Theoretical Physics VI: Statistical Physics - Theory of Heat

Problem Set 6

due: 28. 11. 2007, 10:15 am

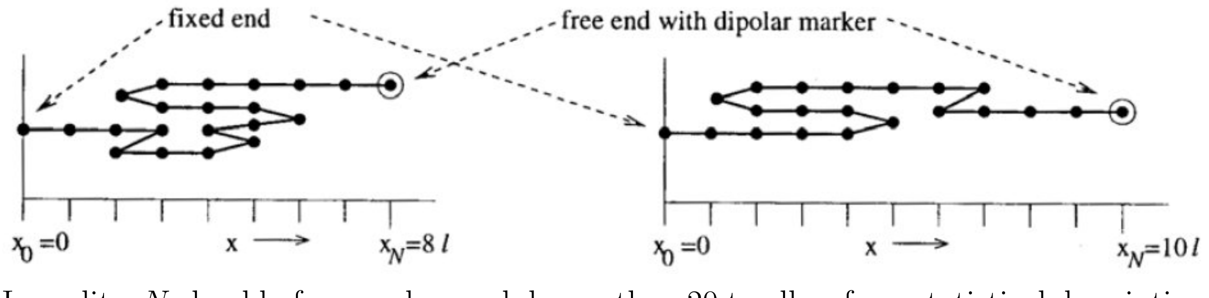
Problem 6.1 *Debye theory of the heat capacity in solids: 1D* (3 pts.)
The Hamiltonian of a chain of linearly coupled harmonic oscillators is given by

$$\hat{\mathbf{H}}_{1\mathrm{D}} = \sum_{j=1}^{N} \frac{\hat{\mathbf{p}}_j^2}{2m} + \frac{k}{2}\sum_{j=1}^{N-1}\left(\hat{\mathbf{u}}_{j+1} - \hat{\mathbf{u}}_j\right)^2 + \frac{k}{2}\hat{\mathbf{u}}_1^2 + \frac{k}{2}\hat{\mathbf{u}}_N^2 \,.$$

Determine the orthogonal transformation $\hat{\mathbf{X}}$ which relates $\hat{\mathbf{p}}_j$, $\hat{\mathbf{u}}_j$ to the normal mode coordinates $\hat{\mathbf{P}}_i$, $\hat{\mathbf{Q}}_i$. What are the frequencies ω_i of the normal modes?

Problem 6.2 *Debye theory of the heat capacity in solids: 3D* (6 pts.)
In Debye's theory, a solid consisting of N atoms in a lattice is modelled by coupled harmonic oscillators. This system is most easily treated in a normal mode picture (cf. problem 6.1).
(a) Derive the density of states for a single normal mode by considering standing waves in a cube. Calculate the total density of states in terms of the number of atoms and the Debye frequency.
Hint: In Debye's theory, the sum over all degrees of freedom is approximated by an integral over the density of states.
(b) Calculate the mean energy and the heat capacity.

Problem 6.3 *Simplified polymer model* (8 pts.)
Consider a polymer, i.e. a long molecule such as a protein or DNA. Since such a molecule has many degrees of freedom, statistical mechanics can be employed to model its behavior. Let one end of the polymer be attached to a substrate. The other end is free to move and has a dipolar marker attached to it. A uniform electric field can be used to exert a constant force on the marker. The polymer shall be modelled as a one-dimensional chain of N links of length l where each link can point left or right. Two examples of the possible configurations of the polymer are shown below for $N = 20$:



In reality, N should of course be much larger than 20 to allow for a statistical description. The second dimension is added in the figure only for the sake of clarity. As indicated, the fixed end of the chain is located at $x_0 = 0$ while the free end is at position x_N. The energy of the polymer is given by

$$E = -a x_N \,,$$

where a is a positive constant which is proportional to the dipole moment of the marker and the electric field gradient. Since $-Nl \leq x_N \leq Nl$, the energy is bounded $-Nal \leq E \leq Nal$.
(a) Show that the number of configurations $\Omega(E)$ for which the energy of the polymer is between E and δE is equal to

$$\Omega(E) = \frac{2^N \delta E}{al\sqrt{2\pi N}}\, e^{-\frac{E^2}{2Nl^2a^2}}$$

for $N \gg 1$, $al \ll \delta E \ll E$ and $|E| \ll Nal$.
Hint: Use Stirling's formula up to orders of $\ln(N)$,

$$\ln N! \approx N \ln N - N + \frac{1}{2}\ln(2\pi N)$$

(b) Find the entropy of the polymer at energy E.
(c) Let the polymer be immersed in a solution at temperature T. Assuming thermal equilibrium between polymer and solution, what is the average energy $\langle E \rangle$ of the polymer? What are the fluctuations in energy?
(d) What is the force which the polymer exerts on the marker? State your answer in terms of the polymer's extension x_N, temperature T, link length l and number of links N.

Problem 6.4 *Rotating ideal gas* (8 pts.)
A cubic box with infinitely hard walls of volume, $V = L^3$, contains an ideal gas of N rigid HCl molecules. Assume that the effective distance between the H atom and the Cl atom is $d = 1.3\,\text{Å}$.
(a) If $L = 1.0\,\text{cm}$, what is the spacing between translational energy levels?
(b) Write down the partition function for this system, including translational and rotational contributions. At what temperature do rotations become important?
Hint: The Hamiltonian for a rigid rotor is given by

$$\hat{\mathbf{H}}_{rot} = \frac{\hbar^2}{2\mu d^2}\hat{\mathbf{L}}^2\,,$$

where μ is the reduced mass.
(c) What are the free energy, entropy and heat capacity for this system at temperatures where rotational degrees of freedom make an important contribution?