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Effects of partial miscibility on drop-wall and drop-drop interactions

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Synopsis

The effect of the mutual diffusion of two polymeric phases on the interaction and coalescence of two nearby drops in quiescent conditions is investigated for two *partially miscible* systems, differing in the miscibility of the components. Transient interfacial tension measurements show that the polybutene (PB)/polydimethylsiloxane (PDMS) system is *highly diffusive* in terms of diffusing low-molecular weight species, while the polybutadiene (PBD)/PDMS system is less miscible. Drops of the highly diffusive PB/PDMS system at distances closer than their equivalent radius attract each other and coalesce with a rate that, in the last stage of the coalescence process, is the same for all drop combinations. For the *slightly diffusive* PBD/PDMS system, no coalescence occurs, and, in contrast, repulsion between the drops is observed. These phenomena are qualitatively explained in terms of the overlap of diffuse layers formed at the drop surfaces of two, close enough drops, yielding concentration gradients that cause gradients in the interfacial tension. These gradients yield Marangoni stresses that induce flow leading either to attraction or repulsion. To determine whether Marangoni stresses are strong enough to displace a drop in quiescent conditions, single drops of PB and PBD are placed in a PDMS matrix in the vicinity of a wall. A lateral drop motion toward the wall is observed for the highly diffusive PB/PDMS system only, while PBD drops do not move. The diffuse-interface model is considered as a good candidate to capture these phenomena described since it couples the mutual diffusion of the low-molecular weight component with both drop and matrix, while including hydrodynamic forces. The presented numerical simulations indeed show a diffusion-induced macroscopic motion that qualitatively reproduces the experimental phenomena observed and support our interpretations.

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I. INTRODUCTION

Interfacial properties in multi-phase systems are important because they affect break-up and coalescence events during the processing of blends, defining the transient and steady morphologies, which result from the dynamic equilibrium between these phenomena. Usually, polymers are considered fully immiscible [e.g., Jones and Richards (1999); Fortelny and Kovar (1988); Lyu *et al.* (2000); Elmendorp and van der Vegt (1986); Rusu and Peuvrel-Disdier (1999); Verdier and Brizard (2002); Vinckier *et al.* (1996)]; however, cases exist where diffusion of low-molecular weight species across an

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interface occurs in the experimental time scale [Shi *et al.* (2004); Peters *et al.* (2005); Tufano *et al.* (2008a, 2008b)], and where mass transfer between the two phases, although limited, creates a gradient in the concentration of migrating molecules, changing the interface properties, thus, affecting drop deformation dynamics and film drainage between two approaching drops [Klaseboer *et al.* (2000); Chevaillier *et al.* (2006)]. Hu *et al.* (2000) reported that a reduction of 3% in the interfacial tension reduces the critical capillary number for coalescence by a factor of 6. Mutual miscibility can cause gradients in interfacial tension since the low-molecular weight fraction accumulated at the interface behaves as a surfactant. To balance this gradient, tangential stresses appear at the drop interface influencing film drainage, usually referred to as Marangoni flow [Scriven and Sterlino (1960); Levich and Krylon (1969)]. Depending on the direction of mass transfer along the drop surface, gradients in the interfacial tension differ in sign and can accelerate or decelerate film drainage, promoting or suppressing coalescence, respectively.

Mackay and Mason (1963) showed that the rate of thinning of the film separating two approaching drops increases when diffusion of a third component (mutual solvent) occurs from the drop phase into the matrix and decreases in the opposite case. Pu and Chen (2001) and Chen and Pu (2001) investigated jump-like coalescence between two captive drops of oil in water and in the absence of external forces, showing that the presence of a third diffusing component enhances coalescence, while the binary coalescence time is retarded by the addition of a surfactant. They proposed an equation to express the binary coalescence time as a function of a so-called thin-film coefficient, which reflects the thin-film properties: the molecular properties of the inner phase, the interface and the continuous phase, thus, the interfacial concentration gradients of surfactant, the viscosity of continuous phase, and the influence of steric hindrance and temperature on interdiffusion. By interpreting the experimental data by using this expression, they found support that the larger the difference in drop size, the shorter the coalescence time. Velev *et al.* (1995) found thick and very stable aqueous films between oil phases when a surfactant is diffusing from the interface toward the film and attributed the film stability to the aggregation of surfactant micelles in the film area, generating an osmotic pressure difference between the film interior and the aqueous meniscus. Film drainage between two captive polyethylene oxide (PEO)-water drops in a polydimethylsiloxane (PDMS) matrix is found to be very sensitive to an increase in film radius, and Zdravkov *et al.* (2003) attributed the effect to a depletion of PEO molecules adsorbed on the drop interfaces into the film. The same authors [Zdravkov *et al.* (2006)] carried out further investigations on the effects of mutual diffusion on film drainage, showing that for highly diffusive systems, the drainage rate is 100 times faster than predicted by existing theoretical models, while, when a slightly diffusive system is considered, good agreement with the partially mobile model prediction is found. The results are explained in terms of Marangoni convection flows, which promote film drainage when the overlap of the diffusion layers formed around the drop surface occurs, and slow it down in the opposite case.

Extensive numerical studies have been carried out to describe the interface between two or more liquids defined as a space in which a rapid but smooth transition of physical quantities between the bulk fluid values occurs. Equilibrium thermodynamics of interfaces was developed by Poisson (1831), Maxwell (1876), and Gibbs (1876). Rayleigh (1892) and van der Waals (1979) developed a model to describe a diffuse-interface based on gradient theories that predict the interface thickness; thus, an interphase, which tends to become infinite once the critical temperature is approached. A review on diffuse-interface methods in fluid mechanics was given by Anderson *et al.* (1998). Lamorgese

TABLE I. Selected model components.

Sample	M_n^a (g/mol)	M_w/M_n^a	ρ (g/cm ³)	σ (mN/m)	η (Pa s)	R_0 (mm)	ΔR_{4h} (μ m)
PB/PDMS	635/62700	2.1/1.8	0.874/0.975	2.2	3.7/10.9	1.13	209
PBD/PDMS	8000/62700	1.1/1.8	0.891/0.975	4.2	13.6/10.9	1.22	6

^aProvided by the supplier.

and Mauri (2006) used a similar approach to simulate the mixing process of a quiescent binary mixture that is instantaneously brought from the two to the one-phase region of its phase diagram.

In this work, a *highly diffusive* system, polybutene (PB) in PDMS, and a *slightly diffusive* system, polybutadiene (PBD) in PDMS, are used to investigate the effects of partial miscibility between the two polymeric phases (i) transient interfacial tension, (ii) the lateral motion of a single drop, and (iii) coalescence of two drops in quiescent conditions. Details on the experimental approach of the transient interfacial tension are given in Tufano *et al.* (2008b).

The results are compared to predictions of the diffuse-interface model modified to account for three components: the drop phase, the low-molecular weight fraction of migrating molecules, and the matrix phase. Drop coalescence under quiescent conditions is experimentally investigated for different drop radii and distances between them. The results are interpreted in terms of diffusivity of low-molecular weight component, in drop and matrix phases, which induce gradients in interfacial tension on the drop surface. In addition, we show that similar phenomena can be observed for a drop close to a wall.

II. MATERIALS AND METHODS

A. Materials

The polymers used as dispersed phase are PB (Indopol H-25, BP Chemicals, UK) and PBD (Ricon 134, Sartomer). The continuous phase is PDMS (UCT). The materials are liquid and transparent at room temperature. The number average molecular weights M_n and the polydispersities M_w/M_n of the materials are given in Table I. Densities measured with a digital density meter (DMA 5000, Anton Paar) and steady interfacial tension measured with a pendent drop apparatus, at room temperature, are also listed in Table I. Zero shear viscosities are measured using a rotational rheometer (Rheometrics, ARES) equipped with a parallel-plate geometry, applying steady shear. All polymers exhibit Newtonian behavior in the range of shear rates applied (0.01–10 s⁻¹) and the viscosities at room temperature are added to Table I. While measuring the interfacial tension, also the changes in the droplet radii are measured. Variations in the drop radius in 4 h (ΔR_{4h}) are used as a measure for the blend diffusivity (see the last column in Table I). Assuming that the thickness of the diffusion layer around the drop is proportional to ΔR_{4h} , the system PB/PDMS is more diffusive compared to the system PBD/PDMS and will have a thick diffusive layer, while the PBD/PDMS system will have a thin diffuse layer.

B. Experimental methods

Coalescence experiments are performed in a home-made Couette device, ensuring simple shear flow between the concentric cylinders. The diameters of the inner and outer cylinders are 25×10^{-3} m and 75×10^{-3} m, respectively. The cylinders are actuated by two dc motors (Maxon) and can rotate independently in both directions. The motors are

controlled by a TUEDAC, an in-house developed digital $\rightarrow$ analog converter, and two amplifiers are used to strengthen the signals. The real time control of the motors is guaranteed by a home-made software. Images are acquired via a 45° oriented polished surface placed below the cylinders. A stereo-microscope (Olympus) and a digital camera serve the acquisition of images, which are further analyzed. In all experiments, a single droplet is introduced in the stagnation plane obtained by concentric counter-rotating conditions, using a syringe, and the critical capillary number is reached to break the droplet in two or more daughter droplets. The angular velocities of the two cylinders are controlled such that the droplet position is stationary and images can be acquired during the whole process. When droplets of the required sizes are created, the flow is reversed, bringing the droplets at the required distance. The reversed flow is chosen to be very slow to avoid any *a priori* drop deformation. Once the flow is stopped, quiescent coalescence is investigated.

To further investigate the drop motion induced by gradients in interfacial tension, a cubic cell with flat glass surfaces is used. Drops of PB and PBD are placed in the cell filled with PDMS, in the proximity of the wall. Images are acquired from the bottom of the cell following the same procedure as described for the Couette device. In order to exclude wetting effects on the possible lateral migration of the drops, the same experiments are carried out in a cubic cell with polytetrafluorethylene (PTFE) (Teflon) side walls.

III. DIFFUSE-INTERFACE MODEL

Diffuse-interface modeling allows us to account for interfaces with nonzero thickness. The method is based on the van der Waals's approach of the interface problem [van der Waals \(1979\)](#) and developed by [Cahn and Hilliard \(1958\)](#). The interface thickness is not explicitly prescribed but follows from the governing equations that couple the thermodynamic and hydrodynamic forces in the interface. The main elements of the theory and the coupling of thermodynamics and hydrodynamics are summarized by [Anderson *et al.* \(1998\)](#). In this work, the diffuse-interface model is applied to describe a three-phase systems, consisting of a low-molecular weight fraction, a drop phase, and a matrix. First, the governing equations are summarized, the numerical methods are outlined, and one- and two-dimensional results are presented and compared with experimental observations.

A. Governing equations

For a chemical inert N -component system, the mass balance can be written as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0, \quad (1)$$

with ρ as the density of the mixture, defined as the sum of the N -component densities, $\rho = \sum_{i=1}^N \rho_i$, and $\mathbf{v}$ is the barycentric velocity,

$$\mathbf{v} = \frac{1}{\rho} \sum_{i=1}^N \rho_i \mathbf{v}_i, \quad (2)$$

where ρ_i , $\mathbf{v}_i$ are the density and velocity of the i th component, respectively. The composition equation reads as

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{v} = -\nabla \cdot \mathbf{j}_i, \quad (3)$$

where $\mathbf{j}_i$ is the mass flux of the i th component of the considered fluid, with i ranging between 1 and N .

The momentum balance, taking into account the mass balance [Eq. (1)], can be written as

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho(\mathbf{v} \cdot \nabla) \mathbf{v} = \rho \mathbf{f}^{\text{ex}} + \nabla \cdot \boldsymbol{\sigma}, \quad (4)$$

where $\mathbf{f}^{\text{ex}}$ denotes external forces such as gravity, $\boldsymbol{\sigma}$ is the Cauchy stress tensor. To complete this set of equations, constitutive relations are required for the Cauchy stress tensor $\boldsymbol{\sigma}$. Different from classical thermodynamics, in which the internal energy u is a function of s , the specific entropy, and the density of the components, $u=u(s, \rho)$, in Cahn–Hilliard case an extra non-local term is introduced to describe inhomogeneous fluids, and the internal energy is defined as $u=u(s, \rho, \nabla \rho)$. Applying gradient theory, the Cauchy stress tensor is given by [see Lowengrub and Truskinovsky (1998)]

$$\boldsymbol{\sigma} = \boldsymbol{\tau} - p\mathbf{I} - \sum_{i=1}^N \frac{\partial \rho u}{\partial \nabla \rho_i} \nabla \rho_i, \quad (5)$$

where p is the pressure, $\boldsymbol{\tau}$ is the extra stress tensor that, assuming isothermal conditions, for a Newtonian system is taken to be $\boldsymbol{\tau} = 2\eta \mathbf{D}$, $\mathbf{D}$ is the deformation tensor given by $\mathbf{D} = (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)/2$, and η is the viscosity of the mixture [for a more complete description of the model, see Khatavkar *et al.* (2007a) and Prusty *et al.* (2007)]. An additional gradient term, similar to the Cauchy stress tensor, is added to the chemical potential of each of the N species, and to the pressure,

$$\mu_i = \mu_{0i} - \nabla \cdot \frac{\partial \rho u}{\partial \nabla \rho_i}, \quad (6)$$

$$p\mathbf{I} = p_0\mathbf{I} - \sum_{i=1}^N \rho_i \nabla \cdot \frac{\partial \rho u}{\partial \nabla \rho_i}, \quad (7)$$

in which μ_{0i} and p_0 are defined with respect to the homogeneous reference state. Substituting the expression of $\boldsymbol{\tau}$ and $\boldsymbol{\sigma}$ in the momentum balance, and writing ρ_i as $c_i \rho$, with $c_i = \rho_i / \rho$, the momentum balance reads as

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho(\mathbf{v} \cdot \nabla) \mathbf{v} = \rho \mathbf{f}^{\text{ex}} + \nabla \cdot (2\eta \mathbf{D}) - \nabla p - \nabla \sum_{i=1}^N \frac{\partial \rho u}{\partial \nabla c_i} \nabla c_i. \quad (8)$$

It was shown by Lowengrub and Truskinovsky (1998) that

$$-\nabla \sum_{i=1}^N \frac{\partial \rho u}{\partial \nabla c_i} \nabla c_i = -\rho \nabla f + \rho \sum_{i=1}^{N-1} (\mu_i - \mu_N) \nabla c_i, \quad (9)$$

where $f = u - Ts$ is the specific Helmholtz free energy of the system, T is the temperature, and s is the entropy. Substituting Eq. (9) and the specific Gibbs free energy defined as $g = f + p/\rho$, in Eq. (8), and dividing all terms by ρ , the momentum balance reduces to

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = \mathbf{f}^{\text{ex}} + \frac{1}{\rho} \nabla \cdot (2\eta \mathbf{D}) - \nabla g + \sum_{i=1}^{N-1} (\mu_i - \mu_N) \nabla c_i. \quad (10)$$

The ∇g term can be considered as a modified pressure and the interfacial tension is now evaluated as a body force ($\sum_{i=1}^{N-1} (\mu_i - \mu_N) \nabla c_i$), as shown by [Lowengrub and Truskinovsky \(1998\)](#). If we substitute the density of each component (ρ_i) with its mass fraction ($c_i = \rho_i / \rho$), and we express $\mathbf{j}_i$ in terms of μ_i , Eq. (3) can be written as

$$\frac{\partial c_i}{\partial t} + \mathbf{v} \cdot \nabla c_i = \nabla \cdot \mathbf{M} \nabla \mu_i. \quad (11)$$

Finally, writing the internal energy u in terms of the specific Helmholtz free energy of the system f , the chemical potential follows:

$$\mu_i - \mu_N = \frac{\partial f}{\partial c_i} - \frac{1}{\rho} \nabla \cdot \left(\rho \frac{\partial f}{\partial \nabla c_i} \right). \quad (12)$$

B. Governing equations for a three-phase system

When a three-phase non-homogeneous system is investigated assuming isothermal conditions, density-matched phases, incompressible fluids, constant viscosities of the phases and neglecting inertia and external forces, and using μ_1 and μ_2 in the momentum balance to express the chemical potential differences with respect to the third component, the system of governing equations reduces to:

- Mass balance

$$\nabla \cdot \mathbf{v} = 0. \quad (13)$$

- Momentum balance

$$0 = -\nabla g + \eta \nabla^2 \mathbf{v} + \mu_1 \nabla c_1 + \mu_2 \nabla c_2. \quad (14)$$

- Composition equation

$$\frac{\partial c_i}{\partial t} + \mathbf{v} \cdot \nabla c_i = M_i \nabla^2 \mu_i \quad i = 1, 2. \quad (15)$$

- Chemical potential

$$\mu_i - \mu_N = \frac{\partial f}{\partial c_i} - \nabla \cdot \left(\frac{\partial c}{\partial \nabla c_i} \right) \quad i = 1, 2. \quad (16)$$

For this three-phase system, we used

$$\mathbf{M} = \begin{bmatrix} M_1 & 0 \\ 0 & M_2 \end{bmatrix}, \quad (17)$$

where M_1 and M_2 are input parameters in the model, describing the mobility between low-molecular weight and drop, and matrix and drop, respectively. Note that, in general, M_1 and M_2 can be a function of c_i , but they are taken constant here. In the Cahn–Hilliard theory, the specific Helmholtz free energy of the system is given by the sum of a homogeneous part and a gradient contribution

FIG. 1. Contour plot of the free energy [Eq. (20)] on the Gibbs triangle for $a=b=d=1/4$ (left) and for $a=4$, $b=2$, and $d=1$ (right).

$$f(\mathbf{c}, \nabla \mathbf{c}) = f_0(\mathbf{c}) + \frac{1}{2} |\boldsymbol{\epsilon} \nabla \mathbf{c}|^2, \quad (18)$$

where f_0 is the homogeneous part, and $\frac{1}{2} |\boldsymbol{\epsilon} \nabla \mathbf{c}|^2$ the non-local term of the free energy, and $\boldsymbol{\epsilon}$ is the gradient energy parameter assumed to be constant, i.e., $\boldsymbol{\epsilon} = \epsilon \mathbf{I}$, where we neglect any possible off-diagonal terms. The model requires one more equation of state to describe the free energy in order to solve the system of Eqs. (13)–(16).

C. Ginzburg–Landau approximation

Based on the classical Flory–Huggins theory, the intensive free energy f_0 (per monomer) of a three-phase system, at a given temperature and pressure, can be written as

$$\frac{f_0}{KT} = \left(\frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \frac{\phi_3}{N_3} \ln \phi_3 + \chi_{12} \phi_1 \phi_2 + \chi_{13} \phi_1 \phi_3 + \chi_{23} \phi_2 \phi_3 \right), \quad (19)$$

where K is the Boltzmann constant, T is the temperature, N_i and ϕ_i with $i=1, 2, 3$ are the chain length and volume fraction of the three components, respectively, and χ_{ij} the Flory–Huggins interaction parameter between the components i and j . Chosen a three-phase system, this interaction parameter defines whether mixing or demixing occurs.

For numerical purposes, a Taylor expansion of Eq. (19) around the critical point is used as an approximation and as such the system of equations is correct only in the vicinity of the critical point, and therefore, when applied to the present, far-from-criticality case, only provides a qualitative picture of the phenomenon. In Kim *et al.* (2004), the approximation for the free-energy formulation proposed for a three-phase system reads as

$$f_0(\mathbf{c}) = f_0(c_1, c_2) = \frac{1}{4} [ac_1^2 c_2^2 + b(c_1^2 + c_2^2)c_3^2 - dc_1 c_2 c_3], \quad (20)$$

where $c_3 = 1 - c_1 - c_2$, and a , b , and d are constants. When these three constants are assumed equal to $1/4$, as proposed by Kim *et al.* (2004), the surface plot of the free energy for the ternary system presents free-energy minima in the corners of the diagram and at the center of it, where the system is fully miscible (see Fig. 1, left). We will use this expression to validate our numerical code by comparing with results from Kim *et al.* (2004). Our system consists of low-molecular weight species partially miscible with the drop and matrix phases, while drop and matrix are immiscible. This requires different values of the parameters in Eq. (20) or another free-energy expression since by just changing the parameter values ($a=4$, $b=2$, and $d=1$) (see Fig. 1, right), it can be ob-

FIG. 2. Surface plot (left) and contour plot (right) of the free energy [Eq. (21)] on the Gibbs triangle.

served that the free-energy contour plot remains symmetrical around one of the axes.

Changing the parameter values therefore does not solve the problem, and we use an alternative free-energy formulation for ternary partially miscible systems proposed by [Kim and Lowengrub \(2005\)](#),

$$f_0(c_1, c_2) = ac_1^2(1 - c_1 - c_2)^2 + (c_1 + b)(c_2 - d)^2 + (e - c_1 - c_2)(c_2 - l)^2. \quad (21)$$

Using values of $a=2$, $b=0.2$, $d=0.2$, $e=1.2$, and $l=0.4$, the surface and contour plot of this free-energy formulation are shown in Fig. 2. The contour plot corresponding to Eq. (21) is no longer symmetric; therefore, it is suitable to describe our three-component system.

D. Numerical method

The resulting system that needs to be solved, i.e., Eqs. (13)–(16), is non-linear and time-dependent. For the temporal discretization, a first-order Euler implicit scheme is used. The non-linear term in the chemical potential equation is linearized by a standard Picard method in each time step. Instead of substituting the chemical potential in the composition equation, it is treated as a separate unknown. The main advantage of this approach is that only second-order derivatives need to be evaluated. So within each cycle of a time step, the chemical potential μ and concentration c are solved together, using the velocity from the previous time. The velocity and pressure are determined by using the composition c and chemical potential μ from the previous time step. Roughly within five iterations, a solution is found for the non-linear problem of each time step. More details about the iteration scheme can be found in [Keestra *et al.* \(2003\)](#) and [Khatavkar *et al.* \(2006\)](#). A second-order finite element method is used for spatial discretization of the set of equations. The flow problem is solved using the velocity-pressure formulation and discretized by a standard Galerkin finite element method. The effect of the interface is included as a known volume source term. Taylor–Hood quadrilateral elements with continuous pressure that employ a biquadratic approximation for the velocity and a bilinear approximation for the pressure are used. The resulting discretized second-order linear algebraic equation is solved using a direct method based on a sparse multifrontal variant of Gaussian elimination (HSL/MA41), [[Amestoy and Duff \(1989\)](#); [Amestoy and Puglisi \(2002\)](#)].

E. Validation of the model

To validate the ternary diffuse-interface model and its implementation, a test case as described by [Kim *et al.* \(2004\)](#) is simulated. Here, a ternary system in a one-dimensional domain is defined with the free-energy formulation of Eq. (20). The one-dimensional

FIG. 3. Time evolution of the concentrations c_1 , c_2 , and c_3 at three different dimensionless times, i.e., $t=0$, 50, and 100.

domain with dimensionless length 1 is defined ranging from 0 to 1. The domain is discretized with 200 s-order elements yielding 401 nodes and the uniform time step is $\Delta t = 1 \times 10^{-4}$. The simulations are started with the following initial conditions:

$$c_i(x) = 0.25 + 0.01 \cos(3\pi x) + 0.04 \cos(5\pi x) \quad i = 1, 2,$$

$$c_3(x) = 1 - c_1(x) - c_2(x), \quad (22)$$

where $0 \leq x \leq 1$. The resulting time evolutions of the three-component concentrations are shown in Fig. 3 at three different times, i.e., $t=0$, 50, and 100. The obtained results fully agree with those reported as in [Kim et al. \(2004\)](#). This validated model is used hereafter to compute and interpret the experimental results.

F. Influence of the mobility parameters

The ternary diffuse-interface model as described in Sec. III B needs five material parameters, i.e., M_1 , M_2 , ϵ , ρ , and η , once the choice for the homogeneous part of the free energy has been defined. In general, these parameters are not known or easily obtained for a given polymeric system and, therefore here, we will restrict ourselves to a qualitative analysis.

In this paper, the main objective of the use of the ternary diffuse-interface model is to be able to distinguish the expected diffusion-induced flow behavior of the highly diffusive PB/PDMS system and the slightly diffusive PBD/PDMS system and compare with our experimental observations. Since for these polymeric systems the material parameters and ternary phase diagram are unknown, Eqs. (13)–(16) are solved in their dimensionless form. For a large range of the parameters, one-dimensional simulations were carried out, where purely diffusion is considered, to obtain insight in the relevant magnitude of the parameters and their effect on the diffusion process of the drops. The knowledge obtained from this exercise then serves as input for the two-dimensional simulations presented and discussed further on.

The free-energy expression adopted is given in Eq. (21), and the gradient-energy parameter ϵ is fixed to 2×10^{-4} . The viscosity η and density ρ are both set equal to 1. The influence of changes in the mobility parameters M_1 (low-molecular weight-drop) and M_2 (matrix-drop) is now investigated. The one-dimensional domain with dimensionless length 1 is defined ranging from 0 to 1. The domain is discretized with 200 s-order elements yielding 401 nodes. The drop is placed in the middle, with an initial diameter equal to the 5% of the domain. The concentration of the low-molecular weight component is taken to be 30% and time steps of $\Delta t = 1 \times 10^{-4}$ are used. A schematic picture of the domain and the initial concentration is shown in Fig. 4.

FIG. 4. Schematic representation of the initial conditions.

The transient concentration profiles of the low-molecular weight species, drop and matrix, are shown in Fig. 5 for $M_1 = 1 \times 10^{-2}$ and in Fig. 6 for $M_1 = 9 \times 10^{-2}$, respectively. In both cases, M_2 is taken equal to 4×10^{-4} . It is seen that the shapes of the concentration

FIG. 5. Concentration profiles in time for low-molecular weight component (top left), drop (top right), and matrix (bottom) for a 0.3 low-molecular weight concentrated blend. Mobility parameters: $M_1 = 1 \times 10^{-2}$ and $M_2 = 4 \times 10^{-4}$.

FIG. 6. As in Fig. 5, now with: $M_1=9 \times 10^{-2}$ and $M_2=4 \times 10^{-4}$ (case A).

profiles do not change much, but the time scale of reaching a certain profile changes considerably. For such a system, the interfacial tension can be related to the composition as

$$\bar{\sigma} = \int_0^1 \left(\frac{dc_{LMW}}{dx} \right)^2 dx. \quad (23)$$

The resulting interfacial tension behavior is shown in Fig. 7 (left) when changing M_1 gradually, in the middle when changing M_2 and on the right when lowering M_1 by orders of magnitude. For these parameter sets, a clear minimum in interfacial tension is observed that is reached at shorter times for a gradually increasing M_1 value, and it is not changing its value. Changes in M_1 affect the transient behavior of the system in the way it reaches the steady state. When M_2 is increased gradually, the time at which the minimum value in interfacial tension is reached stays the same but its value reduces. When M_1 is lowered by orders of magnitude (Fig. 7, right), the minimum disappears and the interfacial tension decreases only in a much slower way. The cases when a minimum appears are representative of highly diffusive systems, when the minimum disappears the systems behave as a slightly diffusive one. In conclusion, diffusivity can be controlled by M_1 .

G. Influence of the low-molecular weight fraction

To show how changes in the initial concentration of low-molecular weight species affect the interfacial tension of the system, we choose the case with a clear minimum $M_1=9 \times 10^{-2}$ and $M_2=4 \times 10^{-4}$, which we will address as case A, and three different

FIG. 7. Interfacial tension computed with Eq. (23) for a 0.3 low-molecular weight concentrated blend. The influence of gradual changes in the mobility parameters M_1 (top left) and M_2 (top right) when they differ two orders of magnitude and when reducing this difference (bottom) are shown.

FIG. 8. LMW concentration profiles when $M_1 = 9 \times 10^{-2}$ and $M_2 = 4 \times 10^{-4}$ (case A) for initial concentrations of LMW species of 0.3 (top left), 0.1 (top right), and 0.01 (bottom).

FIG. 9. Transient interfacial tension experiments (left) and numerical predictions (right).

initial concentrations of low-molecular weight component, respectively, 30%, 10%, and 1% are investigated. The same drop size and time steps are used as in the previous case. The concentration profiles along the drop diameter at different time steps are shown in Fig. 8. Reducing the initial concentration of migrating molecules reduces the typical radial length scale over which diffusion is observed and it shortens the time needed to complete the diffusion process. We now have sets of interfacial tension evolutions that can be compared with our experimental results.

H. Interfacial tension results

Measured transient interfacial tensions are shown for the two systems used in Fig. 9 (left). For the highly diffusive system, the interfacial tension decreases first, corresponding to thickening of the interphase, followed by an increase attributed to depletion where after it reaches a plateau value in the late stages. The slightly diffusive system shows only thinning (i.e., an increase in the interfacial tension thickness) before the plateau value is approached [Tufano *et al.* (2008b)]. In Tufano *et al.* (2008b), the differences in the interfacial behavior of these two systems are partially attributed to their different polydispersities. The PB has higher polydispersity compared to the PBD, i.e., in the system PB/PDMS a larger amount of molecules will participate to the diffusion process compared to the PBD/PDMS system. Based on that, our first approach is to model the two systems by using the three-phase diffuse-interface model described in Sec. III, with the free-energy formulation reported in Eq. (21). The mobility parameters are chosen to be $M_1 = 9 \times 10^{-2}$ and $M_2 = 4 \times 10^{-4}$ (case A), and the parameter $\epsilon = 2 \times 10^{-4}$. To distinguish the two cases, the highly diffusive system is simulated imposing 30% low-molecular weight (LMW) concentration, while, for the slightly diffusive case, this concentration is set equal to 1%. The computed behavior of interfacial tension in time in the two cases is shown in Fig. 9 (right). Given all complexities at hand, the model describes the experimentally observed behavior qualitatively quite well.

We remark again that the results from the simulations are dimensionless in contrast to the presented experimental transient interfacial tension for the two polymeric systems; apparently, the time scales associated with the diffusion of the drops are on the order of 1. Within a dimensionless time of 1, we observe in Fig. 9 (right) that the computed interfacial tension shows a similar transient behavior as in the experiments and that after about a dimensionless time of 1.5 a steady value of $\bar{\sigma}$ is reached.

FIG. 10. Mutual attraction and coalescence between two drops of PB in PDMS. Radii are 341 and 313 μm , distance at the time $t=0$ s is 110 μm . Residence time at $t=0$ s and $t_r=1800$ s.

IV. EXPERIMENTAL RESULTS

A. Drop-drop interaction: PB/PDMS system

Figure 10 shows an example of two drops of PB with nearly the same diameter and at a distance where, normally in a sharp interface regime, no interaction is expected. The initial distance between the drops is created by applying a weak flow during drop approach, ensuring that the drops keep their spherical shape and that there is no influence of flow on coalescence. Once the desired distance d between the drops is reached, the flow is stopped and no other external forces are applied denoted as time $t=0$ s in Fig. 10. At $t=0$ s, the residence time of the drops in the matrix is $t_r=30$ min and it is clearly seen that the drops attract each other, the film is drained, and when rupture occurs the drops coalesce. Figure 11 shows an example of mutual attraction of drops with different radii and with a shorter residence time at $t=0$ s ($t_r=4$ min). A large number of such experiments are carried out, using drops of different sizes, placed at different distances and having different residence times. Drops of PB always attract each other when they are at a distance less than an order of the drop radius. In order to compare the results obtained with different drop size, the ratio distance over equivalent radius is considered. The equivalent radius R_{eq} is defined as

$$\frac{2}{R_{\text{eq}}} = \frac{1}{R_1} + \frac{1}{R_2}, \quad (24)$$

where R_1 and R_2 are the radii of the two drops. Figure 12 shows the time evolution of the distance between the drops for all experiments. In the inset plot, all curves are horizontally shifted to the most right curve to compensate for differences in their initial distance. In the final stages of the measurements, approximately the last 100 s before coalescence occurs, the drops all attract with the same rate. Aging effects are also investigated monitoring drops with different resident times. In the first 30 min after the introduction of the drops in the matrix, diffusion is in progress and the interfacial tension reduces due to thickening of the interface. However, as shown in Fig. 12, no serious variations in the rate of attraction in the late stages before coalescence occurs could be detected. Zdravkov *et al.* (2006) reported for a similar PB/PDMS blend that film drainage is approximately 100 times faster compared to the partially mobile model predictions. They attributed the high

FIG. 11. As in Fig. 10, now radii are 220 and 275 μm , distance at the time $t=0$ s is 95 μm . Residence time at $t=0$ s and $t_r=240$ s.

FIG. 12. Time evolution of the scaled drop distance d/R_{eq} for the PB/PDMS system. Inset plot: curves shifted to the most right experimental curve.

drainage rate to Marangoni flow, acting in the same direction as the film drainage flow. Note that in the diffuse-interface model, the Marangoni stresses are the macroscopic manifestation of the Korteweg stresses. This high drainage rate is confirmed in the experiments presented here. In conclusion, for highly diffusive systems, mutual diffusion cannot be neglected since it has an overruling effect on drop coalescence and, therefore, it plays a crucial role in the morphology evolution of polymer blends, as also shown by [Tufano *et al.* \(2008b\)](#) for diluted blends of PB/PDMS.

B. Drop-drop interaction: PBD/PDMS system

The system PBD/PDMS shows a continuous increasing interfacial tension related to a thin diffusive layer, which approach a plateau value faster than the PB/PDMS system (see Fig. 9). When two PBD drops are brought in close contact and left in quiescent conditions, it is observed that they repel each other (see Fig. 13). In all the cases investigated, i.e., drops with different sizes and at different distances, repulsion is observed. For a similar PBD/PDMS blend, [Zdravkov *et al.* \(2006\)](#) reported that the film drainage slows down with time and eventually reverses. This was again attributed in that case to Marangoni stresses, which may cause reversal of the film drainage and explain the repulsion observed for this system.

FIG. 13. Mutual repulsion between two drops of PBD in PDMS. The radii are 597 and 572 μm .

When diffusion occurs from the drop into the matrix phase, a gradient in the concentration of the migrating molecules is generated in the radial direction forming a diffuse layer that develops around the drops. The more diffusive the material, the thicker this layer. When two drops approach, the thickness of this layer determines whether and when overlap occurs. In the space where two layers overlap, a higher concentration of migrating molecules is found compared to their concentration on the remaining of the drop surface. Gradients in molecule concentration result in a gradient in interfacial tension, and in the overlap zone a lower interfacial tension is found. This gradient in interfacial tension generates tangential Marangoni stresses along the drop surface that act to reduce the interfacial tension gradient. Therefore, they induce a convective flow from the zone of overlap to the sides. This flow acts in the same direction of the film drainage, accelerating this process, and, therefore, attraction between drops occurs and coalescence is promoted. The system PB/PDMS is an example of such a diffusive system.

When the material presents a thin diffuse layer, the overlap does not occur. The film drainage will then drag molecules from the zone between the drops to the sides. It generates the opposite concentration gradients, and, therefore, opposite interfacial tension gradients. The tangential Marangoni stresses act in this case in the direction opposite to the film drainage, retarding coalescence. While thinning of the film between the drops occurs, the drainage rate reduces. It can happen that the convective flow induced by Marangoni stresses overrules film drainage, reversing the thinning rate. The matrix flows back between the drops that move further a part and the experimentally observed repulsion occurs. To support the idea that Marangoni stresses can induce lateral migration of drops and, eventually, enhanced coalescence when highly diffusive systems are used, single-drop measurements are performed. Single PB and PBD drops are created in the vicinity of a flat wall and their possible motion, attributed to diffusion, is recorded. To exclude any effect due to wetting, glass and PTFE walls are used.

C. Drop-wall interaction: PB/PDMS system

When a PB drop is placed in the matrix, diffusion of short molecules from the drop into the matrix occurs. If the drop is close enough to a wall ($d \leq R$), there is less space for migration of the shorter molecules on the wall side and, as a consequence, their concentration will be larger than on the rest of the drop surface. This induced gradient in concentration, i.e., in interfacial tension, along the drop surface, generates Marangoni flows, which will act as to balance the concentration gradient. Movement of the migrating molecules accumulated between the drop and the wall, toward the sides of the drop, will also drag molecules of the matrix. The immediate consequence is the thinning of the matrix film between the drop and the wall. The drop then moves toward the wall, touches it, and eventually wets it (see Fig. 14, where a glass wall is used, and Fig. 15, where a Teflon wall is used).

FIG. 14. Lateral PB-drops migration toward a glass wall. The diameters are 580 and 333 μm . The initial distances from the wall are 163 and 59 μm , respectively. The solid line represents the wall.

FIG. 15. Lateral PB-drops migration toward a Teflon wall. The diameter is $247\ \mu\text{m}$ and the initial distance from the wall is $45\ \mu\text{m}$. Line represents the wall.

D. Drop-wall interaction: PBD/PDMS system

When a drop of PBD is placed close to a wall, no lateral migration is found experimentally. The time scale of the experiment is limited by the vertical movement of the drop, due to the difference in density. The acquisition is stopped when the drops start to move out of focus. In Figs. 16(a) and 16(b), a drop of PBD is placed close to a glass and a Teflon wall, respectively. In the time scale investigated, no lateral movement is seen.

V. COMPUTATIONAL RESULTS

In the previous sections, the described experimental results demonstrated the different diffusion-induced flow behavior for the two different polymeric systems, i.e., the drops are attracted and may coalesce, or repulsion is observed. Earlier, we saw that the ternary diffuse-interface method describes the transient behavior of the interfacial tension in a qualitative sense and that parameters for the mobilities and surface interaction parameter are defined. Now the full model including hydrodynamic interactions is applied, using the parameters from the one-dimensional model, to simulate the two drops in close proximity.

Figure 17 gives a schematic representation of the two cases considered here. First, we deal with drop-drop interaction; second, with drop-wall interaction. For the drop-wall simulations, the number of elements used in the x and y direction are $N_x=N_y=60$, while for the drop-drop simulations $N_x=160$ and $N_y=80$. If we indicate with $\mathbf{v}=(v_x, v_y)$, the following boundary conditions are defined. For the drop-drop case homogeneous Dirichlet for the velocity and homogeneous Neumann boundary conditions for the concentration and chemical potential are prescribed

FIG. 16. No lateral PBD-drops migration toward a wall is found. (a) Glass wall, $d_{\text{drop}}=650\ \mu\text{m}$; residence time 600 s. (b) Teflon wall, $d_{\text{drop}}=900\ \mu\text{m}$; residence time 720 s. The solid line represents the wall.

FIG. 17. Schematic representation of the computational domain used for the drop-drop (left) and drop-wall (right) simulations.

$$\left. \begin{array}{l} \mathbf{v} = \mathbf{0} \\ \frac{\partial c_i}{\partial n} = \frac{\partial \mu_i}{\partial n} = 0 \end{array} \right\} \text{ at } \Gamma_j \text{ } j = 1, 2, 3, 4. \quad (25)$$

For the drop-wall case, similar boundary conditions are prescribed except for the solid wall

FIG. 18. Concentration profiles in time for LMW component (top left), drop (top right), and matrix (bottom) for a 30% LMW concentrated blend. Mobility parameters: $M_1 = 9 \times 10^{-2}$ and $M_2 = 4 \times 10^{-4}$ (case A).

FIG. 19. Concentration profiles in time for LMW component (top left), drop (top right), and matrix (bottom) for a 30% in LMW concentrated blend. Mobility parameters: $M_1=4 \times 10^{-4}$ and $M_2=4 \times 10^{-4}$ (case B).

$$\left. \begin{array}{l} \mathbf{v} = \mathbf{0} \\ \frac{\partial c_i}{\partial n} = \frac{\partial \mu_i}{\partial n} = 0 \end{array} \right\} \text{ at } \Gamma_4, \quad (26)$$

$$\left. \begin{array}{l} \frac{\partial v_x}{\partial n} = \frac{\partial v_y}{\partial n} = 0 \\ \frac{\partial c_i}{\partial n} = \frac{\partial \mu_i}{\partial n} = 0 \end{array} \right\} \text{ at } \Gamma_j \text{ } j = 1, 2, 3. \quad (27)$$

Note that the subscript i in above boundary conditions refers to the two different phases. The initial velocity is set to zero at the start of the simulation, where the initial concentrations c_1 and c_2 are spatially dependent and define the location of the drop, similar as in the one-dimensional simulations.

A. Drop-drop interaction

First, the numerical results for the drop-drop interaction case are discussed. For the two cases (A30%, B30%), the concentration profiles over the drop-drop center line are shown in Figs. 18 and 19 at four different characteristic times. Results are presented for c_1 , c_2 , and $c_3=1-c_1-c_2$. For case A, the mobility parameters are $M_1=9 \times 10^{-2}$ and $M_2=4 \times 10^{-4}$, while, for case B, $M_1=M_2=4 \times 10^{-4}$. Clearly for the A30% system in Fig. 18, the highly diffusive system, large variations in the concentrations are observed and the

FIG. 20. Top row: x -component velocity for A30 at times $t=0.005$ and 0.08 ; the drops approach each other. Bottom row: x -component velocity for A30 at times $t=0.1$ and 0.2 ; the drops slowly move apart.

two drops merge after sufficient time. Focusing on the concentration, it is seen that the drop-drop attraction is present for the A30%; although not shown here, but this is even the case for an increased drop-drop distance. For the B30% system, the drops appear to remain stationary. To determine without doubt if the two drops are really moving by attraction or repulsion, the induced velocity field is studied in more detail.

In Fig. 20, the x component of the velocity is shown for the A30% and B30% cases at two different characteristic times. Isoline of the velocity in the figures denotes the regions of positive and negative velocities. The results from the diffuse-interface model capture the trends as shown in the experiments remarkably well; i.e., for the A30% case, we see that the left drop has a positive velocity, while the drop on the right has a negative velocity. In other words, the drops attract each other. For the B30% case, an opposite velocity direction is observed; thus, the drops repulse. Similar as observed in the experiments, the time scale for attraction is much faster than for repulsion. The separation between the components stays clearly present in the range of time, and for the two drop-drop distances, investigated for the B-cases. These results indicate that sufficient low-molecular weight species that can diffuse fast enough into the matrix (A30% versus B30%) are needed to activate the drop-drop attraction. In addition, they confirm the idea that concentration-gradient induced Marangoni stresses promote the drainage of the film between two droplets in case of a highly diffusive system.

FIG. 21. Concentration profiles in time for LMW component (top left), drop (top right), and matrix (bottom) for a 30% LMW concentrated blend. Mobility parameters: and $M_2 = 4 \times 10^{-4}$ (case A).

B. Drop-wall interaction

As the A30% and A1% systems have the right time-dependent behavior for the interfacial tension, these two systems seem to be good candidates to investigate the drop-wall interaction of a highly diffusive and a slightly diffusive system, respectively. The concentration profiles over a line through the drop center and perpendicular to the wall are shown in Figs. 21–23, respectively. The A30% and the B30% cases show, indeed, the behavior that is anticipated from the drop-drop results: a clear interaction of the drop with the wall for the A30% case and a stationary drop for the B30% case. The A1% case also shows drop-wall interaction, although not as strong as the A30% case (see the concentration levels). This is also caused by the implicitly resulting 90° contact angle for the drop-wall interaction. To generate more realistic results, the modeling should be extended with an extra free-energy function at the wall that defines this contact angle [Khatavkar *et al.* (2007b)] (for the drop-drop interaction, the contact angle is not an issue). Note that a variation in the drop-wall distance did not give any new insights and no results are presented here for these cases.

From the results presented, it is concluded that the diffusive-interface model can generate, so far only in a qualitative way given the difficulties to obtain all parameters for the model, the phenomena observed in the experiments, even though a number of assumptions are used. The diffuse-interface method is therefore considered as a good candidate to describe these phenomena. For a more quantitative comparison, as discussed earlier, besides an experimentally validated free-energy formulation, also input for the mobility, viscosity, and non-local interaction are needed.

FIG. 22. As Fig. 21, now with 1% LMW concentration.

VI. CONCLUSIONS

The effects of mutual diffusion on interfacial tension, drop-drop, and drop-wall interactions in quiescent conditions are investigated experimentally and numerically. A highly diffusive system (PB/PDMS) and a slightly diffusive system (PBD/PDMS) are used at room temperature. Just after contact between the phases is made, the transient interfacial tension of the highly diffusive system reduces as a consequence of the low-molecular weight fraction migration from the drop into the interphase, yielding the formation of a thick diffuse layer around the drop surface. While time proceeds, after reaching a minimum, the interfacial tension increases due to low-molecular weight species migration from the interphase into the matrix, leading to depletion of the diffusive layer. Once the diffusion process is exhausted, a plateau in interfacial tension is reached and sustained. The slightly diffusive PBD/PDMS system, in contrast, shows only an increase in the interfacial tension, corresponding to the migration of the fewer migrating molecules (polydispersity is close to one) into the matrix followed by leveling off to a plateau value that is higher compared to the PB/PDMS system, which is attributed to the higher molecular weight of the drop phase.

Drop-drop interaction experiments, carried out with isolated pairs of drops and in quiescent conditions, show that partial miscibility affects the final morphology of the system. Drops of the highly diffusive PB/PDMS system attract and coalesce when placed at initial distances smaller than their equivalent radius. The rate of attraction, in the last ≈ 100 s of the experiments, is the same for a wide range of drop sizes (radii ranging

FIG. 23. As Fig. 21, now with mobility parameters $M_1=4 \times 10^{-4}$ and $M_2=4 \times 10^{-4}$ (case B).

between 90 and 350 μm) and different initial distances between them. The attraction is explained in terms of the overlap of the diffusive layers around the drops, yielding gradients in interfacial tension and, thus, Marangoni flows acting in the film drainage direction, enhancing coalescence. When the slightly diffusive system (PBD/PDMS) is considered, with a thin diffuse-interface, no attraction occurs and, when the drops are placed close together, repulsion between them is observed. Numerical simulations with a three-component diffuse-interface method predict qualitatively the transient interfacial tension, drop-drop, and drop-wall interactions, as observed in the experiments. However, for a more quantitative comparison, more studies are needed to define an experimentally validated free-energy formulation and realistic values to use as input parameters for our systems.

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