polymer papers

Scattering from a polymer solution at an arbitrary concentration

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The elastic coherent scattering intensity for a polymer solution at an arbitrary concentration has been calculated. We introduce an approximate model of contacts between many chains which is a generalization of the well known Zimm single contact model. The results are consistent with the predictions of the random phase approximation[2-4] and can be considered as a direct application of the theory of Ornstein and Zernike[8]. It is shown that the effect of higher order contacts between chains simply reduces to a redefining of an apparent second virial coefficient which would be a function of concentration only. The model is applied to a mixture of deuterated and ordinary homopolymers and the results are not affected by the polydispersity.

(Keywords: polymer solution; light scattering; small-angle neutron scattering; thermodynamics; concentration effects)

INTRODUCTION

The single contact approximation

In a classic paper[1], Zimm calculated the scattering intensity for a solution of homopolymers at low concentration c using the single contact approximation between different chains. He obtained the following result:

$$I(q)=K_0cM[P(q)-2A_2McP^2(q)] \tag{1}$$

where $I(q)$ is the scattering intensity, q the magnitude of the wave vector i.e. $q=(4\pi/\lambda)\sin(\theta/2)$. λ is the wavelength of the incident radiation, and θ, the scattering angle. c is the total monomer concentration in weight fraction, M is the polymer molecular weight, A_2 the second virial coefficient. K_0 is a constant that characterizes both the apparatus and the type of radiation (light or neutrons). $P(q)$ is the normalized single chain form factor which is defined by the relation:

$$n^2P(q)=g(q)=\sum_j^n\sum_l^n\langle\exp(i\cdot\underline{q}\cdot\underline{R}_{jl})\rangle \tag{2}$$

$g(q)$ and $P(q)$ differ by the constant normalization factor n^2, only. n is the number of monomers per chain and $\underline{R}_{jl}$ represents the vector distance between monomer j and monomer l on the same chain.

To interpret the data, one usually uses the reciprocal form of equation (1) which can be obtained by assuming $2A_2McP(q)\ll 1$:

$$\frac{K_0c}{I(q)}=\frac{1}{MP(q)}+2A_2c \tag{3}$$

This form is used by most workers when trying to interpret scattering data over a wide range of concentrations. It has been shown to be rigourous by Edwards[2] and Jannink and de Gennes[3] when the meanfield approximation is valid i.e. in concentrated solutions. In the semidilute case it is well known that meanfield theory does not apply and that critical exponents have to be used. Daoud *et al.*[4] assume that the form of equation (3) is still valid if a renormalization argument, replacing the term $2A_2c$ by a more correct expression, is used. One can obtain such an expression by using the result of des Cloizeaux showing that the osmotic pressure π is proportional to $c^{9/4}$. We shall come back to this problem later.

Here, we consider a concentration model along the lines of these ideas, and generalize it to the cases of a mixture and a copolymer solution in a forthcoming paper. Let us recall that the scattering intensity $I(q)$ is defined by:

$$I(q)=K\sum_\alpha^N\sum_\beta^N\sum_{j\in\alpha}^n\sum_{l\in\beta}^n\langle\exp(i\underline{q}\cdot\underline{R}_{\alpha j\beta l})\rangle \tag{4}$$

where $K=K_0m^2/N_A$, m being the molecular weight of a monomer and N_A Avogadro's number. $\underline{R}_{\alpha j\beta l}$ is the vector distance between monomer j of chain α and monomer l of chain β. N is the number of chains per unit volume in the solution. Separating the intramolecular from the intermolecular terms, equation (4) becomes:

$$K^{-1}I(q)=Ng(q)+N^2\sum_{j_1}\sum_{l_2}\langle\exp(i\underline{q}\cdot\underline{R}_{j_1l_2})\rangle \tag{5}$$

where 1 and 2 refer to any pair of chains. The symbol $\langle\cdots\rangle$ represents the ensemble average with respect to the

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equilibrium distribution which, in the case of equation (5), can be explicitly written as follows:

$$\langle \exp(i\underline{q}\cdot\underline{R}_{j_1l_2})\rangle = \int d^3R_{j_1l_2}W(\underline{R}_{j_1l_2})\exp(i\underline{q}\cdot\underline{R}_{j_1l_2})$$

where $W(\underline{R}_{j_1l_2})$ represents the probability distribution of the vector distance $\underline{R}_{j_1l_2}$. Following Zimm, one writes this quantity as the product of intrachain distributions $W_s(1)W_s(2)$ and an interaction term $\exp(-U_{12}/k_\beta T)$, where (1) and (2) are symbols for the internal coordinates of chains 1 and 2, U_{12} is the potential of interaction between 1 and 2 and $k_\beta T$ is the temperature in units of the Boltzman constant k_β.

$$W(\underline{R}_{j_1l_2}) = W_S(1)W_S(2)\exp(-U_{12}/k_\beta T) \qquad (7a)$$

Furthermore, one assumes that the energy U_{12} is the sum of the pair of interaction energies between all monomers and that these are of short range:

$$\exp(-U_{12}|k_\beta T) = 1 - \sum_{\mu_1}\sum_{\nu_2} v_{\mu_1\nu_2}\delta(R_{\mu_1\nu_2}) \qquad (7b)$$

where $v_{\mu_1\nu_2}$ is the interaction strength, or the excluded volume for a pair of monomers μ_1 and ν_2 and δ is the Dirac delta function. The minus sign in front of the interaction parameter v is introduced to insure that it has a positive value when it corresponds to a repulsion. One notes that the second term in the right-hand side of equation (5) is different from zero only when the pair (1)(2) interacts, namely, when there is at least one contact between them.

SCATTERING INTENSITY USING MANY CHAIN MODELS

Model for a chain of single contacts

Consider the case of a single contact as illustrated by *Figure 1*. If, in equation (6) we express $\underline{R}_{j_1l_2}$ as a sum $\underline{R}_{l_1\mu_1} + \underline{R}_{\mu_1\nu_2} + \underline{R}_{\nu_2l_2}$, and assume that these 3 vector components are independent, we obtain after summation over all possible contact points, the following expression:

$$\langle \exp(i\underline{q}\cdot\underline{R}_{j_1l_2})\rangle = \sum_{\mu_1}^{n}\sum_{\nu_2}^{n}\langle \exp(i\underline{q}\cdot\underline{R}_{j_1\mu_1})\rangle \times \langle \exp(i\underline{q}\cdot R_{\mu_1\nu_2})\rangle\langle \exp(i\underline{q}\cdot R_{\nu_2l_2})\rangle \qquad (8)$$

Combining this and equation (5), and letting $v_{\mu_1\nu_2} = v$, yields:

$$K^{-1}I(q) = Ng(q,c) - vN^2g^2(q,c) \qquad (9)$$

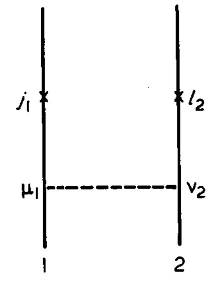

Figure 1 Single contact representation. Vertical lines represent chains (1) and (2) and the broken horizontal line the contact. j_1 and l_2 are the scattering points, μ_1 and ν_2 the contact points

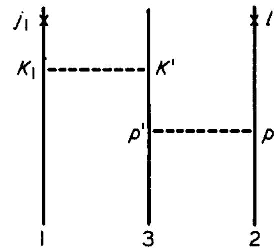

Figure 2 Double contact representation

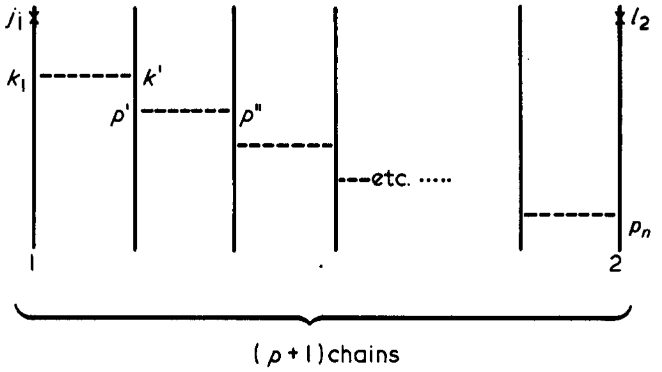

Figure 3 Chain of single contacts

Using the standard notation $A_2 = vN_A/2m^2$, $M = nm$, and $c = Nnm/N_A$, equation (9) can be written in the known form:

$$(KcM)^{-1}I(q) = P(q,c) - 2A_2McP^2(q,c) \qquad (10)$$

This is a classical Zimm result (see equation (1)) which shows that the angular distribution of the scattered intensity depends only on the single chain form factor.

Another type of interaction is illustrated in *Figure 2*, where, instead of having a direct contact, the pair (1)(2) interacts via a third chain (3). The situation in *Figure 2* leads to a term proportional to N^3 or C^3 since 3 different chains are involved. Using a similar procedure as in the single contact limit, namely $\underline{R}_{j_1l_2} = \underline{R}_{j_1k_1} + \underline{R}_{k_1k'} + \underline{R}_{k'p'} + \underline{R}_{p'p_2} + \underline{R}_{p_2l_2}$, assuming that the monomer concentration is uniform in the solution, and that the vector components of $\underline{R}_{j_1l_2}$ are independent, we obtain a sixth order summation. The averages over the distributions of vectors $\underline{R}_{j_1k_1}$, $\underline{R}_{k'p'}$, and $\underline{R}_{p_2l_2}$, combined with the double summation over the appropriate indices leads to a factor $g^3(q,c)$, whereas the averages over the distributions of vectors $\underline{R}_{k_1k'}$ and $\underline{R}_{p'p_2}$ lead to a factor v^2 as explained in the previous case. Therefore, it becomes clear that the contributing term from *Figure 2* takes the form:

$$v^2N^2g^3(q,c) \qquad (11a)$$

One may generalize this procedure to the case illustrated in *Figure 3* and involving a total of $p+1$ chains. It is easy to verify that the term corresponding to this type of figure is of the form:

$$(-v)^pN^{p+1}g^{p+1} \qquad (11b)$$

We shall drop the explicit (q, c) dependence of P and g to ease the notation. Collecting these results, we can obtain $I(q)$ as follows:

$$K^{-1}I(q) = Ng - vN^2g^2 + v^2N^3g^3 - \cdots (-v)^\alpha N^{\alpha+1}g^{\alpha+1} + \cdots \qquad (12)$$

If we assume that $vNg < 1$, this series can be summed and we obtain:

$$K^{-1}I(q) = \frac{Ng}{1+vNg} = \frac{Nn^2P(q,c)}{1+vNn^2P(q,c)} \qquad (13a)$$

and in the reciprocal form, we have:

$$KI^{-1}(q) = \frac{1}{Nn^2P(q,c)} + v \qquad (13b)$$

As we have pointed out earlier, this result has already been obtained by various authors[2-4] using more or less similar arguments. If we consider the reciprocal form given by equation (13b) and use the standard notation defined earlier, again we obtain equation (3). However, one must keep in mind that the validity of equation (3) is subject to the condition that $vNn^2P = 2A_2McP$ is very small compared with 1. Hence, although we have assumed $vNg = 2A_2McP < 1$ in order to sum the infinite series, we shall demonstrate that the result in equation (13) is in fact valid even when $2A_2Mc$ is much larger than 1. Furthermore, by assuming that any pair of chains do not have more than one direct contact, we have neglected a large number of configurations in which chains interact at more than one point in space. We shall assume, in what follows, that these types of configurations modify only the internal structure of the chains and keep the structure of our equation unchanged. This is equivalent to a renormalization of the form of $P(q)$ as a function of concentration. Therefore, we shall assume that our equation is correct if we replace $P(q)$ by $P(q,c)$.

Model for a chain of higher order contacts

In this section we present a generalization of the previous model which accounts for contacts of higher order. The simplest example corresponds to the case in which 3 chains have one segment at the same location in space (see *Figure 4*). The case of *Figure 4* can be considered as the limit of the situation illustrated by *Figure 2* in which we let $\underline{R}_{k'p'} = 0$. Hence, the contribution of *Figure 4* is given by:

$$N^2g^2(nNv_3) \qquad (14)$$

where v_3 is the interaction parameter corresponding to a triple contact; note that, in general, $v_3 \neq v^2$ since the probability of a triple contact is different from the product of probabilities of double contacts involving 3 chains two by two. The factor Nn comes from the summation over all possible chain segments[5]. As a generalization of this procedure, one can immediately write the term corresponding to a contact of order $(v+2)$ by drawing v lines between (1) and (2) in *Figure 4*:

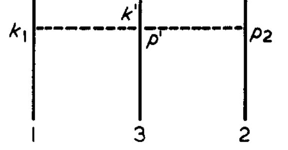

Figure 4 Third order contact representation

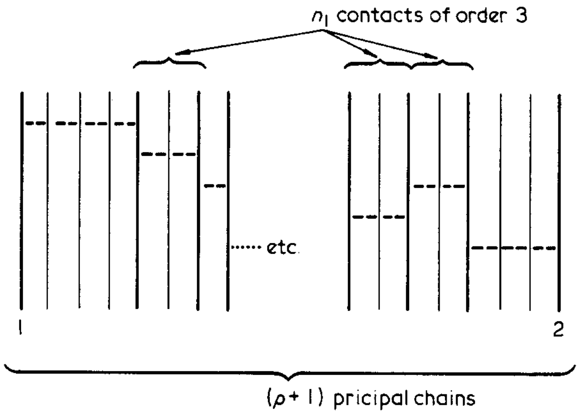

Figure 5 Chain of higher order contacts. Heavy lines are the principal molecules making the chain of contacts from (1) to (2). Light lines represent the chains which contribute to a contact of order $v+2$. There are n_v contacts involving $(v+2)$ molecules, $v = 0, 1, 2, \ldots$

$$(-1)^{v+1}N^2g^2(nN)^v v_{v+2}$$

where v_{v+2} is the interaction parameter for a contact of order $v+2$.

$$N^2g^2\sum_v(-nN)^v v_{v+2} = N^2g^2F(nN) \qquad (15)$$

where $F(nN)$ is given by:

$$F(nN) = v - Nnv_3 + N^2n^2v_4 - \cdots \qquad (16)$$

and since nN is proportional to the concentration c, we shall use the notation

$$F(nN) = v(c)$$

Let us generalize this analysis, first to the case of *Figure 2* where the pair (1)–(2) interacts via another chain (3). The introduction of higher order contacts between (1)–(3) and (3)–(2), and more precisely, of order v_1+2 between (1)–(3), and v_2+2 between (3)–(2), comes to drawing v_1 lines between (1)–(3), and v_2 lines between (3)–(2). This leads to the following term:

$$N^3q^3v_{v_1+2}v_{v_2+2}(=Nn)^{v_1+v_2}$$

and since v_1 and v_2 can take any value, we have:

$$N^3q^3\sum_{v_1}\sum_{v_2}v_{v_1+2}$$

which can be written simply as:

$$N^3g^3\left[\sum_v v_{v+2}(-Nn)^v\right]^2 = N^3g^3v^2(c) \qquad (17)$$

Now, we can generalize further this procedure by considering the case of an arbitrary number of interacting chains (see *Figure 5*). For the sake of simplicity we introduce a new variable X defined by:

$$X_{v+2} = -v_{v+2}(-Nn)^v$$

such that

$$v(c) = -\sum_v X_{v+2}$$

Let us assume that we have $(p+1)$ principal chains making the chain of single contacts which we discussed earlier. There are p sites of contacts that can be of an arbitrary order. If ν additional chains are in contact at the same point, we obtain a contact of order $\nu+2$. n_ν represents the number of sites corresponding to a contact of order $\nu+2$. Clearly, we have

$$\sum n_\nu = p \tag{18}$$

From combinatorial analysis, we know that there are $p!(\prod_\nu n_\nu!)$ ways of arranging p sites in groups of $n_0, n_1, \ldots, n_\nu$. A given realization will contribute to the scattering signal by the expression

$$N^{p+1} g^{p+1} p! \frac{\prod_\nu X_{\nu+2}^{n_\nu}}{\prod_\nu n_\nu!}$$

and summing over all possible realizations (i.e. all possible values of n_ν satisfying equation (18)), one obtains:

$$N^{p+1} g^{p+1} \sum_{n_\nu} p! \frac{\prod_\nu X_{\nu+2}^{n_\nu}}{\prod_\nu n_\nu!}$$

It is easy to verify that this gives:

$$N^{p+1} g^{p+1} \left[\sum_\nu X_{\nu+2}\right]^p = N^{p+1} g^{p+1} [-v(c)]^p$$

Therefore, the final form for $I(q)$ is obtained as:

$$K^{-1} I(q) = Ng[1 - Ngv(c) + N^2 g^2 v^2(c) - \cdots] \tag{19}$$

which is $Ngv(c) < 1$, gives:

$$K^{-1} I(q) = \frac{Ng}{1 + v(c) Ng} \tag{20a}$$

or equivalently,

$$KI^{-1}(q) = \frac{1}{Ng} + v(c) \tag{20b}$$

It is convenient to write this result in the standard form by defining an apparent second virial coefficient $A_2(c)$:

$$A_2(c) = \frac{v(c) N_A}{2m^2}$$

then equation (20b) becomes:

$$KcI^{-1}(q) = \frac{1}{MP} + 2A_2(c)c \tag{20c}$$

The present procedure allows the introduction of contacts of higher order and leads to an excluded volume parameter $v(c)$:

$$v(c) = v + v_3 Nn + v_4 (Nn)^2 - \cdots = \frac{2m^2}{N_A} A_2(c)$$

Hence, it is sufficient to replace v or A_2 in the formalism of the chains with single contacts by the concentration dependent parameters $v(c)$ or $A_2(c)$. This justifies the statement of Daoud *et al.*[4] stating that they renormalize the excluded volume as a function of the concentration.

At zero scattering angle, equation (20c) gives:

$$KcI^{-1}(o) = M^{-1} + 2A_2(c)c \tag{21}$$

However, we know that $I(o)$ is related to the osmotic pressure π as follows:

$$KcI^{-1}(o) = (RT)^{-1} (\partial\pi/\partial c)_T \tag{22}$$

where R is the ideal gas constant. Combining equations (21) and (22) yields:

$$2A_2(c)c = (RT)^{-1} (\partial\pi/\partial c)_T - M^{-1} \tag{23}$$

and substituting this into equation (20c) yields:

$$KcI^{-1}(q) = \frac{1}{M}\left[\frac{1}{P} - 1\right] + \frac{1}{RT}\left(\frac{\partial\pi}{\partial c}\right)_T \tag{24a}$$

which relates the scattered intensity to the structure factor of the molecules and the thermodynamic behaviour of the solution. One notes that by using the classical virial expansion, equation (24a) can be written as:

$$KcI^{-1} = \frac{1}{MP} + 2A_2C + 3A_3c^2 + 4A_4C^3 + \cdots + pApc^{p-1} + \cdots \tag{24b}$$

Another interesting problem is finding how the result in equation (20a) can be applied to the bulk. If we write equation (20a) as:

$$K^{-1} I(q) = Ng + N^2 Q$$

by identification, we obtain:

$$Q = -\frac{v(c) g^2}{1 + v(c) Ng}$$

For an incompressible bulk one has the relation[6]:

$$NQ = -g$$

In order to extrapolate our result to the bulk state, we have to assume that v tends to infinity when the solvent concentration reaches zero. This problem will be discussed later.

Following the argument of de Gennes[7] on the effect of 'correlation hole', we note that in the dilute regime this effect is represented by $-vg^2$ whereas in bulk state it is given by $-g/N$. Therefore, when the concentration increases, the range of the correlation hole decreases continuously from $\sqrt{2}Rg$ in the dilute regime to Rg in the bulk.

Relation with the Ornstein–Zernike theory

In the preceeding section we have selected, among all the interaction diagrams, a series of linear chains leading to a simple equation. It would be useful to show that the contribution of all the other diagrams can be neglected. Here we shall assume that this is correct chiefly because the rigorous calculations of Edwards, Jannink and de Gennes leads to the same result in the concentrated regime.

Furthermore, it is interesting to show that the Ornstein and Zernike[8] approximation also leads to the same result.

Let us first summarize their argument, by considering a system of N pointlike particles for which the scattering intensity given by equation (5) becomes:

$$K^{-1}I(q)=N+N^2\langle\exp(i\underline{q}\cdot\underline{R}_{12})\rangle \tag{25}$$

where $\underline{R}_{12}$ is the vector distance between the two scattering centres 1 and 2.

In order to evaluate the thermal average in this equation, one introduces the pair correlation function $\Gamma(\underline{R}_{12})$ which is related to the more classical $g(R)$ by $\Gamma(\underline{R})=g(R)-1$ (note that Γ tends to zero as R tends to infinity). Equation (25) can be expressed in terms of the Fourier transform $\Gamma(q)$ as:

$$K^{-1}I(q)=N+N^2\Gamma(q) \tag{26}$$

In the case of a dilute solution, Γ is replaced by the direct correlation $\mathscr{C}(\underline{R})$ which is given by $\mathscr{C}(\underline{R})=-v\delta(\underline{R})$ or $\mathscr{C}(q)=-v$, assuming that the interactions are of very short distances as compared with the range of q^{-1} values available experimentally.

Ornstein and Zernike established a relation between $\mathscr{C}(q)$ and $\Gamma(q)$ by considering the interaction between molecules (1) and (2) as being described as the sum of a direct correlation $\mathscr{C}$ between (1) and (2) and an indirect correlation going from (1) to (2) via other molecules. In order to establish the functional relationship between Γ and $\mathscr{C}$, Ornstein and Zernike write:

$$\Gamma(\underline{R}_{12})=\mathscr{C}(\underline{R}_{12})+N\int\Gamma(\underline{R}_{13})\mathscr{C}(\underline{R}_{32})\mathrm{d}^3R_3 \tag{27}$$

This implies that the interaction between (1) and (2) can either be direct through $\mathscr{C}$ or indirect by the means of an indirect contact between (1) and (3) and a direct contact between (3) and (2). The integration is extended to all positions of (3) and the corresponding term is multiplied by N since there are N molecules in the sytem. In Fourier space, equation (27) reads:

$$\Gamma(q)=\mathscr{C}(q)+N\Gamma(q)\mathscr{C}(q) \tag{28}$$

solving for $\Gamma(q)$, one has:

$$\Gamma(q)=\frac{\mathscr{C}(q)}{1-N\mathscr{C}(q)} \tag{29}$$

and substituting this into equation (26) gives the scattered intensity as:

$$KI^{-1}(q)=N^{-1}-\mathscr{C}(q) \tag{30}$$

This equation is similar to equation (13b).

Now let us extend this method to the problem of macromolecules. The direct correlation function between two molecules has been calculated already in equations (5) and (9)

$$\mathscr{C}(q)=\sum_{j_1}\sum_{l_2}\langle\exp(i\underline{q}\cdot\underline{R}_{j_1l_2})\rangle=-vn^4P^2(q) \tag{31}$$

In order to obtain the indirect interaction between (1) and (2), we shall consider the following diagram (see *Figure 6*). We go from j_1 to l_2 either directly (one contact p_1, q_2) or indirectly by an indirect interaction between (1) and (3) and a direct correlation between (2) and (3).

This indirect method $\mathscr{C}'(q)\Gamma(q)$ (which has been called $\mathscr{C}(q)\Gamma(q)$ above) is obtained by writing:

$$\underline{R}_{j_1l_2}=\underline{R}_{j_1k_1}+\underline{R}_{k_1m_3}+\underline{R}_{m_3n_3}+\underline{R}_{n_3k_2}+\underline{R}_{k_2l_2} \tag{32}$$

Now, assuming complete independence between these vectors, one can write $\langle\exp(iq\cdot\underline{R}_{j_1l_2})\rangle$ as the product of five independent quantities and after summation over all the indices, one obtains:

$$\mathscr{C}'(q)\Gamma(q)=-Nn^6P^3v\gamma \tag{33}$$

calling γ the quantity $\langle\exp(iq\cdot\underline{R}_{k_1m_3})\rangle$.

Now, if we go from (1) to (2) by one indirect interaction, we obtain

$$\Gamma(q)=\gamma n^4P^4(q) \tag{34}$$

The functional relationship from Ornstein and Zernicke can be written as:

$$\gamma n^4P^2=-vn^4P^4[1+N\gamma n^2P]$$

which yields:

$$\gamma=-\frac{v}{1+nNn^2P(q)} \tag{35}$$

Substituting equation (35) into (34) and the resulting form of $\Gamma(q)$ into:

$$K^{-1}I(q)=Nn^2P(q)+N^2\Gamma(q) \tag{36}$$

one obtains the scattered intensity $I(q)$ as:

$$K^{-1}I(q)=\frac{Nn^2P(q)}{1+Nn_v^2P(q)} \tag{37}$$

This is the same result as in equation (20a) but, this time without making any assumption on the value of $Nn^2vP(q)$ (in fact since an intensity is always positive, we must have $Nn^2vP(q)>-1$).

Application to a mixture of differently labelled homopolymers

It would be of some interest to test the results of these calculations against experimental values. First of all, one must verify that $I(q)$ is a function of q through the single chain form factor P only. The easiest method of achieving

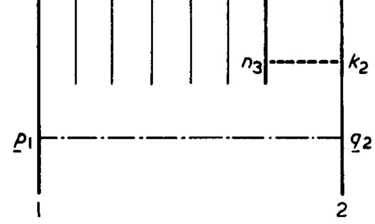

Figure 6 Diagram illustrating the application of the Ornstein–Zernike theory to polymers

this is to use neutron scattering on a mixture of deuterated and ordinary polymers. If all polymers are identical, one goes back to the previous discussion and uses, for example, equation (24a). However, if a small fraction, xN, of deuterated chains is added to a mixture of solvent and $(1-x)N$ ordinary polymers of the same molecular weight, by letting $x \to 0$, one obtains $P(q,c)$. Then, comparing this result with the total scattering intensity $I(q)$, one may be able to test the validity of our model and, if it is correct, one can determine $(\partial\pi/\partial c)_T$ without having to extrapolate the scattering curve to angle zero. Since it seems interesting experimentally to study mixtures of deuterated and protonated homopolymers, let us calculate the scattered intensity for an arbitrary value of x. We start with the general, and classical form:

$$I(q)=(a-s)^2S_{\mathrm{DD}}+(b-s)^2S_{\mathrm{HH}}+2(a-s)(b-s)S_{\mathrm{HD}} \quad (38)$$

where a, b and s are the coherent scattering lengths corresponding to the deuterated and protonated monomers, and to the solvent, respectively. S_{DD}, S_{HH} and S_{HD} are the scattering intensities due to the deuterated and hydrogenated polymers, and the cross terms, respectively, i.e.,

$$S_{\alpha\beta}=\sum_{\alpha}^{N}\sum_{\beta}^{N}\sum_{j}^{n}\sum_{l}^{n}\langle\exp(i\underline{q}\cdot\underline{R}_{j\alpha l\alpha})\rangle; \quad (\alpha,\beta=\mathrm{H},\mathrm{D})$$

These quantities can be immediately obtained from our model as follows:

$$S_{\mathrm{DD}}=xNg-\frac{x^2N^2g^2v(c)}{1+v(c)Ng} \quad (39)$$

where x is the fraction of deuterated chains $x=N_{\mathrm{D}}/N$. One notes that the quantity $v(c)Ng$ appears in the denominator and not $xNgv(c)$ because the chains of interaction between a pair of deuterated chains can be either of type D or H, knowing that they have the same thermodynamic properties. We also have:

$$S_{\mathrm{HH}}=(1-x)Ng-\frac{(1-x)^2N^2g^2v(c)}{1+v(c)Ng} \quad (40)$$

and

$$S_{\mathrm{HD}}=S_{\mathrm{DH}}=-\frac{x(1-x)N^2g^2v(c)}{1+v(c)Ng} \quad (41)$$

Combining equations (25) to (28) and rearranging the terms, we obtain:

$$I(q)=x(1-x)(a-b)^2Ng+\bar{a}^2\left[Ng-\frac{N^2g^2v(c)}{1+v(c)Ng}\right] \quad (42)$$

where $\bar{a}$ is the average scattering length

$$\bar{a}=(a-s)x+(b-s)(1-x) \quad (43)$$

The result from equation (29) is an application of the theory of Akcasu *et al.*[9], and Benoit *et al.*[6] to the model developed here. Letting $\bar{a}=0$ in equation (29) yields as expected:

$$I(q)=(a-b)^2x(1-x)Ng \quad (44)$$

which shows that $I(q)$ becomes independent of the intermolecular interaction. Usually, in neutron scattering experiments, one chooses a solvent such that $b=s$, in which case equation (42) gives:

$$I(q)=(a-s)^2\left[xNg-\frac{x^2N^2g^2v(c)}{1+v(c)Ng}\right] \quad (45)$$

In the reciprocal form, this equation can be written as:

$$(a-s)^2I^{-1}(q)=\frac{1}{xNg}+\frac{v(c)}{1+(1-x)v(c)Ng} \quad (46)$$

It is worth noting here that the single contact model would give, in this case:

$$I(q)=(a-s)^2[xNg-x^2N^2g^2v(c)]$$

and by using the reciprocal approximation, one obtains:

$$(a-s)^2I^{-1}(q)=\frac{1}{xNg}+v(c) \quad (47)$$

where the second term in the right-hand-side (rhs) is independent of q. If we assume that both H and D monomers have the same molecular weight, we can write equation (46) using more practical symbols as:

$$\frac{Mkxc}{I(q)}=\frac{1}{P}+\frac{2A_2(c)Mxc}{1+2A_2(c)M(1-x)cP} \quad (48)$$

If the latter assumption is found to be too crude, one has to use equation (46) with the required modifications. The limiting form of this equation at $q=0$, has been derived by Alexander and Pincus[10] using self consistent field arguments. One notes that the second term on the rhs of this equation depends on q for $x<1$, as opposed to equation (47). Hence, the interesting feature of equation (48) is its strong dependence on x which implies that the apparent $P(q)$ may be very different from its true value. In order to make this point more explicit, we have made several Zimm plots of equation (48) representing the variation of $KMc_{\mathrm{D}}/I(q)$ as a function of $q^2Rg^2+2A_2Mc_{\mathrm{D}}$. In these plots we assume that the molecular weights are the same and the form factor is independent of the concentration and is given by the Debye function.

Figure 7 represents an ordinary Zimm plot which is obtained by using the single contact and the reciprocal approximation (see equation (47)). This Figure is plotted for the sake of comparison with *Figures 8, 9* and *10* which

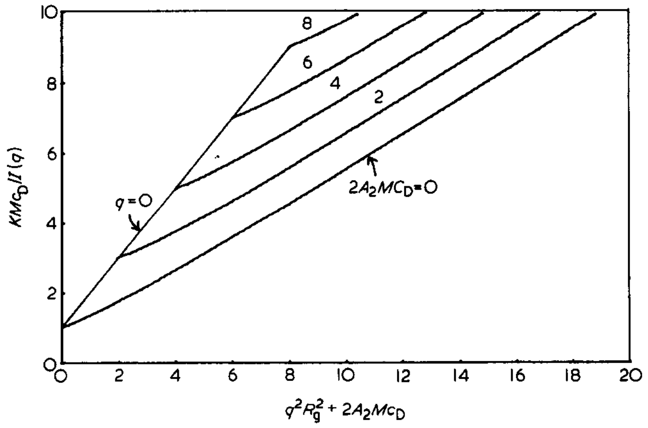

Figure 7 Zimm plot for a mixture of deuterated and ordinary, otherwise identical homopolymers, using equation (47) (single contact with the reciprocal approximation)

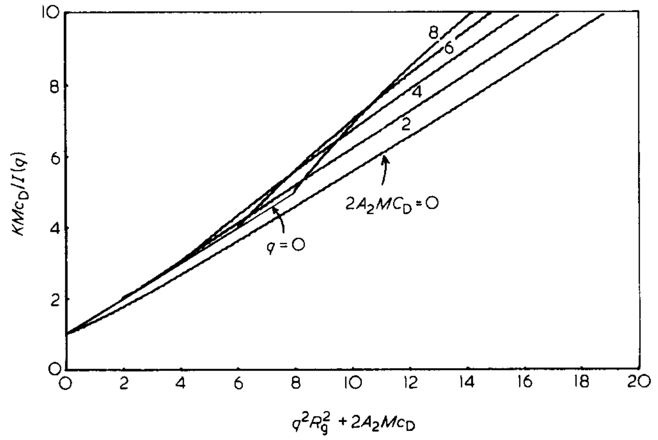

Figure 8 Zimm plot for the same system using equation (48) (chain of single contacts model) and for a concentration C_H given by $2A_2MC_H=1$

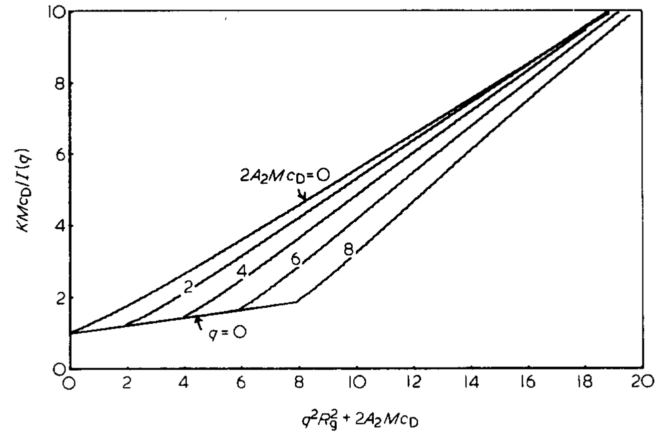

Figure 9 Similar Zimm plot for a concentration C_H eight times higher than in the case of *Figure 8* (i.e. $2A_2MC_H=8$)

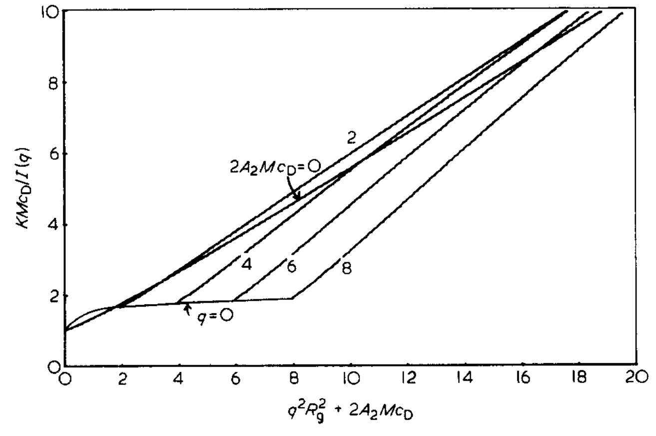

Figure 10 Zimm plot for a 50/50 mixture of H and D homopolymers ($C_H=C_D$)

are plotted using equation (48). In *Figure 8*, we kept the concentration C_H constant (i.e. $2A_2MC_H=1$) and changed C_D. This shows a strong distortion of the Zimm plot.

Figure 9 gives a similar Zimm plot but with a concentration C_H eight times higher (i.e. $2A_2MC_H=8$). We observe that the slope of the straight line $q=0$ decreases which implies that the H-component behaves as a poor solvent.

In *Figure 10*, we assumed that $C_D=C_H$. Here we observe that the concentration dependence quickly reaches a plateau value. An experimentalist who misses the initial curvature, may conclude that he is observing a theta behaviour.

In the last three Figures, the angular distribution of the intensity is highly distorted, mainly in the lower range of qRg and the curves intersect each other. Note that we have used the same scale in these Figures to make the comparison easier.

In *Figure 11*, we have plotted $KMC_D/I(q)$ as a function of q^2Rg^2+x $(x=C_D/C)$ using again equation (48) and keeping the total concentration c constant (i.e. $2A_2Mc=6$). We observe that the curves corresponding to x between 0 and 1 are distorted and may present an inflection point. The curves $x=0$ and $x=1$ representing P^{-1} and $P^{-1}+2A_2MC$, respectively, can be superimposed by translation.

Finally, if v is very large (we shall see that this is always the case when the solvent volume fraction goes to zero i.e. in the bulk limit) equations (46) and (48) become independent of v and one arrives at the result already obtained by Daoud *et al.*[4]:

$$I(q)=(a-s)^2x(1-x)Ng$$

DISCUSSION

The calculations presented in this paper can be seen as an extension of the classical Ornstein and Zernike (OZ) theory to polymer solutions. The final result is very simple but it is important to keep in mind the assumptions made in its derivation.

Either using our sets of diagrams, or the OZ theory, we disregard a large number of diagrams, particularly those for which there are many single contacts on a chain. We tried to take this into account by introducing a form factor $P(q,c)$ function of c as we did for the excluded volume parameter $v(c)$. Only the experiments can tell of this procedure is legitimate. By doing so, we did neglect a number of efforts that have been made to solve this problem and which are well described in Yamakawa's book[11].

We have also assumed a uniform distribution of segments in the solution. This assumption is markedly incorrect at low concentration i.e. $c<c^*$, c^* being the

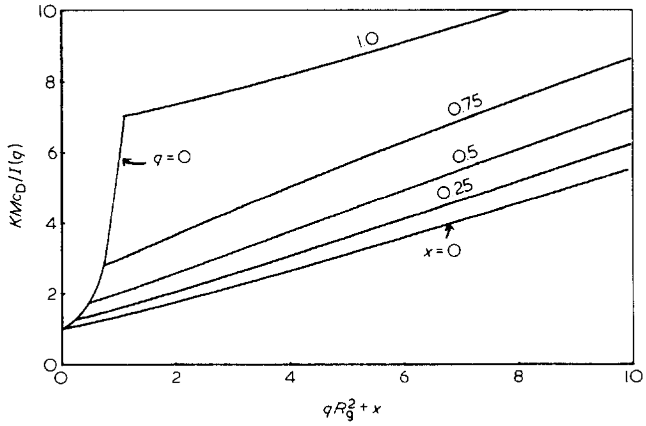

Figure 11 Zimm plot for the same system but keeping the total concentration $C=C_H+C_D$ constant (i.e. $2A_2Mc=6$) and changing the relative composition of deuterated polymers ($x=C_D/C$) from 0 to 1. In all cases, we used Debye's function for $P(q)$ which we assumed to be independent of the concentration

overlap concentration, and therefore our model cannot replace any theory which is capable of accounting for the non-uniform distribution of the concentration below c^*. Our model should work better above c^* where the density fluctuations of monomeric units are much less important.

Furthermore, it would be interesting to see how $v(c)$ varies with the concentration. In the semi-dilute regime, one can use the des Cloizeaux[12] law which gives the osmotic pressure $\pi \sim C^{9/5}$, and therefore, $v \sim c^{1/4}$ varying slowly with the concentration.

In both the lower and higher concentration ranges, this power law does not hold. In order to have a model for the variation of $v(c)$, we shall use the classical Flory–Huggins theory[13] which gives for the chemical potential of the solvent:

$$\mu_1 - \mu_1^0 = RT\left[\ln(1-\varphi_2) + \varphi_2\left(1-\frac{1}{n}\right) + \chi\varphi_2^2\right] \tag{49}$$

where φ_2 is the volume fraction of the polymer and χ the Flory interaction parameter. Knowing that $\pi v_1 = -(\mu_1 - \mu_1^0)$, v_1 being the molar volume of the solvent and using equation (23) and (20b), one obtains:

$$v(c) = \frac{2}{N_t}\left[\frac{1}{2} - \chi + \frac{1}{2}\frac{\varphi_2}{\varphi_1}\right] \tag{50}$$

where N_t is the total number of solvent molecules and monomer units $((v_1/N_A)N_t = 1, \varphi_1 = 1 - \varphi_2)$. In the dilute regime $\varphi_2 \to 0$ and we obtain a classical result. In the high concentration regime, we see that $v(c)$ goes to infinity as expected, in order for the scattered intensity to go to zero. It is important to note that in these limits, the value of $v(c)$ extracted from equation (50) are correct since at low or very high concentrations, all solutions behave like ideal solutions. This legitimates also the procedure we adopted in extrapolating to the bulk state, in the case of a mixture of deuterated and ordinary polymers.

Since we have slightly different results from those of Daoud *et al.*[4], it would be interesting to re-examine the scattering laws in the intermediate range of q and for various concentration regimes. Assuming the chain to be Gaussian, we have in the intermediate q-range, $P^{-1}(q) = (q^2R^2/12) + \frac{1}{2}$ so that $I(q)$ becomes

$$I^{-1}(q) \simeq \frac{1}{Nn^2}\left(\frac{q^2R^2}{12} + \frac{1}{2}\right) + \frac{2}{N_t}\left[\left(\frac{1}{2} - \chi\right) + \frac{1}{2}\frac{\varphi_2}{\varphi_1}\right]$$

which can be put in the Lorentzian form $I(q) \sim 1/(q^2 + \zeta^{-2})$ with a correlation length ξ defined by:

$$\xi^{-2} = \frac{6}{R^2} + \frac{12Nn^2}{R^2N_t}\left[2(\tfrac{1}{2} - \chi) + \frac{\varphi_2}{\varphi_1}\right] \tag{51}$$

ξ^{-2} is the sum of three terms. The first one can be neglected when n (the molecular weight) is large. The second term gives, in the Gaussian approximation $\xi^{-2} \sim c$ but disappears in a theta solvent. The third term has the form const. $(c\varphi_2/\varphi_1)$ which is proportional to c^2 when $\varphi_2 < 1$ but goes to infinity as φ_2 approaches unity in the limit of a pure polymer. Therefore, the situation is rather complex at high concentration and in a theta solvent. In order to have ξ^{-2} proportional to c (Edwards law[2]), one has to assume that the excluded volume is large since, if it is zero, ξ^{-2} is proportional to $c\varphi_2/\varphi_1$ which means that if $\varphi_2 \ll 1$, $\xi \sim c^{-1}$.

In the semi-dilute regime, one can use the des Cloizeaux law ($\pi \sim c^9/^4$) and find $v \sim c^{1/4}$ and nothing can be added to what is said in ref. (4).

All these discussions have been presented having in mind the case of flexible linear chains. In fact the only assumption which made this theory possible is the unidimensionality of the scattering objects. All we have said applies as well to branched polymers, and rigid polymers. In fact, in the latter case, the model should work better because it is not possible to have multiple contacts between two chains, but one has to neglect the angular correlations. This can be done only in dilute solution. At higher concentrations, it is clear that the angular correlations are important and give rise to mesomorphic phases[14].

One of the difficulties in our results is that we cannot introduce the effect of molecular weight on $A_2(c)$ and we have no argument to renormalize A_2 as a function of M. This brings an advantage, however, if we want to apply this theory to polydisperse systems. By a quick inspection of the structure of the formulae, one notes that the only thing to do is to replace the quantity Nn^2P by the expression $\sum_i N_i n_i^2 P_i(q,c)$ where N_i is the number of molecules having n_i segments and P_i as a form factor.

In conclusion, by summing an infinite series or by using the method of Ornstein and Zernike, we obtained a general equation which gives the scattered intensity of a polymer solution at any concentration. As was pointed out earlier, our method reproduces the exact results both in the concentrated regime (Edwards, Jannink and de Gennes) and in the dilute regime (Zimm). It is very important to check from an experimental point of view if the renormalization of the excluded volume as suggested in ref. 4 is sufficient to make it useful in the intermediate range of concentrations. However, the main advantage of this procedure is its direct and immediate generalization to mixtures of homopolymers and copolymers which we shall discuss in a forthcoming paper[15].

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