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Kinetics of phase ordering of nematic liquid crystals in a confined geometry

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Employing a time-dependent Ginzburg-Landau model, we investigate the phase ordering kinetics of nematic liquid crystals confined in a narrow pore. We consider various orientations of the surface field and compute domain growth laws and scaling functions. In the absence of any anchoring field we find that (and in contrast to a confined binary liquid mixture) mere confinement of the liquid crystals is insufficient to produce slow growth of the nematic domains owing to the vector nature of the order parameter. In the presence of a strong homogeneous anchoring, the system quickly reaches a nematic state. On the other hand, for homeotropic anchoring, the liquid crystal takes on an XY character and the growth law exponent crosses over from $\frac{1}{2}$ to $\frac{1}{4}$ as the field strength is increased. [S1063-651X(96)10105-7]

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I. INTRODUCTION

Nematic liquid crystals, like 5CB (where CB denotes cyano biphenyl), are strongly distorted by anchoring conditions at a confining surface [1–3]. These equilibrium configurations reflect the competition between surface anchoring and bulk elasticity [4]. Such equilibrium studies in simple geometries have provided a complete picture of the nature of defects induced by the anchoring. The complexity of the situation increases considerably when the confining medium has a disordered geometric structure. More recent work [5–10] has been directed to address the effect of randomly constraining media (such as porous glasses like Vycor, or silica gels) on both statics and dynamics of the nematic-isotropic phase transition. Results from various experiments indicate that the random preferential orientation of the liquid crystals along the pore surface (whose normal changes direction randomly over a persistence length) profoundly influences the dynamics of the isotropic to nematic phase transition and fluctuations of the orientational order parameter relax at a much slower rate than in bulk liquid crystals. These experimental findings have stimulated intense theoretical work [11,12], leading to the proposal that this glassy relaxation of nematic liquid crystals could be understood by studying the kinetics of a spin model in the presence of a quenched random field.

In contrast to the studies carried out with silica gels as the confining medium [5], experimental results of ordering of nematic liquid crystals in Vycor glass show that the random-field model (with Gaussian randomness) is clearly inapplicable [6]. These studies reveal that the nematic ordering in different cavities of the Vycor glass is only weakly correlated. One could therefore model a porous system as a network of independent pores joined by weak links (junctions) [6]. Indeed, such a ''single-pore'' model for the nematic liquid crystals seems to explain the static measurements reasonably well. Similar models have been proposed by Liu *et al.* [13] to explain the metastability and the slow kinetics of domain growth seen in experiments on binary liquid mixtures confined in a low-porosity medium. In fact, *single-pore models* without any randomness have been used as model systems [13–16] to understand various effects observed in experiments of binary liquid mixtures in Vycor glasses [17,18]. Such simulations [14–16] have shown that the kinetics of domain growth slows down radically when the average domain size and the pore radius become comparable. However, there has been no such study of the kinetics of phase ordering of nematic liquid crystals confined within a single pore.

As a first step towards understanding the kinetics of ne matic ordering in a porous medium following a quench from the isotropic phase, we consider the ordering process in a simple confining geometry (parallelopiped pore), subject to a variety of anchoring conditions at the boundaries of the pore.

Our work draws inspiration from similar studies, carried out in the context of phase separation of binary fluids in porous media, which reveal that the slow dynamics seen in low-porosity media (such as Vycor glass) originates from the *geometrical confinement* of the binary fluid mixture inside the pores. Carrying out a detailed numerical study of the appropriate time-dependent Ginzburg-Landau model, we show that the ordering process of nematic liquid crystals is dramatically different from binary liquid mixtures confined in a pore.

II. MODEL AND NUMERICAL PROCEDURE

Nematic liquid crystals can be described by a vector director field $\vec{\phi}(r,t)$ with the constraint that local inversions, $\vec{\phi}(r,t)\rightarrow-\vec{\phi}(r,t)$, do not change the configuration. We model the nematics by a rigid rotor Hamiltonian [19–21]

$$H=-J\sum_{(i,j)}(\hat{\vec{\phi}}_i\cdot\hat{\vec{\phi}}_j)^2, \tag{1}$$

where $\hat{\vec{\phi}}_i$ is the unit director field on a three-dimensional cubic lattice. As required, this Hamiltonian is invariant under local spin inversion $\hat{\vec{\phi}}_i\rightarrow-\hat{\vec{\phi}}_i$, and further, under separate discrete spatial rotations and internal O(3) rotations. The model shares the global symmetries of the standard Franck elastic Hamiltonian [1] when the moduli for splay, bend, and twist are equal (equal constants approximation). One thus expects that the qualitative features of the dynamics of the two models are similar [20]. The equations of motion for the director field are given by the nonconserved, time-dependent Ginzburg-Landau equation [22]. For numerical expediency, we replace the ''hard constraint'' of unit magnitude with a ''soft constraint,'' by including the a $\Sigma_i\{-1/2\vec{\phi}_i\cdot\vec{\phi}_i+1/4(\vec{\phi}_i\cdot\vec{\phi}_i)^2\}$ in the Hamiltonian. With this term, the equations of motion for a zero-temperature quench read (we set $J=1$) [20]

$$\frac{\partial\vec{\phi}_i}{\partial t}=-\frac{\delta H}{\delta\vec{\phi}_i}=\vec{\phi}_i-|\vec{\phi}_i|^2\vec{\phi}_i+\sum_{j\in\text{nn of }i}(\hat{\vec{\phi}}_i\cdot\hat{\vec{\phi}}_j)\vec{\phi}_j. \tag{2}$$

The initial conditions on the director are such that the components of $\vec{\phi}_i(t=0)$ are independent random variables between -0.1 and 0.1. Physical quantities are averaged over 50 realizations of $\vec{\phi}_i(t=0)$. We solve the discretized form of Eq. (2), with a time step $\delta t=0.01$, up to a time $t_{\max}=500$.

III. RESULTS

It is well known that at late times, vector spin models in d dimensions having O(n) symmetry [23] enter a scaling regime, where the correlation function $g(r,t)\equiv\langle\vec{\phi}(\vec{r},t)\cdot\vec{\phi}(0,t)\rangle$ obeys the scaling relation $g(r,t)=g(r/R(t))$. This implies the existence of a single dominant length scale $R(t)$, related to the ''domain size,'' which grows as $R(t)\sim t^{1/z}$ (z is the dynamical exponent). It has been shown [23] that the asymptotic structure factor [Fourier transform of $g(r,t)$] $S(k,t)\sim\rho_{\text{def}}k^{-(d+n)}$ at large k, where ρ_{def} is the defect density. This generalized Porod's law [24] is related to the type of stable localized defect allowed by the theory [23]. Unlike the Heisenberg spin, which is an O(3) vector, the director field ϕ of nematic liquid crystals belongs to the projective plane $P^2\equiv\text{O}(3)/Z_2$, which is not homotopically equivalent to O(3). This gives rise to $\pm\frac{1}{2}$ line [O(2)] defects, in addition to the usual point [O(3)] defects [2,3].

In our simulations, we first started with a study of *bulk* dynamics (on a 80^3 system) following a quench from the high-temperature isotropic phase to the $T=0$ nematically ordered phase. In the absence of any symmetry breaking field, the continuous infinity of ground states will compete with each other to establish equilibrium. These degenerate ground states are separated by the stable topological point and line defects. Away from these defects, the order parameter saturates to its bulk value in the scaling regime. Subsequent evolution occurs with the monotonic decay of these defects. Since the bulk dynamics of this system has already been studied by Blundell and Bray [20] by a cell-dynamics simulation method [25], we will just briefly mention our results for the simulation of a Langevin model for the bulk kinetics.

The natural order parameter describing the nematic configuration is the traceless second-rank tensor, $\psi_{\alpha\beta}(\vec{r},t)=\langle\phi_\alpha(\vec{r},t)\phi_\beta(\vec{r},t)-(\vec{\phi}(\vec{r},t)\cdot\vec{\phi}(\vec{r},t))\rangle$ (where α and β run from 1 to 3). This is invariant under local inversion of $\phi(\vec{r},t)$. We compute the equal-time pair correlation function defined as

$$g(r;t)\equiv\tfrac{1}{2}\langle 3(\hat{\vec{\phi}}(0;t)\cdot\hat{\vec{\phi}}(r;t))^2-1\rangle. \tag{3}$$

Note that in our definition of the correlation function, the spins are hardened to give $g(0;t)=1$. This makes the size of the defect core ξ_{core} microscopic, which gives better scaling even at early times [20]. The domain size $R_g(t)$ is extracted from the correlation function in the following way:

$$g(r=R_g;t)=g(0;t)/2.$$

At late times, the domain size grows as $R_g(t)\sim t^{1/z}$ with $1/z=0.45\pm0.02$. The correlation function at these late times shows good scaling $g(r,t)=g(r/R_g(t))$. The structure factor $S(k,t)$ decays as k^{-5} for large k. This is consistent with scattering from $\pm\frac{1}{2}$ line defects (corresponding to $n=2$, $d=3$ in the expression for the generalized Porod's law [23]). We take this as concrete evidence that the late-time dynamics is controlled by these $\pm\frac{1}{2}$ line defects. Our results are in general agreement with those of Blundell and Bray [20]; however, we note that these authors have obtained an exponent of -5.3 from their structure factor data. It seems, then, that one needs to run to a much longer time than probed by Blundell and Bray to obtain the asymptotic scaling exponent of -5.

Next we introduce the liquid crystal in its isotropic phase into a parallelopiped pore with dimensions $L_x\gg L_y=L_z$, where $\hat{\mathbf{x}}$ is along the pore axis (in our simulations, $L_x=256$ and $L_y=4$ or 8). We study the evolution of the nematic phase following a quench to $T=0$. We consider periodic boundary conditions at $x=\pm L_z/2$ and open boundary conditions at $y=\pm L_z/2$, and $z=\pm L_z/2$. Surface anchoring fields are incorporated by adding a term $-\Sigma_{i\in\mathscr{S}}(\vec{h}_i\cdot\vec{\phi}_i)^2$ term in the Hamiltonian (where the sum is restricted to sites on the surface $i\in\mathscr{S}$). We distinguish between two kinds of anchoring: (1) homogeneous anchoring, where the surface field $\vec{h}=(h,0,0)$ points along the $\hat{\mathbf{x}}$ direction and (2) homeotropic

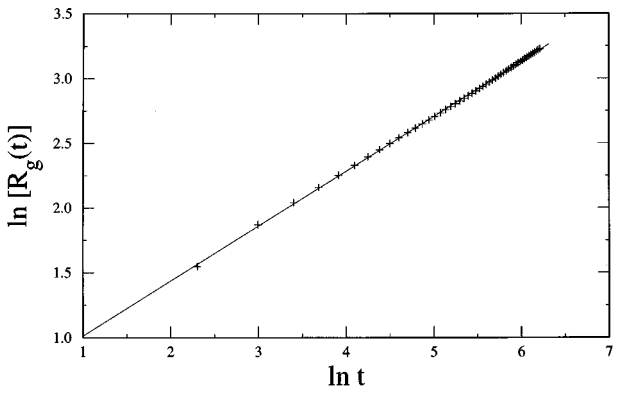

FIG. 1. Log-log plot of domain size $R_g(t)$ vs time for zero anchoring field. The straight line fit yields an exponent of 0.43 $\pm$0.03, which is similar to the bulk value of 0.45$\pm$0.02 (see text).

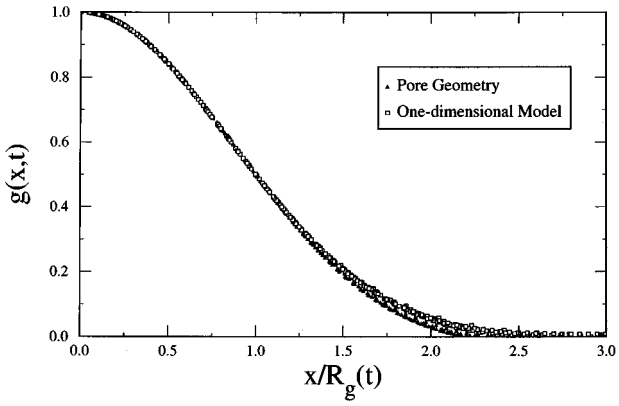

FIG. 3. Comparison of the scaled pair correlation functions for the one-dimensional model (see text) with the corresponding scaling function for the pore geometry.

anchoring, where the surface field points in a direction normal to the local tangent plane at the surface [26]. We compute the pair correlation function, averaged over the $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ directions, as

$$g(\Delta x;t)\equiv\tfrac{1}{2}\langle 3(\hat{\vec{\phi}}(x,y,z;t)\cdot\hat{\vec{\phi}}(x+\Delta x,y,z;t))^2-1\rangle. \quad (4)$$

The domain size in the $\hat{\mathbf{x}}$ direction $R_g(t)$ is computed from the correlation function as described before.

Zero anchoring: The Langevin dynamics following a quench from the isotropic phase to $T=0$ leads to algebraic growth of the domain size $R_g(t)\sim t^{1/z}$ with $1/z=0.43\pm0.03$, which is similar to the bulk value (Fig. 1). The correlation function shows good scaling $g(\Delta x,t)=g(\Delta x/R_g(t))\equiv g(s)$ (Fig. 2). It seems then that the ground state possesses long-ranged orientational order. These features should be contrasted with the dynamics of binary fluids in a pore, where complete phase separation is preempted by the formation of long-lived ''microplugs'' of one of the phases, as soon as the domain size is comparable to the pore size [13–16], which alters the growth from $R\sim t^{1/3}$ to $R\sim\ln t$. Thus mere confinement is insufficient to produce slow growth of the nematic domains.

Why does a nematic liquid crystal behave differently from a binary liquid mixture in a single pore? The answer to this question involves the symmetry of the order parameter, which is a vector quantity for the liquid crystals, in contrast to the binary fluid case where the order parameter is a scalar quantity. As soon as the domain size $R_g(t)$ gets larger than the pore size, the dynamics of the director field is one dimensional. There can exist no stable topological defects, since the dimension of the order parameter n is larger than the spatial dimension d. We check this by performing a simulation of the model described by Eqs. (1) and (2) in one dimension on a system of size $L=1024$. We find that the growth exponent is given by 0.47$\pm$0.03 and the correlation function obeys dynamical scaling. This scaling function in one dimension is plotted in Fig. 3, along with the scaling function for the pore. As can be seen, these two scaling functions compare quite well over a large range of rescaled distances. This indicates that the defects present initially in the confining space of the pore disappear at late times by escap-

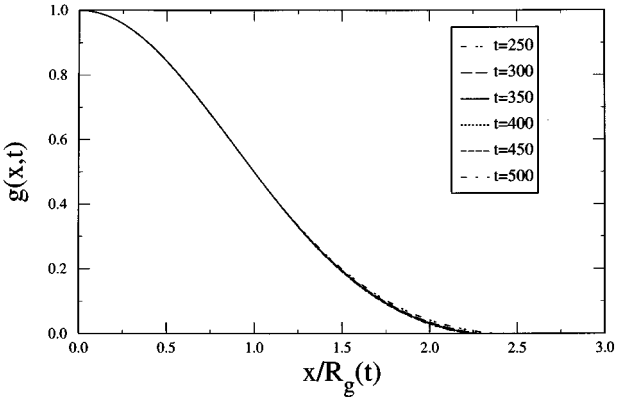

FIG. 2. Scaling function for the pair correlation function along the long direction of the pore ($\hat{\mathbf{x}}$) for the zero anchoring case. Clearly dynamical scaling holds.

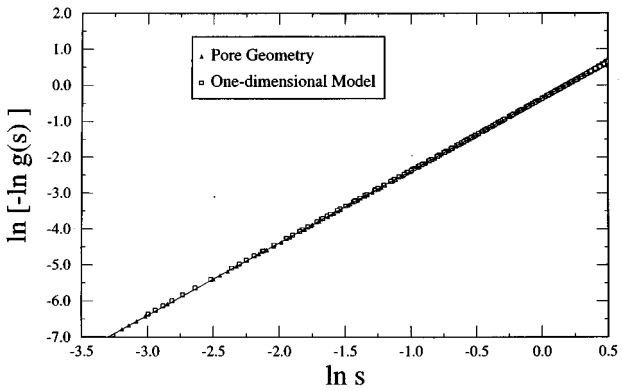

FIG. 4. Plot of $\ln\{-\ln[g(s)]\}$ vs $\ln(s)$ for the scaling function of the one-dimensional model and for the pore geometry with zero anchoring. Here, $s=r/R_g(t)$ and the straight line is the best fit to the data with a slope of 2$\pm$0.05.

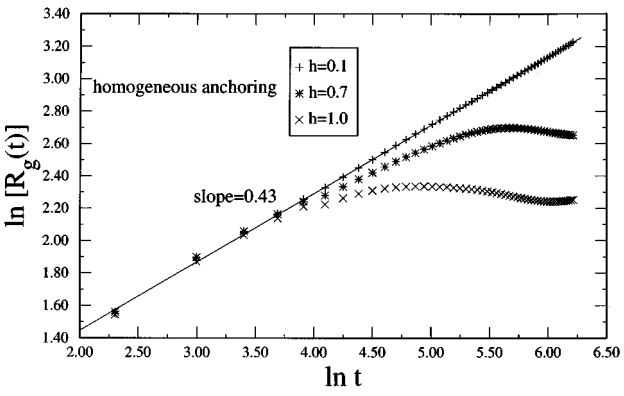

FIG. 5. Log-log plot of domain size $R_g(t)$ (along the long direction of the pore) vs time t for various strengths of the homogeneous anchoring field.

ing to the pore boundary. Theoretical studies in both conserved and nonconserved O(n) models [23,27] suggest that the generalized Porod's law breaks down for cases with $n>d$. Equivalently, the scaled (real-space) correlation function would have a different functional form at small distances than that found in three dimensions. Indeed, our results indicate that this is true. We find that, for small rescaled distance s, the scaled correlation function can be better described by an $\exp(-as^2)$ form (see Fig. 4) instead of the $1-bs^2\ln s+\cdots$ form found in three-dimensional systems [20] [the latter leads to the Porod tail, $S(k)\sim k^{-5}$]. A similar exponential form for the correlation function has been observed for the O(n) model in the absence of topological defects ($n>d$) [23,27].

Homogeneous anchoring: A symmetry breaking surface field in the $\hat{\mathbf{x}}$ direction establishes a unique ground state, where the director points along $\hat{\mathbf{x}}$ at every site. After a quench from the isotropic phase, the growth behavior depends on the strength of the anchoring field. The influence of the surface field can be parametrized by a dimensionless ratio μ of the pore width and the *extrapolation length* $l\equiv J/h^2$. If $\mu\equiv L_y/l\gg 1$ (strong anchoring), the nematic director at the surface points along the easy axis provided by the field. For *weak anchoring*, $\mu\ll 1$, the energetics is ''elasticity dominated,'' but for $\mu>1$, effectively the field dictates the growth that is reflected in the very fast saturation of the correlation function. We compute the ''connected part'' of the correlation function defined as

$$g_{\rm conn}(\Delta x;t)\equiv\frac{g(\Delta x;t)-g(\infty;t)}{1-g(\infty;t)} \tag{5}$$

and extract a length scale $R_g(t)$ from this quantity as before. In Fig. 5 we show a log-log plot of $R_g(t)$ versus t for various strengths of the homogeneous anchoring. For weak anchoring, $R_g(t)$ grows diffusively as in the bulk, $R_g\sim t^{1/2}$. For larger anchoring strengths, after an initial bulk diffusive behavior for a very short period of time, the domain size saturates quickly.

Homeotropic anchoring: As before, we compute the average domain size $R_g(t)$ from the connected part of the correlation function. A log-log plot of $R_g(t)$ versus t is shown in Fig. 6 for $L_y=L_s=4$. We find that the growth law exponent crosses over from a value of $\frac{1}{2}$ to a value of $\frac{1}{4}$ as the strength of the surface field is increased. Snapshots for the liquid crystal conformations help us understand the situation. For the field values considered in our simulation, we find that at late times, all the nematics in a given yz plane prefer to point along a common director. A simple calculation of the energetics in the yz plane reveals that this is due to the domination of the exchange contribution to the energy over the field energy for the field values considered here. After the quench then, the system chooses a particular direction for the director (at every yz plane) and therefore the configuration along the long axis is a twist along the $\hat{\mathbf{x}}$ axis. Our simulation results show that the coarsening occurs through an unwinding of this twisted configuration. An escape to the long axis is not favorable due to the large cost in field energy. Moreover, since the fields act only in the y or z direction, the x component of $\phi(\vec{r})$ is found to much smaller than the y and z components. Thus, in effect, the system behaves like a two-component ($n=2$) nematic in one dimension. Simulations and analytic theories of the dynamics of a nonconserved, XY model in one dimension have shown that the growth law exponent in this case is $\frac{1}{4}$ [23,28]. One expects that two-component ''nematics'' in one dimension would also yield the same growth law exponent. Indeed, our direct simulations of a Lebwohl-Lasher model with two-component nematics in one dimension show that this is true. Thus, in the presence of a homeotropic anchoring, the growth kinetics of liquid crystals in a narrow pore is identical to that of a two-component liquid crystal in one dimension.

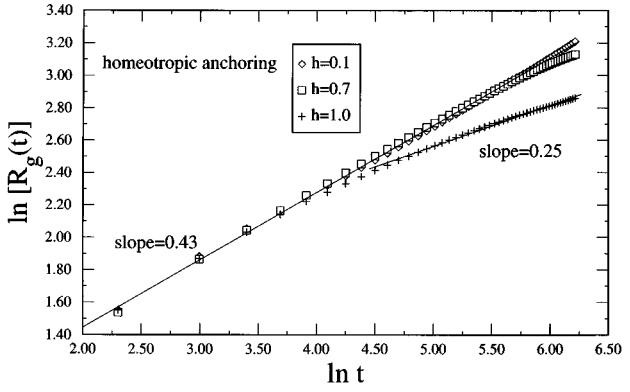

FIG. 6. Log-log plot of domain size $R_g(t)$ (along the long direction of the pore) vs time t for various strengths of the homeotropic anchoring fields. The straight lines are the best fit to the data.

IV. SUMMARY AND CONCLUDING REMARKS

In summary, we have carried out a numerical study of growth kinetics of nematic liquid crystals confined in a narrow pore. We have considered various orientations of surface fields and computed the domain growth law and the scaling functions. In the absence of any anchoring field we find that, in contrast to a binary liquid mixture confined in a narrow pore, mere confinement of the liquid crystals is insufficient to produce slow growth of the nematic domains due to the vector nature of the order parameter. The system in this case behaves as an one-dimensional system and shows dynamical

scaling. In the presence of a strong homogeneous anchoring, the system quickly reaches a nematic state. On the other hand, for homeotropic anchoring, the liquid crystals take a two-component character and the growth law exponent crosses over from $\frac{1}{2}$ to $\frac{1}{4}$ as the field strength is increased.

Although our results are obtained in a simple pore geometry, we believe that they are relevant for growth of nematic domains in a low-porosity medium such as Vycor glass. This is consistent with recent static measurements in Vycor glass, which have been explained in terms of a suitable distribution of single, independent pores that mimic the confining medium. It would be interesting to study the effect of pore junctions, variation in pore radius, and other nontrivial geometrical features, on the growth kinetics of such orientationally ordered systems.

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