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HYDRODYNAMIC BOUNDARY CONDITIONS FOR ONE-COMPONENT LIQUID-GAS FLOWS ON NON-ISOTHERMAL SOLID SUBSTRATES*

XINPENG XU†, CHUN LIU‡, AND TIEZHENG QIAN§

Abstract. Recently, liquid-gas flows related to droplets, bubbles, and thin films on solid surfaces with thermal and wettability gradients have attracted widespread attention because of the many physical processes involved and their promising potential applications in biology, chemistry, and industry. Various new physical effects have been discovered at fluid-solid interfaces by experiments and molecular dynamics simulations, e.g., fluid velocity slip, temperature slip (Kapitza resistance), mechanical-thermal cross coupling, etc. There have been various models and theories proposed to explain these experimental and numerical observations. However, to the best of our knowledge, a continuum hydrodynamic model capable of predicting the temperature and velocity profiles of liquid-gas flows on non-isothermal, heterogeneous solid substrates is still absent. The purpose of this work is to construct a continuum model for simulating the liquid-gas flows on solid surfaces that are flat and rigid, and may involve wettability gradients and thermal gradients. This model is able to describe fluid velocity slip, temperature slip, and mechanical-thermal coupling that may occur at fluid-solid interfaces. For this purpose, we first employ the diffuse interface modeling to formulate the hydrodynamic equations for one-component liquid-gas flows in the bulk region. This reproduces the dynamic van der Waals theory of Onuki [Phys. Rev. Lett., 94: 054501, 2005]. We then extend Waldmann's method [Z. Naturforsch. A, 22: 1269-1280, 1967] to formulate the boundary conditions at the fluid-solid interface that match the hydrodynamic equations in the bulk. The effects of the solid surface curvature are also briefly discussed in the appendix. The guiding principles of our model derivation are the conservation laws and the positive definiteness of entropy production together with the Onsager reciprocal relation. The derived model is self-consistent in the sense that the boundary conditions are mathematically demanded by the bulk equations. A finite difference scheme is presented for numerically solving the model system. We show that some widely used boundary conditions can actually be recovered by taking appropriate limits. We also point out that the framework presented here for modeling two-phase flows on solid surfaces, from bulk equations to boundary conditions, is in a form that can be readily generalized to model other fluid-solid interfacial phenomena.

Key words. One-component two-phase flow, liquid-gas phase transition, fluid-solid interface, wall slip.

AMS subject classifications. 76T10, 82C21.

1. Introduction

Various two-phase flows on solid walls have attracted widespread attention in both scientific research and industrial applications for decades [1, 2, 3]. Over the years, numerous models and theories have been proposed [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15], and a consensus has been formed regarding the guiding principles and constraints that are to be imposed on these models and theories. Physically, the validity of a continuum hydrodynamic model lies in an accurate description of the dynamical processes in the (fluid-fluid and fluid-solid) interfacial regions. Based on this understanding, we first review the two most popular methods developed for interface modeling:

Sharp interface model – The interfacial region is geometrically described as a singular surface [16] of zero thickness across which one or more quantities are discontinuous.

Diffuse interface model – The interfacial region is described through a so-called phase field variable which shows a fast but smooth variation across the intervening interface between the two bulk phases.

In the sharp interface model, the interfacial dynamics are typically taken into account by introducing some surface properties and imposing necessary boundary conditions (sometimes also called jump conditions) at the singular surface. However, the formulation of the boundary conditions necessitated by the hydrodynamic equations in the bulk region is not a trivial task, as they have to be consistent with the principles of continuum mechanics and thermodynamics. Although the general philosophy of formulating these boundary conditions was considered clear in the beginning, great efforts [16, 17, 18, 19, 20, 21, 22] have actually been made for decades with successes gradually achieved. Here we would like to emphasize that the principles of continuum mechanics and thermodynamics in their integral forms should always hold for systems with singular surface(s). The boundary conditions at a surface without mass, momentum, and energy densities were put into general form by Kotchine [17] in 1926 as the dynamical compatibility conditions at shock discontinuities, though special cases had been worked out earlier. After that, many authors [16, 18, 19, 20] have tried to extend Kotchine's theorem [16] in a hydrodynamic framework by introducing various interfacial densities and fluxes (e.g., interfacial tension and viscous stress). However, the constraints imposed by the principles of thermodynamics were not fully taken into consideration until Waldmann [21] applied the method of nonequilibrium thermodynamics [23] to the derivation of boundary conditions at the interface between two immiscible fluids. Later, Bedeaux *et al.* [22] reformulated Waldmann's method for the study of capillary effects in the presence of surface stress, surface energy, and surface entropy. In recent years, the extended Kotchine's theorem and Waldmann's method have proven to be useful and effective in deriving the boundary conditions in various interfacial problems, e.g., solidification of binary alloys [24], viscoelasticity of nematic interfaces [25], dynamics of lipid-protein membranes [26, 27, 28], rarefied gases flowing on the solid walls [29, 30], molecular liquids [31, 32] flowing on the solid walls, viscous flows on chemically patterned solid walls [33], etc.

Unlike the sharp interface models supplemented by boundary conditions, the diffuse interface models allow us to describe the interfacial phenomena by solving a set of partial differential equations applied to the whole system (including the bulk and interfacial regions). This avoids treating the interface by using the boundary conditions. The history of diffuse interface models actually dates back to van der Waals' pioneering work [34] on the thermodynamics of liquid-gas interfaces. Many years later, van der Waals's approach was presented by Cahn and Hilliard [35] in a more modern guise. Since then the diffuse interface modeling has been widely used for studying the equilibrium properties of various two-phase systems. However, to apply the diffuse interface models to the study of dynamical processes is more difficult, as it necessarily involves the coupling of the phase field with hydrodynamics. Recently, applicable models have been formulated and validated by Jasnow *et al.* [36], Anderson [37], etc. for immiscible two-phase flows, by Onuki [38] for two-phase hydrodynamics involving liquid-gas transition, and by Liu *et al.* [39], Onuki *et al.* [40] for fluid-solid systems. Due to its unique simplicity and also the flexibility in incorporating new physics, the diffuse interface modeling has become a widely used method for studying

the equilibrium and dynamic properties of many two-phase systems.

From the two types of models reviewed above, it is now clear that for two-phase flows on solid walls which involve three interfaces (one fluid-fluid interface and two fluid-solid interfaces), there can be three different types of models:

All-sharp-interface model with all the three interfaces treated as sharp interface;

All-diffuse-interface model with all the three interfaces treated as diffuse interface;

Composite-interface model with the fluid-fluid interface treated as diffuse interface and the two fluid-solid interfaces as sharp interface.

Boundary conditions are essential to an accurate (mathematical) description of two-phase flows on solid walls. It is worth emphasizing that the physics associated with boundary conditions can not be simply deduced from that associated with hydrodynamic equations in the bulk region. That is, the boundary conditions should not be regarded as just a routine or conventional mathematical hypothesis associated with the partial differential equations in the bulk region. Presumably, the hydrodynamic length scale involved in the physics in the bulk is well separated from the microscopic/mesoscopic length scale involved in the physics at the boundary.

It has been known for decades that the classical no-slip boundary condition would lead to infinite viscous dissipation in the vicinity of a moving contact line (where the fluid-fluid interface intersects the solid wall), a classical fluid mechanical problem first presented by Huh and Scriven [8, 41]. By analyzing a simplified all-sharp-interface model with the no-slip boundary condition at the fluid-solid interface, they found a non-integrable singularity for shear viscous stress at the moving contact line. Since then, numerous models have been proposed to remove this unphysical stress singularity. The first few models employed the all-sharp-interface description, with the no-slip condition relaxed within a small region around the contact line [42, 43, 44, 45] or with a hypothetical interface formation/disappearance mechanism [9, 46]. Recently, quite a few diffuse interface models have been developed to resolve the moving contact line paradox by introducing mechanisms that are missing in the classical sharp interface treatments. These mechanisms include diffusive transport across the fluid-fluid interface in binary fluids and mass transport in one-component liquid-gas systems with phase transition. By making full use of the advantages of the diffuse interface method, Sun *et al.* [15] have proposed an all-diffuse-interface model capable of describing three phases (e.g., two fluid phases and one solid phase) with two phase fields. However, the all-diffuse-interface method does involve a rather complicated description of the phase field mechanics and thermodynamics, which would become even more difficult if heat conduction enters into the model. In comparison, a balanced approach can be achieved by using the composite-interface models, e.g., Seppecher [4], Chen *et al.* [5], Jacqmin [6], Pismen *et al.* [7], Qian *et al.* [8, 10, 12, 14], Onuki *et al.* [11, 13], Ren *et al.* [47], through which much of the physics involved in contact line motion has been gradually clarified. In the present work, our efforts will be devoted to a composite-interface model for one-component liquid-gas flows on non-isothermal, heterogeneous solid substrates.

Physically, the microscopic length scale associated with the fluid-solid interface is determined by the short-range fluid-solid interactions while the mesoscopic length scale associated with the liquid-gas interface depends on the temperature: it diverges as the critical point is approached. Based on this understanding, we will model the fluid-solid interface as a sharp interface and the liquid-gas interface as a diffuse interface. While this composite modeling has been widely employed to investigate the fluid-solid interfacial phenomena in two-phase flows, a corresponding framework

for the derivation of boundary conditions that match the hydrodynamic equations in the bulk region is still absent. In fact, the boundary conditions have been derived/proposed on a problem-by-problem basis using methods like

(i) Ad hoc methods based on physical intuitions [6, 48];

(ii) Various variational methods based on energy (or entropy) and its dissipation (or production) [10];

(iii) Scaling analysis for the dynamics within the surface layer next to the solid surface [12].

While these methods have proven to be effective for their respective problems, it would be more fruitful if a framework can be developed to incorporate all the possibly involved physical mechanisms into the boundary conditions, without violating any constraint imposed by the principles of continuum mechanics and thermodynamics. Recently, various new physical effects have been discovered at fluid-solid interfaces by experiments and molecular dynamics simulations, including fluid velocity slip [49, 50, 51], temperature slip (Kapitza resistance) [52, 53], and mechanical-thermal cross coupling [54]. Meanwhile, the dynamic van der Waals theory [11, 38] has been well established for the description of two-phase hydrodynamics involving the liquid-gas transition in nonuniform temperature. To the best of our knowledge, the hydrodynamic boundary conditions, general enough to describe the fluid-solid interfacial phenomena mentioned above, have not been fully developed for the dynamic van der Waals theory. In fact, we have derived a model to introduce the boundary slip effects, but only for isothermal fluid-solid interfaces [14]. The purpose of this work is to construct a model for simulating the liquid-gas flows on solid surfaces that may involve wettability gradient and thermal gradient, and exhibit velocity slip [49, 50, 51], temperature slip [52, 53], and mechanical-thermal coupling [54]. Technically, we will combine the dynamic van der Waals theory [11, 38] for the hydrodynamic equations in the bulk region with Waldmann's method [21] for formulating the boundary conditions at the fluid-solid interface. Our derivation focuses on the balance equations for various fluxes and the positive definiteness of local entropy production.

This paper is organized as follows. In Section 2, we review the dynamic van der Waals theory in the bulk region. This review introduces the flux quantities for later use at the fluid-solid interface. In Section 3, we first describe the general assumptions and concepts involved in our derivation of the boundary conditions at a singular surface. Then, by combining the dynamic van der Waals theory with Waldmann's method applied at the singular surface, we construct a model *with all the necessary hydrodynamic boundary conditions* for one-component liquid-gas flows on non-isothermal, heterogeneous solid surfaces. In Section 4, we present a finite difference scheme for numerically solving the model. In Section 5, we show that some widely used boundary conditions, e.g., no-slip boundary condition for velocity and continuity conditions for temperature and heat flux, can be recovered by taking appropriate limits of the present model. We also point out the following. (i) In our previous study [14], while the temperature is nonuniform in the bulk region, the fluid-solid interface is still isothermal. (ii) Although the fluid temperature is allowed to vary at the interface in the recent work by Onuki and Teshigawara [13], there is no dissipative process occurring at the interface, and hence no entropy production there. We emphasize that our boundary conditions are derived from the interfacial entropy production. The paper is concluded in Section 6 with a few remarks.

2. Diffuse interface model for liquid-gas flows in the bulk region

In this section, we review the dynamic van der Waals theory [11, 13, 14, 55],

which is a diffuse interface model for one-component liquid-gas systems in the linear response regime. We present this theory in a framework that is suitable for the later derivation of hydrodynamic boundary conditions in Section 3.

2.1. Thermodynamics. For a one-component homogeneous system in equilibrium, we have the Euler equation, Gibbs equation, and Gibbs-Duhem equation:

$$e - Tns + p - \mu n = 0, \tag{2.1}$$

$$d(ns) = \frac{1}{T}de - \frac{\mu}{T}dn, \tag{2.2}$$

$$-nsdT + dp - nd\mu = 0, \tag{2.3}$$

in which n, e, s, T, p, and μ are the number density, internal energy density, entropy per molecule, temperature, pressure, and chemical potential, respectively. Choosing n and T as the independent state variables, we have the Helmholtz free energy density as the corresponding thermodynamic potential, which is defined by $f(n,T) = e - Tns$ and satisfies

$$df = -nsdT + \mu dn. \tag{2.4}$$

For a one-component homogeneous fluid, van der Waals [56] constructed a simple yet very successful model, with the Helmholtz free energy density $f(n,T)$ given by

$$f(n,T) = nk_BT\left[\ln\left(\lambda_{\mathrm{th}}^3 n\right) - 1 - \ln(1 - v_0 n)\right] - \varepsilon v_0 n^2, \tag{2.5}$$

where k_B is the Boltzmann constant, m the molecular mass, $\lambda_{\mathrm{th}} = \hbar(2\pi/mk_BT)^{1/2}$ the thermal de Broglie length, v_0 the molecular volume, and ε the strength of attractive interaction. The mass density is $\rho = nm$. From $f(n,T)$, we have

$$e(n,T) = 3nk_BT/2 - \varepsilon v_0 n^2, \tag{2.6}$$

$$s(n,T) = -k_B\ln\left[\lambda_{\mathrm{th}}^3 n/(1 - v_0 n)\right] + 5k_B/2, \tag{2.7}$$

$$p(n,T) = nk_BT/(1 - v_0 n) - \varepsilon v_0 n^2. \tag{2.8}$$

In order to treat systems with liquid-gas coexistence, van der Waals [34] further introduced a density gradient contribution to the free energy functional for inhomogeneous systems. However, his theory is only applicable to systems in thermal equilibrium. Recently, a dynamic version of van der Waals theory, namely the dynamic van der Waals theory [11], has been developed, capable of describing two-phase hydrodynamics with liquid-gas transition in non-uniform temperature. As a diffuse interface model, this theory chooses the number density n as the order parameter distinguishing the liquid and gas phases and the intervening interface. The first two assumptions underlying the theory may be stated as follows:

(i) The gradient contributions to the internal energy density $\hat{e}$ and entropy density $\hat{S}$ are given by

$$\hat{e} = e + \frac{K(n)}{2}|\nabla n|^2, \tag{2.9}$$

$$\hat{S} = ns(n,e) - \frac{C(n)}{2} |\nabla n|^2, \tag{2.10}$$

in which $K(n)$ and $C(n)$ are positive, indicating an increase of energy and a decrease of entropy due to the density inhomogeneity. Here $s(n,e)$ denotes the quantity s as a function of n and e. To obtain the explicit form of $s(n,e)$, T is first expressed as a function of n and e, i.e., $T(n,e)$, which can be derived from equation (2.6). Then, substituting $T(n,e)$ into $s(n,T)$ in equation (2.7) gives $s(n,T(n,e)) \equiv s(n,e)$. An immediate consequence of the gradient contributions in equations (2.9) and (2.10) is the elasticity in one-component liquid-gas systems, manifested through a reversible stress tensor $-\overset{\leftrightarrow}{\mathbf{\Pi}}$, which is anisotropic.

(ii) Local equilibria are established in systems out of global equilibrium. Therefore the thermodynamic relations, i.e., equations (2.1)-(2.8), are still valid locally.

The entropy in the bulk region is $S_b = \int d\mathbf{r} \hat{S}$ with $\hat{S}$ given by equation (2.10). The variation of S_b is given by

$$\delta S_b = \int d\mathbf{r} \left\{ \frac{1}{T} \delta e - \frac{\mu}{T} \delta n - \delta \left[\frac{C(n)}{2} |\nabla n|^2 \right] \right\},$$

in which $\delta[ns(n,e)] = \frac{1}{T}\delta e - \frac{\mu}{T}\delta n$ (from equation (2.2) for the homogeneous part) has been used. Substituting $\delta \hat{e} = \delta e + \delta \left[\frac{K(n)}{2} |\nabla n|^2 \right]$ into the above expression for δS_b, we have

$$\delta S_b = \int d\mathbf{r} \left\{ \frac{1}{T} \delta \hat{e} - \frac{\mu}{T} \delta n - \frac{1}{T} \delta \left[\frac{M(n,T)}{2} |\nabla n|^2 \right]_T \right\},$$

in which $M(n,T) \equiv K(n) + C(n)T$, and $\delta[\cdots]_T$ denotes the variation with respect to n only. Using

$$\int d\mathbf{r} \left\{ -\frac{1}{T} \delta \left[\frac{M(n,T)}{2} |\nabla n|^2 \right]_T \right\}$$
$$= \int d\mathbf{r} \left\{ -\frac{1}{T} \left[\frac{M_n(n,T)}{2} |\nabla n|^2 \right] \delta n - \nabla \cdot \left[\frac{1}{T} M(n,T) \nabla n \delta n \right] + \nabla \cdot \left[\frac{1}{T} M(n,T) \nabla n \right] \delta n \right\}$$

with $M_n \equiv (\partial M/\partial n)_T$, we have

$$\delta S_b = \int d\mathbf{r} \left[\frac{1}{T} \delta \hat{e} - \frac{\hat{\mu}}{T} \delta n - \nabla \cdot \left(\frac{M}{T} \nabla n \delta n \right) \right],$$

in which $\hat{\mu}$ denotes the generalized chemical potential

$$\hat{\mu} = \mu + \frac{M_n}{2} |\nabla n|^2 - T \nabla \cdot \left(\frac{M}{T} \nabla n \right). \tag{2.11}$$

We then introduce the generalized pressure $\hat{p}$ through the generalized Euler equation:

$$\hat{e} - T\hat{S} + \hat{p} - n\hat{\mu} = 0, \tag{2.12}$$

with

$$\hat{p} = p - \frac{M}{2} |\nabla n|^2 + \frac{nM_n}{2} |\nabla n|^2 - Tn\nabla n \cdot \nabla \frac{M}{T} - Mn\nabla^2 n, \tag{2.13}$$

which is actually the isotropic part of $\overset{\leftrightarrow}{\mathbf{\Pi}}$, to be derived later.

To obtain the equilibrium conditions in the bulk region, we consider a system of entropy $S_b = \int d\mathbf{r} \hat{S}$ with fixed particle number $N = \int d\mathbf{r} n$ and fixed internal energy $E_b = \int d\mathbf{r} \hat{e}$. Maximizing S_b with respect to $\hat{e}$ and n yields the bulk equilibrium conditions [11]: (i) the homogeneity of temperature T and (ii) the homogeneity of the generalized chemical potential $\hat{\mu}$.

2.2. General balance equations. In order to derive the hydrodynamic equations in the bulk region, we start from a general balance equation for an arbitrary extensive quantity.

A diffuse interface model for two-phase flows adopts the Eulerian description. Let's consider a fluid volume Ω bounded by a closed surface Σ. The rate of change of an extensive quantity $\Phi \equiv \int_\Omega d\mathbf{r} \phi$ (a scalar, vector, or tensor) defined in Ω is given by the general balance equation

$$\dot{\Phi} = -\dot{\Phi}^* + \Pi. \tag{2.14}$$

Here $\dot{\Phi} \equiv d\Phi/dt$ denotes the rate of change of Φ (whose volume density is ϕ), $\dot{\Phi}^* \equiv \int_\Sigma dA \hat{\gamma} \cdot \mathbf{J}$ is the corresponding outgoing (integrated) flux with $\int_\Sigma dA$ denoting the surface integral, $\hat{\gamma}$ being the outward unit vector normal to Σ, and $\mathbf{J}$ being the *non-convective* flux, respectively, and Π is the rate of production of Φ, given by

$$\Pi \equiv \int_\Omega d\mathbf{r} \pi, \tag{2.15}$$

with π being the corresponding density quantity.

Using the Reynolds transport theorem and Gauss' divergence theorem, we rewrite $\dot{\Phi}$ and $\dot{\Phi}^*$ as

$$\dot{\Phi} = \int_\Omega d\mathbf{r} \left[\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{v}\phi) \right], \tag{2.16}$$

$$\dot{\Phi}^* = \int_\Omega d\mathbf{r} \nabla \cdot \mathbf{J}. \tag{2.17}$$

Substituting equations (2.15)-(2.17) into the general balance equation (2.14) then gives

$$\int_\Omega d\mathbf{r} \left[\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{v}\phi + \mathbf{J}) - \pi \right] = 0. \tag{2.18}$$

As the control volume Ω is arbitrarily chosen, equation (2.18) leads to the general differential balance equation

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{v}\phi) = -\nabla \cdot \mathbf{J} + \pi. \tag{2.19}$$

If $\pi = 0$, then the above equation means the conservation of Φ.

It is worth emphasizing that the differential balance equation (2.19) is valid only in regions without any discontinuities (in $\mathbf{v}$, ϕ, and $\mathbf{J}$). Nevertheless, the integral balance equation (2.14) is more general, applicable to control volumes that include singular surface(s) [16].

2.3. Balance equations for particle number, momentum, and energy.
Below we derive the balance equations for particle number, momentum, and energy. The continuity equation for n,

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{v}) = 0, \tag{2.20}$$

is obtained from the differential balance equation (2.19) with $\phi \to n$, $\mathbf{J} \to 0$, $\pi \to 0$. The momentum equation

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v}\mathbf{v}) = \nabla \cdot \overset{\leftrightarrow}{\mathbf{M}}, \tag{2.21}$$

is obtained from the same equation with $\phi \to \rho \mathbf{v}$, $\mathbf{J} \to -\overset{\leftrightarrow}{\mathbf{M}}$, $\pi \to 0$. Here $\overset{\leftrightarrow}{\mathbf{M}}$ denotes the total stress tensor, which is composed of a reversible part $-\overset{\leftrightarrow}{\mathbf{\Pi}}$ and an irreversible (viscous) part $\overset{\leftrightarrow}{\boldsymbol{\sigma}}$, i.e., $\overset{\leftrightarrow}{\mathbf{M}} \equiv -\overset{\leftrightarrow}{\mathbf{\Pi}} + \overset{\leftrightarrow}{\boldsymbol{\sigma}}$. The stress tensors $\overset{\leftrightarrow}{\mathbf{M}}$, $-\overset{\leftrightarrow}{\mathbf{\Pi}}$, and $\overset{\leftrightarrow}{\boldsymbol{\sigma}}$ must be symmetric as required by the conservation of angular momentum for an isotropic fluid [23].

For the total energy density e_T, we have

$$\frac{\partial e_T}{\partial t} + \nabla \cdot (e_T \mathbf{v}) = -\nabla \cdot \left(-\overset{\leftrightarrow}{\mathbf{M}} \cdot \mathbf{v} + \mathbf{q} \right), \tag{2.22}$$

obtained from the general balance equation with $\phi \to e_T$, $\mathbf{J} \to -\overset{\leftrightarrow}{\mathbf{M}} \cdot \mathbf{v} + \mathbf{q}$, $\pi \to 0$. Here $\mathbf{q}$ denotes the heat flux, and $e_T = \hat{e} + e_K$ with $\hat{e}$ being the internal energy density and $e_K \equiv \rho \mathbf{v}^2/2$ being the kinetic energy density. For the kinetic energy density e_K, we have

$$\frac{\partial e_K}{\partial t} + \nabla \cdot (e_K \mathbf{v}) = \mathbf{v} \cdot \left(\nabla \cdot \overset{\leftrightarrow}{\mathbf{M}} \right), \tag{2.23}$$

obtained by multiplying the momentum equation by $\mathbf{v}$. Subtracting equation (2.23) from (2.22) gives the balance equation for internal energy density $\hat{e}$:

$$\frac{\partial \hat{e}}{\partial t} + \nabla \cdot (\hat{e}\mathbf{v}) = -\overset{\leftrightarrow}{\mathbf{\Pi}} : \nabla \mathbf{v} + \overset{\leftrightarrow}{\boldsymbol{\sigma}} : \nabla \mathbf{v} - \nabla \cdot \mathbf{q}. \tag{2.24}$$

2.4. Entropy production and constitutive relations.   We have presented the balance equations for particle number, momentum, and energy by introducing the fluxes $\overset{\leftrightarrow}{\mathbf{M}} \equiv -\overset{\leftrightarrow}{\mathbf{\Pi}} + \overset{\leftrightarrow}{\boldsymbol{\sigma}}$ and $\mathbf{q}$. In order to close the equation system for the state variables n, $\mathbf{v}$, and T, the balance equations must be supplemented with the necessary constitutive relations, which are constrained by the second law of thermodynamics. For this purpose, we need to derive the balance equation for the total entropy density $\hat{S}$, i.e., equation (2.19) for $\phi \to \hat{S}$. This will enable us to obtain explicit expressions for the entropy flux and entropy production, from which the constitutive relations necessitated by the equation system can be derived in accordance with the principles of thermodynamics.

The rate of change of the entropy $S_b = \int_{\Omega_0} d\mathbf{r} \hat{S}$ in the bulk region is given by

$$\frac{dS_b}{dt} = \int_{\Omega_0} d\mathbf{r} \frac{\partial \hat{S}}{\partial t} = \int_{\Omega_0} d\mathbf{r} \left[\frac{1}{T} \frac{\partial \hat{e}}{\partial t} - \frac{\hat{\mu}}{T} \frac{\partial n}{\partial t} - \nabla \cdot \left(\frac{M}{T} \nabla n \frac{\partial n}{\partial t} \right) \right], \tag{2.25}$$

which comes directly from the variational expression for δS_b derived in Section 2 Subsection 2.1. Note that the volume Ω_0 is fixed here. As Ω_0 can be arbitrarily chosen, we have

$$\frac{\partial \hat{S}}{\partial t} = \frac{1}{T}\frac{\partial \hat{e}}{\partial t} - \frac{\hat{\mu}}{T}\frac{\partial n}{\partial t} - \nabla \cdot \left(\frac{M}{T}\nabla n \frac{\partial n}{\partial t}\right) \qquad (2.26)$$

for $\hat{S}$ as a necessary generalization of the Gibbs Equation (2.2). Substituting equations (2.20) and (2.24) into (2.26), we obtain the balance equation for $\hat{S}$:

$$\frac{\partial \hat{S}}{\partial t} + \nabla \cdot \left(\hat{S}\mathbf{v}\right) = -\nabla \cdot \hat{\mathbf{J}}_f^S + \frac{1}{T}\overset{\leftrightarrow}{\boldsymbol{\sigma}}:\nabla\mathbf{v} - \frac{1}{T^2}\mathbf{q}\cdot\nabla T + \frac{1}{T}\left(-\overset{\leftrightarrow}{\mathbf{\Pi}}+\hat{p}\overset{\leftrightarrow}{\mathbf{I}}+M\nabla n\nabla n\right):\nabla\mathbf{v}, \qquad (2.27)$$

in which $\hat{\mathbf{J}}_f^S \equiv [M\nabla n(\partial n/\partial t + \mathbf{v}\cdot\nabla n) + \mathbf{q}]/T$ is the total entropy flux in the bulk region, and the identity $\nabla \cdot \left[\left(\hat{p}\overset{\leftrightarrow}{\mathbf{I}}+M\nabla n\nabla n\right)/T\right] = -\hat{e}\nabla(1/T) + n\nabla(\hat{\mu}/T)$ has been used [11]. (This identity is a generalization of the relation $d(p/T) = -ed(1/T) + nd(\mu/T)$ following the Gibbs-Duhem Equation (2.3) for homogeneous systems.) Comparing equation (2.27) with the general balance equation (2.19), we find the density of the entropy production rate is of the form

$$\sigma = \frac{1}{T}\overset{\leftrightarrow}{\boldsymbol{\sigma}}:\nabla\mathbf{v} - \frac{1}{T^2}\mathbf{q}\cdot\nabla T + \frac{1}{T}\left(-\overset{\leftrightarrow}{\mathbf{\Pi}}+\hat{p}\overset{\leftrightarrow}{\mathbf{I}}+M\nabla n\nabla n\right):\nabla\mathbf{v}. \qquad (2.28)$$

Physically, the density inhomogeneity leads to a reversible entropy flux $[M\nabla n(\partial n/\partial t + \mathbf{v}\cdot\nabla n)]/T$, but it does not contribute to entropy production. Therefore, $\left[\left(-\overset{\leftrightarrow}{\mathbf{\Pi}}+\hat{p}\overset{\leftrightarrow}{\mathbf{I}}+M\nabla n\nabla n\right):\nabla\mathbf{v}\right]/T$ in σ must vanish. It follows that the reversible part of the total stress tensor is given by

$$-\overset{\leftrightarrow}{\mathbf{\Pi}} = -M\nabla n\nabla n - \hat{p}\overset{\leftrightarrow}{\mathbf{I}}, \qquad (2.29)$$

with $\hat{p}$ already given by equation (2.13). In summary, comparing equations (2.19) and (2.27) with (2.29), we have the correspondences $\phi \to \hat{S}$, $\mathbf{J} \to \hat{\mathbf{J}}_f^S$, and $\pi \to \sigma = \frac{1}{T}\overset{\leftrightarrow}{\boldsymbol{\sigma}}:\nabla\mathbf{v} - \frac{1}{T^2}\mathbf{q}\cdot\nabla T$.

In deriving the balance equation for entropy, we have obtained the explicit expression for the reversible stress tensor $-\overset{\leftrightarrow}{\mathbf{\Pi}}$ and also the entropy production σ in the bilinear form

$$\sigma = \sum_i J_i X_i \geq 0, \qquad (2.30)$$

with J_i and X_i regarded as conjugate thermodynamic fluxes and forces. The positive definiteness of

$$\sigma = \frac{1}{T}\overset{\leftrightarrow}{\boldsymbol{\sigma}}:\nabla\mathbf{v} - \frac{1}{T^2}\mathbf{q}\cdot\nabla T \qquad (2.31)$$

can be ensured by the constitutive relations

$$\overset{\leftrightarrow}{\boldsymbol{\sigma}} = \eta\left(\nabla\mathbf{v}+\nabla\mathbf{v}^T\right) + (\zeta - 2\eta/3)\overset{\leftrightarrow}{\mathbf{I}}\nabla\cdot\mathbf{v}, \qquad (2.32)$$

$$\mathbf{q} = -\lambda\nabla T, \qquad (2.33)$$

for the viscous stress tensor and heat flux, respectively. Here the positive coefficients η, ζ, and λ denote the shear viscosity, bulk viscosity, and heat conductivity, respectively. Note that according to Curie's symmetry principle [23], which is a mathematical constraint on constitutive relations, the viscous dissipation in tensorial form and the thermal dissipation in vectorial form have no cross coupling.

To conclude, the hydrodynamic equations for one-component liquid-gas flows consist of the continuity equation (2.20), the momentum equation (2.21), and the balance equation (2.24) for internal energy, supplemented by equations (2.6), (2.8), (2.9), (2.13), (2.29), (2.32), and (2.33). Alternatively, as suggested by Teshigawara and Onuki [55], the balance equation for entropy (2.27) may be used to replace the energy equation (2.24), together with a replacement of (2.6) and (2.9) by (2.7) and (2.10).

3. Sharp interface model for fluid-solid interfaces

In this section, we will treat the fluid-solid interfaces as sharp interfaces and derive the boundary conditions demanded by the bulk hydrodynamic equations of the dynamic van der Waals theory. Physically, these boundary conditions account for the effects of those dissipative processes at the fluid-solid interface. Our derivation is based on Waldmann's method [21] and its later developments [22], which apply the principles of nonequilibrium thermodynamics [23] to interfacial hydrodynamics. We first introduce the surface entropy and surface energy according to Onuki [11]. We then allow the stress tensor and heat flux to be discontinuous across the fluid-solid interface. From the jump conditions (for momentum and energy) and a Gibbs-type equation for various interfacial quantities, we can obtain an expression for the entropy production at the interface. The constitutive relations for various dissipative processes at the interface are then derived from this entropy production expression in accordance with the principles of thermodynamics. Combining the jump conditions and these constitutive relations, we obtain the hydrodynamic boundary conditions necessitated by the hydrodynamic equations in the bulk region.

For simplicity, the solid walls are modeled to be flat, rigid, impermeable, and insoluble. The temperature in the solid, hereafter denoted by T_w, satisfies the heat equation

$$C_w \frac{\partial T_w}{\partial t} = \lambda_w \nabla^2 T_w, \tag{3.1}$$

where C_w is the heat capacity per unit volume, and λ_w is the heat conductivity with $\mathbf{q}_w = -\lambda_w \nabla T_w$ being the heat flux. Note that equation (3.1) is valid only in the reference frame moving with the rigid wall. In general, $\partial T_w/\partial t$ should be replaced by the material derivative $dT_w/dt = \partial T_w/\partial t + \mathbf{w} \cdot \nabla T_w$ with $\mathbf{w}$ denoting the velocity of the wall.

For a fluid in contact with a rigid solid wall, the fluid-solid interfacial region, which is responsible for the fluid-solid coupling, is actually formed by a fluid layer of small but finite thickness [57, 58]. In order to take into account the hydrodynamic effects of this interfacial region *without resolving the dynamics therein*, we need to model the fluid-solid interface as a sharp interface and derive the boundary conditions there, which are necessitated by the hydrodynamic description in the bulk regions. Mathematically, these boundary conditions describe the *integrated* effects of interfacial dynamics.

3.1. Thermodynamics.   The interactions of a fluid with the solid wall can considerably modify the fluid's equilibrium and dynamic properties. In the study of wetting phenomena, Cahn [59] considered the effects of the solid wall by introducing

a surface free energy, which is a function of n, the boundary value of fluid density at the fluid-solid interface. The use of free energy, however, is only valid for describing isothermal systems with a uniform temperature [4, 7, 8, 37]. For the present study, the temperature is in general non-uniform due to liquid-gas transition. According to Onuki [11], it is necessary to introduce the surface entropy S_s and surface energy E_s as

$$S_s = \int dA\sigma'_s(n), \tag{3.2}$$

$$E_s = \int dAe'_s(n), \tag{3.3}$$

where σ'_s and e'_s are entropy and energy per unit area, and $\int dA$ denotes the surface integral at the fluid-solid interface. Note that σ'_s and e'_s are functions of n only. Here the prime denotes the surface quantities whose dimensions are different from the corresponding bulk quantities. Below the prime will be used again in this sense. Furthermore, the Helmholtz free energy per unit area can be defined as

$$f'_s(n,T) = e'_s(n) - T\sigma'_s(n), \tag{3.4}$$

in which T is the boundary value of the fluid's temperature at the fluid-solid interface. It follows that $\sigma'_s = -(\partial f'_s/\partial T)_n$, and hence

$$df'_s = -\sigma'_s dT + \left(\frac{\partial f'_s}{\partial n}\right)_T dn. \tag{3.5}$$

Substituting equation (3.4) into (3.5) then gives a Gibbs-type equation

$$d\sigma'_s = \frac{1}{T}de'_s - \frac{1}{T}\left(\frac{\partial f'_s}{\partial n}\right)_T dn. \tag{3.6}$$

Furthermore, the fluid-solid interfacial tension for one-component fluids satisfies [60] $e'_s - T\sigma'_s - \gamma_{fs} = 0$, an equation of Euler type in analogy with equation (2.1). It follows that

$$\gamma_{fs} = f'_s, \tag{3.7}$$

which is locally temperature dependent. Consequently, a thermal gradient on the solid surface leads to a tangential gradient of γ_{fs}, by which some flow phenomena may be induced [3]. A gradient of γ_{fs} can be induced by wettability gradients as well, which are usually introduced to solid surfaces by chemical treatments [1, 2, 3].

To derive the equilibrium condition at the fluid-solid interface we maximize the total entropy $S_{tot} = S_b + S_s$ with respect to e and n (as in a microcanonical ensemble) for fixed particle number $N = \int d\mathbf{r}n$ and fixed total internal energy $E_{tot} = E_b + E_s$. This leads to the homogeneity of temperature and that of generalized chemical potential $\hat{\mu}$ in the bulk, and

$$L \equiv M\nabla_\gamma n + \left(\frac{\partial f'_s}{\partial n}\right)_T = 0 \tag{3.8}$$

at the fluid-solid interface. Here the scalar operator ∇_γ is defined by $\nabla_\gamma \equiv \hat{\gamma}\cdot\nabla$ with $\hat{\gamma}$ denoting the outward unit vector normal to the interface.

Finally, it is worth emphasizing that to model the interfacial hydrodynamical processes, it is necessary to assume the *local* validity of equations (3.5)-(3.7) at the fluid-solid interface. This will be made clear in Section 3 Subsection 3.3.

3.2. General boundary (jump) conditions.   As presented in Section 2 Subsection 2.2, the integral balance equation reduces to the differential balance equation if there is no discontinuity in the relevant quantities. This is obviously not true at the fluid-solid interface where various discontinuities occur. Therefore, the balance equations to be applied at the interface can not be simply formulated as differential equations. Rather, they appear as boundary (jump) conditions by which the boundary values of those concerned quantities in fluid and solid are related.

As mentioned before, we consider solid walls that are flat, rigid, and impermeable. It follows that the normal components of the fluid velocity $\mathbf{v}$ and wall velocity $\mathbf{w}$ at the fluid-solid interface are equal, i.e.,

$$v_\gamma = w_\gamma, \tag{3.9}$$

with $v_\gamma \equiv \hat{\boldsymbol{\gamma}} \cdot \mathbf{v}$ and $w_\gamma \equiv \hat{\boldsymbol{\gamma}} \cdot \mathbf{w}$. However, the tangential components of these two boundary velocities may differ. That is, slip may occur at the fluid-solid interface, and the (tangential) slip velocity is defined as

$$\mathbf{v}_\tau^{slip} = \mathbf{v}_\tau - \mathbf{w}_\tau, \tag{3.10}$$

with $\mathbf{v}_\tau = \mathbf{v} - v_\gamma \hat{\boldsymbol{\gamma}}$ and $\mathbf{w}_\tau = \mathbf{w} - w_\gamma \hat{\boldsymbol{\gamma}}$. Physically, the slip velocity is the rate associated with an interfacial dissipative process, i.e., slip. In Section 3 Subsection 3.4, the entropy production at the fluid-solid interface will be obtained by deriving a balance equation for the surface entropy. From this entropy production, a constitutive relation can be established for the slip velocity.

Now we turn to the derivation of general boundary (jump) conditions. We first consider the integral balance equation for an extensive quantity Φ_s (a scalar, vector, or tensor) defined at the fluid-solid interface, treated as a singular surface here. Let's consider a surface region Σ_s bounded by the closed curve $\mathcal{C}_s$ (see figure 3.1). The rate of change of the extensive quantity $\Phi_s = \int_{\Sigma_s} dA \phi'_s$ defined over Σ_s is given by the integral balance equation

$$\dot{\Phi}_s = -\dot{\Phi}_s^* + \Pi_s, \tag{3.11}$$

where $\dot{\Phi}_s \equiv d\Phi_s/dt$ denotes the rate of change of Φ_s (whose area density is ϕ'_s), $\dot{\Phi}_s^*$ is the corresponding outgoing (integrated) flux, and Π_s is the rate of production of Φ_s, given by

$$\Pi_s = \int_{\Sigma_s} dA \pi'_s, \tag{3.12}$$

with π'_s being the corresponding area density. Here, the integrated flux $\dot{\Phi}_s^*$ can be expressed as

$$\dot{\Phi}_s^* = \int_{\mathcal{C}_s} dl \hat{\boldsymbol{\gamma}}_C \cdot \mathbf{J}'_s - \int_{\Sigma_s} dA [\![\hat{\boldsymbol{\gamma}} \cdot \mathbf{J}]\!],$$

where $\int_{\mathcal{C}_s} dl$ denotes the line integral along $\mathcal{C}_s$, $\hat{\boldsymbol{\gamma}}_C$ is the outward unit vector normal to $\mathcal{C}_s$ and tangent to Σ_s, $\mathbf{J}'_s$ is the *non-convective* surface flux (per unit length) tangent to Σ_s, and $[\![\hat{\boldsymbol{\gamma}} \cdot \mathbf{J}]\!]$ represents $\hat{\boldsymbol{\gamma}} \cdot (\mathbf{J} - \mathbf{J}_w)$ with $\mathbf{J}$ (or $\mathbf{J}_w$) being the corresponding flux (per unit area) in fluid (or solid) at the interface.

Using the surface transport theorem and surface divergence theorem [61, 62], we rewrite $\dot{\Phi}_s$ and $\dot{\Phi}_s^*$ as

$$\dot{\Phi}_s = \int_{\Sigma_s} dA \left[\frac{\partial \phi'_s}{\partial t} + \nabla_\tau \cdot (\phi'_s \mathbf{v}_\tau) \right], \tag{3.13}$$
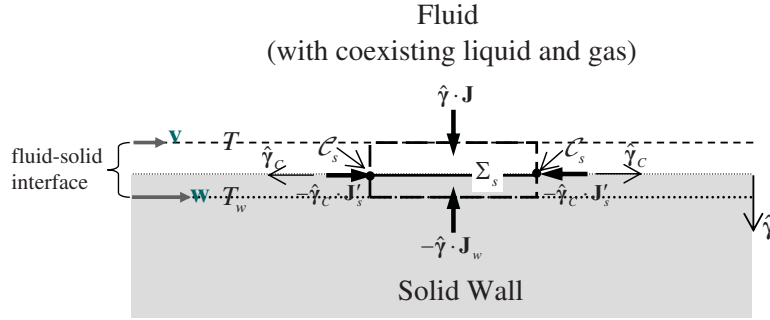
Fluid
(with coexisting liquid and gas)

FIG. 3.1. *A schematic illustration of the fluxes into the surface region Σ_s bounded by the closed curve $\mathcal{C}_s$. Here $\hat{\boldsymbol{\gamma}}_C$ is the outward unit vector normal to $\mathcal{C}_s$ and tangent to Σ_s, $-\hat{\boldsymbol{\gamma}}_C \cdot \mathbf{J}'_s$ is the non-convective surface flux (per unit length) tangent to Σ_s, and $\hat{\boldsymbol{\gamma}} \cdot \mathbf{J}$ (or $-\hat{\boldsymbol{\gamma}} \cdot \mathbf{J}_w$) is the corresponding flux (per unit area) in fluid (or solid) at the interface. The upper dashed line denotes the boundary of the bulk fluid and the lower dotted line denotes the boundary of the solid wall. As the fluid-solid interface is treated as a sharp interface, the surface Σ_s, the fluid boundary, and the solid boundary actually overlap. Here they are slightly separated just for the convenience of illustration. Note that a diffuse liquid-gas interface can exist in the fluid region and intersect with the solid surface because its existence lies in the density variation in a phase field description.*

$$\dot{\Phi}^*_s = \int_{\Sigma_s} dA\,(\nabla_\tau \cdot \mathbf{J}'_s) - \int_{\Sigma_s} dA[\![\hat{\boldsymbol{\gamma}} \cdot \mathbf{J}]\!]. \tag{3.14}$$

Note that every point of Σ_s moves with the local fluid velocity $\mathbf{v}$ as Σ_s is just a singular surface representing a boundary layer of fluid. This fact leads to equation (3.13), in which $\partial \phi'_s / \partial t$ is the normal time derivative [63] of ϕ'_s defined in the direction of $\hat{\boldsymbol{\gamma}}$ and the surface divergence of a vector field $\mathbf{a}$ is defined as $\nabla_\tau \cdot \mathbf{a} \equiv \nabla \cdot \mathbf{a} - \nabla_\gamma (\hat{\boldsymbol{\gamma}} \cdot \mathbf{a})$. As the solid walls considered in the present study are flat, rigid, and impermeable, our reference frame will be chosen in such a way that $v_\gamma = w_\gamma = 0$. This makes the normal time derivative $\partial \phi'_s / \partial t$ equal the usual partial derivative with respect to t for fixed Eulerian coordinates. Substituting equations (3.12), (3.13), and (3.14) into (3.11), we obtain

$$\int_{\Sigma_s} dA \left\{ \frac{\partial \phi'_s}{\partial t} + \nabla_\tau \cdot (\phi'_s \mathbf{v}_\tau) + \nabla_\tau \cdot \mathbf{J}'_s - [\![\hat{\boldsymbol{\gamma}} \cdot \mathbf{J}]\!] - \pi'_s \right\} = 0. \tag{3.15}$$

As Σ_s is arbitrarily chosen, equation (3.15) leads to the general boundary (jump) condition in differential form:

$$\frac{\partial \phi'_s}{\partial t} + \nabla_\tau \cdot (\phi'_s \mathbf{v}_\tau) = -\nabla_\tau \cdot \mathbf{J}'_s + [\![\hat{\boldsymbol{\gamma}} \cdot \mathbf{J}]\!] + \pi'_s, \tag{3.16}$$

which is a special case of the extended Kotchine's theorem [16] (see equation (A.13) in the Appendix) for flat, rigid, and impermeable solid walls.

3.3. Jump conditions for momentum and energy. Now we are ready to derive the jump conditions for momentum and energy from the general condition (3.16). There are three assumptions made for the dynamic van der Waals theory:

(i) The area density of fluid mass vanishes at the fluid-solid interface. That means no adsorption. Consequently, the area densities of momentum and kinetic energy vanish as well.

(ii) As already stated in Section 3 Subsection3.1, the area densities of surface energy and surface entropy, denoted by e'_s and σ'_s, are functions of n, the boundary value of fluid density. The surface free energy density f'_s is then defined as $f'_s(n,T) = e'_s(n) - T\sigma'_s(n)$ with T being the boundary value of fluid temperature.

(iii) The surface stress tensor $\overset{\leftrightarrow}{\mathbf{M}}{}'_s$ and surface heat flux $\mathbf{q}'_s$ (tangent to the surface) are present at the interface. However, there is no surface viscosity.

The jump condition for momentum

$$\nabla_\tau \cdot \overset{\leftrightarrow}{\mathbf{M}}{}'_s - [\![\hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}}]\!] = 0, \tag{3.17}$$

is obtained from equation (3.16) with $\phi'_s \to 0$, $\mathbf{J}'_s \to -\overset{\leftrightarrow}{\mathbf{M}}{}'_s$, $\mathbf{J} \to -\overset{\leftrightarrow}{\mathbf{M}}$, $\pi'_s \to 0$. Here, $-[\![\hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}}]\!] = -\hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}} + \hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}}_w$ with $-\hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}} \equiv \hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{\Pi}} - \hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\boldsymbol{\sigma}}$ being the stress force exerted by the fluid and $\hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}}_w \equiv \mathbf{F}$ being the stress force exerted by the solid. As to the surface stress $\overset{\leftrightarrow}{\mathbf{M}}{}'_s$, angular momentum conservation requires it to be tangential and symmetric [21], i.e., $\overset{\leftrightarrow}{\mathbf{M}}{}'_s \cdot \hat{\boldsymbol{\gamma}} = 0$ and $\overset{\leftrightarrow}{\mathbf{M}}{}'_s = \overset{\leftrightarrow}{\mathbf{M}}{}'^T_s$. Combining the above, we obtain

$$\nabla_\tau \cdot \overset{\leftrightarrow}{\mathbf{M}}{}'_s - \hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}} + \mathbf{F} = 0$$

as the equation for local force balance. In the absence of surface viscosity, $\overset{\leftrightarrow}{\mathbf{M}}{}'_s$ only has the reversible part due to the interfacial tension γ_{fs}, given by

$$\overset{\leftrightarrow}{\mathbf{M}}{}'_s \equiv \gamma_{fs} \overset{\leftrightarrow}{\boldsymbol{\tau}} = f'_s \overset{\leftrightarrow}{\boldsymbol{\tau}}, \tag{3.18}$$

with $\overset{\leftrightarrow}{\boldsymbol{\tau}} \equiv \overset{\leftrightarrow}{\mathbf{I}} - \hat{\boldsymbol{\gamma}}\hat{\boldsymbol{\gamma}}$. This surface stress tensor further gives

$$\nabla_\tau f'_s - \hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}} + \mathbf{F} = 0, \tag{3.19}$$

whose tangential and normal components are

$$\nabla_\tau f'_s - \hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}} \cdot \overset{\leftrightarrow}{\boldsymbol{\tau}} + \mathbf{F}_\tau = 0 \tag{3.20}$$

and

$$-\hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}} \cdot \hat{\boldsymbol{\gamma}} + F_\gamma = 0, \tag{3.21}$$

respectively. Here $\nabla_\tau f'_s = \nabla_\tau \cdot \left(f'_s \overset{\leftrightarrow}{\boldsymbol{\tau}} \right)$ while $F_\gamma \equiv \hat{\boldsymbol{\gamma}} \cdot \mathbf{F}$ and $\mathbf{F}_\tau = \mathbf{F} - F_\gamma \hat{\boldsymbol{\gamma}}$ are the normal (scalar) and tangential (vector) wall force (per unit area), respectively.

With the area density of surface kinetic energy being zero, we obtain

$$\frac{\partial e'_s}{\partial t} + \nabla_\tau \cdot (e'_s \mathbf{v}_\tau) = \nabla_\tau \cdot \left(\overset{\leftrightarrow}{\mathbf{M}}{}'_s \cdot \mathbf{v}_\tau \right) - \nabla_\tau \cdot \mathbf{q}'_s + [\![-\hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}} \cdot \mathbf{v} + \hat{\boldsymbol{\gamma}} \cdot \mathbf{q}]\!] \tag{3.22}$$

as the equation for local energy balance from equation (3.16) with $\phi'_s \to e'_s$, $\mathbf{J}'_s \to -\overset{\leftrightarrow}{\mathbf{M}}{}'_s \cdot \mathbf{v}_\tau + \mathbf{q}'_s$, $\mathbf{J} \to -\overset{\leftrightarrow}{\mathbf{M}} \cdot \mathbf{v} + \mathbf{q}$, $\pi'_s \to 0$. Here the surface heat flux $\mathbf{q}'_s$ is actually defined through the non-convective surface energy flux $-\overset{\leftrightarrow}{\mathbf{M}}{}'_s \cdot \mathbf{v} + \mathbf{q}'_s$. Substituting equations (3.18) and (3.19) into (3.22), we obtain

$$\frac{\partial e'_s}{\partial t} + \nabla_\tau \cdot (e'_s \mathbf{v}_\tau) = \nabla_\tau \cdot (f'_s \mathbf{v}_\tau) - \nabla_\tau \cdot \mathbf{q}'_s + [\![\hat{\boldsymbol{\gamma}} \cdot \mathbf{q}]\!] - \hat{\boldsymbol{\gamma}} \cdot \overset{\leftrightarrow}{\mathbf{M}} \cdot \mathbf{v}^{slip}_\tau - \mathbf{w}_\tau \cdot \nabla_\tau f'_s, \tag{3.23}$$

with $\mathbf{v}^{slip}_\tau = \mathbf{v}_\tau - \mathbf{w}_\tau$ defined in equation (3.10).

3.4. Entropy production and constitutive relations.   Using the Gibbs-type equation (3.6), we obtain

$$\frac{\partial \sigma_s'}{\partial t} = \frac{1}{T}\frac{\partial e_s'}{\partial t} - \frac{1}{T}\left(\frac{\partial f_s'}{\partial n}\right)_T \frac{\partial n}{\partial t}, \tag{3.24}$$

for the rate of change of the surface entropy density σ_s'. Substituting equation (3.23) into (3.24), we obtain

$$\frac{\partial \sigma_s'}{\partial t} + \nabla_\tau \cdot (\sigma_s' \mathbf{v}_\tau) = -\nabla_\tau \cdot \left(\frac{\mathbf{q}_s'}{T}\right) + [\![\hat{\boldsymbol{\gamma}}\cdot \hat{\mathbf{J}}^S]\!] + \mathbf{q}_s' \cdot \nabla_\tau \frac{1}{T}$$

$$-\left[\!\left[\frac{1}{T}\right]\!\right]\hat{\boldsymbol{\gamma}}\cdot \mathbf{q}_w - \frac{1}{T}\mathbf{F}_\tau \cdot \mathbf{v}_\tau^{slip} - \frac{1}{T}L\dot{n} \tag{3.25}$$

as the jump condition for σ_s'. Here $[\![\hat{\boldsymbol{\gamma}}\cdot \hat{\mathbf{J}}^S]\!] = \hat{\boldsymbol{\gamma}}\cdot\hat{\mathbf{J}}_f^S - \hat{\boldsymbol{\gamma}}\cdot\hat{\mathbf{J}}_w^S$ represents the total entropy flux from the fluid and solid bulks, with $\hat{\boldsymbol{\gamma}}\cdot\hat{\mathbf{J}}_f^S \equiv (\hat{\boldsymbol{\gamma}}\cdot\mathbf{q} + M\dot{n}\nabla_\gamma n)/T$ and $-\hat{\boldsymbol{\gamma}}\cdot\hat{\mathbf{J}}_w^S \equiv -\hat{\boldsymbol{\gamma}}\cdot\mathbf{q}_w/T_w$ being the fluid and solid contributions, respectively, $L = M\nabla_\gamma n + (\partial f_s'/\partial n)_T$ is the quantity already defined in equation (3.8), and $\dot{n} \equiv \partial n/\partial t + \mathbf{v}_\tau \cdot\nabla_\tau n$ is the material derivative of n at surface. A comparison between equations (3.25) and (3.16) shows that the density of the rate of entropy production at surface is of the form

$$\sigma_{surf} \equiv \mathbf{q}_s' \cdot \nabla_\tau \frac{1}{T} - \left[\!\left[\frac{1}{T}\right]\!\right]\hat{\boldsymbol{\gamma}}\cdot \mathbf{q}_w - \frac{1}{T}\mathbf{F}_\tau \cdot \mathbf{v}_\tau^{slip} - \frac{1}{T}L\dot{n}, \tag{3.26}$$

which must be positive definite according to the second law of thermodynamics. In summary, comparing equation (3.25) with (3.16) shows the correspondences $\phi_s' \to \sigma_s'$, $\mathbf{J}_s' \to \mathbf{q}_s'/T$, $\mathbf{J} \to \hat{\mathbf{J}}^S$, and $\pi_s' \to \sigma_{surf}$.

The surface entropy production σ_{surf} in equation (3.26) is already written in terms of conjugate surface forces and fluxes. Among the four force-flux pairs, $\mathbf{q}_s' \cdot \nabla_\tau(1/T)$ and $-\mathbf{F}_\tau \cdot \mathbf{v}_\tau^{slip}/T$ involve two-dimensional vectors while $-[\![1/T]\!]\hat{\boldsymbol{\gamma}}\cdot\mathbf{q}_w$ and $-L\dot{n}/T$ involve scalars. In the linear response regime [23, 64], the constitutive relations governing the interfacial dissipative processes can be obtained. Here we note that according to Curie's symmetry principle [23], there can be cross coupling between the vectorial pairs $\mathbf{q}_s' \cdot \nabla_\tau(1/T)$ and $-\mathbf{F}_\tau \cdot \mathbf{v}_\tau^{slip}/T$ and/or between the scalarial pairs $-[\![1/T]\!]\hat{\boldsymbol{\gamma}}\cdot\mathbf{q}_w$ and $-L\dot{n}/T$.

For the two vectorial pairs, the constitutive relations, which take into account the cross coupling, are given by

$$\mathbf{q}_s' = L_{11}\nabla_\tau \frac{1}{T} + L_{12}\left(-\frac{\mathbf{F}_\tau}{T}\right), \tag{3.27}$$

$$\mathbf{v}_\tau^{slip} = L_{21}\nabla_\tau \frac{1}{T} + L_{22}\left(-\frac{\mathbf{F}_\tau}{T}\right), \tag{3.28}$$

in which the cross coefficients L_{12} and L_{21} must satisfy the Onsager-Casimir reciprocal relation [23, 64]. Since the forces $-\mathbf{F}_\tau/T$ and $\nabla_\tau(1/T)$ are both even under time reversal, the reciprocal relation is $L_{12} = L_{21}$. In addition, the positive definiteness of σ_{surf} requires L_{11} and L_{22} to be both positive, with $L_{11}L_{22} > L_{12}L_{21} = L_{12}^2$. We may rewrite the above two constitutive relations in a more convenient and illustrative form:

$$\mathbf{q}_s' = -\lambda_s'\nabla_\tau T - \chi\mathbf{F}_\tau, \tag{3.29}$$

$$\beta \mathbf{v}_\tau^{slip} = -\beta \frac{\chi}{T} \nabla_\tau T - \mathbf{F}_\tau, \tag{3.30}$$

where $\lambda_s' \equiv L_{11}/T^2 > 0$ is the surface heat conductivity, $\beta \equiv T/L_{22} > 0$ is the slip coefficient, and $\chi \equiv L_{12}/T$ is a coefficient measuring the mechanical-thermal cross coupling. It is interesting to note that if there is mechanical-thermal coupling with $\chi \neq 0$, then according to $L_{11}L_{22} > L_{12}^2$, λ_s' must be nonzero for surface heat conductance and β cannot reach $+\infty$, i.e., there has to be some velocity slip. However, the sign of χ cannot be simply determined by thermodynamic constraints. It is expected that molecular dynamics simulations can reveal how χ is influenced by fluid-solid interactions at microscopic length scales [30, 54, 65].

For the two scalarial pairs, cross coupling is not considered here. Consequently, the constitutive relations are given by

$$\kappa \hat{\boldsymbol{\gamma}} \cdot \mathbf{q}_w = -\left[\!\left[\frac{1}{T} \right]\!\right], \tag{3.31}$$

$$\alpha \dot{n} = -L, \tag{3.32}$$

where κ is an interfacial parameter directly related to the thermal boundary resistance (namely Kapitza resistance) [52], and α is another interfacial parameter controlling the density relaxation at solid surfaces [14]. The positive definiteness of σ_{surf} requires κ and α to be positive.

Below we present the boundary conditions in the form which can be directly used by the hydrodynamic equations in the bulk region. Substituting equations (2.29), (2.32), (3.5), and (3.30) into (3.20), we obtain

$$\beta \mathbf{v}_\tau^{slip} = -\eta \nabla_\gamma \mathbf{v}_\tau + \left[M \nabla_\gamma n + \left(\frac{\partial f_s'}{\partial n} \right)_T \right] \nabla_\tau n - \left(\sigma_s' + \beta \frac{\chi}{T} \right) \nabla_\tau T, \tag{3.33}$$

as the boundary condition for tangential force balance. This slip boundary condition is a generalization of that derived in our previous study, where uniform temperature was assumed at the fluid-solid interface [14].

Substituting equations (3.4), (2.33), $\mathbf{q}_w = -\lambda_w \nabla T_w$, (3.29), (3.10), (3.20), and (3.30) into the energy equation (3.23), we obtain

$$-\lambda \nabla_\gamma T + \lambda_w \nabla_\gamma T_w = \frac{\partial e_s'}{\partial t} + \nabla_\tau \cdot (T \sigma_s' \mathbf{v}_\tau) + \mathbf{v}_\tau \cdot \nabla_\tau f_s' - \nabla_\tau \cdot (\lambda_s' \nabla_\tau T)$$
$$- \frac{1}{\beta} \mathbf{F}_\tau \cdot \mathbf{F}_\tau - \nabla_\tau \cdot (\chi \mathbf{F}_\tau) - \frac{\chi}{T} \mathbf{F}_\tau \cdot \nabla_\tau T, \tag{3.34}$$

as the boundary condition for energy balance. Here the tangential wall force $\mathbf{F}_\tau$ is in the form of $\mathbf{F}_\tau = \eta \nabla_\gamma \mathbf{v}_\tau - M \nabla_\gamma n \nabla_\tau n - \nabla_\tau f_s'$, which is obtained from equation (3.20), and $\nabla_\tau f_s'$ is given by $\nabla_\tau f_s' = -\sigma_s' \nabla_\tau T + (\partial f_s'/\partial n)_T \nabla_\tau n$, which is obtained from equation (3.5). In our previous study, the fluid temperature was assumed to be a uniform constant at the fluid-solid interface (a Dirichlet condition) [14]. Now this assumption is replaced by equation (3.34), which serves as a boundary condition for fluid temperature.

Substituting $\mathbf{q}_w = -\lambda_w \nabla T_w$ into equation (3.31), we obtain

$$\kappa \lambda_w \nabla_\gamma T_w = \left[\!\left[\frac{1}{T} \right]\!\right] \equiv \frac{1}{T} - \frac{1}{T_w} \tag{3.35}$$

as the boundary condition for temperature slip across the fluid-solid interface. It serves as a boundary condition for solid temperature governed by equation (3.1). In the limit of $\lambda_w \to \infty$, the temperature in the solid becomes a constant. Nevertheless, heat exchange between the fluid and solid still exists, i.e., $\lambda_w \to \infty$, $\nabla_\gamma T_w \to 0$, and $\kappa \lambda_w \nabla_\gamma T_w = [\![1/T]\!]$ remains finite.

Finally, substituting the definition of L in equation (3.8) into equation (3.32), we obtain

$$\alpha \dot{n} = -M \nabla_\gamma n - \left(\frac{\partial f'_s}{\partial n} \right)_T \tag{3.36}$$

as the boundary condition for density relaxation at solid surfaces, in the same form of that derived in our previous study [14].

4. Numerical algorithm

The model formulated in sections 2 and 3 is formed by a set of partial differential equations supplemented with all the necessary boundary conditions:

(a) Equation (3.1) as the heat equation for solid temperature,

(b) Equation (2.20) as the balance equation for fluid particle number,

(c) Equation (2.21) as the balance equation for fluid momentum,

(d) Equation (2.27) as the balance equation for fluid entropy,

(e) Equation (2.29), together with equations (2.8) and (2.13), for the reversible part of fluid stress tensor, which is involved in equation (2.21),

(f) Equation (2.32) for the irreversible part of fluid stress tensor, which is involved in equation (2.21),

(g) Equation (2.33) for the heat flux in the fluid bulk region, which is involved in equation (2.27),

(h) the kinematic boundary condition $v_\gamma = w_\gamma = 0$,

(i) Equation (3.33) as the slip boundary condition for tangential force balance,

(j) Equation (3.34) as the boundary condition for energy balance,

(k) Equation (3.35) as the boundary condition for temperature slip across the fluid-solid interface,

(l) Equation (3.36) as the boundary condition for density relaxation,

(m) Equation $T = T\left(n, \nabla n, \hat{S}\right)$ for local fluid temperature. This equation, which locally expresses T as a function of n, ∇n, and $\hat{S}$, can be readily derived from equations (2.7) and (2.10).

From the above system, we can solve the number density n, velocity $\mathbf{v}$, and temperature T in the fluid, and the temperature T_w in the solid.

Below we present an algorithm for solving this model by using a finite difference method, with a focus on the use of boundary conditions. According to Teshigawara and Onuki [55], the artificial parasitic flow can be avoided if the equation for $\hat{S}$ is used instead of that for $\hat{e}$. We integrate the heat equation (3.1) in the solid and the hydrodynamic equations (2.20), (2.21), and (2.27) with the constitutive relations (2.29), (2.32), (2.33), supplemented by the kinematic boundary condition $v_\gamma = w_\gamma = 0$, and the dynamic boundary conditions (3.33)-(3.36). In addition, equations (2.8) and (2.13) for pressure have to be used by equation (2.29), and equations (2.7) and (2.10) gives $T = T\left(n, \nabla n, \hat{S}\right)$ for local temperature as a function of n, ∇n, and $\hat{S}$.

The state variables n, $\mathbf{v}$, T in the fluid and T_w in the solid are defined in an unstaggered, uniformly discretized mesh. The solid temperature T_w can be updated by the heat equation (3.1), supplemented with the boundary condition (3.35). As to the state variables in the fluid, the number density n, tangential velocity $\mathbf{v}_\tau$, and entropy density $\hat{S}$ are updated at the interior sites and at the fluid-solid interface as well, while the normal velocity v_γ is updated at the interior sites only. This involves the use of hydrodynamic equations (2.20), (2.21), and (2.27). Obviously, values of n, $\mathbf{v}_\tau$, v_γ, and T at some "ghost" sites are needed for updating n, $\mathbf{v}_\tau$, $\hat{S}$ at the fluid-solid interface and also updating v_γ at the sites nearest to the fluid-solid interface. (Note that in updating v_γ at the sites nearest to the fluid-solid interface, the term $-Mn\nabla^2 n$ in $\hat{p}$ (equation (2.13)) leads to a third-order derivative of n in the normal direction, and hence the values of n at the ghost sites out of the fluid space are still needed.) With $\dot{n}$ evaluated in the continuity equation (2.20), the ghost values of n can be first determined by the boundary condition (3.36) through $\nabla_\gamma n$. The ghost values of $\mathbf{v}_\tau$ are then determined by the boundary condition (3.33) through $\nabla_\gamma \mathbf{v}_\tau$. The ghost values of T can be determined by (3.34) and (3.35) through $\nabla_\gamma T$. As for the ghost values of v_γ, they are determined through $\nabla_\gamma v_\gamma$ at the fluid-solid interface, which can be evaluated using one-sided extrapolation. Finally, the temperature T in the fluid (from the interior to the interface) can be directly obtained from the function $T = T\left(n, \nabla n, \hat{S}\right)$. We have solved the model in two-dimensional space by using an explicit finite-difference scheme. The mesh size is taken to be small enough to resolve the density variations in the liquid-gas interfacial region. The time step is mostly constrained by the large gradients associated with the heat flux and viscous stress in the bulk region. The numerical stability is checked and found to be increased by defining the heat flux and viscous stress at midpoints of the Cartesian mesh (and then expressing them using more neighboring mesh points). This is attributed to a better discretization of the balance equations.

We would like to emphasize that the boundary conditions derived from thermodynamic considerations are just enough for the numerical implementation of the model. This has been confirmed by the stable numerical solutions obtained for liquid-gas systems bounded by solid surfaces. This indicates that as a system of partial differential equations, the model is well posed, being neither under-determined nor over-determined. We think that the validity of the model is supported by the consistency between its physical and mathematical aspects.

5. Boundary conditions in limiting situations

In this section, we consider the various limits of the boundary conditions derived in Section 3 Subsection 3.4. Some of these limits have already been obtained and used in our previous study [14] and the works by Onuki and Teshigawara [11, 13]. We would like to point out that in our previous study [14], although the temperature is nonuniform in the bulk region, the fluid-solid interface is assumed to be isothermal. On the other hand, although the fluid temperature is allowed to vary at the interface in the recent work by Onuki and Teshigawara [13], there is no dissipative process occurring at the interface, and hence no entropy production. It is worth emphasizing that our boundary conditions are derived from the interfacial entropy production expressed in equation (3.26).

We start from the boundary condition (3.36) for density relaxation. In the limit of $\alpha \to 0$, this surface relaxation becomes very fast, and consequently the density distribution at the solid surface approaches the local equilibrium described by equation (3.8): $L \equiv M\nabla_\gamma n + (\partial f_s'/\partial n)_T = 0$. Local equilibrium conditions of this type have been

discussed by Jacqmin [48] and by Qian *et al.* [8, 10, 12] for immiscible two-phase flows, and by Onuki *et al.* [11, 13] and by Xu *et al.* [14] for one-component liquid-gas flows.

We then consider the various limits of the slip boundary condition (3.33). If there is no cross coupling ($\chi \to 0$ in equations (3.29) and (3.30)), then this boundary condition reduces to

$$\beta \mathbf{v}_\tau^{slip} = -\eta \nabla_\gamma \mathbf{v}_\tau + \left[M \nabla_\gamma n + \left(\frac{\partial f_s'}{\partial n} \right)_T \right] \nabla_\tau n - \sigma_s' \nabla_\tau T, \qquad (5.1)$$

which can also be written as $\beta \mathbf{v}_\tau^{slip} = -\eta \nabla_\gamma \mathbf{v}_\tau + M \nabla_\gamma n \nabla_\tau n + \nabla_\tau f_s'$, in which the meaning of each term is quite clear. Furthermore, if the fluid temperature variation at the fluid-solid interface can be neglected ($\nabla_\tau T \to 0$ in the limit of isothermal interface), then equation (5.1) becomes

$$\beta \mathbf{v}_\tau^{slip} = -\eta \nabla_\gamma \mathbf{v}_\tau + \left[M \nabla_\gamma n + \left(\frac{\partial f_s'}{\partial n} \right)_T \right] \nabla_\tau n, \qquad (5.2)$$

which is exactly the slip boundary condition, namely the generalized Navier boundary condition, obtained in our previous study [14]. The no slip condition

$$\mathbf{v}_\tau^{slip} = \mathbf{v}_\tau - \mathbf{w}_\tau = 0 \qquad (5.3)$$

is obtained in the limit of $\beta \to \infty$ in equations (3.33), (5.1), or (5.2). Physically, this limit occurs in the fluid-solid systems with vanishingly small slip length defined by η / β [50, 66].

Finally, we turn to the temperature slip condition (3.35) and the boundary condition (3.34) for energy balance. In the limit of $\kappa \to 0$ corresponding with vanishingly small Kapitza length [52], the temperature slip condition (3.35) yields

$$T = T_w, \qquad (5.4)$$

i.e., there is no temperature discontinuity across the fluid-solid interface. For $\kappa \to 0$ and finite λ_w, the fluid temperature and solid temperature need to be solved simultaneously and this requires two temperature boundary conditions, i.e., equations (3.34) and (5.4). Furthermore, if the relaxation toward thermal equilibrium is very fast in the solid (due to very large λ_w), then the temperature distribution in the solid becomes decoupled from that in the fluid. In this limit, the fluid temperature is equal to the solid temperature at the fluid-solid interface, and the latter can be solved independently. Therefore, equation (5.4) can serve as a Dirichlet temperature boundary condition [11, 14] for the fluid part. On the other hand, if temperature slip does occur (for finite κ) while the relaxation toward equilibrium is still very fast in the solid, then we can obtain a boundary condition by substituting equation (3.35) into (3.34), with T_w considered as a parameter (obtained separately from the solid part). Note that the boundary condition so obtained is neither a Dirichlet condition nor a Neumann condition.

For isothermal fluid-solid interface, numerical simulations have been carried out for a simplified model for confined one-component liquid-gas flows [14]. In that model, the slip boundary condition is given by equation (5.2), the boundary condition for fluid temperature is the Dirichlet condition $T = T_w$ with T_w being a constant, and the boundary condition for density relaxation remains as equation (3.36).

It is interesting to examine the limiting forms of the energy equation (3.34). In the limit of $\chi \to 0$ (no cross coupling) and $\beta \to \infty$ (no slip), this boundary condition

reduces to

$$-\lambda\nabla_\gamma T + \lambda_w\nabla_\gamma T_w = \frac{\partial e'_s}{\partial t} + \nabla_\tau\cdot(T\sigma'_s\mathbf{v}_\tau) + \mathbf{v}_\tau\cdot\nabla_\tau f'_s - \nabla_\tau\cdot(\lambda'_s\nabla_\tau T). \tag{5.5}$$

If the tangential heat conduction at the fluid-solid interface is negligible, e.g., $\lambda'_s\to 0$ or $\lambda'_s\nabla_\tau T\to 0$, then equation (5.5) further reduces to

$$-\lambda\nabla_\gamma T + \lambda_w\nabla_\gamma T_w = \frac{\partial e'_s}{\partial t} + \nabla_\tau\cdot(T\sigma'_s\mathbf{v}_\tau) + \mathbf{v}_\tau\cdot\nabla_\tau f'_s. \tag{5.6}$$

In addition, if there are no appreciable (spatial or temporal) variations in the surface quantities e'_s, σ'_s, f'_s, and $\mathbf{v}_\tau$ such that the three terms in the right hand side of the above equation can be neglected, then we obtain

$$-\lambda\nabla_\gamma T = -\lambda_w\nabla_\gamma T_w \tag{5.7}$$

for the continuity of the heat flux across the fluid-solid interface. In the recent work by Teshigawara and Onuki [13], the fluid and solid temperatures were solved simultaneously using equations (5.4) and (5.7) as the two boundary conditions.

In molecular dynamics simulations [52, 53], the fluid-solid interfaces are typically uniform and the use of $-\lambda\nabla_\gamma T = -\lambda_w\nabla_\gamma T_w$ can be justified. Substituting equation (3.35) into (5.7) gives

$$\kappa\lambda\nabla_\gamma T = \frac{1}{T} - \frac{1}{T_w}, \tag{5.8}$$

which can be directly used for the measurement of the Kapitza resistance.

6. Concluding remarks

In this work, we have presented a continuum hydrodynamic model for one-component liquid-gas flows on non-isothermal, heterogeneous solid substrates. Technically, the liquid-gas interface is modeled as a diffuse interface while the fluid-solid interface is modeled as a sharp interface. As a generalization of the dynamic van der Waals theory [11], this model is capable of predicting the velocity and temperature fields of the liquid-gas flows on flat, rigid, and non-isothermal, heterogeneous solid surfaces. Based on continuum mechanical and thermodynamical principles, we have derived the hydrodynamic boundary conditions at the fluid-solid interface, which are able to describe velocity slip [49, 50, 51], temperature slip (Kapitza resistance) [52, 53], and mechanical-thermal cross coupling [54] that contribute to interfacial entropy production. Our model is self-consistent in the sense that the boundary conditions derived from physical (continuum mechanical and thermodynamical) considerations are actually mathematically demanded by the partial differential equations in the bulk region. In particular, our numerical results indicate that the model is well posed, being neither under-determined nor over-determined. We have also shown that some widely used boundary conditions can actually be derived from the boundary conditions presented here by taking appropriate limits.

We would like to point out that the curvature effects of the rigid solid surfaces can be readily formulated based on the discussions in the appendix. However, we have completely neglected the elasticity of the solid due to the complexity in modeling the fluid-solid coupling. In fact, there have been experimental observations that the deformation of solid substrates can affect the wetting properties [67, 68]. To incorporate the solid deformation into a more general continuum model represents a future work

to pursue. We also would like to point out that the framework presented here for modeling two-phase flows at solid surfaces, from bulk equations to boundary conditions, is already in a form that can be used for modeling other fluid-solid interfacial phenomena, e.g., binary alloy solidification with convection [69] and liquid crystals moving on solid surfaces [12].

An important continuation of the present work is the numerical implementation of the model, by which we can simulate the motion of liquid drops with evaporation/condensation on the solid surfaces possessing thermal gradient and/or wettability gradient. This kind of motion may involve the thermal Marangoni effect, velocity slip, temperature slip, and mechanical-thermal cross coupling. It is worth emphasizing that non-isothermal fluid-solid interfaces are inevitably encountered in this kind of motion, and therefore the general boundary conditions derived in this work have to be used. Numerical simulations for droplet motion driven by wettability gradients and temperature gradients will be reported elsewhere.

Appendix A. Curvature effects of solid surfaces on liquid-gas flows.
Recently, a great amount of attention has been paid to the effects of surface roughness on wetting statics and dynamics [70, 71, 72]. For liquid-gas flows on curved, rigid, and impermeable solid walls, we will briefly discuss two issues arising from the curvature of solid surfaces: (i) the modifications of boundary (jump) conditions, and (ii) the effective slip length.

We first present a derivation of the surface transport theorem [61, 62, 63] using a phase field φ to describe the fluid-solid interface, which is treated as a diffuse interface here. The "free energy" functional associated with φ is given by $F = \int d\mathbf{r} \left[\frac{1}{2} |\nabla \varphi|^2 + f(\varphi) \right]$, with $f(\varphi) \equiv \left(\varphi^2 - 1 \right)^2 / 4\varepsilon^2$ being the double well potential which stabilizes the fluid phase $\varphi = -1$ and the solid phase $\varphi = +1$. The fluid-solid interfacial profile is locally a minimizer of the free energy F. That is, in the direction of the interface normal, the variation of φ satisfies $-\nabla_\gamma^2 \varphi + f'(\varphi) = 0$. Here $\nabla_\gamma = \hat{\gamma} \cdot \nabla$ with the unit vector $\hat{\gamma}$ defined in the direction of $\nabla \varphi$ at the level surface $\varphi = 0$, which is taken as the nominal location of fluid-solid interface. Note that $\hat{\gamma}$ points from the fluid into the solid as usual. We would like to point out that in the sharp interface limit, $-\nabla_\gamma^2 \varphi + f'(\varphi) = 0$ is maintained by the energetics associated with φ. This property immediately leads to the following:

$$(1) \qquad -\frac{1}{2} \left(\nabla_\gamma \varphi \right)^2 + f(\varphi) = 0, \qquad (A.1)$$

with $\nabla_\gamma \varphi = d\varphi / d\xi$. Here ξ is the coordinate along the direction of $\hat{\gamma}$, with $\xi = 0$ at $\varphi = 0$ (the nominal interface).

$$(2) \qquad \varphi(\xi) = \tanh \left(\frac{\xi}{\sqrt{2}\varepsilon} \right). \qquad (A.2)$$

This variation of φ across the diffuse interface indicates that ε is the characteristic length scale for interfacial thickness.

$$(3) \qquad \int d\xi \left[\frac{1}{2} \left(\nabla_\gamma \varphi \right)^2 + f(\varphi) \right] = \frac{2\sqrt{2}}{3\varepsilon}, \qquad (A.3)$$

which is the excess free energy per unit area (surface tension).

$$(4) \qquad \int d\xi \left[\left(-\nabla^2 \varphi + f'(\varphi) \right) \nabla_\gamma \varphi \right] = \int d\xi \left[\left(\nabla_\gamma \varphi \right)^2 \left(-\frac{\nabla_\tau^2 \varphi}{\nabla_\gamma \varphi} \right) \right] = \frac{2\sqrt{2}}{3\varepsilon} (2H), \qquad (A.4)$$

with $-\nabla^2\varphi + f'(\varphi) = -\nabla_\tau^2\varphi$ and $-\nabla_\tau^2\varphi/\nabla_\gamma\varphi = 2H$. Here ∇_τ is the del operator defined in the plane tangent to the level surface $\varphi = 0$, and H is the mean curvature of the interface.

Due to the impermeability of the solid, the phase field φ is transported according to

$$\frac{\partial\varphi}{\partial t} + \mathbf{v}\cdot\nabla\varphi = 0. \tag{A.5}$$

We consider the rate of change of the integral $\int_\Omega d\mathbf{r}\phi\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right]$, where the domain Ω contains both the fluid and the solid. The boundary of Ω, denoted by $\partial\Omega$, moves with the fluid/solid velocity $\mathbf{v}$. The field ϕ, originally defined over the domain Ω, will be related to the surface quantity ϕ_s'. Note that ϕ_s' is first introduced (in Section 3 Subsection 3.2) as the area density of $\Phi_s = \int_{\Sigma_s} dA\phi_s'$ defined over the surface region Σ_s, with every point of Σ_s moving with the local fluid velocity. Therefore, the integral $\int_\Omega d\mathbf{r}\phi\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right]$ has a direct correspondence with $\Phi_s = \int_{\Sigma_s} dA\phi_s'$. This will be made clear below. The time derivative of $\int_\Omega d\mathbf{r}\phi\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right]$ is given by

$$\frac{d}{dt}\int_\Omega d\mathbf{r}\phi\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right] = \int_\Omega d\mathbf{r}\frac{\partial\phi}{\partial t}\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right] + \int_\Omega d\mathbf{r}\phi\frac{\partial}{\partial t}\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right]$$
$$+ \int_{\partial\Omega} dA_\Omega \hat{\mathbf{n}}\cdot\mathbf{v}\phi\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right], \tag{A.6}$$

where $\hat{\mathbf{n}}$ denotes the outward unit vector normal to the boundary $\partial\Omega$ and dA_Ω is the surface area element there. With a simple manipulation of the second term in the right hand side of equation (A.6), we have

$$\frac{d}{dt}\int_\Omega d\mathbf{r}\phi\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right]$$
$$= \int_\Omega d\mathbf{r}\left[\frac{\partial\phi}{\partial t}\left(\frac{1}{2}|\nabla\varphi|^2 + f\right) + (\mathbf{v}\cdot\nabla\varphi)(\nabla\phi\cdot\nabla\varphi)\right] + \int_\Omega d\mathbf{r}\phi(\mathbf{v}\cdot\nabla\varphi)\left(-f' + \nabla^2\varphi\right)$$
$$+ \int_{\partial\Omega} dA_\Omega\left[\phi\left(\frac{1}{2}|\nabla\varphi|^2 + f\right)(\hat{\mathbf{n}}\cdot\mathbf{v}) - \phi(\mathbf{v}\cdot\nabla\varphi)(\hat{\mathbf{n}}\cdot\nabla\varphi)\right]. \tag{A.7}$$

In the sharp interface limit, $\nabla\varphi = \hat{\gamma}\nabla_\gamma\varphi$ in the narrow interfacial region, and hence $\hat{\mathbf{n}}\cdot\nabla\varphi = \hat{\mathbf{n}}\cdot\hat{\gamma}\nabla_\gamma\varphi$ and $\mathbf{v}\cdot\nabla\varphi = v_\gamma\nabla_\gamma\varphi$. Using these relations plus $\hat{\mathbf{n}}\cdot\mathbf{v} = \hat{\mathbf{n}}\cdot\hat{\gamma}v_\gamma + \hat{\mathbf{n}}\cdot\mathbf{v}_\tau$, we have

$$\frac{d}{dt}\int_\Omega d\mathbf{r}\phi\left[\frac{1}{2}|\nabla\varphi|^2 + f\right]$$
$$= \int_\Omega d\mathbf{r}\left[\frac{\partial\phi}{\partial t}\left(\frac{1}{2}(\nabla_\gamma\varphi)^2 + f\right) + (v_\gamma\nabla_\gamma\phi)(\nabla_\gamma\varphi)^2\right] + \int_\Omega d\mathbf{r}\phi(v_\gamma\nabla_\gamma\varphi)\left(-f' + \nabla^2\varphi\right)$$
$$+ \int_{\partial\Omega} dA_\Omega\left[\phi\left(-\frac{1}{2}(\nabla_\gamma\varphi)^2 + f\right)(v_\gamma\hat{\mathbf{n}}\cdot\hat{\gamma})\right] + \int_{\partial\Omega} dA_\Omega\left[\phi\left(\frac{1}{2}(\nabla_\gamma\varphi)^2 + f\right)(\hat{\mathbf{n}}\cdot\mathbf{v}_\tau)\right]. \tag{A.8}$$

With the help of the identity (A.1), we obtain

$$\frac{d}{dt}\int_\Omega d\mathbf{r}\phi\left[\frac{1}{2}|\nabla\varphi|^2 + f(\varphi)\right] = \int_\Omega d\mathbf{r}\left(\frac{1}{2}(\nabla_\gamma\varphi)^2 + f\right)\left(\frac{\partial\phi}{\partial t} + v_\gamma\nabla_\gamma\phi\right)$$

$$+ \int_{\Omega} d\mathbf{r} \left(\phi v_{\gamma} \right) \left[\left(-f' + \nabla^2 \varphi \right) \nabla_{\gamma} \varphi \right]$$

$$+ \int_{\partial\Omega} dA_{\Omega} \left[\left(\frac{1}{2} \left(\nabla_{\gamma} \varphi \right)^2 + f \right) \left(\phi \hat{\mathbf{n}} \cdot \mathbf{v}_{\tau} \right) \right], \qquad \text{(A.9)}$$

from which the surface transport theorem can be readily derived.

In order to proceed, we take the level surface $\varphi = 0$ within the domain Ω as the surface region Σ_s (see figure A.1). It follows that this level surface intersects the domain boundary $\partial\Omega$ at a closed curve, which is the boundary of Σ_s, denoted by $\mathcal{C}_s$. Without loss of generality, we simplify the derivation by choosing two orthogonal base vectors $\hat{\boldsymbol{\tau}}_1$ and $\hat{\boldsymbol{\tau}}_2$ at Σ_s. At the boundary, $\hat{\boldsymbol{\tau}}_1$ is normal to the closed curve $\mathcal{C}_s$ while $\hat{\boldsymbol{\tau}}_2$ is tangent to $\mathcal{C}_s$. In addition, the unit vector $\hat{\mathbf{n}}$, defined to be normal to $\partial\Omega$, must be in the plane of $\hat{\boldsymbol{\tau}}_1$ and $\hat{\boldsymbol{\gamma}}$, with $\hat{\mathbf{n}} \cdot \hat{\boldsymbol{\tau}}_1 = \sin\theta$ and $\hat{\mathbf{n}} \cdot \hat{\boldsymbol{\tau}}_2 = 0$. Here θ is the angle between Σ_s and $\partial\Omega$, i.e., the angle between $\hat{\boldsymbol{\gamma}}$ and $\hat{\mathbf{n}}$. The tangential velocity $\mathbf{v}_{\tau}$ (defined as $\mathbf{v}_{\tau} = \overset{\leftrightarrow}{\boldsymbol{\tau}} \cdot \mathbf{v}$ with $\overset{\leftrightarrow}{\boldsymbol{\tau}} = \hat{\boldsymbol{\tau}}_1 \hat{\boldsymbol{\tau}}_1 + \hat{\boldsymbol{\tau}}_2 \hat{\boldsymbol{\tau}}_2$) can be decomposed as $\mathbf{v}_{\tau} = v_{\tau} \hat{\boldsymbol{\tau}}_1 + \tilde{v}_{\tau} \hat{\boldsymbol{\tau}}_2$. It follows that $\hat{\mathbf{n}} \cdot \mathbf{v}_{\tau} = v_{\tau} \sin\theta$. In the vicinity of the level surface $\varphi = 0$, we also have $d\mathbf{r} = dA d\xi$ and $dA_{\Omega} = (1/\sin\theta) dl d\xi$, where dA is the area element at Σ_s, ξ is the coordinate along $\hat{\boldsymbol{\gamma}}$, and l is the coordinate along $\hat{\boldsymbol{\tau}}_2$.
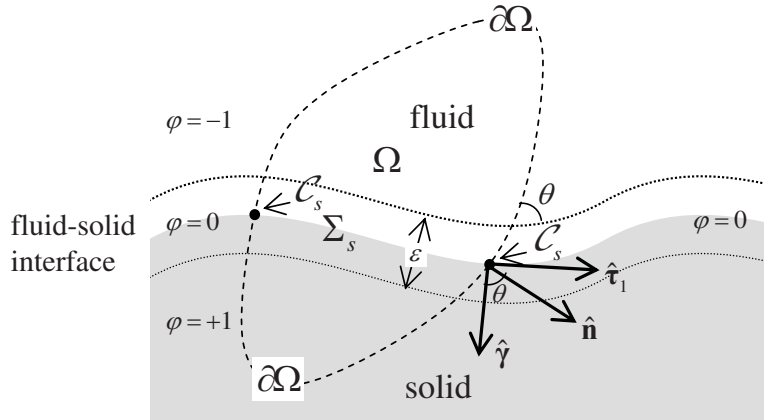

FIG. A.1. *A schematic illustration for the level surface $\varphi = 0$, the domain Ω, the domain boundary $\partial\Omega$, the surface region Σ_s, and the closed curve $\mathcal{C}_s$. We use ε to denote the width of the interfacial region. As to the unit vectors, $\hat{\boldsymbol{\gamma}}$ is normal to Σ_s, $\hat{\mathbf{n}}$ is normal to $\partial\Omega$, $\hat{\boldsymbol{\tau}}_1$ and $\hat{\boldsymbol{\tau}}_2$ are orthogonal base vectors tangent to Σ_s, and $\hat{\boldsymbol{\tau}}_2$ is also tangent to $\mathcal{C}_s$. Note that $\hat{\mathbf{n}}$, $\hat{\boldsymbol{\gamma}}$, and $\hat{\boldsymbol{\tau}}_1$ are in the same plane.*

Based on the above, equation (A.9) can be written as

$$\frac{d}{dt} \int_{\Omega} dA d\xi \left(\frac{1}{2} \left(\nabla_{\gamma} \varphi \right)^2 + f \right) \phi = \int_{\Omega} dA d\xi \left(\frac{1}{2} \left(\nabla_{\gamma} \varphi \right)^2 + f \right) \left(\frac{\partial \phi}{\partial t} + v_{\gamma} \nabla_{\gamma} \phi \right)$$

$$+ \int_{\Omega} dA d\xi \left[\left(-f' + \nabla^2 \varphi \right) \nabla_{\gamma} \varphi \right] \left(\phi v_{\gamma} \right)$$

$$+ \int_{\partial\Omega} dl d\xi \left(\frac{1}{2} \left(\nabla_{\gamma} \varphi \right)^2 + f \right) \left(\phi v_{\tau} \right). \qquad \text{(A.10)}$$

By carrying out the integration across the interface and using equations (A.3) and

(A.4), we obtain the well-known surface transport theorem

$$\frac{d}{dt}\int_{\Sigma_s}dA\phi'_s=\int_{\Sigma_s}dA\left(\frac{\partial\phi'_s}{\partial t}-2H\phi'_sv_\gamma\right)+\int_{\mathcal{C}_s}dl\phi'_sv_\tau$$

$$=\int_{\Sigma_s}dA\left[\frac{\partial\phi'_s}{\partial t}+\nabla_\tau\cdot(\phi'_s\mathbf{v}_\tau)-2H\phi'_sv_\gamma\right], \quad\quad (A.11)$$

in which $\int_{\mathcal{C}_s}dl\phi'_sv_\tau=\int_{\Sigma_s}dA\nabla_\tau\cdot(\phi'_s\mathbf{v}_\tau)$ has been used according to the surface divergence theorem [61, 62, 63]. Here we note that the integration across the interface, with $\frac{1}{2}(\nabla_\gamma\varphi)^2+f$ playing the role of a distribution function, should be regarded as an averaging across the interface, through which various surface quantities defined at Σ_s are obtained from the corresponding quantities defined in the phase field description. Finally, we mention that $\partial\phi'_s/\partial t$ in equation (A.11) comes from the first term in the right hand side of equation (A.10), and hence it is the normal time derivative [63] of ϕ'_s defined in the direction of $\hat{\gamma}$.

Now we turn to the modifications of general boundary (jump) conditions. Substituting equations (A.11), (3.12), and (3.14) into the balance equation (3.11), we obtain

$$\int_{\Sigma_s}dA\left\{\frac{\partial\phi'_s}{\partial t}+\nabla_\tau\cdot(\phi'_s\mathbf{v}_\tau)-2H\phi'_sv_\gamma+\nabla_\tau\cdot\mathbf{J}'_s-[\![\hat{\gamma}\cdot\mathbf{J}]\!]-\pi'_s\right\}=0. \quad\quad (A.12)$$

As the surface region Σ_s is arbitrarily chosen, we have the differential boundary (jump) condition:

$$\frac{\partial\phi'_s}{\partial t}+\nabla_\tau\cdot(\phi'_s\mathbf{v}_\tau)-2H\phi'_sv_\gamma=-\nabla_\tau\cdot\mathbf{J}'_s+[\![\hat{\gamma}\cdot\mathbf{J}]\!]+\pi'_s, \quad\quad (A.13)$$

which is referred to as the extended Kotchine theorem [16, 17, 20].

Below we discuss the curvature effects of solid walls on liquid-gas flows. From a comparison between equations (A.13) and (3.16), an immediate consequence is the modification of the jump condition for the surface energy density e'_s:

$$\frac{\partial e'_s}{\partial t}+\nabla_\tau\cdot(e'_s\mathbf{v}_\tau)-2He'_sv_\gamma=\nabla_\tau\cdot(f'_s\mathbf{v}_\tau)-\nabla_\tau\cdot\mathbf{q}'_s+[\![\hat{\gamma}\cdot\mathbf{q}]\!]-\hat{\gamma}\cdot\overset{\leftrightarrow}{\mathbf{M}}\cdot\mathbf{v}_\tau^{slip}-\mathbf{w}_\tau\cdot\nabla_\tau f'_s. \quad\quad (A.14)$$

A physically more interesting curvature effect is the modification of the slip boundary condition (3.33). Using $\hat{\gamma}\cdot(\nabla\mathbf{v})\cdot\overset{\leftrightarrow}{\boldsymbol{\tau}}=\nabla_\gamma v_\tau$ and $\hat{\gamma}\cdot(\nabla\mathbf{v})^T\cdot\overset{\leftrightarrow}{\boldsymbol{\tau}}=\nabla_\tau v_\gamma+\mathbf{v}_\tau\cdot\overset{\leftrightarrow}{\mathbf{K}}$, we have $\eta\hat{\gamma}\cdot\left[(\nabla\mathbf{v})+(\nabla\mathbf{v})^T\right]\cdot\overset{\leftrightarrow}{\boldsymbol{\tau}}=\eta\nabla_\gamma v_\tau+\eta\mathbf{v}_\tau^{slip}\cdot\overset{\leftrightarrow}{\mathbf{K}}$ for the $\gamma\tau$ component of the viscous stress. Here $v_\gamma=\hat{\gamma}\cdot\mathbf{w}$ (impermeability condition) and $\nabla_\tau v_\gamma=-\mathbf{w}_\tau\cdot\overset{\leftrightarrow}{\mathbf{K}}$, with $\mathbf{v}_\tau^{slip}=\mathbf{v}_\tau-\mathbf{w}_\tau$ and $\overset{\leftrightarrow}{\mathbf{K}}$ being the curvature tensor defined by $\overset{\leftrightarrow}{\mathbf{K}}\equiv-\nabla_\tau\hat{\gamma}$. Accordingly, the slip boundary condition becomes

$$\beta\mathbf{v}_\tau^{slip}=-\eta\nabla_\gamma v_\tau-\eta\mathbf{v}_\tau^{slip}\cdot\overset{\leftrightarrow}{\mathbf{K}}+\left[M\nabla_\gamma n+\left(\frac{\partial f'_s}{\partial n}\right)_T\right]\nabla_\tau n-\left(\sigma'_s+\beta\frac{\chi}{T}\right)\nabla_\tau T. \quad\quad (A.15)$$

For a special solid surface with curvature tensor $\overset{\leftrightarrow}{\mathbf{K}}=-\overset{\leftrightarrow}{\boldsymbol{\tau}}/R$, the slip boundary condition (I.15) takes the form

$$\mathbf{v}_\tau^{slip}=-\tilde{\ell}_s\nabla_\gamma v_\tau+\frac{\tilde{\ell}_s}{\ell_s}\frac{1}{\beta}\left\{\left[M\nabla_\gamma n+\left(\frac{\partial f'_s}{\partial n}\right)_T\right]\nabla_\tau n-\left(\sigma'_s+\beta\frac{\chi}{T}\right)\nabla_\tau T\right\}, \quad\quad (A.16)$$

where $\tilde{\ell}_s$ is the effective slip length defined by $1/\tilde{\ell}_s \equiv 1/\ell_s - 1/R$ with $\ell_s \equiv \eta/\beta$ being the slip length associated with a flat surface [70]. This effective slip length corresponds to the experimentally measured slip length for a fluid on rough solid surface. Physically, the slip length ℓ_s is determined by microscopic fluid-solid interactions while R is a parameter determined by the mesoscopic curvature radius of the solid surface. It is interesting to note that for $0 < R < \ell_s$, the effective slip length may even become negative, i.e. $\tilde{\ell}_s < 0$, with the extrapolated velocity vanishing inside the fluid (rather than the solid). For illustration purposes, we may consider a two-dimensional case where the fluid is above the solid. The curvature radius R is positive if the fluid-solid interface is concave up. Then, if $\ell_s > R$, the effective slip length $\tilde{\ell}_s$ is negative according to $1/\tilde{\ell}_s \equiv 1/\ell_s - 1/R$.

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