ICFP – Soft Matter

Single chain – Solution

Anke Lindner, Vincent Démery

1 Ideal chain

1. b stands for the persistence length of the polymer (sometimes denoted ℓ_p) and $N = L/b$, where L is the total length of the polymer.

2. This is a standard random walk:

$$R_g^2 = \langle \boldsymbol{R}_N^2 \rangle = Nb^2, \tag{1}$$

giving $\nu = 1/2$.

3. For large N, the distribution of $\boldsymbol{R}_N$ is Gaussian:

$$p(\boldsymbol{R}_N) = \left(\frac{3}{2\pi Nb^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{R}_N^2}{2Nb^2}\right). \tag{2}$$

Note that for a given direction, say 1, $\langle (\boldsymbol{e}_1 \cdot \boldsymbol{R}_N)^2 \rangle = Nb^2/3$.

Integrating over the orientation, we get

$$p(R) = 4\pi R^2 \times \left(\frac{3}{2\pi Nb^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2Nb^2}\right). \tag{3}$$

4. Up to a constant,

$$p'(R) \propto \left(2R - \frac{3R^3}{Nb^2}\right) \exp\left(-\frac{3R^2}{2Nb^2}\right). \tag{4}$$

The maximum is at

$$R^* = \sqrt{\frac{2Nb^2}{3}} \propto R_g. \tag{5}$$

The prefactor is different, but we focus on scaling relations; we will thus use R^* and R_g indifferently.

2 Excluded volume effect

5. To estimate $p(R)$, we assume that the N monomers of volume v_m are evenly distributed in a volume of size R^3. Two given monomers avoid self-contact with probability $1 - v_m/R^3$. Since there are $N(N-1)/2$ pairs,

$$p(R) = \left(1 - \frac{v_m}{R^3}\right)^{N(N-1)/2}. \tag{6}$$

assuming that $v_m \ll R^3$ and $N \gg 1$,

$$p(R) \simeq \exp\left(-\frac{N^2 v_m}{2R^3}\right) \tag{7}$$

6. Taking for $W_0(R)$ the distribution of the end to end distance (3), we have

$$W(R) \propto R^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2 v_m}{2R^3}\right). \tag{8}$$

Here the typical size R^* solves

$$\frac{2}{R^*} - \frac{3R^*}{Nb^2} + \frac{3N^2 v_m}{2{R^*}^4} = 0, \tag{9}$$

which we rewrite

$$\left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 = \frac{9\sqrt{6}}{16}\frac{v_m}{b^3}N^{1/2}. \tag{10}$$

7. Excluded volume effects are important if the right hand side is large. In this case $(R_g/R_{g0})^3$ can be neglected and

$$R_g \sim (b^2 v_m)^{1/5} N^{3/5}, \tag{11}$$

corresponding to $\nu = 3/5$.

3 Effect of the solvent

8. The polymer volume fraction is $\phi = Nv_m/R^3$.

9. The number of monomer-monomer, monomer-solvent and solvent-solvent pairs are

$$N_{\rm pp} \simeq \frac{z}{2}N\phi, \tag{12}$$

$$N_{\rm ps} \simeq zN(1-\phi), \tag{13}$$

$$N_{\rm ss} \simeq N_{\rm ss}^0 - N_{\rm pp} - N_{\rm ss}, \tag{14}$$

where z is the number of neighbors of a given site, $z = 6$ in dimension 3.

10. The associated energy is

$$E = -\frac{z}{2}N\phi(\epsilon_{\rm pp} - \epsilon_{\rm ss}) - zN(1-\phi)(\epsilon_{\rm ps} - \epsilon_{\rm ss}) + E_0 = -\frac{z}{2}N\phi(\epsilon_{\rm pp} + \epsilon_{\rm ss} - 2\epsilon_{\rm ps}) + E_1, \tag{15}$$

where E_0 is the interaction energy of the solvent molecules in the absence of polymer, and E_1 does not depend on ϕ (but does depend on N). We thus retain

$$E = -\frac{zN^2 v_m}{R^3}\Delta\epsilon, \tag{16}$$

with

$$\Delta\epsilon = \frac{1}{2}(\epsilon_{\rm pp} + \epsilon_{\rm ss} - 2\epsilon_{\rm ps}). \tag{17}$$

The probability to observe a chain with gyration radius R is thus

$$p(R) \propto W(R)\exp\left(\frac{zN^2 v_m \Delta\epsilon}{kTR^3}\right) \propto R^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2(1-2\chi)v_m}{2R^3}\right), \tag{18}$$

with

$$\chi = \frac{z\Delta\epsilon}{T}. \tag{19}$$

The interaction energy thus renormalizes the monomer volume v_m: $v_m' = (1-2\chi)v_m$.

11. For good solvents, $1-2\chi > 0$ and the chain is extended; for bad solvents, $1-2\chi < 0$ and the polymer collapses. The state can also change depending on the temperature, with a coil (collapsed)-globule (extended) transition at the temperature

$$\Theta = \frac{2z\Delta\epsilon}{k}. \tag{20}$$

Close to the transition,

$$R_g \sim (1-2\chi)^{1/5} \sim \left(1 - \frac{\Theta}{T}\right)^{1/5} \sim (T-\Theta)^{1/5}: \tag{21}$$

the transition is very sharp, which has been observed in [3].

4 Polymer solution

12. Overlap concentration c^* given by

$$c^* = R_g^{-3}. \tag{22}$$

Note that the number of monomer segments per unit volume at the transition is

$$Nc^* \sim N^{-4/5}. \tag{23}$$

Larger polymers overlap at lower volume fraction.

13. The arguments given above for R_g do not hold in a concentrated solution: the interactions are screened. In this situation each polymer recovers the ideal chain configuration.

References

[1] Masao Doi. *Introduction to polymer physics*. Oxford university press, 1996.

[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.