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Viscous fingering–the fluid-mechanical instability that takes place when a low-viscosity fluid displaces a high-viscosity fluid–has traditionally been studied under either fully miscible or fully immiscible fluid systems. Here we study the impact of partial miscibility (a common occurrence in practice) on the fingering dynamics. Through a careful design of the thermodynamic free energy of a binary mixture, we develop a phase-field model of fluid-fluid displacements in a Hele-Shaw cell for the general case in which the two fluids have limited (but nonzero) solubility into one another. We show, by means of high-resolution numerical simulations, that partial miscibility exerts a powerful control on the degree of fingering: fluid dissolution hinders fingering while fluid exsolution enhances fingering. We also show that, as a result of the interplay between compositional exchange and the hydrodynamic pattern-forming process, stronger fingering promotes that the system approach thermodynamic equilibrium faster.

I.   INTRODUCTION

When a less viscous fluid displaces a more viscous fluid, the contrast in viscosity destabilizes the fluid-fluid interface, leading to the formation of viscous fingers [1–3]. Fluid-fluid miscibility plays an important role in the fingering dynamics, and the fingering pattern can change appreciably based on the miscibility of two fluids. Thus, the subject is traditionally divided into *immiscible* and *miscible* viscous fingering. In both cases, it is viscous forces that drive the hydrodynamic instability. When two fluids are immiscible, surface tension stabilizes short-wavelength perturbations at the interface, allowing some proto-protrusions to spread readily, resulting in less ramified patterns [3–5]. When the two fluids are fully miscible, the absence of surface tension suggests a more intense fingering pattern, as demonstrated by experiments [3, 5–7] and simulations [8–12]. Nevertheless, without surface tension, complete suppression of the onset of miscible viscous fingering is possible under certain unfavorable viscosity contrast [6, 13] due to 3D effects. Beyond the onset regime, [7] has shown that molecular diffusion along the interface leads to shutdown of instability at late times during radial injections. Further, it has been suggested that Korteweg stresses and other non-equilibrium surface tension effects can act to stabilize miscible displacement [14–17].

Despite the conventional categorization into fully immiscible and fully miscible, the miscibility of two fluids can vary based on local conditions such as pressure and temperature [18]. Between the two extremes lie fluid pairs that are *partially miscible*, exhibiting limited, but nonzero, solubility into each other. For such fluid pairs, compositional effects are introduced to two-phase problems where component exchange between phases occurs even in the presence of surface tension. This effect is relevant, for instance, during immiscible gas-in-oil injection for oil recovery where the gas and oil can become partially miscible under high pressure reservoir conditions, leading to swelling of the oil phase and enhanced recovery [19]. Under this context, the coupling of viscous fingering with thermodynamic effects could provide new insights to controlling of the viscous instability, which has received increased attention in recent studies [12, 20–24]. Additionally, addressing the role of compositional effects in low Reynolds number two-phase flows is also essential to our understanding of mixing in multiphase mixtures [25], biological cell assembly [26] and geologic sequestration of CO_2 [27].

Our current understanding of viscous fingering with partially miscible fluids is very lim-

ited. In an effort to address this gap, an experimental study on viscous fingering with partially miscible fluids is performed recently [28]. The experiments use a ternary system made of water, PEG and Na_2SO_4 to produce viscously-contrasting fluid pairs that are fully miscible, immiscible or partially miscible. The experiments provide an excellent illustration on how thermodynamic effects can exert a powerful control on hydrodynamic instabilities: as the fluid pairs transition from being immiscible to partially miscible, the authors observe that formation of droplets become more common than formation of fingers. The detailed mechanisms behind the droplets formation remain to be understood. On the modeling front, a recent study [29] investigated radial injection under different fluid miscibility conditions using a Darcy-Cahn-Hilliard model, where the fluid miscibility is prescribed through the design of a Cahn-Hilliard type free energy [30]. Though the model is limited in its ability to explore the truly partially miscible regime, where one would expect to see effects such as finger swelling due to supersaturation, the study provides a consistent comparison between immiscible and miscible viscous fingering to demonstrate the role of compositional effects in controlling the vigor of the instability. As presented in earlier work [7, 14], the study confirms that the degree of fingering instability, as measured by interface length, peaks at a transition time followed by a decay due to diffusive mixing at the interface for *miscible* systems; in *immiscible* simulations, however, where surface tension is present and component diffusion is negligible, a decay in interfacial length is not observed [29].

In this work, we study the interplay between hydrodynamics and nonequilibrium compositional effects in partially miscible systems. To develop new insights into the physics of a nonlinear hydrodynamic instability out of thermodynamic equilibrium, here we develop a 2D gap-averaged model, in the spirit of a large body of literature on Hele-Shaw flows for both miscible and immiscible fluids [8, 11, 12, 20, 22, 23, 31–36]. While a full 3D flow model might be desirable to eventually provide a more detailed description of the flow (as is the case for fully miscible [6, 13, 37–42] and fully immiscible systems [35, 36, 43–45]), it should build on the insights of the nonlinear analysis in 2D. We adopt a phase-field modeling approach, which has been successful at describing immiscible two-phase flow in Hele-Shaw geometry [35, 36, 46–52] and in porous media [53] and, more recently, the coarsening dynamics of partially miscible binary mixtures under viscous fingering [54]. Under the phase-field framework, the design of thermodynamic free energy allows us to readily incorporate partial miscibility into multiphase flow. In its minimal description, the free energy of a two-phase

two-component mixture follows the Cahn-Hilliard form [30], formulated as a functional of component concentration and its gradients. Under the Cahn-Hilliard framework, fluid phase is inferred from component concentration, and not independently described. This approach is successful in capturing the dynamics of binary mixtures with fast phase-transition time scale (e.g. immiscible fluids) [29, 55–60]. In contrast, our proposed model [54] allows fluid concentrations to evolve independently from the phase variable, in order to capture the essence of *partially miscible* systems, where components can exchange between the two phases at time scales comparable to that of flow. During injection, the evolution of the invading phase variable (e.g. volume fraction of the invading phase) is driven by viscous instability, accompanied by redistribution of composition between phases and phase trans-formations that are driven by chemical potentials. Capturing the duality of the dynamics requires having separate evolution equations for phase and concentration, and defining a free energy that is a function of both variables. Similar two-field formulations have been extensively adopted for the simulation of binary alloys solidification [61], but, thus far, not for interfacial flows with compositional effects. With this more general framework, we are able to investigate the two-way coupling between hydrodynamics (viscous fingering) and thermodynamics (compositional exchange between phases and phase transformation). We apply our model to the viscous fingering problem in a rectangular Hele-Shaw cell, where initially a gas band is surrounded by a liquid (Fig. 1, left). Gas fingers are then created by pushing the gas band leftwards with an imposed constant flux of the liquid phase of the same initial composition (Fig. 1, right).
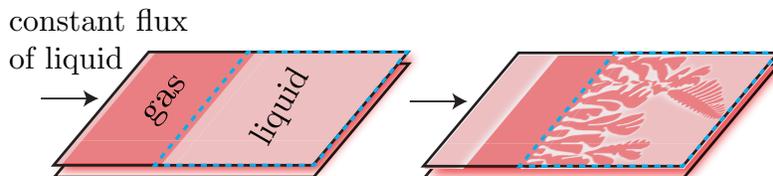
FIG. 1. Displacement of a gas band through liquid phase in a Hele-Shaw cell: (a) initial set up (b) the displacement leads to viscous fingering due to viscosity contrast. Meanwhile, compositional exchange occurs along the fingering interface if the two fluids are out of thermodynamic equilibrium. For example, in this sample image, the liquid phase is initially supersaturated with respect to gas and will swell the gas fingers as they evolve (see Sec. IV A). The blue dashed box indicates the area of study in our discussions.

II.   MATHEMATICAL MODEL

In our recent work [54], we propose a phase-field model of two-phase Darcy flow with two-component transport. Here we provide an extended and detailed description of the model and use it to study the problem described in Fig. 1. Without loss of generality, we focus on a binary mixture that is an analogy for a $CO_2(g)$-water(l) system. The two fluids, denoted *gas* (g) and *liquid* (l), have different viscosities with $\mu_l > \mu_g$. Upon contact, they seek to reach compositional equilibrium through mutual component exchange. The result should be a gas phase that is rich in the primary component (e.g. CO_2) and a liquid that is rich in the secondary component (e.g. H_2O). We introduce two variables, defined pointwise, to describe the state of the binary mixture: the gas volume fraction, ϕ, is a nonconserved quantity due to dissolution/expansion of the gas phase; the molar fraction of CO_2, c, is conservative in the entire domain. The model describes the evolution of ϕ and c when the binary mixture is subjected to hydrodynamic instabilities.

A.   Phase-field modeling of two-phase Darcy flow with compositional effects

We introduce the following dimensional governing equations to describe incompressible, isothermal, two-phase flow with two-component transport in a Hele-Shaw cell, with a uniform gap thickness b:

$$\nabla \cdot \mathbf{u} = 0, \quad \mathbf{u} = -\frac{k}{\mu(\phi)}\nabla P, \tag{1}$$

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{u}\phi) + \lambda^\phi \Psi_\phi = 0; \tag{2}$$

$$\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{u}c) - \nabla \cdot (\lambda^c \nabla \Psi_c) = 0. \tag{3}$$

Equations (1) are the continuity equation for an incompressible mixture and Darcy's law, where $\mathbf{u}$ is the mixture velocity, P is a kinematic pressure, k is a constant permeability and μ is the mixture viscosity, assumed to follow an exponential dependence on phase fraction, $\mu(\phi) = \mu_g \exp(R(1 - \phi))$, where $R = \log(\mu_l/\mu_g)$ is the viscosity contrast.

In the context of phase-field modeling, we understand ϕ also as a phase variable, which takes a value of 1 in the gas and 0 in the liquid, and interpolates smoothly between the two

bulk phases over a well-resolved, diffuse numerical interface. Time evolution of ϕ simulates gas dissolution/exsolution [Eq. (2)], and can be considered a relaxation process towards a minimum of the free energy function of the system F [62]. The gradient towards minimization, obtained by taking the variational derivative of F with respect to ϕ, can be understood as a phase potential that drives phase-transformations:

$$\Psi_\phi \equiv \delta F/\delta\phi = \partial F/\partial\phi - \nabla \cdot [\partial F/\partial(\nabla\phi)]. \tag{4}$$

The dynamics of phase transformation [Eq. (2)] are formulated using Allen–Cahn dynamics [63]. The evolution of c is described by a nonlinear advection–diffusion equation [Eq. (13)], where the component diffusion is driven by gradients in chemical potentials, defined similarly to Eq. 4:

$$\Psi_c \equiv \delta F/\delta c = \partial F/\partial c - \nabla \cdot [\partial F/\partial(\nabla c)]. \tag{5}$$

In Eqs. (2) and (3), λ^ϕ and λ^c are mobilities for ϕ and c respectively. Here we assume that both mobilities are only a function of c:

$$\lambda^\phi b^2 = \lambda^c = \frac{D/\nu}{R_{\text{ideal}}T}(c(1-c) + 0.01), \tag{6}$$

where D is the diffusion coefficient, ν is the molar density, R_{ideal} is the ideal gas constant and T is temperature (assumed constant here). We define the characteristic composition mobility as:

$$\lambda_c = \frac{D/\nu}{R_{\text{ideal}}T}, \tag{7}$$

and the characteristic phase mobility as:

$$\lambda_c^\phi = \frac{D/\nu}{b^2 R_{\text{ideal}}T}. \tag{8}$$

B.   Design of free energy

The free energy functional $F(\phi, c)$ plays a central role in the thermodynamic behavior of our binary mixture. Following the classical Cahn–Hilliard formulation for a binary sys-

152 tem [30], our F subsumes interfacial and bulk energy contributions:

$$F(\phi, c) = \int_V \left\{ \frac{1}{2}\epsilon_\phi^2 T(\nabla\phi)^2 + \frac{1}{2}\epsilon_c^2 T(\nabla c)^2 + \omega T W(\phi) \right.$$
$$\left. + \omega_{\text{mix}} T \left[f_l(c)(1 - g(\phi)) + f_g(c)g(\phi) \right] \right\} dV. \tag{9}$$

The first two terms in Eq. (9) capture the interfacial energy associated with phase and compositional boundaries. The characteristic interfacial energy per unit volume associated with ϕ and c are $\epsilon_\phi^2 T$ and $\epsilon_c^2 T$ respectively. The third term is the part of the bulk free energy responsible for phase separation, where $W(\phi) = \frac{1}{4}\phi^2(1 - \phi)^2$ adopts the shape of a double-well, determining the two stable states of F: $\phi = 0$ or $\phi = 1$. Here, ω is the energy (per unit volume) associated with the double-well energy. The last term, known as the bulk mixing energy, is the part of the bulk free energy responsible for partially miscible behavior. We adopt a form for mixing energy that is commonly used in the field of binary alloy solidification [64], where the energy is an interpolation in ϕ between liquid and gas excess energies (f_l and f_g), which are functions of c only. Here, $\omega_{\text{mix}} T$ is the energy (per unit volume) associated with mixing. The interpolation function $g(\phi) = -\phi^2(2\phi - 3)$ satisfies that the system approaches the stable states $\phi = 0, 1$ with zero slope, which ensures positivity of the phase variable [64]. The excess free energy of each phase are due to compositional effects; here we adopt the Wilson model [65]:

$$f_l(c) = c \log c + (1 - c) \log(1 - c)$$
$$- c \log(c + \alpha_l(1 - c)) - (1 - c) \log(1 - c + \beta_l c),$$
$$f_g(c) = c \log c + (1 - c) \log(1 - c)$$
$$- c \log(c + \alpha_g(1 - c)) - (1 - c) \log(1 - c + \beta_g c), \tag{10}$$

153 where α_l, α_g, β_l and β_g are assigned parameters. The equilibrium concentrations within
154 each phase are then obtained by the common tangent construction of f_l and f_g [66, 67]
156 (Fig. 2). Note here that both $f_l(c)$ and $f_g(c)$ are dimensionless.
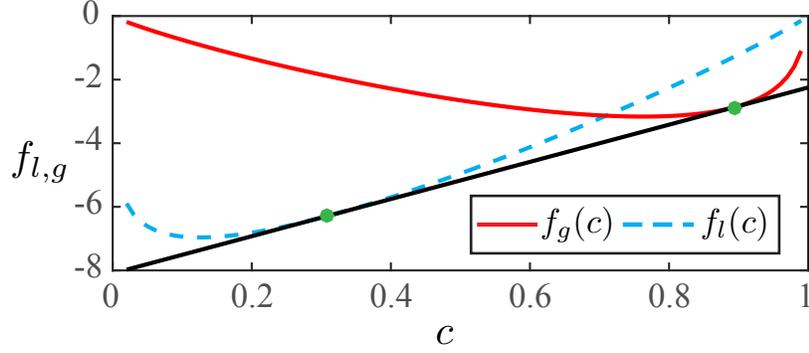
FIG. 2. Common tangent construction: here we assign the parameters in Eq. (10) as $\alpha_l = 2 \times 10^{-7}$, $\beta_l = 2 \times 10^4$, $\alpha_g = 200$, $\beta_g = 2 \times 10^{-4}$ so that the common tangent construction yields the equilibrium composition of the two fluids : $c_g^{\mathrm{eq}} \approx 0.89$, $c_l^{\mathrm{eq}} \approx 0.33$

C.   Scaling analysis

We identify the following characteristic scales in our system: $\epsilon_\phi^2 T/b^2$ is the characteristic energy, b is the length scale, $t_c = b/u_c$ is the characteristic time with $u_c = (k_c \Delta p_c)/(\mu_g b)$, where k_c, Δp_c are the characteristic permeability and pressure drop respectively. Additionally, we introduce λ_c as the characteristic composition mobility [Eq. (7)] and λ_c^ϕ as the characteristic phase mobility [Eq. (8)]. In its dimensionless form, the system of equations reads:

$$\nabla \cdot \mathbf{u} = 0, \quad \mathbf{u} = -\frac{1}{\mu(\phi)} \nabla P, \tag{11}$$

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{u}\phi) + \frac{1}{\mathrm{Ca}} \lambda \Psi_\phi = 0, \tag{12}$$

$$\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{u}c) - \frac{1}{\mathrm{Pe}} \nabla \cdot (\lambda \nabla \Psi_c) = 0. \tag{13}$$

where $\mu(\phi) = e^{R(1-\phi)}$ and $\lambda = 0.01 + c(1-c)$. The first dimensionless group, the capillary number Ca, sets the ratio between time scales associated with phase change and advection:

$$\mathrm{Ca} = (u_c b)/(\lambda_c^\phi \epsilon_\phi^2 T), \tag{14}$$

where $\epsilon_\phi^2 T/b$ is the interfacial tension. We expect that Ca controls the characteristic length scale of the instability pattern, such that the characteristic length decreases with increasing

Ca [54]. The second dimensionless group, the Péclet number, sets the ratio between rate of advection and diffusion:

$$\mathrm{Pe} = (u_c b)/(\lambda_c \epsilon_\phi^2 T). \tag{15}$$

Pe controls the rate of diffusion within a single phase, and therefore directly affects the rate of gas dissolution/exsolution. We expect that for large values of Pe, the finger morphology will approach that of an immiscible system. In dimensionless form, the free energy is described with three additional dimensionless groups:

$$
F(\phi, c) = \int_V \left\{ \frac{1}{2}(\nabla \phi)^2 + \epsilon \frac{1}{2}(\nabla c)^2 + \frac{1}{\mathrm{Ch}} W(\phi) \right. \\
\left. + \frac{1}{\mathrm{Ma}} \left[f_l(c)(1 - g(\phi)) + f_g(c)g(\phi) \right] \right\} dV. \tag{16}
$$

We introduce the third dimensionless group as the ratio between the two energy scales associated with compositional and phase boundaries:

$$\epsilon = \epsilon_c^2 / \epsilon_\phi^2. \tag{17}$$

An increase in ϵ would mean that the numerical profile of concentration (c) becomes sharper and the numerical profile of phases (ϕ) becomes smoother. The fourth group is the Cahn number, which controls the thickness of the numerical interface:

$$\mathrm{Ch} = (\epsilon_\phi^2/b^2)/\omega. \tag{18}$$

A larger Ch would require more grid points to resolve the fluid-fluid interface. Phenomenologically, a larger Ch also corresponds to a system with larger surface tension. Finally, we define a solutal Marangoni number, which sets the ratio between interfacial energy and mixing energy:

$$\mathrm{Ma} = (\epsilon_\phi^2/b^2)/\omega_{\mathrm{mix}}. \tag{19}$$

As Ma increases, the system becomes dominated by interfacial effects and we expect non-equilibrium thermodynamics to play a weaker role in the pattern forming process.

III.   PROBLEM SETUP AND NUMERICAL METHODS

We conduct high-resolution numerical simulations of our model for the problem described in Fig. 1, in which we displace a band of less viscous gas through the more viscous ambient liquid under a constant flux of liquid of the same initial composition. Our simulations are on a domain of size 200×80 ($L_x \times L_y$) and parameter values Ch=1/2000, Ma=1/200 and ϵ=200 (and parameters of the Wilson model given in Fig. 2). We perform a straight-forward calculation of Ca and Pe in order to mimic an experimental fluid pairs analogous to water and methane gas (weakly soluble in water). We approximate the typical injection rate in a rectilinear geometry to be $U = 1.9 \times 10^{-3}$cm/s, based on the values reported in [44]. The surface tension is take as that of water and air at room temperature: $\epsilon_\phi^2 T/b = 72$ dyn/cm. The diffusion coefficient of gas in water at 25°C is taken from [68] as $D = 2 \times 10^{-5}$ cm^2/s. The molar density of pure water is about 0.056 mol/cm^3, and that of gas is about 0.00005 mol/cm^3. Here we take an intermediate value of 0.01 mol/cm^3 for ν. Based on these values, we calculate that $\lambda_c^\phi = 1.29 \times 10^{-5}$cm^3/($J \cdot s$) and $\lambda_c = 8.1 \times 10^{-7}$cm^5/($J \cdot s$). The key dimensionless parameters in our system are computed as: Ca $= U/(\lambda_c^\phi \gamma) \approx 2$ and Pe $= U/\lambda_c \gamma \approx 32$.

We are interested in exploring the coupling between hydrodynamic instabilities and thermodynamic effects. Consequentially, we focus on two parameters, each of which controls one aspect of the coupling: (a) the viscosity contrast R between the two fluids and (b) the initial composition of the liquid phase c_l^0. The parameter R is chosen here to be $R = 0, 1, 2, 3, 4$ and 5, where the gas phase is always less (or equally) viscous than the liquid. The value of c_l^0 determines the thermodynamic response of the two fluids when interacting, where three scenarios may occur: (i) the gas dissolves, transferring CO_2 into the liquid; (i) the gas and liquid are at equilibrium, no component exchange occurs; or (iii) the gas expands in volume by exsolving CO_2 from the liquid. As shown in Fig. 2, the common tangent construction of the bulk free energies yields the equilibrium composition of the two fluids as: $c_g^{eq} \approx 0.89, c_l^{eq} \approx 0.33$. Instructed by this calculation, we can re-create the three scenarios by setting the defending liquid to be initially (at $t = 0$):

(a) *undersaturated* with respect to the gas phase: $c_l^0 = 0.05 < c_l^{eq}$;

(b) *near-saturated* with respect to the gas phase: $c_l^0 = 0.33 \approx c_l^{eq}$;

215 (c) *supersaturated* with respect to the gas phase: $c_l^0 = 0.5 > c_l^{eq}$.

216 In all the simulations performed, we only vary R and c_l^0 while all other parameters are

217 unchanged. We initialize the gas phase with a composition that is close to equilibrium

218 values: $c_g^0 = 0.89 \approx c_g^{eq}$. Further, all simulations start with the same initial configuration in

219 ϕ (as shown in Fig. 1 left):

$$\phi_0 = \begin{cases} 1, & \text{if } 0.05 L_x \leq x \leq 0.4 L_x \\ 0, & \text{otherwise} \end{cases} \tag{20}$$

220 The initial concentration field c_0 is computed as an affine mapping from ϕ_0:

$$c_0 = (c_l^0 - c_g^0)(1 - \phi_0) + c_g^0. \tag{21}$$

221 We solve Eqs. (11)–(13) sequentially. We first obtain the pressure and velocity using a

222 finite volume method with a two-point flux approximation. Next we update c and ϕ using a

223 Fourier pseudo-spectral discretization and using a biharmonic-modified time stepping [69].

224 The domain is discretized with 2560×1024 ($N_x \times N_y$) points. The boundary conditions

225 are periodic, but we show results only in a window of the simulation domain ($80 \leq L_x \leq$

226 200, indicated as the blue dashed box in Fig. 1) unaffected by the boundaries during the

227 simulation period reported (that is, until the fingers reach the right boundary).

228 ## IV. RESULTS

229 ### A. Fingering pattern under the influence of gas dissolution and exsolution

230 We present a summary of the final displacement pattern (in c) in a c_l^0–R phase diagram

231 in Fig. 3. The middle row of the phase diagram corresponds to a displacement scenario

232 where the two fluids are near-saturated, analogous to immiscible displacement [4, 70]. In

233 this regime, viscosity ratio is understood as the control parameter for large scale structure of

234 the pattern [2, 71]. With this series of simulations, we recover the classic features of immis-

235 cible viscous fingering: shielding, spreading and tip-splitting [2], as well as side-branching,

236 merging, pinchoff of fingers, and entrapment of the defending phase towards the injection

237 side [72, 73]. The rest of the phase diagram (top and bottom rows) illustrates the effects of
238 gas dissolution/exsolution on the displacement patterns.

239
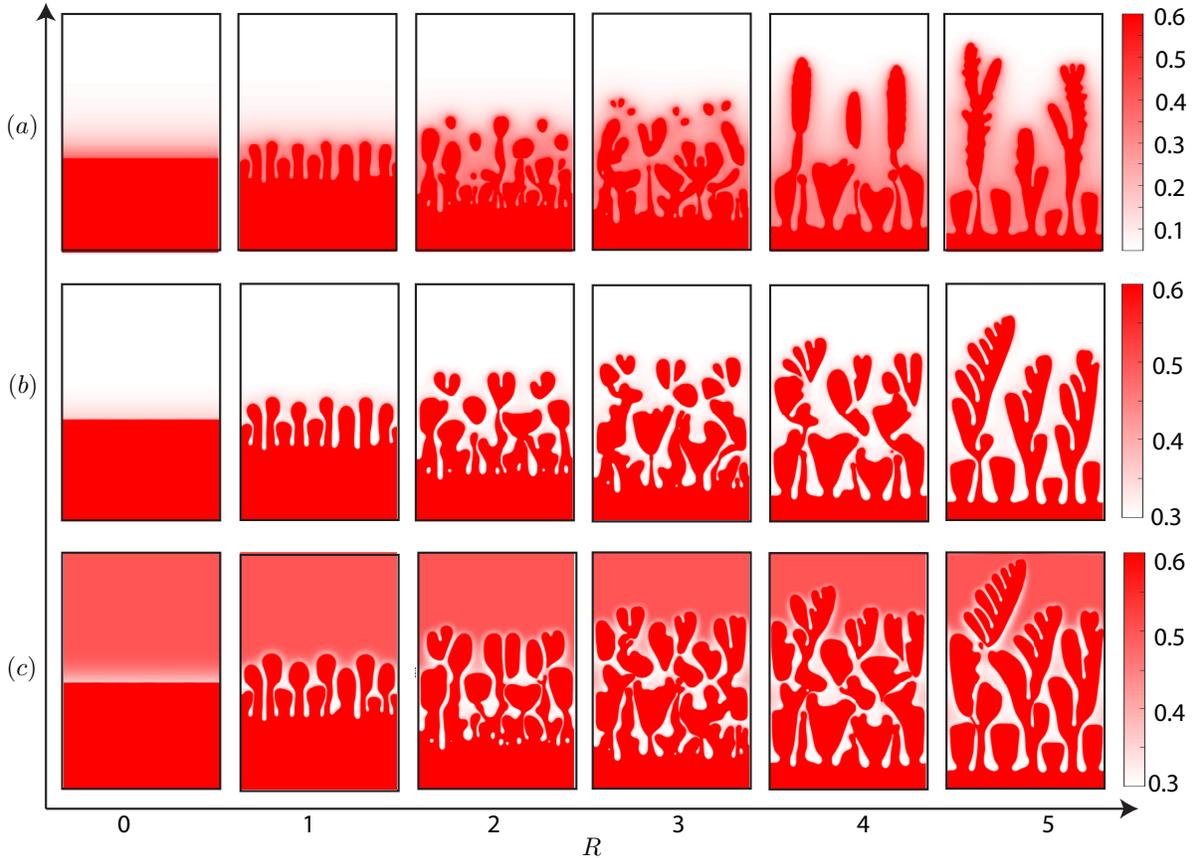
240 FIG. 3. The coupling between different viscosity contrast and compositional effects lead to a rich
241 set of viscous fingering patterns. Here we show snapshots of c at $t = 50$ for six different R values
242 (across each row). Each of the three rows correspond to different c_l^0 values: defending liquid is (a)
243 undersaturated ($c_l^0 = 0.05$); (b) near-saturated ($c_l^0 = 0.33$) and (c) oversaturated ($c_l^0 = 0.5$). Note
244 that the colormap differs between each row to reveal the detailed structures in the concentration
245 field.

246   In the top row, the defending liquid is undersaturated with respect to the gas. Upon
247 contact, the gas volume dissolves locally to replenish the CO_2 concentration level in the
248 ambient liquid. This dissolution process hinders the growth of young fingers, or proto-
249 protrusions, that form along the sides of dominant fingers. By immediately stripping away
250 any gas accumulation that fuels the growth of instability, the dissolution process inhibits
251 proto-protrusions developing into mature fingers. As a result, it has significantly weakened
252 development of side branches as well as the shielding and merging processes. The dissolution
253 effect is most active towards the front of the invasion, where the gas phase is persistently

²⁵⁴ met with undersaturated liquid. Under this effect, the un-bifurcated fingers appear slimmer

²⁵⁵ ($R = 1$), and we observe disconnected droplets that become rounded due to dissolution for

²⁵⁶ intermediate viscosity contrast ($R = 2, 3$); for larger viscosity contrast ($R = 4, 5$), we

²⁵⁷ observe "bald" dominant fingers that lack active side branches.

²⁵⁸   An important distinction between partially and fully miscible fluids pair is the direction

²⁵⁹ of component diffusion. In a fully miscible system, molecular diffusion of the components

²⁶⁰ follow the direction of positive concentration gradient. In the case of partially miscible fluids,

²⁶¹ however, component diffusion is directed in the direction of chemical potential gradient,

²⁶² which can sometimes be the reverse of the concentration gradient. Such is the case when

²⁶³ the gas phase is exposed to an oversaturated liquid (bottom row of the phase diagram),

²⁶⁴ where the invading fingers swell by exsolving the excess CO_2 from the liquid, against the

²⁶⁵ direction of concentration gradient. Exsolution into the gas phase increases the volume of

²⁶⁶ gas (ϕ) and thus promotes instability in the system as it expands the radius of invading

²⁶⁷ front for tip-splitting [4]. This results in an enhanced shielding and merging effect and more

²⁶⁸ prominent side branches. Such promotion of instability is observed across all values of R

²⁶⁹ where fingering occurs, and the effect is most apparent for $R = 4, 5$. In addition, the fingers

²⁷⁰ also appear larger overall in comparison to the middle row.

²⁷¹   **B.   The coupling between ϕ and c**

²⁷²   We illustrate the fingering pattern using the c-field in Fig. 3; however, it is important to

²⁷³ note that both ϕ and c are independently solved using separate evolution equations in our

²⁷⁴ model. To demonstrate this, Fig. 4 shows snapshots of 1D cross section profiles of both ϕ and

²⁷⁵ c side-by-side for $R = 5$ with *unsaturated* (left) and *oversaturated* (right) defending fluid.

²⁷⁶ From this we observe that both ϕ and c, although independently solved, follow each other

²⁷⁷ closely. The pattern in c emulates that of ϕ, although c provides more details on component

²⁷⁸ distribution within each phase. There are, however, fundamental differences in how these

²⁷⁹ two variables behave under their own evolution equation. The 1D profile of ϕ (Fig. 4 bottom,

²⁸⁰ dashed blue line) is continuous but compact—a feature of immiscible invasion under diffuse-

²⁸¹ interface descriptions. Meanwhile the 1D profile of c (Fig. 4 bottom, solid red line) exhibits

²⁸² a diffuse profile that is inherent to diffusive component transport. The coupling between ϕ

²⁸³ and c is not merely a modeling construct: rather, it provides compositional details of the

²⁸⁴ two-phase system that either variable alone would not be able to reveal. This is further
²⁸⁵ discussed in Sec. IV E.
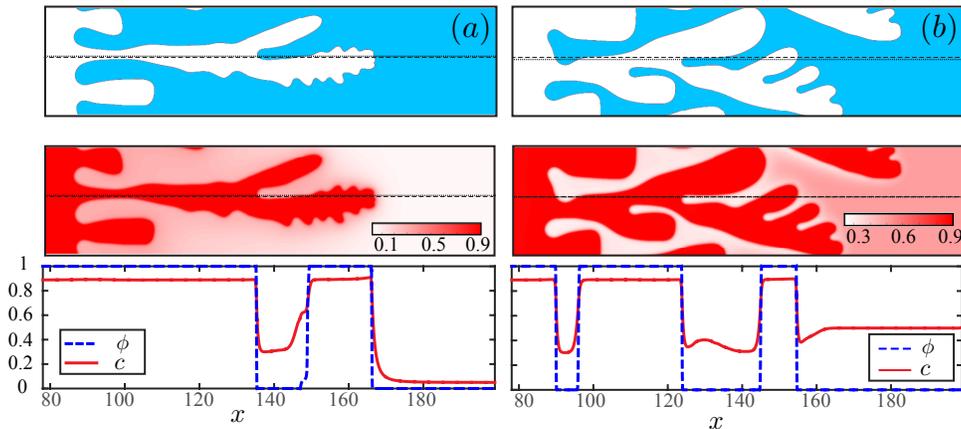
²⁸⁷ FIG. 4. Defending fluid is (a) undersaturated or (b) supersaturated. Top: snapshots of ϕ at $t = 46$.
²⁸⁸ Middle: snapshots of c at $t = 46$. Bottom: horizontal transects of ϕ (dashed) and c (solid) at $t = 46$
²⁸⁹ along the dashed lines indicated in the 2D plots in the top and middle rows. Note that regions
²⁹⁰ where $c \approx 0.33$ indicate area in which local thermodynamic equilibrium is in place.

²⁹¹ ## C.   Thermodynamic control on the degree of fingering

²⁹² Thermodynamic effects such as chemical reactions can lead to a myriad of interesting be-
²⁹³ haviors when coupled with hydrodynamic instabilities [24, 74–77]. In this work, we explore
²⁹⁴ such coupling in the form of thermodynamics-driven phase transformation that leads to fin-
²⁹⁵ ger dissolution and exsolution during viscous fingering. The coupling can be of particular
²⁹⁶ interest in the context of controlling of the viscous instability, which has received increased
²⁹⁷ attention in recent studies [12, 20–24]. Proposed mechanisms include use of chemical reac-
²⁹⁸ tions [24], alternating injections [12], control of injection rate [20, 78], imposing a gradient
²⁹⁹ in flow pathway [22, 79], or confining the flow by elastic membranes [23].

³⁰⁰ In Section IV A, we demonstrate qualitatively that thermodynamic-driven phase transfor-
³⁰¹ mations, resulting in fluid dissolution or exsolution, can hinder or enhance viscous fingering
³⁰² instabilities beyond onset regime. Here we quantify such effect by inferring the degree of
³⁰³ fingering with direct measurement of the total interfacial length generated by the instabil-
³⁰⁴ ity, using image segmentation (see examples in Fig. 5 insets). The interfacial length of the
³⁰⁵ fingering front, $\mathcal{L}$, is scaled by the transversal domain length, $L_y = 80$, so that initially
³⁰⁶ $\mathcal{L}/L_y = 1$ and will increase as fingers form and grow (Fig. 5). When $R = 0$, $\mathcal{L}/L_y = 1$
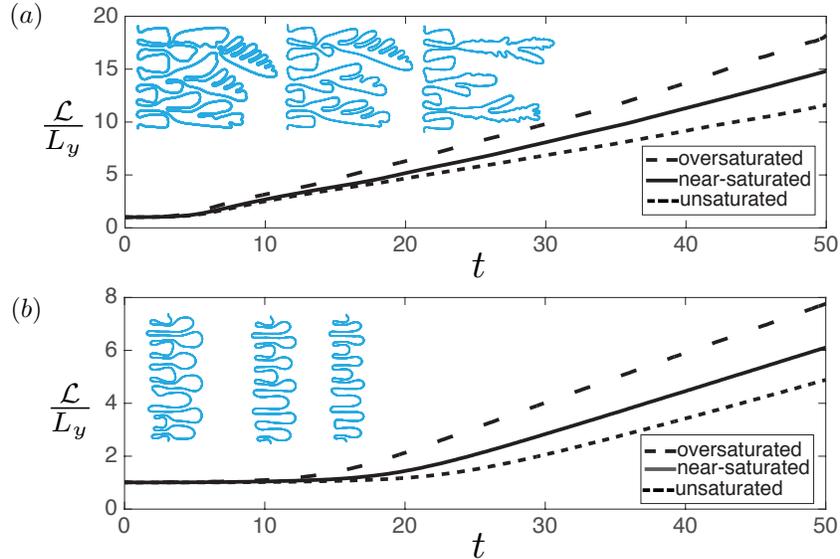
FIG. 5. Normalized interfacial length, $\mathcal{L}/L_y$, as a function of time for three compositional scenarios with (a) $R = 5$ and (b) $R = 1$. In both plots, colored insets show the traced outline of the fingering front at $t = 50$ for oversaturated, near-saturated and unsaturated defending liquid (left to right).

for the entirety of the simulation. In Fig. 5, we show the evolution of $\mathcal{L}/L_y$ under $R = 1$ (bottom) and $R = 5$ (top) for all three compositional scenarios. The degree of fingering persistently increases under all scenarios; the instability is not suppressed due to gas dissolution. However, compared to the second scenario (the immiscible analog, solid lines), the interfacial growth is slowed down under gas dissolution (short dashed line), indicating weakening of the instability; on the other hand, the growth is significant enhanced under finger swelling (long dashed line), indicating promotion of the instability.

The insets in Fig. 5(b) also illustrates a greater finger competition for the oversaturated case. This is due to the fact that under an oversaturated scenario, gas exsolution leads to finger swelling and a space-fling competition that promotes of some fingers while suppressing some others. This enhanced competition is not observed for the unsaturated cases at $R = 1$.

D. Impact of viscous fingering on the rate of gas dissolution/exsolution

The total gas volume fraction in the system should decrease due to gas dissolution or increase due to gas exsolution. In other words, the amount of gas volume change in the domain is a global measure that reflects how much the system has progressed towards thermodynamic equilibrium.
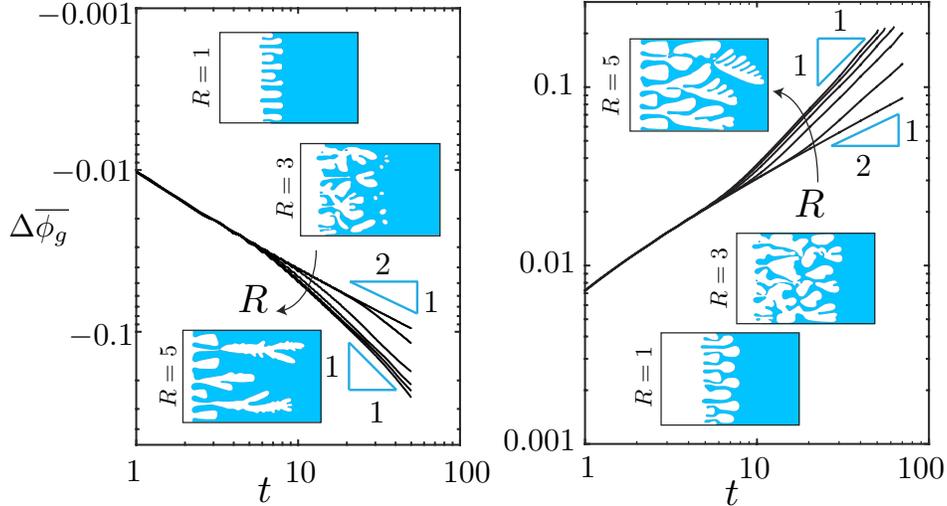
FIG. 6. $\Delta\overline{\phi_g}(t)$ for $R = 0, 1, 2, 3, 4, 5$ (arrows indicating increasing order) when the defending phase is undersaturated (left) and supersaturated (right). The insets in both plots show snapshots of ϕ at $t = 50$ for the different values of R.

Locally, the reduction or increase in gas volume is a direct consequence of component exchange across the phase-phase boundary. We expect that hydrodynamic instability will play an important role in this process because phase transformations take place at the invasion front where the two fluids are out-of-equilibrium, and viscous fingering deforms and lengthens such front.

Here, we define the change in gas volume fraction across the whole domain over time as:

$$\Delta\overline{\phi_g}(t) = \frac{\iint \phi(t)dxdy - \iint \phi_0 dxdy}{\iint \phi_0 dxdy}. \tag{22}$$

In Fig. 6, we show $\Delta\overline{\phi_g}(t)$ for different values of R when the defending fluid is undersaturated (left) and supersaturated (right). When no viscosity contrast is present ($R = 0$), the invasion front remains stable and phase transformation is limited by the rate at which CO_2 diffuses in the liquid phase in order to be transported away or towards the gas phase. This explains $|\Delta\overline{\phi_g}| \sim t^{1/2}$ for $R = 0$ in both composition scenarios. In the presence of the hydrodynamic instability ($R > 0$), the invasion-front deformation provides more interfacial area over which the two fluids can equilibrate. This mass-transfer enhancement is clearly shown in the scaling $|\Delta\overline{\phi_g}| \sim t^1$, observed for $R = 2, 3, 4, 5$.

E.   Heterogeneity in phase compositions

While gas volume fraction is a measure of how the system progresses towards its thermodynamic equilibrium globally, here we show that progress towards equilibrium can be very heterogeneous within the domain. To do this, we track the liquid phase concentration, computed pointwise as:

$$c_l(x, y) = (1 - \phi(x, y))c(x, y). \tag{23}$$

We introduce $\overline{c}_{l_y}(x)$ as the y-averaged liquid phase concentration along the x-axis. If a thermodynamic equilibrium is reached locally, $\overline{c}_{l_y} \approx c_l^{\mathrm{eq}}$ at that point; otherwise, $\overline{c}_{l_y}$ should be larger or smaller than c_l^{eq}. In Fig. 7 (left column), we plot $\overline{c}_{l_y}(x)$ at six different times with $R = 5$ for undersaturated [Fig. 7(a)] and supersaturated [Fig. 7(b)] defending liquid. The shaded red region indicates *metastability*, where the system is close to thermodynamic equilibrium (red dashed lines Fig. 7). From this, we observe that the system reaches metastability towards the roots of the fingers, where two fluids have more time to equilibrate. Towards the fingering front, the fluid-fluid interface is newly created, leaving little time for component exchange to occur; therefore, the liquid composition appears to be far away from thermodynamic equilibrium at the fingering front. The spatial heterogeneity in the phase compositions and consequently in the thermodynamic equilibrium state between the fluids has implications on the pattern forming process: towards the roots of the fingers, where the system has established a thermodynamic equilibrium earlier, the fingering morphology is no longer subject to dissolution/exsolution effects; towards the invasion front, freshly created fingers are subject to constant shrinkage/expansion due to gas dissolution/exsolution.

F.   Fingering pattern as controlled by Ch and Ma

The Cahn number (Ch) controls the effective surface tension between the two fluids. As Ch increases, the system experiences increasing surface tension. Here we verify this effect by simulating viscous fingering at four different values of Ch at a fixed Ma $= 1/200$ (all other parameters are kept the same as introduced in Sec. III). The results as shown in Fig. 8 demonstrate that as Ch increases from left to right, an increasing surface tension results in more prominent finger pinch-off.

The solutal Marangoni number (Ma) controls the thermodynamic forcing that leads to
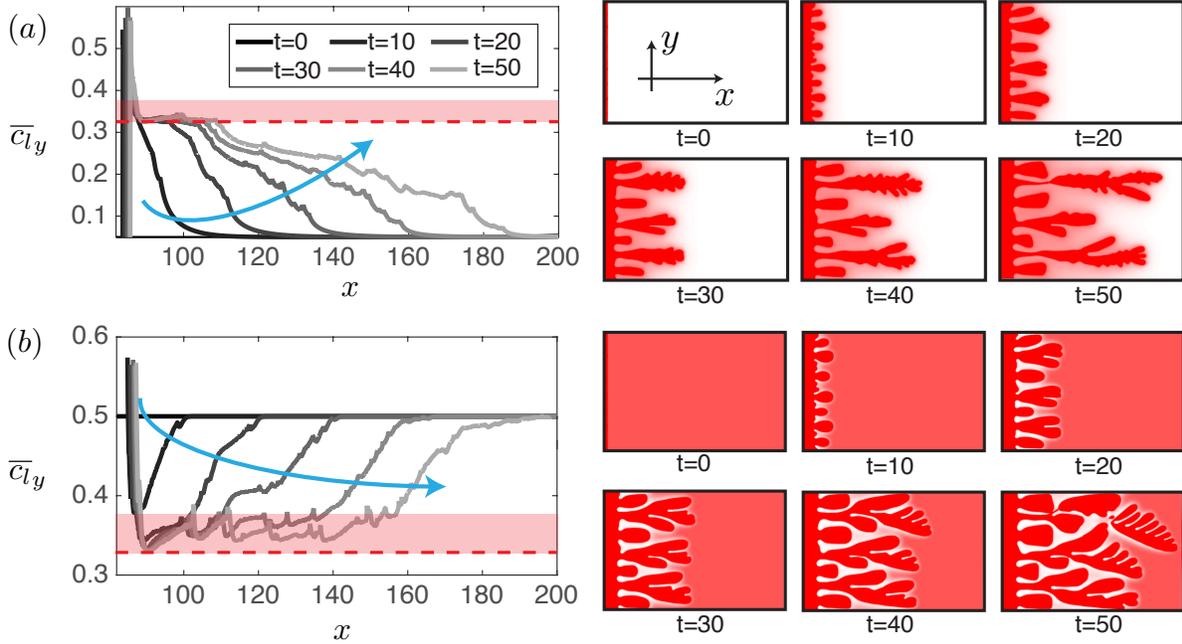
FIG. 7. (Left) $\overline{c}_{ly}(x)$ at $t = 0$, 10, 20, 30, 40 and 50. Blue arrow indicates direction of time. Red dashed line indicates thermodynamic equilibrium: $c_l^{\mathrm{eq}} \approx 0.33$. Red shaded area indicates metastability. (Right) snapshots of c for the corresponding times. The defending liquid is initially undersaturated in (a) and supersaturated in (b), and all simulations correspond to $R = 5$.
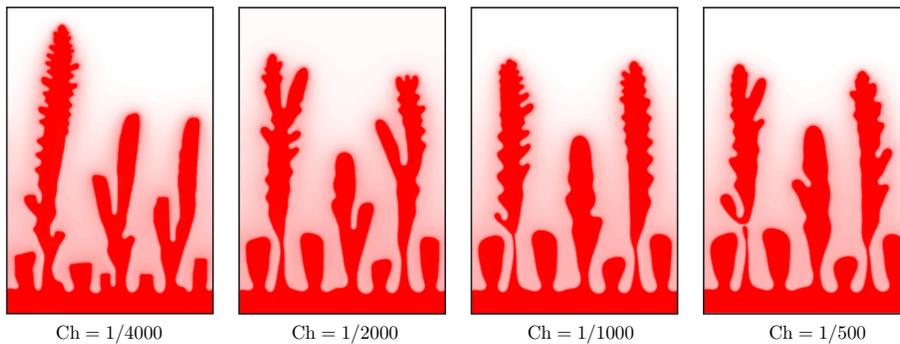
FIG. 8. Impact of Cahn number at $\mathrm{Ma} = 1/200$ and other parameters kept the same as in Sec. III. We simulate for four values of Ch differing by a factor of two each. Shown here are snapshots of c at $t = 40$. The colormap range is $[0.05, 0.9]$ for all figures.

partial miscibility. It appears as a coefficient of the chemical potential, which is defined as:

$$\Psi_c = \epsilon \nabla^2 c + \frac{1}{\mathrm{Ma}} \left[f_l'(c)(1 - g(\phi)) + f_g'(c) g(\phi) \right]. \tag{24}$$

Although Ma does not change the compositional equilibrium, one can treat $1/\mathrm{Ma}$ as a kinetic rate coefficient that drives component diffusion within each phase. Such diffusion is

proportional to the gradient in Ψ_c and will diminish as the system approaches equilibrium (the expression multiplied by 1/Ma will be zero at equilibrium). As Ma increases, the rate of diffusion decreases within each phase and the system takes longer to reach compositional equilibrium. This effect is confirmed by Fig. 9, where we see that as Ma increases from left to right, the liquid phase composition is more heterogeneous and farther away from equilibrium (supersaturated in many regions for Ma = 1/50 and 1/25).
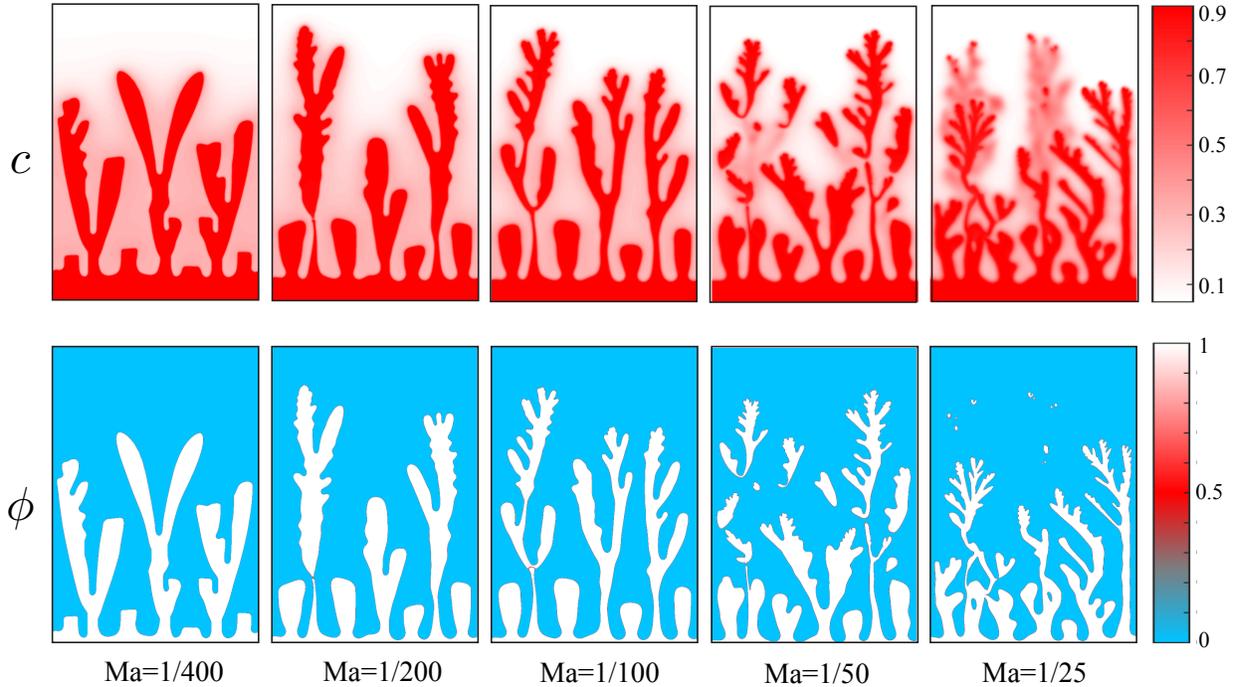
FIG. 9. Impact of solutal Marangoni number at Ch = 1/2000 and other parameters kept the same as in Sec. III. We simulate for five values of Ma differing by a factor of two each. Shown here are snapshots of c (top) and ϕ (bottom) at $t = 50$.

It is also important to note that a decrease in 1/Ma also indirectly promotes the strength of surface tension in the system. This is due to the structure of the free energy design [Eq. (16)]. As a result, an increase in Ma indicates an increase in surface tension, allowing the system to favor more pinch-off and tip-splitting events (Fig. 9). Such nonlinear interactions between compositional effects and fluid instability lead to interesting dynamics in fluid mixing. Here, we use the variance of the concentration field to measure fluid mixing:

$$\sigma^2 = \langle c^2 \rangle - \langle c \rangle^2. \tag{25}$$

In Fig. 10, we study the effect of Ma on fluid mixing by analyzing the temporal dynamics

385 of σ^2 from the set of simulations shown in Fig. 9. We conclude that the rate of mixing

386 is initially enhanced by smaller Ma (enlarged figure to the left), which is consistent with

387 the implication from Eq. (24). However, as a result of nonlinear coupling between fingering

388 instability and dissolution effects, a larger Ma (e.g. Ma = 1/25) produces significantly more

389 tip-splitting and pinch-off events, which results in the creation of more interfacial area and

390 faster mixing at later times (Fig. 10, $t > 20$).
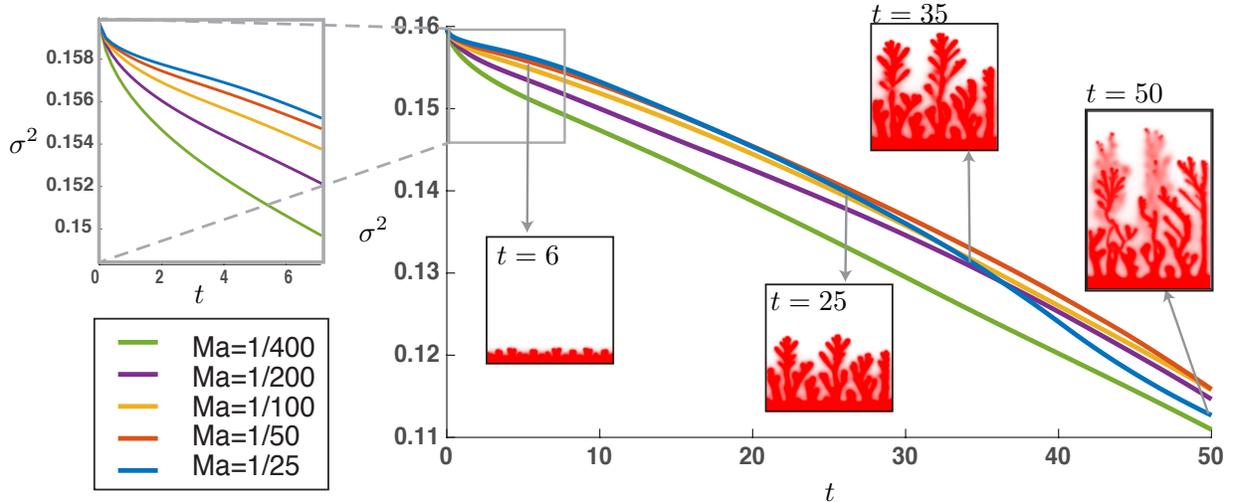
392 FIG. 10. Concentration variance σ^2 as a function of time for different values of Ma. The enlarged
393 portion on the left corresponds to the early time regime when the fluid interface has not been
394 significantly destabilized. The insets in the main figure correspond to snapshots of c for the
395 Ma = 1/25 simulation.

G.   Fingering pattern with decreasing miscibility gap

397   The miscibility gap of a fluids pair is defined here as the difference in compositions between

398 the two fluids once they reach compositional equilibrium: $c_g^{\mathrm{eq}} - c_l^{\mathrm{eq}}$. In our current model, the

399 miscibility gap is determined solely by the description of the bulk mixing energy functions

400 $f_l(c)$ and $f_g(c)$. By changing the parameter values in Eq. (10), we explore the ability of our

401 model framework to describe fluid pairs with different levels of partial miscibility. We stress

402 here that the miscibility gap is determined solely by the shape of the bulk mixing energy

403 curves $f_l(c)$ and $f_g(c)$; tuning the parameters Ma, Ch, ϵ, Pe and Ca will only change the

404 dynamics as the system approaches equilibrium.

405   In Fig. 11, we explore the pattern-forming dynamics as we inject fluid pairs with a

different miscibility gap. This is done by tuning the parameters (α_l, α_g, β_l and β_g) in the bulk mixing energy curves of each phase [Eq. (10)]. As we close the miscibility gap (top to bottom), we also change the initial condition in concentration so that the liquid phase is always undersaturated and the gas phase is at-saturation. Specifically,

- The top row corresponds to the majority of the simulations discussed in this work, where $\alpha_l = 2 \times 10^{-7}$, $\beta_l = 2 \times 10^4$, $\alpha_g = 200$, $\beta_g = 2 \times 10^{-4}$ so that the common tangent construction yields the equilibrium composition of the two fluids: $c_g^{\text{eq}} \approx 0.89$, $c_l^{\text{eq}} \approx 0.33$;

- The middle row corresponds to $\alpha_l = 20$, $\beta_l = 200$, $\alpha_g = 200$, $\beta_g = 20$ so that the common tangent construction yields the equilibrium composition of the two fluids: $c_g^{\text{eq}} \approx 0.65$, $c_l^{\text{eq}} \approx 0.35$;

- The bottom row corresponds to $\alpha_l = 100$, $\beta_l = 200$, $\alpha_g = 200$, $\beta_g = 100$ so that the common tangent construction yields the equilibrium composition of the two fluids: $c_g^{\text{eq}} \approx 0.55$, $c_l^{\text{eq}} \approx 0.45$.

We keep all the other parameters the same as introduced in Sec. III. In Fig. 11, we observe that even as the miscibility gap narrows (approaching the fully miscible limit), where one might expect a transition to a miscible viscous fingering pattern [11], the system always exhibits the effect of interfacial tension and the fingering pattern resembles that of immiscible displacement. This effect is due to our simplified description of mixture viscosity and surface tension. Currently, viscosity in our model is a function of ϕ only, and the effective surface tension is independent of fluid composition. Incorporating a more sophisticated design of viscosity as a function of both ϕ and c and a concentration-dependent surface tension term may allow our model to capture more accurately the transitions towards the fully miscible limit. Nevertheless, the model is robust in capturing the correct thermodynamics, where the fluids arrive at their respective equilibrium compositions as predicted by the bulk mixing energy curves in all three cases.

V. CONCLUSIONS

In this paper, we study viscous fingering with partially miscible fluids. We introduce a phase-field model to describe two-phase two-component flow and transport in a Hele-Shaw
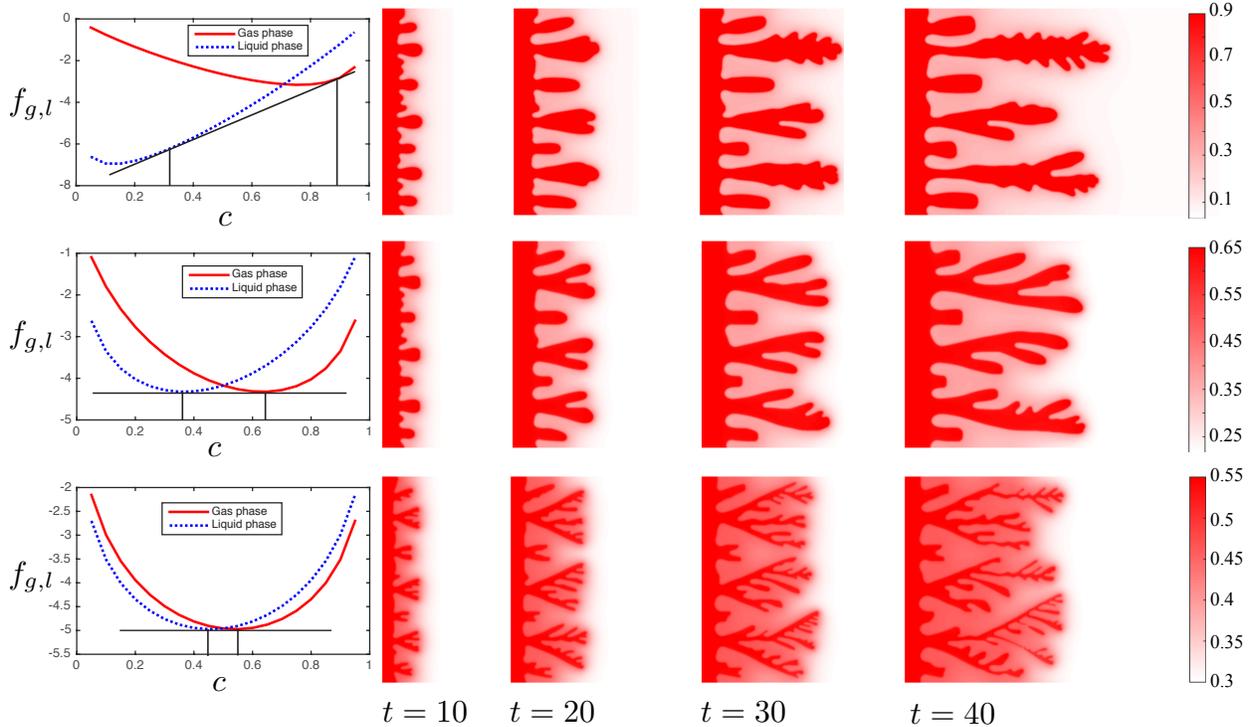
FIG. 11. Impact of miscibility gap in the bulk mixing energy curves. (Left): $f_l(c)$ and $f_g(c)$ and their common tangent constructions. (Right): snapshots of c from simulations using the bulk mixing energy described in the left column. Note that the colormap ranges are different and correspond to the initial composition (slightly wider than miscibility gap).

435 cell. We present high-resolution numerical simulations of the model applied to the viscous

436 fingering problem for various viscosity contrasts and different initial fluid compositions.

437 From the perspective of pattern formation, our results demonstrate that fluid dissolution or

438 exsolution due to partial miscibility can hinder or enhance viscous fingering, respectively.

439 This is shown by both directly visualizing the fingering pattern (Sec. IV A), and also by

440 quantifying the degree of fingering through the measure of interfacial length (Sec. IV C).

441   Conversely, we also explore how the pattern forming process can impact the rate at which

442 the two fluids reach compositional equilibrium. By measuring globally the amount of gas

443 dissolution/expansion from component mass transfer, we show that the increase in degree of

444 fingering—and associated increase in interfacial length—is directly linked to a faster rate of

445 thermodynamic equilibration (Sec. IV D). By measuring locally the degree of equilibrium,

446 we show that equilibrium is reached earlier towards the roots of the fingers, where the two

447 fluids have more time to exchange components (Sec. IV E). The spatial heterogeneity in the

448 degree of thermodynamic equilibrium implies that the gas fingers are subjected to different

levels of dissolution/expansion effects throughout the domain. As a result, the final fingering pattern we observe is a result of the complex nonlinear coupling between hydrodynamic instabilities and thermodynamic effects. Through additional simulations in Sec. IV F, we show that both Ch and Ma can affect the fingering pattern. As Ch increases, the system experiences increasing surface tension and more pinch-off events. As Ma increases, the system takes longer to reach compositional equilibrium and the liquid composition appears more heterogeneous. Further, because a larger Ma also indirectly promotes the strength of surface tension, we also observe more tip-splitting and pinch-off events at larger Ma. Such nonlinear coupling between fingering instability and dissolution effects results in a non-monotonic trend in mixing efficiency as a function of Ma.

An important assumption we make in this paper is that the thermodynamic-driven component exchange does not change the density or viscosity of either fluid, or the interfacial tension between the two phases. This assumption allows us to simplify the parameter space for our simulations and thus focus on the effect of viscosity contrast and initial fluid compositions. However, these assumptions may no longer be valid for realistic fluid pairs where density, viscosity and interfacial tension can change appreciably due to mass transfer across phases. As explained in Sec. IV G, our current model does not reproduce miscible viscous fingering pattern as we close the miscibility gap; surface tension plays a significant role in the fingering instability for all values of fluid miscibility gap in our model. We attribute this to an oversimplified design of viscosity and surface tension, which we plan to extend in future work. Further, the effect of component exchange on fluid properties could yield interesting displacement dynamics. For instance, while we only explore the displacement dynamics under a viscously unstable configuration ($R > 0$) in this work, unstable displacement could still arise under an initially viscously stable configuration ($R < 0$). Under constant fluid-fluid component exchange, this instability could be caused by, for example, nonuniform changes in local surface tension at the fluid interface (a Marangoni effect) or changes in local fluid viscosity that eventually reverse the viscosity contrast. It would be interesting to incorporate these effects in our current model in the future to fully understand ongoing experimental studies [28].

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