Crossover between 2D and 3D Fluid Dynamics in the Diffusion of Islands in Ultrathin Freely Suspended Smectic Films

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The Stokes paradox, that moving a disk at finite velocity through an infinite two-dimensional (2D) viscous fluid requires no force, leads, via the Einstein relation, to an infinite diffusion coefficient D for the disk. Saffman and Delbrück proposed that if the 2D fluid is a thin film immersed in a 3D viscous medium, then the film should behave as if it were of finite size, and $D \sim -\ln(a\eta')$, where a is the inclusion radius and η' is the viscosity of the 3D medium. By studying the Brownian motion of islands in freely suspended smectic liquid crystal films a few molecular layers thick, we verify this dependence using no free parameters, and confirm the subsequent prediction by Hughes, Pailthorpe, and White of a crossover to 3D Stokes-like behavior when the diffusing island is sufficiently large.

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In the early 1970s, Saffman and Delbrück (SD) considered the problem of calculating the diffusivity of a protein included in a thin, bilayer lipid membrane, and realized that both the viscosity of the membrane η and that of the surrounding fluid η' affect the dynamics of the protein [1]. In what became a classic paper, Saffman presented a full fluid mechanical description of the translational motion of an inclusion in a membrane surrounded by another viscous fluid, using no-slip boundary conditions [2]. Saffman pointed out that the viscosity of the surrounding fluid η', however small compared to the viscosity of the membrane η, provides a significant contribution to the momentum dissipation. The characteristic Saffman length $l_S = \eta h/2\eta'$ is found by balancing the drag from the membrane with that of the surrounding fluid, and is proportional to the membrane's thickness h. The Saffman length represents the distance beyond which fluid flow in the membrane caused by the motion of the inclusion, which normally shows a long-ranged logarithmic decay, may be ignored [3]. In this picture, an inclusion of radius a may be thought of as carrying with it a part of the membrane extending a distance l_S around it, increasing the effective drag and leading, in the case $a \ll l_S$, to a finite mobility

$$\mu = \frac{1}{4\pi\eta h}\left[\ln\left(\frac{2l_S}{a}\right) - \gamma\right], \tag{1}$$

where γ is the Euler constant.

Hughes, Pailthorpe, and White (HPW) extended Saffman's model to determine analytically the mobility of an inclusion of arbitrary radius in a 2D fluid [4]. They predicted that for $a \gg l_S$, the mobility would exhibit 3D-like behavior, varying as $\mu \sim 1/a$ but with a prefactor different from the bulk theory [5]. Petrov and Schwille (PS) derived a simple but accurate approximation to the rather complicated HPW mobility expression [6]:

$$\mu = \frac{1}{4\pi\eta h}\left[\frac{\ln(\frac{2}{\epsilon}) - \gamma + \frac{4\epsilon}{\pi} - \frac{\epsilon^2}{2}\ln(\frac{2}{\epsilon})}{1 - \frac{\epsilon^3}{\pi}\ln(\frac{2}{\epsilon}) + \frac{c_1\epsilon^{b_1}}{1+c_2\epsilon^{b_2}}}\right], \tag{2}$$

where $\epsilon = a/l_S$ is the reduced radius and $c_1 = 0.737\,61$, $b_1 = 2.748\,19$, $c_2 = 0.521\,19$, $b_2 = 0.614\,65$ are constants. The reduced mobility $m = \mu(4\pi\eta h)$ derived from Eq. (2) is shown as the solid curve in Fig. 1, predicting asymptotic 2D behavior $m \sim \ln(2/\epsilon)$ for $\epsilon \ll 1$, and 3D behavior $m \sim 1/\epsilon$ for $\epsilon \gg 1$.

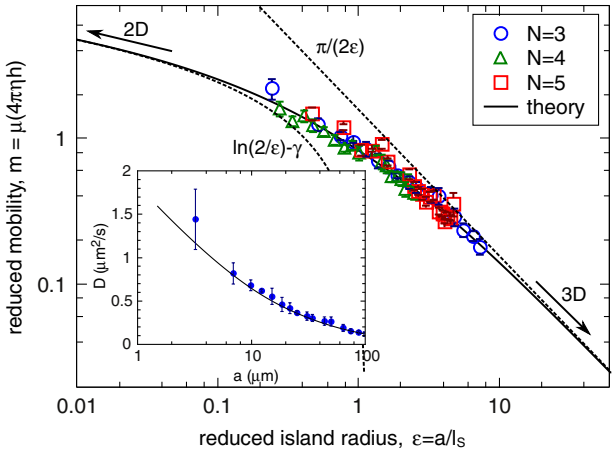

FIG. 1 (color online). Island mobility as a function of radius in smectic films. Experimental data for three different film thicknesses ($N = 3$, 4, and 5) and a range of island radii follow the predictions of the SD-HPW-PS theory (solid curve) and illustrate the crossover from 2D to 3D behavior with increasing island radius. Both mobility and radius are scaled here to be dimensionless. The dotted curves show the predictions of 2D and 3D theory, valid in the limits $a \ll l_S$ and $a \gg l_S$, respectively. The inset shows the diffusion coefficients of islands of different radii in an $N = 3$ film. The error bars correspond to the standard deviations obtained by analyzing several subsets at each radius extracted from a given trajectory.

The SD-HPW-PS picture has been widely used to interpret experimental measurements of the 2D hydrodynamics of inclusions in fluid membranes [7,8], and to extract membrane viscosity [9] or inclusion size [10] from diffusion data. However, in some cases the measurements in the SD regime give a much stronger dependence of $\mu(a)$ on a than predicted, leading to doubts about the validity of the theory in describing complex membrane systems [11]. Here we exploit the unique character of fluid, freely suspended films of smectic liquid crystal to extend parameter-free quantitative testing of the SD-HPW-PS model into the SD regime.

Fluid smectics are particularly well suited for measuring diffusion in 2D because they form homogeneous, ultrathin freely suspended films that are quantized in thickness (consisting of an integer number of smectic layers, which can be selected), and are stable for many hours (or days if not disturbed) [12]. Films as thin as two layers ($h = 6.3$ nm) can be created with an area as large as 10 cm^2, making them the thinnest stable condensed matter system for probing 2D hydrodynamics. Smectic A films have positional ordering in the direction perpendicular to the film, but are liquidlike within each layer, making them ideal for studying 2D physics in general [12,13] and 2D hydrodynamics in particular [14].

In our experiments, we observe the diffusion of mobile inclusions called islands, thicker, pancake-like domains with more smectic layers than the surrounding film, sketched in Fig. 2. These disk-shaped regions are made of the same material as the film, and can be manipulated

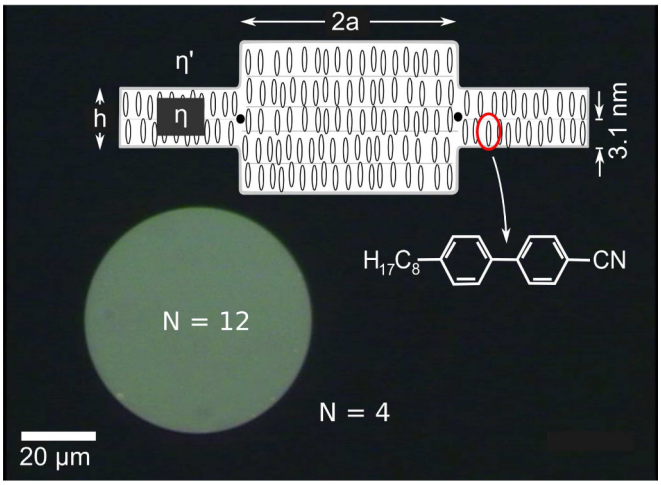

FIG. 2 (color online). A 35 μm-radius island in a freely suspended smectic A film of 8CB. The film and island are an integer number of layers thick, and are separated by an edge dislocation loop (●), which provides a line tension and gives the island its circular shape. The inset shows in cross section an island of radius a in a smectic A film of thickness h. The rodlike 8CB molecules are arranged in 2D fluid layers and are oriented along the layer normal. The low climb mobility of the edge dislocation ensures that the material in the surrounding film diverts around the diffusing island. 8CB has the phase sequence: crystal $\overset{22\,^\circ\mathrm{C}}{\longleftrightarrow}$ smectic A $\overset{33.5\,^\circ\mathrm{C}}{\longleftrightarrow}$ nematic $\overset{40.5\,^\circ\mathrm{C}}{\longleftrightarrow}$ isotropic.

using optical tweezers [15,16]. Moreover, the island radius a can be varied over a wide range ($4 \lesssim a \lesssim 100$ μm) that brackets the typical Saffman lengths in this system (for example, $l_S = 8.4$ μm in a two-layer film), enabling the study of the crossover region between 2D and 3D behavior. Islands, once made, have constant thickness and, in 8CB films, a radius that decreases only very slowly over time, enabling the measurement of translational diffusion coefficients using conventional video microscopy. The mobility is derived from the diffusion coefficient using the Einstein relation $\mu = D/k_BT$.

While the mobilities of inclusions in thin membranes have been studied experimentally before, the crossover between 2D and 3D behavior when the size of the inclusion is varied has not previously been explored. Prasad and Weeks recently reported a crossover of a different nature in soap films, demonstrating that a particle embedded within the film shows a transition from 2D to bulk 3D behavior when the film thickness is made much greater than the particle diameter [8].

The liquid crystal used in our experiment is 8CB (4′-*n*-octyl-4-cyanobiphenyl, Sigma-Aldrich), which has an in-plane viscosity of $\eta = 0.052$ Pa s [17] at temperature $T = 22°$, and a layer thickness $d = 3.17$ nm [18]. The air is assumed to have a viscosity $\eta' = 1.827 \times 10^{-5}$ Pa s [19]. Films are spread at room temperature across a 1 cm-diameter circular hole in a glass cover slip. Islands are then created by blowing obliquely either on the thicker parts of the film or on the meniscus along the edge of the film holder. This process yields islands of 1 μm–1 mm radius, but we typically select those in the range 4–100 μm for ease of observation. We can consistently make films of $N = 2$ to eight smectic layers, with Saffman lengths ranging from 8.4–33 μm. The reflectivity of thin smectic films ($N \lesssim 15$) is quadratic in the thickness, giving excellent contrast between islands and the background film as shown in Fig. 2, and providing a convenient way of determining the number of layers, a measurement typically made using a laser [20,21]. In the present experiments, we used the intensity of the green channel of the calibrated video camera signal to measure the reflectivity.

The films are enclosed in a sealed chamber in order to minimize disturbances from the surrounding air, and are leveled on a goniometer to within 0.5°. This allows us to record the motion of a selected, isolated island with a video camera for up to ten minutes (acquiring ~18 000 frames at 30 frames per second) without its drifting out of the field of view. Because of the lower pressure in the film meniscus, the selected island gradually shrinks over the course of the experiment. This enables us to determine the diffusion coefficient for islands of different radii by analyzing sections of longer video clips in which the radius typically decreases only by a few percent.

The optical contrast between an island and the surrounding background film makes it easy to identify and track the islands by thresholding the video frames and then using image analysis to determine the position of the center of

the island and its size. A typical trajectory of the center of an island is shown in Fig. 3(a). Comparison with video recordings of 10–40 μm-diameter stationary, circular disks etched on a glass slide using electron beam lithography suggests that the tracking method is accurate to within 10 nm, far better than the nominal resolution of the imaging system, which is about 250 nm.

To measure the diffusion coefficient of an island directly from the trajectory of its center, we need to distinguish systematic drift from Brownian motion. Since islands generally have very small diffusion coefficients [on the order of 0.5 μm^2/s, see Fig. 1], even drifts as small as 0.1 μm/s

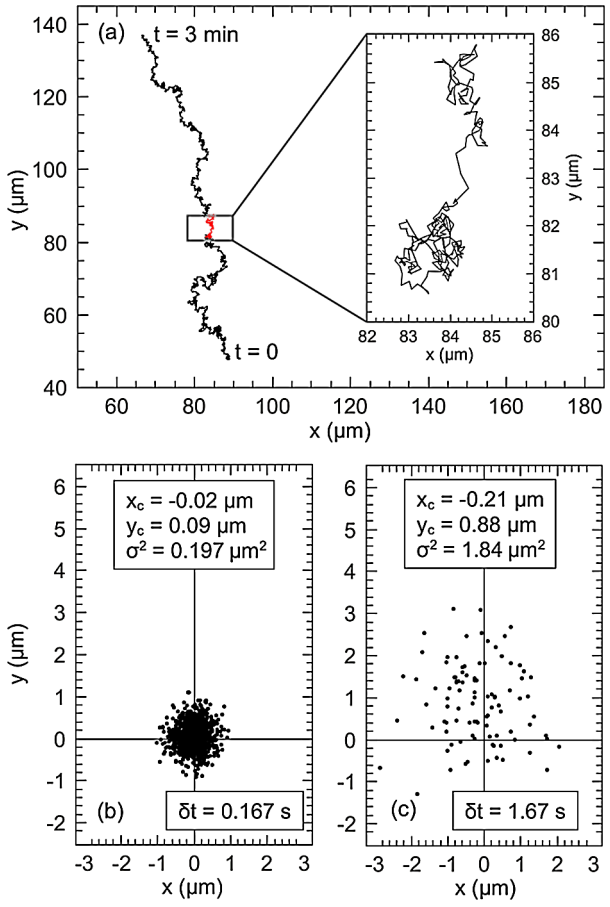

FIG. 3 (color online). Island diffusion in a smectic A liquid crystal film. (a) Three-minute trajectory of a 13 μm-radius island diffusing in an $N = 4$ layer 8CB film, with the inset showing a ten-second extract. The trajectory shows both Brownian motion and a systematic drift. The location of the center of the island is determined to an accuracy of ± 10 nm. The lower plots show the distributions of displacements measured between two points along this trajectory separated by time intervals of (b) 0.167 and (c) 1.67 s. As the time interval increases, the distribution shifts away from the origin and spreads out, with both the distance of the center of the distribution from the origin and the variance of the distribution increasing linearly with the chosen time interval. The rate of change of the center's position gives the drift velocity while that of the variance gives the diffusion coefficient.

may add a significant [$O(60\%)$] systematic error to a typical 1000-frame trajectory if they are neglected. Larger islands are especially susceptible to this kind of artifact since their random diffusion is slower and they drift faster if the film is not properly leveled.

Systematic drift may be analytically separated from diffusion as follows. Let us consider all displacements between pairs of points on the island trajectory that are separated by a prescribed time interval. If we shift those displacements so that they have a common origin, they form a distribution in which the mean displacement corresponds to the net drift in this time interval, while the variance gives the diffusion [Figs. 3(b) and 3(c)]. Assuming that the drift velocity is constant over the entire trajectory, we can extract the drift velocity and the diffusion coefficient, respectively, from the rates of change of the mean and variance with time interval. We verified the accuracy of this drift extraction method using simulated data obtained by generating random walk trajectories comprising diffusion steps with random length and direction, themselves obtained from random walk trajectories with a prescribed number of steps of fixed size. Constant drifts are then superimposed onto the diffusive motion. Both the diffusion coefficients and the drift velocities are extracted correctly for over more than two decades of drift velocity, as shown in Fig. 4.

Smectic A islands are fluid and are therefore susceptible, in principle, to shape fluctuations. Since the island position is obtained by computing its centroid, deviations from perfect circularity of the boundary could be misinterpreted as a change of position. The roughness of the perimeter of an island of radius $a = 10$ μm and line tension $\lambda = 80$ pN

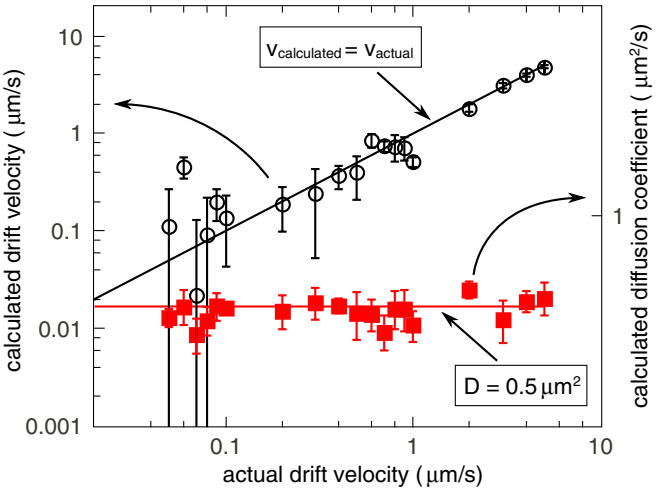

FIG. 4 (color online). Tests of the analysis method using simulated random walk data with a fixed diffusion coefficient of 0.5 μm^2/s, and drift velocities ranging from 0.05 μm/s to 5.0 μm/s. The values extracted for both the drift velocity (○) and the diffusion coefficient (■) are in good agreement with the parameters used to generate the test data. The error bars correspond to the standard deviations obtained from analyzing a set of different random walk sequences generated using the same parameters.

due to thermal fluctuations is estimated to be on the order of $\delta \simeq \sqrt{(k_B T \cdot a)/(\pi\lambda)} \approx 10$ nm, a variation which is too small to observe in our system.

We now compare our experimental results with the predictions of the SD-HPW-PS theory. The mobilities of 7–20 layer-thick islands on 8CB films of three different thicknesses ($N = 3$, 4, and 5) are shown in Fig. 1. The scaled experimental measurements, plotted directly with no free parameters, are in very good agreement with theory, collapsing nicely onto the theoretical curve given by Eq. (2). In performing this comparison, we make three key assumptions. First, since permeative flow in smectics away from the nematic—smectic A phase transition is very slow [22], as evidenced in this case by the very slow change in island radius versus time, we can, for the purposes of this measurement, take the excess island layers as having a fixed number of molecules. If the flow of material through the boundary of the island is negligible on the experimental time scale, the island may be viewed as a thicker, isolated region bounded by an edge dislocation loop. Second, since the islands used here are substantially thicker than the surrounding film, and consequently much more viscous, we neglect fluid flow within the islands, assuming that the islands behave as solid disks under no-slip boundary conditions. Third, we assume that the mass density and the viscosity of the liquid crystal material in a thin film are the same as in the bulk.

In an independent measurement of island drift induced by gravity in slightly tilted films, we observed a terminal drift velocity proportional to the component of the island's weight along the film plane and with a magnitude corresponding to a film viscosity of $\eta \approx 0.044$ Pa s [23], which is within 15% of values reported in the literature. We looked for any dependence of the island mobility on island thickness by measuring the diffusion coefficients of 8- and 17-layer islands of similar size on a three-layer 8CB film but found no significant difference in their (scaled) mobility.

In summary, the diffusion of circular islands in ultrathin, freely suspended smectic A liquid crystal films is in excellent agreement with the SD-HPW-PS theory of Brownian motion of inclusions in thin 2D membranes immersed in a 3D fluid. The freely suspended film system allows the measurement of diffusion under systematic variation of both the radius of the inclusions and the thickness of the membrane. The experimental parameters are such that we are able to measure precisely the mobility of islands with radii both smaller and larger than the Saffman length. The results confirm that this indeed marks a crossover between 2D and 3D hydrodynamic behavior.

In future experiments, we plan to test the SD-HPW-PS theory over a wider range of reduced radius $\epsilon = a/l_S$, especially in the small ϵ regime, which can be achieved either with thicker films (large l_S) or with smaller a. Since freely suspended smectic films have proven to be an excellent system for investigating 2D diffusion in fluids, we should also be able to use them to explore such phenomena as rotational diffusion and the hydrodynamic interactions of multiple inclusions.

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