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Diffuse-interface field approach to modeling arbitrarily-shaped particles at fluid–fluid interfaces

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ABSTRACT

We present a novel mesoscale simulation approach to modeling the evolution of solid particles segregated at fluid–fluid interfaces. The approach involves a diffuse-interface field description of each fluid phase in addition to the set of solid particles. The unique strength of the model is its generality to include particles of arbitrary shapes and orientations, as well as the ability to incorporate electrostatic particle interactions and external forces via a previous work [P.C. Millett, Y.U. Wang, Acta Mater. 57 (2009) 3101]. In this work, we verify that the model produces the correct capillary forces and contact angles by comparing with a well-defined analytical solution. In addition, simulation results of rotations of various-shaped particles at fluid–fluid interfaces, external force-induced capillary attraction/repulsion between particles, and spinodal decomposition arrest due to colloidal particle jamming at the interfaces are presented.

1. Introduction

Interfacial phenomena govern a wide range of processes in solid-state materials, multi-phase fluids, and systems combining solid–fluid components. The interactions of solid-state particles, ranging from millimeter down to nanometer sizes, segregated at fluid–fluid interfaces represent an emerging field of study [1]. From a technological standpoint, particles in multi-phase fluids can be used for self-assembly processing [2] with implications for materials synthesis [3] and biological drug delivery [4,5], among other things. From a purely scientific standpoint, studying particle–fluid–fluid interactions is motivated by an incomplete understanding of (i) the capillary forces exerted on particles by fluid–fluid interfaces, and (ii) how fluid–fluid interfaces modify particle–particle interactions, including electrostatic and van der Waals forces. These issues become particularly complex for particles that are non-spherically shaped and/or have complex charge characteristics (e.g., permanent dipole moments). The fabrication of non-spherically shaped micro- and nano-particles [6] is becoming increasingly better understood and controlled. Hence, there is an abundance of potential self-assembly processes that may occur due to the capillary forces on irregularly-shaped particles at fluid–fluid interfaces that deserves investigation. Experimental studies have begun to investigate non-spherically-shapes particles are interfaces [7]. The computational methods required to simulate such phenomenon is unfortunately lacking.

In this paper, we present a novel mesoscale simulation method that utilizes diffuse-interface fields to model the capillary forces and torques applied to particles suspended at fluid–fluid interfaces. The approach is general enough to encompass arbitrary particle shapes, and builds on the authors' previous model [8,9] that allows the calculation of electrostatic interactions due to particle charge densities and/or permanent particle dipole moments. The diffuse-interface field approach (DIFA) presented here is similar to, although more general than, the commonly-known phase-field method [10], in the sense that both techniques evolve complex microstructural geometries without explicit interface tracking. This approach is considered a mesoscale simulation model, and therefore is most applicable to colloidal particles of size 100 nm–100 μm (i.e., we do not consider non-uniform electron clouds or atomic/molecular structuring in the fluid phase, both of which become non-trivial for particles that are tens of nanometers in size or below). In this paper, we will present results that demonstrate the method's ability to capture the correct capillary forces and contact angles for a variety of fluid–fluid and fluid–particle interfacial energies. In addition, simulations of coarsening arrest in bi-phase fluids due to particle jamming at the fluid–fluid interfaces will be presented.

2. Formulation

Before we discuss the derivation of the capillary forces and torques, the fluid–fluid model must be established. Here, we assume a highly-viscous two-phase mixture, in which inertial forces are non-existent and transport is governed by diffusion alone. Such

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an assumption is appropriate for polymer melts [11], for example. We therefore adopt a Cahn–Hilliard description [12] of diffusion-governed multi-phase morphology. In such a description, diffuse-interface fields are used to represent the relative concentrations of each fluid phase $\{c_\alpha\}$ and each particle $\{\eta_\beta\}$. The term *diffuse interface* refers to the fact that in such models, the interfacial width is finite and larger than the computational grid spacing [10]. Across the interfaces, the concentration fields $\{c_\alpha\}$ and order parameters $\{\eta_\beta\}$ transition continuously, yet rapidly, from one bulk value to the other. The total free energy of the fluid–fluid–particle system is described by

$$F = \int_V \left[f(\{c_\alpha\},\{\eta_\beta\}) + \sum_\alpha \frac{\kappa_\alpha}{2} |\nabla c_\alpha|^2 \right] dV, \tag{1}$$

where $f(\{c_\alpha\},\{\eta_\beta\})$ is the energy density described by

$$f(\{c_\alpha\},\{\eta_\beta\}) = f_c(\{c_\alpha\}) + f_\eta(\{\eta_\beta\}) + f_{c,\eta}(\{c_\alpha\},\{\eta_\beta\}). \tag{2}$$

The terms $f_c(\{c_\alpha\})$, $f_\eta(\{\eta_\beta\})$, and $f_{c,\eta}(\{c_\alpha\},\{\eta_\beta\})$ are the energy densities of the multiple liquid phases, the solid particles, and the interactions among liquid phases and solid particles, respectively. They are defined as

$$f_c(\{c_\alpha\}) = A \sum_\alpha (3c_\alpha^4 - 4c_\alpha^3), \tag{3}$$

$$f_\eta(\{\eta_\beta\}) = A \sum_\beta (3\eta_\beta^4 - 4\eta_\beta^3), \tag{4}$$

$$f_{c,\eta}(\{c_\alpha\},\{\eta_\beta\}) = 6A \left(\sum_{\alpha,\alpha'} B_{\alpha\alpha'} c_\alpha^2 c_{\alpha'}^2 + \sum_{\beta,\beta'} B_{\beta\beta'} \eta_\beta^2 \eta_{\beta'}^2 + \sum_{\alpha,\beta} B_{\alpha\beta} c_\alpha^2 \eta_\beta^2 \right). \tag{5}$$

These free energy functions are phenomenological in nature, and are constructed in the spirit of Landau theory to produce the energy landscape required for such a system, i.e., energy minima at $\{c_{\alpha=i} = 1, c_{\alpha\neq i} = 0, \eta_\beta = 0\}$ or $\{c_\alpha = 0, \eta_{\beta=j} = 1, \eta_{\beta\neq j} = 0\}$, that is, a spatial position is occupied by either fluid i or particle j. Here, A is a scaling coefficient and $B_{\alpha\alpha'}$, $B_{\beta\beta'}$, and $B_{\alpha\beta}$ are coefficients that effectively raise or lower the barrier height between fluid–fluid and fluid–particle energy wells. This allows control over the interfacial energies of any interface in the system, allowing simulations of, for example, fully and/or partially hydrophobic or hydrophilic particles. The fluid concentration fields are updated in time according to the Cahn–Hilliard equation

$$\frac{\partial c_\alpha}{\partial t} = \nabla \cdot \left(M_\alpha \nabla \frac{\delta F}{\delta c_\alpha} \right) \tag{6}$$

where M_α is the mobility of fluid species α. We note that, as described in our previous article [8,9], the diffuse-interface fields describing particle shapes, $\{\eta_\beta\}$, evolve by rigid-body translations and rotations, and therefore Eq. (4) is not solved, although we include it for generality (for the same reason, we do not include the gradient term for $\{\eta_\beta\}$ in Eq. (1)). We note that Eq. (6) is effective for evolving interfaces; however, fluid mechanics are not included in this paper. The Navier–Stokes equations have been integrated into a diffuse-interface approach previously (see e.g. [13]), and the current model can be expanded to include them.

The capillary forces acting on any given particle segregated at a fluid–fluid interface are obtained using a force density that can be integrated around the entire particle–fluid–fluid interface. We note that due to the diffuse interface widths of the fluid fields $\{c_\alpha\}$ and particle fields $\{\eta_\beta\}$, this triple junction region is actually a three-dimensional volume rather than a one-dimensional line (or for two-dimensional simulations, a two-dimensional area rather than a zero-dimensional point). The force density at any point inside the triple junction region, say, formed by fluid fields c_1, c_2 and particle field η is taken as

$$d\mathbf{F} = \kappa[\nabla c \times (\nabla c \times \nabla \eta)], \tag{7}$$

or

$$d\mathbf{F} = \kappa[(\nabla c \cdot \nabla \eta)\nabla c - |\nabla c|^2 \nabla \eta]. \tag{8}$$

Here, κ is a scaling coefficient that can be calibrated for any given, well-defined system. The ∇c vector in Eqs. (7) and (8) is defined as

$$\nabla c = c_1 c_2 (\nabla c_1 - \nabla c_2). \tag{9}$$

This vector defines the local orientation of the interface between fluids 1 and 2, and its magnitude is zero everywhere outside of this fluid–fluid interface (where either $c_1 = 0$ or $c_2 = 0$). Fig. 1 provides a schematic illustration of each of the gradient terms given in Eq. (7). The cross product terms in Eq. (7) ensure that the capillary force exerted on a particle is directed along the fluid–fluid interface and away from the particle. Thus, this capillary force density is applicable to any particle shape or particle orientation.

The total capillary force on the α^{th} particle is obtained by integrating around the particle diffuse interface

$$\mathbf{F}^{cap}(\alpha) = \int_V d\mathbf{F}(\alpha) dV. \tag{10}$$

In addition, the torque produced on a particle due to this capillary force at the particle surface is

$$\mathbf{T}^{cap}(\alpha) = \int_V [\mathbf{r} - \mathbf{r}_c(\alpha)] \times d\mathbf{F}(\alpha) dV, \tag{11}$$

where $[\mathbf{r} - \mathbf{r}_c(\alpha)]$ is the separation vector between the location of the particle–fluid–fluid interface and the particle center-of-mass $\mathbf{r}_c(\alpha)$.

The overall force and torque on the α^{th} particle are calculated by summing the long-range electrostatic components, $\mathbf{F}^{el}(\alpha)$ and $\mathbf{T}^{el}(\alpha)$, the short-range repulsive components, $\mathbf{F}^{sr}(\alpha)$ and $\mathbf{T}^{sr}(\alpha)$, and the capillary components

$$\mathbf{F}(\alpha) = \mathbf{F}^{el}(\alpha) + \mathbf{F}^{sr}(\alpha) + \mathbf{F}^{cap}(\alpha) + \xi^f(\alpha), \tag{12}$$

$$\mathbf{T}(\alpha) = \mathbf{T}^{el}(\alpha) + \mathbf{T}^{sr}(\alpha) + \mathbf{T}^{cap}(\alpha) + \xi^t(\alpha). \tag{13}$$

The long-range electrostatic and short-range repulsive forces and torques are defined in our previous paper [8,9], and are not considered in this work. The short-range particle interaction is treated in a manner of soft-particle potential and is formulated through an effective local force density acting on the surface of the α^{th} particle by its neighbors [8,9]:

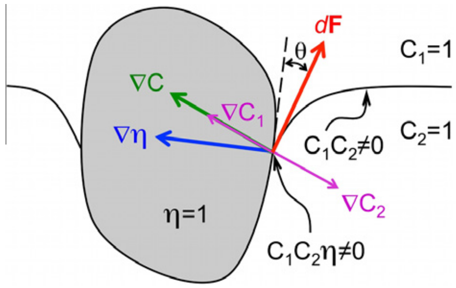

Fig. 1. Schematic depiction of the gradient terms (existing within the diffuse interfaces) presented in Eqs. (7)–(9) for an arbitrarily-shaped particle at a fluid–fluid interface. The term ∇c represents the normal direction at any location on the fluid–fluid interface, and $\nabla \eta$ represents the inward normal direction of the particle surface. Eq. (7) dictates that at any point on the fluid–fluid–particle triple junction, the force density $d\mathbf{F}$ acts in the direction along the fluid–fluid interface and away from the particle.