Statistical Mechanics II

Problem Set 2
Aug 29, 2012

1. **Equipartition Theorem:** Let x_i denote any of the canonical variables p_i or q_i ($i = 1, 2, \ldots, 3N$), and $\mathcal{H}$ be the Hamiltonian. The classical equipartition theorem states that

$$\langle x_i \frac{\delta \mathcal{H}}{\delta x_j} \rangle = \delta_{ij} k_B T.$$

(a) Prove the equipartition theorem by taking the ensemble average $\langle x_i \frac{\delta \mathcal{H}}{\delta x_j} \rangle$ over a canonical ensemble.

(b) Using the equipartition theorem in combination with the Hamiltonian equations of motion, prove the **Virial Theorem**:

$$\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = -3N k_B T.$$

The sum of the ith coordinate times the ith component of the generalized force — $\sum q_i \dot{p}_i$ — is known as the *virial* in classical mechanics.

(c) Many physical systems have Hamiltonians of the form

$$\mathcal{H} = \sum_i A_i P_i^2 + \sum_i B_i Q_i^2,$$

where P_i, Q_i are canonically conjugate variables and A_i, B_i are constants. Suppose f of the constants A_i and B_i are non-vanishing, show that,

$$< \mathcal{H} >= \frac{1}{2} f k_B T.$$

This is the *theorem of equipartition of energy*: each *harmonic* term in the Hamiltonian contributes $\frac{1}{2} k_B T$ to the average energy of the system.

(d) Use this to find the heat capacity (C_V) of a solid crystal comprising N atoms, each of which is modeled as a harmonic oscillator. This remarkable universal result for the specific heat of solids is often called the *Dulong-Petit Law.*

2. **Two-level Systems:** Consider a system of N free particles in which the energy of each particle can assume two and only two distinct values, 0 and E ($E > 0$). Let n_0 and n_1 denote the occupation numbers of the energy levels 0 and E, respectively (n_0 particles have energy 0 and n_1 of them are at energy E). The total energy of the system is U.

(a) Find the entropy of the system as function of U and N.

(b) Find the most probable values of n_0 and n_1, and the mean square fluctuations of these quantities.

(c) Find the temperature as a function of U and show it can be negative. What happens when a system of negative temperature is allowed to exchange heat with a system of positive temperature?

3. **Diatomic Molecules:** Consider a classical system of N non-interacting diatomic molecules enclosed in a box of volume V at temperature T. The Hamiltonian of a single molecule is taken to be

$$\mathcal{H}(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{1}{2m}(p_1^2 + p_2^2) + \frac{1}{2}K|\vec{r}_1 - \vec{r}_2|^2,$$

where $\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2$ are the momentum and position coordinates of the two atoms in a molecule. Find

(a) the Helmholtz free energy of the system;

(b) the specific heats at constant volume(C_V) and constant pressure(C_P) , and hence the ratio $\gamma = C_P/C_V$.

(c) the mean square diameter of a molecule $\langle\, |\vec{r}_1 - \vec{r}_2|^2 \,\rangle$.

4. **Non-harmonic Gas:** Consider a gas of N non-interacting atoms in a d-dimensional box of volume V, with a kinetic energy

$$\mathcal{H} = \sum_{i=1}^{N} A|\vec{p}_i|^s,$$

where $\vec{p}_i$ is the momentum of the ith particle.

(a) Calculate the partition function $Z(N,T)$, at a temperature T.

(b) Calculate the pressure and internal energy of this gas. Note how the usual equipartition theorem is modified for non-quadratic degrees of freedom.

5. **Semi-flexible Polymer:** Consider a 2-dimensional polymer molecule which consists of N almost rigid segments of length ℓ each. It's configurations can be described by a set of vectors $\vec{y}_i$ of length ℓ. Imagine it is placed in a solvent which plays the role of heat bath, and that an experimenter is pulling two ends of the chain in opposite directions by forces f and $-f$ using optical tweezers. The potential energy provided by the external force is $\vec{f}.\vec{R}$, where $\vec{R} = \sum_{i=1}^{N} \vec{y}_i$ is the end-to-end vector of the whole chain.

(a) Find the partition function of this system and the corresponding free energy.

(b) Knowing the free energy as a function of the applied force f, find the average distance between polymer ends in the limits of *weak* ($f \ll T/\ell$) and *strong* ($f \gg T/\ell$) forces.