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Depletion at solid/liquid interfaces: Flowing hexadecane on functionalized surfaces

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We present a neutron reflectivity study on interfaces in contact with flowing hexadecane, which is known to exhibit surface slip on functionalized solid surfaces. The single crystalline silicon substrates were either chemically cleaned Si(100) or Si(100) coated by octadecyl-trichlorosilane (OTS), which resulted in different interfacial energies. The liquid was sheared *in situ* and changes in reflectivity profiles were compared to the static case. For the OTS surface, the temperature dependence was also recorded. For both types of interfaces, density depletion of the liquid at the interface was observed. In the case of the bare Si substrate, shear load altered the structure of the depletion layer, whereas for the OTS covered surface no effect of shear was observed. Possible links between the depletion layer and surface slip are discussed. The results show that, in contrast to water, for hexadecane the enhancement of the depletion layer with temperature and interfacial energy reduces the amount of slip. Thus a density depletion cannot be the origin of surface slip in this system. © 2011 American Institute of Physics. [doi:10.1063/1.3549895]

I. INTRODUCTION

In fluid mechanics, the classical assumption of a flowing liquid featuring a stationary molecular layer adjacent to a solid boundary [no-slip boundary condition (BC)], has been disproved by various experiments with microscopic resolution.^{1,2} In order to have a quantitative measure of this effect, the slip length b is defined as the distance from the solid interface at which the flow profile of the liquid extrapolates to zero,

$$b = v(0) \left(\frac{\partial v(z)}{\partial z} \right)^{-1}, \quad (1)$$

where v denotes the velocity of the liquid and z is the distance from the interface. However, a microscopic picture of surface slip is still missing. Two theoretical scenarios have been proposed. In the case of real slip, the liquid slides over the solid interface on an atomic length scale. This implies either very high shear rates² or a roughness of the solid boundary which considerably differs from the size of the liquid molecules.³ The second, more realistic, scenario for moderate shear over molecularly smooth surfaces is termed “apparent slip.” In this case, a microscopic boundary layer is assumed to exist, which is different structurally and/or dynamically from the bulk liquid. One example of a dynamical near-surface change is the so-called shark-skin effect where, at a critical shear rate, microscopic corrugation of the interface leads to turbulent flow

in the adjacent liquid.⁴ This dynamical change appears as a thin layer of different viscosity. Likewise, a structural change of the boundary layer may produce a different viscosity that is observed as surface slip on a larger length scale, although the no-slip BC is still valid microscopically. Nevertheless, to the best of our knowledge, none of these models have been confirmed as the origin of slip in Newtonian liquids on molecularly smooth surfaces.

At present, two models explaining apparent surface slip are under discussion. In the first model, a microscopic layer with depleted liquid density near the solid interface has been proposed.⁵ Depletion layers at liquid/solid interfaces have been observed in various cases⁶ using x-ray and neutron reflectometry (NR), but only recently they have been recorded under shear load⁷ with NR. In the latter study, however, no influence of shear stress on the structure of the depletion layer was observed. The other model proposes an alignment of the near surface molecules with shear stress as the cause of apparent slip.⁸ This interpretation is consistent with a greater observed slip length for hexadecane, in which the molecules can be elongated, in comparison with squalane, which is a more symmetric molecule.⁹ Surface-induced molecular layering of flowing liquids has been observed in confined propanol¹⁰ using a surface force apparatus (SFA), and in eicosane¹¹ using an atomic force microscope (AFM) after quenching the flowing alkane. However, these techniques are either indirect or require direct contact with the interfacial liquid and thus may perturb the system.

The present study comprises an extension of an earlier work⁷ where we used NR combined with a cone/plate shear

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cell to record the liquid density profile perpendicular to the interface while shearing the liquid *in situ*. As a model system, we use hexadecane on differently treated silicon substrates. In the current study, newly commissioned instruments were used, namely the Liquids Reflectometer at the Spallation Neutron Source (SNS) in Oak Ridge, Tennessee, as well as the FIGARO reflectometer at the Institut Laue-Langevin (ILL) in Grenoble, France, enabling us to access a wider q -range and thus to considerably increase the experimental resolution. Moreover, the use of octadecyl-trichlorosilane (OTS)-covered substrate allows a direct comparison of our structural results with dynamical studies on the same system,⁹ building a bridge from depletion to slip.

Slippage of hexadecane has been examined by several techniques yielding slip lengths of 0–110 nm for a wetted interface and slip lengths of 20–350 nm for low interfacial energy substrates (hexadecane contact angle of about 40°).^{2,9,12} In spite of the wide variation of reported slip lengths, the qualitative result showing that higher interfacial energy impairs or suppresses slippage of hexadecane is consistent and intuitive. In the present study, we try to establish a connection between the presence of a density depleted liquid layer at the interface and slip. Surprisingly, in our study, the interfacial energy has the opposite influence on the extension of the depletion layer as compared to the slip length. The reduction of the depletion layer with increasing interfacial energy is confirmed by the other studies of static alkanes on solid surfaces.⁶ The main result is that the density depletion of liquids at solid boundaries cannot be generally attributed to surface slip.

II. EXPERIMENTAL DETAILS

In order to measure the reflectivity of the silicon/hexadecane interface while shearing the liquid *in situ*, a shear device with a cone/plate geometry was mounted onto the sample stage of a neutron reflectometer. We used a scattering geometry in which the neutron beam passes through the silicon substrate and is reflected downward from the horizontal solid/liquid interface. The sample geometry is described in more detail elsewhere.⁷ Two functionalized single crystalline silicon (100) substrates (70 mm × 70 mm × 10 mm, optically polished, obtained from CrysTec, Germany) were used throughout the experiments. To provide high surface energy, one wafer was chemically cleaned in freshly prepared Piranha solution [50/50 v/v H₂SO₄(concentrated) and H₂O₂(30% aqueous)] (Oxidizing! Do not mix with organic solvents/materials. Acid-resistant gloves, protective goggles, and lab coats must be worn handling the Piranha solution.) for 30 min and rinsed with Millipore water. Then the substrate was kept in Millipore water (as long as 12 h) up to the drying of the sample with a clean nitrogen stream just before the measurement. As a result, we obtained a surface which was completely wetted by hexadecane, corresponding to an interfacial energy of $\gamma_{sl} = 34 \text{ mJ/m}^2$ at room temperature.^{6,13} For the lower interfacial energy substrate another identically cleaned silicon wafer was subsequently chemically coated with an OTS monolayer by immersing it in a solution of 50 g bicyclohexane, 2.8 g carbon tetrachloride, and 0.8 g OTS for 15 min and flushing

afterward with chloroform to remove any cross-linked OTS chains. This procedure was repeated three times to ensure a fully covered substrate, and the resulting advancing contact angle of hexadecane was $40^\circ \pm 2^\circ$ at 22°C, $39^\circ \pm 2^\circ$ at 40°C, and $37.3^\circ \pm 2^\circ$ at 60°C. This corresponds to an interfacial energy of $\gamma_{sl} = 7.2 \text{ mJ/m}^2$ at room temperature. The contact angle error corresponds to variations on different spots on the surface. The contact angle hysteresis was always smaller than 2.8°. The OTS substrate was prepared 2 weeks prior to the experiment and was kept in air until the final ultrasonic cleaning in ethanol, acetone, and toluene and drying of the surface with a clean nitrogen gas stream just before the measurement. All relevant surface parameters of this study and our previous article are summarized in Table I.

The NR measurements with the OTS substrate in contact with fully deuterated hexadecane (deuteration > 98.4%, purity 98.9% from Polymer Source, Montreal, Canada) were performed on the Liquids Reflectometer at the SNS. A wavelength band of 2.5–5.5 Å was chosen with a resolution of $\Delta\lambda/\lambda = 0.5\%$. Seven incident beam angles ($\theta = 0.15^\circ, 0.25^\circ, 0.4^\circ, 0.7^\circ, 1.2^\circ, 2.2^\circ$, and 3.0° for liquid/solid measurements and $\theta = 0.15^\circ, 0.25^\circ, 0.45^\circ, 0.85^\circ, 1.6^\circ, 3.0^\circ$, and 5.5° for air/solid measurements) were used to cover a q -range up to 0.25 Å^{-1} for the liquid/solid interface and 0.48 Å^{-1} in the case of air/solid measurements with a constant angular resolution of 4.4%. A complete reflectivity curve was obtained in 2 h. After background subtraction, the raw data were normalized to a direct beam pattern recorded on the same day and divided by a constant factor for the corresponding slit size. Measurements with fluctuating neutron flux due to spallation source instabilities were discarded.

The NR curves of the cleaned Si wafer in contact with 44% deuterated hexadecane (diluted with protonated hexadecane from BDH Prolabo) were recorded on the FIGARO reflectometer at the ILL. Wavelengths from 2 to 22 Å were used with $\Delta\lambda/\lambda = 5.6\%$ resolution, while the angular resolution varied for the three incident angles ($\theta = 0.6^\circ, 2.0^\circ$, and 3.8°) between 1% and 2%. The background corrected raw data were normalized to the direct beam pattern measured for each slit setting.

Characterization of the OTS substrate by means of x-ray reflectometry was done on a Panalytical X'Pert Pro laboratory reflectometer. The substrate structure was determined by simultaneously fitting the x-ray and neutron reflectivities of the bare substrate in air, as well as the neutron

TABLE I. Interface properties at room temperature of the surfaces used in this study and in Ref. 7. The interfacial energy γ_{sl} was calculated by using $\gamma_{sl} = \gamma_{sg} - \gamma_g \cos \theta$, where γ_g is the surface tension of hexadecane (27.1 mJ/m^2), γ_{sg} the free surface energy (Ref. 13) and θ the contact angle of hexadecane.

Sample	γ_{sg} (mJ/m ²)	θ	γ_{sl} (mJ/m ²)
OTS	28	40°	7.2
HMDS	44	30°	20
Native Si	61	10°	34
UV/ozone treated Si	61	0°	34
Piranha treated Si	61	0°	34

data of the static OTS/*d*-hexadecane interface at 22 °C. The resulting substrate parameters were subsequently fixed and only a change of the liquid density due to temperature was allowed. Fitting of the reflectivity data was accomplished using corefination of a slab model with Motofit.¹⁴ The depletion layer at the substrate/*d*-hexadecane interface was modeled using an additional layer with reduced liquid density. Due to poor statistics in the reflectivity tail, negative numbers may appear after the background deduction. In order to take into account omitted negative numbers when fitting on a logarithmic scale, a constant background was included in the fits, even though the physical background has already been subtracted in the data reduction process. The given errors correspond to an impairment of the standard deviation (χ^2) by 5%, unless otherwise stated. For the determination of the contact angles, a DataPhysics OCA15EC was used.

III. RESULTS

A. Low interfacial energy surface

The OTS substrate was measured with x-ray and neutron reflectometry before and after the shear experiments, and no change was observed, apart from a slightly increased roughness of the OTS up to 5 Å; however, this roughness increase was not observed in contact with hexadecane. The resulting fitting parameters of the bare substrates are summarized in Table II. Note that the fitted roughnesses are on the same length scale as the thicknesses, especially in case of the silicon oxide layers, which makes it impossible to consider adjacent layers as independent from each other. Thus the corresponding densities and layer thicknesses have to be considered as effective parameters. The reflectivity curves themselves as well as the reflectivity curve for the static *d*-hexadecane/OTS interface at room temperature are shown in Fig. 1. A three slab model for the OTS substrate, consisting of a low and a high density hydrocarbon part and the silicon oxide layer was sufficient to obtain a consistent fit for the x-ray and neutron data simultaneously. This approach has already been

TABLE II. Fitting parameters of the bare substrates before the shear experiment measured with X-ray and neutron reflectometry. SiO₂ denotes the natural silicon oxide layer. *d*, ρ , and σ correspond to the thickness, scattering length density (SLD) for neutrons, and roughness (error function) of the respective layers. Note that the lower SLD for the low density OTS part comes from the hydrogen termination of the OTS tail. The given errors correspond to one standard deviation.

Parameter	Piranha	OTS
$\sigma_{\text{Si/SiO}_2}$ [Å]	1.6 ± 0.4	3.8 ± 0.18
d_{SiO_2} [Å]	8.24 ± 0.08	13.1 ± 0.18
ρ_{SiO_2} [10^{-6}Å^{-2}]	3.26 ± 0.01	3.42 ± 0.01
$\sigma_{\text{SiO}_2/\text{air}}$ [Å]	2 ± 0.3	
$\sigma_{\text{SiO}_2/\text{crystOTS}}$ [Å]		4.78 ± 0.03
d_{crystOTS} [Å]		19.9 ± 0.2
ρ_{crystOTS} [10^{-6}Å^{-2}]		-0.32 ± 0.001
$\sigma_{\text{crystOTS/amorphOTS}}$ [Å]		0.43 ± 0.43
$d_{\text{amorphOTS}}$ [Å]		5.3 ± 0.2
$\rho_{\text{amorphOTS}}$ [10^{-6}Å^{-2}]		-0.626 ± 0.002
$\sigma_{\text{amorphOTS/air}}$ [Å]		2.88 ± 0.02

FIG. 1. (a) Neutron (blue bars) and x-ray (black bars) reflectivity curves on a logarithmic scale of the bare silicon wafer covered with OTS; NR for the same substrate in contact with static *d*-hexadecane at 22 °C (red bars). The solid, dotted and dashed lines represent the best fits, respectively. (b) The corresponding SLD profiles obtained with the fits. The color code corresponds to the one used in (a).

successfully used in Ref. 15. In our case, the high density OTS part was 19.9 ± 0.2 Å thick, which corresponds to 14 fully stretched hydrocarbon monomers,¹⁶ with a density of $0.895 \pm 0.002 \text{ g/cm}^3$, close to the density of crystalline octadecane (0.93 g/cm^3).¹⁷ The low density layer had a thickness of 5.3 ± 0.2 Å corresponding to four hydrocarbon monomers and a density of $0.888 \pm 0.003 \text{ g/cm}^3$. The minor density difference between the two OTS parts was clearly visible by using neutrons due to the hydrogen termination of the OTS tail, which can be easily resolved in deuterated hexadecane due to the negative coherent scattering length density (SLD) of the protons in natural hydrogen. This model resulted in a χ^2 of 4.175 when fitting the three contrasts simultaneously. The assumption of an OTS head group between the OTS tail and the silicon oxide, as proposed in Ref. 16 and later used in Refs. 18 and 19, leads to a considerably worse fit with a χ^2 of 4.659. However, the overall OTS thickness of 25.2 Å in our model is comparable to the values reported in the latter studies.

A possible swelling or increased density of the OTS in contact with hexadecane was modeled as well, but this did not improve the fit quality, even though the number of free

FIG. 2. (a) Logarithmic neutron reflectivity curves from the OTS wafer in *d*-hexadecane (black bars) with the conformable fit (red line). The blue line is a simulation of the reflectivity without depletion. (b) Corresponding SLD profiles. (c) Fresnel normalized neutron reflectivity curves for the OTS/*d*-hexadecane interface at different temperatures. The 22 °C (blue squares) and 60 °C (red diamonds) curves are shifted by one for clarity. (d) The corresponding SLD profiles.

parameters increased. The only change of the substrate structure in contact with the liquid was the OTS roughness which decreased from 2.88 to 0.5 Å. According to the fit, swelling of the OTS layer with increasing temperature did not occur either. Thus, in the following, the bare substrate parameters were kept constant during the fitting.

As one can derive from Fig. 2(b), a 14 Å thick hexadecane layer with a density depletion of 30% must be introduced to fit the data with a standard deviation of 1.4. If no depletion layer is assumed, the best alternative fit has to assume swelling of the OTS layer and leads to a χ^2 of 4.1 [see Fig. 2(a)]. This impairment of the fit quality is much larger than 5% and obviously does not fit the measured reflectivity. Thus, this possibility was excluded. All other parameters determined from the bare substrate fit were kept constant in fitting the hexadecane data. In order to compare the resulting depletion effects, the depletion distance d_2 (Ref. 20) is introduced,

$$d_2 = \int_{\text{liquid phase}} \left(1 - \frac{\rho(z)}{\rho_{\text{bulk}}}\right) dz, \quad (2)$$

where $\rho(z)$ denotes the density of the depleted liquid at a distance z from the interface and ρ_{bulk} represents the bulk liquid density. d_2 reduces the smeared-out density profile of the

depletion to a steplike function that represents an equivalent layer of zero density.

The depletion distance calculated in the case of the OTS/hexadecane interface at 22 °C is 3.8 ± 0.24 Å. The subsequent application of shear at 500 s^{-1} does not change the depletion distance within the error bars. Increasing the temperature enlarges the depletion distance slightly to $d_2 = 4.6 \pm 0.45$ Å at 60 °C, as shown in Fig. 3, but no effect of shear is visible.²¹

B. High interfacial energy surface

Next we discuss the interfacial structure at the wetted surface. In this case, only a model with a considerably stronger SLD depletion of up to 100% and of 16–25 Å thickness fits the data, as seen in Fig. 4. The derived depletion distance is 20.5 ± 2.5 Å. Contrary to the OTS surface, the application of shear at 500 s^{-1} changes the reflectivity curve as can be seen in Fig. 4(a). The resulting depletion shrinks slightly to 16.5 ± 0.9 Å.

Due to the highly hydrophilic surface, the presence of a thin layer of protonated water cannot be excluded, even though the substrate was dried with a clean nitrogen stream

FIG. 3. Depletion distances calculated from the fitted SLD profiles of the OTS/*d*-hexadecane interface.

until no water was optically visible. From SFA studies, it is known that even the low solubility of water in oils can affect the hydrodynamic forces between hydrophilic surfaces on a length scale of several nm when working under a humid atmosphere.²² The assumption of a 13 Å thick protonated water layer instead of the depletion layer leads to the same fit quality, due to the small SLD difference between protonated water and air. Thus the depletion distances for the chemically cleaned SiO₂ interface have to be understood as an upper limit, as in the previous study.⁷

IV. DISCUSSION

A. Low interfacial energy surface

The calculated depletion distances, ranging from 3.4 to 5 Å in the case of the OTS coated surface, are consistent with previously measured values at the interface between octane and self-assembled monolayers (SAM).⁶ Note that in the present study the depletion layer can be modeled separately from the SAM due to the high resolution of the instrument, and, therefore, no reference system is needed anymore, which could introduce a systematic error. A further indication of the intrinsic nature of the observed depletion at the OTS/*d*-hexadecane interface is the enhancement of the depletion distance with temperature. The growth of the depletion layer with increasing temperature has already been observed for water in contact with a SAM and predicted by molecular dynamics (MD) simulations.⁶ A possible contamination of the OTS layer due to contact with air²³ is unlikely, as dust layers do not show any change with temperature, but increase with time,⁶ which was not the case for the depletion at OTS, even after 2 days. Furthermore, the contamination layer observed in Ref. 23 was only 2 Å thick, much thinner than the depletion layer at OTS, which spans about 14 Å.

Several properties of the OTS layer are crucial for the amount of slip, namely, the surface roughness²⁴ and the homogeneous surface coverage of the film.²⁵ Regarding our own experience and findings in the literature,²⁶ a nonhomogeneously grown or cross-linked OTS film, e.g., due to the presence of too much water during the growth process, shows up as a 12–15 Å thin film with a roughness of more than 5 Å. In our case, the overall OTS thickness was 25.2 Å with a roughness of 2.88 Å. Hence, we infer that

FIG. 4. (a) Logarithmic neutron reflectivity curves from the cleaned Si wafer in contact with 44% deuterated hexadecane at 22 °C. The blue squares correspond to the static case, the red ones to the sheared liquid. Open and closed symbols indicate reproduction measurements. The solid lines are fits, respectively. Additionally, the theoretical reflectivity without any depletion is shown by the dashed line. (b) The SLD profiles corresponding to the fits.

our OTS film is complete and comparable to the ones used in the cited literature. To the best of our knowledge, two research groups have investigated surface slip of hexadecane on silanated surfaces up to now. Fluorescence recovery after photobleaching (FRAP) has been used to measure a slip length of 3500 Å for hexadecane in contact with an OTS layer, which was 24.5 Å thick and 3.5 Å rough and thus directly comparable to ours.⁹ In a surface force study of hexadecane on hexadecyltrichlorosilane (HTS), a slip length of 200 Å was observed.¹² In this case the roughness was 3 Å.

As mentioned in the Introduction, viscosity change due to the depleted liquid at the interface may be a possible explanation of surface slip. If one considers this interfacial layer as a density depleted region solely (no change of the liquid structure), it can be related to the slip length b introduced in Eq. (1).²⁷ A straightforward calculation yields

$$b = \int_{\text{liquid phase}} \left(\frac{\rho_{\text{bulk}}}{\rho(z)} - 1 \right) dz. \quad (3)$$

The calculated slip length of flowing hexadecane over OTS at 22 °C is 5.18 ± 0.15 Å in our case. This is far too small to explain the reported hexadecane slip lengths mentioned

FIG. 5. Depletion distances for hexadecane calculated from the fitted SLD profiles of the liquid/solid interfaces using Eq. (3). The numbers for the HMDS surface, the untreated silicon, and the UV/ozone treated substrate are from Ref. 7. As comparison the depletion distance measured for *d*-octane in contact with a *d*-dodecanthiol SAM from Ref. 6 is included. The dotted line is a guide to the eye.

above. Accordingly, this result argues against the appearance of surface slip by a pure density depletion of the interfacial liquid.

B. High interfacial energy surface

Concerning the bare silicon substrate, considerably larger depletion distances of about 16–23 Å are indicated by the results. Moreover, this is the first system where we have been able to observe a change in the interfacial structure while applying shear. This shows that even a moderate shear rate of 500 s⁻¹ can affect the structure of the interfacial liquid featuring a bulk structural relaxation time on the order of ps. This dependence might imply discontinuous dynamics near the interface, e.g., surface slip. Unfortunately, the presence of a thin water layer cannot be excluded, thus these numbers have to be considered as upper limits on the depletion. Nevertheless, the calculated slip length via Eq. (3) lies between 41 and 133 Å. If part or all of the depleted SLD would be due to water the calculated slip length would be even smaller because the viscosity of water is greater than 0 and Eq. (3) assumes slip due to a viscosity reduction at the interface. In any case, this value is too small to explain the 1100 Å slip length measured with FRAP for hexadecane on a mica surface,⁹ in spite of the comparable surface roughnesses and surface energies in both studies. On the other hand, SFA based studies report no slip of hexadecane on mica surfaces.²² Here the liquids were degassed and the measurement was performed under a dry atmosphere. Perhaps this could be the origin of the discrepancy between the reported slip lengths.

V. CONCLUSION

All our results show the same trend with increasing interfacial energy, namely, an enhancement of the depletion layer. The same effect was observed, when the interfacial structures of different liquids in contact with the same solid were

compared.⁶ In Fig. 5 all depletion distances measured in this work as well as in our previous study⁷ and in Ref. 6 are plotted versus the interfacial energy γ_{sl} . The obvious connection between the interfacial energy and the extension of the depletion layer is in contrast with the trend of surface slippage of alkanes, which is more pronounced for lower interfacial energy surfaces.^{9,12} The enhancement of the depletion layer with temperature is also contrary to the temperature dependent reduction of slip length observed in polystyrene on OTS.²⁸ Accordingly, the enhancement of the depleted layer contradicts the amount of surface slip. Thus, in addition to slip lengths calculated via formula (3), which are orders of magnitude smaller than the reported literature values, the opposite trend of the depletion effect with interfacial energy we observe shows that the presence of a depletion layer alone cannot explain surface slippage of hexadecane. This result is in sharp contrast to the findings in a recent MD simulation study²⁹ of water on a diamond surface, where the calculated slip length increased for thicker depletion layers. This result shows that interfacial liquid structure has different effects on the boundary conditions of flowing liquids, dependent on the type of liquid used, and that the depletion layer cannot be generally attributed to surface slip. Therefore, structural investigations via surface sensitive diffraction techniques are necessary.

VI. SUMMARY

In summary, we have studied the interface of flowing hexadecane at functionalized solid boundaries by neutron reflectivity. For both high- and low-energy interfaces a layer with depleted liquid density at the hexadecane/solid interface is indicated by the results. But these depletion effects cannot explain reported slip lengths in similar systems if only a density depleted layer is assumed. The opposing influences of interfacial energy and temperature on depletion, as compared to surface slip, point out that the appearance of a depletion layer even contradicts slippage of hexadecane. Thus, different structural rearrangements, e.g., molecular alignments, are more likely to mediate surface slip as proposed in Refs. 8 and 9. Such surface-induced order under shear stress has already been observed in the case of micelles^{30,31} using neutron scattering and indirectly in confined propanol¹⁰ and eicosane¹¹ using SFA and AFM based techniques, as well as in MD simulations³² and theoretical calculations³³ of confined liquids.

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