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Nonrandom Distribution of Molecules in Polymer Systems. 1. Theory and Model Calculations†

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ABSTRACT: The average space distribution of molecules in a mixture is nonrandom when polymers are present. Such nonrandomness can be characterized by the so-called Kirkwood–Buff–Zimm integrals, G_{ij}, which gives information about the relative tendency of the molecules of components i and j to solvate each other. The G_{ij}'s can be obtained from experimental data such as the scattering structure factor or the colligative properties. Theoretical equations to calculate G_{ij} from such experimental data in polymer system are given. They are applied to study nonrandomness arising from the large size of macromolecules and from interactions in model systems. Application to real systems follows in the subsequent paper.

Introduction

In this work we study the average space distribution of molecules in systems composed of a polymer plus another species, be it a solvent or another polymer.[1] The method used for this study is based on the so-called Kirkwood–Buff–Zimm integrals (KBZ). These are defined in terms of the pair correlation function for the system, g_{ij}. If $\vec{R}$ is the vector distance separating a pair of molecules, i and j, the KBZ integrals, G_{ij}, are defined by[2-8]

$$G_{ij} = \int [g_{ij}(R) - 1]\, \mathrm{d}\vec{R} \tag{1}$$

The pair correlation function g_{ij} tends to unity at long distances and differs from unity only at short R. Hence, the difference $g_{ij}(R) - 1$ measures the molecular correlation occurring at a local level, and integration over $\vec{R}$ gives the average value of this correlation in the whole system.

The KBZ integrals have an intuitive physical meaning which is useful for the interpretation of the space distribution of molecules. Let f_i be the average number of i molecules per unit volume of the system. Then f_iG_{ij} is the excess (or deficiency) over the mean value (given by the global concentration) of molecules of class i which, on the average, surround a molecule of class j.[2-8] Likewise, the difference $G_{ij} - G_{jj}$ gives the sign of the preferential solvation of i molecules around a j molecule.[7,8] Thus, the KBZ integrals represent a useful picture about the local distribution of molecules and about the relative affinity of i and j molecules in the system.

The KBZ integrals could be calculated from the pair correlation function, g_{ij}, if the form of this function would be known with some detail. For simple liquid mixtures, model functions for the intermolecular potential are used for this purpose.[3] This is the direct way of obtaining the KBZ integrals. But there is also an inverse way, in which the KBZ integrals are obtained from experimental properties instead of from g_{ij}. This inverse way obviates the need of any model about the intermolecular potential or distribution.

In this inverse way, the KBZ integrals can be obtained from thermodynamic or scattering properties of the system.[3] The composition dependence of the chemical potential and the scattering structure factor at zero angle are useful experimental data from which G_{ij} can be calculated. This has the advantage that the values of the KBZ integrals are then experimental quantities which do not depend on any theoretical assumption about the form of the pair correlation function. Hence, it is possible to get information about the average space distribution of molecules, as expressed by the G_{ij}'s, without specifying the form of g_{ij}.

The actual average space distribution of molecules in a mixture is determined by several factors. One, very important in polymer systems, is the large size of the macromolecules. Another factor, common to all systems, is the balance of interactions between components. And another, also very important, is related to the packing of molecules. Due to the different equation of state properties of the components, there are fluctuations in volume,[9] which affect the average molecular distribution. In this and the subsequent paper,[1] we analyze the relative importance of these three factors.

First, we deduce the equations needed to calculate the KBZ integrals from experimental data in polymer systems (Theory). Then, we give some numerical results on model systems, to show the importance of macromolecular size under different regimes of interactions (Model Systems). And in the subsequent paper,[1] we analyze the influence of volume fluctuations and of interactions in real systems. To obtain the volume fluctuations contribution we first deduce the equations needed by using thermodynamic theory.

Theory

The intensity of radiation in a scattering experiment gives the scattering structure factor of the system, $S(\vec{q})$ ($\vec{q}$ = scattering wave vector). At zero scattering angle (q = 0), this structure factor, $S(0)$, is related to the concentration–concentration correlation function, $S_{cc}(0)$. This function is usually defined using mole fractions, x_i, for the composition of the system, as[2]

$$S_{cc}(0) = RTx_1x_2\left(\frac{\partial \mu_i}{\partial \ln x_i}\right)^{-1} \tag{2}$$

where μ_i is the chemical potential. However, in polymer systems mole fractions are not useful and the composition is usually expressed in terms of volume fractions, ϕ_i, defined by $\phi_i = N_iV_i/V$, where N_i is the amount of substance, V_i is the molar volume, and V is the total volume (both volumes referred to the system before mixing).

We now define a new concentration–concentration correlation function, based on the volume fraction scale,

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ϕ_i. We call such a function $S_{cc}^{\phi}(0)$. Our definition is as follows:

$$S_{cc}^{\phi}(0) = RT\phi_1\phi_2\left(\frac{\partial(\mu_i/V_i)}{\partial \ln \phi_i}\right)^{-1} \tag{3}$$

In the volume fraction scale, we have to use chemical potential per unit volume, μ_i/V_i, in order to make the defined function symmetrical with respect to indices i and j, since μ_i/V_i is the quantity which obeys the Gibbs–Duhem equality:

$$\frac{1}{V_1}\frac{\partial\mu_1}{\partial \ln \phi_1} = \frac{1}{V_2}\frac{\partial\mu_2}{\partial \ln \phi_2} \tag{4}$$

The correlation function thus defined has dimensions of volume per amount of substance. We can make it dimensionless by dividing by a reference volume, V_o (the lattice site volume, the solvent molar volume, or any other convenient reference). Benoit, Benmouna, and Wu[10] have defined a function similar to $S_{cc}^{\phi}(0)$ but written in terms of exchange chemical potentials, $\bar{\mu}_i$ (in our notation: $\bar{\mu}_2 = \mu_2 V_1/V_2 - \mu_1$).

In terms of this $S_{cc}^{\phi}(0)$, the KBZ integrals are

$$G_{ii} = RT\beta + \left(\frac{S_{cc}^{\phi}(0)}{\phi_i} - V_i\right)\phi_i^{-1} \tag{5}$$

$$G_{ij} = RT\beta - \frac{S_{cc}^{\phi}(0)}{\phi_1\phi_2} \tag{6}$$

where β is the isothermal compressibility. The $RT\beta$ term in G_{ii},G_{ij} is much smaller than the other terms of eqs 5 and 6. The isothermal compressibility of solvents has values ranging $(7–17) \times 10^{-10}$ Pa^{-1}, and that for polymers is usually smaller than that for solvents. Molar volumes of organic solvents are usually in the range $(40–130) \times 10^{-6}$ m^3·mol^{-1}. Thus, for T = 25 °C, the value of $RT\beta/V_i$ is of the order 0.05, very small compared to 1, which is the absolute value of G_{ii}/V_i,G_{ij}/V_j in an ideal system (see below). Besides, $RT\beta$ disappears when taking the differences $G_{ii} - G_{ij}$. For the sake of simplicity, we neglect, from now on, this $RT\beta$ term in G_{ii},G_{ij}.

The experimental data of polymer solutions and blends are usually expressed in a reduced form by means of the interaction parameter for the system. In a scattering experiment, the interaction parameter is χ_s, obtained from the structure factor at zero angle, $S(0)$, as

$$\frac{1}{S(0)} = \frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} - 2\frac{\chi_s}{r_1} \tag{7}$$

where $S(0) = S_{cc}^{\phi}(0)/V_o$, and $r_i = V_i/V_o$. But, in an experiment determining a colligative property, the interaction paramenter is χ, which is obtained from the chemical potential, $\Delta\mu_i$, as

$$\frac{\Delta\mu_1}{RT} = \ln\phi_1 + \left(1 - \frac{r_1}{r_2}\right)\phi_2 + \phi_2^2\chi \tag{8}$$

The relationship between both interaction parameters is

$$\chi_s = \frac{1}{2\phi_2}\frac{\partial}{\partial\phi_2}(\phi_2^2\chi) \tag{9}$$

The KBZ integrals can be obtained from these interaction parameters, either from the concentration dependence of χ or from χ_s directly. In both cases, the equations to be used are (5) and (6), together with the definition of $S_{cc}^{\phi}(0)$.

The interaction parameters χ and χ_s defined in eqs 7 and 8 are mere empirical quantities, whose values are obtained from the experimental results of $S(0)$ and $\Delta\mu_1$, respectively. Hence, they contain all kinds of contributions, including nonrandomness, and their use does not presuppose validity of the Flory–Huggins theory.

For calculations, it is easier to deal with the dimensionless quantities G_{ii}/V_i and G_{ij}/V_j, instead of with the G_{ij}'s themselves. In this way, the G_{ij}/V_j's depend only on the ratio of molecular sizes, r

$$r = r_2/r_1 = V_2/V_1 \tag{10}$$

and not on the size parameters of the two components separately. The equations used in the calculation are then

$$G_{11}/V_1 = \phi_1^{-1}\left(\frac{\tilde{S}_{cc}^{\phi}(0)}{\phi_1} - 1\right) \tag{11}$$

$$G_{22}/V_2 = \phi_2^{-1}\left(\frac{\tilde{S}_{cc}^{\phi}(0)}{r\phi_2} - 1\right) \tag{12}$$

$$G_{12}/V_2 = -\frac{\tilde{S}_{cc}^{\phi}(0)}{r\phi_1\phi_2} \tag{13}$$

$$G_{21}/V_1 = -\frac{\tilde{S}_{cc}^{\phi}(0)}{\phi_1\phi_2} \tag{14}$$

with

$$\tilde{S}_{cc}^{\phi}(0) = S_{cc}^{\phi}(0)/V_1 = \left(\frac{1}{\phi_1} + \frac{1}{r\phi_2} - 2\chi_s\right)^{-1} \tag{15}$$

We present the results by giving G_{ij}/V_i and $(G_{ij} - G_{jj})/V_j$ as functions of concentration. These quantities have the intuitive meaning explained in the Introduction. Thus, G_{ij}/V_j gives information about the average excess number of i molecules surrounding each j molecule, and $G_{ij} - G_{jj}$ information about the sign of the preferential solvation of i molecules around a j molecule.[7,8] In fact, f_iG_{ij} is the quantity which gives the average excess number of i around j, not G_{ij}/V_i, but $f_i = \phi_i/V_i$ (neglecting variations of volume on mixing) and thus G_{ij}/V_i differ from f_iG_{ij} only in the factor ϕ_i. This is no limitation, since we can discuss differences between systems equally well. For each value of concentration, ϕ_i, the difference between systems lies in G_{ij}/V_i. Thus, for a given ϕ_i, a larger G_{ii}/V_i means greater tendency of the molecules of kind i to gather together, and a larger G_{ij}/V_i means a greater tendency for the i molecules to surround a j molecule, at that ϕ_i. Likewise, the preferential solvation of i around j is given by $x_ix_j(G_{ij} - G_{jj})$, and not by $(G_{ij} - G_{jj})/V_j$, but the sign is the same in both quantities. Thus, for each given concentration, we can use $(G_{ij} - G_{jj})/V_j$ to compare preferential solvation in different systems.

Model Systems

We analyze first the influence of the large size of macromolecules. To this end, we compare the results for the simple liquid case $r = 1$, with the macromolecular case $r \gg 1$, in model systems. The interactions between components are taken into account by using different values of the interaction parameter. In these model systems no other complication is introduced, and χ is taken as a constant parameter, for simplicity. In the subsequent paper,[1] we shall consider real systems with the actual concentration dependence of the interaction parameter determined experimentally.

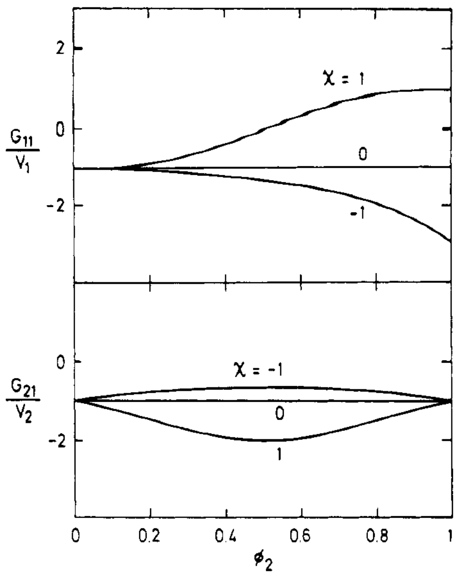

Figure 1. KBZ integrals for $r = 1$, at different values of the interaction parametrer. Curves for G_{22}/V_2 and G_{21}/V_1 vs ϕ_1 are the same as the ones shown for G_{11}/V_1 and G_{21}/V_2 vs ϕ_2.

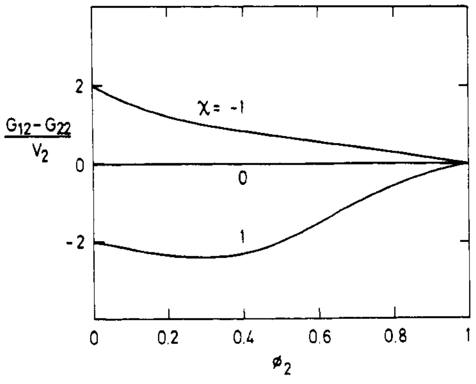

Figure 2. Same as in Figure 1. Curves for $(G_{21} - G_{11})/V_1$ vs ϕ_1 are the same as those shown for $(G_{12} - G_{22})/V_2$ vs ϕ_2.

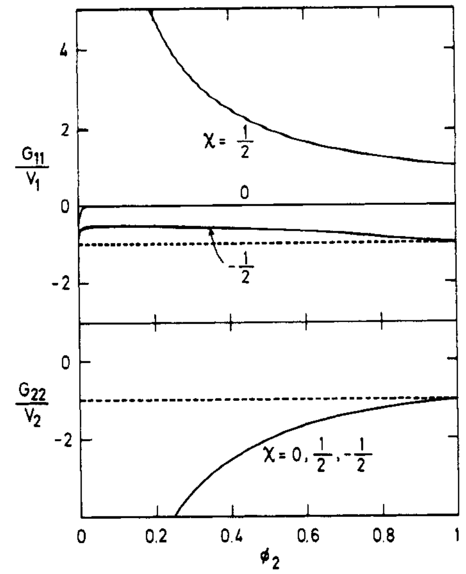

Figure 3. KBZ integrals for $r = 10^3$, at different values of the interaction parameter (continuous curves). Broken curves are for $r = 1$, $\chi = 0$.

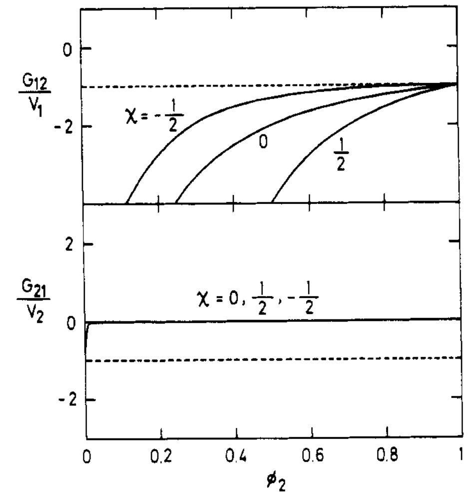

Figure 4. Same as in Figure 3.

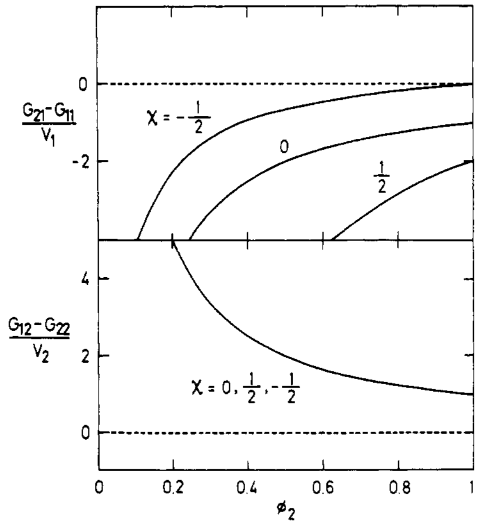

Figure 5. Same as in Figure 3.

For the case $r = 1$ we choose the value $\chi = 0$, which corresponds to the ideal mixture, namely equal molecular sizes and no interactions. Two other cases are also considered: $\chi = 1$, endothermic liquid mixture, and $\chi = -1$, exothermic liquid mixture.

To represent a high molecular weight polymer solution, we take $r = 10^3$. For this system the "quasi ideal" situation is that of a Θ solvent, for which $\chi = {}^1/_2$. Two other cases are considered: $\chi = 0$ and $\chi = -{}^1/_2$. In the $r \gg 1$ system, any value of χ lower than the Θ value $\chi = {}^1/_2$ corresponds to a good solvent. The negative case $\chi = -{}^1/_2$ would correspond to strong specific interactions between polymer and solvent.

$\boldsymbol{r = 1}$. The results are shown on Figures 1 and 2. Only G_{11}, G_{21}, and $G_{12} - G_{22}$ are given, because the results for G_{22}, G_{12}, and $G_{21} - G_{11}$ are the same as these, when they are plotted vs ϕ_1 instead of vs ϕ_2.

$\chi = 0$ gives the ideal random distribution, $G_{ii}/V_i = -1$, in which the excess number of molecules around a given molecule is just given by the exclusion which the chosen molecule exerts on all others. In such random distribution there is no preferential solvation and $(G_{ij} - G_{jj})/V_j = 0$.

Positive χ produces gathering of like molecules, $G_{ij}/V_i > 0$ when $i = j$, and preferential solvation by molecules of the same kind, $(G_{ij} - G_{jj})/V_j < 0$.

Negative χ produces the cross complexation of unlike molecules, $G_{ij}/V_i > 0$ $(i = j)$ and $G_{ii}/V_i < 0$, and preferential solvation by molecules of the other kind $(G_{ij} - G_{jj})V_j > 0$.

$\boldsymbol{r \gg 1}$. The results for $r = 10^3$ are shown on Figures 3–5 as continuous curves. Here, there is no symmetry in the interchange of indices 1 and 2, and all six curves for G_{11}/V_1, G_{22}/V_2, G_{12}/V_1, G_{21}/V_2, $(G_{12} - G_{22})/V_2$, and $(G_{12} - G_{11})/V_1$ are needed. The broken curves correspond to $r = 1$, $\chi = 0$, which is taken as the reference random system for comparison.

The effects caused by the large difference in molecular size can be considered by comparing the curves of $r = 1$ and $r = 10^3$, both with $\chi = 0$. The sign of the G_{ij}'s is not changed by going from $r = 1$ to $r = 10^3$, although the values are very much altered.

The solvent molecules tend to surround each other, rather than to surround macromolecules (higher G_{11}/V_1 and lower G_{12}/V_1 than in the ideal reference), thus producing gathering of solvent. The macromolecules tend to be separated from each other and prefer surrounding solvent molecules (lower G_{22}/V_2 and higher G_{21}/V_2 than in the ideal reference), thus producing segregation among macromolecules.

The tendencies are best seen when preferential solvation is considered. The sign for the preferential solvation of solvent molecules around macromolecules, $(G_{12} - G_{22})/V_2$, is positive, and the sign for the preferential solvation of macromolecules around solvent molecules, $(G_{21} - G_{11})/V_1$, is negative. Thus, solvent molecules tend to solvate preferentially each macromolecule, but macromolecules do not solvate preferentially each solvent molecule.

Again, the picture is that of gathering of solvent molecules and segregation among macromolecules. Both tendencies increase as the system gets more dilute (as ϕ_2 decreases). Thus, nonrandomness created by the size difference gets increasingly more important as the concentration diminishes.

Let us consider now the superimposed influence of interactions. The case $\chi = {}^1/_2$ is the critical value of the interaction parameter for $r \gg 1$. In dilute solution, this value of χ represents the Θ state in which interactions (polymer–polymer, polymer–solvent, solvent–solvent) are compensated. We can see that the effect of $\chi = {}^1/_2$ is large on G_{11}/V_1 and G_{12}/V_2 but negligible on G_{22}/V_2 and G_{21}/V_1.

The most dramatic change occurring with $\chi = {}^1/_2$ is that G_{11}/V_1 has now positive values. Thus, under Θ conditions a much more important gathering of solvent molecules takes place. Also, the negative preferential solvation of macromolecules around solvent molecules, $(G_{21} - G_{11})/V_1$, is enhanced in a Θ solvent.

The reverse situation occurs for these quantities when $\chi = -{}^1/_2$. Thus, the effect of $\chi = -{}^1/_2$ is that the $r = 10^3$ results approach those of the ideal mixture. The nonrandomness created by the large size difference is then counteracted by the strong attractive interactions between components. Such attraction contributes (to a certain degree) in reestablishing a more random distribution in the mixture.

On the other hand, the positive tendency of the solvent molecules to solvate preferentially macromolecules, $(G_{12} - G_{22})/V_2$, is insentitive to the interactions and is affected only by the size dissimilarity, r. The same is true with the tendency of the macromolecules to remain segregated, G_{22}/V_2.

In conclusion, we may say that the mere size difference ($r \gg 1$) is an important source of nonrandomness in the average space distribution of molecules, that this nonrandomness is much more important in a Θ solvent than in a good solvent, and that with strong attractive interactions such nonrandomness can be to a certain degree counteracted.

This analysis is based on model calculations. For real systems, the actual value of interaction parameter and its concentration dependence has to be used.

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