Physics H190
Spring 2005
Homework 10
Due Wednesday, April 27, 2005

Reading Assignment: The lecture notes for this week contain the basics of the statistical mechanics of Gibbs and Einstein in the microcanonical ensemble, with some calculations on the ideal gas.

Note: I have changed my office hour from Tu 4–5 to Tu 5–6, since that seems to be more convenient for most people.

1. In class we worked out the entropy $S = k \ln \Omega$ for an ideal gas of noninteracting point particles, using the microcanonical ensemble. The result is given at the end of the lecture notes. In this problem we consider what happens if the particles have internal structure. We are thinking of a crude model of a diatomic molecule with equal masses, such as O_2. All the Hamiltonians in this problem are classical.

The Hamiltonian for two particles of equal mass m interacting by means of a harmonic oscillator potential can be written,

$$H = \frac{|\mathbf{p}_1|^2}{2m} + \frac{|\mathbf{p}_2|^2}{2m} + \frac{m\omega^2}{4}|\mathbf{r}_2 - \mathbf{r}_1|^2. \tag{1}$$

We write the potential energy with 4 in the denominator instead of 2, because otherwise the ω parameter of the potential would not be the frequency of vibrations. This is because the reduced mass of the system is $\mu = m/2$.

We do the following transformation on the coordinates and momenta of the two particles:

$$\begin{aligned} \mathbf{R} &= \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \qquad & \mathbf{P} &= \mathbf{p}_1 + \mathbf{p}_2, \\ \mathbf{r} &= \mathbf{r}_2 - \mathbf{r}_1, \qquad & \mathbf{p} &= \frac{\mathbf{p}_2 - \mathbf{p}_1}{2}, \end{aligned} \tag{2}$$

which is a canonical transformation (one which preserves the Poisson brackets). Physically, $\mathbf{R}$ is the center of mass position, $\mathbf{P}$ is the total momentum of the two-particle system, and $\mathbf{r}$ is the separation between the particles. After carrying out this coordinate transformation, the Hamiltonian becomes

$$H = \frac{|\mathbf{P}|^2}{2M} + \frac{|\mathbf{p}|^2}{2\mu} + \frac{\mu\omega^2}{2}|\mathbf{r}|^2. \tag{3}$$

It consists of a free particle Hamiltonian for the center-of-mass motion, plus an effective harmonic oscillator for the relative motion. Here $M = 2m$ is the total mass, and $\mu = m/2$ is the reduced mass of the system.

Now consider a gas of N noninteracting systems of this type, where N is very large, confined to a volume V. The Hamiltonian for the whole system is

$$H = \sum_{\alpha=0}^{N} \left(\frac{|\mathbf{P}_\alpha|^2}{2M} + \frac{|\mathbf{p}_\alpha|^2}{2\mu} + \frac{\mu\omega^2}{2} |\mathbf{r}_\alpha|^2 \right). \tag{4}$$

The center-of-mass coordinates $(\mathbf{R}_\alpha, \mathbf{P}_\alpha)$ correspond to the coordinates $(\mathbf{r}_\alpha, \mathbf{p}_\alpha)$ in the lecture notes (where structureless particles were treated), whereas the variables $(\mathbf{r}_\alpha, \mathbf{p}_\alpha)$ in this problem describe the harmonic oscillator, and are new. Thus, the system now has $6N$ degrees of freedom, and a $12N$-dimensional phase space (in the notes, we had $3N$ degrees of freedom and a $6N$-dimensional phase space).

(a) Using the method of the notes, compute the entropy $S = k \ln \Omega(E, \delta E)$. Drop all terms that are insignificant in the thermodynamic limit (one in which N, E and V all go to ∞, while holding their ratios constant).

Of course if there are no interactions between the molecules, then there is no mechanism (collisions) to bring about thermal equilibrium. Also, Einstein's assumption that the total Hamiltonian is the only constant of motion is incorrect, since the kinetic energy and internal (harmonic oscillator) vibrational energy of each molecule is conserved. We rationalize this by saying that there actually are interactions between the molecules, which are large enough to bring about thermal equilibrium, but small enough to be neglected in the computation of the entropy.

(b) In the microcanonical ensemble, the entropy S emerges as a function of (E, V, N). The total energy E is the same as the internal energy U of thermodynamics. Use

$$T\,dS = dE + P\,dV \tag{5}$$

to get an expression for the internal energy $E = E(T, V, N)$ and the equation of state $P = P(T, V, N)$.

The microcanonical ensemble is not as easy to use as the canonical ensemble (which we will discuss next week), but it is worthwhile to do at least one calculation with it once in your life.