Examples Sheet #1

1. Complete the derivation outlined in class of the van der Waals interaction between two hydrogen atoms.

2. Under the assumption that the 3-particle potential energy U_3 can be written as $U_3 = u(r_{12}) + u(r_{13}) + u(r_{23})$, show that the third virial coefficient can be expressed in terms of the Mayer f-functions as

$$B_3(T) = -\frac{1}{3V}\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 f_{12} f_{13} f_{23} \ .$$

3. Approximating yourself as a conducting sphere of radius R at thermodynamic equilibrium at temperature T, estimate your root-mean-square charge q.

4. Prove the law of corresponding states. That is, show that if the underlying potential energy function of a classical statistical system is "conformal," having just a single energy scale ϵ and a single length scale σ,

$$U = \frac{1}{2}\sum_{i,j} u(r_{ij}) = \frac{1}{2}\sum_{ij} \epsilon\phi(r_{ij}/\sigma) \ ,$$

then an appropriately nondimensionalized pressure will be a universal function of the reduced temperature $T^* = k_B T/\epsilon$ and volume $v = V/N\sigma^3$. You will find it useful to consider that the free energy per particle is an intensive quantity, depending only on intensive properties.

5. Calculate (analytically) the properties of the coexistence curve for the mean field lattice gas equation of state in the immediate neighborhood of the critical point. Numerically find the coexistence curve from the critical point down to low temperatures.

6. *Scaling of the Surface Tension of Polymer Solutions.* Using the Flory-Huggins form of the free energy density of a polymer solution,

$$f \equiv \frac{F}{k_B T V} = (1-\phi)\ln(1-\phi) + \frac{1}{N}\phi\ln(\phi) + \chi\phi(1-\phi) \ ,$$

in a free energy functional

$$\mathcal{F}[\phi] = \int dz \left\{ \frac{1}{2} m \left(\frac{d\phi}{dz}\right)^2 + f(\phi) \right\} \ ,$$

and assuming that m is independent of N, find the scaling form for the coexistence curve and the surface tension in the neighborhood of the critical point, in the limit $N \to \infty$, $\chi \to \chi_c$ as a function of the scaled variable $x = N^{1/2}(\chi - \chi_c)$.