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Studies of Dynamical Layering in Adsorbed Organic Films

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ABSTRACT

We are using state-of-the-art quasi-elastic neutron scattering (QNS) to study how molecular diffusive motion in prototypical films may correlate with their lubricating properties. Our experiments have demonstrated that the High Flux Backscattering Spectrometer at the National Institute of Standards and Technology Center for Neutron Research has sufficient energy resolution and throughput for probing relatively slow diffusive motions in molecular monolayers of model lubricants such as tetracosane ($C_{24}H_{50}$ or C24). In particular, these measurements are sensitive to the molecular conformational dynamics on a nanosecond time scale. It is well known from experiments using a surface force apparatus that organic fluids confined between two surfaces exhibit a layered structure at the molecular level. This static layering has motivated us to consider the possibility that the individual molecular layers in fluid films may also have different dynamical properties. Here we report high-resolution QNS measurements on fluid monolayer, bilayer, and trilayer films of C24 adsorbed on exfoliated graphite (Grafoil). The results indicate slower molecular diffusive motion in the bottom layer of a bilayer C24 film compared to that in a monolayer, while the rate of diffusive motion in the bottom two layers of the trilayer film is comparable to that in a monolayer.

INTRODUCTION

Alkane molecules of intermediate length [C_nH_{2n+2}; $20 < n < 40$] are of interest as the principal constituents of commercial lubricants. They also serve as prototypes for studies of interfacial dynamics of more complex polymer molecules [1]. In recent experiments, we have demonstrated that the High Flux Backscattering Spectrometer (HFBS) at NIST has sufficient energy resolution and throughput to probe relatively slow diffusive motions in a single layer of alkane molecules adsorbed on a graphite basal-plane surface [2–4]. In a tetracosane (n-$C_{24}H_{50}$ denoted C24) monolayer, these motions occur on a time scale of ~0.1–4.0 ns and have not been observed using other instruments. In this work, we address the issue of how to interpret such measurements on multilayer films.

It is well known that organic fluids confined between two surfaces exhibit a layered structure at molecular level. The first evidence of this microscopic layering came from

experiments using a surface force apparatus [5]. Using this technique, Christenson et al. [6] have measured the solvation forces between mica surfaces confining fluids of even numbered *n*-alkanes from hexane to hexadecane. They observed the force to be an oscillatory function of the distance between the surfaces with a period comparable to the width of the alkane molecules. This behavior is consistent with the molecules lying in layers next to the mica surface with their long axis oriented predominantly parallel to it.

More recently, Yu et al. have used synchrotron x-ray scattering to study different liquids including tetrakis(2-ethylhexoxy)silane (TEHOS) [7] next to diamond and silicon surfaces, respectively. For both ultrathin and thick liquids on silicon substrates, they found that the molecules form 3–6 layers at the solid interface with a plane spacing close to the molecular dimensions [7].

Molecular dynamics simulations on a variety of fluids confined between two gold surfaces have also provided evidence of molecular layering [8]. The fluids investigated included the alkanes *n*-hexadecane (C16) and *n*-tetracosane (C24) as well as a branched alkane (squalane) and spherical molecules.

This evidence of static layering in organic films from both experiments and simulations has motivated us to consider the possibility that individual molecular layers in fluid films may also behave differently dynamically. In fact, evidence of such dynamical layering effects has been found in computer simulations of fluid heptane (n-C_7H_{16}) films by one of us (FYH) [9]. We have therefore begun investigating the possibility of layering effects in the diffusive motion in films of longer alkanes relevant to lubrication. In this study, we report high-resolution quasi-elastic neutron scattering (QNS) measurements on fluid monolayer, bilayer, and trilayer C24 films adsorbed on an exfoliated graphite substrate. We believe this is a favorable system for studies of dynamical layering because the large aspect ratio of the C24 molecule is likely to inhibit interlayer exchanges compared to more spherical molecules.

EXPERIMENT DETAILS

The measurements were carried out on the HFBS spectrometer [10] at the NIST Center for Neutron Research. The measurements were done over the energy range ±35 μeV with an energy resolution of ~1.0 μeV. Spectra were collected in a neutron wave vector transfer (Q) range from 0.6 to 1.7 $Å^{-1}$. The typical data collection time was about 24 h up to 48 h maximum at each temperature. We ran three different samples at coverages of a monolayer, a bilayer, and a trilayer of C24, respectively. The samples were prepared by depositing C24 from its vapor phase onto an exfoliated graphite substrate (Grafoil) in an evacuated cell at a temperature of ~200°C. The cell had an annular shape (to reduce multiple scattering) with inner and outer diameters of 20 mm and 26 mm, respectively. Preparation details have been described elsewhere [11,12].

DISCUSSION

Before the quasi-elastic measurements began, the sample was cooled to 100 K. While the sample was cooling down, we measured the elastically scattered neutron intensity with the Doppler drive at rest so that the monochromator was fixed in position. In Figure 1(a), we compare the elastic intensity as a function of temperature for the monolayer, bilayer, and trilayer

C24 samples. For all three cases, we see that the elastic intensity decreases monotonically as the temperature increases, consistent with an increase in the diffusive motion within the film. Above 300 K, the elastic intensity levels off indicating that virtually all motion within the film is taking place on a time scale faster than ~4.0 ns, corresponding to the ~1 μeV energy resolution of the HFBS so that only the graphite substrate is contributing to the elastic scattering. Figure 1(b) shows an enlarged view of the intensity of the elastic scattering from the monolayer. The change in slope occurring near 210 K appears to be consistent with a transition from a crystalline to "smectic" phase as was inferred from elastic neutron diffraction measurements and molecular dynamics simulations of a C24 monolayer [13]. These studies also show evidence of a transition from the "smectic" to an isotropic fluid phase at 340 K, which is beyond the temperature range in Figure 1(b).

As described in Ref. 2, we fit the quasi-elastic spectrum at each wave vector transfer Q to the sum of a Lorentzian and a δ function convoluted with the instrumental resolution function. These terms represented the QNS and elastic incoherent scattering, respectively. In Figure 2, we use a typical HFBS spectrum to illustrate the decomposition into the resolution-limited elastic and the Lorentzian quasi-elastic components. The fit parameters of interest are the half-width-at-half-maximum (HWHM) and the integrated intensities of the Lorentzian component and the resolution limited elastic component.

To compare the intensity of the QNS from different samples, we normalized the Lorentzian intensity to the δ function intensity at each Q. This procedure is justified because, as discussed above, in the temperature range of these measurements (> 300 K) the δ function intensity is, to a good approximation, due entirely to the elastic scattering from Grafoil substrate and hence to the amount of Grafoil in the cell. Therefore, this procedure allows us to compare the quasi-elastic intensity from samples containing different amounts of Grafoil.

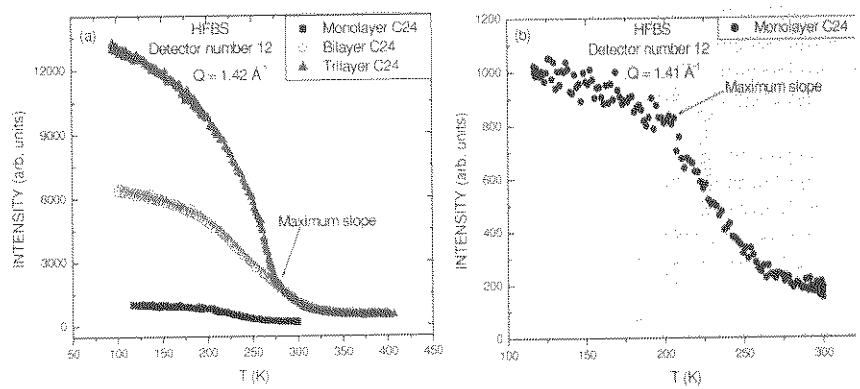

Figure 1. (a) Elastic intensity as a function of temperature as measured on the HFBS for a 0.95- (monolayer), 1.99- (bilayer), and 2.99-layer (trilayer) film of C24 adsorbed on a Grafoil substrate. These fixed window scans were done by setting the temperature ramp to 1 K/min. (b) Enlarged view of the elastic intensity as function of temperature for the monolayer film.

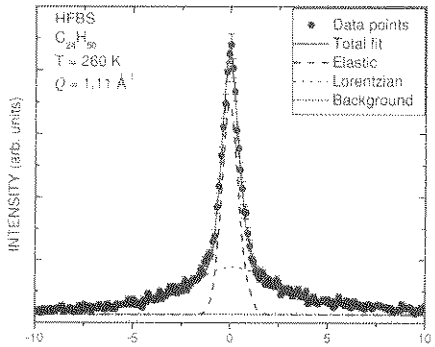

Figure 2. Typical spectrum for a C24 film of thickness 0.95 layer measured at a wave vector transfer $Q = 1.11$ Å^{-1} on the HFBS, illustrating the decomposition into resolution limited elastic and quasi-elastic (Lorentzian) components.

Figure 3 compares the QNS from the monolayer and bilayer films at a temperature near 330 K. This temperature is about 10 K below the monolayer melting point of C24. In Figure 3(a), we see a smaller width of the Lorentzian component of the QNS for the bilayer than the monolayer film, while the normalized intensity of the QNS from the monolayer and bilayer in Figure 3(b) are comparable.

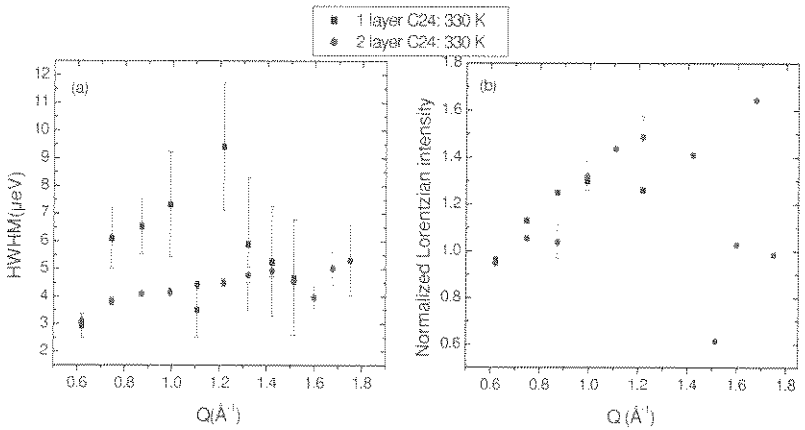

Figure 3. Comparison of the QNS measured on the HFBS from monolayer and bilayer films of C24 absorbed on Grafoil at a temperature of about 330 K. (a) Half-width-at-half-maximum (HWHM) of the Lorentzian component in the QNS vs. Q; and (b) intensity of the Lorentzian component vs. Q. In (b), only representative error bars have been included to improve clarity.

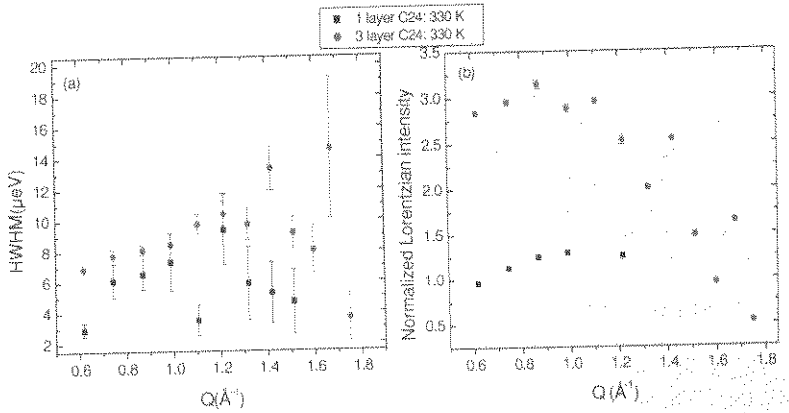

Figure 4. Comparison of the QNS measured on the HFBS from monolayer and trilayer films of C24 adsorbed on Grafoil at a temperature of about 330 K, which is about 10 K below the monolayer melting point of C24. (a) Half-width-at-half-maximum (HWHM) of the Lorentzian component in the QNS vs. Q; and (b) intensity of the Lorentzian component vs. Q. In (b), only representative error bars have been included to improve clarity.

If all of the molecules in the bilayer film were performing the same diffusive motion as those in the monolayer film, we would expect about twice the intensity of the QNS from the bilayer film. Thus the comparable quasi-elastic intensity for the monolayer and bilayer films suggests that only about half the molecules in the bilayer may be contributing to QNS. This could occur, for example, if the molecules in the top layer of the bilayer were moving too fast to be within the energy window of the HFBS (±35 μeV). The smaller energy width observed for the bilayer sample could then be attributed to the slower motion of the molecules in the layer immediately adjacent to the graphite surface.

In Figure 4, we compare the energy width and the intensity of the QNS in the monolayer and trilayer films at a temperature near 330 K. The intensity of the QNS from the trilayer in Figure 4(b) is two to three times larger than for the monolayer, depending on Q. As in the case of the bilayer film, we expect that the molecular diffusive motion in the top layer of the trilayer is too rapid to be in the energy range of the HFBS. The intensity of the QNS from the trilayer film is consistent with both of the two lower layers contributing to the spectra.

CONCLUSIONS

Our preliminary interpretation of these measurements is that the bilayer tetracosane film shows evidence of slower molecular diffusive motion in the bottom layer than in its top layer; and, moreover, the rate in the bottom layer is slower than in a monolayer film. Apparently, the presence of the upper layer inhibits diffusive motion in the bottom layer. On the other hand, in

the case of the trilayer film, the HFBS spectra are consistent with the molecular diffusive motion in the bottom two layers having a rate comparable to that in the monolayer film. This could occur, for example, if interlayer molecular exchanges between the first two layers facilitated diffusive motion within them. Apparently, such interlayer exchanges either do not occur or are less effective in the bilayer film.

It would be very desirable to use molecular dynamics simulations to study the types of diffusive motion in bilayer and trilayer C24 films for comparison with previous simulations of molecular diffusion in a monolayer film. One may then hope to verify whether the tentative interpretation that we have given here in terms of a layered fluid with a different rate of diffusion in each layer is valid.

ACKNOWLEDGMENTS

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