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Diffuse interface modeling of the morphology and rheology of immiscible polymer blends

B. J. Keestra

*Materials Technology, Faculty of Mechanical Engineering, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

P. C. J. Van Puyvelde

K.U. Leuven, Department of Chemical Engineering, W. de Croylaan 46, 3001 Leuven, Belgium

P. D. Anderson and H. E. H. Meijer

*Materials Technology, Faculty of Mechanical Engineering, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

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A diffuse interface model is used to simulate a step-shear experiment of a binary immiscible polymer blend. The gradient theory used in diffuse interface modeling makes it possible to incorporate interfacial tension and governs the process of coalescence and breakup without any additional decision criteria. The interface tensor $\mathbf{q}$, a direct outcome of the model, is used to relate microstructural information to the first-normal stress difference N_1 . The results obtained are in qualitative agreement with experiments reported in the literature. © 2003 American Institute of Physics. [DOI: 10.1063/1.1597454]

I. INTRODUCTION

Blending of immiscible polymers offers an attractive route to produce new materials with tailor-made properties. The mechanical properties of such two-phase or more phases polymer blends are intimately connected with the morphology imparted during processing. Hence, understanding the connection between applied flow fields and morphology development is vital to optimize the processing and therefore the resulting properties of blends. Over the years, a number of comprehensive experimental and theoretical studies of the morphology development in simple (shear) flow fields has been reported. Some of this work is summarized in a recent review by Tucker and Moldenaers,¹ and although considerable fundamental understanding of morphology changes during (shear) flow has been obtained already, the prediction of the (transient) rheology coupled with the microstructure development still remains a challenge.

Any theory that aims to predict microstructure development must contain variables that describe the microstructural state and evolution equations for the change of these variables over time. Moreover, an expression for the stress as a function of microstructure and deformation rate would be rather useful. The latter was provided already by Batchelor,² who coupled the average stress to the interfacial tension and, for an incompressible Newtonian two component system, his expression reads

$$\boldsymbol{\sigma} = -p\mathbf{I} + 2\eta_m\mathbf{D} + \phi\eta_m(\lambda - 1)\mathbf{D}_d - \Gamma\mathbf{q}. \quad (1)$$

The first two terms on the right-hand side of Eq. (1) represent the Newtonian response of the matrix (with viscosity η_m and rate of deformation tensor $\mathbf{D}$), the third term is a viscous contribution of the drops (volume fraction ϕ , viscosity ratio $\lambda = \eta_d/\eta_m$ with η_d the viscosity of the dispersed

phase and $\mathbf{D}_d$ the average deformation rate in the drops), while the last term represents the excess stress due to the presence of an interface with interfacial tension Γ . The orientation and anisotropy of the interface is characterized by the interface tensor $\mathbf{q}$ (Doi and Ohta³):

$$\mathbf{q} = \frac{1}{V} \int_S \left(\mathbf{n}\mathbf{n} - \frac{1}{3}\mathbf{I} \right) dS, \quad (2)$$

where S represents the interfacial surface contained in a volume V and $\mathbf{n}$ the unit normal vector. Equation (1) shows that the (excess) stress, and hence the rheology of the material, can be directly calculated once the microstructure of the material is known. This, however, is not that straightforward. Doi and Ohta³ derived semi-phenomenological kinetic equations describing the time evolution of the interfacial area and anisotropy for a given flow field. Accordingly, these equations could be used to describe the dynamics of the interfacial stress tensor and thus the total stress. A drawback of this approach is, however, that empirical relaxation times which depend in an unknown manner on the morphology of the interfaces have to be specified (see, e.g., Doi and Ohta³). In this paper we use a more direct alternative approach based on the framework of diffuse interface models, which predict the dynamics of the morphology. Interfaces are not modeled explicitly, but result implicitly from the composition field. Hence dramatic changes in topology of complex interfaces occurring during coalescence and breakup are present in the model without the need for making any additional assumptions about the underlying structure. Diffuse interface models have a long history in fluid mechanics (see, e.g., the review by Anderson *et al.*,⁴ Lowengrub *et al.*,⁵ and Naumann and He⁶), especially in the field of phase separation. Recently the method has been applied to study various phenomena that

occur in immiscible fluids (e.g., Chella and Vinals;⁷ Jacqmin;⁸ Roths *et al.*⁹). Here, we will investigate to what extent the diffuse interface method can be applied to the prediction of rheology and morphology of two-phase immiscible blends.

II. MODEL EQUATIONS

The classical expression for the specific Helmholtz free energy used in diffuse interface modeling is based on the work of Cahn and Hilliard:¹⁰

$$f(c, \nabla c) = f_0(c) + \frac{1}{2} \varepsilon |\nabla c|^2$$

$$= -\frac{1}{2} \alpha c^2 + \frac{1}{4} \beta c^4 + \frac{1}{2} \varepsilon |\nabla c|^2, \quad (3)$$

where α and β are positive constants and ε is the gradient energy parameter that is proportional to the interaction parameter χ and c is the mass fraction of one of the two components. The chemical potential is obtained from the variational derivative with respect to concentration:

$$\mu = \frac{\delta f}{\delta c} = -\alpha c + \beta c^3 - \varepsilon \nabla^2 c. \quad (4)$$

This generalized chemical potential allows for the description of the interface between the two fluids simply by a continuously varying concentration profile. For example, for a planar interface, with x being the direction normal to the interface, the analytical solution of Eq. (4) reads

$$c(x) = \sqrt{\frac{\alpha}{\beta}} \tanh \frac{x}{\sqrt{2} \xi}, \quad (5)$$

with $\pm \sqrt{\alpha/\beta}$ the equilibrium bulk solutions (in the approach outlined here ± 1) and $\xi (= \sqrt{\varepsilon/\alpha})$ the measure for the interfacial thickness. In order to comply with mass conservation for both components, the balance equation should be fulfilled:

$$\frac{dc}{dt} = \frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) = M \nabla^2 \mu, \quad (6)$$

with M the mobility coefficient, here for simplicity taken constant. The diffusion flux is assumed to be proportional to the gradient of the chemical potential, which is more general than the common Fickian diffusion, based on the concentration gradients (∇c), which does not hold for multiphase systems, even at equilibrium. The more general expression used of Eq. (6) reflects Gibbs' findings that the chemical potential becomes uniform in non-ideal mixture at equilibrium, and is known as the Cahn–Hilliard equation¹¹ and was used to describe the initial stages of spinodal decomposition.¹² To obtain momentum conservation, a generalized Navier–Stokes equation can be derived for the velocity field:⁵

$$\rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] = -\rho \nabla g + \nabla \cdot \eta (\nabla \mathbf{v} + \nabla \mathbf{v}^T) + \rho \mu \nabla c. \quad (7)$$

Here g is the Gibbs free energy $g = f + p/\rho$, with p the local pressure and ρ the density. The viscosity η generally

FIG. 1. Free energy as a function of concentration for $\chi = 2.3$ (○) and $\chi = 2.6$ (+). With higher χ the system becomes more immiscible.

depends on c but only here, without any serious restrictions, the iso-viscous case will be considered. Compared to the Navier–Stokes equations, in Eq. (7) only one extra capillary term $\rho \mu \nabla c$ appears reflecting the interfacial tension Γ via μ . This modification accounts for hydrodynamic interactions, i.e., the influence of the concentration c or the morphology on the velocity field and, hence, describes the spatial variations of the velocity field due to the presence of interfaces. In the following, we will only consider viscous fluids at moderate velocities, and hence the left-hand side of Eq. (7), the inertia forces can be neglected. For viscosity matched fluids and in the absence of the inertia forces, it is convenient to rewrite the Stokes equations in terms of a stream function ($\mathbf{v} = (\partial \psi / \partial y, -\partial \psi / \partial x)$). Conservation of mass is then automatically satisfied and the Gibbs free energy term drops out of the equation:

$$\eta \nabla^4 \psi = \rho \nabla \times \mu \nabla c. \quad (8)$$

A. Scaling of the equations

Using $c^* = c/c_B$, $\mathbf{v}^* = \mathbf{v}/V$, $\mu^* = \mu \xi^2 / (\varepsilon c_B)$, $t^* = tV/L$, with $c_B = \sqrt{\alpha/\beta}$ the bulk concentration, V a characteristic velocity, and L a characteristic domain size, and omitting the asterix notation, Eqs. (4), (6), and (8) read in dimensionless form

$$\frac{dc}{dt} = \frac{1}{\text{Pe}} \nabla^2 \mu, \quad (9)$$

$$\mu = c^3 - c - C^2 \nabla^2 c, \quad (10)$$

$$\nabla^4 \psi = \frac{1}{\text{Ca}} \frac{1}{C} \nabla \times \mu \nabla c. \quad (11)$$

Three dimensionless groups are appearing in the governing equations: the Péclet number Pe , the capillary number Ca , and the Cahn number C , defined as

$$\text{Pe} = \frac{\xi^2 LV}{M \varepsilon}, \quad \text{Ca} = \frac{\xi \eta V}{\rho \varepsilon c_B^2}, \quad C = \frac{\xi}{L}.$$

FIG. 2. Chemical potential as a function of concentration with $N=3$ ($\circ$), $N=7$ ($+$), and $N=13$ ($*$) [in Eq. (14)], creating a more immiscible system.

The capillary number can be related to the more classical definition ($\eta V/\Gamma$),¹³

$$\text{Ca} = \frac{2\sqrt{2}}{3} \frac{\eta V}{\Gamma}.$$

This system of three partial differential equations, completed with proper initial and boundary conditions, is capable of describing the dynamics of viscous two phase systems (like polymer blends) in the case of phases separating of separated systems in the presence of flow.

B. Choice of the free energy formulation

Since here we try to describe the morphology evolution in immiscible polymer blends, an important aspect is the exact choice of the formulation of the free energy. We will use the so-called “ c^4 ” approximation for the homogeneous part of the free energy¹⁴

$$f_0(c) = \frac{1}{4}\beta c^4 - \frac{1}{2}\alpha c^2, \quad (12)$$

also called the Ginzburg–Landau approximation, which is a Taylor expansion around the critical point of the Flory–Huggins equation:

$$f_0(c) \propto c \ln c + (1-c) \ln(1-c) + \chi c(1-c), \quad (13)$$

with χ the Flory–Huggins interaction parameter. Figure 1 shows, schematically, a typical “double-well potential”

shape of the free energy curve as a function of concentration. For increasing values of χ (i.e., a more immiscible combination of polymers), the concentrations of the spinodal points are forced to the concentrations of the pure components. This is of course the limiting case of real immiscible polymers. The increase of the interaction parameter has an important repercussion on the shape of the chemical potential as schematically shown in Fig. 2: a higher value of the interaction parameter yields a steeper chemical potential.¹⁵ We will examine to what extent the “ c^4 ” approximation can be applied to the study of immiscible polymer blends and additionally other formulations for the homogeneous part of the free energy (and hence the chemical potential) will be used, as an alternative for Eq. (10):

$$\mu = c^N - c - C^2 \nabla^2 c. \quad (14)$$

$N=3$ forms the “classical diffuse interface” case, while higher values of N correspond to steeper chemical potential formulations and hence, as N increases, the materials approach the immiscible behavior.

III. NUMERICAL IMPLEMENTATION

To discretize the governing equations a spectral element method^{16,17} is used, since this method is suitable for capturing interfaces with a small interfacial thickness.¹⁸ Similar to any regular finite element method, the computational domain Ω is divided into N_{el} non-overlapping sub-domains Ω_e , but now a spectral approximation is applied on each element. Essentially, the basis functions ϕ are high-order Lagrange interpolation polynomials through the Legendre–Gauss–Lobatto integration points defined per element.

The momentum equation (11), is a fourth-order differential equation in ψ . Since the basis functions ϕ are elements of H^1 , that is $H^1(\Omega) = \{\phi | \phi \in L^2(\Omega), \nabla \phi \in L^2(\Omega) \times L^2(\Omega)\}$, we split Eq. (11) into two second-order differential equations:

$$-\nabla^2 Q = h, \quad (15)$$

$$-\nabla^2 \psi = Q, \quad (16)$$

where $h = -Ca^{-1}C^{-1}\nabla \times \mu \nabla c$, the inner product $(a, w)_\Omega = \int_\Omega a w d^2\Omega$, and w is the standard Galerkin test function. Partial integration of the Galerkin residual representation of Eqs. (15) and (16) yields the weak or variational forms:

$$(\nabla Q, \nabla w)_\Omega = (h, w), \quad (17)$$

$$(\nabla \psi, \nabla w)_\Omega = (Q, w), \quad (18)$$

FIG. 3. Morphology pictures at different time steps for a single drop and a classical free energy formulation ($N=3$) with $C=0.02$, $\text{Pe}=5$, and $\text{Ca}=10$. The smallest drops in the center dissolve as a result of a too small ratio of volume over interface.

FIG. 4. 1-D simulations showing the balance of interfacial and bulk energy for different free energy formulations. The Péclet number is fixed ($Pe=5$).

where the boundary integrals vanish because of the homogeneous boundary conditions. Next, the domain Ω is decomposed into N_{el} non-overlapping sub-domains Ω_e and a spectral approximation is applied on each element, where $\mathbf{S}$ is the Laplacian stiffness matrix, $\mathbf{M}$ is the mass matrix and $\tilde{\psi}$, $\tilde{Q}$, and $\tilde{h}$ are the discrete vector representations of ψ , Q , and h , respectively,

$$\mathbf{S}\tilde{Q} = \mathbf{M}\tilde{h}, \quad (19)$$

$$\mathbf{S}\tilde{\psi} = \mathbf{M}\tilde{Q}. \quad (20)$$

The local balance equation for c and the chemical potential μ form a set of two second-order differential equations, which are solved in a coupled way. Using Euler implicit time discretization we obtain

$$\begin{bmatrix} \mathbf{M} - \Delta t \mathbf{N}^n & \frac{\Delta t}{Pe_n} \mathbf{S} \\ [1 - (c_i^{n+1})^2] \mathbf{M} - C_n^2 \mathbf{S} & \mathbf{M} \end{bmatrix} \begin{bmatrix} \mathbf{c}_{i+1}^{n+1} \\ \boldsymbol{\mu}_{i+1}^{n+1} \end{bmatrix} = \begin{bmatrix} \mathbf{M} \mathbf{c}_0^n \\ 0 \end{bmatrix}, \quad (21)$$

where N is the convection matrix. The superscript n denotes time t and $n+1$ denotes $t + \Delta t$. A Picard iteration is used to deal with the non-linearity in c term ($i=1, \dots, I$): the iteration starts using $c_1^{n+1} = c_0^n$ and as a stopping criterion we use $\max |c_{i+1}^{n+1} - c_i^{n+1}| < \delta$, in which δ is typically of the order 10^{-4} . After convergence, μ_{i+1}^{n+1} and c_{i+1}^{n+1} are used to update h and we can move to the next time step. Details can be found in Verschueren.¹⁹

IV. RESULTS AND DISCUSSION

Results of the simulations are presented in increasing order of complexity. First two-dimensional simulations with one drop are shown and the importance of the free energy formulation is discussed. Second, a more general case is addressed where breakup and coalescence of drops occur simultaneously. In addition, the prediction of the rheology through the first-normal stress difference is presented. Finally, the aspect of scaling the differential equations is investigated.

FIG. 5. Morphology pictures at different time steps for a single drop and a different free energy formulation ($N=7$) with $C=0.02$, $Pe=5$, and $Ca=10$.

FIG. 6. Morphology pictures at different time steps (0, 0.18, 0.36, 0.54, 0.72, 0.90) defined as the base case with 18 drops and $C=0.02$, $Pe=5$, and $Ca=10$.

A. Problem statement

Simulations are performed on a rectangular mesh with periodic boundary conditions on the left and right side of the domain. On the top and bottom sides, boundary conditions are prescribed to introduce shear. Since Eq. (11) is split into two second-order differential equations, a set of two boundary conditions is applied and bearing in mind the stream function $\mathbf{v}=(\partial\psi/\partial y, -\partial\psi/\partial x)$, on the top and bottom wall $\psi=\frac{1}{2}ay^2$ and $Q=a$ are prescribed. For a typical simulation with $C=0.02$, $Pe=10$, and $Ca=10$ on the rectangle with dimensions $(-4, -1)$ in the left bottom corner and $(4, 1)$ in the top right corner, 100 elements are used in the x direction and 50 elements in the y direction with spectral order $p=4$ and a time step $\Delta t=10^{-3}$. Consistency is tested in simulations with $p=2$ (normal quadratic elements) and $p=6$. The deviations between $p=2$ and $p=4$ are substantial, however, the results of $p=4$ and $p=6$ show no difference. The simulations with spectral order $p=4$ are therefore assumed to be sufficiently accurate.

B. Single drop problem

We start with a rather severe case, where drastic topological changes to a drop are imposed, via deformation and breakup, see Fig. 3. The value of Péclet ($Pe=5$) is taken to be representative for real polymers under these relatively weak shearing conditions. It is observed that the drop is ini-

tially deformed and oriented in the flow direction until, at a certain point, interfacial forces become dominant and the drop breaks in the flow field. Topological changes such as breakup are taken into account implicitly without making any assumptions of the structure related relaxation time. However, as can be seen at $t=0.9$, failure of the diffuse interface method occurs, since the small satellite drops, formed during the breakup process, disappear. The structure size is apparently too small to maintain a phase-separated state and the material returns to a homogeneous state. The occurrence is physically real and is not a numerical artifact, since simulation with a higher spectral order or simulations with more elements showed the same effects. It can be rationalized by considering the expression of the free energy [Eq. (3)]. Phase separation lowers the free energy through the homogeneous part $f_0(c)$ but necessarily causes a gradient in concentration and this raises the free energy through the $\varepsilon|\nabla c|^2$ term. A consequence of the trade-off between bulk and surface energies is that small systems do not bifurcate into two phases but remain a single phase at equilibrium. Naumann and He⁶ calculated the minimal bifurcation size below which a system remains a single phase at equilibrium. Based on the Cahn–Hilliard expression of the free energy, the critical size L_c was calculated to be⁶

$$L_c \approx \pi C, \quad (22)$$

with C the Cahn number. For the Cahn number used in the simulations shown in Fig. 3, the predicted critical size is in good agreement with the simulated one. Of course, it can be argued that, in order to circumvent this problem, a smaller Cahn number should be used. However, small interfacial thicknesses would require extremely small mesh sizes and, hence, require excessive computation times.

In order to study the effect of the Cahn number on this critical size, a one-dimensional problem is considered, where flow has no physical meaning and merely the effects of diffusion are captured. Typical results are summarized in Fig. 4. Three concentration profiles are followed as a function of time. The smallest concentration profile has dimensions below the critical size as predicted by Eq. (22). As can be seen in Fig. 4(a), this phase-separated system returns to the homogeneous state while the other situations—with dimensions larger than the critical one—remain in the phase-separated state. In order to test the scaling of $L_c \sim C$, simulations were performed with $C=0.04$, and, as can be learned from Fig. 4(c), the structure with an original size twice as big as the smallest one is now also disappearing. These results confirm

FIG. 7. Anisotropy plot of 18 drop simulation with cessation of shear at different times for $C=0.02$, $Pe=5$, and $Ca=10$.

FIG. 8. Morphology pictures at different time steps (0.54, 0.72, 0.90) for step-shear and subsequent cessation of shear (top to bottom: $t_c = 0.3, 0.53, 0.6, 0.75$), for $C = 0.02$, $Pe = 5$, and $Ca = 10$.

the physical nature of the disappearing drops put forth in Fig. 3, and these findings clearly limit the applicability of the diffuse interface model.

As stated in Sec. II B, a different chemical potential formulation was proposed to approach the ideal limiting case of immiscible fluids. Now we investigate whether this formulation has a repercussion on the dissolution of the system and results are presented in Figs. 4(b) and 4(d). In Fig. 4(b), a formulation with $N=9$ [see Eq. (14)] is used with $C=0.02$ and the initial concentration identical to the concentrations used in Fig. 4(a). From Figs. 4(b) and 4(d), compared to Figs. 4(a) and 4(c) it is seen that the new formulation has an influence on the phase-separated state. The equilibrium conditions still hold, but drops with dimensions below the critical size do not disappear that rapidly, since the higher order formulation changes the kinetics and makes the system less soluble. These instructive one-dimensional experiments show that a different formulation of the free energy, and hence the chemical potential, might be beneficial in the description of the morphology evolution of perfectly immiscible polymers, but do not resolve the total problem of the disappearing drops!

In Fig. 5, the calculation of Fig. 3 is redone, with a different formulation of the chemical potential ($N=7$), and the drop breaks up into a series of drops which nicely remain in the phase-separated state. Figures reinforces the conclusion on a proper description of the chemical potential.

C. Multi-drop problem

Now a more complex problem is handled, where a large number of drops is present. The high-order expression for the free energy [$N=7$ in Eq. (14)] is used and, additionally, the rheological properties due to the presence of anisotropic interfaces are addressed. Hereto the anisotropy tensor as defined in Eq. (2) is used,

$$\frac{N_1 V}{\gamma} = q_{yy} - q_{xx} = \sum (n_{yy,i} - n_{xx,i}) d\Omega_i. \quad (23)$$

The first-normal stress difference has proven to be extremely sensitive to morphological changes in immiscible blends (e.g., Tucker and Moldenaers¹). The normal vector

used in the anisotropy tensor can be calculated straightforwardly by using the results of the diffuse interface simulations. Figure 6 shows a few snapshots of the morphology development of a blend consisting of a drop-matrix morphology during shear flow for 18 drops with $C=0.02$, $Pe=5$, and $Ca=10$. This is referred to as the base case. Topological changes such as breakup and coalescence are indeed present, and the results are obtained in a natural way without making any assumptions on underlying structure dependent relaxation times.

Figure 7 shows the corresponding, 2-D, scaled, first-normal stress difference N_1 . Qualitatively, it can be concluded that the evolution of the calculated N_1 is similar to the experimentally observed evolutions of N_1 (Vinckier,²⁰ Janssuene *et al.*,²¹ and Takahashi *et al.*²²). Initially, during the deformation of the drops, N_1 increases. When the drops breakup, the anisotropy of the structure decreases and consequently the first-normal stress difference is reduced. Finally, a steady state deformation and hence constant N_1 is

FIG. 9. Anisotropy plot of 18 drop simulation with capillary number $Ca = 10$ (base case) and $Ca = 1$. The effect of increased interfacial tension becomes clear in the simulation with cessation of shear at $t_c = 0.3$ ($C = 0.02$, $Pe = 5$).

FIG. 10. Anisotropy plot of the scaling results. The capillary number is fixed ($Ca = 10$). $C = 0.02$ in the base case. The numerical Cahn number is doubled with respect to the base case ($C_n = 0.04$) and the numerical Péclet number Pe_n is calculated according to the different scaling laws.

reached. The noise in the curve in Fig. 7 is due to the fact that only a relatively small number of drops is used in the calculations. Increasing their number will reduce the statistical noise and smooth the curve. In Fig. 7, and also the snapshots in Fig. 8, the effect of cessation of shear for four different cessation times $t_c = 0.3, 0.53, 0.6, 0.75$ can be observed. Drops that are initially deformed and stretched relax back due to interface tension to shapes with a high volume to surface ratio. Compared to the experimental results the curves fall off rather slowly. This is due to the high capillary number ($Ca = 10$) used in these simulations. If this number is decreased to $Ca = 1$, the interfacial tension becomes more important and influences the relaxation process. Also in the initial deformation and stretching part, the influence of the

interfacial tension counteracts the stretching, as can be seen in Fig. 9.

D. Scaling

The diffuse interface model is essentially a small scale model. For Cahn numbers, typically used in the simulations ($C = 0.02$), and the typical interfacial thicknesses (order of magnitude 10 nm), the computational domain used in for instance Fig. 6 has a length of the order of 500 nm.⁹ If we want to extend to larger systems, the real interfacial thickness cannot be captured numerically in general. This requires the use of a numerical thickness that is much larger than the real one. Scaling of such systems needs special attention: it has to be verified that, when the interfacial thickness is changed, still the same system with the same interfacial tension and diffusion is described. Different possibilities have been proposed in literature. Lowengrub *et al.*⁵ proposed to scale the numerical Péclet number as $Pe_n = (C/C_n)Pe$, where C_n denotes the numerical Cahn number and C the real Cahn number, which converges to the sharp-interface limit when $C \rightarrow 0$. The reasoning behind this approach is that for a sharp interface (i.e., $C \rightarrow 0$), diffusion should not play any role and the dynamics should be governed solely by convection. Using matched asymptotics, Lowengrub *et al.*⁵ showed that the diffuse-interface equations reduce to the classical sharp-interface limit. However, when comparing simulation results with different interfacial thicknesses, one has to ascertain that interfacial tension in both cases remains the same. Based on this argument, the definition of the dimensionless groups shows that this is equivalent to keeping ε/ξ constant. Keeping ε/ξ constant in the Péclet number yields a numerical Péclet number which is proportional to C_n [$Pe_n = (C_n/C)Pe$] rather than $1/C_n$ if the other parameters are kept constant. This scaling, originally proposed by Verschueren,¹⁹ states that, if a larger interfacial thickness is chosen, the Péclet number has to be replaced by a larger one,

FIG. 11. Morphology pictures of the zero contour line ($c = 0$) with different scalings at times $t = 0.18, 0.24, 0.30$ in the initial stage of shear. The top row is the base case with $C = 0.02$ and $Pe = 5$ and $Ca = 10$. The scaling laws are tested with a thicker interface ($C = 0.04$) and different Péclet numbers. The morphology pictures in the second row with the quadratic scaling for the Péclet number closely resemble the snapshots in the base case with the thinner interface.

FIG. 12. Morphology pictures with different scalings at times $t=0.36, 0.66, 0.96$, the later stage of shear, where large topological changes occur. The top row is the base case with $C=0.02$, $Pe=5$, and $Ca=10$. The scaling laws are tested with a thicker interface ($C=0.04$) and different Péclet numbers.

such that the effect of diffusion is smaller. A third scaling is based on the analysis of the Cahn–Hilliard equations. In the composition-diffusion equation the only variable is the Péclet number and the chemical potential equation contains only a squared Cahn number. This relation is reflected in the proposed scaling with a quadratic term: $Pe_n = (C_n/C)^2 Pe$. The results are summarized in Fig. 10. In Fig. 11 and the morphology development is depicted for the early stage and the latter stage with the larger topological changes. The results of scaling clearly show that in the initial part of the step-shear the quadratic scaling [$Pe_n = (C_n/C)^2 Pe$] of the Péclet number shows the best result. In the later stage all proposed scalings deviate from the base case. In Fig. 12 it can clearly be observed that for the quadratic scaling (second row from the top) the stretched drops disappear instead of break up. The Péclet number is relatively high and the interfaces are out of equilibrium and tend to disappear due to dominant convective forces. The other scalings seem to have sufficient diffusion, but do not reach this high degree of anisotropy, and therefore deviate already in an earlier stage. None of the proposed scaling strategies appears to be appropriate to cover all phenomena.

V. CONCLUSIONS

In this paper the diffuse interface method is applied to model the morphology evolution of immiscible polymer blends. The method has been applied on a variety of problems ranging from a single drop to a large set of drops. It is shown that topological changes such as breakup and coalescence of drops is implicitly present in the model approach. The simulations can contribute to the understanding of the structure formation and rheological properties of immiscible blends. For example, though restricted to two dimensions, the simulations show that the first-normal stress difference corresponds qualitatively with experimental results. The hydrodynamic coupling makes it possible to incorporate interfacial tension and describe the related phenomena, such as breakup and coalescence. Moreover, the influence of interfa-

cial tension relative to the convective forces, through the capillary number, was clearly demonstrated. This also opens new perspectives in the modeling of the morphology and rheology of blends consisting of viscoelastic materials. Next to the advantages of the method, also some drawbacks have been discussed. It has been shown that the formulation of the free energy is important in the description of the morphology in perfectly immiscible blends. An alternative formulation, based on a higher order function of the chemical potential, has been proposed. Second, the important point of scaling has been addressed, but none of the proposed scalings strategies is capable of describing all topological changes that occur during flow. However, the quadratic scaling [$Pe_n = (C_n/C)^2 Pe$] is able to describe the affine deformation part accurately in the initial stages of the process. The issue of proper scaling clearly remains open for further investigation in order to be able to analyze larger systems. Of course local adaptive mesh refinement could be an—be it limited—alternative.

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- ¹C. L. Tucker and P. Moldenaers, "Microstructural evolution in polymer blends," *Annu. Rev. Fluid Mech.* **34**, 177 (2002).
- ²G. K. Batchelor, "The stress system in a suspension of force-free particles," *J. Fluid Mech.* **41**, 420 (1970).
- ³M. Doi and T. Ohta, "Dynamics and rheology of complex interfaces. I," *J. Chem. Phys.* **95**, 1242 (1991).
- ⁴D. M. Anderson, G. B. McFadden, and A. A. Wheeler, "Diffuse-interface methods in fluid mechanics," *Annu. Rev. Fluid Mech.* **30**, 139 (1998).
- ⁵J. Lowengrub, J. Goodman, H. Lee, E. Longmire, M. J. Shelley, and L. Truskinovsky, in *Proceedings of the 1997 International Congress on Free Boundary Problems*, edited by I. Athanasopoulos, M. Makrakis, and J. F. Rodrigues (Addison–Wesley–Longman, Reading, MA, 1998), Pitman Research Notes.
- ⁶E. B. Naumann and D. Q. He, "Nonlinear diffusion and phase separation," *Chem. Eng. Sci.* **56**, 1999 (2001).

- ⁷R. Chella and J. Viñals, "Mixing of a two-phase fluid by cavity flow," *Phys. Rev. E* **53**, 3832 (1996).
- ⁸D. Jacqmin, in *Proceedings of the 34th Aerospace Science Meeting Exhibition, AIAA 96-0858*, Reno, 1996.
- ⁹T. Roths, C. Friedrich, M. Marth, and J. Honerkamp, "Dynamics and rheology of the morphology of immiscible polymer blends—On modeling and simulation," *Rheol. Acta* **41**, 211 (2002).
- ¹⁰J. W. Cahn and J. E. Hilliard, "Free energy of a nonuniform system. I. Interfacial energy," *J. Chem. Phys.* **28**, 258 (1958).
- ¹¹J. W. Cahn and J. E. Hilliard, "Free energy of a nonuniform system. III," *J. Chem. Phys.* **31**, 688 (1959).
- ¹²J. W. Cahn, "Phase separation by spinodal decomposition in isotropic systems," *J. Chem. Phys.* **42**, 93 (1964).
- ¹³H. T. Davis and L. E. Scriven, "Stress and structure in fluid interfaces," *Adv. Chem. Phys.* **49**, 357 (1982).
- ¹⁴J. D. Gunton, M. S. Miguel, and P. S. Sahni, *The Dynamics of First-order Phase Transitions*, Phase Transitions and Critical Phenomena Vol. 8 (Academic, London, 1983).
- ¹⁵D. Jacqmin, in *Workshop on Diffuse Interface Models* (ENS Lyon, Lyon, 2002).
- ¹⁶A. T. Patera, "A spectral element method for fluid dynamics," *J. Comput. Phys.* **54**, 468 (1984).
- ¹⁷L. J. P. Timmermans, F. N. van de Vosse, and P. D. Mineev, "Taylor–Galerkin-based spectral element methods for convection-diffusion problems," *Int. J. Numer. Methods Fluids* **18**, 853 (1994).
- ¹⁸M. Verschuere, P. D. Anderson, and F. N. van de Vosse, ICOSAHOM'98, Herzliya, Israel, 22–26 June 1998.
- ¹⁹M. Verschuere, Ph.D. thesis, Eindhoven University of Technology, The Netherlands, 1999.
- ²⁰I. Vinckier, Ph.D. thesis, Katholieke Universiteit Leuven, Belgium, 1996.
- ²¹T. Jansseune, J. Mewis, P. Moldenaers, M. Minale, and P. L. Maffettone, "Rheology and rheological morphology determination in immiscible two-phase polymer model blends," *J. Non-Newtonian Fluid Mech.* **93**, 153 (2000).
- ²²Y. Takahashi, N. Kurashima, I. Noda, and M. Doi, "Experimental tests of the scaling relation for textured materials in mixtures of two immiscible fluids," *J. Rheol.* **38**, 699 (1994).