The rheology and morphology of phase-separating fluids with viscosity contrast

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In this paper, the effects of viscosity contrast between the components on the rheology and morphology of phase-separating binary fluids have been studied by numerically solving time-dependent Ginzburg–Landau equation and Navier–Stokes equation. It is found that, the viscosity contrast between the components strongly affects the bulk contribution to the overall rheological behavior. When the viscosity of the minor phase is higher, the trend of bulk contribution is contrary with that of interfacial contribution. Therefore, the non-Newtonian behavior is weakened. When the viscosity of the minor phases is lower, the evolution of bulk contribution is the same as interfacial contribution, and thus the non-Newtonian behavior is strengthened. However, the interfacial contribution still plays the crucial role in the overall rheological behavior. When the system contains two droplets or many domains, due to the merging of domains induced by shear flow, there is a decrease of interfacial volume fraction. Therefore, the interfacial contribution of rheology decreases and forms a peak at small shear strain. Correspondingly, the bulk contribution has also been altered. However, whether the bulk contribution increases or decreases will depend on the viscosity contrast. © 2001 American Institute of Physics. [DOI: 10.1063/1.1407294]

I. INTRODUCTION

The kinetics of phase separation has been extensively studied in the past years. The main features of this process have been understood after efforts of theoretical and experimental scientists. In the early stage the dynamics of phase separation is controlled by concentration fluctuation. In late stage the dynamics of phase separation is controlled by diffusion and surface tension. The growth of domain size in late stage obeys some simple relations, i.e., the domain growth follows $R(t) \sim t^a$, and the maximum intensity of scattering functions increases as $I_{\text{max}}(t) \sim t^b$ with $b = 3a$. The values of $a$, $b$ depend on the space dimension, hydrodynamic effect and composition. When the internal asymmetry is considered, such as viscoelastic contrast and elastic contrast between components, the characteristic scaling relation will be broken and particular morphology evolution can be observed such as network structure and phase inversion.6–10

Rheology and morphology of phase-separating system is one of important topics in the field of phase separation dynamics. It has been received more and more attentions of the scientists in recent years.11–16 The interests are mainly originated from two aspects. The first is that, to study the critical dynamics under symmetry-broken field itself is an important topic in the field of condensed matter physics. The second is that it has great potential value in application area. People want to control the morphology by proper processing condition and monitor morphology evolution by rheological measurements.

The previous works show that the phase-separating system under shear flow usually has anisotropic morphology evolution even some ordering structure can be induced. And particular rheological behavior is often observed in the process.11–16 Based on Model B, Ohta and Doi17 solve time-dependent Ginzburg–Landau (TDGL) equation numerically to study the phase separation under steady shear. Some empirical power laws of the morphology evolution and rheological behavior were given. A semiphenomenological model has ever been presented by Ohta and Doi18 to explore the rheological behavior of multiphase fluids under steady shear. It was found that the steady-state shear viscosity is independent of shear rate while the normal stress difference is non-zero and proportional to magnitude of the shear rate. However, the effect of phase separation dynamics has been ignored in that model. Coberi et al.19–21 analyzed phase separation dynamics under shear with renormalization group approach and TDGL equations. Some numerical solutions of structure factor and excessive viscosity were obtained. It should be mentioned that the hydrodynamic effect is neglected in their works. To investigate the hydrodynamic effect, Shou et al.22 simulated phase separation under shear with TDGL solver based on Model H and found that the shear can induce layered structure normal to shear direction. But the finite size effect makes his conclusion questionable. Based on Model B and Model H, Zhang et al.23 performed three-dimensional simulations to investigate the steady shear effect on rheology and morphology of binary mixtures. It is found that, for deep and critical quench, there are two peaks appeared in the shear viscosity as a function of shear strain at low shear rate, which agrees with the experimentally observations quite well.11

Compared to the steady shear, the effect of oscillatory
shear on the morphology and SD kinetics is relatively less studied.\textsuperscript{23} Many experimental and theoretical works have revealed that, for block copolymers, depending on the shear frequency and shear amplitude, the oscillatory can induce different ordering structure and exhibits different rheological behavior. Qiu et al.\textsuperscript{24} have ever performed the three-dimensional computer simulation to clarify the oscillatory shear effect on phase separation for polymer blends. It was also found that, depending on the quench depth and shear frequency, the oscillatory shear could induce different ordering structures and various rheological characters.

From the brief review of rheology and morphology of phase-separating mixtures under shear flow given above, we could see that the asymmetry of properties of the components such as viscoelastic contrast, elastic contrast, and viscosity contrast have been ignored. In fact it is necessary to handle with this problem. Previous study shows that the viscoelastic contrast and elastic contrast of components can break the scaling law of phase separation dynamics. And they are responsible for the formation of network structure or phase inversion that has been proved by the experimental results. Therefore, we believe that the property contrast of components will also affect the phase separation dynamics under shear. Moreover, we believe the effect is more important than that in phase separation dynamics without shear, especially its effects on the rheological behavior, because we think that the contrast of mechanical properties will show more obviously in the symmetry-broken field of shear flow. Besides we believe that only the theory which takes the contrast of properties of components into account is valuable to the applications and can be comparable with experimental results, because it is usual that the properties of the components are different in real experimental systems and application area.

In this paper, a new method is proposed to study the rheology and morphology of phase-separating fluids with viscosity contrast between the components. Due to the technical importance and theoretical simplicity, the effect of viscosity ratio on dynamics and rheology of droplets in emulsions (where both the phases can be considered as simple Newtonian fluids) has been extensively studied.\textsuperscript{25–28} However, the limitations of their models used in these works are obvious. First, their models are only applicable for system of droplet matrix. Second, the interface was assumed to be sharp, i.e., only the interaction between the shear and surface tension is considered. The diffusion process in phase separation has been neglected. Third, an assumption that the rheological measurements are fast compared with the rate of coarsening was made, i.e., the rheological measurements have been considered as nondstructive tool. These assumptions do not make their models to be far away from the real fact in application area. In this paper, we modify the Model H by introducing order parameter dependence of viscosity to study the effect of viscosity contrast on phase separation dynamics under shear. This model was first proposed by Tanaka\textsuperscript{29,30} to study the viscosity difference on the kinetics of phase separation under quiescent condition. In order to consider the shear flow, we further define new variables in order to modify the Navier–Stokes equation in the form of “modified Model H.” By this method, the effect of viscosity contrast on shear viscosity and morphology evolution of phase separating fluids can be studied. The method of introducing new variables is first proposed and used by Onuki et al.\textsuperscript{31} to study the complex problem of highly viscous polymer solutions under steady shear. However, when the viscosity contrast is introduced, the calculation equation of velocity will be different. We will give it in Sec. II, where the model and the simulation algorithm used in this paper will be described in detail. The rest of the paper is organized as follows. In Sec. III, the effects of steady shear on rheology and morphology of phase separating binary mixtures will be presented and discussed. We finally conclude with a summary of our results in Sec. IV.

\section{II. MODEL AND SIMULATION ALGORITHM}

From the theoretical point of view, the most relevant progress of phase separation dynamics has been achieved in the framework of the continuous approach based on the time-dependent Ginzburg–Landau (TDGL) model. With this approach, the properties of the phase-separation kinetics can be efficiently studied by means of numerical simulations or analytically in the context of approximate theories.

The kinetics of phase separating fluids can be described by Model H as follows:

\begin{equation}
\frac{\partial \psi(r,t)}{\partial t} = -\nabla \cdot (\psi \nabla \mu) + \frac{\delta F}{\delta \psi(r,t)} + \frac{\delta \psi(r,t)}{\partial t},
\end{equation}

\begin{equation}
\frac{\partial \eta(r,t)}{\partial t} = \left( \nabla \cdot \left[ \eta \left( \nabla \psi + \nabla \psi^T \right) \right] - \psi \nabla \frac{\delta F}{\delta \psi(r,t)} \right),
\end{equation}

where $\psi(r,t)$ is local order parameter, which is defined as local concentration difference between the two components ($\phi_1 - \phi_2$). $\nabla \psi(r,t)$ is local velocity. The first equation is the TDGL equation. The time evolution of order parameter is governed by this equation. The second equation is the Navier–Stokes equation, which describes the time evolution of local velocity. $[\cdots]^\dagger$ denotes the transpose operator. $\rho$ and $\eta$ are local density and viscosity, respectively. $F[\psi(r,t)]$ is free energy functional of the system with the Landau form:

\begin{equation}
F[\psi(r,t)] = \int d\mathbf{r} \left\{ -\frac{\tau}{2} \psi^2 + \frac{g}{4} \psi^4 + \frac{K}{2} \left( \nabla \psi \right)^2 \right\},
\end{equation}

where $\tau$ and $g$ are both positive phenomenological parameter which control the rate of phase separation. $K$ is also a positive parameter, which characterizes the interfacial free energy derived from the spatial composition inhomogeneity.

We define $\psi_c = \sqrt{g/\tau}$, $\xi = \sqrt{K/\tau}$, $\omega = D_{app}/\xi^2 = M \tau^2/K$, $\eta = \eta^2 = D_{app}/\xi = (M \tau) \sqrt{\tau/K}$, and $\nu_h = \sigma/\eta$, where $\sigma$ is the surface tension. Then we introduce the dimensionless variables $\psi' = \psi/\psi_c$, $\tau' = r/\tau$, $\xi' = r/\xi$, and $\eta = \eta/\eta^2$ is the surface tension. Then we introduce the dimensionless variables $\psi' = \psi/\psi_c$, $\tau' = r/\tau$, $\xi' = r/\xi$, and $\eta = \eta/\eta^2$ is the surface tension. Then we introduce the dimensionless variables $\psi' = \psi/\psi_c$, $\tau' = r/\tau$, $\xi' = r/\xi$, and $\eta = \eta/\eta^2$. Then Eqs. (1) and (2) can be rewritten as

\begin{equation}
\frac{\partial \psi}{\partial \tau} = \nabla \cdot \left( \psi \nabla \mu \right) + \nabla^2 (\psi - \psi^3 - \nabla^2 \psi),
\end{equation}
Moreover, we use the form of chemical potential \( m \) instead of Landau form \( -\psi + \psi^3 - \nabla^2\psi \) to acquire the better numerical stability. This form is first used in the cell dynamics scheme (CDS) proposed by Onoo and Puri. Where \( A \) is a phenomenological parameter greater than 1, which characterizes the quench depth, and \( D \) is an interfacial parameter. The greater \( A \) is, the more incompatible the system becomes.

Here we should make a remark. From a physical point of view, the asymmetry of phase separation should come from three aspects: viscosity contrast, mobility differences and difference of driving force of diffusion. The driving force of diffusion is actually decided by the form of free energy of the mixtures. In fact, Eqs. (4) and (5) contains two assumptions. The first is that the mobility of the components has been assumed to be a constant. In other words, the mobility is independent of the order parameter, which implies that the diffusion is controlled by bulk diffusion, not by the diffusion in the vicinity of the interface. The second assumption is that a symmetric chemical potential is assumed. Therefore, the driving force for diffusion is symmetric. The viscosity contrast does not cause asymmetric distribution of driving force. (According to the two-fluid model, except the mixing free energy, the total free energy should include the contribution of the asymmetric force.) We think it is a plausible assumption because the viscous stress caused by frictions of small molecules is a kind of dissipative force, which is quite different from viscoelastic force caused by conformation changes of macromolecular chains. The rheological time of the material is quite shorter than the characteristic growth time of domains. Therefore the distribution of local force has enough time to reach an equilibrium state within characteristic time of domain growth.

Equation (4) is solved in the real space (r space) while Eq. (5) is solved in the reciprocal space (k space). The form of Eq. (5) in k space is written as

\[
\frac{\partial \mathbf{v}(k,t)}{\partial t} = (\mathbf{I} - \mathbf{k}k^2) \cdot \mathbf{F}(k,t),
\]  

where \( \mathbf{v}(k,t) \) and \( \mathbf{F}(k,t) \) are, respectively, the Fourier transforms of local velocity \( \mathbf{v}(r,t) \) and driving force \( \mathbf{F}(r,t) \). \( \mathbf{F}(r,t) \) represents the quantity of \( \nabla \cdot [\eta(\psi)(\nabla \psi + \nabla \mathbf{v}^T)] - \psi \nabla \mu \), which is calculated in r space.

The steady shear flow is defined by

\[
\mathbf{v}_0(r,t) = (\dot{\gamma}y,0).
\]

In this paper, we have chosen x axis as the flow direction, y axis as the velocity gradient direction.

The simulation is carried out in \( L \times L \) two-dimensional square lattices. The simple Euler–Scheme is used. To solve TDGL equation with shear flow in real space, a shear periodic boundary condition proposed by Ohta et al. should be applied to y direction. With the shear strain \( \gamma = \dot{\gamma}t \), this boundary condition is written as

\[
\psi(n_x, n_y, \tau) = \psi(n_x + N_x L + \gamma(\tau)N_y L, n_y, n_x + N_y L, \tau),
\]

where \( N_x \) and \( N_y \) are arbitrary integers.

When the steady shear flow is exerted, we introduce new variable \( k' = k_x + \gamma t k_y \) to reduce Eq. (6). After the simple derivation, we can obtain the following iteration equation of \( \mathbf{v}(k',t) \) in k’ space:

\[
\frac{\partial \mathbf{v}(k',t)}{\partial t} = (I - kkk^2) \left[ \mathbf{F}(k',t) - \dot{\gamma} k'y^2 \frac{\partial \mathbf{v}(k',t)}{\partial k'} \right] - kv(k',t)k^2 \frac{\partial k}{\partial t},
\]

where \( k \) has the following relations with \( k': k_x = k_{x}', k_y = k_y' - \dot{\gamma} t k_{y}'. \)

It should be mentioned that, in order to consider the shear flow, the remeshing technique has been used by Shou et al. In their work, the remeshing is only done at every integer strain. Therefore, we think it is not a right way since this remeshing technique is quite far away from the physical fact of shear flow. Here, by using the new variable, the remesh of the lattices is not necessary and the Navier–Stokes equation can be solved by fast Fourier transform (FFT).

We assume the viscosity of the system is the linear combination of that of the individual component, i.e.,

\[
\eta(\phi_1) = \eta_1 \phi_1 + \eta_2 \phi_2,
\]

where the viscosity contrast between the two components has been chosen as \( \eta_1 : \eta_2 = 3 : 1 \). It implies that the viscosity of the viscous phase is 3 and the viscosity of dilute phase is 1, i.e., \( \eta(\psi) = 2 + \psi \). The other parameters are set as follows, \( A = 1.3, D = 0.25, \Delta l = 1.0, \) and \( \Delta t = 0.05 \).

For the binary fluids with viscosity contrast between two components, the total stress tensor of the system should be written as

\[
\sigma_{a\beta}^T = \sigma_{a\beta}^\text{Int} + \sigma_{a\beta}^\text{Bulk},
\]

where \( \sigma_{a\beta}^\text{Int} \) is the stress contributed from the interfaces, \( \sigma_{a\beta}^\text{Bulk} \) is the stress contributed from bulk phases.

The bulk contribution of stress is written as

\[
\sigma_{a\beta}^\text{Bulk} = \frac{1}{L^4} \int \left[ \eta(\psi)(\nabla \psi + \nabla \mathbf{v}^T) + p \delta_{a\beta} \right] (\alpha, \beta = x, y),
\]

where \( p \) is the pressure, \( \eta(\psi) \) is the order parameter dependent viscosity and \( \nabla \psi \) is tensor of velocity gradient.

Kawasaki has derived the stress contributed from the interface relaxation. It reads

\[
\sigma_{a\beta}^\text{Int} = -\frac{D}{L^4} \int \frac{\partial \psi(r,t)}{\partial r_a} \frac{\partial \psi(r,t)}{\partial r_\beta} (\alpha, \beta = x, y).
\]

The shear viscosity \( \eta \) is calculated by

\[
\eta = \sigma_{xy} / \dot{\gamma}.
\]
In this paper, in order to study the effect of viscosity contrast on the rheology of phase separating fluids in detail, the bulk contribution of stress tensor, the interfacial contribution of stress tensor and the total stress tensor, respectively, is calculated according to Eqs. \(\ldots\), \(\ldots\), and \(\ldots\). Equation (14) is used to calculate the shear viscosity contributed from three different sources.

III. RESULTS AND DISCUSSIONS

A. Single droplet in the matrix subjected to steady shear

For simplicity and clarification, our study starts from a simple case of a single droplet in the matrix. The simulation is carried in a system \(64 \times 64\). Initially, a droplet with radius \(R = 10.5\) was put at the center of the lattice \((n_x = 33\) and \(n_y = 33)\), then the shear is exerted to study the morphology evolution and corresponding rheology. When the quench depth \(A = 1.3\) and interfacial energy coefficient \(D = 0.25\), the order parameter at equilibrium should be \(\psi_e = 0.978\). Therefore, we set the initial order parameter of the droplet to be \(\psi = \psi_e = 0.978\) and that of the matrix to be \(\psi = -\psi_e = -0.978\). To study the effect of viscosity contrast, the viscosity ratio between the droplet and the matrix are set to be \(\eta_d : \eta_m = 3:1\), \(\eta_d : \eta_m = 1:3\), \(\eta_d : \eta_m = 2:2\), respectively.

Case 1A: A viscous droplet immersed in a dilute matrix \((\eta_d : \eta_m = 3:1)\). The evolutions of morphology and shear stress distribution at \(\dot{\gamma} = 0.002\) is shown in Fig. 1(a). It is seen that, as the shear strain proceeds, the droplet is elongated into elliptic shape and it induces high stress distribution near the droplet interface. Figure 2 shows the corresponding shear viscosity contributed from three sources (interfacial, bulk and total contributions). From this figure, we can see the bulk contribution to the total viscosity decreases initially. After reaching a minimum value, it increases a little and then goes into a steady state. The oscillations of the shear viscosity at integer shear strains are due to the artifacts of the shear periodic boundary condition. It should be noted that, the bulk contribution of shear stress inside the droplet is negative [refer to Fig. 1(a)]. A plausible explanation is that the higher viscosity of the droplet results in a resisting force and thus the viscous droplet is difficult to be deformed by shear flow. In contrast with the bulk contribution, the interfacial contribution to the total viscosity increases in the beginning. After reaching a maximum value, it decreases a little and then goes into a steady value. Actually the non-Newtonian behavior has been weakened since the two trends are contrary. As the shear rate increases, the bulk contribution increases like inflating fluid while the interfacial contribution decreases like plastic fluid. The trend of total shear viscosity and the gray plot of the shear stress distribution show that the interfacial contribution plays more important role in determining the whole rheological behavior.
Therefore, it still behaves as non-Newtonian plastic fluid. Combining the results of rheology and morphology, the whole process can be roughly separated into three stages. In stage I, the droplet is deformed into elliptic shape. Due to the elongation of the droplet, the interfacial volume fraction increases as well until it reaches a maximum value. Correspondingly, the shear viscosity shows an increase in this stage. In stage II, the relaxation of the droplet and the shear is a pair of competing force. As the droplet is elongating the relaxation rate of the droplet also increases. When the rate of relaxation exceeds the shear rate, the droplet shrinks and leads to a decrease of the shear viscosity. In stage III, the equilibrium between the deformation and relaxation has been reached and thus the viscosity eventually reaches a steady state.

Case 1B: A dilute droplet immersed in a viscous matrix \( (\eta_d: \eta_m = 1:3) \). Figure 1(b) illustrates the evolutions of morphology and shear stress distribution at \( \dot{\gamma} = 0.002 \). Compared with Fig. 1(a) it is seen that the bulk contribution of shear stress inside the droplet is much less negative. According to the previous explanation, it should be attributed to the easier deformation of the dilute droplet. Figure 3 shows the corresponding strain dependence of the shear viscosity. From Fig. 3, we can see that the interfacial contribution of the shear viscosity in this case is very similar to that in Case 1A, i.e., it increases initially and then goes into a steady state after reaching a maximum value. As the shear rate increases, it decreases just like plastic fluid. But the behavior of bulk contribution of the shear viscosity in this case is contrary to Case 1A. It increases initially and then goes into steady state after reaching a maximum value. It decreases just like plastic fluid as the shear rate increases. In fact, in this case the non-Newtonian behavior has been strengthened since the two contributions are in the same trend. From the whole rheological behavior and stress distribution, it is seen that the interfacial contribution still play more important role in determining the whole rheological behavior than the bulk contribution. The whole process can also be roughly separated into three stages. In stage I, the droplet is deformed by the shear flow. In stage II, the interfacial relaxation starts. During this stage, the relaxation of the droplet causes a decrease of the shear viscosity. In stage III, an equilibrium state between the relaxation and the external shear is eventually reached.

Case 1C: A droplet in matrix with the same viscosity \( (\eta_d: \eta_m = 2:2) \). The corresponding morphology evolution and shear stress distribution are illustrated in Fig. 1(c). The strain dependent shear viscosity is plotted in Fig. 4. The trend of interfacial contribution of shear viscosity is similar with Cases 1A and 1B. However, the bulk contribution to the shear viscosity is a constant \( (\eta = 2) \) although there is still an
asymmetric stress distribution observed in Fig. 1(c). In other words, the non-Newtonian behavior is only caused by interfacial stress. It is very different from the previous two cases.

The simulation of single droplet in the matrix reveals that introducing of the viscosity contrast does not affect the interfacial contribution of rheology but brings obvious changes of bulk contribution to the rheological property. It is not difficult to understand the first point, i.e., the effect of viscosity contrast on interfacial contribution. From Eq. (13), which calculates the interfacial stress tensor, we can see that the interfacial contribution of stress tensor only depends on how the domain is deformed. Under steady shear, the domain always tilts to the shear direction. Since the shear flow is exerted in the constant direction, the interfacial contribution should exhibit the similar trend, which weakly relates to the viscosity contrast. However, the reasons for the effect of viscosity contrast on bulk contribution of shear stress are not so straightforward as that on interfacial contribution of shear stress. To explore the possible physical reasons, we further make a numerical statistics on the bulk shear stress contributed from the droplet and matrix, respectively, which is shown in Fig. 5. From Fig. 5 we can see that although the viscosity ratio is different, the trend of bulk shear stress contributed from the droplet always decreases and the bulk shear stress contributed from the matrix always increase when shear proceeds. This implies that, with the shear proceeds, the matrix not the droplet eventually supports the bulk shear stress, which is not dependent on the viscosity ratio. However, the detailed changes of bulk shear stress contributed from the droplet and the matrix among different viscosity ratios are quite different due to the different deformability of the matrix and the droplet. For \( \eta_d: \eta_m = 3:1 \) [Fig. 5(a)], the bulk shear stress contributed from the matrix changes a little (about from 8.0 to 8.8) but the bulk shear stress contributed from the droplet changes a lot (it decreases from 1.2 to \(-0.3\)). Thus the total bulk shear stress shows a decrease in the process. However for \( \eta_d: \eta_m = 1:3 \) [Fig. 5(b)], the bulk shear stress contributed from the matrix changes a lot (from 21.8 to 23.4). And that of the droplet changes a little (about from 0.95 to 0.35). Therefore the total bulk shear stress shows an increasing trend. For \( \eta_d: \eta_m = 2:2 \) [Fig. 5(c)], the changes of bulk shear stress contributed from the matrix and the droplet are totally symmetric. Then the total bulk shear stress is unchanged in the whole process.

If the system contains many domains, the dynamics becomes more complicated. Not only the deformation, but also the merging and burst of the domain will happen. In order to explore the relationship between the morphology and rheology further, we will perform the simulations on the morphology and rheology of two droplets in a matrix.

B. Double droplets in a matrix subjected to steady shear

One droplet with radius 7.0 was put at \( n_x = 23, n_y = 33 \), and another droplet with radius 8.0 was put at \( n_x = 45, n_y = 28 \). In order to compare with the case of single droplet, we also set the viscosity ratio of the two phases to be \( \eta_d: \eta_m = 3:1 \), \( \eta_d: \eta_m = 1:3 \), \( \eta_d: \eta_m = 2:2 \) respectively.

Figure 6(a) shows the morphology evolution and shear stress distribution of double viscous droplets immersed in a dilute matrix (\( \eta_d: \eta_m = 3:1 \)). It is seen that the two small droplets initially deform then coagulate together into one
larger droplet. And after that, the big droplet continues to be deformed under shear. The corresponding shear viscosity is illustrated in Fig. 7. Compared with the corresponding situation of single droplet, the rheological behavior observed here becomes more complicated. The interfacial contribution to shear viscosity increases initially then experiences a decrease at a small shear strain ($\gamma = 0.45$ for shear rate 0.002) due to the merging of the droplets. After reaching a minimum value, it increases again until it reaches a steady state. Correspondingly, there is a peak in the curve of bulk contribution. It is also observed that, as the shear rate decreases, the critical strain, at which the droplets coagulate, will move to smaller value. This can be explained by the fact that, at lower shear rate, the diffusion has accelerated the merge of droplets. Except the abnormal behavior due to merging of droplets, the other phenomena are similar to the case of single droplet. The whole process can be divided into four stages. During stage I, both droplets are deformed by steady shear flow. In stage II, two droplets begin to contact and merge into a larger droplet as the shear proceeds. In stage III, the merged larger droplet continues to be elongated by the shear flow. Finally, in stage IV, the competition between the shape relaxation of the droplet and the external shear flow reaches an equilibrium state.

The morphology and shear stress distribution for double dilute droplets immersed in a viscous matrix ($\eta_d: \eta_m = 1:3$) is illustrated in Fig. 6(b). In Fig. 8, the corresponding shear viscosity has been plotted. Just like the case of $\eta_d: \eta_m = 3:1$, there is abnormal behavior appears due to the merging of droplets. At shear strain $\gamma = 0.45$ (for shear rate 0.002)}
The shear viscosity curve of double droplets in matrix with the same viscosity (merging, redeformation and steady state) can be separated into four stages as well, i.e., deformation, II merging, III re-deformation, IV steady state.

The viscosity ratio \( \eta_d: \eta_m = 1:3 \), and the other parameters are the same as in Fig. 6. The four stages are divided by the dashed–dotted lines: I deformation, II merging, III re-deformation, IV steady state.

For double droplets immersed in a matrix with the same viscosity (\( \eta_d: \eta_m = 2:2 \)), the morphology evolution and corresponding shear stress distribution for this case are illustrated in Fig. 6(c). Correspondingly, the trend of shear viscosity is plotted in Fig. 9. Although there is a droplets merging process, Fig. 9 reveals that the bulk contribution to the non-Newtonian behavior is a constant. Except that there is abnormal rheological behavior appears in the interfacial contribution, other phenomena are quite similar to the case of single droplet immersed in a matrix.

Although the simulations of simple system (single and double droplets in a matrix) reveal some basic features of the effects of viscosity contrast on dynamics of phase-separating fluids under shear, it still deserves further simulation in a large system that contains many domains.

C. Rheology and morphology of phase-separating fluids with viscosity contrast (in a system of \( 256 \times 256 \))

In the simulation, the shear is exerted after an initial period (\( t_0=250 \)) of phase separation has been proceeded under quiescent condition. It is expected that, the rheology of system, which has internal structure, will more obviously reveal the effect of viscosity contrast between the two components. The volume fraction of minor phase is always set to be 0.35. For the sake of comparison with the systems of single and double droplets, the viscosity ratios of the two phases have been set to be \( \eta_d: \eta_m = 3:1, 1:3, \) and 2:2, respectively.

Figure 10 illustrates the morphology evolution of binary fluids with different viscosity contrast at steady shear (\( \dot{\gamma} = 0.002 \)). It is observed that the shear flow induces the merging of domains and eventually the domains are elongated into stringlike structures. The corresponding shear viscosity is plotted in Figs. 11–13 for different viscosity contrast. It is also found that, when the viscosity of minor phases is greater than that of major phase (Fig. 11), the bulk contribution of shear viscosity initially decreases, and then increases until reaching a maximum value. After that it decreases again. The evolution of interfacial contribution is basically on the contrary way of bulk contribution. It increases initially and then decreases to form the first peak in the curve. When it reaches a minimum value it increases again to form the second peak. With increasing of the shear rate, the critical shear strain, at which the first peak appears, moves to higher value and the interfacial contribution decreases just like a plastic fluid while the bulk contribution increases like a inflating fluid. The trend of total shear viscosity reveals that the interfacial contribution plays more important role in the process. In the whole, the fluid behaves like a plastic fluid. When the viscosity of minor phases is less than that of major phase (Fig. 12), the interfacial contribution of shear viscosity shows similar behavior as that in Fig. 11. However, the bulk contribution runs in a contrary way compared with that in Fig. 11. When the two phases of binary mixtures have the same viscosity (Fig. 13), it is seen that the bulk contribution of shear viscosity is a constant (\( \eta = 2.0 \)). In other words, the whole rheological behavior is only determined by interfacial contribution.

All the observations indicate that the features showed in the above simple systems are basically recovered in the multi-domain systems except the following two points:

1. The interfacial contribution plays a more important role in determining the whole rheological behavior.

2. The interfacial contribution decreases just like a plastic fluid while the bulk contribution increases like a inflating fluid.
easy to be understood because there is more interface volume fraction in the multi-domain systems.

(2) After the second peak in the curves of shear viscosity, the shear viscosity decreases but cannot reach steady state. This is caused by the decrease of interfacial volume fraction due to domain growth. It is easy to imagine that the steady state cannot be reached unless the phase separation is over.

In general, the whole shear process of phase-separating binary fluids for multidomain system can also be roughly divided into four stages. In stage I, the domains are deformed by the shear flow but still keep isolated. In stage II, the deformed domains contacted and merged together. In stage III, the merged domains continue to be elongated along the shear direction. Finally, in stage IV, the merged domains begin to align in the shear direction and re-merging as the shear proceeds. The boundaries between different stages have been schematically present by dashed straight lines in Figs. 11–13.
IV. SUMMARY

In this paper, by introducing the order parameter dependent viscosity, the TDGL and Navier–Stokes equations have been solved numerically to investigate the effects of viscosity contrast between components on the rheology and morphology of phase-separating binary fluids. The shear viscosity contributed from interfaces and bulk phases are calculated, respectively. The main conclusions can be summarized as follows.

(1) The viscosity contrast between the components of phase-separating binary fluids affects the bulk contribution to the whole rheological behavior. Its effect strongly depends on the volume fraction of the components. When the viscous phase is the minor phase, the viscosity of the bulk contribution is contrary with that of interfacial contribution, and thus the non-Newtonian behavior is weakened. When the viscous phase is the major phase, the bulk contribution is comparable to the interfacial contribution and thus the non-Newtonian behavior is strengthened. However, the interfacial contribution still plays crucial role in the overall rheological behavior.

(2) When the system contains two droplets or many domains, due to the merging of domains induced by shear flow, there is a decrease of interfacial volume fraction. The interfacial contribution to the rheological properties decreases, which is responsible for the appearance of a peak in the shear viscosity curve at small shear strain. Correspondingly, the bulk contribution is also altered. However, whether the bulk contribution increases or decreases will depend on the viscosity contrast between the components. As decreasing the shear rate, the critical strain, at which the first peak appears, moves to smaller value due to the fact that the diffusion will also accelerate the domain merging.

At last, we should mention that, since the merging of domains triggers the appearance of the first peak of shear viscosity, one could acquire important information about initial morphology such as domain size and its distribution and domain growth rate, etc., by monitoring this peak.

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