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Molecular force mechanism of hydrodynamics in clay nanopores

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Abstract: Nanopores are prevalent within various clay morphologies, and water flow in clay nanopores is significant for various engineering applications. In this study, we performed non-equilibrium molecular dynamics (NEMD) simulations to reveal the molecular force mechanisms of water flow in clay nanopores. The water dynamic viscosity, slip length, and average flow velocity were obtained to verify the NEMD models. Since the water confined in the nanopores maintained a dynamic mechanical equilibrium state, each water lamina can be regarded as a simply supported beam. The applied driving force, the force from clay crystal layers, the force from compensating sodium ions, and the force from other water laminae were further calculated to investigate the force mechanisms. The van der Waals barrier above the surface and hydraulic gradient lead to distribution differences in water oxygen atoms, which contribute to a net van der Waals resistance component of the force from clay crystal layers. Meanwhile, the water molecules tend to rotate to generate the electrostatic resistance component of the force from clay crystal layers and balance the increasing hydraulic gradient. Due to the velocity difference, the water molecules in the slower lamina have a higher tendency to lag and generate a net electrostatic resistance force as well as a net van der Waals driving force on the water molecules in the faster lamina, which together make up the viscous force.

Key words: Molecular dynamics; Hydrodynamics; Clay; Nanopore; Molecular force; Boundary effect; Viscous force

1 Introduction

Clays are natural geomaterials with various particle morphologies under different environmental conditions (i.e., single crystal layers, quasi-crystals formed by stacking layers, and aggregates assembled by quasicrystals) (Quirk and Aylmore, 1971; Ahmed and Abduljauwad, 2017). Nanopores are prevalent within various clay morphologies and water flow in clay nanopores is significant for various engineering applications, such as the design of cut-off walls and anti-pollutant barriers (Wasak and Akkutlu, 2015; Li et al., 2017), and petroleum engineering (Xiong et al., 2020). However, because the length scale of clay nanopores is of the same order of magnitude as the molecular size, there are excessive molecular fluctuations in water behavior and the hydrodynamics properties become inhomogeneous (Daivis and Todd, 2018), making the accuracy and validity of continuous description by means of the Navier-Stokes equation questionable (Sam et al., 2021).

Since classic fluid mechanics is unable to accurately describe nanoscale water-flow behaviors, gaining insights into the micro-physical mechanisms can aid in better controlling the process of water flow in clay nanopores. Due to the limitations of nanofluidic experimental technology and the development of computational capacity, numerical simulation has become an indispensable way for studying the process.

Among various kinds of simulation methods, molecular dynamics (MD) method was known as the bridge between macroscopic properties and molecular mechanisms of nanoscale water flow (Cao, 2017). In the MD simulations, interactions between water molecules and those between water and clay matrix (i.e., clay crystal layers and compensating cations) were chiefly described by non-bonded interactions, including van der Waals and electrostatic interactions (Cygan et al., 2004; Cao, 2017). The short-range van der Waals interaction was generally described by the Lennard-Jones potential, while part of the long-range electrostatic

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interaction within cutoff distance was described by Coulombic potential and the other part beyond the cutoff distance was calculated by Ewald summation algorithm (Wei et al., 2023). Particularly, as one of the specific kinds of MD simulations, non-equilibrium molecular dynamics (NEMD) simulation, with an external perturbation (e.g., pressure gradient) driving the system out of the original equilibrium state (Allen and Tildesley, 2017), has allowed for better simulations of pressure-driven nanofluidic behaviors (Ramos-Alvarado et al., 2016). To generate stable pressure differences, dual-reservoir model (Wang et al., 2012), fluid piston model (Hanasaki and Nakatani, 2006a, 2006b), reflecting particle model (Li et al., 1998), and quasi-gravity-driven model (Boțan et al., 2011; Wei et al., 2023) were widely applied. So far, researchers have used these models to primarily investigate the relationships between two aspects of water flow in clay nanopores: microscopic structure of water (i.e., density, orientation, and hydrogen bonds) and hydrodynamics properties of flow (i.e., velocity, viscosity, and slip length). It was found that water density in nanoflow was dominated by water-substrate interactions rather than water-water interactions (Alexiadis and Kassinos, 2008), and slip length showed a predictable relation to the spatial distribution and morphological organization of interfacial water molecules (Ramos-Alvarado, et al., 2016). Further simulations illustrated that the types and concentrations of cations highly influenced the orientations of water molecules (Simonnin et al., 2018), and the increasing concentrations densified the hydrogen-bonding networks to increase the viscosity of water (Yin and Zhao, 2020). Furthermore, simulated slip lengths by NEMD were adopted to modify the continuous description by the Navier-Stokes equation for a better prediction of flow velocity of water flow in clay nanopores (Zhan et al., 2020), but the modification with local viscosity was still unable to eliminate the offsets near the mineral surface (Hansen et al., 2011).

Although previous molecular simulations have made great progress in the insights on the influencing factors (e.g., mineral type, size/geometry of pores, and type/concentration of cations) on the hydrodynamics properties (i.e., slip length and viscosity) of the confined water molecules in clay nanopores by means of density profile and planar distribution of water molecules, few studies have explored the force mechanisms of those properties straightforward. In this study, NEMD simulations on water flow in montmorillonite nanopores were performed. The model was verified in terms of water viscosity, slip length, and flow velocity. After investigation of the time fluctuation of total force on the pore water, we calculated the distributed molecular forces on the pore water. Finally, we looked at the relationship between the molecular forces on water molecules and the morphological organization of water molecules. This study revealed the force mechanisms of the slip length and water viscosity on hydrodynamics in clay nanopores at molecular scale.

2 Models and methods

The clay substrate of nanopore was constructed by randomly substituting aluminum atoms in the octahedral sheet of pyrophyllite with magnesium atoms. The lattice parameters and fractional coordinates of atoms used for pyrophyllite were obtained from the model developed by Skipper et al. (1995). All of the isomorphic substitutions followed Loewenstein's rule (that is, no substitution site was adjacent to another) (Loewenstein, 1954), and the negative charges due to isomorphic substitutions were neutralized by 24 compensating Na⁺ atoms. Three different pore sizes h (3.5, 5.0, and 6.5 nm) were considered, and the number of water molecules $N_{\rm w}$ for different pore sizes was determined based on the bulk density of water (Botan et al., 2011). More details on the molecular models could be found in our previous work (Wei et al., 2023).

As for the atomic interactions, the ClayFF force field (Cygan et al., 2004), the Smith-Dang parameters (Smith, 1998), and the extended simple point charge (SPC/E) model (Berendsen et al., 1981) were utilized for the clay crystal layers, compensating sodium cations, and water molecules, respectively. The rigidity of water molecules was constrained by the SHAKE algorithm (Ryckaert et al., 1977). The cutoff distance for short-range interactions was set to be 1 nm. We adopted the open source code LAMMPS to perform the simulations (Plimpton, 1995) and the OVITO software for post-visualization (Stukowski, 2010).

2.1 Equilibrium molecular dynamics

Equilibrium molecular dynamics (EMD) simulations in canonical ensemble were performed to obtain the properties of the quasi-static water confined in clay

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nanopores. The clay crystal layers were frozen and an initial velocity distribution based on the initial temperature of 10 K was assigned to the water molecules and mobile cations. The minimum timestep was set to be 1.0 fs and the temperature was controlled with a Nosé-Hoover thermostat (Martyna et al., 1994). After the initial structure was optimized by means of energy minimization, the water molecules and mobile cations were heated from 10 to 300 K after 100 ps. Following the equilibration period of 1 ns, the trajectories of atoms for water molecules and Na⁺ were collected every 0.1 ps for 2 ns. The final configurations of the EMD simulations were taken as the initial configura-tions for the subsequent NEMD simulations.

Fig. S1 of the electronic supplementary materials (ESM) illustrated the number density profiles of water molecules and compensating sodium cations calculated by EMD simulations. We divided the clay nanopores into three zones: Stern layer, diffusion layer, and bulk region (Wei et al., 2023). The Stern layer was characterized as a single water layer with highly-polarized molecules, and the width of the layer (about 3.5 Å) maintained unchanged with the increasing pore sizes. In the Stern layer, the location of the first density peak of water oxygen atoms (2.5-3.0 Å from the clay mineral surface) was generally used as the indicator of the first adsorbed water layer and the accessible width for water molecules h^* enlarged with pore sizes (Kannam et al., 2013). Followed the Stern layer, the diffusion layer was considered as the transition layer for water molecules from being polarized to being free. Due to the reduction of salt concentration (Mitchell and Soga, 2005), its width enlarged with pore sizes (9.0, 11.5, and 18.5 Å for 3.5, 5.0, and 6.5 nm, respectively). Since all of the substitutions occurred at the octahedral sheet, hydrated sodium cations tended to form outer-sphere complexes in the diffusion layer. Water molecules in the bulk region were not affected by the clay crystal layer and the compensating cations, and the number density did not change with the distance from clay crystal layers.

2.2 Non-equilibrium molecular dynamics

By adopting appropriate external perturbation to ensure the linear response of the system, we were able to adapt the molecular dynamics method to treat the non-equilibrium system (Hoover and Hoover, 2005). According to the quasi-gravity-driven method, we

generated different total driving forces F^{d} on the pore water by assigning additional accelerations in the y-direction a_v (5.5×10¹², 16.5×10¹², 32.9×10¹², and 65.9×10^{12} m/s²) to the fluid particles. Subsequently, the equivalent differential pressures ($\Delta P=20, 60, 120,$ and 240 MPa) between two sides of the simulation box along the y-direction (i.e., the flow direction) could be generated based on F^{d} and the flow area (Liu et al., 2018). Obviously, the additional accelerations would generate fictitious high temperature because the net velocity of water molecules was not zero. To solve this problem, the y-component of the velocity of the mass center of water molecules was subtracted out during the thermostatic process (Botan et al., 2011; Wei et al., 2023). For NEMD simulations with different pore sizes and driving pressures, a 2-ns equilibrium period was required to achieve a steady flow and a 2-ns sampling period was used for collecting thermodynamics properties of each particle. During the sampling time, the hydrodynamics properties were obtained to verify the NEMD simulation models. Subsequently, the clay crystal layers, the compensating cations, and the water molecules in nanopores were respectively placed in three independent groups, and the interaction forces between the groups were calculated via the compute group/group command in LAMMPS (Plimpton, 1995) to conduct the mechanical analyses of water flow in clay nanopores and reveal the force mechanisms of hydrodynamics in clay nanopores.

3 Hydrodynamics properties

The flow velocity of the *i*th water lamina v_i can be calculated as follows:

$$v_i = \frac{1}{N_t} \sum_{k=1}^{N_t} \frac{\sum_{j \in i \text{th lamina}} m_j v_{j,k}}{\sum_{j \in i \text{th lamina}} m_j}, \qquad (1)$$

where m_j is the mass of particle *j* within the *i*th lamina, $v_{j,k}$ is the *y*-velocity of particle *j* at timestep *k*, and N_i is the number of total timesteps considered. The velocity profiles under different equivalent flowdriving pressures for *h*=3.5 nm are illustrated in Fig. 1, while the profiles for *h*=5.0 and 6.5 nm are plotted in Fig. S2 of the ESM. It is noteworthy that the NEMD simulation was unable to adapt to the non-equilibrium



Fig. 1 Velocity profiles of water flow in clay nanopores under different pressures (h=3.5 nm)

system if the applied flow-driving force on the pore water was too great to ensure the linear response of the system (Hoover and Hoover, 2005). The results showed that $\Delta P=240$ MPa for h=5.0 nm as well as $\Delta P=$ 120 and 240 MPa for h=6.5 nm was unacceptable for the NEMD method. Thus, the results obtained with these three cases are excluded from this paper.

The NEMD models were quantitatively verified in terms of the hydrodynamics properties of water flow in clay nanopores (i.e., water dynamic viscosity μ , slip length l_s , and average flow velocity ν). The parabolic part of the velocity profile in Fig. 1 can be fitted by the Navier-Stokes equation:

$$v_{y}(z) = -\frac{1}{2\mu} \frac{\Delta P}{L_{y}} \left(z^{2} - \frac{h^{*2}}{4} - h^{*} \cdot l_{s} \right), \qquad (2)$$

where L_y is the y-dimension of the simulation box. The values of μ and l_s are determined by fitting the obtained velocity profiles and the results are summarized in Table 1. The dynamic viscosity of water (μ = (0.71±0.05) cP) remained stable with various pore sizes and equivalent flow-driving pressures. To verify this, the viscosity for bulk water was also obtained according to the Green-Kubo equation (Kondratyuk, 2019) in the EMD simulations (Fig. S3 of the ESM). The value of μ obtained via NEMD simulations basically conformed to that obtained from EMD simulations (about 0.69 cP), but was slightly larger than the other published results with SPC/E water model (Hess, 2002). The slip length l_s is a simple parameter to characterize the slip magnitude along the interface between the fluid and the solid surface. For $l_{s} \leq 0$, there was a strong boundary interaction on the water molecules near the clay mineral surfaces and the water flow had a sticky boundary; otherwise, the water molecules tended to slide near the boundary and the water flow had a slip boundary. As shown in Table 1, all values of l_s were greater than 0 and enlarged with the increase of ΔP . Besides, we adopted two methods to calculate average flow velocity. One (v_1) involved averaging the fitting velocity profile along the z-axis; the other (v_2) was based on the total outflow volume Q during the 2-ns sampling time from the NEMD simulations (calculation details are shown in Note S4 of the ESM). The relative error between v_1 and v_2 was less than 6% (Table 1) and cross-validation between these two methods confirmed that the system had achieved a thermodynamic equilibrium state.

4 Molecular forces on water molecules in clay nanopores

In the following sections, we described the link between the morphological organization and molecular forces of the water molecules to reveal the force mechanisms of water flow in clay nanopores. For the sake of convenience, all of the following force variables refer to the force components along the flow direction. The value of a driving force is positive, while

Dama sina <i>k</i> (see)			$S_{1} = 1 = 1 = 1$	Average flow velocity (m/s)	
Pore size, n (nm)	re size, n (nm) ΔP (MPa) Dynamic viscosity, μ (cP) Slip length, l_s (Slip length, $l_s(A)$	Velocity profile, v_1	Outflow rate, v_2
3.5	20	0.76	2.24	8.93	8.84
	60	0.71	2.81	27.09	26.23
	120	0.73	3.70	58.89	57.74
	240	0.66	5.96	162.62	158.52
5.0	20	0.69	1.84	16.71	16.86
	60	0.71	2.50	52.18	53.30
	120	0.68	3.86	124.03	126.60
6.5	20	0.73	2.17	27.31	27.35
	60	0.72	3.45	92.97	93.88

Table 1 Obtained values of hydrodynamics parameters for water flow

the value of a resistant force is negative. The width of a nanopore has little influence on the distribution and mechanism of the forces on water molecules; therefore, for the sake of simplicity, we considered the forces on water molecules in a 3.5-nm clay nanopore as typical.

4.1 Total forces on pore water

A total of 20000 values of the total force of clay matrix on pore water F^{sc} for $\Delta P=0$ and 240 MPa were sampled and illustrated with dots in Fig. 2. It can be found that the values of F^{sc} continued to fluctuate after the 2-ns equilibrium period. To investigate the fluctuation patterns of F^{sc} , we divided the fluctuant range equally into 100 intervals and counted the number of timesteps when the value of F^{sc} fell into the corresponding interval. The occurrence frequencies of the corresponding F^{sc} are plotted with black circles in Fig. 2. We found that the fluctuation of F^{sc} conformed to the Gaussian function and the mean value of the distribution decreased with the increment of ΔP . The difference between the absolute time-averaged value of F^{sc} and F^{d} for $\Delta P=240$ MPa was 2×10^{-12} N and the relative error was 0.1%. This indicates that the water flow in clay nanopores reached a dynamic mechanical equilibrium state (Wei et al., 2023) and further force analyses can be conducted on them. Moreover, the standard deviations of the Gaussian distribution of F^{∞} for $\Delta P=$ 0 and 240 MPa were basically the same, which indicated the dispersion degree of F^{∞} was basically independent of ΔP at an identical temperature.

4.2 Force analyses for water laminae

Each water lamina can be equivalent as a simply supported beam with four forces acting on it: the



Fig. 2 Time fluctuation and occurrence frequency distribution of F^{sc} for $\Delta P=0$ MPa (a) and $\Delta P=240$ MPa (b)

applied driving force (f°) , the force from clay crystal layers (f°) , the force from compensating sodium ions (f°) , and the force from other water laminae (f°) (Wei et al., 2023). Undoubtedly, with the increase of ΔP , the forces on pore water were less susceptible to thermodynamic disturbance, and the distribution patterns of forces were more prominent. Hence, we took the profile of these forces along the *z*-axis with ΔP = 240 MPa as an example; it is plotted in Fig. 3.



Fig. 3 Profile of forces acting on water molecules in each water lamina with ΔP =240 MPa

Obviously, f^{d} (represented by the curve with circles in Fig. 3) was proportional to the number density of water molecules. f^{s} (the curve with squares in Fig. 3) was a resistance force (i.e., $f^{s}<0$) mainly acting in the Stern layer, while f^{e} (the curve with crosses in Fig. 3) was chiefly concentrated in the diffusion layer. Within a range of 3.5–5.0 Å from the clay surface, f^{e} was characterized as a driving force (i.e., $f^{e}>0$) due to ion hydration. Subsequently, f^{e} became a resistance force and gradually decayed to zero with further diffusion of Na⁺. f^{w} (the curve with triangles in Fig. 3) served as a dominant viscous force to balance the shear force induced by the other three forces.

5 Force mechanism of clay crystal layers on water molecules

 f^{s} was symmetric around the center of the nanopores and concentrated on the water molecules in the Stern layer. It played a similar role to the pedestal counterforce of a simply supported beam, and influenced the boundary effect of the water flow in the clay nanopores. As ΔP increased, the resistant effect of the clay surface was enhanced (Note S6 of the ESM). f^{s} consisted of the van der Waals force component f^{s}_{vdW} and the Coulomb electrostatic force component f_{Coul}^{s} , which were based on the non-bonded interactions in ClayFF. As ΔP increased, the resistant f_{vdW}^s was enhanced while the f_{Coul}^{s} gradually changed from a driving force to a resistance force, and played a leading role in f^{s} (Fig. S10 of the ESM). The mechanisms of the changes in f_{vdW}^{s} and f_{Coul}^{s} with the increasing hydraulic gradient are described in the following sections.

5.1 van der Waals component

 $f_{\rm vdW}^s$ was concentrated on water molecules within a range of 2.0–2.5 Å away from the clay mineral surface (Fig. S10) and was highly dependent on the planar distribution of the water oxygens. Hence, the planar distribution of water oxygen in the plane 2.25 Å away from the clay mineral surface could be summarized according to the flow trajectories (Fig. 4a). For



Fig. 4 Cloud maps for a single water molecule in the plane 2.25 Å away from the mineral surface: (a) distribution probability; (b) van der Waals potential $U_{vdW}^{s^*}$; (c) van der Waals force $f_{vdW}^{s^*}$. The notation '*' is used to distinguish the force on an individual water molecule from the distributed force along the z-axis

each single water molecule located at different positions in the plane, we calculated the van der Waals potential $U_{vdW}^{s^*}$ (Fig. 4b) and force $f_{vdW}^{s^*}$ (Fig. 4c) and plotted them as cloud maps in a unit cell of the clay crystal.

As shown in Fig. 4a, water molecules tended to stay above the center of the hexagonal cavity (Marry et al., 2008) due to the van der Waals repulsive barrier (Fig. 4b) between the bridging oxygen atoms and water oxygen atoms. Based on the planar distribution of $f_{\rm vdW}^{s^*}$ (Fig. 4c), the unit cell of the clay crystal could be divided into four areas (i.e., Areas a, b, c, and d) along the contour lines with values of zero. Clearly, the v-component of the van der Waals repulsive force on water molecules in Areas a and c served as a resistance force, while the corresponding y-component acting on water molecules in Areas b and d served as a driving force. As water flowed along the y-direction, it was easy to figure out that water molecules had a higher probability of residing downstream (i.e., Area a) than upstream (i.e., Area b). Hence, the probability of molecules being in the resistance-force areas (Areas a and c) was slightly larger than that of them being in the driving-force areas (Areas b and d), and the difference generated a net resistant van der Waals force, which enlarged with the increase of ΔP (as listed in Table 2). It can be concluded that, with the increase of ΔP , more water molecules moved from Area b to Area a and generated an increasing resistance force $f_{\rm vdW}^{\rm s}$ to respond to the increase of flow-driving force.

5.2 Coulomb electrostatic component

Compared to f_{vdW}^{s} , the peak of f_{Coul}^{s} was slightly farther and occurred within a range of 2.5–3.0 Å away from the surface (Fig. S10). Based on the planar distribution of water oxygen atoms in the plane 2.75 Å from the clay surface (Fig. S6 of the ESM), the hexagonal cavity could be divided into six equilateral triangular areas (i.e., Areas I–VI), and the water oxygen atoms

were generally located near the geometric centroid of the areas (Table S1 of the ESM), which basically remained the same under different pressures. Apart from the planar distribution, three characteristic angles were used to describe the morphology of water molecules, that is, orientation angle α , interplanar angle β , and rotation angle γ , and the schematic diagrams of these angles are illustrated in Fig. S5 of the ESM. Further investigations showed that the distributions of angles α and β along the z-axis were all independent of ΔP (Fig. S8 of the ESM), while the distribution of rotation angle y changed with ΔP . For water molecules located in the six areas, we calculated the distributionprobability difference of rotation angle γ between ΔP = 0 MPa and $\Delta P=240$ MPa and found that the variation trends were approximately identical for all six areas. Hence, Fig. 5 shows only the result for Area III (complete results for all six equilateral triangular areas are plotted in Fig. S9 of the ESM).

As ΔP rose from 0 to 240 MPa, water molecules with γ less than 180° multiplied, while water molecules with γ greater than 180° decreased, revealing that water molecules were apt to rotate around oxygen atoms to point their orientation vectors in the flow direction. We also calculated the electrostatic force $f_{\text{Coul}}^{s^*}$ on a single water molecule rotating counterclockwise around the z-axis to form the rotation angle γ from 0° to 360°; this is plotted by a dashed curve in Fig. 5. It is evident that the $f_{\text{Coul}}^{s^*}$ on water molecules with γ less than 180° was a resistance force, but was a driving force on water molecules with γ greater than 180°. Hence, it was possible to conclude that changes in $f_{\text{Coul}}^{\text{s}}$ with different ΔP mainly resulted from rotation of the orientation vectors of partial water molecules around the normal vector of the clay mineral surface. The rotation led to the increase of water molecules with a resistant $f_{\text{Coul}}^{s^*}$, which generated the resistance force to balance the increasing flow-driving force.

Table 2 Distribution probability and weighted average force of a single water molecule in each area of a unit cell

	Resistance-force area				Driving-force area			
ΔP (MPa)	Distribution probability			Weighted average	Distribution probability			Weighted average
	Area a	Area c	Total	force (×10 ⁻¹⁰ N)	Area b	Area d	Total	force (×10 ⁻¹⁰ N)
0	0.499	0.033	0.532	-9.717	0.442	0.026	0.468	8.798
20	0.509	0.032	0.541	-10.00	0.433	0.026	0.459	8.597
60	0.518	0.030	0.548	-10.35	0.424	0.028	0.452	8.554
120	0.540	0.027	0.567	-10.97	0.404	0.029	0.433	8.354
240	0.555	0.025	0.580	-11.90	0.386	0.034	0.420	8.284



Fig. 5 Electrostatic forces on a single water molecule and probability differences between ΔP =240 MPa and ΔP =0 MPa for water molecules with different rotation angles γ in Area III. μ_{xy} is the projection of the orientation vector of water molecule μ on the *xy*-plane

6 Mechanism of internal viscous force within pore water

In a non-uniform velocity field, momentum transfer occurs between the water molecules in adjacent laminae with different velocities (Zhu and Xu, 2009), which results in a viscous force that reduces relative motion, that is, a resistance force acting on the faster lamina (FL) and a driving force on the slower lamina (SL). As mentioned above, the internal force f^{w} served as the viscous force within pore water. The profiles of f^{w} , f^{w}_{vdw} , and f^{w}_{Coul} under $\Delta P=240$ MPa (Fig. S11 of the ESM) showed that all of these forces were concentrated on the water molecules in the Stern layer and the front part of the diffusion layer, while the values of f^{w}_{vdw} ; this is similar to findings in the decomposition results for the viscosity integral (Fig. S4 of the ESM). To determine the mechanism of f^{w} , we performed the following analyses using the spatial distribution function (SDF) calculation method (Chen et al., 2019), but in a two-dimensional way. An arbitrary water lamina was taken as the central lamina (CL), and for each water molecule in CL, we calculate the *y*-component forces from the water molecules that satisfied the hydrogen bonding criterion (Kumar et al., 2007) in the adjacent laminae (i.e., FL or SL). Afterwards, with respect to each water oxygen atom in the CL, the relative *xy*-planar distributions of forces from water molecules in the SL are elucidated as an example.

It can be concluded from Fig. 6 that the Coulomb electrostatic force between water molecules in the adjacent laminae was attractive, and thus generated a driving force from downstream water molecules and a resistance force from upstream water molecules. Similarly, we noted that the van der Waals force between water molecules was repulsive. Due to the velocity difference between adjacent laminae, the water molecules in the SL were more likely to reside upstream with respect to the water molecules in the CL. Therefore, in the SL, the values of forces from upstream water molecules were always higher than those from downstream ones. It was the retention that induced the net electrostatic resistance force and the net van der Waals driving force from the water molecules in the SL to the water molecules in the CL. Furthermore, the net electrostatic force was always greater than the net van der Waals force, so the water molecules in the SL exerted a net resistance force, while the water molecules in the FL exerted a net driving force to the water molecules in the CL, which was the mechanism of the viscous force. Obviously, the different probabilities of being downstream or upstream were dependent on the velocity gradient between adjacent laminae. Hence, as the hydraulic gradient increased, the velocity gradient between the adjacent laminae increased, eventually resulting in a stronger viscous force within the flowing pore water.

7 Conclusions

In this study, we simulated the nanoflow in the clay nanopores via the NEMD simulation method. The hydrodynamics properties were obtained to verify the simulation model, and the molecular forces from clay



Fig. 6 Planar distribution of forces from water molecules in the SL. vdW represents van der Waals; $r_{0.0}$ is the length of the oxygen vector, which is the vector from the central water oxygen atom to another water oxygen atom in the SL; $\theta_{0.0}$ is the angle between the oxygen vector and x-axis

matrix and the viscous force within the pore water were calculated. The mechanisms of the van der Waals and Coulomb electrostatic components of these molecular forces were revealed by analyzing the planar distribution and morphology of water molecules. The following conclusions can be drawn:

Concentrated on water molecules in the Stern layer, the resistance force f^s is similar to a pedestal counterforce of the simply supported beam. It is composed of the van der Waals component f^s_{vdW} and the Coulomb electrostatic component f^s_{Coul} , the latter of which takes a leading role in f^s .

 $f_{\rm vdw}^{\rm s}$ crests within a range of 2.0–2.5 Å away from the clay mineral surface and is highly dependent on the planar distributions of the water oxygens. Due to the van der Waals repulsive barrier and directed flow, it is more favorable for a water molecule to reside in resistance-force areas (i.e., Area a) rather than drivingforce areas (i.e., Area b), and the differences widen to generate a stronger net resistance force as the hydraulic gradient increases.

 $f_{\text{Coul}}^{\text{s}}$ concentrates within a range of 2.5–3.0 Å away from the clay mineral surface and the variation of $f_{\text{Coul}}^{\text{s}}$ under different ΔP mainly results from the rotation of the orientation vectors of partial water molecules. This rotation leads to the increase of water molecules with a resistant $f_{\text{Coul}}^{s^*}$ and generation of the resistant force to balance the increasing driving force.

As for f^{*} within the flowing pore water, due to the velocity difference between adjacent laminae, the water molecules in the slower lamina have a higher probability of residing upstream, resulting in a net electrostatic resistance force and a net van der Waals driving force. The increasing velocity gradient raises the probability of water molecules in the slower lamina lagging behind, and results in a correspondingly stronger viscous force within the pore water.

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Author contributions

Yuchao LI and Shengjie WEI designed the research. Shengjie WEI and Peng SHEN processed the corresponding data. Shengjie WEI wrote the first draft of the manuscript. Yuchao LI helped to organize the manuscript. Yuchao LI and Shengjie WEI revised and edited the final version. Yunmin CHEN and Yuchao LI acquired the financial support.

Conflict of interest

Shengjie WEI, Yuchao LI, Peng SHEN, and Yunmin CHEN declare that they have no conflict of interest.

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Electronic supplementary materials

Notes S1-S8, Table S1, Figs. S1-S12