Nonrandom Distribution of Molecules in Polymer Systems. 2. Volume Fluctuations and Interactions in Real Systems†

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ABSTRACT: The nonrandom average space distribution of molecules in polymer solutions and blends can be studied by means of the Kirkwood–Buff–Zimm integrals, using the equations developed in the preceding paper. Several systems covering a wide range of strength of interactions, from purely nonpolar to strongly interacting with specific hydrogen bonds, are studied here. Their nonrandomness depends both on interactions and on macromolecular size. But, another very important factor is the difference in free volume between components, which gives rise to volume fluctuations. Thermodynamic theory is used to deduce the influence of such volume fluctuations. Their contribution to the interaction parameter can be quite large. Volume fluctuations and attractive interactions act in opposite senses with regard to nonrandomness and can thus mask each other.

Introduction

Information about the average space distribution of molecules in a mixture can be obtained from common experimental results of chemical potential or of scattering structure factor. In the case of polymer systems, this type of information has not been exploited for this purpose up to the present. In the preceding paper,[1] we have shown how such information can be obtained by calculating the so-called Kirkwood–Buff–Zimm integrals (KBZ) from experimental results. These integrals allow the discussion of the molecular distribution in terms of quantities having very intuitive meaning, for example, in terms of the composition of the mixture surrounding a given molecule, by giving the average number of molecules of each component which is in excess over the mean value determined by the global or analytical concentration or, in other words, by giving the preferential solvation of the components in the mixture around a given molecule.

This information can be obtained by studying the KBZ integrals, G_{ij}, as defined in the previous paper.[1] All that is needed is the experimental interaction parameter, determined either directly from scattering experiments or from the composition dependence of the chemical potential (as in colligative properties).

In the present paper we show how this information can be obtained in real systems. We study several examples, chosen to cover a wide range of strength of interactions between components.

But interactions are not the only factor to consider. We shall see that the space distribution of molecules depends also on the molecular packing of the components. When the components have different equation of state properties, they yield mixtures in which there are large volume fluctuations. As we shall show, these volume fluctuations make a substantial contribution to the experimental interaction parameter and can be as important as the exchange interactions in determining the average space distribution of molecules.

Three examples of polymer–solvent systems and one example of a polymer–polymer system are studied. The three polymer–solvent systems differ widely in their interactions. Polyisobutylene + cyclohexane (PIB + CH) is completely nonpolar with only weak dispersion interactions. Polystyrene + methyl ethyl ketone (PS + MEK) is also weakly interacting, but with one of its components polar and the other aromatic. Poly(4-hydroxystyrene) + acetone (P4HS + AC) is a typical case having strong specific interactions due to hydrogen bonding. The example of a polymer–polymer system is the much studied compatible blend poly(vinyl methyl ether) + polystyrene (PVME + PS).

Interaction Parameters

The interaction parameter data needed are taken from the literature. For the three polymer–solvent systems the experimental data are colligative properties (solvent vapor pressure, vapor osmometry), and therefore the interaction parameter obtained is χ. Its concentration dependence can be well represented by a polynomial:

$$\chi = a + b\phi_2 + c\phi_2^{\,2} + ... \qquad (1)$$

Since the interaction parameter needed to obtain the KBZ integrals is χ_s (see the definition in part 1),[1] we have to convert χ into χ_s, which according to eq 9 in part 1,[1] is simply

$$\chi_s = a + (3/2)b\phi_2 + 2c\phi_2^{\,2} + ... \qquad (2)$$

For the polymer–polymer system, the experimental interaction parameter is from neutron-scattering experiments, which yield χ_s directly:

$$\chi_s = a + b_s\phi_2 + c_s\phi_2^{\,2} + ... \qquad (3)$$

Volume Fluctuations

The average space distribution of molecules, as described by the KBZ integrals, depends on the volume properties of the system in two ways. One is through its compressibility β (term $RT\beta$ in eqs 5 and 6 of part 1).[1] But this is unimportant, as we have seen.[1] The other is through the influence of volume fluctuations on the interaction parameter.[2] As we shall see below in the Results, this is a very important contribution and affects substantially the distribution of molecules. It arises because the volume of the system fluctuates with concentration when the components forming the mixture have different equation of state properties.

To calculate the effect of this contribution we use thermodynamic theory. We start from the Gibbs mixing function (ΔG_M) expressed per unit volume: $g = \Delta G_M/V$.

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This g is composed of a combinatorial part, $RT[(\phi_1/V_1)\ln\phi_1 + (\phi_2/V_2)\ln\phi_2]$, plus a residual part, g^R. The interaction parameter, χ_s, is given by the second derivative of g^R with respect to volume fraction:

$$\chi_s = -\frac{V_1}{2RT}\frac{\partial^2 g^R}{\partial \phi_2^{\,2}} \tag{4}$$

Now, according to the volume fluctation thermodynamics recently developed by Sanchez,[2] this derivative of g^R can be written

$$\frac{\partial^2 g^R}{\partial \phi_2^{\,2}} = g^R_{\{\phi\phi\}} - v\beta P_\phi^{\,2} \tag{5}$$

where P_ϕ is defined as[2]

$$P_\phi = \frac{1}{\beta}\frac{\partial \ln v}{\partial \phi_2} \tag{6}$$

v being an intensive volume and $g^R_{\{\phi\phi\}}$ having the meaning of the second derivative of g with respect to ϕ_2, but taken at constant v.[2]

The pressure coefficient thus defined, P_ϕ, is large whenever the mixture is formed by components with dissimilar free volume or different equation of state properties, because then the variation of v with composition (eq 6) is large (even if the mixing volume is ideal). Thus, the difference in free volume or equation of state of the components represented by this P_ϕ term is a very important factor in determining the experimental value of the interaction parameter in a system. Since $v\beta P_\phi^2$ is always positive, the contribution of volume fluctuations to the value of χ_s is also positive (compare eqs 4 and 5). Because of its origin in the dissimilarity of free volume or equation of state of the components, this P_ϕ contribution to the interaction parameter increases with temperature and is higher for polymer–solvent systems than for polymer–polymer ones.

In order to quantify the relative importance of this volume fluctuation contribution, we use the following procedure. We define a hypothetical interaction parameter, which the system would have in the absence of volume fluctuations, namely the interaction parameter determined solely by the derivative $g^R_{\{\phi\phi\}}$ taken at fixed volume v. This hypothetical χ_s we call χ_s': $\chi_s' = (V_1/2RT)g^R_{\{\phi\phi\}}$. We obtain it from the real χ_s by subtracting the P_ϕ term due to volume fluctuations:

$$\chi_s' = \chi_s - (V_1/2RT)v\beta P_\phi^{\,2} \tag{7}$$

Then we calculate the KBZ integrals deduced from this constant volume χ_s' and compare the results with the ones obtained using the real χ_s. The difference between both sets of results is due to the volume fluctuation contribution represented by $(V_1/2RT)v\beta P_\phi^2$.

We choose as examples to study this effect the systems PIB + CH, PS + MEK, and PVME + PS, which are well documented with respect to their equation of state properties needed for the calculation of $v\beta P_\phi^2$. We identify v with the reduced volume, $\tilde{V}$. We take the simpler approach of assuming volume fraction additivity of isothermal compressibility and of reduced volume in the mixtures.

Results

The KBZ integrals are calculated using eqs 11–15 of part 1.[1] The results are presented in Figures 1–8 in the form of the dimensionless quantities G_{ij}/V_i, the same as in part 1. In order to make the figures simpler, each curve is designated only by the symbol of the corresponding KBZ integral. Thus, the curve for G_{11}/V_1 is denoted as G_{11} and the curve for $(G_{12} - G_{22})/V_2$ is denoted as $G_{12} - G_{22}$. The results obtained using the real interaction parameter from experimental data are shown as continuous curves with unprimed symbols. The broken curves with primed symbols show the results of KBZ integrals calculated using the hypothetical χ_s' instead of the real χ_s. Thus the importance of volume fluctuations on the distribution of molecules can be appreciated by comparing these broken curves with the corresponding continuous ones. The difference between the broken and continuous curve for each KBZ integral represents the contribution due to volume fluctuations in the system.

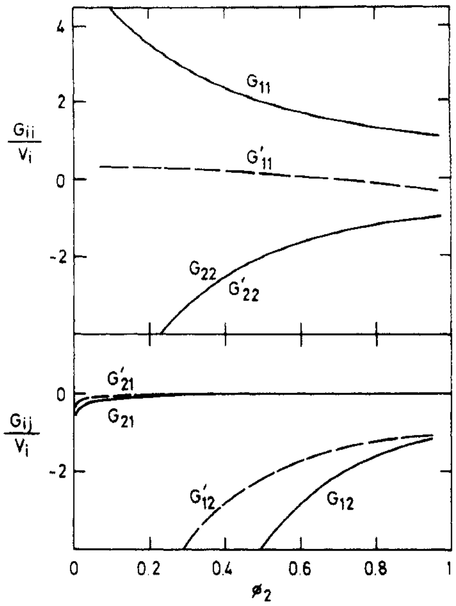

Figure 1. KBZ integrals for polyisobutylene + cyclohexane, from the experimental interaction parameter, at 25 °C. The continuous curves with unprimed symbols are calculations for the real system. The broken curves with primed symbols are hypothetical calculations assuming no volume fluctuations in the system.

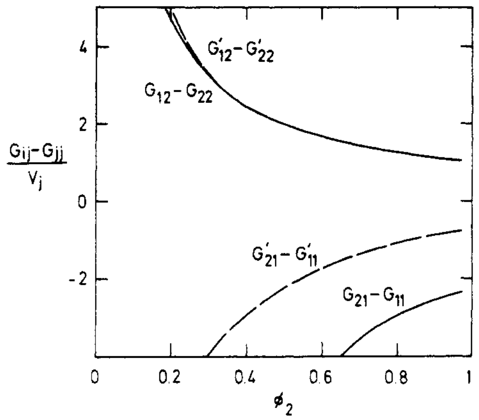

Figure 2. Same as in Figure 1.

PIB + CH. The results are shown on Figures 1 and 2. They have been obtained using experimental data at 25 °C.[3-7] χ varies only slightly with concentration. We take $a = 0.450$, $b = 0.063$, $c = 0$ (eq 1), and $r = 350$.[3,4]

Since r is large enough and χ is almost constant around 0.5, the results of the KBZ integrals (continuous curves) are very similar to those of the model system studied in part 1[1] for $r = 10^3$, $\chi = {}^1/_2$. In this nonpolar system the dominant source of nonrandomness is the large molecular size difference, together with the positive value of the interaction parameter. Thus, there is gathering of solvent

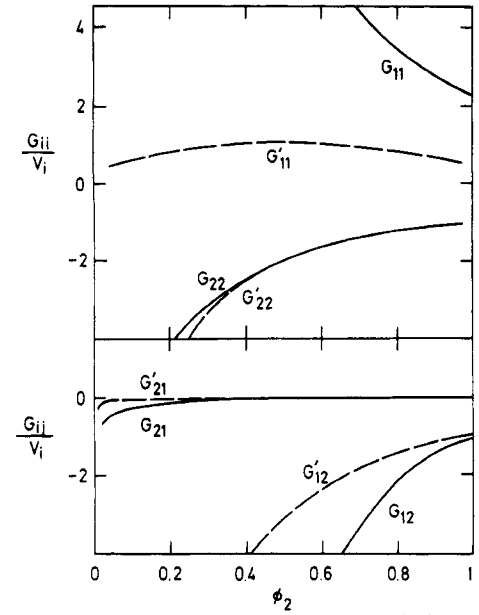

Figure 3. KBZ integrals for polystyrene + methyl ethyl ketone, from the experimental interaction parameter, at 25 °C. Symbols are as in Figure 1.

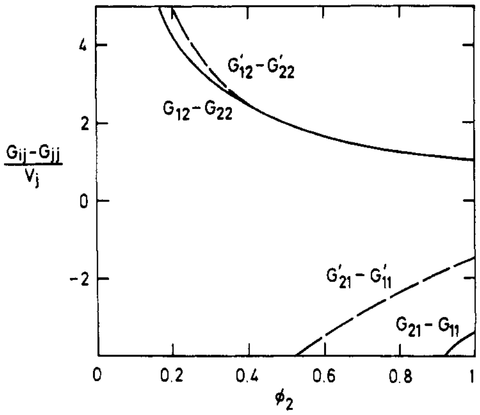

Figure 4. Same as in Figure 3.

molecules, segregation among macromolecules, preferential solvation of solvent around macromolecules, and preferential desolvation of macromolecules around solvent molecules, and all these effects become aggravated as the polymer concentration diminishes.

Considering now the results for the hypothetical rigid system (broken curves), we see that G_{11}', G_{12}', and $G_{21}' - G_{11}'$ are very similar to the model system $r = 10^3$, $\chi = 0$ (the other curves are unaffected). Thus, interactions alone in the hypothetical rigid system would give a behavior much closer to the random ideal mixture than is actually observed. It is when we include volume fluctuations by considering the real χ_s that the system appears greatly nonrandom.

PS + MEK. The results for the KBZ integrals are shown on Figures 3 and 4. The experimental data are taken at 25 °C.[3,8,9] The interaction parameter has here a larger variation with concentration but still can be approximated by a linear fit. We take $a = 0.458$, $b = 0.470$, $c = 0$ (eq 1), and $r = 700$.[3,8]

The continuous curves show that the nonrandom effects of solvent gathering are more important than in the PIB + CH case, but segregation among macromolecules is similar or slightly smaller. Also, preferential solvation of solvent around macromolecules is similar or slightly smaller than in PIB + CH, but preferential desolvation of macromolecules around solvent molecules is clearly more important in the present system.

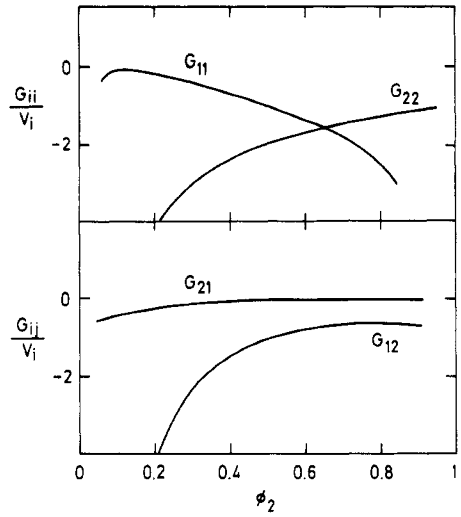

Figure 5. KBZ integrals for poly(4-hydroxystyrene) + acetone, from the experimental interaction parameter, at 25 °C.

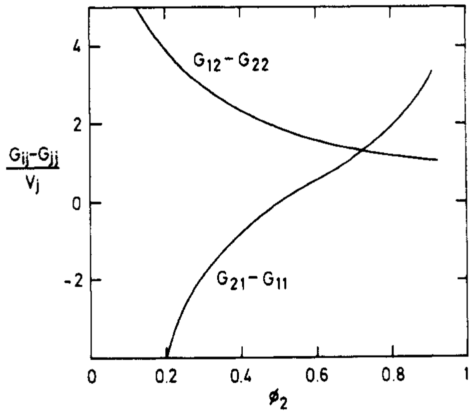

Figure 6. Same as in Figure 5.

The contribution from volume fluctuations is similar to that of the PIB + CH case. If we consider the broken curves G_{11}', G_{12}', and $G_{21}' - G_{11}'$, they have values much closer to the random mixture than their corresponding unprimed counterparts. Thus, volume fluctuations contribute greatly to the nonrandomness of the system.

P4HS + AC. The results for the KBZ integrals are shown on Figures 5 and 6. The interaction parameter, at 25 °C, varies strongly with concentration and a second-degree polynomial is needed. Contrary to the two previous cases, χ decreases on increasing polymer concentration. We take $a = 0.30$, $b = -0.50$, $c = -1.7$ (eq 1), and $r = 20$.[10]

The behavior of this system has similarities with the model system studied in part 1[1] corresponding to $r = 10^3$, $\chi = -{}^1/_2$. The size difference is the dominant factor, and superimposed on it are the strong interactions. Here, the interaction parameter varies steeply with concentration, reaching very negative values for high concentrations (the very high ϕ_2 range is not covered by the original experimental data). The strong specific interactions in this system give a peculiar behavior at high concentrations. Namely, G_{11}/V_1 continues its decreasing tendency as $\phi_2 \rightarrow 1$, instead of leveling off as in the model system. More interestingly, the preferential solvation of macromolecules around solvent, which starts negative in the low ϕ_2 range, instead of tending to zero for $\phi_2 \rightarrow 1$ as in the model, changes sign and becomes increasingly positive. For $\phi_2 > 0.5$, both the solvent molecules and the macromolecules solvate preferentially around the other component, as a consequence of their strong mutual interaction.

PVME + PS. The results are shown on Figures 7 and 8. In this system results for two series of molecular weights

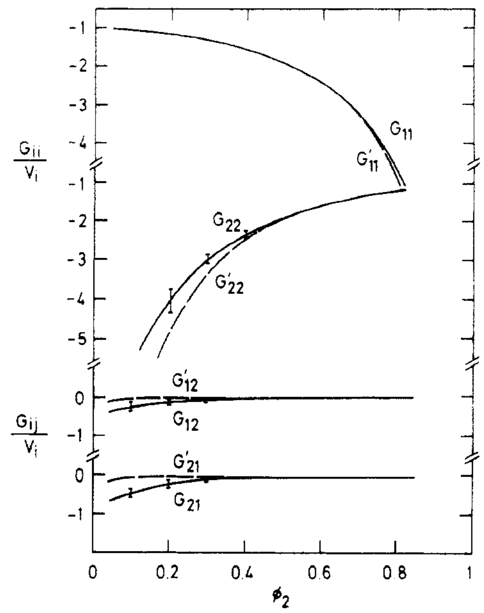

Figure 7. KBZ integrals for poly(vinyl methyl ether) + polystyrene, from the experimental interaction parameter, at 130 °C. Error bars denote two series of molecular weights. Symbols are as in Figure 1.

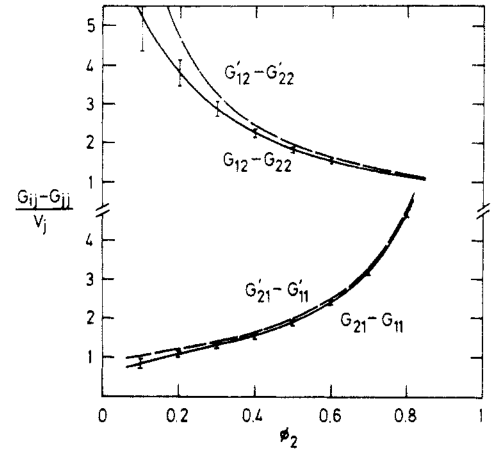

Figure 8. Same as in Figure 7.

(M's) are represented. Blends prepared with samples having different M's yield slightly different results. They are shown separately in the figures in the form of error bars. One end point of the error bar represents the value for one of the series, the other end point represents the value for the other series. The curves are drawn through the middle points.

The interaction parameter has been determined by neutron scattering at several temperatures approaching the LCST of the system. We take the values for T = 130 °C. χ_s is negative and varies linearly with concentration. The series of molecular weights which we consider are the ones designated as L and H in the original work.[11] For these, the coefficients of eq 3 (expressing χ_s per monomer of PVME) are[11] $a = -4.057 \times 10^{-4}$, $b_s = -7.507 \times 10^{-3}$, and $c_s = 0$. In series L, $r = 0.61$; and in series H, $r = 0.48$.[11] For β_1, β_2 and $\tilde{V}_1$, $\tilde{V}_2$ we use data at 100 °C from ref 12.

The negative value of the interaction parameter, together with the low r, determines the nonrandom behavior of this system. G_{11}/V_1 and G_{22}/V_2 start from the ideal value -1 at low concentration of the other component, but they decrease below -1 very fast at high concentration. G_{12}/V_1 and G_{21}/V_2 are higher than the ideal -1. This means that there is a certain tendency of each polymer to distribute nonrandomly around the other. The preferential solvation is positive both for PS around PVME and for PS around PVME, and in both cases it increases with concentration. In summary, the nonrandomness is important in this system.

The contribution from volume fluctuations to nonrandomness is not large in this system. Differences in equation of state between the two polymers are not as large as between polymer and solvent. Hence, the discontinuous curves for primed G's are all very close to the continuous curves for the unprimed ones, in Figures 7 and 8. However, the contribution of volume fluctuations to the actual value of the interaction parameter is far from being negligible. Since the experimental χ_s is small, the term arising from volume fluctuations (although small in itself) results in a major contribution to χ_s.

Discussion

The present analysis of experimental data gives information about the average distribution of molecules in the polymer solutions and blends, disclosing the relative importance of interactions and of free volume differences in creating nonrandomness in the system. As we have seen, the importance of free volume difference can be very large. In general, this factor contributes to nonrandomness in the sense of favoring like contacts and disfavoring unlike contacts, thus the reverse effect of mutual attractive interactions between components. Both factors, volume fluctuations and attractive interactions, can be of comparable magnitude, and since they act in opposite senses with regard to nonrandomness, they can mask each other.

All the information about nonrandomness deduced by the present method is already contained in the experimental data used for the calculation, mainly the interaction parameters as a function of composition. But the analysis of these data in terms of KBZ integrals allows a more illuminating view of them in terms of space distribution of molecules and not just as a mere empirical description.

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