Problem Set 4

Due Wednesday Oct 8, 2014

4.1 Equilibrium Fluctuations

Consider a monatomic ideal gas consisteing of N gas atoms in a container of volume V.

(a) How does the number $\Omega(E, V, N)$ of accessible microstates at energy E and volume V depend on E and on V? You may ignore numerical prefactors that depend on N only.

(b) The gas brought in thermal equilibrium with a "heat reservoir" at tmperature T. (A heat reservoir is a macroscopic system that is so large that its temperature remains unaffected if energy is absorbed or emitted.) As a result the enrgy E of the gas shows random fluctuations as a function of time. For these fluctuations, find the average energy $\bar{E}$ and the variance of the energy $var(E) = \overline{(E - \bar{E})^2}$.

(c) The cas is brought in thermal equilibrium with a heat and pressure bath at temperature T and pressure p. (A "pressure reservoir is a macroscopic system that is so large that its pressure remains unaffected if its volume is changed. Our local atmosphere is an example of a heat and pressure reservoir.) As a result, the energy E and the volume V of the gas show random fluctuations as a function of time. For these fluctuations, find the averages $\bar{E}$ and $\bar{V}$ and the variances $var(E)$ and $var(V)$. Are the fluctuations of enegy and volume statistically independant?

4.2 Calorimetry

Reif §4.2

4.3 Pulling on a Polymer

With the help of (bio)chemical methods, it has become possible to study the mechanical properties of long molecules or polymers, such as proteins or DNA. In this exercise, you are asked to consider one such molecule. Although a polymer is only one molecule, it has many degrees of freedom because it is flexible. That's why we can use methods from statistcal mechanics to describe polymers.

One end of the polymer is attached to a substrate. To the other end, which is free to move, a dipolar marker is attached. With the hlep of a uniform electric field gradient, a constant force can be exerted on the dipole.
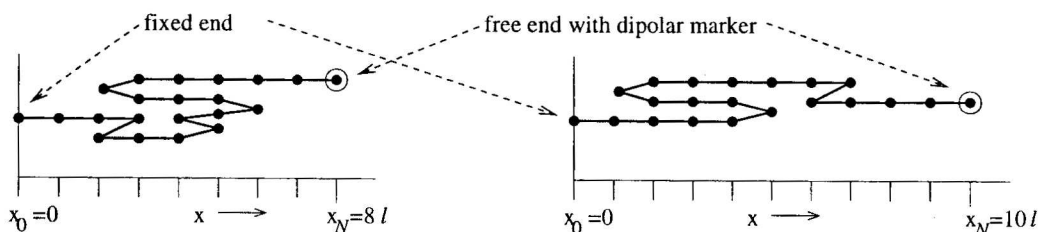
We will model the polymer as a one-dimensional chain of N links of length l. Each link can point left or right. Two examples of the possible configurations of the polymer are shown in the figure below for $N = 20$. The real polymer is of course has a much larger number of links N. (In the figure for clarity a second dimension has been added.) One end of hte chain is kept at fixed position $x_o = 0$ (since it is attached to the substrate), whereas the other end at position x_N, is free to move.

The energy of the polymer is

$$E = -ax_N \tag{1}$$

The constant a is positive and proportional to the marker's dipole moment and the electric field gradient. Since $-Nl \leq x_N \leq Nl$, the energy E can take values between $-Nal$ and Nal.

(a) Show that for $N \gg 1$ the number of "microstates" (configurations) $\Omega(E)$ for which the energy of the polymer is between E and $E + \delta E$ is equal to

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

if $al \ll \delta E \ll E$ and $|E| \ll Nal$.

(b) Find the entropy of S of the polymer at energy E.

(c) The polymer is immersed in a solution at temperature T. If the polymer and the surrounding liquid are in thermal equilibrium, what is the (average) energy $\bar{E}$ of the polymer? what are the fluctuations of the energy?

(d) What is the force the polymer exerts on the marker? Formulate your answer in terms of the polymer's extension x_N, the temperature T, the link length l, and the numer of links N.

4.4 Ideal Work

Reif §5.2

4.5 Elastic Rod

Reif §5.14

4.6 Van der Waals Gas

Van der Waals proposed an equation of state for a nonideal gas,

$$(p + a(N/V)^2)(V - Nb) = NkT.$$

This equation is obtained from the ideal gas law $pV = NkT$ by subtracting a constant Nb from the volume V, which models the effect of the short-range repulsive potential between the gas molecules, and tho add a density-dependent term $a(N/V)^2$ to the pressure, which represents the effect of the long-range attraction between the gas molecules.

In this exercise we consider the free expansion of a Van der Waals gas. (Free expansion is an expansion at a fixed total energy E.)

(a) Express $(\partial T/\partial V)_E$ in terms of p, T, $(\partial p/\partial T)_V$, and C_V.

(b) Express $(\partial S/\partial V)_E$ in terms of p and T.

(c) Calculate the temperature change $\Delta T = T_1 - T_2$ for the free exapansion from volume V_1 to volume V_2. Give explicit results for the Van der Waals gas. You may assume that the heat capacity C_V is temperature-independent.

4.7 Email three questions