Spinodal decomposition to a lamellar phase: effects of hydrodynamic flow

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Results are presented for the kinetics of domain growth of a two-dimensional fluid quenched from a disordered to a lamellar phase. At early times when a Lifshitz-Slyozov mechanism is operative the growth process proceeds logarithmically in time to a frozen state with locked-in defects. However when hydrodynamic modes become important, or the fluid is subjected to shear, the frustration of the system is alleviated and the size and orientation of the lamellae attain their equilibrium values.

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The kinetics of the growth of ordered phases as a system is quenched from a one- to a two-phase region provides a wealth of interesting physical questions[3]. Our aim here is to present results for phase separation in a two-dimensional binary fluid in the case where equilibrium corresponds to a lamellar structure where the two coexisting phases arrange themselves in stripes. We consider both the early-time regime, where the growth is driven by a Lifshitz-Slyozov evaporation-condensation mechanism[4], and later times (or equivalently lower viscosities) where hydrodynamic modes alter the kinetic behaviour. Our main conclusions are that when the former mechanism is operative the lamellae initially grow logarithmically but then become frozen in a tangled configuration. It is only when hydrodynamic movement becomes effective that topological defects can be removed allowing the lamellae to line up and attain their correct equilibrium width. We show that the frustration of the system can also be alleviated by subjecting it to shear.

Our results are relevant to a wide variety of physical systems where competing interactions result in stable lamellar phases. One example is a di-block copolymer melt comprising A- and B-type chains covalently bonded end-to-end in pairs. If the A–B interaction is repulsive the tendency towards bulk phase separation at low temperatures is halted by the covalent bond and a lamellar phase can be stabilised[5]. In microemulsions similar structures result from the presence of surfactant at the (say) oil–water interface which leads to competition between a negative surface tension and positive interfacial curvature free energy[6]. Other examples include dipolar fluids with long-range Coulombic interactions[7] and chemically reactive binary mixtures where the ordering tendency of the two components is counterbalanced by the mixing effect of the reaction[8].

The problem is addressed using lattice Boltzmann simulations[9] of the Navier-Stokes and convection-diffusion equations for a binary fluid. These simulations follow the behaviour of a set of distribution functions, related to the fluid densities and velocity, which evolve according to a discretised Boltzmann equation. The densities and momenta are conserved at each step of the simulation thus approximating the continuum equations of fluid flow.

The technique has two advantages which are particularly relevant here. Firstly it allows simulations on long enough time scales to access hydrodynamic behaviour. Secondly by using an implementation of the method described by Orlandini et. al.[10] it is possible to introduce a free energy into the model such that the fluid relaxes to an equilibrium state determined by the minimisation of the input free energy. Hence we are able to accurately control the equilibrium state that the fluid is trying to reach.

The numerical method is described in detail in reference[11]. Here we consider a model which corresponds to an equilibrium free energy density[11]

$$F\{\varphi\} = \int d^d x \left\{ \frac{a}{2} \varphi^2 + \frac{b}{4} \varphi^4 + \frac{\kappa}{2} \nabla \varphi^2 + \frac{c}{2} (\nabla^2 \varphi)^2 \right\}$$

where \( \varphi \) is a scalar order parameter describing the concentration difference between the two binary components. We take \( b, c > 0 \) to ensure stability. For \( a > 0 \) the fluid is disordered; for \( a < 0 \) it prefers an ordered state. The nature of this depends on the value of the surface tension. For \( \kappa \) sufficiently large for fixed \( c \) the surface tension is positive and the fluid prefers to phase separate into two homogeneous phases. As \( \kappa \) is decreased, however, at some \( \kappa = \kappa_c \approx -0.8 \) for \( c = 1 \) the surface tension becomes negative and it becomes favourable to introduce interfaces into the system. The ordered state is now a lamellar or striped phase with spacing determined by the competition between the free energy gain due to interface creation and the repulsive force between interfaces. We shall compare the behaviour of the fluid under sudden quenches from the disordered to the ordered phases for \( \kappa \) greater than and less than \( \kappa_c \).

Before presenting our results it is useful to summarise the known behaviour of a binary fluid quenched into the ordered homogeneous phase[12]. Once domains of the two phases are well established experimental and numerical data indicates that the growth is self-similar with a typical length scale \( R \) scaling with time as \( R \sim t^{\alpha} \). The exponent \( \alpha \) is universal depending only on a small number of parameters; the dimensionality, conservation laws applicable to the order parameter and the presence or absence of hydrodynamic degrees of freedom. Three growth mechanisms are believed to be operative in two
dimensions: (i) Lifshitz-Slyozov evaporation of particles from interfaces of high curvature to recondense on interfaces of lower curvature with $\alpha = 1/3$, (ii) a regime with $\alpha = 1/2$ which has been explained as being due to Brownian diffusion of interfaces and droplets\cite{12}, (iii) inertial hydrodynamic flow with $\alpha = 2/3$\cite{13}. Previous lattice Boltzmann simulations\cite{14} have shown a crossover from (i) to (iii) with decreasing viscosity with (ii) not seen as might be expected because of the lack of noise in the simulations. Lattice gas simulations, which do include noise, show a crossover from (ii) to (iii)\cite{15}. However puzzles do remain. For example, a simulation by Lookman et. al.\cite{16} using a Ginzburg-Landau approach, shows a crossover from (ii) to (iii) independent of whether or not noise is present.

Results for the evolution of the domain size $R(t)$ with time following a quench to the ordered phase $a < 0$ for different values of $\kappa$ are shown in Fig. 1. $R(t)$ was calculated as the first moment of the circularly averaged structure factor. These simulations were run with high values of the viscosity where the diffusive Lifshitz-Slyozov growth mechanism is expected to be operative.

For $\kappa \geq -0.8$, where the surface tension is positive, all systems reach the scaling regime (i) after a sufficiently long time. As $\kappa$ is decreased the domains take longer to reach a given size. This is as expected because the driving force for the Lifshitz-Slyozov growth, provided by the surface tension, is lower. It is interesting to note that the scaling regime sets in at approximately the same domain size in each of the runs. The data presented in Fig. 1 is from a single run on a lattice of size $128 \times 128$ as our aim here is to provide a qualitative comparison of the results as $\kappa$ is decreased rather than the best quantitative value for $\alpha$ which has been done elsewhere\cite{14}.

For $\kappa < \kappa_c$ where the system prefers to order in a lamellar phase a significantly different behaviour is apparent. After initial transients there is a region of logarithmic growth which corresponds to formation of the lamellae. The growth then slows down and the fluid becomes frozen. A similar pattern of growth has been observed for quenches into microemulsion phases\cite{17,15} and for systems with quenched defects\cite{18}.

![FIG. 1. Logarithm of a typical domain size as a function of the logarithm of the time for different values of the surface tension and a sufficiently high viscosity that the growth proceeds by the Lifshitz-Slyozov mechanism. The straight line corresponds to a growth exponent $\alpha = 1/3$. For $\kappa$ sufficiently negative the domain size grows logarithmically and then saturates as the system reaches a frozen state of tangled lamellae.](image)

![FIG. 2. Snapshots of the growth of domains with time. Each line, reading from left to right, represents a different physical situation: (a) a quench to the homogeneous two phase region $\kappa > \kappa_c$; (b) a quench to the lamellar phase $\kappa < \kappa_c$ in a high viscosity fluid. The lamellae form in a tangled pattern which becomes frozen in time; (c) a quench to the same final parameters as (b) but for a low viscosity fluid. Hydrodynamic modes allow the lamellae to reorder giving, locally, well-defined striped regions.](image)
ever this does not impede growth into two homogeneous phases and the lamellae grow and become more isotropic throughout the simulation. For \( \kappa < \kappa_c \), however, (Fig. 2b), the lamellae form in a tangled pattern which becomes frozen in time.

We now turn to a primary aim of this Letter which is to report the effect of hydrodynamic modes on the quench to the lamellar state. To investigate this we ran the simulations for \( \kappa = -0.9 \) for a low value of the viscosity. A pictorial comparison of the domain growth in the long time regime for the high and low viscosity cases are given in Figs. 2b and 2c respectively. It is apparent that in the latter case it becomes easier for the lamellae to grow and shrink along their length thus allowing a decrease in the frustration in the system. This is because the long-range nature of the hydrodynamic modes are allowing the fluid to reorder in such a way as to remove topological defects from the fluid. For the latest accessible times some defects remain although the system is locally lamellar.

The rearrangements of the lamellae also have the effect of allowing them to attain their equilibrium width. The growth of the domain size with time following a quench to the lamellar phase for high and low viscosities is compared in Fig. 3. In the latter case there is a relatively rapid decrease in the domain width as hydrodynamic modes become effective. As evidence that equilibrium is indeed being achieved we also show in Fig. 3 a quench for the same (high viscosity) parameters but with a one-dimensional sine wave as the initial condition. This allows the lamellae to grow easily in an ordered pattern. The final domain size achieved is very similar to that obtained after hydrodynamic rearrangements of the frozen state.

As a further check on the mechanism causing the unlocking of the frustrated lamellar state we simulated the behaviour of simple topological defects. Examples are a broken lamella or an extra portion of lamella inserted in an otherwise regular pattern. In each case diffusive growth was only able to cause small changes of interface shape whereas hydrodynamic rearrangements succeeded in removing the defect from the fluid.

Finally we consider another mechanism which allows topological disorder in the lamellar state to be removed, the introduction of a shear. To simulate the shear we imposed rigid walls moving with velocity \( \pm v \) on the left and right of the simulation area. A natural way to implement rigid walls is to use bounce-back conditions at the boundary sites[20]. The other edges of the system were linked with periodic boundary conditions.

The fluid was quenched into the lamellar state giving the disordered configuration shown in Fig. 4(a). As the shear was applied ordered lamellae quickly formed, aligned at an angle to the direction of shear, as shown in Figure 4(b). A further increase in the shear rate resulted in a decrease in the angle between the direction of the lamellae and that of the shear (Figure 4(c)). We believe that this angle is determined by a balance between the force on the lamellae due to the shear and the elastic force which results because they are compressed. Presumably on much longer time scales lamellae could be lost from the system, releasing the elastic energy and allowing the lamellae to turn towards the shear direction.
Thermal fluctuations are not included in the lattice Boltzmann simulations and it is important to ask whether noise could be responsible for unpinning the metastable state before the onset of hydrodynamics. To test this we ran a simulation of Langevin dynamics for the free energy \[1\]. Tangled lamellar were formed in the same way as in the lattice Boltzmann simulations suggesting that noise is ineffective in bringing the system to a global thermodynamic equilibrium. This conclusion is supported by cell dynamical calculations\[3\] but disagrees with results based on a time-dependent Ginzburg-Landau simulation\[21\].

To conclude, we have studied domain growth in a fluid with a well-characterised, lamellar, equilibrium state. Diffusive growth leads to a frozen pattern of tangled lamellae. The topological defects in the fluid can be removed by hydrodynamic modes or applied shear. It would be interesting to extend this work to three dimensions where a new physical mechanism, the Rayleigh instability of tubes, is expected to be operative\[22\]. However such calculations would be extremely demanding computationally.

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