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Molecular dynamics simulation of nanoconfined *n*-decane

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ABSTRACT

Liquid *n*-decane nanoconfined between parallel graphene surfaces has been simulated using a new method, to quantify the effect of fluid layering in the pore on a number of its structural and dynamical properties. It is shown that the solvation force curve shows oscillatory behavior with maxima corresponding to well-organized fluid layers. The relaxation times for end-to-end vector decorrelations are much higher than the corresponding bulk values in narrow pores and show oscillatory behavior, corresponding to the solvation force oscillations. The *n*-decane molecules diffuse much slower in the pore, compared to the bulk. A comparison of the results for chain dynamics in the case of pore widths with positive and negative solvation forces shows that the origin of slow dynamics in the pore is the formation of organized fluid layers.

1. Introduction

Understanding the properties of ultrathin films of fluids, confined between solid surfaces with separations of a few nanometers, is of particular importance in many technologically and scientifically important areas such as adhesion, nanotribology, nanocomposites, coating, and wetting [1]. From the experimental point of view, such systems are studied using recent experimental techniques including the surface forces apparatus, atomic force microscopy, and friction force microscopy [2]. In the surface force apparatus one measures the solvation forces, the forces acting on two solid surfaces immersed in a liquid, as a function of surface separation. The results of such measurements indicate that the solvation force is sensitive to the chemical architecture of the fluid molecules, confined between solid surfaces with separations of a few nanometers. As an example of the sensitivity of the solvation force on the chemical structure, we may address the differences between the solvation force curves of linear and branched alkanes [3]. The addition of side groups to the main alkane chain changes the solvation force patterns from strongly oscillatory to nonoscillatory with just one attractive minimum [3]. It is obvious that such a phenomenon could be given address to in terms of the molecular level structure of the confined fluid. However, such detailed information cannot be directly detected by current experimental measurements.

Molecular simulation techniques, on the other hand, are known as well established techniques in providing insight to the microscopic phenomena underlying the macroscopic behavior of condensed matter systems. So far molecular dynamics and Monte Carlo simulation techniques have been applied on simple [4,5] as well as complex liquids [6,7] to reveal interfacial local liquid density oscillations and variations in transport and dynamic properties a function of distance from the interface. The molecular dynamics simulations of confined alkanes, between simple solid surfaces, have frequently been addressed in the literature. Of these studies we can address the molecular dynamics simulation studies by Huang et al. [8] on the adsorption mechanism of *n*-alkanes on the model fcc surfaces and by Wang et al. [9] on the simulation of solvation force of *n*-octane confined between model surfaces. Other studies consist of works by Dijkstra [10] who employed a configurational bias Monte Carlo method to perform grand canonical ensemble simulation of decane confined between solid surfaces, by Porcheron et al. [11] on the grand canonical ensemble simulation of *n*-decane confined between structureless surfaces, and by Subramanian and Wang [12] on the diffusion of *n*-decane adsorbed on the pt(111) surfaces. In all these methods a united atom model is used to describe the *n*-decane chains. Similar studies on longer chain *n*-alkanes consist of works by Harmandaris et al. [13,14] on the united atom molecular dynamics simulation of thin polyethylene supported by crystalline graphite. They concluded that the local mobility of polymer melt near the surface is highly anisotropic.

This work is motivated by the necessity to simulate the surface force apparatus experiments, in which the confined fluid is in equilibrium with the bulk fluid. In most of the simulations in the literature, the fluid in confinement is not kept in equilibrium with the bulk fluid. In the surface force apparatus the measured pressure (or pressure) is described as a disjoining force (or pressure), which is the difference between the force (pressure) in the confinement and that in the parallel direction. Such an experiment can be simulated in the grand canonical ensemble [15], in which the equality of chemical

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potentials is regarded as the equilibrium condition. However, practically it is a hard task to do simulations in the grand canonical ensemble, in the case of big molecules. This is due to the fact that insertion of big molecules is a very rare event. Therefore, one should invoke other methods. Recently, a new simulation scheme has been developed by Eslami et al. [16] in which a constant number of fluid particles, confined in a nanometric pore, are simulated at constant temperature and a constant parallel component of pressure. While this method is shown to be able to reproduce the results of grand canonical ensemble simulations, it is easy to be employed in the case of solvation force calculation. In the present work, this method is employed to simulate the liquid decane confined between solid graphene surfaces. The results of this simulation are shown to well agree with the grand canonical ensemble simulation results of Dijkstra [10] and Porcheron et al. [11].

2. Simulation method

Confining a liquid between two solid surfaces with surface area A, equilibrium molecular dynamics simulations are done in the so-called NAPT ensemble, developed by Eslami et al. [16]. The method, as described by Eslami et al. [16], couples the system to a Berendsen thermostat [17]. The coupling to the barostat is done in such a way to keep the parallel component of pressure fixed. The parallel component of pressure is defined as:

$$\begin{aligned}P_{\|} &= \frac{P_{xx}+P_{yy}}{2}\\ &= \frac{1}{3V}\sum_i m_i v_i^2 + \frac{1}{2V}\left[\sum_i\sum_j\left(X_{ij}.F_{x,ij}+Y_{ij}.F_{y,ij}\right)+\sum_i\sum_s\left(X_{is}.F_{x,is}+Y_{is}.F_{y,is}\right)\right]\end{aligned} \tag{1}$$

where P_{xx} and P_{yy} are the x- and y-components of pressure tensor, respectively, m is the atomic mass, v is the velocity, V is the volume, subscripts i and j refer to the fluid particles in the confinement, subscript s stands for the surface atoms, $\mathbf{X}$ and $\mathbf{Y}$ are the relative distances between particles in the x and y directions, respectively, and $\mathbf{F}_x$ and $\mathbf{F}_y$ are their corresponding forces. According to Eslami et al. [16], by changing the intersurface distance, h, during the simulation one can keep the parallel component of pressure fixed. This amounts to scaling the z-coordinates of all particles per time step from z to αz, with

$$\alpha = 1-\beta\Delta t\frac{\left(P_{0,\|}-P_{\|}\right)}{\tau_P} \tag{2}$$

where β is the isothermal compressibility, $P_{||}$ is the parallel component of pressure, P_0 is the target pressure, and τ_P is the time constant for pressure coupling. This method is shown to simulate the fluid in the confined region in equilibrium with the bulk fluid.

In this work we employ this method to simulate an atomistic model of n-decane films confined between parallel graphene surfaces. The simulation results are compared with the grand canonical ensemble simulation results of the same system, confined between model solid surfaces [10,11].

3. Simulation details

In this work several systems consisting of different numbers of n-decane molecules are confined between parallel graphene surfaces of different surface areas, to be able to prepare systems of varieties of pore widths. The studied systems are summarized in Table 1. The atomistic force filed for n-decane molecules are taken from [18]. The carbon atoms in the graphene surfaces are kept frozen during the simulation. The interaction between carbon atoms in the graphene surface and the alkane atoms is modeled by a Lennard–Jones (12–6) potential [6,7]. The force field parameters for carbon atoms in graphene are taken from Ref. [6]. All nonbonded interactions were truncated at 1.0 nm. An atomic Verlet neighbor list was used, which was updated every 15 time steps, and the neighbors were included if they were closer to 1.1 nm. The unlike interactions are calculated by means of Jorgensen mixing rules [19].

Table 1
Characteristics of systems simulated in this work.

System	Number of n-decane molecules	x (nm)	y (nm)	<h> (nm)
S_1	100	8.36	8.09	0.66
S_2	115	8.11	8.09	0.91
S_3	150	7.37	7.24	1.04
S_4	130	6.14	6.39	1.41
S_5	120	5.16	5.11	1.56
S_6	145	3.44	3.40	4.12
S_7	150			

The simulation box is periodic in the x and y directions, but not in the z direction. Molecular dynamics simulations were carried out using a simulation package, YASP [20]. The temperature was kept fixed at 300 K and the parallel component of pressure was kept at 101.3 kPa. The time constant for temperature and pressure couplings were 0.2 ps and 2.0 ps, respectively. The time step for the leapfrog integration scheme was 2.0 fs. Simulations were performed for 5.0 ns for equilibration and 6.0 ns for the sake of data collection. The results are indicated in the following sections.

4. Results and discussions

4.1. Solvation force

The solvation force is the force which would be required to keep the confining surfaces at a fixed separation. In the present simulation scheme, keeping fixed the parallel component of pressure, the perpendicular component can easily be calculated during the course of simulation. The solvation force is then defines as:

$$\langle f_s\rangle = \frac{\langle P_{\|}\rangle-\langle P_{\perp}\rangle}{A} \tag{3}$$

where f_s is the solvation force, $P_{\perp}$ is the vertical component of pressure, and brackets indicate the average. In Fig. 1 we have shown the average solvation force as a function of average intersurface

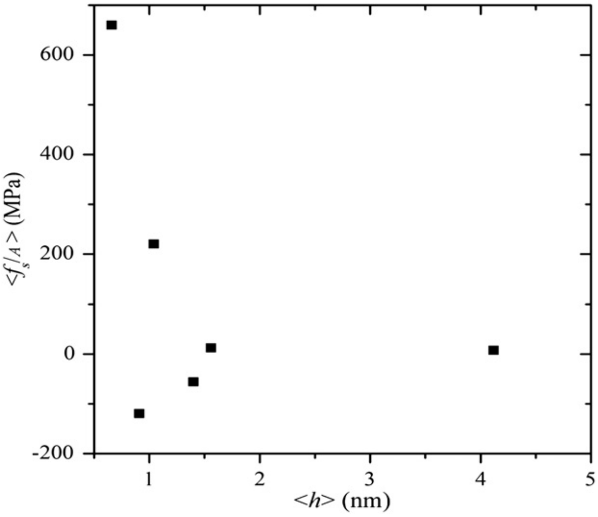

Fig. 1. The calculated solvation force as a function of average intersurface separation for nanoconfined n-decane at $T = 300$ K and $P_{\|} = 101.3$ kPa.