Effect of Phase Change and Solute Diffusion on Spreading on a Dissolving Substrate

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Abstract

Dissolutive wetting is investigated numerically using a diffuse-interface model that incorporates fluid flow, solute diffusion, and phase change. A range of materials parameters are investigated that: 1) permits recovery of the hydrodynamic limit by suppressing the dissolution of the substrate and 2) evaluates the role of diffusion. The time history of droplet size, droplet concentration, and angles between the interfaces are given. For convectiondominated case the dynamics of spreading agrees with a known hydrodynamic model for spreading of inert fluids. We have found that phase change increases wetting speed, which is due to a condensation that takes place near the triple junction. There is also a strong dependence of the wetting kinetics on the solute diffusivities. Details of composition changes during spreading are also discussed, such as the composition path of the bulk liquid probed at different locations in the drop.

Key words: Dissolutive Wetting, Diffusion, Navier-Stokes flow, Multicomponent and multiphase model, Phase-field method

1. Introduction

The spreading of molten solder over a solid substrate to form a joint is a common technological process. It may appear simple but the underlying mechanisms of reactive

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wetting are quite complicated (see [1] for general discussion). The process involves fluid flow, heat and mass transfer, capillary phenomena, and phase transformations. Although considerable progress has been made, a thorough understanding of reactive wetting and improved models are still required. Reactive wetting can be divided into two classes. The first is where partial dissolution of the substrate alters the concentration of the spreading liquid but no new phase forms between the liquid and the substrate. The second is when such a phase or phases form between the wetting liquid and the solid substrate [2-6].

Early experimental and theoretical investigation of dissolutive wetting has been performed by Yost et al. [7]. Their experimental work involved the spreading of Sn-Bi alloys on Bi-substrates and measurement of the wetted area of the drop with respect to time. They developed a kinetic description for the wetted area and found good agreement with their experiment. Warren et al. [8] also investigated dissolutive wetting of Sn-Bi alloys on Bi-substrates and have developed a model that incorporates solute transport and fluid flow effects in a sharp interface model. Their model describes the shape evolution of the spreading liquid and dissolving solid and they have shown qualitative agreement with their experiment. The Gibbs-Thomson effect for the solid-liquid interface plays a significant role at the triple junction. Yin et al. [9] also performed a detailed experimental study of various Sn-Bi alloys on pure Bi-substrates. They showed that the dynamics of spreading (dynamic apparent contact angle versus triple junction speed) have certain similarities to a universal correlation for nonreactive wetting systems. In a succeeding work [10], they employed the model of Warren et al. [8] to study the same system and found good agreement with the experiments on the dynamic apparent contact angles for cases with low contents of Sn (10, 15, and 20 wt%) in the liquid drop.

Webb et al. [11] studied dissolutive wetting of Ag on Cu through molecular dynamics simulation. They used the time dependent radius of the spreading droplet to quantify the wetting kinetics in a cylindrical geometry.

Recently, a general diffuse-interface model of a multicomponent and multiphase system [12] has been developed that incorporates solute transport, fluid flow, and phase transformation (melting, solidification, evaporation, condensation). The numerical simulations have revealed two stages in the wetting process, a convection-dominated stage during rapid spreading, and a diffusion-dominated stage with dissolution of the substrate into the liquid and an elevation of the contact line from the original horizontal plane of the substrate.

In this study, we use the multicomponent and multiphase model introduced in [12] to analyze details at the triple junction and investigate the effects of variable solute diffusivities and phase change kinetics on the dynamics of wetting. In Section 2, we review the mathematical model in a compact form, and in Section 3 give a description of a base set of input parameters and their relationship to sharp interface parameters. The numerical treatment is given in Section 4. In Section 5 we first give detailed results for the base set of parameters; viz., composition and flow near the triple junction, extent of the phase changes (evaporation, condensation, dissolution, etc.), dynamic contact angle and changes in substrate shape. We then investigate the effect of altered materials parameter that prohibit phase change to permit comparison to a known hydrodynamic model for spreading of inert fluids. Subsequently the diffusion mobilities are varied to investigate the effect their role in the spreading dynamics.

2. Mathematical Model

We start by setting the total molar Gibbs energy G of a ternary system of substitutional elements A, B and C with three phases, L (spreading liquid), S (solid substrate) and V(vapor), given by,

$$G = \int_{\Omega} \left(\frac{G_m(x_A, x_B, x_C, \phi_L, \phi_S, \phi_V, T)}{V_m} + \sum_{i=L, S, V} \frac{\epsilon_i^2}{2} (\nabla \phi_i)^2 \right) d\Omega$$
(1)

where T is temperature, V_m is the molar volume, and $x_{A,B,C}$ are the mole fractions of A, B, C-atoms with $x_A + x_B + x_C = 1$. The phase-field variables ϕ_i 's vary smoothly between 0 and 1 and we set the condition that $\phi_L + \phi_S + \phi_V = 1$. The coefficients ϵ_i 's and W_{ij} 's are related to the thicknesses and interfacial energies and G_m denotes the molar Gibbs energy,

$$G_m = (1 - P(\phi_L) - P(\phi_S))G_m^V + P(\phi_L)G_m^L + P(\phi_S)G_m^S + W_{LS}\phi_L^2\phi_S^2 + W_{LV}\phi_L^2(1 - \phi_L - \phi_S)^2 + W_{SV}\phi_S^2(1 - \phi_L - \phi_S)^2 + W_{LSV}\phi_L^2\phi_S^2(1 - \phi_L - \phi_S)^2$$
(2)



Figure 1: Schematic diagram of the initial configuration $(t = t_0)$ (dashed lines) with three phases L (spreading liquid), S (solid substrate), and V (vapor) and later time (t = t') dissolutive spreading (solid lines). The three interfaces form three included angles θ_L , θ_S , and θ_V but here we also define the dynamic angles $\theta_1(t)$ (the angle the spreading liquid makes with respect to the horizontal surface), $\theta_2(t)$ (the angle between the liquid-solid interface and the horizontal), and $\theta_3(t)$ (inclination angle of the solid-vapor interface). In addition, we define the dynamic contact angle $\theta_L(t) = \theta_1(t) + \theta_2(t)$.

with the smoothed step-interpolation function $P(\phi_i) = \phi_i^3(10 - 15\phi_i + 6\phi_i^2)$ [14, 15].

For simplicity, we assume ideal solutions for $G_m^{L,S,V}$, thus each molar Gibbs energy takes the form,

$$G_m^i = x_A{}^o G_A^i + x_B{}^o G_B^i + (1 - x_A - x_B){}^o G_C^i + RT(x_A \ln x_A + x_B \ln x_B + (1 - x_A - x_B) \ln(1 - x_A - x_B)), \quad i = L, S, V$$
(3)

where, for example, ${}^{o}G_{A}^{L}$ is the molar Gibbs energy of pure A in the liquid phase and R is the gas constant.

Considering an isothermal, viscous, and incompressible system, the governing equations are the following:

(i) conservative convective concentration equations,

$$\frac{1}{V_m} \left(\frac{\partial x_A}{\partial t} + \mathbf{u} \cdot \nabla x_A \right) = -\nabla \cdot J_A \tag{4}$$

$$\frac{1}{V_m} \left(\frac{\partial x_B}{\partial t} + \mathbf{u} \cdot \nabla x_B \right) = -\nabla \cdot J_B \tag{5}$$

where **u** is the flow velocity and J_A and J_B are fluxes of A and B atoms measured with respect to the local flow,

(ii) non-conservative convective Allen-Cahn equations for the phase-field variables,

$$\frac{\partial \phi_L}{\partial t} + \mathbf{u} \cdot \nabla \phi_L = -M_{\phi_L} \frac{\delta G}{\delta \phi_L} \tag{6}$$

$$\frac{\partial \phi_S}{\partial t} + \mathbf{u} \cdot \nabla \phi_S = -M_{\phi_S} \frac{\delta G}{\delta \phi_S} \tag{7}$$

where M_{ϕ_L} and M_{ϕ_S} are kinetic mobilities and with natural boundary conditions $\mathbf{n} \cdot \nabla \phi_L = 0$ and $\mathbf{n} \cdot \nabla \phi_S = 0$,

(iii) a mass continuity equation for incompressible flow,

$$\nabla \cdot \mathbf{u} = 0. \tag{8}$$

(iv) and the Navier-Stokes equations for incompressible flow with added surface tension forces,

$$\rho(\phi) \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla \tilde{p} + \nabla \cdot \mu(\phi) (\nabla \mathbf{u} + \nabla \mathbf{u}^T) - \sum_{i=L,S,V} \phi_i \nabla \left(\frac{\delta G}{\delta \phi_i} \right) - \sum_{i=L,S,V} x_i \nabla \left(\frac{\delta G}{\delta x_i} \right)$$
(9)

where \tilde{p} is a nonclassical pressure. The surface tension forcing is based on the derivation of Jacqmin [16]. If we set the nonclassical pressure $\tilde{p} = -\sum_{i=L,S,V} \phi_i \frac{\delta G}{\delta \phi_i}$ in the above equation and apply the Gibbs-Duhem relation, the equation becomes identical to the approach of Sekerka and Bi [17] wherein the surface tension forcing is equal to $-\sum_{i=L,S,V} \nabla \cdot \frac{\partial q}{\partial \nabla \phi_i} \nabla \phi_i$ where q is the gradient energy term and p is the classical pressure. The density $\rho(\phi)$ and

viscosity $\mu(\phi)$ are defined as

$$\rho(\phi) = \rho_L \phi_L + \rho_S \phi_S + \rho_V (1 - \phi_L - \phi_S), \tag{10}$$

$$\mu(\phi) = \begin{cases} \mu_L \phi_L + \mu_V (1 - \phi_L - \phi_S), & \text{if } \phi_S \le 0.8\\ \mu_V + 0.5(\mu_S - \mu_V)(1 + \tanh(\frac{2\pi(\phi_S - 0.8)}{0.6})), & \text{if } \phi_S > 0.8. \end{cases}$$
(11)

To complete the concentration equations (Eqns. 4-5), we write the interdiffusion flux of solutes J_A and J_B (with $J_A + J_B + J_C = 0$)

$$J_A = -L_{AA} \nabla \left(\frac{\delta G}{\delta x_A}\right) - L_{AB} \nabla \left(\frac{\delta G}{\delta x_B}\right) \tag{12}$$

$$J_B = -L_{AB} \nabla \left(\frac{\delta G}{\delta x_A}\right) - L_{BB} \nabla \left(\frac{\delta G}{\delta x_B}\right) \tag{13}$$

where the variation in G with respect to the compositions x_j are given by

$$\frac{\delta G}{\delta x_j} = \frac{1}{V_m} \frac{\partial G_m}{\partial x_j}, \quad j = A, B \tag{14}$$

and the L_{ij} 's are

$$L_{AA} = (1 - x_A)^2 x_A M_A(\phi_L, \phi_S, \phi_V) + x_A^2 x_B M_B(\phi_L, \phi_S, \phi_V) + x_A^2 (1 - x_A - x_B) M_C(\phi_L, \phi_S, \phi_V)$$
(15)

$$L_{BB} = x_B^2 x_A M_A(\phi_L, \phi_S, \phi_V) + (1 - x_B)^2 x_B M_B(\phi_L, \phi_S, \phi_V) + x_B^2 (1 - x_A - x_B) M_C(\phi_L, \phi_S, \phi_V)$$
(16)

$$L_{AB} = -(1 - x_A)x_A x_B M_A(\phi_L, \phi_S, \phi_V) - x_A x_B(1 - x_B) M_B(\phi_L, \phi_S, \phi_V) + x_A(1 - x_A - x_B) x_B M_C(\phi_L, \phi_S, \phi_V).$$
(17)

The mobilities of A, B, and C can be different in each phase and are given by

$$M_{j}(\phi_{L},\phi_{S},\phi_{V}) = M_{j}^{L}\phi_{L} + M_{j}^{S}\phi_{S} + M_{j}^{V}(1-\phi_{L}-\phi_{S}), \quad j = A, B, C$$
(18)

where $1 - \phi_L - \phi_S$ has been substituted for ϕ_V . In the interior of the phases, the diffusivities, D_{ij} , are defined through the expressions,

$$J_A = -\frac{D_{AA}}{V_m} \nabla x_A - \frac{D_{AB}}{V_m} \nabla x_B \tag{19}$$

$$J_B = -\frac{D_{BA}}{V_m} \nabla x_A - \frac{D_{BB}}{V_m} \nabla x_B.$$
⁽²⁰⁾



Figure 2: Idealized phase diagram of a ternary A-B-C system at 450K. The blue circles represent the initial compositions of the 3 phases and the red squares represent the equilibrium compositions. The initial composition in the solid is taken to be the equilibrium composition of a flat interface.

Because we have assumed ideal solutions for the molar Gibbs energy of each phase, $D_{AB} = D_{BA} = 0$ in each phases and $D_{AA}^{\text{phase}} = D_{BB}^{\text{phase}} = D_{\text{phase}} = M_x^{\text{phase}} RTf(x_A, x_B).$

3. Input parameters

The model allows for a ternary phase diagram such as the one shown as an isothermal section in Figure 2. The phase diagram is idealized and the parameters are given in Table 1 along with other input parameters.

Given the parameters in Table 1, we can estimate more familiar material parameters such as the interface energies σ_{ij} , interface thicknesses δ_{ij} , diffusivities D_i , and interface kinetic

Table 1: Base set of parameters.

${}^{o}G_{A}^{L} = -5.0 \times 10^{3} \frac{J}{mol}$	$T = 450 \ K$
${}^oG^S_A = {}^oG^L_B = {}^oG^L_C = {}^oG^S_C = -1/2 \cdot {}^oG^L_A$	$W_{LS} = 1.24 \times 10^5 \frac{J}{mol}$
${}^oG^V_A = -{}^oG^L_A$	$W_{LV} = 1.54 \times 10^5 \ \frac{J}{mol}$
${}^oG_B^S = 1/4 \cdot {}^oG_A^L$	$W_{SV} = 3.22 \times 10^5 \ \frac{J}{mol}$
${}^oG^V_B = -2 \cdot {}^oG^L_A$	$\epsilon_L^2 = 7.38 \times 10^{-11} \frac{J}{m}$
${}^oG_C^V = 1/2 \cdot {}^oG_A^L$	$\epsilon_S^2 = 4.32 \times 10^{-9} \ \frac{J}{m}$
$M_A^L = M_B^L = M_C^L = M_A^V = M_B^V = M_C^V = 2.67 \times 10^{-13} \ \frac{mol \ m^2}{Js}$	$\epsilon_V^2 = 4.54 \times 10^{-9} \frac{J}{m}$
$M_{A}^{S} = M_{B}^{S} = M_{C}^{S} = 10^{-3} \cdot M_{A}^{L}$	$R = 8.31 \frac{J}{mol K}$
$\mu_L = \mu_V = 4.0 \times 10^{-3} Pa \cdot s$	$M_{\phi_L} = M_{\phi_S} = 5.0 \ \frac{m^3}{Js}$
$\mu_S = 10^5 \cdot \mu_L$	$\rho_L = \rho_S = 8.9 \times 10^3 \ \frac{kg}{m^3}$
$V_M = 1.0 \times 10^{-5} \frac{m^3}{mol}$	$ \rho_V = 0.1 \cdot \rho_L $

*Note that we keep $M_A^i = M_B^i = M_C^i = M_x^i$ (i = L, S, V) and the ratios of the solute mobilities between the phases, M_x^S/M_x^L and M_x^V/M_x^L , fixed in all simulations.

coefficients k_{coeff} with the following formulas,

$$\sigma_{LS} = \frac{1}{4} \sqrt{\frac{W_{LS}(\epsilon_L^2 + \epsilon_S^2)}{V_m}}, \quad \text{etc.}$$
(21)

$$\delta_{LS} = 2\sqrt{\frac{V_m(\epsilon_L^2 + \epsilon_S^2)}{W_{LS}}}, \quad \text{etc.}$$
(22)

$$D_L = M_x^L RT, \quad \text{etc.} \tag{23}$$

$$k_{\rm coeff} = \frac{V_m}{3RM_\phi\delta} \tag{24}$$

where $M_x^i = M_A^i = M_B^i = M_C^i$, i = L, S, V. These derived familiar parameters are given in Table 2.

The formulas given in Eqn. 21 provide estimates of the interface energies without solving the governing equations. Exact values for the interface energies must be obtained from 1D simulations of each pair of phases (LS, LV, and SV). The interface energies are then computed

Table 2: Derived familiar parameters from the input parameters given in Table 1.

	-	
$\sigma_{LS} = 1.85 \ \frac{J}{m^2} \ (2.06 \ \frac{J}{m^2})$	$\delta_{LS} = 1.19 \times 10^{-9} m$	$^{\dagger}D_L = D_V = 1.00 \times 10^{-9} \ \frac{m^2}{s}$
$\sigma_{LV} = 2.11 \ \frac{J}{m^2} \ (2.16 \ \frac{J}{m^2})$	$\delta_{LV} = 1.09 \times 10^{-9} m$	$^{\dagger}D_S = 1.00 \times 10^{-12} \frac{m^2}{s}$
$\sigma_{SV} = 4.22 \ \frac{J}{m^2} \ (4.15 \ \frac{J}{m^2})$	$\delta_{SV} = 1.05 \times 10^{-9} m$	$k_{\text{coeff}} = 80 \frac{sK}{m}$

*The kinetic coefficient is taken as the same for all interfaces. In a non-isothermal transformation it corresponds to an interface supercooling ΔT given by $\Delta T = k_{\text{coeff}} \cdot v$ where v is the interface speed.

[†]The exact values of D_i at corners of the 3-phase triangle differ by only 10^{-3} from estimated values.

from the expression [18],

$$\sigma = \int_{-\infty}^{\infty} \left[\frac{1}{V_m} \left((G_m(x_i(z), \phi_i(z); T) - G_m(x_i(\pm \infty), \phi_i(\pm \infty); T)) - \sum_{i=1}^{2} \frac{\partial G_m(x_i, \phi_i; T)}{\partial x_i} \right|_{z=\pm\infty} \cdot (x_i(z) - x_i(\pm \infty)) \right) + \sum_i \frac{\epsilon_i^2}{2} \left(\frac{\partial \phi_i}{\partial z} \right)^2 dz.$$
(25)

The calculated interface energies are $\sigma_{LS} = 2.06 \frac{J}{m^2}$, $\sigma_{LV} = 2.16 \frac{J}{m^2}$, and $\sigma_{SV} = 4.15 \frac{J}{m^2}$ for compositions at the corners of the 3-phase triangle. We note that one may also compute the equilibrium interface adsorption [18] through a procedure developed by Cahn [19] that is independent of choice of dividing surface and that obeys the Gibbs adsorption equation. For the present choice of constant values of ϵ and W, the concentration variation of the interface energies is small. For example the LS energy varies by 0.2% from the binary AB edge to 25% C.

Previous work [18] has shown that triple junction angles in phase field calculations agree with classical surface tension balance laws. Thus, given the exact interfacial energies, the equilibrium contact angle of the drop according to Young's equation if the substrate is assumed to be smooth, rigid, and planar, is given by

$$\theta_{YE} = \cos^{-1} \left(\frac{\sigma_{SV} - \sigma_{LS}}{\sigma_{LV}} \right) = 14.53^{\circ}, \tag{26}$$

where we have employed the exact interface energies. No finite equilibrium contact angle can be obtained using the estimated interface energies.

If the substrate is nonplanar, we can calculate equilibrium contact angles with the assumption that the horizontal and vertical components of the surface tension forces must sum up to zero, hence

$$\theta_{L}^{E} = \cos^{-1} \left(\frac{\sigma_{SV}^{2} - \sigma_{LS}^{2} - \sigma_{LV}^{2}}{2 \sigma_{LS} \sigma_{LV}} \right) = 20.77^{o}$$

$$\theta_{S}^{E} = \cos^{-1} \left(\frac{\sigma_{LV}^{2} - \sigma_{LS}^{2} - \sigma_{SV}^{2}}{2 \sigma_{LS} \sigma_{SV}} \right) = 169.37^{o}$$

$$\theta_{V}^{E} = \cos^{-1} \left(\frac{\sigma_{LS}^{2} - \sigma_{LV}^{2} - \sigma_{SV}^{2}}{2 \sigma_{LV} \sigma_{SV}} \right) = 169.86^{o}.$$
(27)

We will compare these angles to those 'observed' in the simulations.

4. Numerical Treatment

The partial differential equations are solved using a mesh adaptive finite element method which is detailed in [12]. In the numerical implementation, we have assumed cylindrical symmetry about the z axis perpendicular to the solid substrate (see Figure 1).

The choice of materials parameters is generally constrained by limits on computational time; specifically the interface energies, kinetic coefficients and viscosity. If we use Sn on a Cu substrate as an example, the interface energies that we employ are generally larger than realistic values. The interface energy of the liquid-vapor interface of Sn at the melting point is in the range $0.47 - 0.63 J/m^2$ as summarized in Yuan et.al. [20]. Values for the liquid-solid interface of Sn are between $0.044 - 0.077 J/m^2$ as summarized in Saatci et al. [21]. The solid-vapor interface energy for a clean Cu substrate is ~ $1.7 J/m^2$ [22] but this varies widely due to oxide/flux reaction in soldering applications.

The kinetic coefficient for the liquid-solid interface of pure Sn is probably close to that of Pb, which is 3.33 sK/m [23]. This is much less than the 80 sK/m we employ (Table 2). We have used the corresponding mobility value for all the interfaces and thus our interfaces are sluggish in the sense that they respond more slowly to disequilibrium than is realistic. The viscosity of the liquid is about twice the viscosity of liquid Sn at 523K which is $1.9 \times 10^{-3} Pa \cdot s$ [24]. Also, to give a constant V_m for the specified densities, the atomic weight of the components depends on the phase.

Another practical limitation of a phase-field calculation is the ratio between the interface thickness and the characteristic length scale of the system (i.e., drop size) typically being of the order of 0.1 - 0.01. This implies that if we take the interface thickness to be realistic, say 1 nm, the characteristic length scale of the drop is of the range 10 - 100 nm. The other alternative is to choose the characteristic length to be realistic, say 1 mm, and the interface thickness δ is in the range 0.1 - 0.01 mm. In our calculation, we have chosen the former and have the interface thickness realistic, $\delta = 1 nm$. The initial radius of the drop is $R_0 = 10 nm$ and the domain size is $(60 nm \times 80 nm)$. This is too small compared to many experimental conditions which is of the order of millimeter size droplets. Nevertheless, the results show that the dynamics of wetting in the hydrodynamic limit at the small scale agrees with analytical theories that are also used to compare with experimental data in the millimeter-size range.

Because we employ a diffuse interface model, our use of the terms "triple junction", "interface", and "apparent contact angle" require definition as shown in the Appendix. Briefly the triple junction is the point where all three phase fields are 1/3. Contact angles are obtained from the slopes of $\phi_i = 0.5$ contours at a distance of 2δ from the triple junction point. Beyond contours at 0.9 "bulk" behavior dominates. We employ terms such as triple junction and interface using these definitions but with the caveat that they are always diffuse.

We have considered two time scales in the model to be especially important, the capillary time scale $t_c = \mu_L R_0 / \sigma_{LV}$ and the diffusive time scale $t_d = R_0^2 / D_L$. The ratio of these time scales in the calculation is $t_d / t_c = 5.4 \times 10^3$. The capillary time scale represents the natural response time of the system to reach mechanical equilibrium and the diffusive time scale represents the natural response time of the system to reach bulk chemical equilibrium.

5. Results and Discussion

5.1. Results for selected base parameter set

Examples of the flow pattern and concentration field near the moving triple junction for early $(t/t_c = 1)$ and later $(t/t_c = 100)$ times are shown in Figure 3. In general, the liquidvapor interface can move by both advection and phase change (condensation/evaporation). Whereas the vapor-solid and liquid-solid interfaces effectively can only move by phase change



Figure 3: Concentration profiles of B with the base set of parameters at (a) early fast-spreading stage $t/t_c = 1$ (b) late slow-spreading stage $t/t_c = 100$ with superimposed isoconcentrate lines and normalized velocity profiles. The maximum flow velocity in (b) is 3 orders of magnitude smaller than in the early stage (a). The triple junction speeds are (a) $U_{CL}\mu_L/\sigma_{LV} = 0.25$ and (b) $U_{CL}\mu_L/\sigma_{LV} = 0.002$. The 0.1, 0.5, and 0.9 contour levels of the liquid phase are also plotted. The triple junction is defined as the location where all the phase fields are 1/3.

(condensation/sublimation and solidification/melting, respectively) because the solid is practically motionless due to its high viscosity. For the liquid-vapor interface the motion is primarily by advection as shown by the flow arrows: a downward and outward flow from the interior of the liquid that moves the triple junction outward. At $t/t_c = 1$, there is also some condensation near the triple junction that increases the spreading rate beyond advection. The amount of phase change can only be accessed through the difference between the local interface speed and the normal component of the fluid flow. This will be described in more detail below. At $t/t_c = 100$ (see Figure 3b), the maximum flow velocity is 3 orders of magnitude smaller than in the early stage and the velocity vectors are more parallel to the liquid-gas interface, indicating a much reduced rate of shape change of the droplet.

For the composition field, we observe features on two length scales. On a fine scale within the diffuse interface between the 0.9 phase field contours of the interfaces can be seen variations in composition associated with the adsorption. This can also be seen most clearly by the zig-zag in the top black concentration contours in Figure 3a-b. On a larger scale in the liquid and outside the diffuse interface regions one can observe the relatively homogenous dark blue color ($x_B \approx 0.04$) of Figure 3a and the lighter blue color ($x_B \approx 0.19$) of Figure 3b. At early time very little dissolution has occurred whereas at later time the diffusion of component B from the dissolving substrate has changed the liquid concentration. In Figure 3b at $t/t_c = 100$, the isoconcentrates in the liquid outside of the interfacial zone beyond the 0.9 contour level of the liquid are nearly orthogonal to the liquid-vapor interface. This 90° behavior is consistent with the theoretical description of Warren, et al.[8] and the experiments of Yin, et al.[9].

Figure 4a shows the segments of the $\phi_L = 0.5$ and $\phi_V = 0.5$ contours at $t/t_c = 1$ where the red line indicates condensation/dissolution and the blue line indicates evaporation. Condensation or dissolution is determined by $S = v_n - \mathbf{u}_L \cdot \mathbf{n} > 0$, where v_n , \mathbf{u}_L , and $\mathbf{n} = \nabla \phi_L / |\nabla \phi_L|$ are the normal speed, fluid velocity, and normal vector at the $\phi_L = 0.5$, respectively. Evaporation is determined by S < 0 and not surprisingly in Figure 4a, it takes place over most of the liquid-vapor interface. There is dissolution along the liquid-solid interface that is expected while condensation takes place along the solid-vapor interface.



Figure 4: (a) Plot of $\phi_L = 0.5$ and $\phi_V = 0.5$ contours at $t/t_c = 1$ with the red line segment indicating condensation/dissolution and the blue line segment indicating evaporation. The circle has a radius $\delta = 0.1R_0 \approx \delta_{LV}$ centered at the triple junction. (b) Plot of $S = v_n - \mathbf{u}_L \cdot \mathbf{n}$ against the arc length that starts from the top center of the drop down to the bottom of the drop, where v_n , \mathbf{u}_L , and $\mathbf{n} = \nabla \phi_L / |\nabla \phi_L|$ are the normal speed, fluid velocity, and normal vector at the $\phi_L = 0.5$, respectively.



Figure 5: Contact angles plotted against time that is scaled with $\mu_L R_0 / \sigma_{LV}$.

Figure 4b shows the plot of S scaled with σ_{LV}/μ_L against the arc length starting from the top center of the drop down to the bottom of the drop. The peak in condensation takes place in the region enclosed by a circle of radius δ centered at the triple junction. A corresponding peak in evaporation takes place within 2δ but this is only about a third of the peak in condensation.

As the droplet spreads and the substrate dissolves the angles defined in Figure 1 change with time as shown in Figure 5. The early stage shows rapid decreases in the angles θ_1 and θ_L followed by slower decreases as diffusion becomes the dominant process. The angle θ_2 , which characterizes the extent of solid dissolution just behind the moving triple junction, appears to rise to about 10° monotonically with time. On the other hand the angle θ_3 , which characterizes the tilting of the solid surface in advance of the moving triple junction increases to about 8° and then decreases at longer time. Superimposed on the plot for reference are the equilibrium angles θ_{YE} and θ_L^E , the former obtained using Young's equation with the assumption that the substrate had remained planar and rigid (i.e., $\theta_2 = \theta_3 = 0$) and the latter obtained using Neumann's construction where the substrate does not remain planar. The angle θ_L approaches θ_L^E as expected. The angle θ_1 also appears to approach θ_{YE} but only because θ_2 is small.

The nonmonotonic behavior of θ_3 in Figure 5 is indicative of a solid ridge that forms at the triple junction that should eventually flatten if the substrate has infinite extent. The ridge at the triple junction has been observed experimentally in [6]. The ridge rises above the initial plane of the substrate in the present simulation due to solidification along the liquidsolid interface and condensation along the vapor-solid interface. The ridge is small, however, being only several interface widths high and hence has the properties of the adsorbed layer.

In Figure 6, we show the composition at points along a circle of radius 2δ with center at the triple junction (see inner circles in Figure 14 in Appendix A for illustration) at fixed times. These 'composition paths' sample in the interior of each of the three phases (sharp corners) and across each of the three interfaces (sides). The black dots correspond to the initial compositions in each phase while the corners of the phase diagram triangle correspond to the equilibrium compositions of the phases with flat interfaces. At $t/t_c = 1$ (blue dots), the composition path along the side for the liquid-vapor interface nearly follows a tie-line between the liquid phase and the vapor phase. Similarly, the composition path along the side for the solid-vapor interface nearly follows a tie-line between the solid phase and the vapor phase. The liquid-solid interface has more structure where we see a significant increase in composition x_C along the path that is attributed to the rapid spreading in the early stage with excess component C adsorbed from the C-rich vapor. At an intermediate time $t/t_c = 5$ (red dots), the composition at the bulk liquid changes as does the path followed through the interface between the liquid and the vapor with decreasing adsorption of C in the liquid-solid interface. In the liquid-solid interface at $t/t_c = 300$ (green dots), the path between liquid and solid is closer to the tie-line indicating a reduction in the adsorbed component C. The fact that the adsorption changes with triple junction speed is an interesting feature of this model.

Figure 7 shows the composition path versus time of the bulk liquid taken from two different locations: at the center of the drop, and at a location on a circle of radius 2δ (centered at the triple junction) midway between the LV and LS interface (see the star symbol in Figure 14 in Appendix A for illustration). There is an increase in composition x_B



Figure 6: Composition path of equi-distant points along the circle with center at the triple junction.

in both. However, the composition close to the triple junction approaches the equilibrium composition (the liquid corner in the 3-phase triangle) faster than at the center of the drop as the LS and LV interfaces quickly relax to local equilibrium concentrations. Interestingly, the composition x_C at the center of the drop decreases and reaches a minimum then increases approaching the equilibrium composition; while the composition x_C close to the triple line increases rapidly reaching a maximum then decreases to the equilibrium composition.

5.2. Influence of Solute Diffusivities

In order to gain more insight into the behavior of the model, we now explore variations in the solute mobilities (diffusivites) while keeping the ratios of the solute mobilities between the phases, M_x^S/M_x^L and M_x^V/M_x^L fixed.

In Figure 8, the composition x_B taken at the center of the liquid drop plotted against the two different time scales is shown. The composition x_B as a function of the capillary time scale (Figure 8a) for the diffusivity $D_L = 10^{-9} m^2/s$ shows that the composition slowly progresses to the equilibrium composition. At $t/t_c = 30$, the composition x_B has only increased 3% of the difference between the initial and final equilibrium composition, but at this point, the drop has spread considerably with the dynamic contact angle θ_L equal to



Figure 7: Composition path of the bulk liquid taken from two different locations: center of the drop and near the triple junction about a distance 2δ from the triple junction midway between the liquid-vapor and liquid-solid interface (see star symbol in Figure 14 in Appendix A for illustration).

43.5° from an initial angle of about 175°. For an order of magnitude decrease in diffusivity, $D_L = 10^{-10} m^2/s$ from the base set, the increase in composition is even slower. In practice, solder is often quenched very rapidly and the diffusivity could decrease up to 3 orders of magnitude, thus the composition in the bulk liquid could take orders of magnitude in time longer before it reaches its equilibrium composition. Figure 8b shows the same information plotted versus the diffusive time scale which incorporates the different diffusivities. Note the curves essentially collapse under this change of composition x_B at a diffusive time scale with different scaling as would be expected to changes in concentration in the center of the drop.

The evolution of the base radius R/R_0 plotted versus the different time scales is shown in Figure 9. The base radius rapidly increases up to about its initial radius and the influence of the diffusivities is negligible at this stage. From this point until about $t/t_c = 20$, the higher the diffusivity the greater the spread of the drop. With diffusivities $D_L = 10^{-6} m^2/s$ and $D_L = 10^{-5} m^2/s$, the behavior is nearly identical for the computed time. With $D_L \leq$



Figure 8: Composition x_B probed at the center of the drop at different time scales: (a) capillary time scale, (b) diffusive time scale.

 $10^{-8} m^2/s$, the drop spreads continuously. However, for $D_L > 10^{-8} m^2/s$, the drop spreads, reaches a maximum, and then starts to recede. This effect was also obtained in [8]. The droplet retracts at long time as the non-constant curvature of the liquid-solid interface produced during the rapid spreading stage slowly evolves towards a final equilibrium with constant curvature. If we simulate long enough, this retraction can be observed for all the simulations given the initial conditions. For the case with $D_L = 10^{-9} m^2/s$, the drop spreads with a relatively constant rate until it reaches a base radius R/R_0 of about 1.4 then slows down but still continuously spreads. Similarly with $D_L = 10^{-10} m^2/s$, the drop also spreads at a relatively constant rate until it reaches a base radius R/R_0 of about 1.4 then slows down but with a rate of increase lower than with the previous case.

Figure 10a shows the θ_L as function of capillary time for different values of diffusivities. We observe that at an early stage in the spreading process, the dynamic contact angle of the drop decreases from about 150° to about 90° at $t/t_c = 1$ regardless of the diffusivity D_L . As time progresses the effect of diffusion gets more significant. With diffusivity $D_L = 10^{-9} m^2/s$ (our base set given in Table 1) which is also shown in Figure 5, the dynamic contact angle decreases rapidly then slowly approaches the equilibrium value. With an order of magnitude



Figure 9: Base radius R/R_0 vs. capillary time scale.

lower in diffusivity, $D_L = 10^{-10} m^2/s$, the behavior is similar but approaches the expected equilibrium contact angle at a slower rate. Higher diffusivities give the same behavior but approach the expected equilibrium contact angle faster. At $t/t_c = 50$, the dynamic contact angle has reached 22.9° with $D_L = 10^{-7} m^2/s$ while the dynamic contact angle is 37.4° with $D_L = 10^{-9} m^2/s$.

It is common in hydrodynamic spreading experiments and models on inert substrate to plot angle θ_1 vs. the scaled contact line speed as this relationship captures the essential information about spreading kinetics. Even though we have dissolution of the substrate, an examination of our results for θ_1 is interesting. Figure 10b compares the present results to the hydrodynamic prediction of Cox described in Section 5.3.1 (black line). In the early stage (large values of θ_1) all cases spread faster than the hydrodynamic limit; i.e., for a fixed value of angle, the speed is faster. In all cases except the two lowest values of diffusion coefficient ($D_L \leq 10^{-9} m^2/s$), this increased spreading rate is also retained for later times. The larger the diffusivity the faster the spreading. This is a major result of this study. As noted for some cases from Figure 9, the droplet retracts and so the contact line speed is negative. These few results are shown in Figure 10b by having taken the absolute value of the spreading speed. For these cases the contact angle decreases below that observed on



Figure 10: (a) Dynamic contact angles θ_L plotted vs. capillary time scale for various values of liquid diffusion coefficient, and (b) θ_1 vs. contact line speed. The black line is the hydrodynamic limit described in Section 5.3.1.

spreading as expected (see [30] for more discussion of retracting contact lines).

5.3. Comparison to hydrodynamic theories

By decreasing the phase field mobilities we can slow and essentially prevent the rates of the various phase transformations (dissolution, condensation, etc.). In the process we will mimic the spreading of a system where the three phases are chemically inert and permit comparison to existing hydrodynamic notions of droplet spreading. This limiting case will also highlight the contribution of the diffusion and phase transformation on spreading dynamics. In particular we compare the contact angle vs. triple line speed behavior to the model of Cox [29] and the details of the flow pattern near the triple junction to that predicted by a modification to the creeping flow model developed by Huh and Scriven [31].

5.3.1. Comparison to Cox's model

A number of models have been proposed to explain how the dynamic contact angle θ_d relates to the parameters in the system. Hoffman [26] has first postulated from experimental data that the dynamic apparent contact angle depends solely on the capillary number Ca = $\mu_{LV}U_{CL}/\sigma_{LV}$. Independent derivations by Tanner [27] and Voinov [28] of a power law from a hydrodynamic analysis has lead to the well known Hoffman-Voinov-Tanner (HVT) law, given by $\theta_d \approx \text{const} \cdot \text{Ca}^{1/3}$ that is valid for Ca $\ll 1$.

Later, Cox [29] derived a more general analysis of the dynamics of wetting using matched asymptotic expansions. The theory assumes a negligible effect of phase change, solute diffusion, and inertia and it is applicable to two immiscible fluids with a viscosity ratio $\lambda = \mu_2/\mu_1$. At a leading order in Ca,

$$g(\theta_d, \lambda) - g(\theta_e, \lambda) = \operatorname{Ca} \ln(\xi^{-1})$$
(28)

where θ_d is the apparent dynamic contact angle, θ_e is the static equilibrium contact angle, ξ is a small constant parameter that relates the ratio of the slip length to the system size, and the function $g(\psi, \lambda)$ is given by

$$g(\psi,\lambda) = \int_0^{\psi} \left(\lambda(\theta^2 - \sin^2\theta) [(\pi - \theta) + \sin\theta\cos\theta] + [(\pi - \theta)^2 - \sin^2\theta](\theta - \sin\theta\cos\theta) \right) \Big/ \left(2\sin\theta \{\lambda^2(\theta^2 - \sin^2\theta) + 2\lambda[\theta(\pi - \theta) + \sin^2\theta] + [(\pi - \theta)^2 - \sin^2\theta] \} \right) d\theta.$$
(29)

In the hydrodynamic limit the instantaneous velocity of the liquid at the interface is equal to the normal speed of the interface (i.e., they are moving together), that is, the movement of interfaces is only the result of flow field (advection) and not due to phase change or diffusion. To see this clearly in the model, we nondimensionalize the concentration equations and the phase-field (but consider only ϕ_L for simplicity),

$$\frac{\partial x_i}{\partial t} + \mathbf{u} \cdot \nabla x_i = -\frac{1}{\operatorname{Pe}_{x_i}} \nabla \cdot J_i, \quad i = A, B$$
(30)

$$\frac{\partial \phi_L}{\partial t} + \mathbf{u} \cdot \nabla \phi_L = -\frac{1}{\operatorname{Pe}_{\phi_L}} \frac{\delta G}{\delta \phi_L}$$
(31)

where the solutal Peclet number $\operatorname{Pe}_{x_i} = U_{CL}R_0/(M_i^L RT)$ relates the ratio between the transport due to convection and transport due to solute diffusion (see [12] for details of the nondimensionalization). The phase-field Peclet number $\operatorname{Pe}_{\phi_L} = U_{CL}\delta_{LV}/(M_{\phi_L}\sigma_{LV}R_0)$, relates the ratio between the transport due to convection and transport due to phase change. The hydrodynamic limit is when $\operatorname{Pe}_{x_i} \to \infty$ and $\operatorname{Pe}_{\phi_L} \to \infty$, that is, the concentrations and

phase-field ϕ_L are only advected by a velocity **u** at any time *t*. An alternative way to let the right-hand sides of Eqns. 30-31 approach 0 is to set up a system such that $\nabla \cdot J_i \approx 0$ and $\delta G/\delta \phi_L \approx 0$.

In practice, however, the right-hand sides of the concentration and phase-field equation are never set to zero and the equations are solved given finite solutal and phase-field Peclet numbers. The system is considered convection-dominated when $\text{Pe}_{x_i} \gg 1$ and $\text{Pe}_{\phi_L} \gg 1$. We have a diffusion-dominated process when $\text{Pe}_{x_i} \ll 1$ and $\text{Pe}_{x_i}/\text{Pe}_{\phi_L} \ll 1$ while a phasechange-dominated system has $\text{Pe}_{\phi_L} \ll 1$ and $\text{Pe}_{x_i}/\text{Pe}_{\phi_L} \gg 1$.

Generally, the spreading of the liquid drop is faster in the early stage then slows down, i.e. $U_{CL} \rightarrow 0$ as time $t \rightarrow \infty$. This implies that as U_{CL} decreases, the transport due to convection slows down which allows other effects such as phase change and solute diffusion to take effect. In some cases, however, phase change plays a significant role even in the early stage, i.e. $\operatorname{Pe}_{\phi_L}$ is of order 1. If we approximate the contact line speed in the early stage of spreading to be of the order σ_{LV}/μ_{LV} , we can define a nominal phase-field Peclet number, $\operatorname{Pe}_{\phi_L} = \delta_{LV}/(\mu_{LV}M_{\phi_L}R_0)$. Given the base set of parameters in Table 1 with $M_{\phi} = 5 m^3/Js$, $\operatorname{Pe}_{\phi_L} = 5$, which implies that phase change plays a significant role in the spreading process. The nominal solutal Peclet numbers are defined by $\operatorname{Pe}_{x_i} = \sigma_{LV}R_0/(\mu_{LV}M_i^LRT)$, i = A, B, for the given base set of parameters are both 10³ that means solute diffusion does not play a significant role in the early stage of spreading.

On the other hand, with $M_{\phi} = 0.25 \, m^3/Js$, $\hat{P}e_{\phi_L} = 10^2$ and $\hat{P}e_{x_A} = \hat{P}e_{x_B} = 10^3$ which are both much greater than 1. This system, based on the above argument, can be considered convection-dominated in the early stage of spreading. Thus we expect that the dynamics of wetting for this system agrees with known hydrodynamic theories for spreading of inert fluids.

To test the hypothesis about the hydrodynamic limit, in Figure 11a the dynamics of the spreading with phase-field mobilities $M_{\phi} = 0.25 \, m^3/Js$ and $M_{\phi} = 5 \, m^3/Js$ (base state in our calculations) are compared to Cox's model. The velocity of the triple junction U_{CL} is equal to dR/dt. To match our phase field calculations with Cox's model, we also set a viscosity ratio of 1, an equilibrium contact angle $\theta_e = 14.53^{\circ}$ calculated from Young's equation, and a



Figure 11: The dynamic contact angle θ_1 plotted against the Capillary number Ca = $U_{CL}\mu_L/\sigma_{LV}$. Results for phase-field mobilities $M_{\phi} = 0.25, 5 \ m^3/Js$ with $D_L = 10^{-9} \ m^2/s$ are compared to Cox's model with constant $\xi = 0.1$, viscosity ratio of 1, and equilibrium contact angle $\theta_e = 14.53^o$ calculated from Young's equation.

constant parameter ϵ that is related to the ratio between the slip length and characteristic size of the drop. Setting the slip length proportional to the LV-interface thickness, we have $\xi \approx \delta_{LV}/R_0 = 0.1$. For $M_{\phi} = 5 \ m^3/Js$, the dynamics of the spreading does not agree well with Cox's model. In the early stage, the drop spreads faster than the predictions of Cox, then gets closer to Cox's predictions in the final stage. This is expected since phase change should increase interface motion (see Figure 4). With a lower $M_{\phi} = 0.25 \ m^3/Js$, a better agreement with Cox is obtained.

5.3.2. Comparison to a creeping flow model

Huh and Scriven [31] has provided a steady-state analysis of the flow in the vicinity of the contact line in which it is assumed that the stream functions Ψ satisfy a biharmonic equation with conditions that the solid boundary and the liquid-vapor interface are streamlines and there is a continuity of velocity and tangential stress across the interface (see Appendix B for details). Two sets of biharmonic equations that correspond to the streamlines in the spreading liquid and the vapor are solved with matched boundary conditions at the fluid



Figure 12: Streamlines calculated using (a) the modified creeping flow model in a lab frame with viscosity ratio $\mu_2/\mu_1 = 1$, angle of incidence $\theta_1 = 38.7^o$, and angle of depression $\theta_2 = 6.8^o$, (b) numerical simulation at $t/t_c = 40$ with (superimposed) measured contact angles $\theta_1 = 38.7^o$ and $\theta_2 = 6.8^o$.

interface.

As is detailed in Appendix B, we modify this creeping flow model (CFM) to incorporate a non-planar solid substrate and recognize the importance of new boundary conditions as well as a new geometry. Figure 12a correspond to the case with viscosity ratio $\mu_2/\mu_1 = 1$, angle of incidence $\theta_1 = 38.7^{\circ}$, and angle of depression $\theta_2 = 6.8^{\circ}$. The streamlines are shown in a lab frame and the color shades correspond to the magnitude of the velocities (normalized by the magnitude of the velocity of the triple junction). In addition, the flow is two-dimensional and steady-state while the flow in the numerical simulation is transient and axisymmetric. Figure 12b shows a streamline profile of a particular case with a viscosity ratio of 1 at a late time spreading $t/t_c = 40$. The measured contact angles which are superimposed are $\theta_1 = 38.7^{\circ}$ and $\theta_2 = 6.8^{\circ}$. The streamlines are also shown in a lab frame and the color shades correspond to the velocities that is normalized by the magnitude of the velocity of the triple junction. The streamlines inside the spreading drop are nearly parallel to the horizontal substrate but slightly bent towards the triple junction as the height increases. This behavior agrees with the creeping flow model in Figure 12a. Moreover, with both CFM and the numerical simulation, the high velocities are located along the liquidvapor interface which is expected. However, the magnitude of the velocities with the CFM could reach up to a factor of 2.9 of the triple junction speed while the magnitude of the velocities in the simulation could only reach up to 1.1 times the corresponding triple junction speed. Lastly, the streamlines outside the drop with the CFM qualitatively differs with the numerical simulation especially in the area close to the substrate. The streamlines inside the spreading drop agrees with the theory (Figure 12c) while the streamlines outside the drop differs especially close to the substrate. This is due to the fact that in the theoretical analysis, it was assumed that the effective Reynolds number right at the substrate is exactly 0 as a consequence of the imposed no-slip boundary condition. While in the numerical simulation, where no boundary condition is imposed on the diffuse interface but only a highly-steep viscosity gradient, the effective Reynolds number is close but not exactly 0. The difference in the location of the corresponding vortices in both CFM and numerical simulation is also attributed to the effective Reynolds number right at the substrate. Still the disparity in streamlines in the vapor does not significantly affect the flow inside the spreading drop and most importantly the motion of the contact line.

6. Conclusion

We have studied dissolutive wetting numerically using a diffuse-interface model that incorporates fluid flow, solute diffusion, and phase change. We have shown that for convectiondominated cases (i.e., transport due to phase change and solute diffusion is minimum compared to transport due to convection), the dynamics of spreading agrees with a known hydrodynamic theory for spreading inert fluids. However, for cases where phase change plays a significant role, as in most realistic systems, agreement with a known hydrodynamic theory is no longer observed and we found that phase change increases wetting speed. This is due to a strong condensation that takes place near the triple junction. Moreover, there is a strong dependence of the wetting kinetics to the solutal diffusivities. An analysis of the details in composition changes during spreading have revealed that the composition path of the bulk liquid probed at the center of the drop behaves differently compared to the composition path of the bulk liquid probed close to the triple junction, although both locations approach the final equilibrium compositions simultaneously. The difference in behavior is attributed to a lateral flow sweeping solute from the center of the liquid drop to the region close to the triple junction. In addition, we have also found that the rapid spreading traps composition from the vapor to the bulk liquid close to the triple junction.

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Appendix

A. Contact angle measurement

The model presented assumes that all interfaces involved are diffuse but have a finite thickness. The local equilibrium of the phase-field variables varies rapidly but smoothly from a phase-field value of 0 to 1. We can define the thickness of the interface, for example, to be the distance between the phase-field value of 0.1 and phase-field value of 0.9.

However, in order to facilitate an effective measurement of contact angles, a sharpinterface analogue is needed. There are two possible ways of locating a 'sharp-interface' from the diffuse-interface profiles. First is to simply take the level 0.5 contours of all the phase-field variables as seen in Figure 13a. This methodology does not directly identify a triple junction but rather a contact line region.

The second method is to use the following equation,

$$\max(\phi_1(\mathbf{x}, \cdot), \phi_2(\mathbf{x}, \cdot), \phi_3(\mathbf{x}, \cdot)) = \begin{cases} \phi_1 & \text{red} \\ \phi_2 & \text{blue} \\ \phi_3 & \text{green} \end{cases}$$
(32)

that means at every discrete point in the domain we find the phase-field variables that has the maximum value and then designate a corresponding color; red for ϕ_1 , blue for ϕ_2 , and green for ϕ_3 (see Figure 13b). The curvatures of the phases using this method is identical



Figure 13: Level 0.5 contours of all the phase-field variables (white lines) and maximum phase-field value plot given by equation 32 where a color is designated at every discrete point. If ϕ_1 has the maximum value at a point compared to the other phases it is designated a red color. The color blue is designated for ϕ_2 and green for ϕ_3 . The triple junction (TJ) is the point where ($\phi_1 = 1/3, \phi_2 = 1/3, \phi_3 = 1/3$).



Figure 14: Contact angle measurement with a blow-up of the vicinity of the contact line. Following the schematic diagram in Figure 1 for the three contact angles, the measured angles at an early time $(t/t_c = 1)$ using the algorithm in the Appendix are (a) $\theta_1 = 118.1^\circ$, $\theta_2 = 4.6^\circ$, $\theta_3 = 3.4^\circ$, and in the late time $t/t_c = 100$ (b) $\theta_1 = 24.0^\circ$, $\theta_2 = 8.0^\circ$, $\theta_3 = 4.6^\circ$. The star symbol on the outer circle midway between the liquid-vapor and liquid-solid interfaces is the location where composition values of the bulk liquid are taken (see Figure 7).

to the previous method except in the vicinity of the contact line region where this method directly identifies the triple junction that is the point with $(\phi_1 = 1/3, \phi_2 = 1/3, \phi_3 = 1/3)$.

For the measurement of the dynamic contact angles $\theta_1(t)$, $\theta_2(t)$, and $\theta_3(t)$ as described in the schematic diagram in Figure 1, we employ the following algorithm that is illustrated in Figure 14, (i) Plot the 0.5 contours of the phase field variables.

(ii) Define the triple junction (TJ) as the $(\phi_1 = 1/3, \phi_2 = 1/3, \phi_3 = 1/3)$ point.

(iii) Set an inner circle with radius R_1 (typically, 2 - 5x the interface thickness).

(iv) Determine the inner points as the intersection of the inner circle with the $(\phi_i = \phi_j)$ point along the interfaces.

(v) Repeat steps iii-iv with an outer circle with radius $R_2 > R_1$.

The corresponding points along the interfaces (LS, LV, and SV) determine the angles from the horizontal lines. In Figure 14, two examples at different times from the simulations that corresponds to the base set of parameters are shown. The dynamic contact angle θ_1 typically changes from greater than 90° in (a) to less than 90° in (b) while the angles θ_2 and θ_3 remain to be less than 90°. The reason for a certain choice of the radius R_1 is mainly to exclude the complex structure of the triple junction region wherein contact angles that correspond to the interfaces can not be clearly defined. In Figure 15a, the angles from the hozontal lines of the phase fields plotted against the radius from the triple junction are shown. As expected in the triple junction region at a radius $r < \delta$ where δ is the interface thickness, contact angles that correspond to the interfaces (LS, LV, and SV) can not be clearly determined. On the other hand, at radius $r > \delta$, the contact angles of the interfaces can be clearly determined since the curvature of one phase almost coincide with the other corresponding phase. For example, the curvature of the liquid phase along the liquid-vapor interface almost coincides with the curvature of the vapor phase along the same interface (see Figure 14). Figure 15b shows the liquid dynamic contact angle $\theta_L = \theta_1 + \theta_2$ evaluated at radius $r = \delta$ and 2δ and plotted against capillary time. The dynamic contact angle at time $t/t_c = 300$ with $r = 2\delta$ is 26.3° which is closer to the the equilibrium contact angle given by the Neumann's construction ($\theta_L^E = 20.77^\circ$) than with $r = \delta$ where $\theta_L(300) = 37.7^\circ$. In addition, with $r = 3\delta$, 4δ , 5δ , the dynamic contact angles θ_L at time $t/t_c = 300$ are



Figure 15: (a) Angles at the $\phi = 0.5$ contour of the phases with respect to the horizontal axis plotted against radius from the triple junction at $t/t_c = 1$, and (b) dynamic contact angle $\theta_L = \theta_1 + \theta_2$ versus capillary time evaluated at two radii from the triple junction.

25.3°, 25.7°, 26.6°, respectively, which is within $\pm 1^{\circ}$ of the case with $r = 2\delta$. In this paper, we evaluate all contact angles at the radius $r = 2\delta$ from the triple junction.

B. Creeping flow model

Following Huh and Scriven [31], we analyze the motion in the vicinity of the contact line between the fluid interface and the nonplanar solid boundary (see Figure 16). In the creeping flow approximation, the Reynolds number based on the length scale of the contact line region is small enough that the Stokes equations are valid. The flow is locally twodimensional in which the fluid interface is a plane moving with a constant speed U in the direction perpendicular to the contact line.

Polar co-ordinates (r, θ) are defined such that the origin is on the contact line and the fluid interface is in the plane $\theta = 0$. A fluid of viscosity μ_1 occupies the sector $0 < \theta < \alpha_1 + \beta$ while a fluid of viscosity μ_2 occupies the other sector $0 < \theta < \alpha_2$. Both fluid phases are incompressible Newtonian fluids and extend indefinitely large distances from the triple junction. The velocity components in terms of the stream function $\Psi(r, \theta)$ are



Figure 16: Schematic diagram for the creeping flow model with nonplanar substrate.

 $u_r = -r^{-1}\partial\Psi/\partial\theta$ and $u_{\theta} = \partial\Psi/\partial r$. In the fluid with viscosity μ_1 the stream function is denoted by $\Psi_1(r,\theta)$ while in the other fluid, it is denoted by $\Psi_2(r,\theta)$. The stream functions satisfy the following biharmonic equation

$$\left[\frac{\partial^2}{\partial r^2} + \frac{\partial}{r\partial r} + \frac{\partial^2}{r^2\partial\theta^2}\right]^2 \Psi = 0,$$
(33)

and the general solution is given by

$$\Psi_i(r,\theta) = Ur(a_i \sin \theta + b_i \cos \theta + c_i \theta \sin \theta + d_i \theta \cos \theta), \quad i = 1, 2.$$
(34)

The eight constants are determined from the boundary conditions

$$\Psi_1(r,0) = \Psi_2(r,0) = \Psi_1(r,\alpha_2) = 0, \ \Psi_1(r,\alpha_1+\beta) = Ur\sin\beta,$$
(35)

$$\frac{\partial \Psi_1(r,0)}{\partial \theta} = \frac{\partial \Psi_2(r,0)}{\partial \theta}, \ \frac{\mu_1 \partial^2 \Psi_1(r,0)}{\partial \theta^2} = \frac{\mu_2 \partial^2 \Psi_2(r,0)}{\partial \theta^2}, \tag{36}$$

$$\frac{\partial \Psi_1(r,\alpha_1+\beta)}{r\partial\theta} = U\cos\beta, \ \frac{\partial \Psi_2(r,\alpha_2)}{r\partial\theta} = -U.$$
(37)

The equations in (37) correspond to a no-slip boundary condition which result in a force singularity at the contact line. We are mainly interested, however, in the motion in the vicinity of the triple junction and the removal of the force singularity by a slip flow is beyond the scope of this paper (for discussion see [32]). Note that setting $\beta = 0$ in equations (35)-(37) reduces to the original analysis of Huh and Scriven; as an example, see Figure 12a for



Figure 17: Motion in the vicinity of the contact line with the creeping flow model in a moving reference frame with dimensionless velocity U = 1, viscosity ratio $\mu_2/\mu_1 = 0.001$ and (a) angle of incidence $\alpha_1 = 27^o$ and angle of depression $\beta = 5^o$, (b) $\alpha_1 = 27^o$ and $\beta = 15^o$, (c) $\alpha_1 = 45^o$ and $\beta = 15^o$, and (d) reversal of flow with the line corresponds to a zero radial speed of the interface.

the case with dimensionless velocity U = 1, angle of incidence $\alpha_1 = 27^{\circ}$ and viscosity ratio $\mu_2/\mu_1 = 0.001$ in a moving reference frame. In this case, the direction of the flow at the fluid interface is inward to the contact line. With $\beta = 5^{\circ}$ (shown in Figure 17a), the motion in the vicinity of the contact line is generally similar to the previous case with the flow at the fluid interface also inward to the contact line. However, with a higher $\beta = 15^{\circ}$, the motion drastically changes with the flow at the *LV*-interface now outward from the contact line (see Figure 17b). If we keep $\beta = 15^{\circ}$ and increase $\alpha_1 = 45^{\circ}$ (see Figure 17c), the motion becomes similar to the behavior in Figure 17a. Figure 17d shows the pair of angles β and α_1 that corresponds to a zero radial speed of the interface. The area below the line corresponds to a positive radial speed (away from the triple point) of the interface. This reversal of flow did not occur in our simulations, but one could imagine a large effect on dissolutive wetting. In one case fresh (not contaminated by solute from the dissolving solid) would sweep the triple junction; whereas in the other case liquid rich in solid component would wash the triple junction region. A change in contact angle might occur when the flow reverses.

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