There has been long-standing debate about the physical state and possible phase transformations of confined liquids. In this report we show that a model confined liquid can behave both as a Newtonian liquid with very little change in its dynamics or as a pseudo-solid depending solely on the rate of approach of the confining surfaces. Thus, the confined liquid does not exhibit any confinement induced solidification in thermodynamic equilibrium. Instead, solidification is induced kinetically, when the two confining surfaces are approached with a minimum critical rate. This critical rate is surprisingly slow, of the order of 6 Å/s, explaining the frequent observation of confinement induced solidification.

The structure and dynamics of confined liquids is of great importance in interfacial phenomena from cell membranes to nanotribology. In nanoscale confined liquids, continuum theories break down and geometrically induced molecular layering is observed. New tools to study confined liquids include Surface Force Apparatus (SFA) and Atomic Force
Microscopy (AFM) \(^7\) and spectroscopic techniques \(^8\), such as Fluorescence Correlation Spectroscopy (FCS) \(^9\). Various experiments have yielded mutually exclusive findings on the dynamics of these confined systems. In OMCTS (octamethylcyclotetrasiloxane), a non-polar, roughly spherical, ‘model’ liquid, different research groups have reported behavior ranging from crystallization, glass formation, to no transition at all \(^10, 11\). The same is true for water, the primary biological solvent \(^13, 12, 14\). Here, we report on recent measurements of confined OMCTS using AFM. By systematically altering measurement conditions, we found that dynamical properties change profoundly as a result of a small change in the compression rate. Thus the observation of confinement induced solidification may be due to a kinetically induced transition from liquid to solid.

Measurements were performed with a home-built AFM that incorporates a fiber interferometer to measure changes in the cantilever’s amplitude and phase \(^15\). We vibrated the AFM cantilever far below the resonance frequency and monitored the amplitude and phase using a lock-in amplifier as the sample was approached toward the tip. By using small cantilever amplitudes, smaller than the size of a single molecule, we linearized the measurement allowing us to directly relate the measured cantilever phase and amplitude to the stiffness and damping coefficient of the confined liquid \(^14\). The sample consisted of OMCTS, sandwiched between a flat silicon dioxide surface and the silicon AFM tip. The OMCTS was purified by passing it through molecular sieves and filtering it through a 20 nm filter just prior to each measurement. The silicon oxide surfaces were prepared by oxidation in a heated Piranha solution (1:3 \(\text{H}_2\text{O}_2, \text{H}_2\text{SO}_4\)) and drying in an oven at 120 °C overnight. Experiments were performed at room temperature (25 °C).

To model the dynamic behavior of the liquid we found it convenient to use the simplest viscoelastic model for a liquid, the Maxwell model \(^16\). It consists of a linear spring and linear
viscous element in series and exhibits time-dependent stress dissipation under application of an external strain. The characteristic relaxation time is given by $t_R = k/(\gamma \omega^2)$, where $k$ is the measured junction stiffness, $\gamma$ is the measured damping coefficient and $\omega$ is the oscillation (angular) frequency of the cantilever. In a liquid, stresses will dissipate quickly and $t_R$ is expected to be low. In ideal (elastic) solids, stresses can be sustained indefinitely, so $t_R$ is expected to be large if the system behaves more solid-like.

Fig. 1a shows the stiffness and normalized damping coefficient measured at an approach rate of 3 Å/s. The damping coefficient is normalized to the measured bulk value far from the surface. This value varied between different levers, but was generally in the range of $10^{-5}$ Ns/m. It can be seen that the stiffness and damping coefficient are 'in-phase', i.e., maxima of the stiffness are aligned with maxima in the damping coefficient. Since a higher stiffness implies an increased density of the confined liquid, the confined liquid acts like a Newtonian fluid, where the viscosity is expected to increase with density. Fig. 1b shows the normalized mechanical relaxation time of the liquid, $t_R$, calculated from the data in Fig. 1a. Again the relaxation time is normalized to the measured bulk value, which typically was of order $2 \times 10^{-4}$ seconds. The mechanical relaxation time does not show any systematic changes associated with either confinement or layering. Thus, the dynamics of the system seems to be unaffected by confinement and the liquid remains liquid-like even at small separations. The only change that is induced is a density oscillation as a function of separation associated with the geometrically induced layering of the liquid molecules.

By contrast, Fig. 2a shows stiffness and damping at an approach rate of 12 Å/s. We can see a dramatic change in the relative magnitude of stiffness and damping coefficient. They are now 'out-of-phase', and the liquid shows reduced damping in the 'ordered', high stiffness state and liquid-like damping in the disordered, low stiffness state. This suggests that in the ordered state
Figure 1: (a) Junction stiffness (open circles) and normalized damping coefficient (line graph) versus displacement for OMCTS confined between the AFM cantilever tip and a silicon oxide surface. Cantilever frequency and free amplitude were 460 Hz and 3.5 Å, respectively. The sample was approached towards the tip at a ‘slow’ rate of 3 Å/s. Clear stiffness oscillations can be seen with an average separation of about 9 Å, consistent with the diameter of OMCTS molecules. The stiffness and the damping coefficient are in-phase in this case. (b) Junction stiffness (open circles) and Maxwell mechanical relaxation time (filled circles) versus displacement. Note that the relaxation time does not systematically change with displacement.

the liquid now behaves more like an elastic solid. Fig. 2b shows the corresponding relaxation time which now shows clear oscillations, with prominent maxima associated with the ‘solid’, ordered state of the liquid.

Fig. 3 summarizes our measurements. We plotted our observations in a matrix of two crucial parameters: The oscillation frequency of the cantilever and the approach rate. In our experiments, we also explored different cantilever amplitudes in a restricted range from 1.5 Å to 7 Å, but except for an attenuation of the peak heights in the stiffness at larger amplitudes, we did not find any systematic dependence in this range of small amplitudes. As can be seen in Fig. 3, the approach rate, rather than the oscillation frequency of the lever, is the crucial parameter that determines the dynamical behavior of the liquid. This may seem surprising since the maximum speed of the cantilever during each oscillation cycle is of the order of 1000 Å/s, i.e. much larger than the approach speed. However, the lever is oscillated at small amplitudes compressing the
Figure 2: (a) Junction stiffness (open circles) and normalized damping coefficient (line graph) versus displacement for OMCTS confined between the AFM cantilever tip and a silicon oxide surface. Cantilever frequency and free amplitude were 400 Hz and 2.4 Å, respectively. In this case, the sample was approached towards the tip at a ‘fast’ rate of 12 Å/s. Clear stiffness oscillations can be seen with an average separation of about 9 Å, consistent with the diameter of OMCTS molecules. The stiffness and the damping coefficient are now out-of-phase with respect to each other. (b) Junction stiffness (open circles) and Maxwell mechanical relaxation time (filled circles) versus displacement. Note that the relaxation time shows strong peaks associated with the high stiffness regions of the sample.

liquid film only slightly without squeeze-out of a complete molecular layer. Thus, the oscillation of the lever probes the mechanical and dynamical properties of the confined liquid film, and the slow approach of the tip actually forces molecular layers to be pushed out of the tip-sample gap. We can thus postulate that the observed kinetic phase transformation may be due to the fact that at a rate of 6 Å/sec and above, the molecular layers are ‘jammed’ and are not able to react to the narrowing of the gap fast enough.

It is useful to compare our results with recent experiments by Xhu and Granick (17) who report the onset of strong friction in confined OMCTS layers only if the layers were squeezed at a rate exceeding 5 Å/s. If the surfaces were approached much slower, friction was immeasurably small. Thus, the confined liquid became ‘solidified’ at approach rates of $\geq 5$ Å/s, almost identical to our observations. If we define a critical time scale by dividing the thickness of one
Figure 3: Summary of all measurements that showed stiffness oscillations plotted in a matrix of approach speed and cantilever oscillation frequency. Due to local roughness of the sample, not all measurements showed stiffness oscillations. The typical ‘success’ rate in our measurements was of the order of 20%. Open circles denote cases in which stiffness and damping were in-phase and the mechanical relaxation time was essentially constant with displacement - as in Figure 1 (liquid-like behavior). Filled circles denote measurements where stiffness and damping were out-of-phase and the mechanical relaxation time showed distinct peaks associated with the high stiffness phase of the confined fluid - as in Figure 2 (solid-like behavior). It can be seen that liquid- or solid-like behavior depends merely on the approach speed and not on the oscillation frequency of the cantilever. Size of circles denotes confidence in data - small circles denote cases where stiffness and damping peaks were aligned either in-phase or out-of-phase, but data was noisy or alignment of peaks changed as surface was approached (in these cases the alignment closer to the surface was used). In all other cases (large circles) the relative alignment of stiffness and damping peaks was clearly either in or out-of phase over the full range of observed peaks.
molecular layer by the critical approach rate, we find a critical time of the order of 9 Å/(6 Å/s) = 1.5 s, which is 12-14 orders of magnitude longer than typical molecular relaxation times. The identical time-scale observed in the SFA experiments by Xhu and Granick (17) and our present observations - despite the vastly different lateral dimensions of the confined region (∼10 µm versus ∼10 nm) - suggest that this behavior is independent of the lateral size of the confined region. Rather it must be intrinsic to characteristic properties of the confined liquid and the thickness of the film (number of layers).

There are few models describing the squeeze-out dynamics of confined liquids. Persson et al. (18) proposed a nucleation model. However, we found that the critical parameters obtained from this theory (in particular the pressure) do not match well with our experimental observations. Moreover, these parameters do not change much if the approach rate is varied in the range of 3 - 12 Å/s because of the logarithmic dependence of the critical values on the nucleation rate. Thus this approach cannot explain the dramatic shift in behavior from 3 to 6 Å/s approach rate.

How about the time to expel the layer after a 'hole' has nucleated? In a recent measurement by Becker et al. (19), an OMCTS layer of 25 µm radius was expelled in about 2 seconds. According to Persson et al. (18), the squeeze-out time is proportional to the area of film that needs to be expelled. Thus, with a 100 nm radius tip, a layer should be expelled in about 10 - 100 µs. This is much too fast to be observed in our measurements.

The mechanical behavior of this simple system changes profoundly from liquid to solid depending on an experimentally imposed (macroscopically long) time scale. The system exhibits a sharp kinetically induced transition in response to a rather small change in this time scale. This change (a factor of two) is very small indeed, if we consider thermodynamic arguments where rates are typically exponentially dependent on activation energies (like the nucleation model discussed above). This suggests that under confinement, i.e. effectively in two dimensions, it is difficult for the molecules to move out of the way of the approaching surfaces except by a slow
cooperative process, involving a characteristic number of molecules (which may depend on the specific interactions between the molecules). If the molecules are not given enough time, they become 'jammed', and the system is forced into a non-equilibrium 'solid' state, exhibiting high friction (Xhu and Granick) and an elastic response to normal pressure (present work).

How can we estimate the number of molecules that have to act cooperatively in order to arrive at a characteristic time of a few seconds for one complete squeeze-out? A typical molecular relaxation time (i.e. the average time a molecules moves freely before colliding with another molecule) is of the order of $\tau_0 = 10^{-14}$ s. Now, in order to move out of a layer beneath the tip, the molecules have to move away from a central point, opening up a hole in the layer. Treating the problem as a 2-dimensional problem, we can see that the probability that a molecule will move away from a central point, rather than towards it, is approximately 1/2 (since 1/2 of all possible angles of motion will point away from a central point). Thus the probability that $N$ molecules will all move away from a central point at the same time is of order $p_N = (1/2)^N$. Then the mean time for the event of $N$ molecules moving away from a central point, opening up a hole in the layer, to happen randomly is of the order of $\tau_0/p_N$. For this time to be 1.5 seconds, $N$ would have to be about 47 molecules. Thus it does not take a very large number of cooperatively moving molecules to arrive at macroscopic times.

These observations are reminiscent of the jamming transition in suspensions of colloidal particles, granular materials or glassy systems near the glass transition (20). In granular materials, for instance, fast compaction leads to an elastic response, while slow compaction speeds allow for a more plastic response and 'greater internal rearrangement' (21). Comparing the present observations to glassy systems, we find some similarities as well (indeed, 'solidified' OMCTS has been described as a glassy solid): The role of cooperativity and the rate dependence (cooling rate in the case of glass transitions). However, there are some important differences: The temperature in our experiments was constant, and the kinetic transition was induced by the
rate of volume reduction and not by cooling. A more striking difference is that OMCTS is a very simple system, consisting of small globular molecules, unlike the typical glass-forming systems, such as polymers or heterogeneous mixtures of several constituents.

What are the practical implications of these observations? In macroscopic systems, even in the absence of a lubricant, friction is dominated by confined layers of contaminant hydrocarbon and water layers (22). In such systems, lateral motions are typically not well controlled on a molecular scale and any shear motion will be accompanied by a normal motion far exceeding 3 Å/s. Thus, we could expect that macroscopic friction is partially due to molecular jamming of lubricant molecules. However, lubricants are often a mixture of different molecules. Thus layering may be greatly disrupted.

In microscopic situation, including Nano-electromechanical systems (NEMS), our findings may provide insight for the management of frictional dissipation. As long as approach rates can be kept very low, lateral friction could be kept very low as well. This should be possible in systems that are approaching molecular dimensions. Furthermore, the fact that under faster approach rates the system behaves elastically may lead to designs that exploit the confined lubricant as a 'smart liquid' to control approach rates in small devices.

Looking further afield, the important observation that even simple systems can alter their properties profoundly as a function of time scale, and that the critical time scale can be macroscopically long could have important implications in many areas of nanoscience and molecular biology.

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Supporting Online Material

**Instrument:** In our experiments, we use the dynamic mode of a home-built Atomic Force Microscope (AFM). We impose a small oscillation on the AFM cantilever using a piezoelectric element and then monitor amplitude and phase angle between the piezo motion and the cantilever end. The deflection of the cantilever is measured using a highly sensitive fiber interferometer with a measured base noise level of $600 \, \text{fm}/\sqrt{\text{Hz}}$. The end of the fiber is coated with a $30\%$ reflective thin film. This allows for multiple reflections between the mirrored cantilever back and the fiber end, before the light couples back into the fiber. To optimally align the fiber with respect to the cantilever we built a five degree-of-freedom inertial positioner with $\approx 50$ nm step size on which the fiber is mounted. Once we achieve the desired sensitivity the fiber is locked in that position using a feedback loop. This allows us to use small amplitudes of an angstrom or less, linearizing the measurement. Jump-to-contact is avoided by using sufficiently stiff levers. The cantilever is oscillated far below the resonance to avoid resonance enhancement of the amplitude and simplify data interpretation. The junction stiffness and the damping coefficient is then directly related to amplitude and phase in the following way.

$$ k = k_L \left( \frac{A_0}{A} \cos \phi - 1 \right) \quad (1) $$

and

$$ \gamma = -\frac{k_L A_0}{A \omega} \sin \phi \quad (2) $$

where $A_0$ is the free amplitude of the cantilever, $A$ is the measured amplitude during the approach, $k_L$ is the stiffness of the cantilever, $\phi$ is the phase angle between the cantilever drive and the cantilever end, and $\omega$ is the angular frequency of the cantilever oscillation.

**Sample Preparation:** In AFM and SFA studies of confined liquids ordering is only observed if the confining surfaces are atomically smooth. In AFM, the tip needs to be sharp, such that the measurement is dominated by forces acting on the very end of the tip. If the tip is blunt,
it is also typically rough on a molecular scale and due to 'destructive interference' of layering in different regions, no layering is observed in the measurements. Any roughness in the sample also disrupts layering. In our studies the OMCTS is confined between a silicon oxide substrate and a silicon tip. For producing smooth silicon oxide, silicon wafers are immersed in a strong oxidizer (hydrogen peroxide and sulfuric acid in the proportion 1:3) and heated for 20 minutes at 100°C for 20 minutes. The process of simultaneous etching and oxidation makes the surface free from any contaminants. The wafers are then rinsed in DI water and kept in the oven overnight at 120°C to remove any remaining water from the surface.

**Humidity control:** The liquid under study, OMCTS, is known to be hygroscopic. Before use, OMCTS is stored overnight in a sealed bottle containing molecular sieves which absorb the water. The OMCTS is then passed through a syringe filter of .02 nm pore size. If humidity is high, OMCTS gets contaminated by atmospheric water during the course of the experiment. In some of our measurements, where the sample was exposed to the air for long times, we saw a clear attractive background in the force profiles. To avoid this we place the AFM in a de-humidified chamber which is isolated from the rest of the room. A de-humidifier is used to maintain the humidity level below 30 % throughout the experiments.