

Is Compressibility Important in the Thermodynamics of Polymer Mixtures?

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The effect of compressibility on the static scattering from polymer mixtures is critically evaluated through a general thermodynamic analysis. We find that compressibility plays an important role for blends comprised of chains with disparate chemical structures, and that it is effectively irrelevant for blends with similar chemical structures. [S0031-9007(97)04029-5]

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The mixing thermodynamics of polymers are usually described by Flory-Huggins theory [1], according to which the Helmholtz energy per unit volume, a/v_0 , for binary mixtures is

$$\frac{a}{v_0 RT} = \frac{\phi}{N_1 v_1} \ln \phi + \frac{1-\phi}{N_2 v_2} \ln(1-\phi) + \frac{\chi}{v_0} \phi(1-\phi). \quad (1)$$

Here ϕ is the volume fraction of component 1, N_i and v_i are the degree of polymerization and molar volume of monomer units, respectively, of component i , R is the gas constant, T is the temperature, and v_0 is the volume of a mole of lattice sites. In the context of this model χ , the interchange energy parameter, is a pair-specific function of temperature, and depends neither on the blend composition, ϕ , nor on the chain lengths. Values for χ can be obtained, for example, from small angle neutron scattering (SANS) data. The experimentally determined zero wave vector limit of the static structure factor $S(0)$ [2] is related to χ through the incompressible Flory model expression for $S(0)$ [2],

$$\frac{1}{v_0 S_{\text{incomp}}(0)} \equiv \frac{1}{RT v_0} \left[\frac{\partial^2 a}{\partial \phi^2} \right]_T = \frac{1}{N_1 v_1 \phi} + \frac{1}{N_2 v_2 (1-\phi)} - 2 \frac{\chi}{v_0}, \quad (2)$$

where $S(0) = [I(0)]_{\text{coh}}/k_N$, in which $I(0)$ is the coherent SANS intensity extrapolated to zero wave vector, and k_N is the SANS contrast factor.

Contrary to the model, values of χ_{SANS} obtained in this way are found to vary significantly with blend composition [3–7]. The systems showing these effects have been tentatively classified into two categories [8]. Isotopic mixtures [3,6], or saturated hydrocarbon mixtures [5,7], which show a parabolic dependence of χ_{SANS} on ϕ , will be referred to in this work as “quadratic” blends. Other blends, which are generally comprised of chains with dissimilar chemical structures, show a linear composition dependence

of χ_{SANS} [6] and will be referred to as “linear” blends. The origin of the unexpected composition dependence of χ_{SANS} is an unresolved issue. Some of the various proposed possibilities—non-mean-field effects, nonrandom mixing, compressibility effects—have been reviewed recently [5,7,8]. The role of compressibility has been controversial. It has been argued by various groups that it is either an important variable [8–11] or irrelevant [12].

It appears generally accepted that current methods for the extrapolation of coherent scattering data to the zero wave vector limit, such as the Ornstein-Zernike method, remain valid even in the case of compressible systems [8]. Further, the neutron contrast factor, k_N , is relatively unaffected by system compressibility for mixtures of typical polymer liquids. Consequently, the quantity $S(0)$ derived from scattering techniques contains only thermodynamic information of the mixture of interest.

Here, a generally applicable thermodynamic approach is utilized to critically evaluate the role of compressibility on $S(0)$, and hence on the composition dependence of the interaction parameter, χ_{SANS} . A dimensionless parameter, which identifies the importance of compressibility effects, is derived without resort to a specific model. Through this approach we show that the finite compressibility of polymers plays a significant role in determining the static structure factor for linear blends. However, it is effectively irrelevant in the case of quadratic mixtures. While these results rationalize and explain our recent numerical findings [13] based on the lattice fluid model [14], it is important to stress that the model presented here is general and contains the lattice fluid and other compressible models as special cases.

The zero angle scattering from compressible binary mixtures, $S_{\text{comp}}(0)$, was derived in the 1940s [15],

$$S_{\text{comp}}(0) = \frac{\langle b \rangle^2}{v_0 k_N} (RT \rho^2 \kappa_T) + [\rho v_0]^3 \left[\frac{\partial^2 (g/RT)}{\partial x^2} \right]_{T,P}^{-1}. \quad (3)$$

Here κ_T is the isothermal compressibility of the mixture, ρ is the monomer density, $v_0 = \sqrt{v_1 v_2}$ is a reference volume, and v_i is the molar volume of pure component i [16]. $\langle b \rangle = b_1 x + b_2(1 - x)$ is the average scattering length of the sample, and $k_N \equiv (\frac{b_1}{v_1} - \frac{b_2}{v_2})^2$ is the scattering contrast factor, where b_i is the scattering length of species i . Note that we have considered experimentally relevant isothermal-isobaric conditions, and hence x , the mole fraction of monomers of species 1, and g , the Gibbs free energy of mixing per mole of monomers, are the natural variables. The first term on the right side of Eq. (3) derives directly from density fluctuations, and is one manifestation of system compressibility. Since this term is typically 100–1000 times smaller than $S_{\text{comp}}(0)$ [8], it is ignored in the analysis that follows. The contribution of system compressibility to the second term in Eq. (3), which is purely thermodynamic in origin, is then the primary focus of this analysis.

We begin with the identity $g(v) \equiv a(v) + P_v$, where P and v are the pressure and the volume per mole of monomers, respectively, and $a(v)$ is the Helmholtz energy per mole of monomers. Consider a Taylor expansion of a

about the experimental state, which is characterized by a volume v ,

$$a(v') = a(v) - P_v(v' - v) - \left[\frac{\partial P}{\partial v} \right]_T \times \frac{(v' - v)^2}{2} \dots, \quad (4)$$

where P_v and $\partial P/\partial v|_T$ are evaluated at experimental conditions [17]. To isolate the role of compressibility we set $v' = v^*$, the system volume in the incompressible limit, i.e., $P \rightarrow \infty$. We stress that this Taylor series is convergent and appropriate to extrapolate from atmospheric pressure to the incompressible limit as can be illustrated, for example, by adopting the Sanchez-Lacombe lattice formalism [14]. After rearranging we obtain

$$g(v) = a(v^*) + P_v v^* + \left[\frac{\partial P}{\partial v} \right]_T \times \frac{(v^* - v)^2}{2} + \dots \quad (5)$$

Since $v^* = x v_1^* + (1 - x) v_2^*$ it follows that

$$\left[\frac{\partial^2 g(v)}{\partial x^2} \right]_{T,P} = \left[\frac{\partial^2 a(v^*)}{\partial x^2} \right]_{T,P} + \frac{[(\bar{v}_1 - \bar{v}_2) - (v_1^* - v_2^*)]^2}{v \kappa_T} - \frac{1}{\kappa_T} \left(1 - \frac{v^*}{v} \right) \frac{1}{1 - x} \left[\frac{\partial \bar{v}_1}{\partial x} \right]_{T,P} + \dots, \quad (6)$$

where the Gibbs-Duhem relationship has been utilized. \bar{v}_i and v_i^* are the partial molar volume and hard core volume, respectively, of component i , and κ_T is the isothermal compressibility of the experimental system. Note that the first term on the right-hand side corresponds to the result obtained from an incompressible system, such as the one considered by Flory-Huggins theory. The remaining terms describe the contribution of compressibility to scattering. To emphasize the role of compressibility consider the case where the system is characterized by zero excess volume on mixing. The third term in Eq. (6) would be equal to zero. Even in this situation, which is traditionally considered to be equivalent to the incompressible limit

[2,12], it is clear that the second term does not vanish except in the special case where $(v_1 - v_2) = (v_1^* - v_2^*)$. Consequently, the scattering obtained from a system where mixing occurs under additive volume conditions is not, in general, equivalent to that obtained in the hypothetical incompressible limit [2,12].

To more quantitatively assess the importance of compressibility we define a parameter, Λ , which is derived from Eqs. (6) and (1) [18],

$$\frac{1}{S_{\text{comp}}(0)} = \frac{1}{S_{\text{incomp}}(0)} \times (1 + \Lambda), \quad (7)$$

where

$$\Lambda \equiv \left\{ \frac{1}{\rho^3 [x v_1 + (1 - x) v_2]^3} - 1 \right\} + \frac{S_{\text{incomp}}(0)}{\rho \kappa_T R T} \frac{1}{(\rho v_0)^3} \times \left\{ \left[\frac{(\bar{v}_1 - v_1^*) - (\bar{v}_2 - v_2^*)}{v} \right]^2 - \rho \left(1 - \frac{v^*}{v} \right) \frac{1}{1 - x} \left[\frac{\partial \bar{v}_1}{\partial x} \right]_{T,P} \dots \right\}. \quad (8)$$

The magnitude of Λ determines the importance of compressibility. If $\Lambda \ll 1$ then compressibility is irrelevant to the analysis of scattering data, and hence the composition dependence of χ_{SANS} , while the opposite conclusion arises if $\Lambda \approx 1$. To obtain estimates of Λ of typical polymer blends it is necessary to quantify the partial molar volumes of the mixture components. As a convenient approximation we assume that the molar volume

of a polymer mixture can be described by the empirical relation [8], $v \approx (v_1 x + v_2 [1 - x]) \times [1 + \alpha \phi (1 - \phi)]$ where $\phi = x v_1 / (x v_1 + [1 - x] v_2)$. The absolute value of α is of order 10^{-4} for quadratic blends [8], while it is $\approx 10^{-2}$ for linear blends [19]. From here the partial molar volumes can be readily derived: $\bar{v}_1 = v_1 [1 + \alpha (1 - \phi)^2]$. For many typical systems [4,5] the dimensionless value of $S_{\text{incomp}}(0)$, as defined in Eq. (1), is of

order 10^2 , $\rho v_0 \approx 1$, and $\rho \kappa_T RT \approx 0.1$ [8]. Therefore,

$$\Lambda \approx 10^3 \times \left\{ \left[\frac{(v_1 - v_1^*) - (v_2 - v_2^*)}{v} \right]^2 + 2\alpha \rho^4 v_1^2 v_2^2 \left(1 - \frac{v^*}{v} \right) + \dots \right\}. \quad (9)$$

Note that the first term on the right-hand side of Eq. (8), which is of order α , is ignored since it is much smaller than the other terms in the expansion. Further, the partial molar volumes in the second and third terms on the right-hand side of Eq. (8) have been replaced by the molar volumes with negligible errors.

Let us now consider a few specific examples. For quadratic blends, such as hydrocarbon polymer mixtures or isotopic blends, if one utilizes a typical equation of state, such as the one derived by Sanchez [14], $\frac{(v_1 - v_1^*) - (v_2 - v_2^*)}{v} \approx 10^{-3}$. Further, $\frac{v^*}{v} \approx 0.9$ [8], and the term $\rho^4 v_1^2 v_2^2 \approx 1$. Consequently, $\Lambda \approx 10^{-2}$. Since the typical uncertainties in scattering experiments are of the order of 5%, it is clear that the contributions of compressibility are within these uncertainties. In contrast to past work [8,10,11], we therefore conclude that compressibility by itself cannot explain the unusual composition dependence of χ_{SANS} for these “weakly” interacting (or quadratic) systems. For linear blends, such as PS/PVME [4], $\frac{(v_1 - v_1^*) - (v_2 - v_2^*)}{v} \approx 0.04$, suggesting that $\Lambda \approx 1$ in this case. Thus, compressibility can play an important role in the scattering obtained from these more strongly interacting systems.

In this context we stress that the contribution of the last term in Eq. (9), which reflects the role of excess volumes on mixing, is comparable in magnitude to the first term in this equation. Consequently, the assumption of additive volumes is not appropriate when one assesses the importance of compressibility effects on the scattering from polymer mixtures.

To verify these order of magnitude analyses we have performed numerical calculations using the Sanchez-Lacombe theory [13]. There was one mixture specific unknown quantity, ε_{12} , the energy of interaction between a monomer of type 1 and one of type 2, which was fit separately at each composition to experimental SANS $S(0)$ data. These results are compared to the composition dependent χ_{SANS} values obtained from fitting the incompressible Flory model to the same data. To facilitate the comparison of the two models, in the case of the compressible formalism we define a parameter, χ_0 , analogous to the Flory χ , $\chi_0 \equiv \frac{2}{2k_B T} (2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22})$, where z is the lattice coordination number. In Fig. 1 we compare the χ and χ_0 for a quadratic blend. Both curves show virtually identical composition dependences suggesting that the introduction of compressibility does not affect the composition dependence of χ_{SANS} in this case [20]. We also compare the incompressible χ to the χ_0 for the case of a linear blend in Fig. 2. It is clear that, while

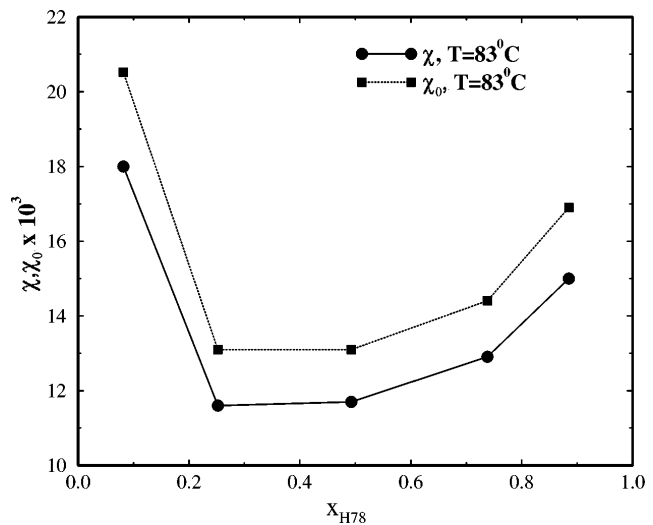


FIG. 1. χ and χ_0 for a “quadratic” system. The data correspond to a hydrocarbon polymer blend, which is denoted as H78/D66 [5]. Lines are guides to the eye.

the χ parameter varies linearly with composition, χ_0 is effectively composition independent. Consequently, in this case, the introduction of compressibility significantly affects the composition dependence of the interaction parameter.

In a qualitative sense these results can be understood as follows. In the case of quadratic blends, the components possess similar molar volumes and compressibilities. Consequently, the free volume, which can be viewed as a nonselective solvent, does not contribute significantly to the scattering. In the case of linear blends, the molar volume and the compressibility change with composition. Further, past work of Sanchez [14] has shown that compressibility intimately affects the thermodynamics of

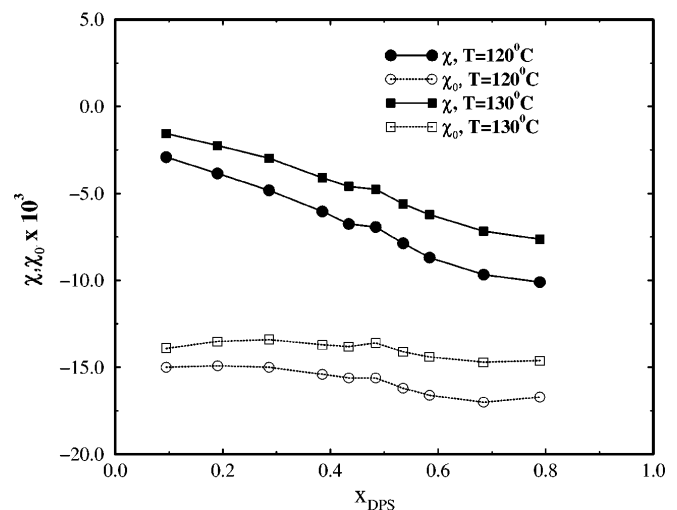


FIG. 2. χ and χ_0 for a “linear” blend at three different temperatures. The data correspond to a polystyrene and polyvinylmethylether blend [4]. Lines are guides to the eye.

these systems in that unusual behavior, such as lower critical solution behavior observed for the PS/PVME blend, cannot be reproduced by an incompressible model. Consequently, it is not surprising that compressibility plays an important role in determining the scattering in these cases.

In conclusion, we have examined the role of compressibility on the scattering from a polymer mixture. The finite, but small, compressibility of a polymer liquid can play a significant role in determining the scattering from linear systems, while it is effectively irrelevant for quadratic systems. Since the scattering and the composition dependence of the χ_{SANS} for isotopic blends and hydrocarbon mixtures have been the focus of much attention, we emphasize that compressibility by itself is not the origin of these anomalous experimental results.

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- [16] Note that the selection of a monomer is arbitrary. However, the molar volume of a pure component, v_i is fixed by the expression, $v_i = [\frac{\partial V}{\partial n_i}]$, where n_i is the number of corresponding monomers. It should be noted that physically meaningful results should only depend on such combinations of v_i and n_i that are not arbitrary.
- [17] Note that we expand around the system volume v , not the hard core volume, v^* , because $[\frac{\partial a(v)}{\partial v}]_{T, v=v^*}$ and higher order derivatives are infinite in the incompressible limit.
- [18] We have to relate the quantity $[\frac{\partial^2 a(v)}{\partial x^2}]_{T, v=v^*}$ with $S_{\text{incomp}}(0)$ as defined in Eq. (2). To facilitate this we define the effective volume fraction, $\phi \equiv xv_1/(xv_1 + [1-x]v_2)$, and the effective molar volume $v_{\text{eff}} = xv_1 + [1-x]v_2$. From here it follows that

$$\begin{aligned} \left[\frac{\partial^2 [a(v^*)/RT v_{\text{eff}}]}{\partial \phi^2} \right]_T &\equiv \frac{1}{v_0 S_{\text{incomp}}(0)} \\ &= \frac{v_{\text{eff}}^3}{(v_1 v_2)^2} \left[\frac{\partial^2 [a(v^*)/RT]}{\partial x^2} \right]_T. \end{aligned}$$

Equation (7) then results directly.

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- [20] Note that the values of χ and χ_0 are offset in this case. An analysis of the Sanchez-Lacombe model [13] shows that $\chi_0 \equiv \frac{\chi}{1+\phi_v \varepsilon}$. Here ϕ_v is the "void" fraction on the lattice, while $\varepsilon \approx \varepsilon_{11} \approx \varepsilon_{22} \approx \varepsilon_{12}$ in this case. So this offset is to be expected, and is a consequence of the finite compressibility of the system.