Homework #3

due: Thursday, 10/29/09

1. Calculate the probability of observing an energy that differs by 10^{-6} from the average energy of 1 mole of an ideal gas (hint: use the Gaussian distribution for P(E) derived in class).

Solution:

When looking at fluctuations, we derived

$$P(\Delta E) \approx \frac{1}{\sqrt{2\pi k T^2 C_v}} \exp\left[-\frac{\left(E-\overline{E}\right)^2}{2kT^2C_v}\right]$$

For an ideal monatomic gas (derived explicitly in chapter 5)

$$\overline{E} = \frac{3}{2}NkT$$

$$C_v = \frac{\partial \overline{E}}{\partial T} = \frac{3}{2}Nk$$

We are now asked what is the probability that the N-particle system will sample an energy that differs by $10^{-4}\%$ from the average energy, $\overline{E} = \frac{3}{2}NkT$? (We can let $N = N_A = 6.022 \times 10^{23} M$)

$$\Delta E = \left(\frac{10^{-4}}{100}\right)\overline{E} = 10^{-6}\overline{E} = \left(10^{-6}\right)\frac{3}{2}NkT$$

$$\frac{(\Delta E)^2}{2kT^2C_v} = \frac{\left(10^{-6}\right)^2 \frac{9}{4}N^2k^2T^2}{2kT^2 \cdot \frac{3}{2}Nk} = \frac{3}{4}\left(10^{-6}\right)^2 N$$

$$P(\Delta E) \approx \frac{1}{kT\sqrt{3\pi N}} \exp\left[-4.5 \times 10^{11}\right]$$

This is an extremely small probability which validates our earlier assumptions.

2. Derive the principal thermodynamic connection formulas of the grand canonical ensemble starting from.

$$pV = kT ln\Xi$$

and

$$d(pV) = SdT + Nd\mu + pdV$$

Solution:

$$S = \left(\frac{\partial(pV)}{\partial T}\right)_{\mu,V} = k\left(\frac{\partial(T ln\Xi)}{\partial T}\right)_{\mu,V} = k\ln\Xi + kT\left(\frac{\partial \ln\Xi}{\partial T}\right)_{\mu,V}$$

and

$$N = \left(\frac{\partial(pV)}{\partial\mu}\right)_{T,V} = kT\left(\frac{\partial \ln\Xi}{\partial\mu}\right)_{T,V}$$

and

$$p = \left(\frac{\partial(pV)}{\partial V}\right)_{\mu,T} = kT\left(\frac{\partial \ln\Xi}{\partial V}\right)_{\mu,T}$$

3. Show that the partition function appropriate to an isothermal-isobaric ensemble is

$$\Delta(\mathrm{N,p,T}) = \sum\nolimits_E \sum\nolimits_V \Omega(N,V,E) e^{-\beta E}\, e^{-\beta p V}$$

Derive the thermodynamic connection formulas for this ensemble.

Solution:

Begin with the Gibbs entropy formula for the probabilities in the isothermal-isobaric ensemble

$$S = -k \sum\nolimits_i \sum\nolimits_V P_{Vi} \ln P_{Vi}$$

We now need to obtain a set $\{P_{Vi}^*\}$ that maximizes S with respect to the following constraints

$$\sum\nolimits_i \sum\nolimits_V P_{Vi} = 1$$

$$\sum\nolimits_i \sum\nolimits_V n_{Vi}\, E_{Vi} = \mathbb{E}$$

$$\sum\nolimits_i \sum\nolimits_V n_{Vi}\, V = \mathbb{V}$$

where $n_{Vi}$is the number of subsystems with energy E_{Vi} and volume V, $\mathbb{E}$ is the total energy of the ensemble and $\mathbb{V}$ is the total volume of the ensemble. Use the method of Lagrange multipliers to find each P_{Vi}^*.

$$\left.\frac{\partial\left(\frac{S_{Vi}}{k}\right)}{\partial P_{Vi}}\right|_{P_{Vi}^*} - \alpha\left(\frac{\partial(P_{Vi})}{\partial P_{Vi}}\right) - \beta\left(\frac{\partial(n_{Vi}E_{Vi})}{\partial P_{Vi}}\right) - \gamma\left(\frac{\partial(n_{Vi}V)}{\partial P_{Vi}}\right) = 0$$

$$-\left.\frac{\partial(P_{Vi}\ln P_{Vi})}{\partial P_{Vi}}\right|_{P_{Vi}^*} - \alpha\left(\frac{\partial(P_{Vi})}{\partial P_{Vi}}\right) - \beta\left(\frac{\partial(n_{Vi}E_{Vi})}{\partial n_{Vi}}\right)\left(\frac{\partial n_{Vi}}{\partial P_{Vi}}\right) - \gamma\left(\frac{\partial(n_{Vi}V)}{\partial P_{Vi}}\right)\left(\frac{\partial n_{Vi}}{\partial P_{Vi}}\right) = 0$$

Since $P_{Vi} = n_{Vi}/\mathbb{A}$ where $\mathbb{A}$ is the number of subsystems in the ensemble, $\partial P_{Vi}/\partial n_{Vi} = 1$ and the above equation becomes

$$-1 - \ln P_{Vi}^* - \alpha - \beta E_{Vi} - \gamma V = 0$$

Solve for P_{Vi}^* to get

$$P_{Vi}^{*} \;=\; e^{-(1+\alpha)}e^{-\beta E_{Vi}}e^{-\gamma V}$$

Our set $\{P_{Vi}^{*}\}$ must be properly normalized to obtain a general solution for the probability distribution.

$$P_{Vi} \;=\; \frac{e^{-(1+\alpha)}e^{-\beta E_{Vi}}e^{-\gamma V}}{\sum_i \sum_V e^{-(1+\alpha)}e^{-\beta E_{Vi}}e^{-\gamma V}} \;=\; \frac{e^{-\beta E_{Vi}}e^{-\gamma V}}{\sum_i \sum_V e^{-\beta E_{Vi}}e^{-\gamma V}} \;=\; \frac{e^{-\beta E_{Vi}}e^{-\gamma V}}{\Delta}$$

where

$$\Delta \equiv \Delta(N,p,T) \;=\; \sum_i \sum_V e^{-\beta E_{Vi}}e^{-\gamma V}$$

Now we can obtain the multipliers β and γ by comparing this partition function with the partition functions obtained for the canonical and grand canonical ensemble. The multiplier β is the same as the other two (i.e. $\beta = 1/kT$) and the multiplier γ is a function of β. Furthermore, the argument of the exponential must be unitless, which means that based on our previous experience $\gamma V = \beta pV = pV/kT$, and $\gamma = \beta p$. This means that the partition function is

$$\Delta(N,p,T) \;=\; \sum_i \sum_V e^{-\beta E_{Vi}}e^{-\beta pV}$$

If we sum over the energy levels instead of the states we have

$$\Delta(N,p,T) \;=\; \sum_E \sum_V \Omega(N,V,E)e^{-\beta E}e^{-\beta pV}$$

where $\Omega(N,V,E)$ is the degeneracy of the energy level E. The characteristic function can be obtained from fluctuation theory (see problem 4) if we assume that the fluctuations in energy are very small relative to the average energy (i.e. $\sigma_E/\langle E\rangle \rightarrow 0$) and that the fluctuations in volume are very small relative to the average volume (i.e. $\sigma_V/\langle V\rangle \rightarrow 0$) then

$$\Delta(N,p,T) \;=\; \sum_E \sum_V \Omega(N,V,E)e^{-\beta E}e^{-\beta pV} \;\cong\; \Omega(N,\langle V\rangle,\langle E\rangle)e^{-\beta\langle E\rangle}e^{-\beta p\langle V\rangle}$$

and

$$\ln\Delta = \ln\Omega - \beta\langle E\rangle - \beta p\langle V\rangle \;=\; \ln\Omega - \beta E - \beta pV$$

which can be simplified to

$$kT\ln\Delta \;=\; T(k\ln\Omega) \;-\; E - pV \;=\; TS - E - pV \;=\; TS - H \;=\; -G$$

and the characteristic function is

$$G \;=\; -kT\ln\Delta$$

To get the thermodynamic connection formulas we need an expression for dG as a function of dT, dp and dN. We know from thermodynamics that in a single component system

$$dG = -SdT + Vdp + \mu dN$$

The connection formulas are then found in the same way as problem 2.

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,N} = k\left(\frac{\partial(T ln\Delta)}{\partial T}\right)_{p,N} = k\ln\Delta + kT\left(\frac{\partial \ln\Delta}{\partial T}\right)_{p,N}$$

and

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,N} = -kT\left(\frac{\partial \ln\Delta}{\partial p}\right)_{T,N}$$

and

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{p,T} = -kT\left(\frac{\partial \ln\Delta}{\partial N}\right)_{p,T}$$

4. One can derive the characteristic function for the grand canonical ensemble (see the first equation in problem 3) using fluctuation theory as we did for the canonical ensemble in class. The grand canonical partition function is given by

$$\Xi\,(V,T,\mu) = \sum_N Q(N,V,T)\, e^{\beta\mu N}$$

where Q(N,V,T) is the canonical partition function

Solution:

The characteristic function can be obtained from fluctuation theory if we assume that the fluctuations in energy are very small relative to the average energy (i.e. $\sigma_E/\langle E\rangle \rightarrow 0$) and that the fluctuations in particle number are very small relative to the average particle number (i.e. $\sigma_N/\langle N\rangle \rightarrow 0$) then

$$\Xi\,(V,T,\mu) = \sum_N Q(N,V,T)\, e^{\beta\mu N} = \sum_N \sum_E \Omega(N,V,E) e^{-\beta E} e^{\beta\mu N}$$
$$\cong \Omega(\langle N\rangle, V, \langle E\rangle) e^{-\beta\langle E\rangle} e^{\beta\mu\langle N\rangle} = \Omega e^{-\beta E} e^{\beta\mu N}$$

Taking the natural log

$$\ln\Xi = \ln\Omega - \beta E + \beta\,\mu N$$

which then simplifies to

$$kT\ln\Delta = T(k\ln\Omega) - E + \mu N = TS - E + G = TS - E + (H - TS) = -E + H$$
$$= -E + (E + pV) = pV$$

Thus, the characteristic function of the grand canonical ensemble is

$$pV = kT\ln\Xi$$