New Approach to the Problem of Elastic Scattering from a Mixture of Homopolymers in a Concentrated Solution

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ABSTRACT: The coherent elastic scattering intensity for a mixture of homopolymers is calculated as a function of the wave vector and the concentrations using the chain of single contacts model. This model, which we developed elsewhere for identical homopolymers, is extended here to the case of a ternary mixture of two arbitrary homopolymers and a solvent. The polymers can have not only different contrast factors but also different excluded volume parameters, different molecular weights, and different form factors. The q dependence is expressed in terms of the single-chain form factors only. The result is valid at any concentration from the dilute regime to the high-concentration regime, and in the bulk limit we obtain the random phase approximation result. At zero scattering angle, we obtain the same result as Stockmayer, who used a thermodynamical approach.

I. Introduction

In a preceding paper,[1] we have calculated the scattering intensity from a solution of homopolymers as a function of the concentration c and the wave vector q. We have developed in detail a model for the interaction between chains which is based on a generalization of the well-known single-contact approximation of Zimm.[2] We have also shown that our model gives a result that can be obtained by the Ornstein–Zernike[3] theory, which takes elegantly into account the indirect interaction between molecules.

Since our approach seems to describe correctly the scattering function for solutions of one polymer in a solvent, from zero concentration to the bulk, it would be interesting to generalize it to a three-component system of two polymers in a solvent. This is the purpose of the present work, where we show that it is possible to obtain a formula which, at zero scattering angle, coincides with the well-known Stockmayer[4] result and which, in the bulk limit, gives the random phase approximation (RPA) result of de Gennes[5] for a mixture of two polymers.

To summarize the main ideas of this model, let us consider a solution of N identical homopolymers per unit volume all having the same number of monomers n. (We choose, following Flory,[6] the size of a monomer to be equal to that of a solvent molecule.) The scattered intensity per unit volume $I(q)$ is given by the general formula

$$I(q) = Nn^2P(q) + Q(q) \tag{1}$$

where $q = (4\pi/\lambda) \sin(\theta/2)$, λ being the wavelength of the incident radiation (light, X-rays, or neutrons) and θ the scattering angle. $P(q)$ is the single-chain form factor and $Q(q)$ the intermolecular scattering function. These last two quantities are defined by

$$n^2P(q) = \sum_{j=1}^{n}\sum_{l=1}^{n}\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jl})\rangle \tag{2}$$

$$Q(q) = N^2\sum_{j_1=1}^{n}\sum_{l_2=1}^{n}\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{j_1l_2})\rangle \tag{3}$$

where $\mathbf{R}_{jl}$ is the vector distance between monomers j and l belonging to the same chain and $\mathbf{R}_{j_1l_2}$ corresponds to the distance between two monomers j_1 and l_2 on two different chains. The angular brackets denote the average with respect to the equilibrium distribution of monomers. In the single-contact approximation (see Figure 1) one takes into account only the interaction between two chains by one pair of contact points, which we call k and k'. One writes

$$\mathbf{R}_{j_1l_2} = \mathbf{R}_{j_1k} + \mathbf{R}_{kk'} + \mathbf{R}_{k'l_2}$$

and assumes that $\mathbf{R}_{j_1k}$ and $\mathbf{R}_{k'l_2}$ are independent. $\mathbf{R}_{kk'}$ does not depend on the indices and we have

$$\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{kk'})\rangle = \int d^3R\, [g(R) - 1] \exp(i\mathbf{q}\cdot\mathbf{R})$$

where $g(R)$ is the pair distribution function. Assuming short-range interaction gives $g(R) - 1 = -\vartheta\delta(\mathbf{R})$, δ being the Dirac delta function and ϑ the excluded volume parameter. Hence, we have

$$\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{kk'})\rangle = -\vartheta \tag{4}$$

Using these results yields

$$Q(q) = -\vartheta N^2\sum_{j_1}\sum_{k}\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{j_1k})\rangle\sum_{l_2}\sum_{k'}\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{l_2k'})\rangle = -\vartheta N^2(n^2P)^2 \tag{5}$$

The generalization to a chain of single contacts involving many polymers is illustrated by Figure 2. Here also one uses the same procedure by writing

$$\mathbf{R}_{j_1l_2} = \mathbf{R}_{j_1k} + \mathbf{R}_{kk'} + \mathbf{R}_{k'p} + \ldots + \mathbf{R}_{hl_2}$$

and assuming that these vectors are distributed independently. The type of diagram in this figure involving $p + 1$ chains and hence p contacts contributes to Q by the quantity

$$Q_{p+1} = (-\vartheta)^p(Nn^2P)^{p+1}$$

Adding the terms corresponding to all possible chains of contacts, for p going from one to infinity, we obtain $Q = \sum_{p=1}^{\infty}Q_{p+1}$ and hence

$$I(q) = \frac{Nn^2P(q)}{1 + \vartheta Nn^2P(q)} \tag{6}$$

In reciprocal form, this reads

$$I^{-1}(q) = \frac{1}{Nn^2P(q)} + \vartheta \tag{7}$$

This method is valid only if $\vartheta Nn^2P < 1$. In fact, we have shown using the Ornstein–Zernike theory that this limitation is not real and that if one considers other types of diagrams,[7] the only limitation is $\vartheta Nn^2P > -1$ in order to have a positive scattering intensity. We showed that the

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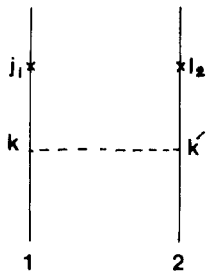


Figure 1. Single-contact approximation. The vertical solid lines are the chains 1 and 2. The horizontal dotted line represents the interaction between chains 1 and 2.

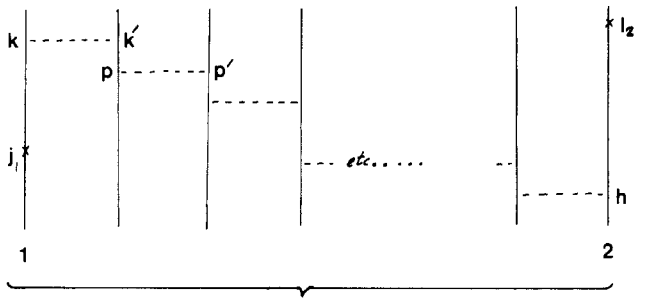


Figure 2. Chain of single contacts involving $p + 1$ macromolecules.

introduction of multiple contacts renormalizes the excluded volume parameter ϑ as a function of the concentration c and leads to the general formula

$$\frac{Kc}{I(q)} = \frac{1}{MP(q,c)} - \frac{1}{M} + \frac{1}{RT}\left(\frac{\partial \Pi}{\partial c}\right)_T \tag{8}$$

where Π is the osmotic pressure, c the concentration in weight fraction, M the molecular weight, R the ideal gas constant, and K a constant that depends on the type of radiation used (light, X-rays, or neutrons) and the apparatus. These quantities are all available in a given experiment. These results justify the use of Zimm's formula and perhaps its success in interpreting scattering data even in the range of concentrations exceeding the overlap threshold c^*.[8]

Now we propose to extend this model to a mixture of homopolymers. For the sake of simplicity, we consider the case of two components A and B, but it is possible to extend this model to a multicomponent system. We consider all possible characteristics of the two species, including their contrast factors.

II. Scattering from a Mixture of Two Homopolymers

Consider a solution where two species of homopolymers A and B are embedded in a solvent S. We assume that there are N_A polymers of types A and N_B polymers of type B per unit volume and that their polymerization indices are respectively n_A and n_B. The contrast factors with respect to the solvent for the monomers A and B are called a and b. In the case of neutrons, a and b are the differences of the coherent scattering lengths, respectively, between monomer A and a solvent molecule and between monomer B and a solvent molecule. In the case of light, we have

$$a = \partial\eta/\partial c_A; \qquad b = \partial\eta/\partial c_B$$

where η is the refractive index. The scattering intensity for this mixture is given by the general formula

$$I(q) = a^2 S_A(q) + b^2 S_B(q) + 2ab S_{AB}(q) \tag{9}$$

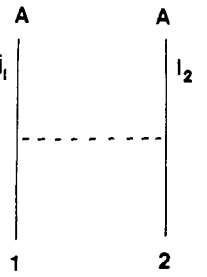


Figure 3. Single contact between two chains of type A.

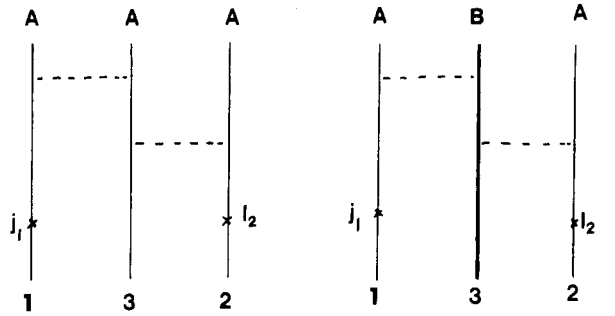


Figure 4. Case of three chains.

S_A, S_B, and S_{AB} are due to two interfering points when both of them are on chains A, when both are on chains B, or when one is on chain A and the other is on chain B, respectively. They can be expressed in terms of the form factors P_A and P_B and the interaction scattering functions Q_A, Q_B, and Q_{AB}:

$$S_A = N_A n_A^2 P_A + Q_A \tag{10a}$$

$$S_B = N_B n_B^2 P_B + Q_B \tag{10b}$$

$$S_{AB} = Q_{AB} \tag{10c}$$

The purpose of this paper is to evaluate Q_A, Q_B, and Q_{AB} using the chain of interaction model which we have developed in ref 1.

Calculation of Q_A. Since in Q_A the scattering points are each on a different chain A, the single-contact approximation leads to the unique type of diagram represented by Figure 3. The contribution of this contact is

$$Q_{A2} = -\vartheta_A (N_A n_A^2 P_A)^2 \tag{11}$$

where ϑ_A is the excluded volume parameter for a contact between two A monomers. To improve this result, we shall consider as in ref 1 different chains of contacts and evaluate their contributions to the scattering signal. Let us start with three chains. Since the terminal ones are of A type, we can have the two diagrams in Figure 4. These diagrams give the following contributions:

$$\vartheta_A^2 (N_A n_A^2 P_A)^3; \qquad \vartheta_{AB}^2 (N_A n_A^2 P_A)^2 (N_B n_B^2 P_B)$$

ϑ_{AB} denotes the excluded volume parameter for a pair AB. Introducing the new variables

$$\chi_A = N_A n_A^2 P_A$$

$$\chi_B = N_B n_B^2 P_B \tag{12}$$

the total contribution for the three-chain series will be

$$Q_{A3} = \vartheta_A \chi_A^2 \left[\vartheta_A \chi_A + \frac{\vartheta_{AB}^2}{\vartheta_A} \chi_B \right] \tag{13}$$

We need now to generalize this calculation to a series involving a large number of polymers A and B. Following the procedure described in ref 1, we consider a system made of p_A chains A and p_B chains B. In this system, we

count p_{AA} contacts of type AA, p_{BB} contacts of type BB, and p_{AB} contacts of type AB. These numbers must satisfy the conditions

$$p_A + p_B = p + 1 \qquad \text{(total number of chains)}$$

$$p_{AA} + p_{BB} + p_{AB} = p \qquad \text{(total number of contacts)}$$

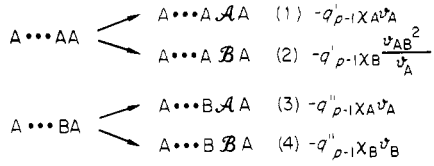
The contribution Q_{Ap} of such systems to the interchain scattering function Q_A will be the sum over all possible diagrams of the quantity

$$Q_{Ap} = \sum \chi_A^{p_A} \chi_B^{p_B} \vartheta_A^{p_{AA}} \vartheta_B^{p_{BB}} \vartheta_{AB}^{p_{AB}}$$

and

$$Q_A = \sum_{p=2}^{\infty} Q_{Ap}$$

The exact counting of the number of arrangements for a given system can be made by a combinatorial analysis technique. It seemed more convenient to establish a recurrence relation between Q_{Ap+1} and Q_{Ap}. Since we are dealing with a series having A chains at both ends, in order to go from Q_{Ap-1} to Q_{Ap}, we have to insert a chain, A or B, at a certain location within the series but not at the ends; we choose to insert it just before the last one. We see that we have to distinguish between two types of configurations whose contributions are called q'_{p-1} and q''_{p-1} for a series of $p-1$ chains. q'_{p-1} corresponds to a series finishing by a sequence AA, and q''_{p-1} by a sequence BA. Adding the pth chain, either A or B, will lead to four terms in q'_p and q''_p as indicated by the following scheme:



In cases 1 and 3 we add a chain A and a contact AA. In case 4 we add a chain B and a contact BB. Case 2 is more subtle since by putting a chain B inside a sequence AA, we replace a contact AA by two contacts AB, therefore leading to the factor $(-\vartheta_{AB}^2/\vartheta_A)\chi_B$. The minus sign is introduced to ensure that the interaction parameter be positive when it corresponds to a repulsion.

From this analysis, we obtain the following recurrence relations:

$$q'_p = -(\chi_A\vartheta_A q'_{p-1} + \chi_A\vartheta_A q''_{p-1})$$

$$q''_p = -\left(\chi_B\frac{\vartheta_{AB}^2}{\vartheta_A} q'_{p-1} + \chi_B\vartheta_B q''_{p-1}\right) \qquad (14)$$

Writing $\mathbf{q}_p$ as a column vector

$$\mathbf{q}_p = \begin{pmatrix} q'_p \\ q''_p \end{pmatrix} \qquad (15)$$

and introducing the square matrix $\mathbf{M}$

$$\mathbf{M} = -\begin{pmatrix} \chi_A\vartheta_A & \chi_A\vartheta_A \\ \chi_B\dfrac{\vartheta_{AB}^2}{\vartheta_A} & \chi_B\vartheta_B \end{pmatrix} \qquad (16)$$

one can put relations (14) into the matrix form

$$\mathbf{q}_p = \mathbf{M}\cdot\mathbf{q}_{p-1} \qquad (17)$$

Then one applies this recurrence relation repeatedly to obtain

$$\mathbf{q}_p = \mathbf{M}^{p-2}\cdot\mathbf{q}_2, \qquad \text{for } p+1 \text{ chains} \qquad (18)$$

where we have directly evaluated the vector column

$$\mathbf{q}_2 = \vartheta_A\chi_A^2\begin{pmatrix} \vartheta_A\chi_A \\ \dfrac{\vartheta_{AB}^2}{\vartheta_A}\chi_B \end{pmatrix} \qquad (19)$$

In order to have the total contribution due to all possible arrangements of the chains of contacts, we have to make the sum of all the Q_{Ap} contributions. From eq 18 we obtain by letting $\nu = p - 2$

$$\sum \mathbf{q}_p = (\sum_{\nu=0}^{\infty}\mathbf{M}^\nu)\cdot\mathbf{q}_2 = (\mathbf{I} - \mathbf{M})^{-1}\cdot\mathbf{q}_2 \qquad (20)$$

where $\mathbf{I}$ in the two-by-two unit matrix. This result is valid only if the sum $\sum_{\nu=0}^{\infty}\mathbf{M}^\nu$ converges, which implies that the magnitude of both eigenvalues of $\mathbf{M}$ are less than 1. We will discuss later the physical implications of these restrictions. Note that the actual result we are seeking is the sum of the elements of the column matrix $\sum(q'_p + q''_p)$. To treat this problem in a more general way, one shows that if

$$\mathbf{q}_2 = \begin{pmatrix} q'_2 \\ q''_2 \end{pmatrix}$$

and

$$\mathbf{M} = -\begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

then one would have the following result for the sum:

$$\sum_{p=2}^{\infty}(q'_p + q''_p) = \frac{q'_2(1 - c + d) + q''_2(1 + a - b)}{1 + a + d + ad - bc} \qquad (21)$$

This gives us immediately the result

$$\chi_A^2[\vartheta_A^2\chi_A + \vartheta_{AB}^2\chi_B + \vartheta_A(\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B]/ [1 + \vartheta_A\chi_A + \vartheta_B\chi_B + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B] \qquad (22)$$

The final form for Q_A is obtained by adding the single-contact term to eq 22:

$$Q_A = -\chi_A^2[\vartheta_A + \chi_B(\vartheta_A\vartheta_B - \vartheta_{AB}^2)]/[1 + \vartheta_A\chi_A + \vartheta_B\chi_B + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B] \qquad (23)$$

To obtain Q_B one simply interchanges A and B in this equation, namely,

$$Q_B = -\chi_B^2[\vartheta_B + \chi_A(\vartheta_A\vartheta_B - \vartheta_{AB}^2)]/[1 + \vartheta_A\chi_A + \vartheta_B\chi_B + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B] \qquad (24)$$

The determination of Q_{BA} is easy. Since we assume that the series ends with a chain A, we can use the same matrix $\mathbf{M}$. Furthermore, a close examination of the case involving three chains gives

$$q'_2 = \vartheta_{AB}\chi_A\chi_B\begin{pmatrix} \vartheta_A\chi_A \\ \vartheta_B\chi_B \end{pmatrix} \qquad (25)$$

Combining eq 16, 21, and 25 and adding the single-contact term (i.e., $-\vartheta_{AB}\chi_A\chi_B$), one finds

$$Q_{AB} = Q_{BA} = -\vartheta_{AB}\chi_A\chi_B/[1 + \vartheta_A\chi_A + \vartheta_B\chi_B + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B] \qquad (26)$$

Substituting eq 23, 24, and 26 into eq 10 yields

$$S_A = [\chi_A(1 + \vartheta_B\chi_B)]/[1 + \vartheta_A\chi_A + \vartheta_B\chi_B + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B] \quad (27)$$

$$S_B = [\chi_B(1 + \vartheta_A\chi_A)]/[1 + \vartheta_A\chi_A + \vartheta_B\chi_B + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B] \quad (28)$$

$$S_{AB} = -\vartheta_{AB}\chi_A\chi_B/[1 + \vartheta_A\chi_A + \vartheta_B\chi_B + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B] \quad (29)$$

and using eq 9, one obtains

$$I(q) = [(a^2\chi_A + b^2\chi_B) + (a^2\vartheta_B + b^2\vartheta_A - 2ab\vartheta_{AB})\chi_A\chi_B]/[1 + \vartheta_A\chi_A + \vartheta_B\chi_B + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)\chi_A\chi_B] \quad (30)$$

This is the central result of this work. It gives the scattering intensity one would obtain from a solution containing a mixture of two arbitrary homopolymers. It accommodates for differences in their contrast factors a and b, their thermodynamical parameters ϑ_A, ϑ_B, and ϑ_{AB}, their relative compositions inherent in the numbers of chains N_A and N_B, their internal structures P_A and P_B, and their degrees of polymerization n_A and n_B. This result assumes imcompressibility of the system (it is actually the excess scattering due to concentration fluctuations). Before going further, two remarks need to be made:

1. As has been shown in ref 1, ϑ_A, ϑ_B, and ϑ_{AB} as well as P_A and P_B are functions of c_A and c_B and have to be renormalized in terms of these concentrations. The renormalization of ϑ_A, ϑ_B, and ϑ_{AB} is a thermodynamical problem (since at $q = 0$, $I(0,c)$ is a thermodynamical quantity). The renormalization of the chain conformations is a difficult problem which we do not intend to discuss here.

2. We mentioned earlier that for the series in eq 20 to be convergent, one has to have $||\mathbf{M}|| < 1$. We have seen in the case of homopolymers that the application of the Ornstein–Zernike theory gives exactly the same results as our summation procedure, but without any limitation regarding the value of the denominator. Since in the case of a mixture, we use exactly the same procedure, we can expect that our results are also valid even if the condition $||\mathbf{M}|| < 1$ is not fulfilled. This is also supported by the fact that at $q = 0$, our result is identical with the one obtained by Stockmayer by a pure statistical thermodynamical approach. Since in Stockmayer's formula, there is absolutely no restriction, our formula is good (at $q = 0$) for any value of the matrix. This strongly supports the idea that eq 30 is valid without restriction. It is worth noting that eq 30 is good for any value of q as opposed to the result obtained by Vrij and Van den Esker,[9] which is restricted to the lower range of q, since these authors assumed a spherical distribution of monomers about the center of mass.

III. Discussion

1. Special Cases. In order to test the validity of our theory, it would be interesting to check a few special cases and see if we can recover already known results. (a) If we let $\vartheta_{AB} = 0$, there would be no interaction between chains of different species; these evolve independently and the scattered intensity should be the superposition of the intensities due to the two species. We indeed obtain from eq 30

$$I(q) = \frac{a^2\chi_A}{1 + \vartheta_A\chi_A} + \frac{b^2\chi_B}{1 + \vartheta_B\chi_B} \quad (31)$$

(b) If the two polymers are identical and differ only by their scattering amplitude, as in the case of deuterated and protonated polymers,[1] we have

$$\vartheta = \vartheta_A = \vartheta_B = \vartheta_{AB}$$

$$\chi_A = \varphi N n^2 P$$

$$\chi_B = (1 - \varphi)Nn^2P$$

$$\varphi = N_A/N, \qquad N = N_A + N_B \quad (32)$$

and hence $I(q)$ becomes

$$I(q) = (a - b)^2\varphi(1 - \varphi)Nn^2P + \bar{a}^2\frac{Nn^2P}{1 + \vartheta Nn^2P} \quad (33)$$

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

$$\bar{a} = a\varphi + b(1 - \varphi) \quad (34)$$

It would be interesting to see what happens when there is a slight interaction between the deuterated and protonated monomers. In order to obtain a simple expression, let us assume that $\vartheta_A = \vartheta_B = 0$ (the solvent is Θ for both species) but $\vartheta_{AB} = \epsilon$. If we use a solvent for which either a or b is equal to zero, we do not see any effect of this interaction. Therefore, let us assume that $\bar{a} = 0$, and in this case, we obtain the following expression for $I(q)$, keeping the first order in ϵ only:

$$I(q) = (a - b)^2\varphi(1 - \varphi)Nn^2P[1 + 2Nn^2P\epsilon\varphi(1 - \varphi)] \quad (35)$$

This suggests the following experiment. One prepares various mixtures of identical deuterated and hydrogenated polymers and measures $I(q)/\varphi(1 - \varphi)$ as a function of φ. If the results depend on φ, this can be explained by assuming a nonzero value for our parameter ϵ. But deviation from eq 35 can also occur if the two species do not have exactly the same molecular weight, which is practically always the case. Now, if we assume $n_AP_A \neq n_BP_B$ and write

$$n_BP_B - n_AP_A = (n_B - n_A)\Delta P$$

and if $\vartheta_A = \vartheta_B = \vartheta_{AB} = 0$, we obtain

$$\frac{I(q)}{N_An_A + N_Bn_B} = (a - b)^2\varphi(1 - \varphi)P_A + b^2(1 - \varphi)(n_B - n_A)\Delta P \quad (36)$$

It could be possible, in principle, to make the difference between eq 35 and 36 by carefully examining the structure of the function I of φ and q. We have written these equations assuming $\vartheta_A = \vartheta_B = 0$. This assumption does not change the physical implications of our discussions but makes the arithmetic much easier.

In ref 1, we investigated the angular distribution of the scattered intensity for a mixture of deuterated and ordinary homopolymers by presenting various Zimm plots of $KMc_D/I(q)$ as a function of $q^2R_g^2 + 2A_2Mc_D$ for various values of c_H. Here we present similar plots but we introduce the effect of the interaction parameters between the two polymers A and B. For simplicity, we let $b = 0$, $M_A = M_B = M$, $P_A = P_B = P$, and $A_{2A} = A_{2B} = A_2$ so that eq 30 rewritten in the standard notation gives

$$KMc_A/I(q) = [1 + 2A_2McP + 4(A_2^2 - A_{2AB}^2)M^2P^2c_Ac_B]/(P[1 + 2A_2Mc_BP]) = \frac{1}{P} + 2A_2Mc_A - \frac{A_{2AB}^2}{A_2^2}2A_2Mc_A\left(\frac{2A_2Mc_BP}{1 + 2A_2Mc_BP}\right) \quad (37)$$

In Figure 5, we present a Zimm plot of this equation by choosing the interaction A_{2AB} such that $A_{2AB}/A_2 = 1$ and the concentration c_B such that $2A_2Mc_B = 1$. We observe a strong distortion of the Zimm plot which is of type similar to that seen in the previous case of deuterated and

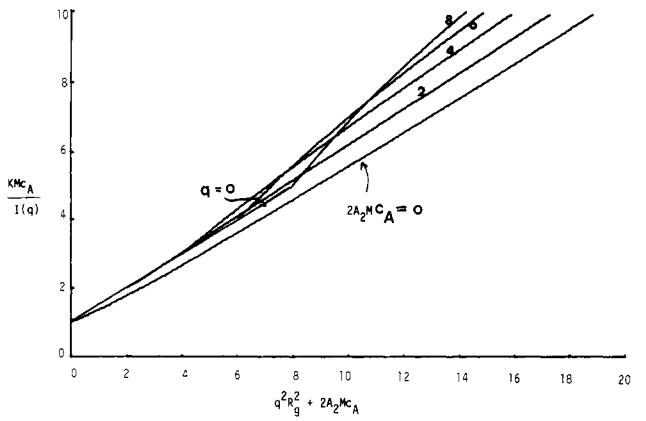


Figure 5. Zimm plot for a mixture of two polymers A and B and a solvent representing $KMc_A/I(q)$ as a function of $q^2R_g^2 + 2A_2Mc_A$ using eq 37 and letting $2A_{2B}Mc_B = 1$ and $A_{2AB}/A_2 = 1$.

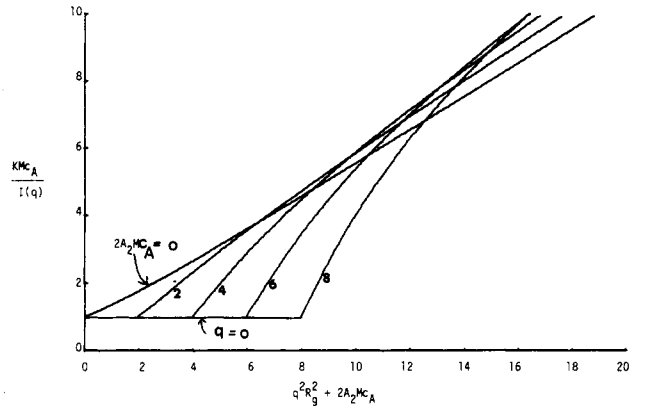


Figure 6. Plot similar to Figure 5 for a higher interaction parameter corresponding to $A_{2AB}/A_2 = 1.41$.

ordinary homopolymers.[1] To see the effect of a higher interaction, we have made a similar plot in Figure 6 with $A_{2AB}/A_2 = 1.41$. We note that the slope of the concentration line ($q = 0$) vanishes. This behavior is expected since the two polymers repel each other. A similar behavior is observed by increasing the concentration of B and keeping the interaction constant. This is illustrated by Figure 7, where we let $A_{2AB}/A_2 = 1$ and $2A_2Mc_B = 8$. In Figure 8, we show a similar plot for $A_{2AB}/A_2 = 1.1$ and $2A_2Mc_B = 8$. The slope of the concentration line is negative, indicating a negative apparent virial coefficient. Note that if the concentration or the interaction parameter or both are increased further, one may reach the demixing point, where $I(q) = \infty$. The angular distribution is highly distorted in all these figures, which are plotted on the same scale to make the comparison easier.

2. Polydispersity. It is evident by inspection of eq 30 and the way it has been obtained that polydispersity has no effect on the results. If one deals with two polydisperse polymers A and B, it is sufficient to replace χ_A and χ_B by the corresponding sums:

$$\chi_A = \sum_i N_{iA} n_{iA}^2 P_{iA}(q)$$

$$\chi_B = \sum_i N_{iB} n_{iB}^2 P_{iB}(q)$$

3. Forward Scattering $I(0,c)$. As we have pointed out earlier, eq 30 gives for $q = 0$, the intensity due to fluctuations in a ternary system. This has been evaluated by many authors[9,10] using thermodynamical methods, which give correct results. Therefore, it was interesting to write the thermodynamical equation and to compare it with ours. For this purpose, we write Stockmayer's[4]

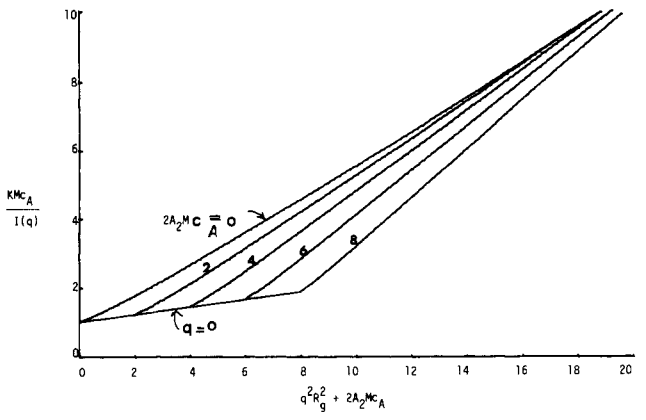


Figure 7. Plot similar to Figure 5 using $A_{2AB}/A_2 = 1$ and $2A_2Mc_B = 8$.

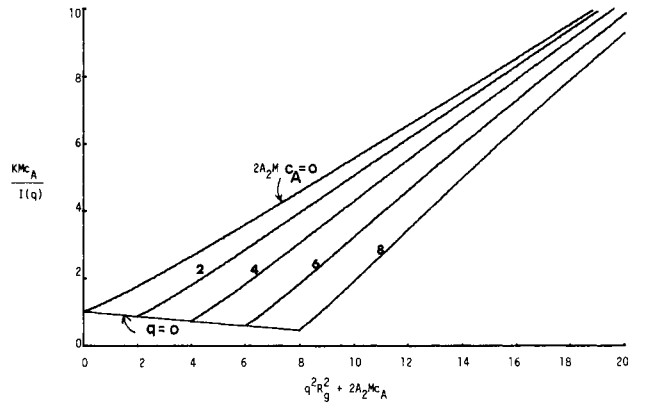


Figure 8. Plot similar to Figure 5 using $A_{2AB}/A_2 = 1.1$ and $2A_2Mc_B = 8$.

result in the form given by Kratochvil et al.[11] with a slight modification:

$$I(0,c) = [\psi_A^2 m_A + \psi_B^2 m_B + (\psi_A^2\beta_B + \psi_B\beta_A^2 - 2\psi_A\psi_B\beta_{AB})m_A m_B]/[1 + m_A\beta_A + m_B\beta_B + (\beta_A\beta_B - \beta_{AB}^2)m_A m_B] \quad (38)$$

which is to be compared with our result:

$$I(0,c) = [a^2 N_A n_A^2 + b^2 N_B n_B^2 + (a^2\vartheta_B + b^2\vartheta_A - 2ab\vartheta_{AB})N_A n_A^2 N_B n_B^2]/[1 + \vartheta_A N_A n_A^2 + \vartheta_B N_B n_B^2 + (\vartheta_A\vartheta_B - \vartheta_{AB}^2)N_A n_A^2 N_B n_B^2] \quad (39)$$

The equations are identical if we replace ϑ_A, ϑ_B, and ϑ_{AB} by their thermodynamical counterparts β_A, β_B, and β_{AB} and we identify the other parameters as $\psi_A = a$, $\psi_B = b$, $n_A^2 N_A = m_A$, and $n_B^2 N_B = m_B$. This observation is very satisfying since it proves that, regardless of its approximation, this model leads to a correct result, at least for $q = 0$.

Since we obtain for $I(0,c)$ a formula which has been known for a very long time, there is no need to elaborate more on its applications.[13]

4. Extrapolation to the Limit of a Pure Mixture of Polymers (Bulk Limit). Before considering the limit of a pure mixture of polymers A and B, let us examine the relations between our parameters ϑ_A, ϑ_B, and ϑ_{AB} and those appearing in the classical Flory–Huggins theory χ_A, χ_B, and χ_{AB}. To avoid a cumbersome manipulation of the thermodynamical functions, we can just remark that if $N_B = 0$, we obtain a binary system for which we write

$$\frac{K}{I} = \frac{1}{M_A c_A} + 2A_{2A}(c_A) = \frac{1}{m_A^2}\left[\frac{1}{N_A n_A^2} + 2A_{2A}(c_A)m_A^2\right] \quad (40)$$

where m_A is the molecular weight of a monomer A and $A_{2A}(c_A) = \vartheta_A(c_A)/2m_A^2$. Therefore we have

$$2A_{2A}(c_A)c_A = \frac{1}{RT}\left(\frac{\partial \Pi}{\partial c_A}\right) - \frac{1}{M_A} \tag{41}$$

Flory–Huggins theory gives

$$\frac{1}{RT}\Pi v_1 = \ln(1-\varphi_A) + \varphi_A\left(1 - \frac{1}{n_A}\right) + \chi_{AS}\varphi_A^2 \tag{42}$$

From the last three equations, one obtains[1,6]

$$\vartheta_A = \vartheta_S(1/\varphi_S - 2\chi_{AS}) \tag{43}$$

where ϑ_S is the volume of a solvent molecule and φ_S the volume fraction of the solvent in the mixture. By a similar argument, one also obtains

$$\vartheta_B = \vartheta_S(1/\varphi_S - 2\chi_{BS}) \tag{44}$$

$$\vartheta_{AB} = \vartheta_S(1/\varphi_S - 2\chi_S) \tag{45a}$$

$$2\chi_S = \chi_{AS} + \chi_{BS} - \chi_{AB} \tag{45b}$$

This shows that the excluded volume parameters are far from being constants and they go to infinity when the solvent volume fraction goes to zero. This is a general observation which does not depend on the form of eq 40, since in this limit the system behaves like an ideal solution. It is only for a dilute solution that one can assume ϑ_A, ϑ_B, and ϑ_{AB} to be constant. For a Θ solvent, $\vartheta_A = 0$ at infinite dilution and it is proportional to φ_A in the dilute range $\varphi_A \ll 1$.

In order to see what kind of results one can obtain from eq 30 in the bulk limit, one can substitute these values of ϑ_A, ϑ_B, and ϑ_{AB} into eq 30, multiply both the numerator and denominator by φ_S, and let $\varphi_S \to 0$. Using this procedure, one obtains

$$I(q) = (a-b)^2 \frac{\chi_A\chi_B}{\chi_A + \chi_B - 2\vartheta_S\chi\chi_A\chi_B} \tag{46}$$

where

$$\chi = \chi_{AB} \tag{47}$$

Taking the inverse of eq 46 yields

$$I^{-1}(q) = \frac{1}{\chi_A} + \frac{1}{\chi_B} - \frac{2\chi}{N} \tag{48}$$

which is very similar to the formula obtained by de Gennes using the RPA technique.[5,12] We note, however, that in his formula de Gennes gives the intensity per site. In our presentation we give the intensity per unit volume. Therefore assuming that there are N sites per unit volume, de Gennes' formula becomes

$$I^{-1}(q) = \frac{1}{N_A n_A^2 P_A} + \frac{1}{N_B n_B^2 P_B} - \frac{2\chi}{N} \tag{49}$$

Now it is interesting to see how de Gennes' formula, which is valid for a mixture of two polymers, can be applied to a polymer–solvent system. If in eq 49 we assume that polymer B is a monomer, or a simple liquid, then $n_B = P_B = 1$, $Nv_S = 1$, and eq 49 can be written as

$$I(q) = \frac{1}{Nn^2P} + \frac{1}{N}\left[\frac{1}{\varphi_S} - 2\chi\right] = \frac{1}{Nn^2P} + v_S\left[\frac{1}{\varphi_S} - 2\chi\right] \tag{50}$$

which is exactly the result we obtained.[1] Therefore the approximation made in the RPA calculations is exactly the same as in the Flory–Huggins theory. Starting from eq 50, it is possible by two integrations, assuming χ to be constant, to obtain the free energy of mixing of the Flory–Huggins theory.

This shows from the study of scattering in the forward direction that three routes, the Flory–Huggins theory, de Gennes' RPA, and our approach based on a generalization of the Ornstein–Zernike theory, are completely equivalent. For the scattering at a finite angle, our theory and the RPA are equivalent.

Finally, it should be noted that if the denominator of eq 30 goes to zero, the scattered intensity becomes infinite, which means that we reach the spinodal (for this problem one may refer to Tompa's book[13]). Therefore, equating our denominator to zero gives the equation of the spinodal in a three-component polymer A/polymer B/solvent system.

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References and Notes

(1) Benoit, H.; Benmouna, M., submitted to *Polymer*.
(2) Zimm, B. *J. Chem. Phys.* **1948**, *16*, 1093.
(3) Ornstein, L. S.; Zernike, F. *Proc. Acad. Sci., Amsterdam* **1914**, *17*, 793.
(4) Stockmayer, W. *J. Chem. Phys.* **1950**, *18*, 58.
(5) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press, Ithaca, NY, 1979.
(6) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1967.
(7) Rushbrooke, G. S. "Physics of Simple Liquids"; Temperley, H. N. V., Rowlinson, J. S., Rushbrooke, G. S., Eds.; Wiley-Interscience: New York, 1968.
(8) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(9) Vrij, A.; Van den Esker, M. W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 727.
(10) Strazielle, C. "Light Scattering from Polymer Solutions"; Huglin, M. B., Ed.; Academic Press: New York, 1972. See also: Hyde, A. J. *Ibid.*, p 459.
(11) Kratochvil, P.; Vorlicek, J.; Stakova, D.; Tuzar, Z. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2321.
(12) Leibler, L. *Macromolecules* **1982**, *15*, 1283.
(13) Tompa, H. "Polymer Solutions"; Academic Press: New York, 1956.