Physics 112, Fall 2017: Holzapfel
Problem Set 3 (6 problems). Due Friday, September 22, 5 PM

Problem 1: **Energy fluctuations**
(a) Kittel, Problem 3.4

(b) Consider the case of the ideal gas and calculate $\frac{\sqrt{<(\Delta U)^2>}}{U}$. For what value of N do the fluctuations become of order 10 percent of the total energy?

Problem 2: **Diatomic molecules**
Kittel, Problem 3.6

Problem 3: **DNA denaturation**
a) Kittel, Problem 3.7

b) A more realistic model allows for the DNA to unzip from either the left or the right side of the molecule. Calculate the partition function for this case.

Problem 4: **Rubber Band**
Kittel, Problem 3.10

Problem 5: **Entropy of Mixing**
Consider two ideal monatomic gases. The partition function for each can be be written as:

$$Z_{N_a} = \frac{Z_a^{N_a}}{N_a!},\ Z_{N_b} = \frac{Z_b^{N_b}}{N_b!}; \tag{1}$$

where Z_a is the partition function of a single particle of gas a of which there are N_a particles, and Z_b is the partition function of a single particle of gas b of which there are N_b particles. Now assume that a barrier separating the two different chambers of gas is removed and they are combined in a final system with total number of particles, $N = N_a + N_b$.
(a) Write down expressions for the partition function for the combined system in the two cases in which the particles are distinguishable and indistinguishable.
(b) Calculate the free energy in the two cases assuming that $Z_a = Z_b$.
(c) Show that in the case in which particles a and b are distinguishable, there is an additional mixing entropy term for the combined system:

$$S_{mix} = -k_b \left[N_a \ln\left(\frac{N_a}{N}\right) + N_b \ln\left(\frac{N_b}{N}\right) \right]. \tag{2}$$

(d) Express your result from part (c) as the ratio of the multiplicities for the two cases after the gas has been mixed. Evaluate your expression for the case in which $N_a = N_b$.

Problem 6: **Thermal expansion and anharmonicity**
In this problem we want to derive a simple expression for the thermal expansion coefficient of a solid. To start off, we'll treat each atom as bound to its neighbors by a harmonic potential

$$U(x) = ax^2 \tag{3}$$

Here U(x) is the potential felt by a particular atom at a displacement x from its equilibrium position and "a" is a constant.

(a) Using the Boltzmann factor, write down an expression for $< x >$, the average displacement of an atom from its equilibrium position. Note that because the displacement is a continuous variable, your expression will look like the ratio of two integrals.

(b) Show that in this approximation, $< x >= 0$, independent of temperature. In other words, as you increase the temperature, the atoms oscillate more and more wildly, but the average displacement is always zero.

(c) You have thus shown that treating the nearest neighbor interactions as purely harmonic gives a thermal expansion coefficient equal to zero, which of course is incorrect. So let's suppose there are what are termed anharmonic terms in the potential. For example, you know a spring has potential energy $U = kx^2/2$ for small displacements. When x becomes large, higher order terms in this expansion become important so that $U = kx^2/2 - bx^3 + \cdots$. Thus suppose that

$$U(x) = ax^2 - bx^3 \tag{4}$$

Write down another formal expression for the average displacement $< x >$ as the ratio of two integrals.

(d) Approximate this expression to first order in b and thus find the thermal expansion coefficient in this model. You might find the following integral useful:

$$\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = \frac{3\sqrt{\pi}}{4\alpha^{5/2}} \tag{5}$$