Sheet 7

Please hand in your solutions before the Monday lecture at 10:15.

Problem 1 : Grand Canonical Ensemble (10 points)

Consider a system of $n = 1, 2, \cdots, M$ energy states, so that the number of particles in each state is N_n and the energy of each state is E_n. The rescaled entropy $\tilde{S} = S/k_B$ is defined as

$$\tilde{S} = -\sum_{n=1}^{M} p_n \ln p_n, \tag{1}$$

where p_n is the probability for the system being in a state "n".

a) (1 point): Write down the conservation of probability relation.

b) (1 point): Write down the average total energy E in terms of E_n, p_n and M.

c) (1 point): Write down the average particle total number N in terms of N_n, p_n and M..

d) (7 points): Calculate the probabilities p_n that maximize the entropy $\tilde{S}$, constrained by the conservation of probability, the average total energy E, and the average particle total number N.

** For the calculations in d), use the Lagrange variational method for a function $f(x_i)$:

$$\frac{\partial f}{\partial x_i} + \sum_{k=1}^{K} \lambda_k \frac{\partial \phi_k}{\partial x_i} = 0, \tag{2}$$

where $\phi_k(x_i) = 0$ is a set of K constraints, and λ_k are the Lagrange multipliers. Evaluate λ_k if possible.

Problem 2 : Fluctuations (20 points)

Consider a system described by the grand canonical ensemble, where Ξ is the grand partition function and μ is the chemical potential.

a) (3 points) Show that the average number of particles in equilibrium is

$$\langle N \rangle = \frac{k_B T}{\Xi} \left(\frac{\partial \Xi}{\partial \mu} \right)_{T,V}. \tag{3}$$

b) (3 points) Show that the mean-square number is

$$\langle N^2 \rangle = \frac{(k_B T)^2}{\Xi} \left(\frac{\partial^2 \Xi}{\partial \mu^2} \right)_{T,V}. \tag{4}$$

c) (4 points) Using the above results, show that the relative root-mean-square fluctuation $\sigma/\langle N \rangle \equiv \sqrt{(\langle N^2 \rangle - \langle N \rangle^2)}/\langle N \rangle$ is

$$\frac{\sigma}{\langle N \rangle} = \sqrt{\frac{k_B T}{\langle N \rangle^2} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V}}. \tag{5}$$

d) (5 points) By applying the above a), b) and c) to the ideal gas, express b) and c) as functions of $\langle N \rangle$. Sketch a plot of $\sigma/\langle N \rangle$ as a function of $\langle N \rangle$.

e) (5 points) By applying the above a), b) and c) to the harmonic oscillators, express b) and c) as functions of $\langle N \rangle$. Sketch a plot of $\sigma/\langle N \rangle$ as a function of $\langle N \rangle$.

Problem 3 : Isothermal-isobaric Ensemble (20 points)

a) (7 points) Using the canonical ensemble partition function and approaching the summation to an integral, obtain the partition function Δ for an ideal gas in the isothermal-isobaric ensemble [Hint: $\int_0^\infty e^{-x} x^N dx = N!$].

b) (7 points) Obtain the entropy for the isothermal-isobaric ensemble using the information entropy description and in terms of the average volume, the average energy and the partition function. Also, obtain the Gibbs free energy in these terms.

c) (6 points) Obtain $\langle E \rangle$, $\langle V \rangle$ and the Gibbs free energy for the monoatomic ideal gas in the isothermal-isobaric ensemble,

$$\langle E \rangle = -\left(\frac{\partial \ln \Delta(T, P, N)}{\partial \beta} \right) \tag{6}$$

$$\langle V \rangle = -k_B T \left(\frac{\partial \ln \Delta(T, P, N)}{\partial P} \right). \tag{7}$$