Diffusive motion in model soft matter systems: quasielastic neutron scattering study of short- and intermediate-length alkane layers

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Abstract

Among organic-chain molecules, normal alkanes $\text{[CH}_3\text{(CH}_2\text{)}_{n-2}\text{CH}_3; \quad n < 40]$ provide model systems in which to study the effect of molecular flexibility on diffusion in adsorbed films. Here we give an overview of our quasielastic neutron scattering studies of alkane films adsorbed on a graphite substrate, emphasizing the dependence of the observed spectra on the molecular length. © 2000 Elsevier Science B.V. All rights reserved.

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A quantitative understanding of diffusion in \textit{n}-alkane films, one of the simplest families of chain-like organic molecules, may assist in the development of methods for investigating the interfacial diffusive motion of complex polymers.

In this paper, we extend previous studies to monolayers of longer alkanes. Our main objective here is to investigate how the quasielastic scattering from these alkane monolayers depends on the molecular length. We have conducted quasielastic neutron scattering (QNS) experiments on the QENS spectrometer \cite{1} at the intense pulsed neutron source (IPNS) of Argonne National Laboratory (USA) on bulk heptane (\textit{n}-C\textsubscript{7}H\textsubscript{16}) and the heptane monolayer on an exfoliated graphite substrate, and a heptane monolayer vapor-deposited over the dotriacontane (\textit{n}-C\textsubscript{32}H\textsubscript{66}) monolayer. The latter system was of interest as a first step in studying diffusive processes related to selective adsorption \cite{2}.

The QNS spectra were first analyzed by fitting a model-independent scattering function consisting of a sum of elastic and Lorentzian components to the data. The results of the model-independent analysis of the QNS spectra at room temperature are shown in Fig. 1. In the upper panel, the HWHM of the Lorentzian versus the wave vector transfer is plotted. There is very good agreement between bulk heptane (\textit{n}-C\textsubscript{7}H\textsubscript{16}) and the heptane monolayer in the low-$Q$ region, while the longer-chain dotriacontane (\textit{n}-C\textsubscript{32}H\textsubscript{66}) monolayer has a lower HWHM in this $Q$ range. At higher $Q$, however, the HWHM of the QENS spectra of the heptane and dotriacontane monolayers become comparable in magnitude but are smaller than that of the bulk heptane.

At the bottom of Fig. 1, the Lorentzian intensity versus $Q$ for the same three systems at room temperature is displayed. For both bulk heptane and the heptane monolayer, the Lorentzian intensity decreases as a function of $Q$. The $\textit{n}$-C\textsubscript{32}H\textsubscript{66} monolayer shows a pronounced maximum around 1.5 \AA$^{-1}$ followed by a minimum at 2.1 \AA$^{-1}$.
In order to extract diffusion constants from the quasielastic spectra, the data were analyzed using specific models of diffusive motion. The bulk heptane data were fitted with a scattering law consisting of 3D translational scattering function convoluted with that for isotropic rotation. Spectra at 12 different \( Q \) values spanning the spectrometer’s accessible range were fit simultaneously to this model. At 294 K, the best fit yielded a translational diffusion constant \( D_t = 1.2 \pm 0.2 \times 10^{-5} \text{cm}^2/\text{s} \) and a rotational diffusion constant \( D_r = 10 \pm 5 \times 10^6 \text{s}^{-1} \). The diffusion constants of butane, the only other alkane whose bulk diffusive motion has been studied by QNS [3] are compared with those of bulk heptane in Table 1.

Applying the analysis described above to the room-temperature spectra to the C\(_7\)H\(_{16}\)/C\(_{32}\)D\(_{66}\)/graphite system obtained over the full \( Q \)-range of the spectrometer yielded the diffusion constants \( D_t = 1.2 \pm 0.2 \times 10^{-5} \text{cm}^2/\text{s} \) and \( D_r = 22 \pm 5 \times 10^6 \text{s}^{-1} \). We see that the diffusion constant in the heptane monolayer for translational motion parallel to the surface is, within error bars, the same as in the bulk.

The dotriacontane monolayer spectra at room temperature and above could not reproduced by the above models. Recent molecular dynamics simulations [4] suggest that the ends of the dotriacontane molecules are raised above the surface so that their motion may be approximated by isotropic rotation about a point near the chain end. For this reason, we are extending our analysis to include isotropic rotational diffusion about a smaller radius of gyration.

In Table 1, the extracted diffusion constants for alkane layers of this study are also compared to previous investigations. We see that the heptane layer has a smaller translational diffusion constant than the butane and hexane monolayers adsorbed on graphite.

Our study demonstrates that quasielastic neutron scattering can be used to study the diffusive motion in prototypical polymers in the time domain of 1–40 ps. Both translational and intramolecular degrees of freedom contribute to the diffusive motion on this time scale. Molecular dynamics simulations are now being used to determine the relative contribution of each type of motion.

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References


\begin{table}
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\begin{tabular}{|c|c|c|c|c|}
\hline
System & \( T(K) \) & \( T/T_{\text{melt}} \) & \( D_t \) (\(10^{-5}\text{cm}^2/\text{sec})\) & \( D_r \) (\(10^6\text{s}^{-1})\) & Ref \tabularnewline
\hline
Bulk C\(_7\)H\(_{10}\) & 190 (1.41) & 2.3 & 277 & [3] \tabularnewline
Bulk C\(_7\)H\(_{16}\) & 298 (1.63) & 1.2 & 10 & This work \tabularnewline
CH\(_4\)/graphite & 71.5 (1.49) & 8.3 & - & [5] \tabularnewline
C\(_7\)H\(_6\)/graphite & 122 (1.88) & 5.0 & 50 & [6] \tabularnewline
C\(_7\)H\(_{10}\)/graphite & 149 (1.28) & 1.7 & 7.9 & [7] \tabularnewline
C\(_7\)H\(_{14}\)/graphite & 215 (1.26) & 1.7 & 45 & [7] \tabularnewline
C\(_7\)H\(_{16}\)/C\(_{32}\)D\(_{66}\)/graphite & 298 (1.75) & 1.2 & 22 & This work \tabularnewline
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\caption{Diffusion constants for bulk \( n \)-alkanes and alkane layers of various chain length determined by quasielastic neutron scattering.}
\end{table}