Due May 6, Monday

Problem 1 (20 points) *Gas 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. However, 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) Comment on what happens to your results, if the outside atmospheric pressure is not negligible (but is kept constant at any time).

Problem 2 (20 points) *Microcanonical ensemble and canonical ensemble.* N diatomic molecules are stuck on the surface of a crystal of a hexagonal symmetry ("honeycomb lattice"). Each molecule is positioned at the vertex of a hexagon, where three identical regular hexagons meet, as part of the honeycomb lattice on the surface of the crystal. Each molecule can either lie flat on the surface, or it can stand up along the z direction, the direction normal to the surface. When it lies flat on the surface, it can be only in one the three definite directions, determined by the crystal structure. We shall assume that each stuck molecule is completely independent of one another (assume that their density is low). The energy of each molecule is given by $\varepsilon > 0$, when it is up, and 0, when it is flat.

(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 (leading order non-zero terms) for $C(T)$ as $T \to 0$ and $T \to \infty$.

(c) Derive the entropy, starting from the partition function $Z(T, N)$ of the canonical ensemble, and verify that you get the same result as above. Be sure to make use of Eq. 8.3.

(d) 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.

Problem 3 (20 points) Problem 3.30 of P & B. (Anharmonic oscillator.)

Problem 4 (20 points) Problem 3.35 of P & B. (Canonical ensemble.)

Problem 5 (10 points) Problem 3.43 of P & B. (Simple and interesting theorem! Straight application of the partition function technique.)

Problem 6 (25 points) Problem 4.10 & 4.11 of P & B. (Grand canonical ensemble problem involving gas adsorption on surface.)

Problem 7 (20 points) Problem 1.4 of P & B. (Excluded volume by interaction.)

Problem 8 (20 points) Problem 3.12 of P & B. (Excluded volume by interaction.) **Additional questions**: Find the energy E, and express S as $S(E, V, N)$ assuming that $\bar{V} = V - Nb'$, where b' is a constant representing a small atomic scale volume. Then, calculate the equation of state, by evaluating P from S. **Note**: $U(\vec{\mathbf{q}}_i) \equiv \sum_{i>j} U(\vec{q}_i - \vec{q}_j)$, and $\bar{U}$ is its thermal average. **Hint**: Start by calculating Z.

Addendum ✎ *Derivation of the van-der Waals equation of state.*

The above two problems provide a quite convenient starting point for deriving the famous van der Waals equation of state. For this, we assume that (1) U has the hard core repulsion, and (2) U has an additional long range attractive part. That is, we assume that the two particle potential $u_{ij} = \infty$ if $|\vec{r}_i - \vec{r}_j| < 2D$, as in problem 7, and some attractive potential if $|\vec{r}_i - \vec{r}_j| > 2D$, and the total potential energy is given by $U = \frac{1}{2}\sum_{i,j} u_{ij}$. The van-der Waals theory is **a mean field theory**, where the attractive part of the potential is replaced by its average. So, $\bar{V}$ is the same as the last part of problem 8, or what we got in problem 7, $\bar{V} = V - Nv_0/2$, since $U = \bar{U}$ for the attractive part, by the mean field assumption. Now, carrying out the calculation of $\bar{U}$, we get $\bar{U} \approx \frac{1}{2}N^2\bar{u}$, where $\bar{u}$ is the average of $u_{i,j}$. On general grounds, we expect that $\bar{u} \sim -\frac{v_a}{V}u_0$, where v_a is an atomic volume scale, and u_0 is the energy scale (> 0) of the inter-particle attraction. We shall postpone a specific example for the actual calculation of $\bar{u}$ until after we establish the van-der Waals equation. For now, we will simply define a positive *constant*

$a \equiv -\frac{1}{2}\bar{u}V \sim \frac{1}{2}v_a u_0$. Then, $\bar{U} = -\frac{N^2}{V}a$, and from the above expression of Z, we get

$$F = Nk_BT\left(\log\frac{N}{\bar{V}} - 1 + 3\log\lambda\right) - \frac{N^2}{V}a.$$

Now, in order to get P from F, we note that

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{\bar{V}} - an^2.$$

Defining $b \equiv v_0/2$, $\bar{V} = (V - bN)$, and so we get the van der Waals equation:

$$\boxed{(P + an^2)(V - bN) = Nk_BT.}$$

For a specific example of $\bar{u}$, let us calculate it assuming that the interparticle potential has the followin form

$$u_{ij} = -u_0\left(\frac{2D}{r}\right)^6, \qquad r \ge 2D, \quad \text{van-der Waals attraction}$$

where $u_0 > 0$ is an energy scale, and $r = |\vec{r}_i - \vec{r}_j|$. Within the mean field theory, there is no Boltzman factors to worry about for calculating $\bar{u}$, and we get

$$\begin{aligned}\bar{u} &= \frac{4\pi\int_{2D}^{\infty} dr r^2\,(-u_0)\left(\frac{2D}{r}\right)^6}{4\pi\int_{2D}^{\infty} dr r^2} = \frac{-\frac{4\pi}{3}(2D)^3 u_0}{V - v_0} = \frac{-v_0u_0}{V - v_0}\\ &\approx \frac{-v_0}{V}u_0.\end{aligned}$$

The form of $\bar{u}$ is as we precisely anticipated above, with v_a identified as v_0, the excluded volume per pair. So, we have

$$a = \frac{v_0\,u_0}{2}, \quad b = \frac{v_0}{2}.$$

Note that a is indeed a postive constant, as is b. ✎