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On the Buoyancy-Driven Detachment of a Wall-Bound Pendant Drop: Results of Phase-Field Simulations

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We investigate numerically the critical conditions for detachment of an isolated, wall-bound pendant emulsion droplet acted upon by surface tension and wall-normal buoyancy forces alone. To that end, we present a simple extension of a diffuse interface model for partially miscible binary mixtures that was previously employed for simulating several two-phase flow phenomena far and near the critical point ["Phase-Field Approach to Multiphase Flow Modeling," Milan J. Math. **79**, 597 (2011)] to allow for static contact angles other than 90°. Initially, we show that a formulation of the Cahn boundary condition based on a linear interpolation of surface tensions between the wall and each phase at equilibrium can be readily implemented in our numerical procedures by introducing a contact line indicator function and changes to our numerical algorithm that include an iterative method of enforcing inhomogeneous boundary conditions within a semi-implicit temporal scheme for the Cahn-Hilliard equation. Subsequently, the classical formulation of the Cahn boundary condition as first proposed by Jacqmin ["Contact-line dynamics of a diffuse fluid interface," J. Fluid Mech. **402**, 57 (2000)], which accommodates a cubic (Hermite) interpolation of surface tensions between the wall and each phase at equilibrium, has also been incorporated into our numerical code. We show that the resulting phase-field models can be successfully employed for simulating three-phase contact line problems in stable emulsions with nearly immiscible components. We also show the first numerical determination of critical Bond numbers as a function of static contact angle by phase-field simulation. In addition, results of 3D simulations are compared to critical Bond numbers from a static stability analysis based on a numerical integration of the Young-Laplace equation. We argue that the discrepancy between our numerically determined static contact angle dependence of the critical Bond number and its sharp-interface counterpart is mainly due to the inability of the sharp interface analysis to describe the necking regime of drop detachment, where a sharpening of concentration gradients in the necking region produces an effective increase in (dynamic) surface tension, ultimately leading to a reduced tendency to detachment or an increase in the critical Bond number.

1. Introduction

We simulate the influence of static contact angle on the buoyancy-driven detachment of an isolated emulsion droplet initially adhering to a wall under gravitational forcing, as a sequel to our previous study of Marangoni migration of a wall-bound drop in a temperature gradient (Lamorgese and Mauri, 2011), wherein simulations with a static contact angle of 90° were presented showing the existence of a critical gradient strength for detachment and subsequent migration to the hot wall, for an isolated droplet initially adhering to the cold wall. In this work, we intend to study the mechanics of buoyancy-driven detachment in greater detail by determining the critical Bond number as a function of static contact angle. In fact, although the buoyancy-driven detachment of oily deposits (and liquid emulsion droplets in particular) from a solid substrate is of considerable interest in many industrial applications, due to the complexity of the removal process and the large variations in soils and substrates encountered, the details of the detachment process remain poorly understood and have long been the subject of active research. Although experiments and simulations on the buoyancy-driven detachment of liquid emulsion droplets from solid substrates have been carried out in the past (Schwartz, 1972; Dillan *et al.*, 1979; Gum and Goddard, 1982; Aronson *et al.,* 1983; Raney and Miller, 1987; Thompson, 1994; Kolev *et al*., 2003; Kralchevsky *et al*., 2005; Liu *et al*., 2012), none of these previous studies has

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addressed the critical Bond number as a function of the relevant nondimensional parameters systematically. In fact, in addition to the works cited above, a number of theoretical, numerical and experimental investigations have been focused on the influence of a shear flow on the conditions for drop removal from solid surfaces (Basu *et al.*, 1997; Dimitrakopoulos and Higdon, 1998; Theodorakakos *et al.*, 2006; Golpaygan and Ashgriz, 2008), neglecting the more fundamental case of a pendant drop acted upon by surface tension and wall-normal buoyancy forces alone. Although the critical Bond number for buoyancy-driven detachment as a function of static contact angle has been addressed previously by numerical integration of the Young-Laplace equation (Chatterjee, 2002a,b; Chen *et al.*, 2005), to our knowledge computations of that dependence based on a phase-field model have not been presented in the literature before and are reported here for the first time. In the remainder of this paper, we present in Section 2 definitions of nondimensional parameters arising in our phase-field model, along with a brief discussion of the linear interpolation formulation of the Cahn boundary condition as opposed to its classical formulation, as first proposed by Jacqmin (2000). Then, in Section 3 we show the first numerical determination of critical Bond numbers as a function of static contact angle by phase-field simulation. Conclusions are then presented.

2. The governing equations

The derivation of the governing equations has been presented elsewhere (Lamorgese and Mauri, 2014). There, the equations of motion for a regular binary mixture with partially miscible components at low Reynolds number were derived rigorously, starting from the fundamental conservation principles, together with constitutive modelling for the diffusive volumetric flux based on irreversible thermodynamics. After diffusive scaling of the Stokes/Cahn-Hilliard system, the dimensionless parameters that appear in the governing equations were shown to be the standard fluidity coefficient (Tanaka and Araki, 1998) together with a Bond number, defined as $Bo \equiv (d/l_c)^2$, where d is the initial droplet diameter and $l_c \equiv \sqrt{\sigma / g\rho\Delta\phi_{eq}}$ is a capillary length. (Here and below, $\Delta\phi_{eq} \equiv \phi_{eq}^{\alpha} - \phi_{eq}^{\beta}$ denotes the composition difference in terms of mass fractions between the two phases at equilibrium while σ denotes their surface tension.) Also, wettability effects were included in our phase-field formulation by introducing the simplest additional surface contribution to the free energy functional, which is based on the assumption that wettability is a local quantity, solely depending on the local concentration of the two-phase fluid at the wall (Cahn, 1977). A derivation of the Cahn boundary condition was then presented by considering the first variation of the augmented free energy functional along with a surface free energy consisting of a linear interpolation of the surface tensions between the wall and each phase at equilibrium, i.e.,

$$g_s(\phi) = \sigma_{\beta,s} + \frac{\Delta\sigma}{\Delta\phi_{eq}}(\phi - \phi_{eq}^{\beta}), \tag{1}$$

where $\Delta\sigma \equiv \sigma_{\alpha,s} - \sigma_{\beta,s}$ expresses the affinity of the wall to the equilibrium α phase, as compared to the equilibrium β phase. Note that the resulting formulation of the Cahn boundary condition can only be correct at the contact line since there is no contact angle for any wall region where a single phase at equilibrium wets the wall. However, since in such regions Eq. (1) is able to reproduce a constant surface tension, then after variation of the augmented functional the Cahn boundary condition correctly reduces to a trivial identity in all such regions (as it should). This observation can be incorporated into the Cahn boundary condition by introducing a contact line indicator function (i.e., equal to one at the contact line and zero elsewhere), which makes this linear interpolation formulation viable as a boundary condition for the Cahn-Hilliard equation.

In fact, it can be argued that as a consequence of considering values of contact angle other than 90°, two Margules coefficients should be employed for modelling the surface free energy at the wall (Smith and Van Ness, 1987). Hence, any modelling expression which interpolates $\sigma_{\alpha,s}$ (at $\phi = \phi_{eq}^{\alpha}$) and $\sigma_{\beta,s}$ (at $\phi = \phi_{eq}^{\beta}$) should be based on a cubic expression in powers of ϕ, which is uniquely determined by the following conditions: (i) $g_s(\phi_{eq}^{\alpha}) = \sigma_{s,\alpha}$ and $g_s(\phi_{eq}^{\beta}) = \sigma_{s,\beta}$, (ii) $g_s'(\phi_{eq}^{\alpha}) = g_s'(\phi_{eq}^{\beta}) = 0$. Finally we obtain (Jacqmin, 2000):

$$g_s(\phi) = \sigma_{\beta,s} + \frac{\Delta\sigma}{(\Delta\phi_{eq})^3}(\phi - \phi_{eq}^{\beta})^2(3\phi_{eq}^{\alpha} - \phi_{eq}^{\beta} - 2\phi). \tag{2}$$

In both cases, the right-hand side of the Cahn boundary condition involves a factor of $\Delta\sigma / \sigma$ which can be handled by means of Young's equation, $\cos\theta = -\Delta\sigma / \sigma.$ This is an additional relation (lying outside of the diffuse interface framework) that must be invoked to make the connection with the equilibirum contact angle $\theta.$ Consequently, the Cahn boundary condition for the Hermite interpolation formulation can be rearranged to the form:

$$\hat{\mathbf{n}}\cdot\nabla\phi=-12\frac{\mathrm{K}\cos\theta}{a(\Delta\phi_{eq})^{3}}(\phi-\phi_{eq}^{\alpha})(\phi-\phi_{eq}^{\beta}), \tag{3}$$

where $\mathrm{K}\equiv\frac{\sigma M_W}{\rho RTa}$ is a (dimensionless) surface tension coefficient while a denotes a (coarse-grained) sub-micron scale length, which represents the typical interface thickness at equilibrium. This formulation of the Cahn boundary condition has been employed for obtaining the principal result reported in this paper, i.e., the dependence of the critical Bond number for detachment of an isolated, wall-bound droplet as a function of the static contact angle. Numerical results based on the linear interpolation formulation in comparison to the Hermite interpolation formulation will be reported in future work.

3. Numerical results

Numerical methods are the same as in our previous works (Lamorgese and Mauri, 2008, 2011). However, it is worth noting that in our previous work (Lamorgese and Mauri, 2008) homogeneous boundary conditions on the first- and third-order *y*-derivatives of the concentration at the wall had been imposed using an influence-matrix technique (Canuto *et al*., 1988). In this work, inhomogeneous conditions on those derivatives have been dealt with in either one of two ways: (i) by interpolating the inhomogeneous boundary conditions as a body force so that our previous influence matrix solver could still be utilized (Shen, 1994), (ii) by making changes to our influence matrix solver that allow for inhomogeneous boundary conditions. In fact, although a modified influence matrix solver for inhomogeneous conditions was implemented in our code, in our production runs we chose the former method of boundary condition interpolation as a body force due to its lower complexity. In what follows, the static contact angle dependence of the critical Bond number will be discussed by first using dimensionless parameters that are readily accessible in our numerical setup. Subsequently, using a change of variables that dependence will also be presented in terms of standard

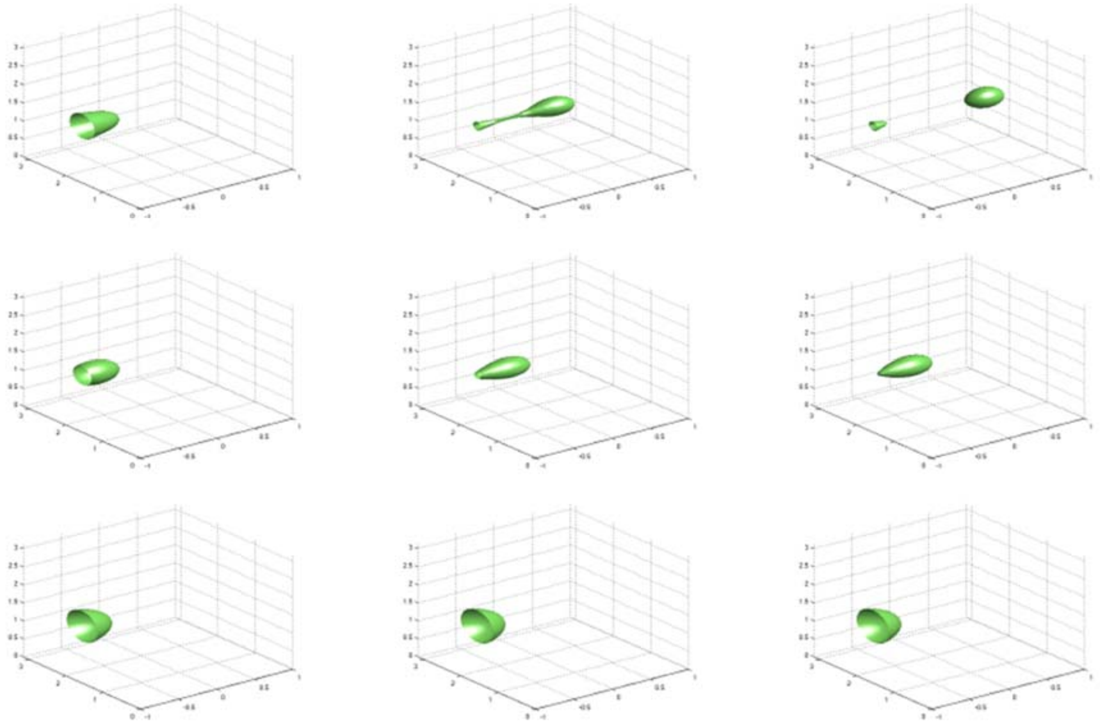

Figure 1: Snapshots of mass fraction isosurfaces at different (nondimensional) times $t=5\cdot10^{-3}$, $3.8\cdot10^{-2}$ *and* $4.3\cdot10^{-2}$ *from phase-field computations with* $\Psi=2.7$, $\alpha=100$ *and* $\langle\phi\rangle=0.1127$ *on a* $64\times65\times64$ *grid corresponding to* $\Delta\tilde{\sigma}=-6.56\cdot10^{-2}$ *with* $\mathrm{G}=1.6\mathrm{G}_c$ *(top row),* $\Delta\tilde{\sigma}=6.56\cdot10^{-2}$ *with* $\mathrm{G}=1.5\mathrm{G}_c$ *(middle row) and* $\Delta\tilde{\sigma}=-3.28\cdot10^{-2}$ *with* $\mathrm{G}=0.8\mathrm{G}_c$ *(bottom row).*

(i.e., θ and Bo). In fact, the actual dimensionless groups that appear in the governing equations after diffusive scaling of the Stokes/Cahn-Hilliard system are the previously noted fluidity coefficient and a (dimensionless) magnitude of the buoyancy force, defined as

$$\alpha \equiv \frac{RTa^2}{M_W \nu D}, \text{ a } \quad \mathrm{G} \equiv \frac{g\Delta\phi_{eq} d^3}{\alpha\nu D} = \frac{GaSc}{\alpha}, \tag{4}$$

where $Ga \equiv g\Delta\phi_{eq} d^3 / \nu^2$ is a Galileo number while $Sc \equiv \nu / D$ is the Schmidt number (M_W being the molecular mass of both component species). Hence it becomes clear that the critical conditions for detachment of an isolated, wall-bound drop can be uniquely identified through the dependence $\mathrm{G}_c = fn(\Delta\tilde{\sigma})$, where $\Delta\tilde{\sigma} \equiv \frac{\Delta\sigma}{\rho RTa / M_W}$ is the dimensionless surface tension difference at the wall. Note that, based on our previous definitions, we have

$$\cos\theta = -\frac{\Delta\tilde{\sigma}}{\mathrm{K}}, \quad \text{and} \quad Bo = \mathrm{G}\frac{a/d}{\mathrm{K}}. \tag{5}$$

The presence of K in the denominator of both of these relations (due to a reciprocal dependence on σ when rearranged in terms of dimensional quantities) indicates that θ and the Bond number are not readily available in our numerical setup and can only be evaluated after a numerical determination of K (further addressed below). Simulations of buoyancy-driven detachment were carried out in a computational domain of size $L_x = L_z = \frac{\pi}{2}Na,\ L_y = Na \quad (N = 64)$, with a pendant droplet (having a radius of $12a$) of the minority phase embedded in a continuous phase (with both phases at equilibrium), corresponding to $\langle\phi\rangle = 0.1127$. In the first set of simulations, we chose $\Psi = 2.7$ (corresponding to equilibrium mass fractions $\phi_{eq}^{\beta} = 0.1069$ and

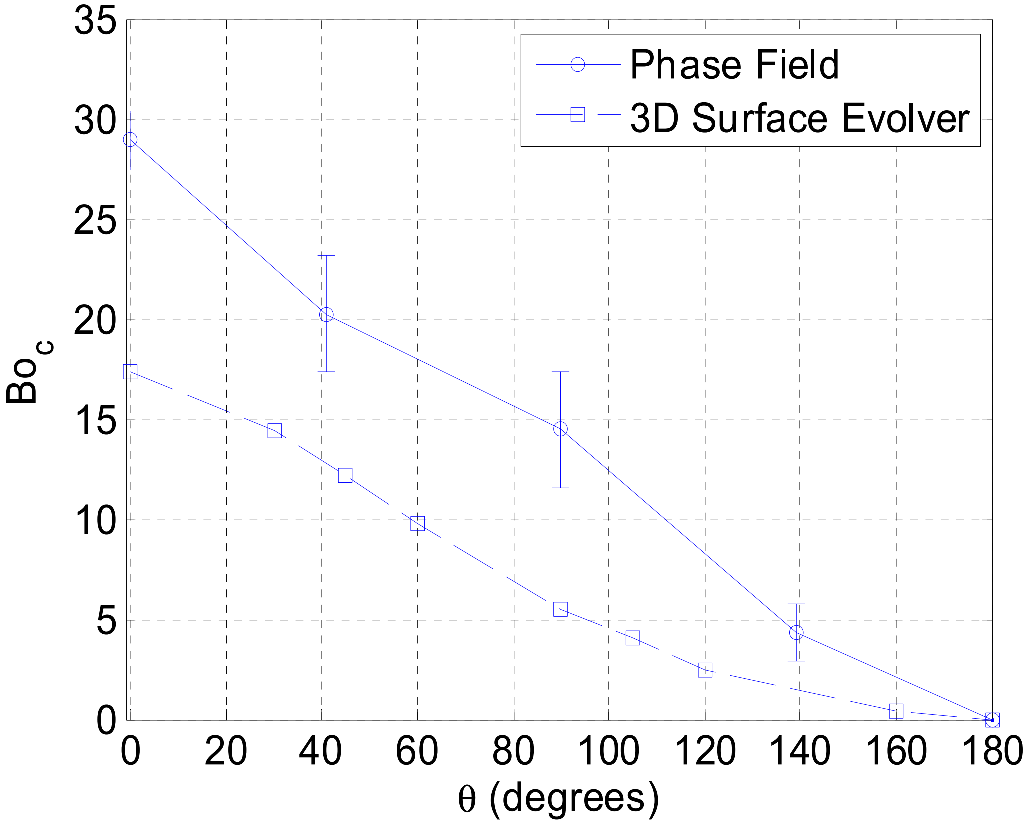

Figure 2: Critical Bond numbers as a function of static contact angle from phase-field computations with $\Psi = 2.7$, $\alpha = 100$ *and* $\langle\phi\rangle = 0.1127$ *on a* $64 \times 65 \times 64$ *grid (solid) vs. static stability analysis of equilibrium shapes obtained from the Young-Laplace equation (dashed).*

$\phi_{eq}^{\alpha} = 0.8929$) and $\alpha = 100$, yielding results that could be considered as roughly representative of a binary mixture with nearly immiscible components. Values of dimensionless surface tension difference were chosen in a discrete set $\Delta\tilde{\sigma} = \{-8.68 \cdot 10^{-2}, -6.56 \cdot 10^{-2}, 0, 6.56 \cdot 10^{-2}, 8.68 \cdot 10^{-2}\}$. For each such value, we ran simulations for different (nondimensional) buoyancy magnitudes to identify the critical magnitude corresponding to a pinch-off event. This is documented in Figure 1 showing snapshots of mass fraction isosurfaces at different (nondimensional) times for three cases corresponding to detachment with $\Delta\tilde{\sigma} < 0$ and $\Delta\tilde{\sigma} > 0$ and to no detachment with $\Delta\tilde{\sigma} < 0$. In particular, we found $\Delta\tilde{\sigma} = 8.68 \cdot 10^{-2}$ as the smallest (positive) surface tension difference for which a drop would detach from the wall under a zero gravity magnitude. This value of surface tension difference can be interpreted (in dimensional terms) as defining the reference surface tension needed for introducing θ as an alternative abscissa in place of $\Delta\tilde{\sigma}$ (i.e., $\Delta\sigma = \sigma$ with $G_c = 0$ corresponds to $\theta = 180^{\circ}$). Based on the first relation in (5), this then identifies the value $K^{*} = 8.68 \cdot 10^{-2}$ for switching to a $Bo_c = fn(\theta)$ description. The corresponding values of θ are in the discrete set $\{0^{\circ}, 40.9^{\circ}, 90^{\circ}, 139^{\circ}, 180^{\circ}\}$. Hence we see that the cases shown in Figure 1 correspond to detachment with $\theta < 90^{\circ}$ and $\theta > 90^{\circ}$ and to no detachment with $\theta < 90^{\circ}$. For each value of $\theta < 90^{\circ}$, we found that for all Bond numbers larger than critical a partial detachment event occurs. In contrast, for values $\theta \geq 90^{\circ}$ we found that a Bond number much larger than critical corresponds to a partial drop detachment from the solid surface, while for Bond numbers only slightly larger than critical a complete detachment is achieved.

These numerical results are summarized in Figure 2, showing the critical Bond number as a function of static contact angle. Also shown in this Figure are critical Bond numbers for axisymmetric droplets as a function of contact angle from sharp-interface equilibrium calculations based on Surface Evolver (Chen *et al*., 2005). As can be seen, these values are approximately half of those determined by phase-field simulation. We can only speculate on the factors leading to such a discrepancy, since a more precise assessment should be based on a large database of buoyancy-driven detachment simulations (missing in our case). It should be borne in mind that in all simulations reported herein a drop of the minority phase displaces continuous phase fluid when settling in the gravity direction, and this creates a backflow in its vicinity which could tend to further hinder the detachment process as the backflow strength increases. Although the effects of a backflow are likely to be significant for Bond numbers much larger than the critical value at a given contact angle, based on the observation of an extremely slow process of detachment very near to the critical condition (i.e., for Bond numbers only slightly larger than critical), a backflow is expected to have a negligible influence on the critical Bond number.

Another, more important, factor contributing to the discrepancy in Figure 2 is the static stability analysis ignoring the dynamics of the detachment process. In particular, a sharp-interface description together with its assumption of constant surface tension are expected to fail in the necking regime of drop detachment, where a sharpening of concentration gradients in the necking region leads to an effective increase in (dynamic) surface tension, ultimately leading to a reduced tendency to detachment or an increase in the critical Bond number.

4. Conclusions

We have discussed results of 3D phase-field simulations of buoyancy-driven detachment of a pendant emulsion droplet with the main objective of determining the critical Bond number as a function of static contact angle. Starting from the basic conservation principles, we have shown that a diffuse interface description of partially miscible binary liquid mixtures far from the critical point can be successfully employed for simulating triphase contact line problems in stable emulsions with nearly immiscible components. In addition, our numerical results have shown a characteristic monotonic behaviour of the critical Bond number as a function of static contact angle. We argue that the discrepancy between our numerically determined static contact angle dependence of the critical Bond number and its sharp-interface counterpart from a static stability analysis based on a numerical integration of the Young-Laplace equation can be explained in terms of (i) the inability of the sharp-interface analysis to describe the later stages of the detachment process and, in particular, the sharpening of concentration gradients leading to an effective increase in (dynamic) surface tension and critical Bond number, and (ii) a nonnegligible dependence on mean mass fraction of the critical Bond number at a given contact angle, due to a backflow which tends to hinder the detachment process as the backflow strength increases. However, that dependence cannot be properly resolved using the present dataset and is left for future work.

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