Static Structure Factors of Compressible Polymer Blends and Diblock Copolymer Melts. 2. Constraints on Density Fluctuations

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ABSTRACT: An upper bound constraint on the allowable density fluctuations is introduced into the McMullen–Freed formulation of the compressible random-phase approximation (RPA). We use this compressible RPA approximation to derive the three independent static structure factors for the monomer correlations within a binary polymer blend and within a diblock copolymer melt as a function of the three excluded-volume parameters that are required for describing a compressible binary system. The compressible RPA scattering functions approach the well-known incompressible results when the free volume tends toward zero. However, even small amounts of free volume (finite compressibility) introduce some significant changes in the structure factor. For instance, the extrapolated zero-angle scattering from a binary blend is consistent with a compressible Flory–Huggins model as investigated by Dudowicz and Freed. Under certain circumstances the latter difference produces significant alterations of the structure factor from the incompressible theory. Rather high values of $k^2R_G^2$ can sometimes be required before the blend structure factor enters the asymptotic k^{-2} region. Likewise, the structure factor for a compressible diblock copolymer melt does not vanish in the limit of zero angle and displays a nontrivial dependence on the additional interaction parameters that are absent in the incompressible limit. We discuss how the compressible RPA may affect theories of the interfacial profiles in binary blend phase separations and of microphase separations for diblock copolymers.

I. Introduction

Small-angle neutron-scattering data for polymer blends are generally analyzed with the random-phase approximation (RPA) for the scattering intensity. de Gennes has used a simple linear response formalism to derive the RPA structure factor for incompressible blends,[1,2] and this structure factor is widely used in extrapolating the scattering data to zero angle, in extracting an effective interaction parameter χ, and in determining the radii of gyration of the polymers in the blend. The same structure factor enters prominently into theories of the phase separation and interfacial profile of blends[3-5] and the microphase separation of block copolymers.[2,6]

Polymer melts and blends, however, are at least as compressible as the monomeric liquids, and this must have measurable effects on both the neutron-scattering and phase-separation processes. However, some of these effects are difficult to discern unless there are independent measurements of the interaction parameter and radii of gyration that are not obtained through use of the incompressibility assumption. For instance, the extrapolated zero-angle scattering intensity provides one empirical definition of the Flory interaction parameter χ for a blend, but if the blend is compressible, there must, in fact, be three measurable independent interaction parameters determining the thermodynamic properties of the blend.[7-9]

Recent work by Dudowicz and Freed[9] uses the simplest Flory–Huggins[7] model of a compressible blend (with three independent polymer–polymer interaction parameters) to compute the extrapolated zero-angle neutron scattering and thus the effective χ_{inc} parameter that would be deduced from a standard incompressible RPA analysis.[2] They find that χ_{inc} depends on all three independent interaction parameters and exhibits a molecular weight and composition dependence, solely due to the inappropriate use of an incompressible model for interpreting the properties of a compressible system. They suggest that compressibility might likewise affect the scattering intensity at nonzero angles and therefore the interpretation of radii of gyration and phase-separation processes.

McMullen and Freed[8] have lifted the incompressibility assumption within an Edwards path integral formalism[10-12] to evaluate a compressible RPA structure factor. A similar formalism is employed by Brereton and Vilgis[13] to study both the effective screened interactions and the radius of gyration of a single chain in a blend. The McMullen–Freed scattering function only depends on a single effective interaction parameter, and after a reinterpretation of the effective volume fractions to include compressibility, their scattering function has the same form as in the incompressible RPA. The subsequent compressible Flory–Huggins computations of Dudowicz and Freed,[9] however, demonstrate a limitation of the McMullen and Freed compressible blend structure factor. The extrapolated zero-angle scattering from the latter does not coincide with the scattering intensity that is obtained by simple thermodynamics from the compressible Flory–Huggins model. The difference between the two involves a term depending separately on the three interaction parameters in the system. This additional term appears because the creation of free volume in a compressible blend destroys polymer–polymer contacts, thereby altering the free energy of the blend and hence its second derivatives that equal the extrapolated zero-angle scattering.

The difference between the zero-angle scattering in the McMullen–Freed structure factor and the Flory–Huggins compressible blend model implies a need for alterations of the compressible blend calculations to include the cost in free energy of the creation of free volume. The appropriate extension may simply be understood with reference to the standard lattice model for describing a compressible blend, since the Flory–Huggins compressible model may be derived as an approximation to such a model.[14] The lattice model requires that each lattice site be occupied either by a monomer of spcies A, species B, or a void. This implies that the sum of the species A monomer density, $\rho_A(\mathbf{r}_i)$, on the site i at a position $\mathbf{r}_i$, with $\rho_B(\mathbf{r}_i)$ for species B and with $\rho_v(\mathbf{r}_i)$ for the free volume, must be a constant (single occupancy). Passing to the continuum limit this leads to the constraint that

$$\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) + \rho_v(\mathbf{r}) = \rho \tag{1.1}$$

where ρ is the constant maximum density of the system. The condition (1.1) places an upper bound on the allowable density fluctuations at a spatial position $\mathbf{r}$ and therefore implies that the creation of free volume in a region destroys polymer–polymer contacts, thereby costing energy. The compressible RPA formulation of McMullen and Freed and the related work of Brereton and Vilgis do not introduce constraints on allowable density fluctuations. Thus, the creation of free volume in a spatial region does not require the breaking of polymer–polymer contacts in that formulation, which consequently involves only a single effective interaction parameter.

Section II modifies the McMullen–Freed compressible RPA theory to incorporate the constraint (1.1). Since the calculations parallel those given in ref 8, the details are only briefly sketched in this section. The extension to a compressible RPA for diblock copolymers is likewise only briefly sketched in section IV. While explicit calculations are provided for binary systems, it is straightforward to extend them to systems with any number of components. The small-angle scattering from blends is analyzed in section II, where the theory is shown to recover in the limit of zero scattering angle the results obtained from the compressible Flory–Huggins model.[9] Deviations from the incompressible RPA enter in the correlation length, but these appear to be too small to be readily measurable. However, these deviations should be of consequence for describing density profiles of inhomogeneous phase-separated systems, particularly the density profile of a free surface of a polymer melt for which compressibility is a crucial factor. When the self-interaction (A–A and B–B) parameters differ significantly, the compressible RPA scattering functions depart from their compressible counterparts. The differences for binary blends are more pronounced for smaller $k^2R_G^2$, where k is the magnitude of the scattering vector and R_G is the radius of gyration of the scattering component, while those for diblock copolymers are centered about the maximum in the scattering function. Illustrations are provided in sections III and IV.

After submission of this manuscript, a paper appeared by Benoit et al.[22] in which they use the traditional (one-loop) diagram summation method to obtain RPA structure factors for multicomponent. While they note that their theory is not applicable to melts and blends, it turns out that if the solvent in their work is replaced by free volume and the monomer–void interactions are taken to vanish, their results for two-component systems (of homopolymers or of diblock copolymers) become formally identical with those presented here. Apart from the independence of the two derivations, there are other reasons why the present one is of interest as follows: The Edwards path integral formulation, as applied to the RPA structure factor by de la Cruz and Sanchez,[6] is a major theoretical technique for describing polymer systems. Consequently, it is important to ascertain the physical assumptions and computational alterations within the formalism that are necessary to describe correctly the properties of compressible polymer systems. In addition, the Edwards style approach is readily amenable to systematic extension, as described in section II, to consider nonideality effects on labeled chain radii of gyration, structure factors, higher order correlations functions, etc., whereas we would hesitate to use the Benoit style diagram summation to pass onto the next order (two-loop) approximation. In fact, it is partly to obviate this complicated diagram summation, which is necessary to obtain the RPA in other contexts, that led Edwards in his seminal paper on polymer screening[10] to employ the random-field methods for obtaining the RPA approximation from the leading simple (despite the apparent complexity of the path integral formulas) Gaussian integrals. Our paper extends beyond that of Benoit et al., which focuses on multicomponent polymer solutions in the semidilute region. Here we analyze the importance of the compressibility corrections to the RPA for the partial structure factors and for polymer phase separations.

II. Compressible RPA Theory for the Structure Factor

We consider a compressible binary blend with n_α polymers of type α (α = A, B) and n_v voids that are employed to model free volume. If, for simplicity, the monomers and voids are assumed to occupy equal volumes as in lattice models, then the volume fraction of the free volume is $\varphi_v = n_v/(n_AN_A + n_BN_B + n_v)$, where N_α is the polymerization index for chains of species α. The free volume may be eliminated from the theory by use of the equation of state for a constant-pressure system.[9] As is clear from the discussion in section III, the appropriate thermodynamic model is obtained from a compressible Flory–Huggins theory, such as that used by Dudowicz and Freed. Other models of free volume may be introduced, such as those describing the free volume, say, as nonoverlapping spherical volumes with an exponential distribution of sizes. This would provide a thermodynamic model more akin to those discussed by Dickman and Hall,[15] but such a treatment would enormously complicate the algebra, so we retain the simplest Flory–Huggins form.

The density operators for the monomers and voids are defined, respectively, by

$$\rho_\alpha(\mathbf{r}) = \sum_{j=1}^{n_\alpha} \int_0^{L_\alpha} \mathrm{d}\tau_j{}^\alpha\, (l_\alpha)^{-1}\, \delta(\mathbf{r}-\mathbf{r}_j{}^\alpha) \tag{2.1a}$$

$$\rho_v(\mathbf{r}) = \sum_{j=1}^{n_v} \delta(\mathbf{r}-\mathbf{r}_j{}^v) \tag{2.1b}$$

where the α polymer is composed of monomers with Kuhn length l_α, the chain has polymerization index N_α, and the overall contour length is $L_\alpha = l_\alpha N_\alpha$ with α = A or B.

Introducing Fourier transforms converts (2.1) into

$$\rho_\mathbf{q}{}^\alpha = \sum_{j=1}^{n_\alpha} \int_0^{L_\alpha} \mathrm{d}\tau_j{}^\alpha\, (l_\alpha)^{-1} \exp(i\mathbf{q}\cdot\mathbf{r}_j{}^\alpha) \tag{2.2a}$$

$$\rho_\mathbf{q}{}^v = \sum_{j=1}^{n_v} \exp(i\mathbf{q}\cdot\mathbf{r}_j{}^v) \tag{2.2b}$$

with the inverse relations

$$\rho_\alpha(\mathbf{r}) = V^{-1} \sum_\mathbf{q} \rho_\mathbf{q}{}^\alpha \exp(-i\mathbf{q}\cdot\mathbf{r}) \tag{2.3a}$$

$$\rho_v(\mathbf{r}) = V^{-1} \sum_\mathbf{q} \rho_\mathbf{q}{}^v \exp(-i\mathbf{q}\cdot\mathbf{r}) \tag{2.3b}$$

where V denotes the volume of the system.

The Edwards Hamiltonian for the compressible blend is

$$H = \frac{3}{2} \sum_{\alpha=A,B} \sum_{j=1}^{n_\alpha} \int_0^{L_\alpha} \mathrm{d}\tau_j{}^\alpha\, (l_\alpha)^{-1} |\dot{\mathbf{r}}_j{}^\alpha(\tau_j{}^\alpha)|^2 + \frac{1}{2} \sum_{\alpha_1,\alpha_2=A,B} \upsilon_{\alpha_1\alpha_2} \sum_{j_1=1}^{n_{\alpha_1}} \sum_{j_2=1}^{n_{\alpha_2}} \int_0^{L_{\alpha_1}} \mathrm{d}\tau_{j_1}{}^{\alpha_1}\, (l_{\alpha_1})^{-1} \times \int_0^{L_{\alpha_2}} \mathrm{d}\tau_{j_2}{}^{\alpha_2}\, (l_{\alpha_2})^{-1}\, \delta[\mathbf{r}_{j_1}{}^{\alpha_1}(\tau_{j_1}{}^{\alpha_1}) - \mathbf{r}_{j_2}{}^{\alpha_2}(\tau_{j_2}{}^{\alpha_2})] \tag{2.4}$$

The first term in (2.4) describes the usual continuous Gaussian chain with configuration specified by the continuous curve $\mathbf{r}_j^\alpha(\tau_j^\alpha)$, while the remainder provides the excluded volume, which is expressed in terms of the excluded volume $v_{\alpha_1\alpha_2}$ due to α_1–α_2 monomer interactions. Notice that reference to the voids is absent in (2.4) as they do not affect the interaction energies. They do, however, alter the number of polymer–polymer contacts and thereby affecting the thermodynamic properties and fluctuations in the system. The extension to multicomponent systems merely involves allowing the summation indices α, α_1, and α_2 in (2.4) to range over the additional components.

It is convenient to transform the second term on the right-hand side of (2.4) to matrix notation

$$u_{\alpha_1\alpha_2} = v_{\alpha_1\alpha_2}/V \tag{2.5}$$

$$\mathbf{u} = \begin{pmatrix} u_{\mathrm{AA}} & u_{\mathrm{AB}} \\ u_{\mathrm{AB}} & u_{\mathrm{BB}} \end{pmatrix} \tag{2.6}$$

$$\rho_p = \begin{pmatrix} \rho_{\mathbf{q}}^{\mathrm{A}} \\ \rho_{\mathbf{q}}^{\mathrm{B}} \end{pmatrix} \tag{2.7}$$

Then the interaction contributions in (2.4) may be rewritten compactly in terms of the density fluctuations as

$$U = \frac{1}{2}\sum_{\mathbf{q}} \rho_{\mathbf{q}}^{\mathrm{T}} \mathbf{u} \rho_{\mathbf{q}}^* \tag{2.8}$$

where the superscript T designates the matrix transpose.

Partial structure factors of the compressible blend are defined by

$$S_{\mu\nu}(\mathbf{k}) = M^{-1}\int \mathrm{d}\mathbf{r}_2 \int \mathrm{d}\mathbf{r}_1 \exp[i\mathbf{k}\cdot(\mathbf{r}_2 - \mathbf{r}_1)] \times \\ \langle \rho_\mu(\mathbf{r}_1)\rho_\nu(\mathbf{r}_2)\rangle \equiv M^{-1}\langle \rho_{\mathbf{k}}^{\mu}\rho_{\mathbf{k}}^{\nu*}\rangle \tag{2.9}$$

with M the equivalent of the total number of lattice sites

$$M = n_{\mathrm{A}}N_{\mathrm{A}} + n_{\mathrm{B}}N_{\mathrm{B}} + n_{\mathrm{v}} \tag{2.10}$$

which is proportional to the volume V. (When $\mu = \nu$, the normalization in (2.9) is often chosen as $(n_\mu N_\mu)^{-1}$, leading to an overall factor of volume fraction difference between the two choices.) The average in the second line of (2.9) may be written in terms of the Edwards Hamiltonain (2.4) in the usual fashion

$$\langle \rho_{\mathbf{k}}^{\mu}\rho_{\mathbf{k}}^{\nu*}\rangle = Z^{-1} \prod_{\alpha=\mathrm{A,B}} \prod_{j=1}^{n_\alpha} \prod_{i=1}^{n_{\mathrm{v}}} \int \mathrm{d}\mathbf{r}_i^{\mathrm{v}} \int \mathcal{D}[\mathbf{r}_j^\alpha] \times \\ \exp(-H)\rho_{\mathbf{k}}^{\mu}\rho_{\mathbf{k}}^{\nu*}\Delta \tag{2.11}$$

where Z is the partition function, which equals the numerator in (2.11) without the factors of $\rho_{\mathbf{k}}^{\mu}\rho_{\mathbf{k}}^{\nu*}$, and the quantity Δ represents the constraint (1.1) in a fashion to be introduced below. It is this constraint that is lacking in the two previous papers on the compressible RPA. Notice that eq 2.11 permits the presence of a random spatial distribution of voids to model the free volume. The voids enter into the constraint Δ below in (2.13) and thereby account for the existence of density fluctuations. Were we to use a model of spherical voids with an exponential distribution of void sizes (a possible extension within the path integral formulation), it would be necessary to include additional constraints that the voids be nonoverlapping, and this would introduce severe complications into the calculations. Instead, eq 2.11 treats the voids as being pointlike in the same fashion that it treats the monomers.

Following the previous treatment of McMullen and Freed[8] we insert unity in the form of the left-hand side of the identity

$$\prod_{\mathbf{q}}\{\prod_{\alpha=\mathrm{A,B}}\int \mathrm{d}\rho_{\mathbf{q}}^{\alpha}\,\delta[\rho_{\mathbf{q}}^{\alpha} - \sum_j \int_0^{L_\alpha}(l_\alpha)^{-1}\,\mathrm{d}\tau_j^\alpha \exp(i\mathbf{q}\cdot\mathbf{r}_j^\alpha)]\} \times \\ \{\int \mathrm{d}\rho_{\mathbf{q}}^{\mathrm{v}}\,\delta[\rho_{\mathbf{q}}^{\mathrm{v}} - \sum_j \exp(i\mathbf{q}\cdot\mathbf{r}_j^{\mathrm{v}})]\} = 1 \tag{2.12}$$

into the integrand of (2.11) and into the corresponding expression for Z. In order to prohibit unphysical unbounded density fluctuations of the polymers, the continuum analogues of the single site occupancy constraint (1.1) is enforced at each position $\mathbf{r}$ in space. Introducing Fourier transforms permits this constraint to be represented in the continuum limit as

$$\Delta \equiv \delta(\sum_{\alpha=\mathrm{A,B,v}} \rho_0^{\alpha} - \rho)\prod_{\mathbf{q}\neq 0}\delta(\sum_{\alpha=\mathrm{A,B,v}} \rho_{\mathbf{q}}^{\alpha}) \tag{2.13}$$

where Δ is understood to be inserted into (2.11). The condition (2.13) and the definition of the void density in (2.12) are the main physical ingredients necessary to extend the Edwards style formulation of de la Cruz and Sanchez[6] and others[8,13] to compressible systems.

Rewriting the δ functions in (2.12) as Fourier integrals converts the expression for $\langle \rho_{\mathbf{k}}^{\mu}\rho_{\mathbf{k}}^{\nu*}\rangle$ into

$$\langle \rho_{\mathbf{k}}^{\mu}\rho_{\mathbf{k}}^{\nu*}\rangle = Z^{-1}\Bigg\{\Bigg[\prod_{\alpha=\mathrm{A,B,v}}\int \mathrm{d}\rho_0^{\alpha}\frac{\mathrm{d}\lambda_0^{\alpha}}{2\pi}\exp(i\lambda_0^{\alpha}\rho_0^{\alpha})\Bigg] \times \\ \exp(-\rho_0^{\mathrm{T}}\mathbf{u}\rho_0/2)\;\delta(\sum_{\alpha=\mathrm{A,B,v}}\rho_0^{\alpha} - \rho) \times \\ \prod_{\mathbf{q}\neq 0}\Bigg\{\Bigg[\prod_{\alpha=\mathrm{A,B,v}}\int \mathrm{d}\rho_{\mathbf{q}}^{\alpha}\frac{\mathrm{d}\lambda_{\mathbf{q}}^{\alpha}}{2\pi} \times \\ \exp(i\lambda_{\mathbf{q}}^{\alpha}\rho_{\mathbf{q}}^{\alpha})\Bigg]\exp(-\rho_{\mathbf{q}}^{\mathrm{T}}\mathbf{u}\rho_{\mathbf{q}}^*/2)\;\delta(\sum_{\alpha=\mathrm{A,B,v}}\rho_{\mathbf{q}}^{\alpha})\Bigg\}\rho_{\mathbf{k}}^{\mu}\rho_{\mathbf{k}}^{\nu*} \times \\ \Bigg\{\prod_{\beta=\mathrm{A,B}}\prod_{j=1}^{n_\beta}\int \mathcal{D}[\mathbf{r}_j^\beta]\exp\Bigg\{-\frac{3}{2}\int_0^{L_\beta}\mathrm{d}\tau_j^\beta\,(l_\beta)^{-1}\Big|\dot{\mathbf{r}}_j^\beta(\tau_j^\beta)\Big|^2 - \\ i\sum_{\mathbf{q}}\lambda_{\mathbf{q}}^{\beta}\int_0^{L_\beta}\mathrm{d}\tau_j^\beta\,(l_\beta)^{-1}\exp[i\mathbf{q}\cdot\mathbf{r}_j^\beta(\tau_j^\beta)]\Bigg\}\Bigg\}\prod_{i=1}^{n_{\mathrm{v}}}\int \mathrm{d}\mathbf{r}_i^{\mathrm{v}} \times \\ \exp[-i\sum_{\mathbf{q}}\lambda_{\mathbf{q}}^{\mathrm{v}}\exp(i\mathbf{q}\cdot\mathbf{r}_i^{\mathrm{v}})] \tag{2.14}$$

We now switch the order of integrations and first perform the path integrals

$$F_{\beta j}[\{\lambda_{\mathbf{q}}^{\beta}\}] = \int \mathcal{D}[\mathbf{r}_j^\beta]\exp\Bigg\{-\frac{3}{2}\int_0^{L_\beta}\mathrm{d}\tau_j^\beta\,(l_\beta)^{-1}\Big|\dot{\mathbf{r}}_j^\beta(\tau_j^\beta)\Big|^2 - \\ i\sum_{\mathbf{q}}\lambda_{\mathbf{q}}^{\beta}\int_0^{L_\beta}\mathrm{d}\tau_j^\beta\,(l_\beta)^{-1}\exp[i\mathbf{q}\cdot\mathbf{r}_j^\beta(\tau_j^\beta)]\Bigg\} \tag{2.15}$$

that appear in (2.14). Expansion of the second term in the exponential of (2.15) and retention of terms through quadratic order lead to the lowest order approximation

$$F_{\beta j}[\{\lambda_{\mathbf{q}}^{\beta}\}] \approx \exp(-i\lambda_0^{\beta}N_\beta)\exp\Bigg[-\frac{N_\beta^2}{2}\sum_{\mathbf{q}\neq 0}|\lambda_{\mathbf{q}}^{\beta}|^2 S_{\mathrm{D}}^{\beta}(\mathbf{q})\Bigg] \tag{2.16}$$

where the unperturbed single-chain Debye scattering function is

$$S_{\mathrm{D}}^{\beta}(\mathbf{q}) = \frac{12}{q^2 l_\beta^2 N_\beta}\Bigg\{1 - \frac{6}{q^2 l_\beta^2 N_\beta}[1 - \exp(-q^2 l_\beta^2 N_\beta/6)]\Bigg\} \tag{2.17}$$

with the well-known long-wavelength ($\mathbf{q} \to 0$) limit

$$S_{\mathrm{D}}^{\beta}(\mathbf{q}) \to 1 - \tfrac{1}{3}R_{\mathrm{G},\beta}^{\;2}q^2, \quad \mathbf{q} \to 0 \tag{2.18}$$

providing the mean radius of gyration $R_{\mathrm{G},\beta}^{\;2} = (1/6)\,l_\beta^2 N_\beta$

of the βth polymer. For notational convenience, we define the quantity

$$G_\beta(q) = n_\beta N_\beta^2 S_D^\beta(\mathbf{q}) \qquad (2.19)$$

Equation 2.16 embodies the main assumption of the random-phase approximation within the Edwards formalism[10] whereby the single-chain correlations are replaced by those for ideal unperturbed chains. It is computationally straightforward, although algebraically tedious, to retain higher cumulants in (2.16) and thereby describe nonideality effects on the scattering factors arising from changes in chain dimensions in the blend. This is accomplished in next order by retention of cubic and quartic contributions in the $\{\lambda_\mathbf{q}^\beta\}$, while the analogous process in the diagram summation method of Benoit et al.[22] would require infinite (two-loop) diagram summations.

The integral over void positions in (2.14) is likewise performed in the lowest order approximation analogous to (2.16) to give

$$F_{\mathrm{v}j}[\{\lambda_\mathbf{q}^\mathrm{v}\}] = \int \mathrm{d}\mathbf{r}_j^\mathrm{v} \exp[-i\sum_\mathbf{q}\lambda_\mathbf{q}^\mathrm{v} \exp(i\mathbf{q}\cdot\mathbf{r}_j^\mathrm{v})] \approx \exp(-i\lambda_0^\mathrm{v}) \exp\left(-\frac{1}{2}\sum_{\mathbf{q}\neq 0} \lambda_\mathbf{q}^{\mathrm{v}\ 2}\right) \qquad (2.20)$$

Notice that (2.20) follows from (2.16) by simply taking the limit of $N_\mathrm{v} \to 1$, with the functional integral transformed into an ordinary integral over $\mathbf{r}_j^\mathrm{v}$. Substituting the approximations (2.16) and (2.20) into (2.14), we find that the integrals factor into a product of terms for each $\mathbf{q}$ (likewise in Z). Thus, the integrals over $\rho_\mathbf{q}^\beta$ and $\lambda_\mathbf{q}^\beta$ for $\mathbf{q} \neq \mathbf{k}$ cancel between the numerator and Z, leaving only the integrals in $\rho_\mathbf{k}^\beta$ and $\lambda_\mathbf{k}^\beta$

$$\begin{aligned}\langle\rho_\mathbf{k}^\mu\rho_\mathbf{k}^{\nu *}\rangle = {} & Z_\mathbf{k}^{-1}\prod_{\beta=\mathrm{A,B}}\{\int \mathrm{d}\rho_\mathbf{k}^\beta\, \mathrm{d}\rho_\mathbf{k}^{\beta *}\, \mathrm{d}\lambda_\mathbf{k}^\beta\, \mathrm{d}\lambda_\mathbf{k}^{\beta *} \times \\ & \exp[-|\lambda_\mathbf{k}^\beta|^2 G_\beta(\mathbf{k})] \exp[i(\lambda_\mathbf{k}^\beta\rho_\mathbf{k}^\beta + \lambda_\mathbf{k}^{\beta *}\rho_\mathbf{k}^{\beta *})]\}\rho_\mathbf{k}^\mu\rho_\mathbf{k}^{\nu *} \times \\ & \exp(-\rho_\mathbf{k}^\mathrm{T}\mathbf{u}\rho_\mathbf{k}^*)\int \mathrm{d}\rho_\mathbf{k}^\mathrm{v}\, \mathrm{d}\rho_\mathbf{k}^{\mathrm{v}*}\, \mathrm{d}\lambda_\mathbf{k}^\mathrm{v}\, \mathrm{d}\lambda_\mathbf{k}^{\mathrm{v}*} \exp[-n_\mathrm{v}|\lambda_\mathbf{k}^\mathrm{v}|^2] \times \\ & \exp[i(\lambda_\mathbf{k}^\mathrm{v}\rho_\mathbf{k}^\mathrm{v} + \lambda_\mathbf{k}^{\mathrm{v}*}\rho_\mathbf{k}^{\mathrm{v}*})]\, \delta(\sum_{\alpha=\mathrm{A,B,v}}\rho_\mathbf{k}^\alpha)\, \delta(\sum_{\alpha=\mathrm{A,B,v}}\rho_\mathbf{k}^{\alpha *})\end{aligned} \qquad (2.21)$$

where $Z_\mathbf{k}$ is defined as the integral in the numerator of (2.21) but without the factor of $\rho_\mathbf{k}^\mu\rho_\mathbf{k}^{\nu *}$. Equation 2.21 is similar to intermediate results of McMullen and Freed, apart from the extra δ function constraints in the right most two factors, constraints that trivially permit the evaluation of the $\rho_\mathbf{k}^\mathrm{v}$ integral. Multicomponent systems are treated by simply adding the extra components to the range of the summation indices α and β. It follows from (2.21) that the density–density correlation functions (as well as higher order analogues) may be generated from $Z_\mathbf{k}$ by differentiation

$$\langle\rho_\mathbf{k}^\alpha\rho_\mathbf{k}^{\alpha *}\rangle = -\frac{\partial \ln Z_\mathbf{k}}{\partial u_{\alpha\alpha}} \qquad (2.22a)$$

$$\langle\rho_\mathbf{k}^\alpha\rho_\mathbf{k}^{\beta *}\rangle = -\frac{1}{2}\frac{\partial \ln Z_\mathbf{k}}{\partial u_{\alpha\beta}}, \quad \alpha \neq \beta \qquad (2.22b)$$

Straightforward integration of eq 2.21 and application of (2.22) enable us to obtain the density–density correlation functions as

$$\langle\rho_\mathbf{k}^\mathrm{A}\rho_\mathbf{k}^{\mathrm{A}*}\rangle = Q_\mathbf{k}^{-1}[G_\mathrm{B}^{-1}(\mathbf{k}) + u_\mathrm{BB} + n_\mathrm{v}^{-1}] \qquad (2.23a)$$

$$\langle\rho_\mathbf{k}^\mathrm{A}\rho_\mathbf{k}^{\mathrm{B}*}\rangle = -Q_\mathbf{k}^{-1}[u_\mathrm{AB} + n_\mathrm{v}^{-1}] \qquad (2.23b)$$

where the denominator function is

$$Q_\mathbf{k} = [G_\mathrm{A}^{-1}(\mathbf{k}) + u_\mathrm{AA} + n_\mathrm{v}^{-1}][G_\mathrm{B}^{-1}(\mathbf{k}) + u_\mathrm{BB} + n_\mathrm{v}^{-1}] - [u_\mathrm{AB} + n_\mathrm{v}^{-1}]^2 \qquad (2.24)$$

While our eqs 2.9, 2.23, and 2.24 are equivalent to the two homopolymer cases of Benoit et al.[22] when the solvent is replaced by voids and monomer–void interactions are taken to vanish, refs 22 subsumes all dependence on solvent (which becomes void here) volume fractions into effective excluded-volume interactions in their eqs 17 and 18 with the implicit further implications that these excluded-volume parameters are constants at a given temperature. It is important, however, to specifically retain the void volume fraction dependence to consider questions of pressure dependence, etc. (See also section III for numerical examples.)

Since monomers and voids are taken, for simplicity, to occupy identical volumes, the volume fractions may be written as

$$\varphi_\alpha = n_\alpha N_\alpha/M, \quad \alpha = \mathrm{A, B} \qquad (2.25a)$$

$$\varphi_\mathrm{v} = n_\mathrm{v}/M \qquad (2.25b)$$

Introduce the interaction parameters

$$\chi_{\alpha\beta} = -(M/2)u_{\alpha\beta}, \quad \alpha, \beta = \mathrm{A, B} \qquad (2.26)$$

and the definitions

$$F_{\alpha\alpha} = -2\chi_{\alpha\alpha} + \frac{1}{N_\alpha\varphi_\alpha} + \frac{1}{\varphi_\mathrm{v}}, \quad \alpha = \mathrm{A, B} \qquad (2.27a)$$

$$F_\mathrm{AB} = -2\chi_\mathrm{AB} + \frac{1}{\varphi_\mathrm{v}} \qquad (2.27b)$$

$$F = F_\mathrm{AA}F_\mathrm{BB} - F_\mathrm{AB}^2 \qquad (2.28)$$

Use of (2.18) and (2.19) in the long-wavelength limit of $\mathbf{k} \to 0$ converts the denominator function of (2.24) into the expression

$$M^2 Q_\mathbf{k} \approx F + \frac{k^2}{3}\left(\frac{R_{\mathrm{G,A}}^{\ 2}}{N_\mathrm{A}\varphi_\mathrm{A}}F_\mathrm{BB} + \frac{R_{\mathrm{G,B}}^{\ 2}}{N_\mathrm{B}\varphi_\mathrm{B}}F_\mathrm{AA}\right) + O(k^4) \qquad (2.29)$$

Therefore, substitution of (2.29) into (2.23) gives the partial structure factors

$$\frac{1}{S_\mathrm{AA}(\mathbf{k})} \approx \frac{F}{F_\mathrm{BB}} + \frac{k^2}{3}\left(\frac{R_{\mathrm{G,A}}^{\ 2}}{N_\mathrm{A}\varphi_\mathrm{A}} + \frac{R_{\mathrm{G,B}}^{\ 2}F_\mathrm{AB}^{\ 2}}{N_\mathrm{B}\varphi_\mathrm{B}F_\mathrm{BB}^{\ 2}}\right) + O(k^4) \qquad (2.30a)$$

$$\frac{1}{S_\mathrm{AB}(\mathbf{k})} \approx -\frac{F}{F_\mathrm{AB}} - \frac{k^2}{3}\left(\frac{R_{\mathrm{G,A}}^{\ 2}F_\mathrm{BB}}{N_\mathrm{A}\varphi_\mathrm{A}F_\mathrm{AB}} + \frac{R_{\mathrm{G,B}}^{\ 2}F_\mathrm{AA}}{N_\mathrm{B}\varphi_\mathrm{B}F_\mathrm{AB}}\right) + O(k^4) \qquad (2.30b)$$

The $\mathbf{k} \to 0$ limit intercepts in (2.30) are identical with the expressions obtained independently by Dudowicz and Freed[9] from purely thermodynamic considerations based on a compressible Flory–Huggins model and by Benoit et al.[22] for polymer solutions if the solvent is replaced by free volume and the monomer–void interactions are set to zero. The departure from unity of the additional factors of $F_\mathrm{AB}^2/F_\mathrm{BB}^2$ in (2.30a) and of $F_\mathrm{BB}/F_\mathrm{AA}$ and $F_\mathrm{AA}/F_\mathrm{AB}$ provides corrections to the incompressible RPA correlation lengths due to blend compressibility. Notice also that the compressible blend generally has $S_\mathrm{AB}(\mathbf{k}) \neq -S_\mathrm{AA}(\mathbf{k})$ in contrast to the incompressible case where these partial structure factors are equal.

In general, both polymer species may scatter light or neutrons with different efficiencies. Thus, it is necessary to introduce the effective blend structure factor

$$S(\mathbf{k}) = (\alpha_A - \alpha_B)^{-2}[\alpha_A{}^2 S_{AA}(\mathbf{k}) + 2\alpha_A\alpha_B S_{AB}(\mathbf{k}) + \alpha_B{}^2 S_{BB}(\mathbf{k})] \quad (2.31)$$

where the α_i, i = A, B, are scattering lengths for monomers of chains i. It is convenient to define the reduced scattering lengths

$$p_i = \frac{\alpha_i}{\alpha_A - \alpha_B}, \quad i = \mathrm{A, B} \quad (2.32)$$

Then, inserting (2.30) and (2.32) into (2.31) produces the final experimental scattering function for the compressible blend as

$$\frac{1}{S(\mathbf{k})} = \frac{F}{R} + \frac{k^2}{3R^2}\left[\frac{R_{G,A}{}^2}{N_A\varphi_A}(p_A F_{BB} - p_B F_{AB})^2 + \frac{R_{G,B}{}^2}{N_B\varphi_B}(p_B F_{AA} - p_A F_{AB})^2\right] + O(k^4) \quad (2.33)$$

where

$$R = p_A{}^2 F_{BB} - 2p_A p_B F_{AB} + p_B{}^2 F_{AA} \quad (2.34)$$

III. Discussion of Results for the Blend

We begin by comparing the compressible and incompressible RPA's. The incompressible blend has volume fractions

$$\Phi_\alpha = n_\alpha N_\alpha/(n_A N_A + n_B N_B), \quad \alpha = \mathrm{A, B} \quad (3.1)$$

and the well-known incompressible RPA structure factor[1,2]

$$\frac{1}{S(\mathbf{k})} = \frac{1}{N_A\Phi_A S_D{}^A(\mathbf{k})} + \frac{1}{N_B\Phi_B S_D{}^B(\mathbf{k})} - 2\chi_{FH} \quad (3.2)$$

where the Flory interaction parameter is

$$\chi_{FH} = (M/2)(2u_{AB} - u_{AA} - u_{BB}) = \chi_{AA} + \chi_{BB} - 2\chi_{AB} \quad (3.3)$$

The $\mathbf{k} \to 0$ limit of (3.2) is used to define the correlation length $\xi_{RPA}{}^2$

$$\frac{1}{S(\mathbf{k})} = \frac{1}{N_A\Phi_A} + \frac{1}{N_B\Phi_B} - 2\chi_{FH} + \frac{1}{3}k^2\xi_{RPA}{}^2 + O(k^4) \quad (3.4)$$

$$\xi_{RPA}{}^2 = \frac{R_{G,A}{}^2}{N_A\Phi_A} + \frac{R_{G,B}{}^2}{N_B\Phi_B} \quad (3.5)$$

A. Effective Interactions and Correlation Lengths in the Compressible Blend. Consider now a compressible blend with the structure factors given in (2.30) that is analyzed in the traditional fashion by the incompressible RPA of (3.2)–(3.4). Thus, for instance the AA structure factor is written as

$$\frac{1}{S_{AA}(\mathbf{k})} = \frac{1}{N_A\varphi_A} + \frac{1}{N_B\varphi_B} - 2\chi_{\mathrm{eff}}{}^{AA} + \frac{1}{3}k^2\xi_{AA}{}^2 + O(k^4) \quad (3.6)$$

Comparing (2.30a) with (3.6) and use of the relationship

$$\varphi_\alpha = (1 - \varphi_v)\Phi_\alpha \quad (3.7)$$

show that $\chi_{\mathrm{eff}}{}^{AA}$ is identical with the expression derived by Dudowicz and Freed from the Flory–Huggins model free energy for a compressible blend. This $\chi_{\mathrm{eff}}{}^{AA}$ equals the sum of (3.3) plus two correction terms. The first correction accounts for the difference in volume fractions Φ_α for the incompressible blend ($\Phi_A + \Phi_B = 1$) and those of a compressible system where $\varphi_A + \varphi_B = 1 - \varphi_v$.[16] The second correection accounts for the fact that the creation of free volume removes polymer–polymer contacts and makes $\chi_{\mathrm{eff}}{}^{AA}$ depend on the three independent interaction parameters. Similarly, comparing (2.30a) with (3.5) shows that $\xi_{AA}{}^2$ can be written in the form

$$\xi_{AA}{}^2 = \xi_{RPA}{}^2 + \frac{R_{G,A}{}^2\varphi_v}{N_A\Phi_A(1 - \varphi_v)} + \frac{R_{G,B}{}^2}{N_B\Phi_B} \times \left[\frac{\left(-2\chi_{AB} + \dfrac{1}{\varphi_v}\right)^2}{(1 - \varphi_v)\left\{-2\chi_{BB} + \dfrac{1}{N_B\Phi_B(1 - \varphi_v)} + \dfrac{1}{\varphi_v}\right\}^2} - 1\right] \quad (3.8)$$

Apart from the difference between the volume fractions φ_α and Φ_α, so long as φ_B is not so small and φ_v is not too large, the right most correction term in (3.8) becomes

$$\frac{R_{G,B}{}^2\varphi_v}{N_B\Phi_B(1 - \varphi_v)}\left[1 + 4(\chi_{BB} - \chi_{AB}) - \frac{2}{N_B\Phi_B(1 - \varphi_v)}\right] + O(\varphi_v{}^2) \quad (3.8a)$$

and is generally probably small. Compressibility cannot, therefore, describe observed deviations from the standard RPA that have been ascribed to the nonzero range of the polymer–polymer interactions.[17]

Compressible blends have $S_{AA}(\mathbf{k})$ depart from $-S_{AB}(\mathbf{k})$, thereby differing from the incompressible case where they are equal. Unfortunately, $S_{AB}(\mathbf{k})$ is not readily determined by neutron scattering, but analysis according to the above procedure would yield a $\chi_{\mathrm{eff}}{}^{AB}$ that differs from $\chi_{\mathrm{eff}}{}^{AA}$ and a correlation length $\xi_{AB}{}^2$ that likewise differs slightly from $\xi_{RPA}{}^2$ in terms of order φ_v multiplied by a weighted average of the two components' radii of gyration. Because of the difference between $S_{AA}(\mathbf{k})$ and $-S_{AB}(\mathbf{k})$ and the fact that both components of the blend generally produce some scattering, the actual measured structure factor is the weighted average given in (2.31). This leads to somewhat more complicated expressions for χ_{eff} and $\xi_{\mathrm{eff}}{}^2$ from (2.33) than the expressions presented above in the ideal limit where only component A may scatter the incident neutrons or radiation.

The above analysis, along with that of Dudowicz and Freed, indicates that compressibility may have a substantial influence on the interpretation of the composition and molecular weight dependence of χ_{eff}, but the corrections to $\xi_{RPA}{}^2$ do not appear to be so great. However, the correlation lengths figure centrally into theories of the phase separation and interfacial profile of binary blends[3-5] and is in this case that compressibility may lead to stronger consequences. The correction terms in (3.8a) are proportional to φ_v and therefore may become considerable near the free surface of a binary blend.

B. Applications to Interfacial Profiles in Phase-Separated Blends. The incompressible blend RPA is used to express the inhomogeneous system free energy in terms of $\varphi = \Phi_A$ and $\Phi_B = 1 - \Phi_A$ as[18]

$$\frac{\Delta F}{kT} = \int \mathrm{d}\mathbf{r}\left\{f[\varphi(\mathbf{r})] + \frac{1}{6}\xi_{RPA}{}^2[\nabla\varphi(\mathbf{r})]^2\right\} \quad (3.9)$$

where $f[\varphi(\mathbf{r})]$ is the free energy functional of a homogeneous blend and $\xi_{RPA}{}^2$ is given by (3.5). While the square gradient term in (3.9) remains finite as is evident from the identity

$$\frac{1}{6}\xi_{RPA}{}^2(\nabla\varphi)^2 = \frac{1}{9}[l_A{}^2(\nabla\varphi^{1/2})^2 + l_B{}^2(\nabla(1 - \varphi)^{1/2})^2] \quad (3.10)$$

Eq 3.9 cannot possibly properly describe the transition to a pure substance in the limit of $\varphi \to 0$ because the RPA in this limit yields an incompressible rather than a compressible pure B phase. This deficiency precludes the incompressible RPA from describing such interesting phenomena as the free surface of a melt. The treatment of these and many other problems requires the generalization to compressible systems where φ_A and φ_B are independent variables.[19]

A full theory of the interfacial profile of a compressible binary blend is beyond the scope of the present article, but it is pertinent to mention some results in order to understand how the square gradient coefficients properly tend to the pure-component limits as they must. The treatment employs the rigorous density functional methods of McMullen and Freed[19] with extensions that are applicable to cases of thick interfaces (interfacial widths that exceed the unperturbed chain radii of gyration).[25] Upon incorporating compressibility into the theory, eq 3.9 is converted into[25]

$$\frac{\Delta F}{kT} = \int \mathrm{d}\mathbf{r}\left\{f[\varphi_A(\mathbf{r}),\varphi_B(\mathbf{r})] + \frac{{R_{G,A}}^2}{6\varphi_A N_A}[\nabla\varphi_A(\mathbf{r})]^2 + \frac{{R_{G,B}}^2}{6\varphi_B N_B}[\nabla\varphi_B(\mathbf{r})]^2\right\} \quad (3.11)$$

where $f[\varphi_A(\mathbf{r}),\varphi_B(\mathbf{r})]$ is the appropriate homogeneous blend compressible free energy functional that is obtained[25] from the density functional formalism[19] as the compressible local Flory–Huggins free energy

$$f[\varphi_A(\mathbf{r}),\varphi_B(\mathbf{r})] = \frac{\varphi_A(\mathbf{r})}{N_A}\ln[\varphi_A(\mathbf{r})] + \frac{\varphi_B(\mathbf{r})}{N_B}\ln[\varphi_B(\mathbf{r})] + \varphi_v(\mathbf{r})\ln[\varphi_v(\mathbf{r})] - \chi_{AA}[\varphi_A(\mathbf{r})]^2 - \chi_{BB}[\varphi_B(\mathbf{r})]^2 - 2\chi_{AB}\varphi_A(\mathbf{r})\,\varphi_B(\mathbf{r}) \quad (3.12)$$

The coefficients in (3.11) ensure that the incompressible blend limit is recovered when $\varphi_v \to 0$, $\varphi_A \to \varphi$, and $\varphi_B \to 1 - \varphi$, whereupon this equation reduces to (3.9) as it must. Considerations like those applied to (3.10) above permit us to apply (3.11) in the melt limit, where either φ_A or φ_B tends toward zero, and this simply produces

$$\frac{\Delta F}{kT} = \int \mathrm{d}\mathbf{r}\left\{f[\varphi_A(\mathbf{r})] + \frac{{R_{G,A}}^2}{6\varphi_A N_A}[\nabla\varphi_A(\mathbf{r})]^2\right\} \quad (3.13)$$

which contains the correct correlation length appropriate to a compressible A melt. Consequently, a compressible RPA is required for treatment of free surfaces of melts and blends, and possibly for interfaces in phase-separated systems where the transition is accompanied by a considerable change in volume.

C. Illustration of the Influence of Compressibility on the Blend Scattering Function. Dudowicz and Freed[9] find that the compressible blend $S_{AA}(0)$ differs maximally from the incompressible case when $|\chi_{AA} - \chi_{BB}|$ is largest. Hence, the greatest deviations between the two $S_{AA}(\mathbf{k})$ should also appear for this highly unsymmetrical situation. For convenience, we illustrate $S_{AA}(\mathbf{k})$ in Figures 1 and 2 for a binary blend with $N_A = N_B = 100$, $\varphi_A = \varphi_B$, and $l_A = l_B$, but $\chi_{AA} = 2.0$ and $\chi_{BB} = 1.8$. (This is still an unsymmetrical blend because $\chi_{AA} \neq \chi_{BB}$). Figure 1 has $\chi_{FH} = 0$ and exhibits significant deviations between the incompressible $S_{AA}(\mathbf{k})$ for $\varphi_v = 0$ and the compressible cases for $\varphi_v = 0.05$ and 0.10. Sariban and Binder[20] discuss the scattering functions for a binary blend with free volume under the assumption (adequate for the analysis of their Monte Carlo simulations) that the free-volume fraction, φ_v, is constant. In this case the single effective interaction parameter, χ_{eff}, is renormalized as $\chi_{eff} = \chi(1 - \varphi_v)$, and consequently it would be expected that the incompressible $S_{AA}(0)$ should be the largest in Figures 1 and 2. The opposite actually appears in these figures and indicates the importance of a more complete treatment of the compressible blend thermodynamics as given by Dudowicz and Freed.[9] Figure 2 has $\chi_{FH} = 0.018$ and therefore represents a situation closer to the phase-separation temperature than that in Figure 1. Compressibility introduces significant quantitative (but not qualitative) differences in the range of smaller $k^2R_G^2$. The large k limit of $S_{AA}(\mathbf{k})$ behaves as k^{-2} only at rather high values of $k^2R_G^2$, and it is perhaps useful to specialize (2.9), (2.23a), and (2.24) to this large k limit, where we obtain

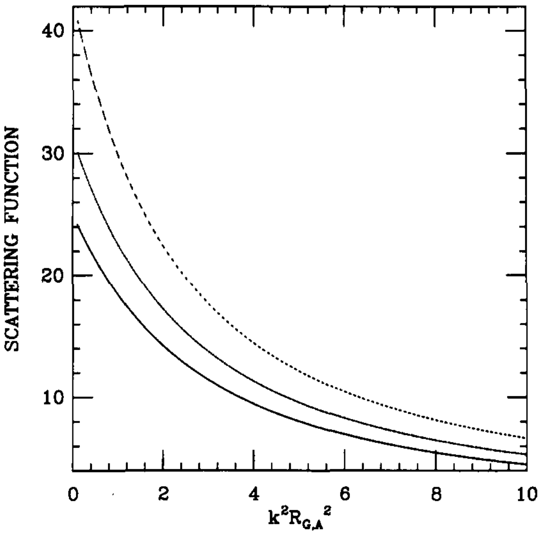

Figure 1. Coherent scattering function, $S_{AA}(\mathbf{k})$, as a function of $k^2{R_{G,A}}^2$ for a blend with $\chi_{AA} = 2.0$, $\chi_{BB} = 1.8$, $N_A = N_B = 100$, $l_A = l_B$, $\varphi_A = \varphi_B$, and $\chi_{FH} = 0$ and for $\varphi_v = 0$ (incompressible), 0.05, and 0.10. The solid curve is for the incompressible case ($\varphi_v = 0$), the dotted curve is for $\varphi_v = 0.05$, and the dashed curve is for $\varphi_v = 0.1$.

$$\lim_{k\to\infty} S_{AA}(\mathbf{k}) = \left\{1 + \varphi_v\left[\frac{k^2{R_{G,B}}^2}{2N_B\varphi_B} - 2\chi_{BB}\right]\right\}\left\{\frac{k^2{R_{G,A}}^2}{2N_A\varphi_A} + \frac{k^2{R_{G,B}}^2}{2N_B\varphi_B} - 2\chi_{FH} + \varphi_v\left[\left(\frac{k^2{R_{G,B}}^2}{2N_B\varphi_B} - 2\chi_{BB}\right) \times \left(\frac{k^2{R_{G,A}}^2}{2N_A\varphi_A} - 2\chi_{AA}\right) - 4{\chi_{AB}}^2\right]\right\}^{-1} \quad (3.14)$$

which requires rather large $k^2{R_{G,A}}^2/2N_A\varphi_A$ for the asymptotic k^{-2} limit to be reached. This large k limit may have implications for experimental analyses in which the nonzero base line for large k is used as a subtraction to account for scattering from simple density fluctuations.[23] When applied to the above $S(0)$, alternative subtraction methods[24] are found by Dudowicz and Freed[9] to have minor influence on the zero-angle scattering, so these are not discussed further here.

Figures 1 and 2 could be analyzed by using in the incompressible RPA theory an effective interaction parameter, χ_{eff}, as given in ref 9, that applies to the compressible system and that would be obtained from the extrapolated zero-angle scattering. This amounts to shifting the incompressible RPA curve to have the same value as $S(0)$ for the compressible cases and thus also to have the same spinoidal temperature. While this curve shifting would diminish the difference between the compressible RPA scattering curves and the adjusted incompressible ones in Figure 1, large differences would persist in Figure 2. Consequently, it is generally impossible to subsume the compressibility effects solely into a compressible χ_{eff}.

D. Generalization to Blends in Which Monomers and Voids Occupy Different Volumes. The A and B monomers, in general, may occupy volumes that differ

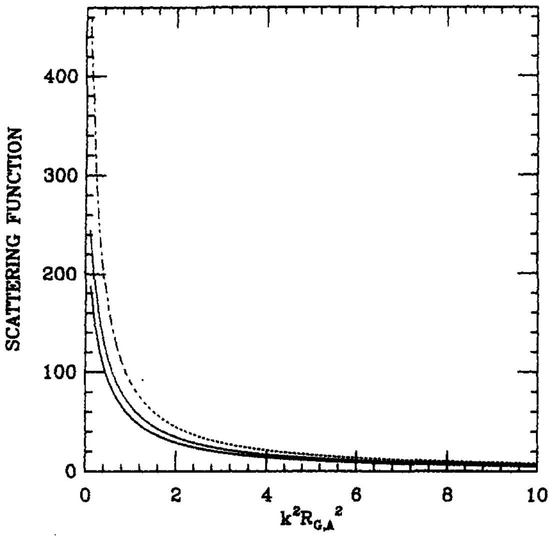

Figure 2. Same as in Figure 1 but with $\chi_{FH} = 0.018$.

from each other and from that of the voids; i.e., $v_A \neq v_B \neq v_v$. The generalization of the RPA structure factors presented in section III to this general case follows straightforwardly by replacing the constraint Δ of (2.13) by

$$\Delta \equiv \delta(\sum_{\alpha=A,B,v} \rho_0{}^{\alpha} v_{\alpha} - 1)\prod_{\mathbf{q}\neq 0}\delta(\sum_{\alpha=A,B,v} \rho_{\mathbf{q}}{}^{\alpha} v_{\alpha}) \qquad (3.15)$$

The calculation of the RPA structure factors then follows identically as in section III and yields

$$\langle \rho_{\mathbf{k}}{}^{A}\rho_{\mathbf{k}}{}^{A*}\rangle = \frac{1}{v_A{}^2}Q_{\mathbf{k}}{}^{-1}\left[\frac{1}{n_B N_B{}^2 v_B{}^2 S_D{}^B(\mathbf{k})} + \frac{u_{BB}}{v_B{}^2} + \frac{1}{n_v v_v{}^2}\right] \qquad (3.16a)$$

$$\langle \rho_{\mathbf{k}}{}^{A}\rho_{\mathbf{k}}{}^{B*}\rangle = -\frac{1}{v_A v_B}Q_{\mathbf{k}}{}^{-1}\left[\frac{u_{AB}}{v_A v_B} + \frac{1}{n_v v_v{}^2}\right] \qquad (3.16b)$$

where

$$Q_{\mathbf{k}} = \left[\frac{1}{n_A N_A{}^2 v_A{}^2 S_D{}^A(\mathbf{k})} + \frac{u_{AA}}{v_A{}^2} + \frac{1}{n_v v_v{}^2}\right] \times \left[\frac{1}{n_B N_B{}^2 v_B{}^2 S_D{}^B(\mathbf{k})} + \frac{u_{BB}}{v_B{}^2} + \frac{1}{n_v v_v{}^2}\right] - \left[\frac{u_{AB}}{v_A v_B} + \frac{1}{n_v v_v{}^2}\right]^2 \qquad (3.17)$$

In the incompressible limit, eq 3.16a reduces to

$$\frac{\rho_0}{v_A{}^2}S_{AA}{}^{-1}(\mathbf{k}) = \frac{1}{N_A\varphi_A v_A S_D{}^A(\mathbf{k})} + \frac{u_{AA}V}{v_A{}^2} + \frac{1}{N_B\varphi_B v_B S_D{}^B(\mathbf{k})} + \frac{u_{BB}V}{v_B{}^2} + \frac{2u_{AB}V}{v_A v_B} \qquad (3.18)$$

where φ_α is the density fraction of α monomers as defined by

$$\varphi_\alpha = n_\alpha N_\alpha v_\alpha / V \qquad (3.19)$$

Equation 3.18 is equivalent to the forms used in the literature with the replacement

$$\frac{2\chi}{v_0} \equiv V\left(\frac{2u_{AB}}{v_A v_B} - \frac{u_{AA}}{v_A{}^2} - \frac{u_{BB}}{v_B{}^2}\right) \qquad (3.20)$$

E. Comparison with RISM Partial Structure Factors. After acceptance of this paper, an analysis was made[26] of the relationship of our compressible RPA structure factors to those which emerge from the RISM integral equation formulation of Curro and Schweizer.[27] The binary blend partial structure factors of the RISM theory are summarized in eqs 2.16 to 2.18 of ref 27a and need not be reporduced here. They are written in terms of the ideal-chain scattering functions, the monomer densities, and the Fourier transforms of the direct correlation functions $\hat{C}_{\alpha\beta}(k)$ which are determined from the approximate integral equation theory. It is natural to expect that the RPA follows from a mean spherical type approximation for these direct correlation function. Given the pointlike character of the interactions in the Edwards Hamiltonian of (2.4), the appropriate correspondence turns out to be[26]

$$\hat{C}_{\alpha\beta}(k) \rightarrow 2\chi_{\alpha\beta} - (\varphi_v)^{-1} \qquad (3.21)$$

for the simplest case in which monomers and voids are taken to have identical volumes. Thus, introduction of (3.21) into eqs 2.16 to 2.18 of ref 27a lead identically to our compressible blend RPA partial structure factors. The calculations of Curro and Schweizer have considerable excess free volumes (i.e., φ_v), and they note[27a] that the incompressible RPA structure factors are often in poor agreement with the RISM calculations. We look forward to comparisons of RISM theory with the approximation in (3.21) in order to determine the conditions under which the RPA becomes inadequate and further theoretical studies are necessary.

IV. Compressible RPA for Block Copolymers

One potentially interesting application of the compressible RPA is to describe the pressure dependence of microphase separation in block copolymers.[2,6] The computation of the structure factor for a compressible block copolymer melt follows as a straightforward but tedious generalization of the methods described in section II. Thus, we only sketch the main results.

The Hamiltonian for block copolymers is

$$H = \frac{3}{2}\sum_{j=1}^{n}[\int_0^{L_A}\mathrm{d}\tau_j\,(l_A)^{-1}|\dot{\mathbf{r}}_j(\tau_j)|^2 + \int_{L_A}^{L_A+L_B}\mathrm{d}\tau_j\,(l_B)^{-1}|\dot{\mathbf{r}}_j(\tau_j)|^2] + \frac{1}{2}\sum_{j_1,j_2=1}^{n}\{v_{AA}\int_0^{L_A}\mathrm{d}\tau_{j_1}\,(l_A)^{-1}\int_0^{L_A}\mathrm{d}\tau_{j_2}\,(l_A)^{-1} + v_{BB}\int_{L_A}^{L_A+L_B}\mathrm{d}\tau_{j_1}\,(l_B)^{-1}\int_{L_A}^{L_A+L_B}\mathrm{d}\tau_{j_2}\,(l_B)^{-1} + 2v_{AB}\int_0^{L_A}\mathrm{d}\tau_{j_1}\,(l_A)^{-1}\int_{L_A}^{L_A+L_B}\mathrm{d}\tau_{j_2}\,(l_B)^{-1}\}\,\delta[\mathbf{r}_{j_1}(\tau_{j_1}) - \mathbf{r}_{j_2}(\tau_{j_2})] \qquad (4.1)$$

and is obtained from (2.4) by merely attaching the end of an A chain to a B chain. Following the steps in (2.5)–(2.22), we obtain

$$\langle \rho_{\mathbf{k}}{}^{A}\rho_{\mathbf{k}}{}^{A*}\rangle = Q'_{\mathbf{k}}{}^{-1}\{(u_{BB} + n_v{}^{-1})[G_A(\mathbf{k})\,G_B(\mathbf{k}) - G_{AB}{}^2(\mathbf{k})] + G_A(\mathbf{k})\} \qquad (4.2a)$$

$$\langle \rho_{\mathbf{k}}{}^{A}\rho_{\mathbf{k}}{}^{B*}\rangle = -Q'_{\mathbf{k}}{}^{-1}\{(u_{AB} + n_v{}^{-1})[G_A(\mathbf{k})\,G_B(\mathbf{k}) - G_{AB}{}^2(\mathbf{k})] - G_{AB}(\mathbf{k})\} \qquad (4.2b)$$

where the denominator

$$Q'_{\mathbf{k}} = [(u_{AA} + n_v{}^{-1})(u_{BB} + n_v{}^{-1}) - (u_{AB} + n_v{}^{-1})^2] \times [G_A(\mathbf{k})\,G_B(\mathbf{k}) - G_{AB}{}^2(\mathbf{k})] + G_A(\mathbf{k})(u_{AA} + n_v{}^{-1}) + G_B(\mathbf{k})(u_{BB} + n_v{}^{-1}) + 2G_{AB}(\mathbf{k})(u_{AB} + n_v{}^{-1}) + 1 \qquad (4.3)$$

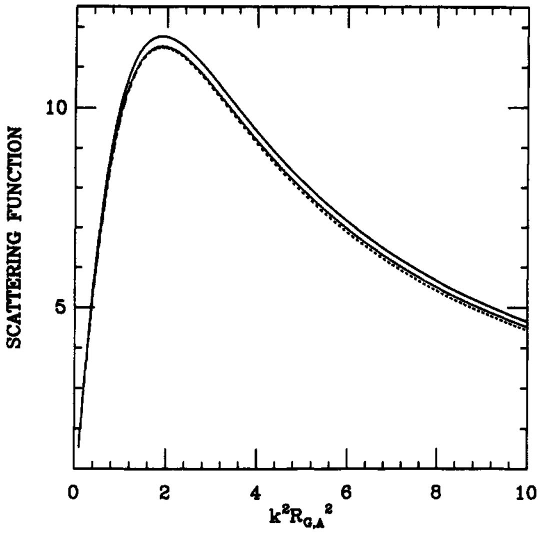

Figure 3. $S_{AA}(\mathbf{k})$ as a function of $k^2R_{G,A}^2$ for a diblock copolymer melt. Same parameters as in Figure 1, except that $\chi_{FH} = 0.01$.

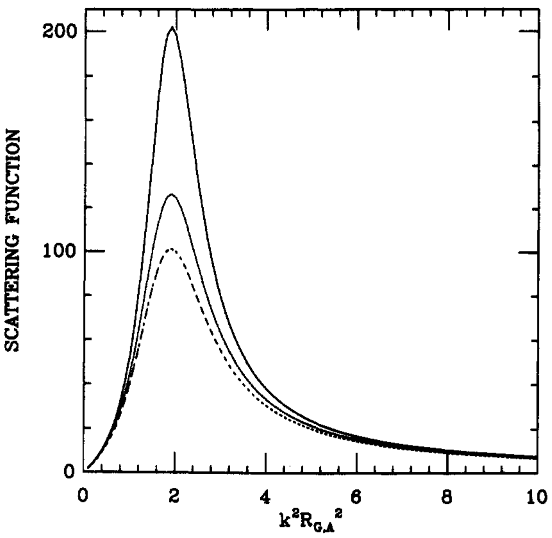

Figure 4. As in Figure 3, except that $\chi_{FH} = 0.05$.

is written in terms of the function

$$G_{AB}(\mathbf{k}) = nN_AN_B\left[1 - \frac{1}{2}k^2R_{G,A}^2S_D^A(\mathbf{k})\right] \times \left[1 - \frac{1}{2}k^2R_{G,B}^2S_D^B(\mathbf{k})\right] \quad (4.4)$$

and the radii of gyration are defined following eq 2.18. The mean-square radius of gyration for the block copolymer is given as

$$R_G^2 = R_{G,A}^2 + R_{G,B}^2 \quad (4.5)$$

It is straightforward, albeit tedious, to obtain the compressible higher order block copolymer density-density correlation functions that are necessary in theories of microphase separation.[2]

The incompressible limit is obtained from (4.2) by passage to the limit of $n_v \to 0$, in which case eq 4.2 reduces to

$$\frac{1}{S_{AA}(\mathbf{k})} = -\frac{1}{S_{AB}(\mathbf{k})} = M\frac{G_A(\mathbf{k}) + G_B(\mathbf{k}) + 2G_{AB}(\mathbf{k})}{G_A(\mathbf{k})\,G_B(\mathbf{k}) - G_{AB}^2(\mathbf{k})} - 2\chi_{FH} \quad (4.6)$$

which may be shown to be identical with the incompressible RPA structure factor as given by eq 21 of de la Cruz and Sanchez.[6] Compressibility corrections may be evident from rewriting, for instance, (4.2a) in the form

$$\frac{1}{S_{AA}(\mathbf{k})} = \frac{\left\{M\dfrac{G_A + G_B + 2G_{AB}}{G_AG_B - G_{AB}^2} - 2\chi_{FH}\right\} + C_1}{1 + C_2} \quad (4.7)$$

where the argument ($\mathbf{k}$) is dropped in the G's for convenience and the correction terms are explicitly represented as

$$C_1 = Mn_v\left[u_{AA}u_{BB} - u_{AB}^2 + \frac{u_{AA}G_A + u_{BB}G_B + 2u_{AB}G_{AB} + 1}{G_AG_B - G_{AB}^2}\right] \quad (4.7a)$$

$$C_2 = n_v\left[u_{BB} + \frac{G_A}{G_AG_B - G_{AB}^2}\right] \quad (4.7b)$$

One particular limit of interest is the $\mathbf{k} \to 0$ limit where $S_{AA}(\mathbf{k})$ vanishes for incompressible block copolymers but where (4.7) produces the nonzero limit

$$S_{AA}(0) = N_A\varphi_A\varphi_v[N_A\varphi_A(1 - 2\chi_{AA}\varphi_v) + N_B\varphi_B(1 - 2\chi_{BB}\varphi_v) + 2N_A\varphi_B(1 - 2\chi_{AB}\varphi_v) + \varphi_v]^{-1} \quad (4.8)$$

which may explain experimental observations of values for $S_{AA}(0)$ that are somewhat in excess of estimates computed as arising from polydispersity.[21] Experimental difficulties preclude direct determination of $S_{AA}(0)$, which is usually obtained from extrapolations to $k \to 0$. Because both k and φ_v are small quantities, it is perhaps most useful if both the numerator and denominator of (4.7) are separately expanded in k to obtain

$$S_{AA}(\mathbf{k}) = \varphi_AN_A\left\{\frac{2}{3}k^2R_G^2N_B\varphi_B(1 - 2\chi_{BB}\varphi_v) + \varphi_v - \frac{1}{3}\varphi_vk^2R_{G,A}^2\right\}\Big\{(N_A + N_B)(1 - \varphi_v) - \frac{1}{3}k^2[N_A\varphi_AR_{G,A}^2 + N_B\varphi_BR_{G,B}^2 + 3N_A\varphi_BR_G^2 + 4\chi_{FH}N_A\varphi_AN_B\varphi_BR_G^2] + \varphi_v - 2\varphi_v[\chi_{AA}N_A\varphi_A + \chi_{BB}N_B\varphi_B + 2\chi_{AB}(N_A\varphi_B + N_B\varphi_A)] + \frac{2}{3}k^2\varphi_v[\chi_{AA}N_A\varphi_AR_{G,A}^2 + \chi_{BB}N_B\varphi_BR_{G,B}^2 + 3\chi_{AB}N_A\varphi_BR_G^2] + \frac{8}{3}\varphi_vk^2R_G^2N_A\varphi_AN_B\varphi_B(\chi_{AA}\chi_{BB} - \chi_{AB}^2)\Big\}^{-1}, \quad k \to 0 \quad (4.9)$$

which is written in terms of experimentally relevant variables.

The full expression (4.7) is rather involved, and the behavior of the scattering function is illustrated in Figures 3–5 for quasi-symmetric diblocks with $N_A = N_B$ and $l_A = l_B$ but $\chi_{AA} = 2.0$ and $\chi_{BB} = 1.8$. Figures 3 and 4 have $N_A = 100$ and χ_{FH} equal, respectively, to 0.01 and 0.05. The former is rather far from the microphase-separation transition, and the compressible and incompressible $S_{AA}(\mathbf{k})$ curves in Figure 3 are rather similar to each other. The differences are quite significant in Figure 4, which corresponds to a situation that is closer to the transition. Figures 3 and 4 have the incompressible curve lying above the compressible ones, but Figure 5 presents a situation (for $N_A = N_B = 1000$ and $\chi_{FH} = 0.001$) in which the ordering is reversed. There are slight shifts with φ_v of the q corresponding to the maxima in Figures 4 and 5. It will be interesting to determine the influence these compressibility corrections have on predictions of microphase separation in block copolymers and, in particular, on the previously unexplored nature of the pressure dependence

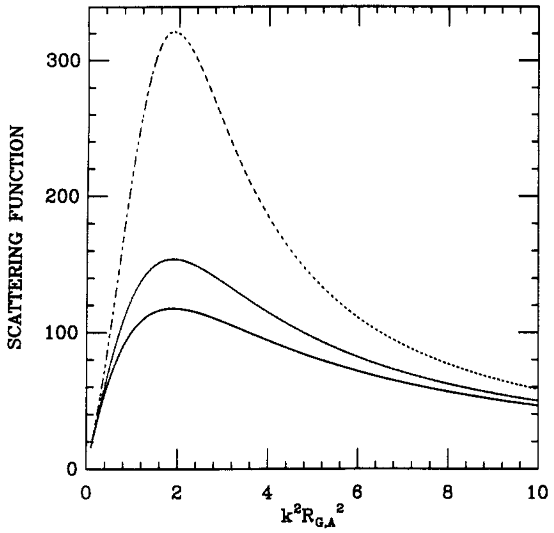

Figure 5. As in Figure 3, except that $N_A = N_B = 1000$ and $\chi_{FH} = 0.001$.

of this phenomenon. (Comparisons with neutron-scattering data should utilize the effective structure factor (2.31) because the A and B components no longer have the same structure factors for compressible systems.)

V. Discussion

The compressible random-phase approximation (RPA) scattering functions for binary blends and diblock copolymers are generalized by imposing upper bound constraints on total density fluctuations at a point. These constraints introduce into the RPA structure factors the energetic cost, associated with the creation of free volume, that is absent in two prior works on the role of compressibility on scattering functions, effective screened interactions, and labeled chain radii of gyration. The extrapolated zero-angle scattering corresponds to that derivable by thermodynamics from a compressible Flory–Huggins model.[9,22] If such a compressible system is analyzed by using the conventional incompressible RPA model, the effective interaction parameter so deduced incurs a spurious molecular weight and composition dependence because the incompressible model is inadequate for describing the extrapolated zero-angle scattering, which depends on three separate polymer–polymer interaction parameters in the compressible case. The compressible block copolymer structure factor, for instance, is nonzero in the $\mathbf{k} \to 0$ limit, while it vanishes in this limit for incompressible polymers.

The leading small-angle scattering provides a definition of the correlation length and the radii of gyration of individual chains, and here compressibility leads to very small and probably unmeasurable corrections to the incompressible RPA. Nevertheless, these leading correction terms are essential ingredients in theories of interfacial profiles. Thus, the compressible RPA structure factors may yield significant effects, especially in density profiles near free surfaces (polymer–vacuum) or in phase separations with moderate volume changes. It is also of interest to apply the compressible RPA for studying the pressure dependence of these phase separations. The RPA approximation has been used to consider the role of density fluctuations on the thermodynamics[11] and phase behavior of polymer systems. It is straightforward to introduce compressibility into treatments of contributions from the density fluctuations based upon the present RPA formalism.

The calculations proceed by using the Edwards style path integral treatment of the screening of polymer excluded volume. Other properties, such as the screened interactions and individual chain radii, may likewise be considered by using this formalism, and calculations are possible to higher orders when necessary. Further refinements might involve the treatment of the nonzero extent of both monomers and voids, but this poses quite severe additional mathematical difficulties in order to provide a much more realistic description of the blend, etc., thermodynamics, and structure.

Significant differences between compressible and incompressible RPA structure factors arise in binary blends and diblock copolymer melts when the intraspecies interaction parameters differ considerably, and the differences are magnified closer to phase- or microphase-separation transitions, in part, because of the shift in the transition temperature that is induced by the introduction into the theory of compressibility. Analysis of experimental data with the compressible RPA structure factors is expected to be more complicated than for the incompressible case because of the presence of the three independent interaction parameters. It will probably be necessary to supplement neutron scattering experiments with thermodynamic data for these systems in order to overdetermine these three temperature- and composition-dependent parameters.[26]

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