Hydrodynamic Interaction Model for Two Droplets under Large Step Shear Strains

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A hydrodynamic interaction model is presented to predict the behaviors of two droplets in a medium after application of large step shear strains. The model expresses the droplets by arrays of rigid spheres. Because of retraction rate ε in time differentials for the rigid spheres, they move toward the center of mass of them in each array and this motion of the rigid spheres generates flow field in the medium similar to the field caused by recovery of droplets owing to the interfacial tension. The interaction between the rigid spheres is calculated using the hydrodynamic interaction tensor. The model predicts that the distance between the droplets in deformation direction decreases with increasing time and that the shape of the droplets becomes sigmoidal. In addition, the model calculation shows change in the distance in the deformation direction is independent of initial distance between the droplets providing that the initial distance is less than a certain value. These three predictions agree with the experimental results and strongly indicate that the origin of the interaction between the droplets is the hydrodynamic interaction.

Key Words: Hydrodynamic interaction / Droplets / Interfacial tension / Immiscible blend

1. INTRODUCTION

Polymer blends are important materials in industry and fascinating materials for academic research. Especially, rheological behaviors of polymer blends have been studied in many years. One of the most successful achievements in the previous decades is the theoretical prediction of linear viscoelasticity for polymer blends by Palierne.1 His theory predicts the linear viscoelasticity quite well.2-6 In addition, interfacial tension between two polymer components can be evaluated using the Palierne theory with observation of size of dispersed phase.5-7

Other important achievements are for non-linear rheology, which Onuki8 and Doi and Ohta9 studied theoretically. Onuki derived the interface tensor to express the contribution of the interface to the stress tensor in binary mixtures of fluids.8 Doi and Ohta applied the interface tensor to explain rheological behaviors for binary mixtures of Newtonian fluids with the same viscosities under steady-state and step up of strain rate, and found scaling laws between the stress and strain rate.9 These scaling laws agree fairly well with the experimental results for immiscible polymer blends.10,11 In addition, it was shown that the interface tensor roughly expresses the stress due to the interface.12,13

The other theory for rheological behaviors of polymer blends was developed by Batchelor14 and Mellema and Willemse15 which is the oldest but the most general one. Their theory considers the stress contribution both from the Laplace pressure and the interface velocity. The stress contribution from the Laplace pressure corresponds to the stress expressed by the interface tensor. Recently, the other contribution, the interface velocity, is widely studied.16-22 Recent experimental results revealed that the contribution from the interface velocity is not small compared with the contribution from the Laplace pressure when viscosities of droplet and matrix phases are different.17,20 In addition, our recent experiments20,23 suggest that the stress due to the interface cannot be expressed by the interface tensor nor the expression by Batchelor14 and Mellema and Willemse15 during the last stage of stress relaxation under large step shear strains. Our experimental results indicate that the stress is affected by droplet size distribution and/or interaction between adjacent droplets.20,23
Concerning the interaction between adjacent droplets, our recent observation\textsuperscript{24,25} revealed that attractive interaction acts on two polyisobutylene (PIB) droplets in polydimethylsiloxane (PDMS) matrix on the same shear plane during the shape recovery of the droplets after application of large step shear strains: The droplets approach by each strain. We have shown that the origin of the interaction is hydrodynamic interaction between the droplets based on a simple model using the hydrodynamic interaction tensor. The flow field around the droplets explains approach of the droplets during shape recovery, which explains the experimental results well.\textsuperscript{25} In the present study, details of the above model which explains the origin of the approach of the droplets are described and the model is evaluated more crucially by comparing with our experimental results.\textsuperscript{25} To do this, we will clarify the origin and effects of the interaction between adjacent droplets in polymer blends.

### 2. MODEL

The model is valid for the initial stage of the shape recovery of the droplet. Figure 1 shows scheme of the model where \(x\) and \(y\) -axes respectively correspond to directions of deformation and deformation gradient of the large step shear strains. This model represents a deformed droplet by an array of rigid spheres with radius \(a\). In Fig. 1, \(N\), \(D_0\), \(\theta\) and \(\eta_s\) denote the number of the rigid spheres in the array, distance between centers of mass for the arrays of the rigid spheres which consist in each deformed droplet, orientation angle from the \(x\)-axis and viscosity of medium, respectively. \(R_{A,i}\) and \(R_{B,i}\) are position vectors of centers for \(i\)-th rigid spheres in the droplets A and B, respectively. The origins of \(R_{A,i}\) and \(R_{B,i}\) are the centers of mass of the arrays for each droplet. In Fig. 1, an example of \(N = 11\), \(i = 9\) for \(R_{A,i}\) and \(i = 10\) for \(R_{B,i}\) is schematically shown.

![Scheme of the hydrodynamic interaction model.](image)

<table>
<thead>
<tr>
<th>Time differentials of (R_{A,i}) and (R_{B,i}) are respectively given by</th>
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<tbody>
<tr>
<td>(\dot{R}<em>{A,i} = -\dot{\epsilon} R</em>{A,i} + v(R_{A,i} + x_A)) (1)</td>
</tr>
<tr>
<td>(\dot{R}<em>{B,i} = -\dot{\epsilon} R</em>{B,i} + v(R_{B,i} + x_B)) (2)</td>
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where \(\dot{\epsilon}\) represents retraction rate of the arrays of the rigid spheres, \(x_A\) and \(x_B\) position of the centers of mass for the arrays corresponding to the droplet A and B, respectively. \(v(x)\) is velocity vector due to the hydrodynamic interaction at position \(x\) in the fluid and given by

\[
v(x) = \sum_{j=1}^{N} \left[ H(x - (R_{A,j} + x_A)) \cdot F_{A,j} + H(x - (R_{B,j} + x_B)) \cdot F_{B,j} \right]
\]

(3)

where \(H(r)\) denotes hydrodynamic interaction tensor. \(F_{A,i}\) and \(F_{B,i}\) are friction forces acting on the \(j\)-th rigid spheres in the droplet A and B, and given by

\[
F_{A,j} = \zeta \left( \dot{R}_{A,j} - v(R_{A,j} + x_A) \right)
\]

(4)

\[
F_{B,j} = \zeta \left( \dot{R}_{B,j} - v(R_{B,j} + x_B) \right),
\]

(5)

respectively, where \(\zeta = 6\pi \eta_s a\) represents friction coefficient of the rigid spheres. For the hydrodynamic interaction tensor \(H(r)\), various forms can be used.\textsuperscript{26-28} In the present study, we adopt the simplest form as follows.

\[
H(r) = \delta / r (r = 0)
\]

\[
H(r) = \frac{1}{8\pi \eta_s r^2} \left( \delta + \frac{\delta r r}{r^2} \right) (r \neq 0),
\]

(6)

where \(\delta\) denotes the unit tensor, \(r\) an vector between two anonymous points in the fluid and \(r = |r|\). Substituting Eqs. (4) and (5) into Eq. (3) gives

\[
v(x) = -\zeta \dot{\epsilon} \sum_{j=1}^{N} \left[ H(x - (R_{A,j} + x_A)) \cdot R_{A,j} + H(x - (R_{B,j} + x_B)) \cdot R_{B,j} \right].
\]

(7)

Eqs. (1) and (2) with Eq. (7) determine time evolution of \(R_{A,i}\) and \(R_{B,i}\), respectively.

In the present study, the time evolution of \(R_{A,i}\) and \(R_{B,i}\) are numerically calculated using forward difference equations corresponding to Eqs. (1) and (2). Time step \(\Delta t\) for the calculation is fixed to be \(\Delta t = 0.004\ \dot{\epsilon}^{-1}\) since calculations for \(\Delta t < 0.004\ \dot{\epsilon}^{-1}\) gives the same results as that obtained.
for $\Delta t = 0.004 \dot{\epsilon}^{-1}$. Initial conditions $\mathbf{R}_{i,j} = 0$ and $\mathbf{\dot{R}}_{i,j} = 0$ are always used. Other initial conditions are described for each calculation.

3. RESULTS AND DISCUSSION

In this section, calculated results are shown using units $a$ for length and $\dot{\epsilon}^{-1}$ for time. Because of the first terms in the right hand sides of Eqs. (1) and (2), the rigid spheres move toward the center of mass in each array of the rigid spheres, which corresponds to the recovery of the deformed droplet owing to the interfacial tension. Since the first and the second terms in the summation symbol of the right hand side in Eq. (7) represent the hydrodynamic interaction from the droplet A and the droplet B, respectively, the former corresponds to intra-droplet interaction and the latter inter-droplet interaction for the droplet A, and vice-versa for the droplet B.

At first, we show retraction process of the arrays of the rigid spheres without inter-droplet interaction, i.e., the calculated results in which the second term in the summation symbol in Eq. (7) is neglected for the droplet A and the first term is neglected for the droplet B. Figures 2 (a)-(d) show time dependence of shape for the two arrays, where number of rigid spheres, $N = 100$, initial distance between centers of mass for the two arrays, $D_0 = 300$, and orientation angle $\theta = \pi/20$. It is clear that both arrays retract with time keeping initial straight shape until $t = 0.32$. In addition, distance between the centers of mass for the arrays does not change. Figure 3 shows semi-logarithmic plot of length, which is defined by distance between centers of the rigid spheres at both ends, for the arrays versus $t$. In this plot, the length linearly decreases with increasing $t$ at $t < 0.6$. This means that the arrays retract with time exponentially.

The exponential decay of the major axis of an isolated droplet was observed for polyisobutylene (PIB) droplet in polydimethylsiloxane (PDMS) at initial stage of recovery after application of large step shear strains. Symmetric shape of the isolated droplet was also observed for PIB droplet in PDMS during the recovery. Therefore, the calculated results without inter-droplet interaction reproduce the experimental results for the isolated droplet at the initial stage of the recovery after application of large step shear strains. This means that the arrays of the rigid spheres and the time differentials in Eqs. (1) and (2) are good approximations for the initial stage of the recovery of the isolated droplets.

Now we demonstrate results with the inter-droplet interaction, i.e., results for calculations which include both terms in summation symbol of Eq. (7). Figures 4 (a)-(d) show time dependence of shape for the two arrays, where number of rigid spheres, $N = 100$, distance between centers of mass for the two arrays $D_0 = 300$ and orientation angle $\theta = \pi/20$. At $t = 0$, length of the droplets, $L_0$, which is defined by distance between the centers of the rigid spheres at both ends of each droplet, is $L_0 = 1000$. This means distance between the centers

![Fig. 2. Time dependence of shapes of the two arrays without inter-droplet interaction for initial distance $D_0 = 300$, orientation angle $\theta = \pi/20$ and $N = 100$. (a) $t = 0.00$, (b) $t = 0.08$, (c) $t = 0.16$ and (d) $t = 0.32$.](image-url)
of the rigid spheres in each droplet is \( L_0/N = 10 \). In Fig. 4, the rigid spheres are indicated by open circles with 20 times size for clarity.

At \( t = 0.0 \) (Fig. 4 (a)), rigid spheres align on a straight line according to the initial condition above. At \( t = 0.08 \) and \( t = 0.16 \) (Figs. 4 (b) and (c)), rigid spheres move toward their centers of mass and \( L_0 \) decreases with \( t \), which corresponds to retraction of droplets. Though it is difficult to see from these figures, shape of the droplets, which is expressed by configuration of the rigid spheres, slightly becomes sigmoidal.

At \( t = 0.32 \), (Fig. 4 (d)), the configuration of the rigid spheres obviously exhibits sigmoidal shape. For comparison, we also calculated time dependence of shape for the two arrays using the same \( \theta \) as Figs. 4 (a)-(d). Figures 5 (a)-(d) show the calculated results for \( D_0 = 75 \), \( L_0 = 250 \) and \( N = 25 \), which is the same \( L_0/D_0 \) and \( L_0/N \) as that in Figs. 4 (a)-(d). The results in Figs. 5 (a)-(d) are the same as Figs. 4 (a)-(d) except for the length scale.

Figure 6 shows shapes of the droplets in Fig. 4 using deviation in the position of the rigid spheres perpendicular to the initial line, on which the rigid spheres align at \( t = 0.0 \), as functions of \( x \) coordinate of the spheres. Since the two droplets exhibit the same shape except for their direction, the deviation for the droplet A only is shown in Fig. 6, where positive deviation means that the rigid spheres are above the initial line, negative deviation below the line and absolute value of the deviation corresponds to distance of the center of the rigid spheres perpendicular to the initial line. Figure 6 shows the sigmoidal shape of the droplet at \( t = 0.08 \), \( t = 0.16 \) and \( t = 0.32 \) more clearly, in which right part of the droplet exhibits positive and middle part negative deviation, where the positive deviation means that the rigid spheres moved above the initial line and the negative deviation means the spheres moved below the line. Such sigmoidal shapes are observed in the experiments for the two PIB droplets in the PDMS matrix\(^{25}\) and are not found during recovery of an isolated PIB droplet in PDMS matrix.\(^{30}\) The calculated results

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Fig. 3. Semi-logarithmic plot of length of the arrays versus \( t \) without inter-droplet interaction for initial distance \( D_0 = 300 \), orientation angle \( \theta = \pi/20 \) and \( N = 100 \).

Fig. 4. Time dependence of shapes of the two arrays for initial distance \( D_0 = 300 \), orientation angle \( \theta = \pi/20 \) and \( N = 100 \). (a) \( t = 0.00 \), (b) \( t = 0.08 \), (c) \( t = 0.16 \) and (d) \( t = 0.32 \).
without inter-droplet interaction shown in Fig. 2 also does not show the sigmoidal shapes. Thus the sigmoidal shape can be due to the inter-droplet interaction. Since the hydrodynamic interaction is the only inter-droplet interaction in the present model, the hydrodynamic interaction can be the origin of the experimentally observed sigmoidal shapes of the droplets.\(^{(25)}\)

Figure 7 demonstrates time dependence of distance between the centers of mass of the rigid spheres for the droplets A and B in Fig. 6, where \(D_x\) indicates the distance in the \(x\) direction, and \(D_y\) is relative \(y\) coordinate of the droplet A to the droplet B. It is clear that \(D_x\) decreases with increasing \(t\) while \(D_y\) increases with increasing \(t\) at \(t < 0.26\) and decreases with increasing \(t\) at \(t > 0.26\). In the experimental results,\(^{(25)}\) distance in the direction of deformation (i.e. the \(x\) direction in the present model) between the droplets decreases during shape recovery of the droplets after application of large step shear strains. This qualitatively agrees with the time dependence of \(D_x\) in Fig. 7.

It is worth mentioning that such decrease in the distance

Fig. 5. Time dependence of shapes of the two arrays for initial distance \(D_0 = 75\), orientation angle \(\theta = \pi/20\) and \(N=25\). (a) \(t = 0.00\), (b) \(t = 0.08\), (c) \(t = 0.16\) and (d) \(t = 0.32\).

Fig. 6. Time dependence of deviation in the shape of the array A from its initial shape for initial distance \(D_0 = 300\), orientation angle \(\theta = \pi/20\) and \(N=100\).

Fig. 7. Time dependence of distance between the arrays in the \(x\) direction, \(D_x\), and the relative \(y\) coordinate of the array A to the array B, \(D_y\), for initial distance \(D_0 = 300\), orientation angle \(\theta = \pi/20\) and \(N=100\).
between the droplets is not observed in the calculation without inter-droplet interaction shown in Fig. 2. This indicates that the inter-droplet hydrodynamic interaction causes the decrease in the distance between the droplets. On the other hand, distance in direction of deformation gradient (the y direction) is nearly constant in the same experiments, which does not agree with the time dependence of \( D_y \) in Fig. 7. This difference between the model prediction and the experimental results can be caused by the way to apply deformation in the experiments. In the experiments, direction to apply the large step shear strains is alternate. Thus, the relative distance of the droplet A to the droplet B in the y direction, \( D_y \), is positive for the deformation in the +x direction as shown in Fig. 7 while \( D_y \) decreases for the deformation in the -x direction and becomes close to zero after the two times of the large step deformation. As a result, the height of the two droplets becomes almost the same.

Figures 8 (a)-(d) illustrate flow fields in the medium around the droplets for the same initial conditions and \( t \) as Figs. 6 (a)-(d), respectively, which is calculated using Eq. (7). An arrow starts from a point \( x \) in the medium, and length and direction of the arrow represent velocity vector of the flow at the point \( x \), \( v(x) \). The rigid spheres are shown by filled circles with about 60 times size. At \( t = 0.0 \), the flow field is strongest and the flow field becomes weaker with increasing \( t \). Though both droplets are influenced by flow from -x to x as well as flow from x to -x, closer look at the figure reveals that left side of the droplet A have large influence of the flow from -x to x and the flow from x to -x at right side of the droplet A is smaller.

As a result, total flow acting on the droplet A is from -x to x. For the droplet B, the situation is opposite and total flow acting on the droplet B is from x to -x. Consequently, total flows acting on the droplets make them closer. At \( t = 0.08 \), \( t = 0.16 \) and \( t = 0.32 \), similar effect of flow fields to \( t = 0.0 \) is observed, and the droplets become closer and closer with increasing \( t \) in the x direction as shown in Fig. 7.

Concerning the sigmoidal shapes of the droplets, Figs. 8 (a) and (b) show that right part of the droplet A is in the flow field which causes the positive deviation from the initial line at \( t = 0.0 \) and that middle part is in the flow field which causes the negative deviation. These flow fields obviously make the droplet shape sigmoidal. On the other hand, Fig. 8 (c) shows different flow field, in which the right and left parts of the droplet A are in flow fields heading toward the positive deviation. These flow fields can make the droplet shape bending rather than sigmoidal. Provided that the rigid spheres are connected each other, the bending flow fields can enhance the sigmoidal shape. Though direct connections between the rigid spheres are not assumed in the present model, Eq. (7) includes both intra- and inter-droplet hydrodynamic interaction between the arrays of the rigid spheres. The intra-droplet interaction can tend to connect the rigid spheres in the droplet A and the bending flow fields can result in more enhanced sigmoidal shape of the droplets at \( t = 0.32 \) in Figs. 4 (d) and 8 (d).

Figure 9 shows double-logarithmic plots of \( D_0 - D_x \) versus \( t \) for \( \theta = \pi/10 \) and various \( D_0 \). \( D_0 - D_x \) increases with increasing...
t at \( t \leq 0.29 \), which means that \( D_x \) decreases with \( t \) at \( t \leq 0.29 \) and indicates approach of the droplets during the recovery process. At \( t > 0.29 \), \( D_x - D_y \) has maxima except for \( D_y = 600 \) and decreases with increasing \( t \) after the maxima. A particular feature of the behavior in \( D_y - D_x \) is that variation of \( D_y - D_x \) for different \( D_y \) at the same \( t \) is within \( \pm 8\% \) for \( 200 \leq D_y \leq 500 \) and \( t < 0.4 \). This means that the time dependence of \( D_y \) during one recovery is almost independent of \( D_y \) in these conditions.

Figures 10 and 11 show double-logarithmic plots of \( D_y - D_x \) versus \( t \) at various \( D_y \) for \( \theta = \pi/20 \) and \( \theta = \pi/30 \), respectively. \( D_y - D_x \) increases with increasing \( t \) at \( t \leq 0.32 \) for \( \theta = \pi/20 \) and at \( t \leq 0.34 \) for \( \theta = \pi/30 \). After these time region, \( D_y - D_x \) exhibits maxima except for \( D_y = 500 \) and \( D_y = 600 \). For \( \theta = \pi/20 \) and \( \theta = \pi/30 \), variation of \( D_y - D_x \) for \( 200 \leq D_y \leq 500 \) and \( t < 0.4 \) is within \( \pm 8\% \) and \( 9\% \), respectively, which is similar to that for \( \theta = \pi/10 \). In Figs. 9-11, the utilized values of \( \theta \) roughly correspond to that in the experiments.\(^\text{25}\)

In the present model, the concept of the initial radius of the droplets is missing. Therefore, it is not possible to compare our model with the experimental results directly. Nevertheless, \( D_y \) independence of \( D_y - D_x \) in the model prediction in Figs. 9-11 might correspond to the experimental results that change in the distance between the droplets for one recovery process is independent of the distance before the recovery. In the experimental results,\(^\text{25}\) we found that \( d_0/r_0 \) is linear to \( \gamma_{\text{total}} \) at \( d_0/r_0 < 3.8 \), where \( d_0 \) and \( r_0 \) respectively denote distance between the centers of the droplets before each deformation and initial radius of the droplets. \( \gamma_{\text{total}} \) is total strain applied to the droplets which is defined by product of step strain \( \gamma \) and number of the application of the step strain. This linear relationship means that change in \( d_0/r_0 \) for one recovery process is independent of \( d_0/r_0 \) at \( d_0/r_0 < 3.8 \) and agrees with the model predictions in Figs. 9-11. Concerning the results for \( D_y = 100 \), \( D_y \) can be too small to reproduce the experimental results. This may be a limitation of the present model in which actual shape of the interface is not apparent.

4. CONCLUSIONS

We calculated time dependence of shape for two droplets and flow field around the droplets after application of large step shear strain based on a model which considers inter- and intra- droplet hydrodynamic interaction. The droplets are represented by arrays of rigid spheres in the model and retraction rate \( \dot{c} \) is introduced to time differentials of positions of the rigid spheres to retract the arrays. Because of \( \dot{c} \), the process is independent of \( d_0/r_0 \) at \( d_0/r_0 < 3.8 \) and agrees with the model predictions in Figs. 9-11. Concerning the results for \( D_y = 100 \), \( D_y \) can be too small to reproduce the experimental results. This may be a limitation of the present model in which actual shape of the interface is not apparent.

\[ \text{Fig. 10. Double-logarithmic plots of change in distance between the arrays in the } x \text{ direction, } D_y - D_x, \text{ versus time } t \text{ at various initial distance } D_y \text{ for orientation angle } \theta = \pi/20 \text{ and } N = 100. \]

\[ \text{Fig. 11. Double-logarithmic plots of change in distance between the arrays in the } x \text{ direction, } D_y - D_x, \text{ versus time } t \text{ at various initial distance } D_y \text{ for orientation angle } \theta = \pi/20 \text{ and } N = 100. \]
rigid spheres move toward the center of mass in each array and generates flow field in the medium similar to what is caused by recovery of droplets owing to the interfacial tension. The model reproduces three experimental results: (1) the two droplets approach each other in the direction of the deformation with increasing time, (2) shape of the droplets becomes sigmoidal during the retraction, (3) change in distance between the droplets in the direction of deformation for one recovery process is roughly independent of initial distance provided that the initial distance is less than a certain value. These three agreements between the model predictions and the experimental results strongly indicate that the behaviors of the two droplets after application of large step shear strains are dominated by the hydrodynamic interaction.

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