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# Molecular force mechanism of hydrodynamics in clay nanopores

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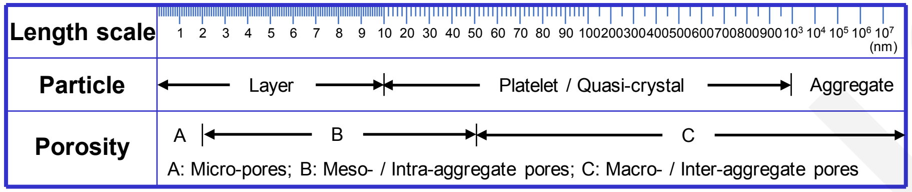
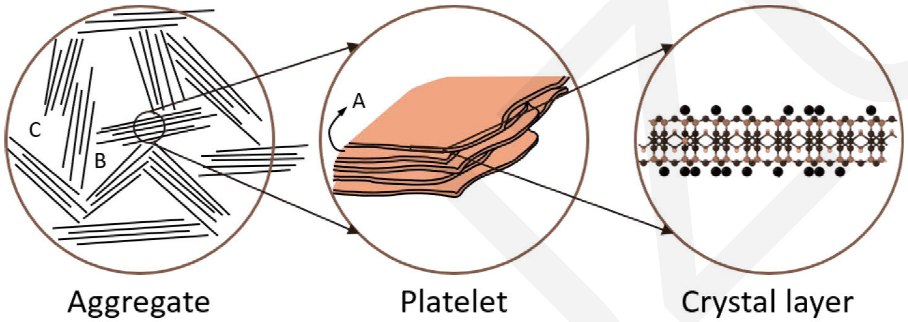
# Challenges in continuous descriptions of flow in clay nanopores

## ■ Multi-scale nature



| Length scale | 1 2 3 4 5 6 7 8 9 10 20 30 40 50 60 70 80 90 100 200 300 400 500 600 700 800 900 $10^3$ $10^4$ $10^5$ $10^6$ $10^7$ (nm) |
|---|---|
| Particle | ← Layer →\|← Platelet / Quasi-crystal →\| Aggregate |
| Porosity | A \|← B →\|← C →<br>A: Micro-pores; B: Meso- / Intra-aggregate pores; C: Macro- / Inter-aggregate pores |



## ■ Navier-Stokes equation

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t}+(\mathbf{v}\cdot\nabla)\mathbf{v}\right)=-\nabla \mathbf{P}+\mu\nabla^2\mathbf{v}+\rho\mathbf{g}$$

- excessive molecular fluctuations
- inhomogeneous hydrodynamics properties (i.e., density and viscosity)
- limitations of nanofluidic experimental technology

# Molecular model and inter-atomic force field

- Planar size: 4.2 nm ($L_x$) × 3.7 nm ($L_y$)
- Pore size $h$: 3.5, 5.0, and 6.5 nm
- Accessible width $h^*$: between the first adsorbed layer
- Water number: 1665 (3.5 nm), 2437 (5.0 nm) and 3209 (6.5 nm)

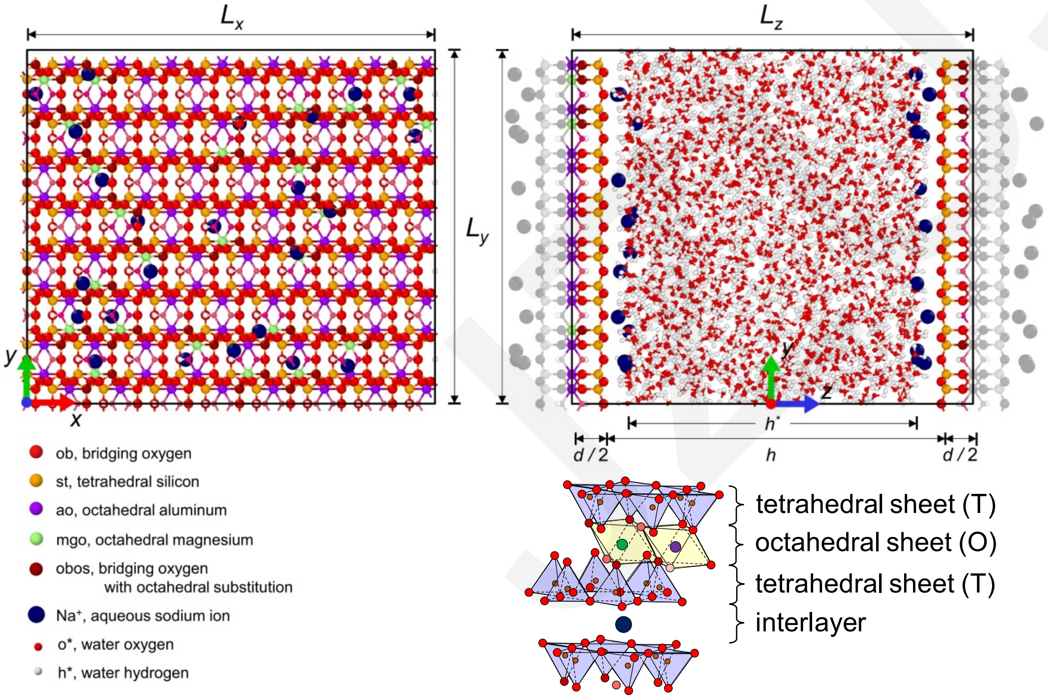


**Fig. 1 Molecular model for water flow in Na-MMT nanopores**

**Clay matrix**: CLAYFF

$$U^{\text{total}} = U^{\text{vdW}} + U^{\text{Coul}} + U^{\text{bond}} + U^{\text{angle}}$$

$$U^{\text{vdW}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad (r \le 1 \text{ nm})$$

$$U^{\text{Coul}} = \frac{kq_iq_j}{\epsilon_r r} \quad (r \le 1 \text{ nm; Ewald summation for } r > 1 \text{ nm})$$

$$U^{\text{bond}} = k_b(r_{ij} - r_0)^2$$

$$U^{\text{angle}} = k_a(\theta_{ijk} - \theta_0)^2$$

**Water molecules**: SPC/E model

# Hydrodynamics properties

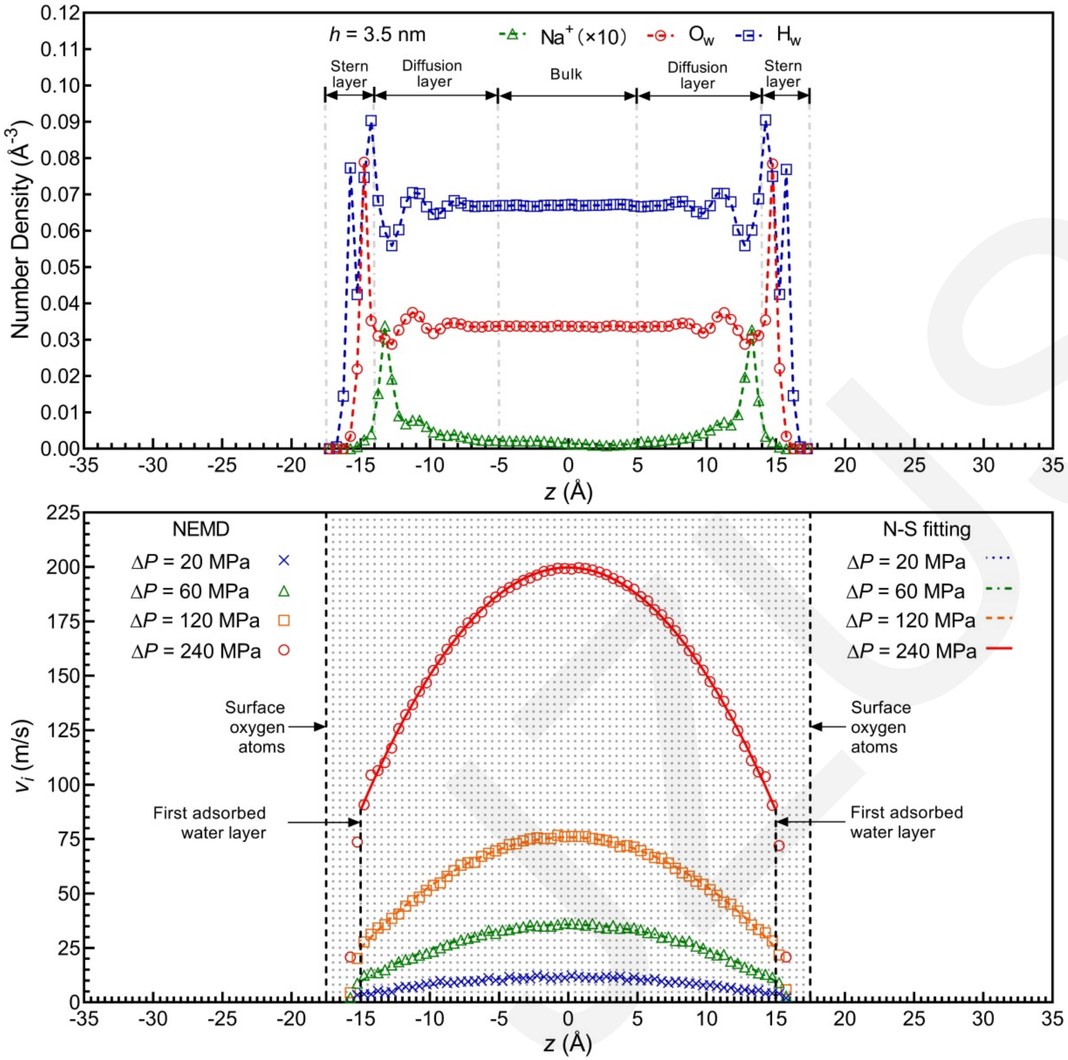


**Fig. 2 Density profile and velocity profile of water flow in clay nanopore with *h* = 3.5 nm**

## ■ Density profile

- Stern layer (~0.35 nm): equals to the diameter of a single water molecule
- Diffusion layer: conformed to the EDL theory; hydrated $Na^+$ formed outer-sphere complexes
- Bulk region: water remained constant

## ■ Velocity profile

$$v_y = -\frac{1}{2\mu}\frac{\Delta P}{L_y}\left(z^2 - \frac{h^{*2}}{4} - h^* l_s\right)$$

- parabolic between first adsorbed layers but offsets were observed near mineral surfaces
- dynamics viscosity $\mu = 0.71 \pm 0.05$ cP
- slip length $l_s > 0$ (slip boundary) and increased with $\Delta P$
- hydraulic conductivity: $(1.79 \pm 0.63)$, $(3.23 \pm 0.55)$, $(5.22 \pm 0.34) \times 10^{-11}$ m/s

# Molecular forces on water molecules in clay nanopores

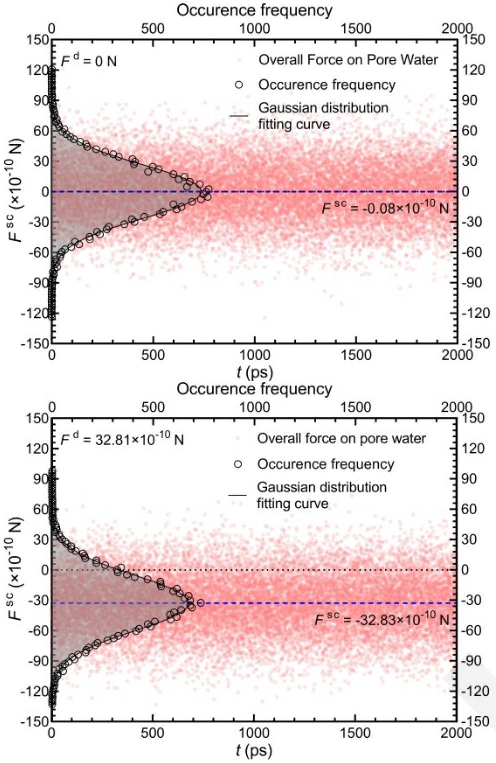


**Fig. 3 Time-fluctuation and occurrence-frequency distribution of total forces on pore water**

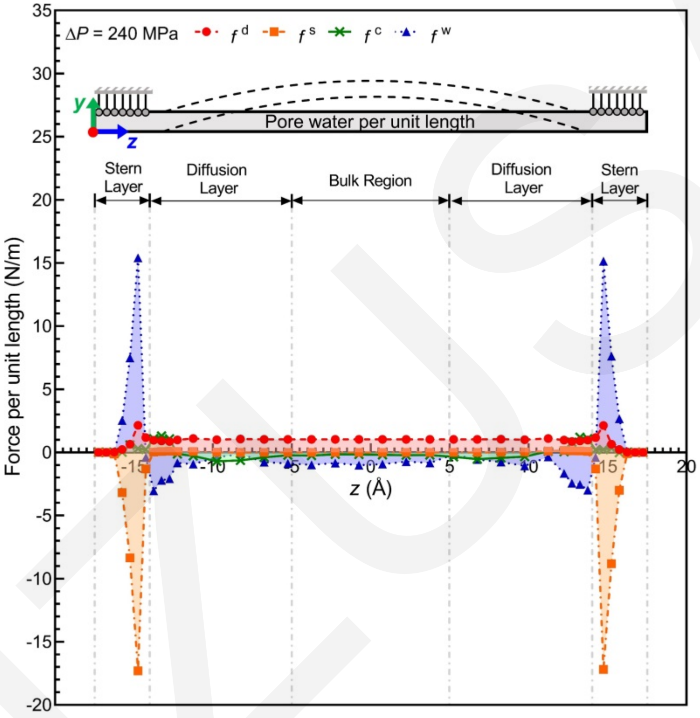


**Fig. 4 Profile of forces acting on water molecules in each water lamina for ΔP = 240 MPa**

## ■ Total forces

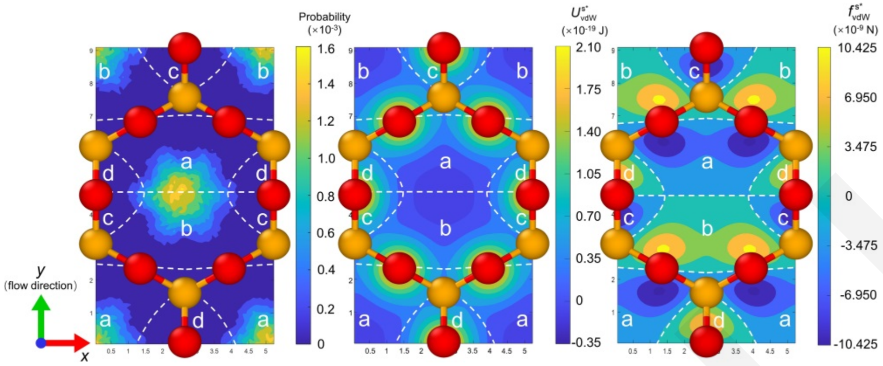
- fluctuation satisfied the Gaussian distribution and the time-averaged value of $F^{sc}$ equaled $F^d$ to maintain dynamic mechanical equilibrium
- dispersion degree was independent of ΔP with identical temperature

## ■ Force analyses

- $f^d$: proportional to water number
- $f^s$: resistance force in the Stern layer
- $f^c$: mainly in the diffusion layer
- $f^w$: served as viscous force to resist shear deformation

# Force mechanisms of clay crystal layer on water molecules

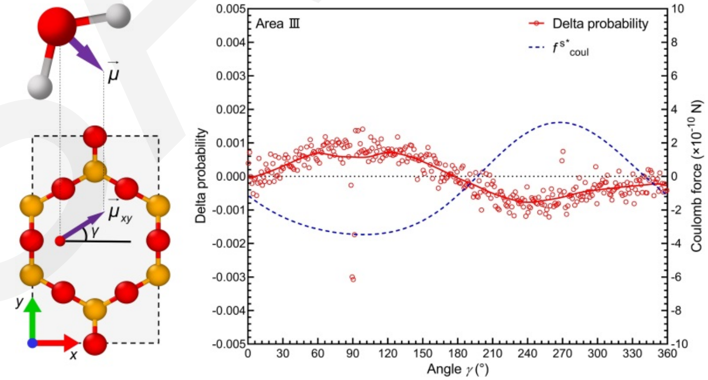
## ■ van der Waals component



| ΔP (MPa) | Resistant force areas | | | | Driving force areas | | | |
|---|---|---|---|---|---|---|---|---|
| | Distribution probability | | | Average force (×$10^{-10}$ N) | Distribution probability | | | Average force (×$10^{-10}$ N) |
| | a | c | Sum | | b | d | Sum | |
| 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 |

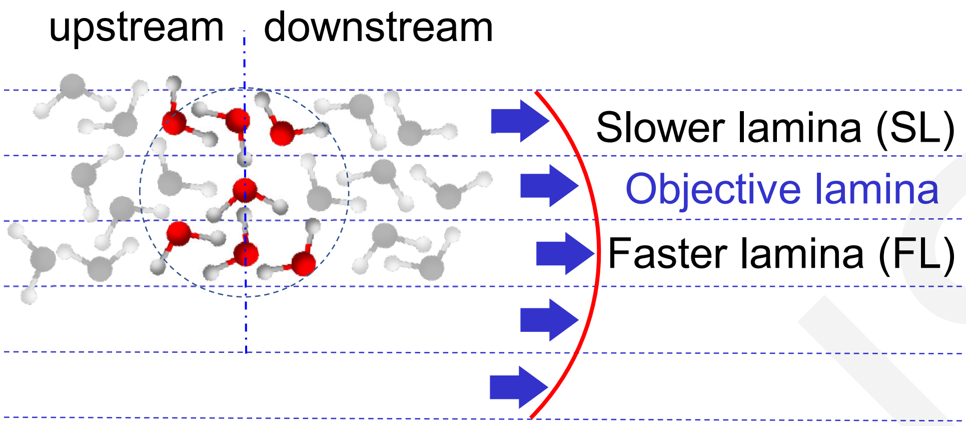
- tend to reside at the center of cavity due to repulsive barrier
- distribution differences generated net resistance van der Waals force from clay crystal layer and increased with Δ*P*

## ■ electrostatic component



- orientation angle *α* and interplanar angle *β* stay unchanged with Δ*P*
- water with rotation angle *γ* < 180° increased, showing a tendency of rotation around the normal vector to point towards the flow direction
- electrostatic force on water with *γ* < 180° was resistant
- the changes in electrostatic force resulted from the rotation of water

# Mechanism of internal viscous force within pore water



Slower lamina (SL)

Objective lamina

Faster lamina (FL)

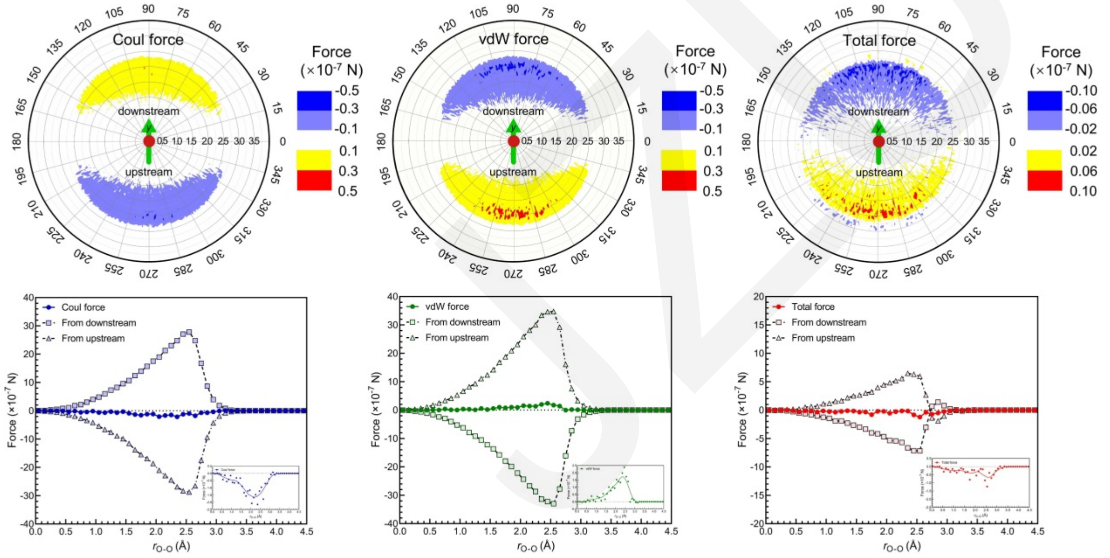


Fig. 7 Planar distribution of forces from water molecules in SL

- Coulombic electrostatic force from adjacent water lamina was **attractive** while van der Waals force was **repulsive**
- Water molecules in the SL were apt to **reside upstream** with respect to the water molecules in the objective lamina, generating **a net resistance Coulombic force** and **a net driving van der Waals force**
- The probability difference of being upstream or downstream was **dependent on the velocity gradient**
- The increasing external driving pressures **induced an increasing velocity gradient and a stronger viscous force**

# Conclusions

- During the NEMD simulations, pore water reached **a dynamic mechanical equilibrium state** and each water lamina could be regarded as **a simply supported beam**

- **Boundary effect:**

  The resistance force from clay crystal layer was similar to **a pedestal counterforce**. Water molecules **preferred the resistance-force area than the driving-force area at the cavity** and the differences enlarged to generate a stronger net resistance van der Waals force. **The rotation of water molecules around the surface normal vector** attributed to the generation of the resistance electrostatic force

- **Viscous effect:**

  Water molecules in the slower lamina have **a higher probability of residing upstream** with respect to the water molecules in the faster lamina, resulting **a net resistance electrostatic force**, **a net driving van der Waals force** and thus, **a net resistance resultant force**