PROBLEMS AND SOLUTIONS IN
STATISTICAL MECHANICS

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Contents

Notice

These exercises appear in my textbook *Statistical Mechanics in a Nutshell* (2nd ed.) (Princeton: Princeton U. P., 2023). In a large part, they were submitted during my teaching of Statistical Mechanics at the University of Naples "Federico II". I am grateful to my colleagues and especially to my students, who helped shape the problems and their answers.

Part I

Problems

CHAPTER 1

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 Prove that the only distribution that satisfies the postulates of independence of the components and isotropy in space is a Gaussian:

$$\phi(\boldsymbol{v}) \propto \exp\left(-\lambda v^2\right),$$

where λ is a positive constant. Show that

$$\left\langle v^2 \right\rangle = \frac{3}{2\lambda},$$

and that therefore the average kinetic energy is given by

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3m}{4\lambda}.$$

Exercise 1.3 (On Maxwell's distribution)

1. Evaluate the root mean square speed $v_{\mathrm{RMS}} = \sqrt{\langle v^2 \rangle}$ of a gas obeying Maxwell's distribution $\phi(\boldsymbol{v})$ 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:

$$f(\kappa) = \int \mathrm{d}^d\boldsymbol{v}\; \delta\left(\kappa - \frac{1}{2}mv^2\right) \phi(\boldsymbol{v}).$$

Exercise 1.4 (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 $\boldsymbol{g}$ 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 1.5 (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 1.6 (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 $\boldsymbol{v}$, where $\boldsymbol{v}$ 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.

CHAPTER 2

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

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

Exercise 2.3 Let the fundamental equation for systems A and B be given by

$$S = \kappa \left(NVE\right)^{1/3}.$$

Let $N^{(\mathrm{A})}$ and $V^{(\mathrm{A})}$ be the number of particles and volume of system A, and similarly for B. Assume that the total internal energy of the system $\mathrm{A} \cup \mathrm{B}$ is equal to E_0, and that the systems can exchange energy but neither particles nor volume. Evaluate the internal energies of the two systems at equilibrium.

Exercise 2.4 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 2.5 Consider the thermodynamic potential

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

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

Exercise 2.6 Prove that among all states that have the same temperature and pressure values, the state of equilibrium is that in which the Gibbs free energy assumes the minimum value.

Exercise 2.7 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 2.8 Prove that the heat released by a system that is relaxing at equilibrium at constant pressure is less then (or equal to) its change in enthalpy:

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

Exercise 2.9 (Law of adiabatic processes) Prove that for an ideal gas, one gets

$$C_p - C_V = Nk_{\text{B}}.$$

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 2.10 (Reech's relation) Show that the ratio $\gamma_C = C_p/C_V$ is equal to the ratio κ_T/κ_S of the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right)_T,$$

to the adiabatic compressibility

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right)_S.$$

Exercise 2.11 (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:

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

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

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

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

Exercise 2.12 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 2.13 (Theory of elasticity) Consider an elastic band with a fixed cross section as a thermodynamic system. The thermodynamic variables that characterize it within the energy scheme are its entropy S, length L, and a measure N of its mass, all assumed to be extensive. The expression of $\mathrm{d}E$ is given by

$$\mathrm{d}E = T\,\mathrm{d}S + f\,\mathrm{d}L + \mu\,\mathrm{d}N,$$

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

One observes experimentally that the tension f, when the length L and the mass m are constant, increases proportionally to temperature. Thus the equation of state is given by

$$f = \kappa(L, N)\,T,$$

where κ depends on L and N. Hooke's law, on the other hand, implies that the relative lengthening is proportional to tension (at least in the case of not too large length changes), and therefore,

$$f \simeq \phi \frac{L - L_0}{N}, \qquad |L - L_0| \ll L_0,$$

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

1. Derive the analogue of the Gibbs-Duhem equation.
2. Show that ϕ is proportional to the temperature T:

$$\phi = bT.$$

3. Show that the internal energy E depends only on T, and that the entropy S is the sum of a term depending only on T and one depending only on L.
4. Show how to obtain the fundamental equation in both the entropy and energy schemes.

CHAPTER 3

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 n. In this case, the possible energy values are $E_n = \hbar^2\pi^2 n^2/L^2$, where $n = 1, 2\ldots$ Prove that in this case too, the phase space volume "occupied" by each quantum state is equal to h.

Exercise 3.2 (The Bohr-van Leeuwen theorem) Prove that when statistical mechanics and classical mechanics are applied consistently, and the particles have no intrinsic magnetic moment, the thermal average of the magnetization is always zero.

1. Express the hamiltonian $\mathcal{H}(\boldsymbol{p}, \boldsymbol{r})$ of a system of N charged particles as a function of the coordinates $\boldsymbol{r} = (\boldsymbol{r}_i)$ and the momenta $\boldsymbol{p} = (\boldsymbol{p}_i)$ of the particles, and of the vector potential $\boldsymbol{A}(\boldsymbol{r})$ of the field, such that the magnetic induction field $\boldsymbol{B} = \nabla \times \boldsymbol{A}$.

2. Evaluate the magnetization $\boldsymbol{M} = -\left\langle \partial\mathcal{H}/\partial\boldsymbol{B} \right\rangle$ in the canonical ensemble.

Thus diamagnetism in materials have a quantum origin. This theorem was discovered by N. Bohr in his doctoral dissertation, and rediscovered a few years later by H. J. van Leeuwen.

Exercise 3.3 (Langevin theory of paramagnetism) Suppose that the system is made by N *classical* magnetic dipoles of magnitude μ, whose direction is identified by the spherical angles θ (latitude) and ϕ (longitude). The dipoles have a moment of inertia I for rotations normal to their axis.

1. Write the classical Lagrangian for such a system, supposing that the potential energy derives only from the interaction with an external magnetic field of magnitude B directed along the z-axis. Obtain the corresponding hamiltonian.
2. Evaluate the canonical partition function of the system by a suitable phase-space integral.
3. Obtain the isotherm of the system, that is, the average magnetization per spin $m(B)$ at a given temperature T. Check if the Curie law applies to it.

Exercise 3.4 (An elementary model of elasticity) Consider a fibre made by N molecules of length ℓ_0 and width $\ell_1 > \ell_0$, bound one after the other along the x axis. Each molecule can be in two positions: either normal to the x axis or parallel to it. In the first case, it occupies a length equal to ℓ_0, and in the second, a length equal to ℓ_1. The first molecule is fixed at the origin, and on the last one is applied a force F that pulls in the direction of the positive x axis. We denote by L the abscissa of the last molecule.

1. Write the hamiltonian of the system, as a function of the configuration $\tau = (\tau_1, \ldots, \tau_N)$, where $\tau_i = 0$ if the molecule normal to the x axis, and $\tau_i = 1$ if it is parallel to it.
2. Evaluate the equation of state $L = L(N, F, T)$. Deduce that the system follows Hooke's law for small values of F, and evaluate the Hooke constant.

Exercise 3.5 Making use of the Maxwell relations and of the expression $p = -\partial F/\partial V)_T$ of pressure, prove the equality

$$\left.\frac{\partial E}{\partial T}\right)_p + \left.\frac{\partial E}{\partial p}\right)_T \left.\frac{\partial p}{\partial T}\right)_{p/k_\mathrm{B}T} = \left.\frac{\partial E}{\partial T}\right)_V - \frac{1}{T}\left.\frac{\partial E}{\partial V}\right)_T^2 \left.\frac{\partial V}{\partial p}\right)_T .$$

Exercise 3.6 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 ($N \to \infty$ with constant pressure).

Exercise 3.7 Consider a simple fluid, described by a grand canonical ensemble. Express the following quantities in terms of the grand canonical partition function:

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

Exercise 3.8 Show that the energy fluctuations in the grand canonical (GC) ensemble are always greater than the corresponding fluctuations in the canonical (C) ensemble:

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

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

Exercise 3.9 Consider a system described by the hamiltonian $\mathcal{H}(x)$. Show that the quantity

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

is largest for the canonical distribution

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

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

$$\langle \mathcal{H} \rangle = \sum_x p(x) \, \mathcal{H}(x).$$

Chapter 4

Interaction-Free Systems

Exercise 4.1 (Kappler's experiment) In his thesis Kappler [1931], E. Kappler measured the angular fluctuations of a mirror hanging on a thin vertical wire fixed at both ends, above and below, and immersed in a room at the temperature $T = 287.1\,\mathrm{K}$. He carefully measured the angular Hooke constant of the wire, obtaining $\kappa = 9.428 \cdot 10^{-9}\,\mathrm{g\,cm^2\,s^{-2}}$. He obtained a value of the variance of the angular deviation from equilibrium equal to $\langle \varphi^2 \rangle = 4.178 \cdot 10^{-6}\,\mathrm{rad}^2$. Calculate the value of k_B starting from these data.

Exercise 4.2 (Stefan-Boltzmann law) By integrating equation (4.25), one obtains the total power emitted by a body at temperature T per unit surface:

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

where the constant κ is equal to

$$\kappa = \frac{2\pi^5 k_\mathrm{B}^4}{15 c^2 h^3} = 5.6710\ 10^{-8}\ \mathrm{J\,m^{-2}s^{-1}K^4}.$$

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:

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

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

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

   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.

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

Exercise 4.3 Evaluate the power needed to keep the human body at the constant temperature of 37°C, under the following hypotheses;

- The body behaves like a black body, with an emissivity $E = 0.7$ (fraction of the radiation emitted or received);
- The surface area is approximately $2\,\mathrm{m}^2$;
- The body receives the radiation of the environment at 27°C.

Compare it with the basal metabolism rate, estimated at $1.1 \cdot 10^7\,\mathrm{J/day}$.

Exercise 4.4 Evaluate the corrections to the classical equation of state of the quantum gases to order ξ^2, where ξ is the degeneration parameter defined by $\xi = N\lambda_{\mathrm{B}}^3/V$.

Exercise 4.5 (Pauli paramagnetism) The paramagnetic properties of a number of metals can be explained by considering the effect of a magnetic field on a degenerate electron gas.

Assume that each electron has a magnetic dipole of magnitude μ_{m} parallel to its spin, and that a magnetic field of induction vector $\boldsymbol{B}$ is applied to the system. Then states with spin parallel or antiparallel to the field have different energies.

1. Evaluate the total magnetization $\boldsymbol{M}$ of the system as a function of $\boldsymbol{H}$ at zero temperature for a three-dimensional system of N free electrons.
2. Same question for a two-dimensional system.

Exercise 4.6 Show that for a quantum gas in d dimensions, whose single-particle energy $\epsilon(\boldsymbol{p})$ is proportional to p^α, one has $C_p/C_V = 1 + d/\alpha$.

Exercise 4.7 (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 $\omega(\epsilon) = \sum_{\boldsymbol{k},\sigma} \delta(\epsilon - \epsilon(\boldsymbol{k},\sigma))$, where $\boldsymbol{k}$ are the allowed values of the wave vector, σ the possible values of the spin, and $\epsilon(\boldsymbol{k},\sigma)$ the corresponding single-particle energy.
2. Evaluate the Fermi energy ϵ_F as a function of the particle 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 $T \to 0$.

Exercise 4.8 (Neutrino density in the universe) Current cosmological theories do not only predict a uniform backgound radiation density in thermal equilibrium at the temperature of 2.725 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 $\boldsymbol{p}$. Thus there is only one possible state for the spin for each value of the momentum. Moreover, their mass is indistinguishable from zero and therefore the energy of a state of momentum $\boldsymbol{p}$ is equal to $c\,|\boldsymbol{p}|$, 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:

- $c \simeq 3.00 \cdot 10^8\,\mathrm{ms}^{-1}$;
- $k_\mathrm{B} \simeq 1.38 \cdot 10^{-23}\,\mathrm{JK}^{-1}$;
- $\int_0^\infty x^2 \mathrm{d}x/(1+\mathrm{e}^x) = \frac{3}{2}\zeta_\mathrm{R}(3) \simeq 1.80$;

- $\int_0^\infty x^3 \mathrm{d}x/(1+\mathrm{e}^x) = 7\pi^4/120 \simeq 5.67$.

Exercise 4.9 (Classical theory of diamagnetism) Quite surprisingly, diamagnetism was explained by P. Langevin in 1905 via a completely classical reasoning, that we shall follow in the present exercise.

Consider a classical atom subject to a uniform magnetic field $\boldsymbol{B}$ of magnitude B directed along the z-axis.

1. According to the Larmor theorem, the system undergoes a precession at the angular frequancy ω_L. Evaluate this frequency.
2. This precession is equivalent to an added circular current. Evaluate the added current density at point $\boldsymbol{r}$ assuming the electron density $\rho(\boldsymbol{r})$ to be given and spherically symmetric.
3. Using this result, evaluate the total magnetic moment of the atom, again exploiting spherical symmetry, and compare this result with the preceding one.

In this derivation, where did we violate the assumptions of the Bohr-van Leeuwen theorem?

Exercise 4.10 We consider a typical white dwarf of mass $M = 2.0 \cdot 10^{30}$ kg.

1. Evaluate the Fermi momentum p_F of the electrons in the star. Compare its kinetic energy $p_\mathrm{F}c$ with its rest energy mc^2. Is the ultrarelativistic approximation warranted?
2. Evaluate the Fermi temperature of the electrons in the white dwarf and compare it with the typical value of 10^7 K.
3. Evaluate the pressure due to the nuclei, considered as a perfect non-relativistic gas, and compare it to the pressure of the electron gas. (One can take equal ratios of oxygen and carbon.)

Exercise 4.11 (Neutron stars) Massive stars (whose mass exceeds about ten solar masses) avoid the white dwarf fate, because their gravitational energy is large enough to allow the continuation of nuclear synthesis even if all hydrogen is transformed into helium. Then, after a number of processes that we do not attempt to summarize here, the star relinquishes a ball entirely made of neutrons, with mass about 1.4 times the solar mass, kept together by their gravitational attraction. This state is known as a **neutron star**. Here we assume that the neutron gas is a nonrelativistic Fermi gas at zero temperature.

1. Given the mass M of the star and its radius R, give the expression of the internal kinetic energy of the star.
2. Give the expression of the total energy of the star, including its gravitational contribution, and assuming that its density is uniform. Evaluate its equilibrium radius as a function of M.
3. Evaluate the radius R for a star with mass M of the order of 1.4 times the solar mass. Evaluate the Fermi temperature of the neutrons and compare it with the initial temperature of the star. Is the zero-temperature approximation warranted?
4. Evaluate the escape speed of an object of mass m placed at the surface of the neutron star. Evaluate the value M_{BH} of a star for which this speed equals the speed of light.

Exercise 4.12 Evaluate the behavior of the internal energy and specific heat of a boson gas in the vicinity of the Einstein condensation.

Exercise 4.13 (Einstein condensation of zero-mass particles) Consider a system of quantum particles with spin zero, whose energy, as a function of the wave vector $\boldsymbol{k}$, is given by

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

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 Einsten'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 4.14 (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

$$u(\boldsymbol{r}) = \frac{1}{2}m\omega_0^2 r^2, \tag{4.1}$$

where $\boldsymbol{r} = (r_1, \ldots, r_d)$ 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 $N - N_0$ 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 $N \to \infty$, $N/R_0^d = \rho = \text{const.}$, which implies $\omega_0 \to 0$. 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 4.15 (A simplified model of hemoglobin) Let us associate each of the four units i, $(i = 1, \ldots, 4)$ 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 $x = \exp[(\epsilon_0 + \mu)/k_{\mathrm{B}}T]$ and of $y = \exp(J/k_{\mathrm{B}}T)$.

Exercise 4.16 (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 4.17 (Frustrated spins) A system is made up by N Ising spins, $\sigma_i \in \{-1, +1\}$, $i = 1, \ldots, N$ which interact in groups of three, with the hamitonian

$$\begin{aligned} \mathcal{H}_\ell^{(3)} &= J\left(\sigma_{3\ell-1}\sigma_{3\ell-2} + \sigma_{3\ell-2}\sigma_{3\ell} + \sigma_{3\ell}\sigma_{3\ell-1}\right) - h\sum_{i=0}^{2}\sigma_{3\ell-i}, \\ \ell &= 1, \ldots, N/3. \end{aligned}$$

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

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

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.

CHAPTER 5

Phase Transitions

Exercise 5.1 Show that the Maxwell construction corresponds to the double tangent construction discussed in sec. 2.21.

Exercise 5.2 Evaluate the discontinuity of the specific heat in a fluid following the van der Waals equation for $v = v_\mathrm{c}$ and T close to T_c:

1. Express the specific heat per particle at constant volume, evaluated at the critical volume v_c, in terms of the fractions x_liq and x_vap at coexistence, of the specific heat c_{v_liq} and c_{v_vap} of the specific heats for the coexisting liqued and vapor phases, of the derivatives $\partial p_\mathrm{liq}/\partial v_\mathrm{liq})_T$ and $\partial p_\mathrm{vap}/\partial v_\mathrm{vap})_T$ of the equation of state at coexistence, and of the derivatives $\mathrm{d}v_\mathrm{liq}/\mathrm{d}T)_\mathrm{coex}$ and $\mathrm{d}v_\mathrm{vap}/\mathrm{d}T)_\mathrm{coex}$ of the specific volumes of the two phases at coexistence.
2. Show that the specific heat at constant volume of a van der Waals fluid in a homogeneous phase does not depend on the temperature.
3. Evaluate the relevant quantities mentioned above close to the critical point in a van der Waals fluid. Deduce the jump in the specific heat per particle at constant volume equal to the critical volume around the critical temperature.

It is convenient to use *reduced units*, namely, to measure quantities like the temperature T, the specific volume v and the pressure p in units of the corresponding critical values T_c, v_c, p_c.

Exercise 5.3 (Phase coexistence) Consider the following grand canonical partition function

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

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 5.4 An electrostatic analog of the equation of state of the Lee-Yang model can be found as follows:

1. Consider a circular cylinder of unit radius perpendicular to the complex z plane, cutting it on the unit circle. Suppose that the cylinder is charged with a surface charge density $g(\theta)$ that depends only on the angle θ and that satisfies $g(-\theta) = g(\theta)$. Let then $\Phi(z)$ and $E(z)$ be respectively the electrostatic potential and the electric field at a point z on the real axis. Show that we then have

$$\frac{p}{k_{\mathrm{B}}T} = -\frac{1}{2}\Phi(z); \qquad \rho = \frac{1}{2}zE(z).$$

2. Assume $g(0) \neq 0$. Show by electrostatic arguments that $p(z)$ is continuous at $z = 1$, but ρ jumps discontinuously. By means of Gauss's theorem, show that the discontinuity is given by $\Delta\rho = 2\pi g(0)$.

Exercise 5.5 Generalize the Peierls argument to $d = 3$ dimensions.

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 $|i-j|^{-\alpha}$, where α is a positive constant. Show that Landau's argument does not rule out a transition if $\alpha < 2$.

Exercise 5.7 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

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

where $K = J/k_{\mathrm{B}}T$.

Exercise 5.8 Show that in the one-dimensional Ising model in the presence of a nonvanishing magnetic field h, one has

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

where $\lambda = h/k_{\mathrm{B}}T$.

Exercise 5.9 Obtain the same result with the following method, introduced by 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 $N \to \infty$, it is necessary that $z \to z^*$, where z^* is the value of z closest to the origin for which Z admits a singularity. Evaluate z^*.
5. Show that $f = \lim_{N\to\infty} \ln Z/N = -\ln z^*$, and compare the result with what was obtained in the previous exercise.

Exercise 5.10 (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

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

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

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

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

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

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

   show that one has

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

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

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

where $\lambda_\pm$ 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 5.11 (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 5.12 (Mean-field theory of the Ising antiferromagnet) The Ising antiferromagnet in d dimensions is described by the hamiltonian

$$\mathcal{H}(\sigma) = \sum_{<ij>} J\sigma_i\sigma_j - \sum_i h\sigma_i,$$

where $\sigma = (\sigma_1, \ldots, \sigma_N)$, $\sigma_i = \pm 1$, $\forall i$, and the first sum runs over all pairs $<ij>$ of nearest-neighbor lattice sites. Here J is a positive constant, and the lattice is a simple cubic lattice in d dimensions. As a consequence, the lattice breaks down into two intertwined sublattices, that we denote by '$+$' and '$-$', such that, if i is a site that belong to one lattice, its $2d$ nearest neighbors all belong to the other lattice.

Since the hamiltonian favors antiparallel nearest-neighbor orientations, there is the possibility of spontaneous breaking of the symmetry between the two sublattices.

1. Define a trial free energy for the model, as a function of the magnetization per spin $m_\pm$ of each sublattice: $m_+ = \langle \sigma_i \rangle$, with i belonging to the '$+$' sublattice, and analogously for m_-.

2. Write down the self-consistency equations that determine the values of $m_\pm$ as a function of $K = J/k_\mathrm{B}T$ and $\lambda = h/k_\mathrm{B}T$.

3. Express the critical value $K_c(h)$ of K as a function of the applied magnetic field.
4. Show that the transition is *reentrant* in the (T, h) plane: for a certain interval of h, there are two critical values T_c of T, such that the system exhibits spontaneous symmetry breaking for values of T between them.

Exercise 5.13 Consider the Landau theory applied to a system with a vector order parameter $\boldsymbol{m}$. Show that we can distinguish between the effect of a field applied in the direction of the order parameter $\boldsymbol{m}$, or normal to it. For $T < T_c$, the susceptibility to a field parallel to $\boldsymbol{m}$ is finite for $h \to 0$, while the susceptibility to a field normal to it diverges like h^{-1}.

Exercise 5.14 (Tricritical point) Consider a system whose free energy density is given by

$$f(T, h, b; m) = \text{const.} + \frac{1}{2}am^2 + \frac{1}{4}bm^4 + \frac{1}{6}cm^6 - hm, \tag{5.1}$$

where m is a scalar and $c > 0$ is fixed. Set $h = 0$ at first.

1. Evaluate for fixed $b > 0$ the extrema of the free energy density as a function of a, and discuss their stability. Find the location of the critical point and evaluate the magnitude of the order parameter in the broken-symmetry phase.
2. Identify for fixed $b < 0$ the minima of the free energy and show that there is a point in which the symmetry breaks spontaneously. Discuss the nature of the transition. Sketch the phase diagram in the (a, b) plane, distinguishing between continuous and discontinuous transitions.
3. Show that for $h = 0$ there are surfaces in the (a, b, h) space where a discontinuous transition between two different broken-symmetry phases take place, and identify what bounds these surfaces.
4. The point $(a, b, h) = (0, 0, 0)$ is called the **tricritical point**. Evaluate the thermodynamic critical exponents approaching the tricritical point along the line $b = 0$.
5. Show that for b small but positive, as one approaches the critical temperature, one should first observe a behavior dictated by the tricritical point, and eventually those characteristic of the critical one.

Exercise 5.15 (Spherical model) Consider a model defined by the hamiltonian $\mathcal{H}(\sigma) = -J\sum_{<ij>}\sigma_i\sigma_j - h\sum_i \sigma_i$, defined on a lattice in d dimensions. Here the variables σ_i do not satisfy $\sigma_i^2 = 1$, $\forall i$, but the much weaker constraint

$$\sum_i \sigma_i^2 = N,$$

where N is the number of points in the lattice. Thus $\sigma = (\sigma_i)$ belongs to a sphere in N dimensions, what justifies the name "spherical model". Show that this model can be solved exactly, and that its behavior corresponds to that of the $n \to \infty$ limit.

Exercise 5.16 Obtain a scaling relation connecting δ, d and η. Evaluate the exponent δ of the $n \to \infty$ model and check on it the relation.

Exercise 5.17 (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

$$\mathcal{H}_1 = \sum_{i=1}^{N_1} \frac{p_i^2}{2m}.$$

   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 $\mu(T, N, \lambda_\mathrm{B})$, where $\lambda_\mathrm{B} = \sqrt{h^2/(2\pi m k_\mathrm{B} T)}$ 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

$$\mathcal{H}_2 = \sum_{i=1}^{N_2} \left(\frac{p_i^2}{2m} + \frac{1}{2} m\omega^2 r_i^2 - \epsilon_0 \right),$$

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

a) Write the expression of the partition function of the crystal.
b) Derive the expression of its chemical potential.
c) Imposing the equilibrium between the crystal and the gas phases, express the equilibrium pressure as a function of λ_{B}, T and $\theta = \hbar\omega/k_{\mathrm{B}}$.
d) Is the model thus obtained physically reasonable?

Exercise 5.18 (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

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

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:

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

where

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

is associated with odd-numbered spins, and

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

is associated with even-numbered spins.

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

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

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 5.19 (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

$$\mathcal{H} = -J \sum_{<i,j>} \sigma_i^z \sigma_j^z - \Gamma \sum_i \sigma_i^x,$$

where

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

This operator acts on the Hilbert space

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

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

$$\mathcal{F}(K,h;J,\Gamma) = \langle (\mathcal{H} - \mathcal{H}_0) \rangle_0 - \beta^{-1} \ln Z_0,$$

where we have introduced the trial hamiltonian

$$\mathcal{H}_0 = -\beta^{-1} \sum_i \left(K\sigma_i^z + h\sigma_i^x \right),$$

and where we respectively have

$$\begin{aligned} \langle A \rangle_0 &= \frac{1}{Z_0} \mathrm{Tr}\, A\, \mathrm{e}^{-\beta \mathcal{H}_0} \\ Z_0 &= \mathrm{Tr}\, \mathrm{e}^{-\beta \mathcal{H}_0}. \end{aligned}$$

Exploit the relations

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

1. Evaluate the trace by diagonalizing the matrix
$$\mathsf{T} = K\sigma^z + h\sigma^x.$$
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 5.20 (Mean-field theory of the 3-state Potts model) Let us consider a system made up of N units placed on a simple cubic lattice in d dimensions. The state of each unit i is identified by a variable τ_i that can assume the values $\tau_i \in \{1,2,3\}$. It two neighboring units have the same value of τ, the energy is lowered. We obtain therefore the hamiltonian
$$\mathcal{H}(\tau) = J\sum_{<i,j>}\left(1-\delta_{\tau_i\tau_j}\right).$$
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 $\tau_i = a$, $a \in \{1,2,3\}$. 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 express the entropy $S(m)$ of a system of N independent units as a function of m via Gibbs' formula.
2. Let us assume that the units are independent, identically distributed random variables, and that we have therefore $\mathrm{Prob}(\tau_i,\tau_j) = p_{\tau_i}p_{\tau_j}$ 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 (5.20) 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 a 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.

CHAPTER 6

Renormalization Group

Exercise 6.1 Derive the relation

$$\frac{\beta\delta}{\nu} = \frac{\ln \kappa_h}{\ln b},$$

where β, δ and ν are critical exponents, and κ_h is defined by the relation

$$\mathbb{T}(h, t = 0) = \kappa_h\, h + \mathrm{O}\left(h^3\right),$$

where $t = T - T_c$ and $\mathbb{T}$ is Kadanoff's transformation.

Exercise 6.2 Solve numerically the equation

$$K^* = \frac{3}{8} \ln\cosh 4K^*.$$

(Hint: How do you transform a fixed point from unstable into stable?)

Exercise 6.3 Show that all the coefficients of $k^n\, \phi_k \phi_{-k}$ with $n \neq 0$ are irrelevant parameters around the infinite temperature fixed point ($r > 0$, $c = 0$, etc.)

Exercise 6.4 Show that all the coefficients of $k^n\, \phi_k \phi_{-k}$ 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 6.5 Obtain the value of the exponent α for the Gaussian model and $d < 4$ from the relation

$$C_h \propto |T - T_{\mathrm{c}}|^{-\alpha},$$

where C_h is the thermal capacity at zero field, given by

$$C_h = -T \left.\frac{\partial^2 F}{\partial T^2}\right)_{h=0},$$

in which $F = -k_{\mathrm{B}} T \ln Z$ is the Helmholtz free energy.

Exercise 6.6 (Critical isotherm) Discuss the behavior of the $n \to \infty$ model for $h \neq 0$, and obtain the value of exponent δ directly. Compare this with the result obtained from the scaling laws:

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

Exercise 6.7 (Cubic anisotropy) Obtain the flow equations:

$$\begin{aligned}
\frac{\mathrm{d}r}{\mathrm{d}\ell} &= 2r + 4\left[(n+2)u + 3v\right]\frac{1}{1+r},\\
\frac{\mathrm{d}u}{\mathrm{d}\ell} &= \epsilon u - 4\left[(n+8)u^2 + 6uv\right]\frac{1}{(1+r)^2},\\
\frac{\mathrm{d}v}{\mathrm{d}\ell} &= \epsilon v - 4\left[12uv + 9v^2\right]\frac{1}{(1+r)^2}.
\end{aligned}$$

Exercise 6.8 Obtain explicitly the classical exponents for the ϕ^3 and the ϕ^6 case and evaluate d_{c} from the Toulouse criterion.

Exercise 6.9 Show that, in $2d$, the circuitation of a vector field $\boldsymbol{V}(\boldsymbol{r})$ over a closed circuit $\mathcal{C}$ is equal to the flux of a suitably rotated vector field $\boldsymbol{W}(\boldsymbol{r})$ across the same circuit $\mathcal{C}$. Using this analogy, obtain the expressions of the energy of an isolated vortex and of a vortex-antivortex pair by using Coulomb's law and the divergence theorem.

CHAPTER 7

Classical Fluids

Exercise 7.1 Consider the Gibbs entropy associated with the one-particle reduced density $\rho^{(1)}$, defined by

$$\mathcal{S}(\rho^{(1)}) = -k_{\mathrm{B}} \int \mathrm{d}x\, \rho^{(1)}(x) \ln \rho^{(1)}(x),$$

where $x = (\boldsymbol{r}, \boldsymbol{p})$ 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.

Exercise 7.2 Derive the **compressibility equation of state**:

$$\rho \int \mathrm{d}^3\boldsymbol{r}\ [g(\boldsymbol{r}) - 1] + 1 = \rho k_{\mathrm{B}} T K_{\mathrm{T}}.$$

Exercise 7.3 Evaluate $F[\rho]$ for the case of a fluid of non-interacting particles and show that this equation yields the Boltzmann distribution in an external potential $v(\boldsymbol{x})$.

Exercise 7.4 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.

Exercise 7.5 (Joule-Thomson 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.

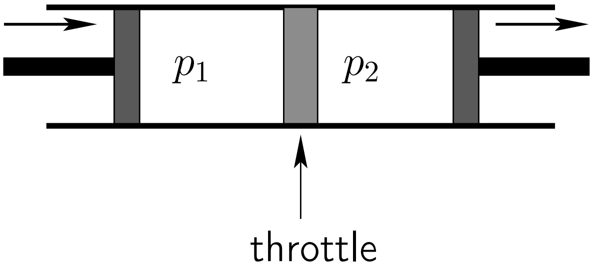

Figure 7.1: The Joule-Thomson process.

1. Show that the process occurs at constant enthalpy H.
2. Evaluate the temperature variation at constant enthalpy $\partial T/\partial p)_H$, as a function of both the specific heat at constant pressure C_p and of the expansion coefficient $\partial V/\partial T)_p$ for a small pressure drop.
3. Given the equation of state expressing p as a power series in ρ truncated at ρ^2, express this quantity as a function of the second virial coefficient $B_2(T)$, and evaluate the temperature T^* in which $\partial T/\partial p)_H$ changes sign.
4. Evaluate the relation between the inversion temperature T^* and the pressure p for a van der Waals gas.

Exercise 7.6 Generalize the equation

$$F_{\mathrm{el}} = -\frac{e^3}{3\pi}\left(\frac{2N_{\mathrm{salt}}}{\epsilon_0\epsilon_{\mathrm{r}}}\right)^{3/2}(V\,k_{\mathrm{B}}T)^{-1/2},$$

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.)

Chapter 8

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 $r_i \geq 0$, $i = 1, 2, \ldots, N$ 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.

Solve 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 conserved. Check the conservation of enthalpy $E + pL$. 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:

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

1. Solve the equations of motion for $\theta(t)$ numerically by the Verlet algorithm, and check energy conservation.
2. Experiment with the initial conditions, and evaluate numerically how the oscillation period grows when the initial angle approaches 180° (supposing that it starts at rest).

Exercise 8.3 Consider a one-dimensional fluid defined by the hamiltonian

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

with periodic boundary conditions:

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

Let $u(r)$ have the Lennard-Jones expression:

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

where it is assumed that only nearest-neighbor particles interact.

1. Introduce suitable length and time scales to make the differential equation adimensional. This leaves an explicit dependence on the adimensional particle density.
2. Write the program for the solution of the equations of motion by means of the velocity Verlet algorithm.
3. Write the expressions of the temperature and pressure as a function of the calculated trajectories obtained 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 in your PC, assuming $m \sim 10^{-23}\,\mathrm{g}$, $\epsilon_0 \sim 1\,\mathrm{eV}$, and $r_0 \sim 1\,\text{Å}$.
5. Choose the initial conditions so that the r_i are arranged on a regular lattice and the p_i follow a Gaussian distribution. Launch the simulation. 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 too small values for the energy, because the Fermi-Pasta-Ulam-Tsingou 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:

$$p_\sigma^{\text{micr}} = \begin{cases} 1/\left|\Gamma\right|, & \text{if } E < \mathcal{H}(\sigma) < E + \Delta E, \\ 0, & \text{otherwise,} \end{cases} \tag{8.1}$$

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 relation $C = \operatorname{Var}\mathcal{H}/k_\mathrm{B}T^2$ and the relation $C \simeq \Delta\left\langle\mathcal{H}\right\rangle/\Delta T$. 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.

Exercise 8.9 (Widom insertion method) The chemical potential of a fluid can be evaluated via a molecular dynamics or Monte Carlo simulation by the following method, due to Widom [1963].

1. Express the chemical potential μ of a simple fluid with N particles in terms of the partition functions Z_{N+1} and Z_N of a system with respectively $N+1$ and N particles. Deduce its expression in terms of the configuration integrals Ω_{N+1} and Ω_N.
2. Express Ω_{N+1} as the average of the Boltzmann factor of a "ghost particle" inserted at random positions within the system, expressed in terms of its interaction with the N remaining particles. Deduce the expression of μ.

CHAPTER 9

Dynamics

Exercise 9.1 Defining

$$\left\langle \Delta r^2(t) \right\rangle = \int \mathrm{d}\boldsymbol{r}\; r^2\, P(\boldsymbol{r},t \mid 0,0),$$

show that

$$\frac{\mathrm{d}}{\mathrm{d}t} \left\langle \Delta r^2(t) \right\rangle = 2dD,$$

where $P(\boldsymbol{r},t \mid 0,0)$ satisfies the equations

$$\int \mathrm{d}\boldsymbol{r}\; P(\boldsymbol{r},t \mid 0,0) = 1; \qquad \frac{\partial P}{\partial t} = D\nabla^2 P.$$

Exercise 9.2 (Kappler's experiment) In Kappler's experiment a mirror with moment of inertia equal to I is suspended to a taut wire. The torque exerted on the mirror for an angular displacement φ from the equilibrium point is given by $-\kappa\,\varphi$. The mirror is enclosed in a room at the temperature T and the resistance torque exerted on it when its angular velocity equals ω is given by $\tau = -\mu\omega$.

1. Write down the Kramers equation governing the evolution of its angular displacement φ from its equilibrium position.

2. By evaluating the Kramers equation for the equilibrium (Boltzmann) distribution, obtain the Einstein relation connecting the noise intensity and the resistance coefficient μ.

3. Write down the Langevin equation satisfied by the angular displacement $\varphi(t)$. Derive from it the differential equation satisfied by the correlation function $C(t) = \langle \varphi(t)\varphi(0) \rangle$ for $t > 0$.

4. Assuming $C(t) = \alpha\, \mathrm{e}^{-\lambda_+ t} + \beta\, \mathrm{e}^{-\lambda_- t}$, where $\lambda_\pm$ are constants to be determined, and suitable initial conditions, give the expression of $C(t)$. Notice that there are two regimes, one for small values of μ, and one for large values of μ. Identify the value μ_c of μ separating these regimes.

Exercise 9.3 From the relation

$$\frac{\mathrm{d}}{\mathrm{d}t} \left\langle \Delta r^2(t) \right\rangle = 2 \int_0^t \mathrm{d}t' \; \left\langle \boldsymbol{v}(t') \cdot \boldsymbol{v}(0) \right\rangle ,$$

assuming

$$\langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(0) \rangle = \left\langle v^2 \right\rangle \mathrm{e}^{-t/\tau}, \qquad t > 0,$$

evaluate $\left\langle \Delta r^2(t) \right\rangle$. Given that the diffusion constant in most liquids is of the order of $10^{-5}\,\mathrm{cm}^2\mathrm{s}^{-1}$, estimate the order of magnitude of τ.

Exercise 9.4 We describe a reaction chain of the form

$$\mathrm{A} \leftrightharpoons \mathrm{A}^* \leftrightharpoons \mathrm{B}.$$

Here A and B are two stable isomers of the same molecule, and A* is an unstable (energy-rich) transition form. The change from A to A* and then to B is described by a reaction coordinate x that moves in a one-dimensional bistable potential $U(x)$. Thus the phase space for this degree of freedom is divided into three regions, one close to A, one to A* and the third one to B. The non-equilibrium concentrations of species in the three regions are $[\mathrm{A}](t)$, $[\mathrm{A}^*](t)$ and $[\mathrm{B}](t)$. The rate equations for this reaction chain read

$$\begin{aligned}
\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} &= k_{\mathrm{AA}^*}[\mathrm{A}^*] - k_{\mathrm{A}^*\mathrm{A}}[\mathrm{A}];\\
\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} &= -\left(k_{\mathrm{AA}^*} + k_{\mathrm{BA}^*}\right)[\mathrm{A}^*] + k_{\mathrm{A}^*\mathrm{A}}[\mathrm{A}] + k_{\mathrm{A}^*\mathrm{B}}[\mathrm{B}];\\
\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} &= k_{\mathrm{BA}^*}[\mathrm{A}^*] - k_{\mathrm{A}^*\mathrm{B}}[\mathrm{B}].
\end{aligned}$$

These equations imply the conservation law

$$\mathrm{A} + [\mathrm{A}^*] + [\mathrm{B}] = \mathrm{const.}$$

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

$$\frac{k_{ij}}{k_{ji}} = \frac{[i]_{\mathrm{eq}}}{[j]_{\mathrm{eq}}} = \mathrm{e}^{-\Delta U_{ij}/k_{\mathrm{B}}T},$$

where (i,j) is either $(\mathrm{A}^*, \mathrm{A})$ or $(\mathrm{A}^*, \mathrm{B})$, and $\Delta U_{ij} = U_i - U_j$. Thus, if $\Delta U_{\mathrm{A}^*\mathrm{A}} \gg k_{\mathrm{B}}T$, one has $k_{\mathrm{A}^*\mathrm{A}} \ll k_{\mathrm{AA}^*}$, and analogously for $k_{\mathrm{A}^*\mathrm{B}}$, k_{BA^*}.

1. Evaluate the behavior of

$$\Delta[\mathrm{A}](t) = [\mathrm{A}](t) - [\mathrm{A}]_{\mathrm{eq}}.$$

2. Show that, if $\Delta U_{\mathrm{A}^*\mathrm{A}} \gg k_{\mathrm{B}}T$, and analogously for $\Delta U_{\mathrm{A}^*\mathrm{B}}$, the relaxation is dominated by a single relaxation time, τ, and that

$$\tau^{-1} \approx k_{\mathrm{A}^*\mathrm{A}} \text{ or } k_{\mathrm{A}^*\mathrm{B}}.$$

Exercise 9.5 (Brownian motion of a harmonic oscillator) Consider a Brownian particle of mass m subject to a harmonic potential of Hooke's constant $m\omega_0^2$ in one dimension, immersed in a fluid at the temperature T, with a damping coefficient equal to γ.

1. Write down the evolution equation of the system when the system is subjected to a time-dependent applied force $f(t)$.
2. Assuming that the system was in equilibrium at $t = 0$, express the average instantaneous position $\langle x(t) \rangle$ in terms of the response function $\chi(t)$ and $f(t)$. By solving the Langevin equation, give the expressions of the response function.
3. Evaluate the correlation function $C(t) = \langle x(t)x(0) \rangle$, assuming that $\langle x^2(0) \rangle$ is equal to the equilibrium value.
4. Evaluate the Fourier transform $C(\omega) = \int_{-\infty}^{+\infty} \mathrm{d}t\ \mathrm{e}^{\mathrm{i}\omega t}\, C(t)$ and compare it with the imaginary part $\chi''(\omega)$ of the Fourier transform of the corresponding response function $\chi(t)$.

Exercise 9.6 Consider a Brownian particle in contact with a heat reservoir. We denote by x the coordinate of the particle and by $(y_1, \dots, y_N)$ the coordinates of the reservoir. The hamiltonian of the system is given by

$$\mathcal{H} = \mathcal{H}_0(x) - xf + \mathcal{H}_{\mathrm{b}}(y_1, \dots, y_N).$$

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 $\mathcal{H}_\mathrm{b}$ is the hamiltonian for a system of classical oscillators. This imples the exact validity of linear-response theory, yielding

$$f(t) = f_\mathrm{b}(t) + \int_{-\infty}^{+\infty} \mathrm{d}t'\, \chi_\mathrm{b}(t-t')x(t'),$$

where

$$\chi_\mathrm{b}(t) = \begin{cases} -\beta \mathrm{d}C_\mathrm{b}(t)/\mathrm{d}t, & \text{for } t > 0; \\ 0, & \text{otherwise.} \end{cases}$$

Here, $C_\mathrm{b}(t)$ is the correlation function of the isolated reservoir:

$$C_\mathrm{b}(t) = \langle \delta f(t)\, \delta f(0) \rangle_\mathrm{b} \,.$$

Show that $x(t)$ satisfies the equation

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

where

$$\begin{aligned} \tilde{f}(x) &= -\frac{\mathrm{d}\tilde{V}}{\mathrm{d}x}; \\ \tilde{V}(x) &= V(x) - \beta C(0)\frac{x^2}{2}; \\ \delta f(t) &= f_\mathrm{b}(t) - \beta C_\mathrm{b}(t) x(0). \end{aligned}$$

Thus $\delta f(t)$ is a Gaussian force with vanishing average and correlation equal to $C_\mathrm{b}(t-t')$.

CHAPTER 10

Stochastic Thermodynamics

Exercise 10.1 Consider a system in contact with a reservoir at the temperature T, but in a nonequilibrium state described by the probability distribution $p = (p_x)$, when the equilibrium distribution p^{eq} is the canonical one $p_x^{\text{eq}} = \mathrm{e}^{(F-\epsilon_x)/k_{\mathrm{B}}T}$. Show that the work W that can be extracted by allowing the system to relax to equilibrium satisfies the inequality

$$W \le k_{\mathrm{B}} T D_{\mathrm{KL}}(p \| p^{\text{eq}}),$$

where $D_{\mathrm{KL}}(p\|q)$ is the Kullback-Leibler divergence between the probability distributions p and q.

Exercise 10.2 Prove that, if $p^{\text{st}} = (p_x^{\text{st}})$ is the stationary solution of the master equation defined by the ergodic transition-rate matrix $\mathsf{K} = (k_{xx'})$, and $\psi = (\psi_x)$ is an arbitrary vector, one has

$$\sum_{xx'} k_{xx'} p_{x'}^{\text{st}} \left(\psi_x - \psi_{x'}\right) = 0.$$

Exercise 10.3 Discuss the behavior of $D_{\mathrm{KL}}(p\|p^{\text{st}})$ when the transition rate matrix K is non-ergodic.

Exercise 10.4 Find an alternate proof of the inequality

$$\frac{\mathrm{d}}{\mathrm{d}t}D_{\mathrm{KL}}(p(t)\|p^{\mathrm{eq}}) \leq 0$$

when $p(t)$ is a solution of a master equation defined by the ergodic matrix $\mathsf{K} = (k_{xx'})$ satisfying detailed balance, and $p^{\mathrm{eq}} = (p_x^{\mathrm{eq}})$ is its equilibrium solution.

Exercise 10.5 Show that the value W of the work that contributes the most to the Jarzynski average $\left\langle \mathrm{e}^{-W/k_{\mathrm{B}}T} \right\rangle$ is equal to the opposite of the most probable value of W in the backward protocol $\widehat{\lambda}$.

Exercise 10.6 Show that the Jarzynski equality holds for a system undergoing an instantaneous quench, defined by the protocol

$$\lambda(t) = \begin{cases} \lambda_0, & \text{for } 0 \leq t_0 < t_{\mathrm{q}}; \\ \lambda_{\mathrm{f}}, & \text{for } t_{\mathrm{q}} \leq t \leq t_{\mathrm{f}}. \end{cases}$$

Assume that the system is at equilibrium with $\lambda = \lambda_0$ at the temperature T for $t = t_0$.

Exercise 10.7 Show that, if the entropy production $\Delta\mathcal{S}^{\mathrm{tot}}$ is gaussianly distributed, one has

$$2k_{\mathrm{B}}\left\langle \Delta\mathcal{S}^{\mathrm{tot}} \right\rangle = \sigma_{\mathrm{tot}}^2,$$

where σ_{tot}^2 is the variance of $\Delta\mathcal{S}^{\mathrm{tot}}$.

Exercise 10.8 (Onsager reciprocal relations) In a non-equilibrium steady state produced by the affinities $\mathcal{A} = (\mathcal{A}_\alpha)$, the entropy produced during a time interval of duration $\mathcal{T}$ is given by the equation

$$\mathcal{S} = \mathcal{T}\sum_\alpha \mathcal{A}_\alpha \mathcal{J}_\alpha,$$

where $\mathcal{J} = (\mathcal{J}_\alpha)$ are the fluctuating currents conjugate to the affinities $\mathcal{A} = (\mathcal{A}_\alpha)$.

Using the detailed fluctuation relation, show that the quantity

$$\psi(q) = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \ln \left\langle \exp\left(\mathcal{T} \sum_\alpha q_\alpha \mathcal{J}_\alpha\right)\right\rangle,$$

where $q = (q_\alpha)$, possesses the Gallavotti-Cohen symmetry $q_\alpha - A_\alpha/k_\mathrm{B} \longrightarrow -q_\alpha$, that is,

$$\psi\left(q - \frac{\mathcal{A}}{k_\mathrm{B}}\right) = \psi(-q).$$

Using this result and the relations

$$\langle \mathcal{J}_\alpha\rangle = \left.\frac{\partial\psi}{\partial q_\alpha}\right|_{q=0}, \qquad L_{\alpha\beta} = \left.\frac{\partial\langle \mathcal{J}_\alpha\rangle}{\partial \mathcal{A}_\alpha}\right|_{q=0,A=0} = \left.\frac{\partial^2\psi}{\partial q_\alpha\,\partial \mathcal{A}_\alpha}\right|_{q=0,A=0},$$

prove that the matrix $\mathsf{L} = (L_{\alpha\beta})$ is symmetric. Thus the Onsager reciprocity relations are a consequence of the Gallavotti-Cohen symmetry.

Exercise 10.9 Consider a Brownian particle of mobility μ, immersed in a fluid at temperature T and subject to a force $\boldsymbol{f}$ parallel to the x axis. In this situation, the average displacement of the particle during a time interval of duration $\mathcal{T}$ is given by

$$\Delta\boldsymbol{r} = \mu\, f\, \mathcal{T}\,\boldsymbol{i},$$

where $\boldsymbol{r} = (x, y, z)$ and $\boldsymbol{i}$ is the unit vector of the x-axis. Show that the Jarzynski equality applied to this system implies the Einstein relation between the mobility and the diffusion coefficient D, that is,

$$D = k_\mathrm{B} T\,\mu.$$

Exercise 10.10 (Hamiltonian system) Consider a system satisfying the canonical equations of motion with state vector $x = ((q_1, p_1), \ldots, (q_n, p_n))$ and hamiltonian $\mathcal{H}(x;\lambda) = \mathcal{H}(q_1, p_1, \ldots, q_n, p_n; \lambda)$. Assume that the system is in equilibrium at the temperature T for $t = t_0$, and is then manipulated according to a protocol $\boldsymbol{\lambda} = (\lambda(t))$ for $t_0 \le t \le t_\mathrm{f}$. During the manipulation, the system is isolated. Show that the Jarzynski equality holds for this system, where the work $\mathcal{W}(\boldsymbol{x};\boldsymbol{\lambda})$ is defined in terms of the phase-space trajectory $\boldsymbol{x} = (x(t))$ and the protocol $\boldsymbol{\lambda}$ by

$$\mathcal{W}(\boldsymbol{x};\boldsymbol{\lambda}) = \int_{t_0}^{t_\mathrm{f}} \mathrm{d}t\, \frac{\mathrm{d}\lambda(t)}{\mathrm{d}t}\, \frac{\partial\mathcal{H}(x(t);\lambda(t))}{\partial\lambda},$$

and ΔF is given by $F(\lambda_{\mathrm{f}}) - F(\lambda_0)$, with

$$F(\lambda) = -k_{\mathrm{B}}T \ln \int \mathrm{d}x \, \mathrm{e}^{-\mathcal{H}(x;\lambda)/k_{\mathrm{B}}T}.$$

Exercise 10.11 Show that the Crooks relation implies that the probability $P(\mathcal{W} \leq \Delta F - \zeta)$ that the work $\mathcal{W}$ is smaller than the free energy difference ΔF by at least the amount $\zeta > 0$ satisfies the inequality

$$P(\mathcal{W} \leq \Delta F - \zeta) \leq \mathrm{e}^{-\zeta/k_{\mathrm{B}}T}.$$

Exercise 10.12 Imagine that you are shown a movie of a mesoscopic system undergoing manipulation while in contact with a reservoir at temperature T. The movie can be either the record of the forward (F) process, in which the system is manipulated out of an initial equilibrium state, or the record of the backward (B) process, projected in reverse order. Taking advantage of the Crooks relation, show that, to assess the probability that the movie shows the F process, it is sufficient to evaluate the dissipated work $\mathcal{W} - \Delta F$, where the work $\mathcal{W}$ is computed from the trajectory exhibited in the movie. Evaluate the probability $p_{\mathrm{F}|\mathcal{W}}$ as a function of $\mathcal{W}$.

Exercise 10.13 Consider a weakly interacting, dilute gas contained in a cylinder with a piston, initially at equilibrium at the temperature T. The system is then thermally isolated and undergoes an adiabatic quasi-static transformation in which its volume changes from V_0 to V_{f}. Assuming that transformation is performed infinitely slowly, verify the Jarzynski equality for this system. Where does stochasticity come from in this case?

Exercise 10.14 Show that the Widom insertion method for the evaluation of the chemical potential can be justified by the Jarzynski equality.

Exercise 10.15 Derive explicitly the relations

$$\Delta\mathcal{S}^{\mathrm{a}}[x;\lambda] = k_{\mathrm{B}} \ln \frac{\mathcal{P}[x;\lambda]}{\mathcal{P}^{+}[x;\lambda]};$$
$$\Delta\mathcal{S}^{\mathrm{na}}[x;\lambda] = k_{\mathrm{B}} \ln \frac{\mathcal{P}[x;\lambda]}{\mathcal{P}^{+}[\widehat{x};\widehat{\lambda}]}.$$

Exercise 10.16 A 1-bit memory is represented by a system with three states: $x \in \{-1, 0, +1\}$, where $\epsilon_{\pm 1} = 0$ and $\epsilon_0 \gg k_{\mathrm{B}}T$, and only the jumps $0 \leftrightharpoons \pm 1$ are allowed, all with equal attempt frequency. The state 0 therefore acts as a barrier between the ± 1 states. The dynamics satisfies detailed balance. One can erase the contents of the memory by manipulating the energies according to the following protocol:

1. The energy barrier ϵ_0 is continuously lowered to 0.
2. Then the energies ϵ_0 and ϵ_{+1} are tilted by setting $\epsilon_0(t) = -\epsilon(t)/2$, $\epsilon_{+1}(t) = -\epsilon(t)$, where $\epsilon(t)$ grows from 0 to a positive value ϵ_{f}. This biases the occupation towards the state $+1$.
3. The energy barrier ϵ_0 is continuously reset to its initial value.
4. Finally, the energy ϵ_{+1} is continuously reset to its initial value.

The outcome of the process is that, independent of the initial state, the final state of the system is equal to $+1$ with high probability. Evaluate W numerically for different values of the duration $\mathcal{T}$ of the manipulation and check that the Landauer bound is approached as $\mathcal{T} \to \infty$. Also show numerically that the average work W in the reverse process, with the initial condition $p_x(t_0) = \delta_{x,+1}$, satisfies the inequality $W \geq -k_{\mathrm{B}}T \ln 2$, and interpret this result.

Exercise 10.17 The evolution equation

$$\frac{\mathrm{d}p_u}{\mathrm{d}t} = \left(k^{\uparrow} + \tilde{k}^{\uparrow}\right) p_d - \left(k^{\downarrow} + \tilde{k}^{\downarrow}\right) p_u;$$
$$\frac{\mathrm{d}p_d}{\mathrm{d}t} = \left(k^{\downarrow} + \tilde{k}^{\downarrow}\right) p_u - \left(k^{\uparrow} + \tilde{k}^{\uparrow}\right) p_d.$$

can also be interpreted in the measurement-and-feedback scheme. In this interpretation, the information reservoir is a device that measures the state of the system at a rate γ, obtaining a result $y \in \{0, 1\}$, where 1 corresponds to u and 0 to d. The parameter r represents the error probability of the measurement, that is, $p_{u|1} = p_{d|0} = 1 - r$ and $p_{u|0} = p_{d|1} = r$. We assume $0 < r \leq 1/2$. If the outcome of the measurement is 1, the states are swapped. Evaluate the average work per unit time performed by the system and the total entropy production in this interpretation and connect these quantities to the mutual entropy of the measurement via the Sagawa-Ueda inequality.

Exercise 10.18 (System interacting with two tapes) Consider a two-state system with two edges between the states, labeled I and II. Both edges are associated with information-mediated jumps, driven by interaction with tapes. The fraction of 1s in the two incoming tapes are $r_{\mathrm{I}} \leq \frac{1}{2}$, and $r_{\mathrm{II}} \leq \frac{1}{2}$. The jump rates from 0 to 1 are $\gamma_{\mathrm{I}} r_{\mathrm{I}}$ for edge I and $\gamma_{\mathrm{II}} r_{\mathrm{II}}$ for edge II. The reverse jump rates are $\gamma_{\mathrm{I}}(1-r_{\mathrm{I}})$ and $\gamma_{\mathrm{II}}(1-r_{\mathrm{II}})$.

Evaluate the entropy production rate. Assuming $r_{\mathrm{I}} < r_{\mathrm{II}} \leq \frac{1}{2}$, information is written on tape I and erased from tape II. Evaluate the efficiency η of the process, defined by

$$\eta = -\frac{\dot{S}^{\mathrm{erase}}}{\dot{S}^{\mathrm{write}}},$$

in the regimes $\gamma_{\mathrm{II}} \gg \gamma_{\mathrm{I}}$ and $\gamma_{\mathrm{II}} \ll \gamma_{\mathrm{I}}$, respectively.

CHAPTER

11

Complex Systems

Exercise 11.1 Evaluate $\left\langle R_{\mathrm{G}}^{2}\right\rangle$ and its relation with $\left\langle r_{N}^{2}\right\rangle$ in the Gaussian model of a linear polymer.

Exercise 11.2 (Polymer on a lattice) Suppose that a polymer is placed over a simple cubic lattice in d dimensions with lattice constant a_0, imposing the constraint that monomers following along the chain must sit on nearest-neighbor lattice points, but that there is no bound on the number of monomers that can occupy a single lattice point. Show that one obtains an expression of the form

$$\Gamma_{\mathrm{GC}}(\boldsymbol{k}, z) \propto \frac{1}{z_{\mathrm{c}} - z + c k^2},$$

for $\Gamma_{\mathrm{GC}}(\boldsymbol{k}, z) = \sum_{N=0}^{\infty} z^N \Gamma_N(\boldsymbol{k})$, and calculate the corresponding values of z_{c} and of the constant c.

Exercise 11.3 Show that if $\Gamma_{\mathrm{GC}}(\boldsymbol{k}{=}0, z) \propto |z_{\mathrm{c}} - z|^{-\gamma}$, one has in the

$$\Gamma_N = \int \mathrm{d}^d\boldsymbol{r}\, \Gamma_N(\boldsymbol{r}) \propto z_{\mathrm{c}}^{-N}\, N^{\gamma-1}.$$

In our case, therefore, $\Gamma_N \propto z_{\mathrm{c}}^{-N}$, while the factor $N^{\gamma-1}$ (which is called the **enhancement factor**) is equal to 1, and γ has the classical value 1.

Exercise 11.4 Show that, for $2 < d < 4$, one has

$$\Gamma(\boldsymbol{r}{=}0, z) = \int \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d}\, \Gamma_{\mathrm{GC}}(\boldsymbol{k}) \simeq \text{const.} + \text{const.} \times |z_{\mathrm{c}} - z|^{(d-2)/2}.$$

Show that this result implies that, for $2 < d < 4$, one has $\Gamma_N(\boldsymbol{r}{=}0) \sim N^{-d/2}$. What occurs for $d = 4$? And what about $d > 4$?

Exercise 11.5 Show that the coefficient of h^{2p} in $\lim_{n \to 0} \ln Z/n$ is given by graphs that represent the configurations of p excluded-volume polymers over the lattice. The contribution of each graph is proportional to K^N, where N is the total number of bonds present in the configuration.

Exercise 11.6 Show that the magnetic susceptibility χ per site for a diluted ferromagnet with strong spin-spin interaction J, with vanishing magnetic field, is given by

$$\chi = \frac{J}{k_{\mathrm{B}} T} \sum_s s^2\, \nu_s(p).$$

Exercise 11.7 Show that the analog of the magnetic correlation function between site i and site j in a diluted ferromagnet with strong spin-spin interaction J is given by the probability that i and j belong to the same finite cluster.

Exercise 11.8 Prove the following two relations for $S(p)$ and $T(p)$ in the percolation problem on the Bethe lattice:

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

Exercise 11.9 Prove the following relation:

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

between the size s of a cluster and the size s' of its boundary in the percolation problem on the Bethe lattice.

Exercise 11.10 Define the exponents σ and τ in terms of the the density $\nu_s(p)$ of clusters of size s per lattice point, as a function of the occupation probability p, by

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

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

$$M_k \propto |p-p_{\mathrm{c}}|^{\Delta_k},$$

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

Exercise 11.11 Show that $\lim_{q\to 0} G(\boldsymbol{r},\boldsymbol{r}') = \langle \Delta(\boldsymbol{r},\boldsymbol{r}')\rangle_{\mathrm{t}}$ in the q-state Potts model, where $\langle \ldots \rangle_{\mathrm{t}}$ represents the average with respect to the distribution $K^{\mathcal{B}(\mathcal{T})}/\mathcal{Z}'_N$. Moreover, show that in the limit $K \to \infty$, one obtains the average with respect to the **spanning trees**—in other words, to those trees that visit all the sites.

Exercise 11.12 Calculate the exponent ν for $d = 3$ in the bond percolation problem by the Migdal-Kadanoff recursion relation

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

and compare it with the numerical value $\nu \simeq 0.9$.

Exercise 11.13 (Migdal-Kadanoff renormalization of the Ising model) 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 obtain the recurrence relation for $K = J/k_{\mathrm{B}}T$ corresponding to a scaling factor b. Calculate the equation for the infinitesimal transformation corresponding to

$b \to 1^+$. Identify the fixed point for $d = 2$ and $d = 3$, and compare the value for the critical temperature and the exponent ν obtained in this way with the exact solution or available numerical values. Discuss the limits $d \to 1$ and $d \to 3$.

Exercise 11.14 Calculate the Hausdorff dimension of the **Sierpiński triangle**, recursively defined as follows. 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 $1 < d_\mathrm{H} < 2$.

Exercise 11.15 Calculate the Hausdorff dimension of the **von Koch curve**, recursively defined as follows. Consider a segment of unit length in the plane. The middle third of the segment is replaced with two segments of length $1/3$ each, as in the figure. The construction is repeated for each of the four segments thus obtained.

Exercise 11.16 Derive the Hausdorff dimensions of the Cantor set, the Sierpiński triangle and the von Koch curve according to the following definition: for a figure immersed in a d-dimensional space, the Hausdorff dimension d_H is given by the behavior of the mass $M(\ell)$ of the figure contained in a sphere of radius ℓ by

$$M(\ell) \sim \ell^{d_\mathrm{H}}.$$

Exercise 11.17 Show that the Gumbel distribution holds for the minimum value of a collection of M random variables E_α, 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 11.18 Show that, if the E_α are distributed approximately exponentially for large and negative E, the Boltzmann factors z_α decay like a power law:

$$P_z(z) \sim z^{-1-\mu}, \tag{11.1}$$

and give the expression of the power μ.

Exercise 11.19 (Large deviations) Let $\mathcal{N}(\epsilon, \delta)$ be the total number of configurations j such that $N\epsilon < \left|E_j\right| < N(\epsilon + \delta)$, with $|\epsilon| > \epsilon_* = \sqrt{\ln 2}$ and $\delta > 0$. Show that the fraction of samples in which there exist such configurations is exponentially small.

Exercise 11.20 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' $M \in \{-N, -N+2, \ldots, N-2, N\}$, and includes $\binom{N}{(N+M)/2}$ configurations. Their energies $\{E_j\}$ are indipendent Gaussian variables with variance $\sqrt{N/2}$ and mean $\left[E_j\right]_{\text{av}} = -MB$, 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:

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

Plot the magnetic susceptibility

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

vs. $T = 1/\beta$.

Exercise 11.21 Consider a generalization of the REM where the pdf of energies, instead of being Gaussian, is $P(E) \propto \mathrm{e}^{-C|E|^{\delta}}$, 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 $N \to \infty$ 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 $\delta < 1$?

Exercise 11.22 Show that, in the Hopfield model of associative memory, if $k_{\mathrm{B}}T < 1$ there exist solutions to the equations

$$f(T) = \frac{1}{2}m^2 - k_{\mathrm{B}}T\,\overline{\ln\left[2\cosh\left(\frac{\boldsymbol{m}\cdot\boldsymbol{\xi}}{k_{\mathrm{B}}T}\right)\right]},$$

$$\boldsymbol{m} = \overline{\boldsymbol{\xi}\tanh\left(\frac{\boldsymbol{m}\cdot\boldsymbol{\xi}}{k_{\mathrm{B}}T}\right)},$$

of the form

$$\boldsymbol{m} = (m^i), \qquad m^i = m, \quad i = 1, \ldots, r; \qquad m^i = 0, \quad i = r+1, \ldots, p.$$

Show that these solutions are metastable, since the corresponding free energy is larger than that of the solution with $r = 1$.

Exercise 11.23 (Capacity of a Hopfield network) The maximal number p_{max} of patterns that can be stored error-free in a Hopfield network can be evaluated as follows. Define the Hopfield hamiltonian $\mathcal{H}(\sigma; \xi)$ by the (slightly modified) expression

$$\mathcal{H}(\sigma; \xi) = -\sum_{\alpha=1}^{p} \left(\sum_{i=1}^{N} \xi_i^\alpha \sigma_i \right)^n , \tag{11.2}$$

where $n = 2$ and σ and the ξ^α are vectors of length N with entries equal to ± 1. Assume that the entries ξ_i^α are independent and identically distributed, equal to $+1$ with probability $\frac{1}{2}$.

1. Give the expression of the energy difference $\Delta E = \mathcal{H}(\hat{\xi}^1; \xi) - \mathcal{H}(\xi^1; \xi)$, where $\hat{\xi}^1$ differs from the stored pattern ξ^1 by a single spin flip: $\hat{\xi}_i^1 - \xi_i^1 = -2\xi_i^1 \delta_{ii_0}$. Evaluate the average $\langle \Delta E \rangle$ and variance $\Sigma^2 = \operatorname{Var} \Delta E$ of ΔE as a function of p and N, provided p and N are large.
2. The i_0-th bit becomes unstable when the magnitude of the fluctuation exceeds the energy gap $\langle \Delta E \rangle$ and the sign of the fluctuation is opposite to the sign of the energy gap. Evaluate the probability that this takes place.
3. Deduce the maximal value of p such that this probability does not exceed a small threshold (say, of 0.5%).
4. Repeat the evaluation for $n > 2$. How does the capacity depend on n?

Part II

Solutions

Chapter 1

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

$$R_\mathrm{T} = \frac{40 \cdot 10^6}{2\pi} = 6.37 \cdot 10^6\,\mathrm{m}. \tag{1.1}$$

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

$$V = 0.71 \cdot 4\pi R_\mathrm{T}^2 h = 1.37 \cdot 10^{18}\,\mathrm{m}^3. \tag{1.2}$$

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

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

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 $nN_\mathrm{A} = 33 \cdot 10^{23}$ molecules, where $N_\mathrm{A} = 6.02 \cdot 10^{23}\,\mathrm{mol}^{-1}$ is Avogadro's number. The expected number of molecules to be found in the flask after the dilution is given by

$$N = nN_\mathrm{A}x = 2.4 \cdot 10^2. \tag{1.4}$$

Solution to exercise 1.2 Due to the independence of the components, the distribution $\phi(\boldsymbol{v})$ must satisfy

$$\phi(\boldsymbol{v}) = f_x(v_x) f_y(v_y) f_z(v_z), \tag{1.5}$$

where the $f_\alpha(v)$ ($\alpha = x, y, z$) are some functions of their arguments. On the other hand, due to isotropy, one has

$$\phi(\boldsymbol{v}) = \psi(v^2), \tag{1.6}$$

where $\psi(z)$ is a suitable function. We then have

$$\frac{\partial \ln \phi(\boldsymbol{v})}{\partial v_x} = 2v_x \frac{\psi'(v^2)}{\psi(v^2)} = \frac{f'(v_x)}{f(v_x)}. \tag{1.7}$$

The last term is independent of v^2, and therefore we must have

$$\frac{\psi'(v^2)}{\psi(v^2)} = -\lambda = \text{const.}, \tag{1.8}$$

where $\lambda > 0$ to ensure normalizability. We thus obtain

$$\phi(\boldsymbol{v}) \propto \mathrm{e}^{-\lambda v^2}. \tag{1.9}$$

Since

$$\int_{-\infty}^{+\infty} \mathrm{d}z \; \mathrm{e}^{-\lambda z^2} = \sqrt{\frac{\pi}{\lambda}}, \tag{1.10}$$

we obtain, by imposing the normalization of $\phi(\boldsymbol{v})$,

$$\phi(\boldsymbol{v}) = \left(\frac{\lambda}{\pi}\right)^{3/2} \mathrm{e}^{-\lambda v^2}. \tag{1.11}$$

To obtain $\left\langle v^2 \right\rangle$, observe that

$$\left\langle v^2 \right\rangle = -\frac{\mathrm{d}}{\mathrm{d}\lambda} \ln \int \mathrm{d}\boldsymbol{v} \; \mathrm{e}^{-\lambda v^2} = \frac{3}{2\lambda}. \tag{1.12}$$

Thus

$$\left\langle \frac{1}{2} m v^3 \right\rangle = \frac{3m}{4\lambda}. \tag{1.13}$$

Solution to exercise 1.3 (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

$$\left\langle v_i^2 \right\rangle = \int_{-\infty}^{\infty} \frac{\mathrm{d}v_i}{\sqrt{2\pi k_\mathrm{B} T/m}}\, v_i^2\, \mathrm{e}^{-m v_i^2/k_\mathrm{B}T} = \frac{k_\mathrm{B}T}{m}. \tag{1.14}$$

Thus

$$\left\langle v^2 \right\rangle = \left\langle \sum_{i=1}^{d} v_i^2 \right\rangle = \frac{d\, k_\mathrm{B}T}{m}. \tag{1.15}$$

and therefore

$$v_\mathrm{RMS} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{d\, k_\mathrm{B}T}{m}}. \tag{1.16}$$

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

$$\left\langle v^2 \right\rangle = 3 k_\mathrm{B} T \left(\frac{p}{m_{\mathrm{O}_2}} + \frac{q}{m_{\mathrm{N}_2}} \right) = \frac{3 k_\mathrm{B} T}{m_\mathrm{Harm}}, \tag{1.17}$$

where m_Harm is the harmonic mean of the components' masses:

$$m_\mathrm{Harm} = \left[\frac{p}{m_{\mathrm{O}_2}} + \frac{q}{m_{\mathrm{N}_2}} \right]^{-1} = 29.2\,\mathrm{g}/N_\mathrm{A}. \tag{1.18}$$

We obtain therefore

$$\left\langle v^2 \right\rangle = \frac{3 \cdot R \cdot 300}{N_\mathrm{A} \cdot m_\mathrm{Harm}} = \frac{3 \cdot 8.31 \cdot 300}{29.2 \cdot 10^{-3}} = 2.56 \cdot 10^5\,\mathrm{m}^2\mathrm{s}^{-2}, \tag{1.19}$$

where $R = 8.31 \mathrm{JK}^{-1}$ is the gas constant, leading to

$$v_\mathrm{RMS} = \sqrt{\langle v^2 \rangle} = 5.06 \cdot 10^2\,\mathrm{ms}^{-1}. \tag{1.20}$$

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

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

$$\phi(v) = \left(\frac{m}{2\pi k_\mathrm{B} T} \right)^{d/2} \exp\left(- \sum_{i=1}^{d} \frac{m v_i^2}{2 k_\mathrm{B} T} \right). \tag{1.21}$$

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

$$\phi(v) = S_d \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{d/2} v^{d-1} \exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right). \tag{1.22}$$

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

$$p_v'(v) = \text{const.} \left[\frac{d-1}{v} - \frac{mv}{k_\mathrm{B}T}\right] v^{d-1} \exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right) = 0. \tag{1.23}$$

The factor in brackets vanishes for

$$mv^2 = (d-1)k_\mathrm{B}T. \tag{1.24}$$

We must of course choose the positive solution:

$$v_\mathrm{prob} = \sqrt{\frac{(d-1)k_\mathrm{B}T}{m}} = \sqrt{\frac{d-1}{d}} v_\mathrm{RMS}. \tag{1.25}$$

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

$$\phi(v_0)\,\mathrm{d}v_0 = p_v\left(\sqrt{\frac{2\kappa_0}{m}}\right) \frac{\mathrm{d}\kappa_0}{\sqrt{2m\kappa_0}} = p_\kappa(\kappa_0)\,\mathrm{d}\kappa_0, \tag{1.26}$$

yielding

$$\begin{aligned} p_\kappa(\kappa_0) &= S_d \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{d/2} \frac{1}{\sqrt{2m\kappa_0}} p_v\left(\sqrt{\frac{2\kappa_0}{m}}\right) \\ &= S_d \frac{1}{2\kappa_0} \left(\frac{\kappa_0}{\pi k_\mathrm{B}T}\right)^{d/2} \exp\left(-\frac{\kappa_0}{k_\mathrm{B}T}\right). \end{aligned} \tag{1.27}$$

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

Solution to exercise 1.4 (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

$$\Delta\mathcal{N}_2 = \rho_2 \left\langle v_z\, \theta(-v_z)\right\rangle\, A\,\Delta t, \tag{1.28}$$

where, from Maxwell's distribution, we have

$$\langle v_z\,\theta(-v_z)\rangle = \int_{-\infty}^{0} \frac{\mathrm{d}v_z}{\sqrt{2\pi k_{\mathrm{B}}T/m}}\,\mathrm{e}^{-mv_z^2/(2k_{\mathrm{B}}T)} = \sqrt{\frac{k_{\mathrm{B}}T}{2\pi m}}. \tag{1.29}$$

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

$$\Delta\mathcal{N}_1 = \rho_1 \left\langle v_z\,\theta\left(v_z - \sqrt{2gh}\right)\right\rangle A\,\Delta t, \tag{1.30}$$

where

$$\left\langle v_z\,\theta\left(v_z - \sqrt{2gh}\right)\right\rangle = \int_{\sqrt{2gh}}^{\infty} \frac{\mathrm{d}v_z}{\sqrt{2\pi k_{\mathrm{B}}T/m}}\,\mathrm{e}^{-mv_z^2/(2k_{\mathrm{B}}T)} = \sqrt{\frac{k_{\mathrm{B}}T}{2\pi m}}\mathrm{e}^{-mgh/k_{\mathrm{B}}T}. \tag{1.31}$$

Equating these two quantities we obtain

$$\rho_2 = \rho_1\,\mathrm{e}^{-mgh/k_{\mathrm{B}}T}. \tag{1.32}$$

Solution to exercise 1.5 (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

$$\Delta\mathcal{N}_1 = \rho_1\,\langle v_x\,\theta(-v_x)\rangle_1\, A\,\Delta t, \tag{1.33}$$

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

$$\langle v_x\,\theta(v_x)\rangle_1 = \int_{0}^{\infty} \frac{\mathrm{d}v_x}{\sqrt{2\pi k_{\mathrm{B}}T_1/m}}\,\mathrm{e}^{-mv_x^2/(2k_{\mathrm{B}}T_1)} = \sqrt{\frac{k_{\mathrm{B}}T_1}{2\pi m}}. \tag{1.34}$$

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

$$\Delta\mathcal{N}_2 = \rho_2\,\langle v_x\,\theta(-v_x)\rangle\, A\,\Delta t, \tag{1.35}$$

where

$$\langle v_x\,\theta(-v_x)\rangle_2 = \int_{-\infty}^{0} \frac{\mathrm{d}v_x}{\sqrt{2\pi k_{\mathrm{B}}T_2/m}}\,\mathrm{e}^{-mv_x^2/(2k_{\mathrm{B}}T_2)} = \sqrt{\frac{k_{\mathrm{B}}T_2}{2\pi m}}. \tag{1.36}$$

The two rates are equal if

$$\rho_1\sqrt{T_1} = \rho_2\sqrt{T_2}, \tag{1.37}$$

i.e., exploiting the equation of state $\rho = p/k_{\mathrm{B}}T$,

$$\frac{p_1}{\sqrt{T_1}} = \frac{p_2}{\sqrt{T_2}}. \tag{1.38}$$

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

$$\Delta E = \rho_1 \left\langle v_x\,\theta(v_x)\,\frac{1}{2}m\left(v_x^2+v_y^2+v_z^2\right)\right\rangle_1 A\,\Delta t. \tag{1.39}$$

Now

$$\begin{aligned}
&\left\langle v_x\,\theta(v_x)\,\frac{1}{2}m\left(v_x^2+v_y^2+v_z^2\right)\right\rangle_1 \\
&\quad= \int_0^{\infty}\frac{\mathrm{d}v_x}{\sqrt{2\pi k_{\mathrm{B}}T_1/m}}\int_{-\infty}^{+\infty}\frac{\mathrm{d}v_y}{\sqrt{2\pi k_{\mathrm{B}}T_1/m}}\int_{-\infty}^{+\infty}\frac{\mathrm{d}v_z}{\sqrt{2\pi k_{\mathrm{B}}T_1/m}} \\
&\qquad\times v_x\,\theta(-v_x)\,\frac{1}{2}m\left(v_x^2+v_y^2+v_z^2\right)\exp\left[-\frac{m\left(v_x^2+v_y^2+v_z^2\right)}{k_{\mathrm{B}}T}\right].
\end{aligned} \tag{1.40}$$

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

$$\begin{aligned}
\left\langle v_x\,\theta(v_x)\,\frac{1}{2}mv_y^2\right\rangle_1 &= \langle v_x\,\theta(v_x)\rangle_1\left\langle\frac{1}{2}mv_y^2\right\rangle_1 \\
&= \sqrt{\frac{k_{\mathrm{B}}T_1}{2\pi m}}\,\frac{1}{2}k_{\mathrm{B}}T_1 = \frac{1}{\sqrt{\pi m}}\left(\frac{k_{\mathrm{B}}T}{2}\right)^{3/2}.
\end{aligned} \tag{1.41}$$

The term containing v_x yields

$$\frac{1}{2}m\left\langle v_x^3\,\theta(v_x)\right\rangle_1 = \frac{1}{\sqrt{\pi m}}\frac{1}{2}\left(\frac{k_{\mathrm{B}}T}{2}\right)^{3/2}. \tag{1.42}$$

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

$$\begin{aligned}
J_E = \frac{\Delta E_1 - \Delta E_2}{A\,\Delta t} &= \frac{1}{\sqrt{\pi m}}\frac{5}{2^{5/2}}\left[\rho_2\left(k_{\mathrm{B}}T_1\right)^{3/2} - \rho_1\left(k_{\mathrm{B}}T_2\right)^{3/2}\right] \\
&= \frac{1}{\sqrt{\pi m}}\frac{5}{2^{5/2}}\frac{p_i}{\sqrt{k_{\mathrm{B}}T_i}}\left(k_{\mathrm{B}}T_1 - k_{\mathrm{B}}T_2\right),
\end{aligned} \tag{1.43}$$

where we have assumed that the condition (1.38) is satisfied.

Solution to exercise 1.6 (Drag in a gas) Let us set the axes so that 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 $\boldsymbol{w} = (w_x, w_y, w_z)$ hitting the disk *from the right* (and thus with $w_x < 0$) releases to it a momentum

$$\Delta \boldsymbol{p} = 2m(w_x, 0, 0). \tag{1.44}$$

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

$$\mathrm{d}\mathcal{N}(\boldsymbol{w})\Delta t = \rho \mathcal{P}(\boldsymbol{w}) d\boldsymbol{w}\, w_x\, \Delta t, \tag{1.45}$$

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

$$\mathcal{P}(\boldsymbol{w}) = f_0(w_x + v) f_0(w_y) f_0(w_z), \tag{1.46}$$

where

$$f_0(w) = \left(\frac{2\pi k_\mathrm{B} T}{m}\right)^{-1/2} \exp\left(-\frac{m w^2}{2 k_\mathrm{B} T}\right). \tag{1.47}$$

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

$$P_x^{(-)} = -\rho S\, \Delta t \int_{-\infty}^{0} \mathrm{d}w_x\; f_0(w_x + v) 2 m w_x^2. \tag{1.48}$$

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

$$P_x^{(+)} = \rho S\, \Delta t \int_{0}^{+\infty} \mathrm{d}w_x\; f_0(w_x + v) 2 m w_x^2. \tag{1.49}$$

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

$$\begin{aligned} P_x = P_x^{(+)} + P_x^{(-)} &= \rho S \Delta t \int_0^{+\infty} \mathrm{d}w_x\; 2 m w_x^2 \left[f_0(w_x + v) - f_0(-w_x + v) \right] \\ &\simeq \rho S\, \Delta t\, 4 m v \int_0^{\infty} \mathrm{d}w_x\; w_x^2 f_0'(w_x). \end{aligned} \tag{1.50}$$

The integral over w_x is evaluated by successive partial integrations:

$$\begin{aligned} \mathcal{I} &= \int_0^{\infty} \mathrm{d}w_x\; w_x^2 f_0'(w_x) = \Big[w^2 f_0(w) \Big]_0^{\infty} - 2 \int_0^{\infty} \mathrm{d}w\; w\; f_0(w) \\ &= \left(-2 \frac{k_\mathrm{B} T}{m} \right) \int_0^{\infty} \mathrm{d}w\; \frac{\mathrm{d} f_0(w)}{\mathrm{d}w} = -\left(\frac{2 k_\mathrm{B} T}{m \pi} \right)^{1/2}. \end{aligned} \tag{1.51}$$

The force acting on the disk is thus given by

$$F = \frac{P_x}{\Delta t} = -4 v \rho S \sqrt{\frac{2 m k_\mathrm{B} T}{\pi}}. \tag{1.52}$$

CHAPTER 2

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

$$S_{\mathrm{i}} = S^{(1)}\left(E_{\mathrm{i}}^{(1)}, N_{\mathrm{i}}^{(1)}\right) + S^{(2)}\left(E_{\mathrm{i}}^{(2)}, N_{\mathrm{i}}^{(2)}\right). \tag{2.1}$$

The final value is given by

$$S_{\mathrm{f}} = S^{(1)}\left(E_{\mathrm{f}}^{(1)}, N_{\mathrm{f}}^{(1)}\right) + S^{(2)}\left(E_{\mathrm{f}}^{(2)}, N_{\mathrm{f}}^{(2)}\right). \tag{2.2}$$

By the concavity properties of the entropy, we have

$$\begin{aligned} S^{(1)}\left(E_{\mathrm{f}}^{(1)}, N_{\mathrm{f}}^{(1)}\right) \leq S^{(1)}\left(E_{\mathrm{i}}^{(1)}, N_{\mathrm{i}}^{(1)}\right) &+ \left.\frac{\partial S^{(1)}}{\partial E^{(1)}}\right|_{E_{\mathrm{i}}^{(1)}, N_{\mathrm{i}}^{(1)}} \left(E_{\mathrm{f}}^{(1)} - E_{\mathrm{i}}^{(1)}\right) \\ &+ \left.\frac{\partial S^{(1)}}{\partial N^{(1)}}\right|_{E_{\mathrm{i}}^{(1)}, N_{\mathrm{i}}^{(1)}} \left(N_{\mathrm{f}}^{(1)} - N_{\mathrm{i}}^{(1)}\right), \end{aligned} \tag{2.3}$$

and analogously for the second system. Therefore, since

$$\left(E_{\mathrm{f}}^{(2)} - E_{\mathrm{i}}^{(2)}\right) = -\left(E_{\mathrm{f}}^{(1)} - E_{\mathrm{i}}^{(1)}\right), \tag{2.4}$$

and analogously for N, we have

$$\begin{aligned} S_{\mathrm{f}} - S_{\mathrm{i}} \le & \left[\left.\frac{\partial S^{(1)}}{\partial E^{(1)}}\right|_{E_{\mathrm{i}}^{(1)},N_{\mathrm{i}}^{(1)}} - \left.\frac{\partial S^{(2)}}{\partial E^{(2)}}\right|_{E_{\mathrm{i}}^{(2)},N_{\mathrm{i}}^{(2)}} \right] \left(E_{\mathrm{f}}^{(1)} - E_{\mathrm{i}}^{(1)} \right) \\ & + \left[\left.\frac{\partial S^{(1)}}{\partial N^{(1)}}\right|_{E_{\mathrm{i}}^{(1)},N_{\mathrm{i}}^{(1)}} - \left.\frac{\partial S^{(2)}}{\partial N^{(2)}}\right|_{E_{\mathrm{i}}^{(2)},N_{\mathrm{i}}^{(2)}} \right] \left(N_{\mathrm{f}}^{(1)} - N_{\mathrm{i}}^{(1)} \right). \end{aligned} \tag{2.5}$$

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

$$\left[\left.\frac{\partial S^{(1)}}{\partial N^{(1)}}\right|_{E_{\mathrm{i}}^{(1)},N_{\mathrm{i}}^{(1)}} - \left.\frac{\partial S^{(2)}}{\partial N^{(2)}}\right|_{E_{\mathrm{i}}^{(2)},N_{\mathrm{i}}^{(2)}} \right] \left(N_{\mathrm{f}}^{(1)} - N_{\mathrm{i}}^{(1)} \right) = -\frac{\mu_{\mathrm{i}}^{(1)} - \mu_{\mathrm{i}}^{(2)}}{T} \left(N_{\mathrm{f}}^{(1)} - N_{\mathrm{i}}^{(1)} \right) \ge 0. \tag{2.6}$$

Thus, if $\mu_{\mathrm{i}}^{(1)} \ge \mu_{\mathrm{i}}^{(2)}$, we have $N_{\mathrm{f}}^{(1)} \le N_{\mathrm{i}}^{(1)}$ (assuming $T > 0$).

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

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

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

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

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 Since

$$\left.\frac{\partial S}{\partial E}\right)_{V,N} = \frac{\kappa}{3}\left(\frac{NV}{E^2}\right)^{1/3}, \tag{2.7}$$

the equilibrium condition reads

$$\frac{N^{(\mathrm{A})}V^{(\mathrm{A})}}{E^{(\mathrm{A})^2}} = \frac{N^{(\mathrm{B})}V^{(\mathrm{B})}}{E^{(\mathrm{B})^2}}, \tag{2.8}$$

with

$$E^{(\mathrm{A})} + E^{(\mathrm{B})} = E_0. \tag{2.9}$$

We thus obtain

$$E^{(\mathrm{A})} = \frac{E_0}{1+\sqrt{N^{(\mathrm{B})}V^{(\mathrm{B})}/N^{(\mathrm{A})}V^{(\mathrm{A})}}}, \qquad E^{(\mathrm{B})} = \frac{E_0}{1+\sqrt{N^{(\mathrm{A})}V^{(\mathrm{A})}/N^{(\mathrm{B})}V^{(\mathrm{B})}}}. \tag{2.10}$$

Solution to exercise 2.4

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

Solution to exercise 2.5 Let us consider an arbitrary change $\mathrm{d}\boldsymbol{f} = (\mathrm{d}f_0, \dots, \mathrm{d}f_k)$, which induces a corresponding change $\mathrm{d}\boldsymbol{X} = (\mathrm{d}X_0, \dots, \mathrm{d}X_k)$, where, with obvious notation, one has

$$\mathrm{d}X_\ell = \sum_{i=0}^{k} \left.\frac{\partial X_\ell}{\partial f_i}\right)_f \mathrm{d}f_i. \tag{2.11}$$

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

$$\begin{aligned} \mathrm{d}^2\Phi &= \sum_{i,j=0}^{k} \frac{\partial^2 \Phi}{\partial f_i \, \partial f_j} \mathrm{d}f_i \, \mathrm{d}f_j = -\sum_{i,j=0}^{k} \left.\frac{\partial X_i}{\partial f_j}\right)_f \mathrm{d}f_i \, \mathrm{d}f_j \\ &= -\sum_{j=0}^{k} \mathrm{d}X_j \, \mathrm{d}f_j. \end{aligned} \tag{2.12}$$

Now we have

$$\mathrm{d}f_j = \sum_{i=0}^{k} \left.\frac{\partial f_j}{\partial X_i}\right)_X \mathrm{d}X_i. \tag{2.13}$$

Therefore

$$\begin{aligned} -\sum_{j=0}^{k} \mathrm{d}X_j \, \mathrm{d}f_j &= -\sum_{i,j=0}^{k} \mathrm{d}X_j \left.\frac{\partial f_j}{\partial X_i}\right)_X \mathrm{d}X_i = -\sum_{j=0}^{k} \mathrm{d}X_j \frac{\partial^2 E}{\partial X_j \, \partial X_i} \mathrm{d}X_i \\ &= -\mathrm{d}^2 E \le 0. \end{aligned} \tag{2.14}$$

Solution to exercise 2.6 Let the system (s) be in contact with the reservoir (r). The total entropy change for a virtual transformation in which the system energy changes by $\Delta E^{(\mathrm{s})}$ and its volume by $\Delta V^{(\mathrm{s})}$, and analogously for (r), is given by

$$\Delta S^{\mathrm{tot}} = \Delta S^{(\mathrm{s})} + \Delta S^{(\mathrm{r})} = \Delta S^{(\mathrm{s})} + \frac{1}{T}\,\Delta E^{(\mathrm{r})} + \frac{p}{T}\,\Delta V^{(\mathrm{r})}. \tag{2.15}$$

Now, in our case, we have $\Delta E^{(\mathrm{r})} = -\Delta E^{(\mathrm{s})}$ and $\Delta V^{(\mathrm{r})} = -\Delta V^{(\mathrm{s})}$. Thus we have

$$\Delta S^{\mathrm{tot}} = -\frac{1}{T}\left(\Delta E^{(\mathrm{s})} + p\,\Delta V^{(\mathrm{s})} - T\Delta S^{(\mathrm{s})}\right). \tag{2.16}$$

If the system is at equilibrium, $\Delta S^{\mathrm{tot}} \leq 0$ for all virtual transformation. Thus we have

$$\Delta G = \Delta E^{(\mathrm{s})} + p\,\Delta V^{(\mathrm{s})} - T\Delta S^{(\mathrm{s})} \geq 0, \tag{2.17}$$

that is, G is minimal.

Solution to exercise 2.7 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 $W = -\left(\Delta E^{(\mathrm{r})} + \Delta E^{(\mathrm{s})}\right)$. On the other hand, we have $\Delta S^{(\mathrm{s})} + \Delta S^{(\mathrm{r})} \geq 0$. We have moreover $\Delta S^{(\mathrm{r})} = \left(\Delta E^{(\mathrm{r})} + p\,\Delta V^{(\mathrm{r})}\right)/T$, where $\Delta V^{(\mathrm{r})} = -\Delta V^{(\mathrm{s})}$ Thus

$$\frac{1}{T}\left(-W - \Delta E^{(\mathrm{s})} + p\,\Delta V^{(\mathrm{s})}\right) + \Delta S^{(\mathrm{s})} \geq 0. \tag{2.18}$$

Multiplying by T (assumed to be positive) we obtain

$$W \leq -\left(\Delta E^{(\mathrm{s})} - T\,\Delta S^{(\mathrm{s})} + p\,\Delta V^{(\mathrm{s})}\right). \tag{2.19}$$

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 2.8 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

$$Q \leq T\,\Delta S. \tag{2.20}$$

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

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

$$\Delta S^{(\mathrm{r})} = \frac{1}{T}\left(\Delta E^{(\mathrm{r})} + p\,\Delta V^{(\mathrm{r})}\right). \tag{2.21}$$

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

$$Q \leq \Delta H^{(\mathrm{s})}. \tag{2.22}$$

Solution to exercise 2.9 (Law of adiabatic processes) Let the gas undergo a reversible temperature change of size $\mathrm{d}T$ at constant pressure by receiving heat from a reservoir at temperature $T + \mathrm{d}T$ and releasing work to the exterior via an adiabatic piston. One has

$$\mathrm{d}S = C_p \frac{\mathrm{d}T}{T + \mathrm{d}T} \simeq C_p \frac{\mathrm{d}T}{T}. \tag{2.23}$$

In this transformation, the change in internal energy is given by $\mathrm{d}E = C_V\,\mathrm{d}T$, 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 $\mathrm{d}T$ at constant pressure p, we have

$$\mathrm{d}V = \frac{Nk_\mathrm{B}\,\mathrm{d}T}{p}. \tag{2.24}$$

Thus, by the First Principle, we have

$$\mathrm{d}E = C_V\,\mathrm{d}T = T\,\mathrm{d}S - p\,\mathrm{d}V = C_p\,\mathrm{d}T - p\,\mathrm{d}V = \left(C_p - Nk_\mathrm{B}\right)\mathrm{d}T. \tag{2.25}$$

When $\mathrm{d}S = 0$, we have

$$\mathrm{d}E = C_V\,\mathrm{d}T = -p\,\mathrm{d}V. \tag{2.26}$$

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

$$\mathrm{d}T = \frac{1}{Nk_\mathrm{B}}\,\mathrm{d}\left(pV\right) = \frac{1}{C_p - C_V}\left(p\,\mathrm{d}V + V\,\mathrm{d}p\right). \tag{2.27}$$

Thus

$$p\,\mathrm{d}V + V\,\mathrm{d}p = -\frac{C_p - C_V}{C_V}p\,\mathrm{d}V, \tag{2.28}$$

which implies

$$\left.\frac{\partial p}{\partial V}\right)_S = -\frac{C_p}{C_V}\frac{p}{V} = -\gamma\frac{p}{V}. \tag{2.29}$$

Differentiating the equation of state in the form

$$V = \frac{Nk_\mathrm{B}T}{p}, \tag{2.30}$$

we obtain

$$\mathrm{d}V = Nk_\mathrm{B}\left(\frac{\mathrm{d}T}{p} - \frac{T\,\mathrm{d}p}{p^2}\right). \tag{2.31}$$

Thus from $V\,\mathrm{d}p = -\gamma p\,\mathrm{d}V$ we obtain

$$Nk_\mathrm{B}T\frac{\mathrm{d}p}{p} = -\gamma Nk_\mathrm{B}\left(\mathrm{d}T - \frac{T\,\mathrm{d}p}{p}\right), \tag{2.32}$$

and thus

$$\gamma\,\frac{\mathrm{d}T}{T} + (1-\gamma)\frac{\mathrm{d}p}{p} = 0, \tag{2.33}$$

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

Solution to exercise 2.10 (Reech's relation) We have

$$\gamma = \frac{C_p}{C_V}, \tag{2.34}$$

where

$$C_p = T\left.\frac{\partial S}{\partial T}\right)_p, \qquad C_V = T\left.\frac{\partial S}{\partial T}\right)_V. \tag{2.35}$$

By the relation

$$\left.\frac{\partial x}{\partial y}\right)_z\left.\frac{\partial y}{\partial z}\right)_x\left.\frac{\partial z}{\partial x}\right)_y = -1, \tag{2.36}$$

that holds when x, y and z satisfy a relation of the form $f(x,y,z) = 0$, we have

$$\left.\frac{\partial S}{\partial T}\right)_p\left.\frac{\partial T}{\partial p}\right)_S\left.\frac{\partial p}{\partial S}\right)_T = -1, \tag{2.37}$$

$$\left.\frac{\partial S}{\partial T}\right)_V\left.\frac{\partial T}{\partial V}\right)_S\left.\frac{\partial V}{\partial S}\right)_T = -1. \tag{2.38}$$

Therefore, taking advantage of Maxwell's relations,

$$\gamma = \frac{\left.\frac{\partial T}{\partial V}\right)_S\left.\frac{\partial V}{\partial S}\right)_T}{\left.\frac{\partial T}{\partial p}\right)_S\left.\frac{\partial p}{\partial S}\right)_T} = \frac{\left.\frac{\partial S}{\partial p}\right)_T\left.\frac{\partial V}{\partial S}\right)_T}{\left.\frac{\partial T}{\partial p}\right)_S\left.\frac{\partial V}{\partial T}\right)_S} = \frac{\left.\frac{\partial V}{\partial p}\right)_T}{\left.\frac{\partial V}{\partial p}\right)_S}. \tag{2.39}$$

Solution to exercise 2.11 (Adiabatic atmosphere) Denoting the numerical density N/V by ρ, we obtain, from the equation of state $k_{\mathrm{B}}T = p/\rho$,

$$\mathrm{d}T = \frac{1}{k_{\mathrm{B}}}\left(\frac{\mathrm{d}p}{\rho} - \frac{p\,\mathrm{d}\rho}{\rho^2}\right). \tag{2.40}$$

From the Law of the Reversible Adiabatics we obtain

$$\frac{\mathrm{d}\rho}{\rho} = \frac{1}{\gamma}\frac{\mathrm{d}p}{p}. \tag{2.41}$$

Thus

$$\mathrm{d}T = \frac{1}{k_{\mathrm{B}}}\left(1 - \frac{1}{\gamma}\right)\frac{\mathrm{d}p}{\rho}. \tag{2.42}$$

From Stevin's law we have

$$\frac{\mathrm{d}p}{\rho} = -m_{\mathrm{mol}}g\,\mathrm{d}z. \tag{2.43}$$

Thus we have

$$\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{m_{\mathrm{mol}}g}{k_{\mathrm{B}}}\left(1 - \frac{1}{\gamma}\right). \tag{2.44}$$

Solution to exercise 2.12 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_0V_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

$$T = T_0 + \frac{p_0V_0}{C_V} = T_0\left(1 + \frac{C_p - C_V}{C_V}\right) = \gamma T_0. \tag{2.45}$$

Solution to exercise 2.13 (Theory of elasticity)

1. Since $E(S, L, N)$ is homogeneous in its arguments, it satisfies the Euler equation
$$E = TS + fL + \mu N. \tag{2.46}$$
Taking the differential of this equation, we obtain
$$\mathrm{d}E = T\,\mathrm{d}S + S\,\mathrm{d}T + f\,\mathrm{d}L + L\,\mathrm{d}f + \nu\,\mathrm{d}N + N\,\mathrm{d}\mu. \tag{2.47}$$
Comparing with the expression of $\mathrm{d}E$, we obtain the analogue of the Gibbs-Duhem equation:
$$S\,\mathrm{d}T + L\,\mathrm{d}f + N\,\mathrm{d}\mu = 0. \tag{2.48}$$

2. From the equation of state, since both f and T are intensive quantities, $\kappa(L, N)$ can only be a function of the density L/N. We obtain therefore
$$\kappa\left(\frac{L}{N}\right) T = \phi\,\frac{L - L_0}{N}, \tag{2.49}$$
that leads to
$$\phi = \frac{N}{L - L_0}\kappa\left(\frac{L}{N}\right) T \simeq \kappa'\left(\frac{L_0}{N}\right) T, \tag{2.50}$$
where we have exploited the fact that $\kappa(L_0/N) = 0$.

3. Let us evaluate $\partial E/\partial L)_T$:
$$\left.\frac{\partial E}{\partial L}\right)_T = \left.\frac{\partial E}{\partial L}\right)_S + \left.\frac{\partial E}{\partial S}\right)_L \left.\frac{\partial S}{\partial L}\right)_T = f - T\left.\frac{\partial f}{\partial T}\right)_L = 0, \tag{2.51}$$
where we used a Maxwell relation and the fact that $f \propto T$ when L is fixed.
By the same token let us evaluate the mixed derivative $\partial^2 S/(\partial T\,\partial L)$:
$$\frac{\partial^2 S}{\partial T\,\partial L} = \frac{\partial}{\partial T}\left.\frac{\partial S}{\partial L}\right)_T = -\frac{\partial}{\partial T}\left.\frac{\partial f}{\partial T}\right)_L = 0. \tag{2.52}$$
Therefore $S(T, L) = S_1(T) + S_2(L)$.

4. Denoting by $C(T) = \partial E/\partial T)_L$ the specific heat at fixed L, we have
$$E(T) = \int_0^T \mathrm{d}T'\; C(T'), \tag{2.53}$$
and
$$S_2(L) = \int_0^T \mathrm{d}T'\; \frac{C(T')}{T'}. \tag{2.54}$$
We have moreover, setting arbitrarily $S_2(L_0) = 0$,
$$S_1(L) = \int_{L_0}^{L} \mathrm{d}L'\; \left.\frac{\partial S}{\partial L}\right)_T = -\int_{L_0}^{L} \mathrm{d}L'\; \left.\frac{\partial f}{\partial T}\right)_L = \int_{L_0}^{L} \mathrm{d}L'\; \kappa\left(\frac{L'}{N}\right). \tag{2.55}$$

5. Since $C(T) > 0$, $\forall T$, one can express T as a function of E. We can thus also express S_1 as a function of E, via $\mathcal{S}_1(E) = S_1(T(E))$. We thus have, for a fixed value of N,
$$S = \mathcal{S}_1(E) + S_2(L). \tag{2.56}$$
By extensivity, we obtain the fundamental equation in the entropy scheme:
$$S(E, L, N) = N\left[\mathcal{S}_1\left(\frac{E}{N}\right) + S_2\left(\frac{L}{N}\right)\right]. \tag{2.57}$$
On the other hand, given S, L and N, it is possible to evaluate $\mathcal{S}_1$ as $\mathcal{S}_1 = S - S_2(L)$. Since $\mathcal{S}_1(E)$ is a monotonically increasing function of E, we can express E as a function of $\mathcal{S}_1$, and therefore of S, L, and N. This yields the fundamental equation in the energy scheme, in terms of the two functions $E(T)$ and $S_1(T)$ and their inverses.

CHAPTER 3

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 (The Bohr-van Leeuwen theorem)

1. We have
$$\mathcal{H}(\boldsymbol{p}^N, \boldsymbol{r}^N) = \sum_{\alpha=1}^{N} \left[\frac{1}{2}\left(\boldsymbol{p}_\alpha - q\boldsymbol{A}(\boldsymbol{r}_\alpha)\right)^2 + U(\boldsymbol{r}^N)\right], \tag{3.1}$$
where q is the charge of the particle. Indeed the canonical equations of motion read
$$\begin{aligned} \dot{\boldsymbol{p}}_\alpha &= -\nabla_\alpha U + \frac{q}{m}\left(\boldsymbol{p}_\alpha - q\boldsymbol{A}(\boldsymbol{r}_\alpha)\right) \cdot \nabla_\alpha \boldsymbol{A}, \\ \dot{\boldsymbol{r}}_\alpha &= \frac{1}{m}\left(\boldsymbol{p}_\alpha - q\boldsymbol{A}(\boldsymbol{r}_\alpha)\right), \end{aligned} \tag{3.2}$$
where $\nabla_\alpha = \partial/\partial\boldsymbol{r}_\alpha$. We thus have
$$\dot{\boldsymbol{p}}_\alpha = m\ddot{\boldsymbol{r}}_\alpha + q\left(\dot{\boldsymbol{r}}_\alpha \cdot \nabla_\alpha\right)\boldsymbol{A} + q\frac{\partial A(\boldsymbol{r}_\alpha)}{\partial t}, \tag{3.3}$$
Solving for $m\ddot{\boldsymbol{r}}_\alpha$, we obtain
$$m\ddot{\boldsymbol{r}}_\alpha = -q\left(\nabla_\alpha U + \frac{\partial A(\boldsymbol{r}_\alpha)}{\partial t}\right) + q\left[\nabla_\alpha\left(\dot{\boldsymbol{r}} \cdot \boldsymbol{A}\right) - \left(\dot{\boldsymbol{r}}_\alpha \cdot \nabla_\alpha\right)\boldsymbol{A}\right]. \tag{3.4}$$

By the identity

$$\dot{\boldsymbol{r}} \times (\nabla \times \boldsymbol{A}) = \nabla (\dot{\boldsymbol{r}} \cdot \boldsymbol{A}) - (\dot{\boldsymbol{r}} \cdot \nabla) \boldsymbol{A}, \tag{3.5}$$

the last term in the right-hand side is shown to be equal to

$$q\dot{\boldsymbol{r}}_\alpha \times (\nabla_\alpha \times \boldsymbol{A}) = q\dot{\boldsymbol{r}} \times \boldsymbol{B}(\boldsymbol{r}_\alpha), \tag{3.6}$$

where $\boldsymbol{B} = \nabla \times \boldsymbol{A}$ is the magnetic induction field.

2. The partition function is given by

$$Z = \frac{1}{N!} \int \prod_{\alpha=1}^{N} \left(\frac{\mathrm{d}\boldsymbol{p}_\alpha \mathrm{d}\boldsymbol{r}_\alpha}{h^3} \right) \exp \left\{ -\frac{1}{k_\mathrm{B}T} \left[\frac{1}{2m} \sum_{\alpha=1}^{N} (\boldsymbol{p}_\alpha - q\boldsymbol{A}(\boldsymbol{r}_\alpha))^2 + U(\boldsymbol{r}^N) \right] \right\}. \tag{3.7}$$

Change the integration variable according to

$$\boldsymbol{p}_\alpha - q\boldsymbol{A}(\boldsymbol{r}_\alpha) = \boldsymbol{p}'_\alpha, \quad \boldsymbol{r}_\alpha = \boldsymbol{r}'_\alpha, \qquad \alpha = 1, \ldots, N. \tag{3.8}$$

The Jacobian equals 1. Thus the partition function is independent of $\boldsymbol{A}$, that is, of the applied magnetic field. Therefore the magnetization vanishes.

Solution to exercise 3.3 (Langevin theory of paramagnetism)

1. The kinetic energy for a single dipole reads

$$K = \frac{1}{2} I \dot{\theta}^2 + \frac{1}{2} I \sin^2\theta\, \dot{\phi}^2, \tag{3.9}$$

and the potential energy is given by $U(\theta, \phi) = -\mu \cos\theta\, B$. Thus we have

$$\mathcal{L} = K - U = \frac{1}{2} I \dot{\theta}^2 + \frac{1}{2} I \sin^2\theta\, \dot{\phi}^2 + \mu \cos\theta\, B, \tag{3.10}$$

and

$$p_\theta = \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = I\dot{\theta}, \qquad p_\phi = \frac{\partial \mathcal{L}}{\partial \dot{\phi}} = I \sin^2\theta\, \dot{\phi}. \tag{3.11}$$

Thus the hamiltonian is given by

$$\mathcal{H} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2\theta} - \mu \cos\theta\, B. \tag{3.12}$$

2. The partition function of the system is given by ζ^N, where ζ is the single-particle partition function, given by

$$\begin{aligned}\zeta &= \frac{1}{h^2}\int \mathrm{d}p_\theta\,\mathrm{d}p_\phi\,\mathrm{d}\theta\,\mathrm{d}\phi\;\exp\left(-\frac{\mathcal{H}}{k_\mathrm{B}T}\right)\\ &= \frac{1}{h^2}\int \mathrm{d}\theta\,\mathrm{d}\phi\int \mathrm{d}p_\theta\,\mathrm{d}p_\phi\;\exp\left(-\frac{p_\theta^2}{2Ik_\mathrm{B}T}-\frac{p_\phi^2}{2I\sin^2\theta\,k_\mathrm{B}T}\right)\exp\left(\frac{\mu\cos\theta\,B}{k_\mathrm{B}T}\right)\\ &= \frac{2\pi I k_\mathrm{B}T}{h^2}\int \mathrm{d}\theta\,\mathrm{d}\phi\;\sin\theta\,\exp\left(\frac{\mu\cos\theta\,B}{k_\mathrm{B}T}\right).\end{aligned} \tag{3.13}$$

Thus the spherical angle element $\mathrm{d}\Omega=\mathrm{d}\theta\,\sin\theta\,\mathrm{d}\phi$ arises from the integration over the conjugate momenta.

3. We have

$$m = k_\mathrm{B}T\frac{\partial\ln\zeta}{\partial B} = \mu\left.\frac{\partial\ln\zeta(\lambda)}{\partial\lambda}\right|_{\lambda=\mu B/k_\mathrm{B}T}, \tag{3.14}$$

where

$$\zeta(\lambda)=\int \mathrm{d}\theta\,\mathrm{d}\phi\;\sin\theta\,\mathrm{e}^{\lambda\cos\theta}=4\pi\frac{\sinh\lambda}{\lambda}. \tag{3.15}$$

We thus obtain

$$m=\frac{\mu}{\tanh\lambda}-\frac{\mu}{\lambda}, \tag{3.16}$$

where $\lambda=\mu B/k_\mathrm{B}T$. For $\lambda \ll 1$ we have $m\simeq \mu^2/(3k_\mathrm{B}T)B$, in agreement with Curie's law.

Solution to exercise 3.4 (An elementary model of elasticity)

1. We have

$$\mathcal{H}(\tau)=-F\left[N\ell_0+\sum_{i=1}^N \tau_i(\ell_1-\ell_0)\right]. \tag{3.17}$$

2. The partition function is given by

$$Z=\sum_\tau \mathrm{e}^{-\mathcal{H}(\tau)/k_\mathrm{B}T}=\left(\mathrm{e}^{F\ell_0/k_\mathrm{B}T}+\mathrm{e}^{F\ell_1/k_\mathrm{B}T}\right)^N. \tag{3.18}$$

Thus we have

$$\langle L\rangle = k_\mathrm{B}T\frac{\partial\ln Z}{\partial F}=N\frac{\ell_0\mathrm{e}^{F\ell_0/k_\mathrm{B}T}+\ell_1\mathrm{e}^{F\ell_1/k_\mathrm{B}T}}{\mathrm{e}^{F\ell_0/k_\mathrm{B}T}+\mathrm{e}^{F\ell_1/k_\mathrm{B}T}}. \tag{3.19}$$

Notice that $\langle L\rangle \to N(\ell_0+\ell_1)/2$ for $F \to 0$ and $\langle L\rangle \to N\max(\ell_0,\ell_1)$ for $F\to\infty$. For $F\,\delta\ell/k_{\mathrm{B}}T \ll 1$, where $\delta\ell = \ell_1-\ell_0$, one obtains

$$\langle L\rangle = N\left(\frac{\ell_0+\ell_1}{2}\right) + N\frac{\delta\ell^2}{4k_{\mathrm{B}}T}F. \tag{3.20}$$

Thus Hooke's constant is given by

$$\kappa = \frac{4k_{\mathrm{B}}T}{N\delta\ell^2}. \tag{3.21}$$

Solution to exercise 3.5 Apart from the $k_{\mathrm{B}}T^2$ factor, the lhs of the identity can be rewritten as follows:

$$\begin{aligned}\left.\frac{\partial E}{\partial T}\right)_p + \frac{p}{T}\left.\frac{\partial E}{\partial p}\right)_T &= \left.\frac{\partial E}{\partial T}\right)_V + \left.\frac{\partial E}{\partial V}\right)_T\left.\frac{\partial V}{\partial T}\right)_p - \frac{1}{T}\left.\frac{\partial F}{\partial V}\right)_T\left.\frac{\partial E}{\partial p}\right)_T\\ &= \left.\frac{\partial E}{\partial T}\right)_V + \left.\frac{\partial E}{\partial V}\right)_T\left.\frac{\partial V}{\partial T}\right)_p - \frac{1}{T}\left.\frac{\partial F}{\partial V}\right)_T\left.\frac{\partial E}{\partial V}\right)_T\left.\frac{\partial V}{\partial p}\right)_T.\end{aligned} \tag{3.22}$$

Thus the difference between the two sides reads

$$\Delta\mathfrak{S} = \frac{1}{T}\left.\frac{\partial E}{\partial V}\right)_T\left[\left.\frac{\partial E}{\partial V}\right)_T\left.\frac{\partial V}{\partial p}\right)_T - \left.\frac{\partial F}{\partial V}\right)_T\left.\frac{\partial V}{\partial p}\right)_T + T\left.\frac{\partial V}{\partial T}\right)_p\right]. \tag{3.23}$$

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

$$\begin{aligned}\Delta\mathfrak{S} &= \frac{1}{T}\left.\frac{\partial E}{\partial V}\right)_T\left[T\left.\frac{\partial S}{\partial V}\right)_T\left.\frac{\partial V}{\partial p}\right)_T + T\left.\frac{\partial V}{\partial T}\right)_p\right]\\ &= \frac{1}{T}\left.\frac{\partial E}{\partial V}\right)_T\left[T\left.\frac{\partial p}{\partial T}\right)_V\left.\frac{\partial V}{\partial p}\right)_T + T\left.\frac{\partial V}{\partial T}\right)_p\right] = 0,\end{aligned} \tag{3.24}$$

where we have exploited Maxwell's relations and the identity

$$\left.\frac{\partial x}{\partial y}\right)_z = -\frac{\partial x/\partial z)_y}{\partial y/\partial z)_x}. \tag{3.25}$$

Solution to exercise 3.6 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

$$Z_N(X,T) = \int_0^X \mathrm{d}x_1\int_{x_1}^X \mathrm{d}x_2\cdots\int_{x_{N-2}}^X \mathrm{d}x_{N-1}\,\exp\left(-\frac{1}{k_{\mathrm{B}}T}\sum_{i=1}^N u(x_i-x_0)\right). \tag{3.26}$$

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

$$Z_N(p,T) = \int_0^\infty \mathrm{d}X\ \exp\left(-\frac{pX}{k_\mathrm{B}T}\right) Z_N(X,T). \tag{3.27}$$

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

$$Z_N(X,T) = \int_0^X \mathrm{d}x\ \exp\left(-\frac{u(X-x)}{k_\mathrm{B}T}\right) Z_{N-1}(x,T), \tag{3.28}$$

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

$$\tilde{Z}_N(z,T) = \int_0^\infty \mathrm{d}X\ \mathrm{e}^{-zX}\, Z_N(X,T) = \tilde{\phi}(z,T)\tilde{Z}_{N-1}(z,T). \tag{3.29}$$

Taking into account the initial condition we obtain

$$\tilde{Z}_N(z,T) = \tilde{\phi}(z,T)^N. \tag{3.30}$$

Thus we have

$$Z_N(p,T) = \tilde{\phi}\left(\frac{p}{k_\mathrm{B}T}, T\right)^N. \tag{3.31}$$

We have

$$\langle X\rangle_{p,T,N} = -\frac{\partial \ln Z_N}{\partial(p/k_\mathrm{B}T)} = -N\, \frac{\partial_z\tilde{\phi}(z,T)}{\tilde{\phi}(z,T)}\bigg|_{z=p/k_\mathrm{B}T}, \tag{3.32}$$

i.e.,

$$\langle X\rangle_{p,T,N} = N\,\langle X\rangle_{p,T,N=1} = N\frac{\int_0^\infty \mathrm{d}X\ X\,\mathrm{e}^{-(u(X)+pX)/k_\mathrm{B}T}}{\int_0^\infty \mathrm{d}X\ \mathrm{e}^{-(u(X)+pX)/k_\mathrm{B}T}}. \tag{3.33}$$

Solution to exercise 3.7 The grand canonical partition function is defined by

$$Z_\mathrm{GC}(\alpha,\beta) = \sum_x \mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)}, \tag{3.34}$$

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 $\mu/k_\mathrm{B}T$ and $1/k_\mathrm{B}T$ respectively. Then we have

$$\langle \mathcal{H}\rangle = \frac{1}{Z_\mathrm{GC}}\sum_x \epsilon(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)} = -\left.\frac{\partial \ln Z_\mathrm{GC}}{\partial\beta}\right)_\alpha; \tag{3.35}$$

$$\langle N\rangle = \frac{1}{Z_\mathrm{GC}}\sum_x N(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)} = \left.\frac{\partial \ln Z_\mathrm{GC}}{\partial\alpha}\right)_\beta. \tag{3.36}$$

Taking second derivatives, we obtain

$$\begin{aligned}
\frac{\partial^2 \ln Z_{\mathrm{GC}}}{\partial \beta^2} &= \frac{1}{Z_{\mathrm{GC}}}\sum_x \epsilon^2(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)} - \left[\frac{1}{Z_{\mathrm{GC}}}\sum_x \epsilon(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)}\right]^2 \\
&= \left\langle \mathcal{H}^2 \right\rangle - \langle \mathcal{H} \rangle^2 ; \qquad (3.37)\\
\frac{\partial^2 \ln Z_{\mathrm{GC}}}{\partial \alpha^2} &= \frac{1}{Z_{\mathrm{GC}}}\sum_x N^2(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)} - \left[\frac{1}{Z_{\mathrm{GC}}}\sum_x N(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)}\right]^2 \\
&= \left\langle N^2 \right\rangle - \langle N \rangle^2 ; \qquad (3.38)\\
-\frac{\partial^2 \ln Z_{\mathrm{GC}}}{\partial \alpha\, \partial \beta} &= \frac{1}{Z_{\mathrm{GC}}}\sum_x N(x)\, \epsilon(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)} \\
&\quad - \left[\frac{1}{Z_{\mathrm{GC}}}\sum_x N(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)}\right]\left[\frac{1}{Z_{\mathrm{GC}}}\sum_x \epsilon(x)\mathrm{e}^{-\beta\epsilon(x)+\alpha N(x)}\right] \\
&= \langle N\, \mathcal{H} \rangle - \langle N \rangle \langle \mathcal{H} \rangle . \qquad (3.39)
\end{aligned}$$

Solution to exercise 3.8 The grand canonical partition function can be written in the following form:

$$Z_{\mathrm{GC}} = \sum_N \sum_x \delta_{N,N(x)} \mathrm{e}^{-\beta\epsilon(x)+\alpha N} = \sum_N \mathrm{e}^{\alpha N} Z_N, \qquad (3.40)$$

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

$$Z_N = \sum_x \delta_{N,N(x)} \mathrm{e}^{-\beta\epsilon(x)}. \qquad (3.41)$$

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

$$p_N = \frac{\mathrm{e}^{\alpha N} Z_N}{Z_{\mathrm{GC}}}. \qquad (3.42)$$

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

$$\begin{aligned}
\left\langle \Delta E^2 \right\rangle_{\mathrm{GC}} &= \sum_N \left\langle \Delta E^2 \right\rangle_N p_N + \sum_N p_N \left.\frac{\partial \langle E \rangle_N}{\partial N}\right)_T^2 (N - N^{\mathrm{eq}})^2 \\
&\simeq \left\langle \Delta E^2 \right\rangle_{N^{\mathrm{eq}}} + \left.\frac{\partial E}{\partial N}\right|_{N^{\mathrm{eq}}}^2 \left\langle \Delta N^2 \right\rangle_{\mathrm{GC}} \ge \left\langle \Delta E^2 \right\rangle_{N^{\mathrm{eq}}} .
\end{aligned} \qquad (3.43)$$

Solution to exercise 3.9 Given two distributions $p(x)$ and $p'(x)$, define the quantity

$$D(p\|p') = \sum_x p(x) \ln \frac{p(x)}{p'(x)}. \tag{3.44}$$

From the inequality

$$\ln x \le x - 1, \tag{3.45}$$

it follows that

$$D(p\|p') \ge 0, \tag{3.46}$$

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

$$\begin{aligned} D(p\|p') &= -\sum_x p(x) \ln \frac{p'(x)}{p(x)} \ge -\sum_x p(x) \left[\frac{p'(x)}{p(x)} - 1 \right] \\ &= -\sum_x p'(x) + \sum_x p(x) = 0, \end{aligned} \tag{3.47}$$

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

Consider now

$$D(p\|p^{\mathrm{eq}}) = \sum_x p(x) \ln \frac{p(x)}{p^{\mathrm{eq}}(x)}. \tag{3.48}$$

We have

$$D(p\|p^{\mathrm{eq}}) = -\mathcal{S}(p) + \sum_x p(x) \ln p^{\mathrm{eq}}(x) = \mathcal{S}(p) - \langle H \rangle_p - \ln Z. \tag{3.49}$$

We have, on the other hand

$$\begin{aligned} \mathcal{S}(p^{\mathrm{eq}}) &= -\sum_x p^{\mathrm{eq}}(x) \ln p^{\mathrm{eq}}(x) = \sum_x p^{\mathrm{eq}}(x) \frac{H(x)}{k_{\mathrm{B}}T} + \sum_x p^{\mathrm{eq}}(x) \ln Z \\ &= \frac{\langle H \rangle_{p^{\mathrm{eq}}}}{k_{\mathrm{B}}T} + \ln Z. \end{aligned} \tag{3.50}$$

Thus we have

$$\begin{aligned} 0 \le D(p\|p^{\mathrm{eq}}) &= -\mathcal{S}(p) - \langle H \rangle_p - \ln Z \\ &= \mathcal{S}(p) - \langle H \rangle_p + \langle H \rangle_{p^{\mathrm{eq}}} + \mathcal{S}(p^{\mathrm{eq}}) = \mathcal{S}(p^{\mathrm{eq}}) - \mathcal{S}(p), \end{aligned} \tag{3.51}$$

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

Chapter 4

Interaction-Free Systems

Solution to exercise 4.1 (Kappler's experiment) In SI units, we have $\kappa = 9.428 \cdot 10^{-16}\,\mathrm{J}$. Thus we obtain the following estimation:

$$k_{\mathrm{B}} = \frac{\kappa \left\langle \varphi^2 \right\rangle}{T} = \frac{9.428 \cdot 4.178}{2.871} \cdot 10^{-24} = 1.372 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}, \tag{4.1}$$

to be compared with the presently accepted value of $1.3806 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}$.

Solution to exercise 4.2 (Stefan-Boltzmann law) From $E = 3pV$, by differentiation, we obtain $\mathrm{d}E = 3p\,\mathrm{d}V + 3V\,\mathrm{d}p$. On the other hand, from the First Principle we have $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V$. Thus we have $T\,\mathrm{d}S = 4p\,\mathrm{d}V + 3V\,\mathrm{d}p$, from which follow the following relations:

$$\left.\frac{\partial S}{\partial V}\right)_p = \frac{4p}{T}; \tag{4.2}$$

$$\left.\frac{\partial S}{\partial p}\right)_V = \frac{3V}{T}. \tag{4.3}$$

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

$$4\left.\frac{\partial(p/T)}{\partial p}\right)_V = 3\left.\frac{\partial(V/T)}{\partial V}\right)_p. \tag{4.4}$$

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 $(4/T) - (4p/T^2)\,\mathrm{d}T/\mathrm{d}p$. Thus we obtain

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{4p}{T}. \tag{4.5}$$

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

Solution to exercise 4.3 A simple calculation yields $7.87 \cdot 10^6\,\mathrm{J/day}$, that is, about 70% of the basal metabolism rate.

Solution to exercise 4.4 Introducing the notation

$$\xi' = \frac{\xi}{2s+1} = \frac{\rho\lambda_{\mathrm{B}}^3}{2s+1}, \tag{4.6}$$

we have

$$\xi' \simeq z\left(1 \mp \frac{z}{2^{3/2}}\right) \tag{4.7}$$

$$\frac{p\lambda_{\mathrm{B}}^3}{k_{\mathrm{B}}T} \simeq (2s+1)\, z\left(1 \mp \frac{z}{2^{5/2}}\right). \tag{4.8}$$

From (4.7) we obtain

$$z \simeq \xi'\left(1 \pm \frac{\xi'}{2^{3/2}}\right). \tag{4.9}$$

Thus

$$\frac{p\lambda_{\mathrm{B}}^3}{k_{\mathrm{B}}T} \simeq (2s+1)\xi'\left[1 \pm \xi'\left(\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}}\right)\right] = \xi\left(1 \pm \frac{\xi}{(2s+1)2^{5/2}}\right). \tag{4.10}$$

Solution to exercise 4.5 (Pauli paramagnetism)

1. Suppose the filed $\boldsymbol{B}$ is directed parallel to the z-axis. Identify the single-electron states by their momentum $\boldsymbol{p}$ and their z-component of the spin σ. Then the energy of the state $(\boldsymbol{p},\sigma)$ is given by

$$\epsilon(\boldsymbol{p},\sigma) = \frac{p^2}{2m} - \sigma\,\mu_{\mathrm{m}}H, \tag{4.11}$$

where μ_m is the intrinsic magnetic moment of the electron. At zero temperature, all the states whose energy ϵ lies below the fermi energy ϵ_F are occupied, and all the others are empty. Denote by $\omega(\epsilon)$ the density of states per unit volume and unit energy of states with a given value of σ:

$$\omega(\epsilon) = \frac{1}{V} \sum_{p} \delta \left(\epsilon - \frac{p^2}{2m} \right), \tag{4.12}$$

where V is the volume of the system. Then the Fermi energy ϵ_F is given by the condition

$$\frac{N}{V} = \int_{-\infty}^{\epsilon_\mathrm{F}} \mathrm{d}\epsilon \, \sum_{\sigma} \omega \left(\epsilon - \sigma \, \mu_\mathrm{m} B \right) = \frac{1}{V} \left(N_+ + N_- \right), \tag{4.13}$$

where N is the total number of electrons, N_+ the number of electrons with spins "up" (that is, with $\sigma = 1$), and N_- that of electrons with spins "down". For small values of H obtain

$$N_\pm \simeq \frac{N}{2} \pm V \, \omega(\epsilon_\mathrm{F}) \, \mu_\mathrm{m} B. \tag{4.14}$$

Thus ϵ_F remains unchanged to first order in B. On the other hand, the z-component of the total magnetic moment of the system is given by

$$M = \mu_\mathrm{m} \left(N_+ - N_- \right) \simeq V \, \omega(\epsilon_\mathrm{F}) \, \mu_\mathrm{m}^2 \, B. \tag{4.15}$$

For a three-dimensional system we have

$$\omega(\epsilon) = \frac{2\pi}{h^3} (2m)^{3/2} \, \epsilon^{1/2}. \tag{4.16}$$

We thus obtain the susceptibility at zero temperature:

$$\chi_0 = \lim_{B \to 0} \frac{1}{V} \frac{\partial M}{\partial B} = \frac{2\pi}{h^3} (2m)^{3/2} \, \epsilon_\mathrm{F}^{1/2} \, \mu_\mathrm{m}^2. \tag{4.17}$$

Using the relation, valid for $\boldsymbol{B} = 0$,

$$\epsilon_\mathrm{F} = \left(\frac{3N}{8\pi V} \right)^{2/3} \frac{h^2}{2m}, \tag{4.18}$$

we obtain

$$\chi_0 = \frac{N}{V} \frac{3\mu_\mathrm{m}^2}{4\epsilon_\mathrm{F}}. \tag{4.19}$$

2. In a two-dimensional system, we have

$$\omega(\epsilon) = \frac{2\pi \, m}{h^2}, \tag{4.20}$$

and therefore

$$\chi_0 = \frac{2\pi \, m}{h^2} \, \mu_\mathrm{m}^2. \tag{4.21}$$

Remarkably, the susceptivity is independent of the electron density in $d = 2$.

Solution to exercise 4.6 In our case, the pressure p is related to the internal energy E and the volume V by the equation

$$p = \frac{d}{\alpha}\frac{E}{V}. \tag{4.22}$$

As a consequence, when E changes by $\mathrm{d}E$ and V by $\mathrm{d}V$, keeping p constant, one has

$$\mathrm{d}V = V\,\frac{\mathrm{d}E}{E}. \tag{4.23}$$

In this transformation, the heat $\mathrm{d}Q$ released to the system is given by

$$\mathrm{d}Q = \mathrm{d}E + p\,\mathrm{d}V = \mathrm{d}E + \frac{d}{\alpha}\frac{E}{V}\,V\,\frac{\mathrm{d}E}{E} = \mathrm{d}E\left(1+\frac{d}{\alpha}\right). \tag{4.24}$$

On the other hand, when $\mathrm{d}V = 0$, no work is performed, and one has $\mathrm{d}Q = \mathrm{d}E$. The result follows by dividing by the temperature increment $\mathrm{d}T$.

Solution to exercise 4.7 (Fermions in two dimensions)

1. Since there are, for each acceptable value of $\boldsymbol{k}$, two spin states, we obtain

$$\begin{aligned} D(\epsilon) &= 2\frac{L^2}{(2\pi)^2}\int \mathrm{d}^2\boldsymbol{k}\;\delta\left(\epsilon - \frac{\hbar^2k^2}{2m}\right) = 4\pi\frac{L^2}{(2\pi)^2}\int_0^\infty k\,\mathrm{d}k\;\delta\left(\epsilon - \frac{\hbar^2k^2}{2m}\right)\\ &= L^2\frac{4\pi m}{h^2}\int_0^\infty \mathrm{d}x\;\delta\left(\epsilon - x\right) = \theta(\epsilon)\frac{4\pi m L^2}{h^2}. \end{aligned} \tag{4.25}$$

2. From the condition

$$N = \int_0^{\epsilon_{\mathrm{F}}} \mathrm{d}\epsilon\;D(\epsilon) = \frac{4\pi m L^2}{h^2}\epsilon_{\mathrm{F}}, \tag{4.26}$$

we obtain

$$\epsilon_{\mathrm{F}} = \frac{h^2}{4\pi m}\rho, \tag{4.27}$$

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

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

$$\langle E\rangle = \int_0^{\epsilon_F} \mathrm{d}\epsilon\;\epsilon\,D(\epsilon) = \frac{h^2}{8\pi m}\frac{N^2}{L^2}, \tag{4.28}$$

we obtain

$$p = \frac{h^2}{8\pi m}\rho^2. \tag{4.29}$$

4. The equation fixing the chemical potential μ is

$$N = \int_0^\infty \mathrm{d}\epsilon \, \frac{D(\epsilon)}{\mathrm{e}^{(\epsilon-\mu)/k_\mathrm{B}T}+1}, \tag{4.30}$$

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

$$\begin{aligned} \mathcal{N}(\mu, T) &= \int_0^\infty \mathrm{d}\epsilon \, \frac{D(\epsilon)}{\mathrm{e}^{(\epsilon-\mu)/k_\mathrm{B}T}+1} \\ &= D\,k_\mathrm{B}T \int_0^\infty \mathrm{d}\epsilon \, \frac{\mathrm{d}}{\mathrm{d}\epsilon} \ln\left(1+\mathrm{e}^{-(\epsilon-\mu)/kt}\right) \\ &= D\,k_\mathrm{B}T\,\ln\left(1+\mathrm{e}^{\mu/k_\mathrm{B}T}\right) \\ &= D\mu + D\,k_\mathrm{B}T\,\ln\left(1+\mathrm{e}^{-\mu/k_\mathrm{B}T}\right). \end{aligned} \tag{4.31}$$

Since we have $N = D\,\epsilon_\mathrm{F}$ we obtain for $T \to 0$

$$\mu \simeq \epsilon_\mathrm{F} - k_\mathrm{B}T\mathrm{e}^{-\epsilon_\mathrm{F}/k_\mathrm{B}T}. \tag{4.32}$$

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

$$f(\epsilon) = \frac{1}{\mathrm{e}^{\epsilon/k_\mathrm{B}T}+1}. \tag{4.33}$$

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

$$D(p)\,\mathrm{d}p = \frac{V}{h^3}\,4\pi\,p^2\,\mathrm{d}p, \tag{4.34}$$

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

$$D(\epsilon)\,\mathrm{d}\epsilon = \frac{V}{h^3c^3}4\pi\,\epsilon^2\,\mathrm{d}\epsilon. \tag{4.35}$$

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

$$\begin{aligned} \langle N \rangle = \int_0^\infty \mathrm{d}\epsilon\, f(\epsilon)\,D(\epsilon) &= \frac{4\pi\,V}{h^3c^3} \int_0^\infty \mathrm{d}\epsilon \, \frac{\epsilon^2}{\mathrm{e}^{\epsilon/k_\mathrm{B}T}+1} \\ &= \frac{4\pi\,V}{h^3c^3}(k_\mathrm{B}T)^3 \int_0^\infty \frac{x^2\,\mathrm{d}x}{\mathrm{e}^x+1}. \end{aligned} \tag{4.36}$$

Substituting the numerical values, one obtains for $T = 2.7\,\mathrm{K}$,

$$\frac{\langle N \rangle}{V} = 7.6 \cdot 10^6\,T^3\,\mathrm{m}^{-3} \simeq 150 \cdot 10^6\,\mathrm{m}^{-3}. \tag{4.37}$$

2. The average energy is given by

$$\begin{aligned}\langle \mathcal{H} \rangle &= \int_0^\infty \mathrm{d}\epsilon \, f(\epsilon)\, \epsilon \, D(\epsilon) = \frac{4\pi\, V}{h^3 c^3} \int_0^\infty \mathrm{d}\epsilon \, \frac{\epsilon^3}{\mathrm{e}^{\epsilon/k_\mathrm{B}T} + 1} \\ &= \frac{4\pi\, V}{h^3 c^3} (k_\mathrm{B}T)^4 \int_0^\infty \frac{x^4\, \mathrm{d}x}{\mathrm{e}^x + 1} = \frac{V}{h^3 c^3} (k_\mathrm{B}T)^4 \frac{7\,\pi^5}{30}.\end{aligned} \tag{4.38}$$

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

$$\frac{\langle \mathcal{H} \rangle}{V} = 3.3 \cdot 10^{-10}\, T^4 \, \mathrm{J m^{-3}} = 1.8 \cdot 10^{-14} \, \mathrm{J m^{-3}}. \tag{4.39}$$

3. The energy spectrum is given by (cf. fig.4.1)

$$u(\epsilon) = \frac{1}{V}\, \epsilon\, f(\epsilon)\, D(\epsilon) = \frac{4\pi}{h^3 c^3} \frac{\epsilon^3}{\mathrm{e}^{\epsilon/k_\mathrm{B}T} + 1}. \tag{4.40}$$

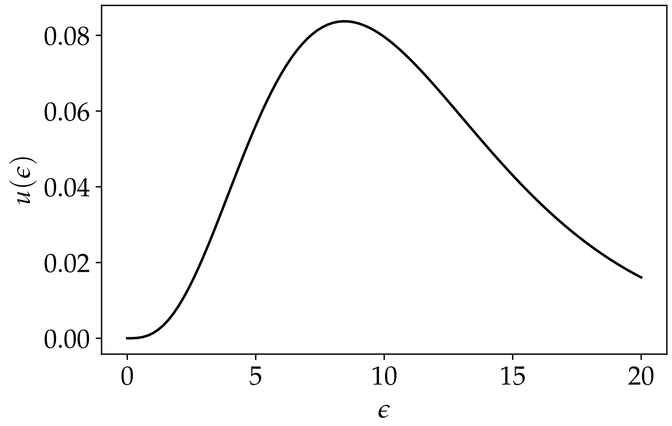

Figure 4.1: Energy spectrum for neutrinos in the background radiation. Energies are measured in units of $k_\mathrm{B}T$. The integral of the density is normalized to one.

Solution to exercise 4.9 (Classical theory of diamagnetism)

1. To fix our ideas, consider an electron of charge $-e$ and mass m on a Bohr orbit of radius r around a nucleus. Let the orbit lie in the xy-plane, and the magnetic

induction $\boldsymbol{B}$ bi directed along the z-axis. Then, by Newton's law, and taking into account the Lorentz force, we have

$$\boldsymbol{F}_{\text{el}} - e\boldsymbol{v} \times \boldsymbol{B} = -m\frac{v^2}{r}\,\hat{\boldsymbol{r}}, \tag{4.41}$$

where $\boldsymbol{F}_{\text{el}}$ is the electrostatic force acting on the electron and $\hat{\boldsymbol{r}}$ is the unit vector parallel to the radius vector $\boldsymbol{r}$ from the nucleus to the electron. Expanding $\boldsymbol{v}$ to first order in B we obtain $\boldsymbol{v} = \boldsymbol{v}_0 + \boldsymbol{v}_1$, and we readily see that $\boldsymbol{v}_1$ satisfies

$$-e\boldsymbol{v}_0 \times \boldsymbol{B} = -2mv_0\,\frac{v_1}{r}\,\hat{\boldsymbol{r}}. \tag{4.42}$$

We thus obtain

$$\frac{v_1}{r} = \frac{e}{2m}\,B. \tag{4.43}$$

This corresponds to an angular precession around the direction of $\boldsymbol{B}$ with angular frequency ω_{L} given by

$$\omega_{\text{L}} = \frac{e}{2m}\,B. \tag{4.44}$$

2. According to Larmor's theorem, the effect of a uniform magnetic field of induction B on an atom with a given electron density $\rho(\boldsymbol{r})$ is to let its magnetic moment precede with an angular frequency ω_{L}. This corresponds to adding to the system an electron current of density $-e\,\rho(\boldsymbol{r})\,\omega_{\text{L}} \times \boldsymbol{r}$.

3. A loop carrying a current of intensity I and enclosing an area A contributes to the magnetic moment of the system an amount equal to $I\,A$. Consider a spherically symmetric charge distribution $\rho(\boldsymbol{r})$, and an area element $\mathrm{d}S = \mathrm{d}x\,\mathrm{d}z$ at a position $\boldsymbol{r} = (r_\perp, 0, z)$ in the xz-plane, with $r > 0$. The current going through this area element is given by $\mathrm{d}I = (-e)\omega_{\text{L}}\,r_\perp\,\rho(\boldsymbol{r})\mathrm{d}S$, and the enclosed area is equal to $\pi r_\perp^2$. Thus the contribution of this loop to the magnetic moment of the system is given by

$$\mathrm{d}\boldsymbol{\mu} = \omega_{\boldsymbol{L}}\,r_\perp\;\mathrm{d}S\,\pi\,r_\perp^2\,\boldsymbol{n} = \frac{1}{2}\omega_{\text{L}}\int_0^{2\pi} r_\perp\,\mathrm{d}\phi\,r_\perp^2\,\mathrm{d}r_\perp\,\mathrm{d}z, \tag{4.45}$$

where we have denoted by $\boldsymbol{n}$ the unit vector parallel to $\boldsymbol{B}$ and in the last equality we have switched to cylindrical coordinates. Thus the total contribution of the charge distribution to the magnetic moment is given by

$$\boldsymbol{\mu} = (-e)\,\omega_{\text{L}}\,Z\,\left\langle r_\perp^2 \right\rangle, \tag{4.46}$$

where we have defined

$$Z = \int \mathrm{d}\boldsymbol{r}\;\rho(\boldsymbol{r}), \qquad \left\langle r_\perp^2 \right\rangle = \frac{1}{Z}\int \mathrm{d}\boldsymbol{r}\;r_\perp^2\,\rho(\boldsymbol{r}). \tag{4.47}$$

Clearly, Z is the total number of electrons of the atom, that is, its atomic number. For a spherically symmetric distribution $\rho(\boldsymbol{r})$, we have

$$\left\langle r_{\perp}^2 \right\rangle = \frac{2}{3} \left\langle r^2 \right\rangle, \tag{4.48}$$

where

$$\left\langle r^2 \right\rangle = \frac{1}{Z} \int \mathrm{d}\boldsymbol{r}\, r^2 \rho(\boldsymbol{r}). \tag{4.49}$$

We thus obtain the contribution of the Larmor precession to the magnetic moment $\boldsymbol{\mu}$ of a single atom:

$$\boldsymbol{\mu} = -\frac{Ze^2}{6m} \left\langle r^2 \right\rangle \boldsymbol{B}. \tag{4.50}$$

The magnetic susceptibility of a material is given by

$$\chi = \frac{1}{V} \frac{\partial M}{\partial B}, \tag{4.51}$$

where V is the sample volume, M the total magnetic moment, and B the applied magnetic field. Summing up, we obtain

$$\chi = -n \frac{Ze^2}{6m} \left\langle r^2 \right\rangle, \tag{4.52}$$

where n is the number of atoms per unit volume. For system made of several chemical species, one sums the contributions of each different species.

Note that we have assumed that the electron density $\rho(\boldsymbol{r})$ does not change with the application of the magnetic field.

Solution to exercise 4.10

1. Given the mass of the star M_0, one can evaluate the number N of electrons by dividing M_0 by twice the proton mass. (We neglect the difference between neutron and proto mass, and we count one neutron for each proton.) We thus have

   $$N = \frac{M_0}{2m_{\mathrm{p}}} = \frac{2.0 \cdot 10^{30}}{2\,1.673 \cdot 10^{-27}} = 5.97 \cdot 10^{56}. \tag{4.53}$$

   The radius R of the star is given by eq. (4.181), where the factor $\sqrt{\gamma/\beta}$ is approximately equal to $3.38 \cdot 10^{-14}$ in SI units, and we take the mass $M_0 \simeq 2.49 \cdot 10^{30}$ kg, since we work with the uniform density approximation. We thus have

   $$R = \sqrt{\frac{\gamma}{\beta}} M^{2/3} \left(\frac{M_0}{M}\right)^{1/3} \sqrt{1 - \left(\frac{M}{M_0}\right)^{2/3}} = 2.03 \cdot 10^6\,\mathrm{m}. \tag{4.54}$$

Therefore the volume of the star is given by

$$V = \frac{4\pi}{3} R^3 = 3.53 \cdot 10^{19}\,\mathrm{m}^3. \tag{4.55}$$

The Fermi momentum p_F is given by the condition

$$\frac{1}{h^3}\frac{4\pi}{3}p_\mathrm{F}^3 = \frac{N}{2V}. \tag{4.56}$$

This yields

$$p_\mathrm{F} = 8.38 \cdot 10^{-22}\,\mathrm{kg\,m\,s^{-1}}, \tag{4.57}$$

to which corresponds the relativistic energy

$$\epsilon_\mathrm{F} = c p_\mathrm{F} = 2.51 \cdot 10^{-13}\,\mathrm{J}, \tag{4.58}$$

while the rest energy is given by

$$\epsilon_0 = m_\mathrm{e}\, c^2 = 8.19 \cdot 10^{-14}\,\mathrm{J}. \tag{4.59}$$

Therefore using the ultrarelativistic approximation does not make too much damage.

2. We obtain the Fermi temperature by the relation

$$T_\mathrm{F} = \frac{\epsilon_\mathrm{F}}{k_\mathrm{B}} = 1.82 \cdot 10^{10}\,\mathrm{K}. \tag{4.60}$$

This is safely larger than the star temperature, which is typically of order 10^7 K.

3. The pressure of the electron gas can be obtained by using the relation (4.123) for $d = 3$ and $\alpha = 1$. We need therefore to evaluate the internal energy E of the electron gas. Using the relativistic approximation, we obtain

$$\frac{E}{V} = \int_0^{p_\mathrm{F}} \mathrm{d}p\, \frac{4\pi\, p^2}{h^3}\, cp = \frac{\pi c}{h^3}\, p_\mathrm{F}^4 = 1.59 \cdot 10^{24}\,\mathrm{J}. \tag{4.61}$$

The pressure is then given by

$$p_\mathrm{el} = \frac{E}{3V} = 5.31 \cdot 10^{23}\,\mathrm{N\,m^{-2}}. \tag{4.62}$$

In order to evaluate the pressure of the gas of nuclei, we estimate the number of independent particles by dividing the mass M by the average mass of a nucleus, given by $(12+16)/2 = 14$ times the mass of a proton (totally neglecting the electron contribution). We thus obtain

$$N_\mathrm{ion} = \frac{M}{14\, m_\mathrm{p}} = 8.54 \cdot 10^{55}. \tag{4.63}$$

The corresponding pressure at the temperature $T = 10^7$ K is given by

$$p_\mathrm{ion} = \frac{N_\mathrm{ion}\, k_\mathrm{B} T}{V} = 3{,}34 \cdot 10^{20}\,\mathrm{N\,m^{-2}}. \tag{4.64}$$

Solution to exercise 4.11 (Neutron stars)

1. The neutron number is given by $N = M/m_{\mathrm{p}}$, where $m_{\mathrm{n}} \simeq 1.675 \cdot 10^{-27}\,\mathrm{kg}$ is the neutron mass. Thus the neutron density is given by $\rho = N/V = M/(m_{\mathrm{n}}\,V)$ where $V = 4\pi\,R^3/3$ is the volume of the star. Thus the Fermi momentum is given by the relation
$$\frac{4\pi}{3h^3} 2 p_{\mathrm{F}}^3 = \rho, \tag{4.65}$$
where the factor 2 comes from the spin. We thus obtain
$$p_{\mathrm{F}} = \frac{h}{2}\left(\frac{3\rho}{\pi}\right)^{1/3}. \tag{4.66}$$
Since the density of states $\omega(p)$ per unit volume and increment $\mathrm{d}p$ of momentum is given by $8\pi\,p^2/h^3$, a straightforward integration yields the kinetic energy density
$$\frac{T}{V} = \int_0^{p_{\mathrm{F}}} \mathrm{d}p\;\omega(p)\,\frac{p^2}{2m_{\mathrm{n}}} = \frac{8\pi}{h^3}\frac{1}{2m_{\mathrm{n}}}\frac{p_{\mathrm{F}}^5}{5} = \frac{3}{5}\,\epsilon_{\mathrm{F}}\,\rho, \tag{4.67}$$
where $\epsilon_{\mathrm{F}} = p_{\mathrm{F}}^2/2m_{\mathrm{n}}$ is the Fermi energy. Thus the total kinetic energy is given by
$$T = \frac{3N}{5}\epsilon_{\mathrm{F}} = \alpha\,\frac{M^{5/3}}{R^2}, \tag{4.68}$$
where α is given by
$$\alpha = \frac{3}{5}\frac{\hbar^2}{2m_{\mathrm{n}}^{8/3}}\left(\frac{9\pi}{4}\right)^{2/3}. \tag{4.69}$$

2. The gravitational energy of the star is given by
$$\begin{aligned} E_{\mathrm{g}} &= -G\int_0^R 4\pi\,r^2\,\mathrm{d}r\,(\rho m_{\mathrm{n}})\left(\frac{4\pi}{3}r^3\,\rho m_{\mathrm{n}}\right)\frac{1}{r} \\ &= -G\left(\frac{4\pi}{3}R^3\,\rho m_{\mathrm{n}}\right)^2\frac{3}{5R} = -\frac{3}{5}G\,\frac{M^2}{R}, \end{aligned} \tag{4.70}$$
where $G \simeq 6.674 \cdot 10^{-11}\,\mathrm{m^3kg^{-1}s^{-2}}$ is the gravitational constant. Thus the total energy of the star is given by
$$E = T + E_{\mathrm{g}} = \alpha\frac{M^{5/3}}{R^2} - \beta\frac{M^2}{R}. \tag{4.71}$$
This energy is minimal for the radius R^* given by
$$R^* = \frac{2\alpha}{\beta M^{1/3}} = \left(\frac{9\pi}{4}\right)^{2/3}\frac{\hbar^2}{G m_{\mathrm{n}}^{8/3}}\cdot\frac{1}{M^{1/3}}. \tag{4.72}$$

3. The equilibrium radius for a star of mass equal to the solar mass $M_\odot \simeq 1.989 \cdot 10^{30}\,\mathrm{kg}$ is approximately 12.34 km. We thus have $\rho \simeq 1.507 \cdot 10^{44}\,\mathrm{m}^{-3}$, $p_\mathrm{F} \simeq 1.737 \cdot 10^{-19}\,\mathrm{kg\,ms}^{-1}$ and $\epsilon_\mathrm{F} \simeq 9.007 \cdot 10^{-12}$, corresponding to a Fermi temperature of $6.527 \cdot 10^{11}\,\mathrm{K}$, thus much larger than the star temperature of about $10^7\,\mathrm{K}$.

Solution to exercise 4.12 Let us define the function $g_\alpha(z)$, for $\alpha > 0$ and $|z| < 1$ by the series

$$g_\alpha(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^\alpha}. \tag{4.73}$$

This function has the integral representation

$$g_\alpha(z) = \frac{1}{\Gamma(\alpha)} \int_0^\infty \mathrm{d}x\; x^{\alpha-1} \frac{z\,\mathrm{e}^{-x}}{1 - z\,\mathrm{e}^{-x}}, \tag{4.74}$$

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

$$\rho = \frac{1}{\lambda_\mathrm{B}^3(T_0)}, \tag{4.75}$$

where

$$\lambda_B(T) = \left(\frac{h^2}{2\pi k_\mathrm{B} T}\right)^{1/2} \tag{4.76}$$

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

$$p(T) = T \left(\frac{T}{T_0}\right)^{3/2} g_{5/2}(\zeta(T)), \tag{4.77}$$

where $\zeta(T)$ satisfies the equation

$$\left(\frac{T}{T_0}\right)^{3/2} g_{3/2}(\zeta(T)) = 1. \tag{4.78}$$

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

$$\epsilon(T) = \frac{3}{2} p(T) = \frac{3}{2} T \left(\frac{T}{T_0}\right)^{3/2} g_{5/2}(\zeta(T)). \tag{4.79}$$

These expressions hold for $T > T_\mathrm{c}$, where the condensation temperature T_c is given by

$$\left(\frac{T_\mathrm{c}}{T_0}\right)^{3/2} g_{3/2}(1) = 1. \tag{4.80}$$

We have

$$g_{3/2}(1) = \zeta_{\mathrm{R}}\left(\frac{3}{2}\right) = 2.61238\ldots \tag{4.81}$$

where $\zeta_{\mathrm{R}}(\alpha)$ Riemann's zeta function:

$$\zeta_{\mathrm{R}}(\alpha) = \sum_{k=1}^{\infty} \frac{1}{k^{\alpha}}. \tag{4.82}$$

We obtain therefore

$$T_{\mathrm{c}} = \left(\zeta_{\mathrm{R}}\left(\frac{3}{2}\right)\right)^{-2/3} T_0 \simeq 0.527201\, T_0. \tag{4.83}$$

For $T < T_{\mathrm{c}}$ we have $z = 1$ and therefore

$$p(T) = T\left(\frac{T}{T_0}\right)^{5/2} g_{5/2}(1) \simeq 1.34149\, T\left(\frac{T}{T_0}\right)^{3/2}, \tag{4.84}$$

and analogously for the energy density.

Let us now evaluate the specific heat per particle $C = \partial\epsilon/\partial T$. For $T > T_{\mathrm{c}}$ we have

$$\frac{\partial\epsilon}{\partial T} = \frac{15}{4}\left(\frac{T}{T_0}\right)^{3/2} g_{5/2}(\zeta(T)) + \frac{3}{2}T\left(\frac{T}{T_0}\right)^{3/2} g'_{5/2}(\zeta(T))\zeta'(T). \tag{4.85}$$

We can evaluate the derivative $\zeta'(T)$ by differentiating equation (4.78):

$$\frac{3}{2T}\left(\frac{T}{T_0}\right)^{3/2} g_{3/2}(\zeta(T)) + \left(\frac{T}{T_0}\right)^{3/2} g'_{3/2}(\zeta(T))\zeta'(T) = 0. \tag{4.86}$$

On the other hand it is easy to see that

$$g'_{\alpha}(z) = \frac{\mathrm{d}}{\mathrm{d}z}\sum_{k=1}^{\infty}\frac{z^k}{k^{\alpha}} = \sum_{k=1}^{\infty}\frac{z^{k-1}}{k^{\alpha-1}} = \frac{1}{z}g_{\alpha-1}(z). \tag{4.87}$$

We obtain therefore

$$\begin{aligned} C(T) = \frac{\partial\epsilon}{\partial T} &= \left(\frac{T}{T_0}\right)^{3/2}\left[\frac{15}{4}g_{5/2}(\zeta(T)) - \frac{9}{4}\frac{g^2_{3/2}(\zeta(T))}{g_{1/2}(\zeta(T))}\right] \\ &= \left(\frac{T}{T_0}\right)^{3/2} g_{3/2}(\zeta(T))\left[\frac{15}{4}\frac{g_{5/2}(\zeta(T))}{g_{3/2}(\zeta(T))} - \frac{9}{4}\frac{g_{3/2}(\zeta(T))}{g_{1/2}(\zeta(T))}\right] \\ &= \frac{15}{4}\frac{g_{5/2}(\zeta(T))}{g_{3/2}(\zeta(T))} - \frac{9}{4}\frac{g_{3/2}(\zeta(T))}{g_{1/2}(\zeta(T))}. \end{aligned} \tag{4.88}$$

In the last equality we have exploited equation (4.78). Since $g_{\alpha}(z) \simeq z$ for $|z| \ll 1$, we see that $\lim_{T\to\infty} C(T) = \frac{3}{2}$.

To evaluate the expression on the rhs we can use equation (4.74). However, for $\alpha = 1/2$ and $z \to 1$ the function $g_\alpha(z)$ diverges, and the integration routine can have problems. One can extract the singularity as follows:

$$\begin{aligned} g_\alpha(z) &= \frac{1}{\Gamma(\alpha)} \int_0^\infty \mathrm{d}x \; x^{\alpha-1} \frac{z\,\mathrm{e}^{-x}}{1 - z\,\mathrm{e}^{-x}} \\ &= \frac{z}{\Gamma(\alpha)} \int_0^\infty \mathrm{d}x \; x^{\alpha-1}\,\mathrm{e}^{-x} \left[\frac{1}{1-z} + \left(\frac{1}{1-z\,\mathrm{e}^{-x}} - \frac{1}{1-z}\right)\right] \\ &= \frac{z}{1-z}\left[1 - \frac{z}{\Gamma(\alpha)} \int_0^\infty \mathrm{d}x \; x^{\alpha-1}\,\mathrm{e}^{-x} \frac{1-\mathrm{e}^{-x}}{1-z\,\mathrm{e}^{-x}}\right]. \end{aligned} \tag{4.89}$$

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

We have thus obtained a parametric representation of the specific heat of the Bose gas for $T > T_\mathrm{c}$. From (4.78) we obtain T as a function of the fugacity$z$:

$$T(z) = \left(g_{3/2}(z)\right)^{-2/3}, \tag{4.90}$$

while equation (5.8) yields the specific heat $C = \partial\epsilon/\partial T$ as a function of z. For $T < T_\mathrm{c}$, $z \equiv 1$, and therefore one has

$$\epsilon = \frac{3}{2} T \left(\frac{T}{T_0}\right)^{3/2} g_{3/2}(1), \tag{4.91}$$

from which it follows

$$C(T) = \frac{15}{4} \left(\frac{T}{T_0}\right)^{3/2} g_{3/2}(1). \tag{4.92}$$

The resulting graph is shown in figure 4.2: it appears that the derivative of $C(T)$ exhibits a discontinuity at $T = T_\mathrm{c}$. Evaluation of the discontinuity requires further mathematical analysis (see, e.g., Wang [2004].)

Solution to exercise 4.13 (Einstein condensation of zero-mass particles)

1. *Grand canonical partition function.* The allowed values of the wave vector $\boldsymbol{k}$ are given by

   $$\boldsymbol{k} = \frac{2\pi}{L}\left(n_1, \ldots, n_d\right), \tag{4.93}$$

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

   $$\epsilon_{\boldsymbol{k}} = ck = \frac{2\pi c}{L}\sqrt{\sum_{k=1}^{d} n_k^2}. \tag{4.94}$$

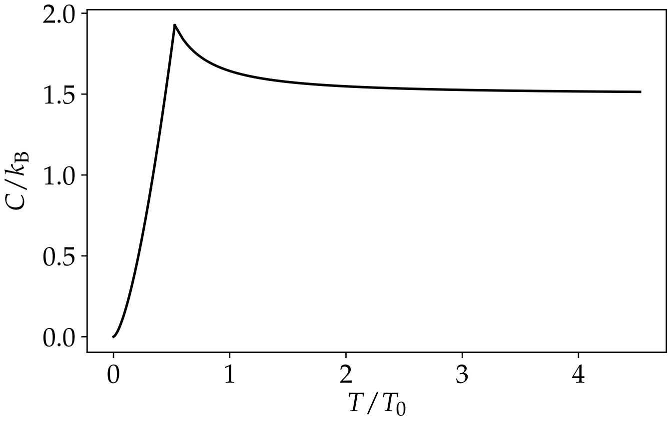

Figure 4.2: Specific heat per particle $C(T)$ of an ideal Bose gas. Temperatures are shown in units of T_0 (see eq. (4.75)), and the specific heat in units of k_B. The derivative of $C(T)$ exhibits a discontinuity for $T = T_\mathrm{c} = 0.527201\, T_0$.

Given the chemical potential μ, we have

$$\ln Z_\mathrm{GC} = -\sum_{\boldsymbol{k}} \ln\left[1 - \mathrm{e}^{-(\epsilon_k-\mu)/k_\mathrm{B}T}\right], \tag{4.95}$$

where the sum runs over the values allowed by eq. (4.93).

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

$$N = \left.\frac{\partial \ln Z_\mathrm{GC}}{\partial(\mu/k_\mathrm{B}T)}\right)_{V,1/k_\mathrm{B}T} = \sum_{\boldsymbol{k}} \frac{1}{\mathrm{e}^{(\epsilon_k-\mu)/k_\mathrm{B}T}-1}. \tag{4.96}$$

For large volumes, this expression can be approximated by

$$N = L^d \int_0^\infty \mathrm{d}k\, \frac{S_d}{(2\pi)^d}\, k^{d-1} \frac{1}{\mathrm{e}^{(ck-\mu)/k_\mathrm{B}T}-1}, \tag{4.97}$$

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.,

$$N_\mathrm{c} = \left(\frac{k_\mathrm{B}TL}{2\pi c}\right)^d \int_0^\infty \mathrm{d}x\; S_d\, x^{d-1} \frac{1}{\mathrm{e}^x - 1}. \tag{4.98}$$

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

Solution to exercise 4.14 (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 $\boldsymbol{k} = (k_1, \ldots, k_d)$ and are given by

$$\epsilon_{\boldsymbol{k}} = \hbar\omega_0 \left(\sum_{i=1}^{d} k_i + \frac{d}{2} \right). \tag{4.99}$$

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

$$\ln Z = -\sum_{\boldsymbol{k}} \ln \left[1 - \mathrm{e}^{-(\epsilon_{\boldsymbol{k}} - \mu)/k_{\mathrm{B}}T} \right]. \tag{4.100}$$

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

$$N' = \sum_{\boldsymbol{k}}{}' \frac{1}{\mathrm{e}^{\epsilon_{\boldsymbol{k}}/k_{\mathrm{B}}T}/z - 1} = \sum_{n=1}^{\infty} \frac{\mathcal{N}_d(n)}{\mathrm{e}^{\epsilon_{\boldsymbol{k}}/k_{\mathrm{B}}T}/z - 1}, \tag{4.101}$$

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:

$$\mathcal{N}_d(n) = \sum_{k_1, \ldots, k_d} \delta_{\sum_i k_i, n}. \tag{4.102}$$

To evaluate this number, let us define the generating function

$$\Gamma_d(z) = \sum_{n=0}^{\infty} z^n \mathcal{N}_d(n). \tag{4.103}$$

We have

$$\Gamma_d(z) = \sum_{n=0}^{\infty} \sum_{k_1, \ldots, k_d} \delta_{\sum_i k_i, n} z^n = \left(\sum_{n=0}^{\infty} z^n \right)^d = \frac{1}{(1-z)^d}. \tag{4.104}$$

By Newton's theorem we have therefore

$$\mathcal{N}_d(n) = (-1)^d \binom{-d}{n} = \frac{d(d+1)\cdots(d+n-1)}{n!}. \tag{4.105}$$

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

$$\mathcal{N}_2(n) = n + 1; \tag{4.106}$$

$$\mathcal{N}_3(n) = \frac{n(n+1)}{2}. \tag{4.107}$$

Thus we obtain

$$\ln Z = -\sum_{n=0}^{\infty} \mathcal{N}_d(n) \ln\left(1 - z\mathrm{e}^{-\kappa n}\right) \tag{4.108}$$

where we have introduced the fugacity

$$z = \mathrm{e}^{-(\mu_0-\mu)/k_\mathrm{B}T}, \tag{4.109}$$

and the shorthand

$$\kappa = \frac{\hbar\omega_0}{k_\mathrm{B}T}. \tag{4.110}$$

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

$$N = \sum_{n=0}^{\infty} \frac{\mathcal{N}_d(n)}{\mathrm{e}^{\kappa n}/z - 1}. \tag{4.111}$$

As $\mu \to \mu_0$, we have $z \to 1$ and the term corresponding to $n = 0$ in the sum (4.111) diverges. Let us thus separate this term from the others:

$$N = \frac{z}{1-z} + \sum_{n=1}^{\infty} \frac{\mathcal{N}_d(n)}{\mathrm{e}^{\kappa n}/z - 1}. \tag{4.112}$$

The number of particles in the excited states is given by

$$N' = \sum_{n=1}^{\infty} \frac{\mathcal{N}_d(n)}{\mathrm{e}^{\kappa n}/z - 1}. \tag{4.113}$$

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

$$N' = \sum_{n=1}^{\infty} \frac{\mathcal{N}_d(n)}{\mathrm{e}^{\kappa n}/z - 1}. \tag{4.114}$$

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

$$\begin{aligned}\sum_{i=m}^{n} f(n) &= \int_m^n \mathrm{d}x\, f(x) + \frac{1}{2}\left[f(n) + f(m)\right] \\ &\quad + \sum_{k=1}^{p} \frac{B_{2k}}{(2k)!}\left[f^{(2k-1)}(n) - f^{(2k-1)}(m)\right] + R \\ &= \int_m^n \mathrm{d}x\, f(x) + \frac{1}{2}\left[f(n) + f(m)\right] + \frac{1}{12}\left[f'(n) - f'(m)\right] + \cdots,\end{aligned} \tag{4.115}$$

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 if 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:

$$N' = \sum_{p=0}^{\infty} \frac{\mathcal{N}_d(p+1)}{\mathrm{e}^{\kappa p}/z' - 1}, \tag{4.116}$$

where

$$z' = z\mathrm{e}^{-\kappa}. \tag{4.117}$$

Let us evaluate the integral:

$$I_k(z') = \int_0^{\infty} \mathrm{d}x \, \frac{x^k}{\mathrm{e}^{\kappa x}/z' - 1}. \tag{4.118}$$

We have

$$\begin{aligned} I_k(z') &= \int_0^{\infty} \mathrm{d}x \; x^k \sum_{\ell=1}^{\infty} z'^{\ell} \mathrm{e}^{-\kappa \ell \, x} \\ &= \sum_{\ell=1}^{\infty} (\kappa \ell)^{-(k+1)} z'^{\ell} \int_0^{\infty} \mathrm{d}x \; x^k \mathrm{e}^{-x} = \Gamma(k+1)\kappa^{-(k+1)} \sum_{\ell=1}^{\infty} \frac{z'^{\ell}}{\ell^{k+1}} \\ &= \Gamma(k+1)\kappa^{-(k+1)} g_{k+1}(z'), \end{aligned} \tag{4.119}$$

where

$$g_k(z) = \sum_{\ell=1}^{\infty} \frac{z^{\ell}}{\ell^k} \tag{4.120}$$

is the polylog function.

We obtain therefore

$$N' \simeq \begin{cases} \kappa^{-2} g_2(z') + 2\kappa^{-1} g_1(z'), & \text{for } d = 2; \\ \kappa^{-3} g_3(z') + \frac{3}{2}\kappa^{-2} g_2(z') + \kappa^{-1} g_1(z'), & \text{for } d = 3. \end{cases} \tag{4.121}$$

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

   $$m\omega_0^2 = \frac{u_0}{R_0^2}, \tag{4.122}$$

   thus

   $$\omega_0 = \sqrt{\frac{u_0}{m}} \frac{1}{R_0}. \tag{4.123}$$

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

   $$\omega_0 = \sqrt{\frac{u_0}{m}} \left(\frac{\rho}{N}\right)^{1/d}, \tag{4.124}$$

and

$$\kappa = \frac{\hbar\omega_0}{k_{\mathrm{B}}T} = \frac{\hbar}{k_{\mathrm{B}}T}\sqrt{\frac{u_0}{m}}\left(\frac{\rho}{N}\right)^{1/d} = \frac{T_0}{T}N^{-1/d}, \tag{4.125}$$

where T_0 is defined by

$$T_0 = \frac{\hbar}{k_{\mathrm{B}}}\sqrt{\frac{u_0}{m}}\rho^{1/d}. \tag{4.126}$$

Thus we have

$$N' \simeq \begin{cases} N\left(\frac{T}{T_0}\right)^2 g_2(z') + 2\sqrt{N}\frac{T}{T_0}g_1(z'), & \text{for } d = 2; \\ N\left(\frac{T}{T_0}\right)^3 g_3(z') + \frac{3}{2}N^{2/3}\left(\frac{T}{T_0}\right)^2 g_2(z') + N^{1/3}\left(\frac{T}{T_0}\right)\kappa^{-1}g_1(z'), & \text{for } d = 3. \end{cases} \tag{4.127}$$

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

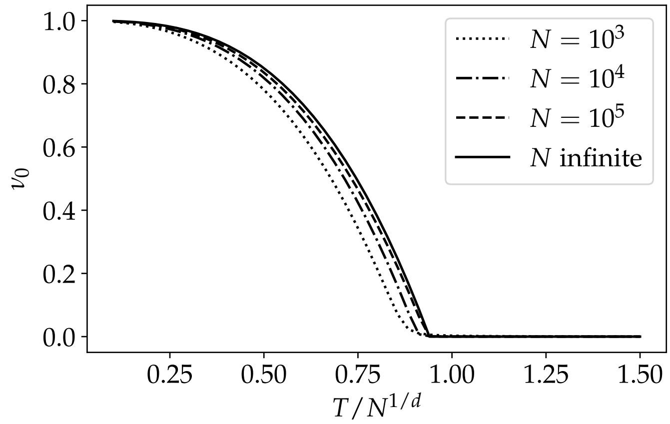

Figure 4.3: Condensate fraction of the Bose gas in a harmonic potential vs. $T/N^{1/d}$, for $d = 3$ and different values of N. The broken line corresponds to the thermodynamic limit expression $\nu_0 = 1 - (T/T_{\mathrm{c}})^d$.

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

$$N'_{\max} = \begin{cases} N\left(\frac{T}{T_0}\right)^2 g_2(1) = N\left(\frac{T}{T_0}\right)^2 \frac{\pi^2}{6}, & \text{for } d = 2; \\ N\left(\frac{T}{T_0}\right)^3 \zeta_{\mathrm{R}}(3), & \text{for } d = 3. \end{cases} \tag{4.128}$$

Here $\zeta_{\mathrm{R}}(z)$ is Riemann's zeta function. Thus we find the transition temperature:

$$T_{\mathrm{c}} = T_0 \cdot \begin{cases} \sqrt{6}/\pi = 0.7797, & \text{for } d = 2; \\ \sqrt[3]{1/\zeta_R(3)} = 0.9405, & \text{for } d = 3. \end{cases} \tag{4.129}$$

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

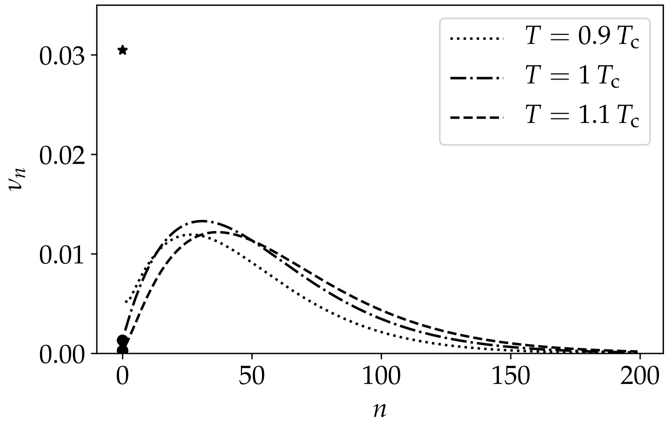

Figure 4.4: Occupation fractions ν_n of levels of energy $\hbar\omega_0(n + d/2)$ vs. n for $d = 3$, $N = 10000$ and different values of the temperature. The fraction ν_0 is marked by a symbol: point above and star below the condensation point.

> diverges for $z \to 1$, 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 4.3. 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 4.4. The occupation number of the ground state is marked with a symbol. Figure 4.5 shows the fraction of particles in the condensate for $d = 2$.

Solution to exercise 4.15 (A simplified model of hemoglobin) The grand canonical partition function of the system reads

$$Z_N(x, y) = \zeta^{N/4}(x, y), \tag{4.130}$$

where

$$\zeta(x, y) = \sum_{\{\tau\}} e^{[(\epsilon_0+\mu)\nu+Jk]/k_B T} = \sum_{\{\tau\}} x^{\nu(\{\tau\})} y^{k(\{\tau\})}, \tag{4.131}$$

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

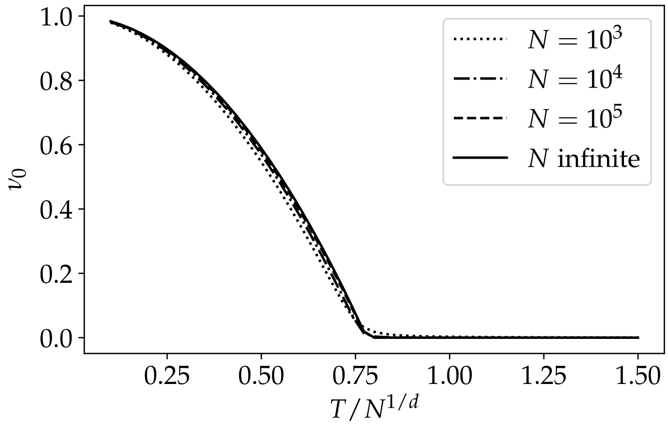

Figure 4.5: Condensate fraction of the Bose gas in a harmonic potential vs. $T/N^{1/d}$, for $d = 2$ and different values of N. The broken line corresponds to the thermodynamic limit expression $\nu_0 = 1 - (T/T_c)^d$. Notice that to evaluate numerically the condensate fraction the sum in Eq. (4.114) must be extended to substantially larger values of n than for $d = 3$.

$\nu = k = 0$, 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

$$\zeta(x, y) = 1 + 4x + 2x^2 + 4x^2y + 4x^3y^2 + x^4y^4. \tag{4.132}$$

Since

$$\left\langle \sum_{i=1}^{4} \tau_i \right\rangle = x \frac{\partial \ln \zeta}{\partial x}, \tag{4.133}$$

we have

$$\langle M \rangle = N \langle \tau \rangle = N \frac{x + x^2(1 + 2y) + 3x^3y^2 + x^4y^4}{1 + 4x + 2x^2 + 4x^2y + 4x^3y^2 + x^4y^4}. \tag{4.134}$$

One can use $x_0 = \mathrm{e}^{\epsilon_0/k_\mathrm{B}T}$ and y as fitting parameters. The fit is shown in figure 4.6. The ratio between the expected value and the observed one is shown in figure 4.7. One sees a systematic underestimate at low pressure.

Solution to exercise 4.16 (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

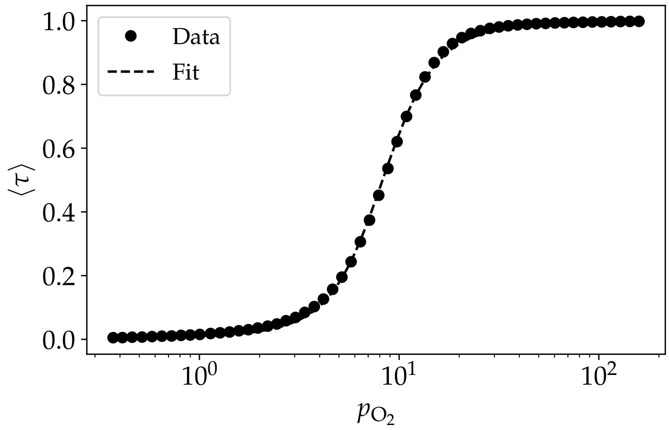

Figure 4.6: Fit of the function $\langle\tau\rangle\,(p_{O_2})$ with respect to the data by Imai [1990]. The x-axis is logarithmic.

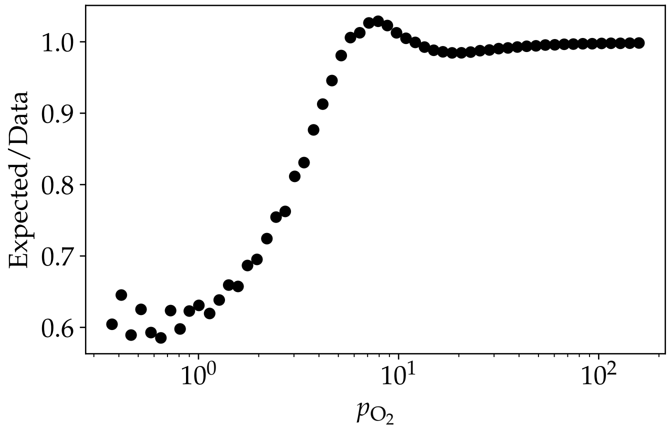

Figure 4.7: Ratio between the expected $\langle\tau\rangle\,(p_{O_2})$ and the observed one. The x-axis is logarithmic.

partition function:

$$Z = \sum_{\{k_i\}} \exp\left[-\beta \sum_i \epsilon(k_i)\right] = \prod_i \sum_{k_i} e^{-\beta\epsilon(k_i)}. \tag{4.135}$$

We obtain

$$\epsilon(0) = 0; \tag{4.136}$$

$$\epsilon(1) = \epsilon_0 + h; \tag{4.137}$$

$$\epsilon(2) = \epsilon_0; \tag{4.138}$$

$$\epsilon(3) = \epsilon_0 - h. \tag{4.139}$$

Thus

$$Z = \left[1 + \mathrm{e}^{-\beta\epsilon_0}\left(1 + \mathrm{e}^{-\beta h} + \mathrm{e}^{\beta h}\right)\right]^N. \tag{4.140}$$

2. We obtain, since $\beta = 1/k_\mathrm{B}T$,

$$E = -\left.\frac{\partial \ln Z}{\partial \beta}\right)_{\beta h} = \frac{N\mathrm{e}^{-\beta\epsilon_0}\left(1 + \mathrm{e}^{-\beta h} + \mathrm{e}^{\beta h}\right)}{1 + \mathrm{e}^{-\beta\epsilon_0}\left(1 + \mathrm{e}^{-\beta h} + \mathrm{e}^{\beta h}\right)}; \tag{4.141}$$

$$M = \left.\frac{\partial \ln Z}{\partial \beta h}\right)_{\beta} = \frac{N\mathrm{e}^{-\beta\epsilon_0} 2\sinh\beta h}{1 + \mathrm{e}^{-\beta\epsilon_0}\left(1 + \mathrm{e}^{-\beta h} + \mathrm{e}^{\beta h}\right)}. \tag{4.142}$$

.

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

$$M \simeq N\chi h, \tag{4.143}$$

where

$$\chi = \frac{2\beta\mathrm{e}^{-\beta\epsilon_0}}{1 + 3\mathrm{e}^{-\beta\epsilon_0}}. \tag{4.144}$$

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

Solution to exercise 4.17 (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 thus obtain the single-particle partition function $\zeta = \sum_m g_m \exp(-E_m/k_\mathrm{B}T)$:

   $$\zeta = 2\left[\mathrm{e}^{-3J/k_\mathrm{B}T}\cosh(3h/k_\mathrm{B}T) + 3\mathrm{e}^{-J/k_\mathrm{B}T}\cosh(h/k_\mathrm{B}T)\right]. \tag{4.145}$$

   The magnetization per spin m is obtained by evaluating $\partial \ln\zeta/\partial(h/k_\mathrm{B}T)$:

   $$3m = 3\frac{\mathrm{e}^{-3J/k_\mathrm{B}T}\sinh(3h/k_\mathrm{B}T) + \mathrm{e}^{-J/k_\mathrm{B}T}\sinh(h/k_\mathrm{B}T)}{\mathrm{e}^{-3J/k_\mathrm{B}T}\cosh(3h/k_\mathrm{B}T) + 3\mathrm{e}^{-J/k_\mathrm{B}T}\cosh(h/k_\mathrm{B}T)}, \tag{4.146}$$

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

CHAPTER 5

Phase Transitions

Solution to exercise 5.1 The Helmholtz free energy of a system which obeys the equation of state

$$p = p_{\mathrm{vdW}}(V,T), \tag{5.1}$$

where $p_{\mathrm{vdW}}(V,T)$ is given by the van der Waals equation, can be obtained by setting

$$\mathcal{F}(V,T) = F(V_0,T) - \int_{V_0}^{V} \mathrm{d}V'\; p(V',T), \tag{5.2}$$

where V_0 is chosen large enough, so that its Helmholtz free energy is close to the ideal gas free energy for that value of the volume. However, since in the van der Waals equation there is a range of V in which $\partial p/\partial V)_T$ is negative, the resulting function $\mathcal{F}(V,T)$ is not convex with respect to V. Thus, the actual Helmholtz free energy $F(V,T)$ is given by the convex envelope of $\mathcal{F}(V,T)$. The convex envelope is obtained by the double-tangent construction: we have $F(V,T) = \mathcal{F}(V,T)$ for V outside of an interval $[V_{\mathrm{L}}, V_{\mathrm{G}}]$, where V_{L} and V_{G} satisfy the following conditions:

$$\begin{aligned} \left.\frac{\partial \mathcal{F}}{\partial V}\right|_{V_{\mathrm{L}}} = \left.\frac{\partial \mathcal{F}}{\partial V}\right|_{V_{\mathrm{G}}} &= p_{\mathrm{t}}, \\ \frac{\mathcal{F}(V_{\mathrm{G}},T) - \mathcal{F}(V_{\mathrm{L}},T)}{V_{\mathrm{G}} - V_{\mathrm{L}}} &= p_{\mathrm{t}}. \end{aligned} \tag{5.3}$$

For $V_{\mathrm{L}} < V < V_{\mathrm{G}}$ we have

$$F(V,T) = \mathcal{F}(V_{\mathrm{L}},T) + \frac{V - V_{\mathrm{L}}}{V_{\mathrm{G}} - V_{\mathrm{L}}} \left(\mathcal{F}(V_{\mathrm{G}},T) - \mathcal{F}(V_{\mathrm{L}},T)\right). \tag{5.4}$$

Given the definition of $\mathcal{F}(V,T)$, the conditions (5.3) can be expressed by

$$\int_{V_{\mathrm{L}}}^{V_{\mathrm{G}}} \mathrm{d}V' \; p_{\mathrm{vdW}}(V',T) = p_{\mathrm{t}} \left(V_{\mathrm{G}} - V_{\mathrm{L}}\right), \tag{5.5}$$

which corresponds to Maxwell's construction.

Solution to exercise 5.2

1. We wish to evaluate the specific heat c_v per molecule of a van der Waals fluid for $v = v_{\mathrm{c}}$ and T close to T_{c}. Notice that the specific heat at constant pressure c_p becomes infinite for $T < T_{\mathrm{c}}$, since an arbitrary amount of liquid can be transformed into vapor without letting the temperature raise. Since $v = \text{const.}$, we have

$$c_v = T \left.\frac{\partial s}{\partial T}\right)_v = \left.\frac{\partial \epsilon}{\partial T}\right)_v, \tag{5.6}$$

where ϵ is the internal energy per molecule. At coexistence, let us denote by x_{liq} the fraction of molecules in the liquid state (and analogously for the vapor state). We then have

$$\epsilon = x_{\mathrm{liq}}\, \epsilon_{\mathrm{liq}} + x_{\mathrm{vap}}\, \epsilon_{\mathrm{vap}}. \tag{5.7}$$

Thus the specific heat is given by

$$c_{v_{\mathrm{c}}} = \left.\frac{\partial \epsilon_{\mathrm{liq}}}{\partial T}\right)_{v_{\mathrm{c}}} = x_{\mathrm{liq}} \left.\frac{\partial \epsilon}{\partial T}\right)_{v_{\mathrm{c}}} + x_{\mathrm{vap}} \left.\frac{\partial \epsilon_{\mathrm{vap}}}{\partial T}\right)_{v_{\mathrm{c}}} + \left(\epsilon_{\mathrm{liq}} - \epsilon_{\mathrm{vap}}\right) \left.\frac{\partial x_{\mathrm{liq}}}{\partial T}\right)_{v_{\mathrm{c}}}. \tag{5.8}$$

Now, from the Clausius-Clapeyron equation

$$\frac{\mathrm{d}p_{\mathrm{coex}}}{\mathrm{d}T} = \frac{\Delta s}{\Delta v}, \tag{5.9}$$

using the relation $\Delta H = \Delta E + p\,\Delta V$, where H is the enthalpy, we obtain

$$\frac{\mathrm{d}p_{\mathrm{coex}}}{\mathrm{d}T} = \frac{1}{T}\frac{\Delta \epsilon}{\Delta v} + \frac{p}{T}, \tag{5.10}$$

leading to

$$\Delta\epsilon = \epsilon_{\mathrm{liq}} - \epsilon_{\mathrm{vap}} = \left(T\,\frac{\mathrm{d}p_{\mathrm{coex}}}{\mathrm{d}T} - p_{\mathrm{coex}}\right)\left(v_{\mathrm{vap}} - v_{\mathrm{liq}}\right). \tag{5.11}$$

We next evaluate $\partial x_{\mathrm{liq}}/\partial T)_{v_{\mathrm{c}}}$. We have, since the total volume per molecule does not change,

$$\left.\frac{\partial x_{\mathrm{liq}}}{\partial T}\right)_{v_{\mathrm{c}}} \left(v_{\mathrm{vap}} - v_{\mathrm{liq}}\right) = x_{\mathrm{liq}} \left.\frac{\partial v_{\mathrm{liq}}}{\partial T}\right)_{\mathrm{coex}} + x_{\mathrm{vap}} \left.\frac{\partial v_{\mathrm{vap}}}{\partial T}\right)_{\mathrm{coex}}, \tag{5.12}$$

where the index denotes that the derivatives are taken along the coexistence line. Substituting eqs. (5.11) and (5.12) in eq. (5.8), we obtain

$$\begin{aligned} c_{v_\mathrm{c}} &= x_\mathrm{liq} \left.\frac{\partial \epsilon_\mathrm{liq}}{\partial T}\right)_{v_\mathrm{c}} + x_\mathrm{vap} \left.\frac{\partial \epsilon_\mathrm{vap}}{\partial T}\right)_{v_\mathrm{c}} \\ &\quad + \left(T \frac{\mathrm{d}p_\mathrm{coex}}{\mathrm{d}T} - p_\mathrm{coex} \right) \left[x_\mathrm{liq} \left.\frac{\partial v_\mathrm{liq}}{\partial T}\right)_\mathrm{coex} + x_\mathrm{vap} \left.\frac{\partial v_\mathrm{vap}}{\partial T}\right)_\mathrm{coex} \right]. \end{aligned} \tag{5.13}$$

We now have

$$\begin{aligned} \left.\frac{\partial \epsilon_\mathrm{liq}}{\partial T}\right)_{v_\mathrm{c}} &= \left.\frac{\partial \epsilon_\mathrm{liq}}{\partial T}\right)_{v_\mathrm{liq}} + \left.\frac{\partial \epsilon_\mathrm{liq}}{\partial v}\right)_T \left.\frac{\mathrm{d}v_\mathrm{liq}}{\mathrm{d}T}\right)_\mathrm{coex} \\ &= c_{v_\mathrm{liq}} + \left.\frac{\partial \epsilon_\mathrm{liq}}{\partial v}\right)_T \left.\frac{\mathrm{d}v_\mathrm{liq}}{\mathrm{d}T}\right)_\mathrm{coex}, \end{aligned} \tag{5.14}$$

and analogously for the vapor. On the other hand, we have

$$\left.\frac{\partial \epsilon_\mathrm{liq}}{\partial v}\right)_T = T \left.\frac{\partial p_\mathrm{liq}}{\partial T}\right)_{v_\mathrm{liq}} - p_\mathrm{liq}, \tag{5.15}$$

and

$$\left.\frac{\partial p_\mathrm{liq}}{\partial T}\right)_{v_\mathrm{liq}} = \left.\frac{\partial p}{\partial T}\right)_\mathrm{coex} - \left.\frac{\partial p_\mathrm{liq}}{\partial v_\mathrm{liq}}\right)_T \left.\frac{\mathrm{d}v_\mathrm{liq}}{\mathrm{d}T}\right)_\mathrm{coex}. \tag{5.16}$$

Substituting these equations, and the ones for the vapor, in the expression (5.13) of the specific heat, we obtain

$$\begin{aligned} c_{v_\mathrm{c}} &= x_\mathrm{liq} \left[c_{v_\mathrm{liq}} - T \left.\frac{\partial p_\mathrm{liq}}{\partial v_\mathrm{liq}}\right)_T \left(\frac{\mathrm{d}v_\mathrm{liq}}{\mathrm{d}T}\right)^2_\mathrm{coex} \right] \\ &\quad + x_\mathrm{vap} \left[c_{v_\mathrm{vap}} - T \left.\frac{\partial p_\mathrm{vap}}{\partial v_\mathrm{vap}}\right)_T \left(\frac{\mathrm{d}v_\mathrm{vap}}{\mathrm{d}T}\right)^2_\mathrm{coex} \right]. \end{aligned} \tag{5.17}$$

2. It is convenient to consider the van der Waals equation of state in reduced variables:

$$p_\mathrm{r} = \frac{8T_\mathrm{r}}{3v_\mathrm{r} - 1} - \frac{3}{v_\mathrm{r}^2}, \tag{5.18}$$

where

$$p_\mathrm{r} = \frac{p}{p_\mathrm{c}}, \qquad T_\mathrm{r} = \frac{T}{T_\mathrm{c}}, \qquad v_\mathrm{r} = \frac{v}{v_\mathrm{c}}. \tag{5.19}$$

We omit the subscript r in what follows.

From the Gibbs-Duhem relation

$$\mathrm{d}\mu = v\,\mathrm{d}p - s\,\mathrm{d}T, \tag{5.20}$$

the relation identifying the specific volumes of the liquid and of the vapor at coexistence is given by

$$\Delta\mu = \mu_{\text{vap}} - \mu_{\text{liq}} = 0, \tag{5.21}$$

yielding

$$\int_{v_{\text{liq}}}^{v_{\text{vap}}} \mathrm{d}v \; p(v,T) = p_{\text{coex}}\,(v_{\text{vap}} - v_{\text{liq}}), \tag{5.22}$$

where p_{coex} is the coexistence pressure. Equation (5.22) yields

$$p_{\text{coex}}\,(v_{\text{vap}} - v_{\text{liq}}) = \frac{8T}{3}\ln\frac{3v_{\text{vap}}-1}{3v_{\text{liq}}-1} + \frac{3}{v_{\text{vap}}} - \frac{3}{v_{\text{liq}}}. \tag{5.23}$$

This relation and the van der Waals equation correspond to the condition that v_{liq} and v_{vap} identify the minima of the function

$$\mathcal{F}(v,T,p) = pv - \int_{v_0}^{v} \mathrm{d}v' \; p(v',T), \tag{5.24}$$

for the value $p_{\text{coex}}(T)$ of p such that

$$\mathcal{F}(v_{\text{liq}}, T, p_{\text{coex}}(T)) = \mathcal{F}(v_{\text{vap}}, T, p_{\text{coex}}(T)). \tag{5.25}$$

On the other hand, we have, from the Maxwell relation

$$\left.\frac{\partial s}{\partial v}\right)_T = \left.\frac{\partial p}{\partial T}\right)_v, \tag{5.26}$$

the entropy difference between the vapor and liquid phase, that is, the latent heat divided by the temperature:

$$\Delta s = \int_{v_{\text{liq}}}^{v_{\text{vap}}} \mathrm{d}v \; \left.\frac{\partial s}{\partial v}\right)_T = \frac{8}{3}\ln\frac{3v_{\text{vap}}-1}{3v_{\text{liq}}-1}. \tag{5.27}$$

The same Maxwell relation implies

$$\frac{\partial^2 s}{\partial T\,\partial v} = \frac{\partial^2 p}{\partial T^2}, \tag{5.28}$$

which vanishes for the van der Waals fluid. Thus the specific heat of a homogeneous van der Waals fluid does not depend on v. To evaluate it, we take the $v \to \infty$ limit, where the fluid reduces to an ideal gas. We thus have (in non-reduced units)

$$c_v = \alpha\, k_{\text{B}}, \tag{5.29}$$

where $\alpha = 3/2$ for a monoatomic gas, $\alpha = 5/2$ for a biatomic one, or $\alpha = 3$ for a more complex molecule.

3. Let us now set, in reduced units,

$$p = 1 + \pi, \qquad T = 1 + \tau, \qquad v = 1 + \omega. \tag{5.30}$$

We then obtain

$$\begin{aligned}\mathcal{F}(1+\omega, 1+\tau, 1+\pi) \simeq \text{const.} + (-4\tau + \pi)\omega + 3\tau\,\omega^2 - 3\tau\,\omega^3 \\ + \left(\frac{3}{8} + \frac{27\tau}{8}\right)\omega^4,\end{aligned} \tag{5.31}$$

where the "const." does not depend on ω. Taking the minimum condition, we obtain

$$\pi = 4\tau - 6\tau\omega + 9\tau\omega^2 - \frac{3}{2}\omega^3, \tag{5.32}$$

plus negligible terms. To obtain coexistence, we must set $\pi = 4\tau$, and $\tau < 0$. We then obtain

$$\omega_{\text{coex}}^2 = -4\tau + \text{o}(\tau) > 0. \tag{5.33}$$

Thus $v_{\text{vap}} - v_{\text{liq}} \simeq 2\omega_{\text{coex}}$, and we obtain

$$\Delta s = \frac{8}{3}\ln\frac{2 + 3\omega_{\text{coex}}}{2 - 3\omega_{\text{coex}}} \simeq 8\omega_{\text{coex}}. \tag{5.34}$$

Substituting in the Clausius-Clapeyron equation we obtain, in reduced units

$$\left.\frac{\mathrm{d}p_{\text{coex}}}{\mathrm{d}T}\right|_{T_\text{c}} = 4, \tag{5.35}$$

which corresponds to the ansatz $\pi = 4\tau$ we made above. We also obtain, for small values of τ,

$$\left.\frac{\mathrm{d}v_{\text{liq}}}{\mathrm{d}T}\right)_{\text{coex}} = -\frac{\mathrm{d}\omega_{\text{coex}}}{\mathrm{d}\tau} = -\frac{1}{|\tau|^{1/2}}, \tag{5.36}$$

and analogously (with the opposite sign) for the vapor side. We have, on the other hand,

$$\left.\frac{\partial p_{\text{liq}}}{\partial v_{\text{liq}}}\right)_T = \frac{\partial \pi}{\partial \omega} \simeq 6\,|\tau| - \frac{9}{2}\omega_{\text{coex}}^2 = -12\,|\tau|\,. \tag{5.37}$$

Plugging these results in eq. (5.13), we obtain, for $T = T_\text{c} - \epsilon$, where $\epsilon > 0$ is infinitesimal,

$$c_{v_\text{c}} = c_v(T_\text{c} + \epsilon) + 12, \tag{5.38}$$

where the first term comes from the "regular" contributions $c_{v_{\text{liq}}}$, $c_{v_{\text{vap}}}$. To convert this result in ordinary units, observe that, in the van der Waals equation, we have $p_\text{c}v_\text{c} = (3/8)k_\text{B}T_\text{c}$. We thus obtain

$$\Delta c_v = c_{v_\text{c}}(T_\text{c} + \epsilon) - c_{v_\text{c}}(T_\text{c} - \epsilon) = 12\frac{p_\text{c}v_\text{c}}{T_\text{c}} = \frac{9}{2}k_\text{B}. \tag{5.39}$$

Solution to exercise 5.3 (Phase coexistence) We evaluate the partition function as follows.

1. We have
$$N = z\frac{\partial \ln Z_{\mathrm{GC}}}{\partial z} = V\frac{z}{1+z} + \alpha V \frac{z^{\alpha V}}{1+z^{\alpha V}}. \tag{5.40}$$
In the thermodynamic limit, the second term vanishes if $z < 1$, whereas it approaches αV for $z > 1$. Thus phase coexistence obtains for $z = z_{\mathrm{t}} = 1$, and the two densities are respectively equal to $N/V = \frac{1}{2}$ and $N/V = \frac{1}{2} + \alpha$.

2. Since
$$\frac{p}{k_{\mathrm{B}}T} = \frac{1}{V}\ln Z_{\mathrm{GC}}, \tag{5.41}$$
one has
$$p_{\mathrm{t}} = k_{\mathrm{B}}T\ln(1+z_{\mathrm{t}}) = k_{\mathrm{B}}T\ln 2. \tag{5.42}$$

Solution to exercise 5.4

1. We use units in which the electric field in $\boldsymbol{r}$ due to a charge q at rest at the origin is given by
$$\boldsymbol{E} = \frac{q\,\boldsymbol{r}}{r^3}. \tag{5.43}$$
Denote by $z = (x, y, 0)$ a generic point in the $h = 0$ plane. Consider the electrostatic field $\boldsymbol{E}(z)$ due to due to a charge uniformly distributed on the h axis, with linear charge density σ. We then obtain that $\boldsymbol{E}(z)$ is parallel to z and its component along this direction is given by
$$E(z) = \sigma\int_{-\infty}^{+\infty}\mathrm{d}h\,\frac{d}{(d^2+h^2)^{3/2}} = \frac{2\sigma}{d}, \tag{5.44}$$
where d is the length of z, that is,
$$d = \sqrt{x^2+y^2}. \tag{5.45}$$
This can be obtained from the potential
$$\Phi(z) = -2\sigma\,\ln d. \tag{5.46}$$

If we have N such lines, with linear density σ_k and intercepts on the $h = 0$ plane $z_k = (x_k, y_k, 0)$, for $k = 1, \dots, N$, the total potential will be given by

$$\Phi(z) = -2 \sum_{k=1}^{N} \sigma_k \ln |z - z_k| . \tag{5.47}$$

Let us now assume that z belongs to the positive x axis, and that the distribution of the lines is symmetrical with respect to the x axis, that is, for each $z_k = (x_k, y_k, 0)$ there is a k' such that $z_{k'} = (x_k, -y_k, 0)$ and $\sigma_{k'} = \sigma_k$. Then

$$\sum_{k=1}^{N} \sigma_k \ln |z - z_k| = \sum_{k=1}^{N} \sigma_k \ln(z - z_k), \tag{5.48}$$

where the logarithm is the complex logarithm of the complex variable $z - z_k$, where $z = x + \mathrm{i}y$, and $z_k = x_k + \mathrm{i}y_k$, $k = 1, \dots, N$. Indeed, for any complex number z, one has

$$\operatorname{Re} \ln z = \ln |z| , \qquad \operatorname{Im} \ln z = \arg z, \tag{5.49}$$

and the imaginary parts cancel out due to the symmetry.

Let us now have a large number (N) of charged lines, with intercepts disposed along the unit circle in the $h = 0$ plane. Let the line charge density of all lines be equal to $1/N$, and the number of lines per unit length around point $\zeta = \mathrm{e}^{\mathrm{i}\theta}$ be given by $N\,g(\theta)$. We assume moreover that $g(-\theta) = g(\theta)$. We then have, for any point z on the positive x axis,

$$\Phi(z) = -4\pi \int_0^{2\pi} \mathrm{d}\theta\; g(\theta)\; \ln(z - \mathrm{e}^{\mathrm{i}\theta}), \tag{5.50}$$

where the factor 2π comes from the fact that the length $\mathrm{d}\ell$ of an arc of angle $\mathrm{d}\theta$ of the unit circle is equal to $2\pi\,\mathrm{d}\theta$.

Let the grand partition function $Z(z)$ of a system as a function of the fugacity z have zeros at $z = z_k$, $k = 1, \dots, N$. The distribution of zeros is necessarily symmetric with respect to the real axis, since $Z(z)$ is real for real and positive z. We thus have

$$Z(z) = \prod_k (z - z_k). \tag{5.51}$$

Hence we have the following expression of the thermodynamic potential $G(z)$ per unit volume

$$\Omega(z) = -\frac{k_{\mathrm{B}}T}{N} \ln Z = -\frac{k_{\mathrm{B}}T}{N} \sum_k \ln(z - z_k), \tag{5.52}$$

due to the symmetry of the zeros distribution. If the number of zeros per unit length around $\zeta = \mathrm{e}^{\mathrm{i}\theta}$ is given by $g(\theta)$, we obtain

$$\frac{\Omega(z)}{k_{\mathrm{B}}T} = -2\pi \int_0^{2\pi} \mathrm{d}\theta\; g(\theta)\; \ln(z - \mathrm{e}^{\mathrm{i}\theta}) = \frac{\Phi(z)}{2}, \tag{5.53}$$

where $\Phi(z)$ is the potential associated with a distribution of charges on a cylinder insisting on the unit circle and with surface charge density given by $g(\theta)$.

Let $Z(z)$ be the grand partition function of a lattice gas with N sites, each of unit volume. We then have

$$\frac{\Omega(z)}{k_\mathrm{B}T} = -\frac{p}{k_\mathrm{B}T}, \qquad -z\frac{\partial}{\partial z}\left(\frac{\Omega(z)}{k_\mathrm{B}T}\right) = \rho = \frac{z}{2}E(z), \tag{5.54}$$

where ρ is the average occupation number per site. Let N go to infinity and set the linear change density to $1/N$, so that $g(\theta)$ remains constant. Then $g(\theta)$ can be interpreted as a surface charge density. We thus obtain the first result.

2. If $g(0) \neq 0$, consider a small Gauss surface formed by two small identical vertical rectangles symmetrically placed on one side and the other of the plane $x = 1$ and near to it, connected by rectangular faces (see fig. 5.1). The net flux of

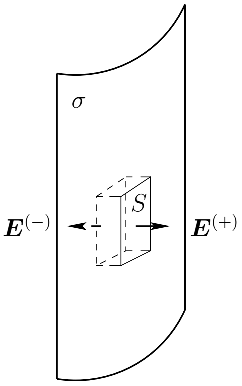

Figure 5.1: Evaluating the field discontinuity due to a surface distribution of charges. By Gauss's theorem the flux of the electric field across the parallelopipedal surface is equal to 4π times the enclosed charge, which is equal to σS. The net flux is given by $E^{(+)}S - E^{(-)}S$. Therefore we obtain $\Delta E = E^{(+)} - E^{(-)} = 4\pi\,\sigma$.

the field due to far away charges vanishes if the Gauss surface is small enough. The flux of the enclosed charges is only due to the rectangular faces, since the field is parallel to the connecting faces, and is given by $S\,\left(E^{(+)} - E^{(-)}\right)$, where $E^{(+,-)}$ are the x components of the field for $x = 1 \pm \epsilon$. From Gauss's theorem we then have, since the enclosed charge is equal to $S\,g(0)$,

$$4\pi\,S\,g(0) = S\,\left(E^{(+)} - E^{(-)}\right), \tag{5.55}$$

yielding $\Delta E = 4\pi\,g(0)$. By the above relation between E and ρ, taking into account that $z = 1$, we obtain

$$\Delta\rho = \frac{1}{2}z\,\Delta E = 2\pi\,g(0). \tag{5.56}$$

Solution to exercise 5.5 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 $p_+ = \mathrm{Prob}(\sigma_0 = +1)$. 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

$$\mathcal{N}_S < 3^S \cdot \text{power of } S, \tag{5.57}$$

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 5.6 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

$$\Delta E = \sum_{i=L+1}^{N} \sum_{j=1}^{L} \frac{2J}{|i-j|^a}. \tag{5.58}$$

If $1 < a < 2$ this quantity increases faster than $\ln N$ 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 Let us consider the one-dimensional Ising model with free boundary conditions, defined by the namiltonian $\mathcal{H} = -\sum_{i=1}^{N-1} J\sigma_i\sigma_{i+1}$. With the change of variables

$$\sigma'_i = \sigma_i\sigma_{i+1}, \quad 1 \le i < N, \tag{5.59}$$

the hamiltonian can be rewritten as

$$\mathcal{H}(\sigma') = -\sum_{i=1}^{N-1} J\sigma'_i. \tag{5.60}$$

Thus the partition function Z is given by

$$Z = \sum_{\sigma'} \mathrm{e}^{-\mathcal{H}(\sigma')/k_{\mathrm{B}}T} = [2\cosh K]^{N-1}, \tag{5.61}$$

where $K = J/k_{\mathrm{B}}T$. In the same way, we obtain, assuming $1 \le i < j \le N$,

$$\begin{aligned} C_{ij} &= \frac{1}{Z}\sum_{\sigma} \mathrm{e}^{-H(\sigma)/k_{\mathrm{B}}T}\sigma_i\sigma_j = \frac{1}{Z}\frac{1}{Z}\sum_{\sigma'}\prod_{\ell=1}^{i-1}\mathrm{e}^{K\sigma'_\ell}\prod_{m=i}^{j-1}\sigma'_m\mathrm{e}^{K\sigma'_m}\prod_{n=j}^{N-1}\mathrm{e}^{K\sigma'_n} \\ &= \frac{1}{Z}[2\sinh K]^{|i-j|}\,[2\cosh K]^{N-1-|i-j|}. \end{aligned} \tag{5.62}$$

We obtain therefore

$$C_{ij} = [\tanh K]^{|i-j|}. \tag{5.63}$$

Solution to exercise 5.8 Let us consider periodic boundary conditions. Then the partition function

$$Z = \sum_{\sigma_1,\dots,\sigma_N}\prod_{i=1}^{N}\mathrm{e}^{K\sigma_i\sigma_{i+1}+\lambda\sigma_i}, \tag{5.64}$$

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

$$Z = \mathrm{Tr}\,\mathsf{T}^N, \tag{5.65}$$

where

$$\mathsf{T} = \left(\mathrm{e}^{K\sigma\sigma'+(\lambda/2)(\sigma+\sigma')}\right) = \begin{pmatrix} \mathrm{e}^{K+h}, & \mathrm{e}^{-K} \\ \mathrm{e}^{-K}, & \mathrm{e}^{K-h} \end{pmatrix}, \tag{5.66}$$

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

$$\tau_\pm = \mathrm{e}^K\cosh\lambda \pm \sqrt{\mathrm{e}^{2K}\sinh^2\lambda + \mathrm{e}^{-2K}}. \tag{5.67}$$

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

$$f = \ln\tau_+ = \ln\left[\mathrm{e}^K\cosh\lambda + \sqrt{\mathrm{e}^{2K}\sinh^2\lambda + \mathrm{e}^{-2K}}\right]. \tag{5.68}$$

Solution to exercise 5.9

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 $(\ell_1, \dots, \ell_n)$, where $\sum_{i=1}^{n} \ell_i = N$, has the weight

$$W^{(n)}(\ell_1, \dots, \ell_n) = \mathrm{e}^{NK} x^{n-1} y^{\left(\sum_{i\,\mathrm{odd}} \ell_i - \sum_{i\,\mathrm{even}} \ell_i\right)}, \tag{5.69}$$

where we have defined

$$x = \mathrm{e}^{-2K}; \tag{5.70}$$

$$y = \mathrm{e}^{\lambda}. \tag{5.71}$$

(We use the notations $K = J/k_{\mathrm{B}}T$ and $\lambda = h/k_{\mathrm{B}}T$.) Thus the partition function has the expression

$$Z_N = \mathrm{e}^{NK} \sum_{n=1}^{N} x^{n-1} \sum_{\ell_1, \dots, \ell_n} \delta_{N, \sum_i \ell_i} y^{\left(\sum_{i\,\mathrm{odd}} \ell_i - \sum_{i\,\mathrm{even}} \ell_i\right)}. \tag{5.72}$$

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

$$Z(z) = \sum_{N=0}^{\infty} \left(z\,\mathrm{e}^{-K}\right)^N Z_N = \sum_{n=1}^{\infty} x^{n-1} \sum_{\ell_1, \dots, \ell_n} y^{\left(\sum_{i\,\mathrm{odd}} \ell_i - \sum_{i\,\mathrm{even}} \ell_i\right)} z^{\sum_i \ell_i}. \tag{5.73}$$

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

$$\begin{aligned} Z(z) &= Z_{\mathrm{odd}}(z) \left(1 + x \sum_{\ell=1}^{\infty} \left(\frac{z}{y}\right)^{\ell}\right) \\ &= Z_{\mathrm{odd}}(z) \left(1 + x \frac{z/y}{1 - z/y}\right) = Z_{\mathrm{odd}}(z) R(z). \end{aligned} \tag{5.74}$$

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

$$Q(z) = x^2 \sum_{\ell=1}^{\infty} (zy)^{\ell_1} \sum_{\ell_2=1}^{\infty} \left(\frac{z}{y}\right)^{\ell_2} = \frac{x^2 z^2}{(1 - zy)(1 - z/y)}. \tag{5.75}$$

The initial stretch of positive spins yields

$$P(z) = \sum_{\ell=1}^{\infty} (zy)^{\ell} = \frac{zy}{1 - zy}. \tag{5.76}$$

Thus the partition function reads

$$Z(z) = P(z) \left(\sum_{n=0}^{\infty} Q^n(z) \right) R(z) = \frac{P(z)\, R(z)}{1 - Q(z)}. \tag{5.77}$$

4. Since

$$\langle N \rangle = z \frac{\partial \ln Z}{\partial z} = z \left[\frac{P'(z)}{P(z)} + \frac{R'(z)}{R(z)} + \frac{Q'(z)}{1 - Q(z)} \right], \tag{5.78}$$

   the limit $N \to \infty$ 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

$$Q(z^*) = 1. \tag{5.79}$$

   This equation reads

$$\left(1 - x^2\right) z^2 - \left(y + \frac{1}{y}\right) z + 1 = 0, \tag{5.80}$$

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

$$z^* = \left[\frac{1}{2}\left(y + \frac{1}{y}\right) + \sqrt{\frac{1}{4}\left(y - \frac{1}{y}\right)^2 + x^2} \right]^{-1}. \tag{5.81}$$

   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 $Z(z) \sim \mathrm{e}^{N(z)[f_{N(z)} + \ln z]}$. It is easy to see that $\lim_{z \to z^*} \ln Z(z)/N(z) = 0$. Thus $\lim_{z \to z^*} f_{N(z)} = \lim_{N \to \infty} f_N = -\ln z^*$. Substituting for x and y their values, and remembering that we had rescaled z by e^K we recover equation (5.68).

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 5.10 (The Chinese philosophers' problem) The problem can be tackled in the following way.

1. Let us denote by $i \in \{1, \ldots, N\}$ 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

$$\mathcal{N}_N = \mathcal{N}(+1) + \mathcal{N}(-1) \tag{5.82}$$

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

$$\mathcal{N}_{N+1}(-1) = \mathcal{N}_N + \mathcal{N}_{N-1}(+1). \tag{5.83}$$

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

$$\mathcal{N}_{N+1}(+1) = \mathcal{N}_{N-1}(-1). \tag{5.84}$$

We obtain therefore

$$\mathcal{N}_{N+1} = \mathcal{N}_N + \mathcal{N}_{N-1}. \tag{5.85}$$

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

$$\Delta\mathcal{H}(\sigma, \sigma') = -J\sigma\sigma' - \frac{h}{2}\left(\sigma + \sigma'\right). \tag{5.86}$$

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

σ/σ'	$+1$	-1
$+1$	3	-1
-1	-1	-1

.

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

7. We have

$$\begin{aligned}\lambda_\pm &= \mathrm{e}^{\beta J}\cosh(\beta h) \pm \sqrt{\mathrm{e}^{2\beta J}\sinh^2(\beta h) + \mathrm{e}^{-2\beta J}}\\ &= \mathrm{e}^{-\beta}\cosh(2\beta) \pm \sqrt{\mathrm{e}^{-2\beta}\sinh^2(2\beta) + \mathrm{e}^{2\beta}}.\end{aligned} \tag{5.87}$$

For $\beta \to \infty$ one has

$$\lambda_\pm \to \mathrm{e}^{\beta}\frac{1 \pm \sqrt{5}}{2} = \mathrm{e}^{\beta}\lambda^0_\pm. \tag{5.88}$$

An explicit calculation shows that in this limit

$$p_N = \lim_{\beta\to\infty} \mathrm{e}^{\beta E_0(N)}\left(\lambda_+^N + \lambda_-^N\right) = (\lambda^0_+)^N + (\lambda^0_-)^N \tag{5.89}$$

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

Notice that the recursion relation (5.85) 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 5.11 (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 $\mathrm{e}^{-E_0/k_\mathrm{B}T}$, where E_0 is the ground-state energy, is given by $\mathrm{e}^{-2\mathcal{N}K}$ where $K = J/k_\mathrm{B}T$ 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:

$$Z = \mathrm{e}^{-E_0/k_\mathrm{B}T} \sum_{\mathcal{C}} \mathrm{e}^{-2\mathcal{N}(\mathcal{C})K}, \tag{5.90}$$

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

$$\mathcal{H} = -J' \sum_{\mathcal{P}} \prod_{i \in \mathcal{P}} \sigma_i, \tag{5.91}$$

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

$$Z' = \sum_{\sigma} \exp\left[K' \sum_{\mathcal{P}} \prod_{i \in \mathcal{P}} \sigma_i\right] = (2\cosh K')^{N_\mathcal{P}} \sum_{\sigma} \prod_{\mathcal{P}} \left(1 + \tanh K' \prod_{i \in \mathcal{P}} \sigma_i\right), \tag{5.92}$$

where $K' = J'/k_\mathrm{B}T$ 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 $(\tanh K')^{\mathcal{N}_\mathcal{P}}$. Thus, apart form the explicit configuration-independent factors, the two partition functions correspond where

$$\mathrm{e}^{-2K} = \tanh K'. \tag{5.93}$$

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

Solution to exercise 5.12 (Mean-field theory of the Ising antiferromagnet)

1. Let us denote by m_+ and m_-, respectively, the magnetization per spin for each of the two sublattices. The trial free energy then reads

$$\mathcal{F}(m_+, m_-) = \frac{1}{2} J m_+ m_- - \frac{h}{2}(m_+ + m_-) - \frac{T}{2}\left[S(m_+) + S(m_-)\right], \tag{5.94}$$

where $S(m)$ is the entropy per spin of an Ising paramagnet of average magnetization m:

$$S(m) = -k_\mathrm{B}\left[\frac{1+m}{2}\ln\frac{1+m}{2} + \frac{1-m}{2}\ln\frac{1-m}{2}\right]. \tag{5.95}$$

2. Since

$$\frac{\mathrm{d}S}{\mathrm{d}m} = -k_\mathrm{B} \tanh^{-1} m, \tag{5.96}$$

the variational principle yields the self-consistency equations

$$\frac{\zeta J m_- - h}{k_\mathrm{B} T} = -\tanh^{-1} m_+; \tag{5.97}$$

$$\frac{\zeta J m_+ - h}{k_\mathrm{B} T} = -\tanh^{-1} m_-. \tag{5.98}$$

3. Introducing the variables K and λ, these equations take the form

$$K m_- - \lambda = -\tanh^{-1} m_+; \tag{5.99}$$

$$K m_+ - \lambda = -\tanh^{-1} m_-. \tag{5.100}$$

In the absence of the applied field, we can look at solutions where $m_+ = -m_- = m$. We then obtain the equation

$$K m = \tanh^{-1} m, \tag{5.101}$$

that coincides with that of the Ising ferromagnet. We thus obtain $K_\mathrm{c}(\lambda{=}0) = 1$.

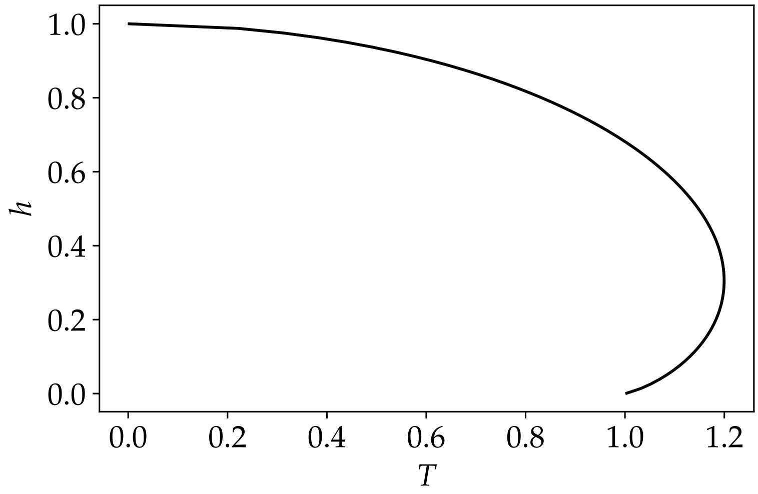

Figure 5.2: Phase diagram in the (T, h) plane for the Ising antiferromagnet in mean-field theory. The region below the curve corresponds to $m_+ - m_- \neq 0$. Both T and h are normalized by $\zeta J / k_\mathrm{B}$. Notice the reentrant behavior for $T < T^* \simeq 0.3$. Therefore, for $1 < |h| < h^* \simeq 1.2$, there are a lower and an upper critical temperature.

When $\lambda \neq 0$, we look for a solution where $m_+ - m_- = \delta \ll 1$. We then have

$$\tanh^{-1} m_+ = \tanh^{-1} m_- + \frac{\delta}{1 - m_-^2}. \tag{5.102}$$

On the other hand, we have $\tanh^{-1} m_- = \lambda - K m_+$. We thus obtain the self-consistency equation to first order in δ:

$$K\delta = \frac{\delta}{1 - m_-^2}. \tag{5.103}$$

We have the solution $\delta = 0$. But, if $K = 1/(1 - m_-^2)$, we also have a solution with $m_+ \neq m_-$, i.e., where the symmetry between the two lattices is broken. We express the condition in terms of K and λ by solving for m in terms of K:

$$m = \sqrt{1 - \frac{1}{K}}. \tag{5.104}$$

Substituting in the self-consistency equation (with $m_+ = m_- = m$) we obtain

$$\lambda = K\sqrt{1 - \frac{1}{K}} + \tanh^{-1} \sqrt{1 - \frac{1}{K}}. \tag{5.105}$$

4. We see that $\lambda \to 0$ for $K \to K_\mathrm{c} = 1$. For $T \to 0$, i.e., $K \to \infty$, we obtain $\lambda \approx K$ (since the $\tanh^{-1}$ diverges only logarithmically). Since $K = \zeta J/k_\mathrm{B}T$ and $\lambda = h/k_\mathrm{B}T$, this means that $\lim_{T\to 0} h_\mathrm{c} = \zeta J$. On the other hand, this limit is reached *from above*, as shown in fig. 5.2. There is therefore a range of values of h where a lower and an upper transition temperature are present, and the symmetry is broken only between them.

Solution to exercise 5.13 Consider a system to which a field $h_\parallel$ is applied, say, in the x direction. Then the order parameter m also lies in the x direction. If we add a small field, $h_\perp$, say, in the y direction, we obtain to first order a field $\boldsymbol{h}$ of equal magnitude, but directed at an angle θ with the x direction, where

$$\theta \simeq \sin\theta \simeq \frac{h_\perp}{h_\parallel}. \tag{5.106}$$

To this order, the magnitude of $\boldsymbol{m}$ remains unchanged, but its direction is aligned with the field. Therefore the order parameter acquires a component in the y direction given by

$$m_\perp = \sin\theta \simeq m\,\frac{h_\perp}{h_\parallel}, \tag{5.107}$$

where $m = |\boldsymbol{m}|$. Therefore the susceptibility to a transverse field is given by

$$\chi_\perp = \frac{\partial m_\perp}{\partial h_\perp} = \frac{m}{h_\parallel}, \tag{5.108}$$

and diverges for $h_\parallel \to 0$ if $\lim_{h_\parallel \to 0} m \neq 0$, that is, below the critical temperature.

Solution to exercise 5.14 (Tricritical point)

1. The extremum of the free energy is given by the equation

   $$h = m\left(a + bm^2 + cm^4\right). \tag{5.109}$$

   For $h = 0$ and $a > 0$ this has a minimum at $m = 0$. If $b > 0$ and $a < 0$, it exhibits a *maximum* for $m = 0$ and two minima at the points $m = \pm m_0$, where

   $$m_0^2 = \frac{-b + \sqrt{b^2 - 4ac}}{2c}. \tag{5.110}$$

   Thus the critical point corresponds to $a = 0$.

2. When $b < 0$ and a is positive, but small enough, there are, beyond the minimum at $m = 0$, two minima at $m = \pm m_0$, where m_0 satisfies the condition

   $$a + bm_0^2 + cm_0^4 = 0. \tag{5.111}$$

   When the free energy of these minima is equal to that at $m = 0$, that is, when m satisfies

   $$\frac{1}{2}a + \frac{1}{4}bm_0^2 + \frac{1}{6}cm_0^4 = 0, \tag{5.112}$$

   one has coexistence. Requiring these two equations to have a common nonzero solution yields

   $$m_0^2 = -\frac{3b}{4c}, \tag{5.113}$$

   and substituting in the equations yields

   $$a = \frac{3b^2}{16c} > 0. \tag{5.114}$$

   Thus the equation for the first-order transition line is

   $$a = \frac{3b^2}{16c} = 0. \tag{5.115}$$

The slope of this line, taking into accoun the dependence of the coefficients on the temperature T and an extra parameter r, is given by

$$\frac{\mathrm{d}T}{\mathrm{d}r} = -\frac{c(\partial a/\partial r) + a(\partial c/\partial r) - (3/8)b(\partial b/\partial r)}{c(\partial a/\partial T) + a(\partial c/\partial T) - (3/8)b(\partial b/\partial T)}. \tag{5.116}$$

Since both a and b approach zero as T approaches T_t from the side of the first-order transition, the slope approaches $-(\partial a/\partial r)/(\partial a/\partial T)$, that is the slope of the line of critical points on the other side. Thus the transition line is continuous with its derivative at $(T_\mathrm{t}, r_\mathrm{t})$, as shown in fig. 5.3.

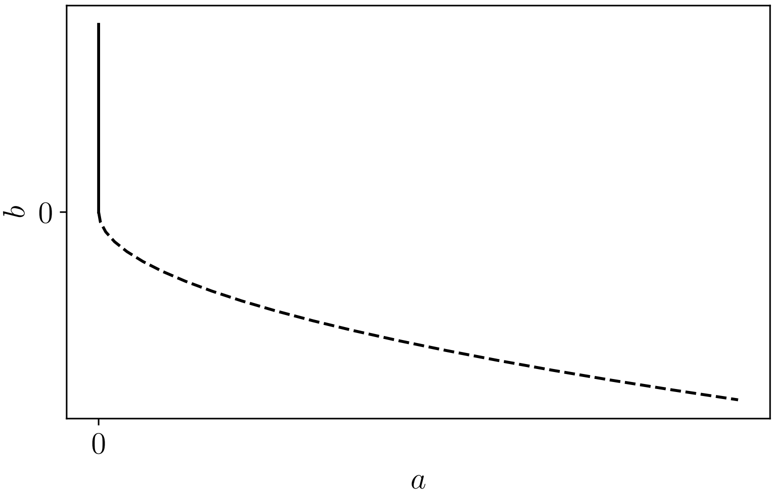

Figure 5.3: Phase diagram in the (a, b) plane. The continuous line corresponds to the critical line $(a = 0, b > 0)$. The dashed line corresponds to the line of triple points $a = b^2/(4c)$, $b < 0$. The point $(a = 0, b = 0)$ is the tricritical point. The points below the curve correspond to a first-order transition as h changes sign.

3. When $h \neq 0$ and $b < 0$, the magnetization m satisfies

$$h = am + bm^3 + cm^5. \tag{5.117}$$

This equation has in general more than one solution. Requiring that two of these solutions have the same value of the free energy for the given value of h imposes a condition between a and b for a fixed value of c. We obtain therefore a coexistence surface in the (a, h, b) space. This surface ends on the one hand for $h = 0$ on the line of first-order transitions obtained above, when the two non-vanishing minima become symmetric. On the other hand, it ends on a line of critical points. Indeed, requiring that m, given above, corresponds to a critical point imposes two extra conditions: the first, $\partial^2 f/\partial m^2 = 0$, yields

$$a + 3bm^2 + 5cm^4 = 0. \tag{5.118}$$

The second, $\partial^3 f/\partial m^3 = 0$, is required by stability and yields

$$6b + 20cm^2 = 0. \tag{5.119}$$

We thus obtain

$$m^2 = -\frac{3b}{10c}, \tag{5.120}$$

leading to

$$a = \frac{9b^2}{20c}, \tag{5.121}$$

and

$$h = \pm\sqrt{-\frac{3b}{10c}} \cdot \frac{6b^2}{25c}. \tag{5.122}$$

The diagram is shown in fig. 5.4.

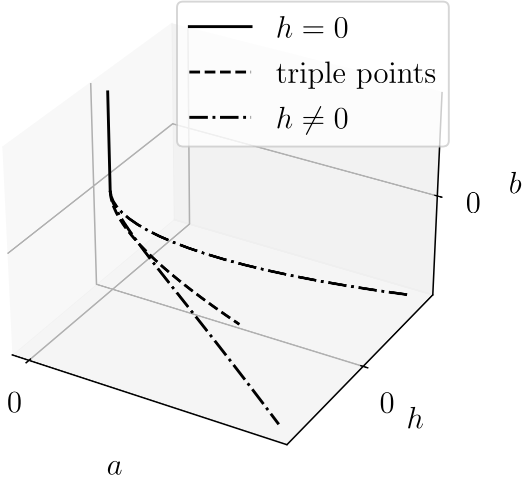

Figure 5.4: Phase diagram in the (a, h, b) space. Beyond the lines shown in fig. 5.3, we see the two critical lines given by $a = 9b^2/(20c)$, $h = \pm m_0\, 6b^2/(25c)$, $b < 0$, with $m_0^2 = -3b/(10c)$. A surface of first-order transitions is bounded by each such line and the line of triple points. Another such surface is bounded by the line of critical and triple points on the $h = 0$ plane.

4. When $b = 0$ and $a = 0$, we obtain $h = cm^5$, yielding the exponent $\delta_t = 5$. On the other hand, assuming $a < 0$ and taking $h = 0$, we obtain $m_0 = (-a/c)^{1/4}$, yielding an exponent $\beta_t = 1/4$.

5. Let us consider how the spontaneous magnetization m_0 behaves on approaching the critical line when $h = 0$ and $b > 0$ but very small. We have

$$m_0^2 = \frac{-b + \sqrt{b^2 - 4ac}}{2c}, \tag{5.123}$$

where $a < 0$. When we are far from the critical line, such that $4\,|a|\,c \gg b^2$, we have

$$m_0^2 \simeq \sqrt{-\frac{a}{c}} \sim |a|^{1/2}, \tag{5.124}$$

and therefore

$$m_0 \propto (T_\mathrm{c} - T)^{1/4}. \tag{5.125}$$

On the other hand, when we get closer to the transition temperature, so that $4\,|a|\,c \ll b^2$, we obtain

$$m_0^2 \simeq -\frac{2a}{b^2}, \tag{5.126}$$

yielding

$$m_0 \propto (T_\mathrm{c} - T)^{1/2}, \tag{5.127}$$

as in the usual mean-field case. Thus the system exhibits a crossover from the tricritical behavior to the critical one. In $d = 3$, while the tricritical exponent is still equal to its mean-field value (but the behavior exhibits logarithmic corrections), the critical one will be of course that pertinent to the universality class of the considered model.

Solution to exercise 5.15 (Spherical model) The hamiltonian of the spherical model, defined on a simple cubic lattice in d dimensions, is given by

$$\mathcal{H}(\sigma) = -\sum_{<ij>} J\sigma_i\sigma_j, \tag{5.128}$$

where the first sum runs over nearest-neighbor pairs of lattice points, $J > 0$, and the real variables σ_i satisfy the constraint

$$\sum_i \sigma_i^2 = N, \tag{5.129}$$

where N is the number of lattice points in the system. The partition function of the model is given by

$$Z = \int \prod_i \mathrm{d}\sigma_i\, \delta\left(\sum_i \sigma_i^2 - N\right) \exp\left[\frac{1}{2}\sum_{ij} K_{ij}\sigma_i\sigma_j\right], \tag{5.130}$$

where we have defined the matrix $\mathsf{K} = (K_{ij})$:

$$K_{ij} = \begin{cases} J/k_{\mathrm{B}}T = K, & \text{if } i \text{ and } j \text{ are nearest neighbors,} \\ 0, & \text{otherwise.} \end{cases} \tag{5.131}$$

By using the integral representation of the delta function, we can express Z by

$$\begin{aligned} Z &= \int \frac{\mathrm{d}\lambda}{2\pi} \int \prod_i \mathrm{d}\sigma_i \, \exp\left[\frac{1}{2}\sum_{ij} K_{ij}\sigma_i\sigma_j - \lambda\left(\sum_i \sigma_i^2 - N\right)\right] \\ &= \int \frac{\mathrm{d}\lambda}{2\pi} \int \prod_i \mathrm{d}\sigma_i \, \exp\left[-\frac{1}{2}\sum_{ij} Q_{ij}(\lambda)\sigma_i\sigma_j + \lambda N\right], \end{aligned} \tag{5.132}$$

where we have defined

$$Q_{ij}(\lambda) = 2\lambda\,\delta_{ij} - K_{ij}. \tag{5.133}$$

The Gaussian integral over the σ can now be performed, and we obtain

$$Z = \int \frac{\mathrm{d}\lambda}{2\pi\mathrm{i}} \, \exp\left[-\frac{1}{2}\operatorname{Tr}\ln\left(\mathsf{Q}'(\lambda)\right) - \lambda N\right], \tag{5.134}$$

by using the relation

$$\det \mathsf{A} = \exp\left(\operatorname{Tr}\ln \mathsf{A}\right). \tag{5.135}$$

The trace can be evaluated in Fourier space:

$$\operatorname{Tr}\ln \mathsf{Q}(\lambda) = \sum_{\boldsymbol{k}} \ln\left(2\lambda - K(\boldsymbol{k})\right), \tag{5.136}$$

where

$$K(\boldsymbol{k}) = \sum_i \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i} K_{ij}, \tag{5.137}$$

is the Fourier transform of K_{ij} (which is independent of i if the system is translationally invariant) and where the sum over $\boldsymbol{k}$ runs over wavenumbers of the form

$$\boldsymbol{k} = (k_1, \ldots, k_d) = \left(\frac{2\pi n_1}{L}, \ldots, \frac{2\pi n_d}{L}\right), \tag{5.138}$$

where L is the side length of the system, and which satisfy the condition

$$|k_\alpha| \leq \frac{\pi}{a_0}, \qquad \alpha = 1, \ldots, d, \tag{5.139}$$

where a_0 is the lattice spacing. We obtain

$$K(\boldsymbol{k}) = 2K \sum_{\alpha=1}^{d} \cos(k_\alpha a_0), \tag{5.140}$$

and

$$\mathrm{Tr}\ln \mathrm{Q}(\lambda) = \frac{Na_0^3}{(2\pi)^d}\int_{\mathrm{B.Z.}} \mathrm{d}\boldsymbol{k}\ \ln\left(2\lambda - K(\boldsymbol{k})\right), \tag{5.141}$$

where the integral is extended to the first Brillouin zone, that is, the region in which the relations (5.139) are satisfied.

Thus the integral in eq. (5.134) can be evaluated by the saddle-point method. We then have the saddle point equation

$$-\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\lambda}\,\mathrm{Tr}\ln \mathrm{Q}(\lambda)\bigg|_{\lambda^*} = N. \tag{5.142}$$

We have

$$-\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\mu}\,\mathrm{Tr}\ln \mathrm{Q}(\lambda) = \frac{Na_0^3}{(2\pi)^d}\int_{\mathrm{B.Z.}} \mathrm{d}\boldsymbol{k}\ \frac{1}{2\lambda - K(\boldsymbol{k})}. \tag{5.143}$$

Now, $K(\boldsymbol{k})$ is non-negative, and assumes its maximum value $K_0 = 2d\,K$ for $\boldsymbol{k} = 0$. In order to avoid a divergence in the integration, λ should not be not smaller than K_0. This expression monotonically increases as λ decreases. Therefore its maximum value is reached for $\lambda = \lambda_{\mathrm{c}} = K_0/2$. When $d > 2$, it is easy to see that it reaches a finite value, behaving like $1/K$. (On the other hand, for $d \leq 2$, the expression diverges as λ approaches $K_0/2$, and no transition takes place.) We thus obtain, for $d > 2$, a critical value K_{c} of K (that is, of T) such that, if $K > K_{\mathrm{c}}$, the saddle-point equation cannot be satisfied. This value is given by

$$K_{\mathrm{c}} = \frac{a_0^2}{2\,(2\pi)^d}\int_{\mathrm{B.Z.}} \mathrm{d}\boldsymbol{k}\ \frac{1}{d - \sum_\alpha \cos(k_\alpha a_0)}. \tag{5.144}$$

When $K > K_{\mathrm{c}}$ (that is, $T < T_{\mathrm{c}}$), the average of σ_i is different from zero. Let $\sigma_i = m + \sigma_i'$, with $\left\langle \sigma_i' \right\rangle = 0$. Then m must be such that

$$\left\langle \sigma_i^2 \right\rangle = m^2 + \left\langle \sigma_i'^2 \right\rangle = 1. \tag{5.145}$$

We have, on the other hand

$$\left\langle \sigma_i'^2 \right\rangle = \frac{a_0^3}{(2\pi)^d}\int_{\mathrm{B.Z.}} \mathrm{d}\boldsymbol{k}\ \frac{1}{K_0 - K(\boldsymbol{k})} = \frac{K_{\mathrm{c}}}{K}. \tag{5.146}$$

We thus obtain

$$m = \sqrt{1 - \frac{K_{\mathrm{c}}}{K}}, \tag{5.147}$$

corresponding to $\beta = 1/2$. Other exponents can be obtained by observing that the correlation function for $K < K_{\mathrm{c}}$ is given by

$$C(\boldsymbol{k}) = \frac{1}{2\lambda - K(\boldsymbol{k})}. \tag{5.148}$$

One thus obtains, for example, $\nu = 1/2$.

Solution to exercise 5.16 From the relation

$$\beta = 2 - \alpha - \beta\delta, \tag{5.149}$$

we obtain

$$\beta(\delta + 1) = 2 - \alpha = d\nu. \tag{5.150}$$

On the other hand, from the relation

$$\gamma + \beta = \beta\delta, \tag{5.151}$$

we obtain

$$\beta(\delta - 1) = \gamma = (2 - \eta)\nu. \tag{5.152}$$

Dividing both sides of these relations, we obtain

$$\frac{\delta + 1}{\delta - 1} = \frac{d}{2 - \eta}. \tag{5.153}$$

In the $n \to \infty$ model one has $\eta = 0$ and therefore

$$\delta = \frac{d + 2}{d - 2}. \tag{5.154}$$

Since $\beta = 1/2$ and $\gamma = 2/(d-2)$ for this model, we obtain, using eq. (5.151),

$$\delta - 1 = \frac{\gamma}{\beta} = \frac{4}{d - 2}, \tag{5.155}$$

that yields the above value.

To evaluate δ directly, let us set $K = K_c$ and introduce an external field h along the first direction. We then have the saddle-point equations

$$(2\lambda - K_0\omega(0))\,\sigma = h, \tag{5.156a}$$
$$-\sigma^2 + n = nf(\lambda), \tag{5.156b}$$

where σ is the average value of the first component of $\boldsymbol{\phi}$. Since $K = K_c$, we have $\lambda \to \lambda_c$, with $\lambda_c = K_0\omega(0)/2$ as h approaches 0. Then $f(\lambda) - f(\lambda_c) \sim r^{(d-2)/2}$, where $r = \lambda - \lambda_c$. From eq. (5.156a) we obtain $\sigma \sim h/r$, and from eq. (5.156b) we obtain $\sigma^2 \propto f(\lambda) - f(\lambda_c) \sim r^{(d-2)/2}$. Hence $h \sim r^{(d+2)/2}$ and $\sigma \sim h^{1/\delta} \sim h/r \sim h^{(d-2)/(d+2)}$. Therefore

$$\delta = \frac{d + 2}{d - 2}. \tag{5.157}$$

Solution to exercise 5.17 (A simple model of sublimation)

1. We have

$$Z = \frac{1}{N_1!} \int \prod_{i=1}^{N_1} \frac{\mathrm{d}\boldsymbol{p}_i \, \mathrm{d}\boldsymbol{r}_i}{h^3} \; \exp\left[-\frac{1}{k_{\mathrm{B}}T} \sum_{i=1}^{N_1} \frac{p_i^2}{2m} \right], \tag{5.158}$$

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

$$Z_1 = \frac{1}{N_1!} \left(\frac{V}{\lambda_{\mathrm{B}}^3} \right)^{N_1} \approx \left(\frac{\mathrm{e}\, V}{N_1 \lambda_{\mathrm{B}}^3} \right)^{N_1}. \tag{5.159}$$

We obtain therefore

$$\mu_1 = -k_{\mathrm{B}}T \frac{\partial \ln Z_1}{\partial N_1} = -k_{\mathrm{B}}T \ln \left(\frac{V}{N_1 \lambda_{\mathrm{B}}^3} \right). \tag{5.160}$$

By the ideal gas law we have

$$p = \frac{N_1 k_{\mathrm{B}} T}{V}, \tag{5.161}$$

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

$$\mu_1 = -k_{\mathrm{B}}T \ln \left(\frac{k_{\mathrm{B}}T}{p\, \lambda_{\mathrm{B}}^3} \right). \tag{5.162}$$

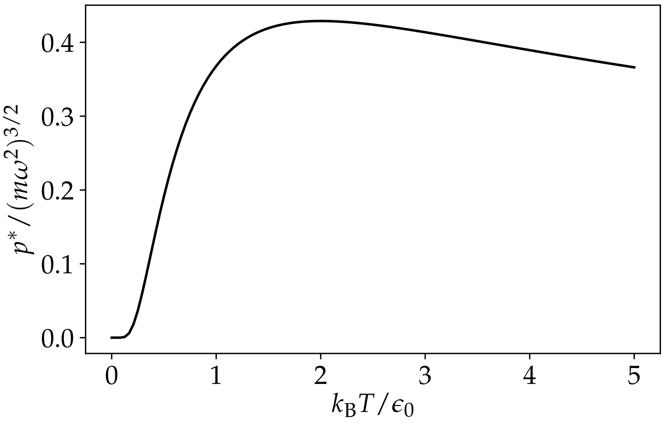

Figure 5.5: Sublimation pressure p^* as a function of T/ϵ_0, in units $(m\omega^2)^{3/2}$. We have set $k_{\mathrm{B}} = 1$.

2. We obtain

$$\begin{aligned} Z_2 &= \int \prod_{i=1}^{N_1} \frac{\mathrm{d}\boldsymbol{p}_i\,\mathrm{d}\boldsymbol{r}_i}{h^3}\ \exp\left[-\frac{1}{2k_\mathrm{B}T}\sum_{i=1}^{N_1}\left(\frac{p_i^2}{m}+m\omega^2 r_i^2-\epsilon_0\right)\right] \\ &= \left(\frac{k_\mathrm{B}T}{\hbar\omega}\right)^{3N_2} \mathrm{e}^{N_2\epsilon_0/k_\mathrm{B}T}. \end{aligned} \tag{5.163}$$

Thus we obtain

$$\mu_2 = -k_\mathrm{B}T\frac{\partial \ln Z_2}{\partial N_2} = -3k_\mathrm{B}T\ln\left(\frac{k_\mathrm{B}T}{\hbar\omega}\right)-\epsilon_0. \tag{5.164}$$

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

$$\ln\left(\frac{k_\mathrm{B}T^*}{p\,\lambda_\mathrm{B}^3}\right) = 3\ln\left(\frac{k_\mathrm{B}T^*}{\hbar\omega}\right)+\frac{\epsilon_0}{k_\mathrm{B}T^*}. \tag{5.165}$$

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

$$p^* = \left(\frac{\hbar\omega}{\lambda_\mathrm{B}(T)}\right)^3\frac{\mathrm{e}^{-\epsilon_0/k_\mathrm{B}T}}{(k_\mathrm{B}T)^2} = \frac{(m\omega^2)^{3/2}}{(k_\mathrm{B}T)^{1/2}}\,\mathrm{e}^{-\epsilon_0/k_\mathrm{B}T}. \tag{5.166}$$

The model is not reliable for $k_\mathrm{B}T \gg \epsilon_0$, 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 5.18 (Spin-elasticity coupling)

1. The hamiltonian of the model is given by

$$\mathcal{H}(\sigma,\epsilon) = -\sum_{i=1}^{N}\left[1+(-)^i\epsilon\right]\sigma_i\sigma_{i+1}+N\omega\epsilon^2. \tag{5.167}$$

Thus the partition function is given by

$$Z(\beta) = \int_{-\infty}^{+\infty}\mathrm{d}\epsilon\ \mathrm{e}^{-N\beta\omega\epsilon^2}Z_N(\epsilon,\beta), \tag{5.168}$$

where

$$Z_N(\epsilon,\beta) = \sum_{\{\sigma\}}\exp\left\{\beta\sum_{i=1}^{N}\left[1+(-\epsilon)^i\right]\sigma_i\sigma_{i+1}\right\}. \tag{5.169}$$

Introducing the transfer matrices

$$\mathsf{P} = \begin{pmatrix} \mathrm{e}^{\beta(1+\epsilon)}, & \mathrm{e}^{-\beta(1+\epsilon)} \\ \mathrm{e}^{-\beta(1+\epsilon)}, & \mathrm{e}^{\beta(1+\epsilon)} \end{pmatrix}; \tag{5.170}$$

$$\mathsf{Q} = \begin{pmatrix} \mathrm{e}^{\beta(1-\epsilon)}, & \mathrm{e}^{-\beta(1-\epsilon)} \\ \mathrm{e}^{-\beta(1-\epsilon)}, & \mathrm{e}^{\beta(1-\epsilon)} \end{pmatrix}. \tag{5.171}$$

we obtain

$$Z_N(\epsilon, \beta) = \mathrm{Tr}\,(\mathsf{PQ})^{N/2} \simeq \lambda_+^{N/2}, \tag{5.172}$$

where λ_+ is the largest eigenvalue of PQ:

$$\mathsf{PQ} = \begin{pmatrix} \mathrm{e}^{2\beta} + \mathrm{e}^{-2\beta}, & \mathrm{e}^{2\beta\epsilon} + \mathrm{e}^{-2\beta\epsilon} \\ \mathrm{e}^{2\beta\epsilon} + \mathrm{e}^{-2\beta\epsilon}, & \mathrm{e}^{2\beta} + \mathrm{e}^{-2\beta} \end{pmatrix}. \tag{5.173}$$

It is easy to see that

$$\lambda_+ = 2\left(\cosh 2\beta + \cosh 2\beta\epsilon\right). \tag{5.174}$$

We can thus evaluate the integral (5.168) by the saddle-point method, obtaining

$$Z(\beta) \sim \mathrm{e}^{-N\beta g(\epsilon^*, \beta)}, \tag{5.175}$$

where

$$g(\epsilon, \beta) = \omega\epsilon^2 - \frac{1}{2\beta}\ln\lambda_+, \tag{5.176}$$

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

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

$$\begin{aligned} -\ln\lambda_+ = {} & -\ln 2 - \ln\left(1 + \cosh 2\beta\right) - \frac{2\beta^2\epsilon^2}{1 + \cosh 2\beta} \\ & - \frac{2\left(\cosh 2\beta - 2\right)\beta^4\epsilon^4}{3(1 + \cosh 2\beta)^2} + \mathrm{O}\left(\epsilon^6\right) \end{aligned} \tag{5.177}$$

Let us define

$$u(\beta) = \frac{2\beta}{1 + \cosh 2\beta}. \tag{5.178}$$

It is easy to see that $\lim_{\beta\to 0} u(\beta) = \lim_{\beta\to\infty} u(\beta) = 0$, 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 $\epsilon = \pm 2$, whee 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 $g(\epsilon, \beta)$:

$$\frac{\partial g}{\partial \epsilon} = 2\omega\epsilon - \frac{\sinh(2\beta\epsilon)}{\cosh(2\beta) + \cosh(2\beta\epsilon)}. \tag{5.179}$$

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 5.6. One sees that the transition disappears for $\omega > \lim_{\beta\to\infty} \omega(\beta) = 0.25$.

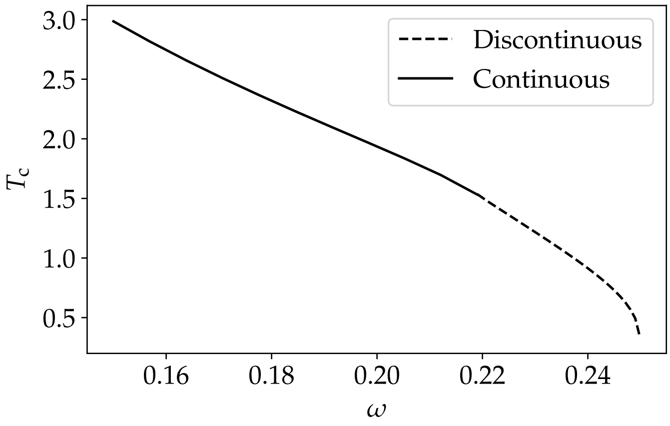

Figure 5.6: Phase diagram for the spin-elasticity coupling model.

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 $\omega_t = 0.219$.

Solution to exercise 5.19 (Mean-field theory of the Ising model in a transverse

field) The model is defined by the hamiltonian

$$\mathcal{H} = -J \sum_{<i,j>} \sigma_i^z \sigma_j^z - \Gamma \sum_i \sigma_i^x, \tag{5.180}$$

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

$$\sigma^z = \begin{pmatrix} 1, & 0 \\ 0, & -1 \end{pmatrix}; \qquad \sigma^x = \begin{pmatrix} 0, & 1 \\ 1, & 0 \end{pmatrix}. \tag{5.181}$$

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

$$\mathcal{H}_0(K,h) = -k_{\mathrm{B}}T \left[\sum_i \left(K\sigma_i^z + h\sigma_i^x \right) \right]. \tag{5.182}$$

We now look for the minimum of the trial free energy

$$\mathcal{F}(K,h) = \langle (\mathcal{H} - \mathcal{H}_0) \rangle_0 - k_{\mathrm{B}}T \ln Z_0, \tag{5.183}$$

where

$$Z_0 = \mathrm{Tr}\, \mathrm{e}^{-\beta H_0}; \tag{5.184}$$

$$\langle A \rangle_0 = \frac{1}{Z_0} \mathrm{Tr}\, A E^{-\beta H_0}. \tag{5.185}$$

1. Since

   $$\mathcal{H}_0 = -\beta^{-1} \begin{pmatrix} K, & h \\ h, & -K \end{pmatrix}, \tag{5.186}$$

   the secular equation has the expression

   $$\lambda^2 - \beta^{-2} \left(K^2 + h^2 \right) = 0. \tag{5.187}$$

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

   $$\lambda_\pm = \pm\sqrt{K^2 + h^2}. \tag{5.188}$$

   We thus obtain

   $$\ln Z_0 = N \ln 2 \cosh \sqrt{K^2 + h^2}. \tag{5.189}$$

2. On the other hand we have

   $$m = \langle \sigma^z \rangle_0 = \frac{\partial}{\partial K} \ln Z_0 = \frac{K}{\sqrt{K^2 + h^2}} \tanh \sqrt{K^2 + h^2}; \tag{5.190}$$

   $$\tau = \langle \sigma^x \rangle_0 = \frac{\partial}{\partial h} \ln Z_0 = \frac{h}{\sqrt{K^2 + h^2}} \tanh \sqrt{K^2 + h^2}. \tag{5.191}$$

Therefore

$$\langle(\mathcal{H}-\mathcal{H}_0)\rangle_0 = -\frac{NJ\zeta}{2}m^2 - N\left(\Gamma - k_{\mathrm{B}}Th\right)\tau + Nk_{\mathrm{B}}TKm. \tag{5.192}$$

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

$$\begin{aligned}\mathcal{F}(K,h) = -\frac{NJ\zeta}{2}m^2 &- N\left(\Gamma - k_{\mathrm{B}}Th\right)\tau + Nk_{\mathrm{B}}TKm \\ &- Nk_{\mathrm{B}}T\ln 2\cosh\sqrt{K^2+h^2}.\end{aligned} \tag{5.193}$$

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

$$0 = -NJ\zeta mm_K - N\left(\Gamma - k_{\mathrm{B}}Th\right)\tau_K + Nk_{\mathrm{B}}TKm_K; \tag{5.194}$$

$$0 = -NJ\zeta mm_h + Nk_{\mathrm{B}}TKm_h - N\left(\Gamma - k_{\mathrm{B}}Th\right)\tau_h. \tag{5.195}$$

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

$$K = \frac{Jm\zeta}{k_{\mathrm{B}}T}; \qquad h = \frac{\Gamma}{k_{\mathrm{B}}T}. \tag{5.196}$$

Since m is expressed as a function of K via eq. (5.190), we obtain the self-consistency equation

$$\frac{T}{T_0}K = \frac{K}{\sqrt{K^2+h^2}}\tanh\sqrt{K^2+h^2}, \tag{5.197}$$

where we have defined

$$T_0 = \frac{J\zeta}{k_{\mathrm{B}}}. \tag{5.198}$$

Equation (5.197) always allows for the solution $K = 0$. The solutions with $K \neq 0$ must satisfy

$$\frac{T}{T_0}\sqrt{K^2+h^2} = \tanh\sqrt{K^2+h^2} \tag{5.199}$$

Let us define ω via the equation

$$\omega = \frac{T}{T_0}\sqrt{K^2+h^2}. \tag{5.200}$$

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

$$m(T,\Gamma) = \pm\sqrt{\omega_0^2 - \left(\frac{\Gamma}{k_{\mathrm{B}}T_0}\right)^2}. \tag{5.201}$$

Of course this solution is acceptable only if the argument of the square root is

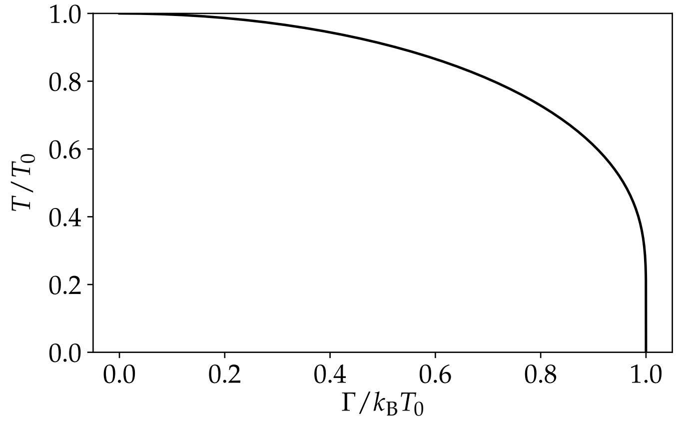

Figure 5.7: Phase diagram of the Ising model in a transverse field in the (Γ, T)-plane. Below the curve, one has $m \neq 0$. Notice the vertical asymptote for $\Gamma/k_\mathrm{B}T_0 \to 1$.

positive. Thus the transition between a regime with $m = 0$ and one with $m \neq 0$ will take place at the temperature $T_\mathrm{c}(\Gamma)$ defined by

$$\omega_0(T_\mathrm{c}) = \frac{\Gamma}{k_\mathrm{B}T_0}. \tag{5.202}$$

For temperatures smaller than T_c we shall have a non-vanishing magnetization, given by

$$m_0(T) = \pm\frac{T}{T_0}\sqrt{\omega_0^2(T) - \left(\frac{\Gamma}{k_\mathrm{B}T}\right)^2} \propto \sqrt{T_\mathrm{c} - T}. \tag{5.203}$$

The phase diagram (Γ, T) described by equation (5.202) is shown in figure 5.7.

Solution to exercise 5.20 (Mean-field theory of the three-state Potts model)

1. We have

$$1 = p + 2\pi = p + 2(p - m) = 3p - 2m, \tag{5.204}$$

and thus

$$p = \frac{1+2m}{3}; \tag{5.205}$$

$$\pi = p - m = \frac{1+2m}{3} - m = \frac{1-m}{3}. \tag{5.206}$$

Thus, by Gibbs' formula

$$\begin{aligned} S(m) &= -k_\mathrm{B} \sum_a p_a \ln p_a \\ &= -k_\mathrm{B} \left[\left(\frac{1+2m}{3} \right) \ln \left(\frac{1+2m}{3} \right) + 2 \left(\frac{1-m}{3} \right) \ln \left(\frac{1-m}{3} \right) \right]. \end{aligned} \tag{5.207}$$

2. We have

$$\begin{aligned} E(m) = \langle \mathcal{H} \rangle &= \frac{N\zeta J}{2} \sum_{a=1}^{3} p_a(1-p_a) \\ &= \frac{NJ\zeta}{2} \left[\frac{1+2m}{3} \frac{2}{3}(1-m) + 2 \frac{1-m}{3} \frac{2+m}{3} \right] = \frac{NJ\zeta}{3}(1-m^2). \end{aligned} \tag{5.208}$$

3. We thus obtain

$$\begin{aligned} F(m,T) = E(m) - TS(m) = \frac{NJ\zeta}{3}(1-m^2) \\ + Nk_\mathrm{B}T \left[\left(\frac{1+2m}{3} \right) \ln \left(\frac{1+2m}{3} \right) \right. \\ \left. + 2 \left(\frac{1-m}{3} \right) \ln \left(\frac{1-m}{3} \right) \right]. \end{aligned} \tag{5.209}$$

Imposing that the derivative with respect to m vanishes we obtain the self-consistency equation

$$0 = -\frac{2NJ\zeta}{3} m + \frac{2Nk_\mathrm{B}T}{3} \ln \frac{1+2m}{1-m}, \tag{5.210}$$

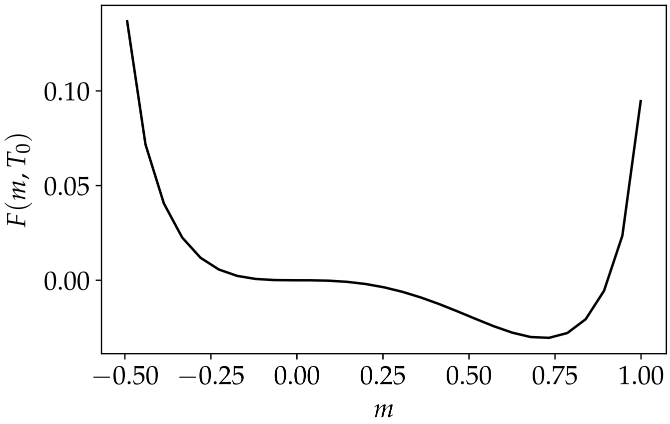

Figure 5.8: Trial free energy $F(m, T_0) - F(0, T_0)$, for the value T_0 of the temperature in which $\partial^2 F / \partial m^2|_{m=0}$ vanishes.

i.e.,

$$\ln\frac{1+2m}{1-m}=\frac{J\zeta}{k_\mathrm{B}T}m. \tag{5.211}$$

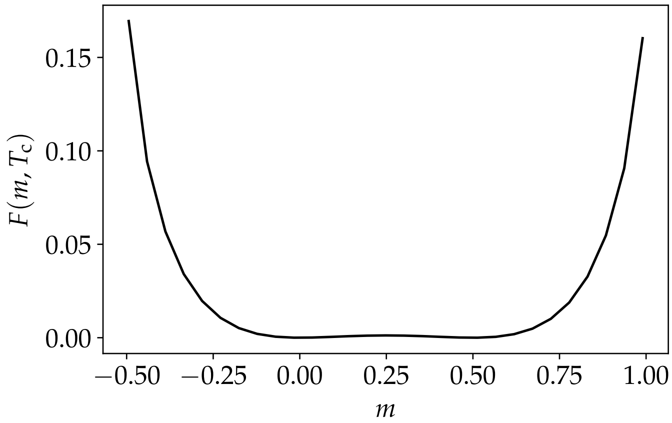

Figure 5.9: Trial free energy $F(m,T_\mathrm{c})-F(0,T_\mathrm{c})$, for the value T_c of the temperature in which the transition takes place.

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

   $$\phi(m)=\ln\frac{1+2m}{1-m}, \tag{5.212}$$

   it is easy to obtain

   $$\phi(m)=3m-\frac{3}{2}m^2+\mathrm{O}\left(m^3\right). \tag{5.213}$$

   Thus, for $k_\mathrm{B}T_0=J\zeta/3$ 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 can evaluate numerically the critical value T_c of T and the corresponding value of the minimum $m^*(T_\mathrm{c})$ for which we have $F(m^*,T_\mathrm{c})=F(m^*,T_\mathrm{c})$. One thus obtains $T_\mathrm{c}=0.7213=1/\ln 4$, with $m^*=0.5$. The figures shows $F(m,T_\mathrm{c})-F(0,T_\mathrm{c})$ as a function of m. Thus there will be a discontinuous transition for $T=T_\mathrm{c}$, where m jumps from 0 to $m^*=\frac{1}{2}$.

   For $T<T_\mathrm{c}$ one has $m=m^*(T)$, which rapidly approaches 1 as T decreases, as shown.

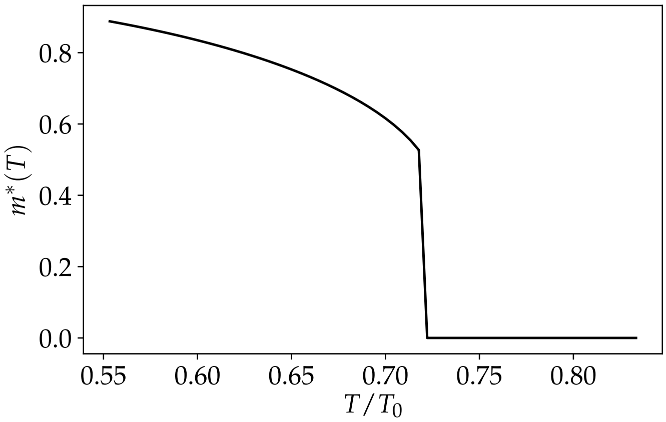

Figure 5.10: Order parameter $m^*(T)$ as a function of T/T_0 for the three-state Potts model.

CHAPTER 6

Renormalization Group

Solution to exercise 6.1 Assuming both t and h are small, and applying Kadanoff's transformation once, we obtain the relation

$$m(\kappa t, \kappa_h h) = \kappa^{\beta}\, m(t,h), \tag{6.1}$$

which can be compared with the scaling law relation (5.217)

$$m(\lambda t, \lambda^{\beta\delta} h) = \lambda^{\beta}\, m(t,h). \tag{6.2}$$

We can thus set

$$\kappa_h = \kappa^{\beta\delta}, \tag{6.3}$$

and taking into account the relation

$$\frac{1}{\nu} = \frac{\ln \kappa}{\ln b}, \tag{6.4}$$

we obtain

$$\frac{\ln \kappa_h}{\ln b} = \frac{\beta\delta}{\nu}. \tag{6.5}$$

Solution to exercise 6.2 Given the relation

$$K' = \frac{3}{8} \ln \cosh(4K), \tag{6.6}$$

we have

$$K = \frac{1}{4} \cosh^{-1}\left(\mathrm{e}^{8K'/3}\right) = f(K'). \tag{6.7}$$

If K^* is an unstable fixed point for the transformation $K \longrightarrow K'$, it is a stable fixed point for the inverse transformation $K' \longrightarrow K$. It suffices therefore to iterate $f(K')$ starting from any initial point (except 0 or ∞). We have, for instance, starting from $K' = 1/2$, $K^* = 0.50698$ with 25 iterations. Ona can of course use more sophisticated methods, like the Newton method.

Solution to exercise 6.3 Let c_n be the coefficient of $k^n\,\phi_{\boldsymbol{k}}\phi_{-\boldsymbol{k}}$. Under the transformation, since $\zeta = b^{d/2}$, we obtain

$$c_n' = c_n b^{-(d+n)\zeta^2} = b^{-n} c_n < c_n. \tag{6.8}$$

Solution to exercise 6.4 Let us denote by c_n the coefficient of $k^n\,\phi_{\boldsymbol{k}}\phi_{-\boldsymbol{k}}$ in $\Delta(\boldsymbol{k})$. We then have, instead of eq. (6.96b)

$$c_n' = c_n b^{-(d+n)}\zeta^2.$$

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 6.5 The partition function has the expression

$$Z \propto \int \prod_{\boldsymbol{k}} \mathrm{d}\phi_{\boldsymbol{k}}\ \exp\left[-\frac{N}{2}\int_{\text{Z.B.}} \mathrm{d}\boldsymbol{k}\ \phi_{-\boldsymbol{k}}\Delta(\boldsymbol{k})\phi_{\boldsymbol{k}}\right], \tag{6.9}$$

where

$$\Delta(\boldsymbol{k}) = r + ck^2 + \cdots \tag{6.10}$$

Since

$$F = -k_{\mathrm{B}}T \ln Z, \tag{6.11}$$

and the Gaussian integral can be directly performed, we obtain

$$F = \frac{Vk_{\mathrm{B}}T}{2}\int_{\text{Z.B.}} \mathrm{d}\boldsymbol{k}\ \ln\Delta(\boldsymbol{k}). \tag{6.12}$$

The singular part of the specific heat is obtained by differentiating $\Delta(\boldsymbol{k})$ with respect to T, and therefore with respect to r, since $r \propto T - T_{\mathrm{c}}$. We thus obtain

$$C_h \propto \frac{Nk_{\mathrm{B}}T}{2}\int_{\text{Z.B.}} \mathrm{d}\boldsymbol{k}\ \frac{1}{(r + ck^2 + \cdots)^2}, \tag{6.13}$$

where r vanishes as $T \to T_c$. The dominant contribution comes from the small values of k. Changing variables to $k' = k\sqrt{c/r}$ the integral appears to be proportional to $r^{(d-4)/2}$, that is, to $(T - T_c)^{(d-4)/2}$. Comparing with $C_h \sim (T - T_c)^{-\alpha}$, we obtain $\alpha = (4 - d)/2$.

Solution to exercise 6.6 (Critical isotherm) 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 $\sigma \sim h/r \sim h^{(d-2)/(d+2)}$.

Solution to exercise 6.7 Let us first evaluate

$$\mathcal{H}_1 = u \sum_j \left(\sum_\alpha \phi_i^\alpha \right) + v \sum_i \sum_\alpha (\phi_i^\alpha)^4 . \tag{6.14}$$

Thus we obtain

$$\sum_j G_{ij}^{-1} \left\langle \phi_i^\alpha \phi_j^\alpha \right\rangle + 4u \sum_j \sum_\beta \left\langle \phi_i^\alpha \phi_j^\alpha \left(\phi_j^\beta\right)^2 \right\rangle + 4v \sum_j \left\langle \phi_i^\alpha \left(\phi_j^\alpha\right)^3 \right\rangle = 1. \tag{6.15}$$

At the lowest order we obtain

$$\begin{gathered} \sum_\beta \left\langle \phi_i^\alpha \phi_j^\alpha \left(\phi_j^\beta\right)^2 \right\rangle = (n+2) \left\langle \phi_i^\alpha \phi_j^\alpha \right\rangle \left\langle \left(\phi_j^\beta\right)^2 \right\rangle, \\ \left\langle \phi_i^\alpha (\phi_j^\alpha)^3 \right\rangle = 3 \left\langle \phi_i^\alpha \phi_j^\alpha \right\rangle \left\langle \left(\phi_j^\alpha\right)^2 \right\rangle, \end{gathered} \tag{6.16}$$

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.

To proceed, we must evaluate the expression

$$\left\langle \mathcal{H}_1^2 \right\rangle_0 - \langle \mathcal{H}_1 \rangle_0^2 , \tag{6.17}$$

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

$$(\phi_i^<)^4 \left\langle (\phi_i^>)^4 \right\rangle_0 \tag{6.18}$$

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

$$-36v^2 \frac{1}{(1+r)^2} \tag{6.19}$$

to the renormalization of v.

The terms proportional to uv contain a factor of 2 from the double product. They are proportional to

$$\left\langle (\phi^\alpha)^2 \left(\phi^\beta\right)^2 (\phi^\gamma)^4 \right\rangle_0 . \tag{6.20}$$

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 6.8 By looking at the case $T > T_\mathrm{c}$ one sees that $\gamma = 1$ and $\nu = 1/2$ for both ϕ^3 and ϕ^6. By looking at the case $T < T_\mathrm{c}$ one obtains $\langle \phi \rangle \propto |T - T_\mathrm{c}|^\beta$, with $\beta = 1$ for ϕ^3 and $\beta = 1/4$ for ϕ^6. Using the scaling law

$$2\beta + \gamma = 2 - \alpha = d\nu, \tag{6.21}$$

we obtain the critical dimension by the Toulouse argument:

$$d_\mathrm{c} = \begin{cases} 2\,(2+1) = 6, & \text{for } \phi^3, \\ 2\,(1/2+1) = 3, & \text{for } \phi^6. \end{cases} \tag{6.22}$$

Solution to exercise 6.9 Given the $2d$ vector field $\boldsymbol{v} = \big(v_x(\boldsymbol{r}), v_y(\boldsymbol{r})\big)$ and the circuit $\mathcal{C}$, the circulation Γ is given by

$$\Gamma = \oint_{\mathcal{C}} \mathrm{d}\boldsymbol{r} \cdot \boldsymbol{v} = \oint_{\mathcal{C}} \left(v_x \,\mathrm{d}x + v_y \,\mathrm{d}y\right). \tag{6.23}$$

Define the rotated field $\boldsymbol{w} = (-v_y, v_x)$: it is the $\boldsymbol{v}$ field rotated by $\pi/4$ counterclockwise. We then have

$$\Gamma = \oint_{\mathcal{C}} \left(w_y \,\mathrm{d}x - w_x \,\mathrm{d}y\right) = \oint_{\mathcal{C}} \boldsymbol{w} \cdot \boldsymbol{n} \,\mathrm{d}r, \tag{6.24}$$

where $\boldsymbol{n}$ is the normal versor to $\boldsymbol{r}$:

$$\boldsymbol{n} = \frac{(-\mathrm{d}y, \mathrm{d}x)}{\sqrt{\mathrm{d}x^2 + \mathrm{d}y^2}}. \tag{6.25}$$

Thus Γ is the flux of $\boldsymbol{w}$ across $\mathcal{C}$. Therefore the quantization condition on $\boldsymbol{\psi} = \nabla\theta$ corresponds to the charge quantization for the rotated field $\boldsymbol{w}$. The equation expressing $\nabla \times \boldsymbol{\psi}$ goes over to the Gauss-like expression $\nabla \cdot \boldsymbol{w} = 2\pi\,\delta(\boldsymbol{r})$. The rest follows easily.

CHAPTER 7

Classical Fluids

Solution to exercise 7.1 Define

$$\rho_0(x_1,\dots,x_N)=\prod_{i=1}^{N}\rho^{(1)}(x_i), \tag{7.1}$$

and denote the canonical probability distribution by $\rho^{\mathrm{eq}}(x_1,\dots,x_N)$. Then we have

$$D_{\mathrm{KL}}(\rho^{\mathrm{eq}}\|\rho_0)\geq 0, \tag{7.2}$$

where

$$D_{\mathrm{KL}}(p\|p')=\int\prod_{i=1}^{N}\mathrm{d}x_i\;p(\{x_i\})\ln\frac{p(\{x_i\})}{p'(\{x_i\})}. \tag{7.3}$$

Now

$$\begin{aligned}
k_{\mathrm{B}}D_{\mathrm{KL}}(\rho^{\mathrm{eq}}\|\rho_0)&=\int\prod_{i=1}^{N}\mathrm{d}x_i\;\rho^{\mathrm{eq}}(\{x_i\})\left[\ln\rho^{\mathrm{eq}}(\{x_i\})-\ln\rho_0(\{x_i\})\right]\\
&=-\mathcal{S}(\rho^{\mathrm{eq}})-k_{\mathrm{B}}\sum_{j=1}^{N}\int\prod_{i=1}^{N}\mathrm{d}x_i\;\rho^{\mathrm{eq}}(\{x_i\})\ln\rho^{(1)}(x_j)\\
&=-\mathcal{S}(\rho^{\mathrm{eq}})-Nk_{\mathrm{B}}\int\mathrm{d}x\;\rho^{(1)}(x)\ln\rho^{(1)}(x)=-S+N\mathcal{S}(\rho^{(1)}),
\end{aligned} \tag{7.4}$$

since $\mathcal{S}(\rho^{\mathrm{eq}})$ 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.

Solution to exercise 7.2 By integrating the expression of $\rho^{(\ell)}(x_1,\ldots,x_\ell)$, we obtain, in the canonical ensemble

$$\int \mathrm{d}\boldsymbol{x}_1\cdots\mathrm{d}\boldsymbol{x}_\ell\;\rho^{(\ell)}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_\ell)=N(N-1)\cdots(N-\ell+1)=\frac{N!}{(N-\ell)!}. \tag{7.5}$$

Let us evaluate the same quantity in the grand canonical ensemble:

$$\rho^{(\ell)}_{\mathrm{GC}}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_\ell)=\frac{1}{\Omega_{\mathrm{GC}}[\mu,v]}\sum_N \mathrm{e}^{\mu N/k_{\mathrm{B}}T}\Omega_N[v]\rho^{(\ell)}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_\ell), \tag{7.6}$$

where

$$\Omega_{\mathrm{GC}}[\mu,v]=\sum_N \mathrm{e}^{\mu N/k_{\mathrm{B}}T}\Omega_N[v]. \tag{7.7}$$

We have

$$\int \mathrm{d}\boldsymbol{x}_1\cdots\mathrm{d}\boldsymbol{x}_\ell\;\rho^{(\ell)}_{\mathrm{GC}}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_\ell)=\left\langle\frac{N!}{(N-\ell)!}\right\rangle, \tag{7.8}$$

where the average is taken in the grand canonical ensemble. We have in particular

$$\int \mathrm{d}\boldsymbol{x}_1\;\rho^{(1)}_{\mathrm{GC}}(\boldsymbol{x}_1)=\langle N\rangle; \tag{7.9}$$

$$\int \mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2\;\rho^{(2)}_{\mathrm{GC}}(\boldsymbol{x}_1,\boldsymbol{x}_2)=\left\langle N^2\right\rangle-\langle N\rangle. \tag{7.10}$$

Thus we have

$$\begin{aligned}&\int \mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2\;\left[\rho^{(2)}_{\mathrm{GC}}(\boldsymbol{x}_1,\boldsymbol{x}_2)-\rho^{(1)}_{\mathrm{GC}}(\boldsymbol{x}_1)\rho^{(1)}_{\mathrm{GC}}(\boldsymbol{x}_2)\right]\\&\qquad=N\int\mathrm{d}\boldsymbol{x}\;\left[g(\boldsymbol{x})-1\right]=\left\langle N^2\right\rangle-\langle N\rangle-\langle N\rangle^2.\end{aligned} \tag{7.11}$$

On the other hand we have

$$\left\langle N^2\right\rangle-\langle N\rangle^2=k_{\mathrm{B}}T\left.\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T}. \tag{7.12}$$

The rhs is related to the susceptibility. We have indeed

$$\ln Z_{\mathrm{GC}}=\frac{p(\mu,T)V}{k_{\mathrm{B}}T}. \tag{7.13}$$

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

$$\frac{1}{\rho K_T}=\left.\frac{\partial p}{\partial\rho}\right)_{V,T}=V\left.\frac{\partial p}{\partial\langle N\rangle}\right)_{V,T}=\langle N\rangle\left.\frac{\partial\mu}{\partial\langle N\rangle}\right)_{V,T}. \tag{7.14}$$

From equations (7.11,7.14) we obtain

$$1+\rho\int \mathrm{d}\boldsymbol{x}\ \left[g(\boldsymbol{x})-1\right]=\rho k_{\mathrm{B}}TK_T. \tag{7.15}$$

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 7.3 The grand canonical partition function for non-interacting particles, in the presence of a single-particle potential $v(\boldsymbol{r})$ is given by

$$Z_{\mathrm{GC}}=\sum_{N=0}^{\infty}\frac{\mathrm{e}^{\mu N/k_{\mathrm{B}}T}}{N!}\left(\int\frac{\mathrm{d}\boldsymbol{r}}{\lambda_{\mathrm{B}}^3}\,\mathrm{e}^{-v(\boldsymbol{r})/k_{\mathrm{B}}T}\right)^N=\exp\left[\int\frac{\mathrm{d}\boldsymbol{r}}{\lambda_{\mathrm{B}}^3}\,\mathrm{e}^{(\mu-v(\boldsymbol{r}))/k_{\mathrm{B}}T}\right], \tag{7.16}$$

where μ is the chemical potential. Thus the thermodynamic potential is given by

$$\mathcal{F}[v]=-k_{\mathrm{B}}T\ln Z_{\mathrm{GC}}=-k_{\mathrm{B}}T\int\frac{\mathrm{d}\boldsymbol{r}}{\lambda_{\mathrm{B}}^3}\,\mathrm{e}^{(\mu-v(\boldsymbol{r}))/k_{\mathrm{B}}T}. \tag{7.17}$$

We thus obtain

$$\rho(\boldsymbol{r})=\frac{\delta\mathcal{F}}{\delta v(\boldsymbol{r})}=\frac{1}{\lambda_{\mathrm{B}}^3}\mathrm{e}^{(\mu-v(\boldsymbol{r}))/k_{\mathrm{B}}T}. \tag{7.18}$$

We can thus express $v(\boldsymbol{r})$ in terms of $\rho(\boldsymbol{r})$ as follows:

$$v(\boldsymbol{r})=\mu-k_{\mathrm{B}}T\ln\left(\rho(\boldsymbol{r})\lambda_{\mathrm{B}}^3\right). \tag{7.19}$$

We obtain therefore

$$\begin{aligned}F[\rho]&=\int\mathrm{d}\boldsymbol{r}\ v(\boldsymbol{r})\rho(\boldsymbol{r})-\mathcal{F}[v]\\&=\int\mathrm{d}\boldsymbol{r}\ \left[\mu-k_{\mathrm{B}}T\ln\left(\rho(\boldsymbol{r})\lambda_{\mathrm{B}}^3\right)\right]\rho(\boldsymbol{r})+k_{\mathrm{B}}T\int\mathrm{d}\boldsymbol{r}\ \rho(\boldsymbol{r}).\end{aligned} \tag{7.20}$$

One may check that

$$\frac{\delta F}{\delta\rho(\boldsymbol{r})}=\mu-k_{\mathrm{B}}T\ln\left(\rho(\boldsymbol{r})\lambda_{\mathrm{B}}^3\right)=v(\boldsymbol{r}). \tag{7.21}$$

Solution to exercise 7.4 The weight of a configuration $(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$ of N particles can be expressed in terms of the $f_{ij}=f(\boldsymbol{r}_i-\boldsymbol{r}_j)$ as

$$P(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)=\frac{1}{\Omega_N}\,\mathrm{e}^{-\beta U(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)}=\frac{1}{\Omega_N}\prod_{(k\ell)}\mathrm{e}^{-\beta u(\boldsymbol{r}_k-\boldsymbol{r}_\ell)}=\frac{1}{\Omega_N}\prod_{(k\ell)}\left(1+f_{k\ell}\right). \tag{7.22}$$

Thus the weight of all configurations in which one particle is at x and another is at x' is given by

$$\begin{aligned}
\rho^{(2)}(x,x') &= \sum_{ij}\int \mathrm{d}r_1\cdots\mathrm{d}r_N\,\delta(r_i-x)\delta(r_j-x')P(r_1,\ldots,r_N)\\
&= \frac{N(N-1)}{\Omega_N}\int \mathrm{d}r_1\cdots\mathrm{d}r_N\,\delta(r_1-x)\delta(r_2-x')\prod_{k\ell}(1+f_{k\ell}) \qquad (7.23)\\
&= \frac{N(N-1)}{\Omega_N}\int \mathrm{d}r_1\cdots\mathrm{d}r_N\,\delta(r_1-x)\delta(r_2-x')[1+f(x-x')]\prod_{(k\ell)}{}'(1+f_{k\ell}),
\end{aligned}$$

where the sum runs over all pairs (i,j) different from $(1,2)$. Now we have

$$\int \mathrm{d}r_3\cdots\mathrm{d}r_N \prod_{(k,\ell)\in\{3,\ldots,N\}}(1+f_{k\ell}) = \Omega_{N-2} \simeq \Omega_N V^{-2}. \qquad (7.24)$$

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

$$\rho^{(2)}(x,x') = \rho^2 g\left(|x-x'|\right) = \rho^2\left(1+f\left(|x-x'|\right)\right). \qquad (7.25)$$

Solution to exercise 7.5 (Joule-Thomson process)

1. The system exchanges energy with the environment only via the work $\delta W = \sum_{i=1,2} p_i\,\mathrm{d}V_i$. Thus we have $\mathrm{d}E = \mathrm{d}(E_1+E_2) = -\delta W = -\sum_{i=1,2} p_i\,\mathrm{d}V_i$. On the other hand, since the p_i's are constant, one has $\mathrm{d}H_i = \mathrm{d}E_i + p_i\,\mathrm{d}V_i$, and the result follows.

2. Since $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p$, we have

$$\mathrm{d}H = T\left.\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left[V + T\left.\frac{\partial S}{\partial p}\right)_T\right]\mathrm{d}p. \qquad (7.26)$$

   On the other hand, $C_p = T\,\partial S/\partial T)_p$, while, by Maxwell's relations, we have

$$\left.\frac{\partial S}{\partial p}\right)_T = -\left.\frac{\partial V}{\partial T}\right)_p. \qquad (7.27)$$

   Thus, when $\mathrm{d}H = 0$, we have

$$\left.\frac{\partial T}{\partial p}\right)_H = \frac{T\,\partial V/\partial T)_p - V}{C_p}. \qquad (7.28)$$

3. Therefore, the condition defining T^* is the following:

$$\frac{T}{V}\left.\frac{\partial V}{\partial T}\right)_p = -\frac{T}{\rho}\left.\frac{\partial \rho}{\partial T}\right)_p = 1, \tag{7.29}$$

where $\rho = N/V$. By differentiating both sides of the equation

$$p = \rho k_{\mathrm{B}} T \left(1 + \rho B_2(T)\right), \tag{7.30}$$

at constant pressure, we obtain

$$\frac{T}{\rho}\left.\frac{\partial \rho}{\partial T}\right)_p = -\frac{1 + \rho B_2(T) + \rho T B_2'(T)}{1 + 2\rho B_2(T)}. \tag{7.31}$$

Thus by simple algebra one obtains the equation for T^*:

$$T^* B_2'(T^*) = B_2(T^*). \tag{7.32}$$

4. Let us write the van der Waals equation in terms of ρ in the following form:

$$\left(p + \rho^2 a\right)(1 - \rho b)\,\frac{1}{\rho} = k_{\mathrm{B}} T. \tag{7.33}$$

Taking the logarithmic derivative of this equation with respect to T at constant pressure, we obtain

$$\frac{T}{\rho}\left.\frac{\partial \rho}{\partial T}\right)_p \left[\frac{2\rho a}{p + \rho^2 a} - \frac{b}{1 - \rho b} - 1\right] = 1. \tag{7.34}$$

Thus equation (7.29) reads, for a van der Waals gas,

$$\frac{2\rho a}{p + \rho^2 a} = \frac{b}{1 - \rho b}, \tag{7.35}$$

that, by substituting the van der Waals equation, leads to

$$\frac{k_{\mathrm{B}} T^*}{(1 - \rho b)^2} = \frac{2a}{b}. \tag{7.36}$$

Expressing ρ as a function of T^* via this equation, and substituting in the van der Waals equation of state, we obtain the pressure as a function of the inversion temperature T^*:

$$p = \frac{2}{b}\sqrt{\frac{2a k_{\mathrm{B}} T^*}{b}} - \frac{3}{2}\frac{k_{\mathrm{B}} T^*}{b} - \frac{a}{b^2}. \tag{7.37}$$

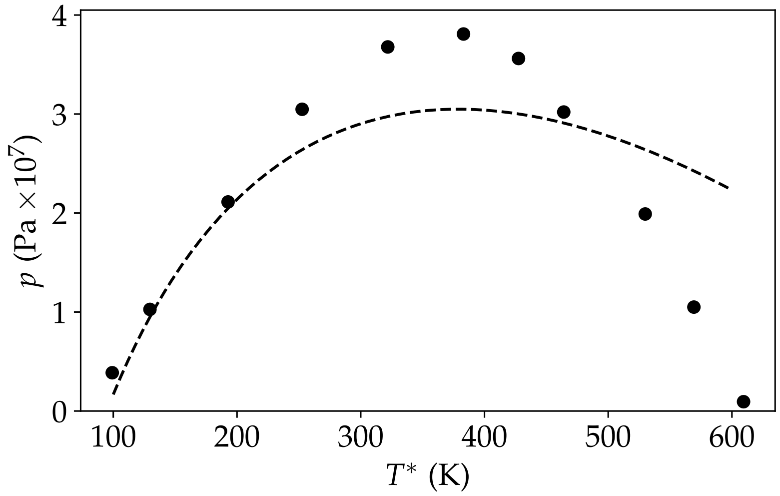

Figure 7.1: Pressure vs. inversion temperature T^* for N_2. Points: data [Zemansky, 1957, p. 282]. Dashed line: Prediction of (7.37) with the van der Waals parameters $a = 137.0\,\mathrm{J\,m^6/mol}$, $b = 0.0387\,\mathrm{m^3/mol}$ (*Wikipedia*).

Solution to exercise 7.6 Denoting by $\nu_i(\boldsymbol{r})$ the local density of ions of species i at $\boldsymbol{r}$, the electric potential ϕ satisfies Poisson's equation

$$\nabla^2\phi = -\frac{1}{\epsilon_\mathrm{r}\epsilon_0}\sum_i e z_i \nu_i(\boldsymbol{r}). \tag{7.38}$$

On the other hand, by the Boltzmann distribution, we expect

$$\nu_i(\boldsymbol{r}) = \nu_i^0 \mathrm{e}^{-ez_i\phi(r)/k_\mathrm{B}T} \simeq \nu_i^0\left(1 - \frac{ez_i\phi(\boldsymbol{r})}{k_\mathrm{B}T}\right). \tag{7.39}$$

Thus we have

$$\nabla^2\phi = \frac{1}{\epsilon_\mathrm{r}\epsilon_0}\sum_i e^2\nu_i^0 z_i^2\phi(\boldsymbol{r}) - \frac{1}{\epsilon_\mathrm{r}\epsilon_0}\sum_i e z_i \nu_i^0\phi(\boldsymbol{r}). \tag{7.40}$$

The last term vanishes because of the neutrality condition. We obtain therefore the equation

$$\nabla^2\phi = \frac{\phi}{\ell_\mathrm{D}^2}, \tag{7.41}$$

where the Debye length ℓ_D is given by

$$\ell_\mathrm{D} = \left(\frac{\sum_i e^2\nu_i^0 z_i^2}{\epsilon_\mathrm{r}\epsilon_0}\right)^{-1/2}. \tag{7.42}$$

CHAPTER 8

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

$$E = \sum_{i=1}^{N} \frac{1}{2} m v_i^2 + \frac{1}{2} M V^2 + p_0 L. \tag{8.1}$$

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 $(x_1, v_1, \ldots, x_N, v_N, L, V)$ at time t_0, where of course $-L \leq x_i \leq +L$, $\forall i$. The motion of the i-th particle satisfies

$$x_i(t) = x_i + v_i(t - t_0), \tag{8.2}$$

and that of the piston satisfies

$$L(t) = L + V(t - t_0) - \frac{1}{2} \frac{p_0}{M} (t - t_0)^2. \tag{8.3}$$

Thus the waiting time τ_i^* till the impact of the particle on the piston is given by

$$\tau_i^* = \frac{M}{p_0} \left(V - v + \sqrt{(V - v)^2 - 2p_0(r - L)/M} \right), \tag{8.4}$$

if $v > 0$, or by

$$\tau_i^* = \frac{M}{p_0}\left(-V - v + \sqrt{(V+v)^2 + 2p(r+L)/M}\right), \tag{8.5}$$

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

$$W = \frac{\pm 2mv + (M-m)V_0}{m+M}; \tag{8.6}$$

$$w = \frac{\pm 2MV_0 + (m-M)v}{m+M}. \tag{8.7}$$

Here one should take upper signs when $v > 0$ and lower ones when $v < 0$.

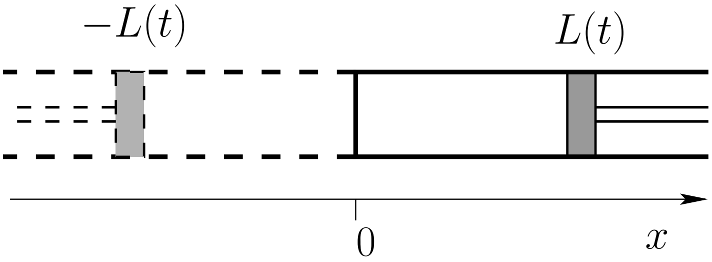

Figure 8.1: The “negative copy” of the piston which simplifies the treatment of collisions with the back wall of the cylinder.

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

$$E = \sum_{i=1}^{N} \frac{1}{2} m v_i^2 + \frac{1}{2} M V^2 + p_0 L. \tag{8.8}$$

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:

$$\langle L \rangle = \frac{N k_\mathrm{B} T}{p_0}. \tag{8.9}$$

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.

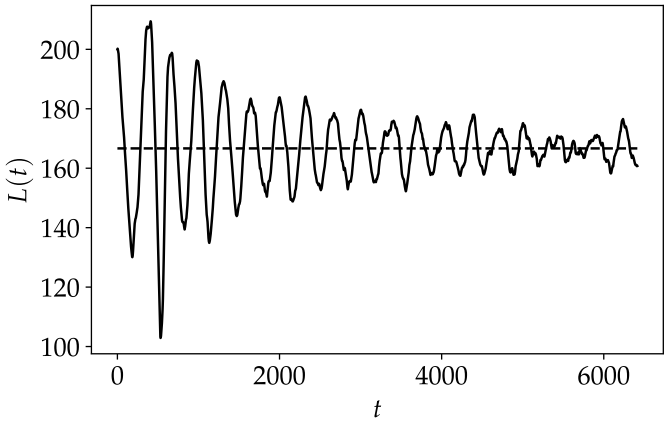

Figure 8.2: Piston position $L(t)$ as a function of time for a simulations with $N = 1000$ particles, with $p = 10$ and a mass ratio $M/m = 100$ with $k_\mathrm{B} T_0 = 1$. The initial position is $L_0 = 2Nk_\mathrm{B}T_0/p$. The dashed line corresponds to the equlibrium position $2H/3p$, where $H = 3Nk_\mathrm{B}T_0/2 + pL_0$ 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
```

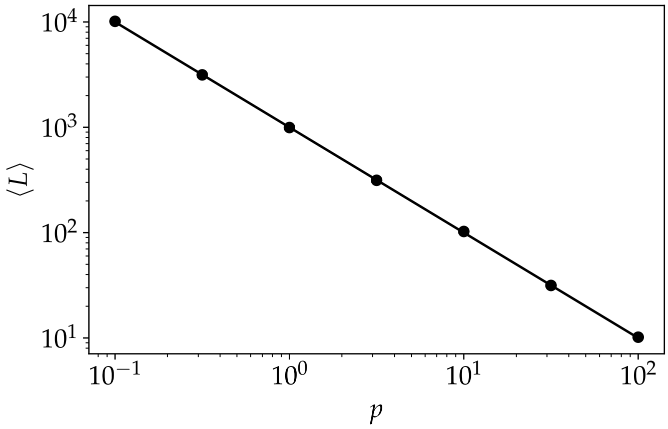

Figure 8.3: Log-log plot of the equation of state obtained from the simulation of the model with $N = 1000$ particles, for $M/m = 100$ and $k_B T = 1$. The line corresponds to the ideal-gas law.

```
def collision(v, V, M):
    """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 piston position: x0 times the equilibrium pos.
    V = np.random.randn()*np.sqrt(T0/M) # Initial piston velocity
    x0 = np.zeros((N, 2))
    x0[:, 0] = np.random.uniform(low=-L, high=L, size=N) # x: Uniform distr.
    if mode == 'delta':
        x0[:, 1] = np.random.choice([-sqT0, sqT0], size=N) # v = +-sqrt(T0)
    else:
        x0[:, 1] = np.random.randn(N)*sqT0  # Gaussian distribution
    return L, V, x0
```

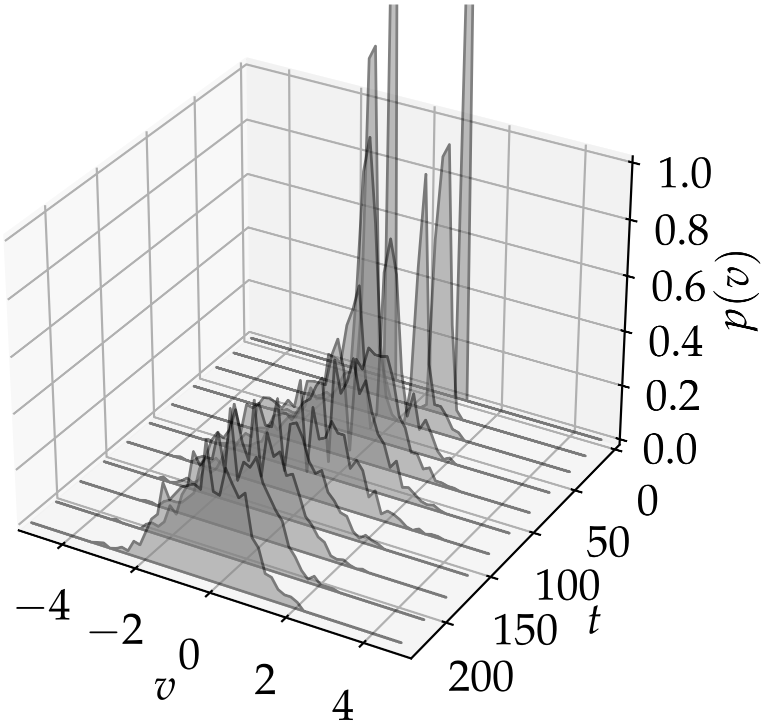

Figure 8.4: Approach of the velocity distribution to the Maxwell form, starting from an initial distribution allowing for only two (opposite) values of v. Parameters: $N = 1000$, $M/m = 100$, $p = 100$, $k_{\mathrm{B}}T = 1$.

```
def iterate(N, T0, p, x0, M, itermax, interval = 100, mode='gaussian'):
    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)
        # 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 $\frac{1}{2}M\left\langle V^2\right\rangle = \frac{1}{2}k_\mathrm{B}T$, 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

$$\frac{3N+1}{2}k_\mathrm{B}T = H. \tag{8.10}$$

   Indeed, each particle contributes $k_\mathrm{B}T/2$ to E and $k_\mathrm{B}T$ 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 $\theta_i = \theta(i\,h)$. Then one has

$$\theta_{i+1} = 2\theta_i - \theta_{i-1} - h^2 \sin\theta_i. \tag{8.11}$$

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

$$\theta_1 = \theta_0 + hv_0 - \frac{h^2}{2}\sin\theta_0. \tag{8.12}$$

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

$$v_{i-1} = \frac{1}{2h}\left(\theta_i - \theta_{i-2}\right), \tag{8.13}$$

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 $E = 1 - \cos\theta + \frac{1}{2}\dot\theta^2$.

To evaluate the period $\mathcal{T}$, we identify the time coordinates in which the pendulum crosses the line $\theta = 0$, first with a negative velocity v, then with a positive velocity. The semiperiod $\mathcal{T}/2$ is then given by the difference of these two times. We set $\theta_0 = \pi - 10^k$, for $k = 0, 1, \ldots, 7$. We then plot $\mathcal{T}/2$ vs. k, and compare it with the asymptotic form $\mathcal{T}/2 = 2\ln(4/\cos(\theta_0/2))$ suggested by Cromer [1995].

This algorithm is implemented in the following Python program.

```
import numpy as np
import matplotlib.pyplot as plt

def verlet(tmax, theta0, v0, h):
        """Solution of the ODE via the Verlet algorithm"""
    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])
```

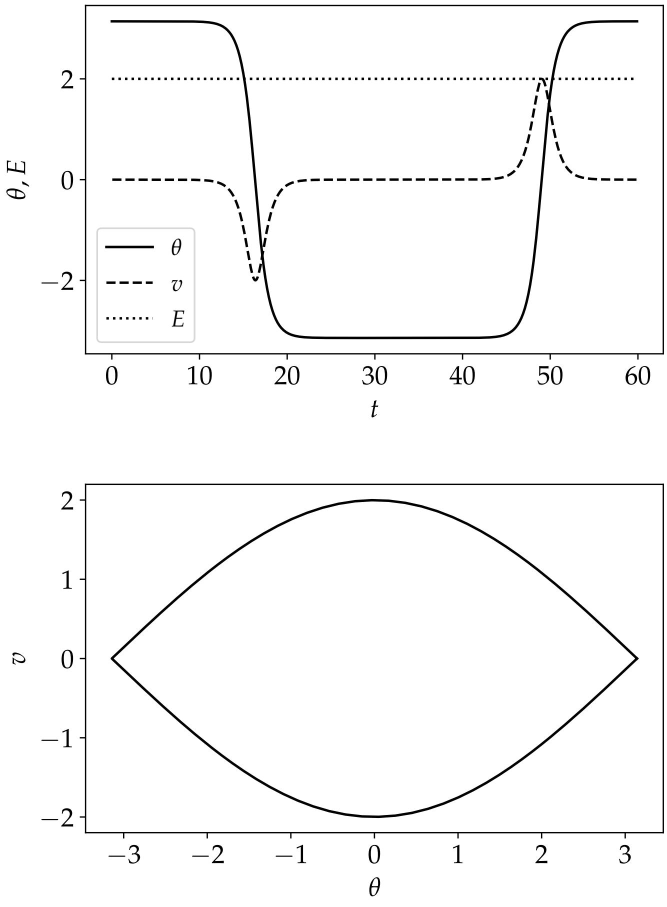

Figure 8.5: Solution of the pendulum equation of motion via the Verlet algorithm. Above: $\theta(t)$, $v(t) = \mathrm{d}\theta/\mathrm{d}t$ and the corresponding evolution of $E(t)$. Below: trajectory in the (θ, v) plane, showing the periodicity of the motion. The figure corresponds to one level curve of $E(\theta, v)$.

```
    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))]
    return t, theta

def velocity(t, theta):
        """Evaluation of the velocity from the trajectory"""
    N = len(t)
    v = np.zeros(N)
    h = t[1] - t[0]
```

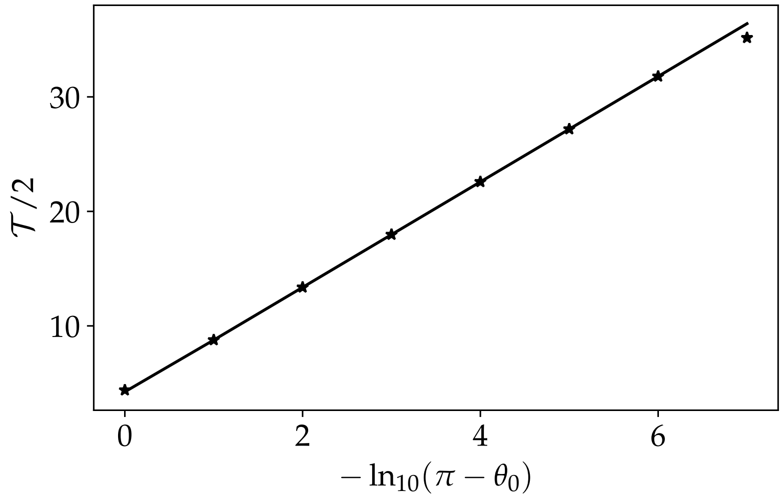

Figure 8.6: Semiperiod $\mathcal{T}/2$ vs. $-\ln_{10}(\pi-\theta_0)$, obtained by the Verlet algorithm, compared with Cromer's asymptotic behavior $\mathcal{T}/2 \simeq 2\ln(4/\cos(\theta_0/2))$.

```
    v[0] = (theta[1]-theta[0])/h
    for i in range(2,N):
        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))]
    return tv, v

def find_zero(t, theta):
        """Identifying the times where theta=0"""
    t0 = []
    for k in range(1, len(theta)):
        if ((theta[k-1] > theta[k] and theta[k-1]*theta[k] < 0) or
            (theta[k-1] < theta[k] and theta[k-1]*theta[k] < 0)):
            # Linear interpolation to find the zero of theta
                t0.append((np.abs(theta[k])*t[k-1]+np.abs(theta[k-1])*t[k])
                          /(np.abs(theta[k-1])+np.abs(theta[k])))
    return t0

def cromer(theta0):
        """Asymptotic behavior of the semiperiod"""
    return 2*np.log(4/np.cos(theta0/2))

theta0 = 3.14
v0 = 0.0
h = 0.1
```

```
tmax = 60

t, theta = verlet(tmax, theta0, v0, h)
tv, v = velocity(t, theta)

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.plot('pendulum.pdf')


plt.plot(theta[:-1],v[:-1], 'k-')
plt.xlabel(r'$\theta$')
plt.ylabel('$v$')
plt.plot('phaseGraph.pdf')


theta0 = [np.pi - 10**(-k) for k in range(0, 8)]
tmax = 480
h = 0.05
dt = []
for th0 in theta0:
    t, theta = verlet(tmax, th0, h)
    t0 = find_zero(t, theta)
    dt.append((t0[1]-t0[0]))

plt.plot(dt, 'k*')
plt.plot(cromer(np.array(theta0)), 'k-')
plt.xlabel(r'$-\ln_{10}(\pi-\theta_0)$')
plt.ylabel(r'$\mathcal{T}/2$')
plt.savefig('semiperiod.pdf')
```

The results are shown in figures 8.5 and 8.6.

Solution to exercise 8.3

1. The dimensional equations of motion read

$$\frac{\mathrm{d}^2 r_i}{\mathrm{d}t^2} = \frac{1}{m}\left[u'(r_{i+1}-r_i) - u'(r_i - r_{i-1})\right], \tag{8.14}$$

   where $u(r)$ is the two-particle interaction potential. Defining

$$x_i = \frac{r_i}{r_0}, \qquad \tau = \sqrt{\frac{mr_0^2}{\epsilon_0}}, \quad t_1 = \frac{t}{\tau}, \tag{8.15}$$

   we obtain

$$\frac{\mathrm{d}^2 x_i}{\mathrm{d}t_1^2} = \left[f(x_{i+1}-x_i) - f(x_i - x_{i-1})\right], \tag{8.16}$$

   where

$$f(x) = \frac{6}{x}\left(\frac{2}{x^{12}} - \frac{1}{x^6}\right). \tag{8.17}$$

2. See the program that follows.
3. We have

$$T = \frac{\epsilon_0}{k_\mathrm{B}}\left\langle \left(\frac{\mathrm{d}x_i}{\mathrm{d}\tau}\right)^2 \right\rangle, \qquad p = \frac{1}{L}\left(k_\mathrm{B}T + \epsilon_0\left\langle (x_{i+1}-x_i)\, f(x_{i+1}-x_i)\right\rangle\right). \tag{8.18}$$

4. We have

$$r_0 = 1.0 \cdot 10^{-10}\,\mathrm{m}; \qquad \epsilon_0 \approx 1.6 \cdot 10^{-19}\,\mathrm{J}; \qquad m = 1.0 \cdot 10^{-26}\,\mathrm{kg}. \tag{8.19}$$

   This yields $\tau \approx 2.5 \cdot 10^{-14}$ s. Running 10000 steps on a system with 100 units with $\mathrm{d}t_1 = 10^{-2}$ 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('energyLJ.pdf')

plt.plot(t, pressure, 'k-')
plt.xlabel('$t$')
plt.ylabel('$p$')
plt.plot('pressureLJ.pdf')

plt.plot(t, temp, 'k-')
plt.xlabel('$t$')
plt.ylabel('$T$')
plt.plot('temperatureLJ.pdf')
```

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

$$p_b = \frac{W_{ba_{n-1}} \cdots W_{a_1 a_0}}{W_{a_{n-1}b} \cdots W_{a_0 a_1}} p_{a_0}. \tag{8.20}$$

According to $\mathcal{C}'$ we can assign it the probability

$$p'_b = \frac{W_{ba'_{m-1}} \cdots W_{a'_1 a_0}}{W_{a'_{m-1}b} \cdots W_{a_0 a'_1}} p_{a_0}. \tag{8.21}$$

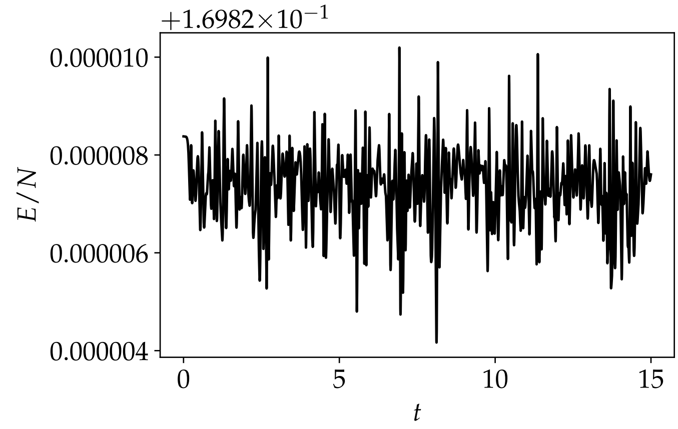

Figure 8.7: Check of energy conservation in the velocity Verlet algorithm for the 1D Lennard-Jones fluid. One sees that the total energy is conserved to the 6-th significant digit. The energy is measured in units of ϵ_0.

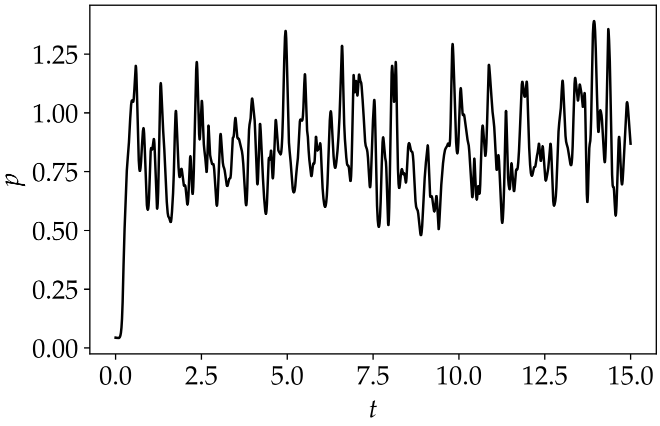

Figure 8.8: Pressure (in units ϵ_0/r_0) in the velocity Verlet algorithm for the 1D Lennard-Jones fluid.

The ratio between these two probabilities is given by

$$\frac{p_b}{p'_b} = \frac{W_{a_0 a'_1} W_{a'_1 a'_2} \cdots W_{a'_{m-1} b} W_{b a_{n-1}} W_{a_{n-1} a_{n-2}} \cdots W_{a_1 a_0}}{W_{a_0 a_1} W_{a_1 a_2} \cdots W_{a_{n-1} b} W_{b a'_{m-1}} W_{a'_{m-1} a'_{m-1}} \cdots W_{a'_1 a_0}}. \tag{8.22}$$

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

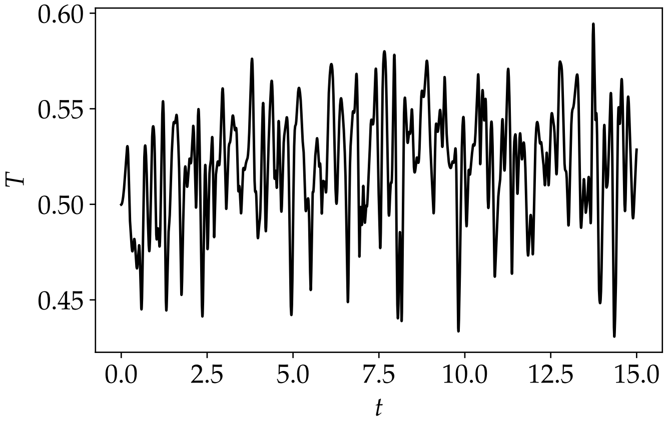

Figure 8.9: Observed temperature $T = m \left\langle v^2 \right\rangle$ (in units $\epsilon_0/k_{\mathrm{B}}$) in the velocity Verlet algorithm for the 1D Lennard-Jones fluid.

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 $\sigma \longrightarrow \sigma'$ is equal to $\frac{1}{4}$ and the probability that $\sigma' \longrightarrow \sigma$ 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 "demon") 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 $E'_{\mathrm{D}} = E_D - (H(\sigma') - H(\sigma))$ 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

$$Z = \sum_{\sigma} \sum_{E_\mathrm{D} \in [0, \Delta E]} \delta \left[H(\sigma) + E_\mathrm{D} - E \right]. \tag{8.23}$$

By standard statistical mechanics arguments, the demon's energy will be exponentially distributed, $p(E_\mathrm{D}) \propto \mathrm{e}^{-E_\mathrm{D}/k_\mathrm{B}T}$. 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 $\langle E_\mathrm{D} \rangle$. For the case of an Ising model, in which energy values are of the form $4nJ$, where n is an integer, we have

$$\frac{1}{k_\mathrm{B}T} = \frac{1}{4J} \ln \left(1 + \frac{4J}{\langle E_\mathrm{D} \rangle} \right). \tag{8.24}$$

For a continuous system where the energy can take any positive value, this simplifies to

$$k_\mathrm{B}T = \langle E_\mathrm{D} \rangle. \tag{8.25}$$

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

$$\langle E \rangle_{\beta + \mathrm{d}\beta} = \frac{1}{Z'} \sum_{i=1}^{\mathcal{N}\mathcal{N}} H(\sigma_i)\, \mathrm{e}^{-\mathrm{d}\beta H(\sigma_i)}, \tag{8.26}$$

where

$$Z' = \sum_{i=1}^{\mathcal{N}\mathcal{N}} H(\sigma_i)\, \mathrm{e}^{-\mathrm{d}\beta H(\sigma_i)}, \tag{8.27}$$

and the configurations σ_i are evaluated with a weight proportional to $\mathrm{e}^{-\beta H(\sigma_i)}$ by the Metropolis algorithm. We then have

$$\frac{C}{k_\mathrm{B}} \simeq -\beta^2 \frac{\langle E \rangle_{\beta + \mathrm{d}\beta} - \langle E \rangle_{\beta}}{\mathrm{d}\beta}. \tag{8.28}$$

```
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]:
```

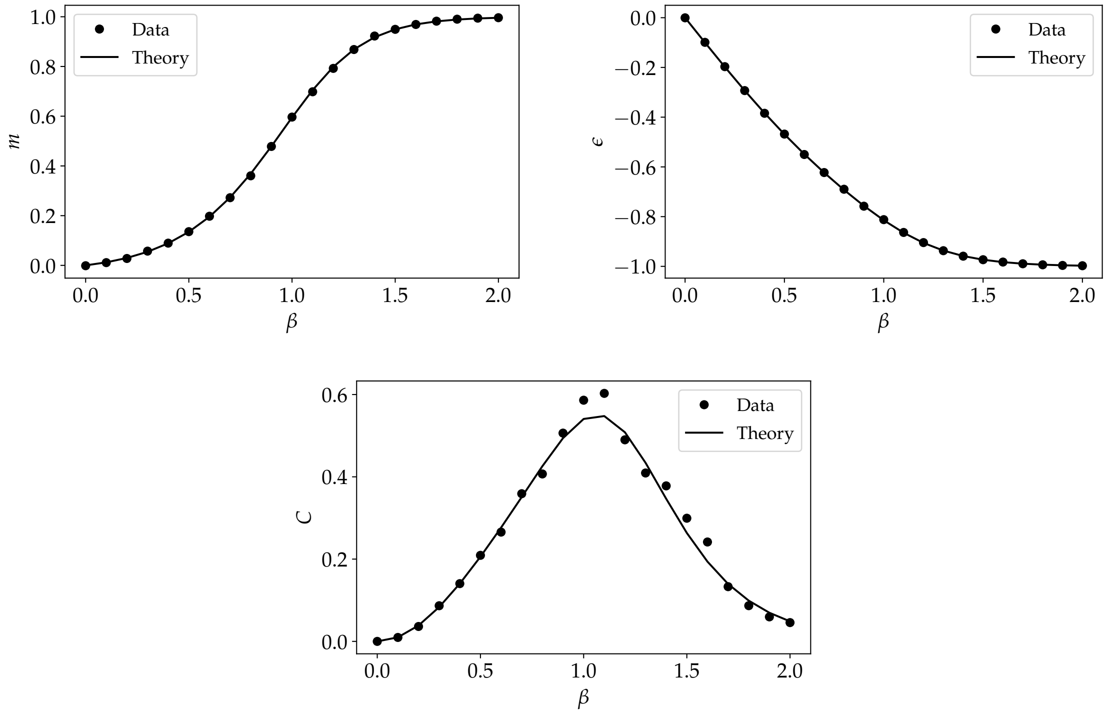

Figure 8.10: Simulation of the 1D Ising model. Above: Left: Magnetization per spin $\langle\sigma_i\rangle$. Right: Internal energy per spin $-\langle\sigma_i\sigma_{i+1}\rangle$. The theoretical values are also plotted. Bottom: Specific heat. Number of spins $N = 1000$, applied field $h = 0.1$. Units are such that $k_B = 1$. Notice that the sampling errors are larger for the specific heat than for the magnetization and internal energy.

```
        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)

    W = weight(w, u)

    mtot = 0
    etot = 0
    ntot = 0
    ztot = 0
    e1tot = 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
            e1tot += (ek/n)*dw

    magn = mtot/ntot
    en = etot/ntot
    en1 = e1tot/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 (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

$$\langle E \rangle_\beta = \frac{1}{\mathcal{N}} \sum_{i=1}^{\mathcal{N}} E_i, \tag{8.29}$$

and

$$\langle E \rangle_{\beta+\mathrm{d}\beta} = \frac{1}{Z} \sum_{i=1}^{\mathcal{N}} E_i \, \mathrm{e}^{-\mathrm{d}\beta\, E_i}, \tag{8.30}$$

where

$$Z = \sum_{i=1}^{\mathcal{N}} \mathrm{e}^{-\mathrm{d}\beta\, E_i}. \tag{8.31}$$

The specific heat is then obtained by

$$C = \frac{1}{N k_\mathrm{B}} \frac{\beta^2}{\mathrm{d}\beta} \left(\langle E \rangle_{\beta+\mathrm{d}\beta} - \langle E \rangle_\beta \right). \tag{8.32}$$

We can also check the relation

$$\frac{1}{\mathrm{d}\beta} \left(\langle E \rangle_{\beta+\mathrm{d}\beta} - \langle E \rangle_\beta \right) = \left\langle E^2 \right\rangle_\beta - \langle E \rangle_\beta^2. \tag{8.33}$$

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 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

    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
    # Specific heat from differentiation:
    spec_heat = beta**2*((energy - energy1))/dbeta

    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)
plt.savefig('spec1D_Umbrella.pdf')

# 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'$\left<\Delta E^2\right>$')
plt.savefig('fluct_diss.pdf')
```

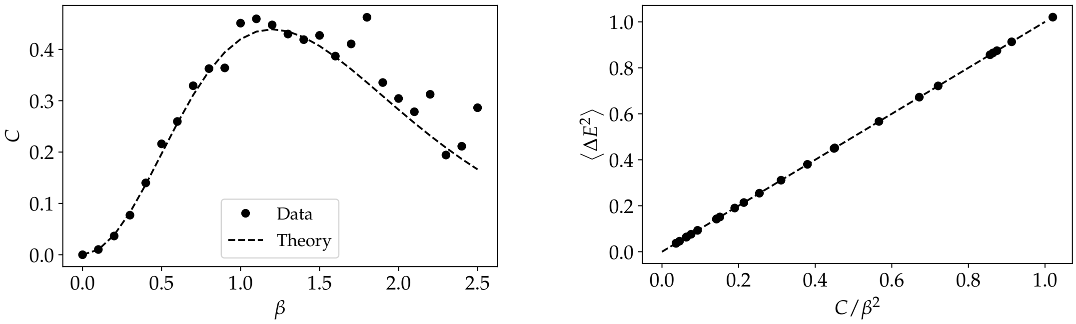

Figure 8.11: Left: Specific heat of the 1D Ising model, obtained by umbrella sampling, vs. the theoretical prediction. Right: Comparison of the energy fluctuations obtained in the Monte Carlo sampling with the specific heat obtained by the umbrella sampling. The dashed line corresponds to $y = x$.

Solution to exercise 8.9 (Widom insertion method)

1. The chemical potential μ is given by

$$\mu = F(N+1, V, T) - F(N, V, T) = -k_\mathrm{B} T \ln \frac{Z_{N+1}}{Z_N}, \tag{8.34}$$

where $F(N, V, T)$ is the Helmholtz free energy and Z_N the partition function of the system. In the simple case of spherical particles, we can express the activity $z = \mathrm{e}^{\mu/k_\mathrm{B}T}$ by

$$z = (N+1)\lambda_\mathrm{B}^3 \frac{\Omega_N}{\Omega_{N+1}}, \tag{8.35}$$

where λ_B is the de Broglie thermal wavelength, and Ω_N is the configuration integral of the system of N particles.

---

2. In evaluating Ω_{N+1} we can split the potential energy of the system into $U\left(\boldsymbol{r}^N\right)$, due to the N particles, and the contribution $W\left(\boldsymbol{r}_{N+1}, \boldsymbol{r}^N\right)$ of the $(N+1)$-th one:

$$\begin{aligned} \Omega_{N+1} &= \int \mathrm{d}\boldsymbol{r}^N \int \mathrm{d}\boldsymbol{r}_{N+1}\ \exp\left[-\left(U\left(\boldsymbol{r}^N\right)+W\left(\boldsymbol{r}_{N+1},\boldsymbol{r}^N\right)\right)/k_\mathrm{B}T\right] \\ &= \Omega_N \int \mathrm{d}\boldsymbol{r}_{N+1}\ \left\langle \exp\left[-W\left(\boldsymbol{r}_{N+1},\boldsymbol{r}^N\right)/k_\mathrm{B}T\right]\right\rangle_N, \end{aligned} \tag{8.36}$$

where $\langle\ldots\rangle_N$ is the canonical average over the N-particle system:

$$\langle A(\boldsymbol{r})\rangle_N = \frac{1}{\Omega_N}\int \mathrm{d}\boldsymbol{r}^N\ A\left(\boldsymbol{r}^N\right)\ \exp\left[-U\left(\boldsymbol{r}^N\right)/k_\mathrm{B}T\right]. \tag{8.37}$$

We can evaluate the integral appearing in the last line of eq. (8.36) by inserting a "ghost particle" at random positions $\boldsymbol{r}_{N+1}$ in the volume occupied by the system, evaluating its interaction energy $W\left(\boldsymbol{r}_{N+1},\boldsymbol{r}^N\right)$ with the remaining N particles, and averaging over the position of the particle and those of the other N ones:

$$\begin{aligned} \Psi &= \frac{1}{V}\int \mathrm{d}\boldsymbol{r}_{N+1}\ \left\langle \exp\left[-W\left(\boldsymbol{r}_{N+1},\boldsymbol{r}^N\right)/k_\mathrm{B}T\right]\right\rangle_N \\ &\simeq \overline{\exp\left[-W\left(\boldsymbol{r}_{N+1},\boldsymbol{r}^N\right)/k_\mathrm{B}T\right]}. \end{aligned} \tag{8.38}$$

Here the overline represents the mean of $\mathrm{e}^{-W/k_\mathrm{B}T}$ over a number of trials, where the position of the particle is chosen at random within the container, and the positions of the particles in background are sampled either by molecular dynamics or by Monte-Carlo. The particle is a "ghost" in the sense that it does not modify the dynamics of the remaining particles in any way. We thus obtain

$$z = \frac{(N+1)\lambda_\mathrm{B}^3}{V}\frac{1}{\Psi}, \tag{8.39}$$

that yields

$$\mu = \mu^{(0)} - k_\mathrm{B}T\ln\Psi, \tag{8.40}$$

where $\mu^{(0)} = k_\mathrm{B}T\ln\left(\rho\lambda_\mathrm{B}^3\right)$ is the chemical potential of the ideal gas in the given conditions.

In the simple case of hard spheres, the Boltzmann factor $\mathrm{e}^{-W/k_\mathrm{B}T}$ is either 0, if the ghost particle overlaps with one or more of the fluid particles, or 1, if it doesn't. Then Ψ is given by the success rate of the ghost particle insertion. This success rate becomes small very fast as the system density increases. Thus the method becomes less efficient at higher densities.

CHAPTER 9

Dynamics

Solution to exercise 9.1 We have

$$\frac{\mathrm{d}}{\mathrm{d}t}\Delta R^2(t) = \int \mathrm{d}^d\boldsymbol{r}\, r^2 \frac{\partial}{\partial t} P(\boldsymbol{r},t \mid 0,0) = \int \mathrm{d}^d\boldsymbol{r}\, r^2\, D\nabla^2 P(\boldsymbol{r},t \mid 0,0). \tag{9.1}$$

We integrate twice by parts. The boundary terms vanish because $P(\boldsymbol{r},t \mid 0,0)$ vanishes at infinity. On the other hand we have

$$\nabla^2 r^2 = \sum_{i=1}^{d} \frac{\partial^2}{\partial x_i^2}\left(\sum_{j=1}^{2} x_j^2\right) = 2d. \tag{9.2}$$

Thus we obtain

$$\frac{\mathrm{d}\Delta R^2}{\mathrm{d}t} = 2dD. \tag{9.3}$$

Solution to exercise 9.2 (Kappler's experiment)

1. The hamiltonian of the mirror is given by

$$\mathcal{H}(\varphi, p_\varphi) = \frac{p_\varphi^2}{2I} + \frac{1}{2}\kappa\varphi^2, \tag{9.4}$$

where $p_\varphi = I\,\dot{\varphi}$ is the momentum conjugate to φ. Thus the Klein-Kramers equation for the system reads, by analogy with that of a particle,

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \varphi}\left(-\frac{p_\varphi}{I}P\right) + \frac{\partial}{\partial p_\varphi}\left\{\left[\kappa\varphi + \mu\frac{p_\varphi}{I}\right]P\right\} + \Gamma\frac{\partial^2 P}{\partial p_\varphi^2}, \tag{9.5}$$

where Γ is defined by the noise correlation:

$$\left\langle \eta(t)\eta(t')\right\rangle = 2\Gamma\,\delta(t-t'). \tag{9.6}$$

2. The Boltzmann distribution for the system is given by

$$P^{\mathrm{eq}} \propto \mathrm{e}^{-\mathcal{H}(\varphi,p_\varphi)/k_{\mathrm{B}}T} = \exp\left(-\frac{p_\varphi^2}{2Ik_{\mathrm{B}}T} - \frac{1}{2}\kappa\varphi^2\right). \tag{9.7}$$

Substituting in the Klein-Kramers equation, we obtain

$$\frac{\partial P^{\mathrm{eq}}}{\partial t} = -\frac{\mu}{I^2k_{\mathrm{B}}T}p_\varphi^2\,P^{\mathrm{eq}} + \frac{\mu}{I}\,P^{\mathrm{eq}} + \Gamma\left(-\frac{1}{I\,k_{\mathrm{B}}T} + \frac{p_\varphi^2}{(I\,k_{\mathrm{B}}T)^2}\right)P^{\mathrm{eq}}. \tag{9.8}$$

Imposing that the derivative vanishes, we obtain Einstein's relation in the form

$$\Gamma = \mu\,k_{\mathrm{B}}T. \tag{9.9}$$

3. The Langevin equation for the angular displacement $\varphi(t)$ reads

$$\frac{\mathrm{d}^2\varphi}{\mathrm{d}t^2} = -\frac{\kappa}{I}\varphi - \frac{\mu}{I}\frac{\mathrm{d}\varphi}{\mathrm{d}t} + \frac{1}{I}f(t). \tag{9.10}$$

From this we obtain the differential equation for $C(t)$, for positive values of t:

$$\frac{\mathrm{d}^2C}{\mathrm{d}t^2} = -\frac{\kappa}{I},C - \frac{\mu}{I}\frac{\mathrm{d}C}{\mathrm{d}t}, \tag{9.11}$$

since the noise for $t > 0$ is uncorrelated with that at $t = 0$.

4. Assuming $C(t) = \alpha\,\mathrm{e}^{-\lambda_+t} + \beta\mathrm{e}^{-\lambda_-t}$, and substituting in the equation, we obtain that $\lambda_\pm$ are the two solutions of the equation

$$\lambda^2 = -\frac{\kappa}{I} + \frac{\mu}{I}\lambda. \tag{9.12}$$

The discriminant of this equation is given by

$$\Delta = \frac{1}{I}\sqrt{\mu^2 - 4I\kappa}. \tag{9.13}$$

When $\Delta > 0$, both values of λ are real. Otherwise, they are imaginary. In the second regime, which obtains for small values of λ, the correlation function exhibits damped oscillations. In the first one, it exhibits at most one sign change before relaxing to zero. The value of μ separating the two regimes is $\mu_{\mathrm{c}} = 2\sqrt{I\kappa}$. For this value of μ, the correlation function behaves like $(\alpha + \beta t)\,\mathrm{e}^{-\lambda t}$, where λ is the sole solution of eq. (9.12), and α and β are constants.

Solution to exercise 9.3 Since we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\Delta R^2(t) = 6D, \tag{9.14}$$

and, on the other hand,

$$\int_0^\infty \mathrm{d}t' \, \langle \boldsymbol{v}(t') \cdot \boldsymbol{v}(0) \rangle = \left\langle v^2 \right\rangle \int_0^\infty \mathrm{d}t' \, \mathrm{e}^{-t'/\tau} = \left\langle v^2 \right\rangle \tau, \tag{9.15}$$

we obtain

$$D = \frac{1}{3}\left\langle v^2 \right\rangle \tau. \tag{9.16}$$

From equipartition we obtain

$$\left\langle v^2 \right\rangle = \frac{3k_\mathrm{B}T}{m} \tag{9.17}$$

yielding

$$\tau = \frac{mD}{k_\mathrm{B}T}. \tag{9.18}$$

Taking $m = 18\,\mathrm{amu}$ (as for water), $D \simeq 10^{-5}\,\mathrm{cm}^2\mathrm{s}^{-1}$, i.e., $D \simeq 10^{-9}\,\mathrm{m}^2\mathrm{s}^{-2}$, we obtain $\tau \simeq 7 \cdot 10^{-15}\,\mathrm{s}$, at 300 K, i.e., 7 femtoseconds.

Solution to exercise 9.4 Since the energy ϵ_{A^*} is much larger than that of either A or B, we have $k_{\mathrm{AA}^*} \sim k_{\mathrm{BA}^*} \gg k_{\mathrm{A}^*\mathrm{A}} \sim k_{\mathrm{A}^*\mathrm{B}}$. Thus the equation for $[\mathrm{A}^*]$ reaches fast a steady state, depending on the instantaneous values of [A] and [B]:

$$[\mathrm{A}^*] \simeq \frac{k_{\mathrm{A}^*\mathrm{A}}[\mathrm{A}] + k_{\mathrm{A}^*\mathrm{B}}[\mathrm{B}]}{k_{\mathrm{AA}^*} + k_{\mathrm{BA}^*}}. \tag{9.19}$$

Substituting in the rate equations for [A] and [B] we obtain the equations

$$\begin{aligned}
\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} &= -\frac{k_{\mathrm{A}^*\mathrm{A}}k_{\mathrm{BA}^*}}{k_{\mathrm{AA}^*} + k_{\mathrm{BA}^*}}[\mathrm{A}] + \frac{k_{\mathrm{AA}^*}k_{\mathrm{A}^*\mathrm{B}}}{k_{\mathrm{AA}^*} + k_{\mathrm{BA}^*}}[\mathrm{B}], \\
\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} &= \frac{k_{\mathrm{A}^*\mathrm{A}}k_{\mathrm{BA}^*}}{k_{\mathrm{AA}^*} + k_{\mathrm{BA}^*}}[\mathrm{A}] - \frac{k_{\mathrm{AA}^*}k_{\mathrm{A}^*\mathrm{B}}}{k_{\mathrm{AA}^*} + k_{\mathrm{BA}^*}}[\mathrm{B}].
\end{aligned} \tag{9.20}$$

We can check that the equation conserves $[\mathrm{A}] + [\mathrm{B}]$ (this is due to the fact that we are effectively neglecting $[\mathrm{A}^*]$). Thus there is only one decay rate $\lambda > 0$, given by

$$\lambda = \frac{k_{\mathrm{A}^*\mathrm{A}}k_{\mathrm{BA}^*} + k_{\mathrm{AA}^*}k_{\mathrm{A}^*\mathrm{B}}}{k_{\mathrm{AA}^*} + k_{\mathrm{BA}^*}}. \tag{9.21}$$

Assuming $k_{\mathrm{A^*A}} \sim k_{\mathrm{A^*B}}$ much smaller than the rates for the reverse reaction, we obtain as an order of magnitude of the relaxation time τ

$$\tau = \lambda^{-1} \sim k_{\mathrm{A^*A}}^{-1} \sim k_{\mathrm{A^*B}}^{-1}. \tag{9.22}$$

Solution to exercise 9.5 (Brownian motion of a harmonic oscillator)

1. We have

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -\omega_0^2 x - \frac{\gamma}{m}\frac{\mathrm{d}x}{\mathrm{d}t} + \frac{f(t)}{m} + \frac{\eta(t)}{m}, \tag{9.23}$$

where $\eta(t)$ is the thermal noise, that satisfies

$$\langle \eta(t) \rangle = 0, \quad \langle \eta(t)\eta(t') \rangle = 2\gamma k_{\mathrm{B}} T\, \delta(t-t'), \qquad \forall t, t'. \tag{9.24}$$

2. Denoting by $x_0(t)$ the system's trajectory in the absence of the applied force $f(t)$, and by $\delta x(t)$ the difference of the actual trajectory $x(t)$ from $x_0(t)$, we obtain the evolution equation

$$\frac{\mathrm{d}^2 \delta x}{\mathrm{d}t^2} = -\omega_0^2 \delta x - \frac{\gamma}{m}\frac{\mathrm{d}\delta x}{\mathrm{d}t} + \frac{f(t)}{m}, \tag{9.25}$$

We have therefore, assuming $f(t) = \delta(t)$, i.e., a delta-like impulse at $t = 0$,

$$\lim_{t\to 0^+} \delta x(t) = 0, \qquad \lim_{t\to 0^+} \frac{\mathrm{d}\delta x(t)}{\mathrm{d}t} = \frac{1}{m}. \tag{9.26}$$

We have, on the other hand, for $t > 0$,

$$\delta x(t) = \alpha \mathrm{e}^{-\lambda_+ t} + \beta \mathrm{e}^{-\lambda_- t}, \tag{9.27}$$

where α and β are as yet undetermined coefficients and $-\lambda_\pm$ are the two solutions of the equation

$$\lambda^2 + \frac{\gamma}{m}\lambda + \omega_0^2 = 0, \tag{9.28}$$

i.e.,

$$\lambda_\pm = \frac{\gamma}{2m} \pm \frac{1}{2}\sqrt{\frac{\gamma^2}{m^2} - 4\omega_0^2}. \tag{9.29}$$

Imposing the initial conditions, we obtain

$$\alpha = -\beta = -\frac{1}{\sqrt{\gamma^2 - 4m^2\omega_0^2}}. \tag{9.30}$$

Thus we have

$$\chi(t) = \frac{1}{\sqrt{\gamma^2 - 4m^2\omega_0^2}} \left(\mathrm{e}^{-\lambda_- t} - \mathrm{e}^{-\lambda_+ t} \right). \tag{9.31}$$

3. The correlation function $C(t)$ satisfies the same equation for $t > 0$, but its initial conditions are different: one has indeed

$$C(0) = \left\langle x^2 \right\rangle^{\mathrm{eq}} = \frac{k_\mathrm{B}T}{m\omega_0^2}, \qquad \lim_{x\to 0^+} \frac{\mathrm{d}C(t)}{\mathrm{d}t} = 0. \tag{9.32}$$

We thus obtain

$$\alpha = \frac{k_\mathrm{B}T}{m\omega_0^2}\frac{\lambda_-}{\lambda_- - \lambda_+}, \qquad \beta = \frac{k_\mathrm{B}T}{m\omega_0^2}\frac{\lambda_+}{\lambda_+ - \lambda_-}, \tag{9.33}$$

that corresponds to

$$C(t) = \frac{k_\mathrm{B}T}{\omega_0^2\sqrt{\gamma^2 - 4m^2\omega_0^2}}\left(\lambda_+ \mathrm{e}^{-\lambda_- t} - \lambda_- \mathrm{e}^{-\lambda_+ t}\right). \tag{9.34}$$

We also have $C(-t) = C(t)$, by time-reversal symmetry. One can easily chack that the fluctuation-dissipation relation

$$\chi(t) = -\frac{\theta_\mathrm{H}(t)}{k_\mathrm{B}T}\frac{\mathrm{d}C(t)}{\mathrm{d}t}, \tag{9.35}$$

is satisfied. We have here to distinguish three cases:

- $\gamma > 2m\omega_0$. Then both λ_+ and λ_- are real and positive, and $C(t)$ is straightforwardly given by eq. (9.34).
- $\gamma < 2m\omega_0$. Then λ_+ and λ_- are complex conjugate:

  $$\lambda_\pm = \frac{\gamma}{2m} \pm \mathrm{i}\Omega, \tag{9.36}$$

  where

  $$\Omega = \sqrt{\omega_0^2 - (\gamma/2m)^2}. \tag{9.37}$$

  We then have

  $$C(t) = \frac{k_\mathrm{B}T}{m\omega_0^2}\,\mathrm{e}^{-\gamma t/2m}\left(\frac{\gamma}{2m}\frac{\sin\Omega t}{\Omega} + \cos\Omega t\right). \tag{9.38}$$

- $\gamma = 2m\omega_0$. This corresponds to $\lambda_+ = \lambda_- = \gamma/2m$. We then have

  $$C(t) = \frac{k_\mathrm{B}T}{m\omega_0^2}\,\mathrm{e}^{-\gamma t/2m}\left(1 + \frac{\gamma t}{2m}\right). \tag{9.39}$$

4. Performing the integral, taking into account eq. (9.34) and the relation $C(-t) = C(t)$, one obtains

$$\begin{aligned} C(\omega) &= \int_{-\infty}^{+\infty} \mathrm{d}t \; \mathrm{e}^{\mathrm{i}\omega t}\, C(t) \\ &= \frac{k_{\mathrm{B}}T}{\omega_0^2\sqrt{\gamma^2 - 4m^2\omega_0^2}} \left[\lambda_+ \left(\frac{1}{-\mathrm{i}\omega + \lambda_-} + \frac{1}{\mathrm{i}\omega + \lambda_-}\right)\right. \\ &\qquad \left. - \lambda_- \left(\frac{1}{-\mathrm{i}\omega + \lambda_+} + \frac{1}{\mathrm{i}\omega + \lambda_+}\right)\right] \\ &= \frac{k_{\mathrm{B}}T}{\sqrt{\gamma^2 - 4m^2\omega_0^2}} \left(\frac{1}{\lambda_-^2 + \omega^2} - \frac{1}{\lambda_+^2 + \omega^2}\right), \end{aligned} \tag{9.40}$$

where we have taken into account that $\lambda_-\lambda_+ = \omega_0^2$.

On the other hand, by straightforwardly evaluating the Fourier transform of $\chi(t)$, we obtain

$$\chi(\omega) = \int_0^{\infty} \mathrm{d}t \; \mathrm{e}^{\mathrm{i}\omega t}\, \chi(t) = \frac{1}{\sqrt{\gamma^2 - 4m^2\omega_0^2}} \left(\frac{1}{-\mathrm{i}\omega + \lambda_-} - \frac{1}{-\mathrm{i}\omega + \lambda_+}\right). \tag{9.41}$$

This can be shown to imply

$$\chi''(\omega) = \frac{\omega}{k_{\mathrm{B}}T} C(\omega), \tag{9.42}$$

for the three cases considered above, by straightforward but tedious algebra.

Solution to exercise 9.6 The primary variable $x(t)$ drives the bath, and the driven bath affects the primary variable through the force

$$\begin{aligned} f(t) &= f_{\mathrm{b}}(t) + \int_{-\infty}^{\infty} \mathrm{d}t' \; \chi_{\mathrm{b}}(t - t')\, x(t') \\ &= f_{\mathrm{b}}(t) - \beta \int_{-\infty}^{t} \mathrm{d}t' \; \left[\frac{\mathrm{d}}{\mathrm{d}(t - t')} C_{\mathrm{b}}(t - t')\right] x(t') \\ &= f_{\mathrm{b}}(t) + \beta C_{\mathrm{b}}(0)\, x(t) - \beta C_{\mathrm{b}}(0)\, x(t) - \beta \int_0^t \mathrm{d}t' \; C_{\mathrm{b}}(t - t')\, \dot{x}(t'). \end{aligned} \tag{9.43}$$

Now we have

$$\left\langle f_{\mathrm{b}}(t) \right\rangle\big|_{x(0),\dot{x}(0)\ \mathrm{fixed}} = \left\langle f_{\mathrm{b}}(t; x, \dot{x}, \{y, \dot{y}\}) \mathrm{e}^{\beta x f} \right\rangle_{\mathrm{b}} \frac{1}{\left\langle \mathrm{e}^{\beta x f} \right\rangle_{\mathrm{b}}}. \tag{9.44}$$

This equation follows from the fact that the distribution of the initial variables for the bath differs by the factor $\mathrm{e}^{\beta x f}$ 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

$$\begin{aligned}
\langle f_{\mathrm{b}}(t)\rangle|_{x(0),\dot{x}(0)\ \text{fixed}} &= \sum_i c_i \left\langle \left[y_i \cos\omega_i t + \frac{\dot{y}_i}{\omega_i}\sin\omega_i t \right] \mathrm{e}^{\beta x c_i y_i} \right\rangle_{\mathrm{b}} \frac{1}{\left\langle \mathrm{e}^{\beta x f}\right\rangle_{\mathrm{b}}} \\
&= \sum_i c_i \cos\omega_i t \, \frac{\partial}{\partial \beta x c_i} \ln \left\langle \mathrm{e}^{\beta x c_i y_i} \right\rangle_{\mathrm{b}} \\
&= \beta x \sum_i c_i^2 \left\langle y_i^2 \right\rangle_{\mathrm{b}} \cos\omega_i t = \beta x C_{\mathrm{b}}(t),
\end{aligned} \tag{9.45}$$

where the last equality stems from the fact that the y_i's are independent classical oscillators and obey a Gaussian distribution, and since $\langle y_i y_j \rangle_{\mathrm{b}} = \langle y_i^2 \rangle_{\mathrm{b}} \, \delta_{ij}$, yielding

$$\sum_{i,j} c_i c_j \langle y_i y_j \rangle_{\mathrm{b}} \cos\omega_j t = \sum_i c_i^2 \left\langle y_i^2 \right\rangle_{\mathrm{b}} \cos\omega_i t. \tag{9.46}$$

By combining eq. (9.43) and eq. (9.45) with Newton's law and averaging over initial conditions we obtain the generalized Langevin equation.

Chapter 10

Stochastic Thermodynamics

Solution to exercise 10.1 In a transformation ending in the equilibrium state described by p_x^{eq}, the work W performed on the system and the heat Q released to the reservoir satisfy the first law:

$$\langle \epsilon \rangle_p - \langle \epsilon \rangle_{p^{\mathrm{eq}}} = Q - W. \tag{10.1}$$

The total entropy change during the transformation is given by

$$S^{\mathrm{tot}} = \Delta S^{\mathrm{sys}} + S^{\mathrm{res}} = k_{\mathrm{B}} \left(H(p^{\mathrm{eq}}) - H(p) \right) + \frac{Q}{T} \geq 0, \tag{10.2}$$

where $H(p)$ is the Shannon entropy of the distribution p and we have exploited the Gibbs relation. We have therefore

$$\begin{aligned} -W &= \langle \epsilon \rangle_p - \langle \epsilon \rangle_{p^{\mathrm{eq}}} - Q \geq \left[\langle \epsilon \rangle_p - k_{\mathrm{B}} T H(p) \right] - \left[\langle \epsilon \rangle_{p^{\mathrm{eq}}} - k_{\mathrm{B}} T H(p^{\mathrm{eq}}) \right] \\ &= F^{\mathrm{neq}}(p) - F. \end{aligned} \tag{10.3}$$

This difference can be expressed in terms of the Kullback-Leibler divergence between p and p_{eq}:

$$\begin{aligned} D_{\mathrm{KL}}(p \| p^{\mathrm{eq}}) &= \sum_x p_x \ln \frac{p_x}{p_x^{\mathrm{eq}}} \\ &= -\frac{1}{k_{\mathrm{B}} T} \sum_x p_x \left(F - \epsilon_x - \ln p_x \right) = \langle \epsilon \rangle_p - k_{\mathrm{B}} T \, H_{\mathrm{S}}(p) - F. \end{aligned} \tag{10.4}$$

Solution to exercise 10.2 Since p^{st} is stationary, we have

$$\sum_{x'} k_{xx'} p^{\mathrm{st}}_{x'} = \sum_{x'} k_{x'x} p^{\mathrm{st}}_{x}. \tag{10.5}$$

We have therefore

$$\sum_{x,x'} \psi_x k_{xx'} p^{\mathrm{st}}_{x'} = \sum_{x,x'} \psi_x k_{x'x} p^{\mathrm{st}}_{x}. \tag{10.6}$$

Exchange x with x' in the right-hand side, and the result follows.

Solution to exercise 10.3 If the matrix is non-ergodic, the states x fall into several equivalence classes, such that $k_{xx'}$ vanishes if x and x' belong to different classes, and the restriction of the transition matrix within each class is ergodic. Thus the result we obtained only proves that w_x tends to a constant within each class. Therefore the stationary solution approached by the system is of the form

$$p^{\mathrm{st}} = \sum_{\alpha} c_\alpha p^{(\alpha)}, \tag{10.7}$$

where $p^{(\alpha)} = (p^{(\alpha)}_x)$ is the normalized stationary solution within each class α, and the coefficients c_α satisfy

$$0 \le c_\alpha, \quad \forall \alpha; \qquad \sum_{\alpha} c_\alpha = 1. \tag{10.8}$$

Solution to exercise 10.4 We have, with $f(x) = x \ln x$ and $w_x = p_x / p^{\mathrm{eq}}_x$, where p^{eq} is the stationary distribution,

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} D_{\mathrm{KL}}(p(t) \| p^{\mathrm{eq}}) &= \sum_x f'(w_x) \left[\sum_{x'} \left(k_{xx'} p_{x'} - k_{x'x} p_x \right) \right] \\ &= \sum_{xx'} k_{xx'} f'(w_x) \left(p_{x'} - \frac{p^{\mathrm{eq}}_{x'}}{p^{\mathrm{eq}}_x} p_x \right) \\ &= \sum_{xx'} k_{xx'} p^{\mathrm{eq}}_{x'} f'(w_x) \left(w_{x'} - w_x \right). \end{aligned} \tag{10.9}$$

Exchanging x with x' we have

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} D_{\mathrm{KL}}(p(t) \| p^{\mathrm{eq}}) &= \sum_{xx'} k_{x'x} p^{\mathrm{eq}}_{x} f'(w_{x'}) \left(w_x - w_{x'} \right) \\ &= \sum_{xx'} k_{xx'} p^{\mathrm{eq}}_{x'} f'(w_{x'}) \left(w_x - w_{x'} \right), \end{aligned} \tag{10.10}$$

where we have used the detailed-balance condition. Taking the half-sum of these relations, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t} D_{\mathrm{KL}}(p(t)\|p^{\mathrm{eq}}) = \frac{1}{2}\sum_{xx'} k_{xx'} p^{\mathrm{eq}}_{x'} \left(f'(w_x) - f'(w_{x'})\right)(w_{x'} - w_x), \tag{10.11}$$

which is readily seen to be negative, since $f'(x)$ is a monotonically increasing function.

Solution to exercise 10.5 The Jarzinsky average is given by

$$\left\langle \mathrm{e}^{-\mathcal{W}/k_{\mathrm{B}}T} \right\rangle = \int \mathrm{d}\mathcal{W}\; P(\mathcal{W};\boldsymbol{\lambda})\, \mathrm{e}^{-\mathcal{W}/k_{\mathrm{B}}T}, \tag{10.12}$$

where $P(\mathcal{W};\boldsymbol{\lambda})$ is the probability distribution of the fluctuating work $\mathcal{W}$ under the protocol $\boldsymbol{\lambda}$.

By the Crooks relation one has

$$P(-\mathcal{W};\widehat{\boldsymbol{\lambda}}) = P(\mathcal{W};\boldsymbol{\lambda})\mathrm{e}^{(\Delta F-\mathcal{W})/k_{\mathrm{B}}T}, \tag{10.13}$$

where $\widehat{\boldsymbol{\lambda}}$ is the reverse of the protocol $\boldsymbol{\lambda}$. Thus the maximum of the integrand $P(\mathcal{W};\boldsymbol{\lambda})\,\mathrm{e}^{-\mathcal{W}/k_{\mathrm{B}}T}$ corresponds to the opposite of the maximum of $P(-\mathcal{W};\widehat{\boldsymbol{\lambda}})$.

Solution to exercise 10.6 Let x be the state the system is in when the quench takes place. Then the fluctuating work $\mathcal{W}$ is given by

$$\mathcal{W}_x = \epsilon(\lambda_{\mathrm{f}})_x - \epsilon(\lambda_0)_x. \tag{10.14}$$

We have therefore, since the system is at equilibrium with the distribution $p^{\mathrm{eq}}(\lambda_0)$ at that instant,

$$\begin{aligned}\left\langle \mathrm{e}^{-\mathcal{W}/k_{\mathrm{B}}T} \right\rangle &= \sum_x p^{\mathrm{eq}}(\lambda_0)_x\, \mathrm{e}^{-(\epsilon(\lambda_{\mathrm{f}})_x-\epsilon(\lambda_0)_x)/k_{\mathrm{B}}T}\\ &= \sum_x \mathrm{e}^{(F(\lambda_0)-\epsilon(\lambda_0)_x)/kt}\, \mathrm{e}^{-(\epsilon(\lambda_{\mathrm{f}})_x-\epsilon(\lambda_0)_x)/k_{\mathrm{B}}T}\\ &= \sum_x \mathrm{e}^{(F(\lambda_0)-\epsilon(\lambda_{\mathrm{f}})_x)/k_{\mathrm{B}}T} = \mathrm{e}^{-(F(\lambda_{\mathrm{f}})-F(\lambda_0))/k_{\mathrm{B}}T}.\end{aligned} \tag{10.15}$$

Solution to exercise 10.7 This problem can be solved by direct integration. We call S^{tot} the average of $\mathcal{S}^{\mathrm{tot}}$ and σ^2 its variance. The integral fluctuation relation imposes that

$$
\begin{aligned}
1 &= \int_{-\infty}^{\infty} \frac{\mathrm{d}\mathcal{S}^{\mathrm{tot}}}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(\mathcal{S}^{\mathrm{tot}} - S^{\mathrm{tot}})^2}{2\sigma^2}\right] \mathrm{e}^{-s^{\mathrm{tot}}/k_{\mathrm{B}}} \\
&= \exp\left[-\frac{1}{2\sigma^2}\left(S^{\mathrm{tot}2} - \left(S^{\mathrm{tot}} - \frac{\sigma^2}{k_{\mathrm{B}}}\right)^2\right)\right] = \exp\left(-\frac{S^{\mathrm{tot}}}{k_{\mathrm{B}}} + \frac{\sigma^2}{2k_{\mathrm{B}}^2}\right).
\end{aligned}
\tag{10.16}
$$

To satisfy this condition, we require $2S^{\mathrm{tot}} = \sigma^2/k_{\mathrm{B}}$.

Solution to exercise 10.8 (Onsager reciprocal relations) We recall the expression of the entropy production along a trajectory $\boldsymbol{x}$,

$$
\mathcal{S}[\boldsymbol{x}] = \mathcal{T}\sum_{\alpha} \mathcal{A}_\alpha \mathcal{J}_\alpha[\boldsymbol{x}], \tag{10.17}
$$

and the relation,

$$
\mathcal{J}_\alpha[\widehat{\boldsymbol{x}}] = -\mathcal{J}_\alpha[\boldsymbol{x}]. \tag{10.18}
$$

We then have, by the detailed fluctuation relation,

$$
P(\mathcal{J}) = \mathrm{e}^{\mathcal{S}/k_{\mathrm{B}}}\, P(-\mathcal{J}) = \exp\left(\frac{\mathcal{T}}{k_{\mathrm{B}}}\sum_{\alpha}\mathcal{A}_\alpha\mathcal{J}_\alpha\right) P(-\mathcal{J}), \tag{10.19}
$$

where $\mathcal{J} = (\mathcal{J}_\alpha)$. Therefore

$$
\begin{aligned}
\left\langle \exp\left(-\mathcal{T}\sum_{\alpha}\mathcal{A}_\alpha\mathcal{J}_\alpha\right)\right\rangle &= \int\prod_{\alpha}\mathrm{d}\mathcal{J}_\alpha\, \mathrm{e}^{-\mathcal{T}\sum_\alpha q_\alpha\mathcal{J}_\alpha}\, P(-\mathcal{J}) \\
&= \int\prod_{\alpha}\mathrm{d}\mathcal{J}_\alpha\, \mathrm{e}^{\mathcal{T}\sum_\alpha(-q_\alpha+\mathcal{A}_\alpha/k_{\mathrm{B}})\mathcal{J}_\alpha} P(-\mathcal{J}_\alpha) \\
&= \int\prod_{\alpha}\mathrm{d}\mathcal{J}_\alpha\, \mathrm{e}^{-\mathcal{T}\sum_\alpha(q_\alpha-\mathcal{A}_\alpha/k_{\mathrm{B}})\mathcal{J}_\alpha} P(\mathcal{J}_\alpha).
\end{aligned}
\tag{10.20}
$$

Therefore

$$
\psi(-q) = \psi\left(q - \frac{\mathcal{A}}{k_{\mathrm{B}}}\right). \tag{10.21}
$$

From this relation, we obtain

$$
\left.\frac{\partial^2\psi}{\partial q_\alpha\,\partial q_\beta}\right|_{q,\mathcal{A}} = \frac{1}{k_{\mathrm{B}}}\left.\frac{\partial^2\psi}{\partial q_\alpha\,\partial q_\beta}\right|_{-q-\mathcal{A}/k_{\mathrm{B}},\mathcal{A}} - \left.\frac{\partial^2\psi}{\partial q_\alpha\,\partial\mathcal{A}_\beta}\right|_{-q-\mathcal{A}/k_{\mathrm{B}},\mathcal{A}}. \tag{10.22}
$$

Going to the $q \to 0$, $\mathcal{A} \to 0$ limit, we obtain

$$
L_{\alpha\beta} = \frac{1}{2k_{\mathrm{B}}}\left.\frac{\partial^2\psi}{\partial q_\alpha\,\partial q_\beta}\right|_{q=0,\mathcal{A}=0} = L_{\beta\alpha}, \tag{10.23}
$$

that are Onsager's reciprocity relations.

Solution to exercise 10.9 The position of the particle evolves according to the Langevin equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \mu f + \sigma \xi(t), \tag{10.24}$$

where σ is a constant. The force f does not arise from a potential, and therefore the free energy at the end of the process is equal to its initial value. We arbitrarily set the initial position of the particle at $x = 0$. Then the probability distribution x at time $t > t_0$ is a Gaussian of mean $\mu f \Delta t$ (where $\Delta t = t - t_0$) and of variance $\sigma^2 \Delta t$. For each value of x, the work performed on the particle is given by $W(x) = f x$. We then obtain

$$\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle = \frac{1}{Z} \int \mathrm{d}x \ \exp\left[-\frac{f x}{k_\mathrm{B}T} - \frac{(x - \mu f \Delta t)^2}{2\sigma^2 \Delta t} \right], \tag{10.25}$$

where Z is a normalization constant. Completing the square and integrating, we obtain

$$\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle = \exp\left[\left(\mu - \frac{1}{2}\frac{\sigma^2}{k_\mathrm{B}T} \right) \frac{f^2 \Delta t}{k_\mathrm{B}T} \right]. \tag{10.26}$$

Comparing with the Jarzynski equality, we obtain

$$\sigma^2 = 2k_\mathrm{B}T\,\mu. \tag{10.27}$$

The diffusion constant D is equal to $D = \sigma^2/2$. We thus obtain the Einstein relation

$$D = k_\mathrm{B}T\,\mu. \tag{10.28}$$

Solution to exercise 10.10 (Hamiltonian system) Since the system is isolated, one has

$$\mathcal{W} = \mathcal{H}(x_\mathrm{f}(x_0, \boldsymbol{\lambda}); \lambda_\mathrm{f}) - \mathcal{H}(x_0; \lambda_0), \tag{10.29}$$

where $x_0 = x(t_0)$ is the microstate of the system at the beginning of the manipulation, and $x_\mathrm{f}(x_0, \boldsymbol{\lambda})$ its state at time t_f, given its initial state x_0 and the protocol $\boldsymbol{\lambda}$. This quantity can be considered as a function of x_0 when the protocol $\boldsymbol{\lambda}$ is given. We then have

$$\begin{aligned}
\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle &= \int \mathrm{d}x_0 \; P^{\mathrm{eq}}(x_0)\, \mathrm{e}^{-\mathcal{W}(x_0)/k_\mathrm{B}T} \\
&= \int \mathrm{d}x_0 \; \mathrm{e}^{(F(\lambda_0) - \mathcal{H}(x_0;\lambda_0))/k_\mathrm{B}T}\, \mathrm{e}^{-(\mathcal{H}(x_\mathrm{f}(x_0,\boldsymbol{\lambda});\lambda_\mathrm{f}) - \mathcal{H}(x_0;\lambda_0))/k_\mathrm{B}T} \\
&= \int \mathrm{d}x_0 \; \mathrm{e}^{(F(\lambda_0) - (\mathcal{H}(x_\mathrm{f}(x_0,\boldsymbol{\lambda});\lambda_\mathrm{f}))/k_\mathrm{B}T} = \int \mathrm{d}x_\mathrm{f} \; \mathrm{e}^{(F(\lambda_0) - \mathcal{H}(x_\mathrm{f};\lambda_\mathrm{f}))/k_\mathrm{B}T} \\
&= \mathrm{e}^{-(F(\lambda_\mathrm{f}) - F(\lambda_0))/k_\mathrm{B}T},
\end{aligned} \tag{10.30}$$

where we have exploited the fact that $\mathrm{d}x_\mathrm{f} = \mathrm{d}x_0$, due to Liouville's theorem.

Solution to exercise 10.11 From the Crooks relation

$$p(\mathcal{W};\boldsymbol{\lambda}) = \mathrm{e}^{(\mathcal{W}-\Delta F)/k_\mathrm{B}T} p(-\mathcal{W};\widehat{\boldsymbol{\lambda}}), \tag{10.31}$$

we obtain

$$\begin{aligned}\int_{-\infty}^{\Delta F-\zeta} \mathrm{d}\mathcal{W}\; p(\mathcal{W};\boldsymbol{\lambda}) &= \int_{-\infty}^{\Delta F-\zeta} \mathrm{d}\mathcal{W}\; \mathrm{e}^{(\mathcal{W}-\Delta F)/k_\mathrm{B}T} p(-\mathcal{W};\widehat{\boldsymbol{\lambda}}) \\ &\le \mathrm{e}^{-\zeta/k_\mathrm{B}T} \int_{-\infty}^{\Delta F-\zeta} \mathrm{d}\mathcal{W}\; p(\mathcal{W};\widehat{\boldsymbol{\lambda}}) \le \mathrm{e}^{-\zeta/k_\mathrm{B}T}.\end{aligned} \tag{10.32}$$

Solution to exercise 10.12 (Work as a sufficient statistics) The work $\mathcal{W}^\mathrm{movie}$ evaluated from the movie is equal to $\mathcal{W}$ if the process that is being shown is the forward one, and $-\mathcal{W}$ if it is the backward one. The Crooks relation states that

$$\frac{p_\mathrm{F}(\mathcal{W})}{p_\mathrm{B}(-\mathcal{W})} = \mathrm{e}^{(\Delta F-\mathcal{W})/k_\mathrm{B}T}. \tag{10.33}$$

According to the Bayes formula, the likelihood $p_{\mathrm{F}|\mathcal{W}^\mathrm{movie}}$ is given by

$$p_{\mathrm{F}|\mathcal{W}^\mathrm{movie}} = \frac{p_\mathrm{F}(\mathcal{W})}{p(\mathcal{W}^\mathrm{movie})} = \frac{p_\mathrm{F}(\mathcal{W})}{p_\mathrm{F}(\mathcal{W}) + p_\mathrm{B}(-\mathcal{W})}. \tag{10.34}$$

By the Crooks relation, we obtain

$$p_{\mathrm{F}|\mathcal{W}^\mathrm{movie}} = \frac{1}{1+\mathrm{e}^{(\Delta F-\mathcal{W}^\mathrm{movie})/k_\mathrm{B}T}}. \tag{10.35}$$

Solution to exercise 10.13 (Jarzynski Equality close to the thermodynamic limit) We denote by d the number of degrees of freedom per molecule. For examples, $d = 3, 5, 6$ for monoatomic, diatomic or polyatomic gas molecules, respectively. The internal energy at temperature T is given by $E = N d k_\mathrm{B} T/2$ and the free energy $F(V,T)$ is given by

$$F(V,T) = -N k_\mathrm{B} T \left[\ln V + \frac{d}{2}\ln T + \text{const.}\right]. \tag{10.36}$$

For any positive factor ρ, $F(\beta, V)$ satisfies $\rho F(V, T/\rho) = F(\rho^{-d/2} V, T)$. Moreover, during a quasistatic adiabatic transformation, the product $EV^{2/d}$ remains constant.

We denote by ϵ_0 the internal energy at the beginning of the manipulation. The energy at the end of the manipulation is given by $\epsilon_\mathrm{f} = (\alpha + 1)\epsilon_0$, where

$$\alpha = \left(\frac{V_\mathrm{f}}{V_0}\right)^{2/d} - 1. \tag{10.37}$$

The work performed during the manipulation is given by

$$\mathcal{W}(\epsilon_0) = \epsilon_\mathrm{f} - \epsilon_0 = \alpha\,\epsilon_0. \tag{10.38}$$

The random quantity ϵ_0 is distributed according to

$$p(\epsilon_0; T, V_0) = \mathrm{e}^{(F(T,V_0)-\epsilon_0)/k_\mathrm{B}T}\,\Omega(\epsilon_0; V_0), \tag{10.39}$$

where $\Omega(\epsilon; V)$ is the density of states. We now evaluate

$$\begin{aligned}
\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle &= \int \mathrm{d}\epsilon_0\; p(\epsilon_0; T, V_0)\, \mathrm{e}^{-\alpha\,\epsilon_0/k_\mathrm{B}T} \\
&= \int \mathrm{d}\epsilon_0\; \Omega(\epsilon_0; V_0)\, \mathrm{e}^{(F(V_0,T)-\epsilon_0-\alpha\,\epsilon_0)/k_\mathrm{B}T} \\
&= \mathrm{e}^{F(V_0,T)/k_\mathrm{B}T} \int \mathrm{d}\epsilon_0\; \Omega(\epsilon_0; V_0)\, \mathrm{e}^{-(1+\alpha)\,\epsilon_0/k_\mathrm{B}T} \\
&= \mathrm{e}^{F(V_0,T)/k_\mathrm{B}T} \int \mathrm{d}\epsilon_0\; \Omega(\epsilon_0; V_0)\, \mathrm{e}^{-(V_0/V_f)^{2/d}\,\epsilon_0/k_\mathrm{B}T} \\
&= \mathrm{e}^{(F(V_0,T)-(V_0/V_\mathrm{f})^{2/d}F(V_0,T(V_0/V_\mathrm{f})^{-2/d}))/k_\mathrm{B}T}.
\end{aligned} \tag{10.40}$$

Using the scaling relation for $F(V, T)$, with $\rho = (V_0/V_\mathrm{f})^{2/d}$, we obtain the Jarzynski equality. The fluctuations in the initial value of the energy, even if small, are sufficient to entail such large fluctuations in $\mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T}$ to ensure the validity of the Jarzynski equality.

We obtain the work distribution in the case of a monoatomic gas for definiteness. The density of states is given by

$$\Omega(E; V) = \frac{1}{\Gamma_\mathrm{E}(3N/2)} \frac{V^N}{N!} \left(\frac{2\pi m}{h^2}\right)^{3N/2} \mathrm{e}^{(3N/2)-1}, \tag{10.41}$$

where m is the particle mass, h is the Planck constant and $\Gamma_\mathrm{E}(x)$ is the Euler gamma function. The free energy $F(V, T)$ is given by

$$\begin{aligned}
F(V, T) &= -N\,k_\mathrm{B}T \ln \int \mathrm{d}E\; \Omega(E, V)\, \mathrm{e}^{-E/k_\mathrm{B}T} \\
&= -N\,k_\mathrm{B}T \left[\ln\frac{V}{N} + \frac{3}{2}\ln\frac{2\pi m k_\mathrm{B}T}{h^2} + \text{const.}\right].
\end{aligned} \tag{10.42}$$

The density of states is the derivative with respect to E of the phase-space volume $\Phi(E; V)$ bounded by the surface $E = \text{const.}$ Thus $\Phi(E; V)$ depends only on the product $E\,V^{2/3}$.

During a quasistatic transformation, on the one hand the system is able to explore the whole surface $E =$ const. corresponding to the instantaneous value of its energy, and on the other hand the phase-space volume $\Phi(E; V)$, which is an adiabatic invariant, remains constant. Therefore the value $\epsilon(V; \epsilon_0)$ of the energy of a system whose energy equals ϵ_0 when its volume is V_0 is given by

$$\epsilon(V; \epsilon_0) = \left(\frac{V_0}{V}\right)^{2/3} \epsilon_0. \tag{10.43}$$

This implies that the work $\mathcal{W}$ depends only on ϵ_0 and on $\alpha = (V_0/V_\mathrm{f})^{2/3} - 1$:

$$\mathcal{W}(\epsilon_0; \alpha) = \alpha\, \epsilon_0. \tag{10.44}$$

Therefore the distribution of the work is given by

$$\begin{aligned} p(\mathcal{W}; \alpha) &= \int \mathrm{d}\epsilon_0\; p(\epsilon_0; T, V_0)\, \delta(\mathcal{W} - \alpha\, \epsilon_0) \\ &= \int \mathrm{d}\epsilon_0\; \Omega(\epsilon_0; V_0)\, \mathrm{e}^{(F(V_0,T) - \epsilon_0)/k_\mathrm{B}T}\, \delta(\mathcal{W} - \alpha\, \epsilon_0) \\ &= \frac{1}{\mathcal{N}} \left(\frac{\mathcal{W}}{\alpha\, k_\mathrm{B}T}\right)^{(3N/2)-1} \mathrm{e}^{-\mathcal{W}/(\alpha\, k_\mathrm{B}T)}\, \theta(\alpha\, \mathcal{W}). \end{aligned} \tag{10.45}$$

Here $\mathcal{N}$ is a normalization constant and the Heaviside function $\theta(x)$ ensures that $\mathcal{W}$ has the same sign as α. This is a gamma distribution for $|\mathcal{W}|$ with shape parameter $s = 3N/2$ and scale parameter given by $|\alpha|\; k_\mathrm{B}T$. It is shown in fig. 10.1 for $\alpha = (3/4)^{2/3} - 1$ and $N = 3$, corresponding to $V_\mathrm{f}/V_0 = \frac{3}{4}$.

We now evaluate the average of $\mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T}$. For $\alpha > 0$ we obtain

$$\begin{aligned} \left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle &= \int \mathrm{d}\mathcal{W}\; p(\mathcal{W}; \alpha)\, \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \\ &= \frac{1}{\mathcal{N}} \int_0^\infty \mathrm{d}\mathcal{W} \left(\frac{\mathcal{W}}{\alpha\, k_\mathrm{B}T}\right)^{(3N/2)-1} \mathrm{e}^{-(\mathcal{W}/k_\mathrm{B}T)\left(\alpha^{-1}+1\right)} \\ &= (\alpha+1)^{3N/2} \frac{1}{\mathcal{N}} \int_0^\infty \mathrm{d}\mathcal{W} \left(\frac{\mathcal{W}}{\alpha\, k_\mathrm{B}T}\right)^{(3N/2)-1} \mathrm{e}^{-\mathcal{W}/(\alpha\, k_\mathrm{B}T)} \\ &= (\alpha+1)^{3N/2} = \left(\frac{V_\mathrm{f}}{V_0}\right)^N = \mathrm{e}^{-(F(V_\mathrm{f},T) - F(V_0,T))/k_\mathrm{B}T}. \end{aligned} \tag{10.46}$$

For $\alpha < 0$ we have

$$\begin{aligned} \left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle &= \frac{1}{\mathcal{N}} \int_{-\infty}^0 \mathrm{d}\mathcal{W} \left(\frac{\mathcal{W}}{\alpha\, k_\mathrm{B}T}\right)^{(3N/2)-1} \mathrm{e}^{-(\mathcal{W}/k_\mathrm{B}T)(\alpha^{-1}+1)} \\ &= \frac{1}{\mathcal{N}} \int_0^{+\infty} \mathrm{d}\,|\mathcal{W}| \left(\frac{|\mathcal{W}|}{|\alpha|\; k_\mathrm{B}T}\right)^{(3N/2)-1} \mathrm{e}^{-(|\mathcal{W}|/k_\mathrm{B}T)(-|\alpha|^{-1}+1)} \\ &= (\alpha+1)^{3N/2} = \left(\frac{V_\mathrm{f}}{V_0}\right)^N = \mathrm{e}^{-(F(V_\mathrm{f},T) - F(V_0,T))/k_\mathrm{B}T}. \end{aligned} \tag{10.47}$$

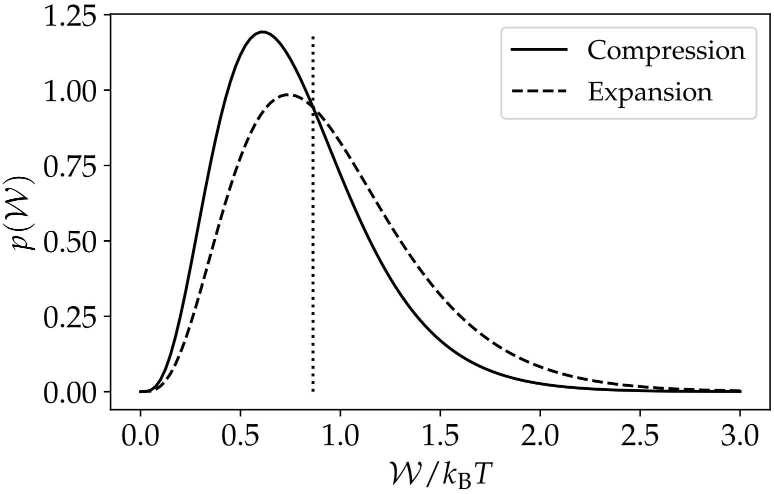

Figure 10.1: Work distribution (continuous line) for $V_\mathrm{f}/V_0 = \frac{3}{4}$ and $N = 3$. Work is measured in units of $k_\mathrm{B}T$. Also shown the distribution for $V_\mathrm{f}/V_0 = 4/3$ (dashed line), corresponding to the reverse transformation. The two distributions cross for $\mathcal{W} = \Delta F = 3k_\mathrm{B}T\ln(4/3)$, denoted by the dotted line.

These results can also be directly obtained by the detailed relation

$$\frac{p(\mathcal{W};\alpha)}{p(-\mathcal{W},-\alpha/(\alpha+1))} = \mathrm{e}^{(\Delta F-\mathcal{W})/k_\mathrm{B}T}, \tag{10.48}$$

which corresponds to the ratio of the distributions for a transformation and its reverse. The result is easily generalized to diatomic and polyatomic gases. If we approximate the initial distribution by a Gaussian, we obtain the result only for $|\alpha| \ll 1$. The contribution of the tail of the distribution is essential in the general case.

Solution to exercise 10.14 In the Widom insertion method, the chemical potential μ is given by

$$\mu = \mu^{(0)} - k_\mathrm{B}T\,\ln\Psi, \tag{10.49}$$

where $\mu^{(0)} = k_\mathrm{B}T\,\ln(\rho\lambda_\mathrm{B}^3)$ is the chemical potential of the ideal gas in the given conditions, and Ψ is given in terms of the interaction energy $W(\boldsymbol{r}_{N+1},\boldsymbol{r}^N)$ of a "ghost" particle inserted at $\boldsymbol{r}_{N+1}$ in the presence of N particles placed at $\boldsymbol{r}^N = (\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$, by

$$\Psi = \frac{1}{V}\int \mathrm{d}\boldsymbol{r}_{N+1}\,\left\langle \exp\left[-W(\boldsymbol{r}_{N+1},\boldsymbol{r}^N)/k_\mathrm{B}T\right]\right\rangle_N, \tag{10.50}$$

where the average is taken with respect to the canonical distribution of the N particles. This can be considered as a quench in which the system suddenly acquires an extra particle placed at a random position with probability density $1/V$. Therefore the expression on the right-hand side of this equation is equal to $\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T}\rangle$, where the random work $\mathcal{W}$ is given by $W(\boldsymbol{r}_{N+1}, \boldsymbol{r}^N)$. By the Jarzynski equality we have

$$\left\langle \mathrm{e}^{-\mathcal{W}/k_\mathrm{B}T} \right\rangle = \mathrm{e}^{-(F_{N+1}-F_N)/k_\mathrm{B}T}, \tag{10.51}$$

where F_{N+1} is the free energy of the system with $N+1$ particles, with the ghost particle motionless in the random position $\boldsymbol{r}_{N+1}$. Taking into account the contribution of its kinetic energy we obtain the result.

Solution to exercise 10.15 From the stationarity condition

$$\sum_x k_{x'x}(t)p_x^{\mathrm{st}}(t) = \sum_x k_{xx'}(t)p_{x'}^{\mathrm{st}}(t), \qquad \forall x', \tag{10.52}$$

we obtain

$$\sum_x k^+_{xx'}(t) = \sum_x k_{x'x}(t)\frac{p_x^{\mathrm{st}}(t)}{p_{x'}^{\mathrm{st}}(t)} = \sum_x k_{xx'}(t). \tag{10.53}$$

Therefore the probability outflow of the conjugate master equation is equal to that of the original master equation. This implies that in evaluating the ratios of the probability trajectory $\mathcal{P}[\boldsymbol{x};\boldsymbol{\lambda}]$ with either $\mathcal{P}^+[\boldsymbol{x};\boldsymbol{\lambda}]$ or $\mathcal{P}^+[\widehat{\boldsymbol{x}};\widehat{\boldsymbol{\lambda}}]$ the contributions of the dwells cancel out between numerator and denominator. As a consequence the contributions only come from the jumps.

One then has

$$\Delta\mathcal{S}^{\mathrm{a}}[\boldsymbol{x};\boldsymbol{\lambda}] = k_\mathrm{B}\sum_{k=1}^n \ln\frac{k_{x_kx_{k-1}}(t_k)}{k^+_{x_kx_{k-1}}(t_k)} = k_\mathrm{B}\sum_{k=1}^n \ln\frac{k_{x_kx_{k-1}}(t_k)p^{\mathrm{st}}_{x_{k-1}}(t_k)}{k^+_{x_{k-1}x_k}(t_k)p^{\mathrm{st}}_{x_k}(t_k)}. \tag{10.54}$$

One similarly has

$$\begin{aligned}\Delta\mathcal{S}^{\mathrm{naa}}[\boldsymbol{x};\boldsymbol{\lambda}] &= k_\mathrm{B}\sum_{k=1}^n \ln\frac{k_{x_kx_{k-1}}(t_k)}{k^+_{x_{k-1}x_k}(t_k)} + k_\mathrm{B}\ln\frac{p_{x_0}(t_0)}{p_{x_\mathrm{f}}(t_\mathrm{f})}\\ &= k_\mathrm{B}\sum_{k=1}^n \ln\frac{p^{\mathrm{st}}_{x_k}(t_k)}{p^{\mathrm{st}}_{x_{k-1}}(t_k)} + k_\mathrm{B}\ln\frac{p_{x_0}(t_0)}{p_{x_\mathrm{f}}(t_\mathrm{f})},\end{aligned} \tag{10.55}$$

where the last term comes from the initial conditions (they cancel out in the expression for $\Delta\mathcal{S}^{\mathrm{a}}$).

Solution to exercise 10.16 (Landauer bound) Consider the distribution for $t = t_\mathrm{f}$ for the forward process that has been described and the reverse process that starts from the equilibrium distribution. We have $p(x, t_\mathrm{f}; \boldsymbol{\lambda}) \approx \delta^\mathrm{K}_{x,+1}$, while $p(x, t_\mathrm{f}; \hat{\boldsymbol{\lambda}}) \approx \left(\delta^\mathrm{K}_{x,+1} + \delta^\mathrm{K}_{x,-1}\right)/2$. Therefore

$$D_\mathrm{KL}\left(p(x, t_\mathrm{f}; \boldsymbol{\lambda}) \| p(x, t_\mathrm{f}; \hat{\boldsymbol{\lambda}})\right) \approx \ln 2, \tag{10.56}$$

and, since $\Delta F = 0$ for the process, the Landauer bound follows.

A numerical solution of the model can be obtained by the following Python code. The result is shown in fig. 10.2.

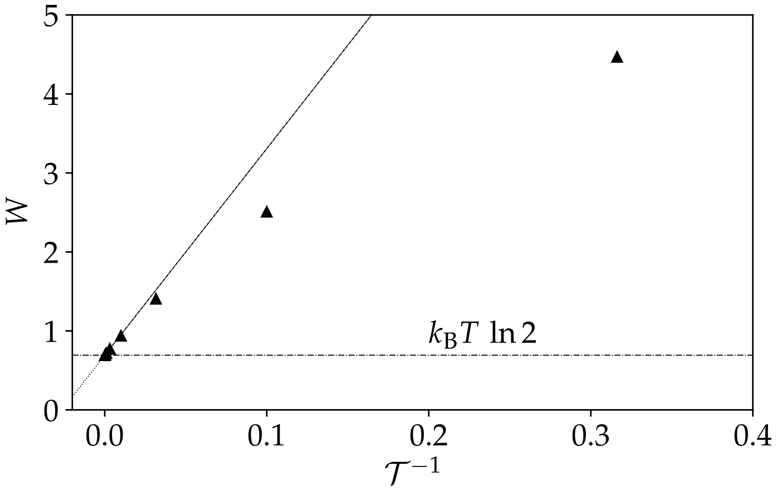

Figure 10.2: Dissipated work W for the three-state memory in the erasure protocol. The manipulation duration $\mathcal{T}$ is measured in units of the inverse $k_{\pm1,0}$ jump rate, and the initial energy ϵ_0 is set to 10 in units of $k_\mathrm{B}T$. The tilted line is a fit to $y = a + b/x$. The horizontal line corresponds to the Landauer bound.

```python
import numpy as np
import matplotlib.pyplot as plt
from scipy import integrate, optimize

def linear(t, e0, e1, t0, t1):
    """Linear function going from e0 at t0 to e1 at t1"""
    return e0+(e1-e0)*(t-t0)/(t1-t0)

def eps(t, tmax, e0):
```

```
    """Manipulation protocol"""
    energy = np.zeros(3)
    energy[1] = e0    # State 0
    t0 = tmax/4
    if t < t0:
        energy[1] = linear(t, e0, 0, 0, t0)
    elif t0 <= t and t < 2*t0:
        energy[1] = linear(t, 0, -e0/2, t0, 2*t0)
        energy[2] = linear(t, 0, -e0, t0, 2*t0)   # State +1
    elif 2*t0 <= t and t < 3*t0:
        energy[1] = linear(t, -e0/2, e0, 2*t0, 3*t0)
        energy[2] = -e0
    else:
        energy[1] = e0
        energy[2] = linear(t, -e0, 0, 3*t0, tmax)
    return energy

def endot(t, tmax, e0):
    """Time derivative of the state energies"""
    edot = np.zeros(3)
    t0 = tmax/4
    if t < t0:
        edot[1] = -e0/t0
    elif t0 <= t and t < 2*t0:
        edot[1] = -(e0/2)/t0
        edot[2] = -e0/t0
    elif 2*t0 <= t and t < 3*t0:
        edot[1] = (3*e0/2)/t0
        edot[2] = 0.
    else:
        edot[1] = 0.
        edot[2] = e0/t0
    return edot

def master(p, t, tmax, e0):
    """Definition of the master equation

    The jumps 0->+1 and 0->-1 take place with unit frequency."""
    en = eps(t, tmax, e0)
    pdot = np.zeros(3)
    pdot[0] = p[1] - np.exp(-en[1])*p[0]       # State -1
    pdot[1] = np.exp(-en[1])*p[0]+np.exp(en[2]-en[1])*p[2]-2.0*p[1]   # State 0
    pdot[2] = p[1] - np.exp(en[2]-en[1])*p[2] # State +1
    return pdot
```

```
def wdiss(tmax, e0, npoints):
    """Evaluating the dissipated work"""
    tspan = np.linspace(0, tmax, npoints)
    q0 = np.exp(-e0)
    p0 = np.array([1., q0, 1.])/(2+q0)    # Initial condition
    y = integrate.odeint(master, p0, tspan, args=(tmax, e0))
    W = 0.
    for k in range(len(tspan)-1):
        ed0 = endot(tspan[k], tmax, e0)
        ed1 = endot(tspan[k+1], tmax, e0)
        # Evaluating the integral by the trapezoid rule
        W += sum( [0.5*(y[k, ell]*ed0[ell]+y[k+1,ell]*ed1[ell])*(tmax/(npoints-1))
                for ell in range(3)])
    return W

def inv(x, a, b):
    return b+a/x

tau = np.logspace(0.5, 4, 8)
npoints = 50001
e0 = 10.
W = np.zeros_like(tau)
for k in range(len(tau)):
    W[k] = wdiss(tau[k], e0, npoints)
popt, pcov = optimize.curve_fit(inv, tau[4:], W[4:])

plt.plot(1/tau, W, 'k^', ms=5)
plt.plot(1/tau, inv(tau, popt[0], popt[1]), 'k--', lw=0.5)
plt.plot((-0.02, 0.4), (popt[1]-0.02*popt[0], popt[1]+0.4*popt[0]), 'k:', lw=0.5)
plt.plot((-0.02, 0.4), np.log(2)*np.ones(2), 'k-.', lw=0.5)
plt.xlim((-0.02, 0.4))
plt.ylim((0, 5))
plt.annotate('$k_\mathrm{B}T\,\ln 2$', (0.2, 0.85))
plt.xlabel('$\mathcal{T}^{-1}$')
plt.ylabel('$W^\mathrm{diss}$')
```

To interpret the reverse process, assume that the states ± 1 have initially the same energy, and that by a measurement one finds that $x = +1$. We can then apply the reverse protocol to extract energy from the reservoir. With this protocol, at the end of the manipulation, the distribution $p_x(t_\mathrm{f}) \approx \left(\delta^\mathrm{K}_{x,-1} + \delta^\mathrm{K}_{x,+1}\right)/2$. Therefore the initial and final conditions of the process are the exact reverse of those in the erasure protocol, and the work W is the opposite of that in the erasure protocol. We can thus obtain for the reverse protocol (since $\Delta F = 0$)

$$W \geq -k_{\mathrm{B}} \ln 2. \tag{10.57}$$

The following code analyzes this setting. It should be considered as a continuation of the code of the previous exercise.

```
def eps1(t, tmax, e0):
        """Reverse protocol"""
    return eps(tmax-t, tmax, e0)

def endot1(t,tmax, e0):
    return -endot(tmax-t, tmax, e0)

def master1(p, t, tmax, e0):
    """Definition of the master equation for the reverse process"""
    en = eps1(t, tmax, e0)
    pdot = np.zeros(3)
    pdot[0] = p[1] - np.exp(-en[1])*p[0]
    pdot[1] = np.exp(-en[1])*p[0]+np.exp(en[2]-en[1])*p[2]-2.0*p[1]
    pdot[2] = p[1] - np.exp(en[2]-en[1])*p[2]
    return pdot

def wdiss1(tmax, e0, npoints):
    """Evaluating the dissipated work for the reverse process"""
    tspan = np.linspace(0, tmax, npoints)
    q0 = np.exp(-e0)
    p0 = [0., 0., 1.]    # Initial condition: x=+1
    y = integrate.odeint(master1, p0, tspan, args=(tmax, e0))
    W = 0.
    for k in range(len(tspan)-1):
        ed0 = endot1(tspan[k], tmax, e0)
        ed1 = endot1(tspan[k+1], tmax, e0)
        W += sum( [ 0.5*(y[k, ell]*ed0[ell]+y[k+1,ell]*ed1[ell])
                *(tmax/(npoints-1)) for ell in range(3)])
    return W

tau = np.logspace(1, 4.5, 8)
npoints = 50001
W = np.zeros_like(tau)
for k in range(len(tau)):
    W[k] = wdiss1(tau[k], e0, npoints)
popt, pcov = optimize.curve_fit(inv, tau, W)
```

```
plt.plot(1/tau, W, 'k^', ms=5)
plt.plot((-0.02, 0.4), (popt[1]-0.02*popt[0], popt[1]+0.4*popt[0]), 'k:', lw=0.5)
plt.plot((-0.02, 0.4), -np.log(2)*np.ones(2), 'k-.', lw=0.5)
plt.xlim(-0.02,0.2)
plt.ylim((-1, 2))
plt.annotate('$-k_\mathrm{B}T\,\ln 2$', (0.1, -0.6))
plt.xlabel('$\mathcal{T}^{-1}$')
plt.ylabel('$W$')
```

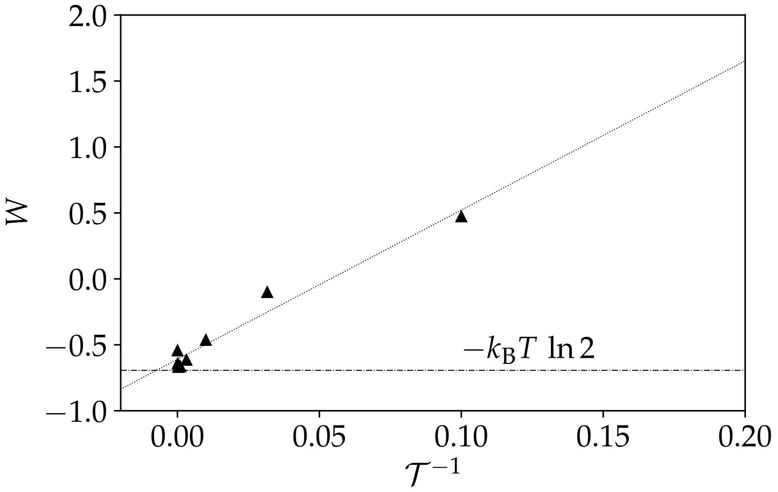

Figure 10.3: Work performed on the three-state model in the Szilard setting, assuming $p_x(t_0) = \delta^{\mathrm{K}}_{x,+1}$, and with the same parameters as in the previous exercise. The bound $W \geq -k_\mathrm{B}T\ln 2$ is shown. The tilted line is a fit to $y = a + b/x$.

Solution to exercise 10.17 Denote by $p_{d,u}$ the probabilities of being in state d or u, respectively, immediately before the interaction, and by $p_{y|x}$ the probability that the measurement yields result y if the system is in state x, that by hypothesis is given by

$$p_{y|x} = (1-r)\delta_{xy} + r(1-\delta_{xy}). \tag{10.58}$$

The steady-state distribution is then given by

$$p_u^{\mathrm{st}} = \frac{k^{\uparrow} + \tilde{k}^{\uparrow}}{k+\gamma}, \qquad p_d^{\mathrm{st}} = \frac{k^{\downarrow} + \tilde{k}^{\downarrow}}{k+\gamma}, \tag{10.59}$$

where

$$k = k^{\uparrow} + k^{\downarrow}, \qquad \gamma = \tilde{k}^{\uparrow} + \tilde{k}^{\downarrow}. \tag{10.60}$$

The measurement-mediated transition takes place when the measurement yields 1, what happens with probability

$$p_1 = (1-r)p_u^{\mathrm{st}} + r p_d^{\mathrm{st}}. \tag{10.61}$$

If it takes place, the average work per transition is given by

$$\langle \mathcal{W} \rangle = \epsilon \left(r p_d^{\mathrm{st}} - (1-r) p_u^{\mathrm{st}} \right) = -\epsilon_0 \left(p_u^{\mathrm{st}} - r \right). \tag{10.62}$$

Thus the average work released to the reservoir per unit time is given by

$$\dot{W} = -\gamma \epsilon \left(p_u^{\mathrm{st}} - r \right), \tag{10.63}$$

which is equal to $T\,\dot{S}^{\mathrm{res}}$, where $\dot{S}^{\mathrm{res}}$ is the total entropy increase in the reservoir per unit time. To this we have to add the contribution of the entropy change due to the measurement. The mutual information between the system and the measuring device for a single interaction is given on average by

$$\begin{aligned} I &= \sum_{x,y} p_{x,y} \ln \frac{p_{x,y}}{p_x p_y} = \sum_{x,y} p_{x,y} \ln p_{y|x} - \sum_y p_y \ln p_y \\ &= H_{\mathrm{S}}(\mathrm{dev}) - \langle H_{\mathrm{S}}(\mathrm{dev}|\mathrm{sys}) \rangle . \end{aligned} \tag{10.64}$$

This is the average decrease in information due to the measurement, that takes place with rate γ. Thus the condition $\dot{S}^{\mathrm{tot}} \geq 0$ boils down to the Sagawa-Ueda relation

$$\dot{W} + \gamma\, k_{\mathrm{B}} T\, I \geq 0, \tag{10.65}$$

where I is given by eq. (10.64).

Solution to exercise 10.18 (System interacting with two tapes) The relative probability of a 0 ⟶ 1 jump is given by

$$p = \frac{\gamma_{\mathrm{I}} r_{\mathrm{I}} + \gamma_{\mathrm{II}} r_{\mathrm{II}}}{\gamma_{\mathrm{I}} + \gamma_{\mathrm{II}}}. \tag{10.66}$$

The entropy production rate is given by

$$\dot{S} = \gamma_{\mathrm{I}} \left(H_{\mathrm{S}}(p_\tau) - H_{\mathrm{S}}(r_{\mathrm{I}}) \right) + \gamma_{\mathrm{II}} \left(H_{\mathrm{S}}(p_\tau) - H_{\mathrm{S}}(r_{\mathrm{II}}) \right). \tag{10.67}$$

Assuming $r_{\mathrm{I}} < r_{\mathrm{II}}$, information is erased from tape II and written on tape I. We can define the erasing efficiency by

$$\eta_I = -\frac{\dot{S}^{\mathrm{eras}}}{\dot{S}^{\mathrm{write}}} = -\frac{\gamma_{\mathrm{II}} \left(H_{\mathrm{S}}(p_\tau) - H_{\mathrm{S}}(r_{\mathrm{II}}) \right)}{\gamma_{\mathrm{I}} \left(H_{\mathrm{S}}(p_\tau) - H(r_{\mathrm{I}}) \right)} \leq 1. \tag{10.68}$$

We obtain

$$\begin{aligned}\lim_{\gamma_{\mathrm{II}}/\gamma_{\mathrm{I}}\to\infty}\eta_I &= \frac{H_{\mathrm{S}}(r_{\mathrm{II}}) - H_{\mathrm{S}}(r_{\mathrm{I}}) - D_{\mathrm{KL}}(r_{\mathrm{I}}\|r_{\mathrm{II}})}{H_{\mathrm{S}}(r_{\mathrm{II}}) - H_{\mathrm{S}}(r_{\mathrm{I}})};\\ \lim_{\gamma_{\mathrm{II}}/\gamma_{\mathrm{I}}\to 0}\eta_I &= \frac{H_{\mathrm{S}}(r_{\mathrm{II}}) - H_{\mathrm{S}}(r_{\mathrm{I}})}{H_{\mathrm{S}}(r_{\mathrm{II}}) - H_{\mathrm{S}}(r_{\mathrm{I}}) - D_{\mathrm{KL}}(r_{\mathrm{II}}\|r_{\mathrm{I}})}.\end{aligned} \tag{10.69}$$

Contrary to the case of heat engines, there are no conservation laws in the present case.

Chapter 11

Complex Systems

Solution to exercise 11.1 Suppose that the polymer is made by particles of equal mass m, successively bound by an inextensible bond of length a_0, and that the first particle is placed at the origin. Then the position $\boldsymbol{r}_i$ of the i-th monomer is given by

$$\boldsymbol{r}_i = \sum_{k=1}^{i} \boldsymbol{y}_k, \qquad k = 1, \ldots, N, \tag{11.1}$$

where $\boldsymbol{y}_k$ is a d-dimensional vector, whose distribution satisfies

$$\langle \boldsymbol{y}_k \rangle = 0, \quad \left\langle y_k^2 \right\rangle = a_0^2, \qquad k = 1, \ldots, N. \tag{11.2}$$

We then have, straightforwardly,

$$\left\langle r_N^2 \right\rangle = N a_0^2. \tag{11.3}$$

On the other hand, R_G^2 is defined by

$$R_\mathrm{G}^2 = \frac{1}{N+1} \sum_{i=0}^{N} \left(\boldsymbol{r}_i - \boldsymbol{R}_\mathrm{CM} \right)^2, \tag{11.4}$$

where the center of mass $\boldsymbol{R}_\mathrm{CM}$ is given by

$$\boldsymbol{R}_\mathrm{CM} = \frac{1}{N+1} \sum_i \boldsymbol{r}_i. \tag{11.5}$$

Define the empirical mean by

$$\overline{A_i} = \frac{1}{N+1} \sum_i A_i. \tag{11.6}$$

We then have

$$R_{\mathrm{G}}^2 = \overline{r_i^2} - \overline{\boldsymbol{r}_i}^2. \tag{11.7}$$

One readily sees that

$$\left\langle \overline{\boldsymbol{r}_i}^2 \right\rangle = \frac{1}{N+1} a_0^2, \tag{11.8}$$

where the $\langle \ldots \rangle$ is taken with respect to all possible conformations of the polymer. We have, on the other hand

$$\left\langle \overline{r_i^2} \right\rangle = \frac{1}{N+1} \left\langle \sum_i \left(\sum_{k=1}^{i} a_0^2 \right) \right\rangle = \frac{1}{N+1} \sum_i i\, a_0^2 = \frac{N}{2} a_0^2. \tag{11.9}$$

We thus obtain

$$\left\langle r_{\mathrm{G}}^2 \right\rangle = \frac{N}{2} a_0^2 + \mathrm{O}\left(N^{-1}\right). \tag{11.10}$$

Solution to exercise 11.2 (Polymer over Lattice) Let us first consider $\Gamma_N(\boldsymbol{r})$, defined as the number of paths of a polymer of length N that reaches point $\boldsymbol{r}$ starting from the origin. This quantity satisfies the recursion relation

$$\Gamma_{N+1}(\boldsymbol{r}) = \sum_{\alpha=1}^{d} \Gamma_N(\boldsymbol{r} - a_0 \boldsymbol{e}_\alpha), \tag{11.11}$$

since to reach $\boldsymbol{r}$ in $(N+1)$ steps the path must reach in N steps one if its neighbors.

Multiplying both sides by $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}$ and summing, we obtain

$$\tilde{\Gamma}_{N+1}(\boldsymbol{k}) = \left(2 \sum_{\alpha=1}^{d} \cos(a_0 k_\alpha) \right) \tilde{\Gamma}_N(\boldsymbol{k}), \tag{11.12}$$

where we have taken into account that $\boldsymbol{k} \cdot \boldsymbol{e}_a = k_\alpha$ ($\alpha = 1, \ldots, d$). Given the initial condition $\Gamma_0(\boldsymbol{r}) = \delta_{\boldsymbol{r},0}$ one obtains

$$\tilde{\Gamma}_N(\boldsymbol{k}) = \left[2 \sum_{\alpha=1}^{d} \cos(a_0 k_\alpha) \right]^N. \tag{11.13}$$

Thus we have

$$\tilde{\Gamma}_{\mathrm{GC}}(\boldsymbol{k}, z) = \sum_{N=0}^{\infty} z^N \tilde{\Gamma}_N(\boldsymbol{k}) = \left[1 - 2z \sum_{\alpha=1}^{d} \cos(a_0 k_\alpha) \right]^{-1}. \tag{11.14}$$

For $|x| \ll 1$ one has $\cos x \simeq 1 - \frac{x^2}{2}$. Thus, for $|k| \ll a_0^{-1}$ one has

$$\tilde{\Gamma}_{\mathrm{GC}}(\boldsymbol{k}, z) \simeq \left[1 - z \left(2d - k^2 a_0^2 \right) \right]^{-1}. \tag{11.15}$$

This expression is equivalent to

$$\tilde{\Gamma}_{\mathrm{GC}}(\boldsymbol{k},z) \simeq \frac{1/(2d)}{1/(2d) - z + z a_0^2 k^2}, \tag{11.16}$$

so that we can set (for $z \simeq z_{\mathrm{c}}$)

$$z_{\mathrm{c}} = \frac{1}{2d}; \qquad c = \frac{a_0^2}{2d}. \tag{11.17}$$

Solution to exercise 11.3 Use the relation

$$f_N = \oint \frac{\mathrm{d}z}{2\pi \mathrm{i}}\, z^{-(N+1)} f(z), \tag{11.18}$$

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 $|z - z_{\mathrm{c}}|^{-\gamma}$, one can change the path of integration to move along the cut. The integral is thus transformed to

$$f_N \propto \int_{z_{\mathrm{c}}}^{\infty} \mathrm{d}z\, z^{-(N+1)} \left(z - z_{\mathrm{c}}\right)^{-\gamma}. \tag{11.19}$$

Set $z = z_{\mathrm{c}} \mathrm{e}^{w}$ so that the integral becomes

$$z_{\mathrm{c}}^{\gamma-(N+1)} \int_0^{\infty} \mathrm{d}w\, \mathrm{e}^{-Nw} \left(\mathrm{e}^{w} - 1\right)^{-\gamma}. \tag{11.20}$$

The singularity appears for $w \to 0$. One then has $\mathrm{e}^{w} - 1 \simeq w$. Then we have

$$f_N \propto z_{\mathrm{c}}^{-N} \int_0^{\infty} \mathrm{d}w\, \mathrm{e}^{-Nw} w^{-\gamma} = z_{\mathrm{c}}^{-N} \Gamma_{\mathrm{E}}(1-\gamma) N^{\gamma-1}, \tag{11.21}$$

where $\Gamma_{\mathrm{E}}(z)$ is Euler's gamma function.

It is easier to show the converse. Assume $\Gamma_N \sim z_{\mathrm{c}}^{-N} N^{\gamma-1}$, and define $\Gamma(z)$ by

$$\Gamma(z) = \sum_N z^N \Gamma_N. \tag{11.22}$$

Then

$$\Gamma(z) \sim \sum_N \left(\frac{z}{z_{\mathrm{c}}}\right)^N N^{\gamma-1}. \tag{11.23}$$

For $z \simeq z_{\mathrm{c}}$ we can set $w = -\ln(z/z_{\mathrm{c}})$ and (since the summand is slowly varying) approximate the sum by an integral:

$$\Gamma(z) \sim \int_0^{\infty} \mathrm{d}N\, \mathrm{e}^{-Nw} N^{\gamma-1} = \Gamma_{\mathrm{E}}(\gamma) w^{-\gamma}. \tag{11.24}$$

When $z \simeq z_\mathrm{c}$ one has $w \simeq (z_\mathrm{c} - z)/z_\mathrm{c}$ and the result follows.

Solution to exercise 11.4 For $|\boldsymbol{k}|\, a_0 \ll 1$ one has

$$\tilde{\Gamma}_\mathrm{GC}(\boldsymbol{k}, z) \sim \frac{1}{z_\mathrm{c} - z + ck^2}. \tag{11.25}$$

To simplify the discussion, let us set $z_\mathrm{c} - z = ct$, with $t > 0$. Then we have

$$\tilde{\Gamma}_\mathrm{GC}(\boldsymbol{k}, z) \propto \frac{1}{t + k^2}, \tag{11.26}$$

and

$$\Gamma(0, z) \propto I_d(t) = \int_\mathrm{Z.B.} \frac{\mathrm{d}^d \boldsymbol{k}}{t + k^2}. \tag{11.27}$$

For $d > 2$ the integral converges for $t = 0$. We can thus evaluate $I_d'(t) = \mathrm{d}I_d/\mathrm{d}t$, and set

$$I_d(t) = I_d(0) + \int_0^t \mathrm{d}t'\ I_d'(t'), \tag{11.28}$$

where

$$I_d'(t) = -\int_\mathrm{Z.B.} \frac{\mathrm{d}^d \boldsymbol{k}}{(t + k^2)^2}. \tag{11.29}$$

For $d < 4$ the integral converges if the upper integration limit is moved to infinity. Thus we have

$$I_d'(t) = -\int \frac{\mathrm{d}\boldsymbol{k}}{(t + k^2)^2} + \text{regular terms}, \tag{11.30}$$

where the integral extends to infinity. We can now exploit the identity

$$\frac{1}{X^2} = \int_0^\infty \mathrm{d}u\ u\, \mathrm{e}^{-uX}, \tag{11.31}$$

to obtain (up to regular terms)

$$I_d'(t) \simeq -\int_0^\infty \mathrm{d}u \int \mathrm{d}^d \boldsymbol{k}\ u\, \mathrm{e}^{-u(t+k^2)}. \tag{11.32}$$

The integral over $\boldsymbol{k}$ yields $(\pi/u)^{d/2}$. We have therefore

$$\begin{aligned} I_d'(t) &\simeq -\pi^{d/2} \int_0^\infty \mathrm{d}u\ u^{1-d/2}\, \mathrm{e}^{-ut} = -t^{d/2-2} \int_0 \mathrm{d}w\ w^{1-d/2}\, \mathrm{e}^{-w} \\ &= -\pi^{d/2} \Gamma_\mathrm{E}(2 - d/2)\, t^{d/2-2}. \end{aligned} \tag{11.33}$$

We have therefore, for $2 < d < 4$,

$$\begin{aligned} I_d(t) &\simeq I_d(0) - \pi^{d/2}\Gamma_{\mathrm{E}}(2-d/2)\int_0^t \mathrm{d}t'\ (t')^{d/2-2} \\ &= I_d(0) + \pi^{d/2}\frac{\Gamma_{\mathrm{E}}(2-d/2)}{1-d/2}t^{1-d/2} \\ &= I_d(0) + \pi^{d/2}\Gamma_{\mathrm{E}}(1-d/2)t^{d/2-1}. \end{aligned} \tag{11.34}$$

We obtain therefore, for $2 < d < 4$,

$$\Gamma(0,z) \simeq \text{const.} + \text{const.} \times |z_{\mathrm{c}} - z|^{(d-2)/2}. \tag{11.35}$$

By using the technique used in the solution of exercise 11.3 one obtains

$$\Gamma_N(0) \sim N^{-d/2}. \tag{11.36}$$

For $d = 4$ $I_d'(t)$ diverges if the integration over $\boldsymbol{k}$ extends to infinity. Differentiating once more with respect to t we obtain

$$I_4''(t) \simeq 2\int_{\mathrm{Z.B.}} \frac{\mathrm{d}\boldsymbol{k}}{(t+k^2)^3}, \tag{11.37}$$

in which we can now safely extend the integration to infinity. Evaluating the integral as above we obtain

$$I_4''(t) \simeq 2\pi^2\Gamma_{\mathrm{E}}(1)\,t^{-1}, \tag{11.38}$$

and therefore

$$I_4'(t) \propto \ln t + \text{const.} \tag{11.39}$$

yielding

$$I_4(t) \simeq \text{const.} + \text{const.} \times t\ln t. \tag{11.40}$$

Thus we have

$$\Gamma_N(0) \sim \frac{\ln N}{N}. \tag{11.41}$$

For $d > 4$, by the same token, we obtain

$$I_d(t) = \text{const.} + \text{const.} \times t + \mathrm{o}(t), \tag{11.42}$$

and therefore

$$\Gamma_N(0) \sim N^{-1}. \tag{11.43}$$

Solution to exercise 11.5 Let us consider the expression of Z_n:

$$Z_n = \int \prod_i \left[\mathrm{d}^n\boldsymbol{\phi}_i\,\delta\left(\phi_i^2 - n\right)\right]\ \exp\left[\sum_{<i,j>} K\boldsymbol{\phi}_i\cdot\boldsymbol{\phi}_j + h_1\sum_i \phi_{1i}\right], \tag{11.44}$$

where $\boldsymbol{\phi}_i = (\phi_{1i}, \ldots, \phi_{ni})$, $\mathrm{d}^n\boldsymbol{\phi} = \mathrm{d}\phi_{1i} \cdots \mathrm{d}\phi_{ni}$, and $\sum_{<i,j>}$ 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}:

$$\begin{aligned}\Gamma^{(2p)} = \frac{1}{(2p)!} \int \prod_i \left[\mathrm{d}^n \boldsymbol{\phi}_i \, \delta\left(\phi_i^2 - n\right)\right] \\ \times \sum_{i_1,\ldots,i_{2p}} \phi_{1i_1} \cdots \phi_{1i_{2p}} \, \exp\left[\sum_{<i,j>} K \boldsymbol{\phi}_i \cdot \boldsymbol{\phi}_j\right].\end{aligned} \tag{11.45}$$

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 $\exp\left[\sum K \boldsymbol{\phi} \cdot \boldsymbol{\phi}\right]$. 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 $n \to 0$ 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 $i_1, \ldots i_{2p}$, 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 11.6 Let us consider a single cluster of size s of the ferromagnet. We assume throughout that the interaction constant J satisfies $J \gg k_\mathrm{B}T$. 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

$$m = s \tanh \frac{sh}{k_\mathrm{B}T}. \tag{11.46}$$

For $h \ll k_\mathrm{B}T$ we have

$$m \simeq s^2 \frac{h}{k_\mathrm{B}T}. \tag{11.47}$$

Summing over the whole cluster, we obtain the magnetization per unit site

$$m = \sum_s s^2 \, \nu_s(p) \frac{h}{k_\mathrm{B}T}, \tag{11.48}$$

yielding

$$\chi = \frac{1}{k_\mathrm{B}T} \sum_s s^2 \, \nu_s(p). \tag{11.49}$$

Solution to exercise 11.7 Let us assume that if two neighboring spins are occupied, the interaction constant J between them is much larger than $k_{\mathrm{B}}T$. 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 11.8 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

$$S(p) = p(1 + \zeta T(p)). \tag{11.50}$$

Now let us consider the root of the branch. It 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

$$T(p) = p\left[1 + (\zeta - 1)T(p)\right]. \tag{11.51}$$

Solution to exercise 11.9 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 11.10 Let us evaluate M_k via

$$M_k \simeq \sum_k s^k \nu_s(p) \simeq \sum_k s^{k-\tau} \mathrm{e}^{-c(p)s} \simeq [c(p)]^{\tau-k-1}, \tag{11.52}$$

where we have approached the sum as an integral. Substituting the behavior of $c(p)$ we obtain the result.

Solution to exercise 11.11 From the expression of Z' we obtain the following expression for the rescaled partition function Z':

$$\lim_{q \to 0} Z' = \sum_{\mathcal{G}_{\mathrm{t}}} \prod_s (1 + hs)^{N\mathcal{K}_{\mathrm{t}}(\mathcal{G}_{\mathrm{t}};h,s)}, \tag{11.53}$$

where the sum runs on all graphs $\mathcal{G}_\mathrm{t}$ without loops and $N\mathcal{K}_\mathrm{t}(\mathcal{G}_\mathrm{t}; h, s)$ is the number of clusters in configuration $\mathcal{G}_\mathrm{t}$ that contain s sites. We have therefore

$$\lim_{q\to 0} D_q(\boldsymbol{r},\boldsymbol{r}') = \sum_{\mathcal{G}_\mathrm{t}} P(\mathcal{G}_t) C(\boldsymbol{r},\boldsymbol{r}') = \left\langle C(\boldsymbol{r},\boldsymbol{r}')\right\rangle_\mathrm{t}. \tag{11.54}$$

On the other hand, as $K \to \infty$, the weight is dominated by trees with the maximum number N_b of bonds. Since $N_\mathrm{b} = N - N_\mathrm{c}$ for trees, this corresponds to $N_\mathrm{b} = N - 1$, i.e., to spanning trees.

Solution to exercise 11.12 Let us define $\beta(p, d)$ by

$$\beta(p,d) = \left.\frac{\mathrm{d}p'}{\mathrm{d}b}\right|_{b=1}. \tag{11.55}$$

The equation $\beta(p, 3) = 0$ allows, beyond the trivial fixed points $p = 0, 1$, for the nontrivial one

$$p = p_\mathrm{c} = 0.160365. \tag{11.56}$$

We have

$$\lambda = \left.\frac{\partial\beta}{\partial p}\right|_{p=p_\mathrm{c}} = 0.820122. \tag{11.57}$$

From the relation

$$\nu = \frac{1}{\lambda} \tag{11.58}$$

we obtain

$$\nu = 1.21933. \tag{11.59}$$

Solution to exercise 11.13 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 mutliple bond (cf. fig. 11.1). By bond moving each bond in the x direction gets surrounded by $(b-1)(d-1)$ bonds. Thus we have

$$K_1 = (1 + (b-1)(d-1))\, K, \tag{11.60}$$

where $K = J/k_\mathrm{B}T$ is the bond's strength. We can now decimate the $(b-1)$ spins 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

$$\mathsf{T} = \begin{pmatrix} \mathrm{e}^{K_1}, & \mathrm{e}^{-K_1} \\ \mathrm{e}^{-K_1}, & \mathrm{e}^{K_1} \end{pmatrix}. \tag{11.61}$$

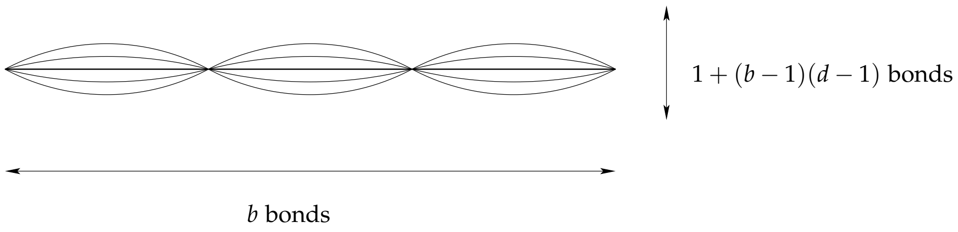

Figure 11.1: Bond moving in the d-dimensional Ising model

This matrix allows for the eigenvectors

$$|\pm\rangle = \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}, \tag{11.62}$$

with the corresponding eigenvalues

$$\lambda_\pm = \mathrm{e}^{K_1} \pm \mathrm{e}^{-K_1}. \tag{11.63}$$

Thus we have

$$\mathsf{T}^b = \lambda_+^b \, |+\rangle \, \langle +| + \lambda_-^b \, |-\rangle \, \langle -| \, . \tag{11.64}$$

We can write this expression in the form

$$\mathsf{T}^b = \cosh^{b/2}(K_1) \begin{pmatrix} \mathrm{e}^{K'}, & \mathrm{e}^{-K'} \\ \mathrm{e}^{-K'}, & \mathrm{e}^{K'} \end{pmatrix}, \tag{11.65}$$

where

$$\mathrm{e}^{-2K'} = \frac{\lambda_+^b - \lambda_-^b}{\lambda_+^b + \lambda_-^b} = \frac{\cosh^b K_1 - \sinh^b K_1}{\cosh^b K_1 + \sinh^b K_1}. \tag{11.66}$$

By taking the derivative of this expression, and setting $b \to 1$, we obtain

$$\beta(K,d) = \left.\frac{\mathrm{d}K'}{\mathrm{d}K}\right|_{b=1} = (d-1)K + \frac{1}{2}\sinh 2K \ln\tanh K. \tag{11.67}$$

This function always allows for the trivial zeros $K = 0$ and $K = +\infty$. There is a nontrivial zero K_* satisfying the equation

$$(d-1)K_* = \frac{1}{2}\sinh 2K_* \left|\ln\tanh K_*\right| . \tag{11.68}$$

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

$$\frac{1}{\nu} = \left.\frac{\mathrm{d}\beta(K,d)}{\mathrm{d}K}\right|_{K=K_*} = 0.75355, \tag{11.69}$$

yielding $\nu = 1.32705$ rather than the exact value 1. For $d = 3$ we obtain $K_* = 0.75355$ with $1/\nu = 0.948169$. For $d \to 1$ we have $K_* \to 1/(d-1)$ and eventually the nontrivial fixed point disappears. On the other hand, for $d \to \infty$ we obtain $K \sim \mathrm{e}^{-(d-1)}$ with $1/\nu \to 1$, which has nothing to do with the classical behavior.

Solution to exercise 11.14 Let us denote by $\mathcal{N}_\ell$ the number of circles of diameter equal to ℓ needed to cover the triangle, 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

$$\mathcal{N}_\ell \propto \ell^{\ln 3/\ln 2)}. \tag{11.70}$$

We obtain therefore

$$d_{\mathrm{H}} = \frac{\ln 3}{\ln 2} = 1.58. \tag{11.71}$$

Solution to exercise 11.15 Reasoning as in the previous case, we obtain

$$\mathcal{N}_\ell \propto \ell^{\ln 4/\ln 3}, \tag{11.72}$$

leading to

$$d_{\mathrm{H}} = \frac{\ln 4}{\ln 3} = 1.26. \tag{11.73}$$

Solution to exercise 11.16 Given a Sierpiński triangle 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 $\mathcal{N} \propto \ell^{\ln 3}/\ln 2$. The reasoning for the other two cases is similar.

Solution to exercise 11.17 Let us denote by $\Phi(E)$ the cumulative pdf of E:

$$\Phi(E) = \int_{-\infty}^{E} \mathrm{d}E'\, P(E'). \tag{11.74}$$

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

$$\Phi_M(E) = [1 - \Phi(E)]^M. \tag{11.75}$$

For large values of M, we expect typical values of E to be large and negative, so that $\Phi(E) \ll 1$, yielding

$$\Phi_M(E) \simeq \exp\left[-M\Phi(E)\right]. \tag{11.76}$$

Let us identify the critical value E_{c} by the condition

$$M\Phi(E_{\mathrm{c}}) = 1. \tag{11.77}$$

From the asymptotic behavior of $P(E)$ we obtain the following estimate of E_{c}:

$$E_{\mathrm{c}} \simeq -\left(\frac{\ln M}{B}\right)^{1/\delta}. \tag{11.78}$$

For $E \simeq E_{\mathrm{c}} + \epsilon$, with $|\epsilon| \ll |E_{\mathrm{c}}|$, we have

$$\Phi(E) \simeq \Phi(E_c) \cdot \exp\left(\left.\frac{\mathrm{d}\ln\Phi}{\mathrm{d}E}\right|_{E_{\mathrm{c}}} \epsilon\right) = \frac{1}{M}\exp\left(-B\delta\,|E_{\mathrm{c}}|^{\delta-1}\,\epsilon\right), \tag{11.79}$$

that yields

$$\Phi_M(E) \simeq \exp\left[-\exp\left(B\delta\,|E_{\mathrm{c}}|^{\delta-1}\,\epsilon\right)\right]. \tag{11.80}$$

Let us introduce the variable

$$x = B\delta\,|E_{\mathrm{c}}|^{\delta-1}\,\epsilon. \tag{11.81}$$

Then the cumulative pdf of the variable x is given by

$$\Phi(x) = \exp\left[-\exp(x)\right], \tag{11.82}$$

and the corresponding probability density is given by the **Gumbel's law**:

$$P(x) = -\frac{\mathrm{d}\Phi}{\mathrm{d}x} = \exp\left[x - \exp(x)\right]. \tag{11.83}$$

Solution to exercise 11.18 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

$$E_{\mathrm{c}} = -NJ_0\sqrt{\ln 2}, \tag{11.84}$$

and

$$\Phi_M(E) \simeq \mathrm{e}^{2\sqrt{\ln 2}\epsilon/J_0} = \mathrm{e}^{\epsilon/T_0}, \tag{11.85}$$

where $\epsilon = E - E_{\mathrm{c}}$ and

$$\frac{1}{T_0} = \frac{2\sqrt{\ln 2}}{J_0}. \tag{11.86}$$

Since $E = -T \ln z$ we have therefore

$$\Phi_M(z) \propto \mathrm{e}^{(\ln \epsilon + |E_c|)/T_0} = z^{-\mu}, \tag{11.87}$$

with

$$\mu = \frac{T}{T_0}. \tag{11.88}$$

Taking the derivative, we obtain the pdf $P(z)$:

$$P(z) \propto z^{-1-\mu}. \tag{11.89}$$

Solution to exercise 11.19 By Chebyshev's inequality, the probability that a random variable X deviates from its average $[X]_{\mathrm{av}}$ by more than a ($a > 0$) is related to the variance $\mathrm{Var}(X) = \left[X^2\right]_{\mathrm{av}} - [X]_{\mathrm{av}}^2$ by

$$P\left(|E - [E]_{\mathrm{av}}| \geq a\right) \leq \frac{\mathrm{Var}(X)}{a^2}. \tag{11.90}$$

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

$$[\mathcal{N}(\epsilon, \delta)]_{\mathrm{av}} = 2^N \int_{N\epsilon}^{N(\epsilon+\delta)} \mathrm{d}E\ P(E) \simeq \frac{N\delta}{\sqrt{\pi N}} \mathrm{e}^{N(\ln 2 - \epsilon^2)}. \tag{11.91}$$

Since $\mathcal{N}(\epsilon, \delta)$ is Poisson distributed, its variance is equal to its average. Let us assume that $|\epsilon| > \epsilon_* = \sqrt{\ln 2}$. Letting $a = 1$ into Chebyshev's inequality we obtain that the probability that $\mathcal{N}(\epsilon, \delta) \geq 1$ satisfies

$$P\left(\mathcal{N}(\epsilon, \delta) \geq 1\right) \leq \delta \sqrt{\frac{N}{\pi}}\, \mathrm{e}^{-N\left|\ln 2 - \epsilon^2\right|} \ll 1, \tag{11.92}$$

for $|\epsilon| > \epsilon_*$ and N large enough.

Solution to exercise 11.20 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

$$[\mathcal{N}(\epsilon, \delta, m)]_{\mathrm{av}} \simeq \binom{N}{(N+M)/2} \frac{\mu\, \delta}{\sqrt{\pi N}}\, \mathrm{e}^{-N(\epsilon + mB)^2}. \tag{11.93}$$

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

$$s(\epsilon, m) = \lim_{N \to \infty} \frac{1}{N} \ln\left[\mathcal{N}(\epsilon, \delta, m)\right]_{\mathrm{av}} = s_0(m) - (\epsilon + mB)^2, \tag{11.94}$$

where

$$s_0(m) = -\left[\frac{1+m}{2}\ln\frac{1+m}{2} + \frac{1-m}{2}\ln\frac{1-m}{2}\right]. \qquad (11.95)$$

This relation holds as long as we have $s(\epsilon, m) > 0$, i.e.,

$$|\epsilon + mB| < \sqrt{s_0(m)}. \qquad (11.96)$$

In this regime, the equilibrium value m_0 of m is obtained from the equation

$$\left.\frac{\partial s}{\partial m}\right|_{m=m_0} = 0. \qquad (11.97)$$

We obtain

$$\tanh^{-1} m_0 = -2B\left(\epsilon + m_0 B\right). \qquad (11.98)$$

Then the temperature $T = 1/\beta$ is given by

$$\beta = \left.\frac{\partial s}{\partial \epsilon}\right)_m = -2\left(\epsilon + m_0 B\right). \qquad (11.99)$$

When these conditions are satisfied, we obtain

$$m_0(\beta, B) = \tanh(\beta B), \qquad (11.100)$$

corresponding to the usual paramagnetic behavior. However, there is a transition line corresponding to the condition

$$\beta_{\mathrm{c}} = \frac{1}{2}\sqrt{s_0\left(m_0(\beta_{\mathrm{c}}, B)\right)}. \qquad (11.101)$$

To identify the transition line, let us take as an independent variable m_0. We then have

$$\beta_{\mathrm{c}}(m_0) = \frac{1}{2}\sqrt{s_0(m_0)}; \qquad (11.102)$$

$$B = \frac{\tanh^{-1} m_0}{\beta_c(m_0)}. \qquad (11.103)$$

To obtain the expression of the susceptibility χ we must distinguish between the paramagnetic phase $\beta < \beta_{\mathrm{c}}(B)$ and the “frozen” phase $\beta > \beta_{\mathrm{c}}(B)$. In the former case we obtain

$$\chi = \beta(1 - m_0^2), \qquad (11.104)$$

which leads to the Curie law $\chi = \beta$ for $B = 0$.

On the other hand, for $\beta > \beta_{\mathrm{c}}(B)$, the system remains “frozen” in one of the relevant configurations at temperature $1/\beta_{\mathrm{c}}$. Thus we have

$$\chi = \beta_{\mathrm{c}}, \quad \text{for } \beta > \beta_{\mathrm{c}}. \qquad (11.105)$$

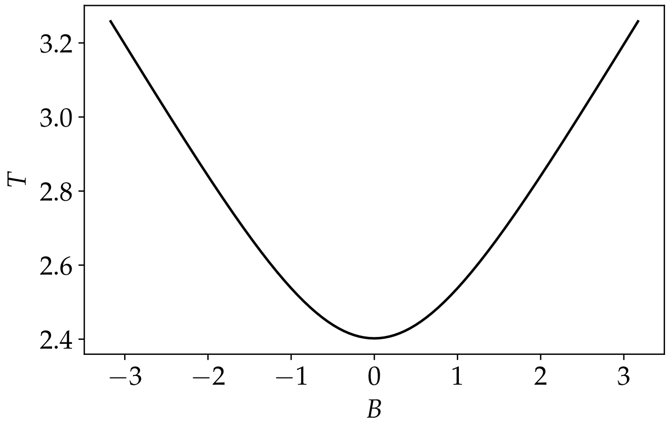

Figure 11.2: Phase diagram of the REM in external field in the $(B, T = 1/\beta)$ plane. The “frozen” phase lies below the line.

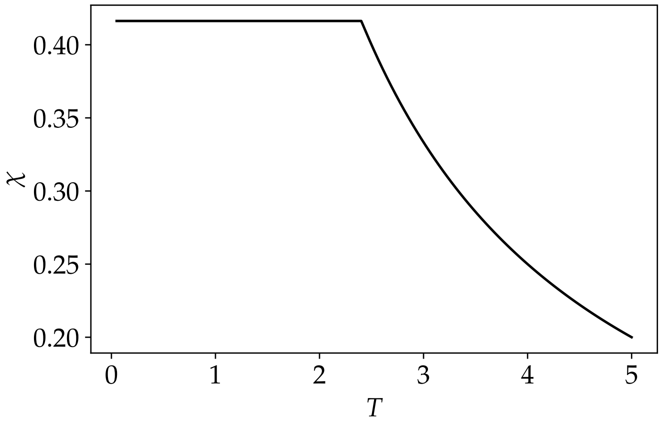

Figure 11.3: Zero-field susceptibility χ of the REM as a function of the temperature T.

Solution to exercise 11.21 For $\delta > 1$, we can evaluate the entropy per spin in the same way as above. For $|\epsilon|$ small enough we have

$$s(\epsilon) = \lim_{N\to\infty} [\ln \mathcal{N}(\epsilon, \delta)] = \ln 2 - CN^{\delta-1} |\epsilon|^{\delta} . \tag{11.106}$$

To obtain an N-independent limit we must set

$$CN^{\delta-1} = \hat{C}. \tag{11.107}$$

The expression vanishes for

$$|\epsilon| = \epsilon_* = \left(\frac{\ln 2}{\hat{C}}\right)^{1/\delta}. \tag{11.108}$$

The temperature is obtained by the expression

$$\beta = \frac{\partial s}{\partial \epsilon} = \hat{C}\delta\,|\epsilon|^{\delta-1}. \tag{11.109}$$

Thus the critical temperature β_{c} is given by

$$\beta_{\mathrm{c}} = \hat{C}\delta\epsilon_*^{\delta-1} = \delta\ln 2^{1-1/\delta}\hat{C}^{1/\delta}. \tag{11.110}$$

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

$$Z = \int_{-\epsilon_*}^{0} \mathrm{e}^{N[s(\epsilon)-\beta\epsilon]}. \tag{11.111}$$

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 $\beta < \beta_{\mathrm{c}}$, where β_{c} is the solution of the equation

$$\beta\epsilon_* = \ln 2. \tag{11.112}$$

In this state the entropy per spin is equal to $\ln 2$. For $\beta > \beta_{\mathrm{c}}$ we have $\langle E\rangle = -N\epsilon_*$ and the entropy per spin vanishes. Thus the transition at β_{c} is first order.

Solution to exercise 11.22 Given a solution of the form

$$\boldsymbol{m} = (m^i), \qquad m^i = m, \quad i = 1,\ldots,r; \qquad m^i = 0, \quad i = r+1,\ldots,p,$$

the mean-field equations become

$$\overline{f(T)} = \frac{r}{2}m^2 - k_{\mathrm{B}}T\,\overline{\ln\left[2\cosh\left(\frac{mz_r}{k_{\mathrm{B}}T}\right)\right]}, \tag{11.113}$$

$$m = \frac{1}{r}\overline{z_r\tanh\left(\frac{mz_r}{k_{\mathrm{B}}T}\right)}, \tag{11.114}$$

where

$$z_r = \sum_{i=1}^{r} \xi_i. \tag{11.115}$$

The distribution of z_r is given by

$$p(z_r) = \frac{1}{2^r} \binom{r}{k}, \tag{11.116}$$

where $k = (r + z_r)/2$ is the number of positive ξ_i that contribute to z_r. We have therefore

$$\overline{z_r^2} = r, \qquad \overline{z_r^4} = r(3r-2). \tag{11.117}$$

Expanding the self-consistency equation for small values of m we obtain

$$m \simeq \frac{\overline{z_r^2}}{r} \frac{m}{k_{\mathrm{B}}T} - \frac{\overline{z_r^4}}{3r} \left(\frac{m}{k_{\mathrm{B}}T} \right)^3. \tag{11.118}$$

We thus obtain

$$m^2 \simeq \frac{3t}{3r-2}, \tag{11.119}$$

where $t = k_{\mathrm{B}}\,(T_{\mathrm{c}} - T)$, with $k_{\mathrm{B}}T_{\mathrm{c}} = 1$. Substituting in the expression of $f(T)$ we obtain

$$\overline{f(T)} \simeq -\frac{3rt^2}{4(3r-2)}. \tag{11.120}$$

The average free energy increases monotonically with r, therefore the solutions with $r > 1$ are at most metastable. One can check that they are locally stable, since the second derivative of $\overline{f}$ with respect to m is positive.

Solution to exercise 11.23 (Capacity of a Hopfield network)

1. We have

$$\begin{aligned}\Delta E &= \sum_{\alpha=1}^{p}\left(\xi_{i_0}^1\xi_{i_0}^\alpha + \sum_{i\neq i_0}\xi_i^1\xi_i^\alpha\right)^n - \sum_{\alpha=1}^{p}\left(-\xi_{i_0}^1\xi_{i_0}^\alpha + \sum_{i\neq i_0}\xi_i^1\xi_i^\alpha\right)^n \\ &\simeq 2n\sum_{\alpha=1}^{p}\xi_{i_0}^1\xi_{i_0}^\alpha\left(\sum_{i\neq i_0}\xi_i^1\xi_i^\alpha\right)^{n-1} \\ &= 2n\left[(N-1)^{n-1} + \sum_{\alpha=2}^{p}\xi_{i_0}^1\xi_{i_0}^\alpha\left(\sum_{i\neq i_0}\xi_i^1\xi_i^\alpha\right)^{n-1}\right].\end{aligned} \tag{11.121}$$

   Now, for $\alpha > 1$, the quantity

$$Y = \sum_{i\neq i_0}\xi_i^1\xi_i^\alpha, \tag{11.122}$$

   is a random (approximately Gaussian) variable of vanishing average and variance equal to $N-1$. We thus obtain, for $n=2$,

$$\langle\Delta E\rangle = N^2 - (N-2)^2 \simeq 4N, \tag{11.123}$$

   and, for $N, p \gg 1$,

$$\Sigma^2 \simeq 16pN. \tag{11.124}$$

2. We obtain

$$\begin{aligned}p_{\text{err}} &= \int_{\langle\Delta E\rangle}^{\infty}\frac{\mathrm{d}\epsilon}{\sqrt{2\pi\Sigma^2}}\,\mathrm{e}^{-\epsilon^2/2\Sigma^2} \\ &= \frac{1}{2}\operatorname{erfc}\left(\sqrt{\frac{N}{2p}}\right) \simeq \sqrt{\frac{p}{2\pi N}}\,\mathrm{e}^{-N/(2p)}.\end{aligned} \tag{11.125}$$

   Requiring this to be smaller than 0.5% yields $p_{\text{max}} \simeq 0.1462\,N$.

3. When $n > 2$ and even, we obtain

$$\langle\Delta E\rangle \simeq 2n\,N^{n-1}, \tag{11.126}$$

   and

$$\Sigma^2 \simeq 4n^2(2n-3)!!(p-1)N^{n-1}. \tag{11.127}$$

   One thus obtains, for $p, N \gg 1$,

$$p_{\text{err}} \simeq \sqrt{\frac{(2n-3)!!}{2\pi}\,\frac{p}{N^{n-1}}}\,\mathrm{e}^{-N^{n-1}/(2p\,(2n-3)!!)}. \tag{11.128}$$

Requiring $p_{\mathrm{err}} < 0.5\%$ yields $p_{\max} = 0.0098\,N^3$ for $n = 4$. Thus the capacity grows much faster than the system size N and grows the faster, the larger n is. If we require perfect retrieval, that is, $p_{\mathrm{err}} < 1/N$, we obtain

$$p_{\max} \simeq \frac{1}{2(2n-3)!!}\frac{N^{n-1}}{\ln N}. \tag{11.129}$$

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