T} \quad (3.5)$$

In order to perform the differentiation with respect to volume in the configuration integral we use Green's transformation of particle coordinates:

$$\mathbf{r}_i = L\mathbf{r}_i^*, \quad L = V^{1/3}; \quad i = 1, \dots, N \quad (3.6)$$

The dimensionless coordinates $\mathbf{r}_i^*$ belong to the unit cube:

$$V = L^3 \int d\mathbf{r}^* \rightarrow \int d\mathbf{r}^* = 1$$

In changing L we change the volume of the system. Thus,

$$p = \frac{k_B T}{Q_N} \left(\frac{\partial Q_N}{\partial L} \right)_{N,T} \frac{1}{3L^2} \quad (3.7)$$

and $Q_N(L)$ becomes

$$Q_N(L) = L^{3N} \int \exp[-\beta U_N(L\mathbf{r}_1^*, \dots, L\mathbf{r}_N^*)] d\mathbf{r}^{*N}$$

Differentiation with respect to L gives

$$\frac{1}{Q_N} \frac{\partial Q_N}{\partial L} = \frac{3N}{L} - \beta \int \frac{\partial U_N}{\partial L} \left(\frac{e^{-\beta U_N}}{Q_N} \right) d\mathbf{r}^N = \frac{3N}{L} - \beta \left\langle \frac{\partial U_N}{\partial L} \right\rangle \quad (3.8)$$

In the second term one recognizes the average of a pairwise additive function

$$\frac{\partial U_N(L\mathbf{r}_1^*, \dots, L\mathbf{r}_N^*)}{\partial L} = \sum_{1 \leq i < j \leq N} \frac{du}{dr_{ij}} \frac{r_{ij}}{L}$$

Using the theorem of averaging (2.8), $\langle \frac{\partial U_N}{\partial L} \rangle$ can be expressed

$$\frac{1}{L} \frac{1}{2} \int \frac{du}{dr_{12}} r_{12} \rho^{(2)}(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{L} \frac{N^2}{V} 2\pi \int_0^\infty u'(r_{12}) g(r_{12}) r_{12}^3 dr_{12} \quad (3.9)$$

Substitution of (3.8)–(3.9) into Eq. (3.7) gives the final result:

$$p = \rho k_B T - \frac{2\pi}{3} \rho^2 \int_0^\infty u'(r_{12}) g(r_{12}; \rho, T) r_{12}^3 dr_{12} \quad (3.10)$$

The first term is the ideal gas contribution (cf. (1.52)), whereas the second is due to intermolecular interactions. The latter expression is also known as the virial equation of state since it can be derived from the mechanical virial theorem of Clausius (the product $ru'(r)$ is called the virial of the potential u). Note that (3.10) is an exact expression and not a truncated series in powers of the density: there is an implicit dependence of g on ρ . Later we shall discuss an expansion in ρ (virial expansion), that holds for dilute systems (e.g. rare gas) and not for systems (such as liquids and solids) where the density is not a small parameter.

3.3 Compressibility equation

This equation relates the isothermal compressibility

$$\chi_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{T,V} \quad (3.11)$$

to the total correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$. Since the derivative of ρ is taken at fixed volume, this means that we study a system in which the number of particles can vary. Hence, the most natural approach is to perform derivations in the grand ensemble. Using the thermodynamic relationship $\Omega = -pV$ we have

$$\left(\frac{\partial \rho}{\partial p} \right)_{T,V} = \frac{1}{V} \left(\frac{\partial \bar{N}}{\partial p} \right)_{T,V} = - \left(\frac{\partial \bar{N}}{\partial \Omega} \right)_{T,V} = \frac{\left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T,V}}{- \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V}}$$

Equations (1.82) and (1.87) yield

$$\chi_T = \frac{V}{(\bar{N})^2} \frac{\bar{N}^2 - (\bar{N})^2}{k_B T} \quad (3.12)$$

Thus, χ_T is proportional to the mean-square fluctuation of the number of particles in the system. For a uniform system ($U_{\text{ext}} = 0$) the singlet distribution function $\rho^{(1)} = \rho$ is independent of $\mathbf{r}$. Rewriting the definition of the total correlation function, we have

$$\rho^2 h(\mathbf{r}_1, \mathbf{r}_2) = \rho^{(2)}(\mathbf{r}_{12}) - \rho^2$$

Integration over $d\mathbf{r}_1 d\mathbf{r}_2$ results in

$$\rho^2 V \int h(r_{12}) d\mathbf{r}_{12} = \int \rho^{(2)}(\mathbf{r}_{12}) d\mathbf{r}_1 d\mathbf{r}_2 - (\bar{N})^2$$

The integral on the right-hand side represents normalization of the pair distribution function, which according to (2.3) is equal to $\bar{N}(\bar{N} - 1) = \bar{N}^2 - \bar{N}$. Then using (3.12) we have

$$\rho^2 V \int h(r_{12}) d\mathbf{r}_{12} = [\bar{N}^2 - (\bar{N})^2] - \bar{N} = \frac{(\bar{N})^2}{V} k_B T \chi_T - \bar{N}$$

Dividing both sides by $\bar{N}$, we obtain the compressibility equation:

$$k_B T \rho \chi_T = 1 + \rho \int h(r_{12}) d\mathbf{r}_{12} \quad (3.13)$$

Note that this result is independent of any special assumptions about the interaction energy U_N , such as pairwise additivity; recall that derivation of the pressure equation and the energy equation was based on the assumption of pairwise additivity. From the compressibility equation and (2.17) it follows that χ_T can be related to the static structure factor in the long-wavelength limit:

$$\chi_T = \frac{S(0)}{\rho k_B T} \quad (3.14)$$

3.4 Thermodynamic consistency

At the beginning of this chapter we briefly mentioned a problem of thermodynamic consistency. Let us demonstrate it in an explicit way by calculating the pressure from the compressibility equation and comparing with the virial equation. Using (3.13) and the definition of the isothermal compressibility, we find

$$(p)_C = k_B T \int_0^{\bar{\rho}} d\bar{\rho} \left[\frac{1}{1 + \bar{\rho} \int_V dr \{g(r; \bar{\rho}, T) - 1\}} \right] \quad (3.15)$$

where the subscript C indicates that the pressure was obtained by means of the compressibility route. The virial equation for the same quantity gives

$$(p)_P = \rho k_B T - \frac{2\pi}{3} \rho^2 \int_0^\infty \frac{du(r)}{dr} g(r; \rho, T) r^3 dr \quad (3.16)$$

where the subscript p indicates that the pressure was obtained by means of the pressure route. For an ideal gas ($u(r) \equiv 0$) the pair correlation function is known exactly, $g(r; \rho, T) \equiv 1$, and the two equations are consistent:

$$(p)_C = (p)_P = \rho k_B T$$

However, for an arbitrary interaction potential the exact form of $g(r)$ is unknown. Use of approximations for $g(r)$ can lead to different values for p : $(p)_C \neq (p)_P$ resulting in a loss of thermodynamic consistency.

3.5 Hard spheres

A hard-sphere system is characterized by a purely repulsive pairwise potential $u_d(r)$:

$$u_d(r) = \begin{cases} +\infty & \text{for } r < d \\ 0 & \text{for } r \geq d \end{cases} \quad (3.17)$$

where d is called the hard-sphere diameter (see Fig. 3.1); quantities with the subscript d will refer to the hard-sphere system. This model system plays, as we shall see later, an exceptionally important role in the perturbation theory of liquids, similar to the role of the ideal gas in the theory of imperfect gases or the harmonic crystal in solid-state physics.

Furthermore, this is the simplest colloidal system that can be realized in the laboratory (see also the discussion in Chap. 14). Silica particles with diameter $d \sim 10$ – 100 nm, stabilized against aggregation with a thin organophilic layer and dispersed in a nonpolar solvent (e.g. cyclohexane) with a refractive

index close to that of the particles, provides an example of a model hard-sphere colloid [145], [75]. Matching of refractive indexes enables the suppression of electrostatic and dispersion forces between particles [128]. The only (effective) interparticle interaction left is repulsion, which is approximately of the hard-sphere type.

From (3.17) it follows that $e^{-\beta u_d(r)}$ is a unit step function of $(r - d)$: it is zero at $r < d$ and unity at $r \geq d$. Therefore its derivative is the Dirac δ -function:

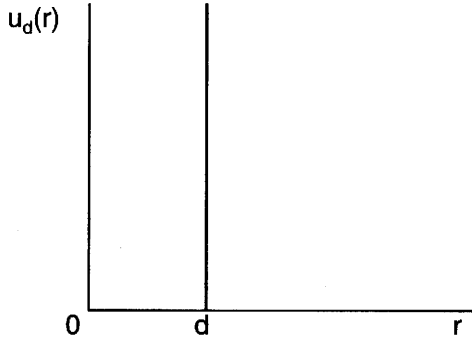


Fig. 3.1. Hard-sphere interaction potential; d is the hard sphere diameter

$$\frac{d}{dr} [e^{-\beta u_d(r)}] = \delta(r - d)$$

Differentiating the left-hand side, we have

$$\frac{du_d(r)}{dr} = -k_B T e^{\beta u_d(r)} \delta(r - d) \quad (3.18)$$

Using this result, we derive from (3.10) the virial equation for hard spheres:

$$\frac{p}{\rho k_B T} = 1 + \frac{2\pi}{3} \rho d^3 y_d(d) \equiv 1 + 4\phi_d y_d(d) \quad (3.19)$$

where

$$\phi_d = \frac{\pi}{6} d^3 \rho \quad (3.20)$$

is the volume fraction and

$$y_d(r) \equiv g_d(r) e^{\beta u_d(r)} \quad (3.21)$$

is called the cavity function of hard spheres (since it describes the distribution of cavities in a hard-sphere fluid). The cavity function can be defined similarly in the general case:

$$y(r) \equiv g(r)e^{\beta u(r)} \quad (3.22)$$

It is important to note that the cavity function is continuous even if the correlation function is not (as in the case of hard spheres). This can easily be shown by recalling the definition of the pair correlation function:

$$g(r_{12}) = \frac{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2} = \frac{V^2}{N^2} N(N-1) \int D_N \, d\mathbf{r}_3 \dots d\mathbf{r}_N$$

where D_N is the Gibbs distribution. For large N this gives

$$g(r_{12}) = V^2 \frac{e^{-\beta u(r_{12})}}{Q_N} \int d\mathbf{r}_3 \dots d\mathbf{r}_N \prod_{(i,j) \neq (1,2)} e^{-\beta u(r_{ij})}$$

A possible discontinuity of g is due to $e^{-\beta u(r_{12})}$. In the cavity function this factor disappears:

$$y = \frac{V^2}{Q_N} \int d\mathbf{r}_3 \dots d\mathbf{r}_N \prod_{(i,j) \neq (1,2)} e^{-\beta u(r_{ij})}$$

Because of the integration, all possible discontinuities in the Boltzmann factors in the integrand are smoothed and therefore y remains continuous and positive. We also note that y depends implicitly on density (for dilute systems $y(r) \approx 1$).

Thus, the pressure equation for hard spheres is determined solely by the value of the cavity function at contact.¹ Once $y_d(d; \phi)$ is known one can obtain the full thermodynamic description of a hard-sphere system by integrating the virial equation. Several approximate models for $y_d(d)$ have been proposed. Here we recall one of them – the Carnahan–Starling model – which is widely used in the theory of liquids (other approximations are discussed in Chap. 8). On the basis of empirical considerations Carnahan and Starling [20] proposed an approximation:

$$y_d(d) = \frac{4 - 2\phi_d}{4(1 - \phi_d)^3} \quad (3.23)$$

Substitution of (3.23) into (3.19) results in the Carnahan–Starling equation of state:

$$\frac{p}{\rho k_B T} = \frac{1 + \phi_d + \phi_d^2 - \phi_d^3}{(1 - \phi_d)^3} \quad (3.24)$$

The pressure of a hard-sphere system is a monotonically increasing function of a volume fraction tending to infinity when the latter tends to unity.

¹ Equation (3.19) is often written with $g_d(d)$ instead of $y_d(d)$. Strictly speaking it must then be $g_d(d+) \equiv \lim_{r \rightarrow d+0} g_d(r)$.

Nevertheless one should bear in mind that the singularity at $\phi_d = 1$ cannot be achieved because ϕ_d cannot exceed the close packing value

$$\phi_{\text{cl.p.}} = \pi\sqrt{2}/6 \approx 0.7405$$

We may recall other useful thermodynamic consequences resulting from the Carnahan–Starling theory. Integration of (3.24) over the volume yields the Helmholtz free energy:

$$\frac{\mathcal{F}_d}{Nk_B T} = \ln \frac{\rho \Lambda^3}{e} + \frac{4\phi_d - 3\phi_d^2}{(1 - \phi_d)^2} \quad (3.25)$$

The chemical potential is

$$\frac{\mu_d}{k_B T} = \ln(\rho \Lambda^3) + \frac{8\phi_d - 9\phi_d^2 + 3\phi_d^3}{(1 - \phi_d)^3} \quad (3.26)$$

The Carnahan–Starling model accurately describes the hard-sphere fluid up to crystalline densities, although it does not predict a transition from a disordered fluid for $\phi_d < 0.495$ to an ordered face-centered-cubic solid for $0.545 < \phi_d < 0.74$. This transition, which is of purely entropic origin, because all of the energies are either zero or infinite, was found in a number of Monte Carlo and molecular dynamics simulations (for a review see [47], Chap. 9). Piazza et al. [111] performed direct experimental measurements of the hard-sphere equation of state over the wide density range, which for the first time unambiguously demonstrated the possibility of the crystallization transition.

3.6 Virial expansion

The virial expansion is the expansion of pressure in powers of the density:

$$\frac{p}{k_B T} = \sum_{l=1}^{\infty} \beta_l(T) \rho^l \quad (3.27)$$

It takes into account deviations from nonideality due to interparticle interactions; $\beta_l(T)$, $l = 1, 2, \dots$ are called virial coefficients. It is clear that $\beta_1 \equiv 1$. Although (3.27) does not provide the basis for a satisfactory theory of dense systems, this expansion is useful for imperfect gases at low densities.

The virial coefficients can be calculated for some model or real potentials and can be regarded as another source of quasi-experimental data similar to computer simulations. First, let us recall some basic facts from the theory of power series. The formal expression for a power series is

$$\sum_{l=0}^{\infty} a_l z^l \equiv f(z) \quad (3.28)$$

where z is a complex variable and the a_l are complex coefficients. At some values of z the series (3.28) can diverge; divergence of the series at some $z = z_1$ corresponds to a singularity of the function $f(z)$ at the point z_1 . One can speak of a radius of convergence of the power series defined by

$$r_0 = \lim_{l \rightarrow \infty} |a_l|^{-1/l} \quad (3.29)$$

On the circle $|z| = r_0$ there must be at least one singular point z_0 of the function $f(z)$, and no other singularities in the complex plane can lie closer to the origin.

The grand partition function can be written as a power series in *fugacity*, defined as

$$z \equiv \frac{\lambda}{\Lambda^3} \quad (3.30)$$

Using (1.42) we have:

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} z^N Q_N = 1 + f(z) \quad (3.31)$$

where

$$f(z) = \sum_{N=1}^{\infty} \frac{1}{N!} z^N Q_N = zV + \frac{1}{2!} z^2 \int e^{-\beta u_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{3!} z^3 \int e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 + \dots \quad (3.32)$$

Taking the logarithm of (3.31) and expanding it formally in powers of f , we obtain

$$\ln \Xi = f(z) - \frac{1}{2} [f(z)]^2 + \dots \quad (3.33)$$

Each term on the right-hand side represents a power series in z ; collecting terms with equal powers of z , we rewrite (3.33) as

$$\ln \Xi = V \sum_{l=1}^{\infty} \frac{J_l}{l!} z^l$$

The first two coefficients are

$$J_1 = 1, \quad J_2 = \int \left(e^{-\beta u(r)} - 1 \right) d\mathbf{r} \quad (3.34)$$

Thermodynamics in the grand ensemble follows from the relationship

$$pV = k_B T \ln \Xi$$

from which we obtain the expansion of the pressure in powers of z :

$$\frac{p}{k_B T} = \sum_{l=1}^{\infty} \frac{J_l}{l!} z^l \quad (3.35)$$

Note, that this must be regarded as a formal power series (see (3.28)) whose radius of convergence must be discussed as a separate problem. A similar expansion can be written for the number density using (1.86):

$$\rho \equiv \frac{\bar{N}}{V} = \sum_{l=1}^{\infty} \frac{J_l}{(l-1)!} z^l \quad (3.36)$$

To derive the virial coefficients we substitute the series (3.36) for ρ in (3.27) and compare it with the series (3.35) for the pressure:

$$\sum_{l=1}^{\infty} \frac{J_l}{l!} z^l = \sum_{k=1}^{\infty} \beta_k \left[\sum_{n=1}^{\infty} \frac{J_n}{(n-1)!} z^n \right]^k \quad (3.37)$$

Equating coefficients of equal powers of z on both sides gives the desired β_k . Specifically, for $l = 1$ and 2 :

- $l = 1$. Contribution to the term z^1 comes from the only combination of powers on the right-hand side of (3.37): $n = 1$, $k = 1$. We have $J_1 = \beta_1 J_1 \Rightarrow \beta_1 = 1$, as expected.
- $l = 2$. Contribution to the term z^2 comes from n and k satisfying $nk = 2$. The latter is provided by two terms: $n = 2$, $k = 1$ and $n = 1$, $k = 2$. We then have $\frac{1}{2}J_2 = \beta_1 J_2 + \beta_2 J_1^2$, which yields (recalling that $J_1 = \beta_1 = 1$) $\beta_2 = -\frac{1}{2}J_2$.

The second virial coefficient, usually denoted by B , is

$$B(T) = \frac{1}{2} \int \left(1 - e^{-\beta u(r)} \right) \mathrm{d}\mathbf{r} \quad (3.38)$$

At low temperatures the attractive part of the potential (if any!) dominates the integrand and $B(T)$ is negative; at high temperatures $B(T)$ is positive due to the excluded volume effect. The second virial coefficient for the Lennard–Jones fluid is shown in Fig. 3.2. The temperature at which $B(T)$ passes zero is called the Boyle temperature T_B . For the Lennard–Jones potential $k_B T_B / \epsilon \approx 3.45$, while the critical temperature $k_B T_c / \epsilon \approx 1.3$ [47]. Thus, for the Lennard–Jones fluid $T_B > T_c$. For a hard-sphere fluid the second virial coefficient does not depend on temperature and can be calculated straightforwardly to give

$$B = B_d = \frac{2\pi}{3} d^3$$

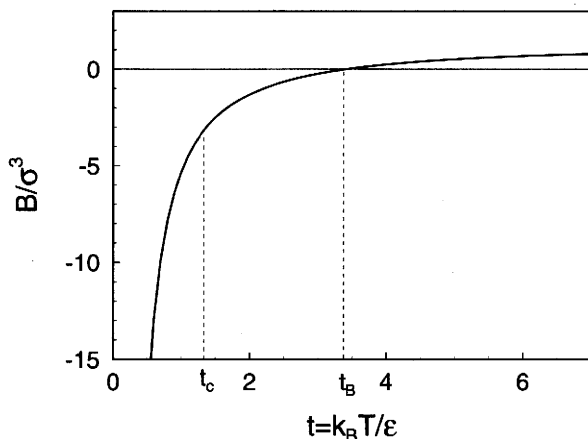


Fig. 3.2. Second virial coefficient B/σ^3 for the Lennard-Jones fluid vs. dimensionless temperature $t = k_B T/\epsilon$. The critical temperature $t_c \approx 1.3$, the Boyle temperature $t_B \approx 3.45$

which is four times the volume of a sphere. For long-range potentials, in particular for the Coulomb interaction $u_C \sim 1/r$, the second virial coefficient is not defined because the integral in (3.38) diverges.

Finally, we note two other useful forms of the virial expansion. The compressibility factor as a series in powers of pressure reads [100]

$$\frac{p}{\rho k_B T} = 1 + \frac{B}{k_B T} p + \frac{C - B^2}{(k_B T)^2} p^2 \quad (3.39)$$

If we rewrite it as

$$\rho k_B T = \frac{p}{1 + \frac{B}{k_B T} p + \frac{(C - B^2)}{(k_B T)^2} p^2}$$

and use the expansion $(1 + x)^{-1} = 1 - x + x^2 + \dots$, we obtain for the density in powers of the pressure:

$$\rho = \frac{p}{k_B T} - \frac{B}{(k_B T)^2} p^2 + \frac{2B^2 - C}{(k_B T)^3} p^3 \quad (3.40)$$

3.7 Law of corresponding states

Let us assume that an interaction potential has the two-parameter form (e.g., Lennard-Jones potential (1.27)):

$$u(r) = \epsilon \Phi\left(\frac{r}{\sigma}\right) \quad (3.41)$$

where ϵ is a depth of the interaction and σ the molecular size. One can assume that (3.41) is sufficiently accurate for real atoms and molecules regardless of the choice of the exact form $\Phi(x)$. We then transform coordinates: $\mathbf{r}_i = \sigma \mathbf{r}'_i$, $i = 1, \dots, N$. Then the total potential energy becomes

$$U_N = \epsilon U'_N(\mathbf{r}'_1, \dots, \mathbf{r}'_N)$$

where U'_N is a dimensionless function. The configuration integral can be written

$$Q_N = \sigma^{3N} \int_{V/\sigma^3} \dots \int_{V/\sigma^3} \exp \left[-\frac{\epsilon}{k_B T} U'_N(\mathbf{r}'^N) \right] d\mathbf{r}'^N = \sigma^{3N} f_N \left(\frac{k_B T}{\epsilon}, \frac{V}{\sigma^3} \right) \quad (3.42)$$

where f_N is a dimensionless “universal” function for a given type of interaction potential. This equation is a manifestation of the law of corresponding states. Using the standard thermodynamic relationships, we obtain:

$$p = \frac{\epsilon}{\sigma^3} \xi \left(\frac{k_B T}{\epsilon}, \frac{V}{\sigma^3} \right)$$

$$E = \epsilon \psi \left(\frac{k_B T}{\epsilon}, \frac{V}{\sigma^3} \right)$$

Introducing the dimensionless quantities

$$p^* = \frac{p\sigma^3}{\epsilon}, \quad E^* = \frac{E}{\epsilon}, \quad T^* = \frac{k_B T}{\epsilon}, \quad V^* = \frac{V}{\sigma^3}$$

one can express thermodynamic relationships in a universal form:

$$p^* = p^*(T^*, V^*); \quad E^* = E^*(T^*, V^*)$$

This means that for all substances with interaction potentials of the type (3.41), the behavior of dimensionless thermodynamic functions must be identical.

4. Liquid–vapor interface

4.1 Thermodynamics of the interface

In the previous chapters we studied the bulk properties of fluids. Now we shall discuss the interface properties of a two-phase system consisting of a liquid and its saturated vapor at temperature T . The two-phase equilibrium is characterized by equality of temperature, pressure, and chemical potentials in both bulk phases (see Chap. 6). The density, however, is not constant but varies continuously along the interface between two bulk equilibrium values $\rho^v(T)$ and $\rho^l(T)$. Superscripts “v” and “l” refer to the vapor and liquid phase. Local fluctuations of density take place even in homogeneous fluid, where, however, they are small and short-ranged and therefore can be neglected. In the two-phase system these fluctuations are macroscopic: at low temperatures ρ^v and ρ^l can differ by 3–4 orders of magnitude.

Density variations give rise to an extra contribution to thermodynamic functions. In the presence of an interface the Helmholtz and Gibbs free energies and the grand potential of the two-phase system are modified to include the work γdA which has to be imposed by external forces in order to change the interface area A by dA :

$$d\mathcal{F} = -p dV - S dT + \gamma dA + \mu dN \quad (4.1)$$

$$dG = V dp - S dT + \gamma dA + \mu dN \quad (4.2)$$

$$d\Omega = -p dV - S dT + \gamma dA - N d\mu \quad (4.3)$$

(in the last expression N is the mean number of particles in the system). The coefficient γ is the surface tension; its thermodynamic definition follows from the above expressions:

$$\gamma = \left(\frac{\partial \mathcal{F}}{\partial A} \right)_{N,V,T} \quad (4.4)$$

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{N,p,T} \quad (4.5)$$

$$\gamma = \left(\frac{\partial \Omega}{\partial A} \right)_{\mu,V,T} \quad (4.6)$$

Let us discuss a two-phase system contained in a volume V with a planar interface between vapor and liquid with area A . Inhomogeneity is along the z direction; $z \rightarrow +\infty$ corresponds to bulk vapor, and $z \rightarrow -\infty$ to bulk liquid (see Fig. 4.1).

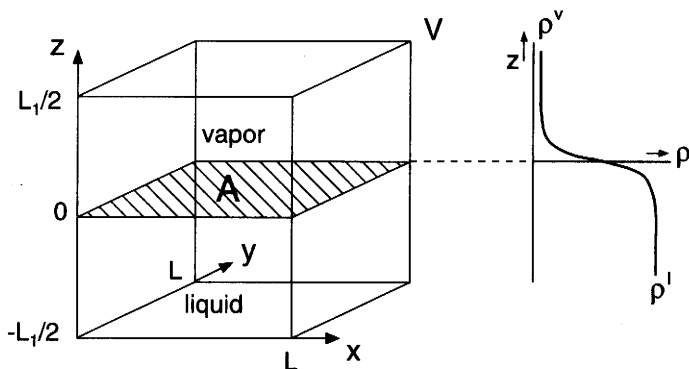


Fig. 4.1. Schematic representation of the vapor-liquid system contained in volume $V = L^2 L_1$. Inhomogeneity is along the z axis

Following Gibbs we introduce a so called dividing surface, a mathematical surface (of zero width) which establishes a boundary between bulk phases as shown in Fig. 4.2. Although its position is arbitrary, it is convenient to locate it somewhere in the transition zone. Once the position of a dividing surface is chosen, the volumes of the two phases are fixed, and satisfy

$$V^v + V^l = V$$

The idea of Gibbs was that any extensive thermodynamic quantity $\mathcal{M}$ (the number of particles, energy, entropy, etc.) can be written as a sum of bulk contributions $\mathcal{M}^v$ and $\mathcal{M}^l$ and an excess contribution $\mathcal{M}^s$ that is assigned to the chosen dividing surface:

$$\mathcal{M} = \mathcal{M}^v + \mathcal{M}^l + \mathcal{M}^s \quad (4.7)$$

Equation (4.7) is in fact a definition of $\mathcal{M}^s$; its value depends on the location of the dividing surface, and so do the values of $\mathcal{M}^v$ and $\mathcal{M}^l$ (as opposed to $\mathcal{M}$). Thus, excess quantities are assumed to be located on the dividing surface. Since its location is totally arbitrary, the excess quantities can be either positive or negative. Several important examples are

$$\begin{aligned} N &= N^v + N^l + N^s \\ S &= S^v + S^l + S^s \end{aligned}$$

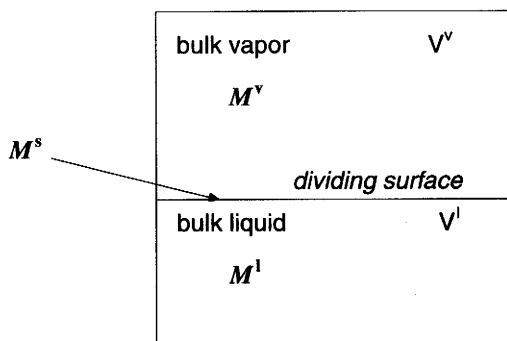


Fig. 4.2. Gibbs dividing surface

$$\Omega = \Omega^v + \Omega^l + \Omega^s$$

$$\mathcal{F} = \mathcal{F}^v + \mathcal{F}^l + \mathcal{F}^s$$

$$V = V^v + V^l$$

(by definition V^s is always zero).

One special case that will be useful for future discussions is an equimolar surface defined through the requirement that $N^s = 0$, where N^s is the excess number of particles. The surface density of this quantity

$$\Gamma = \frac{N^s}{A} \quad (4.8)$$

is called *adsorption*. Thus, equimolar surface corresponds to zero adsorption. Integration of (4.3) using the Gibbs–Duhem equation

$$S dT - V dp + N d\mu = 0$$

results in the appearance of an extra term γA in the grand potential of the two-phase system:

$$\Omega = -pV + \gamma A \quad (4.9)$$

whereas in each of the bulk phases

$$\Omega^v = -pV^v, \quad \Omega^l = -pV^l \quad (4.10)$$

Here we explicitly used the equality of pressures in the coexisting phases. Thus,

$$\Omega^s = \gamma A \quad (4.11)$$

irrespective of the choice of the dividing surface. Integration of (4.1) combined with the Gibbs–Duhem equation (or using Legendre transformation) give

$$\mathcal{F} = -pV + \gamma A + \mu N \quad (4.12)$$

implying that the surface part of the Helmholtz free energy is

$$\mathcal{F}^s = \gamma A + \mu N^s \quad (4.13)$$

It becomes equal to γA only in the case of equimolar surface.¹ A thermodynamic route to the surface tension given by (4.9) is used in modern density functional theories of fluids discussed in Chap. 9. By definition

$$\Omega^s = \Omega - \Omega^v - \Omega^l$$

Differentiating this expression using (4.3) for $d\Omega$ and (1.65) for each of the bulk phases yields

$$d\Omega^s = -S^s dT + \gamma dA - N^s d\mu$$

On the other hand, from (4.11) we have

$$d\Omega^s = \gamma dA + A d\gamma$$

Comparison of these two equalities leads to the Gibbs adsorption equation

$$A d\gamma + S^s dT + N^s d\mu = 0 \quad (4.14)$$

which describes the change of the surface tension resulting from the changes in T and μ . An important consequence is the expression for adsorption:

$$\Gamma = - \left(\frac{\partial \gamma}{\partial \mu} \right)_T \quad (4.15)$$

4.2 Statistical mechanical calculation of surface tension

A statistical mechanical derivation of the surface tension for a planar liquid-vapor interface can be obtained from the definition of γ in the canonical ensemble (4.4):

$$\gamma = - \frac{k_B T}{Q_N} \left(\frac{\partial Q_N}{\partial A} \right)_{N, V, T} \quad (4.16)$$

We assume that the interaction energy is pairwise additive and the intermolecular potential u is spherically symmetric. Let us write the volume of the two-phase system as

¹ Note that for a mixture it is not possible to choose a dividing surface in such a way that adsorption of all the components on it vanishes [125]. Preferential adsorption of one of the components can lead to surface enrichment.

$$V = L^2 L_1$$

where

$$L^2 = A$$

is the cross section in the xy plane and L_1 is the length in the z direction along which the system is inhomogeneous (see Fig. 4.1). Note that for the calculations to be presented we do not need to introduce the Gibbs surface²; in other words its location is irrelevant for the value of γ . As A varies, both L and L_1 change in such a way that the volume V remains constant. In order to calculate $\partial Q_N / \partial A$ we use Green's transformation (cf. Sect. 3.2):

$$x_i = Lx'_i, y_i = Ly'_i, z_i = L_1 z'_i \quad (4.17)$$

Primed coordinates belong to unit intervals, $0 \leq x'_i, y'_i \leq 1$, $-1/2 \leq z'_i \leq 1/2$, which remain unchanged when the surface area is changed. Then

$$Q_N = Q_N(L(A), L_1(A)) = V^N \int \exp[-\beta U_N(Lx'_1, Ly'_1, L_1 z'_1, \dots, L_1 z'_N)] d\mathbf{r}'^N$$

Now the dependence on A is contained only in the integrand in which it enters U_N via $L(A)$ and $L_1(A)$. Differentiation with respect to A and substitution into (4.16) yields

$$\gamma = V^N \int \frac{e^{-\beta U_N}}{Q_N} \frac{\partial U_N}{\partial A} d\mathbf{r}'^N$$

Returning to the original coordinates, we have:

$$\gamma = \int \left(\frac{e^{-\beta U_N}}{Q_N} \right) \frac{\partial U_N}{\partial A} d\mathbf{r}^N = \left\langle \frac{\partial U_N}{\partial A} \right\rangle \quad (4.18)$$

where we recognize a canonical average of the pairwise-additive quantity $\frac{\partial U_N}{\partial A}$. Using (2.8) it can be written as

$$\gamma = \frac{1}{2} \int \frac{\partial u_{12}}{\partial A} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

where $\rho^{(2)}$ describes pair correlations over the entire two-phase region including the transition zone. Taking into account that inhomogeneity is along the z direction, which implies $d\mathbf{r}_1 d\mathbf{r}_2 = A dz_1 d\mathbf{r}_{12}$, we can rewrite this as

$$\gamma = \frac{1}{2} \int_{-\infty}^{+\infty} dz_1 \int d\mathbf{r}_{12} A \frac{\partial u_{12}}{\partial A} \rho^{(2)}(z_1, r_{12}) \quad (4.19)$$

Calculating $\frac{\partial u}{\partial A}$ Green's transformation

$$x_{12} = Lx'_{12}, y_{12} = Ly'_{12}, z_{12} = L_1 z'_{12}$$

² This concept becomes necessary for curved interfaces.

yields

$$\frac{\partial u_{12}}{\partial A} = \frac{\partial u_{12}}{\partial x_{12}} x'_{12} \frac{\partial L}{\partial A} + \frac{\partial u_{12}}{\partial y_{12}} y'_{12} \frac{\partial L}{\partial A} + \frac{\partial u_{12}}{\partial z_{12}} z'_{12} \frac{\partial L}{\partial A}$$

Simple algebra gives

$$A \frac{\partial u_{12}}{\partial A} = \frac{1}{2} r_{12} \frac{\partial u_{12}}{\partial r_{12}} \left(1 - 3 \frac{z_{12}^2}{r_{12}^2} \right)$$

Substituting this expression into (4.19) we obtain

$$\gamma = \frac{1}{4} \int_{-\infty}^{+\infty} dz_1 \int d\mathbf{r}_{12} r_{12} \left(1 - 3 \frac{z_{12}^2}{r_{12}^2} \right) u'(r_{12}) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \rho^{(1)}) \quad (4.20)$$

This result, known as the Kirkwood–Buff formula, was originally derived from the microscopic pressure tensor $\hat{\mathbf{p}}$ by Kirkwood and Buff in 1949.³

Application of (4.20) for the calculation of surface tension requires a knowledge of singlet and pair distribution functions $\rho^{(1)}$ and $\rho^{(2)}$. In Chap. 8 we discuss integral equation theories describing their behavior. As we shall see, even for the bulk homogeneous phases this is not a simple task and one has to invoke several approximations. Unfortunately, no practicable and exact routes exist to determine distribution functions in the interface domain of a two-phase system from a knowledge of $u(r)$ only.

Serious progress in the statistical theory of fluids during the last two decades was achieved due to implementation of the perturbation theory (discussed in Chap. 5). Its application to the problem of surface tension is presented in Sect. 5.6. A more refined approach, pioneered by Evans [38], is based on the ideas of the density functional theory (see Chap. 9). One can deduce γ from computer simulations (Monte Carlo or molecular dynamics). To do so the Kirkwood–Buff equation is written

$$\gamma = \frac{1}{2A} \left\{ \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)} \left[\left(1 - 3 \frac{z_{12}^2}{r_{12}^2} \right) u'(r_{12}) r_{12} \right] \right\}$$

Recalling the theorem of averaging, we recognize in curly brackets the thermal average of the pairwise additive quantity

$$X_\gamma = \sum_{i < j} \left[\left(1 - 3 \frac{z_{ij}^2}{r_{ij}^2} \right) u'(r_{ij}) r_{ij} \right]$$

Thus,

$$\gamma = \frac{1}{2A} \langle X_\gamma \rangle \quad (4.21)$$

The average $\langle X_\gamma \rangle$ can be accumulated during simulation runs.

³ As found by Schofield and Henderson [129], the form of $\hat{\mathbf{p}}$ is not unique, that is why the derivation presented here is more general.

4.2.1 Fowler approximation

Here we discuss a considerable simplification of the Kirkwood–Buff equation that is appropriate if the temperature is not close to the critical point. In view of the large difference in density between the liquid and its saturated vapor, it is feasible to shrink the physical transition zone to a mathematical surface of density discontinuity; in Fig. 4.1 we placed it at $z = 0$. The density profile $\rho^{(1)} = \rho(z)$ then becomes a step function:

$$\rho(z) = \rho^l \quad \text{at } z < 0, \quad \rho(z) = 0 \quad \text{at } z > 0 \quad (4.22)$$

Hence, this approximation, first proposed by Fowler in 1937, neglects $\rho^v(T)$ compared to $\rho^l(T)$. The pair distribution function is written in the form

$$\rho^{(2)}(r_{12}, z_1, z_2) = \rho(z_1)\rho(z_2)g(r_{12}; \rho^l)$$

where $g(r_{12}; \rho^l)$ is the pair correlation function in the bulk liquid. Then (4.20) in spherical coordinates reads

$$\gamma = -\pi (\rho^l)^2 \int_0^\infty dr_{12} r_{12}^3 u'(r_{12}) g(r_{12}; \rho^l) \int_{-\infty}^0 dz_1 \int d\theta_{12} \sin \theta_{12} P_2(\cos \theta_{12}) \quad (4.23)$$

where $P_2(x) = \frac{1}{2}(3x^2 - 1)$ is the Legendre polynomial of the second order. Let us fix r_{12} and examine possible limits of variation of z_1 . If $|z_1| > r_{12}$ the integral over θ_{12} vanishes:

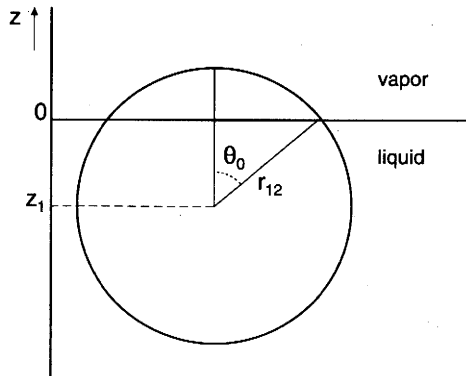


Fig. 4.3. Range of integration over θ_{12} in the Fowler approximation. The lower limit is $\theta_0 = \arccos \frac{|z_1|}{r_{12}}$

$$\int_0^\pi d\theta_{12} \sin \theta_{12} P_2(\cos \theta_{12}) = \int_{-1}^1 P_2(x) dx = 0.$$

This is a manifestation of the fact that the mean density fluctuation in the bulk (liquid or vapor) is equal to zero. Hence $|z_1|$ should not exceed r_{12} (see Fig. 4.3). Integration over θ_{12} yields

$$\int_{\arccos a}^\pi d\theta_{12} \sin \theta_{12} P_2(\cos \theta_{12}) = \frac{1}{2}(a^3 - a)$$

where $a = \frac{|z_1|}{r_{12}}$. Integration over z_1 yields

$$r_{12} \int_0^1 da \left[-\frac{1}{2}(a - a^3) \right] = -\frac{1}{8}r_{12}$$

Substituting into (4.23), we obtain

$$\gamma = \frac{\pi}{8} (\rho^l)^2 \int_0^\infty dr r^4 u'(r) g(r; \rho^l) \quad (4.24)$$

The short-range repulsive part of the interaction potential makes a negative contribution to γ , whereas the long-range attractive part makes a positive contribution. Note that g has a strong dependence on the liquid density ρ^l ; the latter cannot be considered a small parameter.

5. Perturbation approach

5.1 General remarks

Perturbation theories became a powerful technique in the theory of liquids in the early 1970s. The main idea of a perturbation approach in general terms reduces to the following. The system under consideration is decomposed into a reference model, characterized by some reference interaction potential and the same density and temperature as the original system, and a perturbation which, strictly speaking, must be small.¹ Properties of the reference model are assumed to be known to appreciable accuracy. The thermodynamics of the full system is obtained by appropriate averaging of the perturbation over the reference model. It is important to bear in mind that the perturbation is in the interaction potential (and not in density). The peculiar thing about application of this approach to liquids is that the reference model must be nonideal. In most cases it is a hard-sphere system with an appropriately chosen effective diameter. Hard spheres are a starting point in the theory of liquids, as an ideal gas is in the theory of gases and a harmonic solid in solid-state physics. Nowadays a lot of data is available from computer simulations of hard spheres and from integral theories of correlation functions. The reason for the success of perturbation theories is that the structure of a liquid is determined primarily by the repulsive (hard-core) part of the interaction, while the attractive part provides a uniform background potential in which the molecules move. This is the main concept of the perturbation approach. Throughout this chapter we assume a pairwise additive interaction energy with spherical potentials.

5.2 Van der Waals theory

The idea of a perturbation approach in the theory of liquids belongs to van der Waals, who used it as a basis for his equation of state formulated in 1873. Following van der Waals we assume that molecules have a hard core, i.e.

¹ The choice of a decomposition scheme is not unique.

$$u(r) = \begin{cases} +\infty & \text{for } r < \sigma \\ u_1(r) & \text{for } r \geq \sigma \end{cases}, \quad (5.1)$$

where σ is a molecular diameter, and $u_1(r) < 0$. Using the main concept of the perturbation approach we write the free energy as

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{2}N\psi \quad (5.2)$$

Here $\mathcal{F}_0$ is the free energy of hard spheres with the diameter σ ; the latter is chosen as a reference model. The second term is the average energy of background interactions with potential $u_1(r)$ viewed as a perturbation; ψ is the average perturbation energy per particle. It makes a negative contribution to $\mathcal{F}$. The factor $\frac{1}{2}$ appears because the energy ψ is shared by two molecules.

Note an important difference between $u_1(r)$ and ψ : the latter is an averaged (over all configurations) interaction energy per particle, and therefore ψ does not depend on r . Van der Waals' idea to decompose the free energy and not the internal energy (as Lord Rayleigh was proposing) anticipated the modern development of the theory in the 1970s (almost a century after van der Waals' work!). Recalling the definition of a pair correlation function describing a local arrangement of particles around the tagged one at the origin, we observe that

$$\rho g(r) 4\pi r^2 dr$$

is the average number of molecules in a spherical shell of thickness dr and radius r surrounding a tagged molecule at the origin. As a result of the conjecture that the structure is determined primarily by the hard-core part of the potential, we can replace g by g_0 , implying that

$$\psi = 4\pi\rho \int u_1(r)g_0(r)r^2 dr$$

Van der Waals made a further assumption that molecules are randomly distributed, which means that $g_0(r) = 1$ for $r > \sigma$ (and $g_0(r) = 0$ for $r < \sigma$). In fact, this is nothing but the low density limit of the hard-sphere pair correlation function (cf. Sect. 8.2). Thus,

$$\psi = -2\rho a$$

where

$$a = -2\pi \int_{\sigma}^{\infty} u_1(r)r^2 dr \quad (5.3)$$

In van der Waals' time the properties of the hard-sphere system were not known; he approximated $\mathcal{F}_0$ by assuming that it is equal to the free energy of an ideal gas contained in a "free volume" V_f that is smaller than the

total volume V due to the hard-sphere exclusion effects. This is a reasonable assumption since hard spheres behave as noninteracting particles at distances greater than their diameter. The configuration integral of such an ideal gas is equal to V_f^N , and using the general expression (1.46) for the free energy of an ideal gas we have

$$\mathcal{F}_0 = Nk_B T \ln(N\Lambda^3/e) - Nk_B T \ln V_f$$

For the free volume one can write

$$V_f = V - Nb,$$

where the parameter b , called the van der Waals covolume, is the excluded volume per particle. When two molecules collide (only pair collisions are taken into account) the center of mass of one of them is excluded from a volume of $4\pi\sigma^3/3$ (Fig. 5.1). The latter must be divided by 2 because it is shared by two molecules:

$$b = 2\pi\sigma^3/3 \quad (5.4)$$

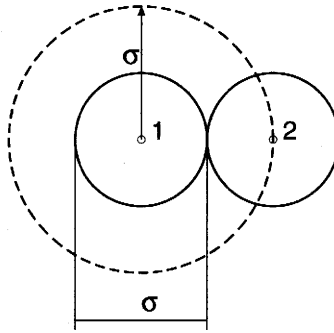


Fig. 5.1. Excluded volume in the van der Waals theory; σ is the diameter of a molecule. The dashed circle has a radius σ

Summing up these results we obtain for the free energy

$$\mathcal{F} = [Nk_B T \ln(N\Lambda^3/e) - Nk_B T \ln(V - Nb)] - N\rho a \quad (5.5)$$

where the expression in square brackets corresponds to the reference part. Differentiation of $\mathcal{F}$ with respect to volume yields the van der Waals equation of state:

$$p = -\rho^2 a + \frac{\rho k_B T}{1 - b\rho} \quad (5.6)$$

with parameters a and b given by (5.3)–(5.4). The van der Waals equation represents an interpolation formula, which gives a qualitative description of the liquid-gas transition. It is widely used due to its simplicity. As an interpolation formula (5.6) gives correct results in the two limiting cases:

- for a dilute gas in the limit $\rho \rightarrow 0$ it gives the ideal gas equation of state
- when ρ increases it takes into account the finite compressibility of the liquid: $\rho < 1/b$

Quantities a and b can be related to the parameters of the critical state. The critical point satisfies (see Sect. 6.3):

$$\left. \frac{dp}{d\rho} \right|_{T_c} = \left. \frac{d^2p}{d\rho^2} \right|_{T_c} = 0 \quad (5.7)$$

Applying (5.7) to (5.6), we obtain

$$b = \frac{1}{3\rho_c}, \quad a = \frac{9}{8} \frac{k_B T_c}{\rho_c} \quad (5.8)$$

These relationships form the basis for practical applications of the van der Waals equation to various substances: if information about the critical parameters is available (for a large number substances one can find it, for example, in [119]), we can apply the van der Waals equation without exact knowledge of the microscopic interaction potential (assuming, however, its two-parameter spherically symmetric form). Note also that according to (5.5) and (5.8) it is impossible to compress the liquid beyond three times its critical density.

Let us introduce the reduced variables

$$\rho^* = \frac{\rho}{\rho_c}, \quad T^* = \frac{T}{T_c}, \quad p^* = \frac{p}{p_c} \quad (5.9)$$

Then the van der Waals equation combined with (5.8) reads:

$$p^* = \frac{1}{Z_c} \left[-\frac{9}{8} \rho^{*2} + \frac{3\rho^* T^*}{3 - \rho^*} \right], \quad \rho^* < 3 \quad (5.10)$$

where

$$Z_c \equiv \frac{p_c}{\rho_c k_B T_c} \quad (5.11)$$

is the critical compressibility factor. By applying Eq. (5.10) to the critical point $p_c^* = \rho_c^* = T_c^* = 1$, we conclude that all fluids, that can be described by the van der Waals equation of state, have the universal critical compressibility factor

$$Z_c^{\text{vdW}} = \frac{3}{8} = 0.375$$

Then (5.10) reads

$$p^* = -3\rho^{*2} + \frac{8\rho^*T^*}{3 - \rho^*} \quad (5.12)$$

This equation contains no individual characteristics of a substance; it is a manifestation of the law of corresponding states studied in Sect. 3.7. All gases with the same values of two out of the three parameters p^* , ρ^* , T^* have the same value of the third parameter. Van der Waals isotherms are shown in Fig. 5.2 for $T^* < 1$, $T^* = 1$, and $T^* > 1$. Each subcritical ($T^* < 1$) isotherm possesses a loop containing an unstable part corresponding to negative compressibility. This loop has to be replaced by a "Maxwell construction" that manifests the equality of the chemical potentials of the two coexisting phases:

$$\int_{\rho^{*v}}^{\rho^{*l}} \frac{1}{\rho^*} dp^* = 0 \quad (5.13)$$

where ρ^{*v} and ρ^{*l} are the densities of the coexisting phases. The part of the van der Waals curve $p^*(\rho^*)_{T^*}$ between these two values is replaced by a horizontal line $p^* = p_{\text{sat}}^*(T^*)$, where the quantity on the right-hand side is the saturation pressure at temperature T^* .

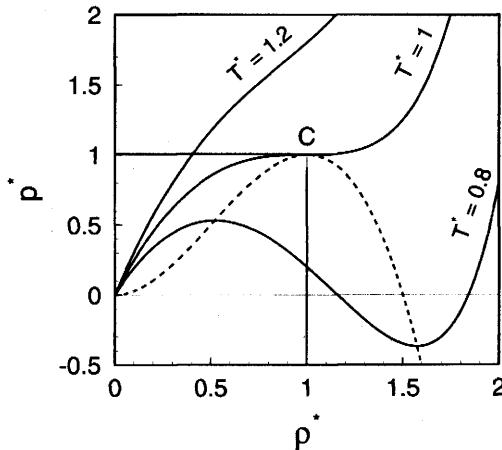


Fig. 5.2. Van der Waals isotherms for $T^* = 0.8$, $T^* = 1$, $T^* = 1.2$ in dimensionless units (solid lines). Dashed curve is a spinodal, C is the critical point

The locus of points where the compressibility becomes infinite $\partial p^* / \partial \rho^* = 0$ corresponds to a *spinodal*. For the van der Waals fluid the spinodal equation reads

$$T^* = \frac{\rho^*}{4}(3 - \rho^*)^2, \quad 0 < \rho^* < 3 \quad (5.14)$$

The maximum of the spinodal coincides with the critical point. The locus of coexistence points satisfying the Maxwell construction is called a *binodal*.

5.3 First-order perturbation theories

In this section we give a generalized description of the perturbation approach. For simplicity we restrict ourselves to first-order perturbation theories. There exist several possibilities to formulate such an approach and an expansion parameter can be chosen in different ways. In what follows we will use the technique of Mayer functions. A Mayer function of potential $u(r)$ is defined as

$$f(r) = e^{-\beta u(r)} - 1 \quad (5.15)$$

It is clear that the range of $f(r)$ coincides with the range of $u(r)$. We write the interaction potential as the sum of a reference part $u_0(r)$ and a perturbation $u_1(r)$:

$$u(r) = u_0(r) + u_1(r)$$

The perturbation is considered to be small; the exact meaning of “small perturbation” will become clear below. The total interaction energy can be written

$$U_N = U_N^0 + \sum_{i < j} u_1(r_{ij})$$

where U_N^0 is the interaction energy of the reference model. The configuration integral is

$$Q_N = \int e^{-\beta U_N^0} e^{-\beta \sum_{i < j} u_1(r_{ij})} d\mathbf{r}^N \quad (5.16)$$

With the help of the Mayer function of the perturbation

$$f_{ij} = e^{-\beta u_1(r_{ij})} - 1 \quad (5.17)$$

the second exponential in (5.16) can be written

$$e^{-\beta \sum_{i < j} u_1(r_{ij})} = \prod_{i < j} (1 + f_{ij}) = 1 + [f_{12} + f_{13} + f_{23} + \dots] +$$

$$[f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + \dots] + [f_{12}f_{13}f_{23} + \dots] + \dots$$

Each square bracket represents a sum over all connected products of the same order. Substitution of this series into (5.16) yields the group expansion of the configuration integral.

In our perturbation approach we assume f_{ij} to be small and cut off the series at the second term:

$$Q_N = Q_N^0 + Q_N^0 \int \frac{e^{-\beta U_N^0}}{Q_N^0} \sum_{i < j} f_{ij} \, d\mathbf{r}^N$$

In the integral on the right-hand side one can recognize averaging of the pairwise additive function $\sum_{i < j} f_{ij}$ over the reference system. The theorem of averaging yields

$$Q_N = Q_N^0 \left[1 + \frac{N^2}{2V} \int f_{12} g_0(r_{12}) \, d\mathbf{r}_{12} \right]$$

where $g_0(r)$ is the pair correlation function of the reference system.

The free energy linearized in the perturbative term reads:

$$\mathcal{F} = \mathcal{F}_0 - \frac{k_B T}{2} N \rho \int f(r) g_0(r) \, d\mathbf{r} \quad (5.18)$$

where $\mathcal{F}_0$ refers to the reference system. This form of the perturbation expansion can be particularly useful for systems in which potential u_1 is large and positive (e.g. charged colloidal particles); its Mayer function nevertheless remains bounded. In liquids u_1 refers to attractive interactions and it is usually assumed that $\beta\epsilon \ll 1$, where ϵ is the depth of $u_1(r)$. Then expanding the Mayer function one obtains

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{2} N \rho \int u_1(r) g_0(r) \, d\mathbf{r} \quad (5.19)$$

This is an example of the energy route to thermodynamics. From our assumptions it follows that (5.19) is a high-temperature approximation. It is easy to verify that this expression is similar to the van der Waals result (5.2). An important observation is that the first-order perturbation term (of van der Waals type) changes the energy of the system without changes in entropy (structure). This term yields the average contribution of attractive interactions to the free energy, and is often called the *mean-field term*, and the free energy expansion truncated at the first order is called a *mean-field theory*.

The higher-order terms take into account effects of changing structure resulting from the perturbation. If the density is high, as in liquids, these changes in structure become increasingly difficult since particles are closely packed. Therefore, at high densities the higher-order perturbation terms become small and the perturbation expansion converges rapidly even if $\beta\epsilon$ is not small. This is one of the main reasons for the success of the perturbation approach in the theory of liquids. At lower densities, convergence of the perturbation expansion is slow and the first-order scheme is not sufficient.

We have discussed a general construction of a first order perturbation theory. It remains to study how to choose a reference model and how to

calculate its properties: $\mathcal{F}_0$ and $g_0(r)$. From the ideas of van der Waals we know that a reasonable choice of the reference model must include a repulsive part of the interaction potential.² Then the actual reference model with soft-core repulsion can be represented by a hard-sphere system with some effective hard-sphere diameter d .

One of the first decomposition schemes was proposed by Barker and Henderson [8]. It reads

$$u_0(r) = \begin{cases} u(r) & \text{for } r < \sigma \\ 0 & \text{for } r \geq \sigma \end{cases} \quad (5.20)$$

and

$$u_1(r) = \begin{cases} 0 & \text{for } r < \sigma \\ u(r) & \text{for } r \geq \sigma \end{cases} \quad (5.21)$$

Although the difference between $u_0(r)$ and the hard-sphere potential can be large, the difference between their Mayer functions

$$\Delta f = f_0 - f_d$$

can be quite small. Δf has the form of an oscillographic “blip”, which is nonzero only over a short range of distances as shown in Fig. 5.3. The soft core is treated by means of an effective hard-sphere system with effective diameter satisfying the integral condition³

$$\int_0^\infty \Delta f \, dr = 0 \quad (5.22)$$

which yields

$$d(T) = \int_0^\infty \left[1 - e^{-\beta u_0(r)} \right] dr \quad (5.23)$$

Thus, in the Barker–Henderson theory the effective diameter is temperature-dependent but not density-dependent. For a Lennard–Jones fluid (5.23) can be accurately approximated by an algebraic formula found by Lu et al. [97] by fitting to the Monte Carlo simulation of the coexistence curve

$$d(T) = \frac{a_1 T + b_1}{a_2 T + a_3} \sigma \quad (5.24)$$

² In the van der Waals theory it is represented by the hard-sphere potential, i.e. the soft core is neglected.

³ A rigorous derivation of (5.23) will be given in the next section; it appears to be a first-order approximation for the effective diameter given by the Weeks–Chandler–Andersen theory.

where

$$a_1 = 0.56165 \frac{k_B}{\epsilon}, \quad a_2 = 0.60899 \frac{k_B}{\epsilon}, \quad a_3 = 0.92868, \quad b_1 = 0.9718$$

Finally, the quantities in (5.19) related to the reference model are approximated as

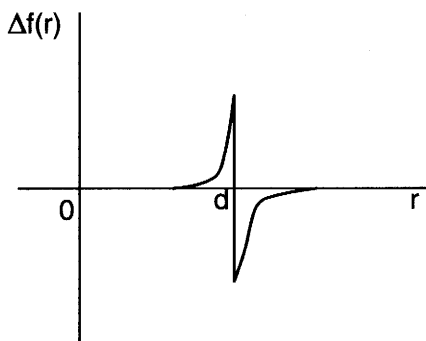


Fig. 5.3. Function $\Delta f = f_0 - f_d$

$$\mathcal{F}_0 \approx \mathcal{F}_d, \quad g_0(r) \approx g_d(r)$$

5.4 Weeks–Chandler–Andersen theory

Probably the most successful of the perturbation theories is that of Weeks, Chandler and Andersen (WCA) [146]. WCA proposed the following decomposition of the interaction potential (see Fig. 5.4):

$$u_0(r) = \begin{cases} u(r) + \epsilon & \text{for } r < r_m \\ 0 & \text{for } r \geq r_m \end{cases} \quad (5.25)$$

$$u_1(r) = \begin{cases} -\epsilon & \text{for } r < r_m \\ u(r) & \text{for } r \geq r_m \end{cases} \quad (5.26)$$

where ϵ is the depth of the potential and r_m the corresponding value of r : $u(r_m) = -\epsilon$. This is an excellent division because all strongly varying parts of the potential are subsumed by the reference model, whereas $u_1(r)$ varies slowly and therefore the importance of fluctuations in the free energy expansion (the second-order term) is reduced.

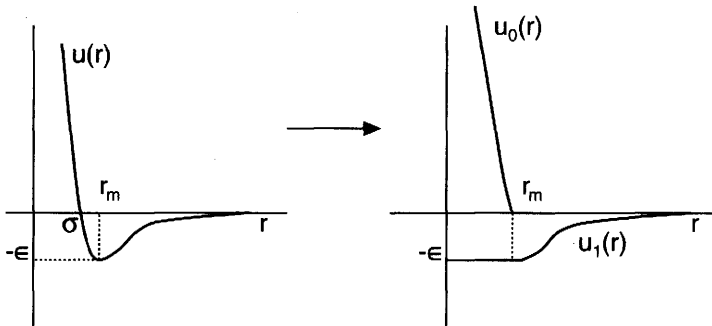


Fig. 5.4. Weeks-Chandler-Andersen decomposition of the interaction potential $u(r)$; $u_0(r)$ is the reference interaction, $u_1(r)$ is the perturbation

5.4.1 Reference model

We now discuss the properties of the reference model, and their description in terms of an equivalent hard-sphere system using the technique of Mayer functions. Although the difference between the soft-core potential u_0 and the hard-sphere potential u_d can be large (even infinite), the difference between their Mayer functions

$$f_0 = e^{-\beta u_0} - 1 \quad \text{and} \quad f_d = e^{-\beta u_d} - 1$$

can be small. Indeed, if we choose the diameter d in a reasonable way, then for a harshly repulsive u_0 its Mayer function f_0 will differ from f_d only over a small domain (see Fig. 5.5).

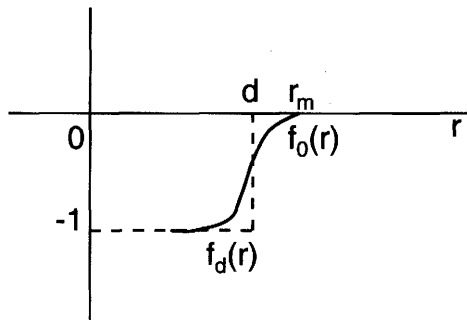


Fig. 5.5. Mayer function $f_0(r)$ of the original reference system (solid line), and of hard spheres $f_d(r)$ (dashed line)s

Let us assume for a moment that d has been chosen, and consider a “test system” characterized by the Mayer function

$$f_\nu(r) = f_d(r) + \nu \Delta f(r), \quad \Delta f(r) = f_0 - f_d \quad (5.27)$$

where $0 \leq \nu \leq 1$. By changing ν gradually from 0 to 1 we change f_ν from f_d to f_0 :

$$f_{\nu=0} = f_d, \quad f_{\nu=1} = f_0$$

In fact, by (5.27) we have introduced a family of systems parametrized by ν . By choosing the Mayer function f_ν we fix the corresponding interaction potential u_ν :

$$e^{-\beta u_\nu(r)} - 1 = f_d(r) + \nu \Delta f(r) \quad (5.28)$$

The configuration integral of a ν -system is

$$Q_\nu = \int e^{-\beta U_\nu} d\mathbf{r}^N, \quad U_\nu = \sum_{i < j} u_\nu(r_{ij})$$

The derivative of the free energy $\mathcal{F}_\nu = -k_B T \ln Q_\nu$ with respect to ν is

$$\frac{\partial \mathcal{F}_\nu}{\partial \nu} = -\frac{k_B T}{Q_\nu} \int \frac{\partial}{\partial \nu} e^{-\beta U_\nu} d\mathbf{r}^N = \left\langle \sum_{i < j} \frac{\partial u_\nu(r_{ij})}{\partial \nu} \right\rangle_\nu$$

Using the theorem of averaging we obtain

$$\frac{\partial \mathcal{F}_\nu}{\partial \nu} = \frac{\rho^2}{2} \int \frac{\partial u_\nu}{\partial \nu} g_\nu d\mathbf{r}_1 d\mathbf{r}_2 \quad (5.29)$$

where g_ν is the pair correlation function of the ν -system. Finding $du_\nu/d\nu$ from (5.28) we obtain

$$\frac{\partial \mathcal{F}_\nu}{\partial \nu} = -\frac{1}{2} \rho^2 k_B T V \int \Delta f(r) e^{\beta u_\nu(r)} g_\nu(r) d\mathbf{r}$$

Using the cavity function

$$y_\nu(r) = e^{\beta u_\nu(r)} g_\nu(r)$$

we rewrite this result as

$$\frac{\partial \mathcal{F}_\nu}{\partial \nu} = -\frac{1}{2} \rho^2 k_B T V \int \Delta f(r) y_\nu(r) d\mathbf{r}$$

Integration of both parts with respect to ν from $\nu = 0$ to $\nu = 1$ yields

$$\frac{\mathcal{F}_0 - \mathcal{F}_d}{-k_B T V} = \frac{\rho^2}{2} \int_0^1 d\nu \int d\mathbf{r} \Delta f(r) y_\nu(r) \quad (5.30)$$

This is an *exact* relation. The right-hand side gives the difference between the reference free energy and the free energy of an equivalent hard-sphere system. Our aim is to choose the latter in such a way that this difference is minimized. For a reasonable choice of a hard-sphere diameter d the relative difference

$$\Delta y_\nu(r) = \frac{y_\nu(r) - y_d(r)}{y_d(r)}$$

will be small. Substituting $y_\nu(r) = y_d(r) + y_d(r)\Delta y_\nu(r)$ into (5.30) we obtain

$$\frac{\mathcal{F}_0 - \mathcal{F}_d}{-k_B TV} = \frac{\rho^2}{2} \int dr B_d(r) + \frac{\rho^2}{2} \int_0^1 d\nu \int dr B_d(r) \Delta y_\nu(r) \quad (5.31)$$

where

$$B_d(r) = y_d(r)\Delta f(r)$$

is called a “blip” function. Note that $B_d(r)$ and not simply $\Delta f(r)$ appears on the right-hand side of (5.31) (compare with the Barker–Henderson theory (5.22)).⁴ Both $\Delta f(r)$ and (consequently) $B_d(r)$ are nonzero only over a small range of distances near $r = d$ (recall the Barker–Henderson theory and Fig. 5.3). Let ξd denote the total range of $B_d(r)$ (see Fig. 5.6), i.e.

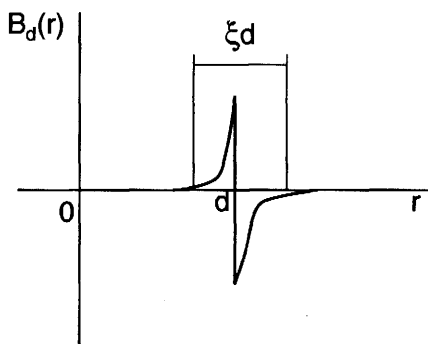


Fig. 5.6. Blip function $B_d(r)$. The range of distances where it appreciably differs from zero is ξd ; ξ is a softness parameter

⁴ Equation (5.31) is a functional Taylor series in $\Delta f(r)$ for the functional $\mathcal{A} \equiv \frac{\mathcal{F}}{-k_B TV}$:

$$\begin{aligned} \mathcal{A}[f_0] &= \mathcal{A}[f_d] + \int dr \left(\frac{\Delta \mathcal{A}}{\Delta f(r)} \right)_{f_d} \Delta f(r) \\ &\quad + \frac{1}{2} \int dr dr' \left(\frac{\Delta^2 \mathcal{A}}{\Delta f(r) \Delta f(r')} \right)_{f_d} \Delta f(r) \Delta f(r') + \dots \end{aligned}$$

with $\left(\frac{\Delta \mathcal{A}}{\Delta f(r)} \right)_{f_d(r)} = \frac{e^2}{2} y_d(r)$. We discuss functional derivatives in Chap. 9.

$$\int_0^\infty |B_d(r)| dr \equiv \xi d$$

This relationship defines the softness parameter ξ . In view of the obvious identity $\xi d = \xi d \times 1$, ξd also gives the order of the range of distances for which the blip function is finite. Therefore

$$\xi \equiv \frac{1}{d} \int_0^\infty |B_d(r)| dr \approx \frac{1}{4\pi d^3} \int |B_d(r)| dr$$

For harshly repulsive reference potentials $\xi \ll 1$; it vanishes for the hard-sphere interaction (in this case $\Delta f = B_d = 0$). Apparently, the first term in (5.31) is of order ξ . A natural choice of the effective hard-sphere diameter will be the one that makes the first term vanish:

$$\int d\mathbf{r} B_d(r) = \int d\mathbf{r} y_d(r) [e^{-\beta u_0} - e^{-\beta u_d}] = 0 \quad (5.32)$$

With this choice of d , Weeks, Chandler and Andersen showed [146] that the second term in (5.31) is of order ξ^4 . We have

$$\mathcal{F}_0 = \mathcal{F}_d[1 + O(\xi^4)]$$

(note that in the Barker–Henderson scheme $\mathcal{F}_0 = \mathcal{F}_d[1 + O(\xi^2)]$) and

$$y_0(r) = y_d(r)[1 + O(\xi^2)]$$

From the latter relation we obtain an approximation for the reference pair correlation function:

$$g_0(r) = e^{-\beta u_0(r)} y_d(r)[1 + O(\xi^2)] \quad (5.33)$$

Compared to the van der Waals and Barker–Henderson theories, the WCA is more subtle, for it takes into account the difference between g_0 and g_d , whereas the other two set $g_0 = g_d$. Physically, the cavity function $y_0(r; \rho, T)$ gives the correlations that exist in the reference system beyond the range of the reference interaction $u_0(r)$; $y_0(r)$ is a more slowly varying function of r than $g_0(r)$.

To find the physical meaning of (5.32) we rewrite it as

$$\int g_0(r) d\mathbf{r} = \int g_d(r) d\mathbf{r}$$

from which it follows that the structure factors of the reference model and the effective hard spheres must be equal at the long-wavelength limit implying the equality of isothermal compressibilities (see (3.14)):

$$\chi_0 = \chi_d \quad (5.34)$$

The function $y_d(r)$ can be found from one of the integral theories of correlation functions. Note that $y_d(r) = g_d(r)$ for $r > d$, as follows from the definition of the cavity function, and at $r = d$, y_d remains continuous, whereas g_d has a finite jump, becoming zero for $r < d$.

5.4.2 Total free energy

To complete the formulation of the WCA theory we combine the results for the reference system with the general perturbation expression (5.19):

$$\mathcal{F} = \mathcal{F}_d + \frac{1}{2} N \rho \int u_1(r) e^{-\beta u_0(r)} y_d(r) dr \quad (5.35)$$

where d is defined from

$$\int dr y_d(r) [e^{-\beta u_0} - e^{-\beta u_d}] = 0 \quad (5.36)$$

From (5.36) one can see that in the WCA theory the effective diameter depends both on the temperature and density, and therefore must be found by iteration of the integral equation (5.36). The WCA theory shows very good agreement with computer simulations by virtue of its fast convergence, $O(\xi^4)$, in the free energy.

We now show that the Barker–Henderson formula (5.23) is an approximation of the WCA result (5.36). Because the function

$$\Delta f = e^{-\beta u_0} - e^{-\beta u_d}$$

is nonzero only over a narrow range of distances, we expand $r^2 y_d(r)$ about $r = d$:

$$r^2 y_d(r) = a_0 + a_1(r - d) + a_2(r - d)^2 + \dots$$

with

$$a_k = \frac{1}{k!} \left(\frac{d^k}{dr^k} r^2 y_d(r) \right)_{r=d}$$

Equation (5.36) becomes

$$\sum_{k=0}^{\infty} a_k \int_0^{\infty} dr (r - d)^k \Delta f(r) = 0$$

The series converges rapidly. Retaining only the first term (with $k = 0$), we obtain

$$\int_0^{\infty} dr \Delta f(r) = 0$$

which coincides with the Barker–Henderson formula.

5.5 Song and Mason theory

In 1989 Song and Mason (SM) [133] formulated a new variant of the perturbation theory in which the starting point is the virial equation (3.10) (recall that thermodynamics in the WCA is derived via the energy route):

$$\frac{p}{\rho k_B T} = 1 - \frac{2\pi}{3} \frac{\rho}{k_B T} \int_0^\infty u'(r) g(r; \rho, T) r^3 dr \quad (5.37)$$

Using the Mayer function representation we write

$$u'(r) = -k_B T f'(r) e^{\beta u(r)} \quad (5.38)$$

where $f(r)$ is the Mayer function of the potential u . Then

$$\int_0^\infty u'(r) g(r; \rho, T) r^3 dr = -k_B T \int_0^\infty f'(r) y(r; \rho, T) r^3 dr$$

where $y(r; \rho, T)$ is the cavity function of the system. The latter integral can be rewritten as

$$-k_B T \int_0^\infty f'(r) r^3 dr - k_B T \int_0^\infty f'(r) [y(r; \rho, T) - 1] r^3 dr$$

The first term integrated by parts yields the second virial coefficient of the system $B(T)$:

$$-k_B T \int_0^\infty f'(r) r^3 dr = -\frac{3k_B T}{2\pi} B(T)$$

where we used the short-range nature of the Mayer function. Thus, the virial equation takes the form

$$\frac{p}{\rho k_B T} = 1 + \rho B + \rho I, \quad (5.39)$$

where

$$I(\rho, T) = \frac{2\pi}{3} \int_0^\infty r^3 f'(r) [y(r; \rho, T) - 1] dr \quad (5.40)$$

We have separated out the term with the second virial coefficient, which is calculated exactly. Recalling the virial expansion, we can say that $\rho I(\rho, T)$ represents the sum of the infinite virial series starting with the third virial coefficient.

The following discussion is devoted to the evaluation of $I(\rho, T)$. One can expect that I is dominated by repulsion over the whole (ρ, T) domain. The reasons for this expectation are as follows. At high densities, $\rho > \rho_c$, the pressure of a liquid or a highly compressed gas is large and positive, so I for all temperatures must make a large and positive contribution, which obviously must come from repulsion. At lower densities, $\rho < \rho_c$ one can think about the virial expansion starting with the third virial coefficient. If the temperature is above T_c the third, fourth, and fifth virial coefficients are all positive or small [100]. Thus, I is again positive and dominated by repulsion. Below T_c at low densities we have a dilute vapor, and its behavior can be largely described by $B(T)$, whereas the contribution of I is negligible.

Based on this observation, to calculate $I(\rho, T)$ we apply the perturbation approach using the WCA decomposition of the potential (5.25)–(5.26). In the domain $r < r_m$ the derivative of the Mayer function $f'(r)$ has a sharp positive peak at some r_0 close to r_m , whereas the cavity function $y(r; \rho, T)$ monotonically decreases. In the region $r > r_m$, $f'(r)$ is negative and asymptotically tends to zero, whereas $[y(r; \rho, T) - 1]$ oscillates about zero (see Fig. 5.7). In view of these oscillations we can set the upper limit of the integral in (5.40) equal to r_m . For $r < r_m$, $f'(r) = f'_0(r) \exp(\beta\epsilon)$, where the reference Mayer function

$$f_0(r) = e^{-\beta u_0(r)} - 1$$

is equal to zero for $r > r_m$. In the framework of the perturbation approach we expand

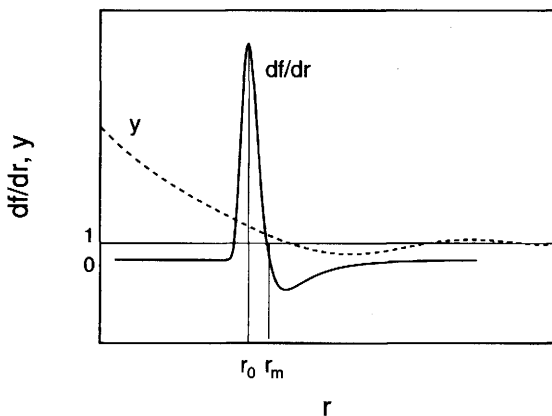


Fig. 5.7. Behavior of $f'(r)$ and $y(r)$ for a typical interaction potential

$$f'(r) \simeq f'_0(r)(1 + \beta\epsilon), \quad r < r_m$$

In the same domain $r < r_m$ one can replace the function $y(r)$ by its repulsive counterpart

$$y_0(r) = e^{\beta u_0(r)} g_0(r)$$

where $g_0(r; \rho, T)$ is the reference pair correlation function, because $y(r)$ and $y_0(r)$ are quite similar. (Note that in the van der Waals theory the similarity between correlation functions $g(r)$ and $g_0(r)$ was exploited, whereas SM use the similarity between cavity functions.) Thus, I can be approximated as

$$I \simeq \frac{2\pi}{3} \int_0^{r_m} dr f'_0(r) (1 + \beta\epsilon) [y_0(r; \rho, T) - 1] r^3 \quad (5.41)$$

The function $f'_0(r)$ has a sharp peak at the same $r_0 < r_m$ as $f'(r)$, and therefore the major contribution to the integral comes from the vicinity of r_0 , where y_0 behaves to first order as a straight line:

$$y_0(r; \rho, T) = y_0(R; \rho, T) + \left. \frac{dy_0}{dr} \right|_R (r - R) + \dots$$

with a negative slope $\left. \frac{dy_0}{dr} \right|_R$; R is a point near r_0 which will be specified below. Substitution of this expression into (5.41) gives $I \simeq I_0 + I_+ + I_- + \dots$, where

$$\begin{aligned} I_0 &= \frac{2\pi}{3} [y_0(R; \rho, T) - 1] \int_0^{r_m} dr f'_0(r) r^3 \\ I_+ &= \frac{2\pi}{3} \beta\epsilon [y_0(R; \rho, T) - 1] \int_0^{r_m} dr f'_0(r) r^3 \\ I_- &= \frac{2\pi}{3} \left. \frac{dy_0}{dr} \right|_R \int_0^{r_m} dr f'_0(r) r^3 (r - R) \end{aligned}$$

One can see that $I_+ > 0$ and $I_- < 0$ at all temperatures (for a reasonable choice of R). At intermediate to high temperatures both I_+ and I_- are negligible compared to I_0 ; I_+ becomes small because of $\beta\epsilon$ and I_- becomes small because in this temperature domain $y_0 \rightarrow 1$, $dy_0/dr \rightarrow 0$. At low temperatures they are not individually negligible but cancel one another. Thus,

$$I \simeq I_0 = \alpha[y_0(R) - 1] \quad (5.42)$$

where

$$\alpha(T) = \frac{2\pi}{3} \int_0^{r_m} dr f'_0(r) r^3 = 2\pi \int_0^{r_m} (1 - e^{-\beta u_0}) r^2 dr \quad (5.43)$$

appears to be the second virial coefficient of the reference system. Since the reference interaction is strongly repulsive, y_0 is fairly insensitive to the particular form of the repulsive potential, and therefore can be approximated by a similar function appropriate to a hard-sphere system of some effective diameter d :

$$y_0(R) \simeq y_d(d) \quad (5.44)$$

For $y_d(d)$ we use the Carnahan–Starling formula

$$y_d(d) = \frac{4 - 2\phi_d}{4(1 - \phi_d)^3}, \quad \phi_d = \frac{\pi}{6} \rho d^3$$

Substituting (5.42)–(5.44) into (5.39), we obtain the SM equation of state:

$$\frac{p}{\rho k_B T} = 1 + \rho B + \rho \alpha [y_d(d) - 1] \quad (5.45)$$

It contains three parameters: the second virial coefficient of the original system (B), the second virial coefficient of the reference system (α), and the effective hard-sphere diameter (d). The first two are given explicitly in terms of the intermolecular potential $u(r)$; they are functions of temperature only.

The choice of an effective hard-sphere diameter is not dictated by the SM model, but represents an independent problem. Recall that in the WCA theory, d is found by minimizing the free energy difference between the reference model and the effective hard spheres, and results in equality of their isothermal compressibilities; d depends on temperature and density and is calculated numerically.

To preserve the complete analyticity of their model, Song and Mason propose an interpolation formula for d . We will discuss it in terms of the van der Waals covolume

$$b = \frac{2\pi}{3} d^3$$

Instead of presenting a definite expression for b , let us examine two limiting cases: low and high temperature regimes. At low temperatures ($T \rightarrow 0$) the WCA theory (Eq. (5.36)) gives $d \rightarrow r_m$; therefore

$$b(T \rightarrow 0) = \frac{2\pi}{3} r_m^3$$

Let us discuss the high temperature range, namely the vicinity of the Boyle temperature, T_B , where by definition, $B(T_B) = 0$. For high T the behavior of the second virial coefficient can be approximated by the expression resulting from the van der Waals theory. Using the definition of $B(T)$, we have:

$$B(T) = 2\pi \int_0^\sigma r^2 dr + 2\pi \int_\sigma^\infty (1 - e^{-\beta u_1}) r^2 dr \approx \frac{2\pi}{3} \sigma^3 + 2\pi\beta \int_\sigma^\infty u_1(r) r^2 dr$$

Thus,

$$B(T) = b - \frac{a}{k_B T} \quad (5.46)$$

with constant a and b ; a is due to the background interaction and b is responsible for the excluded volume effect. Then $\frac{dB}{dT} = \frac{1}{T} \frac{a}{k_B T}$ and expression (5.46) can be written in the form

$$b(T \rightarrow \text{high}) = B + T \frac{dB}{dT} = 2\pi \int_0^\infty [1 - (1 + \beta u) e^{-\beta u}] r^2 dr$$

It is obvious that for low temperatures this expression is not valid: for $T \rightarrow 0$ it gives an infinite value of b . This difficulty can be avoided and we can satisfy both temperature limits if we assume that the excluded volume

effect is due only to the repulsive forces. Then u_0 can be written instead of u , and the upper limit of integration becomes r_m . This yields the expression for b :

$$b(T) = 2\pi \int_0^{r_m} [1 - (1 + \beta u_0)e^{-\beta u_0}] r^2 dr \quad (5.47)$$

which satisfies both temperature limits and behaves smoothly in between. Thus, the effective diameter d depends only on temperature, whereas in the WCA theory $d = d(T, \rho)$.⁵ Finally we write the full set of equalities of the SM theory, applying for $y_d(d)$ the Carnahan–Starling approximation:

$$\frac{p}{\rho k_B T} = 1 + \rho B + \rho \alpha \left[\frac{8(8 - b\rho)}{(4 - b\rho)^3} - 1 \right] \quad (5.48)$$

$$B(T) = 2\pi \int_0^\infty (1 - e^{-\beta u}) r^2 dr \quad (5.49)$$

$$\alpha(T) = 2\pi \int_0^{r_m} (1 - e^{-\beta u_0}) r^2 dr \quad (5.50)$$

$$b(T) = 2\pi \int_0^{r_m} [1 - (1 + \beta u_0)e^{-\beta u_0}] r^2 dr \quad (5.51)$$

Note that the SM equation is fifth-order in density (the van der Waals equation is cubic). Figure 5.8 shows the compressibility factor $Z = p/\rho k_B T$ vs. density $\rho\sigma^3$ for an Lennard–Jones fluid for several reduced temperatures $t = k_B T/\epsilon$. The critical temperature $t_c \approx 1.3$, so that a part of the isotherm for $t = 0.75$ is located in a metastable region with negative pressures, where the Maxwell construction must be applied. Other two isotherms correspond to the gas at $t > t_c$. Simulation results [69] demonstrate good agreement with theoretical predictions, which according to [133] are better than 1%.

5.6 Perturbation approach to surface tension

The perturbation approach turns out to be useful not only for the bulk properties but also for the analysis of interface phenomena, and in particular for the surface tension [63]. When the liquid–vapor system has a temperature not too close to T_c , the Fowler approximation can be used:

$$\gamma = \frac{\pi}{8} (\rho^l)^2 \int_0^\infty dr r^4 u'(r) g(r; \rho^l) \quad (5.52)$$

⁵ In view of the preceding remark one is not restricted to this interpolation formula and can use other recipes, like Barker–Henderson or WCA.

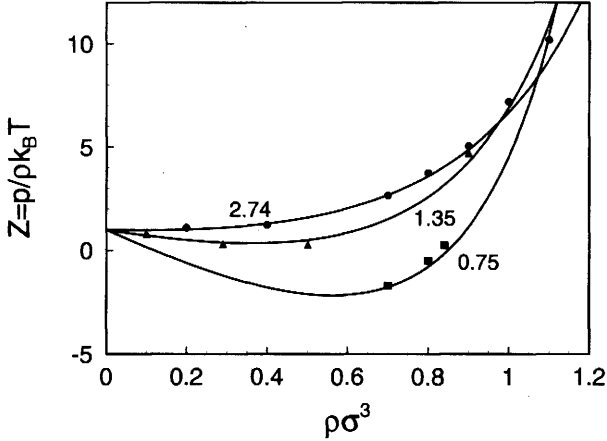


Fig. 5.8. Compressibility factor $Z = p/\rho k_B T$ vs. density $\rho\sigma^3$ for a Lennard-Jones fluid. Solid lines: SM theory, symbols: simulation results [69]. Labels correspond to the value of the reduced temperature $t = k_B T/\epsilon$

where the pair correlation function of the bulk liquid strongly depends on the liquid density ρ^l . As in the SM theory we use a representation of $u'(r)$ in terms of the Mayer function (5.38), which yields

$$\gamma = \frac{\pi}{8} (\rho^l)^2 [A_1(T) + A_2(T, \rho^l)], \quad (5.53)$$

where

$$A_1(T) = 4k_B T \int_0^\infty dr f(r) r^3 \quad (5.54)$$

$$A_2(T, \rho^l) = -k_B T \int_0^\infty dr f'(r) r^4 [y(r; \rho^l) - 1] \quad (5.55)$$

The quantity A_2 has a structure similar to I in the SM theory (cf. (5.40)). Repeating the arguments based on the WCA decomposition and the perturbation ideas, we find that A_2 is dominated by repulsions, and can be approximated by

$$A_2 \simeq 4k_B T [y_0(R; \rho^l) - 1] \int_0^{r_m} dr f_0(r) r^3$$

With the hard-sphere approximation for the reference cavity function

$$y_0(R; \rho^l) \simeq y_d(d; \rho^l),$$

we finally derive an analytical expression for the surface tension explicit in density:

$$\gamma = \frac{\pi}{2} (\rho^l)^2 k_B T \left\{ \int_0^\infty dr f(r) r^3 + [y_d(d; \rho^l) - 1] \int_0^{r_m} dr f_0(r) r^3 \right\} \quad (5.56)$$

This result must be supplemented by an equation of state for determination of $\rho^l(T)$ and by an expression for the effective hard-sphere diameter; ρ^l can be found from (5.48) by imposing the conditions of phase equilibrium:

$$p(\rho^l, T) = p(\rho^v, T)$$

$$\mu(\rho^l, T) = \mu(\rho^v, T)$$

To be consistent with the Fowler approximation we must treat the vapor as an ideal gas with a vanishingly small density. In this case we need only the first equation: if it is satisfied, the equality of chemical potentials (to the same degree of accuracy in ρ^v/ρ^l) follows automatically. Then $\rho^l(T)$ becomes a solution of the fourth-order algebraic equation $p(\rho^l, T) = 0$

$$\alpha(T)\rho^l[y_d(d; \rho^l) - 1] = -B(T)\rho^l - 1 \quad (5.57)$$

which reflects the incompressibility of the liquid phase at sufficiently low temperatures. Calculations of the surface tension using (5.56) (with ρ^l given by (5.57)) for the Lennard-Jones system are presented in Fig. 5.9. For the effective hard-sphere diameter the Barker-Henderson formula (5.23) is chosen. The reduced surface tension $\gamma\sigma^2/\epsilon$ is shown as a function of the reduced temperature $k_B T/\epsilon$. Chapela et al. [22] performed Monte Carlo and molecular dynamics simulations of a gas-liquid interface for a Lennard-Jones fluid. In simulations the Lennard-Jones potential was truncated at a distance $r_c = 2.5\sigma$. Truncation of a potential at some point of its attractive branch results in reduced surface tension, since the integrated strength of attractive interactions is smaller than that for the full system.

The underestimation of surface tension in simulations by not taking the tail of the potential into account can be quite substantial. It can be eliminated (though not fully) by means of a so-called tail correction. Blokhuis et al. [17] obtained an expression for the tail correction based on the Kirkwood-Buff formula. In Fig. 5.9 we show the simulation results of [22] taking tail corrections into account (triangles). One can see that theoretical predictions are in good agreement with simulations. This is due to the fact that (5.56) is exact in the liquid density.

5.7 Algebraic method of Ruelle

In his book [126] Ruelle proposed a formal algebraic technique, developed further by Zelener, Norman, and Filinov [152], which can be useful for a number of problems in which the perturbation series converges slowly. An example

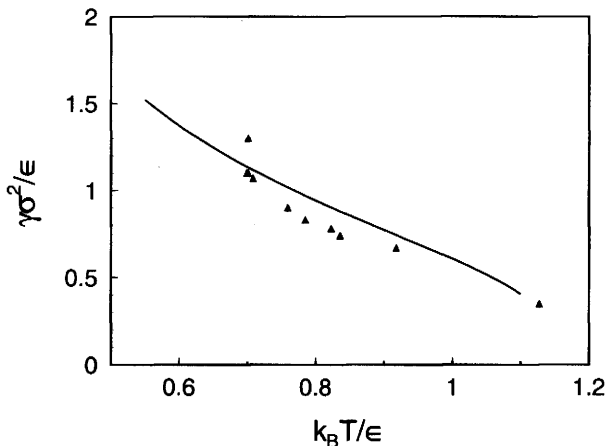


Fig. 5.9. Surface tension of the Lennard-Jones fluid: theoretical predictions (solid line) and computer simulation results of Chapela et al. [22] (triangles)

of such a problem will be given in Chap. 12. Here we discuss the formulation and the main result of Ruelle's technique. We consider an infinite set of arbitrary bounded and integrable real functions that depend on various generalized coordinate vectors $\tilde{\mathbf{r}}_i$, which can include space coordinates, angular coordinates, etc. An infinite sequence of such functions will be denoted by just one letter:

$$\mathbf{a} = \{a_0, a_1(\tilde{\mathbf{r}}_1), \dots, a_n(\tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_n), \dots\} \quad (5.58)$$

We can say that $\mathbf{a}$ is a vector of infinite dimension with coordinates

$$a_0 = \text{const}, a_1(\tilde{\mathbf{r}}_1), \dots, a_n(\tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_n), \dots$$

Vectors $\mathbf{a}$ form a linear space $\mathcal{A}$ since they can be summed component-wise and multiplied by a constant. We introduce some useful notation:

$$\mathbf{a} = \{a(\tilde{\mathbf{R}})_n\}_{n \geq 0}$$

where

$$(\tilde{\mathbf{R}})_n = (\tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_n)$$

In the linear space $\mathcal{A}$ one can introduce multiplication of vectors. Let $\mathbf{q}$ and $\mathbf{a}$ be elements of $\mathcal{A}$. We construct the vector $\mathbf{x}$, whose n -th component is defined as

$$x(\tilde{\mathbf{R}})_n = \sum_{\mathbf{Y} \subset (\tilde{\mathbf{R}})_n} q(\mathbf{Y}) a[(\tilde{\mathbf{R}})_n \setminus (\mathbf{Y})] \quad (5.59)$$

where summation is over all subsequences $\mathbf{Y}$ of coordinate sequence $(\tilde{\mathbf{R}})_n$; $(\tilde{\mathbf{R}})_n \setminus (\mathbf{Y})$ denotes the subsequence obtained by extracting from $(\tilde{\mathbf{R}})_n$ all elements of the subsequence $(\mathbf{Y})$. The sum in (5.59) is finite and contains $\sum_{k=0}^n C_n^k = 2^n$ terms. Therefore, the n -th component of $\mathbf{x}$ contains 2^n terms. Vector $\mathbf{x}$ belongs to $\mathcal{A}$, and we shall say that (5.59) defines multiplication of vectors in the linear space $\mathcal{A}$:

$$\mathbf{x} = \mathbf{q} \times \mathbf{a}$$

This definition implies that multiplication is commutative:

$$\mathbf{x} = \mathbf{q} \times \mathbf{a} = \mathbf{a} \times \mathbf{q}$$

Let us write out several components of vector $\mathbf{x}$:

$$\begin{aligned} x_0 &= q_0 a_0 \\ x(\tilde{\mathbf{r}}_1) &= q_0 a(\tilde{\mathbf{r}}_1) + q(\tilde{\mathbf{r}}_1) a_0 \\ x(\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2) &= q_0 a(\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2) + q(\tilde{\mathbf{r}}_1) a(\tilde{\mathbf{r}}_2) + q(\tilde{\mathbf{r}}_2) a(\tilde{\mathbf{r}}_1) + q(\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2) a_0 \\ &\dots \end{aligned} \tag{5.60}$$

We define a unit element $\mathbf{1}$ in $\mathcal{A}$ such that

$$1_0 = 1, \quad 1(\tilde{\mathbf{R}})_n = 0 \quad \text{for all } n \geq 1$$

Then for every vector $\mathbf{a}$

$$\mathbf{a} = \mathbf{1} \times \mathbf{a} = \mathbf{a} \times \mathbf{1}$$

Thus, we have defined three binary operations in $\mathcal{A}$: summation and multiplication of vectors and multiplication of a vector by a constant. This implies that $\mathcal{A}$ is a commutative linear algebra with a unit element. Let $\mathcal{A}_+$ be a subspace of $\mathcal{A}$ such that all its elements $\mathbf{b}$ are characterized by $b_0 = 0$. Then for any vector $\mathbf{a} \in \mathcal{A}$ and $\mathbf{b} \in \mathcal{A}_+$, the products $\mathbf{b} \times \mathbf{a}$ and $\mathbf{a} \times \mathbf{b}$ obviously belong to $\mathcal{A}_+$. Consider a mapping

$$\Gamma: \mathcal{A}_+ \Rightarrow \mathbf{1} + \mathcal{A}_+$$

which transfers elements from $\mathcal{A}_+$ to elements of $(\mathbf{1} + \mathcal{A}_+)$, defined by

$$\mathbf{a} \equiv \Gamma \mathbf{b} = \mathbf{1} + \mathbf{b} + \frac{\mathbf{b} \times \mathbf{b}}{2!} + \frac{\mathbf{b} \times \mathbf{b} \times \mathbf{b}}{3!} + \dots \tag{5.61}$$

Although (5.61) contains an infinite number of terms, each component of $\Gamma \mathbf{b}$ is a finite sum containing products of components of vector $\mathbf{b}$. This mapping is single-valued; therefore there exists an inverse mapping

$$\Gamma^{-1}: \mathbf{1} + \mathcal{A}_+ \Rightarrow \mathcal{A}_+$$

which for every vector $\mathbf{a}_+ \in \mathcal{A}_+$ is defined by

$$\mathbf{b} \equiv \Gamma^{-1}(\mathbf{1} + \mathbf{a}_+) = \mathbf{a}_+ - \frac{\mathbf{a}_+ \times \mathbf{a}_+}{2} + \frac{\mathbf{a}_+ \times \mathbf{a}_+ \times \mathbf{a}_+}{3} - \dots \quad (5.62)$$

Note that (5.61) and (5.62) have a simple meaning. If b were just a number then (5.61) would become a formal series representation of the exponential function $\Gamma b = e^b$, whereas (5.62) is a series representation of $\ln(1 + a_+)$. Therefore there is a unique solution of the equation

$$\Gamma \mathbf{b} = \mathbf{a}, \quad \text{with } \mathbf{a} = \mathbf{1} + \mathbf{a}_+$$

with components

$$\begin{aligned} b_0 &= 0 \\ b_1(\tilde{\mathbf{r}}_1) &= a_+(\tilde{\mathbf{r}}_1) \\ b_2(\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2) &= a_+(\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2) - a_+(\tilde{\mathbf{r}}_1)a_+(\tilde{\mathbf{r}}_2) \\ &\dots \end{aligned} \quad (5.63)$$

With each $\mathbf{a} \in \mathcal{A}$ we associate a power series

$$a(z) = \sum_{n=0}^{\infty} \frac{z^n}{n!} a_n \quad (5.64)$$

where z is a formal parameter and the numerical coefficients a_n are constructed in the following way:

$$a_0 = 1, \quad a_n = \int d^n \tilde{\mathbf{r}} a(\tilde{\mathbf{R}})_n, \quad n \geq 1 \quad (5.65)$$

It is easy to see that $a(z)$ is the generating function for the sequence $\{a_n\}$ (a_n are just real numbers). Ruelle [126] proved a theorem stating that if

$$\mathbf{x} = \mathbf{q} \times \mathbf{a}, \quad \mathbf{x}, \mathbf{q}, \mathbf{a} \in \mathcal{A}$$

then the corresponding power series $x(z)$, $q(z)$ and $a(z)$ (all of the type (5.64)–(5.65)) satisfy the similar relationship:

$$x(z) = q(z)a(z) \quad (5.66)$$

In other words the mapping $\mathbf{a} \Rightarrow a(z)$ is a homomorphism of the algebra $\mathcal{A}$ into the algebra of power series. This implies that all transformations made in one algebra are “copied” in the other. In particular, if $\mathbf{a} = \Gamma \mathbf{b}$ in the algebra $\mathcal{A}$ with the operator Γ defined in (5.61), then

$$a(z) = \Gamma [b(z)] = 1 + b(z) + \frac{[b(z)]^2}{2!} + \frac{[b(z)]^3}{3!} + \dots$$

The right-hand side of this equation is an exponential function $e^{b(z)}$. Thus,

$$a(z) = \exp[b(z)] = \exp \left[\sum_{n=0}^{\infty} \frac{z^n}{n!} b_n \right] \quad (5.67)$$

with

$$b_0 = 0, \quad b_n = \int d^n \tilde{\mathbf{r}} b(\tilde{\mathbf{R}})_n, \quad n \geq 1 \quad (5.68)$$

The components of vector $\mathbf{b}$ in the integrand are *algebraic combinations* of the components of vector $a(\tilde{\mathbf{R}})_n$

$$b(\tilde{\mathbf{R}})_n = \mathcal{R}_n \left[a(\tilde{\mathbf{R}})_n \right] \quad (5.69)$$

constructed unambiguously according to (5.63).

Summarizing, Ruelle's technique makes it possible to represent a series of the type (5.64)–(5.65) as an exponential function of some other series (5.67)–(5.68) without making any a priori assumptions. The advantage of Ruelle's method stems from the fact that usually the series (5.67) converges faster than the original one. This is a very important result because in statistical physics one frequently faces the problem of summing a certain perturbation series for a partition function of the form (5.64).

6. Equilibrium phase transitions

6.1 Classification of phase transitions

Condensation of vapor, evaporation of liquid, melting of a crystal, crystallization of a liquid are examples of phase transitions. Their characteristic common feature is an abrupt change in certain properties. For example, when ice is heated, its state first changes continuously up to the moment when the temperature reaches 0°C (at normal pressure), at which point ice begins transforming into liquid water with absolutely different properties.

The states of a substance between which a transition takes place are called phases. To start a discussion of general features inherent to phase transitions it is necessary to introduce a proper (rigorous) definition. For clues as to how this can be done let us examine the p - T diagram of a fluid depicted schematically in Fig. 6.1.

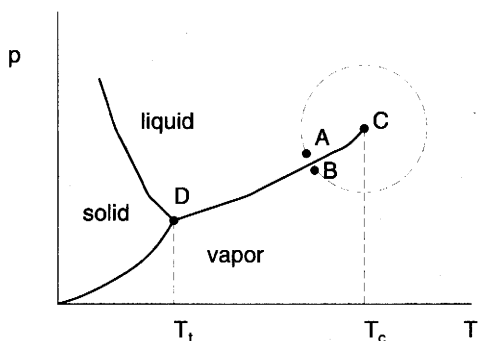


Fig. 6.1. Phase diagram of a fluid

Liquid and vapor coexist along the line connecting the triple point D corresponding to three-phase (solid, liquid, and vapor) coexistence and the critical point C . Below T_c we can easily discriminate between liquid and gas by measuring their density. At T_c the difference between them disappears. The existence of the critical point makes it possible to convert any state A of a liquid phase to any state B of a vapor phase without phase separation by

going round the critical point C along any (dashed) curve that does not intersect the line D–C. By doing so we avoid phase separation, the system always remains continuous, and we cannot identify where the substance stopped being a liquid and became a gas. In general it is clear that an isolated critical point can exist if the difference between phases is of a purely quantitative nature. One manifestation of the gas–liquid transition is the difference in densities, which can in principle be detected with a microscope. If the difference between phases is qualitative in nature it cannot be detected by examination of a microscopic sample of the substance. A phase transition in this case is associated with a change in symmetry, known as *symmetry breaking*. This change is abrupt, though the state of the system changes continuously. The two phases are characterized by different internal symmetries (e.g. symmetry of a crystal lattice).

Examination of the main common feature in these two cases leads us to a definition of a phase transition based on the concept of analyticity of an appropriate thermodynamic potential. Let us recall that an auxiliary function $f(x)$ is called analytic, or regular, at a point x_0 if its Taylor series at *every* point $x = x_0 + \Delta x$ in the vicinity of x_0 converges to the value of the function at this point, i.e. if there exists a positive δ such that for every $|\Delta x| < \delta$

$$f(x_0 + \Delta x) = f(x_0) + \sum_{k=1}^{\infty} \left. \frac{d^k f}{dx^k} \right|_{x_0} \frac{(\Delta x)^k}{k!} \quad (6.1)$$

So, if a function is analytic at x_0 , then all its derivatives at this point exist. A simple but important example for our future considerations that illustrates this definition is the power-law function

$$f(x) = x^a$$

with a noninteger power a . It is analytic everywhere except $x_0 = 0$, where its derivatives of order higher than the integral part of a become infinite (e.g. for $a = 3/2$ the second derivative diverges at $x = 0$ as $x^{-1/2}$).

The definition of an analytic function is naturally extended to the case of many variables. Since our interest is ultimately related to thermodynamic potentials, we formulate it for the case of two variables. A function $f(x, y)$ is analytic at the point (x_0, y_0) if

$$f(x_0 + \Delta x, y_0 + \Delta y) = f(x_0, y_0) + \sum_{k+l \geq 1} \left. \frac{\partial^{k+l} f}{\partial x^k \partial y^l} \right|_{x_0, y_0} \frac{(\Delta x)^k (\Delta y)^l}{k!l!} \quad (6.2)$$

for all Δx and Δy located inside a circle of radius δ :

$$(\Delta x)^2 + (\Delta y)^2 < \delta^2$$

Nonexistence (divergence) of one of the derivatives of a thermodynamic potential is a manifestation of a phase transition. Coming back to the p – T

diagram of Fig. 6.1 we can say that within the single-phase regions the Gibbs free energy G is analytic. These regions are bounded by a curve (D–C) at which G is nonanalytic, or *singular*. Singularity means that the value of G at the point B cannot be obtained by expanding G about the point A situated on the other side of the boundary curve, no matter how close these points are. Along the coexistence line any thermodynamic potential can be written as a sum of a regular and singular parts:

$$\mathcal{F} = \mathcal{F}_{\text{reg}} + \mathcal{F}_{\text{sing}} \quad (6.3)$$

$$G = G_{\text{reg}} + G_{\text{sing}} \quad (6.4)$$

A phase transition is ultimately related to a singularity of a corresponding thermodynamic potential. This is how the term “abrupt change” used in the definition of a phase transition can be interpreted. A thermodynamic potential is proportional to the logarithm of a corresponding partition function, which is an integral over a finite phase-space volume (or a finite sum for the case of a lattice system) of exponentials (Boltzmann factors).

Now an important question can be raised: how in principle can a thermodynamic potential be nonanalytic? The answer can be found if we recall that statistical thermodynamics is valid only in the thermodynamic limit. So the proper function to be analyzed is a *specific* free energy, i.e. free energy per particle

$$g_N = \frac{G(N, p, T)}{N}$$

The limit

$$\lim_{N \rightarrow \infty} g_N = g$$

exists for all reasonable Hamiltonians. Possible nonanalyticity of the specific free energy g can occur due to the fact that although the sequence of functions $\{g_N\}$ converges to the limiting function g , the sequence of derivatives $\{dg_N/dx\}$ need not necessarily converge to dg/dx . This implies that in the thermodynamic limit, derivatives of a free energy can diverge resulting in nonanalyticity.

It is important to realize that the notation of a phase has a broader physical meaning than just an aggregate state of matter. Having focused on common features of phase transitions, let us introduce their classification. In the most general form it can be based on the following criterion: any phase transition that can be detected by observing a microscopically finite sample for a finite time is of first order. All others are called second-order (or continuous). The latter cannot be detected by direct observation of a microscopic sample, since it does not invoke a change in the physical state of the system at the transition point, which means that all state parameters (S, E, V, p) remain unchanged. Examples of second-order transitions include

- ferromagnetic–paramagnetic transition in the absence of an external field (Curie point) in which the symmetry of magnetic moments is changed
- transition of a metal from a normal to a superconducting state
- transition of liquid helium to a superfluid state

According to this classification, the vapor-liquid transition is of first order below the critical temperature; at $T = T_c$ the transition is continuous. Note that one experimental verification of a striking difference between the behavior of a liquid–vapor system below T_c and at T_c is critical opalescence: below T_c the scattered pattern of water is clear whereas at T_c it becomes milky white.

6.2 Phase equilibrium and stability conditions

Two phases (1 and 2) can coexist if they are in thermal and mechanical equilibrium. The former implies that there is no heat flux and therefore $T_1 = T_2$, and the latter implies that there is no mass flux, which yields equal pressures $p_1 = p_2$. However, this is not sufficient. Let N be the total number of particles in the two-phase system $N = N_1 + N_2$. The number of particles in either phase can vary while N is kept fixed. If the whole system is at equilibrium, its total entropy $S = S_1 + S_2$ is maximized, which means in particular that

$$\frac{\partial S}{\partial N_1} = 0$$

Using the additivity of S , this condition can be expressed as

$$\frac{\partial S}{\partial N_1} = \frac{\partial S_1}{\partial N_1} + \frac{\partial S_2}{\partial N_1} = \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} = 0 \quad (6.5)$$

The basic thermodynamic relationship written as

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

yields

$$\frac{\partial S}{\partial N} = -\frac{\mu}{T}$$

at constant E and V . Thus, from (6.5) $\mu_1/T_1 = \mu_2/T_2$. Since $T_1 = T_2$ the chemical potentials must be equal:

$$\mu_1 = \mu_2$$

Hence, two phases in equilibrium at a temperature T and pressure p must satisfy the equation

$$\mu_1(p, T) = \mu_2(p, T) \quad (6.6)$$

which determines the phase equilibrium curve $p(T)$ shown in Fig. 6.1. Thus, T and p cannot be fixed independently, but have to provide for equality of the chemical potentials of the two phases. Differentiating this equation with respect to temperature and bearing in mind that $p = p(T)$, we obtain:

$$\frac{\partial \mu_1}{\partial T} + \frac{\partial \mu_1}{\partial p} \frac{dp}{dT} = \frac{\partial \mu_2}{\partial T} + \frac{\partial \mu_2}{\partial p} \frac{dp}{dT} \quad (6.7)$$

From the Gibbs–Duhem equation

$$d\mu = -s dT + v dp$$

where $s = \frac{S}{N}$ and $v = \frac{V}{N}$ are entropy and volume per particle, we have

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -s, \quad \left(\frac{\partial \mu}{\partial p} \right)_T = v$$

Using (6.7), we obtain the Clapeyron equation:

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1} \quad (6.8)$$

describing the form of the p - T diagram.

Many first-order phase transitions are characterized by the absorption or release of so-called *latent heat*.¹ For processes at constant pressure the latent heat L is given by the change in enthalpy:

$$L \equiv \delta Q = \delta U + \delta A = \delta(U + pV) \equiv \delta H$$

The latent heat per molecule is then

$$l = \frac{L}{N} = T(s_2 - s_1) \quad (6.9)$$

Therefore at $T < T_c$ the Clapeyron equation can be written as:

$$\frac{dp}{dT} = \frac{l}{T(v_2 - v_1)} \quad (6.10)$$

A phase transition takes place when the state of the system becomes unstable with respect to external perturbations. The condition of phase stability is given by Le Chatelier's principle:

¹ Note that most but not all first-order phase transitions have latent heat. For example, the ferromagnetic–paramagnetic transition in metals in the presence of external field is of first order, but has no latent heat.

An external perturbation that disturbs the system in its equilibrium state gives rise to processes within the system that tend to oppose the effect of that perturbation.

This principle can be expressed in the form of thermodynamic inequalities [80]. Let us single out a small (but macroscopic) part of the system. With respect to this subsystem the remaining parts of the system play the role of the environment. The subsystem and the environment are in equilibrium, implying equality of their temperature T_0 and pressure p_0 . If E , S , and V are the energy, entropy, and volume of the given subsystem, then in equilibrium the quantity

$$G = E - T_0 S + p_0 V$$

is minimized. This means that for every small perturbation from equilibrium

$$\delta G = \delta E - T_0 \delta S + p_0 \delta V > 0 \quad (6.11)$$

Considering E to be a function of S and V , we expand δE to second order:

$$\delta E = \frac{\partial E}{\partial S} \delta S + \frac{\partial E}{\partial V} \delta V + \frac{1}{2} \left[\frac{\partial^2 E}{\partial S^2} (\delta S)^2 + 2 \frac{\partial^2 E}{\partial S \partial V} \delta S \delta V + \frac{\partial^2 E}{\partial V^2} (\delta V)^2 \right]$$

Taking into account that $\frac{\partial E}{\partial S} = T_0$ and $\frac{\partial E}{\partial V} = -p_0$ and substituting this expansion into (6.11), we obtain the condition

$$\frac{\partial^2 E}{\partial S^2} (\delta S)^2 + 2 \frac{\partial^2 E}{\partial S \partial V} \delta S \delta V + \frac{\partial^2 E}{\partial V^2} (\delta V)^2 > 0 \quad (6.12)$$

which must be valid for arbitrary values of δS and δV . This leads to the requirement of the positiveness of the quadratic form: all its minors must be positive. This implies

$$\frac{\partial^2 E}{\partial S^2} > 0 \quad (6.13)$$

$$\frac{\partial^2 E}{\partial S^2} \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V} \right)^2 > 0 \quad (6.14)$$

The first inequality (omitting subscripts) yields

$$\frac{\partial^2 E}{\partial S^2} = \left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V} > 0$$

where C_V is the heat capacity at constant volume. Thus,

$$C_V > 0 \quad (6.15)$$

The condition (6.14) can be written in the form of a Jacobian:

$$\frac{\partial \left[\left(\frac{\partial E}{\partial S} \right)_V, \left(\frac{\partial E}{\partial V} \right)_S \right]}{\partial(S, V)} > 0$$

or

$$\frac{\partial(T, p)}{\partial(S, V)} < 0$$

Working this out, we obtain:

$$\frac{\partial(T, p)}{\partial(S, V)} = \frac{\frac{\partial(T, p)}{\partial(T, V)}}{\frac{\partial(S, V)}{\partial(T, V)}} = \frac{\left(\frac{\partial p}{\partial V} \right)_T}{\left(\frac{\partial S}{\partial T} \right)_V} = \frac{T}{C_V} \left(\frac{\partial p}{\partial V} \right)_T < 0$$

Since $C_V > 0$ this gives

$$\left(\frac{\partial p}{\partial V} \right)_T < 0$$

We can express this condition as the positiveness of the isothermal compressibility:

$$\chi_T > 0 \quad \text{and finite} \quad (6.16)$$

The states for which the conditions (6.15) and (6.16) are violated are unstable and cannot be realized. Note that the locus of points where $\chi_T = \infty$ defines the *spinodal line* (recall the van der Waals theory).

6.3 Critical point

By definition quantitative differences between phases disappear at the critical point. Therefore at T_c

$$v_1 = v_2, \quad s_1 = s_2$$

Thus, $l = 0$ and the transition is continuous; the Clapeyron equation becomes undefined. One, however, can discuss the behavior of the p - T curve in the vicinity of the critical point by taking the limit $\left(\frac{dp}{dT} \right)_{T \rightarrow T_c^-}$. Let us find conditions determining the critical point. Near T_c the specific volumes of liquid and vapor are close to each other. If V is the liquid volume and $V + \delta V$ is the vapor volume, then equality of pressures in the two phases in equilibrium is

$$p(V, T) = p(V + \delta V, T)$$

Expanding the right-hand side in δV , we obtain

$$p(V, T) = p(V, T) + \left(\frac{\partial p}{\partial V} \right)_T \delta V + \frac{1}{2} \left(\frac{\partial^2 p}{\partial V^2} \right)_T (\delta V)^2 + \dots$$

which after dividing by a small but finite δV yields

$$\left(\frac{\partial p}{\partial V} \right)_T + \frac{1}{2} \left(\frac{\partial^2 p}{\partial V^2} \right)_T \delta V + \dots = 0$$

In the limit $\delta V \rightarrow 0$, corresponding to the critical point, this equation yields

$$\left(\frac{\partial p}{\partial V} \right)_{T=T_c} = 0 \quad (6.17)$$

Now we perform a similar expansion of the Helmholtz free energy near T_c :

$$\begin{aligned} \delta \mathcal{F} &= \mathcal{F}(V + \delta V) - \mathcal{F}(V) = \frac{\partial \mathcal{F}}{\partial V} \delta V + \frac{1}{2} \frac{\partial^2 \mathcal{F}}{\partial V^2} (\delta V)^2 + \\ &\quad \frac{1}{3!} \left(\frac{\partial^3 \mathcal{F}}{\partial V^3} \right) (\delta V)^3 + \frac{1}{4!} \left(\frac{\partial^4 \mathcal{F}}{\partial V^4} \right) (\delta V)^4 + \dots \end{aligned}$$

and note that $\frac{\partial \mathcal{F}}{\partial V} = -p$ and therefore $\frac{\partial^2 \mathcal{F}}{\partial V^2} = -\frac{\partial p}{\partial V}$, which vanishes at T_c . Thus,

$$\delta \mathcal{F} = -p \delta V - \frac{1}{3!} \left(\frac{\partial^2 p}{\partial V^2} \right) (\delta V)^3 - \frac{1}{4!} \left(\frac{\partial^3 p}{\partial V^3} \right) (\delta V)^4 + \dots$$

Equilibrium at a given pressure and temperature corresponds to the minimum of the Gibbs energy, which results in $\delta G = \delta \mathcal{F} + p \delta V = 0$. Substituting the expression for $\delta \mathcal{F}$ and dividing by small but finite $(\delta V)^3$, we obtain

$$\frac{1}{3!} \left(\frac{\partial^2 p}{\partial V^2} \right) + \frac{1}{4!} \left(\frac{\partial^3 p}{\partial V^3} \right) \delta V + \dots = 0$$

which in the limit $\delta V \rightarrow 0$ yields

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_{T=T_c} = 0 \quad (6.18)$$

Equations (6.17) and (6.18) define an isolated critical point (p_c, V_c, T_c) . In the p - V plane it corresponds to a horizontal inflection point of the isotherm $T = T_c$.

6.4 Universality hypothesis and critical exponents

The behavior of a system in the vicinity of a critical point is called *critical phenomena*. It was established experimentally and in computer simulations

(though not proven rigorously) that critical phenomena related to physically distinct systems possess striking similarity. In other words, they do not depend on the details of microscopic interactions between particles constituting a particular substance. This fact lies in the heart of the *universality hypothesis*, the cornerstone of the modern theory of critical phenomena (see e.g. [15]). The universality hypothesis can be expressed by means of two basic conjectures [149]:

1. In whatever guise it might appear, there is only one free energy density of fundamental importance in the critical phenomena; this free energy density corresponds to the singular contribution in (6.3).
2. In whatever guise it might appear, there is only one length scale of fundamental importance in the critical phenomena; this length scale is given by the correlation length characterizing the behavior of the total correlation function $h(r)$ at large r .

The Ornstein–Zernike theory (see Sect. 8.3) predicts that at large distances $h(r)$ decreases as

$$\frac{1}{r} e^{-r/\xi},$$

where the parameter ξ is called the correlation length. Mathematically, universality is expressed in the form of scaling relationships describing the behavior of various quantities in the critical region. They are power-law functions with some universal critical exponents (also called *critical indices*).

We now write out the scaling relationships for the properties of the liquid–vapor system (though in view of the conjectures described above they have universal character). An important characteristic of the system is the difference between the equilibrium liquid and vapor density at temperature T , $\rho_{\text{sat}}^l(T) - \rho_{\text{sat}}^v(T)$, which decreases and tends to zero as T approaches T_c . In order to characterize this decrease we introduce a critical index β (which should not be confused with the same notation used for the inverse temperature $1/(k_B T)$):

$$\rho^l - \rho^v \sim (T_c - T)^\beta$$

Introducing the reduced temperature

$$t = \frac{T - T_c}{T_c} \quad (6.19)$$

we represent this relationship as

$$\rho^l - \rho^v \sim |t|^\beta \quad (6.20)$$

Another critical index, γ , characterizes the divergence of the isothermal compressibility:

$$\chi_T \sim |t|^{-\gamma} \quad (6.21)$$

The constant volume specific heat is defined as

$$c_v = \frac{1}{N} \left. \frac{dQ}{dT} \right|_V = T \left. \frac{\partial s}{\partial T} \right|_V \quad (6.22)$$

Using (1.47) it can be related to the second derivative of the Helmholtz free energy density $f = \mathcal{F}/N$:

$$c_v = -T \left. \frac{\partial^2 f}{\partial T^2} \right|_V \quad (6.23)$$

Near T_c , c_v diverges and its behavior is described by

$$c_v \sim |t|^{-\alpha} \quad (6.24)$$

By integrating twice over the temperature, we find that the singular part of the free energy density (the part that carries the specific heat singularity) behaves as

$$f_{\text{sing}} \sim |t|^{2-\alpha} \quad (6.25)$$

The shape of the critical isotherm $T = T_c$ is given by the exponent δ :

$$p - p_c \sim |\rho - \rho_c|^\delta, \quad T = T_c \quad (6.26)$$

Two other critical indices are related to the behavior of the total correlation function $h(r)$. As $T \rightarrow T_c$ the correlation length diverges as

$$\xi \sim |t|^{-\nu} \quad (6.27)$$

which defines the critical exponent ν . At the critical point exponential decay of the total correlation functions is replaced by an algebraic one characterized by the exponent η :

$$h(r) \sim r^{-(d-2+\eta)}, \quad T = T_c \quad (6.28)$$

where d is the dimensionality of space. Finally, the exponent μ characterizes the decrease in surface tension γ_0 as T tends to T_c :

$$\gamma_0 \sim (T_c - T)^\mu \quad (6.29)$$

Not all the critical exponents are independent of one another. In fact it turns out that it is sufficient to know any two of them in order to find all the rest. We show this by deriving several scaling relations, i.e. expressions involving various critical exponents. Pressure is related to the free energy by

$$p = - \left. \frac{\partial \mathcal{F}}{\partial V} \right|_{N,T} = \rho^2 \frac{\partial f}{\partial \rho}$$

Near T_c it is a sum of regular and singular terms resulting from (6.3):

$$p = p_{\text{reg}} + p_{\text{sing}}, \quad p_{\text{sing}} = \rho^2 \frac{\partial f_{\text{sing}}}{\partial \rho}$$

We stress that all quantities are taken at coexistence. Since f_{sing} scales as $|t|^{2-\alpha}$, we obtain using (6.20)

$$p_{\text{sing}} \sim |t|^{2-\alpha-\beta}$$

Then

$$\frac{\partial p_{\text{sing}}}{\partial \rho} \sim |t|^{2-\alpha-2\beta}$$

and therefore the isothermal compressibility scales as

$$\chi_T \sim |t|^{-(2-\alpha-2\beta)}$$

Comparison with (6.21) yields the relation

$$\gamma + 2\beta = 2 - \alpha \quad (6.30)$$

Note that in order to establish scaling relations we do not need to know the prefactors, just the exponents. Recall from the previous chapter that the surface tension of plane interface with area A is given by

$$\mathcal{F}^s = \gamma_0 A$$

for the equimolar Gibbs dividing surface. $\mathcal{F}^s \equiv \mathcal{F} - \mathcal{F}^l - \mathcal{F}^v$ is the excess free energy due to the presence of an interface. The interface thickness is of the order of the correlation length ξ , hence $\mathcal{F}^s$ is “accumulated” in a volume ξA . The excess free energy per unit volume of the interfacial fluid is γ_0/ξ . This is a singular function near T_c . According to the universality conjecture it is a manifestation of the singular part of the bulk free energy density in either of the bulk phases; the latter scales as $(T_c - T)^{2-\alpha}$. Therefore,

$$\frac{\gamma_0}{\xi} \sim (T_c - T)^{2-\alpha}$$

Thus, from (6.27) and (6.29)

$$\mu + \nu = 2 - \alpha \quad (6.31)$$

There exist a number of relations that directly involve the dimensionality of space d . These are called *hyperscaling relations*. The fact that ξ is the only significant length scale near T_c means that density fluctuations are correlated at distances of order ξ , and density fluctuations in volume elements ξ^d are independent. The average free energy associated with an independent fluctuation in a fluid is of order $k_B T \approx k_B T_c$. Thus, the free energy density of

fluctuations near the critical point is $\sim k_B T_c / \xi^d$. Comparing this with (6.25) we find

$$d\nu = 2 - \alpha \quad (6.32)$$

Combining (6.31) and (6.32) yields a simple hyperscaling relation between μ and ν :

$$\mu = (d - 1)\nu \quad (6.33)$$

Kadanoff [61] formulated a scaling hypothesis that combines the behavior of the total correlation function $h(r)$ in the vicinity of T_c and at T_c itself:

$$h(r) = r^{-(d-2+\eta)} \Psi\left(\frac{r}{\xi}\right) \quad (6.34)$$

where $\Psi(x)$ is some function of one argument x . For small x , $\Psi(x) \approx \text{const}$, since this is the case $\xi \rightarrow \infty$, corresponding to the algebraic decay of h . In the limit of large x , i.e. for $r > \xi$

$$\Psi(x) \sim x^{d-2+\eta} e^{-x}$$

Thus, in the vicinity of T_c the total correlation function at separations larger than the correlation length behaves as

$$h(r) \sim \xi^{-(d-2+\eta)} e^{-r/\xi}, \quad r > \xi \quad (6.35)$$

Recall that $h(r)$ is related to χ_T via the compressibility equation of state (3.13), which near T_c in a d -dimensional space reads

$$\int h(r) d^d \mathbf{r} \approx k_B T_c \chi_T$$

Since χ_T diverges near T_c the integral must diverge, and therefore the main contribution comes from large r . Therefore

$$\int h(r) d^d \mathbf{r} \sim \int \xi^{-(d-2+\eta)} e^{-\frac{r}{\xi}} d^d \mathbf{r} = \xi^{-(d-2+\eta)} \xi^d \Omega_{d-1} \int_0^\infty x^{d-1} e^{-x} dx$$

where Ω_d is the area of the unit d -sphere (e.g. $\Omega_2 = 4\pi$). Thus,

$$\int h(r) d^d \mathbf{r} \sim \xi^{2-\eta} \sim |t|^{-(2-\eta)\nu}$$

which yields Fisher's scaling law [45]:

$$(2 - \eta)\nu = \gamma \quad (6.36)$$

We have stated that critical exponents are universal numbers that do not depend on the details of microscopic interactions. Are there physical

parameters they *do* depend on? A partial (but not a full) answer is given by the preceding discussion: critical exponents depend on the dimensionality of space. An important characteristic of a second-order phase transition is the so-called order parameter, φ , introduced by Landau. This is the quantity which by definition is equal to zero in a (more) symmetrical phase (usually the high-temperature side) and is nonzero in a nonsymmetrical phase. Its definition is not unique, and depends on particular physical problem. It can be a scalar (real or complex), or a vector.

For the gas-liquid transition the order parameter can be defined as the difference between densities of liquid and gas:

$$\varphi = \rho^l(T) - \rho^v(T) \quad (6.37)$$

This is a real scalar. At the critical point the difference between phases disappears, so at T_c , $\varphi = 0$.

Dimensionality of the order parameter is the second factor that governs the values of critical indices. The fundamental statement of the theory of critical phenomena is:

All second-order phase transitions in physically different systems can be attached to universality classes characterized by dimensionality of space and dimensionality of the order parameter.

As an implication of this fact we observe that the liquid-vapor transition at T_c belongs to the same universality class as the ferromagnetic-paramagnetic transition in a uniaxial ferromagnet.

To complete the description of critical indices we present in Table 6.1 their numerical values for the three-dimensional space and a one-dimensional order parameter [117]. It is easy to check that the scaling and hyperscaling relations are satisfied.

Table 6.1. Critical exponents for the one-dimensional order parameter and three-dimensional space [117]

α	β	γ	ν	η	δ	μ
0.107	0.328	1.237	0.631	0.040	4.769	1.262

6.5 Critical behavior of the van der Waals fluid

A system for which we can derive critical exponents explicitly is a van der Waals fluid. Let us first recall the van der Waals equation in dimensionless form (5.12):

$$p^* + \frac{3}{v^{*2}} = \frac{8T^*}{3v^* - 1} \quad (6.38)$$

where for mathematical convenience we used a reduced volume

$$v^* \equiv \frac{v}{v_c} = \frac{\rho_c}{\rho} = \frac{1}{\rho^*}$$

instead of a reduced density ρ^* . To analyze the behavior in the vicinity of the critical point we introduce small quantities ω , τ , π by

$$v^* = 1 + \omega, \quad T^* = 1 + \tau, \quad p^* = 1 + \pi$$

Then, (6.38) takes a universal form

$$(1 + \pi) + \frac{3}{(1 + \omega)^2} = \frac{8(1 + \tau)}{2 + 3\omega} \quad (6.39)$$

Expanding both sides in all variables up to third order, we find:

$$\pi = 4\tau - 6\tau\omega + 9\tau\omega^2 - \frac{3}{2}\omega^3 \quad (6.40)$$

On the critical isotherm $\tau = 0$ we have $\pi \sim \omega^3$, so the critical isotherm is a cubic curve yielding $\delta = 3$ (cf. (6.26)). The isothermal compressibility is

$$\chi_T = -\frac{1}{v} \frac{\partial v}{\partial p} = -\frac{1}{p_c(1 + \omega)} \left. \frac{\partial \omega}{\partial \pi} \right|_\tau$$

By differentiating (6.40) we find that on the critical isochore ($\omega = 0$)

$$\chi_T = \frac{1}{6p_c\tau}$$

Thus, the compressibility diverges as $\chi_T \sim \tau^{-1}$, yielding another critical index: $\gamma = 1$.

Below T_c phase separation takes place. To find the critical exponent β we have to apply the Maxwell construction (5.13) in order to determine the equilibrium liquid and vapor volumes:

$$\int_{v^{*v}}^{v^{*l}} v^* dp^* = 0$$

Integrating by parts and noting that at coexistence $p^{*l} = p^{*v} = p_0^*$, we obtain:

$$\int_{v^{*v}}^{v^{*l}} p^*(v^*) dv^* = p_0^*(v^{*l} - v^{*v}) \quad (6.41)$$

In the π , ω , τ notations the Maxwell construction becomes

$$\int_{\omega_1}^{\omega_2} \pi'(\omega; \tau) d\omega = \pi_0(\omega_2 - \omega_1) \quad (6.42)$$

Here $v^{*v} = 1 + \omega_1$, $v^{*1} = 1 + \omega_2$, $p_0^* = 1 + \pi_0$ and $\pi'(\omega; \tau)$ is the current value of $\pi(\omega)$. Performing the integration and using (6.40), we obtain after some algebra:

$$\pi = 4\tau - 3\tau(\omega_1 + \omega_2) + 3\tau(\omega_1^2 + \omega_1\omega_2 + \omega_2^2) - \frac{3}{8}(\omega_1 + \omega_2)(\omega_1^2 + \omega_2^2) \quad (6.43)$$

(note that $\tau < 0$ below T_c). This must be combined with the van der Waals equation written for each of the equilibrium phases:

$$\pi_0 = 4\tau - 6\tau\omega_1 + 9\tau\omega_1^2 - \frac{3}{2}\omega_1^3 \quad (6.44)$$

$$\pi_0 = 4\tau - 6\tau\omega_2 + 9\tau\omega_2^2 - \frac{3}{2}\omega_2^3 \quad (6.45)$$

Subtracting (6.45) from (6.44), we have

$$-6\tau + 9\tau(\omega_1 + \omega_2) - \frac{3}{2}(\omega_1^2 + \omega_1\omega_2 + \omega_2^2) = 0$$

To lowest order in τ the solution is

$$\omega_1 = -\omega_2 = 2\sqrt{-\tau} \quad (6.46)$$

$$\pi_0 = 4\tau \quad (6.47)$$

Equation (6.46) implies that

$$|v^1 - v_c| \sim (T_c - T)^{1/2}$$

yielding the exponent $\beta = 1/2$.

6.6 Landau theory of second-order phase transitions

Landau formulated a general approach to second order phase transitions [80]. Let φ be a corresponding order parameter which, as we have mentioned, can have different physical meaning depending on the nature of the transition. Since phase equilibrium is characterized by equality of pressures and temperatures, we discuss the behavior of the Gibbs energy G , for which p and T are natural variables.

Landau proposed to consider G as a function of not only p and T but also of the order parameter φ : $G = G(p, T, \varphi)$. However, in contrast to p

and T , which can be given arbitrary values, the value of φ corresponding to equilibrium, $\varphi = \varphi_0$, is determined by minimization of the Gibbs energy:

$$\left. \frac{\partial G}{\partial \varphi} \right|_{p,T} = 0, \quad \left. \frac{\partial^2 G}{\partial \varphi^2} \right|_{\varphi=\varphi_0} > 0 \quad (6.48)$$

Thus, the roles of p and T on the one hand, and φ on the other, are different: in equilibrium $\varphi = \varphi(p, T)$. We identify the critical point with $T = T_c$. It is important to note that in contrast to a first-order transition, there is no coexistence of phases for a second order-transition: above T_c the system is in the symmetric phase, while below T_c it is in the nonsymmetric phase. Continuity of the state of the system at the critical point yields that in its vicinity the order parameter can attain infinitesimally small values, since at the critical point itself $\varphi = 0$.

Landau proposed to present the Gibbs free energy in the vicinity of the critical point as a series in powers of the order parameter

$$G(p, T, \varphi) = G_0 + V(a_1\varphi + a_2\varphi^2 + a_3\varphi^3 + \frac{b}{4}\varphi^4 + \dots) \quad (6.49)$$

with the coefficients a_1 , a_2 , a_3 , b that depend on p and T ; V is the volume of the system. The possibility of such an expansion is not obvious. Moreover, we know that at the critical point, thermodynamic potentials become singular! However, (6.49) applies to the vicinity of the critical point, and it does lead (as we shall see later) to singular behavior of G at T_c . Even with this explanation this expansion is not yet fully justified mathematically. To use it we have to assume that singularities of G are of higher order than the terms used in the Landau theory.

The dependence of G on φ means that one can associate with φ a *conjugate field* H such that

$$dG = V dp - S dT + H d\varphi$$

or in other words

$$\left(\frac{\partial G}{\partial \varphi} \right)_{p,T} = H \quad (6.50)$$

The physical meaning of H depends on the physical meaning of φ for a particular transition. For example, for a paramagnetic-ferromagnetic transition φ is the average magnetization and H is an external magnetic field; for a vapor-liquid transition $H = \mu - \mu_c$, where μ_c is the chemical potential at the critical point; etc. Above T_c , i.e. in the symmetric phase, φ must be zero if its conjugate field is zero. A simple illustration of this in the magnetic language is that at temperatures higher than the Curie point $T_c \equiv T_{\text{Curie}}$, i.e. in the paramagnetic state, the average magnetization in the absence of an external magnetic field is zero. From (6.49)

$$\left. \frac{\partial G}{\partial \varphi} \right|_{\varphi=0} = V a_1(p, T)$$

Comparing this with (6.50) and taking into account that a_1 is independent of H , we conclude that $a_1(p, T) \equiv 0$. Thus, the Landau expansion of the free energy does not contain a linear term.

Let us discuss the second-order term. In the symmetric phase in equilibrium $\varphi = 0$, and this value must correspond to the minimum of G which implies, that

$$\left. \frac{\partial G}{\partial \varphi} \right|_{\varphi=0} = 0 \quad \text{and} \quad \left. \frac{\partial^2 G}{\partial \varphi^2} \right|_{\varphi=0} > 0$$

From (6.49) it then follows that in the symmetric phase $a_2 > 0$ and $\min G = G_0$. The equilibrium value of the order parameter for the nonsymmetric phase is nonzero (by definition) and $\min G$ is therefore lower than G_0 , which can be possible only if $a_2 < 0$. Hence $a_2(p, T) > 0$ for the symmetric phase and $a_2(p, T) < 0$ for the nonsymmetric one. Continuity of G at the transition point (which is a manifestation of the second-order transition) requires that $a_2(p, T_c) = 0$ (see Fig. 6.2).

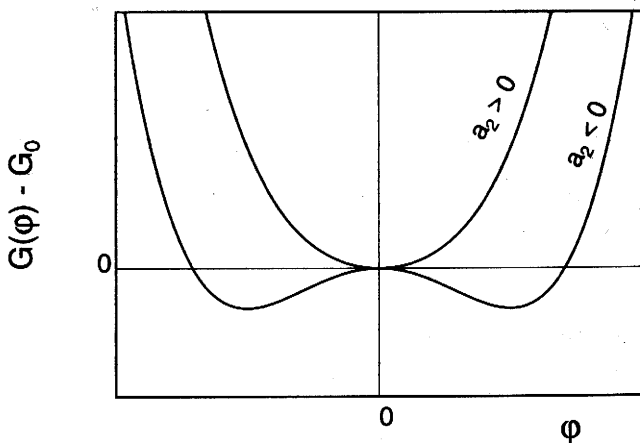


Fig. 6.2. Landau theory: Gibbs free energy as a function of the order parameter

These features imply that in the critical region a_2 can be written to leading order in $T - T_c$ as

$$a_2 = \frac{a}{2}t, \quad a > 0 \quad (6.51)$$

where

$$t = \frac{T - T_c}{T_c}$$

is the reduced temperature and a is the material parameter. For the thermodynamic stability of the system at the critical point it is necessary that $\partial^2 G(T_c)/\partial \varphi^2 > 0$. Since $a_2 = 0$ at T_c this implies that

$$a_3(p, T_c) = 0 \quad \text{and} \quad b(p, T_c) > 0$$

Here one can distinguish two possibilities. If $a_3(p, T) \equiv 0$ for all T then we have a locus of critical points $p(T_c)$ in the p - T plane given by $a_2(p, T_c) = 0$. If $a_3 = 0$ only at T_c then the system of equations $a_2(p, T) = a_3(p, T) = 0$ determines isolated critical points. Let us discuss, following Landau, the former case: $a_3(p, T) \equiv 0$. Expansion (6.49) becomes

$$G(p, T, \varphi) = G_0 + V \left(\frac{a}{2} t \varphi^2 + \frac{b}{4} \varphi^4 \right) \quad (6.52)$$

Equilibrium corresponds to $\min G$, which results in the equation

$$\varphi(at + b\varphi^2) = 0 \quad (6.53)$$

For $t > 0$ (i.e. for $T > T_c$) there exists only one solution: $\varphi_0 = 0$. For $t < 0$ a second solution appears:

$$\varphi_0 = \sqrt{\frac{-at}{b}}, \quad t < 0 \quad (6.54)$$

which corresponds to the minimum of G and is therefore stable, whereas $\varphi_0 = 0$ becomes unstable. Substituting (6.54) into (6.52) we obtain the equilibrium Gibbs free energy in the nonsymmetric phase:

$$G = G_0 - V \frac{(at)^2}{4b} \quad (6.55)$$

This important result allows us to draw several conclusions, revealing general features of the second-order phase transitions. Let us first analyze the entropy,

$$S = - \left. \frac{\partial G}{\partial T} \right|_p = S_0 + V \frac{a^2 t}{2bT_c} \quad (6.56)$$

where S_0 is the entropy of the symmetric phase, for which $\varphi_0 = 0$, and $G = G_0$. As expected at the critical point ($t = 0$) the entropy remains continuous: $S = S_0$ in both phases. The heat capacity at constant pressure is

$$C_p = T \left. \frac{\partial S}{\partial T} \right|_p = C_{p0} + VT \frac{a^2}{2bT_c^2}$$

where C_{p0} is the heat capacity in the symmetric phase. Thus, at the critical point C_p has a finite jump:

$$C_p - C_{p0} = V \frac{a^2}{2bT_c}, \quad T = T_c \quad (6.57)$$

which manifests nonanalyticity of the Gibbs energy at the critical point: its second derivative with respect to temperature is discontinuous. Thus, in the Landau theory the heat capacity increases discontinuously when the system undergoes a transition from a symmetric to a nonsymmetric phase. This fact yields the value of the critical exponent α in the Landau theory:

$$\alpha = 0$$

Exponent β , describing the behavior of the order parameter as a function of temperature, is found from (6.54):

$$\beta = 1/2$$

We have thus far completely ignored fluctuations in the system by assuming that $\varphi = \text{const}$ throughout the volume. One can improve the original Landau treatment by considering the order parameter to be a function of space coordinates $\varphi = \varphi(\mathbf{r})$, to include the effect of correlations. Then (6.52) takes the form of the Ginzburg–Landau functional:

$$G(p, T, [\varphi]) = G_0 + \int_V d\mathbf{r} \left[\frac{1}{2} a t \varphi^2 + \frac{b}{4} \varphi^4 + \frac{1}{2} c |\nabla \varphi|^2 \right] \quad (6.58)$$

where c is a positive coefficient. Note that for φ independent of $\mathbf{r}$ we recover the original expansion (6.52). Now equilibrium corresponds to the functional minimization

$$\frac{\delta G}{\delta \varphi} = 0$$

which results in the Euler–Lagrange equation:

$$a t \varphi + b \varphi^3 - c \Delta \varphi = 0 \quad (6.59)$$

We assume that φ is close to φ_0 given by (6.54). Then setting

$$\varphi = \varphi_0 + \varphi_1$$

substituting into (6.59), and linearizing in φ_1 we obtain the linear equation of Helmholtz type

$$\Delta \varphi_1 - \kappa^2 \varphi_1 = 0 \quad (6.60)$$

where

$$\kappa^2 = \frac{at + 3b\varphi_0^2}{c} \quad (6.61)$$

For the spherically symmetric case $\varphi_1(\mathbf{r}) = \varphi_1(r)$ and the Laplacian in spherical coordinates becomes

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}$$

The spherically symmetric solution of (6.60) has the form of the Yukawa function

$$\varphi_1 = \text{const} \frac{1}{r} e^{-\kappa r} \quad (6.62)$$

The quantity $\xi = 1/\kappa$ characterizes the length scale of fluctuations of the order parameter. At separations larger than ξ , $\varphi_1 \approx 0$, meaning that the corresponding parts of the system are uncorrelated. Thus, ξ is a correlation length. From (6.61) and (6.54)

$$\xi = \begin{cases} \sqrt{\frac{c}{-2at}} & \text{for } t < 0, \\ \sqrt{\frac{c}{at}} & \text{for } t > 0 \end{cases}$$

Thus, the correlation length diverges as

$$\xi \sim |t|^{-1/2} \quad (6.63)$$

yielding the value of the critical exponent ν :

$$\nu = 1/2$$

At the critical point ($t = 0$) the correlation length becomes infinite, so from (6.62) $\varphi_1 \sim 1/r$, implying that

$$\eta = 0$$

7. Monte Carlo methods

7.1 Basic principles of Monte Carlo. Original capabilities and typical drawbacks

Since the beginning of 1950s the Monte Carlo method (MC) has served as one of the major numerical tools of computer modeling of physical processes. Its specific feature is based on *statistical* modeling as opposed to *deterministic calculations* of finite difference type. In performing MC calculations one literally tries to counterfeit random quantities distributed according to the known laws of physics, or – especially in statistical physics – to counterfeit processes leading to known physical behavior, e.g. to the settlement of thermodynamic equilibrium. Such counterfeits are known by various names, such as “imitation”, “simulation”, “modeling”, and also “numerical experiment.” To make the terminology more precise, the words “statistical” and “computational” are often added. This refinement is related to the fact that statistics requires a lot of observations, attempts or trials, and one cannot do without modern computers.

Recalling the history of scientific development over the last 50 years, it turns out that the pioneers of Monte Carlo belonged to the same cohort of physicists and mathematicians who, in the 1940s, created the first nuclear reactor and the first nuclear bomb. Those people also developed many of the earliest electronic computers and assessed the future capabilities of computational machines – which have turned out to be more astonishing than anyone originally expected. Probably the best definition of MC would be the following:

Monte Carlo is a method of solving physical problems by simulating on computers the observations of random variables with subsequent statistical processing.

In statistical physics MC is applied mostly to calculate integrals over configuration space. To be more specific, let us consider a canonical (NVT) ensemble of pairwise interacting particles (molecules) in an external field. The integral (7.1) gives the average value of some function of coordinates $X(\mathbf{r}^N)$

$$\langle X(\mathbf{r}^N) \rangle = \int X(\mathbf{r}^N) w(\mathbf{r}^N) d\mathbf{r}^N \quad (7.1)$$

where $w(\mathbf{r}^N)$ is the Gibbs probability density function

$$w(\mathbf{r}^N) = D_N(\mathbf{r}^N) = \frac{1}{Q_N} \exp \left[-\frac{U(\mathbf{r}^N)}{k_B T} \right] \quad (7.2)$$

and the potential energy is

$$U(\mathbf{r}^N) = \sum_{i < j} u(\mathbf{r}_i, \mathbf{r}_j) + \sum_i u_{\text{ext}}(\mathbf{r}_i)$$

From the standpoint of probability theory and mathematical statistics (7.1) defines the mathematical expectation of $X(\mathbf{r}^N)$. Imagine that we have a digital camera that can instantaneously take photos, and that we use it to scan and memorize the 3D coordinates of all N fluid molecules in the volume V . We can repeat these actions M times per second. Then the computer memory will contain the set of coordinates $(\mathbf{r}^N)_1, (\mathbf{r}^N)_2, \dots, (\mathbf{r}^N)_M$ and it would not be difficult to write a program performing standard statistical processing of these observations [73]. The average *observed* value of X

$$\text{AVRG}(X) = (1/M) \sum_{c=1}^M X[(\mathbf{r}^N)_c] \quad (7.3)$$

gives an estimate of the *true* value $\langle X(\mathbf{r}^N) \rangle$.¹ Its mean square deviation from the latter is

$$\sigma^2 = (1/M) \sum_{c=1}^M X^2[(\mathbf{r}^N)_c] - [\text{AVRG}(X)]^2 \quad (7.4)$$

Finally, the integral (7.1) is approximated by [73]

$$\langle X(\mathbf{r}^N) \rangle \approx \text{AVRG}(X) \left[1 \pm \frac{\sigma}{\sqrt{M}} \right] \quad (7.5)$$

Note that σ becomes independent of the number of “photo pictures” (observations) for large M , implying that the error is inversely proportional to the square root of the number of observations, which is typical for mathematical statistics (and MC).

MC plays the role of such a microscope that produces a skillful counterfeit of these pictures by a computer program, their scanning and processing according to (7.5). Unlike the microscope, which does not care about the form of intermolecular interaction, MC imitates the picture just by proceeding from the form of this interaction. To do this one has to be able to

¹ Terminologically one should not confuse the mathematical expectation with $\text{AVRG}(X)$ (as it historically appears in physical theories since the nineteenth century). The former is a theoretically exact quantity (as if we were able to calculate the integral (7.1)) while the latter is an estimate (as if we were able to observe the coordinates $\mathbf{r}^N$ M times).

1. simulate randomness as a phenomenon, and
2. generate random configurations corresponding to a given system, e.g. a fluid with a given interaction potential under given external conditions.

It is important that the error of the approximation (7.5) does not depend on the dimension of the integral, but is determined by the number of observations M (the function $X(\mathbf{r}^N)$ is calculated at M random points), being of the order $O(M^{-1/2})$. It is useful to compare MC accuracy with the accuracy one can reach by performing approximate integration using standard deterministic quadrature formulas (Gaussian, trapezoidal, etc.) with the same number M of specially chosen points. One-dimensional integrals can be much more efficiently calculated deterministically: the order of accuracy is $O(M^{-3})$ or even better. However, for a $3N$ -dimensional integral the order of deterministic error at fixed M is $O[(M^{-3})^{1/3N}] = O(M^{-1/N})$; i.e. even for two particles ($N = 2$) it becomes $O(M^{-1/2})$ – the same order of magnitude as for MC. For $N > 3$ the accuracy of quadrature methods is much worse, tending to 100% as $N \rightarrow \infty$: $O(M^0) = O(1)$. Thus, MC has no deterministic competitors when one needs to calculate $3N$ -multiple integrals starting with $N = 2-3$.

Comparing MC with molecular dynamics (MD) [53], let us point out their common features and differences when applied to statistical physics. In MD one chooses an initial state of the system in phase space, i.e. fixes coordinates and momenta of particles, and then solves the classical equations of motion by means of finite differences. To do this a temporal grid is created. Thus, MD models the actual approach to thermodynamic equilibrium – rather than simulating it! MC is able to *simulate* this process without using such dynamical variables as momenta. In other words, MC's dynamics is artificial. One chooses initial conditions in configuration space (not in phase space) and creates there a fictitious approach to equilibrium on the basis of the master equation. An important remark is that the time scale of this process differs from the real time scale and can be made “faster,” thereby greatly simplifying the calculations.

However, strictly speaking as far as fluids are concerned, neither MC nor MD is able to cope with the problem of a huge number of particles $\sim 10^{23}$ (of the order of Avogadro's number N_A), and even in the case of pairwise interactions are content with usually not more than $\sim 10^5$ particles, resulting in $\sim 10^{10}$ terms in the potential energy. In this context, the amazing computer progress over the past 30 years, having reduced the time per arithmetic operation from milliseconds to nanoseconds, i.e. by factor $\sim 10^6$, has not led to any appreciable proximity to N_A : the number of simulated particles has risen by “only” two orders of magnitude,² from $\sim 10^3$ to $\sim 10^5$.

² However, MC calculations can be facilitated by other means. While the speed of computer operations has almost reached its physical limit, rapid progress in the design of chips for computer memory does not seem to be slowing down. The accessible amount of computer memory doubles every year, and can reach

Finally, a general statement is that MC does not compete with analytical physics: no numerical method is superior to a good model of a phenomenon and its analytical treatment if the latter is available. At the same time, if a good model has been proposed, MC can significantly improve its estimates. On the other hand, there are plenty of fundamental and applied problems that are too complicated (at least for now) to be treated analytically. For those, MC can become not only a quantitative tool but also a qualitative method that yields insight into the physical picture.

7.2 Computer simulation of randomness

Since there exist a variety of random distributions it is useful to find out how many counterfeits are necessary to cover them. Surprisingly enough it turns out that it is theoretically sufficient to simulate independent random variables characterized by just a single distribution function – *a standard of randomness* – and, moreover, it doesn't matter which one, even the simplest, as long as it is known exactly. Probability theory guarantees the same degree of randomness to variables with other known distribution functions if they can be recalculated from the standard one by means of deterministic formulas.

The unexpected appearance of MC in the middle of the twentieth century contributed to the very philosophy of the problem “what is a random sequence?”. A traditional task of mathematical statistics is to estimate unambiguously probabilities of random events. MC gave birth to the reverse task: given a probability function simulate a random event and express it by means of a computer number. Rigorously speaking such a problem is not only ambiguous but simply unsolvable, since every truly random event is by its very mathematical definition unpredictable. Lehmer in 1951 [91] was the first to propose an escape from this deadlock. He introduced two terms: “unpredictability to the uninitiated” and “pseudorandom sequence”:

“A pseudorandom sequence is a vague notion embodying the idea of a sequence in which each term is unpredictable to the uninitiated and whose digits pass a certain number of tests traditional with statisticians and depending somewhat on the uses to which the sequence is to be put.”

At first sight one might consider this quotation more philological than mathematical. However, after a little thought, one might admit that there was probably (and still is!) no other way to introduce artificial randomness. Lehmer's

at present about 40 GB, i.e. 10^{10} 4-byte numbers, making it possible to store an $N \times N$ matrix of pairwise interaction potentials of $N = 10^5$ particles! Then a “Metropolis step” (7.26)–(7.27), described in Sect. 7.4, requiring calculation of the energy change ΔU for a single particle move $\mathbf{r}_i \rightarrow \mathbf{r}'_i$, results in the correction of only N of the stored potentials, not N^2 . Parallel calculations on several processors are another possibility.

“philology” seemed puzzling to some and astonished others. The random number generator proposed by Lehmer (we discuss it below) has so far successfully competed with other generators (of Fibonacci type and other types).

From the preceding discussion it is clear that it is appropriate to choose as a standard of randomness the simplest variable, namely the independent random quantities $q_1, q_2, \dots$, uniformly distributed over the interval $(0, 1)$. These variables are called *random numbers*; we reserve the notation q for them throughout this chapter. To make a distinction, variables described by other probability distributions will be referred to as *random quantities*.

There are many ways to generate random numbers (for a review see [60]). Among the latest “Lehmer-like” works we refer to [34]–[36]. In [34], [35] the sequence of q is generated with the help of a recursive sequence of 64-bit integers Q :

$$q_{n+1} = Q_{n+1}/2.0^{64}, \quad \text{where} \quad (7.6)$$

$$Q_0 = 1, \quad Q_{n+1} = (Q_n A) \bmod 2^{64}, \quad n = 0, 1, 2, \dots \quad (7.7)$$

The 64-bit integer A is called the *multiplier* and 2^{64} the *modulus* of the sequence. Thus, two 64-bit integer numbers Q_n and A are multiplied exactly (without roundoff) and from the 128-bit product the least significant 64 bits are retained as the next Q_{n+1} . After that it is normalized, divided by the modulus, and presented as the next standard q_{n+1} . Pseudorandomness stems from the fact that the most significant bits in the middle of the product are produced by adding many bits. One has to be careful when choosing the multipliers A ; the resulting sequence (7.6) must be tested by statistical methods to verify independence of the numbers q with the different as well as the same multipliers. These tests are carried out in [34], where 200 multipliers are selected.³

Let us discuss how the random numbers can be recalculated into random quantities satisfying other given distribution functions. In some cases these recalculation formulas are obvious. For example, random quantities α uniformly distributed at $(-1, 1)$ are realized according to

$$\alpha = 2q - 1, \quad \text{or equivalently} \quad \alpha = 1 - 2q \quad (7.8)$$

In the simplest case of a one-dimensional probability density $w(x)$ (subject by definition to the normalization $\int_{-\infty}^{\infty} w(X) dX = 1$) the recalculation formula can be derived by solving one of the equivalent “integral probability equalities” [132]:

³ The corresponding Fortran codes are available via the Computer Physics Communications Program Library. Randomness is guaranteed for up to 10^{18} numbers produced by each generator. Recently the same authors [36] have studied a “more random” 128-bit sequence $Q_0 = 1, Q_{n+1} = (Q_n A) \bmod 2^{128}, q_{n+1} = Q_{n+1}/2.0^{128}$ and selected more than 2000 multipliers for it.

$$\int_{-\infty}^x w(X) dX = q \quad \text{or equivalently} \quad (7.9)$$

$$\int_x^{\infty} w(X) dX = q \quad (7.10)$$

To clarify these expressions note that the left-hand side of the first one is the probability $P\{X < x\}$ that the random variable X is less than x , while the left-hand side of the other is complementary to it: $P\{X > x\} = 1 - P\{X < x\}$. For random quantities with the exponential probability distribution

$$e^{-\xi}, \quad \xi > 0$$

(we reserve the notation ξ for them throughout this chapter) we obtain from (7.10)

$$\xi = -\ln q \quad (7.11)$$

Thus, if the energy E of a certain system is always positive and distributed according to the Boltzmann factor $w(E) = \exp(-E/k_B T)$ then it can be simulated by

$$E = -k_B T \ln q = k_B T \xi$$

Because of the exceptional role the quantities ξ and α , discussed above, play in MC calculations we will also call them standards of randomness.⁴ If X is given by the Gaussian distribution

$$w(X) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{X^2}{2\sigma^2}\right)$$

then one could in principle make use of (7.9), but this would lead to the integral equation

$$\text{erf}(x/\sigma) = q$$

where

$$\text{erf}(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^z e^{-u^2/2} du \quad (7.12)$$

is the error function. There exists, however, a more elegant way to do it, based on the principle of superfluous randomness, using not one but several standards of randomness, which leads to elementary simulation formulas.

In fact these formulas solve, in a probabilistic sense, integral equations of the type (7.9)–(7.10) and their multidimensional analogs. The normal (Gaussian) distribution is simulated by the Box–Muller formula [18] (see also [132]) using two standard quantities q and ξ :

⁴ The library [34] contains the subroutines simulating not only q but also α , ξ , normally distributed (with mean zero and variance = 1) and some other random quantities.

$$X = \sigma(2\xi)^{1/2} \cos(2\pi q) \quad (7.13)$$

Note that for the two-dimensional normal density

$$w(X, Y) = \frac{1}{2\pi\sigma^2} \exp\left(-\frac{X^2 + Y^2}{2\sigma^2}\right)$$

one still needs only two standard quantities:

$$X = \sigma(2\xi)^{1/2} \cos(2\pi q), \quad Y = \sigma(2\xi)^{1/2} \sin(2\pi q) \quad (7.14)$$

7.2.1 Rejection method

One of the efficient techniques of recalculating the standards into a given distribution $w(X)$, where X can be multidimensional, is called the rejection method. It uses a random amount of superfluous standards and is useful for a variety of complicated distribution functions $w(X)$. Imagine that we can find a trial density distribution function $v(X)$ satisfying the following requirements:

1. with its help we can generate X ;
2. $v(X)$ does not vanish anywhere that $w(X)$ is finite (this is the ergodicity requirement: a trial density should cover all points accessible for $w(X)$);
3. the trial weight

$$s_{w/v}(X) \equiv \frac{w(X)}{v(X)}$$

has a finite maximum:

$$\sup_X s_{w/v}(X) \equiv S_{w/v} < \infty$$

(in other words a trial density $v(X)$ can have singularities at the same points and of the same order as the original density $w(X)$). Then the following simple algorithm for simulation of X distributed with $w(X)$ can be proposed:

Algorithm 7.1 (Rejection method) *A trial X is simulated from the trial density $v(X)$ to give $X = x$ and with the next q the inequality of weights is checked:*

$$S(x) \equiv \frac{s_{w/v}(x)}{S_{w/v}} > q \quad (7.15)$$

If “yes”, $X = x$ is accepted as a simulation from $w(X)$; if “no”, it is rejected and the procedure repeats with another trial simulation X from $v(X)$.

The left-hand side, $S(x)$, of (7.15) is often called a *rejection umbrella* (or *umbrella curve*) and the inequality itself is associated with *hiding under the rejection umbrella*. Note that $0 < S(x) < 1$.

Figure 7.1 illustrates how the rejection algorithm works. It is notable that the inequality check (7.15) does not require any knowledge of normalizing constants for the two probability densities, since the normalizing constants cancel – a feature that (as we shall see later) becomes crucial for application of the Monte Carlo method to statistical physics problems.

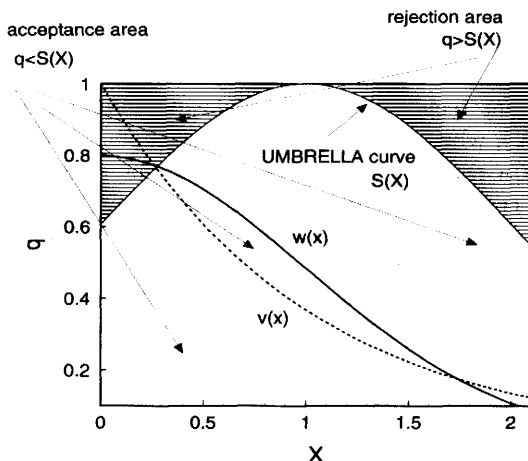


Fig. 7.1. Illustration of the rejection method. X is a positive random quantity with the probability density $w(X)$; $v(X)$ is a trial density for simulation of a trial X . $S(X) = s_{w/v}(X)/\sup_X[s_{w/v}(X)]$ is the umbrella curve; q , a random number. The rejection area for pairs (X, q) is filled; the acceptance area is open

A simple proof of the validity of this scheme stems from the fact that the probability $dP(x)$ of accepting X from the interval $(x, x + dx)$ is a product of two quantities:

- (a) the probability $v(x)dx$ of a trial X simulated from $v(X)$ being within this interval, and
- (b) the probability of accepting this trial value, which is given by the inequality (7.15); the latter, read from left to right, can be expressed as the probability that a random number is less than $S(X)$. Thus,

$$dP(x) = [v(x) dx] S(x) = v(x) dx \left[\frac{w(x)}{v(x)S_{w/v}} \right] = \frac{1}{S_{w/v}} w(x) dx$$

Hence, as required, $dP(x)$ is proportional to the original distribution function $w(x)$. The efficiency of the rejection algorithm is characterized by the proba-

bility P_{yes} of accepting any trial X from the first attempt. By integrating we find

$$P_{\text{yes}} = \int dP(x) = \frac{1}{S_{w/v}} \quad (7.16)$$

since $w(x)$ is normalized to unity. This result reflects a trivial observation: the closer the trial density is to the simulated one, the smaller the number of rejections.

As an example, let us apply the rejection method to simulate the standard normal distribution with mean 0 and variance 1:

$$w(X) = \sqrt{\frac{2}{\pi}} \exp\left(-\frac{X^2}{2}\right), \quad 0 < X < \infty$$

Let us choose the exponential density as a trial

$$v(X) = e^{-X}, \quad X > 0$$

We already know how to simulate it: $X = \xi$. The trial weight is

$$s_{w/v}(X) = \sqrt{\frac{2}{\pi}} \exp\left(-\frac{X^2}{2} + X\right),$$

its absolute maximum being

$$S_{w/v} = \sqrt{\frac{2}{\pi}} \exp(1/2)$$

The umbrella curve is given by the function

$$S(X) = \exp\left[-\frac{(X-1)^2}{2}\right]$$

which does not contain the normalizing constant. The inequality (7.15) reads

$$\exp[-(X-1)^2/2] > q$$

Taking the logarithm and using (7.11), we obtain the following

Algorithm 7.2 (Simulation of the standard normal distribution)

$$X = \xi \quad \text{if } (\xi - 1)^2 < 2\xi_1,$$

otherwise ξ and ξ_1 are rejected and replaced by the new values.

The probability of accepting the trial X from the first attempt is

$$\frac{1}{S_{w/v}} = \left[\frac{\pi}{(2e)} \right]^{1/2} \approx 0.76$$

Thus, on average one needs to generate about four pairs (ξ_1, ξ_2) for every three simulations.

7.3 Simulation of “observations of random variables” for statistical ensembles

The rejection algorithm described above indicates a possible way to simulate the Gibbs density function (7.2) but it is still far from practical use. Even for the simplest Lennard–Jones potential it is not easy to choose a trial density $v(\mathbf{r}^N)$ close to the equilibrium canonical form (7.2):

$$P_{\text{eq}} = w(\mathbf{r}^N) = \frac{1}{Q_N} \exp \left[-\frac{U(\mathbf{r}^N)}{k_{\text{B}}T} \right] \quad (7.17)$$

The easiest way to satisfy the requirements 1 and 2 is to choose as a trial a uniform distribution within the volume V for every particle, which for N particles gives

$$v(\mathbf{r}^N) = \frac{1}{V^N}$$

It is not possible, however, to find the supremum of the weight. And even if it were it would be of no use. Indeed, as is known from thermodynamic fluctuation theory, a rather narrow domain of the configuration space in the vicinity of the sharp maximum of the Gibbs function (7.17) makes the dominant contribution to the thermal averages, and in practice it is virtually impossible that by means of a trial simulation *all molecules simultaneously* find themselves in this domain. What one can do is to simulate the transition process from less probable to more probable configurations. This can be done by performing a random walk in configuration space. The question becomes how one can guarantee that MC simulation of particle coordinates will “forget” the initial trial distribution and relax to the equilibrium fluctuating around it (as it does in Nature). The answer is that this will be the case provided that the simulated relaxation process satisfies the detailed balance condition framed in terms of the master equation [53].

The master equation describes evolution of an ensemble of particles from some initial configuration ($\mathbf{r}^N$) at time $t = 0$ (we denote its probability by $P(\mathbf{r}^N, t = 0)$) to another one ($\mathbf{r}'^N$) at time t , characterized by the probability $P(\mathbf{r}'^N, t)$. The evolution depends on the rates of forward and backward transitions between two configurations, $W(\mathbf{r}^N \rightarrow \mathbf{r}'^N)$ and $W(\mathbf{r}'^N \rightarrow \mathbf{r}^N)$, respectively

$$\begin{aligned} \frac{\partial P(\mathbf{r}^N, t)}{\partial t} = & - \int d\mathbf{r}'^N P(\mathbf{r}^N, t) W(\mathbf{r}^N \rightarrow \mathbf{r}'^N) \\ & + \int d\mathbf{r}'^N [P(\mathbf{r}'^N, t) W(\mathbf{r}'^N \rightarrow \mathbf{r}^N)] \end{aligned} \quad (7.18)$$

The first term here gives the total rate of transitions from the given configuration $\mathbf{r}^N$ to others, and the second term describes the total rate of transitions

from other configurations to $\mathbf{r}^N$. Relaxation to equilibrium means that at $t \rightarrow \infty$

$$\frac{\partial P(\mathbf{r}^N, t)}{\partial t} \rightarrow 0, \quad P(\mathbf{r}^N, t) \rightarrow P_{\text{eq}}(\mathbf{r}^N)$$

which can be achieved if (the detailed balance condition) for every two points $\mathbf{r}^N$ and $\mathbf{r}'^N$ of the configuration space the following time-independent relationship is satisfied:

$$P_{\text{eq}}(\mathbf{r}'^N)W(\mathbf{r}'^N \rightarrow \mathbf{r}^N) - P_{\text{eq}}(\mathbf{r}^N)W(\mathbf{r}^N \rightarrow \mathbf{r}'^N) = 0, \quad \text{or} \quad (7.19)$$

$$\frac{W(\mathbf{r}^N \rightarrow \mathbf{r}'^N)}{W(\mathbf{r}'^N \rightarrow \mathbf{r}^N)} = \frac{P_{\text{eq}}(\mathbf{r}'^N)}{P_{\text{eq}}(\mathbf{r}^N)} \quad (7.20)$$

From the standpoint of simulation it is notable that this condition can be satisfied by choosing transition probabilities W in a variety of ways. One can call the simplest one a “step forward or step in place”:

$$W(\mathbf{r}^N \rightarrow \mathbf{r}'^N) = \min \left\{ 1, \frac{P_{\text{eq}}(\mathbf{r}'^N)}{P_{\text{eq}}(\mathbf{r}^N)} \right\} \quad (7.21)$$

Metropolis criterion. An elegant way to perform a step for the master equation was proposed by Metropolis and his colleagues in 1953 [101]:

- a new configuration is generated by means of an arbitrary trial density probability v satisfying the above written criteria 1 and 2 (e.g. the uniform density): $\mathbf{r}^N = \mathbf{r}'^N[v]$
- the next random number q is generated and the condition

$$s_{w/v} \equiv \frac{P_{\text{eq}}(\mathbf{r}'^N)}{P_{\text{eq}}(\mathbf{r}^N)} > q \quad (7.22)$$

is checked

- if it is satisfied, $\mathbf{r}'^N$ is accepted as the new configuration (step forward), otherwise the old one, $\mathbf{r}^N$, is retained (step in place, increasing the weight of the old configuration).

Taking the logarithm of (7.22) and using (7.11) and (7.17) we convert it into a more elegant form

$$\Delta U < k_B T \xi \quad (7.23)$$

where $\Delta U \equiv U(\mathbf{r}'^N) - U(\mathbf{r}^N)$ is the energy difference between the two configurations and ξ is the exponential standard.⁵

⁵ The inequality (7.22) covers both possibilities appearing under the min sign in (7.21) since q is always smaller than unity. It is possible to first check

The physical meaning is transparent: if the weight of the new configuration exceeds unity, $s_{w/v} > 1$, then (note that q is always less than unity) it is *unconditionally* accepted (thereby providing relaxation to equilibrium). If the new configuration is less probable, $s_{w/v} < 1$, it is accepted (but now on condition) with the probability $s_{w/v}$ and rejected with the complementary probability $1 - s_{w/v}$ (providing fluctuations near equilibrium after the relaxation period). One can easily see by interchanging $\mathbf{r}^N$ and $\mathbf{r}'^N$ that detailed balance (7.21) is satisfied.

A nice feature of the scheme (originally pointed out by its authors [101]) is that a new configuration can be obtained from the old one by changing the coordinates of only one particle at each MC step, keeping the positions of the rest fixed. A particle to be displaced can be chosen at random or in turn. Compared to the naive approach of moving all particles simultaneously, this idea significantly facilitates approach to the sharp maximum of the equilibrium distribution function.

Finally, analyzing the detailed balance condition (7.20), we observe that it allows the multiplicative inclusion of an arbitrary symmetric function $\omega(\mathbf{r}^N, \mathbf{r}'^N) = \omega(\mathbf{r}'^N, \mathbf{r}^N)$, which can be continuous or discrete, into W . If ω is positive and normalized to unity it can be also simulated by means of MC. Usually, the transition probability is chosen to be continuous in coordinates and discrete in a particle's number:

$$W(\mathbf{r}^N \rightarrow \mathbf{r}'^N) = \sum_{i=1}^N p_i W(\dots, \mathbf{r}_i \rightarrow \mathbf{r}'_i, \dots) \quad (7.24)$$

(by “...” we denote the coordinates of particles other than i , which remain unchanged) with

$$p_i = \omega(\mathbf{r}^N, \mathbf{r}'^N) = \frac{1}{N}, \quad \sum_{i=1}^N p_i = 1$$

7.4 Metropolis algorithm for canonical ensemble

Combining all these features and considering the volume V to be a cube with a side L , we can formulate

$P_{\text{eq}}(\mathbf{r}'^N)/P_{\text{eq}}(\mathbf{r}^N) > 1$ and if “yes” then there is no need to generate q (equivalently there is no need to generate ξ in (7.23) if $\Delta U < 0$). However, a small (compared to the ΔU calculation) savings in time is not always favorable. It can be outweighed by using the *method of dependent trials* (see Sect. 7.8.2) whereupon equal number of standards of randomness per MC step becomes important.

Algorithm 7.3 (Metropolis algorithm for canonical ensemble)*Step 0. Simulation of initial configuration*

Set the configuration and relaxation counters to zero: $k_{\text{con}} = 0$, $k_{\text{eq}} = 0$ (no relaxation). For each particle $i = 1, 2, \dots, N$ simulate coordinates uniformly distributed in the cube V :

$$\mathbf{r}_i = L(q_{x,i}\mathbf{e}_x + q_{y,i}\mathbf{e}_y + q_{z,i}\mathbf{e}_z) \quad (7.25)$$

where $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ are unit vectors of the cube and q with various indices are independent random numbers (if the particles have hard cores it is reasonable to rule out overlap). Find the initial configuration energy $U(k_{\text{con}} = 0)$.

Step 1. Simulation of a new configuration by displacing particles one by one
Increase the configuration counter by 1: $k_{\text{con}} \rightarrow k_{\text{con}} + 1$. Sequentially (or randomly with the equal probability $1/N$) simulate new coordinates of the particle i ($i = 1, 2, \dots, N$) according to

$$\mathbf{r}'_i = L(q_{x,i}\mathbf{e}_x + q_{y,i}\mathbf{e}_y + q_{z,i}\mathbf{e}_z)$$

(with the next independent random numbers), every time calculating the energy change ΔU and checking the inequality

$$\Delta U < k_B T \xi \quad (7.26)$$

where

$$\Delta U = \sum_{j \neq i} [u(\mathbf{r}'_i, \mathbf{r}_j)] - u(\mathbf{r}_i, \mathbf{r}_j) + u_{\text{ext}}(\mathbf{r}'_i) - u_{\text{ext}}(\mathbf{r}_i) \quad (7.27)$$

If “yes”, replace the old coordinates by the new ones (the old are forgotten); if “no”, the particle retains its old position. Store the new configuration energy $U(k_{\text{con}})$. If $k_{\text{eq}} = 1$, go to Step 3 (averaging), otherwise - to Step 2 (relaxation).

Step 2. Analysis of the relaxation process

Comparing the terms in the sequence $U(0)$, $U(1)$, $U(k_{\text{con}})$ estimate whether the relaxation process has finished and the system has started to fluctuate about some average value. If “no”, go to Step 1 for a new configuration. If “yes”, set $k_{\text{eq}} = 1$ (end of relaxation), $k_{\text{con}} = 0$ (begin counting equilibrium configurations) and go to Step 3.

Step 3. Calculation of averages over equilibrium configurations

The sums (7.3)–(7.4) are accumulated, where $M = k_{\text{con}}$ (due to Step 2, the nonequilibrium relaxation configurations are excluded from k_{con}). Go to Step 1 until the desired number of trials M is reached. *End of algorithm.*

The Metropolis algorithm performs importance sampling of configurations by generating them already with a probability proportional to the Boltzmann factor $e^{-\beta U}$. All thermal averages then become simple arithmetic averages over the generated configurations. The remarkable feature of this scheme is

that although the constant of proportionality $1/Q_N$ is not known, it does not enter into the algorithm.

7.5 Simulation of boundary conditions for canonical ensemble

As already discussed, the number of simulated particles accessible to modern computers is $\sim 10^5$, far less than the desired number $N_A \sim 10^{23}$. This fact gives rise to a systematic error (the latter should not be confused with the typical MC error $\sim O(M^{-1/2})$) that depends on the number of simulated particles N_{MC} . Its order is $O(N_{MC}^{-\epsilon})$, $\epsilon > 0$ and at best $\epsilon > 1/2$. In other words if computers allowed simulation of N_A particles this systematic error would not occur, but at present its reduction is problematic. The main idea for the solution of the “Avogadro-MC” problem is simulation of the boundary conditions.

Let us first simplify the problem by eliminating the external field contribution and assuming short-range pairwise potentials. The latter are those which decay with distance faster than $1/r^3$ (e.g. Lennard-Jones, exponential etc.). Compare the cube with the Avogadro number of particles N_A in the volume $V_A = L_A^3$ with the internal MC cube of the volume $V_{MC} = L_{MC}^3$ which is only

$$V_{MC}/V_A = 10^5/10^{23} = 10^{-18}$$

of the Avogadro volume and its side $L_{MC} = 10^{-18/3}L_A = 10^{-6}L_A$. Only a reasonable extrapolation at the volume boundaries makes it still possible to study real ensembles. A particle effectively interacts with neighbors within a distance of the order of L_{near} , which can be identified with the correlation length (at the given temperature). Assume that $L_{MC} > L_{near}$.⁶ Then a configuration in the MC cell, which is inside the Avogadro cell of the real ensemble, possesses translational symmetry in the probabilistic sense; specifically the average configuration for all translational images of the MC cell along all three directions x, y, z will coincide with the average configuration for the original cell. But configurations in different cells will fluctuate independently. The idea of MC boundary conditions, reducing the error $O(N_{MC}^{-\epsilon})$, is to assume in all translationally symmetric cells exactly the same configuration as in the original one. Thus, we assume that fluctuations in all these cells are 100% correlated with fluctuations in the original cell. This idea introduces periodic boundary conditions.

In the Metropolis algorithm one must decide which neighbors take part in the pairwise interactions with a given particle from the main MC cell.

⁶ This condition cannot be satisfied in the vicinity of a critical point, where the correlation length tends to infinity. In this case, *finite-size scaling* is applied [13].

For short-range interactions it is plausible to take into account contributions from particles located in a cube with the same side length L_{MC} centered at the given particle; this is the condition of the cut-off, toroidal periodicity.

Long-ranged potentials like Coulomb ($\sim 1/r$) and dipole-dipole ($\sim 1/r^3$), require a special treatment. We cannot truncate the potential at some distance, but instead we must sum over an infinitely large number of cells. Such sums are poorly convergent. There exists, however, a procedure originally proposed in 1921 by Ewald [37] and rigorously developed by de Leeuw, Peram, and Smith [86]–[88] (see also the discussion of the Ewald summation method in [47]) which makes it possible to overcome this difficulty by converting the original poorly convergent sum into two rapidly convergent sums in physical and Fourier space.

Obviously translational manipulations are forbidden if they violate the physical symmetry of the system under consideration. For example a fluid in the absence of an external field allows for full 3D periodic translational symmetry. However a fluid in the gravitational field near the surface of the Earth allows for periodic cylindrical boundary conditions only in the layer below the upper boundary and above the lower boundary of the MC cell; the upper boundary must be free, while the lower must be impenetrable.

7.6 Grand ensemble simulation

In the grand (μVT) ensemble the average of an arbitrary physical quantity X is given by (1.85):

$$\bar{X} = \sum_{N \geq 0} \frac{z_0^N}{N!} \int d\mathbf{r}^N X(\mathbf{r}^N) \frac{e^{-\beta U(N, \mathbf{r}^N)}}{\Xi} \quad (7.28)$$

where $z_0 = \lambda/\Lambda^3$ is the fugacity and

$$\Xi = \sum_{N \geq 0} \frac{z_0^N}{N!} \int d\mathbf{r}^N e^{-\beta U(N, \mathbf{r}^N)} \quad (7.29)$$

is the grand partition function. It is clear that the detailed balance condition results in relations between the forward and backward probabilities, including, in addition to (7.19)–(7.20), changing the number of particles due to the particle exchange with the heat bath.

To make the application of MC more transparent it is reasonable to unify all integrals to a fixed dimension, that can be done in a simple way. First of all note that due to the finite size of particles their number in a fixed volume V is bounded from above by some N_0 (since the number density is always below the close packing limit).⁷ This means that for N exceeding N_0 ,

⁷ We do not discuss here an ideal gas (point-like particles) for which calculations become trivial: $\Xi = \exp(z_0 V)$.

$U(N, \mathbf{r}^N) = \infty$, $\exp[-\beta U(N, \mathbf{r}^N)] = 0$ whatever the configuration $\mathbf{r}^N$. Using this concept of the maximum number of particles proposed by Rowley et al. [123], we conclude that summation in (7.28)–(7.29) is up to N_0 .

Now to extend all integrals in the sum (i.e. for each $0 \leq N \leq N_0$) to the fixed dimension N_0 we add $N_0 - N$ fictitious particles, considering them to be an ideal gas environment; physically, this is a way to model the heat bath. Because fictitious particles are passive, the energy U can be thought of as being dependent on all coordinates $\mathbf{r}^{N_0}$ rather than on $\mathbf{r}^N$ only. All extra integrations lead simply to multiplication by V^{N_0-N} , which must be canceled by the inverse quantity V^{N-N_0} , resulting in

$$\bar{X} = V^{-N_0} \sum_{N=0}^{N_0} \frac{(z_0 V)^N}{N!} \int d\mathbf{r}^{N_0} X(\mathbf{r}^N) \frac{e^{-\beta U(N, \mathbf{r}^{N_0})}}{\Xi} \quad (7.30)$$

$$\Xi = V^{-N_0} \sum_{N=0}^{N_0} \frac{(z_0 V)^N}{N!} \int d\mathbf{r}^{N_0} e^{-\beta U(N, \mathbf{r}^{N_0})} \quad (7.31)$$

The detailed balance condition becomes (note that, as expected, it does not depend on N_0)

$$\frac{W[(N, \mathbf{r}^N) \rightarrow (N', \mathbf{r}'^{N'})]}{W[(N', \mathbf{r}'^{N'}) \rightarrow (N, \mathbf{r}^N)]} = \frac{(z_0 V)^N / N!}{(z_0 V)^{N'} / N'!} \exp \left\{ -\frac{[U(N, \mathbf{r}^{N_0}) - U(N', \mathbf{r}'^{N_0})]}{k_B T} \right\} \quad (7.32)$$

In the Metropolis algorithm an elementary trial step is performed for a single particle i . Now it should include probabilities W_0 , W_{+1} , W_{-1} , of three elementary transitions:

- W_0 : changing coordinates of the particle i ,
- W_{+1} : gaining a new particle: $N' = N + 1$, and
- W_{-1} : losing a particle: $N' = N - 1$

The general expression for W_k is

$$W_k = \min \left\{ 1, a_k \exp \left[-\frac{\Delta U_k}{k_B T} \right] \right\}, \quad k = 0, +1, -1 \quad (7.33)$$

where

$$\Delta U_0 = U(N, \dots, \mathbf{r}'_i, \dots) - U(N, \dots, \mathbf{r}_i, \dots), \quad a_0 = 1 \quad (7.34)$$

$$\Delta U_{+1} = U(N+1, \mathbf{r}^{N+1}) - U(N, \mathbf{r}^N), \quad a_{+1} = \frac{z_0 V}{N+1} \quad (7.35)$$

$$\Delta U_{-1} = U(N-1, \mathbf{r}^{N-1}) - U(N, \mathbf{r}^N), \quad a_{-1} = \frac{N}{z_0 V} \quad (7.36)$$

From these expressions we can deduce

Algorithm 7.4 (Metropolis algorithm for grand ensemble)*Step 0. Simulation of initial configuration and number of particles*

Choose an arbitrary N and as in the canonical Metropolis scheme set the configuration and relaxation counters to zero: $k_{\text{con}} = 0$, $k_{\text{eq}} = 0$. For each particle $i = 1, 2, \dots, N$ simulate coordinates uniformly distributed in the volume V . Find the initial configuration energy $U(k_{\text{con}} = 0)$.

Step 1. Cycle over particles

Sequentially (or randomly with the uniform probability $1/N$) for every particle $i = 1, 2, \dots, N$ perform Step 1a, simulation of one of the three elementary events (index k) with equal probability $1/3$.

Step 1a

$k_{\text{con}} \rightarrow k_{\text{con}} + 1$. With the next random number q calculate $k = \text{integer}(3q) - 1$, ΔU_k and a_k , and check the inequality

$$\Delta U_k < k_B T (\xi + \ln a_k) \quad (7.37)$$

which is an obvious generalization of (7.26). If “yes”, change the old parameters – the number of particles N or particle coordinates, or both (if a new particle is introduced). If “no”, keep them unchanged. Store the new configuration energy $U(k_{\text{con}})$. If $k_{\text{eq}} = 1$, go to Step 3 (averaging), otherwise go to Step 2 (relaxation).

Step 2. Analysis of the relaxation process

Comparing the terms in the sequence $U(0)$, $U(1)$, $U(k_{\text{con}})$, assess whether the relaxation process has finished and whether the system has started to fluctuate about some average value. If “no”, go to Step 1 for a new configuration. If “yes”, set $k_{\text{eq}} = 1$ (end of relaxation), $k_{\text{con}} = 0$ (begin counting equilibrium configurations), and go to Step 3.

Step 3. Calculation of averages over equilibrium configurations The sums (7.3)–(7.4) are accumulated where $M = k_{\text{con}}$ (due to Step 2, nonequilibrium relaxation configurations are excluded from k_{con}). Go to Step 1 until the desired number of trials M is reached. *End of algorithm.*

7.6.1 Monte Carlo with fictitious particles

The simulation strategy described above is efficient predominantly for low chemical potentials, i.e. for dilute systems. If a system is dense, inserting a new particle into the volume V without overlapping of hard cores can be rather time consuming. Instead one can apply a more efficient technique proposed by Yao et al. [151], which makes use the concept of fictitious particles in an elegant way. The system in a given volume V can be thought of as N_0 particles which can belong to one of two species:

- *real*, of which there are N , with $0 \leq N \leq N_0$, and
- *fictitious*, numbering $N_0 - N$

Fictitious particles, as previously discussed, are passive, and constitute “ideal gas background”: they do not interact either with each other or with real ones. At the same time there exists the possibility of *converting* a real particle into a fictitious one and vice versa. Conceptually, fictitious particles are analogous but not identical (!) to a heat bath: they are located not outside but inside the same volume as the real particles belonging to the simulated ensemble. The average $\bar{X}$ of a physical quantity X in (7.30) can be rewritten as

$$\bar{X} = \frac{\sum_{N=0}^{N_0} \int d\mathbf{r}^{N_0} X(N, \mathbf{r}^{N_0}) h(N, \mathbf{r}^{N_0})}{\sum_{N=0}^{N_0} \int d\mathbf{r}^{N_0} h(N, \mathbf{r}^{N_0})} \quad (7.38)$$

where

$$h(N, \mathbf{r}^{N_0}) = \frac{1}{N!} (z_0 V)^N e^{-\beta U(N, \mathbf{r}^{N_0})} \quad (7.39)$$

Subdividing the volume V into a large number of identical elementary cells $(\Delta L)^3$ and replacing the configuration integral by summation over configurations, $\sum_{\text{conf}}$, as $d\mathbf{r}$ approaches $(\Delta L)^3$ we obtain:

$$\bar{X} = \sum_{N=0}^{N_0} \sum_{\text{conf}} X(N, \mathbf{r}^{N_0}) \nu(N, \mathbf{r}^{N_0}) \quad (7.40)$$

$$\nu = \frac{h(N, \mathbf{r}^{N_0})}{\sum_{N=0}^{N_0} \sum_{\text{conf}} h(N, \mathbf{r}^{N_0})} \quad (7.41)$$

Using MC to calculate this expression means generating a Markov chain of configurations, so that $X(N, \mathbf{r}^{N_0})$ occurs with probability proportional to ν . Then as usual,

$$\bar{X} \approx \frac{1}{M} \sum_{c=1}^M X[(N, \mathbf{r}^{N_0})_c] \quad (7.42)$$

Thus, we have the following

Algorithm 7.5 (MC sampling with fictitious particles)

Step 0. Simulation of an initial configuration of N_0 particles and initial number of real particles N

Set the configuration and relaxation counters to zero: $k_{\text{con}} = 0$, $k_{\text{eq}} = 0$ and for $i = 1, 2, \dots, N_0$ simulate particles coordinates uniformly distributed in the volume V (taking into account hard-core exclusion). Choose an initial number of real particles $N = N_{\text{init}} < N_0$. The rest $N_0 - N_{\text{init}}$ of the particles are fictitious (potentially real). Find the initial configuration energy $U(N_0, N; k_{\text{con}} = 0)$ taking into account that fictitious particles are passive (and therefore only the contribution from real ones counts).

Step 1

For a current configuration k_{con} characterized by the number of real particles N and energy $U(N_0, N; k_{\text{con}})$ decide at random with uniform probability (1/3) which of the steps 1a, 1b, or 1c to perform.

Step 1a. Move of a real particle

Choose at random with uniform probability $1/N$ one of the real particles, say i , and make a trial move (simulate new coordinates of the particle i) calculating

$$\Delta U = U(N_0, N; \dots, \mathbf{r}'_i, \dots) - U(N_0, N; \dots, \mathbf{r}_i, \dots)$$

Check whether

$$\Delta U < k_B T \xi$$

If “yes”, the new configuration is accepted, if “no”, the old one is retained (clearly Step 1a is the canonical Metropolis sampling). Go to Step 1d.

Step 1b. Annihilation of a real particle

Choose at random one of the real particles, say i_R , and calculate the difference of configuration energies without and with the particle i_R :

$$\Delta U = U(N_0, N-1; \mathbf{r}_{-i_R}^{N-1}) - U(N_0, N; \mathbf{r}^N)$$

(here $\mathbf{r}_{-i_R}^{N-1}$ denotes the configuration of $(N-1)$ real particles after annihilation of the particle i_R). Check whether

$$\frac{\nu_{N-1}}{\nu_N} = \frac{N}{z_0 V} e^{-\beta \Delta U} > q$$

or equivalently

$$\Delta U < k_B T \left[\xi + \ln \left(\frac{N}{z_0 V} \right) \right]$$

If “yes”, convert the particle i to fictitious (annihilation), $N \rightarrow N-1$; if “no”, keep it real. Go to Step 1d.

Step 1c. Creation of a real particle

Choose at random one of the fictitious particles, say j_F , and calculate the difference of configuration energies considering that in the new configuration the particle j_F becomes real:

$$\Delta U = U(N_0, N+1; \mathbf{r}_{+j_F}^{N+1}) - U(N_0, N; \mathbf{r}^N)$$

(here $\mathbf{r}_{+j_F}^{N+1}$ denotes the configuration of $(N+1)$ real particles after creation of the particle j_F). Check whether

$$\frac{\nu_{N+1}}{\nu_N} = \frac{z_0 V}{N+1} e^{-\beta \Delta U} > q$$

or equivalently

$$\Delta U < k_B T \left[\xi + \ln \left(\frac{z_0 V}{N+1} \right) \right]$$

If “yes”, convert the particle j_f to real (creation), $N \rightarrow N+1$; if “no”, keep it fictitious.

Step 1d. Fix new configuration

Increase the configuration counter: $k_{\text{con}} \rightarrow k_{\text{con}} + 1$. Store the energy corresponding to the new configuration $U(N_0, N; k_{\text{con}})$. If the relaxation index $k_{\text{eq}} = 1$, go to Step 3 (averaging), otherwise go to Step 2 (relaxation).

Step 2. Analysis of the relaxation process

Comparing the terms in the sequence

$$U(N_0, N_{\text{init}}; k_{\text{con}} = 0), \dots, U(N_0, N; k_{\text{con}})$$

assess whether the relaxation process has finished and the system has started to fluctuate about some average value. If not, go to Step 1. If it has, set $k_{\text{eq}} = 1$ (end of relaxation), $k_{\text{con}} = 0$ (begin counting equilibrium configurations) and go to Step 3.

Step 3. Calculation of averages over equilibrium configurations

The sums (7.3), (7.4) are accumulated where $M = k_{\text{con}}$ (due to Step 2, nonequilibrium relaxation configurations are excluded from k_{con}). Go to Step 1 until the desired number of trials M is reached. *End of algorithm.*

The advantage of this algorithm is that in creating a particle, we do not have to insert it into the volume V (searching for a new location), but instead convert one of the fictitious particles, which are already present but hidden, into a real one. Thus, we do not search for a new location but pick up a fictitious particle with known coordinates and attempt to declare it real. It may be possible that it overlaps with one of the real particles, in which case the attempt is not accepted and it remains fictitious. Another important feature of this strategy is that one need store in computer memory only the interaction energies of the real molecules.

Yao et al. [151] applied this algorithm to a Lennard-Jones fluid with the pair interaction potential

$$u(r) = 4\epsilon_{\text{LJ}} \left[\left(\frac{\sigma_{\text{LJ}}}{r} \right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{r} \right)^6 \right],$$

where r is the center-to-center distance between two particles, and analyzed the dependence of the chemical potential on number density. It is convenient to introduce the reduced independent variables

$$T^* = k_B T / \epsilon_{\text{LJ}}, \quad V^* = V / \sigma_{\text{LJ}}^3, \quad z_0^* = z_0 \sigma_{\text{LJ}}^3$$

From the definition of fugacity we have

$$z_0^* = \frac{e^{\beta\mu}\sigma_{LJ}^3}{\Lambda^3} = \exp \left\{ \beta \left[\mu + k_B T \ln \left(\frac{\sigma_{LJ}}{\Lambda} \right)^3 \right] \right\} = e^{\beta\mu_{conf}}$$

where

$$\mu_{conf} = \mu + k_B T \ln \left(\frac{\sigma_{LJ}}{\Lambda} \right)^3 \quad (7.43)$$

is the configuration chemical potential. The corresponding reduced quantity is

$$\mu_{conf}^* = \mu_{conf} / \epsilon_{LJ}$$

The quantity we wish to determine in simulations is the number density

$$\rho(\mu, V, T) = \frac{\bar{N}}{V}$$

or in reduced units

$$\rho^* = \rho \sigma_{LJ}^3 = \frac{\bar{N}}{V^*}$$

The Lennard–Jones potential is truncated at a cutoff distance $L/2$, where L is the size of the MC cell ($V = L^3$), and periodic boundary conditions are imposed in all three directions. We choose the maximum number of particles N_0 as the one corresponding to close packing of spheres of diameter $0.8\sigma_{LJ}$ in a cube of volume V ; $d = 0.8\sigma_{LJ}$ is a reasonable choice of effective hard-sphere diameter (recall, the Barker–Henderson formula of Sect. 5.3). In [151] N_0 was 500 and 864. The total number of MC steps was approximately 2×10^6 .

Simulations were performed at temperatures $T^* = 1.15$ and $T^* = 1.25$, both below the critical temperature, which according to various estimates [143], [131], [94] lies in the range $T_c^* \approx 1.31$ – 1.35 . This means that the system undergoes a first-order phase transition manifested by two-phase vapor-liquid coexistence at a certain $\mu_{coex}(T)$ which in the chemical potential–density plot should correspond to a horizontal line given by the Maxwell construction. At each temperature three simulations were performed for the liquid phase, and three for the vapor phase. Figure 7.2 shows the configuration chemical potential μ_{conf}^* versus density ρ^* .

The results are in agreement with simulations by Adams [4] based on the Metropolis strategy for the grand ensemble, but calculations using fictitious particles are significantly faster, since a much smaller number of particles is used. For comparison we also show in Fig. 7.2 predictions of the density functional theory, discussed in detail in Chap. 9, for the same system. The chemical potential is given by (9.25):

$$\mu = \mu_d(\rho) - 2\rho a, \quad (7.44)$$

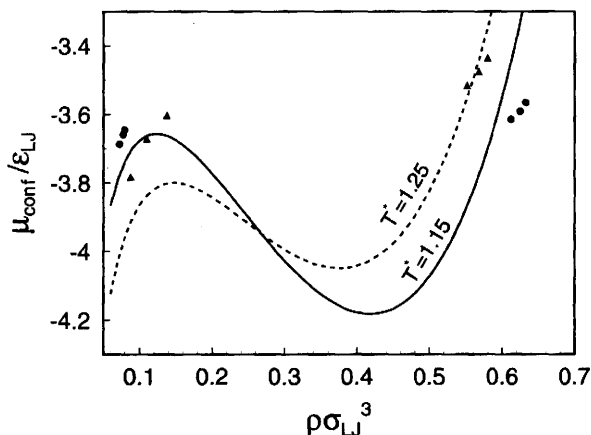


Fig. 7.2. Configuration chemical potential vs. density for a Lennard-Jones fluid obtained by grand ensemble Monte Carlo simulations at $T^* = 1.15$ (circles) and $T^* = 1.25$ (triangles). Solid and dashed lines: results of the density functional calculations for $T^* = 1.15$ and $T^* = 1.25$, respectively

where $\mu_d(\rho)$ is the chemical potential of hard spheres with effective diameter d , and the number density ρ , and the background interaction parameter a for the Lennard-Jones fluid with the WCA decomposition of the interaction potential is given by (9.28):

$$a = \frac{16\pi\sqrt{2}}{9}\epsilon_{LJ}\sigma_{LJ}^3 \quad (7.45)$$

The effective hard-sphere diameter was calculated using the Barker-Henderson formula, and the hard-sphere chemical potential is that of the Carnahan-Starling theory (3.26).

Note that a common feature of first-order phase transitions is appreciable hysteresis, which is the manifestation of the fact that two coexisting phases are separated by an energy barrier; its height is equal to the free energy of the interface between the two phases. It is rather difficult to determine directly in simulations the coexistence point at a given temperature: if we start our simulations in a stable phase 1 and change the temperature, we soon enter the metastable region being trapped in the phase 1 (due to the presence of the energy barrier), and changing the temperature further leads to an irreversible transition to a new phase which is well beyond the coexistence point. That is why in order to detect a coexistence point in simulations it is desirable to get rid of the interface by placing “vapor” and “liquid” molecules into different boxes. This is an idea of the Gibbs ensemble method proposed by Panagiotopoulos [107]. A deficiency of this method is that exchange of particles between the boxes becomes effectively impossible if one of the phases (liquid) is sufficiently dense. An alternative to the Gibbs ensemble method is

the thermodynamic integration method described in detail in [47], in which one determines which phase is stable under given conditions by comparing the free energies of the two phases.

7.7 Simulation of lattice systems

Usually the intermolecular interaction in fluids has a hard core (or at least very strong repulsion at short separations), a potential well, and a rapidly decaying tail. Instead of letting molecules occupy arbitrary positions in space, we can impose a restriction demanding that the centers of the molecules occupy only the sites of some lattice. By doing so we obtain what is called a lattice gas model of a fluid [11]. If the lattice spacing is small enough, such a restriction sounds reasonable; moreover it is necessary for almost every numerical calculation. MC simulation of such systems is significantly faster than that of a continuum, since one deals with a limited number of possible positions.

Let us assume that the total number of lattice sites is N_0 and the coordination number is l , which means that each particle has l nearest neighbors. We also assume that the lattice is *bichromatic*, which means that it can be partitioned into two interpenetrating sublattices, so that nearest neighbors belong to different sublattices.⁸

With each site i ($i = 1, \dots, N_0$) we associate a variable p_i which is equal to unity if the site is occupied and zero otherwise. During simulations we store in computer memory the $N_0 \times N_0$ occupancy matrix, in which each element is just one bit. Simulation of hard-core repulsion becomes trivial: a trial move or insertion of a particle (in the grand ensemble) at a site i with $p_i = 1$ (meaning that the site is already occupied) is rejected.

As an example let us study a lattice gas with short-range repulsive interaction $u > 0$ between nearest neighbors. This means that we are dealing with a “positive potential well,” which is not typical of fluids, where the potential well is usually negative. The underlying physical system might be equally charged ions on a lattice where electrostatic interactions are strongly screened by counterions (the system as a whole is electroneutral). If the screening radius is of the order of the lattice spacing, this ionic system can be modeled as a lattice gas with repulsion between nearest neighbors. The interaction energy of a specific configuration becomes

$$U(p_1, \dots, p_N) = u \sum_{(i,j)} p_i p_j$$

where parentheses in the sum denote summation over pairs of nearest neighbors, with each pair counted only once. This expression implies that all sites are equivalent. The number of occupied sites for a given configuration is

⁸ This is a purely geometrical property. Such partitioning is possible for example in a square, simple cubic, or diamond lattice, but not in a triangular lattice.

$$N(\{p_i\}) = \sum_{i=1}^{N_0} p_i$$

The average concentration (fraction of occupied sites) is given by

$$x = \bar{N}/N_0$$

Let us first discuss some qualitative features of the system behavior. Since interactions are purely repulsive, the equilibrium configuration results from competition between energetic and entropic terms in the free energy. If the repulsion is weak, the entropic contribution prevails for all fractions, which means that particles occupy sites at random. If the repulsion is strong enough, random occupation is favorable for fractions smaller than some critical $x_c^{(1)}$. Beyond $x_c^{(1)}$ the energy contribution becomes comparable to the entropic one, which results in a disorder–order transition: particles occupy preferably one of the sublattices up to $x = 1/2$, whereupon preferable occupation of the second sublattice starts. At high concentrations, in view of a large number of mutually repelling particles, it becomes again favorable to place them at random in order to maximize the entropy. Thus, at some $x_c^{(2)}$ the order–disorder transition takes place. The particle–hole symmetry of the model yields: $x_c^{(2)} = 1 - x_c^{(1)}$. The phase transition is second-order, the order parameter being the difference in average concentrations of the sublattices:

$$x_s = \bar{\rho}_s,$$

where

$$\rho_s = \frac{N_1 - N_2}{N_0}$$

N_1 and N_2 are occupation numbers of sublattices. Average concentrations of sublattices are expressed as

$$x_1 = \bar{N}_1/N_0, \quad x_2 = \bar{N}_2/N_0,$$

so that $x = x_1 + x_2$. It is important to note that this transition is purely an effect of the lattice; it does not occur in a continuum system.

Let us investigate the phase diagram. The grand ensemble ($\mu N_0 T$) is an obvious choice for these calculations. Note that instead of fixing the volume V we fix N_0 , which for a lattice is equivalent. The grand partition function for the lattice gas is

$$\Xi = \sum_{\{p\}} \exp \left[\frac{N\mu - U(\{p\})}{k_B T} \right]$$

where the sum is over all configurations. The average number of occupied sites is given by the thermodynamic relationship [80]

$$x = -\frac{1}{N_0} \left. \frac{\partial \Omega}{\partial \mu} \right|_{N_0, T} \quad (7.46)$$

where $\Omega(\mu, N_0, T) = -k_B T \ln \Xi$ is the grand potential. Equation (7.46) determines the concentration as a function of the chemical potential and temperature $x = x(\mu, T)$. In a second-order phase transition we are not confronted with coexisting phases. Therefore the density at the transition point remains continuous while its derivative $\partial x / \partial \mu$, which is proportional to the isothermal compressibility

$$\chi_T = \frac{N_0}{(\bar{N})^2} \frac{\overline{N^2} - (\bar{N})^2}{k_B T} \quad (7.47)$$

diverges, resulting in nonanalyticity of the function $x = x(\mu, T)$ and its inverse $\mu(x, T)$ at corresponding critical concentrations.

Thus, divergence of χ_T signals a phase transition. However, it is more convenient to detect a transition point by studying the *staggered* compressibility

$$\chi_s \sim \overline{\rho_s^2} - (\overline{\rho_s})^2$$

rather than χ_T . Let us apply the lattice version of the MC algorithm for the grand ensemble with fictitious particles and calculate the order parameter x_s , which is zero in the disordered phase (where the densities of sublattices are equal, $x_1 = x_2 = x$, implying that the sublattices are indistinguishable) and zero in the ordered phase, and the staggered compressibility χ_s , which is sharply peaked in the vicinity of the transition point. Note that a serious problem in simulations is that near the transition point the relaxation time tends to infinity, leading to the so-called critical slowing down; fluctuations dominate the behavior, reducing the accuracy of simulation data. Methods to tackle this problem are described in [135], [13], [150]. The phase diagram for the simple cubic lattice ($l = 6$) emerging from the simulations is shown in Fig. 7.3 in coordinates (x, t) and (μ, t) , where

$$t = 4k_B T / u$$

is the reduced temperature. Areas bounded by the critical curves and the vertical axis correspond to the ordered state.⁹

⁹ Note that this system is equivalent to an antiferromagnetic Ising model [11] in an external field; the order-disorder transition is the one from the antiferromagnetic to the paramagnetic state.

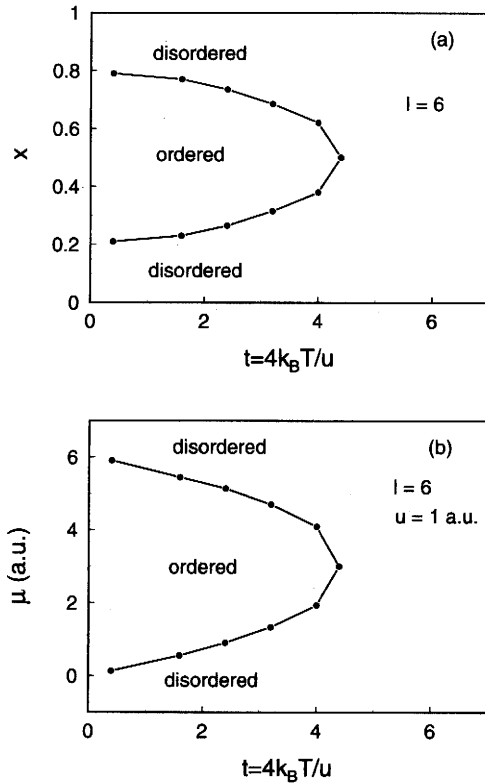


Fig. 7.3. Lattice-gas phase diagram for the simple cubic lattice ($l = 6$). (a) (x, t) plane, (b) (μ, t) plane. Filled circles: MC results. Lines are shown for visual convenience. Domain inside the curve corresponds to ordered states, and outside to disordered states

7.8 Some advanced Monte Carlo techniques

There are a variety of ways to speed up MC calculations and to extend the areas of MC applications. The abilities of modern hardware were already mentioned: large volumes of accessible computer memory (progressing in a geometrical way) and nanosecond time per arithmetic operation, enabling one to store all elements of the pairwise potential matrix, parallel processing, etc. From a number of specific MC possibilities to reduce the calculation time and extend applications (see e.g. [47]), we briefly discuss two (opposing!) trends

- *superfluous randomness* (mentioned in Sect. 7.2), and
- *method of dependent trials*, diminishing unnecessary randomness.

7.8.1 Superfluous randomness to simulate microcanonical ensemble

The microcanonical distribution discussed in Sect. 1.3 contains the Dirac δ -function to ensure conservation of total energy. It is impossible to perform MC steps in a random way on the infinitely thin energy surface. That is why Creutz [24] proposed a superfluous randomness that simulates the kinetic energy of the system but in an indirect way. Recall that the direct way implies solving the Hamiltonian equations in phase space by the deterministic MD-method. As we know, MC simulation of canonical ensembles totally ignores the momenta. The idea of Creutz is to introduce a fictitious demon (leading to extra one-dimensional randomness) instead of the real $3N$ -dimensional momentum subspace. The demon energy must always be positive (like the kinetic energy it is simulating). The idea of the simulation algorithm in the microcanonical (NVE) ensemble is as follows.

1. Start with some random configuration with the potential energy $U(\mathbf{r}^N)$ and fix a total energy $E > U$. The remainder $E_D = E - U$ is assigned to the demon; E_D must always be positive.
2. Take a trial step for each particle and calculate ΔU .
3. If $\Delta U < 0$ the step is accepted and the demon energy increases: $E_D \rightarrow E_D + |\Delta U|$.
If $\Delta U > 0$ check whether $E_D > \Delta U$. If so, the step is accepted and the demon energy decreases: $E_D \rightarrow E_D - \Delta U$; otherwise the step is rejected.

Relaxation in this scenario means that the Maxwell-Boltzmann distribution of the demon (kinetic) energy is established, and one can calculate the demon temperature using the Boltzmann factor with E_D .

7.8.2 Method of dependent trials – eliminating unnecessary randomness

MC “observations” obtained using the *method of dependent trials* have an important advantage over real statistical ones. This stems from the fact that any series of pseudorandom numbers for simulation of one ensemble can be precisely repeated for simulation of another one.¹⁰ Suppose we wish to calculate an average $\bar{X}$ as a function of temperature T for the NVT ensemble. We simulate several ensembles with different $T = T_1, T_2, \dots$. To clarify the idea let us consider just two temperatures T_1 and T_2 close to each other and calculate averages $\bar{X}_1 = \overline{X(T_1)}$ and $\bar{X}_2 = \overline{X(T_2)}$ and their estimated absolute mean square errors ϵ_1 and ϵ_2 . Then the difference $\bar{X}_1 - \bar{X}_2$ has an error

$$\epsilon = \sqrt{\epsilon_1^2 - 2\rho_{12}\epsilon_1\epsilon_2 + \epsilon_2^2} \quad (7.48)$$

¹⁰ This technique becomes particularly useful for studying phase transitions [41].

where $-1 < \varrho_{12} < 1$ is the correlation coefficient [142]. If the statistical errors ϵ_1 and ϵ_2 are independent, then $\varrho_{12} = 0$ and

$$\epsilon = \sqrt{\epsilon_1^2 + \epsilon_2^2}$$

which can easily exceed the average value $\overline{X_1} - \overline{X_2}$ itself, especially if the latter is small. As a result, the curve $\overline{X}(T)$ becomes erratic, showing appreciable jumps at neighboring temperatures.

If on the contrary ϵ_1 and ϵ_2 are substantially positively correlated, so that ϱ_{12} is close to 1, the errors are subtracted:

$$\epsilon \approx |\epsilon_1 - \epsilon_2|$$

and we obtain a smooth curve $\overline{X}(T)$. This situation is impossible for real observations, but in MC “observations” it may be achieved. One of the simplest ways to realize it is to use in an appropriate manner the same set of random numbers to simulate *all* NVT ensembles with different temperatures. According to (7.6)–(7.7) a pseudorandom sequence $\mathbf{q}^{(k)}$ (i.e. a sequence of pseudorandom numbers) can be characterized by the value of the multiplier $A = A_k$ that generates it (as mentioned previously 200 such multipliers were selected and tested in [34] for 64-bit sequences, and 2000 for 128-bit sequences in [36]). Thus, we can generate q indicating a particular sequence number:

$$\mathbf{q}^{(1)}, \mathbf{q}^{(2)}, \dots$$

The same can be done for other standards of randomness: $\alpha^{(k)}$, $\xi^{(k)}$, Gaussian random quantities.

Now let us analyze the Metropolis Algorithm 7.3 of Sect. 7.4, searching for an appropriate way to use the $\mathbf{q}^{(k)}$ -sequences to ensure substantial positive correlations.

Step 0

Use $\mathbf{q}^{(1)}$ to emulate the initial configuration. The latter will be exactly the same for all T .

Step 1

Regularly, one by one, pick up a particle¹¹ and make a trial move. New coordinates for this move are simulated using another sequence $\mathbf{q}^{(2)}$. So new trial coordinates in all T -variants will be the same. Check the inequality (7.26) with $\xi^{(3)}$ (not to check preliminary $\Delta U < 0$, but to provide that in all variants the same number of random values is used).

Steps 2 and 3

are unchanged for all variants.

¹¹ A general rule is: avoid randomness whenever possible and act regularly, since it diminishes the statistical error.

As a result, many particles will at neighboring temperatures occupy the same positions, leading to a smooth variation of physical quantities with T . It is clear that this scheme is suitable for parallel processing.¹²

Even stronger positive correlations can be achieved by the following idea. When relaxation for the T_1 variant is over

- the corresponding equilibrium configuration is stored to serve as the initial one for the T_2 variant, and
- from then on Step 1 operates with $\mathbf{q}^{(4)}, \xi^{(5)}$ (instead of $\mathbf{q}^{(2)}, \xi^{(3)}$).

The T_2 variant begins with the stored configuration as the initial one and proceeds towards equilibrium using $\mathbf{q}^{(4)}$, and $\xi^{(5)}$ sequences.

A simulation strategy analogous to this one is successfully used in nuclear geophysics (see e.g. [141]) when one must analyze the nuclear contents of a rock medium. In logging experiments neutrons are emitted by a source placed in a borehole with a detector; a neutron can be either absorbed by the rock medium or captured by the detector. The goal is to assess the nuclear content of rocks by measuring detector indications during neutron logging.

Monte Carlo is used for the *prediction* problem: *given* a nuclear composition of the rock medium, simulate neutron trajectories in order to find the average fraction of neutrons captured by the detector as a function of nuclei (say, hydrogen) content. Applying the method of dependent trials, one simulates neutron trajectories in the media with differing hydrogen content in such a way that all trajectories start and propagate by means of one and the same random number sequence. The resulting curve, the fraction of captured neutrons versus hydrogen content, proves to be significantly smoother than for independent trials.

¹² Note that if $\Delta T = T_2 - T_1$ is large, simulation lengths for T_1 and T_2 will differ considerably and statistical errors will be uncorrelated. In this case, however, physical quantities corresponding to these temperatures will be significantly different, and therefore the absence of correlations of statistical errors does not play a role.

8. Theories of correlation functions

8.1 General remarks

In the previous chapters we obtained expressions for various thermodynamic properties containing distribution functions, but did not present recipes for calculating them. At low densities $\rho^{(n)}$ can be found by means of density expansions (cf. Sect. 3.6). When this procedure is used, the resulting distribution functions are exact to a given order in the number density ρ , and the resulting properties are also exact to some order in ρ no matter which route to thermodynamics is used: the energy, pressure, or compressibility equation of state. Thus, in using density expansion techniques, one does not confront the problem of thermodynamic consistency.

Clearly, the expansion in density does not work for dense systems. In what follows we discuss approximate methods, resulting in the derivation of approximate distribution functions that are especially suitable at high densities. Note that this approach inevitably leads to the loss of thermodynamic consistency. Throughout this chapter we assume that the potential energy U_N is pairwise additive and u is spherically symmetric.

8.2 Bogolubov–Born–Green–Kirkwood–Yvon hierarchy

The definition of the n -particle distribution function is

$$\rho^{(n)}(\mathbf{r}^n) = \frac{N!}{(N-n)!} \int D_N(\mathbf{r}^N) d\mathbf{r}_{n+1} \dots d\mathbf{r}_N \quad (8.1)$$

where

$$D_N \equiv \frac{1}{Q_N} \exp[-\beta(U_N + U_{N,\text{ext}})]$$

Let us separate terms in U_N and $U_{N,\text{ext}}$ containing $\mathbf{r}_1$:

$$U_N = \sum_{i=2}^N u(r_{1i}) + \sum_{2 \leq i < j \leq N} u(r_{ij})$$

$$U_{N,\text{ext}} = u_{\text{ext}}(\mathbf{r}_1) + \sum_{i=2}^N u_{\text{ext}}(\mathbf{r}_i)$$

and differentiate (8.1) with respect to the coordinates of particle 1:

$$\nabla_1 \rho^{(n)} = -\beta \frac{N!}{(N-n)!} \int D_N \sum_{i=2}^N \nabla_1 u(r_{1i}) \mathbf{dr}_{n+1} \dots \mathbf{dr}_N - \beta \rho^{(n)} \nabla_1 u_{\text{ext}}(\mathbf{r}_1) \quad (8.2)$$

where

$$\nabla_1 \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \equiv \frac{\partial}{\partial \mathbf{r}_1} \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$$

In the integral we break the sum into two parts:

$$\sum_{i=2}^N = \sum_{i=2}^n + \sum_{i=n+1}^N$$

Integration does not depend on the first n variables, so the first summation can be taken out of the integrand, yielding the term $-\beta \rho^{(n)} \sum_{i=2}^n \nabla_1 u(r_{1i})$. Multiplication of the right-hand side of (8.2) by $-k_B T$ gives

$$\begin{aligned} & \rho^{(n)} \sum_{i=2}^n \nabla_1 u(r_{1i}) + \rho^{(n)} \nabla_1 u_{\text{ext}}(\mathbf{r}_1) \\ & + \left\{ \frac{N!}{(N-n)!} \sum_{i=n+1}^N \left[\int D_N \nabla_1 u(r_{1i}) \mathbf{dr}_{n+1} \dots \mathbf{dr}_N \right] \right\} \quad (8.3) \end{aligned}$$

The sum contains $N - n$ terms, all equal (due to integration). Therefore the term in curly brackets becomes

$$\int \mathbf{dr}_{n+1} \nabla_1 u(r_{1,n+1}) \left[\frac{N!}{(N-n-1)!} \int D_N \mathbf{dr}_{n+2} \dots \mathbf{dr}_N \right]$$

which, using (8.1), can be expressed as

$$\int \nabla_1 u(r_{1,n+1}) \rho^{(n+1)} \mathbf{dr}_{n+1}$$

The final result is:

$$\begin{aligned} -k_B T \nabla_1 \rho^{(n)} &= \rho^{(n)} \nabla_1 u_{\text{ext}}(\mathbf{r}_1) + \rho^{(n)} \sum_{i=2}^n \nabla_1 u(r_{1i}) \\ &+ \int \nabla_1 u(r_{1,n+1}) \rho^{(n+1)} \mathbf{dr}_{n+1} \quad (8.4) \end{aligned}$$

This infinite set of equations ($n = 1, 2, \dots$) is called the Bogolubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy. It expresses $\rho^{(n)}$ in terms of $\rho^{(n+1)}$, and therefore cannot be solved for $\rho^{(n)}$ unless some independent approximation (closure) relating $\rho^{(n+1)}$ to distribution functions of order $m \leq n$ is used. As we discuss only pairwise interactions, the most interesting are the BBGKY equations for $n = 1$ and 2:

$$-k_B T \nabla_1 \rho^{(1)}(\mathbf{r}_1) = \rho^{(1)}(\mathbf{r}_1) \nabla_1 u_{\text{ext}}(\mathbf{r}_1) + \int \nabla_1 u(r_{12}) \rho^{(2)} \, d\mathbf{r}_2 \quad (8.5)$$

and

$$-k_B T \nabla_1 \rho^{(2)} = \rho^{(2)} \nabla_1 u_{\text{ext}}(\mathbf{r}_1) + \rho^{(2)} \nabla_1 u(r_{12}) + \int \rho^{(3)} \nabla_1 u(r_{13}) \, d\mathbf{r}_3 \quad (8.6)$$

In the absence of interactions ($u = 0$) the first one reads

$$\nabla_1 (\ln \rho^{(1)}(\mathbf{r}_1)) = \nabla_1 (-\beta u_{\text{ext}}(\mathbf{r}_1))$$

which yields the barometric formula discussed in Sect. 1.5. If $u_{\text{ext}} = 0$ and the system is homogeneous, (8.5) becomes trivial, as all parts vanish: the integral on the right-hand side is proportional to the net force on particle 1, which in homogeneous fluid is equal to zero.

The second equation of the BBGKY hierarchy is nontrivial even in a homogeneous fluid. With a suitable approximation for $\rho^{(3)}$ it constitutes the basis for the Born–Green theory. A widely used closure is Kirkwood’s superposition approximation:

$$\rho^{(3)}(123) = \frac{\rho^{(2)}(12) \rho^{(2)}(13) \rho^{(2)}(23)}{\rho^{(1)}(1) \rho^{(1)}(2) \rho^{(1)}(3)} \quad (8.7)$$

For uniform fluids this becomes

$$g_3(123) = g(12) g(13) g(23) \quad (8.8)$$

Its possible origin can be understood from the following considerations. At sufficiently low densities $g_n(\mathbf{r}^n) \rightarrow \prod_{i=1}^n g_1(\mathbf{r}_i)$, and in particular $g_3(\mathbf{r}^3) \rightarrow \prod_{i=1}^3 g_1(\mathbf{r}_i)$. This means that particles are individually independent. In the next order of approximation in density one can represent the three-particle correlation as a product of all possible pair correlations. So we assume independence of pairs and not of individual particles. However, it still remains a low-density approximation. It is significantly in error at intermediate densities. Surprisingly, for the hard-sphere system at high densities (8.8) becomes reasonably accurate as found in computer simulations of Alder [5]. The validity of the superposition approximation at high densities may possibly be the

result of mutual reductions of the higher-order terms in the group expansion of g_3 [23]. For a uniform fluid ($u_{\text{ext}} = 0$)

$$\rho^{(2)}(12) = \rho^2 g(12), \quad \rho^{(3)}(123) = \rho^3 g(12) g(13) g(23)$$

and combining (8.6) with the superposition approximation results in the Born–Green equation:

$$-k_B T \nabla_1 \ln g(12) = \nabla_1 u(12) + \rho \int g(13) g(23) \nabla_1 u(13) d\mathbf{r}_3 \quad (8.9)$$

This is a nonlinear integro-differential equation relating the pair correlation function to the pairwise interaction potential. Application of (8.9) to hard spheres shows that for volume fractions greater than $\phi_{d,\text{crit}} \approx 0.495$, the integral of the total correlation function does not converge, and the equation has no admissible solutions. Divergence of $\int h(r) d\mathbf{r}$ yields the divergence of the isothermal compressibility (see (3.13)). The latter signals a thermodynamic instability. That is why such behavior of the Born–Green equation was interpreted as an indication of a peculiar phase transition in the system of hard spheres – crystallization – despite the absence of any attractive forces. This is an example of an entropically driven phase transition (see also the discussion in Sect. 3.5). From (8.9) it follows that in the limit of low densities the pair correlation function has the Boltzmann form

$$g(12) = e^{-\beta u(12)}, \quad \rho \rightarrow 0 \quad (8.10)$$

If we substitute this solution into the pressure equation (3.10), it results in the virial expansion truncated at the second-order term and the second virial coefficient is recovered. In the general case one can still write $g(12)$ in the Boltzmann form

$$g(12) = e^{-\beta \Psi(12)} \quad (8.11)$$

but now with a potential of mean force, $\Psi(12)$ that takes into account the influence of a third particle: $\Psi(12) = u(12) + W(12)$. It is seen that $W(12)$ is related to the cavity function via¹

$$y(12) = e^{-\beta W(12)}$$

At low densities

$$\Psi(12) \rightarrow u(12), \quad \rho \rightarrow 0 \quad (8.12)$$

¹ These considerations support the statement, discussed in Chap. 5, that the cavity function describes correlations beyond the range of the pairwise potential.

8.3 Ornstein–Zernike equation

8.3.1 Formulation and main features

In this section we discuss another class of integral equations for correlation functions which are based on stronger physical arguments than the BBGKY hierarchy. We start by splitting the total correlation between a pair of molecules 1 and 2 into direct and indirect correlation. The latter results from the influence of other particles (which is important for dense systems) and must be averaged over all positions of a third particle that directly correlates with particle 1. This idea is manifested by the Ornstein–Zernike (OZ) equation

$$h(12) = c(12) + \rho \int c(13)h(23) d\mathbf{3} \quad (8.13)$$

which can be viewed as the definition of a direct pair correlation function $c(r)$ (for simplicity we discuss a homogeneous fluid). One can notice that the right-hand side represents an infinite series comprised of various direct correlations:

$$h(12) = c(12) + \rho \int c(13)c(23) d\mathbf{3} + \rho^2 \int c(13)c(34)c(42) d\mathbf{3} d\mathbf{4} + \dots$$

which means that the second term in (8.13) remains invariant under the permutation $1 \rightarrow 2$ in the integrand.

The OZ relationship can be viewed as an integral equation for the pair correlation function $g(r) = h(r) + 1$ once information about $c(r)$ is available. Several approximations (closures) for $c(r)$ have been proposed; we discuss them in the next section. It is possible to predict some features of $c(r)$ on the basis of reasonable physical arguments. At low densities the influence of indirect correlations vanishes and $h(12) \rightarrow c(12)$, implying

$$g(12) \rightarrow 1 + c(12)$$

which, using (8.10), can be written

$$c(12) \rightarrow e^{-\beta u(12)} - 1, \quad \rho \rightarrow 0 \quad (8.14)$$

This means that at low densities the direct correlation function reduces to the Mayer function

$$f(r) = e^{-\beta u(r)} - 1$$

(see Fig. 8.1). The relationship (8.14) suggests that $c(r)$ must be short-range, its radius being determined by the radius of intermolecular forces. The second term in the OZ equation has the form of a convolution integral. Taking the Fourier transform of (8.13), we obtain

$$\tilde{h}(k) = \tilde{c}(k) + \rho \tilde{c}(k) \tilde{h}(k) \quad (8.15)$$

where the Fourier transforms of $h(r)$ and $c(r)$ are

$$\tilde{h}(k) = \int \mathbf{dr} h(r) e^{-ikr}, \quad \tilde{c}(k) = \int \mathbf{dr} c(r) e^{-ikr} \quad (8.16)$$

The structure factor introduced in (2.17) is related to $\tilde{h}(k)$ by

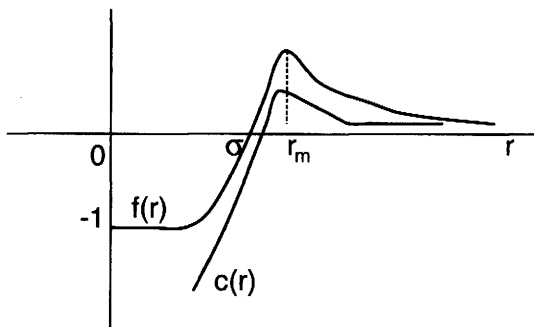


Fig. 8.1. Mayer function $f(r)$ and direct pair correlation function $c(r)$ for a potential of a Lennard-Jones type. At low densities $c(r) \rightarrow f(r)$

$$S(k) = 1 + \rho \tilde{h}(k)$$

According to (3.14) its long-wavelength limit is proportional to the isothermal compressibility. Thus,

$$\chi_T = \frac{1}{\rho k_B T} \frac{1}{1 - \rho \tilde{c}(0)}$$

which yields another form of the compressibility equation:

$$1 - \rho \int c(r) \mathbf{dr} = (\rho k_B T \chi_T)^{-1} \quad (8.17)$$

From the definition of χ_T and (8.17) we obtain

$$\frac{\partial p}{\partial \rho} = k_B T \left[1 - \rho \int c(r) \mathbf{dr} \right]$$

which after integration over density gives the pressure

$$p = \rho k_B T - \int d\rho \left[\rho \int \mathbf{dr} c(r; \rho) \right] \quad (8.18)$$

As already mentioned the values, of p calculated from the compressibility equation can differ from those found from the virial equation when an approximation for $c(r)$ is used. This thermodynamic inconsistency will be demonstrated in the next section for a system of hard spheres.

We now discuss the behavior of the OZ equation in the vicinity of the critical point: $T \rightarrow T_c$. We saw in Sect. 6.3 that at the critical point the isothermal compressibility diverges. Then, from (8.17)

$$\int c(\mathbf{r}) d\mathbf{r} \rightarrow \frac{1}{\rho_c} \quad (8.19)$$

which means that the second moment of $c(r)$ remains finite at T_c . The structure factor $S(0) \rightarrow \infty$, implying that

$$\int h(\mathbf{r}) d\mathbf{r} \rightarrow \infty \quad (8.20)$$

We conclude that near the critical point $c(r)$ is more short-range than $h(r)$.

Let us write the OZ equation in the vector form

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) h(|\mathbf{r}'|) d\mathbf{r}' \quad (8.21)$$

and expand $h(|\mathbf{r}'|)$ in Taylor series about the point $\mathbf{r}$. The first term gives $h(r)$. The term with ∇h vanishes since $c(r)$ is spherically symmetric. The next term can be written

$$\frac{1}{2} \nabla^2 h \int d\mathbf{r} c(r) r^2$$

We are interested in the behavior at large r , i.e. in the region where $c(r)$ becomes vanishingly small. Neglecting the first term on the right-hand side of (8.21), we obtain after substitution of the Taylor expansion

$$\nabla^2 h = \frac{1}{\xi^2} h \quad (8.22)$$

where

$$\xi^2 \equiv \frac{1}{2} \frac{\rho \int d\mathbf{r} c(r) r^2}{1 - \rho \tilde{c}(0)} \quad (8.23)$$

The spherically symmetric solution of (8.22) that vanishes at infinity has the form

$$h(r) = \text{const} \frac{e^{-r/\xi}}{r} \quad (8.24)$$

This result leads to identification of the correlation length ξ . At the critical temperature ξ becomes infinite, leading to

$$h(r) \sim \frac{1}{r}, \quad T = T_c \quad (8.25)$$

i.e. at the critical point the total correlation function decays algebraically (and not exponentially) at large r . This result is corrected in the modern theory of critical phenomena where the scaling of $h(r)$ at T_c is characterized by the critical exponent η ; for three-dimensional physical space it reads (see (6.28))

$$h(r) \sim \frac{1}{r^{1+\eta}}, \quad T = T_c \quad (8.26)$$

Taking the Fourier transform of both sides of this expression, we conclude that the structure factor behaves as

$$S(k) \sim \frac{1}{k^{2-\eta}}, \quad T = T_c, \quad k \rightarrow 0 \quad (8.27)$$

Our analysis of the OZ equation shows that the radius of $c(r)$ is determined by the radius of intermolecular forces, whereas the radius of $h(r)$ is of the order of the correlation length.

8.3.2 Closures

Having studied the main features of the OZ equation we now formulate several approximations for the direct pair correlation function which in combination with the OZ equation constitute a closed system of equations for $h(r)$. All of them represent modifications of the simple relationship (8.14). The most widely used closures are:

- hypernetted chain approximation (HNC) developed by several authors (Morita, van Leeuwen, Rushbrooke, Verlet) [8]:

$$c_{\text{HNC}}(12) = h(12) - \ln g(12) - \beta u(12) \quad (8.28)$$

- Percus-Yevick (PY) theory [110]

$$c_{\text{PY}}(12) = g(12) \left[1 - e^{\beta u(12)} \right] = y(12) f(12) \quad (8.29)$$

The domain of existence of $c_{\text{PY}}(r)$ coincides with the characteristic range of the pairwise potential.

- mean spherical approximation (MSA) proposed by Lebowitz and Percus [82]:

$$\begin{aligned} h_{\text{MSA}}(r) &= -1, & r < \sigma \\ c_{\text{MSA}}(r) &= -\beta u(r), & r > \sigma \end{aligned} \quad (8.30)$$

where σ is the hard-core diameter. MSA originates from the observation that for large separation the right-hand side of (8.14) becomes simply $-\beta u(12)$. Lebowitz and Percus suggested using this relationship not just for large r_{12} but for all r_{12} in the region where the potential u is attractive.

In the MSA the direct correlation function does not depend on density, which makes MSA an attractive tool for development of theoretical models since for a wide variety of systems it can be solved analytically. Note that MSA is identical to PY when $\beta = 0$. Since the hard-sphere system is insensitive to temperature, MSA and PY approximations are identical for hard spheres.

It has been found by many authors (see e.g. [10]) that the PY theory is satisfactory for hard spheres but does not work for systems with attractive tails. The HNC theory is complementary to PY in the sense that it is unsatisfactory for hard spheres but appears to account satisfactorily for the effects of attractive tails and nonhard cores. Finally, the MSA seems to combine the virtues of HNC and PY theories and gives good results for systems with attractive forces. Another compromise between the properties of PY and HNC closures is the

- Rogers-Young (RY) approximation [120]

$$g_{\text{RY}}(r) = e^{-\beta u(r)} \left[1 + \frac{e^{f_{\text{RY}}(r)[h(r)-c(r)]} - 1}{f_{\text{RY}}} \right] \quad (8.31)$$

where f_{RY} is a “switching function” satisfying

$$\lim_{r \rightarrow 0} f_{\text{RY}} = 0, \quad \lim_{r \rightarrow \infty} f_{\text{RY}} = 1 \quad (8.32)$$

In the limit $r \rightarrow 0$ it reduces to PY, whereas the second limit recovers HNC. Rogers and Young proposed to choose f_{RY} in the form

$$f_{\text{RY}} = 1 - e^{-\alpha r}$$

where the parameter α is found from the “virial-compressibility consistency” condition, i.e. equality of pressures found by means of the virial and compressibility routes. Using (3.10) and (8.18), we can express it as

$$\frac{2\pi}{3} \rho^2 \int_0^\infty u'(r_{12}) g(r_{12}) r_{12}^3 dr_{12} = \int d\rho \left[\rho \int dr c(r; \rho) \right] \quad (8.33)$$

RY closure has been successfully applied to hard spheres and systems with inverse-power potentials [120].

8.3.3 Percus-Yevick theory for hard spheres

The PY theory has an important feature: its equations can be solved analytically for the system of hard spheres. The solution derived by Wertheim [147] is discussed in the present section. For hard spheres the Mayer function $f_d(r)$ is nonpositive and has a step-like form:

$$f_d(r) = \begin{cases} -1 & \text{for } r < d \\ 0 & \text{for } r \geq d \end{cases} \quad (8.34)$$

This implies that the PY closure (8.29) becomes

$$c_{PY}(r_{12}) = 0 \quad \text{for } r_{12} > d \quad (8.35)$$

and

$$c_{PY}(r_{12}) = -y_d(r_{12}) \quad \text{for } r_{12} < d \quad (8.36)$$

The problem of finding the direct correlation function (and, consequently, $g(r)$) for the whole range of distances will be solved if we find the cavity function $y_d(r)$ for $r < d$.

Let us write the OZ equation with the PY closure in terms of $y_d(r)$, using the identity $h_d = g_d - 1 = y_d e^{-\beta u_d} - 1$:

$$y_d(12) = 1 + \rho \int y_d(13) f_d(13) y_d(23) e^{-\beta u(23)} d\mathbf{3} - \rho \int y_d(13) f_d(13) d\mathbf{3} \quad (8.37)$$

Taking into account the step-function nature of f_d this equation can be simplified:

$$y_d(12) = 1 - \rho \int_{13 < d, 23 > d} y(13) y(23) d\mathbf{3} + \rho \int_{13 < d} y(13) d\mathbf{3}$$

In vector form it reads

$$y_d(r) = 1 - \rho \int_{r' < d, |\mathbf{r} - \mathbf{r}'| > d} y(r') y_d(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' + \rho \int_{r' < d} y_d(r') d\mathbf{r}' \quad (8.38)$$

The second term is a convolution integral, so it is natural to search for a solution by means of the Laplace transform. Let us define the functions

$$F(p) = \frac{1}{d^2} \int_0^d r y_d(r) e^{-\frac{pr}{d}} dr, \quad \text{and} \quad G(p) = \frac{1}{d^2} \int_d^\infty r y_d(r) e^{-\frac{pr}{d}} dr \quad (8.39)$$

Then the Laplace transform of (8.38) yields

$$p[F(p) + G(p)] = \frac{1}{p} \left[1 + \frac{24\phi}{d^3} \int_0^d y_d(r) r^2 dr \right] - 12\phi[F(-p) - F(p)]G(p) \quad (8.40)$$

where $\phi = \frac{\pi}{6} \rho d^3$ is the volume fraction.

Wertheim suggested a trial solution in the form of a cubic polynomial²:

² This suggestion is based on expansion of the PY equation in powers of the density.

$$y_d(x) = a_0 + a_1x + a_2x^2 + a_3x^3 \quad (8.41)$$

where $x = r/d$. The four unknown-composition dependent coefficients are found from (8.40) [147]:

$$(1 - \phi)^4 a_0 = (1 + 2\phi)^2 \quad (8.42)$$

$$(1 - \phi)^4 a_1 = -6\phi(1 + \phi/2)^2 \quad (8.43)$$

$$(1 - \phi)^4 a_3 = \frac{1}{2}\phi(1 + 2\phi)^2 \quad (8.44)$$

The quadratic term is absent ($a_2 = 0$). The solution of the PY equation finally becomes

$$\begin{aligned} -c(x) = y_d(x) &= a_0 + a_1x + a_3x^3, & x = r/d < 1 \\ c(x) &= 0, & x = r/d > 1 \end{aligned} \quad (8.45)$$

The behavior of $c(r)$ for various values of the volume fraction is shown in Fig. 8.2. Using (8.15) the PY structure factor for hard spheres can be written as

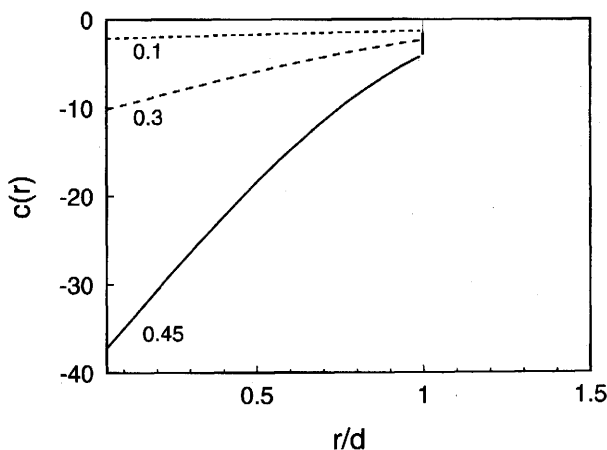


Fig. 8.2. Percus-Yevick direct correlation function for hard spheres. Labels correspond to the volume fraction. It can be seen that for small ϕ , $c(r)$ tends to the Mayer function of hard spheres.

$$S(k) = \frac{1}{1 - \rho \tilde{c}(k)} = \left[1 - 24 \frac{\phi}{k^*} \int_0^1 dx x c(x) \sin(k^* x) \right]^{-1}, \quad k^* = kd \quad (8.46)$$

The main peak of $S(k)$ grows, becoming sharper and shifting towards large k as the volume fraction is increased, as shown in Fig. 8.3. The value of k at first maximum is

$$k_{\max} \approx \frac{2\pi}{r_{\text{av}}}$$

where $r_{\text{av}} = \rho^{-1/3}$ is the average interparticle distance. Thus,

$$k_{\max} d \approx 2\pi \left(\frac{6}{\pi}\right)^{1/3} \phi^{1/3}$$

The direct correlation function of hard spheres is discontinuous at $r = d$, while the cavity function remains continuous everywhere. Applying (8.45) at $r = d$ we obtain its value at contact $y_d(d) = a_0 + a_1 + a_3$:

$$y_d(d)_{\text{PY}} = \frac{1 + \phi_d/2}{(1 - \phi_d)^2} \quad (8.47)$$

Substitution of this expression into (3.19) yields the PY equation of state for hard spheres:

$$\left(\frac{p}{\rho k_B T}\right)_{\text{PY(P)}} = \frac{1 + 2\phi_d + 3\phi_d^2}{(1 - \phi_d)^2} = \frac{1 + \phi_d + \phi_d^2 - 3\phi_d^3}{(1 - \phi_d)^3} \quad (8.48)$$

The symbol (P) denotes that pressure is obtained by means of the pressure equation of state. We have mentioned an important feature of integral theories of correlation functions: the loss of thermodynamic consistency. Here we demonstrate it for the PY theory. Let us calculate the pressure obtained from the compressibility equation using Wertheim's exact solution for $c(r)$. Integration in (8.18), in which we replace the upper limit by d , results in

$$\left(\frac{p}{\rho k_B T}\right)_{\text{PY(C)}} = \frac{1 + \phi_d + \phi_d^2}{(1 - \phi_d)^3} \quad (8.49)$$

where the index (C) refers to calculations on the basis of the compressibility equation. Comparison with (8.48) shows that the latter predicts lower pressures; the difference between the two expressions becomes important at relatively high volume fractions.

We obtained the value of the pair correlation function at contact. For a number of perturbation theories discussed in Chap. 5 the hard-sphere system serves as a reference model, for which it is necessary to know the behavior of $g(r)$ over the whole range of distances $r > d$ (remember that for $r < d$, $g(r) = 0$). To find it we obtain the Laplace transform of $rg(r)$ from (8.40):

$$G(p) = \frac{\frac{1}{p} \left[1 + \frac{24\phi}{d^3} \int_0^d y(r) r^2 dr \right] - pF(p)}{p + 12\phi[F(-p) - F(p)]}$$

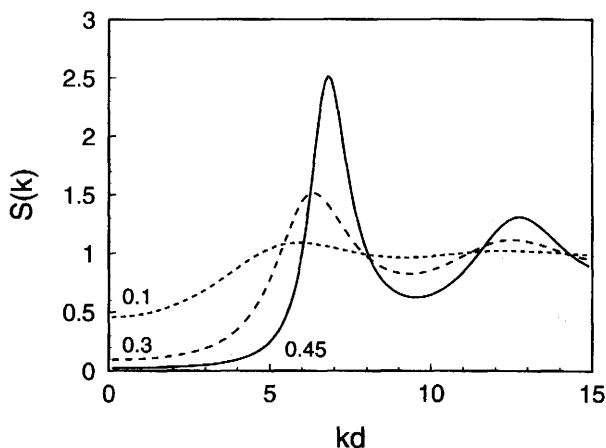


Fig. 8.3. Percus-Yevick structure factor for hard spheres. Labels correspond to the volume fraction

All integrations on the right-hand side can be performed analytically, since they involve the cavity function at $r < d$ given by Wertheim's solution (8.45). Routine calculations yield

$$G(p) = \frac{pL(p)}{12\phi L(p) + M(p)e^p} \quad (8.50)$$

where

$$L(p) = \left(1 + \frac{\phi}{2}\right)p + 1 + 2\phi \quad (8.51)$$

$$M(p) = (1 - \phi)^2 p^3 + 6\phi(1 - \phi)p^2 + 18\phi^2 p - 12\phi(1 + 2\phi) \quad (8.52)$$

The inverse Laplace transform of (8.50) gives the final answer:

$$rg(r) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} dp \frac{pL(p)}{12\phi[L(p) + M(p)e^p]}, \quad r > d \quad (8.53)$$

In a number of Monte Carlo simulations it was found that the PY correlation function has two deficiencies [85]:

- At large r it oscillated out of phase with respect to the "exact" correlation function
- The value at contact $g(d)$ is too low at high densities.

In order to improve on the PY result, Verlet and Weis [144] proposed an analytic construction which behaves accurately at high densities. The first deficiency is corrected by introducing a modified volume fraction into Wertheim's solution

$$\phi_m = \phi - \frac{\phi^2}{16} \quad (8.54)$$

The modified hard-sphere diameter then becomes (the number density remains unchanged)

$$d_m = \left(\frac{\phi_m}{\phi} \right)^{1/3} d$$

As a result the modified PY correlation function $g_m(r/d_m)$ oscillates in phase with the “exact” one (found in simulations) for $r > 1.6d$. On the other hand, it is clear that (8.54) makes the second deficiency even worse. In order to improve on that, Verlet and Weiss added a correction term to $g_m(r/d_m)$:

$$g(r/d; \phi) = g_m(r/d_m; \phi_m) + \Delta g(r) \quad (8.55)$$

where $\Delta g(r)$ has the form

$$\Delta g(r) = \frac{A}{r} e^{-\alpha(r-d)} \cos[\alpha(r-d)] \quad (8.56)$$

and the constants A and α are related to the packing fraction by

$$A = \frac{3}{4} \frac{\phi_m^2 (1 - 0.7117\phi_m - 0.114\phi_m^2)}{(1 - \phi_m)^4} \quad (8.57)$$

$$\alpha = \frac{1}{d^2} \frac{A}{\phi_m g_m(1; \phi_m)} \quad (8.58)$$

This construction is found to reproduce the exact hard-sphere correlation function to within 1% accuracy.

Low density approximation. For a system characterized by low particle density (e.g. colloidal suspensions), the PY correlation function for hard spheres can be represented analytically. In the zeroth order approximation in ρ , both h_{PY} and c_{PY} are step functions coinciding with the hard-sphere Mayer function. Let us find the first-order correction to $h_{PY}(r; \rho)$. For $r < d$ it remains equal to -1 , as required by the PY closure. For $r > d$ the linearized Ornstein–Zernike equation (8.13) reads

$$h(r; \rho) = \rho \int d\mathbf{r}_3 c(r_{13}; \rho = 0) h(r_{23}; \rho = 0) + o(\rho^2), \quad r > d \quad (8.59)$$

We place the origin at the point $\mathbf{r}_1$, making the linear transformation of coordinates

$$\begin{aligned}\mathbf{r}'_1 &= \mathbf{r}_1 \\ \mathbf{r}'_2 &= \mathbf{r}_2 - \mathbf{r}_1 \equiv \mathbf{r}_{12} \\ \mathbf{r}'_3 &= \mathbf{r}_3 - \mathbf{r}_1 \equiv \mathbf{r}_{13}\end{aligned}$$

and rewrite the integral in (8.59) in dimensionless form (for notational simplicity we set $R \equiv r_{12}$, $r \equiv r_{13}$):

$$h(R; \rho) = \rho d^3 \int d\mathbf{r}_{13} \Theta(r < 1) \Theta(r_{23} < 1) \Theta(R > 1) \quad (8.60)$$

where the step function $\Theta(a < b)$ is unity when $a < b$, and zero otherwise. It is obvious that the three inequalities can be simultaneously satisfied if and only if

$$1 < R < 2$$

which means that the first-order density correction to h is nonzero at $1 < R < 2$ and zero beyond this interval. In spherical coordinates (8.60) reads

$$\begin{aligned}h(R) \\ = 2\pi\rho d^3 \int dr r^2 \int_{-1}^1 d(\cos \theta_{13}) \Theta(r < 1) \Theta(R > 1) \Theta(R^2 + r^2 - 2Rr \cos \theta_{13} < 1)\end{aligned}$$

Writing $\mu \equiv \cos \theta_{13}$, we have

$$\frac{h(R; \rho)}{12\phi} = \int dr r^2 \int_{-1}^1 d\mu \Theta(r < 1) \Theta(R > 1) \Theta(R^2 + r^2 - 2Rr\mu < 1) \quad (8.61)$$

The condition $R^2 + r^2 - 2Rr\mu < 1$ can be written

$$\mu > q(r, R) \equiv \frac{R^2 + r^2 - 1}{2rR} \quad (8.62)$$

Since $R > 1$, the function $q(r, R)$ is positive. By definition the upper limit of μ is unity, so the function q must be less than unity implying

$$R^2 - 2Rr + r^2 < 1 \quad (8.63)$$

Combining (8.63) with the condition $0 < r < 1 < R < 2$, the limits of integration over r become

$$R - 1 < r < 1 \quad (8.64)$$

Using (8.62) and (8.64), we obtain

$$\frac{h(R; \rho)}{12\phi} = \int_{R-1}^1 dr r^2 [1 - q(r, R)]$$

Routine calculations on the right-hand side result in

$$\frac{h(R)}{12\phi} = \frac{2}{3} - \frac{R}{2} + \frac{R^3}{24} \quad (8.65)$$

The $O(\rho)$ approximation of the hard-sphere total pair correlation function is thus

$$h_{PY}(R; \phi) = \begin{cases} -1 & \text{for } R < 1 \\ \phi\Phi(R) & \text{for } 1 < R < 2 \\ 0 & \text{for } R > 2 \end{cases} \quad (8.66)$$

where

$$\Phi(R) = 8 - 6R + \frac{R^3}{2} \quad (8.67)$$

It is easy to see that the value of $g_{PY} = 1 + h_{PY}$ at contact is:

$$\lim_{R \rightarrow 1+} g_{PY}(R) = 1 + \frac{5}{2}\phi$$

As expected, it is equal to the cavity function at contact, $y_d(d)$, in the same order of approximation (cf. (8.47)). At $R = 2$, $\Phi(R) = 0$ ensuring continuity of h .

Shinomoto [130] proposed a closed form expression for $h(R; \phi)$ for arbitrary volume fractions, based on semi-empirical considerations:

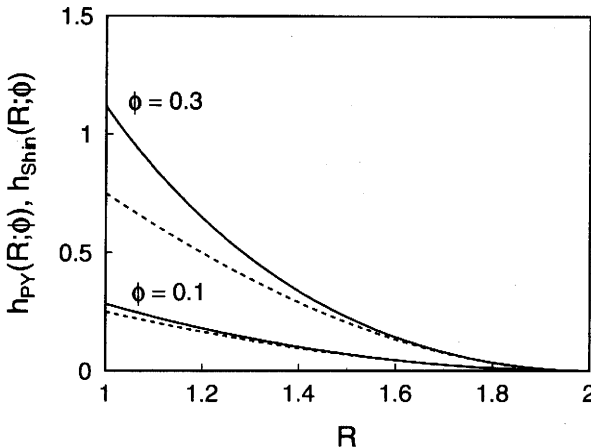


Fig. 8.4. Shinomoto (solid lines) and linearized Percus–Yevick (dashed lines) total correlation functions for hard spheres. Labels correspond to the volume fraction

$$h_{\text{Shin}}(R; \phi) = \begin{cases} -1 & \text{for } R < 1 \\ e^{\phi\Phi(R)} - 1 & \text{for } 1 < R < 2 \\ 0 & \text{for } R > 2 \end{cases} \quad (8.68)$$

The first-order term in the expansion of the exponent gives the linear PY result (8.66). Figure 8.4 shows the behavior of the linearized PY and Shinomoto correlation functions for $\phi = 0.1$ and $\phi = 0.3$. In the former case both theories are close while in the latter case their predictions differ significantly.

9. Density functional theory

9.1 Foundations of the density functional theory

Conventional statistical thermodynamics studied in the previous chapters usually is not able to provide information about the behavior of systems exhibiting spatial variations of the average one-body distribution function (or simply, the number density) $\rho(\mathbf{r})$.¹ An important example of an inhomogeneous system is the liquid–vapor interface. Within the framework of classical statistical mechanics we derived the Kirkwood–Buff formula for the surface tension, which contains the pair distribution function in the two-phase region. The latter, however, is unknown in the transition zone and conventional techniques are not able to predict it. It turns out to be productive to postulate the existence of thermodynamic functions, such as the free energy, for arbitrary values of their natural arguments, i.e. not necessarily corresponding to equilibrium conditions. This leads us to the concept of functionals (the free energy, the grand potential, etc.) of arbitrary distribution functions; this approach is called the density functional theory (DFT) (for a review see [40]). We will show that these functionals have two important properties:

- they reach extrema when the distribution functions are those of the equilibrium state, and
- those extremal values are the equilibrium values of the corresponding thermodynamic potentials.

The cornerstone of DFT is the statement that the free energy of an inhomogeneous fluid is a functional of $\rho(\mathbf{r})$. On the basis of the knowledge of this functional one can calculate interfacial tensions (vapor–liquid, liquid–liquid, liquid–solid), properties of confined systems, adsorption properties, determine depletion forces, study phase transitions, etc. From these introductory remarks it is clear that DFT represents an alternative (variational) formulation of statistical mechanics. Determining the exact form of the free-energy functional is equivalent to calculating the partition function, which, as we know, is not possible for realistic potentials. Thus, one has to formulate approximations to this functional which can lead to computationally tractable results, and at the same time be applicable to a number of practical problems.

¹ An exception is the ideal gas in an external field (see the barometric formula).

Historically the density functional approach in its modern form was formulated first in quantum mechanics by Hohenberg and Kohn [56] and Kohn and Sham [72]. The main issue there is that the intrinsic part of the ground state energy of an inhomogeneous electron liquid can be cast in the form of a unique functional of the electron density $n(\mathbf{r})$ that is the analogue of $\rho(\mathbf{r})$ in the classical case. The quantum many-body problem (i.e. solution of the many-electron Schrödinger equation) is replaced by a variational one-body problem for an electron in an effective potential field arising from the exchange and correlation energy functional $E_{xc}[n(\mathbf{r})]$ for which various approximations have been proposed.

Being concerned with classical systems, we can always consider the momentum part of the Hamiltonian to be described by the equilibrium Maxwellian distribution. So the arbitrariness refers only to the configurational part of $\mathcal{H}$. Let us consider an arbitrary distribution function of order N , $\hat{\rho}^N(\mathbf{r}^N)$, subject to the normalization

$$\int \hat{\rho}^{(N)}(\mathbf{r}^N) d\mathbf{r}^N = N!, \quad \hat{\rho}^{(N)}(\mathbf{r}^N) > 0 \quad (9.1)$$

The “hat” indicates that ρ does not necessarily have its equilibrium form; the equilibrium function will be denoted without the “hat”. Hence, we demand that $\hat{\rho}^{(N)}$ be positive, like any probability measure, and be subject to the same normalization as the equilibrium distribution function (cf. (2.3)). In other respects it is almost arbitrary.

To limit the class of functions $\hat{\rho}^{(N)}$, we employ the following considerations [125]. For a given interaction potential $u(r)$ every fixed external field $u_{\text{ext}}(\mathbf{r})$ gives rise to a certain equilibrium one-particle distribution function $\rho(\mathbf{r})[u_{\text{ext}}(\mathbf{r})]$, i.e. only one $u_{\text{ext}}(\mathbf{r})$ can determine a given $\rho(\mathbf{r})$. Using $\rho(\mathbf{r})$ we can generate a set of functions $\hat{\rho}(\mathbf{r})$ so that each of them will be an equilibrium density corresponding to some other external field, $\hat{u}_{\text{ext}}(\mathbf{r})$, but is nonequilibrium with respect to the original field $u_{\text{ext}}(\mathbf{r})$:

$$\hat{\rho}(\mathbf{r}) = \rho(\mathbf{r})[\hat{u}_{\text{ext}}(\mathbf{r})]$$

For every $\hat{\rho}(\mathbf{r})$ there exists a unique N -particle distribution function $\hat{\rho}^{(N)}$ (for a proof see [38]). Thus, any functional of $\hat{\rho}^{(N)}(\mathbf{r}^N)$ can be equally considered a functional of the one-particle distribution function $\hat{\rho}(\mathbf{r})$.

Let us first assume that there is no external field: $u_{\text{ext}}(\mathbf{r}) \equiv 0$. We formally define an intrinsic free energy functional

$$\mathcal{F}_{\text{int}}[\hat{\rho}] = \frac{1}{N!} \int d\mathbf{r}^N \hat{\rho}^{(N)} [U_N + k_B T \ln(\Lambda^{3N} \hat{\rho}^{(N)})] \quad (9.2)$$

which, as we have found, is a unique functional of $\rho(\mathbf{r})$ for a given interaction potential u . This means that $\mathcal{F}_{\text{int}}$ has the same dependence on $\hat{\rho}(\mathbf{r})$ for all systems with the same interaction potential irrespective of the external field producing inhomogeneity. As an implication of this statement $\mathcal{F}_{\text{int}}$ will

look the same for the vapor–liquid or liquid–solid interface as soon as the substances are characterized by the same interaction potential.

9.1.1 Ideal gas

In order to understand the origin of the functional (9.2) let us first discuss an ideal gas ($U_N = 0$) (not necessarily in equilibrium). The singlet distribution function satisfies the normalization

$$\int \hat{\rho}(\mathbf{r}) \, d\mathbf{r} = N,$$

so the probability of finding a molecule i in a volume element $d\mathbf{r}_i$ about $\mathbf{r}_i$ is

$$\frac{\hat{\rho}(\mathbf{r}_i)}{N} \, d\mathbf{r}_i.$$

Normalized to unity $\hat{\rho}(\mathbf{r}_i)/N$ plays the role of a probability density function.

In an ideal gas the positions of molecules are independent, so

$$\frac{\hat{\rho}^{(N)}}{N!} = \prod_{i=1}^N \frac{\hat{\rho}(\mathbf{r}_i)}{N} = \frac{1}{N^N} \prod_{i=1}^N \hat{\rho}(\mathbf{r}_i)$$

Substitution of $\hat{\rho}^{(N)}$ into the functional (9.2) (where we set $U_N = 0$) gives

$$\mathcal{F}_{\text{int}}[\hat{\rho}] = k_B T \ln(\Lambda^{3N} N!) + k_B T I_2$$

where

$$I_2 = \int d\mathbf{r}^N \prod_{i=1}^N \frac{\hat{\rho}(\mathbf{r}_i)}{N} \ln \left[\prod_{j=1}^N \frac{\hat{\rho}(\mathbf{r}_j)}{N} \right] = \int d\mathbf{r}^N \sum_{j=1}^N \left[\ln \left(\frac{\hat{\rho}(\mathbf{r}_j)}{N} \right) \prod_{i=1}^N \frac{\hat{\rho}(\mathbf{r}_i)}{N} \right]$$

All terms of the sum make an equal contribution to the integral, so

$$\begin{aligned} I_2 &= N \int d\mathbf{r}^N \left[\ln \left(\frac{\hat{\rho}(\mathbf{r}_1)}{N} \right) \prod_{i=1}^N \frac{\hat{\rho}(\mathbf{r}_i)}{N} \right] \\ &= \int d\mathbf{r}_1 \ln \left(\frac{\hat{\rho}(\mathbf{r}_1)}{N} \right) \hat{\rho}(\mathbf{r}_1) \prod_{i=2}^N \int d\mathbf{r}_i \frac{\hat{\rho}(\mathbf{r}_i)}{N} \end{aligned}$$

All terms in the product are equal to unity due to the normalization condition, so only integration over $d\mathbf{r}_1$ remains, which yields:

$$I_2 = \int d\mathbf{r} \ln \left(\frac{\hat{\rho}(\mathbf{r})}{N} \right) \hat{\rho}(\mathbf{r})$$

Then $\mathcal{F}_{\text{int}}[\hat{\rho}] \equiv \mathcal{F}_{\text{ideal}}[\hat{\rho}]$ can be written

$$\mathcal{F}_{\text{ideal}}[\hat{\rho}] = k_B T \left[\int d\mathbf{r} \frac{\hat{\rho}(\mathbf{r})}{N} \ln(\Lambda^{3N} N!) + \int d\mathbf{r} \ln \left(\frac{\hat{\rho}(\mathbf{r})}{N} \right) \hat{\rho}(\mathbf{r}) \right]$$

Using Stirling's formula we finally obtain

$$\mathcal{F}_{\text{ideal}}[\hat{\rho}] = k_B T \int d\mathbf{r} \hat{\rho}(\mathbf{r}) [\ln(\Lambda^3 \hat{\rho}(\mathbf{r})) - 1] \quad (9.3)$$

If $\hat{\rho}(\mathbf{r}) = \rho$, the familiar result for the free energy of an ideal gas (in equilibrium) is recovered:

$$\mathcal{F}_{\text{ideal}} = N k_B T \ln \left(\frac{\rho \Lambda^3}{e} \right)$$

Equation (9.3) gives the free energy of an ideal gas in the absence of external fields when its density is not necessarily equal to the equilibrium value.

9.1.2 General case

Returning to the general case, let us calculate the value of the intrinsic free energy functional for equilibrium conditions. Substitution of the equilibrium distribution function

$$\rho^{(N)} = N! D_N = \frac{e^{-\beta U_N}}{\Lambda^{3N} Z_N} \quad (9.4)$$

into (9.2) results in

$$\mathcal{F}_{\text{int}}[\rho] = -k_B T \ln Z_N = \mathcal{F}$$

Thus, for the equilibrium density, $\mathcal{F}_{\text{int}}$ gives exactly the free energy in the absence of external fields (justifying the term *intrinsic free energy*).

This description can be extended by including an external field contribution. Let us define another functional:

$$\mathcal{F}[\hat{\rho}] = \frac{1}{N!} \int d\mathbf{r}^N \hat{\rho}^{(N)} [U_N + U_{N,\text{ext}} + k_B T \ln(\Lambda^{3N} \hat{\rho}^{(N)})] \quad (9.5)$$

which, using the definition of $\mathcal{F}_{\text{int}}$, can be expressed as

$$\mathcal{F}[\hat{\rho}] = \mathcal{F}_{\text{int}}[\hat{\rho}] + \int d\mathbf{r}^N \frac{\hat{\rho}^{(N)}}{N!} \sum_{i=1}^N u_{\text{ext}}(\mathbf{r}_i)$$

It is easy to see that the integral contains N equal terms. Integration of the N -particle probability density $\hat{\rho}^{(N)}/N!$ over the positions of $(N-1)$ particles results in the singlet distribution function:

$$\int d\mathbf{r}_2 \dots d\mathbf{r}_N \frac{\hat{\rho}^{(N)}}{N!} = \frac{\hat{\rho}^{(1)}(\mathbf{r}_1)}{N}$$

Thus,

$$\mathcal{F}[\hat{\rho}] = \mathcal{F}_{\text{int}}[\hat{\rho}] + \int \mathbf{d}\mathbf{r} u_{\text{ext}}(\mathbf{r}) \hat{\rho}(\mathbf{r}) \quad (9.6)$$

The last term is the energy of the system in an external field. We apply this as before for the equilibrium case. Substituting

$$\rho^{(N)} = \frac{e^{-\beta(U_N + U_{N,\text{ext}})}}{\Lambda^{3N} Z_N} \quad (9.7)$$

into (9.5), we recover the total free energy

$$\mathcal{F}[\rho] = -k_B T \ln Z_N = \mathcal{F}$$

Finally, let us define the grand potential functional:

$$\Omega[\hat{\rho}; u_{\text{ext}}] = \mathcal{F}_{\text{int}}[\hat{\rho}] + \int u_{\text{ext}}(\mathbf{r}) \hat{\rho}(\mathbf{r}) \mathbf{d}\mathbf{r} - \mu N \quad (9.8)$$

Obviously, for the equilibrium density this reduces to the grand potential: $\Omega[\rho; U_{\text{ext}}] = \mathcal{F} - \mu N = \Omega$. The key feature of DFT is that among all density profiles with the normalization

$$\int \hat{\rho}(\mathbf{r}) \mathbf{d}\mathbf{r} = N \quad (9.9)$$

the equilibrium profile minimizes the free energy functional. To prove this let us express the total energy $U_N^{\text{tot}} \equiv U_N + U_{N,\text{ext}}$ in terms of the equilibrium distribution function using (9.7):

$$U_N^{\text{tot}} = -k_B T \ln \rho^{(N)} - k_B T \ln \Lambda^{3N} + \mathcal{F}[\rho]$$

The free energy functional can be written

$$\mathcal{F}[\hat{\rho}] = \mathcal{F}[\rho] + k_B T \frac{1}{N!} \int \mathbf{d}\mathbf{r}^N [\hat{\rho}^{(N)} \ln \hat{\rho}^{(N)} - \hat{\rho}^{(N)} \ln \rho^{(N)}]$$

where the nonequilibrium features are contained in the second term. We now prove that it is always positive. The latter statement follows from the following general:

Theorem 9.1.1. *If for two arbitrary positive functions $A(\mathbf{r}^N)$ and $B(\mathbf{r}^N)$*

$$\int \mathbf{d}\mathbf{r}^N A(\mathbf{r}^N) = \int \mathbf{d}\mathbf{r}^N B(\mathbf{r}^N) \quad (9.10)$$

then the Gibbs inequality is satisfied

$$\int \mathbf{d}\mathbf{r}^N A \ln A \geq \int \mathbf{d}\mathbf{r}^N A \ln B \quad (9.11)$$

Proof. Let us study the difference between the left- and right-hand side of (9.11):

$$\Delta = \int d\mathbf{r}^N A \ln \left(\frac{A}{B} \right)$$

Using (9.10) we add to the right-hand side the expression $\int d\mathbf{r}^N B - \int d\mathbf{r}^N A$ (which is equal to zero). This yields

$$\Delta = \int d\mathbf{r}^N B \left[\frac{A}{B} \ln \left(\frac{A}{B} \right) - \frac{A}{B} + 1 \right]$$

To prove that the integrand on the right-hand side is always positive, we must prove the simple inequality

$$x \ln x \geq x - 1$$

for any positive x . Dividing both sides by x we can rewrite it as

$$-\ln x \leq \frac{1}{x} - 1$$

Introducing $y \equiv 1/x$ the latter expression reduces to the obvious inequality:

$$\ln y \leq y - 1$$

which is valid for all positive y ; equality corresponds to $y = 1$ or $A = B$. Thus, $\mathcal{F}[\hat{\rho}] \geq \mathcal{F}[\rho]$.

We have proved the minimizing property for $\mathcal{F}$ under the condition (9.9). Using the Lagrange multipliers, one can say that the equilibrium density provides an unconditional minimum of the grand potential functional:

$$\left. \frac{\delta \Omega}{\delta \hat{\rho}(\mathbf{r})} \right|_{\rho(\mathbf{r})} = 0 \quad (9.12)$$

Recall that for an arbitrary functional

$$\mathcal{A}[f(\mathbf{r})] = \int d\mathbf{r} L(f(\mathbf{r}), \nabla f(\mathbf{r}), \mathbf{r})$$

the variational derivative is given by

$$\frac{\delta \mathcal{A}}{\delta f(\mathbf{r})} = \frac{\partial L}{\partial f} - \nabla \cdot \left(\frac{\partial L}{\partial \nabla f} \right)$$

With this in mind we rewrite the variational equation (9.12) using the definition of $\Omega[\hat{\rho}]$ and (9.9) :

$$\mu = \mu_{\text{int}}(\mathbf{r}) + u_{\text{ext}}(\mathbf{r}) \quad (9.13)$$

where

$$\mu_{\text{int}}(\mathbf{r}) \equiv \left. \frac{\delta \mathcal{F}_{\text{int}}[\hat{\rho}]}{\delta \hat{\rho}(\mathbf{r})} \right|_{\rho(\mathbf{r})} \quad (9.14)$$

is the *intrinsic chemical potential*. The spatial dependence of μ_{int} must be exactly cancelled by the radial dependence of u_{ext} , since the “full” chemical potential μ (which is the Lagrange parameter in this variational problem) is constant.

Equation (9.13) represents the fundamental result of the DFT of nonuniform systems. If we had some means of determining μ_{int} or equivalently $\mathcal{F}_{\text{int}}$, then (9.13) would be an explicit equation for the equilibrium density.

For an ideal gas in an external field, the intrinsic chemical potential can be calculated exactly from (9.3):

$$\mu_{\text{int,ideal}}(\rho(\mathbf{r})) = k_{\text{B}}T \ln[\rho(\mathbf{r})\Lambda^3] \quad (9.15)$$

Then (9.13) results in the Boltzmann barometric formula:

$$\rho(\mathbf{r}) = \frac{e^{\beta\mu}}{\Lambda^3} e^{-\beta u_{\text{ext}}(\mathbf{r})}$$

9.2 Intrinsic free energy

Since for realistic interactions the exact intrinsic free energy functional is not available, one has to invoke approximations. The basic assumption of all density-functional theories is that the thermodynamic potential of a nonuniform system can be approximated using known structural and thermodynamic properties of the corresponding uniform system. What distinguishes various theories from one another is the detailed manner in which each formulates the approximation.

Let us study the response of the system to a small change in the pairwise potentials $\delta u(r_{ij})$ that alters the total interaction energy

$$\delta U_N(\mathbf{r}^N) = \sum_{i < j} \delta u(r_{ij})$$

The macroscopic reaction of the system will be described by the change in the grand potential $\Omega(\mu, V, T) = -k_{\text{B}}T \ln \Xi(\mu, V, T)$:

$$\delta \Omega = -k_{\text{B}}T \frac{\delta \Xi}{\Xi} = \frac{1}{\Xi} \sum_{N \geq 0} \lambda^N \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N e^{-\beta(U_N + U_{N,\text{ext}})} \sum_{i < j} \delta u(r_{ij})$$

Examination of the right-hand side and comparison with (1.84) reveals that

$$\delta \Omega = \overline{\delta U_N}$$

In view of the pairwise additivity of δU_N , this result can be transformed by means of the theorem of averaging (see Chap. 1) to give

$$\delta\Omega = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \delta u(r_{12})$$

Using the definition of a variational derivative this result can be expressed as

$$\frac{\delta\Omega}{\delta u(r_{12})} = \frac{1}{2} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (9.16)$$

From the definition of $\Omega[\rho]$ it follows that the same expression is valid for $\mathcal{F}_{\text{int}}$:

$$\frac{\delta\mathcal{F}_{\text{int}}[\rho]}{\delta u(r_{12})} = \frac{1}{2} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (9.17)$$

This equation can be functionally integrated. One way to do this is by using the ideas of the perturbation approach of Chap. 5. Let us decompose the interaction potential $u = u_0 + u_1$, where u_0 is some reference interaction and u_1 a perturbation, and introduce a “test system” characterized by a potential

$$u_\alpha(r_{12}) = u_0(r) + \alpha u_1(r), \quad 0 \leq \alpha \leq 1 \quad (9.18)$$

which gradually changes from u_0 to u when the formal parameter α changes from zero to unity. The functional integration of (9.17) gives:

$$\mathcal{F}_{\text{int}}[\rho] = \mathcal{F}_{\text{int},0}[\rho] + \frac{1}{2} \int_0^1 d\alpha \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_\alpha^{(2)}(\mathbf{r}_1, \mathbf{r}_2) u_1(r_{12}) \quad (9.19)$$

where we have expressed δu_α as

$$\frac{\partial u_\alpha}{\partial \alpha} d\alpha = u_1 d\alpha$$

The first term in (9.19) is the reference contribution and the second one refers to the perturbative part. The pair distribution function $\rho_\alpha^{(2)}$ is that of a system with the density ρ and the interaction potential u_α . This second fundamental equation of the DFT gives the *exact* (but intractable!) expression for the intrinsic free energy. To make the theory work we imply the perturbation approach in which u_1 is considered to be a small perturbation. Expanding (9.19) in u_1 in the spirit of the general scheme of the first order perturbation theories we obtain

$$\mathcal{F}_{\text{int}}[\rho] = \mathcal{F}_{\text{int},0}[\rho] + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2) u_1(r_{12}) + O(u_1^2)$$

where the distribution function $\rho_0^{(2)}$ is now that of the reference system with the density $\rho(\mathbf{r})$ and interaction potential $u_0(r)$. One can go further and treat the reference part in the *local density approximation* (LDA):

$$\mathcal{F}_{int,0}[\rho] \approx \int d\mathbf{r} \psi_0(\rho(\mathbf{r})) \quad (9.20)$$

and

$$\rho_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \approx \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) g_0(\bar{\rho}; r_{12}) \quad (9.21)$$

where $\psi_0(\rho)$ is the free energy density of uniform reference system with number density ρ ; $g_0(\bar{\rho}; r_{12})$ is the pair correlation function of the uniform reference system evaluated at some mean density $\bar{\rho}$, e.g. $\bar{\rho} = [\rho(\mathbf{r}_1) + \rho(\mathbf{r}_2)]/2$. The LDA is valid for weakly inhomogeneous systems, such as a liquid-vapor interface. For strongly inhomogeneous systems, e.g. liquid at a wall, it becomes too crude and one has to use a nonlocal approximation, such as the smoothed density or weighted density approximations.

As discussed in Chap. 5, the preferable decomposition of the interaction potential is given by the WCA theory, in which the reference potential describes the harshly repulsive interaction. The free energy of the reference model can be expressed as the free energy of a hard-sphere system with a suitably defined effective diameter d . The free energy density $\psi_0 = \psi_d$ is readily available (e.g. from the Carnahan-Starling theory, (3.25)). One can go further and ignore all correlations between particles in the perturbative term which results in setting $g_0 = 1$ in (9.21); this is the so-called random phase approximation (RPA), equivalent to the mean field theory (similar to that used by van der Waals).

Many investigations have shown that for systems with weak inhomogeneities, the RPA is sufficient when the system is not too close to the critical point. Combining LDA and RPA, we obtain the intrinsic free energy in its simplest form:

$$\mathcal{F}_{int}[\rho] = \int d\mathbf{r} \psi_d(\rho(\mathbf{r})) + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) u_1(r_{12}) \quad (9.22)$$

In the same approximation the DFT equation (9.13) becomes

$$\mu = \mu_d(\rho(\mathbf{r})) + \int d\mathbf{r}' \rho(\mathbf{r}') u_1(|\mathbf{r} - \mathbf{r}'|) + u_{ext}(\mathbf{r}) \quad (9.23)$$

where $\mu_d(\rho(\mathbf{r}))$ is the local chemical potential of the hard-sphere fluid (in the Carnahan-Starling theory μ_d is given by (3.26)). The integral equation (9.23) can be solved iteratively for $\rho(\mathbf{r})$.

The DFT can also be useful for the description of a uniform system ($\rho = \text{const}$). Equations (9.22)–(9.23) then become

$$\mathcal{F}[\rho] = \mathcal{F}_d[\rho] - \rho^2 aV \quad (9.24)$$

$$\mu = \mu_d(\rho) - 2\rho a, \quad (9.25)$$

where

$$a = -\frac{1}{2} \int d\mathbf{r} u_1(r) \quad (9.26)$$

is the background interaction parameter, which has the same form as in the van der Waals theory. Differentiation of $\mathcal{F}$ with respect to volume yields the virial equation of state:

$$p = p_d - \rho^2 a \quad (9.27)$$

where p_d is the pressure of the hard-sphere system. For a Lennard–Jones fluid with the WCA decomposition of interaction potential

$$a_{\text{LJ}}^{\text{WCA}} = \frac{16\pi\sqrt{2}}{9} \epsilon \sigma^3 \quad (9.28)$$

There is an obvious resemblance between (9.27) and the van der Waals equation (5.6). However, there is also an important difference: DFT uses a more sophisticated approach to describe the repulsive part of the potential than the simple free volume considerations of van der Waals. Furthermore, due to the different decomposition scheme, the background interaction parameter in the van der Waals theory differs from (9.28):

$$a_{\text{LJ}}^{\text{vdW}} = \frac{16\pi}{9} \epsilon \sigma^3 \quad (9.29)$$

9.3 Surface tension

The density-functional perturbation approach is directly applicable to calculating the density profile $\rho(z)$ (inhomogeneity in the z direction) and the surface tension γ for a planar liquid–vapor interface. We start with the thermodynamic relationship (4.11) for the surface tension

$$\gamma = \frac{\Omega^s}{A} = \frac{\Omega[\rho] + pV}{A} \quad (9.30)$$

where A is the surface area. We use the intrinsic free energy functional in the form given by (9.22). Applying the Legendre transformation $\mathcal{F}_d \rightarrow \Omega_d$, the free energy density of hard spheres can be written

$$\psi_d = \rho\mu_d - p_d$$

The grand potential functional (9.8) with $u_{\text{ext}} = 0$ then reads

$$\begin{aligned} \Omega[\rho] = & - \int d\mathbf{r} p_d(\rho) + \int d\mathbf{r} \rho \mu_d(\rho) \\ & + \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') u_1(|\mathbf{r} - \mathbf{r}'|) - \mu \int d\mathbf{r} \rho(\mathbf{r}) \end{aligned}$$

which, after substitution of the DFT equation (9.23) and taking into account that $d\mathbf{r} = A dz$ yields

$$\gamma = - \int dz \left\{ p_d(\rho(z)) + \frac{1}{2} \rho(z) \int d\mathbf{r}' \rho(z') u_1(|\mathbf{r} - \mathbf{r}'|) - p \right\} \quad (9.31)$$

where the equilibrium vapor-liquid density profile $\rho(z)$ satisfies (9.23):

$$\mu_d(\rho(z)) = \mu - \int d\mathbf{r}' \rho(\mathbf{r}') u_1(|\mathbf{r} - \mathbf{r}'|) \quad (9.32)$$

We illustrate the DFT technique by considering the surface tension for a Lennard-Jones system [95], [153]. As usual the Lennard-Jones interaction parameters are denoted by σ and ϵ . We begin by searching for the bulk equilibrium conditions at a given temperature $T < T_c$. Performing the WCA decomposition, we determine the effective hard-sphere diameter d for the reference model (for which both the WCA and Barker-Henderson recipes can be applied). Then the reference pressure and chemical potential follow from the Carnahan-Starling theory:

$$\frac{p}{\rho k_B T} = \frac{1 + \phi_d + \phi_d^2 - \phi_d^3}{(1 - \phi_d)^3} \quad (9.33)$$

$$\frac{\mu_d}{k_B T} = \ln(\rho \Lambda^3) + \frac{8\phi_d - 9\phi_d^2 + 3\phi_d^3}{(1 - \phi_d)^3} \quad (9.34)$$

where $\phi_d = (\pi/6)\rho d^3$ is the volume fraction of effective hard spheres.

Densities in the bulk phases, together with the equilibrium chemical potential and pressure, are found from the coupled nonlinear equations (9.25)–(9.27)

$$\begin{aligned} \mu &= \mu_d(\rho^v) - 2\rho^v a = \mu_d(\rho^l) - 2\rho^l a \\ p &= p_d(\rho^v) - (\rho^v)^2 a = p_d(\rho^l) - (\rho^l)^2 a \end{aligned}$$

with

$$a = a_{LJ}^{\text{WCA}} = \frac{16\pi\sqrt{2}}{9} \epsilon \sigma^3$$

Given the bulk limits

$$\rho(z) \rightarrow \rho^v \quad \text{in the bulk vapor } (z \rightarrow 0)$$

$$\rho(z) \rightarrow \rho^l \quad \text{in the bulk liquid } (z \rightarrow \infty)$$

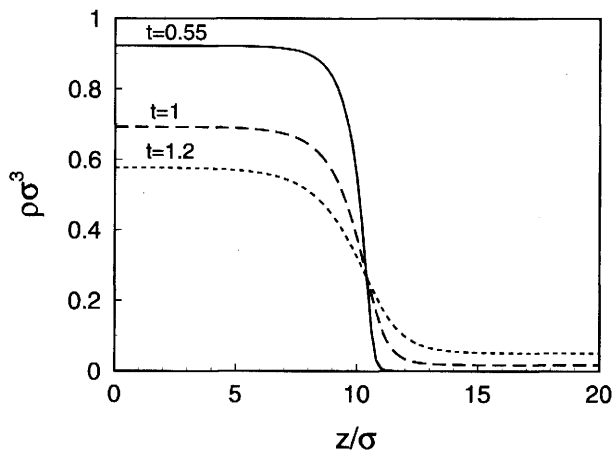


Fig. 9.1. Density profiles for two-phase the Lennard-Jones fluid for various dimensionless temperatures $t = k_B T / \epsilon$

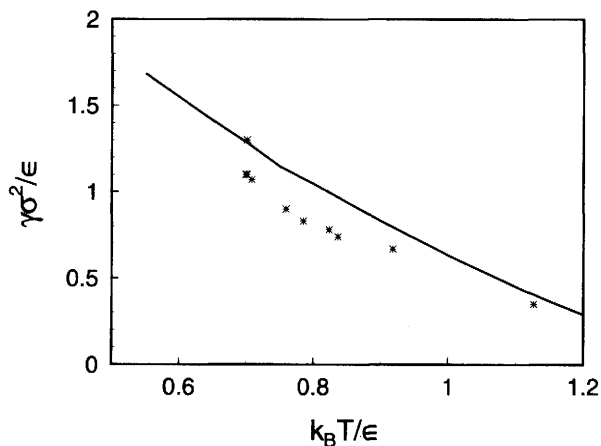


Fig. 9.2. Surface tension of the Lennard-Jones fluid: DFT predictions and simulation results of [22]

the density profile is calculated iteratively from (9.32), starting with an initial guess for $\rho(z)$, which can be a step function or a continuous function (like $\tanh$) that varies between the two bulk limits. At each iteration step a new density profile is derived: for each value of z , the right-hand side of (9.32) is evaluated using the known profile from the previous step, after which $\rho(z)$ is found by inverting the Carnahan–Starling expression for μ_d .

The calculated density profiles for different dimensionless temperatures

$$t \equiv \frac{k_B T}{\epsilon}$$

are shown in Fig. 9.1. The higher the temperature, the smaller the difference between the two bulk densities and the broader the transition zone: for $t = 0.55$ it is $\approx 2\sigma$, while for $t = 1.2$ it is about 7σ . Using the equilibrium $\rho(z)$ for each temperature, we find the surface tension by integration in (9.31) (note that the integrand in this expression vanishes outside the transition zone).

One important remark concerning these results must be made. The presented approximate theory is strictly mean-field in character, and therefore does not take into account fluctuations, which become increasingly important at high temperatures close to the critical point of the gas-liquid transition. This means that this treatment is not valid in the critical region. Several models have been proposed to improve this approach (for a review see [40]). In spite of this difficulty, the perturbation DFT turns out to be very productive in giving an insight into various problems of the liquid state, such as adsorption and wetting phenomena [32], phase transitions in confined fluids [39], depletion interactions [49], etc.

9.4 Nonlocal density functional theories

Local density approach can be a bad approximation for systems with large density fluctuations. This difficulty arises, for example in problems where a liquid-solid equilibrium is involved; note that a solid can be viewed as a liquid with giant density fluctuations, or in other words as a highly inhomogeneous liquid. The liquid-vapor interface, which can be quite accurately described by a local density theory like the one presented in the previous section shows, increasingly nonlocal behavior near the critical point.

In these cases one must apply nonlocal DFT schemes. One feature common to all these models is that the intrinsic free energy functional can be represented as the sum of an ideal contribution and excess (over and above the ideal):

$$\mathcal{F}_{\text{int}} = \mathcal{F}_{\text{ideal}} + \mathcal{F}_{\text{ex,int}} \quad (9.35)$$

Note that this decomposition differs from the one discussed in the previous section. The ideal term is known exactly, and $\mathcal{F}_{\text{ex,int}}$ is calculated in an approximate manner using as an input the direct correlation functions of the uniform liquid.

In order to introduce the general ideas of nonlocal DFT models we start with the familiar barometric formula for the density profile:

$$\rho^{(1)}(\mathbf{r}) = \frac{\lambda}{\Lambda^3} \exp[-\beta u_{\text{ext}}(\mathbf{r})],$$

which is valid for an ideal gas in an external field u_{ext} . If the system is non-ideal (i.e. $u(r) \neq 0$) we retain the Boltzmann form for $\rho^{(1)}$ by introducing a singlet direct correlation function $c^{(1)}(\mathbf{r})$:

$$\rho^{(1)}(\mathbf{r}) = \frac{e^{\beta\mu}}{\Lambda^3} \exp \left[-\beta u_{\text{ext}}(\mathbf{r}) + c^{(1)}(\mathbf{r}) \right], \quad (9.36)$$

For an ideal gas $c^{(1)}(\mathbf{r})$ is equal to zero. The expression (9.36) can be interpreted as a self-consistent equation determining the one-body distribution function $\rho^{(1)}(\mathbf{r})$, where

$$-k_{\text{B}}Tc^{(1)}(\mathbf{r})$$

plays the role of an effective one-body potential (originating from interactions in the system under consideration); we stress that $c^{(1)}(\mathbf{r})$ is itself a functional of $\rho^{(1)}(\mathbf{r})$. This is analogous to the Kohn–Sham theory [72], where the effective one-body potential

$$\int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}$$

which contains the Coulombic interaction term calculated exactly, and the exchange and correlation energy E_{xc} calculated approximately, is incorporated into the Schrödinger equation for the noninteracting electron liquid. With the help of the Yvon equation [125] one can show that the direct pair correlation function is the functional derivative of the singlet function:

$$c(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta c^{(1)}(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)} \quad (9.37)$$

The intrinsic chemical potential can be expressed using (9.15) and (9.35) as

$$\mu_{\text{int}} = k_{\text{B}}T \ln[\rho(\mathbf{r})\Lambda^3] + \frac{\delta \mathcal{F}_{\text{ex,int}}}{\delta \rho(\mathbf{r})} \quad (9.38)$$

From the definition of $c^{(1)}(\mathbf{r})$ we can write

$$k_{\text{B}}T \ln[\rho(\mathbf{r})\Lambda^3] = \mu - u_{\text{ext}}(\mathbf{r}) + c^{(1)}(\mathbf{r}) \quad (9.39)$$

Substitution of (9.38)–(9.39) into the DFT equation (9.13) results in

$$c^{(1)}(\mathbf{r}) = -\beta \frac{\delta \mathcal{F}_{\text{ex,int}}}{\delta \rho(\mathbf{r})} \quad (9.40)$$

Thus, another physical interpretation of the singlet direct correlation function is that $-k_{\text{B}}Tc^{(1)}(\mathbf{r})$ is the contribution to the intrinsic chemical potential arising from the interactions between particles. From (9.37) we obtain

$$c(\mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\delta^2 \mathcal{F}_{\text{ex,int}}}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \quad (9.41)$$

In the next two sections we briefly formulate two nonlocal theories: the weighted-density approximation (WDA) of Curtin and Ashcroft [25] and the modified weighted-density approximation (MWDA) of Denton and Ashcroft [31].

9.4.1 Weighted-density approximation

The functional of the excess intrinsic free energy can be expressed in the form

$$\mathcal{F}_{\text{ex,int}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) f_{\text{ex}}(\mathbf{r}; [\rho]) \quad (9.42)$$

which serves as the definition of a local excess free energy per particle $f_{\text{ex}}(\mathbf{r}; [\rho])$. In the WDA this relationship is approximated as

$$\mathcal{F}_{\text{ex,int}}^{\text{WDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) f_{\text{ex,u}}(\bar{\rho}(\mathbf{r})), \quad (9.43)$$

where $f_{\text{ex,u}}(\bar{\rho}(\mathbf{r}))$ is the excess free energy per particle of a uniform liquid (assumed to be known for any density) taken at some weighted density $\bar{\rho}(\mathbf{r})$ (note that setting $\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r})$ leads to the LDA). In (9.43) $\rho(\mathbf{r}) d\mathbf{r}$ gives the number of particles in the spherical shell $d\mathbf{r}$ about point $\mathbf{r}$; to each particle in this shell WDA assigns the free energy of a uniform fluid with some weighted density $\bar{\rho}$ different from the actual density ρ at point $\mathbf{r}$. The weighted density is defined as a weighted average of $\rho(\mathbf{r})$ with respect to a weight function w according to

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w(\mathbf{r} - \mathbf{r}'; \bar{\rho}(\mathbf{r})) \quad (9.44)$$

Note the important feature of this definition, its self-consistency with respect to $\bar{\rho}(\mathbf{r})$ ($\bar{\rho}$ appears on both sides of (9.44)). The form of the weight function has yet to be specified. We have to ensure that the WDA becomes exact for a uniform system, i.e. when $\rho(\mathbf{r}) \rightarrow \rho_u$, where ρ_u is the density of the uniform system. This yields the normalization

$$\int d\mathbf{r}' w(\mathbf{r} - \mathbf{r}'; \bar{\rho}(\mathbf{r})) = 1 \quad \text{for all } \mathbf{r} \quad (9.45)$$

(note that setting $w(\mathbf{r}) = \delta(\mathbf{r})$ leads to a local formulation: $\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r})$).

In order to find a unique specification of w we demand that the general relationship (9.41) for the direct pair correlation function become exact when we replace $\mathcal{F}_{\text{ex,int}}$ by $\mathcal{F}_{\text{ex,int}}^{\text{WDA}}$ and take the limit of the uniform system. This means that

$$c_u(\mathbf{r} - \mathbf{r}'; \rho_u) = -\beta \lim_{\rho \rightarrow \rho_u} \left\{ \frac{\delta^2 \mathcal{F}_{\text{ex,int}}^{\text{WDA}}[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right\} \quad (9.46)$$

where c_u is the direct pair correlation function of the uniform system. Performing variational differentiation in (9.43), we find the singlet direct correlation function:

$$-k_B T c^{(1)}([\rho]; \mathbf{r}_1) = \frac{\delta \mathcal{F}_{\text{ex,int}}[\rho]}{\delta \rho(\mathbf{r}_1)} = \int d\mathbf{r}_2 \rho(\mathbf{r}_2) f'_{\text{ex,u}}(\bar{\rho}(\mathbf{r}_2)) \frac{\delta \bar{\rho}(\mathbf{r}_2)}{\delta \rho(\mathbf{r}_1)} + f'_{\text{ex,u}}(\bar{\rho}(\mathbf{r}_1))$$

where a prime denotes a derivative with respect to density, and from (9.45)

$$\frac{\delta \bar{\rho}(\mathbf{r}_2)}{\delta \rho(\mathbf{r}_1)} = \frac{w(\mathbf{r}_2 - \mathbf{r}_1; \bar{\rho}(\mathbf{r}_2))}{1 - \int d\mathbf{r}_3 w'(\mathbf{r}_2 - \mathbf{r}_3; \bar{\rho}(\mathbf{r}_2)) \rho(\mathbf{r}_3)}$$

In the uniform limit w does not depend on density, therefore $w' = 0$ and the integral in the denominator vanishes. The second variational differentiation gives in the uniform limit

$$\begin{aligned} & -k_{\text{B}} T c^{(2)}(\rho_{\text{u}}; r_{12}) \\ & = 2f'_{\text{ex,u}}(\rho_{\text{u}})w(r_{12}, \rho_{\text{u}}) + \rho_{\text{u}} f''_{\text{ex,u}}(\rho_{\text{u}}) \int d\mathbf{r}_3 w(r_{13}, \rho_{\text{u}}) w(r_{23}, \rho_{\text{u}}) \\ & \quad + \rho_{\text{u}} f'_{\text{ex,u}}(\rho_{\text{u}}) \int d\mathbf{r}_3 [w'(r_{13}, \rho_{\text{u}}) w(r_{23}, \rho_{\text{u}}) + w(r_{13}, \rho_{\text{u}}) w'(r_{23}, \rho_{\text{u}})] \end{aligned}$$

This is an integrodifferential equation with respect to the unknown weight function w , in which c_{u} and $f_{\text{ex,u}}$ are assumed known. In the Fourier space it has the form of a nonlinear differential equation:

$$\begin{aligned} -k_{\text{B}} T c_{\text{u}}^{(2)}(k; \rho_{\text{u}}) & = 2f'_{\text{ex,u}}(\rho_{\text{u}})w(k; \rho_{\text{u}}) + \rho_{\text{u}} f''_{\text{ex,u}}(\rho_{\text{u}})[w(k; \rho_{\text{u}})]^2 \\ & \quad + 2\rho_{\text{u}} f'_{\text{ex,u}}(\rho_{\text{u}})w'(k; \rho_{\text{u}})w(k; \rho_{\text{u}}) \end{aligned} \quad (9.47)$$

where the Fourier transforms are defined as

$$c_{\text{u}}^{(2)}(k; \rho_{\text{u}}) = \int d\mathbf{r} c_{\text{u}}^{(2)}(r; \rho_{\text{u}}) e^{i\mathbf{k}\mathbf{r}}, \quad w(k; \rho_{\text{u}}) = \int d\mathbf{r} w(r; \rho_{\text{u}}) e^{i\mathbf{k}\mathbf{r}}$$

In view of normalization for w it is clear that $w(k=0; \rho_{\text{u}}) = 1$. An obvious candidate to apply the WDA is the hard-sphere system for which the direct pair correlation function and the excess free energy are given analytically in the Percus–Yevick approximation, and therefore the nonlinear differential equation (9.47) can be solved numerically for $w(k)$ for all densities. WDA was successfully applied in [25]–[27], [74] to studying the hard-sphere freezing transition, and to determine of the density profile of hard spheres near a hard wall.

9.4.2 Modified weighted-density approximation

Formulation of the MWDA follows the ideas of WDA with one new concept: instead of introducing the local quantity $f_{\text{ex}}(\mathbf{r}, [\rho])$ one starts with the global excess free energy per particle

$$\mathcal{F}_{\text{ex,int}}[\rho]/N,$$

where N is the number of particles in the system. Since $\mathcal{F}_{\text{ex,int}}[\rho]/N$ is independent of position, the theory must involve a position-independent weighted density, which we denote by $\bar{\rho}$. Thus MWDA can be expressed as

$$\mathcal{F}_{\text{ex,int}}^{\text{MWDA}}[\rho]/N = f_{\text{ex,u}}(\tilde{\rho}), \quad (9.48)$$

The weighted density $\tilde{\rho}$ is defined by

$$\tilde{\rho} = \frac{1}{N} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') \tilde{w}(\mathbf{r} - \mathbf{r}'; \tilde{\rho}) \quad (9.49)$$

Comparing of (9.44) and (9.49), one can see that $\tilde{\rho}$ (which is just a number, not a function of $\mathbf{r}$) is an average of $\bar{\rho}(\mathbf{r})$. The normalization of the weight function remains the same (in order to satisfy the uniform liquid limit), namely

$$\int d\mathbf{r}' \tilde{w}(\mathbf{r} - \mathbf{r}'; \tilde{\rho}) = 1, \quad \text{for all } \mathbf{r} \quad (9.50)$$

and its unique specification follows from the same requirement as in the WDA (cf. (9.46)):

$$c_u(\mathbf{r} - \mathbf{r}'; \rho_u) = -\beta \lim_{\rho \rightarrow \rho_u} \left\{ \frac{\delta^2 \mathcal{F}_{\text{ex,int}}^{\text{MWDA}}[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right\} \quad (9.51)$$

To find the weight function $\tilde{w}$, we calculate variational derivatives of $\mathcal{F}_{\text{ex,int}}^{\text{MWDA}}$. From (9.48)

$$\frac{\delta \mathcal{F}_{\text{ex,int}}^{\text{MWDA}}[\rho]}{\delta \rho(\mathbf{r})} = f_{\text{ex,u}} + N \frac{\delta f_{\text{ex,u}}}{\delta \rho(\mathbf{r})}$$

where we took into account that $\delta N / \delta \rho(\mathbf{r}) = 1$, since $N = \int d\mathbf{r} \rho(\mathbf{r})$. Then the second variational derivative becomes

$$\frac{\delta^2 \mathcal{F}_{\text{ex,int}}^{\text{MWDA}}[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = 2 \frac{\delta f_{\text{ex,u}}}{\delta \rho(\mathbf{r})} + N \frac{\delta^2 f_{\text{ex,u}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \quad (9.52)$$

The global excess free energy per particle is a function of the weighted density $\tilde{\rho}$, which in turn is a functional of the actual density $\rho(\mathbf{r})$. Therefore,

$$\frac{\delta f_{\text{ex,u}}}{\delta \rho(\mathbf{r})} = f'_{\text{ex,u}} \frac{\delta \tilde{\rho}}{\delta \rho(\mathbf{r})} \quad (9.53)$$

and

$$\frac{\delta^2 f_{\text{ex,u}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = f''_{\text{ex,u}} \left[\frac{\delta \tilde{\rho}}{\delta \rho(\mathbf{r})} \right]^2 + f'_{\text{ex,u}} \frac{\delta^2 \tilde{\rho}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \quad (9.54)$$

Variational derivatives of $\tilde{\rho}$ follow from the definition (9.49). We have

$$\frac{\delta \tilde{\rho}}{\delta \rho(\mathbf{r})} = \frac{2}{N} \int d\mathbf{r}' \rho(\mathbf{r}') \tilde{w}(\mathbf{r} - \mathbf{r}'; \tilde{\rho}) - \frac{1}{N} \tilde{\rho}$$

For the uniform liquid, this yields, taking into account normalization of the weight function,

$$\left. \frac{\delta \tilde{\rho}}{\delta \rho(\mathbf{r})} \right|_{\rho_u} = \frac{\rho_u}{N} \quad (9.55)$$

In the same manner we find

$$\frac{\delta^2 \tilde{\rho}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = -\frac{2}{N} \frac{\delta \tilde{\rho}}{\delta \rho(\mathbf{r})} + \frac{2}{N} \tilde{w}$$

which in the uniform limit reduces to

$$\left. \frac{\delta^2 \tilde{\rho}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right|_{\rho_u} = -\frac{2\rho_u}{N^2} + \frac{2}{N} \tilde{w} \quad (9.56)$$

Summarizing (9.51)–(9.56), we obtain:

$$\tilde{w}(\mathbf{r} - \mathbf{r}'; \rho_u) = -\frac{1}{2f'_{\text{ex},u}(\rho_u)} \left[k_B T c_u(\mathbf{r} - \mathbf{r}'; \rho_u) + \frac{1}{V} \rho_u f''_{\text{ex},u}(\rho_u) \right] \quad (9.57)$$

In Fourier space this result has a simpler form:

$$\tilde{w}(k; \rho_u) = -\frac{1}{2f'_{\text{ex},u}(\rho_u)} \left[k_B T c_u(k; \rho_u) + \delta_{k,0} \rho_u f''_{\text{ex},u}(\rho_u) \right] \quad (9.58)$$

where $\delta_{i,j}$ is the Kronecker delta. It is notable that for $k \neq 0$, $\tilde{w}$ is simply proportional to the Fourier transform of the direct pair correlation function (which is assumed to be known). Thus, MWDA provides a closed form expression for the weight function that makes its practical implementation more attractive compared to WDA, since it requires considerably less computational effort and at the same time, as shown in [31], the MWDA results for a hard-sphere freezing transition accurately reproduce those obtained by means of WDA.

10. Real gases

We have studied a number of approaches to the description of the liquid state. With this knowledge the question “Do we understand the properties of real gases on a satisfactory level?” might seem rather trivial. However, it is not. The simplest thermodynamic description of a real gas can be obtained from the virial expansion, which for low densities one can truncate at the second-order term:

$$\frac{p}{k_B T} = \rho + \rho^2 B(T) \quad (10.1)$$

which contains the second virial coefficient $B(T)$. We know from experiment that even at low densities the gas can condense into liquid. This is a first-order phase transition in which the density abruptly changes from its value in the gas phase to the value in the liquid phase. Like any phase transition it must result in a singularity of the free energy density. A simple inspection of (10.1) shows that pressure is an analytic function over its entire domain of definition and so is the free energy. Thus, by no means can the virial expansion signal condensation.

Similar considerations also apply to the van der Waals theory. The gaseous part of the isotherm remains smooth and analytic below and above the saturation (condensation) point. This is the reason why it can be extended into the metastable region with $p > p_{\text{sat}}(T)$, and why it develops the “van der Waals loop.” Thus, the van der Waals equation, as it is, turns out to be insensitive to the presence of the condensation point; for a description of “true” equilibrium it must be supplemented by the Maxwell construction.

On the basis of general arguments presented in Chap. 6 one can formulate the converse statement: a gaseous isotherm *must* contain a singularity that corresponds to the condensation point. A rigorous proof of this statement within the framework of statistical mechanics requires calculation of the configuration integral, which, as we know, is an unrealistic problem for realistic interaction potentials. However, it is possible to put forward some heuristic considerations that appear to be very helpful.

A typical interaction between gas molecules consists of a harshly repulsive core and a short-range attraction. The most probable configurations of the gas at low densities and temperatures will be isolated clusters of $n = 1, 2, 3, \dots$ molecules. Hence, to a reasonable approximation we can describe a gas as

a system of noninteracting clusters (at the same time intracluster interactions are significant). They all are in statistical equilibrium, associating and dissociating. Even large clusters have a certain probability of appearing. A simple but important observation is that a cluster can be associated with a droplet of the liquid phase in a gas at the same temperature. Growth of a macroscopic liquid droplet corresponds to condensation in this picture.

10.1 Fisher droplet model

In this section we discuss the droplet model of a real gas formulated by Fisher [44]. The internal (potential) energy of an n -cluster can be expressed as

$$U_n = -nE_0 + W_n \quad (10.2)$$

Here $-E_0$ ($E_0 > 0$) is the binding energy per molecule; it can be related to the depth of interparticle attraction $-\epsilon_0$. In close packing of spherical molecules (face-centered cubic lattice), each molecule is surrounded by 12 nearest neighbors, and due to the fact that interaction is shared by two molecules we can write $E_0 = 6\epsilon_0$. The second term in (10.2) is the surface energy related to the surface area s_n of an n -cluster:

$$W_n = ws_n, \quad W_n > 0$$

The coefficient w can be associated with a “microscopic” surface tension. This term provides stability of the cluster: at low temperatures there is a tendency to form compact droplets with minimal surface. This tendency is opposed by an entropic contribution to the free energy. The entropy of an n -cluster can be written as a sum of bulk and surface terms similar to (10.2):

$$S_n = nS_0 + \omega s_n \quad (10.3)$$

where S_0 is the entropy per molecule in the bulk liquid, the factor ω characterizes the number of distinct configurations with the same surface area s_n .

Let us consider the configuration integral of an n -cluster in a domain of volume V :

$$q_n = \frac{1}{n!} \int d\mathbf{r}^n e^{-\beta U_n}$$

For convenience we have incorporated the factor $\frac{1}{n!}$ into the configuration integral (cf. (1.44)). It is important to understand the difference between the n -particle configuration integral Q_n discussed in the previous chapters and q_n . The latter includes only those molecular configurations in the volume V that form an n -cluster, while Q_n contains all possible configurations; therefore $Q_n \geq q_n$. Consider formally the quantity:

$$A \equiv \exp \left[\sum_{n=1}^{\infty} q_n z^n \right] = 1 + \frac{1}{1!} \sum_{n=1}^{\infty} q_n z^n + \frac{1}{2!} \left[\sum_{n=1}^{\infty} q_n z^n \right]^2 + \dots \quad (10.4)$$

where

$$z = e^{\beta\mu} / \Lambda^3 \quad (10.5)$$

is the fugacity and μ the chemical potential of a molecule. Each term on the right-hand side represents a power series in z . We collect terms in z^N for all $N = 0, 1, 2, \dots$

$$A = \sum_{N=0}^{\infty} z^N A_N(\beta, V) \quad (10.6)$$

Due to the neglect of intercluster interactions, the coefficient $A_N(\beta, V)$ is nothing but the configuration integral of an N -particle system, $Q_N(\beta, V)$. To verify this, recall that Q_N is proportional to the probability of having exactly N particles in the system. These particles can be organized in various possible clusters, so Q_N must contain all q_n with $1 \leq n \leq N$. For instance, a two-particle system can contain

- one 2-cluster or
- two 1-clusters

and, since they are mutually independent,

$$Q_2 = q_2 + \frac{1}{2!} q_1^2$$

A 3-particle system can comprise

- one 3-cluster or
- one 2-cluster and one 1-cluster, or
- three 1-clusters,

resulting in

$$Q_3 = q_3 + q_2 q_1 + \frac{1}{3!} q_1^3$$

For a 4-particle system

$$Q_4 = q_4 + q_3 q_1 + \frac{1}{2!} q_2^2 + \frac{1}{2!} q_2 q_1^2 + \frac{1}{4!} q_1^4, \text{ etc.}$$

Permutations of molecules inside a cluster are taken into account in the definition of q_n , and in Q_N we take into account only permutations of clusters themselves (as independent entities). Expressions for $A_2, A_3, A_4, \dots$ which

emerge from (10.4), are exactly the same. Thus, the series on the right-hand side of (10.6) represents the grand partition function,

$$\Xi = \sum_{N \geq 0} \lambda^N Z_N = \sum_{N \geq 0} z^N Q_N$$

and from the definition of A we derive an important result stating that Ξ can be expressed in exponential form:

$$\Xi = \exp \left[\sum_{n=1}^{\infty} q_n z^n \right] \quad (10.7)$$

Then the grand potential becomes

$$\Omega = -k_B T \sum_{n=1}^{\infty} q_n z^n$$

Using the thermodynamic relationship $\Omega = -pV$ we obtain the pressure equation of state

$$\frac{p}{k_B T} = \sum_{n=1}^{\infty} \left(\frac{q_n}{V} \right) z^n \equiv \Pi(\beta, z), \quad (10.8)$$

which has the form of a virial series (3.35). The overall (macroscopic) number density can be written (see (3.36))

$$\rho = \sum_{n=1}^{\infty} n \frac{q_n}{V} z^n \quad (10.9)$$

On the other hand ρ can be expressed via the densities ρ_n of n -clusters:

$$\rho = \sum_{n=1}^{\infty} n \rho_n$$

implying that

$$\rho_n = \frac{q_n}{V} z^n \quad (10.10)$$

and

$$\frac{p}{k_B T} = \sum_{n=1}^{\infty} \rho_n \quad (10.11)$$

By neglecting intercluster interactions we have been able to reduce calculation of the equation of state to calculation of the n -cluster configuration integrals. $\Pi(\beta, z)$ defined in (10.8) plays the role of a generating function for

various thermodynamic quantities. This can be easily shown if we introduce the sequence of functions $\Pi^{(k)}(\beta, z)$, $k = 0, 1, 2, \dots$ defined by

$$\Pi^{(0)}(\beta, z) = \Pi(\beta, z), \quad \Pi^{(1)} = z \frac{\partial \Pi^{(0)}}{\partial z}, \dots, \quad \Pi^{(k)} = z \frac{\partial \Pi^{(k-1)}}{\partial z}, \dots$$

Then for the overall number density we get

$$\rho = \Pi^{(1)} \quad (10.12)$$

The isothermal compressibility can be expressed as

$$\chi_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial z} \right)_{T,V} \left(\frac{\partial z}{\partial p} \right)_{T,V} = \frac{1}{\rho k_B T} \frac{\Pi^{(2)}}{\Pi^{(1)}}$$

Thus,

$$\rho^2 k_B T \chi_T = \Pi^{(2)} \quad (10.13)$$

The energy, specific heat, etc. can be similarly expressed in terms of derivatives of the function Π with respect to the temperature.

If we move the origin to the center of mass of the n -cluster (let it be molecule 1), then q_n can be written

$$q_n = V \frac{1}{n!} \int d\mathbf{r}_{12} \dots d\mathbf{r}_{1n} e^{-\beta U_n} = V \sum_{s_n} g(n, s_n) e^{n\beta E_0 - \beta w s_n} \quad (10.14)$$

We replaced integration over $3(n-1)$ configuration space by summation over all possible surface areas s_n . Several different configurations may have the same surface area, so the degeneracy factor $g(n, s_n)$ appears, which represents the number (or more correctly the volume in $3(n-1)$ configuration space) of configurations of n indistinguishable molecules with a fixed center of mass forming a cluster with surface area s_n .

Intuitively it is clear that $g(n, s_n)$ must be related to the entropy of an n -cluster. In order to verify this hypothesis let us calculate S_n ; note that we are concerned with the *configurational* entropy, which is related to the configurational Helmholtz free energy $\mathcal{F}_n^{\text{conf}} = -k_B T \ln q_n$ of the cluster via

$$S_n = - \frac{\partial \mathcal{F}_n^{\text{conf}}}{\partial T}$$

Thus,

$$S_n = k_B \left[\ln q_n - \beta \frac{1}{q_n} \frac{\partial q_n}{\partial \beta} \right]$$

From (10.14) the last term becomes

$$\frac{1}{q_n} \frac{\partial q_n}{\partial \beta} = nE_0 - \frac{V \sum_{s_n} g(n, s_n) e^{-\beta U_n} w s_n}{q_n} = nE_0 - \langle W_n \rangle$$

where $\langle W_n \rangle$ is the thermal average of the microscopic surface energy. The n -cluster entropy then becomes

$$S_n(\beta) = k_B [\ln q_n - \beta nE_0 + \beta \langle W_n \rangle] \quad (10.15)$$

In (10.3) S_n was divided into the bulk and surface terms. The bulk entropy per particle, S_0 , can be determined from (10.15) if we take $\lim_{n \rightarrow \infty} S_n/n$. Then the surface term vanishes and we obtain

$$S_0(\beta) = k_B \left[\lim_{n \rightarrow \infty} \frac{1}{n} \ln q_n - \beta E_0 \right]$$

We can write this in a more compact form by introducing the function

$$G_n(\beta) = \frac{q_n}{V} e^{-\beta nE_0} \equiv \sum_{s_n} g(n, s_n) e^{-\beta w s_n} \quad (10.16)$$

Its logarithm is

$$\ln G_n = \ln q_n - \beta nE_0 - \ln V$$

For large n ,

$$\frac{\ln V}{n} \sim \frac{\ln n}{n} \rightarrow 0$$

so

$$\lim_{n \rightarrow \infty} \frac{1}{n} \ln G_n = \lim_{n \rightarrow \infty} \left[\frac{1}{n} \ln q_n - \beta E_0 \right]$$

and therefore S_0 can be expressed in terms of G_n :

$$S_0(\beta) = k_B \lim_{n \rightarrow \infty} \left[\frac{1}{n} \ln G_n(\beta) \right] \quad (10.17)$$

Now let us discuss possible upper and lower limits for the surface area of an n -cluster. It is clear that the lower limit corresponds to the most compact object, a sphere in 3D, or a circle in 2D. The upper limit is achieved when a cluster represents a string of molecules. Thus,

$$a_1 n^{1-(1/d)} \leq s_n \leq a_2 n \quad (10.18)$$

where a_1 and a_2 are appropriate positive constants, and d is dimensionality of space. The series (10.16) contains only positive terms, and we can use the standard argument: G_n is larger than the maximal term and smaller than the maximal term times the maximal value of s_n . This yields

$$\max_{s_n} \{g(n, s_n) e^{-\beta w s_n}\} \leq G_n(\beta) \leq a_2 n \max_{s_n} \{g(n, s_n) e^{-\beta w s_n}\}$$

If this maximum is attained for $\overline{s_n}$ it means that $\overline{s_n}(\beta)$ is the most probable surface area. In other words $\overline{s_n}$ corresponds to the configuration with the maximum statistical weight: $e^{-\beta U_n} \rightarrow \max$. Then

$$\ln G_n(\beta) = \ln g(n, \overline{s_n}(\beta)) - \beta w \overline{s_n}(\beta) + O(\ln n) \quad (10.19)$$

At low temperatures clusters will be close to relatively compact objects, so the mean surface area will increase with n more slowly than n :

$$\frac{\overline{s_n}(\beta)}{n} \rightarrow 0 \quad \text{as } n \rightarrow \infty \quad (10.20)$$

On the other hand, by virtue of the lower limit, we can write from (10.18)

$$\frac{\overline{s_n}(\beta)}{\ln n} \geq \frac{a_1 n^{1-(1/d)}}{\ln n} \rightarrow \infty \quad \text{as } n \rightarrow \infty$$

Thus, $\overline{s_n}$ (as a function of n) grows slower than n but faster than $\ln n$. Combining these two constraints results in

$$\overline{s_n}(\beta) = a_0 n^\sigma \quad (10.21)$$

with $a_0 = a_0(\beta)$ and $\sigma = \sigma(\beta)$, and

$$0 < \sigma < 1$$

At low temperatures we can expect that $\sigma = 2/3$ for $d = 3$ and $\sigma = 1/2$ for $d = 2$. From (10.19) and (10.20) we obtain in the limit of large n

$$\frac{1}{n} \ln G_n(\beta) \rightarrow_{n \rightarrow \infty} \frac{1}{n} \ln g(n, \overline{s_n}(\beta))$$

Comparison with (10.17) shows that at large n

$$k_B \ln g(n, \overline{s_n}(\beta)) \rightarrow_{n \rightarrow \infty} n S_0$$

It is natural to assume that the residual entropy related to the second and third terms on the right-hand side of (10.19) satisfies

$$k_B \ln g(n, \overline{s_n}(\beta)) - n S_0 \approx \omega \overline{s_n} \quad (10.22)$$

The right-hand side represents the surface entropy of the cluster. We have found the degeneracy factor for the most probable surface area of an n -cluster:

$$\ln g(n, \overline{s_n}) = \frac{n S_0}{k_B} + \frac{\omega \overline{s_n}}{k_B} \quad (10.23)$$

Combining (10.19) and (10.23), we obtain

$$\ln G_n(\beta) = n \frac{S_0}{k_B} - \beta(w - \omega T) \bar{s}_n - \tau \ln n + \ln q_0 \quad (10.24)$$

where the terms proportional to $\ln n$ and of order unity are introduced. For convenience we denote the latter term by $\ln q_0$, and the unknown coefficient of $\ln n$ is denoted by $-\tau$; their numerical values will be discussed later.

Now we can return to our main goal, the calculation of the n -cluster configuration integral. From (10.16) we have

$$\frac{q_n}{V} = e^{\beta n E_0} \exp \left[n \frac{S_0}{k_B} - \beta(w - \omega T) \bar{s}_n \right] n^{-\tau} q_0$$

With the help of (10.21), the latter expression can be written as:

$$\frac{q_n}{V} = \left\{ \exp \left[\beta E_0 + \frac{S_0}{k_B} \right] \right\}^n \{ \exp [-a_0 \beta (w - \omega T)] \}^{n^\sigma} n^{-\tau} q_0 \quad (10.25)$$

This is the basic result of the Fisher droplet model. With its help the pressure equation takes the form

$$\frac{p}{k_B T} = \Pi(\beta, z) = q_0 \sum_{n=1}^{\infty} y^n x^{n^\sigma} n^{-\tau} \quad (10.26)$$

where

$$y = z \exp \left[\beta E_0 + \frac{S_0}{k_B} \right] \quad (10.27)$$

is proportional to the activity and

$$x = \exp [-a_0 \beta (w - \omega T)] \quad (10.28)$$

measures the temperature. The number density of n -clusters is thus

$$\rho_n = q_0 y^n x^{n^\sigma} n^{-\tau} \quad (10.29)$$

The overall density and isothermal compressibility are, respectively (see (10.12)–(10.13))

$$\rho = q_0 \sum_{n=1}^{\infty} n^{1-\tau} y^n x^{n^\sigma} \quad (10.30)$$

$$\rho^2 k_B T \chi_T = q_0 \sum_{n=1}^{\infty} n^{2-\tau} y^n x^{n^\sigma} \quad (10.31)$$

Let us discuss the probability of finding an n -cluster. First of all, we note that it is proportional to ρ_n . At low temperatures ($\beta \rightarrow \infty$) x is small; if

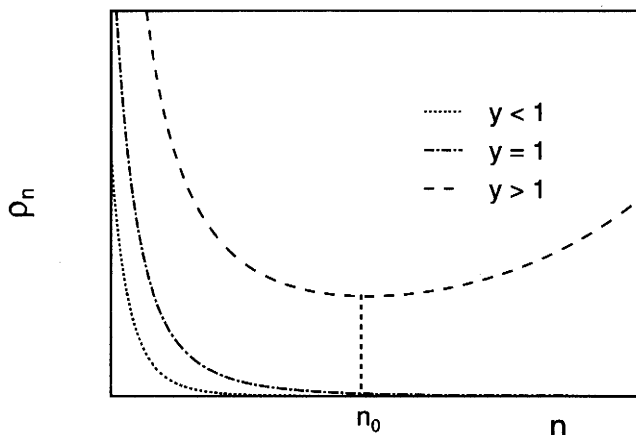


Fig. 10.1. The number density of n -clusters as a function of n for various values of the activity, or equivalently, parameter y . For $y > 1$ ρ_n attains a minimum at $n = n_0$ and for $n > n_0$ it diverges

at the same time the activity is small (the chemical potential is large and negative), implying that $y < 1$, then ρ_n rapidly (exponentially) decays to zero as n grows. As y approaches unity the decrease in ρ_n becomes slower. When $y = 1$, ρ_n still decays but only as $\exp[-\text{const } n^\sigma]$.

Finally, if y slightly exceeds unity, then ρ_n first decreases, reaching a minimum at $n = n_0$, and then increases. The large (divergent) probability of finding a very large cluster indicates that condensation has taken place (see Fig. 10.1). We identify

$$y_{\text{sat}} = 1$$

with the saturation point (corresponding to the bulk liquid-vapor equilibrium). From (10.27)

$$z_{\text{sat}} = \exp[\beta(-E_0 - TS_0)]$$

Using (10.5) we find the chemical potential at saturation:

$$\mu_{\text{sat}} = -E_0 - TS_0 + k_B T \ln \Lambda^3 \quad (10.32)$$

Let us discuss what happens if y becomes slightly larger than y_{sat} :

$$y = 1 + \delta y, \quad 0 < \delta y \ll 1 \quad (10.33)$$

Physically this situation corresponds to a metastable state of supersaturated vapor. Rewriting (10.33) for the chemical potentials and linearizing in δy we have

$$\mu - \mu_{\text{sat}} = k_{\text{B}}T \ln \left(\frac{z}{z_{\text{sat}}} \right) \simeq k_{\text{B}}T \delta y$$

The value of n_0 corresponding to the minimum of ρ_n can be found from the condition: $\partial \ln \rho_n / \partial n = 0$:

$$n_0 = \left[\frac{\delta y}{\sigma |\ln x|} \right]^{\frac{1}{\sigma-1}}$$

which can be rewritten as

$$n_0 = \left[\frac{a_0 \sigma (w - \omega T)}{\mu - \mu_{\text{sat}}} \right]^{\frac{1}{1-\sigma}} \quad (10.34)$$

The extreme limit of metastability can be defined, somewhat arbitrarily, by the condition $n_0 = 1$, which yields

$$|\mu - \mu_{\text{sat}}|_{\text{max}} = a_0 \sigma (w - \omega T)$$

The right-hand side of this expression must be positive, implying that the metastability cannot occur if T exceeds

$$T_c = w/\omega$$

which may be identified with the critical temperature. The quantity

$$\gamma_{\text{micro}} = w \left(1 - \frac{T}{T_c} \right) \quad (10.35)$$

is the microscopic surface tension. Equations (10.32) and (10.35) yield another useful form of the Fisher configuration integral:

$$\frac{q_n}{V} = q_0 \Lambda^{3n} \exp[-n\beta\mu_{\text{sat}}] \exp[-a_0 n^\sigma \beta \gamma_{\text{micro}}] n^{-\tau} \quad (10.36)$$

which relates q_n to the chemical potential at the saturation point and to the surface energy of an n -cluster. At $T < T_c$ the right-hand side of the pressure equation becomes a power series in y

$$\frac{p}{k_{\text{B}}T} = \sum_{n=1}^{\infty} a_n y^n$$

with coefficients

$$a_n = q_0 x^{n^\sigma} n^{-\tau}, \quad x \equiv \exp(-a_0 \beta \gamma_{\text{micro}}) \quad (10.37)$$

Its radius of convergence according to (3.29) is

$$y_0 = \lim_{n \rightarrow \infty} |a_n|^{-1/n} = \lim_{n \rightarrow \infty} x^{-n^\sigma/n} = 1$$

Hence, y_{sat} coincides with the radius of convergence, and since all terms of the series are positive, y_{sat} is a singular point of the function $p(z)/k_B T$.

Thus, the gaseous isotherm exhibits a mathematical singularity at y_{sat} . As we know, the behavior of various thermodynamic properties at the saturation point is determined by the functions $\Pi_{\text{sat}}^{(k)} \equiv \Pi_{y=1}^{(k)}$:

$$\Pi_{\text{sat}}^{(k)} = q_0 \sum_{n=1}^{\infty} x^{n^\sigma} n^{k-\tau} \quad (10.38)$$

For $x < 1$ (i.e. for $T < T_c$) the series on the right-hand side converges for all k , which means that properties remain finite and therefore $y = y_{\text{sat}}$ is an *essential* singularity.¹ Evidently it can hardly be detected by thermodynamic measurements. At $x > 1$ the series diverges. Thus, in the Fisher theory the isothermal compressibility remains finite for all $T < T_c$ and at the critical point diverges.

10.1.1 Fisher parameters and critical exponents

To complete the description of the model it is necessary to present a recipe for calculating the Fisher parameters q_0 and τ and the microscopic surface tension γ_{micro} . Following Fisher, we pursue the consequences of the model in the vicinity of the critical point (although at high temperatures one can be less confident of the correctness of the assumptions). At $T = T_c$ (i.e. for $x = 1$) the exponential convergence of $\Pi_{\text{sat}}^{(k)}$ goes at a slower algebraic rate:

$$\Pi_c^{(k)} = q_0 \sum_{n=1}^{\infty} n^{k-\tau} = q_0 \zeta(\tau - k) \quad (10.39)$$

where

$$\zeta(u) = \sum_{n=1}^{\infty} n^{-u}$$

is the Riemann zeta function, which converges for $u > 1$ and diverges for $u \leq 1$. Setting $k = 1$ and $k = 2$ in (10.39) leads to ρ_c and $\chi_T(T_c)$, respectively. The former quantity is finite whereas the latter diverges, so τ must satisfy

$$2 < \tau < 3$$

In the vicinity of T_c the main contribution to $\Pi_{\text{sat}}^{(k)}$ comes from the terms with large n , and therefore we can replace summation by integration:

$$\Pi_{\text{sat}}^{(k)} = q_0 \int_0^{\infty} n^{k-\tau} e^{-\theta n^\sigma} dn \quad (10.40)$$

¹ An example of such a singularity is the function $f(t) = \exp(-1/t^2)$, for which all derivatives at $t = 0$ remain finite.

where

$$\theta = \frac{a_0 w}{k_B T} \left(\frac{T_c - T}{T_c} \right) \quad (10.41)$$

Introducing the new variable

$$t = \theta n^\sigma$$

we rewrite (10.40) as

$$\Pi_{\text{sat}}^{(k)} = \frac{q_0}{\sigma \theta^{\frac{k-\tau+1}{\sigma}}} \int_0^\infty t^{\left(\frac{k-\tau+1}{\sigma}-1\right)} e^{-t} dt$$

The integral on the right-hand side is the gamma function

$$\Gamma(u) \equiv \int_0^\infty t^{u-1} e^{-t} dt$$

Its argument must be positive implying, that $k > \tau - 1$. Hence,

$$\Pi_{\text{sat}}^{(k)} = \frac{q_0}{\sigma \theta^{\frac{k-\tau+1}{\sigma}}} \Gamma\left(\frac{k-\tau+1}{\sigma}\right), \quad k > \tau - 1 \quad (10.42)$$

Since $\tau > 2$, this representation is valid for $k \geq 2$. For the compressibility ($k = 2$) we obtain:

$$\chi_T \sim (T_c - T)^{-\frac{3-\tau}{\sigma}}$$

Comparing this with the scaling law $\chi_T \sim (T_c - T)^{-\gamma}$ from Chap. 6, we find the scaling relationship

$$\gamma = \frac{3-\tau}{\sigma} \quad (10.43)$$

The gaseous side of the coexistence curve is described by

$$\rho_c - \rho_{\text{sat}}^v = q_0 \sum_{n=0}^{\infty} n^{1-\tau} \left(1 - e^{-\theta n^\sigma} \right) \quad (10.44)$$

Note that we cannot apply (10.42) to this case since $k = 1$. No matter how small (but finite) θ can be, there always exists an n_* such that for $n > n_*$, the exponential term becomes vanishingly small; the smaller θ is (i.e. the closer to T_c), the larger n_* . We can estimate n_* by the requirement

$$\theta n_*^\sigma \approx 1$$

which implies that

$$n_* \approx \theta^{-1/\sigma} \quad (10.45)$$

Then (10.44) can be approximated as

$$\rho_c - \rho_{\text{sat}}^v \approx q_0 \theta \sum_{n=0}^{n_*} n^{1-\tau+\sigma} + q_0 \sum_{n=n_*}^{\infty} n^{1-\tau}$$

Replacing summation by integration in both series and taking into account (10.45), we obtain:

$$\rho_c - \rho_{\text{sat}}^v = \theta^{\frac{\tau-2}{\sigma}} \left[q_0 \left(\frac{1}{2-\tau+\sigma} + \frac{1}{\tau-2} \right) \right]$$

Thus,

$$\rho_c - \rho_{\text{sat}}^v \sim (T_c - T)^{\frac{\tau-2}{\sigma}}$$

This yields a relationship involving the critical exponent β :

$$\beta = \frac{\tau-2}{\sigma} \quad (10.46)$$

Eliminating σ from (10.43)–(10.46) we obtain

$$\tau = 2 + \frac{\beta}{\gamma + \beta} \quad (10.47)$$

Using the universal values for the critical exponents $\beta \approx 0.32$, $\gamma \approx 1.24$ [125] we find

$$\tau \approx 2.2$$

Thus, τ is a universal exponent. Kiang [71] proposed an alternative, substance-dependent model for the Fisher parameters. According to (10.39), at the critical point

$$\frac{p_c}{k_B T_c} = q_0 \zeta(\tau), \quad \rho_c = q_0 \zeta(\tau-1) \quad (10.48)$$

and therefore τ is a solution of the equation:

$$Z_c \equiv \frac{p_c}{\rho_c k_B T_c} = \zeta(\tau)/\zeta(\tau-1) \quad (10.49)$$

where Z_c is the critical compressibility factor. For the vast majority of substances Z_c is between 0.2 and 0.3 [119], which implies that τ lies in the narrow range (see Fig. 10.2)

$$2.1 \leq \tau \leq 2.2 \quad (10.50)$$

confirming the universal nature of this quantity, which was predicted by Fisher. Once τ is found, q_0 can be obtained from (10.48)

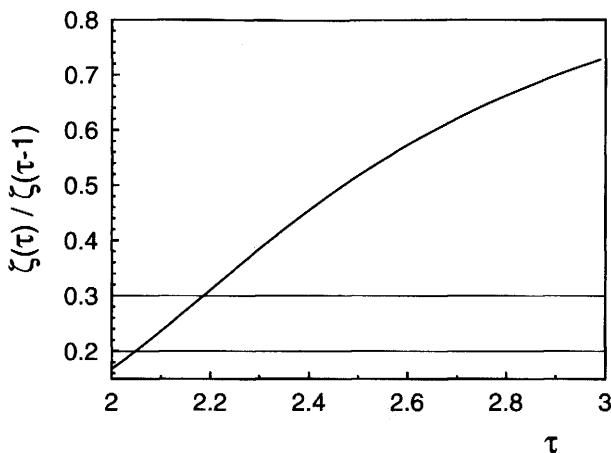


Fig. 10.2. Calculation of the Fisher parameter τ : graphical representation of (10.49). Horizontal lines correspond to $Z_c = 0.2$ and $Z_c = 0.3$

$$q_0 = \frac{\rho_c}{\zeta(\tau - 1)} \quad \left(\simeq \frac{\rho_c}{5} \right) \quad (10.51)$$

We have shown that the Fisher parameters can be related to the critical state parameters. Note that this is not the only possible way to determine them. Various other choices are discussed in the literature (see e.g. [30], [78]); however, controversies between them are not yet fully resolved [70].

As for the microscopic surface tension γ_{micro} postulated in the theory, we only know that it does not coincide with its macroscopic counterpart, but its exact value remains undetermined. We note, that the Fisher model, combined with an appropriate choice of γ_{micro} , is a basic ingredient of the semi-phenomenological theories of homogeneous nucleation [33], [30], [64].

11. Surface tension of a curved interface

11.1 Thermodynamics of a spherical interface

An arbitrary curved surface is characterized by two radii of curvature. For simplicity we shall focus on a spherical interface for which these two are equal. As discussed in Chap. 4, Gibbs' notion of a dividing surface is a useful concept for thermodynamic description of an interface. However, the planar surface tension is not effected by a particular location of a dividing surface since the surface area remains constant at any position of the latter. Hence, this concept is not necessary for calculation of the planar surface tension.

The situation drastically changes when we discuss a spherical interface. Here the position of the dividing surface determines not only the volumes of the two bulk phases (as in the planar case) but also the interfacial area. Let us consider a spherical liquid droplet inside a fixed volume V containing in total N molecules at temperature T . The "radius" of the droplet is smeared out on the microscopic level since it can be defined to within the width of the interfacial zone, which is of the order of the correlation length. Let us choose a spherical dividing surface with radius R . This choice determines the bulk liquid and vapor volumes V^l and V^v :

$$V^l = \frac{4\pi}{3}R^3, \quad V^v = V - \frac{4\pi}{3}R^3$$

The Helmholtz free energy of this two-phase system is

$$\mathcal{F} = -p^l V^l - p^v V^v + \mu N + 4\pi R^2 \gamma \quad (11.1)$$

where p^l and p^v are pressures in the two bulk phases, and μ is the chemical potential (the same for both phases in equilibrium). The last term is the surface energy for a given dividing surface.

It is clear that $\mathcal{F}$, p^l , p^v , μ and N are independent of R . This implies that the surface tension must depend on the choice of dividing surface. We denote by a differential in square brackets a virtual change of a thermodynamic parameter, corresponding to a change in R . This notation is meant to stress that a change in position of a (mathematical) dividing surface does not affect the physical parameters of the system, since it does not correspond to a change in the actual size of a drop. From (11.1) we have

$$[d\mathcal{F}] = -\Delta p 4\pi R^2 [dR] + 8\pi R \gamma [dR] + 4\pi R^2 [d\gamma], \quad \Delta p \equiv p^l - p^v$$

At the same time $[d\mathcal{F}]$ must be equal to zero, since no change in the actual physical state takes place when the location of the dividing surface is changed. This leads to the generalized Laplace equation:

$$\Delta p = \frac{2\gamma}{R} + \left[\frac{d\gamma}{dR} \right] \quad (11.2)$$

A particular choice $R = R_s$, such that

$$\left[\frac{d\gamma}{dR} \right]_{R=R_s} = 0, \quad (11.3)$$

corresponding to the so-called surface of tension, converts (11.2) into the standard Laplace equation

$$\Delta p = \frac{2\gamma_s}{R_s} \quad (11.4)$$

where $\gamma_s = \gamma[R_s]$.

In view of (11.4) one says that the surface tension acts on the surface of tension (see Fig. 11.1). An important alternative choice is the equimolar surface of radius R_e at which adsorption is equal to zero ($N^s = 0$), resulting in

$$N = \rho^l \frac{4\pi}{3} R_e^3 + \rho^v \left(V - \frac{4\pi}{3} R_e^3 \right) \quad (11.5)$$

Thus, R_e is fixed by fixing N , V , and T , since in equilibrium $\rho^l = \rho^l(T)$, $\rho^v = \rho^v(T)$. For $R = R_e$ the generalized Laplace equation becomes

$$\Delta p = \frac{2\gamma_e}{R_e} + \left[\frac{d\gamma}{dR} \right]_{R=R_e} \quad (11.6)$$

The equimolar surface possesses the property

$$\left[\frac{d\gamma}{dR} \right]_{R=R_e} = \left(\frac{\partial \gamma_e}{\partial R_e} \right)_{T,V} \quad (11.7)$$

To prove this, one has to bear in mind that a change in R_e on the right-hand side does correspond to a real (not virtual) change in the free energy since $R_e = R_e(N, V, T)$. At $R = R_e$, in view of (11.1) and (11.5)

$$\mathcal{F} = -\Delta p \frac{4\pi}{3} R_e^3 - p^v V + \mu \left(\Delta \rho \frac{4\pi}{3} R_e^3 + \rho^v V \right) + 4\pi R_e^2 \gamma_e$$

where $\Delta \rho = \rho^l - \rho^v$. The change in free energy at fixed T and V is then

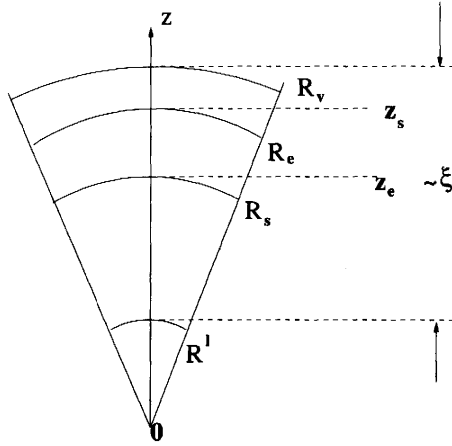


Fig. 11.1. Sketch of a spherical interface. The z axis is perpendicular to the interface pointing away from the center of curvature. R_e and R_s denote the location of the equimolar surface and surface of tension, respectively. The width of the transition zone between bulk vapor and bulk liquid is of the order of the correlation length ξ

$$(d\mathcal{F})_{T,V} = 4\pi R_e^2 dR_e \left\{ -\Delta p + \frac{2\gamma_e}{R_e} + \left(\frac{\partial \gamma_e}{\partial R_e} \right)_{T,V} + \mu \Delta \rho \right\}, \quad \Delta \rho \equiv \rho^l - \rho^v$$

Using (11.6) we have

$$\left(\frac{\partial \mathcal{F}}{\partial R_e} \right)_{T,V} = 4\pi R_e^2 \left\{ - \left[\frac{d\gamma}{dR} \right]_{R=R_e} + \left(\frac{\partial \gamma_e}{\partial R_e} \right)_{T,V} + \mu \Delta \rho \right\} \quad (11.8)$$

On the other hand $\mathcal{F} = \mathcal{F}(N, V, T)$, and thus

$$\left(\frac{\partial \mathcal{F}}{\partial R_e} \right)_{T,V} = \left(\frac{\partial \mathcal{F}}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial R_e} \right)_{T,V} = \mu \Delta \rho \quad (11.9)$$

Comparison of (11.8) and (11.9) completes the proof of (11.7).

Let us characterize the droplet radius by its value at the surface of tension $R = R_s$; then $\gamma = \gamma_s$ and for Δp the standard Laplace equation (11.4) holds. Bulk equilibrium implies the equality of the chemical potentials: $\mu_{\text{bulk}}^v = \mu_{\text{bulk}}^l$. The coexistence of a liquid droplet with the ambient vapor is characterized by $\mu_R^v = \mu_R^l$, where μ_R^l and μ_R^v are the chemical potentials of a molecule inside and outside a droplet of radius R . Thus,

$$\mu_R^v - \mu_{\text{bulk}}^v = \mu_R^l - \mu_{\text{bulk}}^l$$

which can be rewritten as

$$\int_{p_{\text{sat}}}^{p^v} v^v dp = \int_{p_{\text{sat}}}^{p^l} v^l dp$$

where p_{sat} is the saturation pressure (bulk equilibrium property). Assuming that the liquid is incompressible ($v^l = \text{const}$) and the vapor is ideal ($p v^v = k_B T$) we find after integration

$$k_B T \ln \left(\frac{p^v}{p_{\text{sat}}} \right) = v^l (p^l - p_{\text{sat}})$$

Combining this with (11.4) we obtain

$$k_B T \ln \left(\frac{p^v}{p_{\text{sat}}} \right) = v^l \left(p^v - p_{\text{sat}} + \frac{2\gamma}{R} \right) \quad (11.10)$$

This is Kelvin's equation for the vapor pressure over a spherical liquid drop. If

$$k_B T \ln \left(\frac{p^v}{p_{\text{sat}}} \right) \gg v^l p_{\text{sat}} \left(\frac{p^v}{p_{\text{sat}}} - 1 \right)$$

then (11.10) can be written in the approximate form:

$$k_B T \ln \left(\frac{p^v}{p_{\text{sat}}} \right) = \frac{2\gamma v^l}{R} \quad (11.11)$$

Kelvin's equation has been confirmed experimentally [43] for R ranging from 19 nm down to 4 nm.

11.2 Tolman length

It is plausible to expand the surface tension in powers of the curvature:

$$\gamma(R) = \gamma_0 \left(1 - \frac{2\delta_T}{R} \right) + \text{h.o.t.} \quad (11.12)$$

where the leading term, γ_0 , refers to zero curvature (planar interface) and h.o.t. denotes higher order terms in $1/R$. The parameter δ_T introduced by Tolman [140] is called the *Tolman length*.

Let us write the generalized Laplace equation (11.2) in the form

$$\Delta p R^2 = \left[\frac{d}{dR} \right] R^2 \gamma$$

and integrate it from R_s to an arbitrary R :

$$\gamma(R) = \left(\frac{R_s}{R} \right)^2 \gamma_s + \frac{1}{3} \Delta p \left(\frac{R^3}{R_s^2} - R_s \right)$$

Substituting Δp from (11.4) we have

$$\gamma(R) = \gamma_s f\left(\frac{R}{R_s}\right)$$

where

$$f(x) = \frac{1}{x^2} + \frac{2}{3}(x^3 - 1)$$

Elementary analysis shows that $f(x)$ has a minimum at $x = 1$ corresponding to $R = R_s$. Thus, γ_s is the minimum surface tension among all possible choices of the Gibbs dividing surface:

$$\gamma(R) = \gamma_s \left[1 + O\left(\frac{R - R_s}{R_s}\right)^2 \right] \quad (11.13)$$

When R differs from R_s by a small value, $\gamma(R)$ remains constant to within terms of order $1/R_s^2$. This implies that the Tolman length is independent of the choice of dividing surface. The term of order $\gamma_0(\delta_T/R)^2$ in (11.12) is of no physical significance; being multiplied by the surface area, it results in a constant term in the thermodynamic potential. This means that it cannot contribute to the restoring force that opposes distortions of the surface (see also the discussion in [55]). That is why we restrict ourselves to the first-order term, i.e. to the Tolman correction.

Let us discuss the relationship between the Tolman length and other microscopic quantities. From (11.4), (11.6) and (11.7) we have

$$\left(\frac{\partial \gamma_e}{\partial R_e}\right)_{T,V} = 2 \left(\frac{\gamma_s}{R_s} - \frac{\gamma_e}{R_e}\right)$$

Applying the Tolman formula to both sides of this equation we obtain

$$2\gamma_0 \frac{\delta_T}{R_e^2} = 2\gamma_0 \left[\frac{1 - \frac{2\delta_T}{R_s}}{R_s} - \frac{1 - \frac{2\delta_T}{R_e}}{R_e} \right]$$

In the planar limit $R_e, R_s \rightarrow \infty$ this yields

$$\delta_T = (R_e - R_s)_\infty \equiv z_e - z_s \quad (11.14)$$

where the z axis is taken perpendicular to the interface, pointing away from the center of curvature. This result means that the Tolman length is a well-defined microscopic length. From (11.14) it follows that δ_T is of the order of the correlation length, since both dividing surfaces are situated in the interface zone. However, (11.14) does not prescribe the sign of δ_T and its temperature dependence. Although there are no reliable experimental data on δ_T , one can estimate it using several analytical and simulation results.

A general statement is that when the two coexisting phases are symmetric, δ_T vanishes exactly at all temperatures. This statement was first formulated and proved by Fisher and Wortis [46]. Following their arguments, let us imagine a planar interface between two fluid phases α and β (e.g. liquid and vapor) (Fig. 11.2). According to its definition (11.14), δ_T is equal to the difference between the positions of the equimolar surface and the surface of tension, which are well defined in the planar limit. Additionally we assume that z_s and z_e vary continuously as the system moves from configuration A to C , passing through planar configuration B . Configurations A and C differ from each other only in the sign of the curvature. Due to the assumed symmetry of the coexisting phases we can write

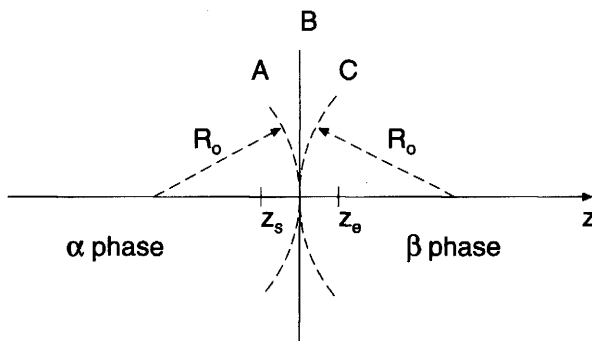


Fig. 11.2. Diagram for Fisher-Wortis theorem (see text)

$$(z_e - z_s)_A = -(z_e - z_s)_C \quad (11.15)$$

where the subscripts denote corresponding configurations. When $R_0 \rightarrow \infty$ both configurations tend to the planar limit, i.e. to the configuration B .¹ Thus, (11.15) becomes

$$\delta_T = -\delta_T$$

implying that

$$\delta_T = 0 \quad \text{for all } T \quad (11.16)$$

Equation (11.16) can be obtained on the basis of the Irving-Kirkwood expression for the microscopic pressure tensor in an inhomogeneous fluid [16]. This approach, however, cannot be considered quite satisfactory, since the result varies with the choice of pressure tensor, all choices being equally valid [55], [129].

¹ This argument fails if the limit (11.14) does not exist or z_e and z_s change discontinuously when passing through configuration B .

It is important to realize that in the presence of asymmetry (which is always the case in real fluids) the general conclusion (11.16) does not hold.

Nijmeijer et al. [103] performed molecular dynamics simulations of liquid droplets with molecules interacting via the Lennard-Jones potential. Simulations at one particular temperature $T/T_c \approx 0.83$ gave the estimate

$$|\delta_T| < 0.7\sigma,$$

where σ is the hard-core molecular diameter. Haye and Bruin [52] evaluated the temperature dependence of δ_T for a Lennard-Jones fluid from simulations of a planar interface using the relation proposed by Blokhuis and Bedeaux [16]:

$$\delta_T = -\frac{1}{8\gamma_0} \int dz_1 \int d\mathbf{r}_{12} r u'(r_{12}) (1 - 3s^2)(z_1 + z_2 - 2z_e) \rho^{(2)}(z_1, z_2, r_{12}) \quad (11.17)$$

where $s = z_{12}/r_{12}$ and $\rho^{(2)}(z_1, z_2, r_{12})$ is the pair distribution function of a planar interface – the function entering the Kirkwood-Buff formula. Simulation results of [52] are characterized by much higher accuracy than the estimate of [103] (though not in conflict with the latter). They show that within the range $0.69 \leq T/T_c \leq 0.92$, δ_T is positive and small. However, at high temperatures, $T/T_c \geq 0.87$, simulation results exhibit large fluctuations due to proximity of the critical point.

Critical behavior of the Tolman length was studied by Fisher and Wortis [46] on the basis of density functional considerations. They found that in the Landau theory when $T \rightarrow T_c^-$ the Tolman length approaches a constant value of the order of the molecular size; its sign is determined solely by the coefficient of the fifth-order term in the free energy expansion. Furthermore, within the framework of the van der Waals theory this limiting value turns out to be negative. Near the critical point fluctuations, become extremely important and one has to go beyond the mean-field Landau theory. A scaling hypothesis and renormalization group analysis [46] predict the divergence of δ_T at T_c (for asymmetric phase transitions).

Recent interest in this problem has been stimulated by the development of semiphenomenological theories of homogeneous vapor-liquid nucleation [33], [30], [64], [65], [96] where the concept of curvature-dependent surface tension of nuclei (droplets) plays an important role. The nucleation rate J , the number of critical nuclei formed per unit time per unit volume, is an extremely strong function of the surface tension γ : $J \sim e^{\gamma^3}$. Critical nuclei are usually quite small, being of the order of several nanometers. Therefore, even a small correction to γ can have a dramatic effect (orders of magnitude) on the nucleation rate. Thus, the Tolman length, originally a purely academic problem, turns out to be a matter of practical importance.

11.3 Semiphenomenological theory of the Tolman length

As already mentioned, explicit microscopic determination of the Tolman length as a function of temperature meets with serious difficulties. In this section we formulate a semiphenomenological approach that combines the statistical mechanics of clusters in terms of the Fisher droplet model of Chap. 10 with macroscopic (phenomenological) data on the bulk coexistence properties of a substance [66]. Consider a real gas, and following the lines of Chap. 10, assume that it can be regarded as a collection of noninteracting spherical clusters. The virial equation (10.11), which we apply at the coexistence line, i.e. at the saturation point for a given temperature T , reads

$$\frac{p_{\text{sat}}}{k_B T} = \sum_{n=1}^{\infty} \rho_{\text{sat}}(n) \quad (11.18)$$

where the number density of n -clusters is given by

$$\rho_{\text{sat}}(n) = \frac{1}{V} q_n \frac{e^{\beta n \mu_{\text{sat}}}}{\Lambda^{3n}} \quad (11.19)$$

and $\mu_{\text{sat}}(T)$ is the chemical potential at coexistence. The configuration integral of an n -cluster has the form (10.36)

$$q_n = q_0 V \Lambda^{3n} \exp \left[-n\beta\mu_{\text{sat}} - \beta\gamma_{\text{micro}} s_1 n^{2/3} - \tau \ln n \right] \quad (11.20)$$

The terms in the argument of the exponential refer to the bulk energy, surface energy, and entropic contributions, respectively. We have used the fact that the radius of the n -cluster scales as $r_n = r_1 n^{1/3}$, where

$$r_1 = \left(\frac{3}{4\pi\rho^l} \right)^{1/3} \quad (11.21)$$

is the mean intermolecular distance in the liquid phase, and

$$s_1 = 4\pi r_1^2 = (36\pi)^{1/3} 3^{2/3} (\rho^l)^{-2/3} \quad (11.22)$$

The Fisher parameters q_0 and τ are related to the critical state parameters via (10.48)–(10.49). From (11.19)–(11.20) we find:

$$\rho_{\text{sat}}(n) = q_0 \exp \left[-\beta\gamma_{\text{micro}} s_1 n^{2/3} - \tau \ln n \right] \quad (11.23)$$

The surface energy contains the “microscopic surface tension” γ_{micro} which, as pointed out in Sect. 10.1, is not identical to its macroscopic counterpart (plane interface value) γ_0 . In Fisher’s model γ_{micro} remains undetermined.

One can view an n -cluster as a microscopic liquid droplet containing n molecules in the surrounding vapor. Then it is reasonable to associate γ_{micro} with the surface tension of a spherical surface with radius $r_n = r_1 n^{1/3}$, and write it in the Tolman form

$$\gamma_{\text{micro}}(n) = \gamma_0 \left(1 - \frac{2\delta_T}{r_n} \right) \quad (11.24)$$

Combining this ansatz with (11.18) and (11.23), we obtain

$$\frac{p_{\text{sat}}}{q_0 k_B T} = \sum_{n=1}^{\infty} n^{-\tau} \exp \left[-\theta_0 \left(1 + \alpha_\gamma n^{-1/3} \right) n^{2/3} \right] , \quad (11.25)$$

where

$$\theta_0 \equiv \frac{\gamma_0 s_1}{k_B T} \quad (11.26)$$

and for convenience we introduce a new unknown variable α_γ :

$$\alpha_\gamma \equiv -\frac{2\delta_T}{r_1} \quad (11.27)$$

Equation (11.25) relates the Tolman length to the macroscopic equilibrium properties $p_{\text{sat}}(T)$, $\gamma_0(T)$, $\rho^l(T)$. The saturation pressure and liquid density are empirically well-defined and tabulated for various substances for a wide temperature range up to T_c [119]. There are also several empirical correlations for $\gamma_0(T)$ based on the law of corresponding states (see Appendix A). The right-hand side of (11.25)

$$f = \sum_{n=1}^{\infty} n^{-\tau} \exp \left[-\theta_0 \left(1 + \alpha_\gamma n^{-1/3} \right) n^{2/3} \right] \quad (11.28)$$

is a positive-term series containing the unknown α_γ in the argument of the exponential function. For each T we search for the root in the interval

$$-1 \leq \alpha_\gamma < \infty$$

The condition $\alpha_\gamma \geq -1$ requires that the microscopic surface tension for all clusters be positive. The derivative

$$\left(\frac{\partial f}{\partial \alpha_\gamma} \right)_T < 0$$

for all T , implying that $f(\alpha_\gamma)$ is a monotonically decreasing function, yielding the uniqueness of the solution of Eq. (11.25). At low temperatures the planar surface tension is large ($\theta_0 > 1$) and the Tolman length is expected to be small ($|\alpha_\gamma| \ll 1$). To high accuracy we can then truncate the series at $n = 1$ which results in the analytic solution

$$\alpha_\gamma = -\frac{1}{\theta_0} \ln \left[\frac{p_{\text{sat}}}{q_0 k_B T} \right] - 1 , \quad |\alpha_\gamma| \ll 1 \quad (11.29)$$

At high temperatures θ_0 is small, and truncation of the series at the first term is impossible. In the general case (11.25) must be solved iteratively. The fast (exponential) convergence of (11.28) at each iteration step k is provided by the terms with large absolute values of the argument of the exponential. We can truncate the series at $n = N^{(k)}$ satisfying

$$\theta_0 \left(N^{(k)} \right)^{2/3} + \theta_0 \alpha_\gamma^{(k)} \left(N^{(k)} \right)^{1/3} = G_0, \quad (11.30)$$

where $\alpha_\gamma^{(k)}$ is the value of α_γ at the k -th step, and $G_0 \gg 1$ is an arbitrary large number; for calculations displayed in Fig. 11.3 we choose $G_0 = 100$. For each iteration step the truncation limit is given by

$$N^{(k)} \left(\theta_0; \alpha_\gamma^{(k)} \right) = \frac{1}{8} \left[-\alpha_\gamma^{(k)} + \sqrt{\left(\alpha_\gamma^{(k)} \right)^2 + \frac{4G_0}{\theta_0}} \right]^3 \quad (11.31)$$

Figure 11.3 shows the reduced Tolman length

$$\delta_T^* \equiv \frac{\delta_T}{\sigma} = -\frac{\alpha_\gamma}{2} \frac{r_1}{\sigma}$$

for 3 nonpolar substances – argon, benzene and n -nonane (the empirical correlations for their macroscopic properties are given in Appendix A)– as a function of the reduced temperature

$$t = \frac{T - T_c}{T_c} \quad (11.32)$$

Comparison of the theoretical predictions with the simulations of [103] and [52] shows good agreement over the temperature range in which reliable simulations were performed: except for one point, all theoretical curves lie within the error bars of MD simulations. Not too close to T_c the Tolman length for all substances is positive and is about 0.2σ .

For small $|t|$ ($|t| < 2 \times 10^{-2}$) it changes sign at a certain temperature T_δ and becomes negative.² At T_δ the surface tension of a droplet is equal to that of the planar interface. Finally, there is an indication that δ_T diverges when the critical point is approached as predicted by the density-functional analysis of [46]. For this reason the numerical procedure fails near T_c . According to (11.14), a negative Tolman length means that the surface of tension is located on the gas side of the equimolar surface. These results suggest that at $T > T_\delta$ the microscopic surface tension increases with increasing curvature, the effect being greater the higher the temperature. This trend is opposite to the one usually discussed far from T_c . Note that the possibility of negative δ_T for the model system of penetrable spheres is pointed out by Hemingway et al. [54].

² The analytic low-temperature result (11.29) appears to be a good approximation to the “exact” numerical solution for $|t| > 0.3$, but closer to the critical region it is in error.

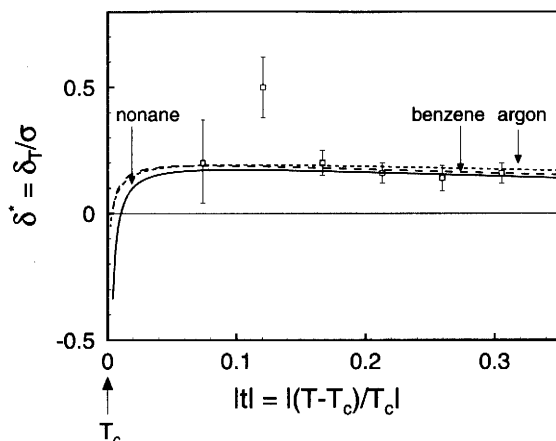


Fig. 11.3. Temperature dependence of the Tolman length; $\delta_T^* = \delta_T/\sigma$, σ is a hard-core molecular diameter. Lines: theoretical predictions (solution of equation (11.25)) for argon, benzene and *n*-nonane. Squares: MD results of Haye et al. [52]; the MD estimate of Nijmeijer et al. [103] is $|\delta_T^*(|t| = 0.17)| < 0.7$

It would be desirable to derive a critical exponent for δ_T on the basis of the proposed semiphenomenological theory. However, given the present state of the theory, this does not seem possible. The reason is that Fisher's model neglects cluster-cluster interactions (excluded volume effects), which become important in the critical region. Therefore, in this region the theory is suggestive, but cannot be taken literally for calculating a critical exponent.

12. Polar fluids

12.1 Algebraic perturbation theory of a polar fluid

Throughout the previous chapters we were mainly concerned with systems in which the interparticle interaction is spherically symmetric. In a number of fluids the presence of a dipole moment, permanent and/or induced, can play an important role in their thermodynamic behavior. A vivid example from everyday life is water, in which the strength of dipole–dipole interactions is comparable to the van der Waals attraction. The dipole–dipole interactions are long-range – the interaction energy decreases with the distance as $1/r^3$ – and anisotropic, i.e. it depends on the orientations of dipoles. An adequate description of long-range and anisotropic interactions comprises the main source of difficulties that arise in theoretical models and simulation studies. A full microscopic theory of a polar fluid is an immensely difficult problem also due to the fact that:

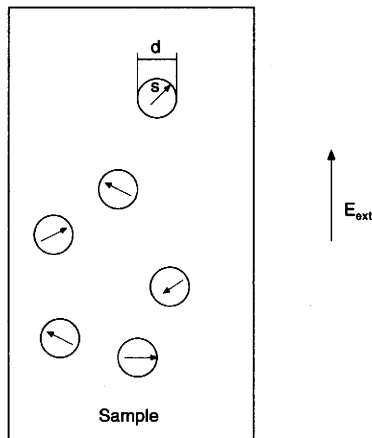


Fig. 12.1. A model of a polar nonpolarizable fluid

- besides dipoles one must also take into account multipole terms (quadrupole, octupole, etc.)

- polarizability effects related to induced moments can be as important as the effects due to permanent moments.

In this chapter we consider a simplified model of a polar fluid, in which polarizability effects and effects due to multipole interactions are neglected. We describe a polar fluid as a system of N hard spheres with point dipoles at their centers contained in a volume V at temperature T and located in a weak external homogeneous electric field $\mathbf{E}_{\text{ext}}$; this is the field that would exist in the absence of the fluid. We also assume that the container is an (infinitely) long cylinder with its axis parallel to $\mathbf{E}_{\text{ext}}$ (Fig. 12.1). This ensures the absence of a depolarization field inside the sample (the depolarization factor of a long cylinder is zero [81]) and therefore the macroscopic electric field in it is

$$\mathbf{E} = \mathbf{E}_{\text{ext}} \quad (12.1)$$

Each particle is characterized by a 5-dimensional vector $\tilde{\mathbf{r}}_i = (\mathbf{r}_i, \omega_i)$, where $\mathbf{r}_i$ is the radius vector of its center of mass and $\omega_i = (\theta_i, \varphi_i)$ denotes the orientation of the dipole moment $\mathbf{s}_i$. We assume that the particles are identical with the hard-sphere diameter d and $|\mathbf{s}_i| = s$. The potential energy for an arbitrary configuration consists of the interparticle interaction energy and the external field contribution:

$$U(\tilde{\mathbf{r}}^N) = U_0(\tilde{\mathbf{r}}^N) + U_1(\omega^N),$$

$$U_0 = \sum_{i < j} \left[u_{d,ij} + u_{ij}^{(\text{dd})} \right] \quad (12.2)$$

$$U_1 = -sE_{\text{ext}} \sum_i \cos \theta_i \quad (12.3)$$

Here $u_{d,ij} = u_d(r_{ij})$ is the hard-sphere interaction, θ_i the angle between $\mathbf{s}_i$ and $\mathbf{E}_{\text{ext}}$,

$$u_{ij}^{(\text{dd})} = \frac{s^2}{r_{ij}^3} D(i, j)$$

is the dipole-dipole potential with the angular part $D(i, j)$ given by

$$D(i, j) = \hat{\mathbf{s}}_i \hat{\mathbf{s}}_j - 3(\hat{\mathbf{s}}_i \hat{\mathbf{r}}_{ij})(\hat{\mathbf{s}}_j \hat{\mathbf{r}}_{ij}) \quad (12.4)$$

where $\hat{\mathbf{x}}$ denotes the unit vector corresponding to $\mathbf{x}$.

We now apply the ideas of a perturbation approach discussed in Chap. 5. The formulation of any perturbation theory starts from decomposing the system into a reference and perturbative parts. Since we are aiming at a detailed description of the interparticle interactions, it is reasonable to include them in the reference model. The latter is characterized by the energy U_0 and represents the system of dipolar hard spheres in zero field. Interaction with

an external field is treated as a perturbation. Introducing the perturbation Mayer function

$$f_i = e^{\alpha \cos \theta_i} - 1$$

where

$$\alpha = \frac{sE_{\text{ext}}}{k_B T} \quad (12.5)$$

is the Langevin parameter, which characterizes the relative strength of the external field, we write the configuration integral as

$$\begin{aligned} Q &= \int d\mathbf{r}^N e^{-\beta U_0} \prod_{i=1}^N (1 + f_i) \\ &= \int d\mathbf{r}^N e^{-\beta U_0} \left[1 + \sum_{n=1}^N \left(\sum_{1 \leq i_1 < \dots < i_n \leq N} f_{i_1} \cdots f_{i_n} \right) \right] \end{aligned} \quad (12.6)$$

The same quantity for the reference model is

$$Q_0 = \int d\mathbf{r}^N e^{-\beta U_0}$$

Equation (12.6) can be written

$$\frac{Q}{Q_0} = 1 + \sum_{n=1}^N \left[\int d\mathbf{r}^N \frac{e^{-\beta U_0}}{Q_0} \left(\sum_{1 \leq i_1 < \dots < i_n \leq N} f_{i_1} \cdots f_{i_n} \right) \right]$$

Each term of the outer sum is a thermal average over the reference model of the quantity in parentheses:

$$\frac{Q}{Q_0} = 1 + \sum_{n=1}^N \langle X_n \rangle_0, \quad X_n \equiv \sum_{1 \leq i_1 < \dots < i_n \leq N} f_{i_1} \cdots f_{i_n}$$

With the help of the theorem of averaging we obtain

$$\frac{Q}{Q_0} = 1 + \sum_{n=1}^N \frac{1}{n!} \int d\mathbf{r}^n \left(\prod_{i=1}^n f_i \right) \rho_0^{(n)}(\mathbf{r}^n) \quad (12.7)$$

where

$$\rho_0^{(n)}(\mathbf{r}^n) = \frac{N!}{(N-n)!} \int d\mathbf{r}_{n+1} \dots d\mathbf{r}_N \frac{e^{-\beta U_0}}{Q_0}$$

is the n -particle distribution function of the reference model (cf. (2.2)). The n -particle correlation function g_n^0 is given by

$$\rho_0^{(n)} = \left(\frac{\rho}{4\pi}\right)^n g_n^0, \quad n = 1, 2, \dots$$

where 4π appears because of $\int d\tilde{\mathbf{r}} = 4\pi V$. Thus,

$$\frac{Q}{Q_0} = 1 + \sum_{n=1}^N \frac{1}{n!} \left(\frac{\rho}{4\pi}\right)^n \int d\tilde{\mathbf{r}}^n \left(\prod_{i=1}^n f_i\right) g_n^0(\tilde{\mathbf{r}}^n) \quad (12.8)$$

The standard scheme of the perturbation approach of Chap. 5 is based on the expansion of the configuration integral in terms of the Mayer functions. In our case, however, this is not appropriate, since f_i is purely orientational and therefore does not compensate for the long-range behavior of g_n^0 : $g_n^0 \rightarrow 1$ when separations between particles become large.

Instead of the standard route we use an approach based on the algebraic technique of Ruelle described in Sect. 5.7. Let us rewrite (12.7) as

$$a(z) = \sum_{n=0}^{\infty} \frac{z^n}{n!} a_n \quad (12.9)$$

where

$$z \equiv \frac{\rho}{4\pi}, \quad a(z) \equiv \frac{Q}{Q_0}$$

and coefficients a_n are given by

$$a_0 = 1, \quad a_n = \int d\tilde{\mathbf{r}}^n q_n^a(\tilde{\mathbf{r}}^n), \quad n \geq 1 \quad (12.10)$$

with

$$q_n^a \equiv \left(\prod_{i=1}^n f_i\right) g_n^0, \quad n = 1, 2, \dots$$

The summation is extended to infinity as we are interested in the thermodynamic limit. Equations (12.9)–(12.10) are identical to (5.64)–(5.65). Then, according to Sect. 5.7, $a(z)$ can be written as the exponential of another series:

$$\frac{Q}{Q_0} = \exp \left[\sum_{n=0}^{\infty} \frac{(\rho/4\pi)^n}{n!} b_n \right] \quad (12.11)$$

where

$$b_0 = 0, \quad b_n = \int d\tilde{\mathbf{r}}^n q_n^b(\tilde{\mathbf{r}}^n), \quad n \geq 1 \quad (12.12)$$

and functions q_n^b are algebraic combinations of functions q_n^a . The first terms of the sequence $\{q_n^b\}$ are found from (5.63):

$$q_1^b = f_1 g_1^0 = f_1 \quad (12.13)$$

$$q_2^b = \left(\prod_{i=1}^2 f_i \right) [g_2^0 - 1] = \left(\prod_{i=1}^2 f_i \right) h_2^0 \quad (12.14)$$

$$q_3^b = \left(\prod_{i=1}^3 f_i \right) [h_3^0 - \sum_{1 \leq i < j \leq 3} h_2^0(\tilde{\mathbf{r}}_i, \tilde{\mathbf{r}}_j)] \quad (12.15)$$

We stress that taking into account each term in (12.11) is equivalent to taking into account an infinite number of terms in (12.7). The free energy becomes

$$\beta \mathcal{F} = \beta \mathcal{F}_0 - \sum_{n=1}^{\infty} \frac{(\rho/4\pi)^n}{n!} b_n \quad (12.16)$$

where $\mathcal{F}_0$ is the reference contribution. Equation (12.16) is exact: no approximations have been imposed so far. Given the expression for the free energy one can calculate the thermodynamics of a polar fluid once information about the reference system (its free energy and correlation functions) is available. In the next section we will show how this algebraic perturbation theory (APT) [68] can be used to calculate the dielectric constant.

12.2 Dielectric constant

The theory of the dielectric constant, ε , pioneered in 1912 by Debye [28], still remains an actively developing area. Its fundamental and practical importance has motivated much theoretical work and computer simulation studies (for reviews see, for example, [134] and [89]). However, agreement among the various models and simulations remains rather poor, especially for condensed systems at relatively low temperatures, when interparticle interactions play an increasingly important role.

In a seminal paper [28], Debye obtained ε by studying the response of a dilute gas of particles to an applied external electrical field $\mathbf{E}_{\text{ext}}$ (in the same fashion as Langevin's work on a paramagnetic gas in an external magnetic field). Subsequent models mainly used an approach which relates ε to the properties of the system in the absence of $\mathbf{E}_{\text{ext}}$. In these theories each particle is regarded as the source of the field acting on its neighbors, and ε describes the response of the system to this field.

We will formulate a theory of the dielectric constant for a polar nonpolarizable fluid in the spirit of the original Debye–Langevin approach: by studying the response of a dielectric system to a weak external field, taking into account dipole–dipole interactions. For this purpose we use the APT approach presented in the previous section. To derive the dielectric constant we need to find the linear response of the system to a weak external field, which corresponds to keeping only the leading term in the expansion of the free energy in

powers of the external field strength, or equivalently the Langevin parameter α . Since $\mathcal{F}$ is an even function of the field, we must cut off the series (12.16), keeping the term that is $O(\alpha^2)$ and neglecting all the rest. The cutoff is only possible if the b_n contain converging integrals. This is really the case, since the g_n^0 in (12.8) are replaced by $h_n^0 = g_n^0 - 1$ in (12.14)–(12.15), that vanish at large separations, thus ensuring convergence of (12.16) for $n \geq 2$.

Substituting (12.13)–(12.14) into (12.12) and expanding the Mayer functions to second order in α

$$f_i = \alpha \cos \theta_i + \frac{1}{2} \alpha^2 \cos^2 \theta_i + o(\alpha^3)$$

we find that

$$b_1 = \int \mathbf{dr} \int d\omega \left(\alpha \cos \theta + \frac{1}{2} \alpha^2 \cos^2 \theta \right) = 4\pi V \frac{\alpha^2}{6} \quad (12.17)$$

and the free energy becomes

$$\beta \mathcal{F} = \beta \mathcal{F}_0 - N \frac{\alpha^2}{6} - \frac{1}{2} \left(\frac{\rho}{4\pi} \right)^2 b_2 + o(\alpha^4) \quad (12.18)$$

The first term is the reference free energy, the second gives the energy of independent dipoles in an external field, and the third accounts for interparticle interactions in the presence of E_{ext} . The pair correlation function of dipolar hard spheres in the absence of the field can be written as a series in powers of s^2 [10]:

$$g_2^0(r_{12}, \omega_1, \omega_2) = g_d(r_{12}) + \sum_{m=1}^{\infty} (\beta s^2)^m g_m(r_{12}, \omega_1, \omega_2) \quad (12.19)$$

The first two terms are available:

$$g_1 = -\frac{g_d(r_{12})}{r_{12}^3} D(1, 2) \quad (12.20)$$

$$g_2 = \frac{1}{2} \frac{g_d(r_{12})}{r_{12}^6} D^2(1, 2) \quad (12.21)$$

$$+ \frac{1}{6} \rho D(1, 2) \int d\mathbf{r}_3 \frac{1 + 3 \cos \alpha_1 \cos \alpha_2 \cos \alpha_3}{(r_{13} r_{23})^3} g_d(123) \quad (12.22)$$

$$+ \frac{1}{3} \rho \Delta(1, 2) \int d\mathbf{r}_3 \frac{3 \cos^2 \alpha_3 - 1}{(r_{13} r_{23})^3} g_d(123) \quad (12.23)$$

Here

$$\Delta(1, 2) = \hat{\mathbf{s}}_1 \hat{\mathbf{s}}_2$$

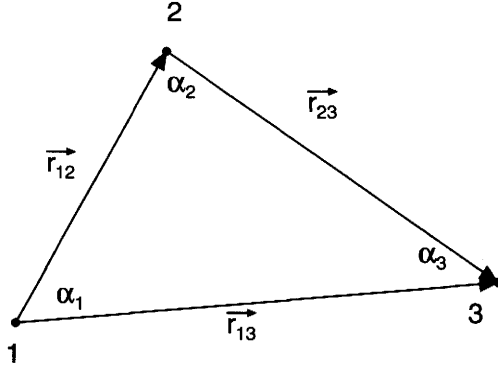


Fig. 12.2. Three-particle contribution to the pair correlation function of dipolar hard spheres (12.22)–(12.23)

$g_d(r)$ and $g_d(123)$ are the two- and three-body hard-sphere correlation functions, and α_1 , α_2 , α_3 are the angles of the triangle formed by the three particles as shown in Fig. 12.2. A cutoff of (12.19) at $m = 2$ implies

$$b_2 = \alpha^2 V \sum_{m=0}^2 b_2^{(m)} \quad (12.24)$$

where

$$\begin{aligned} b_2^{(0)} &= \int d\mathbf{r}_{12} \int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 [g_d(r_{12}) - 1] \\ b_2^{(1)} &= (\beta s^2) \int d\mathbf{r}_{12} \int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 g_1(r_{12}, \omega_1, \omega_2) \\ b_2^{(2)} &= (\beta s^2)^2 \int d\mathbf{r}_{12} \int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 g_2(r_{12}, \omega_1, \omega_2) \end{aligned} \quad (12.25)$$

First the integration over solid angles ω_1 , ω_2 is performed (Appendix B contains the table of angular dipole integrals). This implies

$$b_2^{(0)} = 0 \quad (12.26)$$

and the next term is (see (B.5))

$$b_2^{(1)} = -\beta s^2 \left(\frac{4\pi}{3} \right)^2 \int_{r_{12} > d} d\mathbf{r}_{12} \frac{1}{r_{12}^3} (1 - 3 \cos^2 \theta_{12}) \quad (12.27)$$

In the spirit of van der Waals we replace $g_d(r_{12})$ by the step function $\Theta(r_{12} > d)$:

$$\Theta(r_{12} > d) \equiv \Theta_{12} = \begin{cases} 1 & \text{for } r_{12} > d \\ 0 & \text{for } r_{12} < d \end{cases} \quad (12.28)$$

The integral in (12.27) yields (the rigorous derivation is given in Appendix C)

$$\int_{r_{12} > d}^{\text{cyl}} d\mathbf{r}_{12} \frac{1}{r_{12}^3} (1 - 3 \cos^2 \theta_{12}) = -\frac{4\pi}{3} \quad (12.29)$$

where the superscript "cyl" means integration over an (infinitely) elongated cylinder,¹ thus implying

$$b_2^{(1)} = \beta s^2 \left(\frac{4\pi}{3} \right)^3 \quad (12.30)$$

The last contribution to b_2 consists of three terms arising from (12.21)–(12.23). The first, which contains $D^2(1, 2)$, vanishes in view of (B.4). Thus, $b_2^{(2)}$ is a sum of two contributions, originating from (12.22) and (12.23):

$$b_2^{(2)} = b_D + b_\Delta \quad (12.31)$$

Here (after integration over ω_1 and ω_2)

$$b_D = \frac{1}{6} \rho (\beta s^2)^2 \left(\frac{4\pi}{3} \right)^2 \gamma_D \quad (12.32)$$

$$\gamma_D = \int d\mathbf{r}_{12} (1 - 3 \cos^2 \theta_{12}) a_D \quad (12.33)$$

$$a_D = \int d\mathbf{r}_3 \frac{1 + 3 \cos \alpha_1 \cos \alpha_2 \cos \alpha_3}{(r_{13} r_{23})^3} g_d(123) \quad (12.34)$$

and

$$b_\Delta = \frac{1}{3} \rho (\beta s^2)^2 \left(\frac{4\pi}{3} \right)^2 \gamma_\Delta \quad (12.35)$$

$$\gamma_\Delta = \int d\mathbf{r}_{12} a_\Delta \quad (12.36)$$

$$a_\Delta = \int d\mathbf{r}_3 \frac{3 \cos^2 \alpha_3 - 1}{(r_{13} r_{23})^3} g_d(123) \quad (12.37)$$

The three-particle hard-sphere correlation function can be written using Kirkwood's superposition approximation

$$g_d(123) \cong g_d(12) g_d(13) g_d(23) \cong \Theta(r_{12} > d) \Theta(r_{13} > d) \Theta(r_{23} > d) \quad (12.38)$$

¹ It is easy to see that for a spherical container this integral vanishes.

The detailed analytic calculation of dimensionless quantities γ_D and γ_Δ , presented in Appendix D, yields

$$\gamma_D = -\frac{32\pi^2}{9}, \quad \gamma_\Delta = \frac{17\pi^2}{9} \quad (12.39)$$

implying that these terms bring competing contributions to $b_2^{(2)}$:

$$b_D = \frac{1}{3} \left(\frac{4\pi}{3} \right)^2 \rho (\beta s^2)^2 \left(-\frac{16\pi^2}{9} \right), \quad b_\Delta = \frac{1}{3} \left(\frac{4\pi}{3} \right)^2 \rho (\beta s^2)^2 \left(\frac{17\pi^2}{9} \right)$$

and

$$b_2^{(2)} = \frac{1}{3} \left(\frac{4\pi}{3} \right)^2 \rho (\beta s^2)^2 \left(\frac{1}{9} \pi^2 \right) \quad (12.40)$$

Substituting (12.26), (12.30) and (12.40) into (12.24), we obtain

$$b_2 = \frac{1}{3} \alpha^2 V d^3 \left(\frac{4\pi}{3} \right)^2 \left(4\pi\lambda + \frac{1}{9} \pi^2 \rho d^3 \lambda^2 \right) \quad (12.41)$$

where

$$\lambda = \frac{s^2}{k_B T d^3} \quad (12.42)$$

is the coupling constant that characterizes the strength of the dipole-dipole interaction.

Summarizing, we can write the free energy (12.18) in closed form:

$$\beta \mathcal{F} = \beta \mathcal{F}_0 - N \frac{\alpha^2}{6} - \frac{\alpha^2}{54} \rho^2 V d^3 \left(4\pi\lambda + \frac{1}{9} \pi^2 \rho d^3 \lambda^2 \right) \quad (12.43)$$

The macroscopic polarization $\mathbf{P}$ is related to the free energy via [81]

$$\mathbf{P} = -\frac{1}{V} \left. \frac{\partial \mathcal{F}}{\partial \mathbf{E}_{\text{ext}}} \right|_{N,V,T}$$

yielding

$$P = \frac{\alpha}{3} \rho s \left[1 + \frac{4\pi}{9} \rho d^3 \lambda + \frac{1}{81} \pi^2 (\rho d^3 \lambda)^2 \right] \quad (12.44)$$

On the other hand

$$(\varepsilon - 1) \mathbf{E} = 4\pi \mathbf{P} \quad (12.45)$$

where the field $\mathbf{E}$ inside the long cylindrical container coincides with $\mathbf{E}_{\text{ext}}$. Comparing (12.44) and (12.45), we obtain for the dielectric constant

$$\varepsilon - 1 = 3y \left[1 + y + \frac{1}{16} y^2 \right] \quad (12.46)$$

where

$$y \equiv \frac{4\pi}{9}\beta\rho s^2 \quad (12.47)$$

12.2.1 Extrapolation to arbitrary densities

The results obtained thus far may be called the low-density limit of the APT since we used the low-density form of the hard-sphere pair correlation function, specifically we replaced it by the step function $\theta(r > d)$. As an implication of this the dielectric constant can be expressed as a function of only one parameter, y – the feature shared by other theoretical models (see discussion below). Physically, one can expect, however, in the general case a dependence of ε separately on two parameters, λ and the reduced density

$$\rho^* = \rho d^3$$

rather than on their product. Of course, this feature becomes appreciable at moderate and high densities, while at low densities one can apply (12.46) which is exact to order $O(\rho^3)$.

The generalization of the theory to higher densities can be constructed by taking into account the density dependence of g_d , which can be introduced as

$$g_d(r; \rho) = \theta(r > d) + \psi(r; \rho) \quad (12.48)$$

It is important that in contrast to the first term, which is long-range, the function $\psi(r; \rho)$ is short-range persisting over distances of the order of the correlation length, which under normal conditions is roughly several diameters. As a result it will not contribute to $b_2^{(1)}$, and the only contribution to $b_2^{(2)}$ affected by this correction is γ_Δ , which now becomes

$$\gamma_\Delta = \frac{17}{9}\pi^2 I(\rho^*) \quad (12.49)$$

The density correction factor $I(\rho^*)$ can be found using the method of Padé approximants [113] yielding [9], [137]

$$I(\rho^*) = \frac{1 - 0.93952\rho^* + 0.36714\rho^{*2}}{1 - 0.92398\rho^* + 0.23323\rho^{*2}} \quad (12.50)$$

Thus,

$$b_2^{(2)} = \frac{1}{3} \left(\frac{4\pi}{3} \right)^2 \rho (\beta s^2)^2 \left(\frac{1}{9} \pi^2 \right) (-16 + 17I) \quad (12.51)$$

which implies for the free energy

$$\beta\mathcal{F} = \beta\mathcal{F}_0 - N\frac{\alpha^2}{6} - \frac{\alpha^2}{54}\rho^2 V d^3 \left\{ 4\pi\lambda + \left[-\frac{16}{9} + \frac{17}{9}I(\rho^*) \right] \pi^2 \rho d^3 \lambda^2 \right\} \quad (12.52)$$

This expression can serve as the basis for a thermodynamic description of polar fluids at low electrical fields. For the dielectric constant, this yields:

$$\varepsilon - 1 = 3y \left[1 + y + \left(-1 + \frac{17}{16}I \right) y^2 \right] \quad (12.53)$$

12.2.2 Comparison of the algebraic perturbation theory with other models and computer simulations

In the earliest theory of the dielectric constant, formulated by Debye [28], the polarization has the same functional form as for a gas of noninteracting dipoles in an effective external field

$$E_{\text{eff}} = E_{\text{ext}} + \frac{4\pi}{3}P \quad (12.54)$$

where the second term takes into account in mean-field fashion the interaction of a particle with the environment. Then

$$P = \rho s L(\alpha_{\text{eff}}), \quad (12.55)$$

where

$$L(x) = \coth x - \frac{1}{x}$$

is the Langevin function,

$$\alpha_{\text{eff}} = \frac{sE_{\text{eff}}}{k_B T}$$

and ρs is the maximum polarization, which corresponds to complete alignment of dipoles along the field. The dielectric constant is found from the self-consistent equation (12.54), resulting in

$$\varepsilon - 1 = 3y \left(1 + \frac{\varepsilon - 1}{3} \right)$$

Solving this equation for ε , we obtain

$$\varepsilon - 1 = \frac{3y}{1 - y} \quad (12.56)$$

where y is given by (12.47). This expression leads to a singularity at $y = 1$, which is known to be incorrect [10].

In the Onsager theory [105] each particle is considered to be embedded in a continuum with a dielectric constant ε , the quantity to be determined. The theory results in a quadratic equation for ε :

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = y \quad (12.57)$$

from which

$$\varepsilon - 1 = \frac{3}{4} \left(3y - 1 + \sqrt{1 + 2y + 9y^2} \right) \quad (12.58)$$

The singularity is avoided but ε is underestimated [134].

Integral equation theories of ε are based on the Ornstein–Zernike equation supplemented by various closures. Among other models belonging to this class we mention the linearized hypernetted-chain (LHNC) [108] and the mean-spherical (MSA) [148] approximations.

Let us discuss the latter in somewhat more detail. The MSA is based on Wertheim's analytic solution for the total pair correlation function of dipolar hard spheres [148]:

$$h_0(1, 2) = h_d(r_{12}) - h_D(r_{12})D(1, 2) + h_\Delta(r_{12})\Delta(12) \quad (12.59)$$

Radial functions h_D and h_Δ can be expressed via the total pair correlation function of hard spheres h_d . For $r > d$

$$\begin{aligned} h_\Delta(r) &= 2a [h_d(r; 2a\rho) - h_d(r; -a\rho)] \\ h_D(r) &= \tilde{h}_D(r) - \frac{3}{r^3} \int_0^r dp p^2 \tilde{h}_D(p) \end{aligned}$$

where

$$\tilde{h}_D(r) = a [2h_d(r; 2a\rho) + h_d(r; -a\rho)]$$

For $r < d$, $h_\Delta(r) = h_D(r) = 0$. The parameter a is given by $a = \zeta/\phi$, where $\phi = (\pi/6)\rho d^3$ is the volume fraction of hard spheres, and $0 < \zeta < 1/2$ is a real root of the algebraic equation

$$q(2\zeta) - q(-\zeta) = 3y, \quad q(x) \equiv \frac{(1 + 2x)^2}{(1 - x)^4} \quad (12.60)$$

In the MSA ε is written in parametric form:

$$\varepsilon - 1 = \frac{q(2\zeta) - q(-\zeta)}{q(-\zeta)} \quad (12.61)$$

In all likelihood MSA also underestimates ε [134].² In view of the long-range nature of dipolar forces, computer simulation of ε proves to be a very

² Note that if orientational correlation is completely ignored in the APT, the reference pair correlation function will reduce to that of hard spheres, $g_2^0 = g_d$, providing that $b_2 = 0$, and the APT expression (12.53) will become $\varepsilon - 1 = 3y$. Exactly the same result follows from all the other theories in the limit of small y .

difficult problem [134], [89]. None of the simulation methods gives ϵ for truly infinite systems described by approximate theories. Nevertheless simulation results can give an idea about the accuracy of various models. Simulation of dipolar hard spheres appear to be technically more difficult than the simulation of a Stockmayer fluid [89], for which a larger amount of data is available. The latter is characterized by a potential that is a sum of the Lennard-Jones and dipole-dipole interaction:

$$u_{ST} = 4\epsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r} \right)^{12} - \left(\frac{\sigma_{LJ}}{r} \right)^6 \right] + u^{(dd)} \quad (12.62)$$

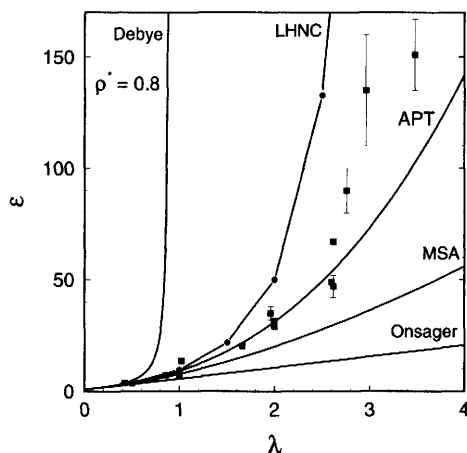


Fig. 12.3. Dielectric constant ϵ as a function of λ for $\rho^* = 0.8$. Labels correspond to various theoretical models: Debye theory, Onsager theory, mean-spherical approximation (MSA), linearized hypernetted-chain approximation (LHNC), algebraic perturbation theory (APT) Eq.(12.53). Squares are simulation results of [1], [2], [90], [76], [77], [92], [104], [109], [112]

It is found in [108] that for $\lambda < 2$, ϵ of a Stockmayer fluid is close to that of equivalent dipolar hard spheres; for larger λ the Stockmayer ϵ is considerably lower than that of the corresponding dipolar hard-sphere system. Figure 12.3 shows the dielectric constant as a function of λ for $\rho^* \equiv \rho d^3 = 0.8$ predicted by various theoretical models – Debye, Onsager, MSA, LHNC, APT (Eq.(12.53)) – and that found in simulation studies [1], [2], [90], [76], [77], [92], [104], [109], [112]; simulation data are presented for both dipolar hard spheres and Stockmayer fluids. Compared to other models mentioned, the APT provides better agreement with simulations for low and intermediate values of λ : $\lambda < 2.5$. For $\lambda > 2.5$ theoretical predictions are below simulation

data. It is clear that at low densities $I(\rho^*) \rightarrow 1$, and the low-density limit of the APT is recovered.³

In the beginning of this chapter we pointed out that real molecules can have both dipole and quadrupole moments and possess induced dipolar moments, which makes a straightforward comparison of the APT predictions with real dielectric liquids problematic. However, by changing from the electric to magnetic language, APT can be straightforwardly compared with experimental data on the initial magnetic susceptibility of a ferrofluid (see Chap. 14), where quadrupole interactions and induced dipolar moments are absent.

13. Mixtures

13.1 Generalization of basic concepts

Basic thermodynamic relationships discussed in Chap. 1 can be straightforwardly generalized for a M -component mixture:

$$dE = TdS - p dV + \sum_{I=1}^M \mu_I dN_I \quad (13.1)$$

$$d\mathcal{F} = -p dV - SdT + \sum_{I=1}^M \mu_I dN_I \quad (13.2)$$

$$dG = -SdT + Vdp + \sum_{I=1}^M \mu_I dN_I \quad (13.3)$$

$$d\Omega = -p dV - SdT - \sum_{I=1}^M \bar{N}_I d\mu_I \quad (13.4)$$

where N_I and μ_I are the number of particles and the chemical potential of component I . The canonical partition function takes the form

$$Z = \frac{1}{\prod_{I=1}^M N_I! \Lambda_I^{3N_I}} Q \quad (13.5)$$

where Λ_I is the de Broglie wave length of component I and

$$Q = \int e^{-\beta U} \prod_{I=1}^M d\mathbf{r}_I^{N_I} \quad (13.6)$$

is the configuration integral (for simplicity we assume that there is no external field). The total interaction energy U comprises interaction between the molecules of the same species as well as the unlike terms. It is due to the latter that for nonideal mixtures Q cannot be decomposed into the product of the individual configuration integrals: $Q \neq \prod_I Q_{N_I}$.

Let us first discuss the case of a binary mixture of components A and B . The results that we obtain can be easily generalized for mixtures with

an arbitrary number of components. Assuming that interactions are pairwise additive we can write

$$U \equiv U_{N_A N_B} = U^{(AA)} + U^{(BB)} + U^{(AB)} \quad (13.7)$$

where

$$\begin{aligned} U^{(AA)} &= \sum_{1 \leq i < j \leq N_A} u_{AA,ij} \\ U^{(BB)} &= \sum_{1 \leq i < j \leq N_B} u_{BB,ij} \\ U^{(AB)} &= \sum_{1 \leq i \leq N_A} \sum_{1 \leq j \leq N_B} u_{AB,ij} \end{aligned}$$

Equation(13.7) must be completed by a mixing rule describing the treatment of unlike interactions u_{AB} . For a system of Lennard-Jones fluids with parameters $\sigma_I \equiv \sigma_{II}$ and $\epsilon_I \equiv \epsilon_{II}$ ($I = A, B$) the Lorentz-Berthelot mixing rule is most widely used:

$$\sigma_{AB} = \frac{\sigma_{AA} + \sigma_{BB}}{2}, \quad \epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}} \quad (13.8)$$

A pair distribution function describes the unlabeled probability of finding a pair of particles around certain positions. In mixtures one must distinguish among the types of the particles in the pair. For a binary mixture three distribution functions are to be defined: $\rho_{AA}^{(2)}$, $\rho_{BB}^{(2)}$ and $\rho_{AB}^{(2)}$, describing correlations of particles of the same species (AA or BB) and correlations of particle belonging to different species (AB). A unified definition can be formulated with the help of two nonnegative integers s_A and s_B satisfying $s_A + s_B = 2$. Then the AA function will correspond to $s_A = 2$, $s_B = 0$, the BB function to $s_A = 0$, $s_B = 2$, and the AB function to $s_A = 1$, $s_B = 1$. Thus, we define:

$$\begin{aligned} \rho_{s_A s_B}^{(2)} &= \frac{N_A! N_B!}{(N_A - s_A)!(N_B - s_B)!} \\ &\times \int D_{N_A N_B} \, d\mathbf{r}_{A, s_A+1} \dots d\mathbf{r}_{A, N_A} \, d\mathbf{r}_{B, s_B+1} \dots d\mathbf{r}_{B, N_B} \quad (13.9) \end{aligned}$$

where the Gibbs function reads

$$D_{N_A N_B} = \frac{e^{-\beta U_{N_A N_B}}}{Q}$$

The presence of unlike interactions implies that the distribution function of like particles, say AA , is influenced by other species, i.e. by species B . The pair correlation functions can be defined by analogy with (2.9):

$$\begin{aligned}
g_{AA}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{\rho_{AA}^{(2)}}{\rho_A^{(1)}(\mathbf{r}_1) \rho_A^{(1)}(\mathbf{r}_2)} \\
g_{BB}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{\rho_{BB}^{(2)}}{\rho_B^{(1)}(\mathbf{r}_1) \rho_B^{(1)}(\mathbf{r}_2)} \\
g_{AB}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{\rho_{AB}^{(2)}}{\rho_A^{(1)}(\mathbf{r}_1) \rho_B^{(1)}(\mathbf{r}_2)}
\end{aligned}$$

Following the steps described in Chap. 3 we can formulate equations of state for a mixture. The energy equation is

$$E = \frac{3}{2}(N_A + N_B)k_B T + \langle U^{(AA)} \rangle + \langle U^{(BB)} \rangle + \langle U^{(AB)} \rangle$$

where the thermal averages are calculated with the help of the theorem of averaging

$$\begin{aligned}
\langle U^{(II)} \rangle &= 2\pi \frac{N_I^2}{V} \int_0^\infty u_{II}(r) g_{II}(r) r^2 dr, \quad I = A, B \\
\langle U^{(AB)} \rangle &= 4\pi \frac{N_A N_B}{V} \int_0^\infty u_{AB}(r) g_{AB}(r) r^2 dr
\end{aligned}$$

These relationships can be written in terms of the overall density $\rho = N/V$ (where $N = N_A + N_B$ is the total number of particles) and compositions (molar fractions)

$$x_I = \frac{N_I}{N}, \quad I = A, B$$

which satisfy $\sum_I x_I = 1$. The energy equation takes the form

$$E = N \left[\frac{3}{2} k_B T + 2\pi \rho \sum_I \sum_J x_I x_J \int_0^\infty u_{IJ}(r) g_{IJ}(r) r^2 dr \right] \quad (13.10)$$

It is easy to see that the one-component case is recovered from (13.10) by setting $x_A = 1$, $x_B = 0$. The virial equation is obtained from the relationship

$$p = \frac{k_B T}{Q} \left(\frac{\partial Q}{\partial V} \right)_{N_A, N_B, T}$$

Green's transformation

$$\mathbf{r}_I = L \mathbf{r}_I^*, \quad L = V^{1/3}, \quad I = A, B$$

yields

$$p = \rho k_B T - \frac{2\pi}{3} \rho^2 \sum_I \sum_J x_I x_J \int_0^\infty u'_{IJ}(r) g_{IJ}(r) r^3 dr \quad (13.11)$$

where a prime denotes a derivative with respect to distance. Note that (13.10) and (13.11) are valid for the general case of an M -component system ($M \geq 1$) provided that there are only pairwise interactions. The Gibbs–Duhem equation and Gibbs adsorption equations for a mixture are natural generalizations of the single-component analogs (1.68) and (4.14)

$$S dT - V dp + \sum_I N_I d\mu_I = 0 \quad (13.12)$$

$$A d\gamma + S^s dT + \sum_I N_I^s d\mu_I = 0 \quad (13.13)$$

It is important to note that it is not possible to choose a Gibbs dividing surface in a such a way that adsorption of all components vanishes there. The surface tension of a binary vapor–liquid system is defined by

$$\gamma = \left(\frac{\partial \mathcal{F}}{\partial A} \right)_{N_A, N_B, V, T} \quad (13.14)$$

where A is the surface area. For the pairwise interaction energy this expression yields (cf. (4.18))

$$\gamma = \left\langle \frac{\partial U^{(AA)}}{\partial A} \right\rangle + \left\langle \frac{\partial U^{(BB)}}{\partial A} \right\rangle + \left\langle \frac{\partial U^{(AB)}}{\partial A} \right\rangle \quad (13.15)$$

Working out each contribution on the right-hand side in the same way as in Chap. 4 we obtain the Kirkwood–Buff equation for a binary mixture (cf. (4.20)):

$$\gamma = \frac{1}{4} \int_{-\infty}^{+\infty} dz_1 \int d\mathbf{r}_{12} r_{12} \left(1 - 3 \frac{z_{12}^2}{r_{12}^2} \right) \sum_I \sum_J \left[u'_{IJ}(r_{12}) \rho_{IJ}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right] \quad (13.16)$$

13.2 One-fluid approximation

Let us write the virial equation (13.11) in a reduced form:

$$\frac{p}{\rho k_B T} = 1 - \frac{2\pi}{3} \sum_{I=1}^M \sum_{J=1}^M x_I x_J \frac{\rho \sigma_{IJ}^3 \epsilon_{IJ}}{k_B T} \int_0^\infty dr_{IJ}^* r_{IJ}^{*3} u'_{IJ} g_{IJ}(r_{IJ}^*; \rho, T, \mathbf{x}) \quad (13.17)$$

where

$$r_{IJ}^* = r/\sigma_{IJ}, \quad u_{IJ}^*(r_{IJ}^*) = u_{IJ}/\epsilon_{IJ}$$

The reduced potential $u_{IJ}^* \equiv u^*(z)$ does not contain information about a particular species, e.g. for the LJ system $u^*(z) = 4(z^{-12} - z^{-6})$. Composition dependence of the integrand is contained only in the correlation functions. This fact suggests an important simplification of the problem known as the one-fluid approximation. It reads

$$g_{IJ} \left(\frac{r}{\sigma_{IJ}}; \rho, T, \mathbf{x} \right) \approx g \left(\frac{r}{\sigma_x}; \rho \sigma_x^3, \frac{k_B T}{\epsilon_x} \right), \quad I, J = 1, \dots, M \quad (13.18)$$

Here g on the right-hand side is the pair correlation function of a hypothetical pure fluid with reduced potential u^* and molecular parameters σ_x and ϵ_x given by

$$\sigma_x^3 = \sum_I \sum_J x_I x_J \sigma_{IJ}^3 \quad (13.19)$$

and

$$\epsilon_x \sigma_x^3 = \sum_I \sum_J x_I x_J \epsilon_{IJ} \sigma_{IJ}^3, \quad (13.20)$$

even though these parameters are composition dependent. Equation (13.17) becomes

$$\frac{p}{\rho k_B T} = 1 - \frac{2\pi}{3} \rho \sigma_x^3 \frac{\epsilon_x}{k_B T} \int_0^\infty dr^* (r^*)^3 \frac{du^*}{dr^*} g \left(r^*; \rho \sigma_x^3, \frac{k_B T}{\epsilon_x} \right) \quad (13.21)$$

Thus, our hypothetical pure fluid is isomorphic to the original multi-component fluid at the reduced density $\rho^* = \rho \sigma_x^3$ and reduced temperature $T^* = k_B T / \epsilon_x$. As found in various simulations (see [85], [124] and references therein), the one-fluid theory (OFT), can be viewed as a serious contender for the representation of the properties of mixtures of simple molecules of arbitrary size.

13.3 Density functional theory for mixtures

Following the lines of Chap. 9, the main concepts of the density functional theory can be straightforwardly generalized to a binary mixture. The free energy and the grand potential for a mixture now become functionals of two one-body density distributions $\hat{\rho}_1$ and $\hat{\rho}_2$:

$$\Omega[\hat{\rho}_1, \hat{\rho}_2; u_{\text{ext}}] = \mathcal{F}_{\text{int}}[\hat{\rho}_1, \hat{\rho}_2] + \sum_{I=1}^2 \int u_{\text{ext}}(\mathbf{r}) \hat{\rho}_I(\mathbf{r}) d\mathbf{r} - \sum_{I=1}^2 \mu_I N_I \quad (13.22)$$

where $\hat{\rho}_1$ and $\hat{\rho}_2$ are normalized in the usual way:

$$\int \hat{\rho}_I(\mathbf{r}_I) d\mathbf{r}_I = N_I, \quad I = 1, 2$$

The equilibrium condition corresponds to minimization of the grand potential functional with respect to the density profiles of both components:

$$\left. \frac{\delta \Omega}{\delta \hat{\rho}_1(\mathbf{r})} \right|_{\rho_1(\mathbf{r}), \rho_2(\mathbf{r})} = \left. \frac{\delta \Omega}{\delta \hat{\rho}_2(\mathbf{r})} \right|_{\rho_1(\mathbf{r}), \rho_2(\mathbf{r})} = 0 \quad (13.23)$$

Variational differentiation results in the fundamental DFT equations for a mixture (cf. (9.13)):

$$\mu_I = \mu_{\text{int}, I}(\mathbf{r}) + u_{\text{ext}}(\mathbf{r}), \quad I = 1, 2 \quad (13.24)$$

where

$$\mu_{\text{int}, I}(\mathbf{r}) \equiv \left. \frac{\delta \mathcal{F}_{\text{int}}[\hat{\rho}]}{\delta \hat{\rho}_I(\mathbf{r})} \right|_{\rho_1(\mathbf{r}), \rho_2(\mathbf{r})} \quad (13.25)$$

is the intrinsic chemical potential of species I . As in the case of a single-component system we construct a functional of the intrinsic free energy by means of the mean-field perturbation approach. Each of the potentials is decomposed into a reference part and a perturbation

$$u = u^{\text{ref}} + u^{\text{pert}}$$

The reference system is represented by a hard-sphere mixture with the effective diameters d_1 and d_2 calculated by means of the known recipes (Barker-Henderson, WCA, Song-Mason). Using the local-density approximation for the reference contribution and the random-phase approximation for the perturbation, we obtain a generalization of (9.22):

$$\mathcal{F}_{\text{int}}[\rho_1, \rho_2] = \int d\mathbf{r} \psi_d(\rho_1(\mathbf{r}), \rho_2(\mathbf{r})) + \frac{1}{2} \sum_{I, J=1}^2 \int d\mathbf{r} d\mathbf{r}' \rho_I(\mathbf{r}) \rho_J(\mathbf{r}') u_{IJ}^{\text{pert}}(|\mathbf{r} - \mathbf{r}'|) \quad (13.26)$$

where ψ_d is the free energy density of the mixture of hard spheres. Taking variational derivatives with respect to $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ we present the DFT equations for a mixture (13.23) as

$$\mu_I = \mu_{d,I}(\rho_1(\mathbf{r}), \rho_2(\mathbf{r})) + \sum_{J=1}^2 \int d\mathbf{r}' \rho_J(\mathbf{r}') u_{IJ}^{\text{pert}}(|\mathbf{r} - \mathbf{r}'|) + u_{\text{ext}}(\mathbf{r}) \quad (13.27)$$

For a homogeneous binary mixture in the absence of external fields $\rho_I(\mathbf{r}) = \rho_I$, and the DFT equations are significantly simplified:

$$\mathcal{F}(\rho_1, \rho_2) = \mathcal{F}_d(\rho_1, \rho_2) - V \sum_{I,J=1}^2 \rho_I \rho_J a_{IJ} \quad (13.28)$$

$$\mu_I = \mu_{d,I}(\rho_1, \rho_2) - 2 \sum_{J=1}^2 \rho_J a_{IJ} \quad (13.29)$$

where

$$a_{IJ} = -\frac{1}{2} \int d\mathbf{r} u_{IJ}^{\text{pert}}(r)$$

is the background interaction parameter. Finally, the virial equation for a mixture reads

$$p = p_d(\rho_1, \rho_2) - \sum_{I,J=1}^2 \rho_I \rho_J a_{IJ} \quad (13.30)$$

where $p_d(\rho_1, \rho_2)$ is the pressure of the hard-sphere mixture. Analytic approximations developed by various authors [98], [121] for the thermodynamic properties (the Helmholtz free energy, chemical potentials of the species, the virial equation) of a hard-sphere mixture based on the Carnahan–Starling theory are presented in Appendix E.

Note the close resemblance of (13.30) to the van der Waals equation for a single-component fluid. If for hard spheres we use simple excluded-volume considerations, then (13.30) can be written in the van der Waals form

$$p = \frac{\rho k_B T}{1 - b_m \rho} - \rho^2 a_m \quad (13.31)$$

with

$$a_m = \sum_{I,J=1}^2 x_I x_J \sqrt{a_I a_J} = \left[\sum_{I=1}^2 x_I \sqrt{a_I} \right]^2, \quad b_m = \sum_{I=1}^2 x_I b_I$$

where a_I and b_I are the van der Waals parameters of individual species I .

13.4 Surface tension

13.4.1 Density functional approach

Study of the liquid–vapor interface of multicomponent mixtures by means of theoretical models and computer simulation has become a field of growing

interest during last two decades. Great progress was achieved in implementation of the density functional theory in combination with a perturbation treatment of attractive interactions (see e.g. [139], [153],[96]). Calculations based on the DFT use the thermodynamic route

$$\gamma = (\Omega[\{\rho_I\}] + pV)/A \quad (13.32)$$

where Ω is the grand potential of a nonuniform multicomponent mixture, p the equilibrium pressure, V the volume and A interface area.

Let us study in more detail a binary vapor-liquid mixture of Lennard-Jones fluids with a flat interface and inhomogeneity in the z direction. Using the Legendre transformation $\mathcal{F}_d \rightarrow \Omega_d$, the free energy density of a hard-sphere mixture can be written as

$$\psi_d(z) = \sum_{I=1}^2 \rho_I \mu_{d,I} - p_d[\rho_1(z), \rho_2(z)]$$

The grand potential functional (13.22) with $u_{\text{ext}} = 0$ then reads

$$\begin{aligned} \Omega[\rho_1, \rho_2] = & - \int d\mathbf{r} p_d(\rho_1, \rho_2) + \sum_{I=1}^2 \int d\mathbf{r} \rho_I \mu_{d,I}(\rho_I) + \\ & \frac{1}{2} \sum_{I,J=1}^2 \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') u_{IJ}^{\text{pert}}(|\mathbf{r} - \mathbf{r}'|) - \sum_{I=1}^2 \mu_I \int d\mathbf{r} \rho_I(\mathbf{r}) \end{aligned}$$

which after substitution of the DFT equation (13.27) yields:

$$\gamma = - \int dz \left\{ p_d(z) + \frac{1}{2} \sum_{I=1}^2 \rho_I(z) \int d\mathbf{r}' \rho_J(z') u_{IJ}^{\text{pert}}(|\mathbf{r} - \mathbf{r}'|) - p \right\} \quad (13.33)$$

The equilibrium density profiles $\rho_I(z)$ satisfy (13.27):

$$\mu_{d,I}(\rho_1(z), \rho_2(z)) = \mu_I - \sum_{J=1}^2 \int d\mathbf{r}' \rho_J(\mathbf{r}') u_{IJ}^{\text{pert}}(|\mathbf{r} - \mathbf{r}'|) \quad (13.34)$$

Two-phase equilibrium for a binary mixture is specified by fixing two thermodynamic degrees of freedom, e.g. temperature and one of the bulk densities, or temperature and the total pressure p . Choosing the latter possibility (i.e. fixing T and p), the equilibrium bulk densities ρ_I^v and ρ_I^l ($I = 1, 2$) are found from the equality of pressures in the bulk phases and equality of chemical potentials of each species:

$$p_d(\rho_1^v, \rho_2^v) - \sum_{I,J=1}^2 \rho_I^v \rho_J^v a_{IJ} = p_d(\rho_1^l, \rho_2^l) - \sum_{I,J=1}^2 \rho_I^l \rho_J^l a_{IJ} = p$$

$$\mu_{d,I}(\rho_1^v, \rho_2^v) - 2 \sum_{J=1}^2 \rho_J^v a_{IJ} = \mu_{d,I}(\rho_1^l, \rho_2^l) - 2 \sum_{J=1}^2 \rho_J^l a_{IJ}, \quad I = 1, 2$$

Given the bulk limits

$$\rho_I(z) \rightarrow \rho_I^v \quad \text{in the bulk vapor}$$

$$\rho_I(z) \rightarrow \rho_I^l \quad \text{in the bulk liquid}$$

the density profiles of the components are calculated iteratively from (13.34), starting with an initial guess for each $\rho_I(z)$, which can be a step function or a continuous function (like $\tanh$) that varies between the bulk limits.

One feature of a binary (or, more generally, any multicomponent) system is a possibility of nonmonotonic behavior of the density profile $\rho_I(z)$ in the liquid–vapor transition region for some of the components due to high relative adsorption (i.e. adsorption of one species with respect to the equimolar Gibbs dividing surface of the other) – an effect known as surface enrichment. This effect is pronounced when the species differ significantly in their critical temperatures and molecular masses.

We apply these techniques for a mixture of *n*-hexane (C_6H_{14}) and methane (CH_4) at room temperature $T = 300$ K. The interaction parameters and thermodynamic data are given in Table 13.1 [119]. At room temperature methane is in a supercritical condition, since its critical temperature is lower than 300 K. Thus, if it were pure methane, it could not be transformed into the liquid phase at 300 K. Figure 13.1 shows the density profiles of the two species at a total pressure $p = 40$ bar. The surface enrichment effect is clearly seen: methane molecules under high pressure penetrate the liquid phase, but they concentrate more easily in the interface region than in the bulk. This relative adsorption increases with pressure.

Two important effects are observed:

- at high pressure the more volatile component (methane) is dissolved into the liquid phase, thereby reducing the liquid number density of the less volatile component (*n*-hexane) (compared to pure liquid *n*-hexane at the same temperature)
- the more volatile component preferentially concentrates at the interface

These two effects lead to a significant reduction in surface tension with pressure at a given temperature.

The temperature dependence of γ is more unusual. At a low pressure $\gamma(T)$ monotonically decreases, as shown in Fig. 13.2 for $p = 5$ bar. At a high enough pressure (e.g. at $p = 40$ bar) the surface tension **first** increases with

temperature: at low T methane is more soluble in n -hexane which causes a considerable reduction in surface tension. As temperature increases the solubility decreases (methane partly evaporates), resulting in an increase in γ . Thus, at low T the effect of liquid composition on γ dominates the effect of temperature. For higher temperatures the second effect becomes dominant. As a result the surface tension as a function of T has a maximum at high pressures.

Table 13.1. Lennard-Jones parameters ϵ/k_B (K) and σ (Å), molecular weight M (g/mol) and critical temperature T_c (K) for n -hexane and methane [119]

Component	ϵ/k_B (K)	σ (Å)	M (g/mol)	T_c (K)
C_6H_{14}	471.5	5.587	86	507.5
CH_4	148.6	3.758	16	190

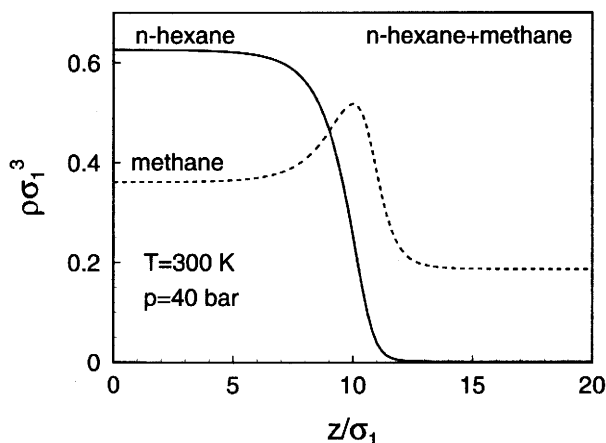


Fig. 13.1. Liquid-vapor density profiles of n -hexane and methane at total pressure $p = 40$ bar predicted by the DFT. Distances and densities are scaled with respect to $\sigma_1 = \sigma_{C_6H_{14}}$. Methane is preferentially adsorbed at the surface (surface enrichment)

13.4.2 One-fluid theory

As the complexity of the system (i.e. the number of components) grows, theoretical calculations using the DFT become increasingly difficult, since one must calculate the density profiles of individual components iteratively, solving a large set of coupled nonlinear equations. This difficulty can be avoided (at the cost of the losing information about the details of density profiles of

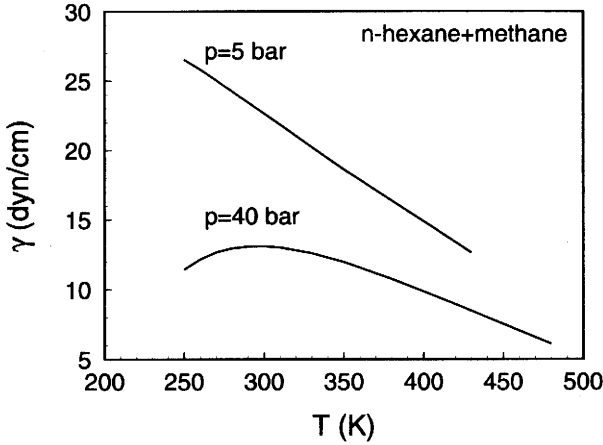


Fig. 13.2. Surface tension for the mixture *n*-hexane-methane predicted by the DFT

individual components) within the framework of the one-fluid theory (OFT) for the surface tension [67].

Consider the liquid-vapor equilibrium at a given temperature and given equilibrium liquid molar fractions $x_1^l, \dots, x_M^l$, $\sum_{I=1}^M x_I^l = 1$; inhomogeneity is in the z direction. In spite of the possible surface enrichment of one of the components, the profile of the total density

$$\rho^{(1)} = \sum_{I=1}^M \rho_I^{(1)}$$

exhibits a monotonic behavior and moreover is quite sharp far from the critical domain [138]. This observation leads us to formulation of the Fowler approximation for a mixture in terms of its total density. To be more precise we will discuss a hypothetical pure inhomogeneous fluid at the same temperature T which possesses an (average) density profile which coincides with the total density profile of the original multicomponent system. This transformation, performed within the framework of OFT, yields (13.19)–(13.20) for composition-dependent interaction parameters. For the two-phase system in equilibrium, the molar fractions x_I vary through the interface, implying that σ_x and ϵ_x are functions of z . However, if the vapor density is negligible compared to the liquid, we can apply the Fowler approximation for the hypothetical pure fluid, which means that the surface tension γ_{OFT} can be related exclusively to the bulk liquid properties. This yields a straightforward generalization of (5.56), derived in Chap. 5 for a single-component vapor-liquid system:

$$\gamma_{\text{OFT}} = \frac{\pi}{2} (\rho^l)^2 k_B T \left\{ \int_0^\infty dr f^l(r) r^3 + [y_d^l(d^l; \rho^l) - 1] \int_0^{r_m^l} dr f_0^l(r) r^3 \right\} \quad (13.35)$$

where the superscript "l" denotes the dependence on equilibrium liquid composition $\mathbf{x}^l$ fixed by the input conditions. Specifically, the interaction potential

$$u = u^l(r; \sigma_x, \epsilon_x) \equiv \epsilon_x u^* \left(\frac{r}{\sigma_x} \right)$$

is characterized by

$$\sigma_x^3 = \sum_I \sum_J x_I^l x_J^l \sigma_{IJ}^3, \quad \epsilon_x \sigma_x^3 = \sum_I \sum_J x_I^l x_J^l \epsilon_{IJ} \sigma_{IJ}^3, \quad (13.36)$$

Here f^l is the Mayer function for u^l , f_0^l the Mayer function for the reference potential u_0^l , obtained by means of the Weeks–Chandler–Andersen decomposition of u^l , $u^l(r_m^l) = -\epsilon_x$. The equilibrium liquid density is found from the analog of (5.57)

$$1 + B^l \rho^l + \alpha^l \rho^l [y_d^l(d^l; \rho^l) - 1] = 0 \quad (13.37)$$

where

$$B^l(T; \mathbf{x}^l) = 2\pi \int_0^\infty dr r^2 \left[1 - e^{-\beta u^l(r)} \right] \quad (13.38)$$

and

$$\alpha^l(T; \mathbf{x}^l) = 2\pi \int_0^{r_m^l} dr r^2 \left[1 - e^{-\beta u_0^l(r)} \right] \quad (13.39)$$

The cavity function at contact has the Carnahan–Starling form (3.23) in which the effective hard-sphere diameter is

$$d^l(\mathbf{x}^l) = \int_0^{r_m^l} dr [1 - \exp(-\beta u_0^l)] \quad (13.40)$$

Consider a binary Lennard–Jones mixture Ar/Kr at $T = 115.77$ K with the parameters [84]:

$$\begin{aligned} \sigma_{\text{Ar,Ar}} &= 3.405 \text{ \AA}, & \frac{\epsilon_{\text{Ar,Ar}}}{k_B} &= 119.8 \text{ K} \\ \sigma_{\text{Kr,Kr}} &= 3.630 \text{ \AA}, & \frac{\epsilon_{\text{Kr,Kr}}}{k_B} &= 163.1 \text{ K} \end{aligned}$$

Binary Ar/Kr mixture: truncated LJ potential. Lee et al. [84] performed computer simulations for the mixture of truncated and shifted LJ potentials: potentials were truncated at $r_c = 2.5\sigma_{IJ}$ and shifted by $u_{IJ}(r_c)$ in order to preserve continuity at r_c . Table 13.2 shows the simulation results of [84] and predictions of OFT for the same cutoff and shifted LJ potentials for several equilibrium liquid molar fractions of Ar, x_{Ar}^l , and temperature $T = 115.77$ K. There is good qualitative agreement for the surface tension; the main difference between theory and simulations is due to the fact that OFT underestimates the total liquid density by ~ 10 –13%. Note that the density dependence of γ_{OFT} in (13.35) is nonmonotonic, since the second term in curly brackets is negative and decreases as ρ^l grows, competing with $(\rho^l)^2$ in the prefactor. Figure 13.3 summarizes the comparison of γ_{OFT} with both DFT results and simulation data of [84].

Table 13.2. Surface tension γ in dyne/cm and total equilibrium liquid density ρ^l in $\text{\AA}^{-3}$ for an Ar/Kr mixture at $T = 115.77$ K; truncated and shifted LJ potential. x_{Ar}^l : liquid molar fraction of Ar; the subscript “sim” refers to simulation results of [84]; “OFT” refers to the one-fluid theory

x_{Ar}^l	γ_{sim}	ρ_{sim}^l	γ_{OFT}	ρ_{OFT}^l
0.458	5.55 ± 0.05	0.0166	7.87	0.0144
0.445	6.95 ± 0.05	0.0164	7.96	0.0144
0.249	7.2 ± 0.01	0.0165	9.23	0.0148
0.219	8.5 ± 0.01	0.0164	9.42	0.0148

Binary Ar/Kr mixture: full LJ potential. Truncation of a potential at some point r_c of its attractive branch reduces the surface tension since the integrated strength of attractive interactions is less than for the full LJ mixture. The underestimation of surface tension in simulations by not taking into account the tail of the potential can be quite substantial. For pure fluids it can be eliminated (though not fully) by means of the tail correction [17]; similar calculations for mixtures are not available.

Figure 13.4 displays the surface tension of Ar/Kr as a function of the equilibrium liquid molar fraction of Ar; γ_{OFT} for the full potentials is approximately two times larger than for the truncated potentials. Predictions of this model are compared with the DFT calculations of [84] and [153] for full LJ potentials. We observe that γ_{OFT} is located between the two DFT curves.

The OFT calculations are very fast, since they do not involve iterations for finding equilibrium density profiles inherent to DFT models. This advantage becomes crucial for systems with relatively large complexity ($M \geq 3$). In spite of its simplicity OFT appears to provide a quantitative description of surface tension (to within 15–20 %). Though the present model completely disregards the structure of the interface, good agreement with simulation results seems

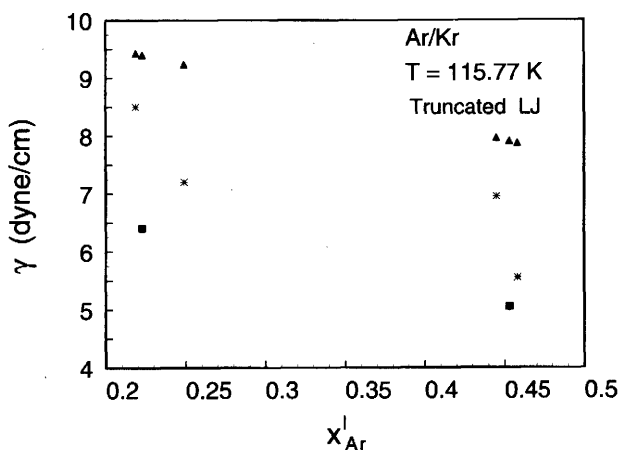


Fig. 13.3. Surface tension for the Ar/Kr mixture at $T = 115.77$ K for truncated LJ potentials as a function of equilibrium liquid molar fraction of Ar, x_{Ar}^l . Squares: DFT results of [84]; stars: MD simulation data of [84]; triangles: OFT

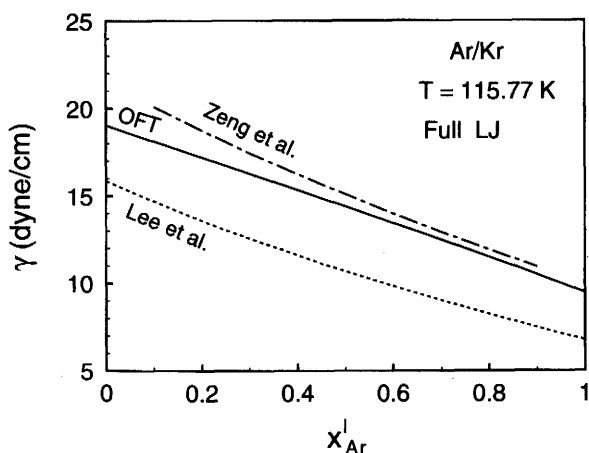


Fig. 13.4. Surface tension for the Ar/Kr mixture at $T = 115.77$ K as a function of equilibrium liquid molar fraction of Ar, x_{Ar}^l ; full LJ potentials. Shown are predictions of OFT (solid line) and DFT results of [84] (dashed line) and [153] (dashed-dotted line)

to suggest that the value of the surface tension (far from critical conditions) is insensitive to the interface density profiles.

14. Ferrofluids

A colloidal suspension is an example of a mixture containing species characterized by different length and time scales. It consists of mesoscopic particles with a diameter σ ranging between 1 nm and 1 μm dispersed in a microscopic molecular liquid solvent (water, organic solvent, etc.). The interaction between two spherical colloidal particles can be derived by summing van der Waals attractions between pairs of atoms distributed uniformly over the spherical volumes. This summation yields the Hamacker potential [128]

$$u_{\text{Ham}}(r) = -\frac{A}{12} \left[\frac{\sigma^2}{r^2 - \sigma^2} + \frac{\sigma^2}{r^2} + \ln \left(1 - \frac{\sigma^2}{r^2} \right) \right] \quad (14.1)$$

where $A > 0$ is the Hamacker constant (of the order of $k_{\text{B}}T$), and r the distance between centers of the particles. Due to the long-range nature of the Hamacker potential, particles have a tendency to coagulate. In order to prevent irreversible coagulation induced by singularity of u_{Ham} at $r \rightarrow \sigma$, stabilization is needed. The latter can be achieved by means of two mechanisms.

In steric stabilization one adds a surfactant, which consists of short polymer chains stuck to the surface of colloidal particles. These chains form a mechanical “mattress” surrounding a particle; when two particles come close to each other they experience a repulsion of entropic origin, due to the phase space reduction of the grafted chains.

It is possible to construct a dispersion in such a way that the Hamacker interactions are almost totally suppressed; this is achieved by matching the refractive indexes of the solvent and colloidal particle material. A sterically stabilized colloidal suspension can be accurately described in terms of a hard-sphere model with an effective diameter somewhat larger than the bare colloid diameter (approximately by the width of the surfactant layer).

Charge stabilization is achieved when colloidal particles are dispersed in a polar solvent (e.g. water). In this case surface radicals of particles dissociate in the solvent producing an electric double layer formed by the surface charges and microscopic counterions carrying one or two elementary charges. In view of its mesoscopic size, a particle becomes highly charged carrying typically $\sim 10^2$ – 10^4 elementary charges. Due to the “microion cloud” around a colloidal particle, the electrostatic repulsion of macroions is screened and can be presented in the form of a repulsive Yukawa potential with a screening

(Debye) length r_D depending on the total density of microions. This means that repulsion persists up to r_D . Thus, in charge stabilized colloidal suspension, one can speak about an electrostatic "mattress" surrounding each colloidal particle.

For some types of suspensions the problem of statistical mechanical description becomes complicated due to long-range anisotropic interactions between colloidal particles with permanent dipole moments. This is the case for a ferrofluid (or magnetic fluid), a colloidal suspension of single-domain ferromagnetic particles (Fe_3O_4 , Co, Fe, etc.) of mean diameter ~ 100 Å dispersed in a solvent (water, kerosene, oil, etc.) (for an excellent description of ferrofluid properties see [122]). Its main feature, which is of fundamental and practical interest, is that it is a paramagnetic fluid with strong magnetic properties: its initial magnetic susceptibility lies in the range

$$4\pi\chi \sim 1-10$$

whereas for natural paramagnets $4\pi\chi \sim 10^{-3}-10^{-4}$.

One can therefore say that a ferrofluid is a superparamagnetic medium. In a number of experiments (for a review see e.g. [114]) a substantial deviation of magnetic properties of ferrofluid from the classical (Langevin) behavior of noninteracting magnetic moments was observed. These results indicate that ferroparticles form a strongly interacting system that can exert a significant influence on ferrofluid properties and structure.

An adequate description of ferrofluid properties requires a statistical thermodynamic approach that takes into account anisotropic long-range interparticle interactions. To simplify the description it is desirable to distinguish the degrees of freedom of solvent molecules from those of ferroparticles.¹ This can be done within the framework of a cell model that allows for the difference in the length and time scales of molecules and ferroparticles [14], [62].

14.1 Cell model of a ferrofluid

Consider a volume V of a ferrofluid containing N_s molecules and N ferroparticles and placed in an external magnetic field $\mathbf{H}_{\text{ext}}$ (Fig. 14.1). As in Chap. 12 the container is an (infinitely) long cylinder with an axis parallel to $\mathbf{H}_{\text{ext}}$. This ensures the absence of a demagnetization field inside the sample so that the macroscopic magnetic field in it is

$$\mathbf{H} = \mathbf{H}_{\text{ext}}$$

Particles are assumed to be rigid spheres of a bare diameter d_0 ($d_0 \sim 50-150$ Å). For simplicity we discuss a monodisperse suspension, but the results can

¹ Throughout this chapter the term "molecule" refers to a solvent molecule and the term "particle" refers to a ferromagnetic particle.

be straightforwardly generalized for a polydisperse system by averaging over the corresponding size distribution. Each particle carries a permanent magnetic moment $\mathbf{s}_i$, $|\mathbf{s}_i| = s$ ($i = 1, \dots, N$). The small size of a particle makes it possible to consider it single-domain; the absolute value of the magnetic moment can be estimated as

$$s = M_f \frac{\pi d_0^3}{6}$$

where $M_f(T)$ is the saturation magnetization of the ferromagnetic material; a typical value is $s \sim 10^5 \mu_B$ (where the Bohr magneton $\mu_B = 9.27 \times 10^{-21}$ erg/Gs). Brownian motion destroys ordering of magnetic moments imposed by the field.

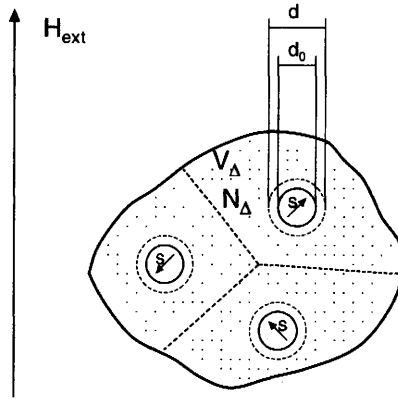


Fig. 14.1. Cell model of a ferrofluid (see explanation in the text)

We discuss the case of steric stabilization achieved by means of a surfactant forming a layer of thickness σ_{surf} (usually $\sim 20\text{--}40 \text{ \AA}$) around a particle.² The solvent is dielectric and nonmagnetic. The volume fraction of the disperse phase

$$\phi = \rho \frac{\pi d^3}{6}, \quad d = d_0 + 2\sigma_{\text{surf}} \quad (14.2)$$

is assumed to be small. Typically, the number density of particles is $\rho \sim 10^{16} - 10^{18} \text{ cm}^{-3}$. A presence of a surfactant can be taken into account by imposing hard-sphere repulsion between particles with an effective hard-sphere diameter d . Let us denote by $\mathbf{q}_\alpha$, ($\alpha = 1, \dots, N_s$) the radius vectors of the molecules. A ferroparticle is characterized by its radius vector $\mathbf{r}_i$ ($i = 1, \dots, N$) and by the angular coordinates of its magnetic moment $\omega_i = (\theta_i, \varphi_i)$; thus a particle is described by a five-dimensional vector $\bar{\mathbf{r}}_i = (\mathbf{r}_i, \omega_i)$. One can distinguish four types of interaction:

² A description of ionic ferrofluids with charge stabilization follows the same lines.

1. Interparticle interaction

$$u_{ij} = u_{d,ij} + u_{ij}^{(dd)}$$

consisting of hard-sphere repulsion $u_{d,ij}$ and dipole-dipole interaction $u_{ij}^{(dd)}$ (dipolar hard spheres), similar to that discussed for polar fluids in Chap. 12;

2. Interaction of a particle with the external magnetic field:

$$u_{\text{ext},i} = -\mathbf{s}_i \mathbf{H}_{\text{ext}}$$

3. Molecule-particle interaction $u_{i\alpha}^{(fs)}$; and4. Solvent-solvent (intermolecular) interaction $u_{\alpha\gamma}^{(ss)}$.

According to (13.5) the partition function of a ferrofluid is

$$Z_{\text{FF}} = \frac{1}{N! \Lambda^{3N}} \frac{1}{N_s! \Lambda_s^{3N_s}} Q_{\text{FF}}$$

where Λ and Λ_s are the values of the de Broglie wavelength for particles and molecules, respectively. The total potential energy is

$$U_{\text{FF}}(\mathbf{r}^N, \mathbf{q}^{N_s}) = U + \bar{U}$$

where

$$U(\mathbf{r}^N) = \sum_{i < j} u_{ij} + \sum_i u_{\text{ext},i}$$

and

$$\bar{U}(\mathbf{r}^N, \mathbf{q}^{N_s}) = \sum_{\alpha < \gamma} u_{\alpha\gamma}^{(ss)} + \sum_i \sum_{\alpha} u_{i\alpha}^{(fs)}$$

U does not depend on the coordinates of solvent molecules (but $\bar{U}$ does), so the configuration integral becomes

$$Q_{\text{FF}} = \int d\mathbf{r}^N \left\{ e^{-\beta U(\mathbf{r}^N)} \left[\int d\mathbf{q}^{N_s} e^{-\beta \bar{U}(\mathbf{r}^N, \mathbf{q}^{N_s})} \right] \right\}$$

It can be simplified if we take into account the smallness of ϕ and the large difference in sizes of particles and molecules. Let us divide the physical space V into N cells in such a way that each cell Δ contains one particle and $N_{\Delta} = \rho_s / \rho$ molecules (ρ_s is the number density of the solvent); on average $N_{\Delta} \sim 10^5$ – 10^7 . The following assumptions are adopted:

- Interactions of molecules belonging to different cells are neglected compared to interactions of molecules within cells.

- For each particle only its interaction with molecules of the same cell is taken into account.

For both assumptions a relative error in the energy calculation is $\sim N_{\Delta}^{-1/3}$. Then cells can be considered independent and

$$\bar{U} \approx \sum_{i=1}^N \left[\sum_{\alpha < \gamma} 'u_{\alpha\gamma}^{(ss)} + \sum_{\alpha} 'u_{i\alpha}^{(fs)} \right] = N\bar{U}_{\Delta}(\mathbf{q}^N\Delta)$$

where $\sum'$ means that the summation is taken over a single cell, $\bar{U}_{\Delta}(\mathbf{q}^N\Delta)$ being the average energy of a cell.

The configuration integral can be written in factorized form:

$$Q_{\text{FF}} = \frac{N_s!}{(N_{\Delta}!)^N} Q_m Q_{\Delta}^N$$

where

$$Q_m = \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \quad (14.3)$$

$$Q_{\Delta} = \int d\mathbf{q}^N e^{-\beta \bar{U}_{\Delta}(\mathbf{q}^N\Delta)} \quad (14.4)$$

The symbol Δ under the integral indicates that integration is over the configuration space of a single cell. The combinatorial factor $N_s!/(N_{\Delta}!)^N$ gives the number of ways of partitioning of N_s molecules among N cells with N_{Δ} molecules in each cell. The Helmholtz free energy $\mathcal{F}_{\text{FF}} = -k_B T \ln Z_{\text{FF}}$ can be expressed in an additive form:

$$\mathcal{F}_{\text{FF}} = -k_B T \ln Q_m - N k_B T \ln Q_{\Delta} - k_B T \ln \left(\frac{1}{N! \Lambda^{3N}} \frac{1}{(N_{\Delta}!)^N \Lambda_s^{3N_s}} \right) \quad (14.5)$$

This result shows that within the cell model a ferrofluid can be treated as a combination of two independent subsystems: “magnetic” and “solvent,” with configuration integrals Q_m and Q_{Δ}^N , respectively. The magnetic subsystem consists of N ferroparticles interacting with one another and with the external magnetic field. The solvent subsystem consists of N identical cells, i.e. N identical elementary subsystems with configuration integrals Q_{Δ} . Inside a cell N_{Δ} molecules interact with one another and with the external field created by the particle situated in its center. Therefore, thermodynamic properties of a ferrofluid can be studied separately for the two subsystems. We proceed by using the perturbation approach for the magnetic subsystem.

14.2 Magnetic subsystem in a low field.

Algebraic perturbation theory

For a magnetic subsystem in a low external magnetic field we can apply the algebraic perturbation theory (APT) formulated in Chap. 12 for a polar fluid, switching from electric to magnetic language: $\mathbf{s}$ becomes the magnetic moment of a ferroparticle, $\mathbf{E}_{\text{ext}}$ is replaced by $\mathbf{H}_{\text{ext}}$, and ε is replaced by the magnetic permeability μ . The APT expression for the free energy (12.43) in a low magnetic field reads

$$\mathcal{F} = \mathcal{F}_0 - Nk_B T \frac{\alpha^2}{6} - k_B T \frac{\alpha^2}{54} \rho^2 V d^3 \left(4\pi\lambda + \frac{1}{9} \pi^2 \rho d^3 \lambda^2 \right) \quad (14.6)$$

where $\mathcal{F}_0$ is the reference free energy,

$$\alpha = \frac{sH_{\text{ext}}}{k_B T}$$

is the Langevin parameter, assumed to be small, and

$$\lambda = \frac{s^2}{k_B T d^3}$$

is the coupling constant. The magnetization is given by the thermodynamic relationship [81]

$$\mathbf{M} = - \frac{1}{V} \left. \frac{\partial \mathcal{F}}{\partial \mathbf{H}_{\text{ext}}} \right|_{N, V, T} \quad (14.7)$$

The reference free energy gives no contribution to $\mathbf{M}$ unless there exists spontaneous magnetization of dipolar hard spheres. The possibility of spontaneous magnetization in a ferrofluid has been discussed by several authors [154], [50], [106]. However, no experimental evidence has been obtained so far supporting this statement. But even assuming that an order-disorder transition in dipolar hard spheres does take place it would correspond, according to theoretical estimates [154], [50], [106], to relatively high volume fractions $\phi > 0.35$, which are beyond the scope of the model.

Thus, in the present theory magnetization is determined entirely by the perturbative part of the free energy. From (14.6)–(14.7) in the leading order in the Langevin parameter

$$M = \frac{\alpha}{3} \rho s \left[1 + \frac{4\pi}{9} \rho d^3 \lambda + \frac{1}{81} \pi^2 (\rho d^3 \lambda)^2 \right] \quad (14.8)$$

The saturation magnetization $M_s = \rho s$ corresponds to complete alignment of dipoles along the field. The first term gives the Langevin magnetization (i.e. the magnetization of an ideal gas of dipoles) in a low field

$$M_L = \frac{\alpha}{3} M_s \quad (14.9)$$

The initial susceptibility is a reaction of the magnetization to application of an infinitesimal field $\mathbf{H}$. Taking into account that $\mathbf{H} = \mathbf{H}_{\text{ext}}$, we write

$$\chi = \left. \frac{\partial M}{\partial H_{\text{ext}}} \right|_{H_{\text{ext}} \rightarrow 0} \quad (14.10)$$

From (14.8)–(14.10) we obtain

$$\chi = \chi_L \left(1 + \frac{4\pi}{3} \chi_L + \frac{1}{9} \pi^2 \chi_L^2 \right) \quad (14.11)$$

where

$$\chi_L = \frac{1}{3} \frac{\rho s^2}{k_B T} \quad (14.12)$$

is the Langevin susceptibility. In terms of the magnetic permeability $\mu = 1 + 4\pi\chi$, this result becomes

$$\mu - 1 = 3y \left(1 + y + \frac{1}{16} y^2 \right) \quad (14.13)$$

where

$$y = \frac{4\pi}{9} \frac{\rho s^2}{k_B T} = \frac{4\pi}{3} \chi_L$$

Analogous to the corresponding expression (12.46) for the dielectric constant, (14.11) and (14.13) can be called the low-density limits of μ and χ . A more general form includes the density correction factor in the form of Padé approximation (12.50)

$$I(\rho^*) = \frac{1 - 0.93952\rho^* + 0.36714\rho^{*2}}{1 - 0.92398\rho^* + 0.23323\rho^{*2}}, \quad \rho^* = \rho d^3$$

yielding

$$\chi = \chi_L \left\{ 1 + \frac{4\pi}{3} \chi_L + \left[-1 + \frac{17}{16} I(\rho^*) \right] \left(\frac{4\pi}{3} \right)^2 \chi_L^2 \right\} \quad (14.14)$$

In the low-density limit $I(\rho^*) \rightarrow 1$ and (14.11) is recovered. In Fig. 14.2 we plot χ as a function of the Langevin susceptibility for various values of the coupling constant. Being rescaled, these curves show the density dependence of χ , since for a given λ

$$\rho^* = 3\chi_L/\lambda$$

The theoretical predictions for $\lambda = 3$ and $\lambda = 4$ are hardly distinguishable except at high values of χ_L because they correspond to low densities, for which $I \approx 1$. Recalling that the APT predictions for the dielectric constant (see Fig. 12.3) are in good agreement with simulations for $\lambda < 2.5$, we expect the same reliability range for the initial susceptibility of a ferrofluid. This expectation is supported by Monte Carlo simulations of Pshenichnikov and Mekhonoshin [116] shown in Fig. 14.2. For $\lambda = 1$ MC data (closed circles) agrees well with the theory, while for $\lambda = 3$ (triangles) the discrepancy between theory and simulations is appreciable.

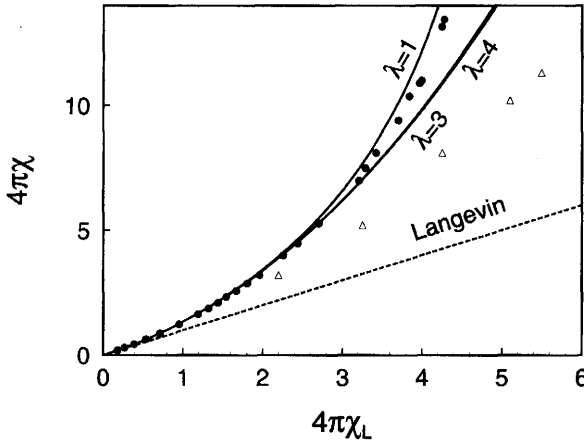


Fig. 14.2. Density dependence of the initial magnetic susceptibility. Solid lines labeled by the value of the coupling constant λ : predictions of the APT. Curves for $\lambda = 3$ and $\lambda = 4$ are hardly distinguishable except at high values of χ_L . Dashed line corresponds to the Langevin gas $\chi = \chi_L$ (no interactions). Closed circles and triangles: Monte Carlo simulation results of [116] for $\lambda = 1$ and $\lambda = 3$, respectively

Figure 14.3 shows the temperature dependence of the initial susceptibility for a colloidal solution of magnetite in kerosene predicted by various models, and experimental results of Pshenichnikov and Lebedev [115]. To calculate $\chi_L(T)$ we assume that at the highest experimental temperature $T^{\text{ref}} = 343.15$ K, where interparticle interactions are at a minimum, the experimental value $4\pi\chi^{\text{ref}} = 24.7$ is described by (14.11). The experimental value of the reduced density at T^{ref} was $\rho^{*,\text{ref}} = 0.342$. Applying the APT we first solve the cubic equation (14.11) to find the Langevin susceptibility at the reference point ($T = T^{\text{ref}}$, $\rho^* = \rho^{*,\text{ref}}$):

$$\chi^{\text{ref}} = \chi_L^{\text{ref}} \left\{ 1 + \frac{4\pi\chi_L^{\text{ref}}}{3} + \left[-1 + \frac{17}{16} I(\rho^{*,\text{ref}}) \right] \left(\frac{4\pi\chi_L^{\text{ref}}}{3} \right)^2 \right\}$$

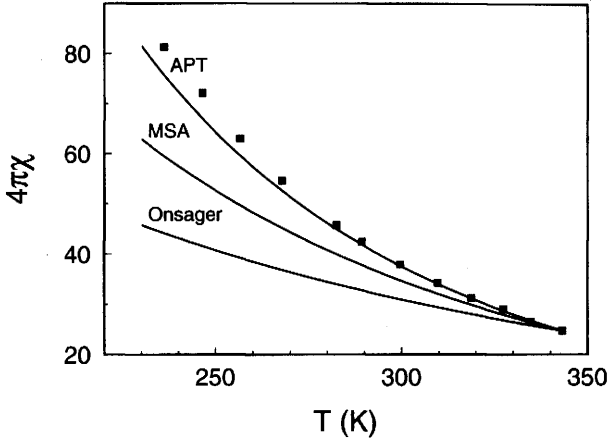


Fig. 14.3. Temperature dependence of the initial magnetic susceptibility of a ferrofluid “magnetite in kerosene”. Squares: experiment [115]; solid lines: theoretical predictions (notation is the same as in Fig. 12.3). Comparison with experiment is made by adjusting the corresponding theoretical $4\pi\chi$ to the experimental value $4\pi\chi^{\text{ref}} = 24.7$ at the temperature $T^{\text{ref}} = 343.15$ K

which gives $4\pi\chi_L^{\text{ref}} \approx 6.76$. For other temperatures the Langevin susceptibility is given by

$$\chi_L(T) = \frac{T^{\text{ref}}}{T} \chi_L^{\text{ref}} \left\{ \left[1 - \beta_1(T - T^{\text{ref}}) \right] \left[\frac{1 - \beta_2 T^2}{1 - \beta_2 (T^{\text{ref}})^2} \right]^2 \right\} \quad (14.15)$$

Terms in curly brackets take into account corrections to the leading temperature dependence (14.12) of χ_L due to two effects: the thermal expansion of the solvent (kerosene) with expansion coefficient $\beta_1 \approx 0.9 \times 10^{-3} \text{ K}^{-1}$, and a decrease of the spontaneous magnetization of the ferromagnetic material with temperature, where for magnetite $\beta_2 \approx 8 \times 10^{-7} \text{ K}^{-2}$ [114].

APT (Eq. (14.14)) shows good agreement with the experimental data for the whole temperature range studied. In the same figure predictions of the Onsager theory and the MSA [102]) are also shown. To be consistent we use the same procedure for all of these models, adjusting the corresponding theoretical $4\pi\chi$ to the experimental value $4\pi\chi^{\text{ref}} = 24.7$ at $T^{\text{ref}} = 343.15$ K to calculate χ_L^{ref} . This implies that the reference Langevin susceptibility is different for different models. Among the theories presented in Fig. 14.3, APT demonstrates the best agreement with experiment.

14.2.1 Equation of state

For the free energy of the reference model (dipolar hard spheres) we use the result of Rushbrooke et al. [127]:

$$\mathcal{F}_0 = \mathcal{F}_d - Nk_B T \left[\frac{2\pi}{9}(\rho d^3)\lambda^2 - \frac{5\pi^2}{162}(\rho d^3)^2\lambda^3 \right] \quad (14.16)$$

where $\mathcal{F}_d$ is the free energy of hard spheres (see (3.25)). Then the virial equation for the ferrofluid becomes

$$p = p_d - \rho k_B T \left[\frac{2\pi}{9}(\rho d^3)\lambda \left(\lambda + \frac{\alpha^2}{3} \right) - \frac{\pi^2}{81}(\rho d^3)^2\lambda^2 \left(5\lambda - \frac{\alpha^2}{3} \right) \right] \quad (14.17)$$

Due to the contribution from the square brackets, (14.17) develops a van der Waals loop, signaling a first-order phase transition of the vapor-liquid type, resulting in formation of a condensed phase in the homogeneous ferrofluid. The simplest estimate of the critical point for this transition $[\phi_c(\alpha), \lambda_c(\alpha)]$ can be made if for the hard-sphere pressure we adopt the van der Waals form:

$$p_d^{\text{vdW}} = \frac{\rho k_B T}{1 - b\rho}, \quad b = \frac{2\pi}{3}d^3$$

and neglect the term of order ρ^3 in (14.17). The van der Waals parameter a becomes

$$a = k_B T \frac{2\pi}{9}d^3\lambda \left(\lambda + \frac{\alpha^2}{3} \right)$$

The critical point is found from (5.8):

$$\phi_c = \frac{1}{12} \approx 0.083 \quad (14.18)$$

$$\lambda_c(\alpha) = \lambda_c(0) \left[1 - \alpha^2 \frac{\sqrt{2}}{27} \right] \quad (14.19)$$

where

$$\lambda_c(0) = \frac{9}{2\sqrt{2}} \approx 3.182 \quad (14.20)$$

Thus, in the van der Waals limit the critical volume fraction in low fields is independent of H_{ext} , whereas the critical coupling constant weakly decreases with H_{ext} . This stems from the fact that the external field enhances effective attraction between particles, thereby making phase separation easier. In terms of the reduced density ρ^* and temperature $T^* = k_B T d^3/s^2 \equiv 1/\lambda$ these results read

$$\rho_c^*(\alpha) = \frac{1}{2\pi} \approx 0.159 \quad \text{for all (small) } \alpha \quad (14.21)$$

$$T_c^*(\alpha) = T_c^*(0) \left[1 + \alpha^2 \frac{\sqrt{2}}{27} + o(\alpha^4) \right], \quad T_c^*(0) = \frac{2\sqrt{2}}{9} \approx 0.314 \quad (14.22)$$

14.3 Magnetic subsystem in an arbitrary field.

High-temperature approximation

Partitioning the potential energy into reference and perturbative parts is not unique. In this section we discuss another decomposition scheme, which can be called a high-temperature approximation (HTA) [62], [19]. The external field in the HTA is included in the reference model, thus implying that it need not be weak, but can be arbitrary.

We define a reference model as a system of “independent” dipoles in an external field; quotation marks mean that the interparticle interaction is purely entropic (hard spheres). The reference potential energy reads:

$$U_0 = \sum_{i < j} u_{d,ij} + \sum_i u_{\text{ext},i}$$

The dipole–dipole interaction is considered a perturbation:

$$U_1 = \sum_{i < j} u_{ij}^{(\text{dd})}$$

The perturbation Mayer function

$$f_{ij} = \begin{cases} \exp(-\beta u_{ij}^{(\text{dd})}) - 1 & \text{for } r_{ij} > d \\ 0 & \text{for } r_{ij} < d \end{cases} \quad (14.23)$$

in this case depends on particle separation, and we can follow the standard route of the first-order perturbation theory described in Sect. 5.3.

The configuration integral is:

$$\frac{Q_m}{Q_0} = \int d\tilde{\mathbf{r}}^N \frac{e^{-\beta U_0}}{Q_0} \prod_{i < j} (1 + f_{ij})$$

where Q_0 is the configuration integral of the reference model. Assuming smallness of f_{ij} , we keep the first two terms of the product, neglecting the others:

$$\prod_{i < j} (1 + f_{ij}) \approx 1 + \sum_{i < j} f_{ij}$$

which yields for the free energy (cf. (5.19))

$$\mathcal{F} = \mathcal{F}_0 - \frac{k_B T}{2} \left(\frac{\rho}{4\pi} \right)^2 V \int d\mathbf{r}_{12} \int d\omega_1 d\omega_2 f_{12} g_2^0(r_{12}, \omega_1, \omega_2) \quad (14.24)$$

where $g_2^0(r_{12}, \omega_1, \omega_2)$ is the reference pair correlation function which in this case can be obtained in a straightforward manner.

14.3.1 Properties of the reference system

Independence of the spatial and angular coordinates of particles in the reference model implies that g_2^0 is a product of the hard-sphere correlation $g_d(r_{12})$ and the purely orientational correlation $\psi_2(\omega_1, \omega_2)$, which in turn is decoupled due to mutual independence in orientations of magnetic moments:

$$\psi_2(\omega_1, \omega_2) = \psi_1(\omega_1) \psi_1(\omega_2)$$

Here the probability $\psi_1(\omega)d\omega$ that a magnetic moment will be within the solid angle $(\omega, \omega + d\omega)$ is given by the Gibbs distribution $\psi_1(\omega) = c_1 \exp(\alpha \cos \theta)$, where the normalizing constant c_1 is found from the condition

$$\frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \psi_1(\theta) = 1$$

yielding $c_1 = \alpha / \sinh \alpha$. Thus,

$$g_2^0(r_{12}, \omega_1, \omega_2) = \left(\frac{\alpha}{\sinh \alpha} \right)^2 g_d(r_{12}) e_1 e_2 \quad (14.25)$$

where

$$e_i = e^{\alpha \cos \theta_i}, \quad i = 1, 2$$

Independence of the spatial and orientational degrees of freedom results in factorization of Q_0

$$Q_0 = Q_d \left[\int d\omega e^{\alpha \cos \theta} \right]^N \quad (14.26)$$

where Q_d is the configuration integral of hard spheres. The reference free energy becomes

$$\mathcal{F}_0 = \mathcal{F}_d - N k_B T \ln \left(\frac{4\pi \sinh \alpha}{\alpha} \right) \quad (14.27)$$

where the second term gives the free energy of the Langevin gas.

14.3.2 Free energy and magnetostatics

Expanding the Mayer function in (14.24) to the second order and replacing $g_d(r_{12})$ in the perturbative part by the step function $\Theta(r_{12} > d)$, we obtain:

$$\mathcal{F} = \mathcal{F}_0 + \Delta \mathcal{F}_1 + \Delta \mathcal{F}_2 \quad (14.28)$$

where

$$\Delta\mathcal{F}_1 = -\frac{k_B T}{2} \left(\frac{\rho}{4\pi}\right)^2 V (-\beta s^2) \left(\frac{\alpha}{\sinh \alpha}\right)^2 \\ \times \int_{r_{12} > d} d\mathbf{r}_{12} \frac{1}{r_{12}^3} \int d\omega_1 d\omega_2 D(1, 2) e_1 e_2 \quad (14.29)$$

and

$$\Delta\mathcal{F}_2 = -\frac{k_B T}{2} \left(\frac{\rho}{4\pi}\right)^2 V \left[\frac{1}{2}(\beta s^2)^2\right] \left(\frac{\alpha}{\sinh \alpha}\right)^2 \\ \times \int_{r_{12} > d} d\mathbf{r}_{12} \frac{1}{r_{12}^6} \int d\omega_1 d\omega_2 D^2(1, 2) e_1 e_2 \quad (14.30)$$

Integration over solid angles in $\Delta\mathcal{F}_1$ gives (see (B.11))

$$\left[\frac{4\pi \sinh \alpha}{\alpha} L(\alpha) \right]^2 (1 - 3 \cos^2 \theta_{12})$$

Since the container is a long cylinder with its axis along the external field, the long-range $1/r^3$ nature of (14.29) yields the de Gennes–Pincus integral (C.6), thus implying that

$$\Delta\mathcal{F}_1 = -\frac{2\pi}{3} k_B T V \rho^2 d^3 \lambda L^2(\alpha) \quad (14.31)$$

Simple but tedious integration over solid angles in $\Delta\mathcal{F}_2$ gives (see (B.10))

$$\int d\omega_1 d\omega_2 D^2 e_1 e_2 = \pi^2 (4a^2 + 2c^2 - 6c^2 \sin^2 \theta_{12} - 24a^2 \cos^2 \theta_{12} \\ + 36a^2 \cos^4 \theta_{12} + 9c^2 \sin^4 \theta_{12} + 36ac \cos^2 \theta_{12} \sin^2 \theta_{12}) \quad (14.32)$$

where

$$a = \frac{2}{\alpha} \sinh \alpha \left[1 - \frac{2}{\alpha} L(\alpha) \right], \quad c = \frac{4}{\alpha^2} \sinh \alpha L(\alpha)$$

$\Delta\mathcal{F}_2$ is short-range, so the spatial integration can be performed over a spherical volume $\int d\mathbf{r}_{12}$ to obtain

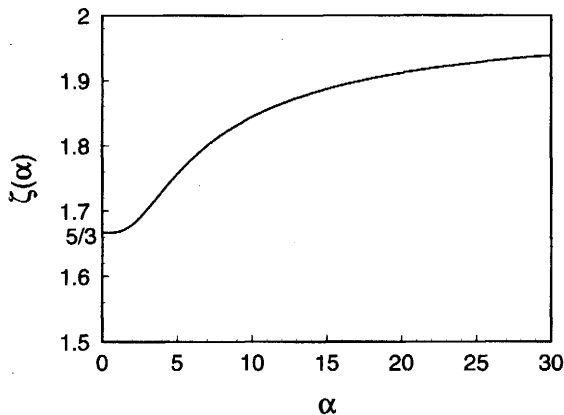
$$\Delta\mathcal{F}_2 = -\frac{2\pi}{15} k_B T V \rho^2 d^3 \lambda^2 \zeta(\alpha) \quad (14.33)$$

where

$$\zeta(\alpha) = 2 - 2 \left[\frac{L(\alpha)}{\alpha} \right] + 3 \left[\frac{L(\alpha)}{\alpha} \right]^2 \quad (14.34)$$

The function $\zeta(\alpha)$ shown in Fig. 14.4 increases monotonically from 5/3 as $\alpha \rightarrow 0$ to 2 as $\alpha \rightarrow \infty$. Substitution of (14.27), (14.31) and (14.33) into (14.28) yields the total free energy:

$$\mathcal{F} = \mathcal{F}_d - N k_B T \ln \left(\frac{4\pi \sinh \alpha}{\alpha} \right) - \frac{2\pi}{3} k_B T V \rho^2 d^3 \lambda L^2(\alpha) - \frac{2\pi}{15} k_B T V \rho^2 d^3 \lambda^2 \zeta(\alpha) \quad (14.35)$$

Fig. 14.4. Function $\zeta(\alpha)$

Differentiating $\mathcal{F}$ with respect to the field, we obtain the magnetization:

$$M = M_L \left[1 + \frac{4\pi}{3} \rho d^3 \lambda \left(\frac{1}{\alpha^2} - \frac{1}{\sinh^2 \alpha} \right) \right] + M_s \frac{2\pi}{15} \rho d^3 \lambda^2 \frac{\partial \zeta}{\partial \alpha} \quad (14.36)$$

Interparticle interaction enhances magnetization over the Langevin value M_L . We can rewrite this result in another useful form:

$$M = M_L \left[1 + 4\pi \chi_L \left(\frac{1}{\alpha^2} - \frac{1}{\sinh^2 \alpha} \right) \right] + M_s \frac{2\pi}{5} \chi_L \lambda \frac{\partial \zeta}{\partial \alpha} \quad (14.37)$$

Figure 14.5 shows the behavior of the reduced magnetization M/M_s as a function of α for $\rho^* = 0.2$ and two values of the coupling constant, $\lambda = 1$ and $\lambda = 3$.

Let us study HTA for low fields, where we must keep terms of order α^2 in the free energy. For small α

$$\zeta(\alpha) = \frac{5}{3} + o(\alpha^4) \quad (14.38)$$

implying that

$$\mathcal{F} = \mathcal{F}_d - N k_B T \ln(4\pi) - N k_B T \frac{\alpha^2}{6} - \frac{2\pi}{27} k_B T V \rho^2 d^3 \lambda \alpha^2 - \frac{2\pi}{9} k_B T V \rho^2 d^3 \lambda^2 \quad (14.39)$$

The last term has no effect on the low-field magnetization which reads:

$$M = M_L \left(1 + \frac{4\pi}{3} \chi_L \right)$$

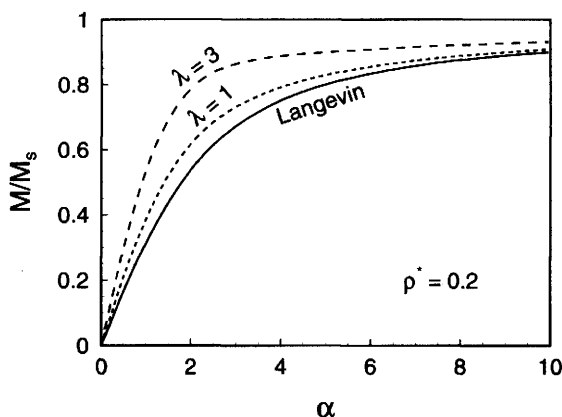


Fig. 14.5. Reduced magnetization M/M_s as a function of α for $\rho^* \equiv \rho d^3 = 0.2$ and two values of the coupling constant $\lambda = 1$ and $\lambda = 3$. Lowest curve corresponds to the Langevin case $M/M_s = L(\alpha)$

The initial susceptibility becomes

$$\chi_{\text{HTA}} = \chi_L \left(1 + \frac{4\pi}{3} \chi_L \right) \quad (14.40)$$

Thus, HTA intrinsically contains only the mean-field correction to the Langevin susceptibility. Its predictions are close to the MSA.

14.4 Perturbation approach for the solvent

In the cell model the solvent is represented by a collection of N identical cells; each cell being an elementary subsystem for which we can formulate a perturbation approach. Molecules in the cell experience the “external field” of a particle located in its center. Decomposition of a cell energy $\bar{U}_\Delta = \bar{U}_{\Delta,0} + \bar{U}_{\Delta,1}$ can be obtained in the following way. First we split the energy of a molecule in this field $u^{(\text{fs})}$ into the repulsive and attractive parts:

$$u^{(\text{fs})} = u_+^{(\text{fs})} + u_-^{(\text{fs})}$$

The repulsive part $u_+^{(\text{fs})}$ is included in the reference model as well as the intermolecular interactions:

$$\bar{U}_{\Delta,0} = \sum_{\alpha < \gamma} 'u_{\alpha\gamma}^{(\text{ss})} + \sum_{\alpha} 'u_{\alpha,+}^{(\text{fs})}$$

This reference model is known in the literature as a “molecular system at an ideal hard wall” [42]. Such a choice ensures convergence of the perturbation series. The attractive part $u_-^{(\text{fs})}$ is considered a perturbation:

$$\bar{U}_{\Delta,1} = \sum_{\alpha} u_{\alpha,-}^{(\text{fs})}$$

We proceed by using the algebraic technique of Sect. 5.7, which yields for the free energy of a cell

$$\mathcal{F}_{\Delta} = \mathcal{F}_{\Delta,0} - k_B T \left[\sum_{n=1}^{\infty} \frac{\rho_s^n}{n!} b_{\Delta,n} \right] \quad (14.41)$$

where $\mathcal{F}_{\Delta,0}$ is the free energy of the reference cell model and $b_{\Delta,n}$ has the structure described in Sect. 5.7. The total free energy of the solvent becomes $\mathcal{F}_s = N\mathcal{F}_{\Delta}$.

A. Empirical correlations for macroscopic properties of argon, benzene and *n*-nonane

In this section we present empirical correlations for the saturation vapor pressure p_{sat} , the equilibrium liquid number density ρ^l , and the surface tension γ_0 for argon, benzene and *n*-nonane, used in calculations of the Tolman length from (11.25).

The saturation vapor pressure, p_{sat} , for all of these substances has the form [119]

$$\ln \frac{p_{\text{sat}}}{p_c} = (1 - |t|)^{-1} [a|t| + b|t|^{1.5} + c|t|^3 + d|t|^4] \quad (\text{A.1})$$

where

$$t = \frac{T - T_c}{T_c}$$

is the reduced temperature, and the values of parameters a , b , c , and d are given in Table A.1.

Table A.1. Thermophysical properties of argon, benzene and *n*-nonane [119]. p_c : critical pressure in bar; T_c : critical temperature in K; ρ_c : critical number density in mol/cm³; T_b : normal boiling point in K; σ : molecular diameter in Å; a , b , c , d : parameters of the saturation vapor pressure (A.1)

	p_c	T_c	ρ_c^{-1}	T_b	σ	a	b	c	d
argon	48.7	150.8	74.9	87.3	3.542	-5.90501	1.12627	-0.76787	-1.62721
benzene	48.9	562.2	259.	353.2	5.349	-6.98273	1.33213	-2.62863	-3.33399
<i>n</i> -nonane	22.9	594.6	548.	424.	6.567	-8.24480	1.57885	-4.38155	-4.04412

The liquid mass densities ρ_m^l (g/cm³) of the compounds are

- argon [59]

$$\rho_m^l = 1.37396 [1 - 4.65 \times 10^{-3}(t_{\text{Cels}} + 183.15)]$$

- benzene [59]:

$$\rho_m^l = 0.90005 - 1.0636 \times 10^{-3}t_{\text{Cels}} - 0.0376 \times 10^{-6}t_{\text{Cels}}^2 - 2.213 \times 10^{-9}t_{\text{Cels}}^3$$

- *n*-nonane [58]:

$$\rho_m^l = 0.733503 - 7.87562 \times 10^{-4} t_{\text{Cels}} - 9.68937 \times 10^{-8} t_{\text{Cels}}^2 - 1.29616 \times 10^{-9} t_{\text{Cels}}^3$$

where t_{Cels} is Celsius temperature. The number density is expressed via the mass density as

$$\rho^l = \frac{\rho_m^l N_A}{M}$$

where M (g/mol) is a molar mass and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ Avogadro's number.

A widely used correlation for the macroscopic (planar) surface tension of nonpolar fluids reads [119]

$$\gamma_0(t) = A_\gamma |t|^{1.26} \quad (\text{A.2})$$

$$A_\gamma = p_c^{2/3} T_c^{1/3} B_\gamma, \quad B_\gamma = 0.1196 \left[1 + \frac{T_{\text{br}} \ln(p_c/1.01325)}{1 - T_{\text{br}}} \right] - 0.279 \quad (\text{A.3})$$

Here A_γ is in dyn/cm, p_c is in bars, $T_{\text{br}} = T_b/T_c$, T_b is the normal boiling point in K. Values of T_c , T_b , and p_c are given in Table A.1.

B. Angular dipole integrals

We present here angular dipole integrals used in Chap. 14. The following notation is used:

$$D \equiv D(1, 2) = \hat{\mathbf{s}}_1 \hat{\mathbf{s}}_2 - 3(\hat{\mathbf{s}}_1 \hat{\mathbf{r}}_{12})(\hat{\mathbf{s}}_2 \hat{\mathbf{r}}_{12})$$

$$\Delta \equiv \Delta(1, 2) = \hat{\mathbf{s}}_1 \hat{\mathbf{s}}_2$$

$$L(\alpha) = \coth \alpha - \frac{1}{\alpha} \quad \text{is the Langevin function}$$

$$a = \frac{2}{\alpha} \sinh \alpha \left[1 - \frac{2}{\alpha} L(\alpha) \right], \quad c = \frac{4}{\alpha^2} \sinh \alpha L(\alpha)$$

$$\int d\omega_1 d\omega_2 = \int_0^{2\pi} d\phi_1 \int_0^\pi \sin \theta_1 d\theta_1 \int_0^{2\pi} d\phi_2 \int_0^\pi \sin \theta_2 d\theta_2$$

$$\int d\omega_1 d\omega_2 D = 0 \tag{B.1}$$

$$\int d\omega_1 d\omega_2 \Delta = 0 \tag{B.2}$$

$$\int d\omega_1 d\omega_2 D^2 = 6 \left(\frac{4\pi}{3} \right)^2 \tag{B.3}$$

$$\int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 D^2 = 0 \tag{B.4}$$

$$\int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 D = \left(\frac{4\pi}{3} \right)^2 (1 - 3 \cos^2 \theta) \tag{B.5}$$

$$\int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 \Delta = \left(\frac{4\pi}{3} \right)^2 \tag{B.6}$$

$$\int d\omega_1 d\omega_2 D \Delta = 0 \tag{B.7}$$

$$\int d\omega_1 d\omega_2 \Delta^2 e^{\alpha \cos \theta_1} e^{\alpha \cos \theta_2} = 2\pi^2 (2a^2 + c^2) \tag{B.8}$$

$$\int d\omega_1 d\omega_2 e^{\alpha \cos \theta_1} e^{\alpha \cos \theta_2} \Delta = \left[\frac{4\pi \sinh \alpha}{\alpha} L(\alpha) \right]^2 \quad (\text{B.9})$$

$$\begin{aligned} \int d\omega_1 d\omega_2 D^2 e^{\alpha \cos \theta_1} e^{\alpha \cos \theta_2} &= \pi^2 (4a^2 + 2c^2 - 6c^2 \sin^2 \theta_{12} - 24a^2 \cos^2 \theta_{12} \\ &+ 36a^2 \cos^4 \theta_{12} + 9c^2 \sin^4 \theta_{12} + 36ac \cos^2 \theta_{12} \sin^2 \theta_{12}) \end{aligned} \quad (\text{B.10})$$

$$\int d\omega_1 d\omega_2 e^{\alpha \cos \theta_1} e^{\alpha \cos \theta_2} D = \left[\frac{4\pi \sinh \alpha}{\alpha} L(\alpha) \right]^2 (1 - 3 \cos^2 \theta_{12}) \quad (\text{B.11})$$

where θ_{12} is the angle between vector $\mathbf{r}_{12}$ and the z axis.

C. De Gennes–Pincus integral

We calculate the integral

$$I_{\text{GP}} = \int_{r>d}^{\text{cyl}} d\mathbf{r} \frac{1 - 3 \cos^2 \theta}{r^3} \quad (\text{C.1})$$

which first appeared in the paper of de Gennes and Pincus [48] in connection with their derivation of the second virial coefficient of a ferrofluid. The superscript “cyl” means integration over an infinitely long cylinder; θ is the angle between $\mathbf{r}$ and the cylinder axis. Since I_{GP} is dimensionless, we can scale all distances by d to obtain

$$I_{\text{GP}} = \int_{r>1}^{\text{cyl}} d\mathbf{r} \frac{1 - 3 \cos^2 \theta}{r^3} \quad (\text{C.2})$$

First of all, we note that for a spherical region, angular integration (in spherical coordinates) results in

$$\int_0^\pi d\theta \sin \theta (1 - 3 \cos^2 \theta) = 0$$

but this is not the case if the domain is an infinitely long cylinder. In cylindrical coordinates (p, ϕ, z)

$$r = (p^2 + z^2)^{1/2}, \quad \cos \theta = z/(p^2 + z^2)^{1/2}$$

and the integrand in (C.2), which we denote by $F(p, z)$, becomes

$$F(p, z) = \frac{1}{(p^2 + z^2)^{3/2}} - \frac{3z^2}{(p^2 + z^2)^{5/2}}$$

and

$$I_{\text{GP}} = \pi \lim_{A \rightarrow \infty} \int_{-\infty}^{\infty} dz \int_0^{A^2} d(p^2) F(p, z)$$

$F(p, z)$ is an even function of both arguments implying that

$$I_{\text{GP}} = 2\pi \lim_{A \rightarrow \infty} \int_0^\infty dz \int d(p^2) F(p, z) \quad (\text{C.3})$$

Indefinite integration in the internal integral gives

$$\int d(p^2) F(p, z) = -2(p^2 + z^2)^{-1/2} + 2z^2(p^2 + z^2)^{-3/2} \quad (\text{C.4})$$

To satisfy the condition $r > 1$ in cylindrical coordinates, we split the integration over dz into $\int_0^1 dz$ and $\int_1^\infty dz$:

$$I_{\text{GP}} = 2\pi \lim_{A \rightarrow \infty} \left[\int_0^1 dz \int_{1-z^2}^{A^2} d(p^2) F(p, z) + \int_1^\infty dz \int_0^{A^2} d(p^2) F(p, z) \right] \quad (\text{C.5})$$

Using (C.4), we find that the first term is

$$\int_{1-z^2}^{A^2} d(p^2) F(p, z) = 2 \left[(1 - z^2) - (A^2 + z^2)^{-1/2} + z^2(A^2 + z^2)^{-3/2} \right]$$

while the second yields

$$\int_0^{A^2} d(p^2) F(p, z) = 2 \left[-(A^2 + z^2)^{-1/2} + z^2(A^2 + z^2)^{-3/2} \right]$$

Substitution of these results into (C.5) yields

$$I_{\text{GP}} = 4\pi \lim_{A \rightarrow \infty} \left\{ \int_0^1 dz (1 - z^2) + \int_0^\infty dz \left[\frac{z^2}{(A^2 + z^2)^{3/2}} - \frac{1}{(A^2 + z^2)^{1/2}} \right] \right\}$$

After simple algebra we obtain

$$I_{\text{GP}} = 4\pi \left[\frac{2}{3} - \int_0^\infty dx \frac{1}{(1 + x^2)^{3/2}} \right], \quad x \equiv \frac{z}{A}$$

where the last integral equals unity. The final result reads

$$I_{\text{GP}} \equiv \int_{r>1}^{\text{cyl}} d\mathbf{r} \frac{1 - 3 \cos^2 \theta}{r^3} = -\frac{4\pi}{3} \quad (\text{C.6})$$

D. Calculation of γ_D and γ_Δ in the algebraic perturbation theory

In this Appendix we calculate the three-body integrals γ_D and γ_Δ (Eqs. (12.33) and (12.36)) in the algebraic perturbation theory for the polar fluids of Sect. 12. Since both are dimensionless we scale all distances by the hard-sphere diameter d . Placing the origin of the coordinate system in point 1, we replace $d\mathbf{r}_3$ by $d\mathbf{r}_{13}$:

$$\gamma_D = \int d\mathbf{r}_{12} (1 - 3 \cos^2 \theta_{12}) a_D \quad (\text{D.1})$$

$$a_D = \int d\mathbf{r}_{13} \frac{1 + 3 \cos \alpha_1 \cos \alpha_2 \cos \alpha_3}{(r_{13} r_{23})^3} \prod_{i < j} \Theta(r_{ij} - 1) \quad (\text{D.2})$$

$$\gamma_\Delta = \int d\mathbf{r}_{12} a_\Delta \quad (\text{D.3})$$

$$a_\Delta = \int d\mathbf{r}_{13} \frac{3 \cos^2 \alpha_3 - 1}{(r_{13} r_{23})^3} \prod_{i < j} \Theta(r_{ij} - 1) \quad (\text{D.4})$$

where $\Theta(x)$ is the step function.

Note that if the dependence on particle separation is short-range, it is possible to replace integration over a cylinder (which is the assumed form of the container) by integration over a sphere. This follows from the general statement (which can be straightforwardly proven) that

$$\int_{r>1}^{\text{sphere}} d\mathbf{r} \frac{1}{r^m} = \int_{r>1}^{\text{cyl}} d\mathbf{r} \frac{1}{r^m} = \frac{4\pi}{m-3} \quad \text{for all } m > 3$$

(so $m = 3$ is indeed a special case, giving different results for a sphere and a cylinder). To simplify notation we set

$$\mathbf{r}_{12} = \mathbf{R}, \quad \mathbf{r}_{13} = \mathbf{r}, \quad \mathbf{r}_{23} = \mathbf{x}, \quad \cos \alpha_1 = \mu$$

and choose the z -axis to be along $\mathbf{r}_{12}$ (see Fig. D.1). Then all the elements of the 123-triangle are expressed in terms of R , r and μ :

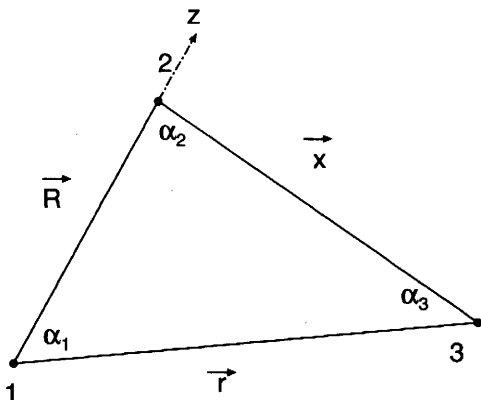


Fig. D.1. Three-particle configuration

$$x = \sqrt{R^2 + r^2 - 2rR\mu} \quad (\text{D.5})$$

$$\cos \alpha_2 = \frac{R - r\mu}{x} \quad (\text{D.6})$$

$$\cos \alpha_3 = \frac{r - R\mu}{x} \quad (\text{D.7})$$

The volume element $d\mathbf{r}_{13}$ becomes:

$$d\mathbf{r} = -2\pi r^2 dr d\mu$$

D.1 Calculation of γ_D

We start with the function a_D , which after substitution of (D.5)–(D.7) reads

$$a_D = 2\pi \int dr \frac{1}{r} \int_{-1}^1 d\mu f_D(r, R, \mu) \Theta(R > 1) \Theta(r > 1) \Theta(x(r, R, \mu) > 1)$$

with

$$f_D = \frac{1}{x^5} [(r^2 + R^2)(1 - 3\mu^2) + \mu r R(1 + 3\mu^2)]$$

The condition $x > 1$ can be written using (D.5) as

$$\mu < h \equiv \frac{r^2 + R^2 - 1}{2rR} \quad (\text{D.8})$$

Since both r and R are larger than unity, h is always positive. By definition μ is cosine, therefore its values are limited by $-1 < \mu < 1$. Thus, two cases are possible:

- $h > 1$, implying that integration over μ is from -1 to 1 , and
- $h < 1$, implying that integration over μ is from -1 to h

The first case makes no contribution to γ_D because

$$\int_{-1}^1 d\mu f_D = 0$$

(the easiest way to verify this is by means of one of the symbolic calculations software, e.g. *Mathematica*). Thus, $h < 1$, or equivalently $|r - R| < 1$. For a fixed R this determines the domain of r :

$$R - 1 < r < R + 1, \quad \text{if } R > 2$$

and

$$1 < r < R + 1, \quad \text{if } 1 < R < 2$$

Hence,

$$\gamma_D = \int_{1 < R < 2} d\mathbf{r} a_D(R) (1 - 3 \cos^2 \theta_R) + \int_{R > 2} d\mathbf{r} a_D(R) (1 - 3 \cos^2 \theta_R) \quad (\text{D.9})$$

where we denoted $\theta_R \equiv \theta_{12}$. Integration in the first term is over a finite domain, and therefore can be performed in spherical coordinates, yielding zero:

$$\int_0^\pi d\theta_R \sin \theta_R (1 - 3 \cos^2 \theta_R) = 0$$

Thus, the only nontrivial contribution comes from the second term, in which

$$a_D(R) = 2\pi \int_{R-1}^{R+1} dr \frac{1}{r} \int_{-1}^h d\mu f_D(r, R, \mu)$$

Integrating these algebraic functions we find that $a_D(R)$ is long-range:

$$a_D(R) = \frac{8\pi}{3} \frac{1}{R^3} \quad (\text{D.10})$$

Substituting it into (D.9) we obtain an integral of de Gennes–Pincus type (C.1):

$$\gamma_D = \frac{8\pi}{3} \int_{R>1} d\mathbf{r} \frac{1}{R^3} (1 - 3 \cos^2 \theta_R)$$

where integration domain is extended to $R > 1$ (contribution of the interval $1 < R < 2$ is zero). Using (C.6) we obtain

$$\gamma_D = -\frac{32}{9} \pi^2 \quad (\text{D.11})$$

D.2 Calculation of γ_Δ

The function a_Δ in (D.4) reads

$$a_\Delta = 2\pi \int dr \frac{1}{r} \int_{-1}^{\infty} d\mu f_\Delta(r, R, \mu) \Theta(R > 1) \Theta(r > 1) \Theta(x(r, R, \mu) > 1)$$

with

$$f_\Delta = \frac{1}{x^5} [(2r^2 - 4rR\mu + R^2(3\mu^2 - 1))]$$

As in D.1 the condition $x > 1$ can be expressed in the form of (D.8). Let us begin with dividing the R -domain into $1 < R < 2$ and $R > 2$.

D.2.1 Short-range part: $1 < R < 2$

As previously we proceed by discussing two possibilities:

- $h > 1$, implying that integration over μ is from -1 to 1
- $h < 1$, implying that integration over μ is from -1 to h

The case $h > 1$ implies that $r > R + 1$. Integration over μ gives

$$\int_{-1}^1 d\mu f_\Delta(r, R, \mu) = \frac{2}{r^3} \left(\frac{|r - R|}{r - R} + 1 \right) \quad (\text{D.12})$$

which for $r > R + 1$ results in

$$\int_{-1}^1 d\mu f_\Delta(r, R, \mu) = \frac{4}{r^3}, \quad r > R + 1$$

Its contribution to a_Δ is

$$a_{\Delta, h > 1}^{(1 < R < 2)} = 8\pi \int_{R+1}^{\infty} dr \frac{1}{r^4} = \frac{8\pi}{3} \frac{1}{(R+1)^3} \quad (\text{D.13})$$

The opposite case $h < 1$ implies that $1 < r < R + 1$. Integration over μ gives

$$\int_{-1}^h d\mu f_\Delta(r, R, \mu) = \frac{1}{4r^3 R} (-3 + 2r^2 + r^4 + 8R - 6R^2 - 2r^2 R^2 + R^4) \quad (\text{D.14})$$

Contribution to a_Δ becomes

$$\begin{aligned} a_{\Delta, h < 1}^{(1 < R < 2)} &= 2\pi \int_1^{R+1} dr \frac{1}{r} \int_{-1}^h d\mu f_\Delta \\ &= 2\pi \frac{R}{12(1+R)^3} (36 + 12R - 19R^2 - 9R^3 + 3R^4 + R^5) \end{aligned} \quad (\text{D.15})$$

Hence,

$$a_{\Delta, h>1}^{(1<R<2)} + a_{\Delta, h<1}^{(1<R<2)} = 2\pi \left(\frac{4}{3} - R + \frac{R^3}{12} \right)$$

and the corresponding contribution to γ_Δ is

$$\gamma_\Delta^{(1<R<2)} = \frac{17}{9}\pi^2 \quad (\text{D.16})$$

D.2.2 Long-range part: $2 < R < \infty$

We follow the same route first studying the case $h > 1$, which now can be realized for r belonging to one of the two domains

$$r > R + 1 \quad \text{and/or} \quad 1 < r < R - 1$$

According to (D.12), integration over μ yields

$$\int_{-1}^1 d\mu f_\Delta(r, R, \mu) = \frac{4}{r^3}, \quad \text{for } r > R + 1$$

and

$$\int_{-1}^1 d\mu f_\Delta(r, R, \mu) = 0, \quad \text{for } 1 < r < R - 1$$

Thus,

$$a_{\Delta, h>1}^{(R>2)} = a_{\Delta, h>1}^{(1<R<2)} = \frac{8\pi}{3} \frac{1}{(R+1)^3}$$

For $h < 1$ we use (D.14) to obtain

$$a_{\Delta, h<1}^{(R>2)} = 2\pi \int_{R-1}^{R+1} dr \frac{1}{r} \int_{-1}^h d\mu f_\Delta = -\frac{8\pi}{3} \frac{1}{(R+1)^3}$$

The long-range quantities $a_{\Delta, h>1}^{(R>2)}$ and $a_{\Delta, h<1}^{(R>2)}$ cancel:

$$a_{\Delta, h>1}^{(R>2)} + a_{\Delta, h<1}^{(R>2)} = 0$$

yielding¹

$$\gamma_\Delta = \frac{17}{9}\pi^2 \quad (\text{D.17})$$

¹ Note that the same results for γ_D and γ_Δ can be derived using the “Fourier-transform-convolution method” of Høye and Stell [57], [136].

E. Mixtures of hard spheres

This appendix summarizes the relations describing the thermodynamic properties of a binary mixture of hard spheres [98], [121], [95]. The diameters of the components are d_1 and d_2 ; their respective number densities are ρ_1 and ρ_2 .

E.1 Pressure

We start with defining the first three “moments” of the hard-sphere diameters:

$$\begin{aligned}R_I &= d_I/2 \\ A_I &= \pi d_I^2 \\ V_I &= \pi d_I^3/6\end{aligned}$$

Note that A_I can be regarded as a molecular surface area, whereas V_I denotes the molecular volume of component I . Next, the parameters $\xi^{(k)}$ are defined as

$$\begin{aligned}\xi^{(0)} &= \rho_1 + \rho_2 \\ \xi^{(1)} &= \rho_1 R_1 + \rho_2 R_2 \\ \xi^{(2)} &= \rho_1 A_1 + \rho_2 A_2 \\ \xi^{(3)} &= \rho_1 V_1 + \rho_2 V_2.\end{aligned}$$

Note that $\xi^{(3)}$ is the total volume fraction occupied by hard spheres. For notational convenience, we also introduce

$$\eta = 1 - \xi^{(3)}.$$

On the basis of $\xi^{(k)}$, new parameters $c^{(k)}$ are calculated according to

$$\begin{aligned}
c^{(0)} &= -\ln \eta \\
c^{(1)} &= \frac{\xi^{(2)}}{\eta} \\
c^{(2)} &= \frac{\xi^{(1)}}{\eta} + \frac{(\xi^{(2)})^2}{8\pi\eta^2} \\
c^{(3)} &= \frac{\xi^{(0)}}{\eta} + \frac{\xi^{(1)}\xi^{(2)}}{\eta^2} + \frac{(\xi^{(2)})^3}{12\pi\eta^3}.
\end{aligned}$$

The pressure p_d of the hard-sphere mixture follows from

$$p_3 = c^{(3)} k_B T \quad (\text{E.1})$$

$$p_2 = p_3 - \frac{(\xi^{(2)})^3 \xi^{(3)}}{12\pi\eta^3} k_B T \quad (\text{E.2})$$

$$p_d = \frac{2p_3 + p_2}{3}. \quad (\text{E.3})$$

E.2 Chemical potentials

Let us introduce for brevity of notation two additional quantities:

$$\begin{aligned}
Y^{(1)} &= 3 \left[\frac{1 - \frac{3}{2}\xi^{(3)}}{\eta^2} + \frac{\ln \eta}{\xi^{(3)}} \right] \\
Y^{(2)} &= \frac{\xi^{(2)}}{6\xi^{(3)}} \left[\frac{\eta + (1 - 2\xi^{(3)})^2}{\eta^3} + \frac{2 \ln \eta}{\xi^{(3)}} \right].
\end{aligned}$$

The chemical potentials $\mu_{d,I}$ can be derived from the virial equation using standard thermodynamic relationships:

$$\mu_I^{(3)} = c^{(0)} + c^{(1)} R_I + c^{(2)} A_I + c^{(3)} V_I \quad (\text{E.4})$$

$$\mu_I^{(2)} = \mu_I^{(3)} + \frac{(R_I \xi^{(2)})^2}{3\xi^{(3)}} \left(Y^{(1)} - 2R_I Y^{(2)} \right) \quad (\text{E.5})$$

$$\mu_I^{\text{ex}} = k_B T \frac{2\mu_I^{(3)} + \mu_I^{(2)}}{3} \quad (\text{E.6})$$

$$\mu_{d,I} = k_B T \left[\ln (\rho_I \Lambda_I^3) \right] + \mu_I^{\text{ex}} \quad (\text{E.7})$$

The last expression presents the chemical potential of a species as a sum of an ideal and excess contributions.

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