ICFP M2 – SOFT MATTER PHYSICS
Tutorial 3. Polymers in dilute solutions

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We wish to understand the effects of molecular interactions on the spatial extent of macromolecules in dilute solutions. We first introduce and exploit Flory's thermodynamical model. Then, we retrieve Flory's results by making the ideal-chain statistical description more realistic. This is performed by adding two energetic ingredients to the previous entropic one : the excluded volume associated with the impossibility of the monomers to overlap, and the intermolecular attractive interactions. We place ourselves in dimension d, where $1 < d < 4$, and consider a chain made of $N \gg 1$ monomers of size a, uniformly distributed in a region of space with radius R, within a solution at temperature T. We forget about the numerical prefactors and focus on the scaling laws only.

I   Flory's model

1   What is the average monomeric concentration c in the space pervaded by the chain ?

2   We assume the interaction energy per unit volume to read :

$$u \sim k_{\mathrm{B}} T v(T) c^2 \ , \tag{1}$$

where k_{B} is the Boltzmann constant. What is the dimension of the unknown quantity v ? Justify the proposed expression.

3   What sign of v ensures a good (bad) solvant ?

4   Estimate the average interaction energy $U(R, N, T)$ over the entire chain.

5   Propose a free energy form $F(R, N, T)$ that includes also the entropic elasticity of the ideal chain. Comment on the effects of the different terms.

6   For $v > 0$, obtain the scaling law $R \sim N^\nu$ at equilibrium by minimizing the free energy. Compare the obtained exponent ν to the one of the ideal case.

II   Excluded volume

1   Deduce from Tutorial 1 the density of probability per unit volume $P_0(R, N)$ to find the two extremities of an ideal chain separated by a (scalar) distance R. What were the limits of the underlying model ?

2   What scaling law $R \sim N^\nu$ does correspond to the maximum of this distribution ?

3 Justify why the probability p that two given monomers overlap in the volume pervaded by the chain typically scales as $p \sim (a/R)^d$.

4 What is the number of possible monomeric pairs to be taken into account for the entire chain?

5 Deduce from above the probability $\pi(N, a, R, d)$[1] at large N for a given chain conformation to have no internal monomeric overlap.

6 Provide the modified probability distribution $P_1(R, N)$ that includes those excluded-volume effects.

7 What scaling law $R \sim N^\nu$ does correspond to the maximum of P_1?

8 Using numerical simulations of 3D self-avoiding random walks, one finds $\nu \approx 0.588$. Comment.

III   Solvant effect

We assume the solvent molecules (s) to have a size comparable to the one of the monomers of the polymer (p). We denote by $-\epsilon_{\alpha,\beta}$ the intermolecular interaction energy, where α and β stand for s or p.

1 What is the typical number $z(d)$ of nearest neighbours (no matter s or p) of a given monomer?

2 Estimate the volume fraction ϕ occupied by the monomers within the volume pervaded by the chain.

3 What is the average number $n_{\alpha,\beta}(N, \phi, z)$ of neighbour pairs, for each α-β combination?

4 Evaluate the energy $E(R, N)$ of a given configuration. Why can we neglect the terms that are independent of R?

5 Provide the modified probability distribution $P_2(R, N)$ that includes the above interactions.

6 Show that we recover $P_1(R, N)$ by replacing the monomeric volume a^d by :

$$v(T) = a^d \left[1 - 2\chi(T) \right] , \tag{2}$$

and determine the so-called Flory parameter χ.

7 In the case of Van der Waals interactions, the energy is proportional to the product of the individual polarisabilities. Comment on the sign of χ. Guess what is referred to as an "athermal" solvent.

8 Compare the results to Flory's phenomenology and exhibit a transition between two distinct regimes.

9 What are the critical temperature and critical exponent?

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1. No link with Bordeaux.