# Thermodynamically consistent modelling of two-phase flows with moving contact line and soluble surfactants

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Droplet dynamics on a solid substrate is significantly influenced by surfactants. It remains a challenging task to model and simulate the moving contact line dynamics with soluble surfactants. In this work, we present a derivation of the phase-field moving contact line model with soluble surfactants through the first law of thermodynamics, associated thermodynamic relations and the Onsager variational principle. The derived thermodynamically consistent model consists of two Cahn-Hilliard type of equations governing the evolution of interface and surfactant concentration, the incompressible Navier-Stokes equations and the generalized Navier boundary condition for the moving contact line. With chemical potentials derived from the free energy functional, we analytically obtain certain equilibrium properties of surfactant adsorption, including equilibrium profiles for phase-field variables, the Langmuir isotherm and the equilibrium equation of state. A classical droplet spread case is used to numerically validate the moving contact line model and equilibrium properties of surfactant adsorption. The influence of surfactants on the contact line dynamics observed in our simulations is consistent with the results obtained using sharp interface models. Using the proposed model, we investigate the droplet dynamics with soluble surfactants on a chemically patterned surface. It is observed that droplets will form three typical flow states as a result of different surfactant bulk concentrations and defect strengths, specifically the coalescence mode, the non-coalescence mode and the detachment mode. In addition, a phase diagram for the three flow states is presented. Finally, we study the unbalanced Young stress acting on triple-phase contact points. The unbalanced Young stress could be a driving or resistance force, which is determined by the critical defect strength.

Key words: contact lines, Navier-Stokes equations, multiphase flow

## 1. Introduction

The flow of droplets on a solid surface is ubiquitous in nature and many industrial applications, ranging from spray coating, crude oil recovery and microfluidics to ink-jet printing (Dupuis & Yeomans 2005; Blake et al. 2015; Patil et al. 2016). The droplet dynamics is significantly dependent on the properties of the solid surface, e.g. the wettability (Blake et al. 2015; Shang, Luo & Bai 2019). Surfactants, interface active agents, can change the wetting properties of a solid surface by altering the contact angle (Lai, Tseng & Huang 2010; Xu & Ren 2014; Zhang, Xu & Ren 2014). An interesting example in daily life is that detergents (surfactants) are added into a washing machine to clean clothes effectively. Oil droplets that stick to clothes becomes less 'sticky' under the effect of surfactants, and the water currents can readily wash away the droplets. Another typical example is surfactant-based enhanced oil recovery in the petroleum industry. Adding surfactants into injected water can greatly improve the efficiency of drainage, since oil droplets attached on the surface of hydrophobic rock are easier to be displaced away (Raffa, Broekhuis & Picchioni 2016). Surfactants and wettability of reservoir rocks determine the efficiency of drainage and the distribution of residual oil in porous media. In the above examples, water, oil droplets, clothes (rock) and surfactants make up a typical multiphase system involving the moving contact line (MCL) and surfactants. Therefore, an interesting and practically important issue arises concerning how surfactants affect the dynamics of the MCL.

Numerical modelling is taking an increasingly significant position in the investigation of droplet dynamics on a solid surface with surfactants, as it can provide easier access to some quantities such as surfactant concentration, pressure and velocity, which are difficult to measure experimentally (Liu et al. 2018). However, the efficient and accurate computational modelling of contact line dynamics with surfactants remains a challenging task. The first challenge comes from the modelling of interfacial dynamics with surfactants. The presence of surfactants brings some difficulties to simulations (Booty & Siegel 2010; Zhang et al. 2014; Liu et al. 2018), including the following: (1) a suitable equation of state is needed to account for the effect of surfactants in reducing the interfacial tension; (2) in addition to the hydrodynamic equations, an advection-diffusion equation should be introduced to describe the evolution of surfactant concentration (Khatri & Tornberg 2014); (3) the non-uniform distribution of surfactants along the interface creates a Marangoni stress, and this effect should be considered in the governing system; and (4) for soluble surfactants, adsorption and desorption of surfactants on the interface further increase the difficulty of modelling (Cuenot, Magnaudet & Spennato 1997). To address these difficulties, numerous numerical methods have been developed, such as the level set method (Xu, Yang & Lowengrub 2012; Xu & Ren 2014; Titta et al. 2018), the volume of fluid method (James & Lowengrub 2004; Alke & Bothe 2009), the front tracking method (Zhang, Eckmann & Ayyaswamy 2006; Muradoglu & Tryggvason 2008), the immersed boundary method (Lai et al. 2010) and the lattice Boltzmann method (Van der Sman & Van der Graaf 2006; Zhang et al. 2015; Zhao et al. 2018; Wei et al. 2019). Although these methods have allowed great progress in the simulation of interfacial flows with surfactants, they still suffer from several drawbacks (Liu et al. 2018), including the following: (1) the level set and volume of fluid methods require either non-physical re-initialization processes or complex interface reconstruction algorithms to represent the interface and surfactant concentration; (2) the front tracking and immersed boundary methods have difficulty in dealing with large topological changes, for example droplet breakup and coalescence; and (3) most lattice Boltzmann models

do not consider the Marangoni stress (Liu et al. 2018), which is unphysical and could have an important impact on the droplet dynamics. The second challenge is the MCL problem. It is well known that under the usual hydrodynamic assumptions, namely the incompressible Navier-Stokes equations and no-slip boundary condition, non-physical singularities will occur in the vicinity of the MCL, and the velocity field is multi-valued at the contact line (Wang, Oian & Sheng 2008; Xu, Di & Yu 2018). To remove the singularities at the MCL, various continuous models have been proposed, and reviews of these models are available (Snoeijer & Andreotti 2013; Sui, Ding & Spelt 2014). Among these models, the Navier boundary condition (NBC) is a classical and natural boundary condition (Yang et al. 2017; Alpak, Samardžić & Frank 2018; Zampogna, Magnaudet & Bottaro 2019), and it has been used in simulations of contact line dynamics with insoluble surfactants. Lai et al. (2010) used an immersed boundary method to simulate the MCL problem, and studied the effect of insoluble surfactants on contact angles. A level set method for two-phase flows with the MCL and insoluble surfactants was proposed by Xu & Ren (2014). Zhang et al. (2014) derived a continuous model for the dynamics of two immiscible fluids with the MCL and insoluble surfactants based on thermodynamic principles. Their pioneering studies have greatly promoted the development of simulations for droplet dynamics with the MCL and surfactants. However, the dynamic contact line condition and soluble surfactants were not considered in these studies.

Recently, the phase-field model has shown great potential for the modelling of two-phase flows with the MCL and surfactants. In this model, the interface is treated as a thin diffuse layer between different fluids represented by a phase-field variable (Shen & Yang 2015; Alpak, Riviere & Frank 2016; Frank et al. 2018; Kou & Sun 2018a,b). Compared with sharp interface models, the phase-field model has several obvious advantages: (1) it does not need to track the interface explicitly, and the interface is captured implicitly and automatically by the evolution of a phase-field variable (Xu et al. 2018), and thus computations and analysis for the phase-field model are much easier than for other methods and (2) the phase-field model has a firm physical basis for multiphase flow (Liu & Zhang 2010; Chen, Sun & Wang 2014), since the governing system can be derived from an energy-based variational formalism, and the developed model normally satisfies thermodynamically consistent energy dissipation law (Shen & Yang 2015; Yang et al. 2017; Zhu et al. 2019a). These advantages mean that the phase-field model is widely used to simulate interfacial phenomena, e.g. surfactant-driven interfacial flows (Teigen et al. 2011; Yun, Li & Kim 2014). Laradji et al. (1992) proposed the first phase-field surfactant model. In their pioneering work, two phase-field variables were introduced in the free energy functional, which formed the general framework of phase-field surfactant models, to represent fluid components and surfactant concentration, respectively. Since then, numerous phase-field surfactant models (Copetti & Elliott 1992; Komura & Kodama 1997: Van der Sman & Van der Graaf 2006) have been proposed and reviews of these models can be found in Li & Kim (2012), Yang & Ju (2017) and Zhu et al. (2018). In this study, we adopt a typical representative phase-field surfactant model (free energy functional) developed by Engblom et al. (2013). In the proposed free energy functional, the classical Cahn-Hilliard potential determines the dynamics of a diffuse interface, and the logarithmic Flory-Huggins potential controls the entropy of mixing surfactants with the bulk phases and restricts the range of concentration variable. The nonlinearly coupled surface energy potential locally attracts surfactants to the interface of fluids, while the enthalpic term globally penalizes free surfactants in the bulk phases and stabilizes the phase-field model. Recently, we coupled this model

with the hydrodynamic equations to simulate the interfacial flows with surfactants. Several linear, decoupled and energy-stable schemes were also constructed to solve this complex system effectively (Zhu *et al.* 2019*b*). Our three-dimensional results successfully demonstrate the effect of surfactants on the interfacial dynamics. To date, a series of hydrodynamics coupled phase-field surfactant models have been developed (Pätzold & Dawson 1995; Liu & Zhang 2010; Teigen *et al.* 2011; Garcke, Lam & Stinner 2014), but none of them has considered the MCL problem. Hence, it is necessary to extend our current work to the modelling of the MCL problem.

Although the no-slip velocity boundary condition leads to the well-known contact line paradox for sharp interface models, it works well for the phase-field model. The chemical diffusion in a thin interface, arising from the non-equilibrium of chemical potential, can cause the motion of the contact line. Hence, the singularities at the MCL can be successfully removed in the phase-field model when a no-slip boundary condition is imposed. On the other hand, a slip boundary condition also works well for the phase-field model. Using careful molecular dynamics studies of the slip behaviour near the MCL (Qian, Wang & Sheng 2004, 2006) and principles of thermodynamics, Oian, Wang & Sheng (2003) proposed a generalized Navier boundary condition (GNBC). The GNBC states that the slip velocity at the MCL is proportional to the sum of viscous stress and unbalanced Young stress; the latter arises from the deviation of the fluid-fluid interface from its equilibrium configuration (Wang et al. 2008). They further demonstrated that the GNBC can quantitatively reproduce the MCL slip velocity profiles obtained by molecular dynamics simulations (Qian et al. 2006). The GNBC can reduce to the typical NBC (Fan et al. 2019) in equilibrium, and the NBC would reduce to the no-slip boundary condition when the slip length of fluid on a solid substrate is zero (Yu & Yang 2017). For the wetting boundary condition, the GNBC uses the typical surface-energy approach (Jacqmin 2000; Frank et al. 2018) to prescribe a dynamic contact angle between diffuse interface and solid substrate. Note that there are also some other well-known approaches to describe contact angles in the framework of the phase-field model, for example, the geometric contact angle approach derived by Ding & Spelt (2007) and the extended geometric approach developed by Alpak et al. (2016). The GNBC shows great advantages and prospects for simulating the MCL dynamics, and several attempts have been made to develop energy-stable schemes for the GNBC-based phase-field models. In this work, the GNBC is adopted to handle the slip boundary condition and dynamic contact angle at the fluid-solid interface.

As a first attempt, we present a derivation of the phase-field MCL model with soluble surfactants through the first law of thermodynamics, associated thermodynamic relations and the Onsager variational principle. The derived thermodynamically consistent model consists of two Cahn–Hilliard type of equations governing the evolution of interface and surfactant concentration, the incompressible Navier–Stokes equations and the GNBC for the MCL. With chemical potentials derived from the free energy functional, we analytically obtain certain equilibrium properties of surfactant adsorption, including equilibrium profiles for phase-field variables, the Langmuir isotherm and the equilibrium equation of state. A classical droplet spread case is used to numerically validate the MCL model and equilibrium properties of surfactant adsorption. Using the proposed model, we investigate the droplet dynamics with soluble surfactants on a chemically patterned surface.

### 2. Derivation of MCL hydrodynamics with surfactants

In this section, we present a derivation of the phase-field MCL model with soluble surfactants. The governing equation is derived through three key steps: (1) the first

law of thermodynamics and associated thermodynamic relations are used to derive an entropy equation; (2) the momentum equation and the slip boundary condition are obtained through the Galilean invariance; and (3) the Onsager variational principle is used to obtain diffusive fluxes and the stress tensor. The derived model consists of two Cahn–Hilliard type of equations for phase-field variables, the incompressible Navier–Stokes equations and the GNBC for the MCL.

## 2.1. Free energy functional and entropy equation

In an immiscible two-phase system with soluble surfactants, there are three types of free energy. These are the mixing energy, free energies associated with surfactants and the surface energy at the fluid–solid interface.

*Mixing energy*. In the phase-field model, a phase-field variable is introduced to distinguish two phases, and the interface is treated as a thin and continuous layer, inside which the two phases are mixed and store the mixing energy. The classical Cahn–Hilliard free energy functional (Gao & Wang 2012; Engblom *et al.* 2013) is used to represent the mixing energy,

$$F_{mix}(\phi) = \int \left[ -\frac{A}{2}\phi^2 + \frac{B}{4}\phi^4 + \frac{A}{4} + \frac{\kappa}{2}|\nabla\phi|^2 \right] d\Omega, \qquad (2.1)$$

where  $\phi$  is the phase-field variable measuring the local composition of fluids. Parameters A, B and  $\kappa$  can be determined from the two equilibrium phases  $\phi_{\pm} = \pm \sqrt{A/B}$ , and the interfacial thickness parameter  $\varepsilon = \sqrt{\kappa/A}$ . The polynomial part  $-A\phi^2/2 + B\phi^4/4 + A/4$  in  $F_{mix}$  prefers the total separation of two phases and produces the classical sharp-interface picture (Yue *et al.* 2004). The square gradient term  $\kappa |\nabla \phi|^2/2$  represents weakly non-local interactions between fluids that prefers the complete mixing of phases. Competition between the two terms leads to a diffuse interface in equilibrium (Shen & Yang 2015), where  $F_{mix}$  reaches a minimum.

*Free energies associated with surfactants.* The presence of surfactants would greatly affect the dynamics of fluid mixtures. To account for the effect of surfactants, additional energy terms are introduced to the Cahn–Hilliard free energy functional, including a logarithmic free energy, a nonlinearly coupled surface energy and an energy term measuring the cost of free surfactants.

Free energy  $F_1$  is a typical logarithmic free energy (Yang & Ju 2017) governing the entropy of mixing surfactants with the bulk phases

$$F_{1}(\psi) = \int [k_{b}T_{e}G(\psi)] d\Omega,$$
  

$$G(\psi) = \psi \ln \psi + (1 - \psi) \ln(1 - \psi),$$
(2.2)

where  $\psi$  is a phase-field variable representing the surfactant concentration,  $k_b$  is the Boltzmann constant and  $T_e$  denotes the temperature. The constant  $k_bT_e$  takes the role of a diffusion coefficient for  $\psi$  at a given temperature. The first term  $\psi \ln \psi$  in the Flory–Huggins potential  $G(\psi)$  models the ideal mixing of surfactants in the bulk phases and guarantees the value of  $\psi$  being positive, and the second term  $(1 - \psi) \log(1 - \psi)$  restricts  $\psi < 1$ . Thus, the surfactant concentration  $\psi$  varies within the range of 0 to 1 in this study.

Surfactants can automatically adsorb onto the interface and form a buffer zone to reduce the system energy. A surface energy  $F_2$  (Engblom *et al.* 2013) is adopted to account for the high surfactant concentration near the interface

$$F_{2}(\phi, \psi) = \int \left[ -\frac{\zeta}{4} \psi (1 - \phi^{2})^{2} \right] d\Omega.$$
 (2.3)

Here we set  $\zeta = A$  to reduce unnecessary free parameters (Engblom *et al.* 2013). Theoretically, the surface energy  $F_2$  is inactive in the bulk phases and reaches a minimum on the interface. The energy term  $F_3$  is used to penalize free surfactants in the bulk phases:

$$F_{3}(\phi, \psi) = \int \left[\frac{W}{2}\psi\phi^{2}\right] d\Omega, \qquad (2.4)$$

where W is a positive parameter. Surface energy  $F_3$  also plays a significant role in stabilizing the phase-field model (Liu & Zhang 2010). It is obvious that  $F_3$  is inactive on the interface where  $\phi \approx 0$  and reaches a maximum in the bulk phases. To some extent,  $F_2$  and  $F_3$  are complementary;  $F_2$  locally attracts surfactants to the interface while  $F_3$  globally counteracts the occurrence of free surfactants (Engblom *et al.* 2013).

Surface energy at the fluid-solid interface. When the diffuse interface touches a solid surface, the MCL problem arises. The interfacial free energy per unit area  $M(\phi)$  at the fluid-solid interface is determined by the interfacial tension  $\sigma$  between fluids, the contact angle  $\theta_s$  between the diffuse interface and solid surface, and the local composition of fluids on the solid surface. The typical free energy at the fluid-solid surface (Gao & Wang 2014) reads

$$F_{wf}(\phi) = \int M(\phi) \, \mathrm{d}S = \int \left[ -\frac{\sigma}{2} \cos \theta_s \sin \left( \frac{\pi}{2} \phi \right) \right] \, \mathrm{d}S. \tag{2.5}$$

The total free energy F of a two-phase system with soluble surfactants can be written as the sum of the mixing energy, free energies associated with surfactants and the free energy at the fluid-solid interface:

$$F(\phi, \psi) = F_{mix}(\phi) + F_1(\psi) + F_2(\phi, \psi) + F_3(\phi, \psi) + F_{wf}(\phi).$$
(2.6)

The three quantities  $w_{\phi}$ ,  $w_{\psi}$  and L can be variationally derived from the total free energy F as

$$\delta F(\phi, \psi) = \int [w_{\phi} \delta \phi] \, \mathrm{d}\Omega + \int [w_{\psi} \, \delta \psi] \, \mathrm{d}\Omega + \int [L \, \delta \phi] \, \mathrm{d}S, \qquad (2.7)$$

where  $w_{\phi}$  is the chemical potential determining the composition diffusion as follows:

$$w_{\phi} = -A\phi + B\phi^3 - \kappa \Delta\phi + W\psi\phi - \zeta \psi\phi(\phi^2 - 1).$$
(2.8)

Equation (2.8) indicates that the surfactant concentration may greatly affect the composition diffusion, and change the equilibrium profile of the phase-field variable  $\phi$ . A detailed discussion of this issue will be presented in § 3. The variable  $w_{\psi}$  is the chemical potential governing the diffusion of surfactants,

$$w_{\psi} = k_b T_e \ln\left(\frac{\psi}{1-\psi}\right) + \frac{W}{2}\phi^2 - \frac{\zeta}{4}(\phi^2 - 1)^2, \qquad (2.9)$$

and L is the chemical potential at the solid surface,

$$L = \kappa \partial_n \phi + M'(\phi). \tag{2.10}$$

By minimizing the total free energy F with respect to phase-field variables  $\phi$  and  $\psi$ , we can obtain equilibrium conditions, where chemical potentials are constants throughout the whole system. Deviations from equilibrium conditions, measured by the chemical potential gradients  $\nabla w_{\phi}$  and  $\nabla w_{\psi}$  in the bulk phases and L at the fluid-solid interface (Qian *et al.* 2006), will lead to composition diffusion, surfactant diffusion in the bulk phases and relaxation at the fluid-solid interface. The conservation of  $\phi$  and  $\psi$  requires that diffusive fluxes and material derivatives of phase-field variables satisfy the continuity equation, namely

$$\phi = \phi_t + \boldsymbol{u} \cdot \nabla \phi = -\nabla \cdot \boldsymbol{J}_{\phi} \tag{2.11}$$

and

$$\dot{\boldsymbol{\psi}} = \boldsymbol{\psi}_t + \boldsymbol{u} \cdot \boldsymbol{\nabla} \boldsymbol{\psi} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_{\boldsymbol{\psi}}, \qquad (2.12)$$

where  $J_{\phi}$  and  $J_{\psi}$  are diffusive fluxes resulting from the composition diffusion and surfactant diffusion, respectively. The variable u is the flow velocity field. The relaxation arising from L can be described by the material derivative  $\phi$  at the solid surface, i.e.

 $\dot{\phi} = \phi_t + u_\tau \partial_\tau \phi$ , where  $u_\tau$  is the tangential velocity of fluid on the solid surface. The mass conservation of system requires that

$$\dot{\rho} = \rho_t + \boldsymbol{u} \cdot \boldsymbol{\nabla} \rho = -\boldsymbol{\nabla} \cdot \boldsymbol{J}, \qquad (2.13)$$

where  $\rho$  is the fluid density and J is the diffusive mass flux, which is determined by the diffusive flux  $J_{\phi}$  and density difference between fluids.

Now we will combine the first law of thermodynamics and classical thermodynamic relations to derive the entropy balance equation. Then, we can obtain the momentum equation and the slip boundary condition using the Galilean invariance.

Similar to the variation of the total free energy F, the rate of change of F can be written as

$$\dot{F} = \int [w_{\phi}\phi_t] \,\mathrm{d}\Omega + \int [w_{\psi}\psi_t] \,\mathrm{d}\Omega + \int [L\phi_t] \,\mathrm{d}S.$$
(2.14)

Substituting (2.11), (2.12) and  $\phi_t = \dot{\phi} - u_\tau \partial_\tau \phi$  into (2.14), we obtain

$$\dot{F} = \int [-w_{\phi} \nabla \cdot \boldsymbol{J}_{\phi} - w_{\phi} \boldsymbol{u} \cdot \nabla \phi] \, \mathrm{d}\Omega + \int [-w_{\psi} \nabla \cdot \boldsymbol{J}_{\psi} - w_{\psi} \boldsymbol{u} \cdot \nabla \psi] \, \mathrm{d}\Omega + \int [L(\dot{\phi} - \boldsymbol{u}_{\tau} \partial_{\tau} \phi)] \, \mathrm{d}S.$$
(2.15)

Considering the fact that normal diffusion fluxes disappear at the solid surface because of the impermeability condition, specifically  $J_{\phi} \cdot \boldsymbol{n}|_{s} = 0$  and  $J_{\psi} \cdot \boldsymbol{n}|_{s} = 0$ , we obtain identities

$$-\int [w_{\phi} \nabla \cdot \boldsymbol{J}_{\phi}] \, \mathrm{d}\Omega = -\int [w_{\phi} \boldsymbol{J}_{\phi} \cdot \boldsymbol{n}] \, \mathrm{d}S + \int [\nabla w_{\phi} \cdot \boldsymbol{J}_{\phi}] \, \mathrm{d}\Omega = \int [\nabla w_{\phi} \cdot \boldsymbol{J}_{\phi}] \, \mathrm{d}\Omega \quad (2.16)$$

and  $-\int [w_{\psi} \nabla \cdot J_{\psi}] d\Omega = \int [\nabla w_{\psi} \cdot J_{\psi}] d\Omega$ . Similarly, we can obtain  $-\int [w_{\phi} u \cdot \nabla \phi] d\Omega = \int [\phi u \cdot \nabla w_{\phi}] d\Omega$  and  $-\int [w_{\psi} u \cdot \nabla \psi] d\Omega = \int [\psi u \cdot \nabla w_{\psi}] d\Omega$  using the

boundary condition  $\mathbf{u} \cdot \mathbf{n}|_{s} = 0$ , where  $\mathbf{n}$  is the unit vector orthogonal to boundaries. Then (2.15) can be rewritten as

$$\dot{F} = \int \left[ \nabla w_{\phi} \cdot \boldsymbol{J}_{\phi} + \nabla w_{\psi} \cdot \boldsymbol{J}_{\psi} \right] d\Omega + \int \left[ \phi \boldsymbol{u} \cdot \nabla w_{\phi} + \psi \boldsymbol{u} \cdot \nabla w_{\psi} \right] d\Omega + \int \left[ L \dot{\phi} - L \boldsymbol{u}_{\tau} \partial_{\tau} \phi \right] dS.$$
(2.17)

The first law of thermodynamics states that

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$$(\dot{U} + \dot{E}_k) = \dot{W} + \dot{Q},$$
 (2.18)

where U is the internal energy, W is the work done by the face force  $F_t$  and Q denotes the heat from the surroundings that keeps the system temperature constant. The variable  $E_k$  is the kinetic energy, and it is defined as  $E_k = \frac{1}{2} \int [\rho |\mathbf{u}|^2] d\Omega$ . The total entropy S is contributed by two components, namely the entropy of the system  $S_{sys}$  and the entropy of the surroundings  $S_{surr}$ , the latter of which is related to Q as  $\dot{S}_{surr} = -\dot{Q}/T$ . Using the thermodynamic relation  $\dot{U} = \dot{F} + T\dot{S}_{sys}$ , we have

$$\dot{S} = \dot{S}_{sys} + \dot{S}_{surr} = \dot{S}_{sys} - \frac{\dot{Q}}{T} = -\frac{1}{T}(\dot{F} + \dot{E}_k) + \frac{1}{T}\dot{W}.$$
(2.19)

Applying the Reynolds transport theorem and the Gauss divergence theorem, we can derive that

$$\dot{E}_{k} = \frac{1}{2} \int \left[ \frac{\partial (\rho \boldsymbol{u} \cdot \boldsymbol{u})}{\partial t} \right] d\Omega + \frac{1}{2} \int [\nabla \cdot ([\rho \boldsymbol{u} \cdot \boldsymbol{u}]\boldsymbol{u})] d\Omega$$

$$= \int \left[ \rho \boldsymbol{u} \cdot \boldsymbol{u}_{t} + \frac{1}{2} \boldsymbol{u} \cdot \boldsymbol{u} \rho_{t} \right] d\Omega$$

$$+ \frac{1}{2} \int \left[ (\rho \boldsymbol{u} \cdot \boldsymbol{u}) \nabla \cdot \boldsymbol{u} + (\boldsymbol{u} \cdot \boldsymbol{u}) \boldsymbol{u} \cdot \nabla \rho + \rho \boldsymbol{u} \cdot \nabla (\boldsymbol{u} \cdot \boldsymbol{u}) \right] d\Omega$$

$$= \int \left[ \boldsymbol{u} \cdot (\rho \boldsymbol{u}_{t} + \rho \boldsymbol{u} \cdot \nabla \boldsymbol{u}) \right] d\Omega + \frac{1}{2} \int \left[ (\boldsymbol{u} \cdot \boldsymbol{u}) (\rho_{t} + \boldsymbol{u} \cdot \nabla \rho) \right] d\Omega. \quad (2.20)$$

Substituting (2.13) into (2.20), and using integration by parts, we have

$$\dot{E}_k = \int [\boldsymbol{u} \cdot (\rho \boldsymbol{u}_t + \rho \boldsymbol{u} \cdot \nabla \boldsymbol{u} + \boldsymbol{J} \cdot \nabla \boldsymbol{u})] \, \mathrm{d}\Omega.$$
(2.21)

The work done by the stress  $\sigma$  and the fraction force  $f_s$  at the fluid-solid interface is expressed as

$$\dot{W} = -\int [\boldsymbol{\sigma}^{\mathrm{T}} : \boldsymbol{\nabla} \boldsymbol{u} + \boldsymbol{u} \cdot (\boldsymbol{\nabla} \cdot \boldsymbol{\sigma})] \,\mathrm{d}\Omega + \int [(\boldsymbol{\sigma} \cdot \boldsymbol{n}) \cdot \boldsymbol{u}_{s}] \,\mathrm{d}S + \int [\boldsymbol{f}_{\tau} \cdot \boldsymbol{u}_{s}] \,\mathrm{d}S, \quad (2.22)$$

where  $u_s$  is the slip velocity of fluids relative to the solid wall. Note that  $u_s$  is equal to  $u_{\tau}$  when the solid wall is static.

Substituting (2.17), (2.21) and (2.22) into (2.19), we can obtain the entropy balance equation

$$T\dot{S} = -\int [\boldsymbol{u} \cdot (\rho \boldsymbol{u}_t + \rho \boldsymbol{u} \cdot \nabla \boldsymbol{u} + \boldsymbol{J} \cdot \nabla \boldsymbol{u} + \nabla \cdot \boldsymbol{\sigma} + \phi \nabla \boldsymbol{w}_{\phi} + \psi \nabla \boldsymbol{w}_{\psi})] d\Omega$$

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$$-\int [\boldsymbol{\sigma}^{\mathrm{T}} : \boldsymbol{\nabla} \boldsymbol{u} - \boldsymbol{J}_{\phi} \cdot \boldsymbol{\nabla} w_{\phi} - \boldsymbol{J}_{\psi} \cdot \boldsymbol{\nabla} w_{\psi}] \, \mathrm{d}\Omega - \int [L\dot{\phi}] \, \mathrm{d}S \\ + \int \boldsymbol{u}_{\tau} \cdot [\boldsymbol{\sigma} \cdot \boldsymbol{n} + \boldsymbol{f}_{s} + L\partial_{\tau}\phi] \, \mathrm{d}S.$$
(2.23)

The Galilean invariance yields from (2.23)

$$\rho \boldsymbol{u}_t + \rho \boldsymbol{u} \cdot \nabla \boldsymbol{u} + \boldsymbol{J} \cdot \nabla \boldsymbol{u} + \nabla \cdot \boldsymbol{\sigma} + \phi \nabla w_{\phi} + \psi \nabla w_{\psi} = 0 \qquad (2.24)$$

in the bulk phases and

$$(\boldsymbol{\sigma} \cdot \boldsymbol{n} + \boldsymbol{f}_s + L\partial_\tau \phi) \cdot \boldsymbol{\tau} = 0 \tag{2.25}$$

at the fluid-solid interface. Equation (2.24) is the Navier-Stokes equation for twophase flows with soluble surfactants and equation (2.25) is the slip boundary condition. The total stress tensor can be split into  $\boldsymbol{\sigma} = p\boldsymbol{I} + \boldsymbol{\sigma}_{irrev}$ , where *p* is the reversible part, i.e. the pressure, and  $\boldsymbol{\sigma}_{irrev}$  is the irreversible part. With the incompressibility constraint  $\nabla \cdot \boldsymbol{u} = 0$ , we can derive that

$$\boldsymbol{\sigma}^{\mathrm{T}} \colon \boldsymbol{\nabla} \boldsymbol{u} = p \boldsymbol{\nabla} \cdot \boldsymbol{u} + \boldsymbol{\sigma}_{irrev}^{\mathrm{T}} \colon \boldsymbol{\nabla} \boldsymbol{u} = \boldsymbol{\sigma}_{irrev}^{\mathrm{T}} \colon \boldsymbol{\nabla} \boldsymbol{u}, \qquad (2.26)$$

and (2.25) can reduce to

$$(\boldsymbol{\sigma}_{irrev} \cdot \boldsymbol{n} + \boldsymbol{f}_s + L\partial_\tau \phi) \cdot \boldsymbol{\tau} = 0.$$
(2.27)

Thus, the entropy balance equation (2.23) is simplified as

$$-T\dot{S} = \int [\boldsymbol{\sigma}_{irrev}^{\mathrm{T}} : \boldsymbol{\nabla} \boldsymbol{u} + \boldsymbol{J}_{\phi} \cdot \boldsymbol{\nabla} w_{\phi} + \boldsymbol{J}_{\psi} \cdot \boldsymbol{\nabla} w_{\psi}] \,\mathrm{d}\Omega + \int [L\dot{\phi}] \,\mathrm{d}S.$$
(2.28)

Next, we will use the entropy balance equation (2.28) and the dissipation function to obtain diffusive fluxes and the irreversible stress tensor.

#### 2.2. Onsager's variational principle

An irreversible process (e.g. diffusion) taking place in a thermodynamic system leads to dissipation, and the principle of minimum energy dissipation produces the most probable course of an irreversible process when deviations from equilibrium conditions are small. For a multiphase system with MCL and soluble surfactants, there are several physically distinct sources of dissipations, and now we will discuss them in detail. The work done by a fluid on adjacent layers due to the action of shear force is transformed into heat, and this irreversible process is called viscous dissipation. The rate of viscous dissipation in the bulk phases  $R_v$  can be written as

$$R_{v}(\boldsymbol{u}) = \int \left[\frac{\boldsymbol{\sigma}_{irrev}^{2}}{\eta}\right] \mathrm{d}\Omega, \qquad (2.29)$$

where  $\eta$  is the fluid viscosity. Obviously,  $R_v$  is positive definite and quadratic in the rate  $\sigma_{irrev}$ .

As we mentioned before, chemical potential gradients in the bulk phases and L at the fluid-solid interface measure deviations from equilibrium conditions. The diffusive flux  $J_{\phi}$  arising from  $\nabla w_{\phi}$ , the diffusive flux  $J_{\psi}$  resulting from  $\nabla w_{\psi}$  and the composition relaxation  $\dot{\phi}$  at the solid surface coming from L are sources of additional

energy dissipation. According to the general rule governing entropy production in a thermodynamic process, the addition rate of dissipation  $R_t$  should be positive definite and quadratic in the rates  $\{J_{\phi}, \dot{\phi} \text{ and } J_{\psi}\}$ , e.g.  $R_t = R_d + R_{ds} + R_r$ , where

$$R_d(\phi) = \int \left[\frac{J_{\phi}^2}{M_{\phi}}\right] d\Omega, \quad R_{ds}(\psi) = \int \left[\frac{J_{\psi}^2}{M_{\psi}}\right] d\Omega, \quad R_r(\phi) = \int \left[\frac{\dot{\phi}^2}{\Gamma}\right] dS. \quad (2.30a-c)$$

Here  $R_d$  comes from the composition diffusion,  $R_{ds}$  arises from the diffusion associated with surfactants and  $R_r$  is attributed to the composition relaxation at the solid surface. Parameters  $M_{\phi}$ ,  $M_{\psi}$  and  $\Gamma$  are phenomenological parameters. Now we can obtain the free energy dissipation for a two-phase system with MCL and soluble surfactants  $R = R_v + R_d + R_{ds} + R_r$ .

The Onsager variation principle (Onsager 1931*a,b*; Qian *et al.* 2006) states that for an open system, the state evolution equation can be obtained by minimizing  $\Phi - T\dot{S}$ with respect to the rates  $\{J_{\phi}, J_{\psi}, \dot{\phi} \text{ and } \sigma_{irrev}\}$ . Here  $\Phi$  is the dissipation functional, which equals half the free energy dissipation R:

$$\Phi = \int \left[ \frac{\sigma_{irrev}^2}{2\eta} + \frac{J_{\phi}^2}{2M_{\phi}} + \frac{J_{\psi}^2}{2M_{\psi}} \right] d\Omega + \int \left[ \frac{\dot{\phi}^2}{2\Gamma} \right] dS.$$
(2.31)

Adding (2.28) and (2.31) together, we have

$$\Phi - T\dot{S} = \int \left[ \frac{\boldsymbol{\sigma}_{irrev}^2}{2\eta} + \frac{\boldsymbol{J}_{\phi}^2}{2M_{\phi}} + \frac{\boldsymbol{J}_{\psi}^2}{2M_{\psi}} + \boldsymbol{\sigma}_{irrev}^{\mathrm{T}} : \boldsymbol{\nabla}\boldsymbol{u} + \boldsymbol{J}_{\phi} \cdot \boldsymbol{\nabla}\boldsymbol{w}_{\phi} + \boldsymbol{J}_{\psi} \cdot \boldsymbol{\nabla}\boldsymbol{w}_{\psi} \right] \mathrm{d}\Omega + \int \left[ \frac{\dot{\phi}^2}{2\Gamma} + L\dot{\phi} \right] \mathrm{d}S.$$
(2.32)

By minimizing  $\Phi - T\dot{S}$  with respect to the rates  $\{J_{\phi}, J_{\psi}, \dot{\phi} \text{ and } \sigma_{irrev}\}$ , we can obtain the phase-field MCL model with soluble surfactants.

The Euler-Lagrange equation for minimizing  $\Phi - T\dot{S}$  with respect to  $J_{\phi}$  is

$$\boldsymbol{J}_{\phi} = -\boldsymbol{M}_{\phi} \boldsymbol{\nabla} \boldsymbol{w}_{\phi}, \qquad (2.33)$$

where the phenomenological parameter  $M_{\phi}$  can be viewed as a mobility coefficient, and is usually taken as a constant. Equation (2.33) indicates that the diffusive flux  $J_{\phi}$ and the chemical potential  $w_{\phi}$  satisfy the classical Fick's first law. Substituting (2.33) into the continuity equation (2.11) yields the desired Cahn-Hilliard type of equation for  $\phi$ :

$$\dot{\phi} = \phi_t + \boldsymbol{u} \cdot \nabla \phi = -\nabla \cdot \boldsymbol{J}_{\phi}, = \nabla \cdot M_{\phi} \nabla w_{\phi}.$$
(2.34)

Similarly, we can obtain the Cahn–Hilliard type of equation for  $\psi$ :

$$\dot{\psi} = \psi_t + \boldsymbol{u} \cdot \nabla \psi = -\nabla \cdot \boldsymbol{J}_{\psi}, = \nabla \cdot M_{\psi} \nabla w_{\psi}.$$
(2.35)

To combine with the logarithmic chemical potential  $w_{\psi}$ , the mobility coefficient  $M_{\psi}$  for  $\psi$  usually takes the form of  $m_{\psi}\psi(1-\psi)$ , where  $m_{\psi}$  is a constant. Coefficient  $M_{\psi}$  vanishes at the extreme points  $\psi = 0$  and  $\psi = 1$ . Substituting  $M_{\psi}$  into (2.35), and using (2.9), we have

$$\psi_t + \boldsymbol{u} \cdot \nabla \psi = \nabla \cdot \left( M_{\psi} \frac{\partial w_{\psi}}{\partial \psi} \nabla \psi \right) = \nabla \cdot \left( M_{\psi} \frac{k_b T_e}{\psi (1 - \psi)} \nabla \psi \right)$$
$$= \nabla \cdot (m_{\psi} k_b T_e \nabla \psi) = \nabla \cdot (D_{\psi} \nabla \psi), \qquad (2.36)$$

where  $D_{\psi}$  can be seen as the surfactant diffusive coefficient in the bulk phases. Then (2.35) is translated into the widely used bulk surfactant transport equation in sharp interface models.

By minimizing  $\Phi - T\dot{S}$  with respect to  $\dot{\phi}$  at the fluid-solid interface, we have

$$\dot{\phi} = \phi_t + \boldsymbol{u}_\tau \partial_\tau \phi = -\Gamma L. \tag{2.37}$$

Equation (2.37) is the dynamic contact line condition. It can be observed that the relaxation dynamics for  $\phi$  at the fluid-solid interface is proportional to the deviation of L from its equilibrium value zero.

Considering the variation of  $\Phi - T\dot{S}$  with respect to  $\sigma_{irrev}$ , we have

$$\boldsymbol{\sigma}_{irrev} = -\eta \boldsymbol{\nabla} \boldsymbol{u}. \tag{2.38}$$

Substituting (2.38) into (2.24), we obtain the desired Navier–Stokes equation for twophase flows with soluble surfactants

$$\rho \boldsymbol{u}_t + \rho \boldsymbol{u} \cdot \nabla \boldsymbol{u} + \boldsymbol{J} \cdot \nabla \boldsymbol{u} - \eta \Delta \boldsymbol{u} + \phi \nabla \boldsymbol{w}_{\phi} + \psi \nabla \boldsymbol{w}_{\psi} = 0.$$
(2.39)

Note that the viscous term  $\eta \Delta u$  can be readily generalized to  $\nabla \cdot \eta D(u)$  if  $\sigma_{irrev}$  is symmetric, where  $D(u) = \nabla u + \nabla^{T} u$ . For two phases with variable densities and viscosities, the density  $\rho$  and viscosity  $\eta$  usually have the following linear relations:

$$\rho = \frac{\rho_1 - \rho_2}{2}\phi + \frac{\rho_1 + \rho_2}{2}, \quad \eta = \frac{\eta_1 - \eta_2}{2}\phi + \frac{\eta_1 + \eta_2}{2}.$$
 (2.40*a*,*b*)

Substituting the density equation in (2.40) into the Cahn–Hilliard type of equation for  $\phi$ , and using the incompressibility constraint  $\nabla \cdot \boldsymbol{u} = 0$ , we get

$$\boldsymbol{J} = \frac{\rho_2 - \rho_1}{2} M_{\phi} \nabla w_{\phi} = \frac{\rho_1 - \rho_2}{2} \boldsymbol{J}_{\phi}.$$
 (2.41)

We naturally assume that the fraction force is linear to the slip velocity of fluids  $u_s$ , i.e.  $f_s = -\beta u_s$ , where  $\beta$  is the slip coefficient and it can be used to define a slip length  $l_s = \eta/\beta$ . Substituting (2.38) into (2.27), we obtain

$$\beta \boldsymbol{u}_s = -\eta \partial_n \boldsymbol{u}_\tau + L \partial_\tau \boldsymbol{\phi} \tag{2.42}$$

at the fluid-solid interface. The unbalanced Young stress  $L\partial_{\tau}\phi$  and  $\eta\partial_{n}u_{\tau}$  in (2.42) are manifestations of the interfacial tension and the viscous stress at the solid surface, respectively. In general, we denote the dynamic contact line condition (2.37) and the slip boundary condition (2.42) together as the GNBC.

When the relaxation parameter  $\Gamma$  in (2.37) tends to infinity, the dynamic contact line condition reduces to the static contact line condition as

$$L = \kappa \partial_n \phi + M'(\phi) = 0, \qquad (2.43)$$

and the slip boundary condition (2.42) becomes  $\beta u_s = -\eta \partial_n u_\tau$ , which is the wellknown NBC. The contact line effect disappears if we further set  $M'(\phi) = 0$  in (2.43). As the slip length  $l_s$  ( $l_s = \eta/\beta$ ) approaches zero, the NBC reduces to the traditional no-slip boundary condition. In the other limit,  $l_s$  approaches infinity, the tangential viscous stress on the boundary disappears. Thus the NBC interpolates between the no-slip limit and the limit of zero tangential viscous stress (Qian *et al.* 2006).

Two Cahn–Hilliard type of equations for phase-field variables, the incompressible Navier–Stokes equation and the GNBC for the MCL form the phase-field MCL model with soluble surfactants.

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#### 2.3. Dimensionless governing equation and numerical scheme

We use a global characteristic length scale  $L_c$ , a characteristic velocity  $U_c$  and properties (density  $\rho_1$  and viscosity  $\eta_1$ ) of fluid I to define some dimensionless parameters. With defined parameters, we obtain dimensionless Cahn–Hilliard type of equations:

$$\psi_t + \nabla \cdot (\boldsymbol{u}\psi) = \frac{1}{Pe_{\psi}} \nabla \cdot M_d \nabla w_{\psi}, \qquad (2.44)$$

$$w_{\psi} = Pi \ln\left(\frac{\psi}{1-\psi}\right) + \frac{1}{2Ex}\phi^2 - \frac{(\phi^2 - 1)^2}{4},$$
(2.45)

$$\phi_t + \nabla \cdot (\boldsymbol{u}\phi) = \frac{1}{Pe_{\phi}} \Delta w_{\phi}, \qquad (2.46)$$

$$w_{\phi} = -\phi + \phi^{3} - Cn^{2}\Delta\phi + \frac{1}{Ex}\psi\phi - \psi\phi(\phi^{2} - 1), \qquad (2.47)$$

where  $M_d = \psi(1 - \psi)$ . The dimensionless Navier–Stokes equations are

$$\rho \boldsymbol{u}_{t} + \rho \boldsymbol{u} \cdot \nabla \boldsymbol{u} + \boldsymbol{J} \cdot \nabla \boldsymbol{u} - \frac{1}{Re} \nabla \cdot \eta D(\boldsymbol{u}) + \nabla p + \frac{1}{ReCaCn} (\phi \nabla w_{\phi} + \psi \nabla w_{\psi}) = 0, \quad (2.48)$$
$$\nabla \cdot \boldsymbol{u} = 0, \quad (2.49)$$

where

$$\boldsymbol{J} = \frac{\lambda_{\rho} - 1}{2Pe_{\phi}} \boldsymbol{\nabla} w_{\phi}, \quad \rho = \frac{1 - \lambda_{\rho}}{2} \phi + \frac{1 + \lambda_{\rho}}{2}, \quad \eta = \frac{1 - \lambda_{\eta}}{2} \phi + \frac{1 + \lambda_{\eta}}{2}. \quad (2.50a - c)$$

The impermeability boundary condition of the solid surface is

$$\partial_n \psi = 0, \quad \partial_n w_\phi = 0, \quad \partial_n w_\psi = 0, \quad \boldsymbol{u} \cdot \boldsymbol{n} = 0, \quad \text{on } S.$$
 (2.51*a*-*c*)

The dimensionless dynamic contact line condition for  $\phi$  at the solid surface is

$$\phi_t + \boldsymbol{u}_\tau \cdot \partial_\tau \phi = -\frac{1}{Pe_s}L, \quad \text{on } S,$$
(2.52)

where  $L = Cn\partial_n \phi + M'(\phi)$  and  $M(\phi) = -(\sqrt{2}/3) \cos \theta_s \sin(\pi \phi/2)$ . The slip boundary condition can be written as

$$\frac{Ca\eta}{L_s}\boldsymbol{u}_s = -Ca\eta\partial_n\boldsymbol{u}_\tau + L\partial_\tau\phi, \quad \text{on } S.$$
(2.53)

Several dimensionless parameters are used in the above governing equation. These are (1) the Reynolds number  $Re = \rho_1 L_c U_c / \eta_1$ , (2) the capillary number  $Ca = 2\sqrt{2}\eta_1 U_c/3\sigma$ , (3) the Cahn number  $Cn = \varepsilon/L_c$ , (4) Péclet numbers  $Pe_{\phi} = L_c U_c / (M_{\phi}A)$  and  $Pe_{\psi} = L_c U_c / (m_{\psi}A)$ , (5)  $Pe_s = U_c Cn/(\kappa\Gamma)$ , (6)  $Ex = \kappa/(W\varepsilon^2)$ , which determines the bulk solubility, (7)  $Pi = k_b T_e / (A\phi_{\pm}^2)$ , which is a temperature-dependent constant, (8) the slip length  $L_s = \eta/(\beta L_c)$  and (9) the density ratio  $\lambda_{\rho} = \rho_2 / \rho_1$  and viscosity ratio  $\lambda_{\eta} = \eta_2 / \eta_1$ .

If we consider the extra body force in the momentum equation, e.g. the gravitational force, (2.48) can be modified into

$$\rho \boldsymbol{u}_{t} + \rho \boldsymbol{u} \cdot \nabla \boldsymbol{u} + \boldsymbol{J} \cdot \nabla \boldsymbol{u} - \frac{1}{Re} \nabla \cdot \eta D(\boldsymbol{u}) + \nabla p + \frac{1}{BoCn} (\phi \nabla w_{\phi} + \psi \nabla w_{\psi}) - \rho \boldsymbol{g} = 0,$$
(2.54)

where Bo is the Bond number and g is the unit vector denoting the direction of body force.

The governing system (2.44)-(2.53) satisfies the following energy dissipation law:

$$\dot{F}_{tot}(\boldsymbol{u}, \phi, \psi) = -\frac{1}{Pe_{\phi}} \|\nabla w_{\phi}\|^{2} - \frac{1}{Pe_{\psi}} \|\sqrt{m_{\psi}} \nabla w_{\psi}\|^{2} - \frac{CaCn}{2} \|\sqrt{\eta}D(\boldsymbol{u})\|^{2} - \frac{Cn}{Pe_{s}} \|L\|_{s}^{2} - \frac{CaCn}{L_{s}} \|\sqrt{\eta}\boldsymbol{u}_{s}\|_{s}^{2} \leq 0,$$
(2.55)

where  $F_{tot}$  is the dimensionless total energy, which is the sum of the kinetic energy and the total free energy F:

$$F_{tot}(\boldsymbol{u}, \phi, \psi) = \int_{\Omega} \left( \frac{ReCaCn}{2} \rho |\boldsymbol{u}|^2 + \frac{Cn^2}{2} |\nabla \phi|^2 + \frac{(\phi^2 - 1)^2}{4} + PiG(\psi) - \frac{\psi(\phi^2 - 1)^2}{4} + \frac{\psi\phi^2}{2Ex} \right) d\Omega + Cn \int_{S} M(\phi) dS.$$
(2.56)

Physically, the energy dissipation law (2.55) states that the total energy of a twophase system with MCL and soluble surfactants will decrease from internal dissipation. Note that the energy dissipation law in (2.55) is actually guaranteed as a part of the thermodynamic consistency by the Onsager variational principle.

The nonlinearly coupled governing system (2.44)–(2.53) can be transformed into an equivalent one by introducing appropriate scalar auxiliary variables, and nonlinear potentials, e.g. the double-well potential and the logarithmic Flory-Huggins potential, are then treated semi-explicitly (Kou, Sun & Wang 2018; Shen, Xu & Yang 2018; Zhu et al. 2018). For the stress and convection terms, which come from the nonlinear couplings between phase-field variables and velocity, we use some subtle implicit-explicit treatments of them (Yu & Yang 2017). For the Navier-Stokes equation, a splitting method based on pressure stabilization is implemented to decouple the computation of velocity from pressure (Guermond & Salgado 2009; Shen & Yang 2015). A stabilization term is artificially added to balance the explicit nonlinear term associated with the surface energy at the fluid-solid interface (Shen, Yang & Yu 2015). We use a finite difference method on staggered grids to complete the spatial discretization (Chen, Sun & Zhang 2018; Aniszewski et al. 2019; Malan et al. 2019). Note that advection terms in the Cahn-Hilliard and Navier-Stokes equations are discretized by the MINMOD scheme (Li et al. 2015; Moukalled, Mangani & Darwish 2016; Liu et al. 2019), which is a combination of the central difference, first-order and second-order upwind schemes. The MINMOD scheme not only achieves second-order accuracy in space, but also preserves the physical properties of convection. Other spatial derivatives are discretized using the standard central difference schemes. A preconditioned biconjugate gradient stabilized method (BICGSTAB) is used to solve the above variables (Zhu et al. 2016; Yan et al. 2019; Zeng, Yao & Shao 2019).

### 3. Equilibrium properties of surfactant adsorption

In equilibrium, chemical potentials throughout the whole system are constants. Using this fact, we can obtain certain equilibrium properties and adsorption isotherm relations, including equilibrium profiles for phase-field variables, the Langmuir isotherm and the equilibrium equation of state. We first consider the equilibrium profile for  $\phi$  at constant surfactant concentration. For a two-phase system without surfactants, the chemical potential  $w_{\phi}$  reads

$$w_{\phi} = -\phi + \phi^3 - Cn^2 \Delta \phi, \qquad (3.1)$$

and the equilibrium profile for  $\phi$  can be written as

$$\phi(x) = \tanh(x/[\sqrt{2Cn}]). \tag{3.2}$$

We denote  $\psi_b$  and  $\phi_b$  as the surfactant bulk concentration and phase bulk value, respectively. Here  $\psi_b$  is far smaller than 1 ( $\psi_b \ll 1$ ). Considering the fact that the chemical potential  $w_{\phi}$  is equal throughout the system, we have

$$w_{\phi} = -\phi + \phi^{3} - Cn^{2}\Delta\phi + \frac{1}{Ex}\psi_{b}\phi - \psi_{b}\phi(\phi^{2} - 1) = 0.$$
(3.3)

Equation (3.3) can be rewritten as

$$w_{\phi} = -\left(1 + \frac{1}{Ex} - \frac{1}{Ex(1 - \psi_b)}\right)\phi + \phi^3 - \frac{Cn^2}{1 - \psi_b}\Delta\phi$$
  
=  $-\left(1 + \frac{1}{Ex} - \frac{1}{Ex(1 - \psi_b)}\right)\phi_b^3\phi_b^{-2}(\phi_b^{-1}\phi) + \phi_b^3(\phi_b^{-1}\phi)^3$   
 $-\phi_b^3\frac{Cn^2}{\phi_b^2(1 - \psi_b)}\Delta(\phi_b^{-1}\phi).$  (3.4)

We can further reformulate (3.4) as

$$w_{\phi} = \phi_b^3 [-(\phi_b^{-1}\phi) + (\phi_b^{-1}\phi)^3 - Cn_{\psi}^2 \Delta(\phi_b^{-1}\phi)]$$
(3.5)

by using

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$$\phi_b^2$$
: = 1 +  $\frac{1}{Ex} - \frac{1}{Ex(1 - \psi_b)}, \quad Cn_{\psi}^2$ : =  $\frac{Cn^2}{\phi_b^2(1 - \psi_b)}.$  (3.6*a*,*b*)

Equation (3.5) has a similar form to (3.1). Referring to (3.2), the equilibrium profile for the scaled variable  $\phi_b^{-1}\phi$  can be written as  $\phi_b^{-1}\phi = \tanh(x/\sqrt{2}Cn_{\psi})$ . Replacing  $Cn_{\psi}$  with Cn, we obtain

$$\phi(x) = \phi_b \tanh\left(\phi_b \sqrt{1 - \psi_b} \frac{x}{\sqrt{2}Cn}\right), \qquad (3.7)$$

with

$$\phi_b^2 = 1 + \frac{1}{Ex} - \frac{1}{Ex(1 - \psi_b)}.$$
(3.8)

Using (3.7) and (3.8), we can derive the gradient at the interface (x = 0):

$$\partial_x \phi|_{x=0} = \frac{\phi_b^2 \sqrt{1 - \psi_b}}{\sqrt{2}Cn} = \frac{\sqrt{1 - \psi_b}}{\sqrt{2}Cn} \left(1 - \frac{\psi_b}{Ex(1 - \psi_b)}\right) < \frac{1}{\sqrt{2}Cn}.$$
 (3.9)

It can be observed from (3.9) that the introduction of surfactants increases the interface thickness, which is determined by the Cahn number Cn, the surfactant bulk concentration  $\psi_b$  and the parameter Ex. The decrease in Ex or increase in  $\psi_b$  will further decrease the gradient of  $\phi$  on the interface, leading to a more diffuse interface. Since the surfactant bulk concentration  $\psi_b$  is far smaller than unity ( $\psi_b \ll 1$ ), the variation of the interface thickness is small even at high surfactant bulk concentration. Thus, to some extent, it is reasonable to assume that the interface thickness is unchanged when we analytically derive some equilibrium properties of surfactant adsorption, especially at low surfactant bulk concentration. This simplification will greatly facilitate our derivations. Then (3.9) can be reduced to

$$\partial_x \phi|_{x=0} = 1/(\sqrt{2Cn}).$$
 (3.10)

Now we analyse the equilibrium properties of surfactant adsorption (Liu & Zhang 2010; Engblom *et al.* 2013). The chemical potential  $w_{\psi}$  at any position can be written as

$$w_{\psi} = Pi \ln\left(\frac{\psi}{1-\psi}\right) + \frac{1}{2Ex}\phi^2 - \frac{(\phi^2 - 1)^2}{4}$$
(3.11)

and  $w_{\psi}$  in the pure phases reads

$$w_{\psi_b} = Pi \ln\left(\frac{\psi_b}{1 - \psi_b}\right) + \frac{1}{2Ex}\phi_b^2 - \frac{(\phi_b^2 - 1)^2}{4}.$$
(3.12)

Since  $w_{\psi}$  is constant at equilibrium, subtracting (3.12) from (3.11), and introducing the intermediate variable  $\psi_c$ , we get the relation

$$Pi\ln\psi_c = -\frac{1}{2Ex}(\phi_b^2 - \phi^2) - \frac{1}{4}[(\phi^2 - \phi_b^2)(\phi_b^2 + \phi^2 - 2)].$$
(3.13)

Then the equilibrium profile for  $\psi$  can be obtained as

$$\psi = \frac{\psi_b}{\psi_b + \psi_c (1 - \psi_b)}.$$
(3.14)

Considering the fact that  $\phi = 0$  on the interface of fluids, phase bulk value  $\phi_b = \pm 1$  and  $\psi_b \ll 1$ , (3.14) and (3.13) can be simplified as

$$\psi_0 = \frac{\psi_b}{\psi_b + \psi_c},\tag{3.15}$$

$$Pi \ln \psi_c = -\frac{1}{4} \left( 1 + \frac{2}{Ex} \right),$$
 (3.16)

where  $\psi_0$  is the equilibrium surfactant concentration on the interface. Equation (3.15) is the typical Langmuir isotherm and the intermediate variable  $\psi_c$  can be viewed as the Langmuir adsorption constant. Given specific *Pi* (temperature-dependent constant) and  $\psi_c$ , the parameter *Ex* can be obtained from (3.16). The adsorption isotherm is important for the following simulations.

Shape interface models simulate interfacial flows with surfactants using an equilibrium equation of state, which relates the dynamic interfacial tension to the surfactant concentration on the interface, and the equilibrium equation of state can

be derived by integration of the Gibbs equation  $d\sigma = -\psi_0 dw_{\psi,0}$  (isothermal system), where  $w_{\psi,0}$  is the chemical potential on the interface. However, for the phase-field model, the excess amount of surfactants has to be obtained via integration over the whole diffuse interface, and thus there exists no analytical solution for the equilibrium equation of state. Following the idea in Van der Sman & Van der Graaf (2006), we assume that the excess amount of surfactants is proportional to  $\psi_0$ , so that the interfacial lowering  $d\sigma$  is proportional to that of the sharp interface with a coefficient k, i.e.

$$\mathrm{d}\sigma = -k\psi_0 \,\mathrm{d}w_{\psi,0},\tag{3.17}$$

where the coefficient k should be independent of  $\psi_0$ . We know that k = 1 for the sharp interface model, while  $k \neq 1$  for the diffuse interface model due to the finite interface thickness. As we mentioned above, k depends on the excess amount of surfactants. Considering the fact that the Langmuir isotherm determines the equilibrium profile of surfactants (diffuse interface), we can infer from (3.15) and (3.16) that, for the given Langmuir adsorption constant  $\psi_c$ , the excess surfactant concentration is a function of the interfacial thickness Cn,  $\psi_0$  and Ex (*Pi* can be determined by Ex and  $\psi_c$ ). As k is independent of  $\psi_0$ , k only depends on Ex once the interfacial thickness Cn is specified.

Substituting (3.11) into (3.17), and integrating on both sides of (3.17), we obtain the equation of state

$$\Delta \sigma = \sigma - \sigma_0 = kPi \ln(1 - \psi_0). \tag{3.18}$$

Equation (3.18) will be validated in §4.1.

#### 4. Numerical results

In this section, we first use the classical droplet spread case to validate the MCL model and the analytically derived equilibrium properties. Then we investigate the droplet dynamics with soluble surfactants on a chemically patterned surface.

#### 4.1. Numerical validation

Most previous studies of two-phase flows with MCL utilized sharp interface models with an equilibrium equation of state, and their models only considered insoluble surfactants on the interface, which are quite different from the diffuse interface model with soluble surfactants in this study. Thus, it is difficult to find an appropriate benchmark to validate our model. If the surfactant concentration is set to zero (clean droplet), then the derived model reduces to the phase-field MCL model, which can be easily validated. We first use a classical benchmark to verify the phase-field MCL model, as shown in figure 1. The rectangular computational domain  $\Omega$  is set as  $[0, 1] \times [0, 2]$ , and periodic boundary conditions are applied in the horizontal direction. Initially, a semicircular droplet with radius  $R_0 = 0.5$  and contact angle  $\theta_0 = 90^\circ$  is placed on the bottom surface (figure 1a). The gravitational effect is neglected in this case. The Reynolds number Re, the capillary number Ca and the Péclet number  $Pe_{\phi}$  are taken as 10, 0.1 and 10, respectively. The Cahn number Cn, measuring the thickness of the diffuse interface, is 0.01. The relaxation parameter  $Pe_s$  and slip length  $L_s$  are set to 0.005 and 0.0038, respectively. Both density ratio  $\lambda_{\rho}$  and viscosity ratio  $\lambda_{\nu}$  of the droplet to the surrounding fluid are 1.1. We use a grid size of  $300 \times 150$ and time step size  $\delta t = 2.5 \times 10^{-4}$  in all simulations.

The droplet driven by the unbalanced Young stress will spread or recoil to the equilibrium shape with the prescribed static contact angle  $\theta_s$  ( $\theta_s$  is equal to the



FIGURE 1. (Colour online) Illustration of (a) initial shape of the droplet with a radius of  $R_0$  released on the bottom surface and (b) equilibrium shape of the droplet. The size of the computational domain is  $[0, L_x] \times [0, L_y]$ . In (a), the droplet centre is located at  $(L_x/2, 0)$ . In (b), L is the spreading length and H is the droplet height. The gravitational effect is neglected in this case. Angle  $\theta_0$  is the initial contact angle and  $\theta_e$  is the equilibrium contact angle. Note that  $\theta_e$  is equal to the static contact angle  $\theta_s$  for a clean droplet.



FIGURE 2. (Colour online) Comparison of analytical and numerical values of spreading length L and droplet height H at different static contact angles  $\theta_s$ . Here  $\theta_s$  ranges from 45° to 135° with an interval 15°.

equilibrium contact angle  $\theta_e$  for a clean droplet). In equilibrium, the spreading length L and droplet height H in figure 1(b) can be analytically obtained by the law of mass conservation (Cai *et al.* 2014):

$$L = 2R_0 \sqrt{\frac{\pi}{2(\theta_s - \sin\theta_s \cos\theta_s)}} \sin\theta_s, \quad H = R_0 \sqrt{\frac{\pi}{2(\theta_s - \sin\theta_s \cos\theta_s)}} (1 - \cos\theta_s).$$
(4.1*a*,*b*)

We conduct several simulations in a wide range of surface wettability for both hydrophilic and hydrophobic cases ( $\theta_s$  varies from 45° to 135°). Analytical and numerical values of *L* and *H* are compared in figure 2, and a good agreement is observed for all values of  $\theta_s$ .

To clearly demonstrate the effect of surfactants on the MCL, we compare the dynamics of clean and contaminated (with surfactants) droplets. The Langmuir adsorption constant  $\psi_c$  and the parameter Ex take values of 0.017 and 1, respectively, with the value of Pi determined from (3.16). Other parameters are taken as before. Both hydrophilic ( $\theta_s = 60^\circ$ ) and hydrophobic ( $\theta_s = 120^\circ$ ) cases are considered in this study. For the contaminated droplet, the initialization of surfactant concentration is



FIGURE 3. (Colour online) Profiles of (a) contaminated droplet at different times and (b) clean and contaminated droplets in equilibrium on a hydrophilic surface with static contact angle  $\theta_s = 60^\circ$ . For the contaminated droplet, the initial surfactant bulk concentration  $\psi_b$  is  $1.5 \times 10^{-2}$ . In (b), equilibrium contact angles  $\theta_e$  for clean and contaminated droplets are  $60^\circ$  and  $52^\circ$ , respectively.



FIGURE 4. (Colour online) Profiles of (a) contaminated droplet at different times and (b) clean and contaminated droplets in equilibrium on a hydrophobic surface with static contact angle  $\theta_s = 120^\circ$ . For the contaminated droplet, the initial surfactant bulk concentration  $\psi_b$  is  $1.5 \times 10^{-2}$ . In (b), equilibrium contact angles for clean and contaminated droplets are  $120^\circ$  and  $129^\circ$ , respectively.

performed using the analytical prediction in (3.15) for  $\psi$  with the initial surfactant bulk concentration  $\psi_b = 1.5 \times 10^{-2}$ .

Figure 3(a) gives the evolution of a contaminated droplet on a hydrophilic surface at different times (t ranges from 0 to 10). The contaminated droplet constantly spreads until the steady state is reached. Equilibrium contact angles  $\theta_e$  for clean and contaminated droplets in figure 3(b) are  $60^{\circ}$  and  $52^{\circ}$ , respectively. Obviously, the presence of surfactants makes the droplet more hydrophilic on a hydrophilic surface. In contrast to the hydrophilic surface, surfactants make the droplet more hydrophobic on a hydrophobic surface by increasing the equilibrium contact angle  $\theta_e$  from 120° to 129°, as shown in figure 4. Results in figures 3 and 4 are consistent with the results obtained for sharp interface models (Lai et al. 2010; Xu & Ren 2014; Zhang et al. 2014). We further calculate the spreading length L, the droplet height H and  $\theta_e$  for the contaminated droplet ( $\psi_b = 1.5 \times 10^{-2}$ ) in a wide range of surface wettability ( $\theta_s$ varies from 45° to 135°). Analytical L and H for the clean droplet in figure 5 serve as a comparison. It is observed from figure 5 that the effect of surfactants is more obvious on the strong hydrophilic or hydrophobic surface. The inset gives  $\theta_{e}$  of the contaminated droplet. The blue line in the inset represents static contact angles  $\theta_s$ of the clean droplet (the slope of this line is 1), and it serves as a reference. We



FIGURE 5. (Colour online) Numerical spreading length L (points) and droplet height H (points) for the contaminated droplet, and analytical values (lines) calculated from static contact angles serve as a comparison. For the contaminated droplet, the initial surfactant bulk concentration  $\psi_b$  is  $1.5 \times 10^{-2}$ . The inset gives  $\theta_e$  of the contaminated droplet. It can be observed that  $\theta_e$  can be approximately predicted by  $\theta_s$  through a linear relationship:  $\theta_e = 1.3\theta_s - 25.7$ .

found that  $\theta_e$  can be approximately predicted by  $\theta_s$  through a linear relationship:  $\theta_e = 1.3\theta_s - 25.7$ .

We also extend our work to a three-dimensional computational domain  $[0, 0.8]^2 \times [0, 0.4]$ . A grid size of  $110^2 \times 55$  and time step size  $\delta t = 8 \times 10^{-4}$  are used in simulations. For the contaminated droplet, the initial surfactant bulk concentration  $\psi_b$  is  $2.5 \times 10^{-2}$ . Results in figure 6 clearly demonstrate the effect of surfactants on the contact line dynamics. The presence of surfactants reduces  $\theta_e$  from 60° to 42° on the hydrophilic surface, and increases  $\theta_e$  from 120° to 139° on the hydrophobic surface.

The Young equation can well explain the effect of surfactants on the droplet dynamics on the solid surface. As in Wang *et al.* (2008), we can derive that

$$\int_{int} [L\partial_{\tau}\phi] \,\mathrm{d}\tau = \int_{int} [Cn\partial_{n}\phi\partial_{\tau}\phi + M'(\phi)\partial_{\tau}\phi] \,\mathrm{d}\tau = \sigma_{e}\cos\theta_{e} + \Delta\sigma_{fs}, \qquad (4.2)$$

where  $\int_{int} d\tau$  denotes the integration across the fluid-fluid interface along the  $\tau$ -direction,  $\Delta \sigma_{fs}$  is a function of the local composition at the solid surface measuring the fluid-solid interfacial free energy per unit area and  $\sigma_e$  is the interfacial tension of a contaminated droplet in equilibrium. Equation (4.2) indicates that the unbalanced Young stress dominates the evolution of contact angle. It drives the droplet at two contact points to spread on a hydrophilic surface or to recoil on a hydrophobic surface. In equilibrium, the unbalanced Young stress decreases to zero (figure 7), namely L = 0, and (4.2) reduces to the classical Young equation

$$\sigma_e \cos \theta_e + \Delta \sigma_{fs} = 0. \tag{4.3}$$

The boundary condition  $\partial_n \psi = 0$  allows the presence of free surfactants on the fluidsolid interface, but these surfactants do not affect the fluid-solid interfacial tension



FIGURE 6. (Colour online) Profiles of clean and contaminated droplets on (*a*) hydrophilic  $(\theta_s = 60^\circ)$  and (*b*) hydrophobic  $(\theta_s = 120^\circ)$  surfaces. For the contaminated droplet, the initial surfactant bulk concentration  $\psi_b$  is  $2.5 \times 10^{-2}$ . The computation domain is  $[0, 0.8]^2 \times [0, 0.4]$ . We use a grid size of  $110^2 \times 55$  and time step size  $\delta t = 8 \times 10^{-4}$  in simulations. In (*a*), equilibrium contact angles  $\theta_e$  of clean and contaminated droplets are  $60^\circ$  and  $42^\circ$ , respectively. In (*b*), equilibrium contact angles  $\theta_e$  of clean and contaminated droplets are  $120^\circ$  and  $139^\circ$ , respectively.



FIGURE 7. (Colour online) Evolutions of unbalanced Young stresses at right contact points of clean and contaminated droplets ( $\psi_b = 1.5 \times 10^{-2}$ ). The static contact angle  $\theta_s$  of the hydrophilic surface is 60°.

through adsorption or the like, so clean and contaminated droplets have the same  $\Delta \sigma_{fs}$ . Then we have

$$\sigma_e \cos \theta_e = \sigma_0 \cos \theta_s, \tag{4.4}$$

where  $\sigma_0$  is the interfacial tension of a clean droplet. The addition of surfactants greatly reduces the interfacial tension between fluids, resulting in  $\sigma_e < \sigma_0$ . We can



FIGURE 8. (Colour online) The linear relationship between the interfacial tension lowering  $\Delta\sigma/\sigma_0$  and  $\ln(1 - \psi_0)$ . Fitted formulas of green and blue lines can be approximated as  $\Delta\sigma/\sigma_0 = 0.3396 \ln(1 - \psi_0)$  and  $\Delta\sigma/\sigma_0 = 0.1942 \ln(1 - \psi_0)$ , respectively. These results directly validate the equilibrium equation of state (3.18).

derive that  $\cos \theta_e > \cos \theta_s$  from (4.4). Thus,  $\theta_e$  is smaller than  $\theta_s$  in the hydrophilic case (the contaminated droplet becomes more hydrophilic), and  $\theta_e$  is larger than  $\theta_s$  in the hydrophobic case (the contaminated droplet becomes more hydrophobic).

We denote the unbalanced Young stresses at right contact points of clean and contaminated droplets as  $F_{Rc}$  and  $F_{Rs}$ , respectively. Figure 7 gives evolutions of  $F_{Rc}$  and  $F_{Rs}$ , and the whole process can be divided into three stages. In the first stage, the contaminated droplet spreads faster than the clean droplet since  $F_{Rs}$  is larger than  $F_{Rc}$ . During the droplet spreading process, the unbalanced Young stress always drags the right contact point forward to reduce the contact angle, and it decreases as the contact angle changes until equilibrium. Thus, to some extent, the unbalanced Young stress can be reflected in the contact angle than the clean droplet, which explains why the change in  $F_{Rs}$  is more dramatic in the second stage. It can be observed that  $F_{Rs}$  is larger than  $F_{Rc}$  in the third stage, and this fact may account for a smaller equilibrium contact angle of the contaminated droplet.

The interfacial tension lowering  $\Delta \sigma$  of a contaminated droplet in equilibrium can be calculated from

$$\Delta \sigma = \sigma_e - \sigma_0 = \sigma_0 \left( \frac{\cos \theta_s - \cos \theta_e}{\cos \theta_e} \right). \tag{4.5}$$

Now we perform a series of numerical experiments to verify the linear relationship between  $\Delta\sigma$  and  $\ln(1-\psi_0)$  analytically obtained in (3.18). Two different scenarios are considered in this study: Ex = 0.5 and Ex = 1. In each scenario, we conduct simulations with different surfactant bulk concentrations, e.g.  $\psi_b = 1 \times 10^{-2}$ ,  $1.5 \times 10^{-2}$ and  $2 \times 10^{-2}$ . The static contact angle  $\theta_s$  of the bottom surface is taken to be 60°. From the resulting profile of surfactant concentration in equilibrium, the surfactant loading of interface  $\psi_0$  can be directly obtained. The equilibrium contact angle  $\theta_e$ can be easily calculated when the contaminated droplet reaches the steady state, and then we get the interfacial tension lowering  $\Delta\sigma$  from (4.5). Obviously, there is a linear relationship between  $\Delta\sigma$  and  $\ln(1 - \psi_0)$ , as plotted in figure 8, which



FIGURE 9. (Colour online) The relative interfacial tension  $\sigma_e/\sigma_0$  at different surfactant bulk concentrations  $\psi_b$ . The Langmuir adsorption constant  $\psi_c$  is 0.017. The analytical equation (4.6) fits the simulated values very well.

directly validates the equilibrium equation of state (3.18). We use linear formulas to fit simulated values at different Ex, and fitted equations of green and blue lines can be approximated as  $\Delta \sigma / \sigma_0 = 0.3396 \ln(1 - \psi_0)$  and  $\Delta \sigma / \sigma_0 = 0.1942 \ln(1 - \psi_0)$ , respectively. It worth noting that Ex plays an important role in reducing the interfacial tension, and its effect is more obvious at higher interfacial surfactant concentration. We infer, in the last part of § 3, that the coefficient k is determined by Ex for the given Langmuir adsorption constant  $\psi_c$  and interfacial thickness Cn. It can be observed that the slopes (kPi) of two fitted curves in figure 8 equal 0.1942 (Ex = 1)and 0.3396 (Ex = 0.5), respectively. The dimensionless parameter Pi can be calculated from (3.16). Then we can obtain that k equals 1.05 and 1.11 for the cases of Ex = 1and Ex = 0.5, respectively. This result verifies our inference that k depends on Ex.

Using the Langmuir isotherm in (3.15) and equilibrium equation of state (3.18), we obtain the relationship between the relative interfacial tension  $\sigma_e/\sigma_0$  and surfactant bulk concentration  $\psi_b$ :

$$\frac{\sigma_e}{\sigma_0} = -\frac{kPi}{\sigma_0}\ln(\psi_b + \psi_c) + \frac{kPi}{\sigma_0}\ln\psi_c + 1, \qquad (4.6)$$

where the Langmuir adsorption constant  $\psi_c$  is 0.017 in this study. It can be observed that (4.6) fits the simulated values very well in figure 9, indicating the correctness of the Langmuir isotherm and the equilibrium equation of state to some extent. Again, we can see that the coefficient k is determined by Ex.

#### 4.2. Droplet dynamics on a chemically patterned surface

## 4.2.1. Phase diagram of flow states

Having validated the MCL model, we investigate the droplet dynamics with soluble surfactants on a chemically patterned surface. The computational domain is  $\Omega = [0, 4] \times [0, 1]$  with periodic boundary conditions applied on the horizontal direction, as shown in figure 10. Initially, a semicircular droplet with a radius of 0.5 is placed on the bottom surface with static contact angles  $\theta_1$  ( $\theta_1 < 90^\circ$ ) for the hydrophilic A-type stripe and  $\theta_2$  ( $\theta_2 > 90^\circ$ ) for the hydrophobic B-type stripe. The droplet centre is located at (1, 0). A constant body force along the horizontal



FIGURE 10. (Colour online) Schematic of computation domain  $\Omega = [0, L] \times [0, H]$ . A semicircular droplet with a radius of L/8 is placed on a chemically patterned surface with static contact angles  $\theta_1$  ( $\theta_1 < 90^\circ$ ) for the hydrophilic A-type stripe (black stripe) and  $\theta_2$  ( $\theta_2 > 90^\circ$ ) for the hydrophobic B-type stripe (green stripe). The droplet centre is located at (L/4, 0). The droplet is pushed along the horizontal direction by a constant body force.

direction is applied on the droplet. A grid size of  $600 \times 150$  and time step size  $\delta t = 5 \times 10^{-4}$  are used in all simulations. The Reynolds number Re and Péclet numbers  $Pe_{\phi}$  and  $Pe_{\psi}$  are taken as 20, 100 and 10, respectively. The value of Cahn number Cn is 0.01. The relaxation parameter  $Pe_s$  and slip length  $L_s$  are set to 0.005 and 0.0038, respectively. Both density ratio  $\lambda_{\rho}$  and viscosity ratio  $\lambda_{\nu}$  of the droplet to the surrounding fluid are 2. The initial surfactant bulk concentration  $\psi_b$  is  $1.5 \times 10^{-2}$ . To clearly demonstrate the effect of surfactants, we compare the dynamics of clean and contaminated droplets.

Figure 11 gives the evolution of droplets on a chemically patterned surface. At first, both clean and contaminated droplets spread out over the hydrophilic surface due to the unbalanced Young stress, and then move forward under the action of a constant body force (figure 11b). After crossing the junction of wettability transition, both droplets suffer from large deformation and break up into daughter droplets. Obviously, compared with the clean droplet, the contaminated droplet has a larger advancing angle on the hydrophobic B-type stripe and a smaller receding angle on the hydrophilic A-type stripe (figure 11c). We also note that the break-up of the contaminated droplet occurs earlier than that of the clean droplet (figure 11d). After the break-up, the spreading droplets left on the hydrophobic stripe begin to contract (figure 11e). Subsequently, daughter droplets detached from the solid surface move towards daughter droplets in contact with the B-type stripe (figure 11f). As two clean daughter droplets approach each other, the film between them becomes very thin, and then they merge together due to the effect of interfacial tension. The merging droplet continues to slide on the hydrophilic A-type stripe (figure 11*i*). While the thin film between two contaminated daughter droplets is always maintained at a certain thickness until they slide over each other (figure 11h). Note that both contaminated daughter droplets eventually detach from the bottom surface. Figure 12 shows the evolution of surfactant concentration. The surfactant concentration around the interface is much larger than that for other regions, and the distribution of surfactants is non-uniform along the interface. In fact, the different behaviour between contaminated and clean droplets is caused by (1) the uniform reduction of interfacial tension and (2) the non-uniform effects from the non-uniform interfacial tension and the Marangoni stress along the interface. We also see that surfactants are swept into the bulk phases when concentration reaches a maximum at the droplet tip (figure 12e). Figure 13 presents the evolutions of pressure field and surfactant concentration during the collision of two contaminated droplets. It can be observed that the pressure in the gap between two contaminated droplets increases significantly as they approach each



FIGURE 11. (Colour online) Dynamics of clean (blue) and contaminated (red) droplets on a chemically patterned surface with static contact angles  $\theta_1 = 60^\circ$  for the A-type stripe (black stripe) and  $\theta_2 = 120^\circ$  for the B-type stripe (green stripe). Droplets are pushed by a constant body force along the horizontal direction.



FIGURE 12. (Colour online) Evolution of the surfactant concentration for a contaminated droplet. The initial surfactant bulk concentration  $\psi_b$  is  $1.5 \times 10^{-2}$ .



FIGURE 13. (Colour online) Evolutions of (a) pressure field (background colour), (b) surfactant concentration and (c) pressure during the separation of two contaminated droplets. The initial surfactant bulk concentration  $\psi_b$  is  $1.5 \times 10^{-2}$ .

other (point A to point C). The increasing pressure pushes surfactants away from the near-contact region, and the resulting Marangoni force acts as a repulsive force to prevent droplet coalescence (Liu & Zhang 2010; Wodlei *et al.* 2018). The pressure in the gap decreases (point D to point E) as two contaminated droplets slide over each other.

There are several parameters that potentially influence the dynamics of a contaminated droplet on a chemically patterned surface, e.g. the surfactant bulk concentration  $\psi_b$ , the defect strength  $\Delta \theta_e = \theta_2 - \theta_1$ , the Reynolds number Re, etc. In this work, we only consider the effect of  $\psi_b$  and  $\Delta \theta_e$  on the behaviour of a contaminated droplet. A series of numerical simulations, with  $\psi_b$  ranging from  $1 \times 10^{-3}$  to  $1.5 \times 10^{-2}$  and  $\Delta \theta_e$  ranging from 20° to 100°, are conducted to obtain a clear understanding of the droplet dynamics. Other parameters and boundary conditions remain unchanged. Results demonstrate that all contaminated droplets at various conditions suffer from large deformation and break-up, just as in figure 11(c,d). After droplet break-up, we observe three typical flow states, specifically the coalescence mode, the non-coalescence mode and the detachment mode, as shown in figure 14. At low  $\psi_b$  and medium  $\Delta \theta_e$  ( $\psi_b = 1 \times 10^{-3}$  and  $\Delta \theta_e = 70^{\circ}$ ), the coalescence occurs as two contaminated droplets move towards each other because of the interfacial tension. At high  $\psi_b$  and low  $\Delta \theta_e$  ( $\psi_b = 1.5 \times 10^{-2}$  and  $\Delta \theta_e = 50^\circ$ ), the repulsive Marangoni force together with the low interfacial tension leads to the separation of two daughter droplets, and the droplet in contact with the bottom wall will continue to slide on the hydrophilic A-type stripe. This phenomenon is called 'non-coalescence'. If we increase  $\Delta \theta_e$  on the basis of the non-coalescence event ( $\psi_b = 1.5 \times 10^{-2}$  and



FIGURE 14. (Colour online) Three typical flow states of contaminated droplets at various surfactant bulk concentrations  $\psi_b$  and defect strengths  $\Delta \theta_e$ : coalescence, non-coalescence and detachment. The A-type stripe (black stripe) with static contact angle  $\theta_1$  is hydrophilic and the B-type stripe (green stripe) with static contact angle  $\theta_2$  is hydrophobic. We define the defect strength  $\Delta \theta_e$  as the difference of  $\theta_1$  and  $\theta_2$ , namely  $\Delta \theta_e = \theta_2 - \theta_1$ .

 $\Delta \theta_e = 70^\circ$ ), the detachment event will occur, when the droplet sliding on the bottom wall (green stripe) leaves the patterned surface. Note that the droplet can only detach from the solid surface on the hydrophobic B-type stripe (green stripe).

A phase diagram of flow states for contaminated droplets at different  $\psi_b$  and  $\Delta \theta_e$ is further shown in figure 15. A black star identifies a coalescence event, a red diamond marks a non-coalescence event and a blue circle represents a detachment event. As we can see, only non-coalescence occurs for all  $\psi_b$  when  $\Delta \theta_e$  is less than 60°. The surfactant bulk concentration  $\psi_b$  begins to affect the flow state of a droplet as the defect strength  $\Delta \theta_e$  increases to 60°. Detachment events occur at high  $\psi_{h}$  since surfactants reduce the adsorption effect of the B-type stripe by increasing advancing contact angles of droplets. With a decrease of  $\psi_b$ , droplets cannot detach from the B-type stripe due to the weak effect of surfactants, and non-coalescence phenomena appear. If we further reduce  $\psi_b$ , a large interfacial tension will lead to the coalescence of two contaminated droplets. It can be observed that non-coalescence events occur on a narrower range of  $\psi_b$  at  $\Delta \theta_e = 70^\circ$  and completely disappear when  $\Delta \theta_e$  is larger than 70°. Detachment and coalescence events dominate flow states of droplets at  $\Delta \theta_e = 80^\circ$ . Coalescence events only occur at specific surfactant bulk concentrations when  $\Delta \theta_e$  is larger than 80°. Overall, the non-coalescence event is the only flow state of contaminated droplets at low defect strength ( $\Delta \theta_e \leq 50^\circ$ ) and completely disappears at high defect strength ( $\Delta \theta_e \ge 80^\circ$ ). All three flow states occur at medium defect strength (50° <  $\Delta \theta_e$  < 80°). The detachment event dominates the flow behaviour of droplets at high defect strength.



 $\star$  Coalescence  $\blacklozenge$  Non-coalescence  $\bigcirc$  Detachment

FIGURE 15. (Colour online) A phase diagram of flow states for contaminated droplets at different surfactant bulk concentrations  $\psi_b$  and defect strengths  $\Delta \theta_e$ . A black star identifies a coalescence event, a red diamond marks a non-coalescence event and a blue circle represents a detachment event.



FIGURE 16. (Colour online) Illustration of unbalanced Young stresses  $F_A$  and  $F_R$  at the triple-phase contact points A and R. Angle  $\theta_A$  is the advancing contact angle and  $\theta_R$  is the receding contact angle.

#### 4.2.2. Unbalanced Young stress at the MCL

In this section, we focus on the evolution of the unbalanced Young stress  $L\partial_{\tau}\phi$  when a contaminated droplet moves across the junction of wettability transition. As a contaminated droplet moves along the x direction, the advancing contact angle and receding contact angle are denoted as  $\theta_A$  and  $\theta_R$ , respectively. Stresses  $F_A$  and  $F_R$  are unbalanced Young stresses acting on the triple-phase contact points A and R, respectively. As shown in figure 16, the unbalanced Young stress is defined as positive when it points from left to right; otherwise, it is defined as negative. We calculate unbalanced Young stresses  $F_A$  and  $F_R$  within the time range 0–2.8, and details of droplet dynamics in this period are depicted in figure 11(*a*-*c*). During the process, the triple-phase contact point A moves from the hydrophilic A-type stripe to the hydrophobic B-type stripe, while the point R never crosses the junction.

The chemical potential L in the unbalanced Young stress measures the deviation from the equilibrium condition (L = 0) at the solid surface, and the main role of the unbalanced Young stress is to adjust the droplet to its equilibrium condition (equilibrium contact angle  $\theta_e$ ). Figure 17 gives the evolutions of unbalanced Young



FIGURE 17. (Colour online) Evolutions of unbalanced Young stresses (a)  $F_R$  and (b)  $F_A$  at different defect strengths  $\Delta \theta_e$ . The initial surfactant bulk concentration  $\psi_b$  is  $1.5 \times 10^{-2}$ .

stresses  $F_R$  and  $F_A$ . Initially, the static droplet ( $\theta_0 = 90^\circ$ ) spreads on the hydrophilic surface under the action of  $F_R$  and  $F_A$ . Stress  $F_R$  points to the left (negative) and  $F_A$  points in the opposite direction (positive). Both  $F_R$  and  $F_A$  decrease dramatically as  $\theta_R$  and  $\theta_A$  approach the equilibrium contact angle  $\theta_e$  ( $\theta_e < \theta_s$  on a hydrophilic surface). Meanwhile, the droplet keeps deforming as a constant body force drives it forward. The receding contact angle  $\theta_R$  decreases with the deformation of the droplet, and  $F_R$  becomes zero when  $\theta_R$  decreases to  $\theta_e$ , as shown in figure 17(*a*). The continuous deformation of the droplet causes the receding contact angle  $\theta_R$  to continue to decrease ( $\theta_R < \theta_e$ ). In order to adjust the contact point R to the equilibrium condition,  $F_R$  changes its direction (now it points to the right, positive) and pushes the contact point R to move forward. During the whole process, the contact point R never moves across the junction of wettability transition.

The evolution of  $F_A$  is more complicated than that of  $F_R$ . Before  $\theta_A$  decreases to the equilibrium contact angle  $\theta_e$ , droplet deformation leads to an increase of  $\theta_A$ , which is contrary to the expectation of  $F_A$ . Thus,  $F_A$  begins to increase (point M in figure 17b) and drags the contact point A forward to reduce  $\theta_A$ . As the contact point A meets the junction,  $F_A$  experiences a dramatic decrease (point N). According to the GNBC, the decrease of  $F_A$  must be accompanied by the decrease of fraction force due to the contact line slip. Thus, the classical phenomenon of the contact line sticking to the solid surface is expected to occur at the point N, and this is actually observed in figure 18.

In figure 17(*b*), we can see that the defect strength  $\Delta \theta_e$  has a significant impact on the behaviour of  $F_A$ . When the defect strength  $\Delta \theta_e$  is less than 80°,  $\theta_A$  immediately arrives at the equilibrium contact angle  $\theta_e$  of the hydrophobic B-type stripe. With droplet deformation,  $\theta_A$  continues to increase and exceeds  $\theta_e$ , and correspondingly  $F_A$ increases to reduce  $\theta_A$ . Throughout the whole process,  $F_A$  never changes direction, and always drags the contact point A forward. The behaviour of  $F_A$  becomes complicated when  $\Delta \theta_e$  is larger than 80°. As the droplet moves across the junction,  $\theta_A$  ( $\theta_A < 90^\circ$ ) is less than  $\theta_e$  ( $\theta_e > 90^\circ$  on a hydrophobic surface). In order to adjust  $\theta_A$ , the unbalanced Young stress  $F_A$ , acting as the drag force before (positive), decreases dramatically and changes its direction (negative). Stress  $F_A$  decreases to zero when  $\theta_A$  arrives at  $\theta_e$ , and it becomes the drag force again as  $\theta_A$  exceeds  $\theta_e$  with droplet deformation. Based on the above analysis, we can conclude that the unbalanced Young stress could be



FIGURE 18. (Colour online) Profiles of phase-field variable  $\phi$  at different times. The initial surfactant bulk concentration  $\psi_b$  is  $1.5 \times 10^{-2}$ .

a driving or resistance force, which is determined by the critical defect strength  $\Delta \theta_e$ , and  $\Delta \theta_e$  is between 60° and 80°.

#### 5. Conclusions

In this work, we present a derivation of the phase-field MCL model with soluble surfactants through the first law of thermodynamics, associated thermodynamic relations and the Onsager variational principle. The derived thermodynamically consistent model consists of two Cahn-Hilliard type of equations governing the evolution of interface and surfactant concentration, the incompressible Navier-Stokes equations and the GNBC for the MCL. With chemical potentials derived from the free energy functional, we analytically obtain certain equilibrium properties of surfactant adsorption, including equilibrium profiles for phase-field variables, the Langmuir isotherm and the equilibrium equation of state. A classical droplet spread case is used to numerically validate the MCL model and equilibrium properties of surfactant adsorption. The influence of surfactants on the contact line dynamics observed in our simulations is consistent with the results obtained using sharp interface models. Numerical results also demonstrate that the equilibrium contact angle of a contaminated droplet can be approximately predicted by the static contact angle of a clean droplet through a linear relationship. Using the proposed model, we investigate the droplet dynamics with soluble surfactants on a chemically patterned surface. It is observed that droplets will form three typical flow states as a result of different surfactant bulk concentrations and defect strengths, specifically the coalescence mode, the non-coalescence mode and the detachment mode. In addition, a phase diagram for the three flow states is presented. Finally, we study the unbalanced Young stress acting on triple-phase contact points. The unbalanced Young stress could be a driving or resistance force, which is determined by the critical defect strength.

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