Elastic scattering from asymmetric, polydisperse block copolymer systems in the disordered state

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We present the scattering function for AB diblock copolymers, and their mixtures with homopolymers A and/or B, in the single-phase state. The calculation is a generalization of earlier random-phase approximation calculations to include differences in monomer volumes and statistical segment lengths, as well as homopolymer molecular-weight distributions and copolymer composition distributions. Their individual and combined effects on the scattering profiles $I(q)$ and on the Flory interaction parameter determined from $I(q)$ are discussed. Using poly(styrene-*b*-isoprene) as a specific example, we found that for pure block copolymer the asymmetry effects are negligible if the volume fraction of one of the blocks, f_A, is close to 0.5, but that they become significant as f_A approaches zero or unity. For a blend, we found asymmetry effects over a wide range of system characteristics.

(Keywords: block copolymer; blends; small-angle X-ray scattering; small-angle neutron scattering; χ parameter random-phase approximation)

INTRODUCTION

Investigation of the spectrum of thermally induced spatial composition fluctuations of AB block copolymers and their mixtures with corresponding homopolymers A and/or B in a bulk, disordered, single phase is an area of active research in polymer physics. The spectrum can be studied experimentally by small-angle X-ray scattering (SAXS)[1] and small-angle neutron scattering (SANS)[2]. The scattering profile can depend on the constituent molecules' architectures, average degrees of polymerization as well as molecular-weight distributions, statistical segment lengths a_κ, monomer volumes v_κ and Flory interaction parameter χ.

A theoretical treatment of scattering from binary homopolymer blends was given by de Gennes[3] for the case of equal statistical segment lengths and monomer volumes. This case is what we refer to as 'symmetric' in this paper. It was generalized to asymmetric homopolymer blends (unequal monomer volumes) by Warner *et al.*[4] and Shibayama *et al.*[5]. Scattering from monodisperse, symmetric AB diblock copolymers has been treated by Leibler[6] and Fredrickson and Helfand[7]. The Leibler theory was generalized to polydisperse symmetric copolymers by Leibler and Benoit[8] and Bates and Hartney[9], as well as by Mori *et al.*[10], who also introduced a partial correction for asymmetry (discussed in the fourth section). The Leibler theory was also generalized by Bates *et al.*[11] to monodisperse but asymmetric copolymers. Hong and Noolandi formally treated polydisperse, asymmetric copolymers[12], but concentrated on the effects of polydispersity. Symmetric, copolymer/homopolymer blends have been treated by Leibler and Benoit[8] and Benoit *et al.*[13].

In this paper we generalize the scattering equation, taking into account the combined effects of polydispersity and asymmetry for diblock copolymer/homopolymer blends. Using the Schultz–Zimm molecular-weight distributions, we demonstrate numerically their effects on the scattering profiles and on the estimated χ parameter.

SYSTEMS TREATED

We consider a ternary mixture of AB diblock copolymer with A and B homopolymers in a bulk, disordered, single phase. To simplify the notation we denote homopolymers A and B as polymers D and E, respectively, as shown in *Figure 1*. The overall volume fractions of copolymer and homopolymers in the mixture are denoted by ϕ_C, ϕ_D and ϕ_E, respectively, and the statistical segment length by a_κ for each component. We associate with each component a monomer volume v_κ by the relation $v_\kappa = 1/\rho_{0\kappa}$, where $\rho_{0\kappa}$ is the density of pure component κ, in monomers per unit volume. Each statistical segment length depends at least in part on, for example, chain stiffness, and so is independent of monomer volume (although of course to within a numerical factor $v_\kappa \simeq a_\kappa^3$). The intrinsic

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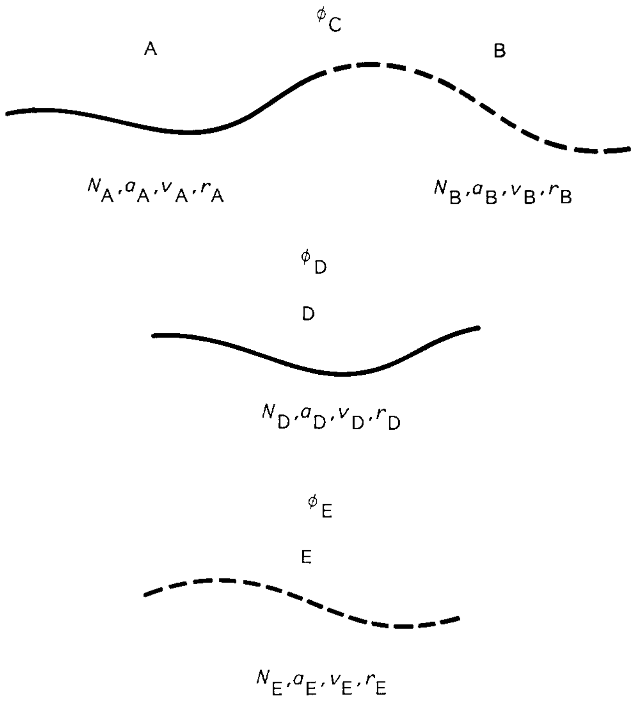

Figure 1 Block copolymer/homopolymer systems considered in this paper. They consist of AB diblock copolymers, together with D and E homopolymers which are chemically identical to the A-block and B-block chains, respectively. The volume fractions of the respective components are ϕ_C (copolymer), ϕ_D and ϕ_E. N_κ, a_κ, v_κ and r_κ (κ = A, B, D or E) are, respectively, the degree of polymerization, statistical segment length, monomer molecular volume and effective degree of polymerization defined by equation (5) in the text

asymmetry of the A and B chains exists in the fact that $v_A \neq v_B$ and $a_A \neq a_B$. On the other hand, in assuming that the A and D blocks are chemically identical, we do assume that $v_A = v_D$ and $a_A = a_D$, and likewise that $v_B = v_E$ and $a_B = a_E$.

In addition to the asymmetry, each chain has a distribution of molecular weights which we model here using a Schultz–Zimm distribution, i.e.

$$\Psi_\kappa(N_\kappa) = \frac{1}{\Gamma(k_\kappa + 1)} v_\kappa^{k_\kappa + 1} N_\kappa^{k_\kappa} \exp(-v_\kappa N_\kappa) \qquad (1)$$

where

$$v_\kappa = \frac{k_\kappa}{N_{\kappa,\mathrm{n}}} = \frac{k_\kappa + 1}{N_{\kappa,\mathrm{w}}} \qquad (2)$$

or

$$N_{\kappa,\mathrm{w}}/N_{\kappa,\mathrm{n}} = (k_\kappa + 1)/k_\kappa \equiv \lambda_\kappa \qquad (3)$$

$N_{\kappa,\mathrm{n}}$ and $N_{\kappa,\mathrm{w}}$ are the number-average and weight-average degrees of polymerization of the κ chain, and λ_κ is the heterogeneity index. The constants k_κ and v_κ characterize the polydispersity in molecular weight for the κ chain. We assume that the k_κ and v_κ for A, B, D and E are mutually independent, as in previous treatments[8–10,12,13]. Note that the $\Psi_\kappa(N_\kappa)$ given by equations (1) and (2) is the normalized weight-distribution function.

GENERAL FORMALISM

The scattering function can be calculated as a generalization of the result of Hong and Noolandi[12]. We need to calculate the free energy associated with small fluctuations in the concentration profiles for the system of polydisperse AB copolymers and D and E homopolymers. The basis of the calculation is the general expression for the free energy of polymer blends[14]. In the present case we assume that the interaction energy depends only on the local volume fractions of A and B type monomers at each point, independent of whether the monomers belong to copolymer or homopolymer, which we denote $\phi_\alpha(\boldsymbol{r})$ and $\phi_\beta(\boldsymbol{r})$. In the language of Hong and Noolandi, we need to introduce only two fields $\omega_\alpha(\boldsymbol{r})$ and $\omega_\beta(\boldsymbol{r})$. The free energy density associated with small fluctuations in the concentration profiles, in units of $k_B T$ where k_B is the Boltzmann constant and T is the temperature, can be expressed to second order as[15]:

$$\begin{aligned}\frac{\Delta f}{\rho_0} &\simeq \frac{\Delta f_2}{\rho_0} \\ &= \frac{1}{V}\int \frac{\mathrm{d}^3 q}{(2\pi)^3}\Bigg(\frac{1}{2}\sum_{i,j=\alpha}^{\beta} \chi_{ij}\psi_i(\boldsymbol{q})\psi_j(-\boldsymbol{q}) \\ &\quad - \sum_{i=\alpha}^{\beta} \psi_i(\boldsymbol{q})\omega_i(-\boldsymbol{q}) \\ &\quad - \frac{1}{2}\sum_{\kappa}\sum_{i,j=\alpha}^{\beta} r_\kappa \phi_\kappa g_{ij}^{\kappa}(\boldsymbol{q}, -\boldsymbol{q})\omega_i(\boldsymbol{q})\omega_j(-\boldsymbol{q})\Bigg) \qquad (4)\end{aligned}$$

In this expression, ρ_0 is the reference density, which is used for defining the Flory interaction parameters χ_{ij}, $i, j = \alpha$ or β, which describe interactions between components i and j; $\chi_{\alpha\beta}$ describes interactions between A or D with B or E, and $\chi_{\alpha\alpha} = \chi_{\beta\beta} = 0$. As well, $\psi_i(\boldsymbol{q})$, $i = \alpha$ or β, is the Fourier transform of the fluctuation of the local volume fraction of constituent i from its overall value, $\psi_i(\boldsymbol{r}) = \phi_i(\boldsymbol{r}) - \phi_i$. The summation over κ is over molecules, i.e. κ = C, D and E, where C stands for an AB copolymer. Polydispersity is incorporated here in that molecules of differing molecular weight, even if otherwise identical, are treated as separate components κ. For each such component, the r_κ, sometimes referred to as the 'effective degree of polymerization', is:

$$r_\kappa = (v_\kappa/v_0)N_\kappa \qquad (5)$$

where $\rho_0 = 1/v_0$ is the reference density used in defining the Flory interaction parameters. For block copolymers, $r_C = r_A + r_B$. Similarly, each ϕ_κ in equation (4) is the volume fraction of the corresponding component with degree of polymerization N_κ.

For homopolymers, κ = D or E, the $g_{ij}^{\kappa}(\boldsymbol{q}, -\boldsymbol{q})$ vanishes unless $i = j = \kappa$, in which case:

$$g_{ij}^{\kappa}(\boldsymbol{q}, -\boldsymbol{q}) = g_\kappa^{(2)}(\boldsymbol{q}, -\boldsymbol{q}) \qquad (6)$$

with

$$g_\kappa^{(2)}(\boldsymbol{q}, -\boldsymbol{q}) = \frac{2}{x^2}(\mathrm{e}^{-x} + x - 1) \qquad (7)$$

which is the Debye function, in which $x = N_\kappa a_\kappa^2 q^2/6$. For copolymers, κ = C, there are three independent functions:

$$\begin{aligned} g_{AA}^{C}(\boldsymbol{q}, -\boldsymbol{q}) &= f_A^2 g_A^{(2)}(\boldsymbol{q}, -\boldsymbol{q}) \\ g_{AB}^{C}(\boldsymbol{q}, -\boldsymbol{q}) &= g_{BA}^{C}(\boldsymbol{q}, -\boldsymbol{q}) = f_A f_B g_A^{(1)}(\boldsymbol{q}) g_B^{(1)}(-\boldsymbol{q}) \qquad (8) \\ g_{BB}^{C}(\boldsymbol{q}, -\boldsymbol{q}) &= f_B^2 g_B^{(2)}(\boldsymbol{q}, -\boldsymbol{q}) \end{aligned}$$

with

$$g_\kappa^{(1)}(\boldsymbol{q}) = \frac{1}{x}(1 - \mathrm{e}^{-x}) \qquad (9)$$

and

$$f_\kappa = \frac{r_\kappa}{r_C} = \frac{N_\kappa v_\kappa}{N_A v_A + N_B v_B} \tag{10}$$

These factors f_A and f_B are the volume fractions of components A and B within each copolymer. Note that the actual degrees of polymerization, N_κ, appear in the arguments of the Debye function, whereas the effective degrees of polymerization, r_κ, appear in the prefactors f_κ.

Equation (4) can be rewritten as:

$$\begin{aligned}\frac{\Delta f_2}{\rho_0} = \frac{1}{V}\int \frac{d^3q}{(2\pi)^3} \\ \times\Bigg(\frac{1}{2}\sum_{i,j=\alpha}^{\beta} \chi_{ij}\psi_i(\boldsymbol{q})\psi_j(-\boldsymbol{q}) - \sum_{i=\alpha}^{\beta}\psi_i(\boldsymbol{q})\omega_i(-\boldsymbol{q}) \\ -\frac{1}{2}\sum_{i,j=\alpha}^{\beta}\overline{S_{ij}(q)}\omega_i(\boldsymbol{q})\omega_j(-\boldsymbol{q})\Bigg)\end{aligned} \tag{11}$$

where the elements of the matrix S, which depend on only $|\boldsymbol{q}|$, are given by:

$$\begin{aligned}\overline{S_{\alpha\alpha}(q)} &= \phi_C\langle r_C g^C_{AA}(\boldsymbol{q}, -\boldsymbol{q})\rangle_v + \phi_D\langle r_D g^D_{DD}(\boldsymbol{q}, -\boldsymbol{q})\rangle_v \\ \overline{S_{\alpha\beta}(q)} &= \overline{S_{\beta\alpha}(q)} = \phi_C\langle r_C g^C_{AB}(\boldsymbol{q}, -\boldsymbol{q})\rangle_v \\ \overline{S_{\beta\beta}(q)} &= \phi_C\langle r_C g^C_{BB}(\boldsymbol{q}, -\boldsymbol{q})\rangle_v + \phi_E\langle r_E g^E_{EE}(\boldsymbol{q}, -\boldsymbol{q})\rangle_v\end{aligned} \tag{12}$$

where $\langle\ \rangle_v$ designates a volume average, and the line over a quantity, e.g. $\overline{S_{\alpha\beta}(q)}$, indicates that it contains volume-average quantities. For homopolymer, volume average is equivalent to weight average, and using a weight-distribution function such as equation (1) can be written (for homopolymer D):

$$\langle r_D g^D_{DD}(\boldsymbol{q}, -\boldsymbol{q})\rangle_v = \int dN_D \Psi_D(N_D) r_D g^D_{DD}(\boldsymbol{q}, -\boldsymbol{q}) \tag{13}$$

with an equivalent expression for homopolymer E. For polydisperse, asymmetric copolymers, the volume and weight fractions are not equivalent, but in this paper we approximate the volume average by the weight average, and have for example:

$$\begin{aligned}&\langle r_C g^C_{AA}(\boldsymbol{q}, -\boldsymbol{q})\rangle_v \\ &\quad\simeq \int dN_A\, dN_B \Psi_A(N_A)\Psi_B(N_B) r_C g^C_{AA}(\boldsymbol{q}, -\boldsymbol{q})\end{aligned} \tag{14}$$

The next step is eliminating the potentials ω_i, which is done by minimizing Δf_2 with respect to each ω_i. This results in an expression for ψ_i, which is easily inverted to give (to leading order):

$$\omega_i(\boldsymbol{q}) \simeq -\sum_{j=\alpha}^{\beta}[\overline{S(q)}]^{-1}_{ij}\psi_j(-\boldsymbol{q}) \tag{15}$$

which can be substituted into equation (11) to give:

$$\frac{\Delta f_2}{\rho_0} = \frac{1}{2V}\int\frac{d^3q}{(2\pi)^3}\sum_{i,j=\alpha}^{\beta}\{\chi_{ij} + [\overline{S(q)}]^{-1}_{ij}\}\psi_i(\boldsymbol{q})\psi_j(-\boldsymbol{q}) \tag{16}$$

Finally, we use the incompressibility condition to eliminate the ψ_β, arriving at:

$$\begin{aligned}\frac{\Delta f_2}{\rho_0} = \frac{1}{2V}\int\frac{d^3q}{(2\pi)^3}\{-2\chi + [\overline{S(q)}]^{-1}_{\alpha\alpha} \\ - 2[\overline{S(q)}]^{-1}_{\alpha\beta} + [\overline{S(q)}]^{-1}_{\beta\beta}\}|\psi_\alpha(\boldsymbol{q})|^2\end{aligned} \tag{17}$$

where we have denoted $\chi_{\alpha\beta}$ simply by χ. From equation (17) it follows that the scattering profile in the disordered phase, $I(q)$, is given by:

$$I(q) \propto \frac{1}{[\overline{S(q)}]^{-1}_{\alpha\alpha} - 2[\overline{S(q)}]^{-1}_{\alpha\beta} + [\overline{S(q)}]^{-1}_{\beta\beta} - 2\chi} \tag{18}$$

where q is the magnitude of the scattering vector:

$$q = (4\pi/\lambda)\sin(\theta/2) \tag{19}$$

and λ is the wavelength of the radiation and θ is the scattering angle. Expressing the elements of $[\bar{S}]^{-1}$ in terms of the elements of $\bar{S}$, equation (18) can be written:

$$I(q) \propto [\overline{S(q)}/\overline{W(q)} - 2\chi]^{-1} \tag{20}$$

with

$$\frac{\overline{S(q)}}{\overline{W(q)}} = \frac{\overline{S_{\alpha\alpha}(q)} + 2\overline{S_{\alpha\beta}(q)} + \overline{S_{\beta\beta}(q)}}{\overline{S_{\alpha\alpha}(q)}\,\overline{S_{\beta\beta}(q)} - \overline{S_{\alpha\beta}(q)}^2} \tag{21}$$

Equations (5)–(10), (12)–(14), (20) and (21) constitute our general result for the scattering from the AB/A/B blend of polydisperse homopolymers and polydisperse, asymmetric diblock copolymers. The detailed evaluations of the weight-average functions, using the Schultz–Zimm distributions, are given in the Appendix.

These results reduce to the cases referred to in the 'Introduction' (except for the theory presented by Fredrickson and Helfand[7]) by appropriate choices of volume fractions, statistical segment lengths, monomer volumes and distribution functions. In particular, the partial correction for asymmetry used in refs 1 and 10 is equivalent to using the equations for the symmetric case, but with the effective degree of polymerization used in both the prefactors f_κ in equation (8) and the arguments of the correlation functions. In this paper we compare our calculated asymmetry corrections with those of that approach, which we hereafter refer to as the 'conventional' correction.

NUMERICAL ANALYSIS OF ASYMMETRY EFFECTS AND DISCUSSION

In this section we show and discuss results obtained using the scattering equations presented above and the Schultz–Zimm distributions. For these calculations, we have chosen the reference volume $v_0 = \sqrt{v_A v_B}$.

Pure copolymer

Figures 2 and *3* show the results of numerical calculations for pure AB diblock copolymers, i.e. the case of $\phi_C = 1$ and $\phi_D = \phi_E = 0$ in equation (12). The profiles $r_C\overline{S(q)}/\overline{W(q)}$ in *Figure 2* and $r_C^{-1}\overline{W(q)}/\overline{S(q)}$ in *Figure 3* can be calculated for a given set of parameters (λ, $f_{A,n}$, $m_{A,n}$) as a function of qR_g. Here λ is the heterogeneity index for the A-block and B-block chains (equation (3)) which for these figures are assumed to be equal:

$$\lambda \equiv \lambda_A = \lambda_B \tag{22}$$

$f_{A,n}$ is the effective volume fraction of A-block chain in the copolymer as defined by equation (A.5), and $m_{A,n}$ is defined by:

$$m_{A,n} \equiv R^2_{g,A,n}/R^2_{g,n} = [1 + (a_B/a_A)^2(N_{B,n}/N_{A,n})]^{-1} \tag{23}$$

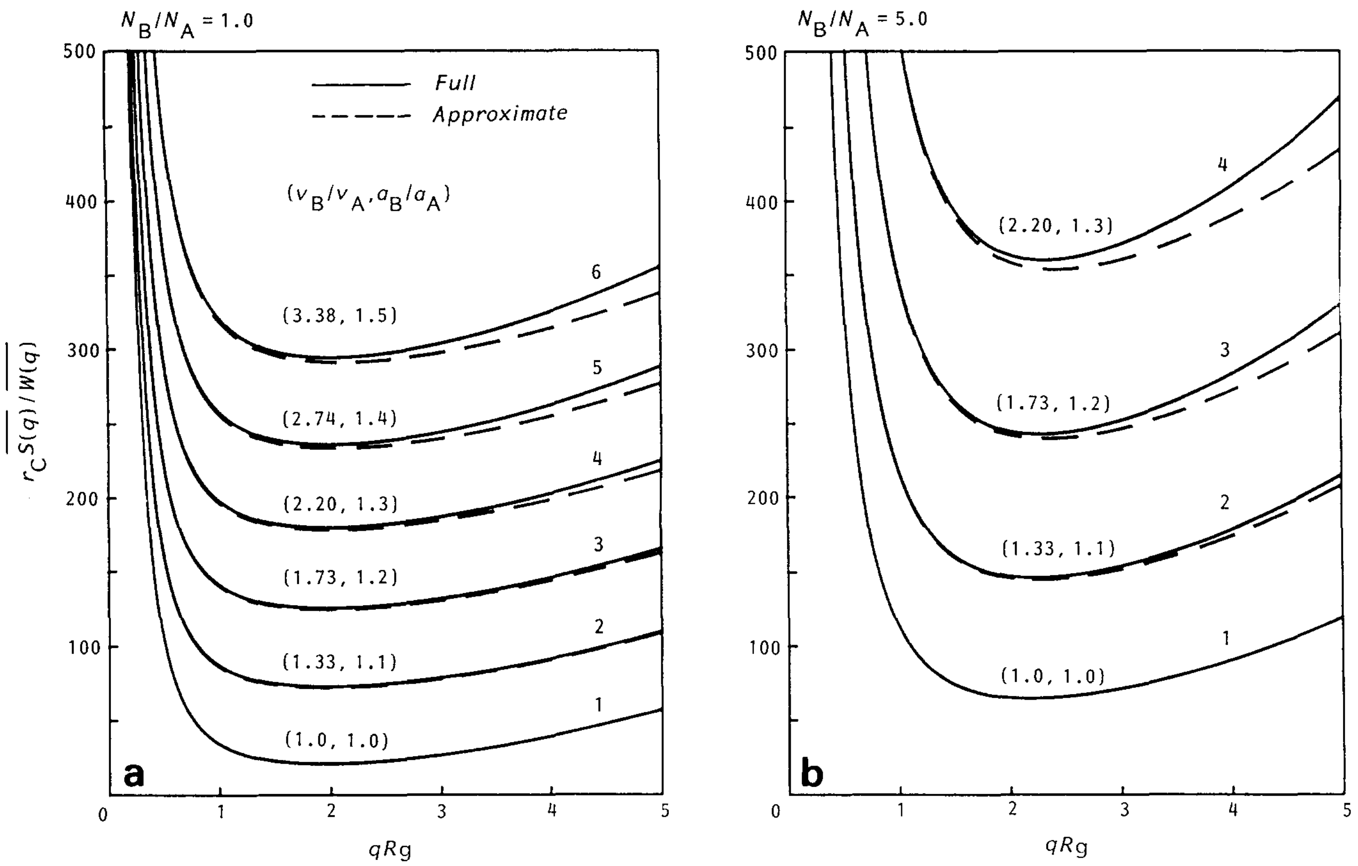

Figure 2 Effect of asymmetry on $r_C\overline{S(q)}/\overline{W(q)}$ for monodisperse AB diblock copolymers, $\lambda \equiv N_w/N_n = 1$; (a) $N_B/N_A = 1$ and (b) $N_B/N_A = 5$. The profiles $r_C\overline{S(q)}/\overline{W(q)}$ correspond to various sets of the asymmetry parameters (v_B/v_A, a_B/a_A). The solid and broken curves are results of the *full* and *approximate* treatments of the asymmetry effect, respectively (see text). Each set of profiles is vertically shifted to avoid overlap except for the lines labelled by number 1; the ($i + 1$)th set of profiles is shifted by 50 units relative to the ith set ($i = 1$ to 6 for part (a), $i = 1$ to 4 for part (b))

and

$$R_{g,n}^2 = R_{g,A,n}^2 + R_{g,B,n}^2 \tag{24}$$

where $R_{g,\kappa,n} = (\frac{1}{6}a_\kappa^2 N_{\kappa,n})^{1/2}$, the number-average radius of gyration of the κ-block chain, and $R_{g,n}$ is that of the entire diblock chain. Alternatively, (λ, v_B/v_A, a_B/a_A) can be used as an equivalent set of parameters. It should be noted that the profile $r_C^{-1}\overline{W(q)}/\overline{S(q)}$ is proportional to the scattering intensity $I(q)$ in the limit of $\chi = 0$ (see equation (20)), i.e. the stable limit of the systems against the thermally induced spatial composition fluctuations, far away from the spinodal point. As the system approaches the spinodal point the asymmetry and polydispersity effects become increasingly important.

Figure 2 shows the asymmetric effect on $r_C\overline{S(q)}/\overline{W(q)}$ for monodisperse AB block copolymers, i.e. $\lambda = 1$. The profiles for equal block lengths, $N_B/N_A = 1$, and highly disparate block lengths, $N_B/N_A = 5$, are shown in panels (a) and (b) respectively, for various sets of the asymmetry parameters (v_B/v_A, a_B/a_A). In order to highlight the asymmetry effects, for each set of parameters two profiles are shown; the ones shown by the solid curves were calculated using the equations for the asymmetric copolymers, equations (12), (21) and (A.6)–(A.19), and the profiles shown by the broken curves were calculated for symmetric copolymers with $v_A = v_B = v_0$ and $a_A = a_B = a_0$, but using the 'conventional' asymmetry correction discussed at the end of the previous section. For the sake of convenience we designate hereafter the analysis yielding the solid and broken profiles as *full* and *approximate* treatments, respectively. In *Figure 2* each set of profiles is vertically shifted to avoid overlap (see figure caption).

As indicated in *Figure 2a*, the asymmetry effect is rather minor for the case of block copolymers with equal degrees of polymerization, except for the cases of the large asymmetry parameters such as (v_B/v_A, a_B/a_A) = (2.20, 1.3), (2.74, 1.4) and (3.38, 1.5). However, the effect is much enhanced for the case of highly disparate block degrees of polymerization, as shown in *Figure 2b*; the difference between the solid and broken profiles is much larger than for the case of $N_B/N_A = 1$. This is reasonable since the asymmetry in the statistical segment lengths tends to enhance the asymmetry in $R_{g,A,n}$ and $R_{g,B,n}$ in equation (23) in these cases (both $a_B > a_A$ and $N_B > N_A$). For conventional block copolymers such as poly(styrene-*b*-isoprene) (PS-*b*-PI) and poly(styrene-*b*-butadiene) having $v_B/v_A \simeq 0.77$ and $a_B/a_A \simeq 0.86$, the *approximate* treatment based upon the theory for the symmetric copolymer with effective f_A would suffice for the copolymers with nearly identical N_B and N_A. However as the difference between N_B and N_A becomes large, the accuracy of the *approximate* theory worsens, and the *full* theory should be used.

Figure 3 shows comparisons of the scattering profiles $r_C^{-1}\overline{W(q)}/\overline{S(q)}$ obtained for the cases of: no asymmetry and no polydispersity (curve 1), asymmetry but no polydispersity (curve 2), no asymmetry but polydispersity (curve 3), and asymmetry and polydispersity (curve 4), for the cases of $N_{B,n}/N_{A,n} = 1$ in part (a) and $N_{B,n}/N_{A,n} = 3$ in part (b). All the profiles were calculated

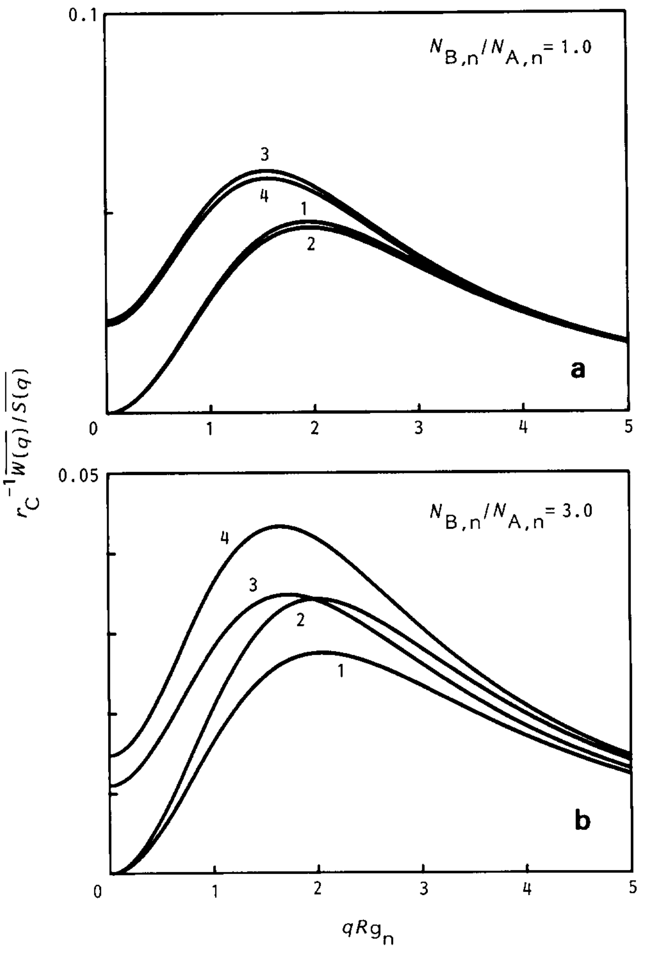

Figure 3 Comparison of the scattering profiles $r_C^{-1}\overline{W(q)}/\overline{S(q)}$ (proportional to $I(q)$ for the case $\chi = 0$) for AB diblock copolymer obtained for the cases of no asymmetry and no polydispersity (curve 1), asymmetry but no polydispersity (curve 2), no asymmetry but polydispersity (curve 3), and asymmetry and polydispersity (curve 4), for the cases (a) $N_{B,n}/N_{A,n} = 1$ and (b) $N_{B,n}/N_{A,n} = 3$. All the profiles are calculated for the case $\chi = 0$, $v_A = 100\,\text{cm}^3\,\text{mol}^{-1}$, $v_B = 77\,\text{cm}^3\,\text{mol}^{-1}$, $a_A = 7$ Å, $a_B = 6$ Å and $\lambda_C = N_{C,w}/N_{C,n} = 1.1$. These values correspond approximately to PS – *b* – PI copolymers

for the case of $\chi = 0$, $v_A = 100\,\text{cm}^3\,\text{mol}^{-1}$, $v_B = 77\,\text{cm}^3\,\text{mol}^{-1}$, $a_A = 7$ Å, $a_B = 6$ Å and $N_w/N_n = 1.1$ for the entire block chain. Note that $a_B/a_A = 1$ in equation (23) and $v_B/v_A = 1$ in equation (A.5) for the case of no asymmetry. This set of parameters approximately corresponds to that for PS-*b*-PI diblock copolymers where A and B correspond to PS and PI, respectively. The set of parameters in part (a) gives $f_{A,n} = 0.565$ and $m_{A,n} = 0.576$, while that in part (b) gives $f_{A,n} = 0.302$ and $m_{A,n} = 0.312$.

For PS-*b*-PI copolymers with $N_A = N_B$, the asymmetry effect is seen to be insignificant by comparing profiles 1 with 2 and 3 with 4 in *Figure 3a*. The molecular-weight distributions of PS-block and PI-block chains affect the profiles much more than the asymmetry, as clearly observed by comparing profiles 1 with 3 and 2 with 4. The small suppression of the intensity due to the asymmetry can be traced to the slight increase in $f_{A,n}$ beyond 0.5 (see the changes in the profiles from curve 1 to 2 or from curve 3 to 4). In this case, neglecting asymmetry leads to an underestimate of the value of χ determined by the best fit between experimental and theoretical SAXS and SANS profiles. On the other hand, neglecting polydispersity tends to overestimate χ.

For PS-*b*-PI copolymers for which $N_A \neq N_B$, the effect of asymmetry is comparable with that of polydispersity, as shown in *Figure 3b*. Once again,the asymmetry effect is seen by comparing profile 1 with 2 or 3 with 4,while the polydispersity effect is seen by comparing profile 1 with 3 or 2 with 4. In this case the asymmetry tends to enhance the scattered intensity, contrary to the case of *Figure 3a*. This is due to the fact that the asymmetry tends to suppress the asymmetry in the effective volume of the PS-block and PI-block chains in this case, causing $f_{A,n}$ to be closer to 0.5. In this case neglecting either the asymmetry or polydispersity tends to overestimate χ, and *both* significantly affect the scattering profiles and hence the fitted value of χ.

Copolymer/homopolymer blends

Figure 4 shows scattering profiles $r_C^{-1}\overline{W(q)}/\overline{S(q)}$ for binary mixtures of AB diblock copolymer and D homopolymer plotted as a function of $qR_{g,n}$ where $R_{g,n}$ is the number-average radius of gyration of the AB diblock copolymer. The four panels of the figure correspond to: (a) $N_{D,n}/N_{A,n} = 0.1$ and $\phi_C = 0.8$; (b) $N_{D,n}/N_{A,n} = 0.1$ and $\phi_C = 0.2$; (c) $N_{D,n}/N_{A,n} = 3$ and $\phi_C = 0.8$; and (d) $N_{D,n}/N_{A,n} = 3$ and $\phi_C = 0.2$. In each panel, curves 1 to 4 have the same meanings as those in *Figure 3*. All panels are calculated using $f_{A,n} = 0.565$, $m_{A,n} = 0.576$, $\lambda_C = \lambda_D = 1.1$, $v_B/v_A = v_B/v_D = 0.77$ and $a_B/a_A = a_B/a_D = 0.86$, values which correspond approximately to binary mixtures of PS-*b*-PI with homopolystyrene. (The copolymer characteristics are the same as in *Figure 3a*.)

Effects of the copolymer volume fraction, ϕ_C for a given $N_{D,n}/N_{A,n}$ on the scattering profiles are seen by comparing panels (a) with (b) and panels (c) with (d). The asymmetry effects are found to be greater for lower ϕ_C than for higher ϕ_C, for this particular case where the diblock copolymer by itself exhibits little asymmetry effect. Effects of $N_{D,n}/N_{A,n}$ for a given ϕ_C on the scattering profiles are seen by comparing panels (a) with (c) and panels (b) with (d). The asymmetry effects are found to be greater for a greater $N_{D,n}/N_{A,n}$ than for a smaller $N_{D,n}/N_{A,n}$. The asymmetry effect is very small in the case of part (a) so that the *approximate* treatment as discussed earlier would suffice. However, it becomes significant, to varying degrees, for the other cases. In general, the effect becomes increasingly important with increasing value of $r_D\phi_D/r_C\phi_C$ for this particular diblock copolymer system having $f_{A,n} = 0.565$.

In conclusion, we have derived a set of scattering equations for copolymer/homopolymer blends which incorporate polydispersity and asymmetry, and have found that the effects of each can be comparable, and that both can be significant. These equations are no harder to use than previous scattering equations.

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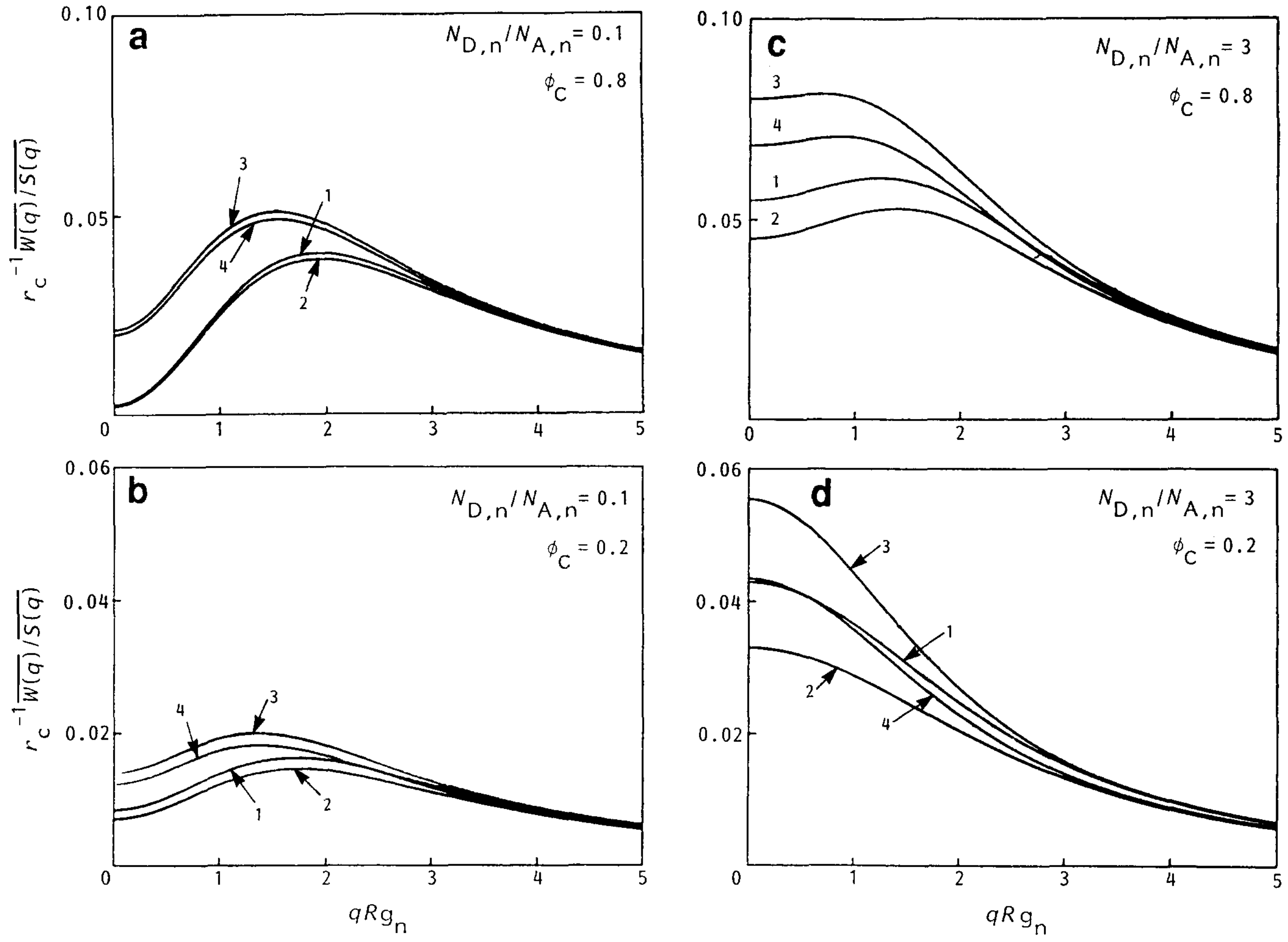

Figure 4 Comparison of the scattering profiles $r_C^{-1}\overline{W(q)}/\overline{S(q)}$ (proportional to $I(q)$ for the case $\chi = 0$) obtained for a binary mixture of AB diblock copolymer and D homopolymer plotted as a function of $qR_{g,n}$ where $R_{g,n}$ is the number-average radius of gyration of the AB diblock copolymer: (a) $N_{D,n}/N_{A,n} = 0.1$ and $\phi_C = 0.8$; (b) $N_{D,n}/N_{A,n} = 0.1$ and $\phi_C = 0.2$; (c) $N_{D,n}/N_{A,n} = 3$ and $\phi_C = 0.8$; and (d) $N_{D,n}/N_{A,n} = 3$ and $\phi_C = 0.2$. In each panel, curves 1 to 4 have the same meanings as those in *Figure 3*. All these profiles were calculated for the following sets of parameters: $f_{A,n} = 0.565$, $m_{A,n} = 0.576$, $N_w/N_n = 1.1$ (for the entire chain), $\lambda_D = 1.1$, $\chi = 0$, $v_B/v_A = v_B/v_D = 0.77$ and $a_B/a_A = a_B/a_D = 0.86$

Program. The authors thank Mr Taie for preparing figures.

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APPENDIX

Detailed scattering formulae

In this appendix we outline the calculation of the weight averages appearing in equation (12) using the Schultz–Zimm weight-distribution function of equation (1), and exhibit results. Throughout, we assume that the reference volume used in defining the Flory interaction parameter is $v_0 = \sqrt{v_A v_B}$.

The copolymer contribution to $\overline{S_{\alpha\alpha}(q)}$ contains $\langle r_C g_{AA}^C(\boldsymbol{q}, -\boldsymbol{q})\rangle_v$. Approximating this by the weight average, and using the Schultz–Zimm distribution, it can be expressed as:

$$\langle r_C g_{AA}^C(\boldsymbol{q}, -\boldsymbol{q})\rangle_v$$

$$\simeq \frac{\nu_A^{k_A+1}\nu_B^{k_B+1}}{\Gamma(k_A+1)\Gamma(k_B+1)}\int_0^\infty\int_0^\infty \mathrm{d}N_A\,\mathrm{d}N_B$$

$$\times N_A^{k_A}[\exp(-\nu_A N_A)]N_B^{k_B}[\exp(-\nu_B N_B)]$$

$$\times\left(\frac{v_A}{v_0}\right)^2 N_A^2\frac{1}{r_C}\frac{2}{y_A^2N_A^2}[y_AN_A+\exp(-y_AN_A)-1]$$

$$= \frac{\nu_{\mathrm{A}}^{k_{\mathrm{A}}+1}\nu_{\mathrm{B}}^{k_{\mathrm{B}}+1}}{\Gamma(k_{\mathrm{A}}+1)\Gamma(k_{\mathrm{B}}+1)}(H_1 + H_2 - H_3) \qquad (\mathrm{A.1})$$

where

$$\begin{pmatrix} H_1 \\ H_2 \\ H_3 \end{pmatrix} = \int_0^\infty \int_0^\infty \mathrm{d}N_{\mathrm{A}}\,\mathrm{d}N_{\mathrm{B}} \times N_{\mathrm{A}}^{k_{\mathrm{A}}}[\exp(-\nu_{\mathrm{A}}N_{\mathrm{A}})]N_{\mathrm{B}}^{k_{\mathrm{B}}}[\exp(-\nu_{\mathrm{B}}N_{\mathrm{B}})] \times \left(\frac{v_{\mathrm{A}}}{v_0}\right)^2 \begin{pmatrix} 2N_{\mathrm{A}}/(y_{\mathrm{A}}r_{\mathrm{C}}) \\ [2/(y_{\mathrm{A}}^2 r_{\mathrm{C}})]\exp(-y_{\mathrm{A}}N_{\mathrm{A}}) \\ 2/(y_{\mathrm{A}}^2 r_{\mathrm{C}}) \end{pmatrix} \qquad (\mathrm{A.2})$$

The integrand contains asymmetry parameters explicitly through v_{A}/v_0 and implicitly through r_{C} and y_κ. It is worth while to note that the calculations for the symmetric systems can be adapted to the asymmetric systems by the replacements:

$$\begin{array}{lll} fN \rightarrow r_{\mathrm{A}} & (1-f)N \rightarrow r_{\mathrm{B}} & \\ y \rightarrow y_{\mathrm{A}}(v_0/v_{\mathrm{A}}) & f \rightarrow f_{\mathrm{A}} & 1/N \rightarrow 1/r_{\mathrm{C}} \end{array} \qquad (\mathrm{A.3})$$

The final result for H_3, for example, is given by:

$$H_3 = \left(\frac{v_{\mathrm{A}}}{v_0}\right)^3 \frac{2\Gamma(k_{\mathrm{A}}+1)\Gamma(k_{\mathrm{B}}+1)}{y_{\mathrm{A}}^2(k_{\mathrm{A}}+k_{\mathrm{B}}+1)\nu_{\mathrm{A}}^{k_{\mathrm{A}}+k_{\mathrm{B}}+1}} \left(\frac{\nu_{\mathrm{B}}}{\nu_{\mathrm{A}}}\right)^{-k_{\mathrm{B}}} \times F\left(1, k_{\mathrm{A}}+1, k_{\mathrm{A}}+k_{\mathrm{B}}+2; \frac{\nu_{\mathrm{A}} - (v_{\mathrm{A}}/v_0)^2\nu_{\mathrm{B}}}{\nu_{\mathrm{A}}}\right) \qquad (\mathrm{A.4})$$

for

$$f_{\mathrm{A,n}} \equiv \frac{N_{\mathrm{A,n}}v_{\mathrm{A}}}{N_{\mathrm{A,n}}v_{\mathrm{A}} + N_{\mathrm{B,n}}v_{\mathrm{B}}} \leqslant \frac{k_{\mathrm{A}}}{k_{\mathrm{A}}+k_{\mathrm{B}}} \qquad (\mathrm{A.5})$$

where $F(\alpha, \beta, \gamma; z)$ is the Gauss hypergeometric function. The condition stated by equation (A.5) arises from the convergence condition of the Laplace transformation of the Whittaker function[10]. The expression for H_3 corresponding to the condition $f_{\mathrm{A,n}} > k_{\mathrm{A}}/(k_{\mathrm{A}}+k_{\mathrm{B}})$, as well as the other contributions to the scattering equations, can be obtained similarly.

We summarize here the equations for the simplified case where the A-block and B-block chains have identical polydispersity parameters, $k_{\mathrm{A}} = k_{\mathrm{B}} = k$ or $\lambda_{\mathrm{A}} = \lambda_{\mathrm{B}} = \lambda$, and for the case when equation (A.5) is satisfied. (This latter condition can always be satisfied by designating the block with volume fraction less than 1/2 as the A block.) Beginning with the copolymer contributions:

$$\langle r_{\mathrm{C}} g_{\mathrm{AA}}^{\mathrm{C}}(\boldsymbol{q}, -\boldsymbol{q})\rangle_{\mathrm{v}} \simeq \frac{2r_{\mathrm{C,n}}}{x_{\mathrm{A,n}}^2} f_{\mathrm{A,n}}^2 \left\{ \frac{x_{\mathrm{A,n}}}{2f_{\mathrm{B,n}}} F\left(1, k+2, 2k+3; 1 - \frac{f_{\mathrm{A,n}}}{f_{\mathrm{B,n}}}\right) + \frac{1}{f_{\mathrm{B,n}}}\frac{1}{\lambda+1}\left[z_2^{\lambda/(\lambda-1)} F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{A,n}}}{f_{\mathrm{B,n}}}z_2\right) - F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{A,n}}}{f_{\mathrm{B,n}}}\right)\right]\right\} \qquad (\mathrm{A.6})$$

where

$$z_2 = [1 + x_{\mathrm{A,n}}(\lambda - 1)]^{-1} \qquad (\mathrm{A.7})$$

$$f_{\mathrm{B,n}} = 1 - f_{\mathrm{A,n}} \qquad (\mathrm{A.8})$$

$$r_{\mathrm{C,n}} = (v_{\mathrm{A}}/v_0)N_{\mathrm{A,n}} + (v_{\mathrm{B}}/v_0)N_{\mathrm{B,n}} \qquad (\mathrm{A.9})$$

which is the number average of the effective degree of polymerization, and

$$x_{\kappa,\mathrm{n}} = y_\kappa N_{\kappa,\mathrm{n}} \qquad (\mathrm{A.10})$$

for $\kappa = \mathrm{A}$ or B. Next:

$$\langle r_{\mathrm{C}} g_{\mathrm{BB}}^{\mathrm{C}}(\boldsymbol{q}, -\boldsymbol{q})\rangle_{\mathrm{v}} \simeq \frac{2r_{\mathrm{C,n}}}{x_{\mathrm{B,n}}^2} f_{\mathrm{B,n}}^2 \left[\frac{x_{\mathrm{B,n}}}{2f_{\mathrm{B,n}}} F\left(1, k+1, 2k+3; 1 - \frac{f_{\mathrm{A,n}}}{f_{\mathrm{B,n}}}\right) - \frac{1}{f_{\mathrm{B,n}}}\frac{1}{\lambda+1} F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{A,n}}}{f_{\mathrm{B,n}}}\right) + G_1 \right] \qquad (\mathrm{A.11})$$

where

$$G_1 = \frac{z_5^{1/(\lambda-1)}}{f_{\mathrm{B,n}}(\lambda+1)} F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{A,n}}}{f_{\mathrm{B,n}}} z_5^{-1}\right) \qquad (\mathrm{A.12})$$

for

$$x_{\mathrm{B,n}} \leqslant k f_{\mathrm{B,n}}(1/f_{\mathrm{A,n}} - 1/f_{\mathrm{B,n}}) \qquad (\mathrm{A.13})$$

and

$$G_1 = \frac{z_5^{\lambda/(\lambda-1)}}{f_{\mathrm{A,n}}(\lambda+1)} F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{B,n}}}{f_{\mathrm{A,n}}} z_5\right) \qquad (\mathrm{A.14})$$

otherwise. In these equations:

$$z_5 = [1 + x_{\mathrm{B,n}}(\lambda - 1)]^{-1} \qquad (\mathrm{A.15})$$

Finally:

$$\langle r_{\mathrm{C}} g_{\mathrm{AB}}^{\mathrm{C}}(\boldsymbol{q}, -\boldsymbol{q})\rangle_{\mathrm{v}} \simeq \frac{r_{\mathrm{C,n}}}{x_{\mathrm{A,n}}x_{\mathrm{B,n}}} f_{\mathrm{A,n}}f_{\mathrm{B,n}} \left[\frac{1}{f_{\mathrm{B,n}}(\lambda+1)} \times F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{A,n}}}{f_{\mathrm{B,n}}}\right) - \frac{z_2^{\lambda/(\lambda-1)}}{f_{\mathrm{B,n}}(\lambda+1)} F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{A,n}}}{f_{\mathrm{B,n}}} z_2\right) - G_1 + G_2 \right] \qquad (\mathrm{A.16})$$

where

$$G_2 = \frac{z_2^{\lambda/(\lambda-1)} z_5^{1/(\lambda-1)}}{f_{\mathrm{B,n}}(\lambda+1)} F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{A,n}}z_2}{f_{\mathrm{B,n}}z_5}\right) \qquad (\mathrm{A.17})$$

for

$$f_{\mathrm{A,n}}z_2/(f_{\mathrm{B,n}}z_5) \leqslant 1 \qquad (\mathrm{A.18})$$

and

$$G_2 = \frac{z_2^{1/(\lambda-1)} z_5^{\lambda/(\lambda-1)}}{f_{\mathrm{A,n}}(\lambda+1)} F\left(1, k+1, 2k+2; 1 - \frac{f_{\mathrm{B,n}}z_5}{f_{\mathrm{A,n}}z_2}\right) \qquad (\mathrm{A.19})$$

It should be noted that equations (A.4) to (A.19) reduce to those given previously (equations (42) to (48) in ref. 10) for the symmetric block copolymers with $v_A = v_B = v_0$ and $a_A = a_B = a$.

The contribution from homopolymers D is given by:

$$\langle r_D g_{DD}^{D}(\boldsymbol{q}, -\boldsymbol{q}) \rangle_v = \frac{2r_{D,n}}{x_{D,n}^2} \{ x_{D,n} - 1 + [1 + (\lambda_D - 1) x_{D,n}]^{-1/(\lambda_D - 1)} \} \tag{A.20}$$

and from homopolymers E is obtained from equation (A.20) by replacing the subscript D with E. The $r_{\kappa,n}$ is the number-average effective degree of polymerization for homopolymer κ:

$$r_{\kappa,n} = (v_\kappa / v_0) N_{\kappa,n} \tag{A.21}$$

for κ = D or E, with $x_{\kappa,n}$ given by equation (A.10), and each λ_κ is the heterogeneity index for homopolymer κ, which may differ from that of the copolymer blocks ($\lambda_A = \lambda_B = \lambda$).