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A COARSE GRAINED APPROACH TO THERMOCAPILLARITY EFFECTS IN BINARY SYSTEMS

Jorge Llambías, Aritomo Shinozaki and David Jasnow
Department of Physics and Astronomy
University of Pittsburgh
Pittsburgh, PA 15260

ABSTRACT

An coarse-grained approach to thermocapillarity effects in binary fluid systems is discussed along with example numerical results.

1. INTRODUCTION

Coarse grained models have played an important role in developing a theoretical understanding of a variety of dynamical phenomena. Particularly important examples include the elucidation of universality classes in critical dynamics [1], developments in nucleation theory [2], and the kinetics of phase separation and spinodal decomposition [3]. There has been considerable success in developing “minimal” models which correctly predict the essential, universal features of a variety of non-equilibrium growth processes while at the same time exhibiting computational efficiency. A particularly successful example is the modeling of the coarsening during microphase separation in diblock copolymer melts. [4]

There are many problems in which the interest is in phenomena occurring on length scales from the correlation length on up to “macroscopic” scales. The coarse grained approach is ideally suited for this, and can be supplemented by, for example, molecular dynamics for dealing with phenomena on shorter scales.

In this brief paper we present a coarse grained model for the study of a variety of thermocapillarity effects in binary systems which should provide a correct description even far from equilibrium, e.g., for deep quenches such as one considers in typical spinodal decomposition phase separation experiments. As examples we show preliminary results of numerical integrations of the appropriate dynamical equations for phase separation in a temperature gradient, both in a “solid” and liquid system and with the temperature either as a passively imposed or fluctuating field. We comment on the new features introduced by the temperature variations in comparison to the related isothermal phenomena.

2. OVERVIEW

The full problem of interest contains the essential features of a binary system over a range of parameters which allows both miscibility and phase coexistence. Here we consider the case of a conserved order parameter (such as the concentration of one of the species) coupling to a conserved energy density as well as to the fluid velocity field. The basic ideas at the macroscopic level are discussed, for example, by Landau and Lifshitz [5]. At an appropriate point features of a coarse grained free energy are introduced which then specifies the model.

Our general aim is to express the equations of motion for a phase separating, two component fluid. The new ingredient for a binary system is the (conserved) order parameter ϕ , corresponding to the concentration, and its associated chemical potential, μ . Along with a conservation equation

for the total density there is an additional conservation

$$\rho \left(\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \vec{\nabla} \phi \right) = -\vec{\nabla} \cdot \mathbf{j}_c \quad (1)$$

where \mathbf{j}_c is an as yet undetermined concentration flux. As discussed below, the specifics of the coarse grained modeling will determine \mathbf{j}_c . The “mode-coupling” advective term in Eq. (1) represents an important coupling in the studies of critical dynamics.

The energy and entropy equations, which are developed in detail in Ref. [5], require a heat current, also to be specified. For the energy equation one may introduce an enthalpy $w(s, p, \phi)$ with s and p the entropy and the pressure, and

$$dw = Tds + (1/\rho)dp + \mu d\phi \quad , \quad (2)$$

leading to

$$\vec{\nabla} p = \rho \vec{\nabla} w - \rho T \vec{\nabla} s - \rho \mu \vec{\nabla} \phi \quad . \quad (3)$$

This is an important equation since it contains the corresponding mode coupling between concentration fluctuations and the velocity field. Since $\vec{\nabla} p$ enters the Navier-Stokes equation, one finds the additional driving force for velocity field, $\mu \vec{\nabla} \phi$.

Details of the thermodynamic analysis are standard, and the reader may refer to Ref. [5]. In particular, the energy or entropy equation is turned into an equation for the temperature field via $ds = \frac{\partial s}{\partial T} dT + \frac{\partial s}{\partial \phi} d\phi$ and using the equation of motion for ϕ [5].

We point out here a few features relevant to the specific models which follow. The entropy production, as discussed in Ref. [5] can be made positive using the constitutive equations for concentration and heat currents

$$\mathbf{j}_c = -\alpha \vec{\nabla} \mu - \beta \vec{\nabla} T \quad (4)$$

$$\mathbf{j}_q = (\mu + \beta T / \alpha) \mathbf{j}_c - \kappa \vec{\nabla} T \quad , \quad (5)$$

if $\kappa, \alpha > 0$. The kinetic coefficient β , related to the Soret effect, can play a role in the ensuing dynamics.

Within this approach there remains the question of specifying the thermodynamic functions. In particular one must specify the chemical potential to describe the system and obtain the relevant currents. It is here that the particular choice of coarse grained free energy is made. Note that the interesting behavior resides in the dynamics of the order parameter ϕ and that the total density can be taken as constant. Hence, one can effectively ignore any density fluctuations and consider the fluid as incompressible. In doing so, the pressure gradient entering the Navier-Stokes equation as in Eq. (3), introduces the enthalpy, which will essentially be determined as part of the solution to guarantee incompressibility.

For our purposes here it is sufficient to specify a free energy density of the form [6]

$$F(\phi, T) = f(\phi, T) + \frac{1}{2} R^2 (\vec{\nabla} \phi)^2 \quad (6)$$

where $f(\phi, T)$ represents the local free energy. The parameter R is taken as a constant, but the phenomenology certainly admits functional dependence on ϕ and T . The chemical potential, energy density and entropy all follow, closing the equations.

3. EXAMPLES

We turn now to some applications of the general system of equations, beginning first with simplifications.

(i) Conserved order parameter with temperature gradient

There are thermocapillarity effects, or, perhaps more precisely, effects driven by the interfacial free energy, even in the absence of velocity fields, i.e., in purely diffusive systems. One may think of phase separation in a "solid" or an extremely viscous fluid. Furthermore one may imagine heat diffusion to be much more rapid than concentration diffusion. The model considered corresponds in the critical dynamics context to Model B [1] in the presence of an imposed temperature gradient. This is interesting in that the model is the usually accepted one to describe phase separation, but the coupling of the temperature field to the order parameter is very weak if the two phases are made symmetric. One takes the local free energy of the form $f(\phi, T) = \frac{1}{2}r(T)\phi^2 + \frac{1}{4}u\phi^4$ leading to the chemical potential of the form

$$\mu = -R^2\nabla^2\phi + r(T)\phi + u\phi^3 \quad (7)$$

where $r(T) = r_1(T/T_0 - 1)$. Here T_0 is a reference temperature (playing the role of the value at criticality), and r_1 and u are positive constants. The phase boundary in this symmetric model lies at $\mu = 0$. An additional term on the right of Eq. (7) can be added to introduce a latent heat, which will become more important when temperature is included as an active, fluctuating variable. This model reasonably describes a binary system; there are coexisting phases at sufficiently low temperature, and the surface tension is naturally a function of temperature, vanishing in this mean field model as $|T - T_0|^{3/2}$ as $T \rightarrow T_0^-$. Considerable effort has gone into studying phase separation kinetics and domain growth starting typically from a high temperature configuration and quenching to a uniform temperature below T_0 . [3]

Since it is being assumed that thermal conductivity is relatively large, we impose a constant temperature gradient $T = T_l(1 + \gamma x)$ where x measures distance from one side of the sample and $T_l = T(x = 0) < T_0$. The dynamics of the model are then described in suitably dimensionless form by the system

$$\frac{\partial\phi}{\partial t} = \nabla^2\mu \quad (8)$$

$$\mu = -\nabla^2\phi - (1 - \gamma x)\phi + \phi^3 \quad (9)$$

In this equation we have neglected the potential dependence of the kinetic coefficient, α , on the order parameter, which dependence is important in studying driven diffusive systems. [7] This point will be reconsidered elsewhere.

Simulations of the system (9) are carried out with large space and time steps which nonetheless are sufficient to reveal the essential features. We have studied the dynamics of phase separation in two dimensions. As noted, temperature couples weakly to this process, favoring neither phase. For example, the asymptotic domain growth exponent is not changed by changing the quench temperature of a homogeneous system, but the amplitude of the growth law is modified. Hence it is important to know whether in a temperature gradient one merely observes ordinary phase separation in each temperature "slice." As will be reported in more detail elsewhere, the temperature gradient induces an anisotropy in the system, with characteristic lengths along the gradient growing more slowly than perpendicular to the gradient. This is an effect of the transport current in the phase separating system.

The system has been specifically chosen to be completely symmetric in the two bulk phases. In a temperature gradient, motion of a domain (or bubble) of one phase in the background of the other is due to the contribution to the free energy of the domain walls, which is temperature-dependent. The total free energy is reduced when the domain drifts to the high temperature side. However, recall that the only dynamics included in the model so far are those of order parameter diffusion, hence the process can be quite slow. Sample motion of a droplet is shown in Fig. 1. By considering slab geometry, which should yield the essential features of a droplet or domain, one can show that for small gradients the drift velocity is proportional to the temperature gradient γ , while the spreading of the drop is a higher order effect. This analysis, including the analytic treatment of the response of a " ϕ^4 -kink" to a temperature gradient, will be presented elsewhere.

(ii) Conserved order parameter and coupled slow mode

The next stage of complexity couples the conserved order parameter (concentration) to a slow, conserved mode like an energy density or other density. For our fluid, the natural example is a heat mode. Such a model corresponds to "Model D" in the study of critical dynamics [8]. As far as critical dynamics are concerned, the conserved dynamics of the order parameter degrees of freedom are not affected by coupling to an additional slow mode. [8] However for deep quenches, and for domain migration in a temperature gradient, it is interesting to consider the effect of the slow heat mode. Our interest will be to detect differences due to finite thermal conductivity, and, for example, to a Soret effect.

To this end we consider the general treatment sketched in the Overview, but for the moment drop all fluid velocity terms. There is a conserved energy density following from a free energy density as in Eq. (6) with the same local part as above. The entropy density follows from $S = -\frac{\partial F}{\partial T}$, while the chemical potential follows from $\mu = \delta/\delta\phi \int F d^d x$ as in Eq. (9).

As an example we show in Fig. 2 the phase separation patterns starting from a high temperature initial condition to a state with a temperature ramp. The overall average order parameter is chosen off-critical, but the left-hand part of the system should be in the unstable regime. Phase separation via spinodal decomposition is affected by the Soret effect (and particularly its relative sign) causing a concentration gradient to advance from the wall. Essentially this is a kinetic finite-size effect. Analysis of the features of this process will be presented elsewhere.

(iii) Imposed temperature gradient and velocity coupling

Now we turn to the full problem which includes the fluid velocity fields, i.e., finite viscosity. In Fig. 3 a sample phase separation sequence is shown. The qualitative change in domain dynamics with the inclusion of velocity fields and the finite system size is significant, as expected. One observes, for example, "boundary forcing" induced by the boundary conditions, and its effect on the dynamics. The full time sequence clearly shows the merging of domains. Detailed analysis including the behavior of separate temperature "slices" to determine anisotropic behavior in domain growth will also be discussed elsewhere.

4. CONCLUDING REMARKS

We have presented here a brief description of modeling in which thermocapillarity effects can be studied at the coarse-grained level. Features such as phase separation kinetics, droplet migration and flow in binary fluid systems can be studied with the aim of extracting universal features. Several specific examples have been provided to demonstrate the range of phenomena that can be considered in this fashion.

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FIGURE CAPTIONS

1. Migration of droplet of one phase in background of other in an imposed temperature gradient. Diffusion only, no hydrodynamics.
2. Phase separation in a temperature gradient. Finite size of system combined with Soret term affect the phase separation kinetics.
3. Phase separation in imposed temperature gradient, with hydrodynamic coupling.

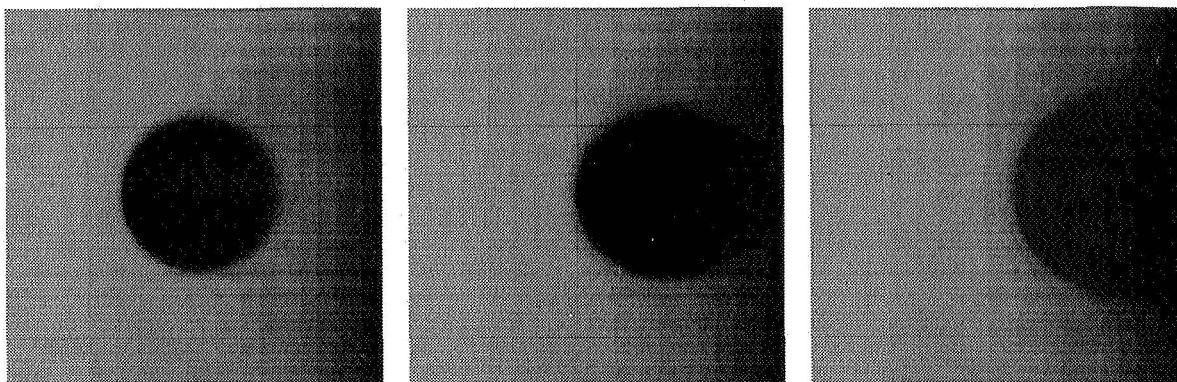


Figure 1

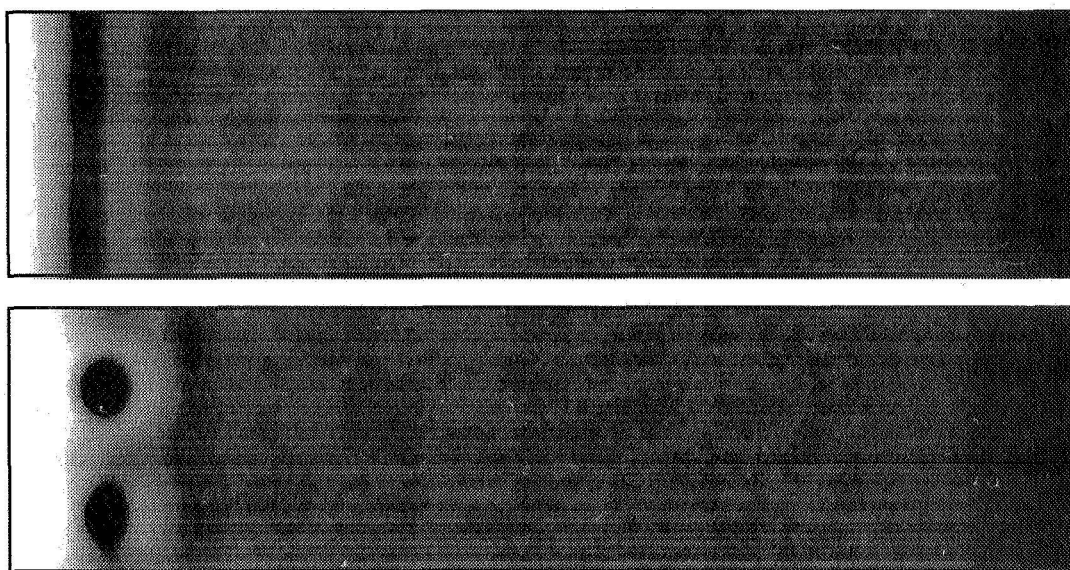


Figure 2

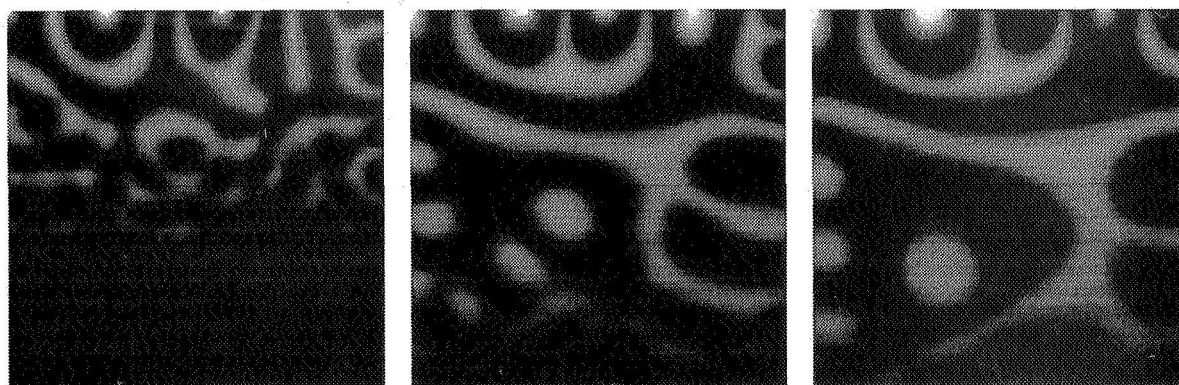


Figure 3