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Orientational Correlations and the Dynamical Behavior of Diblock Copolymers

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ABSTRACT: Strong orientational effects in the static and dynamic structure factors of diblock copolymer melts have been shown to originate from the connected structure and mutual repulsion between the blocks. A collective variable based on the chain bond vectors is introduced and shown to have a dynamics comparable to that of the concentration fluctuations. Coupled equations of motion are derived which illustrate how the concentration fluctuations drive the orientational correlations in diblock chains. The coupling gives rise to two relaxation modes, one of which shows a critical slowing down and is approximately wavenumber independent on scales larger than the chain size. The amplitude of this mode increases as the microphase separation is approached in a manner similar to the static concentration fluctuations. These findings are in qualitative agreement with recent light-scattering experiments.

I. Introduction

The configurational properties of diblock copolymer chains show a rich variety of behavior as the order disorder transition is approached. Computer simulation experiments[1−3] and analytic work[4,5] have clearly showed that near the transition the individual blocks of the copolymer chain contract but that the total radius of gyration increases due to the repulsion between the component chains. The stretching of the diblock copolymer into a dumbell shape[6] creates an anisotropic distribution of monomer segments. The screening of the isotropic excluded volume interactions by anisotropic long chain molecules induces a nematic interaction. For stretched network chains this has been shown[8−10] to give rise to a splitting in the NMR spectrum. In order to describe this orientational effect in the context of diblock copolymer melts, we introduced[11] a simple vector collective variable based on the chain bond vectors. Because of the unique structure of the diblock, it was possible to show that the bond vector variable was coupled to the concentration fluctuations. In contrast, for a binary polymer blend there is no direct structure factor between the two components and the coupling is absent. For the diblock system, a microphase separation can be induced in the concentration fluctuations by isotropic excluded volume interactions. Our theoretical results showed that for diblocks the instability in the concentration fluctuations is communicated to the bond vector correlations. In computer simulation experiments,[1−3] these were seen as a spontaneous orientation of the diblocks chains at the microphase separation—an effect which is absent for phase separating blends.

In this paper, we will extend these results, which were entirely concerned with the static correlation functions, to the collective dynamical behavior of the diblock chains. Our intention is to show that there is a dynamical consequence of the coupling between the concentration fluctuations and the bond vector orientational variable. This work is further motivated by recent light-scattering experiments[7] which indicated that in addition to the expected relaxation processes known to occur in diblock systems there is an additional slow relaxation mode. This is characterized by a wave vector *independent* relaxation rate and a strongly temperature dependent amplitude which is similar to that of the static structure factor at the wave vector q^* at which the microphase separation takes place. We will show that these features are well-described by incorporating the chain end to end collective vector variable into the dynamics of the concentration fluctuations.

There are diverse approaches to the dynamics of concentrated polymer systems. In this paper we will follow the work of Doi and Edwards[13] and consider dynamical equations for the collective variables which can be derived from a free energy $F(\rho_q,\mathbf{u}_q)$ functional, where ρ_q and $\mathbf{u}_q$ are collective variables describing the monomer concentration fluctuations and bond vector fluctuations, respectively [$F(\rho_q,\mathbf{u}_q)$, ρ_q, and $\mathbf{u}_q$ will be defined in the next section]. The equations of motion are assumed to have the form

$$\frac{\mathrm{d}\mathbf{u}_q}{\mathrm{d}t} = L_u \frac{\partial F_q}{\partial \mathbf{u}_{-q}} + \boldsymbol{\eta}_q \tag{1}$$

$$\frac{\mathrm{d}\rho_q}{\mathrm{d}t} = L_\rho \frac{\partial F_q}{\partial \rho_{-q}} + \xi_q$$

where L_u and L_ρ are Onsager coefficients and $\boldsymbol{\eta}_q$ and ξ_q are random force terms. These will be considered in section 3. In the next section, we will define the collective variables and consider a form for the free energy $F(\rho_q,\mathbf{u}_q)$ which has been considered in a previous work.[11] Note that dense melts are considered only; therefore no hydrodynamic interactions are needed.

II. The Free Energy $F(\rho_q,\mathbf{u}_q)$

A. Collective Variables. The two blocks of the copolymer are labeled A and B and the configuration of the statistical segments in each block is described by the position vectors $\{\mathbf{r}^{\mathrm{A}}_{\alpha i},\mathbf{r}^{\mathrm{B}}_{\beta j}\}$, where α and β are chain labels and i and j locate the monomers on the chain.

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The concentration fluctuations $\hat{\rho}_q$ are defined by

$$\hat{\rho}_q(\mathbf{r}) = \hat{\rho}_q^{\mathrm{A}}\{\mathbf{r}\} - \hat{\rho}_q^{\mathrm{B}}(\mathbf{r})$$

where

$$\hat{\rho}_q^{\mathrm{K}}\{\mathbf{r}\} = \sum_{\alpha i} \exp\, i\mathbf{q}\cdot\mathbf{r}_{\alpha i}^{\mathrm{K}} \tag{2}$$

with K = A, B. The collective bond vector variable $\hat{\mathbf{u}}_q\{\mathbf{r}\}$ is defined by

$$\hat{\mathbf{u}}_q\{\mathbf{r}\} = \frac{1}{\sqrt{\Omega}}\sum_{\alpha i}(\mathbf{b}_{\alpha i}^{\mathrm{A}} \exp\, i\mathbf{q}\cdot\mathbf{r}_{\alpha i}^{\mathrm{A}} + \mathbf{b}_{\alpha i}^{\mathrm{B}} \exp\, i\mathbf{q}\cdot\mathbf{r}_{\alpha i}^{\mathrm{B}}) \tag{3}$$

where the bond vector variable $\mathbf{b}_{\alpha i}^{\mathrm{K}}$ is defined by

$$\mathbf{b}_{\alpha i}^{\mathrm{K}} = \mathbf{r}_{\alpha i+1}^{\mathrm{K}} - \mathbf{r}_{\alpha i}^{\mathrm{K}}$$

and Ω is the volume of the system. In the limit of the wave vector $q \to 0$ this variable measures the correlation functions of the chain end to end vectors $\mathbf{R}_\alpha$.

$$\hat{\mathbf{u}}_{q\to 0} = \frac{1}{\sqrt{\Omega}}\sum_{\alpha}\mathbf{R}_\alpha \tag{4}$$

A spontaneous orientation of chains in the diblock system is signalled by an instability in the correlation function $\langle\hat{\mathbf{u}}_{-q}\hat{\mathbf{u}}_q\rangle$ at a particular wave vector $q = q^*$.

The $\hat{\mathbf{u}}_q$ are vector variables and strictly speaking apply to chains to which a sense of direction along the chain, i.e. an arrow head, can be assigned. The diblock polymers that we are considering do not have this property and we should use the tensorial collective variable

$$\hat{\mathbf{Q}}_q\{\mathbf{r}\} = \frac{1}{\sqrt{\Omega}}\sum_{\alpha i}(\mathbf{b}_{\alpha i}\mathbf{b}_{\alpha i} \exp\, i\mathbf{q}\cdot\mathbf{r}_{\alpha i}) \tag{5}$$

The use of this variable greatly increases the algebraic complexity of the calculations and for the static polymer properties has been considered by Holyst et al.[12] We believe that the essential dynamical features of the diblock system that we wish to discuss are well-illustrated by the simpler vector variable $\hat{\mathbf{u}}_q$. The methods we will use can be directly extended to the tensorial term $\hat{\mathbf{Q}}_q$, but at the cost of a significant increase in algebraic complexity.

B. Free Energy. The monomers are assumed to interact with each other and with those on other chains through isotropic excluded volume interactions V_{AA}, V_{AB}, and V_{BB}. It is worth while emphasizing that at this stage no orientation-dependent interactions are postulated.

The free energy $F(\rho_q,\mathbf{u}_q)$ is defined by evaluating the following partition sum

$$Z(\rho_q,\mathbf{u}_q) = \left\langle \exp - \sum_{\substack{\alpha i\\ \beta j}}\left[\frac{1}{2}V_{\mathrm{AA}}(\mathbf{r}_{\alpha i}^{\mathrm{A}} - \mathbf{r}_{\mathrm{B}j}^{\mathrm{A}}) + V_{\mathrm{AB}}(\mathbf{r}_{\alpha i}^{\mathrm{A}} - \mathbf{r}_{\beta j}^{\mathrm{B}}) + \frac{1}{2}V_{\mathrm{BB}}(\mathbf{r}_{\alpha i}^{\mathrm{B}} - \mathbf{r}_{\beta j}^{\mathrm{B}})\right]\right\rangle = \exp(F(\rho_q,\mathbf{u}_q)) \tag{6}$$

The average is over the unperturbed chain configurations subject to the constraints.

$$\hat{\rho}_q\{\mathbf{r}\} = \rho_q$$

$$\hat{\mathbf{u}}_q\{\mathbf{r}\} = \mathbf{u}_q$$

The evaluation of the constrained partition sum $Z(\rho_q,\mathbf{u}_q)$ is well-established within the mean field approximation. The original method was given by Edwards[13] and was adapted by the present authors to the bond vector collective variable in refs 11 and 15. For simplicity, we confine our attention to the incompressible, symmetric diblock copolymer, where the result for the free energy can be written as

$$F(\rho_q,\mathbf{u}_q) = -|\rho_q|^2\left[\frac{1}{S - S_{\mathrm{AB}}} - \chi_{\mathrm{F}}\right] + \frac{q^2b^4}{18}\left(\frac{S_{\mathrm{AB}}}{S - S_{\mathrm{AB}}}\right)^2\left(\frac{1}{G - \frac{q^2b^4}{18}\frac{S^2}{S - S_{\mathrm{AB}}}}\right) - \frac{|\mathbf{u}_q|^2}{2G} - \frac{b^4}{36G}\frac{S^2}{S - S_{\mathrm{AB}}}\frac{|\mathbf{u}_q\cdot\mathbf{q}|^2}{G - \frac{q^2b^4}{18}\frac{S^2}{S - S_{\mathrm{AB}}}} - \left(\frac{\mathbf{u}_q\cdot i\mathbf{q}}{3}\rho_{-q}\right)\frac{b^2S_{\mathrm{AB}}}{S - S_{\mathrm{AB}}}\frac{1}{G - \frac{q^2b^4}{18}\frac{S^2}{S - S_{\mathrm{AB}}}} \tag{7}$$

The functions $S = S(q)$, $S_{\mathrm{AB}} = S_{\mathrm{AB}}(q)$ are essentially the unperturbed single chain and diblock structure factors.

$$S(q) = \langle\rho_{-q}^{\mathrm{A}}\rho_q^{\mathrm{A}}\rangle_0 = \frac{cN}{4}\left[\frac{2}{x^2} - \frac{2}{x^4}(1 - e^{-x^2})\right] \tag{8}$$

$$S_{\mathrm{AB}}(q) = \langle\rho_{-q}^{\mathrm{A}}\rho_q^{\mathrm{B}}\rangle_0 = \frac{cN}{4x^4}(1 - e^{-x})^2 \tag{9}$$

where c is the number concentration of monomers,

$$c = \frac{(N_{\mathrm{A}} + N_{\mathrm{B}})N_c}{\Omega} = \frac{NN_c}{\Omega}$$

and

$$x^2 = \frac{q^2b^2N}{12}$$

G is the bond vector correlation function, given by

$$G = \langle\mathbf{u}_{-q}\mathbf{u}_q\rangle_0 = cb^2 \tag{10}$$

and χ_{F} is the Flory interaction parameter $2\chi_{\mathrm{F}} = 2V_{\mathrm{AB}} - V_{\mathrm{AA}} - V_{\mathrm{BB}}$.

The free energy contains several important terms (in Gaussian approximation): The first term, which is proportional to the square of the concentration fluctuation, contains the classical random phase approximation (RPA) term and in addition information about the bond vector correlation, i.e., the terms that are proportional to the square of the wave vector q. The terms that are proportional to the square of the bond vector correlation separate into two terms. The first is again only determined by the bare correlation function G. The second selects different directions by the scalar product $\mathbf{u}\cdot\mathbf{q}$. The most important term, which makes the free energy nontrivial even in the Gaussian approximation, is the coupling term proportional to $\mathbf{u}\cdot\mathbf{q}\rho$. It is this term that ensures the interaction between the orientational correlations and the concentration fluctuations. It is, however, remarkable that the coupling is already present in the Gaussian approximation.

At this point we draw attention to the presence of the cross correlation term S_{AB}, which distinguishes the diblock system from a two-component polymer blend. In the binary blend the structure factor $S_{\mathrm{AB}} = 0$ and in the free energy (7) the bond vector and the concentration fluctuations variables are decoupled.

Returning to the diblock case, we confirm that upon integrating over the bond vector variable $\mathbf{u}_q$ the usual Gaussian result is obtained for the concentration fluctuations ρ_q.

$$\int D\mathbf{u}_q \exp(\sum_q F(\rho_q,\mathbf{u}_q)) = \exp\left(-\frac{1}{2}\sum_q \left|\rho_q\right|^2\left[\frac{2}{S - S_{\mathrm{AB}}} - 2\chi_{\mathrm{F}}\right]\right) \quad (11)$$

The microphase separation occurs at $\boldsymbol{q} = \boldsymbol{q}^*$, where

$$\langle\rho_q\rho_{-q}\rangle^{-1} = \frac{2}{S(q^*) - S_{\mathrm{AB}}(q^*)} - 2\chi_{\mathrm{F}} = 0 \qquad (12)$$

Likewise if the concentration variables are integrated out, an effective gaussian free energy $F(\mathbf{u}_q)$ for the bond vector variables is obtained

$$\int D\rho_q \exp(\sum_q F(\rho_q,\mathbf{u}_q)) = \exp(\sum_q F(\mathbf{u}_q))$$

where

$$F(\mathbf{u}_q) = \frac{\mathbf{1}}{2G}\mathbf{u}_q\cdot(\mathbf{1} + K(q)\hat{\mathbf{q}}\hat{\mathbf{q}})\cdot\mathbf{u}_{-q} \qquad (13)$$

and

$$K(q) = \frac{\frac{q^2b^4}{18}(S + S_{\mathrm{AB}} - S^2\chi_{\mathrm{F}})}{G(1 - \chi_{\mathrm{F}}(S - S_{\mathrm{AB}})) - \frac{q^2b^4}{18}(S + S_{\mathrm{AB}} - S^2\chi_{\mathrm{F}})}$$

and $\hat{\mathbf{q}}$ is the unit vector $\mathbf{q}/q$.

The bond vector correlation function $\langle(\mathbf{u}\cdot\hat{\mathbf{q}})^2\rangle$ is given by inverting the matrix in expression 13 for the effective free energy. The result is

$$\langle|\mathbf{u}_q\cdot\hat{\mathbf{q}}|^2\rangle = G - \frac{q^2b^4(S + S_{\mathrm{AB}} - S^2\chi_{\mathrm{F}})}{18(1 - \chi_{\mathrm{F}}(S - S_{\mathrm{AB}}))} \qquad (14)$$

The first term G is the unperturbed direct correlation, while the second term is induced by the coupling to the concentration fluctuations. As a result of this induced term, the bond vector correlation function is also unstable at q^* corresponding to a spontaneous alignment of the diblocks. The importance of the structure of the diblock is seen by setting the cross correlation function $S_{\mathrm{AB}} = 0$, in which case the unstable term in (14) is cancelled. The case when $S_{\mathrm{AB}} = 0$ corresponds to an A/B polymer blend instead of a diblock.

The previous discussion clearly demonstrates that bond vector variables play an important role in the static correlation functions of diblock copolymers. The principal aim of this paper is to explore the further consequences that these variables have for the dynamic correlation functions. We will use the derivatives of the free energy (7) with respect to the concentration and bond vector variables as the driving force terms for the dynamical equations. These are discussed in the next section.

III. Dynamical Equations

The dynamical equations for $\mathbf{u}_q(t)$ and $\rho_q(t)$ are given by the stochastic eq 1. Assuming that the random forces are uncorrelated with the value $\rho_q(0)$ at $t = 0$, we can write down the following equation for the dynamic structure factor correlation functions

$$\frac{\mathrm{d}\langle\rho_q(t)\rho_{-q}(0)\rangle}{\mathrm{d}t} = L_\rho\left\langle\frac{\partial F_q}{\partial\rho_{-q}}\rho_{-q}(0)\right\rangle \qquad (15)$$

We proceed with the free energy term, where it is useful to write the collective bond vector variable $\mathbf{u}_q$ in terms of components parallel and perpendicular to the wave vector $\mathbf{q}$

$$\mathbf{u}_q = (\mathbf{u}_{q\|})\hat{\mathbf{q}} + \mathbf{u}_{q\perp}$$

($\hat{\mathbf{q}}$ is a unit wave vector).

Then the free energy given by (7) can be written in the block form

$$F(\rho_q,\mathbf{u}_q) = -\frac{1}{2}|\rho_q|^2 A(q) - \frac{1}{2}\frac{|u_{q\perp}|^2}{G} - \frac{1}{2}|u_{q\|}|^2 B(q) - u_{q\|}\rho_{-q}C(q) \quad (16)$$

where

$$A(q) = 2\left[\left(\frac{1}{S - S_{\mathrm{AB}}} - \chi_{\mathrm{F}}\right) + \frac{q^2b^4}{18}\left(\frac{S_{\mathrm{AB}}}{S - S_{\mathrm{AB}}}\right)^2\left(\frac{1}{G - \frac{q^2b^4}{18}\frac{S^2}{S - S_{\mathrm{AB}}}}\right)\right]$$

$$B(q) = \frac{1}{G - \frac{q^2b^4}{18}\frac{S^2}{S - S_{\mathrm{AB}}}} \qquad (17)$$

$$C(q) = \frac{iqb^2S_{\mathrm{AB}}}{3(S - S_{\mathrm{AB}})}\frac{1}{G - \frac{q^2b^4}{18}\frac{S^2}{S - S_{\mathrm{AB}}}}$$

Using (15) gives the following coupled equations for $\langle\rho_q(t)\rho_{-q}(0)\rangle$ and $\langle u_{q\|}(t)\rho_{-q}(0)\rangle$, which can be written in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\langle\rho_q(t)\rho_{-q}(0)\rangle\\ \langle u_{q\|}(t)\rho_{-q}(0)\rangle\end{pmatrix} = -\mathbf{M}\begin{pmatrix}\langle\rho_q(t)\rho_{-q}(0)\rangle\\ \langle u_{q\|}(t)\rho_{-q}(0)\rangle\end{pmatrix} \qquad (18)$$

where the dynamic matrix $\mathbf{M}$ is given by

$$\mathbf{M} = \begin{pmatrix} L_\rho A(q) & L_\rho C(q) \\ L_u C(q) & L_u B(q) \end{pmatrix} \tag{19}$$

A. The Onsager Coefficients. The Onsager coefficients L_ρ and L_u are formally related[13] to the correlations of the random force terms in (1)

$$\langle \xi_q(t)\xi_{-q}(0)\rangle = 2kTL_\rho\delta(t)$$

$$\langle \boldsymbol{\eta}_q(t)\boldsymbol{\eta}_{-q}(0)\rangle = 2kTL_u\delta(t)$$

The identification of the random forces in this problem is not entirely straightforward and we adopt an alternative strategy which should be valid in the limit $q \to 0$. We consider first the coefficient L_u. From (4), in the $q \to 0$ limit, the bond vector fluctuations become

$$\langle \mathbf{u}_q(t)\mathbf{u}_{-q}(0)\rangle = \frac{1}{\Omega}\sum_{\alpha,\beta}\langle \mathbf{R}^\alpha(t)\mathbf{R}^\beta(0)\rangle \tag{20}$$

where $\mathbf{R}^\alpha(t)$ is a single diblock chain end to end vector. If we adopt the Rouse model for polymer chain dynamics, then the correlation function in (20) can be evaluated approximately as

$$\langle \mathbf{R}^\alpha(t)\mathbf{R}^\beta(0)\rangle = \delta_{\alpha\beta}\langle R^2\rangle \exp\left(\frac{-3\pi^2 kT}{\nu b^2 N^2}t\right) \tag{21}$$

Here we have only retained the longest Rouse relaxation time. ν is the monomer friction coefficient and kT the usual unit of thermal energy. In the $q \to 0$ limit, the free energy (14) governing the bond vector variables $\mathbf{u}_q$ becomes

$$F(\mathbf{u}_q) = -\frac{1}{2}\frac{|\mathbf{u}_q|^2}{cb^2}$$

and the equations of motion for $\mathbf{u}_q(t)$ give

$$\mathbf{u}_q(t) = \mathbf{u}_q(0)\exp\left(-\frac{L_u}{cb^2}t\right) \tag{22}$$

Comparing (22) with (21) in the $q \to 0$ limit gives

$$L_u = \frac{3\pi^2 ckT}{\nu N^2}$$

For the concentration fluctuations L_ρ is well-known[13] and we quote the result

$$L_\rho = \frac{ckTq^2}{\nu}$$

It will turn out later to be essential that the scaling of the Onsager coefficients is a factor of N^{-2} different. It is this difference that makes both dynamical correlations observable in the same time window.

IV. The Eigenmodes

A. The Relaxation Rates. The dynamic concentration fluctuations are given by the solution of the coupled equations (18) together with (19) and can be written in the form

$$\langle \rho_q(t)\rho_{-q}(0)\rangle = \alpha_+\exp(-\lambda_+ t) + \alpha_-\exp(-\lambda_- t) \tag{23}$$

The relaxation rates $\lambda_\pm$ are given by the eigenvalues of the 2 × 2 matrix **M** as

$$2\lambda_\pm = L_uB(q) + L_\rho A(q) \pm \sqrt{(L_uB(q) - L_\rho A(q))^2 + 4L_uL_\rho C(q)^2} \tag{24}$$

No significant algebraic simplification appears to be possible, and the full expression is not written down. However the $q \to 0$ limit does simplify and we briefly consider it here. From the expressions 8 and 9 the small q expansion of the structure factors is given as

$$S(q) = \frac{1}{4}cN - \frac{1}{144}q^2b^2cN^2 + ...$$

$$S_{\mathrm{AB}}(q) = \frac{1}{4}cN - \frac{1}{48}q^2b^2cN^2 + ...$$

Then

$$A(q) = \frac{16 \times 12}{q^2b^2cN^2}$$

$$B(q) = \frac{4}{3cb^2}$$

$$C(q) = \frac{i8}{cNb^2q}$$

The ($q \to 0$) eigenvalues are readily found as

$$\begin{aligned}\lambda_\pm &= \frac{3kT}{\nu N^2b^2}\left[\left(\frac{\pi^2}{3} + 16\right) \pm \sqrt{\left(\frac{\pi^2}{3} - 16\right)^2 + 16\frac{\pi^2}{3}}\right] \\ &\simeq \frac{3kT}{\nu N^2b^2}\begin{pmatrix}67.85\\ 9.31\end{pmatrix}\end{aligned} \tag{25}$$

What is significant about this result is that the two modes, in this limit, have comparable relaxation rates. In other words, the dynamics of the collective variables $\mathbf{u}_q(t)$ and $\rho_q(t)$ cannot be separated into fast and slow time scales. For polymer blends, the concentration fluctuations are hydrodynamic modes since the relaxation rate is proportional to q^2 in the small q limit. They are therefore naturally slow variables and any other nonhydrodynamic variables, such as the bond vector collective variables $\mathbf{u}_q$, can be considered fast. In forming a free energy functional the fast variables are normally integrated out. In the present case the hydrodynamic mode is absent in the $q \to 0$ limit, since we are dealing with a homogeneous one-component incompressible system. Instead, the finite $q \to 0$ relaxation rate is the so-called breathing mode[14] attributed to the relative motion of the two blocks. However, if the bond vector collective variables $\mathbf{u}_q$ are integrated out, this would lead to the usual free energy (11)

$$\begin{aligned}F(\rho_q) &= \frac{1}{-2}\sum_q|\rho_q|^2\left[\frac{2}{S - S_{\mathrm{AB}}} - 2\chi_{\mathrm{F}}\right] \\ &= -\sum_q|\rho_q|^2[\chi_{\mathrm{F}}^*(q) - \chi_{\mathrm{F}}]\end{aligned}$$

From which the dynamic correlation function for the concentration fluctuations is given by

$$\langle \rho_q(t)\rho_{-q}(0)\rangle = \langle|\rho_q|^2\rangle\exp[-2L_\rho(\chi_{\mathrm{F}}^*(q) - \chi_{\mathrm{F}})t] \tag{26}$$

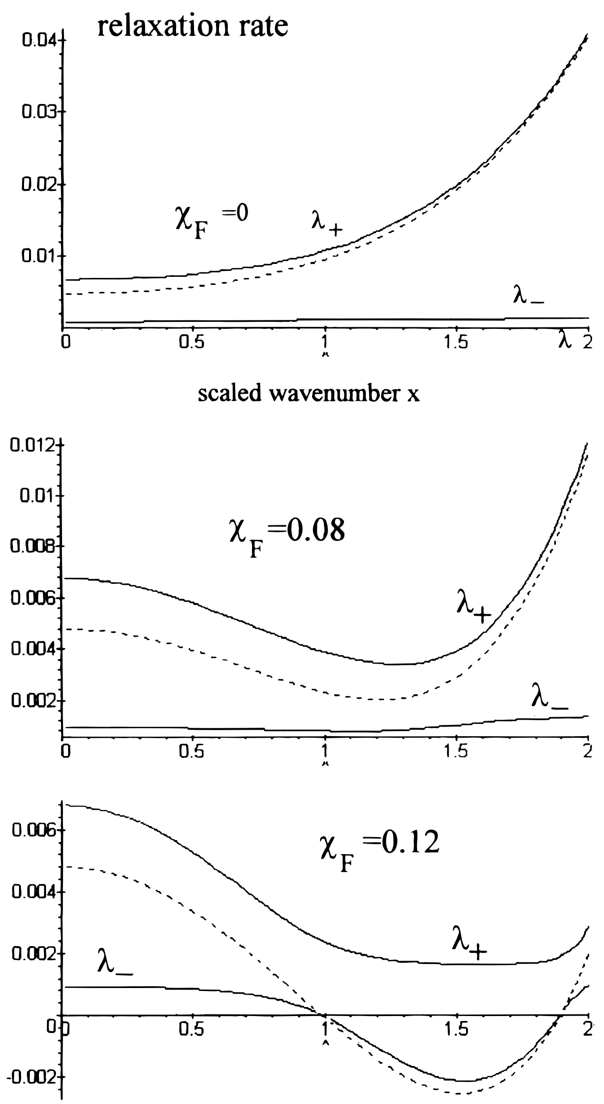

Figure 1. The full lines are the eigenvalues $\lambda_\pm$ of the dynamic matrix Ω, as a function of the scaled wavenumber $x = q^2Nb^2/12$, given by eq 24. The dashed line is the relaxation rate of the concentration fluctuations when the collective bond variable $\mathbf{u}(q)$ is integrated out of the free energy. The microphase separation occurs for $\chi_F = 0.104$. At $\chi_F = 0.12$ the λ_- is unstable, while the λ_+ mode remains stable. Units are used where $b = 1$, $c = 1$, and $N = 100$.

To compare the results of (23) and (24) with (26), the full q-dependence of the eigenvalues $\lambda_\pm$ is found numerically from (24) together with (17) for $A(q)$, $B(q)$, and $C(q)$. The results are shown in Figure 1 for a range of values of the interaction parameter χ_F and a chain length of $N = 100$. Units are used where $b = c = 1$. A dashed line is used for the single relaxation mode result (26) obtained by integrating out the bond vector modes.

As χ_F is increased, it can be seen that only one mode (λ_-) becomes unstable. The stability criterion applied to the eigenmodes, i.e. $\lambda_- \geq 0$, can be shown to be the same as that imposed on the concentration fluctuations, that is

$$\frac{1}{S(q) - S_{AB}(q)} - \chi_F \geq 0$$

The additional mode formed by coupling the concentration fluctuations to the collective bond vector variable is relatively q independent, at least for small q, which is the range seen in light-scattering experiments.

B. The Amplitudes. The amplitudes α and β of the two relaxation modes are given by standard matrix algebra as

$$\alpha_\pm = \frac{\langle|\rho_q|^2\rangle}{2} \pm \frac{(A(q)L_\rho - B(q)L_u)\langle|\rho_q|^2\rangle + 2iC(q)L_\rho\langle u_{q\|}\rho_{-q}\rangle}{2(\lambda_+ - \lambda_-)} \quad (27)$$

The static correlation functions $\langle|\rho_q|^2\rangle$ and $\langle u_{q\|}\rho_{-q}\rangle$ are the $t = 0$ values of the corresponding dynamic functions (18). They can be found in terms of the functions $A(q)$, $B(q)$, and $C(q)$ directly from the free energy form (16) as

$$\langle|\rho_q|^2\rangle = \frac{B}{AB - C^2} \qquad \langle u_{q\|}\rho_{-q}\rangle = \frac{iC}{AB - C^2}$$

and using the expressions (16) for A, B, and C, they are given in terms of the structure factors as

$$\langle|\rho_q|^2\rangle^{-1} = \frac{2}{S - S_{AB}} - 2\chi_F$$

$$\langle|\rho_q|^2\rangle^{-1} = \frac{S - S_{AB}}{2(1 - (S - S_{AB})\chi_F)} \quad (28)$$

$$\langle u_{q\|}\rho_{-q}\rangle = \frac{iqb^2S_{AB}}{6(1 - (S - S_{AB})\chi_F)}$$

Both correlation functions diverge at the microphase separation, given by

$$(1 - (S - S_{AB})\chi_F) = 0$$

However, it is possible to show that only the amplitude α_- associated with the mode λ_- diverges at the microphase separation. At this point, $\lambda_- \to 0$ and the time evolution of this mode is also unstable. The other amplitude α_+ remains finite at the microphase and the relaxation rate λ_+ remains positive, i.e. stable dynamics.

No significant algebraic simplification of the expressions for the amplitudes $\alpha_\pm$ is possible, and they have been numerically evaluated for a series of values for χ_F. The results are shown in Figure 2 for $N = 100$ and in units where $b = c = 1$. On the same plot the static structure factor $\langle|\rho_q|^2\rangle$ for the concentration fluctuations has been plotted as a dashed line for comparison.

Qualitatively these results are in agreement with the light-scattering results of Jian et al.[7] to the following extent: they find that the mode which was approximately q independent far from the microphase separation diverges as the phase point is approached and that the divergence is well-modeled by the static structure factor. In our work this is shown by the relaxation mode λ_-, where in Figure 1 for $\chi_F \approx 0$ it is approximately q independent. Near the microphase separation the amplitude α_- of this mode diverges and is closely modeled by the static structure factor, shown as the dashed line in Figure 2. A more quantitative comparison would require that we used the quadrupolar collective variable $\hat{\mathbf{Q}}_q\{\mathbf{r}\}$ (5).

V. Discussion

The strong orientational effects in the static correlation functions of diblock polymers have been shown to be driven by concentration fluctuations, mediated by the

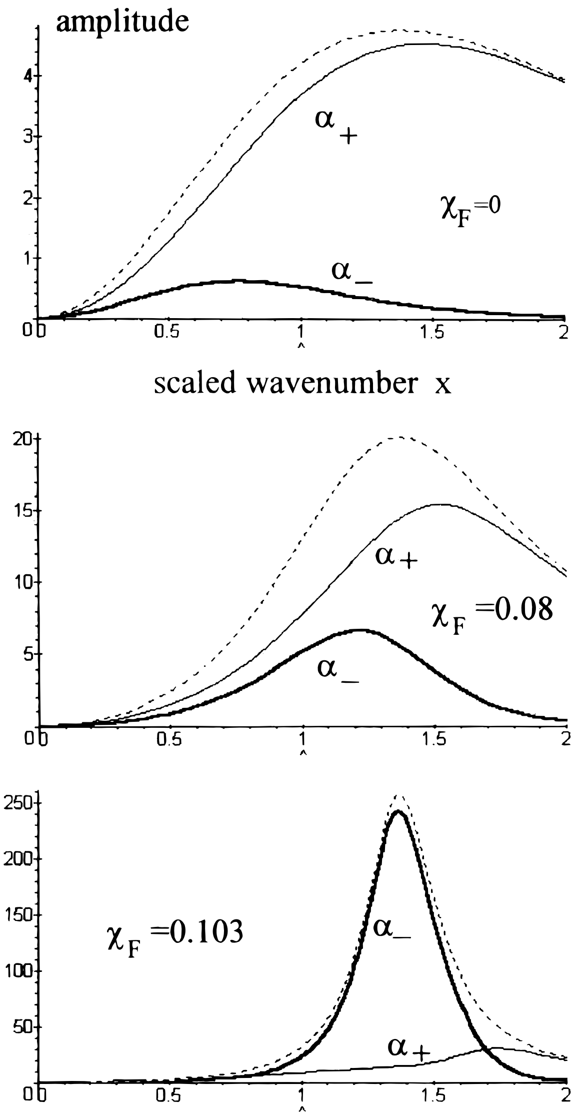

Figure 2. The amplitudes $\alpha_\pm$ of the two modes, given by eq 27, as a function of the scaled wavenumber $x = q^2Nb^2/12$. The thick line is the amplitude α_-, which is associated with the approximately q independent mode and which becomes unstable when $\lambda_- = 0$, i.e. at the microphase separation. The amplitude α_+ remains finite and is associated with the diblock breathing mode for small values of q and the Flory interaction parameter χ_F. For comparison, the static concentration fluctuations, given by eq 28, are shown as a dashed line. Units are used where $b = 1$, $c = 1$, and $N = 100$.

particular structure factor of the diblock. For polymer blends at the same concentrations the orientational coupling to the concentration fluctuations is absent. The simplest collective variable sensitive to these effects was defined in terms of the chain bond vectors. A free energy function of both the concentration and bond vector collective variables was derived from a model of chain interactions based solely on isotropic excluded volume interactions. In terms of an increasing Flory interaction parameter, the static concentration correlation function showed a microphase separation, while the collective bond vector correlations showed a nematic transition. This can be understood in terms of the screening of isotropic excluded volume interactions by anisotropic chains diblock chains leading to an effective nematic interaction.

The effect that these vector collective variables would have on the collective dynamics of a melt of diblock chains was then considered. In polymer blends the concentration variables form a natural set of hydrodynamic (slow) variables with other nonhydrodynamic variables such as the bond vector variable having a much faster dynamics, especially at $q \rightarrow 0$. Under these conditions it is possible to justify the use of a free energy function $F(\rho_q)$. For an incompressible system of identical diblock chains the concentration variables are no longer hydrodynamic in the limit $q \rightarrow 0$. They are associated with breathing modes of the chain and, as we have shown, have a dynamics comparable with the collective bond vector variable. In the small q limit there is no justification for integrating out these variables and we derived a free energy expression involving both variables. The equations of motion were assumed to be driven by derivatives of the free energy with respect to these variables. Again the unique structure of the diblock chain in the form of the cross correlation function S_{AB} was shown to be responsible for a dynamic coupling between the two sets of variables. This coupling gives rise to two relaxation modes, one of which shows a critical slowing down and is approximately q independent on scales larger than the chain size. The amplitude of this mode also increases as the microphase separation is approached. These findings are qualitatively in agreement with experimental light-scattering results.

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References and Notes

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