

System-size effect on the friction at liquid-solid interfaces*

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Abstract The friction at the liquid-solid interfaces is widely involved in various phenomena ranging from nanometer to micrometer scales. By the molecular dynamic (MD) simulation, the friction properties of liquid-solid interfaces at the molecular level are calculated via the Green-Kubo relation. It is found that the system size will influence the value of the friction coefficient, especially for the solid surfaces with the larger polar charge. The value of the friction coefficient decreases with the increase in the system size and converges at large system sizes. The large polar charge will lead to a significant friction coefficient. However, the diffusion of water molecules on this surface is almost a constant, indicating that the diffusion coefficient seems to be independent of the system size and polar charge. This work provides insights for the selection of the system size in modeling the frictional properties of hydrophobic/hydrophilic surfaces.

Key words Green-Kubo relation, liquid-solid interface, system-size effect, friction coefficient

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1 Introduction

The friction at the liquid-solid interfaces plays a central role in diverse systems and phenomena ranging from nanometer to micrometer scales^[1–3], such as the flow of fluid in nanochannel^[4–6], the drainage of thin liquid film between interfaces^[7], and the mass transport of biomolecules on microtubule^[8]. Whether the frictional properties of liquid-solid surfaces

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are properly estimated, it is thus important for the understanding of transport on surface^[9], through the biological membrane or channel^[7-8], the design of microfluid devices^[7], as well as the fabrication of novel material with superlubricity^[10-11]. The frictional properties at the molecular level can be quantitatively studied via the computer simulation^[12].

The solid surface model with tunable polarization is the simplest model to explore various interfacial phenomena, including the wetting/dewetting^[13-14], the molecule binding, and the interfacial friction^[15-18]. The advantage of this model is that only two adjustable variables, i.e., the polar charges^[19] of the solid atoms and lattice constant, are sufficient to reproduce the wetting transition between the hydrophobicity and the hydrophilicity of many kinds of solid material surfaces and capture the underlying mechanisms. Despite its wide applications, the interfacial friction of this surface in the model at the molecular level remains unclear.

In this work, we perform the molecular dynamic (MD) simulation of water films on the solid surface to study the system-size effects on the friction of liquid-solid interfaces^[12,20]. It is found that the size of the system has significant influence on the friction coefficient^[13,21-22]. The value of the friction coefficient decreases with the increase in the system size and converges at large system sizes. The converged value depends on the polar charge of the solid atom, and the large polar charge will lead to a large friction coefficient. Surprisingly, the diffusion of water molecules on this surface is almost a constant, indicating that the diffusion coefficient seems to be independent of the system size and polar charge. To the best of the authors' knowledge, this is the first work to discuss the system-size effect on the interfacial friction and diffusion coefficient at such a model surface. This work provides insights for the selection of system size in modeling the frictional properties of hydrophobic/hydrophilic surfaces in computer simulation.

2 Methods

2.1 Calculation of friction properties

The friction coefficient at liquid-solid interfaces at the molecular level is commonly estimated via the Green-Kubo relation^[19,21,23]. This method is based on the direct calculation of forces and interactions between liquid and solid atoms used in equilibrium simulation, avoiding the complicated settings in the Couette flow method used in the nonequilibrium simulation. The friction coefficient is expressed via the correlation of a fluctuating variable at the equilibrium state

$$\lambda = \frac{1}{2Sk_{\text{B}}T} \int_0^{\infty} \langle F_{\text{P}}(t') \cdot F_{\text{P}}(0) \rangle dt',$$

where S is the system size, T is the temperature, k_{B} is the Boltzmann constant, F_{P} is the projection of the total friction force between the water layer and the solid surface on the xy -plane, and $\langle \cdot \rangle$ denotes the ensemble average at the equilibrium state.

2.2 Simulation settings

The MD simulation is performed at the canonical ensemble by using the GROMACS 5.0.6 Software with a time step of 1 fs. The solid surface is extended infinitely in the xy -plane and the solid atoms is fixed to keep the rigidity of the solid surface^[24]. Liquid water layers of 5 nm thick are initially deposited on the surface. The water molecules have no initial velocities^[25] and their initial positions are randomly given while keeping the average water density at the bulk value. The system size in the xy -plane ranges from $2.56 \times 2.46 \text{ nm}^2$, $3.83 \times 3.69 \text{ nm}^2$, $5.11 \times 4.92 \text{ nm}^2$, $6.39 \times 6.15 \text{ nm}^2$, and $7.67 \times 7.38 \text{ nm}^2$ to $8.95 \times 8.61 \text{ nm}^2$. The system temperature is maintained at $T = 300 \text{ K}$ by using the V-rescale algorithm. The periodic boundary condition is applied in all six directions. The solid surface atoms and water molecules are described by GROMACS and SPC/E force fields, respectively. Lennard-Jones (LJ) parameters of the oxygen atom in water are $\sigma_{\text{OO}} = 0.316 \text{ nm}$, and $\varepsilon_{\text{OO}} = 0.65 \text{ kJ/mol}$, and of the solid atom are $\sigma_{\text{SS}} = 0.334 \text{ nm}$, and $\varepsilon_{\text{SS}} = 0.44 \text{ kJ/mol}$. The solid surface is neutral, while the atoms on the solid surface are

positively and negatively polar charged. The magnitude of the polar charge is tuned from $0.0e$, $0.4e$, and $0.7e$ to $1.0e$ in the unit of electron charge e , respectively. This model returns to graphene for $q = 0.0e$. The particle-mesh Ewald (PME) method with a real space cutoff of 1.2 nm is used to treat the long-range electrostatic interactions. The van der Waals (VDW) interactions are truncated at a cutoff distance of 1.2 nm . Each system is equilibrated for 10 ns . The total simulation time is 16 ns and the data are collected per 10 fs during the last 5 ns for the calculation of friction coefficient.

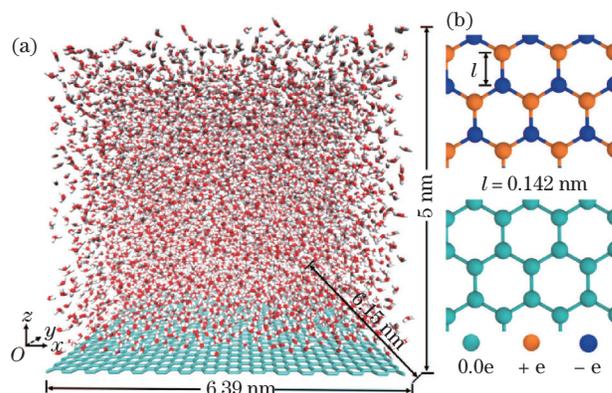


Fig. 1 A snapshot of the initial system configuration and the structure of the solid surface, i.e., (a) the side view snapshot of water layers on the solid surface with the polar charge $q = 0.0e$, of which the water layer is 5 nm in thickness, and the size of the solid surface is $6.39 \times 6.15\text{ nm}^2$, and (b) the orange and blue beads represent the atoms on the solid surface with positive and negative polar charges, respectively. The bond length l of the hexagonal unit is 0.142 nm (color online)

3 Results and discussion

Figure 2 shows the dependence of the friction coefficient between the water layers and the solid surface on the system area. For $q = 0.0e$, as the system area increases, the friction coefficient shows little variance and is almost a constant of about $2.5 \times 10^5\text{ N}\cdot\text{s}/\text{m}^3$. This value is smaller than other values for the solid surfaces with polar charges. Indeed, the solid surface with $q = 0.0e$ in fact returns to a model of graphene sheet, which has been verified to show the low friction at the liquid-solid interface. For $q = 0.4e$, the friction coefficient at the smaller system area increases to $7.5 \times 10^5\text{ N}\cdot\text{s}/\text{m}^3$, larger than $5 \times 10^5\text{ N}\cdot\text{s}/\text{m}^3$ for the solid surface without the polar charge. The friction coefficient becomes larger and increases to $30 \times 10^5\text{ N}\cdot\text{s}/\text{m}^3$ when the polar charge q is $1.0e$, implying that the electrostatic interaction enhances the liquid-solid frictions for smaller system areas. For $q = 0.7e$ and $1.0e$, the values of friction coefficient all decrease rapidly with the increase in the system size, and converge to about $5.7 \times 10^5\text{ N}\cdot\text{s}/\text{m}^3$ and $9.2 \times 10^5\text{ N}\cdot\text{s}/\text{m}^3$ when the system size reaches about 77 nm^2 , respectively. The decaying dependence of the friction coefficient on the system area at various polar charges indicates that the system area influences the values of the friction coefficient of liquid-solid interfaces calculated by MD simulation with periodic boundary conditions.

While the friction coefficient shows a strong dependence on the system size, we would expect that the other water-related properties of interface and diffusion coefficient should also depend on the system size. We thus further analyze the diffusion coefficient of the first layer of water molecules on the solid surface. Water layers are identified by the density distribution functions of oxygen atoms vertical to the solid surface. The first water layer is defined as the vertical

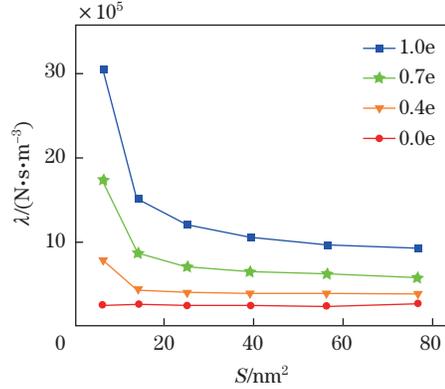


Fig. 2 The system-size dependence of the friction coefficient between the water layers and the solid surface with the different values of the polar charge $q = 0.0e, 0.4e, 0.7e,$ and $1.0e,$ respectively (color online)

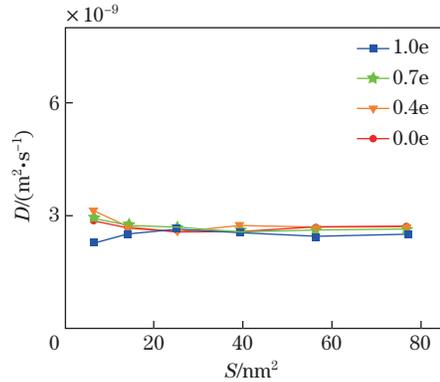


Fig. 3 The system-size dependence of the diffusion coefficient of the first layer of water on the surface area with the different values of the polar charge $q = 0.0e, 0.4e, 0.7e,$ and $1.0e,$ respectively (color online)

distance of oxygen atom to the solid surface less than 0.25 nm. Conversely, in Fig. 3, the diffusion coefficient is independent of the system size, different from the friction coefficient in Fig. 2. For $q = 0.0e$, the solid surface is considered as a graphene sheet and the diffusion coefficient of water molecules within the first layer is almost a constant of $2.6 \times 10^{-9} \text{ m}^2/\text{s}$, indicating that the diffusion coefficient is independent of the system size for the hydrophobic graphene sheet. With the increase in the polar charge q , the value of diffusion coefficient is also almost unchanged at various system areas, which is different from the rapid decay of the friction coefficient as the system size increases. To show the interaction between the water molecules and the graphene sheet ($q = 0.0e$), the LJ interaction between water molecules and carbons of solid surface is calculated. As shown in Fig. 4, the LJ interaction per area is negative for various surface areas, which results from the attraction between carbons on the solid surface and water molecules. The absolute value of LJ interaction energy per area is around $76.6 \text{ kJ}/(\text{mol}\cdot\text{nm}^2)$, which is larger than the surface tension coefficient of water at 300 K, $43.3 \text{ kJ}/(\text{mol}\cdot\text{nm}^2)$, indicating that the LJ interaction is strong enough to capture water molecules.

We further analyze the diffusion of water molecules of other layers in the water film as a control. Taking the solid surface with area $S = 39.3 \text{ nm}^2$ and polar charge $q = 0.7e$ as an example, we calculate the dependence of diffusion coefficient D as a function of the vertical

distance d , which is defined as the vertical distance between the oxygen atom of a water molecule and the solid surface plane. Water molecules are counted if the value of d is within the same spacing of 0.25 nm. The diffusion coefficient D of a water layer is calculated by averaging the diffusion coefficient of each water molecule counted in the same layer. As shown in Fig. 5, with the increase in d , the value of D increases from $2.62 \times 10^{-9} \text{ m}^2/\text{s}$ to the bulk value of $2.71 \times 10^{-9} \text{ m}^2/\text{s}$ at $d = 3.0 \text{ nm}$, representing that the impact of solid surface on the water layer is decreasing. At the regions of several water layers near the liquid-vapor interface, D rapidly increases to $3.78 \times 10^{-9} \text{ m}^2/\text{s}$. This is attributed to the decrease in number in hydrogen bond for each water molecule, allowing the water molecules to move more freely. The diffusion of water molecules of other layers on the solid surface at $q = 0.0e$ shows the similar tendency.

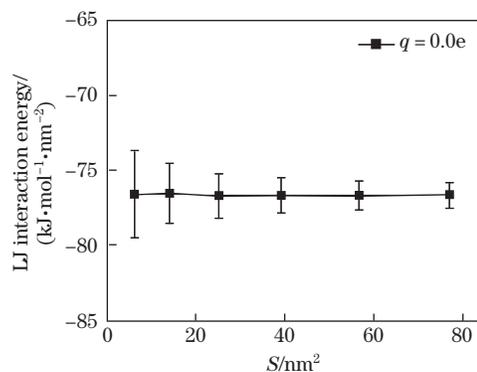


Fig. 4 The LJ interaction energy per area between carbons of the solid surface and water molecules at various surface areas without the polar charge

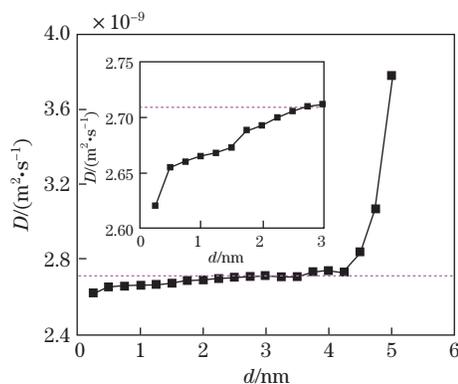


Fig. 5 The diffusion coefficient D as a function of the vertical distance d of water layers to the solid surface with $S = 39.3 \text{ nm}^2$ and $q = 0.7e$. The inset shows the details of D from the solid surface to the bulk water environment. The pink dashed line denotes the diffusion coefficient of the bulk water $D = 2.71 \times 10^{-9} \text{ m}^2/\text{s}$ calculated from the present work (color online)

It should be noted that the value of D is independent of the temperature coupling methods. We perform the simulation for the system with $S = 39.3 \text{ nm}^2$ and polar charge $q = 0.7e$ without temperature coupling, and with Berendsen and Nose-Hoover coupling methods. As shown in Table 1, the value of D is almost unchanged.

Table 1 The temperature coupling effect on the diffusion of water molecules at the surface area $S = 39.3 \text{ nm}^2$ and the polar charge $q = 0.7e$

Temperature coupling method	Without temperature coupling	V-rescale (present work)	Berendsen	Nose-Hoover
$D/(\text{m}^2 \cdot \text{s}^{-1})$	2.65×10^{-9}	2.62×10^{-9}	2.57×10^{-9}	2.64×10^{-9}

We have noticed that the interfacial friction has been extensively involved in the literature, such as the friction on graphitic interfaces with various topologies^[4], the biological lipid membrane^[26], the entangled macromolecules^[27–28], and the microtubules^[4,29–31]. The interfacial properties on these widely spread polarized interfaces are all related to the interfacial friction. Our work for the first time shows the dramatically different dependence of water-related interfacial properties on the system size of the polarized solid surface. The size of system used in the simulation is usually small and the system-size effect is negligible for hydrophobic solid surfaces. While the interfacial friction will show a strong dependence on the system size for polarized surfaces, the system-size effect should be carefully considered.

4 Conclusions

We have studied the system-size effect on the friction properties at the liquid-solid interfaces by the MD simulation. It is found that the system size dramatically influences the value of the friction coefficient of liquid-solid interfaces. With the increase in the system area, the friction coefficient rapidly decays from a larger value at the smaller system area and converge to a constant when the system area is larger than 77 nm^2 . The dependence of the friction coefficient on the system size becomes evident for the solid surface with larger polar charges. With the increase in the polar charge q from $0.0e$ to $1.0e$, the friction coefficient at the smaller system area becomes larger, which is an order larger than that for $q = 0.0e$. The converged value of the friction coefficient also increases as the polar charge increases. However, the diffusion coefficient of water molecules at the solid interfaces shows little response to the system area and the polar charge. This indicates that the appropriate selection of system size is important, and our results provide a reference of selecting system size in the characterization of the friction properties of the liquid-solid interfaces by the MD simulation.

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