

Structural Transition and Solid-like Behavior of Alkane Films Confined in Nano-Spacing

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Abstract: By carrying out accurate molecular simulation of dodecane fluid confined between mica surfaces using molecular models appropriately describing wall-fluid interaction, we show that the state condition of the confined fluid is strongly influenced by the wall-fluid interaction. At ambient condition, for strongly attractive surfaces the effective density is significantly higher than the bulk density and increases with the narrowing of the confinement spacing. This increase results in the density crossing-over into a density region corresponding to bulk solid when the confined film becomes narrower than about six molecular layers, driving the transition to solid-like structure. At six molecular layers, the confined film forms distinct layers as well as in-plane orientational order and inter-plane packing correlation . The results suggest that the strong interfacial interaction is the driving force for the dramatic effects observed in experiment.

Introduction

Interactions at a solid-fluid interface can exert strong influence on the structure, and thermodynamic and rheological properties of the fluid. When an ultra-thin layer of fluid is confined by two solid surfaces separated by a distance of the order of nanometers, the close proximity of the surfaces causes the interfacial effect to correlate and overlap. As a result, the thin layer of fluid exhibits anomalous behavior, different from that of the fluid at a single solid surface, such as the “quantized” nature in the thickness of the film (i.e., the film is stable only at discrete thickness corresponding to integral number of molecular layers) [1,2]. Experimental investigations of the properties of ultra-thin molecular films using the surface force apparatus (SFA) have found that when fluids are confined to six molecular layers or less between mica surfaces, the fluids exhibit solid-like behavior, with viscosity increases by more than six orders of magnitude [3-5]. In some cases, the film showed the ability to sustain a finite yield stress [5,6]. The phenomenon has been experimentally observed for a variety of systems with differing molecular architecture, including OMCTS (octamethylcyclotetrasiloxane), cyclohexane, toluene, and alkanes. The solid-like behavior of ultra-thin fluid films has thus far not been satisfactorily explained.

In this paper, we review the results of an extensive molecular dynamics simulation study of the ultra-thin film confined between solid surfaces [7]. Our results suggest a microscopic mechanism where experimentally observed phenomena can be consistently explained.

Molecular Models and Methods

We briefly describe here the models and methods that we used for the simulation, more details can be found in published literature [8]. The dodecane is described by a united atom model [9]. The solid walls are composed of the simple Lennard-Jones atoms with energy and size parameters reproducing the surface energy of a real mica surface. The wall atoms are placed on an fcc lattice with the (100) surface being the wall surface. The size parameter $\sigma_w = 3.5 \text{ \AA}$, is chosen approximately equal to the size of potassium atoms on mica surface (note that for a fcc crystal, the nearest neighbor distance, d , is related to the Lennard-Jones parameter by $d \cong 1.09\sigma_w$ [10]). Our estimate suggests that for a Lennard-Jones energy parameter $\epsilon_w = 7.815 \text{ kJ/mol}$ for the wall atoms, the surface energy density is about 220 mJ/m^2 , consistent with surface energy density of $\sim 200\text{-}400 \text{ mJ/m}^2$ for a real mica surface [4]. The wall-fluid interaction was obtained by using the Lorentz-Berthelot combining rules, which gives a wall-fluid atom interaction energy parameter $\epsilon_{wf} \cong 4.47\epsilon_{CH_2} \cong 1.747 \text{ kJ/mol}$, and a size parameter $\sigma_{wf} = 3.715 \text{ \AA}$, the values used in this work.

To properly treat the long-range contribution to the interaction and to the pressure tensor, we used a very large cutoff distance, 19.65 \AA (5σ , where $\sigma = 3.93 \text{ \AA}$ is the Lennard-Jones diameter of a united atom of the alkane molecules). Such a long cutoff distance makes the long-range correction beyond the cutoff distance essentially negligible [11]. The pressure tensor of the system is calculated using the method described in ref. [12,13] which has been shown to be exact for fluids under narrow confinement. It is verified in our simulation that the normal pressure in the interior of the confined film is equal to the external normal load, as determined from summing over all the forces of

interaction between the wall atoms and the fluid molecules. Periodic boundary conditions are used in the two lateral directions, and the box lengths in the two directions are fixed during the simulation. This is justified based on the fact that the lateral dimensions in experiment are on the order of micrometers and are at least several hundred times larger than the length of the simulation box. The simulations were performed by thermostating the walls at temperature $T = 300$ K.

In our simulation, the final system widths were adjusted to yield normal pressures of approximately one atmosphere. Although this was not achieved exactly, the method yields accurate equilibrium widths since the width is quite insensitive to the variation in normal pressure (e.g., the isothermal compressibility of dodecane at ambient temperature is on the order of 0.001 MPa^{-1} [14], a change in normal pressure of 10 MPa would result in deviations in width less than 0.5 \AA).

Results and Discussion

Table 1 shows the state conditions of the confined fluid obtained in the simulations for two different wall-fluid interaction strengths and varying confinement width. It is seen that a weak attractive wall-fluid interaction (roughly corresponding to a hydrocarbon coated surface) results in a lower effective density in the confined fluid (the bulk dodecane liquid density is about 0.75 g/cm^3 at ambient condition [15]). On the other hand, for strong attractive wall-fluid interaction, when the confined dodecane film is narrowed to six molecular layers, the effective density has increased to 0.85 g/cm^3 . This is greater than the bulk density of dodecane solid at ambient conditions (0.84 g/cm^3) [15].

Therefore, the transition of the confined film into an ordered solid-like structure is a natural manifestation of the increased density in the confined film.

The configuration structures of the confined dodecane fluid at thickness corresponding to six, seven, and eight molecular layers are shown in Figs. 1(a)-(c). The configuration were obtained from long molecular simulation runs (16.8, 21.3, and 15.7 ns for six, seven, and eight molecular layers, respectively) starting from disordered liquid-like structure. It is seen that at eight molecular layers, the fluid remains a disorder liquid-like structure. At seven molecular layers, part of the system appears to be in ordered structure and part of it appears to be in disordered structure. The state of the system is suggestive of a coexistence of disordered and ordered structures. At six molecular layers, the confined film has transformed into a completely ordered system.

In the past, the study of confined fluids has focused mostly on the oscillatory fluid density structure in the direction normal to the confining surfaces. Such density oscillation, however, occurs commonly for confined films in liquid state, and thus can not be used to explain the solid-like behavior observed in experiment. It has increasingly been realized that for solid-like behavior to occur, in-plane order and interlayer packing correlation need to be present so that local energy minima may exist such that certain external force is needed to overcome the energy barrier. Such an energy barrier would manifest itself as a yield stress in the surface force apparatus experiment. It is therefore evident that for a complete understanding of the behavior of the narrowly confined fluids, it is necessary to examine the in-plane order, and the inter-plane packing correlation of the confined fluids. Such an understanding will provide a structural basis for the dynamical behaviors of the ultra-thin confined fluids.

We studied the in-plane order of the confined films by plotting the particle correlation function in the plane parallel to the confining surfaces for each individual layer (each layer is defined as the spacing between two neighboring minima in the density profile). The results are shown in Fig. 2(a). Since all layers exhibited essentially similar features, in Fig. 2(a) we present the result for one internal layer (layer 3) only. The pronounced peaks in Fig. 2(a) correspond to the intra-molecular correlation of the dodecane molecules. For easy identification of the density peaks, we show in Fig. 2(b) the orientation-averaged two-particle correlation as a function of the in-plane distance. The first peak in Fig. 2(b) corresponds to the united atom directly bonded to the atom in consideration, the second peak corresponds to the second neighbor on the backbone, and so on. It is noted that in Fig. 2(b) that the positions of the first two intermolecular peaks of the correlation function coincides with the fourth and eighth peak of the intra-molecular peak and so are not directly visible in Fig. 2(b). A careful examination of the background, however, can see a slow varying wave corresponding to the intermolecular correlation. To clearly identify the intermolecular peaks, in Fig. 2(c), we plot the intermolecular correlation only as a function of the in-plane distance. It shows that the first intermolecular peak occurs at about 5.0 \AA which corresponds roughly to the distance between two parallel dodecane molecules in trans conformation lying flat in the plane (i.e., the zigzag bonds lying in the plane). From Fig. 2(a), it is also noted that the normal alkane molecules in each layer orient predominantly in one direction, consistent with the configuration in Figs. 1 (d). In Fig. 2(a), the broad bands run in parallel to the series of intra-molecular peaks correspond to the intermolecular peaks (this distance is 5.0 \AA , consistent with the intermolecular peak distance observed in Fig. 2(c)). Fig. 2(d) display

the two-dimensional particle correlation function summing over all six layers. In addition to the intra-molecular peaks similar to that seen in Fig. 2(a) for a single molecular layer, Fig. 2(d) shows the striking feature of stripes of peaks and valleys running parallel to the series of intra-molecular peaks, demonstrating the predominate parallel intermolecular packing. Comparison of Fig. 2(d) with Fig. 2(a) also shows that the number of inter-molecular peaks is twice that of an individual layer and the separation between the peaks is half that for individual layer. This suggests a triangular packing structure for the dodecane molecules, i.e., molecules pack in such a way so as to fit into the grooves formed by molecules in adjacent layers. This can be clearly seen in Fig. 1(d), where a perspective view of the same configuration of Fig. 2(a) is show.

Conclusions

We have shown that a strong wall-fluid interaction can significantly affect the state condition of the confined fluids, leading to solid-like structure. The film thickness at which a structure transition takes place agrees remarkably well with surface force apparatus experiment. On the other hand, when the wall-fluid interaction is weak, the fluids remain in liquid-like even they are geometrically confined. The structure of the dodecane fluid confined with mica-like surfaces at six molecular layers shows not only the layering order in the direction normal to the confining surfaces, but also in-plane orientational order and inter-layer packing correlation. The results found in this study suggest a microscopic mechanism where the increased density and structural order cause the dramatic increase in the viscosity, the ability of the confined fluid to resist flow.

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Figure Captions

1. (a) The configuration for dodecane fluid confined between mica-like surfaces at ambient conditions and thickness corresponding to eight molecular layers.
(b) The same as in (a), but for thickness corresponding to seven molecular layers.
(c) The same as in (a), but for thickness corresponding to six molecular layers.
(d) The same configuration in (c) viewed from a perspective angle and without showing the wall atoms.

2. (a) The two-particle correlation as a function of in-plane coordinates for the united atoms in the dodecane molecules. The sharp peaks correspond to the intramolecular correlation in a molecule, and broad wave bands correspond to intermolecular correlation. The units of the coordinates are in Å.
(b) The angular averaged two-particle correlation as a function of the in-plane distance for an interior layer of the confined dodecane film (layer 3), including intra-molecular contribution.
(c) The same as in (b), but without the intra-molecular contribution.
(e) The two-particle correlation as a function of in-plane coordinates including contribution from all layers. The units of the coordinates are in Å.

Table 1. The state conditions of the confined dodecane fluid.

$\epsilon_{wf}/\epsilon_{CH_2}$	N_f	N_w	$H(\text{\AA})$	1	$P_{\perp}(\text{MPa})$	$\rho_{\text{eff}}(\text{g/cm}^3)$
1.00	128	768	40.87	6	13.2(0.8)	0.714
4.47	170	768	47.16	8	6.1(2.8)	0.785
4.47	149	768	42.05	7	7.1(1.4)	0.829
4.47	128	768	38.24	6	11.3(3.3)	0.850

In the table, ϵ_{wf} , ϵ_{CH_2} , N_f , N_w , H , 1, P_{\perp} , and ρ_{eff} are the wall-fluid, fluid-fluid Lennard-Jones interaction energy parameters, numbers of fluid and wall molecules, the equilibrium system width, number of layers, normal pressure, and the effective density, respectively. The effective density is estimated by using the middle point between the first peak of the fluid layers and the position of the layer of wall atoms adjacent to the fluid as the boundary in calculating the width of the fluid film. The numbers in the parentheses indicate the statistical uncertainty.

Fig. 1

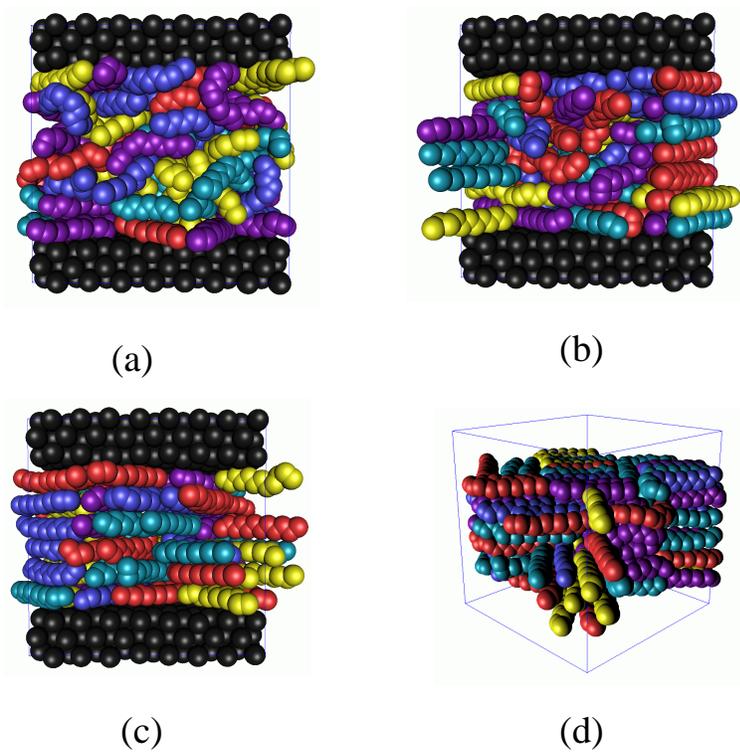


Fig. 2(a)

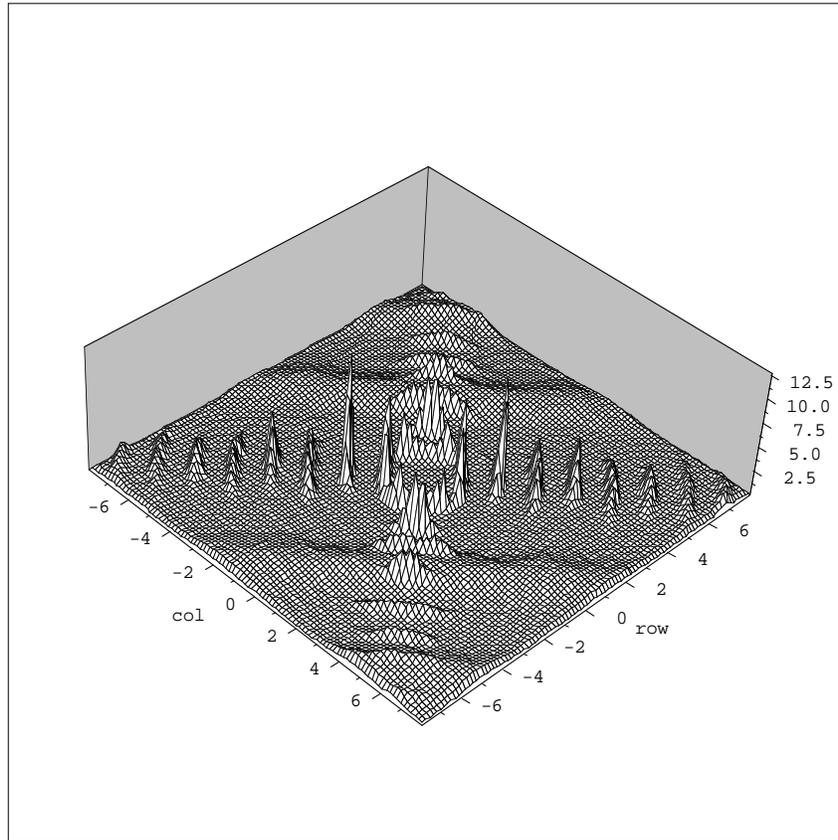


Fig. 2(b)

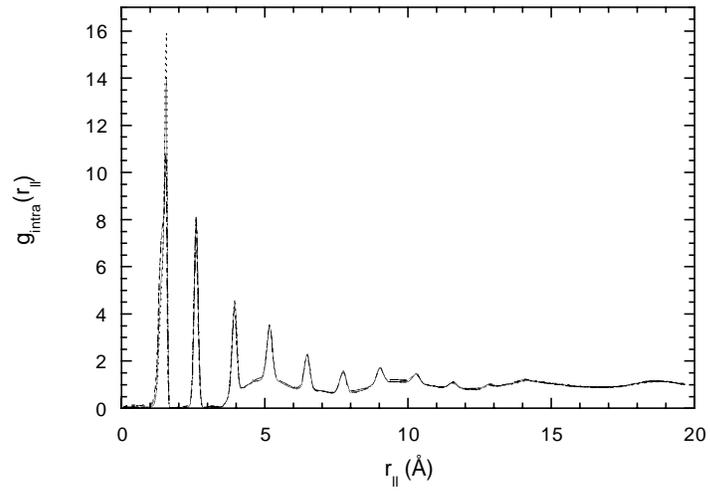


Fig. 2(c)

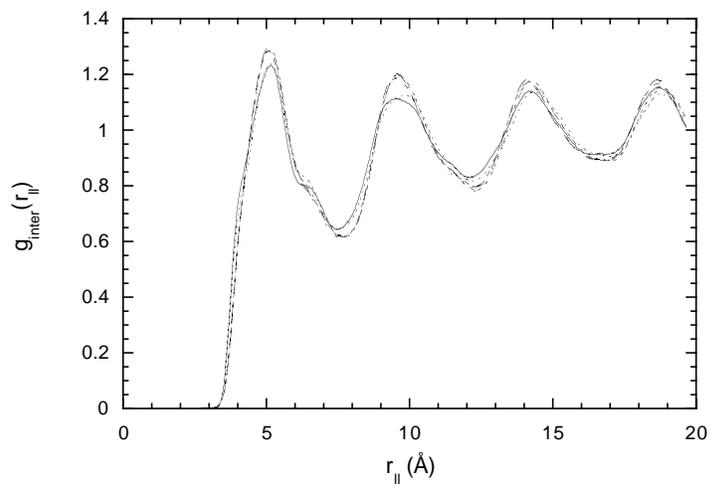


Fig. 2(d)

