Thermal and hydrodynamic effects in the ordering of lamellar fluids

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Phase separation in a complex fluid with lamellar order has been studied in the case of cold thermal fronts propagating diffusively from external walls. The velocity hydrodynamic modes are taken into account by coupling the convection-diffusion equation for the order parameter to a generalised Navier-Stokes equation. The dynamical equations are simulated by implementing a hybrid method based on a lattice Boltzmann algorithm coupled to finite difference schemes. Simulations show that the ordering process occurs with morphologies depending on the speed of the thermal fronts or, equivalently, on the value of the thermal conductivity $\xi$. At large values of $\xi$, as in instantaneous quenching, the system is frozen in entangled configurations at high viscosity while consists of grains with well ordered lamellae at low viscosity. By decreasing the value of $\xi$, a regime with very ordered lamellae parallel to the thermal fronts is found. At very low values of $\xi$ the preferred orientation is perpendicular to the walls in $d = 2$, while perpendicular order is lost moving far from the walls in $d = 3$.

Keywords: Thermal effects; hydrodynamics; lattice Boltzmann method; lamellar order

1. Introduction

Ordering in complex fluids can be a slow process. Thermodynamic equilibrium is often characterised by the presence of organised structures at mesoscopic scales (Larson 1999). However, the dynamical formation of topological defects can make difficult to reach the true equilibrium state (Boyer & Viñals 2002, Benzi et al. 2009). Since there are physically relevant properties related to the degree of order in the system, it can be crucial to control the ordering process by proper driving.

In this paper we will consider fluids with lamellar order, such as symmetric block copolymer melts (Fredrickson & Bates 1996). For recent applications of these systems in micro- and nano-technologies one can for example see the work by Man et al. (2010) where the relevance of having long-range order is discussed. A transient macroscopic sample of a copolymer melt usually consists of different oriented lamellar domains (grains) with defects like dislocations and disclinations. The interplay between the mesoscopic structures and the local velocity field is essential for the evolution of defects (Gonnella et al. 1997). Hydrodynamic modes favour the disentanglement of intertwined patterns but simulations have shown how extended defects between different grains remain at late times slowing down the dynamics of ordering (Xu et al. 2004, 2005).

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Mechanical driving like shear can favour ordering since interfaces generally prefer to be aligned with the flow (Larson 1999). In lamellar systems under shear, however, different stable orientations are possible (Fredrickson 1994) and in the ordering process (Cates & Milner 1989, Corberi et al. 2002) the shear by itself can cause the creation of defects due to the dilatation or compression of the layers (Kumar et al. 2001, Lu et al. 2008). More complex phenomena like shear banding have been also observed (Xu et al. 2006).

A different controlling procedure could be thermal driving. Recently, in simple binary mixtures, it has been shown that in thermally controlled quenches with cold fronts propagating into the system at finite speed, interfaces have a preferred orientation with respect to the fronts (Furukawa 1992; Foard & Wagner 2009; Gonnella et al. 2010). As a result, ordered patterns are obtained. Applications to polymer systems have been considered for example by Voit et al. (2005). In this work we want to investigate how a thermally controlled quench could be used to produce well ordered lamellar systems.

We consider a system described in the continuum by the Navier-Stokes and convection-diffusion equations with the thermodynamics of the lamellar phase encoded in a free-energy functional. The temperature evolves by following a standard diffusion equation with the system between two walls at a temperature below the critical value. In order to solve the dynamical equations we apply a hybrid method with a lattice Boltzmann algorithm for solving the Navier-Stokes equations and a finite difference scheme for the convection-diffusion equation. The model and the method will be described in the next section while the numerical results will be presented Section III. Few conclusions will complete the paper.

2. The model

We consider a binary mixture having total density \( n \) and density difference \( \varphi \), the order parameter, between the two components. The equilibrium properties are described by the free energy (Brazovskii 1975)

\[
\mathcal{F} = \int \left[ nT + nT \ln(nT) + \frac{a}{2} \varphi^2 + \frac{b}{4} \varphi^4 + \frac{k}{2} (\nabla \varphi)^2 + \frac{c}{2} (\nabla^2 \varphi)^2 \right] \, dr. \tag{2.1}
\]

The first two terms depending on \( n \) and on the temperature \( T \) (the Boltzmann constant is assumed to be one) give the ideal gas pressure which does not affect the phase behaviour. We consider \( b, c > 0 \) to ensure stability. The parameter \( a \) can be thought of as a reduced temperature

\[
a = \frac{T - T_c}{T_c} \tag{2.2}
\]

and is the only one depending on temperature in the terms depending on \( \varphi \). For temperatures above the critical value \( T_c \), the fluid is disordered. For \( T < T_c \) and \( \kappa > 0 \) there is the coexistence of two homogeneous phases with equilibrium values \( \varphi = \sqrt{-a/b} \). Negative values of \( \kappa \) favour the formation of interfaces, while a reduction of \( \kappa \) can induce a transition into a lamellar phase. By using a single mode approximation with profiles like \( A \sin k_0 x \) in the direction normal to lamellae, one finds a transition, when \( |a| = b \), at \( a \simeq -1.11 \kappa^2/c \) with \( k_0 = \sqrt{-\kappa/2c} \) and
\[ A^2 = 4(1 + \kappa^2/4c)b/3 \] (Xu et al. 2005). The parameters of this model have been mapped on those of copolymer systems by Binder (1995).

The evolution of the system is described by a set of coupled partial differential equations:
\[
\partial_t n + \partial_\alpha (nu_\alpha) = 0, \quad (2.3)
\]
\[
n(\partial_t u_\alpha + u_\beta \partial_\beta u_\alpha) = -\partial_\beta P_{\alpha\beta} + \partial_\beta \left[ \eta (\partial_\alpha u_\beta + \partial_\beta u_\alpha) + (\zeta - 2\eta/d)\partial_\alpha \partial_\beta u_\alpha \right], \quad (2.4)
\]
\[
\partial_t \varphi + \partial_\alpha (\varphi u_\alpha) = \Gamma \nabla^2 \mu, \quad (2.5)
\]

where \( \mathbf{u} \) is the local velocity of the fluid, \( \eta \) the shear viscosity, \( \zeta \) the bulk viscosity, \( d \) the space dimension, and \( \Gamma \) the mobility coefficient. We model the quench process by taking the reduced temperature \( a \) \((2.2)\) to be the solution of a diffusion equation \( \partial_t a = \xi \nabla^2 a \) where \( \xi \) is the thermal conductivity. The pressure tensor \( P_{\alpha\beta} \) and the chemical potential \( \mu \) can be computed from the free energy functional \((2.1)\) and have the following forms (Gonnella et al. 1997):
\[
P_{\alpha\beta} = \left\{ nt + \frac{a}{3} \varphi^2 + \frac{3b}{4} \varphi^4 - \kappa \left[ \varphi (\nabla^2 \varphi) + \frac{1}{2} (\nabla \varphi)^2 \right] + c \left[ \varphi (\nabla^2 \varphi)^2 + \frac{1}{2} (\nabla^2 \varphi)^2 \right] + \partial_\gamma \varphi \partial_\gamma (\nabla^2 \varphi) \right\} \partial_{\alpha\beta} + \kappa \partial_{\alpha\gamma} \varphi \partial_{\beta\gamma} \varphi - c \left[ \partial_{\alpha\gamma} \varphi \partial_{\beta\gamma} (\nabla^2 \varphi) + \partial_{\beta\gamma} \varphi \partial_{\alpha\gamma} (\nabla^2 \varphi) \right], \quad (2.6)
\]

and
\[
\mu = a \varphi + b \varphi^3 - \kappa \nabla^2 \varphi + c (\nabla^2 \varphi)^2. \quad (2.7)
\]

Equations \((2.3) - (2.5)\) are solved numerically, by using a mixed approach. A lattice Boltzmann scheme is used for the continuity and Navier-Stokes equations \((2.3)\) and \((2.4)\), and a finite-difference approach for equation \((2.5)\) and for the temperature diffusion equation. The full study is limited to bi-dimensional systems while the equations for \( \varphi \) not coupled to hydrodynamics will be solved also in \( d = 3 \).

In the case of a simple fluid (Benzi et al. 1992, Chen & Doolen 1998, Succi 2001) the lattice Boltzmann method (LBM) is defined in terms of a set of distribution functions, \( f_i(\mathbf{r}, t) \), located in each lattice site \( \mathbf{r} \) at each time \( t \), and of a set of nine velocity vectors \( \mathbf{e}_i \), defined on a square lattice, having moduli \( |\mathbf{e}_i| = 0, c, \sqrt{2}c \) with \( c = \Delta x/\Delta t \) being \( \Delta x \) and \( \Delta t \) the lattice and the time step, respectively. The distribution functions evolve according to a single relaxation time Boltzmann equation (Bhatnagar et al. 1954)
\[
f_i(\mathbf{r} + \mathbf{e}_i \Delta t, t + \Delta t) - f_i(\mathbf{r}, t) = -\frac{\Delta t}{\tau} [f_i(\mathbf{r}, t) - f_{eq}^i(\mathbf{r}, t)] + \Delta t F_i(\mathbf{r}, t), \quad (2.8)
\]

where \( \tau \) is the relaxation time, \( f_{eq}^i \) are the equilibrium distribution functions and \( F_i \) are the forcing terms to be properly fixed.

The physical quantities, that is the total density \( n \) and the fluid momentum \( n \mathbf{u} \), are determined by the relations
\[
n = \sum_i f_i, \quad n \mathbf{u} = \sum_i f_i \mathbf{e}_i + \frac{1}{2} \mathbf{F} \Delta t, \quad (2.9)
\]

with \( \mathbf{F} \) the force density acting on the fluid. The equilibrium distribution functions \( f_{eq}^i \) are given by the standard second order expansion in the fluid velocity \( \mathbf{u} \) of the Maxwell-Boltzmann distribution function (Qian et al. 1992).
The forcing term in equation (2.8) is expressed as a second order expansion in the lattice vector velocities (Guo et al. 2002)

\[ F_i = \left(1 - \frac{\Delta t}{2} \right) \omega_i \left[ \frac{e_i - u}{c_s^2} + \frac{e_i \cdot u}{c_s^2} e_i \right] \cdot F, \tag{2.10} \]

where \( c_s = c / \sqrt{3} \) is the speed of sound and \( \omega_i = 4/9, 1/9, 1/36 \) in correspondence of the lattice directions with \( |e_i| = 0, c, \sqrt{2} c \), respectively. The force \( F \) has to have the following expression

\[ F_\beta = \partial_\alpha (n c_s^2 \delta_{\alpha\beta} - P_{\alpha\beta}) \tag{2.11} \]

in order to recover equation (2.4) where it results \( \zeta = \eta = n c_s^2 \Delta t \left( \frac{\tau}{\Delta t} - \frac{1}{2} \right) \). \tag{2.12} \]

The first term on the r.h.s. of equation (2.11) allows to cancel out the athermal ideal gas pressure \( n c_s^2 \) of the LBM. We verified that the Mach number \( Ma = |u|_{\text{max}} / c_s \), where \( |u|_{\text{max}} \) is the maximum value of the fluid velocity during evolution, stays always smaller than 0.1 so that the fluid results practically incompressible with \( n \approx 1 \).

The convection-diffusion (2.5) and the temperature equations are solved by using a finite-difference scheme, which is described with details in the paper by Tiribocchi et al. (2009). The function \( \varphi(r, t) \) is defined on the same sites of the LBM with the same space and time steps. We update \( \varphi \) using an explicit Euler scheme (Strikwerda 1989). The spatial differential operators are calculated by a second-order finite-difference scheme.

Periodic boundary conditions are used along the \( x \)-direction (and \( y \)-direction in \( d = 3 \)) and flat walls are placed at the lower and upper rows of the lattice along the \( y \)-direction (\( z \)-direction in \( d = 3 \)), where the temperature is kept at fixed value \( T_w \). Moreover, neutral wetting condition for the order parameter \( \varphi \) is implemented at walls imposing that \( a \cdot \nabla \varphi \mid_{\text{wall}} = 0 \), being \( a \) an inward normal unit vector to the boundaries. To guarantee exact conservation of the order parameter \( \varphi \) we also require that \( a \nabla (\nabla^2 \varphi) \mid_{\text{wall}} = a \nabla [\nabla^2 \varphi] \mid_{\text{wall}} = 0 \). The bounce-back rule (Lavallee et al. 1991, Desplat et al. 2001) for the LBM is adopted at walls supplemented by the prescription for density exact conservation introduced by Lamura & Gonnella (2001).

### 3. Results and discussion

In this section we will present the results of our simulations of equations (2.3)-(2.5). We used the set of parameters \( b = 0.1, \kappa = -c = -0.03, T_c = 0.005 \), and \( \Gamma = 0.1 \) corresponding to the lamellar phase in the phase diagram. Lattices had sizes \( 256 \times 256 \) in \( d = 2 \) and \( 32 \times 32 \times 256 \) in \( d = 3 \). The system, initially, is in disordered symmetric states with \( \varphi \) fluctuating around zero in the interval \([-0.01, 0.01]\). The initial temperature is above \( T_c \) with the walls at \( T_w = 0.9 T_c \).

We first show in figure 1 typical configurations of systems with very high viscosity. In this case we neglected the coupling with the velocity field by solving equation (2.5) without the convective term. Lamellar domains start to form close
Figure 1. Configurations of the concentration field $\varphi$ without hydrodynamics with thermal conductivity $\xi = 10^{-2}, 10^{-1}, +\infty$ (from left to right) at times $t = 55.7 \times 10^3; 11.7 \times 10^3; 1.95 \times 10^3$, respectively.

Figure 2. Configurations of the concentration field $\varphi$ at low viscosity ($\eta = 1.5$) with thermal conductivity $\xi = 10^{-4}, 10^{-3}, +\infty$ (from left to right) at times $t = 144 \times 10^4; 35.6 \times 10^4; 2.1 \times 10^4$, respectively.

to the walls, where the temperature has become lower than the critical value, with interfaces perpendicular to the walls in agreement with the imposed neutral wetting conditions. Then, following the temperature fronts, the regions with phase separated domains will extend towards the middle of the system. The pattern morphology, however, depends on the value of the thermal conductivity or, equivalently, on the speed of the temperature fronts. At very large $\xi$, the system remains frozen in intertwined noodle-like configurations without long range order, like that on the right of figure 1, as observed in other simulations (see, e.g., Gonnella et al. 1997). However, by decreasing the value of $\xi$, in the interval $[0.1, 1]$, in spite of the adopted boundary conditions, the interfaces tend to follow the temperature fronts, parallel to the walls, and exhibit only few defects. The two fronts separating the regions with ordered lamellae from the central disordered region will approach each other joining at the later times of the simulation. By further decreasing $\xi$, interfaces show the tendency to keep the perpendicular orientation with respect to the walls. This phenomenology has to be compared with that observed in simple binary mixtures where at large $\xi$ usual isotropic phase separation occurs (of course, in binary mixtures, there is no frustration and the average size of domains grows by power law, see, e.g., Bray 1994), while by lowering the values of the thermal conductivity one
observes domains first parallel and then perpendicular to the cold walls (Tiribocchi et al. 2010).

Going to a lower viscosity (ρ = 5, η = 1.5, see figure 2), at very large ξ, one finds that hydrodynamics favours the disentanglement of the network pattern (Gonnella et al. 1997) but one still observes extended defects between grains of different oriented lamellae (see e.g. the grain with vertical orientation on the top-left region of the system opposed to the large horizontal underlying domain). One could see in systems larger than those here considered that these extended defects would slow down the ordering process at very late times (Xu et al. 2005). At lower thermal conductivities, in the range $[5 \times 10^{-4}, 5 \times 10^{-3}]$, one again finds that lamellae are well aligned with the thermal fronts. The velocity helps this ordering and, indeed, very ordered defect-free lamellae can be observed (compare the central snapshots of figure 1 and figure 2) in the regions close to the walls. In the central part, even if structures can be observed, the local values of the field $\varphi$ are not in equilibrium, and further evolution will show a completely ordered lamellar state. Finally, by further decreasing the value of ξ, one sees in the left snapshot of figure 2 that hy-
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drodynamics clearly helps the tendency of the system to prefer the perpendicular orientation.

We also studied three-dimensional lamellar systems without coupling to the velocity field. At large values of $\xi$ the system evolves towards metastable configurations ordered only on short scales, similarly to what occurs in two-dimensional systems, as it can be seen in the bottom snapshot of figure 3. At lower values of $\xi$ ($0.1 \leq \xi \leq 10$) one can see stacks of lamellae parallel to the thermal fronts with very few defects (central snapshot of figure 3), while, again similarly to the two-dimensional case of figure 1, perpendicular order is lost far from the walls at very low values of $\xi$.

4. Conclusions

In this work we have studied the ordering of a lamellar phase where the temperature cold fronts diffusively move from external walls. Phase separation therefore starts close to the walls but develops in the middle of the systems with a phenomenology depending on the speed of the thermal fronts. In an intermediate range of values of thermal conductivity $\xi$, lamellae appear ordered and parallel to the thermal fronts while a perpendicular orientation is preferred at very low values of $\xi$. Hydrodynamics favours these preferred ordering and one can conclude that quenching with moving temperature fronts are effective in producing lamellar states with very few defects. A full analysis of the three-dimensional case will complete this study.

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