Homework 3: Canonical ensemble (continued) and radial distribution function

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1. (Computational) Fill in the missing pieces in the notebook within the rdf folder on the course github:
   https://github.com/hockyg/chem-ga-2600/
   This will demonstrate how to compute a radial distribution function ($g(r)$) for somewhat realistic simulation data.

   When finished, download with File->Download As->ipynb so you have a copy. You can either email this to me or print it out and attach to the other homework.

2. *Ideal gas of molecules* (Adapted from Tuckerman problem 4.12). If you have N identical non-interacting molecules (each with n atoms) in a box, the total partition function factorizes,
   $$Q(N,V,T) = \frac{q(n,V,T)^N}{N!} \tag{1}$$
   Moreover, the single molecule partition function $q(n,V,T) = Vf(n,T)$, where f is a function that only depends on the number of atoms and the temperature.
   Now suppose that the system contains different types of molecules, this factorization still works. For example, with 2 types, A and B,
   $$Q(N_A,N_B,V,T) = \frac{q_A(n_A,V,T)^{N_A}}{N_A!} \cdot \frac{q_B(n_B,V,T)^{N_B}}{N_B!} \tag{2}$$

   (a) An example chemical reaction might be
   $$aA + bB \rightleftharpoons cC + dD \tag{3}$$
   The Helmholtz free energy A is now a function of V,T, and all 4 N's. Let there be a variable called λ which is the reaction extent. Then $dN_A = a\ d\lambda$,

$dN_B = b\, d\lambda$, $dN_C = -c\, d\lambda$, and $dN_D = -d\, d\lambda$. At chemical equilibrium, A is at a minimum, which means that $dA/d\lambda = 0$.

Show that at equilibrium with fixed V and T,

$$a\mu_A + b\mu_B - c\mu_C - d\mu D = 0, \tag{4}$$

where chemical potentials of each species are defined like:

$$\mu_A = -k_B T \frac{\partial \ln Q(V, T, N_A, N_B, N_C, N_D)}{\partial N_A} \tag{5}$$

Hint: This should follow very directly from writing out the chain rule for dA.

(b) By plugging in for Q in the 4 equations like Eq. 5 and substituting this in to Eq. 4, show that you get the following relationship

$$K(T) = \frac{\rho_C^c \rho_D^d}{\rho_A^a \rho_B^b} = \frac{(q_C/V)^c (q_D/V)^d}{(q_A/V)^a (q_B/V)^b}, \tag{6}$$

where $\rho_A = N_A/V$, etc. Hint, you may have to use Sterling's approximation. Do you see why both the middle and right fractions are functions of only temperature?

(c) Using the definition of the Helmholtz free energy and the formula for Q with 4 different species, show that the Helmholtz free energy A can be written as $A_{total} = A_A + A_B + A_C + A_D$. What is the equation for A_X, that is, the contribution to the Helmholtz free energy from species X.

(d) The pressure in the canonical ensemble can be obtained by the formula $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$. The partial pressure of species X can be expressed similarly as $P_X = -\left(\frac{\partial A_X}{\partial V}\right)_{N,T}$, where A_X was defined in the previous part. Given this definition, find the relationship between K(T) above and

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b} \tag{7}$$