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Screening length in semi-dilute polymer solutions

J P Cotton†, B Farnoux†, G Jannink and R Ober‡

† Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay, BP no 2-91, Gif-sur-Yvette, France

‡ Laboratoire de la Matière Condensée, Collège de France, 11 Place Marcellin Berthelot, Paris 5ème, France

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Abstract. Osmotic pressure data in the semi-dilute polymer concentration range are interpreted in terms of excluded volume and Edward's screening length. The values obtained are compared with the results of a neutron scattering experiment.

The statistics of polymer solutions at concentrations high enough for chains to overlap have received considerable and successful theoretical attention. In the Flory-Huggins theory (Flory 1957), the free energy of mixing from which all thermodynamical observables are derived, could be determined by a free volume type of argument. More recently, Edwards (1966) has formulated the problem in a self-consistent field approximation, which in contradistinction to the previous theory is valid only up to a finite concentration, which defines the semi-dilute range. Problems of interest raised by these theories are (i) the existence of the semi-dilute range, (ii) the comparison between the values of the parameters used in both theories and identically defined. In two earlier papers (Cotton *et al* 1972 and to be published) we discussed the first aspect and concluded that the semi-dilute is very distinct from the dilute solution. This statement is often found in the literature (eg Flory 1957). It is based (Kuwahara *et al* 1967, Leonard and Daoust 1965) on the sudden change of slope ϕ of the osmotic pressure concentration ratio against concentration c at the onset of overlap c^* (figure 1). In a scattering experiment, a good observable which reflects this distinction is the screening length introduced by Edwards

$$\xi = \left(\frac{l^2 m}{12c\mathcal{A}v} \right)^{1/2} \quad (1)$$

where c is the concentration in g cm^{-3} and \mathcal{A} is the Avogadro number. The other quantities refer to the statistical element, l^2 the mean square length, m the mass and v the excluded volume. The values obtained for $\xi\sqrt{c}$ by neutron scattering were (Cotton *et al* 1972) $(6.5 \pm 0.5) \times 10^{-8} \text{ g}^{1/2} \text{ cm}^{-1/2}$. The following problems are discussed here.

(i) Is it possible to determine the value of the screening length from the osmotic pressure concentration dependence? Although this is feasible in principle, there is no published data.

(ii) How does such a value of the screening length compare with the neutron scattering result?

(iii) In what sense does the Edwards description better represent the experimental data than the Flory-Huggins theory, and what is the physical difference between the two formulations?

The osmotic pressure concentration dependence given by Edwards (1966) as

$$\frac{\pi}{kT} = \mathcal{N} + \frac{n^2 v}{2} - \frac{1}{24\pi} \xi^{-3}, \quad (2)$$

where \mathcal{N} and n are the number of chains and statistical elements/cm³, contains the screening length as a parameter. Before discussing the possibility of determining this quantity from the experimental data, it is necessary to introduce the following modification into formula (2). According to Edwards (1966), formula (2) is physically acceptable as long as

$$\xi > \left(\frac{1}{\mathcal{N}} \right)^{1/3} = d. \quad (3)$$

If ξ is somewhat smaller than d , that is,

$$\xi \leq \left(\frac{1}{\mathcal{N}} \right)^{1/3} \left\{ 24\pi \left(1 + \frac{Nnv}{2} \right) \right\}^{-1/3},$$

where N is the number of segments per chain, the osmotic pressure (2) becomes negative. The concentration for which the minimum osmotic pressure is zero is given by

$$c = \frac{3vm}{\pi^2 \mathcal{A} l^6}. \quad (4)$$

Condition (3) states that the screening length has to be greater than the average distance d between neighbouring chains. However, use of the random phase approximation in the derivation of the density fluctuations in semi-dilute solutions (Jannink and de Gennes 1968), only requires that

$$nv \ll 1 \quad (5)$$

which yields

$$\xi > l/\sqrt{12} \quad (6)$$

as a sufficient condition. We can write (1) as

$$\xi = \left(\frac{d^3 l^2}{12Nv} \right)^{1/2} \quad (7)$$

or

$$\xi^2 d^{-2} = \frac{dl^2}{12Nv}. \quad (8)$$

In the semi-dilute range the distance d is smaller than the radius of gyration R_g

$$\xi^2 d^{-2} < \frac{R_g l^2}{12Nv} = \frac{l^3}{12\sqrt{6}N^{1/2}v}. \quad (9)$$

The right hand side of this expression is part of the Flory relation (Flory 1957)

$$\frac{N^{1/2}v}{l^3} = \frac{\pi}{3}(\alpha^5 - \alpha^3) \quad (10)$$

where α is the Flory excluded volume polymer expansion factor. For a good solvent

$$\xi^2 d^{-2} < \frac{1}{4\pi\sqrt{6(\alpha^5 - \alpha^3)}} < 1. \tag{11}$$

Hence ξ cannot satisfy inequality (3). On the other hand, using equation (10) we can replace (5) by

$$nl^3 < \frac{N^{1/2}}{\alpha^5 - \alpha^3} \left(\frac{3}{\pi}\right) \\ l < \left(\frac{1}{n}\right)^{1/3} \left(\frac{N^{1/2}}{\alpha^5 - \alpha^3}\right)^{1/3} \left(\frac{3}{\pi}\right)^{1/3}. \tag{12}$$

In a good solvent and for large N , the value of $N^{1/2}(\alpha^5 - \alpha^3)^{-1}$ is never greater than 30 (Brandrup and Immergut 1967). It is therefore sufficient that

$$\xi > \left(\frac{1}{n}\right)^{1/3} \frac{1}{\sqrt{12}} \left(\frac{90}{\pi}\right)^{1/3}.$$

Thus we replace the Edwards condition (3) by the less stringent condition that the screening length must be greater than the mean distance between statistical elements

$$\xi > \left(\frac{1}{n}\right)^{1/3}. \tag{14}$$

The values found for ξ in a neutron scattering experiment satisfy (14) but not (3). In order to measure ξ in an osmotic pressure experiment, we need a formula for which the concentration dependence is positive at all values of ξ satisfying (14). Now the negative term in equation (2) arises from the evaluation of the monomer density-density fluctuation. The latter contributes (de Gennes 1968†) to the free energy of interaction by the term (see the appendix)

$$\Delta F = \frac{kT}{2n} \lim_{R \rightarrow 0} \int_0^\infty \frac{dq}{(2\pi)^3} q^2 \ln \left(1 + \frac{\xi^{-2}}{q^2}\right) e^{-iq \cdot R}. \tag{15}$$

This quantity is usually made finite by subtracting the self-energy of the chain, so that

$$\bar{\Delta F} = \frac{kT}{2n} \int_0^\infty \frac{dq}{(2\pi)^3} q^2 \left\{ \ln \left(1 + \frac{\xi^{-2}}{q^2}\right) - \frac{\xi^{-2}}{q^2} \right\}. \tag{16}$$

The contribution of the self-energy is, however, over estimated in this equation. In particular for $q < 1/l$, no correction to the point-interaction hypothesis is necessary.

Therefore we correct the self-energy by the quantity

$$\frac{kT}{2n} \frac{1}{(2\pi)^3} \frac{\xi^{-2}}{l}. \tag{17}$$

The osmotic pressure becomes now instead of (2)

$$\frac{\pi}{kT} = \mathcal{N} + \frac{n^2 v}{2} \frac{1}{24\pi} \left(\xi^{-3} - \frac{\xi^{-2}}{l} \right). \tag{18}$$

This expression is always positive if relation (14) is satisfied.

A typical osmotic pressure concentration dependence is shown in figure 1. Interpretation of the data with formula (18) faces two difficulties.

† Copies obtainable from G Paillotain, CEN Saclay, 91 Gif-sur-Yvette on request.

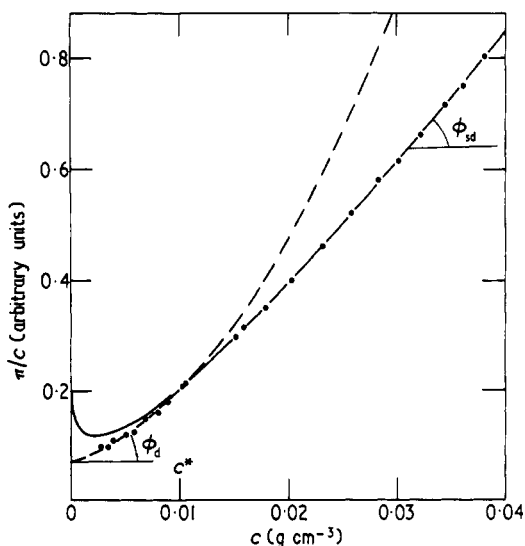


Figure 1. Osmotic pressure data as a function of concentration for polystyrene of molecular mass $M = 5 \times 10^5$, in toluene. The data (●) are taken from Cotton *et al* (1973); broken curve, best fit with the virial expansion, $c < c^*$; full curve, best fit with formula (18), $c > c^*$. Equation (18) was used to interpolate the data in the range $c^* = c_1 = 10^{-2} \text{ g cm}^{-3}$ to $c_2 = 4 \times 10^{-2} \text{ g cm}^{-3}$. This curve below c_1 is an extrapolation of equation (18).

- (i) The lower limit of the semi-dilute range is given by the inequality $d < R_g$, or

$$c > c^* = \frac{mN}{R_g^3 \mathcal{A}}. \quad (19)$$

This limit is thus not precisely defined.

(ii) It is seen that the concentration range over which the screening length modifies the osmotic pressure (by a departure from linearity of π/c) is small. Thus the value obtained for ξ cannot be very precise.

The theoretical curve (18) was fitted to two sets of data, one with a polystyrene of number average molecular weight $M_1 = 3 \times 10^5$ (Cotton *et al* 1973). The other with $M_2 = 5 \times 10^5$. The solvent used in both cases was toluene. Concentrations ranged from 0.01 to 0.04 g cm^{-3} . The unknown parameter ξ in (18) was expressed in terms of number average molecular mass M_N whose value is determined by the zero concentration limit of the osmotic pressure. Values of $\xi\sqrt{c}$ were determined by a best fit method (Tournarie 1969). They are:

$$\begin{aligned} \xi\sqrt{c} &= (4.1 \pm 4) \times 10^{-8} \text{ g}^{1/2} \text{ cm}^{-1/2}, & \text{for } M_1 \\ \xi\sqrt{c} &= (6.5 \pm 5) \times 10^{-8} \text{ g}^{1/2} \text{ cm}^{-1/2}, & \text{for } M_2. \end{aligned}$$

The errors associated with these values of $\xi\sqrt{c}$ are large compared to the errors usually obtained in the determination of the molecular mass and the second virial coefficient by osmotic pressure. It will be difficult to improve the experimental precision, as described above.

Despite the shortcomings of such an experiment, it is possible to infer the following conclusions:

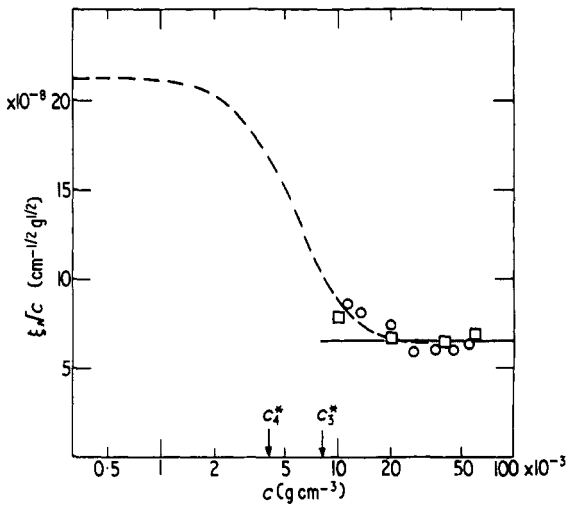


Figure 2. $\xi\sqrt{c}$ values: broken curve, as a function of concentration from the scattering experiment of Cotton *et al* (1972). Molecular mass $M_3 = 6.5 \times 10^5$ (■) and $M_4 = 2.1 \times 10^6$ (●) of polystyrene in C_6D_6 . The upper plateau was measured in the dilute solution range. Full curve, determined by the osmotic pressure data in figure 1, interpreted with formula (18) in the semi-dilute concentration range, for the molecular mass $M_2 = 5 \times 10^5$.

(i) The screening length obtained from osmotic pressure measurements cannot be greater than the distance between chains (3), even if we allow the maximum possible error. This confirms the neutron scattering result. On the other hand, central values of $\xi\sqrt{c}$ are consistent with neutron results and satisfy inequality (14).

(ii) The alternative interpretation of the osmotic pressure-concentration dependence in the semi-dilute range is given by the Flory-Huggins theory. Instead of (2) or (18), one has

$$\frac{\pi}{kT} = \mathcal{N} + \frac{n^2\bar{v}^2}{V_1\mathcal{A}}m^2\left(\frac{1}{2} - \chi\right) + \frac{n^3\bar{v}^3m^3}{V_1\mathcal{A}^2}\left(\frac{1}{3} - \Phi\right), \quad (20)$$

where \bar{v} is the partial specific volume of the polymer and V_1 the molar volume of the solvent, χ is the dimensionless quantity characterizing the interaction energy per solvent molecule and Φ , a dimensionless corrective term for the entropy of mixing. Most experimental data for $c > c^*$ are interpreted with equation (20) (Kuwahara *et al* 1967). The departure from linearity of π/c is produced here by the triple monomer encounters. However, it has been suggested that at concentrations considered ($c \leq 0.04 \text{ g cm}^{-3}$) triple monomer encounters are negligible (Edwards 1966). On the other hand, the monomer density-density fluctuations, which are important at all concentrations, produce in the semi-dilute range an irrational concentration dependence ($c^{3/2}$) of the osmotic pressure, because the radial pair correlation function cannot be expanded in c for $c > c^*$. The latter point has been confirmed by a neutron scattering experiment (Cotton *et al* 1972). Experimentally, the choice between equations (20) and (18) is a question of appreciation of the departure from linearity of π/c against c . In the Flory-Huggins theory this departure increases with c , in the Edwards theory it decreases with c . The π/c dependence in figure 1 is clearly in favour of a decreasing departure from linearity.

We feel that equation (2) is better constructed to fit the concentration dependence especially at the lower end of the semi-dilute range. This is of course of great interest

for a study of the intermediate region between the dilute and the semi-dilute ranges, which has not yet received any theoretical attention.

On the basis of our result, we propose that the weaker inequality (14) holds for semi-dilute solutions. We would expect that inequality (3) holds for dilute solutions, if we use expression (1) in which v is replaced by the chain excluded volume u/N^2 . This is however not the case. As for the interpretation of inequality (14), we may say that ξ is a screening length associated with the screening of statistical elements, rather than chain density fluctuations.

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Appendix. Derivation of formula (16)

This formula, which is formula (3.15) in Edwards (1966), is derived from the monomer density-density fluctuation in de Gennes (1968). Onset of the excluded volume interaction in a semi-dilute solution gives rise to an excess energy per cm^3

$$\langle \Delta E \rangle = kT(\frac{1}{2}vn^2 + \frac{1}{2}v\langle \delta n^2 \rangle), \quad (\text{A.1})$$

where δn is the fluctuation in monomer density. The last term in (A.1) can be written as the Fourier transform of the neutron scattering law (Van Hove 1958)

$$\langle \delta n^2 \rangle = \lim_{R \rightarrow 0} n \int \frac{d^3q}{(2\pi)^3} S(q) e^{-iq \cdot R}, \quad (\text{A.2})$$

where q is the momentum transfer, $S(q)$ the scattering law and R the distance between the space points at which the fluctuation in density is considered. If we insert in (A.2) the scattering law (Jannink and de Gennes 1968) for semi-dilute polymer solutions

$$S(q) = (q^2 + \xi^{-2})^{-1}, \quad (\text{A.3})$$

we obtain the result (16) by quadrature

$$\Delta F = \int_0^v \langle \Delta E \rangle(v') \frac{dv'}{v'}. \quad (\text{A.4})$$

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