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Phase separation in incompressible systems

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We consider phase separation in multicomponent systems in the limit as the free volume goes to zero. Excluded volume effects are taken into account via a pressure field which implicitly relates currents and forces. The pressure, obtainable from a divergence condition, may give rise to circulating currents. A simple description of the dynamics of phase separation at late times follows. [S1063-651X(97)50504-6]

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The dynamics of phase separation in complex fluids, such as polymer blends and liquid crystal mixtures, is of considerable current interest [1–4]. A problem of particular importance is the determination of the Onsager kinetic coefficients which relate material currents to the thermodynamic forces driving the phase separation. Generalized thermodynamics [5] gives a prescription for enumerating the allowed forces; however, the procedure for evaluating the nonvanishing transport coefficients is less clear. In the Cahn-Hilliard theory [6] of binary fluids, the mixture is assumed to be incompressible, and the volume fraction of the second component can be eliminated from the free energy and from the dynamical description. In this approach, the transport coefficient chosen for one component implicitly determines that of the other. In a seminal work, de Gennes [7] considered the thermodynamic forces responsible for incompressibility, and obtained an expression for the transport coefficients in a binary polymer blend. This approach was extended by Binder [8], who allowed for nonlocality of the interactions by making the transport coefficients dependent on the wave vector **q**. Current work, such as that of Liu and Fredrickson [10], generalizes the above method; transport coefficients are obtained by making use of linear or nonlinear response theory and invoking incompressibility.

In this Rapid Communication, we propose a different approach, similar to the one used in deriving the hydrodynamic equations for incompressible fluids [11]. We first consider the dynamics of a compressible multicomponent system where the mobilities of the constituents depend on the free volume; we then take the incompressible limit. In this scheme, there naturally emerges a pressure field, obtainable from a divergence-free condition, whose gradient enforces incompressibility. Rather than making use of a wave-vector expansion, this model is fully nonlocal; it furthermore gives the relevant long-time behavior. We discuss the connection with earlier approaches.

We start with the following approximate expression for the free-energy density of a compressible m component system:

$$F=F_0-kT\sum_{i=1}^{m}\frac{\phi_i}{v_i}\ln\left(1-\sum_{j=1}^{m}\phi_j\right), \tag{1}$$

where v_i is the particle volume and ϕ_i is the volume fraction of the ith component. F_0 is the free-energy density of the incompressible fluid, and $F-F_0$ is the entropic contribution arising from compressibility. If F_0 has the form $F_0=-\Sigma_{ij}a_{ij}\phi_i\phi_j+kT\Sigma_i(\phi_i/v_i)\ln\phi_i$, then Eq. (1) leads to the van der Waals equation of state. One may write $v_i=N_iv_0$, where v_0 is a characteristic volume; for polymers, then, N_i is the degree of polymerization. The last term on the right-hand side of Eq. (1) is due to compressibility. Other than having the entropy of mixing (per volume v_0) equal to $-k\Sigma_i(\phi_i/N_i)\ln\phi_i$, F_0 is general, and may have Flory-Huggins [12] or Cahn-Hilliard [6] form.

From Eq. (1), the chemical potential μ_i of a particle of species i is

$$\mu_i=\mu_{i0}-kT\ \ln\eta\sum_j\frac{\phi_j}{v_j}+\frac{kTv_i}{\eta} \tag{2}$$

where $\eta=(1-\Sigma_j\phi_j)/\Sigma_j(\phi_j/v_j)$ is the free volume per particle. As in Ref. [7], we postulate that the current of any component is proportional to the gradient of the chemical potential of that component. Since we expect the mobility to be proportional to the mean free path, for the volume current of component i we write

$$\mathbf{J}_i=-\Lambda_i(\eta/v_0)^{1/d}\nabla\mu_i/v_ikT, \tag{3}$$

where d is the dimensionality of the system, $\Lambda_i=D_i\phi_iv_i$ and D_i is a ‘‘bare’’ diffusion constant. The dynamics is then obtained from the equation of continuity $(\partial\phi_i/\partial t)+\nabla\cdot J_i=0$.

Next we take the incompressible limit. We note that the pressure is given by $P=-F+\Sigma_i\phi_i(\partial F/\partial\phi_i)=P_o+kT\Sigma_i\phi_i/\eta$ where P_o is the contribution to the pressure from F_o. Away from equilibrium, P, P_o, and η may vary in space and time. It is convenient to write $kT\Sigma_i\phi_i/\eta=P_\infty+\ p(\mathbf{r},t)$, where P_∞ is a large uniform constant background pressure, and $p=P-P_o-P_\infty$ is the local variation. We write P_∞ in terms of a small dimensionless parameter $\varepsilon=kT/P_\infty v_o$; then $\eta=\varepsilon v_0\Sigma_i\phi_i\times[1+\varepsilon(pv_0/kT)]^{-1}$. In the limit when $\varepsilon\to0$, $\Sigma_i\phi_i\to1$, and the chemical potential becomes

$$\mu_i=\mu_{i0}-kT\ \ln\sum_j\frac{\phi_j}{v_j}+pv_i \tag{4}$$

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to within an additive constant. The excluded volume interactions, which are not included in F_0 but which are responsible for the finite density of the system, give rise to the last two terms on the right-hand side of Eq. (4). For small ε, the equation of continuity becomes

$$\frac{\partial \phi_i}{\partial t} \simeq \varepsilon^{1/d} \nabla \cdot (\Lambda_i \nabla \mu_i / v_i kT) \tag{5}$$

Introducing the scaled time $t_l = \varepsilon^{1/d} t$ to obtain the late time behavior, we get

$$\frac{\partial \phi_i}{\partial t_l} = \nabla \cdot \Lambda_i \nabla \mu_i / v_i kT, \tag{6}$$

where μ_i is given by Eq. (4).

The pressure field can be obtained from the incompressibility condition $\eta = 0$, or $\Sigma_i \phi_i = 1$. This gives

$$\nabla \cdot \sum_i \Lambda_i \nabla p = -\nabla \cdot \sum_i \Lambda_i \nabla \left(\mu_{i0} - kT \ln \sum_j \frac{\phi_j}{v_j} \right) \Big/ v_i \tag{7}$$

which may be solved for p. Equations (4), (6), and (7) are our main results. They describe the evolution of the system at late times, where the nonlocal interactions which give rise to volume conservation are taken into account via the pressure field p.

Both our approach and that of de Gennes [7] rely on an augmented chemial potential which enforces volume conservation. Indeed, his potential U corresponds to $-kT \ln \Sigma_j (\phi_j / v_j) + p v_i$ in our scheme. He subsequently argues, however, that since the divergence of the total current must be zero, the Fourier coefficients of the total current must be zero for $q \neq 0$. His results therefore only hold in one dimension, whereas ours hold in general, and allow nonvanishing solenoidal net flux.

In one dimension, Eq. (7) may be solved to give

$$\nabla p = -\frac{\Sigma_i \Lambda_i \nabla [\mu_{i0} - kT \ln \Sigma_j (\phi_j / v_j)] v_i}{\Sigma_i \Lambda_i}. \tag{8}$$

Equation (4) then gives

$$\mathbf{J}_i = \sum_j \Gamma_{ij} \nabla \left(\mu_{j0}/kT - \ln \sum_l \frac{\phi_l}{v_l} \right) \Big/ v_j \tag{9}$$

where $\Gamma_{ij} = (\Lambda_i \Lambda_j / \Sigma_l \Lambda_l) - \delta_{ij} \Lambda_i$. We note that all the thermodynamic forces $-\nabla \mu_{oj}$ contribute to the current $\mathbf{J}_i$ of each component, due to the interactions responsible for incompressibility. The kinetic coefficients Γ_{ij} satisfy the Onsager reciprocity relations $\Gamma_{ij} = \Gamma_{ji}$. For a two-component system, $\Gamma_{AB} = \Gamma_{BA} = -\Gamma_{BB} = -\Gamma_{AA} = \Lambda_A \Lambda_B / (\Lambda_A + \Lambda_B)$, in agreement with expressions currently in use [7,9,10].

The dynamics is given by

$$\frac{\partial \phi_A}{\partial t} = \frac{\partial}{\partial x} \Gamma_{AB} \frac{\partial}{\partial x} \left[\frac{\delta F_0(\phi_A, 1-\phi_A)/kT}{\delta \phi_A} - \left(\frac{1}{v_A} - \frac{1}{v_B} \right) \ln \left(\frac{\phi_A}{v_A} + \frac{1-\phi_A}{v_B} \right) \right], \tag{10}$$

and similarly for ϕ_B. For the growth rate ω_A of a mode with wave number $\mathbf{q}$, linear stability analysis gives

$$\omega_A = \Gamma_{AB} (a q^2 - b q^4 + c q^2), \tag{11}$$

where $a = -\partial^2 F_0 / \partial \phi_A^2$ and $b = \partial^2 F_o / \partial (\partial \phi_A / \partial x)^2$ as usual; $c = [(v_A / v_B) + (v_B / v_A) - 2/(v_B \phi_A + v_A (1 - \phi_A)]$ is a destabilizing entropic contribution originating in the volume difference of particles. Although in the absence of energetic terms in F_0 this effect is not large enough to overcome the entropy of mixing, it is consistent with predictions of phase separation due to size difference via steric interactions [14].

In summary, here we propose that phase separation dynamics of incompressible multicomponent systems may be simply described by a model where the current of each component is proportional to the chemical potential of that component; $\mathbf{J}_i = -\Lambda_i \nabla \mu_i$. The kinetic coefficient is $\Lambda_i = D_i \phi_i v_i$, and the chemical potential is $\mu_i = \mu_{i0} - kT \ln \Sigma (\phi_j / v_j) + p v_i$, where μ_{i0} is the chemical potential obtained from the usual (Flory-Huggins or Cahn-Hilliard type) free energy. The contribution to the current $\mathbf{J}_i$ from the chemical potential gradients of other components is implicitly included in the pressure field p, which may be obtained from the divergence condition of Eq. (7). Due to time scaling, the dynamic equations [Eq. (6)] give the relevant behavior at late times. It is straightforward to show that, following this dynamics, the free energy is nonincreasing in time. This model is also equivalent to the description of multi-component fluids under Darcy's approximation [13]. In $1-d$, our results are consistent with those in the literature. Extension of this approach to systems with orientational order is underway.

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