ChE677 Introduction to Polymer Physics and Rheology

Assignment 2 **Due Date: 6 September 2007**

1. The fundamental equation $S = S(L, E, n)$ (S: entropy; L: length; n: number of molecules) for a rubber band is either

$$S = L_0\gamma \left(\frac{\theta E}{L_0}\right)^{1/2} - L_0\gamma \left[\frac{1}{2}\left(\frac{L}{L_0}\right)^2 + \frac{L_0}{L} - \frac{3}{2}\right], \tag{1}$$

where $L_0 = nl_0$; or

$$S = L_0\gamma \exp[\theta n E/L_0] - L_0\gamma \left[\frac{1}{2}\left(\frac{L}{L_0}\right)^2 + \frac{L_0}{L} - \frac{3}{2}\right] \tag{2}$$

where γ, l_0 and θ are constants. L is the length of the rubber band, and n is the number of molecules in the rubber band.

   (a) Which of the possibilities is thermodynamically acceptable, and why ?

   (b) For the model which is thermodynamically acceptable, derive a relation for the force $f(T, L/n)$.

2. For an ideal gas at constant N, V, E, the entropy of the system is given by (result from statistical mechanics)

$$S(N, V, E) = k_B \log \left[\frac{(2\pi)^{3N/2}}{(3N/2-1)!}(2mE)^{3N/2} V^N \frac{1}{N!}(2\pi h)^{-3N}\frac{1}{2}\right] \tag{3}$$

where h is the Planck's constant, E is the energy, k_B is the Boltzmann's constant and m is the mass of a single molecule.

Consider two boxes A and B which are under thermal contact, but are isolated from the surroundings. Box A has energy E_A and N_A number of gas molecules. Box B has energy E_B and N_B number of gas molecules. Let the boxes be in thermal contact for a long time so that they can equilibrate. Then we shut the thermal contact between the two boxes thereby isolating them and let each system come to equilibrium separately.

Let $E_{tot} = E_A + E_B$. Then, $S_{tot}(E_A) = S_A(E_A) + S_B(E_{tot} - E_A)$. Using the result for the entropy of an ideal gas, what is the most likely value of E_A ?

3. Suppose we have insulated a tank of gas with a partition down in the middle, N molecules on the left and none on the right. Each side has a volume V. At some time an internal clock-work mechanism opens the partition and the gas rearranges. What happens to the entropy, and by how much does it change ? (Use the entropy expression for an ideal gas from the previous problem).

4. Consider an isolated system, but with a sliding piston (see figure 1). The left side consists of N gas molecules initially at temperature T. The right side is empty except for the spring. The system is completely isolated from the surroundings. When the piston is at L the spring exerts a force f directed to the left. Suppose we initially clamp the piston to a certain position $x = L$ and let the gas come to equilibrium.

   (a) Now unclamp the piston and let it freely slide to a new position at $L - \delta$ clamp it there and again let the system come to equilibrium ($\delta \ll L$). Find the difference in entropy between the old and new states.

(b) Suppose we unclamp the piston and let it go where it likes. Its position will wander thermally, but most likely it will be found in a position L_{eq} at equilibrium. Find the position. At this equilibrium position, calculate the force per unit area exerted by the spring on the gas. This must be equal to the pressure exerted by the gas on the piston. What is the relation you get for the pressure in the gas ? Does it look familiar ?

Use the expression for the entropy of the ideal gas given in the previous question.

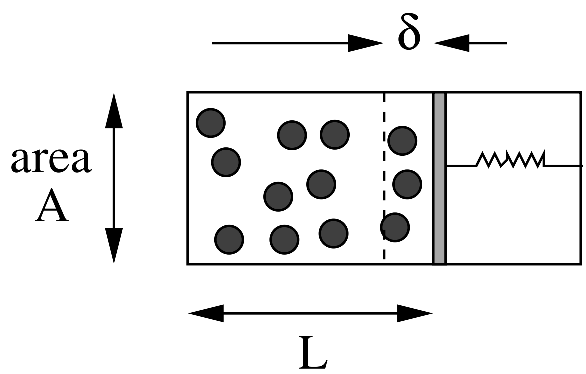

Figure 1: Schematic for problem 4

5. Suppose a microscopic ball (e.g. a colloidal particle!) is tied elastically to some point and is free to move in one dimension (along the x-direction shown in the figure 2). The ball's microstate is described by its position x and velocity v. Total energy $E(x, v) = \frac{1}{2}(mv^2 + k(x - x_o)^2)$ where m is the mass of the ball, k is the spring constant of the elastic spring, and x_o is the rest length of the spring. From the Boltzmann distribution at equilibrium, find the average energy $\langle E \rangle$. What will happen if the ball is allowed to move in 3 directions ? (use equipartition of energy).

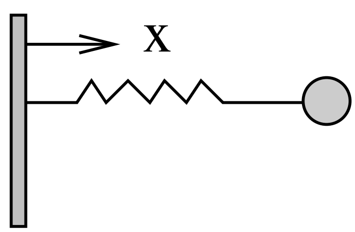

Figure 2: Schematic for problem 5

6. Calculate $\langle (x - x_o)^2 \rangle$ for the colloidal particle (previous problem). The above problem is a good model for a colloidal particle present in an elastic medium (such as the cytoskeleton present in our cells). It is now possible to experimentally measure $\langle (x - x_o)^2 \rangle$ and this turns out to be 35 nm at room temperature (300 K). What is the spring constant of the 'spring' ?