Liquid mixture convection during phase separation in a temperature gradient

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We simulate the phase separation of a low-viscosity binary mixture, assuming that the fluid system is confined between two walls that are cooled down to different temperatures below the critical point of the mixture, corresponding to quenches within the unstable range of its phase diagram. Spinodal decomposition patterns for off-critical mixtures are studied numerically in two dimensions in the creeping flow limit and for a large Lewis number, together with their dependence on the fluidity coefficient. Our numerical results reproduce the large-scale unidirectional migration of phase-separating droplets that was observed experimentally by Califano et al. [“Large-scale, unidirectional convection during phase separation of a density-matched liquid mixture,” Phys. Fluids 17, 094109 (2005)], who measured typical speeds that are quite larger than the Marangoni velocity. To understand this finding, we then studied the temperature-gradient-induced motion of an isolated droplet of the minority phase embedded in a continuous phase, showing that when the drop is near local equilibrium, its speed is of the same order as the Marangoni velocity, i.e., it is proportional to the unperturbed temperature gradient and the fluidity coefficient. However, far from local equilibrium, i.e., for very large unperturbed temperature gradients, the drop first accelerates to a speed that is larger than the Marangoni velocity, then, later, it decelerates, exhibiting an increase-decrease behavior, as described by Yin et al. [“Thermocapillary migration of nondeformable drops,” Phys. Fluids 20, 082101 (2008)]. Such behavior is due to the large nonequilibrium, Korteweg-driven convection, which at first accelerates the droplets to relatively large velocities, and then tends to induce an approximately uniform inside temperature distribution so that the drop experiences an effective temperature gradient that is much smaller than the unperturbed one and, consequently, decelerates. © 2011 American Institute of Physics.
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I. INTRODUCTION

The objective of this work is to study numerically the influence of temperature gradients on the phase separation of a low-viscosity binary system, occurring after quenching its walls to different temperatures below the critical point. In general, a binary mixture that is quenched into the unstable range of its phase diagram phase separates through a process known as spinodal decomposition. In previous works we have shown that, for a low-viscosity binary system in a uniform temperature field, this process is driven by the convection induced by phase transition, which is responsible for the enhanced coalescence between single-phase micro-domains.¹⁻⁶ When the temperature field is inhomogeneous, however, another effect becomes relevant, namely, convective heat transport due to phase transition. This effect is well known in vapor-liquid phase transitions, where the density mismatch between the component phases drives a strong, turbulent convection which enhances heat transfer. However, in liquid-liquid phase transitions, density differences are typically small and the heat transfer enhancement due to this effect is consequently much smaller, as was measured experimentally by Poesio et al.⁷ and predicted numerically by Molin and Mauri.⁸

Temperature-gradient effects on phase-separating binary liquid mixtures have been investigated in the past, both numerically⁸⁻¹⁰ and experimentally.¹¹⁻¹⁵ In particular, Marangoni-like migration of droplets undergoing phase separation has been studied numerically under particular flow conditions,¹⁰,¹⁶ although none of these works have focused on thermocapillary effects systematically. Other numerical studies⁸⁻¹⁰ have focused on the effects of temperature gradients on diffusion-driven phase separation and, specifically, on how the morphology of a very viscous binary system, where both the molar and the thermal Peclet numbers of the mixture can be assumed to be negligible, evolves during phase separation with an imposed temperature gradient. Therefore, the coupling with hydrodynamics was altogether neglected since heat and mass transport were solely diffusive, as in polymer melts and alloys.

For low-viscosity binary mixtures, however, diffusion alone cannot explain the phase segregation process occurring in isothermal spinodal decomposition, as the prevailing mechanism that drives phase separation after the initial diffusion-driven stage is convection-driven coalescence, leading to a linear growth law for the characteristic size of single-phase microdomains.²,³,⁵,⁶,¹⁷ Experimentally, when a nearly isopycnic, low-viscosity binary mixture is quenched...
deeply and rapidly into the spinodal region of its phase diagram in the presence of a temperature gradient, it develops a unidirectional and large-scale motion of the nucleating droplets along the direction of the temperature gradient, which, even in the absence of buoyancy, is responsible for a rapid and complete segregation of the mixture. This was initially observed by Califano and Mauri, who used a nearly isophasic hexadecane-acetone mixture in a temperature-regulated cell for investigating drop size evolution in a phase-separating system. Later on, Califano et al. also observed a large-scale unidirectional motion of the acetone-rich drops toward the warmer region of a condenser tube, and of the hexadecane-rich drops in the opposite direction, with speeds largely exceeding the Marangoni velocity.

In this work, applying the diffuse-interface model, we investigate temperature-gradient effects on the phase separation of off-critical binary mixtures as a function of the Peclet and Lewis numbers. To this end, we first perform two-dimensional (2D) simulations of off-critical phase-separating mixtures which reproduce qualitatively the experimental findings of Califano et al. Next, in order to obtain quantitative measurements of migration velocity as a function of temperature-gradient strength, we simulate the thermocapillary migration of 2D isolated droplets of the minority phase embedded in a continuous phase, comparing our results with the classical result by Young, Goldstein, and Block and with recent simulations by Yin et al.

An outline of the remainder of this paper is as follows. In Secs. II and III, the governing equations and numerical methods are briefly outlined. Then, in Sec. IV, we show the results of numerical simulations for large Lewis and Peclet numbers corresponding to a low-viscosity binary mixture. Conclusions are then presented.

II. THE GOVERNING EQUATIONS

In the absence of external forces, the motion of a regular binary mixture is described by the generalized Cahn–Hilliard, Navier–Stokes, and energy equations, \[ \partial_t \phi + \nabla \cdot (\mathbf{v} \phi) = -\nabla \cdot \mathbf{J}_\phi, \] \[ \partial_t \mathbf{q} + \nabla \cdot (\mathbf{v} \mathbf{q}) = -\nabla \cdot \mathbf{J}_\mathbf{q} + \mathbf{F}_\phi, \] \[ \nabla \cdot \mathbf{v} = 0, \] \[ \partial_t \mathbf{u} + \nabla \cdot (\mathbf{v} \mathbf{u}) = -\nabla \cdot \mathbf{J}_\mathbf{u} + \mathbf{q}, \] where \( \phi, \mathbf{q}, \) and \( u \) are, respectively, the mass fraction of species \( A \), the mixture momentum and internal energy; these latter being simply related to the velocity, \( \mathbf{v} \), and the temperature, \( T \), as \( \mathbf{q} = \rho \mathbf{v} \) and \( u = \rho c T \), with \( \rho \) and \( c \) denoting density and specific heat. Here, \( \mathbf{J}_\phi, \mathbf{J}_\mathbf{q}, \) and \( \mathbf{J}_\mathbf{u} \) are the material, momentum, and internal energy diffusive fluxes, respectively, \( \mathbf{F}_\phi \) is the reversible Korteweg body force, while \( \mathbf{q} \) denotes heat generation. In this work, we will only consider flows with negligible Reynolds number that are governed by the Stokes equation which results from Eq. (2) after dropping the left-hand side. The Korteweg force is given by

\[ \mathbf{F}_\phi = -\phi \nabla \frac{\rho RT}{M_w} \tilde{\mu}, \] where \( R \) is the universal gas constant, \( M_w \) is the molecular weight, while \( \tilde{\mu} = \mu_i - \mu_2 \) is the chemical potential difference, defined as \( \mu = \delta (g/RT)/\delta \phi \), with \( g \) denoting the molar Gibbs free energy of mixing for a nonhomogeneous mixture at temperature \( T \) and pressure \( P \). This last quantity is the sum of a thermodynamic part (i.e., that which we would have for a uniform mixture) plus a nonlocal part, i.e., \[ \tilde{g} = g_{\text{Th}} + g_{\text{NL}}, \] where \( g_{\text{Th}} = RT(\phi \log \phi + (1 - \phi) \log(1 - \phi) + \Psi \phi(1 - \phi)) \) \[ + \frac{1}{2}RT\alpha^2(\nabla \phi)^2, \] so that \( \tilde{\mu} = \mu_{\text{Th}} + \mu_{\text{NL}} \) with \( \mu_{\text{Th}} = \log \frac{\phi}{1 - \phi} + \Psi(1 - 2\phi) \) and \( \mu_{\text{NL}} = -\alpha^2 \nabla^2 \phi. \)

Here, \( \alpha \) is a characteristic microscopic length, while \( \Psi \) is the Margules parameter, which describes the repulsive interaction between unlike molecules versus that between like molecules. At the critical point \( C \), imposing that the free energy have a horizontal inflection point for \( \phi_i = 1/2 \), we see that \( \Psi_C = 2 \). Therefore, since the mixture is assumed to be regular (i.e., its components are van der Waals fluids), we obtain \[ \Psi = \frac{2T_C}{T} \quad \text{and} \quad \alpha = \frac{\hat{a}}{\sqrt{T}}, \] where \( \hat{a} \) is a constant length, independent of the temperature. Note that, as shown by Jasnow and Viñals, Jäcquin, and Pismen and Pomeau, at the late stages of phase separation, when the mixture is composed of well-defined single-phase domains separated by sharp interfaces, the Korteweg body force collapses into the more conventional Marangoni force. In particular, the surface tension can be obtained by integrating the nonlocal part of the volumetric free energy along a direction perpendicular to the interface region, obtaining

\[ \sigma = \frac{\rho RT}{M_w}. \] The Korteweg body force can also be expressed in the following form:

\[ \mathbf{F}_\phi = -\sum_{i=1}^{2} x_i \nabla \psi_i, \] where \( x_i \) is the molar fraction of species \( i \) and

\[ \psi_i = \frac{\rho RT}{M_w} \mu_{\text{NL,i}} \] is the nonlocal chemical potential of species \( i \). Note that since according to the Gibbs–Duhem relation, \( \sum_i x_i \nabla \mu_{\text{Th},i} = 0 \), in the expression above \( \mu_{\text{NL},i} \) can be replaced by \( \mu_i = \mu_{\text{Th},i} + \mu_{\text{NL},i} \) so that, as already seen, the Korteweg force reduces to...
Finally, the total potential energy of the system is

\[ V = \sum_{i=1}^{2} \phi_i \bar{p} \psi_i \]

where \( \psi = \psi_1 - \psi_2 \). For all practical purposes, the Korteweg force can be considered as a potential force; in fact, we can include into \( \psi \) also the contributions of any other potential force. For example, in the Boussinesq, quasi-incompressible approximation, the buoyancy force is \( F_g = -\phi \nabla \left[ g z (\phi \partial z / \partial \phi) \right] \), where \( g \) is the gravity acceleration term and \( z \) is the vertical coordinate. Accordingly, gravity can be accounted for by simply adding the term \( V_{ext} = g z (\phi \partial z / \partial \phi) \) to \( \psi \) in Eq. (12). Finally, the total potential energy of the system is

\[ V = \sum_{i=1}^{2} \phi_i \bar{p} \psi_i = \sum_{i=1}^{2} \frac{\rho R T}{M_w} \phi_i \bar{\mu}_i = \sum_{i=1}^{2} \rho_R T \phi_i \bar{\mu}_i + V_{ext}, \tag{13} \]

where, as we have seen, \( \bar{\mu}_i \) includes also the contribution of all other external, potential forces. As shown in the detailed energy balance in Appendix A, the work done by the Korteweg force, as that done by any other potential force, decreases the potential energy and at the same time increases the kinetic energy, so that it drops out of the balance equation for mechanical (kinetic plus potential) energy. In addition, energy conservation coupled to irreversible thermodynamics determines the following constitutive equations for the diffusive fluxes:

\[ J_{\phi} = -D'(\phi) \left[ \nabla \phi \right]_{T}, \tag{14} \]

\[ J_{\psi} = \rho I - \eta(\phi, T) \left[ \nabla \phi + (\nabla \phi)^* \right], \tag{15} \]

\[ J_{\phi} = -k \nabla T + J_N, \tag{16} \]

where \( D'(\phi) \) is the diffusion coefficient, \( \rho \) is the pressure, \( \eta \) is the viscosity, \( k \) is the heat conductivity, \( \bar{h} \) is the total (i.e., thermodynamic plus nonlocal) partial enthalpy difference, while the subscript \( T \) indicates constant temperature and \( * \) denotes the transpose. In this work, the two components of the mixture are assumed to have the same uniform density, \( \rho \), viscosity, \( \eta \), molecular weights, \( M_w \), heat conductivity, \( k \), and specific heat, \( c \). In addition, imposing that in the dilute limit Eq. (14) reduce to Fick’s law, the simplest expression for the diffusivity is as follows: \( D'(\phi) = D \phi (1 - \phi) \).

As for the heat generation term in Eq. (4), in Appendix A we obtain

\[ \dot{q} = -\frac{\rho R T}{M_w} \frac{d \phi}{dt}, \tag{18} \]

where viscous dissipation has been neglected. This is a new formulation for the heat generation term that is not explicitly discussed in de Groot and Mazur, although our derivations in the Appendixes are based on their analysis of the energy and entropy equations. Equation (18) corrects the expression that was used in a previous work by one of the authors, where the chemical potential difference on the right-hand side (RHS) was erroneously assumed to be equal to the enthalpy of mixing. Since all dissipations were assumed to be negligible, though, all the results of that work are to be considered valid nonetheless. We stress again that here we as-

III. NUMERICAL METHODS

The governing equations (in dimensionless form) can be rewritten as follows:

\[ \left( \partial_t - \nabla^2 \right) \phi = -\nabla^2 \left\{ \phi (1 - \phi) \left[ 2 \phi - 1 + \left( \frac{\alpha}{h} \right)^2 \nabla^2 \phi \right] \psi \right\} \]

\[ + \nabla \cdot \left\{ \left[ 2 \phi - 1 + \left( \frac{\alpha}{h} \right)^2 \nabla^2 \phi \right] \Psi \right\} \]

\[ \times (1 - 2 \phi) \nabla \phi - \alpha \phi u \right\}. \tag{19} \]

\[ \left( \frac{\alpha}{h} \right)^2 \nabla^2 u = 1 \left( \nabla \phi \right) \nabla \left( \frac{\bar{\mu}}{\psi} \right), \quad \nabla \left( \nabla \phi \right) = \delta_{ij} - \nabla^2 \delta_{ij}, \tag{20} \]

\[ \left( \partial_t - \text{Le} \nabla^2 \right) \psi = -\alpha \nabla \cdot u \psi - 2 \text{Le} \frac{\left| \nabla \psi \right|^2}{\psi} - \frac{\Psi^2}{\bar{c}} \left( \frac{\alpha}{h} \right)^2 \nabla^2 \phi, \tag{21} \]

where all lengths and times are scaled by \( h \) and \( h^2/D \), respectively, with \( h \) denoting a macro-length-scale, which in our case coincides with the channel half-width. In Eq. (21), \( \bar{c} = c M_w / R \) is the nondimensional specific heat, \( \text{Le} = \alpha \phi / D \) is the Lewis number (with \( \alpha = k / \rho c \) denoting the thermal diffusivity), whereas \( \alpha \) denotes the fluidity coefficient, \( \alpha = \frac{RT \alpha^2}{M_w \nu D} = \frac{\alpha}{(\eta \bar{U})} \), \tag{22} \]

where we have applied Eq. (9), with \( U=D/a \) denoting a characteristic velocity. Accordingly, the nondimensional parameter \( \alpha \) on one hand, is an inverse capillary number, while, on the other hand, it can also be interpreted as a Peclet number, i.e., the ratio of convective to diffusive mass fluxes in the Cahn–Hilliard equation (19). Equation (20) can be seen as a “static” constraint on the (nondimensional) velocity field, i.e., at each instant in time the velocity can be determined once the concentration and temperature fields are known [so that the \( u \)-dependence on the RHS of Eq. (19) can be formally dropped]. The projector \( \nabla (\nabla) \) in Eq. (20) guarantees a solenoidal velocity at all times. Finally, in the following, we will neglect the heat generation term, which amounts to assuming \( \bar{c} \gg 1 \) in Eq. (21).

Numerical methods here are based on a previous work by Lamorgese and Mauri. We summarize in the following the necessary changes for including the inverse temperature \( \Psi \) as a time-dependent field. Fourier pseudospectral methods are used to discretize the streamwise (x) and spanwise (z) directions, whereas fourth-order compact finite differences are applied to the wall-normal (\( y \)) direction. After Fourier-
transforming in the $x$ and $z$ directions, the Cahn–Hilliard equation [Eq. (19)] can be rewritten as follows:

$$
\frac{d}{dt}[e^{f(k_0)}\phi_h(y,t)] = \mathcal{L}(k)e^{f(k_0)}\phi_h(y,t) + e^{f(k_0)}\dot{N}_h(y,t), \tag{23}
$$

where

$$f(k) := (1 - 2\beta_h)|k|^2 + \beta_h\left(\frac{\hat{a}}{h}\right)^2|k|^4, \tag{24}
$$

$$\mathcal{L}(k) := \left[1 - 2\beta_h + 2\beta_h|k|^2\left(\frac{\hat{a}}{h}\right)^2\right]D_2 - \beta_h\left(\frac{\hat{a}}{h}\right)^2D_4, \tag{25}
$$

$$N := -\nabla^2 \left\{\phi(1 - \phi)\Psi - \beta_h\left[2\phi - 1 + \left(\frac{\hat{a}}{h}\right)^2\nabla^2\phi\right]\right\}
+ \nabla \cdot \left\{\Psi \left[2\phi - 1 + \left(\frac{\hat{a}}{h}\right)^2\nabla^2\phi\right]\right\}
\times(1 - 2\phi) \nabla \phi - \alpha \phi u. \tag{26}
$$

Here, $D_2$ and $D_4$ denote second- and fourth-order differentiation matrices (from the compact finite-difference discretization), whereas $\beta_h$ is a numerical hyperdiffusivity. As previously noted,\textsuperscript{34} for the Cahn–Hilliard equation the following wall-boundary conditions are imposed: (i) a no-flux condition $\hat{n} \cdot J = 0$, with $\hat{n}$ denoting a unit vector perpendicular to the wall, and (ii) a wetting condition based on a local model\textsuperscript{30,36} for the surface Gibbs free energy, $\sigma a^n \cdot \nabla \phi = -\Delta \sigma_w$, where $\Delta \sigma_w = \sigma_{1w} - \sigma_{2w}$, expresses the affinity of the wall to species 1, as compared to species 2. This simple model for the surface free energy is based on the assumption that wettability is a local quantity, depending on the local composition of the mixture at the wall. The resulting wall-boundary condition describes a diffusively controlled local equilibrium at the wall.\textsuperscript{36} With the additional assumption $\sigma_{1w} = \sigma_{2w}$ (expressing the same affinity of both species for the wall or a 90° contact angle), the following wall-boundary conditions for the Cahn–Hilliard equation result:

$$
\frac{\partial \phi}{\partial y} = 0, \quad \frac{\partial^2 \phi}{\partial y^2} = 0, \tag{27}
$$

In our solution algorithm, these are implemented using an influence-matrix technique.\textsuperscript{34,37} Note that we have neglected additional wall interaction terms (i.e., disjoining potential) contributing to the surface Gibbs free energy integral\textsuperscript{22,31,38} since our focus in this work is on the Korteweg-driven convection due to an imposed temperature gradient.

The Cahn–Hilliard equation is integrated in time using a second-order Runge–Kutta/Crank–Nicolson technique.\textsuperscript{39} By means of $\beta_h$, the linear operator $\mathcal{L}$ includes a fourth-order derivative, so as to render enforcement of boundary conditions [Eq. (27)] possible. Through numerical experiments we showed that a stable and accurate temporal advancement is obtained with $\beta_h |\hat{a}| = 5 \times 10^{-6}$ (we used $\beta_h = 5 \times 10^{-6}$ in our production runs).\textsuperscript{34} The Fourier-transformed energy equation can be rewritten in the form,

$$
\frac{d}{dt}[e^{f(k_0)}\phi_h(y,t)] = \mathcal{L}(k)e^{f(k_0)}\phi_h(y,t) + e^{f(k_0)}\dot{N}_h(y,t), \tag{23}
$$

where

$$N := -2 \mathcal{L}(k)\frac{\Psi^2}{\Psi} - \alpha \nabla \cdot u \Psi - \mathcal{L}(k)\frac{\Psi^2}{\Psi} \left(\frac{\hat{a}}{h}\right)^2 \nabla^2 \phi. \tag{29}
$$

This equation is advanced in time using the second-order Runge–Kutta/Crank–Nicolson scheme above, with Dirichlet boundary conditions for $\Psi$ imposed at the channel walls.

To solve the Stokes equation, we use a vertical-velocity/vertical-vorticity formulation.\textsuperscript{34} We first take the curl of Eq. (2), which eliminates the pressure and yields a static equation for the vorticity $\omega$:

$$
-\nabla^2 \omega = \nabla \phi \times \nabla \phi + \frac{h}{\hat{a}} \nabla \times \left[\frac{1}{\Psi} \log \frac{\phi}{1 - \phi} \nabla \phi\right]. \tag{30}
$$

Taking the curl once more yields

$$
\nabla^2 u = \nabla \times (\nabla \phi \times \nabla \phi) + \frac{h}{\hat{a}} \nabla \times \nabla \times \left[\frac{1}{\Psi} \log \frac{\phi}{1 - \phi} \nabla \phi\right]. \tag{31}
$$

Since the contact line at the top and bottom walls of the domain ($y = \pm 1$) is diffuse, no-slip, no-penetration boundary conditions are imposed for the velocity there. With no-slip, no-penetration boundary conditions at the channel walls, we have homogeneous Dirichlet boundary conditions at the walls for the wall-normal vorticity. Therefore, the solution of the Stokes equation is obtained by first projecting Eqs. (30) and (31) into the wall-normal direction and solving the resulting boundary-value problems (with homogeneous boundary conditions) for the vertical velocity and vorticity components. Then, the horizontal velocity components follow from continuity.\textsuperscript{34} Finally, it is noted that the first term on the RHS of Eq. (30) would normally require nine FFTs for its pseudospectral evaluation. However, using the following identity:\textsuperscript{34}

$$
(\nabla \phi \times \nabla \phi)_{ij} = \partial^2_{ij}(\partial^2_{ij} - \partial^2)_{ij} + (\partial^2_{ij} - \partial^2)_{ij}\phi_i \phi_j - \partial^2_{ij}\phi_i \partial^2_{ij} + \partial^2_{ij}\phi_i \phi_j, \tag{32}
$$

where $\{i,j,k\}$ is any cyclic permutation of $\{1,2,3\}$, its computation requires only eight FFTs. It is clear that, being based on a vertical-velocity/vertical-vorticity formulation, our numerical algorithm is more efficient than numerical schemes for the (Navier–)Stokes/Cahn–Hilliard system previously shown in literature, which require a pressure Poisson solver. As previously mentioned, Eqs. (19) and (21) are integrated in time using a hybrid implicit/explicit integration scheme. The nonlinear term in each equation is treated explicitly with a second-order Runge–Kutta method, while the purely diffusive and hyperdiffusive terms are treated implicitly using a Crank–Nicolson scheme. The time step $\Delta t$ is determined by the Courant–Friedrichs–Lewy condition.
such that the scheme is numerically unstable.

\[ 
\Delta t = N_c \frac{\Delta x}{\max_y V(y)}, \tag{33} 
\]

where \( \Delta x \) is the dimensionless grid spacing in the \( x \) direction, while \( N_c \) is the Courant number. In our case, considering that convection is induced by concentration gradients, we have assumed that \( V(y) = \max_{x,z} \phi \), where \( \max_{x,z} \) indicates the maximum attained over all collocation points in an \((x,z)\) plane, so that at each time step the advancement scheme is sensitive to the spatial gradients of \( \phi \). The Courant number is chosen such that the time-advancement scheme is numerically stable and the smallest dynamical motions are accurately computed. Unfortunately, the nonlinearity of the equation prevents a rigorous determination of the stability limit and imposes a trial-and-error determination of the maximum acceptable Courant number. In our simulations, we chose \( N_c = N_c(\alpha, Le) \) with \( N_c(\alpha, Le) = 10^{-4} - 10^{-3} \) depending on the chosen \( \alpha \) and \( Le \), as we found values of \( N_c > N_c(\alpha, Le) \) such that the scheme is numerically unstable.

\section*{IV. RESULTS}

The simulations were carried out in a computational domain of size \( L_x = (N/2) \hat{a}, \ L_y = (\pi/2) \hat{a} \), with \( N = 128, 256 \). First, for a given temperature gradient \( \Delta T = \Psi_w,1 - \Psi_w,2 \) (with subscripts 1 and 2 denoting the cold and hot walls), we studied the spinodal decomposition of off-critical mixtures for a large Lewis number \((Le=100)\) and different values of the Peclet number. Initially, the off-critical mixture was assumed to have a uniform composition \( (\phi_0 = 0.35) \) with a white noise superimposed to it (noise perturbations were only applied close enough to the walls). In the first set of simulations, the right wall is kept at a cold temperature \( T_1 = 2T_c/\Psi_w,1 \), with \( \Psi_w,1 = 2.4 \), while the left wall has a higher temperature \( T_2 = 2T_c/\Psi_w,2 \), with \( \Psi_w,2 = 2.1 \). Both wall temperatures are below the critical value, which corresponds to \( \Psi_c = 2 \) [see Eq. (8)]. Initially, the temperature of the mixture is assumed to be uniform, corresponding to \((\Psi_w,1 + \Psi_w,2)/2\); as the Lewis number is large, i.e., \( Le=100 \), though, heat transport is much faster than mass transport, and therefore, the temperature distribution reaches very rapidly a stationary linear profile, which later evolves, following the changes in the morphology of the mixture. Snapshots of the phase separation process in two dimensions for an off-critical mixture at different values of \( \alpha = 0, 10, 100, 1000 \) are shown in Fig. 1.

First, the phase separation process is diffusion-driven and takes place near the cold wall, forming single-phase droplet-like structures that later start to coalesce and grow, at an increasing rate for larger \( \alpha \). In addition, because of the temperature gradient, they tend to migrate toward the hot wall and, as they grow in size, they also accelerate.

We saw that, when \( \alpha = 10 \) and \( \Delta T = 0.3 \), the typical speed of the phase-separating droplets is about \( 3D/\alpha \), which corresponds to \( 0.1–1 \) mm/s [here we have assumed that \( D = 10^{-5} \) cm\(^2\)/s and \( \alpha = 10^{-5} \) cm, where this latter value can be calculated from Eq. (9) with \( \sigma = 10 \) dyn/cm]. This result is in agreement with the typical velocities observed in previous experimental works\(^{3,5,7,17}\), which are quite larger than the Marangoni speed.

To better understand the coupling between the concentration and temperature fields for a phase-separating system, snapshots of nondimensional temperature corresponding to the phase separation pattern above are presented in Fig. 2. As can be seen, after a rapid transient (due to a high value of the Lewis number \( Le=100)\) toward a linear profile, the temperature field develops spatial gradients as the droplets migrate toward the hot wall. Note that for a non-phase-separating

\[ 
FIG. 1. (Color online) Phase separation of an off-critical mixture with \( Le=100 \) at different nondimensional times \( t = 0.01, 0.1, \) and 0.4, with \( \alpha = 0, 10, 10^2, \) and \( 10^3 \) from top to bottom.
\]

\[ 
FIG. 2. (Color online) Nondimensional offset temperature (after subtraction of the linear profile) corresponding to separation pattern in Fig. 1 at different nondimensional times \( t = 0.01, 0.1, \) and 0.4, with \( \alpha = 0, 10, 10^2, \) and \( 10^3 \) from top to bottom. [Dark to light corresponds to values ranging from 0 to \( 10^{-3} \) (blue to red online).] 
\]
metastable system disturbed by composition fluctuations of small amplitude that are unable to trigger phase separation and with the initial temperature initialized as above, the composition fluctuations induce negligible temperature gradients since changes in the composition affect the inverse temperature only through the velocity field (due to a neglect of the last component of the nonlinear term [Eq. (29)] in the energy equation). Therefore, the temporal evolution of the temperature field is trivial (not shown) as it is smoothed out rapidly toward a linear profile due to the large Lewis number. Consequently, it is expected that for the same imposed gradient strength the average wall heat flux for a phase-separating mixture will always be greater than or equal to that for no phase separation. In a previous work on heat transfer enhancement during phase separation of binary mixtures without an imposed temperature gradient,27 it was found that the heat flux at the wall (as reflected in the dependence of the Nusselt number on the Peclet number) increases roughly by a factor of 2 at a Peclet number of $O(10^3)$ over the case with no convection, as confirmed experimentally by Poesio et al.7

In the case of an imposed temperature gradient, which is the focus of this work, we ran a series of simulations corresponding to phase separation of an off-critical mixture (with $\phi_0=0.35$) for different values of $\alpha=0,10,100,1000$ with a Lewis number $Le=1$ and a quenching depth $\xi=1-\Psi_w/\Psi_{w,1}=1/6$, together with an unperturbed gradient strength expressed as $\Delta\Psi=0.1$. Numerical results (Fig. 3) show a time-varying Nusselt number with an overshoot behavior at early times and a limiting value of 1 at large times (since the wall heat flux for different $\alpha$ must equal the imposed temperature gradient at large times). Consequently, peak values of the Nusselt number at different values of $\alpha$ can be taken as a measure of heat transfer enhancement. These values show a stronger enhancement as compared to the case without imposed temperature gradient, although the values reported here should be considered as preliminary since (i) they were computed from 2D calculations, and (ii) simulations on a 128$^2$ grid lead to smaller values for $\alpha=10,100$, although the same of value of about 3 is found at $\alpha=1000$.

In another simulation, we studied the droplet migration following an instantaneous off-critical quench from a one-phase region, with both wall temperatures specified as above (i.e., $\Psi_{w,1}=2.4$ and $\Psi_{w,2}=2.1$). In this case, drop-like microdomains of the minority phase start to appear at both walls due to spinodal instabilities, and subsequently move away converging toward the center of the domain (Fig. 4) since the dominant interaction between the drops is an attractive force due to chemical potential gradients. This causes coalescence and growth to occur predominantly near the center of the computational domain. Afterwards, since the dominant variations in the Korteweg stresses are due to the temperature gradient, droplets migrate toward the hot wall.

In order to further study the origin of the unusually large velocities of the collective drop migration, we simulated the thermocapillary migration of a single isolated droplet of the minority phase embedded in a continuous phase and initially located close to the cold (right) wall but not in contact with it (see Fig. 5, third and fourth rows). Again, the right wall is kept at a cold temperature $T_1=2T_c/\Psi_{w,1}$, with $\Psi_{w,1}=2.025,2.05,2.1,\ldots,2.8$, while the opposite wall is kept at an almost critical temperature, $T_2=2T_c/\Psi_{w,2}$, with $\Psi_{w,2}=2.001$. The droplet, of radius $R=12\delta$ and with composition $\phi_{eq}^A(T_1)$, is initially located close to the right (i.e., cold) wall, while the continuous phase has initially a uniform composition $\phi_{eq}^B(T_1)$, where $\phi_{eq}^A(T_1)$ and $\phi_{eq}^B(T_1)$ are the equilibrium compositions of the mixture at temperature $T_1$. Accordingly, the right side of the drop is at equilibrium while the left side is not, so the droplet will tend to change its composition (and that of the continuous phase as well) on its left side, “eating” material and moving toward the hot wall. Temperature profiles along the channel width for $\Delta\Psi=0.8$ with $\alpha=100$ and $Le=100$ (at midchannel in the $x$ direction) are presented in Fig. 6, showing that while the initial temperature profile corresponds to strong nonequilibrium, it tends to become linear at the late stages of drop migration. It appears that, for small enough values of the temperature gradient,

![Image](https://example.com/image.png)

**FIG. 3.** Nusselt number vs nondimensional time for different values of the fluidity with $Le=1$ and $\xi=1-\Psi_w/\Psi_{w,1}=1/6$ (at cold wall) together with gradient strength $\Delta\Psi=\Psi_{w,1}-\Psi_{w,2}=0.1$.

**FIG. 4.** (Color online) Phase separation of off-critical mixture with $\alpha=1000$ and $Le=100$ at different nondimensional times $t=0.1, 0.15,0.2,0.25,0.3,0.35,0.4,0.45,0.55$ (left to right and top to bottom).
ΔΨ ≤ 0.3, the droplet does not deform appreciably as it migrates to the hot wall; however, migration with appreciable droplet deformation occurs for ΔΨ ≈ 0.4. Using these results, the center locations of the equilibrium level set of the droplet composition field were tracked. However, because of high-frequency numerical noise in the time series, migration velocity could not be reliably obtained by straightforward numerical differentiation. Therefore, each time series was interpolated using an analytical expression, which then allowed to determine the migration velocity \( v \). First, we validated our results by considering the migration of a single drop for small temperature gradients, \( ΔΨ ≤ 0.1 \). In fact, temporal histories of droplet center location (Fig. 7) for small values of the Marangoni number (\( ΔΨ ≤ 0.1 \)) show that the drop moves with a nearly constant velocity \( v_m \), which is proportional to the temperature gradient and the radius of the drop, and whose value agrees well with the Marangoni velocity (see the classical solution of Young, Goldstein, and Block) for a nondeformable bubble in the limit of vanishing Reynolds and Marangoni numbers, \( U_m = (R / \eta) |\nabla \sigma| = \alpha(D / \bar{a})(RΔΨ / h), \) where \( |\nabla \sigma| \approx (\partial \sigma / \partial \Psi)ΔΨ / h \) has been evaluated using Eq. (9). In particular, our numerical simulations for small enough values of the Marangoni number and with \( \alpha = 10 \) show that migration velocities can be fitted to the following expression:

\[
v_m = 0.029 \frac{Ma}{R} \alpha_T, \tag{34}
\]

where \( Ma \) is the Marangoni number,

\[
Ma = \frac{U_m R}{\alpha_T} = \frac{\alpha R^2}{Le h \bar{a}} \Delta \Psi. \tag{35}
\]

The degree of agreement can be judged from Fig. 9, showing nondimensional maximum velocities versus the Marangoni number [Eq. (34)]. Although the smaller values of \( \Delta \Psi < 0.1 \) can be fitted accurately using Eq. (34), the agreement starts deteriorating at \( \Delta \Psi = 0.1 \).

This result is not obvious since numerical simulations were performed in two dimensions and, in addition, in our case the Marangoni number is not very small as \( Ma = 0.225ΔΨ \) when \( \alpha = 10 \). For larger temperature gradients, i.e., when \( \Delta \Psi ≥ 0.2 \), the drops initially accelerate, reaching a maximum speed, \( \nu \), and then decelerate (see Fig. 8). Therefore, the velocity of a far-from-equilibrium isolated drop exhibits an increase-decrease behavior, as was previously computed by Yin et al. for a spherical liquid droplet at large Marangoni number using a sharp-interface approach. Although a similar result (much less pronounced) was also found for gas bubbles by Oliver and DeWitt, it should be
noted that since the unperturbed temperature gradient from our simulations scales as \((\Delta \Psi / N_c) / (T_\ell / \dot{a})\) (with \(N_c = h / \dot{a}\)), the chosen \(\Delta \Psi\) values above together with the relatively low resolution of our simulations correspond to very large gradient strengths which cannot be achieved experimentally. The nondimensional maximum velocity \(v\) made dimensionless in \(D / h\) units is plotted in Fig. 9 versus the Marangoni velocity [Eq. (34)], showing a nonlinear dependence as \(\alpha \Delta \Psi\) increases. In fact, for large temperature gradients, we see that \(v\) can be far larger than the Marangoni velocity, similar to what we saw in the collective drop migration. A qualitative explanation of this behavior is that, as soon as a droplet is introduced within a large temperature-gradient field, it initially experiences a far-from-equilibrium condition, inducing a Korteweg force, which in turn gives rise to droplet speeds that are larger than the Marangoni velocity. Snapshots of temperature and composition (Fig. 5) show that, although the initial droplet location is in a strong temperature gradient, subsequently the temperature of the drop becomes approximately uniform, due to the large temperature-induced internal convection, so that the effective temperature gradient experienced by the drop is much smaller than the unperturbed one and the drop consequently decelerates (see also Fig. 6). On the other hand, in the case of collective drop migrations, drops coalesce with each other and remain therefore far from equilibrium, which is why we do not see the deceleration stage in our simulation.

We also ran simulations with a different concentration initial condition, corresponding to the droplet initially making contact with the cold wall (Fig. 5, first and second rows). Results in this figure and additional simulations for smaller values \(\Psi_{\ell,1} < 2.8\) show a critical gradient strength (expressed as \(\Delta \Psi^* = \Psi_{\ell,1} - \Psi_c\)) \(\Delta \Psi^* \in (0.6, 0.7]\) such that for \(\Delta \Psi \geq \Delta \Psi^*\) a pinch-off event occurs, with the droplet subsequently migrating to the hot wall. (We checked that no pinch-off occurs for \(\Delta \Psi < \Delta \Psi^*\).)

Finally, it should be noted that the latest stage of droplet migration, in view of our assumption of negligible inertial effects in the momentum balance, should be understood as a “quasi-static” approach to the hot wall, with the droplet ultimately adhering to it (see Fig. 5). Therefore, the decrease part of the increase-decrease behavior must include a deceleration to a quiescent state, affected by the finite size of the computational domain. Since our numerical results were computed at relatively low resolution, the terminal velocity of the droplet (which is likely to be smaller than the Marangoni velocity) cannot be resolved by the present dataset and will be addressed in future work using higher resolution simulations.

V. CONCLUSIONS

The objective of this work is to study numerically the effects of an imposed temperature gradient on the phase separation of a low-viscosity binary mixture in a channel-like geometry and, in particular, how phase transition can enhance heat transport. To that end, following the diffuse-interface model, we first simulated spinodal decomposition of a regular, off-critical binary mixture occurring after both of its boundaries are instantaneously cooled down to different temperatures below the critical temperature. The simulation results show a unidirectional Korteweg-driven motion of the phase-separating droplets due to the imposed temperature gradient and, in particular, that the dominant variations in the Korteweg stresses can be either due to chemical potential gradients, such as when the dominant interaction between the phase-separating droplets is an attractive force which causes coalescence, or to the imposed temperature gradient, which causes droplet migration in the direction of the temperature gradient. To investigate further the migration velocity in comparison with the Marangoni velocity, we ran isolated drop simulations in two dimensions showing that for near-equilibrium droplets, when the Marangoni (and Reynolds) number is very small, the drop moves with a constant velocity in good agreement with the Marangoni velocity. However, for larger strength of the imposed temperature gradient, corresponding to far-from-equilibrium conditions, the simulation results show an increase-decrease behavior in the
migration velocity, in agreement with the sharp-interface simulations by Yin et al.,23 with maximum speeds having a nonlinear dependence on the Marangoni velocity. Finally, we investigated a different concentration initial condition in the isolated drop simulations, with the droplet initially making contact with the cold wall, and found a critical strength for the unperturbed temperature gradient beyond which a pinch-off event occurs, with the droplet subsequently migrating toward the hot wall.

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APPENDIX A: THE ENERGY EQUATION

Now we show that the time derivative of the total energy of the system is equal to its energy dissipation through the boundaries, i.e.,

$$\frac{d}{dt} \int_V e d^3x = -\int_S \hat{n} \cdot \mathbf{J}_d d^2x,$$  \hspace{1cm} (A1)

where the integrals are taken over a material volume $V=V(t)$ with its bounding surface $S(t)$. Here, $e$ is the total energy of the mixture per unit volume, i.e., the sum of the kinetic, potential and internal energies, i.e.,

$$e = \frac{1}{2} \rho v^2 + V + u,$$  \hspace{1cm} (A2)

with $u$ denoting the thermodynamic internal energy, which here is simply related to the temperature as $u = \rho c T$, as the mixture is incompressible, while $V=\rho/\mathcal{M}_w \mathcal{G}_{NL}$ is the potential energy [see Eq. (13)] which, as we have seen, includes the nonlocal part of the free energy plus any additional potential energy term due to gravitational, electric, and other potential force fields. The following analysis is basically identical to that in de Groot and Mazur.32

First, we obtain a balance equation for the kinetic energy multiplying Eq. (2) by $v$ and volume integrating,

$$\frac{d}{dt} \int_V \left(\frac{1}{2} \rho v^2 \right) d^3x = -\int_S \hat{n} \cdot (\mathbf{J}_d \cdot v) d^2x$$

$$+ \int_V (\mathbf{J}_d \cdot \nabla v + \mathbf{F}_d \cdot v) d^3x,$$  \hspace{1cm} (A3)

where we have integrated by parts, applying the incompressibility condition. Then, we determine a balance equation for the potential energy, $V = \rho/\mathcal{M}_w \mathcal{G}_{NL}$, as

$$\frac{d}{dt} \int_V V d^3x = \int_V \left[ - (\nabla \cdot \mathbf{J}_d) \psi_{NL} + df \nabla \cdot \psi_{NL} \right] d^3x,$$  \hspace{1cm} (A4)

with $\psi_{NL} = (\rho R T/\mathcal{M}_w) \overline{\mu}_{NL}$. Here we have taken into account that $g_{NL} = \rho R T (\phi \overline{\mu}_{NL})$, $d\overline{\mu}_{NL}/dt = \rho R T \left[ \mu_{NL}(d\phi/dt) + \phi (d\overline{\mu}_{NL}/dt) \right]$, and we have considered that $\mu_{NL}$ is not an explicit function of $t$, so that $d\mu_{NL}/dt = v \nabla \mu_{NL}$. Therefore, integrating by parts, we obtain

$$\frac{d}{dt} \int_V V d^3x = -\int_S (\hat{n} \cdot \mathbf{J}_d) \psi_{NL} d^2x$$

$$+ \int_V (\mathbf{J}_d \cdot \nabla \psi_{NL} - \mathbf{F}_d \cdot \phi) d^3x.$$  \hspace{1cm} (A5)

Note that the work done by the Korteweg force, as that done by any other potential force, decreases the potential energy and at the same time increases the kinetic energy by the same amount [cf. Eqs. (A3) and (A5)]. Accordingly, that term drops out of the balance equation for the mechanical energy:

$$\frac{d}{dt} \int_V \left(\frac{1}{2} \rho v^2 + V \right) d^3x = -\int_S \hat{n} \cdot (\mathbf{J}_d \cdot v + \mathbf{J}_d \psi_{NL}) d^2x$$

$$+ \int_V (\mathbf{J}_d \cdot \nabla v + \mathbf{J}_d \cdot \nabla \psi_{NL}) d^3x.$$  \hspace{1cm} (A6)

Now, imposing that the total energy (A2) satisfy the balance equation (A1), we see that the total energy flux can be written as

$$\mathbf{J}_e = \mathbf{J}_u + \mathbf{J}_v + \mathbf{J}_d \psi_{NL},$$  \hspace{1cm} (A7)

which is the sum of, respectively, the internal energy flux (generally referred to as heat flux), the work dissipated by viscous forces, and the net potential energy loss. This last term describes the fact that when species $i$ diffuses out of the material volume, it carries an energy $\mathbf{J}_i \psi_i$, where $\psi_i$ is the potential energy [Eq. (11)] associated with component $i$. Finally, we derive the integral equation for the internal energy,

$$\frac{d}{dt} \int_V u d^3x = -\int_S \hat{n} \cdot \mathbf{J}_d d^2x$$

$$+ \int_V (-\mathbf{J}_u \cdot \nabla v - \mathbf{J}_d \cdot \nabla \psi_{NL}) d^3x,$$  \hspace{1cm} (A8)

corresponding to the differential form,

$$\frac{du}{dt} + \nabla \cdot \mathbf{J}_u = \dot{q},$$  \hspace{1cm} (A9)

where the heat generation term reads as

$$\dot{q} = -\mathbf{J}_u \cdot \nabla v - \mathbf{J}_d \cdot \nabla \psi_{NL}.$$  \hspace{1cm} (A10)

Naturally, the internal energy flux, $\mathbf{J}_{u,i}$, must be expressed through a constitutive equation. Here, we will consider the simplest case where, based on considerations of Appendix B [see Eqs. (B7) and (B9)], $\mathbf{J}_u$ is the sum of a Fourier diffusive flux and a diffusive term,

$$\mathbf{J}_u = -k \nabla T + \mathbf{J}_d h_{Th},$$  \hspace{1cm} (A11)

where $T$ is the temperature of the mixture, $k$ denotes the heat conductivity that, in general, depends on the composition, i.e., $k = k(\phi)$, while $h_{Th}$ is the thermodynamic partial enthalpy difference. In general, we should also add a Dufour diffusion
thermal flux, which is generally negligible, as discussed by Thiele et al.\textsuperscript{23} In addition, the internal energy density, $u$, is a known function of temperature and density. Considering that the density is a constant, here we will assume the simplest relation, $u = u(T)$, where, in general, $c = c(\phi)$ is the specific heat. The same energy balance was obtained by Antanovskii\textsuperscript{19,41} by maximizing the entropy of the system. Note that, integrating by parts the last term on the RHS of Eq. (A8), the heat generation term can also be written as

$$\dot{q} = -\mathbf{J}_s \cdot \nabla \mathbf{v} - \psi_{NL} \frac{d\phi}{dt}, \quad (A12)$$

while the internal energy flux becomes

$$\mathbf{J}_u = -k \nabla T + \mathbf{J}_h \tilde{h}, \quad (A13)$$

where $\tilde{h} = h_{\text{Th}} + \psi_{NL}$ denotes the total (i.e., thermodynamic plus nonlocal) partial enthalpy difference, considering that the nonlocal part of the chemical potential equals that of the enthalpy, being independent of temperature. The minus sign in the last term in the RHS of Eq. (A12) is due to the fact that heat is drawn to increase the chemical energy of the mixture, i.e., when both $\tilde{\mu}$ and $\phi$ are positive. In addition, Eq. (A13) shows that the internal energy flux for multicomponent mixtures can be written as the sum of a heat diffusive term and a heat transport term due to each diffusing species.

Note that, since $h = u + p/\rho$, the internal energy $u$ can be replaced by the enthalpy $h$ in the energy equation, as the $dp/dt$ term can be neglected in any low Mach number process. As shown by de Groot and Mazur,\textsuperscript{32} these same results are also valid for compressible, multicomponent mixtures. A more recent and complete derivation can be found in Thiele et al.\textsuperscript{23} and Madruga and Thiele.\textsuperscript{42}

**APPENDIX B: THE ENTROPY EQUATION**

Consider the Gibbs equation for an incompressible binary mixture,

$$T \frac{ds}{dt} = \frac{du}{dt} - \mu_{\text{Th}} \frac{d\phi}{dt}, \quad (B1)$$

with $\mu_{\text{Th}}$ denoting the dimensional thermodynamic chemical potential difference. Substituting Eqs. (A9) and (1), we obtain

$$T \frac{ds}{dt} = -\nabla \cdot (\mathbf{J}_u - \mathbf{J}_0 \mu_{\text{Th}}) + \dot{q} - \mathbf{J}_\phi \cdot \nabla \tilde{\mu}_{\text{Th}}. \quad (B2)$$

Rearranging, we have

$$\frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma, \quad (B3)$$

where

$$\mathbf{J}_s = \frac{1}{T} (\mathbf{J}_u - \mathbf{J}_0 \mu_{\text{Th}}) \quad (B4)$$

is the entropy flux, while

$$\sigma = -\frac{1}{T} \mathbf{J}_s \cdot \nabla T - \frac{1}{T} \mathbf{J}_\phi \cdot \nabla \tilde{\mu} - \frac{1}{T} \mathbf{J}_v \cdot \nabla \mathbf{v} \quad (B5)$$

is the entropy production, where $\tilde{\mu} = \mu_{\text{Th}} + \psi_{NL}$ is the total (i.e., thermodynamic plus nonlocal) dimensional chemical potential difference. Different, albeit equivalent, expressions can also be found in de Groot and Mazur\textsuperscript{32}, who used the equality

$$\nabla \tilde{\mu} = [\nabla \tilde{\mu}]_T - \tilde{\sigma} \nabla T, \quad (B6)$$

considering that $\tilde{h} = \tilde{\mu} + \tilde{s} T$, where $\tilde{h}$ and $\tilde{s}$ are the partial molar enthalpy difference and the partial molar entropy difference, respectively, while the subscript “$T$” indicates that the derivative must be taken at constant temperature. These expressions are valid also when $\tilde{h}$, $\tilde{\mu}$, and $\tilde{s}$ are the generalized quantities, i.e., composed of both thermodynamic and nonlocal parts, as the nonlocal part of the chemical potential difference does not depend on temperature and therefore it is equal to the nonlocal part of the partial molar enthalpy difference, while the partial molar entropy difference is identically zero. Finally, we obtain for the entropy flux and the entropy production:

$$\mathbf{J}_s = \frac{1}{T} (\mathbf{J}_u - \mathbf{J}_0 \mu_{\text{Th}}) \quad (B7)$$

and

$$\sigma = -\frac{1}{T} \mathbf{J}_s \cdot \nabla T - \frac{1}{T} \mathbf{J}_\phi \cdot [\nabla \tilde{\mu}]_T - \frac{1}{T} \mathbf{J}_v \cdot \nabla \mathbf{v}. \quad (B8)$$

Considering that the entropy production term is the sum of the products between thermodynamic forces and thermodynamic fluxes which are then related to each other through constitutive relations, this last expression of the entropy production reveals that entropy flux, $\mathbf{J}_s$, material flux, $\mathbf{J}_\phi$, and momentum flux, $\mathbf{J}_v$, must be related to the gradients of temperature, $\nabla T$, chemical potential (thermodynamic plus nonlocal) at constant temperature, $[\nabla \tilde{\mu}]_T$, and velocity, $\nabla \mathbf{v}$. This justifies the constitutive equations for the thermodynamic fluxes that we have shown previously [see Eqs. (14) and (A11)], i.e.,

$$\mathbf{J}_s = -k (\phi, T) \nabla T - C_1 (\phi, T) [\nabla \tilde{\mu}]_T, \quad (B9)$$

$$\mathbf{J}_\phi = -C_2 (\phi, T) \nabla T - D (\phi, T) [\nabla \tilde{\mu}]_T, \quad (B10)$$

$$\mathbf{J}_v - p \mathbf{I} = -\eta (\phi, T) \nabla \mathbf{v} + (\nabla \mathbf{v})^*, \quad (B11)$$

where $C_1$ and $C_2$ are the Dufour and the Soret coefficients, respectively, which, according to Onsager’s principle, are equal to each other. Here we have assumed that the mixture is microscopically isotropic so that, according to Curie’s principle, a vectorial flux, such as a heat or mass diffusion flux, cannot be coupled to a tensorial force, such as strain rate. In addition, we have implicitly assumed that, according to the conservation of angular momentum, the momentum flux is a symmetric tensor so that only the symmetric and traceless part of the velocity gradient can appear in the constitutive relation (B11), where fluid incompressibility has also been accounted for.


