3 Statistical Thermodynamics

3.1: Boundary conditions

The energy eigenstates of a point particle of mass m in a cubic container of size L are labeled by three positive integers n_x, n_y, and n_z,

$$\psi_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\frac{\pi n_x x}{L} \sin\frac{\pi n_y y}{L} \sin\frac{\pi n_z z}{L} \tag{1}$$

and the corresponding energy is

$$E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2).$$

The wavefunction (1), which has the form of a *standing wave*, is calculated using the boundary condition that $\psi(x, y, z) = 0$ for x, y, z on the walls of the container. This boundary condition is referred to as the "Dirichlet boundary condition".

Sometimes it is easier to use a different boundary condition. One often uses the so-called "periodic boundary condition". Instead of requiring that the wavefunction vanishes on the walls of the container, one requires *periodicity*,

$$\psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L) = \psi(x, y, z).$$

For this boundary condition, wavefunctions are *traveling waves*. They are labeled by integers n_x, n_y, n_z, which can be positive, negative, or zero,

$$\psi_{n_x n_y n_z}(x, y, z) = L^{-3/2} e^{2\pi i(n_x x + n_y y + n_z z)/L}.$$

The corresponding energy eigenvalue is

$$E_{n_x n_y n_z} = \frac{2\hbar^2\pi^2}{mL^2}(n_x^2 + n_y^2 + n_z^2).$$

(a) Calculate the microcanonical partition function $\Omega(E)$ for an ideal gas of $N \gg 1$ non-interacting distinguishable point particles in a cubic container of size L with periodic boundary conditions. How does your answer compare to the case of Dirichlet boundary conditions?

(b) Another boundary condition is the "Neumann boundary condition", in which one requires that the normal derivative of the wavefunction vanishes on the walls of the container. What would be the microcanonical partition function in this case? You don't need to show a full calculation.

3.2: Einstein model for lattice vibrations (2)

This exercise continues last week's analysis of Einstein's model for lattice vibrations in a one-dimensional solid. Recall that Einstein's model describes a chain of N atoms. Each atom i is specified by a coordinate x_i and a momentum p_i, $i = 1, 2, \ldots, N$. The Hamiltonian for N lattice atoms is

$$H = \sum_{i=1}^{N} H_i, \quad H_i = \frac{1}{2m}\left(p_i^2 + \omega^2 x_i^2\right).$$

Using quantum mechanics to describe the lattice vibrations, you found that, for large N, the number of accessible quantum states at energy $E = (M + N/2)\hbar\omega$ is given by

$$\Omega(E) \approx \frac{(M+N)^{M+N}}{M^M N^N},$$

where we assumed that M and N are large. You may continue to use the large-N limit in the remainder of this exercise.

(a) What is the entropy for the lattice system? Express your answer in terms of M and N.

(b) The chain of atoms is brought in thermal contact with a heat bath at temperature T. Express the energy per atom, E/N, and the heat capacity per atom, C/N, in terms of the temperature T and the vibration frequency ω.

3.3: Microcanonical Ensemble

In the microcanonical ensemble, one considers an isolated system in equilibrium at energy E and volume V. Thermodynamical quantities can be found by calculation of the number of microstates $\Omega(E, V)$ available to the system, the "microcanonical partition function". The number of microstates is related to the entropy through the relation $S(E, V) = k \ln \Omega(E, V)$.

(a) In practice, it may be advantageous to describe the state of a system by specifying its temperature T and pressure p. Indicate how one could calculate p and T from the microcanonical partition function $\Omega(E, V)$.

(b) For a certain nonideal gas, the microcanonical partition function is given by

$$k \ln \Omega = S = Nk \ln \left(\frac{V}{N} - b \right) + \frac{3}{2} Nk \ln \left(\frac{E}{N} + a\frac{N}{V} \right) + \text{const},$$

where a and b are constants. Find the equation of state for this gas, *i.e.*, find a relation between the pressure p, the volume V, the particle number N, and the temperature T.

Suggested problems for further study:

3.4: Pressure of an ideal gas
Exercise 2.7 from Reif's book. Add:

(c) Calculate the pressure for a monatomic ideal gas of known macroscopic energy E and confined to the same box of volume L^3. Write your answer in terms of E and the number N of gas molecules.

3.5: Punctured partition
Exercise 3.1 from Reif's book

3.6: Mixture of ideal gases
Exercise 3.5 from Reif's book

3.7: Semi-permeable membrane
Exercise 3.6 from Reif's book.

3.8: Spin systems in equilibrium
Consider two collections of weakly interacting but localized (i.e., "pinned") particles with spin 1/2 in an external magnetic field H. The first system consists of $N_1 = N \gg 1$ spins with magnetic moment $\mu_1 = \mu$ per spin; the second system has $N_2 = 2N$ particles with magnetic moment $\mu_2 = \mu/2$. The two systems are measured to be at equal total energies E, with $|E| \ll \mu NH$.

(a) Write down expressions for the densities of states $\omega_1(E)$ and $\omega_2(E)$ for the two spin systems.

The two systems are brought into thermal contact.

(b) What are the average energies $\bar{E}_1$ and $\bar{E}_2$ of each of the two systems after thermal equilibrium has been reached?

(c) What is the heat Q absorbed by system 1 in going from the initial situation to the final situation when it is in equilibrium with system 2?

Although the systems are in thermal contact, the energies E_1 and E_2 of the individual components continue to show small fluctuations around their average values calculated above.

(d) We can characterize the fluctuations by their variance. What is the variance of (the fluctuations of) E_1? And of E_2?