**Phase field modeling of phase separation in a binary mixture in presence of external forces**

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**1.Introduction**

When a partially miscible binary mixture is brought from the stable region to the unstable region of its phase diagram, it separates into two coexisting phases since this corresponds to the minimization of the mixture free energy. Such a phase transition, called spinodal decomposition, is a reordering process that takes place isotropically. However, when an external force field (e.g., gravity or electric/magnetic fields) is applied to the mixture, provided that the force exerts a different acceleration to the species, demixing is enhanced, leading to stratification or to anisotropic phase separation.

In this study the process of phase separation of a regular binary mixture subject to an external force field is studied by extending the thermodynamics-based phase field model developed by the authors in a series of publications [1-3]. Numerical simulations show how the external force field breaks the isotropy of the mixture dynamics when starting from stable, unstable and metastable initial states of the phase diagram.

**2. Methods**

The phase field (a.k.a. diffuse interface) approach assumes that the interface between different phases is not a sharp bidimensional surface but, rather, it occupies a finite volume wherein all the mixture properties vary continuously, from the bulk region of one phase to the bulk region of the other phase [1]. In this way, capillary forces associated to the interfaces, such as the surface tension, are treated as volumetric forces in the governing equations of the mixture.

We basically start from the conservation of mass, species and momentum for a regular binary mixture, as follows [1-3]:

$\frac{∂ρ}{∂t}+∇∙\left(ρv\right)=0$ (1)

$\frac{∂\left(ρv\right)}{∂t}+∇∙\left(ρvv-η\left(∇v+∇v^{T}\right)\right)=-∇p+ρf$ (2)

 $\frac{∂\left(ρϕ\right)}{∂t}+∇∙\left(ρvϕ+J\_{ϕ}\right)=0$ (3)

where *t* is time, *f* is the mass fraction of species *1* in the mixture, *r* and *h* the density and viscosity of the mixture (which are assumed constant), *p* is pressure, **v** is the mass-average velocity, **f** is the force per unit mass and **J***f* is the diffusion flux. In particular, the volumetric force *r***f** is the sum of two contributions: the Korteweg force (first term on the right-hand side of Eq. (4)), which is a non-equilibrium force that encodes the capillary stresses which arise from spatial inhomogeneities, and the applied external force (second term on the right-hand side of Eq. (4)), as follows [1,3]:

$ρf=ρ\frac{RT}{M\_{w}}ϕ∇\left(a^{2}∇^{2}ϕ\right)+ρϕχ\_{12}b$ (4)

where *R* is the universal gas constant, *Mw* the molecular weight of the species (assumed equal for both species), *T* is temperature, *a* is the characteristic length of the diffuse interface, while *c*12 and **b** are difference in species susceptibilities and the external body force, respectively.

The external force, being its effects different on the two species of the mixture, provides an additional contribution to species diffusion, so that the species diffusion flux results as [3]:

$J\_{ϕ}=-ρD\left[\left(1-2Ψϕ\left(1-ϕ\right)\right)∇ϕ-ϕ\left(1-ϕ\right)∇\left(a^{2}∇^{2}ϕ\right)\right]+ρD\frac{M\_{w}}{RT}ϕ\left(1-ϕ\right)χ\_{12}b$ (5)

where *D* is species diffusivity and Y is the Margules coefficient, which describes the non-ideality of the mixture.

**3. Results and discussion**

Figure 1 shows the main results of the numerical solution of the system of Eqs. (1)-(5). The phase diagram of the mixture (Figure 1a) shows that while above the critical temperature *Tc* the mixture is always stable and does not phase separate, below *Tc* there is a miscibility gap, with unstable and metastable regions.

When the external force is applied to a mixture in the stable region of the phase diagram, as in point A, the two species undergo a stratification process, as shown in Figure 1b, where species *1* is pushed along the direction of the force field (which is the vertical one in this case). Even though there is no phase separation, the external force leverages on the thermodynamic repulsion between the species, which segregate following a continuous species distribution.

The application of the external force to an unstable mixture (point B in Figure 1a) leads to a specific directionality to phase separation, as show in Figure 1c. In particular, as small nuclei of the minority phase emerge, these are pushed by the external force, which speeds up demixing and makes it anisotropic, leading to two completely segregated phases at steady-state.

Finally, the external force field can trigger phase separation from the metastable region, as for point C in the phase diagram. If the force is sufficiently strong to stratify the species so that a significant fraction of the domain falls within the unstable region (see Figure 1d, in particular the grey line which denotes the spinodal composition), phase separation starts and proceeds following a nucleation process, where the interface forms first and then moves slowly to its final state.



**Figure 1.** Effect of the external force in a binary mixture. a) Phase diagram, b) stratification induced for the stable point A, c) phase separation from the unstable point B and d) from the metastable point C.

**4. Conclusions**

The phase field model proves to be a versatile modelling framework to simulate the dynamics of multiphase flows from first principles, where external forces can be easily included within the modeling framework. This opens the scope for an extended use of phase field modelling to simulate mixtures subject to gravitational, electric or magnetic force fields.

**References**

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