



Research Paper

A thermodynamically consistent phase-field model and an entropy stable numerical method for simulating two-phase flows with thermocapillary effects

Yanxiao Sun^a, Jiang Wu^b, Maosheng Jiang^c, Steven M. Wise^d, Zhenlin Guo^{a,*}

^a Mechanics Division, Beijing Computational Science Research Center, Building 9, East Zone, ZPark II, No. 10 East Xibeiwang Road, Haidian District, Beijing 100193, People's Republic of China

^b School of Mathematics and Physics, University of Science and Technology Beijing, No. 30, Xueyuan Road, Haidian District, Beijing 100083, People's Republic of China

^c School of Mathematics and Statistics, Qingdao University, Qingdao 266071, People's Republic of China

^d Mathematics Department, University of Tennessee, Knoxville, TN 37996-1320, USA

ARTICLE INFO

Keywords:

Two-phase flows
Thermocapillary effects
Thermodynamic consistency
Phase-field method

ABSTRACT

In this study, we have derived a thermodynamically consistent phase-field model for two-phase flows with thermocapillary effects. This model accommodates variations in physical properties such as density, viscosity, heat capacity, and thermal conductivity between the two components. The model equations encompass a Cahn-Hilliard equation with the volume fraction as the phase variable, a Navier-Stokes equation, and a heat equation, and meanwhile maintains mass conservation, energy conservation, and entropy increase simultaneously. Given the highly coupled and nonlinear nature of the model equations, we developed a semi-decoupled, mass-preserving, and entropy-stable time-discrete numerical method. We conducted several numerical tests to validate both our model and numerical method. Additionally, we have investigated the merging process of two bubbles under non-isothermal conditions and compared the results with those under isothermal conditions. Our findings reveal that temperature gradients influence bubble morphology and lead to earlier merging. Moreover, we have observed that the merging of bubbles slows down with increasing heat Peclet number Pe_T when the initial temperature field increases linearly along the channel, while bubbles merge faster with heat Peclet number Pe_T when the initial temperature field decreases linearly along the channel.

1. Introduction

The variations of surface tension caused by temperature gradients at a fluid-fluid interface usually lead to an interfacial shear force along the interface, and thus induce the movement of fluids in the direction of the temperature gradient. This effect is known as the thermocapillary effect, which plays an important role in various industrial applications involving microgravity or microdevices [1]. Several phase-field models have been developed for simulating the thermocapillary effects for two-phase flows [1–10]. The essential idea for the phase-field model is to introduce an order parameter to characterize the different phases, which varies continuously over

* Corresponding author.

E-mail address: zguo@csrc.ac.cn (Z. Guo).

<https://doi.org/10.1016/j.apnum.2024.08.010>

Received 13 March 2024; Received in revised form 1 July 2024; Accepted 9 August 2024

Available online 13 August 2024

0168-9274/© 2024 IMACS. Published by Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

a thin interfacial layer and is essentially uniform in the bulk phases. However, most of the existing models are not thermodynamically consistent, namely the fluid flow equation (Navier-Stokes), the phase-field equation (Cahn-Hilliard), and the heat equation are simply coupled and thus do not satisfy energy conservation and entropy production laws.

Recently, a thermodynamically consistent phase-field model [1] has been developed for simulating two-phase flows with thermocapillary effects, where the mass concentration is employed as the phase variable. The model equations for the whole computational domain can be derived variationally from energy and entropy functional, which allows the two fluids to have different physical properties (including density, viscosity and thermal conductivity) and meanwhile maintains mass conservation, internal energy conservation, and entropy increase. The model equations are highly nonlinear and coupled, which leave a challenge to the numerical simulations. In [10], another thermodynamically consistent phase-field model was developed for simulating thermocapillary effects, where the volume fraction is employed as the phase variable instead of the mass concentration, and the two components are assumed to be of equal density. Moreover, several stable and efficient numerical methods, including IEQ [11–13], SAV [14–17], extended SAV [18–21] and SVM [10,22,23], have been developed for solving the phase-field models. In some of these methods, extra, auxiliary variables have been introduced to ensure the discrete energy conservation and entropy increase.

In this paper, we propose a thermodynamically consistent phase-field model for two-phase flows with thermocapillary effects, which allows the two components to have different physical properties, including density, viscosity, heat capacity, and thermal conductivity. The model equations consist of a Cahn-Hilliard equation with the volume fraction of one component as the phase variable, a Navier-Stokes equation, and a heat equation. These equations are highly coupled and nonlinear, and meanwhile satisfy mass conservation, total energy conservation, and entropy increase. To carry out the numerical simulations, we develop a first order, semi-decoupled, mass conservative and entropy stable numerical method for solving the model equations, where there is no need to introduce extra auxiliary variables to our method.

The paper is organized as follows. We present the derivations of the phase-field model for two-phase flows with thermocapillary effects in §2, and provide the model validation in §3. The temporal discrete numerical method and the corresponding discrete mass conservation and entropy increase are shown in §4. The fully discrete numerical method is provided in §5. The numerical results are presented in §6, and finally the conclusion is given in §7.

2. Model equations

2.1. Phase-field variable and variable physical properties

We use the phase-field model to represent a two-phase incompressible fluid flow with variable physical properties and thermocapillary effects along the fluid/fluid interface. In particular, we use the following formulation as the variable density for the two-phase fluid:

$$\rho(\Phi_1, \Phi_2) = \rho_1 \Phi_1 + \rho_2 \Phi_2, \quad (1)$$

where $\rho_i > 0$ is the constant density and Φ_i is the volume fraction of the i^{th} fluid, respectively, for $i = 1, 2$. Here, we use the no-voids assumption,

$$\Phi_1 + \Phi_2 = 1. \quad (2)$$

We next treat the two-phase fluid as one mixture, and define the phase variable as

$$\psi = \Phi_1,$$

such that the variable density ρ for the mixture can be rewritten as

$$\rho = \rho_1 \psi + \rho_2 (1 - \psi). \quad (3)$$

Similarly, we define the other variable properties for the mixture:

$$\text{variable viscosity : } \mu(\psi) = \mu_1 \psi + \mu_2 (1 - \psi), \quad (4)$$

$$\text{variable thermal conductivity : } k(\psi) = k_1 \psi + k_2 (1 - \psi), \quad (5)$$

$$\text{variable heat capacity : } C_h(\psi) = C_{h,1} \psi + C_{h,2} (1 - \psi). \quad (6)$$

2.2. Internal energy, free energy, and entropy

To investigate the thermocapillary effects, we expect the surface free energy of the two-phase fluid to be temperature-dependent. To address this, we propose the internal energy density, \hat{u} , free energy density, \hat{f} , and entropy density, \hat{s} , for the mixture as follows:

$$\hat{u}(T, \psi, \nabla \psi) = u(T, \psi) + \lambda_u \delta(\psi, \nabla \psi), \quad (7)$$

$$\hat{f}(T, \psi, \nabla \psi) = f(T, \psi) + \lambda_f \delta(\psi, \nabla \psi), \quad (8)$$

$$\hat{s}(T, \psi, \nabla \psi) = s(T, \psi) + \lambda_s \delta(\psi, \nabla \psi). \quad (9)$$

Here u , f and s represent the classical components that can be defined as [1]

$$u = \rho C_h T, \quad (10)$$

$$f = \rho C_h T - \rho C_h T \ln \left(\frac{T}{T_0} \right), \quad (11)$$

$$s = \rho C_h \ln \left(\frac{T}{T_0} \right), \quad (12)$$

where T denotes the absolute temperature, and T_0 serves as the reference temperature. Furthermore, we note the following thermodynamic relation:

$$f = u - Ts. \quad (13)$$

Additionally, δ represents the interface free energy, defined as:

$$\delta(\psi, \nabla \psi) = \frac{1}{\epsilon} W(\psi) + \epsilon \frac{|\nabla \psi|^2}{2}, \quad (14)$$

where $W(\psi) = \psi^2(1 - \psi)^2/4$ represents a double-well free energy, and ϵ serves as a small parameter denoting the thickness of the diffuse interface.

In the framework of the sharp-interface model, it's common to assume that the surface tension decreases linearly with temperature, given by:

$$\sigma(T) = \sigma_0 - \sigma_T(T - T_0), \quad (15)$$

where σ_0 represents the surface tension at the reference temperature T_0 , and σ_T denotes the rate of change of surface tension with temperature. Consequently, for our phase-field model, we consider λ_u , λ_f , and λ_s as:

$$\lambda_u = \eta(\sigma_0 + \sigma_T T_0), \quad \lambda_f = \eta\sigma(T), \quad \lambda_s = \eta\sigma_T, \quad (16)$$

where $\eta > 0$ is a positive constant that establishes the relationship between the surface tensions of the diffuse-interface model and the sharp-interface model, as discussed in [1]. Moreover, we note the following thermodynamic relations

$$\lambda_f = \lambda_u - T\lambda_s, \quad (17)$$

$$\hat{f} = \hat{u} - T\hat{s}. \quad (18)$$

2.3. Conservation laws

Next, we establish the conservation laws for the flow of the two-phase fluid. Assuming the two-phase fluid occupies a domain Ω , we consider an arbitrary material volume $V(t) \in \Omega$ moving with the mixture. Here, we define the following quantities: the total mass M , volume of a single fluid phase Ψ , momentum \mathbf{P} , and internal energy U :

$$M = \int_{V(t)} \rho \, dV, \quad (19)$$

$$\Psi = \int_{V(t)} \psi \, dV, \quad (20)$$

$$\mathbf{P} = \int_{V(t)} \rho \mathbf{v} \, dV, \quad (21)$$

$$U = \int_{V(t)} \hat{u} \, dV, \quad (22)$$

where ρ is defined in Eq. (3), \mathbf{v} represents the mass-averaged velocity of the mixture as discussed in [24], and \hat{u} denotes the internal energy density as defined in Eq. (7). Given these considerations, the associated conservation laws can be expressed as follows:

$$\frac{dM}{dt} = 0, \quad (23)$$

$$\frac{d\Psi}{dt} = \int_{\partial V(t)} -\frac{\mathbf{J}}{\rho_1} \cdot \mathbf{n} \, dA, \quad (24)$$

$$\frac{d\mathbf{P}}{dt} = \int_{\partial V(t)} \mathbf{T} \cdot \mathbf{n} \, dA - \int_{V(t)} \rho g \hat{\mathbf{z}} \, dV, \quad (25)$$

$$\frac{dU}{dt} = \int_{\partial V(t)} -\mathbf{q}_E \cdot \mathbf{n} dA + \int_{V(t)} \nabla \mathbf{v} : \mathbf{T} dV. \quad (26)$$

Here, \mathbf{n} denotes the unit outward normal vector of the boundary $\partial V(t)$, while $\hat{\mathbf{z}}$ represents the unit vector in the vertical direction. Eq. (23) represents the mass conservation of the mixture within the material volume, and Eq. (24) stands for the volume conservation for a single fluid (here for the fluid 1), where \mathbf{J} is the volume flux of fluid 1 through the boundary of the material volume. The momentum conservation Eq. (25) states that the rate of change in total momentum equals the force (surface forces \mathbf{T}) acting on the volume boundary. Here we assume that

$$\mathbf{T} = \tau - p\mathbf{I} + \mathbf{q}, \quad (27)$$

where $\tau = \mu(\nabla \mathbf{v} + \nabla \mathbf{v}^\top) - \frac{2}{3}\mu(\nabla \cdot \mathbf{v})\mathbf{I}$ represents the deviatoric stress tensor, p denotes the pressure, \mathbf{I} stands for the unit tensor, and \mathbf{q} represents the unknown term that needs to be determined to ensure entropy non-decrease. Additionally, g in Eq. (25) corresponds to the gravitational constant. The internal energy conservation Eq. (26) states that the change in internal energy equals the rate of work done by the forces (\mathbf{T}) on the boundary plus the energy flux (\mathbf{q}_E) through the volume boundary.

2.4. Model derivation

By substituting Eqs. (19) – (22) into the conservation laws (23) – (26), respectively, we derive the following equations:

$$\rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot \mathbf{T} - \rho g \hat{\mathbf{z}}, \quad (28)$$

$$\nabla \cdot \mathbf{v} = -\alpha \frac{\nabla \cdot \mathbf{J}}{\rho_1}, \quad (29)$$

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \mathbf{v}) = -\frac{\nabla \cdot \mathbf{J}}{\rho_1} \quad \text{or} \quad \frac{D\psi}{Dt} + \psi(\nabla \cdot \mathbf{v}) = \frac{-\nabla \cdot \mathbf{J}}{\rho_1}, \quad (30)$$

$$\frac{\partial u}{\partial T} \frac{DT}{Dt} = -\nabla \cdot \mathbf{q}_E + \nabla \mathbf{v} : \mathbf{T} - src, \quad (31)$$

where

$$\begin{aligned} src &= \left(\frac{\partial u}{\partial \psi} + \lambda_u w \right) \frac{D\psi}{Dt} + \lambda_u \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) + \hat{u}(\nabla \cdot \mathbf{v}) \\ &\quad + \lambda_u \epsilon \nabla \cdot (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v}, \end{aligned} \quad (32)$$

$$w = \frac{W'(\psi)}{\epsilon} - \epsilon \Delta \psi, \quad (33)$$

$$\alpha = (\rho_2 - \rho_1)/\rho_2, \quad (34)$$

and $D/Dt = \partial/\partial t + \mathbf{v} \cdot \nabla$ denotes the material derivative. Note that the comprehensive derivation is provided in Appendix A.

We now define the entropy as

$$S = \int_{V(t)} \hat{s} dV, \quad (35)$$

and calculate the time derivative of the entropy. Here \hat{s} represents the entropy density as defined in Eq. (9), and the following relation is used

$$\frac{\partial \hat{s}}{\partial T} \left(\frac{\partial u}{\partial T} \right)^{-1} = \frac{1}{T}. \quad (36)$$

Similar to the derivation of Eq. (A.12), we obtain

$$\frac{\partial \hat{s}}{\partial t} = \frac{\partial \hat{s}}{\partial T} \frac{\partial T}{\partial t} + \left(\frac{\partial \hat{s}}{\partial \psi} + \lambda_s w \right) \frac{\partial \psi}{\partial t} + \lambda_s \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}), \quad (37)$$

such that

$$\begin{aligned} \frac{dS}{dt} &= \int_{V(t)} \left\{ \frac{\partial \hat{s}}{\partial T} \frac{\partial T}{\partial t} + \left(\frac{\partial \hat{s}}{\partial \psi} + \lambda_s w \right) \frac{\partial \psi}{\partial t} + \lambda_s \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) + \nabla \cdot (\hat{s} \mathbf{v}) \right\} dV \\ &= \int_{V(t)} \left\{ \frac{1}{T} \frac{\partial u}{\partial T} \frac{\partial T}{\partial t} + \left(\frac{\partial \hat{s}}{\partial \psi} + \lambda_s w \right) \frac{\partial \psi}{\partial t} + \lambda_s \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) + \nabla \cdot (\hat{s} \mathbf{v}) \right\} dV. \end{aligned} \quad (38)$$

Substituting (31) into (38), we obtain

$$\frac{dS}{dt} = \int_{V(t)} \left\{ -\frac{\partial \hat{s}}{\partial T} \mathbf{v} \cdot \nabla T - \frac{1}{T} \left(\frac{\partial u}{\partial \psi} + \lambda_u w \right) \frac{D\psi}{Dt} - \frac{1}{T} \lambda_u \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) \right\} dV$$

$$\begin{aligned}
& -\frac{1}{T}\hat{u}(\nabla \cdot \mathbf{v}) - \frac{1}{T}\nabla \cdot \mathbf{q}_E + \frac{1}{T}\nabla \mathbf{v} : \mathbf{T} - \frac{1}{T}\lambda_u \epsilon \nabla \cdot (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} \\
& + \left(\frac{\partial s}{\partial \psi} + \lambda_s w \right) \left(\frac{D\psi}{Dt} - \mathbf{v} \cdot \nabla \psi \right) + \lambda_s \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) + \nabla \cdot (\hat{s} \mathbf{v}) \Big\} dV.
\end{aligned} \tag{39}$$

With the help of Eq. (17) and the following identities

$$\frac{1}{T} \frac{\partial f}{\partial \psi} = \frac{1}{T} \frac{\partial u}{\partial \psi} - \frac{\partial s}{\partial \psi}, \tag{40}$$

$$\mathbf{v} \cdot \nabla \hat{s} = \mathbf{v} \cdot \left(\frac{\partial s}{\partial T} \nabla T + \left(\frac{\partial s}{\partial \psi} + \lambda_s w \right) \nabla \psi + \lambda_s \epsilon \nabla \cdot (\nabla \psi \otimes \nabla \psi) \right), \tag{41}$$

Eq. (39) can be rewritten as

$$\begin{aligned}
\frac{dS}{dt} &= \int_{V(t)} \left\{ -\frac{1}{T} \nabla \cdot \mathbf{q}_E + \frac{1}{T} \nabla \mathbf{v} : \mathbf{T} - \frac{1}{T} \lambda_u \epsilon \nabla \cdot (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} \right. \\
& - \frac{1}{T} \lambda_u \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) + \hat{s}(\nabla \cdot \mathbf{v}) + \lambda_s \epsilon \nabla \cdot (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} \\
& \left. - \frac{1}{T} \hat{u}(\nabla \cdot \mathbf{v}) - \frac{1}{T} \left(\frac{\partial f}{\partial \psi} + \lambda_f w \right) \frac{D\psi}{Dt} + \lambda_s \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) \right\} dV.
\end{aligned} \tag{42}$$

In addition, with the help of Eq. (18) and the following identity

$$\nabla \cdot (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} = \nabla \cdot ((\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v}) - \nabla \mathbf{v} : (\nabla \psi \otimes \nabla \psi), \tag{43}$$

we rewrite Eq. (42) as

$$\begin{aligned}
\frac{dS}{dt} &= \int_{V(t)} \left\{ -\frac{1}{T} \nabla \cdot \left(\mathbf{q}_E + \lambda_u \epsilon (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} + \lambda_u \epsilon \nabla \psi \frac{\partial \psi}{\partial t} \right) \right. \\
& + \frac{1}{T} \nabla \mathbf{v} : (\mathbf{T} + \lambda_f \epsilon (\nabla \psi \otimes \nabla \psi)) - \frac{1}{T} \hat{f}(\nabla \cdot \mathbf{v}) \\
& + \lambda_s \epsilon \nabla \cdot ((\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v}) - \frac{1}{T} \left(\frac{\partial f}{\partial \psi} + \lambda_f w \right) \frac{D\psi}{Dt} \\
& \left. + \lambda_s \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) \right\} dV.
\end{aligned} \tag{44}$$

Next, by substituting Eq. (27) (the definition of \mathbf{T}), mass conservation Eq. (29) and volume conservation Eq. (30) into Eq. (44), we obtain

$$\begin{aligned}
\frac{dS}{dt} &= \int_{V(t)} \left\{ -\frac{1}{T} \nabla \cdot \left(\mathbf{q}_E + \lambda_u \epsilon (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} + \lambda_u \epsilon \nabla \psi \frac{\partial \psi}{\partial t} \right) \right. \\
& + \frac{1}{T} \nabla \mathbf{v} : (\boldsymbol{\tau} + \mathbf{q} + \lambda_f \epsilon (\nabla \psi \otimes \nabla \psi) + \mu_0 \psi \mathbf{I}) \\
& - \frac{1}{T} \hat{f}(\nabla \cdot \mathbf{v}) + \frac{1}{T} \mu_c \nabla \cdot \frac{\mathbf{J}}{\rho_1} + \lambda_s \epsilon \nabla \cdot ((\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v}) \\
& \left. + \lambda_s \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) \right\} dV,
\end{aligned} \tag{45}$$

where

$$\mu_0 = \frac{\partial f}{\partial \psi} + \lambda_f w, \tag{46}$$

$$\mu_c = \mu_0 + \alpha p. \tag{47}$$

With the help of the following identity

$$\frac{1}{T} \mu_c \nabla \cdot \frac{\mathbf{J}}{\rho_1} = \nabla \cdot \left(\frac{1}{T} \mu_c \frac{\mathbf{J}}{\rho_1} \right) - \mu_c \frac{\mathbf{J}}{\rho_1} \cdot \nabla \left(\frac{1}{T} \right) - \frac{1}{T} \frac{\mathbf{J}}{\rho_1} \cdot \nabla \mu_c, \tag{48}$$

Eq. (45) can be rewritten as

$$\frac{dS}{dt} = \int_{V(t)} \left\{ -\nabla \cdot \left(\frac{1}{T} \mathbf{q}_E + \frac{1}{T} \lambda_f \epsilon (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} + \frac{1}{T} \lambda_f \epsilon \nabla \psi \frac{\partial \psi}{\partial t} - \frac{1}{T} \mu_c \frac{\mathbf{J}}{\rho_1} \right) \right.$$

$$\begin{aligned}
& + \nabla \left(\frac{1}{T} \right) \cdot \left(\mathbf{q}_E + \lambda_u \epsilon (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} + \lambda_u \epsilon \nabla \psi \frac{\partial \psi}{\partial t} - \mu_c \frac{\mathbf{J}}{\rho_1} \right) \\
& + \frac{1}{T} \nabla \mathbf{v} : (\tau + \mathbf{q} + \lambda_f \epsilon (\nabla \psi \otimes \nabla \psi) + \mu_0 \psi \mathbf{I} - \hat{f} \mathbf{I}) \\
& - \frac{1}{T} \frac{\mathbf{J}}{\rho_1} \cdot \nabla \mu_c \} dV.
\end{aligned} \tag{49}$$

For the above equation, we denote the first part as the entropy flux of the material volume, and the rest parts as the local entropy increase, S_{inc} , which needs to be non-negative according to the second law of thermodynamics, such that

$$\begin{aligned}
S_{inc} = \int_{V(t)} \left\{ \nabla \left(\frac{1}{T} \right) \cdot \left(\mathbf{q}_E + \lambda_u \epsilon (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} + \lambda_u \epsilon \nabla \psi \frac{\partial \psi}{\partial t} - \mu_c \frac{\mathbf{J}}{\rho_1} \right) \right. \\
\left. + \frac{1}{T} \nabla \mathbf{v} : (\tau + \mathbf{q} + \lambda_f \epsilon (\nabla \psi \otimes \nabla \psi) + \mu_0 \psi \mathbf{I} - \hat{f} \mathbf{I}) - \frac{1}{T} \frac{\mathbf{J}}{\rho_1} \cdot \nabla \mu_c \right\} \geq 0.
\end{aligned} \tag{50}$$

To comply with the second law of thermodynamics, which states that local entropy generation must be non-negative for an irreversible process, we specify the unknown terms as:

$$\mathbf{q} = \hat{f} \mathbf{I} - \lambda_f \epsilon (\nabla \psi \otimes \nabla \psi) - \mu_0 \psi \mathbf{I}, \tag{51}$$

$$\mathbf{J} = -\rho_1 m_\psi \nabla \mu_c, \tag{52}$$

$$\mathbf{q}_E = -k \nabla T - \lambda_u \epsilon (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} - \lambda_u \epsilon \nabla \psi \frac{\partial \psi}{\partial t} + \mu_c \frac{\mathbf{J}}{\rho_1}, \tag{53}$$

where $m_\psi = m \sqrt{\psi^2(1-\psi)^2}$ is the degenerate mobility for the diffuse interface, and m is a constant. Substituting Eqs. (51) – (53) into Eq. (50), we obtain the entropy generation for the two-phase fluid system

$$S_{inc} = \int_{V(t)} \left\{ k \frac{|\nabla T|^2}{T^2} + \frac{1}{T} \nabla \mathbf{v} : \tau + \frac{1}{T} m_\psi |\nabla \mu_c|^2 \right\} \geq 0. \tag{54}$$

Substituting Eqs. (51) – (53) into Eqs. (28) – (31), respectively, we finally obtain the model equations for two-phase flow with variable properties and thermocapillary effects:

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = \nabla \cdot \mathbf{T} - \rho g \hat{\mathbf{z}}, \tag{55}$$

$$\nabla \cdot \mathbf{v} = \alpha \nabla \cdot (m_\psi \nabla \mu_c), \tag{56}$$

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \mathbf{v}) = \nabla \cdot (m_\psi \nabla \mu_c), \tag{57}$$

$$\begin{aligned}
\frac{\partial (\rho C_h T)}{\partial t} + \nabla \cdot (\rho C_h T \mathbf{v}) = -\nabla \cdot \mathbf{q}_E + \nabla \mathbf{v} : \mathbf{T} \\
- \lambda_u \left(\frac{\partial \delta}{\partial t} + \nabla \cdot (\delta \mathbf{v}) \right),
\end{aligned} \tag{58}$$

where

$$\Lambda = \Lambda_1 \psi + \Lambda_2 (1 - \psi) \text{ for } \Lambda = \rho, \mu, C_h, k, \tag{59}$$

$$\mathbf{T} = -p \mathbf{I} + \hat{f} \mathbf{I} + \tau - \lambda_f (T) \epsilon (\nabla \psi \otimes \nabla \psi) - \mu_0 \psi \mathbf{I}, \tag{60}$$

$$\hat{f} = f + \lambda_f (T) \delta, \quad f = \rho C_h T - \rho C_h T \ln \left(\frac{T}{T_0} \right), \tag{61}$$

$$\delta = \frac{W(\psi)}{\epsilon} + \epsilon \frac{|\nabla \psi|^2}{2} = \frac{\psi^2(1-\psi)^2}{4\epsilon} + \epsilon \frac{|\nabla \psi|^2}{2}, \tag{62}$$

$$\tau = \mu (\nabla \mathbf{v} + \nabla \mathbf{v}^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{v}) \mathbf{I}, \tag{63}$$

$$\mu_0 = \frac{\partial f}{\partial \psi} + \lambda_f w, \tag{64}$$

$$\frac{\partial f}{\partial \psi} = (\rho_1 - \rho_2) C_h T (1 - \ln \frac{T}{T_0}) + \rho (C_{h,1} - C_{h,2}) T (1 - \ln \frac{T}{T_0}), \tag{65}$$

$$w = \frac{W'(\psi)}{\epsilon} - \epsilon \Delta \psi, \tag{66}$$

$$\mu_c = \mu_0 + \alpha p, \tag{67}$$

$$\mathbf{q}_E = -k\nabla T - \lambda_u \epsilon (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} - \lambda_u \epsilon \nabla \psi \frac{\partial \psi}{\partial t} - m_\psi \mu_c \nabla \mu_c. \quad (68)$$

2.5. Non-dimensionalization

We now non-dimensionalize the model Eqs. (55) – (58). Using the properties of fluid 1 as the characteristic quantities, we non-dimensionalize the variable properties as

$$\bar{\Lambda} = \psi + \zeta_\Lambda (1 - \psi), \quad (69)$$

where Λ stands for ρ, μ, c_{hc} and k , respectively, and $\zeta_\Lambda = \Lambda_2/\Lambda_1$ are the corresponding physical property ratios. By selecting $R^*, V^*,$ and T^* as the characteristic length, velocity, and temperature, respectively, and $\mu_c^* = \rho_1 (V^*)^2$ as the characteristic chemical potential, energy density, and pressure, σ_0 as the characteristic surface tension, and $m_\psi^* = m$ as the characteristic mobility for the phase field, we non-dimensionalize the physical quantities as follows:

$$\begin{aligned} \bar{t} &= \frac{tV^*}{R^*}, \quad \bar{\mathbf{v}} = \frac{\mathbf{v}}{V^*}, \quad \bar{T} = \frac{T}{T^*}, \quad \bar{T}_0 = \frac{T_0}{T^*}, \quad \bar{\epsilon} = \frac{\epsilon}{R^*}, \quad \bar{\mu}_c = \frac{\mu_c}{\rho_1 (V^*)^2}, \\ \bar{f} &= \frac{\hat{f}}{\rho_1 (V^*)^2}, \quad \bar{u} = \frac{\hat{u}}{\rho_1 (V^*)^2}, \quad \bar{s} = \frac{\hat{s} T^*}{\rho_1 (V^*)^2}, \quad \bar{p} = \frac{p}{\rho_1 (V^*)^2}, \\ \bar{\lambda}_u &= \frac{\lambda_u}{\sigma_0}, \quad \bar{\lambda}_f = \frac{\lambda_f}{\sigma_0}, \quad \bar{\lambda}_s = \frac{\lambda_s T^*}{\sigma_0}, \quad \bar{m}_\psi = \frac{m_\psi}{m}. \end{aligned} \quad (70)$$

After dropping the bar notations, the non-dimensional phase-field model for two-phase flows with thermocapillary effects can be given as follows:

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = \nabla \cdot \mathbf{T} - \frac{\rho}{\text{Fr}} \hat{\mathbf{z}}, \quad (71)$$

$$\nabla \cdot \mathbf{v} = \frac{\alpha}{\text{Pe}_\psi} \nabla \cdot (m_\psi \nabla \mu_c), \quad (72)$$

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \mathbf{v}) = \frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi \nabla \mu_c), \quad (73)$$

$$\begin{aligned} \frac{\partial (\rho C_h T)}{\partial t} + \nabla \cdot (\rho C_h T \mathbf{v}) &= -\nabla \cdot \mathbf{q}_E + \text{Ec} \nabla \mathbf{v} : \mathbf{T} \\ &\quad - \frac{\text{Ec}}{\text{We}} \lambda_u \left(\frac{\partial \delta}{\partial t} + \nabla \cdot (\delta \mathbf{v}) \right), \end{aligned} \quad (74)$$

where

$$\Lambda = \psi + \zeta_\Lambda (1 - \psi), \quad \zeta_\Lambda = \Lambda_2/\Lambda_1 \quad \text{for } \Lambda = \rho, \mu, C_h, k, \quad (75)$$

$$\mathbf{T} = -p\mathbf{I} + \hat{\mathbf{f}}\mathbf{I} + \frac{1}{\text{Re}} \tau - \frac{1}{\text{We}} \lambda_f(T) \epsilon (\nabla \psi \otimes \nabla \psi) - \mu_0 \psi \mathbf{I}, \quad (76)$$

$$\hat{f} = f(T, \psi) + \frac{1}{\text{We}} \lambda_f(T) \delta, \quad (77)$$

$$f = \frac{1}{\text{Ec}} \rho C_h T - \frac{1}{\text{Ec}} \rho C_h T \ln \left(\frac{T}{T_0} \right), \quad (78)$$

$$\lambda_f(T) = \eta (1 - \text{Ca} \text{Ma}(T - T_0)), \quad (79)$$

$$\delta = \frac{W(\psi)}{\epsilon} + \epsilon \frac{|\nabla \psi|^2}{2}, \quad (80)$$

$$W(\psi) = \frac{\psi^2(1 - \psi)^2}{4}, \quad (81)$$

$$\tau = \mu (\nabla \mathbf{v} + \nabla \mathbf{v}^\top) - \frac{2}{3} \mu (\nabla \cdot \mathbf{v}) \mathbf{I}, \quad (82)$$

$$\mu_0 = \frac{\partial f}{\partial \psi} + \frac{1}{\text{We}} \lambda_f(T) w, \quad (83)$$

$$\frac{\partial f}{\partial \psi} = \frac{1}{\text{Ec}} \frac{\rho_1 - \rho_2}{\rho_1} C_h T \left(1 - \ln \left(\frac{T}{T_0} \right) \right) + \frac{1}{\text{Ec}} \rho \frac{C_{h,1} - C_{h,2}}{C_{h,1}} T \left(1 - \ln \left(\frac{T}{T_0} \right) \right), \quad (84)$$

$$w = \frac{W'(\psi)}{\epsilon} - \epsilon \Delta \psi, \quad (85)$$

$$W'(\psi) = \psi(\psi - 1)(\psi - \frac{1}{2}), \quad (86)$$

$$m_\psi = \sqrt{\psi^2(1 - \psi)^2}, \quad (87)$$

$$\mu_c = \mu_0 + \alpha p, \quad (88)$$

$$\begin{aligned} q_E = & -\frac{1}{\text{Pe}_T} k \nabla T - \frac{\text{Ec}}{\text{We}} \lambda_u \epsilon (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} - \frac{\text{Ec}}{\text{We}} \lambda_u \epsilon \nabla \psi \frac{\partial \psi}{\partial t} \\ & - \frac{\text{Ec}}{\text{Pe}_\psi} m_\psi \mu_c \nabla \mu_c, \end{aligned} \quad (89)$$

$$\lambda_u = \eta(1 + \text{Ca} \text{ Ma} T_0). \quad (90)$$

Here the non-dimensional parameters are given by

$$\begin{aligned} \text{Re} = \frac{\rho_1 V^* R^*}{\mu_1}, \quad \text{Ca} = \frac{\mu_1 V^*}{\sigma_0}, \quad \text{Ma} = \frac{\sigma_T T^*}{\mu_1 V^*}, \quad \text{Fr} = \frac{(V^*)^2}{g R^*}, \\ \text{Pe}_\psi = \frac{V^* R^*}{m_\psi \mu_c}, \quad \text{Pe}_T = \frac{\rho_1 C_{h,1} V^* R^*}{k_1}, \quad \text{Ec} = \frac{(V^*)^2}{C_{h,1} T^*}, \quad \text{We} = \text{Ca} \text{ Re}, \end{aligned} \quad (91)$$

where Re is the Reynolds number, Ca is the Capillary number, Ma is the thermal Marangoni number, Fr is the Froude number, Pe_ψ and Pe_T are the Peclet numbers for the phase-field and heat equations, respectively, Ec is the Eckert number and We is the Weber number. In addition, the non-dimensional internal energy and entropy densities are given by

$$\hat{u} = u + \frac{1}{\text{We}} \lambda_u \delta, \quad u = \frac{1}{\text{Ec}} \rho C_h T, \quad (92)$$

$$\hat{s} = s + \frac{1}{\text{We}} \lambda_s \delta, \quad s = \frac{1}{\text{Ec}} \rho C_h \ln \left(\frac{T}{T_0} \right), \quad \lambda_s = \eta \text{Ca} \text{ Ma}. \quad (93)$$

3. Model validation

In this section, to validate the model derivations, we demonstrate that the conservation laws of mass and energy, and entropy increase can be derived from the model Eqs. (71)–(74), which can be further served as the foundation for designing numerical methods.

Theorem 3.1. Consider a closed system in Ω with following boundary conditions

$$\mathbf{v}|_{\partial\Omega} = 0, \quad \mathbf{n} \cdot \nabla \mu_c|_{\partial\Omega} = \mathbf{n} \cdot \nabla \psi|_{\partial\Omega} = \mathbf{n} \cdot \nabla T|_{\partial\Omega} = 0, \quad (94)$$

the model Eqs. (71) – (74) satisfy the following mass and energy conservation

$$\frac{d}{dt} \int_{\Omega} \rho \, dx = 0 \quad \text{and} \quad \frac{dE}{dt} = \frac{d}{dt} \int_{\Omega} \left\{ \hat{u} + \frac{1}{2} \rho |\mathbf{v}|^2 + \frac{\rho}{\text{Fr}} z \right\} dx = 0, \quad (95)$$

where E denotes the dimensionless total energy of the system, comprising the internal energy \hat{u} , kinetic energy $\frac{1}{2} \rho |\mathbf{v}|^2$, and potential energy $\frac{\rho}{\text{Fr}} z$.

Proof. We first show the proof for the mass conservation in (95). Multiplying Eq. (73) by α and using Eq. (72), we obtain

$$\alpha \psi_t + \alpha \nabla \cdot (\psi \mathbf{v}) = \nabla \cdot \mathbf{v}. \quad (96)$$

With the help of α (34) and ρ (75), Eq. (96) can be reformulated as

$$\rho_t + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (97)$$

By integrating over Ω and applying the divergence theorem with the boundary conditions in (94), we deduce the mass conservation in (95).

We now show the proof for the energy conservation. Multiplying Eq. (73) by $-\rho_2 \alpha$ and using Eq. (72), we obtain

$$-\rho_2 \alpha \frac{\partial \psi}{\partial t} - \rho_2 \alpha \nabla \cdot (\psi \mathbf{v}) = -\rho_2 \nabla \cdot \mathbf{v}. \quad (98)$$

With the definitions of α (34) and ρ (75), Eq. (98) can be rewritten as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (99)$$

Multiplying Eq. (71) by \mathbf{v} and Eq. (99) by $|\mathbf{v}|^2/2$, and adding them together, we obtain

$$\frac{1}{2} \frac{\partial (\rho |\mathbf{v}|^2)}{\partial t} + \frac{1}{2} \nabla \cdot (\rho |\mathbf{v}|^2 \mathbf{v}) = \nabla \cdot \mathbf{T} \cdot \mathbf{v} - \frac{\rho}{\text{Fr}} \hat{\mathbf{z}} \cdot \mathbf{v}, \quad (100)$$

where the following identity is used

$$\rho(\mathbf{v} \cdot \nabla \mathbf{v}) \cdot \mathbf{v} + \frac{1}{2} \nabla \cdot (\rho \mathbf{v}) |\mathbf{v}|^2 = \frac{1}{2} \nabla \cdot (\rho |\mathbf{v}|^2 \mathbf{v}). \quad (101)$$

In addition, with the help of \hat{u} (92), Eq. (74) can be rewritten as

$$\frac{\partial \hat{u}}{\partial t} + \nabla \cdot (\hat{u} \mathbf{v}) = -\frac{1}{\text{Ec}} \nabla \cdot \mathbf{q}_E + \nabla \mathbf{v} : \mathbf{T}. \quad (102)$$

Combining Eqs. (100) and (102), and integrating over Ω while applying the divergence theorem with the boundary conditions in Eq. (94), we obtain

$$\frac{d}{dt} \int_{\Omega} \left\{ \frac{1}{2} \rho |\mathbf{v}|^2 + \hat{u} \right\} dx = \int_{\Omega} -\frac{\rho}{\text{Fr}} \hat{\mathbf{z}} \cdot \mathbf{v} dx, \quad (103)$$

where the following identity is used

$$\nabla \cdot (\mathbf{T} \cdot \mathbf{v}) = \nabla \cdot \mathbf{T} \cdot \mathbf{v} + \nabla \mathbf{v} : \mathbf{T}. \quad (104)$$

In addition, using Eq. (99), we have

$$\frac{d}{dt} \int_{\Omega} \frac{\rho}{\text{Fr}} z dx = \int_{\Omega} \frac{\partial \rho}{\partial t} \frac{z}{\text{Fr}} dx = \int_{\Omega} -\nabla \cdot (\rho \mathbf{v}) \frac{z}{\text{Fr}} dx. \quad (105)$$

Adding Eqs. (103) and (105) together, and applying the divergence theorem with the boundary conditions in (94), we deduce the energy conservation in (95). \square

Theorem 3.2. Consider a closed system in Ω with following boundary conditions

$$\mathbf{v}|_{\partial\Omega} = 0, \quad \mathbf{n} \cdot \nabla \mu_c|_{\partial\Omega} = \mathbf{n} \cdot \nabla \psi|_{\partial\Omega} = \mathbf{n} \cdot \nabla T|_{\partial\Omega} = 0, \quad (106)$$

the model Eqs. (71) – (74) satisfy the following entropy increase

$$\begin{aligned} \frac{dS}{dt} &= \frac{d}{dt} \int_{\Omega} \left\{ \frac{1}{\text{Ec}} \rho C_h \ln \left(\frac{T}{T_0} \right) + \frac{1}{\text{We}} \lambda_s \delta \right\} dx \\ &= \int_{\Omega} \left\{ \frac{k}{\text{Ec Pe}_T} \frac{|\nabla T|^2}{T^2} + \frac{1}{\text{Re}} \frac{\tau : \nabla \mathbf{v}}{T} + \frac{m_{\psi}}{\text{Pe}_{\psi}} \frac{|\nabla \mu_c|^2}{T} \right\} dx \geq 0, \end{aligned} \quad (107)$$

where the entropy S of the system is defined as

$$S = \int_{\Omega} \hat{s}(T, \psi, \nabla \psi) dx, \quad (108)$$

and \hat{s} is defined in Eq. (93).

Proof. Multiplying Eq. (73) by μ_0 , we obtain

$$\frac{\partial \psi}{\partial t} \mu_0 + \nabla \cdot (\psi \mathbf{v}) \mu_0 = \frac{1}{\text{Pe}_{\psi}} \nabla \cdot (m_{\psi} \nabla \mu_c) \mu_0. \quad (109)$$

Using the definitions of μ_0 (Eq. (83)) and w (Eq. (85)), the first term leads to

$$\frac{\partial \psi}{\partial t} \mu_0 = \frac{\partial \psi}{\partial t} \frac{\partial f}{\partial \psi} + \frac{1}{\text{We}} \lambda_f(T) \frac{\partial \psi}{\partial t} \frac{W'(\psi)}{\epsilon} - \frac{1}{\text{We}} \lambda_f(T) \frac{\partial \psi}{\partial t} \epsilon \Delta \psi. \quad (110)$$

Furthermore, we note that

$$\lambda_f(T) \frac{\partial \psi}{\partial t} \frac{W'(\psi)}{\epsilon} = \lambda_f(T) \frac{1}{\epsilon} \frac{\partial W}{\partial t}, \quad (111)$$

and

$$-\lambda_f(T) \frac{\partial \psi}{\partial t} \epsilon \Delta \psi = -\lambda_f(T) \epsilon \nabla \cdot \left(\frac{\partial \psi}{\partial t} \nabla \psi \right) + \frac{1}{2} \lambda_f(T) \epsilon \frac{\partial |\nabla \psi|^2}{\partial t}. \quad (112)$$

Substituting Eqs. (111) and (112) into Eq. (110), and using the definition of δ (Eq. (80)), the first term of Eq. (109) can be rewritten as

$$\frac{\partial \psi}{\partial t} \mu_0 = \frac{\partial \psi}{\partial t} \frac{\partial f}{\partial \psi} + \frac{1}{\text{We}} \lambda_f(T) \frac{\partial \delta}{\partial t} - \frac{1}{\text{We}} \lambda_f(T) \epsilon \nabla \cdot \left(\frac{\partial \psi}{\partial t} \nabla \psi \right). \quad (113)$$

The second term of Eq. (109) leads to

$$\begin{aligned}\nabla \cdot (\psi \mathbf{v}) \mu_0 &= \mu_0 \psi (\nabla \cdot \mathbf{v}) + \mu_0 (\mathbf{v} \cdot \nabla \psi) \\ &= \mu_0 \psi (\nabla \cdot \mathbf{v}) + \frac{\partial f}{\partial \psi} (\mathbf{v} \cdot \nabla \psi) + \frac{1}{\text{We}} \lambda_f(T) (\mathbf{v} \cdot \nabla \psi) w,\end{aligned}\quad (114)$$

where Eq. (83) (the definition of μ_0) is used. Furthermore, we obtain

$$\begin{aligned}\lambda_f(T) (\mathbf{v} \cdot \nabla \psi) w &= \lambda_f(T) (\mathbf{v} \cdot \nabla \psi) \frac{W'(\psi)}{\epsilon} - \lambda_f(T) (\mathbf{v} \cdot \nabla \psi) \epsilon \Delta \psi \\ &= \lambda_f(T) (\mathbf{v} \cdot \nabla \delta) - \lambda_f(T) \epsilon \nabla \cdot ((\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v}) \\ &\quad + \lambda_f(T) \epsilon \nabla \mathbf{v} : (\nabla \psi \otimes \nabla \psi),\end{aligned}\quad (115)$$

where the following identity and the definition of δ (Eq. (80)) are used

$$\begin{aligned}-(\mathbf{v} \cdot \nabla \psi) \Delta \psi &= -\nabla \cdot ((\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v}) + \nabla \mathbf{v} : (\nabla \psi \otimes \nabla \psi) \\ &\quad + \mathbf{v} \cdot \nabla \frac{|\nabla \psi|^2}{2}.\end{aligned}\quad (116)$$

Substituting Eq. (115) into Eq. (114), the second term of Eq. (109) can be rewritten as

$$\begin{aligned}\nabla \cdot (\psi \mathbf{v}) \mu_0 &= \mu_0 \psi (\nabla \cdot \mathbf{v}) + \frac{\partial f}{\partial \psi} (\mathbf{v} \cdot \nabla \psi) + \frac{1}{\text{We}} \lambda_f(T) (\mathbf{v} \cdot \nabla \delta) \\ &\quad - \frac{1}{\text{We}} \lambda_f(T) \epsilon \nabla \cdot ((\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v}) + \frac{1}{\text{We}} \lambda_f(T) \epsilon \nabla \mathbf{v} : (\nabla \psi \otimes \nabla \psi).\end{aligned}\quad (117)$$

Substituting Eqs. (113) and (117) into Eq. (109), we obtain

$$\begin{aligned}\frac{\partial \psi}{\partial t} \frac{\partial f}{\partial \psi} &= -\frac{\partial f}{\partial \psi} (\mathbf{v} \cdot \nabla \psi) - \frac{1}{\text{We}} \lambda_f(T) \frac{\partial \delta}{\partial t} \\ &\quad + \frac{1}{\text{We}} \lambda_f(T) \epsilon \nabla \cdot \left(\frac{\partial \psi}{\partial t} \nabla \psi + (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} \right) \\ &\quad - \mu_0 \psi (\nabla \cdot \mathbf{v}) - \frac{1}{\text{We}} \lambda_f(T) (\mathbf{v} \cdot \nabla \delta) \\ &\quad - \frac{1}{\text{We}} \lambda_f(T) \epsilon \nabla \mathbf{v} : (\nabla \psi \otimes \nabla \psi) + \frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi \nabla \mu_c) \mu_0.\end{aligned}\quad (118)$$

Multiplying Eq. (72) by p , and adding it to Eq. (118), we obtain

$$\begin{aligned}\frac{\partial \psi}{\partial t} \frac{\partial f}{\partial \psi} &= -\frac{\partial f}{\partial \psi} (\mathbf{v} \cdot \nabla \psi) - \frac{1}{\text{We}} \lambda_f(T) \frac{\partial \delta}{\partial t} \\ &\quad + \frac{1}{\text{We}} \lambda_f(T) \epsilon \nabla \cdot \left(\frac{\partial \psi}{\partial t} \nabla \psi + (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} \right) \\ &\quad - \frac{1}{\text{We}} \lambda_f(T) (\mathbf{v} \cdot \nabla \delta) \\ &\quad - \frac{1}{\text{We}} \lambda_f(T) \epsilon \nabla \mathbf{v} : (\nabla \psi \otimes \nabla \psi) \\ &\quad - \mu_0 \psi (\nabla \cdot \mathbf{v}) - p (\nabla \cdot \mathbf{v}) \\ &\quad + \frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi \mu_c \nabla \mu_c) - \frac{m_\psi}{\text{Pe}_\psi} |\nabla \mu_c|^2,\end{aligned}\quad (119)$$

where the following identity is used

$$\begin{aligned}&\frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi \nabla \mu_c) \mu_0 + \frac{\alpha}{\text{Pe}_\psi} \nabla \cdot (m_\psi \nabla \mu_c) p \\ &= \frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi \nabla \mu_c) \mu_c \\ &= \frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi \mu_c \nabla \mu_c) - \frac{m_\psi}{\text{Pe}_\psi} |\nabla \mu_c|^2.\end{aligned}$$

In addition, with the help of the definition of u (92), Eq. (74) can be rewritten as

$$\frac{\partial u}{\partial t} + \nabla \cdot (u \mathbf{v}) = -\frac{1}{\text{Ec}} \nabla \cdot \mathbf{q}_E + \nabla \mathbf{v} : \mathbf{T} - \frac{1}{\text{We}} \lambda_u \left(\frac{\partial \delta}{\partial t} + \nabla \cdot (\delta \mathbf{v}) \right).\quad (120)$$

Subtracting Eq. (119) from Eq. (120), we obtain

$$\begin{aligned}
\frac{\partial u}{\partial t} - \frac{\partial f}{\partial \psi} \frac{\partial \psi}{\partial t} &= -\mathbf{v} \cdot \nabla u + \frac{\partial f}{\partial \psi} (\mathbf{v} \cdot \nabla \psi) - \frac{1}{\text{We}} T \lambda_s \frac{\partial \delta}{\partial t} \\
&\quad - \frac{1}{\text{We}} T \lambda_s (\mathbf{v} \cdot \nabla \delta) + \frac{1}{\text{Ec Pe}_T} \nabla \cdot (k \nabla T) \\
&\quad + \frac{1}{\text{We}} T \lambda_s \epsilon \nabla \cdot \left(\nabla \psi \frac{\partial \psi}{\partial t} + \nabla \psi (\mathbf{v} \cdot \nabla \psi) \right) \\
&\quad - T \hat{s}(\nabla \cdot \mathbf{v}) + \frac{1}{\text{Re}} \tau : \nabla \mathbf{v} + \frac{m_\psi}{\text{Pe}_\psi} |\nabla \mu_c|^2,
\end{aligned} \tag{121}$$

where the following identities are used

$$\begin{aligned}
\frac{1}{\text{We}} \lambda_u \frac{\partial \delta}{\partial t} - \frac{1}{\text{We}} \lambda_f(T) \frac{\partial \delta}{\partial t} &= \frac{1}{\text{We}} T \lambda_s \frac{\partial \delta}{\partial t}, \\
\nabla \cdot (u \mathbf{v}) + \frac{1}{\text{We}} \lambda_u \nabla \cdot (\delta \mathbf{v}) - \nabla \mathbf{v} : \hat{\mathbf{f}} \mathbf{I} &= \mathbf{v} \cdot \nabla u + T \hat{s}(\nabla \cdot \mathbf{v}) + \frac{1}{\text{We}} \lambda_u (\mathbf{v} \cdot \nabla \delta), \\
\frac{1}{\text{We}} \lambda_u (\mathbf{v} \cdot \nabla \delta) - \frac{1}{\text{We}} \lambda_f(T) (\mathbf{v} \cdot \nabla \delta) &= \frac{1}{\text{We}} T \lambda_s (\mathbf{v} \cdot \nabla \delta).
\end{aligned}$$

Furthermore, with the help of the following identities

$$\begin{aligned}
\frac{\partial u}{\partial t} - \frac{\partial \psi}{\partial t} \frac{\partial f}{\partial \psi} &= T \frac{\partial s}{\partial t}, \\
T \frac{\partial s}{\partial t} + \frac{1}{\text{We}} T \lambda_s \frac{\partial \delta}{\partial t} &= T \frac{\partial \hat{s}}{\partial t}, \\
\mathbf{v} \cdot \nabla u - \frac{\partial f}{\partial \psi} (\mathbf{v} \cdot \nabla \psi) &= T \mathbf{v} \cdot \nabla s, \\
T \mathbf{v} \cdot \nabla s + \frac{1}{\text{We}} T \lambda_s (\mathbf{v} \cdot \nabla \delta) + T \hat{s}(\nabla \cdot \mathbf{v}) &= T \nabla \cdot (\hat{s} \mathbf{v}),
\end{aligned}$$

Eq. (121) can be rewritten as

$$\begin{aligned}
\frac{\partial \hat{s}}{\partial t} &= -\nabla \cdot (\hat{s} \mathbf{v}) + \frac{1}{\text{Ec Pe}_T} \nabla \cdot \left(\frac{1}{T} k \nabla T \right) + \frac{k}{\text{Ec Pe}_T} \frac{|\nabla T|^2}{T^2} \\
&\quad + \frac{1}{\text{We}} \lambda_s \epsilon \nabla \cdot \left(\nabla \psi \frac{\partial \psi}{\partial t} + \nabla \psi (\mathbf{v} \cdot \nabla \psi) \right) \\
&\quad + \frac{1}{\text{Re}} \frac{\tau : \nabla \mathbf{v}}{T} + \frac{m_\psi}{\text{Pe}_\psi} \frac{|\nabla \mu_c|^2}{T}.
\end{aligned} \tag{122}$$

Taking the integral over Ω and applying the divergence theorem with the boundary conditions in Eq. (106), we finally deduce the entropy increasing Eq. (107). \square

4. Temporal discrete numerical method

The continuous model (Eqs. (71) – (74)) is mass conserved, energy conserved and entropy increasing, which is highly nonlinear and coupled, making it challenging to develop an algorithm that preserves all these properties simultaneously. Therefore, we developed an algorithm that maintains the conservation of mass and entropy increase at the temporal discrete level.

We now present a first order, semi-decoupled, mass conserving and entropy increasing temporal discrete numerical method for the model Eqs. (71) – (74):

$$\rho^n \mathbf{v}_i + \rho^n \mathbf{v}^n \cdot \nabla \mathbf{v}^{n+1} = \nabla \cdot \mathbf{T}^{n+1} - \frac{\rho^n}{\text{Fr}} \hat{\mathbf{z}}, \tag{123}$$

$$\nabla \cdot \mathbf{v}^n = \frac{\alpha}{\text{Pe}_\psi} \nabla \cdot \left(m_\psi^n \nabla \mu_c^{n+1} \right), \tag{124}$$

$$\psi_i + \nabla \cdot (\psi^{n+1} \mathbf{v}^n) = \frac{1}{\text{Pe}_\psi} \nabla \cdot \left(m_\psi^n \nabla \mu_c^{n+1} \right), \tag{125}$$

$$(\rho C_h)^{n+1} T_i + (\rho C_h)^{n+1} (\mathbf{v}^n \cdot \nabla T^n) = -\nabla \cdot \mathbf{q}_E^{n+1} + h s. \tag{126}$$

We refer to Appendix B for the detailed definitions. Here, \mathbf{v}^n , p^n , ψ^n , μ_0^n and T^n are the approximations of $\mathbf{v}(n\delta t)$, $p(n\delta t)$, $\psi(n\delta t)$, $\mu_0(n\delta t)$ and $T(n\delta t)$ at time $t = n\delta t$, respectively, δt is the time step, and $*_{\bar{t}} = (*^{n+1} - *)/\delta t$.

Next, we prove that the numerical method (123) – (126) preserves the temporal discrete mass conservation and entropy increase.

Theorem 4.1. Consider a closed system in Ω with following boundary conditions

$$\mathbf{v}^n|_{\partial\Omega} = 0, \quad \mathbf{n} \cdot \nabla \mu_c^n|_{\partial\Omega} = \mathbf{n} \cdot \nabla \psi^n|_{\partial\Omega} = \mathbf{n} \cdot \nabla T^n|_{\partial\Omega} = 0, \tag{127}$$

the numerical method (123) – (126) preserves the following temporal discrete mass conservation

$$\int_{\Omega} \rho_{\bar{t}} dx = 0, \quad (128)$$

and discrete entropy increase corresponding to the continuous counterpart (107)

$$\begin{aligned} S_{\bar{t}} = \int_{\Omega} \frac{\hat{s}^{n+1} - \hat{s}^n}{\delta t} dx = \int_{\Omega} \left\{ \frac{k}{\text{Ec Pe}_T} \frac{|\nabla T^{n+1} + \nabla T^n|^2}{4(T^n)^2} + \frac{1}{\text{Re}} \frac{\tau^{n+1} : \nabla \mathbf{v}^{n+1}}{T^n} \right. \\ \left. + \frac{m_{\psi}^n}{\text{Pe}_{\psi}} \frac{|\nabla \mu_{\epsilon}^{n+1}|^2}{T^n} + res \right\} dx \geq 0, \end{aligned} \quad (129)$$

where $\hat{s}^{n+1} = \frac{1}{\text{Ec}} \rho^{n+1} C_h^{n+1} \ln \left(\frac{T^{n+1}}{T_0} \right) + \frac{1}{\text{We}} \lambda_s \delta^{n+1}$, and res is defined in Eq. (164).

Proof. We first show the proof for the discrete mass conservation. Multiplying Eq. (125) by α and using Eq. (124), we obtain

$$\alpha \psi_{\bar{t}} + \alpha \nabla \cdot (\psi^{n+1} \mathbf{v}^n) = \nabla \cdot \mathbf{v}^n. \quad (130)$$

With the help of the definitions of α (34) and ρ^{n+1} (B.1), Eq. (130) can be rewritten as

$$\rho_{\bar{t}} + \nabla \cdot (\rho^{n+1} \mathbf{v}^n) = 0. \quad (131)$$

Taking the integral over Ω with the boundary conditions in (127), we obtain the discrete mass conservation (128).

We now show the proof for the discrete entropy increasing law. Multiplying Eq. (125) by μ_0^{n+1} , we obtain

$$\psi_{\bar{t}} \mu_0^{n+1} + \nabla \cdot (\psi^{n+1} \mathbf{v}^n) \mu_0^{n+1} = \frac{1}{\text{Pe}_{\psi}} \nabla \cdot \left(m_{\psi}^n \nabla \mu_{\epsilon}^{n+1} \right) \mu_0^{n+1}. \quad (132)$$

Using Eq. (B.4) (the definition of μ_0^{n+1}), the first term leads to

$$\begin{aligned} \psi_{\bar{t}} \mu_0^{n+1} &= \psi_{\bar{t}} \frac{\partial f}{\partial \psi} + \frac{1}{\text{We}} \lambda_f(T^n) \psi_{\bar{t}} \frac{W'(\psi^{n+1})}{\epsilon} \\ &\quad - \frac{1}{\text{We}} \lambda_f(T^n) \psi_{\bar{t}} \epsilon \Delta \psi^{n+1}. \end{aligned} \quad (133)$$

Furthermore, we have

$$\frac{1}{\text{We}} \lambda_f(T^n) \psi_{\bar{t}} \frac{W'(\psi^{n+1})}{\epsilon} = \frac{1}{\text{We}} \lambda_f(T^n) \frac{W_{\bar{t}}}{\epsilon} + err_1, \quad (134)$$

$$err_1 = \frac{1}{\text{We}} \lambda_f(T^n) \frac{W''(\xi)(\psi^n - \psi^{n+1})^2}{2\delta t \epsilon}, \quad (135)$$

where ξ is between ψ^{n+1} and ψ^n , and we have used the following Taylor expansion

$$W'(\psi^{n+1})(\psi^{n+1} - \psi^n) = W(\psi^{n+1}) - W(\psi^n) + \frac{1}{2} W''(\xi)(\psi^n - \psi^{n+1})^2. \quad (136)$$

In addition, we have

$$\begin{aligned} -\frac{1}{\text{We}} \lambda_f(T^n) \psi_{\bar{t}} \epsilon \Delta \psi^{n+1} &= -\frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \cdot \left(\frac{\psi^{n+1} - \psi^n}{\delta t} \nabla \psi^{n+1} \right) \\ &\quad + \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \left(\frac{|\nabla \psi^{n+1}|^2}{\delta t} - \frac{\nabla \psi^n \cdot \nabla \psi^{n+1}}{\delta t} \right) \\ &= -\frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \cdot (\psi_{\bar{t}} \nabla \psi^{n+1}) \\ &\quad + \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \frac{|\nabla \psi|^2_{\bar{t}}}{2} + err_2, \end{aligned} \quad (137)$$

$$err_2 = \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \frac{|\nabla \psi^{n+1} - \nabla \psi^n|^2}{2\delta t}. \quad (138)$$

Substituting Eqs. (134) and (137) into Eq. (133), the first term of Eq. (132) can be rewritten as

$$\begin{aligned} \psi_{\bar{t}} \mu_0^{n+1} &= \psi_{\bar{t}} \frac{\partial f}{\partial \psi} + \frac{1}{\text{We}} \lambda_f(T^n) \delta_{\bar{t}} - \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \cdot (\psi_{\bar{t}} \nabla \psi^{n+1}) \\ &\quad + err_1 + err_2. \end{aligned} \quad (139)$$

The second term of Eq. (132) leads to

$$\begin{aligned}\nabla \cdot (\psi^{n+1} \mathbf{v}^n) \mu_0^{n+1} &= \mu_0^{n+1} \psi^{n+1} (\nabla \cdot \mathbf{v}^n) + \frac{\partial f}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) \\ &\quad + \frac{1}{\text{We}} \lambda_f(T^n) (\mathbf{v}^n \cdot \nabla \psi^{n+1}) w^{n+1},\end{aligned}\quad (140)$$

where the definition of μ_0^{n+1} (Eq. (B.4)) is used. Furthermore, we have

$$\begin{aligned}\lambda_f(T^n) (\mathbf{v}^n \cdot \nabla \psi^{n+1}) w^{n+1} &= \lambda_f(T^n) (\mathbf{v}^n \cdot \nabla \psi^{n+1}) \frac{W'(\psi^{n+1})}{\epsilon} \\ &\quad - \lambda_f(T^n) (\mathbf{v}^n \cdot \nabla \psi^{n+1}) \epsilon \Delta \psi^{n+1} \\ &= \lambda_f(T^n) (\mathbf{v}^n \cdot \nabla \delta^{n+1}) \\ &\quad - \lambda_f(T^n) \epsilon \nabla \cdot ((\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \cdot \mathbf{v}^n) \\ &\quad + \lambda_f(T^n) \epsilon \nabla \mathbf{v}^n : (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}),\end{aligned}\quad (141)$$

where the following identity is used

$$\begin{aligned}-(\mathbf{v}^n \cdot \nabla \psi^{n+1}) \Delta \psi^{n+1} &= -\nabla \cdot ((\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \cdot \mathbf{v}^n) \\ &\quad + \nabla \mathbf{v}^n : (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) + \mathbf{v}^n \cdot \nabla \frac{|\nabla \psi^{n+1}|^2}{2}.\end{aligned}\quad (142)$$

Substituting Eq. (141) into Eq. (140), the second term of Eq. (132) can be rewritten as

$$\begin{aligned}\nabla \cdot (\psi^{n+1} \mathbf{v}^n) \mu_0^{n+1} &= \mu_0^{n+1} \psi^{n+1} (\nabla \cdot \mathbf{v}^n) + \frac{\partial f}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) \\ &\quad + \frac{1}{\text{We}} \lambda_f(T^n) (\mathbf{v}^n \cdot \nabla \delta^{n+1}) \\ &\quad - \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \cdot ((\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \cdot \mathbf{v}^n) \\ &\quad + \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \mathbf{v}^n : (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}).\end{aligned}\quad (143)$$

Substituting Eqs. (139) and (143) into Eq. (132), we obtain

$$\begin{aligned}\psi_{\bar{i}} \frac{\partial f}{\partial \psi} &= -\frac{\partial f}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) - \frac{1}{\text{We}} \lambda_f(T^n) \delta_{\bar{i}} \\ &\quad + \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \cdot (\psi_{\bar{i}} \nabla \psi^{n+1} + (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \cdot \mathbf{v}^n) \\ &\quad - \mu_0^{n+1} \psi^{n+1} (\nabla \cdot \mathbf{v}^n) - \frac{1}{\text{We}} \lambda_f(T^n) (\mathbf{v}^n \cdot \nabla \delta^{n+1}) \\ &\quad - \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \mathbf{v}^n : (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \\ &\quad + \frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi^n \nabla \mu_c^{n+1}) \mu_0^{n+1} - err_1 - err_2.\end{aligned}\quad (144)$$

Multiplying Eq. (124) by p^{n+1} , we obtain

$$p^{n+1} (\nabla \cdot \mathbf{v}^n) = \frac{\alpha}{\text{Pe}_\psi} \nabla \cdot (m_\psi^n \nabla \mu_c^{n+1}) p^{n+1}.\quad (145)$$

Adding Eq. (145) to Eq. (144), we obtain

$$\begin{aligned}\psi_{\bar{i}} \frac{\partial f}{\partial \psi} &= -\frac{\partial f}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) - \frac{1}{\text{We}} \lambda_f(T^n) \delta_{\bar{i}} \\ &\quad + \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \cdot (\psi_{\bar{i}} \nabla \psi^{n+1} + (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \cdot \mathbf{v}^n) \\ &\quad - \frac{1}{\text{We}} \lambda_f(T^n) (\mathbf{v}^n \cdot \nabla \delta^{n+1}) \\ &\quad - \frac{1}{\text{We}} \lambda_f(T^n) \epsilon \nabla \mathbf{v}^n : (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \\ &\quad - \mu_0^{n+1} \psi^{n+1} (\nabla \cdot \mathbf{v}^n) - p^{n+1} (\nabla \cdot \mathbf{v}^n) \\ &\quad + \frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi^n \mu_c^{n+1} \nabla \mu_c^{n+1}) - \frac{m_\psi^n}{\text{Pe}_\psi} |\nabla \mu_c^{n+1}|^2\end{aligned}$$

$$-err_1 - err_2, \quad (146)$$

where the following identity is used

$$\begin{aligned} & \frac{1}{\text{Pe}_\psi} \nabla \cdot \left(m_\psi^n \nabla \mu_c^{n+1} \right) \mu_0^{n+1} + \frac{\alpha}{\text{Pe}_\psi} \nabla \cdot \left(m_\psi^n \nabla \mu_c^{n+1} \right) p^{n+1} \\ &= \frac{1}{\text{Pe}_\psi} \nabla \cdot \left(m_\psi^n \nabla \mu_c^{n+1} \right) \mu_c^{n+1} \\ &= \frac{1}{\text{Pe}_\psi} \nabla \cdot (m_\psi^n \mu_c^{n+1} \nabla \mu_c^{n+1}) - \frac{m_\psi^n}{\text{Pe}_\psi} |\nabla \mu_c^{n+1}|^2. \end{aligned}$$

Next, multiplying Eq. (146) by $-\text{Ec}$, and adding to Eq. (126), we obtain

$$\begin{aligned} (\rho C_h)^{n+1} T_i + \text{Ec} \frac{\partial u}{\partial \psi} \psi_i - \text{Ec} \frac{\partial f}{\partial \psi} \psi_i &= -(\rho C_h)^{n+1} (\mathbf{v}^n \cdot \nabla T^n) \\ &\quad - \text{Ec} \frac{\partial \tilde{u}}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) + \text{Ec} \frac{\partial f}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) \\ &\quad - \frac{\text{Ec}}{\text{We}} T^n \lambda_s \delta_i + \frac{1}{\text{Pe}_T} \nabla \cdot \left(k \frac{\nabla T^{n+1} + \nabla T^n}{2} \right) \\ &\quad + \frac{\text{Ec}}{\text{We}} T^n \lambda_s \epsilon \nabla \cdot (\nabla \psi^{n+1} \psi_i + \nabla \psi^{n+1} (\mathbf{v}^n \cdot \nabla \psi^{n+1})) \\ &\quad - \frac{\text{Ec}}{\text{We}} T^n \lambda_s (\mathbf{v}^n \cdot \nabla \delta^{n+1}) \\ &\quad - \text{Ec} T^n \tilde{s}^{n+1} (\nabla \cdot \mathbf{v}^n) + \frac{\text{Ec}}{\text{Re}} \tau^{n+1} : \nabla \mathbf{v}^{n+1} \\ &\quad + \frac{\text{Ec}}{\text{Pe}_\psi} m_\psi^n |\nabla \mu_c^{n+1}|^2 + corr^n \\ &\quad + \text{Ec} err_1 + \text{Ec} err_2, \end{aligned} \quad (147)$$

where the following identities are used

$$T^n \lambda_s = \lambda_u - \lambda_f(T^n), \quad (148)$$

$$(\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \cdot \mathbf{v}^n = \nabla \psi^{n+1} (\mathbf{v}^n \cdot \nabla \psi^{n+1}), \quad (149)$$

$$\nabla \mathbf{v}^n : \mu_0^{n+1} \psi^{n+1} \mathbf{I} = \mu_0^{n+1} \psi^{n+1} (\nabla \cdot \mathbf{v}^n). \quad (150)$$

Furthermore, using Eqs. (B.5) and (B.10), we obtain

$$\begin{aligned} \text{Ec} \frac{\partial f}{\partial \psi} \psi_i &= \rho_i C_h^{n+1} T^n - \rho_i C_h^{n+1} T^n \ln \left(\frac{T^n}{T_0} \right) \\ &\quad + \rho^n (C_h)_i T^n - \rho^n (C_h)_i T^n \ln \left(\frac{T^n}{T_0} \right) \\ &= (\rho C_h)_i T^n - (\rho C_h)_i T^n \ln \left(\frac{T^n}{T_0} \right), \end{aligned} \quad (151)$$

and

$$\begin{aligned} \text{Ec} \frac{\partial u}{\partial \psi} \psi_i + (\rho C_h)^{n+1} T_i &= (\rho C_h)_i T^n \\ &\quad + \frac{(\rho C_h)^{n+1} T^n}{\delta t} \left(\ln \left(\frac{T^{n+1}}{T_0} \right) - \ln \left(\frac{T^n}{T_0} \right) \right) \\ &\quad + err_3, \end{aligned} \quad (152)$$

$$err_3 = \frac{(\rho C_h)^{n+1} T^n (T^{n+1} - T^n)^2}{2(\tilde{T})^2 \delta t}, \quad (153)$$

where \tilde{T} is between T^{n+1} and T^n , and we have used the following identity

$$T^{n+1} - T^n = \left(\ln \left(\frac{T^{n+1}}{T_0} \right) - \ln \left(\frac{T^n}{T_0} \right) \right) T^n + \frac{T^n}{2(\tilde{T})^2} (T^{n+1} - T^n)^2. \quad (154)$$

Subtracting Eq. (151) from Eq. (152), we obtain

$$\begin{aligned}
(\rho C_h)^{n+1} T_i + \text{Ec} \frac{\partial u}{\partial \psi} \psi_i - \text{Ec} \frac{\partial f}{\partial \psi} \psi_i &= \frac{(\rho C_h)^{n+1} T^n}{\delta t} \ln\left(\frac{T^{n+1}}{T_0}\right) \\
&\quad - \frac{(\rho C_h)^n T^n}{\delta t} \ln\left(\frac{T^n}{T_0}\right) + \text{err}_3 \\
&= \text{Ec} T^n s_i + \text{err}_3.
\end{aligned} \tag{155}$$

In addition, we have

$$\begin{aligned}
&-(\rho C_h)^{n+1} (\mathbf{v}^n \cdot \nabla T^n) - \text{Ec} \frac{\partial \tilde{u}}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) + \text{Ec} \frac{\partial f}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) \\
&= -\text{Ec} T^n (\mathbf{v}^n \cdot \nabla \tilde{S}^{n+1}),
\end{aligned} \tag{156}$$

where the following identities are used

$$-(\rho C_h)^{n+1} (\mathbf{v}^n \cdot \nabla T^n) = -\text{Ec} T^n \frac{\partial \tilde{S}^{n+1}}{\partial T^n} (\mathbf{v}^n \cdot \nabla T^n), \tag{157}$$

$$-\frac{\partial \tilde{u}}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) + \frac{\partial f}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) = -T^n \frac{\partial \tilde{S}^{n+1}}{\partial \psi^{n+1}} (\mathbf{v}^n \cdot \nabla \psi^{n+1}). \tag{158}$$

Substituting Eqs. (155) and (156) into Eq. (147), and recalling the definitions of \hat{s} (Eq. (93)) and \tilde{s}^{n+1} (Eq. (B.12)), we obtain

$$\begin{aligned}
\text{Ec} T^n \hat{s}_i &= \frac{1}{\text{Pe}_T} \nabla \cdot \left(k \frac{\nabla T^{n+1} + \nabla T^n}{2} \right) \\
&\quad + \frac{\text{Ec}}{\text{We}} T^n \lambda_s \epsilon \nabla \cdot (\nabla \psi^{n+1} \psi_i + \nabla \psi^{n+1} (\mathbf{v}^n \cdot \nabla \psi^{n+1})) \\
&\quad - \text{Ec} T^n \nabla \cdot (\tilde{s}^{n+1} \mathbf{v}^n) + \frac{\text{Ec}}{\text{Re}} \tau^{n+1} : \nabla \mathbf{v}^{n+1} \\
&\quad + \frac{\text{Ec}}{\text{Pe}_\psi} m_\psi^n |\nabla \mu_c^{n+1}|^2 + \text{corr}^n + \text{Ec} \text{err}_1 + \text{Ec} \text{err}_2 - \text{err}_3.
\end{aligned} \tag{159}$$

Multiplying Eq. (159) by $1/(\text{Ec} T^n)$, and using the following identities

$$\begin{aligned}
\frac{1}{T^n} \nabla \cdot \left(k \frac{\nabla T^{n+1} + \nabla T^n}{2} \right) &= \nabla \cdot \left(\frac{k}{T^n} \frac{\nabla T^{n+1} + \nabla T^n}{2} \right) + \frac{k |\nabla T^{n+1} + \nabla T^n|^2}{4(T^n)^2} \\
&\quad + \frac{\text{err}_4}{T^n},
\end{aligned} \tag{160}$$

$$\text{err}_4 = \frac{k |\nabla T^n|^2 - k |\nabla T^{n+1}|^2}{4T^n}, \tag{161}$$

we obtain

$$\begin{aligned}
\hat{s}_i &= \frac{k}{\text{Ec} \text{Pe}_T} \frac{|\nabla T^{n+1} + \nabla T^n|^2}{4(T^n)^2} \\
&\quad + \frac{1}{\text{Ec} \text{Pe}_T} \nabla \cdot \left(\frac{k}{T^n} \frac{\nabla T^{n+1} + \nabla T^n}{2} \right) \\
&\quad + \frac{1}{\text{We}} \lambda_s \epsilon \nabla \cdot (\nabla \psi^{n+1} \psi_i + \nabla \psi^{n+1} (\mathbf{v}^n \cdot \nabla \psi^{n+1})) \\
&\quad - \nabla \cdot (\tilde{s}^{n+1} \mathbf{v}^n) + \frac{1}{\text{Re}} \frac{\tau^{n+1} : \nabla \mathbf{v}^{n+1}}{T^n} + \frac{m_\psi^n}{\text{Pe}_\psi} \frac{|\nabla \mu_c^{n+1}|^2}{T^n} + \text{res},
\end{aligned} \tag{162}$$

where

$$\text{res} = \frac{\text{corr}^n + \text{Ec} \text{err}_1 + \text{Ec} \text{err}_2 - \text{err}_3 + \frac{1}{\text{Pe}_T} \text{err}_4}{\text{Ec} T^n}. \tag{163}$$

Recalling the definitions of corr^n (Eq. (B.14)), err_1 (Eq. (135)), err_2 (Eq. (138)), err_3 (Eq. (153)) and err_4 (Eq. (161)), we obtain

$$\begin{aligned}
\text{res} &= \frac{\text{Ec}}{\text{We}} \lambda_f(T^n) \left(\frac{1}{4} + W''(\xi) \right) \frac{(\psi^n - \psi^{n+1})^2}{2T^n \delta t \epsilon} + \frac{(\rho C_h)^{n+1} (T^{n+1} - T^n)^2}{2(T_{\min})^2 \delta t} \\
&\quad - \frac{(\rho C_h)^{n+1} (T^{n+1} - T^n)^2}{2(\tilde{T})^2 \delta t} \geq 0,
\end{aligned} \tag{164}$$

where we have used the relations $W''(\xi) \geq -1/4$, $\lambda_f(T^n) \geq 0$ and $T_{\min} \leq \tilde{T}$.

Taking the integral over Ω and applying the divergence theorem with the boundary conditions in Eq. (127), we finally deduce the discrete entropy increase (128) of our numerical method

$$S_i = \int_{\Omega} \hat{s}_i dx = \int_{\Omega} \left\{ \frac{k}{\text{Ec Pe}_T} \frac{|\nabla T^{n+1} + \nabla T^n|^2}{4(T^n)^2} + \frac{1}{\text{Re}} \frac{\tau^{n+1} : \nabla \mathbf{v}^{n+1}}{T^n} + \frac{m_{\psi}^n}{\text{Pe}_{\psi}} \frac{|\nabla \mu_c^{n+1}|^2}{T^n} + \text{res} \right\} dx \geq 0. \quad \square \quad (165)$$

5. Fully discrete numerical method

5.1. Basic definitions

In this study, we employ the finite difference method on staggered grids for spatial discretization of the model Eqs. (71) – (74). We first show some basic definitions and notations for the finite difference discretization on a staggered grid. Here we use the notation and results from [25]. Let $\Omega = (0, L_x) \times (0, L_y)$, with $L_x = m_1 \cdot h$ and $L_y = m_2 \cdot h$, where m_1 and m_2 are positive integers and $h > 0$ is the spatial step size. For simplicity we assume that $L_x = L_y$. Consider the following four sets

$$E_{m_1} = \{x_{i+\frac{1}{2}} \mid i = 0, \dots, m_1\}, \quad E_{\bar{m}_1} = \{x_{i+\frac{1}{2}} \mid i = -1, \dots, m_1 + 1\}, \\ C_{m_1} = \{x_i \mid i = 1, \dots, m_1\}, \quad C_{\bar{m}_1} = \{x_i \mid i = 0, \dots, m_1 + 1\},$$

where $x_{i+\frac{1}{2}} = (i + \frac{1}{2}) \cdot h$ and $x_i = i \cdot h$. Here the elements of E_{m_1} and $E_{\bar{m}_1}$ are called edge-centered points. The two points belonging to $E_{\bar{m}_1} \setminus E_{m_1}$ are called ghost points. The elements of C_{m_1} and $C_{\bar{m}_1}$ are called cell-centered points. Again, the two points belonging to $C_{\bar{m}_1} \setminus C_{m_1}$ are called ghost points. Analogously, the sets E_{m_2} and $E_{\bar{m}_2}$ contain the edge-centered points, and C_{m_2} and $C_{\bar{m}_2}$ contain the cell-centered points of the interval $[0, L_y]$. We then define the following function spaces

$$C_{m_1 \times m_2} = \left\{ \psi : C_{m_1} \times C_{m_2} \rightarrow \mathbf{R} \right\}, \quad \mathcal{V}_{m_1 \times m_2}^{vc} = \left\{ f : E_{m_1} \times E_{m_2} \rightarrow \mathbf{R} \right\}, \\ \mathcal{E}_{m_1 \times m_2}^{ew} = \left\{ u : E_{m_1} \times C_{m_2} \rightarrow \mathbf{R} \right\}, \quad \mathcal{E}_{m_1 \times m_2}^{ns} = \left\{ v : C_{m_1} \times E_{m_2} \rightarrow \mathbf{R} \right\},$$

for cell-centered functions, vertex-centered functions, east-west edge-centered functions and north-south edge-centered functions, respectively. Due to the different locations of the functions, we define several average and difference operators as follows:

edge to center average and difference: a_x, a_y, d_x, d_y ;
center to edge average and difference: A_x, A_y, D_x, D_y ;
vertex to edge average and difference: $\mathfrak{A}_x, \mathfrak{A}_y, \mathfrak{D}_x, \mathfrak{D}_y$;
edge to vertex average and difference: $\mathcal{A}_x, \mathcal{A}_y, \mathcal{D}_x, \mathcal{D}_y$;
center to vertex average: \mathcal{A} .

We refer the reader to Appendix C for a description of our notations for the above operators. We also define average operators $A = \begin{pmatrix} A_x & 0 \\ 0 & A_y \end{pmatrix}$, $A_a = \begin{pmatrix} a_x & 0 \\ 0 & a_y \end{pmatrix}$ and the following gradient operators:

$$\nabla_d = (d_x, d_y), \quad \nabla_D = (D_x, D_y), \quad \nabla_{(d,D)} = (d_x, D_y), \\ \nabla_{(D,d)} = (D_x, d_y), \quad \nabla_{(D,\mathfrak{D})} = (D_x, \mathfrak{D}_y), \quad \nabla_{(\mathfrak{D},D)} = (\mathfrak{D}_x, D_y).$$

Note that in this paper, the cell-centered functions are the phase variable ψ , chemical potential μ_c , pressure p , and temperature T , the east-west edge-centered function is the x -component of the velocity, u , and the north-south edge-centered function is the y -component of the velocity, v .

5.2. Finite difference discretization on staggered grid

We now apply the finite difference method on staggered grids in space to the temporal discrete numerical method (123) – (126), and let the grid functions $\psi^n, \mu_c^n, p^n, T^n \in C_{\bar{m}_1 \times \bar{m}_2}$, $u^n \in \mathcal{E}_{m_1 \times m_2}^{ew}$ and $v^n \in \mathcal{E}_{m_1 \times m_2}^{ns}$. For convenience, we present the following two-dimensional fully discrete numerical scheme:

$$A \rho^n \mathbf{v}_i^n + \rho^n \mathbf{v}^n \cdot \nabla \mathbf{v}^{n+1} = \nabla \cdot \mathbf{T}^{n+1} - \frac{A \rho^n}{\text{Fr}} \hat{\mathbf{z}}. \quad (166)$$

$$\nabla_d \cdot \mathbf{v}^n = \frac{\alpha}{\text{Pe}_{\psi}} \nabla_d \cdot (A m_{\psi}^n \nabla_D \mu_c^{n+1}), \quad (167)$$

$$\psi_i^n + \nabla_d \cdot (A \psi^{n+1} \mathbf{v}^n) = \frac{1}{\text{Pe}_{\psi}} \nabla_d \cdot (A m_{\psi}^n \nabla_D \mu_c^{n+1}), \quad (168)$$

$$(\rho C_h)^{n+1} T_i^n + (\rho C_h)^{n+1} (A_a \mathbf{v}^n \cdot A_a \nabla_D^T T^n) = -\nabla_d \cdot \mathbf{q}_E^{n+1} + h s, \quad (169)$$

where the terms $\rho^n \mathbf{v}^n \cdot \nabla \mathbf{v}^{n+1}$, $\nabla \cdot \mathbf{T}^{n+1}$, \mathbf{q}_E^{n+1} and $h s$ are defined in Appendix D. The numerical scheme in three-dimensional space can be easily generalized straightforwardly.

Table 1

Comparison of L^2 errors for the phase variable ψ , and velocity components u and v obtained at $t = 0.25$ with various δt on a fixed grid size of 1024×1024 . Refer to §6.1 for details.

δt	L^2 error of ψ	Order	L^2 error of u	Order	L^2 error of v	Order
1/64	4.2312e-2		9.7261e-3		1.0042e-2	
1/128	2.1379e-2	0.9849	4.7447e-3	1.0355	4.9610e-3	1.0174
1/256	1.0806e-2	0.9844	2.3420e-3	1.0186	2.4671e-3	1.0078
1/512	5.4513e-3	0.9871	1.1675e-3	1.0043	1.2358e-3	0.9974
1/1024	2.7434e-3	0.9906	5.8559e-4	0.9955	6.2164e-4	0.9913

For the discretization of boundary conditions, the homogeneous Neumann boundary conditions for ψ^n , μ_c^n and T^n are discretized as

$$\mathbf{n} \cdot \nabla_D \psi^{n+1} \Big|_{\partial\Omega} = \mathbf{n} \cdot \nabla_D \mu_c^{n+1} \Big|_{\partial\Omega} = \mathbf{n} \cdot \nabla_D T^{n+1} \Big|_{\partial\Omega} = 0,$$

and the no-slip boundary condition for velocity \mathbf{v}^{n+1} are discretized as

$$\mathbf{v}^{n+1} \Big|_{\partial\Omega} = 0.$$

After obtaining $(\mathbf{v}^n, p^n, \psi^n, \mu_0^n, T^n)$, we can use the fully discrete numerical scheme (166)–(169) to find $(\mathbf{v}^{n+1}, p^{n+1}, \psi^{n+1}, \mu_0^{n+1}, T^{n+1})$ by the following steps:

Step 1. solve Eqs. (167) and (168) to obtain $\psi^{n+1}, \mu_0^{n+1}, p^{n+1}$;

Step 2. solve Eq. (166) to obtain \mathbf{v}^{n+1} ;

Step 3. solve Eq. (169) to obtain T^{n+1} .

Note that the conservation properties at the fully discrete level are not within our scope of consideration.

6. Numerical results

6.1. Time accuracy test

We first conduct a time accuracy test for our numerical method (166)–(169) in a 2D domain $[0, 2] \times [0, 2]$, while also demonstrating that the entropy remains increasing. Here, we fix the grid size as 1024×1024 , ensuring that errors from spatial discretization are negligible compared to time discretization errors. Without considering gravity, we set the non-dimensional parameters as follows

$$\begin{aligned} \text{Pe}_\psi &= 100, \text{Re} = 1, \text{We} = 10, \text{Ca} = 10, \text{Ma} = 0.01, \text{Pe}_T = 1, \text{Ec} = 1, \\ \zeta_\rho &= 1, \zeta_\mu = 0.1, \zeta_{C_h} = 0.1, \zeta_k = 0.1, \epsilon = 0.05, \eta = 6\sqrt{2}. \end{aligned} \quad (170)$$

The initial conditions are given as

$$\psi(x, y, 0) = 0.5 (\sin(\pi x) \cos(\pi y) + 1), \quad (171)$$

$$\mathbf{v}(x, y, 0) = (u_0, v_0) = (\sin(\pi x) \sin(\pi y), \sin(\pi x) \sin(\pi y)), \quad (172)$$

$$T(x, y, 0) = 0.5 (\cos(\pi x) \cos(\pi y) + 1), \quad (173)$$

$$p(x, y, 0) = \sin(\pi x) \sin(\pi y). \quad (174)$$

On the left and right boundaries of the domain, we apply periodic boundary conditions. On the top and bottom walls, we apply no-slip boundary condition for \mathbf{v} and no-flux boundary conditions for ψ , μ_c and T . As exact solutions are not available, errors in L^2 norms are calculated as the difference between the solution of the coarse time step and that of the adjacent finer time step. The errors of the phase variable ψ and velocity components u and v at $t = 0.25$ with various time step sizes are presented in Table 1. We observe that our numerical method (166)–(169) almost perfectly matches the first-order accuracy in time. Additionally, the numerical results of the entropy and volume of the two-phase fluid system with various time steps are shown in Figs. 1 and 2, where we observe that the entropy remains increasing, and the volume is preserved up to 10^{-12} (all the lines in Fig. 2 are coincident).

6.2. Thermocapillary migration of a droplet with infinitely small Pe_T

In this subsection, we explore the thermocapillary migration of a droplet in a square microchannel with a fixed linearly increasing temperature field imposed along the channel. The temperature gradient is $\partial T / \partial z = \nabla T_\infty > 0$, and the effect of gravity is assumed to be negligible.

The droplet (fluid 2) of radius R is surrounded by another immiscible fluid (fluid 1) in the microchannel. The thermocapillary migration of a droplet was first investigated analytically by Young et al. [26], where both the heat Peclet and Reynolds numbers are assumed to be infinitely small, and the convective transport of momentum and energy is neglected. The terminal velocity (also known as YGB velocity) of the droplet under constant temperature gradient ∇T_∞ is given as

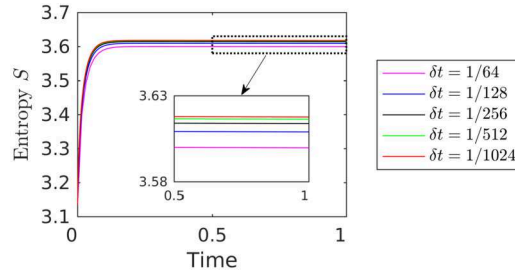


Fig. 1. Entropy (S) computed using Eq. (108) with different time steps on a fixed grid size of 1024×1024 . Refer to §6.1 for details.

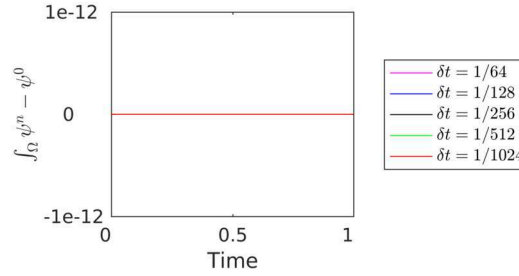


Fig. 2. Discrete volume conservation $\int_{\Omega} \psi^n - \psi^0$ with different time steps on a fixed grid size of 1024×1024 . Refer to §6.1 for details.

$$V_{YGB} = \frac{2\sigma_T \nabla T_{\infty} R}{(2 + k_1/k_2)(2\mu_1 + 3\mu_2)}. \quad (175)$$

To validate our phase-field model, we compare the numerical results to the analytical solution V_{YGB} obtained from the sharp-interface model. The characteristic length, velocity and temperature for this test are $R^* = 10R$, $V^* = V_{YGB}$ and $T^* = \nabla T_{\infty} R$, respectively. Numerical simulations are carried out in a 3D dimensionless domain $[0, 0.75] \times [0, 0.75] \times [0, 1.5]$. We impose periodic boundary conditions on all the side boundaries ($x = 0, 0.75$, $y = 0, 0.75$), and apply no-slip boundary condition for \mathbf{v} and no-flux boundary conditions for ψ and μ_c on the top and bottom boundaries ($z = 0, 1.5$).

The droplet of dimensionless radius 0.1 is initially stationary and centered at $(0.375, 0.375, 0.75)$. Therefore, the initial conditions for velocity and phase variable are given as

$$\mathbf{v}(x, y, z, 0) = 0, \quad (176)$$

$$\psi(x, y, z, 0) = 0.5 + 0.5 \tanh\left((0.1 - r)/2\sqrt{2}\epsilon\right), \quad (177)$$

where $r = \sqrt{(x - 0.375)^2 + (y - 0.375)^2 + (z - 0.75)^2}$. In addition, the dimensionless temperature field is fixed as

$$T(z) = 10z + 1, \quad (178)$$

and thus, the heat Eq. (74) is not considered. The model parameters and ratios of physical properties are set as follows

$$\begin{aligned} \text{Pe}_{\psi} &= 1.5 \times 10^4 / \epsilon, \text{Re} = 1.3 \times 10^{-3}, \text{We} = 8.8 \times 10^{-6}, \text{Ca} = 6.6 \times 10^{-3}, \\ \text{Ma} &= 7.5, \text{Ec} = 1.7 \times 10^{-6}, \zeta_{\rho} = 1, \zeta_{\mu} = 1, \zeta_{C_h} = 1, \eta = 6\sqrt{2}. \end{aligned} \quad (179)$$

In the simulations, the droplet migration velocity, v_d , is calculated numerically by

$$v_d = \frac{\int_{\Omega} \psi \mathbf{v} \cdot \mathbf{k} d\mathbf{x}}{\int_{\Omega} \psi d\mathbf{x}}, \quad (180)$$

where \mathbf{k} is the unit vector in z direction. We first demonstrate the convergence of the model by testing various values of ϵ ($= 0.0025, 0.005, 0.01, 0.02$) with a fixed grid size $128 \times 128 \times 256$ and a time step of 10^{-5} . As shown in Fig. 3(a), the terminal velocity converges to V_{YGB} asymptotically as the value of ϵ decreases. Next, we show the convergence of the results by refining the grid with a fixed $\epsilon = 0.0025$ and a time step of 10^{-5} . Specially, we use four grid sizes ($32 \times 32 \times 64, 64 \times 64 \times 128, 128 \times 128 \times 256, 256 \times 256 \times 512$) for the computations. As shown in Fig. 3(b), the migration velocity converges as the grid size increases, and the results for the grid sizes $128 \times 128 \times 256$ and $256 \times 256 \times 512$ are very close. Therefore, we set the grid size $128 \times 128 \times 256$ and a time step of 10^{-5} for the 3D computations in the subsequent section.

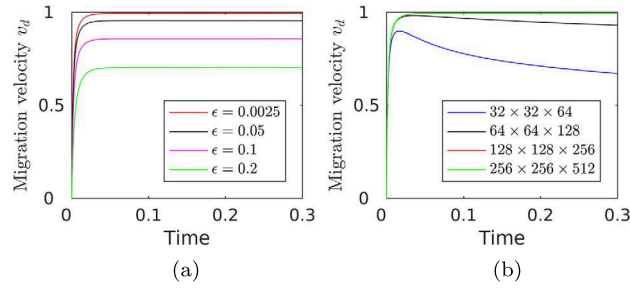


Fig. 3. Time evolution of the thermocapillary migration velocity of a droplet with (a) various ϵ and a fixed grid size $128 \times 128 \times 256$, and (b) various grid sizes and a fixed $\epsilon = 0.0025$. See §6.2 for details.

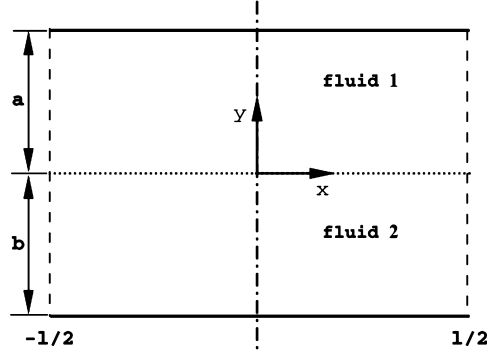


Fig. 4. The diagram depicting two immiscible fluids in a microchannel. The temperatures of the lower and upper walls are given by $T(x, -b) = T_h + T_\theta \cos(\omega x)$ and $T(x, a) = T_c$, respectively, where $T_h > T_c > T_\theta$ and $\omega = \frac{2\pi}{l}$ is the wave number. Refer to §6.3 for further details.

6.3. Thermocapillary-driven convection

We now investigate the thermocapillary-driven convection in a heated microchannel with two superimposed planar fluids [27]. The setup of the problem is illustrated in Fig. 4. The heights of the fluid 1 (upper) and fluid 2 (lower) are a and b , respectively, and the fluids extend infinitely in the horizontal direction. The temperatures of the upper and lower walls are imposed as follows:

$$T(x, a) = T_c, \quad (181)$$

and

$$T(x, -b) = T_h + T_\theta \cos(\omega x), \quad (182)$$

respectively, where $T_h > T_c > T_\theta > 0$, and $\omega = 2\pi/l$ is a wave number with l being the channel length. The given thermal boundary conditions establish a temperature field that is periodic in the horizontal direction with a period length of l . Therefore, it is sufficient to only concentrate on the solution within one period domain $-1/2 < x < 1/2$.

When the heat Peclet number and Reynolds number are negligibly small, it is possible to ignore the convective transport of momentum and energy. In addition, it is assumed that the interface remains flat, and the effect of gravity is assumed to be negligible. By solving the simplified linear governing equations, Pendse and Esmaeeli [27] obtained the analytical solutions for the temperature field $\tilde{T}(x, y)$ and stream-function $\tilde{\Phi}(x, y)$. Specifically, for the upper fluid, the solutions are obtained as follows:

$$\tilde{T}(x, y) = \frac{(T_c - T_h)y + \tilde{k}T_c b + T_h a}{a + \tilde{k}b} + T_\theta f(\alpha, \beta, \tilde{k}) \sinh(\alpha - \omega y) \cos(\omega x), \quad (183)$$

$$\begin{aligned} \tilde{\Phi}(x, y) = & \frac{U_{\max}}{\omega} \frac{1}{\sinh^2(\alpha) - \alpha^2} \{ \omega y \sinh^2(\alpha) \cosh(\omega y) \\ & - \frac{1}{2} [2\alpha^2 + \omega y (\sinh(2\alpha) - 2\alpha)] \sinh(\omega y) \} \sin(\omega x), \end{aligned} \quad (184)$$

and for the lower fluid

$$\begin{aligned} \tilde{T}(x, y) = & \frac{\tilde{k}(T_c - T_h)y + \tilde{k}T_c b + T_h a}{a + \tilde{k}b} + T_\theta f(\alpha, \beta, \tilde{k}) [\sinh(\alpha) \cosh(\omega y) \\ & - \tilde{k} \sinh(\omega y) \cosh(\alpha)] \cos(\omega x), \end{aligned} \quad (185)$$

$$\begin{aligned}\Phi(x, y) = & \frac{U_{\max}}{\omega} \frac{1}{\sinh^2(\beta) - \beta^2} \{ \omega y \sinh^2(\beta) \cosh(\omega y) \\ & - \frac{1}{2} [2\beta^2 - \omega y (\sinh(2\beta) - 2\beta)] \sinh(\omega y) \} \sin(\omega x).\end{aligned}\quad (186)$$

The unknowns in the above equations are defined by

$$\tilde{k} = \frac{k_1}{k_2}, \quad \alpha = a\omega, \quad \beta = b\omega, \quad f(\alpha, \beta, \tilde{k}) = \frac{1}{\tilde{k} \sinh(\beta) \cosh(\alpha) + \sinh(\alpha) \cosh(\beta)}, \quad (187)$$

and

$$U_{\max} = \left(\frac{T_\theta \sigma_T}{\mu_2} \right) g(\alpha, \beta, \tilde{k}) h(\alpha, \beta, \tilde{\mu}), \quad (188)$$

where the subscripts 1 and 2 stand for the fluid 1 and 2, respectively,

$$g(\alpha, \beta, \tilde{k}) = \sinh(\alpha) f(\alpha, \beta, \tilde{k}), \quad (189)$$

$$h(\alpha, \beta, \tilde{\mu}) = \frac{(\sinh^2(\alpha) - \alpha^2)(\sinh^2(\beta) - \beta^2)}{\tilde{\mu} (\sinh^2(\beta) - \beta^2)(\sinh(2\alpha) - 2\alpha) + (\sinh^2(\alpha) - \alpha^2)(\sinh(2\beta) - 2\beta)}, \quad (190)$$

$\tilde{k} = k_1/k_2$ and $\tilde{\mu} = \mu_1/\mu_2$ are the thermal conductivity ratio and viscosity ratio between the two fluids, respectively.

Here, we use a , $T_\theta \sigma_T/\mu_2$, T_c and $T_\theta \sigma_T a/\mu_2$ as the characteristic length, velocity, temperature and stream-function for the present test, respectively. The numerical simulations are carried out in a 2D domain $[-l/2, l/2] \times [-b, a]$, where

$$l = 2, \quad a = b = 1, \quad (191)$$

resulting in a dimensionless domain $[-1, 1] \times [-1, 1]$. To ensure a flat and rigid interface between the two fluids, we specify the phase variable as

$$\psi(y) = \frac{1}{2} + \frac{1}{2} \tanh\left(\frac{y}{2\sqrt{2}\epsilon}\right), \quad \text{for } y \in (-1, 1), \quad (192)$$

where ϵ represents the thickness of the diffuse interface. Periodic boundary conditions are enforced on the left and right boundaries of the domain. On the upper and lower walls, no-slip boundary conditions are imposed. The wall temperatures are prescribed through Eqs. (181) and (182), where dimensional temperatures are $T_h = 20$, $T_c = 10$, and $T_\theta = 4$, yielding dimensionless temperatures $T_h = 2$, $T_c = 1$, and $T_\theta = 0.4$. The ratios of fluid properties and model parameters are specified as:

$$\begin{aligned}Re = 0.05, \quad We = 0.004, \quad Ca = 0.08, \quad Ma = 2.5, \quad Pe_T = 0.01, \\ \zeta_\rho = 1, \quad \zeta_\mu = 1, \quad \zeta_{C_h} = 1, \quad \zeta_k = 1/\tilde{k}, \quad \eta = 6\sqrt{2}.\end{aligned}\quad (193)$$

To show the effect of the thermal conductivity ratio on the stream-function and the temperature field, we examine two cases with different values of \tilde{k} , i.e., $\tilde{k} = 1$ for case 1, and $\tilde{k} = 0.2$ for case 2. According to the definition of the variable thermal conductivity $k(\psi)$, we have a constant k for case 1,

$$k(\psi) = \psi + \frac{k_2}{k_1}(1 - \psi) = 1,$$

and a variable $k(\psi)$ for case 2,

$$k(\psi) = \psi + \frac{k_2}{k_1}(1 - \psi) = 5 - 4\psi.$$

Figs. 5 and 6 depict the temperature field and stream-functions contours for the two cases, respectively. The numerical simulation is conducted on a grid size 1024×1024 with a time step of 10^{-4} and $\epsilon = 0.0025$. It's apparent that the numerical results agree well with the analytical solutions. Moreover, as the thermal conductivity ratio \tilde{k} decreases, the temperature distribution at the interface becomes more nonuniform (See Fig. 5). This results in an enhanced shear force along the interface, and thus strengthens the thermocapillary-driven convection, as reflected in Fig. 6, where the gradient of the stream-function increases as \tilde{k} decreases. Additionally, to demonstrate the convergence of our phase-field model towards the sharp-interface model as the diffuse interface thickness tends to zero, we compute the L^2 norms of the relative differences between the numerical results with five different ϵ values (0.0025, 0.005, 0.01, 0.02, 0.04) and the analytical solutions. The L^2 norms of the relative differences are defined as:

$$E_T = \frac{\|T - \tilde{T}\|_{L^2}}{\|\tilde{T}\|_{L^2}} \quad \text{and} \quad E_\Phi = \frac{\|\Phi - \tilde{\Phi}\|_{L^2}}{\|\tilde{\Phi}\|_{L^2}} \quad (194)$$

for the temperature and stream-function, respectively, where Φ represents the numerical result of the stream-function. The numerical results are shown in Table 2, indicating a decrease in the L^2 norm of the relative differences as the value of ϵ decreases for both the temperature field and the stream-function.

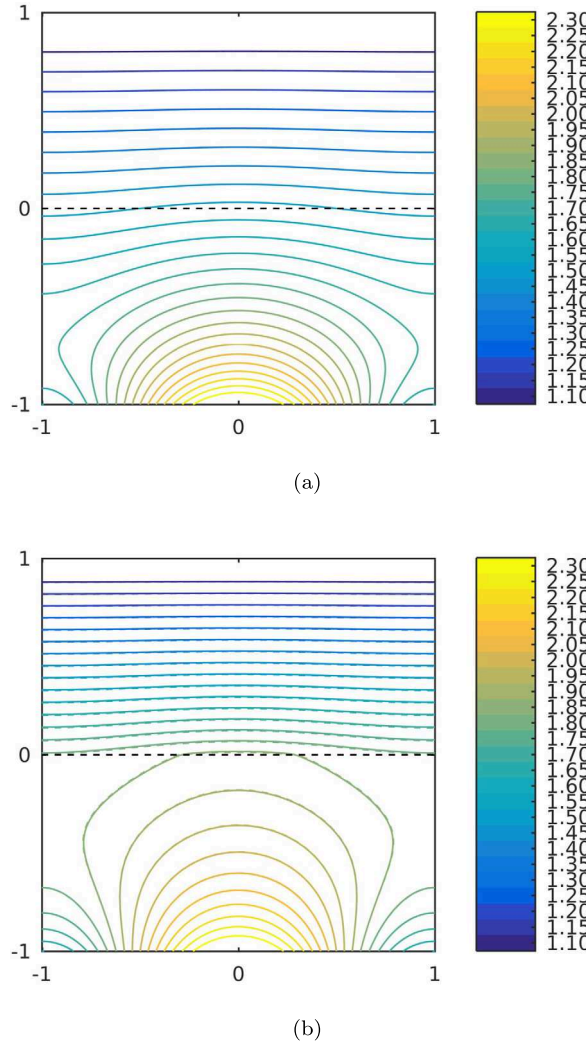


Fig. 5. Isotherms for fluid systems with thermal conductivity ratios of (a) $\tilde{k} = 1$ and (b) $\tilde{k} = 0.2$. Solid lines represent numerical results T , while dashed lines depict analytical solutions \bar{T} . For further details, refer to §6.3.

Table 2

The L^2 norms of the relative differences between the numerical results obtained at the steady state and analytical solutions with various ϵ and a fixed grid size 1024×1024 . For more details, refer to §6.3.

ϵ	$\tilde{k} = 1$		$\tilde{k} = 0.2$	
	E_T	E_Φ	E_T	E_Φ
0.04	1.8290e-07	1.5493e-01	1.0591e-02	1.6071e-01
0.02	1.8290e-07	4.4292e-02	5.7621e-03	6.0471e-02
0.01	1.8290e-07	1.6597e-02	2.9972e-03	2.3082e-02
0.005	1.8290e-07	1.2590e-02	1.5303e-03	1.0508e-02
0.0025	1.8290e-07	1.2233e-02	7.7892e-04	9.1579e-03

6.4. The merging process of two bubbles with thermocapillary effects

We now investigate the merging process of two spherical gas bubbles in a squared channel with an initially linear temperature field imposed along the channel ($\partial T / \partial z = \nabla T_\infty$). The two bubbles, surrounded by a viscous liquid, are initially stationary with the same radius R_0 . We adopt $R^* = R_0$, $V^* = \sqrt{g R_0}$, and $T^* = |\nabla T_\infty| R_0$ as the characteristic length, velocity, and temperature, respectively. The dimensionless computational domain is $[0, 8] \times [0, 8] \times [0, 16]$, and the initial bubbles, each with a radius of 1, are centered at $(4, 4, 5)$ and $(5.6, 4, 2)$, respectively. The following initial conditions are imposed for the numerical simulations:

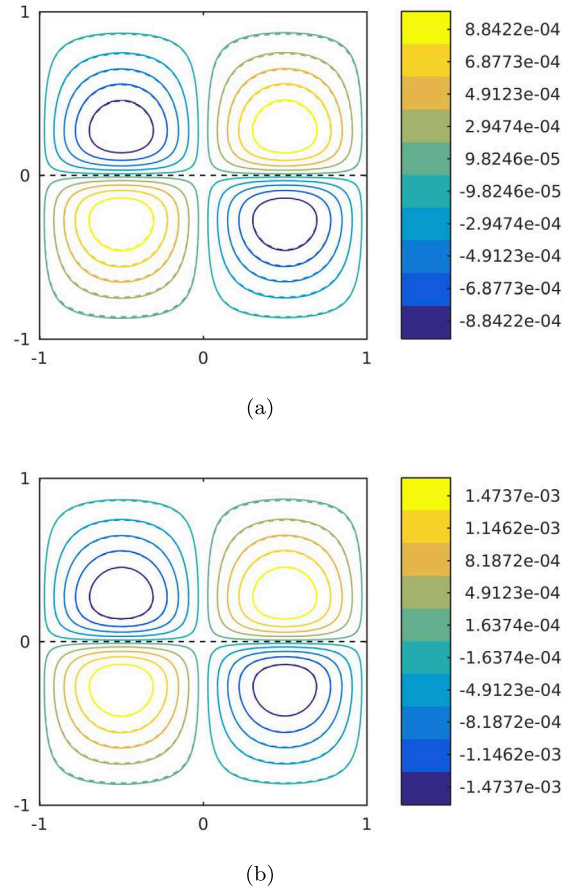


Fig. 6. Streamlines for fluid systems with different thermal conductivity ratios: (a) $\tilde{k} = 1$ and (b) $\tilde{k} = 0.2$. Solid lines represent numerical results Φ , while dashed lines depict analytical solutions Φ . For further details, refer to §6.3.

$$\mathbf{v}(x, y, z, 0) = 0, \quad (195)$$

$$\psi(x, y, z, 0) = 1 + \frac{1}{2} \tanh\left(\frac{1 - \sqrt{r_1}}{2\sqrt{2}\epsilon}\right) + \frac{1}{2} \tanh\left(\frac{1 - \sqrt{r_2}}{2\sqrt{2}\epsilon}\right), \quad (196)$$

$$T(x, y, z, 0) = z + 20, \quad (\text{case 1}) \quad (197)$$

or

$$T(x, y, z, 0) = -z + 36, \quad (\text{case 2}) \quad (198)$$

where $r_1 = (x - 4)^2 + (y - 4)^2 + (z - 5)^2$ and $r_2 = (x - 5.6)^2 + (y - 4)^2 + (z - 2)^2$. No-slip boundary conditions are imposed for \mathbf{v} on all domain boundaries, while no-flux boundary conditions are applied for ψ and μ_c . Additionally, no-flux boundary conditions are set for T on all side boundaries ($x = 0, 8$, $y = 0, 8$), and T is specified on the top and bottom boundaries ($z = 0, 16$) through (197) or (198). The model parameters and ratios of physical properties are given as follows

$$\text{Pe}_\psi = 40, \text{Re} = 0.34, \text{We} = 0.05, \text{Ca} = 0.14, \text{Ma} = 0.2, \text{Ec} = 0.001, \text{Fr} = 1,$$

$$\zeta_\rho = 1000, \zeta_\mu = 100, \zeta_{C_h} = 4, \zeta_k = 23, \epsilon = 0.03, \eta = 6\sqrt{2}. \quad (199)$$

6.4.1. The merging process of two bubbles under isothermal conditions

We first investigate the merging behavior of two bubbles under isothermal conditions. Here, surface tension is assumed to be constant ($\sigma = 1$) over the bubble interfaces, and the heat equation (74) is dropped. The numerical results, as shown in Fig. 7, are found to align well with experimental results [28]. In addition, it is found that the bubbles gradually rise and deform due to the buoyancy force. As two bubbles approach, the lower bubble accelerates because the drag force on lower bubble becomes smaller than the upper bubble.

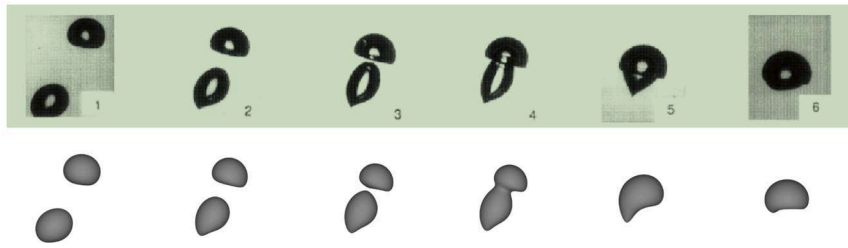


Fig. 7. Comparison of numerical results and experimental results for merging process of two bubbles, adapted from [28]. Refer to §6.4.1 for further details.

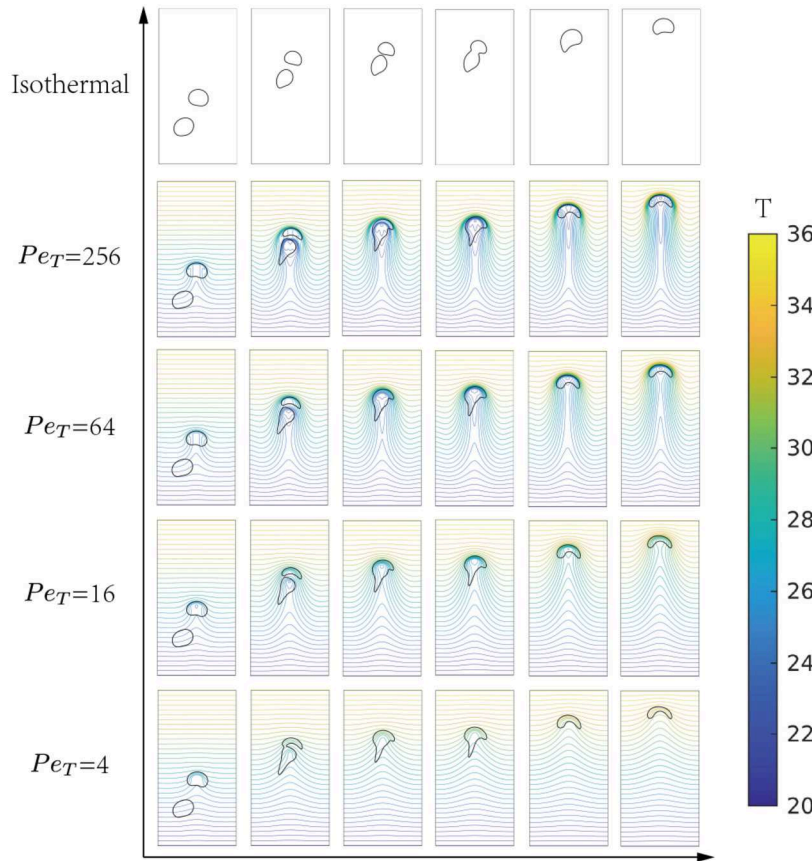


Fig. 8. Time evolution of bubbles interfaces (contour $\psi = 0.5$) on the slice $y = 4$ under isothermal conditions, along with the time evolution of isotherms and bubbles interface on the same slice at different Pe_T numbers when the initial temperature field increases linearly along the channel. See §6.4.2 for details.

6.4.2. Effect of thermocapillarity on the merging of two bubbles

We further investigate the merging behavior of two bubbles under non-isothermal conditions by considering the full model Eqs. (71)–(74). Two cases of initial temperature, given by Eqs. (197) and (198), are examined to analyze the effect of the heat Peclet number Pe_T on the merging process of bubbles. Various Pe_T , specially $Pe_T = 4, 16, 64, 256$, are selected for this examination, with other settings described in §6.4. The numerical results are illustrated in Figs. 8 and 9.

In case 1, where the initial temperature field increases linearly along the channel, the numerical results are presented in Fig. 8. Comparing with the results under isothermal conditions, several observations are made. Firstly, prior to bubble merging, the upper bubble becomes flatter and the lower bubble elongates. Following the merging, the resulting bubble also flattens further. Secondly, the presence of a positive temperature gradient causes bubbles to merge earlier, evident from the second column of Fig. 8. Lastly, as Pe_T increases, the merging process slows down and the isotherms surrounding the bubbles become more distorted.

In case 2, where the initial temperature field decreases linearly long the channel, the numerical results are displayed in Fig. 9. Similar to case 1, prior to merging, the upper bubble flattens while the lower bubble elongates, followed by further flattening of the resulting bubble post-merging. Moreover, the negative temperature gradient accelerates bubble merging, noticeable from the second column of Fig. 9. Furthermore, as Pe_T increases, bubble merging occurs more rapidly, accompanied by greater distortion of the surrounding isotherms.

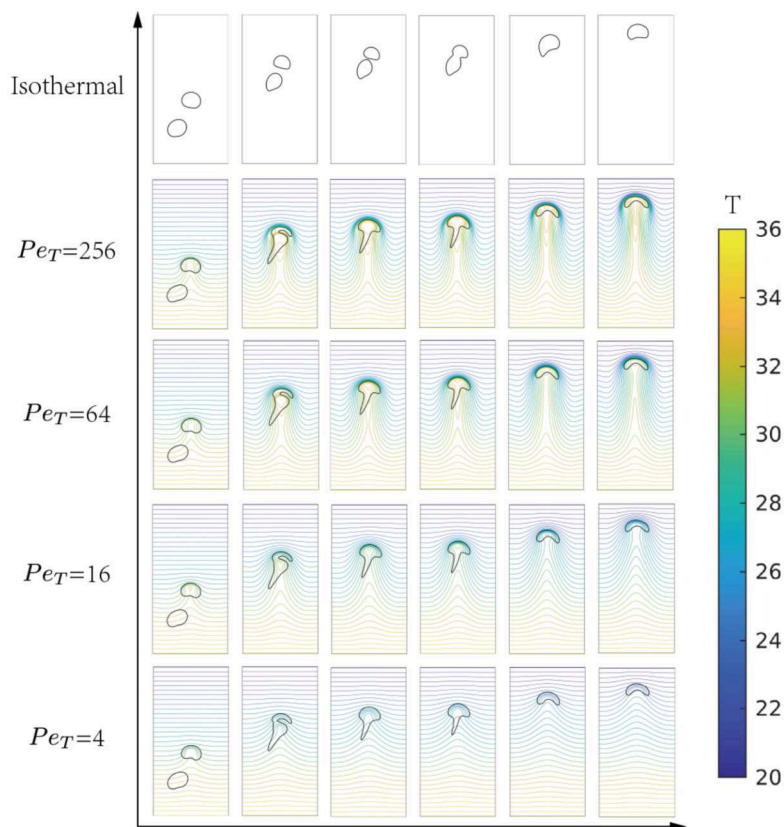


Fig. 9. Time evolution of bubbles interfaces (contour $\psi = 0.5$) on the slice $y = 4$ under isothermal conditions, along with the time evolution of isotherms and bubble interfaces on the same slice at different Pe_T numbers when the initial temperature field decreases linearly along the channel. See §6.4.2 for details.

7. Conclusion

In this study, we present a thermodynamically consistent phase-field model for two-phase flows with thermocapillary effects, which allows the two fluid components to have different physical properties, including density, viscosity, heat capacity, and thermal conductivity, and meanwhile maintains the balance laws of mass, momentum, and energy and entropy increase simultaneously.

Given the highly coupled and nonlinear nature of the model equations, we develop a first order accurate numerical method that satisfies the discrete laws of mass conservation and entropy increasing. We validate both our model and numerical method through a series of numerical tests. These include the thermocapillary migration of a droplet, thermocapillary convection within a heated microchannel featuring two superimposed planar fluids, and the merging dynamics of two bubbles under isothermal conditions. Remarkably, our results align closely with existing analytical solutions or experimental findings. Furthermore, we delve into the merging process of bubbles under non-isothermal conditions. In comparing these scenarios with those under isothermal conditions, we observe significant differences: temperature gradients prompt earlier bubble merging and substantial alterations in bubble morphology. Moreover, as the initial temperature field increases linearly along the channel, the merging rate of bubbles decelerates with rising heat Peclet number (Pe_T). Conversely, for scenarios with a linear decrease in the initial temperature field along the channel, bubbles coalesce at a faster rate as Pe_T increases.

CRediT authorship contribution statement

Yanxiao Sun: Investigation, Validation, Visualization, Writing – original draft. **Jiang Wu:** Investigation, Methodology, Supervision. **Maosheng Jiang:** Writing – review & editing, Supervision. **Steven M. Wise:** Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Zhenlin Guo:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Acknowledgement

This work is partially supported by National Natural Science Foundation of China (Grant No. 12371387 and No. 12071046), U2230402, Natural Science Foundation of Shandong Province (Grant No. ZR2021QA018), China Postdoctoral Science Foundation Funded Projection (Grant No. 2022M721757), and NSF-DMS 2309547.

Appendix A. Derivation of the conservation equations

A.1. Mass and volume conservation equations

Substituting Eq. (19) into Eq. (23), and substituting Eq. (20) into Eq. (24), we obtain the following mass conservation equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (\text{A.1})$$

and volume conservation equation

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \mathbf{v}) = -\frac{\nabla \cdot \mathbf{J}}{\rho_1}. \quad (\text{A.2})$$

Similarly, we assume the volume conservation equation for fluid 2 is

$$\frac{\partial \Phi_2}{\partial t} + \nabla \cdot (\Phi_2 \mathbf{v}) = -\frac{\nabla \cdot \tilde{\mathbf{J}}}{\rho_2}, \quad (\text{A.3})$$

where Φ_2 is the volume fraction of fluid 2, and $\tilde{\mathbf{J}}$ is the volume flux of fluid 2. Multiplying Eq. (A.2) by ρ_1 and Eq. (A.3) by ρ_2 , adding them together, and using Eq. (A.1), we obtain

$$-\nabla \cdot \mathbf{J} - \nabla \cdot \tilde{\mathbf{J}} = 0 \quad (\text{A.4})$$

or

$$\nabla \cdot (\mathbf{J} + \tilde{\mathbf{J}}) = 0.$$

Furthermore, adding Eqs. (A.2) and (A.3) together, we obtain

$$\nabla \cdot \mathbf{v} = -\frac{\nabla \cdot \mathbf{J}}{\rho_1} - \frac{\nabla \cdot \tilde{\mathbf{J}}}{\rho_2} = \frac{\rho_1 - \rho_2}{\rho_1 \rho_2} \nabla \cdot \mathbf{J}. \quad (\text{A.5})$$

Let $\alpha = (\rho_2 - \rho_1)/\rho_2$, thus Eq. (A.5) can be rewritten as

$$\nabla \cdot \mathbf{v} = -\alpha \frac{\nabla \cdot \mathbf{J}}{\rho_1}. \quad (\text{A.6})$$

Recall the definition of the total time derivative:

$$\frac{D\psi}{Dt} = \frac{\partial \psi}{\partial t} + \mathbf{v} \cdot \nabla \psi, \quad (\text{A.7})$$

then (A.2) can be rewritten as

$$\frac{D\psi}{Dt} + \psi(\nabla \cdot \mathbf{v}) = \frac{-\nabla \cdot \mathbf{J}}{\rho_1}. \quad (\text{A.8})$$

A.2. Momentum and energy conservation equations

Substituting Eq. (21) into Eq. (25), and using Eq. (A.1), we obtain the momentum conservation equation

$$\rho \frac{D\mathbf{v}}{Dt} = \nabla \cdot \mathbf{T} - \rho g \hat{\mathbf{z}}. \quad (\text{A.9})$$

In addition, substituting Eq. (22) into Eq. (26), we obtain

$$\frac{\partial \hat{u}}{\partial t} + \nabla \cdot (\hat{u} \mathbf{v}) = -\nabla \cdot \mathbf{q}_E + \nabla \mathbf{v} : \mathbf{T}. \quad (\text{A.10})$$

Using the definition of \hat{u} (in (7)), we obtain

$$\frac{\partial \hat{u}}{\partial t} = \frac{\partial u}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial u}{\partial \psi} \frac{\partial \psi}{\partial t} + \lambda_u \frac{\partial \delta}{\partial t}. \quad (\text{A.11})$$

Substituting the definition of δ (14) into (A.11), we obtain

$$\begin{aligned} \frac{\partial \hat{u}}{\partial t} &= \frac{\partial u}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial u}{\partial \psi} \frac{\partial \psi}{\partial t} + \lambda_u \frac{W'(\psi)}{\epsilon} \frac{\partial \psi}{\partial t} \\ &\quad + \lambda_u \epsilon \nabla \psi \cdot \nabla \left(\frac{\partial \psi}{\partial t} \right) \\ &= \frac{\partial u}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial u}{\partial \psi} \frac{\partial \psi}{\partial t} + \lambda_u \frac{W'(\psi)}{\epsilon} \frac{\partial \psi}{\partial t} \\ &\quad + \lambda_u \epsilon \nabla \cdot \left(\nabla \psi \frac{\partial \psi}{\partial t} \right) - \lambda_u \epsilon \Delta \psi \frac{\partial \psi}{\partial t} \end{aligned}$$

$$= \frac{\partial u}{\partial T} \frac{\partial T}{\partial t} + \left(\frac{\partial u}{\partial \psi} + \lambda_u w \right) \frac{\partial \psi}{\partial t} + \lambda_u \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}), \quad (\text{A.12})$$

where

$$w = \frac{W'(\psi)}{\epsilon} - \epsilon \Delta \psi. \quad (\text{A.13})$$

In addition, we have the following identity:

$$\mathbf{v} \cdot \nabla \hat{u} = \mathbf{v} \cdot \left(\frac{\partial u}{\partial T} \nabla T + \left(\frac{\partial u}{\partial \psi} + \lambda_u w \right) \nabla \psi + \lambda_u \epsilon \nabla \cdot (\nabla \psi \otimes \nabla \psi) \right). \quad (\text{A.14})$$

Substituting (A.12) and (A.14) into (A.10), we obtain the energy conservation equation

$$\begin{aligned} \frac{\partial u}{\partial T} \frac{DT}{Dt} = & - \left(\frac{\partial u}{\partial \psi} + \lambda_u w \right) \frac{D\psi}{Dt} - \lambda_u \epsilon \nabla \cdot (\nabla \psi \frac{\partial \psi}{\partial t}) - \hat{u}(\nabla \cdot \mathbf{v}) \\ & - \lambda_u \epsilon \nabla \cdot (\nabla \psi \otimes \nabla \psi) \cdot \mathbf{v} - \nabla \cdot \mathbf{q}_E + \nabla \mathbf{v} : \mathbf{T}. \end{aligned} \quad (\text{A.15})$$

Appendix B. Specification for temporal discretization

The detailed definitions in Eqs. (123) – (126) are as follows:

$$\Lambda^{n+1} = \psi^{n+1} + \zeta_\Lambda (1 - \psi^{n+1}), \quad \zeta_\Lambda = \Lambda_2 / \Lambda_1 \quad \text{for } \Lambda = \rho, \mu, C_h, k, \quad (\text{B.1})$$

$$\mathbf{T}^{n+1} = \mathbf{m}^{n+1} + \frac{1}{\text{Re}} \tau^{n+1} + \hat{f}^{n+1} \mathbf{I}, \quad (\text{B.2})$$

$$\mathbf{m}^{n+1} = -\rho^{n+1} \mathbf{I} - \frac{1}{\text{We}} \lambda_f(T^n) \epsilon (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) - \mu_0^{n+1} \psi^{n+1} \mathbf{I}, \quad (\text{B.3})$$

$$\mu_0^{n+1} = \frac{\partial f}{\partial \psi} + \frac{1}{\text{We}} \lambda_f(T^n) w^{n+1}, \quad (\text{B.4})$$

$$\frac{\partial f}{\partial \psi} = \frac{1}{\text{Ec}} \left(\frac{\rho_1 - \rho_2}{\rho_1} C_h^{n+1} T^n + \rho^n \frac{C_{h,1} - C_{h,2}}{C_{h,1}} T^n \right) \left(1 - \ln \left(\frac{T^n}{T_0} \right) \right), \quad (\text{B.5})$$

$$\tau^{n+1} = \mu^n (\nabla \mathbf{v}^{n+1} + (\nabla \mathbf{v}^{n+1})^\top) - \frac{2}{3} \mu^n (\nabla \cdot \mathbf{v}^{n+1}) \mathbf{I}, \quad (\text{B.6})$$

$$\hat{f}^{n+1} = \frac{1}{\text{Ec}} \rho^{n+1} C_h^{n+1} T^n \left(1 - \ln \left(\frac{T^n}{T_0} \right) \right) + \frac{1}{\text{We}} \lambda_f(T^n) \delta^{n+1}, \quad (\text{B.7})$$

$$\begin{aligned} \mathbf{q}_E^{n+1} = & -\frac{1}{\text{Pe}_T} k \frac{\nabla T^{n+1} + \nabla T^n}{2} - \frac{\text{Ec}}{\text{Pe}_\psi} m_\psi^n \mu_c^{n+1} \nabla \mu_c^{n+1} \\ & - \frac{\text{Ec}}{\text{We}} \lambda_u \epsilon (\nabla \psi^{n+1} \psi_{\bar{t}} + (\nabla \psi^{n+1} \otimes \nabla \psi^{n+1}) \cdot \mathbf{v}^n), \end{aligned} \quad (\text{B.8})$$

$$\begin{aligned} h_s = & -\text{Ec} \frac{\partial u}{\partial \psi} \psi_{\bar{t}} - \text{Ec} \frac{\partial \tilde{u}}{\partial \psi} (\mathbf{v}^n \cdot \nabla \psi^{n+1}) + \text{Ec} \mathbf{m}^{n+1} : \nabla \mathbf{v}^n \\ & + \frac{\text{Ec}}{\text{Re}} \tau^{n+1} : \nabla \mathbf{v}^{n+1} - \text{Ec} T^n \tilde{s}^{n+1} (\nabla \cdot \mathbf{v}^n) - \frac{\text{Ec}}{\text{We}} \lambda_u \delta_{\bar{t}} \\ & - \frac{\text{Ec}}{\text{We}} \lambda_u (\mathbf{v}^n \cdot \nabla \delta^{n+1}) + \text{corr}^n, \end{aligned} \quad (\text{B.9})$$

$$\frac{\partial u}{\partial \psi} = \frac{1}{\text{Ec}} \left(\frac{\rho_1 - \rho_2}{\rho_1} C_h^{n+1} + \rho^n \frac{C_{h,1} - C_{h,2}}{C_{h,1}} \right) T^n, \quad (\text{B.10})$$

$$\frac{\partial \tilde{u}}{\partial \psi} = \frac{\partial f}{\partial \psi} + T^n \frac{\partial \tilde{s}^{n+1}}{\partial \psi^{n+1}}, \quad (\text{B.11})$$

$$\tilde{s}^{n+1} = \tilde{s}^{n+1} + \frac{1}{\text{We}} \lambda_3 \delta^{n+1}, \quad (\text{B.12})$$

$$\tilde{s}^{n+1} = \frac{1}{\text{Ec}} \rho^{n+1} C_h^{n+1} \ln \left(\frac{T^n}{T_0} \right), \quad (\text{B.13})$$

$$\text{corr}^n = \text{corr}_1 + \text{corr}_2 + \text{corr}_3 + \text{corr}_4, \quad (\text{B.14})$$

$$\text{corr}_1 = \frac{\text{Ec}}{\text{We}} \lambda_f(T^n) \frac{(\psi^{n+1} - \psi^n)^2}{8\delta t \epsilon}, \quad (\text{B.15})$$

$$\text{corr}_2 = -\frac{\text{Ec}}{\text{We}} \lambda_f(T^n) \epsilon \frac{|\nabla \psi^{n+1} - \nabla \psi^n|^2}{2\delta t}, \quad (\text{B.16})$$

$$\text{corr}_3 = \frac{(\rho C_h)^{n+1} T^n (T^{n+1} - T^n)^2}{2(T_{min})^2 \delta t}, \quad (\text{B.17})$$

$$corr_4 = \frac{k|\nabla T^{n+1}|^2 - k|\nabla T^n|^2}{4 \text{Pe}_T T^n}, \quad (\text{B.18})$$

where \tilde{S}^{n+1} is the approximation of s^{n+1} , \tilde{s}^{n+1} is the approximation of \hat{s}^{n+1} , and T_{min} is the global minimum value of the initial temperature.

Appendix C. Average and difference operators

Here we define the edge-to-center average and difference operators $a_x, d_x : \mathcal{E}_{m_1 \times m_2}^{ew} \rightarrow C_{m_1 \times m_2}$ and $a_y, d_y : \mathcal{E}_{m_1 \times m_2}^{ns} \rightarrow C_{m_1 \times m_2}$ as

$$a_x u_{i,j} = \frac{1}{2} \left(u_{i+\frac{1}{2},j} + u_{i-\frac{1}{2},j} \right), \quad d_x u_{i,j} = \frac{1}{h} \left(u_{i+\frac{1}{2},j} - u_{i-\frac{1}{2},j} \right), \quad (\text{C.1})$$

$$a_y v_{i,j} = \frac{1}{2} \left(v_{i,j+\frac{1}{2}} + v_{i,j-\frac{1}{2}} \right), \quad d_y v_{i,j} = \frac{1}{h} \left(v_{i,j+\frac{1}{2}} - v_{i,j-\frac{1}{2}} \right), \quad (\text{C.2})$$

for $i = 1, \dots, m_1$ and $j = 1, \dots, m_2$.

The center-to-edge average and difference operators $A_x, D_x : C_{\bar{m}_1 \times m_2} \rightarrow \mathcal{E}_{m_1 \times m_2}^{ew}$ and $A_y, D_y : C_{m_1 \times \bar{m}_2} \rightarrow \mathcal{E}_{m_1 \times m_2}^{ns}$ are defined as

$$A_x \psi_{i+\frac{1}{2},j} = \frac{1}{2} (\psi_{i+1,j} + \psi_{i,j}), \quad D_x \psi_{i+\frac{1}{2},j} = \frac{1}{h} (\psi_{i+1,j} - \psi_{i,j}), \quad (\text{C.3})$$

$$A_y \psi_{i,j+\frac{1}{2}} = \frac{1}{2} (\psi_{i,j+1} + \psi_{i,j}), \quad D_y \psi_{i,j+\frac{1}{2}} = \frac{1}{h} (\psi_{i,j+1} - \psi_{i,j}), \quad (\text{C.4})$$

for $i = 0, \dots, m_1$ and $j = 0, \dots, m_2$.

The center-to-vertex average operator $\mathcal{A} : C_{\bar{m}_1 \times \bar{m}_2} \rightarrow \mathcal{V}_{m_1 \times m_2}$ is defined as

$$\mathcal{A} \phi_{i+\frac{1}{2},j+\frac{1}{2}} = \frac{1}{4} (\phi_{i+1,j+1} + \phi_{i,j+1} + \phi_{i+1,j} + \phi_{i,j}), \quad (\text{C.5})$$

for $i = 0, \dots, m_1$ and $j = 0, \dots, m_2$.

The edge-to-vertex average and difference operators $\mathcal{A}_x, \mathcal{D}_x : \mathcal{E}_{\bar{m}_1 \times m_2}^{ns} \rightarrow \mathcal{V}_{m_1 \times m_2}$ and $\mathcal{A}_y, \mathcal{D}_y : \mathcal{E}_{m_1 \times \bar{m}_2}^{ew} \rightarrow \mathcal{V}_{m_1 \times m_2}$ are defined as

$$\mathcal{A}_x v_{i+\frac{1}{2},j+\frac{1}{2}} = \frac{1}{2} \left(v_{i+1,j+\frac{1}{2}} + v_{i,j+\frac{1}{2}} \right), \quad \mathcal{D}_x v_{i+\frac{1}{2},j+\frac{1}{2}} = \frac{1}{h} \left(v_{i+1,j+\frac{1}{2}} - v_{i,j+\frac{1}{2}} \right), \quad (\text{C.6})$$

$$\mathcal{A}_y u_{i+\frac{1}{2},j+\frac{1}{2}} = \frac{1}{2} \left(u_{i+\frac{1}{2},j+1} + u_{i+\frac{1}{2},j} \right), \quad \mathcal{D}_y u_{i+\frac{1}{2},j+\frac{1}{2}} = \frac{1}{h} \left(u_{i+\frac{1}{2},j+1} - u_{i+\frac{1}{2},j} \right), \quad (\text{C.7})$$

for $i = 0, \dots, m_1$ and $j = 0, \dots, m_2$.

The vertex-to-edge average and difference operators $\mathfrak{A}_x, \mathfrak{D}_x : \mathcal{V}_{m_1 \times m_2} \rightarrow \mathcal{E}_{m_1 \times m_2}^{ns}$ and $\mathfrak{A}_y, \mathfrak{D}_y : \mathcal{V}_{m_1 \times m_2} \rightarrow \mathcal{E}_{m_1 \times m_2}^{ew}$ are defined as

$$\mathfrak{A}_x f_{i,j+\frac{1}{2}} = \frac{1}{2} \left(f_{i+\frac{1}{2},j+\frac{1}{2}} + f_{i-\frac{1}{2},j+\frac{1}{2}} \right), \quad \mathfrak{D}_x f_{i,j+\frac{1}{2}} = \frac{1}{h} \left(f_{i+\frac{1}{2},j+\frac{1}{2}} - f_{i-\frac{1}{2},j+\frac{1}{2}} \right), \quad (\text{C.8})$$

$$\mathfrak{A}_y g_{i+\frac{1}{2},j} = \frac{1}{2} \left(g_{i+\frac{1}{2},j+\frac{1}{2}} + g_{i+\frac{1}{2},j-\frac{1}{2}} \right), \quad \mathfrak{D}_y g_{i+\frac{1}{2},j} = \frac{1}{h} \left(g_{i+\frac{1}{2},j+\frac{1}{2}} - g_{i+\frac{1}{2},j-\frac{1}{2}} \right), \quad (\text{C.9})$$

for $i = 0, \dots, m_1$ and $j = 1, \dots, m_2$.

Appendix D. Specification for fully discretization

Here we specify the terms $\rho^n \mathbf{v}^n \cdot \nabla \mathbf{v}^{n+1}$, $\nabla \cdot \mathbf{T}^{n+1}$, q_E^{n+1} and h_s in fully discrete numerical method (166)-(169) as follows:

$$\begin{aligned} \rho^n \mathbf{v}^n \cdot \nabla \mathbf{v}^{n+1} &= \left(A_x (\rho^n a_x u^n d_x u^{n+1}) + \mathfrak{A}_y (\mathcal{A} \rho^n \mathcal{A}_x v^n \mathcal{D}_y u^{n+1}) \right), \\ \nabla \cdot \mathbf{T}^{n+1} &= -\frac{\epsilon}{\text{We}} \left(D_x (\lambda_f(T^n) a_x (D_x \psi^{n+1})^2) + \mathfrak{D}_y (\mathcal{A} \lambda_f(T^n) D_x A_y \psi^{n+1} \mathcal{D}_y A_x \psi^{n+1}) \right) \\ &\quad + \frac{1}{\text{Re}} \left(2 D_x (\mu^n d_x u^{n+1}) + \mathfrak{D}_y (\mathcal{A} \mu^n (\mathcal{D}_y u^{n+1} + D_x v^{n+1})) \right) \\ &\quad - \nabla_D (\rho^{n+1} + \mu_0^{n+1} \psi^{n+1}) - \frac{2}{3\text{Re}} \nabla_D (\mu^n \nabla_d \cdot \mathbf{v}^{n+1}) + \nabla_D \hat{f}^{n+1}, \\ \mu_0^{n+1} &= \frac{\partial f}{\partial \psi} + \frac{1}{\text{We}} \lambda_f(T^n) \left(\frac{W'(\psi^{n+1})}{\epsilon} - \epsilon \nabla_d \cdot \nabla_D \psi^{n+1} \right), \\ \hat{f}^{n+1} &= f^{n+1} + \frac{1}{\text{We}} \lambda_f(T^n) \delta^{n+1}, \end{aligned}$$

$$\begin{aligned}
\delta^{n+1} &= \frac{W(\psi^{n+1})}{\epsilon} + \epsilon \frac{|\nabla_d A \psi^{n+1}|^2}{2}, \\
q_E^{n+1} &= -\frac{1}{\text{Pe}_T} A k \frac{\nabla_D T^{n+1} + \nabla_D T^n}{2} - \frac{\text{Ec}}{\text{Pe}_\psi} A(m_\psi^n \mu_c^{n+1}) \nabla_D \mu_c^{n+1} \\
&\quad - \frac{\text{Ec}}{\text{We}} \lambda_u \epsilon \left((u^n D_x \psi^{n+1} + A_x a_y v^n \mathfrak{D}_y A \psi^{n+1}) D_x \psi^{n+1} \right) \\
&\quad - \frac{\text{Ec}}{\text{We}} \lambda_u \epsilon \left((A_y a_x u^n \mathfrak{D}_x A \psi^{n+1} + v^n D_y \psi^{n+1}) D_y \psi^{n+1} \right) \\
&\quad - \frac{\text{Ec}}{\text{We}} \lambda_u \epsilon (\nabla_D \psi^{n+1} \psi_{\bar{t}}), \\
hs &= -\text{Ec} \frac{\partial u}{\partial \psi} \psi_{\bar{t}} - \text{Ec} \frac{\partial \tilde{u}}{\partial \psi} (v^n \cdot \nabla \psi^{n+1}) + \text{Ec} \mathbf{m}^{n+1} : \nabla v^n \\
&\quad + \frac{\text{Ec}}{\text{Re}} \tau^{n+1} : \nabla v^{n+1} - \text{Ec} T^n \tilde{s}^{n+1} (\nabla_d \cdot v^n) - \frac{\text{Ec}}{\text{We}} \lambda_u \delta_{\bar{t}} \\
&\quad - \frac{\text{Ec}}{\text{We}} \lambda_u (v^n \cdot \nabla \delta^{n+1}) + \text{corr}^n, \\
\mathbf{m}^{n+1} &= -\frac{1}{\text{We}} \lambda_f (T^n) \epsilon ((\nabla_d A \psi^{n+1}) \otimes (\nabla_d A \psi^{n+1})) \\
&\quad - (p^{n+1} + \mu_0^{n+1} \psi^{n+1}) \mathbf{I}, \\
\tau^{n+1} &= \mu^n (\nabla v^{n+1} + (\nabla v^{n+1})^\top) - \frac{2}{3} \mu^n (\nabla_d \cdot v^{n+1}) \mathbf{I}, \\
v^n \cdot \nabla \psi^{n+1} &= a_x u^n a_x D_x \psi^{n+1} + a_y v^n a_y D_y \psi^{n+1}, \\
v^n \cdot \nabla \delta^{n+1} &= a_x u^n a_x D_x \delta^{n+1} + a_y v^n a_y D_y \delta^{n+1}, \\
\text{corr}^n &= \text{corr}_1 + \text{corr}_2 + \text{corr}_3 + \text{corr}_4, \\
\text{corr}_1 &= \frac{\text{Ec}}{\text{We}} \lambda_f (T^n) \frac{(\psi^{n+1} - \psi^n)^2}{8 \delta t \epsilon}, \\
\text{corr}_2 &= -\frac{\text{Ec}}{\text{We}} \lambda_f (T^n) \epsilon \frac{|A_a \nabla_D^\top (\psi^{n+1} - \psi^n)|^2}{2 \delta t}, \\
\text{corr}_3 &= \frac{(\rho C_h)^{n+1} T^n (T^{n+1} - T^n)^2}{2 (T_{\min})^2 \delta t}, \\
\text{corr}_4 &= \frac{k |A_a \nabla_D^\top T^{n+1}|^2 - k |A_a \nabla_D^\top T^n|^2}{4 \text{Pe}_T T^n}.
\end{aligned}$$

References

- [1] Z. Guo, P. Lin, A thermodynamically consistent phase-field model for two-phase flows with thermocapillary effects, *J. Fluid Mech.* 766 (2015) 226–271.
- [2] H. Liu, Y. Zhang, A.J. Valocchi, Modeling and simulation of thermocapillary flows using lattice Boltzmann method, *J. Comput. Phys.* 231 (12) (2012) 4433–4453.
- [3] H. Liu, A.J. Valocchi, Y. Zhang, Q. Kang, Phase-field-based lattice Boltzmann finite-difference model for simulating thermocapillary flows, *Phys. Rev. E* 87 (1) (2013) 013010.
- [4] T. Mitchell, M. Majidi, M. Rahimian, C. Leonardi, Computational modeling of three-dimensional thermocapillary flow of recalcitrant bubbles using a coupled lattice Boltzmann-finite difference method, *Phys. Fluids* 33 (3) (2021).
- [5] Y. Hu, D. Li, X. Niu, S. Shu, A diffuse interface lattice Boltzmann model for thermocapillary flows with large density ratio and thermophysical parameters contrasts, *Int. J. Heat Mass Transf.* 138 (2019) 809–824.
- [6] Y. Xiao, Z. Zeng, L. Zhang, J. Wang, Y. Wang, H. Liu, C. Huang, A spectral element-based phase field method for incompressible two-phase flows, *Phys. Fluids* 34 (2) (2022).
- [7] Q. Yang, Y. Liu, X. Jia, T. Zhang, H. Tian, J. Fan, Q. Xu, F. Song, Phase-field numerical study on the dynamic process of thermocapillary patterning, *Phys. Rev. E* 106 (1) (2022) 015111.
- [8] H. Liu, A.J. Valocchi, Y. Zhang, Q. Kang, Lattice Boltzmann phase-field modeling of thermocapillary flows in a confined microchannel, *J. Comput. Phys.* 256 (2014) 334–356.
- [9] L. Yue, Z. Chai, H. Wang, B. Shi, Improved phase-field-based lattice Boltzmann method for thermocapillary flow, *Phys. Rev. E* 105 (1) (2022) 015314.
- [10] S. Sun, J. Li, J. Zhao, Q. Wang, Structure-preserving numerical approximations to a non-isothermal hydrodynamic model of binary fluid flows, *J. Sci. Comput.* 83 (2020) 1–43.
- [11] X. Yang, Linear, first and second-order, unconditionally energy stable numerical schemes for the phase field model of homopolymer blends, *J. Comput. Phys.* 327 (2016) 294–316.
- [12] X. Yang, L. Ju, Efficient linear schemes with unconditional energy stability for the phase field elastic bending energy model, *Comput. Methods Appl. Mech. Eng.* 315 (2017) 691–712.
- [13] X. Yang, Efficient linear, fully-decoupled and energy stable numerical scheme for a variable density and viscosity, volume-conserved, hydrodynamically coupled phase-field elastic bending energy model of lipid vesicles, *Comput. Methods Appl. Mech. Eng.* 400 (2022) 115479.
- [14] J. Shen, J. Xu, J. Yang, The scalar auxiliary variable (SAV) approach for gradient flows, *J. Comput. Phys.* 353 (2018) 407–416.
- [15] J. Shen, J. Xu, J. Yang, A new class of efficient and robust energy stable schemes for gradient flows, *SIAM Rev.* 61 (3) (2019) 474–506.
- [16] G. Zhu, H. Chen, J. Yao, S. Sun, Efficient energy-stable schemes for the hydrodynamics coupled phase-field model, *Appl. Math. Model.* 70 (2019) 82–108.
- [17] M. Wang, Q. Huang, C. Wang, A second order accurate scalar auxiliary variable (SAV) numerical method for the square phase field crystal equation, *J. Sci. Comput.* 88 (2) (2021) 33.
- [18] D. Hou, C. Xu, Robust and stable schemes for time fractional molecular beam epitaxial growth model using SAV approach, *J. Comput. Phys.* 445 (2021) 11062.

- [19] D. Hou, H. Zhu, C. Xu, Highly efficient schemes for time-fractional Allen Cahn equation using extended sav approach, *Numer. Algorithms* 445 (2021) 1–32.
- [20] M. Jiang, Z. Zhang, J. Zhao, Improving the accuracy and consistency of the scalar auxiliary variable (sav) method with relaxation, *J. Comput. Phys.* 456 (2022) 110954.
- [21] D. Hou, M. Azaiez, C. Xu, A variant of scalar auxiliary variable approaches for gradient flows, *J. Comput. Phys.* 395 (2019) 307–332.
- [22] Y. Gong, Q. Hong, Q. Wang, Supplementary variable method for thermodynamically consistent partial differential equations, *Comput. Methods Appl. Mech. Eng.* 381 (2021) 113746.
- [23] Q. Hong, Q. Wang, Y. Gong, High-order supplementary variable methods for thermodynamically consistent partial differential equations, *Comput. Methods Appl. Mech. Eng.* 416 (2023) 116306.
- [24] J. Lowengrub, L. Truskinovsky, Quasi-incompressible Cahn–Hilliard fluids and topological transitions, *Proc. R. Soc. Lond., Ser. A, Math. Phys. Eng. Sci.* 454 (1978) (1998) 2617–2654.
- [25] Z. Guo, P. Lin, J. Lowengrub, S.M. Wise, Mass conservative and energy stable finite difference methods for the quasi-incompressible Navier–Stokes–Cahn–Hilliard system: primitive variable and projection-type schemes, *Comput. Methods Appl. Mech. Eng.* 326 (2017) 144–174.
- [26] N. Young, J.S. Goldstein, M. Block, The motion of bubbles in a vertical temperature gradient, *J. Fluid Mech.* 6 (3) (1959) 350–356.
- [27] B. Pendse, A. Esmaceli, An analytical solution for thermocapillary-driven convection of superimposed fluids at zero Reynolds and Marangoni numbers, *Int. J. Therm. Sci.* 49 (7) (2010) 1147–1155.
- [28] G. Brereton, D. Korotney, Coaxial and oblique coalescence of two rising bubbles, *Dynamics of Bubbles and Vortices Near a Free Surface* 119 (1991) 50–73.