ICFP – Soft Matter

Single polymer chain, effects of exclusion and interaction with the solvent

Anke Lindner, Vincent Démery

In this tutorial we study the conformation of a single polymer molecule in a solvent, using the random walk model. In this model, a configuration of the polymer is modeled as a random walk of length $N \gg 1$ on a cubic lattice of step b [1]. We first derive the properties of the ideal chain, and then use mean-field arguments to evaluate the effects of excluded volume (two monomers cannot occupy the same site) and interaction with the solvent. We focus on the typical extension of the polymer, $R \sim N^\nu$.

1 Ideal chain

In the ideal chain model, the excluded volume interaction is not taken into account: two monomers can overlap.

1. What do b and N represent?

2. We assume that the monomer 0 is at the origin and denote $\boldsymbol{R}_N$ the position of the end monomer. What is the gyration radius R_g, defined by $R_g^2 = \langle \boldsymbol{R}_N^2 \rangle$? What is ν?

3. What is the probability density of $\boldsymbol{R}_N$, $p(\boldsymbol{R}_N)$? What is the probability density of the end-to-end distance of the polymer $R = |\boldsymbol{R}_N|$, $p(R)$?

4. Another way to evaluate the typical size of the polymer is to consider the maximum of $p(R)$, R^*. Determine R^* and compare it with R_g.

2 Excluded volume effect

Here we take into account the effect of excluded volume with a mean-field approach. We assume that a configuration of extension R occupies a volume R^3 in space, and that the monomers are uniformly distributed in this volume. The probability distribution of R is proportional to the number of admissible configurations of extension R, $W(R) = W_0(R)p(R)$, where $W_0(R)$ is the number of ideal chain configurations with size R, obtained above, and $p(R)$ is the probability that there is no overlap in such configuration. We denote v_m the volume occupied by a monomer.

5. * What is the probability that two given monomers overlap? How many pairs of monomer are there? Conclude that

$$p(R) \simeq \exp\left(-\frac{N^2 v_m}{2R^3}\right) \tag{1}$$

6. What equation does the maximum of $W(R)$, R^*, satisfies? You can separate the term containing v_m and write this equation as an equation for R^*/R_0^*, where R_0^* is the typical size of an ideal chain.

7. * Identify two regimes in the above equation and determine when the excluded volume effects are important and what is the new exponent ν in this regime.

Numerical simulations give $\nu \simeq 0.5875$ [2].

3 Effect of the solvent

We use the same random walk model to investigate the interaction with the solvent. We assume that the lattice sites that are not occupied by the polymer are occupied by solvent "molecules", and attribute the energies $-\epsilon_{\mathrm{pp}}$, $-\epsilon_{\mathrm{ps}}$, $-\epsilon_{\mathrm{ss}}$ to monomer-monomer, monomer-solvent and solvent-solvent nearest neighbors, respectively.

8. What is the polymer volume fraction ϕ in a configuration with extension R? We will consider that ϕ is the probability that a lattice site is occupied by the polymer.

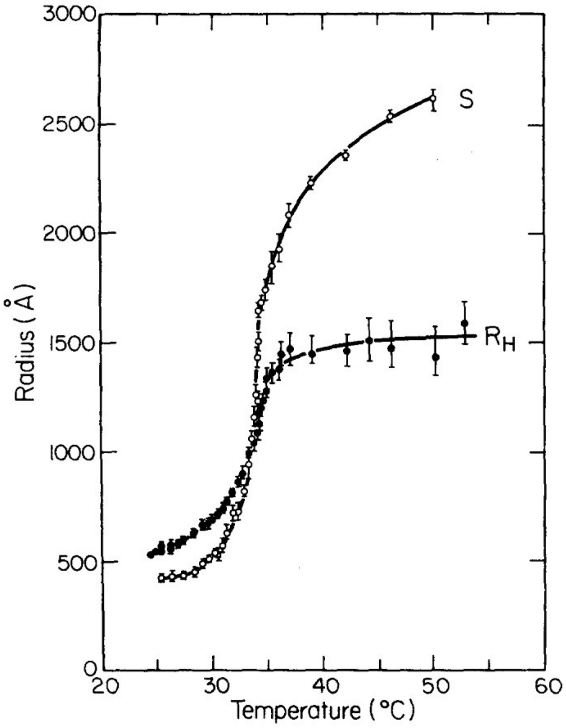

Figure 1: Temperature dependence of the radius of gyration, S, and the hydrodynamic radius, R_H, of polystyrene in cyclohexane [3].

9. * Determine the numbers of monomer-monomer, monomer-solvent and solvent-solvent pairs, $N_{\rm pp}$, $N_{\rm ps}$ and $N_{\rm ss}$, as a function of N, ϕ and z, the number of neighbors of a given site ($z = 6$ for a cubic lattice in dimension 3)?

10. What is the associated energy, and finally the probability to observe a configuration with extension R? Show in particular that the interactions just renormalize the monomer volume.

11. What are good and bad solvents? Interpret the experimental result shown in Fig. 1.

4 Polymer solution

12. What is the overlap concentration c^* of a polymer solution, where the volumes occupied by different chains start to overlap?

13. What are the effects of excluded volume and interaction with the solvent beyond this concentration?

References

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[2] Imtiaz Majid, Zorica V. Djordjevic, and H. Eugene Stanley. Conformation of linear polymers in three dimensions. *Phys. Rev. Lett.*, 51:1282–1285, Oct 1983.

[3] Shao-Tang Sun, Izumi Nishio, Gerald Swislow, and Toyoichi Tanaka. The coil–globule transition: Radius of gyration of polystyrene in cyclohexane. *The Journal of Chemical Physics*, 73(12):5971–5975, 1980.