TEMPERATURE, VISCOSITY, AND CHARGE DENSITY EFFECTS ON THE VELOCITY PROFILE OF A NANOCHANNEL ELECTRO-OSMOTIC FLOW

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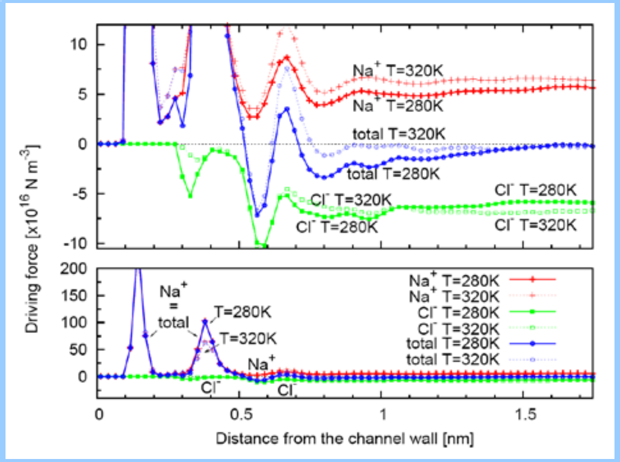
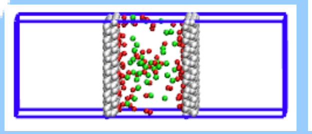
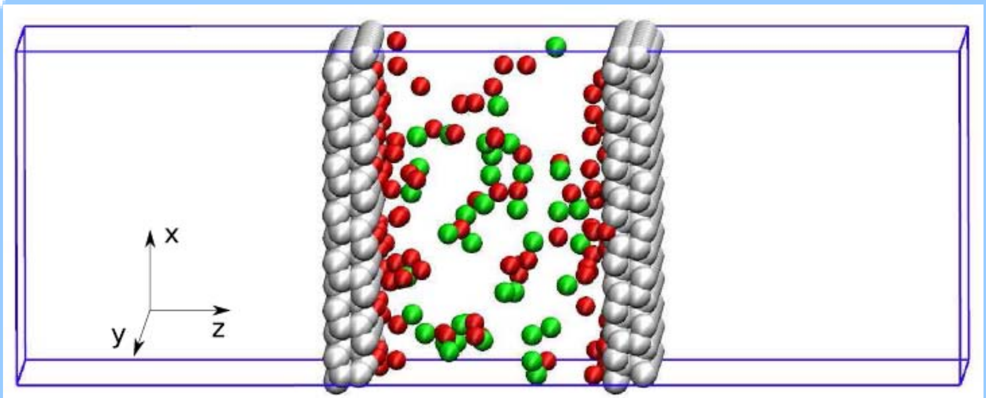
$$\vec{F}_d(z) = e\left[c_{Na^+}(z) - c_{Cl^-}(z)\right]\vec{E}_{ext}$$







Electrokinetic process - definitions

Electorkinetic phenomena: electric field related effects occurring in heterogeneous fluids in porous materials

Electroosmosis: motion of fluid under the influence of electric field

Electrophoresis: motion of particles under the influence of electric field

Streaming potential: electric potential generated by moving fluid

Cause: **Double layer** of charges on solid-liquid interface

Applications: dewatering of concrete structures, decontamination, nanoscale devices, even source of electric energy?

Atomic system configuration

Na^+ and **Cl^- ions** solvated in **water**,
confined between two negatively charged Si walls

Applied **electric field** parallel to the walls

Measured **velocity profiles** and **ionic concentrations**

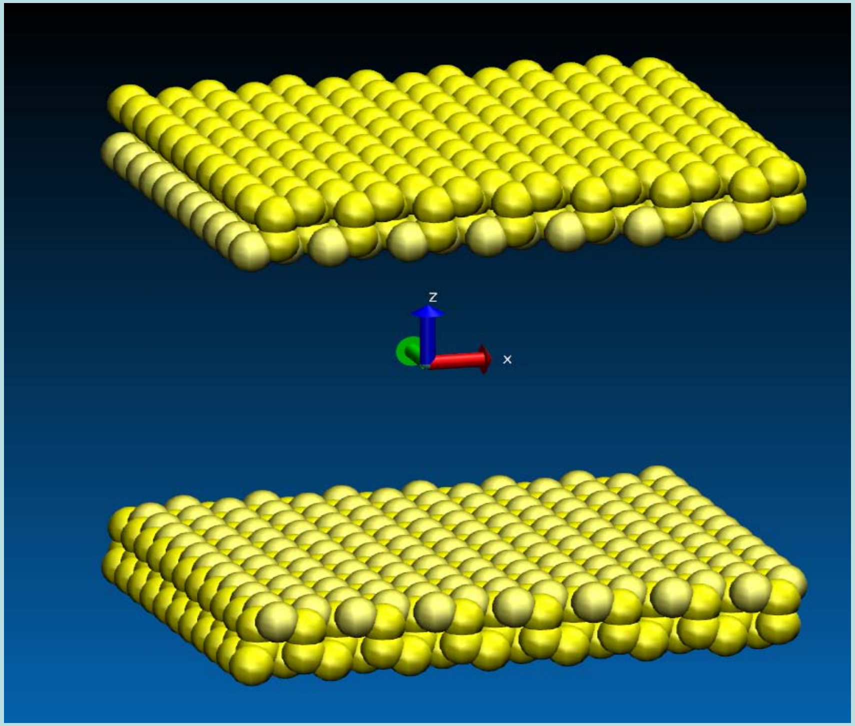
Final goal: obtain effective diffusion coefficients and ionic mobilities to supplement continuum level model

References:

R. Qiao and N. R. Aluru: Charge Inversion and Flow Reversal in a Nanochannel Electro-osmotic Flow, PRL 92 (19) 2004

R. Qiao and N. R. Aluru: Multiscale Simulation of Electroosmotic Transport Using Embedding Techniques, International Journal for Multiscale Computational Engineering 2 (2) 2004

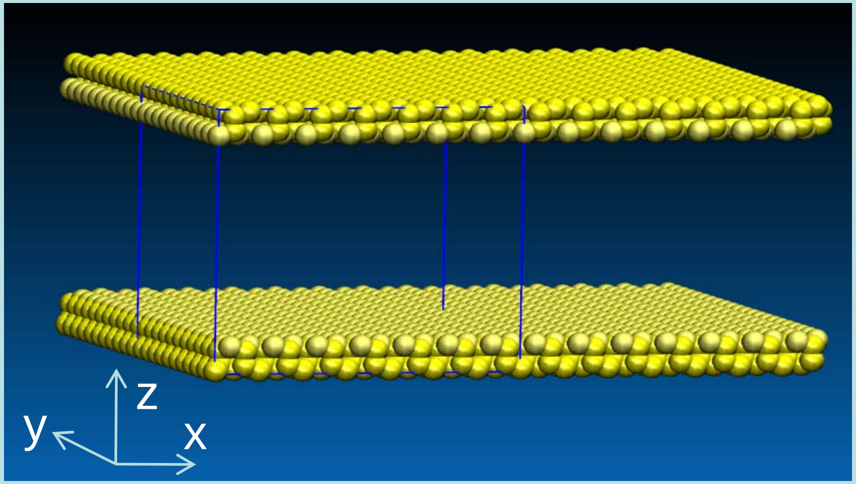
Construction of simulation cell



- Channel walls of silicon crystal surface in (111) direction
- Dimensions 4.66x4.22x3.49 nm
- Uniform negative charge on inner surface layers
- Walls: 924 uncharged Si atoms

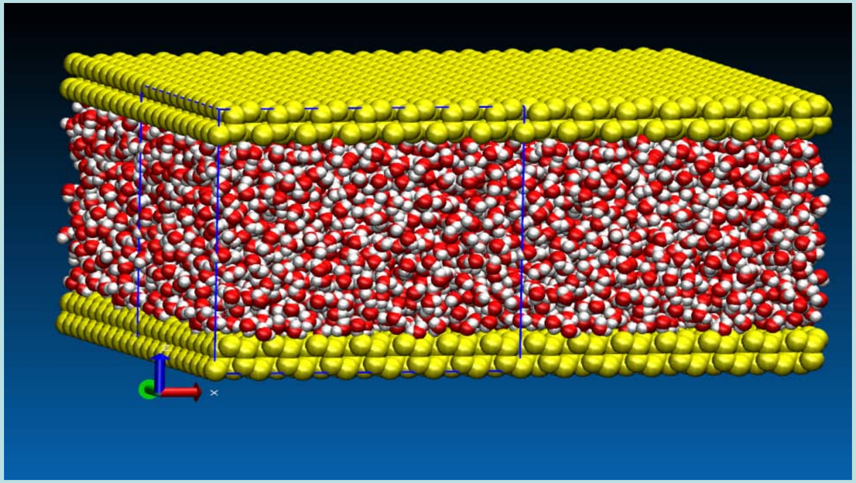
  308 neg. charged Si atoms

Construction of simulation cell



Periodic boundary conditions in x and y directions => slab with infinite surface area

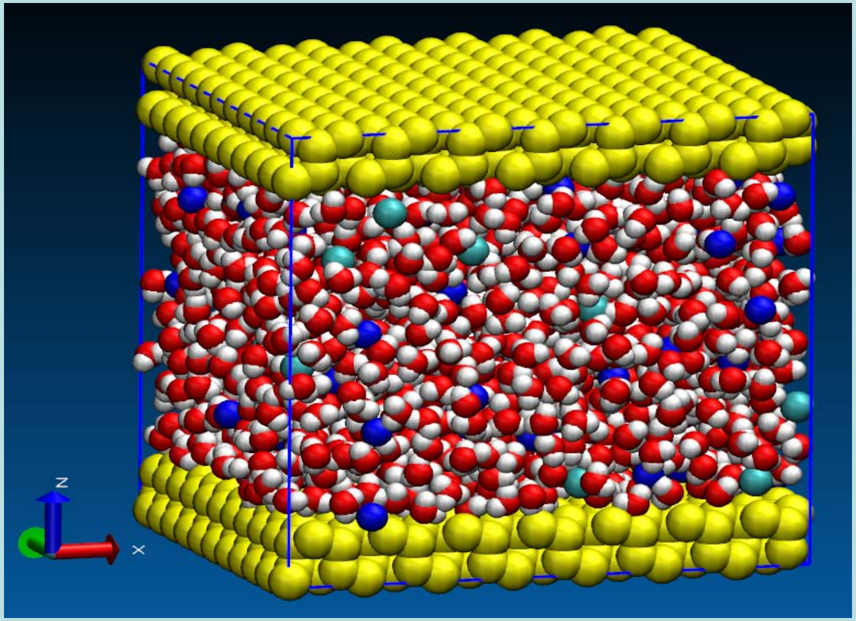
Studied variation along z direction



Solvation:

- Randomly inserted 2290 water molecules
- Avoided overlap, even across PBC boundaries

Construction of simulation cell



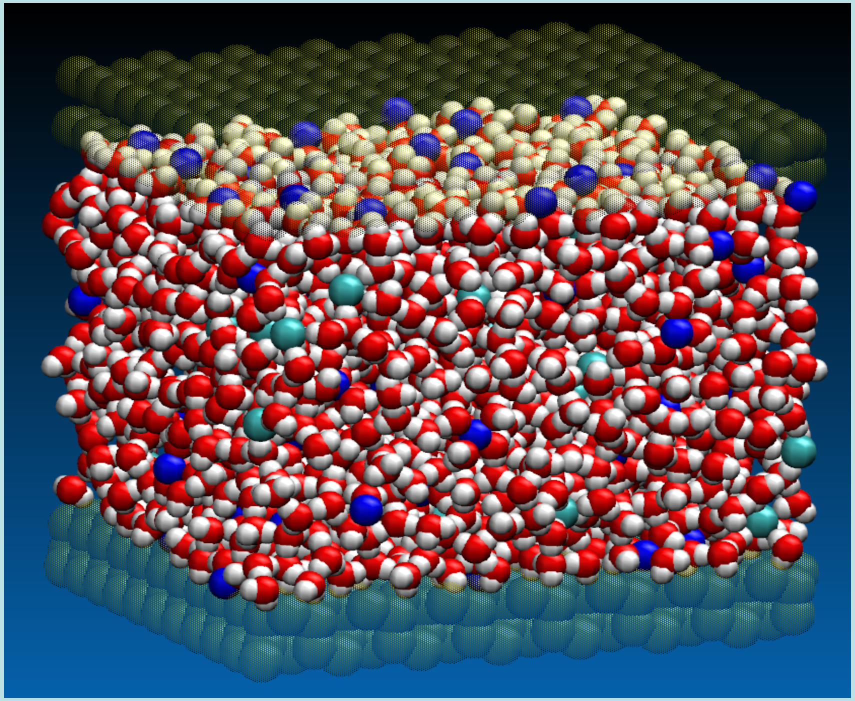
Insertion of ions:

- Replaced random water molecules with Na^+ and Cl^- ions

Ionic solution:

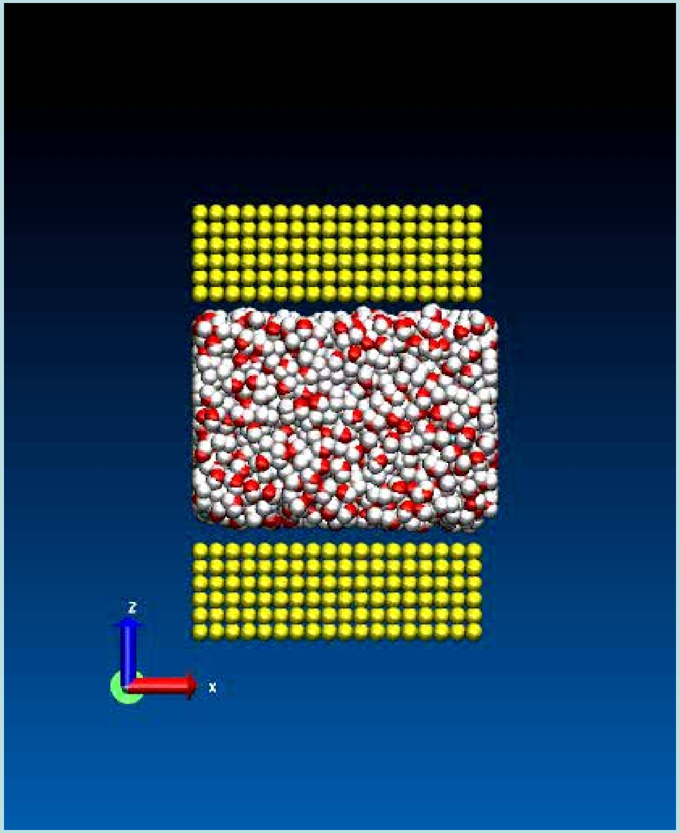
- 2144 water molecules
- 108 Na^+ ions
- 38 Cl^- ions

Energy minimization



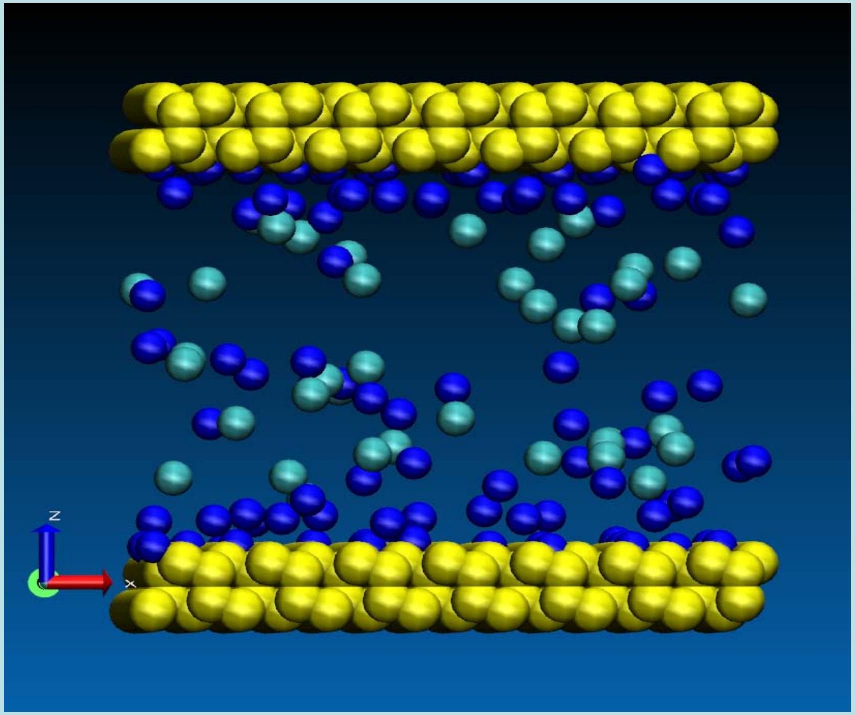
- Molecules reorient and settle to local minimum of energy position
- H from H_2O molecules points to the negative surface
- Na^+ ions move slightly closer to the negatively charged surface
- Cl^- ions move slightly away from the negatively charged surface

Pressure adjustment



- Bottom wall is fixed
- External force is applied on the top wall atoms in the downward direction
- Magnitude of the external force is calculated so that the total force on each atom corresponds to the desired pressure
- External force is balanced by the fluid pressure

Equilibration of atomic system



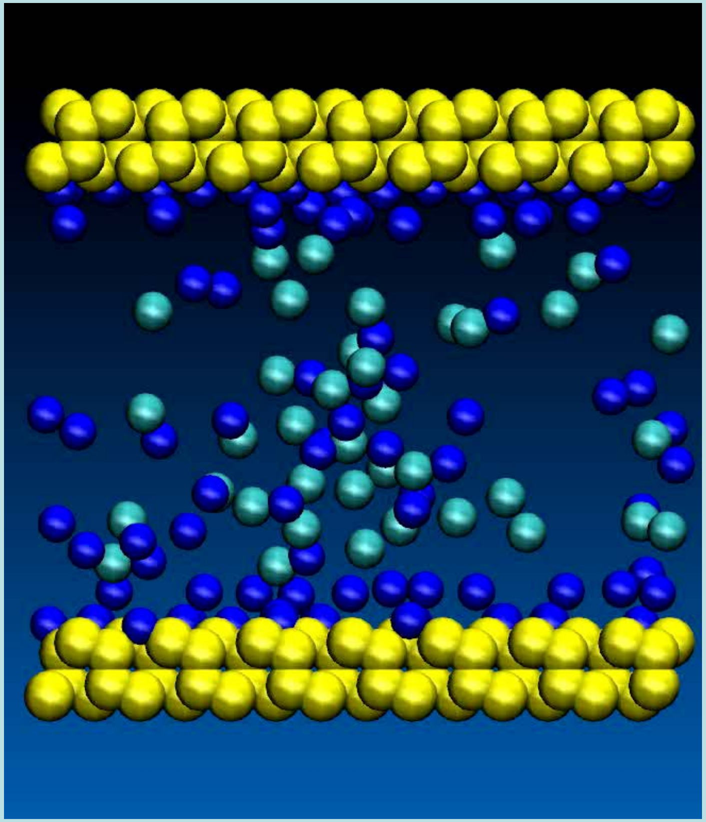
Equilibration:

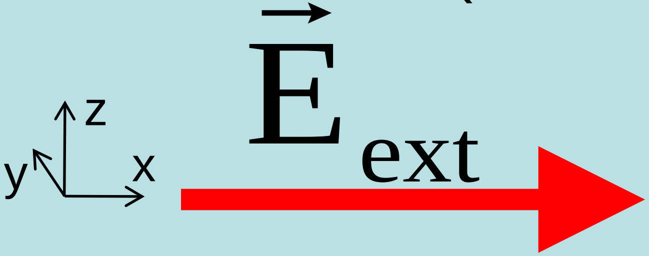
- MD simulation, t = 2 ns
- without ext. electric field
- T = 300 K

Result:

- ionic concentration profile is formed along the z direction

Simulation with applied electric field





Electric field applied in the +x direction (to the right)

Na$^+$ ions (dark blue):

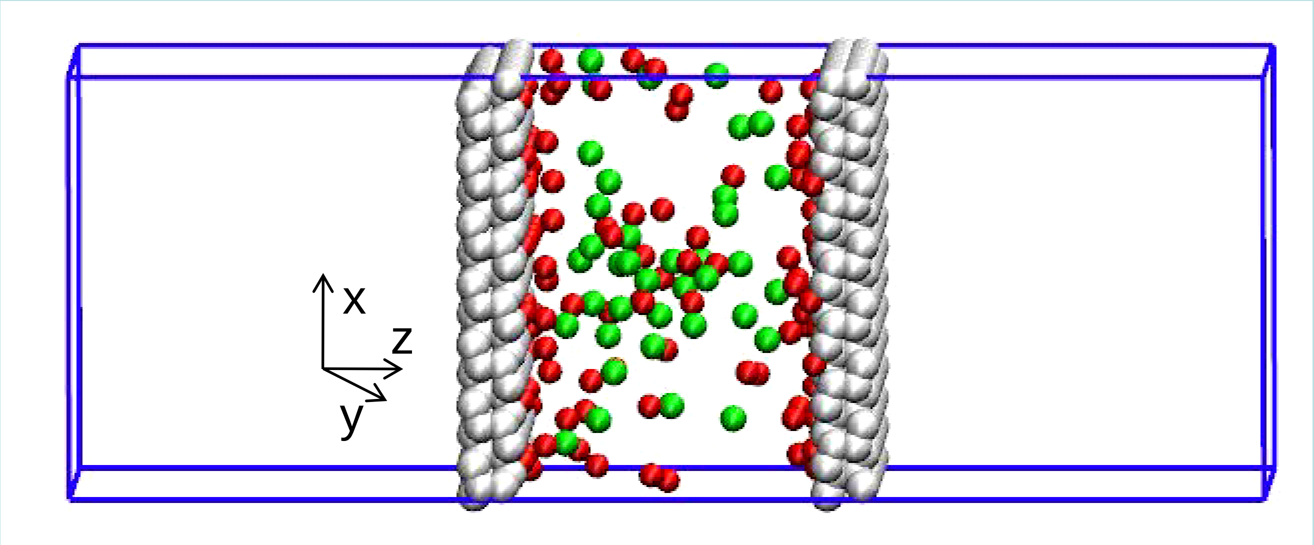
move in the direction of $\vec{E}_{ext}$

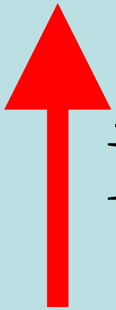
or adsorb at the negatively charged surface

Cl$^-$ ions (light blue):

move opposite to $\vec{E}_{ext}$

Simulation with applied electric field



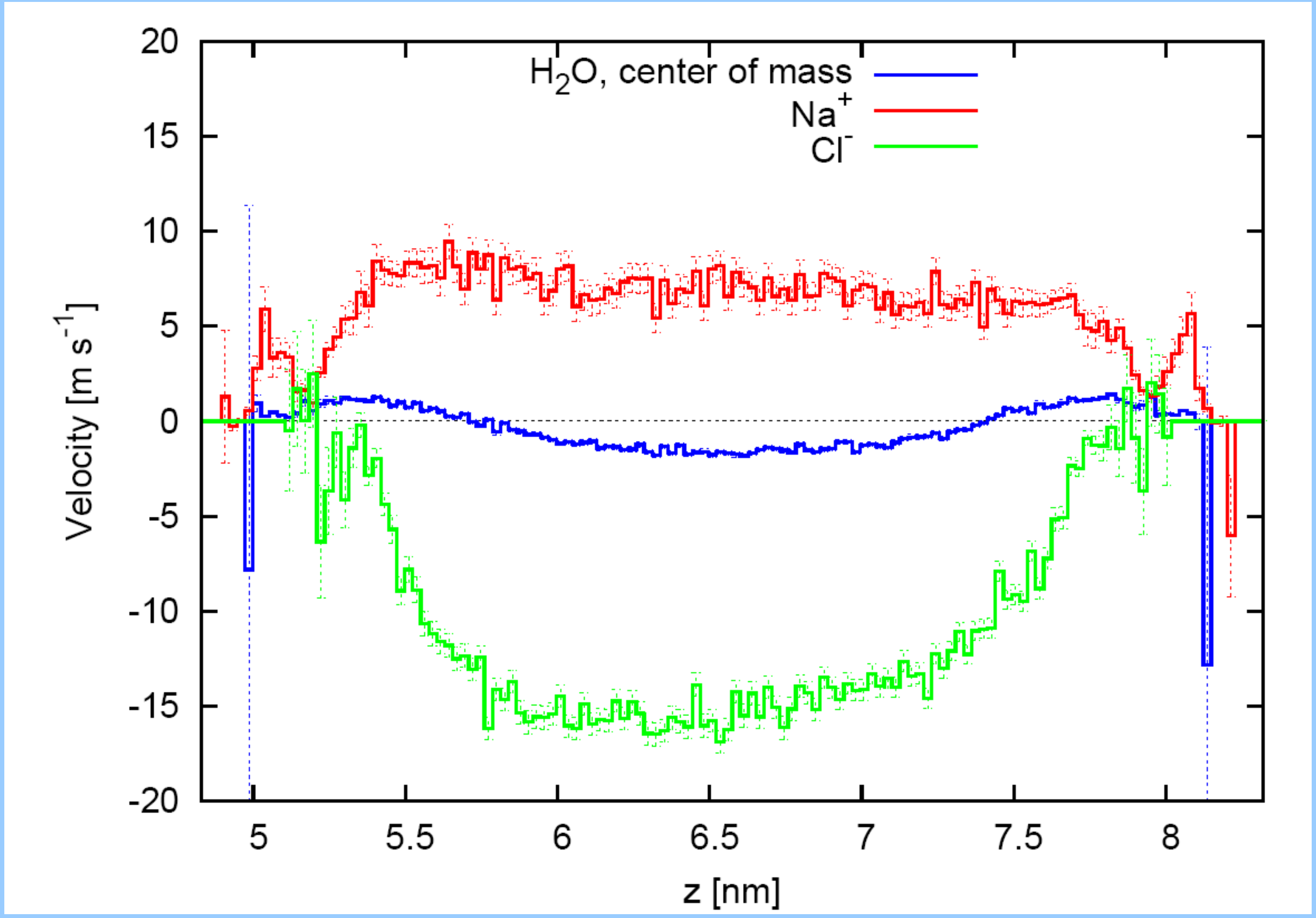


$\vec{E}_{ext}$

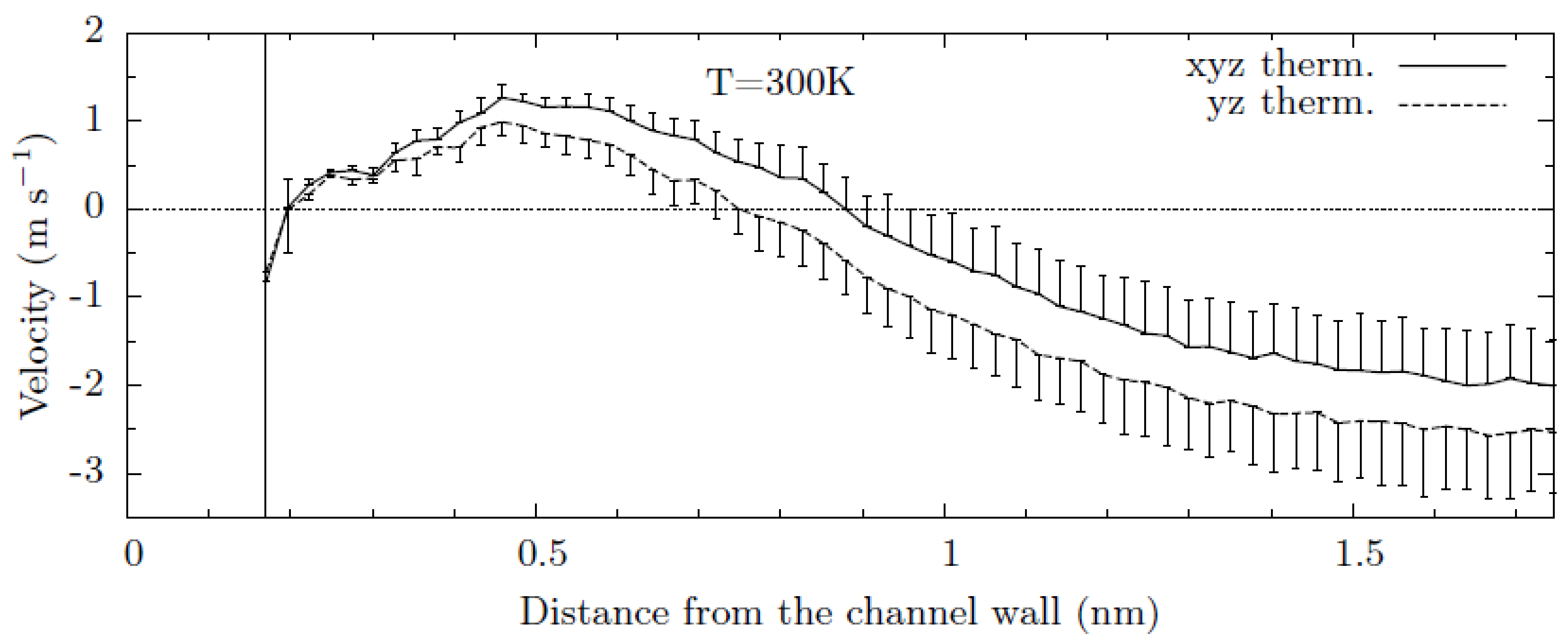
Na^+ adsorb at the negatively charged surface or move in the direction of $\vec{E}_{ext}$

Cl^- move opposite to $\vec{E}_{ext}$

Velocity profiles

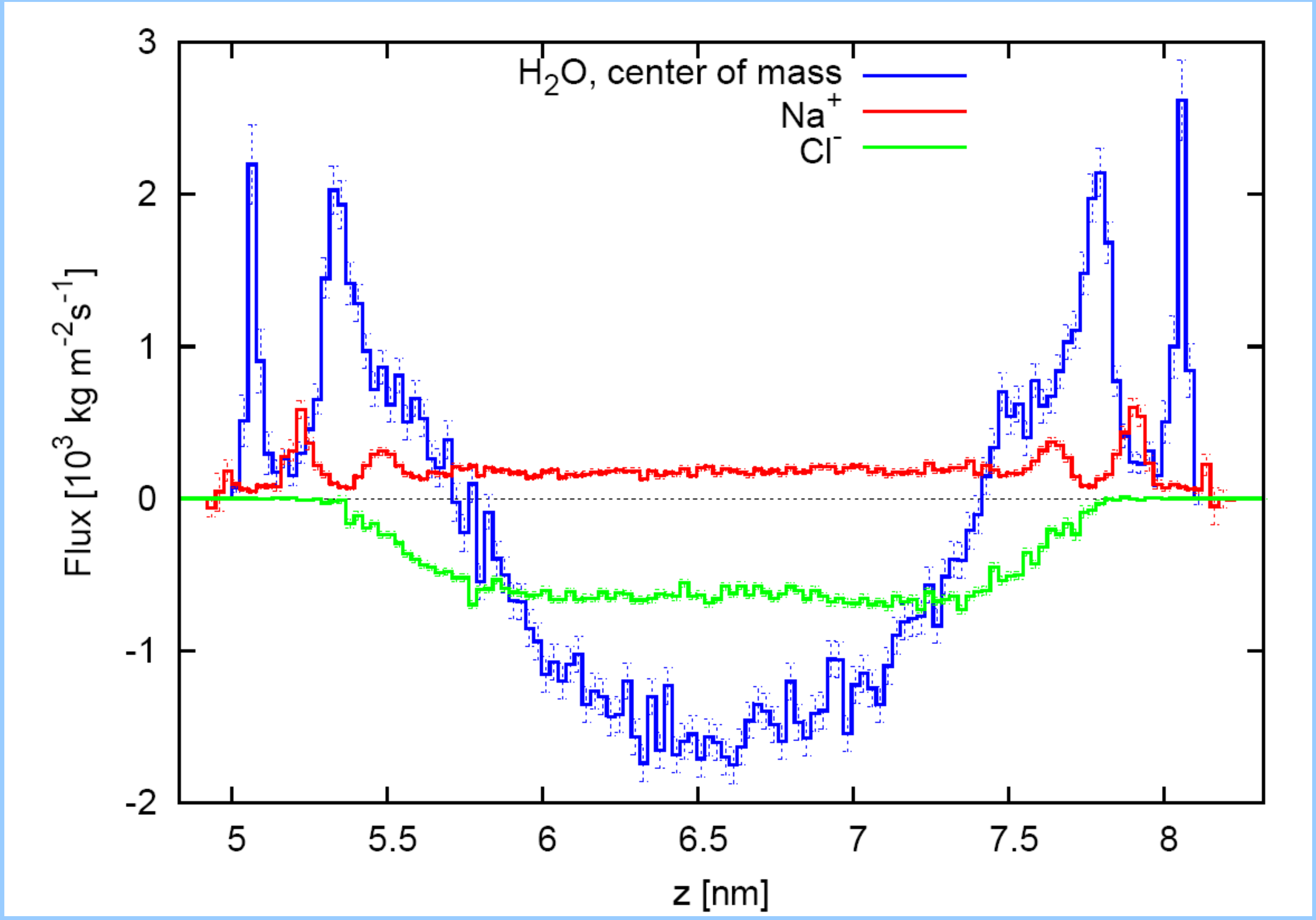


Selective thermostat

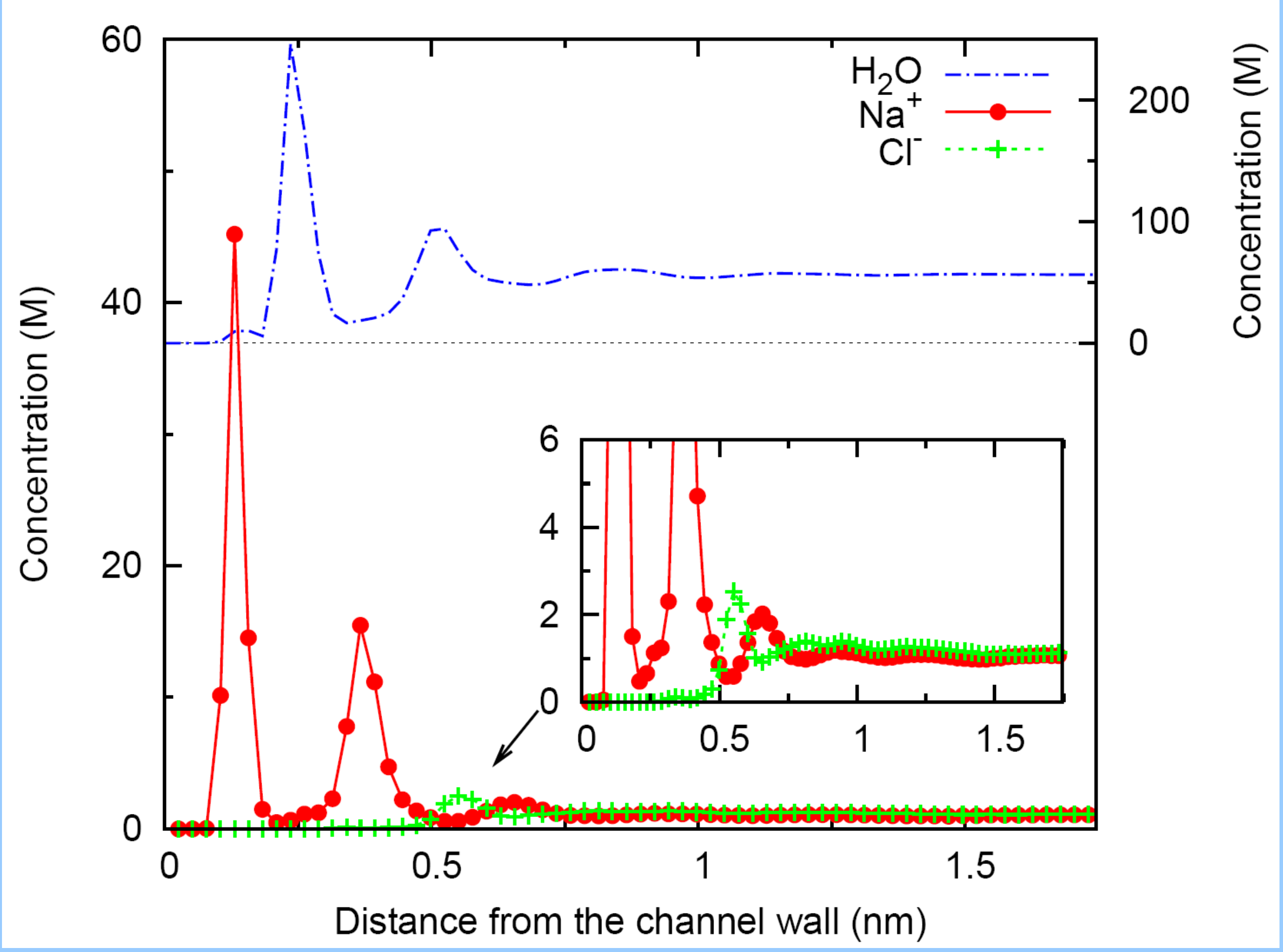


- Themostating of velocity component in the field direction (x) slightly influences velocity profile – we chose to apply selective (yz) thermostat

Mass flux areal density profiles

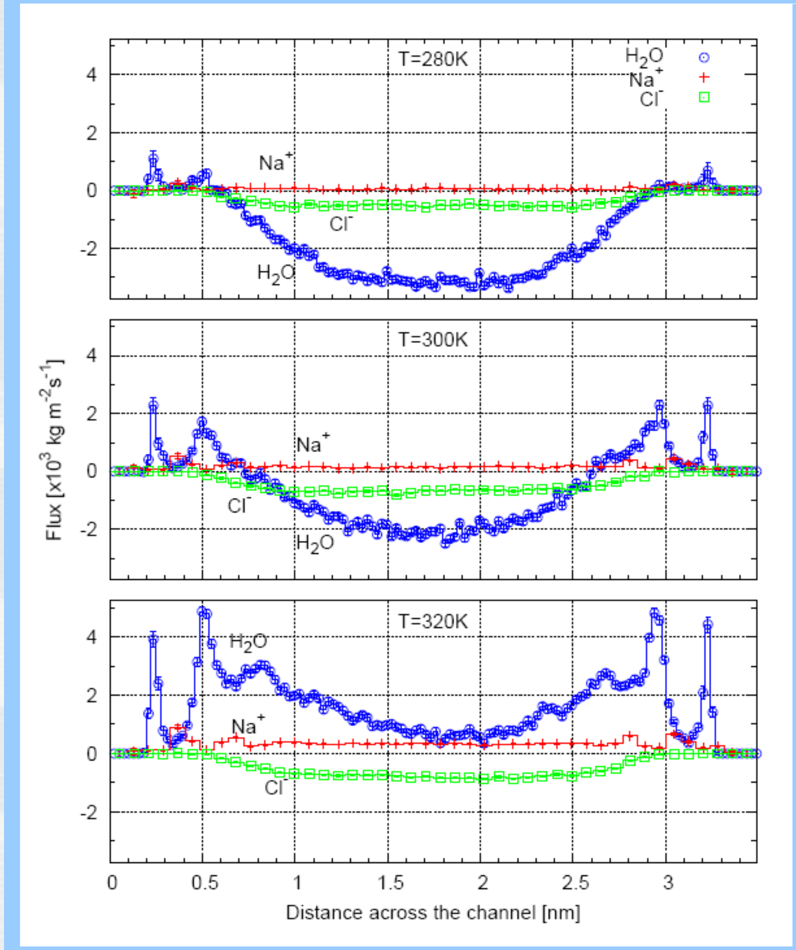


Concentration profiles

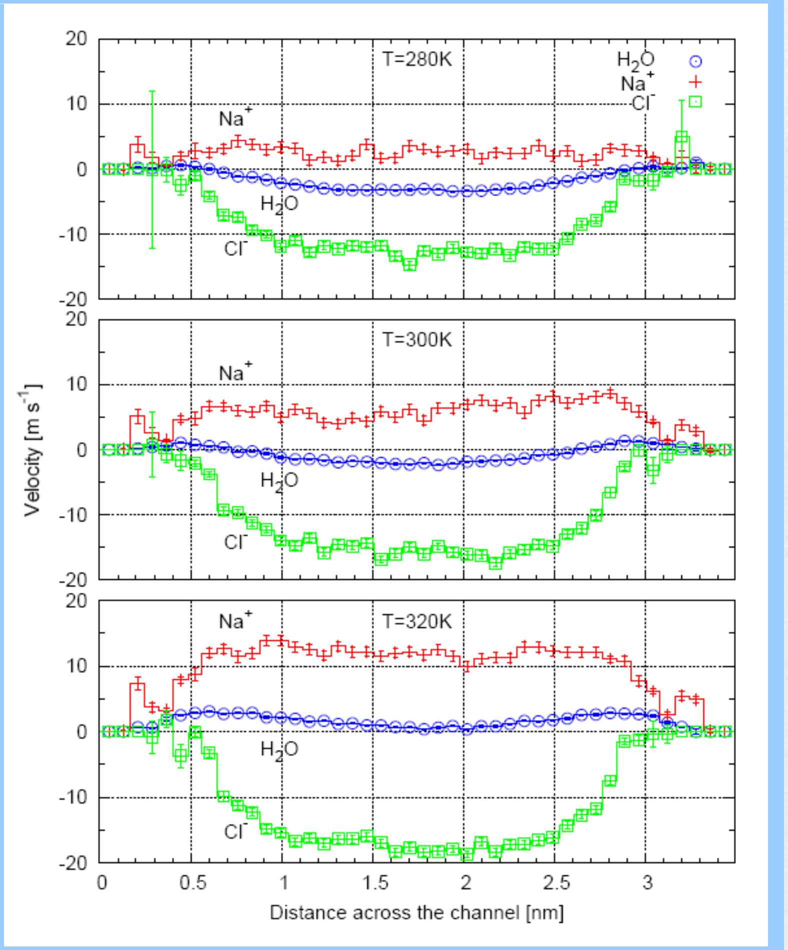


Temperature dependence

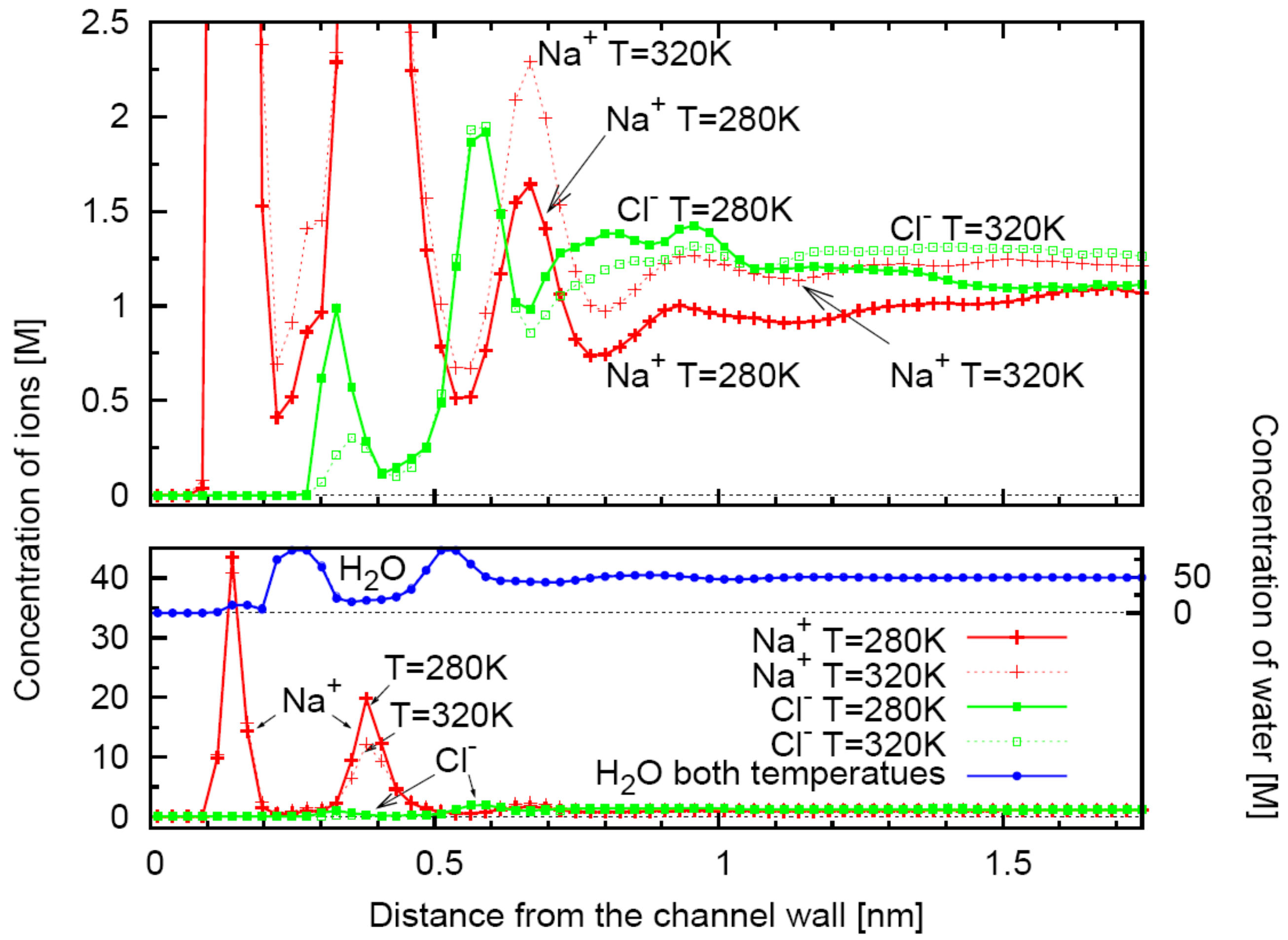
Flux



Velocity

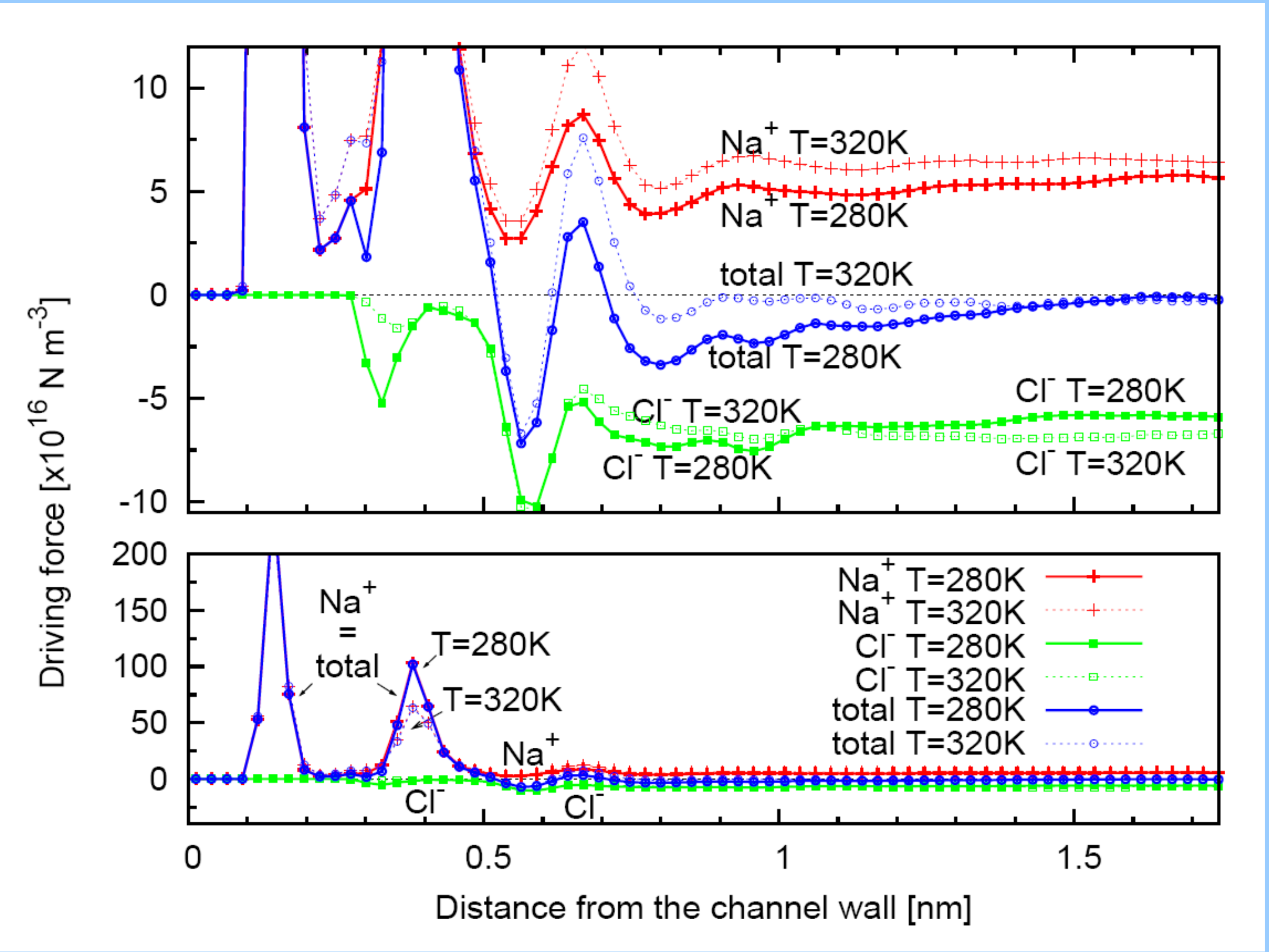


Temperature effects on concentrations

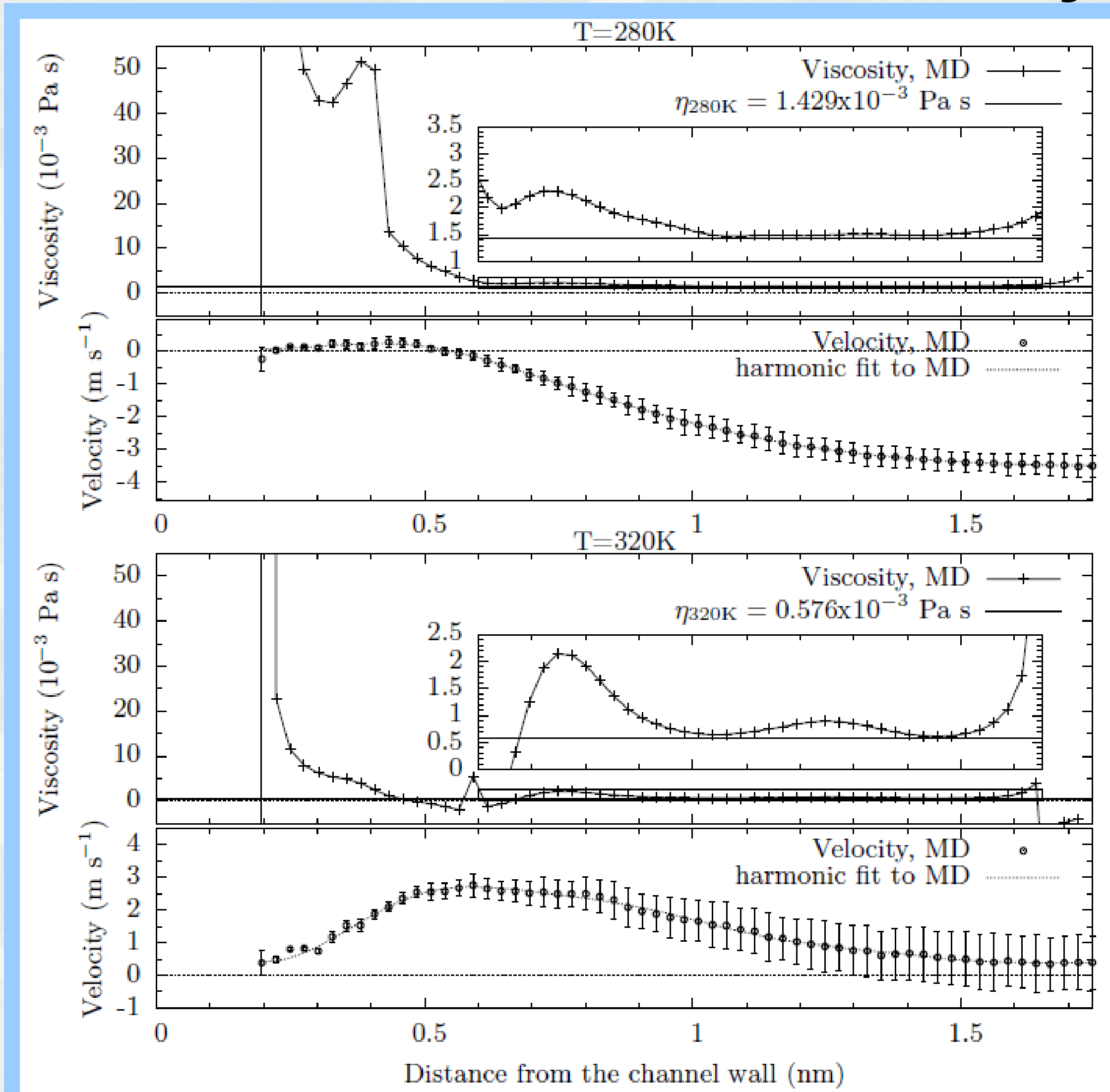


Temperature effects on driving force

$$\vec{F}_d(z) = e\left[c_{Na^+}(z) - c_{Cl^-}(z)\right]\vec{E}_{ext}$$



Viscosity



Stokes equation:

$$\frac{d}{dz}\left[\eta(z)\frac{du_x(z)}{dz}\right] = -F_d(z)$$

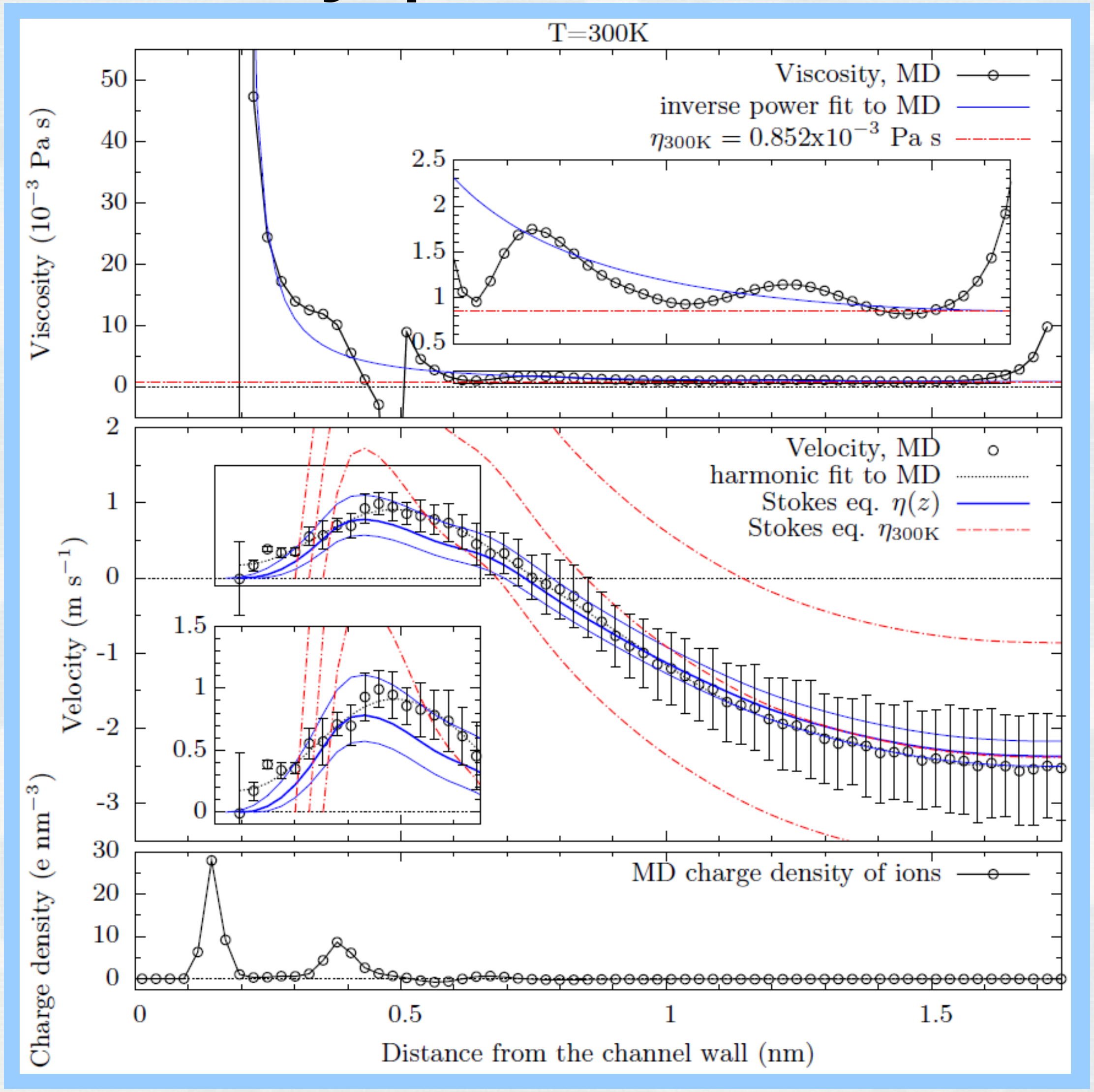
Integrated:

$$\eta(z)|_{z=z_0} = \frac{-\int_0^{z_0} F_d(z)\,dz}{\left.\frac{du_x(z)}{dz}\right|_{z=z_0}}$$

Velocity approximation:

$$u_{xfit}(z) = \sum_{n=0}^{7} a_n \cos\left(n\pi\frac{z}{h}\right)$$

Velocity predicted from charge density



Stokes equation:

$$\frac{d}{dz}\left[\eta(z)\frac{du_x(z)}{dz}\right] = -F_d(z)$$

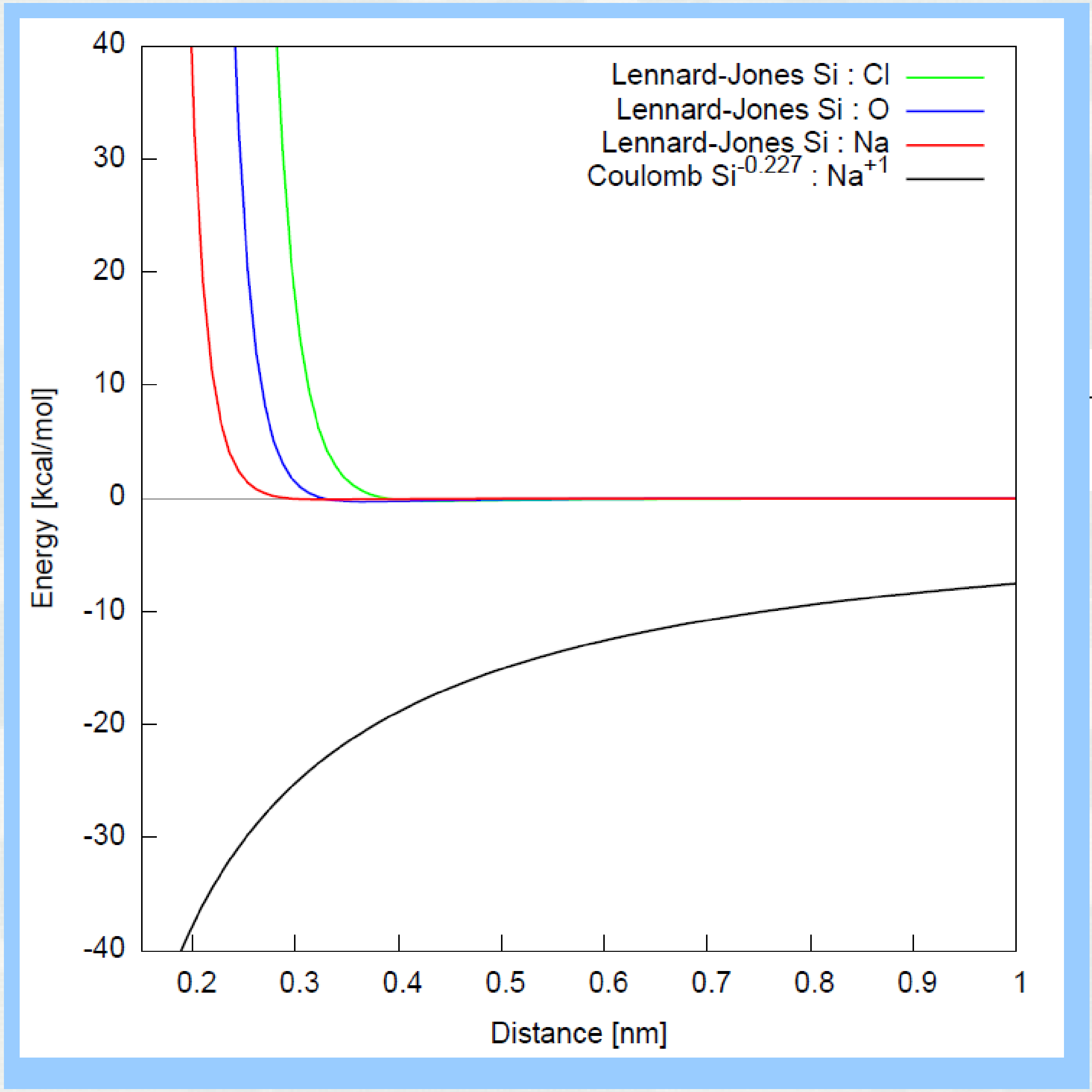
Black:
Molecular Dynamics

Red:
constant viscosity

Blue:
inverse power viscosity

$$\eta(z) = \left[1 - \left(\frac{z}{h}\right)^2\right]^{-p} \eta_{\exp}$$

Lennard-Jones and Coulomb interaction



RGB

Lennard-Jones

$$V_{LJ}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

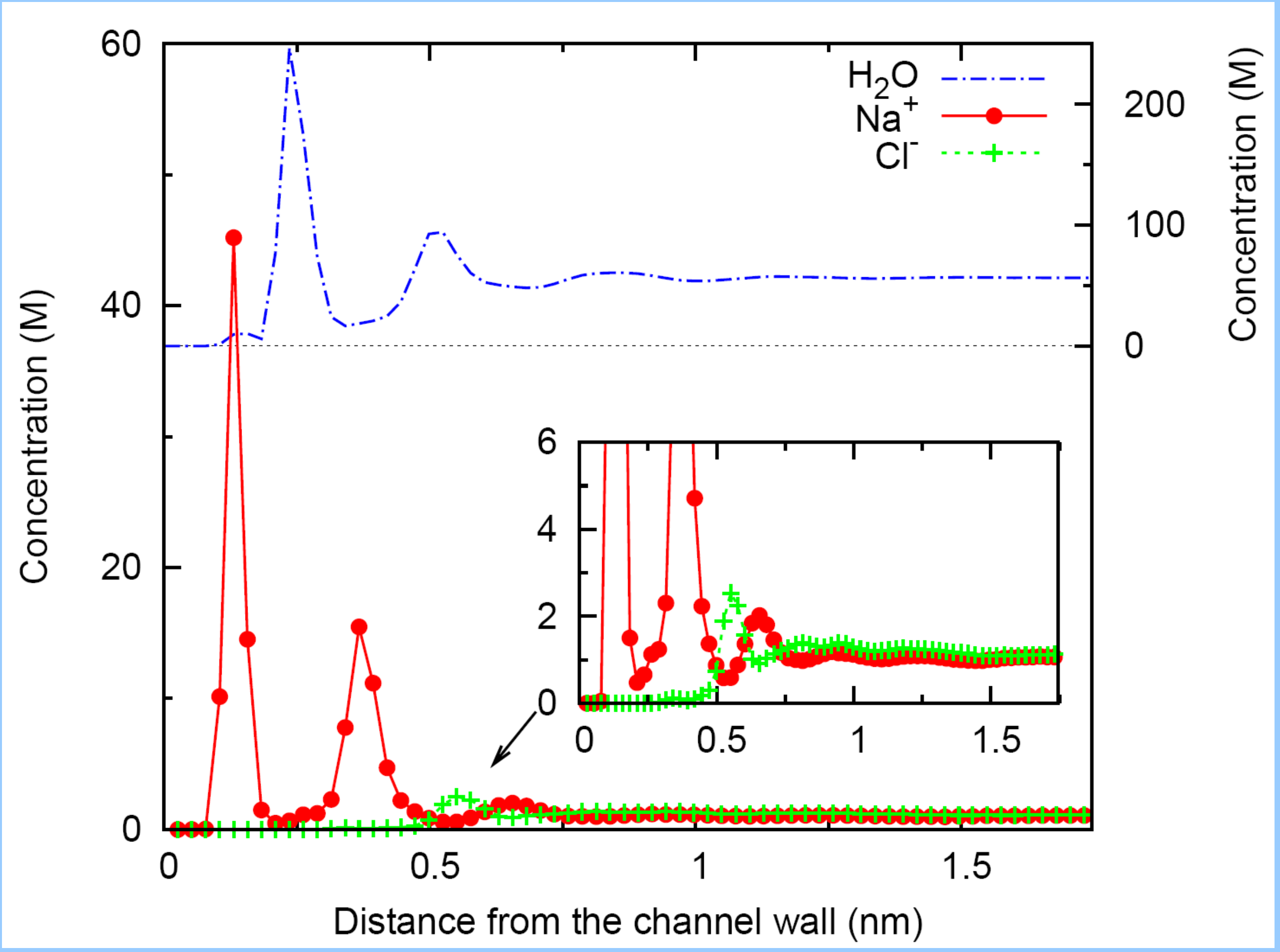
i-j	O-O	O-Si	O-Na	O-Cl	Si-Si	Si-Na	Si-Cl	Na-Na	Na-Cl	Cl-Cl
σ_{ij}	3.17	3.27	2.86	3.75	3.39	2.95	3.88	2.58	3.38	4.45
ϵ_{ij}	155	301	47.9	129	584	92.9	249	14.8	39.6	106

Black

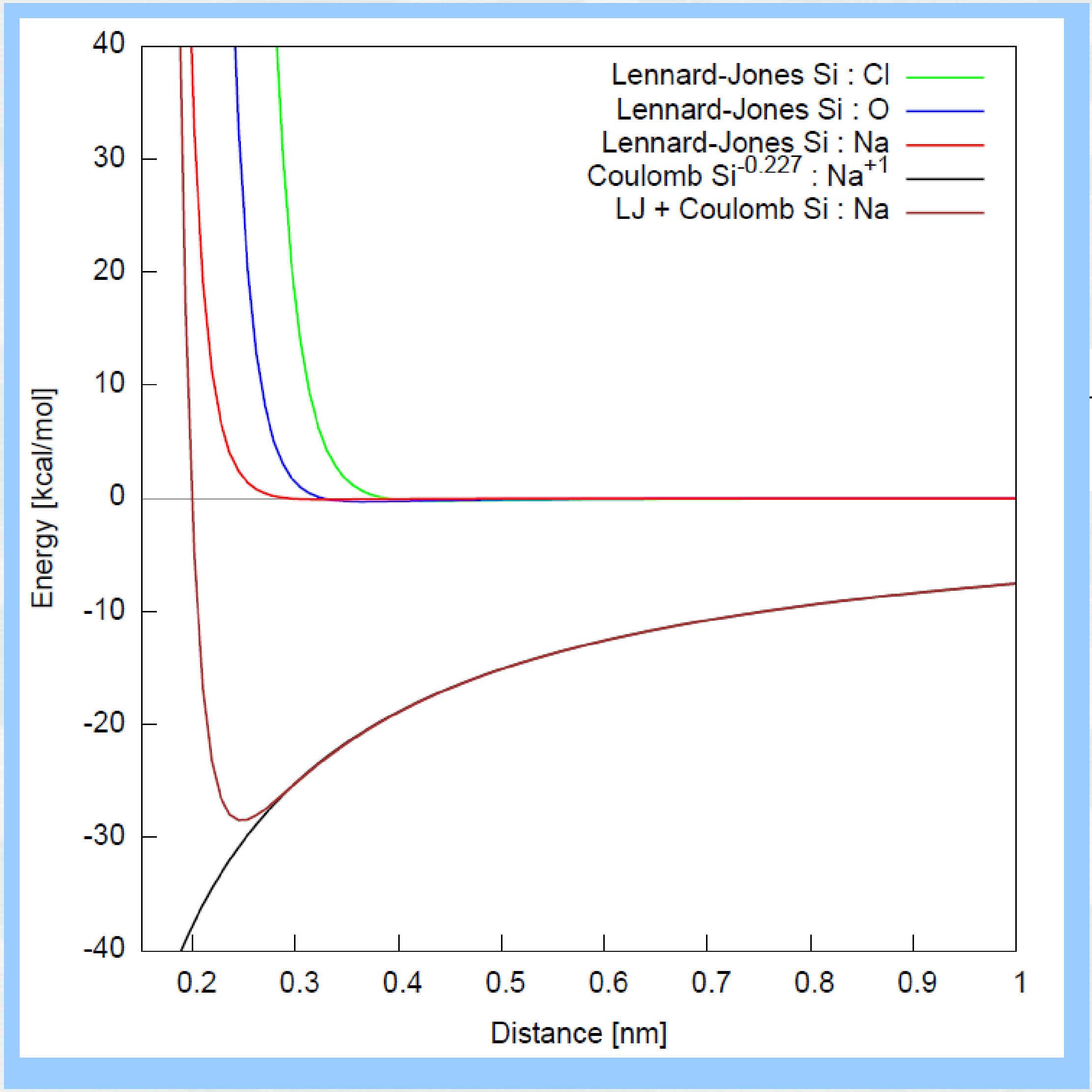
Electrostatic (Coulomb)

$$V_C(r) = \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r}$$

Concentration profiles



Lennard-Jones and Coulomb interaction



RGB
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Black
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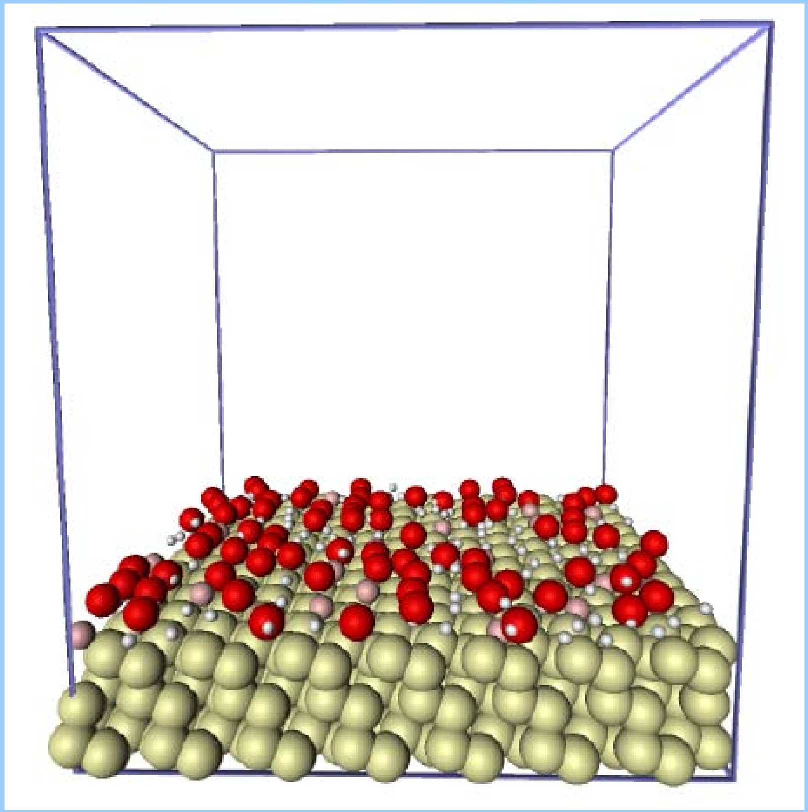
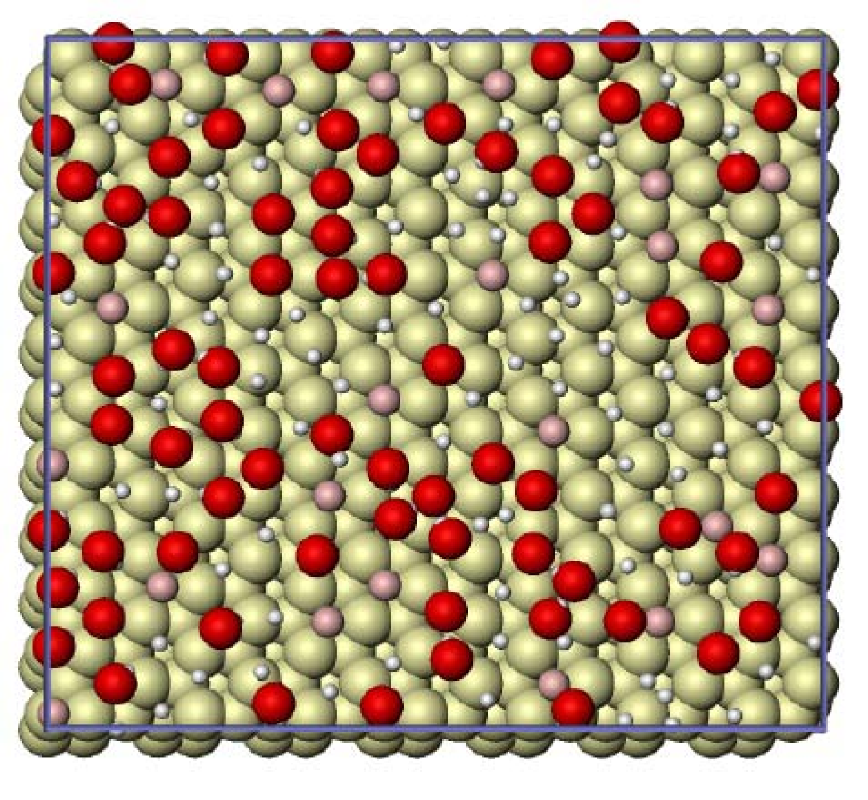
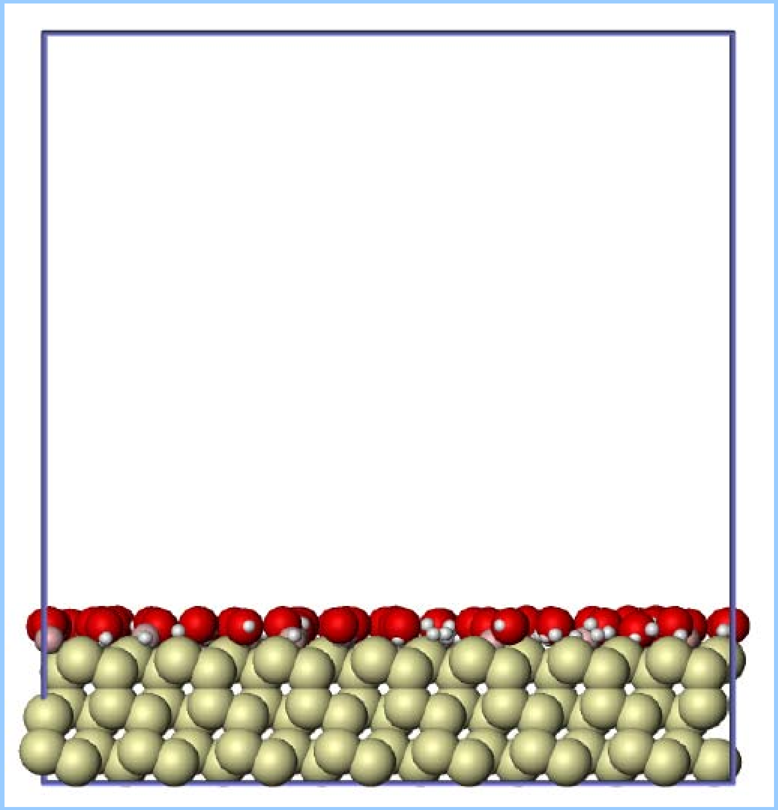
Adsorption sites

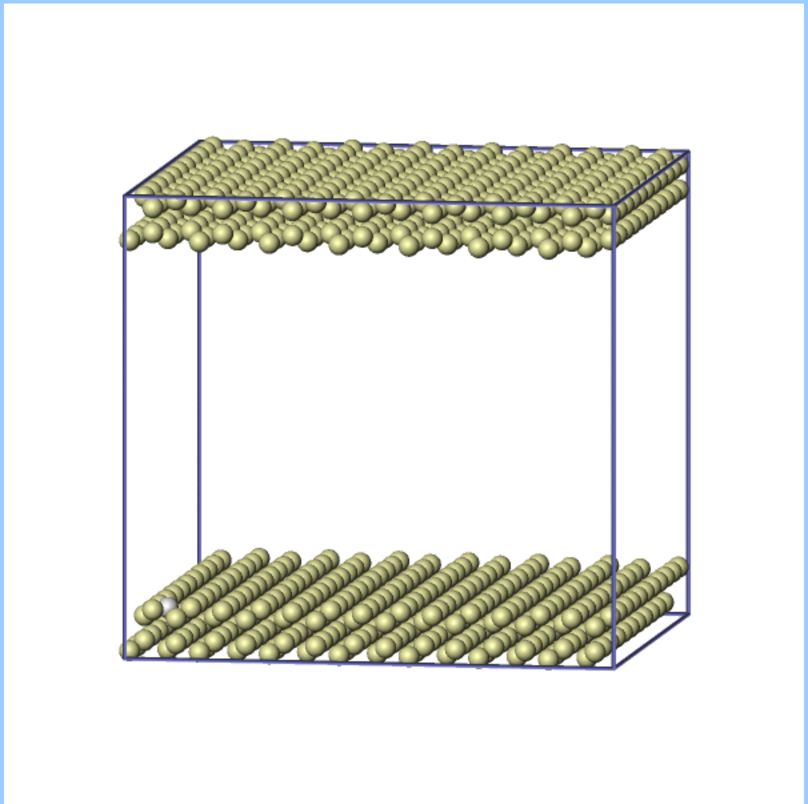




The nearest-to-wall peak of high Na^+ concentration corresponds to the favorable adsorption sites on the silicon surface

Potential energy profile

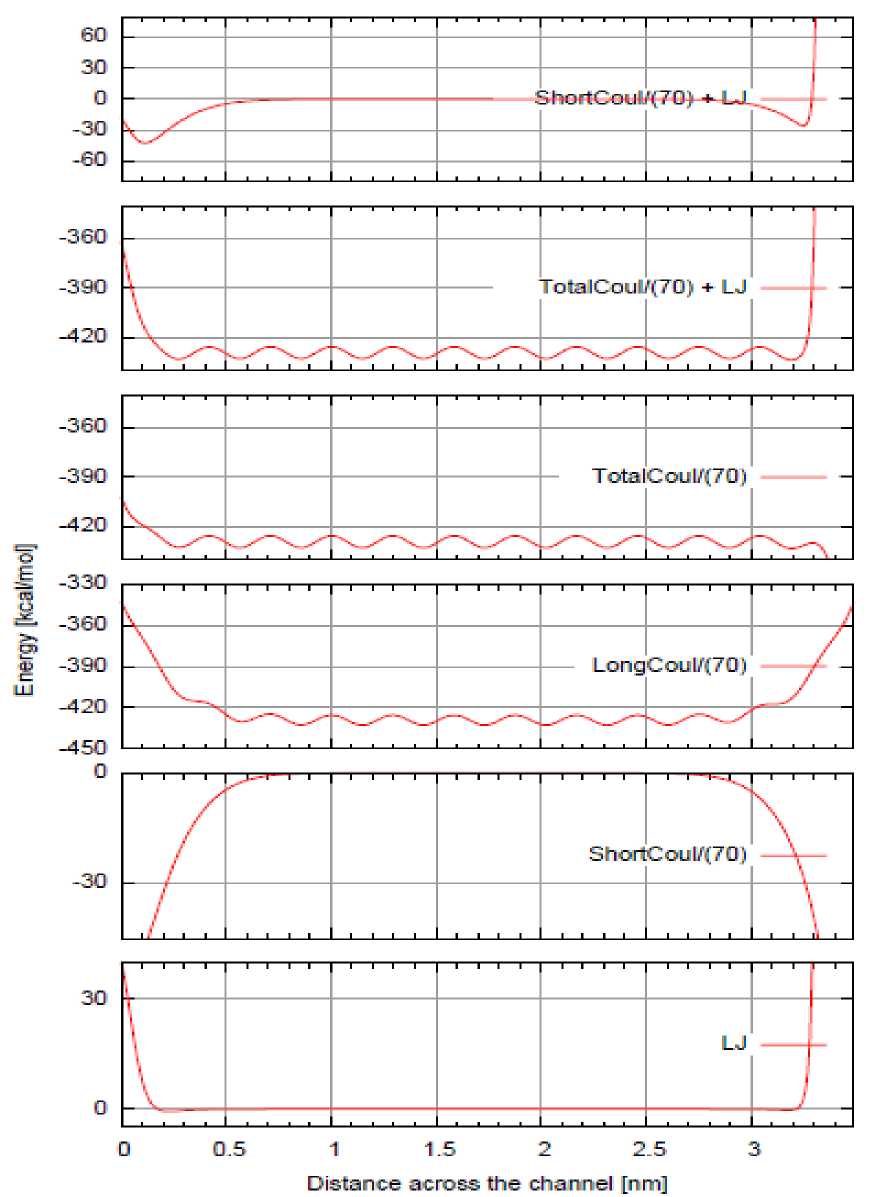




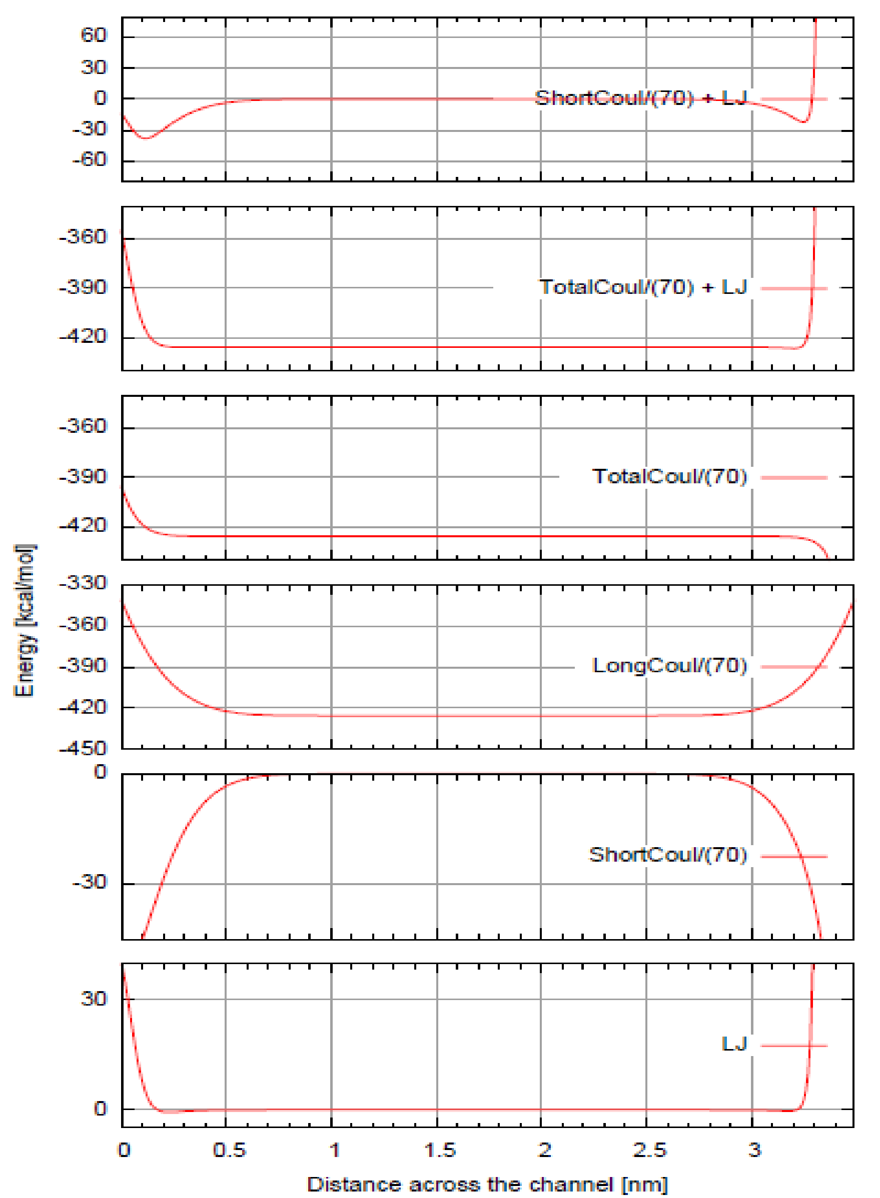
Potential energy profile of an ions was measured along the line perpendicular to the surface

The line passed through different adsorption sites

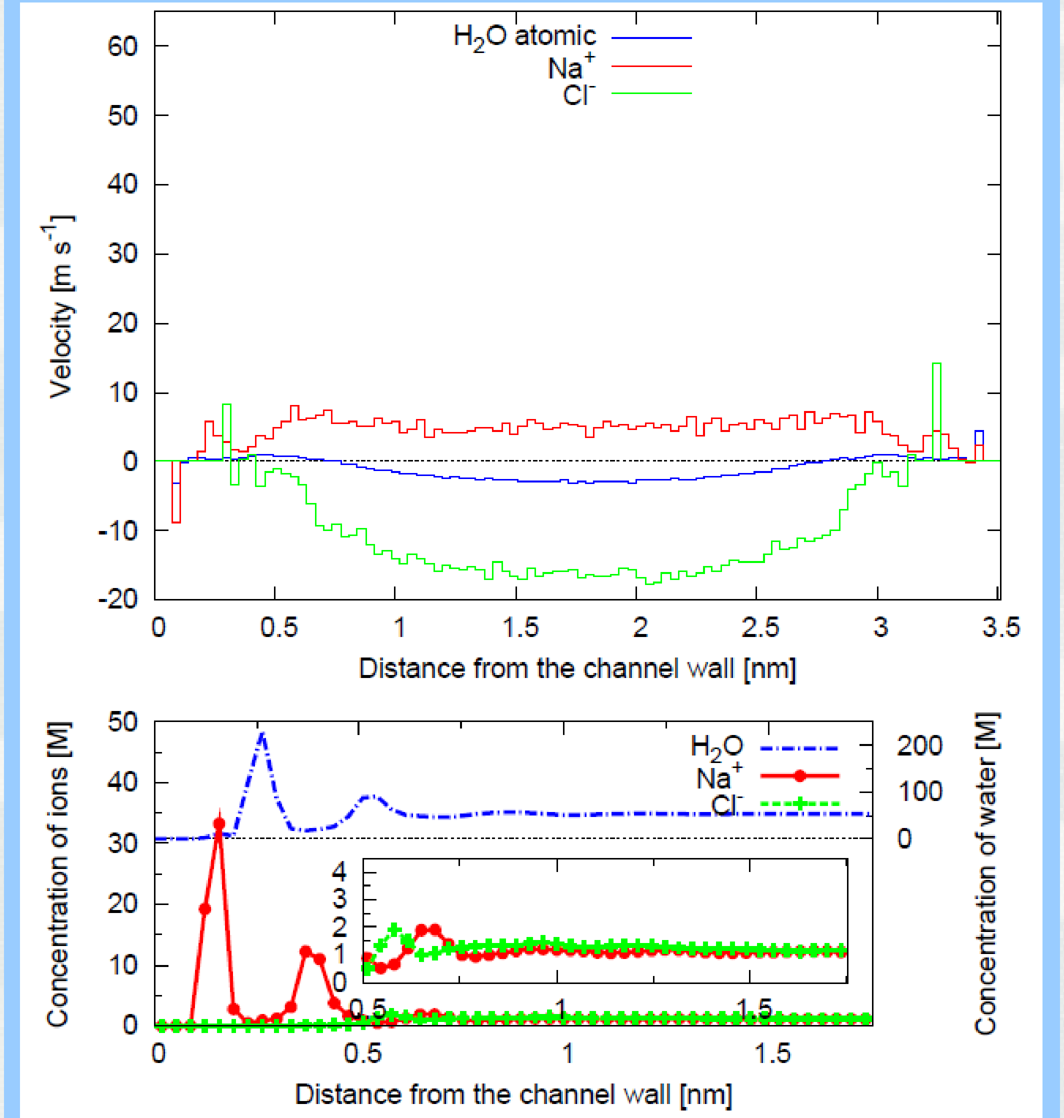
PPPM



Ewald sum



Effects of ionic concentrations



Surface charge:

-70 e

Na^+:

108

Cl^-:

38

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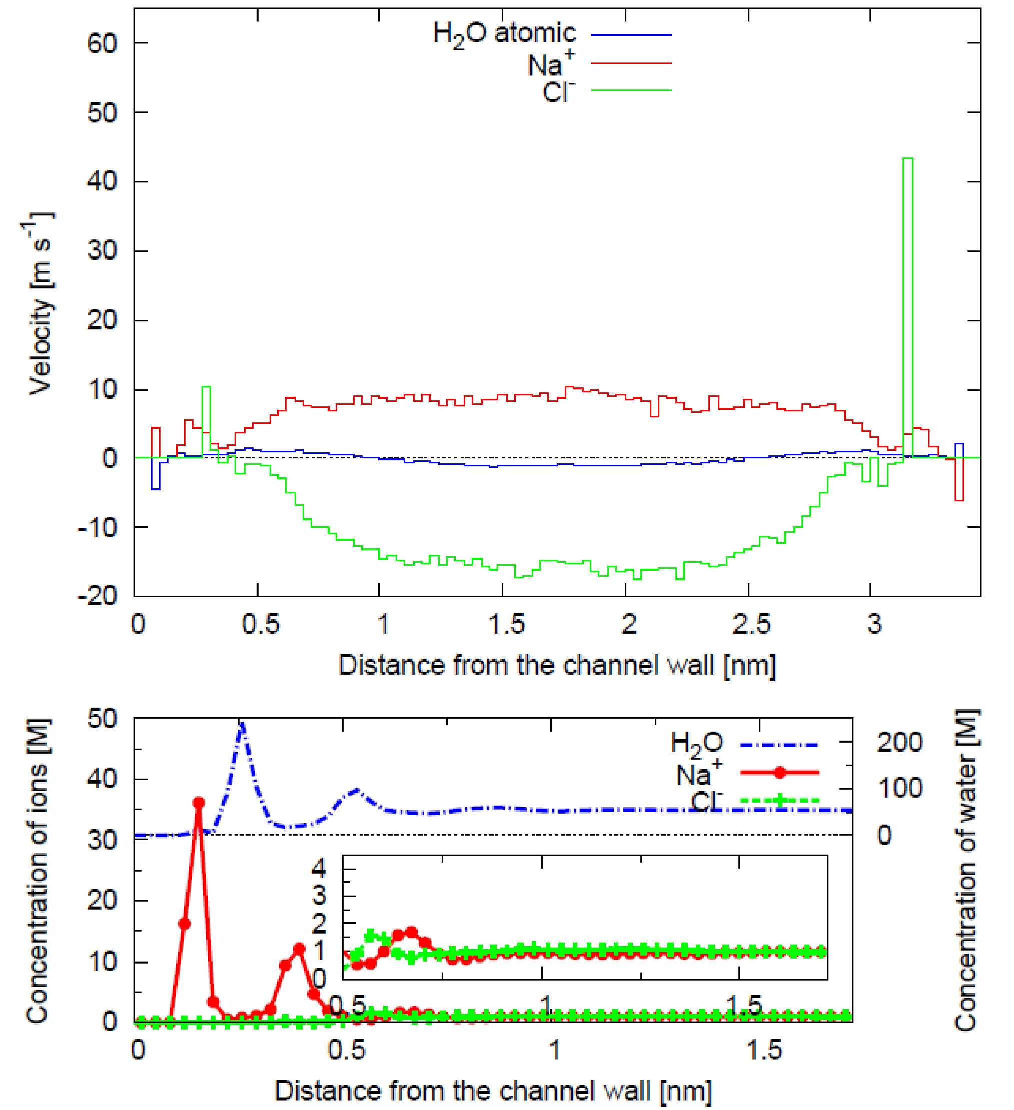
Effects of ionic concentrations



Surface charge:

-70 e

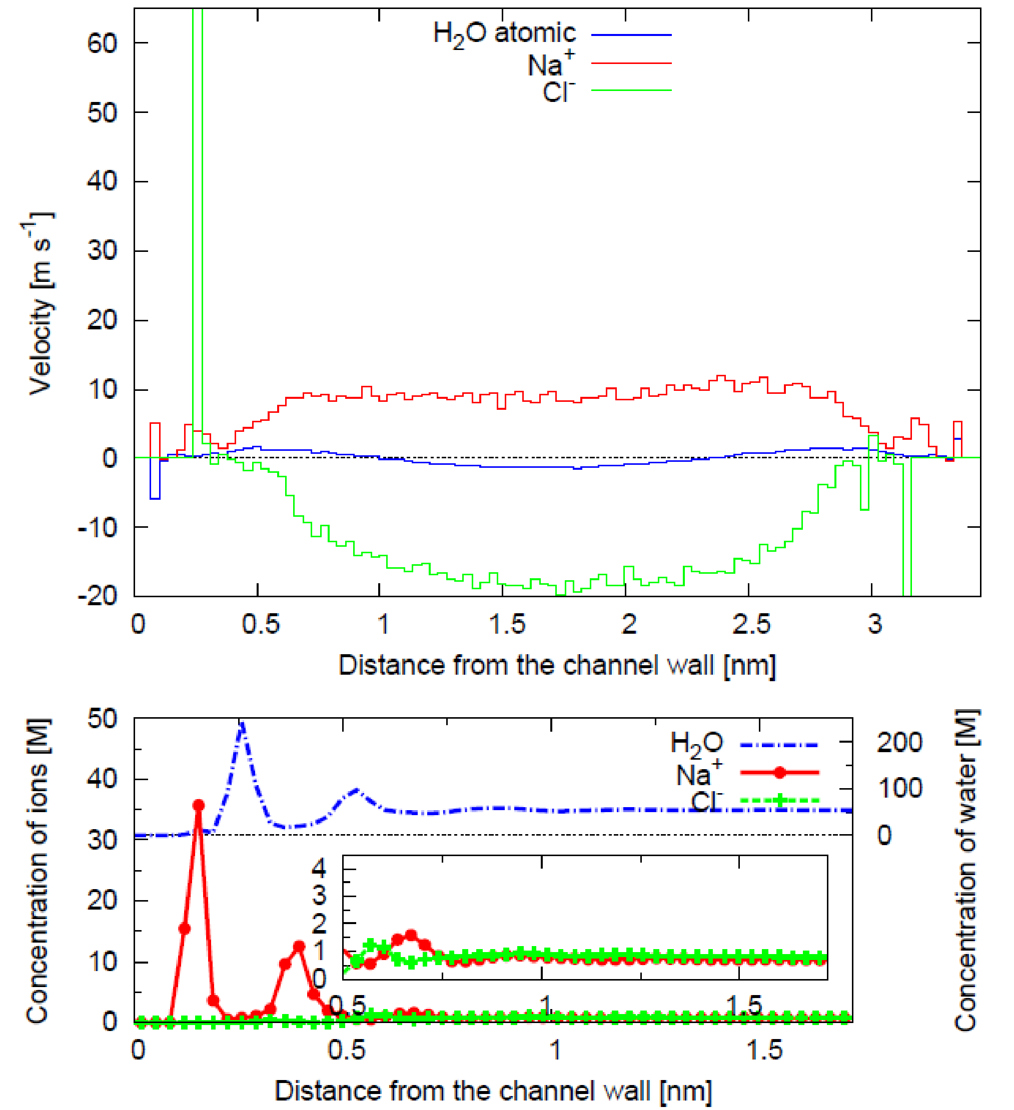
Na$^+$:

100

Cl$^-$:

30

Effects of ionic concentrations



Surface charge:
-70 e

Na$^+$:
93

Cl$^-$:
23

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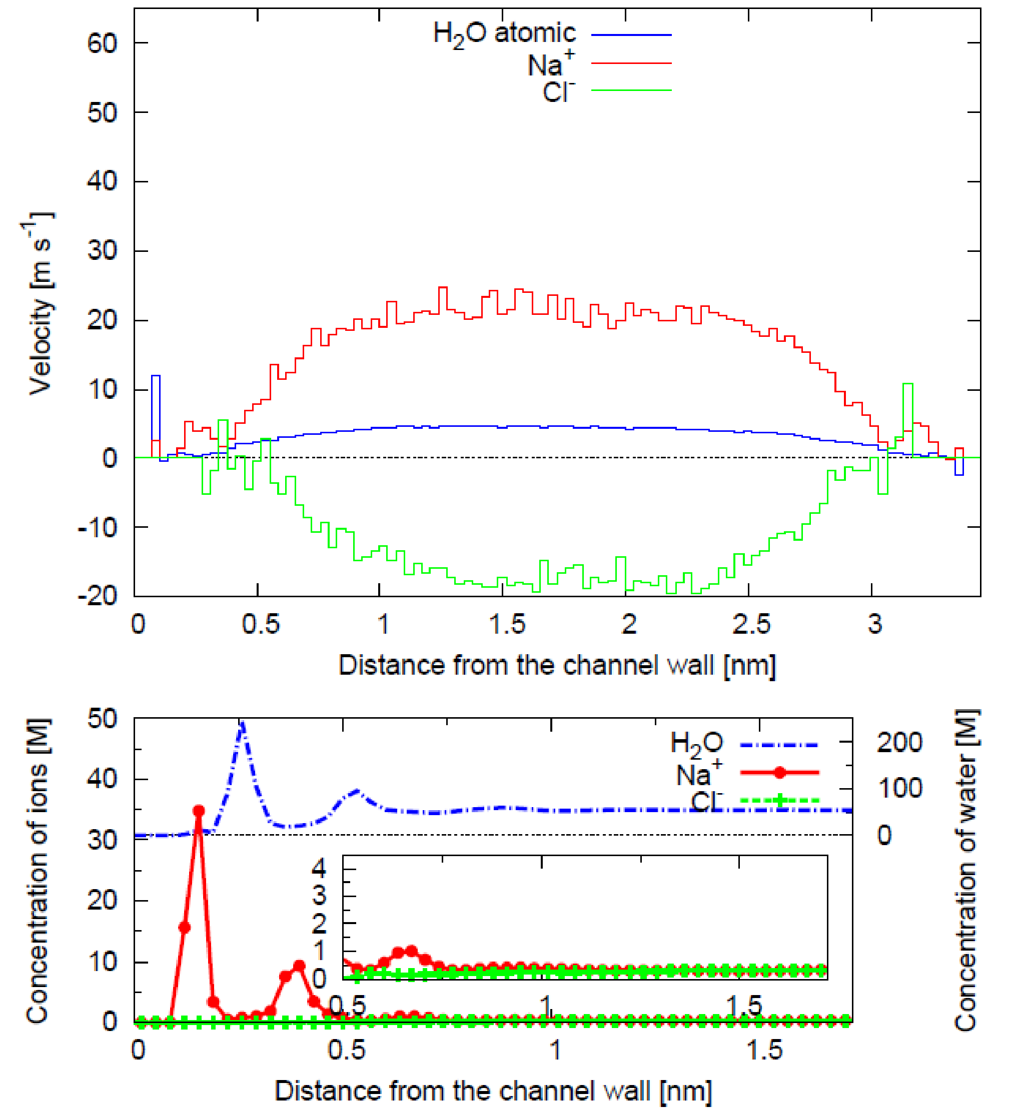
Effects of ionic concentrations



Surface charge:

-70 e

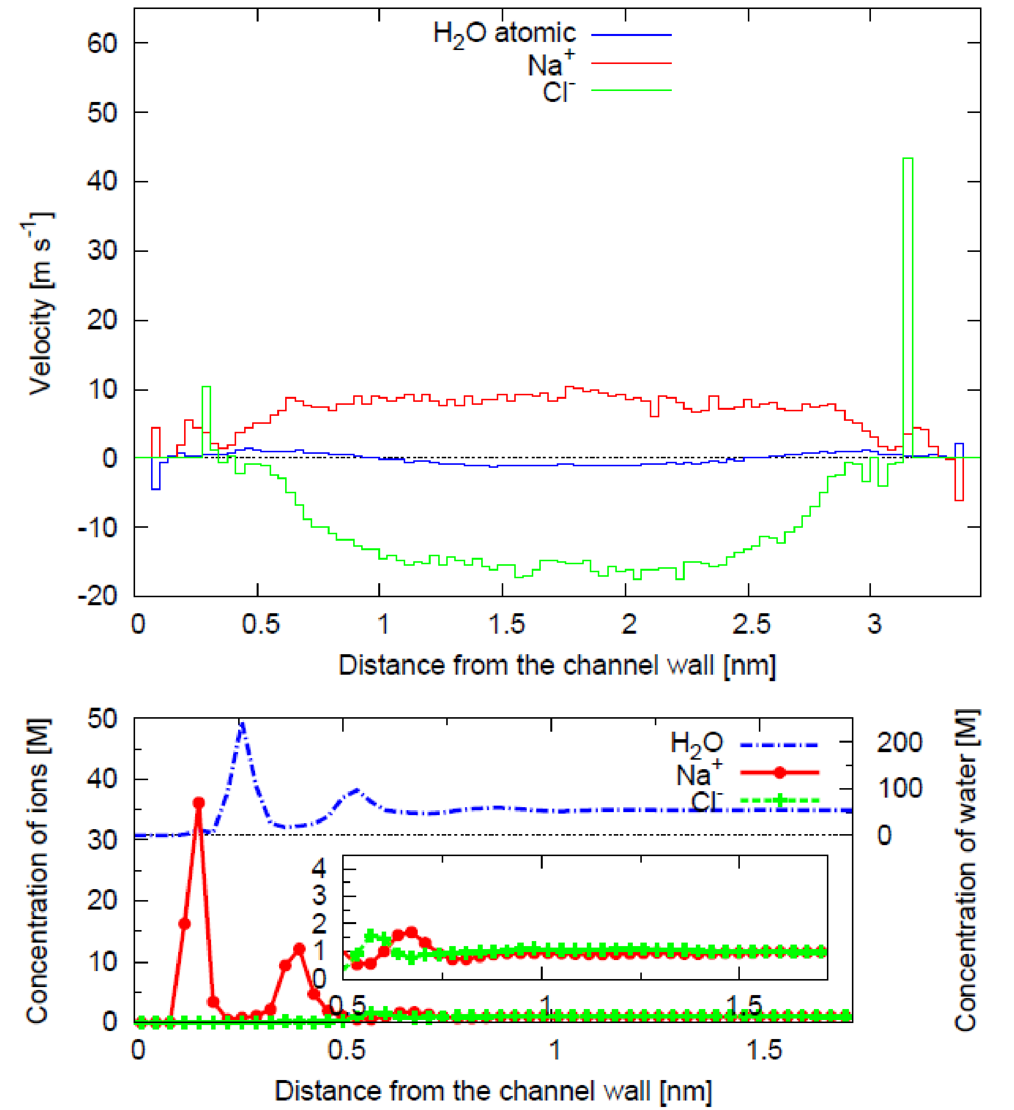
Na^+:

78

Cl^-:

8

Effects of surface charge density



Surface charge:

-70 e

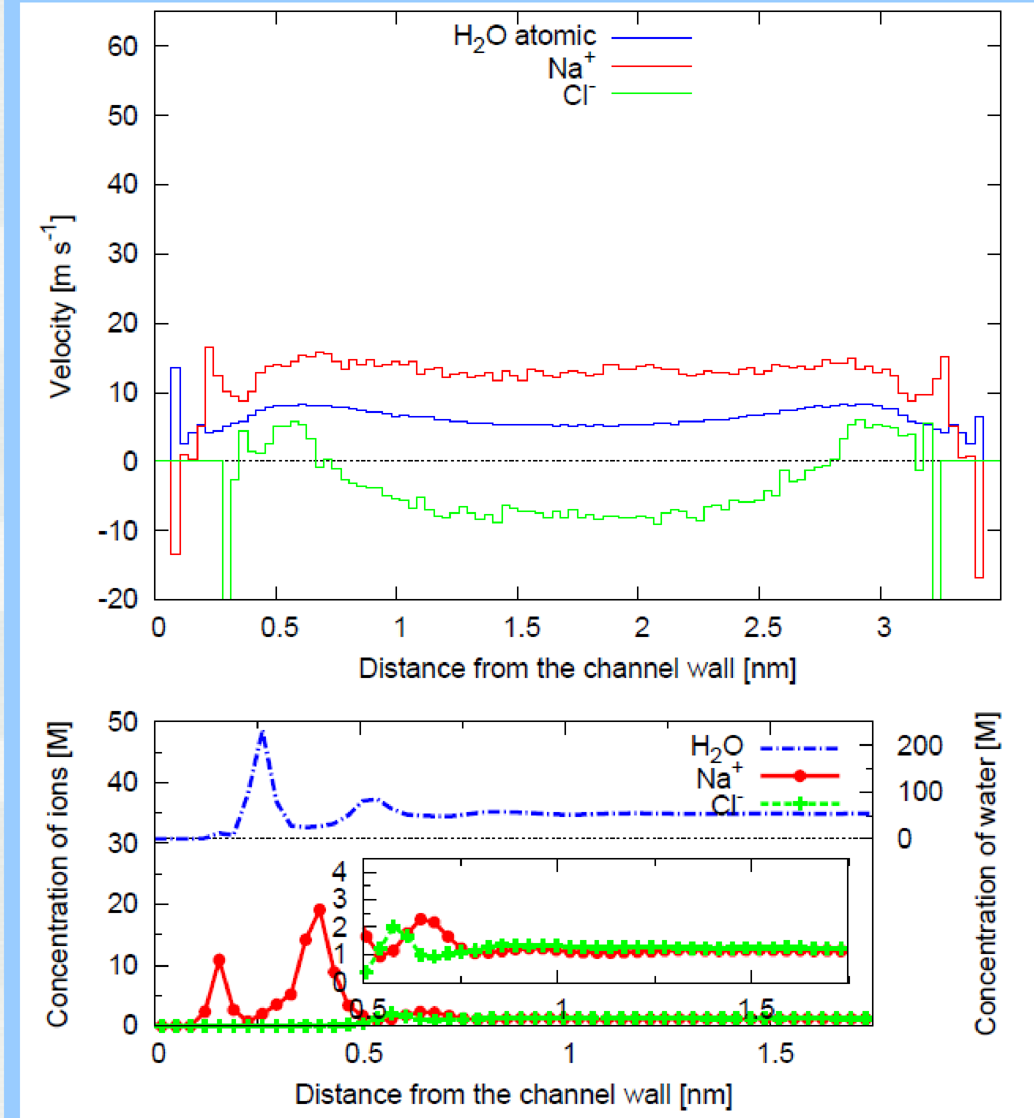
Na^+:

100

Cl^-:

30

Effects of surface charge density



Surface charge:

-60 e

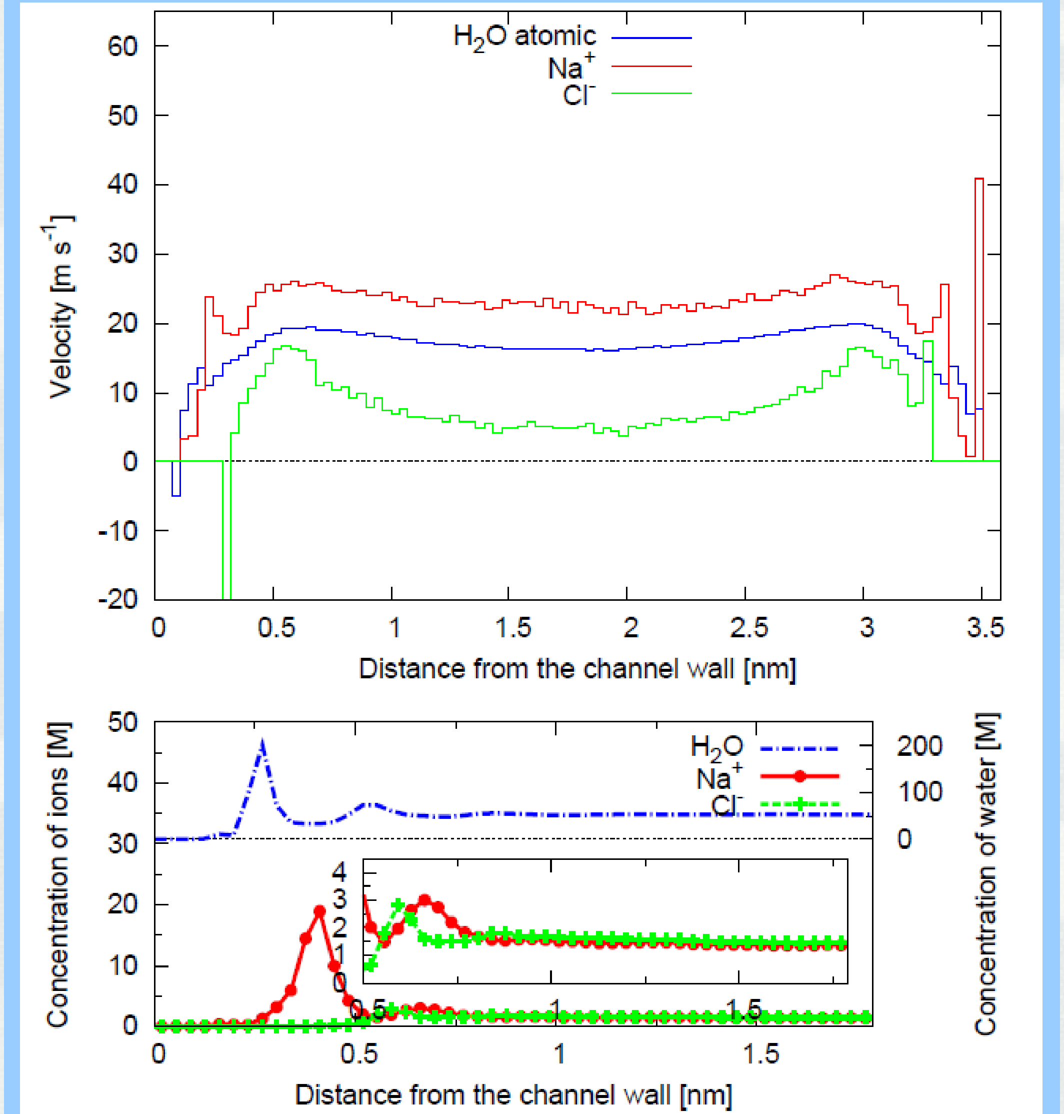
Na$^+$:

100

Cl$^-$:

40

Effects of surface charge density



Surface charge:

-50 e

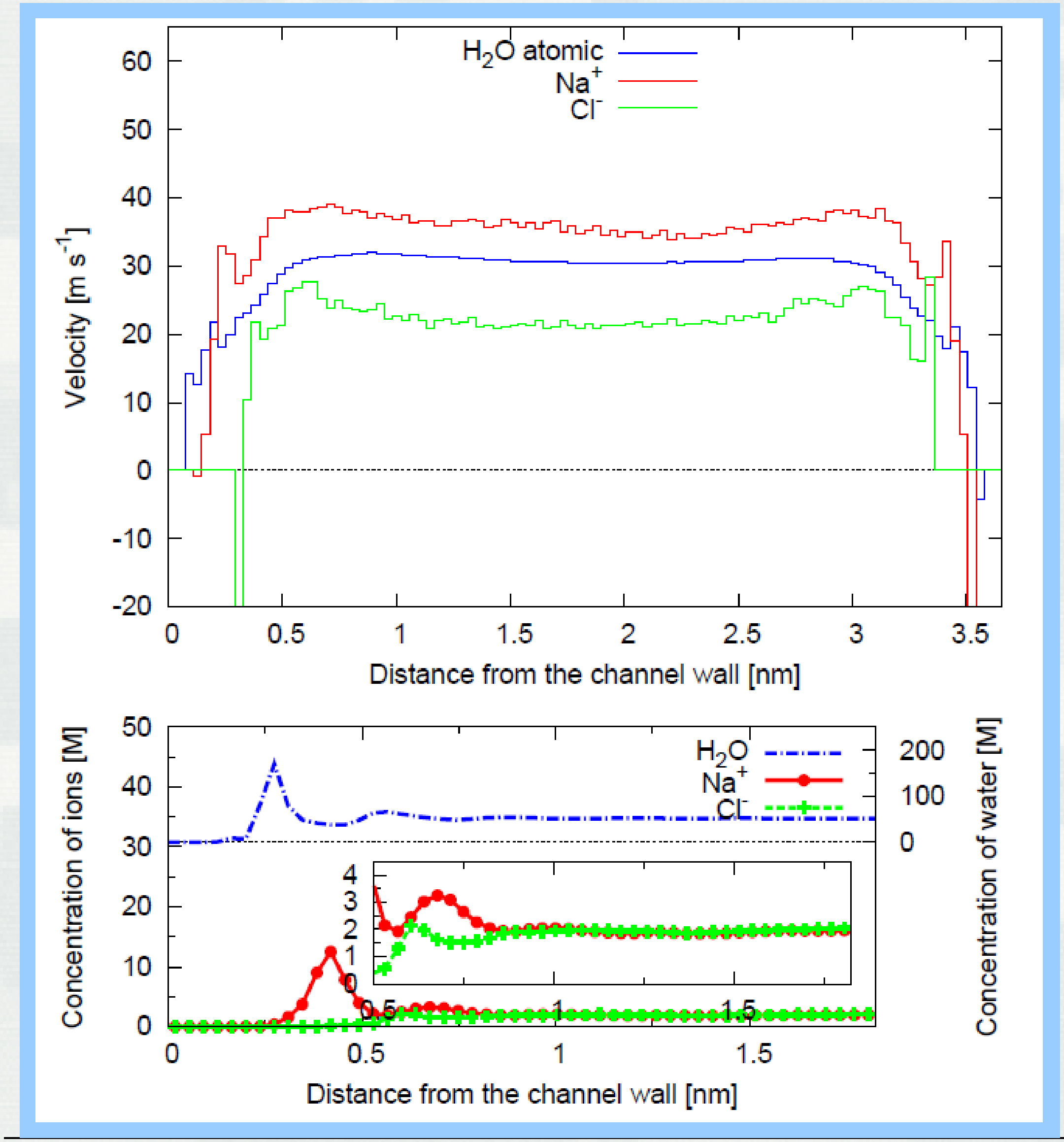
Na^+:

100

Cl^-:

50

Effects of surface charge density



Surface charge:

-40 e

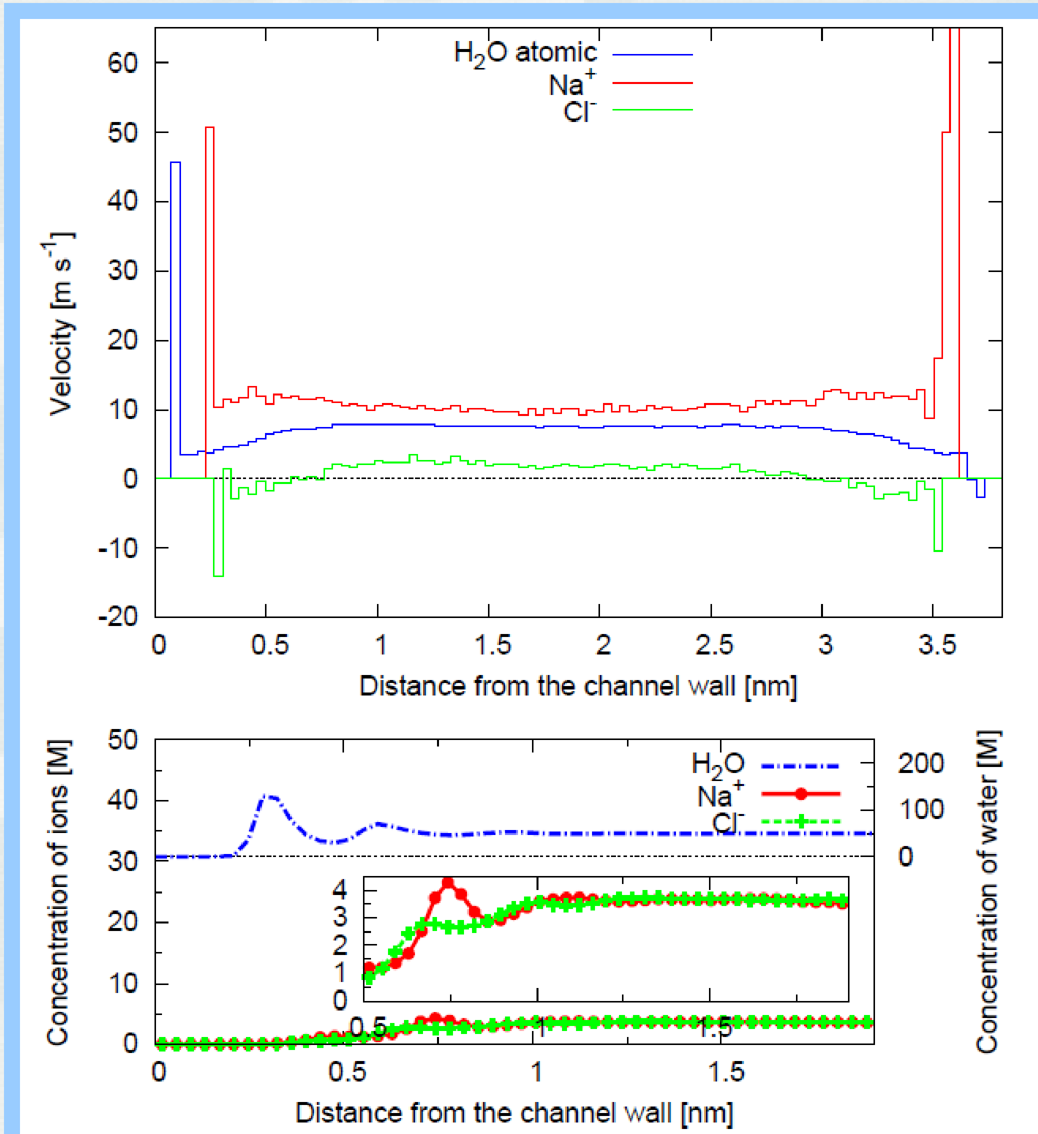
Na^{+}:

100

Cl^{-}:

60

Low surface charge density flow



Surface charge:

-4 e

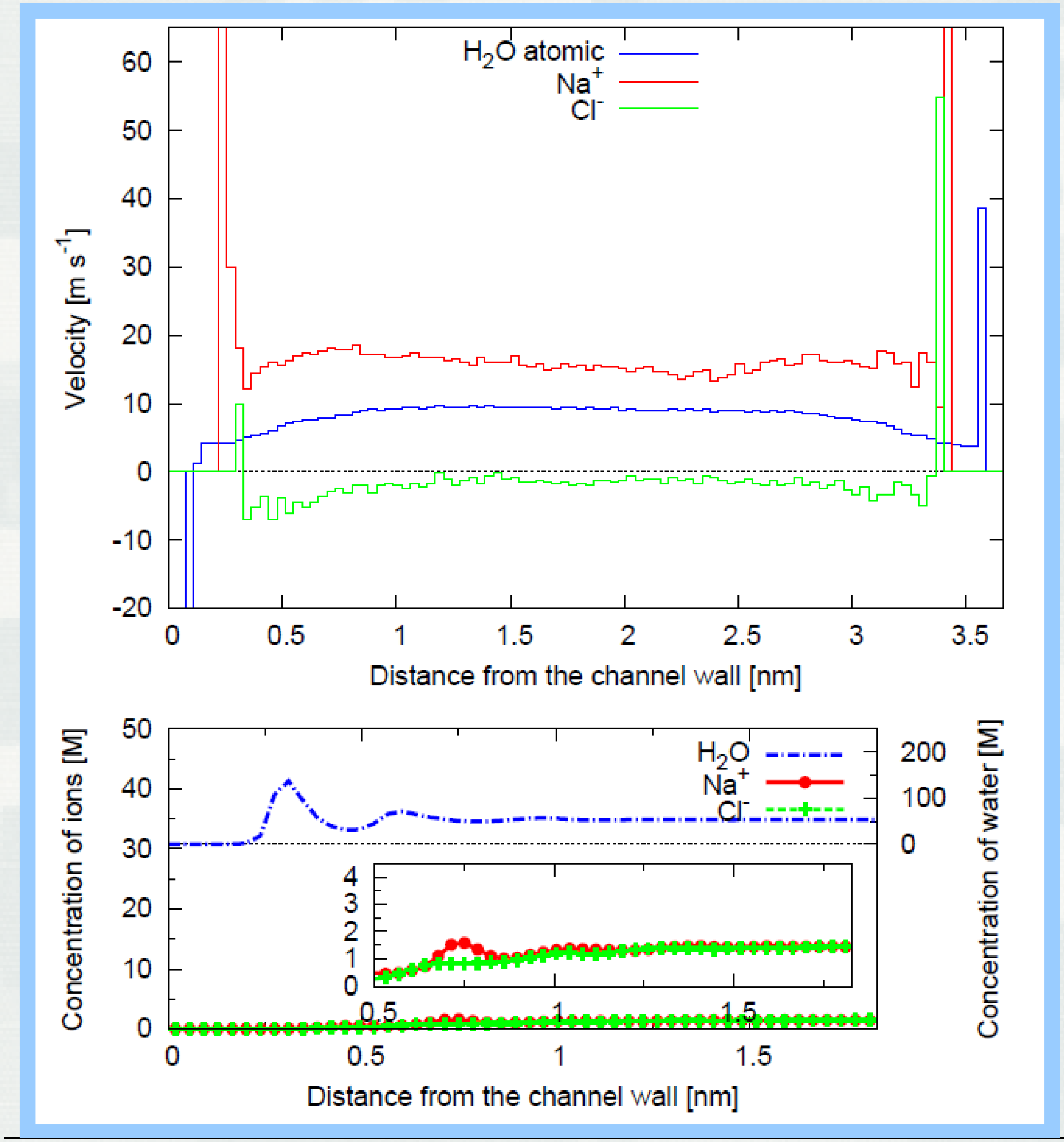
Na^+:

108

Cl^-:

104

Low surface charge density flow



Surface charge:

-4 e

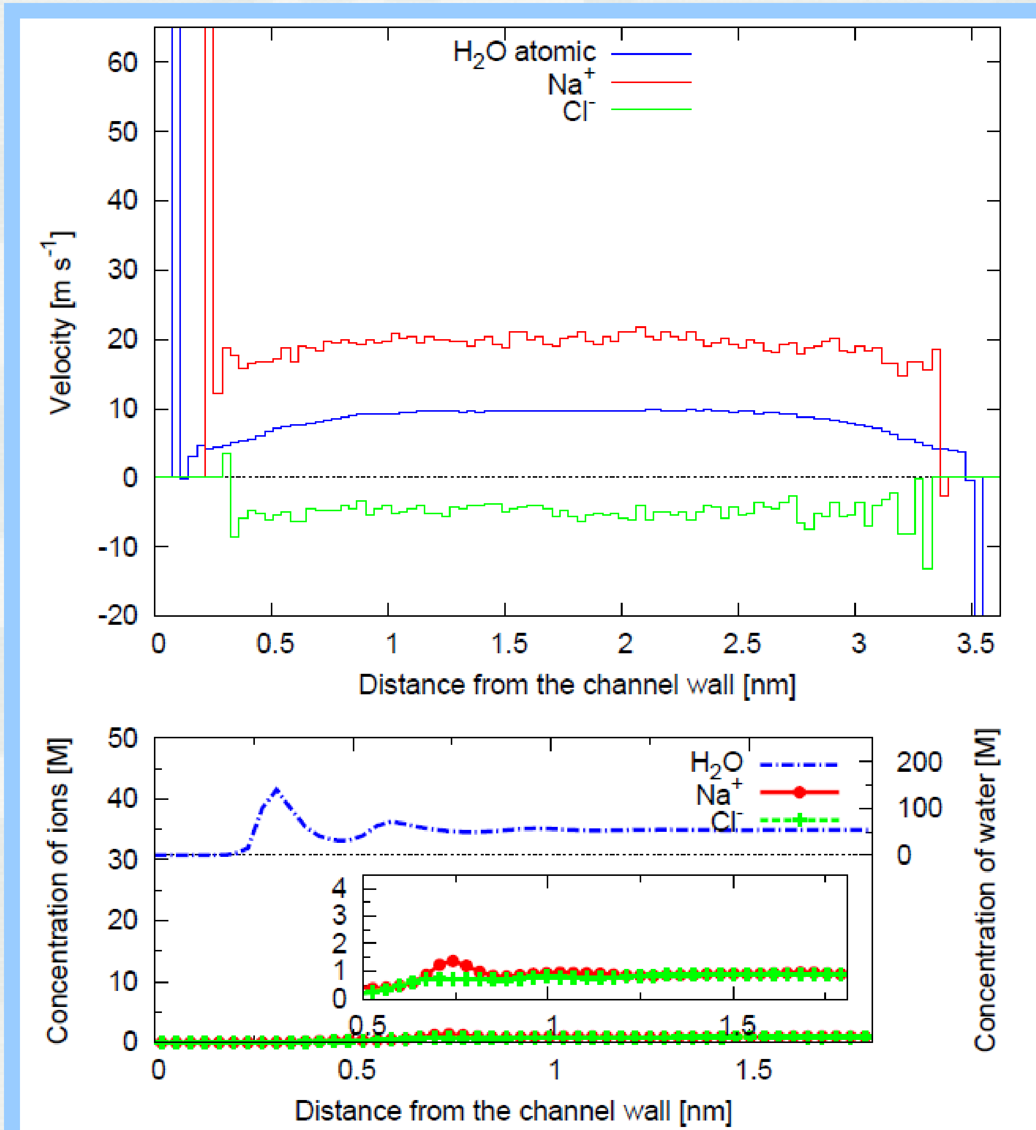
Na^+:

44

Cl^-:

40

Low surface charge density flow



Surface charge:

-4 e

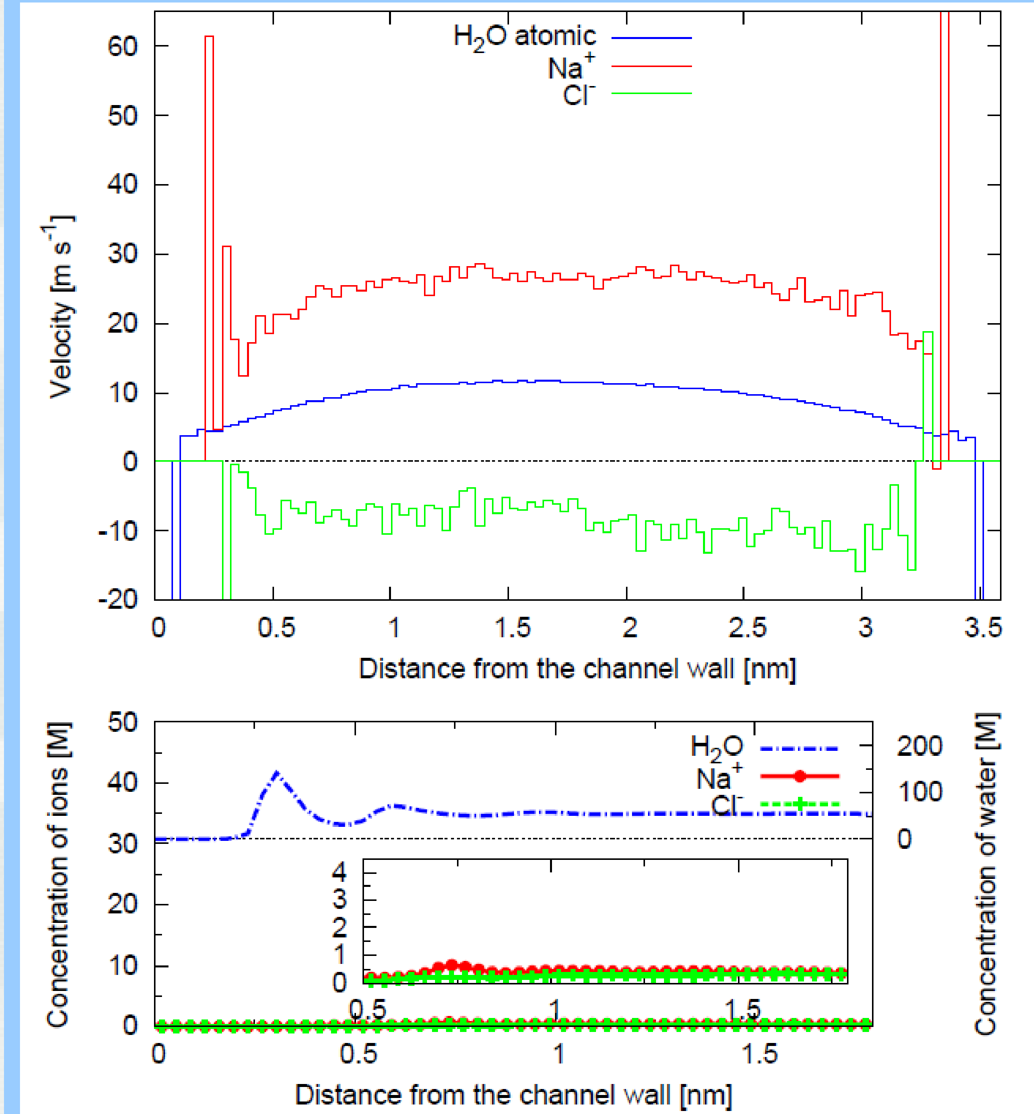
Na$^+$:

28

Cl$^-$:

24

Low surface charge density flow



Surface charge:

-4 e

Na^+:

12

Cl^-:

8

Conclusions

- Studied temperature, viscosity, and charge density effects on a nanochannel electroosmotic flow by MD simulations
- Obtained velocity, mass flux, ionic concentration, and viscosity profiles
- Justified temperature dependence of water flow direction by thermal release of adsorbed Na^+ ions and spatial variation of viscosity
- Demonstrated an improved prediction of velocity profile from charge density using non-constant viscosity
- Revealed the dependence of the flow on surface charge density and ionic concentrations