Phase-field modeling of interfacial dynamics in emulsion flows: Nonequilibrium surface tension

A. Lamorgese*, R. Mauri

Department of Civil and Industrial Engineering, Laboratory of Multiphase Reactive Flows, Università di Pisa, I-56126 Pisa, Italy

A B S T R A C T

A weakly nonlocal phase-field model is used to define the surface tension in liquid binary mixtures in terms of the composition gradient in the interfacial region so that, at equilibrium, it depends linearly on the characteristic length that defines the interfacial width. Contrary to previous works suggesting that the surface tension in a phase-field model is fixed, we define the surface tension for a curved interface and far-from-equilibrium conditions as the integral of the free energy excess (i.e., above the thermodynamic component of the free energy) across the interface profile in a direction parallel to the composition gradient. Consequently, the nonequilibrium surface tension can be widely different from its equilibrium value under dynamic conditions, while it reduces to its thermodynamic value for a flat interface at local equilibrium. In nonequilibrium conditions, the surface tension changes with time: during mixing, it decreases as the inverse square root of time, while in the linear regime of spinodal decomposition, it increases exponentially to its equilibrium value, as nonlinear effects saturate the exponential growth. In addition, since temperature gradients modify the steepness of the concentration profile in the interfacial region, they induce gradients in the nonequilibrium surface tension, leading to the Marangoni thermocapillary migration of an isolated drop. Similarly, Marangoni stresses are induced in a composition gradient, leading to diffusiophoresis. We also review results on the nonequilibrium surface tension for a wall-bound pendant drop near detachment, which help to explain a discrepancy between our numerically determined static contact angle dependence of the critical Bond number and its sharp-interface counterpart from a static stability analysis of equilibrium shapes after numerical integration of the Young-Laplace equation. Finally, we present new results from phase-field simulations of the motion of an isolated droplet down an incline in gravity, showing that dynamic contact angle hysteresis can be explained in terms of the nonequilibrium surface tension.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

In a liquid–vapor system at equilibrium, a molecule in the liquid bulk is surrounded by attractive neighbors, while a molecule at the surface, being attracted by a reduced number of molecules, finds itself in an energetically unfavorable state (see de Gennes et al., 2004). The resulting free energy deficit (i.e., a negative surplus) per unit interfacial area is a thermodynamic equilibrium property of the interface and can be identified macroscopically as the surface tension. This microscopic picture is reflected at the mesoscale in the phase-field model, an approach that goes back to van der Waals (1894) and has been widely used to describe many equilibrium interfacial properties. Here, on one hand, the continuum hypothesis is assumed to be valid, so that thermodynamic quantities such as temperature and pressure can be defined locally,

even when, as it usually occurs in continuum mechanics, they are not uniform in space. In addition, weakly nonlocal effects are taken into consideration, so that thermodynamic potentials depend on the gradients of the order parameter, i.e., density or concentration. Accordingly, an interface is described as a finite thickness transition region where the order parameter is allowed to change continuously, interpolating between the two phases. Naturally, as the surplus interfacial energy is defined in terms of density (or concentration) gradients, it is natural to generalize the concept of surface tension to systems far from equilibrium (see the discussion in Joseph and Renardy, 1993). Many authors have studied nonequilibrium micro- and meso-scale interpretations of the surface tension. For example, Ma et al. (1992) confirmed the microscopic nature of surface tension by numerically simulating a binary system at equilibrium using molecular dynamics. At the mesoscale, several coarse-grained expressions for the free energy can be found in the literature (see Hohenberg and Halperin, 1977), which have allowed to model dynamical processes such as mixing and demixing.

* Corresponding author. Fax: +39(050)2217866

Since the surplus free energy depends on the density (or concentration) gradients in the interfacial region, a nonequilibrium surface tension can be defined, which characterizes the system during the whole process. This, in turn, can be considered as the appropriate jump boundary condition of any macroscopic multiphase flow model, where interfaces are considered to be zero-thickness surfaces (see Sagis, 2011). Applications of the phase-field model to dynamic processes in fluids lead to the introduction into the Navier–Stokes equation of a nonequilibrium capillary force, generally referred to as the Korteweg force. As it arises naturally by applying Hamilton's least action principle, this is a reversible body force, tending to restore the local equilibrium condition (Lamorgese et al., 2011). As such, the Korteweg force tends to accelerate both the mixing process of miscible fluids and the phase separation of unstable or metastable mixtures.

The remainder of this paper is laid out as follows. In Section 2 we review the formulation of a diffuse-interface model of inhomogeneous binary fluids (a.k.a. square-gradient theory or Model H, in the taxonomy of Hohenberg and Halperin, 1977), based on a regular solution model along with a Flory–Huggins and Cahn–Hilliard type of modeling for the excess (i.e., enthalpic) and nonlocal components of the Gibbs free energy of mixing. We then show the definition of the surface tension for a flat interface at local equilibrium and briefly discuss its extension to curved interfaces and far-from-equilibrium conditions. Subsequently, we recall the equations governing dynamic processes (under isothermal conditions) before discussing some previously published results from simulations of binary fluid mixing and demixing, and of the Marangoni migration of isolated drops in a temperature (or concentration) gradient. We also discuss previous results on the nonequilibrium surface tension at pinchoff from simulations of the buoyancy-driven detachment of a wall-bound pendant drop. Finally, we discuss contact angle hysteresis in phase-field simulations of the motion of an isolated drop down an incline in gravity. Conclusions are then presented.

2. Model description

Consider a regular binary mixture, composed of two incompressible liquids A and B having the same molar density, ρ. The phase-field model can be derived assuming that its free energy is the sum of a thermodynamic part and a nonlocal contribution (see Cahn and Hilliard, 1958, 1959; Lamorgese et al., 2011), i.e.,

$$G = \rho RT \int_V \tilde{g} dV, \quad \tilde{g}(\phi, \nabla\phi) = g(\phi) + \frac{1}{2}a^2(\nabla\phi)^2, \quad (1)$$

where g is the dimensionless thermodynamic (i.e., coarse-grained) bulk free energy density, T is the temperature and V the volume, R is the gas constant, while a indicates a typical length. Equation (1) can be justified rigorously starting from Landau's mean-field theory for a nonhomogeneous van der Waals fluid (Landau and Lifshitz, 1980), showing that in addition to the above thermodynamic part, spatial inhomogeneities in the composition give rise to a nonlocal (square-gradient) component of the coarse-grained free energy, typical of the diffuse-interface model. That derivation is valid for equilibrium and nonequilibrium conditions alike. At local equilibrium, when the mixture is separated into two phases α and β by a flat interfacial region, a surface tension can be obtained by integrating the specific (i.e., per unit volume) free energy along a coordinate z perpendicular to the interface, i.e.,

$$\sigma = \frac{1}{2}a^2 \rho RT \int_{-\infty}^{\infty} (\nabla\phi)^2 dz, \quad (2)$$

where we have considered that the composition of the mixture far from the interfacial region is constant. This result was first obtained by van der Waals (1894) in his treatment of the equilibrium liquid–vapor interface for a single-component fluid and was applied by Cahn and Hilliard (1959) to a binary mixture (see also de Gennes, 1985). More recently, Pismen (2001) showed a systematic derivation of the van der Waals square-gradient model based on a mean-field approximation along with a gradient expansion for the order parameter. This derivation was an intermediate result (Pismen and Pomeau, 2000) as they were trying to obtain an expression for the disjoining pressure based on a more accurate free energy functional (with a more realistic representation of nonlocal interactions). On the other hand, Jacqmin (2000) performed a careful matched asymptotic analysis showing that, in the limit of vanishing interfacial width, the diffuse-interface model is consistent with the usual Marangoni-type boundary conditions that arise in the classical formulation of two-phase flow. Note that the asymptotic analysis of diffuse-interface models has been furthered considerably (Magaletti et al., 2013; Sibley et al., 2013a) since the Jacqmin (2000) paper. In particular, recent work by Sibley et al. (2013a) has shown that when a binary fluid diffuse-interface model is employed in conjunction with a tensorial mobility, the model allows the classical two-phase flow equations to be recovered to all orders in the Cahn number, in the limit as it tends to zero.

Considering that the expression for the free energy, Eq. (1), is valid also for systems far from equilibrium, the surface tension as defined in Eq. (2) is not necessarily confined to systems at thermodynamic equilibrium. In fact, a similarly defined nonequilibrium surface tension had already been introduced in Ma et al. (1993), Osborn et al. (1995) and Swift et al. (1996), particularly for checking their lattice Boltzmann scheme in terms of the rate of decay of a flat interface (initially at equilibrium) which is instantaneously brought from the two-phase to the one-phase region. However, these authors did not clarify the role of the nonequilibrium surface tension in diffuse-interface models of emulsion flows far from the critical point, which is the primary objective of the work reported herein.

Again, it should be stressed that Eq. (1) represents a coarse-grained expression of the free energy, so that a is in no way equal to the actual interfacial thickness. Assuming that the mixture has zero excess volume of mixing and zero excess entropy of mixing, the simplest expression for the thermodynamic free energy density, g, corresponding to a perfectly symmetric, partially miscible binary mixture, is the sum of an entropic, ideal part, and a nonideal, so-called excess part, with

$$g = g_0 + \phi \ln \phi + (1 - \phi) \ln (1 - \phi) + \Psi \phi (1 - \phi). \quad (3)$$

Here, g_0 is the free energy of both the pure components (they must be equal, since we are considering an ideally perfectly symmetric binary mixture), ϕ is the molar (and mass) concentration of species A, while Ψ is the temperature-dependent Margules parameter (see Sandler, 2006). Since the entropy of mixing for regular mixtures is equal to that for an ideal gas, the excess free energy of mixing cannot depend on temperature and, therefore, Ψ and a^2 must be inversely proportional to T. Thus, considering that at the critical point (see below), when $T = T_c$, $\Psi = \Psi_c = 2$, we may assume:

$$\Psi = \frac{2T_c}{T}, \quad a = \hat{a}\sqrt{\frac{2T_c}{T}} = \hat{a}\sqrt{\Psi}, \quad (4)$$

where $\hat{a}$ is a constant length, independent of the temperature. Since at constant pressure and temperature $dg = \mu d\phi$, where $\mu = \mu_A - \mu_B$ is the dimensionless chemical potential difference, we obtain:

$$\mu = \frac{dg}{d\phi} = \ln \frac{\phi}{1 - \phi} + \Psi(1 - 2\phi). \quad (5)$$

Phase separation occurs whenever the temperature of the system T is lower than the critical temperature T_c. Imposing that at