Problems, due Thursday, Nov. 21

1. It makes sense to consider a classical ideal gas that can exchange particles with a particle reservoir characterized by a chemical potential $\mu$, just as we can imagine it exchanging energy with a heat bath characterized by temperature $T$. In this problem apply the general method of equilibrium statistical mechanics to this system.

(a) Take the probability of a state with energy $E$ and particle number $N$ to be $P \propto \exp[-\beta(E - \mu N)]$, and form the partition function

$$Z_{gr} = \sum_j e^{-\beta(E_j - \mu N_j)} \quad (1)$$

where $j$ labels multiparticle states. Evaluate $Z_{gr}$ by first fixing the particle number $N$ and integrating over classical space for the fixed number of particles. (Don’t forget the factor $N!$ to make the counting right for indistinguishable particles.) Then sum over all possible values for $N$.

(b) Point out why

$$N = kT \frac{\partial \ln Z_{gr}}{\partial \mu} \quad (2)$$

in general, and find $N$ for given $\mu$, $T$, and $V$ for the classical ideal gas.

(c) Invert the relation in (b) to find $\mu$ as a function of $N$, $T$, and $V$.

(d) In thermodynamics, $\mu = \partial F/\partial N$ is the free energy per particle. Find $F(T, V, N)$ for the classical ideal gas (fixed number of particles!), and compute $\mu$. How does it compare to your expression in (c)? You will need to recall Stirling’s approximation, $\ln(N!) \approx N \ln N - N$.

2. This problem leads you through a famous argument of Einstein, in which he visualizes equilibrium as a balance of currents. The condition of balance leads to what is now called a “fluctuation-dissipation theorem.” The reason for this name is not too apparent here, and has to do with the fact that the diffusion constant $D$ is related to the position fluctuations of a particle in Brownian motion – perhaps we will make this connection in a future problem!
(a) Use the Maxwell-Boltzmann distribution to justify the “Law of Atmospheres”: the number density $\rho$ of a constant-temperature atmosphere, as a function of height (in a gravitational field) falls exponentially. Estimate the “scale height” numerically (i.e., the altitude you would have to reach to begin to notice an appreciably lower density). How does it compare to what you know about Earth’s atmosphere?

(b) Phenomenologically, a number density gradient produces a particle current proportional to the gradient (and in the opposite direction, i.e., from high number density to low number density, tending to equalize the densities). The constant of proportionality is called the “diffusion constant.” That is,

$$\vec{j} = -D \vec{\nabla} \rho \quad (3)$$

The current $\vec{j}$ has the dimensions of $[\text{number density}] \times [\text{velocity}]$. What are the units of the diffusion constant $D$? Compute this current for the isothermal atmosphere.

(c) Molecules falling in the gravitational field reach an average terminal velocity $v_{\text{term}}$ since they are subject to the systematic gravitational force $mg$ and a systematic retarding force $-bv$, as well as random forces that produce no systematic motion. Find the net current due to this “falling.” Be sure it has the same units as the current in (b).

(d) In equilibrium the currents in (b) and (c) must exactly balance. This leads to a relationship between the diffusion constant $D$ and the friction coefficient $b$. Find this relationship.

(e) A small sphere of radius $R$ moving slowly in a medium of viscosity $\eta$ has friction coefficient $6\pi\eta R$, by a famous result of Stokes. Use this to predict the diffusion constant of a spherical particle in a viscous medium.