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Editors' Suggestion

Crystallinelike Ordering of Confined Liquids at the Moving Contact Line

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The friction between a liquid swollen soft elastomer and a solid surface depends on the state of a confined liquid. To measure the physical state of the confined liquid, an interface-sensitive sum frequency generation spectroscopy technique was used to probe the contact region. We find that during sliding (friction) and pull-off (adhesion) experiments of pentadecane-swollen poly(dimethyl siloxane) lenses submerged in linear alkane (pentadecane) on a sapphire substrate, crystallinelike ordering of the liquid occurs only at the contact line, where we anticipate the highest shear. This crystallinelike structure of pentadecane molecules is transient and shows Arrhenius temperature dependence with unusually long relaxation times (hundreds of seconds) and an activation energy (50 kJ/mole), which is twice that of the bulk pentadecane liquid, at temperatures that are 14–70 °C higher than the bulk melting temperature ($T_m = 9\,^\circ$C). This unusual long-lived crystallinelike ordering may explain why these systems show higher friction coefficients (boundary lubrication) compared to values predicted using bulk viscosity of pentadecane (hydrodynamic lubrication).

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The importance of a nanometer-thin lubricating liquid layer is obvious when a car's wiper blades smoothly move across a wet windshield. This lubrication is also vital when we bend our knees or blink our eyes. Thin liquid layers trapped between two solids also play an important role in reducing friction, wear, and energy dissipation [1–4]. The frictional forces are typically represented by a Stribeck curve. On one extreme, at large separations (or low normal forces), the friction is related to the viscosity of the confined liquid and the regime is known as the hydrodynamic lubrication regime. In this work, we are interested in understanding the state of the confined liquid when the gap is very thin (or at high normal loads), where the physical state of this confined liquid could be altered due to confinement. The physical and chemical properties of the thin film and the surface influence the frictional behavior. The friction is independent of the viscosity of the confined liquid in this regime known as the boundary lubrication regime [5–7].

The nature of nanometer-thin confined liquid has intrigued scientists for centuries. Inferences have been drawn from shear experiments where liquids (usually low molecular weight liquids) are confined between two atomically smooth mica surfaces [8]. The shear response resembles that of crystalline solids, or glasses, or unusually highly viscous liquids [9,10]. It is postulated that sliding of these confined liquids occurs by either shear-induced melting or a slip between two ordered liquid layers [8,11–16]. Even though there are no direct measurements on the state of the confined liquid, some indirect measurements using atomic force microscopy (AFM) and fluorescence probes reveal layering and domain formation [17,18]. Optical absorption spectroscopy in combination with a surface force apparatus also showed the alignment of the fluorescent probe molecules upon shear, indicating the shear-induced ordering [18].

Direct measurement of the structure of confined liquids has been challenging because the spectroscopic signals are dominated by bulk molecule vibrations. Recently, interface-sensitive sum frequency generation (SFG) spectroscopy [19] has been used to study the contact between a pentadecane-swollen poly(dimethyl siloxane) (PDMS) lens and a sapphire substrate in static conditions [20]. The experiments revealed that the structure of the confined pentadecane liquid, between a PDMS lens and a sapphire substrate, was very different from the unconfined pentadecane. Surprisingly, the melting temperature of confined pentadecane was lower than that of bulk pentadecane crystals [21–23].

Conventional SFG measurements require scanning the infrared wavelength and hence inhibit fast data collection to observe changes during sliding and pull-off. Using a femtosecond SFG system (with 1 kHz repetition rate) in combination with an *in situ* friction-adhesion setup, we directly probe the changes in the structure of confined liquids during sliding and pull-off [24]. The *in situ* SFG results show crystallinelike ordering during sliding or pull-off only at the moving contact line (not in the center of the contact spot). Surprisingly, the ordered state exists for a relatively long time after sliding or pull-off measurements are stopped. The relaxation of the ordering was much slower than the relaxation time expected for bulk pentadecane molecules. Also, the activation energy for the ordered state was twice the value of the activation energy

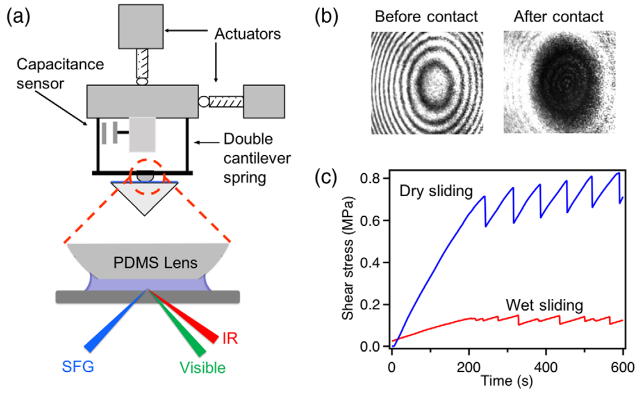

FIG. 1. Schematic of the experimental setup to probe the sliding contact between two surfaces using SFG. (a) Schematic of the friction cell used to probe the molecular structure of liquid pentadecane confined between a soft elastomeric PDMS lens and a hard sapphire substrate using SFG along with shear and normal force measurements. For simplicity, we have only shown the shear module. The normal force module is identical to but perpendicular to the shear module. The capacitance probes measure the deflection of the cantilever beams. The cantilever spring constants were calibrated by hanging known weights and recording the deflection using the capacitance probe. (b) The thickness of the confined pentadecane liquid was measured by monitoring the intensity of the 632.8 nm He-Ne beam in the contact spot. As the liquid is drained out from the contact region, we observe a dark contact region and the intensity in this contact region can be related to the film thickness [26]. We estimate the thickness to be less than 10 nm. A more precise determination of thickness is difficult due to scatter from the PDMS lens along with poor refractive index contrast between PDMS and pentadecane. (c) Shear stress measured for PDMS lens sliding against sapphire with a velocity of 7.5 μm/s in the presence (wet sliding) and absence (dry sliding) of confined pentadecane.

calculated using the viscosity of bulk pentadecane. The anisotropic alignment of pentadecane molecules during sliding explains the high friction coefficients in the boundary lubrication regime.

Figure 1(a) shows the friction and adhesion cell coupled to the SFG system to study the structure of the confined liquid during sliding and pull-off measurements. Pentadecane liquid (melting temperature of 9 °C TCI, purity $\geq 99\%$) was confined between an elastomeric PDMS lens and a sapphire prism at room temperature (23 °C). The PDMS lenses swell upon contact with alkanes and they contain around 15 wt % pentadecane (determined by weighing the lens before and after alkane swelling). The PDMS lens was deformed by applying a normal pressure so that the contact area was $\sim$0.5–1 mm in diameter. This normal pressure was chosen to ensure that the diameter of the laser beams (100–200 μm) was smaller than the contact spot. The contact interface was shown to be covered with pentadecane molecules in our previous study [20] and the thickness of the confined pentadecane was estimated to be less than 10 nm using the optical interferometry method [Fig. 1(b)] [20,26]. A more precise estimate of the thickness of the confined liquid was not possible due to poor refractive index contrast between PDMS (1.43–1.45) and pentadecane (1.41–1.42) and also background scattering from the PDMS lens [27,28].

The sliding stresses in the wet conditions ($\sim$0.13 MPa) are lower than those for dry contact ($\sim$0.71 MPa), but much higher than those expected in the lubrication regime (calculated to be $\sim$2 Pa using a viscosity of 2.9 mPa s, thickness of 10 nm, and sliding speed of 7.5 μm/s), confirming that we are in the boundary lubrication regime [Fig. 1(c)] [20]. The *in situ* sliding experiments involved first positioning the infrared and visible laser beams away from the contact region and then moving the PDMS lens towards the laser beams (velocity of 1.5 μm/s) while collecting SFG spectra every 1 sec. Because we were using a total internal reflection geometry, we can control the interface that we are probing by varying the incident angle of the laser beams [29]. Here, we used an incident angle of 8°, which satisfies total internal reflection conditions for both unconfined and confined liquid alkane next to the sapphire substrate.

Figure 2(a) shows the changes in SFG intensity in the hydrocarbon region as the PDMS lens slides past the laser beams (corresponding waterfall plot of SFG spectra is shown in Supplemental Fig. 1A [24]). The SFG intensity changes significantly at certain wave numbers (2840, 2925, and 2950 cm^{-1}) as the lens moves and the laser beams probe different areas in and out of the contact zone [Fig. 2(b)]. The SFG intensity at 2840 cm^{-1} increases significantly as the laser beams probe the leading and trailing edges of the contact zone. By comparing the SFG spectra at the leading and trailing edge and the center of the lens during sliding with the confined pentadecane liquid and crystal, ordering of the petadecane at the moving edges can be inferred [Fig. 2(c)]. In spectrum (I) the laser beams probe the unconfined pentadecane liquid in contact with the sapphire substrate; in spectrum (II) the laser beams are near the edges of the contact spot during sliding. And in spectrum (III) the laser beams are at the center of the contact spot. We have also shown SFG spectra for confined pentadecane at 23 °C (IV) and after freezing at 5 °C (V) with stationary lens. The SFG spectra collected with the laser beams at the leading and trailing edge of the PDMS lens are very similar to the spectrum of pentadecane crystal at 5 °C in confinement.

Understanding the changes in the spectral features during sliding requires assignment of spectral peaks. The 2925 cm^{-1} and 2950 cm^{-1} peaks are assigned to CH_2 and CH_3 asymmetric vibrations, respectively [30–32]. These peaks are assigned to pentadecane because the Si-CH_3 peaks for PDMS are expected at 2905 and 2965 cm^{-1} [33]. The 2840 cm^{-1} peak observed at the edges corresponds to symmetric CH_2 vibrations of the pentadecane molecules [30–32]. The structuring of pentadecane molecules upon

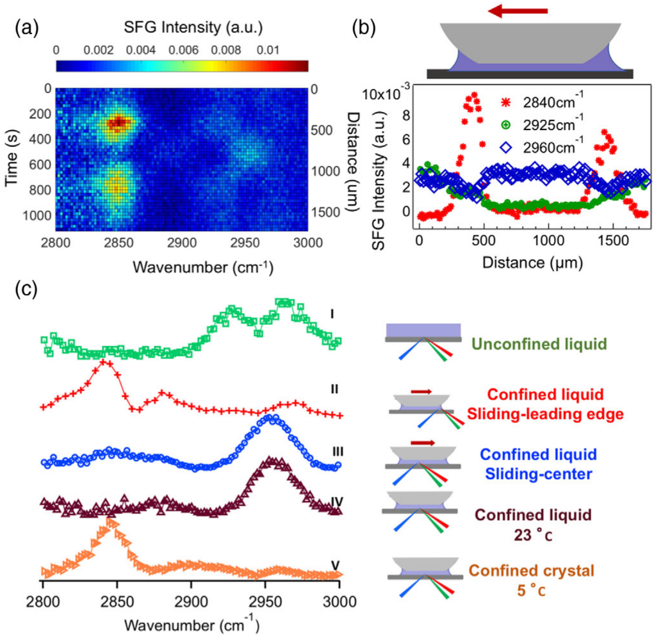

FIG. 2. The changes in the structure of confined pentadecane liquid. (a) A plot of variation in SFG intensity as a function of wave number and distance moved by the PDMS lens as it is brought in and out of the region probed by laser beams. The output SFG, input visible, and input infrared beams were *P*, *P*, and *P* polarized, respectively. The SFG spectra were collected at a 1 sec interval with 1 sec of accumulation time. For clarity, we have only plotted spectra collected every 25 sec interval. (b) The variation in intensity at selected peak positions (2840, 2925, and 2950 cm^{-1}) is plotted as a function of distance as the lens moved in and out the laser spot. (c) SFG spectra taken at different positions of the PDMS lens with respect to the laser spot. The spectra are normalized and scaled for clarity. SFG spectrum taken during sliding when the lens has not moved into the laser spot (square). This spectrum is similar to that of unconfined pentadecane liquid in contact with the sapphire substrate. SFG spectrum of alkane fluid at the leading edge of the lens as the lens enters the laser spot (plus). SFG spectrum of confined liquid when the laser beams overlap with the center of the contact spot (circle). SFG spectra of confined liquid at 23 °C (triangle) and confined crystal at 5 °C (inverted triangle) collected under static conditions.

confinement near the center (III) is different from the unconfined pentadecane structure next to sapphire (I) and is similar to the static confined pentadecane liquid (IV). Confinement induced ordering of pentadecane led to these differences in the alignment of the chains inside and outside of the contact region [20,34]. However, the SFG spectrum collected for the pentadecane in confinement near the leading and the trailing edge (II) shows marked similarities with the static confined crystal (V) and not with static confined liquid (IV) [20]. The resemblance between the spectra collected at the moving contact line and that of confined crystal at 5 °C indicates a strong crystallinelike ordering of pentadecane molecules near the leading and trailing edge. We have used the crystallinelike order to describe the physical state of pentadecane at the leading and trailing edge during sliding because the SFG spectra at the leading and trailing edge during sliding resemble the spectra of confined alkanes below the freezing temperature. We postulate that the changes observed near the edge of the contact line could be due to higher shear forces at the edge compared to the center of the contact spot [11,35]. Previously, the observation of a strong symmetric CH_2 peak upon crystallization had been assigned to the structure of an interfacial layer of molecules aligned with the C-C-C axis parallel to the surface plane [20]. This alignment explains why the methylene groups have a non-centrosymmetric structure, which leads to significant enhancement in the SFG signal at 2840 cm^{-1}. We have also performed the sliding experiments with a higher purity grade of pentadecane to rule out the effect of potential contaminants present in pentadecane [36]. Even though the spectra collected at the center show small differences due to differences in the thickness of the confined film (Supplemental Figs. 2A and 2B), the spectra collected at the moving edge show similar features (Supplemental Figs. 2C and 2D) confirming the observed enhancement in 2840 cm^{-1} is a result of orientation of pentadecane molecules.

The lateral movement of the contact line also takes place when the compressed PDMS lens is retracted back during the pull-off experiments. The variation in SFG intensity as a function of wave number during pull-off is plotted in Fig. 3(a) (corresponding waterfall plot of SFG spectra is shown in Supplemental Fig. 1B). In this experiment, the laser beams were positioned in the center of the contact region and SFG intensity was recorded during pull-off as the contact line approached the laser beams. We have conducted this experiment in two different configurations. In one case, excess pentadecane was added to create a capillary bridge. In the second case, the complete chamber was filled with liquid pentadecane eliminating a triple contact line with the air interface. In both cases, the results were identical; thus, the presence of the air boundary was not the governing factor in the observed increase in SFG signals at the moving edges of the PDMS contact (Supplemental Fig. 3). Here, we only discuss the results for the second case. Figure 3(b) shows the SFG intensity of the 2840 cm^{-1} peak and the normal force recorded during pull-off as a function of scan number and time. The increase in SFG intensity matches with the adhesive pull-off force and the edge overlapping with the laser beams before the PDMS lens is separated from the sapphire substrate. Figure 3(c) compares the SFG spectrum collected before the surfaces are separated during pull-off and SFG spectrum collected when the laser beams are at the edges during sliding. The similarity in the SFG spectra during sliding and pull-off measurements further confirms that the movement of the pentadecane liquid at the edges of the contact line is necessary for aligning the pentadecane molecules. The increase in SFG intensity observed during pull-off

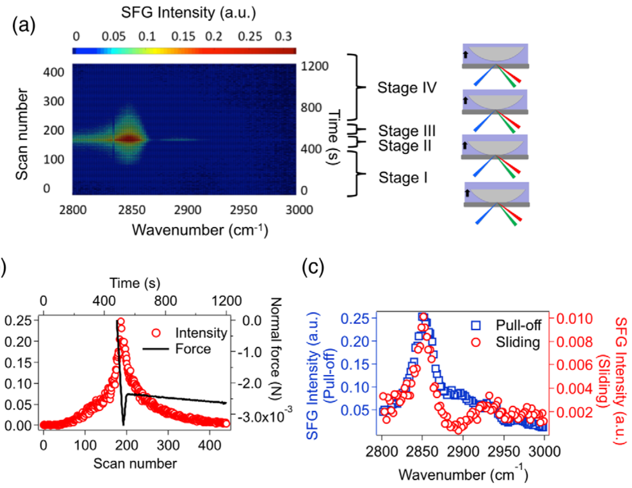

FIG. 3. SFG spectra and normal forces during pull-off experiments. (a) A plot of the variation in SFG intensity as a function of wave number in the hydrocarbon region as the PDMS lens is pulled out of contact. The schematic of the different stages during the pull-off are shown along the plot: stage I—confined center, stage II—confined edges approaching towards center, stage III—confined edge near pull-off, and stage IV—unconfined liquid after pull-off. The output SFG, input visible, and input infrared were P, P, and P polarized, respectively. The SFG spectra were taken at a 1 sec interval with 2 sec accumulation time. (b) The variation in SFG intensity of 2840 cm^{-1} (left axis, circle) and the normal force (right axis,—) is plotted as the lens is pulled-off. (c) SFG spectra collected during pull-off (left axis, square) and sliding (right axis, circle) experiments when the laser beams are close to the moving edges.

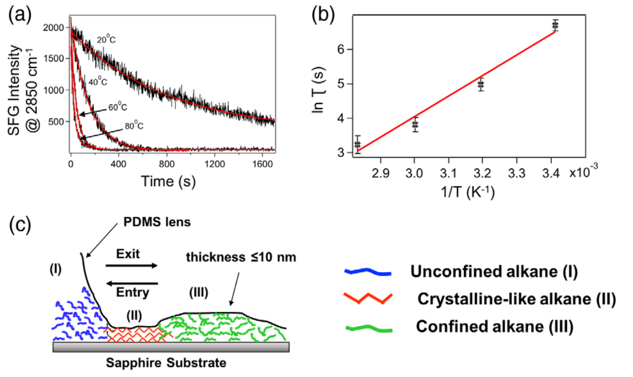

FIG. 4. Relaxation of the aligned pentadecane molecules after pull-off experiments. (a) Relaxation of the SFG signals after the PDMS lens has been pulled-off at 20, 40, 60, and 80 °C. (b) The relaxation curves were fitted using a single exponential function and the relaxation time constants were plotted as a function of $1/T$. (c) A sketch illustrating the alignment of pentadecane molecules at the edge of the moving boundary during sliding and pull-off experiments.

experiments was 25 times of that observed during sliding, which can be explained by the faster movement of the contact line during pull-off compared to sliding experiments. Similar enhancement in SFG intensity has been observed previously upon crystallization of pentadecane and hexadecanol molecules next to the sapphire substrate [20,38]. The higher SFG intensity could be a result of multiple layers of crystallinelike order due to shear during the movement of the contact boundary. However, we did not observe significant dependence of enhancement in SFG intensity on pull-off rates in range of 1–20 $\mu\mathrm{m/s}$ (Supplemental Fig. 4).

Perplexingly, we observed this aligned state of pentadecane molecules at the sapphire substrate in direct contact with the liquid pentadecane phase 20–30 min after the PDMS lens was separated at room temperature. The existence of the ordered state at a temperature more than 14–70 °C above the bulk melting temperature of pentadecane was surprising since the confinement results in depression of the melting point of the alkane crystal [21]. In Fig. 4(a), we plot the relaxation of these SFG signals after the PDMS lenses were retracted at different temperatures. At room temperature, the orientation persisted even after 30 min. The relaxation observed in the present case was much faster at higher temperatures than at room temperature. The relaxation profiles at different temperatures were fitted using a single exponential function and the calculated relaxation time constants were plotted in Fig. 4(b) as a function of $1/T$. These results were modeled using an Arrhenius temperature dependence [$\tau \propto \exp(\Delta E/RT)$, where ΔE is the activation energy and R is the gas constant]. We obtain an activation energy of 50 kJ/mol for the liquid pentadecane to go to the transient ordered pentadecane state. This activation energy is twice the activation energy obtained by plotting changes in viscosity as a function of temperature for liquid pentadecane (25 kJ/mol) [39]. In addition to the differences in the activation energies, the relaxation times in Fig. 4(a) are also very long compared to relaxation time in the bulk of a nonpolar liquid, which is less than 10^{-10} s [40,41].

We have also measured the SFG intensity during pull-off for PDMS lenses submerged in n-tridecane liquid (Sigma-Aldrich, 99.5% purity, $T_m = -5\,^{\circ}\mathrm{C}$) after bringing them in contact with a sapphire substrate. There is a significant increase in the SFG intensity at 2840 cm^{-1} during pull-off (Supplemental Fig. 5), which is consistent with our observation for pentadecane. This suggests that the results presented in the current study are not just specific to pentadecane.

We would like to summarize two intriguing observations. The first observation is the strong crystallinelike ordering of pentadecane molecules after sliding or pull-off experiments at 14–70 °C above the bulk melting temperature. Nonuniform flow-induced alignment of liquids during sliding has not been considered in explaining boundary lubrication [Figure 4(c)]. In addition, the flow-induced alignment may explain the adhesion hysteresis observed during pull-off. The alignment of pentadecane molecules may result in a different energy dissipation mechanism.

The second intriguing observation is the decay rate of the ordered structure (hundreds of seconds at room temperature) even after the lenses have been pulled off. In this case, the ordered structure is in direct contact with the liquid pentadecane. Using a 5-nm-thick layer of confined liquid and a relaxation time of 1000 sec, we obtain a diffusion constant of around 10^{-16} cm^2/s $[D \sim r^2/2t \sim (5 \times 10^{-7})^2/(2 \times 1000)]$, a value expected for a glassy or crystalline layer. Although we do not offer a quantitative connection between crystallinelike order and friction, we anticipate that these observations will spark new ideas towards understanding the friction and adhesion of soft materials in the presence of liquids.

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