Intramolecular Diffusive Motion in Alkane Monolayers Studied by
High-resolution Quasielastic Neutron Scattering and
Molecular Dynamics Simulations

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Abstract

Molecular dynamics simulations of a tetracosane (n-C_{24}H_{50}) monolayer adsorbed on
a graphite basal-plane surface show that there are diffusive motions associated with the
creation and annihilation of gauche defects occurring on a time scale of ~0.1–4 ns. We
present evidence that these relatively slow motions are observable by high-energy-
resolution quasielastic neutron scattering (QNS) thus demonstrating QNS as a
complementary technique to nuclear magnetic resonance for studying conformational
dynamics on a nanosecond time scale in molecular monolayers.
Intermediate-length alkane molecules \((C_nH_{2n+2}; 15 < n < 35)\) adsorbed on solid substrates offer attractive model systems for studying a wide range of interfacial phenomena. Such alkanes are believed to be large enough to exhibit some features of more complex adsorbed polymers and yet small enough to be tractable in detailed molecular dynamics (MD) simulations. They have been used to address a variety of issues of current interest including polymer film growth [1], selective adsorption of polymers [2], microscopic mechanisms of friction and lubrication [3], and the gel-to-fluid transition in bilayer lipid membranes [4].

In the last example, we refer to MD simulations and neutron diffraction measurements [4] that suggest the melting transition in monolayers of tetracosane \((n-C_{24}H_{50} \text{ or } C24)\) and dotriacontane \((n-C_{32}H_{66} \text{ or } C32)\) adsorbed on a graphite basal-plane surface to be analogous to the gel-to-fluid transition in bilayer lipid membranes [5]. That is, MD simulations show evidence of monolayer melting in which intramolecular and translational order are lost simultaneously. Figure 1 presents top views of the C24 molecules in the MD simulation cell both above and below the transition temperature at \(~340\) K. At 230 K (left panel), we see translational order manifested by the lamellar structure of the monolayer [6]. Since both the simulations and quasielastic neutron scattering (QNS) measurements (see below) indicate some translational diffusive motion within the lamellae at this temperature, we refer to this structure as the “smectic” phase. At 350 K (right panel), the individual molecules have transformed to a more globular shape, i.e., they undergo “chain-melting,” and the monolayer has lost its translational order characterized by the lamellar structure [4]. As in the case of the gel-to-fluid
transition in bilayer lipid membranes [5], the MD simulations demonstrate [4] that the simultaneous chain and lattice melting result from an abrupt increase in the number of gauche defects within the central region of the chains.

For over thirty years, nuclear magnetic resonance has been used to investigate the conformational dynamics of the lipid molecules in membranes [7]. Measurements of the nuclear quadrupole splitting at selectively deuterated methylene groups along the alkyl chains have yielded the distribution of gauche defects along the chains in the membrane’s fluid phase [8]. Although cold neutron spectroscopy has proved to be a powerful research tool for investigating molecular dynamics on times scales in the range $10^{-13} - 10^{-9}$ s in many areas of condensed matter research, it has been difficult to apply the technique to biophysical systems such as lipid membranes due to their complexity, small size, and the relatively long time scale of their motions (> 1 ns).

The simpler structure of an alkane monolayer on graphite, a single layer of flexible-chain molecules without headgroups on a well-characterized substrate, motivated us to undertake a study of the molecular conformational dynamics in this system. Here we describe how MD simulations can be combined with high-resolution QNS to investigate the intramolecular diffusive motion in these monolayers associated with the creation and annihilation of gauche defects.

The QNS experiments were performed on the new High Flux Backscattering Spectrometer (HFBS) at the Center for Neutron Research, National Institute of Standards and Technology [9]. The HFBS has a neutron energy resolution of ~1.0 μeV and a dynamic range of 0–36 μeV. Spectra were collected in a neutron wave vector transfer
(Q) range from 0.6 Å\(^{-1}\) to 1.7 Å\(^{-1}\). The large solid angle subtended by the silicon analyzing crystals used to select the final neutron energy makes the HFBS particularly effective for inherently small samples such as adsorbed monolayers.

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. Preparation details have been described elsewhere [10]. The samples had an annular shape (to reduce multiple scattering) with a height of 30 mm and an inner and outer diameter of 16 mm and 22 mm, respectively. Consistent with earlier studies [6], room temperature neutron diffraction measurements at the University of Missouri Research Reactor on the same samples used for the QNS experiments confirmed the presence of the low-density “smectic” monolayer C24 phase shown in Fig. 1 (left panel).

Neutron diffraction measurements on deuterated samples show that the C24 monolayer undergoes a transition from the “smectic” to a commensurate crystalline phase at ~215 K, below which the monolayer contracts by about 8% in a direction parallel to the lamellae boundaries [11]. In this higher-density crystalline phase, the nearest-neighbor molecular separation perpendicular to the chain axes is 4.26 Å = \(\sqrt{3} a_g\) where \(a_g = 2.46\) Å is the graphite basal-plane lattice constant.

In our quasielastic experiments, the C24 molecules are protonated so that the scattered neutron intensity is completely dominated by the incoherent scattering from the hydrogen which is proportional to \(S_{\text{inc}}(Q,\omega)\), the time Fourier transform of the intermediate scattering function \(F_s(Q,t) = \frac{1}{N} \sum_{j=1}^{N} \exp\left\{iQ \cdot (\mathbf{R}_j(t) - \mathbf{R}_j(0))\right\}\). \(F_s(Q,t)\) is in
turn the space Fourier transform of the self-correlation function $G_s(r,t)$, which gives the probability of finding an atom $j$ at $\mathbf{R}_j(t)$ at time $t$ given that the same atom was at $\mathbf{R}_j(0)$ at time zero. In Fig. 3(a), we compare schematically $F_s(\mathbf{Q},t)$ for diffusive processes that are “fast” and “slow” on the time scale accessible to the HFBS. For the “slow” process, one may follow the decay of $F_s(\mathbf{Q},t)$ to a time-independent value due to any elastic component in the scattering (zero in its absence). For the “fast” process, we take an extreme example by describing the time decay of $F_s(\mathbf{Q},t)$ by a $\delta$-function. Figure 3(b) contains $S_{inc}(Q,\omega)$ for the same “fast” and “slow” processes depicted in Fig. 3(a). For the “slow” process, the inelastic part of $S_{inc}(Q,\omega)$ is bell-shaped whereas the “fast” process yields a flat, nearly frequency-independent contribution to the scattering function. Therefore, it is possible to characterize the observed quasielastic scattering contributed by the “slow” process without hindrance from the faster motions in the system.

We began the quasielastic measurements at low temperature where we anticipated that the molecular diffusive motion would be simplest to describe. Upon heating the sample to a temperature of at $\sim 215$ K, close to the crystalline-to-“smectic” phase transition [11], we observe quasielastic scattering with sufficient intensity to determine the $Q$ dependence of its energy width. At each $Q$, the quasielastic intensity is fit to the sum of a Lorentzian and a delta-function convoluted with the instrumental resolution function. We see in Fig. 2 that the half-width at half-maximum (HWHM) of the Lorentzian component is essentially dispersionless at temperatures of 215 K and 230 K.

As suggested by the molecular motions observed in our MD simulations, we use a model of uniaxial rotation about the long molecular axis (aligned parallel to the graphite
surface) to fit the observed quasielastic spectra. This model is also consistent with the $Q$-dependence of the constant level of the intermediate scattering function at long times calculated from the MD simulations. At a temperature of 230 K, the model gives a time constant of $400 \pm 100$ ps for this uniaxial rotational motion [12]. The large uncertainty reflects a corresponding uncertainty in the radius of gyration. At 260 K, the energy width of the quasielastic scattering increases with $Q$ as shown in Fig. 2. We interpret this as the onset of bounded translational motion of the molecules within the lamellae of the “smectic” phase as seen in our MD simulations.

Based on the qualitative time-scale analysis in Fig. 3, our strategy in probing diffusive motion related to the creation and annihilation of gauche defects in the C24 molecules is to use the MD simulations to find a temperature and wave vector range in which all other diffusive motion will be “fast” and therefore contribute only a “flat” background to the quasielastic intensity. For this purpose, we have constructed a matrix operator that projects out the center-of-mass motion, the rigid rotational motion, and the intramolecular motion from the arbitrary displacement of the atoms in a molecule [13]. The intramolecular motion includes vibration, libration, and cooperative motion of atom groups required to create or annihilate a gauche defect.

Figure 4(a) shows the intermediate scattering functions calculated from the MD simulations for the rigid rotational and intramolecular motions at $Q = 1.00 \, \text{Å}^{-1}$ and 260 K. At this temperature, the simulations indicate that there are only a few gauche defects in the molecules and that these are localized at the chain ends [4]. The open triangles show the contribution to the intermediate scattering function from rotational motion
about all three principal axes of the molecule whereas the closed triangles indicate the intermediate scattering function corresponding to the intramolecular motion after both the rotational motion and the center-of-mass motion have been removed. For both cases, we see that the intermediate scattering function at 260 K is very similar to the one for the “fast” process depicted in Fig. 3(a), i.e., well described by a delta-function at time $t = 0$. In this way, we infer that the rigid rotational, vibrational, and librational diffusive motions are too fast to be detected within the dynamical range ($<1–36 \mu eV$) of the HFBS. Furthermore, upon heating, these motions will be even faster so that no observable QNS is expected unless a new, slower motion is activated.

In Fig. 4(b), we show the same intermediate scattering functions calculated from the simulation for rigid rotational motion (open triangles) and for the intramolecular motion (solid triangles) as appeared in Fig. 4(a) but at a temperature of 330 K. It is interesting to see that the intermediate scattering functions now have the qualitative shape expected for the “slow” process depicted in Fig. 3(a), suggesting that, in fact, slower rotational and intramolecular motions have been activated. The temperature of 330 K is 10 K below the C24 monolayer melting point where our MD simulations show that, in addition to a large number of gauche defects at the chain ends, a significant number of these defects have now appeared in the central region of the alkane chains [4,14]. Thus it is appealing to interpret these slow intramolecular diffusive motions as associated with the creation and annihilation of gauche defects near the chain centers. Presumably, these motions are slower than for the defects near the chain ends, since they involve the cooperative motion of larger groups of atoms. The “slow” diffusion indicated
by the intermediate scattering function for rigid molecular rotation may also result from a larger number of gauche defects in the molecules’ central region. These defects produce a more compact shape of the C24 molecules as measured, e.g., by their average end-to-end distance [4,14]. The slower rotational diffusion can then be explained by the larger moment of inertia about each of the principal molecular axes.

In order to obtain further evidence that the dynamics of gauche defects in the alkane molecules can have an observable effect on the QNS spectra, we have performed MD simulations at 330 K with stiffened chains to inhibit defect formation. This was accomplished by tripling the trans-to-gauche energy barrier within the C24 molecule and recalculating the intermediate scattering functions. The results shown in Fig. 4(c) indicate that the intermediate scattering functions are well approximated by a delta-function at time $t = 0$ and that the slow diffusive motions have disappeared as anticipated.

Our measurements support the prediction of these MD simulations that QNS should be observable within the energy window of the HFBS at 330 K, arising from the gauche defect motion in the central region of the C24 chains. In Fig. 5, we have analyzed the $Q$ dependence of the HFBS spectra at temperatures of 285 K and 330 K in the same way as for lower temperatures (see Fig. 2): (a) the Lorentzian HWHM characterizing the energy width of the observed QNS; and (b) the relative intensity of the Lorentzian component in the spectra. Although the intensity becomes very weak at 330 K, it is clear that there is still QNS within the dynamic range of the HFBS. Comparing with Fig. 2, we see that at each $Q$ the energy width of the QNS continues to increase with temperature above 260 K. There is also a large increase in the slope of the HWHM vs. $Q$ between 260 K and 285 K.
For comparison, we have also plotted in Fig. 5 (dashed line) the HWHM of a Lorentzian fitted to $S_{in}(Q,\omega)$ calculated from the MD simulation at 330 K after removing the center-of-mass motion from the C24 molecules. It should reflect the contribution to the width of the quasielastic scattering from both rotational and intramolecular diffusive motions. It shows qualitative agreement with the measured widths. Unlike the experiment, the simulation predicts a temperature range between 260 K and 300 K, a range below the appearance of a large number of gauche defects in the molecular interior, in which rotational and intramolecular diffusive motion is sufficiently rapid to be outside the energy window of the spectrometer. We believe that this is not observed experimentally because the unified-atom representation of the molecule in the simulation [4] underestimates the moment of inertia about the long molecular axis resulting in faster rotational diffusion.

In summary, these experiments demonstrate that neutron spectrometers such as the HFBS combining both high energy resolution with large throughput can be used to probe molecular conformational dynamics on a nanosecond time scale in monolayer films. Future experiments are planned to investigate the lubricating properties of molecularly thin alkane films [15] by correlating the conformational dynamics observed by quasielastic neutron scattering with nanoscale friction measurements by atomic force microscopy.

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11. B. Matthies et al., unpublished.


14. Figure 4 of Ref. 4 contains distributions of gauche bonds along a molecular chain in a C32 monolayer. Similar distributions have been calculated from MD simulations of C24 monolayers [F. Y. Hansen, K. W. Herwig, and H. Taub, unpublished].

Figure captions

Fig. 1. Top view showing configuration of C24 molecules in the MD simulation cell: “smectic” phase (left); fluid phase (right).

Fig. 2. Results of fitting the quasielastic spectra at low temperatures: the energy width of the Lorentzian component (half-width at half-maximum) is plotted versus wave vector transfer $Q$.

Fig. 3. Sketch of the (a) intermediate self scattering function $F_s(Q,t)$ and (b) the incoherent scattering function $S_{inc}(Q,\omega)$ for “slow” and “fast” diffusive processes on the time scale accessible to the HFBS.

Fig. 4. The intermediate self scattering function for the rigid rotational and intramolecular motions in the C24 monolayer calculated from the MD simulation at various temperatures: (a) 260 K; (b) 330 K (which is 10 K below the monolayer melting transition); and (c) at 330 K but with stiffened chains to inhibit formation of gauche defects.

Fig. 5. Results of fitting the quasielastic spectra at higher temperatures: (a) the energy width of the Lorentzian component vs. wave vector transfer $Q$; (b) the intensity of the Lorentzian component vs. $Q$. In (a), the dashed line indicates values calculated from the MD simulations at 330 K.
Fig. 1

"Smectic" ~340 K Fluid
Fig. 2
Fig. 3
Fig. 4

C24 monolayer on graphite

(a) $T = 260 \, \text{K}$

- --- rigid rotational motion
- •- intramolecular motion

(b) $T = 330 \, \text{K}$ (normal molecules)

(c) $T = 330 \, \text{K}$ (stiffened molecules)

Intermediate Scattering Functions at $Q = 1.00 \, \text{Å}^{-1}$

Time (ps)
Fig. 5