CHM328S: Modern Physical Chemistry

Problem Set 3: Ensemble Theory

Notes:

- Please start each problem on a new page.
- This third problem set is due on Tuesday, March 17, 2009.

1. In class, we assumed that the energy micro-states depend on the number of particles to be able to introduce the chemical potential. We will now introduce the chemical potential in a different way, by defining the grand-canonical partition sum as

$$\Xi(\mu, \beta, V) = \sum_{N=0}^{\infty} \sum_{j} e^{-\beta E_j(N,V) + \beta\mu N} = \sum_{N=0}^{\infty} Q_N e^{\beta\mu N}$$

This corresponds to a probability for a micro-state E_j with number of particles N of

$$p_{jN} = \frac{e^{-\beta E_j + \beta\mu N}}{\Xi}.$$

(a) Show that

$$\langle E \rangle = -\left(\frac{\partial \log \Xi}{\partial \beta}\right)_{\beta\mu,V}.$$

(b) Show that

$$\langle N \rangle = k_B T \left(\frac{\partial \log \Xi}{\partial \mu}\right)_{T,V}.$$

(c) Show that

$$(k_B T)^2 \frac{\partial^2 \log \Xi}{\partial \mu^2} = \langle N^2 \rangle - \langle N \rangle^2.$$

What does this quantity measure?

(d) Show that in the grand-canonical ensemble the fluctuations in number of particles is small if it is large, i.e. $N \approx \langle N \rangle$.

(e) Within this approximation, show that

$$\log \Xi = \beta(\mu \langle N \rangle + TS - \langle E \rangle) = \beta p V$$

(The last equality is a thermodynamic identity which you do not have to prove.)

(f) Compute the grand-canonical partition sum for a system of N non-interacting molecules with molecular partition sum q.

2. Show that the temperature at which the fractional population of vibrational level ν is at a maximum is given by:

$$T = \frac{\Theta_v}{\ln(1 + 1/\nu)},$$

where Θ_v us the characteristic vibrational temperature. What is the fractional population of vibrational level ν?

3. Let a system of N particles be such that each particle can only have energy 0 or ϵ.

   (a) Compute the (canonical) partition sum.

   (b) Compute the average energy.

   (c) Compute the entropy (hint: $A = \langle E \rangle - TS$).

   (d) Compute $(\partial S/\partial U)_{N,V}$. What do you notice?

   (e) Compute the pressure.

   (f) Compute the pressure from the grand-canonical ensemble as well.