

## Polymer solutions

difference across a membrane that separates the polymer solution from pure solvent. The membrane allows solvent to pass freely but prevents polymer from crossing. In Chapters 1 and 4, we learned that osmotic pressure measurements in dilute solution determine polymer molar mass, since osmotic pressure is  $kT$  per chain. In this chapter, we learned that the osmotic pressure measurement in semidilute solution provides another means of determining the correlation length because the osmotic pressure is of the order of  $kT$  per correlation volume. The correlation length can also be determined from the osmotic compressibility measured by scattering at low wavevector [Eq. (1.91)].

### 5.8 Summary of polymer solutions

The phase diagram of polymer solutions is shown in Fig. 5.1, assuming the usual case of  $B > 0$  in Eq. (4.31) (with  $\chi = A + B/T$  a decreasing function of temperature). In the poor solvent half of the diagram (at temperatures below  $\theta$ ) the binodal separates the two-phase region from the two single-phase regions.

There are dilute globules with size

$$R_{\text{gl}} \approx \frac{b^2 N^{1/3}}{|\mathbf{v}|^{1/3}}, \quad (5.77)$$

at very low concentrations ( $\phi < \phi'$ ) and concentrated solutions with overlapping ideal chains for  $\phi > \phi''$ .

At temperatures near  $\theta$  (for  $|T - \theta|/\theta < 1/\sqrt{N}$ ) there are two regions. Dilute  $\theta$ -solutions with non-overlapping chains for  $\phi < \phi_\theta^* \approx 1/\sqrt{N}$  and semidilute  $\theta$ -solutions with overlapping chains for  $\phi > \phi_\theta^*$ . Chains in both  $\theta$ -regions have nearly ideal coil size:

$$R \approx R_0 = bN^{1/2}. \quad (5.78)$$

At sufficiently high temperatures, the solvent is good, with three regimes. There is a dilute good solvent regime at concentrations  $\phi < \phi^* \approx (b^3/\mathbf{v})^{6\nu-3} N^{1-3\nu}$ , with non-overlapping swollen chains whose size was determined in Chapter 3:

$$R_{\text{F}} \approx b \left( \frac{\mathbf{v}}{b^3} \right)^{2\nu-1} N^\nu \approx b \left( \frac{\mathbf{v}}{b^3} \right)^{0.18} N^{0.588}. \quad (5.79)$$

At concentrations  $\phi^* < \phi < \phi^{**} \approx \mathbf{v}/b^3$ , there is a semidilute good solvent regime. In semidilute solution, the chain conformation is similar to dilute solutions on small length scales, while the conformation is analogous to polymer melts on large length scales. The overlapping chains in semidilute solution are swollen at intermediate length scales between the thermal blob size and the correlation length  $\xi_T < r < \xi$  and ideal at smaller ( $r < \xi_T$ ) and larger ( $r > \xi$ ) length scales. The chain size in semidilute solutions in a good solvent decreases weakly as the concentration is increased:

$$R \approx R_{\text{F}} \left( \frac{\phi}{\phi^*} \right)^{-(\nu-1/2)/(3\nu-1)} \approx R_0 \left( \frac{\phi}{\phi^{**}} \right)^{-0.12}. \quad (5.80)$$

Concentrated solutions occur above the concentration  $\phi^{**}$  at which the thermal blob size and the correlation length coincide (at  $\phi = \phi^{**} \approx v/b^3$ ). Chains have nearly ideal statistics on all length scales in concentrated solution. This regime is simply an extension of the semidilute  $\theta$ -solution region to higher temperatures (see Fig. 5.1).

Semidilute and concentrated solutions are characterized by a correlation length  $\xi$ , the scale at which a given chain starts to find out about other chains. This correlation length is

$$\xi \approx b \left( \frac{b^3}{v} \right)^{(2\nu-1)/(3\nu-1)} \phi^{-\nu/(3\nu-1)} \approx b \left( \frac{b^3}{v} \right)^{0.23} \phi^{-0.76} \quad (5.81)$$

in good solvents, and

$$\xi \approx \frac{b}{\phi} \quad (5.82)$$

in semidilute  $\theta$  and concentrated solutions. The correlation length is the average distance between segments on neighbouring chains and is independent of the degree of polymerization. Inside the correlation blob, dilute chain statistics apply, whereas the large-scale conformation of the chain is that of a melt of correlation blobs. Hence, the chain size in semidilute solution is always determined as a random walk of correlation blobs.

The semidilute good solvent predictions have been tested using SANS on polystyrene solutions in carbon disulphide in Fig. 5.13, showing remarkable agreement. Carbon disulphide was chosen for the solvent because no deuterium labelling is needed since this solvent has no protons. Apparently,  $\text{CS}_2$  is an athermal solvent for polystyrene, since the radius of gyration continues to decrease all the way to the melt.

The correlation length also determines the osmotic pressure to be of order  $kT$  per blob:

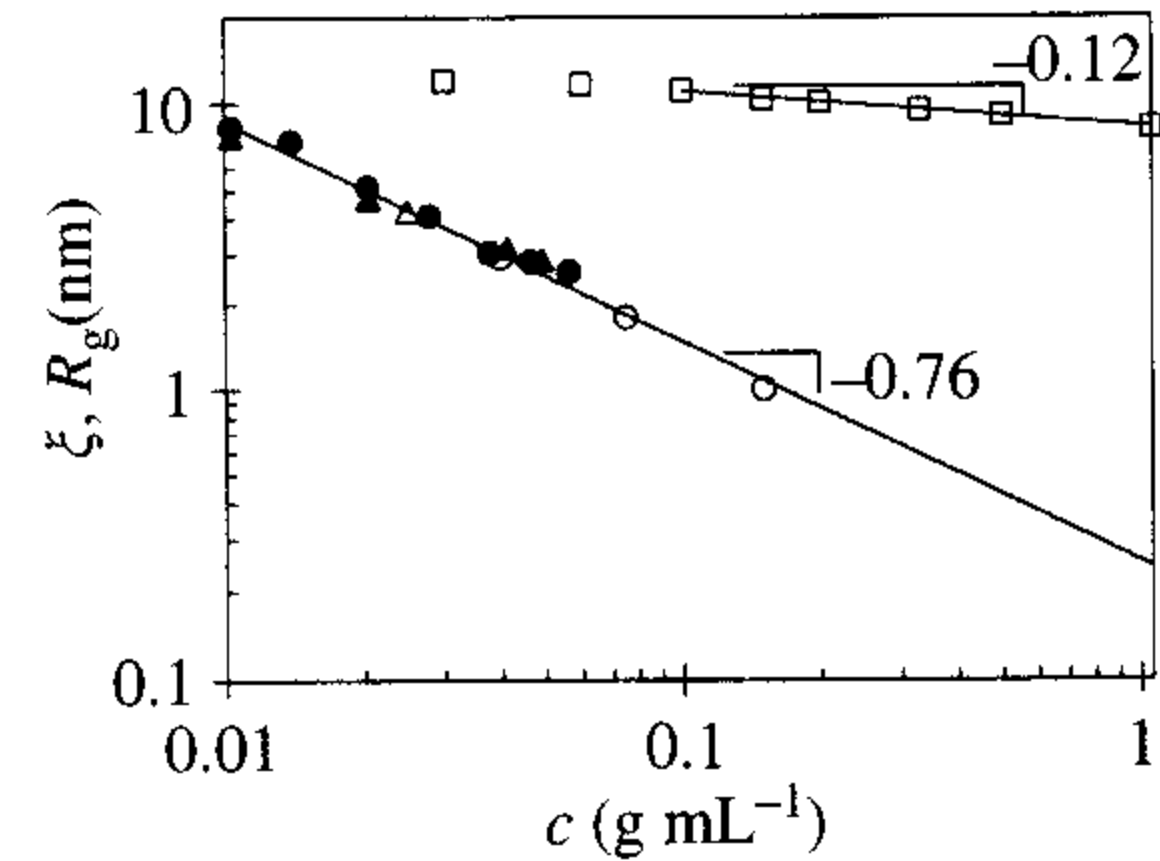
$$\Pi \approx \frac{kT}{\xi^3}. \quad (5.83)$$

This equation holds for theta, good, and athermal solvents. Hence, osmotic pressure or osmotic compressibility measurements provide a convenient means of measuring the correlation length in semidilute solutions.

## Problems

### Section 5.2

- 5.1 Consider a dilute polymer solution with excluded volume  $v = -12.5 \text{ \AA}^3$  and Kuhn monomer length  $b = 5 \text{ \AA}$ . What is the root-mean-square end-to-end distance of this polymer if the number of Kuhn monomers is (i)  $N = 50$ ? (ii)  $N = 10^2$ ? (iii)  $N = 10^3$ ?
- 5.2 A solution is prepared using chains having  $N = 10^4$  Kuhn monomers of length  $b = 4 \text{ \AA}$ , with Flory interaction parameter  $\chi = 0.55$  at volume fraction  $\phi = 0.01$ .
- Will this solution remain homogeneous or phase separate?
  - What is the polymer volume fraction  $\phi''$  in the sediment?



**Fig. 5.13**

Correlation length  $\xi$  and radius of gyration  $R_g$  for polystyrene in carbon disulfide from M. Daoud *et al.*, *Macromolecules* **8**, 804 (1975). Radius of gyration data (open squares  $M = 1.14 \times 10^5 \text{ g mol}^{-1}$ ) above  $c = 0.1 \text{ g ml}^{-1}$  were fit to a power law with slope  $-0.12$  that agrees well with the scaling prediction [Eq. (5.80)]. The correlation length is independent of molar mass (filled circles  $M = 2.1 \times 10^6 \text{ g mol}^{-1}$ , filled triangles  $M = 6.5 \times 10^5 \text{ g mol}^{-1}$ , open circles  $M = 5 \times 10^5 \text{ g mol}^{-1}$ ) and the power law slope of  $-0.76$  for all data agrees well with scaling prediction [Eq. (5.81)]. Note that  $c = 1.06 \text{ g mL}^{-1}$  corresponds to a polystyrene melt.

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- (iii) What is the root-mean-square end-to-end distance of the polymer in the sediment?
- (iv) What is the polymer volume fraction  $\phi'$  in the supernatant?
- (v) What is the root-mean-square end-to-end distance of the polymer in the supernatant?
- (vi) What is the volume fraction within the globule in the supernatant?

### Section 5.3

**5.3** Consider a polymer solution with  $N = 10^3$  Kuhn monomers of length  $b = 7 \text{ \AA}$ , and Flory interaction parameter  $\chi = 0.45$  at volume fraction  $\phi = 0.025$ .

- (i) Do you expect this solution to stay homogeneous or to phase separate? Explain.
- (ii) What is the polymer volume fraction  $\phi$  in the sediment?
- (iii) What is the root-mean-square end-to-end distance of the polymer in the sediment?
- (iv) What is the polymer volume fraction  $\phi$  in this solution?
- (v) What is the root-mean-square end-to-end distance of the polymer in this solution?

**5.4** Consider three polymer solutions with Flory interaction parameter  $\chi = 0.49$ , Kuhn length  $b = 7 \text{ \AA}$ , and the number of Kuhn monomers: (a)  $N = 100$ ; (b)  $N = 1000$ ; and (c)  $N = 10,000$ .

- (i) How many monomers are in a thermal blob?
- (ii) Find the root-mean-square size of these polymers in dilute solutions.
- (iii) Find the overlap volume fraction for each of these three polymers.
- (iv) What is the size of each of these polymers in solutions with volume fraction  $\phi = 0.015$ ?

**5.5** Consider a polymer solution with Flory interaction parameter  $\chi = 0.4$ , consisting of chains with  $N = 10^3$  Kuhn monomers of length  $b = 3 \text{ \AA}$ .

- (i) What is the overlap volume fraction  $\phi^*$  of these chains?
- (ii) What is the  $\phi^{**}$  volume fraction for this solution?

What is the root-mean-square end-to-end distance of the polymer at volume fraction

- (iii)  $\phi = 0.005$ ?
- (iv)  $\phi = 0.05$ ?
- (v)  $\phi = 0.1$ ?
- (vi)  $\phi = 0.2$ ?
- (vii)  $\phi = 0.4$ ?

**5.6** Recall the two-dimensional size of an isolated real chain at the air–water interface  $R = a^{1/4} b^{1/2} N^{3/4}$ , where  $a$  is the excluded area parameter,  $b$  is the monomer size, and  $N$  is the degree of polymerization [Eq. (3.137)].

- (i) What is the overlap surface coverage,  $\sigma^*$ ?
- (ii) What is the thermal blob size,  $\xi_T$ ?
- (iii) What is the correlation length  $\xi$  at surface coverage  $\sigma$ ?
- (iv) What is the size of the polymer  $R$ ? Describe the conformation of the chain at surface coverages  $\sigma$  above the overlap coverage  $\sigma^*$ .
- (v) What is the surface pressure (the two-dimensional analog of osmotic pressure)?

**5.7** Consider an athermal semidilute polymer solution (with excluded volume  $v = 125 \text{ \AA}^3$ , and the Kuhn length  $b = 5 \text{ \AA}$ ) at volume fraction  $\phi = 0.01$ . The

degree of polymerization of chains is  $N = 10^4$ . Estimate the osmotic pressure of this solution at room temperature using

- (i) mean-field theory;
- (ii) scaling theory.

**5.8** Consider a semidilute polymer solution of chains with  $N_B$  monomers, volume fraction  $\phi$  and excluded volume  $v$ . A trace amount of longer chemically identical chains with  $N_A$  monomers is added to the solution. What is the size  $R_A$  of these A-chains, if they are assumed not to overlap with each other and not to change the overall volume fraction  $\phi$ ?

**5.9** Derive Eqs (5.23) and (5.26) for good solvents with  $0 < v < b^3$  from Eqs (5.38) and (5.39) for athermal solvents. *Hint*: Renormalize the monomer to the thermal blob.

**5.10** Plot the size  $r$  of a labelled section of  $n$  consecutive Kuhn monomers of a chain for different regions of the diagram in Fig. 5.1. (i) Dilute  $\theta$ -solvent; (ii) semidilute  $\theta$ -solvent; (iii) dilute poor solvent; (iv) two-phase region; (v) concentrated poor solvent; (vi) dilute good solvent; (vii) semidilute good solvent; (viii) concentrated good solvent.

**5.11** Plot the total number of Kuhn monomers belonging to all chains within a small sphere of radius  $r$  with the centre at one monomer for different regions of the diagram in Fig. 5.1. (i) Dilute  $\theta$ -solvent; (ii) semidilute  $\theta$ -solvent; (iii) dilute poor solvent; (iv) two-phase region; (v) concentrated poor solvent; (vi) dilute good solvent; (vii) semidilute good solvent; (viii) concentrated good solvent.

**5.12** Stretching a chain in semidilute solution.

Consider a semidilute solution with volume fraction  $\phi$  of chains with  $N$  Kuhn monomers of length  $b$  and excluded volume  $v$ . Calculate the free energy cost to stretch a chain to end-to-end distance  $R$  for the following cases:

- (i) Consider the case of relatively weak stretching, with the Pincus blob larger than the correlation length.
- (ii) Consider the case of intermediate stretching, with the Pincus blob smaller than the correlation length but larger than the thermal blob.
- (iii) Consider the case of strong stretching, with the Pincus blob smaller than the thermal blob.
- (iv) Over what range of end-to-end distance does each case apply?

## Section 5.4

**5.13** Consider a semidilute polymer solution at room temperature with Flory interaction parameter  $\chi = 0.4$ , having  $N = 10^3$  Kuhn monomers of length  $b = 3 \text{ \AA}$ .

- (i) Calculate the size of a thermal blob  $\xi_T$ .
- (ii) Calculate the size of a correlation blob  $\xi$  as a function of polymer volume fraction  $\phi$ . Note: separately consider two cases:  $\xi > \xi_T$  and  $\xi < \xi_T$ .
- (iii) What is the concentration dependence of osmotic pressure  $\Pi(\phi)$  at room temperature?

**5.14** In order to better understand why the distance between three-body contacts is of the order of the distance between monomers on neighbouring chains, the problem can be generalized to ideal chains in  $d$  dimensions.

- (i) Calculate the distance  $r_n$  between  $n$ -body contacts in  $d$  dimensions.