Two-dimensional model of phase segregation in liquid binary mixtures with an initial concentration gradient

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Abstract

We simulate the phase segregation of a deeply quenched binary mixture with an initial concentration gradient. Our theoretical model follows the standard model H, where convection and diffusion are coupled via a body force, expressing the tendency of the demixing system to minimize its free energy. This driving force induces a material flux much larger than that due to pure molecular diffusion, as in a typical case the Peclet number $\alpha$, expressing here the ratio of thermal to viscous forces, is of the order of $10^5$.

Integrating the equations of motion in 2D, we show that the behavior of the system depends on the values of the Peclet number $\alpha$ and the non-dimensional initial concentration gradient $\gamma$. In particular, the morphology of the system during the separation process reflects the competition between the capillarity-induced drop migration along the concentration gradient and the random fluctuations generated by the interactions of the drops with the local environment. For large $\alpha$, the nucleating drops grow with time, until they reach a maximum size, whose value decreases as the Peclet number and the initial concentration gradient increase. This behavior is due to the fact that the nucleating drops do not have the chance to grow further, as they tend to move towards the homogeneous regions where they are assimilated.

Keywords: Phase separation; convection-induced spinodal decomposition

1. Introduction

In this work we simulate numerically and explain physically a phenomenon which was observed by Gupta, Mauri, and Shinnar (2000): when a low-viscosity liquid binary mixture with a strong initial concentration gradient is quenched deeply into the unstable region of its phase diagram it phase separates without the appearance of large (i.e. larger than 10 $\mu$m) drops.

In general, when a binary mixture is quenched from its single-phase region to a temperature below the composition-dependent spinodal curve, it phase separates through a process called spinodal decomposition (for a review on spinodal decomposition, see Gunton, San Miguel & Sahni, 1983), which is characterized by the spontaneous formation of single-phase domains which then proceed to grow and coalesce. Unlike nucleation, where an activation energy is required to initiate the separation, spinodal decomposition involves the growth of any fluctuations whose wavelength exceeds a critical value. Experimentally, the typical domain size $R$ is described by a power-law time dependence, $t^n$, where $n \sim 1/3$ when diffusion is the dominant mechanism of material transport, while $n \sim 1$ when hydrodynamic, long-range interactions become important (Chou & Goldburg, 1979; Wong & Knobler, 1981; Guenoun, Gastaud, Perrot & Beysens, 1987; Gupta, Mauri & Shinnar, 1999).

Theoretically, spinodal decomposition in fluids has been described within the framework of the Ginsburg–Landau theory of phase transition (see Le Bellac, 1984, Chapter 2) by Cahn and Hilliard (1959), showing that during the early stages of the process, initial instabilities grow exponentially, forming, at the end, single-phase microdomains whose size corresponds to the fastest-growing mode $\lambda_0$ of the linear regime (Mauri, Shinnar & Triantafyllou, 1996). During the late stages of the
process, i.e. for times \( \tau_0 = \lambda_0^2 / D \), where \( D \) is the molecular diffusivity, the system consists of well-defined patches in which the average concentration is not too far from its equilibrium value, although the condition of local equilibrium is reached much later (Vladimirova, Malagoli & Mauri, 1998). At this point, material transport can occur either by diffusion or by convection. In cases where diffusion is the only transport mechanism, both analytical calculations (Lifshitz & Pitaevski, 1984, Chapter 12) and dimensional analysis (Siggia, 1979) predict a growth law \( R \sim t^{1/3} \), due to the Brownian coagulation of droplets. On the other hand, when hydrodynamic interactions among droplets become important, the effect of convective mass flow resulting from surface tension effects cannot be neglected any more, and dimensional analysis indicates a growth law \( R \sim t \) (Siggia, 1979; Furukawa, 1994). This linear growth has been obtained recently in a series of simulations by Vladimirova, Malagoli and Mauri (1999a,b), showing that phase separation in low-viscosity liquid mixtures is convection-driven, with typical instantaneous fluid velocity being \( O(D/\lambda_0) \). Here, the process is simulated in two dimension, following the so-called model H, in the taxonomy of Hohenberg and Halperin (1977), where the equations of conservation of mass and momentum are coupled via the convective term of the convection–diffusion equation, which is driven by a composition-dependent body force in the Stokes equation. As noted by Jasnow and Viñals (1996), when the system is composed of single-phase domains separated by sharp interfaces, this force incorporates capillary effects, and plays the role of a Marangoni force. After the initial, diffusion-driven stage leads to a non-uniform concentration field, this capillary driving force induces a material flux, which is several orders of magnitude larger than its diffusive counterpart. This convective flux drives the successive process of phase segregation, and can explain the linear growth law which was observed experimentally by Gupta et al. (1999). The agreement, which is both qualitative and quantitative, between 2D numerical simulations and 3D experimental measurements seems to indicate the existence of a universal behavior characterizing all phase separation processes. This conjecture is further strengthened by the results of this work.

After a description of the model in Section 2, in Section 3 we present the numerical results. In Appendixes A and B we show how the constitutive relation of the material flux can be derived, stressing that it can be very different, depending on whether the mean properties of the fluid mixtures are defined in terms of mass or of mole averages. Finally, in Appendix C, the driving force of the Stokes equation is analyzed, showing that it can be interpreted as a capillary force, provided that the system consists of single-phase domains separated by sharp interfaces, as it happens during the late stage of the phase separation process.

2. The governing equations

2.1. The binary mixture at equilibrium

Consider a homogeneous mixture of two species A and B with molar fractions \( x_A \) and \( x_B = 1 - x_A \), respectively, kept at temperature \( T \) and pressure \( P \). For sake of simplicity, in our model we assume that the molecular weights, specific volumes and viscosities of A are equal to those of B, namely \( M_A = M_B = M_W \), \( \bar{V}_A = \bar{V}_B = \bar{V} \) and \( \eta_A = \eta_B = \eta \), respectively, so that molar, volumetric and mass fractions are all equal to each other, and the mixture viscosity is composition-independent. The generalization to binary mixtures composed of species with different physical properties is presented in Appendix A. The equilibrium state of this system is described by the “coarse-grained” free energy functional, that is the molar Gibbs energy of mixing, \( \Delta g_{eq} \),

\[
\Delta g_{eq} = g_{eq} - (g_A x_A + g_B x_B)
\]  

where \( g_{eq} \) is the energy of the mixture at equilibrium, while \( g_A \) and \( g_B \) are the molar free energy of pure species A and B, respectively, at temperature \( T \) and pressure \( P \). The free energy \( \Delta g_{eq} \) is the sum of an ideal part \( \Delta g_{id} \) and a so-called excess part \( g_{ex} \), with

\[
\Delta g_{id} = RT [x_A \log x_A + x_B \log x_B],
\]

where \( R \) is the gas constant, while the excess molar free energy can be expressed as

\[
g_{ex} = RT \Psi x_A x_B,
\]

where \( \Psi \) is a function of \( T \) and \( P \). This expression, which in Chemical Engineering is generally referred to as the one-parameter Margules correlation (Prausnitz, Lichtenthaler & Gomes de Azevedo, 1986), is generally derived by considering the molecular interactions between nearest neighbors or summing all pairwise interactions throughout the whole system (Lifshitz & Pitaevski, 1984). As shown by Mauri et al. (1996), Eq. (3) can also be derived from first principles, assuming that the A–A and the B–B intermolecular forces are equal to each other and larger than the A–B intermolecular forces, i.e.\( F_{AA} = F_{BB} > F_{AB} \), obtaining an expression for \( \Psi \) which depends on \( (F_{AA} - F_{AB}) \). In the following, we shall assume that \( P \) is fixed, so that the physical state of the mixture at equilibrium depends only on \( T \) and \( x_A \). In order to take into account the effects of spatial inhomogeneities, Cahn and Hilliard (1959) introduced the generalized specific free energy \( \tilde{g} \), which for no-flux or periodic boundary conditions is given by the following expression:

\[
\tilde{g} = g_{eq} - \frac{1}{2} RT a^2 (\nabla x_A) (\nabla x_B),
\]

where \( a \) represents the typical length of spatial inhomogeneities in the composition. As shown by van der Waals (1979), \( a \) is proportional to the surface tension.
between the two phases [see Eq. (C.4)] and for a system near its miscibility curve it is typically of the order of 0.1 μm. Below a certain critical temperature \( T_c \), corresponding to values \( Ψ \gtrsim 2 \), the molar free energy can be written as (Prausnitz et al., 1986),

\[
g_{eq}/RT = \mu_A x_A + \mu_B x_B, \tag{5}
\]

where \( \mu_A \) and \( \mu_B \) denote the chemical potential of species A and B in solution, respectively, i.e.

\[
\mu_A = \frac{1}{RT} \frac{\partial (g_{eq})}{\partial c_A}, \quad \mu_B = \frac{1}{RT} \frac{\partial (g_{eq})}{\partial c_B}, \tag{6}
\]

with \( c_A = x_A \) and \( c_B = x_B \) denoting the mole densities, that is the number of moles per unit volume of species A and B, respectively, and \( c = c_A + c_B \) is the total mole density. Consequently, we see that the two quantities \( \phi = x_A \) and \( (\mu_A - \mu_B) \) are thermodynamically conjugated, that is \( (\mu_A - \mu_B) = d(g_{eq}/RT)/d\phi \). This result was extended by Cahn and Hilliard (1959), defining the generalized chemical potential \( \tilde{\mu} \):

\[
\tilde{\mu} = \frac{\delta \tilde{g}/(RT)}{\delta \phi}, \tag{7}
\]

and substituting Eqs. (1)-(4) into Eq. (7) we obtain

\[
\tilde{\mu} = \mu_0 + \log \frac{\phi}{1 - \phi} + \Psi(1 - 2\phi) - \alpha^2 \nabla^2 \phi, \tag{8}
\]

where \( \mu_0 = (g_B - g_A)/RT \).

2.2. The equations of motion

Imposing that the number of particles of each species is conserved, we obtain the continuity equations (see Bird, Stewart & Lightfoot, 1960, Chapter 16)

\[
\frac{\partial c_A}{\partial t} + \mathbf{V} \cdot (c_A \mathbf{v}_A) = 0, \tag{9}
\]

\[
\frac{\partial c_B}{\partial t} + \mathbf{V} \cdot (c_B \mathbf{v}_B) = 0, \tag{10}
\]

where \( \mathbf{v}_A \) and \( \mathbf{v}_B \) are the mean velocities of species A and B, respectively. For an incompressible mixture composed of species with equal physical properties, Eqs. (9) and (10) lead to the following continuity equations in terms of the mass fraction \( \phi \) of the A species (which is equal to its mole fraction):

\[
\frac{\partial \phi}{\partial t} + \mathbf{V} \cdot \nabla \phi = - \frac{1}{\rho} \mathbf{V} \cdot \mathbf{j}, \tag{11}
\]

\[
\mathbf{V} \cdot \mathbf{v} = 0, \tag{12}
\]

where \( \rho = c M_w \) is the mixture mass density, \( \mathbf{j} = \rho \phi (1 - \phi) (\mathbf{v}_A - \mathbf{v}_B) \) is the diffusive mass flux, and \( \mathbf{v} \) is the average velocity of the mixture, \( \mathbf{v} = x_A \mathbf{v}_A + x_B \mathbf{v}_B \). The velocities \( \mathbf{v}_A \) and \( \mathbf{v}_B \) are the sums of a convective part, \( \mathbf{v} \), and a diffusive part:

\[
\mathbf{v}_A = \mathbf{v} - D \nabla \mu_A, \quad \mathbf{v}_B = \mathbf{v} - D \nabla \mu_B, \tag{13}
\]

where \( D \) is a composition-independent diffusion coefficient, and we have assumed that the diffusive parts of \( \mathbf{v}_A \) and \( \mathbf{v}_B \) are proportional to the gradients of the chemical potentials (see Appendix B for a justification of this assumption, where \( D \) is defined as the Onsager mobility coefficient relating the molar flux to its thermodynamically conjugated force). Consequently, the diffusive flux becomes

\[
\mathbf{j} = - \rho \phi (1 - \phi) D \nabla \tilde{\mu}. \tag{14}
\]

Finally, substituting Eq. (8) into Eq. (14), we obtain

\[
\frac{\mathbf{j}}{\rho} = - D \nabla \phi + D \phi (1 - \phi) \nabla^2 \phi, \tag{15}
\]

This expression for \( \mathbf{j} \) coincides with that used in Mauri et al. (1996). The term \( D \nabla \phi \) in Eq. (15) represents the regular diffusion flux, while the last term vanishes for small concentrations of either solvents (\( \phi \to 0 \) or 1) and for ideal mixtures (\( \rho = 1 \)). Note that the \( a^2 \) term is always stabilizing and is relevant only at small length scales, while \( \Psi \) is a known function of the temperature, and near the critical temperature \( T_c \) it is proportional to \( (T_c - T) \). If the flow is slow enough that the dynamic terms in the Navier–Stokes equation can be neglected, conservation of momentum leads to the following Stokes equation:

\[
\eta \nabla^2 \mathbf{v} - \nabla p = - \mathbf{F}_\phi, \tag{16}
\]

where \( \eta \) is the mixture viscosity, which, as we assume, is composition independent, while \( \mathbf{F}_\phi \) is a body force. This latter, in turn, equals the gradient of the free energy, and therefore it is driven by the concentration gradients within the mixture (Valls & Farrell, 1993):

\[
\mathbf{F}_\phi = \frac{\rho}{M_w} \mathbf{V} \mathbf{g} = \left( \frac{\rho RT}{M_w} \right) \mathbf{\tilde{\mu}} \nabla \phi. \tag{17}
\]

In Appendix C we derive the general form of \( \mathbf{F}_\phi \) when the binary mixture is composed of two species having different physical properties. In addition, it is shown that, when the mixture is composed of well-defined single-phase domains separated by a thin interface located at \( r = r_s \), the body force \( \mathbf{F}_\phi \) can be interpreted as a capillary force at \( r_s \), i.e. [cf. Eq. (C.6)]

\[
\mathbf{F}_\phi (r) = \left[ \hat{n} \sigma K + (I - \hat{n} \hat{n}) \nabla \sigma \right] \delta (\hat{n} \cdot (r - r_s)), \tag{18}
\]

where \( \sigma \) is the surface tension, while \( \hat{n} \) and \( \kappa \) are the unit vector perpendicular to the interface and the curvature at \( r_s \), respectively. Physically, \( \mathbf{F}_\phi \) tends to minimize the energy stored at the interface, and therefore it drives, say,
A-rich drops towards A-rich regions, enhancing coalescence. Note that Eq. (16) can also be written as

$$\eta \nabla^2 \mathbf{v} - \mathbf{v} \cdot \nabla \mathbf{v} = \left( \frac{\rho R T}{M_w} \right) \phi \nabla \tilde{\mu},$$

(19)

with \( p' = p - \left( \frac{\rho R T}{M_w} \right) \tilde{\mu} \). Eqs. (11), (12) and (19) constitute the so-called model H (Hohenberg & Halperin, 1977). Now we restrict our analysis to two-dimensional systems, so that the velocity \( \mathbf{v} \) can be expressed in terms of a stream function \( \psi \), i.e., \( v_{\parallel} = \frac{\partial \psi}{\partial x} \) and \( v_{\perp} = - \frac{\partial \psi}{\partial y} \). Consequently, substituting Eq. (15) into Eq. (11) and Eq. (17) into Eq. (16), we obtain

$$\frac{\partial \tilde{\phi}}{\partial t} = \nabla \times \nabla \phi - \frac{1}{\rho} \nabla \cdot \mathbf{j},$$

(20)

$$\eta \nabla^4 \psi = \left( \frac{\rho R T}{M_w} \right) \tilde{\mu} \times \nabla \phi,$$

(21)

where

$$\mathbf{A} \times \mathbf{B} = A_1 B_2 - A_2 B_1.$$  

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

$$\tilde{r} = \frac{1}{a} r, \quad \tilde{t} = \frac{D}{a^2} t, \quad \tilde{\psi} = \frac{1}{\eta} \psi,$$

(22)

and substituting Eq. (15) into Eq. (20) and Eq. (8) into Eq. (21), we obtain

$$\frac{\partial \tilde{\phi}}{\partial \tilde{t}} = \tilde{a}^2 \tilde{\psi} \times \nabla \phi + \nabla \cdot (\tilde{\phi} \nabla \phi - \phi(1 - \phi)(2\tilde{\psi} + \tilde{\nabla}^2 \tilde{\psi}) \nabla \phi),$$

(23)

$$\tilde{\nabla}^4 \tilde{\psi} = - \tilde{\nabla} (\tilde{\nabla}^2 \tilde{\phi}) \times \nabla \phi,$$

(24)

where

$$\tilde{a}^2 = \frac{\rho R T}{D \eta M_w}.$$  

(25)

The non-dimensional number \( \tilde{a} \) is the ratio between thermal and viscous forces, and was interpreted by Jasnow and Viñals (1996) and Vladimirova et al. (1999a) as the inverse capillary number. In this work, however, we prefer to denote \( \tilde{a} \) as the Peclet number, that is the ratio between the diffusion time scale, \( \tilde{t}_{diff} = a^2/D \), and its convective counterpart, \( \tilde{t}_{conv} = a/V \), or, equivalently, the ratio between the convective and the diffusive mass fluxes in the convection–diffusion equation (23), i.e.,

$$\tilde{a} = V a / D.$$  

(26)

We see that when \( \tilde{a} \ll 1 \) random fluctuations prevail and the process is identical to the phase separation of an initially homogeneous system, as described in Vladimirova et al. (1999b). On the other hand, when \( \tilde{a} > 1 \), drift prevails and drops migrate by diffusiophoresis as seen in Vladimirova et al. (1999a). In this article, we will study how these two processes are interrelated.

When it is easier, instead of \( \tilde{a} \) we will use the ratio

$$\gamma = \frac{\beta}{\tilde{a}} = a \nabla \phi_0,$$

(27)

defining the non-dimensional concentration gradient. Clearly, any two of the three non-dimensional numbers \( \tilde{a}, \beta \) and \( \gamma \) completely characterize the phase separation process.

3. Numerical results

The governing equations (23) and (24) were solved on a uniform two-dimensional square grid with constant width \( ((x_i, y_j) = (i \Delta x, j \Delta y), i = 1, N_x, j = 1, N_y) \) and time discretization \( \Delta t = n \Delta t, n = 0, 1, 2, \ldots \). The physical dimensions of the grid were chosen such that \( \Delta x / a, \Delta y / a = 2 \), while the time step \( \Delta t \) satisfied \( \Delta t / (a^2 / D) \approx 0.1 \) – 0.001. The choice of the time step \( \Delta t \) was determined semi-empirically in order to maintain the stability of the numerical scheme. Note that both 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 \( O(\Delta x^3, \Delta y^3) \).
which is the order of the highest operator in the discretized system. The space discretization was based on a cell-centered approximation of both the concentration variable $\phi$ and of the stream function $\psi$. The spatial derivatives in the right-hand side of Eqs. (23) and (24) were discretized using a straightforward second-order-accurate approximation. The time integration from $t^n = n\Delta t$ to $t^{n+1} = (n + 1)\Delta t$ was achieved in two steps. First, we computed the stream function $\psi$ by solving the biharmonic equation (24) with the source term evaluated at time $t^n = n\Delta t$. The biharmonic equations was solved using the DBIWAR routine from NETLIB (Bjorstad, 1980). Second, Eq. (23) was advanced in time, using the velocity field computed from the updated stream function and a straightforward explicit Eulerian step. This makes the entire scheme $O(\Delta t)$ accurate in time, which is acceptable for our problem, since the size of the time step was kept very small anyway by the stability constraints. In addition, it should be stressed that the stream function $\psi$ depends on high-order derivatives of the concentration and therefore it is very sensitive to the concentration profile within the interface.

The boundary conditions were no-flux for the concentration field and no-slip for the velocity field and the discretization of the derivatives near the boundaries was modified to use only interior points. In general, anyway, our results were not very sensitive to the precise treatment of the boundary conditions, since all gradients remained close to zero near the boundaries. Finally, the background noise was simulated generating a random concentration field of amplitude $\delta\phi = 0.01$, which was uncorrelated both in space and in time. Changing the form and the intensity of the noise, however, did not affect the coarsening process, as one would expect since the system is far from equilibrium (see Vladimirova et al. (1998) for a discussion about this point).

Eqs. (23) and (24) were solved with the initial conditions that the mixture is quiescent and a given concentration gradient is imposed along the $y$-direction, i.e. $\phi_0 = 0.5 + \gamma(y/a)$, where $\gamma$ is the constant non-dimensional concentration gradient defined in Eq. (27). Note that, as the axis $y = 0$ is at the center of the cell, the mean concentration is $\langle \phi \rangle = 0.5$.

Eqs. (23) and (24) were solved for different values of the Peclet number $x$ and the concentration gradient $G$. In most simulations, the Margules parameter was kept $\Psi = 2.1$, corresponding to its value for the critical mixture used in the experimental studies by Gupta et al. (1999, 2000). However, simulations with different values of $\Psi$ were also performed, obtaining very similar results. The dependence of the phase separation on the Peclet number is represented in Fig. 1, where $\gamma$ is equal to $0.3 \times 10^{-3}$. Here, the first row of images represents the results for $x = 0$, e.g., for the case when diffusion is the only mechanism of mass transfer, showing that phase separation starts to occur at the center of the system, where $\phi_0 \sim 0.5$, and then propagates towards the walls so that, soon after the quench, the morphology of the system consists of dendroid-like structures near the center of the cell and of isolated drops elsewhere. The mean composition within (and without) these structures changes rapidly, as at time $t = 6 \times 10^4 a^2/D$ we already see two clearly distinguishable phases with almost uniform concentrations equal to 0.59 and 0.41, while at equilibrium their respective compositions are $\phi_{eq}^A = 0.685$ and $\phi_{eq}^B = 0.315$. After this early stage, the structures start to grow, increasing their thickness and reducing the total interface area, while at the same time the composition within the domains approaches its equilibrium value. This, however, is a slow process, driven only by diffusion, and at time $t = 8 \times 10^5 a^2/D$ the phase domains still have a dendroid-like geometry with a characteristic width which is just twice as large as its initial value. For non-zero bulk flow, i.e. for $x \neq 0$, single-phase domains grow much faster than when molecular diffusion is the only transport mechanism. As in the case of systems with homogeneous initial composition, we see that up to $x \approx 10^2$ domain growth still follows the same pattern as for $x = 0$; first, single-phase domains start to appear, separated from each other by sharp interfaces, and only later these structures grow, with increasing growth rate for larger $x$. When $x > 10^2$, however, phase separation occurs simultaneously with the growth process, as circular (due to the effect of surface tension) single-phase domains move fast while they grow, absorbing material from the bulk, colliding with each other and coalescing. The motion of these drops is the effect of the net attractive force between domains of like composition which derives from the previously discussed non-equilibrium capillary force (Gupta et al., 1999). As such, this motion is composed of two parts: a random component, which is observed also for homogeneous mixtures (Vladimirova et al., 1999b), and a drift motion, where A-rich microdomains tend to move upward, i.e. towards the A-rich phase, while B-rich microdomains tend to move downward (Vladimirova et al., 1999a), where they are reabsorbed. Now, while up to $x \approx 10^4$ the random component appears to prevail, a further increase of $x$ delays the formation of sharp interfaces, thus, preserving the initial concentration gradient for a longer time, thus enhancing the reabsorption process. In fact, comparing the last images of Fig. 1 we see that, at the end of the separation process, only a small number of tiny A-rich droplets remain entrapped within the B-rich phase (and likewise B-rich droplets in the A-rich phase) when $x = 10^5$, compared with many more and larger droplets being trapped for smaller $x$. This result is not surprising, as the drift convective bulk flow is proportional to the Peclet number (and to the concentration gradient as well), so that both the drop size and the thickness of the region where drops are confined tend to decrease as $x$ increases. Therefore, drift tends to prevail over random
The composition field of the binary mixture when \( \Psi = 2.1 \) and \( \gamma = 0.3 \times 10^{-2} \), with Peclet number \( x = 0, 10^3 \) and \( 10^5 \). The snapshots correspond to times \( t = 4, 6 \) and \( 8 \) after the instantaneous quenching, expressed in \( 10^3 a^2/D \) units. The color varies between blue and red, corresponding to concentrations \( \phi_{eq}^b \) and \( \phi_{eq}^d \), respectively.

The diffusion as \( x \) increases and, in fact, \( \beta = 0 \) for the first row of Fig. 1, \( \beta = 0.3 \) for the second and \( \beta = 30 \) for the third, where \( \beta \) is defined in Eq. (26).

The dependence of phase separation on the non-dimensional number \( \beta \) is represented in Fig. 2, where the Peclet number is kept equal to \( 10^5 \). Again, we see that both the number of the phase separating drops and the thickness of the region where they are confined decrease as \( \beta \) increases. In addition, we see that at that Peclet number drift and random fluctuations have comparable effects only when \( 1 < \beta < 5 \). In fact, when \( \beta < 1 \), the process reduces to the phase separation of an initially uniform mixture, while on the other hand, when \( \beta > 5 \), phase separation occurs very fast, with hardly any drop forming.

In Fig. 3, we see that in our simulations the number of drops \( N \), after an initial sharp increase, decreases as
$z$ increases. In fact, after forming in the region surrounding the $\phi = 0$ line, drops tend to move towards one of the homogeneous regions, where they are assimilated. Eventually, this process must end with the disappearance of all drops and the formation of a sharp horizontal interface separating the two phases at mutual equilibrium, although our computation time is too short to see that. More important, the average drop size, $R$, as plotted in Fig. 4, is smaller as $z$ increases. Here, $R$ is defined as the average equivalent drop radius:

$$R = \sqrt{\langle A \rangle / \pi}, \quad (28)$$

where $A$ is the area of a single-phase domain, while the bracket indicates, as before, volume and ensemble average. Note that when $z \gg 10^4$ the equivalent radius grows rapidly with time, until it reaches a maximum value, which is smaller as $z$ increases. This behavior is due to the fact that the nucleating drops do not have the chance to grow further, since they are assimilated as soon as they reach the homogeneous region. For smaller value of $z$, i.e. $z \ll 10^3$, $R$ continues to grow, albeit at a slower rate, although, again our computation time is too short to see whether $R$ will reach an asymptotic value at later times or it will keep growing. In a “real” experiment, though, once the drop size becomes equal to the capillary length, $R_{\text{cap}} = O(\sigma / \rho g \Delta \rho)$, where $\sigma$ is the surface tension, $g$ the gravity field, and $\Delta \rho$ the density difference between the two separating phases, then the liquid mixture separates rapidly by gravity (Siggia, 1979).

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Appendix A. Molar vs. mass average

The continuity equation can be written both in terms of number of particles (i.e. moles) and in terms of mass. If all the particles of the system have the same mass, these two approaches are equivalent, as the molar flux can be converted into mass flux by multiplying it by the molar weight, in the same way as the mole density can be converted into mass density. That means that the mole-averaged velocity, defined as the ratio between the molar flux and the mole density, is equal to the mass-averaged velocity, which, in turn, is defined as the ratio between the mass flux and the mass density. Therefore, in the case of a one-component system, we can talk about velocity $v$ without having to specify whether it is mole or mass-averaged. In the same way, in an A–B binary mixture, the velocities of species A and B, $v_A$ and $v_B$, respectively, are well-defined quantities which do not require further explanations. Consequently, the usual continuity equations for the molar concentrations $c_A$ and $c_B$ are still valid for the subsystems of particles A and B, i.e.,

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A v_A) = 0, \quad (A.1)$$

$$\frac{\partial c_B}{\partial t} + \nabla \cdot (c_B v_B) = 0. \quad (A.2)$$

The difference between the mole averaging and the mass averaging approaches arises only when we write the continuity equation for both species. For example, in the mole averaging case, it is convenient to rewrite Eqs. (A.1) and (A.2) in terms of the total mole density $c = c_A + c_B$ and the mole fraction of one of the species, $x = x_A = c_A/c$, as

$$\frac{\partial c}{\partial t} + \nabla \cdot (cv) = 0, \quad (A.3)$$

$$c \left( \frac{\partial x}{\partial t} + v \cdot \nabla x \right) = - \nabla \cdot j^*, \quad (A.4)$$

where

$$v^* = x_A v_A + x_B v_B \quad (A.5)$$

is the mole-averaged velocity, and

$$j^* = c x_A x_B (v_A - v_B) \quad (A.6)$$

is the diffusive molar flux. In the mass averaging case, we obtain similar equations in terms of the total mass density $\rho = \rho_A + \rho_B$ and the mass fraction of one of the species, $y = y_A = \rho_A/\rho$, with $\rho_A = c_A M_A$ and $\rho_B = c_B M_B$ denoting the mass densities of the individual species, i.e.,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = 0, \quad (A.7)$$

$$\rho \left( \frac{\partial v}{\partial t} + v \cdot \nabla v \right) = - \nabla \cdot j, \quad (A.8)$$

where

$$v = y_A v_A + y_B v_B \quad (A.9)$$

is the mass-averaged velocity, and

$$j = \rho y_A y_B (v_A - v_B) \quad (A.10)$$

is the diffusive mass flux (Bird et al., 1960). Here the mass densities of each individual species are defined as the products between their mole densities and their molar weights, i.e. $\rho_A = c_A M_A$ and $\rho_B = c_B M_B$. Therefore, when $\rho_A = \rho_B = \rho$ and $M_A = M_B = M$, the mole- and mass-averaged approaches give identical continuity equations, namely Eqs. (11) and (12).

Appendix B. The constitutive relation for the diffusive flux

For a two-component system, the diffusive mass fluxes of each species A and B are defined as

$$j_A = \rho_A (v_A - v), \quad j_B = \rho_B (v_B - v), \quad (B.1)$$

where $v$ is the mass averaged velocity [cf. Eq. (A.9)]. Applying irreversible thermodynamics, this diffusive mass fluxes can be expressed through the following expressions (Bird et al., 1960; DeGroot & Mazur, 1962):

$$j_A = - \frac{c}{\rho} M_A M_B D c_A \nabla \mu_A, \quad (B.2)$$

$$j_B = - \frac{c}{\rho} M_A M_B D c_B \nabla \mu_B, \quad (B.3)$$

where $\mu_A$ and $\mu_B$ are the chemical potentials of species A and B in solution. Here we have neglected mechanical- and thermal-driven fluxes, as they are both irrelevant in our case. Note that, since $j_A + j_B = 0$, [cf. Eq. (B.1) above, together with Eq. (A.9)], Eqs. (B.2) and (B.3) satisfy identically the Gibbs–Duhem relation

$$x_A \nabla \mu_A + x_B \nabla \mu_B = 0. \quad (B.4)$$

Now we intend to determine the expression for the diffusive flux $j$ appearing in our governing equations. According to Eq. (A.10), it is proportional to $(v_A - v_B)$, where

$$v_A - v_B = \frac{\dot{j}_A}{\rho_A} - \frac{\dot{j}_B}{\rho_B} = - \frac{c}{\rho} M_A M_B D \nabla \left( \frac{\mu_A}{M_A} - \frac{\mu_B}{M_B} \right) \quad (B.5)$$
Chemical potential gradients can be expressed in terms of \( \mu = \mu_A - \mu_B \) [cf. Eq. (7)] by applying the Gibbs–Duhem relation (B.4), to obtain: \( \nabla \mu_A = x_B \nabla \mu \) and \( \nabla \mu_B = x_A \nabla \mu \). Finally, substituting these results into Eq. (A.10) of Appendix A, and considering that \( \rho = c(x_A M_A + x_B M_B) \), we conclude

\[
j = -\rho x_A y_B D \nabla \mu_A , \tag{B.6}
\]

and analogously for the diffusive mole flux,

\[
j^* = -c x_A x_B D \nabla \mu. \tag{B.7}
\]

Therefore, \( D \) can be interpreted as the Onsager mobility coefficient relating the mass (or molar) flux to its thermodynamically conjugated force (DeGroot & Mazur, 1962).

For an ideal mixture, with chemical potential \( \mu = \mu_A^d = \log [x_A/x_B] \), this equation reduces to the “usual”, Fickian constitutive relation, \( j^* = -c D \nabla x_A \).

**Appendix C. The capillary force**

To minimize the classical Gibbs free energy equations (1)–(3), particles of the same kind tend to aggregate, forming single-phase domains separated by narrow regions with sharp concentration gradients. On the other hand, the additional \( a^2(\nabla \phi)^2 \) term in the expression for the generalized free energy (cf. Eq. (4)) forces the different species to rearrange themselves to minimize the concentration gradients in the system. Macroscopically, the motion within the system is induced by the following body force:

\[
F_\phi = \rho \nabla g = \rho \frac{\dot{c} \nabla \phi}{c_0 \phi} \nabla \phi = \mu \nabla \phi, \tag{C.1}
\]

where \( g \) is the energy per unit mass, while the chemical potential \( \mu \) is defined as

\[
\mu = \frac{\dot{c} \nabla \phi}{c_0 \phi} = \rho RT \left( \frac{\mu_A}{M_A} - \frac{\mu_B}{M_B} \right).
\]

An interesting analysis of this force can be found in Jasnow and Vinals (1996). Again, when \( M_A = M_B = M_w \), the expression for \( \mu \) reduces to

\[
\mu = \rho RT \frac{\Delta \mu \dot{c}}{M_w}, \tag{C.2}
\]

where \( \Delta \mu = \mu_A - \mu_B \) is the dimensionless chemical potential (7). Let us consider a well-separated system, that is a mixture composed of single-phase domains of uniform, equilibrium concentration, separated by sharp interfaces. At equilibrium, the line integral of \( F_\phi \) across an interface must equal the surface force \( F_A = \hat{n}\Delta p \), where \( \hat{n} = \hat{n}(r) \) is the unit normal at the location \( r \), on the interface, while \( \Delta p \) is the pressure jump across the interface. This latter, in turn, is related to the surface tension \( \sigma \) through Laplace’s formula, \( \Delta p = \sigma \kappa \), where \( \kappa = \kappa(r) \) is the curvature at \( r \), obtaining

\[
\int F_\phi d(\hat{n} \cdot r) = \hat{n}\sigma\kappa. \tag{C.3}
\]

From this relation, we can easily estimate \( \sigma \) as

\[
\sigma \approx \frac{\rho RT a}{M_w} (\Delta \phi)^2 \sqrt{\frac{\pi}{\ell^2}} - 2, \tag{C.4}
\]

where \( (\Delta \phi)_0 = (\phi_1 - \phi_2)_0 \) is the concentration drop across the interface, while we have considered that the width of the interface \( \ell \) equals the wavelength corresponding to the fastest growing mode of the linear regime, \( \ell \approx a/\sqrt{\pi - 2} \). Expression (C.4) for the surface tension is consistent with the definition of \( \sigma \) as the energy stored in the unit interfacial area, i.e.,

\[
\sigma = \frac{1}{\sqrt{2} M_w} a n \int (\nabla \phi)^2 \mathrm{d}x. \tag{C.5}
\]

When the system is not at equilibrium, Eq. (C.3) should be modified to account for the Marangoni tangential force, which is proportional to the tangential derivative of the surface tension, \((1 - \hat{n} \cdot \nabla) \sigma \). Therefore, in the limit of a vanishing interface width \( \ell \to 0 \), the body force reduces to (see Jasnow & Vinals, 1996, for a formal proof),

\[
F_\phi = [\hat{n}\sigma\kappa + (1 - \hat{n} \cdot \nabla) \sigma] \delta(\hat{n} \cdot (r - r_s)), \tag{C.6}
\]

which yields the conventional surface force at \( r_s \).

**References**


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