

PROBLEMS AND SOLUTIONS IN
STATISTICAL MECHANICS

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Notice

These exercises were submitted during my teaching of Statistical Mechanics at the University of Naples “Federico II”. They occasionally refer to my textbook, L. Peliti, *Statistical Mechanics in a Nutshell* (Princeton: Princeton U. P., 2012). I am grateful to my colleagues and especially to my students, who helped shape the problems and their answers.

Part I
Problems

Kinetic Theory

Exercise 1.1 (On Avogadro's Number) Imagine we could “mark” the water molecules contained in a small flask of 100 cc, and to pour them into the sea. Let us now assume to fill the flask back in, after having waited for the flask's molecules to distribute uniformly in the oceans. How many “marked” molecules can we expect to find back on average?

NOTE. The surface of the oceans equals 71% of the Earth's surface, and its mean depth is 3800 m. The molecular weight of water is equal to 18.

Exercise 1.2 (On Maxwell's Distribution)

1. Evaluate the root mean square speed $v_{\text{RMS}} = \sqrt{\langle v^2 \rangle}$ of a gas obeying Maxwell's distribution in d dimensions. Give the corresponding numerical value for air in 3 dimensions at room temperature ($T = 300$ K). Air is made by 2/3 of nitrogen (molecular weight 28) and 1/3 of oxygen (molecular weight 32).
2. Evaluate the value v of the speed in a Maxwell distribution at temperature T for a gas of molecules of mass m in d dimensions which corresponds to the maximal probability density. Compare it with the root mean square speed.
3. Evaluate the probability distribution function for the kinetic energy of a gas following Maxwell's distribution, i.e., the probability density that the kinetic energy of a randomly chosen particle has the value κ :

$$f(\kappa) = \int d^d v \delta\left(\kappa - \frac{1}{2}mv^2\right) p_{\text{Maxwell}}(v).$$

Exercise 1.3 (Gas in a Gravity Field) Let us consider a gas of particles of mass m , at equilibrium with a uniform temperature T in a gravity field, described by the acceleration g pointing vertically downwards. The gas particles obey the Maxwell distribution. Let S_1 and S_2 be two horizontal surfaces, at heights z_1 and $z_2 > z_1$ respectively. We denote by ρ_i , $i \in \{1, 2\}$, respectively, the numerical density close to S_i .

By considering the condition that, in a time interval of duration Δt , as many particles originating from S_1 cross S_2 as vice-versa, derive a relation between ρ_i and z_i ($i \in \{1, 2\}$). Neglect the effects of collisions between S_1 and S_2 .

Exercise 1.4 (Knudsen Gas) Let us consider a gas distributed in two containers placed side by side, both at a very small density, at pressures and temperatures (p_1, T_1) and (p_2, T_2) respectively. The two containers are connected by a very small opening, such that the thermal equilibrium of the two systems is not perturbed. There is molecular equilibrium when the flux of particles through the opening from container 1 to 2 is equal to the flux of particles from container 2 to 1.

1. Show that in this situation there is a simple relation between (p_1, T_1) and (p_2, T_2) .
2. Evaluate the small change in (p_i, T_i) , $i = 1, 2$, which obtains in a short time interval Δt .

Exercise 1.5 (Drag in a Gas) Let us consider an ideal gas made of particles of mass m , with numerical density $\rho = N/V$, at temperature T . Using Maxwell's distribution, evaluate the drag applied by the gas on a small disk of radius R moving at velocity v , where v is parallel to the axis of the disk. We assume that R is much smaller than the interatomic distance $\rho^{-1/3}$ and that v is much smaller than the characteristic speed of the particles.

Thermodynamics

Exercise 2.1 Consider two systems, initially at the same temperature, that are in contact by means of a semipermeable wall that allows for the passage of particles of the chemical species k . Show that, in this case, the particles flow from the system with a larger value of μ to that with a smaller value.

Exercise 2.2 The following expressions are proposed as possible fundamental equations for various thermodynamic systems. However, some of them violate some of the postulates of entropy and are therefore not acceptable from a physics standpoint. Find the five that are not acceptable from a physics standpoint, and indicate which postulates are violated by each one. The quantities v_0 , θ and R are positive constants. When fractional exponents appear, only the root's positive values should be considered.

1. $S = (R^2/v_0\theta)^{1/3} [NVE]^{1/3}$.
2. $S = (R^2/\theta^2)^{1/3} [NE/V]^{2/3}$.
3. $S = (R/\theta)^{1/2} [NE - R\theta V^2/v_0^2]^{1/2}$.
4. $S = (R^2\theta/v_0^3) [V^3/NE]$.
5. $S = (R^3/v_0\theta^2)^{1/5} [N^2VE^2]^{1/5}$.
6. $S = NR \log (VE/N^2R\theta v_0)$.

$$7. S = (R/\theta)^{1/2} [NE]^{1/2} \exp(-V^2/2N^2v_0^2).$$

$$8. S = (R/\theta)^{1/2} [NE]^{1/2} \exp(-EV/NR\theta v_0).$$

Exercise 2.3 For each of the physically acceptable fundamental equations in exercise 2.2, express its internal energy as a function of S , V and N .

Exercise 2.4 Consider the thermodynamic potential

$$\Phi(f_0, f_1, \dots, f_k, X_{k+1}, \dots, X_r) = E - \sum_{i=0}^k f_i X_i.$$

Prove that the matrix of second derivatives $(\partial^2 \Phi / \partial f_i \partial f_j)$ is negative definite at each point.

Exercise 2.5 Prove that if a system is brought toward equilibrium while temperature and pressure are kept constant, the maximum work that can be performed on its environment is given precisely by the difference between the initial and final values of its Gibbs free energy G .

Exercise 2.6 Prove that the heat released by a system that is relaxing at equilibrium at constant pressure is less than (or equal to) its change in enthalpy:

$$Q \leq H_{\text{in}} - H_{\text{fin}} = -Q_{\text{rev}}.$$

Exercise 2.7 Prove the identity

$$\left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x,$$

where it is assumed that x , y and z satisfy a condition of the form $F(x, y, z) = 0$.

Exercise 2.8 (Law of Adiabatic Processes) Prove that for an ideal gas, one gets

$$C_p - C_V = Nk_B.$$

By defining $\gamma = C_p/C_V$ (which is only a function of temperature), deduce the **law of reversible adiabatic processes**:

$$\left(\frac{\partial p}{\partial V}\right)_S = -\gamma \frac{p}{V}.$$

If we assume that $C_V = \text{const.}$, one can integrate this relation, and obtain

$$pV^\gamma = \text{const.}$$

Deduce that in a reversible adiabatic process one has

$$pT^{\gamma/(1-\gamma)} = \text{const.}$$

Exercise 2.9 (Adiabatic Atmosphere) It is a well-known fact that atmospheric temperature decreases with an increase in elevation. As a first approximation, given air's low thermal conductivity, we can assume that the atmosphere is at equilibrium with respect to vertical *adiabatic* shifts of small quantities of air. By using the equation of states for ideal gases, the law of adiabatic processes, and Stevin's law:

$$\frac{\partial p}{\partial z} = -m_{\text{mol}}g \frac{N}{V},$$

where m_{mol} is air's average molecular mass ($0.67m_{\text{N}_2} + 0.33m_{\text{O}_2}$), prove that the atmosphere's thermal gradient is given by

$$\left(\frac{\partial T}{\partial z}\right)_S = -\frac{m_{\text{mol}}g}{k_B} (1 - \gamma^{-1}).$$

The value of this quantity is about -9.9K km^{-1} .

Exercise 2.10 Let us consider a container whose walls are adiabatic, in which there is an opening closed by a faucet. A void is created inside the container, then it

is placed in contact with the atmosphere at pressure p_0 and temperature T_0 . At his point, the faucet is opened and air rapidly enters the container. After a brief interval, internal pressure has equalized external pressure. Calculate the temperature of the air inside the container under these conditions. We remind the reader that for air, $\gamma = C_p/C_V = 7/5$.

Exercise 2.11 (Theory of Elasticity) Let us consider an elastic band with a fixed cross section as a thermodynamic system. The thermodynamic variables that characterize it within the energy scheme are the entropy S , the length L , and the mass (or number of moles) n . The expression of dE is given by

$$dE = T dS + f dL + \mu dn,$$

where f is the tension acting on the band, and μ is the chemical potential.

1. Derive the analogue of the Gibbs-Duhem equation.

One can observe experimentally that the tension f , when the length L and the mass m are fixed, increases proportionally to temperature. This suggests that the equation of state is

$$E = cnT,$$

where c is a constant. Hooke's law, on the other hand, implies that the relative lengthening is proportional to tension (at least in the case of increases in length that are not too large), and therefore

$$f = \phi \frac{L - L_0}{n},$$

where $L_0 = n\ell_0$ is the length at rest.

2. Show that ϕ is proportional to the temperature T :

$$\phi = bT.$$

3. Derive the expression for the entropy differential as a function of E , L , and N .
4. Derive the fundamental equation in both the entropy and energy schemes.
5. Calculate the relative variation of $L - L_0$ for a small increment in temperature dT .

The Fundamental Postulate

Exercise 3.1 (Particle in a Potential Well) Let us consider a particle of mass m , constrained to moving in one dimension along a segment of length L . In this case, the possible energy values are $E_n = \hbar^2 \pi^2 n^2 / L^2$, where $n = 1, 2, \dots$. Prove that in this case the phase space volume “occupied” by each quantum state is equal to h . (Be careful to calculate the classical phase volume correctly!)

Exercise 3.2 Making use of the Maxwell relations and of the expression $p = -\partial F / \partial V)_T$ of pressure, prove the equality

$$\left. \frac{\partial E}{\partial T} \right)_p + \left. \frac{\partial E}{\partial p} \right)_T \left. \frac{\partial p}{\partial T} \right)_{p/k_B T} = \left. \frac{\partial E}{\partial T} \right)_V - \frac{1}{T} \left. \frac{\partial E}{\partial V} \right)_T \left. \frac{\partial V}{\partial p} \right)_T.$$

Exercise 3.3 Let us suppose that we have some particles arranged on a straight line. Each particle is a hard sphere of diameter ℓ and there is an interaction $u(r)$ between the particles with a range between ℓ , and 2ℓ (such that only close nearest-neighbor particles can interact). Evaluate the partition function at temperature T and the equation of state for this system in the thermodynamic limit ($N \rightarrow \infty$ with constant pressure).

Exercise 3.4 Consider a simple fluid, described by a grand canonical ensemble. Express the following quantities in terms of the grand canonical partition function:

$$\begin{aligned}\langle \Delta E^2 \rangle &= \langle E^2 \rangle - \langle E \rangle^2; \\ \langle \Delta N^2 \rangle &= \langle N^2 \rangle - \langle N \rangle^2; \\ \langle \Delta E \Delta N \rangle &= \langle E N \rangle - \langle E \rangle \langle N \rangle.\end{aligned}$$

Exercise 3.5 Show that the energy fluctuations in the grand canonical (GC) ensemble are always greater than the corresponding fluctuations in the canonical (C) ensemble:

$$\langle \Delta E^2 \rangle_{\text{GC}}(\mu) \geq \langle \Delta E^2 \rangle_{\text{C}}(N),$$

where N is the average value of the number of particles corresponding to μ .

Exercise 3.6 Consider a system described by the hamiltonian $H(x)$. Show that the quantity

$$\mathcal{S}(p) = - \sum_x p(x) \log p(x),$$

is largest for the canonical distribution

$$p^{\text{eq}}(x) = \frac{e^{-H(x)/k_{\text{B}}T}}{Z},$$

among all distributions $p(x)$ which have the same value of the average of H ,

$$\langle H \rangle = \sum_x p(x) H(x).$$

Interaction-Free Systems

Exercise 4.1 (Stefan-Boltzmann Law) By integrating equation (4.25), one obtains the total power emitted by a body at temperature T per unit surface:

$$W_{\text{tot}} = \int_0^{\infty} d\omega W(\omega) = \kappa T^4,$$

where the constant κ is equal to

$$\kappa = \frac{2\pi^5 k_B^4}{15c^2 h^3} = 5.6710 \cdot 10^{-8} \text{Jm}^{-2} \text{s}^{-1} \text{K}^4. \quad (4.1)$$

Show that this result (except for the value of the constant κ) follows from thermodynamics and the following hypotheses:

1. The internal energy of the black body radiation is proportional to the system's volume; the energy density depends only on the temperature:

$$E = \epsilon(T)V. \quad (4.2)$$

2. The pressure p is equal to 1/3 of the energy density:

$$p = \frac{1}{3}\epsilon(T). \quad (4.3)$$

This hypothesis can be justified by taking account of the fact that if the distribution of light is isotropic, only one-third of the light present contributes to the pressure on any given element of the surface.

4. INTERACTION-FREE SYSTEMS

First obtain the expression of $\epsilon(T)$, and from it, derive the value of W_{tot} .

Exercise 4.2 Evaluate the behavior of the internal energy and specific heat of a boson gas in the vicinity of the Einstein condensation.

Exercise 4.3 (A Simplified Model of Hemoglobin) Let us associate each of the four units i , ($i = 1, \dots, 4$) that make up a molecule of hemoglobin with a variable τ_i , which is equal to 1 if an O_2 molecule is adsorbed, and is otherwise 0. The energy of the hemoglobin molecule is given by

- $-\epsilon_0$ times the number of O_2 molecules adsorbed.
- $-J$ times the number of pairs of nearest-neighbor units, each containing a molecule of adsorbed O_2 . (The i and $i + 1$ sites are nearest neighbors, and so are sites 4 and 1).

Consider a system of $N/4$ molecules of hemoglobin. Evaluate the average number $M = \left\langle \sum_{\alpha=1}^{N/4} \sum_{i=1}^4 \tau_{\alpha i} \right\rangle$ of adsorbed molecules as a function of $x = \exp[(\epsilon_0 + \mu)/k_B T]$ and of $y = \exp(J/k_B T)$.

Exercise 4.4 (Frustrated spins) A system is made up by N Ising spins, $\sigma_i \in \{-1, +1\}$, $i = 1, \dots, N$ which interact in groups of three, with the Hamiltonian

$$H_{\ell}^{(3)} = J(\sigma_{3\ell-1}\sigma_{3\ell-2} + \sigma_{3\ell-2}\sigma_{3\ell} + \sigma_{3\ell}\sigma_{3\ell-1}) - h \sum_{i=0}^2 \sigma_{3\ell-i},$$

$$\ell = 1, \dots, N/3.$$

with a *positive* interaction coefficient J . Thus the total Hamiltonian of the system is given by

$$H = \sum_{\ell=1}^{N/3} H_{\ell}^{(3)}.$$

1. Evaluate the possible energy values of each “elementary triangle” and its corresponding degeneration.
2. Evaluate the equation of state for the magnetization per spin $m = \langle \sigma_i \rangle$:

$$m = m(h, T),$$

and discuss its behavior.

Exercise 4.5 (Particles with variable spin) Let us consider a system made up of N particles, each of which can be in a spin $s = 0$ state (with vanishing energy) or in one of three spin $s = 1$ states, where the z -component of the spin is equal to $\sigma = -1, 0, +1$, with energy equal to $\epsilon_0 - h\sigma$, where h is the applied magnetic field, measured in suitable units.

1. Evaluate the partition function of the system at the absolute temperature T . (Hint: introduce the variable N_1 , equal to the number of particles which are in the $s = 1$ state).
2. Provide the expressions of the internal energy E and of the magnetization $M = \langle \sum_i \sigma_i \rangle$ as functions of T and h .
3. Discuss the behavior of the susceptibility per particle $\chi = \partial M / \partial h)_{h=0} / N$ as a function of the temperature.

Exercise 4.6 (Einstein condensation of zero-mass particles) Consider a system of quantum particles with spin zero, whose energy, as a function of the wave vector \mathbf{k} , is given by

$$\epsilon(\mathbf{k}) = c|\mathbf{k}|.$$

The system is contained in a cubic d -dimensional box of volume $V = L^d$.

1. Give the expression of the system's grand canonical partition function.
2. Deduce the expression for the average number N of particles.
3. Obtain, as a function of V , c and T , the value N_c of the particle number in which Einstein's condensation takes place. Does it take place for $d = 2$? And for $d = 1$?

(It is not necessary to evaluate explicitly *convergent* integrals.)

Exercise 4.7 (Einstein condensation in a harmonic potential) Consider a system of N quantum particles of spin zero and mass m in d dimensions, subject to a harmonic potential of the form

$$u(\mathbf{r}) = \frac{1}{2}m\omega_0^2 r^2, \quad (4.4)$$

where $\mathbf{r} = (r_1, \dots, r_d)$ is the position vector, and ω_0 is a parameter with the dimensions of a frequency.

1. Give the expression of the grand canonical partition function and show that the chemical potential cannot exceed a special value μ_0 . Give the expression of μ_0 .
2. Give the expression of the number N' of particles in the excited states. Approximate the resulting expression by an integral for $d = 2, d = 3$.
3. Define $R_0 = \sqrt{u_0/m}/\omega_0$, where u_0 is a parameter with the dimensions of an energy. The thermodynamic limit corresponds to $N \rightarrow \infty, N/R_0^d = \rho = \text{const.}$, which implies $\omega_0 \rightarrow 0$. Show that in this limit the system exhibits an Einstein condensation for $d = 2$ or $d = 3$ and give the expression of the corresponding transition temperature.

Exercise 4.8 (Neutrino density in the universe) Current cosmological theories do not only predict a uniform background radiation density in thermal equilibrium at the temperature of 2.72 K, but also an equilibrium distribution of neutrinos at the same temperature.

Neutrinos are spin- $\frac{1}{2}$ particles (and therefore fermions), but one finds experimentally that their spin is always *parallel* to their momentum \mathbf{p} . Thus there is only one possible state for the spin for each value of the momentum. Moreover, their mass vanishes and therefore the energy of a state of momentum \mathbf{p} is equal to $c|\mathbf{p}|$, where c is the speed of light. Their (weak) interaction with matter implies that the number of neutrinos is not fixed.

Evaluate:

1. The number of neutrinos per unit volume;
2. Their average energy;
3. Their energy spectrum.

Data:

- $c = 3.00 \cdot 10^8 \text{ ms}^{-1}$;
- $k_B = 1.38 \cdot 10^{-23} \text{ JK}^{-1}$;
- $\int_0^\infty x^2 dx / (1 + e^x) = \frac{3}{2} \zeta_R(3) = 1.80$;
- $\int_0^\infty x^3 dx / (1 + e^x) = 7\pi^4/120 = 5.67$.

Exercise 4.9 (Fermions in two dimensions) Let us consider a system of non-interacting fermions of spin $\frac{1}{2}$ and mass m in two dimensions, contained in a square box of side L .

1. Evaluate the density of states $D(\epsilon) = \sum_{k\alpha} \delta(\epsilon - \epsilon_{k\alpha})$, where k are the allowed values of the wave vector, α the possible values of the spin, and $\epsilon_{k\alpha}$ the corresponding single-particle energy.
2. Evaluate the Fermi energy ϵ_F as a function of the numerical density $\rho = N/V$.
3. Evaluate the equation of state $p(\rho)$ at vanishing temperature.
4. Show that the chemical potential μ tends exponentially towards ϵ_F as $T \rightarrow 0$.

Phase Transitions

Exercise 5.1 Generalize the Peierls argument to $d = 3$ dimensions.

Exercise 5.2 Consider the spin correlation function

$$C_{ij} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle,$$

in the one-dimensional Ising model with a vanishing field. Show that one has

$$\lim_{N \rightarrow \infty} C_{ij} = (\tanh K)^{|i-j|},$$

where $K = J/k_B T$.

Exercise 5.3 Show that, in the presence of a nonvanishing magnetic field h , in the one-dimensional Ising model, one has

$$f = \lim_{N \rightarrow \infty} \frac{\ln Z}{N} = \ln \left[e^K \cosh \lambda + \sqrt{e^{2K} \sinh^2 \lambda + e^{-2K}} \right],$$

where $\lambda = h/k_B T$.

Exercise 5.4* Obtain the same result with the following method, introduced by Lifson Lifson [1964]. Let us consider the system with $\sigma_0 = +1$, and with σ_N free.

Then (analogously with what was done with the Peierls argument), the spin configurations σ are univocally defined by the configurations Γ of the boundaries—in other words, of the pairs of nearest-neighbor spins with opposite values. The system is subdivided into n intervals, of length $\ell_i \geq 1$, such that sites belonging to the same interval have the same value σ_i of the spin.

1. Write the canonical partition function as a function of the ℓ_i 's.
2. Move to the corresponding grand canonical partition function by introducing the spin fugacity z .
3. Evaluate the grand canonical partition function as a function of z .
4. Evaluate N and prove that, in order to obtain the thermodynamic limit $N \rightarrow \infty$, it is necessary that $z \rightarrow z^*$, where z^* is the value of z closest to the origin for which Z admits a singularity. Evaluate z^* .
5. Show that $f = \lim_{N \rightarrow \infty} \ln Z/N = -\ln z^*$, and compare the result with what was obtained in the previous exercise.

Exercise 5.5 (The Chinese philosophers' problem) Let us consider N Chinese philosophers sitting at a circular table. Each philosopher can either meditate (state “−1”) or eat (state “+1”). In order to eat he needs two chopsticks: chopsticks are shared between the two neighboring philosophers, one with the left and one with the right one. Thus if a philosopher is eating, his left and right neighbors cannot be eating at the same time. We wish to evaluate the number of possible configurations of the system of N philosophers.

1. Show that the question reduces to the following problem: one considers N sites on a circle, each carrying a spin variable $\sigma_i \in \{-1, +1\}$. The total number of configurations is 2^N . We wish to evaluate the number \mathcal{N}_N of states in which one cannot find two spins +1 one after the other.
2. Evaluate explicitly \mathcal{N}_N for $N = 2, 3, 4, 5$.
3. Check that the calculated \mathcal{N}_N verify the relation $\mathcal{N}_N = \mathcal{N}_{N-1} + \mathcal{N}_{N-2}$, which defines the Fibonacci sequence. The “standard” Fibonacci sequence satisfies this relation and the initial conditions $\mathcal{N}_0 = \mathcal{N}_1 = 1$. In our case the initial conditions will be different.
4. Let us denote by $\mathcal{N}_N(\sigma)$ the number of acceptable configurations in which $\sigma_N = \sigma$, $\sigma \in \{-1, +1\}$. Show that one then has

$$\mathcal{N}_N = \mathcal{N}_N(+1) + \mathcal{N}_N(-1).$$

Evaluate $\mathcal{N}_N(+1)$ as a function of \mathcal{N}_{N-1} and $\mathcal{N}_{N-1}(+1)$, and analogously for $\mathcal{N}_N(-1)$, and show that one can derive the Fibonacci recursion relation.

5. Show that the problem reduces to counting the minimal-energy states of a one-dimensional Ising model defined by the Hamiltonian

$$H(\{\sigma_i\}) = \sum_{i=1}^N \left[-J\sigma_i\sigma_{i+1} - \frac{h}{2}(\sigma_i + \sigma_{i+1}) \right],$$

with periodic boundary conditions ($\sigma_{i+N} = \sigma_i$) and with

$$J = -1; \quad h = -2.$$

Evaluate the corresponding ground-state energy $E_0(N)$.

6. Assuming to be able to evaluate the canonical partition function

$$Z_N(\beta) = \sum_{\{\sigma_i\}} e^{-\beta H(\{\sigma_i\})},$$

show that one has

$$\mathcal{N}_N = \lim_{\beta \rightarrow \infty} e^{\beta E_0(N)} Z_N(\beta).$$

7. Given the following expression for the canonical partition function of the one-dimensional Ising model,

$$Z_N(\beta) = \lambda_+^N + \lambda_-^N.$$

where λ_{\pm} are the two eigenvalues of the transfer matrix of the system, expressed as functions of β , J and h , check the values of \mathcal{N}_N previously obtained.

Exercise 5.6 Let us suppose that the interaction is long range, so that the coupling constant J_{ij} between the i spin and the j spin decays as $|i - j|^{-a}$, where a is a positive constant. Show that Landau's argument for the absence of transitions in one dimension is not valid if $a < 2$.

Exercise 5.7* (Duality in the Three-Dimensional Ising Model) By considering the expansion of the partition function of the three-dimensional Ising model as a

function of the Γ distribution of boundaries, show that the dual of this model is defined by the Hamiltonian

$$\mathcal{H} = -J \sum_{\mathcal{P}} \prod_{i \in \mathcal{P}} \sigma_i,$$

where the sum runs over all the plaquettes \mathcal{P} composed of the dual lattice's four nearest-neighbor pairs of spin. Find the relation between the temperatures of the Ising model and the corresponding dual model. Note that, since the dual of the Ising model is not identical to the initial model, this argument does not provide us with information about the critical temperature for $d = 3$.

Exercise 5.8 (Phase coexistence) Consider the following grand canonical partition function

$$Z_{\text{GC}}(z) = (1+z)^V (1+z^{\alpha V}),$$

where z is the fugacity and α is a positive parameter.

1. Evaluate the density $\rho = N/V$ and show that the system exhibits phase coexistence. Evaluate the two densities at coexistence.
2. Evaluate the equation of state in the low-density phase ("gas") and the pressure at phase coexistence.

Exercise 5.9 (A simple model of sublimation) **Sublimation** is the phase transition corresponding to the change from a solid to a gaseous phase (without going through an intermediate liquid phase). In this exercise we aim at obtaining an extremely simplified description of this transition.

1. In the gaseous phase the system is described as an ideal gas made of N_1 indistinguishable atoms of mass m , with hamiltonian

$$H_1 = \sum_{i=1}^{N_1} \frac{p_i^2}{2m}. \quad (5.1)$$

The gas is held in a container of volume V with rigid and elastic walls, kept at a constant and uniform temperature T .

- a) Write the expression of the canonical partition function of the gas.
- b) Deduce the expression of its chemical potential $\mu(T, N, \lambda_B)$, where $\lambda_B = \sqrt{h^2/(2\pi mk_B T)}$ is the de Broglie wavelength.

2. The crystal is described as a collection of N_2 classical oscillators in three dimensions, distinguishable because of their locations. The hamiltonian of the solid is given by

$$H_2 = \sum_{i=1}^{N_2} \left(\frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 r_i^2 - \epsilon_0 \right), \quad (5.2)$$

where $\mathbf{r}_i = (x_i, y_i, z_i)$ describes the particle's displacement from its equilibrium position and \mathbf{p}_i is the relative conjugate momentum. The energy $\epsilon_0 > 0$ describes the effect of the attractive forces that stabilize the crystal. We assume that the crystal and the gas are at the same temperature.

- Write the expression of the partition function of the crystal.
- Derive the expression of its chemical potential.
- Imposing the equilibrium between the crystal and the gas phases, express the equilibrium pressure as a function of λ_B , T and $\theta = \hbar\omega/k_B$.
- Is the model thus obtained physically reasonable?

Exercise 5.10 (Spin-elasticity coupling) Consider a system of N Ising spins in one dimension, coupled to an elasticity field ϵ . Non-vanishing values of ϵ yield the dimerization of the system, by getting neighboring spins to come closer or further away. The hamiltonian of the system is given by

$$H = - \sum_{i=1}^N \left[1 - \epsilon(-1)^i \right] \sigma_i \sigma_{i+1} + N\omega\epsilon^2,$$

where $\sigma_{i+N} = \sigma_i$. We shall solve the system by the transfer matrix method.

The partition function of the spin system, with fixed ϵ , has the following expression:

$$Z(\epsilon) = \sum_{\{\sigma_i\}} e^{\beta \sum_{i=1}^N [1 - \epsilon(-1)^i] \sigma_i \sigma_{i+1}} = \text{Tr} [\text{PQ}]^{N/2},$$

where

$$\text{P} = \begin{pmatrix} e^{\beta(1+\epsilon)} & e^{-\beta(1+\epsilon)} \\ e^{-\beta(1+\epsilon)} & e^{\beta(1+\epsilon)} \end{pmatrix}$$

is associated with odd-numbered spins, and

$$\text{Q} = \begin{pmatrix} e^{\beta(1-\epsilon)} & e^{-\beta(1-\epsilon)} \\ e^{-\beta(1-\epsilon)} & e^{\beta(1-\epsilon)} \end{pmatrix}$$

is associated with even-numbered spins.

5. PHASE TRANSITIONS

1. Let $\lambda(\epsilon)$ the largest eigenvalue of the transfer matrix PQ . Evaluate $\lambda(\epsilon)$ and show that the system's partition function is given by

$$Z = \int d\epsilon e^{-N\beta\omega\epsilon^2} Z(\epsilon) = \int d\epsilon e^{-N\beta[\omega\epsilon^2 - (k_B T/2) \log \lambda(\epsilon)]}.$$

2. Evaluate this expression by the saddle-point method and show that there is no transition for $\omega > 0.25$. Show that for $\omega = 0.20$ the system undergoes a continuous transition to a dimerized state in which $\epsilon \neq 0$. Evaluate β at the transition.
3. Show that for $\omega = 0.24$ the system undergoes a discontinuous transition to a state with $\epsilon \neq 0$. Evaluate β at the transition.
4. Show that the two regimes are separated by a *tricritical point* for some values ω_t and β_t . Obtain numerically the values β_t and ω_t .

Exercise 5.11 (Mean-field theory of the Ising model in a transverse field) Let us consider a system of N units, placed on a simple cubic lattice in 3 dimensions. Each unit possesses a *quantum* spin $\frac{1}{2}$ degree of freedom. Spins interact by their z -component, but are subject to a magnetic field along their x -component. The hamiltonian is therefore an *operator* defined by

$$H = -J \sum_{\langle i,j \rangle} \sigma_i^z \sigma_j^z - \Gamma \sum_i \sigma_i^x,$$

where

$$\sigma_i^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \quad \sigma_i^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

This operator acts on the Hilbert space

$$\mathcal{H} = \Sigma_1 \otimes \Sigma_2 \cdots \otimes \Sigma_N,$$

where Σ_i is the two-dimensional Hilbert space generated by $\{|+\rangle_i, |-\rangle_i\}$.

Within mean-field theory, we look for the minimum of the trial free energy

$$\mathcal{F}(K, h; J, \Gamma) = \langle (H - H_0) \rangle_0 - \beta^{-1} \log Z_0,$$

where we have introduced the trial hamiltonian

$$H_0 = -\beta^{-1} \sum_i (K\sigma_i^z + h\sigma_i^x),$$

and where we respectively have

$$\begin{aligned}\langle A \rangle_0 &= \frac{1}{Z_0} \text{Tr} A e^{-\beta H_0} \\ Z_0 &= \text{Tr} e^{-\beta H_0}.\end{aligned}$$

Exploit the relations

$$\begin{aligned}m^z &= \langle \sigma^z \rangle_0 = \frac{\text{Tr} [\sigma^z \exp(K\sigma^z + h\sigma^x)]}{\text{Tr} [\exp(K\sigma^z + h\sigma^x)]} \\ &= \frac{\partial}{\partial K} \log \text{Tr} [\exp(K\sigma^z + h\sigma^x)]; \\ m^x &= \langle \sigma^x \rangle_0 = \frac{\partial}{\partial h} \log \text{Tr} [\exp(K\sigma^z + h\sigma^x)].\end{aligned}$$

1. Evaluate the trace by diagonalizing the matrix

$$\mathbb{T} = K\sigma^z + h\sigma^x.$$

2. Obtain the expressions of $m_z(K, h)$ e $m_x(K, h)$.
3. Obtain the equations for the minimum of \mathcal{F}_0 with respect to (K, h) and deduce the relation which connects (K, h) at the minimum with (J, Γ, m^z, β) .
4. Show that these expressions imply the existence of a phase transition between a ferromagnetic and a paramagnetic phase. Identify the transition line in the (β, Γ) -plane.

Exercise 5.12 (Mean-field theory of the 3-state Potts model) Let us consider a system made up of N placed on a simple cubic lattice in d dimensions. The state of each unit is identified by a variable τ that can assume states: $\tau \in \{1, 2, 3\}$. If two neighboring units have the same value of τ , the energy is lowered. We obtain therefore the hamiltonian

$$H(\{\tau\}) = J \sum_{\langle i, j \rangle} (1 - \delta_{\tau_i \tau_j}).$$

We wish to study this hamiltonian by mean-field theory.

1. Let us first consider the paramagnetic state. Let us set $p_1 = p$, $p_2 = p_3 = \pi$, where p_a is the probability that $\tau = a$, $a \in \{1, 2, 3\}$. We define m by the relation $m = p - \pi$, as a measure of symmetry breaking. Evaluate $p_{1,2,3}$ as a function of m and expresso the entropy $S(m)$ of a system of N independent units as a function of m via Gibbs' formula.

5. PHASE TRANSITIONS

2. Let us assume that the units are independent, identically distributed random variables, and that we have therefore $\text{Prob}(\tau_i, \tau_j) = p_{\tau_i} p_{\tau_j}$ if the sites i and j are different. Let us assume that the p_a 's are expressed as functions of m as above. Evaluate the average $E(m)$ of the hamiltonian (5.12) as a function of m .
3. From these results, deduce the expression of the trial free energy $F(m, T) = E(m) - TS(m)$ as a function of m in mean-field theory. Obtain a self-consistency equation for m .
4. Show that this self-consistency equation predicts transition with symmetry breaking. Identify the nature (continuous or discontinuous) of the transition.
5. Evaluate numerically the transition temperature T_c and the behavior of m at the transition.

Renormalization Group

Exercise 6.1 Show that all the coefficients of k^n with $n \neq 0$ are irrelevant parameters around the infinite-temperature fixed point ($r > 0, c = 0$).

Exercise 6.2 Show that all the coefficients of κ^n with $n \geq 4$ are irrelevant parameters with the choice of $\zeta = b^{(d+2)/2}$ around the $r = 0, c > 0$ fixed point.

Exercise 6.3 Obtain the flux equations (6.206–208).

Exercise 6.4 Discuss the behavior of the $n \rightarrow \infty$ model for $h \neq 0$, and obtain the value of exponent δ directly. Compare this with the result obtained from the scaling laws:

$$\delta = \frac{d+2}{d-2}; \quad 2 < d \leq 4.$$

Classical Fluids

Exercise 7.1 Derive the **compressibility equation of state**:

$$\rho \int d^3\mathbf{r} [g(\mathbf{r}) - 1] + 1 = \rho k_B T K_T.$$

Exercise 7.2 Show that to lowest nontrivial order in the density the $g(r)$ is expressed by

$$g(r) = 1 + f(r),$$

where $f(r)$ is the Mayer function, and that therefore equations (7.12) and (7.70) are compatible.

Exercise 7.3 (Joule-Thompson process) Consider a gas that expands through a throttle from a region at pressure p_1 to a region at pressure p_2 , as shown in figure 7.1.

1. Show that the process occurs at constant enthalpy H .
2. Evaluate the temperature variation at constant enthalpy

$$\left. \frac{\partial T}{\partial p} \right)_H'$$

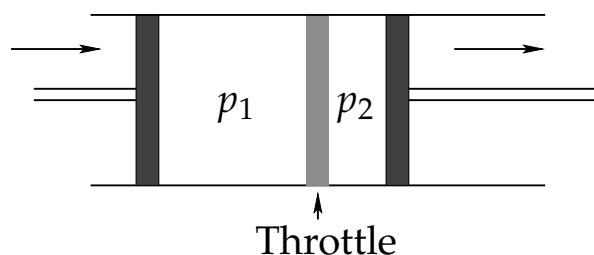


Figure 7.1: The Joule-Thomson process.

as a function of both the specific heat at constant pressure C_p and of the expansion coefficient

$$\left. \frac{\partial V}{\partial T} \right)_p.$$

3. By expressing $\partial V/\partial T)_p$ as a function of the second virial coefficient $B_2(T)$, evaluate the inversion temperature T^* in which $\partial T/\partial p)_H$ changes sign.
4. Estimate the order of magnitude of T^* as a function of the critical temperature T_c for a van der Waals gas.

Exercise 7.4 Show that if $C(T) = \int_0^\infty 4\pi r^2 dr \left| 1 - e^{-u(r)/k_B T} \right|$, where $u(r)$ is a pair potential bounded below by $-B$, is finite for one temperature T , it is also finite for all temperatures $0 < T < \infty$.

Exercise 7.5 Generalize equation (7.176) to the case of a salt with composition $\sum_i n_i X_i$, where the ion X_i has a charge z_i . (One obviously has $\sum_i n_i z_i = 0$ due to neutrality.)

Exercise 7.6 Consider the Gibbs entropy associated with the one-particle reduced density $\rho^{(1)}$, defined by

$$\mathcal{S}(\rho^{(1)}) = -k_B \int dx \rho^{(1)}(x) \log \rho^{(1)}(x),$$

where $x = (\mathbf{r}, \mathbf{p})$ denotes the single-particle state. Here $\rho^{(1)}$ is defined by

$$\rho^{(1)}(x) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta(x - x_i) \right\rangle,$$

where the average is taken with respect to the canonical distribution. Show that

$$\mathcal{S}(\rho^{(1)}) \geq \frac{S}{N},$$

where S is the thermodynamical entropy of the system.

Numerical Simulation

Exercise 8.1 (Ideal Gas in One Dimension) Consider a system composed of N particles of mass m in one dimension, contained in the half-line $r_i \geq 0$, $i = 1, 2, \dots, N$, with an elastic wall at the origin. The particles are confined by a piston of mass M , whose instantaneous position is given by $L(t) > 0$, and which is acted on by a force p oriented toward the origin. Resolve this problem in molecular dynamics, taking into account the fact that the particles interact only with the fixed wall at the origin (where they bounce elastically) and with the piston, by means of impacts in which energy and momentum are preserved. Check the enthalpy conservation $E + pL$. Show (numerically) that the velocity distribution tends to the Maxwell distribution and that the equation of state is given approximately by the law of ideal gases.

Exercise 8.2 Write the Verlet algorithm for the pendulum:

$$l\ddot{\theta} = -g \sin \theta.$$

Solve numerically the equations of motion for θ , and check energy conservation.

Exercise 8.3 Let us consider a one-dimensional fluid defined by the Hamiltonian

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=1}^N u(r_{i+1} - r_i),$$

with periodic boundary conditions:

$$r_{i+N} = r_i, \quad -L/2 \leq r_i \leq L/2, \quad u(r_i + L) = u(r_i), \quad \forall i.$$

Let us assume the Lennard-Jones form for $u(r)$:

$$u(r) = \epsilon_0 \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right].$$

1. By introducing r_0 as the length scale and $\tau = \sqrt{mr_0^2/\epsilon_0}$ as a time scale, make the equations of motion adimensional. The explicit dependence on the adimensional density $\rho = (Nr_0)/L$ will remain.
2. Write the program for the solution of the equations of motion by means of the Verlet algorithm.
3. Write the expression of temperature and pressure as a function of the trajectory calculated by means of the Verlet algorithm.
4. Evaluate the order of magnitude (in real length and time) of the systems and durations you can simulate on your PC, by supposing that $m \sim 10^{-23}$ g, $\epsilon_0 \sim 1$ eV and $r_0 \sim 1$ Å.

If you are courageous, launch the simulation! Choose the initial conditions so that the r_i are arranged on a regular lattice and the p_i follow a Gaussian distribution. Check the conservation of energy and monitor the approach to equilibrium. You can also compare your data to the exact solution. Be careful not to use excessively low values for energy, because the Fermi-Pasta-Ulam phenomenon mentioned earlier can make the approach to equilibrium in finite systems unreliable and slow.

Exercise 8.4 Prove that, if the detailed-balance condition is satisfied, and a given state a is reached by two (or more) different paths, the resulting evaluated probabilities will be the same.

Exercise 8.5 Prove that for sequential sublattice updating in an Ising model the detailed-balance condition is not satisfied, by finding two configurations σ and σ' such that $W_{\sigma'\sigma} \neq 0$ while $W_{\sigma\sigma'} = 0$, for example.

Exercise 8.6 (Microcanonical Ensemble) Describe a Markov chain (defined by the matrix W of the transition probabilities) that can sample the microcanonical ensemble:

$$P_{\sigma}^{\text{M}} = \begin{cases} 1/|\Gamma|, & \text{if } E \leq H(\sigma) \leq E + \Delta E, \\ 0, & \text{otherwise,} \end{cases}$$

where $|\Gamma|$ is the number of accessible configurations.

Exercise 8.7 (One-Dimensional Ising Model) Consider a one-dimensional Ising model of N spins with free boundary conditions. Simulate the system with the Metropolis algorithm, alternately updating the even and odd spins. Evaluate the internal energy and the specific heat, using both the fluctuation–dissipation theorem and the calculation of energy variation. Compare with the exact result.

Exercise 8.8 Evaluate the specific heat in the one-dimensional Ising model using umbrella sampling and check the validity of the fluctuation–dissipation relation.

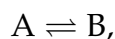
Dynamics

Exercise 9.1 Given a collection $\xi = (\xi_1, \dots, \xi_n)$ of Gaussian variables whose average vanishes, show that for any analytic function $F(\xi)$ one has

$$\langle F(\xi)\xi_i \rangle = \sum_j C_{ij} \left\langle \frac{\partial F}{\partial \xi_j} \right\rangle,$$

where C_{ij} is the correlation matrix of the ξ .

Exercise 9.2 Consider the chemical reaction



described by the kinetic equations

$$\begin{aligned} \frac{d[A]}{dt} &= -k_{BA}[A] + k_{AB}[B]; \\ \frac{d[B]}{dt} &= k_{BA}[A] - k_{AB}[B]. \end{aligned}$$

Show that the equilibrium concentrations $\langle [A] \rangle$ and $\langle [B] \rangle$ satisfy the detailed-balance condition

$$k_{BA} \langle [A] \rangle = k_{AB} \langle [B] \rangle.$$

Show that the solutions to the kinetic equation yield

$$\Delta c_A(t) = [A](t) - \langle [A] \rangle = \Delta c_A(0) e^{-t/\tau},$$

where

$$\tau^{-1} = k_{AB} + k_{BA}.$$

Exercise 9.3 Defining

$$\Delta R^2(t) = \int d^d \mathbf{r} r^2 P(\mathbf{r}, t | 0, 0),$$

show that

$$\frac{d}{dt} \Delta R^2(t) = 2dD,$$

where $P(\mathbf{r}, t | 0, 0)$ satisfies the equations

$$\begin{aligned} \int d^d \mathbf{r} P(\mathbf{r}, t | 0, 0) &= 1; \\ \frac{\partial P}{\partial t} &= D \nabla^2 P. \end{aligned}$$

Exercise 9.4 From the relation

$$\frac{d}{dt} \Delta R^2(t) = 2 \int_0^t dt' \langle \mathbf{v}(t') \cdot \mathbf{v}(0) \rangle,$$

assuming

$$\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = \langle v^2 \rangle e^{-t/\tau}, \quad t > 0,$$

evaluate $\Delta R^2(t)$. Given that the self-diffusion constant in most liquids is of the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, estimate the order of magnitude of τ .

Exercise 9.5 Consider particles in a liquid for which D is $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Determine the percentage of particles which in 15 psec have moved more than 5 \AA from their initial position.

Exercise 9.6 Consider a reaction coordinate q that moves in a one-dimensional bistable potential $V(q)$. Divide phase space for the degree of freedom into three

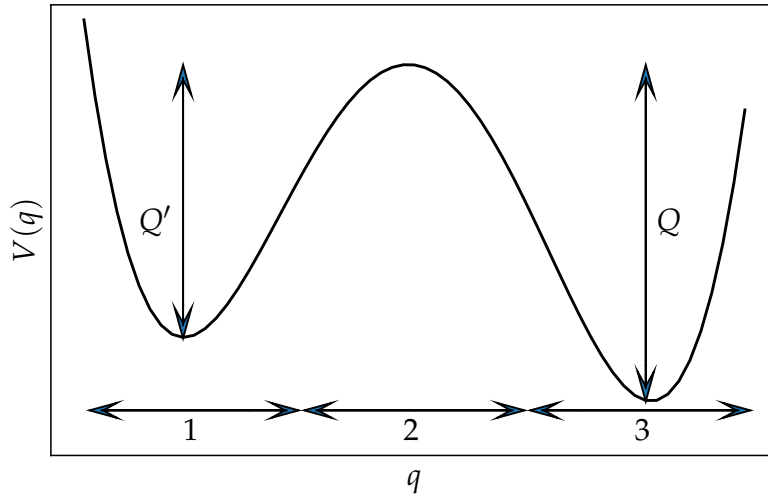


Figure 9.1: Bistable potential and three regions.

regions as illustrated in Fig. 9.1. The non-equilibrium concentrations of species in the three regions are $c_1(t)$, $c_2(t)$ and $c_3(t)$. A reasonable rate law description of the dynamics is

$$\begin{aligned}\frac{dc_1}{dt} &= -k_{31}c_1(t) + k_{13}c_3(t); \\ \frac{dc_2}{dt} &= -k_{32}c_2(t) + k_{23}c_3(t); \\ c &= c_1(t) + c_2(t) + c_3(t) = \text{const.}\end{aligned}$$

Here k_{ij} is the rate of going from region j to region i . From detailed balance we have

$$k_{13} \text{ and } k_{23} \gg k_{31} \text{ and } k_{32},$$

since

$$\frac{k_{31}}{k_{13}} = \frac{\langle c_3 \rangle}{c_1} = e^{-\beta Q},$$

and we assume the barrier height, Q , is large compared to $k_B T$.

(a) Use the simple kinetic model to compute the dependence for

$$\Delta c_1(t) = c_1(t) - \langle c_1 \rangle.$$

(b) Show that, if $\exp(-\beta Q) \ll 1$, the relaxation is dominated by a single relaxation time, τ , and that

$$\tau^{-1} \approx k_{31} \text{ or } k_{32}.$$

- (c) Discuss the transient behavior of $\Delta c(t)$ or its time derivative and show how this behavior disappears in a time of the order of k_{13}^{-1} or k_{23}^{-1} .

Exercise 9.7 Consider a tristable potential (shown in fig. 9.2) for a reaction coor-

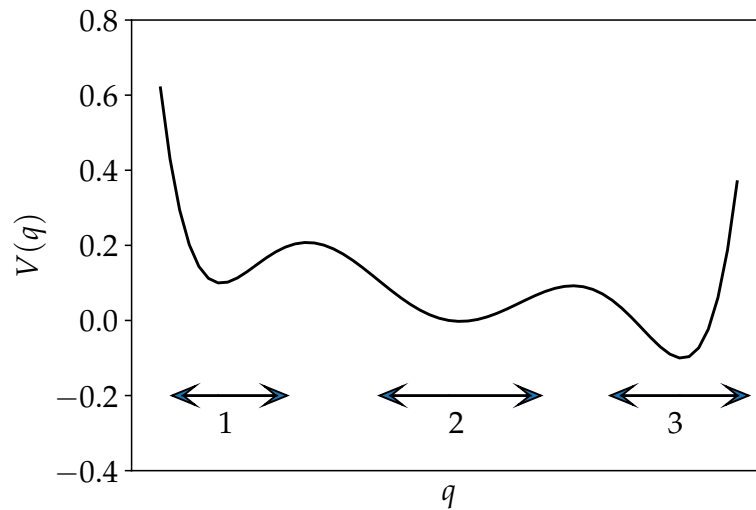


Figure 9.2: Tristable potential.

dinate q . Derive a microscopic expression for the rate constant k_{21} , which is defined by the phenomenological rate equations

$$\begin{aligned}\frac{dc_1}{dt} &= -k_{21}c_1(t) + k_{12}c_2(t); \\ \frac{dc_2}{dt} &= k_{21}c_1(t) - k_{12}c_2(t) + k_{23}c_3(t) - k_{32}c_2(t); \\ c &= c_1(t) + c_2(t) + c_3(t) = \text{const.}\end{aligned}$$

Exercise 9.8 Show that if $A(t)$ satisfies the classical oscillator equation of motion

$$\frac{d^2 A(t)}{dt^2} = -\omega_0^2 A(t),$$

one has

$$\langle \delta A(t) \delta A(0) \rangle = \langle (\delta A)^2 \rangle \cos(\omega_0 t).$$

Exercise 9.9 Consider a Brownian particle in contact with a bath. We denote by x the coordinate of the particle and by (y_1, \dots, y_N) the coordinates of the bath. The hamiltonian of the system is given by

$$\mathcal{H} = \mathcal{H}_0(x) - x f + \mathcal{H}_b(y_1, \dots, y_N).$$

We assume

$$f = \sum_i c_i y_i,$$

and

$$\mathcal{H}_0 = \frac{m\dot{x}^2}{2} + V(x).$$

We also assume that \mathcal{H}_b is the hamiltonian for a system of classical oscillators. This implies the exact validity of linear-response theory, yielding

$$f(t) = f_b(t) + \int_{-\infty}^{+\infty} dt' \chi_b(t-t') x(t'),$$

where

$$\chi_b(t) = \begin{cases} -\beta dC_b(t)/dt, & \text{for } t > 0; \\ 0, & \text{otherwise.} \end{cases}$$

Here, $C_b(t)$ is the correlation function of the pure bath:

$$C_b(t) = \langle \delta f(t) \delta f(0) \rangle_b.$$

Show that $x(t)$ satisfies the equation

$$m\ddot{x}(t) = \tilde{f}[x(t)] + \delta f(t) - \beta \int_0^t dt' C_{b(t-t')} \dot{x}(t'),$$

where

$$\begin{aligned} \tilde{f}(x) &= -\frac{d\tilde{V}}{dx}; \\ \tilde{V}(x) &= V(x) - \beta C(0) \frac{x^2}{2}; \\ \delta f(t) &= f_b(t) - \beta C_b(t) x(0). \end{aligned}$$

Thus $\delta f(t)$ is a Gaussian force with vanishing average and correlation equal to $C_b(t-t')$.

Complex Systems

Exercise 10.1 (Polymer over Lattice) Suppose that you arrange a polymer over a simple cubic lattice, so that the possible values of the \mathbf{r}_i are of the form $\mathbf{r}_i = a_0(n_1, \dots, n_d)$, where the n_a , $a = 1, \dots, d$ are integers. One imposes the constraint that $\mathbf{y}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$ be equal to one of the lattice base vectors $\mathbf{y}_i = a_0 \mathbf{e}_a$, where $\mathbf{e}_a = (\delta_{1a}, \dots, \delta_{da})$. Show that the grand canonical sum $\tilde{\Gamma}_{GC}(\mathbf{k}, z) = \sum_{N=0}^{\infty} z^N \tilde{\Gamma}_N(\mathbf{k})$ has an expression of the form

$$\tilde{\Gamma}_{GC}(\mathbf{k}, z) \propto (z_c - z + ck^2)^{-1},$$

and calculate the corresponding values of z_c and of the constant c .

Exercise 10.2 Show that if $\tilde{\Gamma}_{GC}(\mathbf{k}=0, z) \propto |z - z_c|^{-\gamma}$, one has

$$\Gamma_N = \int d^d \mathbf{r} \Gamma_N(\mathbf{r}) \propto z_c^{-N} N^{\gamma-1}.$$

Exercise 10.3 Show that, for $d < 4$, one has in the Gaussian model of polymers

$$\Gamma(0, z) = \int \frac{d^d \mathbf{k}}{(2\pi)^d} \tilde{\Gamma}_{GC}(\mathbf{k}, z) \simeq \text{const.} + \text{const.} \times |z_c - z|^{(d-2)/2}.$$

What occurs for $d = 4$? And what about $d > 4$? Show that this result implies that, for $2 < d \leq 4$, one has

$$\Gamma_N(0) \sim N^{-d/2}.$$

Exercise 10.4 Show that the coefficient of h_1^{2p} in $\lim_{n \rightarrow 0} Z/n$ can be represented by graphs that represent the configurations of p polymers over an excluded volume lattice. The contribution of each graph is proportional to K^N , where N is the total number of bonds present in the configuration.

Exercise 10.6 Show that the magnetic susceptibility per site in a vanishing magnetic field in a strongly diluted ferromagnet is given by

$$\chi = \frac{1}{k_B T} \sum_s s^2 v_s(p),$$

where $v_s(p)$ is the density of clusters of size s per lattice point, as a function of the occupation probability p .

Exercise 10.7 Show that the percolation analog of the magnetic correlation function between site i and site j is given by the average probability that i and j belong to the same *finite* cluster.

Exercise 10.8 Derive the following relations in the Bethe lattice bond percolation problem, valid for $p < p_c$:

$$\begin{aligned} S(p) &= p(1 + \zeta T(p)); \\ T(p) &= p[1 + (\zeta - 1)T(p)]. \end{aligned}$$

Here $S(p)$ is the average cluster size, and $T(p)$ the average cluster size contained in one branch of the Bethe lattice. p is the link probability and ζ the coordination number.

Exercise 10.9 Show that in the bond percolation problem in a Bethe lattice of coordination number ζ , the number of unconnected neighbors to a cluster of size s is given by

$$s' = (\zeta - 2)s + 2.$$

Exercise 10.10 Define the exponents σ and τ in terms of the density $\nu_s(p)$ of clusters of size s per lattice point, as a function of the occupation probability p , by

$$\begin{aligned}\nu_s(p) &\propto s^{-\tau} e^{-c(p)s}; \\ c(p) &\sim |p - p_c|^{1/\sigma}.\end{aligned}$$

Show that, if $k > \tau - 1$, the k -th moment of the distribution of cluster sizes, defined by

$$M_k = \sum_s s^k \nu_s(p),$$

satisfies

$$M_k \propto |p - p_c|^{\Delta_k},$$

where $\Delta_k = (\tau - 1 - k)/\sigma$.

Exercise 10.12 Given the Migdal-Kadanoff recurrence relation for the percolation problem in $d = 3$

$$\left. \frac{dp'}{db} \right|_{b=1} = p \ln p - (d-1)(1-p) \ln(1-p),$$

calculate the critical exponent ν for $d = 3$ and compare it with the numerical estimate $\nu = 0.9$.

Exercise 10.14 The Migdal-Kadanoff recurrence relation can also be derived for more “traditional” statistical systems. Once the bonds have been shifted, one obtains a one-dimensional system for which decimation is exact. Apply this method to the d -dimensional Ising model, and show that the recurrence relation for $K = J/k_B T$ in a d -dimensional Ising model, with a scaling factor b , is given by

$$e^{2K'} = \frac{\cosh^b(K_1) + \sinh^b(K_1)}{\cosh^b(K_1) - \sinh^b(K_1)},$$

where

$$K_1 = [1 + (d-1)(b-1)] K.$$

Calculate the equation for the infinitesimal transformation corresponding to $b \rightarrow 1^+$. Identify the fixed point for $d = 2$ and $d = 3$, and compare the value for the critical

temperature and for the exponent ν obtained in this fashion with the exact solution or available numerical values. Discuss the limits $d \rightarrow 1$ and $d \rightarrow \infty$.

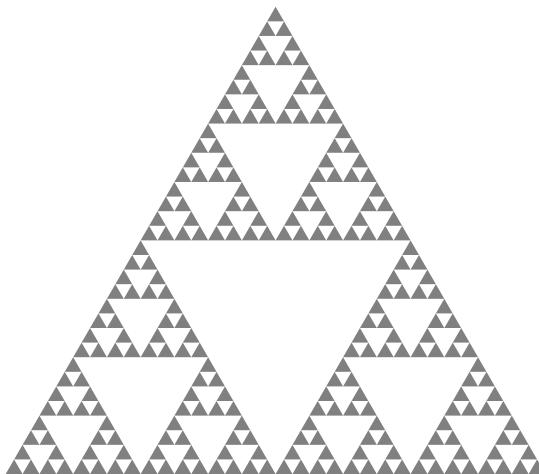


Figure 10.1: The Sierpiński gasket.

Exercise 10.15 Calculate the Hausdorff dimension of the Sierpiński gasket, recursively defined as follows (cf. fig. 10.1). Consider an equilateral triangle, and divide it into four equal triangles. The middle triangle is removed, and the construction is repeated for the remaining three triangles and so forth. Note that the dimension d_H obtained in this manner satisfies $1 < d_H < 2$.

Exercise 10.16 Calculate the Hausdorff dimension of the von Koch curve, recursively defined as follows (cf. fig. 10.2). Consider a segment of unitary length in the plane. The segment's middle third is replaced with two segments of length $1/3$ each, joined at their free ends. The construction is repeated for each of the four segments thus obtained.

Exercise 10.17 Define the covering dimension D of a subset of a d -dimensional space in the following way. Take a point that belongs to the set and trace a sphere of radius ℓ , with a center in that point. If the mass of the part of the set contained in this sphere is proportional to ℓ^D the covering dimension is D .

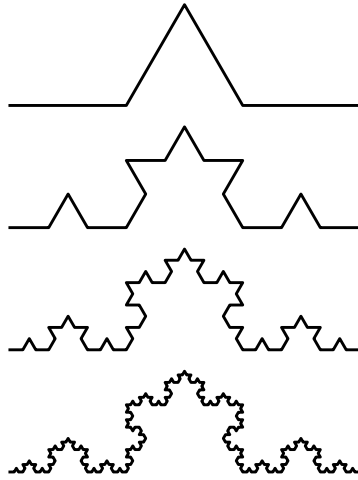


Figure 10.2: The von Koch curve.

Evaluate the covering dimensions of the Cantor set, the von Koch curve and the Sierpiński gasket.

Exercise 10.18 Show the validity of the Gumbel distribution for the minimum value of a collection M of random variables E_i , identically distributed, whose distribution for large and negative E is given by

$$P(E) \sim \exp\left(-B|E|^\delta\right),$$

with $B, \delta > 0$.

Exercise 10.19 Consider a random-energy model with energy probability distribution

$$P(E) \propto \exp\left(-\frac{E^2}{NJ_0^2}\right)$$

Show that, for large values of z , the probability distribution of the Boltzmann factor $z = e^{-E/k_B T}$ behaves as

$$P(z) \sim z^{-1-\mu},$$

where $\mu = T/T_0$ with $k_B T_0 = J_0/(2\sqrt{\ln 2})$.

Exercise 10.20 (Large deviations) Let $\mathcal{N}(\epsilon, \delta)$ be the total number of configurations j such that $N\epsilon < |E_j| < N(\epsilon + \delta)$, with $|\epsilon| > \epsilon_* = \sqrt{\log 2}$ and $\delta > 0$. Show that the fraction of samples in which there exist such configurations is exponentially small.

Exercise 10.21 From the original motivation of the REM as a simple version of a spin glass, one can define a generalization of the REM in the presence of a magnetic field B . The 2^N configurations are divided in $N + 1$ groups. Each group is labelled by its ‘magnetization’ $M \in \{-N, -N + 2, \dots, N - 2, N\}$, and includes $\binom{N}{(N+M)/2}$ configurations. Their energies $\{E_j\}$ are independent Gaussian variables with variance $\sqrt{N/2}$ and mean $[E_j]_{\text{av}} = -MB$, which depends upon the group j belongs to. Show that there exists a phase transition line β_c in the plane (β, B) such that:

$$\frac{1}{N} [\langle M \rangle]_{\text{av}} = \begin{cases} \tanh(\beta B), & \text{for } \beta \leq \beta_c(B); \\ \tanh(\beta_c(B) B), & \text{for } \beta > \beta_c(B). \end{cases}$$

Plot the magnetic susceptibility

$$\chi = \left[\frac{\partial \langle M \rangle}{\partial B} \right]_{\text{av}} \Big|_{B=0},$$

vs. $T = 1/\beta$.

Exercise 10.22 Consider a generalization of the REM where the pdf of energies, instead of being Gaussian, is $P(E) \propto e^{-C|E|^\delta}$, where $\delta > 0$. Show that, in order to have extensive thermodynamic potentials, one should scale C as $C = N^{1-\delta} \hat{C}$ (i.e. the thermodynamic limit $N \rightarrow \infty$ should be taken at fixed \hat{C}). Compute the critical temperature and the ground state energy density. What is the qualitative difference between the cases $\delta > 1$ and $\delta < 1$?

Part II

Solutions

Kinetic Theory

Solution to exercise 1.1 (On Avogadro's Number) It is well known that the length of a maximum circle on the Earth going through the Poles is equal to $40 \cdot 10^6$ m. Approximating the Earth by a sphere, its radius R_T is thus given by

$$R_T = \frac{40 \cdot 10^6}{2\pi} = 6.37 \cdot 10^6 \text{ m.} \quad (1.1)$$

The volume of water in the oceans is equal to 71% of the volume of a spherical shell of radius R_T and thickness h , where $h = 3.8 \cdot 10^3$ m is the mean depth of the oceans. Thus we obtain

$$V = 0.71 \cdot 4\pi R_T^2 h = 1.37 \cdot 10^{18} \text{ m}^3. \quad (1.2)$$

A volume of 100cc corresponds to $1.0 \cdot 10^{-4} \text{ m}^3$. Thus the ratio between the volume of the oceans and that of the flask is given by

$$x = \frac{1.0 \cdot 10^{-4}}{1.37 \cdot 10^{18}} = 7.3 \cdot 10^{-23}. \quad (1.3)$$

100cc of water have a mass of 100g. The molecular weight of water is 18, thus 100cc of water contain $n = 100/18 = 5.6$ mol, corresponding to $nN_A = 33 \cdot 10^{23}$ molecules, where $N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$ is Avogadro's number. The expected number of molecules to be found in the flask after the dilution is given by

$$N = nN_A x = 2.4 \cdot 10^2. \quad (1.4)$$

Solution to exercise 1.2 (On Maxwell's Distribution)

1. *Root mean square velocity.* The average square of any component of the velocity in a Maxwell distribution is given by

$$\langle v_i^2 \rangle = \int_{-\infty}^{\infty} \frac{dv_i}{\sqrt{2\pi k_B T/m}} v_i^2 e^{-mv_i^2/k_B T} = \frac{k_B T}{m}. \quad (1.5)$$

Thus

$$\langle v^2 \rangle = \left\langle \sum_{i=1}^d v_i^2 \right\rangle = \frac{d k_B T}{m}. \quad (1.6)$$

and therefore

$$v_{\text{RMS}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{d k_B T}{m}}. \quad (1.7)$$

In air, a randomly chosen particle is a molecule of O_2 , with molecular weight 32, with probability $p = \frac{1}{3}$ and a molecule of N_2 , with molecular weight 28, with probability $q = \frac{2}{3}$. Thus we have

$$\langle v^2 \rangle = 3k_B T \left(\frac{p}{m_{\text{O}_2}} + \frac{q}{m_{\text{N}_2}} \right) = \frac{3k_B T}{m_{\text{Harm}}}, \quad (1.8)$$

where m_{Harm} is the harmonic mean of the components' masses:

$$m_{\text{Harm}} = \left[\frac{p}{m_{\text{O}_2}} + \frac{q}{m_{\text{N}_2}} \right]^{-1} = 29.2 \text{ g}/N_A. \quad (1.9)$$

We obtain therefore

$$\langle v^2 \rangle = \frac{3 \cdot R \cdot 300}{N_A \cdot m_{\text{Harm}}} = \frac{3 \cdot 8.31 \cdot 300}{29.2 \cdot 10^{-3}} = 2.56 \cdot 10^5 \text{ m}^2\text{s}^{-2}, \quad (1.10)$$

where $R = 8.31 \text{ J K}^{-1}$ is the gas constant, leading to

$$v_{\text{RMS}} = \sqrt{\langle v^2 \rangle} = 5.06 \cdot 10^2 \text{ ms}^{-1}. \quad (1.11)$$

Although one should put m_{Harm} in this expression, the error one makes by introducing the mean mass $\bar{m} = p m_{\text{O}_2} + q m_{\text{N}_2}$ does not affect the first two significant digits.

2. *Most probable speed.* The Maxwell distribution of v in d dimensions is given by

$$p(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{d/2} \exp \left(- \sum_{i=1}^d \frac{m v_i^2}{2k_B T} \right). \quad (1.12)$$

The region in v -space where $v = |v|$ lies between v_0 and $v_0 + dv_0$ is a spherical shell of volume $S_d v_0^{d-1} dv_0$, where S_d the surface of the unit sphere in d dimensions. Thus the distribution of the module v is given by

$$p_v(v) = S_d \left(\frac{m}{2\pi k_B T} \right)^{d/2} v^{d-1} \exp \left(-\frac{mv^2}{2k_B T} \right). \quad (1.13)$$

The most probable speed corresponds to the maximum of this expression. Taking its derivative we obtain the equation

$$p'_v(v) = \text{const.} \left[\frac{d-1}{v} - \frac{mv}{k_B T} \right] v^{d-1} \exp \left(-\frac{mv^2}{2k_B T} \right) = 0. \quad (1.14)$$

The factor in brackets vanishes for

$$mv^2 = (d-1)k_B T. \quad (1.15)$$

We must of course choose the positive solution:

$$v_{\text{prob}} = \sqrt{\frac{(d-1)k_B T}{m}} = \sqrt{\frac{d-1}{d}} v_{\text{RMS}}. \quad (1.16)$$

3. *Kinetic energy distribution.* From the preceding answer, we can evaluate the distribution of the kinetic energy. If v lies between v_0 and $v_0 + dv_0$, the kinetic energy κ lies between $\kappa_0 = \frac{1}{2}mv_0^2$ and $\kappa_0 + d\kappa_0 = \kappa_0 + mv_0 dv_0$. Thus $dv_0 = d\kappa_0 / \sqrt{2m\kappa_0}$. We obtain therefore

$$p_v(v_0) dv_0 = p_v \left(\sqrt{\frac{2\kappa_0}{m}} \right) \frac{d\kappa_0}{\sqrt{2m\kappa_0}} = p_\kappa(\kappa_0) d\kappa_0, \quad (1.17)$$

yielding

$$\begin{aligned} p_\kappa(\kappa_0) &= S_d \left(\frac{m}{2\pi k_B T} \right)^{d/2} \frac{1}{\sqrt{2m\kappa_0}} p_v \left(\sqrt{\frac{2\kappa_0}{m}} \right) \\ &= S_d \frac{1}{2\kappa_0} \left(\frac{\kappa_0}{\pi k_B T} \right)^{d/2} \exp \left(-\frac{\kappa_0}{k_B T} \right). \end{aligned} \quad (1.18)$$

In particular for $d = 3$ the distribution is proportional to $\sqrt{\kappa} e^{-\kappa/k_B T}$.

Solution to exercise 1.3 (Gas in a Gravity Field) According to Bernoulli's argument, the number of particles that cross S_2 downwards through a patch of area A during a time interval of duration Δt is given by

$$\Delta \mathcal{N}_2 = \rho_2 \langle v_z \theta(-v_z) \rangle A \Delta t, \quad (1.19)$$

where, from Maxwell's distribution, we have

$$\langle v_z \theta(-v_z) \rangle = \int_{-\infty}^0 \frac{dv_z}{\sqrt{2\pi k_B T/m}} e^{-mv_z^2/(2k_B T)} = \sqrt{\frac{k_B T}{2\pi m}}. \quad (1.20)$$

All these particles eventually find their way to S_1 . On the other hand, the particles that in the same time interval leave S_1 upwards are only able to reach S_2 if their velocity satisfies $v_z > \sqrt{2gh}$, where $h = z_2 - z_1$. Thus we have

$$\Delta \mathcal{N}_1 = \rho_1 \langle v_z \theta(v_z - \sqrt{2gh}) \rangle A \Delta t, \quad (1.21)$$

where

$$\langle v_z \theta(v_z - \sqrt{2gh}) \rangle = \int_{\sqrt{2gh}}^{\infty} \frac{dv_z}{\sqrt{2\pi k_B T/m}} e^{-mv_z^2/(2k_B T)} = \sqrt{\frac{k_B T}{2\pi m}} e^{-mgh/k_B T}. \quad (1.22)$$

Equating these two quantities we obtain

$$\rho_2 = \rho_1 e^{-mgh/k_B T}. \quad (1.23)$$

Solution to exercise 1.4 (Knudsen Gas) By Bernoulli's argument, the number of particles that pass from container 1 to container 2 through an opening of area A during a time interval of duration Δt is given by

$$\Delta \mathcal{N}_1 = \rho_1 \langle v_x \theta(-v_x) \rangle_1 A \Delta t, \quad (1.24)$$

where we have assumed that the positive x axis leads toward container 2, and where from Maxwell's distribution we have

$$\langle v_x \theta(v_x) \rangle_1 = \int_0^{\infty} \frac{dv_x}{\sqrt{2\pi k_B T_1/m}} e^{-mv_x^2/(2k_B T_1)} = \sqrt{\frac{k_B T_1}{2\pi m}}. \quad (1.25)$$

By the same token, the number of particles that pass from container 2 to container 1 through the same opening is given by

$$\Delta \mathcal{N}_2 = \rho_2 \langle v_x \theta(-v_x) \rangle A \Delta t, \quad (1.26)$$

where

$$\langle v_x \theta(-v_x) \rangle_2 = \int_{-\infty}^0 \frac{dv_x}{\sqrt{2\pi k_B T_2/m}} e^{-mv_x^2/(2k_B T_2)} = \sqrt{\frac{k_B T_2}{2\pi m}}. \quad (1.27)$$

The two rates are equal if

$$\rho_1 \sqrt{T_1} = \rho_2 \sqrt{T_2}, \quad (1.28)$$

i.e., exploiting the equation of state $\rho = p/k_B T$,

$$\frac{p_1}{\sqrt{T_1}} = \frac{p_2}{\sqrt{T_2}}. \quad (1.29)$$

However, if the two temperatures are not equal, the hotter container will yield energy to the colder one. Indeed, the amount of energy carried out by the particles that leave the container 1 during the time interval of duration Δt is given by

$$\Delta E = \rho_1 \left\langle v_x \theta(v_x) \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \right\rangle_1 A \Delta t. \quad (1.30)$$

Now

$$\begin{aligned} & \left\langle v_x \theta(v_x) \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \right\rangle_1 \\ &= \int_0^\infty \frac{dv_x}{\sqrt{2\pi k_B T_1/m}} \int_{-\infty}^{+\infty} \frac{dv_y}{\sqrt{2\pi k_B T_1/m}} \int_{-\infty}^{+\infty} \frac{dv_z}{\sqrt{2\pi k_B T_1/m}} \\ & \quad \times v_x \theta(-v_x) \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \exp \left[-\frac{m (v_x^2 + v_y^2 + v_z^2)}{k_B T} \right]. \end{aligned} \quad (1.31)$$

The terms containing v_y or v_z yield by independent integration, e.g.,

$$\begin{aligned} \left\langle v_x \theta(v_x) \frac{1}{2} m v_y^2 \right\rangle_1 &= \langle v_x \theta(v_x) \rangle_1 \left\langle \frac{1}{2} m v_y^2 \right\rangle_1 \\ &= \sqrt{\frac{k_B T_1}{2\pi m}} \frac{1}{2} k_B T_1 = \frac{1}{\sqrt{\pi m}} \left(\frac{k_B T}{2} \right)^{3/2}. \end{aligned} \quad (1.32)$$

The term containing v_x yields

$$\frac{1}{2} m \left\langle v_x^3 \theta(v_x) \right\rangle_1 = \frac{1}{\sqrt{\pi m}} \frac{1}{2} \left(\frac{k_B T}{2} \right)^{3/2}. \quad (1.33)$$

Thus the net energy flux per unit area leaving container 1 is given by

$$\begin{aligned} J_E &= \frac{\Delta E_1 - \Delta E_2}{A \Delta t} = \frac{1}{\sqrt{\pi m}} \frac{5}{2^{5/2}} \left[\rho_2 (k_B T_1)^{3/2} - \rho_1 (k_B T_2)^{3/2} \right] \\ &= \frac{1}{\sqrt{\pi m}} \frac{5}{2^{5/2}} \frac{p_i}{\sqrt{k_B T_i}} (k_B T_1 - k_B T_2), \end{aligned} \quad (1.34)$$

where we have assumed that the condition (1.29) is satisfied.

Solution to exercise 1.5 (Drag in a Gas) Let us set the axes so that \mathbf{v} is parallel to the positive x -axis, and let us choose a reference frame in which the disk is at

rest. A gas particle with velocity $\mathbf{w} = (w_x, w_y, w_z)$ hitting the disk *from the right* (and thus with $w_x < 0$) releases to it a momentum

$$\Delta \mathbf{p} = 2m(w_x, 0, 0). \quad (1.35)$$

The number of particles with velocity between \mathbf{w} and $\mathbf{w} + d\mathbf{w}$ which hit the disk during a time interval of duration Δt is given by

$$d\mathcal{N}(\mathbf{w})\Delta t = \rho \mathcal{P}(\mathbf{w}) d\mathbf{w} w_x \Delta t, \quad (1.36)$$

where $\mathcal{P}(\mathbf{w})$ is the probability distribution for the particle velocity. It is given by a Maxwell distribution, with average $\langle \mathbf{w} \rangle = -\mathbf{v}$:

$$\mathcal{P}(\mathbf{w}) = f_0(w_x + v) f_0(w_y) f_0(w_z), \quad (1.37)$$

where

$$f_0(w) = \left(\frac{2\pi k_B T}{m} \right)^{-1/2} \exp\left(-\frac{mw^2}{2k_B T} \right). \quad (1.38)$$

We can thus integrate out the transverse components (w_y, w_z) . Thus the total momentum released to the disk by particles coming from the right during a time interval of duration Δt is parallel to the x -axis and is given by

$$P_x^{(-)} = -\rho S \Delta t \int_{-\infty}^0 dw_x f_0(w_x + v) 2mw_x^2. \quad (1.39)$$

Analogously the total momentum released to the disk by particles coming from the left is given by

$$P_x^{(+)} = \rho S \Delta t \int_0^{+\infty} dw_x f_0(w_x + v) 2mw_x^2. \quad (1.40)$$

We obtain therefore the net momentum released on the disk by the collisions with the particles:

$$\begin{aligned} P_x &= P_x^{(+)} + P_x^{(-)} = \rho S \Delta t \int_0^{+\infty} dw_x 2mw_x^2 [f_0(w_x + v) - f_0(-w_x + v)] \\ &\simeq \rho S \Delta t 4mv \int_0^{\infty} dw_x w_x^2 f_0'(w_x). \end{aligned} \quad (1.41)$$

The integral over w_x is evaluated by successive partial integrations:

$$\begin{aligned} \mathcal{I} &= \int_0^{\infty} dw_x w_x^2 f_0'(w_x) = \left[w^2 f_0(w) \right]_0^{\infty} - 2 \int_0^{\infty} dw w f_0(w) \\ &= \left(-2 \frac{k_B T}{m} \right) \int_0^{\infty} dw \frac{df_0(w)}{dw} = - \left(\frac{2k_B T}{m\pi} \right)^{1/2}. \end{aligned} \quad (1.42)$$

The force acting on the disk is thus given by

$$F = \frac{P_x}{\Delta t} = -4v\rho S \sqrt{\frac{2mk_B T}{\pi}}. \quad (1.43)$$

Thermodynamics

Solution to exercise 2.1 Let us denote the first system by (1), and by $E^{(1)}$ and $N^{(1)}$, respectively, its internal energy and its number of particles of species k , and analogously for the second system (2). We shall mark by the index i and f , respectively, the initial and final values of these quantities. Then the initial value of the entropy for the composite system is given by

$$S_i = S^{(1)}(E_i^{(1)}, N_i^{(1)}) + S^{(2)}(E_i^{(2)}, N_i^{(2)}). \quad (2.1)$$

The final value is given by

$$S_f = S^{(1)}(E_f^{(1)}, N_f^{(1)}) + S^{(2)}(E_f^{(2)}, N_f^{(2)}). \quad (2.2)$$

By the convexity properties of the entropy, we have

$$\begin{aligned} S^{(1)}(E_f^{(1)}, N_f^{(1)}) &\leq S^{(1)}(E_i^{(1)}, N_i^{(1)}) + \left. \frac{\partial S^{(1)}}{\partial E^{(1)}} \right|_{E_i^{(1)}, N_i^{(1)}} (E_f^{(1)} - E_i^{(1)}) \\ &\quad + \left. \frac{\partial S^{(1)}}{\partial N^{(1)}} \right|_{E_i^{(1)}, N_i^{(1)}} (N_f^{(1)} - N_i^{(1)}), \end{aligned} \quad (2.3)$$

and analogously for the second system. Therefore, since

$$(E_f^{(2)} - E_i^{(2)}) = - (E_f^{(1)} - E_i^{(1)}), \quad (2.4)$$

and analogously for N , we have

$$S_f - S_i \leq \left[\frac{\partial S^{(1)}}{\partial E^{(1)}} \Big|_{E_i^{(1)}, N_i^{(1)}} - \frac{\partial S^{(2)}}{\partial E^{(2)}} \Big|_{E_i^{(2)}, N_i^{(2)}} \right] (E_f^{(1)} - E_i^{(1)}) + \left[\frac{\partial S^{(1)}}{\partial N^{(1)}} \Big|_{E_i^{(1)}, N_i^{(1)}} - \frac{\partial S^{(2)}}{\partial N^{(2)}} \Big|_{E_i^{(2)}, N_i^{(2)}} \right] (N_f^{(1)} - N_i^{(1)}). \quad (2.5)$$

The left-hand side is nonnegative, and the factor in brackets in the first term in the right-hand side vanishes because the initial temperature is the same for the two systems. Thus we have

$$\left[\frac{\partial S^{(1)}}{\partial N^{(1)}} \Big|_{E_i^{(1)}, N_i^{(1)}} - \frac{\partial S^{(2)}}{\partial N^{(2)}} \Big|_{E_i^{(2)}, N_i^{(2)}} \right] (N_f^{(1)} - N_i^{(1)}) = -\frac{\mu_i^{(1)} - \mu_i^{(2)}}{T} (N_f^{(1)} - N_i^{(1)}) \geq 0. \quad (2.6)$$

Thus, if $\mu_i^{(1)} \geq \mu_i^{(2)}$, we have $N_f^{(1)} \leq N_i^{(1)}$ (assuming $T > 0$).

Solution to exercise 2.2 We recall that the entropy $S(E, V, N)$ must satisfy the following requirements:

Extensivity: If $\lambda > 0$, one has $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$;

Convexity: The surface $S(E, V, N)$ lies always below the tangent plane to any of its points;

Monotonicity: $\partial S / \partial E)_{V, N} \geq 0$.

The first requirement is satisfied by all expressions. The second requirement is not satisfied by the expressions 2., 3., 4., 7., 8. The third requirement is satisfied by the remaining expressions 1., 5. and 6. Thus the acceptable expressions are 1., 5. and 6.

Solution to exercise 2.3

1. $E = (S^3 v_0 \theta) / (NVR^2)$;
5. $E = [(S^5 v_0 \theta^2) / (N^2 VR^3)]^{1/2}$;
6. $E = (N^2 R \theta v_0 / V) e^{S/NR}$.

Solution to exercise 2.4 Let us consider an arbitrary change $df = (df_0, \dots, df_k)$, which induces a corresponding change $dX = (dX_0, \dots, dX_k)$, where, with obvious notation, one has

$$dX_\ell = \sum_{i=0}^k \left. \frac{\partial X_\ell}{\partial f_i} \right)_f df_i. \quad (2.7)$$

Let us evaluate the second variation $d^2\Phi$ for this change. One has

$$\begin{aligned} d^2\Phi &= \sum_{i,j=0}^k \frac{\partial^2\Phi}{\partial f_i \partial f_j} df_i df_j = - \sum_{i,j=0}^k \left. \frac{\partial X_i}{\partial f_j} \right)_f df_i df_j \\ &= - \sum_{j=0}^k dX_j df_j. \end{aligned} \quad (2.8)$$

Now we have

$$df_j = \sum_{i=0}^k \left. \frac{\partial f_j}{\partial X_i} \right)_X dX_i. \quad (2.9)$$

Therefore

$$\begin{aligned} - \sum_{j=0}^k dX_j df_j &= - \sum_{i,j=0}^k dX_j \left. \frac{\partial f_j}{\partial X_i} \right)_X dX_i = - \sum_{j=0}^k dX_j \frac{\partial^2 E}{\partial X_j \partial X_i} dX_i \\ &= -d^2E \leq 0. \end{aligned} \quad (2.10)$$

Solution to exercise 2.5 Let us assume that the system (s) is in contact with a reservoir (r) at temperature T and pressure p , adiabatically isolated from the environment. Then the work W performed by the system will be given by $W = -(\Delta E^{(r)} + \Delta E^{(s)})$. On the other hand, we have $\Delta S^{(s)} + \Delta S^{(r)} \geq 0$. We have moreover $\Delta S^{(r)} = (\Delta E^{(r)} + p \Delta V^{(r)})/T$, where $\Delta V^{(r)} = -\Delta V^{(s)}$. Thus

$$\frac{1}{T} \left(-W - \Delta E^{(s)} + p \Delta V^{(s)} \right) + \Delta S^{(s)} \geq 0. \quad (2.11)$$

Multiplying by T (assumed to be positive) we obtain

$$W \leq - \left(\Delta E^{(s)} - T \Delta S^{(s)} + p \Delta V^{(s)} \right). \quad (2.12)$$

At constant p and T , the right-hand side is equal to the difference between the equilibrium Gibbs free energy and the initial one for the system.

Solution to exercise 2.6 Let us consider a system which exchanges energy in the form of heat with a reservoir at temperature T . Let the system undergo a process resulting in an entropy change ΔS . Then the heat Q received by the system satisfies

$$Q \leq T \Delta S. \quad (2.13)$$

Indeed, denoting by $\Delta S^{(r)}$ the entropy change of the reservoir, one has $\Delta S^{(r)} = -Q/T$, and $\Delta S^{(r)} + \Delta S \geq 0$.

Let us now assume that our system (s) is in contact with a reservoir (r) at a temperature $T > 0$ and pressure p . Note that we are *not* supposing that the system is in thermal equilibrium with the reservoir, only that the reservoir exchanges energy with the system either via heat or by its volume change. Then the entropy change of the reservoir is given by

$$\Delta S^{(r)} = \frac{1}{T} (\Delta E^{(r)} + p \Delta V^{(r)}). \quad (2.14)$$

For the reservoir, one has $Q \leq T \Delta S^{(r)}$, while $\Delta S^{(r)} = (\Delta E^{(r)} + p \Delta V^{(r)}) / T = -(\Delta E^{(s)} + p \Delta V^{(s)})$. When p is constant, $\Delta H^{(s)} = \Delta E^{(s)} + \Delta(pV^{(s)}) = \Delta E^{(s)} + p \Delta V^{(s)}$. Thus we have (for $T > 0$)

$$Q \leq \Delta H^{(s)}. \quad (2.15)$$

Solution to exercise 2.7 Evaluating the differential of the relation $F(x, y, z) = 0$ we obtain the following condition for the differentials dx , dy and dz :

$$\frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy + \frac{\partial F}{\partial z} dz = 0. \quad (2.16)$$

We obtain therefore the following expression for the partial derivatives:

$$\left. \frac{\partial x}{\partial y} \right|_z = -\frac{\partial F / \partial y}{\partial F / \partial x}; \quad (2.17)$$

$$\left. \frac{\partial y}{\partial z} \right|_x = -\frac{\partial F / \partial z}{\partial F / \partial y}; \quad (2.18)$$

$$\left. \frac{\partial z}{\partial x} \right|_y = -\frac{\partial F / \partial x}{\partial F / \partial z}. \quad (2.19)$$

We obtain therefore, exploiting the fact that, e.g., $\partial x/\partial y)_z = 1/\partial y/\partial x)_z$,

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\partial F/\partial y}{\partial F/\partial x} = -\frac{\partial F/\partial y}{\partial F/\partial z} \frac{\partial F/\partial z}{\partial F/\partial x} = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y. \quad (2.20)$$

Solution to exercise 2.8 (Law of Adiabatic Processes) Let the gas undergo a reversible temperature change of size dT at constant pressure by receiving heat from a reservoir at temperature $T + dT$ and releasing work to the exterior via an adiabatic piston. One has

$$dS = C_p \frac{dT}{T + dT} \simeq C_p \frac{dT}{T}. \quad (2.21)$$

In this transformation, the change in internal energy is given by $dE = C_V dT$, since the internal energy of the gas depends only on the temperature. On the other hand, by the equation of state, for a temperature change dT at constant pressure p , we have

$$dV = \frac{Nk_B dT}{p}. \quad (2.22)$$

Thus, by the First Principle, we have

$$dE = C_V dT = T dS - p dV = C_p dT - p dV = (C_p - Nk_B) dT. \quad (2.23)$$

When $dS = 0$, we have

$$dE = C_V dT = -p dV. \quad (2.24)$$

On the other hand, from the equation of state, we have

$$dT = \frac{1}{Nk_B} d(pV) = \frac{1}{C_p - C_V} (p dV + V dp). \quad (2.25)$$

Thus

$$p dV + V dp = -\frac{C_p - C_V}{C_V} p dV, \quad (2.26)$$

which implies

$$\left(\frac{\partial p}{\partial V}\right)_S = -\frac{C_p}{C_V} \frac{p}{V} = -\gamma \frac{p}{V}. \quad (2.27)$$

Differentiating the equation of state in the form

$$V = \frac{Nk_B T}{p}, \quad (2.28)$$

we obtain

$$dV = Nk_B \left(\frac{dT}{p} - \frac{T dp}{p^2} \right). \quad (2.29)$$

Thus from $V dp = -\gamma p dV$ we obtain

$$Nk_B T \frac{dp}{p} = -\gamma Nk_B \left(dT - \frac{T dp}{p} \right), \quad (2.30)$$

and thus

$$\gamma \frac{dT}{T} + (1 - \gamma) \frac{dp}{p} = 0, \quad (2.31)$$

i.e., if γ is constant, $d \log \left(p T^{\gamma/(1-\gamma)} \right) = 0$.

Solution to exercise 2.9 (Adiabatic Atmosphere) Denoting the numerical density N/V by ρ , we obtain, from the equation of state $k_B T = p/\rho$,

$$dT = \frac{1}{k_B} \left(\frac{dp}{\rho} - \frac{p d\rho}{\rho^2} \right). \quad (2.32)$$

From the Law of the Reversible Adiabatics we obtain

$$\frac{d\rho}{\rho} = \frac{1}{\gamma} \frac{dp}{p}. \quad (2.33)$$

Thus

$$dT = \frac{1}{k_B} \left(1 - \frac{1}{\gamma} \right) \frac{dp}{\rho}. \quad (2.34)$$

From Stevin's law we have

$$\frac{dp}{\rho} = -m_{\text{mol}} g dz. \quad (2.35)$$

Thus we have

$$\frac{dT}{dz} = -\frac{m_{\text{mol}} g}{k_B} \left(1 - \frac{1}{\gamma} \right). \quad (2.36)$$

Solution to exercise 2.10 Let us denote by V_0 the (unknown) volume of the external air which will be found in the container at the end of the process. Thus the work W applied by the atmosphere to the system is equal to $p_0 V_0$. This work increases the internal energy of the gas, yielding an increase of temperature ΔT equal to W/C_V . Thus the final temperature of the gas is given by

$$T = T_0 + \frac{p_0 V_0}{C_V} = T_0 \left(1 + \frac{C_p - C_V}{C_V} \right) = \gamma T_0. \quad (2.37)$$

The Fundamental Postulate

Solution to exercise 3.1 (Particle in a Potential Well) Let us consider the phase space of the system, with coordinates (x, p) . The states of energy $E_n = \hbar^2 \pi^2 n^2 / L^2$ correspond to two straight lines with $-L/2 \leq x \leq +L/2$ and $p = \pm \hbar \pi n / L$. The spanned area A_n is equal to $2\hbar \pi n$. Of course, the area pertaining to the n -th state is given by $A_{n+1} - A_n = 2\pi \hbar = h$.

Solution to exercise 3.2 Apart from the $k_B T^2$ factor, the lhs of the identity can be rewritten as follows:

$$\begin{aligned} \left. \frac{\partial E}{\partial T} \right)_p + \frac{p}{T} \left. \frac{\partial E}{\partial p} \right)_T &= \left. \frac{\partial E}{\partial T} \right)_V + \left. \frac{\partial E}{\partial V} \right)_T \left. \frac{\partial V}{\partial T} \right)_p - \frac{1}{T} \left. \frac{\partial F}{\partial V} \right)_T \left. \frac{\partial E}{\partial p} \right)_T \\ &= \left. \frac{\partial E}{\partial T} \right)_V + \left. \frac{\partial E}{\partial V} \right)_T \left. \frac{\partial V}{\partial T} \right)_p - \frac{1}{T} \left. \frac{\partial F}{\partial V} \right)_T \left. \frac{\partial E}{\partial V} \right)_T \left. \frac{\partial V}{\partial p} \right)_T. \end{aligned} \quad (3.1)$$

Thus the difference between the two sides reads

$$\Delta Q = \frac{1}{T} \left. \frac{\partial E}{\partial V} \right)_T \left[\left. \frac{\partial E}{\partial V} \right)_T \left. \frac{\partial V}{\partial p} \right)_T - \left. \frac{\partial F}{\partial V} \right)_T \left. \frac{\partial V}{\partial p} \right)_T + T \left. \frac{\partial V}{\partial T} \right)_p \right]. \quad (3.2)$$

and, using the relation $F = E - TS$, can be rewritten as follows:

$$\begin{aligned} \Delta Q &= \frac{1}{T} \left. \frac{\partial E}{\partial V} \right)_T \left[T \left. \frac{\partial S}{\partial V} \right)_T \left. \frac{\partial V}{\partial p} \right)_T + T \left. \frac{\partial V}{\partial T} \right)_p \right] \\ &= \frac{1}{T} \left. \frac{\partial E}{\partial V} \right)_T \left[T \left. \frac{\partial p}{\partial T} \right)_V \left. \frac{\partial V}{\partial p} \right)_T + T \left. \frac{\partial V}{\partial T} \right)_p \right] = 0, \end{aligned} \quad (3.3)$$

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where we have exploited Maxwell's relations and the identity

$$\left. \frac{\partial x}{\partial y} \right|_z = - \frac{\partial x / \partial z}{\partial y / \partial z} \Big|_x. \quad (3.4)$$

Solution to exercise 3.3 We assume that one particle is kept fixed at the origin ($x_0 = 0$). Let us define $Z_N(X, p, T)$ by the expression

$$Z_N(X, T) = \int_0^X dx_1 \int_{x_1}^X dx_2 \cdots \int_{x_{N-2}}^X dx_{N-1} \exp \left(- \frac{1}{k_B T} \sum_{i=1}^N u(x_i - x_0) \right). \quad (3.5)$$

Then the partition function in the p - T ensemble is given by

$$Z_N(p, T) = \int_0^\infty dX \exp \left(- \frac{pX}{k_B T} \right) Z_N(X, T). \quad (3.6)$$

This is the Laplace transform of $Z_N(X, T)$, evaluated at $z = p/k_B T$. Now it is easy to see that $Z_N(X, T)$ satisfies the recursion relation

$$Z_N(X, T) = \int_0^X dx \exp \left(- \frac{u(X-x)}{k_B T} \right) Z_{N-1}(x, T), \quad (3.7)$$

with the initial condition $Z_0(X, T) = 1$. This is the convolution of $Z_{N-1}(x, T)$ with $\phi(x, T) = \exp(-u(x)/k_B T) \theta(x)$. Thus the Laplace transform of $Z_N(X, T)$ satisfies

$$\tilde{Z}_N(z, T) = \int_0^\infty dX e^{-zX} Z_N(X, T) = \tilde{\phi}(z, T) \tilde{Z}_{N-1}(z, T). \quad (3.8)$$

Taking into account the initial condition we obtain

$$\tilde{Z}_N(z, T) = \tilde{\phi}(z, T)^N. \quad (3.9)$$

Thus we have

$$Z_N(p, T) = \tilde{\phi} \left(\frac{p}{k_B T}, T \right)^N. \quad (3.10)$$

We have

$$\langle X \rangle_{p, T, N} = - \frac{\partial \log Z_N}{\partial (p/k_B T)} = -N \left. \frac{\partial_z \tilde{\phi}(z, T)}{\tilde{\phi}(z, T)} \right|_{z=p/k_B T}, \quad (3.11)$$

i.e.,

$$\langle X \rangle_{p, T, N} = N \langle X \rangle_{p, T, N=1} = N \frac{\int_0^\infty dX X e^{-(u(X)+pX)/k_B T}}{\int_0^\infty dX e^{-(u(X)+pX)/k_B T}}. \quad (3.12)$$

Solution to exercise 3.4 The grand canonical partition function is defined by

$$Z_{GC}(\alpha, \beta) = \sum_x e^{-\beta\epsilon(x) + \alpha N(x)}, \quad (3.13)$$

where x denotes a generic microstate of energy $\epsilon(x)$ and number of particles $N(x)$, and where α and β are eventually set to $\mu/k_B T$ and $1/k_B T$ respectively. Then we have

$$\langle E \rangle = \frac{1}{Z_{GC}} \sum_x \epsilon(x) e^{-\beta\epsilon(x) + \alpha N(x)} = - \left. \frac{\partial \log Z_{GC}}{\partial \beta} \right|_{\alpha}; \quad (3.14)$$

$$\langle N \rangle = \frac{1}{Z_{GC}} \sum_x N(x) e^{-\beta\epsilon(x) + \alpha N(x)} = \left. \frac{\partial \log Z_{GC}}{\partial \alpha} \right|_{\beta}. \quad (3.15)$$

Taking second derivatives, we obtain

$$\begin{aligned} \frac{\partial^2 \log Z_{GC}}{\partial \beta^2} &= \frac{1}{Z_{GC}} \sum_x \epsilon^2(x) e^{-\beta\epsilon(x) + \alpha N(x)} - \left[\frac{1}{Z_{GC}} \sum_x \epsilon(x) e^{-\beta\epsilon(x) + \alpha N(x)} \right]^2 \\ &= \langle E^2 \rangle - \langle E \rangle^2; \end{aligned} \quad (3.16)$$

$$\begin{aligned} \frac{\partial^2 \log Z_{GC}}{\partial \alpha^2} &= \frac{1}{Z_{GC}} \sum_x N^2(x) e^{-\beta\epsilon(x) + \alpha N(x)} - \left[\frac{1}{Z_{GC}} \sum_x N(x) e^{-\beta\epsilon(x) + \alpha N(x)} \right]^2 \\ &= \langle N^2 \rangle - \langle N \rangle^2; \end{aligned} \quad (3.17)$$

$$\begin{aligned} - \frac{\partial^2 \log Z_{GC}}{\partial \alpha \partial \beta} &= \frac{1}{Z_{GC}} \sum_x N(x) \epsilon(x) e^{-\beta\epsilon(x) + \alpha N(x)} \\ &\quad - \left[\frac{1}{Z_{GC}} \sum_x N(x) e^{-\beta\epsilon(x) + \alpha N(x)} \right] \left[\frac{1}{Z_{GC}} \sum_x \epsilon(x) e^{-\beta\epsilon(x) + \alpha N(x)} \right] \\ &= \langle N E \rangle - \langle N \rangle \langle E \rangle. \end{aligned} \quad (3.18)$$

Solution to exercise 3.5 The grand canonical partition function can be written in the following form:

$$Z_{GC} = \sum_N \sum_x \delta_{N, N(x)} e^{-\beta\epsilon(x) + \alpha N} = \sum_N e^{\alpha N} Z_N, \quad (3.19)$$

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where Z_N is the canonical partition function of a system with N particles:

$$Z_N = \sum_x \delta_{N,N(x)} e^{-\beta \epsilon(x)}. \quad (3.20)$$

Thus the probability that the system in the grand canonical ensemble has N particles is given by

$$p_N = \frac{e^{\alpha N} Z_N}{Z_{GC}}. \quad (3.21)$$

Now p_N is strongly peaked around the equilibrium value, N^{eq} , of N . We have therefore

$$\begin{aligned} \langle \Delta E^2 \rangle_{GC} &= \sum_N \langle \Delta E^2 \rangle_N p_N + \sum_N p_N \left. \frac{\partial \langle E \rangle_N}{\partial N} \right|_T^2 (N - N^{\text{eq}})^2 \\ &\simeq \langle \Delta E^2 \rangle_{N^{\text{eq}}} + \left. \frac{\partial E}{\partial N} \right|_{N^{\text{eq}}}^2 \langle \Delta N^2 \rangle_{GC} \geq \langle \Delta E^2 \rangle_{N^{\text{eq}}}. \end{aligned} \quad (3.22)$$

Solution to exercise 3.6 Given two distributions $p(x)$ and $p'(x)$, define the quantity

$$D(p||p') = \sum_x p(x) \log \frac{p(x)}{p'(x)}. \quad (3.23)$$

From the inequality

$$\log x \leq x - 1, \quad (3.24)$$

it follows that

$$D(p||p') \geq 0, \quad (3.25)$$

and that the equality holds only if $p(x)$ is equal to $p'(x)$ almost everywhere, i.e., except in regions of vanishing probability. One has indeed

$$\begin{aligned} D(p||p') &= - \sum_x p(x) \log \frac{p'(x)}{p(x)} \geq - \sum_x p(x) \left[\frac{p'(x)}{p(x)} - 1 \right] \\ &= - \sum_x p'(x) + \sum_x p(x) = 0, \end{aligned} \quad (3.26)$$

because both $p(x)$ and $p'(x)$ are normalized.

Consider now

$$D(p||p^{\text{eq}}) = \sum_x p(x) \log \frac{p(x)}{p^{\text{eq}}(x)}. \quad (3.27)$$

We have

$$D(p||p^{\text{eq}}) = -\mathcal{S}(p) + \sum_x p(x) \log p^{\text{eq}}(x) = \mathcal{S}(p) - \langle H \rangle_p - \log Z. \quad (3.28)$$

We have, on the other hand

$$\begin{aligned}\mathcal{S}(p^{\text{eq}}) &= -\sum_x p^{\text{eq}}(x) \log p^{\text{eq}}(x) = \sum_x p^{\text{eq}}(x) \frac{H(x)}{k_{\text{B}}T} + \sum_x p^{\text{eq}}(x) \log Z \\ &= \frac{\langle H \rangle_{p^{\text{eq}}}}{k_{\text{B}}T} + \log Z.\end{aligned}\tag{3.29}$$

Thus we have

$$\begin{aligned}0 \leq D(p \| p^{\text{eq}}) &= -\mathcal{S}(p) - \langle H \rangle_p - \log Z \\ &= \mathcal{S}(p) - \langle H \rangle_p + \langle H \rangle_{p^{\text{eq}}} + \mathcal{S}(p^{\text{eq}}) = \mathcal{S}(p^{\text{eq}}) - \mathcal{S}(p),\end{aligned}\tag{3.30}$$

since by assumption $\langle H \rangle_p = \langle H \rangle_{p^{\text{eq}}}$.

Interaction-Free Systems

Solution to exercise 4.1 (Stefan-Boltzmann Law) From $E = 3pV$, by differentiation, we obtain $dE = 3p dV + 3V dp$. On the other hand, from the First Principle we have $dE = T dS - p dV$. Thus we have $T dS = 4p dV + 3V dp$, from which follow the following relations:

$$\left. \frac{\partial S}{\partial V} \right)_p = \frac{4p}{T}; \quad (4.1)$$

$$\left. \frac{\partial S}{\partial p} \right)_V = \frac{3V}{T}. \quad (4.2)$$

Taking the derivative of the first with respect to p , of the second with respect to V , and equating, we obtain

$$4 \left. \frac{\partial(p/T)}{\partial p} \right)_V = 3 \left. \frac{\partial(V/T)}{\partial V} \right)_p. \quad (4.3)$$

In the rhs, T can be taken as constant, since the pressure depends only on T , thus the rhs is equal to $3/T$. The lhs is equal to $(4/T) - (4p/T^2) dT/dp$. Thus we obtain

$$\frac{dp}{dT} = \frac{4p}{T}. \quad (4.4)$$

Since $\lim_{T \rightarrow 0} p(T) = 0$, we obtain $p(T) = \text{const } T^4$. This is also true for $\epsilon(t) = 3p(T)$ and, since $W_{\text{tot}} = \epsilon(T) c$, also for W_{tot} .

Solution to exercise 4.2 Let us define the function $g_\alpha(z)$, for $\alpha > 0$ and $|z| < 1$ by

the series

$$g_\alpha(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^\alpha}. \quad (4.5)$$

This function has the integral representation

$$g_\alpha(z) = \frac{1}{\Gamma(\alpha)} \int_0^\infty dx x^{\alpha-1} \frac{z e^{-x}}{1 - z e^{-x}}, \quad (4.6)$$

where $\Gamma(\alpha)$ is Euler's gamma function. Let us now consider a Bose gas at temperature T with number density of particles equal to ρ . Let us define the temperature T_0 via

$$\rho = \frac{1}{\lambda_B^3(T_0)}, \quad (4.7)$$

where

$$\lambda_B(T) = \left(\frac{h^2}{2\pi k_B T} \right)^{1/2} \quad (4.8)$$

is the thermal de Broglie length. We also set Boltzmann's constant to 1. Then the equation of state for temperatures above the condensation temperature is given by

$$p(T) = T \left(\frac{T}{T_0} \right)^{3/2} g_{5/2}(\zeta(T)), \quad (4.9)$$

where $\zeta(T)$ satisfies the equation

$$\left(\frac{T}{T_0} \right)^{3/2} g_{3/2}(\zeta(T)) = 1. \quad (4.10)$$

On the other hand, the energy per particle $\epsilon(T)$ is given by

$$\epsilon(T) = \frac{3}{2} p(T) = \frac{3}{2} T \left(\frac{T}{T_0} \right)^{3/2} g_{5/2}(\zeta(T)). \quad (4.11)$$

These expressions hold for $T > T_c$, where the condensation temperature T_c is given by

$$\left(\frac{T_c}{T_0} \right)^{3/2} g_{3/2}(1) = 1. \quad (4.12)$$

We have

$$g_{3/2}(1) = \zeta_R \left(\frac{3}{2} \right) = 2.61238 \dots \quad (4.13)$$

where $\zeta_R(\alpha)$ Riemann's zeta function:

$$\zeta_R(\alpha) = \sum_{k=1}^{\infty} \frac{1}{k^\alpha}. \quad (4.14)$$

We obtain therefore

$$T_c = \left(\zeta_R \left(\frac{3}{2} \right) \right)^{-2/3} T_0 \simeq 0.527201 T_0. \quad (4.15)$$

For $T < T_c$ we have $z = 1$ and therefore

$$p(T) = T \left(\frac{T}{T_0} \right)^{5/2} g_{5/2}(1) \simeq 1.34149 T \left(\frac{T}{T_0} \right)^{3/2}, \quad (4.16)$$

and analogously for the energy density.

Let us now evaluate the specific heat per particle $C = \partial\epsilon/\partial T$. For $T > T_c$ we have

$$\frac{\partial\epsilon}{\partial T} = \frac{15}{4} \left(\frac{T}{T_0} \right)^{3/2} g_{5/2}(\zeta(T)) + \frac{3}{2} T \left(\frac{T}{T_0} \right)^{3/2} g'_{5/2}(\zeta(T)) \zeta'(T). \quad (4.17)$$

We can evaluate the derivative $\zeta'(T)$ by differentiating equation (4.10):

$$\frac{3}{2T} \left(\frac{T}{T_0} \right)^{3/2} g_{3/2}(\zeta(T)) + \left(\frac{T}{T_0} \right)^{3/2} g'_{3/2}(\zeta(T)) \zeta'(T) = 0. \quad (4.18)$$

On the other hand it is easy to see that

$$g'_\alpha(z) = \frac{d}{dz} \sum_{k=1}^{\infty} \frac{z^k}{k^\alpha} = \sum_{k=1}^{\infty} \frac{z^{k-1}}{k^{\alpha-1}} = \frac{1}{z} g_{\alpha-1}(z). \quad (4.19)$$

We obtain therefore

$$\begin{aligned} C(T) &= \frac{\partial\epsilon}{\partial T} = \left(\frac{T}{T_0} \right)^{3/2} \left[\frac{15}{4} g_{5/2}(\zeta(T)) - \frac{9 g_{3/2}^2(\zeta(T))}{4 g_{1/2}(\zeta(T))} \right] \\ &= \left(\frac{T}{T_0} \right)^{3/2} g_{3/2}(\zeta(T)) \left[\frac{15 g_{5/2}(\zeta(T))}{4 g_{3/2}(\zeta(T))} - \frac{9 g_{3/2}(\zeta(T))}{4 g_{1/2}(\zeta(T))} \right] \\ &= \frac{15 g_{5/2}(\zeta(T))}{4 g_{3/2}(\zeta(T))} - \frac{9 g_{3/2}(\zeta(T))}{4 g_{1/2}(\zeta(T))}. \end{aligned} \quad (4.20)$$

In the last equality we have exploited equation (4.10). Since $g_\alpha(z) \simeq z$ for $|z| \ll 1$, we see that $\lim_{T \rightarrow \infty} C(T) = \frac{3}{2}$.

To evaluate the expression on the rhs we can use equation (4.6). However, for $\alpha = 1/2$ and $z \rightarrow 1$ the function $g_\alpha(z)$ diverges, and the integration routine can have problems. One can extract the singularity as follows:

$$\begin{aligned} g_\alpha(z) &= \frac{1}{\Gamma(\alpha)} \int_0^\infty dx x^{\alpha-1} \frac{z e^{-x}}{1 - z e^{-x}} \\ &= \frac{z}{\Gamma(\alpha)} \int_0^\infty dx x^{\alpha-1} e^{-x} \left[\frac{1}{1-z} + \left(\frac{1}{1-z e^{-x}} - \frac{1}{1-z} \right) \right] \\ &= \frac{z}{1-z} \left[1 - \frac{z}{\Gamma(\alpha)} \int_0^\infty dx x^{\alpha-1} e^{-x} \frac{1 - e^{-x}}{1 - z e^{-x}} \right]. \end{aligned} \quad (4.21)$$

The integrand on the rhs vanishes like x^α for $x \rightarrow 0$ (for $z < 1$) and therefore the integral converges.

We have thus obtained a parametric representation of the specific heat of the Bose gas for $T > T_c$. From (4.10) we obtain T as a function of the fugacity z :

$$T(z) = (g_{3/2}(z))^{-2/3}, \quad (4.22)$$

while equation (4.20) yields the specific heat $C = \partial\epsilon/\partial T$ as a function of z . For $T < T_c$, $z \equiv 1$, and therefore one has

$$\epsilon = \frac{3}{2}T \left(\frac{T}{T_0}\right)^{3/2} g_{3/2}(1), \quad (4.23)$$

from which it follows

$$C(T) = \frac{15}{4} \left(\frac{T}{T_0}\right)^{3/2} g_{3/2}(1). \quad (4.24)$$

The resulting graph is shown in figure 4.1: it appears that the derivative of $C(T)$ exhibits a discontinuity at $T = T_c$. Evaluation of the discontinuity requires further mathematical analysis (see, e.g., Wang [2004].)

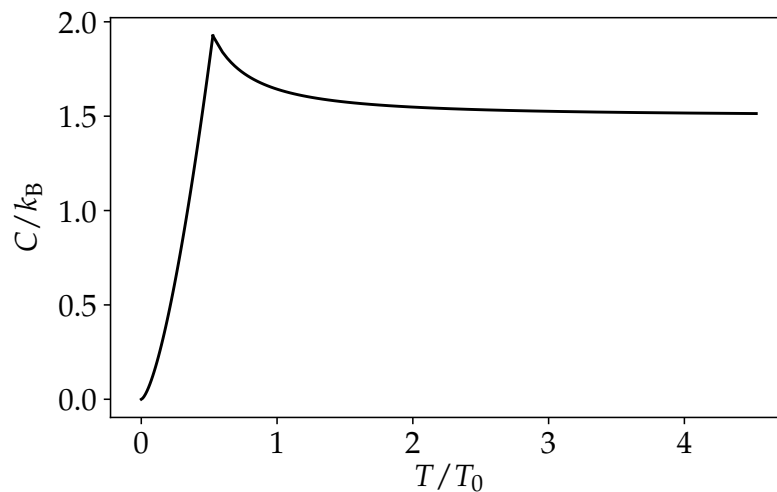


Figure 4.1: Specific heat per particle $C(T)$ of an ideal Bose gas. Temperatures are shown in units of T_0 (see eq. (4.7)), and the specific heat in units of k_B . The derivative of $C(T)$ exhibits a discontinuity for $T = T_c = 0.527201 T_0$.

Solution to exercise 4.3 (A Simplified Model of Hemoglobin) The grand canonical

partition function of the system reads

$$Z_N(x, y) = \zeta^{N/4}(x, y), \quad (4.25)$$

where

$$\zeta(x, y) = \sum_{\{\tau\}} e^{[(\epsilon_0 + \mu)\nu + Jk]/k_B T} = \sum_{\{\tau\}} x^{\nu(\{\tau\})} y^{k(\{\tau\})}, \quad (4.26)$$

where $\{\tau\}$ denotes the set of occupation numbers of the four units of a molecule, $\nu = \sum_i \tau_i$ is the total number of adsorbed sites in a molecule and k is the number of occupied pairs of nearest neighbors sites. It is easy to see that we have 1 state with $\nu = k = 0$, 4 states with $\nu = 1, k = 0$, 2 states with $\nu = 2, k = 0$, 4 states with $\nu = 2, k = 1$, 4 states with $\nu = 3, k = 3$ and finally 1 state with $\nu = k = 4$. Thus we have

$$\zeta(x, y) = 1 + 4x + 2x^2 + 4x^2y + 4x^3y^2 + x^4y^4. \quad (4.27)$$

Since

$$\left\langle \sum_{i=1}^4 \tau_i \right\rangle = x \frac{\partial \log \zeta}{\partial x}, \quad (4.28)$$

we have

$$\langle M \rangle = N \langle \tau \rangle = N \frac{x + x^2(1 + 2y) + 3x^3y^2 + x^4y^4}{1 + 4x + 2x^2 + 4x^2y + 4x^3y^2 + x^4y^4}. \quad (4.29)$$

One can use $x_0 = e^{\epsilon_0/k_B T}$ and y as fitting parameters. The fit is shown in figure 4.2. The ratio between the expected value and the observed one is shown in figure 4.3. One sees a systematic underestimate at low pressure.

Solution to exercise 4.4 (Frustrated spins) The system is made up of $N/3$ independent systems of three spins each.

1. Let us consider a system of three interacting spins, e.g., with $\ell = 1$. The state of the system is identified by the triple $(\sigma_1, \sigma_2, \sigma_3) \in \{-1, +1\}^3$. We can classify these states according to the value of $m = \sum_{i=1}^3 \sigma_i$: the different values have a multiplicity g . Each of them has the energy $E(m)$, given by the following table:

m	g	E
-3	1	$3J + 3h$
-1	3	$J + h$
+1	3	$J - h$
+3	1	$3J - 3h$

2. We can thus evaluate the "partition function" $\zeta = \sum_m g_m \exp(-E_m/k_B T)$:

$$\zeta = 2 \left[e^{-3J/k_B T} \cosh(3h/k_B T) + 3e^{-J/k_B T} \cosh(h/k_B T) \right]. \quad (4.30)$$

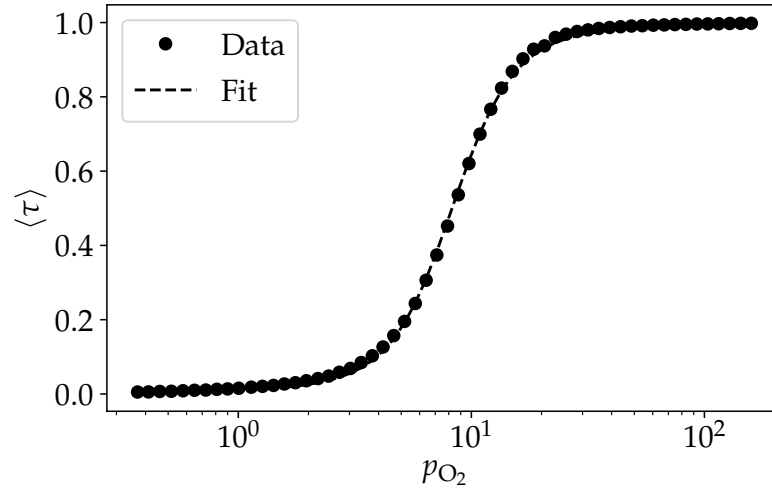


Figure 4.2: Fit of the function $\langle \tau \rangle(p_{O_2})$ with respect to the data from Imai [1990]. The x -axis is logarithmic.

The magnetization per spin m is obtained by evaluating $\partial \log \zeta / \partial (h/k_B T)$:

$$3m = 3 \frac{e^{-3J/k_B T} \sinh(3h/k_B T) + e^{-J/k_B T} \sinh(h/k_B T)}{e^{-3J/k_B T} \cosh(3h/k_B T) + 3e^{-J/k_B T} \cosh(h/k_B T)}, \quad (4.31)$$

and then by dividing this expression by 3. It is easy to see that this quantity exhibits the sigmoidal behavior of $m = \tanh(h/k_B T)$, but with a smaller slope around $h = 0$.

Solution to exercise 4.5 (Particles with variable spin)

1. Each unit can be in one of 4 states: $s = 0$, or $(s = 1, \sigma = -1)$, $(s = 1, \sigma = 0)$, $(s = 1, \sigma = +1)$. Let us denote them by $k \in \{0, 1, 2, 3\}$ and denote the corresponding energy by $\epsilon(k)$. We obtain the following expression for the partition function:

$$Z = \sum_{\{k_i\}} \exp \left[-\beta \sum_i \epsilon(k_i) \right] = \prod_i \sum_{k_i} e^{-\beta \epsilon(k_i)}. \quad (4.32)$$

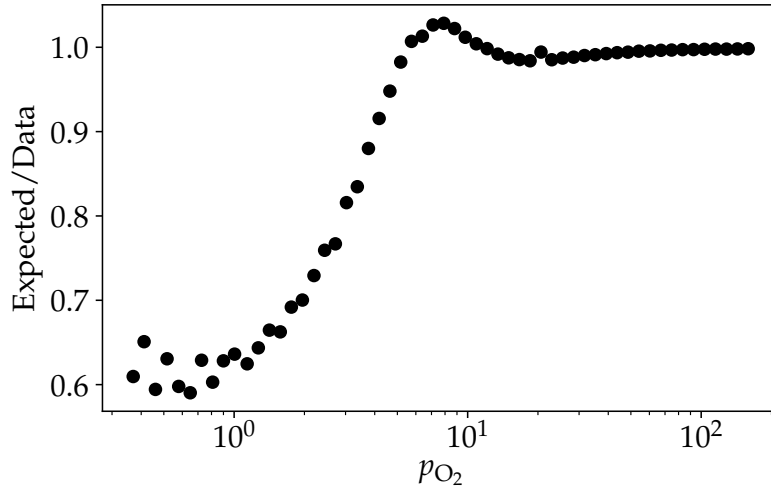


Figure 4.3: Ratio between the expected $\langle \tau \rangle (p_{O_2})$ and the observed one. The x -axis is logarithmic.

We obtain

$$\epsilon(0) = 0; \quad (4.33)$$

$$\epsilon(1) = \epsilon_0 + h; \quad (4.34)$$

$$\epsilon(2) = \epsilon_0; \quad (4.35)$$

$$\epsilon(3) = \epsilon_0 - h. \quad (4.36)$$

Thus

$$Z = \left[1 + e^{-\beta\epsilon_0} (1 + e^{-\beta h} + e^{\beta h}) \right]^N. \quad (4.37)$$

2. We obtain, since $\beta = 1/k_B T$,

$$E = - \left. \frac{\partial \log Z}{\partial \beta} \right)_{\beta h} = \frac{N e^{-\beta\epsilon_0} (1 + e^{-\beta h} + e^{\beta h})}{1 + e^{-\beta\epsilon_0} (1 + e^{-\beta h} + e^{\beta h})}; \quad (4.38)$$

$$M = \left. \frac{\partial \log Z}{\partial \beta h} \right)_{\beta} = \frac{N e^{-\beta\epsilon_0} 2 \sinh \beta h}{1 + e^{-\beta\epsilon_0} (1 + e^{-\beta h} + e^{\beta h})}. \quad (4.39)$$

3. For small values of h we have $\sinh \beta h \simeq \beta h$, so that

$$M \simeq N \chi h, \quad (4.40)$$

where

$$\chi = \frac{2\beta e^{-\beta\epsilon_0}}{1 + 3e^{-\beta\epsilon_0}}. \quad (4.41)$$

4. INTERACTION-FREE SYSTEMS

If $\epsilon_0 > 0$, χ vanishes exponentially for $T \rightarrow 0$, whereas it behaves like $2\beta/3$ if $\epsilon_0 < 0$. For $T \rightarrow \infty$, $\chi \simeq \beta/2$.

Solution to exercise 4.6 (Einstein condensation of zero-mass particles)

1. *Grand canonical partition function.* The allowed values of the wave vector k are given by

$$\mathbf{k} = \frac{2\pi}{L} (n_1, \dots, n_d), \quad (4.42)$$

where the n_i are integers. The corresponding single-particle energy is given by

$$\epsilon_k = ck = \frac{2\pi c}{L} \sqrt{\sum_{k=1}^d n_k^2}. \quad (4.43)$$

Given the chemical potential μ , we have

$$\log Z_{GC} = - \sum_{\mathbf{k}} \log \left[1 - e^{-(\epsilon_k - \mu)/k_B T} \right], \quad (4.44)$$

where the sum runs over the values allowed by eq. (4.42).

2. *Average number N of particles.* We have

$$N = \left. \frac{\partial \log Z_{GC}}{\partial (\mu/k_B T)} \right|_{V, 1/k_B T} = \sum_{\mathbf{k}} \frac{1}{e^{(\epsilon_k - \mu)/k_B T} - 1}. \quad (4.45)$$

For large volumes, this expression can be approximated by

$$N = L^d \int_0^\infty dk \frac{S_d}{(2\pi)^d} k^{d-1} \frac{1}{e^{(ck - \mu)/k_B T} - 1}, \quad (4.46)$$

where S_d is the area of the unit sphere in d dimensions.

3. *Critical value N_c .* The largest value of N corresponds to $\mu = 0$, i.e.,

$$N_c = \left(\frac{k_B T L}{2\pi c} \right)^d \int_0^\infty dx S_d x^{d-1} \frac{1}{e^x - 1}. \quad (4.47)$$

The integral on the rhs converges only for $d > 1$. Thus Einstein's condensation does not take place for $d = 1$.

Solution to exercise 4.7 (Einstein condensation in a harmonic potential)

1. *Grand canonical partition function.* The single-particle energy states are identified by a d -dimensional array of non-negative integers $\mathbf{k} = (k_1, \dots, k_d)$ and are given by

$$\epsilon_{\mathbf{k}} = \hbar\omega_0 \left(\sum_{i=1}^d k_i + \frac{d}{2} \right). \quad (4.48)$$

Thus the grand canonical partition function at temperature T and chemical potential μ is given by

$$\log Z = - \sum_{\mathbf{k}} \log \left[1 - e^{-(\epsilon_{\mathbf{k}} - \mu)/k_B T} \right]. \quad (4.49)$$

This sum can be rearranged introducing n such that $\sum_{i=1}^d k_i = n$:

$$N' = \sum'_{\mathbf{k}} \frac{1}{e^{\epsilon_{\mathbf{k}}/k_B T}/z - 1} = \sum_{n=1}^{\infty} \frac{\mathcal{N}_d(n)}{e^{\epsilon_{\mathbf{k}}/k_B T}/z - 1}, \quad (4.50)$$

where $\mathcal{N}_d(n)$ is the number of d -dimensional arrays with integer non-negative entries such that the sum of the entries has a fixed value n :

$$\mathcal{N}_d(n) = \sum_{k_1, \dots, k_d} \delta_{\sum_i k_i, n}. \quad (4.51)$$

To evaluate this number, let us define the generating function

$$\Gamma_d(z) = \sum_{n=0}^{\infty} z^n \mathcal{N}_d(n). \quad (4.52)$$

We have

$$\Gamma_d(z) = \sum_{n=0}^{\infty} \sum_{k_1, \dots, k_d} \delta_{\sum_i k_i, n} z^n = \left(\sum_{n=0}^{\infty} z^n \right)^d = \frac{1}{(1-z)^d}. \quad (4.53)$$

By Newton's theorem we have therefore

$$\mathcal{N}_d(n) = (-1)^d \binom{-d}{n} = \frac{d(d+1) \cdots (d+n-1)}{n!}. \quad (4.54)$$

Thus $\mathcal{N}_d(n)$ is a polynomial in n of degree $d-1$. We have in particular

$$\mathcal{N}_2(n) = n+1; \quad (4.55)$$

$$\mathcal{N}_3(n) = \frac{n(n+1)}{2}. \quad (4.56)$$

Thus we obtain

$$\log Z = - \sum_{n=0}^{\infty} \mathcal{N}_d(n) \log(1 - ze^{-\kappa n}) \quad (4.57)$$

where we have introduced the fugacity

$$z = e^{-(\mu_0 - \mu)/k_B T}, \quad (4.58)$$

and the shorthand

$$\kappa = \frac{\hbar\omega_0}{k_B T}. \quad (4.59)$$

2. *Number of particles in the excited states.* The average number of particles is given by

$$N = \sum_{n=0}^{\infty} \frac{\mathcal{N}_d(n)}{e^{\kappa n}/z - 1}. \quad (4.60)$$

As $\mu \rightarrow \mu_0$, we have $z \rightarrow 1$ and the term corresponding to $n = 0$ in the sum (4.60) diverges. Let us thus separate this term from the others:

$$N = \frac{z}{1-z} + \sum_{n=1}^{\infty} \frac{\mathcal{N}_d(n)}{e^{\kappa n}/z - 1}. \quad (4.61)$$

The number of particles in the excited states is given by

$$N' = \sum_{n=1}^{\infty} \frac{\mathcal{N}_d(n)}{e^{\kappa n}/z - 1}. \quad (4.62)$$

We evaluate this sum by introducing $n = \sum_{i=1}^d k_i$. Thus we obtain

$$N' = \sum_{n=1}^{\infty} \frac{\mathcal{N}_d(n)}{e^{\kappa n}/z - 1}. \quad (4.63)$$

To evaluate this sum, we take advantage of the Euler-MacLaurin summation formula

$$\begin{aligned} \sum_{i=m}^n f(i) &= \int_m^n dx f(x) + \frac{1}{2} [f(n) + f(m)] \\ &\quad + \sum_{k=1}^p \frac{B_{2k}}{(2k)!} [f^{(2k-1)}(n) - f^{(2k-1)}(m)] + R \\ &= \int_m^n dx f(x) + \frac{1}{2} [f(n) + f(m)] + \frac{1}{12} [f'(n) - f'(m)] + \dots, \end{aligned} \quad (4.64)$$

where B_p are the Bernoulli numbers, R is an error term, and $f^{(p)}(x)$ denotes the p -th derivative of x . However, the use of this expression is made awkward

by the fact that the sum starts with $n = 1$ rather than $n = 0$. Setting $n = p + 1$ we have a more convenient expression:

$$N' = \sum_{p=0}^{\infty} \frac{\mathcal{N}_d(p+1)}{e^{\kappa p}/z' - 1}, \quad (4.65)$$

where

$$z' = ze^{-\kappa}. \quad (4.66)$$

Let us evaluate the integral:

$$I_k(z') = \int_0^{\infty} dx \frac{x^k}{e^{\kappa x}/z' - 1}. \quad (4.67)$$

We have

$$\begin{aligned} I_k(z') &= \int_0^{\infty} dx x^k \sum_{\ell=1}^{\infty} z'^{\ell} e^{-\kappa \ell x} \\ &= \sum_{\ell=1}^{\infty} (\kappa \ell)^{-(k+1)} z'^{\ell} \int_0^{\infty} dx x^k e^{-x} = \Gamma(k+1) \kappa^{-(k+1)} \sum_{\ell=1}^{\infty} \frac{z'^{\ell}}{\ell^{k+1}} \\ &= \Gamma(k+1) \kappa^{-(k+1)} g_{k+1}(z'), \end{aligned} \quad (4.68)$$

where

$$g_k(z) = \sum_{\ell=1}^{\infty} \frac{z^{\ell}}{\ell^k} \quad (4.69)$$

is the polylog function.

We obtain therefore

$$N' \simeq \begin{cases} \kappa^{-2} g_2(z') + 2\kappa^{-1} g_1(z'), & \text{for } d = 2; \\ \kappa^{-3} g_3(z') + \frac{3}{2} \kappa^{-2} g_2(z') + \kappa^{-1} g_1(z'), & \text{for } d = 3. \end{cases} \quad (4.70)$$

3. *Thermodynamic limit.* Let us parametrize the harmonic potential via an energy parameter u_0 and a length parameter R_0 :

$$m\omega_0^2 = \frac{u_0}{R_0^2}, \quad (4.71)$$

thus

$$\omega_0 = \sqrt{\frac{u_0}{m}} \frac{1}{R_0}. \quad (4.72)$$

We define the thermodynamic limit as $N \rightarrow \infty$, $\omega_0 \rightarrow 0$, with $\rho = N/R_0^d = \text{const}$. Thus we have

$$\omega_0 = \sqrt{\frac{u_0}{m}} \left(\frac{\rho}{N} \right)^{1/d}, \quad (4.73)$$

and

$$\kappa = \frac{\hbar\omega_0}{k_B T} = \frac{\hbar}{k_B T} \sqrt{\frac{u_0}{m}} \left(\frac{\rho}{N}\right)^{1/d} = \frac{T_0}{T} N^{-1/d}, \quad (4.74)$$

where T_0 is defined by

$$T_0 = \frac{\hbar}{k_B} \sqrt{\frac{u_0}{m}} \rho^{1/d}. \quad (4.75)$$

Thus we have

$$N' \simeq \begin{cases} N \left(\frac{T}{T_0}\right)^2 g_2(z') + 2\sqrt{N} \frac{T}{T_0} g_1(z'), & \text{for } d = 2; \\ N \left(\frac{T}{T_0}\right)^3 g_3(z') + \frac{3}{2} N^{2/3} \left(\frac{T}{T_0}\right)^2 g_2(z') + N^{1/3} \left(\frac{T}{T_0}\right) \kappa^{-1} g_1(z'), & \text{for } d = 3. \end{cases} \quad (4.76)$$

Only the first term of both expansions dominates in the thermodynamic limit.

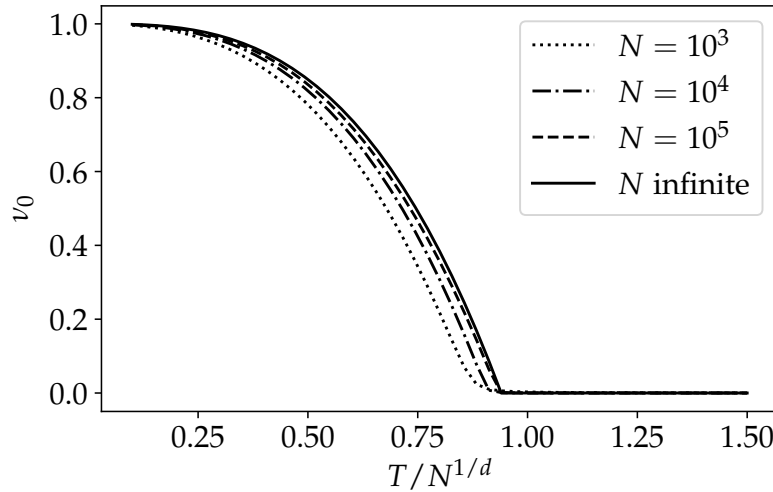


Figure 4.4: Condensate fraction of the Bose gas in a harmonic potential vs. $T/N^{1/d}$, for $d = 3$ and different values of N . The broken line corresponds to the thermodynamic limit expression $\nu_0 = 1 - (T/T_c)^d$.

One can also check that the remaining terms of the expansion in the Euler-MacLaurin formula are negligible. In this limit, the maximum value of z' equals 1. Thus N' cannot exceed

$$N'_{\max} = \begin{cases} N \left(\frac{T}{T_0}\right)^2 g_2(1) = N \left(\frac{T}{T_0}\right)^2 \frac{\pi^2}{6}, & \text{for } d = 2; \\ N \left(\frac{T}{T_0}\right)^3 \zeta_R(3), & \text{for } d = 3. \end{cases} \quad (4.77)$$

Here $\zeta_R(z)$ is Riemann's zeta function. Thus we find the transition temperature:

$$T_c = T_0 \cdot \begin{cases} \sqrt{6}/\pi = 0.7797, & \text{for } d = 2; \\ \sqrt[3]{1/\zeta_R(3)} = 0.9405, & \text{for } d = 3. \end{cases} \quad (4.78)$$

One may also check that there is no transition for $d = 1$. Note that $g_1(z)$

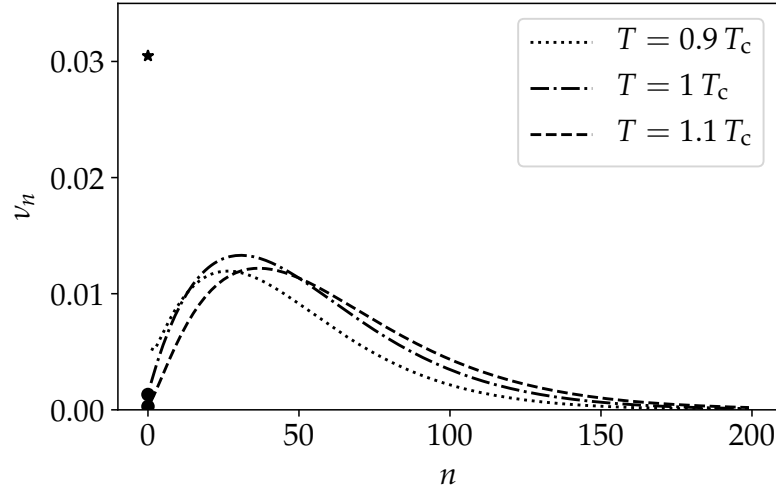


Figure 4.5: Occupation fractions v_n of levels of energy $\hbar\omega_0(n + d/2)$ vs. n for $d = 3$, $N = 10000$ and different values of the temperature. The fraction v_0 is marked by a symbol: point above and star below the condensation point.

diverges for $z \rightarrow 1$, and that therefore it is necessary to go *first* to the thermodynamic limit, and then to lower the temperature, in order to exhibit the transition (see, e.g., Mullin [1997]).

The behavior of the condensate fraction vs. $T/N^{1/d}$ for $d = 3$ is shown in figure 4.4. The fraction of particles occupying an energy level with quantum number n as a function of n , for different values of T , is shown in figure 4.5. The occupation number of the ground state is marked with a symbol. Figure 4.6 shows the fraction of particles in the condensate for $d = 2$.

Solution to exercise 4.8 (Neutrino density in the universe)

1. Since the number of neutrinos in a region of volume V is not fixed, the chemical potential vanishes. Thus the fermi factor reads

$$f(\epsilon) = \frac{1}{e^{\epsilon/k_B T} + 1}. \quad (4.79)$$

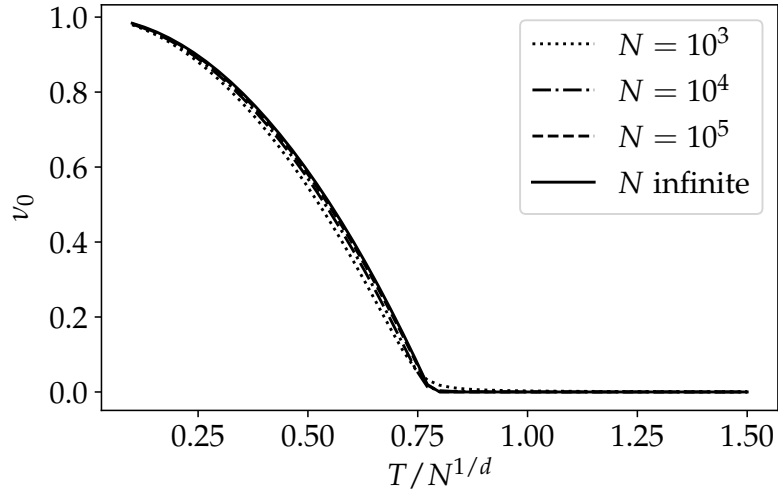


Figure 4.6: Condensate fraction of the Bose gas in a harmonic potential vs. $T/N^{1/d}$, for $d = 2$ and different values of N . The broken line corresponds to the thermodynamic limit expression $v_0 = 1 - (T/T_c)^d$. Notice that to evaluate numerically the condensate fraction the sum in Eq. (4.63) must be extended to substantially larger values of n than for $d = 3$.

The density of states of neutrinos with momentum p , taking into account the fact that there is only one state for each value of p , is given by

$$D(p) dp = \frac{V}{h^3} 4\pi p^2 dp, \quad (4.80)$$

and therefore the density of states of energy $\epsilon = cp$ reads

$$D(\epsilon) d\epsilon = \frac{V}{h^3 c^3} 4\pi \epsilon^2 d\epsilon. \quad (4.81)$$

Thus the average number of neutrinos contained in the region of volume V at the temperature T is given by

$$\begin{aligned} \langle N \rangle &= \int_0^\infty d\epsilon f(\epsilon) D(\epsilon) = \frac{4\pi V}{h^3 c^3} \int_0^\infty d\epsilon \frac{\epsilon^2}{e^{\epsilon/k_B T} + 1} \\ &= \frac{4\pi V}{h^3 c^3} (k_B T)^3 \int_0^\infty \frac{x^2 dx}{e^x + 1}. \end{aligned} \quad (4.82)$$

Substituting the numerical values, one obtains for $T = 2.7$ K,

$$\frac{\langle N \rangle}{V} = 7.6 \cdot 10^6 T^3 \text{ m}^{-3} \simeq 150 \cdot 10^6 \text{ m}^{-3}. \quad (4.83)$$

2. The average energy is given by

$$\begin{aligned}\langle E \rangle &= \int_0^\infty d\epsilon f(\epsilon) \epsilon D(\epsilon) = \frac{4\pi V}{h^3 c^3} \int_0^\infty d\epsilon \frac{\epsilon^3}{e^{\epsilon/k_B T} + 1} \\ &= \frac{4\pi V}{h^3 c^3} (k_B T)^4 \int_0^\infty \frac{x^4 dx}{e^x + 1} = \frac{V}{h^3 c^3} (k_B T)^4 \frac{7\pi^5}{30}.\end{aligned}\quad (4.84)$$

One sees that the contribution of neutrinos to the energy of the black body radiation is equal to 7/16 of that of the photons. This contribution should be multiplied by the number of different neutrino flavors. Numerically one has

$$\frac{\langle E \rangle}{V} = 3.3 \cdot 10^{-10} T^4 \text{ Jm}^{-3} = 1.8 \cdot 10^{-14} \text{ Jm}^{-3}.\quad (4.85)$$

3. The energy spectrum is given by (cf. fig.4.7)

$$u(\epsilon) = \frac{1}{V} \epsilon f(\epsilon) D(\epsilon) = \frac{4\pi}{h^3 c^3} \frac{\epsilon^3}{e^{\epsilon/k_B T} + 1}.\quad (4.86)$$

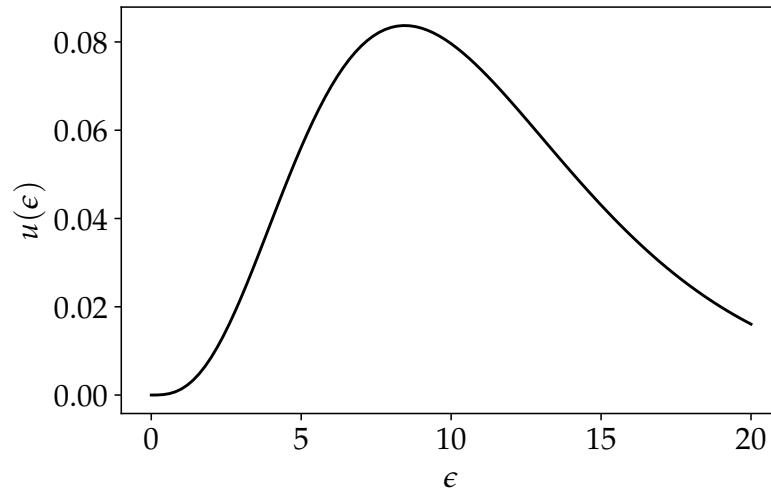


Figure 4.7: Energy spectrum for neutrinos in the background radiation. Energies are measured in units of $k_B T$. The integral of the density is normalized to one.

Solution to exercise 4.9 (Fermions in two dimensions)

1. Since there are, for each acceptable value of k , two spin states, we obtain

$$\begin{aligned} D(\epsilon) &= 2 \frac{L^2}{(2\pi)^2} \int d^2k \delta\left(\epsilon - \frac{\hbar^2 k^2}{2m}\right) = 4\pi \frac{L^2}{(2\pi)^2} \int_0^\infty k dk \delta\left(\epsilon - \frac{\hbar^2 k^2}{2m}\right) \\ &= L^2 \frac{4\pi m}{\hbar^2} \int_0^\infty dx \delta(\epsilon - x) = \theta(\epsilon) \frac{4\pi m L^2}{\hbar^2}. \end{aligned} \quad (4.87)$$

2. From the condition

$$N = \int_0^{\epsilon_F} d\epsilon D(\epsilon) = \frac{4\pi m L^2}{\hbar^2} \epsilon_F, \quad (4.88)$$

we obtain

$$\epsilon_F = \frac{\hbar^2}{4\pi m} \rho, \quad (4.89)$$

with $\rho = N/L^2$.

3. From the relation $p = \langle E \rangle / L^2$, since at $T = 0$ we have

$$\langle E \rangle = \int_0^{\epsilon_F} d\epsilon \epsilon D(\epsilon) = \frac{\hbar^2}{8\pi m} \frac{N^2}{L^2}, \quad (4.90)$$

we obtain

$$p = \frac{\hbar^2}{8\pi m} \rho^2. \quad (4.91)$$

4. The equation fixing the chemical potential μ is

$$N = \int_0^\infty d\epsilon \frac{D(\epsilon)}{e^{(\epsilon-\mu)/k_B T} + 1}, \quad (4.92)$$

where $D(\epsilon) = D$ is a constant in $d = 2$. Thus we can write

$$\begin{aligned} \mathcal{N}(\mu, T) &= \int_0^\infty d\epsilon \frac{D(\epsilon)}{e^{(\epsilon-\mu)/k_B T} + 1} \\ &= D k_B T \int_0^\infty d\epsilon \frac{d}{d\epsilon} \log\left(1 + e^{-(\epsilon-\mu)/k_B T}\right) \\ &= D k_B T \log\left(1 + e^{\mu/k_B T}\right) \\ &= D\mu + D k_B T \log\left(1 + e^{-\mu/k_B T}\right). \end{aligned} \quad (4.93)$$

Since we have $N = D \epsilon_F$ we obtain for $T \rightarrow 0$

$$\mu \simeq \epsilon_F - k_B T e^{-\epsilon_F/k_B T}. \quad (4.94)$$

Phase Transitions

Solution to exercise 5.1 Let us denote by σ_0 the central spin, and assume that the spins on the boundary of the system (a cube of side L) are set to $+$. We wish to evaluate $p_+ = \text{Prob}(\sigma_0 = +1)$. Let us consider a state $(-)$ in which $\sigma_0 = -1$. We can associate to it a state $(+)$ in which $\sigma_0 = +1$ by reversing all spins in the innermost island of -1 spins containing σ_0 . The energy of the corresponding $(+)$ state is smaller than that of $(-)$ by an amount $2JS$, where S is the surface of the boundary (measured in units of the elementary cell). However, there are many $(-)$ states which map onto the same $(+)$ state. Fixing the size S of the boundary, i.e., the number of plaquettes that make it up, we have

$$\mathcal{N}_S < 3^S \cdot \text{power of } S, \quad (5.1)$$

because each plaquette of the surface added at a side of an existing plaquette has at most three possible directions. This is analogous to what happen in two dimensions, and the rest of the Peierls' argument is straightforward.

Solution to exercise 5.2 Let us consider the one-dimensional Ising model with free boundary conditions, defined by the Hamiltonian $H = -\sum_{i=1}^{N-1} J\sigma_i\sigma_{i+1}$. With the change of variables

$$\sigma'_i = \sigma_i\sigma_{i+1}, \quad 1 \leq i < N, \quad (5.2)$$

the Hamiltonian can be rewritten as

$$H(\sigma') = -\sum_{i=1}^{N-1} J\sigma'_i. \quad (5.3)$$

Thus the partition function Z is given by

$$Z = \sum_{\sigma'} e^{-H(\sigma')/k_B T} = [2 \cosh K]^{N-1}, \quad (5.4)$$

where $K = J/k_B T$. In the same way, we obtain, assuming $1 \leq i < j \leq N$,

$$\begin{aligned} C_{ij} &= \frac{1}{Z} \sum_{\sigma} e^{-H(\sigma)/k_B T} \sigma_i \sigma_j = \frac{1}{Z} \frac{1}{Z} \sum_{\sigma'} \prod_{\ell=1}^{i-1} e^{K\sigma'_\ell} \prod_{m=i}^{j-1} \sigma'_m e^{K\sigma'_m} \prod_{n=j}^{N-1} e^{K\sigma'_n} \\ &= \frac{1}{Z} [2 \sinh K]^{|i-j|} [2 \cosh K]^{N-1-|i-j|}. \end{aligned} \quad (5.5)$$

We obtain therefore

$$C_{ij} = [\tanh K]^{|i-j|}. \quad (5.6)$$

Solution to exercise 5.3 Let us consider periodic boundary conditions. Then the partition function

$$Z = \sum_{\sigma_1, \dots, \sigma_N} \prod_{i=1}^N e^{K\sigma_i \sigma_{i+1} + \lambda \sigma_i}, \quad (5.7)$$

where $K = J/k_B T$ and $\lambda = h/k_B T$, and $\sigma_{N+1} = \sigma_1$, can be written in the form

$$Z = \text{Tr } \mathbb{T}^N, \quad (5.8)$$

where

$$\mathbb{T} = \left(e^{K\sigma\sigma' + (\lambda/2)(\sigma + \sigma')} \right) = \begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix}, \quad (5.9)$$

is the transfer matrix. This form is preferred because it is symmetrical. The eigenvalues of \mathbb{T} are given by

$$\tau_{\pm} = e^K \cosh \lambda \pm \sqrt{e^{2K} \sinh^2 \lambda + e^{-2K}}. \quad (5.10)$$

We have $Z = \tau_+^N + \tau_-^N$ that can be approximated by τ_+^N for large N , since τ_+ is the largest eigenvalue. Thus we obtain

$$f = \log \tau_+ = \log \left[e^K \cosh \lambda + \sqrt{e^{2K} \sinh^2 \lambda + e^{-2K}} \right]. \quad (5.11)$$

Solution to exercise 5.4

1. Let us set $\sigma_0 = +1$, and leave σ_N free. A configuration can have n intervals, with $1 \leq n \leq N$, to which correspond $n - 1$ boundaries. Odd-numbered intervals correspond to stretches of positive spins, while even-numbered ones to stretches of negative spins. Thus a configuration with n intervals of lengths (ℓ_1, \dots, ℓ_n) , where $\sum_{i=1}^n \ell_i = N$, has the weight

$$W^{(n)}(\ell_1, \dots, \ell_n) = e^{NK} x^{n-1} y^{(\sum_{i \text{ odd}} \ell_i - \sum_{i \text{ even}} \ell_i)}, \quad (5.12)$$

where we have defined

$$x = e^{-2K}; \quad (5.13)$$

$$y = e^\lambda. \quad (5.14)$$

(We use the notations $K = J/k_B T$ and $\lambda = h/k_B T$.) Thus the partition function has the expression

$$Z_N = e^{NK} \sum_{n=1}^N x^{n-1} \sum_{\ell_1, \dots, \ell_n} \delta_{N, \sum_i \ell_i} y^{(\sum_{i \text{ odd}} \ell_i - \sum_{i \text{ even}} \ell_i)}. \quad (5.15)$$

2. We can get rid of the constraint $\sum_{i=1}^n \ell_i = N$ by switching to a grand canonical ensemble characterized by a fugacity z in which we reabsorb the factor e^K . Thus we set

$$Z(z) = \sum_{N=0}^{\infty} (z e^{-K})^N Z_N = \sum_{n=1}^{\infty} x^{n-1} \sum_{\ell_1, \dots, \ell_n} y^{(\sum_{i \text{ odd}} \ell_i - \sum_{i \text{ even}} \ell_i)} z^{\sum_i \ell_i}. \quad (5.16)$$

3. We can rearrange this sum as follows. Let us focus on a configuration with an odd number of intervals. From this we can obtain a configuration with an even number of intervals adding a boundary and a stretch of negative spins. Thus we have

$$\begin{aligned} Z(z) &= Z_{\text{odd}}(z) \left(1 + x \sum_{\ell=1}^{\infty} \left(\frac{z}{y} \right)^\ell \right) \\ &= Z_{\text{odd}}(z) \left(1 + x \frac{z/y}{1 - z/y} \right) = Z_{\text{odd}}(z) R(z). \end{aligned} \quad (5.17)$$

On the other hand, we can go from one “odd” configuration to the next by adding a successive pair of intervals. Summing over all lengths of the intervals this yields a contribution

$$Q(z) = x^2 \sum_{\ell_1=1}^{\infty} (zy)^{\ell_1} \sum_{\ell_2=1}^{\infty} \left(\frac{z}{y} \right)^{\ell_2} = \frac{x^2 z^2}{(1 - zy)(1 - z/y)}. \quad (5.18)$$

The initial stretch of positive spins yields

$$P(z) = \sum_{\ell=1}^{\infty} (zy)^{\ell} = \frac{zy}{1-zy}. \quad (5.19)$$

Thus the partition function reads

$$Z(z) = P(z) \left(\sum_{n=0}^{\infty} Q^n(z) \right) R(z) = \frac{P(z) R(z)}{1-Q(z)}. \quad (5.20)$$

4. Since

$$\langle N \rangle = z \frac{\partial \log Z}{\partial z} = z \left[\frac{P'(z)}{P(z)} + \frac{R'(z)}{R(z)} + \frac{Q'(z)}{1-Q(z)} \right], \quad (5.21)$$

the limit $N \rightarrow \infty$ requires that z tends to a singular point of at least one of the terms in the bracket. We shall see that the nearest singularity to the origin lies at the point z^* which satisfies

$$Q(z^*) = 1. \quad (5.22)$$

This equation reads

$$\left(1 - x^2\right) z^2 - \left(y + \frac{1}{y}\right) z + 1 = 0, \quad (5.23)$$

and its smaller solution (for positive x and y) reads

$$z^* = \left[\frac{1}{2} \left(y + \frac{1}{y}\right) + \sqrt{\frac{1}{4} \left(y - \frac{1}{y}\right)^2 + x^2} \right]^{-1}. \quad (5.24)$$

One can check that $P(z^*)$ and $R(z^*)$ are both finite.

5. Since $Z(z) = \sum_N z^N Z_N$, by a saddle point integration we obtain $Z(z) \sim e^{N(z)[f_{N(z)} + \log z]}$. It is easy to see that $\lim_{z \rightarrow z^*} \log Z(z) / N(z) = 0$. Thus $\lim_{z \rightarrow z^*} f_{N(z)} = \lim_{N \rightarrow \infty} f_N = -\log z^*$. Substituting for x and y their values, and remembering that we had rescaled z by e^K we recover equation (5.11).

This argument is admittedly quite clumsy for solving the one-dimensional Ising model, but it has the advantage of being more easily generalized to different models, like those describing DNA denaturation (see, e.g., Poland and Scheraga [1966]).

Solution to exercise 5.5 (The Chinese philosophers' problem) The problem can be tackled in the following way.

-
1. Let us denote by $i \in \{1, \dots, N\}$ the philosopher, and by $\sigma_i = \pm 1$ his state. If $\sigma_i = +1$, then necessarily $\sigma_{i-1} = \sigma_{i+1} = -1$ (with periodic boundary conditions: $\sigma_{i+N} = \sigma_i$). Thus one cannot have two nearest neighboring philosophers in the state $\sigma = +1$.
 2. For $N = 2$ we have the three states $(-1, -1)$, $(-1, +1)$, $(+1, -1)$. For $N = 3$ we have the states $\sigma_i = 0, \forall i; \sigma_{i_0} = +1, \sigma_i = -1 (i \neq i_0)$, for $i_0 \in \{1, 2, 3\}$, and thus $\mathcal{N}_3 = 4$. For $N = 4$ we have $\sigma_i = -1, \forall i$ (one state); $\sigma_{i_0} = +1, \sigma_i = -1 (i \neq i_0)$ (4 states), $\sigma_{i_0} = \sigma_{i_0+2} = +1, \sigma_i = -1 (i \neq i_0, i_0 + 2)$ (2 states) for a total of 7. For $N = 5$ we easily see that we have 1 state with no eating philosopher; 5 states with 1 eating philosopher, and 5 states with two eating philosophers, for a total of 11 states.
 3. Check:

N	\mathcal{N}_{N-2}	\mathcal{N}_{N-1}	\mathcal{N}_N
4	3	4	$7 = 3 + 4$
5	4	7	$11 = 4 + 7$

4. The relation

$$\mathcal{N}_N = \mathcal{N}(+1) + \mathcal{N}(-1) \quad (5.25)$$

is evident. Now, it is always possible to add a $(N + 1)$ -th spin -1 to a configuration of N spins. However this does not imply that $\mathcal{N}_{N+1}(-1) = \mathcal{N}_N$, since there are additional configurations: those in which the $(N + 1)$ -th spin disjoins two $+1$ spins. Letting these two spins coincide, we see that these configurations amount to $\mathcal{N}_{N-1}(+1)$. We obtain therefore

$$\mathcal{N}_{N+1}(-1) = \mathcal{N}_N + \mathcal{N}_{N-1}(+1). \quad (5.26)$$

On the other hand, we can only add a $+1$ spin if its neighbors are in the -1 state. Letting these two spins coincide, we see that

$$\mathcal{N}_{N+1}(+1) = \mathcal{N}_{N-1}(-1). \quad (5.27)$$

We obtain therefore

$$\mathcal{N}_{N+1} = \mathcal{N}_N + \mathcal{N}_{N-1}. \quad (5.28)$$

5. Let us consider the contribution to the energy of an Ising model with given values of J and h of a pair of neighboring spins (σ, σ') . We have

$$\Delta H(\sigma, \sigma') = -J\sigma\sigma' - \frac{h}{2}(\sigma + \sigma'). \quad (5.29)$$

We obtain the following table:

σ/σ'	+1	-1
+1	$-J - h$	J
-1	J	$-J + h$

Letting $J = -1$ and $h = -2$ we obtain

$$\frac{\sigma/\sigma'}{\begin{array}{c|cc} +1 & +1 & -1 \\ \hline +1 & 3 & -1 \\ -1 & -1 & -1 \end{array}}.$$

We see that in these conditions all states, except $(+) = (+1, +1)$ have the same energy value, and that of $(+)$ is larger. It is thus enough to evaluate the number of minimal-energy states for this Hamiltonian. The corresponding energy is of course $E_0(N) = -N$.

6. In the $\beta \rightarrow \infty$ limit the partition sum is dominated by the minimal-energy states, each of which contributes with the Boltzmann factor $e^{-\beta E_0(N)}$. We thus obtain the result.
7. We have

$$\begin{aligned} \lambda_{\pm} &= e^{\beta J} \cosh(\beta h) \pm \sqrt{e^{2\beta J} \sinh^2(\beta h) + e^{-2\beta J}} \\ &= e^{-\beta} \cosh(2\beta) \pm \sqrt{e^{-2\beta} \sinh^2(2\beta) + e^{2\beta}}. \end{aligned} \quad (5.30)$$

For $\beta \rightarrow \infty$ one has

$$\lambda_{\pm} \rightarrow e^{\beta} \frac{1 \pm \sqrt{5}}{2} = e^{\beta} \lambda_{\pm}^0. \quad (5.31)$$

An explicit calculation shows that in this limit

$$p_N = \lim_{\beta \rightarrow \infty} e^{\beta E_0(N)} (\lambda_+^N + \lambda_-^N) = (\lambda_+^0)^N + (\lambda_-^0)^N \quad (5.32)$$

reproduces the results we had obtained. It is also possible to obtain this result analytically.

Notice that the recursion relation (5.28) is the one that defines the Fibonacci numbers. However, the initial condition $\mathcal{N}_0 = 2$ and $\mathcal{N}_1 = 1$ (that can be evaluated from the results for $N = 2$ and 3 by inverting the recursion) is different from that of Fibonacci ($\mathcal{N}_0 = 0$ and $\mathcal{N}_1 = 1$) and the resulting sequence is called the Lucas numbers.

Solution to exercise 5.6 Let us consider a system of N spins with free boundary conditions, in the lowest-energy state with magnetization $M = N$. From this we can obtain a state with magnetization $M = N - 2L$ by reversing, say, the first L spins. The change in energy is given by

$$\Delta E = \sum_{i=L+1}^N \sum_{j=1}^L \frac{2J}{|i-j|^a}. \quad (5.33)$$

If $1 < a < 2$ this quantity increases faster than $\log N$ when $L \sim N$. Thus, in this case, the energy cost is not offset by the entropy gain. This allows for long-range order at finite temperature. The case $a = 2$ is especially interesting, see, e.g., Thouless [1969].

Solution to exercise 5.7 (Duality in the Three-Dimensional Ising Model) Let us consider a 3- d Ising model in a cube with (+) boundary conditions: all the spins at the boundary are kept “up”. Then each spin configuration is identified by the configurations of the boundaries between “up” and “down” spins. These boundaries form closed non-intersecting surfaces, made of plaquettes of the dual lattice. The weight of a configuration divided by $e^{-E_0/k_B T}$, where E_0 is the ground-state energy, is given by $e^{-2\mathcal{N}K}$ where $K = J/k_B T$ and \mathcal{N} is the number of plaquettes in the boundaries that correspond to the configuration. Thus we have the following expression of the partition function:

$$Z = e^{-E_0/k_B T} \sum_{\mathcal{C}} e^{-2\mathcal{N}(\mathcal{C})K}, \quad (5.34)$$

where the sum runs over all configurations \mathcal{C} of closed non-intersecting surfaces, and $\mathcal{N}(\mathcal{C})$ is the corresponding plaquette number.

Now let us consider the high-temperature expansion of the model defined by the Hamiltonian

$$\mathcal{H} = -J' \sum_{\mathcal{P}} \prod_{i \in \mathcal{P}} \sigma_i, \quad (5.35)$$

where the sum runs over all the plaquettes \mathcal{P} of dual lattice’s four nearest-neighbor pairs of spin. The partition function reads

$$Z' = \sum_{\sigma} \exp \left[K' \sum_{\mathcal{P}} \prod_{i \in \mathcal{P}} \sigma_i \right] = (2 \cosh K')^{N_{\mathcal{P}}} \sum_{\sigma} \prod_{\mathcal{P}} \left(1 + \tanh K' \prod_{i \in \mathcal{P}} \sigma_i \right), \quad (5.36)$$

where $K' = J'/k_B T$ and $N_{\mathcal{P}}$ is the total number of plaquettes. We can expand the product on the rhs and perform the sum on all spin configurations. By analogy with the two-dimensional model it is easy to see that the only terms which survive the sum are identified by configurations of closed non-intersecting surfaces, each of them contributing a weight $(\tanh K')^{N_{\mathcal{P}}}$. Thus, apart from the explicit configuration-independent factors, the two partition functions correspond where

$$e^{-2K} = \tanh K'. \quad (5.37)$$

This is an interesting duality which maps the Ising model into a Z_2 gauge model.

Solution to exercise 5.8 (Phase coexistence) We evaluate the partition function as follows.

1. We have

$$N = z \frac{\partial \log Z_{GC}}{\partial z} = V \frac{z}{1+z} + \alpha V \frac{z^{\alpha V}}{1+z^{\alpha V}}. \quad (5.38)$$

In the thermodynamic limit, the second term vanishes if $z < 1$, whereas it approaches αV for $z > 1$. Thus phase coexistence obtains for $z = z_t = 1$, and the two densities are respectively equal to $N/V = \frac{1}{2}$ and $N/V = \frac{1}{2} + \alpha$.

2. Since

$$\frac{p}{k_B T} = \frac{1}{V} \log Z_{GC}, \quad (5.39)$$

one has

$$p_t = k_B T \log(1 + z_t) = k_B T \log 2. \quad (5.40)$$

Solution to exercise 5.9

1. We have

$$Z = \frac{1}{N_1!} \int \prod_{i=1}^{N_1} \frac{d\mathbf{p}_i d\mathbf{r}_i}{h^3} \exp \left[-\frac{1}{k_B T} \sum_{i=1}^{N_1} \frac{p_i^2}{2m} \right], \quad (5.41)$$

where the integral in \mathbf{r}_i runs over the available volume V . We obtain

$$Z_1 = \frac{1}{N_1!} \left(\frac{V}{\lambda_B^3} \right)^{N_1} \approx \left(\frac{eV}{N_1 \lambda_B^3} \right)^{N_1}. \quad (5.42)$$

We obtain therefore

$$\mu_1 = -k_B T \frac{\partial \ln Z_1}{\partial N_1} = -k_B T \ln \left(\frac{V}{N_1 \lambda_B^3} \right). \quad (5.43)$$

By the ideal gas law we have

$$p = \frac{N_1 k_B T}{V}, \quad (5.44)$$

and therefore the result can be written as a function of p and T :

$$\mu_1 = -k_B T \ln \left(\frac{k_B T}{p \lambda_B^3} \right). \quad (5.45)$$

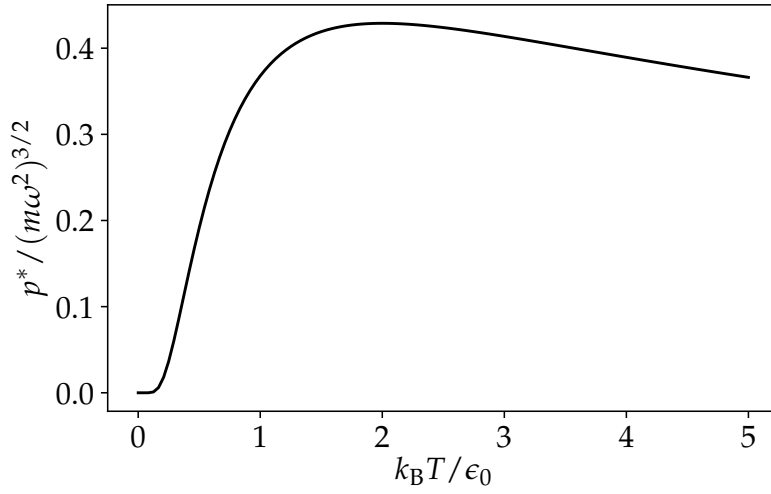


Figure 5.1: Sublimation pressure p^* as a function of T/ϵ_0 , in units $(m\omega^2)^{3/2}$. We have set $k_B = 1$.

2. We obtain

$$\begin{aligned} Z_2 &= \int \prod_{i=1}^{N_1} \frac{d\mathbf{p}_i d\mathbf{r}_i}{h^3} \exp \left[-\frac{1}{2k_B T} \sum_{i=1}^{N_1} \left(\frac{p_i^2}{m} + m\omega^2 r_i^2 - \epsilon_0 \right) \right] \\ &= \left(\frac{k_B T}{\hbar\omega} \right)^{3N_2} e^{N_2 \epsilon_0 / k_B T}. \end{aligned} \quad (5.46)$$

Thus we obtain

$$\mu_2 = -k_B T \frac{\partial \ln Z_2}{\partial N_2} = -3k_B T \ln \left(\frac{k_B T}{\hbar\omega} \right) - \epsilon_0. \quad (5.47)$$

Thus the transition takes place at the temperature T^* such that

$$\ln \left(\frac{k_B T^*}{p \lambda_B^3} \right) = 3 \ln \left(\frac{k_B T^*}{\hbar\omega} \right) + \frac{\epsilon_0}{k_B T^*}. \quad (5.48)$$

Given the temperature, we can solve for the pressure p , obtaining

$$p^* = \left(\frac{\hbar\omega}{\lambda_B(T)} \right)^3 \frac{e^{-\epsilon_0/k_B T}}{(k_B T)^2} = \frac{(m\omega^2)^{3/2}}{(k_B T)^{1/2}} e^{-\epsilon_0/k_B T}. \quad (5.49)$$

The model is not reliable for $k_B T \gg \epsilon_0$, where it is unlikely that the solid remains stable. Thus the slow decrease of p^* for larger values of T is probably unphysical.

Solution to exercise 5.10 (Spin-elasticity coupling)

1. The hamiltonian of the model is given by

$$H(\sigma, \epsilon) = - \sum_{i=1}^N \left[1 + (-\epsilon)^i \right] \sigma_i \sigma_{i+1} + N\omega\epsilon^2. \quad (5.50)$$

Thus the partition function is given by

$$Z(\beta) = \int_{-\infty}^{+\infty} d\epsilon e^{-N\beta\omega\epsilon^2} Z_N(\epsilon, \beta), \quad (5.51)$$

where

$$Z_N(\epsilon, \beta) = \sum_{\{\sigma\}} \exp \left\{ \beta \sum_{i=1}^N \left[1 + (-\epsilon)^i \right] \sigma_i \sigma_{i+1} \right\}. \quad (5.52)$$

Introducing the transfer matrices

$$P = \begin{pmatrix} e^{\beta(1+\epsilon)} & e^{-\beta(1+\epsilon)} \\ e^{-\beta(1+\epsilon)} & e^{\beta(1+\epsilon)} \end{pmatrix}; \quad (5.53)$$

$$Q = \begin{pmatrix} e^{\beta(1-\epsilon)} & e^{-\beta(1-\epsilon)} \\ e^{-\beta(1-\epsilon)} & e^{\beta(1-\epsilon)} \end{pmatrix}. \quad (5.54)$$

we obtain

$$Z_N(\epsilon, \beta) = \text{Tr} (PQ)^{N/2} \simeq \lambda_+^{N/2}, \quad (5.55)$$

where λ_+ is the largest eigenvalue of PQ:

$$PQ = \begin{pmatrix} e^{2\beta} + e^{-2\beta} & e^{2\beta\epsilon} + e^{-2\beta\epsilon} \\ e^{2\beta\epsilon} + e^{-2\beta\epsilon} & e^{2\beta} + e^{-2\beta} \end{pmatrix}. \quad (5.56)$$

It is easy to see that

$$\lambda_+ = 2 (\cosh 2\beta + \cosh 2\beta\epsilon). \quad (5.57)$$

We can thus evaluate the integral (5.51) by the saddle-point method, obtaining

$$Z(\beta) \sim e^{-N\beta g(\epsilon^*, \beta)}, \quad (5.58)$$

where

$$g(\epsilon, \beta) = \omega\epsilon^2 - \frac{1}{2\beta} \log \lambda_+, \quad (5.59)$$

and ϵ^* corresponds to the minimum of $g(\epsilon, \beta)$.

2. Let us now dwell on the behavior of $-\log \lambda_+$ for small values of ϵ . We have

$$-\log \lambda_+ = -\log 2 - \log(1 + \cosh 2\beta) - \frac{2\beta^2 \epsilon^2}{1 + \cosh 2\beta} - \frac{2(\cosh 2\beta - 2)\beta^4 \epsilon^4}{3(1 + \cosh 2\beta)^2} + O(\epsilon^6) \quad (5.60)$$

Let us define

$$u(\beta) = \frac{2\beta}{1 + \cosh 2\beta}. \quad (5.61)$$

It is easy to see that $\lim_{\beta \rightarrow 0} u(\beta) = \lim_{\beta \rightarrow \infty} u(\beta) = 0$, and that $u(\beta) > 0$ for $0 < \beta < +\infty$. Thus there is a maximal value u_{\max} of $u(\beta)$. One obtains $u_{\max} = 0.224$ which is reached for $\beta = 0.772$, and for this value, the coefficient of ϵ^4 in the expansion is positive. Thus for $\omega > u_{\max}$ the point $\epsilon = 0$ corresponds always to a minimum. On the other hand, the coefficient of ϵ^4 in the expansion is positive for $\beta < \beta^* = 0.658$, which corresponds to the value $u(\beta^*) = 0.219$, and negative otherwise. For $\omega \geq 0.25$ one can see that as β varies, the absolute minimum of $g(\epsilon, \beta)$ remains at $\epsilon = 0$, although there are two local minima at $\epsilon = \pm 2$, where the value of g dangerously approaches $g(0, \beta)$.

For $\omega = 0.20$ we can look for the value β_c of β for which $\omega = u(\beta_c)$. We obtain $\beta_c = 0.517$. For this value of β the coefficient of ϵ^4 is positive (it equals 0.00287) and thus the transition is continuous.

3. For $\omega = 0.24$ we do not find a value of β such that $u(\beta) = \omega$. One can check that there are minima for $\epsilon = \pm \epsilon^* \neq 0$, such that $g(\epsilon, \beta)$ becomes smaller than $g(0, \beta)$ for some values of β . We look for these minima and find for which value of β_t one has $g(\epsilon^*, \beta_t) = g(0, \beta_t)$. We evaluate the derivative of $g(\epsilon, \beta)$:

$$\frac{\partial g}{\partial \epsilon} = 2\omega\epsilon - \frac{\sinh(2\beta\epsilon)}{\cosh(2\beta) + \cosh(2\beta\epsilon)}. \quad (5.62)$$

One can then see that the minima lie close to $\epsilon^* \simeq 1.7$. We can find the value of (ϵ^*, β_t) by solving the system of equations formed by $\partial_\epsilon g(\epsilon, \beta) = 0$ and $g(\epsilon, \beta) = g(0, \beta)$. As ω varies, one obtains the phase diagram $\beta_t(\omega)$ for ω between 0.219 and 0.25. The phase diagram is best shown in the form $T_c(\omega)$, where $T_c = 1/\beta_{c,t}$ as in figure 5.2. One sees that the transition disappears for $\omega > \lim_{\beta \rightarrow \infty} \omega(\beta) = 0.25$.

4. The tricritical point corresponds to the coefficients of ϵ^2 and that of ϵ^4 vanishing at the same time as functions of ω and of β . We obtain $\beta_t = 0.658$ and $\omega_t = 0.219$.

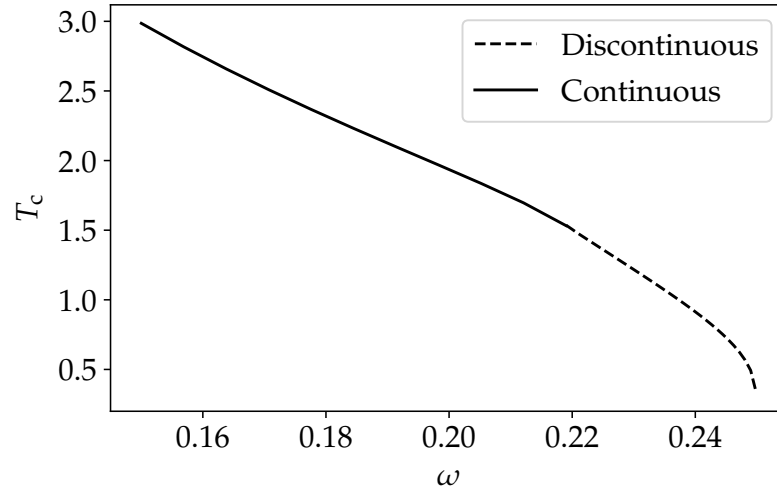


Figure 5.2: Phase diagram for the spin-elasticity coupling model.

Solution to exercise 5.11 (Mean-field theory of the Ising model in a transverse field) The model is defined by the hamiltonian

$$H = -J \sum_{\langle i,j \rangle} \sigma_i^z \sigma_j^z - \Gamma \sum_i \sigma_i^x, \quad (5.63)$$

where $\langle i, j \rangle$ denotes nearest-neighbor pairs, and for each site i the operators σ^z, σ^x are defined by

$$\sigma^z = \begin{pmatrix} 1, & 0 \\ 0, & -1 \end{pmatrix}; \quad \sigma^x = \begin{pmatrix} 0, & 1 \\ 1, & 0 \end{pmatrix}. \quad (5.64)$$

These operators act on the Hilbert space obtained as a product of the spaces Σ_i generated by the vectors $|+\rangle_i, |-\rangle_i$. In the spirit of mean-field theory, we define the trial hamiltonian

$$H_0(K, h) = -k_B T \left[\sum_i (K \sigma_i^z + h \sigma_i^x) \right]. \quad (5.65)$$

We now look for the minimum of the trial free energy

$$\mathcal{F}(K, h) = \langle (H - H_0) \rangle_0 - k_B T \log Z_0, \quad (5.66)$$

where

$$Z_0 = \text{Tr} e^{-\beta H_0}; \quad (5.67)$$

$$\langle A \rangle_0 = \frac{1}{Z_0} \text{Tr} A E^{-\beta H_0}. \quad (5.68)$$

1. Since

$$H_0 = -\beta^{-1} \begin{pmatrix} K, & h \\ h, & -K \end{pmatrix}, \quad (5.69)$$

the secular equation has the expression

$$\lambda^2 - \beta^{-2} (K^2 + h^2) = 0. \quad (5.70)$$

The eigenvalues are therefore $-\beta^{-1}\lambda_{\pm}$, where

$$\lambda_{\pm} = \pm \sqrt{K^2 + h^2}. \quad (5.71)$$

We thus obtain

$$\log Z_0 = N \log 2 \cosh \sqrt{K^2 + h^2}. \quad (5.72)$$

2. On the other side we have

$$m = \langle \sigma^z \rangle_0 = \frac{\partial}{\partial K} \log Z_0 = \frac{K}{\sqrt{K^2 + h^2}} \tanh \sqrt{K^2 + h^2}; \quad (5.73)$$

$$\tau = \langle \sigma^x \rangle_0 = \frac{\partial}{\partial h} \log Z_0 = \frac{h}{\sqrt{K^2 + h^2}} \tanh \sqrt{K^2 + h^2}. \quad (5.74)$$

Therefore

$$\langle (H - H_0) \rangle_0 = -\frac{NJ\zeta}{2} m^2 - N(\Gamma - k_B T h) \tau + Nk_B T K m. \quad (5.75)$$

In this equation $\zeta = 2d$ is the coordination number. We thus obtain

$$\begin{aligned} \mathcal{F}(K, h) = & -\frac{NJ\zeta}{2} m^2 - N(\Gamma - k_B T h) \tau + Nk_B T K m \\ & - Nk_B T \log 2 \cosh \sqrt{K^2 + h^2}. \end{aligned} \quad (5.76)$$

3. The equations for the minimum of \mathcal{F}_0 are given by

$$0 = -NJ\zeta m m_K - N(\Gamma - k_B T h) \tau_K + Nk_B T K m_K; \quad (5.77)$$

$$0 = -NJ\zeta m m_h + Nk_B T K m_h - N(\Gamma - k_B T h) \tau_h. \quad (5.78)$$

In these equations, $m_h = \partial m / \partial h$, and analogously for τ , etc. We thus obtain the conditions

$$K = \frac{Jm\zeta}{k_B T}; \quad h = \frac{\Gamma}{k_B T}. \quad (5.79)$$

Since m is expressed as a function of K via eq. (5.73), we obtain the self-consistency equation

$$\frac{T}{T_0} K = \frac{K}{\sqrt{K^2 + h^2}} \tanh \sqrt{K^2 + h^2}, \quad (5.80)$$

where we have defined

$$T_0 = \frac{J\zeta}{k_B}. \quad (5.81)$$

Equation (5.80) always allows for the solution $K = 0$. The solutions with $K \neq 0$ must satisfy

$$\frac{T}{T_0} \sqrt{K^2 + h^2} = \tanh \sqrt{K^2 + h^2} \quad (5.82)$$

Let us define ω via the equation

$$\omega = \frac{T}{T_0} \sqrt{K^2 + h^2}. \quad (5.83)$$

Of course ω satisfies a self-consistency equation analogue to that of the average magnetization in a classical Ising model. Thus one will have non-vanishing solutions $\omega_0(T)$ for $T < T_0$. At a fixed temperature T and magnetic field Γ , we have

$$m(T, \Gamma) = \pm \sqrt{\omega_0^2 - \left(\frac{\Gamma}{k_B T_0}\right)^2}. \quad (5.84)$$

Of course this solution is acceptable only if the argument of the square root is positive. Thus the transition between a regime with $m = 0$ and one with $m \neq 0$ will take place at the temperature $T_c(\Gamma)$ defined by

$$\omega_0(T_c) = \frac{\Gamma}{k_B T_0}. \quad (5.85)$$

For temperatures smaller than T_c we shall have a non-vanishing magnetization, given by

$$m_0(T) = \pm \frac{T}{T_0} \sqrt{\omega_0^2(T) - \left(\frac{\Gamma}{k_B T}\right)^2} \propto \sqrt{T_c - T}. \quad (5.86)$$

The phase diagram (Γ, T) described by equation (5.85) is shown in figure 5.3.

Solution to exercise 5.12 (Mean-field theory of the three-state Potts model)

1. We have

$$1 = p + 2\pi = p + 2(p - m) = 3p - 2m, \quad (5.87)$$

and thus

$$p = \frac{1 + 2m}{3}; \quad (5.88)$$

$$\pi = p - m = \frac{1 + 2m}{3} - m = \frac{1 - m}{3}. \quad (5.89)$$

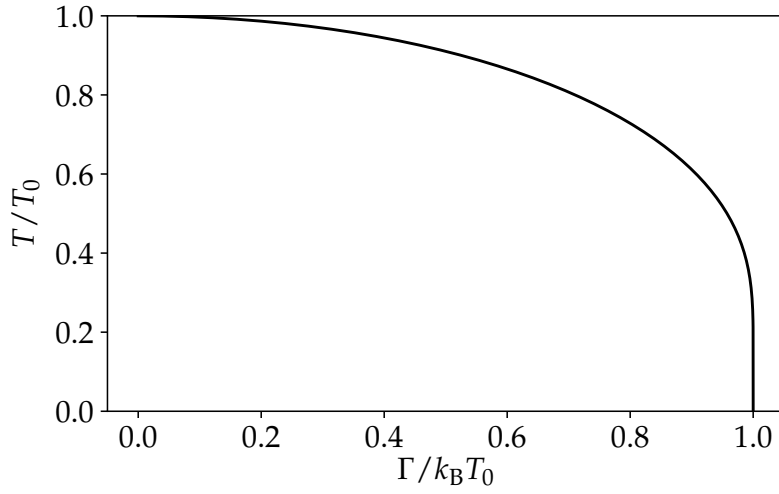


Figure 5.3: Phase diagram of the Ising model in a transverse field in the (Γ, T) -plane. Below the curve, one has $m \neq 0$. Notice the vertical asymptote for $\Gamma/k_B T_0 \rightarrow 1$.

Thus, by Gibbs' formula

$$\begin{aligned} S(m) &= -k_B \sum_a p_a \log p_a \\ &= -k_B \left[\left(\frac{1+2m}{3} \right) \log \left(\frac{1+2m}{3} \right) + 2 \left(\frac{1-m}{3} \right) \log \left(\frac{1-m}{3} \right) \right]. \end{aligned} \quad (5.90)$$

2. We have

$$\begin{aligned} E(m) = \langle H \rangle &= \frac{NJ\zeta}{2} \sum_{a=1}^3 p_a (1 - p_a) \\ &= \frac{NJ\zeta}{2} \left[\frac{1+2m}{3} \frac{2}{3} (1-m) + 2 \frac{1-m}{3} \frac{2+m}{3} \right] = \frac{NJ\zeta}{3} (1 - m^2). \end{aligned} \quad (5.91)$$

3. We thus obtain

$$\begin{aligned} F(m, T) = E(m) - TS(m) &= \frac{NJ\zeta}{3} (1 - m^2) \\ &\quad + Nk_B T \left[\left(\frac{1+2m}{3} \right) \log \left(\frac{1+2m}{3} \right) \right. \\ &\quad \left. + 2 \left(\frac{1-m}{3} \right) \log \left(\frac{1-m}{3} \right) \right]. \end{aligned} \quad (5.92)$$

Imposing that the derivative with respect to m vanishes we obtain the self-consistency equation

$$0 = -\frac{2NJ\zeta}{3} m + \frac{2Nk_B T}{3} \log \frac{1+2m}{1-m}, \quad (5.93)$$

5. PHASE TRANSITIONS

i.e.,

$$\log \frac{1+2m}{1-m} = \frac{J\zeta}{k_B T} m. \quad (5.94)$$

4. The self-consistency equation always allows for the $m = 0$ solution, symmetrical (since it implies $p_a = \frac{1}{3}$ for $a = 1, 2, 3$). On the other hand, for sufficiently small T , it also allows other solutions. Defining the function

$$\phi(m) = \log \frac{1+2m}{1-m}, \quad (5.95)$$

it is easy to obtain

$$\phi(m) = 3m - \frac{3}{2}m^2 + O(m^3). \quad (5.96)$$

Thus, for $k_B T_0 = J\zeta/3$ we have two coinciding solutions for $m = 0$ and one for $m = m^* > 0$. Plotting $F(m, T_0)$ one sees that the minimum of F lies at m^* . One

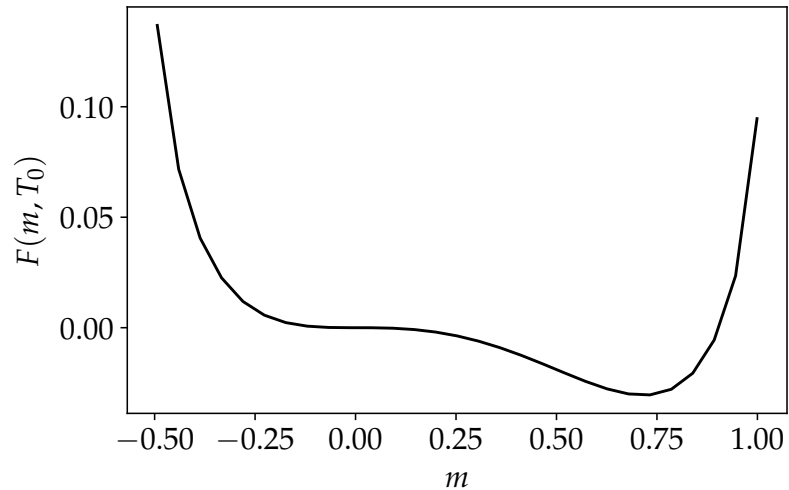


Figure 5.4: Trial free energy $F(m, T_0) - F(0, T_0)$, for the value T_0 of the temperature in which $\partial^2 F / \partial m^2|_{m=0}$ vanishes.

can evaluate numerically the critical value T_c of T and the corresponding value of the minimum $m^*(T_c)$ for which we have $F(m^*, T_c) = F(0, T_c)$. One thus obtains $T_c = 0.7213 = 1/\log 4$, with $m^* = 0.5$. The figure shows $F(m, T_c) - F(0, T_c)$ as a function of m . Thus there will be a discontinuous transition for $T = T_c$, where m jumps from 0 to $m^* = \frac{1}{2}$.

For $T < T_c$ one has $m = m^*(T)$, which rapidly approaches 1 as T decreases, as shown.

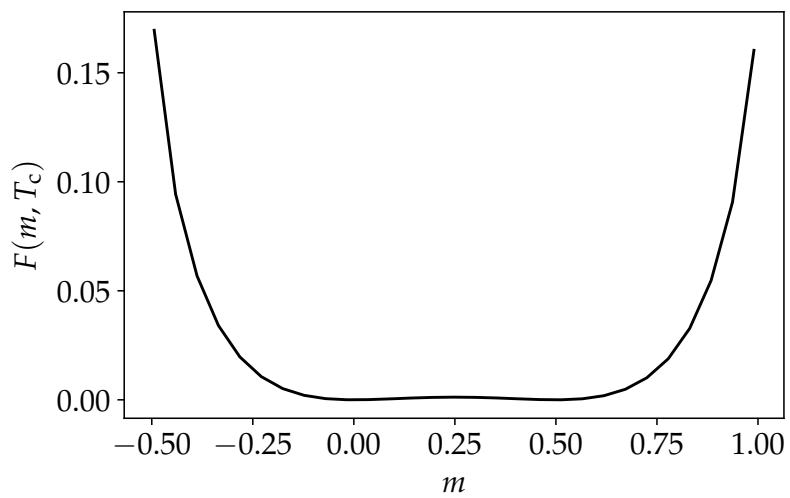


Figure 5.5: Trial free energy $F(m, T_c) - F(0, T_c)$, for the value T_c of the temperature in which the transition takes place.

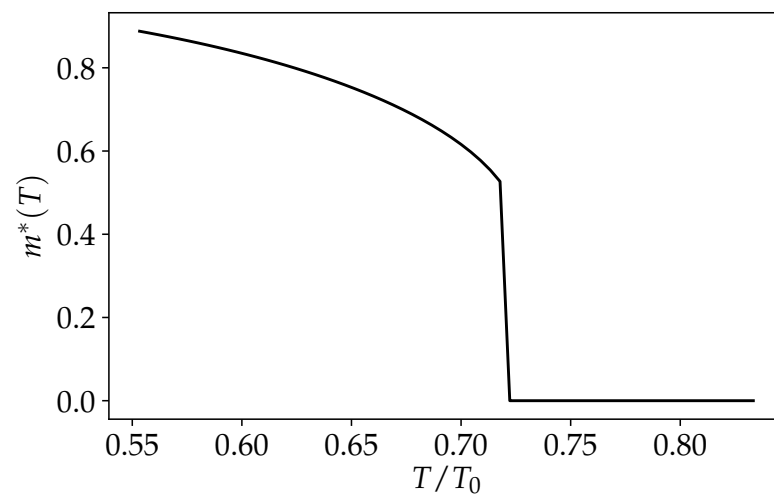


Figure 5.6: Order parameter $m^*(T)$ as a function of T/T_0 for the three-state Potts model.

Renormalization Group

Solution to exercise 6.1 Let us denote by c_n the coefficient of k^n in $\Delta(k)$. We then have, instead of eq. (6.113)

$$c'_n = c_n b^{-(d+2)} \zeta^2. \quad (6.1)$$

Choosing $\zeta = b^{d/2}$ we obtain $c'_n = b^{-n}$. Thus $c'_n < c_n$, and c_n is an irrelevant parameter.

Solution to exercise 6.2 Let us denote by c_n the coefficient of k^n in $\Delta(k)$. We then have, instead of eq. (6.113)

$$c'_n = c_n b^{-(d+2)} \zeta^2.$$

Choosing $\zeta = b^{(d+2)/2}$ we obtain $c'_n = b^{2-n}$. Thus, if $n \geq 4$, we have $c'_n < c_n$, and c_n is an irrelevant parameter.

Solution to exercise 6.3 Let us first evaluate the analog of eq. (6.189), following the calculation of § 6.8.1. We obtain, instead of eq. (6.200),

$$\mathcal{H}_1 = u \sum_j \left(\sum_\alpha \phi_i^\alpha \right) + v \sum_i \sum_\alpha (\phi_i^\alpha)^4. \quad (6.2)$$

Thus we obtain, instead of eq. (6.202),

$$\sum_j G_{ij}^{-1} \langle \phi_i^\alpha \phi_j^\alpha \rangle + 4u \sum_j \sum_\beta \langle \phi_i^\alpha \phi_j^\alpha (\phi_j^\beta)^2 \rangle + 4v \sum_j \langle \phi_i^\alpha (\phi_j^\alpha)^3 \rangle = 1. \quad (6.3)$$

At the lowest order we obtain eq. (6.203) and

$$\langle \phi_i^\alpha (\phi_j^\alpha)^3 \rangle = 3 \langle \phi_i^\alpha \phi_j^\alpha \rangle \langle (\phi_j^\alpha)^2 \rangle, \quad (6.4)$$

where the factor 3 comes from the three ways in which we can choose the ϕ_j^α appearing in the correlation with ϕ_i^α . This yields directly eq. (6.206).

To proceed, we must evaluate the expression

$$\langle \mathcal{H}_1^2 \rangle_0 - \langle \mathcal{H}_1 \rangle_0^2, \quad (6.5)$$

and extract the terms containing four $\phi^<$ factors, to obtain the renormalization of the interaction term. There are terms proportional to u^2 , which contribute to the usual renormalization of u , terms proportional to v^2 , which contribute to the renormalization of v , and terms proportional to uv , which contribute to the renormalization of both u and v .

The terms proportional to v^2 are of the form

$$(\phi_i^<)^4 \langle (\phi_i^>)^4 \rangle_0 \quad (6.6)$$

with a multiplicity 72, just as in the $n = 1$ case, since all the ϕ^α must have the same α . Taking into account the $-1/2$ factor that comes from the cumulant expansion one obtains a contribution

$$-36v^2 \frac{1}{(1+r)^2} \quad (6.7)$$

to the renormalization of v .

The terms proportional to uv contain a factor of 2 from the double product. They are proportional to

$$\langle (\phi^\alpha)^2 (\phi^\beta)^2 (\phi^\gamma)^4 \rangle_0. \quad (6.8)$$

The contribution to the renormalization of u has a multiplicity of 48: there are 4×4 modes of coupling one of the ϕ^γ factors with one of either ϕ^α or ϕ^β , and 3 modes of coupling one of the remaining gamma with the remaining factor of the same component. On the other hand, the contribution to the renormalization of v has an extra factor of 2, since the remaining γ factor must be coupled to one of the two remaining factors of the *other* component (β , if the first coupling was with α , or vice versa). Taking into account the $-1/2$ factor that comes from the cumulant expansion one obtains the result.

Solution to exercise 6.4 From (6.231), setting $K = K_c$ and exploiting the definition of r we obtain $\sigma \sim h/r$ and $\sigma^2 \sim K_c f(\lambda) \sim r^{(d-2)/2}$ from which we obtain $r \sim h^{4/(d+2)}$. One then has $\sigma \sim h/r \sim h^{(d-2)/(d+2)}$.

Classical Fluids

Solution to exercise 7.1 From equation (7.16) we obtain, in the canonical ensemble

$$\int d\mathbf{x}_1 \cdots d\mathbf{x}_\ell \rho^{(\ell)}(\mathbf{x}_1, \dots, \mathbf{x}_\ell) = N(N-1) \cdots (N-\ell+1) = \frac{N!}{(N-\ell)!}. \quad (7.1)$$

Let us evaluate the same quantity in the grand canonical ensemble:

$$\rho_{\text{GC}}^{(\ell)}(\mathbf{x}_1, \dots, \mathbf{x}_\ell) = \frac{1}{\Omega_{\text{GC}}[\mu, v]} \sum_N e^{\mu N/k_B T} \Omega_N[v] \rho^{(\ell)}(\mathbf{x}_1, \dots, \mathbf{x}_\ell), \quad (7.2)$$

where

$$\Omega_{\text{GC}}[\mu, v] = \sum_N e^{\mu N/k_B T} \Omega_N[v]. \quad (7.3)$$

We have

$$\int d\mathbf{x}_1 \cdots d\mathbf{x}_\ell \rho_{\text{GC}}^{(\ell)}(\mathbf{x}_1, \dots, \mathbf{x}_\ell) = \left\langle \frac{N!}{(N-\ell)!} \right\rangle, \quad (7.4)$$

where the average is taken in the grand canonical ensemble. We have in particular

$$\int d\mathbf{x}_1 \rho_{\text{GC}}^{(1)}(\mathbf{x}_1) = \langle N \rangle; \quad (7.5)$$

$$\int d\mathbf{x}_1 d\mathbf{x}_2 \rho_{\text{GC}}^{(2)}(\mathbf{x}_1, \mathbf{x}_2) = \langle N^2 \rangle - \langle N \rangle. \quad (7.6)$$

Thus we have

$$\begin{aligned} & \int d\mathbf{x}_1 d\mathbf{x}_2 \left[\rho_{\text{GC}}^{(2)}(\mathbf{x}_1, \mathbf{x}_2) - \rho_{\text{GC}}^{(1)}(\mathbf{x}_1) \rho_{\text{GC}}^{(1)}(\mathbf{x}_2) \right] \\ &= N \int d\mathbf{x} [g(\mathbf{x}) - 1] = \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2. \end{aligned} \quad (7.7)$$

On the other hand we have

$$\langle N^2 \rangle - \langle N \rangle^2 = k_B T \left. \frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T}. \quad (7.8)$$

The rhs is related to the susceptibility. We have indeed

$$\log Z_{GC} = \frac{p(\mu, T)V}{k_B T}. \quad (7.9)$$

For a small transformation at constant V and T , p and μ can only change via a change in $\langle N \rangle$. Thus we have

$$\left. \frac{1}{\rho K_T} = \frac{\partial p}{\partial \rho} \right)_{V,T} = V \left. \frac{\partial p}{\partial \langle N \rangle} \right)_{V,T} = \langle N \rangle \left. \frac{\partial \mu}{\partial \langle N \rangle} \right)_{V,T}. \quad (7.10)$$

From equations (7.7,7.10) we obtain

$$1 + \rho \int d\mathbf{x} [g(\mathbf{x}) - 1] = \rho k_B T K_T. \quad (7.11)$$

Let us remark that we have made no mention of the form of the potential among the particles. Thus this expression also holds in the presence of three- (or more) body forces.

Solution to exercise 7.2 The weight of a configuration $(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of N particles can be expressed in terms of the $f_{ij} = f(\mathbf{r}_i - \mathbf{r}_j)$ as

$$P(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\Omega_N} e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} = \frac{1}{\Omega_N} \prod_{(kl)} e^{-\beta u(\mathbf{r}_k - \mathbf{r}_\ell)} = \frac{1}{\Omega_N} \prod_{(kl)} (1 + f_{kl}). \quad (7.12)$$

Thus the weight of all configurations in which one particle is at \mathbf{x} and another is at \mathbf{x}' is given by

$$\begin{aligned} \rho^{(2)}(\mathbf{x}, \mathbf{x}') &= \sum_{ij} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \delta(\mathbf{r}_i - \mathbf{x}) \delta(\mathbf{r}_j - \mathbf{x}') P(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ &= \frac{N(N-1)}{\Omega_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \delta(\mathbf{r}_1 - \mathbf{x}) \delta(\mathbf{r}_2 - \mathbf{x}') \prod_{kl} (1 + f_{kl}) \\ &= \frac{N(N-1)}{\Omega_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \delta(\mathbf{r}_1 - \mathbf{x}) \delta(\mathbf{r}_2 - \mathbf{x}') [1 + f(\mathbf{x} - \mathbf{x}')] \prod'_{(kl)} (1 + f_{kl}), \end{aligned} \quad (7.13)$$

where the sum runs over all pairs different from $(1, 2)$. Now we have

$$\int d\mathbf{r}_3 \cdots d\mathbf{r}_N \prod_{(k,\ell) \in \{3, \dots, N\}} (1 + f_{k\ell}) = \Omega_{N-2} \simeq \Omega_N V^{-2}. \quad (7.14)$$

The terms containing one particle at least between 1 and 2 and other particles involve integrals of products of two or more f , which vanish whenever one particle is further away from the others, and therefore yield a contribution which is higher order in ρ . Thus we have

$$\rho^{(2)}(\mathbf{x}, \mathbf{x}') = \rho^2 g(|\mathbf{x} - \mathbf{x}'|) = \rho^2 (1 + f(|\mathbf{x} - \mathbf{x}'|)). \quad (7.15)$$

Thus we have

$$\frac{\partial u}{\partial r} g(r) = -\frac{1}{\beta} \frac{\partial}{\partial r} (1 + f(r)) = -\frac{1}{\beta} \frac{\partial f}{\partial r}. \quad (7.16)$$

Substituting this expression into eq. (7.21) we obtain

$$\begin{aligned} \frac{p}{k_B T} &= \rho - \frac{\beta \rho^2}{2 \cdot 3} \int_0^\infty 4\pi r^2 dr r \left(-\frac{1}{\beta} \frac{\partial f}{\partial r} \right) \\ &= \rho + \frac{\rho^2}{2 \cdot 3} \left[4\pi r^3 f(r) \right]_0^\infty - \frac{\rho^2}{2} \int_0^\infty 4\pi r^2 dr f(r), \end{aligned} \quad (7.17)$$

which, since the integrated term vanishes, compares with (7.70).

Solution to exercise 7.3 (Joule-Thompson process)

1. The system exchanges energy with the environment only via the work $\delta W = \sum_{i=1,2} p_i dV_i$. Thus we have $dE = d(E_1 + E_2) = -\delta W = -\sum_{i=1,2} p_i dV_i$. On the other hand, since the p_i 's are constant, one has $dH_i = dE_i + p_i dV_i$, and the result follows.
2. Since $dH = T dS + V dp$, we have

$$dH = T \left(\frac{\partial S}{\partial T} \right)_p dT + \left[V + T \left(\frac{\partial S}{\partial p} \right)_T \right] dp. \quad (7.18)$$

On the other hand, $C_p = T \partial S / \partial T)_p$, while, by Maxwell's relations, we have

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p. \quad (7.19)$$

Thus, when $dH = 0$, we have

$$\left(\frac{\partial T}{\partial p} \right)_H = \frac{T \partial V / \partial T)_p - V}{C_p}. \quad (7.20)$$

3. The condition defining T^* is the following:

$$\left(\frac{T}{V} \frac{\partial V}{\partial T} \right)_p = 1, \quad (7.21)$$

i.e., $(T/\rho)\partial\rho/\partial T)_p = -1$, where $\rho = N/V$. By differentiating both sides of equation (7.20) at constant pressure, we obtain

$$T \left(\frac{\partial\rho}{\partial T} \right)_p = -\frac{\rho - \rho^2 (B_2(T) + TB_2'(T))}{1 - 2\rho B_2(T)}. \quad (7.22)$$

Thus by simple algebra one obtains the equation for T^* :

$$T^* B_2'(T^*) = B_2(T^*). \quad (7.23)$$

4. Let us write the van der Waals equation in terms of ρ :

$$(p + \rho^2 a)(1 - \rho b) = k_B T. \quad (7.24)$$

Solving for p and neglecting terms of $o(\rho^2)$ yields a virial-like equation of state

$$p = k_B T \rho \left[1 - \rho \left(\frac{a}{k_B T} - b \right) \right]. \quad (7.25)$$

Thus, in the van der Waals gas we have

$$B_2(T) = \frac{a}{k_B T} - b. \quad (7.26)$$

The equation for T^* is thus

$$k_B T^* = \frac{a}{2b} = \frac{16}{27} k_B T_c. \quad (7.27)$$

Solution to exercise 7.4 Given a potential function $u(r)$, with a lower bound $B > -\infty$, we define the quantity $C(T)$ by

$$C(T) = \int d^3\mathbf{r} \left| 1 - e^{-u(r)/k_B T} \right|. \quad (7.28)$$

We wish to show that if there is a value T_0 , $0 < T_0 < +\infty$, such that $C(T_0) < +\infty$, then $C(T) < +\infty$ for $0 < T < +\infty$.

We can write $C(T)$ in the form

$$C(T) = C_+(T) + C_-(T), \quad (7.29)$$

where, having defined

$$u_+(r) = \max(u(r), 0), \quad (7.30)$$

$$u_-(r) = \min(u(r), 0), \quad (7.31)$$

we have

$$C_{\pm}(T) = \int d^3\mathbf{r} \left| 1 - e^{-u_{\pm}(r)/k_B T} \right|. \quad (7.32)$$

Of course, the finiteness of $C(T_0)$ implies the finiteness of both $C_{\pm}(T_0)$, and, vice versa, the finiteness of both $C_{\pm}(T)$ implies that of $C(T)$.

We have

$$C_{-}(T_0) = \int d^3\mathbf{r} \left(e^{|u_{-}(r)|/k_B T_0} - 1 \right) \geq \int d^3\mathbf{r} \frac{|u_{-}(r)|}{k_B T_0}. \quad (7.33)$$

Thus, since $C_{-}(T_0)$ is finite, the integral of $|u_{-}(r)|$ is also finite. In particular, this implies that $\lim_{r \rightarrow \infty} |u_{-}(r)| = 0$. As a consequence, for any $\epsilon > 0$, there is $R < \infty$ such that, if $r > R$, $|u_{-}(r)| < \epsilon$. This implies that $e^{|u_{-}(r)|/k_B T} - 1 < |u_{-}(r)| (e^{\epsilon/k_B T} - 1)$ for $r > R$. Thus we have $C_{-}(T) < (4\pi/3)R^3(e^{\epsilon/k_B T} - 1) + (e^{\epsilon/k_B T} - 1) \int_R^{\infty} 4\pi r^2 dr |u_{-}(r)| < +\infty$.

For $C_{+}(T)$, the reasoning is similar. Since $C_{+}(T_0) < +\infty$, the integral of $1 - e^{-u_{+}(r)/k_B T_0}$ is finite. Thus $\lim_{r \rightarrow \infty} u_{+}(r) = 0$. As a consequence, for any $\epsilon > 0$, there is a R such that $|u_{+}(r)| < \epsilon$ for $r > R$. In this region, $1 - e^{-u_{+}(r)/k_B T_0} > u_{+}(r)(1 - e^{-\epsilon/k_B T_0})$. Thus the integral of $u_{+}(r)$ is finite. Then $C_{+}(T) < (4\pi/3)R^3 + (1/k_B T) \int_R^{\infty} 4\pi r^2 dr u_{+}(r) < +\infty$.

Solution to exercise 7.5 Denoting by $v_i(\mathbf{r})$ the local density of ions of species i at \mathbf{r} , the electric potential ϕ satisfies Poisson's equation

$$\nabla^2 \phi = -\frac{1}{\epsilon_r \epsilon_0} \sum_i e z_i v_i(\mathbf{r}). \quad (7.34)$$

On the other hand, by the Boltzmann distribution, we expect

$$v_i(\mathbf{r}) = v_i^0 e^{-e z_i \phi(\mathbf{r})/k_B T} \simeq v_i^0 \left(1 - \frac{e z_i \phi(\mathbf{r})}{k_B T} \right). \quad (7.35)$$

Thus we have

$$\nabla^2 \phi = \frac{1}{\epsilon_r \epsilon_0} \sum_i e^2 v_i^0 z_i^2 \phi(\mathbf{r}) - \frac{1}{\epsilon_r \epsilon_0} \sum_i e z_i v_i^0 \phi(\mathbf{r}). \quad (7.36)$$

The last term vanishes because of the neutrality condition. We obtain therefore the equation

$$\nabla^2 \phi = \frac{\phi}{\ell_D^2}, \quad (7.37)$$

where the Debye length ℓ_D is given by

$$\ell_D = \left(\frac{\sum_i e^2 v_i^0 z_i^2}{\epsilon_r \epsilon_0} \right)^{-1/2}. \quad (7.38)$$

Solution to exercise 7.6 Define

$$\rho_0(x_1, \dots, x_N) = \prod_{i=1}^N \rho^{(1)}(x_i), \quad (7.39)$$

and denote the canonical probability distribution by $\rho^{\text{eq}}(x_1, \dots, x_N)$. Then we have

$$D(\rho^{\text{eq}} \parallel \rho_0) \geq 0, \quad (7.40)$$

where

$$D(p \parallel p') = k_B \int \prod_{i=1}^N dx_i p(\{x_i\}) \log \frac{p(\{x_i\})}{p'(\{x_i\})}. \quad (7.41)$$

Thus

$$\begin{aligned} D(\rho^{\text{eq}} \parallel \rho_0) &= k_B \int \prod_{i=1}^N dx_i \rho^{\text{eq}}(\{x_i\}) [\log \rho^{\text{eq}}(\{x_i\}) - \log \rho_0(\{x_i\})] \\ &= -\mathcal{S}(\rho^{\text{eq}}) - k_B \sum_{j=1}^N \int \prod_{i=1}^N dx_i \rho^{\text{eq}}(\{x_i\}) \log \rho^{(1)}(x_j) \\ &= -\mathcal{S}(\rho^{\text{eq}}) - Nk_B \int dx \rho^{(1)}(x) \log \rho^{(1)}(x) = -\mathcal{S} + N\mathcal{S}(\rho^{(1)}), \end{aligned} \quad (7.42)$$

since $\mathcal{S}(\rho^{\text{eq}})$ coincides with the thermodynamical entropy, and due to the relation between the canonical probability distribution and the reduced density. Dividing by N we obtain the required result.

Numerical Simulation

Solution to exercise 8.1 (Ideal Gas in One Dimension) The instantaneous state of the system is identified by the collection of the pairs (x_i, v_i) of position and velocities of the particles, plus the corresponding one (L, V) of the piston. The total energy E is given by

$$E = \sum_{i=1}^N \frac{1}{2} m v_i^2 + \frac{1}{2} M V^2 + p_0 L. \quad (8.1)$$

The elastic wall at the origin can be represented by the following trick. We allow the x_i 's to take on negative values. A particle with $x_i < 0$ and velocity v_i would correspond to a particle which has impacted on the wall at the origin an odd number of times, and whose velocity is the opposite of v_i . Thus the impact on the elastic wall will be simply represented by the particle crossing the origin. A “copy” of the piston will be placed at $-L$, with velocity $-V$.

Let us consider a state $(x_1, v_1, \dots, x_N, v_N, L, V)$ at time t_0 , where of course $-L \leq x_i \leq +L, \forall i$. The motion of the i -th particle satisfies

$$x_i(t) = x_i + v_i(t - t_0), \quad (8.2)$$

and that of the piston satisfies

$$L(t) = L + V(t - t_0) - \frac{1}{2} \frac{p_0}{M} (t - t_0)^2. \quad (8.3)$$

Thus the waiting time τ_i^* till the impact of the particle on the piston is given by

$$\tau_i^* = \frac{M}{p_0} \left(V - v + \sqrt{(V - v)^2 - 2p_0(r - L)/M} \right), \quad (8.4)$$

if $v > 0$, or by

$$\tau_i^* = \frac{M}{p_0} \left(-V - v + \sqrt{(V + v)^2 + 2p(r + L)/M} \right), \quad (8.5)$$

if $v < 0$, since in this case the particle collides with the copy of the piston at $-L$.

If the particle and the piston collide, and the piston has velocity V , the velocities after collision are given by

$$W = \frac{\pm 2mv + (M - m)V_0}{m + M}; \quad (8.6)$$

$$w = \frac{\pm 2MV_0 + (m - M)v}{m + M}. \quad (8.7)$$

Here one should take upper signs when $v > 0$ and lower ones when $v < 0$.

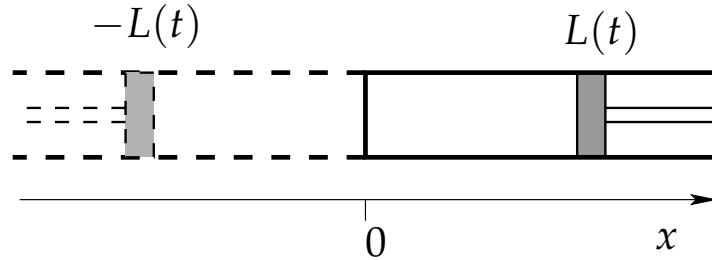


Figure 8.1: The “negative copy” of the piston which simplifies the treatment of collisions with the back wall of the cylinder.

Thus the algorithm for the evolution of the model runs as follows:

1. Initialize the system by distributing the particles in the interval $(-L_0, L_0)$ and assign each of them a velocity v_i^0 and velocity V^0 to the piston. Set the time counter t to 0.
2. Evaluate the time τ_i to the next collision for each particle i , and identify the index i_0 that corresponds to the first collision.
3. Displace each particle i by $v_i \tau_{i_0}$ and set $L = r_{i_0} + v_{i_0} \tau_{i_0}$, $V = V - (p/M) \tau_{i_0}$.
4. Set $V = W$ and $v_{i_0} = w$ after collision by equations (8.6,8.7), according to the sign of v_{i_0} . Add $\tau_{i_0}^*$ to t .
5. Repeat from point 2.

In this way, starting from an initial condition (x_i^0, v_i^0) and L^0, V^0 we obtain a succession of dynamical states which conserve the total energy

$$E = \sum_{i=1}^N \frac{1}{2} m v_i^2 + \frac{1}{2} M V^2 + p_0 L. \quad (8.8)$$

In this way, for $N \gg 1$, we expect the average position $\langle L \rangle$ of the piston to be given by the ideal gas law:

$$\langle L \rangle = \frac{Nk_B T}{p_0}. \quad (8.9)$$

Note that since the time steps have varying durations, when evaluating averages one has to weight each value with its corresponding duration, measured from the time elapsed since the last recorded value.

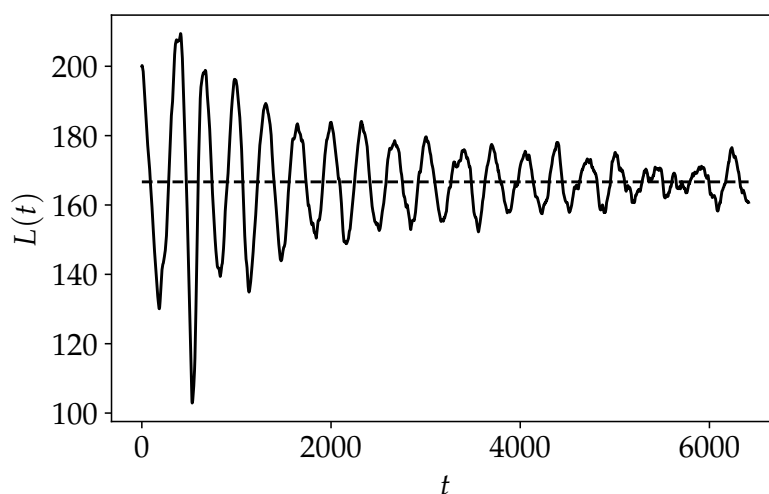


Figure 8.2: Piston position $L(t)$ as a function of time for a simulations with $N = 1000$ particles, with $p = 10$ and a mass ratio $M/m = 100$ with $k_B T_0 = 1$. The initial position is $L_0 = 2Nk_B T_0/p$. The dashed line corresponds to the equilibrium position $2H/3p$, where $H = 3Nk_B T_0/2 + pL_0$ is the enthalpy of the system.

A Python snippet implementing this algorithm follows.

```
import numpy as np
import matplotlib.pyplot as plt

def collision_time(x, v, L, V, f):
    """Evaluates the time till the next collision.
    The particle's velocity and position are (v, x), the piston's are (
        V, L)."""
    if(v > 0):
        t = (V-v+np.sqrt((V-v)**2-2*f*(x-L)))/f
    else:
        t = (V+v+np.sqrt((V+v)**2+2*f*(x+L)))/f
    return t

def collision(v, V, M):
```

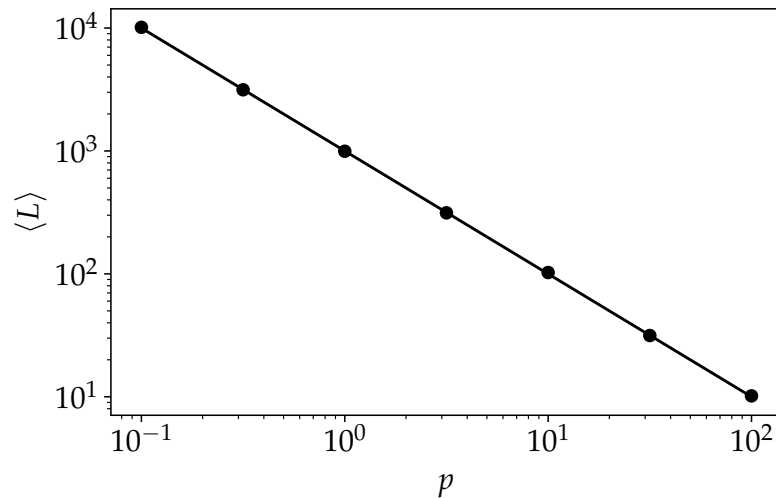


Figure 8.3: Log-log plot of the equation of state obtained from the simulation of the model with $N = 1000$ particles, for $M/m = 100$ and $k_B T = 1$. The line corresponds to the ideal-gas law.

```

"""Evaluates the velocities of the particle after collision.
Particle's velocity: v->w, piston's velocity V->W."""
if(v > 0):
    W = (2*v+(M-1)*V)/(1+M)
    w = (2*M*V+(1-M)*v)/(1+M)
else:
    W = (-2*v+(M-1)*V)/(1+M)
    w = (-2*M*V+(1-M)*v)/(1+M)
return w, W

def initialize(N, T0, p, x0, M, mode='gaussian'):
    sqT0 = np.sqrt(T0)
    L = x0*N*T0/p # Initial position of the piston: x0 times the
                  # equilibrium position
    V = np.random.randn()*np.sqrt(T0/M) # Initial velocity of the
    # piston
    x0 = np.zeros((N, 2))
    x0[:, 0] = np.random.uniform(low=-L, high=L, size=N) # Uniform
    # distribution of positions
    if mode == 'delta':
        x0[:, 1] = np.random.choice([-sqT0, sqT0], size=N) # Velocities
        # : +-sqrt(T0)
    else:
        x0[:, 1] = np.random.randn(N)*sqT0 # Gaussian distribution
    return L, V, x0

def iterate(N, T0, p, x0, M, itermax, interval = 100, mode='gaussian'):

```

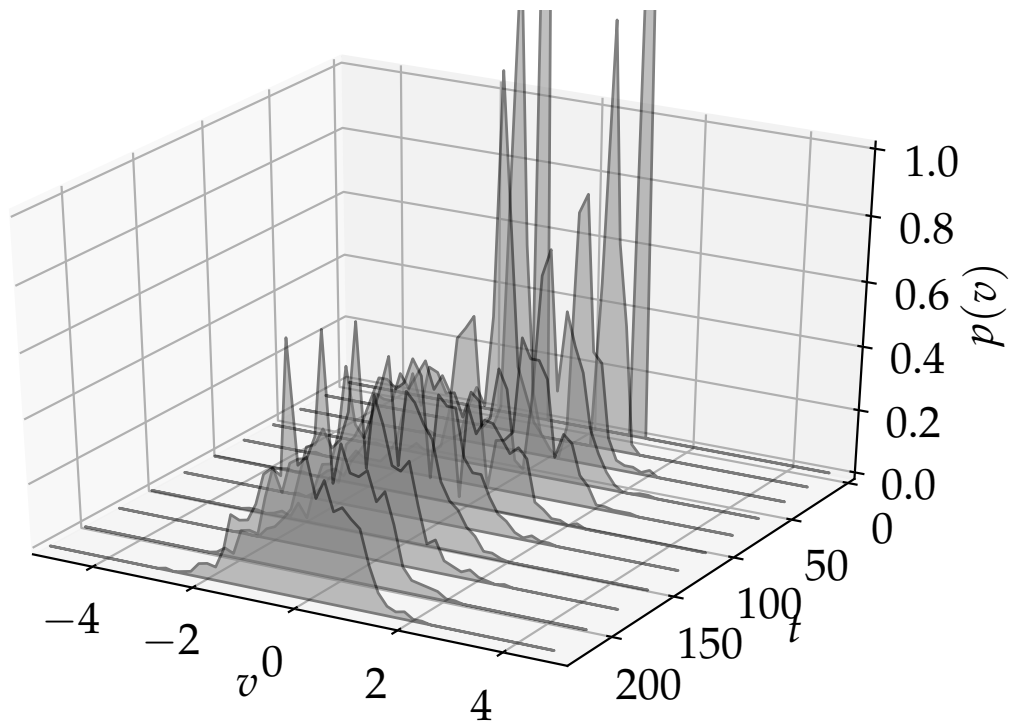


Figure 8.4: Approach of the velocity distribution to the Maxwell form, starting from an initial distribution allowing for only two (opposite) values of v . Parameters: $N = 1000$, $M/m = 100$, $p = 100$, $k_B T = 1$.

```

L, V, x = initialize(N, T0, p, x0, M, mode)
E = 0.5*np.sum([ x[i, 1]**2 for i in range(N)]) + p*L
f = p/M
t = 0.
time = []
ell = []
# Iteration
iteration = 0
while iteration <= itermax*N:
    # Identify the next collision
    tau0, i0 = float("inf"), N
    for i in range(N):
        tau1 = collision_time(x[i, 0], x[i, 1], L, V, f)
        if tau1 < tau0:
            tau0, i0 = tau1, i
    # Evaluate position of the next collision and update velocities
    x[i0, 0] = x[i0, 0] + x[i0, 1]*tau0
    L = np.abs(x[i0, 0])
    V0 = V-f*tau0
    x[i0, 1], V = collision(x[i0, 1], V0, M)

```

8. NUMERICAL SIMULATION

```
# Update the position of the non-colliding particles
for i in range(N):
    x[i, 0] = (x[i, 0]+x[i, 1]*tau0 if i != i0 else x[i0, 0] )
# Update time, yield t, L(t)
t += tau0
time.append(t)
ell.append(L)
iteration +=1
return time, ell

def average_L(time, ell):
    """Evaluate the average of L(t)"""
    ell = np.array(ell)
    dt = np.array([(time[i]-time[i-1]) for i in range(1,len(time))])
    L_ave = np.average(ell[1:], weights=dt)
    L_sq = np.average(ell[1:]**2, weights=dt)
    L_sq -= L_ave**2
    L_std = np.sqrt(L_sq/len(time))
    return L_ave, L_std

N = 1000 # Number of particles
T0 = 1. # Initial temperature
p = 10. # Pressure
x0 = 2. # Initial position of the piston
M = 100.0
itermax = 20 # Duration of the simulation (times N)

np.random.seed(1)
time, ell = iterate(N, T0, p, x0, M, 20, mode='gaussian')

plt.plot(time, ell, 'k-')
plt.plot(time, (2*(x0+(1/2))/3)*(N*T0/p)*np.ones_like(time), 'k--')
plt.xlabel('$t$')
plt.ylabel('$L(t)$')
plt.savefig('volume.pdf')

T1 = 1
x0 = 1.
np.random.seed(1)
fp = open('pistonT%g.dat' % T1, 'w')
fp.write('# %d %g %g %d \n' % (N, T1, M, 20))
p = np.logspace(-1, 2, 7)
L = np.zeros((len(p), 2))
K = np.zeros(len(p))
for k in range(len(p)):
    time, ell = iterate(N, T1, p[k], x0, M, 20, mode='gaussian')
    L_ave, L_std = average_L(time, ell)
    fp.write('%g %g %g \n' % (p[k], L_ave, L_std))
    print('p = %g; L = %g +- %g' % (p[k], L_ave, np.sqrt(L_std)))
    L[k, 0] = L_ave
    L[k, 1] = L_std
fp.close()
```

```

plt.plot(p, L[:, 0], 'ko')
plt.plot(p, N*T1/p, 'k-')
plt.xscale('log')
plt.yscale('log')
plt.xlabel('$p$')
plt.ylabel(r'$\langle L \rangle$')
plt.savefig('idealGas.pdf')

```

Experimenting with this system provides the reader with a number of interesting observations:

1. The enthalpy $H = E + pL$ is *exactly* conserved, provided one takes into account also the kinetic energy $\frac{1}{2}MV^2$ of the piston. Since by the equipartition theorem $\frac{1}{2}M \langle V^2 \rangle = \frac{1}{2}k_B T$, one can neglect this correction in N is large enough.
2. The equilibrium state is identified by the value of the pressure p and of the temperature T . The actual equilibrium temperature of the system is given as a function of the initial H by the equation

$$\frac{3N+1}{2}k_B T = H. \quad (8.10)$$

Indeed, each particle contributes $k_B T/2$ to E and $k_B T$ to pL , but the piston only contributes to E .

3. The system does indeed approach equilibrium, but it does so very slowly, and exhibiting oscillations which become more and more damped as N grows.
4. The system is exactly time-reversal invariant. One can check that, if after some time one suddenly reverses all velocities, the system traces back its recent evolution, only to wander away after some time, due to rounding errors.

The algorithm described above is quite slow, because it requires evaluating τ for every particle to update for just one collision. This can be sped up by some heuristics (e.g., by checking only particles close to the piston for collisions). These ideas can be easily put to test in the context of this model.

Solution to exercise 8.2 The Verlet algorithm, once one sets one's time unit such that $\omega_0 = \sqrt{g/\ell} = 1$, is straightforward. Let h be the time increment, and $\theta_i = \theta(ih)$. Then one has

$$\theta_{i+1} = 2\theta_i - \theta_{i-1} - h^2 \sin \theta_i. \quad (8.11)$$

However, the initial conditions should be treated with care. Assuming that they are given in the form (θ_0, v_0) , where $v_0 = \dot{\theta}(0)$, we can estimate from Taylor's series

$$\theta_1 = \theta_0 + hv_0 - \frac{h^2}{2} \sin \theta_0. \quad (8.12)$$

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Then one can start the simulation, confident that the error will be only of order h^3 . To estimate the velocity $v = \dot{\theta}$, however, we need some care. We can use the expression

$$v_{i-1} = \frac{1}{2h} (\theta_i - \theta_{i-2}), \quad (8.13)$$

to obtain a more symmetric expression. Then, however, we will have evaluated v for one less index than θ . We can then use these quantities to evaluate the instantaneous value of the energy $E = 1 - \cos \theta + \frac{1}{2}\dot{\theta}^2$.

This algorithm is implemented in the following Python program.

```
import numpy as np
import matplotlib.pyplot as plt

theta0 = 3.14
v0 = 0.0
h = 0.1

tmax = 35

t = np.arange(0, tmax, h)
N = len(t)
theta = np.zeros(N)
v = np.zeros(N)

theta[0] = theta0
v[0] = v0
theta[1] = theta0 + v0*h - h**2*0.5*np.sin(theta[0])

for i in range(2,N):
    theta[i] = 2*theta[i-1]-theta[i-2]-h**2*np.sin(theta[i-1])
    v[i-1] = 0.5*(theta[i]-theta[i-2])/h

tv = [ 0.5*(t[i]+t[i-1]) for i in range(1, len(t))]

plt.plot(t, theta, 'k-')
plt.plot(tv, v[:-1], 'k--')
plt.plot(t[:-1], 1-np.cos(theta[:-1])+0.5*v[:-1]**2, 'k:')
plt.xlabel('$t$')
plt.ylabel(r'$\theta$, E$')
plt.legend([r'$\theta$', r'$v$', '$E$'], loc = 'lower left')
plt.savefig('pendulum.pdf')

plt.plot(theta[:-1],v[:-1], 'k-')
plt.xlabel(r'$\theta$')
plt.ylabel('$v$')
plt.savefig('phaseGraph.pdf')
```

The results are shown in figure 8.5.

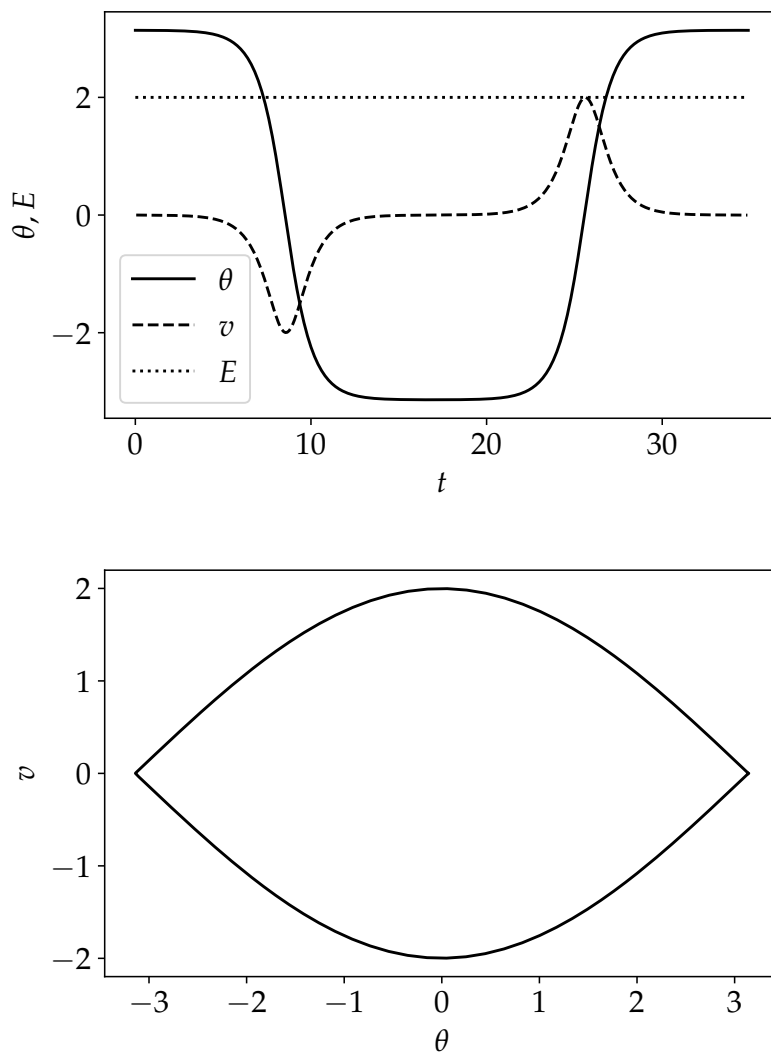


Figure 8.5: Solution of the pendulum equation of motion via the Verlet algorithm. Above: $\theta(t)$, $v(t) = d\theta/dt$ and the corresponding evolution of $E(t)$. Below: trajectory in the (θ, v) plane, showing the periodicity of the motion. The figure corresponds to one level curve of $E(\theta, v)$.

Solution to exercise 8.3

1. The dimensional equations of motion read

$$\frac{d^2 r_i}{dt^2} = \frac{1}{m} [u'(r_{i+1} - r_i) - u'(r_i - r_{i-1})]. \quad (8.14)$$

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Defining

$$x_i = \frac{r_i}{r_0}, \quad \tau = \sqrt{\frac{mr_0^2}{\epsilon_0}}, \quad t_1 = \frac{t}{\tau}, \quad (8.15)$$

we obtain

$$\frac{d^2x_i}{dt_1^2} = [f(x_{i+1} - x_i) - f(x_i - x_{i-1})], \quad (8.16)$$

where

$$f(x) = \frac{6}{x} \left(\frac{2}{x^{12}} - \frac{1}{x^6} \right). \quad (8.17)$$

2. See the program that follows.

3. We have

$$T = \frac{\epsilon_0}{k_B} \left\langle \left(\frac{dx_i}{d\tau} \right)^2 \right\rangle, \quad p = \frac{1}{L} (k_B T + \epsilon_0 \langle (x_{i+1} - x_i) f(x_{i+1} - x_i) \rangle). \quad (8.18)$$

4. We have

$$r_0 = 1.0 \cdot 10^{-10} \text{ m}; \quad \epsilon_0 \approx 1.6 \cdot 10^{-19} \text{ J}; \quad m = 1.0 \cdot 10^{-26} \text{ kg}. \quad (8.19)$$

This yields $\tau \approx 2.5 \cdot 10^{-14}$ s. Running 10000 steps on a system with 100 units with $dt_1 = 10^{-2}$ takes approximately 10 s on a Mac at 4 GHz. This corresponds to approximately $4 \cdot 10^{-12}$ s in real time, on a system of length of approximately 10 nm.

```
import numpy as np
import matplotlib.pyplot as plt

def f(r):
    return (6/r)*(2/r**12-1/r**6)

def u(r):
    return 1/r**12-1/r**6

def force(x0, L):
    N = len(x0)
    f0 = np.zeros(N)
    for i in range(N):
        rp = x0[(i+1)%N] - x0[i]
        rp = rp if rp > 0 else L+rp
        rm = x0[i] - x0[(i-1)%N]
        rm = rm if rm > 0 else L+rm
        f0[i] = -(f(rp)-f(rm))
    return f0

def initialize(N, L, T):
```



```

x0 = np.arange(0, L, L/N)
v0 = np.random.randn(N)*np.sqrt(T)
f0 = force(x0, L)
return x0, v0, f0

def verlet(x0, v0, f0, L, dt):
    N = len(x0)
    x1 = np.zeros(N)
    v1 = np.zeros(N)
    for i in range(N):
        x1[i] = x0[i] + v0[i]*dt + 0.5*f0[i]*dt**2
    f1 = force(x1, L)
    for i in range(N):
        v1[i] = v0[i] + 0.5*dt*(f0[i] + f1[i])
    return x1, v1, f1

def run(N, L0, T, dt, iterations):
    L = L0*N
    x0, v0, f0 = initialize(N, L, T)
    energy = np.zeros(iterations)
    pressure = np.zeros(iterations)
    temp = np.zeros(iterations)
    for k in range(iterations):
        x0, v0, f0 = verlet(x0, v0, f0, L, dt)
        K = np.sum(v0**2)
        temp[k] = K/N
        pressure[k] = K
        U = 0.5*K
        for i in range(N):
            rp = x0[(i+1)%N] - x0[i]
            rp = rp if rp > 0 else L+rp
            U += u(rp)
        pressure[k] += rp*f(rp)
        energy[k] = U
    return temp, energy/N, pressure/L

N = 100
L0 = 1.5
T = 0.5
dt = 1e-3
iterations = 15000
temp, energy, pressure = run(N, L0, T, dt, iterations)

t = np.array(range(iterations))*dt
plt.plot(t, energy, 'k-')
plt.xlabel('$t$')
plt.ylabel('$E/N$')

plt.plot(t, pressure, 'k-')
plt.xlabel('$t$')
plt.ylabel('$p$')

```

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```
plt.plot(t, temp, 'k-')
plt.xlabel('$t$')
plt.ylabel('$T$')
```

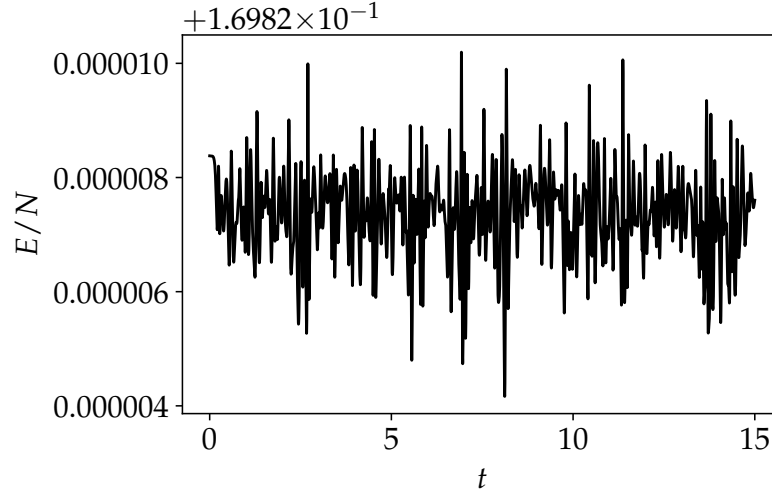


Figure 8.6: Check of energy conservation in the velocity Verlet algorithm for the 1D Lennard-Jones fluid. One sees that the total energy is conserved to the 6-th significant digit. The energy is measured in units ϵ_0 .

Solution to exercise 8.4 Let us assume that the state b can be reached from a_0 via the two different paths $\mathcal{C} = (a_0, a_1, \dots, a_m = b)$ and $\mathcal{C}' = (a_0, a'_1, \dots, a'_m = b)$, such that $W_{ij}, W_{ji} \neq 0$ for each pair (ij) appearing in each path. According to \mathcal{C} , we can assign b the probability

$$p_b = \frac{W_{ba_{n-1}} \cdots W_{a_1 a_0}}{W_{a_{n-1} b} \cdots W_{a_0 a_1}} p_{a_0}. \quad (8.20)$$

According to \mathcal{C}' we can assign it the probability

$$p'_b = \frac{W_{ba'_{m-1}} \cdots W_{a'_1 a_0}}{W_{a'_{m-1} b} \cdots W_{a_0 a'_1}} p_{a_0}. \quad (8.21)$$

The ratio between these two probabilities is given by

$$\frac{p_b}{p'_b} = \frac{W_{a_0 a'_1} W_{a'_1 a'_2} \cdots W_{a'_{m-1} b} W_{ba_{n-1}} W_{a_{n-1} a_{n-2}} \cdots W_{a_1 a_0}}{W_{a_0 a_1} W_{a_1 a_2} \cdots W_{a_{n-1} b} W_{ba'_{m-1}} W_{a'_{m-1} a'_{m-1}} \cdots W_{a'_1 a_0}}. \quad (8.22)$$

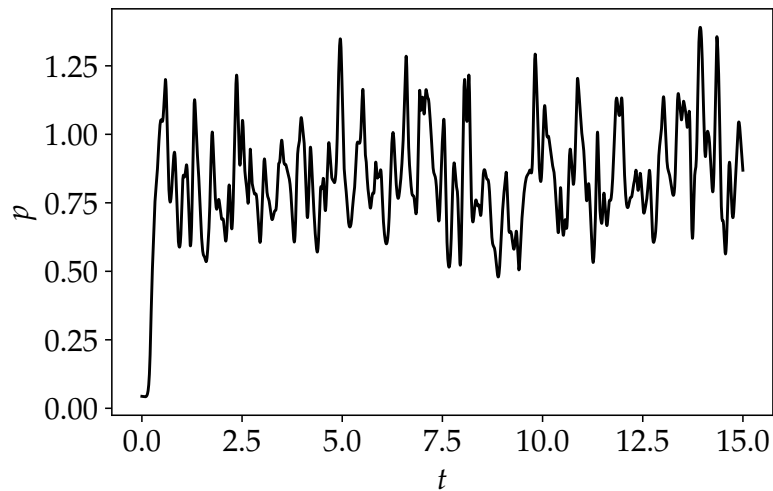


Figure 8.7: Pressure (in units ϵ_0/r_0) in the velocity Verlet algorithm for the 1D Lennard-Jones fluid.

The indices in the numerator (going from right to left) start from a_0 and reach b following \mathcal{C} , then return to a_0 following \mathcal{C}' in the reverse order. Those in the denominator run the same loop in reverse. If we assume that \mathcal{C} and \mathcal{C}' have no point in common other than the endpoints, the ratio is equal to 1 by the detailed-balance assumption. Otherwise the loop decomposes into several loops joined at the common points, and for each of these loops the contribution of the numerator cancels with that of the denominator by the detailed-balance assumption.

Solution to exercise 8.5 We can consider the Metropolis algorithm for a one-dimensional model at $T = 0$. Let the configuration σ be $\sigma_i = +1$ for $i < 0$ and $\sigma_i = -1$ for $i \geq 0$. We first update the spins with even indices, and then those with odd indices. Then with probability $\frac{1}{2}$ the spin σ_0 is flipped in the first half step, and with probability $\frac{1}{2}$ the same happens to spin σ_1 in the second half step. All other spins cannot flip. We thus obtain the configuration σ' , in which $\sigma_i = +1$ for $i \leq 1$ and -1 otherwise. But the spin σ_0 cannot flip from configuration σ' in the first half step. Thus the probability that $\sigma \rightarrow \sigma'$ is equal to $\frac{1}{4}$ and the probability that $\sigma' \rightarrow \sigma$ vanishes.

Solution to exercise 8.6 (Microcanonical Ensemble) Following a suggestion by M. Creutz (Creutz [1983]), one can introduce an extra degree of freedom (a “de-

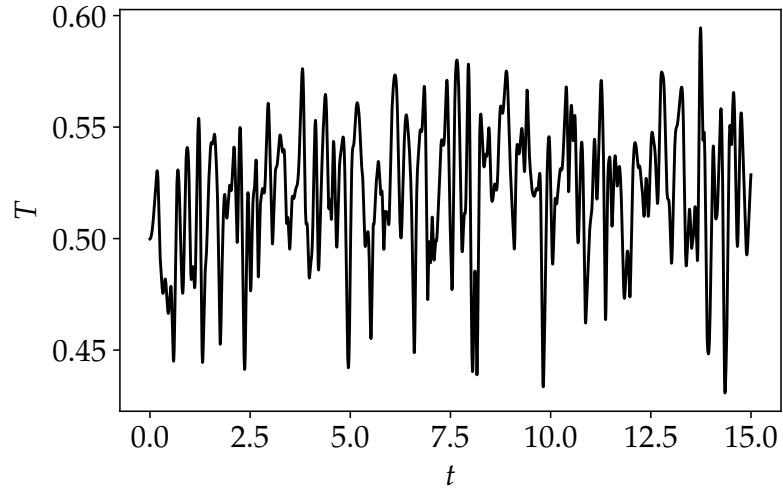


Figure 8.8: Observed temperature $T = m \langle v^2 \rangle$ (in units ϵ_0/k_B) in the velocity Verlet algorithm for the 1D Lennard-Jones fluid.

mon”) which transfers energy as it changes dynamical variables. Let E_D be the energy carried by the demon. The algorithm then proceeds as with the ordinary Metropolis algorithm: given a configuration σ with energy $H(\sigma)$, a different configuration σ' with energy $H(\sigma')$ is generated. The new configuration is accepted if $E'_D = E_D - (H(\sigma') - H(\sigma))$ lies within the interval $[0, \Delta E]$. Then E_D is set equal to E'_D and the algorithm is iterated. In this way one simulates the microcanonical sum

$$Z = \sum_{\sigma} \sum_{E_D \in [0, \Delta E]} \delta [H(\sigma) + E_D - E]. \quad (8.23)$$

By standard statistical mechanics arguments, the demon’s energy will be exponentially distributed, $p(E_D) \propto e^{-E_D/k_B T}$. Thus, if ΔE is macroscopic, the upper bound on E_D can be safely set to infinity. Then one can estimate the temperature of the system from $\langle E_D \rangle$. For the case of an Ising model, in which energy values are of the form $4nJ$, where n is an integer, we have

$$\frac{1}{k_B T} = \frac{1}{4J} \log \left(1 + \frac{4J}{\langle E_D \rangle} \right). \quad (8.24)$$

For a continuous system where the energy can take any positive value, this simplifies to

$$k_B T = \langle E_D \rangle. \quad (8.25)$$

Solution to exercise 8.7 (One-Dimensional Ising Model) The following Python program solves the exercise. Notice that to evaluate the specific heat, we use the expression

$$\langle E \rangle_{\beta+d\beta} = \frac{1}{Z'} \sum_{i=1}^{\mathcal{N}\mathcal{N}} H(\sigma_i) e^{-d\beta H(\sigma_i)}, \quad (8.26)$$

where

$$Z' = \sum_{i=1}^{\mathcal{N}\mathcal{N}} H(\sigma_i) e^{-d\beta H(\sigma_i)}, \quad (8.27)$$

and the configurations σ_i are evaluated with a weight proportional to $e^{-\beta H(\sigma_i)}$ by the Metropolis algorithm. We then have

$$\frac{C}{k_B} \simeq -\beta^2 \frac{\langle E \rangle_{\beta+d\beta} - \langle E \rangle_{\beta}}{d\beta}. \quad (8.28)$$

```
import numpy as np
import matplotlib.pyplot as plt

def weight(w, u):
    """Lookup table for the weights"""
    W = np.zeros((2, 3))
    for s in [-1, 1]:
        for mm in [-2, 0, 2]:
            W[(s+1)//2, (mm+2)//2] = (w**mm*u)**s
    return W

def mtheo(beta, h):
    """Theoretical value of the magnetization per spin"""
    return (np.exp(beta)*np.sinh(beta*h))/np.sqrt(np.exp(-2*beta)+np.
        exp(2*beta)*np.sinh(beta*h)**2)

def etheo(beta, h):
    """Theoretical value of the energy per spin"""
    qw = np.exp(-2*beta)+np.exp(2*beta)*np.sinh(beta*h)**2
    w = np.exp(3*beta)*np.cosh(beta*h)*np.sqrt(qw)+np.exp(4*beta)*np.
        sinh(beta*h)**2
    return (1-w)/(1+w)

def cstheo(beta, h, dbeta):
    """Specific heat by direct differentiation"""
    return -beta**2*(etheo(beta + dbeta, h)-etheo(beta,h))/dbeta

def simulate(beta, h, n, tf, t0):
    sigma = np.random.choice([-1, 1], size=n)

    w = np.exp(-2*betaw[q])
    u = np.exp(-2*betaw[q]*h)
```

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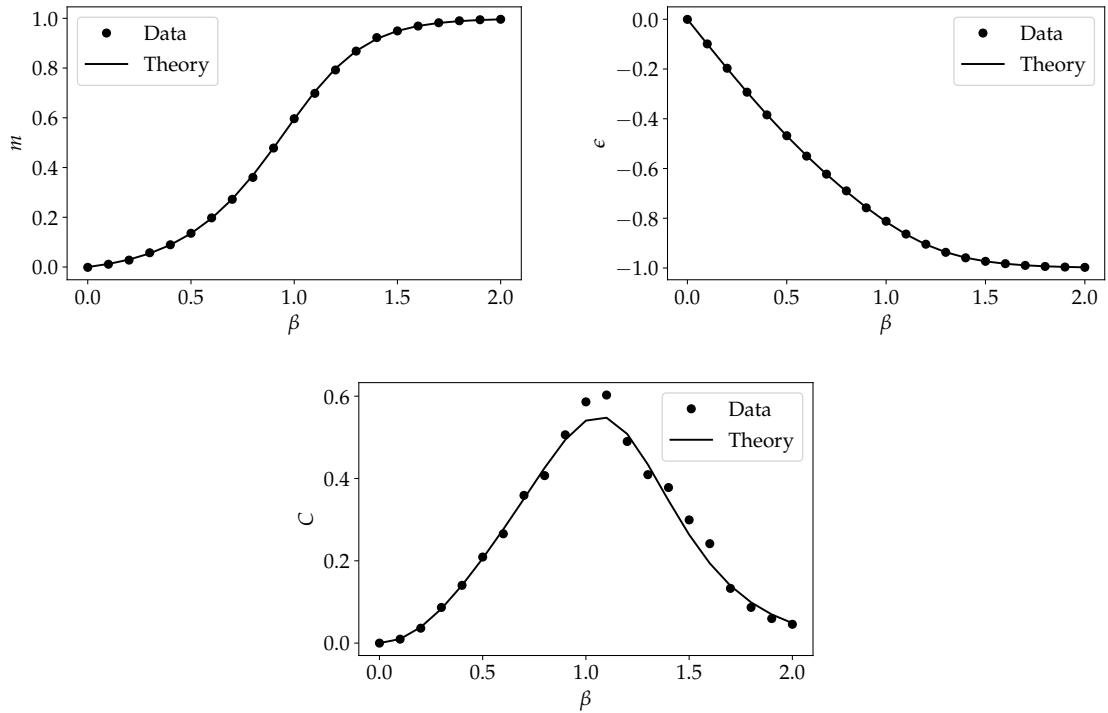


Figure 8.9: Simulation of the 1D Ising model. Above: Left: Magnetization per spin $\langle \sigma_i \rangle$. Right: Internal energy per spin $-\langle \sigma_i \sigma_{i+1} \rangle$. The theoretical values are also plotted. Bottom: Specific heat. Number of spins $N = 1000$, applied field $h = 0.1$. Units are such that $k_B = 1$. Notice that the sampling errors are larger for the specific heat than for the magnetization and internal energy.

```

W = weight(w, u)

mtot = 0
etot = 0
ntot = 0
ztot = 0
eltot = 0

for t in range(tf+t0):
    rnd = np.random.rand(n)
    for i in range(n):
        k = np.random.randint(n)
        mm = sigma[(k+1) % n] + sigma[(k-1) % n]
        if rnd[i] < W[(sigma[k]+1)//2, (mm+2)//2] :
            sigma[k]*=-1
        else:
            pass
    if t > t0 :
        m = np.sum(sigma)

```

```

        ek = - np.sum([sigma[ell]*sigma[(ell+1) % n] for ell in
                                range(n) ])

        dw = np.exp(-dbeta*(ek - h*m))
        mtot += m/n
        etot += ek/n
        ntot += 1
        ztot += dw
        eltot += (ek/n)*dw

    magn = mtot/ntot
    en = etot/ntot
    en1 = eltot/ztot

    # Evaluation of the specific heat
    cs = -betaw[q]**2*(en1-en)/dbeta

    return magn, en, cs

n = 1000
h = 0.1
tf = 1500
t0 = 500

dbeta = 1.0e-2 # Temperature increment for evaluating the specific
               heat
np.random.seed(1) # For reproducibility

# Theoretical value of the specific heat by direct differentiation
betaQ = np.linspace(0, 2.0, 101)
C = np.zeros_like(betaQ)
for q in range(len(betaQ)):
    C[q] = -betaQ[q]**2*(etheo(betaQ[q]+dbeta,h)-etheo(betaQ[q],h))/
           dbeta

betaw = np.linspace(0, 2.0, 21)
magn = np.zeros(len(betaw))
magn_theo = np.zeros(len(betaw))
en = np.zeros(len(betaw))
en_theo = np.zeros(len(betaw))
cs = np.zeros_like(betaw)
cs_theo = np.zeros_like(betaw)

fp = open('ising1D.dat', 'w')
fp.write('# %d %g %g %g \n' % (n, h, tf, t0))
for q in range(len(betaw)):

    magn[q], en[q], cs[q] = simulate(betaw[q], h, n, tf, t0)
    magn_theo[q] = mtheo(betaw[q], h)
    en_theo[q] = etheo(betaw[q], h)
    cs_theo[q] = cstheo(betaw[q], h, dbeta)

    print('beta = %g; m = %g (mtheo = %g); e = %g (etheo = %g); cs = %g

```

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```

                                (cstheo = %g)' %
    (betaw[q], magn[q], magn_theo[q], en[q], en_theo[q], cs[q],
                                cs_theo[q]))
    fp.write('%g %g %g %g %g %g %g\n' % (betaw[q], magn[q], magn_theo[
                                q], en[q], en_theo[q], cs[q],
                                cs_theo[q]))
fp.close()

plt.plot(betaw, magn, 'ko'),
plt.plot(betaw, magn_theo, 'k-')
plt.xlabel(r'$\beta$')
plt.ylabel('$m$')
plt.legend(["Data", "Theory"])
plt.savefig('magn1D.pdf')

plt.plot(betaw, en, 'ko')
plt.plot(betaw, en_theo, 'k-')
plt.xlabel(r'$\beta$')
plt.ylabel('$\epsilon$')
plt.legend(["Data", "Theory"])
plt.savefig('en1D.pdf')

plt.plot(betaw, cs, 'ko')
plt.plot(betaw, cs_theo, 'k-')
plt.xlabel(r'$\beta$')
plt.ylabel('$C$')
plt.legend(["Data", "Theory"])
plt.savefig('specHeat.pdf')

```

Solution to exercise 8.8 Running the Monte Carlo simulation we collect a sequence $E = (E_i)$ of \mathcal{N} energy values at a given value of β . We then estimate $\langle E \rangle_\beta$ by

$$\langle E \rangle_\beta = \frac{1}{\mathcal{N}} \sum_{i=1}^{\mathcal{N}} E_i, \quad (8.29)$$

and

$$\langle E \rangle_{\beta+d\beta} = \frac{1}{Z} \sum_{i=1}^{\mathcal{N}} E_i e^{-d\beta E_i}, \quad (8.30)$$

where

$$Z = \sum_{i=1}^{\mathcal{N}} e^{-d\beta E_i}. \quad (8.31)$$

The specific heat is then obtained by

$$C = \frac{1}{Nk_B} \frac{\beta^2}{d\beta} \left(\langle E \rangle_{\beta+d\beta} - \langle E \rangle_\beta \right). \quad (8.32)$$

We can also check the relation

$$\frac{1}{d\beta} \left(\langle E \rangle_{\beta+d\beta} - \langle E \rangle_{\beta} \right) = \langle E^2 \rangle_{\beta} - \langle E \rangle_{\beta}^2. \quad (8.33)$$

The problem is solved by the following Python program.

```
import numpy as np
import matplotlib.pyplot as plt

def run(beta, dbeta, n, iterations, interval):
    """Umbrella sampling for the evaluation of the specific heat in the
        1D Ising model

    One evaluates the system energy at the inverse temperature beta and
    one reweights
    it at the temperature beta+dbeta. Then the energy difference is
    evaluated."""

    sigma = np.random.choice((-1, +1), size=n) # Initial configuration

    ener = np.zeros(iterations) # Sampled energies at beta
    ener1 = np.zeros(iterations) # Sampled energies at beta+dbeta
    z1 = np.zeros(iterations)

    for k in range(iterations):
        for tau in range(interval):
            index = np.random.choice(range(n), size=n)
            w = np.random.rand(n)
            for i in range(n):
                j = index[i] # Random choice of spin to update
                sm = sigma[j]*(sigma[(j+1)%n] + sigma[(j-1)%n])
                if sm < 0 or w[i] < np.exp(-2*beta*sm): # Monte Carlo
                    update
                    sigma[j] *= -1
            en = 0 # Evaluating the energy
            for ell in range(n):
                en -= sigma[ell]*sigma[(ell+1)%n]
            ener[k] = (en/n) # Storing the energy per spin
            ener1[k] = (en/n)*np.exp(-dbeta*en) # Reweighting the sampled
                energy
            z1[k] = np.exp(-dbeta*en) # Normalization factor for the
                reweighting

    ener = np.array(ener)
    ener1 = np.array(ener1)
    z1 = np.array(z1)
    energy = np.sum(ener)/len(ener)
    var_energy = np.sum(ener*ener)/len(ener)-energy**2
    energy1 = np.sum(ener1)/sum(z1)
    var_energy1 = np.sum(ener1*ener1)/sum(z1)-energy1**2
    spec_heat = beta**2*((energy - energy1))/dbeta # Specific heat
        from direct differentiation
```

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```
    return energy, var_energy, energy1, var_energy1, spec_heat

# Theoretical value of the energy per spin
def etheo(beta):
    return -np.tanh(beta)

# Theoretical value of the specific heat (at h=0)
def ctheo(beta):
    return beta**2*(1-np.tanh(beta)**2)

n = 100
dbeta = 0.1/n
tmax = 1000
interval = 10

npoints = 26
beta = np.linspace(0,2.5, npoints)
energy = np.zeros(npoints)
var_energy = np.zeros(npoints)
energy1 = np.zeros(npoints)
var_energy1 = np.zeros(npoints)
specHeat = np.zeros(npoints)
eny = np.zeros(npoints)
c = np.zeros(npoints)

for kk in range(len(beta)) :

    energ, var_energ, energ1, var_energ1, spec_heat = run(beta[kk],
                                                            dbeta, n, tmax, interval)

    energy[kk] = energ
    var_energy[kk] = var_energ
    energy1[kk] = energ1
    var_energy1[kk] = var_energ1
    specHeat[kk] = spec_heat
    eny[kk] = etheo(beta[kk])
    c[kk] = ctheo(beta[kk])

# Comparing results

# Specific heat by differentiation vs. theory
plt.plot(beta, specHeat, 'ko', label='Data')
plt.plot(beta, c, 'k--', label='Theory')
plt.xlabel(r"$\beta$")
plt.ylabel(r"$C$")
plt.legend(loc=8)

# Comparing energy fluctuations with specific heat
plt.plot(specHeat/beta**2, n*var_energy[:,], 'ko')
t = np.linspace(0, 1, npoints)
plt.plot(t, t, 'k--')
```

```
plt.xlabel(r'$C/\beta^2$')
plt.ylabel(r'$\left\langle\Delta E^2\right\rangle$')
```

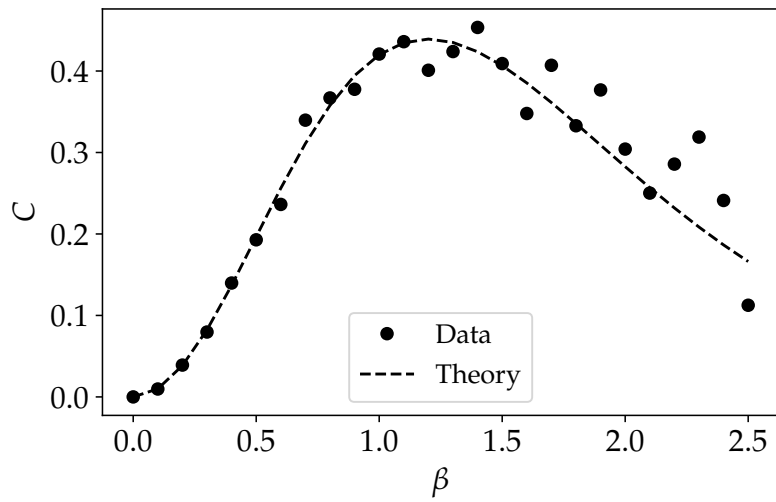


Figure 8.10: Specific heat of the 1D Ising model, obtained by umbrella sampling, vs. the theoretical prediction.

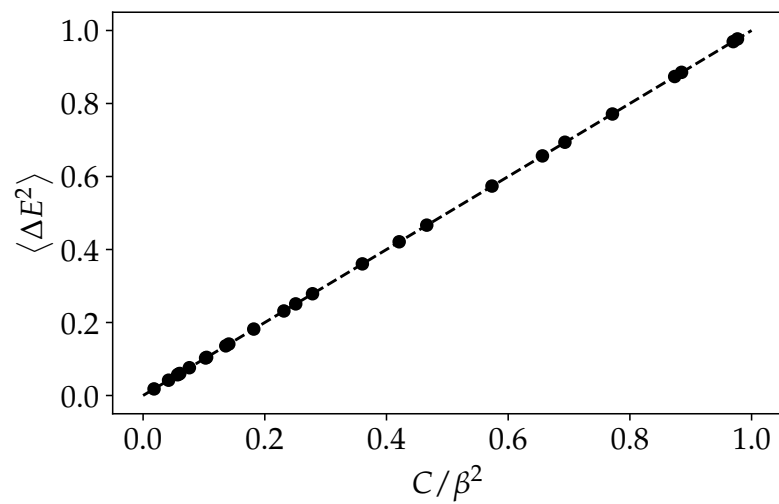


Figure 8.11: Comparison of the energy fluctuations obtained in the Monte Carlo sampling with the specific heat obtained by the umbrella sampling. The dashed line corresponds to $y = x$.

Dynamics

Solution to exercise 9.1 Let us define

$$I = \langle F(\xi) \rangle = \int d\xi_1 \cdots d\xi_n P(\xi) F(\xi), \quad (9.1)$$

where $P(\xi)$ is the probability distribution function of ξ . Let us change the integration variable by setting $\xi = \xi' - c$, where c is an arbitrary constant n -dimensional vector. Then we have

$$I = \int d\xi'_1 \cdots d\xi'_n P(\xi + c) F(\xi + c). \quad (9.2)$$

Since the rhs does not depend on c , we have $\partial I / \partial c_j|_{c=0} = 0$, i.e.,

$$\int d\xi_1 \cdots d\xi_n \left[\frac{\partial P}{\partial \xi_j} F(\xi) + \frac{\partial F}{\partial \xi_j} P(\xi) \right] = 0. \quad (9.3)$$

Now, for a Gaussian distribution with zero average one has

$$\frac{\partial P}{\partial \xi_j} = - \sum_k C_{jk}^{-1} \xi_k P(\xi). \quad (9.4)$$

Thus we have

$$- \sum_j C_{jk}^{-1} \langle \xi_k F(\xi) \rangle + \left\langle \frac{\partial F}{\partial \xi_j} \right\rangle = 0. \quad (9.5)$$

Multiplying both sides by C_{ij} and summing over j we obtain

$$\langle \xi_i F(\xi) \rangle = \sum_j C_{ij} \left\langle \frac{\partial F}{\partial \xi_j} \right\rangle. \quad (9.6)$$

Solution to exercise 9.2 From the condition

$$\frac{d\langle[A]\rangle}{dt} = \frac{d\langle[B]\rangle}{dt} = 0, \quad (9.7)$$

we obtain

$$\frac{\langle[A]\rangle}{\langle[B]\rangle} = \frac{k_{BA}}{k_{AB}}. \quad (9.8)$$

Since we have

$$c = [A] + [B] = \text{const.}, \quad (9.9)$$

we obtain

$$\Delta c_A = [A] - \langle[A]\rangle = -c_B = [B] - \langle[B]\rangle. \quad (9.10)$$

Thus Δc_A satisfies the equation

$$\frac{d\Delta c_A}{dt} = -(k_{AB} + k_{BA}) \Delta c_A, \quad (9.11)$$

whose solution reads

$$\Delta c_A(t) = \Delta c_A(0) e^{-t/\tau}, \quad t > 0, \quad (9.12)$$

with

$$\tau^{-1} = k_{AB} + k_{BA}. \quad (9.13)$$

Solution to exercise 9.3 We have

$$\frac{d}{dt} \Delta R^2(t) = \int d^d \mathbf{r} r^2 \frac{\partial}{\partial t} P(\mathbf{r}, t | 0, 0) = \int d^d \mathbf{r} r^2 D \nabla^2 P(\mathbf{r}, t | 0, 0). \quad (9.14)$$

We integrate twice by parts. The boundary terms vanish because $P(\mathbf{r}, t | 0, 0)$ vanishes at infinity. On the other hand we have

$$\nabla^2 r^2 = \sum_{i=1}^d \frac{\partial^2}{\partial x_i^2} \left(\sum_{j=1}^d x_j^2 \right) = 2d. \quad (9.15)$$

Thus we obtain

$$\frac{d\Delta R^2}{dt} = 2dD. \quad (9.16)$$

Solution to exercise 9.4 Since we have

$$\frac{d}{dt} \Delta R^2(t) = 6D, \quad (9.17)$$

and, on the other hand,

$$\int_0^\infty dt' \langle \mathbf{v}(t') \cdot \mathbf{v}(0) \rangle = \langle v^2 \rangle \int_0^\infty dt' e^{-t'/\tau} = \langle v^2 \rangle \tau, \quad (9.18)$$

we obtain

$$D = \frac{1}{3} \langle v^2 \rangle \tau. \quad (9.19)$$

From equipartition we obtain

$$\langle v^2 \rangle = \frac{3k_B T}{m} \quad (9.20)$$

yielding

$$\tau = \frac{mD}{k_B T}. \quad (9.21)$$

Taking $m = 18 \text{ amu}$ (as for water), $D \simeq 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, i.e., $D \simeq 10^{-9} \text{ m}^2 \text{ s}^{-2}$, we obtain $\tau \simeq 7 \cdot 10^{-15} \text{ s}$, at 300 K, i.e., 7 femtoseconds.

Solution to exercise 9.5 The pdf of the displacement \mathbf{r} is given by

$$P(\mathbf{r}, t | 0, 0) = \frac{1}{\sqrt{\pi Dt}} \exp\left(-\frac{r^2}{Dt}\right). \quad (9.22)$$

Denoting by r_0 a distance of 5 \AA , the probability that a particle moves by more than r_0 in time t is given by

$$p(r_0, t) = \int_{r_0}^\infty 4\pi r^2 dr P(\mathbf{r}, t | 0, 0). \quad (9.23)$$

We have

$$Dt \simeq 10^{-9} \text{ m}^2 \text{ s}^{-1} \cdot 15 \cdot 10^{-12} \text{ s} \simeq 1.5 \cdot 10^{-20} \text{ m}^2. \quad (9.24)$$

On the other hand we have

$$r_0^2 \simeq (5 \cdot 10^{-10})^2 \text{ m}^2 = 25 \cdot 10^{-20} \text{ m}^2. \quad (9.25)$$

We have therefore

$$\frac{r_0^2}{Dt} \simeq 16.7 \gg 1. \quad (9.26)$$

Thus the order of magnitude of $p(r_0, t)$ is $e^{-16.7} \simeq 6 \cdot 10^{-8}$.

Solution to exercise 9.6 At equilibrium, we have

$$c_1^* = \frac{k_{13}c_3^*}{k_{31}}; \quad (9.27)$$

$$c_2^* = \frac{k_{23}c_3^*}{k_{32}}; \quad (9.28)$$

$$c_3^* = \frac{c}{1 + (k_{12}/k_{31}) + (k_{23}/k_{32})}. \quad (9.29)$$

Defining

$$\Delta c_i(t) = c_i(t) - c_i^*, \quad i = 1, 2, \quad (9.30)$$

we obtain the rate equations

$$\frac{d}{dt} \begin{pmatrix} \Delta c_1 \\ \Delta c_2 \end{pmatrix} = \mathbf{K} \begin{pmatrix} \Delta c_1 \\ \Delta c_2 \end{pmatrix}, \quad (9.31)$$

where

$$\mathbf{K} = \begin{pmatrix} k_{31} + k_{13}, & k_{13} \\ k_{23}, & k_{32} + k_{23} \end{pmatrix}. \quad (9.32)$$

From the detailed-balance condition we have

$$\frac{k_{31}}{k_{13}} = e^{-\beta Q'}; \quad \frac{k_{32}}{k_{23}} = e^{-\beta Q}. \quad (9.33)$$

Thus we have $k_{31}, k_{32} \ll k_{13}, k_{23}$. The eigenvalues of \mathbf{K} are given by

$$\begin{aligned} \lambda_{\pm} &= (k_{31} + k_{13} + k_{21} + k_{12}) \pm \sqrt{[(k_{31} + k_{13}) - (k_{21} + k_{12})]^2 / 4 + k_{13}k_{23}} \\ &= \frac{1}{2} (k_{31} + k_{13} + k_{21} + k_{12}) \left[1 \pm \sqrt{1 - \frac{k_{31}k_{32} + k_{31}k_{23} + k_{13}k_{32}}{[(k_{31} + k_{13} + k_{21} + k_{12})/2]^2}} \right] \\ &\simeq \frac{1}{2} (k_{31} + k_{13} + k_{21} + k_{12}) \left\{ 1 \pm \left[1 - \frac{1}{2} \frac{k_{31}k_{32} + k_{31}k_{23} + k_{13}k_{32}}{[(k_{31} + k_{13} + k_{21} + k_{12})/2]^2} \right] \right\}. \end{aligned} \quad (9.34)$$

Thus we have, to lowest nontrivial order,

$$\lambda_+ \simeq k_{13} + k_{23}; \quad (9.35)$$

$$\lambda_- \simeq \frac{k_{31}k_{23} + k_{13}k_{32}}{k_{13} + k_{23}} \ll \lambda_+. \quad (9.36)$$

(a) We obtain therefore

$$\Delta c_1(t) = A e^{-\lambda_+ t} + B e^{-\lambda_- t}, \quad (9.37)$$

where the constants A and B depend on the initial conditions.

(b) For $\lambda_+ t \gg 1$ we have

$$\Delta c_1(t) \simeq B e^{-t/\tau}, \quad (9.38)$$

with

$$\tau^{-1} \simeq \frac{k_{31}k_{23} + k_{32}k_{13}}{k_{13} + k_{23}}, \quad (9.39)$$

which is a time of order $e^{\beta Q}$ or $e^{\beta Q'}$.

(c) As mentioned above, the transient behavior takes place on times of order λ_+^{-1} , i.e., $(k_{13} + k_{23})^{-1}$.

Solution to exercise 9.7 From the detailed balance we have

$$\frac{k_{21}}{k_{12}} = e^{-\beta \Delta V_{21}}; \quad \frac{k_{32}}{k_{23}} = e^{-\beta \Delta V_{32}}, \quad (9.40)$$

where

$$V_{ij} = V(q_i) - V(q_j), \quad i, j = 1, 2, 3, \quad (9.41)$$

and q_i corresponds to the minimum of $V(q)$ in region i . Thus we have, e.g.,

$$k_{12} = \omega_1; \quad k_{21} = \omega_1 e^{-\beta \Delta V_{21}}; \quad k_{23} = \omega_2; \quad k_{32} = \omega_2 e^{-\beta \Delta V_{23}}. \quad (9.42)$$

Here ω_1 and ω_2 depend on the height of the potential barriers between 1 and 2, and 2 and 3 respectively.

Solution to exercise 9.8 Since $A(t)$ satisfies the harmonic oscillator equations of motion, we have

$$A(t) = A(0) \cos \omega_0 t + \frac{\dot{A}(0)}{\omega_0} \sin \omega_0 t. \quad (9.43)$$

On the other hand, we have

$$p^{\text{eq}}(A, \dot{A}) = \frac{e^{-\beta \mathcal{H}(A, \dot{A})}}{Z} = \frac{e^{-\beta m(\omega_0^2 A^2 + \dot{A}^2)/2}}{Z}. \quad (9.44)$$

Thus we have $\langle A \rangle = 0$ and

$$\langle A(t)A(0) \rangle = \langle A^2(0) \rangle \cos^2 \omega_0 t = \langle \delta A^2 \rangle \cos \omega_0 t. \quad (9.45)$$

Solution to exercise 9.9 The primary variable $x(t)$ drives the bath, and the driven bath affects the primary variable through the force

$$\begin{aligned}
 f(t) &= f_b(t) + \int_{-\infty}^{\infty} dt' \chi_b(t-t') x(t') \\
 &= f_b(t) - \beta \int_{-\infty}^t dt' \left[\frac{d}{d(t-t')} C_b(t-t') \right] x(t') \\
 &= f_b(t) + \beta C_b(0) x(t) - \beta C_b(0) x(t) - \beta \int_0^t dt' C_b(t-t') \dot{x}(t').
 \end{aligned} \tag{9.46}$$

Now we have

$$\langle f_b(t) \rangle |_{x(0), \dot{x}(0) \text{ fixed}} = \left\langle f_b(t; x, \dot{x}, \{y, \dot{y}\}) e^{\beta x f} \right\rangle_b \frac{1}{\langle e^{\beta x f} \rangle_b}. \tag{9.47}$$

This equation follows from the fact that the distribution of the initial variables for the bath differs by the factor $e^{\beta x f}$ from that holding when the bath is isolated. Assuming that the y_i 's are the primary modes of the bath, each evolving with its frequency ω_i , we obtain

$$\begin{aligned}
 \langle f_b(t) \rangle |_{x(0), \dot{x}(0) \text{ fixed}} &= \sum_i c_i \left\langle \left[y_i \cos \omega_i t + \frac{\dot{y}_i}{\omega_i} \sin \omega_i t \right] e^{\beta x c_i y_i} \right\rangle_b \frac{1}{\langle e^{\beta x f} \rangle_b} \\
 &= \sum_i c_i \cos \omega_i t \frac{\partial}{\partial \beta x c_i} \log \langle e^{\beta x c_i y_i} \rangle_b \\
 &= \beta x \sum_i c_i^2 \langle y_i^2 \rangle_b \cos \omega_i t = \beta x C_b(t),
 \end{aligned} \tag{9.48}$$

where the last equality stems from the fact that the y_i 's are independent classical oscillators and obey a Gaussian distribution, and since $\langle y_i y_j \rangle_b = \langle y_i^2 \rangle_b \delta_{ij}$, yielding

$$\sum_{i,j} c_i c_j \langle y_i y_j \rangle_b \cos \omega_j t = \sum_i c_i^2 \langle y_i^2 \rangle_b \cos \omega_i t. \tag{9.49}$$

By combining eq. (9.46) and eq. (9.48) with Newton's law and averaging over initial conditions we obtain the generalized Langevin equation.

Complex Systems

Solution to exercise 10.1 (Polymer over Lattice) Let us first consider $\Gamma_N(\mathbf{r})$, defined as the number of paths of a polymer of length N that reaches point \mathbf{r} starting from the origin. This quantity satisfies the recursion relation

$$\Gamma_{N+1}(\mathbf{r}) = \sum_{a=1}^d \Gamma_N(\mathbf{r} - a_0 \mathbf{e}_a), \quad (10.1)$$

since to reach \mathbf{r} in $(N + 1)$ steps the path must reach in N steps one of its neighbors. Multiplying both sides by $e^{i\mathbf{k} \cdot \mathbf{r}}$ and summing, we obtain

$$\tilde{\Gamma}_{N+1}(\mathbf{k}) = \left(2 \sum_{a=1}^d \cos(a_0 k_a) \right) \tilde{\Gamma}_N(\mathbf{k}), \quad (10.2)$$

where we have taken into account that $\mathbf{k} \cdot \mathbf{e}_a = k_a$ ($a = 1, \dots, d$). Given the initial condition $\Gamma_0(\mathbf{r}) = \delta_{\mathbf{r},0}$ one obtains

$$\tilde{\Gamma}_N(\mathbf{k}) = \left[2 \sum_{a=1}^d \cos(a_0 k_a) \right]^N. \quad (10.3)$$

Thus we have

$$\tilde{\Gamma}_{\text{GC}}(\mathbf{k}, z) = \sum_{N=0}^{\infty} z^N \tilde{\Gamma}_N(\mathbf{k}) = \left[1 - 2z \sum_{a=1}^d \cos(a_0 k_a) \right]^{-1}. \quad (10.4)$$

For $|x| \ll 1$ one has $\cos x \simeq 1 - \frac{x^2}{2}$. Thus, for $|k| \ll a_0^{-1}$ one has

$$\tilde{\Gamma}_{\text{GC}}(\mathbf{k}, z) \simeq \left[1 - z \left(2d - k^2 a_0^2 \right) \right]^{-1}. \quad (10.5)$$

This expression is equivalent to

$$\tilde{\Gamma}_{\text{GC}}(\mathbf{k}, z) \simeq \frac{1/(2d)}{1/(2d) - z + za_0^2 k^2}, \quad (10.6)$$

so that we can set (for $z \simeq z_c$)

$$z_c = \frac{1}{2d}; \quad c = \frac{a_0^2}{2d}. \quad (10.7)$$

Solution to exercise 10.2 Use the relation

$$f_N = \oint \frac{dz}{2\pi i} z^{-(N+1)} f(z), \quad (10.8)$$

between $f(z) = \sum_N z^N f_N$ and its Taylor coefficients. Since $f(z)$ has a cut from z_c to infinity, with a discontinuity proportional to $|z - z_c|^{-\gamma}$, one can change the path of integration to move along the cut. The integral is thus transformed to

$$f_N \propto \int_{z_c}^{\infty} dz z^{-(N+1)} (z - z_c)^{-\gamma}. \quad (10.9)$$

Set $z = z_c e^w$ so that the integral becomes

$$z_c^{\gamma-(N+1)} \int_0^{\infty} dw e^{-Nw} (e^w - 1)^{-\gamma}. \quad (10.10)$$

The singularity appears for $w \rightarrow 0$. One then has $e^w - 1 \simeq w$. Then we have

$$f_N \propto z_c^{-N} \int_0^{\infty} dw e^{-Nw} w^{-\gamma} = z_c^{-N} \Gamma_E(1 - \gamma) N^{\gamma-1}, \quad (10.11)$$

where $\Gamma_E(z)$ is Euler's gamma function.

It is easier to show the converse. Assume $\Gamma_N \sim z_c^{-N} N^{\gamma-1}$, and define $\Gamma(z)$ by

$$\Gamma(z) = \sum_N z^N \Gamma_N. \quad (10.12)$$

Then

$$\Gamma(z) \sim \sum_N \left(\frac{z}{z_c} \right)^N N^{\gamma-1}. \quad (10.13)$$

For $z \simeq z_c$ we can set $w = -\log(z/z_c)$ and (since the summand is slowly varying) approximate the sum by an integral:

$$\Gamma(z) \sim \int_0^{\infty} dN e^{-Nw} N^{\gamma-1} = \Gamma_E(\gamma) w^{-\gamma}. \quad (10.14)$$

When $z \simeq z_c$ one has $w \simeq (z_c - z)/z_c$ and the result follows.

Solution to exercise 10.3 For $|k| a_0 \ll 1$ one has

$$\tilde{\Gamma}_{\text{GC}}(\mathbf{k}, z) \sim \frac{1}{z_c - z + ck^2}. \quad (10.15)$$

To simplify the discussion, let us set $z_c - z = ct$, with $t > 0$. Then we have

$$\tilde{\Gamma}_{\text{GC}}(\mathbf{k}, z) \propto \frac{1}{t + k^2}, \quad (10.16)$$

and

$$\Gamma(0, z) \propto I_d(t) = \int_{\text{Z.B.}} \frac{d^d \mathbf{k}}{t + k^2}. \quad (10.17)$$

For $d > 2$ the integral converges for $t = 0$. We can thus evaluate $I'_d(t) = dI_d/dt$, and set

$$I_d(t) = I_d(0) + \int_0^t dt' I'_d(t'), \quad (10.18)$$

where

$$I'_d(t) = - \int_{\text{Z.B.}} \frac{d^d \mathbf{k}}{(t + k^2)^2}. \quad (10.19)$$

For $d < 4$ the integral converges if the upper integration limit is moved to infinity. Thus we have

$$I'_d(t) = - \int \frac{d\mathbf{k}}{(t + k^2)^2} + \text{regular terms}, \quad (10.20)$$

where the integral extends to infinity. We can now exploit the identity

$$\frac{1}{X^2} = \int_0^\infty du u e^{-uX}, \quad (10.21)$$

to obtain (up to regular terms)

$$I'_d(t) \simeq - \int_0^\infty du \int d^d \mathbf{k} u e^{-u(t+k^2)}. \quad (10.22)$$

The integral over k yields $(\pi/u)^{d/2}$. We have therefore

$$\begin{aligned} I'_d(t) &\simeq -\pi^{d/2} \int_0^\infty du u^{1-d/2} e^{-ut} = -t^{d/2-2} \int_0^\infty dw w^{1-d/2} e^{-w} \\ &= -\pi^{d/2} \Gamma_E(2 - d/2) t^{d/2-2}. \end{aligned} \quad (10.23)$$

We have therefore, for $2 < d < 4$,

$$\begin{aligned}
 I_d(t) &\simeq I_d(0) - \pi^{d/2} \Gamma_E(2 - d/2) \int_0^t dt' (t')^{d/2-2} \\
 &= I_d(0) + \pi^{d/2} \frac{\Gamma_E(2 - d/2)}{1 - d/2} t^{1-d/2} \\
 &= I_d(0) + \pi^{d/2} \Gamma_E(1 - d/2) t^{d/2-1}.
 \end{aligned} \tag{10.24}$$

We obtain therefore, for $2 < d < 4$,

$$\Gamma(0, z) \simeq \text{const.} + \text{const.} \times |z_c - z|^{(d-2)/2}. \tag{10.25}$$

By using the technique used in the solution of exercise 10.2 one obtains

$$\Gamma_N(0) \sim N^{-d/2}. \tag{10.26}$$

For $d = 4$ $I'_d(t)$ diverges if the integration over k extends to infinity. Differentiating once more with respect to t we obtain

$$I''_4(t) \simeq 2 \int_{\text{Z.B.}} \frac{dk}{(t + k^2)^3}, \tag{10.27}$$

in which we can now safely extend the integration to infinity. Evaluating the integral as above we obtain

$$I''_4(t) \simeq 2\pi^2 \Gamma_E(1) t^{-1}, \tag{10.28}$$

and therefore

$$I'_4(t) \propto \log t + \text{const.} \tag{10.29}$$

yielding

$$I_4(t) \simeq \text{const.} + \text{const.} \times t \log t. \tag{10.30}$$

Thus we have

$$\Gamma_N(0) \sim \frac{\log N}{N}. \tag{10.31}$$

For $d > 4$, by the same token, we obtain

$$I_d(t) = \text{const.} + \text{const.} \times t + o(t), \tag{10.32}$$

and therefore

$$\Gamma_N(0) \sim N^{-1}. \tag{10.33}$$

Solution to exercise 10.4 Let us consider the expression of Z_n :

$$Z_n = \int \prod_i \left[d^n \boldsymbol{\phi}_i \delta(\phi_i^2 - n) \right] \exp \left[\sum_{\langle i,j \rangle} K \boldsymbol{\phi}_i \cdot \boldsymbol{\phi}_j + h_1 \sum_i \phi_{1i} \right], \tag{10.34}$$

where $\boldsymbol{\phi}_i = (\phi_{1i}, \dots, \phi_{ni})$, $d^n \boldsymbol{\phi} = d\phi_{1i} \cdots d\phi_{ni}$, and $\sum_{\langle i,j \rangle}$ denotes the sum over all pairs of nearest-neighbor sites on the lattice. We can expand as usual the exponential of the last term, obtaining the following expression for the coefficient of h_1^{2p} :

$$\begin{aligned} \Gamma^{(2p)} &= \frac{1}{(2p)!} \int \prod_i [d^n \boldsymbol{\phi}_i \delta(\phi_i^2 - n)] \\ &\quad \times \sum_{i_1, \dots, i_{2p}} \phi_{1i_1} \cdots \phi_{1i_{2p}} \exp \left[\sum_{\langle i,j \rangle} K \boldsymbol{\phi}_i \cdot \boldsymbol{\phi}_j \right]. \end{aligned} \quad (10.35)$$

The expression we obtain this way looks like the average of $\phi_{1i_1} \cdots \phi_{1i_{2p}}$ with the distribution given by the Boltzmann factor $\exp[\sum K \boldsymbol{\phi} \cdot \boldsymbol{\phi}]$. We can expand it as for the case of two points in terms of diagrams. Each bond of such a diagram yields a contribution $K \phi_{\alpha i} \phi_{\alpha j}$, where i and j are first neighbors. Upon integration over the $\boldsymbol{\phi}$'s, and taking the $n \rightarrow 0$ limit, only those diagrams in which exactly 2 ϕ_{1i} factors appear will give a non-vanishing contribution. These are the ones in which exactly one bond stems from each of the points i_1, \dots, i_{2p} , and which are connected by sequences of nearest-neighbor bonds without intersections. One easily sees that the combinatorial factors associated with the relabeling of the vertices and the bonds cancel the factorials in the denominator.

Solution to exercise 10.6 Let us consider a single cluster of size s of the ferromagnet. We assume throughout that the interaction constant J satisfies $J \ll k_B T$. Then the cluster can be in the '+' state, with magnetization $+s$, and in the '-', with magnetization $-s$. In an applied magnetic field h , their respective energies are respectively $\pm hs$. Thus the isotherm magnetization m vs. h has the expression

$$m = s \tanh \frac{sh}{k_B T}. \quad (10.36)$$

For $h \ll k_B T$ we have

$$m \simeq s^2 \frac{h}{k_B T}. \quad (10.37)$$

Summing over the whole cluster, we obtain the magnetization per unit site

$$m = \sum_s s^2 v_s(p) \frac{h}{k_B T}, \quad (10.38)$$

yielding

$$\chi = \frac{1}{k_B T} \sum_s s^2 v_s(p). \quad (10.39)$$

Solution to exercise 10.7 Let us assume that if two neighboring spins are occupied, the interaction constant J between them is much larger than $k_B T$. Then $\langle \sigma_i \sigma_j \rangle$ is given by the probability C_{ij} that the two sites belong to the same cluster, because it vanishes when the lattice points belong to a different cluster.

Solution to exercise 10.8 Let us consider the lattice point at the origin, which is occupied with probability p . Let us denote by $T(p)$ the average cluster size contained in one branch of the Bethe lattice. Then if the lattice point at the origin is occupied it belongs to a cluster of average size $(1 + \zeta T(p))$, since on average each of the ζ branches carry a cluster of size $T(p)$. Thus we have

$$S(p) = p(1 + \zeta T(p)). \quad (10.40)$$

Now let us consider the root of the branch. If it is occupied, it is in contact with $(\zeta - 1)$ roots if any of them is occupied, it belongs to a cluster of average size $T(p)$. Thus we have

$$T(p) = p [1 + (\zeta - 1)T(p)]. \quad (10.41)$$

Solution to exercise 10.9 The relation is trivial for $s = 1$. Let us assume it holds for a given value of s . Let us add a new lattice point to the cluster. Then $s'(s + 1) = s'(s) - 1 + (\zeta - 1)$, because (a) one of the boundary points now becomes a point of the cluster, and (b) $(\zeta - 1)$ new points are added to the boundary. This yields the result.

Solution to exercise 10.10 Let us evaluate M_k via

$$M_k \simeq \sum_k s^k \nu_s(p) \simeq \sum_k s^{k-\tau} e^{-c(p)s} \simeq [c(p)]^{\tau-k-1}, \quad (10.42)$$

where we have approached the sum as an integral. Substituting the behavior of $c(p)$ we obtain the result.

Solution to exercise 10.11 From equation (10.101) we obtain the following expression for the rescaled partition function Z' :

$$\lim_{q \rightarrow 0} Z' = \sum_{\mathcal{G}_t} \prod_s (1 + hs)^{N\mathcal{K}_t(\mathcal{G}_t; h, s)}, \quad (10.43)$$

where the sum runs on all graphs \mathcal{G}_t without loops and $N\mathcal{K}_t(\mathcal{G}_t; h, s)$ is the number of clusters in configuration \mathcal{G}_t that contain s sites. We have therefore

$$\lim_{q \rightarrow 0} D_q(\mathbf{r}, \mathbf{r}') = \sum_{\mathcal{G}_t} P(\mathcal{G}_t) C(\mathbf{r}, \mathbf{r}') = \langle C(\mathbf{r}, \mathbf{r}') \rangle_t. \quad (10.44)$$

On the other hand, as $K \rightarrow \infty$, the weight is dominated by trees with the maximum number N_b of bonds. Since $N_b = N - N_c$ for trees, this corresponds to $N_b = N - 1$, i.e., to spanning trees.

Solution to exercise 10.12 Let us define $\beta(p, d)$ by

$$\beta(p, d) = \left. \frac{dp'}{db} \right|_{b=1}. \quad (10.45)$$

The equation $\beta(p, 3) = 0$ allows, beyond the trivial fixed points $p = 0, 1$, for the nontrivial one

$$p = p_c = 0.160365. \quad (10.46)$$

We have

$$\lambda = \left. \frac{\partial \beta}{\partial p} \right|_{p=p_c} = 0.820122. \quad (10.47)$$

From the relation

$$v = \frac{1}{\lambda} \quad (10.48)$$

we obtain

$$v = 1.21933. \quad (10.49)$$

Solution to exercise 10.13

Reflexivity: Each occupied site i is connected to itself by definition.

For symmetry and transitivity, let us first prove the following lemma: If x and y are connected, there is a path (x_0, x_1, \dots, x_n) of occupied sites such that x_{k+1} and x_k are nearest neighbors, and $x_0 = x$, while $x_n = y$. To prove it, start from y and draw a line to all its occupied nearest neighbors. Then draw a line from each of these neighbors to each of *their* neighbors that have not been reached in the first step. Iterate the procedure until no occupied nearest neighbors are found. We have built a spanning tree with root in y that contains x in one of its branches, since y is connected to x . Thus we can identify a sequence of points that starts from y and

ends in x , where each pair of successive points are nearest neighbors and occupied. Inverting the sequence, we have a path from x to y . **Reflexivity** is now immediate, and **transitivity** follows from the consideration that joining a path from x to y with a path from y to z , if it exists, yields a path from x to z .

Solution to exercise 10.14 Let us fix one direction, say x , in a d -dimensional simple cubic lattice. We wish to replace a block of size b^d with a single bond, by first moving bonds transverse to x and then decimating spins along the resulting multiple bond (cf. fig. 10.1). By bond moving each bond in the x direction gets surrounded by $(b-1)(d-1)$ bonds. Thus we have

$$K_1 = (1 + (b-1)(d-1)) K, \quad (10.50)$$

where $K = J/k_B T$ is the bond's strength. We can now decimate the $(b-1)$ spins

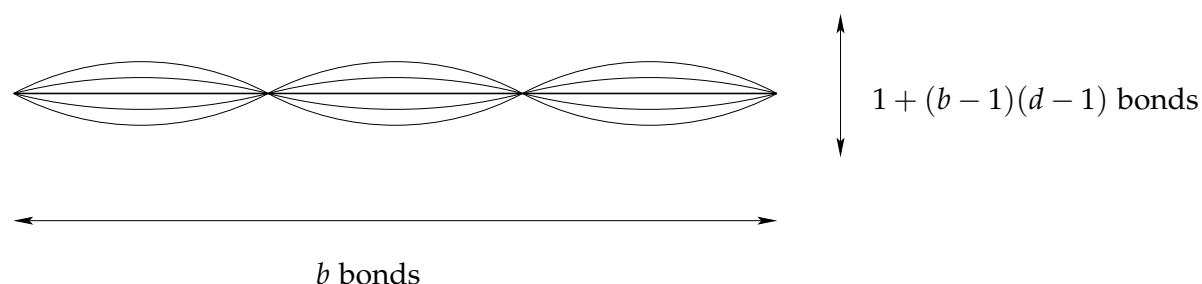


Figure 10.1: Bond moving in the d -dimensional Ising model

internal to the resulting bond in the x direction. This is similar to a 1-dimensional Ising model with bond strength equal to K_1 and of length b . The transfer matrix has the usual form

$$T = \begin{pmatrix} e^{K_1} & e^{-K_1} \\ e^{-K_1} & e^{K_1} \end{pmatrix}. \quad (10.51)$$

This matrix allows for the eigenvectors

$$|\pm\rangle = \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}, \quad (10.52)$$

with the corresponding eigenvalues

$$\lambda_{\pm} = e^{K_1} \pm e^{-K_1}. \quad (10.53)$$

Thus we have

$$T^b = \lambda_+^b |+\rangle \langle +| + \lambda_-^b |-\rangle \langle -|. \quad (10.54)$$

We can write this expression in the form

$$T^b = \cosh^{b/2}(K_1) \begin{pmatrix} e^{K'} & e^{-K'} \\ e^{-K'} & e^{K'} \end{pmatrix}, \quad (10.55)$$

where

$$e^{-2K'} = \frac{\lambda_+^b - \lambda_-^b}{\lambda_+^b + \lambda_-^b} = \frac{\cosh^b K_1 - \sinh^b K_1}{\cosh^b K_1 + \sinh^b K_1}. \quad (10.56)$$

By taking the derivative of this expression, and setting $b \rightarrow 1$, we obtain

$$\beta(K, d) = \left. \frac{dK'}{dK} \right|_{b=1} = (d-1)K + \frac{1}{2} \sinh 2K \log \tanh K. \quad (10.57)$$

This function always allows for the trivial zeros $K = 0$ and $K = +\infty$. There is a nontrivial zero K_* satisfying the equation

$$(d-1)K_* = \frac{1}{2} \sinh 2K_* |\log \tanh K_*|. \quad (10.58)$$

In particular for $d = 2$ this yields $K_* = 0.440687$, i.e., the exact value of the transition temperature for the $d=2$ Ising model. The corresponding exponent ν is given by

$$\frac{1}{\nu} = \left. \frac{d\beta(K, d)}{dK} \right|_{K=K_*} = 0.75355, \quad (10.59)$$

yielding $\nu = 1.32705$ rather than the exact value 1. For $d = 3$ we obtain $K_* = 0.75355$ with $1/\nu = 0.948169$.

For $d \rightarrow 1$ we have $K_* \rightarrow 1/(d-1)$ and eventually the nontrivial fixed point disappears. On the other hand, for $d \rightarrow \infty$ we obtain $K \sim e^{-(d-1)}$ with $1/\nu \rightarrow 1$, which has nothing to do with the classical behavior.

Solution to exercise 10.15 Let us denote by \mathcal{N}_ℓ the number of circles of diameter equal to ℓ needed to cover the gasket, and let us assume that $\ell = 2^{-n}$ in units of the gasket's side. Then when ℓ is divided by 2, \mathcal{N} gets multiplied by 3. Thus we have

$$\mathcal{N}_\ell \propto \ell^{\log 3 / \log 2}. \quad (10.60)$$

We obtain therefore

$$d_H = \frac{\log 3}{\log 2} = 1.58. \quad (10.61)$$

Solution to exercise 10.16 Reasoning as in the previous case, we obtain

$$\mathcal{N}_\ell \propto \ell^{\log 4 / \log 3}, \quad (10.62)$$

leading to

$$d_H = \frac{\log 4}{\log 3} = 1.26. \quad (10.63)$$

Solution to exercise 10.17 Given a Sierpiński gasket of side length equal to 1, let us consider a circle of radius ℓ , with $\ell \ll 1$, centered, e.g., on one vertex. If this radius is multiplied by 2, the number of points it contains is multiplied by 3. Thus we have $\mathcal{N} \propto \ell^{\log 3 / \log 2}$. The reasoning for the von Koch curve is similar.

Solution to exercise 10.18 Let us denote by $\Phi(E)$ the cumulative pdf of E :

$$\Phi(E) = \int_{-\infty}^E dE' P(E'). \quad (10.64)$$

Then the cumulative pdf of the minimum of M i.i.d. variables distributed according to $P(E)$ is given by the probability that each of them is larger than E , i.e., by

$$\Phi_M(E) = [1 - \Phi(E)]^M. \quad (10.65)$$

For large values of M , we expect typical values of E to be large and negative, so that $\Phi(E) \ll 1$, yielding

$$\Phi_M(E) \simeq \exp[-M\Phi(E)]. \quad (10.66)$$

Let us identify the critical value E_c by the condition

$$M\Phi(E) = 1. \quad (10.67)$$

From the asymptotic behavior of $P(E)$ we obtain the following estimate of E_c :

$$E_c \simeq - \left(\frac{\log M}{B} \right)^{1/\delta}. \quad (10.68)$$

For $E \simeq E_c + \epsilon$, with $|\epsilon| \ll |E_c|$, we have

$$\Phi(E) \simeq \Phi(E_c) \cdot \left. \frac{d \log \Phi}{dE} \right|_{E_c} \epsilon = \frac{1}{M} B \delta |E_c|^{\delta-1} \epsilon, \quad (10.69)$$

that yields

$$\Phi_M(E) \simeq \exp \left[-\exp \left(B\delta |E_c|^{\delta-1} \epsilon \right) \right]. \quad (10.70)$$

Let us introduce the variable

$$x = B\delta |E_c|^{\delta-1} \epsilon. \quad (10.71)$$

Then the cumulative pdf of the variable x is given by

$$\Phi(x) = \exp [-\exp(x)], \quad (10.72)$$

and the corresponding probability density is given by the **Gumbel's law**:

$$P(x) = -\frac{d\Phi}{dx} = \exp [x - \exp(x)]. \quad (10.73)$$

Solution to exercise 10.19 The cumulative distribution of z for large values of z over $M = 2^N$ variables can be obtained from the cumulative distribution of the minimum of E over M states, which can be obtained from the Gumbel distribution. Letting $\delta = 2$, $B = 1/(NJ_0^2)$ we obtain

$$E_c = -NJ_0\sqrt{\log 2}, \quad (10.74)$$

and

$$\Phi_M(E) \simeq e^{2\sqrt{\log 2}\epsilon/J_0} = e^{\epsilon/T_0}, \quad (10.75)$$

where $\epsilon = E - E_c$ and

$$\frac{1}{T_0} = \frac{2\sqrt{\log 2}}{J_0}. \quad (10.76)$$

Since $E = -T \log z$ we have therefore

$$\Phi_M(z) \propto e^{(\log \epsilon + |E_c|)/T_0} = z^{-\mu}, \quad (10.77)$$

with

$$\mu = \frac{T}{T_0}. \quad (10.78)$$

Taking the derivative, we obtain the pdf $P(z)$:

$$P(z) \propto z^{-1-\mu}. \quad (10.79)$$

Solution to exercise 10.20 By Chebyshev's inequality, the probability that a random variable X deviates from its average $[X]_{\text{av}}$ by more than a ($a > 0$) is related to the variance $\text{Var}(X) = [X^2]_{\text{av}} - [X]_{\text{av}}^2$ by

$$P(|E - [E]_{\text{av}}| \geq a) \leq \frac{\text{Var}(X)}{a^2}. \quad (10.80)$$

Let us consider the number $\mathcal{N}(\epsilon, \delta)$ of levels j whose energy E_j falls between $N\epsilon$ and $N(\epsilon + \delta)$. This is a random variable, Poisson distributed, whose average is given by

$$[\mathcal{N}(\epsilon, \delta)]_{\text{av}} = 2^N \int_{N\epsilon}^{N(\epsilon+\delta)} dE P(E) \simeq \frac{N\delta}{\sqrt{\pi N}} e^{N(\log 2 - \epsilon^2)}. \quad (10.81)$$

Since $\mathcal{N}(\epsilon, \delta)$ is Poisson distributed, its variance is equal to its average. Let us assume that $|\epsilon| > \epsilon_* = \sqrt{\log 2}$. Letting $a = 1$ into Chebyshev's inequality we obtain that the probability that $\mathcal{N}(\epsilon, \delta) \geq 1$ satisfies

$$P(\mathcal{N}(\epsilon, \delta) \geq 1) \leq \delta \sqrt{\frac{N}{\pi}} e^{-N|\log 2 - \epsilon^2|} \ll 1, \quad (10.82)$$

for $|\epsilon| > \epsilon_*$ and N large enough.

Solution to exercise 10.21 Let $\mathcal{N}(\epsilon, \delta, m, \mu)$, i.e., the number of levels j with energy E_j such that $-N(\epsilon + \delta) < E_j < N\epsilon$ and magnetization $Nm < M < N(m + \mu)$. Then we have

$$[\mathcal{N}(\epsilon, \delta, m)]_{\text{av}} \simeq \binom{N}{(N+M)/2} \frac{\mu \delta}{\sqrt{\pi N}} e^{-N(\epsilon + mB)^2}. \quad (10.83)$$

As long as the average of $\mathcal{N}(\epsilon, \delta, m)$ grows exponentially with N , we can evaluate the entropy per particle $s(\epsilon, m)$ by

$$s(\epsilon, m) = \lim_{N \rightarrow \infty} \frac{1}{N} \log [\mathcal{N}(\epsilon, \delta, m)]_{\text{av}} = s_0(m) - (\epsilon + mB)^2, \quad (10.84)$$

where

$$s_0(m) = - \left[\frac{1+m}{2} \log \frac{1+m}{2} + \frac{1-m}{2} \log \frac{1-m}{2} \right]. \quad (10.85)$$

This relation holds as long as we have $s(\epsilon, m) > 0$, i.e.,

$$|\epsilon + mB| < \sqrt{s_0(m)}. \quad (10.86)$$

In this regime, the equilibrium value m_0 of m is obtained from the equation

$$\left. \frac{\partial s}{\partial m} \right|_{m=m_0} = 0. \quad (10.87)$$

We obtain

$$\tanh^{-1} m_0 = -2B(\epsilon + m_0 B). \quad (10.88)$$

Then the temperature $T = 1/\beta$ is given by

$$\beta = \left. \frac{\partial s}{\partial \epsilon} \right)_m = -2(\epsilon + m_0 B). \quad (10.89)$$

When these conditions are satisfied, we obtain

$$m_0(\beta, B) = \tanh(\beta B), \quad (10.90)$$

corresponding to the usual paramagnetic behavior. However, there is a transition line corresponding to the condition

$$\beta_c = \frac{1}{2} \sqrt{s_0(m_0(\beta_c, B))}. \quad (10.91)$$

To identify the transition line, let us take as an independent variable m_0 . We then have

$$\beta_c(m_0) = \frac{1}{2} \sqrt{s_0(m_0)}; \quad (10.92)$$

$$B = \frac{\tanh^{-1} m_0}{\beta_c(m_0)}. \quad (10.93)$$

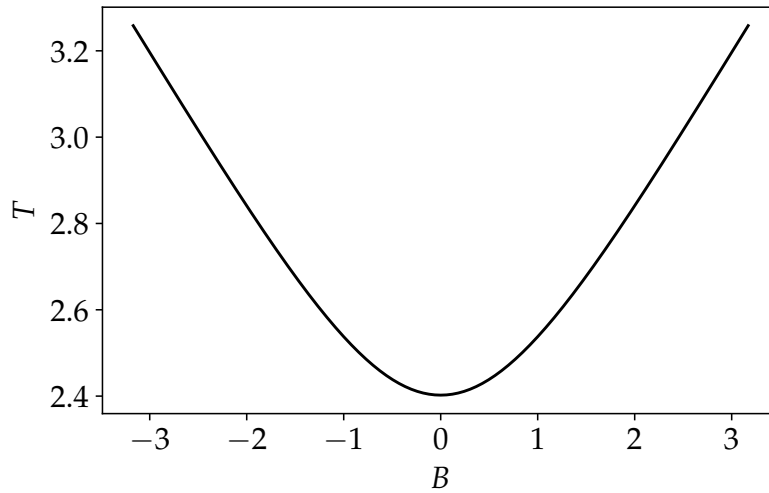


Figure 10.2: Phase diagram of the REM in external field in the $(B, T = 1/\beta)$ plane. The “frozen” phase lies below the line.

To obtain the expression of the susceptibility χ we must distinguish between the paramagnetic phase $\beta < \beta_c(B)$ and the “frozen” phase $\beta > \beta_c(B)$. In the former case we obtain

$$\chi = \beta(1 - m_0^2), \quad (10.94)$$

which leads to the Curie law $\chi = \beta$ for $B = 0$.

On the other hand, for $\beta > \beta_c(B)$, the system remains “frozen” in one of the relevant configurations at temperature $1/\beta_c$. Thus we have

$$\chi = \beta_c, \quad \text{for } \beta > \beta_c. \quad (10.95)$$

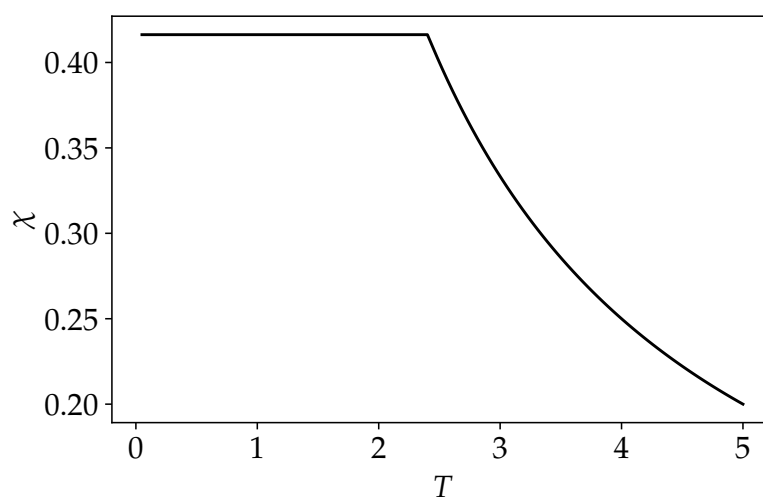


Figure 10.3: Zero-field susceptibility χ of the REM as a function of the temperature T .

Solution to exercise 10.22 For $\delta > 1$, we can evaluate the entropy per spin in the same way as above. For $|\epsilon|$ small enough we have

$$s(\epsilon) = \lim_{N \rightarrow \infty} [\log \mathcal{N}(\epsilon, \delta)] = \log 2 - CN^{\delta-1} |\epsilon|^\delta. \quad (10.96)$$

To obtain an N -independent limit we must set

$$CN^{\delta-1} = \hat{C}. \quad (10.97)$$

The expression vanishes for

$$|\epsilon| = \epsilon_* = \left(\frac{\log 2}{\hat{C}} \right)^{1/\delta}. \quad (10.98)$$

The temperature is obtained by the expression

$$\beta = \frac{\partial s}{\partial \epsilon} = \hat{C} \delta |\epsilon|^{\delta-1}. \quad (10.99)$$

Thus the critical temperature β_c is given by

$$\beta_c = \hat{C} \delta \epsilon_*^{\delta-1} = \delta \log 2^{1-1/\delta} \hat{C}^{1/\delta}. \quad (10.100)$$

The behavior is similar to the case $\delta = 2$.

On the other hand, if $\delta < 1$, the resulting expression of $s(\epsilon)$ is no more downward convex with respect to ϵ . To evaluate the thermodynamic behavior at inverse temperature β , let us evaluate the partition function according to the expression

$$Z = \int_{-\epsilon_*}^0 e^{N[s(\epsilon) - \beta\epsilon]}. \quad (10.101)$$

Since the exponent $\phi(\epsilon, \beta) = s(\epsilon) - \beta\epsilon$ is upwards concave with respect to ϵ , the integral is dominated by the values of $\phi(\epsilon)$ at the boundary of the integration interval, i.e., $-\epsilon_*$ and 0. One sees that $\phi(0) > \phi(-\epsilon_*)$ for $\beta < \beta_c$, where β_c is the solution of the equation

$$\beta\epsilon_* = \log 2. \quad (10.102)$$

In this state the entropy per spin is equal to $\log 2$. For $\beta > \beta_c$ we have $\langle E \rangle = -N\epsilon_*$ and the entropy per spin vanishes. Thus the transition at β_c is first order.

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