Supporting Information

Non-scaling behavior for ionic transport in voltage-gated nanopores

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Solvent velocity profiles for different pore sizes

Figure S1. The solvent velocity distribution in the nanochannels with width varying from $H=2.5$ to 0.6 nm. Here the gating voltage is fixed at 0.1 V.

Figure S2. The solvent velocity distribution in the nanochannels with width varying from $H=2.5$ to 0.6 nm. Here the gating voltage is fixed at 0.5 V.
**Excess chemical potential in DFT**

The excess chemical potential for $i$th ion $\mu_i^{ex}$ in Eq. (4) consists of three parts that result from the external potential, hard-sphere repulsions and electrostatic correlations. The external potential accounts for the hard wall effect of the electrode model and is given by

$$V_i(z) = \begin{cases} \infty, & z \geq 2R \text{ or } z \leq 0 \\ 0, & 0 < z < 2R \end{cases} \quad \* \text{MERGEFORMAT (S1)}$$

The local excess chemical potential due to hard-sphere repulsions is calculated from the modified fundamental measure theory (MFMT)

$$\mu_i^{HS}(q) = \sum_\alpha \phi_\alpha \int dq' \phi_\alpha (q' - q') \quad \* \text{MERGEFORMAT (S2)}$$

where $q$ is the coordinate vector. The summation applies to the six indices for the weighted functions $\omega_i^{(a)}(q)$. Two scalar weight functions are related to the volume and the surface area of a spherical particle of diameter $\sigma_i$:

$$\omega_i^{(3)}(q) = \theta(q - \sigma_i / 2) \quad \* \text{MERGEFORMAT (S3)}$$

$$\omega_i^{(2)}(q) = \delta(q - \sigma_i / 2) \quad \* \text{MERGEFORMAT (S4)}$$

and a surface vector weight function is related to the variance across the particle surface

$$\omega_i^{(v,2)}(q) = \frac{q}{|q|} \delta(q - \sigma_i / 2) \quad \* \text{MERGEFORMAT (S5)}$$

where $q = |q|$, $\delta(q)$ is the Dirac delta function, and $\Theta(q)$ is the Heaviside step function. Other weight functions in FMT are given by
\[ \omega_i(0)(q) = \omega_i(2)(q) / (\pi \sigma_i^2), \quad \omega_i(1)(q) = \omega_i(2)(q) / (2\pi \sigma_i), \quad \omega_i(V)(q) = \omega_i(V2)(q) / (2\pi \sigma_i) \]

In Eq.\(* \text{MERGEFORMAT} \) (S2), the coefficients are defined by the functional derivatives of the local excess Helmholtz energy density with respect to the six weighted densities:

\[ \phi_0 = -\ln(1-n_3) \quad \text{\* MERGEFORMAT (S7)} \]

\[ \phi_i = n_i / (1-n_3) \quad \text{\* MERGEFORMAT (S8)} \]

\[ \phi_2 = \frac{n_i}{1-n_3} + \frac{n_i(1-n_3)^2 \ln(1-n_3)}{12\pi n_i^2 (1-n_3)^2} n_i^2 (1-\xi^2 - \xi^4 + \xi^6) \quad \text{\* MERGEFORMAT (S9)} \]

\[ \phi_3 = \frac{n_0}{1-n_3} + \frac{n_1 n_3}{(1-n_3)^2} (1-\xi^2) - \frac{n_1^3 (1-\xi^2)^3}{36\pi} \left[ \frac{2-5n_3 + n_3^2}{(1-n_3)^3} n_3^3 + \frac{2 \ln(1-n_3)}{n_3} \right] \quad \text{\* MERGEFORMAT (S10)} \]

\[ \phi_1 = -\frac{n_3}{1-n_3} \quad \text{\* MERGEFORMAT (S11)} \]

\[ \phi_2 = -\frac{n_3}{1-n_3} - \frac{n_i(1-n_3)^2 \ln(1-n_3)}{6\pi n_i^2 (1-n_3)^2} n_i^2 n_2 (1-\xi^2) \quad \text{\* MERGEFORMAT (S12)} \]

where \( \xi = n_2 / n_3 \), and the weighted densities are

\[ n_\alpha(q) = \sum_i n_{\alpha,i}(q) = \sum_i \int dq' \rho_i(q') \omega_i(\alpha)(q-q') \quad \text{\* MERGEFORMAT (S13)} \]

For systems with slab geometry, the ionic density profiles vary only in the direction perpendicular to the surface, \( \text{\textit{viz}, } \rho_i(q) = \rho_i(z) \). In that case, the weighted densities are
Similarly, the local excess chemical potentials are

$$\phi_{0,i}(z) = \frac{\phi_{0,i}(z)}{\pi \sigma_i^2} \quad \text{\scriptsize \* MERGEFORMAT (S20)}$$

$$\phi_{1,i}(z) = \frac{\phi_{2,i}(z)}{2 \pi \sigma_i} \quad \text{\scriptsize \* MERGEFORMAT (S21)}$$

$$\phi_{2,i}(z) = \pi \sigma_i \int_{z-\sigma_i/2}^{z+\sigma_i/2} dz' \phi_2(z') \quad \text{\scriptsize \* MERGEFORMAT (S22)}$$

$$\phi_{3,i}(z) = \pi \int_{z-\sigma_i/2}^{z+\sigma_i/2} dz' \phi_3(z')[\sigma_i^2 / 4 - (z'-z)^2] \quad \text{\scriptsize \* MERGEFORMAT (S23)}$$

$$\phi_{1,1,i}(z) = \frac{\phi_{1,1,i}(z)}{2 \pi \sigma_i} \quad \text{\scriptsize \* MERGEFORMAT (S24)}$$
\[ \phi_{i,j}(z) = \pi \sigma \int_{z-z_i}^{z+z_i/2} \phi_{i,j}(z')(z'-z)dz' \]  \text{(S25)}

The reduced excess chemical potential due to the electrostatic correlations is given by

\[ \beta \mu_i^{EL}(q) = \beta \mu_i^{EL}[\rho_i(z = R, x)] - \sum_{j=1}^{N} \int \Delta \rho_j(q') c_{ij}^{EL}(|q-q'|) dq' \]  \text{(S26)}

According to the mean-spherical approximation (MSA)\(^3\), the direct correlation function (DCF) for the range of \(0 \leq q \leq |\sigma_i - \sigma_j|/2\) is

\[ c_{ij}^{EL}(q) = -2l_B \left[ -Z_i N_j + X_i (N_i + \Gamma X_i) - (\sigma_i/3)(N_i + \Gamma X_i)^2 \right] \]  \text{(S27)}

and for \( |\sigma_i - \sigma_j|/2 \leq q \leq \sigma_j \),

\[ c_{ij}^{EL}(q) = l_B \left[ (\sigma_i - \sigma_j) L_1 - rL_2 + q^2 L_3 + q^4 L_4 \right] \]  \text{(S28)}

where

\[ L_1 = \frac{X_i + X_j}{4} (S_i - S_j) - \frac{\sigma_i - \sigma_j}{16} \left[ (S_i + S_j)^2 - 4N_i N_j \right] \]
\[ L_2 = \left( X_i - X_j \right) \left( N_i - N_j \right) + \left( X_i^2 + X_j^2 \right) \Gamma + \left( \sigma_i + \sigma_j \right) N_i N_j \]
\[ + \left[ \sigma_i S_i^2 + \sigma_j S_j^2 \right] / 3 \]  \text{(S29)}

and

\[ L_3 = \frac{X_i}{\sigma_i} S_j + \frac{X_j}{\sigma_j} S_i + N_i N_j - \left[ S_i^2 + S_j^2 \right] / 2 \]
\[ L_4 = \frac{S_i^2}{6\sigma_i^2} + \frac{S_j^2}{6\sigma_j^2} \]
\[ S_i = N_i + \Gamma X_i \]  
\[ \Gamma = \left( \pi l_b \sum \rho_i(z = R, x) X_i^2 \right)^{1/2} \]  
and the parameter \( N_i \) can be obtained from
\[ N_i = \frac{X_i - Z_i}{\sigma_i} \]

where \( X_i \) is solved from the following non-linear equations
\[ (1 + \Gamma \sigma_i) X_i + \alpha \sigma_i^2 \sum_j \rho_j(z = R, x) X_j = Z_i \]
\[ \alpha \equiv \left( \frac{\pi}{2} \right) \left[ 1 - \left( \frac{\pi}{6} \right) \sum \rho_i(z = R, x) \sigma_i^3 \right]^{-1} \]

As shown in our previous work\(^4\), the quadratic expansion is sufficient to capture counter-intuitive electrostatic phenomena such as attraction between like charges and charge inversion in the presence of multivalent ions, which defy the conventional mean-field theories.

**References**