
Problem Sheet 6

for the lecture “Statistical Physics”, Master course “Computational Science”, year 2007/08

due date: Tuesday, December 11, 2007

Problem 1

3.5 points

Consider a classic system of N diatomic molecules without interaction among them. The particles are in a container of volume V at temperature T . The Hamiltonian of a molecule is

$$H(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{(\vec{p}_1^2 + \vec{p}_2^2)}{2m} + \epsilon |r - r_o| \quad (1)$$

where \vec{p}_i and \vec{r}_i are the moments and the coordinates of the two atoms of the molecule, $r = |\vec{r}_1 - \vec{r}_2|$, ϵ and r_o are constant parameters. Find the Helmholtz free energy, the specific heat at constant volume C_V , and the mean square molecular diameter $\langle (\vec{r}_1 - \vec{r}_2)^2 \rangle$. What is the behaviour of the mean square molecular diameter when the temperature is increased?

Problem 2

3.5 points

In class we have calculated the the partition function of an ideal gas by considering only the *translational* energy of the particles. As long as we are looking at mono-atomic gases this procedure is correct, but molecules also have *rotational* degrees of freedom and an energy associated with it. Consider therefore a linear molecule, such as carbon monoxide, made up of two different atoms, one carbon and one oxygen separated by a distance d . The rotational motion of such a diatomic molecule is quantised, and the energy levels are given by

$$\epsilon_\ell = \frac{\hbar^2 \ell(\ell + 1)}{2I}.$$

Here, $I = \mu d^2$ is the moment of inertia of the molecule about the axis perpendicular to the molecule's linear axis, and $\ell = 0, 1, 2, \dots$ is the quantum number associated with the orbital angular momentum. Each energy level of the rotating molecule has degeneracy $g_\ell = 2\ell + 1$. This means that there is one $\ell = 0$ state, three $\ell = 1$ states, five $\ell = 2$ states, et cetera.

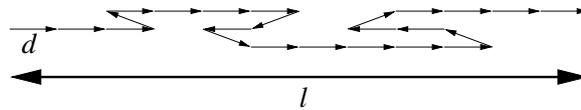
1. Write down the canonical partition function for the rotational states of one molecule.
2. The partition function cannot be summed up analytically. Approximate it for low temperatures, i.e. $\tau \rightarrow 0 \Leftrightarrow \frac{\hbar^2}{2I\tau} \gg 1$. Do this by truncating the sum after the second term.
3. Evaluate the partition function approximately also in the limit of high temperature, i.e. $\tau \rightarrow \infty \Leftrightarrow \frac{\hbar^2}{2I\tau} \rightarrow 0$, by converting the sum to an integral. *Hint: The resulting integral is solved easily after substituting to the new variable $y = 2\ell + 1$.*
4. Calculate the free energy F and the entropy σ in both limits.

5. Calculate the energy U and the heat capacity at constant volume, C_V , in the high and low temperature limit. You should observe that the rotational contribution to the heat capacity, which you have calculated, approaches 1, when $\tau \rightarrow \infty$.
6. Sketch the behaviour of $U(\tau)$ and $C_V(\tau)$, showing the limiting behaviours for $\tau \rightarrow \infty$ and $\tau \rightarrow 0$.

Problem 3

3 points

A simple picture of a rubber band is that of a single long chain of linking groups of atoms, with the links oriented in any direction. When the band is pulled such that the chain of atoms is completely linear, there is only one possible arrangement and the entropy is zero. But when the rubber band is all tangled up, there is a huge number of arrangements of the links leading to a large entropy.



Instead of dealing with a rubber chain in three dimensions, we simplify things by assuming that the links lie in only two directions, either in the direction of increasing z or in the opposite direction. We hence consider a “one-dimensional polymeric chain” of N links. n_+ describes the number of links pointing in the positive z -direction and n_- the number of links pointing in the negative z -direction; $N = n_+ + n_-$. Each link has got the length d . The total extension of the rubber band, i.e. the distance from one end of the chain to the other, is l .

1. There can be of course many different ways of ending up with n_+ links in the $+z$ direction. Compare this situation with the spin system discussed at the beginning of the lecture! What does the multiplicity function $g(N, n_+)$ look like?
2. Calculate the entropy $\sigma(N, n_+)$.
3. The total extension is defined as $l = (n_+ - n_-)d = (2n_+ - N)d$. For convenience introduce the rescaled extension $x = \frac{l}{Nd}$, $0 \leq x \leq 1$. Show that the following relations are true:

$$\frac{n_+}{N} = \frac{1+x}{2} \quad ; \quad \frac{n_-}{N} = \frac{1-x}{2} .$$

4. By using these expressions, you should (after Stirling) end up with the entropy

$$\sigma(N, x) = -N \left\{ \left(\frac{1+x}{2} \right) \ln \left(\frac{1+x}{2} \right) + \left(\frac{1-x}{2} \right) \ln \left(\frac{1-x}{2} \right) \right\} .$$

5. The differential of the internal energy is given by

$$dU = \tau d\sigma + f dl ,$$

where f is the external force (tension) exerted on the line and dl the infinitesimal change in polymer length. Therefore, $f dl$ is the work done by the tension. From that relation we get

$$\frac{f}{\tau} = - \left(\frac{\partial \sigma}{\partial l} \right)_U .$$

Show that this leads to the force-extension-relation

$$f = \frac{\tau}{2d} \ln \left(\frac{1+x}{1-x} \right) \quad \left(\text{ or equivalently: } x = \tanh \frac{fd}{\tau} \right).$$

6. Assume that $x = \frac{l}{Nd}$ is sufficiently small. For that case expand the logarithm (or the hyperbolic tangent) according to its Taylor expansion to the lowest order. How does the tensional force f depend on the temperature and the extension l ?
7. What happens to the rubber band if one heats it up while keeping the tension f constant? Does this behaviour surprise you? Find a physical explanation!

