Viscoelastic Effects on the Dynamics of Spinodal Decomposition in Binary Polymer Mixtures

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Introduction

Although the phase separation and critical phenomena have been extensively studied in the past three decades both theoretically and experimentally,[1, 2] the ordering process of the thermodynamically unstable state (e.g. spinodal decomposition) is still one of the puzzles in the field of phase transition. Analytical and numerical approaches were employed by researchers to tackle this problem. For the highly non-linear properties of phase separation dynamics that exist in nature, the reliability of approximations introduced into the analytical approaches is hard to appraise (especially for the late stage behavior of the phase separation), so numerical simulations have been widely applied to this field.

Enlightened by renormalization group theory, Oono and Puri proposed an efficient method that directly described the phenomena, i.e. the cell dynamics scheme (CDS), to improve computing efficiency.[3–5] Therefore it is not necessary to rigidly adhere to the classical analytical theories based on partial differential equations, and the approach can be applied to investigate the process of phase separation in polymer mixtures efficiently.

In the classical models, the characteristics of polymer chains have not been considered, except for introducing molecular weights of polymers into the Flory-Huggins free energy.[6, 7] It has so far been believed that polymer systems belong to the same dynamic universality class as classical fluids, namely, the so-called model-B for the case without hydrodynamic effect and model-H for the case with hydrodynamic effect in the Hohenberg-Halperin notions.[8] Many experimental results suggest this universality[9, 10] and point out that phase separation in polymer mixtures can be understood in terms of model-H.

Recently, the effects of characteristics unique to polymer system on the phase separation dynamics have drawn more and more attention. It is found that in the polymer systems in which there exists a pronounced contrast of viscoelasticity, modulus, and flexibility of chains, the
process of phase separation will exhibit unusual behaviors, e.g. spinodal pinning, network-like morphology, sponge-like morphology, and phase inversion. Many researchers believe that the phase separation phenomena of polymer blends should be ascribed to a new dynamical universality. Such a class of behavior has been considered as viscoelastic phase separation.

Tanaka has proposed a reasonable explanation for viscoelastic phase separation. During the incubation stage, the appearance of domains has to overcome the elastic barrier. Once the domains come into being, there must be one phase which has much stronger viscoelasticity, and this strong viscoelastic phase exhibits elasticity dominant dynamics characteristics in a relatively short time scale, therefore, elasticity plays a more important role than diffusion in this regime.

It is important to note that the viscoelastic effect cannot be simply described by a normal free energy function, order parameter, and mobility coefficient, due to its relaxation character. Previously, the effects of entanglements on the mobility, late stage growth, and the dynamics of concentration fluctuations in the presence of either a macroscopic flow field or a hypothetical microscopic flow field referred to as the “tube velocity”, have been considered. This work has been explored further by Onuki, who proposed that coupling between stress and the dynamics of concentration fluctuations occurs in asymmetric blends (i.e. those in which the molecular weights of the two components are different). The coupling between the stress field and the order parameter causes the viscoelastic suppression of the order parameter fluctuation during the phase separation process.

Based on the two-fluids model, Onuki and Tanaka proposed similar models for viscoelastic phase separation. Taniguchi and Onuki have carried out numerical simulations and found that the network domain structure is stabilized up to a very late stage. They found that in the absence of viscoelastic stress the growth law exponent was controlled by hydrodynamic interactions and the characteristic size of domains grew with time as $R(t) \propto t^n$, with the growth exponent $n = 2/3$. In our opinion, Tanaka’s model is relatively more universal, and can be used to describe the dynamical behavior both of polymer solutions and polymer bulks. Tanaka’s simulation results reproduce almost all the essential features of viscoelastic phase separation observed experimentally. In Onuki’s model, only the viscoelasticity of one of the components has been considered, and that of the other one has been set to be zero, so the model only can be applied to polymer solutions. On the other hand, Onuki’s model ignores the contribution of bulk relaxation modulus.

In systems with a contrast of molecular weight, especially in polymer solutions, the scaling structure function in late stage exhibits a broader peak than that predicted by Furukawa. Puri et al., Zhang and Ahluwalia have introduced different forms of order-parameter-dependent mobility into the Cahn-Hilliard equation and obtained some valuable results.

Sappelt et al. have studied a binary mixture containing a glassy component, the conjunction of the glass transition with the spinodal decomposition was modeled by a rapid decrease of the mobility coefficient with increasing concentration of the glass-forming component. The growth law for the characteristic length shows a pronounced plateau at the intermediate stage.

Although there are so many research works on the viscoelastic phase separation, the simulation results of Bhatcharya et al. indicate that the true late-time growth kinetics of quenched polymer solutions belong to the same universality class of small molecular mixtures, and the comprehensive experimental studies of Haas and Torckelson strongly suggest that the growth law for quenched polymer solutions is identical to the small molecular systems at late times.

Clarke et al., considering entanglements as an analogy of a permanent cross-linked system, introduced an elastic term into the Flory-Huggins free energy, and successfully explained the experimental results obtained from polystyrene/poly(vinyl methyl ether) (PS/PVME) blends with asymmetric molecular weights.

In this paper, the dynamical asymmetry has been introduced into binary mixtures through the addition of a relaxable elastic term into the mixing free energy. Simulations were carried out through forming a discrete two-dimensional lattice in real space.

**Model and Simulation Algorithm**

In the frame of the time-dependent Ginzburg-Landau (TDGL) equation, the motion equation for the concentration fluctuation in $q$-space is written as

$$\frac{\partial \psi(q,t)}{\partial t} = -q^2 M(q) \frac{\partial H[\psi(q,t)]}{\partial \psi(q,t)}$$

where $H[\psi(q,t)]$ is the free energy function for the system, $\psi(q,t)$ is the Fourier transform of the order parameter, which is defined as the difference of local concentrations between the two components, i.e. $\psi(q) = \phi_1(q) - \phi_2(q)$; $M(q)$ is the $q$-dependent mobility. For simplicity, $M(q)$ is set to 1 as usual. The free energy for the polymer blends is often written in the Flory-Huggins-de Gennes form as

$$H[\psi(q,t)] = \sum_q \left\{ F[\psi(q,t)] + \frac{1}{2} Dq^2 \psi(q,t) \right\}$$

with $F[\psi(q,t)]$ is the usual Flory-Huggins free energy or the Landau-Ginzburg free-energy; $D$ characterizes the strength of the interfacial free energy.
The viscoelastic effect will be dealt with following the procedure of Clarke et al.\textsuperscript{34} In that treatment, the case of entanglement is analogous with that of the system in which the two components are permanently cross-linked. For the case of a permanently cross-linked system, the chain stretching between fixed cross-links gives rise to an elastic term in the free energy and it will affect the concentration fluctuation. According to de Gennes,\textsuperscript{35} to a good approximation, the free energy may be written as:

\[
H[q(q, t)] = \sum_q \left\{ F[q(q, t)] + \frac{1}{2} Dq^2 \psi(q, t) \right\} + H_0[q(q, t)]
\]

\[
= \sum_q \left\{ F[q(q, t)] + \frac{1}{2} Dq^2 \psi(q, t) \right\} + c_0(q) \psi(q, t) - \psi_0(q, t)^2
\]

Hence, the elastic energy is proportional to the square of the difference between magnitudes of the current fluctuations and the "frozen-in" initial fluctuation, \( \psi_0(q, t) \).

The constant \( c_0(q) \) depends on the details of the entanglement. There are two cases of interest: (1) both components are mutually entangled and an A-B network will be formed; (2) only one component which has the higher molecular weight than component-B, in the time scale between the repetition times of short and long polymers, the only topological constraints are the entanglements between long chains (component-A). It is known that, for the case of A-B entanglement the parameter \( c_0 \) should have the form:

\[
c_0(q) = 36/N_c^2 b^2 q^3
\]

In Equation (4), \( N_c \) is the chain length between entanglements and \( b \) is the statistical segment length. While for the case of A-A entanglement, \( c_0 \) can be written as:\textsuperscript{35}

\[
c_0(q) = 3\phi_s/N_c
\]

with \( \phi_s \) is the volume fraction of polymer A. We must mention that Equation (4) and (5) are valid only for length scales greater than the distance between entanglements, i.e. \( 1/q > N_c b^2 \). In this paper, we only focus our attention on the system with A-A entanglements.

In the case of polymer entanglements, the "frozen-in" concentration fluctuation is not permanent, but decays with time. Following the treatment of Clarke et al.,\textsuperscript{34} the fraction of entanglements that keeps unrelaxed and exists at time \( t \) is denoted by \( g(t-t') \). Hence, its contribution to the elastic free energy is the product of \( H_0 \) and the fraction of entanglements unrelaxed, i.e.:

\[
E_s(t, t') = \{ c_0(q) [\psi(q, t) - \psi(q, t')]^2 \} g(t-t')
\]

Since a new set of entanglements is only born after a characteristic lifetime, \( \tau_s \), the total elastic energy may be obtained by summing over the contributions from all previous times. In the continuous limit, it is written as

\[
E_s(t) = c_0(q) \int_0^\infty [\psi(q, t) - \psi(q, t')]^2 g(t-t') \frac{dt'}{\tau_s}
\]

with \( g(t-t') = \exp[-(t-t')/\tau_s] \) and \( \tau_s \) is the characteristic time of entanglement relaxation. Then, the TDGL equation can be written as:

\[
\frac{\partial \psi(q, t)}{\partial t} = -q^2 M(q) \frac{\partial}{\partial \psi(q, t)} \left\{ F[q(q, t)] + \frac{1}{2} Dq^2 \psi(q, t) \right\} + c_0(q) \int_0^\infty \frac{dt'}{\tau_s} \frac{g(t-t')}{\tau_s} [\psi(q, t) - \psi(q, t')]^2
\]

\[
= -q^2 M(q) \frac{\partial}{\partial \psi(q, t)} \left\{ F[q(q, t)] + \frac{1}{2} Dq^2 \psi(q, t) \right\} + 2c_0(q) \int_0^\infty \frac{dt'}{\tau_s} \frac{g(t-t')}{\tau_s} [\psi(q, t) - \psi(q, t')]^2 \]

It is worth noticing that the solution of the linearized form of Equation (8)\textsuperscript{34} is exactly the same as that derived from a two-fluids model.\textsuperscript{23} Following the simple argument above, it confirms the equivalence between the model proposed by Clarke et al.,\textsuperscript{34} and that proposed by Doi and Onuki.\textsuperscript{23}

By using the inverse Fourier transformation technique, and limiting it to the case of A-A entanglement, the real-space form of Equation (8) is written as:

\[
\frac{\partial \psi(r, t)}{\partial t} = M \nabla^2 \left\{ \frac{dF[q(q, t)]}{dy} - D \nabla^2 \psi(r, t) \right\} + 2c_0 \int_0^\infty \frac{dt'}{\tau_s} \frac{g(t-t')}{\tau_s} [\psi(r, t) - \psi(r, t')] \]

with \( \psi(r, t) \) is the order parameter in real space. For the difficulties confronted in the inverse Fourier transformation, \( \phi_s \) in Equation (5) is taken as the average concentration instead of the local concentration.

Because the system is supposed to be in a completely equilibrium stage before \( t = 0 \), the lower limit of the integral can started from zero.\textsuperscript{34} Thus, Equation (9) can be rewritten as:

\[
\frac{\partial \psi(r, t)}{\partial t} = M \nabla^2 \left\{ \frac{dF[q(q, t)]}{dy} - D \nabla^2 \psi(r, t) \right\} + 2c_0 \int_0^\infty \frac{dt'}{\tau_s} \frac{g(t-t')}{\tau_s} [\psi(r, t) - \psi(r, t')] \]

For simplicity, \( dF/dy \) is chosen as\textsuperscript{34, 5}
where $A$ is the phenomenological parameter which is inversely proportional to the temperature. Defining $a_0$ and $\tau_0 = a_0^2/M$ as the unit of length and time scales and using Equation (11), Equation (10) can be rescaled into a dimensionless form

$$
\frac{\partial \psi(r, \tau)}{\partial \tau} = \nabla^2 \left\{ -A \tanh \psi(r, \tau) + \psi(r, \tau) - \frac{\tau}{\tau_0} \right\}
$$

where $\tau = t/\tau_0$, $\tilde{D} = D/a_0^2$.

Equation (12) is simulated with the cell dynamics scheme (CDS). In the two-dimensional version of CDS, the system uses a discrete $L \times L$ square lattice of size $a_0$ and the order parameter for each cell is defined as $\psi(n,t)$ with $n = (n_x, n_y)$ as the lattice position. Here, $n_x$ and $n_y$ are integers between 1 and $L$. The isotropic Laplacian in CDS is approximated by

$$
\nabla^2 \psi(n) = \frac{1}{a_0^2} \left[ \langle \psi(n) \rangle - \psi(n) \right]
$$

where $\langle \psi(n) \rangle$ represents the following summation of $\psi(n)$ for the nearest neighbors ($n.n$), the next-nearest neighbors ($n.n.n$) and the next-next-nearest neighbors ($n.n.n.n$), i.e.

$$
\langle \psi(n) \rangle = B_1 \sum_{n \neq 0} \psi(n) + B_2 \sum_{n \neq 0, n \neq 0} \psi(n) + B_3 \sum_{n \neq 0, n \neq 0, n \neq 0} \psi(n)
$$

with $B_1$, $B_2$, and $B_3$ are 6/80, 3/80, 1/80 for three-dimensional system, and 1/6, 1/12, and 0 for two-dimensional system, respectively. Then, Equation (12) can be transformed into the difference form:

$$
\psi(n, \tau + 1) = \psi(n, \tau) - \langle I(n, \tau) \rangle - I(n, \tau)
$$

$$
I(n, \tau) = -A \tanh \psi(n, \tau) + \psi(n, \tau) - \frac{\tilde{D}}{\tau_0} \left[ \psi(n, \tau) - \psi(n, \tau^*) \right] + 2a_0 \sum_{\tau = 0}^{\tau - 1} \frac{g(\tau - \tau^*)}{\tau_0} \left[ \psi(n, \tau) - \psi(n, \tau^*) \right]
$$

The simulations are based on Equation (15) and (16) and performed on a two-dimensional square lattice of $L \times L = 256 \times 256$. The parameter $\tilde{D}$ is fixed as 0.5. The interface width $\xi$ between two domains is given by $\xi = \sqrt{\tilde{D}/(A - 1)}$ and thus $\xi = 1.29$ for deep quench ($A = 1.3$) and 2.24 for shallow quench ($A = 1.1$), respectively. As the lattice size is very limited compared to the real system, the periodical boundary condition $\psi(n_x, n_y, \tau) = \psi(n_x + N_xL, n_y + N_yL, \tau)$ where $N_x$ and $N_y$ are arbitrary integers has been employed.

There are two important quantities, the pair correlation function and the scattering function, are used to characterize the system. The pair correlation function of the system is defined as

$$
G(r, \tau) = \left\langle \frac{1}{L^2} \sum_{n} [\psi(n + r, \tau) \psi(n, \tau) - \bar{\psi}^2] \right\rangle
$$

where $n$ runs over the whole system; $\bar{\psi}$ is the average order parameter of the system and the section within the outer brackets, $\langle \rangle$, represents the ensemble average. The stochastic nature of the equations requires an average over many realizations. In this work, the ensemble averages are taken over 20 independent runs. The location of the first zero point of the pair correlation function gives a quantitative measurement of the characteristic domain size, $r_s$. The scattering function is defined as

$$
S(q, \tau) = \langle \psi(q, \tau)^2 \rangle
$$

where $q = (2\pi/L)(m_x, m_y)$ with $m_x$ and $m_y$ integers. The Fourier component

$$
\psi(q, \tau) = \int d\tau \exp(-iq \cdot r) \psi(r, \tau)
$$

is evaluated by a fast Fourier transformation (FFT) technique. The first moment of $S(q, \tau)$ is defined as

$$
\langle q(\tau) \rangle = \sum_{\tau} qS(q, \tau) / \sum_{\tau} S(q, \tau)
$$

which is related to the domain size by $\langle q(\tau) \rangle \propto r_s^{-1}(\tau)$. Assuming that the self-similarity exists in the system of the late stage, the normalized and scaled structure function and the correlation function in the late stage behave as

$$
S(q, \tau) = F(x) \langle q(\tau) \rangle^{-d}
$$

$$
G(r, \tau) = g(r, \tau)/r_s(\tau) = g(x')
$$

where $d$ is the dimensionality, $x = q(\tau)/\langle q(\tau) \rangle$ and $x' = r(\tau)/r_s(\tau)$. $F(x)$ and $g(x')$ are scaling functions independent of time, which implies that the scaling functions $F(x)$ and $g(x')$ at different time can be superposed on each other in the late stage.

It is believed that in the late stage the domain growth should reach asymptotic behavior and there exist such scaling relations as

$$
S_{\infty}(q, \tau) \propto \tau^{\beta}
$$

$$
\langle q(\tau) \rangle \propto \tau^{-\alpha}
$$

and $\beta = 3\alpha$. 

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According to the scaling law, Furukawa proposed a universal scaling function in the late stage of phase separation as\(^{37,38}\)

\[
F(x) = \frac{x^2}{2 + x^{\gamma}}
\]

\[
\begin{cases} 
\gamma = d + 1 & \text{for off-critical mixtures} \\
\gamma = 2d & \text{for critical mixture}
\end{cases}
\]

Equation (25) describes the scaling behaviors of the structure functions at different times.

**Simulation Results and Discussions**

**Binary Mixtures without Entanglements**

For the sake of comparison, we first studied the system without entanglements, i.e. \(c_0 = 0\). The evolution of the scaling functions defined in Equation (21) and (22) for the critical system (\(\phi_c = 0.5\)) is summarized in Figure 1. From Figure 1a and b, it is seen that an initial stage characterized by a plateau in the curve of \(\ln g(q)\) vs. \(\ln \tau\), which exists obviously in both shallow and deep quenches. After the initial stage, Figure 1a and b show that the growth exponents defined by Equation (23) and (24) are independent of the final temperature of quench and agree fundamentally with the modified\(^{39}\) Lifshitz-Slyozov law \((R = a + bt^{1/3})\) which has been testified to by many numerical studies.\(^{6,40-43}\) It is also seen that, as the fluctuations are not so strong in the case of a shallow quench, it takes a longer period to reach the late stage of phase separation. Figure 1c and d show that the scaled structure functions in the late stage can be superimposed on each other, and it reveals that the self-similarity of the morphology exists in the late stage of spinodal decomposition. With an increase of quench depth, the initial stage is shortened and the scaled structure functions become

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Figure 1. The effects of quench depth on the non-entangled critical system; a) the first moment of structure functions vs. time in log-log scale; b) the maximum of the structure function \(S_m\) vs. time in log-log scale; c) scaling structure function in log-log scale; d) the scaled pair correlation functions.
broader. This implies that the correlation of the order parameter for the case of a deep quench is slightly weaker than that of a shallow quench. The scaled pair correlation functions depicted in Figure 1d can also confirm this argument. Our simulations have also been performed for an off-critical system. The results are quite similar so that of a critical system, the growth exponents agree with the Lifshitz-Slyozov law, i.e. it follows the evaporation-condensation mechanism and has $\alpha = 1/3$ and $\beta \approx 1$,[44] except that the quench depth effect on the scaled pair correlation functions becomes more remarkable in an off-critical system. It is not difficult to imagine that the off-critical system tends to result in droplet morphology, which results in weaker pair correlations relative to the bicontinuous morphology.

**Polymer Blends with Viscoelastic Effects**

The Effects of Quench Depth

The viscoelastic effects resulting from the A-A chain entanglements are simulated based on Equation (12) with $c_0 > 0$. The simulated typical morphological evolution for the systems with and without entanglements is shown in Figure 2. In Figure 2, the parameters for the entangled system are set as $\tau_v = 1000$ and $c_0 = 0.15$. It’s clearly seen from Figure 2 that the viscoelastic effect resulting from A-A entanglements strongly suppresses concentration fluctuations and thus the spinodal decomposition dynamics is slowed down. Another exclusive character that can be seen from Figure 2 is that the curvature of the domain boundaries for the entangled systems is much rougher than that of the non-entangled system. We believe that this is due to the stress in the A-rich phase originating from the non-relaxed residual elasticity of the A-A entanglements. This stress will destroy the stress equilibrium between two phases and cause the roughening of the domain boundaries. Roughening of the domain boundary reduces the correlation of the order parameter fluctuations. This reduction will be more pronounced by increasing the quench depth. To see this effect more quantitatively, Figure 3 and 4 illustrate the scaled structure function $F(x)$ and the scaled pair correlation function $g(x')$ both for shallow and deeper quenches. Figure 3 shows that the scaled structure function $F(x)$ has a broader peak and the shoulders existing on that of the shallow quench are almost smeared out completely in the case of the deep quench. The scaled pair correlation function $g(x')$ has a shallower correlation hole in the case of the deep quench. All of these observations reveal that the viscoelastic effects reduce the correlation of order parameter fluctuations and this effect becomes weaker when the quench depth is shallower.

It is more interesting to note that the curves of $\ln S_m(\tau)$ vs. $\ln \tau$ and $\ln \langle \rho \rangle$ vs. $\ln \tau$, both for shallow and deep quenches, show an intermediate stage apparently between the early and late stage (around $\tau \approx \tau_v$), in Figure 5 and 6. During the intermediate stage the domain growth rate slows down drastically. When $\tau \gg \tau_v$, the intermediate
stage ends and then both exponents, $\alpha$ and $\beta$, tend to follow the modified Lifshitz-Slyozov law. The physical implication is quite clear. It simply means that the A-A entanglements initially existing in the system prevent the chain diffusion and thus slow down the spinodal decomposition process and they will be relaxed at $\tau \gg \tau_c$. In addition, we must note that the chain length of the B-component is short and thus there is no entanglement among B chains. Therefore, when the phase separation proceeds, the fraction of A-A entanglements will be increased in the A-rich phase and will be decreased in the B-rich phase. This difference will result in the elastic contrast between two phases, i.e. the A-rich phase has higher elasticity while the B-rich phase has lower elasticity. Therefore, when $\tau \gg \tau_c$ the elasticity in the B-rich phase is negligible and thus the domain growth then reaches the asymptotic behavior of the modified Lifshitz-Slyozov law.

The Effects of $\tau_c$

Having seen the general features of the viscoelastic effect on the morphology and domain growth in a binary polymer mixture, we are now ready to investigate the specific effect of model parameters.

Figure 7 shows the curves of $\ln \langle q \rangle$ vs. $\ln \tau$ for the critical system ($\phi_\Lambda = 0.5$) with $A = 1.3$, $c_0 = 0.033$ and $\tau_v = 500, 1000$ and 1500, respectively. For the sake of comparison, the data obtained from the non-entangled system are also shown in the figure. From Figure 7, it is seen that there also exists an intermediate stage, and the intermediate stage shifts to later time with increasing $\tau_c$. After the intermediate stage, the system reaches asymptotic behavior and the curves for the entangled system are nearly parallel to that of non-entangled system. The simi-
lar behaviors can also be observed from the curves of $\ln S_m(s)$ vs. $\ln s$ shown in Figure 8. These results simply reveal that the viscoelastic effects in the system with longer $s_v$ will take a longer time to relax.

We have also performed simulations for the off-critical system ($\phi_A = 0.55$). It is found that the effects of $s_v$ on the spinodal decomposition dynamics of an off-critical system are quite similar to that of a critical system and thus, for simplicity, the data are not shown in this paper.

The Effects of $c_0$

From the results shown in Figure 7 and 8, it is seen that the effect of $\tau_v$ simply shifts the intermediate stage to later time. Comparing the results shown in Figure 5 and 7, it seems that $c_0$ has more pronounced effects on the dynamic behavior of spinodal decomposition than that of $\tau_v$. In order to explore these effects, the data of $\ln q$ vs. $\ln \tau$ and $\ln S_m(\tau)$ vs. $\ln \tau$ for the critical system with $A = 1.3$, $\tau_v = 1000$ and $c_0 = 0.033 \sim 0.165$ are shown in Figure 9 and 10. Figure 9 and 10 show that the larger the $c_0$ value is, the longer the period of the intermediate stage lasts. In the intermediate stage, the growth rate of domains slows down more notably for larger $c_0$. In the late stage, the growth exponents basically restore to the classical behaviors.

In order to understand these effects, it is necessary to recall the definition of $c_0$ given in Equation (5). From Equation (5), $c_0$ is inversely proportional to the chain length between the entanglements, $N_e$, and thus the elasticity of the entanglements will be higher when $N_e$ is smaller. Therefore, a more distinct viscoelastic effect on the spinodal decomposition will be observed.

It is interesting to compare the scaled structure functions of the entangled and non-entangled systems. Figure 11 shows that the scaled structure functions at the late stage can be superimposed both for entangled and non-entangled systems. The difference is that, for the entangled system, the shoulder at $x > 1$, which reflects the structure of the interface, is much broader and appears at larger $x$ value than that of non-entangled system. This also implies that the domain boundary interface for the entangled system is rougher. In addition to that, the peak at $x \approx 1$ for the entangled system is broader than that of the non-entangled system which indicates that the characteristic size of the domains in the entangled system has a distribution that smears out the sharpness of this main peak. The $c_0$ effects on the scaled pair correlation function (Figure 12) are quite similar to quench depth effects.
The Effects of Off-Criticality

Although we have mentioned that the viscoelastic effects on the off-critical system are quite similar to the critical one, there still exist some distinguishable differences. Figure 13–15 demonstrate that the intermediate stage extends when the fraction of the entangled component increases while the asymptotic growth exponents are not altered. It is interesting to note that the scaled pair correlation functions for the critical ($\phi_A = 0.5$) and off-critical systems ($\phi_A = 0.55$) show little distinguishable difference. Therefore, we can conclude that both critical ($\phi_A = 0.5$) and off-critical systems ($\phi_A = 0.55$) result in very similar morphologies.

Summary and Remarks

In this paper we have performed detailed numerical studies of a complicated partial differential equation based on the TDGL equation appropriate for modeling the dynamics of phase separation and pattern formation in polymer blends. The viscoelastic effects were investigated by considering entanglements in polymer blends through introducing an...
stage, the effects of relaxation time decreases. After complete relaxation of polymer chains, the growth exponents reach asymptotic behavior as usual. The distance between the entangled points plays a very important role in the unusual morphology and dynamics. Entanglements enhance quench depth effects on the correlation because of the rough interface, and diminish the discrimination of correlation induced by off-criticality.

We found that the domain growth law in late stage for the model of polymer blends considered here was independent of entanglements and consistent essentially with the modified Lifshitz-Slyozov law. In addition, the pair correlation function and the structure function are shown to exhibit dynamical scaling at late enough times, and the scaled structure function has a broader peak than that of the non-entanglement case, in accordance with the previous results.

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Viscoelastic effects were investigated by including entanglements of polymer chains. As can be seen, there exists an intermediate stage with characteristics of low growth rate around $\tau \sim \tau_e$, in the process of phase separation, which can be attributed to the viscoelastic suppression of concentration fluctuations and the stress induced by the suppression in A-rich phase. It is very interesting that morphologies with a rough interface are also different from the common case, and this kind of morphology causes the correlation reduction of domains. The relaxation time has apparent effects on the intermediate stage, the intermediate stage will be prolonged when the relaxation time increases. When simulated up to a very late

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Figure 15. The entanglement effects on the criticality of the composition ($A = 1.3$, $\tau_e = 1000$). The scaling pair correlation functions.

elastomeric term into the free energy function for the TDGL equation, analogous to the case of gel studied by de Gennes. We focused on the A-A entangled system, in which only one component is mutually entangled. To improve the efficiency of simulation, the cell dynamical scheme (CDS) proposed by Oono and Puri was employed here to carry out the simulation.

In the case without entanglements, an initial stage exists for both shallow and deep quenches, which obeys the Cahn-Hilliard theory. In the late stage, the growth exponents for the critical system agree essentially with the modified Lifshitz-Slyozov law and the growth exponents for the off-critical system are consistent with the Lifshitz-Slyozov law, and self-similarity is also observed. Quench depth has effects on the dynamics, although growth exponents almost exhibit the same relation, the scaled structure function shows a broader peak and the correlation of domains becomes weaker for a deeper quench. We also observed the weakening of the correlation when transferred from critical quench to off-critical quench conditions, just consistent with Qiu’s results. In the off-critical system, correlation weakening resulted from the increase of quench depth is more remarkable.

Viscoelastic effects were investigated by including entanglements of polymer chains. As can be seen, there exists an intermediate stage with characteristics of low growth rate around $\tau \sim \tau_e$, in the process of phase separation, which can be attributed to the viscoelastic suppression of concentration fluctuations and the stress induced by the suppression in A-rich phase. It is very interesting that morphologies with a rough interface are also different from the common case, and this kind of morphology causes the correlation reduction of domains. The relaxation time has apparent effects on the intermediate stage, the intermediate stage will be prolonged when the relaxation time increases. When simulated up to a very late