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A Few Remarks on Classic Problems of Scattering by Polymer Solutions and Mixtures

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SUMMARY: The problem of scattering by multicomponent systems has been the object of many papers. Here it will be shown that the scattering can be split into two terms, one corresponding to the compressibility of the system and the other depending only on fluctuations of the number of molecules of different constituents. In neutron scattering on samples far from critical conditions, the compressibility term is negligible. In the second part, a simple demonstration of the random phase approximation theorem is proposed, which makes the theorem more understandable for nonspecialists.

Introduction

Being at the end of our career, it is no longer time to discuss new theories and new fields of activity. We will try in this paper to be more modest and to present problems on which we have been working for years hoping to have made some progress. We will present a semiquantitative treatment using a minimum of mathematics to explain classic results used every day in interpretation of scattering data. Two problems will be discussed: the interpretation of scattering by multicomponent systems and the other which is usually called the random phase approximation (RPA) introduced by de Gennes(1). It is used by all experimentalists mainly for the interpretation of neutron scattering data as a function of angle. These remarks do not have the pretension to replace what has been written in the classic papers. Since real understanding of a theory includes the ability to explain it in relatively simple terms, we hope that this approach is not useless.

Multicomponent systems

When I (H. B.) began to work in the field of polymers, Professor C. Sadron asked me to study the potentials of light scattering as a tool in macromolecular physical chemistry. I began to learn the subject and to teach it in the frame of initiation of chemistry students to the light scattering. Bravely I decided to demonstrate all the rules used for the interpretation of light scattering data beginning with the perfect gas where the scattering is the sum of the scattering by individual molecules and obtaining thus a very simple equation. This technique was used by

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a French professor J. Cabannes(2,3) in 1920 who used it for the evaluation of Avogadro's number and showed that in a pure liquid, there should be no scattering if its density is constant. This is difficult to prove experimentally since the liquid has to be perfectly clean, without any impurity. Even under these circumstances, as it has been demonstrated by Einstein(4), there is some scattering produced by the density fluctuations due to thermal agitation. This has been verified in benzene by Cabannes(5) only approximately since this scattering is very low. Under the best experimental conditions that could be realized at that time, the ratio between the intensities of incident light and scattered light is of the order of 10^4. This was very difficult to measure with the techniques available (the light source was the sun and the detector a photographic plate which is far from being a linear detector). It is well known that a dilute solution is equivalent to the perfect gas. Therefore, since Avogadro's number can be calculated for a gas with known molar mass, one can also, knowing Avogadro's number, measure the molar mass of an unknown polymer. This is the general idea which was the basis of the work of Puttees and Brosteaux(6) followed by Debye(7). When you teach students on this problem, you want to make the subject complete and to work with both a pure liquid and a dilute solution. This leads to the question: what happens when you have both phenomena together. In an old textbook, you could find the following statement: it is evident that there are no correlations between density fluctuations (responsible for the scattering by pure liquid and depending on the compressibility) and concentration fluctuations making possible the measurements of molar masses. The author was optimistic since, so far, it has been impossible to find how he did reach this conclusion by simple arguments. This was an open question which has been solved only in the 1950's. Since that time many papers have been devoted to the problem and its generalization to scattering by multicomponent systems. The best-known of these papers have been written by Stockmayer(8) and by Kirkwood et al.(9), followed by many others(10-12). The interest in this problem was renewed during the last decade for the following reason. As it is well known, the scattered intensity makes it possible to determine not only the molar mass but also the second virial coefficient or the covolume. This leads first to an estimation of the famous χ parameter of Flory(13) (which is often called the black box where one puts all that is not clearly understood). Different methods leading to different values of χ are still a puzzling problem. It was suggested that the discrepancies between the values obtained by different methods were due to incorrect treatment of the scattering data and to the influence of density fluctuations on composition fluctuations. Now, we are going back to the general problem of multicomponent compressible systems to show again, without complex calculations, that there is complete independence between composition and density fluctuations, justifying a posteriori the work of Stockmayer, which shows that one can completely forget about the effect of density fluctuations in the classic studies on light and neutron scattering by polymers.

The equation

Let us assume that the scattering system consists of n scattering objects (which will be called molecules), having b as scattering length per unit volume.

$$I(q) = \sum_{i=1}^{n}\sum_{j=1}^{n} b_i b_j \exp(-\mathrm{i}q\mathbf{r}_{ij}) \tag{1}$$

calling $\mathbf{q}$ the scattering vector ($q = \frac{4\pi}{\lambda}\sin(\theta/2)$) and $\mathbf{r}_{ij}$ the vector joining the scattering points i and j having neutron scattering length b_i and b_j (or a quantity related to the refractive index increment in light scattering or to the electron density in X-ray scattering).

Since we are interested in the scattering at zero angle ($\theta = 0$), this relation is simplified (the exponential term being equal to unity) and one can collect the terms corresponding to i and j, either on the same species of molecule or on different species of molecules(14,15):

$$I(0) = \sum_{i,j}\sum b_i b_j \int \mathrm{d}^3\mathbf{r}\,\delta\overline{\left(\mathbf{r} - \mathbf{r}_i - \mathbf{r}_j\right)} \tag{2}$$

where the double sum is extended to the p^2 pairs of molecules of different nature and the integral is extended to all the pairs of monomeric units of the molecules of type i and j in the scattering volume. We have written Δn_i and Δn_j since it is well known that it is only the fluctuations in n, the number of molecules, that scatter light. Let us now call S_{ij} the term

$$S_{ij} = \overline{\Delta n_i \Delta n_j} \tag{3}$$

Equation (2) becomes

$$I(0) = \sum_{r,s}^{p} b_r b_s S_{rs} \tag{3'}$$

This is the starting equation which will allow us to explicitly express the result.

The first remark is that, due to symmetry of the system, $S_{ij} = S_{ji}$. The S_{ij}'s can be collected in a p-by-p matrix and the problem is to evaluate this matrix by the classic techniques of statistical mechanics in order to find a relation between the properties of the system and the scattered intensity.

This is a classic exercise which can be found in practically all textbooks and we will just give here the result as a function of chemical potential μ_i

$$\overline{\Delta n_i^2} = k_{\mathrm{B}} T \left(\frac{\partial \bar{n}_i}{\partial \mu_i} \right)_{V,T,k \neq i} \tag{4}$$

$$\overline{\Delta n_i \Delta n_j} = k_{\mathrm{B}} T \left(\frac{\partial \bar{n}_i}{\partial \mu_j} \right)_{V,T,k \neq i,j}$$

where k_{B} is the Boltzmann constant and $\frac{\partial \bar{n}_i}{\partial \mu_j}$ the derivative of the average number of particles of species i ($\bar{n}_i$) per unit volume. The second equation is of the same type but corresponds to a cross-term. In order to solve this problem, one has first to transform the quantities $\left(\frac{\partial \bar{n}_i}{\partial \mu_i} \right)$ and $\left(\frac{\partial \bar{n}_i}{\partial \mu_j} \right)$ into the reciprocals, i.e., $\frac{\partial \mu_i}{\partial \bar{n}_i}$ and $\frac{\partial \mu_j}{\partial \bar{n}_i}$. The main reason for the transformation is that the latter expressions are more familiar and can be handled more easily. But even when put into this form, the quantities are not very useful since they require to work at constant V and T. Changing the number of molecules without changing the volume is practically impossible if the system is incompressible. One has therefore to make a second step and replace $\left(\frac{\partial \mu_i}{\partial \bar{n}_i} \right)_{V,T}$ with $\left(\frac{\partial \mu_i}{\partial \bar{n}_i} \right)_{P,T}$. The first step is a classic procedure for functions with more than one variable and is symbolized by the equation which allows to evaluate the $\frac{\partial \bar{n}_i}{\partial \mu_i}$ matrix as a function of the matrix $\frac{\partial \mu_i}{\partial \bar{n}_i}$. One has just to write

$$\mathbf{S} = \left[\frac{\partial \bar{n}_i}{\partial \bar{\mu}_i} \right] = \left[\left(\frac{\partial \mu_i}{\partial \bar{n}_i} \right) \right]^{-1} \tag{5}$$

In other words, the matrix **S** of the inverse is equal to the inverse of the matrix $\mathbf{S}^{-1}$.

The second step is to go from constant volume and temperature to constant pressure and temperature. This is also a classic result of thermodynamics(16):

$$\left(\frac{\partial \mu_i}{\partial \bar{n}_j} \right)_{V,n,T} = \left(\frac{\partial \mu_i}{\partial \bar{n}_j} \right)_{P,n,T} + \frac{v_i v_j}{\chi_T V} \tag{6}$$

where v_i and v_j are the molecular volumes of constituents i and j, V is the total volume of the scattering system and χ_T the isothermal compressibility of the system,

$$\chi_T = \frac{-1}{V} \left(\frac{\mathrm{d}V}{\mathrm{d}P} \right)_T$$

We have now all the ingredients to write the general formula allowing to evaluate $I(0)$ If one writes for simplification

$$a_{ij} = (\frac{\partial \mu_i}{\partial n_j})_{P,n,T} \tag{7}$$

one obtains for a three-component system

$$\mathbf{S} = \begin{pmatrix} a_{11} + \frac{v_1^2}{V\chi_T} & a_{12} + \frac{v_1 v_2}{V\chi_T} & a_{13} + \frac{v_1 v_3}{V\chi_T} \\ a_{21} + \frac{v_2 v_1}{V\chi_T} & a_{22} + \frac{v_2^2}{V\chi_T} & a_{23} + \frac{v_2 v_3}{V\chi_T} \\ a_{31} + \frac{v_3 v_1}{V\chi_T} & a_{32} + \frac{v_3 v_2}{V\chi_T} & a_{33} + \frac{v_3^2}{V\chi_T} \end{pmatrix}^{1} \tag{8}$$

The calculation of the S_{ij} seems easy but, even for this simple three-component system, it is rather tedious. The classic method to evaluate the inverse matrix of a given matrix is to write the adjunct matrix and divide it by the determinant of the matrix.

Calculation of the denominator

Since each term is the sum of two terms, one can write the determinant of the matrix **S** as the sum of p^2 determinants and to evaluate them separately. Let us follow this method and write the first determinant of the denominator:

$$\text{Det} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{9}$$

This determinant is zero since, at constant pressure and temperature, the Gibbs-Duhem equation can be written as $\Sigma n_j d\mu_j = 0$ or, after derivation with respect to n_j and using our notations,

$$\sum_{j-1}^{p} n_i (\frac{\partial \mu_i}{\partial n_j})_{P,n,T} = \sum_{j=1}^{p} n_i a_{ij} = 0 \tag{10}$$

One can easily see that multiplying the first column by N_1, the second by N_2 and the third by N_3 and adding the three columns gives a line of zero.

In order to study systematically these sums, let us consider the three determinants having one column of v and the other of a_{ij}. They have no reason to be zero and one obtains, after factorization of $V\chi_T$

$$\chi_T V\,\mathrm{Det} = v_1\begin{vmatrix} v_1 & a_{12} & a_{13} \\ v_2 & a_{22} & a_{23} \\ v_3 & a_{23} & a_{33} \end{vmatrix} + v_2\begin{vmatrix} a_{11} & v_1 & a_{13} \\ a_{21} & v_2 & a_{23} \\ a_{31} & v_3 & a_{33} \end{vmatrix} + v_3\begin{vmatrix} a_{11} & a_{12} & v_1 \\ a_{21} & a_{22} & v_2 \\ a_{31} & a_{32} & v_3 \end{vmatrix} \qquad (11)$$

Finally, the determinants having two or more columns in v have, after factorization, two identical columns; they are equal to zero. We are therefore left with Eq. (11) to express the denominator. This shows that the inverse of the compressibility (χ_T^{-1}) factorizes the denominator of the S_{ij} and we can write that the denominator Det of all S_{ij} is of the form

$$\mathrm{Det} = \frac{1}{V\chi_T}\,\alpha \qquad (12)$$

where α is given in the case of $p - 3$ by Eq. (11).

It is evident that this result can be generalized to any value of p.

Calculation of the numerator

The determination of **S** requires the evaluation of the adjunct matrix of the matrix of Eq. (8). The method is well known: one deletes in the determinant of the matrix of Eq. (8) column i and row j obtaining a new determinant C_{ij} which is proportional to the coefficient S_{ij} and has the form

$$C_{ij} = \frac{1}{V\chi_T}C_{ij}^1 + C_{ij}^2 \qquad (13)$$

It is similar to the denominator of Eq. (11). The main difference results from the fact that the component of the determinant with no v columns is not zero since one cannot use the Gibbs-Duhem equation. Therefore we are left with two terms, one independent of χ_T and the other proportional to $(\chi_T V)^{-1}$. This allows to write for the numerator C_{11} of $\mathbf{S}_1$ for instance

$$C_{11} = \begin{vmatrix} a_{22} + \dfrac{v_2^2}{\chi_T} & a_{12} + \dfrac{v_2 v_1}{\chi_T} \\ a_{12} + \dfrac{v_2 v_1}{\chi_T} & a_{33} + \dfrac{v_3^2}{\chi_T} \end{vmatrix} \qquad (14)$$

$$C_{11} = a_{22}a_{33} - a_{23}^2 + \frac{1}{V\chi_T}\left[v_2^2 a_{33} - 2v_2 v_3 a_{23} + v_3^2 a_{22}\right] \qquad (14')$$

confirming the form of Eq. (13), where the C_{ij}^1 and C_{ij}^2 have a clear meaning. One can write, regardless of the value of p,

$$S_{ij} = \frac{V\chi_T C_{ij}^2 + C_{ij}}{\alpha} = S_{ij}^1 + S_{ij}^2 \qquad (15)$$

calling S^{2}_{ij} the contribution of compressibility to scattering and S^{1}_{ij} the contribution of composition fluctuations.

Density fluctuations

This result, which was obtained by different authors$^{(8,10,11)}$, is important since it is in contradiction with recent calculations. It seems that the method that has been used is correct and cannot be criticized since it does not use any new variable and its derivation is straightforward. The result proves unambiguously that, when dealing with compressible systems, one has just to add to the term corresponding to composition fluctuations a term taking into account the compressibility, which obeys the classic relation

$$I(0)=\left(\sum n_i v_i b_i\right)^2 \frac{\chi_T k_\mathrm{B} T}{V} = V\bar{b}^2 \chi_T k_\mathrm{B} T \qquad (16)$$

after introducing the average scattering length $\bar{b}$

$$\bar{b}=\frac{1}{V}\sum n_i v_i b_i \qquad (16')$$

Note that the vector $\mathbf{v}$, defined by its components v_i, is a null space of $\mathbf{S}_1$ for compressible systems and a null space of $\mathbf{S}$ for incompressible systems.

A recent work$^{(17)}$ has shown that the contribution of Eq. (16) is practically negligible in all actual experiments on neutron scattering by polymers. It can be remarked that if one subtracts from the scattering of the sample the scattering by a system without structure in order to eliminate the incoherent scattering, one subtracts also the effect of compressibility. This means that this correction is in some cases already made.

Composition fluctuations

Now we are left with the second part of the S_{ij} which corresponds to the classic fluctuations of composition. If, starting from Eq. (8), all the terms containing χ_T are eliminated, one is left with a matrix which, because of the Gibbs-Duhem equation, is singular and cannot be used to evaluate S^{1}_{ij}. One could take Eq. (13) to evaluate these terms but this is very cumbersome and not easy to read. The problem is that we have too many S_{ij} which are not independent.

If, for instance, $p = 2$, we have three different S_{ij} but need only two parameters for the evaluation of $I(0)$ - the bulk compressibility and the scattering by the solution. The extra parameters must therefore be eliminated. The choice of variables is a difficult problem. Two decades ago, des Cloizeaux and Jannink$^{(11)}$, using linear algebra methods, have shown that there are two ways to perform this elimination. The first is to use the contrast between the scattering species and the average value of the scattering length. Having been used by Williams et al.(18), this is especially useful in the studies on copolymers. The other, the most frequently used method consists in treating one of the constituents as a solvent and to express the result as a function of the contrast between the scatterer and the solvent. More generally, unless there is a large compressibility contribution, the simplest way to eliminate the corresponding term is to utilize the classic methods of neglecting the contribution of compressibility except when one is interested in the effect of pressure on the scattering (in the latter case, the influence of pressure on $(\frac{\partial \mu_i}{\partial n_j})_{P,T}$ must be taken into account). Summarizing the results of the preceding calculations, we write for the scattering matrix **S**

$$\mathbf{S}^{-1} = \mathbf{A} + \frac{\mathbf{v}\mathbf{v}^{\mathrm{Tr}}}{\chi_T V} \qquad \text{with the property } \mathbf{An} = 0,$$

or

$$\mathbf{S} = \mathbf{B} + \mathrm{nn}^{\mathrm{Tr}} \frac{\chi_T}{V} \qquad \text{with the property } \mathbf{Bv} = 0$$

where **B** stands for $\mathbf{S}^{-1}$ in Eq. (15). The system displays symmetry, the condition **Bv** = 0 being conjugated to the Gibbs-Duhem relation **An** = 0.

The method we have used is in some respect pedestrian. Our colleague Prof. Akcasu(19) reminded us of a formula established by Sherman and Morrison(20) which allows to study this problem with more efficient tools. If a matrix **M** can take the form

$$\mathbf{M}^{-1} = [\mathbf{A} + \frac{1}{\Gamma}\,\mathrm{v}\,\mathrm{v}^{\mathrm{Tr}}\,] \tag{17}$$

where **v** is a vector and $\mathbf{v}^{\mathrm{Tr}}$ its transform, and if the matrix **A** is not singular, its inverse can be written as

$$\mathbf{M} = \frac{\mathbf{A}^{-1} + \mathrm{v}\mathrm{v}^{\mathbf{Tr}}\mathbf{A}^{-1}}{\Gamma + \mathrm{v}^{\mathbf{Tr}}\mathbf{A}^{-1}\mathrm{v}} \tag{18}$$

Unfortunately, our matrix **A** (which is the matrix a_{ij}) is singular and this formula cannot be used without modifications.

The random phase approximation

So far we have only discussed the behavior at zero angle but, even though it is an interesting problem, a majority of the experiments require the interpretation of the scattering in a large domain of the scattering vector **q**.

The exploration of this domain was limited to dilute solutions because there was no theory (besides the second-order in concentration) to explain the results. The situation changed dramatically when P G. de Gennes published(21) in 1970 the method he called the random phase approximation (RPA). This method gives correct results for concentrated solutions and for a large domain of q allowing to demonstrate at low q the results which we have just discussed. Unfortunately, its demonstration is rather complex and there are not many experimentalists which are ready to read the de Gennes paper. The idea is that, since the result is simple(15,21), a simple demonstration to prove it should exist and it is worth spending some time to try to find it. In this last part, it will be shown that this demonstration does exist and one can hope that it is easy to understand.

Let us consider a system made by an incompressible mixture of two polymers. There are N_A and N_B molecules of each species. We cut them into units of the same volume, their number being n_a for polymer A and n_b for B. Their scattering length per unit volume are $\tilde{a}$ and $\tilde{b}$. Following the preceding discussion, we can rewrite the equation for the scattering as

$$I(0) = \tilde{a}^2 \sum_i^{n_a} \sum_j^{n_a} \overline{\exp(-iqr_{ij})} + \tilde{b}^2 \sum_i^{n_b} \sum_j^{n_b} \overline{\exp(-iqr_{ij})} + 2\tilde{a}\tilde{b} \sum_i^{n_a} \sum_j^{n_b} \overline{\exp(-iqr_{ij})}$$

$$= \tilde{a}^2 S_{aa} + 2\tilde{a}\tilde{b}\, S_{ab} + \tilde{b}^2\, S_{bb} \qquad (19)$$

where the average has to be taken for all pairs of monomers a-a, b-b, a-b. Consider the term where the average is taken on the monomers a. If the points i_a and j_b are on the same molecule, there are n_a^2 couples and the average value of the interference term will be called $P_a(q)$. Therefore the part corresponding to the couple a-a in the same molecule can be written as $N_A n_a^2 P_a(q)$. But one has also to consider the interferences between different molecules of the same type and this leads to $N_A^2 n_a^2 Q_{aa}(q)$ where $Q_{aa}(q)$ is the average value taken on one pair of molecules. This leads to

$$\begin{aligned} S_{aa}(q) &= N_A n_a^2 P_a(q) + N_A^2 n_a^2 Q_{aa}(q) \\ S_{bb}(q) &= N_B n_b^2 P_b(q) + N_B^2 n_b^2 Q_{bb}(q) \\ S_{ab}(q) &= N_A N_B n_a n_b Q_{ab}(q) \end{aligned} \qquad (20)$$

since there are no molecules having simultaneously a and b monomers. As we have seen, the S_{ij} are not independent. It is easy to show that we have the two relations:

$$\begin{aligned} S_{aa} + S_{bb} &= 0 \\ S_{bb} + S_{ab} &= 0 \end{aligned} \qquad (21)$$

which are a generalization of the Gibbs-Duhem equation (Eq. 10) for $q \neq 0$ and lead to

$$\frac{I(q)}{\left(\tilde{a}-\tilde{b}\right)^2} = N_A n_a^2 P_a(q) + N_A^2 n_a^2 Q_{aa}(q) + N_B n_b^2 P_b(q) + N_B^2 n_b^2 Q_{bb}(q) + N_A N_B n_a n_b Q_{ab}(q) \tag{22}$$

We still need another equation to be able to write the result as a function of the terms P_b, P_{ab}, Q_{aa}, Q_{bb}, and Q_{ab}. For this purpose, let us consider the diagram of Fig. 1.

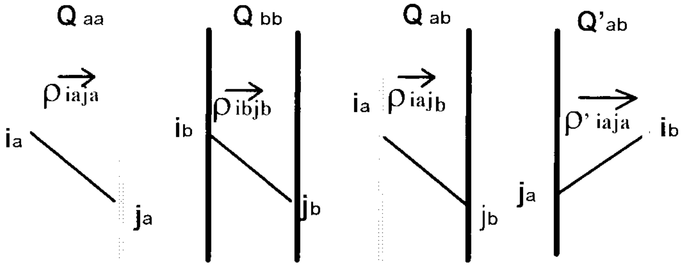

Figure 1 Schematic representation of the interactions between the two species of molecules. The vector joining the two interacting points is called ρ_{ij}. Type A molecules are represented by a gray line, type B by a black line.

This figure is a schematic representation of the terms Q_{aa},Q_{bb} and Q_{ab} (Q'_{ab}). The vertical lines represent the molecules of type A and B. From this diagram one can easily write:

$$\begin{aligned} Q_{aa} &= \overline{\exp(-iq\rho_{i_a j_a})} \\ Q_{bb} &= \overline{\exp(-iq\rho_{i_b j_b})} \\ Q_{ab} = Q'_{ab} &= \overline{\exp(-iq\rho_{i_a j_b})} = \overline{\exp(-iq\rho_{i_b j_a})} \end{aligned} \tag{22'}$$

One writes now the quantities $Q_{aa}Q_{bb}$ and $Q_{ab}Q'_{ab}$, using a common arbitrary origin 0 and this allows to write $\rho_{ij} = r_j - r_i$.

$$\begin{aligned} Q_{aa}Q_{bb} &= \overline{\exp(-iqr_{ja})\exp(-iqr_{ia})\exp(-iqr_{jb})\exp(-iqr_{ib})} \\ Q_{ab}Q'_{ab} &= \overline{\exp(-iqr_{ja})\exp(-iqr_{ia})} \end{aligned} \tag{23}$$

One sees clearly that they are identical if one neglects the average signs; however, this cannot be done without a hypothesis. The random phase approximation introduced by de Gennes(21) in 1970 is just this hypothesis. It assumes that one can write

$$Q_{\mathrm{aa}}Q_{\mathrm{bb}} = Q_{\mathrm{ab}}^2 \tag{24}$$

Assuming this relation to be correct, it is easy to eliminate the Q functions and one obtains

$$\frac{(\tilde{a}-\tilde{b})^2}{I(q)} = \frac{1}{N_{\mathrm{A}}n_{\mathrm{a}}^2 P_{\mathrm{a}}(q)} + \frac{1}{N_{\mathrm{B}}n_{\mathrm{b}}^2 P_{\mathrm{b}}(q)} \tag{25}$$

which is the classic formula for a system with two components. This result has been obtained assuming no interaction between molecules A and B. It can be shown that the χ parameter of Flory can be easily introduced leading to

$$\frac{(\tilde{a}-\tilde{b})^2}{I(q)} = \frac{1}{N_{\mathrm{A}}n_{\mathrm{a}}^2 P_{\mathrm{a}}(q)} + \frac{1}{N_{\mathrm{B}}n_{\mathrm{b}}^2 P_{\mathrm{b}}(q)} - 2\chi \tag{26}$$

The procedure we have used can be extended to any systems containing copolymers and a large number of components. One has only to assume that each pair of constituents satisfies Eq. (24) but the calculations become rapidly tedious.

Assuming that component B is a small molecule ($n_{\mathrm{B}} = P_{\mathrm{B}} = 1$) and that the volume of the A is equal to the volume of solvent molecule, one obtains, using the volume fraction $\varphi = \frac{N_{\mathrm{A}}n_{\mathrm{a}}}{N_{\mathrm{A}}n_{\mathrm{a}} + N_{\mathrm{B}}}$ and introducing the scattering per monomer unit $i(q)$, $i(q) = \frac{I(q)}{N_{\mathrm{A}}n_{\mathrm{a}} + N_{\mathrm{B}}}$ and thus recovers the classic result:

$$\frac{(\tilde{a}-\tilde{b})^2}{i(q)} = \frac{1}{N_{\mathrm{A}}P(q)} + \frac{1}{1-\varphi} - 2\chi \tag{27}$$

This gives a simple explanation to the random phase approximation. It can be reminded that it is a very good approximation, giving at zero angle the rigorous formula obtained by thermodynamics, which is also rigorous when the two polymers are identical. It can be extrapolated to an arbitrary number of constituents. Efforts have been made to improve it but, so far, the results have kept the same form, the improvements consisting mainly in a more rigorous evaluation of the excluded volume parameter $v_{\mathrm{s}} = \frac{1}{\varphi_{\mathrm{s}}} - 2\chi$.

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