

Condensed-Dilute Liquid Phase Separation and Growth of Droplets in 2D

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Liquid-liquid phase separation is an important phenomenon that is observed in various places, from daily life to cellular biology. In this paper, we present a brief theoretical treatment of such phase separations for a binary fluid mixture, and demonstrate theoretical predictions with simulation results.

I. INTRODUCTION

Liquid-liquid phase separation plays an important role in physics. Formation of two phases, where one of the phases are dense and the other dilute, is a phenomenon that is widely observed in daily life. For instance, a field in which this phenomenon is thought to play an important role is cellular physics. According to [SB17], some organelles within cells have membranes to help them stay concentrated and as coherent structures while some other organelles do not have a membrane, yet they still stay as coherent structures that are capable of concentrating specific set of molecules. Recent studies have shown that these membrane-less organelles exhibit liquid-like properties, and the mechanism through which they remain a coherent structure can be modelled as condensed-dilute phase separation of liquids, where the condensed phase structures the organelles and the dilute phase is the intracellular fluid. This plays a role not only in intracellular organization, but also in other biological activity such as facilitating chemical reactions between weakly interacting molecules through concentrating them into the condensed state.

Another example, which is what we will be studying in this paper, is the condensed droplet formation, i.e. on leaves during foggy mornings. This transition where two inhomogeneous coexisting phases emerge from a homogeneous single phase is usually achieved through variation of some parameters of the system such as the temperature or the density. Once the droplets form, depending on external boundary conditions as well as initial conditions, they either dissolve, or grow. [al19]

These systems try to minimize their free energy $F = U - TS$. Phase separation occurs if the interactions between the components of the same type that decrease the free energy are stronger than the negative contribution of entropy to the free energy, which tends the system to remain fixed.

II. RELEVANT THEORY

In what follows, we will first give a brief theoretical treatment of the Ginzburg-Landau free energy and stability of equilibrium states of a binary mixture. Then, we will develop an approximation equation governing the growth of a single droplet. Finally, we will provide numerical simulation results demonstrating the stability of various homogeneous starting concentrations, and growth (or shrink) of the droplet under various initial and boundary conditions.

II.1. Ginzburg-Landau Free Energy of a Binary Mixture

In what follows, we will closely follow the treatment given in [al19].

Although a more sophisticated formula for the free energy density can be obtained by considering a binary fluid mixture of molecules of type A and B on a lattice and employing the mean-field approximation, the physics of the phase separation can be fully captured by the shape of the free energy close to the critical concentration c_c , where concentration here refers to the total concentration of the fluid at a point in space. The shape of the free energy can be obtained through the familiar Ginzburg-Landau expansion:

$$F[c] = \int d^3x \left(f(c) + \frac{\kappa}{2} |\nabla c|^2 \right)$$

where the free energy density $f(c)$ is given by a fourth order polynomial

$$f(c) = -\frac{b}{2}(c - c_c)^2 + \frac{a}{4}(c - c_c)^4$$

Here, c_c is the critical concentration, i.e. where the local maxima of the free energy is. We note that this free energy density is symmetric around c_c .

Now, we wish to find the equilibrium concentrations by finding the minimum of this free energy:

$$\begin{aligned} \frac{df}{dc} = 0 &\Rightarrow \\ -b(c - c_c) + a(c - c_c)^3 &= (c - c_c) (a(c - c_c)^2 - b) = 0 \\ c_1^{(0)} = c_c - \sqrt{b/a}, \quad c_2^{(0)} &= c_c + \sqrt{b/a} \end{aligned}$$

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are the equilibrium concentrations for the dilute and condensed phase, respectively.

Here we define the concentration difference between the two phases as $c_{diff} = 2\sqrt{b/a}$, from which we can find $a = \frac{4b}{c_{diff}^2}$ (1). Also, following eqs. (2.28) and (2.29) in [al19], we define the interfacial width $w = \sqrt{\frac{2\kappa}{b}}$, which is approximately the width over which the equilibrium concentration varies substantially. This is obtained from essentially interpolating the concentration distribution between $c_1^{(0)}$ and $c_2^{(0)}$. This gives us a way to calculate the value of $\kappa = \frac{1}{2}bw^2$ (2) once b and w are chosen. We will use both of these relations when doing the simulation.

II.2. Stability of Equilibrium States

Now we consider the stability of the homogeneous equilibrium state, where $c_{eq}(x) = \bar{c}$. Determining whether inhomogeneous equilibrium state corresponds to a stable solution or not is a bit more involved; we refer the reader to appendix A in [al19].

If small concentration perturbations increase the free energy, then this means \bar{c} is a stable solution. Let $c = \bar{c} + \epsilon$ be a small perturbation. Then

$$\begin{aligned} \Delta F[\bar{c}] &= F[\bar{c} + \epsilon] - F[\bar{c}] \\ &= \int d^3x \left(f(\bar{c} + \epsilon) - f(\bar{c}) + \frac{\kappa}{2} |\nabla \epsilon|^2 \right) \end{aligned}$$

Here

$$\begin{aligned} f(\bar{c} + \epsilon) - f(\bar{c}) &= \\ &= \frac{a}{4} (\bar{c} - c_c + \epsilon)^4 - \frac{b}{2} (\bar{c} - c_c + \epsilon)^2 - \frac{a}{4} (\bar{c} - c_c)^4 + \frac{b}{2} (\bar{c} - c_c)^2 \\ &\approx \frac{a}{4} (4(\bar{c} - c_c)^3 \epsilon + 6(\bar{c} - c_c)^2 \epsilon^2) - \frac{b}{2} (2(\bar{c} - c_c) \epsilon + \epsilon^2) \\ &= \frac{3a}{2} ((\bar{c} - c_c)^2 \epsilon^2) - \frac{b}{2} \epsilon^2 \end{aligned}$$

to lowest order in ϵ , since $a(\bar{c} - c_c)^3 - b(\bar{c} - c_c) = \frac{df}{dc}|_{c=\bar{c}} = 0$ due to \bar{c} being the homogeneous equilibrium state.

Therefore, we end up with

$$\Delta F[\bar{c}] = \int d^3x \left(\frac{\epsilon^2}{2} (3a(\bar{c} - c_c)^2 - b) + \frac{\kappa}{2} |\nabla \epsilon|^2 \right)$$

As the gradient term is always positive, this integral is guaranteed to be positive for all ϵ if the other term is also positive, i.e. if $|\bar{c} - c_c| > \sqrt{\frac{b}{3a}}$ then the homogeneous state is stable. Otherwise, the homogeneous state is unstable.

By a similar, though a bit more involved analysis, it can be shown that the inhomogeneous state is stable if $|\bar{c} - c_c| < \sqrt{\frac{b}{a}}$.

Thus for $|\bar{c} - c_c| > \sqrt{\frac{b}{a}}$, only the homogeneous state is stable, while for $|\bar{c} - c_c| < \sqrt{\frac{b}{3a}}$, only the inhomogeneous state is stable. These observations constitute the first set of theoretical results to be confirmed by the simulations.

II.3. Growth of a Droplet

We now turn our attention to growth of a droplet. Let the particle fluxes for types A and B be $\mathbf{j}_A = \mathbf{j}$ and $\mathbf{j}_B = -\mathbf{j}$. Thus $\mathbf{j} = \frac{\mathbf{j}_A - \mathbf{j}_B}{2}$ is called the exchange current. Due to particle number conservation, these fluxes must be equal in magnitude and opposite in direction. Therefore, for the concentration of A , we can write

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{j}$$

This exchange current is proportional to the gradient of the exchange chemical potential $-\nabla \mu$ (please refer to appendix B of [al19]): $\mathbf{j} = -\Lambda \nabla \mu$. Noting that $\mu = \frac{\delta F[c]}{\delta c}$, we have

$$\frac{\partial c}{\partial t} = \nabla \cdot (\Lambda \nabla (a(c - c_c)^3 - b(c - c_c) - \kappa \nabla^2 c)) \quad (3)$$

This equation is called the Cahn-Hilliard equation. As seen, it involves fourth order derivatives, and therefore very challenging to solve analytically. However, we can solve it numerically by using the finite element method, which is what we will do under simulations. For now, we will solve it by making approximations.

First, we assume that far from the interface between the phases, concentration variations are small and therefore the fourth order derivative can be ignored, and the equation can be linearized around the equilibrium concentrations $c_1^{(0)}$ and $c_2^{(0)}$:

$$\begin{aligned} &a(c_{1,2}^{(0)} + \delta c - c_c)^3 - b(c_{1,2}^{(0)} + \delta c - c_c) \\ &= a(\pm \sqrt{b/a} + \delta c)^3 - b(\pm \sqrt{b/a} + \delta c) \\ &\approx 3b\delta c - b\delta c = 2b\delta c \end{aligned}$$

Setting $D = 2b\Lambda$, we get

$$\frac{\partial c}{\partial t} = -D \nabla^2 c \quad (4)$$

Now we consider the dynamics of a single droplet. Droplets can be thought of small condensed phases immersed in a large dilute phase.

For simplicity, we consider a spherically symmetric system where the droplet is always a sphere in 3D (or a circle in 2D). In this case, only the droplet radius can change:

$$\frac{dR}{dt} = v_r \quad (5)$$

where v_n is the radial velocity component of the droplet-dilute phase interface. Using the familiar relationship from electromagnetism between the charge density, velocity, and current density, the net material flux towards the interface can be written as a difference of the in and out-fluxes at the interface:

$$(c_{in}^{eq} - c_{out}^{eq})v_r = (\mathbf{j}_{in} - \mathbf{j}_{out}) \cdot \hat{r} \Rightarrow v_r = \frac{(\mathbf{j}_{in} - \mathbf{j}_{out}) \cdot \hat{r}}{(c_{in}^{eq} - c_{out}^{eq})}$$

where c_{in}^{eq} and c_{out}^{eq} are the equilibrium concentrations in the condensed and dilute phases.

We make one further approximation: that the droplet radius varies slowly, hence the left hand side of equation 4 can be taken to be approximately 0 at all times. What we are left with to solve is the Laplace equation inside and outside the droplet. The first boundary condition is that the maximum of $c(r)$ must be at the center of the droplet (i.e. $\frac{\partial c(r)}{\partial r} = 0$ at $r = 0$). The second boundary condition is that since the droplet is inside a large system, the concentration as $r \rightarrow \infty$ must be fixed to some value c_∞ .

Using the standard Laplace equation solution and these boundary conditions, we can find the concentrations inside and outside the droplet. From these concentrations, we can calculate the in and out-fluxes at the boundary, and thus v_r . Plugging this v_r into eq. 5, we get

$$\frac{dR}{dt} = \frac{\alpha}{R} \left(\epsilon - \frac{\beta}{R} \right)$$

Here, α and β are some constants, and $\epsilon = \frac{c_\infty}{\gamma} - 1$ (γ being another constant). What's important is that depending on how big the far-away concentration is, $\epsilon - \frac{\beta}{R}$ changes sign, and the droplet either shrinks until it dissolves or grows monotonically. This is the second observation to be confirmed by simulations.

III. SIMULATIONS

We now confirm the two set of observations from sections II.2 and II.3 by numerically solving the full Cahn-Hilliard equation without approximations (eq. 3). In all the simulations, parameters $b = 1$, $c_c = 0.5$, $c_{diff} = 0.25$, $w = 0.1$ were chosen arbitrarily. Based on these, $a = 64$ from eq. (1) and $\kappa = 0.005$ from eq. (2).

For all the simulations, we used the Python Dolfin library available under legacy FEniCS by modifying the Cahn-Hilliard equation demo available at [Dol]. FEniCS is a PDE solver that utilizes finite element methods. For visualization, the internal plot command of Dolfin was used. All the simulations were performed on a unit square in 2D.

III.1. Stability Simulations

We first confirm the two observations made in section II.2: 1) If $|\bar{c} - 0.5| > \sqrt{b/a} = 0.125$, then homogeneous state is the only stable one. 2) If $|\bar{c} - 0.5| < \sqrt{b/3a} \approx 0.073$, then inhomogeneous state is the only stable one.

The simulations in figures 1, 2 and 3 were obtained for different homogeneous starting concentrations \bar{c} (variations of at most 0.01 were added to the starting concentrations).

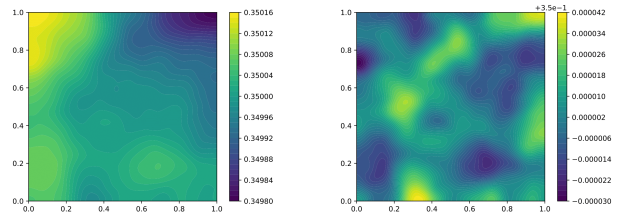


FIG. 1. $\bar{c} = 0.35 < 0.5 - 0.125$. $t = 0.05$; 0.20 from left to right. As seen, the final state of the system is homogeneous with very close to 0 concentration.

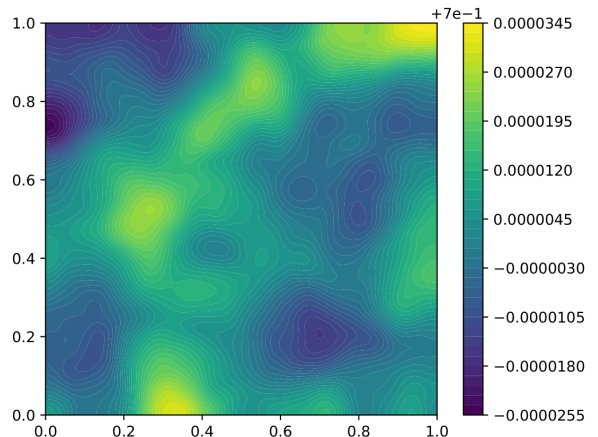


FIG. 2. $\bar{c} = 0.70 > 0.5 + 0.125$. $t = 0.20$. As seen, the final state of the system is homogeneous with very close to 0 concentration.

Similar results to that of figure 3 were obtained when $\bar{c} = 0.55$ (but this time, the condensed phase dominated). Due to space limitations, these will not be provided here.

III.2. Droplet Simulations

We now confirm the observation made in section II.3: Below a certain value of the far-away concentration c_∞ , the droplet shrinks and dilute phase dominates. Above that value, the droplet grows and condensed phase dominates.

This time, in order to fix the far-away concentration, Dirichlet boundary conditions on the boundary of the unit square were imposed for c_∞ (which was varied between different simulations), and $\mu = 0$.

The simulations in figures 4 and 5 were obtained with a configuration where a droplet of radius 0.3 at the center of the square at time $t = 0$ existed. The concentration of the droplet was 0.7 while the dilute phase concentration outside was 0.3.

