Hydrodynamic Coarsening of Binary Fluids

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By suitable interpretation of results from the linear analysis of interface dynamics, it is found that the hydrodynamic growth of the size L of domains that follow spinodal decomposition in fluid mixtures scales with time as $L \sim t^{\alpha}$, with $\alpha = 4/7$ in the inertial regime. The previously proposed exponent $\alpha = 2/3$ is shown to indicate only the scaling of the oscillatory frequency $\omega^{-2/3} \sim L$ of the largest structures of the system. The viscous dissipation in the system occurs within a layer of thickness L_d that also follows a power law of the form $L_d \sim L^{3/4}$ in the inertial regime. In the viscous regime the growth is linear in time $L \sim t$ and the dissipative region remains constant $L_d \sim L^0$.

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Homogeneous binary fluid mixtures phase segregate into two phases with different composition when quenched into thermodynamically unstable regions of the phase diagram. Deep quenches often lead to interconnected and/or highly concentrated branchlike structures with different compositions referred to as spinodal decomposition patterns. As the decomposition evolves, sharp interfaces develop between the regions associated with each phase, and the structures formed coarsen to minimize their interfacial energy. In the late stages of this process the concentrations of the phases are close to their equilibrium values and coarsening is dominated by hydrodynamic rather than thermodynamic (compositional gradient) driving forces. Experimental [1–4] and only recently feasible numerical studies [5–7] have been carried out to determine whether there is an asymptotic hydrodynamic coarsening regime in incompressible fluids in which the characteristic size of the strongly segregated domains L obeys a simple power law in time, $L \sim t^{\alpha}$. Exponents α ranging from $1/2$ to 1 have been reported. Fits are usually attempted to match exponents 1, $2/3$, and $1/2$ predicted by dimensional analysis [8,9] and/or by other physical arguments [10,11].

There are few theoretical coarsening studies in this regime, apparently due to the lack of techniques to deal with such a complicated problem. Only linear analysis has been used to further support the values of some exponents or to explain certain qualitative properties of these systems [8,12]. In this Letter we reassess the information provided by linear analysis of interface dynamics and show that in the late stages of the decomposition the segregated domains are driven towards local stable conformations with a growth exponent $\alpha = 4/7$. This analysis confirms that the exponent $\alpha = 1$ corresponds to asymptotically early times (the viscous regime), while the $\alpha = 2/3$ exponent appears only as characterizing the oscillatory frequency ω of unrelaxed interface inhomogeneities of wavelength λ: $\lambda \sim \omega^{-3/2}$ in the late stages of coarsening (the inertial regime). While the basic results from linear analysis are fairly old, their relevance to the problem of hydrodynamic coarsening has not been exploited, and the asymptotic limits of the problem are not well known.

Some general conditions on the structure of the system are required to interpret the results of linear analysis in the form of a possible power law. The possibility of an asymptotic power law for the hydrodynamic regime requires a degree of self-similarity. We propose that the evolution of the system in the very late stages of the decomposition (sharp interfaces) proceeds by forming locally almost stable structures, dropletlike, that pairwise or many at a time coalesce into larger domains. More precisely, these droplets can be understood as coherent structures whose size corresponds to the average domain size as measured by the structure factor of the system. If the time required for the coalescence of a pair of domains into a larger one obeys a simple scaling relation with respect to the size of the domains, the late stages will exhibit a power law relation. As shown below, the power law is related to the relaxation rate of large domains into stable or metastable structures. In turn, the relaxation rate can be determined from the linear stability analysis of the bigger final domain subject to deformations on length scales of the order of its size.

Consider a region of the mixture with a locally stable configuration, an almost spherical domain. In its final configuration the region will produce a contribution to the structure factor $S_o(k)$ such that, up to a constant, the average size of the system corresponds to the radius of the domain $R_o \sim \langle k^{-1} \rangle = \int d\mathbf{k}\, k^{-1} S_o(k) / \int d\mathbf{k}\, S_o(k)$. Just before reaching this state, at a certain time t, the system takes conformations that can be described by deformations around this spherical shape. The average size for such a deformed structure $R(t)$ is always smaller than the equilibrium size R_o since the structure factor of the deformed shape $S(k)$ has contributions from smaller wavelength modes (larger k) that make $\langle k^{-1} \rangle$ smaller. Decomposing the structure factor into the contribution of the final domain $S_o(k)$ and its perturbation $S_p(k,t)$, the average size of the system is $R(t) = \langle k^{-1} \rangle_t = \int d\mathbf{k}\, k^{-1} [S_o(k) + S_p(k,t)] / \int d\mathbf{k}\, S(k)$. The k modes that appear in the perturbation are stable and their amplitudes $A(k)$ decay according to a relation $\partial_t A(k) = n(k) A(k)$ with $\mathrm{Re}\, n < 0$, so that $\dot{R} \approx \langle k^{-1} n(k) \rangle_t = \int d\mathbf{k}\, k^{-1} \times n(k) S_p(k,t) / \int d\mathbf{k}\, S_o(k)$, since in the hydrodynamic

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regime $\int d\mathbf{k}\, S_o(k) = \int d\mathbf{k}\, S(k,t)$. Note that, since $R_o > R(t)$, the pure k^{-1} average over the perturbation modes is always negative, but the inclusion of the $n(k)$ factor in the average produces a positive growth rate for the size of the domain. If the perturbation is dominated by structures with wavelengths comparable to the size of the system, $k \sim R^{-1}$, and the dispersion relation follows an asymptotic power law $n(k) \sim k^{1/\alpha}$, then it is possible to conclude that the structure of size R under consideration has been formed at a rate $\dot{R} \approx R^{(1-1/\alpha)}$. If the creation of larger structures proceeds in this manner, the growth of the system follows the power law $R \sim t^{\alpha}$, where the exponent α is read from the dispersion relation for *stable* modes, given below.

The linear analysis we need is that of a single large domain. We present a succinct derivation, following the classical text of Chandrasekar [13], of results first obtained by Harrison [14] for a flat interface, and later we quote the results of Miller and Scriven [15] for perturbations of a spherical droplet. The solution for a flat interface is more accessible and serves to show the generality of the final result. Consider deformations of a flat interface between two masses of incompressible fluids of density ρ and viscosity η (the general case of different properties leads to similar results), and a surface tension σ between them. The spectrum that is derived from the analysis corresponds to the normal modes of the fluctuating interface but these are easily seen to be in direct relation to compositional inhomogeneities. The equilibrium surface coincides with the $z = 0$ plane in a suitable Cartesian frame. The initial condition for the interface is given by a deformation of wavelength k and we search for solutions of the form

$$z(t) = Ae^{nt}\cos kx\,. \tag{1}$$

It is also assumed that the velocity fields decay exponentially away from the surface so that, for example, the z component of the velocity is a linear combination of terms of the form $v_z \sim e^{nt}\cos(kx)e^{-qz}$ (for $z > 0$). The task at hand is to calculate the growth or decay rate n of the wave, and the decay length q^{-1}. The linearization of the Navier-Stokes equations and the boundary conditions for the velocity fields at the interface are given in Ref. [13], and only the main steps are sketched here. The problem can be put into dimensionless form by introducing the characteristic length and time $L_0 = \eta^2/\rho\sigma$ and $T_0 = \eta^3/\rho\sigma^2$. Using this convention k, q, and n are dimensionless numbers. The velocity field has a decomposition $\mathbf{v} = \mathbf{v}_o + \mathbf{v}_r$ in which $\mathbf{v}_o$ is irrotational, and the vorticity for the flow is $\boldsymbol{\omega} = \nabla \times \mathbf{v} = \nabla \times \mathbf{v}_r$. The z displacements of the interface at the boundary due to these different velocity components are A_o and A_r, so that $A = A_o + A_r$. The linearization of the Navier-Stokes equations for the bulk of the phases implies $\partial_t \boldsymbol{\omega} = \nabla^2 \boldsymbol{\omega}$ which leads to the following relation for the spectral parameters:

$$n = (q^2 - k^2) = k^2(y^2 - 1)\,, \tag{2}$$

with $y = q/k$. The linear dynamics of the irrotational mode is dictated only by the local pressure so that $\partial_t \mathbf{v}_o = \nabla p$. Therefore, at the interface $n^2 A_o = kp$, since the spatial dependence for the pressure has the form $p \sim \cos(kx)e^{-kz}$. The continuity equations of the velocity fields across the interface imply the relation $yA_r = A_o$, so that $A = A_o(1 - y^{-1})$. Finally, the local curvature of the interface produces a jump in the pressure across the interface, $\Delta p = -(1/2)k^2 A$, from which, after eliminating the pressure amplitude, we obtain $n^2 = -k^3(1 - y^{-1})$. From this last relation, together with Eq. (2), we reach the main result in the form of a single algebraic equation for the ratio y,

$$y^4 + y^3 - y^2 - y + \frac{1}{k} = 0\,. \tag{3}$$

From the analysis of the solutions of this equation, it is found that the system is stable for every wavelength (these systems can be unstable only in the presence of gravity and when the densities are different). The stability of the system is apparently disappointing for the purposes of unstable, explosive behavior, or for structure creation. For the problem of coalescing fluids, however, the stable modes contain the crucial information, and it is necessary to look at the asymptotic limits implied by these relations.

There are two scaling limits encoded in Eq. (3). First we can consider short wavelengths for which $k^{-1} \rightarrow 0$, which due to our choice of units is also equivalent to the viscous regime of the system, or the early stages of growth. The relevant solutions of the equation can be expressed as a power series in k^{-1}, $y = k^{-1} - k^{-2} + \ldots$. This implies that to leading order $q = 1$ and $n = -k$. In this regime, the decay time $\tau = -1/n$ scales linearly with the wavelength of the perturbation. This result is the linear analysis expression of the scaling limit proposed by Siggia [8] for the early stages of the growth, and has also been implicitly confirmed by the 2D analysis of San Miguel *et al.* [12]. For long times after the process of coarsening has started the only surviving modes have long wavelengths, $k \rightarrow 0$, which corresponds to approaching the inviscid limit. In this case the solutions of the characteristic equations are complex, and can be presented as a Laurent series in $k^{1/4}$:

$$y = \frac{1+i}{2^{1/2}}\,k^{-1/4} - \frac{1}{4} + \ldots, \tag{4}$$

so that, to leading order

$$q = \frac{1+i}{2^{1/2}}\,k^{3/4}, \tag{5}$$

$$n = i\omega - \tau^{-1} = ik^{3/2} - 2^{-1/2}k^{7/4}. \tag{6}$$

The leading term of the decay period is complex which implies oscillatory behavior. This is to be expected since the limit $k^{-1} \rightarrow \infty$ is also equivalent to the limit of zero viscosity, in which the system does not dissipate energy and simply oscillates. The waves can decay only by restoring a small amount of viscosity. A naive dimensional analysis of the Navier-Stokes equations for this problem suggests the exponents of 1 and $2/3$ for the growth rate of the system. The first exponent has already been shown to correspond to the early times or viscous regime. The last exponent, however, cannot refer to the growth of the system and provides only the scaling for the asymptotic oscillatory frequency, as is well known in the literature of capillary waves [16]. The next leading order analysis gives rise then to the $1/\alpha = 7/4$ exponent, from which follows the power law growth rate

$$L \sim t^{4/7}. \tag{7}$$

It is also important to note that in both limits the region of viscous dissipation for the perturbation of wavelength L extends not a distance L into the bulk of the fluid, but rather to a different length scale $L_d = q^{-1}$, with asymptotic behavior $L_d \sim L^0 = 1$ and $L_d \sim L^{3/4}$, in the viscous and inertial regimes, respectively. The results thus obtained are also valid in two dimensions since no real use was made of the dimensionality of the system.

The analysis of spherical shapes was performed by Miller and Scriven [15] who considered the fluctuations of a drop immersed in a second fluid. The results are similar to the flat case, showing that the sphere is always stable, and that in the limit of low viscosity perturbations decay in the form of damped oscillations. For the spherical droplet the deformations are decomposed into spherical harmonics, instead of Fourier waves. The first order in the real and imaginary parts of the complex decay rate for the lth wave are given in the inertial limit by

$$n = \omega(l)[iR^{-3/2} - 2^{-5/2}(2l + 1)^2\omega(l)^{-1/2}R^{-7/4}], \tag{8}$$

where R is the radius of the drop and $\omega(l) = [l(l^2 - 1)(l + 1)/(2l + 1)]^{1/2}$. Clearly this case satisfies the same scaling relations obtained for the flat interface. For the case of coalescence of two touching droplets into a larger one it is easy to see that the process can be approximated by considering the two droplet state as a deformation of the final droplet with a large component in the $l = 2$, quadrupolar mode. Note that in that case the precise inverse decay time is given by $\tau^{-1} = -\mathrm{Re}\,n = 3^{1/2}5^{7/4}2^{-9/4}R^{7/4}$, and thus it can be expected that in a fit to a power law from physical or computational data of the form $R = a(t - t_0)^\alpha$, the precoefficient a takes values of order 1.

While the deformations from spherical or planar geometries obey the asymptotic limits given by Eqs. (6) and (8) the average size of the domains will reflect the $4/7$ power law only when the wavelengths and amplitudes that are being relaxed correspond to the size of the system, i.e., when the growth is driven by the coalescing of similarly sized domains. Most of the information produced by the linear approximation can be locally tested by means of time dependent correlation functions $G(k, \omega) = \langle \rho(k, \omega)\rho(k, \omega)\rangle$, even when the state of the system does not belong to a series of self-similar conformations.

It has been argued by Grant and Elder [10] that as the system grows it generates ever larger length scales and velocity fields for which the Reynolds number, which in this case appears to be $\mathrm{Re} = L^2/T = L^{1/4}$, will indicate turbulent behavior. Typically, the Reynolds number predicts turbulent behavior in flows with an externally imposed velocity. While instantaneously the system can be always considered as such, the amount of energy available is always decaying and there is no external source to replace it. Only a fraction of the energy available to the system can be eventually transmitted by means of the turbulent cascade towards smaller scales, leading to the local destruction of the sharp interface. In the coalescence of two large domains at large Reynolds numbers, it is possible that the final state is composed of, for example, one large spherical domain, with satellite droplets that had been expelled from or penetrated from the external phase into the final drop. While the largest scale of the system might still be growing, the creation of the smaller stable structures can slow down the growth rate. It is not clear, however, if the slowing down is sufficient to imply the strict bound $\alpha \leq 1/2$. One way to further study this issue is, for example, to investigate the locus of large vortex stretching fields that might occur in specific geometries relevant to the problem, such as domains with large quadrupolar deformations near the inviscid limit. The localization of possible turbulent structures is not a trivial issue since in the problem at hand there is not one single pair of length and time scales, and indeed, we can form a Reynolds number based in the dissipation length and the oscillatory frequency $\mathrm{Re} = \omega L_d^2 = L^{-3/2}(L^{3/4})^2 = 1$ that is always bounded. It is also possible that the turbulent mixing takes place away from the interface which is then not destroyed. A recent argument by Kendon [11] also shows that different length scales can appear in the inviscid limit and that the largest scale in the system is not equal to the turbulent dissipation scale. The scaling arguments of Kendon assume, however, that all quantities are isotropically distributed, while in our approach all quantities are tied to a local frame set by the sharp interface and there are different dominant scales in the directions transversal and parallel to the surface. Finally, we note that even if the $\alpha \leq 1/2$ bound is correct for the 3D problem, turbulence is not a 2D phenomena, and the $\alpha = 4/7$ exponent should apply to physical systems and simulations for which effectively the dimensionality of the space is $D = 2$.

The conditions for the coalescence of domains are also different depending on the dimensionality of the system. In 3D a tubular structure is unstable [8], and this might hinder the creation of larger structures since the system might be trapped in a state that consists of isolated domains formed by breakup of connecting tubes and relax into a state of many disconnected droplets in the matrix of the second component. In 2D, tubular structures are stable, as shown by San Miguel *et al.* [12], and this analysis has been interpreted as preventing the growth of the system. From our point of view, however, the fact that the oscillations on the tube do not grow simply implies that the tube retains its shape until the regions it connects are joined, or until it is dynamically broken by the flow. It is important also to note that the tube structures, if unstable, disappear rather quickly at the beginning of the hydrodynamic flow. More precisely, while these modes indirectly determine the final state of the system, including the maximum size of the domains that can be formed, they do not modify the rate at which the final size is reached. Finally, we should point out that, upon reaching the maximum size allowed by pure hydrodynamical growth, coarsening may continue either by Brownian motion of droplets [3] or by the diffusional Lifshitz-Slyozov process [17].

Most of the numerical and experimental work to measure a possible power law in the growth of a system has been analyzed by comparing the data against the two, so far believed, more likely candidates, the power laws 1 and $2/3$. The late time asymptotics have been consistently shown to be not 1, but the reduced amount of data does not provide a definitive measurement. The most favorable comparison of numerical data with the predictions presented here comes from 2D simulations in which the best fit for the late stages exponent was measured to be between 0.55 and 0.6 [7].

Since so much work in the field has been done by means of simple dimensional analysis, it is interesting to derive the main result for the inertial regime presented here with such arguments. First, it is clear that the comparison of the density of kinetic energy $\frac{1}{2}\mathbf{v}^2$, and surface energy density proportional to the interface area per volume A/L^3, leads to the relation $\omega^2 L^2 \sim L^{-1}$, or $\omega \sim L^{-3/2}$. Next, the dissipation length L_d is set by matching the frictional forces created by longitudinal stretching $\partial_z^2 v_z$, with the typical inertial term $\partial_t v_z$ in the dissipative layer so that $L_d^{-2} \sim \omega \sim L^{-3/2}$, and $L_d \sim L^{3/4}$. By incompressibility, the typical values of the velocities tangential and normal to interfaces are related by $v_x L_d \sim v_y L$, so that the typical rate of energy dissipation by shear is $v_y \partial_y^2 v_x \sim L_d^{-1} L^{-1} v_y^2$, which should be comparable to the leading term for the kinetic energy decay rate $\partial_t v_y^2 \sim \tau^{-1} v_y^2$, and so $\tau \sim L L_d \sim L^{7/4}$, or as expected, $L \sim \tau^{4/7}$. This rather informal derivation of the exponent can be shown to be right only by making a precise parallel of the steps taken in it with those involved in the linear analysis. More importantly, besides being an argument for the $\alpha = 4/7$ exponent, this derivation shows the dangers implicit in the naive scaling analysis that has often been invoked to justify $\alpha = 2/3$.

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