Part one

Statics

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,

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

where

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

In this book the absolute temperature multiplied by the Boltzmann constant $k_{\rm B} = 1.381 \times 10^{-16}$ 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

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

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

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

where $\delta\mathcal{H}_{\rm ex} = \mathcal{H}_{\rm ex} - \langle \mathcal{H}_{\rm ex} \rangle$ 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,

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

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

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

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

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

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

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

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

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

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[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

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

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,

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

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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]

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

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 $\exp(-\beta\mathcal{H}_{\text{hyd}})$, 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* $\mathcal{H}_{\text{hyd}}$ in terms of $\delta\hat{\psi}$ and $\delta\hat{T}$ is expressed as

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

Another expression for $\mathcal{H}_{\text{hyd}}$ 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

$$\lambda_{\text{th}} = \hbar(2\pi/m_0T)^{1/2} \tag{1.2.5}$$

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 $1/N!$.