Electronic Supplementary Material (ESI) for Soft Matter.

Anisotropic Molecular Hopping at the Solid-Nematic Interface

Electronic Supplementary Information

Saonti Chakraborty, Nathaniel Nelson, and Daniel K. Schwartz*

Department of Chemical and Biological Engineering

University of Colorado Boulder, Boulder, CO 80309

*To whom correspondence should be addressed: daniel.schwartz@colorado.edu

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Single-Molecule Imaging Experimental Details

Sample Preparation – Based on Polarized Optical Microscope measurements, it was found that 4-Cyano-4'-pentylbiphenyl (5CB) had a nematic mesophase in the temperature range 33 °C – 41 °C. The error in these temperatures was found to be ±0.25°C. The fluorescent tracer molecule, AlexaFluor 647 (AF), was first diluted in ethanol, then in toluene and finally in the 5CB melt, where it was mixed directly.

The 5CB-AF mixture was sandwiched between a sapphire wafer and a fused silica coverslip by first heating the sample into the isotropic phase (~41 °C) and then directly pipetting it over the coverslip. Sample thickness was maintained using a 50 μm mylar spacer. Before placing the sapphire wafer over the sample and assembling the top cover of the holder, 5CB was allowed to stand at the isotropic temperature for ~30 min, so that it would fill the entire volume homogeneously with no residual fluid flow.

Surface Preparation – 2-inch diameter sapphire wafers and 1-inch fused silica (FS) coverslips were used to prepare sandwich cells for TIRF studies. The wafers and coverslips were cleaned thoroughly by immersion in warm piranha solution (70% concentrated sulfuric acid and 30% hydrogen peroxide by volume) for ~1 hr. This was followed by UV-ozone cleaning for approximately 1 hr.

On the cleaned sapphire and FS surfaces, a monolayer of (3-glycidoxypropyl)methyldiethoxysilane (GPTMS, Sigma Aldrich) was deposited by overnight vapor deposition. GPTMS was used in order to induce random planar liquid crystal (LC)

anchoring[1]. After deposition, the silane-coated sapphire surface was rubbed unidirectionally using frosted glass (also piranha and UV - ozone cleaned) about 90-100 times in order to homogeneously orient the LC molecules along the direction of rubbing (since 5CB exhibits positive dielectric anisotropy [2]). Care was taken to rub only in one direction and not to apply excessive pressure during the process. A similar process was performed on the coverslip as well. The surfaces were assembled such that the rubbed side of the sapphire and FS surfaces faced each other with their rubbing directions parallel. This sandwich cell uniformly aligned the LC, which was essential for imaging, because the presence of unaligned domains was found to scatter light, making imaging impossible.

Single-Molecule Data Analysis

Immobile trajectories at each temperature comprised a significant fraction of the data and were removed from the data pool prior to performing detailed statistical analysis of interfacial diffusion. This filtering was accomplished by setting a threshold distance of 0.2 μm between the first and the last positions of each trajectory in order to differentiate between immobilization and true motion. All trajectories that failed to meet this criterion were rejected from further analysis. As a sensitivity analysis for the threshold distance of 0.2 μm, this value was changed by a factor of 2. This resulted in a negligible change in the fraction of immobile trajectories as well as the best fit parameters for the cumulative square displacement and waiting time distributions.

Step-Size Distributions – Figure S1 shows the distributions of step sizes parallel and perpendicular to the nematic director. The step lengths have a non Gaussian probability distribution.

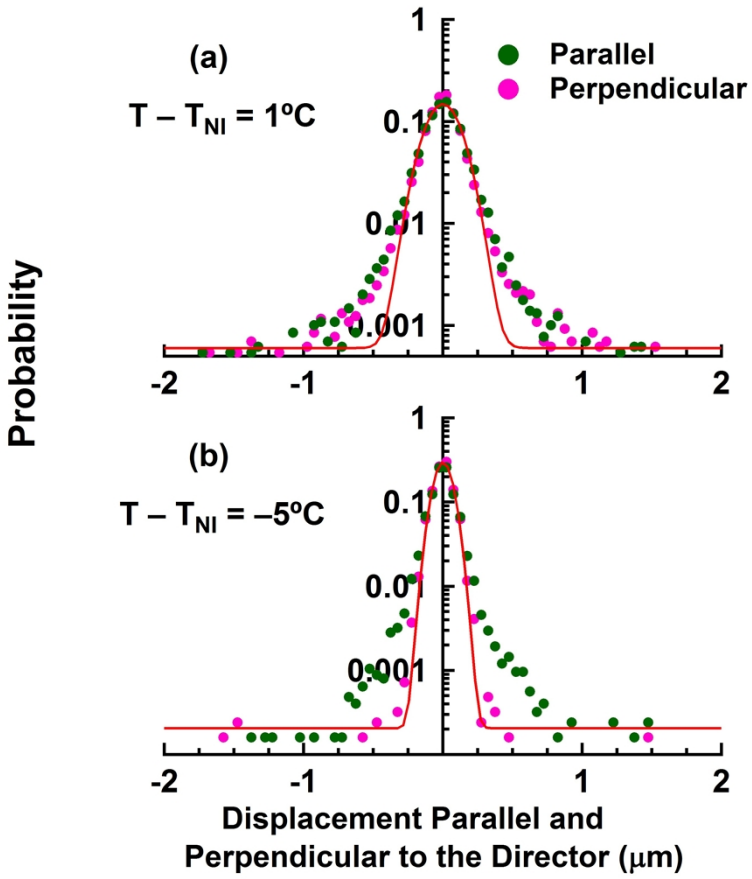

Figure S1. Step-size distributions in directions parallel (green markers) and perpendicular (pink markers) to the nematic director in the (a) isotropic and (b) nematic phases. For comparison, the red line in each plot represents a fit to a Gaussian distribution.

Cumulative Squared Displacement Distributions – The complementary cumulative distributions shown in Figure S2, as well as the distributions shown in figure 2c of the text, were constructed by counting the number of displacements that were equal to or longer than $\frac{r^2}{4\Delta t}$ and dividing by the total number of displacements observed [3].

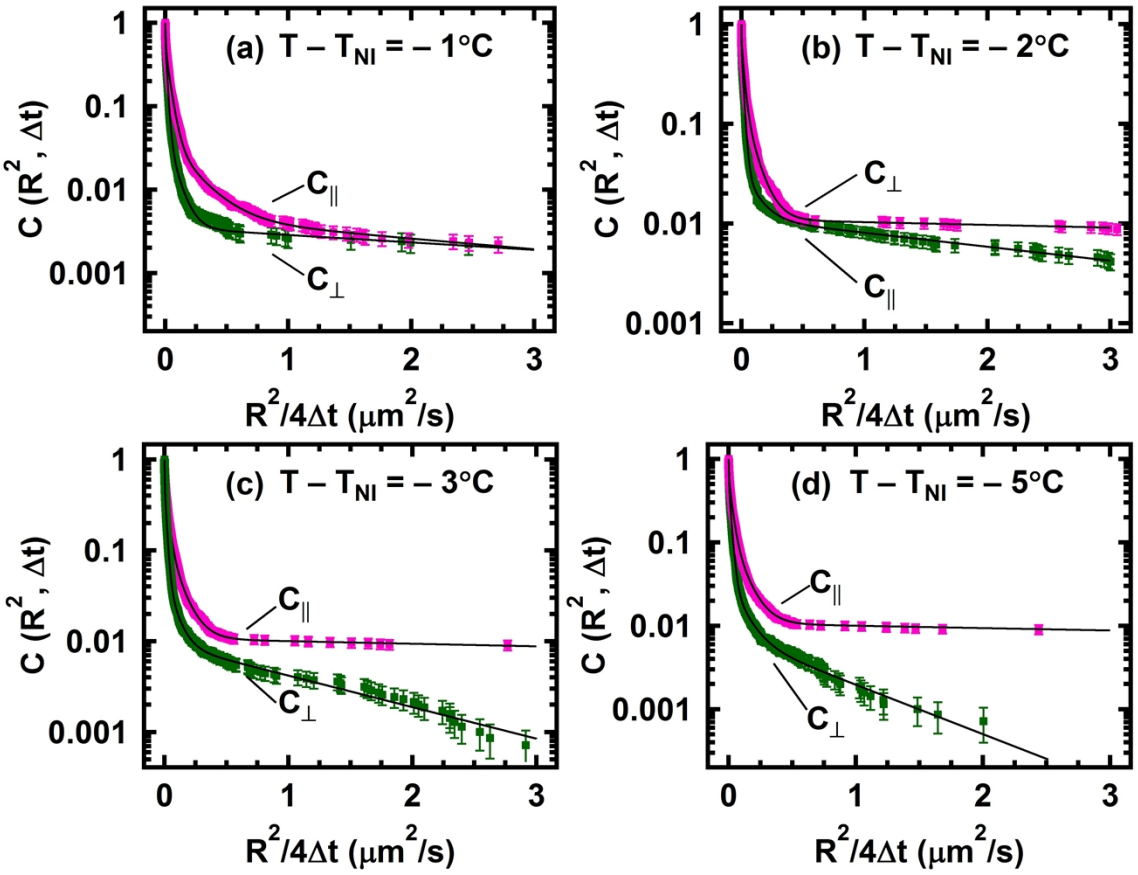

Figure S2. Cumulative probability distribution of the squared displacement divided by 4Δt, where Δt = 200msec was the lag time between successive image acquisitions. The components $C_{\parallel}$ and $C_{\perp}$ indicate the projections of displacements parallel and perpendicular to the rubbing direction.

Cumulative Squared Displacement Analysis – The data shown in Figure S2, as well as the cumulative squared step-size probability distribution of Figure 2c of the main text were fitted using the sum of two Gaussians:

$$C(r^2,\Delta t) = (1 - f_{hopping})\, e^{-r^2/4\Delta t\, D_{confined}} + f_{hopping}\, e^{-r^2/4\Delta t\, D_{hopping}} \quad \text{(S1)}$$

where the variable fitting parameters comprised $f_{hopping}$, $D_{confined}$, and $D_{hopping}$, and represented the fraction of hopping steps, the apparent diffusion coefficient during confinement, and the apparent diffusion coefficient during mobile hopping respectively. For fitting, initially only the first term was used to fit the "immobile" portion of the squared displacement distribution. Using the fitted values of $f_{hopping}$ and $D_{confined}$ as starting parameters, the complete equation was used for fitting the entire range of the plot. The best fit values of $D_{hopping}$ were plotted in Figure 3a of the main text. Tables S1 and S2 give the entire list of fitted parameters using Equation S1. The values of $D_{confined}$ were insensitive to temperature and varied randomly in the range 0.021-0.027 $\mu m^2/s$. Figure S3 shows the fraction of hopping steps as a function of temperature.

Table S1. Fitting parameters for the parallel component ($C_{\parallel}$) of the cumulative squared displacement distribution.

T (°C)	$T - T_{NI}$(°C)	$f_{hopping}$	$D_{hopping}\left(\mu m^2/s\right)$
42	1	0.70±0.11	0.75±0.04
39	-1	0.52±0.08	0.7±0.04
38	-2	0.51±0.02	0.70±0.03
37	-3	0.47±0.03	0.42±0.05
36	-4	0.32±0.04	0.20±0.03

34	-5	0.22±0.03	0.10±0.03

Table S2. Fitting parameters for the perpendicular component ($C_\perp$) of the cumulative squared displacement distribution.

T (°C)	$T - T_{NI}$(°C)	$f_{hopping}$	$D_{hopping}$ $\left(\mu m^2/_s\right)$
42	1	0.58±0.13	0.75±0.04
39	-1	0.56±0.04	0.45±0.07
38	-2	0.51±0.03	0.32±0.03
37	-3	0.48±0.06	0.14±0.05
36	-4	0.26±0.14	0.09±0.01
34	-5	0.14±0.09	0.04±0.04

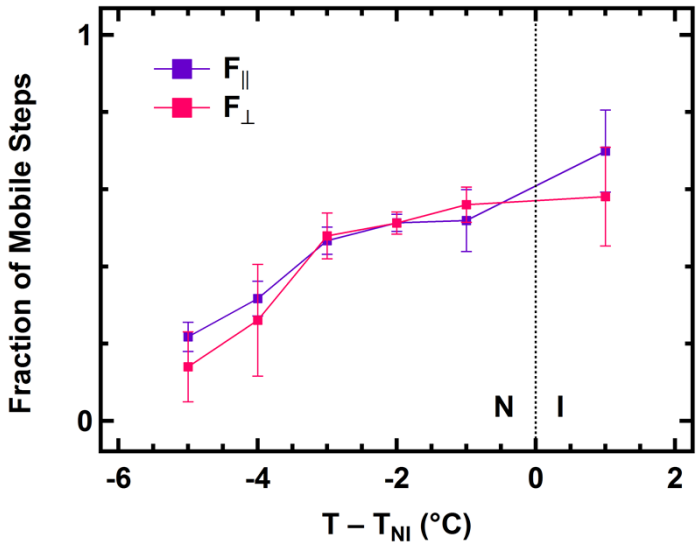

Figure S3. Fraction of mobile hopping steps as a function of temperature, obtained from fitting the cumulative distribution of squared displacements at different temperatures using equation S1.

References

1. S. M. Malone and D. K. Schwartz, *Langmuir*, 2008, **24**, 9790-9794.
2. B. R. Ratna and R. Shashidhar, *Pramana*, 1976, **6**, 278-283.
3. A. Honciuc, A. W. Harant and D. K. Schwartz, *Langmuir*, 2008, **24**, 6562-6566.