

Hydrodynamic delocalization of phase separation in a locally cooled fluid mixture

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Abstract. – We report that phase separation of a fluid mixture, whose temperature is set below the phase separation temperature only locally near one side wall of the container, is strongly delocalized over the entire system if there is density mismatch between the components. We demonstrate that this delocalization is caused by i) gravity-driven convective flow and ii) asymmetric kinetics between fast hydrodynamic coarsening during demixing and slow diffusional mixing through the phase boundary. The relevant physical parameters determining the efficiency of phase separation are clarified.

Phase separation in material processing and in Nature usually proceeds under inhomogeneous temperature fields. Despite this fact, phase separation of a mixture, whose temperature is “spatially homogeneous”, has so far been mainly studied both theoretically and experimentally [1]. For a solid mixture, effects of the temperature gradient on phase separation have been studied in detail [2, 3]. Our intuition tells us that phase separation occurs only locally in the region where $T < T_x$ (T_x : phase separation temperature). This picture has been confirmed to be basically correct, although interesting domain ordering at the cold wall of the cell was found to take place [2, 3]. We also note that couplings between the concentration and the temperature field, such as the so-called Soret effect, make the behavior very rich [4].

For a fluid mixture, on the other hand, it is very difficult to even imagine what would happen in such a situation, due to complex non-linear couplings among the relevant field variables, namely, concentration ϕ [5], temperature T , and flow fields v [6, 7]. It is well known that under a temperature gradient the gravitational and interfacial forces can create convective hydrodynamic flows [1]. Such phenomena are often seen in both laboratories and Nature in a wide spatial range covering from the scale of micrometers to that of the Earth. There are some interesting experimental studies on fluid phase separation under a temperature gradient [8–10]. However, the phenomena observed are still far from being fully understood. For example, Platten *et al.* studied phase separation of classical fluid mixtures under a horizontal temperature gradient field [10]. In their studies, the temperature at the one side of the cell (T_h) is set higher than T_x , while that of the other side (T_c) is set lower than T_x . Interestingly, they found that there coexist two macroscopic phases, which are separated by a distinct, nearly horizontal interface. Surprisingly, a one-phase mixing region was not observed

at all, differently from the above case of a solid mixture, even for the extreme case when $T_x - T_c \sim 2$ K and $T_h - T_x > 100$ K. The mechanism of this phase separation behavior has not yet been clarified even on a qualitative level. In this letter, we aim at elucidating important fundamental effects of hydrodynamic interactions on the phase separation behavior of a binary fluid mixture under a temperature gradient on the Earth.

The geometry studied here is one of the most typical configurations that are often seen in our daily life and industry (the same geometry as that in ref. [10]): The temperature gradient ∇T is horizontal (along the x -axis), while the gravitational field \mathbf{g} is vertical (along the y -axis). We fix the temperatures of both sides of the cell, T_h and T_c , so that $T_h > T_x > T_c$. To simplify the problem and extract the lowest-order effects of hydrodynamic interactions, we make the following simplifications. First, we assume local equilibrium. We also assume that the viscosity η and the material (D_ϕ) and the thermal (κ) diffusion constants are independent of ϕ . We also neglect the off-diagonal kinetic coefficients, which cause the so-called Soret and Dufour effects. Even under these simplifications, the thermal convection and Marangoni effects [11,12] lead to a rich behavior under inhomogeneous temperature fields for the fluid mixture.

Concentration diffusion, momentum conservation, and thermal diffusion are, respectively, described by the following three dynamic equations:

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right)\phi = \nabla^2\mu_m + \theta, \quad (1)$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right)\mathbf{v} = -\Gamma\phi\nabla\mu_m - \nabla\tilde{p} + \Xi\nabla^2\mathbf{v} + \mathbf{G}\phi + \boldsymbol{\nu}, \quad (2)$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right)\tau = \alpha\nabla^2\tau + \iota. \quad (3)$$

Here τ is the scaled temperature defined as $\tau = (T - T_x)/(T_x - T_c)$. Note that $\tau = 0$ corresponds to the phase separation temperature. μ_m is a mixing chemical potential given as $\mu_m = \tau\phi + \phi^3 - \nabla^2\phi$, which can be derived by the functional derivative of the standard Ginzburg-Landau free energy functional [1]. In the above equations, the physical parameters are scaled by using those of isothermal phase separation occurring at $T = T_c$. For example, time and space are scaled by the characteristic length of concentration fluctuations ξ and its lifetime t_ξ at $T = T_c$. $\alpha = \kappa/D_\phi$ (note that $D_\phi = \xi^2/t_\xi$). Γ and Ξ are the non-dimensional parameters defined as $\Gamma = \sigma\xi/D_\phi^2\rho$ (σ : the interface tension between the separated phases at $T = T_c$) and $\Xi = \eta t_\xi/\rho\xi^2$, which are, respectively, the scaled interface tension and viscosity [13]. Here ρ is the average density. We assume that the local density depends only on ϕ and not on T ; namely, we neglect the thermal-expansion effect for simplicity. Thus, $\mathbf{G} = \Delta\rho t_\xi^2\mathbf{g}/\rho\xi$, where $\Delta\rho$ is the density difference of the separated phases at the cold wall. In our model, the only mechanism that creates the density inhomogeneity and induces the gravity effects is the concentration dependence of the density. We employ the Boussinesq approximation for simplicity; namely, we neglect the effects of the density change except for the term that is directly coupled to gravity. \tilde{p} is a part of the pressure, which is imposed to satisfy the incompressible condition $\nabla \cdot \mathbf{v} = 0$. θ , $\boldsymbol{\nu}$, and ι represent the thermal noises of ϕ , \mathbf{v} , and T , respectively. We numerically solve eqs. (1)-(3) using the explicit Euler scheme. We employ the mirror FFT method, whose details will be described elsewhere, to calculate eq. (2) under the non-slip boundary condition for all the cell walls. The cell size is $L \times L$ (the grid size $\Delta x = 1$). The time increment is $\Delta t = 0.01$. We set $\tau_h = 1.0$ and $\tau_c = -1.0$.

A typical phase separation behavior under the temperature gradient is shown in figs. 1(a) and (b), respectively, for a solid and a fluid mixture. First, we explain the case of the solid mixture (see fig. 1(a)). Since we neglect the Onsager coupling coefficient between T and ϕ , the

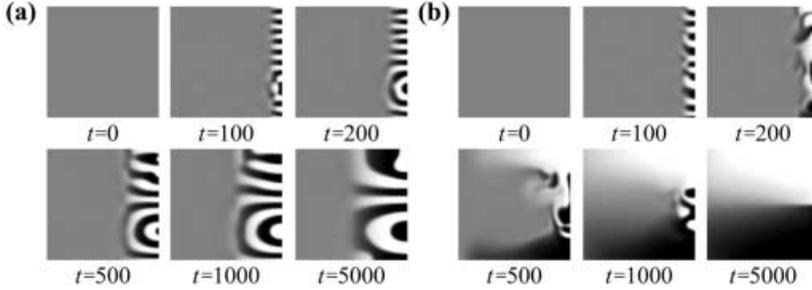


Fig. 1 – (a) Simulated pattern evolution of phase separation of a solid model. Initial conditions are $\phi(\mathbf{r}, t = 0) = 0.0$ and $\tau(\mathbf{r}, t = 0) = 1.0$. Then we start to cool the cell from the right-hand side (cold wall) at $t = 0$ by fixing its temperature to $\tau_c = -1.0$. We set $\alpha = 5.0$. We introduce the Gaussian noises for ϕ and T , whose intensities are $|\theta| = 1 \times 10^{-3}$ and $|\iota| = 1 \times 10^{-3}$, respectively. The simulated cell size is 128×128 . The darkness represents the concentration field. (b) Simulated pattern evolution of phase separation of a fluid model. We set $\Gamma = 5.0$, $|\mathbf{G}| = 0.15$, $\Xi = 1.0$, and $|\nu| = 0.0$. We also set $\mathbf{v}(\mathbf{r}, t = 0) = 0$ as the initial condition for \mathbf{v} . The other parameters and the initial conditions are the same as those for the above solid model.

concentration field does not affect the time development of the temperature. In other words, the temperature field is simply solved by the ordinary diffusion equation (see eq. (3)). Phase separation occurs in the region $\tau < 0$ and the phase-separated region propagates from the right to the left side, following the thermal conduction. Phase separation occurs anisotropically, and the domains tend to align in parallel to the temperature gradient ($\nabla\phi \perp \nabla T$), as first reported by Ball and Essery [2]. In the late stage, the temperature field becomes spatially linear as $T(x, y) = T_h + (T_c - T_h)x/L$. Then, we observe the phase separation state in the region where $\tau < 0$, while the one-phase mixing state where $\tau > 0$. For the solid mixture, thus, phase separation almost exactly reflects the local temperature. Although we include the ϕ -dependence of the density, the gravity effect does not affect the phase separation dynamics in our solid mixture, since we use the ϕ -independent diffusion coefficient D_ϕ [14, 15].

Next, we consider the case of a fluid mixture (see fig. 1(b)). In the early stage, phase separation locally proceeds in the region $\tau < 0$ and the phase-separated region propagates toward the left side as in the case of the above solid mixture. However, once the density difference between the demixed phases is produced near the cold wall, the gravitational force transports the lighter and the heavier phases to the upper and lower parts of the cell, respectively. This induces a macroscopic hydrodynamic flow, which transports the material over the entire system and delocalizes the phase separation. This process is initiated around $t \approx 400$. Since eq. (2) includes the gravitational force, the gravity directly produces the flow, in contrast to the case of the solid model. The one-phase mixing region becomes narrower with time and eventually disappears in the late stage ($t \geq 2000$). Finally, the system enters into a non-equilibrium steady state where it macroscopically phase-separates into the upper and lower phases divided by the horizontal interface. As can be seen from fig. 1(b) ($t = 5000$), the interface between the two phases becomes more diffuse while approaching the hot wall. This is because in the hotter region diffusion takes place to mix the two phases through their interface. The temperature and the flow fields in the nearly steady state are shown in figs. 2(a) and (b), respectively. Note that the steady macroscopic flow remains even when the domain pattern is stationary in the late stage (see fig. 2(b)). Thus, the system is in a dynamically stationary state. The material transported by the flow (in the Lagrange picture) experiences the periodic

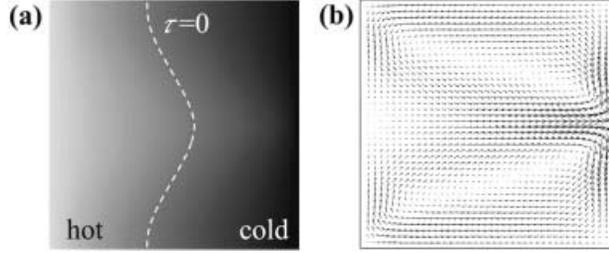


Fig. 2 – Simulated temperature field (a) and flow field (b) of the fluid model in the steady state ($t = 10000$). The brighter contrast means the higher temperature.

temperature oscillation in this steady state (see figs. 2(a) and (b)). It phase-separates when $\tau < 0$ and mixes when $\tau > 0$ repeatedly. Thus, the basic physics behind this phenomenon is similar to that of the periodic spinodal decomposition [1] of a fluid mixture [16], in which the overall temperature is temporally oscillated.

Figure 3 shows the time development of the probability distribution of the concentration $P(\phi)$ averaged over the entire cell for the solid (a) and the fluid model (b). For the solid model (see panel (a)), the distribution is composed of the peak near $\phi \approx 0$ and the plateau, which covers the region $-1 \leq \phi \leq 1$ rather homogeneously. The existence of this peak means that there remains the one-phase mixing region in the hot region even in the late stage. For the fluid model (see panel (b)), on the other hand, the peak near $\phi \approx 0$ exists only in the early stage. It becomes smaller with time and eventually disappears in the late stage ($t \geq 2000$). The distribution in the late stage has the two distinct peaks near $\phi = \pm 1$, which suggests that there is no one-phase region and the system phase-separates macroscopically. Note that the positions of the arrows (A) and (B) in fig. 3(b) correspond to the concentrations at the hot and cold walls, namely, $\phi(x = 0)$ and $\phi(x = L)$, respectively. Here we note that concentration diffusion is the only mechanism to change $P(\phi)$ and hydrodynamic flow can affect only the spatial distribution of the concentration. For a fluid mixture, phase separation occurs near the cold wall continuously via diffusion, and this demixed state is distributed over the entire cell by a macroscopic hydrodynamic flow. It should be stressed that domain coarsening is drastically accelerated by hydrodynamic interactions, while phase mixing slowly takes place *only through the interface*. This strong asymmetry in kinetics between demixing and mixing plays a key role in the delocalization of phase separation [16].

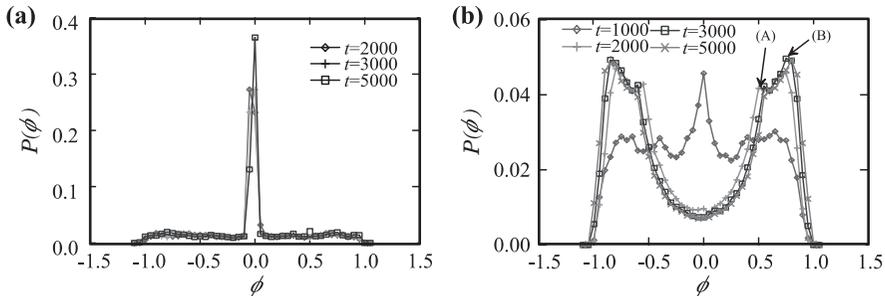


Fig. 3 – Time development of the distribution function of ϕ for the solid (a) and the fluid model (b). $\phi = \pm 1$ corresponds to the equilibrium phase separation in the isothermal phase separation for $\tau_c = -1.0$.

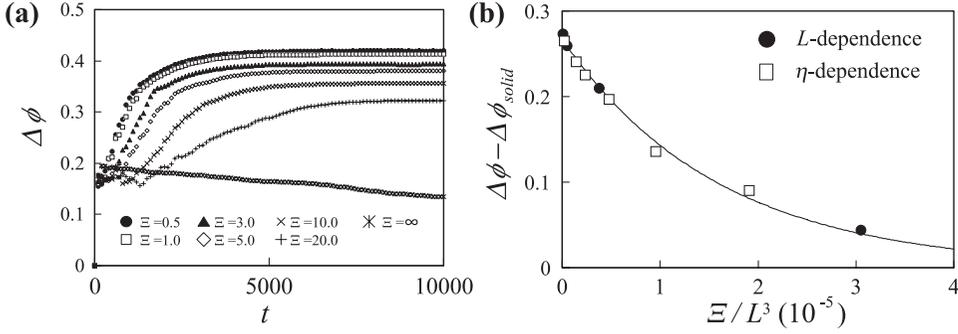


Fig. 4 – (a) Time evolution of $\Delta\phi$ for the solid and fluid mixture. Ξ increases from top to bottom at $t = 10000$. (b) Dependencies of the value of the concentration deviation, $\Delta\phi - \Delta\phi_{\text{solid}}$, at $t = 10000$ on the scaled viscosity Ξ and the scaled system size L .

Time development of the concentration deviation $\Delta\phi(t)$ for various Ξ is also shown in fig. 4(a). Here $\Delta\phi$ is the spatial average of the deviation of the local concentration from the hypothetical equilibrium concentration for isothermal phase separation at the same local temperature, which is defined by $\Delta\phi^2(t) = \int d\mathbf{r}\{\phi(\mathbf{r}, t) - \bar{\phi}(\tau(\mathbf{r}, t))\}_-^2/L^2$, where $\bar{\phi}(\tau(\mathbf{r}, t))$ is the equilibrium concentration for isothermal phase separation at τ : $\bar{\phi}(\tau) = 0$ for $\tau \geq 0$, while $\bar{\phi}(\tau) = \pm\sqrt{-\tau}$ for $\tau < 0$. Since $\bar{\phi}(\tau)$ has the two branches for $\tau < 0$, we chose one of them so that the sign of $\bar{\phi}(\tau(\mathbf{r}, t))$ is the same as that of $\phi(\mathbf{r}, t)$. For the solid mixture ($\Xi = \infty$), the local order parameter is locally determined by the local temperature, as described before. Thus, $\Delta\phi$ is small and decreases with time, reflecting the decrease in the interface area. For the fluid mixture, on the other hand, once flow is generated after the initial stage where the diffusional transport dominates, the phase separation is strongly delocalized by the flow and thus the local order parameter (concentration) is not determined by the local temperature any more. Thus, $\Delta\phi$ keeps increasing with time and approaches its steady-state value. Figure 4(a) also indicates that the larger the viscosity is, the smaller the deviation becomes. This feature is discussed below in detail. Here we note that the system enters into the final stationary state earlier for the smaller cell (not presented here).

Let us consider the physical mechanism responsible for the strong delocalization of phase separation of the fluid mixture. First, we consider the primary cause of the macroscopic flow (see fig. 2(b)). There are two candidates that immediately come to our mind. One is the gravitational effect, and the other is the Marangoni effect that is induced by the gradient of the interface tension due to ∇T . First, we consider the latter. Since there exists a well-developed interface along the temperature gradient in the steady state, the Marangoni effect may cause a macroscopic flow. The force term of eq. (2), $-\Gamma\phi\nabla\mu_m$, is divided into two parts. One is related to the non-local term of μ_m associated with the interface ($\Gamma\phi\nabla\nabla^2\phi$), which is the origin of the Marangoni effect [12]. Since the interface tension is larger in the cooler region, the flow anticipated from the Marangoni effect is consistent with that observed in fig. 2(b). The other is the force caused by the bulk part of the osmotic pressure ($-\Gamma\phi^2\nabla\tau/2$). In the ordinary isothermal phase separation of a fluid mixture, the bulk osmotic pressure should be cancelled out by a part of the pressure to satisfy the incompressible condition and thus never induces flow. Thus, the interface tension is the only origin to cause the flow field in isothermal phase separation. However, since the osmotic pressure depends on not only the concentration but also on the temperature, it does not necessarily violate the incompressible condition and may become the driving force of the hydrodynamic flow under the temperature gradient.

To clarify the roles of this Marangoni effect, thus, we perform the following simulation: We use $\phi(\mathbf{r})$, $T(\mathbf{r})$, and $\mathbf{v}(\mathbf{r})$ of the steady state of the above fluid model simulation (at $t = 5000$ in fig. 1(b)) as the initial condition. Then we continue the simulation while switching off gravity effects by setting $\mathbf{G} = 0$. We found that the macroscopic convective flow field becomes weaker with time and eventually disappears, and as a result, the concentration distribution $P(\phi)$ becomes essentially the same as that of the solid model. This has two important messages: i) The existence of the macroscopic convective flow field is crucial for the macroscopic phase separation and ii) the Marangoni effects play no role in producing the flow in our geometry. The latter can be explained as follows. The sum of the Marangoni force, $\Gamma\phi\nabla\nabla^2\phi$, and the bulk osmotic force coming from the diagonal elements of the osmotic stress, $-\Gamma\phi^2\nabla\tau/2$, is cancelled out by $\nabla\bar{p}$. Thus, the Marangoni effect is not operative for the phase separation geometry considered here, which is characterized by $\nabla T \perp \nabla\phi$. For our system, thus, the gravitational force is the main driving force that produces flow. This clearly indicates that whether the Marangoni effects play a role or not crucially depends upon the orientational relation between ∇T and $\nabla\phi$. This fact has not so far been widely recognized. We believe that this conclusion is not specific to this problem, but may be generic.

Finally, we consider what physical factors determine the degree of the phase separation, or $\Delta\phi$, in the nearly steady state ($t \geq 2000$). The most important point is that even in the steady state phase separation keeps occurring near the cold wall. It is reasonable to assume that the order parameter almost reaches the local equilibrium value near the cold wall; namely, $|\phi(x=L)| \approx 1.0$. This is supported by the fact that the concentration profile is almost given by $\tanh(\zeta/\sqrt{2}\xi)$ near the cold wall (not presented here), where ζ is the distance from the interface. The force balance condition between the gravitational force, which is caused by the concentration difference near the cold wall, and the viscous force is given by $\mathbf{G} - \nabla\bar{p} + \Xi\nabla^2\mathbf{v} \approx 0$. Since the velocity field is delocalized to minimize the viscous dissipation, it is reasonable to assume that its characteristic length is the cell size L . Assuming $\nabla \approx 1/L$, thus, we obtain $v \cong k_v GL^2/\Xi$, where k_v is a constant. This velocity field transports the material to the hot region ($\tau > 0$), where the demixed phases are dissolved by diffusion. Then, we can immediately estimate the duration time of dissolution δt as $\delta t \cong k_{\delta t}(L/v)((T_h - T_x)/(T_h - T_c)) \propto \Xi\tau_h/(GL(\tau_h + 1))$, where $k_{\delta t}$ is a constant. Since diffusion is the only transport mechanism in the mixing process, the mixing process should obey the diffusion equation: $\partial\phi/\partial t \approx \tau_h\nabla^2\phi$. Here, we assume that the mixing proceeds mainly near the hot wall and use its temperature τ_h as the representative value for simplicity. Using the above diffusion equation with $\nabla \sim 1/L$, we can calculate $\phi(x=0)$, to which ϕ decreases by diffusional mixing during δt . Thus, the concentration deviation $\Delta\phi$, which should be proportional to $\phi(x=0) - \bar{\phi}(\tau = \tau_h)$, is straightforwardly estimated as

$$\Delta\phi \propto \exp\left[-k_vk_{\delta t}\frac{\tau_h^2}{(\tau_h + 1)}\frac{\Xi}{GL^3}\right]. \quad (4)$$

Equation (4) provides the condition of macroscopic phase separation. Figure 4(b) clearly indicates that the concentration deviation exponentially decreases with an increase in Ξ/L^3 , which is fully consistent with eq. (4). Here we note that Ξ/L^3 can be written as $\eta D_\phi/(\Delta\rho gl^3)$ (l is the actual cell size). This decrease in $\Delta\phi$ with increasing the viscosity and decreasing the cell size can be explained as follows: The higher viscosity and the smaller system size are both the causes of the increase in the viscous dissipation. Thus, they lead to weaker stationary flow fields, which results in the lower degree of macroscopic phase separation. The weaker stationary flow fields make the behavior more solid-mixture-like.

In conclusion, we performed numerical simulations on phase separation under a horizontal temperature gradient in gravity. For a solid mixture, the mixing and demixing regions coexist,

reflecting its local temperature, as reported previously [2, 3]. For fluid mixtures, on the other hand, the density mismatch between the separated phases near the cold wall leads to a macroscopic convective flow, which strongly delocalizes phase separation and induces macroscopic phase separation of the entire system. A simple scaling argument indicates that the degree of phase separation is more enhanced for the system of smaller viscosity and larger cell size, which is supported by our simulations. We also demonstrate that Marangoni effects do not play any role in producing flow for $\nabla T \perp \nabla \phi$. In this letter, we study the simplest case to elucidate a clear physical picture. In real systems, including the case of ref. [10], the thermal-expansion ratio between the components of a mixture, which is not considered in our study, may play a significant role in creating flow. Thus, further careful studies are necessary for a deeper understanding of the phase separation behavior under a temperature gradient.

Finally, we briefly mention the effects of geometry. We confirm by numerical simulations (not presented here) that for a different geometry of $\nabla T \parallel \mathbf{g}$ (top is hotter) a system macroscopically separates into an upper mixing phase and a lower sedimented one rich in heavier component. In this case, the flow is also convected within each phase. Differently from the case of $\nabla T \perp \mathbf{g}$, however, the material in the upper mixing phase is transported by convective flow but stays only in the hot region, while that in the lower sedimented phase also stays only in the cold region. Thus, the mechanism enhancing phase separation for $\nabla T \perp \mathbf{g}$ does not work for $\nabla T \parallel \mathbf{g}$. Comparison of $\Delta\phi$ between the two geometries reveals that the efficiency of phase separation is much higher for $\nabla T \perp \mathbf{g}$ than for $\nabla T \parallel \mathbf{g}$. This tells us that transporting all material into the cold region by convective flow is a key to delocalizing phase separation and enhancing the degree of phase separation of the fluid mixture. From the energy-saving viewpoint, thus, we may conclude that the most efficient way to induce phase separation is to cool just a side wall of the container. Self-induced hydrodynamic flow can be used to enhance phase separation in this particular geometry. Since this mechanism operates more efficiently in a larger system, it would play a significant role in phase separation in Nature.

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