Diffusion in a smectic liquid crystal with screw dislocations

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(Received 14 September 2001; published 15 April 2002)

Screw dislocations provide barrier-free pathways that enhance interlayer diffusion in smectic liquid crystals and other layered materials. To explore this contribution to interlayer diffusion we study a ''random parking garage'' model in which a random walker can move between layers only by circling a dislocation core. We find that in such a layered system with a density of ρ screw dislocations per unit area, with randomly chosen position, Burgers vector and phase, the ratio of interlayer to intralayer diffusion coefficients is $D_\parallel/D_\perp = (\rho b^2/4\pi)\ln R/a$. Here b is the layer spacing, R is the layer radius, and a is the dislocation core size. Monte Carlo simulations are in agreement with this result. We discuss implications for both molecular simulation and experimental studies of diffusion in smectics.

DOI: 10.1103/PhysRevE.65.051702 PACS number(s): 61.30.Jf, 05.40.Fb, 61.72.Lk

In crystalline solids, transport properties depend sensitively on microstructure, and similar effects may be expected in soft condensed matter. Here we explore one special case where the role of defects is particularly important: diffusion in a layered system such as a smectic *A* liquid crystal.

Self-diffusion in a smectic is anisotropic, as molecules diffuse freely within each liquidlike layer (with diffusion coefficient $D_\perp$) but must overcome a free energy barrier to jump between adjacent layers (diffusion coefficient $D_\parallel$). Self-diffusion between layers may also occur as a two step process with an intermediate state in which a molecule lies in a transverse orientation sandwiched between adjacent layers [1].

Screw dislocations can significantly enhance interlayer diffusion in a smectic by providing barrier-free diffusion pathways. In an experimental study of permeation in smectics, Chan and Webb [2] suggested that the ratio of in plane to interlayer self-diffusion coefficients in a defect-free lyotropic smectic might be as high as $D_\perp/D_\parallel \approx 10^{12}$, but the presence of defects in the microstructure could reduce the ratio to order unity. Molecular dynamics simulation studies of a Gay-Berne smectic also suggest that in the absence of dislocations, the ratio of the two diffusion coefficients is large [3]. A study of aligned hard spherocylinders in a smectic phase with no dislocations [4] produced a ratio of only $D_\perp/D_\parallel \approx 7$, but the suppression of fluctuations in molecular orientation probably increases the frequency of interlayer jumps. Interlayer jumps also increase in frequency close to the smectic-nematic transition [5].

Screw dislocations running vertically through the layers of a smectic contribute to interlayer diffusion in two distinct ways. First, the core region of a dislocation may be disordered, without well-defined layers, so it could serve as a diffusion ''pipe'' in which vertical diffusion is more like that in the nematic phase. From this effect we expect an enhancement of the interlayer diffusion that is simply proportional to the screw dislocation density. Second, screw dislocations make helical connections between layers, providing barrier-free pathways for interlayer diffusion. If a molecule diffusing laterally happens to circle a screw dislocation core, it moves from one layer to another without encountering an energy barrier. If screw dislocations are distributed at random through a sample, then self-diffusion represents diffusion in a disordered medium (see, e.g., [6]) though in this case the ''medium'' is composed of the same material as the random walker.

How does this ''spiral staircase'' effect contribute to the interlayer diffusion? To answer this question, we consider the problem of a random walk in a ''random parking garage.'' In a multilevel parking garage, levels are often connected by spiral paths reminiscent of screw dislocations. Here we imagine a layered system with screw dislocations perpendicular to the layers inserted at random points throughout the structure. While line defects in a smectic could, in principle, be mobile, we treat their positions here as quenched random variables, assuming that they are pinned by heterogeneities on the bounding surfaces of the liquid crystal cell.

To construct the model, we start with a simple cubic lattice of size $L\times L\times L$, then insert screw dislocations with density ρ per unit area, all lying parallel to the z axis. The ith dislocation has Burgers vector b_i, with length of one lattice spacing, pointing randomly in the $+z$ or $-z$ direction; a random phase ϕ_i between $-\pi$ and π; and core centered at a random position (x_i, y_i). For a system with N dislocations, the vertical displacement of any point in the lattice can be expressed as a sum over dislocations [7]

$$z(x,y) = \sum_{i=1,N} \frac{b_i}{2\pi}\left[\arctan\left(\frac{y-y_i}{x-x_i}\right) + \phi_i\right]. \qquad (1)$$

Here the inverse tangent function calculates the angle between the x axis and a line from a dislocation core to the point (x,y). The arbitrary phase ϕ_i ensures that there is rotational symmetry in the xy plane, e.g., there is nothing special about the x axis. We have not taken into account distortions of the nematic director associated with screw dislocations in smectics, but only the layer displacements [8]. After the layer displacements are calculated, connections between layers are made based on nearest neighbor bonding. The result is a random parking garage structure with parallel screw dislocations in random locations.

A random walker starts at an origin in the center of the lattice and makes random steps in the transverse directions only, moving along the xy layer. If the density of screw

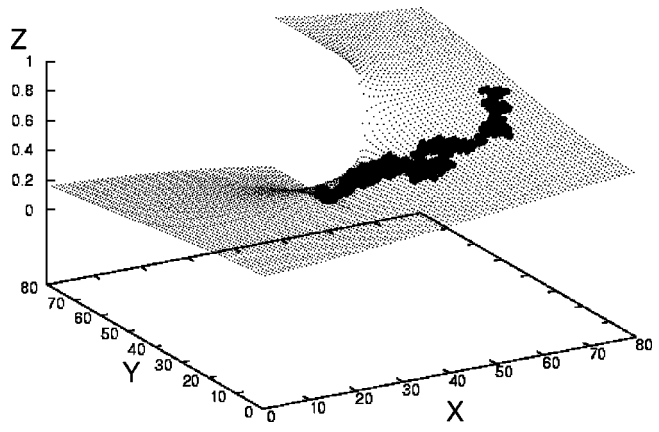

FIG. 1. A screw dislocation provides a barrier-free diffusion pathway for a random walker to get from one layer to another in a layered structure.

dislocations is $\rho=0$, then there is no vertical diffusion at all. However if screw dislocations are present, adjacent layers are bridged by spiral staircases and the random walker can move vertically through the lattice even though it only makes lateral ''in-layer'' steps. A random walker diffusing in this way near a dislocation core is shown in Fig. 1.

Monte Carlo simulations of this system have been carried out for random walks of length 200 steps on systems with dislocation density ranging from $\rho=0.001$–0.005 per unit area. For each value of ρ, 2000 random dislocation configurations were generated, and 10 000 random walks performed on each. In Fig. 2(a) is shown the mean square z displacement vs time for different values of the dislocation density ρ. We find that the effective interlayer diffusion coefficient, the slope of each line, is directly proportional to ρ, as shown in Fig. 2(b). This series of simulations was carried out on a system with lateral dimension $L=500$. We note that it is not practical to implement periodic boundary conditions for a lattice containing a random array of screw dislocations due to incompatible displacements on opposite faces.

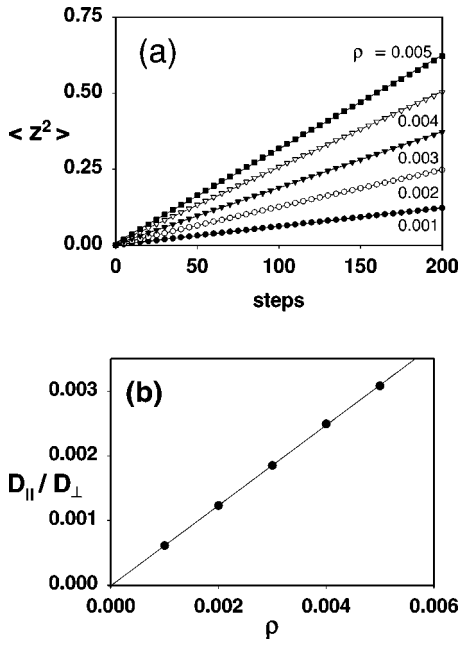

FIG. 2. Monte Carlo simulation results: (a) mean square displacement $\langle z^2\rangle$ vs time measured in steps, for dislocation densities $\rho=0.001$–0.005 per unit area, in a system of size 500^3; (b) ratio of diffusion coefficients $D_\parallel/D_\perp$ as a function of dislocation density ρ.

Curiously, the diffusion coefficient also depends weakly on system size: random walks of length 200 steps produce somewhat different values of the diffusion coefficient if they are carried out on lattices of size $L=500$ or $L=800$. This result seems counterintuitive: why does the size of the lattice matter, as long as it is big enough that random walks do not hit the edge? How could dislocations that are far beyond the range of the random walker change its interlayer diffusion rate?

The answer is that every dislocation contributes to the displacements of each point in the lattice. A larger system size with fixed dislocation density means more dislocations; this in turn increases the overall roughness of the layers. We demonstrate this result via an analytic calculation. At the origin $x=0,y=0$ a random walker's initial z position is

$$z_0=z(x=0,y=0)=\sum_{i=1}^{N}\frac{b_i}{2\pi}\left[\arctan\left(\frac{y_i}{x_i}\right)+\phi_i\right]. \tag{2}$$

The random walker makes a step of length Δx (the lattice constant) each time step Δt. Imagine that its first step is in the $-x$ direction; then its vertical displacement is, again summing over N dislocations:

$$z-z_0=\sum_{i=1}^{N}\frac{b_i}{2\pi}\left[\arctan\left(\frac{y_i}{x_i+\Delta x}\right)-\arctan\left(\frac{y_i}{x_i}\right)\right]. \tag{3}$$

Here the random phases ϕ_i have canceled. Using the approximation $f(x+\Delta x)-f(x)=(df/dx)\Delta x$, we find

$$z-z_0=\sum_{i=1}^{N}\frac{b_i\Delta x}{2\pi}\left[\frac{\partial}{\partial x}\arctan\left(\frac{y_i}{x_i}\right)\right]=\sum_{i=1}^{N}\frac{b_i\Delta x}{2\pi}\left(\frac{-y_i}{x_i^2+y_i^2}\right). \tag{4}$$

To calculate the mean square z displacement $\langle(z-z_0)^2\rangle$, we square this expression and sum over $b_i=\pm b$. (That is, we are averaging over an ensemble of possible dislocation configurations.) Only terms containing b_i^2 are nonzero,

$$(z-z_0)^2=\sum_{i=1}^{N}\left(\frac{b_i\Delta x}{2\pi}\right)^2\left(\frac{y_i^2}{(x_i^2+y_i^2)^2}\right). \tag{5}$$

To complete the ensemble average over dislocation configurations, we convert from a sum over individual dislocations to an integral over the plane in polar coordinates, with a density ρ dislocations per unit area

$$\langle(z-z_0)^2\rangle=\rho\left(\frac{b\Delta x}{2\pi}\right)^2\int\int\frac{r^2\sin^2(\theta)}{r^4}rdrd\theta. \tag{6}$$

Carrying out the integral, we find a logarithmic divergence that requires the use of a system size cutoff R and a microscopic (e.g., core size) cutoff a. R is a layer radius,

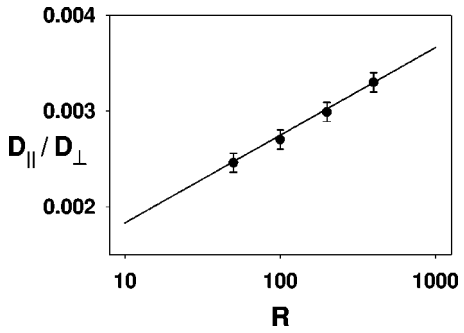

FIG. 3. Ratio of diffusion coefficients $D_\parallel/D_\perp$ as a function of system radius R from Monte Carlo simulations with dislocation density $\rho=0.005$ per unit area. Simulation data are in close agreement with Eq. (8) with one adjustable parameter, the dislocation core size $a=0.1$.

approximately half the system size L if the layers are square. After one step the mean square z displacement is

$$\langle (z-z_0)^2\rangle = \frac{\rho b^2 (\Delta x)^2}{4\pi} \ln\frac{R}{a}. \tag{7}$$

Carrying out this same calculation for a random walk whose first step is in any of the other three directions produces the same result. After one time step, we should have $\langle (z-z_0)^2\rangle = D_\parallel \Delta t$, and with $D_\perp = (\Delta x)^2/\Delta t$, we conclude that the ratio of diffusion constants in the random parking garage model is

$$D_\parallel/D_\perp = \frac{\rho b^2}{4\pi} \ln\frac{R}{a}. \tag{8}$$

Thus the effective interlayer diffusion rate is proportional to the screw dislocation density per unit area, and diverges weakly with system size R. We carried out Monte Carlo simulations of the model with size $L=2R$ ranging from 100 to 800, and find results in agreement with Eq. (8) using a core size $a=0.1$. Comparison of simulation and theory is shown in Fig. 3 and shows close agreement.

In interpreting this result, we must reconsider the validity of our assumption that the spatial distribution of screw dislocations in a smectic is random and not in some way correlated. While elastic interactions of screw dislocations in crystals are normally long ranged, in smectic liquid crystals they are short ranged, dropping off exponentially. For this reason we can safely assume that random surface pinning dominates over elastic forces at least in the low density limit, where the typical distance between neighboring dislocations greatly exceeds the cutoff length for elastic interactions. It is precisely because of this type of pinning that it is difficult to anneal dislocations out of a smectic cell.

However the logarithmic divergence predicted in Eq. (8) cannot go on forever, as the two diffusion coefficients must both remain finite. For a given dislocation density, the predicted behavior must break down above a characteristic system size, because the distortion of an individual smectic layer cannot increase without limit. If the local curvature is too high, the layer structure will simply break up.

Even in systems well below this limiting size, one must also consider whether short-range correlations in dislocation positions could affect diffusion. For instance, consider a smectic threaded by a random distribution of dislocation dipoles, where each dipole consists of two parallel screw dislocations of opposite Burger's vector at fixed separation, in a random orientation. Visualization of a dislocation dipole shows that the region between screw dislocation cores is essentially a narrow ''ramp'' leading from one layer to the next. (This double-screw structure with a central ramp is indeed found in many parking garages.) Without doing a detailed calculation, we can guess that the interlayer diffusion coefficient would be simply linear in the density of such ramps with no system size dependence at all. Thus the introduction of strong correlations may destroy the logarithmic divergence in Eq. (8) entirely, while the linear dependence on overall dislocation density remains.

What are the implications for understanding experimental and computational measures of anisotropic diffusion? Screw dislocations in a smectic do not interrupt the director field and thus cannot be easily observed via microscopy. Yet experimental studies of interlayer diffusion in bulk smectics and other layered materials may give irreproducible results unless dislocation density is taken into account. The logarithmic dependence of $D_\parallel/D_\perp$ on system size is weak, if it exists at all, but could be observable at small length scales.

Smectics containing screw dislocations can be studied via molecular-scale simulation, so it is possible, in principle, to use molecular dynamics to examine competing mechanisms for interlayer diffusion including the spiral staircase effect. Unfortunately simulations containing dislocations can be somewhat complicated by the imposition of periodic boundary conditions. The requirement of compatible displacements on all periodic surfaces greatly restricts accessible dislocation structures. Even a single screw dislocation running parallel to the z axis produces displacements on four sides of the cell that are inconsistent with simple periodic boundary conditions. Slip boundary conditions [9] that also incorporate twist could solve this difficulty at least for some simple cell geometries.

Also, because dislocations cannot terminate within bulk material they either form loops or make connections across periodic boundaries, and this topological constraint restricts straight dislocations to specific angular orientations. A dislocation can lie parallel to a cell boundary, for instance, or an evenly spaced array of like-signed dislocations (e.g., in a twist grain boundary phase [10]) can lie only at a discrete set of angles that allow connections across the periodic cell boundaries.

Because of these topological constraints, researchers simulating dislocation microstructures in crystalline solids tend to use open boundary conditions or a mix of periodic and open boundary conditions on different cell walls. However such a choice is not easily implemented in a liquid crystal simulation, as particles may be ejected if attractive interactions are absent or too weak to hold a droplet together. If a free surface is used, nearby dislocations will be attracted toward it by image forces and can annihilate there. Whether a free surface or a confining wall is used, the material near

the boundary will likely be different in density and degree of order than material in the bulk. In spite of this problem, nonperiodic boundaries may be preferable because they do not impose topological restrictions on available dislocation structures.

In conclusion, we have investigated one mechanism by which screw dislocations in a layered material enhance interlayer self-diffusion, by providing barrier-free diffusion pathways. We find that the ratio of diffusion coefficients $D_{\parallel}/D_{\perp}$ associated with this effect depends linearly on the dislocation density. In the absence of correlations in the spatial distribution of dislocations, the ratio also diverges logarithmically with system size. These results are confirmed by Monte Carlo simulation. Our results demonstrate the general principle that transport properties depend sensitively on microstructure in soft condensed matter.

This work was supported by the National Science Foundation under Grants Nos. NSF-DMR-9702234 and DMR-0116090.

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