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Static Structure Factors of Compressible Polymer Blends and Diblock Copolymer Melts

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ABSTRACT: The incompressibility constraint is removed within the random-phase approximation (RPA). We thereby derive a set of three static structure factors for monomer-monomer correlations within a binary polymer blend as a function of the three excluded-volume interactions that are required for compressible blends. The results are compared to the conventional RPA structure factor. It is shown that the incompressible limit of the blend structure factors recovers the conventional RPA scattering functions when the intrachain excluded-volume parameters are equal. Otherwise, the usual empirical definition of the Flory interaction parameter is a function of all three excluded-volume parameters, the composition of the blend, and the scattering wavevector. Introducing compressibility into the RPA is, however, shown not to alter usual RPA predictions about the behavior of the structure factor and correlation length near the spinodal. The compressible RPA structure factors are also compared with those emerging from integral equation approaches. A brief outline is given of the extensions of the compressible RPA theory to block copolymer melts. We discuss the manner in which overall density fluctuations might affect some experiments on melts and blends and theories of microphase separation in block copolymers.

I. Introduction

Theories of the structure and thermodynamics of polymer blends[1-4] generally place an incompressibility constraint on the monomer concentration fluctuations. These physically motivated approaches have their roots in de Gennes' random-phase approximation (RPA)[1] for the static structure factor of one of the two polymer species. This assumption is entirely adequate for many applications, and the RPA structure factor and free energy of blends have been used to predict their phase diagrams and to determine the Flory–Huggins effective interaction parameter χ from small-angle neutron-scattering (SANS) experiments.[5-7] Similarly, RPA structure factors of block copolymers[8,9] have been inserted into theories of their microphase separation.

Polymer melts, however, are at least as compressible as ordinary liquids or liquid mixtures. It is well appreciated that the latter undergo small, but nonnegligible, density changes upon freezing or phase separation. The incompressibility constraint of the RPA theory nevertheless demands that phase-separated blends occupy the same volume as the unseparated mixture. A related problem concerns block copolymers that undergo *microphase* separations[8,9,11-14] to periodically ordered structures. In this case, it might be expected that the predicted morphology depends crucially on whether or not the theory includes the melt's compressibility in the analysis of monomer–monomer correlations. In order to address this problem, it is at least necessary to generalize the RPA theory to include blend incompressibility. Whereas the description of the structure factor of an incompressible blend requires the use of only a single interaction parameter χ, when the incompressibility constraint is lifted, the structure factor, in principle, may depend on three different interaction parameters. This raises questions about the proper analysis and interpretation of extrapolated zero-angle neutron-scattering data.

Some recent work has investigated the effects that *nonzero* wavevector concentration fluctuations have on polymer blend thermodynamics. Olvera de la Cruz et al.[4] demonstrate that such fluctuations decrease the stability of the homogeneous phase. Once again, however, no effort has been made to estimate the role of zero wavevector contributions (i.e., density changes). Schweizer and Curro[15,16] have generalized the reference interaction site model (RISM) to polymers and have developed an integral equation theory of polymer blends. The effective χ parameter they calculate is significantly smaller than that of the conventional Flory theory and suggests a larger region of blend miscibility. The findings of their approach depend on a number of approximations, including the mean spherical approximation (MSA) closure used to estimate the monomer–monomer correlations, their neglect of chain-end effects, the potential assumed to describe site–site interactions, and the incompressibility constraint employed in the numerical calculations. Different closures should be tested before judging the merits of such schemes. Still, their theory represents a progressive, albeit computationally intensive, approach to blend structure and thermodynamics. Besides the much simpler—and in some ways simplistic—calculations of the present article, we believe that among currently available theoretical techniques, such integral equation methods are perhaps the most promising approach toward the goal of accurately calculating the equilibrium structure factors of compressible blends.

This paper extends the Edwards style formulation of conventional RPA theory of blend static structure factors, as presented by Olvera de la Cruz et al.,[4] to include the melt's compressibility. The same techniques are also applied in section IV to block copolymer melts, and the computations in this case should provide an improved theory of microphase separation that permits density changes upon ordering. In accord with recent SANS measurements, the χ parameter deduced from our analysis depends on composition, three excluded-volume parameters, and the scattering wavevector.

The next section outlines the Edwards style RPA theory of a compressible blend, and section III provides results for compressible block copolymer melts. We compare our findings to the work of Schweizer and Curro.[15,16] After submission of this paper, a complementary short communication appeared by Brereton and Vilgis[17] that likewise lifts the incompressibility constraint for blends and also employs methods analogous to those in ref 4 but that otherwise does not overlap with our work. Brereton and Vilgis focus upon the spatially dependent effective screened excluded-volume interaction potential within a single labeled chain in the blend and the scattering function for this single labeled chain. Their interest lies in explaining the alterations in chain dimensions that have been found[18] in Monte Carlo simulations for blends. We, on the other hand, focus on the influence of compressibility on the *full* coherent scattering function from a single component in a blend and from one of the blocks in diblock copolymers, quantities that are measured in experiments that label all monomers of a given species. These scattering functions are extrapolated to the zero scattering vector to analyze the influence of compressibility on the effective Flory χ parameter for the blend. (This χ differs from the intrachain screened excluded-volume interaction potential in ref 17.) We consider the conceptual problems associated with the existence of three interaction parameters in compressible blends and block copolymers and with the general experimental practice of analyzing data on these systems with a single interaction parameter χ. Our results also pose the question of the role of compressibility on phase or microphase separation in blends or block copolymers, respectively, and we provide necessary ingredients for further analysis of these interesting questions.

Since the acceptance of this paper, there have been several developments suggesting the need for extensions of the present formulation such that the extrapolated zero angle scattering functions be consistent with a compressible Flory–Huggins model. These points are briefly noted in the paper.

II. Theory

The density operators[19,20] for A (B) monomers in a binary melt of n_A (n_B) polymer of length L_A (L_B) and polymerization degree N_A (N_B) are

$$\rho_\alpha(\mathbf{r}) = \sum_{\beta=1}^{n_\alpha} \int_0^{L_\alpha} l_\alpha^{-1}\, \mathrm{d}\tau_\beta\, \delta\,[\mathbf{r} - \mathbf{R}_\beta{}^\alpha(\tau_\beta)]; \quad \alpha = \mathrm{A, B} \quad (1)$$

Introducing Fourier transforms converts (1) into

$$\rho_\alpha(\mathbf{r}) = V^{-1} \sum_{\mathbf{q}} \rho_{\mathbf{q}}{}^\alpha \exp(-i\mathbf{q}\cdot\mathbf{r}); \quad \alpha = \mathrm{A, B} \quad (2)$$

$$\rho_{\mathbf{q}}{}^\alpha = \sum_{\beta=1}^{n_\alpha} \int_0^{L_\alpha} \frac{\mathrm{d}\tau_\beta}{l_\alpha} \exp[i\mathbf{q}\cdot\mathbf{R}_\beta{}^\alpha(\tau_\beta)] \quad (3)$$

where V denotes the system volume and l_A (l_B) the Kuhn length of A (B) monomers. We use the Edwards Hamiltonian[19,20]

$$H = \frac{3}{2} \sum_{\alpha=\mathrm{A,B}} \sum_{\beta=1}^{n_\alpha} \int_0^{L_\alpha} \frac{\mathrm{d}\tau_\beta{}^\alpha}{l_\alpha} |\dot{\mathbf{r}}_\beta{}^\alpha(\tau_\beta{}^\alpha)|^2 + \frac{1}{2} \sum_{\alpha_1,\alpha_2=\mathrm{A,B}} \nu_{\alpha_1\alpha_2} \sum_{\beta_1=1}^{n_{\alpha_1}} \sum_{\beta_2=1}^{n_{\alpha_2}} \int_0^{L_{\alpha_1}} l_{\alpha_1}{}^{-1}\, \mathrm{d}\tau_{\beta_1}{}^{\alpha_1} \times \int_0^{L_{\alpha_2}} l_{\alpha_2}{}^{-1}\, \mathrm{d}\tau_{\beta_2}{}^{\alpha_2}\, \delta[\mathbf{r}_{\beta_1}{}^{\alpha_1}(\tau_{\beta_1}{}^{\alpha_1}) - \mathbf{r}_{\beta_2}{}^{\alpha_2}(\tau_{\beta_2}{}^{\alpha_2})] \quad (4)$$

where the $\nu_{\alpha_1\alpha_2}$ represents the average excluded volumes due to $\alpha_1 - \alpha_2$ monomer binary interactions. It is convenient to define the matrix

$$u = \nu/V \quad (5)$$

and to rewrite the nonideal, second part of eq 4 in terms of the column vector

$$\rho_{\mathbf{q}} = \begin{pmatrix} \rho_{\mathbf{q}}{}^{\mathrm{A}} \\ \rho_{\mathbf{q}}{}^{\mathrm{B}} \end{pmatrix}$$

as

$$U = (1/2) \sum_{\mathbf{q}} \rho_{\mathbf{q}}{}^{\mathrm{T}} u \rho_{\mathbf{q}}{}^* \quad (6)$$

where the superscript T designates a matrix transpose.

For more general monomer–monomer interactions that also possess Fourier transforms, eq 6 can be generalized to

$$U = (1/2) \sum_{\mathbf{q}} \rho_{\mathbf{q}}{}^{\mathrm{T}} u(\mathbf{q}) \rho_{\mathbf{q}}{}^* \quad (7)$$

However, we are primarily interested in very long-wavelength ($\mathbf{q} = 0$) phenomena, and in this limit we may safely take

$$u(\mathbf{q}) \rightarrow u(0) \equiv u$$

The monomer–monomer density correlation functions (partial structure factors) of the quasi-two-component mixture are defined by[21]

$$S_{\alpha\beta}(\mathbf{k}) = M^{-1} \int \mathrm{d}\mathbf{r}_2 \int \mathrm{d}\mathbf{r}_1 \exp(i\mathbf{k}\cdot\mathbf{r}_{21}) \langle \rho_\alpha(\mathbf{r}_1) \rho_\beta(\mathbf{r}_2) \rangle = M^{-1} \langle \rho_{\mathbf{k}}{}^\alpha \rho_{\mathbf{k}}{}^{\beta*} \rangle; \quad \alpha, \beta = \mathrm{A, B} \quad (8)$$

with the total number of monomers

$$M = \sum_{\alpha=\mathrm{A,B}} n_\alpha N_\alpha$$

In an incompressible polymer blend (or any binary mixture) there is but a single independent structure factor, whereas the compressible case has three (since $S_{\alpha\beta} = S_{\beta\alpha}$). Olvera de la Cruz et al.[4] define the incompressible $S(\mathbf{k})$ a little differently: another factor of M^{-1} appears in their expression. Our choice of a single power of M^{-1} is motivated by thermodynamic arguments relating the matrix of $S_{\alpha\beta}$'s to the mixture's number density fluctuations and compressibility.[22] As defined in eq 8, the partial structure factors may be written in terms of the monomer number fractions x_α, the overall bulk monomer density $\bar{\rho} = M/V$, and the pair correlation functions $h_{\alpha\beta}(\mathbf{k})$ as

$$S_{\alpha\beta}(\mathbf{k}) = x_\alpha \delta_{\alpha\beta} + x_\alpha x_\beta \bar{\rho} h_{\alpha\beta}(\mathbf{k})$$

To calculate $S_{\alpha\beta}(\mathbf{k})$ from the Hamiltonian (eq 4), it is necessary to determine the average

$$\langle \rho_\mathbf{k}{}^\alpha \rho_\mathbf{k}{}^{\beta *} \rangle = Z^{-1} \prod_{\alpha=\mathrm{A,B}} \prod_{\beta=1}^{n_\alpha} \int D[\mathbf{r}_\beta{}^\alpha(\tau_\beta{}^\alpha)] \exp(-H) \rho_\mathbf{k}{}^\alpha \rho_\mathbf{k}{}^{\beta *} \tag{9}$$

with the normalization factor Z given by the functional integrals in the numerator without the factor of $\rho_\mathbf{k}{}^\alpha \rho_\mathbf{k}{}^{\beta *}$. Following ref 4, we insert unity in the form

$$\prod_{\alpha=\mathrm{A,B}} \prod_\mathbf{q} \int \mathrm{d}\rho_\mathbf{q}{}^\alpha\, \delta \left\{ \rho_\mathbf{q}{}^\alpha - \sum_{\beta=1}^{n_\alpha} \int_0^{L_\alpha} \frac{\mathrm{d}\tau_\beta{}^\alpha}{l_\alpha} \exp[i\mathbf{q}\cdot\mathbf{R}_\beta(\tau_\beta{}^\alpha)] \right\} = 1 \tag{10}$$

into the functional integrals of eq 9. This procedure transforms them to ordinary integrals over the space of Fourier coefficients—the $\rho_\mathbf{q}{}^\alpha$'s. After rewriting the δ functions in integral form, the average (9) becomes

$$\begin{aligned} \langle \rho_\mathbf{k}{}^\mu \rho_\mathbf{k}{}^{\nu *} \rangle = {} & Z^{-1} \{ \prod_\mathbf{q} [\prod_{\alpha=\mathrm{A,B}} \int \mathrm{d}\rho_\mathbf{q}{}^\alpha\, (\mathrm{d}\lambda_\mathbf{q}{}^\alpha / 2\pi) \exp(i\lambda_\mathbf{q}{}^\alpha \rho_\mathbf{q}{}^\alpha)] \times \\ & \exp(-\rho_\mathbf{q}{}^\mathrm{T} u \rho_\mathbf{q}{}^* / 2) \} \rho_\mathbf{k}{}^\mu \rho_\mathbf{k}{}^{\nu *} \prod_{\alpha=\mathrm{A,B}} \prod_{\beta=1}^{n_\alpha} \int D[\mathbf{r}_\beta{}^\alpha(\tau_\beta{}^\alpha)] \times \\ & \exp\left\{ -\frac{3}{2l_\alpha} \int_0^{L_\alpha} |\dot{\mathbf{r}}(\tau_\beta{}^\alpha)|^2\, \mathrm{d}\tau_\beta{}^\alpha - \frac{i}{l_\alpha} \sum_\mathbf{q} \lambda_\mathbf{q}{}^\alpha \times \right. \\ & \left. \int_0^{L_\alpha} \mathrm{d}\tau_\beta{}^\alpha \exp[i\mathbf{q}\cdot\mathbf{r}_\beta{}^\alpha(\tau_\beta{}^\alpha)] \right\} \end{aligned} \tag{11}$$

Notice that the procedure outlined above decouples the functional integrals into a product of single-chain terms integrated over all possible values of the complex variables $\{\rho_\mathbf{q}{}^\alpha, \lambda_\mathbf{q}{}^\alpha; \alpha = \mathrm{A, B}\}$. To proceed further, we must approximate the expressions

$$\begin{aligned} F_{\alpha\beta}[\{\lambda_\mathbf{q}{}^\alpha\}] = {} & \int D[\mathbf{r}_\beta{}^\alpha(\tau_\beta{}^\alpha)] \exp\left\{ -\frac{3}{2l_\alpha} |\dot{\mathbf{r}}(\tau_\beta{}^\alpha)|^2 - \right. \\ & \left. \frac{i}{l_\alpha} \sum_\mathbf{q} \lambda_\mathbf{q}{}^\alpha \int_0^{L_\alpha} \mathrm{d}\tau_\beta{}^\alpha \exp[i\mathbf{q}\cdot\mathbf{r}_\beta{}^\alpha(\tau_\beta{}^\alpha)] \right\} \end{aligned} \tag{12}$$

The second exponential in the integrand of eq 12 is expanded in a Taylor series, and the lowest order cumulant approximation to $F_{\alpha\beta}[\{\lambda_\mathbf{q}{}^\alpha\}]$ is retained. This leads to

$$F_{\alpha\beta}[\{\lambda_\mathbf{q}{}^\alpha\}] \approx \exp(-i\lambda_0{}^\alpha N_\alpha) \exp\left[-\frac{1}{2} \frac{N_\alpha{}^2}{2} \sum_{\mathbf{q}\neq 0} |\lambda_\mathbf{q}{}^\alpha|^2 S_\mathrm{D}{}^\alpha(\mathbf{q}) \right] \tag{13}$$

where

$$S_\mathrm{D}{}^\alpha(\mathbf{q}) = \frac{12}{q^2 l^2 N_\alpha} \left\{ 1 - \frac{6}{N_\alpha l^2 q^2} [1 - \exp(-N_\alpha l^2 q^2 / 6)] \right\} \tag{14}$$

is the Debye scattering function. Clearly, $F_{\alpha\beta}[\{\lambda_\mathbf{q}{}^\alpha\}]$ does not depend on the index β, so each of the n_α chains of type α contributes the same factor to the right-hand side of eq 11. This enables us to cancel factors in the numerator and denominator of eq 11 containing $\mathbf{q} \neq \mathbf{k}$ and to write

$$\begin{aligned} \langle \rho_\mathbf{k}{}^\mu \rho_\mathbf{k}{}^{\nu *} \rangle \approx {} & Z_\mathbf{k}{}^{-1} \prod_{\alpha=\mathrm{A,B}} \{ \int \mathrm{d}\rho_\mathbf{k}{}^\alpha\, \mathrm{d}\rho_\mathbf{k}{}^{\alpha *}\, \mathrm{d}\lambda_\mathbf{k}{}^\alpha\, \mathrm{d}\lambda_\mathbf{k}{}^{\alpha *} \exp[-|\lambda_\mathbf{k}{}^\alpha|^2 G_\alpha(\mathbf{k})] \times \\ & \exp[i(\lambda_\mathbf{k}{}^\alpha \rho_\mathbf{k}{}^\alpha + \lambda_\mathbf{k}{}^{\alpha *} \rho_\mathbf{k}{}^{\alpha *})] \} \rho_\mathbf{k}{}^\mu \rho_\mathbf{k}{}^{\nu *} \end{aligned} \tag{15}$$

having defined

$$G_\alpha(\mathbf{k}) = n_\alpha N_\alpha{}^2 S_\mathrm{D}{}^\alpha(\mathbf{k}) \tag{16}$$

and

$$\begin{aligned} Z_\mathbf{k} = {} & \prod_{\alpha=\mathrm{A,B}} \{ \int \mathrm{d}\rho_\mathbf{k}{}^\alpha\, \mathrm{d}\rho_\mathbf{k}{}^{\alpha *}\, \mathrm{d}\lambda_\mathbf{k}{}^\alpha\, \mathrm{d}\lambda_\mathbf{k}{}^{\alpha *} \exp[-|\lambda_\mathbf{k}{}^\alpha|^2 G_\alpha(\mathbf{k})] \times \\ & \exp[i(\lambda_\mathbf{k}{}^\alpha \rho_\mathbf{k}{}^\alpha + \lambda_\mathbf{k}{}^{\alpha *} \rho_\mathbf{k}{}^{\alpha *})] \} \exp(-\rho_\mathbf{k}{}^\mathrm{T} u \rho_\mathbf{k}) \end{aligned} \tag{17}$$

The partial structure factors may be determined from the identities

$$\langle \rho_\mathbf{k}{}^\alpha \rho_\mathbf{k}{}^{\alpha *} \rangle = -\frac{\partial \ln Z_\mathbf{k}}{\partial u_{\alpha\alpha}} \tag{18a}$$

and

$$\langle \rho_\mathbf{k}{}^\alpha \rho_\mathbf{k}{}^{\beta *} \rangle = -(1/2) \frac{\partial \ln Z_\mathbf{k}}{\partial u_{\alpha\beta}}; \quad \alpha \neq \beta \tag{18b}$$

Straightforward integration of eq 17 and the application of eq 18a,b lead to the compressible blend correlation functions

$$\begin{aligned} \langle \rho_\mathbf{k}{}^\mathrm{A} \rho_\mathbf{k}{}^{\mathrm{A}*} \rangle = {} & [G_\mathrm{A}(\mathbf{k}) G_\mathrm{B}(\mathbf{k}) u_\mathrm{BB} + G_\mathrm{A}(\mathbf{k})] / [G_\mathrm{A}(\mathbf{k}) G_\mathrm{B}(\mathbf{k}) \times \\ & (u_\mathrm{AA} u_\mathrm{BB} - u_\mathrm{AB}{}^2) + G_\mathrm{A}(\mathbf{k}) u_\mathrm{AA} + G_\mathrm{B}(\mathbf{k}) u_\mathrm{BB} + 1] \end{aligned} \tag{19a}$$

and

$$\begin{aligned} \langle \rho_\mathbf{k}{}^\mathrm{A} \rho_\mathbf{k}{}^{\mathrm{B}*} \rangle = {} & [-G_\mathrm{A}(\mathbf{k}) G_\mathrm{B}(\mathbf{k}) u_\mathrm{AB}] / [G_\mathrm{A}(\mathbf{k}) G_\mathrm{B}(\mathbf{k}) \times \\ & (u_\mathrm{AA} u_\mathrm{BB} - u_\mathrm{AB}{}^2) + G_\mathrm{A}(\mathbf{k}) u_\mathrm{AA} + G_\mathrm{B}(\mathbf{k}) u_\mathrm{BB} + 1] \end{aligned} \tag{19b}$$

III. Discussion of Results for Blends

A. Flory Interaction Parameter χ. An incompressible blend with monomer number fractions

$$x_\alpha = n_\alpha N_\alpha / (n_\mathrm{A} N_\mathrm{A} + n_\mathrm{B} N_\mathrm{B}) \tag{20}$$

has the well-known RPA structure factor

$$[S(\mathbf{k})]^{-1} = 1/[N_\mathrm{A} x_\mathrm{A} S_\mathrm{D}{}^\mathrm{A}(\mathbf{k})] + 1/[N_\mathrm{B} x_\mathrm{B} S_\mathrm{D}{}^\mathrm{B}(\mathbf{k})] - 2\chi^\mathrm{I} \tag{21}$$

The Flory parameter in this case is

$$\chi^\mathrm{I} = (\bar{\rho}/2)(2u_\mathrm{AB} - u_\mathrm{AA} - u_\mathrm{BB}) \tag{22}$$

(The incompressibility limit is designated by a superscript I.) Very often, volume fractions are used instead of the number fractions employed in eq 21. Denoting the volume fractions by ϕ_A and ϕ_B, incompressibility implies

$$\phi_\mathrm{A} + \phi_\mathrm{B} = 1$$

Taking the $\mathbf{k} = 0$ limit of eq 21, with ϕ_α's replacing the

x_α's, yields

$$[S(0)]^{-1} = 1/(N_A\phi_A) + 1/(N_B\phi_B) - 2\chi^I \tag{23}$$

and this agrees with the corresponding thermodynamic quantity that may be derived from the Flory–Huggins lattice model if the two types of monomers are permitted to occupy different numbers of lattice sites.[23] It is also possible to incorporate compressibility into the lattice theory by allowing for voids.[24] However, applying the same arguments used to derive the conventional Flory–Huggins theory of polymer blends leads to additional interaction parameters in the theory. These differences, analogous to eq 22, between monomer–void, void–void, and monomer–monomer interactions are nonnegligible compared to χ^I since it is expected that

$$\nu_{\text{void-void}} = \nu_{\text{void-monomer}} = 0$$

This further complicates the interpretation of χ^I, and we prefer the approach of the present paper in which compressibility is explicitly included in the theory.

B. Compressible Case. By application of the long chain limit N_A, $N_B \gg 1$ to the blend partial structure factors, (19) converts them into a form similar to that of the incompressible RPA. In order to see this, consider the excluded-volume parameter $\nu_{\alpha\alpha}$. We expect that on the average, an α monomer occupies a volume of $\nu_{\alpha\alpha}$. The fraction of the system volume occupied by α monomers then becomes

$$\bar{\phi}_\alpha = n_\alpha N_\alpha \nu_{\alpha\alpha}/V = n_\alpha N_\alpha u_{\alpha\alpha} \tag{24}$$

Substituting eq 16 into eq 19a, using eq 8 and 24 with N_A and $N_B \gg 1$, and defining

$$\chi^C = (1/2)[\nu_{AB}{}^2/(\nu_{AA}\nu_{BB}) - 1] \tag{25}$$

produce the simple result

$$[S_{AA}(\mathbf{k})]^{-1} = \frac{\bar{\phi}_A}{x_A}\{1/[N_A\bar{\phi}_A S_D{}^A(\mathbf{k})] + 1/[N_B\bar{\phi}_B S_D{}^B(\mathbf{k})] - 2\chi^C \tag{26}$$

Similarly, eq 19b may be reexpressed as

$$[S_{AB}(\mathbf{k})]^{-1} = -\left(\frac{\bar{\phi}_A\bar{\phi}_B}{x_A x_B}\right)^{1/2}\{1/[N_A\bar{\phi}_A S_D{}^A(\mathbf{k})] + 1/[N_B\bar{\phi}_B S_D{}^B(\mathbf{k})] - 2\chi^C\} \tag{27}$$

The structure factor $S_{BB}(\mathbf{k})$ is obtained from eq 26 by interchanging A and B. Apart from the prefactors on the right-hand sides of eq 26 and 27, these equations have the same form as the traditional RPA structure factor $S(\mathbf{k})$ for a blend. It may, therefore, appear that considerations of compressibility are irrelevant. However, there is no requirement in (27) that $\bar{\phi}_A + \bar{\phi}_B$ equal unity, and a precise theoretical definition (eq 24) emerges for the polymer volume fractions (see discussion below). Furthermore, the analysis in ref 24 indicates how neglect in compressibility (i.e., the assumption that $\bar{\phi}_A + \bar{\phi}_B = 1$) can lead to a gross change in the molecular weight and composition dependence of the effective interaction parameter. Further discussion of this point is provided in subsection C below.

In the limit that $\bar{\phi}_A \rightarrow \phi_A$ (no voids) and that $\nu_{AA} = \nu_{BB}$, eq 26 and 27 do indeed reduce to the incompressible RPA limit as they must. Otherwise, there are three independent structure factors for the blend, and the results of comparing SANS data to the RPA form (eq 21) depend on which component does the scattering.

Since the excluded-volume parameters ν_{AA}, ν_{AB}, and ν_{BB} are never calculated from first principles but are left as (or combined into) phenomenological parameters to be determined by comparison with experiment, eq 24 exhibits $\{\bar{\phi}_\alpha\}$ likewise a phenomenological parameters. Because the structure factors (26) and (27) reduce in the appropriate limits to the incompressible RPA approximation for which $\bar{\phi}_A$ and $\bar{\phi}_B$ become the volume fractions of the two components, we can safely interpret $\bar{\phi}_\alpha$ as the appropriate volume fractions in the compressible case. Moreover, ref 24 employs a Flory–Huggins model with voids to consider the $\mathbf{k} \rightarrow 0$ limit of (26) (apart from the $\bar{\phi}_A/x_A$ prefactor) with $\bar{\phi}_\alpha$ the volume fractions. The present results merely indicate that the polymer–polymer interactions dictate experimental measures of the volume occupied by the polymers. Although this point is physically obvious, eq 26 and 27 demonstrate that, after definition of volume fractions, only a single interaction parameter remains in the compressible generalization of the RPA.

On a more empirical basis the $\bar{\phi}_\alpha$ variables can be understood as follows: Blends are liquids and are therefore expected to have compressibilities comparable to those for organic liquids. As pressure is increased isothermally, the blend volume changes according to a liquidlike compressibility, until a "log jam" arises where the compressibility becomes solidlike. The difference between the original system volume and the volume at which the "log jam" occurs is a measure of the free volume available in the initial state and may be used to convert nominal volume fractions ϕ_α to the $\bar{\phi}_\alpha$ through $\bar{\phi}_\alpha = (1 - \phi_\nu)\phi_\alpha$ with ϕ_ν the fraction of the original volume that is ascribed to free volume. An alternative is to proceed theoretically by using Flory–Huggins or equation of state theories to compute ϕ_ν directly from the equation of state. Work of the latter variety is currently in progress.[25] The work in ref 25 has been completed after acceptance of this paper. Reference 25 shows that $S_{AA}(0)$ and $S_{AB}(0)$ from (26) and (27), respectively, recover an important contribution that may also be derived from an incompressible Flory–Huggins theory. However, an additional Flory–Huggins theory contribution is absent, suggesting the need for further extensions of the present incompressible RPA formalism. Tang and Freed have recently shown how a minor modification of the present formalism makes $S_{AA}(0)$ and $S_{AB}(0)$ agree with incompressible Flory–Huggins theory, and it also leads to modifications of the q dependence of $S(\mathbf{q})$ from the usual RPA form.[36]

C. Use of the Incompressible RPA for a Compressible System. Let us carry out such a comparison between eq 21 and 26. We assume that the actual system is compressible, is well described by (26), but is analyzed in the traditional method using the incompressible (21). Solving for χ^I in terms of χ^C and defining

$$y = \nu_{BB}/\nu_{AA} \tag{28a}$$

$$\bar{\rho} = (n_A N_A + n_B N_B)V^{-1} \tag{28b}$$

yield the $\mathbf{k} \rightarrow 0$ limit

$$\chi^{I,A} = \bar{\rho}\nu_{AA}\chi^C + \frac{1}{N_A x_A}(1 - 1/y) \tag{29a}$$

$$\chi^{I,B} = \bar{\rho}\nu_{BB}\chi^C + \frac{1}{N_B x_B}(1 - y) \tag{29b}$$

Equation 29 is labeled with superscripts I and A to stress that $\chi^{I,A}$ arises from a comparison to the A–A structure factor.

Equation 29 shows how the Flory parameter of the incompressible RPA varies with composition when the experiment probes long-wavelength ($\mathbf{k} \rightarrow 0$) A–A correlations in the blend. Recent articles[5,7,26] have also discussed the observation that $\chi^{\mathrm{I,A}}$ varies with $\mathbf{k}$ in certain experiments. The incompressible RPA (eq 21) predicts that the Flory parameter is independent of $\mathbf{k}$ unless the ν_{ij} are also taken as dependent on $\mathbf{k}$. It proves convenient to define χ^{I} from the $\mathbf{k} \to 0$ limit, simply because in that limit, the Debye functions equal unity. If we retain the full wavevector dependence of $S_{\mathrm{D}}{}^{\mathrm{A}}(\mathbf{k})$ and $S_{\mathrm{D}}{}^{\mathrm{B}}(\mathbf{k})$ in the algebra leading to eq 29, we obtain

$$\chi^{\mathrm{I,A}}(\mathbf{k}) = \bar{\rho}\nu_{\mathrm{AA}}\chi^{\mathrm{C}} + \frac{1}{N_{\mathrm{B}}x_{\mathrm{B}}S_{\mathrm{D}}{}^{\mathrm{B}}(\mathbf{k})}(1 - 1/y) \qquad (30\mathrm{a})$$

instead. When we retain the leading corrections in the long-wavelength limit

$$k^2 N_{\mathrm{A}} l^2/6 \ll 1$$

eq 30a is well approximated by

$$\chi^{\mathrm{I,A}}(\mathbf{k}) = \bar{\rho}\nu_{\mathrm{AA}}\chi^{\mathrm{C}} + \frac{(1 - 1/y)}{N_{\mathrm{B}}x_{\mathrm{B}}\left(1 - \dfrac{N_{\mathrm{A}}l^2}{18}k^2\right)} \qquad (30\mathrm{b})$$

Equations 30a and 30b emphasize that the apparent Flory parameter may appear to vary with $\mathbf{k}$ if the ratio y of monomer sizes differs from unity and it the incompressible assumption is applied to blends that have nonnegligible free volume. Monomer volumes may be estimated from partial molal volumes of the monomer liquids and clearly may be quite disparate.

Slightly different expressions result from a comparison of the cross-correlation functions (eq 27) and $S(\mathbf{k})$:

$$\chi^{\mathrm{I,AB}}(\mathbf{k}) = \bar{\rho}y^{1/2}\nu_{\mathrm{AA}}\chi^{\mathrm{C}} + \frac{(y^{1/2} - 1)}{2N_{\mathrm{A}}x_{\mathrm{A}}S_{\mathrm{D}}{}^{\mathrm{A}}(\mathbf{k})} + \frac{(1 - y^{-1/2})}{2N_{\mathrm{B}}x_{\mathrm{B}}S_{\mathrm{D}}{}^{\mathrm{B}}(\mathbf{k})} \qquad (31\mathrm{a})$$

and

$$\lim_{\mathbf{k}\to 0} \chi^{\mathrm{I,AB}} = \bar{\rho}y^{1/2}\nu_{\mathrm{AA}}\chi^{\mathrm{C}} + \frac{(y^{1/2} - 1)}{2N_{\mathrm{A}}x_{\mathrm{A}}} + \frac{(1 - y^{-1/2})}{2N_{\mathrm{B}}x_{\mathrm{B}}} \qquad (31\mathrm{b})$$

Again, eq 31b describes the usual experimental extrapolation to $k = 0$. In general, the apparent Flory parameter may depend on which of the partial structure factors the experiment measures. One possible method of determining the relevance of blend compressibility is to separately measure $S_{\mathrm{AA}}(\mathbf{k})$ and $S_{\mathrm{BB}}(\mathbf{k})$ and extract the apparent $\chi^{\mathrm{I,A}}$ and $\chi^{\mathrm{I,B}}$, respectively. Comparison with eq 29 provides an expression for the difference as an explicit function of the controllable N_α and x_α.

D. Comparison with Integral Equation Methods. An interesting feature of eq 19a for the A–A structure factor is that is has exactly the same form as an equation based on the RISM approach of Schweizer and Curro.[15,16] To make a complete analogy between the two theories, we need to recognize that in RPA-type approaches the "Ornstein-Zernike" direct correlation functions $\hat{c}_{\alpha\beta}(\mathbf{k})$ for monomer–monomer correlations are replaced by the negative of the monomer pair potentials, which, in this case, are modeled by the δ-function pseudopotential of our eq 4. Substituting $-\nu_{\alpha\beta}$ for $\hat{c}_{\alpha\beta}(\mathbf{k})$ in eq 4 of ref 15 yields our eq 19a apart from minor notational differences.

The analogy is even more obvious when we generalize our results to include the $\mathbf{r}$ dependence of the $\nu_{\alpha\beta}$'s in the Hamiltonian of eq 4. (See also eq 7.) The generalization leads again to eq 19a,b but with $\mathbf{u}_{\alpha\beta}$ replaced by

$$\hat{u}_{\alpha\beta}(\mathbf{k}) = \hat{\nu}_{\alpha\beta}(\mathbf{k})/V \qquad (32\mathrm{a})$$

and we make the association

$$-\hat{\nu}_{\alpha\beta}(\mathbf{k}) = \hat{c}_{\alpha\beta}(\mathbf{k}) \qquad (32\mathrm{b})$$

This confirms that eq 19a,b are indeed the RPA approximation of the RISM theory.[27] Thus, Schweizer and Curro likewise generate the somewhat different forms in (22) and (25) for the incompressible and compressible cases. However, the individual $u_{\alpha\beta}$ are not separately measurable [or computable within the Edwards style model (4)] to distinguish the forms, so it is only relevant to collect a phenomenological χ parameter.

The apparent χ parameter in eq 29 diverges as $x_{\mathrm{B}} \to 0$ or as x_{A} or $x_{\mathrm{B}} \to 1$ in eq 31 (except when $y = 1$). This does not occur in the previous RISM calculations, perhaps because the authors invoke the incompressibility constraint before proceeding with their numerical analysis. We suspect that the divergences are real and would occur even in the RISM calculations upon properly including the blend's compressibility. Also, it should be clear that when we compare the *compressible* RPA structure factor for $S_{\mathrm{BB}}(\mathbf{k})$ with $S(\mathbf{k})$, the singularity at $x_{\mathrm{B}} = 0$ disappears in favor of one at $x_{\mathrm{A}} = 0$. The compressible RPA theory only predicts consistent behavior among the three possible definitions of χ^{I} when $y = 1$. (See, e.g., eq 29 and 31.)

The number fractions in eq 20 are often replaced with volume fractions.[1,28] The $\mathbf{k} \to 0$ limit used to evaluate χ^{I} in eq 23 of the Flory–Huggins theory establishes the validity of this procedure. If we repeat the analysis that leads to eq 29 and 30 for eq 23, 26, and 27, results similar to eq 24 and 30 are obtained, except that $\chi^{\mathrm{I,A}}(0)$ now diverges at both x_{A} and $x_{\mathrm{B}} \to 0$.

E. Correlation Length and Spinodal. It is convenient to recall results for the well-known incompressible limit before turning to the compressible case. By expansion the Debye functions in eq 20 to lowest order in $\mathbf{k}$ and inversion, the well-known simple and convenient form for the incompressible RPA structure factor emerges as

$$S^{\mathrm{I}}(\mathbf{k}) = \approx S(0)/(1 + \xi_{\mathrm{I}}{}^2 k^2) \qquad (33)$$

where

$$S^{\mathrm{I}}(0) = 1/[2(\chi_{\mathrm{S}}{}^{\mathrm{I}} - \chi^{\mathrm{I}})] \qquad (34\mathrm{a})$$

$$\chi_{\mathrm{S}}{}^{\mathrm{I}} = [1/(N_{\mathrm{A}}\chi_{\mathrm{A}}) + 1/(N_{\mathrm{B}}\chi_{\mathrm{B}})]/2 \qquad (34\mathrm{b})$$

and

$$\xi_{\mathrm{I}}{}^2 = [(l_{\mathrm{A}}/x_{\mathrm{A}})^2 + (l_{\mathrm{B}}/x_{\mathrm{B}})^2]/[36(\chi_{\mathrm{S}}{}^{\mathrm{I}} - \chi^{\mathrm{I}})] \qquad (34\mathrm{c})$$

When the Flory parameter reaches the value of $\chi_{\mathrm{S}}{}^{\mathrm{I}}$, the correlation length of (34c) diverges, and the $\mathbf{k} = 0$ structure factor diverges. At this temperature the blend separates into two phases—one rich in A and the other in B. The spinodal curve associated with the divergences provides the binary system's limit of miscibility. The actual thermodynamic phase transition may occur at a higher temperature.

Any of the partial structure factors may be used to carry out a parallel analysis for the compressible RPA. For example, eq 26 and 27 yield

$$S_{\alpha\beta}(\mathbf{k}) \approx \frac{S_{\alpha\beta}(0)}{1 + \xi_{\mathrm{C}}{}^2 k^2} \qquad (35)$$

$$S_{\alpha\beta}(0) = \pm(1/2)\left(\frac{\bar{\phi}_\alpha\bar{\phi}_\beta}{x_\alpha x_\beta}\right)/(\chi_S{}^C - \chi^C) \qquad (36a)$$

$$\chi_S{}^C = [1/(N_A\bar{\phi}_A) + 1/(N_B\bar{\phi}_B)]/2 \qquad (36b)$$

and

$$\xi_C{}^2 = [(l_A/\bar{\phi}_A)^2 + (l_B/\bar{\phi}_B)^2]/[36(\chi_S{}^C - \chi^C)] \qquad (36c)$$

(The positive sign is used when $\alpha = \beta$ in eq 36a; otherwise the minus sign applies.) Relaxing the compressibility constraint does not affect the qualitative form of the structure factor. Also, despite the nonequivalence of the three partial structure factors, there is but a single correlation length. The mean-field predictions of eq 36a,c are similar to those of eq 34a,c, respectively. Near the spinodal temperature T_S

$$S(0) \sim \xi_I{}^2 \sim (T - T_S)^{-1} \qquad (37)$$

The dilute solution interpretation of $\nu_{\alpha\beta} \sim T^{-1}$ is inappropriate at high polymer volume fractions, because there the $\nu_{\alpha\beta}$'s almost certainly account for a variety of collective interchain and intrachain effects that produce a complicated temperature dependence. (In essence, the simplistic Hamiltonian, eq 4, ignores most of the complexities of polymer interactions by lumping them together into an average ν.) It is still reasonable to expand χ^C about the spinodal by using a Taylor series in the temperature

$$\chi^C - \chi_S{}^C \sim T - T_S \qquad (38)$$

near T_S. Upon substituting eq 38 into eq 35a,c, we find the same dependence of $S_{\alpha\beta}(0)$ and ξ_C on $T - T_S$ as for $S(0)$ and ξ_I. Subsequent work[25] shows that the spinodal evaluated from (33) corresponds to the constant volume spinodal; the spinodal at constant pressure may differ considerably. Also, the Flory–Huggins theory consistent structure factors do indeed depend on three separate interaction parameters.[36]

IV. Extension to Diblock Copolymers

An important application of the RPA is to diblock copolymer scattering functions and to microphase separation. Here we summarize the steps necessary to extend the arguments of the previous sections to diblock copolymers, and we provide the final expression for the RPA scattering functions of compressible diblock copolymer melts.

The Hamiltonian of a system of AB diblock copolymers is similar to that of a two-component blend (eq 4), except for the constraint that $\tau_\beta{}^A = L_A$ and $\tau_\beta{}^B = 0$ refer to the same contour point along the chain backbone and that there is a sum over a single type of chain. Proceeding as in eq 5–16, we arrive at

$$Z_{\mathbf{k}} = \int \prod_{\alpha=A,B} \{d\rho_{\mathbf{k}}{}^\alpha\, d\rho_{\mathbf{k}}{}^{\alpha*}\, d\lambda_{\mathbf{k}}{}^\alpha\, d\lambda_{\mathbf{k}}{}^\alpha \exp[-|\lambda_{\mathbf{k}}{}^\alpha|^2 G_\alpha(\mathbf{k}) \times \exp[i(\lambda_{\mathbf{k}}{}^\alpha\rho_{\mathbf{k}}{}^\alpha + \lambda_{\mathbf{k}}{}^{\alpha*}\rho_{\mathbf{k}}{}^{\alpha*})]]\} \exp(-\rho_{\mathbf{k}}{}^T u \rho_{\mathbf{k}}) \times \exp[-(1/2)G_{AB}(\mathbf{k})(\lambda_{\mathbf{k}}{}^A\lambda_{\mathbf{k}}{}^{B*} + \lambda_{\mathbf{k}}{}^B\lambda_{\mathbf{k}}{}^{\alpha*})] \qquad (39)$$

with

$$G_\alpha(\mathbf{k}) = nN_\alpha{}^2 S_D{}^\alpha(\mathbf{k});\quad \alpha = A, B \qquad (40a)$$

and

$$G_{\alpha\beta}(\mathbf{k}) = nN_AN_B\left[1 - \frac{k^2N_A}{12}S_D{}^A(\mathbf{k})\right]\left[1 - \frac{k^2N_B}{12}S_D{}^B(\mathbf{k})\right] \qquad (40b)$$

Straightforward integration of eq 39 followed by application of eq 18a and 18b yields

$$\langle\rho_{\mathbf{k}}{}^A\rho_{\mathbf{k}}{}^{A*}\rangle = \frac{[G_A(\mathbf{k})G_B(\mathbf{k}) - G_{AB}{}^2(\mathbf{k})]u_{BB} + G_A(\mathbf{k})}{D(\mathbf{k})} \qquad (41a)$$

and

$$\langle\rho_{\mathbf{k}}{}^A\rho_{\mathbf{k}}{}^{B*}\rangle = \frac{G_{AB}(\mathbf{k}) - u_{AB}[G_A(\mathbf{k})G_B(\mathbf{k}) - G_{AB}{}^2(\mathbf{k})]}{D(\mathbf{k})} \qquad (41b)$$

where

$$D(\mathbf{k}) = 1 + u_{AA}G_A(\mathbf{k}) + u_{BB}G_B(\mathbf{k}) + 2u_{AB}G_{AB}(\mathbf{k}) + (u_{AA}u_{BB} - u_{AB}{}^2)[G_A(\mathbf{k})G_B(\mathbf{k}) - G_{AB}{}^2(\mathbf{k})] \qquad (41c)$$

Equations 41a–c are similar to (19a) and (19b) except for the presence of $G_{AB}(\mathbf{k})$ in the diblock case. Besides intrablock cumulants analogous to eq 13, diblocks also have cross terms due to the Gaussian averages over different blocks on the same chain. The methods employed in this article decouple the chains, so that such contributions do not arise for blends, as these would involve different chains.

Diblock copolymers in the incompressible limit yield $\langle\rho_{\mathbf{k}}{}^A\rho_{\mathbf{k}}{}^{A*}\rangle = -\langle\rho_{\mathbf{k}}{}^A\rho_{\mathbf{k}}{}^{B*}\rangle$. Hence, as $\mathbf{k} \to 0$, the scattering functions vanish. Clearly, eq 41a–c display qualitatively different behavior. As $k \to 0$, we find from (41) that

$$S_{AA}(0) = \frac{1}{n(N_A + N_B)}\langle\rho_{\mathbf{k}}{}^A\rho_{\mathbf{k}}{}^{A*}\rangle = x_A{}^2/[\bar{\phi}_Ax_A + \bar{\phi}_Bx_B \pm 2(2\chi^C + 1)^{1/2}(\bar{\phi}_A\bar{\phi}_B)^{1/2}(x_Ax_B)^{1/2}] \qquad (42a)$$

and

$$S_{AB}(0) = x_Ax_B/[\bar{\phi}_Ax_A + \bar{\phi}_Bx_B \pm 2(2\chi^C + 1)^{1/2}(\bar{\phi}_A\bar{\phi}_B)^{1/2}(x_Ax_B)^{1/2}] \qquad (42b)$$

where the sign in the denominator is that of

$$u_{AB}/(u_{AA}u_{BB})$$

and where we have ignored unity compared to N_A and N_B. More generally, eq 41 for $\mathbf{k} \neq 0$ implies

$$S_{AA}(\mathbf{k}) = \left\{N_Ax_Ax_B\bar{\phi}_B\left\{S_D{}^A(\mathbf{k})S_D{}^B(\mathbf{k}) - \left[1 - \frac{k^2N_A}{12}S_D{}^A(\mathbf{k})\right] \times \left[1 - \frac{k^2N_B}{12}S_D{}^B(\mathbf{k})\right]\right\} + x_A{}^2S_D{}^A(\mathbf{k})\right\}/\bar{D}(\mathbf{k}) \qquad (43a)$$

and

$$S_{AB}(\mathbf{k}) = \left\{x_Ax_B\left[1 - \frac{k^2N_A}{12}S_D{}^A(\mathbf{k})\right]\left[1 - \frac{k^2N_B}{12}S_D{}^B(\mathbf{k})\right] \pm (2\chi^C + 1)^{1/2}(\bar{\phi}_A\bar{\phi}_B)^{1/2}(x_Ax_B)^{1/2}\left(S_D{}^A(\mathbf{k})S_D{}^B(\mathbf{k}) - \left[1 - \frac{k^2N_A}{12}S_D{}^A(\mathbf{k})\right]\left[1 - \frac{k^2N_B}{12}S_D{}^B(\mathbf{k})\right]\right)\right\}/\bar{D}(\mathbf{k}) \qquad (43b)$$

where

$$\bar{D}(\mathbf{k}) = \bar{\phi}_Ax_AS_D{}^A(\mathbf{k}) + \bar{\phi}_Bx_BS_D{}^B(\mathbf{k}) \pm 2(2\chi^C + 1)^{1/2} \times (\bar{\phi}_A\bar{\phi}_B)^{1/2}(x_Ax_B)^{1/2}\left[1 - \frac{k^2N_A}{12}S_D{}^A(\mathbf{k})\right]\left[1 - \frac{k^2N_B}{12}S_D{}^B(\mathbf{k})\right] - 2\bar{\phi}_A\bar{\phi}_B\chi^Cx_Ax_B\left\{S_D{}^A(\mathbf{k})S_D{}^B(\mathbf{k}) - \left[1 - \frac{k^2N_AS_D{}^A(\mathbf{k})}{12}\right]\left[1 - \frac{k^2N_BS_D{}^B(\mathbf{k})}{12}\right]\right\} \qquad (43c)$$

It is interesting to note that eq 42a departs from the incompressible RPA limit that $S_{AA}{}^{I}(0) = 0$. Experiments find[29] nonzero values for $S_{AA}(0)$ that are somewhat in excess of estimates computed as arising from polydispersity.[30] Perhaps the compressible system predictions in eq 42a may be employed (by varying block composition) to determine whether a portion of the experimental $S_{AA}(0)$ appears because of compressibility. In the special case of u_{AB} negative, the denominators in (42) may become large, producing a significant excess extrapolated zero-angle scattering.

Unlike a single-component liquid in which the $\mathbf{k} \rightarrow 0$ limit of the structure factor trivially determines the compressibility κ, the compressibility of a blend is not simply related to the matrix of $S_{\alpha\beta}(0)$'s. A theoretical estimate of κ for a blend requires a theory for the free energy from which the chemical potentials and partial molar volumes of the components may be calculated; then the compressibility is obtained from the derivatives of the chemical potentials (at constant volume and temperature) with respect to numbers of A and B monomers. In the present article, we do not obtain the free energy but focus instead on the correlations between the monomers. Without the requisite free energy, the blend compressibility cannot be deduced, but elsewhere an analysis will be provided of the free energy, compressibilities, etc. for blends.[25]

Block copolymer melts also contain two types of monomeric species, but are single-component systems, in contrast to blends. This makes is possible to evaluate the compressibility κ_{BC} of a block copolymer melt directly from the well-known relation involving the number-density fluctuations

$$\kappa_{BC} = \frac{1}{kT}\frac{\langle n^2 \rangle - n^2}{n} \tag{44}$$

and the definition of the $S_{\alpha\beta}(0)$'s in terms of the total correlation functions (the $h_{\alpha\beta}(0)$'s in the expression between eq 8 and 9). Standard manipulations and a little algebra lead to

$$\kappa_{BC} = \frac{1}{\bar{\rho}\kappa T}[\bar{\phi}_A x_A + \bar{\phi}_B x_B \pm 2(2\chi^C + 1)^{1/2}(\bar{\phi}_A \bar{\phi}_B)^{1/2}(x_A x_B)^{1/2}]^{-1}$$

Rough estimates of the parameters appearing on the right-hand side of this equation yield $\kappa_{BC} \sim 10^{-3}$ atm^{-1}, in agreement with Flory–Huggins type model computations[25] and within an order of magnitude of the results of fitting PVT data to model equations of state for homopolymer melts.[31] This crude calculation illustrates how the compressibilities of polymeric fluids are no less important than those of ordinary fluids (e.g.,[32] water at 1 atm and 30 °C has $\kappa \sim 4 \times 10^{-5}$ atm^{-1}). The error here is presumably due to well-known inadequacies of Flory–Huggins type models in modeling the effects of the hard core repulsions in real systems.[33]

V. Conclusions

We have removed the compressibility constraint usually employed in conjunction with the RPA approximation for blend thermodynamics and structure factors. An immediate consequence of our treatment is that the blend possesses three independent structure factors. The empirically determined effective χ parameter depends on which of these structure factors are compared to the RPA structure factor $S(\mathbf{k})$ in eq 20.

Our definition of χ^C in eq 24 differs from the customary one of eq 21 for χ^I. These parameters are primarily of phenomenological importance, and a previous note by one of us[24] indicates that neglect of blend compressibility in comparison with experimental data can lead to a χ^I that contains a spurious dependence on molecular weights even in the long chain limit.[25] Our calculations indicate that compressibility can produce an apparent $\chi^{I,A}$ from scattering by block A that differs from the $\chi^{I,B}$ from block B if the system is incorrectly assumed to be incompressible. The compressible RPA structure factor for block copolymer melts does not vanish for $k \rightarrow 0$ as predicted by the incompressible theory. It will be interesting to see if our predicted composition dependence of this quantity can explain some of the experimental observations. Mean-field predictions, based on eq 32 and 34, about the shape of the spinodal (e.g., T versus x_A), do require a more detailed knowledge of χ^I and χ^C. In this regard, it is easy to rationalize a linear variation of $\chi_S{}^C - \chi^C$ with temperature, so that the compressible and incompressible RPA's lead to exactly the same type of predictions for the spinodal.

We do not expect that the rather simple results and conclusions derived in the present paper will supplant the conventional RPA theory. However, in some applications, it would be wise to examine the older approach critically. Flory parameters that vary with composition, molecular weight, or wavevector may indicate a breakdown of the incompressibility assumption and not a serious defect in the RPA. Also, theory[8,9,34] has already made several predictions, based on incompressible RPA arguments, about preferred morphologies and about the nature (i.e., first order versus second order) of block copolymer microphase separations. Including nonzero density changes at the phase transition could perturb the calculations and change the theoretical conclusions. Calculations of the microphase separation using density functional techniques[35] and the alternative structure factors in eq 43a–c are in progress.

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Θ Temperature of Linear and Star Polymers

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ABSTRACT: The Θ-temperature dependence on chain length and number of arms f for linear and regular star polymers was determined analytically as the temperature at which balance is reached between the repulsive three-body and the attractive two-body interactions; the latter increase with decreasing temperature, unlike the former, which are essentially constant. From an equivalent bead-and-spring model in the Gaussian approximation, Θ is found to *decrease* with increasing molecular weight for linear and lightly branched chains ($f \leqslant 4$), whereas it *increases* if $f \geqslant 5$ to a common asymptotic limit Θ_∞. In fact, for *linear* chains the ratio between the number of the three-body and that of the two-body contacts increases with molecular weight because the minimum chain length for a three-body contact is about twice that for a two-body contact. Therefore, short chains need less temperature lowering to compensate the three-body repulsions than long ones. Conversely, the lower Θ temperature for short *branched* chains with many arms is due to the high density of segments near the star core: this gives rise to a large number of three-body repulsions to be compensated. If the molecular weight is very large, the fraction of segments close to the star core becomes negligible and the same temperature Θ_∞ is attained for any polymer architecture, in agreement with experimental results.

Introduction

It is now accepted that for a given polymer–solvent system the Θ temperature changes in general with polymer architecture and molecular weight, but if the latter is large enough, Θ tends to a common, finite limit.[1–4] This behavior was clearly shown, for example, by well-characterized regular star polymers, synthesized in recent years by linking monodisperse living polymers (mainly polyisoprene and polystyrene) to a multifunctional reactive center. The Θ temperature of these samples, determined by light scattering as the temperature at which the second virial coefficient A_2 vanishes, follows a general pattern: it is lower the shorter the arms are and the larger their number is. However, for very long arms Θ reaches a constant value Θ_∞ independent of both molecular weight and number of arms. Moreover, Θ_∞ turns out to be equal to the Θ temperature of long linear chains.

This finding rules out the widespread assumption that in the Θ state long-range interactions are merely absent. Rather, it suggests that they compensate in a subtle way: a repulsive component, arising from three-body interactions, is balanced by an attractive component, due to the temperature-dependent two-body interactions. In this paper, we follow this approach to calculate the Θ temperature of linear and star polymers using a simple model. The chain comprises $N + 1$ atoms and f equal arms and therefore N/f atoms per arm if one atom sits on the branch point and will be described by an equivalent bead-and-spring chain with a Gaussian distribution of interatomic distances. Θ is obtained as the temperature at which the overall free energy due to the attractive two-body interactions balances that due to the repulsive three-body interactions.

The larger f is, the higher the density at the star core is, hence the larger the number of three-body contacts is. To compensate this increasingly repulsive contribution, a correspondingly lower temperature is needed to strengthen the attractive contribution, unless N/f is so large that only a negligible fraction of chain atoms is near the core. Therefore, Θ should be lower for stars than for linear polymers, the more so the larger f is and the smaller N/f is, but should tend to the same limit if $N/f \to \infty$, no matter what the number of arms is. Note that the linear polymer may be viewed as a special case of a star with $f = 1$ or 2.

By this approach, we are implicitly defining the Θ temperature as the temperature at which the mean-square radius of gyration and the mean-square distances are proportional to the molecular weight and to the topological separation along the chain, respectively. Also, in this context Θ is obtained from consideration of isolated chains, whereas the definition based on A_2 would also require us