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SIMULATION OF THE NUCLEATION AND DOMAIN GROWTH DURING PHASE TRANSITION OF PARTIALLY MISCIBLE SOLVENT SYSTEMS WITH OFF-CRITICAL COMPSTIONS

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ABSTRACT A numerical model based on the diffuse interface approach is developed to simulate the phase separation of binary Upper Critical Solution Temperature (UCST) mixtures with critical and off-critical compositions in 2D geometry. The modeling is intended to simulate the response of such mixtures whilst cooled into the unstable region or to the metastable region. With an off-critical composition, the initial homogeneous mixture may separate via nucleation and growth mechanism, provided it is exposed to a strong enough composition perturbation. In this study, the numerical model is used to explore the response of off-critical composition mixtures to white noise and two different forms of nuclei: a circular drop, and a 2D wavelet. The significant differences in the phase separation processes taking place with critical solution via spinodal decomposition, and off-critical compositions via nucleation and growth, are demonstrated and discussed. While a white noise perturbation in concentration suffices to trigger separation in the unstable region, nuclei exceeding a critical size are required to initiate the separation in the metastable region.

NOMENCLATURE

a	typical length scale of spatial inhomogeneity
â	constant microscopic length
F_{ϕ}	body force due to concentration gradients (Korteweg force)
$\bar{H}_i$	partial molar enthalpy
j_i	diffusive molar flux
q^c	conductive energy flux
q^d	inter-diffusion energy flux
R	nuclei's radius
R_{eq}	equivalent radius of a wavelet or a drop
ϕ	molar fraction
η	mixture's viscosity
μ_{NL}	non-local part of the generalized chemical potential
ψ	stream function
Ψ	Maragules parameter

INTRODUCTION

Partially miscible binary mixture undergoing a temperature quench below its miscibility curve would become either meta-stable or unstable. This depends on the composition and the depth of the temperature quench. A schematic description of the phase diagram of a binary system with an Upper Critical Solution Temperature (UCST) is shown in Figure 1. With a critical composition, any quench below the critical temperature is into the unstable region, which is defined by the spinodal curve, results in phase separation via spinodal decomposition. It is a spontaneous delocalized process with a formation of unstructured domains of the separating phases. With an off-critical composition and a deep enough quench, the system passes the meta-stable region, reaches the unstable region, and separates via nucleation (e.g., Ullmann et al., 2008). However, a shallow quench to the region confined between the miscibility and spinodal curves would lead to a meta-stable state, where a system may remain as a single phase for a long period (similarly to superheated/cooled liquids). In this case, only nuclei with an initial radius larger than a critical value grow, whereas those having an initial radius smaller than the critical one are reabsorbed (Lamorgese and Mauri, 2005). Following the nuclei formation a process of droplets growth by mechanisms of diffusion, convection and coalescence is taking place until eventually two separated phases with compositions corresponding to the binodal (equilibrium) curve will be formed.

We develop a 2D numerical model for phase separation of binary mixtures with off-critical composition. The diffuse interface approach was used to derive the model equations for the conservation of mass, momentum and energy. These conservation equations were previously used to study isothermal and non-isothermal spinodal decomposition of a critical composition mixture (Segal et al., 2012, 2015). In this study, the numerical tool is used to explore the response of off-critical composition mixtures, which are quenched into the metastable region or into the unstable region within the spinodal curve. The significant differences in the phase separation processes taking place in the two-cases, compared to spinodal decomposition of a critical solution, are demonstrated and discussed.

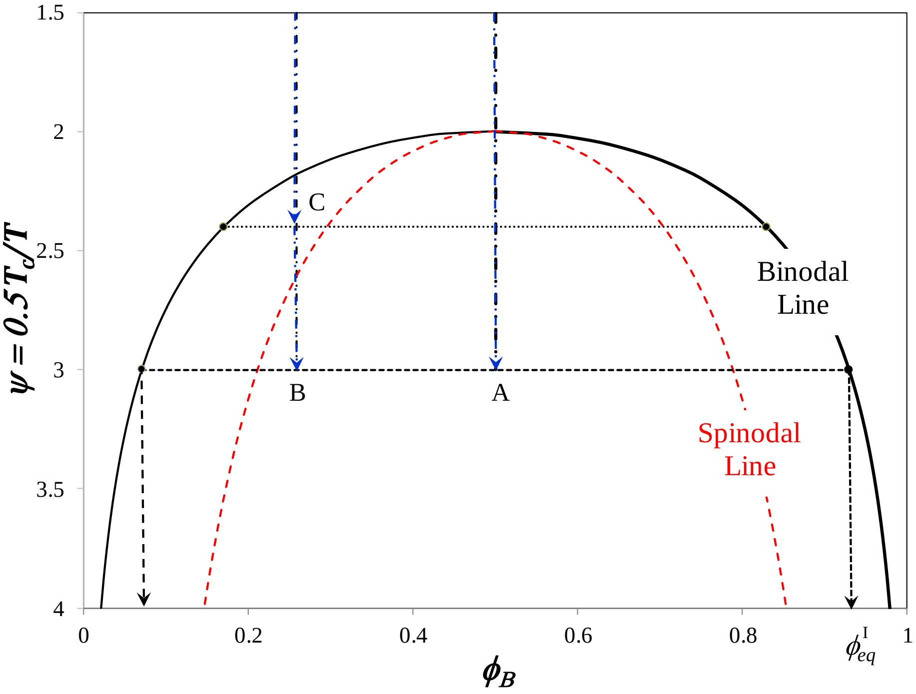

Figure 1. Binodal (coexistence, equilibrium) and spinodal curves obtained by one-parameter Margules equation, showing the quench of a critical solution. (A) critical quench, (B) off-critical quench to the unstable region, (C) off-critical quench to the meta-stable region.

GOVERNING EQUATIONS

As the interface between the separating phases is initially non-existing and gradually evolves in time, the modeling and simulation of the phase separation process can be carried out via the diffuse interface approach, where all properties are considered to vary continuously over the diffuse interface. The governing equations for a two-component system Upper CST (of equal density and equal molar weight), which include the conservation of mass, momentum and energy, were presented in Segal et al. (2012) as follows:

$$\nabla \cdot v = 0 \tag{1}$$

$$\frac{D\phi}{Dt} = \frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = -\frac{1}{\rho} \nabla \cdot j_1 \tag{2}$$

$$\rho \frac{Dv}{Dt} = -\nabla p + \eta \nabla^2 v + F_\phi \tag{3}$$

$$\rho c \frac{DT}{Dt} = -\nabla \cdot q + \sum_{i=1}^{2} \bar{H}_i \left(\nabla \cdot j_i \right) \tag{4}$$

where v is the mixture velocity, ϕ is the concentration field (component B in Figure 1), j is the diffusive mass flux, p is the pressure. ρ , η are the mixture's density and viscosity, respectively. F_ϕ is the Korteweg force given by $F_\phi = (\rho/M)\mu_{NL}\nabla\phi$, where $\mu_{NL} = -RTa^2\nabla^2\phi$ is the non-local part of the generalized chemical potential and (a) is the length scale of the spatial inhomogeneity that is included in the generalized free energy coarse-grained Landau-Ginzburg functional (Cahn and Hilliard, 1958,1959). It is proportional to the surface tension between the separated phases and for low viscosity liquid is of the order of 0.01 to 0.1 μm (e.g., Vladimirova et al., 2000, Poesio et al., 2006). In the energy Eq. (4), c is the specific heat of the mixture, $q = q^c + q^d$ is the sum of conductive ($q^c = -k\nabla T$) and inter-diffusion energy fluxes ($q^d = \sum \bar{H}_i j_i$) and $\bar{H}_i$, j_i are the partial enthalpy and diffusive mass flux of component i, respectively (see Bird et al., (1960)). The typical length scale (a) relates to the surface tension σ between the separated phases (van der Waals, 1979), and takes the form of:

$$a^2 = \hat{a}^2 \frac{2}{T/T_C(1-BT/T_C)} \tag{5}$$

where â is a temperature independent microscopic length scale. Note that the factor B has been introduced to avoid singularity at the critical point (i.e., B=1, except in close proximity to the critical point, where B=1-ε, ε →0 is used). By applying B=0, the typical length scale takes the form of $a = \hat{a}\sqrt{\Psi}$, as was applied in Molin and Mauri (2007). A "regular solution" was adopted as a model for the thermodynamic Gibbs free energy of a non-ideal two-component system, with the one-parameter ($\Psi = 2T_c / T$) Margules model to represent the excess part (e.g., Lupis, 1983). The corresponding binodal (coexistence) curve and spinodal curves are shown in Figure 1.

As the study is restricted to two-dimensional systems, the velocity components can be expressed in terms of a stream function, i.e., $v_1 = \partial\psi/\partial y$, $v_2 = -\partial\psi/\partial x$. The following dimensionless variables are introduced:

$$\tilde{x},\tilde{y} = \frac{1}{\hat{a}}(x,y), \quad \tilde{t} = \frac{D}{\hat{a}^2}t, \quad \tilde{\psi} = \frac{1}{N_{Pe}D}\psi, \quad \tilde{T} = \frac{1}{T_C}T, \quad \tilde{c} = \frac{c}{R} \tag{6}$$

Upon rescaling, the final dimensionless form of the conservation equations (mass, momentum and energy) reads:

$$\frac{\partial\phi}{\partial\tilde{t}} = \tilde{\nabla}\tilde{\psi} \times \tilde{\nabla}\phi + \tilde{\nabla}\cdot\left\{\tilde{\nabla}\phi - \phi(1-\phi)\left[\frac{4}{\tilde{T}}\tilde{\nabla}\phi + \frac{2}{\tilde{T}(1-B\tilde{T})}\tilde{\nabla}^3\phi + \frac{2B}{\tilde{T}(1-B\tilde{T})^2}\tilde{\nabla}^2\phi\tilde{\nabla}\tilde{T}\right]\right\} \tag{7}$$

$$\tilde{\nabla}^4\tilde{\psi} = -N_{Pe}\left[\frac{2}{1-B\tilde{T}}\tilde{\nabla}(\tilde{\nabla}^2\phi) \times \tilde{\nabla}\phi + \frac{2B}{(1-B\tilde{T})^2}\tilde{\nabla}^2\phi(\tilde{\nabla}\tilde{T} \times \tilde{\nabla}\phi)\right] \tag{8}$$

$$\frac{\partial\tilde{T}}{\partial\tilde{t}} = \tilde{\nabla}\tilde{\psi} \times \tilde{\nabla}\tilde{T} + N_{Le}\tilde{\nabla}^2\tilde{T} - 2\tilde{c}^{-1}\left(2\tilde{\nabla}\phi + \frac{1-2B\tilde{T}}{(1-B\tilde{T})^2}\tilde{\nabla}^3\phi + \frac{2B^2\tilde{T}}{(1-B\tilde{T})^3}\tilde{\nabla}\tilde{T}\tilde{\nabla}^2\tilde{\phi}\right)\cdot\left\{\tilde{\nabla}\phi - \phi(1-\phi)\left[\frac{4}{\tilde{T}}\tilde{\nabla}\phi + \frac{2}{\tilde{T}(1-B\tilde{T})}\tilde{\nabla}^3\phi + \frac{2B}{\tilde{T}(1-B\tilde{T})^2}\tilde{\nabla}\tilde{T}\tilde{\nabla}^2\tilde{\phi}\right]\right\} \tag{9}$$

where $N_{Pe} = (\hat{a}^2\rho RT)/(D\eta)$ is the Peclet number, and $N_{Le} = \alpha/D$ is the Lewis number. The boundary conditions are: zero mass flux through the two cooled walls (maintained at constant temperature $T=T_w$) and no-slip condition for the velocity field. To maintain impermeable walls, the boundary conditions are set to $\tilde{\nabla}\phi = 0$ and zero sum of the last two terms in Eq.(7) at the cooled walls. At the other two boundaries, periodic boundary conditions are set.

For off critical quench into the meta-stable region, a single perturbation centered in the middle of the domain is added to the initial uniform concentration field. The initial perturbation takes the form of a 2D Mexican Hat Wavelet, which is defined by:

$$\phi_{wavelet}(r) = (\xi - x^2 - y^2)e^{-\frac{1}{\xi}(x^2+y^2)} \tag{10}$$

where ξ defines the wavelet's maximum height, which was placed to the value of the higher equilibrium concentration ϕ_{eq}^{I} (rich in component B, see Figure 1 and Figures 4,5). As the total contribution of the wavelet's "positive" hill and surrounding "negative" lows (with respect to the initial uniform concentration field) sums to zero, there is no need to readjust the bulk concentration of the entire computational domain (as to maintain the mass balance) upon the introduction of the disturbance.

The governing equations are spatially discretized by a cell-centered second order accurate approximation, and solved on a uniform square grid. The simulation starts with an initial homogeneous concentration field. The initial temperature field is also homogeneous, with a value above the critical temperature. At each time step n, all three equations are solved for the temperature, concentration and velocity fields. The bi-harmonic equation for the velocity field can be solved implicitly using a fast Fourier transform (FFT) algorithm. After achieving the velocity field for the time n+1, it can be used to compute the concentration and temperature fields for the next time step n+1, using a straightforward first order explicit Eulerian scheme. The computations were validated by using various mesh size and time step size, to assure convergent results. The results presented below were obtained by using a 100X100 grid with dx=0.75 $\hat{a}$ and $d\tilde{t}=10^{-3}$. In case immediate quench to a final uniform temperature was assumed in the simulations presented, the energy equation (4) is excluded from the model.

RESULTS AND DISCUSSION

A demonstration of the simulation results for the phase separation process obtained with a critical quench and off-critical quenches are shown in Figures 2-5. Figure 2 shows the simulation results for a critical quench. The solution is initially at a uniform critical composition (i.e., temperature above the CST) and immediately quenched to a constant and uniform temperature below the CST (case A, Figure 1). As shown, the simulated phase separation is, in this case, associated with the formation of unstructured network of domains, which are characteristic to spinodal decomposition (Figure 2a). The domains grow with time and their boundaries become sharper. The corresponding velocity field, which results from the chemical potential gradients, is shown in Figure 2b. Obviously, the highest velocities are at the regions of the diffuse interface between the separating phases. Note that when considering low molecular weight (and low viscosity) liquids, the entire simulation domain is in the range of 1 to 10 μm, and the time scale of $100\tilde{t}$ corresponds to $10^{-3} - 10^{-5}$sec. With these scales the velocities are of the order of few cm/sec.

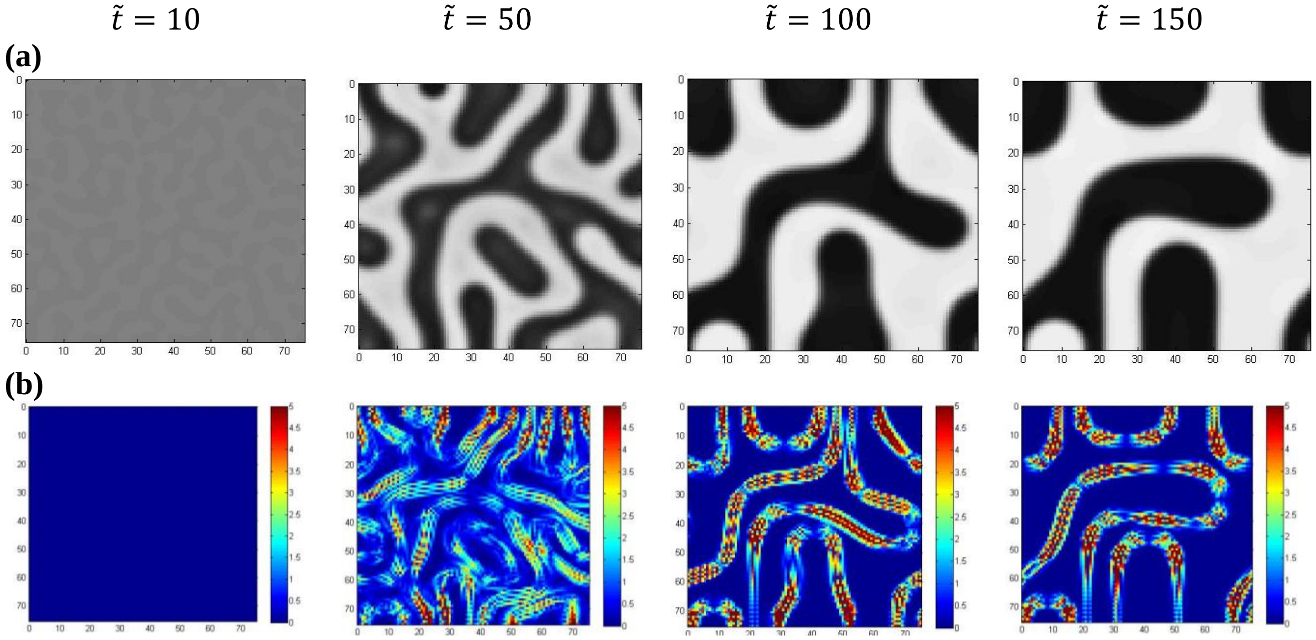

Figure 2. Spinodal Decomposition of a critical composition solution (quenched to $\Psi = 3$ with initial "white noise" in concentration of 10-2), Pe= 10^3. Upper figures (a) – concentration field, lower figures (b) – velocity field.

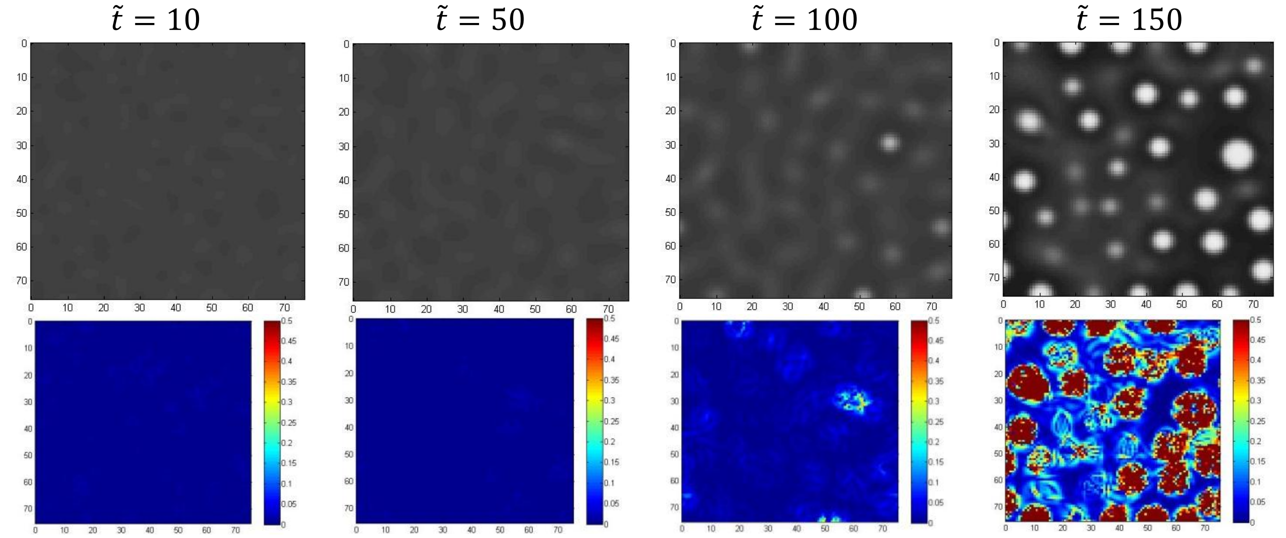

Figure 3. Decomposition of off-critical composition solution, $\phi_0 = 0.258$, quenched to $\Psi = 3$ (with initial "white noise" in concentration of 5*10-2), Pe= 10^3. Upper figures – concentration field, lower figures – velocity field.

The decomposition of off-critical composition solution with initial uniform composition of $\phi_0 = 0.258$, that is quenched into the unstable region (i.e., within the spinodal curve, case B in Figure 1) is shown in Figure 3. The final temperature is the same as that in Figure 2 ($\Psi = 3$). However, as shown, the domain's morphology of the separating phases is definitely different and corresponds to circular structures, which are characteristic to a nucleation and nuclei growth of the minority phase (the phase with the higher concentration of component B). The separation process is much slower compared to spinodal decomposition (although the initial "white noise" introduced is higher), and the velocities induced during the process are lower.

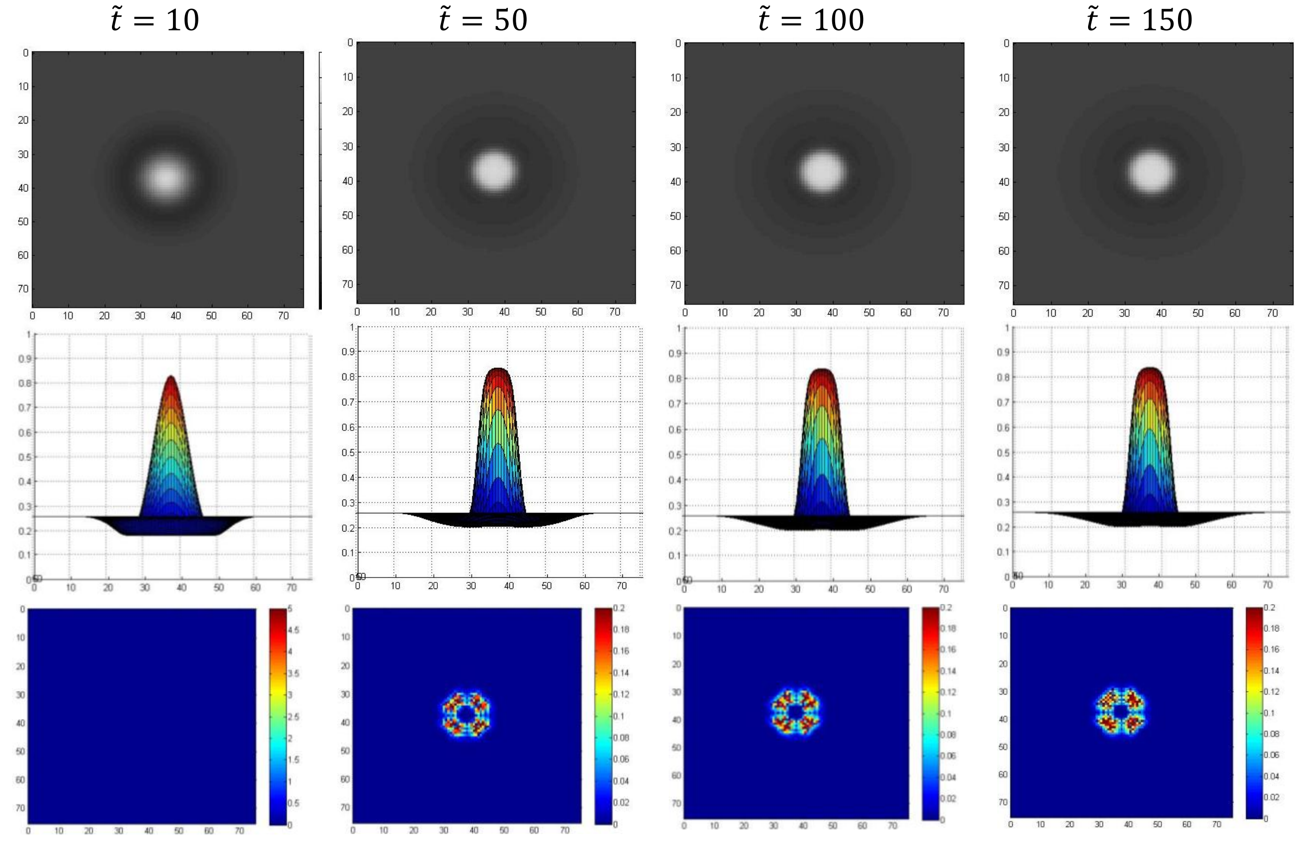
$\tilde{t} = 10$ $\tilde{t} = 50$ $\tilde{t} = 100$ $\tilde{t} = 150$

Figure 4. Nucleus growth in off-critical composition solution, $\phi_0 = 0.258$, Pe= 10^3, quenched into the metastable region, $\Psi = 2.4$ (initial field with a nucleus larger than the critical size, Req=5.16â). Upper figures – concentration field, middle figures – nucleus (wavelet) composition, lower figures – velocity field.

The decomposition of an off-critical composition solution with an initial uniform composition of $\phi_0 = 0.258$ that is quenched into the meta-sable region ($\Psi = 2.4$, case C in Figure 1) is shown in Figures 4 and 5. According to Gibbs, a meta-stable system becomes unstable when the nuclei exceed a critical size, R>Rc, as opposed to the unstable region, where a nucleus of any size would grow spontaneously. As shown, the initial nucleus introduced in Figure 4 exceeds the critical size, and the phase separation proceeds with time. On the other hand, when the initial nucleus size is smaller than a critical value (Figure 5), the nucleus is absorbed and vanishes.

In order to characterize the nucleus radius associated with the wavelet perturbation, its equivalent radius is defined. It corresponds to the radius of an equivalent (2D) drop of a uniform concentration $\phi = \phi_{max} = \phi_{eq}^{I}$. Accordingly, the equivalent radius of the wavelet is the radius of a droplet of concentration ϕ_{eq}^{I}, and a molar mass (of components B, m) that is equal to that of the mass of the wavelet part where the concentration exceeds the initial field concentration. Hence:

$$\mathrm{R_{eq}} = \sqrt{\frac{\mathrm{m}}{\pi(\phi_{\mathrm{max}} - \phi_0)}} \tag{11}$$

Inspection of Figures 4,5 shows that at short times there is a decrease in the maximal concentration of the nucleus. For a large enough initial nucleus ($\mathrm{R_{eq}}$=5.16â in Figure 4) the decrease is followed by a later recovery of the maximal concentration, back towards the equilibrium value, ϕ_{eq}^{I}. However for smaller size nucleus (R_{eq}= 2.06â in Figure 5) the maximal concentration continues to decrease towards the initial concentration value, ϕ_0.

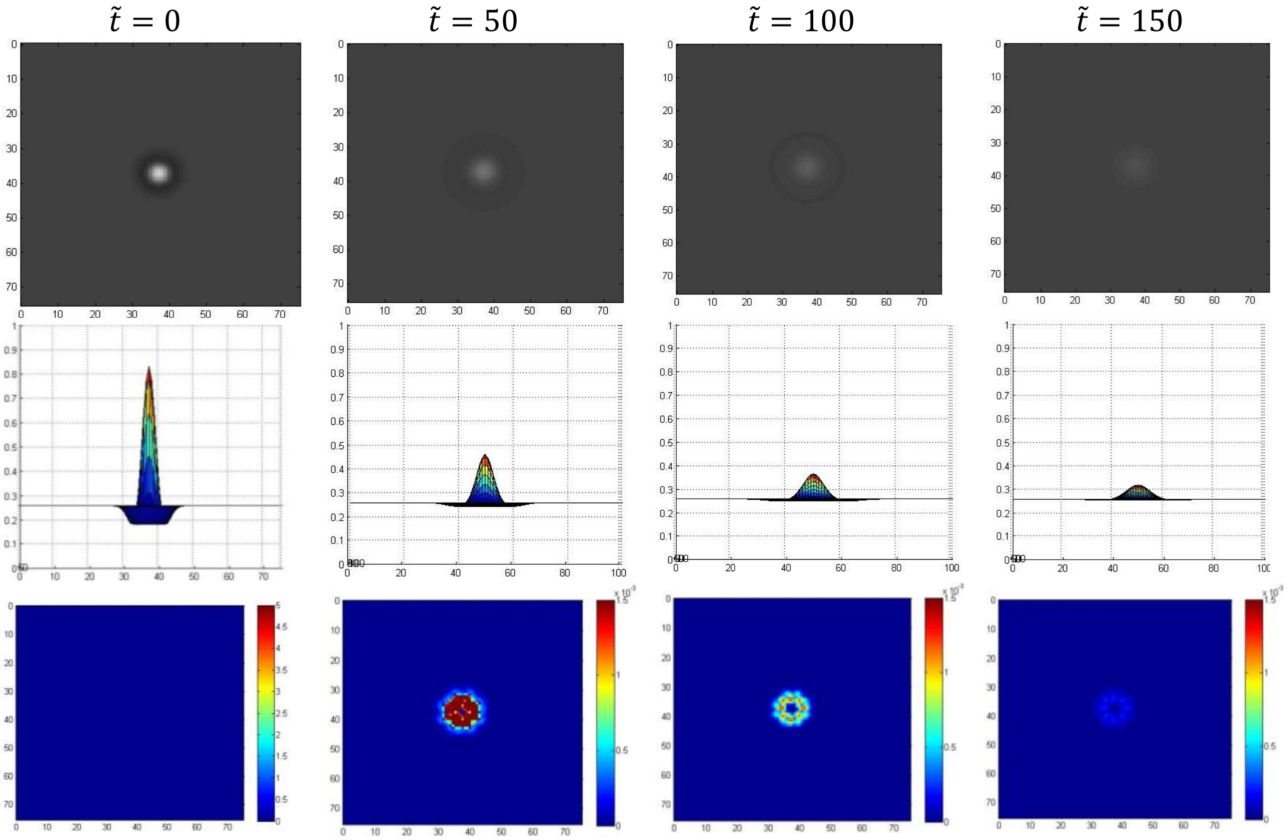

Figure 5. Decay of a nucleus in off-critical composition solution, $\phi_0 = 0.258$, Pe= 10^3, quenched into the metastable region, $\Psi = 2.4$ (initial field with a nucleus smaller than the critical size, Req= 2.06â). Upper figures – concentration field, middle figures – nucleus (wavelet) composition, lower figures – velocity field.

In Lamorgese and Mauri (2005), a simulation of off-critical quench into the meta-stable region was carried out by introducing to the initial uniform concentration field a nucleus in the shape of a circular drop with a uniform concertation of $\phi = \phi_{eq}^{I}$. To avoid a sharp interface between the drop and the bulk, the concentration was assumed to reduce to the surrounding bulk concentration over a length scale a. Accordingly, the concentration distribution of circular drop nucleus introduced is given by:

$$\phi_{\mathrm{drop}}(r) = \left\{ \begin{array}{ll} \phi^{I}_{eq} & \text{if } |r| \le R_0 - a \\ \phi_b + \frac{1}{2}\left\{\phi^{I}_{eq} - \phi_b\right\}\left[1 + \cos\frac{\pi}{a}(|r| - R_0 + a)\right] & \text{if } R_0 - a < |r| \le R_0 \\ \phi_b & \text{if } |r| > R_0 \end{array} \right\} \qquad (12)$$

where R_0 denotes the drop radius, and ϕ_b is the bulk concentration. To maintain the initial overall composition, the bulk concentration of the entire domain has to be readjusted, whereby:

$$\phi_b = \left[\phi_0 - \left(\frac{a}{L}\right)^2 \frac{\pi^2(2\rho^2-4\rho+3)-4}{2\pi}\phi^{I}_{eq}\right]\left[1 - \left(\frac{a}{L}\right)^2 \frac{\pi^2(2\rho^2-1)-4}{2\pi}\right]^{-1} \qquad (13)$$

where $\rho = R_0/a$. Therefore, the effect of introducing such a nucleus is in fact non-local and spread instantaneously over the entire domain.

Figure 6 presents the concentration profile evolution when a circular drop (Eqs.12-13) is introduced and the solution is quenched into the meta-stable region (same parameters as in Figures 4,5). Also in this case, the initial drop size should exceed a critical value to enable its growth (e.g., Figure 6b) and avoid its absorption into the bulk (e.g., Figure 6a). Similarly, to the wavelet nucleus, here too, even with R>Rc, the maximal concentration in the nucleus may initially decrease with time, but eventually it starts growing and reaches the equilibrium (maximal) concentration, ϕ_{eq}^{I} (see Figure 7). The concentration perturbation introduced by a wavelet-shaped nucleus is more moderate compared to a circular nucleus, and therefore its critical R_{eq} is somewhat higher, yet similar to that of a circular nucleus. However, Figure 6 shows that an initial circular drop nucleus evolves in time into a wavelet shape, thus supporting the premise that a wavelet is a more appropriate form of an initial nucleus to simulate phase separation in the meta-stable region. Obviously, a spontaneous formation of a nucleus with a concertation higher than that of the bulk is on the expense of its immediate surrounding, rather than on the expense of entire bulk domain.

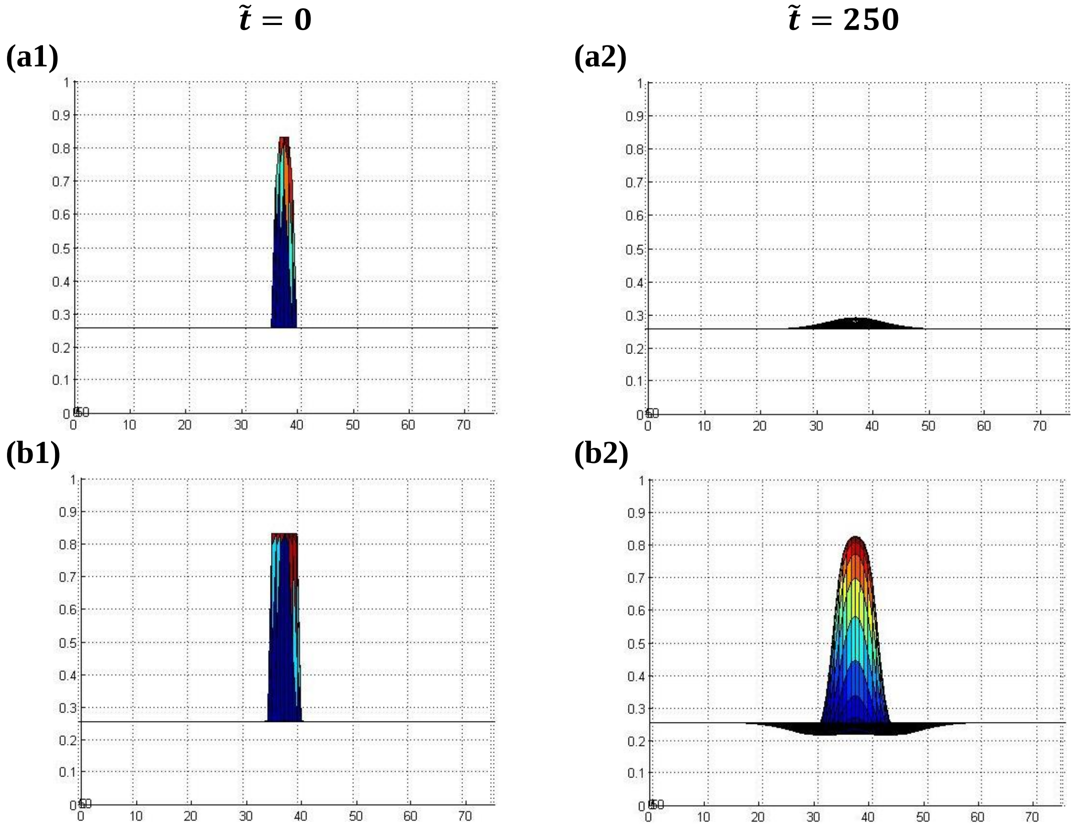

Figure 6. Concentration profile at time 0 (on the left) and 250 (on the right) following: (a) Drop perturbation with R_0 = 1.61â and (b) Drop perturbation with R_0 = 2.09â ($\phi_0 = 0.258$, Pe= 10^3, $\Psi = 2.4$).

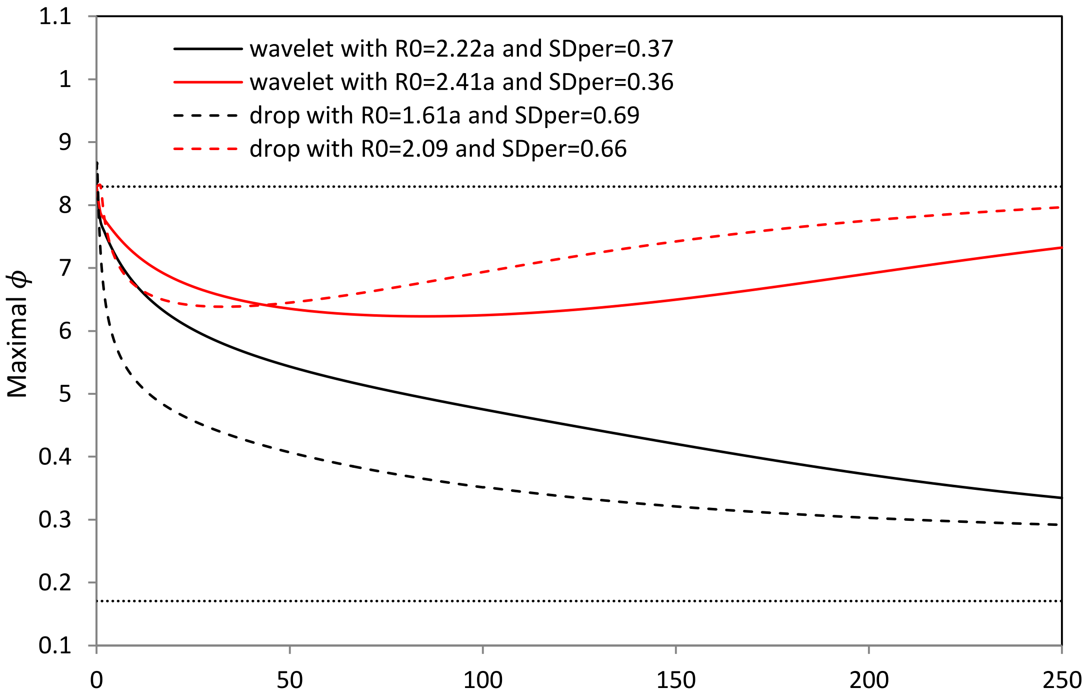

Figure 7. Maximal concentration for wavelet and drop perturbations: $\phi_0 = 0.258$, Pe= 10^3, $\Psi = 2.4$ (dashed horizontal lines mark the equilibrium concentrations of the separating phases).

CONCLUSIONS

A numerical solution of a diffuse interface model has been used to study the phase separation process of a binary Upper Critical Solution Temperature (UCST) mixture when it is quenched below its miscibility curve to the unstable region, or to the meta-stable region. As expected, quenching of a critical composition was shown to result in a spinodal decomposition, while with an off-critical composition, the initial homogeneous mixture separates via nucleation and growth mechanism, provided it is exposed to a strong enough composition perturbation. In this study, the numerical tool is used to explore the response of off-critical composition mixtures to white noise and two different forms of nuclei: a circular drop, and a 2D wavelet. The significant differences in the phase separation processes taking place with a critical composition via spinodal decomposition, and with off-critical compositions via nucleation and growth, are demonstrated and discussed. While a "white noise" perturbation in concentration suffices to trigger separation in the unstable region, nuclei exceeding a critical size are required to initiate the separation in the metastable region.

Inspection of the velocity field reveals the convection driven by the Koteweg forces due to chemical potential gradients. The convection is shown to be pronounced in the vicinity of the diffuse interface formed between the separating phases, where the concertation gradients are the highest. This convective motion enhances the separation process and can augment the transport phenomena accompanying the separation process (e.g., heat transfer). The convection and the rate of phase separation were found to be much faster in spinodal decomposition of solution with critical composition, compared to the nucleation and growth mechanism of off-critical composition mixtures. These findings have implication on the heat transfer rates augmentation via inducing phase separation of CST mixtures when such mixtures are used as coolants or heating fluids (see Ullmann et al., 2014a, Ullmann et al., 2014b).

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