PHY 540 **Statistical Mechanics** Spring 2007

Homework 02 with Solution

Problem 2.1. Find all thermodynamic properties of an ideal classical gas of $N >> 1$ identical atoms contained in volume V at temperature T, starting from the microcanonical distribution (rather than from the Gibbs distribution), neglecting the internal energies of the atoms.

Hints:

(i) Try to make a more accurate calculation than has been done in class for the system of N harmonic oscillators. For that you will need to know the volume of an n-dimensional hypersphere of the unit radius. To avoid being too cruel, I am giving it to you:

$$v_n = \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)},$$

where $\Gamma(x)$ is the gamma-function. (For its definition and properties, see, e.g., Abramowitz and Stegun, Ch. 6.)

(ii) One more piece of math which you will need (and should know!) is the so-called Stirling formula whose crudest form (sufficient for the purposes of our course) is

$$\ln(n!)_{|n\to\infty} \to n\ln n - n.$$

(iii) Think how to account for the exact similarity of the atoms. This will set a good background for our future discussion of the gas-mixing ("Gibbs") paradox.

Solution: The number of quantum states with energies below E is

$$\Sigma(E) = \frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}} \int_{\frac{p^2}{2m}<E} d^{3N}q\, d^{3N}p = \frac{V^N}{N!(2\pi\hbar)^{3N}}\, p_E^{3N} v_{3N},$$

where $p_E=(2mE)^{1/2}$ is the momentum of a particle with energy E, i.e. the radius of the hypersphere in the $3N$-dimensional momentum space, containing the states we are counting, and the factor $1/N!$ provides the "correct Boltzmann counting" which reflects the similarity of the particles. Using the provided formula for v_n, we get

$$\Sigma(E) = \frac{V^N}{N!(2\pi\hbar)^{3N}}(2mE)^{3N/2}\frac{\pi^{3N/2}}{\Gamma(3N/2+1)},$$

so that

$$\Gamma(E)=\frac{d\Sigma}{dE}\approx\frac{V^N}{N!(2\pi\hbar)^{3N}}(2m)^{3N/2}\frac{3N}{2}E^{3N/2-1}\frac{\pi^{3N/2}}{\Gamma(3N/2+1)}$$
$$=\frac{3}{2}\frac{V^N}{(N-1)!\Gamma(3N/2+1)}(\frac{m}{2\pi\hbar^2})^{3N/2}E^{3N/2-1}$$

and

$$S=\ln\Gamma+\text{const}=N\ln V+(\frac{3N}{2}-1)\ln E+\frac{3N}{2}\ln(\frac{m}{2\pi\hbar^2})-\ln[(N-1)!]-\ln\left[\Gamma\left(\frac{3N}{2}+1\right)\right]+\text{const.}$$

Now, going to the limit $N\to\infty$ we can apply the Stirling formula to both $\ln[(N\text{-}1)!]$ and $\ln[\Gamma(3N/2+1)]\approx\ln[(3N/2)!]$, and get

$$S\approx N\ln V+\frac{3N}{2}\ln E+\frac{3N}{2}\ln(\frac{m}{2\pi\hbar^2})-N(\ln N-1)-\frac{3N}{2}(\ln\frac{3N}{2}-1)+\text{const}$$
$$=N\ln\left[\frac{V}{N}\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\left(\frac{2E}{3N}\right)^{3/2}\right]+\frac{5}{2}N+\text{const.}$$

Now we can find temperature:

$$\frac{1}{T}=\left(\frac{\partial S}{\partial E}\right)_V=\frac{3N}{2E},$$

to that $E=(3/2)T$, and entropy may be expressed as a function of T and V:

$$S=N\ln\left[\frac{V}{N}\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}T^{3/2}\right]+\frac{5}{2}N+\text{const},$$

and thus used to calculate the free energy as a function of these two arguments:

$$F=E-TS=-NT\left\{1+\ln\left[\frac{V}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]\right\}=-NT\ln\left(\frac{eV}{N}\right)+Nf(T),$$

where

$$f(T)=-T\ln\left[\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right].$$

This is exactly the expression derived (by Prof. Averin) in class using the *canonical* (Gibbs) distribution (see Sec. 3.2 of the lecture notes) for the particular case of particles with no internal degrees of freedom. From here we can get all the other thermodynamic parameters (including the equation of state, etc.) in exactly the same way as described in the notes.

Please note how shorter was the calculation using the canonical ensemble!