Bounded Amplification of Diffusioosmosis utilizing Hydrophobicity

Vahid Hoshyargar [a], Arman Sadeghi [b], and Seyed Nezameddin Ashrafizadeh [a,1]

[a] Research Lab for Advanced Separation Processes, Department of Chemical Engineering,
Iran University of Science and Technology, Narmak, Tehran 16846-13114, Iran

[b] Department of Mechanical Engineering, University of Kurdistan, Sanandaj 66177-15175, Iran

Supporting Information

The molecular dynamic (MD) is a realistic powerful computational technique for simulating the real behavior of systems only by solving the simple equation of motion of limited particles. The physical properties of materials can also be predicted if an interacting potential between particles are deemed. The so-called "time integration" reveals the trajectory and physical movements of atoms, molecules, and ions in the system. The atoms are interacting with each other and almost all properties (e.g. pressure, temperature, energy, etc) are affected by. One can claim that assuming a proper potential between particles definitely guarantees a good prediction. No limiting assumption in MD makes it an accurate tool to study the properties of systems [1, 2]. In this supporting information, we are summarizing the whole parameters needed to perform molecular dynamics (MD) simulation of DOF by using LAMMPS package (version 2015) [3] and thereafter the method we can obtain the slip length to feed to continuum hydrodynamics from the MD results.

S1. Unit cell structure

A unit cell is constructed by confining the electrolyte in between two parallel walls (See Fig. S1). Each wall consists of multiple duplicates of a closed-packed Face-Centered Cubic (FCC) crystal by 5.3567 Å in lattice size (l_s). The FCC lattice is extended in x, y, and z directions; respectively, 9, 6, and 3 times for each wall. The walls are separated by ~9 lattice spacing times while the exact distance between the walls is determined when the total zz normal component of stress tensor per unit volume of electrolyte is 1 atm in average. In order to constitute an electrolyte, $NaCl$ atoms are dispersed in water molecules to produce a concentration of about 1 M. The SPC/E model is used in the simulation of the water molecules to closely follow the properties of the aqueous solution. Corresponding numbers of water and ions relative to the electrolyte concentration are defined by setting the fluid density equal to 1.083 g/cm^3. The layer of each wall which is in contact with the fluid is carrying a fixed charge corresponding to the electric charge density of the wall, Σ (C/m^2). An important note in this respect is keeping the electroneutrality of the whole system by reducing the charge of coions and increasing the charge of counterion at the same time which sums up an equivalent charge to the prescribed charge of both the walls. To model a slit geometry, periodic boundary conditions are applied only in x and y directions.

S2. Forcefield

The forcefield is established by short-ranged interactions between particles utilizing the Lennard-Jones (LJ) 6-12 force, $F_{ij}^{LJ}(r_{ij}) = 4\epsilon_{ij}\nabla_{r_{ij}}[(\sigma_{ij}/r_{ij})^6 - (\sigma_{ij}/r_{ij})^{12}]$, added to a long-ranged electrostatic Coulomb force, calculated by P^3M method, bearing in mind that dipole interactions should be removed since the system is not periodic in z direction. LJ parameters of homonuclear are listed in Table S1 while those of heteronuclears are calculated via geometric and arithmetic average, respectively for ϵ_{ij} and σ_{ij} (Lorentz-Berthelot rule).

S3. Setting parameters

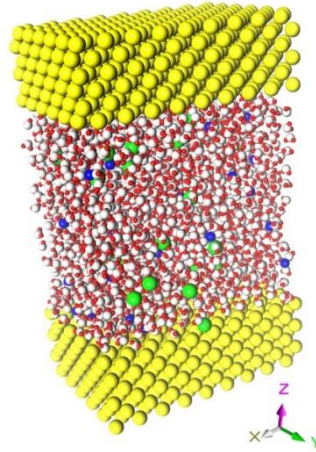Other parameters which are needed to complete the MD model are summarized in Table S2.

Fig S1: Snapshot of a simulated electrolyte confined between two solid walls and system coordinates and origin.

Table S1: Homonuclear LJ parameters and atom charges

Species, i	ϵ_{ii} $(kcal/mol)$ [4, 5]	σ_{ii} (Å) [4, 5]	q_i (e)
Na^+	0.1001	2.5830	$+1-2A\Sigma/(eN_i)$
Cl^-	0.1001	4.4010	$-1+2A\Sigma/(eN_i)$
$O_{SPC/E}^{\delta-}$	0.1555	3.1690	-0.8476
$H_{SPC/E}^{\delta+}$	0.0000	0.0000	$+0.4238$
Wall atoms	0.1500 ~ 2.0000	3.3700	0; except the atoms in contact with water which carry $A\Sigma/(108e)$

[†]The parameter A is the area of the unit cell $= 9 \times 6 \times l_s^2 \times 10^{-20}(m^2)$; Σ is the surface charge density of the wall;

e is the elementary charge, and N_i is the number of type i atoms.

Table S2: Other parameters/constrains for MD simulations

Parameter/Constrain	Value
Temperature	298.0 K
Time step	1.0 fs
Short-range (Long-range) cutoff radius	9.0 (14.0) Å
Skin thickness for neighbor list	2.0 Å which updates every 5 fs
Long-range interaction solver	P3M with 1E-04 as the accuracy
Extended dimension in z	3.0 (relative to actual dimension)
Periodic boundary condition	Only in x, y direction
Constrains on water bonds and angel	SHAKE Algorithm: 1.0 Å for $O-H$ bond and 109.47° for $\angle HOH$ angle.
Thermostat	Nosé only in y-direction (*perpendicular to flow and confinement* [6]) with 100.0 as the damping factor
Dielectric constant	1.0[‡]
Initial conditions	Gaussian velocity distribution with zero total linear and angular momentum or rotation
Total run	6~10 ns (*depending on obtaining invariant output*)

[‡]Although water has a dielectric constant of 68.0 but the partially charged atoms of SPC/E model and that

of 1.0 tacitly screen the coulombic interactions to the same extend.

S4. Performing MD simulation

For a given driving force, 19 number of our model are prepared with regard to different surface energies delineating hydrophilic toward hydrophobic surfaces in which proper inter-wall distance has been determined using the criterion of normal component of stress being 1 atm in average. The calculations of each model are performed using a 48-core node on Sheikh Bahaei National High Performance Computing Center (SBNHPCC) and using 2 GB of memory per core and 4970 hour-core-GHz of calculations on the average. The main physical parameters such as radial distribution function (RDF) are found to be time-invariant in first 1-2 ns but velocity distribution needs 6-10 ns to reach a reliable statistical ensemble.

S5. Velocity distribution

For calculations of the velocity distribution, consider a simulation cell that is binned to N bins in which the statistics and x-component of velocity are gathered for all time-steps[7]. Knowing that during an s-step simulation, at each step k, there are $N_{k,i}$ species in the ith bin, and the velocity of each of these species (denoted by j) is given by $v_{k,i}^{j}$, then the steady state average fluid velocity u_i in the ith bin can be computed by

$$u_i = \sum_{k=1}^{s} \sum_{j=1}^{N_{k,i}} v_{k,i}^{j} \bigg/ \sum_{k=1}^{s} N_{k,i} \qquad (S1)$$

It is noteworthy that the number of bins should be optimized to have simultaneously lower statistical error and finer grids for a better estimation. By considering the size of water molecules, the slab-type bin with 0.5 Å in depth is chosen.

S6. Inducing DOF within our MD model

It is not possible to directly impose a concentration gradient through the microchannel in MD. But it is convenient to indirectly [6, 8] impose the corresponding pressure gradient by using Onsager reciprocal relation:

$$\begin{bmatrix} Q \\ J - 2c_0 Q \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} -\nabla p \\ -k_B T \nabla \ln c_0 \end{bmatrix} \qquad (S2)$$

in which Q is total flow rate (being calculated from the velocity profile), $J = J_+ + J_-$ is total flux of cations and anions (measured by $u_i c_i$), c_0 is the bulk concentration (compatible in unit with J and measured at the center of channel which shows no fluctuation). Considering the particular case in which $\nabla c_0 = 0$ but $\nabla p \neq 0$, we then will have $M_{21} = (J - 2c_0 Q)/(-\nabla p)$ and Onsager reciprocal relations enforce $M_{12} = M_{21}$. Now, antithetical use of such conditions ($\nabla c_0 \neq 0, \nabla p = 0$) results in $Q = M_{12}(-k_B T \nabla c_0 / c_0)$ which gives

$$\nabla p = \left(\frac{J - 2c_0 Q}{Q} \right) \frac{k_B T \nabla c_0}{c_0} \qquad (S3)$$

The pressure gradient is then transformed to an identical force applied to any of the mobile species since $\nabla_x p \approx -\rho_{bulk} f_x$. So one can obtain solute excess current by running a single MD simulation of a Poiseuille flow (in the absence of ∇c_0) to calculate M_{21} and take it in for DOF to find required applicable force corresponding to the desired concentration gradient. The linearity of flows relative to its driving force can also be checked to ensure locating inside the linear response regime.

S7. Derivation of slip length

The velocity distribution is obtained by using chunk/atom and 1D bins with an optimized depth of 0.5 Å in z-direction. At the first glance, it seems that no slip is occurred since the velocity is smoothly decreased to zero; however, the point is that there would absolutely be an empty space very adjacent to the surface in which no mobile atom is appeared. Just

like other parameters in MD near a wall, the number density also rises up and fluctuates to reach its bulk value. It means that to define the boundary at which a tangential line should be added, the electrolyte density distribution should be taken into account. In order to have a global measure between different cases, we chose the position of the first peak in the density distribution. Since a uniform but good accuracy tangential line is desired in all cases, a quadratic polynomial curve is fitted to the velocity profile of the dense phase and thence, simple Newton-Raphson's method is used to determine the slip length, $b^* = u_{i,first\ peak}/Slope$ (see Fig. S2).
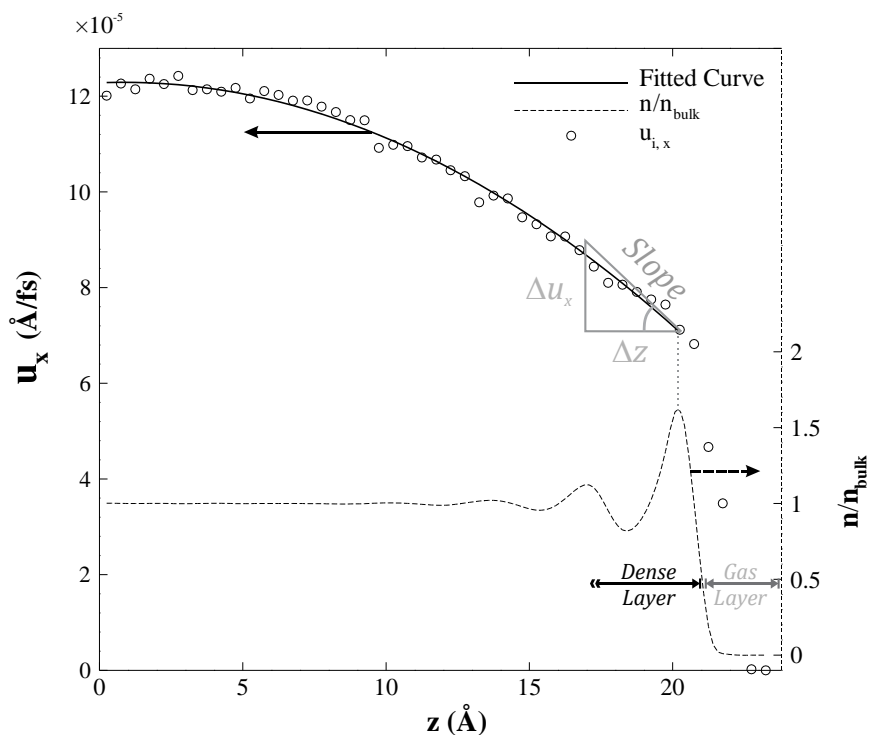

Fig. S2: Simultaneous plot of MD velocity of DOF and number density profiles to derive $b^* = 0.56$.

Repeating this procedure for the next 19 cases reproduces one series of data in Fig. 2.

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