Homework 11

Scaling Theory of Excluded Volume Effects[1]

The Flory theory for chains made of N monomers having a certain excluded volume $v > 0$ and connected by bonds of length b predicts the following behavior of the end-to-end distance R

$$R \sim v^{\frac{1}{5}} b^{\frac{2}{5}} N^{\frac{3}{5}} \tag{1}$$

Remember that the excluded volume measures the net two-body interaction (mediated by the solvent) between monomers. Usually, such an interaction is repulsive at short distances and attractive at relatively larger ones. A positive v means that the repulsive part of the potential is stronger than the attractive one, so that one can roughly think of the monomers as hard spheres of volume v. On the other hand, a negative value of v characterizes the opposite behavior, so that as a result the polymer collapses onto itself, and the result in equation (1) is not anymore valid. A 2-bodies approximation of the Flory theory would predict a collapse of the polymer onto a single point, which is completely unphysical and needs to be corrected by making use of three bodies effects. As a result, in this case the scaling behavior of R is

$$R \sim \frac{b^2}{|v|^{\frac{1}{3}}} N^{\frac{1}{3}} \tag{2}$$

However, both the results for *good* (eqn (1)) and *poor* (eqn (2)) solvents hold at all scales only in the extreme cases where (assuming the monomers to be spherical objects) $v \sim b^3$ or $v \sim -b^3$, i.e. when we are in presence of respectively *athermal* or *non-* solvents. In such cases the leading interaction is not even "tempered" by the weaker one, so that one has exactly hard-spheres or an exactly collapsing polymer. Apart from such cases, one expects the excluded volume to have an effect only starting from a certain length scale.

1. Assuming a sharp transition to take place when changing scales, find the behavior of R as a function of N, v, b in a blob picture. In particular, show that for long enough polymers equations (1) and (2) hold at large scales for the proper ranges of values of the excluded volume.

   Hint: in a Flory framework, the interaction energy due to excluded volume within a polymer made of n monomers and having end-to-end distance ξ is given by

   $$k_B T |v| \frac{n^2}{\xi^3} \tag{3}$$

2. At a first approximation, a DNA molecule can be thought of as a chain made of cylindrical monomers of length $l \simeq 100$ nm and radius $r \simeq 1$ nm. Typical DNA molecules used in single-molecule experiments have lengths of some microns. How do such molecules behave in a good solvent?

   Hint: in this case it can be shown that the excluded volume is roughly $l^2 r$.

[1] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.