

ANA/IPNS/CP-100983

Dynamics of Intermediate-Length Alkane Films Adsorbed on Graphite.
K. W. Herwig, D. Fuhrmann, L. Criswell, H. Taub, F. Y. Hansen, R. Dimeo, D. A. Neumann

RECEIVED
MAR 07 2000
OSTI

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

Abstract. The dynamics of flexible chain molecules near a solid interface is of fundamental interest in polymer science. This paper makes a preliminary report on a quasielastic neutron scattering study of the dynamics of monolayer films of $C_{24}H_{66}$ adsorbed on graphite. Quasielastic scattering was observed at temperatures as low as ~180 K, well below the monolayer melting temperature of 340 K. Preliminary analysis of the data indicates that at 230 K the entire molecule executes a rolling motion about its long axis while the terminal methyl groups exhibit relatively rapid reorientation.

1. INTRODUCTION

The adsorption of long flexible-chains (composed of repeating monomer units) at a solid interface is of great interest in such vital technological fields as lubrication, protective coatings, and adhesion. Monolayer films of intermediate-length linear n -alkanes ($n-C_nH_{2n+2}$; $20 < n < 40$) are prototypical systems for investigating the structure and dynamics of adsorbed flexible chains. Previously, the monolayer structure of $n-C_{32}H_{66}$ (in its deuterated form) adsorbed on the basal planes of graphite has been investigated by neutron diffraction.[1] The low-density phase grown by deposition of the monolayer from the gas phase was observed to transform reversibly to a high-density phase upon the addition of an overlayer of the solvent $n-C_7H_{16}$. Molecular dynamics simulations have been used to interpret the temperature dependence of the diffraction data near the melting transition as a phase transition in which both translational and intramolecular disorder appear simultaneously.[2] The lattice order is lost at the same temperature that the molecular chains collapse to a more globular shape due to the introduction of *gauche* defects. In addition, recent neutron diffraction measurements show a transition from a well-ordered high-density commensurate monolayer at low temperature (~86 K) to a disordered low-density solid phase at high temperature (300 K).[3]

This paper reports on initial quasielastic neutron scattering (QNS) studies of a $n-C_{24}H_{50}$ monolayer (hereafter referred to as C24) exhibiting a low-density structure at room temperature. The data were obtained on two different spectrometers whose energy/time resolutions varied by two orders of magnitude. Interestingly, at 230 K, molecular motions with vastly different time constants are observed on the separate spectrometers.

2. EXPERIMENTAL

Details of the sample preparation have been presented elsewhere.[4] The samples were prepared by depositing C24 from its vapor phase onto an exfoliated graphite substrate (Grafoil) in an evacuated cell at elevated temperature. Neutron diffraction measurements (using the fully protonated C24) verified the presence of the low-density monolayer film at room temperature.

The high-energy resolution QNS experiments were performed using the new backscattering spectrometer, HFBS, at the National Institute of Standards and Technology's National Center for Neutron Research, Gaithersburg, MD, USA. The HFBS has an energy resolution, $\delta\omega$, of $0.85 \mu eV$ (FWHM) at the elastic peak and a Q -range of 0.25 to 1.75 \AA^{-1} . Due to intense small-angle scattering from the sample, useful data was obtained in 11 detectors covering a Q -range of 0.62 to 1.68 \AA^{-1} . Additional data were

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

collected at coarser energy resolution, $\delta\omega = 85 \mu\text{eV}$ (FWHM), using the QENS spectrometer at Argonne National Laboratory's Intense Pulsed Neutron Source. Useable spectra were collected over a Q -range of 0.4 to 2.6 \AA^{-1} , with a gap in Q due to scattering from the (002) reflection of the graphite substrate.

3. Results and Discussion

The experiment on each instrument began by performing an elastic scan from a low temperature of 120 K up to 290 and 370 K on HFBS and QENS respectively. Data were collected for 2 minutes at 2 K intervals using HFBS, with 8 minutes allotted for thermal equilibration of the sample at the next temperature. In order to obtain similar statistics on QENS, data were collected for 15 minutes every 10 K (every 5 K from 180 to 220 K), with thermal equilibration taking an average of 20 minutes. On QENS the data were summed over energy transfers from -0.040 meV to 0.040 meV , while on HFBS the monochromator drive was stopped so that all neutrons counted in the detector were elastically scattered.

Figure 1 compares the elastic scans obtained with the two spectrometers. Each point represents a sum of the counts over all useful detectors normalized to one at 120 K. The contribution from the Grafoil substrate and sample cell is approximately 0.13 for the HFBS data and 0.20 for the QENS data. It is clear from the HFBS data that the onset of diffusive motion in this system occurs at a temperature far below 340 K, the monolayer melting temperature as determined by neutron diffraction. In fact, by 290 K there is very little elastic scattering from the monolayer observable on HFBS. Most of the dynamics is so fast that it lies outside the energy window set by the instrument resolution function. The picture changes greatly when examined with the coarser resolution of QENS. Elastic intensity from the monolayer is observed over the entire temperature range. However, at low temperatures, near the onset of the phase transition indicated by the HFBS data, it would be very difficult to distinguish the temperature dependence of the QENS elastic scan from that expected from the Debye-Waller factor. As discussed below, more rapid diffusive motion can be observed at this temperature using QENS. In fact, it is the combination of the two instruments that allows us to probe the dynamics over a wide time-scale and obtain a more complete picture of the behavior of this system.

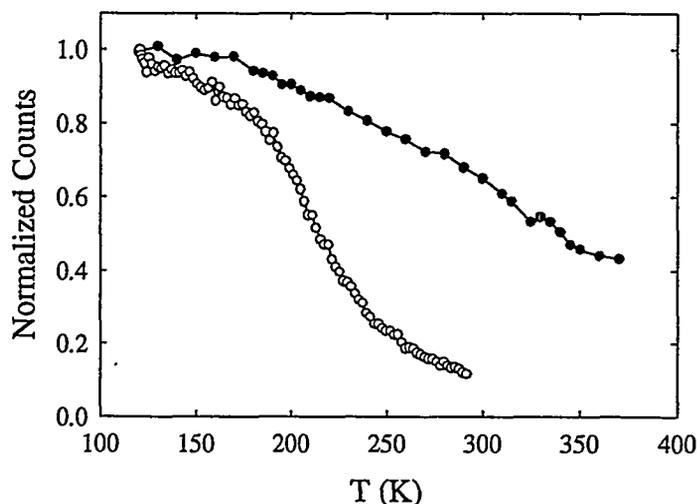


Figure 1. Elastic scan of a C24 monolayer adsorbed on graphite. The open circles are data collected using the HFBS spectrometer while closed circles are data from the QENS spectrometer.

QNS spectra were collected over a range of temperatures with both instruments. Figure 2 shows the spectrum measured from the low-density monolayer phase of C24 obtained on the HFBS at 230 K. For comparison, a spectrum at the same coverage and temperature measured on QENS is shown in Fig. 3 (note that the spectra were obtained at different Q). In both Figs. 2 and 3, the fits are the sum of a single Lorentzian and a delta-function, convoluted with the instrument resolution function (as measured at 100

K). The HFBS fit yielded a Lorentzian FWHM of $\Gamma = 1.6 \pm 0.1 \mu\text{eV}$ while the QENS fit yielded $800 \pm 70 \mu\text{eV}$.

We have also tried to fit the observed quasielastic spectra with simple models in order to infer the type of diffusive motion being probed by each spectrometer. For each instrument, all spectra were fit simultaneously to a model that included the full Q -dependence of the peak shape. A model of uniaxial rotation [5] was applied to data sets from both spectrometers. Preliminary results indicate that the motion observed on the HFBS is one where the entire molecule performs a type of rolling motion about its long axis. The fitted value of the time constant for this motion is 400 ± 100 psec. The large uncertainty in its value reflects a corresponding uncertainty in the appropriate radius of gyration to use in the model. It should be possible to improve this analysis using a radius of gyration estimated from molecular dynamics simulations now in progress. In contrast, a model of uniaxial rotation applied to the QENS data yields a time constant of 0.24 ± 0.01 psec corresponding to motion of only part of the molecule as implied by the radius of gyration, $1.2 \pm 0.05 \text{ \AA}$, inferred from the fit. Preliminary interpretation of this motion is that it involves relatively rapid reorientation of the terminal methyl groups.

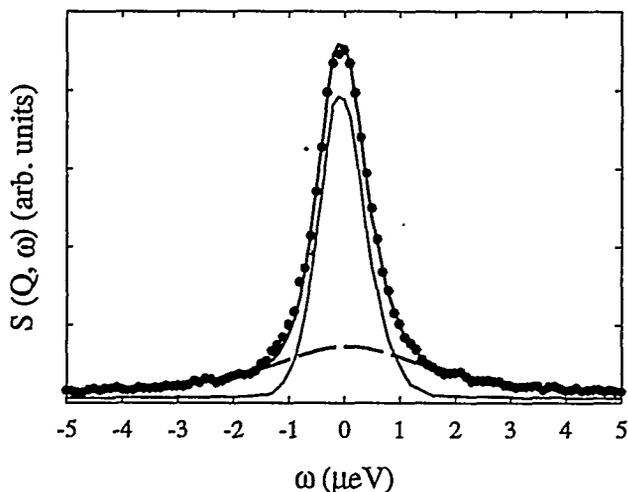


Figure 2. Spectrum obtained from C24 adsorbed on graphite at a sample temperature of 230 K using the HFBS spectrometer. Data are for a Q of 1.32 \AA^{-1} . Circles are the experimentally measured points and the heavy solid line is the full fit as described in the text. The light solid line is the elastic scattering and the dashed curve is the Lorentzian component.

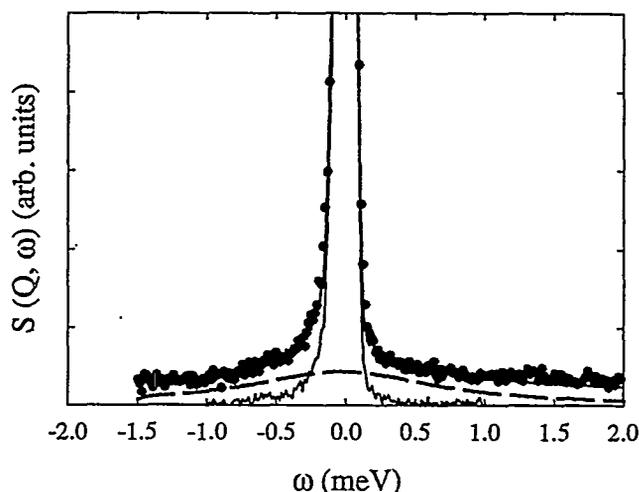


Figure 3. Spectrum obtained from C24 adsorbed on graphite at a sample temperature of 230 K using the QENS spectrometer. Data are for a Q of 2.20 \AA^{-1} . Circles are the experimentally measured points and the heavy solid line is the full fit as described in the text. The light solid line is the elastic scattering and the dashed curve is the Lorentzian component.

Conclusion

Quasielastic neutron scattering is a very useful probe of the dynamics of adsorbed molecules. In the particular case of C24 adsorbed on graphite, diffusive motion over a wide range of time scales was observed at temperatures well below the monolayer melting point. Further work includes using QNS to probe the dependence of the motion on molecular length and degree of branching within the molecule.

Acknowledgements

This research is supported by the U. S. National Science Foundation under Grant No. DMR-9802476 and the Petroleum Research Fund of the ACS. This work has benefited from use of the Intense Pulsed Neutron Source at Argonne National Laboratory, funded by the U. S. Department of Energy, BES-Materials Science under Contract W-31-109-Eng-38. One of us (KWH) wishes to acknowledge the support of the U.S. Department of Energy under contract No. DE-AC05-960R22464.

References

- [1] Herwig K. W., Matthies B. and Taub H., *Phys. Rev. Lett.* **75** (1995) 3154-3157.
- [2] Hansen F. Y., Herwig K. W., Matthies B. and Taub H., *Phys. Rev. Lett.* **83** (1999) 2362-2365.
- [3] Criswell L., Mo H., Fuhrmann D., Herwig K. W., Taub H. and Hansen F. Y., to be published.
- [4] Herwig K. W., Matthies B. and Taub H., in *Neutron Scattering in Materials Science*, edited by Neumann D. A., Russell T. P., and Wuensch B. J., (Mater. Res. Soc. Symp. Proc., Pittsburgh, PA, 1994), Vol. 376.
- [5] Bée M., *Quasielastic Neutron Scattering: Principles and Applications in Solid State Chemistry, biology, and Materials Science* (Adam Hilger, Bristol, England, 1988), 186-188.