Enhanced heat transport during phase separation of liquid binary mixtures

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We show that heat transfer in regular binary fluids is enhanced by induced convection during phase separation. The motion of binary mixtures is simulated using the diffuse interface model, where convection and diffusion are coupled via a nonequilibrium, reversible Korteweg body force. Assuming that the mixture is regular, i.e., its components are van der Waals fluids, we show that the two parameters that describe the mixture, namely the Margules constant and the interfacial thickness, depend on temperature as $T^{-1}$ and $T^{-1/2}$, respectively. Two quantities are used to measure heat transfer, namely the heat flux at the walls and the characteristic cooling time. Comparing these quantities with those of very viscous mixtures, where diffusion prevails over convection, we saw that the ratio between heat fluxes, which defines the Nusselt number, $N_{\text{Nu}}$, equals that between cooling times and remains almost constant in time. The Nusselt number depends on the following: the Peclet number, $N_{\text{Pe}}$, expressing the ratio between convective and diffusive mass fluxes; the Lewis number, $N_{\text{Le}}$, expressing the ratio between thermal and mass diffusivities; the specific heat of the mixture, as it determines how the heat generated by mixing can be stored within the system; and the quenching depth, defined as the distance of the temperature at the wall from its critical value. In particular, the following results were obtained: (a) The Nusselt number grows monotonically with the Peclet number until it reaches an asymptotic value at $N_{\text{Nu}} \approx 2$ when $N_{\text{Pe}} \approx 10^4$; (b) the Nusselt number increases with $N_{\text{Le}}$ when $N_{\text{Le}} < 1$, remains constant at $1 < N_{\text{Le}} < 10$, and then decreases when $N_{\text{Le}} > 1$; (c) the Nusselt number is hardly influenced by the specific heat; (d) the Nusselt number decreases as the quenching rate increases. All these results can be explained by physical considerations. Predictably, considering that convection is within the creeping flow regime, the Nusselt number is always of $o(10)$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2749810]

I. INTRODUCTION

In this work, we study how heat transport in liquid binary mixtures can be enhanced by the convection induced by phase separation. This effect is well known in evaporation and liquefaction, where the strong density difference between the two phases drives a very strong, turbulent convection, which enhances heat transfer. On the other hand, in liquid-liquid phase transitions, density differences are much lower, and for isopycnic systems they can even be negligible. In that case, another effect becomes relevant, namely the motion induced by chemical potential gradients (i.e., the so-called Korteweg reversible body force), which is a typical nonequilibrium phenomenon that has been studied in numerous previous works.\textsuperscript{1,2} Although the enhancement to heat transfer caused by this effect is much smaller than that due to density differences, it is not negligible by any means and, as shown in recent experiments, it can reduce cooling times by a factor 2 or 4.\textsuperscript{3} Surprisingly, as far as we can tell, this effect has not been previously studied.

If we exclude radiation, the transport of heat may occur with two different modalities, namely conduction and convection. In the former, heat propagates from hot to cold regions via a diffusive process, regulated by heat conductivity, while during convection heat is transported by a moving fluid. In turn, fluid motion is either imposed (i.e., forced convection) or it results from the changes in composition or density of the medium that are induced by temperature changes (i.e., natural convection). The mechanism of heat transport that is studied here pertains to this latter category, since convection is caused by the phase change induced by a temperature quench.

In general, when a binary mixture is brought from the single phase region of its phase diagram to the two-phase unstable region, it phase separates through a process that is referred to as spinodal decomposition. As shown in many experimental and numerical works, in low viscosity liquid mixtures this process is driven by the convection that is induced by phase transition, which is responsible for the experimentally observed enhanced coalescence among the droplets.\textsuperscript{4} Accordingly, it becomes natural to assume that during phase separation an effective heat diffusivity could be defined, resulting from the fluctuations of the velocity and temperature fields, just like in turbulent flows.

In this work, we simulated the phase separation of a binary mixture that is confined within a domain whose walls are instantaneously quenched below the critical temperature. Since we are interested in qualitative results, we confine ourselves to 2D simulations, which, as shown in previous works,\textsuperscript{5,6} produce results that are very similar to their 3D...
counterparts. As expected, the mixture starts to demix near the walls, where, correspondingly, a strong convection is induced, enhancing the transport of heat. The mixture is modeled through the diffuse interface model\cite{1,2} (otherwise called model H, in the taxonomy of Hohenberg and Halperin\cite{5}), which is based on the pioneering work of van der Waals,\cite{6} together with the Ginzburg-Landau theory of phase transition.\cite{7} This model was applied to model the spinodal decomposition of binary mixtures by Cahn and Hilliard\cite{8} and was later generalized to include hydrodynamics by Kawasaki.\cite{9} In the diffuse interphase model, convection is driven by a nonequilibrium body force, proportional to the gradient of the chemical potential difference. As noted by Jasnow and Viñals,\cite{10} when the system is composed of single-phase domains separated by sharp interfaces, this force, which is generally referred to as the Korteweg force, incorporates capillary effects, and plays the role of a Marangoni force. This was formally proven by Lowengrub and Truskinovsky\cite{11} and Jacqmin,\cite{12} who performed a careful matched asymptotic expansion and showed that the motion of sharp interfaces between immiscible fluids can be obtained as the outer expansion of the velocity field, calculated using the diffuse interface approach, and it satisfies the usual Marangoni-type boundary conditions at the interfaces. This model shows that during the early stages of phase separation, initial instabilities grow exponentially, forming, at the end, Marangoni-type boundary conditions at the interfaces. In this work, assuming it is in the viscous regime, we show instead that the temperature gradients within the droplet nearly vanish, enhancing the transport of heat. The mixture is modeled through the diffuse interface method,\cite{13,14} see Eq. (A25) in the Appendix. Accordingly, the ideal part of the free energy in Eq. (1) represents an entropic contribution, which is proportional to the temperature, while the excess part is an enthalpic term, depending on interparticle potentials and therefore independent of the temperature, so that $\Psi \propto 1/T$. Consequently, considering that at the critical point, when $T= T_c$ and $\phi= \phi_c=1/2$, the free energy has an inflection point, i.e., $\partial^2 g/\partial \phi^2=0$, so that $\Psi_c=2$, we obtain
\begin{equation}
\Psi = \frac{2T_c}{T}.
\end{equation}
Mixtures that behave in that way are denoted as regular.\cite{22} Since $s_{ex}=-(\partial g_{ex}/\partial T)_{\rho,\phi}$, we see that for regular mixtures $s_{ex}=0$, i.e., their entropy equals that of an ideal mixture. In addition, considering that $v_{ex}= (\partial g_{ex}/\partial \rho)_{T,\phi}$, since $g_{ex}$ is independent of $P$, we see that $v_{ex}=0$, i.e., their specific volume as well equals that of an ideal mixture (in our case, though, this last result is already implicit in the assumption of incompressibility).

II. GOVERNING EQUATIONS

A. Free energy of binary mixtures

Consider a homogeneous mixture of two species $A$ and $B$ with molar fractions $x_A=\phi$ and $x_B=1-\phi$, respectively, which are kept at temperature $T$ and pressure $P$. For simplicity, we assume that the molecular weights, specific volumes, and viscosities of $A$ and $B$ are the same; in particular, that means that we assume the mixture to be incompressible. The thermodynamic molar Gibbs free energy, $g_{th}$, is a coarse-grained free energy functional given by
\begin{equation}
g_{th}(\phi) = g_{id}(\phi) + g_{ex}(\phi),
\end{equation}
where $g_{id}$ is the Gibbs free energy of an ideal mixture,
\begin{equation}
g_{id}(\phi) = RT[\phi \ln \phi + (1-\phi)\ln (1-\phi)],
\end{equation}
where $R$ is the gas constant while $g_{ex}$ is the excess (i.e., nonideal) part of the free energy,
\begin{equation}
g_{ex}(\phi) = RT\Psi \phi(1-\phi),
\end{equation}
where $\Psi$ is a function of $T$ (it cannot depend on $P$, since the mixture is assumed to be incompressible).

This expression, which is generally referred to as the one-parameter Margules correlation,\cite{21} can be derived in terms of the difference between the intermolecular potentials among identical and different neighbors [see Eq. (A25) in the Appendix]. Accordingly, the ideal part of the free energy in Eq. (1) represents an entropic contribution, which is proportional to the temperature, while the excess part is an enthalpic term, depending on interparticle potentials and therefore independent of the temperature, so that $\Psi \propto 1/T$. Consequently, considering that at the critical point, when $T= T_c$ and $\phi= \phi_c=1/2$, the free energy has an inflection point, i.e., $\partial^2 g/\partial \phi^2=0$, so that $\Psi_c=2$, we obtain
\begin{equation}
\Psi = \frac{2T_c}{T}.
\end{equation}
In order to take into account the effects of spatial inhomogeneities, Cahn and Hilliard\textsuperscript{10} introduced the generalized specific molar free energy $g$, which is given by the expression

$$g(\phi, \nabla \phi) = g_{nl}(\phi) + \Delta g_{nl}(\nabla \phi),$$

where

$$\Delta g_{nl}(\nabla \phi) = \frac{a}{2} \sigma \nabla^2 (\nabla \phi)^2$$

is a non local molar free energy due to changes in composition, where $a$ represents the typical length of spatial inhomogeneities. As shown in the Appendix, $a$ depends on the temperature as

$$a = \bar{a} \sqrt{\frac{2T_c}{T}} = \bar{a} \sqrt{\nabla},$$

where $\bar{a}$ is a constant length, independent of the temperature, and we have substituted Eq. (4).

As shown by van der Waals, since the surface tension $\sigma$ is the energy stored in the unit area of the interface separating two phases at local equilibrium, we obtain

$$\sigma = \frac{1}{2} \rho RT a^2 \int (\nabla \phi)^2 dl - a \rho RT (\Delta \phi)^2 \bar{a} \sqrt{\Psi - 2},$$

where $(\Delta \phi)_{eq}$ is the composition difference between the two phases at equilibrium (see the Appendix). This shows that the characteristic length $a$ can be determined once surface tension is known.

From the molar free energy, we may define a generalized chemical potential difference $\bar{\mu}$ as\textsuperscript{10}

$$\bar{\mu} = \frac{\delta (g(\rho R T))}{\delta \phi} = \frac{\delta (g(\rho R T))}{\delta \phi} - \nabla \cdot \frac{\delta (g(\rho R T))}{\delta (\nabla \phi)}.\hspace{1cm}(9)$$

Substituting Eq. (5) into (9), we obtain

$$\bar{\mu} = \ln \frac{\phi}{1 - \phi} + \Psi (1 - 2 \phi) - a^2 \nabla^2 \phi.\hspace{1cm}(10)$$

\section*{B. Equations of motion}

Imposing that the number of particles of each species is conserved, we obtain the continuity equations,$^23$

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A) = 0, \hspace{0.5cm} \frac{\partial \rho_B}{\partial t} + \nabla \cdot (\rho_B \mathbf{v}_B) = 0,\hspace{1cm}(11)$$

where $\rho_A$ and $\rho_B$ are the molar concentrations of species $A$ and $B$, respectively, while $\mathbf{v}_A$ and $\mathbf{v}_B$ are their mean velocities. For an incompressible mixture composed of species with identical physical properties, Eq. (11) leads to the following continuity equations in terms of the molar fractions $x_A = \phi$ of the species $A$ (which is equal to its mass fraction):

$$\frac{d \phi}{dt} = \frac{\delta \phi}{\delta t} + \mathbf{v} \cdot \nabla \phi = - \nabla \cdot \mathbf{j},\hspace{1cm}(12)$$

where $d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla$ is the material derivative, $\mathbf{j} = \phi \mathbf{v} (1 - \phi) (\mathbf{v}_A - \mathbf{v}_B)$ is the diffusive molar flux, and $\mathbf{v}$ is the average velocity of the mixture, $\mathbf{v} = x_A \mathbf{v}_A + x_B \mathbf{v}_B$. In turn, the diffusive molar flux is proportional to the gradient of the generalized chemical potential gradient as (see Vladimirova \textit{et al.}\textsuperscript{24} for a discussion of this constitutive relation)

$$\mathbf{j} = - \phi (1 - \phi) \nabla \bar{\mu}.\hspace{1cm}(13)$$

Finally, substituting (10) into (13), we obtain

$$\mathbf{j} = - D \nabla \phi + D \phi (1 - \phi) \times [a^2 \nabla^2 \phi + 2 \Psi \nabla \phi + (2 \phi - 1) \nabla \Psi].\hspace{1cm}(14)$$

The term $D \nabla \phi$ in Eq. (14) represents the regular diffusion flux, while the term within square brackets vanishes for small concentrations of either solvents, i.e., when $\phi \rightarrow 0$ or $\phi \rightarrow 1$, and for ideal mixtures, i.e., when $\phi = \Psi = 0$. The $a^2$ term is always stabilizing, with $a$ being a function of temperature through Eq. (7). Finally, note that in all previous works, the last term on the right-hand side (RHS) in Eq. (14) was identically zero.

If the flow is slow enough that the dynamic terms in the Navier-Stokes equation can be neglected, the conservation of momentum leads to the following Stokes equation:

$$\nabla p = \eta \nabla^2 \mathbf{v} + \mathbf{F}_\phi, \hspace{0.5cm} \nabla \cdot \mathbf{v} = 0,\hspace{1cm}(15)$$

where $\eta$ is the mixture viscosity, which we assume, is composition-independent, while $\mathbf{F}_\phi$ is a reversible body force, which equals the generalized gradient of the free energy and therefore is driven by the concentration gradients within the mixture,$^{12}$

$$\mathbf{F}_\phi = \rho \frac{\delta g}{\delta \phi} = \rho RT \bar{\mu} \nabla \phi,\hspace{1cm}(16)$$

where $\rho=(\rho_A+\rho_B)$ is the mixture molar density (which we assume to be constant). The assumption of small Reynolds number is supported by previous simulations\textsuperscript{25} and by the experimental observation\textsuperscript{4,26,27} that, during phase separation of liquid mixtures with water-like viscosity, 10 $\mu$m drops move at speeds of $O(100 \mu$m/s). At equilibrium, when the free energy is uniform, the body force $\mathbf{F}_\phi$ is identically zero, and therefore there cannot be any convection of that type. In addition, when the mixture is composed of well-defined single-phase domains separated by a thin interface located at $\mathbf{r}=\mathbf{r}_s$, the body force $\mathbf{F}_\phi$ can be interpreted\textsuperscript{12} as a capillary force at $\mathbf{r}_s$,

$$\mathbf{F}_\phi(\mathbf{r}) = [\hat{n} \sigma \kappa + (1 - \hat{n}) \cdot \nabla \sigma] \delta (\mathbf{r} \cdot (\mathbf{r}_s - \mathbf{r})),\hspace{1cm}(17)$$

where $\sigma$ is the surface tension (8), while $\hat{n}$ and $\kappa$ are the unit vector perpendicular to the interface and the curvature at $\mathbf{r}_s$, respectively. Physically, $\mathbf{F}_\phi$ tends to minimize the energy stored at the interface, and therefore it drives, say, $A$-rich drops toward $A$-rich regions, enhancing coalescence. Note that Eq. (15) can also be written as

$$\nabla p' = \eta \nabla^2 \mathbf{v} - \rho RT \phi \nabla \bar{\mu}, \hspace{0.5cm} \nabla \cdot \mathbf{v} = 0,\hspace{1cm}(18)$$

with $p' = p - \rho RT \bar{\mu} \phi$, showing again that the motion induced by $\mathbf{F}_\phi$ is directed from high chemical potential difference to low, tending to restore chemical equilibrium.

These equations must be coupled to the equation of energy conservation,
\[ \frac{\partial \phi}{\partial t} = N_{pc} \nabla \psi \times \nabla \phi + \nabla \cdot \{ \nabla \phi - \phi (1 - \phi) \} \left( \frac{\Psi^2 + \Psi^2}{\Psi^2} \right) \psi \phi + (2 \phi - 1) \nabla \Psi \right], \]

\[ \psi = \frac{\alpha}{\rho cT} \frac{\partial \Psi}{\partial \tilde{t}}, \]

where \( c \) is the molar specific heat (the same for \( A \) and \( B \)), \( j_x \) is the diffusive heat flux, while \( \tilde{q} \) is the energy dissipation term. Assuming a simple Fourier constitutive relation, we have

\[ j_x = -k \nabla T, \]

where \( k \) is the heat conductivity, which in general depends on the composition, e.g., \( k = k(\phi) \), although here we assume it is independent of \( \phi \). The energy dissipation term is the sum of three contributions: the dissipative work of the external forces, \( F_c \), viscous dissipation, and the enthalpy of mixing,

\[ \tilde{q} = F_c \cdot \nabla + \eta [\nabla \nabla \phi] + \tilde{h}_{\text{mix}}, \]

where \( \tilde{h}_{\text{mix}} = \rho h_{\text{mix}} \phi \) depends on the energy \( h_{\text{ex}} \) that is either generated or consumed when the two components of the mixture are isothermally mixed together. Note that \( F_\phi \) does not contribute to \( \tilde{q} \), since it is a reversible process.\(^5\) In our case, since viscous dissipation is negligible and there are no external forces, dissipation is due exclusively to the enthalpy of mixing. Now, applying classical thermodynamics, we obtain

\[ \tilde{h}_{\text{ex}} = T \left[ \frac{\partial (g_{\text{ex}}/RT)}{\partial T} \right]_P \phi, \]

showing that for regular mixtures, when \( g_{\text{ex}} \) does not depend on \( T \), \( h_{\text{ex}} = g_{\text{ex}} \), and therefore

\[ \tilde{q} = \rho RT \Psi \phi (1 - \phi) \phi. \]

Now we restrict our analysis to two-dimensional systems, so that the velocity \( \nabla \psi \) can be expressed in terms of a stream function \( \psi \), i.e., \( \psi_x = -\partial \phi / \partial y \) and \( \psi_y = -\partial \phi / \partial x \). Consequently, substituting Eq. (16) into (15) and rearranging, we obtain

\[ \frac{\partial \phi}{\partial t} = \nabla \psi \times \nabla \phi - \frac{1}{\rho} \phi \nabla \cdot j, \]

\[ \eta \nabla^4 \psi = \nabla \mu \times \nabla \phi, \]

\[ \frac{\partial T}{\partial \tilde{t}} = \nabla \psi \times \nabla T + \alpha \nabla^2 T + \frac{\tilde{q}}{\rho c}, \]

where \( \alpha = k / \rho c \) is the heat diffusivity, while

\[ A \times B = A_1 B_2 - A_2 B_1. \]

Since the main mechanism of mass transport at the beginning of phase segregation is diffusion, the length scale of the process is the microscopic length \( \alpha \). Therefore, using the scaling

\[ \tilde{r} = \frac{r}{\alpha}, \quad \tilde{\tau} = \frac{D}{\alpha^2}, \quad \tilde{\psi} = \frac{1}{\alpha \Psi} \psi, \]

and substituting Eqs. (4), (7), (14), and (23) into Eqs. (24)–(26), we obtain the governing equations in terms of concentration \( \phi \), stream function \( \psi \), and inverse temperature \( \Psi \),

\[ \tilde{r} = \frac{1}{\alpha}, \quad \tilde{\tau} = \frac{D}{\alpha^2}, \quad \tilde{\psi} = \frac{1}{\alpha \Psi}, \]

where \( \tilde{c} = c/R \) is the nondimensional specific heat, \( N_{le} = \alpha / D \) is the Lewis number, while the nondimensional term,

\[ \tilde{N}_{pc} = \frac{a^2 \rho RT}{D \eta}, \]

III. NUMERICAL RESULTS

The governing equations (29)–(31) were solved on a uniform two-dimensional square grid with constant width \( (x_n,y_n) = (\Delta x_n, \Delta y_n) \), \( i = 1, \ldots, N, j = 1, \ldots, N \), where \( N = 128, 256, 512 \) and time discretization \( \tilde{\tau} = n \Delta \tau, \quad n = 0, 1, 2, \ldots \). The physical dimensions of the grid were chosen such that \( \Delta x / \Delta y = \Delta x / \Delta y = 3/2 \), such space discretization was based on a cell-centered, second-order accurate approximation. The time step \( \Delta \tau \) satisfies \( \Delta \tau / (\tilde{c}^2 / D) = 0.01 \sim 0.001 \), such a choice was determined semiempirically in order to maintain the stability of the numerical scheme. Note that the nonlinearity of the equations prevents a rigorous derivation of the stability constraints on \( \Delta t \), but one can roughly estimate that the size of \( \Delta t \) will scale as \( O(\Delta x^4, \Delta y^4) \), which is the order of the highest operator in the discretized system.

The time integration from \( \tilde{r} = n \Delta \tau \) to \( \tilde{r} = (n+1) \Delta \tau \) was achieved in three steps. First, we computed the stream function by solving the biharmonic equation (25) with the source term evaluated at the time \( \tilde{r} = n \Delta \tau \), using a fast Fourier transform (FFT) algorithm; second, we computed the inverse temperature distribution, using the concentration field evaluated at the previous step; third, Eq. (24) was advanced in time, using the velocity and temperature fields computed from the updated stream function and updated inverse temperature, through a straightforward explicit Eulerian step. This makes the entire scheme \( O(\Delta \tau) \) accurate in time, which is accept-
able for our problem, since the size of the time step was kept very small anyway by the stability constraint. The boundary conditions were no flux for the concentration field and no slip for the velocity field at the two walls where the temperature quench is applied, and periodic boundary conditions at the other two walls. The discretization of the derivatives near the boundaries was modified to use only interior points. We introduced some amount of randomness into the system through a background noise in the concentration field, $\phi$, with $\langle \delta \phi \rangle = 0$ and $\langle (\delta \phi)^2 \rangle^{1/2} = 0.001$, which was uncorrelated both in space and in time. In two separated sets of simulations, the noise was either added in the initial condition only, as in Furukawa, or introduced at each time step and then subtracted at the next time step, only to be replaced with another spatially uncorrelated background noise of the same amplitude, as in Vladimirova et al. This last procedure, which is equivalent to adding noise to the flux $j$ on the right-hand side of Eq. (13), is fully conservative in the sense that the volume integral of the composition $\phi$ is not altered by addition of the ad hoc noise. In fact, since for deep quenches the Ginzburg inequality is satisfied, the background noise does not affect the behavior of the system, and only determines the instant of time when the system departs from its initial uniform state: once the linear regime is reached, the presence of the noise becomes irrelevant.

All our simulations were carried out assuming that, initially, the mixture has a uniform critical composition, $\phi_0 = 0.5$, and a temperature $T(t=0) = T_0$ above the critical temperature $T_c$, so that $\Psi(t=0) = \Psi_0 = 1.9 < \Psi_c = 2$, where $\Psi_c = 2$ is the critical value of the Margules parameter. Then, at time $t=0$, two of the walls of the box are quenched instantaneously to a temperature $T_w$ well below the critical temperature, so that $\Psi_\phi > 2$ at the walls. Different values of $\Psi_w$ have been considered, ranging from $\Psi_w = 2.1$ to 5. Time was measured as $t = (10^6 D^2 / \alpha) \tilde{t}_s$, where $\tilde{t}_s = 10^{-5} \tau$ is a nondimensional coarse time. Since typical values of $D$ and $\alpha$ are $10^{-5}$ cm$^2$/s and $10^{-5}$ cm, respectively, then $\tilde{t}_s \sim t / (1 \text{s})$.

Various simulations were carried out for different box sizes, Peclet and Lewis numbers, and specific and quenching depths. In all cases, the mixture starts to phase-separate at the walls; then, as heat losses penetrate deeper within the domain, demixing takes place everywhere, until, at steady state, the temperature of the mixture reaches its equilibrium value. First, we observed that (see Fig. 1) the process of cooling, as well as that of phase separation, is accelerated by convection. As shown in Fig. 1(a), when $N_p = 0$, the mixture phase-separates through the formation of bicontinuous structures; since the two phases have the same heat conductivity, though, the isothermal lines (not shown here) remain parallel to the walls through the whole process, as they move toward the center of the domain. On the other hand, in the presence of convection, i.e., when $N_p = 10^2$ [see Fig. 1(b)], warm fluid tends to move toward the wall; accordingly, the isothermal lines do not remain parallel to the walls and, most important, they move faster than in the previous case.

The main result of our simulation was to determine how such heat transport enhancement depends on the characteristics of the process, namely the Peclet and Lewis numbers, the specific heat, and the quenching depth. The most obvious way to describe the heat transfer enhancement is through the Nusselt number, which is defined as the ratio between the heat flux $J_q$ at the wall and the heat flux that one would have in the absence of convection, $(J_q)_{N_p = 0}$, i.e.,

$$N_{Nu} = J_q / (J_q)_{N_p = 0}. \quad (33)$$

Although $N_{Nu}$ would seem to be a function of time, we see that it actually remains almost constant and therefore can be used effectively to characterize the enhancement to heat transport due to phase transition.

Another way to characterize heat transport is through the cooling time. In fact, denoting by $\bar{T}$ the average temperature of the fluid, we know that, in the absence of convection, at long times, $t \gg \tau = L^2 / \alpha$, a slab cools down following the equation

$\text{FIG. 1. Evolution of the concentration field for } N_p = 0 \text{ (top) and } N_p = 10^2 \text{ (bottom) when } N_d = 1, \zeta = 0.05, \text{ and with no source term. The snapshots are taken at } t = 50, 70, \text{ and } 120, \text{ where } t \text{ is expressed in } a^2 / D \text{ units.}$
\[ T_w - \bar{T} = \Delta T = \Delta T_0 e^{-\sigma \tau} + O(e^{-\sigma \tau}) \]

where \( \tau \) is a characteristic cooling time and \( L \) is the width of the domain. We saw that in all cases Eq. (34) is satisfied, provided that the heat diffusivity \( \sigma \) is replaced with an effective heat diffusivity \( \sigma^e \). Not surprisingly, we saw that with very good approximation,

\[ N_{Nu} = (\tau)_{Pe=0}/\tau = \sigma^e/\sigma, \]

thus confirming that the Nusselt number represents the enhancement to heat transport due to phase transition.

At this point, we show how \( N_{Nu} \) depends on the Peclet number, the Lewis number, the specific heat, and the quenching depth,

\[ \zeta = 1 - \frac{\Psi_w}{\Psi_c} = 1 - \frac{T_w}{T_e}, \]

where \( \Psi_c = 2.0 \) is the critical value of the Margules coefficient, representing how much below the critical temperature the walls have been cooled down.

First, in Fig. 2 we see that heat transport increases monotonically with \( N_{Pe} \), until it reaches a plateau at \( N_{Nu} = 2.0 \) when \( N_{Pe} = 10^6 \). This result is in agreement with previous findings, showing that the induced fluid velocity grows linearly with \( N_{Pe} \) for \( N_{Pe} < 10^3 \), while at larger \( N_{Pe} \) it reaches a plateau.

In Fig. 3, we show the dependence of \( N_{Nu} \) on \( N_{Le} \), revealing that the cooling speed increases as the Lewis number increases when \( N_{Le} < 1 \), it remains constant at \( N_{Nu} = 1.55 \) when \( 1 < N_{Le} < 10 \), and then it decreases when \( N_{Le} > 1 \). This behavior is due to the fact that, as \( N_{Le} \) increases, i.e., \( \alpha \) increases and/or \( D \) decreases, there are two competing effects. On the one hand, as \( D \) decreases, \( N_{Pe} \) increases, thereby enhancing heat transport, while, on the other hand, as \( \alpha \) increases, heat conduction also increases and therefore \( N_{Nu} \) tends to decrease. When \( N_{Le} \) is small, the first of these effects prevails: in fact, as \( N_{Le} \to 0 \) (i.e., \( D \to \infty \) while \( \alpha \) is kept constant), heat transport is only conductive and therefore \( N_{Nu} \to 1 \). On the other hand, when \( N_{Le} \) increases further, the enhancement due to convection reaches a plateau (see Fig. 2), while conduction continues to increase, so that the Nusselt number starts to decrease and, in fact, \( N_{Nu} \to 1 \) as \( \alpha \to \infty \), i.e., when heat is transported mainly by conduction.

In Fig. 4, we see the dependence of \( N_{Nu} \) on the specific heat \( \tilde{c} \). Now, as \( \tilde{c} \) measures the heat capacity of the mixture, \( N_{Nu} \) decreases as \( \tilde{c} \) increases, as expected. However, we see that the influence of the specific heat on the cooling speed is really very limited, unless \( \tilde{c} \) becomes unreasonably small.

Finally, we determined how the heat transfer enhancement depends on the quenching rate \( \zeta \), defined in Eq. (36). In Fig. 5, we show the results of the simulations conducted by keeping \( \Psi_0 = 1.9 \), \( Pe = 0.0 \) and \( 10^2 \), while \( \Psi_w = 2.1, 2.4, 3.0, \) and \( 4.0 \). Unexpectedly, at first, we see that heat transport is more influenced by convection at low quenching than at high. This is due to the fact that, as \( \zeta \) increases, conductive heat flux increases proportionally, i.e., \( J_q \sim \zeta \), while the increase of its convective counterpart is slower, i.e., \( \sim \zeta^{1/2} \). In fact, when \( \zeta \to \infty \), we see that \( N_{Nu} \to 1 \), as expected. This result complements Fig. 8 of Poesio et al., who found experimentally that, on approaching the critical temperature, i.e., when \( \zeta < 0.03 \), \( N_{Nu} \) tends to 1, as expected. In future works, we intend to simulate this case.

**IV. CONCLUSIONS**

The objective of this work is to investigate how phase transition (and, in general, the fact of being thermodynamically in a state of nonequilibrium) can enhance heat transport. To do that, we simulated the phase separation of a regular liquid binary mixture occurring when the boundaries (i.e.,
FIG. 5. The Nusselt number, $N_{Nu}$, as a function of the quenching depth, $\zeta$, when $N_{Pe}=10^5$, $N_{Le}=1$, and with no source term.

walls of the container where the mixture is kept) are quenched to a temperature below its critical value.

Our theoretical approach follows the diffuse interface model, where convection and diffusion are coupled via a nonequilibrium, reversible body force that is associated with the Korteweg stresses. This, in turn, induces a material flux, which enhances both heat and mass transfer. Unlike previous studies, here the equation of energy conservation is developed in detail, showing that the influence of temperature is twofold: on the one hand, it influences phase transition directly, as the system is brought from the single-phase to the two-phase region of its phase diagram (or vice versa). On the other hand, temperature can also change surface tension, that is, the excess free energy stored within the interface at equilibrium. Assuming that the mixture is regular, i.e., it behaves like a van der Waals fluid, these two effects are described through a $T^{-1}$ dependence of the Margules parameter and through a $T^{-1/2}$ dependence of the characteristic interfacial thickness. In addition, the heat of mixing can also be accounted for, as it equals the excess free energy. Finally, we obtained a set of coupled, strongly nonlinear equations, which we integrated in 2D, using a finite-difference approach.

The results of our simulations showed that, as heat is drawn from the bulk to the walls, the mixture phase-separates at first in the vicinity of the walls, and then, later, deeper and deeper within the bulk. During this process, convection may arise, due to the above-mentioned nonequilibrium, reversible body force, thus enhancing heat transport and, in particular, increasing the heat flux at the walls. As in any type of convective heat transport, this enhancement can be described in terms of the Nusselt number, defined as the ratio between the heat flux at the wall and the heat flux that one would have in the absence of convection. We showed that the Nusselt number is constant in time and it is also equal to the ratio between the characteristic times of cooling in the absence and in the presence of convection, respectively. The Nusselt number is a function of the Peclet and Lewis numbers, the specific heat of the mixture, and the quenching depth, defined through Eq. (36), as shown in Figs. 2–5. In particular, we found that (a) when the Peclet number becomes large, the Nusselt number reaches an asymptotic value (see Fig. 2); (b) the Nusselt number increases with the Lewis number when $N_{Le}<1$, remains constant at $1<N_{Le}<10$, and then it decreases when $N_{Le}>10$ (see Fig. 3); (c) the specific heat hardly influences the Nusselt number, unless $c$ becomes extremely small (see Fig. 4); (d) the Nusselt number decreases as the quenching rate increases (see Fig. 5).

Finally, we should stress that, as the two phases here have the same density and since there is no applied pressure difference, fluid motion is in the viscous regime, i.e., it has very small Reynolds numbers, and therefore it is not surprising that the Nusselt number that we determined is always of $O(10)$, in agreement with recent experimental findings.

On the other hand, when the fluid motion is in the inertial regime, as in a typical evaporator, the density difference between the two phases induces a much stronger, turbulent convection, and consequently typical Nusselt numbers are much larger.

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APPENDIX: FREE ENERGY OF NONHOMOGENEOUS SYSTEMS

1. Pure fluids

In a dense fluid, the Helmholtz free energy depends on the intermolecular forces, which are a combination of weak and strong forces. Fortunately, strong interactions nearly balance each other, so that the net forces acting on each molecule are weak and long-range. In addition, the mean-field approximation is assumed to be applicable, meaning that molecular interactions are smeared out and can be replaced by the action of a continuous effective medium (see Pismen).

Based on these assumptions, the case of dense fluids can be treated as that of nearly ideal gases, so that, allowing for variable density, the molar Helmholtz free energy at constant temperature $T$ can be written as

$$f[\rho(x)] = f_{id} + \frac{1}{2}RTN_A \int \left(1-e^{-U(r)/kT}\right)\rho(x + r)d^3r.$$  \hspace{1cm} (A1)

Here $k$ is Boltzmann’s constant, $R=N_A k$ is the gas constant, with $N_A$ the Avogadro number, $U=U(r)$ is the pair interaction potential, which depends on the distance $r=|r|$, $\rho=N/V$ is the molar density, the factor 1/2 compensates counting twice the interacting molecules, while the first term on the RHS,

$$f_{id} = RT \ln \rho,$$  \hspace{1cm} (A2)

is the molar free energy of an ideal gas (where molecules do not interact). Now, assume that the interaction potential consists of a long-range term, decaying as $r^{-6}$ (like in the Lennard-Jones potential), while the short-range term is replaced by a hard-core repulsion, i.e.,
where $d$ is the nominal hard-core molecular diameter, $\ell$ is a typical intermolecular interaction distance, and the nondimensional constant $U_0$ represents the strength of the intermolecular potential. When the density is constant, Eq. (A1) gives the thermodynamic free energy, $f_{th}$,

$$f_{th} = f_{id} + f_{ex},$$

(A4)

where

$$f_{ex} = RT \rho B(T),$$

(A5)

is the excess (i.e., the nonideal part) of the free energy, with

$$B(T) = \frac{1}{2} N_A \int_0^\infty (1 - e^{-U(r)/kT})4\pi r^2 dr$$

(A6)

denoting the first virial coefficient. This integral can be solved with $U_0 \ll kT$, obtaining the typical virial coefficient of a van der Waals fluid, $B(T) = b - a/(RT)$, where $b = 2/3 \pi \rho \ell^3 N_A$ is the excluded molar volume and $a = 2/3 \pi \rho \ell^6 N_A^2$ is a pressure adding term. From this expression of the free energy, applying the thermodynamic equality $P = (\partial f_{id}/\partial \bar{v})_T$, where $\bar{v} = \rho^{-1}$ is the molar volume, we obtain the van der Waals equation,

$$\left( P + \frac{a}{\bar{v}} \right)(v - b) = RT.$$  

(A7)

Finally, imposing that the critical point in the $P-v$ curve is a horizontal inflection point, the constants $a$ and $b$ in the van der Waals equation can be determined as functions of $T_C$, $P_C$, and $v_C$; and from there, considering that $P_C v_C / RT_C = 3/8$, with easy albeit tedious algebra, we obtain

$$\left( \frac{\ell}{d} \right)^2 = \frac{3}{2} \left( \frac{kT_C}{U_0} \right)^{1/3}.$$  

(A8)

Now, suppose that the molar density of the system is not constant. Accordingly, Eq. (A1) can be rewritten as

$$f(x) = f_{th}(x) + \Delta f_{id}(x),$$  

(A9)

where $f_{th}$ is the molar free energy (A4), corresponding to a system with constant density, while, when $U_0 \ll kT$,

$$\Delta f_{id}(x) = \frac{1}{2} N_A \int_{x > d} U(r)[\rho(x + r) - \rho(x)] d^3 r$$  

(A10)

is a nonlocal molar free energy, due to density changes, typical of the diffuse interface model. In fact, when there is an interface separating two phases at equilibrium, this term corresponds to the interfacial energy. This result is a direct consequence of the “exact” expression (A1), showing that the free energy is nonlocal, that is, its value at any given point does not depend only on the density at that point, but also on the density at neighboring points. As stated by van der Waals, the error that we commit in assuming a dependence on the density only at the point considered vanishes completely when the state of equilibrium is that of a homogeneous distribution of the substance. [...] If, however, the state of equilibrium is one where there is a change of density throughout the vessel, as in a substance under the action of gravity, then the error becomes general, however feeble it may be.”

Now, in (A10) the molar density can be expanded as

$$\rho(x + r) = \rho(x) + r \cdot \nabla \rho(x) + \frac{1}{2} r r \nabla \nabla \rho(x) + \cdots.$$  

(A11)

As we have tacitly assumed that the system is isotropic, we see that the contribution of the linear term vanishes, so that, at leading order, we obtain (see Pismen)

$$\Delta f_{id}(x) = -\frac{1}{2} RT \nabla^2 \rho(x),$$  

(A12)

with

$$K = \frac{2 \pi N_A \ell^6}{3 kT} \frac{d^3}{d} = \frac{9 \pi TC}{4 T} N_A d^6,$$  

(A13)

where we have substituted Eq. (A8). Note that, defining a nondimensional molar density, $\bar{\rho} = N_A d^3 \rho$, the nonlocal free energy can be rewritten as

$$\Delta f_{id}(x) = -\frac{1}{2} RT \nabla^2 \bar{\rho}(x),$$  

(A14)

where

$$a = \sqrt{\frac{9 \pi TC}{4 T} d}$$  

(A15)

is a characteristic length.

The total free energy is, therefore,

$$F = \int \rho f d^3 x,$$  

(A16)

where $\rho f$ is the free energy per unit volume. Now, integrating by part and applying no-flux or periodic boundary conditions, we see that $\rho f$ in Eq. (A16) can be written as

$$\rho f = RT \bar{\rho} f_{th} + \frac{1}{2} \dot{a}^2 \nabla \bar{\rho}^2,$$  

(A17)

where $\bar{f} = f/ (RT N_A d^3)$.

### 2. Regular binary mixtures

The molar free energy of a binary mixture can be determined using the same procedure as for single component systems. Consider a mixture composed of species A and species B, with molar fractions $x_A = \phi$ and $x_B = (1 - \phi)$, assuming that the two species are incompressible and have the same molar weight, so that the total molar density $\rho$ is constant. First, let us determine the free energy of the mixture when its composition is uniform. Starting from Eq. (3), we obtain the thermodynamic molar Gibbs free energy, $g_{th}$, considering the definition of the Gibbs free energy, $g = f + PV = u + TS + PV$:

$$g_{th}(\phi) = g_{id}(\phi) + g_{ex}(\phi).$$  

(A18)

Here, $g_{id}$ is the Gibbs free energy of an ideal mixture, which is a mixture where the intermolecular potentials $U_{ij}$ between molecule i and molecule j are all the same, i.e., $U_{AA} = U_{BB} = U_{AB}$. This statement is a consequence of Eq. (A24) below. Accordingly, $g_{id}$ is the sum of the free energies
of its components, and thus, generalizing the expression of the free energy for a single component fluid, $RT \ln \rho$, we obtain
\[ g_{\text{in}} = RT \left[ x_A \ln(x_A \rho) + x_B \ln(x_B \rho) \right], \quad (A19) \]
that is,
\[ g_{\text{in}} = g_0 + RT \left[ \phi \ln \phi + (1 - \phi) \ln(1 - \phi) \right], \quad (A20) \]
where $g_0 = RT \ln \rho$ is the free energy of the mixture before mixing and, being a constant, has been omitted in Eq. (2). Note that, while for a pure fluid the molar density $\rho$ is a variable, here the total molar density is constant and the variables are the molar densities of the two components, $x_A$ and $x_B$.

The second term on the RHS of Eq. (A18), $g_{\text{ex}}$, is the so-called excess, i.e., nonideal, part of the free energy, whose form is particularly convenient for regular mixtures. In that case, Van Laar assumed\(^{27}\) that (i) the two species composing the mixture are of similar size and energies of interaction, and (ii) the van der Waals equation of state applies to both the pure fluids and the binary mixture. Consequently, regular mixtures have negligible excess volume, $v_{\text{ex}} = 0$, and excess entropy of mixing, $s_{\text{ex}} = 0$, i.e., their volume and entropy coincide with those of an ideal gas mixture. Thus, as the excess Gibbs free energy is equal to the excess Helmholtz free energy, i.e., $g_{\text{ex}} = f_{\text{ex}}$, it can be shown\(^{22}\) that the Gibbs free energy of a regular mixture with molar fractions $x_A$ and $x_B = 1 - x_B$ is
\[ g_{\text{ex}} = x_A a_A + x_B a_B - a_{\text{mix}}, \quad (A21) \]
where we have used obvious notations to indicate the Van der Waals constants ($a$ and $b$) for the pure fluids, $A$ and $B$, and for the mixture, “mix.” Therefore, we see that the excess free energy does not depend on $T$ and on $P$ and, therefore, since $s_{\text{ex}} = -(\partial g_{\text{ex}}/\partial T)_{P, x}$ and $v_{\text{ex}} = (\partial g_{\text{ex}}/\partial P)_{T, x}$, we confirm that $s_{\text{ex}} = 0$ and $v_{\text{ex}} = 0$, i.e., the excess entropy of mixing and the excess volume of mixing of a regular mixture are both zero.

The same conclusion can be reached starting from the fundamental expression (A1) for the Helmholtz free energy and considering that $g_{\text{ex}} = f_{\text{ex}}$ obtaining a generalization of Eq. (A5), i.e., $f_{\text{ex}} = RT \rho B(T)$, where $B$ is the virial coefficient,
\[ B = x_A^2 B_{AA} + 2x_Ax_B B_{AB} + x_B^2 B_{BB}, \quad (A22) \]
and $B_{ij}$ characterizes the repulsive interaction between molecule $i$ and molecule $j$ [see Eq. (A6)]. In particular, for symmetric mixtures, with $U_{AA} = U_{BB} = U_{AB}$, we have $B_{AA} = B_{BB} \neq B_{AB}$. Accordingly, denoting $x_A = \phi$, we obtain:
\[ g_{\text{ex}} = RT \Psi(T, P) \phi (1 - \phi), \quad (A23) \]
where
\[ \Psi(T, P) = 2 \rho(B_{AB} - B_{AA}) \quad (A24) \]
is the so-called Margules coefficient.\(^{22}\) In particular, for an ideal mixture, $B_{AA} = B_{AB} = \rho$ and, therefore, $\Psi = 0$. For a mixture composed of van der Waals fluids at constant pressure, substituting the expression $B = b - a/RT$ [see below Eq. (A6)] for the virial coefficient and assuming that the characteristic lengths $\ell$ and $\ell$ are the same for the two species, we obtain
\[ \Psi = \frac{2 \rho}{RT} (a_{AA} - a_{AB}) = \frac{4 \pi N M_w \ell^6}{3 RT d^3} (U_{0,AA} - U_{0,AB}), \quad (A25) \]
where $U_{0,AA}$ and $U_{0,AB}$ characterize the strength of the potential between molecules of the same species and that of different species, respectively. From this expression, we see that $\Psi$ is proportional to $T^{-1}$ and is independent of $P$, confirming that $g_{\text{ex}}$ is independent of $T$ and $P$. Note that when $\Psi > 0$, the repulsive forces between unlike molecules, $\propto U_{0,AB}/d$, are weaker than those between like molecules, $\propto U_{0,AA}/d$. As shown in Mauri et al.,\(^{14}\) when the solution is not symmetric, this approach is easily generalized by defining two Margules coefficients.

Now, suppose that the composition of the system is not constant. Accordingly, starting from Eq. (A1), we obtain a generalization of Eq. (A9), i.e.,
\[ g(\phi, \nabla \phi) = g_{\text{in}} (\phi) + \Delta g_{\text{ex}} (\nabla \phi), \quad (A26) \]
where $g_{\text{in}}(\phi)$ is the molar free energy (A18) corresponding to a system with uniform composition, while $\Delta g_{\text{ex}}(\nabla \phi)$ is a nonlocal molar free energy, due to changes in composition, typical of the diffuse interface model. In fact, when there is an interface separating two phases at equilibrium, this term corresponds to the interfacial energy. Using the same procedure as that seen in the preceding section, we can derive an expression similar to (A17), originally due to Cahn and Hilliard,\(^9\)
\[ \Delta g_{\text{ex}} (\nabla \phi) = \frac{1}{2} \sigma \ell^2 (\nabla \phi)^2, \quad (A27) \]
where the interface energy per unit area $\sigma$ is a characteristic length, roughly equal to the interface thickness at equilibrium, which, for a regular mixture, has the same value as that seen in Eq. (A15), i.e., $\sigma = (9 \pi \ell^2/4T)d$, where $d$ is the excluded volume length defined in (A3). Now, consider that, at equilibrium, the mixture is segregated in two phases, separated by a sharp interface. By definition, a surface tension $\sigma$ can be defined as the extra energy per unit surface associated with this surface. Accordingly, $\sigma$ is equal to the integral of the Cahn-Hilliard free energy across the interface, so that, as shown by van der Waals,\(^8\) $\sigma = (\rho / M_w) \Delta g_{\text{ex}}$, where $\Delta g_{\text{ex}} \sim RT (\Delta \phi)_{\text{eq}} \ell^2 / \lambda^2$ is a typical value of the change in the Cahn-Hilliard molar free energy within the interface at equilibrium, while $\lambda \sim a/\sqrt{\sigma}$, with $\varphi = (\Psi - 2) / 2$, is the characteristic interface thickness.\(^3\)
Therefore, we obtain Eq. (8), and from there, considering that $(\Delta \phi)^2 \sim \varphi^{1/2}$, we see that $a$ can be determined from $\sigma$ as
\[ a = \sqrt{\varphi} \frac{\sigma M_w}{RT}. \quad (A28) \]


