CE 530
Molecular Simulation

Assignment #3 Due: 28 February 2017

1. The isothermal-isobaric partition function is:

$$\Delta(T,p,N)=\frac{1}{\Lambda^3}\int_0^\infty dV\int_V d\mathbf{r}^N e^{-\beta pV}e^{-\beta U(\mathbf{r}^N)}$$

Using the bridge equation, $G=-kT\ln\Delta$, show that the thermodynamic relation

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

yields an expression representing the average of volume in this ensemble.

2. For an ideal gas the intermolecular potential is zero for all configurations. As a consequence the partition function is greatly simplified, and can be evaluated analytically. Do this for the canonical (*NVT*), isothermal-isobaric (*NPT*), and grand-canonical (μVT) ensembles, and for each derive the ideal-gas equation of state $PV = NRT$.

   As a bonus problem you might wish to do the same for the microcanonical (*EVN*) ensemble (Hint: you might need the formula for the surface area of a hypersphere in arbitrary dimension).