Exercise 1 Dilute polymer solutions under "good solvent" conditions

At this point you should be familiar with the basic statistical mechanics of polymers. Consider once again a dilute polymer solution, where each polymer is represented by a fully flexible linear chain made of spherical monomers. In the last laboratory session we derived the configurational entropy of such an ideal chain as:

$$S_{id}(R) = S_0 + k_B \ln P(R) = S_0 - \frac{3k_B}{2}\frac{R^2}{b^2N} \tag{1}$$

Consider now increasing the temperature beyond the θ-point, so that the repulsive interactions between the monomers of the chain overcomes (on average) the attractive interactions. This kind of unbalance between positive and negative interactions leads to a swelling of the coil which is equivalent with what is observed in *good solvent* conditions. In this exercise, you will rigorously study the behaviour of a dilute polymer solution in such a good solvent (high temperature) regime. In particular, you will be able to prove that, in such a limit, the Flory exponent increases beyond the ideal chain value up to $\nu = 3/5$.

Going beyond the ideal chain limit requires one to compute the portion of free energy that is connected with the interaction between the monomers. Since the polymer is now in an expanded coil configuration, we can approximate the interaction free energy A_{int} as a series of increasing powers of the average density of monomers ρ. Note that this procedure is reminiscent of the virial expansion of the free energy of a real gas beyond the ideal gas state. At the first order in ρ, we have

$$A_{int} = k_B T N \rho B_2(T) \tag{2}$$

As you should have learned during the lecture, $B_2(T)$ is the second virial coefficient, defined as

$$B_2(T) = 2\pi \int_0^\infty dr\, r^2 \left[1 - e^{-\beta v(r)}\right] \tag{3}$$

with $v(r)$ the inter-monomer potential and $g(r)$ the radial distribution function of the monomers.

(a) Assuming that the repulsion between monomers is described by hard-sphere-like interactions, with the hard-sphere diameter corresponding to the average bond distance b, compute the second virial coefficient $B_2(T)$. How can you interpret the result you found in terms of going beyond an ideal polymer condition?

(b) If R represents the end-to-end distance, then we can assume that the polymer is enclosed in a volume $V = cR^3$, with c a constant. Write down the *total* free energy of the polymer as a function of R.

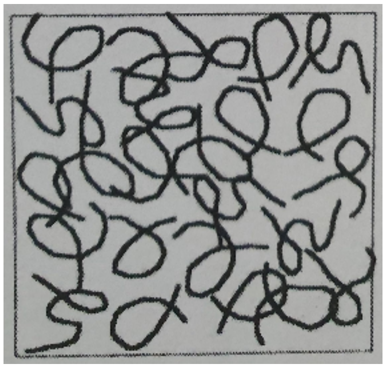
(c) Find the gyration radius R_g as the optimal end-to-end distance value which minimizes the free-energy of the polymer. What is the Flory exponent?

(d) How the previous results would change if the interaction between the monomers was described by a softer repulsion potential? And how "soft" could it possibly be to guarantee the asymptotic convergence of the virial expansion?

Exercise 2 Concentrated polymer solutions and Flory's conjecture

This exercise involves more advanced concepts that are not covered during lectures. Give it a go if you are curious, but do not worry too much if you find it too hard.

In this exercise you will use some fundamental concepts of liquid-state theory to study the properties of a very concentrated polymer solution, or polymer melt, as represented by the figure below.



In these circumstances, the polymer identity is lost, meaning that one can treat on equal footing the interactions between monomers belonging to the same polymer chain and to different polymer chains. In simple liquids, increasing the concentration usually corresponds to an enhancement of the short-range interactions between the system particles, requiring a refined description of the interaction free-energy. Although this is definitely true at the local scale, it turns out that a macroscopic description of a polymer melt is surprisingly pretty close to the one of an ideal chain. Indeed, one can assume that the swelling of a polymer due to the repulsive interactions of the monomers within a chain are screened by the interactions with monomers of the neighbouring chains. This hypothesis takes the name of *Flory's conjecture*.

At the simplest level of theory, one can assume a Gaussian repulsive potential between any two monomers of the melt, i.e.,

$$\nu(r) \sim \exp\left[-\left(\frac{r}{R_0}\right)^2\right] \tag{4}$$

with r the distance between the monomers and R_0 the characteristic interaction length. In this picture, the Flory's hypothesis about the increase of the screening of the interactions with the concentration implies assuming the following limit $\rho R_0^3 \to \infty$. In other words, the characteristic interaction length scale R_0 is assumed to be much larger than the typical distance between two monomers of the melt. This condition identifies the perfect situation for a mean-field treatment of the problem, where the system is described through its collective (macroscopic) behaviour.

Our objective is to derive the pressure P of the melt within a mean-field treatment. As a starting point, consider that the isothermal compressibility of a liquid χ_T is related to the macroscopic ($k \to 0$) limit of the structure factor $S(k)$ of the system as

$$\rho k_B T \chi_T = k_B T \left(\frac{\partial \rho}{\partial P}\right)_T = 1 + \rho \int d\mathbf{r}\,[g(r) - 1] = 1 + \rho \int d\mathbf{r}\, h(r) = \lim_{k\to 0}\left[1 + \rho \hat{h}(k)\right] = \lim_{k\to 0} S(k) = S(0), \tag{5}$$

with $g(r)$ the usual radial distribution function and $h(r) = g(r) - 1$.

(a) Derive a formal expression for the pressure of the polymer melt as a function of S(0).

(b) A fundamental equation of liquid-state theory is the Ornstein-Zernike (OZ) equation. Given $r = |\mathbf{r} - \mathbf{r}'|$, it reads as follows

$$h(r) = c(r) + \rho \int d\mathbf{r}'' c(|\mathbf{r} - \mathbf{r}''|) h(|\mathbf{r}'' - \mathbf{r}'|), \tag{6}$$

Cont.

that is, the total correlation $h(r)$ between two monomers is decomposed in a direct contribution $c(r)$ and an indirect contribution (the convolution integral) that brings information from the other surrounding monomers. Remembering the convolution property of Fourier transforms, and that $S(k) = 1 + \rho\hat{h}(k)$, use the OZ equation to write the structure factor $S(k)$ as a function of $\hat{c}(k)$ only, with $\hat{c}(k)$ the Fourier transform of the direct correlation function $c(r)$.

(c) In a mean-field treatment, where R_0 is much larger than the typical inter-monomer distance, only the asymptotic behaviour of the direct correlation function $c(r)$ can be considered. Bringing information on the direct correlation between two particles, the asymptotic behaviour of $c(r)$ is directly related to the inter-monomer potential, i.e.,

$$\lim_{r\to\infty} c(r) = -\beta v(r). \tag{7}$$

Update the structure factor definition of the previous question based on this knowledge and write a final expression for the pressure of the polymer melt as a function of $\hat{v}(0)$. *Optional: Compute* $\hat{v}(0)$ *explicitly and write the pressure as a function of* R_0.

(d) Can you find an analogy with the virial equation of state? Justify your answer based on the general definition of the second virial coefficient as defined in Eq. (3) of the previous exercise.

Cont.

Solution to Exercise 1

Question (a). A hard-sphere potential is defined as

$$v(r) = \begin{cases} \infty, & \text{if } r \leqslant b \\ 0, & \text{if } r > b \end{cases} \tag{8}$$

which implies a second virial coefficient that is independent from temperature and directly proportional to the excluded volume $\Omega = 4\pi/3\ r^3$ associated with a pair of hard spheres, i.e.,

$$B_2(T) = \frac{2\pi}{3}b^3 = 4\Omega. \tag{9}$$

This result implies that the deviation from the ideal chain behaviour is determined by the fact that two monomers cannot overlap, according to the assumed hard-core repulsion.

Question (b). Making use of the result found for the second virial coefficient, and assuming $\rho = N/cR^3$, the total free energy of the polymer takes the form

$$\begin{aligned} A(R) &= A_{\text{id}}(R) + A_{\text{inter}}(R) = -TS_{\text{id}}(R) + A_{\text{inter}}(R) = \\ &= A_0 + \frac{3}{2}k_B T\frac{R^2}{b^2 N} + 4k_B T\Omega N\rho = A_0 + \frac{3}{2}k_B T\frac{R^2}{b^2 N} + 4k_B T\Omega\frac{N^2}{cR^3} \end{aligned} \tag{10}$$

where we used the definition provided for the entropy of the ideal chain.

Question (c). Minimizing the free energy previously obtained with respect to R, we get

$$\frac{\partial A(R)}{\partial R} = 3\frac{k_B TR}{b^2 N} - 12k_B T\Omega\frac{N^2}{R^4} = 0 \tag{11}$$

which implies an optimal radius of gyration

$$R_g = \left(4\Omega b^2\right)^{\frac{1}{5}} N^{3/5} \tag{12}$$

The Flory exponent is thus $\nu = 3/5$, as expected.

Question (d). If the repulsion potential was "softer", i.e., it is a smooth function of the inter-monomer distance r, the second virial coefficient entering in the definition of the interaction free energy would change, acquiring a dependence on the temperature. As such, the radius of gyration R_g would also become temperature-dependent. The Flory exponent would be however unchanged.

For large inter-monomer distances $r \to \infty$, the second virial coefficient can be approximated as follows

$$B_2(T) \approx \frac{2\pi}{k_B T}\int_0^\infty dr\ r^2\ v(r) \tag{13}$$

This implies that the integral above diverges whenever the inter-monomer potential decays slower than $1/r^3$. As a result, no virial expansion can be defined when considering, for instance, a fluid of charged particles, where the interaction potential follows the Coulomb law $1/r$. This behaviour characterizes the virial expansion as an *asymptotic* expansion, whose convergence is guaranteed only under specific limiting conditions.

Solution to Exercise 2

Question (a) Solving the compressibility equation considering the 0-pressure condition as a reference, we get

$$P = \frac{k_B T}{S(0)} \rho \tag{14}$$

The pressure of the polymer solution is thus proportional to the inverse of the macroscopic ($k \to 0$) limit of the structure factor of the melt.

Question (b) The convolution property of Fourier transforms $\mathcal{F}_k\left[a \star b\right] = \hat{a}(k)\hat{b}(k)$, can be used to write the OZ equation in reciprocal space as

$$\hat{h}(k) = \hat{c}(k) + \rho\ \hat{c}(k)\ \hat{h}(k) \tag{15}$$

from which we can find an explicit solution for $\hat{h}(k)$ as

$$\hat{h}(k) = \frac{\hat{c}(k)}{1 - \rho\ \hat{c}(k)} \tag{16}$$

The structure factor can therefore be rewritten in close form as a function of $\hat{c}(k)$

$$S(k) = 1 + \rho\hat{h}(k) = 1 + \rho\frac{\hat{c}(k)}{1 - \rho\ \hat{c}(k)} = \frac{1}{1 - \rho\ \hat{c}(k)} \tag{17}$$

Question (c) From the asymptotic behaviour of the direct correlation function, we get

$$S(k) = \frac{1}{1 - \rho\ \hat{c}(k)} = \frac{1}{1 + \rho\beta\hat{v}(k)} \tag{18}$$

From the solution at point (a), the pressure of the polymer melt can therefore be rewritten as

$$P = \frac{k_B T}{S(0)}\rho = k_B T\rho + \hat{v}(0)\rho^2 \tag{19}$$

From Eq. (4), we can now compute $\hat{v}(0)$ as

$$\hat{v}(0) = \int d\mathbf{r}\ v(r) = \pi^{3/2} R_0^3 \tag{20}$$

so that

$$P = k_B T\rho + \hat{v}(0)\rho^2 = k_B T\rho + \pi^{3/2} R_0^3\ \rho^2 \tag{21}$$

Question (d) The result found for the pressure of the polymer melt is reminiscent of the virial equation of state, under the correspondence $B_2(T) \sim \frac{\hat{v}(0)}{k_B T}$. This is coherent with considering the asymptotic limit $r \to \infty$ of the the interaction potential $v(r)$, for which we can approximate

$$B_2(T) \approx \frac{2\pi}{k_B T}\int_0^\infty dr\ r^2\ v(r) = \frac{2\pi}{k_B T}\hat{v}(0) \tag{22}$$

This result should not be surprising, since, under Flory's conjecture, the interactions between the monomers of the melt are supposed to take place over an asymptotic (large) length scale, according to having adopted a mean field approach. Note that the possibility of recovering the same formal expression for the pressure of the system by going through different derivation paths is an important property of any theory of liquids which takes the name of *thermodynamic consistency*.

The End.