Effect of Interfacial Liquid Structuring on the Coherence Length in Nanolubrication

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The degree of interfacial structuring of n-hexadecane and octamethylcyclotetrasiloxane (OMCTS) was measured within a nanometer boundary regime to silicon surfaces. Boundary-layer effects on lubricating sliding (in terms of a thermodynamic stress activation parameter) and the layer thickness were determined by scanning force microscopy. A 2.0 ± 0.3 nm thick, entropically cooled layer was found for n-hexadecane. Measurements on spherically shaped OMCTS molecules exhibited only an interfacial "monolayer," and identified the molecular shape of n-hexadecane responsible for augmented interfacial structuring. Interfacial liquid structuring was found to reduce friction.

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It is well known that the frictional resistance between solids is significantly reduced if lubricated. Various characteristic velocity dependencies have been found for liquid lubrication depending on the lubricant thickness (or more generally on the Gumbel number) [1–4]. In surface forces apparatus (SFA) measurements with ultrasmooth mica sheets, it has recently been proposed that due to slow relaxation times in highly confined liquids, it is possible that friction exhibits a logarithmic behavior in velocity [5]. This transient behavior of the fluid finds its counterpart in dry or solid lubrication, where also logarithmic behaviors have been reported. For example, early macroscopic observations on rubber [6], microscopic thin polymer film studies [7], and ultrahigh vacuum (UHV) nanoasperity experiments [8] have all shown a logarithmic friction velocity, $F_F(v)$, relationship.

A discontinuous sliding process causes a logarithmic friction-velocity relationship [6]. It is important to note that in order to generate any sliding discontinuity, the average sliding velocity has to be matched to the material intrinsic characteristic relaxation times [9–11]. For instance, for simple alkane liquids, small sliding velocities on the order of μm/s are necessary to observe sliding discontinuities [10]. From a thermodynamic point of view, sliding discontinuities are caused by activation barriers, which are repeatedly overcome during the sliding process. It has been shown that a thermodynamic activation model provides the means to deduce the microscopic process coherence length or memory function from logarithmic friction-velocity relationships [6,7,12]. The process coherence length is a measure of the length over which the liquid lubricant is capable of building up strain, i.e., to respond to a stress occurrence.

In this Letter we discuss entropic cooling of "simple" liquids, n-hexadecane (n-$C_{16}H_{34}$) (Aldrich, >99% purity) and octamethylcyclotetrasiloxane (OMCTS) (Fluka, >99% purity), in the close vicinity to a single solid boundary (silicon oxide wafer, 5 Å roughness), and show that they are capable of building up strain within a lubricating junction. The two liquids have been selected due to their similar chemical affinity to silicon. They are, however, distinctly different regarding the molecular shapes, i.e., composed of linear chain (n-$C_{16}H_{34}$) and spherically shaped (OMCTS) molecules. We examined the degree of interfacial liquid structuring and its contribution to localized shear processes by scanning force microscopy (SFM) shear modulation approach curves and SFM friction-velocity experiments, respectively. While shear approach curves provide the thickness of entropically cooled boundary layers, a thermal analysis of the friction-velocity data provides information about the molecular coherence length (stress activation length) in the liquid during a lubrication process.

Friction-velocity plots have been obtained with SFM cantilevers that were fully immersed in the liquid lubricant and scanned with μm/s velocity in an apparent contact with a silicon surface at constant load and temperature [13]. As documented in Fig. 1, logarithmic friction-velocity relationships, $F_F(v) = F_0 + \alpha \ln(v[\mu\text{m/s}])$, were found for n-hexadecane and OMCTS. The measurements are compared to "dry" silicon-silicon contact at 18% relative humidity. The fitting constants F_0 and α are found to be lubricant specific and, thus, material process constants. n-hexadecane exceeds OMCTS in its performance as a lubricant for asperity sliding within a velocity range of 0.2–100 μm/s. This cannot be explained from a molecular or bulk liquid perspective alone. The data suggest a substrate-induced change in the liquid properties within the boundary regime to the solid substrate. To obtain liquid rheological information in the solid-liquid boundary regime, we performed a shear modulation analysis of the two liquids as a function of the distance to the silicon surface. The shear modulation analysis, as illustrated in Fig. 2, combines normal tip-sample interaction force measurements with shear amplitude

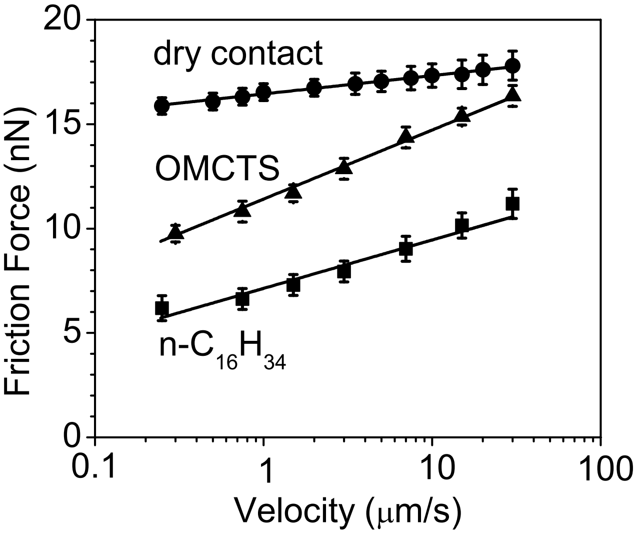

FIG. 1. Logarithmic $F_F(v)$ plots. $F_F(v) = F_0 + \alpha \ln(v[\mu\mathrm{m/s}])$: (●) "dry" contact (18% relative humidity) with $F_0 = 16.4$ nN and $\alpha = 0.91$ nN, (▲) OMCTS lubricated with $F_0 = 11.3$ nN and $\alpha = 3.4$ nN, and (■) n-hexadecane (n-$C_{16}H_{34}$) lubricated with $F_0 = 7.1$ nN and $\alpha = 2.5$ nN. The measurements were obtained with rectangular SFM cantilevers (0.4–0.8 N/m) at 100 nN load and 21 °C, both feedback controlled.

response information that are induced by small sinusoidal local shear distortions. We refer to this method as the shear modulated force displacement (SM-FD) method. The technique is comparable to the normal approach modulation method in liquids [14] and is briefly described in the caption of Fig. 2.

The entropically cooled boundary layer thickness is determined in Figs. 3(a)–3(c) for water, n-hexadecane, and OMCTS. SM-FD data for water, Fig. 3(a), reveal a sudden change in the amplitude response at 0.25 ± 0.2 nm apart from the silicon substrate surface. In lack of a superior method in determining our instrumental accuracy, here this value shall solely serve as a sensitivity limit. The results obtained from n-hexadecane and OMCTS, Figs. 3(b) and 3(c), clearly reveal for both liquids the formation of nanometer-thick boundary layers of 2.0 ± 0.3 nm and 1.6 ± 0.4 nm, respectively.

In theoretical studies on single substrate surfaces, it is proposed that the molecular chains of n-hexadecane close to the solid interface orient parallel to the substrate (i.e., are entropically cooled) [15–17]. A steady-state boundary layer thickness of 1.5–1.8 nm has been proposed [16], which compares well with our measurements. A corresponding boundary layer thickness (by a factor of 2) was found in SFA experiments in which paired "entropically cooling" surfaces must be considered [18]. It is important to note that the SFA confining surfaces exceed by orders of magnitude the size of the liquid molecules, trapping the molecules and inducing density fluctuations (oscillatory solvation forces). In our SFM experiments trapping effects are negligible.

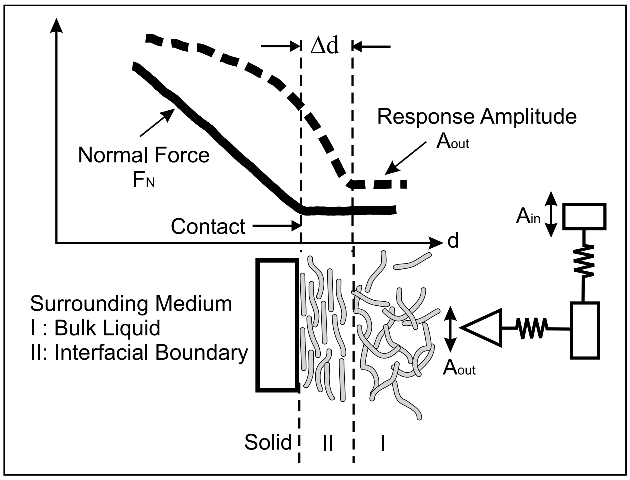

FIG. 2. Generic shear modulated force displacement (SM-FD) method. A cantilever (fully immersed in liquid) approaches the surface with nm/s velocity. "Simple" low molecular weight liquids exhibit no normal restoring forces, F_N, in a slowly approaching cantilever. Nonzero normal forces appear after the cantilever tip contacts the substrate surface (→ displacement reference point). A nanometer-sized lateral sinusoidal disturbance, A_{in}, is superimposed to the normal steady approach motion. The amplitude response, A_{out}, is monitored by the lock-in technique (Standard Research Systems, SR 830) and provides a measure of the rheological property of the liquid as a function of the distance from the solid surface. Δd represents the thickness of the entropically cooled liquid boundary layer.

No correspondence is found for OMCTS between previous SFA measurements and our SM-FD measurements [19]. While in SFA studies the formation of multiple layers was reported [20–22], our SM-FD data suggest only a single interfacial layer. This is not unexpected considering that the OMCTS molecules are spherical in shape and thus not particularly entropically cooled by a planar surface. A very recent synchrotron x-ray reflectivity study of OMCTS between two smooth silicon mirrors confirmed that compression pressures are necessary for inducing multiple layering in OMCTS [23].

The SM-FD measurements suggest that an anisotropic molecular structure of linear chain alkanes induces higher molecular coordination at the solid interface than an isotropic structure of spherically shaped molecules. Consequently, the difference in interfacial structuring of the two liquids can be used to interpret the friction-velocity data above. Further, based on the $F_F(v)$ plots, we find that an increase in molecular coordination (parallel to the sliding direction) in the interfacial regime between liquid lubricant and solid is favorable from a frictional perspective (Fig. 1).

$F_F(v)$ relationships provide two material specific process parameters: namely, F_0 and α. It is possible to gain information about the molecular coordination by analyzing logarithmic $F_F(v)$ plots with a thermodynamic activation barrier analysis [6,7,12]. We consider an overall barrier height, $E = Q + P\Omega - \tau\phi$, that is repeatedly overcome

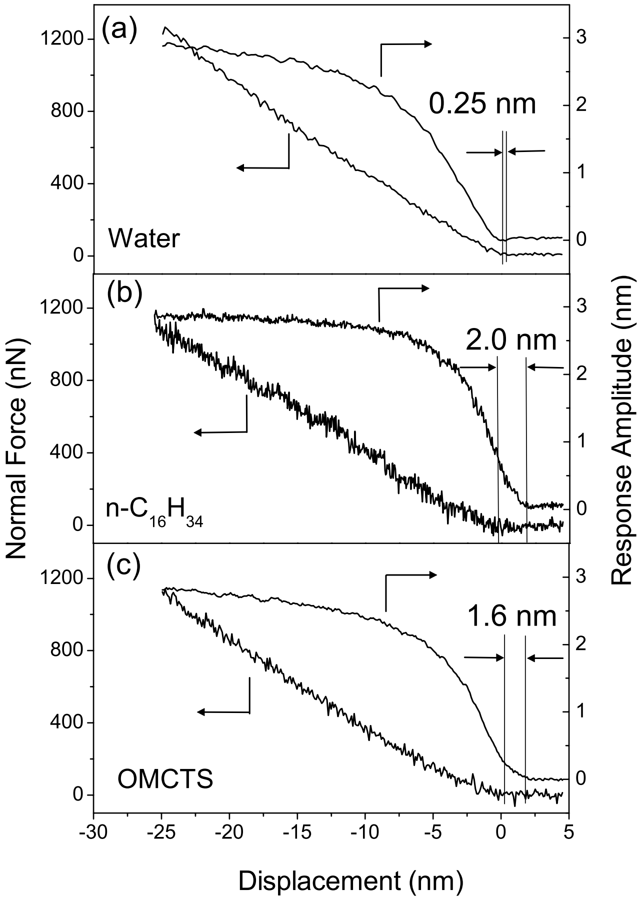

FIG. 3. SM-FD measurements towards silicon oxide surfaces with an approach velocity of 5 nm/s at 21 °C in (a) water, (b) *n*-hexadecane, and (c) OMCTS. The measurements were obtained with stiff rectangular SFM cantilevers (37–55 N/m), to avoid any snap-in instabilities, and with a shear amplitude of 3 nm (rms) at 5 kHz modulation.

during a discontinuous sliding motion. The barrier height, E, is composed of the process activation energy Q, the compression energy $P\Omega$, where P is the pressure acting on the volume of the junction Ω, and the shear energy $\tau\phi$, where τ is the shear strength acting on the stress activation volume ϕ [12]. The stress activation volume ϕ can be conceived as a process coherence volume and be interpreted as the size of the moving segment in the unit shear process, whether it is a part of a molecule or a dislocation line [7]. Introducing an Arrhenius representation for the velocity [6], i.e., $v = v_0 \exp(-E/k_B T)$, which leads to a linear friction-temperature relationship [7] as confirmed in the inset of Fig. 4, the following shear strength versus velocity relationship can be deduced [7]:

$$\tau = \frac{k_B T}{\phi} \ln\left(\frac{v}{v_0}\right) + \frac{1}{\phi}(Q + P\Omega), \qquad (1)$$

where v_0 is a characteristic velocity related to the frequency of the process and a jump distance, k_B is the Boltzmann constant, and T refers to the absolute temperature. Considering that the shear strength can be expressed as the friction force, $F_F(v) = F_0 + \alpha \ln(v)$, per unit area A, the following equation can be directly derived from Eq. (1) for constant temperature and pressure:

$$\frac{\phi}{A} = \frac{k_B T}{\alpha}. \qquad (2)$$

We analyzed the slopes α from Fig. 1 for *n*-hexadecane, OMCTS, and the dry contact situation, with Eq. (2), and plotted the stress activation "radius" ϕ/A in Fig. 4. As expected, the stress activation length (or coherence length) in a dry contact situation dominates the ones in lubricated junctions. However, it has to be pointed out that the origin of the activation barrier (or jump probability) in dry SFM friction experiments is not just caused by phonon excitations in the material, which are too fast to be observable, but by jumps of the cantilever tip. Hence, the logarithmic $F_F(v)$ behavior, as detected in UHV experiments [8], reflects a trapping probability between SFM tip and sample and can be discussed in terms of a white-noise driven system [24]. To what extent lubricated SFM tip-sliding measurements reflect trapping probabilities is unknown. However, since there is a recognizable difference in the stress activation length between *n*-hexadecane and OMTS (see Fig. 4), for two liquids with similar chemical affinity and bulk rheology, we can assume that the intrinsic molecular response time of the liquid (i.e., self-diffusion) is partially responsible for the liquid-specific $F_F(v)$ relationship. Thus, we conclude that *n*-hexadecane shows a higher shear coordination than OMCTS. This interpretation is in accordance with the SM-FD information provided above.

The thermodynamic activation model provides the opportunity to discuss the shear process in more detail.

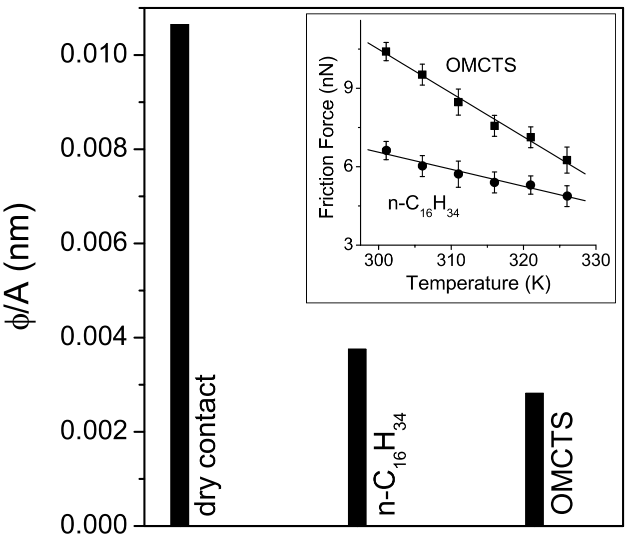

FIG. 4. Stress activation length, ϕ/A, obtained from Fig. 1 and Eq. (2) for OMCTS, *n*-hexadecane, and dry contact. The inset provides a linear relationship between friction and temperature at a velocity of 1 μm/s and a normal load of 100 nN.

The model contains with the characteristic velocity, $v_0 = \nu d$, a process frequency, ν, and a jump distance, d. An upper limit of the process frequency of $10^{13}-10^{15}$ Hz is estimated from infrared absorption data for most organic chemical bonds [25]. Thermal analyses of shear measurements of short chain molecules in Langmuir-Blodgett films [7] provide a lower limit for the relaxation frequency on the order of 10^{11} Hz. This leads to a feasible total energy range of $(4-8) \times 10^{-20}$ J. From the data presented in Figs. 1 and 4, we obtain within the investigated velocity range a shear energy range, $\tau\phi \equiv F_F\phi/A$, of $(3-5) \times 10^{-20}$ J and $(2-4) \times 10^{-20}$ J for OMCTS and n-hexadecane, respectively. From SM-FD measurements, we infer that at a normal load of 100 nN, at a μm/s velocity, and at nanometer confinement, the entropically cooled boundary layer of OMCTS or n-hexadecane cannot oppose the pressure and is penetrated by the tip. No hydrodynamic lift-off is observed in friction experiments. This is confirmed by an estimation of the pressure junction volume per unit area Ω/A. An upper limit for Ω/A of 10^{-4} nm is deduced from $P\Omega \equiv F_N\Omega/A$, which is limited to values on the order of 10^{-20} J by the overall energy balance. Consequently, the process activation energy, Q, is on the order of 10^{-20} J. Although the entropically cooled boundary layer is far from freezing, it shall be noted that the heat of fusion at the melting point is 1.99×10^{-20} J and 8.85×10^{-20} J for OMCTS and n-hexadecane, respectively. The stress activation volume is comparable to the van der Waals volume of both n-hexadecane and OMCTS (about 0.28 nm^3/molecule) for a contact radius of about 5 nm. However, such a comparison is not very informative as the shear process can be expected to be quite different between the two materials. For instance, the layered boundary layer of n-hexadecane is capable of partial shear deformation, while the single surface layer of OMCTS is most likely only plastically deformed by the sliding tip, as indicated by the observed nominally higher friction values for OMCTS in Fig. 1.

In summary, we found that n-hexadecane forms a higher coordinated entropically cooled boundary layer than OMCTS due to the highly anisotropic linear chain molecules. Rheological boundary layer thicknesses of n-hexadecane and OMCTS could be determined. We introduced a thermal activation analysis of nanoscale lubricated frictional sliding, which provides a quantitative measure for the degree of molecular coordination within the fluid phase close to a solid surface.

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