

## Supporting Information

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

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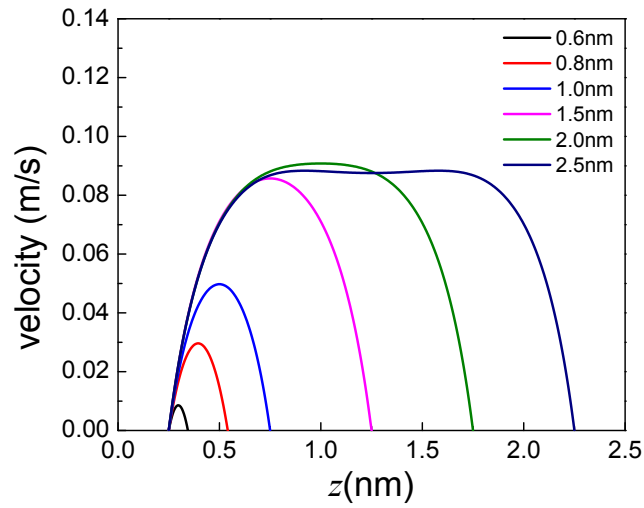
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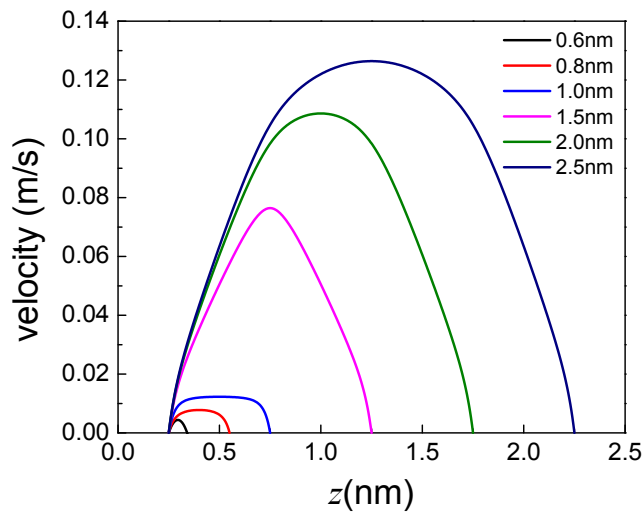
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### Solvent velocity profiles for different pore sizes



**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  $\mu_i^{\text{ex}}$  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

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

The local excess chemical potential due to hard-sphere repulsions is calculated from the modified fundamental measure theory (MFMT)<sup>1,2</sup>

$$\mu_i^{\text{HS}}(\mathbf{q}) = \sum_{\alpha} \phi_{\alpha,i} = \sum_{\alpha} \int d\mathbf{q}' \phi_{\alpha} \omega_i^{(\alpha)}(\mathbf{q} - \mathbf{q}') \quad \backslash * \text{ MERGEFORMAT (S2)}$$

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

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

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

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

$$\omega_i^{(V2)}(\mathbf{q}) = (\mathbf{q} / q) \delta(q - \sigma_i / 2) \quad \backslash * \text{ MERGEFORMAT (S5)}$$

where  $q = |\mathbf{q}|$ ,  $\delta(q)$  is the Dirac delta function, and  $\theta(q)$  is the Heaviside step function. Other weight functions in FMT are given by

$$\omega_i^{(0)}(\mathbf{q}) = \omega_i^{(2)}(\mathbf{q}) / (\pi\sigma_i^2), \quad \omega_i^{(1)}(\mathbf{q}) = \omega_i^{(2)}(\mathbf{q}) / (2\pi\sigma_i), \quad \omega_i^{(V1)}(\mathbf{q}) = \omega_i^{(V2)}(\mathbf{q}) / (2\pi\sigma_i) \quad \text{\* MERGEFORMAT (S6)}$$

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

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

$$\phi_1 = \frac{n_2}{1-n_3} \quad \text{\* MERGEFORMAT (S8)}$$

$$\phi_2 = \frac{n_1}{1-n_3} + \frac{n_3 + (1-n_3)^2 \ln(1-n_3)}{12\pi n_3^2 (1-n_3)^2} n_2^2 (1-\zeta^2 - \zeta^4 + \zeta^6) \quad \text{\* MERGEFORMAT (S9)}$$

$$\phi_3 = \frac{n_0}{1-n_3} + \frac{n_1 n_2}{(1-n_3)^2} (1-\zeta^2) - \frac{n_2^3 (1-\zeta^2)^3}{36\pi} \left[ \frac{2-5n_3+n_3^2}{(1-n_3)^3 n_3^2} + \frac{2\ln(1-n_3)}{n_3^3} \right] \quad \text{\* MERGEFORMAT (S10)}$$

$$\phi_{v1} = -\frac{\mathbf{n}_{v2}}{1-n_3} \quad \text{\* MERGEFORMAT (S11)}$$

$$\phi_{v2} = -\frac{\mathbf{n}_{v1}}{1-n_3} - \frac{n_3 + (1-n_3)^2 \ln(1-n_3)}{6\pi n_3^2 (1-n_3)^2} n_2 \mathbf{n}_{v2} (1-\zeta^2)^2 \quad \text{\* MERGEFORMAT (S12)}$$

where  $\zeta = \mathbf{n}_{v2} / n_2$ , and the weighted densities are

$$n_\alpha(\mathbf{q}) = \sum_i n_{\alpha,i}(\mathbf{q}) = \sum_i \int d\mathbf{q}' \rho_i(\mathbf{q}') \omega_i^{(\alpha)}(\mathbf{q}-\mathbf{q}') \quad \text{\* MERGEFORMAT (S13)}$$

For systems with slab geometry, the ionic density profiles vary only in the direction perpendicular to the surface, *viz*,  $\rho_i(\mathbf{q}) = \rho_i(z)$ . In that case, the weighted densities are

$$n_{0,i}(z) = \frac{n_{2,i}(z)}{\pi\sigma_i^2} \quad \backslash * \text{ MERGEFORMAT (S14)}$$

$$n_{1,i}(z) = \frac{n_{2,i}(z)}{2\pi\sigma_i} \quad \backslash * \text{ MERGEFORMAT (S15)}$$

$$n_{2,i}(z) = \pi\sigma_i \int_{z-\sigma_i/2}^{z+\sigma_i/2} dz' \rho_i(z') \quad \backslash * \text{ MERGEFORMAT (S16)}$$

$$n_{3,i}(z) = \pi \int_{z-\sigma_i/2}^{z+\sigma_i/2} dz' \rho_i(z') [\sigma_i^2 / 4 - (z' - z)^2] \quad \backslash * \text{ MERGEFORMAT (S17)}$$

$$\mathbf{n}_{V1,i}(z) = \frac{\mathbf{n}_{V2,i}(z)}{2\pi\sigma_i} \quad \backslash * \text{ MERGEFORMAT (S18)}$$

$$\mathbf{n}_{V2,i}(z) = -\frac{\mathbf{z}}{z} \pi\sigma_i \int_{z-\sigma_i/2}^{z+\sigma_i/2} \rho_i(z')(z' - z) dz' \quad \backslash * \text{ MERGEFORMAT (S19)}$$

Similarly, the local excess chemical potentials are

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

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

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

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

$$\phi_{V1,i}(z) = \frac{\phi_{V2,i}(z)}{2\pi\sigma_i} \quad \backslash * \text{ MERGEFORMAT (S24)}$$

$$\phi_{V2,i}(z) = \pi\sigma \int_{z-\sigma_i/2}^{z+\sigma_i/2} \phi_{V2}(z')(z'-z)dz' \quad \backslash * \text{MERGEFORMAT (S25)}$$

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

$$\beta\mu_i^{EL}(\mathbf{q}) = \beta\mu_i^{EL}[\rho_i(z=R, x)] - \sum_{j=+,-} \int \Delta\rho_j(\mathbf{q}') c_{ij}^{EL}(|\mathbf{q}-\mathbf{q}'|) d\mathbf{q}' \text{MERGEFORMAT (S26)}$$

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

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

and for  $|\sigma_i - \sigma_j|/2 \leq q \leq \sigma_{ij}$ ,

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

where

$$\begin{aligned} L_1 &= \frac{X_i + X_j}{4} (S_i - S_j) - \frac{\sigma_i - \sigma_j}{16} \left[ (S_i + S_j)^2 - 4N_i N_j \right] \\ L_2 &= (X_i - X_j)(N_i - N_j) + (X_i^2 + X_j^2)\Gamma + (\sigma_i + \sigma_j)N_i N_j \\ &\quad + [\sigma_i S_i^2 + \sigma_j S_j^2]/3 \quad \text{MERGEFORMAT} \\ L_3 &= \frac{X_i}{\sigma_i} S_i + \frac{X_j}{\sigma_j} S_j + N_i N_j - [S_i^2 + S_j^2]/2 \\ L_4 &= \frac{S_i^2}{6\sigma_i^2} + \frac{S_j^2}{6\sigma_j^2} \end{aligned} \text{MERGEFORMAT (S29)}$$

and

$$S_i = N_i + \Gamma X_i \quad \backslash * \text{MERGEFORMAT (S30)}$$

The MSA parameter  $\Gamma$  is given by

$$\Gamma = \left( \pi l_B \sum_i \rho_i(z = R, x) X_i^2 \right)^{1/2} \quad \backslash * \text{MERGEFORMAT (S31)}$$

and the parameter  $N_i$  can be obtained from

$$N_i = \frac{X_i - Z_i}{\sigma_i} \quad \backslash * \text{MERGEFORMAT (S32)}$$

where  $X_i$  is solved from the following non-linear equations

$$(1 + \Gamma \sigma_i) X_i + \alpha \sigma_i^2 \sum_j \rho_j(z = R, x) \sigma_j X_j = Z_i \quad \backslash * \text{MERGEFORMAT (S33)}$$

$$\alpha \equiv (\pi / 2) \left[ 1 - (\pi / 6) \sum_i \rho_i(z = R, x) \sigma_i^3 \right]^{-1} \quad \backslash * \text{MERGEFORMAT (S34)}$$

As shown in our previous work<sup>4</sup>, 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

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