

Molecular dynamics study of viscosity of aqueous NaCl solution confined in nanoscale channels

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Abstract: A physical model of bulk-nanochannel-bulk with buffer baths is built up using nonequilibrium molecular dynamics (MD) simulation to study the effects of vibrating silicon atoms on the viscosity of aqueous NaCl solutions confined in the nanochannel. The simulation is performed under different moving speeds of the upper wall, different heights and different surface charge densities in the nanochannel. The simulation results indicate that with the increase in the surface charge density and the decrease in the nanochannel height and the shear rate, the vibration effect of silicon atoms on the shear viscosity of the confined fluid in the nanochannel cannot be ignored. Compared with still silicon atoms, the vibrating silicon atoms result in the decrease in the viscosity when the height of the nanochannel is less than 0.8 nm and the shear rate is less than $1.0 \times 10^{11} \text{ s}^{-1}$, and the effect of the vibrating silicon atoms on the shear viscosity is significant when the shear rate is small. This is due to the fact that the vibrating silicon atoms weaken the interactions between the counter-ions (Na^+) and the charged surface.

Key words: nanochannel; molecular dynamics simulation; vibrating silicon atom; shear rate; viscosity

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The properties of fluid in a confined nanochannel are critical for the design of nanodevice lubrication and precise control of nanofluidic devices. In nanofluidic devices, the dimensions of the channel are comparable to the thickness of the electric double layer (EDL), so the classical Poisson-Boltzmann equation, which is based on the continuum assumptions, fails to describe the properties of the nanofluid^[1-6], and the ion distribution in the nanochannels mainly depends on the surface-to-volume ratio, surface chemistry and adhesion, and the surface structure and roughness^[7]. The viscosities of nanoscale confined water and aqueous electrolytes have been studied by experiments^[8-17] and simulations^[18-23]. In the surface force measurements, when the distance is within a few nanometers or less between two charged mica surfaces in the salt solution, the strong repulsive hydration forces will develop, which dominates the double layer repulsion and van der Waals at-

traction forces according to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory^[11]. The surface force apparatus proposed by Zhu et al.^[8, 12] shows a very high effective viscosity of liquid films confined between two mica surfaces. In contrast, the surface force balance experiments by Raviv and Klein^[9] on the fluidity of hydration layers were conducted over a broad range of aqueous film thicknesses and demonstrated that the surface-attached hydration layers are fluidic even when the thickness of the film is less than 1.0 nm. The highly purified water under nanometer confinement is found to have a viscosity of three of its bulk values during the process of the “jump into” the adhesive contact between the two mica surfaces^[13-14]. The effective viscosity obtained from the separations which is less than 1 nm in a mechanical model is 2 to 4 times that of a magnitude larger than the bulk value^[15]. The molecular dynamics (MD) simulation results show that the viscosity of the water film with $D = 2.44$ nm is close to that of the bulk water; when $D = 0.92$ nm, the viscosity is increased by 2 times that of the magnitude, which is greater than the experimental results^[15], and the shear responses are fluidic for D of 0.92 to 2.44 nm^[20-22].

In this paper, considering the exchange of ions between the nanochannel and the outside liquid with the silicon atoms vibration, a physical model of the bulk-nanochannel-bulk with buffer baths is set up using MD simulation in order to study the effects of the vibrating silicon atoms on the viscosity of aqueous NaCl solutions confined in the nanochannel, and the ion concentration in a nanochannel is consistent with an actual project.

1 Molecular Dynamics Model and Simulation

1.1 Model

Fig. 1 shows the schematic diagram of the model. The middle part of the model is a nanochannel. Each wall of the channel consists of four layers of silicon atoms oriented in the $\langle 100 \rangle$ direction. The channel height h is defined as the distance between the two innermost wall layers. The three layers of silicon atoms which are next to the fluids vibrate during the simulation, but the rest of them are treated static in their original positions during the simulation. A certain number of surface charges are uniformly distributed on the innermost layers of the silicon atoms in the nanochannel region, giving a certain surface charge density. Two reservoirs are connected to the channel at the two ends, which work as the bulk region. Each bulk region is divided into two parts; bath and buffer. The bath is to provide sufficient ions for the system, and the buffer is to diminish the impact effect while adjusting the atoms in the bath areas to the nanochannel. At the beginning of the simulation, only two

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bath regions of the system are filled with an electrolyte solution of 1 mol/L NaCl. The Na^+ and Cl^- ions in the bath boxes diffuse to the nanochannel through the buffer regions, which gradually leads to a decrease in ions in the bath region and an increase in ions in the channel region. Once the number of ions in the bath decreases to a certain value, the two bath regions are replaced by a new electrolyte solution of 1 mol/L NaCl. After several replacement processes, the number of ions in the buffer will not change greatly and they reach an equilibrated state. When the upper wall is pressed to a set height, the ions exchange freely between the channel and the outside liquid sinks. Using this approach, the concentration of both the counter and the co-ions in the nanochannel region reaches an equilibrium naturally, which is consistent with the actual project.

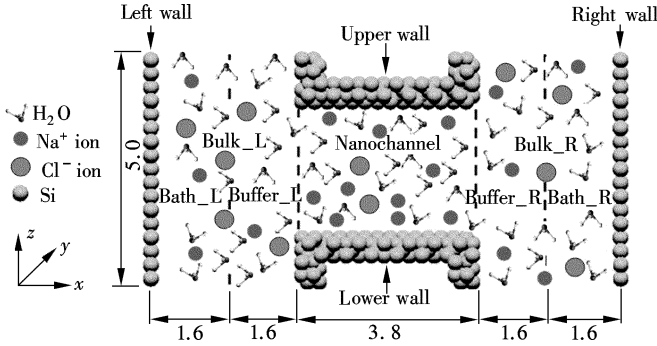


Fig. 1 Schematic diagram of the bulk-nanochannel-bulk model under investigation (unit: nm)

1.2 Simulation

The TIP4P^[24] model is selected to simulate the water molecules and the SETTLE algorithm^[25] is used to maintain the water geometry. The Lennard-Jones (LJ) and Coulomb potentials are used to describe the interactions between the related particles of the system. The LJ potential $U(r) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$ is considered for any atom pair except those pairs including the hydrogen atom and the Si-Si pair, where ϵ and σ are the length and energy parameters, and r_{ij} is the distance between two atoms i and j . The parameters for the LJ potential are listed in Tab. 1^[26]. The cross parameters for the interactions between different atoms are calculated using the Lorentz-Berthelot combination rule^[27]. For the Coulomb potential, all the charges in the system are considered, including mobile ions, charged sites in TIP4P water molecules, and surface charges. The electrostatic interactions among ions, water molecules, and surface charges are modeled by the Ewald summation algorithm^[28]. The simulations are run in the NVT ensemble using the Berendsen thermostat^[29] to maintain a constant temperature of 298.0 K with a time constant of 0.1 ps. A cutoff radius of 1.1 nm is used to compute the LJ and electrostatic potentials in the real space. The IP4P water molecular Na^+ and Cl^- ions are arranged randomly at the beginning of the simulation, and the initial velocity of every particle is given according to the Maxwell-Boltzman distribution. The Newton equations of motion are integrated by the Leap-Frog algorithm^[27] with a time of 2.0 fs. The periodic boundary condition and image convention are applied in the y direction of the system and the z direction of the bulk re-

gion. The Stillinger-Webber (SW) potential^[30] is used to describe the interactions between the vibrating silicon atoms. The temperature of the silicon plates is maintained at 298.0 K by using the Damp force method^[27].

Tab. 1 LJ potential parameters

Atom pair	σ/nm	$\epsilon/(\text{kJ} \cdot \text{mol}^{-1})$
O-O	0.316 9	0.650 2
O- Na^+	0.287 6	0.521 6
O- Cl^-	0.378 5	0.521 6
O-Si	0.327 8	0.327 8
Na^+ - Na^+	0.258 3	0.418 4
Na^+ - Cl^-	0.349 2	0.418 4
Na^+ -Si	0.298 5	1.011 8
Cl^- - Cl^-	0.440 1	0.418 4
Cl^- -Si	0.389 4	1.011 8

Simulations are performed according to the following procedure. First, the upper wall is pressed continuously and slowly to the lower wall in order to obtain the ion distributions at different heights. Once the system reaches an equilibrium at some height, the relative speed along the y direction of the upper wall is introduced to study the viscosity properties of the confined fluid in the nanochannel. The data are saved after equilibrium for analysis, and the schematic diagram of the moving model under investigation is shown in Fig. 2. Thus, the confined fluid of the ensemble in contact with the bulk is much closer to the situation of the surface force apparatus (SFA) experiments. Compared with the traditional method^[3,20,23,31] which sets the thickness of the film artificially to have different thicknesses of the films, this approach can obtain any heights of the nanochannel continuously.

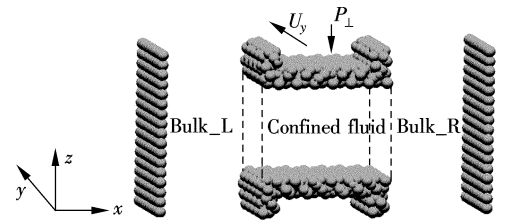


Fig. 2 Schematic diagram of moving model under investigation

2 Results and Discussion

2.1 Viscosity calculation

In a nonequilibrium molecular dynamics calculation, an effective viscosity η is calculated as the ratio of shear stress τ_{yz} to the shear rate γ ^[23].

$$\eta = \frac{\langle \tau_{yz} \rangle}{\gamma} \quad (1)$$

where $\tau_{yz} = \sum_i \sum_j F_y^{ij} / A$, and this expression is the average shear force of the film atoms on the wall atoms divided by the area of the walls. The shear rate γ actually is the velocity gradient, which can be obtained from the fitting velocity profile.

2.2 Viscosity of confined fluid

In this paper, with the surface charge densities increasing

from 0 to -0.2991 C/m^2 and the silicon atoms vibrating, the viscosities of the confined fluid at different nanochannel heights and shear rates are simulated. To investigate the effects of the vibrating silicon atoms on the viscosity of the confined fluid, the still wall with the same charge densities and nanochannel heights is compared with the vibrating ones. Fig. 3 presents the viscosity profiles of the vibrating and the still silicon atoms with different nanochannel heights, shear rates and surface charge densities. The surface charge density of about -0.2991 C/m^2 can be considered very high, but it is still possible in the practical systems [32].

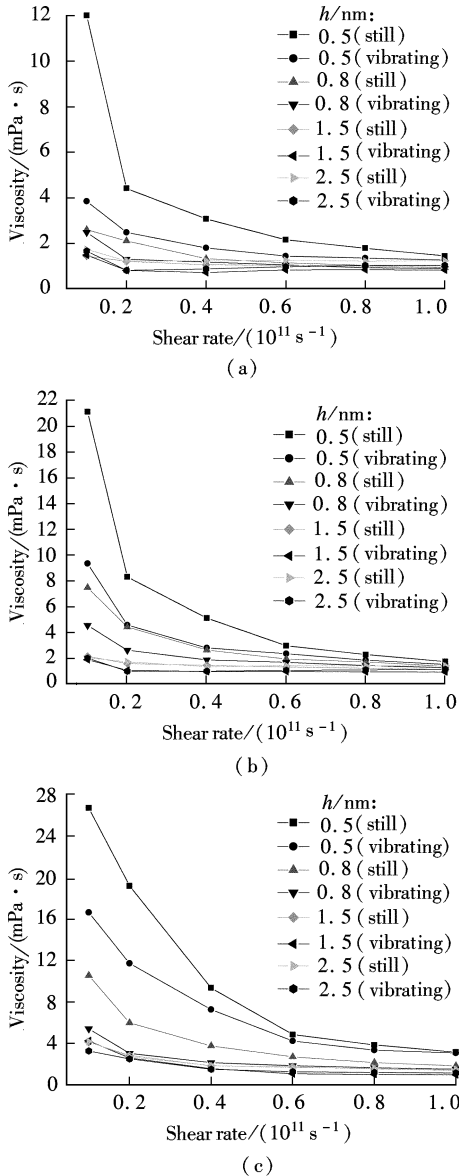


Fig. 3 Variations of shear viscosity vs. shear rate for different heights of channels with still or vibrating wall. (a) For 0 C/m^2 surface charge density; (b) For -0.1496 C/m^2 surface charge density; (c) For -0.2991 C/m^2 surface charge density

As shown in Fig. 3, we can find that when the height of the nanochannel is fixed, the shear viscosity of the confined fluid decreases with the increase in the shear rate. When the shear rate is constant, the viscosity of the fluid shows regularity with the changing nanochannel height, and when the height of the nanochannel is less than 1.0 nm , the value of

the viscosity is greater especially at a lower shear rate. This is because when the water molecules are confined in a narrow nanochannel, the molecular motion is more intense, resulting in an increase in the viscosity.

In more detail, the viscosity values of the 0.5 nm and the 0.8 nm height nanochannels of the system with the vibrating silicon atoms are lower than those with the still ones. But it has little effect on the viscosity of the 1.5 nm and the 2.5 nm high nanochannels whether silicon atoms vibrate or not, and little effect when the shear rate is $1.0 \times 10^{11} \text{ s}^{-1}$. When the shear rate does not exceed $1.0 \times 10^{11} \text{ s}^{-1}$, the vibrating silicon atoms have an obvious effect on the viscosity of the 0.5 nm and the 0.8 nm high nanochannels. The smaller the shear rate is, the more significant the effect is.

As we mentioned in this paper, the charges are evenly distributed among the atoms of the innermost wall layer, and the three layers of silicon atoms which are next to the fluids vibrate during the simulation. The main interactions between the charged silicon and the counter-ion (Na^+) are the Lennard-Jones and Coulomb potentials. The reason is that the vibrations of the charged silicon atoms weaken the interactions between the counter-ion (Na^+) and the charged surface, and that leads to a smaller shear stress compared with the still ones, which is caused by the vibration of the charged silicon atoms that do not have fixed positions. From Eq. (1), we can find that when the shear rate is a constant, the decrease in the shear force leads to the decrease in the viscosity, and this makes the shear viscosity of the vibrating silicon atoms smaller than that of the still ones. But when the nanochannel height is greater than 0.8 nm and the shear rate is greater than $0.8 \times 10^{11} \text{ s}^{-1}$, the impact generated by the vibrating atoms can be ignored when compared with the nanochannel height and the shear rate.

3 Conclusion

Nonequilibrium molecular dynamics simulations are performed to investigate the effects of the thermal vibration of silicon atoms on the viscosity of the confined fluids with a bulk-nanochannel-bulk model. The counter and co-ions distribution in the nanochannel region are calculated with the model. The simulation is performed at various speeds, nanochannel heights and surface charge densities. The simulation results indicate that with the increase in the surface charge density and the decrease in the nanochannel height and the shear rate, the vibration effect of silicon atoms on the shear viscosity of the confined fluid in the nanochannel cannot be ignored. Compared with the still silicon atoms, the vibrating silicon atoms result in the decrease in the viscosity when the height of the nanochannel is less than 0.8 nm and the shear rate is less than $1.0 \times 10^{11} \text{ s}^{-1}$, and the effect of the vibrating silicon atoms on the shear viscosity is significant when the shear rate is small. This is due to the fact that the vibrating silicon atoms weaken the interactions between the counter-ion (Na^+) and the charged surface.

References

- [1] Freund J B. Electro-osmosis in a nanometer-scale channel studied by atomistic simulation [J]. *J Chem Phys*, 2002, **116**(5):2194–2200.

- [2] Qiao R, Aluru N R. Ion concentrations and velocity profiles in nanochannel electro-osmotic flows [J]. *J Chem Phys*, 2003, **118**(10):4692–4701.
- [3] Qiao R, Aluru N R. Charge inversion and flow reversal in a nanochannel electro-osmotic flow [J]. *Phys Rev Lett*, 2004, **92**(19):198301.
- [4] Besteman K, Zevenbergen M A G, Lemay S G. Charge inversion by multivalent ions: dependence on dielectric constant and surface-charge density [J]. *Phys Rev E*, 2005, **72**(6):061501.
- [5] Zhu W, Singer S J, Zheng Z, et al. Electro-osmotic flow of a model electrolyte [J]. *Phys Rev E*, 2005, **71**(4):041501.
- [6] Greberg H, Kjellander R. Charge inversion in electric double layers and effects of different sizes for counterions and co-ions [J]. *J Chem Phys*, 1998, **108**(7):2940–2953.
- [7] Urbakh M, Klafter J, Gourdon D, et al. The nonlinear nature of friction [J]. *Nature*, 2004, **430**(6999):525–528.
- [8] Zhu Y X, Granick S. Viscosity of interfacial water [J]. *Phys Rev Lett*, 2001, **87**(9):096104.
- [9] Raviv U, Klein J. Fluidity of bound hydration layers [J]. *Science*, 2002, **297**(5586):1540–1543.
- [10] Israelachvili J N. Measurement of the viscosity of liquids in very thin-films [J]. *J Colloid Interf Sci*, 1986, **110**(3):263–271.
- [11] Israelachvili J N. *Intermolecular and surface forces* [M]. 3rd ed. New York: Oxford, 2011:341–380.
- [12] Hu H W, Carson G A, Granick S. Relaxation-time of confined liquids under shear [J]. *Phys Rev Lett*, 1991, **66**(21):2758–2761.
- [13] Raviv U, Laurat P, Klein J. Fluidity of water confined to subnanometre films [J]. *Nature*, 2001, **413**(6851):51–54.
- [14] Raviv U, Perkin S, Laurat P, et al. Fluidity of water confined down to subnanometer films [J]. *Langmuir*, 2004, **20**(13):5322–5332.
- [15] Sakuma H, Otsuki K, Kurihara K. Viscosity and lubricity of aqueous NaCl solution confined between mica surfaces studied by shear resonance measurement [J]. *Phys Rev Lett*, 2006, **96**(4):046104.
- [16] Major R C, Houston J E, McGrath M J, et al. Viscous water meniscus under nanoconfinement [J]. *Phys Rev Lett*, 2006, **96**(17):177803.
- [17] Li T D, Gao J P, Szoszkiewicz R, et al. Structured and viscous water in subnanometer gaps [J]. *Phys Rev B*, 2007, **75**(11):115415.
- [18] Lee S H, Rossky P J. A comparison of the structure and dynamics of liquid water at hydrophobic and hydrophilic surfaces—a molecular-dynamics simulation study [J]. *J Chem Phys*, 1994, **100**(4):3334–3345.
- [19] Sakuma H, Tsuchiya T, Kawamura K, et al. Local behavior of water molecules on brucite, talc, and halite surfaces: a molecular dynamics study [J]. *Molecular Simulation*, 2004, **30**(15):861–871.
- [20] Leng Y, Cummings P T. Fluidity of hydration layers nanoconfined between mica surfaces [J]. *Phys Rev Lett*, 2005, **94**(2):026101.
- [21] Leng Y S, Cummings P T. Hydration structure of water confined between mica surfaces [J]. *J Chem Phys*, 2006, **124**(7):074711.
- [22] Leng Y S, Cummings P T. Shear dynamics of hydration layers [J]. *J Chem Phys*, 2006, **125**(10):104701.
- [23] Martini A, Liu Y, Snurr R Q, et al. Molecular dynamics characterization of thin film viscosity for EHL simulation [J]. *Tribol Lett*, 2006, **21**(3):217–225.
- [24] Jorgensen W L, Chandrasekhar J, Madura J D, et al. Comparison of simple potential functions for simulating liquid water [J]. *J Chem Phys*, 1983, **79**(2):926–935.
- [25] Miyamoto S, Kollman P A. SETTLE: an analytical version of the SHAKE and RATTLE algorithm for rigid water models [J]. *J Comput Chem*, 1992, **13**(8):952–962.
- [26] Koneshan S, Rasaiah J C, Lynden-Bell R M, et al. Solvent structure, dynamics, and ion mobility in aqueous solutions at 25°C [J]. *J Phys Chem B*, 1998, **102**(21):4193–4204.
- [27] Allen M P, Tildesley D J. *Computer simulation of Liquids* [M]. New York: Oxford, 1987:152–154.
- [28] Yeh I C, Berkowitz M L. Ewald summation for systems with slab geometry [J]. *J Chem Phys*, 1999, **111**(7):3155–3162.
- [29] Berendsen H J C, Postma J P M, Vangunsteren W F, et al. Molecular-dynamics with coupling to an external bath [J]. *J Chem Phys*, 1984, **81**(8):3684–3690.
- [30] Stillinger F H, Weber T A. Computer-simulation of local order in condensed phases of silicon [J]. *Phys Rev B*, 1985, **31**(8):5262–5271.
- [31] Xu D Y, Leng Y S, Chen Y F, et al. Water structures near charged (100) and (111) silicon surfaces [J]. *Appl Phys Lett*, 2009, **94**(20):201901.
- [32] Poppe H, Cifuentes A, Kok W T. Theoretical description of the influence of external radial fields on the electroosmotic flow in capillary electrophoresis [J]. *Anal Chem*, 1996, **68**(5):888–893.

纳尺度通道中氯化钠溶液黏度的分子动力学研究

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摘要: 建立一个 2 侧带有缓冲池的 bulk-nanochannel-bulk 模型, 采用非平衡态的分子动力学模拟方法研究热运动的硅原子对受限于纳通道中氯化钠溶液黏度的影响. 该模拟在不同的通道上板移动速度、通道高度和通道壁面电荷密度的情况下进行. 模拟结果表明: 随着通道壁面电荷密度的增加、通道高度和剪切率的减小, 热运动的硅原子对受限于纳米通道中流体的剪切黏度有着不可忽视的影响, 当通道高度小于 0.8 nm, 剪切率小于 $1.0 \times 10^{11} \text{ s}^{-1}$ 时, 热运动的硅原子导致了通道中氯化钠溶液的黏度减小, 并且剪切率越小, 这一现象越明显. 这是由于热运动的硅原子减弱了反离子 (Na^+) 和带电的通道壁面之间的相互作用引起的.

关键词: 纳米通道; 分子动力学模拟; 热运动的硅原子; 剪切率; 黏度

中图分类号: O351.2