Hydrodynamics of Binary Fluid Phase Segregation

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Starting with the Vlasov-Boltzmann equation for a binary fluid mixture, we derive an equation for the velocity field $\boldsymbol{u}$ when the system is segregated into two phases (at low temperatures) with a sharp interface between them. $\boldsymbol{u}$ satisfies the incompressible Navier-Stokes equations together with a jump boundary condition for the pressure across the interface which, in turn, moves with a velocity given by the normal component of $\boldsymbol{u}$. Numerical simulations of the Vlasov-Boltzmann equations for shear flows parallel and perpendicular to the interface in a phase segregated mixture support this analysis. We expect similar behavior in real fluid mixtures.

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When a fluid is quenched from a high temperature to a low temperature inside the miscibility gap, it evolves from its initial homogeneous state which is now unstable into a final equilibrium state consisting of two coexisting phases separated by an interface. The phase segregation process, involving hydrodynamical velocity fields $\mathbf{u}(\mathbf{x}, t)$, is more complicated than the corresponding diffusive processes in quenched binary alloys [1]. In a seminal work [2] Siggia pointed out that in the late stages of phase segregation sharp interfaces develop between domains of the two phases, and the coarsening process is mainly due to hydrodynamic flows driven by these elastic interfaces. Following Siggia, there has been much work to investigate the time evolution of this coarsening process [3–5], and this is still going on [6,7].

There has been much less work on the derivation of a quantitative description of the velocity field involving the interface between two phases of macroscopic size, a problem of considerable interest in its own right [8]. To do this, one should start from a microscopic description of the transition region in which the composition varies smoothly on the microscopic scale and end up with boundary conditions on the "membrane" representing this transition layer on the macroscopic scale (the sharp interface limit). This is a difficult task for the case in which the two phases have widely different densities, viscosities, etc., since a reasonable microscopic description valid for both phases is hard to find.

To overcome this difficulty, we consider here a situation in which both the equilibrium and kinetics are as simple as possible. This is a binary fluid model introduced in [9] which provides a description of phase segregation kinetics at the mesoscopic level via the Vlasov-Boltzmann (VB) equations. These equations can be obtained from the microscopic dynamics (in a convincing but not rigorous manner) and in turn allow a derivation, in a suitable limit, of bulk hydrodynamical equations [10]. The hydrodynamic equations we obtain for the bulk mixture are similar but not identical to the heuristic macroscopic equations previously proposed for describing phase segregation in an energy and momentum conserving system [11]. In the present Letter, we consider the case in which the fluid is already well segregated with sharp interfaces between the different phases. We derive hydrodynamic equations involving the interface motion directly from the VB equations and carry out direct simulations for the time evolution of simple hydrodynamical flows, in the presence of such an interface. The resulting free boundary problem was considered phenomenologically, in the context of interface oscillations, by Harrison [12]. We compare our results, with good agreement, with the behavior based on the linearized version [13] of the hydrodynamic equations, recently considered for studying coarsening dynamics [6]. Both the derivation and the numerical analysis are new and we believe that the results have, as is the case of the Navier-Stokes equations of a one component fluid, a universal validity even though their rigorous derivation from microscopic models can be carried out currently only from the Boltzmann equation [14]. In fact, preliminary calculation using the Enskog equation instead of the Boltzmann equation (more appropriate for a dense fluid) leads to the same hydrodynamics.

The model we consider is a mixture of two species of hard spheres with diameter d and unit mass labeled by 1, 2, with a long-range positive potential $\ell^{-3}V(\ell^{-1}r)$ between particles of different species; ℓ is the range of the interaction. The latter causes phase segregation at temperatures lower than a critical temperature T_c, into phases I and II: I is rich in species 1 and II in species 2 [15]. Let n be the total particle density. It was shown in [10] that, when $nd^3 \ll 1$, while $\ell \gg d$, this system is well described by coupled VB kinetic equations for the one-particle distributions $f_i(\boldsymbol{r}, \boldsymbol{v}, \tau)$, $i = 1, 2$

$$\partial_\tau f_i + \boldsymbol{v} \cdot \nabla_{\boldsymbol{r}} f_i + \boldsymbol{F}_i \cdot \nabla_{\boldsymbol{v}} f_i = J[f_i, f_1 + f_2], \quad (1)$$

where $\boldsymbol{F}_i(\boldsymbol{r}, \tau) = -\nabla_{\boldsymbol{r}} V_i(\boldsymbol{r}, \tau)$ with V_i the self-consistent

Vlasov potentials $V_i(\boldsymbol{r}, \tau) = \int_{\mathbb{R}^3} \ell^{-3} V(\ell^{-1}|\boldsymbol{r} - \boldsymbol{r}'|) \times n_j(\boldsymbol{r}', \tau) d\boldsymbol{r}'$, $i \neq j$, $n_j(\boldsymbol{r}, \tau) = \int_{\mathbb{R}^3} f_j(\boldsymbol{r}, \boldsymbol{v}, \tau) d\boldsymbol{v}$, and $J[f, g]$ is the Boltzmann collision operator for hard spheres [16]. We are interested in an equilibrium state at a fixed total density in which the system is split into two regions, one consisting of phase I and the other of phase II. These regions are separated by a transition layer whose local form can be obtained by considering particular 1D stationary "solitonic" (actually kink) solutions of (1): set $f_i = \rho_i(z) M(\boldsymbol{v})$ where $M(\boldsymbol{v})$ is the Maxwellian with unit mass, zero mean velocity and temperature T, $M(\boldsymbol{v}) = (2\pi k_B T)^{-3/2} \exp[-\boldsymbol{v}^2/2k_B T]$. Moreover, $\rho_i(z) = \phi_i(z/\ell)$ with $\phi_i(q)$ smooth functions satisfying the equations

$$k_B T \log \phi_i(q) + \int_{\mathbb{R}} dq' \tilde{V}(|q - q'|) \phi_j(q') = C_i, \qquad (2)$$

where $\tilde{V}(q) = \int_{\mathbb{R}^2} dw V(\sqrt{q^2 + w^2})$ and C_i is a constant. For $T < T_c$, Eqs. (2) have nonhomogeneous solutions with asymptotic values ρ_i^{I} and ρ_i^{II} as $q \to \pm\infty$, corresponding to the densities in phases I and II, respectively: by symmetry $\rho_1^{\mathrm{I}} = \rho_2^{\mathrm{II}}$, $\rho_2^{\mathrm{I}} = \rho_2^{\mathrm{II}}$. The solutions are not explicit but their existence and properties are studied in [9,15]. These are similar to those observed in realistic mixtures, such as oil and water.

We are interested in studying hydrodynamical flows when the width of the interface, which is of order ℓ, is small compared to the mean-free path λ which is, in turn, small compared to L, the characteristic length of the domains occupied by the pure phases. Setting $\boldsymbol{r} = \epsilon^{-1}\boldsymbol{x}$, $\tau = \epsilon^{-2} t$, where $\epsilon = \lambda/L \sim \ell/\lambda$ and $\boldsymbol{x}, t$ are the macroscopic position and time, we wish to study the small ϵ behavior of a solution $f_i^\epsilon(\boldsymbol{x}, \boldsymbol{v}, t) = f_i(\epsilon^{-1}\boldsymbol{x}, \boldsymbol{v}, \epsilon^{-2} t)$ of Eqs. (1), in the incompressible regime, corresponding to low hydrodynamic velocity [14]. We assume far from the interface a solution of the form [14]

$$f_i^\epsilon(\boldsymbol{x}, \boldsymbol{v}, t) = \bar{\rho}_i(\boldsymbol{x}) M(\boldsymbol{v}) + \sum_{s=1}^{\infty} \epsilon^s g_i^s(\boldsymbol{x}, \boldsymbol{v}, t), \qquad (3)$$

where $\bar{\rho}_i(\boldsymbol{x})$ is either ρ_i^{I} or ρ_i^{II} depending on which region $\boldsymbol{x}$ is in. Note that by symmetry $\rho_1^{\mathrm{I}} + \rho_2^{\mathrm{I}} = \rho_1^{\mathrm{II}} + \rho_2^{\mathrm{II}} = \bar{\rho}$, i.e., the total density is the same in both phases but varies in the interface region. Putting $f^\epsilon = f_1^\epsilon + f_2^\epsilon$, we have for the hydrodynamic velocity field

$$\bar{\rho}^{-1} \int_{\mathbb{R}^3} \boldsymbol{v} f^\epsilon(\boldsymbol{x}, \boldsymbol{v}, t) d\boldsymbol{v} = \epsilon \boldsymbol{u}(\boldsymbol{x}, t) + O(\epsilon^2),$$

so that the Mach number is of order ϵ (incompressible regime). Far from the interface the temperature T and the densities are constants, coinciding for $T < T_c$ with the asymptotic values of the solitonic solutions.

To understand what happens near the interface, consider the situation in which the interface is flat. Then $f_i(\boldsymbol{r}, \boldsymbol{v}, \tau) = \rho_i(z) M(\boldsymbol{v})$ with $\rho_i(z) = \phi_i(z/\ell)$ a stationary solution of the Vlasov-Boltzmann equations. If the interface is not flat this is not exactly true, but because of the tendency of the solitonic profile to keep its form and just translate, one expects that the solution is locally close to the solitonic profiles multiplied by the Maxwellian. On the other hand, the force due to the surface tension acts on the particles of the fluid which start to move with some average velocity $\boldsymbol{u}$ and the surface moves accordingly, so that its normal velocity is at any point $\boldsymbol{u} \cdot \boldsymbol{N}$, $\boldsymbol{N}$ being the normal to the surface. To implement this picture, we write the solution near the interface as

$$f_i^\epsilon(z, \tilde{\boldsymbol{x}}, \boldsymbol{v}, t) = \rho_i(z) M(\boldsymbol{v}) + \sum_{s=1}^{\infty} \epsilon^s \tilde{g}_i^s(z, \tilde{\boldsymbol{x}}, \boldsymbol{v}, t). \qquad (4)$$

The notation is as follows: given a point $\boldsymbol{x}$, we call $z = \epsilon^{-1} d(\boldsymbol{x}, \Gamma_t)$, where $d(\boldsymbol{x}, \Gamma_t)$ is the distance of $\boldsymbol{x}$ from the interface Γ_t and $\tilde{\boldsymbol{x}}$ the component of $\boldsymbol{x}$ tangential to the interface; $\rho_i(z) = \phi_i(z/\ell)$ is the solitonic solution centered on $z = 0$. Since we are so close to the interface, we can assume that locally it looks almost flat, so that the solution near the interface has a weak dependence on $\tilde{\boldsymbol{x}}$. Therefore, the profile interpolating between the values of the densities in the bulk on the two sides of the interface should be well approximated by the 1D solitonic profile $\rho_i(z)$, the lowest order term in Eq. (4).

To obtain a solution of Eqs. (1) we have to put these expressions in the equations (after space-time rescaling) and match the two expansions. This can be done in a consistent way and it is possible to compute the terms in the series (the long computation will be reported elsewhere), but the question of the convergence of the series is open (we expect they are asymptotic). The result is that in the limit $\epsilon \to 0$ the velocity field $\boldsymbol{u}(\boldsymbol{x}, t)$ is divergence free and solves the incompressible Navier-Stokes (INS) equation

$$\partial_t \boldsymbol{u} + (\boldsymbol{u} \cdot \boldsymbol{\nabla}) \boldsymbol{u} + \boldsymbol{\nabla} p = \nu \Delta \boldsymbol{u} \qquad (5)$$

with the kinematic viscosity ν obtained from the Boltzmann equation as in [16]. Moreover, $\boldsymbol{u}$ is continuous across the interface Γ_t whose normal velocity is given by

$$v_{\Gamma_t}(\boldsymbol{x}) = \boldsymbol{u}(\boldsymbol{x}, t) \cdot \boldsymbol{N}(\boldsymbol{x}, t), \qquad (6)$$

while the pressure is discontinuous at the surface and satisfies Laplace's law

$$(p_+ - p_-) = \sigma K. \qquad (7)$$

Here (p_-) p_+ is the pressure on the side of Γ_t (not) containing the normal $\boldsymbol{N}$; K is the mean curvature of Γ_t and σ is the surface tension given in terms of solitonic profiles as

$$\sigma = \frac{1}{2} \int (q' - q) \sum_{i \neq j = 1,2} \frac{d\phi_i(q)}{dq} \tilde{V}(q - q') \phi_j(q') dq dq'. \qquad (8)$$

The equation for $\boldsymbol{u}$ is a complicated initial boundary value problem with free boundary Γ_t. The solutions of INS in the two domains separated by Γ_t are coupled by the jump condition for the pressure. Since the solution is

not explicit, we compare our numerical results with the linearized version of this problem, studied in [13].

To obtain numerical solutions of the VB equations, we use the method introduced in [9] to simulate the VB dynamics at the particle level, based on coupling the direct simulation Monte Carlo algorithm for the short-range interaction with the grid-weighting method for the long-range repulsion. The results were obtained using about 5×10^6 particles, in a cube $(L \times L \times L)$ with periodic boundary conditions. The unit of length is the mean-free path $\lambda = (2^{1/2}\pi\bar{\rho}d^2)^{-1}$, and the unit of time is the mean-free time between collisions $\tau = \lambda/c$, $c = (2k_BT)^{1/2}$. For the repulsive interspecies potential we use, as in [9], $V(q) = \alpha\pi^{-(3/2)}\exp(-q^2)$ (note that the mean-field critical temperature is given by $k_BT_c = \bar{\rho}\alpha/2$), with a range of interaction $\ell = 0.4\lambda$. All quenches were performed at total particle density $\bar{\rho}$, with $\bar{\rho}d^3 \approx 0.01$. We focus on the behavior of a simple initial flow perturbation, $u_z(0) = u_0\cos(ky)$, with $k = 2\pi n_k/L$, $n_k = 1, 2, 3, \ldots$, outside and inside the coexistence region; for all simulations we set $u_0 = 0.1c$. For a homogeneous system this shear wave perturbation leads to a time dependent flow $u_z(t) = u(t)\cos(ky)$, where $u(t) = u(0)\exp(-\nu k^2 t)$, $\nu = \eta/\bar{\rho}$, and η is the viscosity.

We first study the behavior of the above initial perturbation in the homogeneous region of the phase diagram at $T/T_c = 1.5$. The initial velocity profile decays exponentially with very high accuracy and we extract a kinematic viscosity ν which agrees with the Boltzmann gas viscosity [16]. We then turn to the study of the system in the presence of interfaces, at two temperatures, $T_1/T_c = 0.51$ and $T_2/T_c = 0.33$. For each of these temperatures the initial configuration contains two interfaces (due to periodic boundary conditions), situated in the $\{xy\}$ plane a distance $L/2$ apart, that separate domains of the two equilibrium phases for the particular temperature. The static structure of these interfaces has been described in [9]. The thickness of the interface is of order ℓ.

For an initial flow perturbation that is parallel with the interfaces, $\mathbf{u}(0) = u_x(0)\hat{\mathbf{x}} = u_0\cos(ky)\hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$ is the unit vector in the x direction, the behavior of the velocity profile is virtually identical with the one in the homogeneous region. The situation is, however, very different if the initial perturbation is perpendicular to the interfaces, i.e., $\mathbf{u}(0) = u_z(0)\hat{\mathbf{z}} = u_0\cos(ky)\hat{\mathbf{z}}$. While $u_z(t)$ is still very well represented by $u(t)\cos(ky)$, $u(t)$ no longer decays exponentially. To fully characterize this situation, we also look at the position of the interface. The order parameter $\varphi = (\rho_1 - \rho_2)/\rho$ is calculated at time t as a function of z and y. We find that $\varphi(z, y, t)$ is very well fitted by the profile $\varphi_0\tanh\{[z - z_0(y, t)]/\xi\}$ [9] and identify $z_0(y, t)$ with the position of the interface. Furthermore, $z_0(y, t)$ is well represented by $z_0(y, t) = A(t)\cos(\kappa y)$. The velocity amplitude $u(t)$ and the interface amplitude $A(t)$ for the temperature T_1 and $n_k = 1$ are shown in Fig. 1, along with fits with the functional

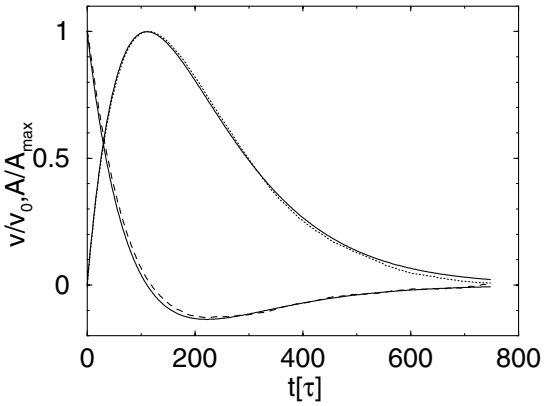

FIG. 1. Interface amplitude $A(t)$ (dotted line) and velocity amplitude $u(t)$ (dashed line) for $T_1/T_c = 0.51$, $n_k = 1$ and corresponding fits (see text) (solid lines).

forms expected for an overdamped harmonic oscillator: $A(t) = u_0\exp(-\gamma t)\sinh(\omega t)/\omega$, $u(t) = u_0\exp(-\gamma t) \times [-\gamma\sinh(\omega t)/\omega + \cosh(\omega t)]$.

We find that these forms can reasonably reproduce the results up to the highest n_k simulated, $n_k = 9$. In Fig. 2 we show the amplitudes of the interface oscillations $A(t)$ up to $n_k = 3$, along with the corresponding best fits, for temperature T_1 (top) and T_2 (bottom). We note that the $n_k = 1$ behavior at T_2 is qualitatively different from the other cases, showing damped oscillations. The functional forms that describe this result are $A(t) = u_0\exp(-\gamma t)\sin(\omega t)/\omega$, $u(t) = u_0\exp(-\gamma t)[-\gamma\sin(\omega t)/\omega + \cos(\omega t)]$.

These simulation results can be compared with those obtained from the linear perturbation analysis of a thin, initially flat interface with surface tension σ separating fluids of matching density $\bar{\rho}$ and viscosity $\eta = \nu\bar{\rho}$. This type of analysis has been carried out in [13] in the full

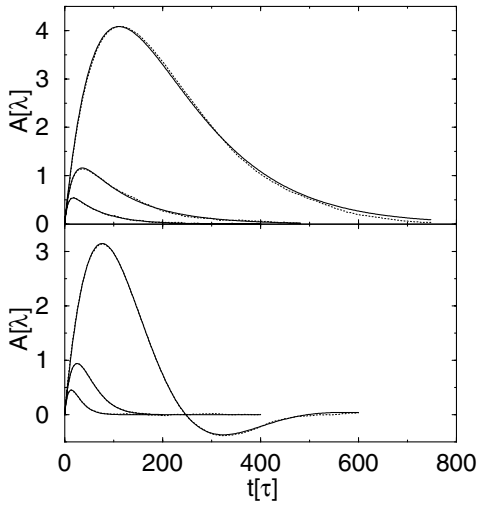

FIG. 2. Interface amplitudes $A(t)$ for $T_1/T_c = 0.51$ (top) and $T_2/T_c = 0.33$ (bottom), $n_k = 1, 2, 3$ (top to bottom) (dotted lines) and corresponding fits (see text) (solid lines).

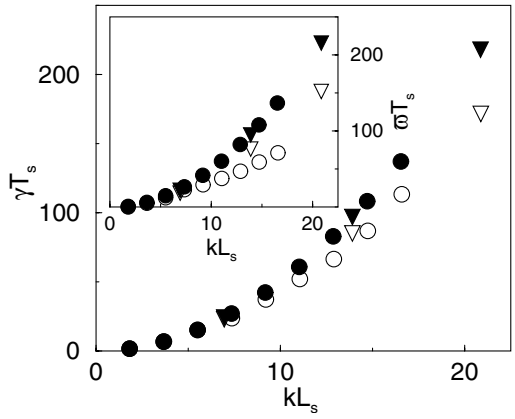

FIG. 3. Coefficients γ and ω (inset): from simulations (open symbols) at T_1 with $\ell = 0.4\lambda$ (circles) and $\ell = 0.2\lambda$ (triangles); oscillator equation (see text) (filled symbols).

space. The idea is to look for flow solutions $u_{x,y,z}(t) \propto e^{\mu t}\cos(k_x x + k_y y)$ following a small velocity perturbation of wave number k. This yields a u_z decaying exponentially as a function of the distance from the interface. We carried out a similar analysis matching the periodic boundary and initial conditions in which u_z is independent of z away from the interfaces. Under these conditions and taking into account the discontinuity of the normal stresses due to surface tension, we can write, following [13] [see, e.g., Chapter X, Eq. (28)]

$$\rho\partial_t u_z = \eta\Delta u_z + \Sigma_s[\sigma(\partial_x^2 + \partial_y^2)\delta z_s]\delta(z - z_s), \qquad (9)$$

where z_s is the position of the interface s, δz_s is the displacement from the initial position and $d\delta z_s/dt = u_{zs}$ is the velocity of the interface. However, we regard the above equation integrated over the torus, along z, as the more fundamental one if u_z is z independent. This yields

$$\rho\partial_t u_z = \eta\Delta u_z + L^{-1}\Sigma_s\sigma(\partial_x^2 + \partial_y^2)\delta z_s. \qquad (10)$$

Using $u_z = u_{zs}$ and assuming $u_z(t) \propto e^{\mu t}\cos(ky)$, which is consistent with the initial conditions, we get $\mu^2\rho + \mu k^2\eta + L^{-1}2\sigma k^2 = 0$. This equation is characteristic of a damped oscillator. Introducing the length scale $L_s = \nu^2\rho/\sigma$ and time scale $T_s = \nu^3\rho^2/\sigma^2$, this becomes

$$\mu_*^2 + \mu_* k_*^2 + L_*^{-1}2k_*^2 = 0, \qquad (11)$$

where $\mu_* = \mu T_s$, $k_* = kL_s$, and $L_* = L/L_s$. Using $k = 2\pi n_k/L$ we find that the above equation predicts damped oscillations for $n_k < n_k^0 = (2L_*)^{1/2}/\pi$ and overdamped behavior (no oscillations) otherwise. For our binary fluid model the surface tension can be related to the interface profile [see Eq. (8)] and easily estimated [17], and, therefore, we can calculate n_k^0. We find that for $T_1/T_c = 0.55$, $n_k^0 = 0.83$, so that for all n_k the oscillations should be overdamped, in agreement with the simulation results. For $T_2/T_c = 0.33$, $n_k^0 = 1.39$, so the $n_k = 1$ case should exhibit damped oscillations, while the others should be overdamped; this is again in agreement with the simulations. We also calculate the coefficients γ and ω that describe the behavior of the velocity profile and compare with the simulation results; see Fig. 3. We find good agreement for small k (n_k) and increasing deviations as k increases; the relative behavior of γ and ω also appears to be qualitatively different from the simulations for large k. This is as expected, since for larger k, i.e., smaller wavelengths, we are far from the hydrodynamic regime. Our hydrodynamic picture is valid if $k\lambda = 2\pi n_k\epsilon$, ℓ/λ, and u/c are of order $\epsilon = \frac{\lambda}{L}$, which is in our simulations 0.028. Better agreement is found in simulations with $\ell/\lambda = 0.2$ (and $\epsilon = 0.056$), see Fig. 3, which indicates that the accuracy of the equations we derive increases when the interface becomes sharper.

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