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Perspective

Phase Transitions in Nanoconfined Fluids: The Evidence from Simulation and Theory

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Introduction

Nanoconfined fluids — that is, fluids confined between surfaces separated by nanometers — play important roles in many natural and man-made processes and products. One example is hard disk drive lubrication where, as data density has increased exponentially, the distance between the read head and rotating platen has been exponentially decreasing for several decades. This distance is now at 10–12 nm, and in the next generation of disk drives will be at 8 nm;[1] currently, monolayers of lubricant are used to protect disk drives in abnormal situations (e.g., power loss), but in the future it is expected that they will be lubricated at all times, including during read/write operations. Additional examples include the lubrication of microelectromechanical systems (MEMS), and nanoelectromechanical systems (NEMS),[2] and a model[3] for the natural lubrication of synovial joints, all of which can involve moving surfaces separated by distances of the order of nm. The latter exhibit very low-sliding friction at normal pressures up to 5 MPa or more; the model system, consisting of polyzwitterionic brushes polymerized directly onto the mica sheets in a surface force balance (SFB), exhibits very similar low-sliding friction (within a factor of 2 of the natural synovial joints) at pressures as high as 7.55 MPa. These three examples highlight the desirability of being able to lubricate effectively between surfaces moving relative to each other while separated by distances on the order of nm. If the lubricant undergoes a fluid-solid phase transition under nanoconfinement, resulting in a many order of magnitude increase in the effective viscosity and the onset of a nonzero yield stress,* then it is clearly not useful as a lubricant. In addition to lubrication at the nanoscale, phase transitions under nanoconfinement are also clearly important in industrial adsorption and catalytic processes (micro- and mesoporous adsorbents, with pore widths of under 2 nm and 2–50 nm, respectively, are widely used in the chemical, petrochemical, gas processing, and pharmaceutical industries for separations, pollution abatement, and as catalysts and catalyst supports).[4] Additional application areas (e.g., in geology, oil recovery and nanofabrication, including nanotemplating through nanoconfinement) are described in the excellent review article by Gelb et al.[4]

Hence, understanding the phase behavior of nanoconfined fluids is key to the rational design and control of many processes and devices, both in the processing industries and in the emerging field of nanotechnology. Specifically, the change in melting temperature as a function of nanoconfinement is an important quantity to understand and predict. Gubbins and coworkers have been leaders in understanding these phenomena

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*For a system consisting of two surfaces enclosing a fluid or solid, the yield stress is defined as the minimum force per unit area that is applied parallel to one of the surfaces in order to make it move relative to the other surface; for a liquid, the yield stress is zero, since for arbitrarily small stress, the two surfaces move. For a solid, and some nonlinear viscoelastic fluids such as suspensions, the stress applied must be greater than a particular material- and surface-specific value (the yield stress) in order to induce relative movement between the two surfaces, and can be associated with shear-induced melting.

at a molecular level, and the global theory of phase transitions under nanoconfinement developed by Radhakishnan et al.[5,6] remains the most complete theory of this phenomenon. The theory is a corresponding states approach, derived from combined classical density functional theory and simulations, that predicts the shift in melting point, as well as the phase of monomeric fluids confined between idealized smooth walls, as a function of the relative strength of the wall-fluid and fluid-fluid attraction, and the wall separation in reduced (relative to the monomer diameter) units. While this theory does not explain quantitatively all the observed experimental and simulation phenomena, it predicts most such phenomena at least qualitatively, and offers a clear and robust insight into the general effect of nanoconfinement. Specifically, the theory predicts that nanoconfinement affects (shifts) the freezing/melting temperature of a confined fluid. When the fluid-wall interaction strength is weaker than the fluid-fluid interaction the freezing/melting temperature is reduced while in the opposite case (fluid-wall interactions stronger than fluid-fluid) the freezing temperature is increased. Note that the theory does not suggest a change in the nature of the transition (e.g., from a first-order to a second-order transition), merely a shift in the temperature at which it occurs. In the theory, the magnitude of the shift is a function of the separation between the surfaces.

Experimentally, confirmation of this theory (i.e., the existence of an order-disorder phase transition) may be found in a large number of works utilizing a variety of techniques. Among these are surface force balance (SFB) experiments such as those performed by Klein and Kumacheva,[7] who have published a series of studies in which a rapid, abrupt and reversible first-order phase transition is observed as a function of confinement. Specifically, Klein and Kumacheva[7] find that as the distance h between the two mica surfaces enclosing the nonpolar liquid octamethylcyclotetrasiloxane (OMCTS) is reduced from seven to six layers of OMCTS, there is an abrupt change in effective viscosity (to a value ~seven-orders of magnitude larger than bulk), and the onset of a nonzero yield stress, indicative of a first-order phase transition to an ordered solid state, associated with a critical value h_c of surface-to-surface separation. Similarly well-characterized results were also found for cyclohexane,[7,8] with the formation of a solid phase again taking place at six layers, while less comprehensive results were reported for toluene[7] that suggested a fluid-solid transition at a fewer number of layers. Further SFB measurements confirming these results have been presented by, among others, Gee et al.[9] and Ohnishi et al.[10] Beyond SFB experiments, additional support for the formation of an ordered solid-like structure is provided by the work of Czwartos et al.,[11] as well as Sliwinska-Bartkowiak et al.[12] and Radhakrishnan et al.[5] who provided evidence of confinement induced freezing in the form of differential scanning calorimetry (DSC) and dielectric relaxation spectroscopy measurements.

Thus, it is perhaps surprising to learn that the idea of order-disorder phase transitions as a function of nanoconfinement (h) is not fully accepted, and that the results of Klein and Kumacheva, in particular, have been disputed by Granick and coworkers. Interestingly, the Klein and Granick groups reported largely similar experimental findings during the 1990s — the major difference between the two groups was in interpretation. Both observed a many-order-of-magnitude increase in effective Newtonian viscosity: Klein and Kumachava for OMCTS and cyclohexane,[7,8,13] Granick for n-dodecane and OMCTS[14] using the surface force apparatus (SFA). At a separation (2.7 nm) corresponding to six layers, Granick reported shear-rate-dependent effective viscosities for n-dodecane and OMCTS that exhibited a transition from Newtonian to shear-thinning behavior at shear rates of $\sim 10^2$–10^3 s^{-1}, or ~seven-orders of magnitude smaller than in bulk.[14,15] In contrast to Klein and Kumacheva's interpretation of their data as evidence for a rapid, abrupt and reversible first-order fluid-solid phase transition, Granick's interpretation of his measurements was that the nanoconfined fluids were undergoing a continuously increasing vitrification with decreasing h. Thus, in the early 2000s, the basic experimental observations — that nonpolar organic molecules undergo a many-order-of-magnitude ($\sim 10^6$-fold) increase in effective viscosity under nanoconfinement between mica sheets at distances of ~six layers — were consistent between the major groups; the difference lay in the interpretation of these data. Detailed molecular simulations of a model for nanoconfined n-dodecane by Cui et al.[15] described in more detail in the next section, yielded results under shear consistent with the measurements of Hu and Granick,[14] and in the absence of shear exhibited the same rapid, abrupt and reversible first-order phase transition observed by Klein and Kumacheva for OMCTS and cyclohexane. Cui et al. reported that nanoconfinement of n-dodecane induced densification of the fluid, and the number of layers at which the fluid underwent the transition to a layered solid structure also corresponded to the separation h at which the density of the confined fluid exceeded that of the corresponding bulk solid. The Cui et al. findings were completely consistent with the Radhakishnan et al.[5,6] theory, even to the point of agreeing with the value of separation at which the fluid-solid transition should occur. In a separate study,[16] Cui et al. showed that a nanoconfined *branched* alkane underwent densification but did not undergo the order-disorder transition. This is consistent with branched alkanes having lower melting points than linear alkanes in bulk; from the Radhakishnan et al.[5,6] theory, we expect that the melting point of the branched alkanes is raised by nanoconfinement, but not sufficiently to bring the melting point to room-temperature.

In 2001, Raviv et al.[17] reported experimental results for water nanoconfined between mica sheets. In this case, water did not exhibit many-order-of-magnitude increases in effective viscosity (the increase in effective viscosity at three and four layers of water was less than two-orders of magnitude), and there was no evidence for a fluid-solid transition under nanoconfinement. From the Radakrishnan et al. model,[6] the very different findings for nonpolar molecules and water are readily reconciled: the wall-fluid attraction in the case of nonpolar molecules and mica is much greater than the fluid-fluid attraction, resulting in elevation of the melting temperature, while for water the fluid-fluid attraction is considerably greater then the wall-fluid attraction. Molecular simulations of water nanoconfined by mica sheets by Leng and Cummings[18,19] reached the same conclusions as the Raviv et al. experiment. Thus, the difference between the behavior of nonpolar fluids and water under nanoconfinement is qualitatively explained by the Radakrishnan et al. model, and is reproduced quantitatively in simulations.

However, a very different explanation was proposed by Christenson and coworkers,[20–22] based on their discovery of the presence of 20–25 nm platinum nanoparticles on the mica surfaces in their own surface force apparatus (SFA). The nanoparticle contamination originated in the method for preparing the mica sheets for the SFA — i.e., by cleaving the mica sheet with a hot platinum wire. The difference in effective viscosity between nanoconfined nonpolar fluids and water was then attributed to the fact that the nanoparticles remained on the mica in the presence of nonpolar fluid, but left the surface in the presence of water. In this scenario, the many-order-of-magnitude increase in viscosity for nanonconfined nonpolar fluids originates from drag induced by the Pt nanoparticles, which is presumed to be absent in the case of water. Granick reported that the mica surfaces in his experiments suffered from Pt nanoparticle contamination,[23] and he adopted a different method of mica preparation[24] which avoided the problem. With this new method of surface preparation, Zhu and Granick[25] reported that for OMCTS the magnitude of the effective viscosity was dependent on the rate at which the mica surfaces were brought together; bringing the surfaces together at speeds of less than 0.01 nm s^{-1} (called quasi-static) yielded very low-effective viscosities, while "rapid quenches" of 0.5–2 nm s^{-1} resulted in many-order-of-magnitude increases in viscosity not dissimilar to previous results reported by Granick. These findings were disputed by Israelachvili and coworkers,[26] and would not be observable in simulation since the movement of surfaces at rates of 0.01–2.0 nm s^{-1} (i.e., 0.01–2.0 $\times$ 10^{-12} nm ps^{-1}) is effectively motionless by molecular simulation standards. Subsequent studies have suggested that the distinction between quasi-static and rapid quenches is related to entrapment of molecules in nonequilibrated structures[27] during squeeze-out of the fluid between the SFA surfaces. As we discuss in relation to the simulations in the next section, the many-order-of-magnitude smaller contact area in simulations appears to be responsible for rapid (i.e., ns time scale) equilibration of nanoconfined structures, and the absence of any observed entrapment in the simulations.

In contrast, Klein and coworkers[28] showed that their standard method of mica preparation did not lead to Pt nanoparticle contamination, and by repeating their experiments with two different surface preparation methods, they confirmed that their previously published results were reproducible and robust.

In the next section, we describe molecular dynamics simulations of nanoconfined fluids, aimed at reconciling the experimental findings. They illustrate the ability of molecular simulation to shed powerful light on complex phenomena.

Molecular Simulations of Nanoconfined Fluids

Molecular simulation is becoming a standard tool for understanding systems at the molecular level,[29,30] and, thus, it is natural to turn to molecular simulation to attempt to resolve the experimental controversies previously outlined. In particular, we note that the SFB/SFA experiments do not directly measure the structure of the confined fluid: rather, the structure and existence/nonexistence of any phase transition is being inferred from SFA/SFB measurements under shear.

Although a number of simulation studies have been performed related to the SFA/SFB experiments, the first simulations to attempt to model the Klein and Granick experiments with a high degree of molecular fidelity were reported by Cui et al.[15] who performed molecular dynamics simulations of n-dodecane nanoconfined between mica-like surfaces. The intermolecular potential used for n-dodecane was the SKS united atom model[31] (in which CH_3 and CH_2 groups are treated as single spheres), the parameters for which are fitted to ensure the model exhibited the experimentally measured phase envelope and critical point of n-dodecane. The mica surface was modeled by an FCC crystal of atoms interacting via the Lennard-Jones (LJ) potential, with the LJ energy parameter designed to reproduce the surface energy of mica; the cross-interactions between the surface and the spheres in n-dodecane were obtained using standard Lorentz-Berthelot combining rules, with the result that the wall-fluid attraction is 4.5 times the fluid-fluid attraction. The simulations were performed, in the presence and absence of shear, in the NVT (constant number of molecules, volume, and temperature of the FCC solid) ensemble, although several were performed at constant normal pressure rather than constant volume. The impact of shear was studied in three different ways (see Figure 1): by moving the mica surfaces to the left and right at constant velocity and volume and measuring stress in the fluid; by applying a constant force per unit area to the left and right on the mica surfaces (i.e., constant applied shear stress at constant volume), and measuring the induced velocity of the surfaces; and by measuring the induced velocity of the surfaces at constant stress and constant normal pressure. These three simulation methods provide three different routes to the effective viscosity, and the consistency between them, shown in Figure 1, suggests the results are reliable. The constant stress simulations measure an effective viscosity in much the same way as the experiment, although the simulations are limited to high-strain rates (beyond those accessible to experiment) due to the small system sizes in the simulation.* As shown in Figure 1, the simulation results are consistent with the sliding data of Hu and Granick.[14] The simulations also suggested the existence of a nonzero yield stress, in agreement with the findings of Klein for OMCTS and cyclohexane.[7,8,13] In the absence of shear, the simulations showed that the structure of the nanoconfined fluid was a layered herringbone solid[32] (see Figure 1), with a sharp transition from fluid to solid at six layers.

While the united atom (UA) approach used by Cui et al.[15,16,32] and subsequently Jabbarzadeh and coworkers[33–37] has provided valuable insight into the effects of nanoconfinement, it could be argued that the simulations introduced some artificialities that potentially affect the results. In particular, the NVT simulations of Cui et al. utilized a relatively small system size which, coupled with the shape and periodic nature of the simulation box, may have promoted and stabilized the herringbone ordered structure. Additionally, the rate at which

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*In nonequilibrium simulations such as those considered here, an external field (shear stress or sliding velocity) is being applied to measure a nonzero quantity (sliding velocity or shear stress, respectively) that on average is zero at equilibrium. Since the thermal fluctuations (noise) in small systems is large compared to macroscopic systems, distinguishing the measured quantity (or signal) from zero is difficult unless the applied field is large. Hence, the problem of sufficient signal-to-noise ratio requires the application of large fields, so that the simulation are at high-effective strain rates.

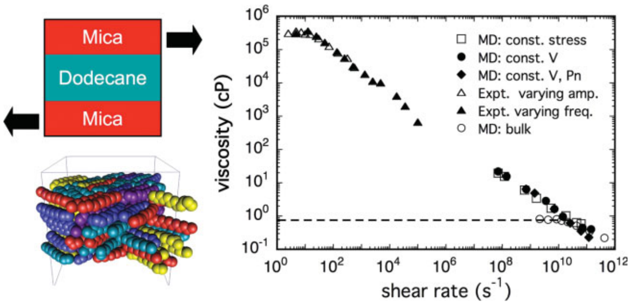

Figure 1. Molecular dynamics simulations of nanoconfined dodecane by Cui et al.[15,32]

Top left: Simulation geometry, showing the mica (modeled as an FCC LJ solid) and dodecane (modeled by UA SKS model). Simulations were performed at equilibrium (no motion of mica surfaces), constant stress (fixed force per unit area applied in direction of arrows, velocity measured to obtain strain), and constant strain (fixed velocity in direction of arrows, stress measured to obtain viscosity). The system is periodically replicated in the horizontal directions. Right: Calculated and experimental viscosity of the six-layer *n*-dodecane film vs. effective shear rate on log-log scales for constant-stress (squares) and constant-velocity (solid circles) simulations at constant film thickness; constant-velocity simulations at atmospheric normal pressure (diamonds), experiment (triangles), and calculated bulk viscosity (open circles). Dashed line indicates the constant Newtonian viscosity plateau of bulk dodecane. Experimental data were taken from the published work of Hu and Granick[14] (Figure reprinted with permission from Cui et al.[15] © 2003 American Institute of Physics (AIP)). Bottom left: Structure of nanoconfined dodecane obtained at equilibrium (in the absence of shear) after ~20 ns of simulation (Image reprinted with permission from Cui et al.[32] © 2001 American Intstitute of Physics (AIP))

the fluid was confined (or quenched) was very rapid compared to experiment, and relatively simplistic models were used, particularly in the description of the mica surfaces, that might not adequately represent the experimental system. To a large degree the choices made in the simulations of Cui et al. were driven by the available computational resources of the time. The question of system size was recently addressed in the work of Jabbarzadeh et al.[36] who studied mica surfaces that have approximately four times the surface area of Cui et al. work (51.84 nm^2 vs. 12.96 nm^2) and exhibit exactly the same behavior (i.e., the formation of a herringbone ordered structure) as observed in the Cui et al. systems. In our own unpublished work, we have used even larger mica sheets (80–400 nm^2), and obtain the same results as Cui et al.[32] and Jabbarzadeh et al.[36] Thus, it seems that system size does not play a determining role in earlier simulation studies.

We now consider the rate of confinement. From an experimental point of view, Zhu and Granick[25] have argued that a rapid quench is when the surfaces approach each other at a rate of 0.5 nm/s or faster; other authors have subsequently conjectured that at surface approach rates higher than this threshold a jammed, nonequilibrium state is created during squeeze-out of the fluid as the surfaces approach.[27] This problem is clearly exacerbated with increasing contact area; for comparison, in the Cui et al.[32] simulations the contact area is ~50 nm^2 ~5 × 10^{-5} μm^2, in the SFB it is ~10^2 μm^2, and in the SFA it is ~10^4 μm^2. Thus, although in simulations the rate of confinement can be very large (e.g., in a constant pressure NPT simulation, the surfaces typically move at speeds of ~1 Å/ps, and, thus, many orders of magnitude larger than experiment), the much smaller contact areas make it feasible that the fast rate of approach is not an issue. Nevertheless, in order to check this, Docherty and Cummings[38] recently performed simulations using the grand canonical molecular dynamics (GCMD) technique of Gao and Landman.[39] As shown in Figure 2a, this method may be thought of as taking the simulation system of Cui et al. and, instead of periodically replicating the simulation cell in the lateral direction, placing a large amount of bulk fluid on two opposite sides of the confining sheets such that molecules are free to enter, and leave, the slit from the bulk fluid (i.e., the confined fluid and surrounding bulk are in equilibrium). The entire system is periodically replicated in three dimensions, and the simulation is performed at constant pressure, with the box length in the lateral direction used to maintain the pressure at 1 bar. The advantage of this NPT-GCMD method is that the surfaces remain stationary relative to each other for the duration of the simulation (i.e., the surface separation h remains constant), thus, eliminating confinement rate as a factor, and the confined fluid is in equilibrium with bulk fluid, so that the number of molecules in the confined region is not predetermined. NPT-GCMD simulations of the n-dodecane/FCC LJ system again result in a herringbone ordered structure with the same structure and orientation relative to the confining surfaces (Figure 2b).

The consistency of the earlier Cui et al. NVT simulations,[32] our NPT simulations[38] (not reported here), and our NPT-GCMD results[38] suggests that confinement rate does not play an important role in the simulations over the simulated time scales (typically 10 –100 ns); in retrospect, this is to be expected based on the contact area in the simulation being ~10-orders of magnitude smaller than that of the SFA. The role of contact surface area—which is directly related to the amount of liquid to be displaced as the surfaces approach, and, thus, is proportional to the time taken for the confined fluid to reach an equilibrium state—suggests a qualitative explanation for Klein and Kumacheva not observing a difference in their results as a function of surface approach speed. Based on their SFB contact area being two-orders of magnitude smaller than the SFA, one could expect that the SFB would reach equilibrium structures much more rapidly than the SFA. From a simulation point of view, the consistent formation of a herringbone structure aligned at 45° to the surface is perhaps unsurprising when one realizes that the n-dodecane molecules are aligning with the "grooves" in the FCC mica surfaces. This is further borne out by the fact that if the FCC surfaces are replaced with BCC surfaces, as in the work of Jabbarzadeh et al.[36] the same herringbone structure is formed, albeit it rotated 45° such that alignment with the surface is maintained. These simulation studies therefore clearly demonstrate that the use of a simplified mica surface structure is influencing the nature of the confined fluid-solid transition.

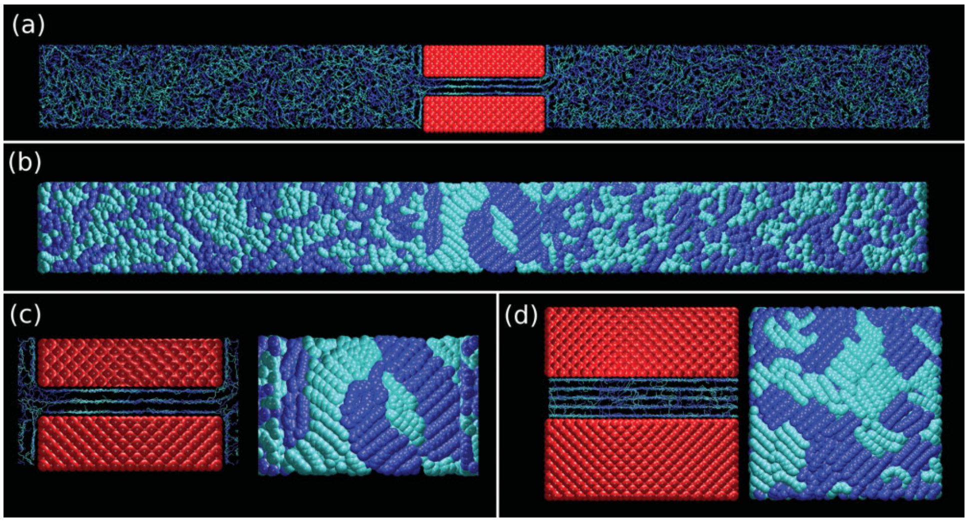

Figure 2. A comparison of GCMD and NPT ensemble simulations.

Panels (a) and (b) depict a side and top view of an equilibrated GCMD simulation with a fixed-surface separation of three dodecane molecular diameters. In the top view, panel (b), the mica is removed to reveal the structure of the confined fluid. Panel (c) shows a close of up the confined dodecane molecules for this same system. The difference between the confined and bulk regions is dramatic, with the confined molecules freely forming three distinct layers, with an intra-layer herringbone structure. Panel (d) depicts an equilibrated NPT simulation for a separation of five molecular diameters. Comparing panels (c) and (d), it is clear that in both simulation techniques, the equilibrated structure is essentially the same, i.e., a layered herringbone structure.

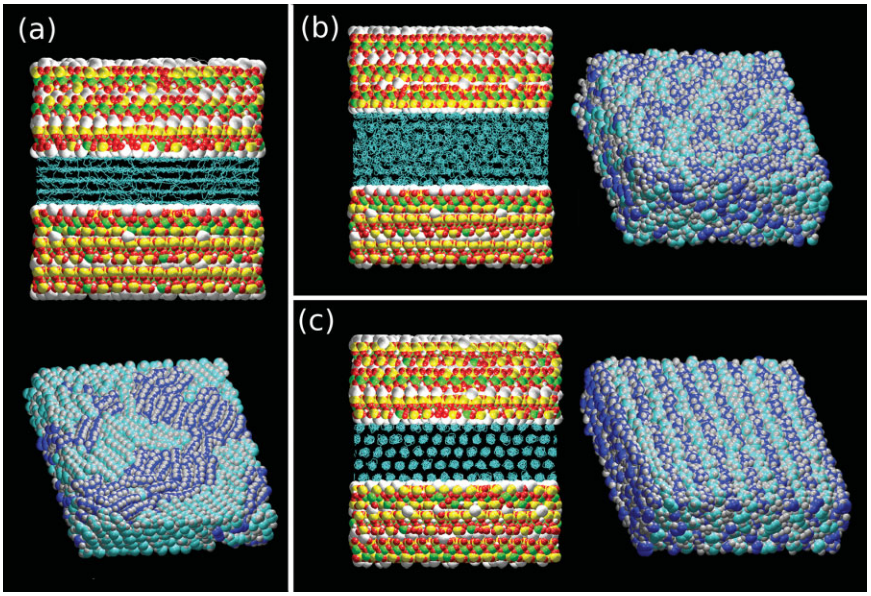

Figure 3. The evidence from atomistic simulation.

Panel (a) depicts an atomistic NPT ensemble simulation of nanoconfined dodecane for a surface separation of five molecular diameters. The top picture shows the full simulation, including mica. The color coding of atoms is: red — oxygen, white — hydrogen or potassium; green — aluminum, and yellow — silicon. Carbon atoms are represented as light or dark blue spheres; the contrast in the carbon atoms is to show the domains of layered herringbone structure. As in the simpler models,[32] the confined fluid undergoes a transition to a layer and ordered structure with an intra-layer structure consisting of regions of parallel molecules. Panel (b) and (c) show an equilibrated atomistic NPT ensemble simulation for cyclohexane with a separation of six and five molecular diameters, respectively. In the case of six diameters, the cyclohexane remains fluid-like (order parameter of 0.34). Conversely, upon moving to a separation of five diameters, the molecules undergo a rapid and abrupt transition to an FCC ordered solid-like structure (order parameter 0.90).

Having established that the NPT and NVT simulation approaches yield results consistent with the much more rigorous NPT-GCMD methodology, we have recently applied the NPT simulation approach but with fully atomistic models of mica and the alkanes. The reason for doing this is many-fold; however, the most important reason is that unless we utilize a true flexible, atomistically detailed model for mica, in which the strong mica-alkane interactions arise naturally as a result of Coulombic and other interactions (as opposed to being fitted into a non-Coulombic effective potential) the simulations are open to the criticism that they may be valid results for a model of mica-alkane, but not indicative of what happens in the real system. For this reason, we implemented NPT simulations using the fully flexible state-of-the-art Heinz et al.[40] forcefield for muscovite mica (which includes partial charges for all ionic species), and the all-atom version of the optimized potentials for liquid simulations (OPLS-AA) of Jorgensen et al.[41] In this simulation, the strong mica-alkane attraction largely arises from electrostatic interactions between the ions in the mica surface and the partial charges on the alkanes. For n-dodecane the atomistically detailed simulations[38] lead to the same conclusions as the Cui et al. simulations: namely, below a critical number of layers, there is a transition to an ordered, layered herringbone structure, with the domains at angles of 120° and 60°, compared to the Cui et al. simulations, where the domains were at angles of 90°, the latter reflecting the FCC structure of the confining surfaces (see Figure 3a). As part of this same study utilizing fully atomistic mica and alkanes,[38] we have also examined cyclohexane, and we find that again there is a critical number of layers below which cyclohexane transitions into a solid state, in agreement with the findings of Klein and Kumachava.[7,8,13] The structure of the confined solid phase of cyclohexane is FCC, and in Figure 3 we present configurations from the fully atomistic simulations, along with order parameters[42] for the nanoconfined cyclohexane.

Conclusions

In this Perspective, we have reviewed simulations that span almost a decade, aimed at understanding the nature of structural and rheological properties of nanoconfined fluids—particularly linear and cyclic nonpolar fluids nanoconfined between molecularly smooth mica surfaces. We find that, as the fidelity and rigor of the simulations has increased over that period, driven in part by the availability of increasingly powerful computational resources, the conclusions have remained the same—namely, that for the linear alkane n-dodecane and for cyclohexane, there is a critical value of surface separation (specific to the fluid) such that for separations less than the critical value, the fluid undergoes an abrupt, reversible phase transition into a solid phase. These simulation results are in agreement with the experimental findings of Klein and coworkers.[7,8,13] Moreover, our simulations agree with the many-order-of-magnitude increase in effective Newtonian viscosity observed by Klein and coworkers, and similarly reported in the early articles of Granick.[14] Although not discussed here, our simulations of nanoconfined water[18,19] show remarkable quantitative agreement with the experimental findings of Klein and coworkers.[17]

We believe that the simulation studies presented here have convincingly demonstrated the existence of phase transitions for linear and cyclic alkanes nanoconfined between molecularly smooth mica sheets. Untangling the structure of nanoconfined fluids, is, thus, an example of how increasingly high-fidelity molecular simulations are providing us the ability to understand complex experimental findings, particularly at the nanoscale.

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