



# Shape-anisotropic particles at curved fluid interfaces and role of Laplace pressure: A computational study

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## ABSTRACT

The self-assembly behavior of shape-anisotropic particles at curved fluid interfaces is computationally investigated by diffuse interface field approach (DIFA). A Gibbs–Duhem-type thermodynamic formalism is introduced to treat heterogeneous pressure within the phenomenological model, in agreement with Young–Laplace equation. Computer simulations are performed to study the effects of capillary forces (interfacial tension and Laplace pressure) on particle self-assembly at fluid interfaces in various two-dimensional cases. For isolated particles, it is found that the equilibrium liquid interface remains circular and particles of different shapes do not disturb the homogeneous curvature of liquid interface, while the equilibrium position, orientation and stability of a particle at the liquid interface depend on its shape and initial location with respect to the liquid interface. For interacting particles, the curvature of local liquid interfaces is different from the apparent curvature of the particle shell; nevertheless, irrespective of the particle shapes, a particle-coated droplet always tends to deform into a circular morphology under positive Laplace pressure, loses mechanical stability and collapses under negative Laplace pressure, while adapts to any morphology and stays in neutral equilibrium under zero Laplace pressure. Finally, the collective behaviors of particles and Laplace pressure evolution in bicontinuous interfacially jammed emulsion gels (bijels) are investigated.

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## 1. Introduction

Colloidal particle self-assembly has become a promising bottom-up route to synthesize advanced materials with novel microstructures and functionalities [1–4]. The basic building blocks, individual particles, have no longer been restricted to simple spherical shape with homogeneous property owing to rapid progress over the last decade in processing techniques to fabricate shape-anisotropic, patchy, and coated particles [1–3,5]. Particles with anisotropic shapes and/or heterogeneous properties (such as non-uniform charge distribution, heterogeneous affinity to liquid phases, and different functionalities of core and shell materials) have greatly enriched the self-assembled structures [1–4,6–9]. Colloidal particle self-assembly directed by liquid interfaces, as inspired by Pickering emulsion, has recently attracted increasing interests [10–13]. New types of soft materials, such as the so-called colloidosome and bijel, are created. The colloidosome [14] (also called colloidal armour [15]) has been exploited for drug encapsulation and delivery. The bijel (bicontinuous interfacially jammed emulsion gel) was first computationally simulated [16] and then

experimentally fabricated [17,18]. Engineered colloidal particles dispersed in multi-phase liquids offer enormous application opportunities, while also pose great challenges to a complete scientific understanding due to the complexities of interaction forces and microstructural evolutions. In order to understand the microstructures and properties of such multi-liquid-phase colloidal systems, the behaviors of colloidal particles at liquid interfaces are one of the most important issues that must be investigated. Realistic computer modeling and simulation is highly desired for such a study, which not only complements experimental studies by providing quantitative details but can also artificially switch on/off various interaction forces at will, enabling researchers to focus on individual interactions separately as well as any combination of them, which are usually difficult or impractical in experiments. The purpose of this paper is to present such a computer modeling and simulation study of shape-anisotropic particles at curved fluid interfaces under the influences of interfacial tension and Laplace pressure (the two distinct contributions to capillary forces) as well as the resultant collective behaviors of colloidal particles and multi-phase fluid.

In this work, we focus on shape-anisotropic particles at curved fluid interfaces. A diffuse interface field approach (DIFA) [19–22] is employed, which is an extension of the phase field method [23,24] extensively used in microstructure evolution simulations.

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A Gibbs–Duhem-type thermodynamic formalism is introduced to treat Laplace pressure, which determines heterogeneous pressure distribution without explicitly tracking inter-phase interfaces, with results in agreement with Young–Laplace equation, while direct application of the latter would be difficult for complex evolving colloidal morphology. After a description of the modeling method including formulation and calibration, computer simulations are performed to study the effects of capillary forces (interfacial tension and Laplace pressure) on particle self-assembly at fluid interfaces in various situations, including isolated particles of various shapes relaxing at curved liquid interfaces, interacting particles at the liquid interfaces of Pickering emulsion droplets under positive, negative and zero Laplace pressures, and the collective behaviors of particles in bijels.

## 2. Modeling method

### 2.1. Basic formulation of diffuse interface field approach (DIFA)

In DIFA model of two-liquid-phase colloidal system, each fluid phase is described by one concentration field variable  $c_\alpha$  and each solid particle by one field  $\eta_\beta$ . The total system free energy assumes the following form

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

where  $f(\{c_\alpha\}, \{\eta_\beta\})$  is the nonequilibrium local bulk chemical free energy density function that defines the thermodynamic properties of a multi-phase system consisting of two liquid phases ( $\alpha = 1, 2$ ) and  $N$  solid particles ( $\beta = 1, \dots, N$ ), and is expressed as

$$f(\{c_\alpha\}, \{\eta_\beta\}) = A \left[ \sum_{\alpha=1}^2 (3c_\alpha^4 - 4c_\alpha^3) + \sum_\beta (3\eta_\beta^4 - 4\eta_\beta^3) + 6 \left( \chi c_1^2 c_2^2 + \sum_{\beta \alpha=1}^2 \lambda_\alpha c_\alpha^2 \eta_\beta^2 \right) \right] \quad (2)$$

This Landau-type free energy function is phenomenological in nature that defines the required energy landscape with minima at  $\{c_{\alpha=i} = 1, c_{\alpha' \neq i} = 0, \eta_\beta = 0\}$  for liquid phase  $i$  and  $\{c_\alpha = 0, \eta_{\beta=j} = 1, \eta_{\beta' \neq j} = 0\}$  for solid particle  $j$ . For partially miscible binary liquid with a miscibility gap, the concentrations  $c_1$  and  $c_2$  are defined, for convenience, as molar fractions of the two liquid phases with respective equilibrium concentrations  $c_{A1}$  and  $c_{A2}$  in terms of component A (or  $c_{B1}$  and  $c_{B2}$  in terms of component B), thus  $c_1 + c_2 = 1$  and the true local concentration in terms of components A and B, respectively, is

$$c_A = c_1 c_{A1} + c_2 c_{A2}, \quad c_B = c_1 c_{B1} + c_2 c_{B2} \quad (3)$$

The gradient terms in Eq. (1) describe the energy contributions from liquid–liquid and liquid–solid interfaces. As a result, all field variables  $\{c_\alpha\}$  smoothly transit from 1 to 0 forming diffuse interfaces at both liquid–liquid interfaces and liquid–solid interfaces. Also,  $\eta_\beta = 1$  inside the particle  $\beta$  and  $\eta_\beta = 0$  outside, and the fields  $\{\eta_\beta\}$  also smoothly transit through diffuse interfaces. Inside liquids ( $\eta_\beta = 0$ ), the free energy function in Eq. (2) describes a double-well potential for binary solution with a miscibility gap. The constant  $A$  is an energy scaling coefficient, and the parameters  $\chi$ ,  $\lambda_\alpha$  and  $\kappa_\alpha$  are used to control the fluid–fluid and fluid–solid interfacial energy densities. Thus, the model is able to simulate colloidal particles of different wettabilities.

In computer simulation, the concentration field variables of liquid phases evolve in time following the Cahn–Hilliard equation:

$$\frac{\partial c_\alpha}{\partial t} = \nabla \cdot \left( M_\alpha \nabla \frac{\delta F}{\delta c_\alpha} \right) \quad (4)$$

where  $M_\alpha$  is chemical mobility, and

$$\frac{\delta F}{\delta c_\alpha} = \frac{\partial f}{\partial c_\alpha} - \kappa_\alpha \Delta c_\alpha \quad (5)$$

is the chemical potential defined within gradient thermodynamics. In the framework of Cahn–Hilliard equation, the two-phase fluid morphology evolves through nonlinear diffusion, thus it is assumed that small colloidal particles are dispersed in viscous binary liquids where Reynolds number ( $Re = VL/\nu$ , with  $V$ ,  $L$  and  $\nu$  being characteristic velocity, length and kinematic viscosity, respectively) and Péclet number ( $Pe = VL/D$ , with  $D$  being liquid diffusivity) are small. As in our previous works [20], colloidal particles in the DIFA model are characterized by diffuse interface fields  $\{\eta_\beta\}$  and evolve via rigid-body motions subjected to various forces including interfacial tension, Laplace pressure, short-range and long-range interactions as well as Stokes' drag force, and the equation of motion is simplified according to low Reynolds number hydrodynamics [21,22].

It is worth noting that coupled Cahn–Hilliard–Navier–Stokes models have been reported for two-phase flows [25–28], however the complex boundary conditions associated with a large number of moving particles in colloid system make their applications to colloid modeling still computationally intractable. An alternative approach to solving the Navier–Stokes equation is the lattice Boltzmann method (LBM) [29–31] with demonstrated capability to treat hydrodynamics with complex geometrical boundary conditions, while study of moving particles with anisotropic shapes has not yet been reported by LBM. Nevertheless, LBM offers a potential approach to combine with the DIFA model to treat colloid assembly processes in large Reynolds number regime.

### 2.2. Laplace pressure

Across a curved liquid interface, there exists a pressure jump (Laplace pressure), which is determined by the well-known Young–Laplace equation. According to thermodynamics, the pressure variation leads to chemical potential variations in the two liquid phases, which obey the Gibbs–Duhem relation (under isothermal condition) [32]

$$c_A d\mu_A + c_B d\mu_B = dp \quad (6)$$

where  $c_A$  and  $c_B$  are the true local concentration respectively in terms of components A and B as given in Eq. (3),  $\mu_A = \partial f / \partial c_A$  and  $\mu_B = \partial f / \partial c_B$  are the chemical potentials in the bulk phases, and  $f(c_A, c_B)$  is the free energy density function. Using chain rules of differentiation yields

$$\mu_A = \frac{\mu_1 c_{B2} - \mu_2 c_{B1}}{c_{A1} c_{B2} - c_{A2} c_{B1}}, \quad \mu_B = \frac{\mu_2 c_{A1} - \mu_1 c_{A2}}{c_{A1} c_{B2} - c_{A2} c_{B1}} \quad (7)$$

where  $\mu_\alpha = \partial f / \partial c_\alpha$ . Eq. (6) can be rewritten with respect to the equilibrium values  $\mu_A^0$ ,  $\mu_B^0$  and  $p^0$  in the case of flat interface as

$$c_A (\mu_A - \mu_A^0) + c_B (\mu_B - \mu_B^0) = p - p^0 \quad (8)$$

For the free energy function given in Eq. (2),  $\mu_1^0 = \mu_2^0 = 0$ , and according to Eq. (7),  $\mu_A^0 = \mu_B^0 = 0$ , which simplifies Eq. (8) to

$$p - p^0 = c_A \mu_A + c_B \mu_B \quad (9)$$

Substituting Eq. (3) and Eq. (7) into Eq. (9) gives

$$p - p^0 = c_1 \mu_1 + c_2 \mu_2 \quad (10)$$

which can be conveniently evaluated from the free energy function  $f(c_1, c_2)$  defined in Eq. (2). That is, the Gibbs–Duhem equation also holds for our phenomenological Landau-type free energy function, which can be understood by thinking in terms of liquid phases 1 and 2 instead of components A and B in the liquid. In particular, the Laplace pressure causes changes in the chemical potentials through slight shifts in compositions away from their equilibrium values. Assuming  $c_1$  and  $c_2$  as equilibrium values in Eq. (10) gives

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