Phase Transition Dynamics

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Contents

1

Spin systems and fluids

To study equilibrium statistical physics, we will start with Ising spin systems (hereafter referred to as Ising systems), because they serve as important reference systems in understanding various phase transitions [1]–[7].[1] We will then proceed to one- and two-component fluids with short-range interaction, which are believed to be isomorphic to Ising systems with respect to static critical behavior. We will treat equilibrium averages of physical quantities such as the spin, number, and energy density and then show that thermodynamic derivatives can be expressed in terms of fluctuation variances of some density variables. Simple examples are the magnetic susceptibility in Ising systems and the isothermal compressibility in one-component fluids expressed in terms of the correlation function of the spin and density, respectively. More complex examples are the constant-volume specific heat and the adiabatic compressibility in one- and two-component fluids. For our purposes, as far as the thermodynamics is concerned, we need equal-time correlations only in the long-wavelength limit. These relations have not been adequately discussed in textbooks, and must be developed here to help us to correctly interpret various experiments of thermodynamic derivatives. They will also be used in dynamic theories in this book. We briefly summarize equilibrium thermodynamics in the light of these equilibrium relations for Ising spin systems in Section 1.1, for one-component fluids in Section 1.2, and for binary fluid mixtures in Section 1.3.

1.1 Spin models

1.1.1 Ising hamiltonian

Let each lattice point of a crystal lattice have two microscopic states. It is convenient to introduce a spin variable s_i, which assumes the values 1 or -1 at lattice point i. The microscopic energy of this system, called the Ising spin hamiltonian, is composed of the exchange interaction energy and the magnetic field energy,

$$\mathcal{H}\{s\} = \mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{mag}}, \tag{1.1.1}$$

where

$$\mathcal{H}_{\text{ex}} = -\sum_{<i,j>} J s_i s_j, \tag{1.1.2}$$

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[1] References are to be found at the end of each chapter.

$$\mathcal{H}_{\rm mag} = -H \sum_i s_i . \tag{1.1.3}$$

The interaction between different spins is short-ranged and the summation in $\mathcal{H}_{\rm ex}$ is taken over the nearest neighbor pairs i, j of the lattice points. The interaction energy between spins is then $-J$ if paired spins have the same sign, while it is J for different signs. In the case $J > 0$ the interaction is ferromagnetic, where all the spins align in one direction at zero temperature. The magnetic field H is scaled appropriately such that it has the dimension of energy. At zero magnetic field the system undergoes a second-order phase transition at a critical temperature $T_{\rm c}$. The hamiltonian $\mathcal{H}$ mimics ferromagnetic systems with uniaxial anisotropy.

In the case $J < 0$, the interaction is antiferromagnetic, where the neighboring paired spins tend to be antiparallel at low temperatures. Let us consider a cubic lattice, which may be divided into two sublattices, A and B, such that each lattice point and its nearest neighbors belong to different sublattices. Here, we define the staggered spin variables S_i by

$$S_i = s_i \quad (i \in A), \qquad S_i = -s_i \quad (i \in B). \tag{1.1.4}$$

Then, $\mathcal{H}_{\rm ex}$ in terms of $\{S_i\}$ has the positive coupling $|J|$ and is isomorphic to the ferromagnetic exchange hamiltonian.

The Ising model may also describe a phase transition of binary alloys consisting of atoms 1 and 2, such as Cu–Zn alloys. If each lattice point i is occupied by a single atom of either of the two species, the occupation numbers n_{1i} and n_{2i} satisfy $n_{1i} + n_{2i} = 1$. Vacancies and interstitials are assumed to be nonexistent. If the nearest neighbor pairs have an interaction energy ϵ_{KL} $(K, L = 1, 2)$, the hamiltonian is written as

$$\mathcal{H}\{n\} = \sum_{<i,j>} \sum_{K,L} \epsilon_{KL} n_{Ki} n_{Lj} - \sum_i \sum_K \mu_K n_{Ki}, \tag{1.1.5}$$

where μ_1 and μ_2 are the chemical potentials of the two components. From (1.1.4) we may introduce a spin variable,

$$s_i = 2n_{1i} - 1 = 1 - 2n_{2i}, \tag{1.1.6}$$

to obtain the Ising model (1.1.1) with

$$J = \frac{1}{4}(-\epsilon_{11} - \epsilon_{22} + 2\epsilon_{12}), \qquad H = \frac{1}{2}(\mu_1 - \mu_2) - \frac{z}{4}(\epsilon_{11} - \epsilon_{22}), \tag{1.1.7}$$

where z is the number of nearest neighbors with respect to each lattice point and is called the coordination number.

1.1.2 Vector spin models

Many variations of spin models defined on lattices have been studied in the literature [8]. If the spin $\boldsymbol{s}_i = (s_{1i}, \ldots, s_{ni})$ on each lattice point is an n-component vector, its simplest hamiltonian reads

$$\mathcal{H}\{\boldsymbol{s}\} = -\sum_{<i,j>} J\boldsymbol{s}_i \cdot \boldsymbol{s}_j - H\sum_i s_{1i}. \tag{1.1.8}$$

The first term, the exchange interaction, is assumed to be invariant with respect to rotation in the spin space. The magnetic field H favors ordering of the first spin components s_{1i}. The model with $n = 2$ is called the xy model, and the model with $n = 3$ the Heisenberg model. It is known that the static critical behavior of the three-dimensional xy model is isomorphic to that of ^{4}He and ^{3}He–^{4}He mixtures near the superfluid transition, as will be discussed later. However, there are many cases in which there is some anisotropy in the spin space and, if one direction is energetically favored, the model reduces to the Ising model asymptotically close to the critical point. Such anisotropy becomes increasingly important near the critical point (or *relevant* in the terminology of renormalization group theory). As another relevant perturbation, we may introduce a long-range interaction such as a dipolar interaction.

1.1.3 Thermodynamics of Ising models

Each microscopic state of the Ising system is determined if all the values of spins $\{s\}$ are given. In thermal equilibrium, the probability of each microscopic state being realized is given by the Boltzmann weight,

$$P_{\text{eq}}(\{s\}) = Z^{-1}\exp(-\beta\mathcal{H}\{s\}), \tag{1.1.9}$$

where

$$\beta = 1/T. \tag{1.1.10}$$

In this book the absolute temperature multiplied by the Boltzmann constant $k_{\text{B}} = 1.381 \times 10^{-16}$ erg/K is simply written as T and is called the temperature [1], so T has the dimension of energy. The normalization factor Z in (1.1.9) is called the partition function,

$$Z = \sum_{\{s\}} \exp(-\beta\mathcal{H}\{s\}), \tag{1.1.11}$$

where the summation is taken over all the microscopic states. The differential form for the logarithm $\ln Z$ becomes

$$d(\ln Z) = -\langle\mathcal{H}\rangle d\beta + \beta\langle\mathcal{M}\rangle dH = -\langle\mathcal{H}_{\text{ex}}\rangle d\beta + \langle\mathcal{M}\rangle dh, \tag{1.1.12}$$

where the increments are infinitesimal,

$$h = \beta H = H/T, \tag{1.1.13}$$

and $\mathcal{M}$ is the sum of the total spins,[2]

$$\mathcal{M} = \sum_i s_i. \tag{1.1.14}$$

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[2] In this book the quantities, $\mathcal{H}$, $\mathcal{M}$, $\mathcal{N}, \ldots$ in script, are fluctuating variables (dependent on the microscopic degrees of freedom) and not thermodynamic ones.

Hereafter $\langle\cdots\rangle$ is the average over the Boltzmann distribution (1.1.9). The usual choice of the thermodynamic potential is the free energy,

$$F = -T\ln Z, \tag{1.1.15}$$

and the independent intensive variables are T and H with

$$dF = -SdT - \langle\mathcal{M}\rangle dH, \tag{1.1.16}$$

where $S = (\langle\mathcal{H}\rangle - F)/T$ is the entropy of the system.

We also consider the small change of the microscopic canonical distribution in (1.1.9) for small changes, $\beta \to \beta + \delta\beta$ and $h \to h + \delta h$. Explicitly writing its dependences on β and h, we obtain

$$P_{\text{eq}}(\{s\};\beta+\delta\beta, h+\delta h) = P_{\text{eq}}(\{s\};\beta, h)\exp\big[-\delta\mathcal{H}_{\text{ex}}\delta\beta + \delta\mathcal{M}\delta h + \cdots\big], \tag{1.1.17}$$

where $\delta\mathcal{H}_{\text{ex}} = \mathcal{H}_{\text{ex}} - \langle\mathcal{H}_{\text{ex}}\rangle$ and $\delta\mathcal{M} = \mathcal{M} - \langle\mathcal{M}\rangle$. To linear order in $\delta\beta$ and δh, the change of the distribution is of the form,

$$\delta P_{\text{eq}}(\{s\}) = P_{\text{eq}}(\{s\})\big[-\delta\mathcal{H}_{\text{ex}}\delta\beta + \delta\mathcal{M}\delta h + \cdots\big]. \tag{1.1.18}$$

Therefore, the average of any physical variable $\mathcal{A} = \mathcal{A}\{s\}$ dependent on the spin configurations is altered with respect to the change (1.1.18) as

$$\delta\langle\mathcal{A}\rangle = -\langle\mathcal{A}\delta\mathcal{H}_{\text{ex}}\rangle\delta\beta + \langle\mathcal{A}\delta\mathcal{M}\rangle\delta h + \cdots. \tag{1.1.19}$$

We set $\mathcal{A} = \mathcal{M}$ and $\mathcal{H}_{\text{ex}}$ to obtain

$$V\chi = \frac{\partial^2 \ln Z}{\partial h^2} = \frac{\partial\langle\mathcal{M}\rangle}{\partial h} = \langle(\delta\mathcal{M})^2\rangle, \tag{1.1.20}$$

$$\frac{\partial^2 \ln Z}{\partial\beta^2} = -\frac{\partial\langle\mathcal{H}_{\text{ex}}\rangle}{\partial\beta} = \langle(\delta\mathcal{H}_{\text{ex}})^2\rangle, \tag{1.1.21}$$

$$\frac{\partial^2 \ln Z}{\partial h\partial\beta} = \frac{\partial\langle M\rangle}{\partial\beta} = -\frac{\partial\langle\mathcal{H}_{\text{ex}}\rangle}{\partial h} = -\langle\delta\mathcal{M}\delta\mathcal{H}_{\text{ex}}\rangle, \tag{1.1.22}$$

where V is the volume of the system, χ is the isothermal magnetic susceptibility per unit volume, h and β are treated as independent variables, and use has been made of (1.1.12). Another frequently discussed quantity is the specific heat C_H at constant magnetic field defined by[3]

$$C_H = \frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_H = \frac{1}{V}\left(\frac{\partial\langle\mathcal{H}\rangle}{\partial T}\right)_H. \tag{1.1.23}$$

Here we use $-(\partial\langle\mathcal{H}\rangle/\partial\beta)_H = (\partial^2\ln Z/\partial\beta^2)_H$ to obtain

$$C_H = \langle(\delta\mathcal{H})^2\rangle/T^2V. \tag{1.1.24}$$

[3] In this book all the specific heats in spin systems and fluids have the dimension of a number density.

Namely, C_H is proportional to the variance of the total energy. We also introduce the specific heat C_M at constant magnetization $\langle \mathcal{M} \rangle$ by

$$VC_M = T\left(\frac{\partial S}{\partial T}\right)_M = VC_H - T\left(\frac{\partial\langle\mathcal{M}\rangle}{\partial T}\right)_H^2 \Bigg/ \left(\frac{\partial\langle\mathcal{M}\rangle}{\partial H}\right)_T. \tag{1.1.25}$$

From $(\partial\langle\mathcal{M}\rangle/\partial\beta)_H = -\langle\delta\mathcal{H}\delta\mathcal{M}\rangle$ we obtain

$$C_M = \left[\langle(\delta\mathcal{H})^2\rangle - \langle\delta\mathcal{H}\delta\mathcal{M}\rangle^2/\langle(\delta\mathcal{M})^2\rangle\right]/VT^2, \tag{1.1.26}$$

where $\delta\mathcal{H}$ may be replaced by $\delta\mathcal{H}_{\rm ex}$ because $\delta\mathcal{H}-\delta\mathcal{H}_{\rm ex} = -H\delta\mathcal{M}$ is linearly proportional to $\mathcal{M}$. It holds the inequality $C_H \geq C_M$. These two specific heats coincide in the disordered phase at $H = 0$ where $\langle\delta\mathcal{H}\delta\mathcal{M}\rangle = 0$. We shall see that C_M in spin systems corresponds to the specific heat C_V at constant volume in one-component fluids.

Positivity of C_M

Combinations of the variances of the form,

$$C_{AB} = \langle(\delta\mathcal{A})^2\rangle - \langle\delta\mathcal{A}\delta\mathcal{B}\rangle^2/\langle(\delta\mathcal{B})^2\rangle \geq 0, \tag{1.1.27}$$

will frequently appear in expressions for thermodynamic derivatives. Obviously C_{AB} is the minimum value of $\langle(\delta\mathcal{A} - x\delta\mathcal{B})^2\rangle = \langle(\delta\mathcal{A})^2\rangle - 2x\langle\delta\mathcal{A}\delta\mathcal{B}\rangle + x^2\langle(\delta\mathcal{B})^2\rangle \geq 0$ as a function of x, so it is positive-definite unless the ratio $\delta\mathcal{A}/\delta\mathcal{B}$ is a constant. Thus we have $C_M > 0$.

1.1.4 Spin density and energy density variables

We may define the spin density variable $\hat{s}(\boldsymbol{r})$ by[4]

$$\hat{\psi}(\boldsymbol{r}) = \sum_i s_i \delta(\boldsymbol{r} - \boldsymbol{r}_i), \tag{1.1.28}$$

where $\boldsymbol{r}_i$ is the position vector of the lattice site i. Then $\mathcal{M} = \int d\boldsymbol{r}\hat{\psi}(\boldsymbol{r})$ is the total spin sum in (1.1.14). Through to Chapter 5 the equilibrium equal-time correlation functions will be considered and the time variable will be suppressed. For the deviation $\delta\hat{\psi} = \hat{\psi} - \langle\hat{\psi}\rangle$ of the spin density, the pair correlation is defined by

$$g(\boldsymbol{r} - \boldsymbol{r}') = \langle\delta\hat{\psi}(\boldsymbol{r})\delta\hat{\psi}(\boldsymbol{r}')\rangle, \tag{1.1.29}$$

which is expected to decay to zero for a distance $|\boldsymbol{r} - \boldsymbol{r}'|$ much longer than a correlation length in the thermodynamic limit ($V \to \infty$). The Fourier transformation of $g(\boldsymbol{r})$ is called the structure factor,

$$I(\boldsymbol{k}) = \int d\boldsymbol{r} g(\boldsymbol{r}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}), \tag{1.1.30}$$

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[4] Hereafter, the quantities with a circumflex such as $\hat{\psi}, \hat{m}, \hat{n}, \ldots$ are fluctuating quantities together with those in script such as $\mathcal{H}, \mathcal{A}, \mathcal{B}, \ldots$. However, the circumflex will be omitted from Chapter 3 onward, to avoid confusion.

which is expected to be isotropic (or independent of the direction of $\boldsymbol{k}$) at long wavelengths ($ka \ll 1$, a being the lattice constant). The susceptibility (1.1.20) is expressed as

$$\chi = \int d\boldsymbol{r} g(\boldsymbol{r}) = \lim_{k\to 0} I(\boldsymbol{k}). \tag{1.1.31}$$

However, in the thermodynamic limit, χ is long-range and the space integral in (1.1.31) is divergent at the critical point. We may also introduce the exchange energy density $\hat{e}(\boldsymbol{r})$ by

$$\hat{e}(\boldsymbol{r}) = -\sum_{<i,j>} J s_i s_j \delta(\boldsymbol{r} - \boldsymbol{r}_i). \tag{1.1.32}$$

Then, $\int d\boldsymbol{r}\hat{e}(\boldsymbol{r}) = \mathcal{H}_{\text{ex}}$, and the (total) energy density is

$$\hat{e}_{\text{T}}(\boldsymbol{r}) = \hat{e}(\boldsymbol{r}) - H\hat{\psi}(\boldsymbol{r}), \tag{1.1.33}$$

including the magnetic field energy. From (1.1.24) C_H is expressed in terms of the deviation $\delta\hat{e}_{\text{T}} = \hat{e}_{\text{T}} - \langle e_{\text{T}}\rangle$ as

$$C_H = T^{-2} \int d\boldsymbol{r} \langle \delta\hat{e}_{\text{T}}(\boldsymbol{r} + \boldsymbol{r}_0)\delta\hat{e}_{\text{T}}(\boldsymbol{r}_0)\rangle, \tag{1.1.34}$$

which is independent of $\boldsymbol{r}_0$ in the thermodynamic limit.

Hereafter, we will use the following abbreviated notation (also for fluid systems),

$$\langle \hat{a} : \hat{b}\rangle = \int d\boldsymbol{r} \langle \delta\hat{a}(\boldsymbol{r})\delta\hat{b}(\boldsymbol{r}')\rangle, \tag{1.1.35}$$

defined for arbitrary density variables $\hat{a}(\boldsymbol{r})$ and $\hat{b}(\boldsymbol{r})$, which are determined by the microscopic degrees of freedom at the space position $\boldsymbol{r}$. The space correlation $\langle \delta\hat{a}(\boldsymbol{r})\delta\hat{b}(\boldsymbol{r}')\rangle$ is taken as its thermodynamic limit, and it is assumed to decay sufficiently rapidly for large $|\boldsymbol{r} - \boldsymbol{r}'|$ ensuring the existence of the long-wavelength limit (1.1.35). Furthermore, for any thermodynamic function $a = a(\psi, e)$, we may introduce a fluctuating variable by

$$\hat{a}(\boldsymbol{r}) = a + \left(\frac{\partial a}{\partial \psi}\right)_e \delta\hat{\psi}(\boldsymbol{r}) + \left(\frac{\partial a}{\partial e}\right)_\psi \delta\hat{e}(\boldsymbol{r}), \tag{1.1.36}$$

where a is treated as a function of the thermodynamic averages $\psi = \langle\hat{\psi}\rangle$ and $e = \langle\hat{e}\rangle$. From (1.1.19) its incremental change for small variations, $\delta\beta = -\delta T/T^2$ and δh, is written as

$$\delta\langle\hat{a}\rangle = \langle\hat{a} : \hat{e}\rangle \frac{\delta T}{T^2} + \langle\hat{a} : \hat{\psi}\rangle\delta h + \cdots. \tag{1.1.37}$$

From the definition, the above quantity is equal to $\delta a = (\partial a/\partial T)_h \delta T + (\partial a/\partial h)_{\text{T}}\delta h$. Thus,

$$T^2\left(\frac{\partial a}{\partial T}\right)_h = \langle\hat{a} : \hat{e}\rangle, \quad \left(\frac{\partial a}{\partial h}\right)_T = \langle\hat{a} : \hat{\psi}\rangle. \tag{1.1.38}$$

The variances among $\hat{\psi}$ and $\hat{e}$ are expressed as

$$\chi = \left(\frac{\partial\psi}{\partial h}\right)_T = \langle\hat{\psi} : \hat{\psi}\rangle, \quad T^2\left(\frac{\partial e}{\partial T}\right)_h = \langle\hat{e} : \hat{e}\rangle,$$
$$T^2\left(\frac{\partial\psi}{\partial T}\right)_h = \left(\frac{\partial e}{\partial h}\right)_T = \langle\hat{\psi} : \hat{e}\rangle. \tag{1.1.39}$$

The specific heats are rewritten as

$$C_H = \frac{1}{T^2}\langle\hat{e}_{\mathrm{T}} : \hat{e}_{\mathrm{T}}\rangle, \quad C_M = \frac{1}{T^2}\big[\langle\hat{e} : \hat{e}\rangle - \langle\hat{e} : \hat{\psi}\rangle^2/\langle\hat{\psi} : \hat{\psi}\rangle\big]. \tag{1.1.40}$$

1.1.5 Hydrodynamic fluctuations of temperature and magnetic field

In the book by Landau and Lifshitz (Ref. [1], Chap. 12), long-wavelength (or hydrodynamic) fluctuations of the temperature and pressure are introduced for one-component fluids. For spin systems we may also consider fluctuations of the temperature and magnetic field around an equilibrium reference state. As special cases of (1.1.36) we define

$$\delta\hat{T}(\boldsymbol{r}) = \left(\frac{\partial T}{\partial\psi}\right)_e \delta\hat{\psi}(\boldsymbol{r}) + \left(\frac{\partial T}{\partial e}\right)_\psi \delta\hat{e}(\boldsymbol{r}), \tag{1.1.41}$$

$$\delta\hat{h}(\boldsymbol{r}) = \left(\frac{\partial h}{\partial\psi}\right)_e \delta\hat{\psi}(\boldsymbol{r}) + \left(\frac{\partial h}{\partial e}\right)_\psi \delta\hat{e}(\boldsymbol{r}). \tag{1.1.42}$$

We may regard $\delta\hat{T}$ and $\delta\hat{H} = T\delta\hat{h} + h\delta\hat{T}$ as local fluctuations superimposed on the homogeneous temperature T and magnetic field $H = Th$, respectively. Therefore, (1.1.38) yields

$$\langle\hat{h} : \hat{\psi}\rangle = \frac{1}{T^2}\langle\hat{T} : \hat{e}\rangle = 1, \quad \langle\hat{h} : \hat{e}\rangle = \langle\hat{T} : \hat{\psi}\rangle = 0. \tag{1.1.43}$$

More generally, the density variable $\hat{a}$ in the form of (1.1.36) satisfies

$$\langle\hat{a} : \hat{T}\rangle = T^2\left(\frac{\partial a}{\partial e}\right)_\psi, \quad \langle\hat{a} : \hat{h}\rangle = \left(\frac{\partial a}{\partial\psi}\right)_e. \tag{1.1.44}$$

In particular, the temperature variance reads[5]

$$\langle\hat{T} : \hat{T}\rangle = T^2/C_M. \tag{1.1.45}$$

The variances among $\delta\hat{h}$ and $\delta\hat{T}/T$ constitute the inverse matrix of those among $\delta\hat{\psi}$ and $\delta\hat{e}/T$. To write them down, it is convenient to define the determinant,

$$\mathcal{D} = \frac{1}{T^2}\big[\langle\hat{\psi} : \hat{\psi}\rangle\langle\hat{e} : \hat{e}\rangle - \langle\hat{\psi} : \hat{e}\rangle^2\big] = \chi C_M. \tag{1.1.46}$$

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[5] In the counterpart of this relation, C_M will be replaced by C_V in (1.2.64) for one-component fluids and by C_{VX} in (1.3.44) for binary fluid mixtures.

The elements of the inverse matrix are written as[6]

$$\begin{aligned} V_{\tau\tau} &\equiv \frac{1}{T^2}\langle \hat{T} : \hat{T}\rangle = \frac{1}{C_M}, \quad V_{hh} \equiv \langle \hat{h} : \hat{h}\rangle = \langle \hat{e} : \hat{e}\rangle / T^2\mathcal{D}, \\ V_{h\tau} &\equiv \frac{1}{T}\langle \hat{T} : \hat{h}\rangle = -\langle \hat{\psi} : \hat{e}\rangle / T\mathcal{D}. \end{aligned} \tag{1.1.47}$$

In the disordered phase with $T > T_c$ and $H = 0$, we have no cross correlation $\langle \hat{\psi} : \hat{e}\rangle = 0$, so that $V_{\tau\tau} = 1/C_H$, $V_{hh} = 1/\chi$, and $V_{h\tau} = 0$. For other values of T and H, there is a nonvanishing cross correlation ($V_{h\tau} \neq 0$). The following dimensionless ratio represents the degree of mixing of the two variables,

$$\begin{aligned} R_v &= \langle \hat{\psi} : \hat{e}\rangle^2 \big/ \big[\langle \hat{\psi} : \hat{\psi}\rangle \langle \hat{e} : \hat{e}\rangle\big] \\ &= T^2\left(\frac{\partial \psi}{\partial T}\right)_h^2 \bigg/ \left(\frac{\partial \psi}{\partial h}\right)_T \left(\frac{\partial e}{\partial T}\right)_h, \end{aligned} \tag{1.1.48}$$

where $0 \leq R_v \leq 1$ and use has been made of (1.1.39) in the second line. From (1.1.40) we have

$$C_M = C_H(1 - R_v), \tag{1.1.49}$$

for $h = 0$ (or for sufficiently small h, as in the critical region). In Chapter 4 we shall see that $R_v \cong 1/2$ as $T \to T_c$ on the coexistence curve ($T < T_c$ and $h = 0$) in 3D Ising systems.

In the long-wavelength limit, the probability distribution of the gross variables, $\hat{\psi}(\boldsymbol{r})$ and $\hat{m}(\boldsymbol{r})$, tends to be gaussian with the form $\exp(-\beta\mathcal{H}_{\rm hyd})$, where the fluctuations with wavelengths shorter than the correlation length have been coarse-grained. From (1.1.39), (1.1.43), and (1.1.46) the *hydrodynamic hamiltonian* $\mathcal{H}_{\rm hyd}$ in terms of $\delta\hat{\psi}$ and $\delta\hat{T}$ is expressed as

$$\mathcal{H}_{\rm hyd} = T\int d\boldsymbol{r}\left\{\frac{1}{2\chi}[\delta\hat{\psi}(\boldsymbol{r})]^2 + \frac{1}{2T^2}C_M[\delta\hat{T}(\boldsymbol{r})]^2\right\}. \tag{1.1.50}$$

Another expression for $\mathcal{H}_{\rm hyd}$ can also be constructed in terms of $\delta\hat{e}$ and $\delta\hat{h}$.

1.2 One-component fluids

1.2.1 Canonical ensemble

Nearly-spherical molecules, such as rare-gas atoms, may be assumed to interact via a pairwise potential $v(r)$ dependent only on the distance r between the two particles [4]–[6]. It consists of a short-range hard-core-like repulsion ($r \lesssim \sigma$) and a long-range attraction ($r \gtrsim \sigma$). These two behaviors may be incorporated in the Lenard-Jones potential,

$$v(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]. \tag{1.2.1}$$

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[6] These relations will be used in (2.2.29)–(2.2.36) for one-component fluids and in (2.3.33)–(2.3.38) for binary fluid mixtures after setting up mapping relations between spin and fluid systems.

This pairwise potential is characterized by the core radius σ and the minimum $-\epsilon$ attained at $r = 2^{1/6}\sigma$. In classical mechanics, the hamiltonian for N identical particles with mass m_0 is written as

$$\mathcal{H} = \frac{1}{2m_0}\sum_i |\boldsymbol{p}_i|^2 + \sum_{<i,j>} v(r_{ij}), \tag{1.2.2}$$

where $\boldsymbol{p}_i$ is the momentum vector of the ith particle, r_{ij} is the distance between the particle pair i, j, and $<i, j>$ denotes summation over particle pairs. The particles are confined in a container with a fixed volume V and the wall potential is not written explicitly in (1.2.2).

In the canonical ensemble T, V, and N are fixed, and the statistical distribution is proportional to the Boltzmann weight as [1]–[3]

$$P_{\text{ca}}(\Gamma) = \frac{1}{Z_N}\exp[-\beta\mathcal{H}], \tag{1.2.3}$$

in the $2dN$-dimensional phase space $\Gamma = (\boldsymbol{p}_1 \cdots \boldsymbol{p}_N, \boldsymbol{r}_1 \cdots \boldsymbol{r}_N)$ (sometimes called the Γ-space). The spatial dimensionality is written as d and may be general. The partition function Z_N of N particles for the canonical ensemble is then given by the multiple integrations,

$$\begin{aligned} Z_N &= \frac{1}{N!(2\pi\hbar)^{dN}}\int d\boldsymbol{p}_1 \cdots \int d\boldsymbol{p}_N \int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_N \exp(-\beta\mathcal{H}) \\ &= \frac{1}{N!\lambda_{\text{th}}^{dN}}\int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_N \exp(-\beta\mathcal{U}), \end{aligned} \tag{1.2.4}$$

where $\hbar = 1.054\,57 \times 10^{-27}$ erg s is the Planck constant. In the second line the momentum integrations over the maxwellian distribution have been performed, where

$$\lambda_{\text{th}} = \hbar(2\pi/m_0 T)^{1/2} \tag{1.2.5}$$

is called the thermal de Broglie wavelength, and

$$\mathcal{U} = \sum_{<i,j>} v(r_{ij}) \tag{1.2.6}$$

is the potential part of the hamiltonian.

The Helmholtz free energy is given by $F = -T \ln Z_N$. The factor $1/N!(2\pi\hbar)^{dN}$ in (1.2.4) naturally arises in the classical limit ($\hbar \to 0$) of the quantum mechanical partition function [2]. Physically, the factor $1/N!$ represents the indistinguishability between particles, which assures the extensive property of the entropy. That is, a set of classical microscopic states obtainable only by the particle exchange, $i \to j$ and $j \to i$, corresponds to a single quantum microscopic state.[7] The factor $1/(2\pi\hbar)^{dN}$ is ascribed to the uncertainty principle ($\Delta p \Delta x \sim 2\pi\hbar$).

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[7] The concept of indistinguishability is intrinsically of quantum mechanical origin as well as the uncertainty principle. It is not necessarily required in the realm of classical statistical mechanics. Observable quantities such as the pressure are not affected by the factor $1/N!$.

1.2.2 Grand canonical ensemble

A fluid region can be in contact with a mass reservoir characterized by a chemical potential μ as well as with a heat reservoir at a temperature T. As an example of such a system, we may choose an arbitrary macroscopic subsystem with a volume much smaller than the volume of the total system. In this case we should consider the grand canonical distribution, in which T, μ, and V are fixed and the energy and the particle number are fluctuating quantities. To make this explicit, the particle number will be written as $\mathcal{N}$ and, to avoid too many symbols, the average $\langle \mathcal{N} \rangle$ will be denoted by N which is now a function of T and μ. The statistical probability of each microscopic state with $\mathcal{N}$ particles being realized is given by [1]–[3]

$$P_{\text{gra}}(\Gamma) = \frac{1}{\Xi} \exp[-\beta \mathcal{H} + \beta \mu \mathcal{N}]. \tag{1.2.7}$$

The equilibrium average is written as $\langle \cdots \rangle = \int d\Gamma (\cdots) P_{\text{gra}}(\Gamma)$, where

$$\int d\Gamma = \sum_{\mathcal{N}} \frac{1}{\mathcal{N}!(2\pi\hbar)^{d\mathcal{N}}} \int d\boldsymbol{p}_1 \cdots \int d\boldsymbol{p}_{\mathcal{N}} \int d\boldsymbol{r}_1 \cdots \int d\boldsymbol{r}_{\mathcal{N}} \tag{1.2.8}$$

represents the integration of the configurations in the Γ-space. The normalization factor or the grand partition function Ξ is expressed as

$$\Xi = \sum_{\mathcal{N}} Z_{\mathcal{N}} \exp(\mathcal{N} \beta \mu). \tag{1.2.9}$$

In this summation the contribution around $\mathcal{N} \cong N = \langle \mathcal{N} \rangle$ is dominant for large N, and the logarithm $\Omega \equiv \ln \Xi$ satisfies

$$\Omega = \ln Z_N + N \beta \mu = pV/T, \tag{1.2.10}$$

in the thermodynamic limit $N \to \infty$. Use has been made of the fact that $G = N\mu$ is the Gibbs free energy.

We may choose Ω as a thermodynamic potential dependent on β and

$$\nu = \beta \mu = \mu / T. \tag{1.2.11}$$

Then, analogous to (1.1.12) for Ising systems, the differential form for Ω is written as [9, 10]

$$d\Omega = -\langle \mathcal{H} \rangle d\beta + \langle \mathcal{N} \rangle d\nu, \tag{1.2.12}$$

where

$$\langle \mathcal{H} \rangle = \frac{3}{2} \langle \mathcal{N} \rangle T + \langle \mathcal{U} \rangle \tag{1.2.13}$$

is the energy consisting of the average kinetic energy and the average potential energy. Notice that (1.2.12) may be transformed into the well-known Gibbs–Duhem relation,

$$d\mu = \frac{1}{n} dp - s dT, \tag{1.2.14}$$

where $n = \langle \mathcal{N} \rangle / V$ is the average number density and $s = (\langle \mathcal{H} \rangle - F)/NT$ is the entropy per particle.

We then find the counterparts of (1.1.20)–(1.1.22) among the thermodynamic derivatives and the fluctuation variances of $\delta\mathcal{N} = \mathcal{N} - \langle \mathcal{N} \rangle$ and $\delta\mathcal{H} = \mathcal{H} - \langle \mathcal{H} \rangle$ as

$$\frac{\partial^2 \Omega}{\partial \nu^2} = \frac{\partial \langle \mathcal{N} \rangle}{\partial \nu} = \langle (\delta\mathcal{N})^2 \rangle, \tag{1.2.15}$$

$$\frac{\partial^2 \Omega}{\partial \beta^2} = -\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} = \langle (\delta\mathcal{H})^2 \rangle, \tag{1.2.16}$$

$$-\frac{\partial^2 \Omega}{\partial \nu \partial \beta} = -\frac{\partial \langle \mathcal{N} \rangle}{\partial \beta} = \frac{\partial \langle \mathcal{H} \rangle}{\partial \nu} = \langle \delta\mathcal{N} \delta\mathcal{H} \rangle, \tag{1.2.17}$$

where all the quantities are regarded as functions of β, and $\nu = \beta\mu$ and the volume V is fixed.

The isothermal compressibility is expressed as

$$K_T = \frac{1}{n}\left(\frac{\partial n}{\partial p}\right)_{VT} = \frac{\beta}{n^2}\left(\frac{\partial}{\partial \nu}\frac{\langle \mathcal{N} \rangle}{V}\right)_{\beta}, \tag{1.2.18}$$

where $n = \langle \mathcal{N} \rangle / V$ is the average number density and use has been made of (1.2.14). The fluctuation variance of $\delta\mathcal{N} = \mathcal{N} - \langle \mathcal{N} \rangle$ is expressed in terms of K_T as

$$\langle (\delta\mathcal{N})^2 \rangle = V n^2 T K_T \quad \text{(grand canonical)}. \tag{1.2.19}$$

As for C_M in (1.1.26), the constant-volume specific heat $C_V = (\partial \langle \mathcal{H} \rangle / \partial T)_{VN} / V$ per unit volume can be calculated in terms of the fluctuation variances as

$$C_V = \left[\langle (\delta\mathcal{H})^2 \rangle - \langle \delta\mathcal{H}\delta\mathcal{N} \rangle^2 / \langle (\delta\mathcal{N})^2 \rangle\right] / VT^2 \quad \text{(grand canonical)}, \tag{1.2.20}$$

where use has been made of

$$(\partial \langle \mathcal{H} \rangle / \partial T)_N = (\partial \langle \mathcal{H} \rangle / \partial T)_\nu + (\partial \langle \mathcal{H} \rangle / \partial N)_{\mathrm{T}} (\partial N / \partial T)_\nu.$$

Field variables and density variables

Following Griffiths and Wheeler [10] and Fisher [11], we refer to T (or β) and h in spin systems and T (or β), $p, \nu, \ldots$ in fluids as *fields*, which have identical values in two coexisting phases. We refer to the spin and energy densities in spin systems and the densities of number, energy, entropy, … in fluids as *densities*. In spin systems, the average spin is discontinuous between the two coexisting phases, but the average energy is continuous. In fluids, the density variables usually have different average values in the two coexisting phases, but can be continuous in accidental cases such as the azeotropic case (see Section 2.3). In this book the density variables (even the entropy and concentration) have microscopic expressions in terms of the spins or the particle positions and momenta. Their equilibrium averages become the usual thermodynamic variables, and their equilibrium fluctuation variances can be related to some thermodynamic derivatives in the long-wavelength limit.

Shift of the origin of the one-particle energy

It would also be appropriate to remark on the arbitrariness of the origin of the energy supported by each particle. That is, let us shift the hamiltonian as

$$\mathcal{H} \to \mathcal{H} + \epsilon_0 \mathcal{N} \tag{1.2.21}$$

and the chemical potential from μ to $\mu + \epsilon_0$. Then, ϵ_0 vanishes in the grand canonical distribution and hence measurable quantities such as the pressure p should remain invariant or independent of ϵ_0 as long as they do not involve the origin of the one-particle energy. We can see that the terms involving ϵ_0 cancel in the variance combination (1.2.20), so C_V is clearly independent of ϵ_0.

Lattice gas model

In the lattice gas model [12], particles are distributed on fixed lattice points in evaluating the potential energy contribution to Ξ. The lattice constant a is taken to be the hard-core size of the pair potential, so each lattice point is supposed to be either vacant ($n_i = 0$) or occupied ($n_i = 1$) by a single particle. Then Ξ is approximated as

$$\Xi = \sum_{\{n\}} \exp(-\beta \mathcal{H}\{n\}), \tag{1.2.22}$$

with

$$\mathcal{H}\{n\} = -\sum_{<i,j>} \epsilon n_i n_j - (\mu + dT \ln \lambda_{\mathrm{th}}) \sum_i n_i, \tag{1.2.23}$$

where the summation in the first term is taken over the nearest neighbor pairs and ϵ represents the magnitude of the attractive part of the pair potential. Obviously, if we set $s_i = 2n_i - 1$, the above hamiltonian becomes isomorphic to the spin hamiltonian (1.1.1) under $J = \epsilon/4$ and

$$H = \frac{1}{2}\mu + \frac{d}{2} T \ln \lambda_{\mathrm{th}} - \frac{1}{4} z\epsilon = \frac{1}{2}\mu - \frac{d}{4} T \ln T + \text{const.}, \tag{1.2.24}$$

z being the coordination number. The pressure p in the lattice gas model is related to the free energy F_{Ising} of the corresponding Ising spin system by

$$p = -V^{-1} F_{\mathrm{Ising}} + a^{-d}\left(H + \frac{1}{8} z\epsilon\right). \tag{1.2.25}$$

1.2.3 Thermodynamic derivatives and fluctuation variances

Analogously to the spin case (1.1.18), the grand canonical distribution function $P_{\mathrm{gra}}(\Gamma)$ in (1.2.7) is changed against small changes, $\beta \to \beta + \delta\beta$ and $\nu \to \nu + \delta\nu$, as [9]

$$\delta P_{\mathrm{gra}} = [-\delta\mathcal{H}\delta\beta + \delta\mathcal{N}\delta\nu] P_{\mathrm{gra}}, \tag{1.2.26}$$

where only the linear deviations are written. Because the choice of β and ν as independent field variables is not usual, we may switch to the usual choice, T and p. Here $\delta T = -T^2\delta\beta$ and

$$\delta p = nT(\delta\nu - \bar{H}\delta\beta), \tag{1.2.27}$$

where

$$\bar{H} = \mu + Ts \tag{1.2.28}$$

is the enthalpy per particle and should not be confused with the magnetic field in the spin system, and s is the entropy per particle. Then (1.2.26) is rewritten as

$$\delta P_{\text{gra}} = \left[n\delta\mathcal{S}\frac{\delta T}{T} + \delta\mathcal{N}\frac{\delta p}{nT} \right] P_{\text{gra}}, \tag{1.2.29}$$

where

$$\delta\mathcal{S} = \frac{1}{nT}[\delta\mathcal{H} - \bar{H}\delta\mathcal{N}] \tag{1.2.30}$$

is the space integral of the entropy density variable to be introduced in (1.2.46) below. Thus, the thermodynamic average of any fluctuating quantity $\mathcal{A}$ changes as

$$\begin{aligned} \delta\langle\mathcal{A}\rangle &= -\langle\mathcal{A}\delta\mathcal{H}\rangle\delta\beta + \langle\mathcal{A}\delta\mathcal{N}\rangle\delta\nu + \cdots, \\ &= \langle\mathcal{A}\delta\mathcal{S}\rangle n\frac{\delta T}{T} + \langle\mathcal{A}\delta\mathcal{N}\rangle\frac{\delta p}{nT} + \cdots. \end{aligned} \tag{1.2.31}$$

Note that $\delta\mathcal{S}$ is invariant with respect to the energy shift in (1.2.21) because the enthalpy $\bar{H}$ is also shifted by ϵ_0.

The familiar constant-pressure specific heat $C_p = nT(\partial s/\partial T)_p$ per unit volume is obtained from $VC_p = nT \lim_{\delta T\to 0} \langle\delta\mathcal{S}\rangle/\delta T$ with $\delta p = 0$. From the second line of (1.2.31) C_p becomes

$$C_p = n^2\langle(\delta\mathcal{S})^2\rangle/V = \langle(\delta\mathcal{H} - \bar{H}\delta\mathcal{N})^2\rangle/VT^2 \quad \text{(grand canonical)}. \tag{1.2.32}$$

In terms of $\delta\mathcal{S}$, the constant-volume specific heat C_V is also expressed as

$$C_V = n^2\big[\langle(\delta\mathcal{S})^2\rangle - \langle\delta\mathcal{S}\delta\mathcal{N}\rangle^2/\langle(\delta\mathcal{N})^2\rangle\big]/V \quad \text{(grand canonical)}, \tag{1.2.33}$$

which is equivalent to (1.2.20). It leads to the inequality $C_p \geq C_V$. Use of the thermodynamic identity $C_p/C_V = K_T/K_s$ yields the adiabatic compressibility $K_s = (\partial n/\partial p)_s/n$ in the form

$$K_s = \big[\langle(\delta\mathcal{N})^2\rangle - \langle\delta\mathcal{S}\delta\mathcal{N}\rangle^2/\langle(\delta\mathcal{S})^2\rangle\big]/Vn^2T \quad \text{(grand canonical)}. \tag{1.2.34}$$

The sound velocity c is given by $c = (\rho K_s)^{-1/2}$, $\rho = m_0 n$ being the mass density.

1.2.4 Gaussian distribution in the long-wavelength limit

We next consider the equilibrium statistical distribution function for the macroscopic gross variables, $\mathcal{H}$ and $\mathcal{N}$, for one-component fluids, which we write as $P(\mathcal{H}, \mathcal{N})$. The entropy $S(E, N)$ as a function of E and N is the logarithm of the number of microscopic configurations at $\mathcal{H} = E$ and $\mathcal{N} = N$. It may be written as

$$\exp[S(E, N)] = \int d\Gamma \delta(\mathcal{H} - E)\delta(\mathcal{N} - N), \tag{1.2.35}$$

where $d\Gamma$ is the configuration integral (1.2.8). This grouping of the microscopic states gives

$$P(\mathcal{H}, \mathcal{N}) = \frac{1}{\Xi} \exp[S(\mathcal{H}, \mathcal{N}) - \beta\mathcal{H} + \nu\mathcal{N}], \tag{1.2.36}$$

with the grand canonical partition function,

$$\Xi = \int d\mathcal{H} \int d\mathcal{N} \exp[S(\mathcal{H}, \mathcal{N}) - \beta\mathcal{H} + \nu\mathcal{N}]. \tag{1.2.37}$$

Each thermodynamic state is characterized by β and ν or by $E = \langle\mathcal{H}\rangle$ and $N = \langle\mathcal{N}\rangle$. We then expand $S(\mathcal{H}, \mathcal{N})$ with respect to the deviations $\delta\mathcal{H} = \mathcal{H} - E$ and $\delta\mathcal{N} = \mathcal{N} - N$ as

$$S(\mathcal{H}, \mathcal{N}) = S(E, N) + \beta\delta\mathcal{H} - \nu\delta\mathcal{N} + (\Delta S)_2 + \cdots, \tag{1.2.38}$$

where $(\delta S)_2$ is the bilinear part,

$$(\Delta S)_2 = \frac{1}{2}\left(\frac{\partial^2 S}{\partial E^2}\right)(\delta\mathcal{H})^2 + \left(\frac{\partial^2 S}{\partial E \partial N}\right)\delta\mathcal{H}\delta\mathcal{N} + \frac{1}{2}\left(\frac{\partial^2 S}{\partial N^2}\right)(\delta\mathcal{N})^2. \tag{1.2.39}$$

In the probability distribution (1.2.36) the linear terms cancel if (1.2.38) is substituted, so the distribution becomes the following well-known gaussian form [1, 3, 7]:

$$P(\mathcal{H}, \mathcal{N}) \propto \exp[(\Delta S)_2]. \tag{1.2.40}$$

From this distribution we can re-derive (1.2.15)–(1.2.17) by using the relations,

$$\begin{aligned} \alpha_{ee} &\equiv V\frac{\partial^2 S}{\partial E^2} = \frac{\partial\beta}{\partial e}, \quad \alpha_{nn} \equiv V\frac{\partial^2 S}{\partial N^2} = -\frac{\partial\nu}{\partial n}, \\ \alpha_{en} &\equiv V\frac{\partial^2 S}{\partial N \partial E} = \frac{\partial\beta}{\partial n} = -\frac{\partial\nu}{\partial e}, \end{aligned} \tag{1.2.41}$$

where β and ν are regarded as functions of $n = N/V$ and $e = E/V$. The three coefficients in (1.2.41) divided by $-V$ constitute the inverse of the matrix whose elements are the variances among $\mathcal{H}$ and $\mathcal{N}$.

Weakly inhomogeneous cases

The above result may be generalized for weakly inhomogeneous cases as follows. Let us consider a small fluid element whose linear dimension is much longer than the correlation length. Because the thermodynamics in the element is described by the grand canonical ensemble, the long-wavelength, number and energy density fluctuations, $\delta\hat{n}(\boldsymbol{r})$ and $\delta\hat{e}(\boldsymbol{r})$, obey a gaussian distribution of the form (1.2.40) with

$$(\Delta S)_2 = \int d\boldsymbol{r}\left[\frac{1}{2}\alpha_{ee}(\delta\hat{e}(\boldsymbol{r}))^2 + \alpha_{en}\delta\hat{e}(\boldsymbol{r})\delta\hat{n}(\boldsymbol{r}) + \frac{1}{2}\alpha_{nn}(\delta\hat{n}(\boldsymbol{r}))^2\right]. \tag{1.2.42}$$

Thermodynamic stability

It has been taken for granted that the probability distribution (1.2.36) is maximum for the equilibrium values, which results in the positive-definiteness of the matrix composed of the coefficients in (1.2.41). In thermodynamics [2, 13] this positive-definiteness (implying the positivity of C_V, K_T, etc.) follows from the thermodynamic stability of equilibrium states. In this book, because we start with statistical–mechanical principles, their positivity is an obvious consequence evident from their variance expressions.

1.2.5 Fluctuating space-dependent variables

The number density variable $\hat{n}(\boldsymbol{r})$ and the energy density variable $\hat{e}(\boldsymbol{r})$ have microscopic expressions,

$$\hat{n}(\boldsymbol{r}) = \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i), \tag{1.2.43}$$

$$\hat{e}(\boldsymbol{r}) = \sum_i \frac{1}{2m_0}|\boldsymbol{p}_i|^2\delta(\boldsymbol{r} - \boldsymbol{r}_i) + \frac{1}{2}\sum_{i\neq j} v(r_{ij})\delta(\boldsymbol{r} - \boldsymbol{r}_i), \tag{1.2.44}$$

in terms of the particle positions and momenta. As in (1.1.36) we may introduce a fluctuating variable by

$$\hat{a}(\boldsymbol{r}) = a + \left(\frac{\partial a}{\partial n}\right)_e \delta\hat{n}(\boldsymbol{r}) + \left(\frac{\partial a}{\partial e}\right)_n \delta\hat{e}(\boldsymbol{r}), \tag{1.2.45}$$

for any thermodynamic variable a given as a function of the averages $n = \langle\hat{n}\rangle$ and $e = \langle\hat{e}\rangle$. The nonlinear terms such as $(\partial^2 a/\partial n^2)(\delta\hat{n})^2$ are not included in the definition. From $ds = (de - \bar{H}dn)/nT$ the space-dependent entropy variable is introduced by

$$\hat{s}(\boldsymbol{r}) = s + \frac{1}{nT}\left[\delta\hat{e}(\boldsymbol{r}) - \bar{H}\delta\hat{n}(\boldsymbol{r})\right], \tag{1.2.46}$$

where $\bar{H} = \mu + Ts = (e + p)/n$ is the enthalpy per particle. The space integral of $\delta\hat{s}(\boldsymbol{r}) = \hat{s}(\boldsymbol{r}) - s$ is equal to $\delta\mathcal{S}$ in (1.2.30). In terms of these density variables, the incremental change of the grand canonical distribution in (1.2.26) and (1.2.29) is expressed as

$$\begin{aligned}\delta P_{\text{gra}} &= P_{\text{gra}}\int d\boldsymbol{r}[-\delta\hat{e}(\boldsymbol{r})\delta\beta + \delta\hat{n}(\boldsymbol{r})\delta\nu] \\ &= P_{\text{gra}}\int d\boldsymbol{r}\left[n\delta\hat{s}(\boldsymbol{r})\frac{\delta T}{T} + \delta\hat{n}(\boldsymbol{r})\frac{\delta p}{nT}\right],\end{aligned} \tag{1.2.47}$$

where δp is the pressure deviation defined in (1.2.27). With these two expressions we may express any thermodynamic derivatives in terms of fluctuation variances of $\hat{n}$, $\hat{e}$, and $\hat{s}$ in the long-wavelength limit. Using the notation $\langle\ :\ \rangle$, as in (1.1.35), we have

$$K_T = (n^2 T)^{-1}\langle \hat{n} : \hat{n}\rangle, \quad C_p = n^2\langle \hat{s} : \hat{s}\rangle, \quad \alpha_p = -T^{-1}\langle \hat{s} : \hat{n}\rangle, \tag{1.2.48}$$

where $\alpha_p = -(\partial n/\partial T)_p/n$ is the thermal expansion coefficient. From (1.2.20) and (1.2.33) the constant-volume specific heat is expressed as

$$\begin{aligned} C_V &= T^{-2}\big[\langle \hat{e} : \hat{e}\rangle - \langle \hat{e} : \hat{n}\rangle^2/\langle \hat{n} : \hat{n}\rangle\big] \\ &= n^2\big[\langle \hat{s} : \hat{s}\rangle - \langle \hat{s} : \hat{n}\rangle^2/\langle \hat{n} : \hat{n}\rangle\big]. \end{aligned} \tag{1.2.49}$$

The first line was obtained by Schofield [see Ref. 18]. From (1.2.34) the adiabatic compressibility is expressed as

$$K_s = (\rho c^2)^{-1} = \big[\langle \hat{n} : \hat{n}\rangle - \langle \hat{n} : \hat{s}\rangle^2/\langle \hat{s} : \hat{s}\rangle\big]\big/ n^2 T. \tag{1.2.50}$$

These expressions are in terms of the long-wavelength limit of the correlation functions. Hence, to their merit, they tend to unique thermodynamic limits, whether the ensemble is canonical or grand canonical, as $N, V \to \infty$ with a fixed density $n = N/V$.

More generally, for any density variable $\hat{a}$ in the form of (1.2.45), we obtain

$$\langle \hat{a} : \hat{e}\rangle = T^2\left(\frac{\partial a}{\partial T}\right)_v, \quad \langle \hat{a} : \hat{n}\rangle = nT\left(\frac{\partial a}{\partial p}\right)_T, \quad \langle \hat{a} : \hat{s}\rangle = \frac{1}{n}T\left(\frac{\partial a}{\partial T}\right)_p. \tag{1.2.51}$$

It then follows that

$$\left(\frac{\partial p}{\partial T}\right)_a = -\left(\frac{\partial a}{\partial T}\right)_p \bigg/ \left(\frac{\partial a}{\partial p}\right)_T = -n^2\langle \hat{a} : \hat{s}\rangle/\langle \hat{a} : \hat{n}\rangle. \tag{1.2.52}$$

Finally, we give some thermodynamic identities,

$$\rho c^2 C_V = T\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial p}{\partial T}\right)_n = T\left(\frac{\partial p}{\partial T}\right)_s^2 (1 - C_V/C_p), \tag{1.2.53}$$

$$C_V/C_p = K_s/K_T = 1 - \left(\frac{\partial p}{\partial T}\right)_n \bigg/ \left(\frac{\partial p}{\partial T}\right)_s. \tag{1.2.54}$$

These are usually proved with the Maxwell relations but can also be derived from the variance relations (1.2.48)–(1.2.54).

1.2.6 Density correlation

In the literature [4]–[6] special attention has been paid to the radial distribution function $g(r)$ defined by

$$\begin{aligned} n^2 g(|\boldsymbol{r} - \boldsymbol{r}'|) &= \sum_{i\neq j}\langle \delta(\boldsymbol{r} - \boldsymbol{r}_i)\delta(\boldsymbol{r}' - \boldsymbol{r}_j)\rangle \\ &= \langle \hat{n}(\boldsymbol{r})\hat{n}(\boldsymbol{r}')\rangle - n\delta(\boldsymbol{r} - \boldsymbol{r}'), \end{aligned} \tag{1.2.55}$$

where the self-part ($i = j$) has been subtracted and $g(r) \to 1$ at long distance in the thermodynamic limit.[8] The structure factor is expressed as

$$I(k) = \int d\boldsymbol{r} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \langle \delta\hat{n}(\boldsymbol{r})\delta\hat{n}(\boldsymbol{0})\rangle = n + n^2 \int d\boldsymbol{r} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}[g(r) - 1]. \tag{1.2.56}$$

An example of $I(k)$ can be found in Fig. 2.3. The isothermal compressibility (1.2.18) is expressed as

$$K_T = (n^2T)^{-1} \lim_{k\to 0} I(k) = (nT)^{-1} + T^{-1} \int d\boldsymbol{r}[g(r) - 1]. \tag{1.2.57}$$

The physical meaning of $g(r)$ is as follows. We place a particle at the origin of the reference frame and consider a volume element $d\boldsymbol{r}$ at a position $\boldsymbol{r}$; then, $ng(r)d\boldsymbol{r}$ is the average particle number in the volume element. In liquid theories another important quantity is the direct correlation function $C(r)$ defined by

$$g(r) = C(r) + \int d\mathbf{r}' C(|\mathbf{r} - \mathbf{r}'|) n g(|\mathbf{r}'|). \tag{1.2.58}$$

Its Fourier transformation C_k satisfies

$$I(k) = n/(1 - nC_k). \tag{1.2.59}$$

Let us assume naively that $C(r)$ decays more rapidly than the pair correlation function $g(r)$ at long distances and C_k can be expanded as $C_k = C_0 - C_1k^2 + \cdots$ at small k with $C_1 > 0$ [14]. Then, (1.2.59) yields a well-known expression called the Ornstein–Zernike form,

$$I(k) \cong n/(1 - nC_0 + nC_1k^2), \tag{1.2.60}$$

at small k. Notice that $C_0 = \lim_{k\to 0} C_k$ approaches to n^{-1} as the critical point (or the *spinodal line* more generally) is approached. The direct correlation functions for binary mixtures will be discussed at the end of Section 1.3.

1.2.7 Hydrodynamic temperature and pressure fluctuations

As in the book by Landau and Lifshitz [1], we introduce the temperature fluctuation $\delta\hat{T}$ as a space-dependent variable by

$$\begin{aligned} \delta\hat{T}(\boldsymbol{r}) &= \left(\frac{\partial T}{\partial e}\right)_n \delta\hat{e}(\boldsymbol{r}) + \left(\frac{\partial T}{\partial n}\right)_e \delta\hat{n}(\boldsymbol{r}) \\ &= \frac{nT}{C_V}\left[\delta\hat{s}(\boldsymbol{r}) + \frac{1}{n^2}\left(\frac{\partial p}{\partial T}\right)_n \delta\hat{n}(\boldsymbol{r})\right], \end{aligned} \tag{1.2.61}$$

where the energy density $\hat{e}(\boldsymbol{r})$, the number density $\hat{n}(\boldsymbol{r})$, and the entropy density $\hat{s}(\boldsymbol{r})$ are defined by (1.2.45)–(1.2.47), and use has been made of $(\partial s/\partial n^{-1})_\mathrm{T} = (\partial p/\partial T)_n$. We assume that these density variables consist only of the Fourier components with wavelengths

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[8] In a finite system, the space integral of (1.2.55) in the volume V would become $N(N - 1)/V$, in apparent contradiction to (1.2.57).

much longer than any correlation lengths ($q \ll \xi^{-1}$, near the critical point, ξ being the correlation length). Then $\hat{a}$ in the form of (1.2.45) satisfies

$$\langle \hat{a} : \hat{T} \rangle = \frac{T}{n}\left(\frac{\partial a}{\partial s}\right)_n = \frac{T^2}{C_V}\left(\frac{\partial a}{\partial T}\right)_n. \tag{1.2.62}$$

This relation gives [1]

$$\langle \hat{n} : \hat{T} \rangle = 0, \quad \langle \hat{s} : \hat{T} \rangle = T/n, \tag{1.2.63}$$

$$\langle \hat{T} : \hat{T} \rangle = T^2/C_V, \tag{1.2.64}$$

The long-wavelength fluctuations obey a gaussian distribution $\propto \exp[-\beta\mathcal{H}_{\mathrm{hyd}}]$. The hydrodynamic hamiltonian is written as

$$\mathcal{H}_{\mathrm{hyd}} = \int d\boldsymbol{r}\left\{\frac{C_V}{2T}[\delta\hat{T}(\boldsymbol{r})]^2 + \frac{1}{2n^2K_T}[\delta\hat{n}(\boldsymbol{r})]^2\right\}, \tag{1.2.65}$$

which is analogous to (1.1.50) for Ising systems.

We may also introduce a hydrodynamic pressure variable $\delta\hat{p}(\boldsymbol{r})$ by

$$\begin{aligned}\delta\hat{p}(\boldsymbol{r}) &= \left(\frac{\partial p}{\partial e}\right)_n \delta\hat{e}(\boldsymbol{r}) + \left(\frac{\partial p}{\partial n}\right)_e \delta\hat{n}(\boldsymbol{r}) \\ &= \rho c^2\left[\frac{1}{n}\delta\hat{n}(\boldsymbol{r}) + n\left(\frac{\partial T}{\partial p}\right)_s \delta\hat{s}(\boldsymbol{r})\right],\end{aligned} \tag{1.2.66}$$

where ρ is the mass density and use has been made of $(\partial n^{-1}/\partial s)_p = (\partial T/\partial p)_s$. For $\hat{a}(\boldsymbol{r})$ in the form of (1.2.45) we obtain

$$\langle \hat{a} : \hat{p} \rangle = Tn\left(\frac{\partial a}{\partial n}\right)_s = T\rho c^2\left(\frac{\partial a}{\partial p}\right)_s. \tag{1.2.67}$$

Substituting $\hat{a} = \hat{p}$ and $\hat{T}$ yields

$$\langle \hat{p} : \hat{p} \rangle = \rho c^2 T, \tag{1.2.68}$$

$$\langle \hat{p} : \hat{T} \rangle = T\rho c^2\left(\frac{\partial T}{\partial p}\right)_s = \frac{T^2}{C_V}\left(\frac{\partial p}{\partial T}\right)_n. \tag{1.2.69}$$

By setting $\hat{a} = \hat{s}$ and $\hat{n}$ we also notice

$$\langle \hat{s} : \hat{p} \rangle = 0, \quad \langle \hat{n} : \hat{p} \rangle = nT. \tag{1.2.70}$$

The $\mathcal{H}_{\mathrm{hyd}}$ may be rewritten in another orthogonal form,

$$\mathcal{H}_{\mathrm{hyd}} = \int d\boldsymbol{r}\left\{\frac{1}{2\rho c^2}[\delta\hat{p}(\boldsymbol{r})]^2 + \frac{n^2T}{2C_p}[\delta\hat{s}(\boldsymbol{r})]^2\right\}. \tag{1.2.71}$$

It goes without saying that $(\Delta S)_2$ in (1.2.42) coincides with $-\beta\mathcal{H}_{\mathrm{hyd}}$.

1.2.8 Projection onto gross variables in the hydrodynamic regime

The pressure fluctuation variable $\delta\hat{p}(\boldsymbol{r})$ in (1.2.66) may be interpreted as the *projection* of the microscopic stress tensor $\hat{\Pi}_{\alpha\beta}(\boldsymbol{r})$ $(\alpha, \beta = x, y, z)$ onto the gross variables $\delta\hat{e}$ (or $\delta\hat{s}$) and $\delta\hat{n}$.[9] In the hydrodynamic regime, for any fluctuating variable $\hat{a}(\boldsymbol{r})$ dependent on space, the projection operator $\mathcal{P}$ is defined as

$$\mathcal{P}\hat{a}(\boldsymbol{r}) = \langle\hat{a}\rangle + A_{en}\delta\hat{e}(\boldsymbol{r}) + A_{ne}\delta\hat{n}(\boldsymbol{r}). \tag{1.2.72}$$

The two coefficients A_{en} and A_{ne} are determined such that the right-hand side and $\delta\hat{a}$ have the same correlations with $\delta\hat{e}$ and $\delta\hat{n}$. Then $\mathcal{P}^2 = \mathcal{P}$. If $\hat{a}$ is of the form (1.2.45), we have $\mathcal{P}\hat{a} = \hat{a}$. We neglect nonlocality in (1.2.72) assuming that $\delta\hat{e}$ and $\delta\hat{n}$ consist of the Fourier components with an upper cut-off wave number Λ much smaller than the inverse thermal correlation length. The calculation of the coefficients is simplified if the above relation is rewritten in terms of $\delta\hat{p}$ and $\delta\hat{s}$ as

$$\mathcal{P}\delta\hat{a}(\boldsymbol{r}) = A_{ps}\delta\hat{p}(\boldsymbol{r}) + A_{sp}\delta\hat{s}(\boldsymbol{r}). \tag{1.2.73}$$

Using $\langle\hat{s} : \hat{p}\rangle = 0$, we find

$$A_{ps} = \langle\hat{a} : \hat{p}\rangle/\langle\hat{p} : \hat{p}\rangle, \quad A_{sp} = \langle\hat{a} : \hat{s}\rangle/\langle\hat{s} : \hat{s}\rangle. \tag{1.2.74}$$

From (1A.11) and (1A.12) in Appendix 1A, we may derive the following variance relations,

$$\langle\hat{n} : \hat{\Pi}_{\alpha\beta}\rangle = nT\delta_{\alpha\beta}, \quad \langle\hat{e} : \hat{\Pi}_{\alpha\beta}\rangle = (e + p)T\delta_{\alpha\beta}. \tag{1.2.75}$$

Then, from the definitions of $\hat{s}$ in (1.2.46) and $\hat{p}$ in (1.2.66) we obtain

$$\langle\hat{s} : \hat{\Pi}_{\alpha\beta}\rangle = 0, \quad \langle\hat{p} : \hat{\Pi}_{\alpha\beta}\rangle = \rho c^2 T\delta_{\alpha\beta}. \tag{1.2.76}$$

Hence, we arrive at

$$\mathcal{P}\delta\hat{\Pi}_{\alpha\beta}(\boldsymbol{r}) = \delta_{\alpha\beta}\delta\hat{p}(\boldsymbol{r}). \tag{1.2.77}$$

This leads to the inequality

$$\rho c^2 \le K_\infty \equiv \left\langle \sum_\alpha \hat{\Pi}_{\alpha\alpha} : \sum_\beta \hat{\Pi}_{\beta\beta} \right\rangle \Big/ d^2 T. \tag{1.2.78}$$

See (1.2.84) below for K_∞ [18]. In fact, at the gas–liquid critical point the sound velocity c goes to zero but K_∞ remains finite. These are consistent with the inequality in (1.2.78).

1.2.9 Pressure, energy, and elastic moduli in terms of $g(r)$

In Appendix 5E we will give the space-dependent microscopic expression for the stress tensor $\hat{\Pi}_{\alpha\beta}(\boldsymbol{r})$. Its space integral has the following microscopic expression [5, 6],

$$\int d\boldsymbol{r}\hat{\Pi}_{\alpha\beta}(\boldsymbol{r}) = \sum_i \frac{p_{i\alpha}p_{i\beta}}{m_0} - \sum_{<i,j>} v'(r_{ij})\frac{1}{r_{ij}}x_{ij\alpha}x_{ij\beta}, \tag{1.2.79}$$

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[9] As will be discussed in Chapter 5, the projection operator method has been developed in the study of irreversible processes.

where $v'(r) = dv(r)/dr$, $x_{i\alpha}$ ($\alpha = x, y, z$) are the cartesian coordinates of the particle position $\boldsymbol{r}_i$, and $x_{ij\alpha} = x_{i\alpha} - x_{j\alpha}$. The pressure is then expressed in terms of the radial distribution function $g(r)$ in (1.2.55) as

$$p = nT - \frac{1}{2d} J_1, \tag{1.2.80}$$

with

$$J_1 = \int d\boldsymbol{r} n^2 g(r) r v'(r), \tag{1.2.81}$$

where d in (1.2.80) is the spatial dimensionality. In addition, the internal energy density is expressed as

$$e = \langle \hat{e} \rangle = \frac{d}{2} nT + \frac{1}{2} \int d\boldsymbol{r} n^2 g(r) v(r). \tag{1.2.82}$$

In an isotropic equilibrium state the variances among the stress tensor $\hat{\Pi}_{\alpha\beta}$ in the long-wavelength limit are written as

$$\frac{1}{T} \langle \hat{\Pi}_{\alpha\beta} : \hat{\Pi}_{\gamma\delta} \rangle = (\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) G_\infty + \delta_{\alpha\beta}\delta_{\gamma\delta} \left(K_\infty - \frac{2}{d} G_\infty \right). \tag{1.2.83}$$

Here K_∞ and G_∞ are called the *elastic moduli* of fluids [6], [15]–[18]. Although elastic deformations are not well defined in fluids, they were interpreted as the infinite-frequency elastic moduli of fluids [17].[10] Interestingly, they can be expressed in terms of $g(r)$ as [17, 18]

$$K_\infty = \frac{1}{d^2 T} \left\langle \sum_\alpha \hat{\Pi}_{\alpha\alpha} : \sum_\beta \hat{\Pi}_{\beta\beta} \right\rangle = \left(1 + \frac{2}{d} \right) nT - \frac{d-1}{2d^2} J_1 + \frac{1}{2d^2} J_2, \tag{1.2.84}$$

$$G_\infty = \frac{1}{T} \langle \hat{\Pi}_{xy} : \hat{\Pi}_{xy} \rangle = nT + \frac{1}{2d(d+2)} \big[(d+1) J_1 + J_2 \big], \tag{1.2.85}$$

where J_1 is defined by (1.2.81) and

$$J_2 = \int d\boldsymbol{r} n^2 g(r) r^2 v''(r), \tag{1.2.86}$$

with $v''(r) = d^2 v(r)/dr^2$. Elimination of J_1 and J_2 yields a general relation,

$$K_\infty - \left(1 + \frac{2}{d} \right) G_\infty = 2(p - nT). \tag{1.2.87}$$

It is not trivial that K_∞ and G_∞ can be expressed in terms of the radial distribution function, although they involve correlations among four particles. We will present a general theory for calculating correlation functions involving the stress tensor in Appendix 1A.

Schofield calculated more general wave number-dependent correlation functions among

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[10] In highly supercooled fluids, a shear modulus becomes well defined and measurable. It is smaller than G_∞ but larger than nT. See Fig. 11.33 and its explanation in Section 11.4.