These problems will serve the purpose of letting you carry out some statistical physics calculations for yourself. Hopefully you will realize how powerful these methods can be once you get over your natural fear of all those integrals!

Problem 1.

One very commonly encountered probability density is the Gaussian or normal distribution given by

$$w(x) = C e^{-\frac{x^2}{2\sigma^2}}.$$

Suppose we are measuring the x-position of a particle and the results scatter around according to a Gaussian distribution, with any value of x between negative infinity and positive infinity being possible, but those near where the distribution is maximum (i.e. near zero) being the most likely. Remember what w(x) actually means. The probability of finding the particle to lie between position x and position x + dx is just given by P(x, x + dx) = w(x)dx.

(a.) To become familiar with this function, calculate the value of the normalization constant *C*. If you look up the integral you will find that  $\int_{-\infty}^{\infty} e^{-a^2x^2} dx = \frac{\sqrt{\pi}}{a}.$ 

(b.) Show that the average value of x is 0, i.e  $\langle x \rangle = 0$ , as you would expect. (c.) Show that  $\langle x^2 \rangle = \sigma^2$ . The fact that  $\int_{-\infty}^{\infty} x^2 e^{-a^2x^2} dx = \frac{\sqrt{\pi}}{2a^3}$  should be useful. You can get this from the fact that  $\int_{-\infty}^{\infty} e^{-a^2x^2} dx = \frac{\sqrt{\pi}}{a}$  by taking the derivative of both sides with respect to *a*, which brings down a factor of  $x^2$  inside the integral, which is a nifty trick!

(d.) Show that the root-mean-square spread in the measured values of x will just equal  $\sigma$ . Root-mean-square spread means the square root of the average of the quantity  $(x - \langle x \rangle)^2$ , so in this case you already know the answer! This number measures how much you should expect results for x to bounce around from one measurement to the next.

Problem 2.

Probably the most fundamental and useful result from all of statistical physics is that the probability of finding a system in a particular state (call it state # *i*) is proportional to  $e^{-\frac{E_i}{k_BT}}$ , where  $E_i$  is the energy of the system when it is in state *i*. That is to say that the probability of finding the system in a particular state is given by  $P(\text{state } \# i) = C e^{-\frac{E_i}{k_BT}}$ . This theorem applies to any system that is in thermal equilibrium at temperature *T*. Such a system might be taken to be a single molecule among many in a container held at fixed temperature, or it might be taken to be the entire container of gas, or some fraction of it.

Of course, to find the actual probability we must impose the requirement that the sum of the probabilities for all possible states must be exactly 1.000, because the system must be in one of its states. It is this requirement that fixes the value of the constant C.

For quantum systems the idea of a state is naturally well-defined. For example, a one-dimensional harmonic oscillator has states that are defined by a single integer, *n*. When the oscillator is in state # *n*, it has energy  $E_n = (n+1/2)\hbar\omega$ , where  $\omega$  is the natural angular frequency of the oscillator, and  $\hbar$  is Planck's constant divided by  $2\pi$ , which is an exceedingly small number  $(1.05 \times 10^{-34}$  Joule seconds). The fact that  $\hbar$  is so small explains why we never notice that we can't give a harmonic oscillator whatever energy we like, but that actually we can only change its energy in increments of  $\hbar\omega$ . The lowest possible energy an oscillator can have is not zero as you might have expected but is instead equal to half the energy difference between levels.

(a.) Using the fact that the oscillator must be in one of its states, i.e. the sum of all the probabilities must be exactly 1.000, show that the probability of finding an oscillator (that is in thermal equilibrium at temperature T) to be in

state # *n* is given by  $P(n) = \left[1 - e^{-\frac{\hbar\omega}{k_B T}}\right] e^{-\frac{n\hbar\omega}{k_B T}}$ . (Hint: You should be trying to

sum a geometric series of the form  $1 + x + x^2 + ...$ , where x < 1 to find the normalization constant *C*, which is all I am asking for.)

(b.) Using the result of part (a.) find the average energy the oscillator has at temperature *T*. (You should get  $\frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\frac{\hbar\omega}{k_BT}}}{1 - e^{-\frac{\hbar\omega}{k_BT}}}$ , if you are sufficiently careful!) You will find it useful to know that  $\sum_{n=0}^{n=\infty} n e^{-nx} = \frac{e^{-x}}{[1 - e^{-x}]^2}$ . If you are mathematically inclined, you can prove this by taking the derivative of  $\sum_{n=0}^{n=\infty} e^{-nx}$ , with respect to x, which sum you already figured out how to calculate in part (a.)

(c.) Now let's try some numbers in our results. Consider diatomic hydrogen, as an oscillator (the two atoms can oscillate back and forth toward and away from each other). The natural angular frequency of this oscillation depends on the mass of the two atoms, and the effective spring constant of their interaction potential, and is about  $8.0 \times 10^{14}$  radians/second for diatomic hydrogen. How hot do you have to get a sample of molecular hydrogen in order for only half the molecules to remain in the lowest vibrational state?

## Problem 3.

Now let's examine the harmonic oscillator using classical physics, which you know and (hopefully) love! The one-dimensional oscillator can now have the spring (of spring constant *k*) extended by an amount *x*, and the point mass (of mass *m*) can be moving in either direction with velocity  $v_x = \dot{x}$ . The state of the oscillator is now not so well-defined as was our quantum oscillator, and we have to use a probability density that describes the chance of finding the position of the mass to be in the range of positions from *x* to x + dx while at the same time having velocity in the range  $v_x$  to  $v_x + dv_x$ . (This is called a joint probability density.) Now the famous theorem gives us this probability density as being  $w(x,v) = C e^{-\frac{(kx^2 + mv^2)}{2k_BT}}$ .

(a.) Show that the constant *C* is equal to 
$$\frac{\sqrt{km}}{2\pi k_B T}$$
 s/m<sup>2</sup>.

(b.) Find the average energy of the oscillator. You should get the result you expect from equi-partition, i.e.  $\frac{k_BT}{2}$  for potential energy and the same for kinetic energy. (Hint: Don't be discouraged by the integrals, they are just the Gaussian ones you used in the first problem, but you will have to be very careful with your algebra.)