Solvation Forces in Branched Molecular Liquids

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The solvation force of squalane confined between a silicon tip and a graphite surface has been measured by atomic force microscopy. This highly branched molecule shows oscillatory force profiles similar to those of spherical and linear chain molecules. Squalane molecules closest to the substrate are tightly bound and finer details imply that interdigitation occurs. This agrees with computer simulations for branched molecules but differs qualitatively from force balance experiments. These differences arise from the smaller confinement area and the different chemical nature of the surfaces.

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Oscillatory-type solvation forces can occur between two surfaces immersed in a liquid. These forces arise from the variation in the molecular density of the liquid between the surfaces [1]. For geometric reasons, the liquid molecules confined between the surfaces may pack (or order) into well-defined layers. The liquid ordering results in force profiles (i.e., the measured force in the direction normal to the surface) which oscillate periodically as successive, discrete layers of liquid molecules are displaced from the gap between the surfaces. The oscillations are characterized by a period approximately equal to the diameter of the liquid molecules and an increasing magnitude as the surface separation decreases (i.e., as the liquid becomes more compressed).

The presence of oscillatory, solvation forces is significant both from a fundamental viewpoint on the behavior of confined materials and for practical applications in tribology and rheology [2]. The behavior of confined liquids and solvation force measurements have been investigated extensively using the surface force apparatus (SFA) [3,4]. SFA results show that geometric asymmetry at the liquid-solid interface (arising from surface roughness, side chain branches of the liquid molecule, etc.) can disrupt molecular layering, resulting in the disappearance of oscillatory-type behavior and a monotonic force profile [5,6]. However, there has been one SFA report [7] showing oscillatory behavior in the force measurements of a molecule having a single side chain methyl group (3-methylundecane, $C_{12}H_{26}$). In the same study, oscillatory forces were not observed in the force profiles of a more heavily branched molecule (squalane, a molecule having a C_{24} backbone with six symmetrically placed methyl sidegroups). Hence, although it is generally agreed that molecular branching can disrupt oscillatory forces, the quantitative influence of branching on the solvation force measurements is not clear [7].

Part of the uncertainty arises from computer simulation studies, which show that simple confined liquids exhibit oscillatory solvation forces [8–10] and density oscillations [8–12] *regardless* of the degree of branching in the liquid. The oscillatory solvation force is associated with density oscillations [8,13], which are in turn dependent on the degree of layering and intralayer ordering of liquid molecules at the liquid-solid interface [8–12]. The simulations reveal that layering should occur in heavily branched alkanes (e.g., squalane and 2-, 6-, 11-, 15-tetramethylhexadecane), although to a lesser degree in comparison with linear chain alkanes, such as *n*-hexadecane [9,11,12]. Additionally, density layering effects have been observed by molecular dynamics for freestanding branched decane isomer films at the liquid-solid interface [14]. Computer simulations do not produce the nonoscillatory, monotonic solvation force profiles observed in SFA experiments for branched alkanes [7]. In this respect, we note that the lateral dimensions of the confining surfaces employed in computer simulations are typically ~5 nm, which is orders of magnitude smaller than in SFA experiments (with a contact area radius of ~10 μm). This suggests that oscillatory solvation force profiles and the corresponding molecular ordering are possibly present for all liquids which are confined at the nanometer length scale. Such a conjecture also has interesting implications for atomic force microscopy (AFM) imaging in liquid environments [15,16].

In this Letter, we report the first experimental evidence of oscillatory behavior in the force profile of squalane, a highly branched molecule. The force profiles are obtained using AFM and we immediately note that the length scale of the AFM tip (~10 nm) is comparable to the dimensions used in computer simulations. Previously, we have shown that AFM force spectroscopy can be used to study the solvation force profiles of the quasispherical molecule octamethylcyclotetrasiloaxane (OMCTS) and linear chain molecules by measuring either the normal force directly [17] or the interaction stiffness (i.e., the tip-sample force gradient) [18]. Recently, we have shown the use of low-amplitude sample-modulation AFM force spectroscopy to measure the force gradient [19] and this is the method adopted in this work.

A standard deflection-type AFM is used (Molecular Imaging Co.). The experimental setup involves oscillating the displacement of the substrate (the sample) with small amplitude (~0.1 nm peak-peak). Force profiles are obtained by varying the tip-sample separation and monitoring the cantilever displacement. In a typical separation cycle the tip is approached and then retracted from the surface. Two cantilever displacement signals are measured simultaneously, namely, the static cantilever deflection (arising from changes in the *force* acting on the tip) and the cantilever oscillation amplitude (arising from induced oscillations in the cantilever as a result of changes in the tip-sample *force gradient*). The oscillation amplitude is measured using a lock-in amplifier (EG&G 7265) and the force gradient can be found from the solution of the equation of motion of a sample-modulated system [20],

$$\frac{d}{A_0} = \frac{k_i[1 + (2m^* \omega \beta_i/k_i)^2]^{1/2}}{\sqrt{(k_i + k_c - m^* \omega^2)^2 + [2m^* \omega(\beta_i + \beta_c)]^2}}, \tag{1}$$

where d is the tip displacement, A_0 is the driving amplitude, ω is the driving frequency, k_i is the tip-sample interaction stiffness (the desired quantity), k_c is the cantilever stiffness, β_i is the interaction damping constant, β_c is the cantilever damping constant, and m^* is the effective mass of the cantilever. In the low frequency limit ($\omega \to 0$), Eq. (1) reduces to

$$\frac{d}{A_0} = \pm \frac{k_i}{k_i + k_c}, \tag{2}$$

which is used for all the data presented in this work since the driving frequency is always orders of magnitude smaller than the fundamental cantilever resonance. Knowing the cantilever stiffness k_c [21] allows us to extract the tip-sample interaction stiffness k_i by measuring the normalized change in amplitude (d/A_0). Note that k_i is simply related to the interaction force law $F(D)$ by $k_i = -dF/dD$, where D is the tip-sample separation distance. A complete description of the experimental method is available elsewhere [19].

The data we present are representative force profiles of squalane confined between a Si AFM tip (Nanosensors) and a freshly cleaved highly oriented pyrolytic graphite (HOPG) substrate. The sample displacement is oscillated at a peak to peak amplitude of 1.2 Å. The measurements are reproducible over consecutive approach/retraction cycles when made with the same tip. Experiments with different tips exhibit oscillatory force profiles of varying magnitude, which we attribute to varying tip roughness and geometry [15,19]. The cantilevers used in this work have typical k_c values of ~3 N/m. After every experiment, scanning electron microscopy is used to characterize the tip radius of curvature (R_{tip}).

Figure 1 shows the applied force (i.e., the static cantilever deflection) collected in a single approach/retract cycle. Three characteristic solvation "jumps" with average periodicity of 5.7 ± 0.6 Å are observed. We assign $D = 0$ to the region where solvation jumps are no longer present. It must be noted, however, that we cannot be certain if the tip is compressing a very tightly bound solvation layer at $D = 0$ rather than being in hard-wall repulsion with the HOPG surface. It is evident that the measured periodicity correlates to the width of a squalane molecule. Single-branched alkane molecules have periodicity in the force profile of 4–5 Å [7] and the value reported here for squalane is slightly larger due to more extensive molecular branching and/or reduced order within each solvation layer. The lack of hysteresis in the approach and retraction curves (Fig. 1) suggests that the ordering of the squalane molecules is in equilibrium over the time scale of the experimental measurement (~10 ms). The normalized adhesive or "pull-off" force (F_{ads}) as measured from the retraction curve is $F_{\text{ads}}/R_{\text{tip}} = 18$ mN/m. The nonretarded van der Waals force (F_{vdW}) between a spherical AFM tip and a plane can be written as $F_{\text{vdW}}/R_{\text{tip}} = -A/6D^2$, where A is the Hamaker constant. Hence using the measured adhesive force and assuming $D = 2$ Å at "contact separation" [3], we find the approximate Hamaker constant to be 0.4×10^{-20} J for the system.

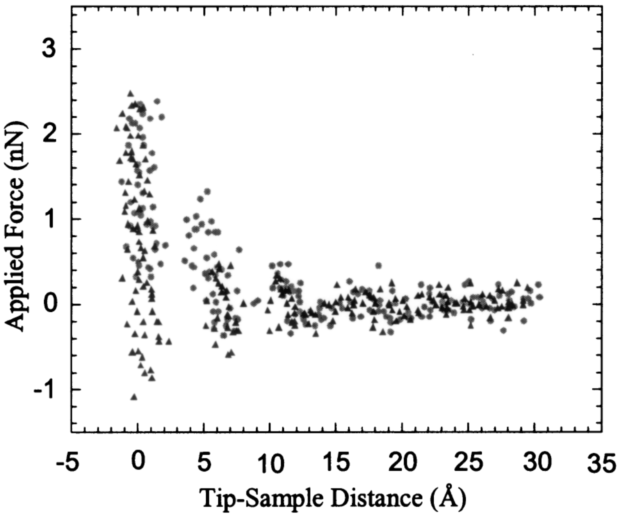

FIG. 1. Plot of approach (●) and retracting (▲) applied force curves for a Si tip ($R_{\text{tip}} = 55$ nm) approaching a HOPG surface in squalane. Solvation jumps with a periodicity of 5.7 ± 0.6 Å correlate to the parallel layering of squalane molecules in the gap. The adhesive force (F_{ads}) is −1.1 nN.

Figure 2 shows the interaction stiffness profile measured in a different experiment. The enhanced sensitivity of the modulation technique reveals six solvation layers. The average periodicity observed in the stiffness data is 5.8 ± 0.6 Å. The stiffness of the first solvation layer (at $D \approx 5$ Å) cannot be measured due to tip instability. Our results show that the squalane system is much stiffer compared with the simple, spherical molecule OMCTS. The peak to peak stiffness values we measure are 4.5, 2.3, 1.0, 0.8, and 0.5 N/m for the second, third, fourth, fifth, and sixth solvation layers, respectively. These values are ~3 times larger than the stiffness of OMCTS measured with a tip of similar size [19]. Closer inspection of Fig. 2 reveals secondary features (indicated by arrows), which extend ~1.5 Å away from the repulsive maxima

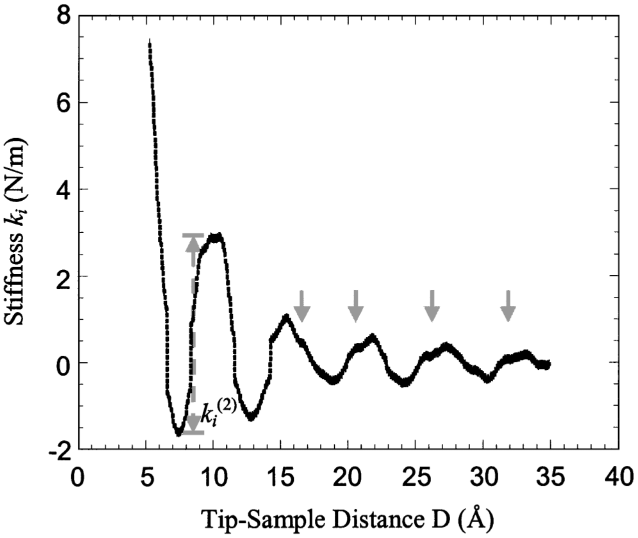

FIG. 2. Measured tip-sample interaction stiffness for a Si tip approaching a HOPG surface in squalane. Secondary features (indicated by arrows) correspond to interdigitation of methyl branches between layers. The peak to peak stiffness values are 4.5, 2.3, 1.0, 0.8, and 0.5 N/m for the second, third, fourth, fifth, and sixth solvation layers, respectively. The dashed arrow (labeled $k_i^{(2)}$) indicates the amplitude measured for the second layer.

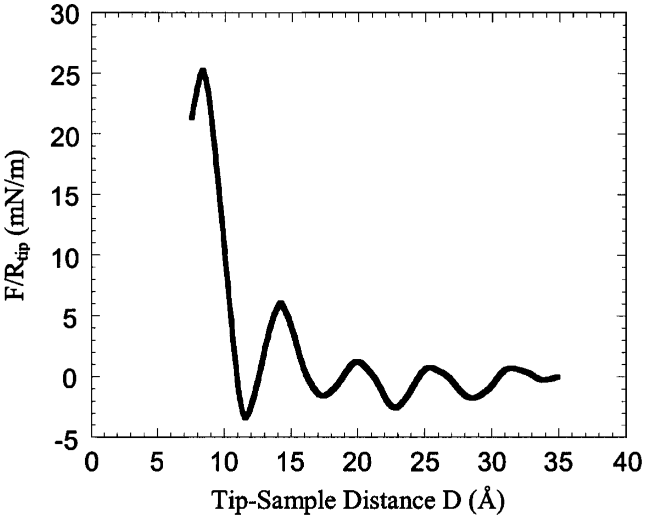

FIG. 3. The normalized force curve (F/R_{tip}) derived from the data of Fig. 2. The rapid decay rate of the repulsive maxima and shallow attractive minima are characteristic of the force profile of squalane as predicted by simulation [9]. This result indicates that solvation layers close to the HOPG surface are tightly bound while layers farther away degrade due to imperfect structuring caused by the interdigitation of methyl branches.

on either slope. These shoulders are especially prominent in the outer solvation layers and are not observed in the solvation force profiles of linear chain alkanes [22] and OMCTS. We associate these shoulders with the interdigitation of the branched methyl groups between the solvation layers. Such interdigitated packing of methyl groups is also found in the computer simulated density profiles of confined squalane [9].

The force can be calculated by integrating k_i with respect to D. Figure 3 shows such a result derived from the data of Fig. 2, with the force normalized by the tip radius (F/R_{tip}). Normalization allows comparison with previous SFA and AFM experiments. A strong repulsive maximum is observed close to the HOPG surface ($D \approx 9$ Å), which quickly decays with increasing separation from 25 mN/m at $D \approx 9$ Å to 6 mN/m at $D \approx 14$ Å. This decay rate is faster than the exponential dependence observed for OMCTS [1]. For the two solvation layers closest to the surface the repulsive forces in squalane are almost twice that of OMCTS, while the attractive minima is about half compared to OMCTS [19]. These observations are in agreement with simulation results, which indicate that the repulsive forces in the squalane film are about twice that of straight chain alkanes and spherical molecules [23]. We cannot calculate reliable forces at separations less than ~8 Å because tip instability occurs and it is not possible to integrate the stiffness data.

The similarities between the features we observe in the force profiles and those observed in the simulation results reported by Gao *et al.* [9] are marked. These are (i) large stiffness and force in the solvation layers closest to the surface, (ii) rapid decay rate, (iii) shallow force minima, and (iv) the presence of secondary "interdigitation" features. The periodicity shows that the molecules lie preferentially parallel to the confining surfaces. There is a slight decrease in the periodicity of the second and third solvation layers, from 5.8 ± 0.6 Å to 5.1 ± 0.2 Å, suggesting a higher packing density, and coupled with the large repulsive forces for these layers implies that these molecules are tightly bound. In comparison, the rapidly decaying force profile of Fig. 3 is indicative of the weakening of molecular order in the outer solvation layers. Simulation results show that confined squalane molecules have poor in-plane ordering due to the interdigitation of the methyl sidegroups [9]. This effect leads to the more widely spaced periodicity observed beyond the second solvation layer. We also find experimental evidence for interdigitation in the broadening of the repulsive maxima shown in Fig. 2. This broadening extends ~1.5 Å about the maxima, the approximate length of a methyl group. Simulations also show that the shallow force minima result from the presence of the methyl side chains of squalane, an effect not observed for spherical and straight chain molecules [23].

The results of this work differ from previous SFA experiments [7] and we believe this arises from two experimental differences, namely, (i) the substrate material is HOPG as distinct from mica and (ii) the smaller interaction area of AFM. HOPG has a surface geometry very similar to that of alkanes. Alkane molecules and their derivatives are known to physisorb strongly on HOPG because of the close registry between the adsorbant and the surface [24,25]. This may be a contributing factor in the strong repulsive forces observed for the first solvation layers. Conversely, it is possible that the absence of an oscillatory force in SFA experiments is a consequence of the surface structure of mica. We have repeated the AFM solvation experiments for the mica-squalane system and the results are inconclusive. There are hints in the force profiles that oscillatory forces are present, but the oscillations are weak and not reproducible. Interestingly, we also find on mica that the net force is always strongly attractive, in contrast to the SFA experiments [7] which show the onset of a strong monotonic repulsion at separations of $D \approx 16$ Å. A possible reason for this is that the AFM tip can more readily penetrate and laterally displace squalane molecules immobilized on the surface.

Clearly, the lateral extent of the interaction area is important in the measurement of oscillatory forces. The effective contact area in AFM is $\sim 10^{-16}$ m^2 compared with $\sim 10^{-10}$ m^2 in SFA. Simulations suggest that spherical and straight chain molecules may develop well-ordered solid-like characteristics when strongly confined [9], whereas branched molecules, such as squalane, exhibit liquid-like characteristics. Thus we anticipate that the correlation between adjacent regions of confined squalane will be much weaker than in the case of comparable straight chain molecules. In this respect, the confined squalane may be considered as an amorphous-like material exhibiting short range order, a view supported by He-atom scattering and neutron-scattering experiments of squalane monolayers at the liquid-graphite interface [26]. The AFM tip is able to probe and measure these localized molecular correlations. In contrast, the lack of long range order in squalane in combination with the measurement over a large interaction area appears to average out any oscillatory-type force behavior being observed in SFA experiments. Further indirect evidence for the lack of long range order at the squalane-HOPG interface comes from experiments using scanning tunneling microscopy (STM). We have attempted to image squalane adsorbed on HOPG by STM, but no molecular images could be obtained. In contrast, when straight chain molecules were used, ordered molecular domains could be readily observed [24,25].

In conclusion, we report the first experiments showing oscillatory solvation forces in squalane. Our results show that the layers closest to the surface of HOPG are tightly bound. Molecular branching, which degrades the quality of layering, is manifest in the rapid decay rate of the force maxima closest to the surface and in the observation of shallow force minima. A broadening of the repulsive peaks indicates that interdigitation occurs between the solvation layers. These results validate computer simulation predictions, which indicate that the molecular ordering of squalane can take place under nanoconfinement, and demonstrate the utility of AFM force measurements in liquids which exhibit only short range order.

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