Chapter 15
Thermodynamic Systems

An important application for computer simulations is the calculation of thermodynamic averages in an equilibrium system. We discuss two different examples:

In the first case the classical equations of motion are solved for a system of particles interacting pairwise by Lennard-Jones forces (Lennard-Jones fluid). The thermodynamic average is taken along the trajectory, i.e. over the calculated coordinates at different times $\mathbf{r}_i(t_n)$. We evaluate the pair distance distribution function

$$g(R) = \frac{1}{N^2 - N}\left\langle \sum_{i \neq j} \delta(r_{ij} - R) \right\rangle, \tag{15.1}$$

the velocity auto-correlation function

$$C(t) = \left\langle \mathbf{v}(t_0)\mathbf{v}(t) \right\rangle \tag{15.2}$$

and the mean square displacement

$$\Delta x^2 = \left\langle \left(\mathbf{x}(t) - \mathbf{x}(t_0)\right)^2 \right\rangle. \tag{15.3}$$

In the second case the Metropolis method is applied to a one- or two-dimensional system of interacting spins (Ising model). The thermodynamic average is taken over a set of random configurations $\mathbf{q}^{(n)}$. We study the average magnetization

$$\langle M \rangle = \mu \langle S \rangle \tag{15.4}$$

in a magnetic field and the phase transition to the ferromagnetic state.

15.1 Simulation of a Lennard-Jones Fluid

The Lennard-Jones fluid is a simple model of a realistic atomic fluid. It has been studied by computer simulations since Verlet's early work [118, 265] and serves as a test case for the theoretical description of liquids [142, 182] and the liquid-gas [270] and liquid-solid phase transitions [146, 176].

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In the following we describe a simple computer model of 125 interacting particles[1] without internal degrees of freedom (see problems section). The force on atom i is given by the gradient of the pairwise Lennard-Jones potential (14.24)

$$\begin{aligned}\mathbf{F}_i &= \sum_{j\neq i}\mathbf{F}_{ij} = -4\varepsilon\sum_{j\neq i}\nabla_i\left(\frac{\sigma^{12}}{r_{ij}^{12}}-\frac{\sigma^6}{r_{ij}^6}\right)\\ &= 4\varepsilon\sum_{j\neq i}\left(\frac{12\sigma^{12}}{r_{ij}^{14}}-\frac{6\sigma^6}{r_{ij}^8}\right)(\mathbf{r}_i-\mathbf{r}_j).\end{aligned} \tag{15.5}$$

We use argon parameters $m = 6.69 \times 10^{-26}$ kg, $\varepsilon = 1.654 \times 10^{-21}$ J, $\sigma = 3.405 \times 10^{-10}$ m [3]. After introduction of reduced units for length $\mathbf{r}^* = \frac{1}{\sigma}\mathbf{r}$, energy $E^* = \frac{1}{\varepsilon}E$ and time $t^* = \sqrt{\varepsilon/m\sigma^2}\,t$, the potential energy

$$U^* = \sum_{ij} 4\left(\frac{1}{r_{ij}^{*12}}-\frac{1}{r_{ij}^{*6}}\right) \tag{15.6}$$

and the equation of motion

$$\frac{\mathrm{d}^2}{\mathrm{d}t^{*2}}\mathbf{r}_i^* = 4\sum_{j\neq i}\left(\frac{12}{r_{ij}^{*14}}-\frac{6}{r_{ij}^{*8}}\right)\left(\mathbf{r}_i^*-\mathbf{r}_j^*\right) \tag{15.7}$$

become universal expressions, i.e. there exists only one universal Lennard-Jones system. To reduce computer time, usually the 6–12 potential is modified at larger distances which can influence the simulation results [239]. In our model a simple cutoff of potential and forces at $r_{\max} = 10$ Å is used.

15.1.1 Integration of the Equations of Motion

The equations of motion are integrated with the Verlet algorithm (Sect. 12.11.5)

$$\Delta\mathbf{r}_i = \mathbf{r}_i(t) - \mathbf{r}_i(t-\Delta t) + \frac{\mathbf{F}_i(t)}{m}\Delta t^2 \tag{15.8}$$

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \Delta\mathbf{r}_i + O\left(\Delta t^4\right). \tag{15.9}$$

We use a higher order expression for the velocities to improve the accuracy of the calculated kinetic energy

$$\mathbf{v}_{i+1} = \frac{\Delta\mathbf{r}_i}{\Delta t} + \frac{5\mathbf{F}_i(t) - 2\mathbf{F}_i(t-\Delta t)}{6m}\Delta t + O\left(\Delta t^3\right). \tag{15.10}$$

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[1] This small number of particles allows a graphical representation of the system during the simulation.

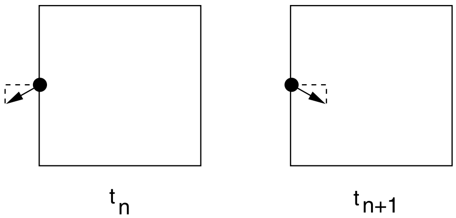

Fig. 15.1 Reflecting walls

15.1.2 Boundary Conditions and Average Pressure

Molecular dynamics simulations often involve periodic boundary conditions to reduce finite size effects. Here we employ an alternative method which simulates a box with elastic walls. This allows us to calculate explicitly the pressure on the walls of the box.

The atoms are kept in the cube by reflecting walls, i.e. whenever an atom passes a face of the cube, the normal component of the velocity vector is changed in sign (Fig. 15.1). Thus the kinetic energy is conserved but a momentum of $m\Delta v = 2mv_\perp$ is transferred to the wall. The average momentum change per time can be interpreted as a force acting upon the wall

$$F_\perp = \left\langle \frac{\sum_{\mathit{refl.}} 2mv_\perp}{dt} \right\rangle. \tag{15.11}$$

The pressure p is given by

$$p = \frac{1}{6L^2} \left\langle \frac{\sum_{\mathit{walls}} \sum_{\mathit{refl.}} 2mv_\perp}{dt} \right\rangle. \tag{15.12}$$

With the Verlet algorithm the reflection can be realized by exchanging the values of the corresponding coordinate at times t_n and t_{n-1}.

15.1.3 Initial Conditions and Average Temperature

At the very beginning the $N = 125$ atoms are distributed over equally spaced lattice points within the cube. Velocities are randomly distributed according to a Gaussian distribution for each Cartesian component v_μ

$$f(v_\mu) = \sqrt{\frac{m}{2\pi k_B T}} \mathrm{e}^{-mv_\mu^2/2k_B T} \tag{15.13}$$

corresponding to a Maxwell speed distribution

$$f(|v|) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \mathrm{e}^{-mv^2/2k_B T}. \tag{15.14}$$

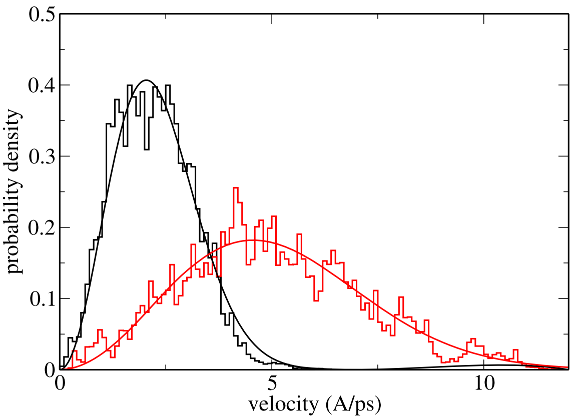

Fig. 15.2 (Velocity distribution) The velocity distribution is shown for $T = 100$ K and $T = 500$ K (*histograms*) and compared to the Maxwell speed distribution (*solid curves*)

Assuming thermal equilibrium, the effective temperature is calculated from the kinetic energy

$$k_B T = \frac{2}{3N} E_{kin}. \tag{15.15}$$

The desired temperature T_o is established by the rescaling procedure

$$\mathbf{v}_i \to \mathbf{v}_i \sqrt{\frac{k_B T_o}{k_B T_{actual}}} \tag{15.16}$$

which is applied repeatedly during an equilibration run. The velocity distribution $f(|v|)$ can be monitored. It approaches quickly a stationary Maxwell distribution (Fig. 15.2).

A smoother method to control temperature is the Berendsen thermostat algorithm [21]

$$\mathbf{v}_i \to \mathbf{v}_i \sqrt{1 + \frac{\Delta t}{\tau_{therm}} \frac{kT_o - kT_{actual}}{kT_{actual}}} \tag{15.17}$$

where τ_{therm} is a suitable relaxation time (for instance $\tau_{therm} = 20\Delta t$). This method can be used also during the simulation. However, it does not generate the trajectory of a true canonical ensemble. If this is necessary, more complicated methods have to be used [128].

15.1.4 Analysis of the Results

After an initial equilibration phase the system is simulated at constant energy (NVE simulation) or at constant temperature (NVT) simulation with the Berendsen thermostat method. Several static and dynamic properties can be determined.

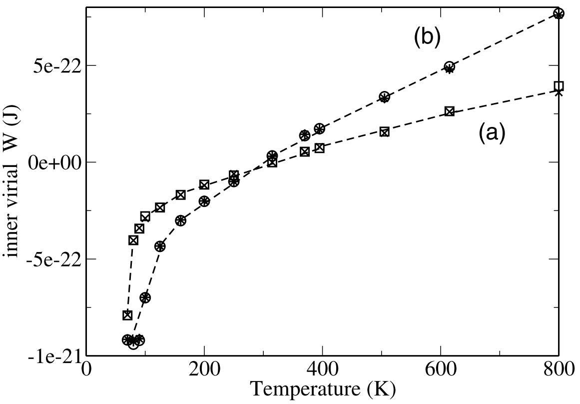

Fig. 15.3 (Inner virial) The inner virial W (15.20, *crosses* and *stars*) is compared to $pV - k_BT$ (*squares* and *circles*) for two values of the particle density $N/V = 10^{-3}$ Å^{-1} (*a*) and 1.95×10^{-3} Å^{-1} (*b*), corresponding to reduced densities $n^* = \sigma^3 N/V$ of 0.040 and 0.077

15.1.4.1 Deviation from the Ideal Gas Behavior

A dilute gas is approximately ideal with

$$pV = Nk_BT. \tag{15.18}$$

For a real gas the interaction between the particles has to be taken into account. From the equipartition theorem it can be found that[2]

$$pV = Nk_BT + W \tag{15.19}$$

with the inner virial (Fig. 15.3)

$$W = \left\langle \frac{1}{3} \sum_i \mathbf{r}_i \mathbf{F}_i \right\rangle \tag{15.20}$$

which can be expanded as a power series of the number density $n = N/V$ [231] to give

$$pV = Nk_BT\left(1 + b(T)\frac{N}{V} + c(T)\left(\frac{N}{V}\right)^2 + \cdots\right). \tag{15.21}$$

The virial coefficient $b(T)$ can be calculated exactly for the Lennard-Jones gas [231]:

$$b(T) = -\frac{2\pi}{3}\sigma^3 \sum_{j=0}^{\infty} \frac{2^{j-3/2}}{j!} \Gamma\left(\frac{2j-1}{4}\right)\left(\frac{\varepsilon}{k_BT}\right)^{(j/2+1/4)}. \tag{15.22}$$

For comparison we calculate the quantity

$$\frac{V}{N}\left(\frac{pV}{Nk_BT} - 1\right) \tag{15.23}$$

which for small values of the particle density $n = N/V$ correlates well (Fig. 15.4) with expression (15.22).

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[2] MD simulations with periodic boundary conditions use this equation to calculate the pressure.

Fig. 15.4 (Second virial coefficient) The value of $\frac{V}{N}(\frac{pV}{k_BT}-1)$ is shown for two values of the particle density $N/V = 10^{-3}$ Å (*crosses*) and 1.95×10^{-3} Å^{-1} (*circles*) and compared to the exact second virial coefficient b (*dashed curve*) (15.22)

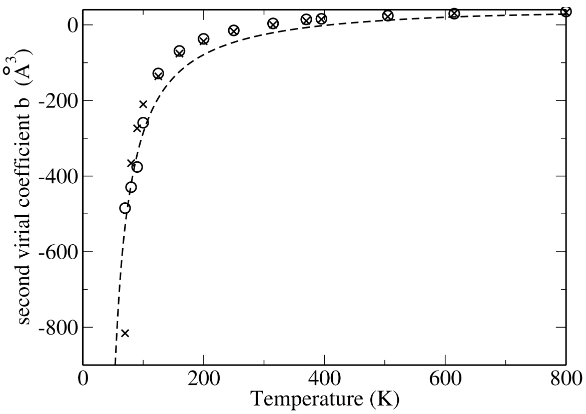
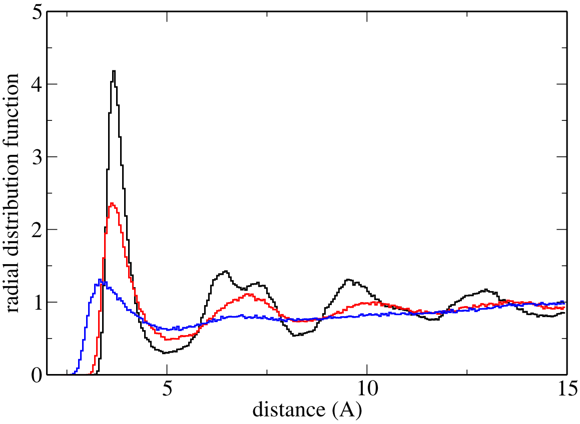


Fig. 15.5 (Radial pair distribution) The normalized radial distribution function $g(R)/g_{ideal}(R)$ is evaluated for $kT = 35$ K, 100 K, 1000 K and a density of $n = 0.025\,A^{-3}$ corresponding to a reduced density $n^* = \sigma^3 N/V$ of 1.0. At this density the Lennard-Jones system shows a liquid-solid transition at a temperature of ca. 180 K [146]



15.1.4.2 Structural Order

A convenient measure for structural order [78] is the radial pair distribution function (Fig. 15.5)

$$g(R) = \left\langle \frac{1}{N(N-1)} \sum_{i \neq j} \delta(r_{ij} - R) \right\rangle = \frac{P(R < r_{ij} < R + dR)}{dR} \tag{15.24}$$

which is usually normalized with respect to an ideal gas, for which

$$g_{ideal}(R) = 4\pi n\, R^2 dR. \tag{15.25}$$

For small distances $g(R)/g_{ideal}(R)$ vanishes due to the strong repulsive force. It peaks at the distance of nearest neighbors and approaches unity at very large distances. In the condensed phase additional maxima appear showing the degree of short (liquid) and long range (solid) order.

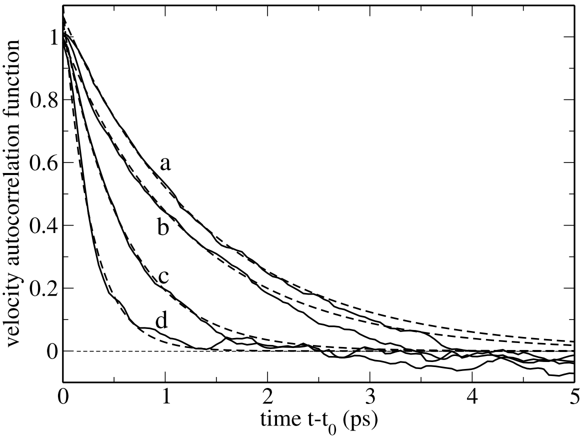


Fig. 15.6 (Velocity auto-correlation function) The Lennard-Jones system is simulated for $k_BT = 200$ K and different values of the density $n^* = 0.12$ (*a*), 0.18 (*b*), 0.32 (*c*), 0.62 (*d*). The velocity auto-correlation function (*full curves*) is averaged over 20 trajectories and fitted by an exponential function (*dashed curves*)

Equation (15.25) is not valid for our small model system without periodic boundary conditions. Therefore g_{ideal} was calculated numerically to normalize the results shown in Fig. 15.5.

15.1.4.3 Ballistic and Diffusive Motion

The velocity auto-correlation function (Fig. 15.6)

$$C(t) = \langle \mathbf{v}(t)\mathbf{v}(t_0) \rangle \tag{15.26}$$

decays as a function of the delay time $t - t_0$ due to collisions of the particles. In a stationary state it does not depend on the initial time t_0. Integration leads to the mean square displacement (Fig. 15.6)

$$\Delta x^2(t) = \langle (\mathbf{x}(t) - \mathbf{x}(t_0))^2 \rangle. \tag{15.27}$$

In the absence of collisions the mean square displacement grows with $(t - t_0)^2$, representing a ballistic type of motion. Collisions lead to a diffusive kind of motion where the mean square displacement grows only linearly with time. The transition between this two types of motion can be analyzed within the model of Brownian motion [219] where the collisions are replaced by a fluctuating random force $\Gamma(t)$ and a damping constant γ.

The equation of motion in one dimension is

$$\dot{v} + \gamma v = \Gamma(t) \tag{15.28}$$

with

$$\langle \Gamma(t) \rangle = 0 \tag{15.29}$$

$$\langle \Gamma(t)\Gamma(t') \rangle = \frac{2\gamma k_B T}{m} \delta(t - t'). \tag{15.30}$$

The velocity correlation decays exponentially

$$\left\langle v(t)v(t_0)\right\rangle = \frac{k_B T}{m} e^{-\gamma|t-t_0|} \tag{15.31}$$

with the average velocity square given by

$$\left\langle v^2\right\rangle = C(t_0) = \frac{k_B T}{m} = \frac{\langle E_{kin}\rangle}{\frac{m}{2}} \tag{15.32}$$

and the integral of the correlation function equals

$$\int_{t_0}^{\infty} C(t)\,dt = \frac{k_B T}{\gamma m}. \tag{15.33}$$

The average of Δx^2 is

$$\left\langle \left(x(t) - x(t_0)\right)^2\right\rangle = \frac{2k_B T}{m\gamma}(t - t_0) - \frac{2k_B T}{m\gamma^2}\left(1 - e^{-\gamma(t-t_0)}\right). \tag{15.34}$$

For small time differences $t - t_0$ the motion is ballistic with the thermal velocity

$$\left\langle \left(x(t) - x(t_0)\right)^2\right\rangle \approx \frac{k_B T}{m}(t - t_0)^2 = \left\langle v^2\right\rangle (t - t_0)^2. \tag{15.35}$$

For large time differences diffusive motion emerges with

$$\left\langle \left(x(t) - x(t_0)\right)^2\right\rangle \approx \frac{2k_B T}{m\gamma}(t - t_0) = 2D(t - t_0) \tag{15.36}$$

with the diffusion constant given by the Einstein relation

$$D = \frac{k_B T}{m\gamma}. \tag{15.37}$$

For a three-dimensional simulation the Cartesian components of the position or velocity vector add up independently. The diffusion coefficient can be determined from

$$D = \frac{1}{6}\lim_{t\to\infty} \frac{\langle (x(t) - x(t_0))^2\rangle}{t - t_0} \tag{15.38}$$

or, alternatively from (15.33) [3]

$$D = \frac{1}{3}\int_{t_0}^{\infty} \left\langle \mathbf{v}(t)\mathbf{v}(t_0)\right\rangle dt. \tag{15.39}$$

This equation is more generally valid also outside the Brownian limit (Green-Kubo formula). The Brownian model represents the simulation data quite well at low particle densities (Figs. 15.6, 15.7). For higher densities the velocity autocorrelation function shows a very rapid decay followed by a more or less structured tail [3, 159, 256].

Fig. 15.7 (Mean square displacement) The Lennard-Jones system is simulated for $k_B T = 200$ K and different values of the density $n^* = 0.12$ (*a*), 0.18 (*b*), 0.32 (*c*), 0.62 (*d*). The mean square displacement (*full curves*) is averaged over 20 trajectories and fitted by a linear function (*dashed lines*) for $t - t_0 > 1.5$ ps

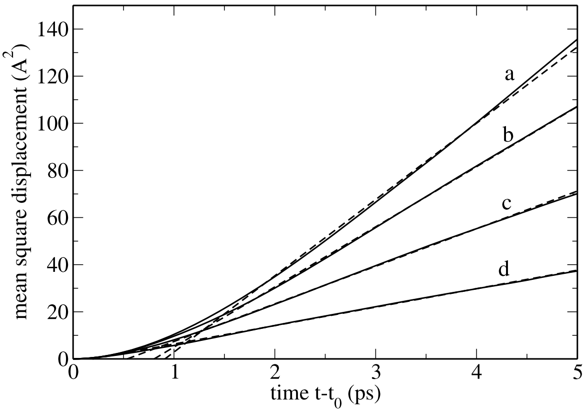
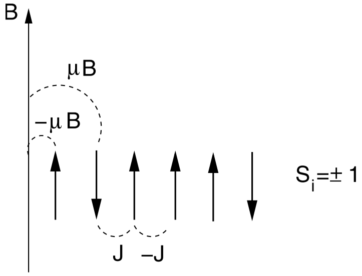


Fig. 15.8 (Ising model) N spins can be up or down. The interaction with the magnetic field is $-\mu B S_i$, the interaction between nearest neighbors is $-J S_i S_j$



15.2 Monte Carlo Simulation

The basic principles of Monte Carlo simulations are discussed in Chap. 8. Here we will apply the Metropolis algorithm to simulate the Ising model in one or two dimensions. The Ising model [26, 134] is primarily a model for the phase transition of a ferromagnetic system. However, it has further applications for instance for a polymer under the influence of an external force or protonation equilibria in proteins.

15.2.1 One-Dimensional Ising Model

We consider a chain consisting of N spins which can be either up ($S_i = 1$) or down ($S_i = -1$). The total energy in a magnetic field is (Fig. 15.8)

$$H = -MB = -B \sum_{i=1}^{N} \mu S_i \tag{15.40}$$

and the average magnetic moment of one spin is

$$\langle M \rangle = \mu \frac{e^{\mu B/kT} - e^{-\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}} = \mu \tanh\left(\frac{\mu B}{kT}\right). \tag{15.41}$$

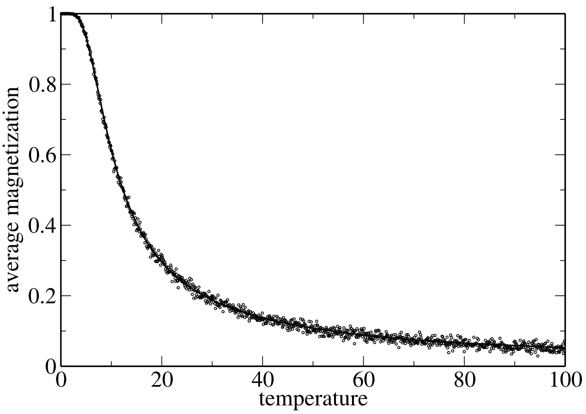


Fig. 15.9 (Numerical simulation of the 1-dimensional Ising model) The average magnetization per spin is calculated from a MC simulation (*circles*) and compared to the exact solution (15.43). Parameters are $\mu B = -5$ and $J = -2$

If interaction between neighboring spins is included the energy of a configuration $(S_1 \cdots S_N)$ becomes

$$H = -\mu B \sum_{i=1}^{N} S_i - J \sum_{i=1}^{N-1} S_i S_{i+1}. \tag{15.42}$$

The 1-dimensional model can be solved analytically [231]. In the limit $N \to \infty$ the magnetization is

$$\langle M \rangle = \mu \frac{\sinh(\frac{\mu B}{kT})}{\sqrt{\sinh^2(\frac{\mu B}{kT}) + e^{4J/kT}}}. \tag{15.43}$$

The numerical simulation (Fig. 15.9) starts either with the ordered state $S_i = 1$ or with a random configuration. New configurations are generated with the Metropolis method as follows:

- flip one randomly chosen spin S_i[3] and calculate the energy change due to the change $\Delta S_i = (-S_i) - S_i = -2S_i$

$$\Delta E = -\mu B \Delta S_i - J \Delta S_i (S_{i+1} + S_{i-1}) = 2\mu B S_i + 2J S_i (S_{i+1} + S_{i-1}) \tag{15.44}$$

- if $\Delta E < 0$ then accept the flip, otherwise accept it with a probability of $P = e^{-\Delta E/kT}$

As a simple example consider $N = 3$ spins which have 8 possible configurations. The probabilities of the trial step $T_{i \to j}$ are shown in Table 15.1.

The table is symmetric and all configurations are connected.

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[3] Or try one spin after the other.

Table 15.1 transition probabilities for a 3-spin system ($p = 1/3$)

	$+++$	$++-$	$+-+$	$+--$	$-++$	$-+-$	$--+$	$---$
$+++$	0	p	p	0	p	0	0	0
$++-$	p	0	0	p	0	p	0	0
$+-+$	p	0	0	p	0	0	p	0
$+--$	0	p	p	0	0	0	0	p
$-++$	p	0	0	0	0	p	p	0
$-+-$	0	p	0	0	p	0	0	p
$--+$	0	0	p	0	p	0	0	p
$---$	0	0	0	p	0	p	p	0

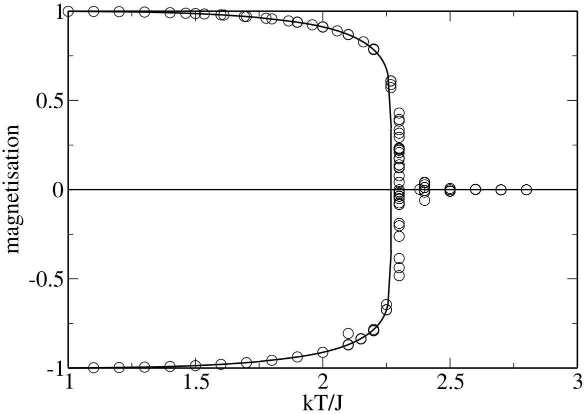


Fig. 15.10 (Numerical simulation of the 2-dimensional Ising model) The average magnetization per spin is calculated for $B = 0$ from a MC simulation (*circles*) and compared to (15.46)

15.2.2 Two-Dimensional Ising Model

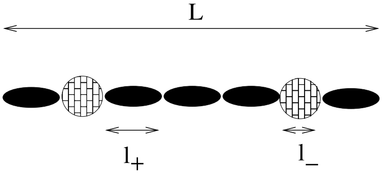
For dimension $d > 1$ the Ising model behaves qualitatively different as a phase transition appears. For $B = 0$ (Fig. 15.10) the 2-dimensional Ising-model with 4 nearest neighbors can be solved analytically [171, 194]. The magnetization disappears above the critical temperature T_c, which is given by

$$\frac{J}{kT_c} = -\frac{1}{2}\ln(\sqrt{2}-1) \approx \frac{1}{2.27}. \tag{15.45}$$

Below T_c the average magnetization is given by

$$\langle M \rangle = \left(1 - \frac{1}{\sinh^4(\frac{2J}{kT})}\right)^{\frac{1}{8}}. \tag{15.46}$$

Fig. 15.11 Two state model



15.3 Problems

Problem 15.1 (Lennard-Jones fluid) In this computer experiment a Lennard-Jones fluid is simulated. The pressure is calculated from the average transfer of momentum (15.12) and compared with expression (15.19).

- Equilibrate the system and observe how the distribution of squared velocities approaches a Maxwell distribution.
- Equilibrate the system for different values of temperature and volume and investigate the relation between pV/N and kT.
- observe the radial distribution function for different values of temperature and densities. Try to locate phase transitions.
- determine the decay time of the velocity correlation function and compare with the behavior of the mean square displacement which shows a transition from ballistic to diffusive motion.

Problem 15.2 (One-dimensional Ising model) In this computer experiment we simulate a linear chain of $N = 500$ spins with periodic boundaries and interaction between nearest neighbors only. We go along the chain and try to flip one spin after the other according to the Metropolis method.

After trying to flip the last spin S_N the total magnetization

$$M = \sum_{i=1}^{N} S_i \tag{15.47}$$

is calculated. It is averaged over 500 such cycles and then compared graphically with the analytical solution for the infinite chain (15.43). Temperature and magnetic field can be varied.

Problem 15.3 (Two-state model for a polymer) Consider a polymer (Fig. 15.11) consisting of N units which can be in two states $S_i = +1$ or $S_i = -1$ with corresponding lengths l_+ and l_-. The interaction between neighboring units takes one of the values w_{++}, w_{+-}, w_{--}. Under the influence of an external force κ the energy of the polymer is

$$E = -\kappa \sum_i l(S_i) + \sum_i w(S_i, S_{i+1}). \tag{15.48}$$

This model is isomorphic to the one-dimensional Ising model,

$$E = -\kappa N \frac{l_- + l_+}{2} - \kappa \frac{l_+ - l_-}{2} \sum S_i \tag{15.49}$$

$$+ \sum \left(w_{+-} + \frac{w_{++} - w_{+-}}{2} S_i + \frac{w_{+-} - w_{--}}{2} S_{i+1} \right.$$
$$\left. + \frac{w_{++} + w_{--} - 2w_{+-}}{2} S_i S_{i+1} \right) \tag{15.50}$$

$$= \kappa N \frac{l_- + l_+}{2} + N w_{+-}$$
$$- \kappa \frac{l_+ - l_-}{2} M + \frac{w_{++} - w_{--}}{2} M$$
$$+ \frac{w_{++} + w_{--} - 2w_{+-}}{2} \sum S_i S_{i+1}. \tag{15.51}$$

Comparison with (15.42) shows the correspondence

$$-J = \frac{w_{++} + w_{--} - 2w_{+-}}{2} \tag{15.52}$$

$$-\mu B = -\kappa \frac{l_+ - l_-}{2} + \frac{w_{++} - w_{--}}{2} \tag{15.53}$$

$$L = \sum l(S_i) = N \frac{l_+ + l_-}{2} + \frac{l_+ - l_-}{2} M. \tag{15.54}$$

In this computer experiment we simulate a linear chain of $N = 20$ units with periodic boundaries and nearest neighbor interaction as in the previous problem.

The fluctuations of the chain conformation are shown graphically and the magnetization of the isomorphic Ising model is compared with the analytical expression for the infinite system (15.43). Temperature and magnetic field can be varied as well as the coupling J. For negative J the anti-ferromagnetic state becomes stable at low magnetic field strengths.

Problem 15.4 (Two-dimensional Ising model) In this computer experiment a 200 × 200 square lattice with periodic boundaries and interaction with the 4 nearest neighbors is simulated. The fluctuations of the spins can be observed. At low temperatures ordered domains with parallel spin appear. The average magnetization is compared with the analytical expression for the infinite system (15.46).