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Numerical study of the ordering properties of lamellar phase

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Abstract

The quench of a binary mixture into a stable lamellar phase is numerically investigated. We present a novel approach to study the phenomenological equations governing the system dynamics based on the combination of lattice Boltzmann and finite difference equations. We can access large systems on time scales long enough to find evidence of dynamical scaling regime in the ordering process when hydrodynamics is operating.

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1. Introduction

When a binary mixture is quenched from a homogeneous phase to a lamellar equilibrium state, the system coarsens and arranges itself in two coexisting phases characterized by spatially periodic patterns. The existence of alternance of stripes is at odds with the typical scenario of macrophase separation when the components form two macroscopic domains that span the system completely. There are several examples of physical systems that present stable lamellar phases: diblock copolymers [1],

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microemulsions at high surfactant concentration [2], Raleigh–Bènard cells above the convective threshold [3].

It is quite well understood that the growth process proceeds via an initial evaporation–condensation mechanism [4] followed by a long-time regime when hydrodynamics comes into play. This last mechanism is crucial in order to drive the system out of patterns of entangled lamellae. Indeed, topological defects can be removed allowing stripes to line up [5]. While the phenomenology is quite clear, considerable theoretical and numerical work is still in progress to enlight quantitatively the ordering process. Namely, there is not yet available a convincing picture of the existence of a dynamical scaling regime when the system can be characterized in terms of a single length scale $\zeta(t)$ growing as a power law in time, $\zeta(t) \sim t^n$, where n is called the growth exponent. Results do not give a definite answer about the growth exponent since different values of $n, \frac{1}{5}, \frac{1}{4}, \frac{1}{3}$, are found [6].

In this paper, we aim to analyze large systems on long time scales. We consider a coarse-grained model in the context of a time-dependent Ginzburg–Landau convection–diffusion equation coupled to the Navier–Stokes equation. We introduce a novel numerical method to solve the system of equations. It consists of a combination of lattice Boltzmann method (LBM) [7] and finite difference equation [8], which allows to reduce memory requirement and to increase numerical stability. We can study quantitatively for the first time the ordering process finding indication of the existence of a scaling regime with a growth exponent $\frac{3}{5}$.

2. The model

We will adopt a coarse-grained continuum description. The equilibrium phase is described by the following free energy:

$$F = \int \mathrm{d}\mathbf{r} \left[\frac{1}{3} n \ln n + \frac{a}{2} \varphi^2 + \frac{b}{4} \varphi^4 + \frac{\kappa}{2} (\nabla \varphi)^2 + \frac{d}{2} (\nabla^2 \varphi)^2 \right] , \tag{1}$$

where n is the total density of the mixture and φ is a scalar order parameter representing the concentration difference between the two components of the mixture. The term in n gives rise to a positive background pressure and does not affect the phase behavior. The terms in φ correspond to the Brazovskii free energy [9]. We take $b, d > 0$ to ensure stability. For $a > 0$, the fluid is disordered; for $a < 0$, it prefers an ordered state whose nature depends on the value of κ. Indeed, for negative values of κ there is a transition into a lamellar state with characteristic wave vector $q = \sqrt{-\kappa/2d}$.

When the order parameter is conserved and hydrodynamics has to be taken into account, the equation of motion describing the diffusive transport as well as the convection of φ by the fluid is

$$\partial_t \varphi + \boldsymbol{\nabla} \cdot (\varphi \mathbf{v}) = \Gamma \nabla^2 \mu , \tag{2}$$

where $\mu = \delta F / \delta \varphi = a\varphi + b\varphi^3 - \kappa \nabla^2 \varphi + d(\nabla^2)^2 \varphi$ is the chemical potential difference between the two components, Γ is a mobility coefficient and $\mathbf{v}$ is the local fluid velocity with components v_α, α denoting the space coordinate. It obeys the Navier–Stokes

equation which, in the incompressibility limit $\nabla \cdot \mathbf{v} = 0$, reads as

$$\partial_t v_\alpha + \mathbf{v} \cdot \nabla v_\alpha = -\frac{1}{n}\,\partial_\beta P^{\mathrm{th}}_{\alpha\beta} + \nu \nabla^2 v_\alpha\,, \tag{3}$$

where ν is the kinematic viscosity and $P^{\mathrm{th}}_{\alpha\beta}$ is the thermodynamic pressure tensor. This is given by

$$\begin{aligned} P^{\mathrm{th}}_{\alpha\beta} &= n\delta F/\delta n + \varphi \delta F/\delta \varphi - f(n,\varphi) + D_{\alpha\beta} \\ &= \frac{1}{3}\, n\delta_{\alpha\beta} + \left[\frac{a}{2}\,\varphi^2 + \frac{3}{4}\, b\varphi^4 - \kappa\varphi(\nabla^2\varphi) - \frac{\kappa}{2}(\nabla\varphi)^2 \right. \\ &\qquad \left. + d\varphi(\nabla^2)^2\varphi + \frac{d}{2}(\nabla^2\varphi)^2 + d\partial_\gamma\varphi\partial_\gamma(\nabla^2\varphi)\right]\delta_{\alpha\beta} \\ &\quad + \kappa\partial_\alpha\varphi\partial_\beta\varphi - d\partial_\alpha\varphi\partial_\beta(\nabla^2\varphi) - d\partial_\beta\varphi\partial_\alpha(\nabla^2\varphi)\,, \end{aligned}$$

where $f(n,\varphi)$ is the free-energy density and the symmetric tensor $D_{\alpha\beta}$ (see Ref. [10] for its expression) has to be added to ensure that the condition of mechanical equilibrium $\partial_\alpha P^{\mathrm{th}}_{\alpha\beta} = 0$ is satisfied [11].

Eqs. (2) and (3) are numerically solved using a mixed approach. We use a finite difference scheme for Eq. (2) and the lattice Boltzmann method for Eq. (3). This allows to control better the numerical stability with respect to the case of simulating both the equations with LBM, to avoid the spurious terms in the convection–diffusion equation (2) which comes into play when standard LBM for binary mixtures is used [12], and to reduce the amount of required memory can be dramatically decreased.

The lattice Boltzmann scheme is based on the 9-velocity model on a square lattice. A set of distribution functions $f_i(\mathbf{r},t)$, $i = 0,1,2,\ldots,8$, is defined on each lattice site $\mathbf{r}$ at each time t. Each function is associated to a lattice speed vector $\mathbf{e}_i$ with $\mathbf{e}_i/c = (\pm1,0),(0,\pm1),(\pm1,\pm1),(0,0)$, where $c = \Delta x/\Delta t$, Δt is the time step, and Δx is the lattice constant. They evolve according to a single relaxation-time Boltzmann equation [13]:

$$f_i(\mathbf{r} + \mathbf{e}_i\Delta t, t + \Delta t) - f_i(\mathbf{r},t) = -\frac{1}{\tau}\,[f_i(\mathbf{r},t) - f_i^{eq}(\mathbf{r},t)]\,, \tag{4}$$

where τ is a relaxation parameter and $f_i^{eq}(\mathbf{r},t)$ are local equilibrium distribution functions. The distribution functions are related to the total density n and to the fluid momentum $n\mathbf{v}$ through $n = \sum_i f_i$, $n\mathbf{v} = \sum_i f_i\mathbf{e}_i$. These quantities are locally conserved in any collision process and, therefore, we require that the local equilibrium distribution functions fulfill the equations $\sum_i f_i^{eq} = n$ and $\sum_i f_i^{eq}\mathbf{e}_i = n\mathbf{v}$. Following Refs. [12,14], the higher moments of the local equilibrium distribution functions are defined so that the Navier–Stokes equation can be obtained and the equilibrium thermodynamic properties of the system can be controlled: $\sum_i f_i^{eq} e_{i\alpha}e_{i\beta} = c^2 P^{\mathrm{th}}_{\alpha\beta} + nv_\alpha v_\beta$. The local equilibrium distribution functions can be expressed as an expansion at the second order in the velocity $\mathbf{v}$ [12,14]. The expansion coefficients depend on the pressure tensor [12]. In order to reduce compressibility effects and force the total density n to stay constant we used the numerical scheme proposed in Ref. [15], which consists

in neglecting terms of the order $o(M^3)$ or higher in the equilibrium distribution functions, M being the Mach number. It has been shown in Ref. [16], using a multi-scale expansion, that the above described lattice Boltzmann scheme simulates at second order in Δt the incompressible Navier–Stokes equation (3) with the kinematic viscosity v given by $v = \Delta t \frac{c^2}{3}(\tau - \frac{1}{2})$. It appears that the relaxation parameter τ can be used to independently tune viscosity. Compressibility errors can be further minimized by reducing the time step and the magnitude of coefficients a, b, κ, d [17].

Eq. (2) is numerically integrated by discretizing the spatial differential operators with a finite difference scheme with lattice spacing Δx, the same as for LBM, and by using an explicit scheme to perform time integration with time step $\Delta t' = \Delta t/2$ since we noticed that the global stability for the coupled Eqs. (2) and (3) could be improved by this choice.

3. Numerical results and discussion

The numerical results presented here were obtained on a lattice with 1024×1024 sites. The following parameters were used: $a = -b = -2 \times 10^{-4}, \kappa = -6 \times 10^{-4}, d = 7.6 \times 10^{-4}, \Gamma = 25, \tau = 0.505, \Delta x = 1$, and $\Delta t = 0.2$. The choice $|a| = b$ is such that the minimum of the polynomial terms in the free energy (1) is in $\varphi = \pm 1$. For the selected parameters, the equilibrium state is lamellar. The width of a lamella is $\lambda/2 = \pi/q = 5$ in units of lattice spacings. The kinematic viscosity is $v = 8.33 \times 10^{-3}$ and corresponds to a value for which hydrodynamic transport is relevant as pointed out in previous study of macrophase separation of binary mixtures [18]. The system was initialized in a disordered state with $\varphi = \varepsilon$ where ε is a random number uniformly distributed in the range $[-0.1, 0.1]$ and $f_i = 1/9,\ i = 0, 1, \ldots, 8$, such that $n = 1$. After the sudden initial quench, the free energy drives the system into its equilibrium configuration. At the beginning the system forms by diffusion portions of lamellae of width approximately equal to the equilibrium value $\lambda/2$. Interfaces separating lamellae are about 3 lattice spacing wide. These lamellae would not be able to shrink along their length if the hydrodynamics were negligible. The reason for having used a low value of viscosity is related to the motivation of studying explicitly the influence of hydrodynamic modes in disentangling lamellae. This can be seen in Fig. 1 where configurations of the system are shown at consecutive times. In the frame at $t = 3400$, domains are well formed and a plenty of topological defects can be clearly seen. A high viscosity system would become frozen at this point giving a final state of tangled lamellae. However, at $t = 4300$ a time scale has been reached where hydrodynamics becomes relevant and the flow alleviates progressively the topological disorder in the system at following times. We show by a black circle in Fig. 1 the evolution of two dislocations. At $t = 3400$, they are clearly visible. Then they get closer and at $t = 5800$ they break to form two disclinations which finally merge at $t = 6300$ so that the initial defects are completely removed.

Since the flow is responsible for the ordering process and the annihilation of defects, we decided to investigate the structure of the fluid velocity. We computed the spherically averaged velocity structure factor $S(k) = \langle |\mathbf{v}(\mathbf{k})|^2 \rangle$ where $\mathbf{v}(\mathbf{k})$ is the Fourier transform of the velocity field and $\langle \cdots \rangle$ denotes the spherical average over $\mathbf{k}$ for fixed

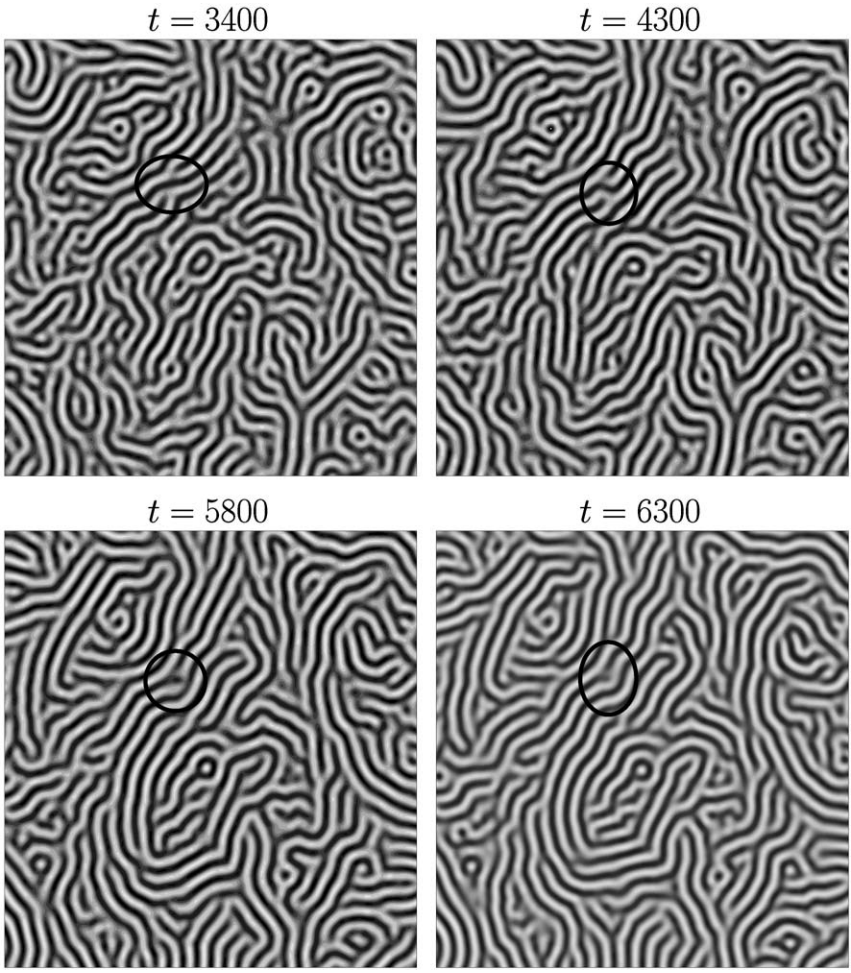

Fig. 1. Configurations of the order parameter φ on a portion 256×256 of the whole lattice at different times. The black circle is a guide to the eye to follow the evolution in time of two dislocations.

$k = |\mathbf{k}|$. The corresponding plot of $S(k)$ as a function of the wave number k is shown in Fig. 2 at different times. We can devise some features. At low wave-numbers S takes the maximum ($\sim 10^{-3}$) and increases at increasing times. This suggests that the elimination of topological defects helps the formation of a velocity structure at scales around 200 ($k \sim 0.03$) lattice spacings comparable with lamellae length. A common trend is that at any time all velocity components decay becoming small at high k and contributing little to the overall dynamics. Two peaks can be clearly seen at two wave-lengths around 4.5 ($k \sim 1.5$) and 2.3 ($k \sim 2.5$) lattice spacings. This would indicate the presence of capillary waves forming around defects and on interfaces giving structure

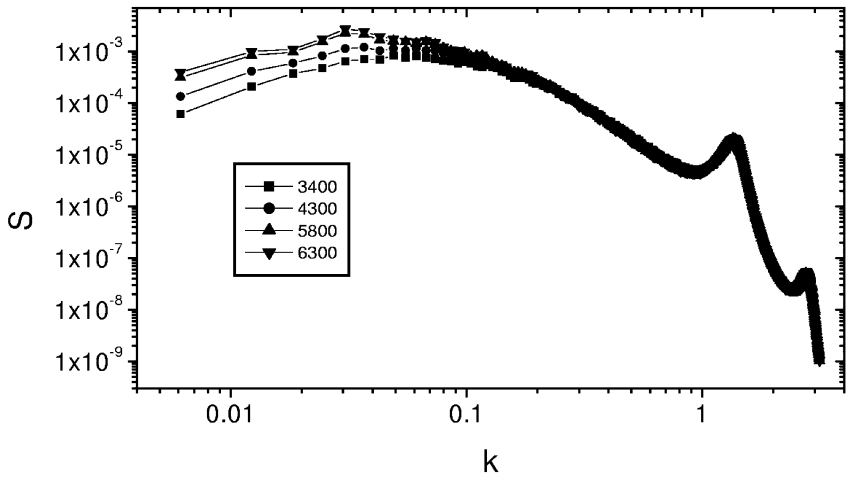

Fig. 2. The velocity structure factor S as a function of the wave number k at different times.

the velocity field on scales of the order of the lamella and interface widths [17]. This last feature is strictly connected to the fact of having a very low viscosity.

A quantitative way to measure the ordering in the system is to evaluate a correlation function of the local orientation field, $\theta(\mathbf{r})$, of the lamellar patterns. We computed the correlation function $C(R,t) = \langle \exp\{2i[\theta(\mathbf{r}+\mathbf{R},t) - \theta(\mathbf{r},t)]\}\rangle$ averaging over the spatial coordinates $\mathbf{r}$ and spherically over $\mathbf{R}$ for fixed $R = |\mathbf{R}|$. The local orientation is extracted from simulation data by considering the director field $\mathbf{n}(\mathbf{r}) = \nabla\varphi(\mathbf{r})/|\nabla\varphi(\mathbf{r})|$ and defining $\theta(\mathbf{r}) = \arctan(n_y(\mathbf{r})/n_x(\mathbf{r}))$. The factor 2 is required by a twofold symmetry of lamellar patterns. The correlation decays with increasing separation r, and from this decay we can extract the orientational correlation length $\zeta(t)$ as the value of r at which $C(R,t)$ reaches a fixed constant value h. The growth exponent n is extracted from the log–log plot of ζ versus time. As shown in Fig. 3, ζ is consistent with the power law $\zeta \sim t^n$ and n assumes the same value independent of h. We found $n = \frac{3}{5}$. This confirms the qualitative observation in Fig. 1 that the order of lamellae increases in time. At long times, a slowing down in the growth of $\zeta(t)$ can be observed. A possible explanation would be the influence of finite size effects. Future work will investigate further this aspect.

4. Conclusions

We have introduced a new method to study complex fluids with lamellar order. Lattice Boltzmann equation is coupled with finite difference scheme to simulate Navier–Stokes and convection–diffusion equations. We confirm previous results on the relevance of hydrodynamics for obtaining lamellar order on large scales in models with

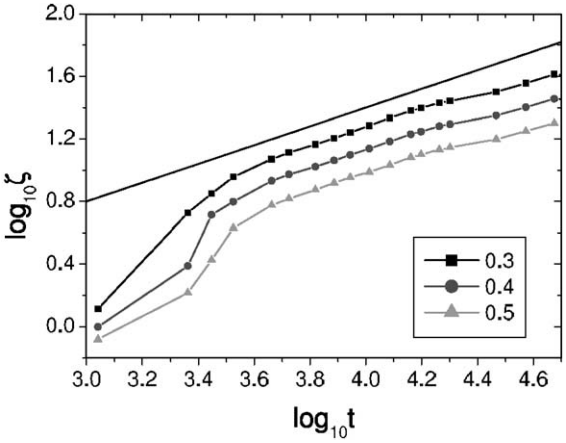

Fig. 3. Time evolution of the length scale ζ for which $C(\zeta, t) = h$, where $h = 0.3, 0.4, 0.5$. The full line has slope $\frac{3}{5}$.

short-range interactions and conserved order parameter. For the first time a power-law behavior with exponent $n = \frac{3}{5}$ is found for the orientational correlation length.

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