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8.044 Statistical Physics I
Spring 2008

Problem Set #8

**Problem 1:** Torsional Pendulum using Canonical Ensemble
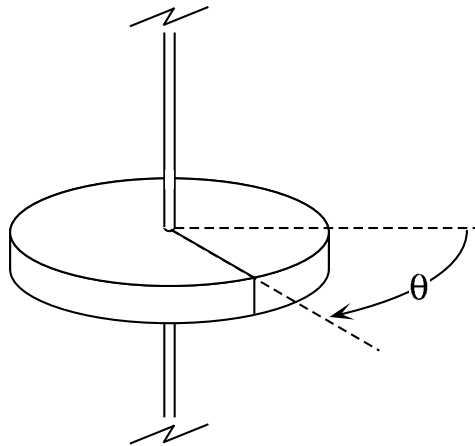
In order to measure a certain physical quantity it is necessary to know the equilibrium angle θ_0 of a torsional pendulum. θ_0 is determined by the minimum in the potential energy of the pendulum $V(\theta) = \frac{1}{2}K(\theta - \theta_0)^2$. The pendulum when rotating has a kinetic energy $T = \frac{1}{2}I\dot{\theta}^2$ where $\dot{\theta} \equiv d\theta/dt$. The precision with which θ_0 can be found is limited because the pendulum is in thermal equilibrium with its environment at a temperature T.

Find the root-mean-square uncertainty $< (\theta - \theta_0)^2 >^{1/2}$ associated with a measurement of θ due to classical thermal noise.

Problem 2: Neutral Atom Trap

A gas of N indistinguishable classical non-interacting atoms is held in a neutral atom trap by a potential of the form $V(r) = ar$ where $r = (x^2 + y^2 + z^2)^{1/2}$. The gas is in thermal equilibrium at a temperature T.
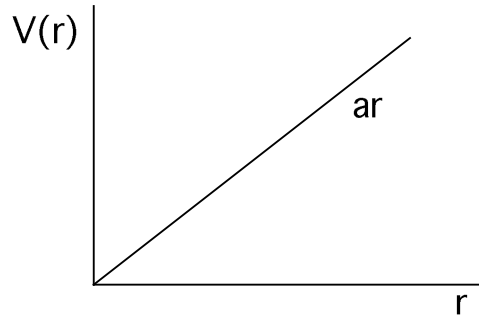
a) Find the single particle partition function Z_1 for a trapped atom. Express your answer in the form $Z_1 = AT^\alpha a^{-\eta}$. Find the prefactor A and the exponents α and η. [Hint: In spherical coordinates the volume element $dx\, dy\, dz$ is replaced by $r^2 \sin\theta\, dr\, d\theta\, d\phi$. A unit sphere subtends a solid angle of 4π steradians.]

b) Find the entropy of the gas in terms of N, k, and $Z_1(T, a)$. Do not leave any derivatives in your answer.

c) The gas can be cooled if the potential is lowered reversibly (by decreasing a) while no heat is allowed to be exchanged with the surroundings, $dQ = 0$. Under these conditions, find T as a function of a and the initial values T_0 and a_0.

Problem 3: The Hydrogen Atom

The bound electronic energy states of the hydrogen atom may be described by the set of quantum numbers (n, l, m_l) where the energy is given by $\epsilon_{n,l,m_l} = -A/n^2$ with $A = 13.6$ eV. The allowed values for the quantum numbers are:

$$
\begin{aligned}
n &= 1, 2, 3, 4, ... \\
l &= 0, 1, 2, 3, ..., n-1 \quad \text{(for a given } n\text{)} \\
m_l &= -l, -l+1, ..., l-1, l \quad \text{(for a given } l\text{)}
\end{aligned}
$$

a) Find the ratio of the number of atoms in the first excited energy level to the number in the lowest energy level at a temperature T. [Hint: Be careful of the difference between energy levels and states of the system.] Evaluate this for $T = 300K$ and $T = 1000K$.

b) To find the actual fraction of atoms in any given state one needs the partition function. Show that the partition function diverges, even when the unbound states are neglected.

c) Any ideas why statistical mechanics does not seem to work for this, one of nature's simplest systems?

Problem 4: Two-Dimensional H_2 Gas
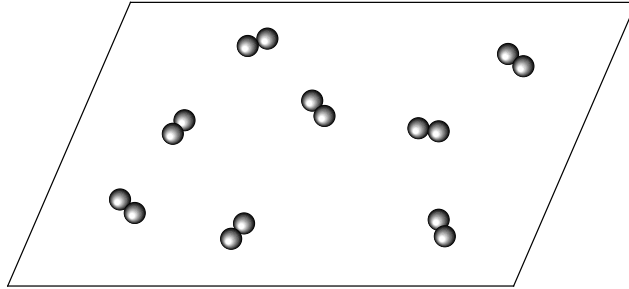
N molecules of molecular hydrogen H_2 adsorbed on a flat surface of area A are in thermal equilibrium at temperature T. On the surface they behave as a non-interacting two-dimensional gas. In particular, the rotational motion of a molecule is confined to the plane of the surface. The quantum state of the planar rotation is specified by a single quantum number m which can take on the values 0, ± 1, ± 2, ± 3, ± 4, etc. There is one quantum state for each allowed value of m. The energies of the rotational states are given by $\epsilon_m = (\hbar^2/2I)m^2$ where I is a moment of inertia.

a) Find an expression for the rotational partition function of a single molecule. Do not try to reduce it to an analytic function.

b) Find the ratio of the two probabilities $p(m = 3)/p(m = 2)$.

c) Find the probability that $m = 3$ given that $\epsilon = 9\hbar^2/2I$. Find the probability that $m = 1$ given that $\epsilon \leq \hbar^2/2I$.

d) Find the rotational contribution to the internal energy of the gas in the high temperature limit where $kT \gg \hbar^2/2I$.

Problem 5: Adsorption on a Realistic Surface

It is unlikely that a clean crystalline face of a real solid would present a flat, featureless landscape to a particular adsorbed atom similar to the model surface assumed in the previous problem. In reality it is more likely that the adsorbed atom would see an energy topography which mirrors the complex atomic structure of the surface. Under these circumstances one often finds that there are only a finite number of

geometrically different sites to which the adsorbed atom may be bound, each with a different binding energy. If these binding energies are comparable to the thermal energy kT, the adsorbed atom may hop from site to site, executing a random walk across the surface.

For simple materials, or ones of technological importance, the structure of the surfaces has been determined and the possible binding sites located for particular adsorbed species. The binding energies of those sites, however, are very hard to determine. Experimental measurements of these binding energies would be valuable to theorists who are trying to make calculations of the electronic structure of the surface and to other scientists who are trying to model surface processes such as growth and catalysis.

The technique of scanning tunneling microscopy (STM) has made it possible to image the surface structure of materials on the atomic scale. The technique also allows one to locate and identify individual foreign atoms adsorbed on the surface. The normal procedure is to move the tip in a raster scan pattern in order to image a rectangular region of the surface. The figure below shows images of several adsorbed molecules on a particular surface of a silicon crystal.

A new development allows one to lock the tip in position above a given foreign atom and follow it as it hops from site to site across the surface. By measuring the fraction of time spent on the different adsorption sites, one can determine the adsorption energies. We will examine here how this is accomplished.

First, we must introduce a new concept which is critical to the application of statistical mechanics to a number of real problems. A process is said to be *ergodic* if statistics determined by examining the behavior of a single system over a long period of time (this is what one usually has in practice) are identical to those that would be determined from an ensemble of similarly prepared systems (the basis for our development of statistical mechanics). A simple consequence of ergodicity is that time

averages are equivalent to ensemble averages. Most systems are ergodic, but some are not. For the purposes of this course we will assume that the systems we study are ergodic; the study of non-ergodic systems is left for a more advanced course. You, however, should be aware that we are making this assumption when comparing the results of statistical mechanics with certain experiments, such as the one described in this problem.

Assume that a certain atom when adsorbed on a given surface of a particular material can occupy any one of 5 geometrically different sites, labeled 1 through 5. There are equal numbers of sites 1, 2, and 5. There are twice as many 3 sites as 1 sites, and twice as many 4 sites as 1 sites. An STM measurement follows one adsorbed atom and finds the following results for the fraction of time spent on each type of site when the material is at a temperature of 300K.

Site Type	1	2	3	4	5
Fraction of Time	0.10	0.15	0.15	0.20	0.40
Number of Sites	N	N	2N	2N	N

In the following, assume that the number of adsorbed atoms is much smaller than the number of available sites. Under these conditions, one can do the statistics by having only one adsorbed atom on the surface at a time.

a) Which site has the lowest energy; that is, which site has the largest binding energy?

b) Find the energy of each of the sites relative to that of the most tightly bound site, $E(i) - E(\text{lowest})$. Express your energies in K (that is, divide by Boltzmann's constant k).

c) If the experiment were repeated with the sample at liquid nitrogen temperature (77K), what would be the fraction of time spent at each type of site?

d) While doing the experiment it is possible to make a histogram of the the different dwell times spent on a given type of site and thereby measure the probability of the waiting time to escape, $p(t)$. Can you predict the functional form of $p(t)$ based on our discussion of Poisson processes earlier in the term?