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Confinement-Induced Ordering of Alkanes between an Elastomer and a Solid Surface

Kumar Nanjundiah and Ali Dhinojwala*

Department of Polymer Science, The University of Akron, Akron, Ohio 44325, USA
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We have studied the molecular structure of liquid alkanes confined between a flexible elastomeric poly(dimethyl siloxane) lens and a rigid sapphire substrate using surface-sensitive infrared-visible sum frequency generation spectroscopy. The reduction in the *gauche* defects suggests ordering of liquid alkanes under confinement. The cooling of confined liquid below the freezing temperature leads to crystallization with alkane molecules lying on the substrate with the symmetry axis parallel to the surface normal. This structure is very different from the bulk alkane crystals next to sapphire or air interfaces.

In recent years, confinement of liquids has generated great interest in understanding friction, lubrication, and wear between solid surfaces [1–7]. Tires on roads, windshield wipers, and the movement of human joints are some examples where flexible-rigid contact interfaces are experienced. The intriguing question is whether the structure and viscosity of confined liquid is different from that in the bulk. No noticeable change in liquid viscosity down to thickness of 25 nm was suggested by Roberts and Tabor for rubber in contact with glass surfaces [1]. Because of surface roughness, Tabor's experiments were inconclusive for thickness less than 25 nm. Using atomically smooth mica surfaces, Israelachvili and co-workers have studied nanometer-thin films and have shown that oscillatory force profiles are observed for a variety of liquids due to layering of molecules under confinement [2]. These results have also been supported by computer simulations [5,8]. As a consequence of layering, the Newtonian liquids show solidlike response under confinement [3,4]. However, more recent measurements using a different procedure to cleave mica show a modest increase in apparent viscosity for nanometer-thin confined liquids [9,10]. We have revisited Tabor's experiment to address the open question of whether confinement affects the structure of liquids between an elastomer [poly(dimethyl siloxane) (PDMS) in our measurements] and a rigid substrate (sapphire). Surface-sensitive infrared-visible sum frequency generation spectroscopy (SFG) was used to directly probe the structure of confined fluids. These results provide the first spectroscopic measurement of molecular structure under confinement between surfaces of practical importance.

SFG involves the spatial and temporal overlap of a high intensity visible laser beam of frequency, ω_1 with a tunable infrared beam of frequency ω_2. According to the dipole approximation, the generation of SFG photons is forbidden in centrosymmetric bulk and permitted only at interfaces where inversion symmetry is broken. The SFG signal is resonantly enhanced when IR frequency overlaps the molecular vibrational mode, which is both Raman and IR active. Further enhancement in signal intensity is achieved when the angle of input beams are close to the critical angle

for total internal reflection [11]. The details of the instrument design are explained elsewhere [12]. The sample geometry used is shown in Fig. 1(a). This novel approach of using a flexible elastomeric lens which deforms against a flat solid surface to confine molecules offsets the need to have perfectly parallel surfaces as we approach separations of molecular dimensions.

PDMS (Sylgard 184, Dow Corning) semispherical lenses of radius 3–4 mm were prepared using the procedure developed by Chaudhury [14] (rms roughness of 0.6 nm). The lenses were extracted with toluene to remove any unreacted PDMS chains. The lenses after drying were soaked in either *n*-hexadecane (Alfa Aesar, 99% purity, $T_m = 291$ K) or *n*-pentadecane (TCI, 99% purity, $T_m = 283$ K). Figure 1(b) shows the shear stresses as a function
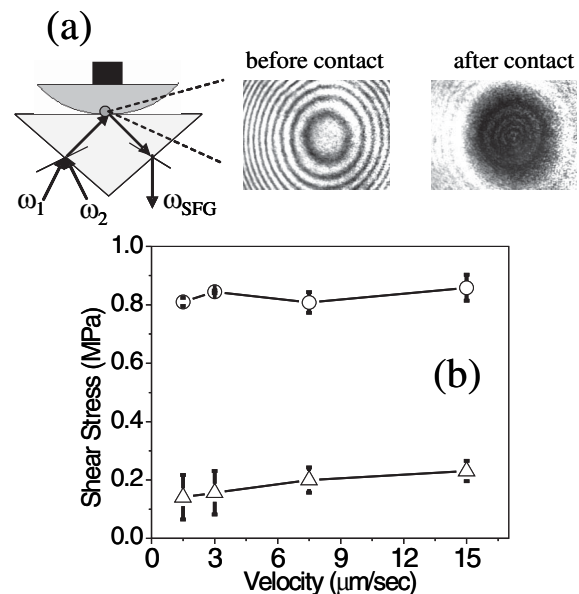

FIG. 1. (a) Schematic diagram of the total internal reflection geometry and the images of Newton rings formed just before contact and the uniform flattened area after contact. (b) Plot of shear stress versus sliding velocity for extracted PDMS lens (○) and hexadecane soaked lens (△) against sapphire. The data presented here are for normal loads of 10–60 mN.

of velocity for extracted PDMS lenses and hexadecane soaked PDMS lenses against sapphire surfaces (rms roughness of 2.4 nm). The soaked lenses show much lower shear stresses in comparison to a dry lens sliding against a sapphire surface. Figure 1 also shows images of Newton rings formed just before contact and the uniform flattened area after contact. The alkane film thickness was estimated, using the procedure described in Ref. [15], to be <10 nm for the normal load of 10 mN–0.3 N. Exact determination of thickness below 10 nm was not possible due to background scattering from PDMS lenses. An estimate from the shear stress of 0.1 MPa, velocity of 10 μm/s, and thickness of 1–10 nm shows the effective viscosity of confined hexadecane to be 10–10^2 Pa s as compared to bulk viscosity of 3×10^{-3} Pa s. This calculation is an approximation since it does not include influence of adhesive forces. Interestingly, this increase in viscosity is similar to that observed for hexadecane confined between mica surfaces [3].

SFG scans using SSP polarization (s-polarized SFG, s-polarized visible and p-polarized IR) in the CH range for alkanes (2750–3050 cm^{-1}) were taken for liquid alkane-sapphire, alkane crystal-sapphire, confined alkane-sapphire and confined crystal alkane-sapphire interfaces. The peak assignments based on bulk IR and Raman measurements for the CH stretches are as follows [16]: peaks between 2875–2880 cm^{-1} are assigned to the CH$_3$ symmetric stretch (r$^+$); two peaks at 2950 cm^{-1} and 2965 cm^{-1} to the CH$_3$ asymmetric stretches (r$^-$); peaks between 2840–2860 cm^{-1} to the symmetric CH$_2$ stretch (d$^+$); peak between 2920–2925 cm^{-1} to the asymmetric CH$_2$ mode (d$^-$); and peak in the range of 2930–2940 cm^{-1} to the CH$_3$ Fermi resonance due to the overlap of symmetric overtone with the bending mode (r$_{FR}^+$). To obtain quantitative information, the spectra were fitted using the following Lorentzian equation [11],

$$I(\text{SFG}) \propto \left| \chi_{\text{eff,NR}} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q - i\Gamma_q} \right|^2, \quad (1)$$

where A_q, Γ_q, and ω_q are the strength, damping constant, and angular frequency of a single resonant vibration, respectively. $\chi_{\text{eff,NR}}$ is the nonresonant part of the signal.

Understanding the structure of confined liquids requires first the characterization of the structure of bulk liquids next to a sapphire surface. SFG spectra of hexadecane and pentadecane liquid in contact with sapphire are shown in Figs. 2(a) and 2(c). For both hexadecane and pentadecane, the SFG spectra show peaks associated with CH$_2$ symmetric, CH$_2$ asymmetric, CH$_3$ Fermi, and CH$_3$ asymmetric modes. The spectra also show an increase in intensity beyond 2970 cm^{-1}, which can be attributed to the surface OH groups on sapphire. The ratios of d$^+$/r$^+$ and r$^-$/r$^+$ obtained from fitting the spectra are shown in Table I. For alkane/sapphire interfaces, the high CH$_2$ and CH$_3$ asymmetric modes indicate the presence of *gauche* defects and the CH$_3$ groups are tilted away from the surface normal.
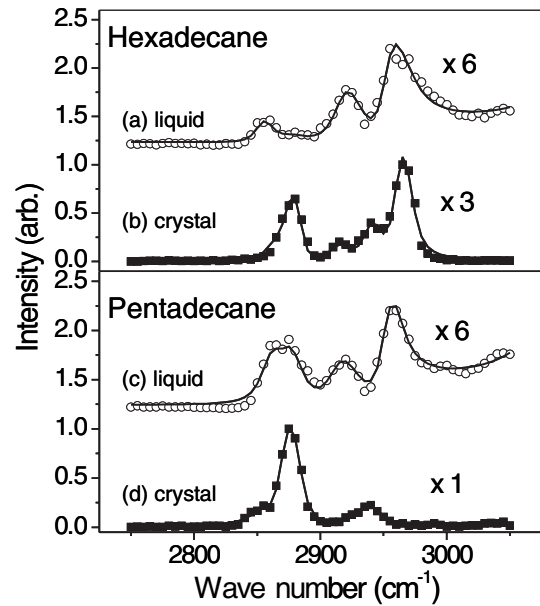

FIG. 2. SSP spectra of hexadecane (a) and pentadecane (c) liquid/-sapphire interfaces at 295 K. The SSP spectra for hexadecane (b) and pentadecane (d) crystal-sapphire interfaces were taken at 287 and 279 K, respectively. The solid lines are fits using Eq. (1). The SFG spectra were offset along the *y* axis by an arbitrary amount and were scaled for clarity.

These spectra for liquid alkanes are similar to those reported for hexadecane next to glass [17].

Figures 2(b) and 2(d) show hexadecane and pentadecane spectra below T_m. The SFG peaks are much sharper and intense in comparison to the broad peaks observed in the liquid spectra. The SFG spectrum for a pentadecane crystal-sapphire interface has two dominant peaks associated with CH$_3$ symmetric and CH$_3$ Fermi. The contribution of CH$_2$ symmetric only appears as a weak shoulder. The presence of strong CH$_3$ peaks suggests that the pentadecane molecules are well ordered in an all-trans conformation. The hexadecane crystal signals are much weaker in comparison to pentadecane. Hexadecane is a symmetric molecule and is expected to be SFG inactive when the molecule is in an all-trans conformation. The SFG data for hexadecane crystals are only presented to make qualitative comparison with the results from odd alkane and to show formation of all-trans conformation when the molecule crystallizes.

The SFG spectra of confined alkane between the PDMS lens and sapphire substrates are shown in Figs. 3(a) and 3(c). The SFG peaks are associated with CH$_3$ and CH$_2$ groups of confined alkanes rather than methyl groups of PDMS. This can also be observed by the control experiment of dry contact between PDMS and the sapphire substrate as shown in Fig. 3(e). The CH$_3$ symmetric and CH$_3$ asymmetric peaks of Si-(CH$_3$)$_2$ are at 2905 cm^{-1} and 2965 cm^{-1}, respectively. In addition, the SFG intensity is much weaker for dry contact. The spectra of confined alkanes-sapphire interfaces have contributions from the

TABLE I.   Ratios of $|A_q|$ of CH_2 (d^+)/CH_3 stretches (r^+) and CH_3 asymmetric (r^-)/CH_3 symmetric (r^+) for hexadecane and pentadecane in contact with sapphire at various conditions.

	Hexadecane		Pentadecane	
	d^+/r^+	r^-/r^+	d^+/r^+	r^-/r^+
Bulk Liquid	1.2	4.3	0.9	1.4
Bulk Crystal	0.2	1.0	0.06	0.1
Confined Liquid	...	0.4	0.05	0.4
Confined Crystal	0.23	0.1	1.4	≈ 0

CH_3 symmetric mode and a broad convoluted peak due to CH_2 asymmetric, CH_3 Fermi, and CH_3 asymmetric modes. The confinement-induced ordering can be inferred from the higher SFG signals (3 times higher than liquid spectra), the presence of CH_3 symmetric mode and the weak CH_2 symmetric mode. Both the confined and bulk pentadecane liquid spectra have strong CH_3 asymmetric signals, which indicates methyl groups are on average tilted with respect to the surface normal.

Surprisingly, the confined liquid does not show differences in signal intensity between odd and even alkanes. This suggest that the order of confined alkane is not similar to that of crystals. To understand this further, we have cooled the confined alkanes below the freezing temperature and the SFG spectra are shown in Figs. 3(b) and 3(d) for hexadecane and pentadecane, respectively. The pentadecane confined crystal-sapphire interface is dominated by the presence of a strong CH_2 symmetric peak at 2840 cm^{-1} along with the CH_3 symmetric and CH_3 Fermi resonance modes. The SFG intensity for confined pentadecane crystals is higher than that of confined liquid-sapphire interface. The presence of a strong CH_2 symmetric mode is surprising and suggest that a confined crystal structure is very different from a bulk pentadecane crystal-sapphire interface. The transition from confined ordered liquid to confined crystal is sluggish with the structure developing with time. In contrast, the bulk liquid to crystal transition shows no time dependent structural change. Also, the absence of an odd-even effect found in confined liquid reappears in the case of confined crystals because the SFG intensity for confined hexadecane crystal-sapphire interface is much lower than that of pentadecane crystal-sapphire interface. These observations confirm that the confined liquid is more ordered but does not crystallize upon confinement and crystallization requires cooling down below the bulk freezing temperature.

The strong methylene intensity in confined crystals cannot be explained by the presence of *gauche* defects as in the case of liquid alkane-sapphire interfaces [17]. With help of a simple model, we postulate that the confined pentadecane chains are crystallizing with the chains lying flat next to the sapphire substrate. The molecular hyperpolarizability was derived by using the IR dipole moment and Raman tensor of a single C-H bond [18] and the normal coordinates for methyl vibrations as given by Snyder [16]. The alkane is
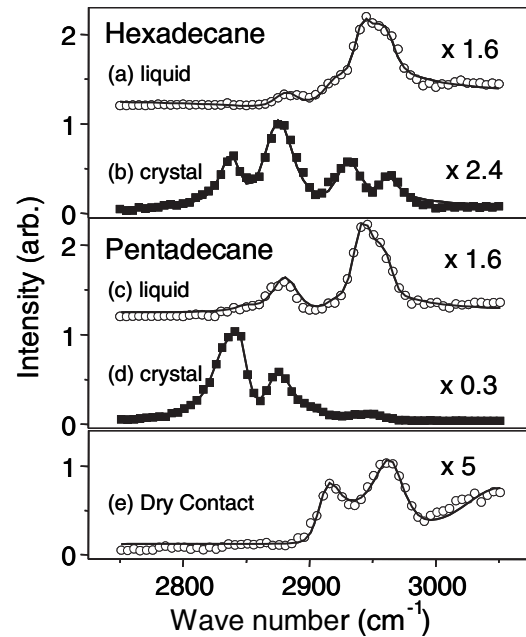

FIG. 3.   SSP spectra of hexadecane (a) and pentadecane (c) confined liquid-sapphire interfaces at 295 K. The SSP spectra for confined hexadecane (b) and pentadecane (d) crystal-sapphire interfaces were taken at 287 and 279 K, respectively. The dry PDMS-sapphire SFG spectrum is shown in (e). The solid lines are fits using Eq. (1). The SFG spectra were offset along the y axis by an arbitrary amount and were scaled with respect to the SFG spectrum for pentadecane crystal in Fig. 2(d) for comparison.

taken as an all-trans chain (a good assumption below T_m) with the coordinates shown in Fig. 4. We have also taken the methyl groups fixed with respect to each other and not freely rotating, which is important since the analysis depends on this assumption. The combined hyperpolarizability of an all-trans alkane can be constructed using Euler transformation of these two individual methyl groups to the new a, b, and c coordinates. Finally, the combined molecule with a, b, and c coordinates can be transformed to the laboratory coordinates x, y, and z as shown in Fig. 4. The molecule is allowed to tilt by an angle θ and rotate around the a axis (in plane, χ is 270°) and around the b axis (out of plane, χ is 0°). All ϕ angles are equally probable, since we do not expect any preferred direction of the alkane chains in the xy plane. A good match between experiments and the model is achieved for $\theta \approx 0$ (symmetry c axis of the molecule parallel to the surface normal). The intensity of SFG signal for bulk pentadecane crystal-sapphire interfaces is comparable to that of self-assembled monolayers with methyl terminal groups (octadecyl trichlorosilane) [19]. Since the SFG intensity is a function of the number density of molecules present at the interfaces, this suggests that the SFG intensity for the alkane crystals is due to more than one layer next to the sapphire surface.

Finally, we would like to comment on the structure of bulk pentadecane crystals next to sapphire substrate.
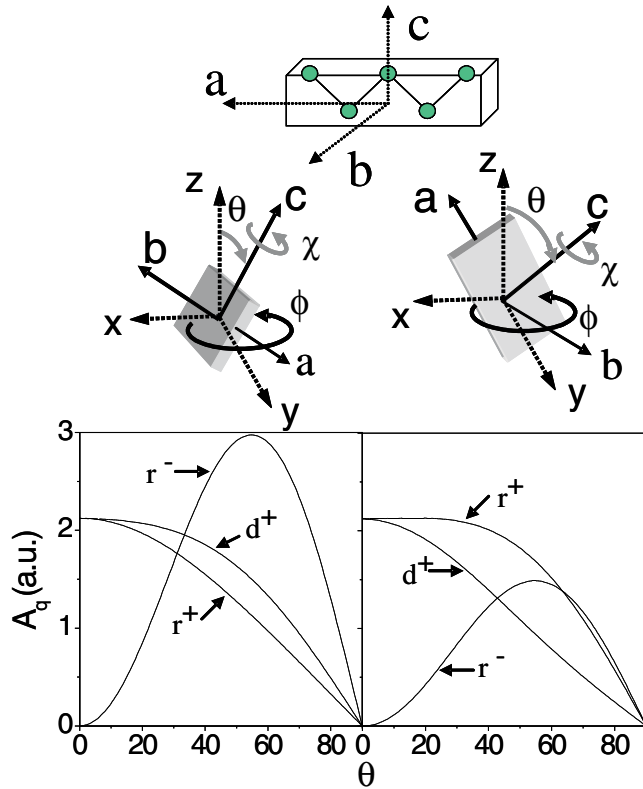
FIG. 4 (color online). Predictions of $|A_{q,\text{SSP}}|$ for CH$_3$ symmetric, CH$_3$ asymmetric, and CH$_2$ symmetric for an all-trans odd alkane rotating along the *a* axis (in plane, left) and *b* axis (out of plane, right) with respect to the laboratory *z* axis.

Yeganeh [20] has interpreted the absence of CH$_3$ asymmetric modes as an indication of chains with $\theta \approx 0$ (Fig. 4). Hence, in this case, there should have been a strong CH$_2$ symmetric peak present in the spectrum [Fig. 2(d)]. By allowing the rotation of the alkane chain out of plane would result in smaller CH$_2$ symmetric signals. However, this would also result in increase in CH$_3$ asymmetric modes, which was not observed in the bulk pentadecane crystal spectrum. There is no solution for this case unless we assume that the symmetry is broken down in the immediate vicinity of the sapphire substrate. This would imply that both the CH$_3$ groups of pentadecane molecule do not contribute equally to the SFG signal. This model has also been used to explain the results for odd and even crystalline alkanes next to the air interface [17]. The experimental data can be explained with the pentadecane chains oriented out of plane with the symmetry axis of the methyl group next to the sapphire surface oriented parallel to the surface normal. The SFG spectra for bulk and confined liquid-sapphire interfaces can be interpreted quantitatively based on average tilt angles of methyl and methylene orientation. However, to obtain a realistic physical picture will require computer simulations, which are in progress.

In summary, for the first time, we have shown that liquid alkanes confined between an elastomer and sapphire surface are much more ordered than bulk liquid. The confined liquid crystallizes below the bulk freezing temperature with the chains lying on the substrate with the symmetry axis parallel to the surface normal. This structure is very different from that of bulk alkane crystals in contact with sapphire. These results have important implications in our understanding of friction and lubrication in confined geometry.

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*Electronic address: ali4@uakron.edu
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