

Accordingly, the product $\Delta t \Delta \nu$, which deviates largely from the Fourier transform limit, provides direct evidence of the laser-induced chirp. The experiment can be interpreted as a measurement of the action associated with the relevant electron trajectory; e.g., for the τ_1 trajectory, we find $\text{Re}S_{\text{free},1} = \alpha \times 10^{-14} \text{ J/(W/cm}^2\text{)}\hbar$ with $\alpha = 3 \pm 2$. The saddle-point Eqs. 3 through 5 yield, for the 19th harmonic at $I = 1.35 \times 10^{14} \text{ W/cm}^2$, $\alpha = 3.0$ ($\alpha = 22$) for the short (long) orbit, corresponding to $\tau_1 = 1.2 \text{ fs}$ and $\tau_2 = 2.2 \text{ fs}$. These results agree nicely with accurate theoretical calculations (28).

Notwithstanding the combined complexities of atomic physics and nonlinear laser-matter interaction, HHG and ATI spectra can be reproduced with a small number of quantum orbits. The identification of these orbits and the measurement of the corresponding action offer a unique way of controlling these processes and opens the possibility of new applications.

References and Notes

1. C. Cohen-Tannoudji, B. Diu, F. Laloë, *Quantum Mechanics* (Wiley and Hermann, Paris, 1977).
2. R. P. Feynman, A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
3. M. Gutzwiller, *Chaos in Classical and Quantum Mechanics* (Springer, Berlin, 1990).
4. K. Kulander, M. Lewenstein, *Atomic, Molecular, and Optical Physics Handbook*, G. W. Drake, Ed. (American Institute of Physics, Woodbury, NY, 1996), chap. 72, pp. 828–838.
5. G. G. Paulus, W. Nicklich, H. Xu, P. Lambropoulos, H. Walther, *Phys. Rev. Lett.* **72**, 2851 (1994).
6. B. Walker, B. Sheehy, K. C. Kulander, L. F. DiMauro, *Phys. Rev. Lett.* **77**, 5031 (1996).
7. Ch. Spielmann *et al.*, *Science* **278**, 661 (1997).
8. Z. Chang, A. Rundquist, H. Wang, M. Murnane, H. C. Kapteyn, *Phys. Rev. Lett.* **79**, 2967 (1997).
9. M. Drescher *et al.*, *Science* **291**, 1923 (2001); published online 15 February 2001 (10.1126/science.1058561).
10. Th. Weber *et al.*, *Nature* **405**, 658 (2000).
11. R. Moshhammer *et al.*, *Phys. Rev. Lett.* **84**, 447 (2000).
12. H. C. Bryant *et al.*, *Phys. Rev. Lett.* **58**, 2412 (1987).
13. M. Bellini *et al.*, *Phys. Rev. Lett.* **81**, 297 (1998).
14. G. G. Paulus *et al.*, *Phys. Rev. Lett.* **84**, 3791 (2000).
15. K. C. Kulander, K. J. Schafer, J. L. Krause, in *Super-Intense Laser-Atom Physics*, B. Piraux, A. L'Huillier, K. Rzażewski, Eds. (Plenum, New York, 1993), pp. 95–110.
16. P. B. Corkum, *Phys. Rev. Lett.* **73**, 1994 (1993).
17. M. Lewenstein, Ph. Balcou, M. Yu. Ivanov, A. L'Huillier, P. B. Corkum, *Phys. Rev. A* **49**, 4998 (1994).
18. R. Kopold, W. Becker, H. Rottke, W. Sandner, *Phys. Rev. Lett.* **85**, 3781 (2000).
19. R. Kopold, D. B. Milošević, W. Becker, *Phys. Rev. Lett.* **84**, 3831 (2000).
20. The acquisition of a single spectrum requires the recording of up to a billion photoelectrons. Therefore, femtosecond lasers with extremely high repetition rates should be used, and the data acquisition must be able to handle electron count rates of 200 kHz and more. The laser system used for the ATI experiment delivers 50-fs pulses with a repetition rate of 100 kHz and intensities up to $3 \times 10^{14} \text{ W/cm}^2$. The photoelectrons are recorded with a high-resolution time-of-flight spectrometer.
21. For the theory of HHG by an elliptically polarized laser field, see (29); for an early experiment, see (30). Similar control is offered by the use of multicolor fields or static magnetic fields; see, for instance (37).
22. A. Rundquist *et al.*, *Science* **280**, 1412 (1998).
23. P. Salières, A. L'Huillier, M. Lewenstein, *Phys. Rev. Lett.* **74**, 3776 (1995).

24. This laser-induced chirp can be compensated by the imposed chirp of the laser. Such control is demonstrated in (32).
25. Shaping the temporal envelope of the harmonic emission results in a corresponding shaping of the spectral profile; see (33).
26. C.-G. Wahlström, J. Larsson, A. Persson, T. Starczewski, S. Svanberg, *Phys. Rev. A* **48**, 4709 (1993).
27. The harmonics generated in an argon jet are sent into an XUV monochromator. By moving the grating in the first diffraction order and closing the exit slit, we measure a well-resolved spectrum. Then, the grating is set in the 0th order (so that the XUV pulse is not time-stretched), the slit is widely opened, and all the harmonic components are directed into a xenon gas target in the source volume of an electron spectrometer, together with a second laser beam, where they produce two-color ATI (harmonic + second laser with variable delay). The corresponding photoelec-

tron lines provide the cross-correlation signal from which the harmonic pulse duration can be derived, as shown in (34).

28. M. B. Gaarde *et al.*, *Phys. Rev. A* **59**, 1367 (1999).
29. P. B. Corkum, N. H. Burnett, M. Y. Ivanov, *Opt. Lett.* **19**, 1870 (1994).
30. K. S. Budil, P. Salières, A. L'Huillier, T. Ditmire, M. D. Perry, *Phys. Rev. A* **48**, R3437 (1993).
31. D. B. Milošević, A. F. Starace, *Phys. Rev. Lett.* **82**, 2653 (1999).
32. Z. Chang *et al.*, *Phys. Rev. A* **58**, R30 (1998).
33. C. Altucci *et al.*, *Phys. Rev. A* **58**, 3934 (1998).
34. T. E. Glover, R. W. Schoenlein, A. H. Shin, C. W. Shank, *Phys. Rev. Lett.* **76**, 2468 (1996).
35. We thank the Deutsche Forschungsgemeinschaft, the Alexander von Humboldt-Foundation, the VolkswagenStiftung, and the European Union TMR networks ERBFMRX-CT96-0002 and ERB-FMRX-CT96-0087.

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Density Fluctuations Under Confinement: When Is a Fluid Not a Fluid?

M. Heuberger,* M. Zäch, N. D. Spencer

Knowing the behavior of a fluid in small volumes is essential for the understanding of a vast array of common problems in science, such as biological interactions, fracture propagation, and molecular tribology and adhesion, as well as pressure solvation and other geophysical processes. When a fluid is confined, its phase behavior is altered and excluded-volume effects become apparent. Pioneering measurements performed with the surface forces apparatus have revealed so-called structural or oscillatory solvation forces as well as the occurrence of a finite shear stress, which was interpreted as a solidification transition. Here, we report measurements obtained with an extended surface forces apparatus, which makes use of fast spectral correlation to gain insight into the behavior of a thin film of cyclohexane confined within attoliter volumes, with simultaneous measurement of film thickness and refractive index. With decreasing pore width, cyclohexane is found to undergo a drastic transition from a three-dimensional bulk fluid to a two-dimensional adsorbate with strikingly different properties. Long-range density fluctuations of unexpected magnitude are observed.

Several experimental techniques, such as the surface forces apparatus (SFA) (1), differential scanning calorimetry (DSC) (2), neutron diffraction (3), or nuclear magnetic resonance (4) in porous materials, are capable of measuring properties of a fluid under molecular-level confinement. Here, an extended surface forces apparatus (eSFA) (5) has been used, comprising two thin (2 to 5 μm) mica sheets, which form a well-defined, single-slit pore of controllable width (i.e., surface separation), D (Fig. 1). The same mica sheets also form an optical interferometer using a 55-nm, silver-mirror coating on their reverse sides. The interferometer is immersed in a fluid, such as cyclohexane, and the fluid is increasingly confined between the surfaces by reducing D .

Cyclohexane becomes the central optical layer of a multilayer interferometer, which selectively filters (infrared-free) white light in transmission. When the optical distance, $\Omega = D \cdot n$ (D = film thickness, n = refractive index), of the thin film varies, the condition for constructive interference is altered, and the wavelength shift of interference fringes with different chromatic orders can be measured. Odd- and even-ordered fringes shift differently as a function of n , an effect that allows D and n to be independently determined. As one would expect, the measurement of n is more difficult for thinner films (5–7). Our measurement errors are $\sigma_D < 25 \text{ pm}$ for distance and $\sigma_n < 0.05$ for refractive index. Detailed error calculations are available (5). This represents a 10- to 30-fold improvement over conventional SFA techniques (6–12). Using imaging optics, transmitted light from a spot of lateral diameter $\varnothing \sim 1 \mu\text{m}$ can be analyzed. For a very thin slit

Laboratory for Surface Science and Technology, ETH Zentrum, CH-8092 Zürich, Switzerland.

*To whom correspondence should be addressed. E-mail: heuberger@surface.mat.ethz.ch

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Fig. 1. Fast spectral correlation (FSC) interferometry allows simultaneous and local measurement of thickness, D , and refractive index, n , of a confined fluid. The focused optical probe has a diameter of $1\ \mu\text{m}$ and is sensitive to attoliter volumes. FSC evaluates small wavelength shifts of interference fringes. One surface (e.g., a 2- to $5\text{-}\mu\text{m}$ -thick mica sheet) is mounted on a force-measuring spring of spring constant, $k = 1002 \pm 21\ \text{N/m}$, while the other surface is fixed. The approximate deflection, Δx , of the spring, which impels an external load, $F = k \cdot \Delta x$, is estimated from the difference between the local film thickness measurement, D , and the distance, M , moved by the loading actuator (39, 40).

between mica surfaces, e.g., $D \sim 1$ nm, the probed volume is thus on the order of $V \sim 10$ attoliter. This corresponds to an ensemble of 10^6 to 10^7 molecules (Fig. 1). When an external force, F , of typically $0 \text{ mN} < F < 1 \text{ mN}$ is applied, pressing the initially cylindrically curved mica surfaces together, they flatten elastically (13–15). The resulting circular contact, which defines the perimeter of the single-slit pore, may grow to a diameter of 10 to 50 μm .

Excluded-volume effects in confined cyclohexane have been previously reported (*16, 17*). When the pore width is reduced to a few molecular diameters, finite shear-stress (*17*) and film-thickness transitions can be observed. Such transitions are often found to be similar in size to a molecular diameter, $d = 530$ pm (*18*). The apparent periodicity of these transitions presumably motivated the hypothesis of a confinement-induced layering

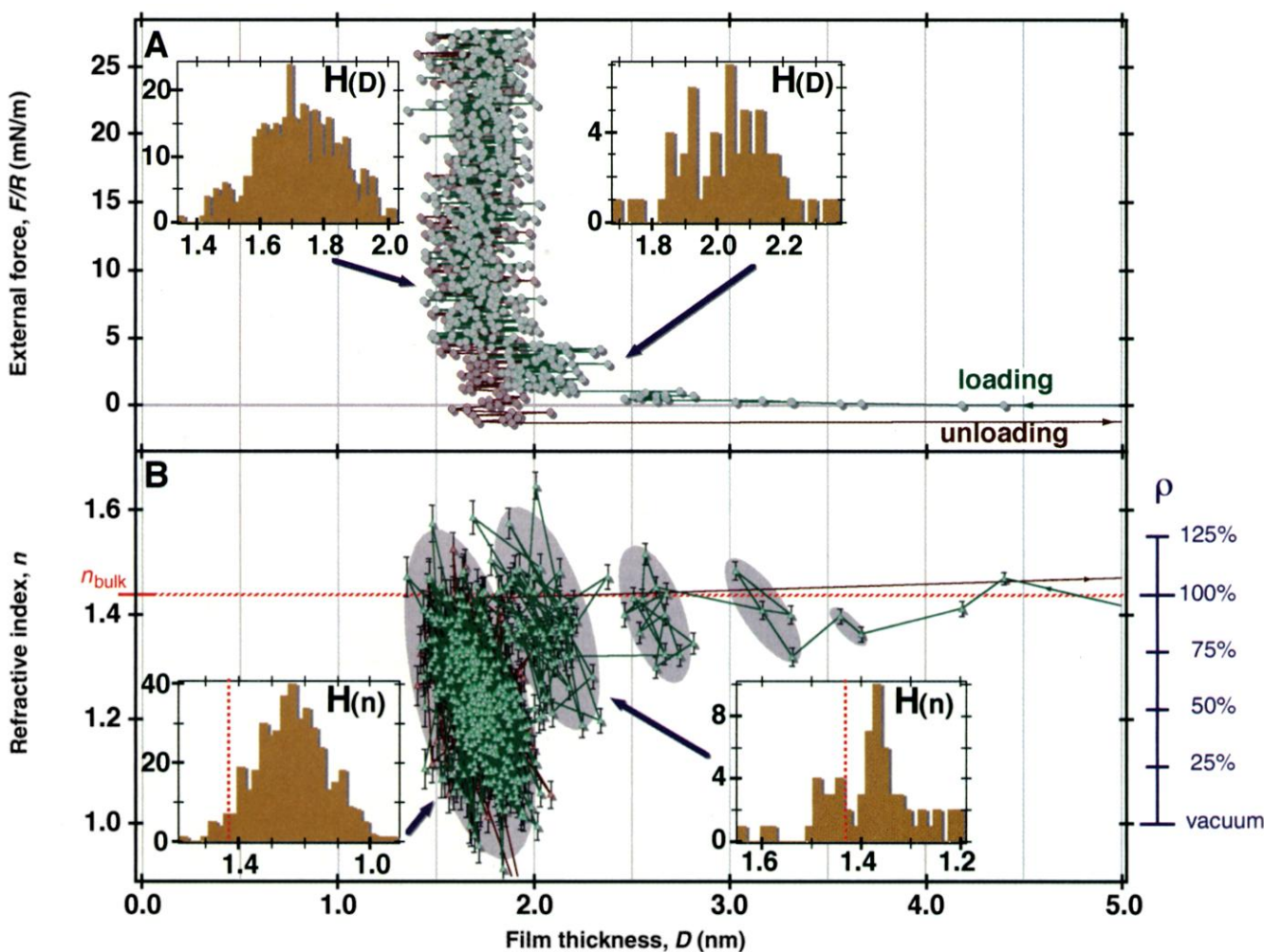


Fig. 2. Simultaneous measurement of D and n during a loading (green)/unloading (red) cycle in cyclohexane. The experiment was conducted in a bath of cyclohexane under isothermal conditions, $T = 24.785^\circ \pm 0.005^\circ\text{C}$, and with controlled actuator approach velocity, $v = 0.330 \pm 0.002 \text{ nm/s}$. Lines between points indicate the sequence of points, which were measured at intervals of $3000 \pm 3 \text{ ms}$. **(A)** Normalized force versus distance in the known regime of excluded-volume effects. Film-thickness transitions are highly reproducible at a

given point on the surface, but may vary by ± 1 nm depending on the surface location. **(B)** Simultaneously measured refractive index as a function of film thickness. We observed an overall 50% reduction of density superimposed on significant fluctuations. The scatter of the points is due to fluctuations, not measurement errors (see also Fig. 3). The fluctuations of D and n are correlated and exhibit distinctive statistics. Statistical measurement errors are only indicated if they are larger than the symbol size.

of molecules. An intimate relationship is commonly assumed between near-surface (time-averaged, mean-field) fluid-density oscillations and the forces required to induce such film-thickness transitions (contact value theorem) (19), which are thought to be reversible. Unfortunately, the SFA cannot measure attractive forces in an oscillatory potential without instrumental instability. During loading, the surfaces jump together when the gradient of the surface force, $dF(D)/dD$, exceeds the spring constant k . For this reason, each local minimum of an oscillatory potential has to be measured during a separate unloading cycle (1). Positions of maxima or minima are thus measured in different situations—during loading or unloading. Experiments of this type do not allow a clear distinction to be made between reversible (e.g., oscillatory potential) and irreversible (e.g., plasticity) effects. Measurements capable of distinguishing between plastic deformation and instrumental instability during film-thickness transitions have not hitherto been reported.

Film-thickness measurements under loading/unloading conditions have been obtained with the eSFA, as shown in Fig. 2A. The force, F , is normalized with the previously measured effective radius of surface curvature, R (19). To facilitate cross-figure readability, the data shown in this report all belong to one selected loading/unloading cycle. Supplementary data are available at *Science* Online (20). More than 1200 interference

spectra were measured and evaluated using fast spectral correlation (FSC) (5). Major transitions of the film thickness are observed while loading at constant velocity, $v = 330 \pm 2$ pm/s. The film thickness is subject to fluctuations of nonrandom statistics and ± 0.2 nm amplitude (see fine structure in Fig. 3). The histogram, $H(D)$ in Fig. 2A, taken at 2.0 nm, suggests that the film exhibits two preferred states, whereas the histogram corresponding to an average film thickness of 1.7 nm shows a considerably broader distribution.

A time-averaged view of D suggests notable deviations from molecular periodicity. The major structural transition occurring at a force of $F/R \sim 5$ mN/m, is smaller ($\Delta D \sim 350$ pm) than d . Indeed, analysis of many eSFA experiments reveals that film-thickness transitions occur neither at a well-defined film thickness and normalized external load, nor over exactly one molecular dimension, nor even in periodic intervals. Irreproducibility and nonperiodicity of structural forces have also been detected in previous studies (1, 21).

Figure 2B depicts the refractive index, n , measured simultaneously with the film thickness. Cyclohexane is nonpolar and is known to be optically isotropic, even in the plastic crystalline state (22). Using the empirical Gladstone-Dale formula (23), $(n - 1)/\rho = \text{constant}$, we can convert n to a mass density ρ (24). The red dashed lines in Fig. 2B indicate the bulk $n = 1.427$, which corresponds to $\rho = 100\%$ ($= 0.779$ g/cm³) (25). Under confinement, we

observe a reduction of the time-averaged density to half the bulk liquid value, which is comparable to the gas/liquid coexistence regime of bulk cyclohexane (26). We also observe significant density fluctuations in the probed volume. Analysis of these fluctuations reveals a correlation with the fine structure of the film thickness. This correlation is graphically indicated in Fig. 2B by tilted gray ovals in the background. The amplitude of the fine structure in Fig. 3A translates into a $<10\%$ volume change in the probed volume, which cannot explain the magnitude of these density fluctuations ($\sim 100\%$). They must have another origin. A statistically significant number of points reveals densities $\sim 9\%$ above that of the bulk liquid (Fig. 2B), which corresponds to the density of the solid S_1 phase in cyclohexane (26).

The evolution of the cyclohexane film during the same loading cycle is illustrated in Fig. 4. For thick films, we measured the expected bulk liquid density. We observed the appearance of long-range fluctuations in both D and n , at the line marked LRF, which coincides exactly with the first detected repulsive forces (visible as a deviation from linearity in Fig. 4A). The observed density fluctuations are of long range, extending over a lateral distance that is similar to or longer than the diameter of the analyzed region (Fig. 1, $\sigma \sim 1$ μm).

Film-thickness transitions may occur over significant times, especially at small values of D . Region R in Fig. 4 designates such a relaxation that evolves over more than 1 min.

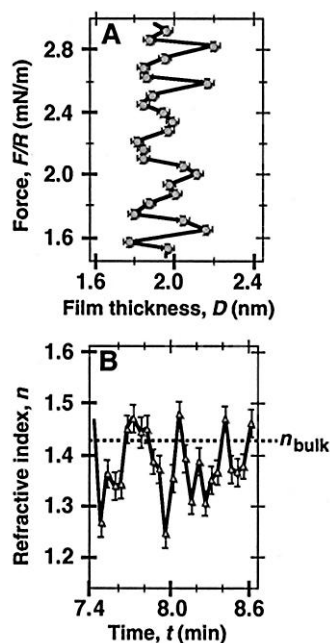


Fig. 3. Fluctuations of D and n during a loading/unloading cycle. (A) Fluctuations of film thickness result in a persistent fine structure in the conventional representation $[F/R(D)]$. (B) Density fluctuations can have a lifetime of several seconds.

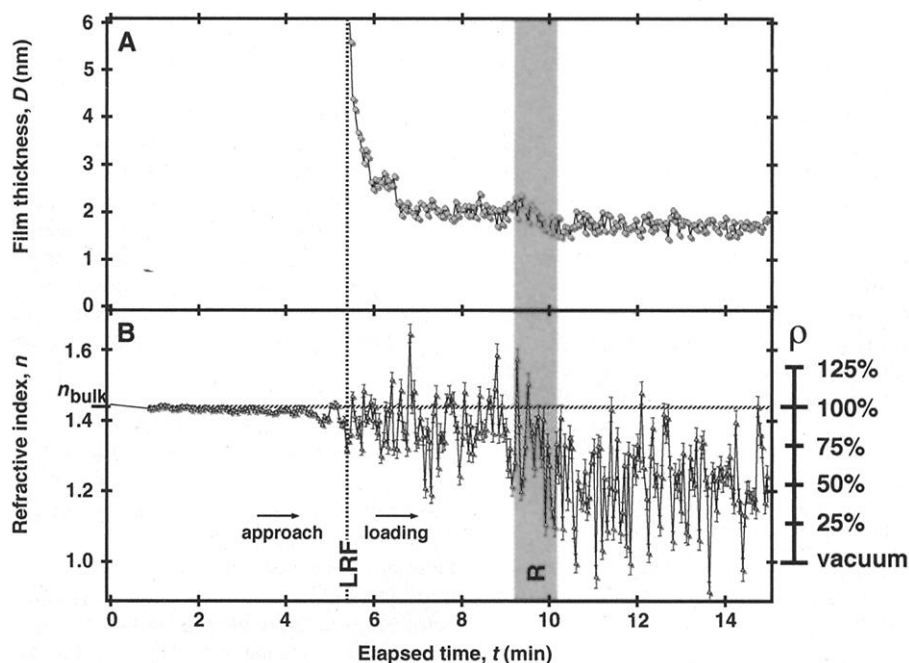


Fig. 4. Evolution of (A) film thickness and (B) simultaneously measured density. The onset of long-range fluctuations (LRF) in D and n coincides with the detection of repulsive forces and the appearance of film-thickness transitions. The transition in region R exhibits a characteristic time constant. Note that the conventional representation $[F/R(D)]$ of the same data (Fig. 2A) does not clearly reveal the evolution of such transitions. Error bars are only indicated if they are larger than the symbol size.

When D is reduced, the surface-to-volume ratio grows roughly as $1/D$. Consequently, volume contributions to the free energy (e.g., intermolecular potential and entropy), which are the basis of the known phase diagram (26–28), are progressively balanced by interfacial contributions (29). Under confinement, cyclohexane is known to exhibit a depression of phase-transition temperatures (2, 30–32) and a reduction of normalized enthalpies (32), as well as lower critical points (31, 33, 34). Macroscopic thermodynamics are inadequate to describe the properties of small volumes, being defined for infinite ensembles of particles. In small volumes, however, thermal fluctuations become increasingly important, and a time-averaged definition of thermodynamic functions is more useful (35).

To change the density of bulk cyclohexane from the solid state to the gas phase, an energy, W , of at least 36 kJ/mol (heat of melting plus heat of vaporization) is required. This energy is more than 10 times the kinetic energy, kT , available for thermal fluctuations. Homogeneous density fluctuations of the observed magnitude can only be thermal in nature if a reduction of W , by at least a factor of 10, is effective in this 2-nm-wide mica pore. This simple estimate is in excellent agreement with the sixfold reduction in transition enthalpies for cyclohexane in 4-nm porous silica, measured by means of DSC (32).

Molecules within 2 to 3 nm of the surface are thought to form a layer of thermally fluctuating optical and mechanical properties, as a consequence of the surface-induced decoupling of energy and density changes. This may explain many observations in confined cyclohexane, such as the time-averaged density reduction (Fig. 2B), density fluctuations (Fig. 2B), critical scattering (36), high surface mobility (4, 37), anomalously fast self diffusion (3, 33), modified molecular dynamics (33, 34) and macroscopic mechanical properties, such as apparent solidification (17, 38), and excluded-volume effects leading to quasi-periodic film-thickness transitions (Fig. 2A). Additional insights into the fascinating properties of confined fluids are expected from a planned laterally resolved real-time measurement of D and n in the eSFA.

References and Notes

- H. K. Christenson, R. G. Horn, J. N. Israelachvili, *J. Colloid Interface Sci.* **88**, 79 (1982).
- C. Faivre, D. Bellet, G. Dolino, *Eur. J. Phys. B* **7**, 19 (1999).
- J. C. Dore, M. Dunn, T. Hasebe, J. H. Strange, *Colloids Surf.* **36**, 199 (1989).
- D. W. Aksnes, L. Gjerde, *J. Mol. Struct.* **475**, 27 (1999).
- M. Heuberger, *Rev. Sci. Instrum.* **72**, 1700 (2001).
- P. Kélicheff, O. Spalla, *Langmuir* **10**, 1584 (1994).
- M. M. Kohonen, H. K. Christenson, *Langmuir* **16**, 7285 (2000).
- J. N. Israelachvili, *J. Colloid Interface Sci.* **44**, 259 (1973).
- B. Gauthier-Manuel, J.-P. Gallinet, *J. Colloid Interface Sci.* **175**, 476 (1995).
- H. K. Christenson, *Colloids Surf. A* **123–124**, 355 (1996).
- J. Janik, R. Tadmor, J. Klein, *Langmuir* **13**, 4466 (1997).
- V. Kitaev, E. Kumacheva, *J. Phys. Chem. B* **104**, 8822 (2000).
- H. Hertz, *J. Reine Angew. Math.* **92**, 156 (1881).
- K. L. Johnson, K. Kendall, A. D. Roberts, *Proc. R. Soc. London A* **324**, 301 (1971).
- R. G. Horn, J. N. Israelachvili, F. Pribac, *J. Colloid Interface Sci.* **115**, 480 (1987).
- M. L. Gee, P. M. McGuigan, J. N. Israelachvili, A. M. Homola, *J. Chem. Phys.* **93**, 1895 (1990).
- E. Kumacheva, J. Klein, *J. Chem. Phys.* **108**, 7010 (1998).
- H. Farman, F. M. Coveney, J. C. Dore, *Physica B* **180–181**, 857 (1992).
- J. Israelachvili, *Intermolecular & Surface Forces* (Academic Press, London, ed. 2, 1991).
- Supplementary data is available at www.sciencemag.org/cgi/content/full/292/5518/905/DC1
- H. K. Christenson, *J. Chem. Phys.* **78**, 6906 (1983).
- O. Hassel, A. M. Sommerfeldt, *Z. Phys. Chem. B* **40**, 391 (1938).
- J. H. Gladstone, J. Dale, *Philosophical Transactions* **153**, 317 (1863).
- G. Godbout, Y. Sicotte, *J. Chim. Phys.* **65**, 1944 (1968).
- C. Wohlfarth, B. Wohlfarth, in *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, M. D. Lechner, Ed., Group III, *Condensed Matter* (Springer, Weinheim, Germany, ed. 5, 1987), vol. 38.
- K. D. Wisotzki, A. Würflinger, *J. Phys. Chem. Solids* **43**, 13 (1982).
- L. Schulte, A. Würflinger, *J. Chem. Thermodyn.* **19**, 363 (1987).
- J. Mayer et al., *Phys. Status Solidi B* **166**, 381 (1991).
- R. Evans, M. B. Marconi, *J. Chem. Phys.* **86**, 7138 (1987).
- S. M. Ross, J. H. Strange, *Mol. Cryst. Liq. Cryst. Sci. Technol.* **33**, 321 (1976).
- C. L. Jackson, G. B. McKenna, *J. Chem. Phys.* **93**, 9002 (1990).
- R. Mu, V. M. Malhotra, *Phys. Rev. B* **44**, 4296 (1991).
- S. Stapf, R. Kimmich, T. Zavada, *Appl. Magn. Reson.* **12**, 199 (1997).
- H. F. Booth, J. H. Strange, *Mol. Phys.* **93**, 263 (1998).
- T. L. Hill, *Thermodynamics of Small Systems* (Dover, New York, 1994).
- J. B. W. Webber, J. C. Dore, H. Fischer, L. Vuillard, *Chem. Phys. Lett.* **253**, 367 (1996).
- H. F. Booth, J. H. Strange, *Magn. Reson. Imaging* **16**, 501 (1998).
- J. Klein, E. Kumacheva, *Science* **269**, 816 (1995).
- J. N. Israelachvili, G. E. Adams, *J. Chem. Soc. Faraday Trans. I* **74**, 975 (1978).
- J. N. Israelachvili, P. M. McGuigan, *J. Mater. Res.* **5**, 2223 (1990).
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Water at Hydrophobic Surfaces: Weak Hydrogen Bonding and Strong Orientation Effects

L. F. Scatena, M. G. Brown, G. L. Richmond*

Vibrational studies that selectively probe molecular structure at $\text{CCl}_4/\text{H}_2\text{O}$ and hydrocarbon/ H_2O interfaces show that the hydrogen bonding between adjacent water molecules at these interfaces is weak, in contrast to generally accepted models of water next to fluid hydrophobic surfaces that suggest strong hydrogen bonding. However, interactions between these water molecules and the organic phase result in substantial orientation of these weakly hydrogen-bonded water molecules in the interfacial region. The results have important implications for understanding water adjacent to hydrophobic surfaces and the penetration of water into hydrophobic phases.

Protein folding, membrane formation, micellar assembly, and wetting are a few of the many processes in which the interaction of water with hydrophobic fluid surfaces plays an important role. A driving force behind these processes is an uncommonly large entropy loss, which is usually explained as an enhanced structuring of water in the immediate vicinity of apolar molecules, biological

macromolecules, and hydrophobic surfaces. Experimental measurements that provide a molecular-level view of interfacial water structure and hydrogen bonding at these interfaces have proven to be problematic because of the difficulty in selectively examining interfacial water molecules. Hence, most of our understanding of the molecular structure of water at hydrophobic surfaces comes from theory (1–7). Here we report surface-specific vibrational spectroscopy experiments on the $\text{CCl}_4/\text{H}_2\text{O}$ and hexane/ H_2O interfaces, which provide detailed information on the structure and orientation of water influenced

Department of Chemistry, University of Oregon, Eugene OR 97403, USA.

*To whom correspondence should be addressed. E-mail: richmond@oregon.uoregon.edu