Homework 10

Excluded Volume Dependence on Temperature[1]

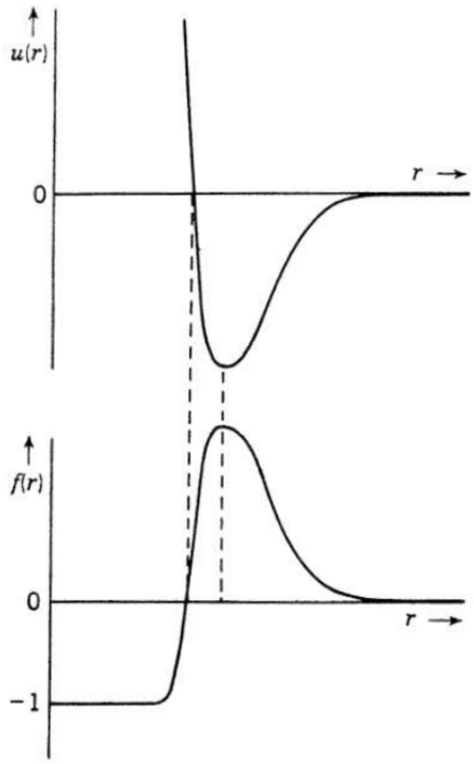
The excluded volume v is the first correction one puts into the free energy of an ideal chain in order to take into account real chain effects. For isotrope monomers, v is given by

$$v = -\int d\vec{r} f(r) \tag{1}$$

In the previous formula, $f(r)$ is the so-called *Mayer f-function* and is given by

$$f(r) = e^{-\frac{u(r)}{k_B T}} - 1 \tag{2}$$

where $u(r)$ is the pairwise potential energy of two monomers at distance r. A typical potential



(think about the famous Lennard-Jones formula) is depicted in the top part in the figure[2]. We note a strong hard-core repulsion up to a typical dimension of the monomer, which can be identified

[1]M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.
[2]Reprinted from T. L. Hill, Statistical Mechanics (McGraw-Hill, New York, 1956).

with its size b, followed by an attractive part, which after reaching a minimum decays relatively fastly to zero. In the bottom part of the figure, the corresponding f-function as defined in eqn (2) is plotted. When integrating the f-function, we basically calculate the difference between the area corresponding to the attractive well and the one coming from the repulsive part. When the latter is larger, the total integral is negative, so that the excluded volume (eqn (1)) is positive. On the other hand, when the attractive well dominates a negative v is found. To make the long story short, v quantifies the net pairwise interaction between monomers. However, notice that while the repulsive part is practically independent on temperature (since the potential rapidly diverges), the attractive part strongly depends on it, being lower for larger values of T. In other words $v = v(T)$. In particular, we expect that for large temperatures $v > 0$, while at low ones $v < 0$. Correspondingly (compare Homework 12), the chain behavior will qualitatively change at the θ-*temperature*, i.e. the temperature corresponding to a θ-solvent (where $v = 0$).
In this exercise, we propose to find an approximate formula for the temperature dependence of the excluded volume. To this aim, at a first approximation we can assume that up to $r = b$, the potential is infinite (i.e. we basically retrieve the hard-spheres model of Homework 10). Moreover, we also assume that the temperature is large enough in order to have $u(r) \ll k_B T$ in the attractive well.

1. Within this approximation, show that apart from numerical constants the excluded volume can be written as

$$v \sim \left(1 - \frac{\theta}{T}\right) b^3 \tag{3}$$

   and provide for an integral formula which permits to calculate θ once the explicit form of $u(r)$ is known.

2. Assuming the monomers to interact with a Lennard-Jones potential

$$u(r) = 4\epsilon \left[\left(\frac{b}{r}\right)^{12} - \left(\frac{b}{r}\right)^{6} \right] \tag{4}$$

   find an explicit formula for θ. Under which conditions does the assumption $u(r) \ll k_B T$ hold?