

Classical equilibrium statistical mechanics

7.1 Basic theory

In this chapter we briefly review the theory of classical statistical mechanics with emphasis on those issues which are relevant to computer simulations. We shall assume that the reader has some background in thermodynamics and statistical mechanics; for further reading, numerous textbooks are available.¹⁻⁸

Statistical mechanics concerns the study of systems with many (in principle infinitely many) degrees of freedom. The degrees of freedom are usually the positions and momenta of particles, or magnetic moments ('spins'). We restrict ourselves to classical systems for which all degrees of freedom commute. The space spanned by the degrees of freedom is called *phase space* – every point in phase space represents a particular configuration of the system. In the course of time, the system follows a path in phase space, determined by the equations of motion. We are obviously not interested in the values of all these degrees of freedom as a function of time: only the time averages of physical quantities such as pressure are measurable. This is because our measuring devices (thermometers, barometers) respond relatively slowly; hence they give a time average of the physical quantity of interest. However, even if we could perform an instantaneous measurement of some quantity we would find a result very close to the time average of that quantity as a result of the law of large numbers, which teaches us that if a quantity is composed of N uncorrelated contributions, fluctuations in that quantity are of order $1/\sqrt{N}$. This implies that for typical macroscopic physical quantities (such as the temperature of your cup of tea) for which $N \sim 10^{24}$, the fluctuations are as small as $\sim 10^{-12}$ if we neglect correlations. If correlations extend over ~ 100 particles, the number of uncorrelated contributions is $\sim 10^{24}/100 = 10^{22}$, so the fluctuations remain extremely small.

Computer simulations always sample relatively few degrees of freedom, since only a restricted amount of data can be stored in memory: system sizes

in simulations are always much smaller than those of experimental systems.[†] Furthermore, a time average of a physical quantity A is given by

$$\bar{A} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(t) dt, \quad (7.1)$$

and we want to obtain results in a finite amount of time! In a molecular dynamics simulation (see Chapter 8), the typical simulation time is of the order of 10^{-9} – 10^{-6} seconds, far below the time in which most measuring devices sample physical quantities. The results of such simulations can only be representative if the spatial correlations extend over ranges smaller than the system size and if the correlation time of the system is smaller than the simulation time. Sometimes it is possible to extract useful information from simulations of systems with a size much smaller than the correlation length by extrapolation – this is done in the finite size scaling method which will be discussed in Section 7.3.2. In this chapter, we shall almost exclusively be concerned with systems in equilibrium.

7.1.1 Ensembles

If a system is thermally and mechanically insulated, the internal energy will remain unchanged in the course of time. If the system is not insulated, it will eventually take on the temperature of its surroundings (we assume that the surroundings have a constant temperature). Such physical quantities, which are either kept fixed or whose average value is controlled externally are called *system parameters*. Different experimental circumstances correspond to different parameters being kept fixed. In the theory of statistical physics, these cases correspond to different *ensembles*. We shall see that adapting the simulation techniques for classical many-particle systems (Monte Carlo and molecular dynamics) to these experimental situations is a nontrivial problem – that is why we consider the ensemble theory in some detail in this section.

The fundamental postulate, or assumption, of statistical mechanics pertains to systems with fixed energy E , volume V and particle number N (in magnetic systems, instead of the volume V , the external magnetic field H is kept constant). The fundamental postulate says that all states accessible to the system and having a prescribed energy, volume and number of particles are equally likely to be visited in the course of time (the ergodic hypothesis). This leads to an identification of the time average \bar{A} (7.1) of the physical quantity A with a uniform average over all

[†]A noticeable exception is formed by the so-called mesoscopic systems which contain typically 10^2 to 10^5 particles.

accessible states – the latter is denoted as $\langle A \rangle$. Denoting the states by X , we have

$$\langle A \rangle = \frac{\sum_{\{X|E\}} A(X)}{\sum_{\{X|E\}} 1} = \frac{\sum_X A(X) \delta[\mathcal{H}(X) - E]}{\sum_X \delta[\mathcal{H}(X) - E]} = \bar{A}. \quad (7.2)$$

$\mathcal{H}(X)$ is the Hamiltonian which gives the energy for a point X in phase space. The denominator ensures proper normalisation. The sum $\sum_{\{X|E\}}$ denotes a sum over all states X with a fixed energy E ; in the unrestricted sums the delta-function takes care of the restriction to the states with energy E (the restriction to a specific volume and particle number is tacitly assumed). In the case of continuous degrees of freedom, the sums will generally be replaced by integrals. In the case of a monatomic liquid consisting of N moving particles with spherically symmetric interactions for example, the sum is replaced by the following integral over the positions \mathbf{r}_i and momenta \mathbf{p}_i of the particles:

$$\sum_X \rightarrow \left(\frac{1}{h}\right)^{3N} \int_V d^3r_1 d^3r_2 \dots d^3r_N \int d^3p_1 d^3p_2 \dots d^3p_N \quad (7.3)$$

where h is Planck's constant. The average (7.2) is called the *ensemble average* and the set of states under consideration (fixed N , V and E) is called the *microcanonical ensemble* or *(NVE) ensemble* [(NHE) ensemble in the magnetic case]. From now on, the volume V of a system of moving particles can be replaced by the external magnetic field H for magnetic systems unless stated otherwise.

The denominator in (7.2) counts the number of states with the prescribed energy. In fact, quantum mechanics imposes a way of counting which for the case of identical particles is quite different from the classical procedure: as the particles are indistinguishable, configurations which can be obtained from each other by permuting the particles should be counted only once – this implies that the sum in the denominator of (7.2) should be divided by $N!$.[†] The number of states with energy E is then given by

$$\Omega(N, V, E) = \frac{1}{N!} \sum_X \delta[\mathcal{H}(X) - E] \quad (7.4)$$

(for mixtures, the factor $N!$ is replaced by the product $N_1!N_2!\dots$, where the subscripts label the different species). The *entropy* is defined in terms of $\Omega(N, V, E)$ as

$$S(N, V, E) = k_B \ln \Omega(N, V, E) \quad (7.5)$$

where k_B is Boltzmann's constant. The quantum counting factor $N!$ is necessary in order to make the entropy thus defined an extensive variable, i.e. a variable which

[†]This only holds for systems in which there is at most one particle per quantum state. Properly taking into account more particles per state leads to quantum statistical distributions.

scales linearly with system size. The thermodynamic quantities temperature T , chemical potential μ , and the pressure P are given as derivatives of the entropy with respect to the system parameters:

$$T = \left(\frac{\partial S}{\partial E} \right)_{N,V}^{-1} \quad \mu = -T \left(\frac{\partial S}{\partial N} \right)_{E,V} \quad P = T \left(\frac{\partial S}{\partial V} \right)_{E,N} \quad (7.6)$$

as can be readily seen from the first law of thermodynamics:[†]

$$dE = TdS - PdV + \mu dN. \quad (7.7)$$

In experimental situations, it is often the temperature which is kept constant and not the energy (for the latter to be constant, the system must be insulated thermally and mechanically). In order to achieve constant temperature, the system under consideration is coupled to a heat bath, a much larger system with which it can exchange heat. It turns out that a time average in the system under consideration is equal to a weighted average over states with fixed volume and particle number (the energy is no longer restricted); the weighting factor is the so-called *Boltzmann factor* $\exp[-\mathcal{H}(X)/(k_B T)]$. Writing $\beta = 1/(k_B T)$, we have

$$\langle A \rangle_{NVT} = \frac{1}{N!Z} \sum_X A(X) e^{-\beta \mathcal{H}(X)}; \quad (7.8a)$$

$$Z(N, V, T) = \frac{1}{N!} \sum_X e^{-\beta \mathcal{H}(X)}. \quad (7.8b)$$

The factor Z ensures proper normalisation – it is called the *partition function* and it is related to the free energy F :

$$F = -k_B T \ln Z(N, V, T) \quad (7.9)$$

which, in terms of thermodynamic quantities, is given by

$$F = E - TS. \quad (7.10)$$

In equilibrium, the free energy assumes its minimum under the constraint of fixed volume and particle number. The average in (7.8) is called the *canonical ensemble average* or (NVT) ensemble average. Note that the partition function can be written as a sum over sets of states with fixed energy:

$$Z(N, V, T) = \sum_E e^{-\beta E} \Omega(N, V, E), \quad (7.11)$$

[†]Often, the first law is stated without including changes in particle number dN .

where $\Omega(N, V, E)$ is the number of states with energy E as defined already in the microcanonical ensemble. The number of states $\Omega(N, V, E)$ is a rapidly increasing function of E and the Boltzmann distribution is a rapidly decreasing function of E . The product of the two functions peaks sharply at some value \bar{E} and the system will be found having an energy very close to this value most of the time. This suggests that there is in practice not much difference between the canonical and the microcanonical system in which the energy is kept rigorously fixed at \bar{E} . This is a manifestation of the so-called ensemble equivalence: because of the law of large numbers, measurable physical quantities exhibit very small fluctuations – hence fixing them to their average value leaves the system essentially unchanged. For finite systems, the differences between the ensembles increase with decreasing system size.

Using the definition of the entropy (7.5), we may write (7.11) as

$$Z(N, V, T) = \sum_E e^{-\beta(E-TS)} = \sum_E e^{-\beta F_E}, \quad (7.12)$$

where F_E is the free energy $E-TS$ with S evaluated in the microcanonical ensemble with energy E , and we see that the sum is indeed dominated by the states for which the free energy is minimal.

Using again the first law of thermodynamics, (7.7), we can derive the following thermodynamic quantities from the free energy:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T} \quad P = - \left(\frac{\partial F}{\partial V} \right)_{N,T} \quad S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}. \quad (7.13)$$

If the pressure P is kept constant and not the volume, as in a cylinder closed by a movable piston, we obtain an average over the isothermal-isobaric or (NPT) ensemble:

$$\langle A \rangle_{NPT} = \frac{1}{N!Q} \int dV e^{-\beta PV} \sum_X e^{-\beta \mathcal{H}(X)} A(X); \quad (7.14a)$$

$$Q(N, P, T) = \int dV e^{-\beta PV} \frac{1}{N!} \sum_X e^{-\beta \mathcal{H}(X)} = \int dV e^{-\beta PV} Z(N, V, T), \quad (7.14b)$$

where $Q(N, P, T)$ is again called the partition function. We see that Q is related to the canonical partition function Z in a similar fashion as Z was related to the function Ω in the microcanonical ensemble – see Eq. (7.11). Q is related to the Gibbs free energy or Gibbs potential G :

$$G = -k_B T \ln Q(N, P, T). \quad (7.15)$$

G can be expressed in terms of thermodynamic quantities as

$$G = E - TS + PV, \quad (7.16)$$

and it assumes its minimum value when the system has reached equilibrium under the condition of fixed temperature and pressure. For magnetic systems, the role of the pressure P is taken over by the total magnetic moment M . The other relevant thermodynamic quantities follow from the definition of $G(N, P, T)$:

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{P,T} \quad V = \left(\frac{\partial G}{\partial P} \right)_{N,T} \quad S = - \left(\frac{\partial G}{\partial T} \right)_{P,N}. \quad (7.17)$$

If the volume is again fixed, but the number of particles is allowed to vary, we obtain the *grand canonical ensemble* average:

$$\langle A \rangle = \frac{1}{Z_G} \sum_N e^{\beta\mu N} \frac{1}{N!} \sum_X e^{-\beta\mathcal{H}(X)} A(X) \quad (7.18a)$$

$$Z_G(\mu, V, T) = \sum_N e^{\beta\mu N} \frac{1}{N!} \sum_X e^{-\beta\mathcal{H}(X)}. \quad (7.18b)$$

Here, μ is the chemical potential for the addition or removal of a particle. $Z_G(\mu, V, T)$ should not be confused with the canonical partition function $Z(N, V, T)$ – it can be expressed in terms of the latter as

$$Z_G(\mu, V, T) = \sum_N e^{\beta\mu N} Z(N, V, T). \quad (7.19)$$

Z_G defines the *grand canonical potential* Ω_G analogous to similar definitions for the other ensembles:

$$\Omega_G(\mu, V, T) = -k_B T \ln Z_G(\mu, V, T). \quad (7.20)$$

In equilibrium, this potential assumes its minimum value for μ , T and V fixed. From the definition of Z_G and from the expression for the average values in the grand canonical ensemble, it follows that

$$\Omega_G(\mu, V, T) = F - \mu N. \quad (7.21)$$

The internal energy can be written in terms of the variables S , V and N and it satisfies the Gibbs-Duhem equation⁴

$$E(S, V, N) = TS - PV + \mu N \quad (7.22)$$

so that we have

$$\Omega_G(\mu, V, T) = -PV. \quad (7.23)$$

From the grand canonical potential we can derive thermodynamic quantities:

$$N = - \left(\frac{\partial \Omega_G}{\partial \mu} \right)_{V,T} \quad P = - \left(\frac{\partial \Omega_G}{\partial V} \right)_{\mu,T} \quad S = - \left(\frac{\partial \Omega_G}{\partial T} \right)_{V,\mu}. \quad (7.24)$$

Expectation values of thermodynamic quantities are either calculated as ensemble averages or as integrals over phase space. As an example of an ensemble average, consider the internal energy. The expectation value of this quantity in the canonical ensemble is given by

$$\langle E \rangle_{NVT} = \frac{\sum_X e^{-\beta \mathcal{H}(X)} \mathcal{H}(X)}{\sum_X e^{-\beta \mathcal{H}(X)}} \quad (7.25)$$

and from this it is readily seen that

$$\langle E \rangle_{NVT} = -\frac{\partial \ln Z}{\partial \beta}. \quad (7.26)$$

The specific heat at constant volume C_V is defined as

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} \quad (7.27)$$

and it can therefore be related to the root mean square (rms) fluctuation of the energy:

$$\begin{aligned} C_V &= \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2} \\ &= \frac{1}{k_B T^2} \left[\frac{\sum_X e^{-\beta \mathcal{H}(X)} \mathcal{H}^2(X)}{\sum_X e^{-\beta \mathcal{H}(X)}} - \left(\frac{\sum_X e^{-\beta \mathcal{H}(X)} \mathcal{H}(X)}{\sum_X e^{-\beta \mathcal{H}(X)}} \right)^2 \right] \\ &= \frac{1}{k_B T^2} (\langle E^2 \rangle_{NVT} - \langle E \rangle_{NVT}^2). \end{aligned} \quad (7.28)$$

Information about the microscopic properties of the system is given by correlation functions, which can sometimes be measured experimentally, for example through neutron scattering experiments.⁹ In the next section we shall encounter several examples of correlation functions.

In later chapters, we shall describe the molecular dynamics and Monte Carlo simulation methods, which enable us to evaluate ensemble averages of different physical quantities which are expressed in terms of the system coordinates – such ensemble averages are called *mechanical averages*. Free energies and chemical potentials are not directly given as mechanical averages but as phase space integrals. Integrals over phase space cannot be estimated directly in simulations, but fortunately differences between free energies at two different temperatures can be formulated as ensemble averages. Suppose, for example, that we know the free energy of system at a temperature T , and we would like to know it at a different

temperature T' . The difference $\beta F(T) - \beta' F(T')$ is then found as

$$\begin{aligned} \exp[\beta F(\beta) - \beta' F(\beta')] &= \frac{Z(\beta')}{Z(\beta)} = \\ &= \frac{\sum_X \exp[-\beta' \mathcal{H}(X)]}{\sum_X \exp[-\beta \mathcal{H}(X)]} = \langle \exp[(-\beta' + \beta) \mathcal{H}] \rangle_\beta \end{aligned} \quad (7.29)$$

where $\langle \cdots \rangle_\beta$ denotes a canonical ensemble average evaluated at inverse temperature β . Determination of this expectation value in a simulation suffers from bad statistics. The reason is that in these simulations the system is pushed into a narrow region around a hypersurface in phase space where the configurational energy is equal to its average value, say \bar{E} , at temperature β . In Eq. (7.29), we want to probe the region where the configurational energy is equal to its average \bar{E}' at temperature β' – hence this region will only be probed correctly if β and β' are fairly close, so that the hypersurface with configurational energy \bar{E}' lies within the narrow region around the \bar{E} -hypersurface probed by the phase space integral. If this is not the case, simulations can be performed for a number of temperatures between T and T' ; the resulting free energy differences are then added to find the desired free energy difference. Such is frequently done, although a slightly more subtle approach is used in practice, see Ref. 10.

Another approach is to integrate the free energy numerically from one value of the volume or temperature to another and is called *thermodynamic integration*. According to Eqs. (7.13) and (7.26), we have¹⁰

$$F(T, V_1) = F(T, V_0) - \int_{V_0}^{V_1} P(T, V) dV \quad (7.30a)$$

$$\frac{F(T_1, V)}{T_1} = \frac{F(T_0, V)}{T_0} + \int_{T_0}^{T_1} \frac{E(T, V)}{T^2} dT. \quad (7.30b)$$

This method can be used to calculate energy differences between systems at different temperatures or with different volumes. Integration over a particular path in phase space can be performed by carrying out simulations for a number of points on that path in order to determine $\langle P \rangle$ or $\langle E \rangle$ and then performing a numerical integration of (7.30). It is advisable to choose these points in accordance with the Gauss-Legendre integration scheme – see Section A.6. At a phase transition (see Section 7.3), the free energy does not behave smoothly as a function of the system parameters and the path must either circumvent the transition line, or two integrations must be performed, one for each phase, with starting points corresponding to appropriate reference systems for which the free energy is known, for example, at zero or infinite temperature.

In Chapter 10 we shall consider additional methods for calculating free energies and chemical potentials. For a review of free energy calculation methods see Ref. 10.

7.2 Examples of statistical models – phase transitions

7.2.1 Molecular systems

A *model* is defined by its degrees of freedom and by the Hamiltonian which assigns an energy to every possible state of the system, that is, a specific set of values of the degrees of freedom. If we consider, for example, a system consisting of N identical point particles, the degrees of freedom are given by all positions \mathbf{r}_i and all momenta \mathbf{p}_i , $i = 1, \dots, N$ of the particles. We shall denote the full sets of positions and momenta by R and P respectively. The Hamiltonian \mathcal{H} is given as

$$\mathcal{H}(R, P) = \sum_{i=1}^N \frac{p_i^2}{2m} + V_N(R). \quad (7.31)$$

$V_N(R)$ denotes the total potential energy of all the particles with positions given by the $3N$ -coordinate R . In simulations one often uses an approximation in which $V_N(R)$ is written as a sum over pair potentials:

$$V_N(R) = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}}^N V_2(|\mathbf{r}_i - \mathbf{r}_j|), \quad (7.32)$$

where the sum is over all pairs i, j , except those with $i = j$. The factor $1/2$ compensates the double counting of pairs in the sum. Pair potentials are so popular because usually the evaluation of all forces or all potentials is the most time consuming part of the program, and the time needed for this calculation increases rapidly with the number of particles involved in the interaction. For pair potentials for example, there are $N(N-1)/2$ interactions, for three-particle interactions we would have $\mathcal{O}(N^3)$ contributions etc.

A Lennard–Jones parametrisation for the pair potential is often adopted:

$$V_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (7.33)$$

Such a potential has already been used in Chapter 2[†] for describing the interaction between a hydrogen and a krypton atom. The $1/r^6$ tail is based on polarisation

[†]Note that this form deviates from that given in Chapter 2. The present form is common in molecular dynamics.

effects of the interacting atoms and the $1/r^{12}$ repulsive is chosen for numerical convenience. For argon, the Lennard-Jones description has been quite successful¹¹ – it has been applied to the solid, liquid and gas phases.

The canonical partition function Z is given as

$$Z(N, V, T) = \frac{1}{h^{3N} N!} \int_V d^{3N} R \, d^{3N} P \, \exp \left[-\beta \left(\sum_{i=1}^N \frac{p_i^2}{2m} + V_N(R) \right) \right]. \quad (7.34)$$

Irrespective of the form of V_N , we can perform the (Gaussian) integration over the momenta since they do not couple with the spatial coordinates, and we find

$$Z(N, V, T) = \frac{1}{N!} \left(\frac{2m\pi}{\beta h^2} \right)^{3N/2} \int_V d^{3N} R \, \exp[-\beta V_N(R)]. \quad (7.35)$$

For systems consisting of rigid polyatomic molecules, the interaction potential is usually taken to be the sum of atomic pair potentials, aside from rigidity constraints. A tantalising problem is the satisfactory description of water in simulations using *ab initio* interaction potentials.¹²

Macroscopic quantities such as pressure, specific heat, etcetera, can be determined relatively easily from simulations and can be compared with experimental results. They give global information concerning the state of the system. The pressure can be found in a simulation using the virial theorem:¹³

$$\frac{\beta P}{n} = 1 - \frac{\beta}{3N} \left\langle \sum_{i=1}^N \mathbf{r}_i \cdot \nabla_i V_N(R) \right\rangle \quad (7.36)$$

where $\langle \dots \rangle$ denotes the usual ensemble average, but in a dynamic system the time average can be used instead.

The specific heat at constant volume can easily be calculated in the canonical ensemble using Eq. (7.28), which relates this quantity to the fluctuation of the total energy. However, in the microcanonical ensemble, the total energy is fixed, so its fluctuation vanishes at all times. Fortunately, it can be calculated from the fluctuation of the kinetic energy from a formula derived by Lebowitz:¹⁴

$$\frac{\langle \delta K^2 \rangle}{\langle K \rangle^2} = \frac{2}{3N} \left(1 - \frac{3N}{2C_V} \right). \quad (7.37)$$

More detailed information can experimentally be obtained via X-ray and neutron scattering experiments. In particular, several correlation functions can be measured experimentally and they can also be determined in simulations. The static pair correlation function $g(\mathbf{r}, \mathbf{r}')$ is proportional to the probability of finding a particle

at \mathbf{r} and simultaneously one at \mathbf{r}' . In the canonical ensemble, it is given by the following expression:

$$g(\mathbf{r}, \mathbf{r}') = V^2 \frac{1}{N! h^{3N} Z} \int_V d^3 r_3 \dots d^3 r_N \exp[-\beta V_N(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)]. \quad (7.38)$$

For a homogeneous system, this function depends on $\Delta\mathbf{r} = \mathbf{r} - \mathbf{r}'$ only and it can hence for large N be written as

$$g(\Delta\mathbf{r}) = \frac{V}{N(N-1)} \left\langle \int d^3 r' \sum_{\substack{i,j \\ i \neq j}}^N \delta(\mathbf{r}' - \mathbf{r}_i) \delta(\mathbf{r}' + \Delta\mathbf{r} - \mathbf{r}_j) \right\rangle. \quad (7.39)$$

For large $\Delta\mathbf{r}$, the correlation function tends to 1, and often the ‘bare’ correlation function $h(\Delta\mathbf{r})$, which is defined as $h(\Delta\mathbf{r}) = g(\Delta\mathbf{r}) - 1$ is used instead.

The pair correlation function contains information concerning the local structure of the fluid. For an isotropic, homogeneous system, the pair correlation function depends only on the distance $\Delta r = |\mathbf{r} - \mathbf{r}'|$. Suppose we were to sit somewhere in the fluid and watch the surroundings for some time, then, on average, we would see a homogeneous structure. If we were to move along with a particular particle, however, and watch the scenery from this particle, we would find no particles close to us because of the strong short-range repulsion. Then we have an increase in density due to a layer of particles surrounding our particle, followed by a drop in density marking the boundary between this layer and a second layer, and so on. Due to the fluctuations, the layer structure becomes more and more diffuse for increasing distances and the correlation function will approach a constant value at large distances. A typical example of a pair distribution function in a fluid is shown in Figure 7.1. For a discussion on the experimental determination of static and dynamic correlation functions, see Ref. 13.

Another important correlation function is the velocity autocorrelation function, which is a function of time. It is the expectation value of the dot product of the velocity of a particular particle (‘tagged particle’) at time 0 with the velocity of the same particle at time t :

$$c_{v_i}(t) = \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle \quad (7.40)$$

for an arbitrary particle i . For a homogeneous system this is independent of i . Since this correlation function is a dynamic quantity, it cannot be found as an ensemble average, as the latter is suitable for evaluation of averages of static quantities only. For identical particles, the velocity autocorrelation function is usually evaluated as a combined time average and an average over the N particles in equilibrium:

$$c_v(t) = \frac{1}{N} \lim_{T \rightarrow \infty} \sum_{i=1}^N \frac{1}{T} \int_0^T dt' \mathbf{v}_i(t') \cdot \mathbf{v}_i(t' + t). \quad (7.41)$$

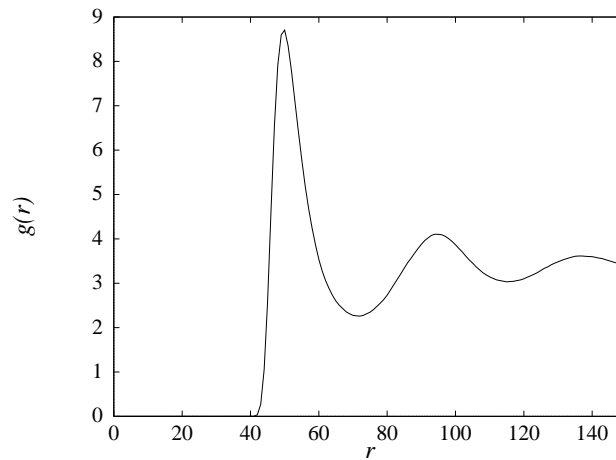


Figure 7.1: The pair correlation function of argon at its triple point.

In 1970, Alder and Wainwright concluded from molecular dynamics simulations for the hard sphere gas that this function decays algebraically as $1/t^{D/2}$ (D is the dimension of the system), in striking contrast to the ‘molecular chaos’ assumption according to which the velocity autocorrelation should decay exponentially. The long time tail implies that a particle moving in a fluid does not so easily ‘forget’ its initial motion. It turns out that the tagged particle causes a pressure rise ahead and a pressure drop behind itself and the resulting pressure difference produces vortices (in two dimensions) or a sideways vortex ring (if $D = 3$) and these persist for a relatively long time. Remarkable quantitative agreement has been found with a hydrodynamic calculation of a sphere moving in a fluid.^{15, 16}

7.2.2 Lattice models

Another model is a ‘magnetic’ one: the famous Ising model.^{17, 18} The quotes are put around the qualification ‘magnetic’ to indicate that the model does not describe magnetic systems satisfactorily, it gives however a good description of atoms adsorbed on surfaces and of two-component alloys. Furthermore, the Ising model is an example of a lattice field theory (lattice field theories will be discussed in Chapter 15). Last but not least: the two-dimensional Ising model on a square lattice was the first model exhibiting a genuine phase transition and which was solved exactly.^{18–20}

The Ising model is defined on a lattice and we shall confine ourselves to the

two-dimensional version on a square lattice of size $L \times L$ (in the thermodynamic limit L goes to infinity). The lattice sites are labelled by a single index i , and with $\langle i, j \rangle$ we denote a pair of neighbouring sites, where it is assumed that the spins on the top row of the lattice are connected to the corresponding ones on the bottom row and similarly for the left and right columns of sites (periodic boundary conditions, see Figure 7.2). On each site i , a ‘spin’ s_i is located, which can assume

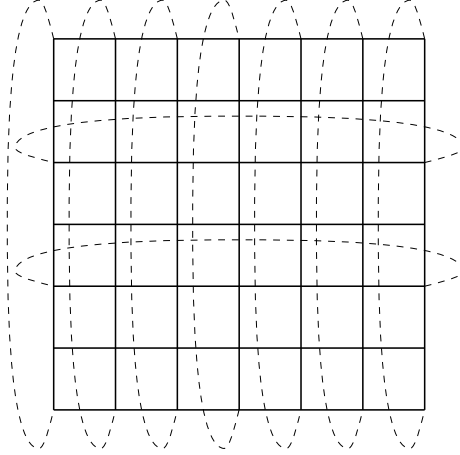


Figure 7.2: Periodic boundary conditions on the square lattice. All sites on the left column are coupled to their counterparts on the right column, but only two of these couplings are shown.

two different values, which we shall take $+1$ and -1 . The spins are the degrees of freedom, and the Hamiltonian assigns an energy to each configuration $\{s_i\}$ of the spins according to

$$\mathcal{H}\{s_i\} = -J \sum_{\langle i, j \rangle} s_i s_j - H \sum_i s_i. \quad (7.42)$$

J is a coupling constant. It couples only nearest neighbour spins: the first sum is over nearest neighbour pairs on the lattice (taking periodic boundary conditions into account). For positive J , the coupling term favours like nearest neighbour pairs as this lowers the total energy: each spin wants to be surrounded by like spins on neighbouring sites – this case is called ferromagnetic – and for negative J -values the model is called antiferromagnetic. The second term favours the spins to have a sign equal to that of the external magnetic field H . The partition function of the Ising model is given by

$$Z = \sum_{\{s_i\}} \exp \left[\beta J \sum_{\langle i, j \rangle} s_i s_j + \beta H \sum_i s_i \right]. \quad (7.43)$$

Notice that the model is defined without any reference to dynamics. Dynamical Ising models have been formulated²¹ and these reflect somehow the behaviour of real systems, but their form is not imposed by physical laws.

An interesting case is zero external magnetic field ($H = 0$), for which the model has been solved analytically. The Hamiltonian is then invariant with respect to global spin reversal. At absolute zero temperature, $\beta \rightarrow \infty$, either of two configurations, with all spins + or all spins –, are allowed. Suppose we start off with all spins +. We are interested in the behaviour of the average value of the spins, which we shall call *magnetisation* and which is denoted m . Flipping a spin with four equal nearest neighbours induces a penalty via the Boltzmann factor being reduced by a factor $e^{-8\beta J}$ (remember the Boltzmann factor gives the weight, i.e. the probability of occurrence in a time sequence) and for low temperature, as β is still large, a particular spin turning over is therefore a very rare event. The relative occurrence of a configuration with an *arbitrary* single spin turned over with respect to one in which all spins are equal is given by $L^2 e^{-8\beta J}$. If we raise the temperature, the probability for having one or more spins turned over increases and therefore the magnetisation decreases (in absolute value). What will happen to the magnetisation when increasing the temperature further? Let us first consider $T \rightarrow \infty$, or $\beta = 0$. In that case all configurations have the same Boltzmann factor of 1 and the coupling between the spins is no longer noticeable. Therefore, each spin will assume values +1 and –1 with equal probability and the average magnetisation will vanish. Two scenarios are possible for intermediate temperatures: either the magnetisation will decay asymptotically with increasing temperature, or it will vanish at some finite temperature. If the latter happens, we shall see a nonanalytic behaviour in the magnetisation curve, which seems highly improbable as the Hamiltonian depends analytically on all spins. Indeed for *finite* systems, all physical variables are analytic functions of the system parameters, but for $N \rightarrow \infty$, nonanalytic behaviour might show up. This is precisely what happens! The magnetisation for the infinite system vanishes at a finite temperature T_c given by $J/k_B T_c \approx 0.44$ and this phenomenon is called *phase transition*.^{18, 19} For reasons to be explained below, this phase transition is often called ‘second order’, ‘critical’ or ‘continuous’. Figure 7.3 shows the (m, T) phase diagram for zero magnetic field. Two branches are shown, one for a system starting off with negative, and the other with positive magnetisation.

The behaviour of the Ising ferromagnet may be described in terms of the balance between entropy and energy. There is only one state with lowest energy (if we restrict ourselves to positive magnetisation at low temperatures, see below), L^2 states with one spin flipped, $L^2(L^2 - 1)/2$ states with two spins flipped and so on: the number of states increases rapidly with energy. It also increases rapidly with decreasing magnetisation for similar reasons. Therefore, there exist a huge number of disordered (zero magnetisation) states, having a relatively small Boltzmann

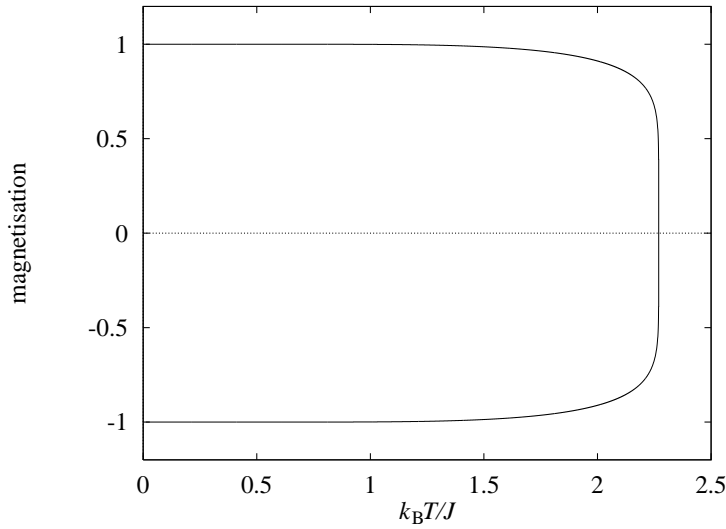


Figure 7.3: Phase diagram of the Ising model. There are two branches, one with negative and one with positive magnetisation, corresponding to the spin-reversal symmetry present in the model.

factor, and a small number of ordered states, with a large Boltzmann factor. The Boltzmann effect is reduced by increasing the temperature. At the point where the numeric abundance (entropy effect) of the disordered states compensates for the Boltzmann effect, energy and entropy of the domain walls separating the spin-up from the spin-down phases are said to be in balance – this is the critical point, where the average magnetisation reaches zero.

This entropy–energy balance can be quantified using an argument given by Peierls.⁵ A domain wall of length N , separating a + from a – region, represents an energy penalty of $2JN$, since each pair of opposite spins on both sides of the wall carries an energy J , as opposed to equal neighbouring spins representing an energy $-J$. We can estimate the number of possible domain wall configurations by realising that at each segment a domain wall has the option of turning left or right, or continuing straight on, leading to three possibilities at each segment. However, a domain wall cannot intersect itself, so at some segments only two of the three options are allowed. Therefore the number of domain wall configurations lies between 2^N and 3^N , and we have for the entropy S :

$$k_B T \ln 2^N < S < k_B T \ln 3^N. \quad (7.44)$$

The point where energy and entropy are in balance satisfies

$$k_{\text{B}}TN\ln 2 < 2NJ < k_{\text{B}}TN\ln 3, \quad (7.45)$$

which leads to $\ln 2 < 2J/(k_{\text{B}}T) < \ln 3$, or $0.3466 < J/(k_{\text{B}}T) < 0.549$, to be compared with the exact value $J/(k_{\text{B}}T) \approx 0.44$.

A remark is in place. The picture sketched so far is a dynamic one: we start off with a particular state (all spins +) and consider what happens when the temperature is increased. According to the postulate of statistical mechanics, average values of physical quantities are given by ensemble averages, and we see immediately that the average magnetisation is always zero, as the Hamiltonian is symmetric with respect to flipping all spins! It is, however, believed that in any realistic system the spins turn over one after another, or perhaps in small groups at a time. Turning over the magnetisation requires a large number of spin flips and the occurrence of a domain wall between two regions of different spin with a length of the order of the linear system size. The probability for this to happen is exceedingly small and the system will never enter the opposite magnetisation phase. This implies ergodicity violation since not all configurations are accessible to the system. A nice way to get round this violation is to switch on a small but positive magnetic field H which causes a difference between the energy of the positive and negative magnetisation phase by an amount $2HL^2$, and therefore the negative magnetisation phase no longer contributes to ensemble averages. After the calculation has been completed, the limit $H \rightarrow 0$ is taken. It is to be noted that for a finite external magnetic field the phase transition disappears.[†]

7.3 Phase transitions

7.3.1 First order and continuous phase transitions

As we have seen already in Section 7.2, phase transitions may occur in thermodynamic systems. These transitions can be of two different types, first order and second order. The latter are also called critical or continuous transitions. In this section we consider phase transitions in more detail, with emphasis on phenomena and techniques which are of interest in numerical simulations. In particular we discuss the finite size scaling technique for studying second order transitions in simulations. The description here is short and simplified and for more detailed accounts the reader is referred to the books by Plischke and Bergersen,⁵ Reichl,³

[†]Switching from a positive magnetic field to a negative one induces a change in sign of the magnetisation m if $T < T_c$. This is a first order phase transition, induced by the magnetic field instead of the temperature.

Pathria,²² Le Bellac⁸ and the various volumes in the Domb and Green/Lebowitz series.²³

The state of a system is usually characterised by a particular value of a physical quantity which is called the *order parameter*. This order parameter is used to distinguish between different phases. In the case of a gas–liquid transition at fixed pressure and temperature, it is the density which plays the role of the order parameter and the transition to the gas phase is indeed characterised by the density being decreased by a large factor. In magnetic systems, with the magnetic field and the temperature as system parameters, the order parameter is the magnetisation m which distinguishes the magnetic ($m \neq 0$) from the nonmagnetic ($m = 0$) phase and which, as we have seen above, is continuous at the zero-field Ising phase transition (the point where it vanishes) but has a discontinuous derivative. The order parameter is a derivative of the free energy (the density is expressed in terms of the volume, which is a derivative with respect to pressure, and magnetisation is a derivative with respect to magnetic field) and therefore a *jump* in the order parameter means a discontinuity in a first derivative of the free energy – hence the name ‘first order’ for this type of transition. If the order parameter is continuous at the phase transition, we speak of a continuous, critical or second order transition. In fact, the discontinuity shows up ‘before the second derivative’, as the free energy generally behaves as a broken power of one of the external parameters, $f \sim (K - K_c)^\alpha$, where K is the external parameter which assumes the value K_c at the critical point, and α lies between 1 and 2.

As we have seen in Section 7.1, any system in equilibrium is characterised by some free energy assuming its minimum for given values of the system parameters, and for this minimum the order parameter assumes a particular value. It is possible to define a free energy for any fixed value of the order parameter by calculating the partition function for exclusively those configurations which have the prescribed value of the order parameter. As an example, we can define the free energy, $F(m)$, for the Ising model with fixed magnetic field in terms of a partition function, $Z(m)$, defined as

$$Z(m) = \sum_{\{s_i\}} e^{-\beta \mathcal{H}} \delta \left(\sum_i s_i - L^d m \right) \quad (7.46a)$$

$$F(m) = -k_B T \ln Z(m), \quad (7.46b)$$

where d is the dimension of the system. Note the delta-function in the definition of $Z(m)$ restricting the sum to configurations with a fixed magnetisation m . It is instructive to consider how this free energy as a function of the order parameter changes with an external parameter (the temperature for example) across the transition for the two different types of phase transitions. Typical examples are

shown in Figure 7.4.

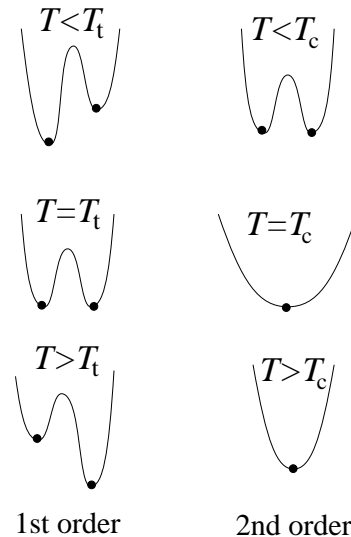


Figure 7.4: Typical behaviour of the free energy as a function of the order parameter and temperature. The left hand side corresponds to the first order case, with transition temperature T_t , and the right hand side to the continuous case, with critical transition temperature T_c .

The equilibrium situation is characterised by the minimum of the free energy. If we imagine the leftmost minimum in the first order case to correspond to the liquid phase and the right hand one to the gas phase, we see that, away from the transition temperature, one of the two phases is stable and the other one metastable. The phase transition is characterised by the liquid phase going from stable to metastable and the gas phase vice versa. In the continuous case (right hand side of Figure 7.4), there are two (or more) minima of equal depth, corresponding to as many ordered phases, and these merge at the phase transition into one, disordered phase – in the Ising model, the ordered phases are the positive and negative magnetisation phases, merging into a single, nonmagnetic, disordered phase. Close to the phase transition the system can easily hop from one (weakly) ordered phase to another, as the phases are separated by weak barriers and therefore fluctuations will increase considerably: the phase transition is announced before it actually happens by an increase in the fluctuations. This is unlike the first order case, in which the order parameter jumps from one well into the other without this being announced by an increase in the fluctuations.

Before focusing on second order transitions, we discuss some problems related to detecting first order transitions in a simulation. From Figure 7.4 it is seen that, in order for the actual transition to take place, the system should overcome a free-energy barrier, and obviously the higher the barrier the longer the time needed for this to happen. In the short time over which a typical system can be simulated, it will not be able to overcome the barrier at or near the first order transition and we shall observe a strong hysteresis: if, in the case of a liquid/gas transition, the system is cooled down from the gas phase, it will remain in that phase well below the transition temperature before it will actually decide to condense into the liquid phase. On the other hand, if a fluid is heated, it will remain in the fluid state above the transition temperature for quite some time before it enters the gas phase. In order to determine the transition temperature it is necessary to obtain the free energy for both phases so that the transition can be determined as the point where they become equal. However, as mentioned already in Section 7.1, the free energy cannot be extracted straightforwardly from molecular dynamics or Monte Carlo simulations, and the special techniques mentioned there and those to be discussed in Chapter 10 must be applied. In transfer matrix calculations (see Chapter 11), the free energy is directly obtainable but this method is restricted to lattice spin models. Panagiatopoulos^{24, 25} has developed a method in which two phases of a molecular system can coexist by adjusting their chemical potentials by the exchange of particles – see Section 10.4.3.

*7.3.2 Critical phase transitions and finite size scaling

Critical phase transitions are characterised by the disappearance of order caused by different ordered phases merging into one disordered phase at the transition. In contrast to first order transitions, critical phase transitions are ‘announced’ by an important increase of the fluctuations. The Ising model on a square lattice described above is an ideal model for visualising what is going on close to a second order phase transition.

An interesting object in connection with phase transitions is the pair correlation function. As the Ising model in itself is not dynamic, only the static correlation function is relevant. It is given by

$$\tilde{g}(m, n) = \langle s_m s_n \rangle = \frac{1}{Z} \sum_{\{s_i\}} s_m s_n \exp \left[\beta J \sum_{\langle ij \rangle} s_i s_j + \beta H \sum_i s_i \right]. \quad (7.47)$$

Instead of the pair correlation function defined in (7.47), the ‘bare’ correlation function is usually considered:

$$g(i, j) = \tilde{g}(i, j) - \langle s_i \rangle^2 \quad (7.48)$$

which decays to zero if i and j are far apart. The physical meaning of the bare pair correlation function is similar to that defined above for molecular systems. Suppose we sit on a site i , then $g(i, j)$ gives us the probability of finding the same spin value on site j in excess of the average spin on the lattice. The correlation function defined here obviously depends on the relative orientation of i and j because the lattice is anisotropic. However, for large distances this dependence is weak and the pair correlation function will depend only on the distance r_{ij} between i and j . The decay of the bare correlation function below the transition temperature is given by

$$g(r) \sim e^{-r/\xi}, \quad \text{large } r. \quad (7.49)$$

ξ is called the *correlation length*: it sets the scale over which each spin has a significant probability of finding like spins in excess of the average probability. One can alternatively interpret ξ as a measure of the average linear size of the domains containing minority spins. If we approach the transition temperature, more and more spins turn over. Below the transition temperature, the system consists of a connected domain (the ‘sea’) of majority spins containing ‘islands’ of minority spin. When approaching the transition temperature, the islands increase in size and at T_c they must grow into a connected land cluster which extends through the whole system in order to equal the surface of the sea, which also extends through the whole system. For higher temperature the system is like a patchwork of unconnected domains of finite size. The picture described here implies that at the transition the correlation length will become of the order of the system size. Indeed, it turns out that at the critical phase transition the correlation length diverges and the physical picture²⁶ is that of huge droplets of one spin containing smaller droplets of the other spin containing still smaller droplets of the first spin and so on. This suggests that the system is self-similar for a large range of different length scales: if we zoomed in on part of a large Ising lattice at the phase transition, we would notice that the resulting picture is essentially indistinguishable from the one presented by the lattice as a whole: the differences only show up at the smallest scales, i.e. comparable to the lattice constant which increases when zooming in. This scale invariance is exploited in renormalisation theory^{27, 28} which has led to a qualitative and quantitative understanding of critical phase transitions.[†]

One of the consequences of the scale invariance at the critical phase transition is that the form of the correlation function should be scale invariant, that is, it should be essentially invariant under a scale transformation with scaling factor b , and it follows from renormalisation theory that at the transition, g transforms under a

[†]More recently, the more extended conformal symmetry has been exploited in a similar fashion as the mere scale invariance. Conformal field theory has turned out a very powerful tool to study phase transitions in two-dimensional systems.^{29–31}

rescaling as

$$g(r) = b^{2(d-y)} g(rb) \quad (7.50)$$

(d is the system dimension). From this, the form of g is found as

$$g(r) = \frac{\text{Constant}}{r^{2(d-y)}}. \quad (7.51)$$

The exponent y is called the *critical exponent*. It turns out that this exponent is *universal*: if we change details in the Hamiltonian, like adding next nearest neighbour interactions to it, the temperature at which the transition takes place will change, but the critical exponent y will remain exactly the same. Systems which are related through such ‘irrelevant’ changes in the Hamiltonian are said to belong to the same *universality class*. If the changes to the Hamiltonian are too drastic, however, like changing the number of possible states of a spin (for example 3 or 4 instead of 2 in the Ising model), or if we add strong next nearest neighbour interactions with a sign opposite to the nearest neighbour ones, the critical behaviour will change: we cross over to a different universality class.

It should be noted that the spin pair-correlation function is not the only correlation function of interest. Other correlation functions can be defined, which we shall not go into, but it is important that these give rise to new exponents. Different correlation functions may have the same exponent, or their exponents may be linearly dependent. The set of independent exponents defines the universality class. In the case of the Ising model this set contains two exponents, the ‘magnetic’ one, y_H , which we have encountered above, and the ‘thermal’ exponent y_T (which is related to a different correlation function).

The critical exponents not only show up in correlation functions, they also describe the behaviour of thermodynamic quantities close to the transition. For example, in magnetic systems, the magnetic susceptibility χ_m , defined as

$$\chi_m = \left(\frac{\partial m}{\partial H} \right)_T, \quad (7.52)$$

exhibits a singularity near the phase transition:

$$\chi_m(T) \sim |T - T_c|^{-\gamma} \quad (7.53)$$

where γ is also called the ‘critical exponent’; its value is related to the y -exponents by $\gamma = (-d + 2y_H)/y_T$. For the specific heat c_H , the correlation length ξ and the magnetisation m we have similar critical exponents:

$$\begin{aligned} c_h(T) &\propto |T - T_c|^{-\alpha} \\ \xi(T) &\propto |T - T_c|^{-\nu} \\ m(T) &\propto (-T + T_c)^\beta; \quad T < T_c \end{aligned} \quad (7.54a)$$

and, moreover, we have an exponent for the behaviour of the magnetisation with varying small magnetic field at the transition temperature:

$$m(H, T_c) = H^{1/\delta}. \quad (7.55)$$

For the case of the two-dimensional Ising model on a square lattice, we know the values of the exponents from the exact solution:

$$\begin{aligned} \alpha = 0, \quad \beta = 1/8, \quad \gamma = 7/4, \\ \delta = 15, \quad \nu = 1. \end{aligned} \quad (7.56)$$

The value 0 of the exponent α denotes a logarithmic divergence:

$$c_H \propto \ln|T - T_c|. \quad (7.57)$$

The fact that there are only two ν -exponents and the fact that the five exponents expressing the divergence of the thermodynamic quantities are expressed in terms of these indicates that there must exist relations between the exponents α , β etc. These relations are called *scaling laws* – examples are:

$$\alpha + 2\beta + \gamma = 2 \quad \text{and} \quad (7.58a)$$

$$2 - \alpha = d\nu, \quad (7.58b)$$

with d the dimension of the system. The Ising exponents listed above satisfy these scaling laws indeed.

In dynamical versions of the Ising model, the relaxation time also diverges with a critical exponent. The correlation time is the time scale over which a physical quantity A relaxes towards its equilibrium value \bar{A} – it is defined by[†]

$$\tau = \frac{\int_0^\infty t [A(t) - \bar{A}] dt}{\int_0^\infty [A(t) - \bar{A}] dt}. \quad (7.59)$$

At the critical point the correlation time diverges according to

$$\tau = \xi^z. \quad (7.60)$$

This divergence implies that close to the critical point the simulation time needed to obtain reliable estimates for physical quantities increases dramatically. This phenomenon is called *critical slowing down*. For most models with a Hamiltonian

[†]In Section 7.4 we shall give another definition of the correlation time which describes the decay of the time correlation function rather than that of the quantity A itself.

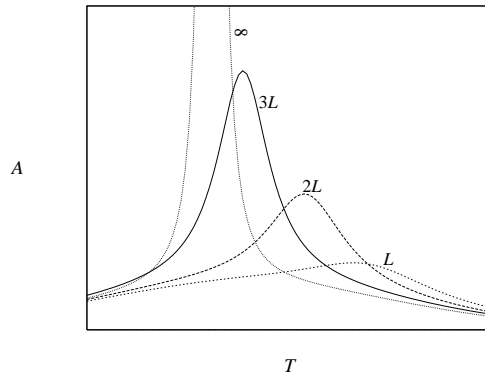


Figure 7.5: Typical behaviour of a physical quantity A vs. temperature close to the critical point for various system sizes.

containing only short-range couplings, the value of the exponent z is close to 2. For the Ising model in two dimensions, the dynamic critical exponent has been determined numerically – its value is $z \approx 2.125$.³²

For systems far from the critical point, the correlation length is small, and it is easy to simulate systems which are considerably larger than the correlation length. The values of physical quantities measured will then converge rapidly to those of the infinite system. Close to the critical point, however, the correlation length of the infinite system might exceed the size of the simulated system – hence the system size will set the scale over which correlations can extend. This part of the phase diagram is called the *finite size scaling region*. It turns out that it is possible to extract information concerning the critical exponents from the behaviour of physical quantities with varying system size close to the critical point. Of course, for a finite system, the partition function and hence the thermodynamic quantities are smooth functions of the system parameters – hence the divergences of the critical point are absent. However, we can still see a signature of these divergences in the occurrence of peaks, which in the scaling region ($\xi \gg L$) become higher and narrower with increasing system size. Also, the location of the peak may be shifted with respect to the location of the critical point. The general behaviour is shown in Figure 7.5. These characteristics of the peak shape as a function of temperature are described in terms of additional exponents, the so-called *finite size scaling exponents*:

- The shift in the position of the maximum with respect to the critical temperature

is described by

$$T_c(L) - T_c(\infty) \propto L^{-\lambda}. \quad (7.61)$$

- The width of the peak scales as

$$\Delta T(L) \propto L^{-\Theta}. \quad (7.62)$$

- The peak height grows with the system size as

$$A_{\max}(L) \propto L^{\sigma_m}. \quad (7.63)$$

The behaviour of a system is determined by two length scales: L/a and ξ/a , with ξ the correlation length of the infinite system, which in the finite size scaling region is larger than the linear system size L . As in the critical region, the fluctuations determining the behaviour of the system extend over large length scales; physical properties should be independent of a . This leaves L/ξ as the only possible parameter in the system and this leads to the so-called finite size scaling *Ansatz*. Defining

$$\epsilon \equiv \frac{T - T_c}{T_c}, \quad (7.64)$$

we can formulate the finite size scaling *Ansatz* as follows:

$$\frac{A_L(\epsilon)}{A_\infty(\epsilon)} = f \left[\frac{L}{\xi_\infty(\epsilon)} \right]. \quad (7.65)$$

Suppose the exponent of the critical divergence of the quantity A is σ :

$$A_\infty \propto \epsilon^{-\sigma}. \quad (7.66)$$

Using, moreover, the scaling form of the correlation length $\xi \propto \epsilon^{-\nu}$, we can write the scaling *Ansatz* as

$$A_L(\epsilon) = \epsilon^{-\sigma} f(L \epsilon^\nu) \quad (7.67)$$

which can be reformulated as

$$A_L(\epsilon) = L^{\sigma/\nu} \phi(L^{1/\nu} \epsilon) \quad (7.68)$$

where we have replaced the scaling function, f , by another one, ϕ , by extracting a factor $(L \epsilon^\nu)^{\sigma/\nu}$ from f and then writing the remaining function in terms of $(L \epsilon^\nu)^{1/\nu}$ rather than $(L \epsilon^\nu)$. Obviously, $\phi(x)$ will have a maximum ϕ_{\max} for some value $x = x_{\max}$ with a peak width Δx . From Eq. (7.68) we then see immediately that:

- The peak height scales as $L^{\sigma/\nu}$, hence $\sigma_m = \sigma/\nu$.

- The peak position scales as $L^{-1/\nu}$, hence $\lambda = 1/\nu$.
- The peak width also scales as $L^{-1/\nu}$, hence $\Theta = 1/\nu$.

These are the finite size scaling laws for any thermodynamic quantity which diverges at the critical point as a power law. We see that if we monitor the peak height, position and width as a function of system size, we can extract the correlation length exponent ν and the exponent σ associated with A from the resulting data.

In reality this approach poses difficulties as the fluctuations increase near the critical point and hence the time needed for obtaining reliable values for the physical quantities measured increases too. This increase is stronger when the system size increases – hence calculations for larger systems require more time, not only because more computational effort is used per time step for a larger system, but also because we need to generate more and more configurations in order to obtain reliable results. An extra complication is that the fluctuations are not only huge, but they correlate over increasing time scales, and the simulation time must be at least a few times the relaxation time in order to obtain reliable estimates for the physical quantities. In Chapter 15 we shall discuss various methods for reducing the dynamic exponent z in Monte Carlo type simulations.

We have presented only the most elementary results of the finite size scaling analysis and the interested reader is invited to consult more specialised literature. There exists a nice collection of key papers on the field³³ and a recent volume on finite size scaling.³⁴

7.4 Determination of averages in simulations

In chapters 8 and 10 we shall encounter two simulation methods for classical many-particle systems: the molecular dynamics (MD) method and the Monte Carlo (MC) method. During a simulation of a many-particle system using either of these methods, we can monitor various physical quantities and determine their expectation values as averages over the configurations generated in the simulation. We denote such averages as ‘time averages’ although the word time does not necessarily denote physical time. For a physical quantity A , the time average is

$$\bar{A} = \frac{1}{M} \sum_{n=1}^M A_n. \quad (7.69)$$

If the system size and the simulation time are large enough, these averages will be very close to the averages in a macroscopic experimental system. Usually, the system sizes and simulation times which can be achieved are limited and it

is important to find an estimate of the error bounds associated with the measured average. These are related to the standard deviation σ of the physical quantity A :

$$\sigma^2 = \langle A^2 \rangle - \langle A \rangle^2. \quad (7.70)$$

The ensemble average $\langle \dots \rangle$ is an average over many independent simulations.

We can estimate the standard deviation as a time average:

$$\sigma^2 = \overline{A^2} - \overline{A}^2. \quad (7.71)$$

For a long enough simulation this reduces to the ensemble average, and the expectation value of this estimate becomes independent of the simulation time. Equation (7.71) estimates the standard deviation irrespective of time correlations between subsequent samples generated by the simulation. However, the *standard deviation of the mean value* of A calculated over M samples generated by the simulation, i.e. the statistical error, depends on the number of *independent* samples generated in the simulation, and this is the total number of samples divided by the correlation ‘time’ τ , measured in simulation steps.

In order to study the standard deviation of the mean (the statistical error), we first analyse the time correlations. These manifest themselves in the time correlation function:

$$c_{AA}(k) = \langle (A_n - \langle A_n \rangle)(A_{n+k} - \langle A_{n+k} \rangle) \rangle = \langle A_n A_{n+k} \rangle - \langle A_n \rangle^2. \quad (7.72)$$

Note that the right hand side of this expression does not depend on n because of time translation symmetry. For $k = 0$ this function is equal to σ^2 , and time correlations manifest themselves in this function assuming nonzero values for $k \neq 0$. The time correlation function can be used to determine the *integrated correlation time* τ , defined as

$$\tau = \frac{1}{2} \sum_{n=-\infty}^{\infty} \frac{c_{AA}(n)}{c_{AA}(0)} \quad (7.73)$$

where the factor 1/2 in front of the sum is chosen such as to guarantee that for a correlation function of the form $\exp(-|t|/\tau)$ with $\tau \gg 1$, the correlation time is equal to τ . Note that this definition of the time correlation is different from that given in Eq. (7.59). The current one is more useful as it can be determined throughout the simulation, and not only at the beginning when the quantity A decays to its equilibrium value. A third definition is the *exponential correlation time* τ_{exp} :

$$\tau_{\text{exp}} = -t / \ln \left| \frac{c_{AA}(t)}{c_{AA}(0)} \right|, \quad \text{large } t. \quad (7.74)$$

This quantity is the slowest decay time with which the system relaxes towards equilibrium (such as happens at the start of a simulation when the system is not yet in equilibrium), and it is in general not equal to the integrated correlation time.

Now let us return to the standard deviation of the mean value of A as determined in a simulation generating M configurations (with time correlations). It is easy to see that the standard deviation in the mean, ϵ , is given by

$$\epsilon^2 = \left\langle \frac{1}{M^2} \sum_{n,m=1}^M A_n A_m \right\rangle - \left(\left\langle \frac{1}{M} \sum_{n=1}^M A_n \right\rangle \right)^2 = \frac{1}{M^2} \sum_{n,m=1}^M c_{AA}(n-m). \quad (7.75)$$

If we define $l = n - m$, then this can be rewritten as

$$\epsilon^2 = \frac{1}{M^2} \sum_{n=1}^M \sum_{l=n-M}^{n-1} c_{AA}(l). \quad (7.76)$$

The lowest and highest values taken on by l are $-(M-1)$ and $M-1$ respectively, and some fixed value of l between these two boundaries occurs $M - |l|$ times. This leads to the expression

$$\epsilon^2 = \frac{1}{M} \sum_{l=-(M-1)}^{M-1} \left(1 - \frac{|l|}{M}\right) c_{AA}(l) \xrightarrow{\text{large } M} 2 \frac{\tau}{M} c_{AA}(0) = 2 \frac{\tau}{M} \sigma^2. \quad (7.77)$$

We see that time correlations cause the error ϵ to be multiplied by a factor of $\sqrt{2\tau}$ w.r.t. the uncorrelated case. The obvious procedure for determining the statistical error is to first estimate the standard deviation and the correlation time, using (7.71) and (7.73) respectively, and then calculate the error using (7.77).

In practice, however, a simpler method is preferred. The values of the physical quantities are recorded in a file. Then the data sequence is chopped into a number of blocks of equal size which is larger than the correlation time. We calculate the averages of A within each block. For blocks of size m , the j -th block average is then given as

$$\bar{A}_j = \frac{1}{m} \sum_{k=jm+1}^{m(j+1)} A_k. \quad (7.78)$$

The averages of the physical quantities in different blocks are uncorrelated and the error can be determined as the standard deviation of the uncorrelated block averages. This method should yield errors which are independent of the block size provided the latter is larger than the correlation time and sufficiently small to have enough blocks to calculate the standard deviation reliably. This method is called *data-blocking*.

Exercises

- 7.1 In this problem we analyse the relation between the differential scattering cross section for elastic X-ray scattering by a collection of particles and the structure factor in more detail. Consider an incoming X-ray with wave vector \mathbf{k}_0 , which is scattered into \mathbf{k}_1 by particle number j at \mathbf{r}_j at time t' . When the wave ‘hits’ particle j at time t' , its phase factor is given by

$$e^{i\mathbf{k}_0\mathbf{r}_j - i\omega t'}$$

- (a) Give the phase of the scattered wave when it arrives at the detector located at \mathbf{r} at time t .
- (b) We assume that the incoming rays have intensity I_0 . Show that the average total intensity of waves with wave vector \mathbf{k}_1 arriving at the detector is given by

$$I(\mathbf{k}_1, \mathbf{r}) = I_0 \left\langle \sum_{l,j=1}^N e^{i\Delta\mathbf{k}(\mathbf{r}_l - \mathbf{r}_j)} \right\rangle$$

with $\Delta\mathbf{k} = \mathbf{k}_1 - \mathbf{k}_0$.

- (c) Show that this expression is equal to $I_0 N S(\Delta\mathbf{k})$, where S is the static structure factor, defined in terms of the correlation function g as

$$S(\mathbf{k}) = 1 + n \int d^3r g(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}}.$$

(n is the particle density N/V .)

- 7.2 The magnetic susceptibility of the Ising model on an $L \times L$ square lattice is defined by $\chi = \partial m / \partial H$, where m is the magnetisation and h the magnetic field.

- (a) Show that the magnetic susceptibility can be written as

$$\chi = \frac{1}{L^2 k_B T} \sum_{i,j} (\langle s_i s_j \rangle - \langle s_i \rangle^2).$$

- (b) A scaling exponent η associated with the magnetic correlation function [see Eq. (7.48)] is defined by

$$g(r) \sim r^{2-d-\eta}.$$

Assuming that close to the critical point this form extends to a distance ξ , where ξ is the correlation length, find the following scaling relation between, γ , η and ν :

$$\gamma = \nu(2 - \eta).$$

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