 FDMP, vol.3, no.4, pp.287-293, 2007

Phase field models and Marangoni flows

Rodica Borcia[1,2] **and Michael Bestehorn**[2]

Abstract: We developed a phase field model for Marangoni convection in compressible fluids of van der Waals type far from criticality. The theoretical description is based on the Navier-Stokes equation with extra terms responsible for describing the Marangoni effect, the classical heat equation, and the continuity equation. The model previously developed for a two-layer geometry is now extended to drops and bubbles. Finally, we report on 2D numerical simulations for drop Marangoni migration in a vertical temperature gradient.

Keyword: Marangoni flow, Pattern formation, Drops and Bubbles, Interface and Surface Thermodynamics

1 Introduction

Composite systems of two or more phases like two immiscible fluids or a fluid with a free surface can be described using an additional phase field. This field contains information about the local state of the composition and permits to distinguish between different phases. With the help of the phase field variable all system parameters can be expressed as functions varying continuously from one medium to another. Therefore, the problem is treated like an entire one phase problem and the interface conditions will be substituted by some extra-terms in the Navier-Stokes equation. Because they reduce the system of equations (they don't need different equations for each medium) and eliminate the explicit interface conditions, the phase field models have been successfully applied to the case of large interface deformations, are more flexible in handling interface geometries, and are very attractive in view of their numerical simplicity.

The present work extends our phase field model previously elaborated for describing Marangoni convection in two-layer systems (Borcia and Bestehorn 2003; Borcia *et al.* 2004; Borcia and Bestehorn 2005; Borcia and Bestehorn 2006; Borcia *et al.* 2006) to drops and bubbles and presents some phase field simulations for Marangoni migration in compressible fluids. Discovered by Young *et al.* (1959), the Marangoni migration consists in the motion of a droplet placed in a temperature gradient towards the hotter wall, "attracted" by the hot objects. This is the motion of the droplet relative to the shearing Marangoni flow induced along its surface by surface tension gradients. Droplet migration appears often in many material processing applications, because temperature gradients occur here in a natural way by using heating or cooling as integral part of the process (see, e.g., Balasubramaniam and Subramanian 2000; Balasubramaniam and Subramanian 2004; Esmaeeli 2005; Hadland *et al.* 1999; Onuki and Kanatoni 2005; Savino *et al.* 2001; Zhang *et al.* 2001 and references therein). Concentration gradients along a surface can also lead to interfacial stress variations. Recently, Lavrenteva *et al.* (2005) report on the drop Marangoni migration on a surface - active substance induced by the concentration gradient of the surfactant.

The outline of the paper is as follows: The phase field formulation for Marangoni convection in a two-phase system is briefly depicted in Sec. 2. The appearance and the coalescence of drops/bubbles in a system without gravity and without temperature gradients is discussed in Sec. 3. The Marangoni migration in a temperature gradient in the frame of the phase field model is presented in Sec. 4. We gather the conclusions in

[1] Email: borcia@physik.tu-cottbus.de
[2] Lehrstuhl Statistische Physik / Nichtlineare Dynamik, Brandenburgische Technische Universität Cottbus, Erich-Weinert-Straβe 1, 03046, Cottbus, Germany

Sec. 5.

2 Model

We study a liquid with its own vapor, a situation for which the most natural phase field variable is the density ρ, scaled by the liquid density. So $\rho = 1$ designates the liquid phase and $\rho \approx 0$ the vapor bulk. For a two-phase system with diffuse interface and without evaporation phenomena the Helmoltz free-energy functional is given by (see, e.g., Jasnow and Viñals 1996; Pismen and Pomeau 2000)

$$\mathscr{F}[\rho] = \int_V \left[f(\rho) + \frac{\mathscr{K}}{2}(\nabla\rho)^2 \right] dV \qquad (1)$$

where the first term in (1) represents the free-energy density for the homogeneous phases and the second term is a "gradient energy" which is a function of the local composition. For a flat interface of area ΔA between two coexisting isotropic phases, we obtain for the total free energy $\mathscr{F}(\rho)$ of the system:

$$\mathscr{F} = \Delta A \int_{-\infty}^{+\infty} \left[f(\rho) + \frac{\mathscr{K}}{2}(\nabla\rho)^2 \right] dz.$$

The specific interfacial free-energy γ is, by definition, the difference per unit area of interface between the actual free energy of the system and that which it would have if the properties of the phases were continuous throughout. Hence the free-energy excess of the interface takes the form (Cahn and Hilliard 1958)

$$\gamma = \int_{-\infty}^{+\infty} \mathscr{K}(\nabla\rho)^2 \, dz.$$

In order to describe thermocapillary convection in the frame of the phase field model we have to consider the generalized surface tension coefficient $\mathscr{K}$ weakly depending on temperature $\mathscr{K} = \mathscr{K}_0 - \mathscr{K}_T T$ ($\mathscr{K}_T > 0$). As already shown in Borcia and Bestehorn (2003) or Borcia *et al.* (2004), minimizing the free-energy functional (1), one can derive the non-classical phase field terms which has to be included in the Navier-Stokes equation for assuring the shear stress balance at the droplet interface:

$$\begin{aligned} \rho \frac{d\vec{v}}{dt} &= -\nabla p + \rho\nabla(\nabla\cdot(\mathscr{K}\nabla\rho)) + \nabla\cdot(\eta\nabla\vec{v}) \\ &\quad + \nabla(\lambda\nabla\cdot\vec{v}) + \rho\vec{g} \qquad \lambda \approx \frac{\eta}{3}. \end{aligned} \qquad (2)$$

To close the system of equations we need another two equations for T and ρ. The temperature field from (2) is described by the energy equation

$$\rho c \frac{dT}{dt} = \nabla\cdot(\kappa\nabla T) \qquad (3)$$

with c as the specific heat capacity, and κ as the thermal conductivity, and the fluid density by the continuity equation

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\vec{v}) = 0. \qquad (4)$$

The energy equation (3) assumes the continuity of the temperature heat transfer at the droplet interface, and the continuity equation (4) fulfils the mass conservation. For a system in equilibrium and without interfacial mass exchange the free-energy density has to be a symmetrical double-well potential with two minima corresponding to the two alternative phases: $\rho = 1$ for the liquid and $\rho = 0$ for the vapor state. We choose the free-energy density given by

$$f(\rho) = \frac{C}{2}\rho^2(\rho-1)^2. \qquad (5)$$

If one represents the thermodynamical pressure $p(\rho) = \rho\frac{\partial f}{\partial\rho} - f(\rho)$ against the unit volume $1/\rho$ for the free-energy density (5) one observes a curve of van der Waals type (see Figure 1).

With (5), the Navier-Stokes equation (2) admits an analytical solution for the stationary state:

$$\rho_0(z) = 1/[1 + \exp\frac{(z-1)}{\ell}], \qquad \ell \propto \sqrt{\mathscr{K}/C}.$$

The parameter ℓ describes the thickness of the interface. For small enough values of ℓ this solution describes two superposed liquid-vapor layers with the liquid boundary at $z = 0$, the vapor boundary at $z = 2$, and the diffuse interface around $z = 1$. Thermocapillary convection in two planar layers vertically heated was investigated in Borcia and Bestehorn (2005), Borcia and Bestehorn

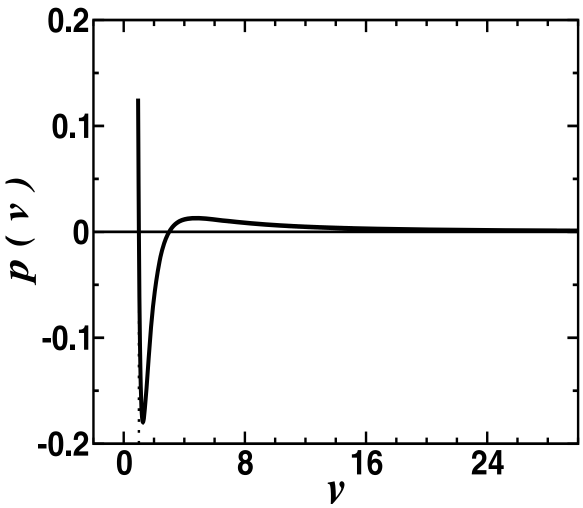


Figure 1: The pressure corresponding to the free-energy density (5) as function of the unit volume $v = 1/\rho$. The unit volumes for liquid and vapor phase are $v_l = 1$ and $v_v = \infty$, respectively.

(2006), and Borcia *et al.* (2006) in the frame of the phase field model. A linear stability analysis and a comparison with the classical models were done in Borcia and Bestehorn (2005). The linear stability analysis shows a good convergence between the phase field model and the regular models in the limit of sharp interfaces, i.e. $\ell \leq 0.03$ for water-vapor parameters. The fully nonlinear evolution for the same problem with evaporation was described in Borcia *et al.* (2006). Figure 2 shows a pattern specific for the short-wave instability at threshold, coming from Eqs. (2)-(4), for a water-vapor system heated from below. This pattern consists of two convective roll systems, one developed in the liquid and the second one in the vapor medium. Convection in the liquid pushes the liquid against the interface which leads to an increase of density at the interface on the liquid side. The advection of vapor from the top plate creates a lower density at the interface. The density perturbations at the diffuse interface induced by Marangoni convection are depicted in Figure 2 in a grey scale (for more details, see Borcia and Bestehorn 2005).

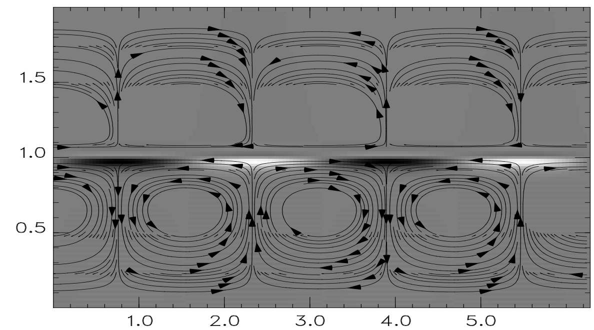


Figure 2: Stream-lines and surface deflections induced by the Marangoni instability with short wavelength in a liquid-vapor system heated from below. The numerical simulations are based on the phase field model described in Sec. 2, for more details see Borcia and Bestehorn (2005).

3 Drops and bubbles

Now we wish to apply the Eqs. (2)-(4) to the formation of drops and bubbles. For this new geometry one has no analytical solution for the stationary state and no linear stability analysis can be done. Instead, one can solve the problem numerically starting from an initial noise density:

$$\rho_{initial}(x,z) = C_m \ \xi \ (x,z), \tag{6}$$

where C_m is the noise intensity and ξ is a random distribution between 0 and 1. The constant C_m controls the total mass of the system. Depending on its value, the asymptotically stable state of lowest free energy corresponds to a single liquid drop in a vapor atmosphere (small C_m) or a gas bubble in a liquid (large C_m). The noise character of (6) may act as seeds for phase separation in the unstable or metastable regime of Figure 1. In the latter, drops or bubbles are found by nucleation and need a finite initial disturbance. In both cases, the dynamical process is dominated by coarsening and relaxes towards one of the "fixed points" described above.

For numerical simulations, first we analyse an isothermal system without gravity. The material parameters η, λ, κ and c are considered linearly coupled to the density. We developed a numerical code in two spatial dimensions based on a finite difference method with 200×200 mesh points for water-vapor parameters (Burelbach *et al.* 1988). The interface is about 3% from the size of the box, that means a resolution around 7 points in the diffuse layer. No-slip conditions for the velocity field were imposed at the wall boundaries ($\vec{\mathbf{v}} = 0$).

For a low total mass the formation of a drop in a vapor system is energetically favoured. Figure 3 displays 2D time series for $C_m = 0.5$ (the time indicated in the labels is scaled by d^2/χ where d is the length of the box and $\chi = \kappa/\rho c$ is the liquid thermal diffusivity). The density distributions are emphasized in a grey scale, where the white regions describe the maxima of fluid density, the dark regions the minima. Small liquid drops are coalescing forming larger and larger drops as the time evolves. When the saturation state is reached ($t > 5000$) a single liquid drop remains.

We have to point out that the boundary conditions for the density at the solid walls play an important role for the contact angle at the solid surface and determine the position of the droplet. In our model we have controlled the contact angle through the density at the solid boundary. For the simulations presented in this paper the boundary conditions constrain the drops to be pushed away from the solid walls (no-wetting properties), fact which explains the symmetry of the Figure 3-b. The influence of the boundary conditions on the droplet contact angle will be described in more detail elsewhere.

4 Drop migration caused by a temperature gradient

We consider the case illustrated in Figure 3 but now with a gravitational field. We obtain a liquid drop falling down (see Figure 4) under a sedimentation force, which is the resultant of the gravity and the Archimedian force. Additionally we apply an external heating at the upper wall in order to simulate the experimental results given by Savino *et al.* (2001), concerning Marangoni migration on Fluorinert drops in a silicone oil. The temperature gradient generates a surface tension gradient along the droplet interface. The lowering of surface tension at its leading pole – hotter than the rear pole – induces Marangoni flows

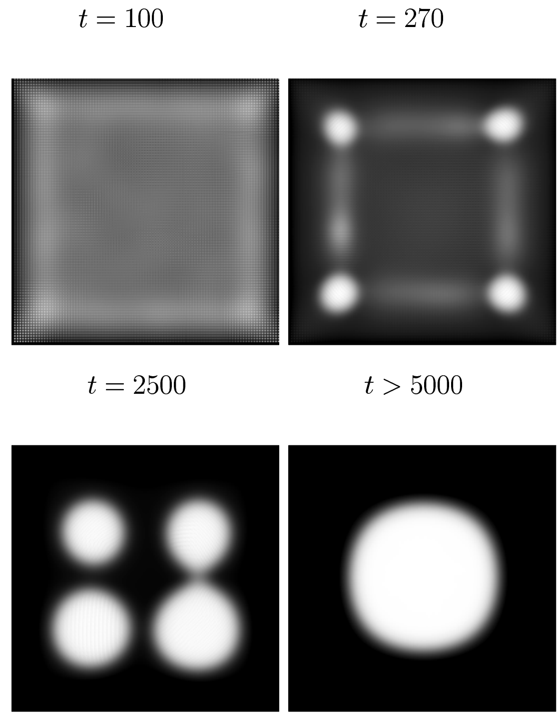


Figure 3: Time series for the formation of a liquid drop in vapor atmosphere for a system without gravity and without external heating ($C_m = 0.5$). The density is represented using grey-scale pictures, with white and black for liquid and vapor, respectively.

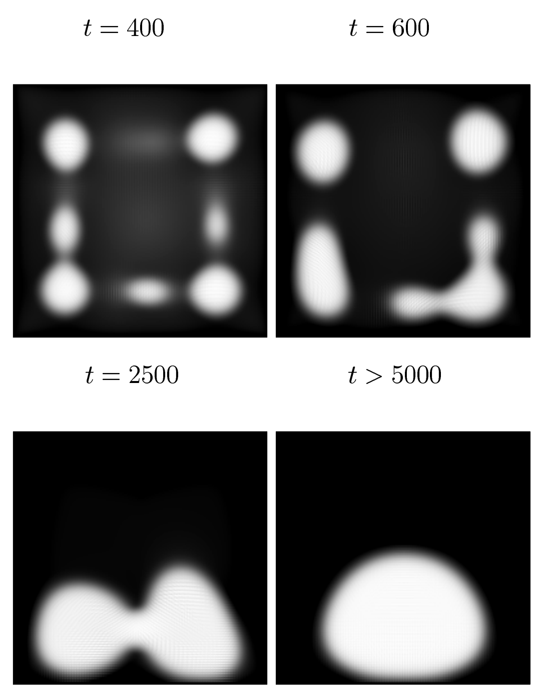
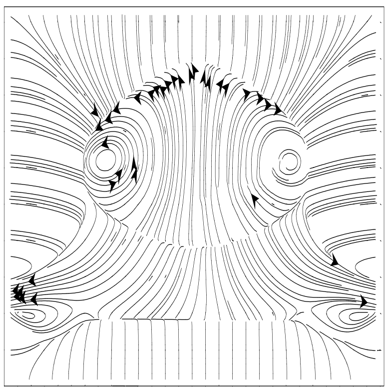
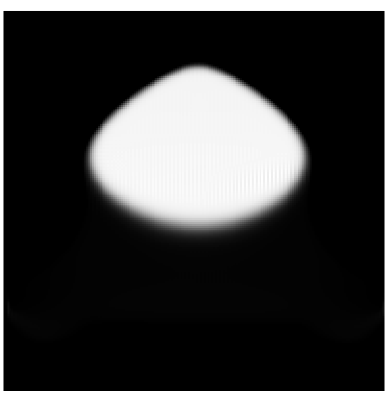


Figure 4: The same as Fig. 3 but now under the gravitational field ($C_m = 0.5$).

(a)



(b)

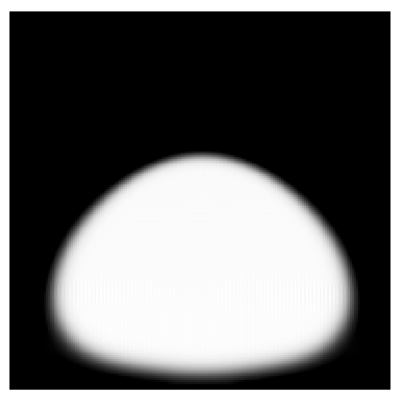


(c)

Figure 5: The balance between Marangoni and gravity effects leads to a floating droplet ($C_m = 0.35$, $\Delta T = 6K$, $d = 0.1\,mm$). Frame (a) shows the profile of the temperature (the system is heated from above), (b) the stream-lines, and (c) the density.

(a)

(b)



(c)

Figure 6: Drop levitation under Marangoni migration for droplets of different sizes, for the same vertical temperature gradient and the same size of the box ($\Delta T = 2K$, $d = 0.1\,mm$). (a) $C_m = 0.35$; (b) $C_m = 0.5$; (c) $C_m = 0.7$.

inside and outside the drop (see the stream-lines plotted in Figure 5-b). The shearing around the droplet surface creates a net force on the drop, a Marangoni pushing force $\vec{F}_M$ directed upwards, towards the hotter wall. This force is the resultant of the viscosity and the pressure forces along the drop [Savino et al. (2001)]:

$$(F_M)_i = \int_S n_j \sigma_{ij} dS - \int_S p n_i dS$$

(σ−the viscous stress tensor).

For a sufficiently high temperature gradient (sufficient Marangoni stress), the Marangoni pushing force $\vec{F}_M$ can balance the sedimentation force caused by the gravitational field. Hence in the steady state a floating liquid drop can occur, as depicted in Figure 5-c. Figure 6 emphasizes drop levitation under Marangoni migration for droplets with different sizes for a fixed vertical temperature gradient.

5 Conclusions

Summarizing, we developed a phase field model for describing Marangoni flows in two–phase systems. The model previously developed for planar layers is now extended to drops and bubbles. A randomly distributed initial density evolves to phase separation and single droplet formation. Depending on the total mass, one can have either a drop in a vapor atmosphere or a bubble in liquid. Simple, flexible and elegant, the actual model can become a useful tool for describing different phenomena with large applications in material and chemical engineering as Marangoni migration induced by a temperature gradient, chemically driven running drops, drop spreading on a solid surface, drop motion on an inclined substrate under gravity effects or oscillatory thermocapillary convection around bubbles heated from above at very large Marangoni numbers.

Acknowledgement: R. Borcia thanks for partial financial support from European Space Agency under the AO-99-110 CIMEX project (Convection and Interfacial Mass Exchange).

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