

# Fluctuation-induced orientational correlations in polymer blends and diblock copolymer melts

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(Received 7 September 1993)

In this paper we study the possibility of fluctuation-induced orientational correlations in interacting polymer systems. We show how orientational correlations can arise solely from isotropic density fluctuations and the screened monomer potentials in the melt. No direct anisotropic interactions are introduced. The case of homopolymer and diblock copolymer blends are considered. For the diblock copolymers the fluctuation-induced anisotropy has a large effect on the shape of the molecule, whereas for homopolymers it is small and not important at the critical point.

PACS number(s): 05.70.Fh, 61.25.Hq, 36.20.-r

## I. INTRODUCTION

The phase behavior of block copolymer melts has been studied extensively during the last decade. The classic paper of Leibler [1] on the collective properties of such systems showed that they differ significantly from polymer blends. The principal difference is that the phase separation occurs at a finite wave vector  $\mathbf{k}^*$ , whereas in homopolymer blends it occurs at zero wave vector.

A more recent result [2] which also clearly shows the difference between homopolymer and copolymer blends was the analytic study by Vilgis and Brereton of the behavior of a tagged chain in a homopolymer blend. It was shown how the individual chains shrink as the phase-separation point of the blend is approached. Similar results have also been obtained in computer simulations by Sariban and Binder [3]. Essentially the same calculation has been done for diblock polymers [4], where it was shown that the individual blocks of the chain shrink. The total radius of gyration increases due to the strong repulsion between the blocks. This result has also been verified numerically [5-7], where it was shown that significant stretching of the chains already occurs before the micro-phase-separation transition (MST). In fact, at the critical point it was found that about 50% of the chain stretching had already occurred. This result was found for all molecular weights and gives the master curve shown in Fig. 1.

Simple scaling arguments show that in the strong segregation limit (in the lamellar case) the typical size of the chains is given by [8]

$$R \sim N^{2/3}, \quad (1.1)$$

i.e., significantly larger than the Gaussian value  $R \sim N^{1/2}$ .

In this paper we will show that the stretching of the block copolymer chains near the micro-phase-separation transition creates additional orientational correlations. We study this problem using only isotropic excluded volume interactions and in contrast to Ref. [9] do not explicitly introduce any orientational interactions. Similar

results have been found in the NMR properties of stretched network chains with only isotropic excluded-volume interactions present [10]. The main result of the paper is a general formalism from which orientational correlations, which depend purely on the structure factors and the individual monomer potential, can be calculated.

## II. EFFECTIVE HAMILTONIAN

The starting point for the model proposed in this paper is the Edwards Hamiltonian for an *A-B* blend or block copolymer melt. Both cases can be treated in the same framework. The Hamiltonian can be written as

$$\beta H(\{\mathbf{R}_\alpha(s)\}) = H_{\text{free}}(\{\mathbf{R}_\alpha(s)\}) + H_{\text{int}}(\{\mathbf{R}_\alpha(s)\}), \quad (2.1)$$

where  $H_{\text{free}}(\{\mathbf{R}_\alpha(s)\})$  describes the free chains, and in the Edwards continuum chain notation it is given by

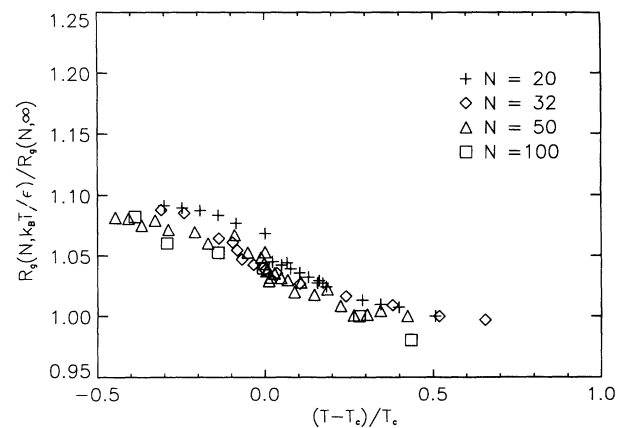


FIG. 1. The effective chain stretching for different molecular weights of the block copolymer is shown. The net effect of the stretching in the simulated range of the molecular weight is of the same order.

$$H_{\text{free}}(\{\mathbf{R}_\alpha(s)\}) = \frac{3}{2l^2} \sum_\alpha \int_0^{N_A} ds \left[ \frac{\partial \mathbf{R}_\alpha^A}{\partial s} \right]^2 + \frac{3}{2l^2} \sum_\alpha \int_0^{N_B} ds \left[ \frac{\partial \mathbf{R}_\alpha^B}{\partial s} \right]^2, \quad (2.2)$$

where  $\mathbf{R}_\alpha^A(s)$  is the chain configuration of chain  $\alpha$  and species  $A$ .  $N_A$  is the degree of polymerization of the species  $A$  and  $l$  the step length, which will be considered to be equal for all species. The sum over the chain label  $\alpha$  runs over all chains.

The interacting term  $H_{\text{int}}(\{\mathbf{R}_\alpha(s)\})$  is more conveniently written in terms of the  $s$  microscopic density fluctuations  $\rho_k^A(\{\mathbf{R}_\alpha(s)\}), \rho_k^B(\{\mathbf{R}_\alpha(s)\})$  as

$$H_{\text{int}}(\{\mathbf{R}_\alpha(s)\}) = + \sum_k V_k^{AA} \rho_k^A \rho_{-k}^A + \sum_k V_k^{AB} \rho_k^A \rho_{-k}^B + \sum_k V_k^{BB} \rho_k^B \rho_{-k}^B, \quad (2.3)$$

where

$$\rho_k^A(\mathbf{R}(s)) = \sum_{\alpha=1}^{n_p^A} \int_0^{N_A} ds e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s)}, \quad (2.4)$$

and similarly for the  $B$  polymer chain.  $n_p^A$  is the number of  $A$ -type chains.

The interactions  $V^{AA}(\mathbf{R}_\alpha^A(s) - \mathbf{R}_\beta^A(s'))$ , etc., are purely isotropic and are *a priori* not sensitive to orientational details. Nevertheless, in this paper we would like to investigate orientational-dependent properties, for example, the behavior of the density of end-to-end vectors of a binary blend or block copolymer as a phase separation is approached. We will show that orientational effects are induced even in isotropic systems.

The simplest orientational-dependent collective variable that can be defined is the local tangent vector density  $\mathbf{u}(\mathbf{r})$  [11]

$$\mathbf{u}^\sigma(\mathbf{r}) = \sum_\alpha \int_0^{N_\sigma} ds \left[ \frac{\partial \mathbf{R}_\alpha^\sigma}{\partial s} \right] \delta(\mathbf{r} - \mathbf{R}_\alpha^\sigma(s)), \quad \sigma = (A, B), \quad (2.5)$$

or in terms of the Fourier transform

$$\mathbf{u}_k^\sigma = \sum_\alpha \int_0^{N_\sigma} ds \left[ \frac{\partial \mathbf{R}_\alpha^\sigma}{\partial s} \right] e^{i\mathbf{k}\cdot\mathbf{R}_\alpha^\sigma}. \quad (2.6)$$

In the limit  $k \rightarrow 0$  the bond-vector density is just the sum of the end-to-end vectors, i.e.,

$$\mathbf{u}_k \rightarrow \sum_\alpha \mathbf{R}_\alpha(N), \quad (2.7)$$

where  $\mathbf{R}_\alpha(N)$  is the chain end-to-end vector of chain  $\alpha$ .

In this paper we will be solely concerned with calculating the bond-vector correlation functions such as

$$\Gamma_{xx}^{AA}(k) = \langle \mathbf{u}_{xk}^A \cdot \mathbf{u}_{xk}^A \rangle, \quad (2.8)$$

and similarly for  $\Gamma_{xy}^{AA}, \Gamma_{xx}^{AB}$ , etc.

The standard procedure (see, for example, Refs. [11,12]) whereby this is achieved is to replace the distribution over the free chain coordinates  $\mathbf{R}_\alpha^A(s), \mathbf{R}_\alpha^B(s)$  by a distribution over the collective variables  $\rho_k^A, \rho_k^B, \mathbf{u}_k^A, \mathbf{u}_k^B$ ,

$$\int \prod_\alpha d\mathbf{R}_\alpha^A d\mathbf{R}_\alpha^B \exp[H_{\text{free}}\{\mathbf{R}_\alpha\}] \rightarrow \int \prod_k d\rho_k^A d\rho_k^B d\mathbf{u}_k^A d\mathbf{u}_k^B \times \exp[-H_0(\{\rho_k^A, \rho_k^B, \mathbf{u}_k^A, \mathbf{u}_k^B\})], \quad (2.9)$$

where  $\exp\{-H_0(\{\rho_k^A, \rho_k^B, \mathbf{u}_k^A, \mathbf{u}_k^B\})\}$  is essentially the Jacobian of the transformation. Some of the details of this transformation are given in Appendix A. The partition sum for the system can be written as

$$Z = \int \prod_k d\rho_k^A d\rho_k^B d\mathbf{u}_k^A d\mathbf{u}_k^B \exp[-\beta H(\{\rho_k^A, \rho_k^B, \mathbf{u}_k^A, \mathbf{u}_k^B\})]. \quad (2.10)$$

The effective Hamiltonian  $H(\{\rho_k^A, \rho_k^B, \mathbf{u}_k^A, \mathbf{u}_k^B\})$  is found to be a general quadratic function of the collective variables. Then, since we are only concerned with correlation functions involving the bond-vector variables  $\{\mathbf{u}_k^A, \mathbf{u}_k^B\}$ , the density fluctuations can be integrated out, leaving an effective Hamiltonian quadratic in these variables. The result is that the bond-vector correlation functions  $\Gamma^{AA}(\mathbf{k}), \Gamma^{AB}(\mathbf{k}), \Gamma^{BB}(\mathbf{k})$  can be calculated immediately and are given in terms of unperturbed correlation functions by the matrix equation

$$\Gamma_{xy}^{AB}(\mathbf{k}) = \Gamma^0(\mathbf{k}) \delta_{xy}^{AB} - \sum_{A,B} \gamma_x^{A0}(\mathbf{k})^T U^{AB}(\mathbf{k}) \gamma_y^{B0}(\mathbf{k}), \quad (2.11)$$

where

$$\underline{\underline{\Gamma}}^0(\mathbf{k}) = \begin{pmatrix} \langle \mathbf{u}_k^A \mathbf{u}_{-k}^A \rangle_0 & \langle \mathbf{u}_k^A \mathbf{u}_{-k}^B \rangle_0 \\ \langle \mathbf{u}_k^B \mathbf{u}_{-k}^A \rangle_0 & \langle \mathbf{u}_k^B \mathbf{u}_{-k}^B \rangle_0 \end{pmatrix}, \quad (2.12)$$

$$\underline{\underline{\gamma}}^0(\mathbf{k}) = \begin{pmatrix} \langle \mathbf{u}_k^A \rho_{-k}^A \rangle_0 & \langle \mathbf{u}_k^A \rho_{-k}^B \rangle_0 \\ \langle \mathbf{u}_k^B \rho_{-k}^A \rangle_0 & \langle \mathbf{u}_k^B \rho_{-k}^B \rangle_0 \end{pmatrix}.$$

The underlines below the symbols are used to denote composition vectors and matrices ( $A, B$ ), where bold-face characters stand for the Cartesian vectors and matrices ( $x, y, z$ ). The matrix  $\underline{\underline{\gamma}}^0(\mathbf{k})$  is written in the following formally as a vector and in the Appendix is shown how this has to be understood. Indeed, the equation can be written such that  $\underline{\underline{\gamma}}^0(\mathbf{k})$  can be used as a vector.  $U(\mathbf{k})$  is the matrix of fluctuation-induced screened monomer potentials. It is related to the direct interactions  $V^{AA}, V^{AB}, V^{BB}$  by the inverse matrix equation [5]

$$\underline{\underline{U}}^{-1}(\mathbf{k}) = \underline{\underline{V}}^{-1}(\mathbf{k}) + \underline{\underline{S}}^0(\mathbf{k}), \quad (2.13)$$

where  $\underline{\underline{S}}^0(\mathbf{k})$  is the matrix of the bare concentration fluctuations

$$\underline{\underline{S}}^0(\mathbf{k}) = \begin{pmatrix} \langle \rho_k^A \rho_{-k}^A \rangle_0 & \langle \rho_k^A \rho_{-k}^B \rangle_0 \\ \langle \rho_k^B \rho_{-k}^A \rangle_0 & \langle \rho_k^B \rho_{-k}^B \rangle_0 \end{pmatrix}, \quad (2.14)$$

and  $\langle \rangle_0$  is an unperturbed average taken with respect to the free chains described by  $H_{\text{free}}(\{\mathbf{R}_\alpha(s)\})$  in Eq.

(2.1,2.2). The structure of Eq. (2.11) clearly demonstrates that although we have not introduced a direct (nematic) interaction between the bond-vector variables, nevertheless a correlation has been induced by the matrix  $\underline{U}$  of effective monomer potentials.

The matrix equation for  $\underline{U}$  can be readily solved. For example in the homopolymer case where  $S_{AB}^0 = 0$ , the results of Ref. [2] are recovered, i.e.,

$$U_{AA} = \frac{V^{AA} - \{(V^{AB})^2 - V^{AA}V^{BB}\}S_{BB}^0}{1 + V^{AA}S_{AA}^0 + V^{BB}S_{BB}^0 - \{(V^{AB})^2 - V^{AA}V^{BB}\}S_{AA}^0S_{BB}^0} . \quad (2.15)$$

Similar expressions hold for  $A \leftrightarrow B$ . Equation (2.15) is greatly simplified by using the incompressibility constraint. This is achieved by setting

$$\begin{aligned} V^{AA} &= V^{BB} = V \rightarrow \infty , \\ (V^{AB})^2 - V^{AA}V^{BB} &= 2\chi_F V , \end{aligned} \quad (2.16)$$

where  $\chi_F$  is the Flory interaction parameter for blends. In the limit  $V \rightarrow \infty$ , the effective monomer potential  $U_{AA}$  becomes

$$U_{AA}(\mathbf{k}) = \frac{1 - 2\chi_{AB}S_{BB}^0(\mathbf{k})}{S_{AA}^0(\mathbf{k}) + S_{BB}^0(\mathbf{k}) - 2\chi_F S_{AA}^0(\mathbf{k})S_{BB}^0(\mathbf{k})} . \quad (2.17)$$

The denominator function in (2.17) is the familiar expres-

$$U_{AA}(\mathbf{k}) = \frac{1 - 2\chi_F S_{BB}^0(\mathbf{k})}{S_{AA}^0(\mathbf{k}) + S_{BB}^0(\mathbf{k}) + 2S_{AB}^0(\mathbf{k}) - 2\chi_F \{S_{AA}^0(\mathbf{k})S_{BB}^0(\mathbf{k}) - S_{AB}^0{}^2(\mathbf{k})\}} . \quad (2.18a)$$

Corresponding expressions can be obtained by interchanging  $A$  and  $B$  and the potential between different types of monomers is given by [5,7]

$$U_{AB}(\mathbf{k}) = \frac{1 + 2\chi_F S_{AB}^0(\mathbf{k})}{S_{AA}^0(\mathbf{k}) + S_{BB}^0(\mathbf{k}) + 2S_{AB}^0(\mathbf{k}) - 2\chi_F \{S_{AA}^0(\mathbf{k})S_{BB}^0(\mathbf{k}) - S_{AB}^0{}^2(\mathbf{k})\}} . \quad (2.18b)$$

It is shown that the strong repulsion of different monomers expressed in Eq. (2.18b) significantly stretches the chain before the phase separation [5-7,15]. In the next section, explicit results for the orientational effects induced in the bond-vector correlation functions by concentration fluctuations will be presented. A simple Gaussian model will be used for both the homopolymer and diblock copolymer systems. Although the model is quite simple it contains already the essential effects we would like to point out. Of course, it can be refined in a similar sense as given in Refs. [7,14], but these extensions do not alter the general conclusion as we will show separately.

### III. RESULTS

#### A. Homopolymers

The main result of this paper for the orientational-dependent bond-vector correlation functions is given by Eq. (2.11) and can be written as

$$\underline{\Gamma}(\mathbf{k}) = \underline{\Gamma}^0(\mathbf{k}) - \underline{\gamma}^0(\mathbf{k})^T \underline{U}(\mathbf{k}) \underline{\gamma}^0(\mathbf{k}) . \quad (3.1)$$

After some algebra this can be written—for the  $A$

sion that leads to the enhancement of the concentration fluctuations and eventually to the phase separation [13]. In the present expression, the screened potentials are enhanced and in turn amplify the bond-vector correlation functions.

The potentials in Eqs. (2.11) and (2.12) have an unphysical singularity that signals the breakdown of the mean-field approximation. By applying a similar “renormalization” approach as in Ref. [14] this case can be regularized also. Although the validity of our results breaks down at the Ginsburg temperature and below, nevertheless simulations [5,6] at high densities confirm these results fairly.

For completeness and later use we already give the screened monomer potentials for the diblock polymer melt, where  $S_{AB} \neq 0$  (in the limit of incompressibility),

chains—as

$$\langle \mathbf{u}^A \mathbf{u}^A \rangle = \langle \mathbf{u}^A \mathbf{u}^A \rangle_0 - \langle \mathbf{u}^A \rho^A \rangle U_{AA}(\mathbf{k}) \langle \rho^A \mathbf{u}^A \rangle , \quad (3.2)$$

where the screened monomer potential  $U_{AA}(\mathbf{k})$  is given by Eq. (2.18a). To evaluate these expressions the following unperturbed correlation functions are needed:

$$\Gamma_{AA}^0 = \langle \mathbf{u}^A \mathbf{u}^A \rangle , \quad \gamma_{AA}^0 = \langle \mathbf{u}^A \rho^A \rangle , \quad S_{AA}^0 = \langle \rho^A \rho^A \rangle , \quad (3.3)$$

and  $A \leftrightarrow B$ . These are evaluated in an appendix, where it is shown that reasonable approximations are given by

$$\begin{aligned} S_{AA}^0(\mathbf{k}) &\cong \frac{\phi_A}{N_A^{-1} + k^2 b^2 / 12} , \\ \gamma_{AA}^0(\mathbf{k}) &\cong -\frac{1}{2} i \mathbf{k} S_{AA}^0(\mathbf{k}) , \\ \Gamma_{AA}^0 &\cong b^2 \mathbf{1} , \end{aligned} \quad (3.4)$$

where  $b$  is the effective monomer step length and is proportional to  $l$ . The screened monomer potential  $U_{AA}(\mathbf{k})$  can be rewritten to a more suitable form,

$$U^{AA}(\mathbf{k}) = \frac{1 - 2\chi_F S_{BB}^0(k)}{S_{AA}^0(k) S_{BB}^0(k) \left\{ \bar{\chi} + \frac{1}{12}(bk)^2 \right\}}, \quad (3.5)$$

where

$$\bar{\chi} = \frac{1}{N_A \phi_A} + \frac{1}{N_B \phi_B} - \chi_F. \quad (3.6)$$

Using these approximations the bond-vector correlation function for, e.g., the  $A$  chains is given by

$$\begin{aligned} \Gamma^{AA}(k) &= b^2 \mathbf{1} + \frac{1}{4} \mathbf{k} \mathbf{k} S_{AA}^0(\mathbf{k}) U_{AA}(\mathbf{k}) S_{AA}^0(\mathbf{k}) \\ &= b^2 \mathbf{1} + \frac{1}{4} \mathbf{k} \mathbf{k} \left[ \frac{S_{AA}^0(\mathbf{k})}{S_{BB}^0(\mathbf{k})} \right] \frac{1 - 2\chi_F S_{BB}^0(\mathbf{k})}{\bar{\chi} + \frac{1}{12}(bk)^2}. \end{aligned} \quad (3.7)$$

One immediate feature of the result (3.1) for  $\underline{\Gamma}(\mathbf{k})$  is that there are orientational couplings between different spatial directions. For example,

$$\begin{aligned} \Gamma_{xy}^{AA}(\mathbf{k}) &= \frac{1}{4} k^2 \sin^2(\theta) \sin(\phi) \cos(\phi) \\ &\times \left[ \frac{S_{AA}^0(\mathbf{k})}{S_{BB}^0(\mathbf{k})} \right] \frac{1 - 2\chi_F S_{BB}^0(\mathbf{k})}{\bar{\chi} + \frac{1}{12}(bk)^2}, \end{aligned} \quad (3.8)$$

where  $\theta, \phi$  are the polar angles between  $\mathbf{k}$  and the  $z$  axis. It is seen that the orientational correlations produced by the interactions are always proportional to  $k^2$ . This factor is responsible for the difference between homopolymer and diblock systems. The phase transition for homopolymers occurs at  $\mathbf{k}=\mathbf{0}$  when  $\bar{\chi}=0$ . However, the singularity  $\mathbf{k}^{-2}$  in the screened monomer potential is cancelled by the  $\mathbf{k}^2$  factor and  $\Gamma_{xy}^{AA}(k)$  remains finite. In other words, there is no instability in the bond-vector correlation function at the phase-separation point. The behavior of the  $\mathbf{k}$  dependent part of  $\Gamma_{xy}^{AA}(\mathbf{k})$  for the symmetric case  $N_A=N_B$  and a range of Flory parameters is shown in Fig. 2.

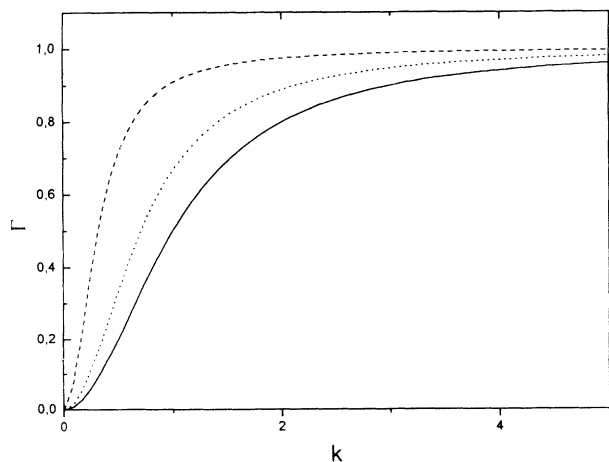


FIG. 2. The wave-vector-dependent singular part of the orientational correlation function for a blend of different polymers. The correlation function does not show a singularity at the phase transition at zero wave vector. The full line corresponds to the case  $\chi_F=0$ , the dotted line corresponds to  $X=(\chi_0-\chi_F)/\chi_0=\frac{1}{2}$  and the broken line corresponds to the system when  $X=0.1$ .

In block copolymer melts the situation is different. Through the permanent connection of the  $A$  and  $B$  part of the chain the micro phase separation takes place at finite wave vectors  $\mathbf{k}^*$  as has been shown by Leibler [1], and significant effects are then expected. This is examined in the next section.

### B. Diblock copolymers

The bond-vector correlation function for, say, the  $A$ -chain part of the diblock is given from Eq. (3.1) as

$$\begin{aligned} \langle \mathbf{u}^A \mathbf{u}^A \rangle &= \langle \mathbf{u}^A \mathbf{u}^A \rangle_0 - \langle \mathbf{u}^A \rho^A \rangle U_{AA}(\mathbf{k}) \langle \rho^A \mathbf{u}^A \rangle \\ &\quad - \langle \mathbf{u}^A \rho^B \rangle U_{BB}(\mathbf{k}) \langle \rho^B \mathbf{u}^A \rangle. \end{aligned} \quad (3.9)$$

The screened monomer potentials for diblock copolymers are more conveniently written from Eq. (2.18) in the form

$$U_{AA}(\mathbf{k}) = \frac{1 - 2\chi_F S_{BB}^0(\mathbf{k})}{S_T^0} \frac{H(\mathbf{k})}{H(\mathbf{k}) - 2\chi_F}, \quad (3.10)$$

and similarly for  $U_{BB}$  where

$$H(\mathbf{k}) = \frac{S_T^0(\mathbf{k})}{S_{AA}^0(\mathbf{k}) S_{BB}^0(\mathbf{k}) - S_{AB}^0{}^2(\mathbf{k})} \quad (3.11)$$

and

$$S_T^0 = S_{AA}^0(\mathbf{k}) + S_{BB}^0(\mathbf{k}) + 2S_{AB}^0(\mathbf{k}). \quad (3.12)$$

For diblock copolymers the block structure factor  $S_{AB}^0$  is not zero and for a Gaussian chain it can be readily found as

$$\begin{aligned} S_{AB} \approx \frac{4}{k^4} \{ &1 - \exp(-k^2 b^2 N_A / 6) - \exp(-k^2 b^2 N_B / 6) \\ &+ \exp(-k^2 b^2 [N_A + N_B] / 6) \}. \end{aligned} \quad (3.13)$$

In practice it is not convenient to parametrize this term; instead Ohta and Kawasaki [8] have given an accurate parametrization of the function  $H(\mathbf{k})$  as

$$H(k) = \frac{1}{k^2} A(N_A, N_B) + k^2 B(N_A, N_B) + \bar{\chi}, \quad (3.14)$$

where

$$\begin{aligned} A(N_A, N_B) &= \frac{1}{4N_A N_B}, \\ B(N_A, N_B) &= \frac{3}{(N_A N_B)^2}, \\ \bar{\chi} &= \frac{(N_A + N_B)}{(N_A N_B)^2} s \{ N_A / (N_A + N_B) \}. \end{aligned} \quad (3.15)$$

$s \{ N_A / (N_A + N_B) \}$  is a numerical factor given by Ohta and Kawasaki, e.g., for the symmetric case  $N_A=N_B$ ,  $s(.5)=0.9$ . The bond-vector correlation function for the  $A$  chain can be written as

$$\Gamma^{AA}(\mathbf{k}) = b^2 + \mathbf{k}\mathbf{k} \frac{H(\mathbf{k})}{H(\mathbf{k}) - 2\chi_F} \left\{ [1 - 2\chi_F S_{BB}^0(\mathbf{k})] \frac{[S_{AA}^0(\mathbf{k})]^2}{S_T^0(\mathbf{k})} + [1 - 2\chi_F S_{AA}^0(\mathbf{k})] \frac{[S_{BB}^0(\mathbf{k})]^2}{S_T^0(\mathbf{k})} \right\}. \quad (3.16)$$

The denominator function has the form

$$\frac{1}{H(k) - 2\chi_F} = \frac{1}{\frac{1}{k^2} A + k^2 B + 2(\bar{\chi} - \chi_F)}, \quad (3.17)$$

which becomes unstable at a finite  $\mathbf{k}$ . Unlike the homopolymer case this instability is no longer canceled by the  $\mathbf{k}^2$  [see Eq. (3.8)] factor in the numerator and the bond-vector correlations also show an instability for the diblock copolymer at the microphase separation. The general behavior is shown in Fig. 3.

#### IV. DISCUSSION

The main result of this paper is that in certain polymer systems orientational correlations can be induced by fluctuations. It is important to realize that no orientational-dependent interaction has been introduced from the beginning. The effective monomer potential mediated these new correlations, which become critical at mesoscopic length scales. This is of great importance especially for block copolymers, where the phase separation takes place at finite wave vectors. As has been shown earlier, the chains already stretch significantly before the microphase separation occurs, because the strong repulsion of the monomer potential between different monomers and the connectivity between the different blocks is in one chain. These effective monomer potentials induce strong orientational correlations and produce nontrivial effects. These can already be seen in the Gaussian approximation

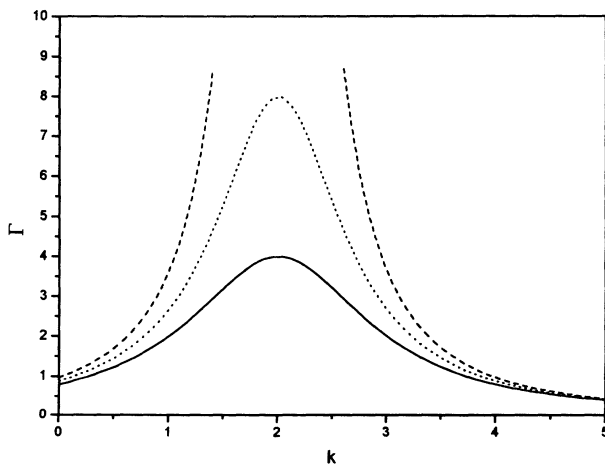


FIG. 3. Same as Fig. 2 but for diblock copolymers. It shows that the orientational correlation function has a peak at the critical wave vector  $k^*$ . As the MST is approached, a singularity occurs.

for the micro-phase-separation. Indeed the Gaussian approximation is not crucial and effective renormalized theories show that the orientational effects persist beyond this technical limitation.

The effect, however, is not important in polymer blends near their macrophase separation since the different kinds of polymers are not connected. This is consistent with the observation that the chains in blends shrink near the macroscopic phase separation [2,3,14]. It is interesting to use these predictions to analyze NMR data along the lines discussed in Ref. [10], where the corresponding NMR functions have been calculated to detect local orientations near the MST.

It is also important to realize that first the initial excluded-volume potentials and the fluctuations which are completely isotropic quantities are responsible for the induced anisotropy. This clearly shows two important features: The first is that the random-phase approximation (RPA) is not bound to isotropic systems, and secondly anisotropies are not necessarily only the result of anisotropic interactions.

#### ACKNOWLEDGMENTS

M.G.B. appreciates financial support from the Max-Planck-Society, Munich, and the warm hospitality of the MPI für Polymerforschung, Mainz. T.A.V. thanks Mr. Don Grolnick (NYC) for his general help and guidance.

#### APPENDIX A: TRANSFORMATION FROM CHAIN VARIABLES TO COLLECTIVE VARIABLES

The collective density variable  $\rho^\sigma(\mathbf{r})$ , where the superscript  $\sigma$  represents the species  $A$  or  $B$ , together with the collective bond-vector density  $u^\sigma(\mathbf{r})$  are introduced into the partition sum (2.1–2.3) by means of the identities

$$\int d\rho_{\mathbf{k}}^\sigma \delta \left[ \rho_{\mathbf{k}}^\sigma - \sum_a \int_0^{N_\sigma} ds e^{i\mathbf{k} \cdot \mathbf{R}_a^\sigma} \right] = 1, \quad (A1)$$

and

$$\int d\mathbf{u}_{\mathbf{k}}^\sigma \delta \left[ \mathbf{u}_{\mathbf{k}}^\sigma - \sum_a \int_0^{N_\sigma} ds \left[ \frac{\partial \mathbf{R}_a^\sigma}{\partial s} \right] e^{i\mathbf{k} \cdot \mathbf{R}_a^\sigma} \right] = 1. \quad (A2)$$

The Dirac  $\delta$  functions are parametrized by fields  $\phi_{\mathbf{k}}, \psi_{\mathbf{k}}$  to give the identities in the following form:

$$\int d\rho_{\mathbf{k}}^\sigma \int \frac{D\phi_{\mathbf{k}}}{2\pi} \exp i\phi_{\mathbf{k}} \left[ \rho_{\mathbf{k}}^\sigma - \sum_a \int_0^{N_\sigma} ds e^{i\mathbf{k} \cdot \mathbf{R}_a^\sigma} \right] = 1, \quad (A3)$$

and

$$\int d\mathbf{u}_k^\sigma \int \frac{\mathcal{D}\psi_k^\sigma}{(2\pi)^3} \exp i \psi_k^\sigma \left[ \mathbf{u}_k^\sigma - \sum_a \int_0^{N_\sigma} ds \left[ \frac{\partial \mathbf{R}_a^\sigma}{\partial s} \right] \exp i \mathbf{k} \cdot \mathbf{R}_a^\sigma \right] = 1. \quad (\text{A4})$$

The partition sum is then written as

$$Z = \int D\mathbf{R}(s) \int D\rho_k \int D\phi_k \int D\underline{\psi}_k \int D\underline{\mathbf{u}}_k \exp \left\{ -\beta H(\{\mathbf{R}, \underline{\rho}, \underline{\phi}, \underline{\mathbf{u}}\}) + i \sum_k \{ \underline{\phi}_k \cdot \underline{\rho}_{-k} + \underline{\mathbf{u}}_{-k} \cdot \underline{\psi}_{-k} \} \right\}. \quad (\text{A5})$$

The standard procedure is now to perform the  $\mathbf{R}_a^\sigma(s)$  functional integral, using the second moment approximation, symbolically written as

$$\int d\mathbf{R} \exp \{ -\beta H\{\mathbf{R}\} \} = \exp \left\{ -\frac{\beta}{2} \int d\mathbf{R} H^2\{\mathbf{R}\} \right\}. \quad (\text{A6})$$

The result is that (A5) can be written as the Legendre transform of an effective Hamiltonian  $H(\{\underline{\rho}_k \underline{\phi}_k, \underline{\mathbf{u}}_k, \underline{\psi}_k\})$ , where

$$\beta H(\{\underline{\rho}_k, \underline{\phi}_k; \underline{\mathbf{u}}_k, \underline{\psi}_k\}) = \sum_k \{ \underline{\phi}_k^T \underline{S}^0(\mathbf{k}) \underline{\phi}_{-k} + \underline{\rho}_k^T \underline{V}(\mathbf{k}) \underline{\rho}_{-k} + \underline{\psi}_k^T \underline{\Gamma}^0(\mathbf{k}) \underline{\psi}_{-k} + 2 \underline{\psi}_k^T \underline{\gamma}_k \cdot \underline{\psi}_{-k} \}. \quad (\text{A7})$$

A shorthand notation has been introduced, i.e.,

$$\underline{\phi}_k = (\phi_k^A, \phi_k^B), \quad \underline{\psi}_k = (\psi_k^A, \psi_k^B); \quad \underline{\mathbf{u}}_k = (\mathbf{u}_k^A, \mathbf{u}_k^B). \quad (\text{A8})$$

such that the underlines below the symbols correspond to the species vectors and the bold-face symbols to the Cartesian vectors.

The correlation functions  $\underline{S}^0(\mathbf{k})$ ,  $\underline{\Gamma}^0(\mathbf{k})$ , and  $\underline{\gamma}_k$  are defined as

$$\underline{S}^0(\mathbf{k}) = \langle \rho(k) \rho(-k) \rangle = \begin{pmatrix} S_{AA}^0(\mathbf{k}) & S_{AB}^0(\mathbf{k}) \\ S_{BA}^0(\mathbf{k}) & S_{BB}^0(\mathbf{k}) \end{pmatrix}, \quad (\text{A9})$$

$$\underline{\Gamma}^0(\mathbf{k}) = \langle \mathbf{u}_k^T \mathbf{u}_{-k} \rangle_0, \quad (\text{A10})$$

$$\underline{\gamma}^0(\mathbf{k}) = \langle \underline{\mathbf{u}}_k^T \cdot \underline{\rho}_{-k} \rangle, \quad (\text{A11})$$

and  $\langle \rangle_0$  is an unperturbed average taken with respect to the free chains described by  $H_{\text{free}}(\{\mathbf{R}_a(s)\})$  in Eq. (2.1). The  $\phi_k, \psi_k$  integrals are standard Gaussians. They are manipulated to give

$$Z = \int D\underline{\mathbf{u}}_k D\underline{\rho}_k \exp \{ -\beta H(\{\underline{\rho}, \underline{\mathbf{u}}\}) \}, \quad (\text{A12})$$

where

$$H(\{\underline{\rho}, \underline{\mathbf{u}}\}) = \sum_k \{ \underline{\rho}_k - \underline{\gamma}_k^0(\underline{\Gamma}_k^0)^{-1} \underline{\mathbf{u}}_{-k} \} \{ \underline{S}^0(\mathbf{k}) - \underline{\gamma}_k^0(\underline{\Gamma}_k^0)^{-1} \underline{\gamma}_{-k}^0 \} \{ \underline{\rho}_{-k} - \underline{\gamma}_{-k}^0(\underline{\Gamma}_{-k}^0)^{-1} \underline{\mathbf{u}}_k \}^T + \sum_k \underline{\mathbf{u}}_k \underline{\Gamma}_k^0 \underline{\mathbf{u}}_{-k} + \sum_k \underline{\rho}_k \underline{V}_k \underline{\rho}_{-k}. \quad (\text{A13})$$

Equation (A13) provides all information in the Gaussian approximation on the physical variable density and bond-vector density needed for further consideration. The integral over  $\underline{\rho}_k$  is done to the partition sum which leads to the bond-vector correlation function given by Eq. (2.11) from the main text.

## APPENDIX B: CORRELATION FUNCTIONS

To be more specific, a block-copolymer melt is considered in more detail. The bare structure matrix  $\mathbf{S}^0(k)$  is known [see Eq. (2.12)] as well as the monomer interactions. The missing matrix  $\underline{\gamma}^0(\mathbf{k})$  is given below. It has the form

$$\underline{\gamma}^0(\mathbf{k}) = \begin{pmatrix} \gamma_x^{011} & \gamma_y^{011} & \gamma_z^{011} & \gamma_x^{012} & \gamma_y^{012} & \gamma_z^{012} \\ \gamma_x^{021} & \gamma_y^{021} & \gamma_z^{021} & \gamma_x^{022} & \gamma_y^{022} & \gamma_z^{022} \end{pmatrix}, \quad (\text{B1})$$

where the individual elements are given by

$$\gamma_v^{0\sigma\tau} = \phi^\sigma \int_0^{N_\sigma} \int_0^{N_\tau} \left[ \frac{\partial \mathbf{R}_v^\sigma}{\partial s} \right]^2 e^{i \mathbf{k} \cdot \mathbf{R}^\sigma(s) - \mathbf{R}^\sigma(s')} ds ds', \quad (\text{B2})$$

$\sigma, \tau = 1, 2$  and  $v = x, y, z$  where  $\phi^\sigma$  is the volume fraction of species  $\sigma$ . It is more convenient to evaluate Eq. (4.2) in terms of discrete bond vectors [10], i.e.,

$$\gamma_x^{0AB} = \phi^A \sum_{i=1}^{fN} \sum_{j=fN+1}^N \left\langle b_{ix}^A \exp \left[ i \mathbf{k} \cdot \left( \sum_{n=1}^{fN} \mathbf{b}_n^A - \sum_{n=fN+1}^N \mathbf{b}_n^B \right) \right] \right\rangle_0, \quad (\text{B3})$$

where the average has to be taken over the discrete Wiener measure

$$P_0(\{\mathbf{b}_n\}) = N \exp \left\{ -\frac{3}{2l^2} \sum_{n=1}^N \mathbf{b}_n^2 \right\}. \quad (\text{B4})$$

It is clear from simple geometry that

$$\gamma_v^{\sigma\tau} = 0 \quad \forall \sigma \neq \tau, \quad v = x, y, z. \quad (\text{B5})$$

Therefore the  $(6 \times 2)$  matrix (B1) reduces to

$$\underline{\underline{\gamma}}^0(\mathbf{k}) = \begin{pmatrix} \gamma^{011}(\mathbf{k}) & \mathbf{0} \\ \mathbf{0} & \gamma^{022}(\mathbf{k}) \end{pmatrix}, \quad (\text{B6})$$

where  $\gamma^{011}(\mathbf{k})$  is the vector

$$\gamma^{011}(\mathbf{k}) = (\gamma_x^{011}, \gamma_y^{011}, \gamma_z^{011}). \quad (\text{B7})$$

Thus the matrix  $\underline{\underline{\gamma}}^0(\mathbf{k})$  can be written as a vector

$$\underline{\underline{\gamma}}^0(\mathbf{k}) = (\gamma_x^{011}, \gamma_y^{011}, \gamma_z^{011}, \gamma_x^{022}, \gamma_y^{022}, \gamma_z^{022}).$$

The individual  $\gamma$ 's themselves can be represented as

$$\gamma_v^{0\sigma\sigma}(\mathbf{k}) = -ik_v p_{\sigma\sigma}(\mathbf{k}), \quad v = x, y, z, \quad (\text{B8})$$

where  $p(\mathbf{k})$  is

$$p_{11}(\mathbf{k}) = \sum_{i>j=1}^{Nf} \exp \left[ -\frac{k^2 l^2}{6} |i-j| \right] \quad (\text{B9a})$$

and

$$p_{11}(\mathbf{k}) = \sum_{i>j=1}^{(1-f)Nf} \exp \left[ -\frac{k^2 l^2}{6} |i-j| \right], \quad (\text{B9b})$$

which are roughly one-half of the value of the Debye function.

For block copolymers the fluctuation-induced correlations are then given by the two typical values

$$\Gamma_{xy}^{AA}(\mathbf{k}) = l^2 + k^2 p_{AA}^2(\mathbf{k}) U^{AA}(\mathbf{k}) \quad (\text{B10a})$$

for the diagonal element and

$$\Gamma_{xy}^{AA}(\mathbf{k}) = k_x k_y p_{AA}^2(\mathbf{k}) U^{AA}(\mathbf{k}) \quad (\text{B10b})$$

for the off-diagonal element. Moreover, a correlation between the species  $A$  and  $B$  is given by

$$\Gamma_{xy}^{AB}(\mathbf{k}) = k_x k_y p_{AA}(\mathbf{k}) U^{AB}(\mathbf{k}) p_{BB}(\mathbf{k}), \quad (\text{B10c})$$

since  $p_{AB} = 0$ .

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