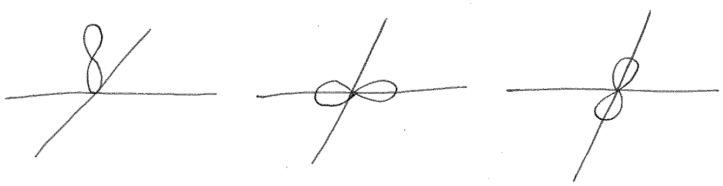
Due May 1, Thursday

Problem 1 (30 points) *Microcanonical ensemble and canonical ensemble.* N diatomic molecules are stuck on the surface of a crystal of a square symmetry ("square lattice"). Each molecule is positioned at the vertex of a square, where four identical squares meet, as part of the square lattice on the surface of the crystal. Each molecule is immobile, but it has three possible orientations: it can either lie flat on the surface, or stand up along the z direction, the direction normal to the surface. When it lies flat on the surface, it can lie only in one the two orthogonal directions, the two major axes of the square lattice. We shall assume that each stuck molecule is completely independent of one another (e.g., due to a low density). The energy of each molecule is given by $\Delta > 0$, when it is up, and 0, when it is lying down.



(a) Use the microcanonical ensemble, to calculate the number of possible states, $\Omega(E, N)$, and the entropy $S(E, N)$.

(b) Calculate the heat capacity $C(T)$ and sketch it. Find the limiting behaviors (non-zero leading order terms) for $C(T)$ as $T \to 0$ and $T \to \infty$.

(c) This problem can be analyzed using different ensembles as well. Let us use the canonical ensemble, for example. It is actually quite convenient to consider the canonical ensemble of just one molecule. Find the partition function, $Z_1(T)$, for one molecule.

(d) Show that $Z(T, N) = Z_1(T)^N$, where $Z(T, N)$ is the full partition function for N molecules.

(e) Find the entropy from $Z(T, N)$ (and F), and verify that your result agrees with the result obtained using the microcanonical ensemble in part (a).

(f) Find the temperature of this system as a function of E and make a plot of T as a function E. Is there a negative temperature regime? Provide a qualitative explanation of your answer, using E, S, and their relation ($dE = TdS$; note that variables such as P and V need not be considered in this problem, since we assumed that molecules are immobile).

(g) What is the largest possible value of E at any positive temperature? Is it what you expected? Explain the value in simple words that catch the relevant physics, by starting with the Helmholtz free energy F.

Problem 2 (30 points) *Under pressure.* A classical ideal gas is contained inside a cylinder with the cross sectional area A. The cylinder is mounted in the upright position and is very long. The bottom of the cylinder is closed, while the top is open. However, there is a freely sliding piston lid, containing the gas between it and the bottom of the cylinder. The lid has mass M and surface area A. Its variable vertical position is y, measured from the bottom of the container. Ignore gravitational force for gas molecules. However, the lid does experience the gravitational force. We assume that M is so large that the atmospheric pressure from the outside air can be neglected. The cylinder does conduct heat and so the temperature of the whole system is that of the atmosphere, in equilibrium.

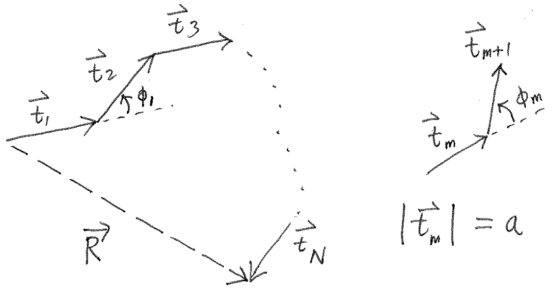
(a) Find the "partition function Z" for the combined system (gas plus lid), in terms of the above parameters, $\lambda = h/\sqrt{2\pi m k_B T}$ for the gas, and relevant fundamental constants.

(b) Show that the potential $-k_B T \log Z$ splits nicely into two contributions, one for gas and the other for the lid.

(c) Consider the gas part of the potential $-k_B T \log Z$. What free energy does it correspond to: the Helmholtz free energy, or the Gibbs free energy, of the gas? Is it consistent with the basic principle of the statistical mechanics: i.e., the principle that governs which partition function or potential results under which constraints?

(d) Find how your results get modified, if the outside atmospheric pressure is not negligible, but is kept at a constant value independent of time.

Problem 3 (30 points) *Polymer and persistent length.* A polymer can be modeled as small rods (i.e., monomers) of length a linked in succession, with orientational degrees of freedom of each rod relative to its neighboring rods. This angular degrees of freedom can be described by ϕ_m's shown in the diagram below.



We can write down the model Hamiltonian as

$$H = \sum_{m=1}^{N-1} f(\vec{t}_m \cdot \vec{t}_{m+1}) = \sum_{m=1}^{N-1} h(\cos\phi_m).$$

Here, we are including interactions of adjacent rods only and $-\pi < \phi_m < \pi$. The function h (or f) is left unspecified, except that $h(x) = 0$ at $x = 1$, $h \geq 0$ and h does not decrease at any point as x decreases over its full range, i.e., from 1 to -1. We imagine that this polymer molecule is immersed in a liquid. We are not interested in any interaction between the polymer molecule and the liquid, which would be approximately independent of the polymer configuration, which is what we are studying with the above Hamiltonian. In this problem, we will use the semi-classical statistical mechanics to analyze the properties of such a polymer. In particular, you are recommended to approach this problem using the canonical ensemble.

(a) A central quantity of interest is the *correlation* between the two vectors $\vec{t}_m$ and $\vec{t}_n$, where m, n are any of $1, \ldots, N$. Considering the rotational symmetry of the whole system, the following correlation is useful[1].

$$\left\langle \vec{t}_m \cdot \vec{t}_n \right\rangle_c \equiv \left\langle \vec{t}_m \cdot \vec{t}_n \right\rangle - \left\langle \vec{t}_m \right\rangle \cdot \left\langle \vec{t}_n \right\rangle .$$

Show that the ensemble average $\left\langle \vec{t}_m \right\rangle = 0$, for any $m = 1, \ldots, N$.

(b) Show that

$$\left\langle \vec{t}_m \cdot \vec{t}_n \right\rangle = a^2 \left\langle \cos\phi_1 \right\rangle^{|m-n|} .$$

Here, you are merely to take note of the independence of ϕ_m variables and reduce the full ensemble average expression to an expression involving an ensemble average of a *single* independent variable, ϕ_m ($m = 1$ is taken in the expression above, without loss of generality).

(c) Show that the correlation is given by

$$\left\langle \vec{t}_m \cdot \vec{t}_n \right\rangle_c = a^2 \exp\left(-\frac{|m-n|}{\xi(T)} \right)$$

where $\xi(T) > 0$ is a function of $\langle \cos\phi_1 \rangle$. You must find this relationship between $\langle \cos\phi_1 \rangle$ and $\xi(T)$, and show that $\xi(T) > 0$.

(d) $\xi(T)$ is an example of a "correlation length," since the correlation between the rods dies off quickly if $|m - n| \gg \xi(T)$. Dimension-wise, $a\xi(T)$ has the dimension of length, and it may be a better quantity to be called the correlation *length*. In polymer physics, this length scale $a\xi(T)$ is known as the *persistence length*. What do you expect the value of $\xi(T)$ to be in the high temperature limit? How about in the low temperature limit (assuming that $h(x) \geq 0$ is zero only at $x = 1$)? Explain your answers in view of the integral expressions for $\xi(T)$ and $\langle \cos\phi_1 \rangle$.

[1]Here, we are *defining* $\left\langle \vec{A} \cdot \vec{B} \right\rangle_c \equiv \sum_i \langle A_i, B_i \rangle_c$, where $i = x, y, z$.

(e) Consider the end-to-end displacement vector $\vec{R} = \sum_m \vec{t}_m$. In analogy with the scalar correlation that we defined above, the rotational symmetry of the system suggests that we can define the *scalar* variance of $\vec{R}$ as

$$\left\langle \vec{R}\cdot\vec{R}\right\rangle_c = \left\langle \vec{R}\cdot\vec{R}\right\rangle - \left\langle \vec{R}\right\rangle\cdot\left\langle \vec{R}\right\rangle.$$

Show that, in the limit of $N\to\infty$,

$$\left\langle \vec{R}\cdot\vec{R}\right\rangle_c \to Na^2\coth\frac{1}{2\xi}.$$

Discuss this result in the high temperature limit and the low temperature limit, making use of your answers in the previous part.

(f) At high temperatures, the correlation is weak, and the orientation of each rod can be seen to do a "random walk." As temperature is lowered, the correlation becomes strong ($\xi(T)$ increases). When the correlation length is finite, we would expect that the central limit theorem hold when $N\to\infty$. Obtain the probability density function $p(\vec{R})$, when $N\gg 1$ under these assumptions. Note that, by symmetry, $p(\vec{R})$ should be an expression dependent only on $R\equiv|\vec{R}|$ and $\langle R^2\rangle$.

(g) Suppose the polymer is pulled apart by an external force so that the Hamiltonian acquires a new term $-\vec{F}\cdot\vec{R}$, where $\vec{F}$ is the external force. Assuming that $\vec{F}$ is small, show that

$$\left\langle \vec{R}\right\rangle = \frac{\vec{F}}{K}+O(F^3), \qquad \text{Hooke's law}$$
$$\frac{1}{K} = \frac{\beta}{2}\left\langle \vec{R}\cdot\vec{R}\right\rangle_{c,0},$$

where the second subscript 0 means $\vec{F}=0$. This last expression is an example of the so-called "fluctuation-dissipation theorem[2]."

Problem 4 (10 points) *van Leeuwen's theorem.* According to semi-classical statistical mechanics, there cannot be any magnetism in equilibrium. This fact is known as van Leeuwen's theorem. You are to prove this theorem, here. To do so, first assume that the initial Hamiltonian consists of the kinetic term, $K(\vec{p}_i)$, and the potential term $U(\vec{q}_i)$, for $i=1,\ldots,N$. Show that in the presence of the magnetic field, $\vec{B}$, the partition function is *not* dependent on $\vec{B}$.

[2]This is to be distinguished from fluctuation theorems, which were mentioned in lecture, lecture note, and past homework. We have yet to discuss the fluctuation-dissipation theorem in class—we will do so in due course.