PHYSICAL REVIEW E **90**, 040501(R) (2014)

Single-molecule diffusion in freely suspended smectic films

Benjamin Schulz,[*] Marco G. Mazza,[†] and Christian Bahr[‡]
Max Planck Institute for Dynamics and Self-Organization (MPIDS), Am Fassberg 17, D-37077 Göttingen, Germany

(Received 5 May 2014; published 7 October 2014)

We present a study of the molecular diffusion in freely suspended smectic-*A* liquid crystal films with thicknesses ranging from 20 down to only two molecular layers. The molecular mobility is directly probed by determining the trajectories of single, fluorescent tracer molecules. We demonstrate, using several different smectic compounds, that a monotonic increase of the diffusion coefficient with decreasing film thickness is a general phenomenon. In two-layer films, the diffusion is enhanced by a factor of 3 to 5 compared to the corresponding bulk smectic phase. Molecular dynamics simulations of freely suspended smectic films are presented which support the experimental results.

DOI: 10.1103/PhysRevE.90.040501 PACS number(s): 61.30.−v, 66.10.cg, 68.15.+e

The dynamic properties of liquids in confinement and at interfaces are of obvious importance for various physical, chemical, and biological systems. For instance, the motion of protein or lipid inclusions in biological membranes [1] can be considered as an example of the Brownian motion of a particle in a two-dimensional fluid. Apart from its biological relevance, this system is also interesting from the viewpoint of fluid mechanics because the Stokes equations cannot describe the viscous flow around a translationally moving disk in a two-dimensional (i.e., infinitely thin) liquid layer. A theoretical description [2–4] can be obtained by taking the finite thickness of a real membrane and the coupling to the surrounding viscous medium (water or air) into account. Recently, freely suspended smectic films were successfully employed [5,6] as experimental model systems for two-dimensional fluid mechanics, confirming the predictions of [2–4].

Freely suspended films of smectic-*A* liquid crystals consist of an integral number of molecular layers, each layer corresponding to a two-dimensional liquid [7,8]. They can be easily prepared with an area of several cm^2 while their thickness can range from thousands of layers down to only two layers, corresponding to a film thickness of about 6 nm. The studies described in [5,6] were concerned with the mobility of micrometer-sized particles or inclusions in the films, mimicking to some extent the behavior of macromolecules in biological membranes. In the present study, we address the question of how the mobility of the constituent molecules themselves, which form the membrane or thin film, changes with the film thickness. We directly probe the mobility on the molecular scale by tracking the Brownian motion of small single molecules in freely suspended smectic films. The film thickness is varied in the range from 20 to 2 molecular layers, thereby exploring the transition to the quasi-two-dimensional regime, for four different smectic liquid crystal compounds. In addition, we determine the temperature dependence of the molecular diffusion coefficient in films of different thickness. We also present results of molecular dynamics simulations that support our experimental observations.

To the best of our knowledge, only one experimental study [9] of molecular diffusion in freely suspended smectic films has been reported so far. Bechhoefer *et al.* [9] used the technique of fluorescence recovery after photobleaching (FRAP) to determine diffusion coefficients for films of different thickness of the common smectic compound 8CB (4-octyl-4′-cyanobiphenyl, [10]). A significant increase of the diffusion coefficient *D* was observed as the film thickness was decreased down to four layers. However, for the three-layer film a considerably smaller value than for the four-layer film was found, whereas *D* increased again for the two-layer film. This nonmonotonic behavior was not explained. In Ref. [9], a fluorescent dye was dissolved at saturation in 8CB and the size of the dye molecules was considerably larger than that of the 8CB molecules. These conditions might have contributed to the unexpected behavior observed in the thin-film limit. The present study is based on the optical tracking of single fluorescent molecules, which directly images the Brownian motion on the molecular level. The size and the shape of the dye molecules are similar to that of the smectic molecules and the dye concentration in the smectic matrix is very low. We can therefore assume that the distortion of the intrinsic behavior of the liquid crystal molecules is minimal. Also, the spatial and temporal resolution of single-molecule tracking is larger than in FRAP studies [11].

Single-molecule tracking has been applied to biological membranes [11,12] and recently to liquid crystal films on solid substrates [13–15]. As fluorescent dye we use Nile red, dissolved in the liquid crystal samples at concentrations around 10^{-8} mol/L (about 3×10^{-7} wt %). The liquid crystal compounds under investigation were 8CB, 9O.4 (4-nonyloxybenzylidene-4′-butylaniline [16]), C7 [4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxybiphenyl [17]], and a pyrimidine compound [2-(4-octyloxyphenyl)-5-octylpyrimidine [18]]. All compounds exhibit a smectic-*A* phase in a certain temperature range.

Freely suspended films were prepared by drawing the material in the smectic state over a rectangular stainless steel frame consisting of two fixed parts ("rails") and two movable parts ("chariots") which enable an adjustment of the film area. Typical lateral dimensions were 1 × 0.5 cm^2. The film was sealed against air flow and the temperature was controlled using a Peltier PID controller (McShane 5R7-002). After preparation, the films, which showed initially domains

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[*] benjamin.schulz@ds.mpg.de
[†] marco.mazza@ds.mpg.de
[‡] christian.bahr@ds.mpg.de

of different thickness, were left to equilibrate (typically for about 30 min) until a homogeneous thickness was attained and any flow between the film and its meniscus came to rest. The film thickness was determined by measuring the reflection spectrum using a UV/VIS spectrometer (AvaSpec-2048-USB2, Avantes) [19].

For the optical tracking of single dye molecules, a homebuilt epifluorescence microscope was used. The sample was illuminated using laser light with a wavelength of 488 nm (sapphire 488, Coherent). The illuminated region of the sample had a size of around 60 μm in diameter. The fluorescence light, detected at wavelengths larger than 510 nm using a longpass filter, was collected through a high magnification objective lens (MPLFLN100×/NA 0.9, Olympus) and imaged on a highly sensitive CCD camera (Andor iXonEM+ 897). This enabled us to follow the movement of individual fluorescent molecules with a frame rate of 50 Hz. A typical trajectory is shown in the inset of Fig. 1. To determine the value of the diffusion coefficient D, a larger number (at least several tens) of trajectories is recorded and for each trajectory a coefficient D_i is determined from the two-dimensional mean square displacement $\Delta r^2 = \Delta x^2 + \Delta y^2$ according to $\Delta r^2 = 4D_i\Delta t$. Only trajectories which could be recorded for a time interval $\Delta t \geqslant 1$ s were evaluated. The frequency of occurrence of the obtained D_i values was fitted to a Gaussian distribution the mean value of which is taken as the value of the diffusion coefficient D. As we observe only the two-dimensional projection of the molecular motion, the determined D values describe the diffusion perpendicular to the molecular axis.

Figure 1 shows the values of D for the compound 8CB, determined as described above, as a function of film thickness. The diffusion coefficient increases monotonically with decreasing thickness. The anomalous behavior of the three-layer film reported in [9] is not observed in our experiments. The thickness dependence of D down to four layers may be described [9] by a functional dependence according to

$$D = D_0\left(1 + \frac{A}{n}\right), \tag{1}$$

TABLE I. Values of the bulk diffusion coefficient D_0 and parameter A obtained by fitting the experimental data shown in Fig. 2 using Eq. (1). The rightmost column gives the temperature at which the measurements were conducted.

Mesogen	D_0 (μm^2/s)	A	T (°C)
C7	1.1	10.4	59
8CB	2.1	7.1	23
Pyrimidine	5.7	5.8	62
9O.4	7.5	2.9	73

with n being the film thickness (number of layers), D_0 the bulk diffusion coefficient ($n \to \infty$), and A a constant. We treat D_0 and A in the first instance as free fitting parameters and discuss the physical significance of Eq. (1) later. As shown in Fig. 1, our data are reasonably described by Eq. (1) over the full range of measured film thicknesses, from 22 down to two layers.

In order to see to what extent the behavior of 8CB is general, three other smectic compounds were studied. The molecules show different physical properties, e.g., different molecular aspect ratios and dipole moments. The measurements were done at a temperature well within the smectic-A phase range of the respective compounds (cf. Table I). The dependence of D (normalized by the respective D_0 values; cf. Table I) on the film thickness for all compounds is shown in Fig. 2. All compounds show qualitatively similar behavior, i.e., a monotonic increase of D with decreasing thickness. For the compounds C7 and 9O.4, we found two-layer films to be not stable enough in our setup for a conclusive measurement of D. However, the data shown in Fig. 2 suggest that the molecular mobility in two-layer films is generally three to six times faster than in the corresponding bulk phase.

A dependence of D on the film thickness as in Eq. (1) results as a leading order approximation if one makes two assumptions: (i) the effects of the two free surfaces on the molecular mobility are additive, and (ii) the local diffusivity

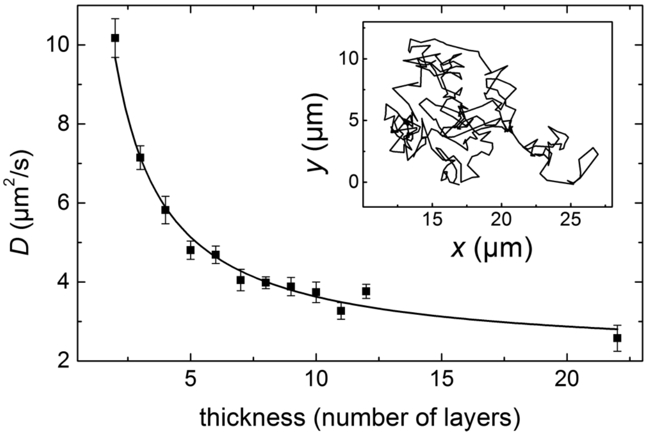

FIG. 1. Diffusion coefficient in freely suspended 8CB films as a function of the film thickness. The solid line is a fit according to Eq. (1). The error bars are determined by the standard error of the mean. The inset shows a typical trajectory for a time interval $\Delta t = 6.5$ s.

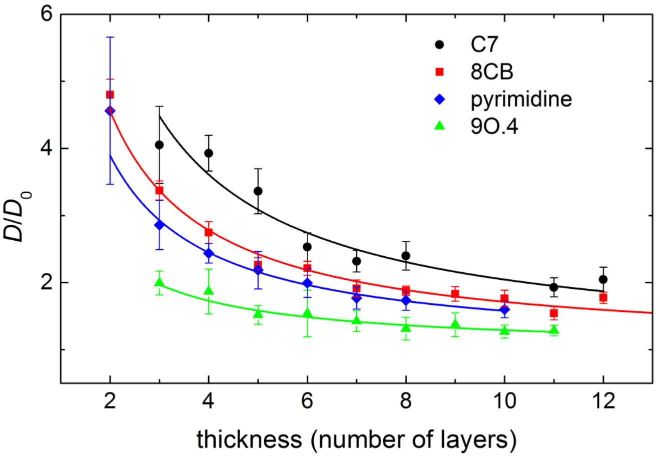

FIG. 2. (Color online) Thickness dependence of the diffusion coefficient D (normalized by the respective bulk diffusion coefficients D_0) in freely suspended films of C7, 8CB, pyrimidine, and 9O.4. The solid lines are fits using Eq. (1).

D_z varies with the distance z from one surface as [9]

$$D_z = D_0\left(1+\frac{\sigma}{2z}\right), \tag{2}$$

with σ being the hydrodynamic radius of the diffusing molecule. Equation (2) can be seen as an approximation of a result from the continuum fluid mechanics description of a spherical particle near a perfect slip interface, which gives $D_z = D_0(1+\frac{3\sigma}{8z})$ [20].

The parameter A in Eq. (1) can be related to the hydrodynamic radius σ: $A = \frac{4\sigma}{d}$ with d being the single smectic layer thickness [9]. The molecular radius r of the Nile red molecule, estimated as the half value of the long molecular axes, is of the order 0.7 nm. However, the values of A used to describe our experimental results (Fig. 2) would lead to values of the hydrodynamic radius σ which are one order of magnitude larger than the molecular radius. Such large values of σ are not physical, particularly as our system is not an ionic liquid. Presumably, a better description could be achieved by introducing a dependence of the surface enhancement of D on the film thickness, i.e., Eq. (2), which describes a semi-infinite system with one surface, should be modified for the case of a confined film with two surfaces and a certain thickness. Our results from molecular dynamics (MD) simulations, described in the following, indeed show that the diffusivity in the smectic layer at the film surface strongly increases with decreasing film thickness.

A recent MD simulation study [21] of freely suspended films of an isotropic glass-forming model system, consisting of a binary mixture of spherical particles, has shown an enhanced diffusion close to the surface. MD studies of thermotropic smectic liquid crystals were reported [22,23], but we are not aware of any MD study of freely suspended smectic films coexisting with their own gas phase. Here, we describe the first MD simulations of realistic model freely suspended smectic films. The simulations are performed for up to $N = 30\,000$ molecules using the Gay-Berne-Kihara potential [24], which models the liquid crystal molecules as spherocylindrical soft particles possessing anistropic interactions. The potential is known [25,26] to generate a smectic-A phase for appropriate parameter settings. The simulation protocol is described in the Supplemental Material [27]. We should note that in the production run, during which the film is in equilibrium with its gas phase and the observables are calculated, the microcanonical ensemble (constant number of molecules, volume, and total energy) is used.

We calculate the mean square displacement perpendicular to the molecular long axis

$$\langle \Delta r_{\perp}^2(t)\rangle \equiv \frac{1}{N}\left\langle \sum_{i=1}^{N} [\boldsymbol{r}_{\perp i}(t+t_0) - \boldsymbol{r}_{\perp i}(t_0)]^2 \right\rangle, \tag{3}$$

where $\boldsymbol{r}_{\perp i} \equiv \boldsymbol{r}_i - (\boldsymbol{u}_i \cdot \boldsymbol{r}_i)\boldsymbol{u}_i$, $\boldsymbol{u}_i$ and $\boldsymbol{r}_i$ describe the orientation and the center-of-mass position of molecule i, respectively, and $\langle \cdots \rangle$ indicates average over the initial times t_0. The value of D is computed first for each layer of a film, from a mean square displacement that is calculated from the average over the position vs time data of all molecules in the layer. In our simulations, we did rarely observe a molecule crossing from one layer to a neighboring layer. The D value of a given film is then calculated as the average of the D values of the individual layers. Figure 3 shows that the simulations give a behavior very similar to that observed in the experiments: when reducing the film thickness at constant temperature, a significant increase of D is predicted. Although the relative increase in the diffusion coefficient appears to be slightly larger than observed in the experiment, the general behavior agrees very well, indicating that the diffusional behaviors of the dye and liquid crystal molecules are not essentially different (as was observed in a recent experimental study [15]) and that the increase of the diffusivity in thinner films is not an artifact of the used dye molecules (caused by a possible solvation effect dominant in thicker films).

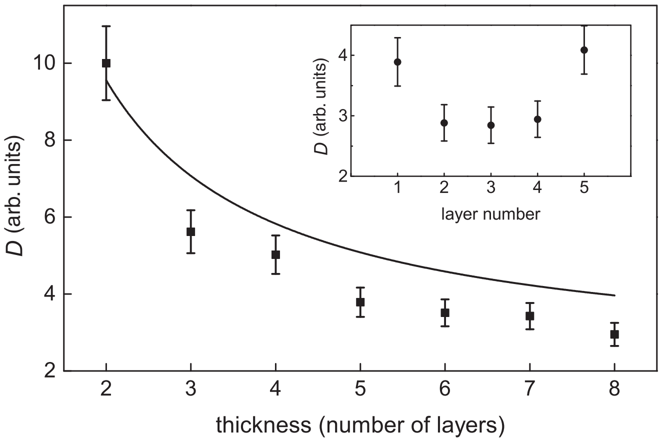

FIG. 3. Diffusion coefficients obtained from MD simulations of freely suspended smectic films. The D values are obtained in arbitrary units and scaled such that the numerical value of the two-layer film is the same as measured experimentally (in $\mu\mathrm{m}^2/\mathrm{s}$) for 8CB. The solid line is the same as in Fig. 1, corresponding to the experimental values obtained for 8CB. The inset shows the D values obtained for the individual layers of a five-layer film, illustrating the larger D values in the two surface layers.

The MD simulations enabled us to determine the diffusion coefficient D in the individual layers of a given film. Typical results, obtained for a five-layer film, are shown in the inset of Fig. 3, demonstrating a significant enhancement of D in the two surface layers of the film. The value of D in the surface layers of the five-layer film is still considerably smaller than that of the two-layer film, indicating that the effects from the two surfaces do not just add but amplify each other. We should also note that we find in the simulations the same value of the number density of molecules in all layers of the film. Thus, the increase of D at the surface is not caused by a lower density. Furthermore, preliminary results of the simulations indicate in the two surface layers a slightly smaller value of the amplitude of the pair correlation function, i.e., the two surface layers may be somewhat more liquidlike in character.

Further insight into the diffusion processes in our freely suspended smectic films may be obtained from the temperature dependence of the diffusion coefficient D. For the case of 8CB, films with thicknesses below ten layers are in the smectic state also in the temperature range of the bulk nematic phase [28] and the temperature dependence of D can be measured over a range of around 18 K. We have measured $D(T)$ for film thicknesses ranging from three to seven layers. As shown in Fig. 4, $D(T)$ can be described in all films by the classical

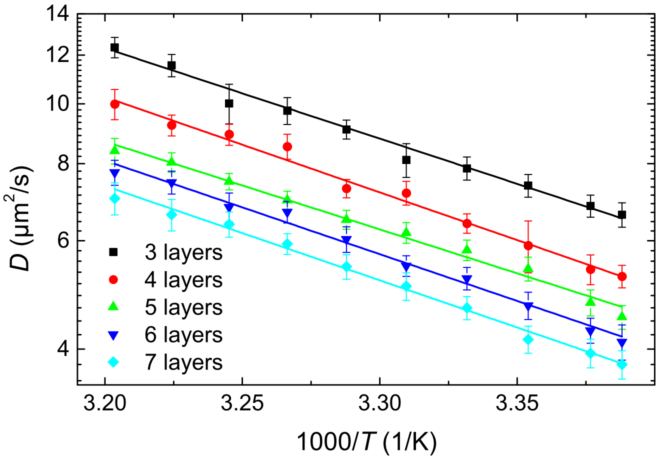

FIG. 4. (Color online) Temperature dependence of the diffusion coefficient in 8CB films for three to seven smectic layers thickness. All films show an Arrhenius behavior with the same activation energy.

Arrhenius law

$$D(T) = D_\infty \exp\left(-\frac{E_a}{RT}\right), \tag{4}$$

with R being the gas constant, E_a the activation energy, and D_∞ the diffusion coefficient at $\frac{1}{T} = 0$. For the seven-layer film, it was possible to cool the smectic film considerably below the bulk melting point of 8CB and we could confirm the Arrhenius-like dependence of D over a range of 40 K and nearly one order of magnitude in D. Remarkably, we find for all films identical values of E_a: Within a 5% margin $E_a = 29$ kJ/mol. This value is close to that observed for isotropic bulk 8CB [29]. The activation energy E_a can be seen as the energy required to create a characteristic void volume in the liquid, enabling a diffusion event [30]. The independence of E_a on the film thickness suggests that the fundamental diffusion processes do not change on approaching the two-dimensional regime. For instance, the increase in D is unlikely to be caused by a lower density or a different transport mechanism in the surface layer as this would show up in a change of E_a. Our observation that E_a does not change with the film thickness is in line with the observation that the viscosity η_3, related to flow parallel to the smectic layer plane, is nearly independent of the film thickness [31]. This behavior appears to contradict the inverse proportionality between D and η of the Stokes-Einstein relation. It is known that the Stokes-Einstein equation becomes invalid when the size of the diffusing particle is similar to or smaller than the size of the solvent molecules, however, also in these cases an inverse relation $D \propto \eta^{-p}$ with the exponent p in a range from $\approx$0.4 to $\approx$0.9 is retained [32]. On the other hand, viscosity data obtained from light scattering measurements showed a clear decrease of the viscosity with decreasing film thickness [33].

The issues described above show that the actual origin of the increase in D in thin films is not obvious. Our finding in the MD simulations that in the two surface layers the pair correlation function is slightly decreased compared to the interior layers appears to be contradictory to the frequently observed surface ordering behavior of freely suspended smectic films. The surface ordering is reflected by the observation that smectic phase transitions occur in many cases in the surface layers at higher temperatures than in the interior layers [8]. For 8CB, this behavior was not observed, but for C7 and 9O.4 it was shown that—at the temperatures of our diffusion measurements—the surface layers are in the smectic-C [34] or smectic-I state [16], respectively. The pyrimidine compound has not been studied in that respect. The surface ordering shows up also in the behavior of the thermal layer fluctuations, which were shown to be suppressed at the surface and in thin freely suspended films of compounds similar to the 9O.4 of the present study [35,36]. Only for a compound with a very low surface tension was an enhancement of the layer fluctuations in thin films observed [37]. It seems that there is no obvious relation between the diffusional behavior observed in the present study and the different surface ordering and layer fluctuation behaviors.

In conclusion, we have reported single-molecule fluorescence experiments and molecular dynamics simulations which directly probe the Brownian motion on the molecular scale in freely suspended smectic-A films. We found a monotonic increase of the diffusion coefficient D as the film thickness is decreased down to the experimental limit of two smectic layers. The increase of D is larger than expected from continuous fluid mechanics calculations for perfect slip interfaces [20]. Measurements of the activation energy indicate that the mechanism of diffusion does not depend on the film thickness. MD simulation results indicate an enhanced diffusion in the surface layers of the films and an increase of this enhancement with decreasing film thickness. Open questions, e.g., the relation to the viscosity and the role of the surface ordering, demonstrate the need for further studies.

Stimulating discussions with Stephan Herminghaus are gratefully acknowledged.

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