Influence of Small-Scale Correlation on the Interface Evolution of Semiflexible Homopolymer Blends

Xinxiang Chen, Shuanhu Qi, Xinghua Zhang, and Dadong Yan

ABSTRACT: Within the framework of a dynamic self-consistent field theory, we study the effect of correlations in a small scale on polymer dynamics, adopting the semiflexible homopolymer blends as the model system. This is accomplished by taking the pair correlation function of ideal semiflexible chains as the Onsager coefficient and the Debye function as an approximation to the Onsager coefficient. Relying on the difference of the two pair correlation functions in the small-scale region, we can identify the effect of small-scale correlations. In the equilibrium state, with the chain length growing, the interface width has a continuous transition from the contour length to radius of gyration. The investigation of interfacial evolution and chain orientation reveals that strong small-scale correlations would accelerate the small-scale dynamic process. We also expect that such a small-scale effect should be highlighted in the process where microscopic phase separation happens.

1. INTRODUCTION

The dynamic process of phase separation and domain growing is interesting and one of the basic problems in the field of polymer physics.1–10 Such a process is typically characterized by the nonlocal coupling and involves generally large-scale polymer translations and small-scale segmental orientations, leading to the multiscale nature of polymer dynamics.7–10 The nonlocal coupling arises from long-range monomer interactions and also their bonding connection. Due to the complicated interactions and rich topological structures of polymer chains, the development of a general dynamics model that could capture completely the collective behavior of polymer systems is still not available so far.

Within the framework of dynamic density functional theory, one popular scheme, which describes the density evolution of polymer systems, is the so-called dynamic self-consistent field (DSCF) theory of the model B-type.11–15 By assuming that the internal structure of chains relaxes faster than the collective motion, Maurits and Fraaije derived the DSCF equations for the nonlocal chain dynamics as11,12

\[
\frac{\partial \phi_\alpha}{\partial t}(\mathbf{r}, t) = \nabla_r \int \mathrm{d}r' \Lambda_{\alpha \beta}(\mathbf{r}, r') \nabla_r \mu_\beta(r', t) \tag{1}
\]

where \(\phi_\alpha\) is the volume fraction of the \(\alpha\)-type polymers and \(\mu_\beta\) \(\equiv (L_a/\rho_0) \partial F/\partial \phi_\beta\) is the chemical potential of the \(\beta\)-type polymers. Here, \(L\) and \(a\) are the contour length and Kuhn length, respectively. \(F\) is the free energy of the system, and \(\rho_0\) is the density of all segments.

The thermodynamic force is the driving force that evolves the system from non-equilibrium to the equilibrium state where this force vanishes. Although an explicit form of the free energy \(F\) is not easily attained, self-consistent field (SCF) theory provides a standard technique to evaluate \(F\) numerically using saddle-point approximation14,16–18 or square-gradient approximation.13,19–22 With regard to the Onsager coefficient, Maurits and Fraaije related \(\Lambda_{\alpha \beta}\) to the density–density correlation function within the Rouse dynamics for polymer chains.13 Unfortunately, the calculation of \(\Lambda_{\alpha \beta}\) is not straightforward. Qi and Schmid proposed a numerical scheme to directly calculate \(\Lambda_{\alpha \beta}\) but it requires more computational time as the additional evaluation of densities is involved in each time step.23 Therefore, in practice, approximations are usually adopted, resulting in simplified versions. One is the local coupling models, where \(\Lambda_{\alpha \beta}(\mathbf{r}, r')\) is assumed to be a position-independent constant or proportional to the local density.11,13,15,24 The other is the nonlocal coupling models without time dependence, as used in eq 1. If \(\Lambda_{\alpha \beta}\) is assumed to have the translational symmetry, the method is then transformed to the external potential dynamics.12,25,26 If it is correlation of the system. According to the dynamic equation (eq 1), the density evolution is controlled mainly by the thermodynamic force \(\nabla \mu_\beta\) and the Onsager coefficient \(\Lambda_{\alpha \beta}\). The thermodynamic force is the driving force that evolves the system from non-equilibrium to the equilibrium state where this force vanishes. Although an explicit form of the free energy \(F\) is not easily attained, self-consistent field (SCF) theory provides a standard technique to evaluate \(F\) numerically using saddle-point approximation14,16–18 or square-gradient approximation.13,19–22 With regard to the Onsager coefficient, Maurits and Fraaije related \(\Lambda_{\alpha \beta}\) to the density–density correlation function within the Rouse dynamics for polymer chains.13 Unfortunately, the calculation of \(\Lambda_{\alpha \beta}\) is not straightforward. Qi and Schmid proposed a numerical scheme to directly calculate \(\Lambda_{\alpha \beta}\) but it requires more computational time as the additional evaluation of densities is involved in each time step.23 Therefore, in practice, approximations are usually adopted, resulting in simplified versions. One is the local coupling models, where \(\Lambda_{\alpha \beta}(\mathbf{r}, r')\) is assumed to be a position-independent constant or proportional to the local density.11,13,15,24 The other is the nonlocal coupling models without time dependence, as used in eq 1. If \(\Lambda_{\alpha \beta}\) is assumed to have the translational symmetry, the method is then transformed to the external potential dynamics.12,25,26 If it is correlation of the system. According to the dynamic equation (eq 1), the density evolution is controlled mainly by the thermodynamic force \(\nabla \mu_\beta\) and the Onsager coefficient \(\Lambda_{\alpha \beta}\). The thermodynamic force is the driving force that evolves the system from non-equilibrium to the equilibrium state where this force vanishes. Although an explicit form of the free energy \(F\) is not easily attained, self-consistent field (SCF) theory provides a standard technique to evaluate \(F\) numerically using saddle-point approximation14,16–18 or square-gradient approximation.13,19–22 With regard to the Onsager coefficient, Maurits and Fraaije related \(\Lambda_{\alpha \beta}\) to the density–density correlation function within the Rouse dynamics for polymer chains.13 Unfortunately, the calculation of \(\Lambda_{\alpha \beta}\) is not straightforward. Qi and Schmid proposed a numerical scheme to directly calculate \(\Lambda_{\alpha \beta}\) but it requires more computational time as the additional evaluation of densities is involved in each time step.23 Therefore, in practice, approximations are usually adopted, resulting in simplified versions. One is the local coupling models, where \(\Lambda_{\alpha \beta}(\mathbf{r}, r')\) is assumed to be a position-independent constant or proportional to the local density.11,13,15,24 The other is the nonlocal coupling models without time dependence, as used in eq 1. If \(\Lambda_{\alpha \beta}\) is assumed to have the translational symmetry, the method is then transformed to the external potential dynamics.12,25,26 If it is
replaced by the pair correlation function \( \Lambda_{\text{pair}}(r, r') \approx g_{\text{pair}}(r - r') \), the model considers the interaction caused by other monomers according to Rouse dynamics.\(^{12,16,25,27}\) Among these different models, the Rouse dynamics has demonstrated to have its advantages, e.g., it has an explicit expression while it still retains the nonlocal coupling feature.

When the Onsager coefficient is approximated by the pair correlation function, the contribution from monomer–monomer interactions is discarded. In this case, the Onsager coefficient represents the connection between the chain structure and the nonlocal correlation. The simplest example is the ideal linear chains. These chains are completely flexible and satisfy the Gaussian distribution function. Meanwhile, the pair correlation can be calculated analytically leading to the Debye function. In a reciprocal space, the Debye function has the shape of the Cauchy distribution in the length scale larger than a few radius of gyration of the polymer (\( R_g \)) and decreases sharply according to the power law \((kR_g)^{-2}\) in the small space within a few \( R_g \) where \( k \) is the magnitude of the wave vector. The correlation behavior of the linear flexible chains stems from their chain structural properties, i.e., the strong large-scale correlation is from the chain connectivity, while the weak small-scale correlation is due to the local rigidity. From this respect, the correlation behavior can be tuned by changing the chain structures including altering the chain topology or introducing some constraint to limit the number of possible conformations. For the latter, we consider semiflexible chains where local rigidity is assumed. The former strategy gives the same structure factor for both flexible and semiflexible chains.\(^{28,29}\)

In our previous research, we found that the structure factors of flexible and semiflexible chains are the same in the large scale corresponding to a small magnitude of wave vector \( k \). However, in a small scale (large \( k \)), the structure factor of semiflexible chains is much larger than that of flexible chains, which is a constant.\(^{30}\) Thus, the difference between semiflexible and flexible chains arises from the small scale. In the semiflexible chain system, the rigidity of the chains will enhance the correlation and the kinetics of diffusion. On the other hand, for the stiff limit, Shi and co-workers studied the structure of rod–coil diblock copolymers around the coil–diblock copolymer transition in the small space.\(^{31}\) They found that there is a strong orientation for rod blocks. For the system of totally flexible chain blends, we know that in the interfacial region, the polymer coil will be stretched, but the orientation of the segments is still random,\(^{16}\) and the small-scale correlation only makes sense for the polymer system including semiflexible or stiff chains. Related results will be shown in the following parts. Such difference in short-length scale provides us the possibility to investigate the effect of small-scale correlation on dynamics, and this is the main objective of the present work, which has not been given by the Gaussian chain model in the previous work.

In this paper, we focus on the binary blends composed of A/B semiflexible homopolymer chains and propagate the system according to the DSCF theory. The interfacial broadening and the segment orientation are investigated by choosing the Debye function of flexible chains and the correlation function of semiflexible chains as the Onsager coefficients, respectively. Since the driving forces of the two kinds of systems are the same, the differences that happened in the dynamic process come from only the difference in local correlations. By comparison, we can examine the effect of Onsager coefficient, i.e., the correlation function, on dynamic properties. Our study indicates that semiflexible chains give rise to strong orientations in the interface region, and this results in favorable distribution of polymer tails in their poor phases, which is in contrast to their flexible counterparts. From the aspect of dynamics, the adoption of correlation functions derived from semiflexible chains in the model generally leads to faster dynamic processes than that of flexible chains. Small-scale correlations affect not only on the speed of component evolution but also on the orientation of segments in the interfacial region. Semiflexible chains in the interfacial region have stronger correlations, so they diffuse themselves and change their orientation faster.

This paper is organized as follows. Section 2 delivers the basic introduction to dynamics evolution equations in worm-like chains and provides the methods. Section 3 presents the results and the comparison of the calculations for two different dynamics models in simulations. Section 4 provides the conclusions and summary.

### 2. MODEL AND METHODS

In this section, the DSCF theory is briefly described for semiflexible chains. The system contains the total number \( n = n_A + n_B \) of A and B polymer chains with a mixing ratio of \( n_A/ n_B \) in the volume \( V \) with periodic boundaries. All A and B chains are identical in structures, i.e., they have the same Kuhn length \( a \), persistent length \( l_p \), and contour length \( L \). According to the Kratky–Porod semiflexible chain model, known as worm-like chain (WLC) model,\(^{7,32,33}\) if bond angles are restricted to small ones, the Kuhn length is twice the persistent length, i.e., \( a = 2l_p \). We utilize this relation in the following discussion, and the rigidity of the chain is then measured only by \( L/a \). For \( L/a \) approaching infinity, it recovers to a flexible chain. For \( L/a \ll 1 \), a rigid rod is recovered. If \( L/a \approx 1 \), the polymer behaves like a semiflexible chain.

The Hamiltonian of the system consists of two parts: \( H = H_0 + H_{\text{int}} \). The first part is the bending energy of WLC

\[
H_0 = \frac{a}{4L} \sum_{i=1}^{n_A} \int_0^{Liat} ds \left[ \frac{d\mathbf{u}(s)}{ds} \right]^2 + \frac{a}{4L} \sum_{i=1}^{n_B} \int_0^{L_0} ds \left[ \frac{d\mathbf{u}(s)}{ds} \right]^2
\]

where \( s \) is the contour variable along the chain and the vector \( \mathbf{u} = (1/L)\mathbf{dr}/ds \) specifies the local orientation of a polymer chain at location \( s \) with \( |\mathbf{u}| = 1 \). The other part is nonbond excluded volume interaction potential

\[
H_{\text{int}} = \int \text{d}r \left[ \chi \left( \frac{L}{a} \right) \phi_A \phi_B + \frac{1}{2} \eta (\phi_A + \phi_B - 1)^2 \right]
\]

where \( \chi \) is the Flory–Huggins interaction parameter and \( \eta \) measures the compressibility. Following the standard SCF theory, the functional form of the free energy has\(^{34}\)

\[
F = \int \text{d}r \left[ \chi \left( \frac{L}{a} \right) \phi_A \phi_B + \frac{1}{2} \eta (\phi_A + \phi_B - 1)^2 \right] - \sum_{a=A,B} \int \text{d}\omega_a \phi_a - V \sum_{a=A,B} \frac{Q_a}{\phi_a}
\]
Here, $\phi_\alpha$ is the average volume fraction of the $\alpha$ polymers. The field $\omega_\alpha(r)$ is the auxiliary potential conjugated to the density $\phi_\alpha(r)$. As there is no orientational interaction in the system, the potential $\omega_\alpha$ is independent of the orientation variable $u$. The single-chain partition function $Q_\alpha$ can be evaluated by $Q_\alpha = (1/4\pi) \int dr dq_\alpha(r, u, 1)$, where the propagator $q_\alpha$ satisfies the following modified diffusion equation (MDE)

$$\frac{\partial q_\alpha(r, u, s)}{\partial s} = \frac{L}{a} \nabla^2 q_\alpha(r, u, s) - L u \nabla q_\alpha(r, u, s) - \alpha_\alpha(r) q_\alpha(r, u, s)$$

with the initial condition $q_\alpha(r, u, 0) = 1$. According to the saddle-point approximation, minimizing the free energy given in eq 4 with respect to the functional variables $\omega_\alpha$ and $\phi_\alpha$, we obtain the SCF equations

$$\phi_\alpha(r) = \frac{\bar{\partial}_\alpha}{4\pi Q_\alpha} \int du \int_0^1 ds q_\alpha(r, -u, 1-s) q_\alpha(r, u, s)$$

$$\alpha_\alpha(r) = \phi_{\alpha\neq\alpha}(r) + \eta[\phi_\alpha(r) + \phi_\beta(r) - 1]$$

from which the interface profile, chain conformation at equilibrium, can be specified.

For homopolymer chains, ignoring hydrodynamic effects, the DSCF equation becomes

$$\frac{\partial}{\partial t} \phi_\alpha(r, t) = \nabla r \int d'r' \Lambda_\alpha(r, r') \nabla r' \phi_\beta(r', t)$$

where $g$ is denoted as the pair correlation function. For flexible chains, the explicit form of the pair correlation function can be obtained in a reciprocal space, which is known as the Debye function

$$g^D(kR_g) = \frac{2}{\pi} (e^{-x} - 1 + x)$$

where $x = k^2 R_g^2$ and $k$ is the magnitude of the wave vector $k$. For semiflexible chains, the corresponding pair correlation function can only be calculated numerically by the single-chain propagator obtained by eq 5 with $\omega_\alpha = 0$, i.e.,

$$g^W(r - r') = (1/4\pi)^2 \int_0^1 ds \int_0^1 ds' \int du \times [q_{\alpha, w=0}(r - r', u, s - s') + q_{\beta, w=0}(r - r', u, s - s')]$$

For practical purposes, it is convenient to solve the dynamic equation in a Fourier space, i.e.,

$$\frac{\partial \phi_\alpha(k, t)}{\partial t} = -\bar{\partial}_\alpha k^2 g(k) \phi_\alpha(k, t)$$

Here, $g(k)$ can be obtained by the Fourier transform as $g(k) = (a/L) \int dr g(r) \exp[-ik \cdot r]$ and $g(k) = g^D(k)$ for flexible chains and $g(k) = g^W(k)$ for WLC. To distinguish these two dynamics, we refer the dynamics with $g^D$ to Debye dynamics while that with $g^W$ to WLC dynamics. As expected, the curve of $g^W$ and $g^D$ overlaps if $L/a$ approaches infinity (see Figure 1). If polymer chains are investigated in a large scale, the linear chain always behaves as flexible chains independent of the local rigidity, so the curves collapse into a single one if $k$ is small. However, deviation appears in small-scale regions. When $kR_g > 3$, $k^2 g(k) L/a$ in semiflexible chains is larger than the case in flexible chains shown in Figure 1,30 It illustrates that the correlation of semiflexible chains is stronger than that of flexible chains within a small scale.

If not specified, all lengths are measured in units of $L$, time is measured by $t_0 = L^2/D_0$, where $D_0$ is the center-of-mass diffusion coefficient for the whole chain, and energy is measured by the thermal energy $k_BT$. In this paper, the normal of the A/B interface aligns parallel to the z axis, and the density distribution varies only along the z direction; therefore, we restrict ourselves to one-dimensional calculations in a space. The polar angle $\theta$ is defined as the angle between the vector $u$ and the axis $z$. Considering the azimuthal symmetry in the system, the propagator becomes a function of $z, \theta$ and $s$. The MDE is solved numerically using pseudo-spectral method.16,35,36 In this method, 256 basic modes are chosen in fast Fourier transformation (FFT), while in polar dimension, Legendre transformation is adopted, where we choose 30 basis functions. The dynamic evolution equation (eq 12) is integrated in a Fourier space using a semi-implicit scheme. These equations are solved iteratively using the simple mixing scheme, and the iteration procedure stops if the iteration error is smaller than $10^{-7}$.

3. RESULTS AND DISCUSSION

The present study considers fully symmetric polymer blends with the average volume fraction of each component $\phi_\alpha = \phi_\beta = 0.5$. The size of the system is $L_z = 3$, and the compressible constant is fixed always as $\eta = 50$. In the following discussion, we only focus on the properties of A chains.

3.1. Equilibrium Properties. The chain conformation and interface properties are first discussed at the equilibrium state. According to our calculation, for sufficiently large $\chi$, i.e., $\chi L/a > 2$, the blend phase separates into A-rich and B-rich regions with an interface in between. For the process of A polymer phase separation, the chains always diffuse from the A-rich phase ($z > 0$) to A-poor phase ($z < 0$). To characterize the interface quantitatively, we define the interfacial width as the inverse of the maximum slope of $\phi_\alpha$, that is,
Figure 2 plots the interfacial width $W$ as a function of $L/a$ in a double logarithmic representation. For convenience, the width $W$ is rescaled by the Kuhn length $a$. It can be seen that with increasing $\chi L/a$, the interface becomes sharper, and this is because the incompatibility between A/B polymers is stronger. For a fixed $\chi L/a$, two main regions can be recognized according to the value of $L/a$. The width satisfies the power law, $W \propto (L/a)^m$. For $L/a \ll 1$, the exponent $m = 1$, while for $L/a \gg 1$, the exponent $m = 0.5$. A continuous crossover region appears at intermediate values of $L/a$, i.e., a semiflexible chain condition.

In the previous work, Helfand and Tagami found that the interface width in the blends of binary flexible homopolymers is given in a infinite molecular weight limit. Then, Broseta and co-workers extended the interfacial analysis to finite molecular weight and polydisperse systems. However, the polymer configuration and orientation in the interfacial region is still unclear. Morse and Fredrickson studied the orientation of the polymers in the interfacial region using the WLC model, in which the chain orientation is well described in ground-state approximation. There are also some other studies on the homopolymer blends in the equilibrium. In the current work, without the infinite length limit, we obtain the property of interface width in WLC for an entire range of $L/a$. In the limit of stiff chains ($L/a \ll 1$), the characteristic size of the chain is the contour length $L$. In a flexible chain limit, the characteristic size is proportional to $L^{1/2}$. This means that the interfacial width has the same scaling relation as that of the size of chains.

In order to describe the configuration of WLC, two monomer distributions are defined. One is the segment distribution for A polymer, which is the probability of finding the $s$-th segment among all the A segments at the position $z$,

$$ P_A(z, s) = \frac{\phi_A(z)}{2Q_A} \int_0^\pi d\theta \sin \theta q_A(z, \theta, s) q_A(z, \pi - \theta, 1 - s) $$

which satisfies the normalization condition $\int_0^\pi d\theta P_A(z, s) = 1$. The other is the orientation distribution for A polymer at the position $z$, which is the probability of finding the A segment with the angle $\theta$ relative to the normal direction of the interface among all the A segments,

$$ P_A(z, \theta) = \frac{\phi_A(z)}{2Q_A} \int_0^\pi d\theta \sin \theta q_A(z, \theta, s) q_A(z, \pi - \theta, 1 - s) $$

which satisfies the normalization condition $\int_0^\pi d\theta P_A(z, \theta) = 1$.

Figure 3 (a, b) shows the distribution $P_A(z, s)$ in the interfacial region for $L/a = 1$ and 100, respectively. The distribution is presented only for $s \in [0, 0.5]$ and $s \in [0, 1]$ because of the symmetry. According to Figure 3a, for semiflexible chains, e.g., $L/a = 1$, their ends prefer to stay at the poor-phase side near the interface. Such a property is weaker for flexible chains, e.g., $L/a = 100$, as illustrated in Figure 3b. In the A-rich side, the distribution of segments is relatively uniform, so the end effect is not obvious for the arbitrary chain length.

Figure 3c,d displays the distribution $P_A(z, \theta)$ in the interfacial region, and only the region of $\theta \in [0, \pi/2]$ is shown because of symmetry. For semiflexible chains with $L/a = 1$, in the A-poor region, segments tend to align to the normal of the interface. However, for flexible chains, no obvious orientation preference can be observed.

For the segment behavior, semiflexible chains tend to distribute more ends in the poor-phase region near the interface and favor to align themselves perpendicular to the interface. Such features should originate from the interplay between enthalpic and entropic effects. Indeed, when the incompatibility of A/B polymers becomes stronger, the interface becomes sharper, and the distribution of the tail segments in the poor phase becomes higher as well as the distribution of $P_A(z, \theta)$ around $\theta = 0$. To save the space, we do not show these results here.

To further characterize the orientation of the polymer chains, we have a so-called orientation order parameter

$$ S_{zz}^A(z) = \frac{1}{2} \langle 3\cos^2 \theta - 1 \rangle $$

$$ = \frac{1}{2} \int_0^\pi d\theta \sin \theta (3\cos^2 \theta - 1) P_A(z, \theta) $$

According to the definition, if all chains are aligned perpendicular to the interface, $S_{zz}^A = 1$, and if they are parallel to the interface, $S_{zz}^A = -0.5$, while for randomly oriented polymers, $S_{zz}^A = 0$.

Figure 4 compares the orientation order parameter $S_{zz}^A(z)$ for $L/a = 1$ and $L/a = 100$ with different $\chi L/a$. For flexible chains with $L/a = 100$, the order parameter $S_{zz}^A$ is almost zero, independent of the position in the space and also not sensitive
to the position. This is consistent with the prediction shown in Figure 3d, i.e., all bonds could rotate completely freely for flexible chains. For semiflexible chains, however, the preferential orientation appears, and this is illustrated by the extremes in the curves with \( L/a = 1 \). In the A-polymer-poor phase, \( S_\infty(z) \) has the maximum around \( z = -0.25 \) larger than zero, which indicates that A chains tend to align perpendicular to the interface. On the other hand, the negative minimum around \( z = 0.1 \) indicates that A chains tend to be parallel to the interface. Liu and Fredrickson showed such a weaker orientation in the infinite molecule weight limit. It is noted that the chain preferential orientation happens only in regions close to the interface. In the bulk phase, no confinement is imposed, and all polymers are rotationally isotropic.

**3.2. Dynamic Properties.** The interface formation process contains the diffusion of polymers A and B. The initial density is assumed to have the format of

\[
\phi_A^{(0)} = \frac{\phi_{\min} + \phi_{\max}}{2} + \frac{\phi_{\min} - \phi_{\max}}{2 \tanh \xi} \times \tanh \left( \frac{\xi}{L} \cos \left( \frac{\pi}{L} \left( z + \frac{L}{2} \right) \right) \right) 
\]

where the parameter \( \xi \) controls the width of the initial interface. Here, we take \( \phi_{\min} = 0.01, \phi_{\max} = 0.99, \) and \( \xi = 100 \). Such initial profiles were also adopted in the theoretical studies to the DSCF theory for the interface of totally flexible chain blends.

Figure 5 shows the evolution of the A polymer density profile, in which panel a is obtained using the WLC dynamics for semiflexible chain \( L/a = 1 \) and panel b is obtained using the Debye dynamics for flexible chain \( L/a = 100 \). With the diffusion of A polymers, the amount in the A-rich region decreases, while that in the A-poor region increases monotonically and leads to the broadening of the interface. It notes that the initial width of the interface is the same in the two subfigures. Polymers with different rigidities have different diffusion rates. The diffusion of semiflexible chains is faster than that of flexible chains. At \( t = t_p \), the diffusion for \( L/a = 1 \) is already close to equilibrium; however, the flexible chains are still interdiffusing. The other is the different width of the interface. The flexible chain system forms a wider interface, which is also shown in the Figure 2.

Figure 6 shows the interfacial width as a function of time, which is rescaled by the interfacial width of the equilibrium state. The interfacial width is extracted from the density profile at some time \( t \) according to eq 13, and the initial interfacial width is calculated as \( W_{\infty} \approx 0.048L \). Figure 6a shows the case of \( \chi L/a = 2.5 \). The curves predicted by Debye dynamics can coincide with that predicted by the WLC dynamics if the chains are flexible, e.g., \( L/a = 25 \) and \( L/a = 100 \). This is inevitable since for flexible chains, their pair correlation function is almost the same as the Debye function. In contrast, deviation appears from the beginning to the final saturation stage if the chains are semiflexible, e.g., \( L/a = 1 \) and \( L/a = 5 \). In the early stage, the WLC dynamic predicts a fast evolution for semiflexible chains. In the later stage, e.g., \( t > 0.1 \), the density profiles from the two dynamic calculations at the same time can overlap each other. Similar features hold for \( \chi L/a = 4 \), where the interface is sharper and the equilibrium state can be reached at an earlier time, as shown in Figure 6b.

Now, we focus on the case of semiflexible chains since only in this case that one can find the difference between the WLC and Debye dynamic processes. For the structure factors shown in Figure 1, the difference is only in larger \( k \) (corresponding to the small scale in a real space), and the structure factor of
WLC is larger than that of the Gaussian chain. Based on this argument, we can conclude that the influence of small-scale correlation plays a key role in the interface evolution for the semiflexible chains.

Figure 7 shows the evolution of the orientation order parameter $S^A_{zz}(z, t)$ for semiflexible chains with $L/a = 1$ and $\chi = 4.0$. The corresponding equilibrium profiles can also be found in Figure 8. As discussed, the positive maximum in the A-polymer-poor region is a sign that A chains prefer to be parallel to the interface, while the negative minimum in the A-polymer-rich region represents that A chains prefer to be perpendicular to the interface. With the elapse of time, the absolute values of the maximum and minimum decrease, while the width of the protrusion broadens.

In order to quantify the chain orientation, the maximum and minimum value in the curves of $S^A_{zz}(z, t)$ are plotted at some chosen time $t$ for $\chi L/a = 4.0$ in Figure 8. The initial state is chosen from the maximum and minimum values in Figure 7 at $t = 10^{-5}$. With time going, $S_{zz}^{\text{max}}$ decreases and $S_{zz}^{\text{min}}$ increases gradually, and they finally get to their equilibrium values. In Figure 8a, the evolution of $S_{zz}^{\text{max}}$ obtained by WLC dynamics and Debye dynamics differs from each other only in the case of $L/a = 1$. However, for $S_{zz}^{\text{min}}$, as shown in Figure 8b, there is still this difference even at $L/a = 5$. In any case, the evolution of WLC dynamics reaches the equilibrium state first. The curves from WLC and Debye dynamics start to merge at some point, depending on the chain rigidity. Although the exact merge time and merging process are not analyzed here, the main point delivered by Figure 8 is clear, i.e., the orientation dynamics are faster predicted using the WLC dynamics model for stiffer chains at the early stage of evolution. The dynamic features for chain orientation are consistent with the evolution of interfacial width, as shown in the Figure 6.

4. SUMMARY AND CONCLUSIONS

To summarize, within the framework of the DSCF theory, we have investigated the effect of small-scale correlation on collective dynamics using WLC polymer blends as the model system. As we know, the correlation function is proportional to the Onsager coefficient, i.e., the mobility matrix. For comparison, two different correlation functions are chosen. One is the Debye function for ideal flexible chains, which accounts for the flexible chain limit and has an explicit expression in reciprocal space; the other is the pair correlation function of semiflexible chains, which can only be calculated numerically. These two correlation functions differ from each other only in the small scale for the semiflexible chains.

The segment distribution shows that the inhomogeneity appears only near the interface. With the increasing chain flexibility, the scaling relation of the interfacial continuously changes from $W \propto L$ for highly stiffer chains to $W \propto L^{1/2}$ for completely flexible chains. Furthermore, near the interface, the end segments of A polymers prefer to distribute in the A-polymer-poor region, while in the A-polymer-rich region, the segment distribution is relatively uniform. The study of polar angle distribution and chain orientation shows that A polymers prefer to be perpendicular to the interface in their poor-phase region and prefer to be parallel to the interface in their rich-phase region. This propensity is enhanced when the A/B interface is sharper.

The investigation of both interfacial broadening and polymer orientation evolution shows that the WLC and Debye dynamic processes overlap each other if the chains become more flexible. On the other limit, when chains become stiffer, the correlation of the semiflexible chains is stronger compared with their flexible counterparts. In this case, the interfacial evolution shows that small-scale correlation can affect the dynamics of interfacial broadening. Precisely, if the small-scale correlation is neglected, the dynamic evolution at the early stage will be slowed down. The acceleration of the dynamics by the small-scale correlation is also confirmed by the investigation of the chain orientation process.

From Figure 6, one can also find that for the semiflexible polymers even if the WLC dynamics is faster than the Debye dynamics in the early stage, they will merge each other in the late stage. This process corresponds to the diffusion of the center of polymer chains since it is a macrophase separation. In this sense, the polymer blends may not be a perfect model system, demonstrating the effect of small-scale correlations on evolution dynamics. The better model system may be the block copolymer system since it is the microphase separation in the small scale. We hope to study this system in the future investigation.

Furthermore, we argue that in order to highlight the small-scale correlation effect, we adopt the DSCF theory of the Maurits and Fraaije scheme, where the Onsager coefficient is memory-free. However, this should generally not be the case, and indeed, Müller and co-workers recently have extended the
conventional DSCF to include the memory effect and demonstrated its significance.5 We believe that identifying the contribution of orientational order and spatial and temporal correlations separately should be crucial for the construction of a more accurate and complete DSCF theory. Such a DSCF theory is expected to be able to investigate various dynamics problems of polymer systems where orientation and correlation effects have to be involved.

Finally, we hope that theoretical results may provide guidance to the related experiments. Neutron scattering techniques may be a good candidate to measure the small-scale correlations and the dynamic process in the semiflexible system, although we have not found the experimental results up to present. Béziel and co-workers investigated the formation to interfacial width of two thin flexible films in the capillary-wave mode.7 It just shows large-scale hydrodynamic flows.

AUTHOR INFORMATION

Corresponding Authors

Shuahan Qi — School of Chemistry, Beihang University, Beijing 100191, China; orcid.org/0000-0002-4260-4641; Email: qishuahuan@buaa.edu.cn

Xinghua Zhang — School of Science, Beijing Jiaotong University, Beijing 100044, China; Email: zhangxh@bjtu.edu.cn

Dadong Yan — Department of Physics, Beijing Normal University, Beijing 100875, China; orcid.org/0000-0002-9944-6381; Email: yandd@bnu.edu.cn

Author

Xinxiang Chen — Department of Physics, Beijing Normal University, Beijing 100875, China

Complete contact information is available at:

https://pubs.acs.org/10.1021/acsomega.0c00421

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (nos. 21873015, 21873010, 21774013, and 21434001) and Beijing Natural Science Foundation (no. 2182057).

REFERENCES

(1) Gao, Q. Polymer morphology: principles, characterization, and processing; Wiley: 2016.

(2) Boudenne, A.; Ibos, L.; Candau, Y.; Thomas, S. Handbook of multiphase polymer systems; Wiley: 2011.

(3) Bailey, A. E.; Poon, W. C. K.; Christianson, R. J.; Schofield, A. B.; Gasser, U.; Prasad, V.; Manley, S.; Segre, P. N.; Cipelletti, L.; Meyer, W. V.; et al. Spinodal decomposition in a model colloid-polymer mixture in microgravity. Phys. Rev. Lett. 2007, 99, 205701.

(4) Béziel, W.; Fragneto, G.; Cousin, F.; Serrazza, M. Neutron reflectivity study of the kinetics of polymer-polymer interface formation. Phys. Rev. E 2008, 78, No. 022801.

(5) Zhang, C.; Fan, Y.; Zhang, Y.; Yu, C.; Li, H.; Chen, Y.; Hanley, I. W.; Jiang, S. Self-assembly kinetics of amphiphilic dendritic copolymers. Macromolecules 2017, 50, 1657–1665.

(6) Pearson, A. J.; Wang, T.; Lidzey, D. G. The role of dynamic measurements in correlating structure with optoelectronic properties in polymer: fullerene bulk-heterojunction solar cells. Rep. Prog. Phys. 2013, 76, No. 022501.

(7) Chen, J. Z. Y.; Sullivan, D. E. Free energy of a wormlike polymer chain confined in a slit: crossover between two scaling regimes. Macromolecules 2006, 39, 7769–7773.

(8) Li, Y.; Abberton, B. C.; Kröger, M.; Liu, W. K. Challenges in multiscale modeling of polymer dynamics. Polymer 2013, 5, 751–832.

(9) Kawasaki, K.; Sekimoto, K. Dynamical theory of polymer melt morphology. Phys. A 1987, 143, 349–413.

(10) Harden, J. L. Kinetics of interface formation between weakly incompatible polymer blends. J. Phys. (Paris) 1990, 51, 1777–1784.

(11) Fraiøj, J. G. E. M.; Van Vlimmeren, B. A. C.; Maurits, N. M.; Postma, M.; Evers, O. A.; Hoffmann, C.; Altevogt, P.; Goldbeck-Wood, G. The dynamic mean-field density functional method and its application to the mesoscopic dynamics of quenched block copolymer melts. J. Chem. Phys. 1997, 106, 4260–4269.

(12) Maurits, N. M.; Fraiøj, J. G. E. M. Mesoscopic dynamics of copolymer melts: From density dynamics to external potential dynamics using nonlocal kinetic coupling. J. Chem. Phys. 1997, 107, 5879–5889.

(13) Yeung, C.; Shi, A.-C. Formation of interfaces in incompatible polymer blends: A dynamical mean field study. Macromolecules 1999, 32, 3637–3642.

(14) Müller, M.; Schmid, F. Incorporating fluctuations and dynamics in self-consistent field theory for polymer blends. Adv. Polym. Sci. 2005, 185, 1–58.

(15) Morita, H.; Kawakatsu, T.; Doi, M. Dynamic density functional study on the structure of thin polymer blend films with a free surface. Macromolecules 2001, 34, 8777–8783.

(16) Fredrickson, G. H. The equilibrium theory of inhomogeneous polymers; Oxford University Press: 2006; Vol. 134.

(17) Laradji, M.; Shi, A.-C.; Noolandi, J.; Desai, R. C. Stability of ordered phases in diblock copolymer melts. Macromolecules 1997, 30, 3242–3255.

(18) Cooke, D. M.; Shi, A.-C. Effects of polydispersity on phase behavior of diblock copolymers. Macromolecules 2006, 39, 6661–6671.

(19) de Gennes, P.-G. Dynamics of fluctuations and spinodal decomposition in polymer blends. J. Chem. Phys. 1980, 72, 4756–4763.

(20) Tang, H.; Freed, K. F. Free energy functional expansion for inhomogeneous polymer blends. J. Chem. Phys. 1991, 94, 1572–1583.

(21) Zhang, X.; Man, X.; Han, C. C.; Yan, D. Nucleation induced by phase separation in the interface of polyelefin blend. Polymer 2008, 49, 2368–2372.

(22) Wang, S. Q.; Shi, Q. Interdiffusion in binary polymer mixtures. Macromolecules 1993, 26, 1091–1096.

(23) Qi, S.; Schmid, F. Dynamic density functional theories for inhomogeneous polymer systems compared to Brownian dynamics simulations. Macromolecules 2017, 50, 9831–9845.

(24) Hasegawa, R.; Doi, M. Adsorption dynamics. Extension of self-consistent field theory to dynamical problems. Macromolecules 1997, 30, 3086–3089.

(25) Reister, E.; Müller, M.; Binder, K. Spinodal decomposition in a binary polymer mixture: dynamic self-consistent-field theory and Monte Carlo simulations. Phys. Rev. E 2001, 64, No. 041804.

(26) Qi, S.; Zhang, X.; Yan, D. External potential dynamic studies on the formation of interface in polypdisperse polymer blends. J. Chem. Phys. 2010, 132, No. 064903.

(27) Rouse, P. E., Jr. A theory of the linear viscoelastic properties of inhomogeneous polymer blends: A dynamical mean field study. Macromolecules 2001, 34, 2372.

(28) Rubinstein, M.; Colby, R. H. Polymer physics; Oxford university press: New York, 2003; Vol. 23.

(29) Jiang, Y.; Chen, J. Z. Y. Isotropic-nematic interface in a lyotropic system of wormlike chains with the Onsager interaction. Macromolecules 2010, 43, 10668–10678.

(30) Zhang, X.; Jiang, Y.; Miao, B.; Chen, Y.; Yan, D.; Chen, J. Z. Y. The structure factor of a wormlike chain and the random-phase-approximation solution for the spinodal line of a diblock copolymer melt. Soft Matter 2014, 10, 5405–5416.
(31) Cai, Y.; Zhang, P.; Shi, A.-C. Liquid crystalline bilayers self-assembled from rod−coil diblock copolymers. *Soft Matter* 2017, 13, 4607−4615.

(32) Kratky, O.; Porod, G. Röntgenuntersuchung gelöster fadenmoleküle. *Recl. Trav. Chim. Pays-Bas* 1949, 68, 1106−1122.

(33) Saitō, N.; Takahashi, K.; Yunoki, Y. The statistical mechanical theory of stiff chains. *J. Phys. Soc. Jpn.* 1967, 22, 219−226.

(34) Morse, D. C.; Fredrickson, G. H. Semiflexible polymers near interfaces. *Phys. Rev. Lett.* 1994, 73, 3235.

(35) Matsen, M. W. Melts of semiflexible diblock copolymer. *J. Chem. Phys.* 1996, 104, 7758−7764.

(36) Jiang, Y.; Zhang, W.-Y.; Chen, J. Z. Y. Dependence of the disorder-lamellar stability boundary of a melt of asymmetric wormlike AB diblock copolymers on the chain rigidity. *Phys. Rev. E* 2011, 84, No. 041803.

(37) Helfand, E.; Tagami, Y. Theory of the interface between immiscible polymers. *J. Polym. Sci., Part B: Polym. Lett.* 1971, 9, 741−746.

(38) Helfand, E.; Tagami, Y. Theory of the interface between immiscible polymers. II. *J. Chem. Phys.* 1972, 56, 3592−3601.

(39) Broseta, D.; Fredrickson, G. H.; Helfand, E.; Leibler, L. Molecular weight and polydispersity effects at polymer-polymer interfaces. *Macromolecules* 1990, 23, 132−139.

(40) Ermoshkin, A. V.; Semenov, A. N. Interfacial tension in binary polymer mixtures. *Macromolecules* 1996, 29, 6294−6300.

(41) Tang, H.; Freed, K. F. Interfacial studies of incompressible binary blends. *J. Chem. Phys.* 1991, 94, 6307−6322.

(42) Schmid, F.; Mueller, M. Quantitative comparison of self-consistent field theories for polymers near interfaces with monte carlo simulations. *Macromolecules* 1995, 28, 8639−8645.

(43) Carelli, C.; Jones, R. A. L.; Young, R. N.; Cubitt, R.; Dalglish, R.; Schmid, F.; Sferrazza, M. Approaching criticality in polymer-polymer systems. *Phys. Rev. E* 2005, 72, No. 031807.

(44) Liu, A. J.; Fredrickson, G. H. Interfacial properties of isotropic semi-flexible polymer blends. *Mater. Res. Soc. Symp. Proc.* 1992, 290, 37.

(45) Wang, G.; Ren, Y.; Müller, M. Collective short-Time dynamics in multicomponent polymer melts. *Macromolecules* 2019, 52, 7704−7720.