Supporting information for: Electrostatics of Nanoparticle-Wall Interactions within Nanochannels: Role of Double-Layer Structure and Ion-Ion Correlations

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S.1 Electrostatics of Channels

For channels having a slit geometry consisting of two parallel walls, the electrostatics exhibit a few interesting features. For channels of finite extent with wall edges immersed in a reservior, the wall surface charges generate the strongest electric fields near the edges in the reservior. Through cancellations in the Coulombic interactions the wall charges do not generate significant net electric forces on the ions toward the middle region of the channel away from reservior edges. As a result, in the idealized limit of two infinite walls having equal and uniform surface charge, the electric fields generated by the wall-charges exactly cancel throughout the channel interior.

This can be seen by considering a single wall with charge σ^* . This contributes to the electric potential for the ion wall-interactions as

$$\phi_{\text{coul-w}}(z) = \int \frac{q_1 \sigma(\mathbf{r}')}{\epsilon |z\mathbf{e}_z - \mathbf{r}'|} dx dy,$$
(S1)

where $\mathbf{r}' = x\mathbf{e}_x + y\mathbf{e}_y$. The \mathbf{e}_i denotes the standard basis vector pointing in the i^{th} coordinate direction. For a constant uniform surface charge σ^* this can be integrated to obtain the equivalent potential

$$\phi_{\text{coul-w}}(z) = -(2\pi q_1 \sigma^* / \epsilon) z. \tag{S2}$$

For two equally charged parallel walls of infinite extent the net electric field has a Coulombic potential that is independent of z. We can see this from

$$\phi(z) = \phi_{\text{coul-w}}(z) + \phi_{\text{coul-w}}(L-z) = -(2\pi q_1 \sigma^*/\epsilon)(z+L-z) = -(2\pi q_1 \sigma^*/\epsilon)L.$$
(S3)

As a consequence, we find $E = -d\phi/dz = 0$ so the net electric field that acts on ions confined between the walls is in fact zero. It is worth mentioning that such cancellations would not hold in the case of two walls that have a finite extent or non-uniform surface charge. For equal uniform charges this can be seen by integrating Equation (S1) in polar coordinates for two disk-like walls of radius R. Our results show that for uniformly charged walls as their extent becomes large the electric fields contribute negligably toward the middle region of the channel away from the reserviors.

These results suggest a few interesting mechanisms by which ion concentrations are determined in the middle region of the channel and overall electric neutrality is achieved. The results indicate that the electric fields generated by the walls near the reservior edges of the channel are primarily responsible for driving ions into the channel or expelling them to acheive electric neutrality. Also, in the middle region of an infinite channel, the lack of net electric force acting on the ions from the walls gives an interesting perspective on the electric double-layers. Rather than conceiving of ions being pulled toward the charged walls, our results indicate once ionic concentrations are setup from the edge effects, the double-layer structures should be viewed as arising from how the walls break symmetry. In particular, since like-charged ions repel one another within the confined region and there are no balancing forces from ion charges on the other side of the walls, the like-charged ion repulsions can be viewed as pushing ions from each other from the channel interior towards the walls. This occurs in a manner very similar to mechanisms underlying generation of osmotic pressures.^{S1,S2} It is in this manner that the double layers can arise in the channel middle region without the need for local net electric forces generated by the two walls. From electric neutrality the ion concentrations are determined and such double-layers can be related to the Poisson-Boltzmann theory (PB) for single and two charged walls.

Our simulations capture such phenomena in the middle region of charged channels. We use periodic boundary conditions to capture behaviors similar to the limit of walls of infinite extent. Since in this limit the walls exert no net electric force on the ions, we handle implicitly the contributions of the wall charge. Our approach is similar to the Ewald summation method of Ballenegger et al.^{S3} In this approach the energy of the charged slab system is regularized

by placing two charged walls above and below the simulation system, with charge densities that neutralize the system. Thus, we are simulating a system that is overall electrically neutral with two walls of an appropriately chosen equal charge that serve to balance the ions.

For mean-field Poisson-Boltzmann theory (PB), charged walls are often handled by employing Neumann boundary conditions to account for surface charge explicitly.^{S4–S7} A crucial consideration linking this to our molecular perspective is the condition of electric neutrality. For channels this implies the implicit determination of a surface charge for the walls. For our model, electric neutrality allows us to distinguish different choices for the wall charge which result in an excess or deficit of ionic species in the interior region driven by the edge electric fields. In this manner our molecular model gives overall results that can be directly related to continuum models with explicit Neumann boundary conditions for the wall charge.^{S5,S7} We discuss how the ionic species concentrations in the channel interior are related to the implicit choice of the wall charge in Section 2.1.1 in the main text.

S.2 Classical Density Functional Theory (cDFT) Formulation

We provide here some additional discussion and details concerning our formulation of the cDFT. As we discussed in Section 2.2, the Helmholtz free energy consists of the terms:

$$F[\rho_{\alpha}(\mathbf{r})] = F_{id}[\rho_{\alpha}(\mathbf{r})] + F_{hs}[\rho_{\alpha}(\mathbf{r})]$$

$$+ F_{coul}[\rho_{\alpha}(\mathbf{r})] + F_{corr}[\rho_{\alpha}(\mathbf{r})].$$
(S4)

The terms represent respectively the Helmholtz free energies for the ideal gas (id), hard spheres (hs), mean-field Coulombic interactions (coul), and second order charge correlations (corr). The term F_{id} is the free energy of an ideal gas which incorporates the translational free energy as

$$F_{id}[\rho_{\alpha}(\mathbf{r})] = k_B T \sum_{\alpha} \int d\mathbf{r} \rho_{\alpha}(\mathbf{r}) \left[\ln(\Lambda_{\alpha}^3 \rho_{\alpha}(\mathbf{r})) - 1 \right].$$
(S5)

Here the thermal de Broglie wavelengths Λ_{α} are constants throughout and do not influence the free energy of the system, so they will be neglected.

For the hard sphere contribution F_{hs} we use the fundamental measure theory of ^{S8,S9} given by

$$F_{hs}\left[\rho_{\alpha}(\mathbf{r})\right] = k_B T \int d\mathbf{r} \,\Phi[n_{\gamma}(\mathbf{r})]. \tag{S6}$$

We mention this is based on the earlier work^{S10} and related to the work.^{S11} The energy density for the hard sphere system Φ is a functional of the Rosenfeld nonlocal (weighted) densities n_{γ} given by

$$\Phi = -n_0 \ln (1 - n_3) \frac{n_1 n_2 - n_{V1} \cdot n_{V2}}{1 - n_3}$$

$$+ (n_2^3 - 3n_2 n_{V2} \cdot n_{V2}) \cdot$$

$$\cdot \frac{n_3 + (1 - n_3)^2 \ln (1 - n_3)}{36 \pi n_3^2 (1 - n_3)^2}.$$
(S7)

The nonlocal densities are

$$n_{\gamma}(\mathbf{r}) = \sum_{\alpha} \int d\mathbf{r}' \,\rho_{\alpha}(\mathbf{r}) \omega_{\alpha}^{(\gamma)}(\mathbf{r} - \mathbf{r}'), \qquad (S8)$$

where $\omega_{\alpha}^{(\gamma)}$ are the weight functions. The weight functions are based on geometric properties

of the interactions between hard spheres and are given by the specific forms

$$\begin{aligned}
\omega_{\alpha}^{(2)}(\mathbf{r}) &= \delta(R_{\alpha} - |\mathbf{r}|), & \omega_{\alpha}^{(3)}(\mathbf{r}) &= \theta(R_{\alpha} - |\mathbf{r}|), \\
\omega_{\alpha}^{(0)}(\mathbf{r}) &= \frac{\omega_{\alpha}^{(2)}(\mathbf{r})}{4\pi R_{\alpha}^{2}}, & \omega_{\alpha}^{(1)}(\mathbf{r}) &= \frac{\omega_{\alpha}^{(2)}(\mathbf{r})}{4\pi R_{\alpha}}, \\
\omega_{\alpha}^{(V2)}(\mathbf{r}) &= \frac{\mathbf{r}}{r} \delta(R_{\alpha} - |\mathbf{r}|), & \omega_{\alpha}^{(V1)}(\mathbf{r}) &= \frac{\omega_{\alpha}^{(V2)}(\mathbf{r})}{4\pi R_{\alpha}}.
\end{aligned}$$
(S9)

The $\delta(\mathbf{r})$ denotes the Dirac delta function and the $\theta(\mathbf{r})$ denotes the Heaviside step function. The functional consisting of Equations (S6)–(S9) is designed to match the Mansoori-Carnahan-Starling-Leland (MCSL) equation of state for multi-component hard-sphere fluids.^{S12}

The contribution to the free energy F_{coul} accounts for the mean-field part of the electrostatic interactions as

$$\begin{aligned} F_{coul}\left[\rho_{\alpha}(\mathbf{r})\right] &= \frac{1}{2} \sum_{\alpha\beta} \int d\mathbf{r} \int d\mathbf{r}' \rho_{\alpha}(\mathbf{r}) \rho_{\beta}(\mathbf{r}') \frac{q_{\alpha}q_{\beta}}{4\pi\epsilon_{0}\epsilon|\mathbf{r}-\mathbf{r}'|} \\ &= \frac{1}{2} \sum_{\alpha} \int d\mathbf{r} q_{\alpha} \rho_{\alpha}(\mathbf{r}) \phi(\mathbf{r}). \end{aligned}$$

Here q_{α} is the charge of species α , ϵ_0 is the permittivity of free space, ϵ is the dielectric constant, and $\phi(\mathbf{r})$ is the electrostatic potential.

The contribution to the free energy F_{corr} accounts for the charge correlations of the electrostatic interactions. We use for the charge correlation the approach in ^{S13} with

$$F_{corr}\left[\rho_{\alpha}(\mathbf{r})\right] = -\frac{1}{2}k_{B}T\sum_{\alpha\beta}\int d\mathbf{r}\int d\mathbf{r}'\rho_{\alpha}(\mathbf{r})\rho_{\beta}(\mathbf{r}')\Delta c_{\alpha\beta}(|\mathbf{r}-\mathbf{r}'|).$$

The correlation operator is

$$\Delta c_{\alpha\beta}(|\mathbf{r} - \mathbf{r}'|)c_{\alpha\beta}(r)\frac{q_{\alpha}q_{\beta}}{4\pi\epsilon_{0}\epsilon k_{B}T|\mathbf{r} - \mathbf{r}'|}c_{\alpha\beta}^{HS}(r).$$
(S10)

where $c_{\alpha\beta}(r)$ is the direct correlation function for the bulk charged system.^{S13} The hard sphere and Coulombic terms are subtracted from the full direct correlation function $c_{\alpha\beta}(r)$ in equation S10 to avoid double counting relative to the contributions already in the F_{hs} and F_{coul} terms. The form of $c_{\alpha\beta}(r)$ is taken from the known analytic solution of the meanspherical-approximation (MSA) for a mixture of charged hard spheres. Detailed expressions can be found in the reference.^{S13}

The grand free energy for the density field of Equation (12) is minimized, see Eq. (13). This leads to a set of residual Euler-Lagrange equations given by

$$R_{1} = \ln \rho_{\alpha}(\mathbf{r}) + V_{\alpha}(\mathbf{r}) - \mu_{\alpha} + \int \sum_{\gamma} \frac{\partial \Phi}{\partial n_{\gamma}}(\mathbf{r}') \omega_{\alpha}^{(\gamma)}(\mathbf{r} - \mathbf{r}') d\mathbf{r}'$$

$$+ \sum_{\beta} \int d\mathbf{r}' \rho_{\beta}(\mathbf{r}') u_{\alpha\beta}(\mathbf{r} - \mathbf{r}') - \sum_{\beta} \int d\mathbf{r}' \rho_{\beta}(\mathbf{r}') \Delta c_{\alpha\beta}(\mathbf{r} - \mathbf{r}') + Z_{\alpha}\phi(\mathbf{r})$$
(S11)

$$R_2 = n_{\gamma}(\mathbf{r}) - \sum_{\alpha} \int d\mathbf{r}' \,\rho_{\alpha}(\mathbf{r}) \omega_{\alpha}^{(\gamma)}(\mathbf{r} - \mathbf{r}') \tag{S12}$$

$$R_3 = \nabla^2 \phi(\mathbf{r}) - \frac{4\pi \ell_B}{d} \sum_{\alpha} q_{\alpha} \rho_{\alpha}(\mathbf{r}).$$
(S13)

In these expressions we have adopted the convention that all quantities are in reduced units, so energies are in units of k_BT , lengths in units of d, and valence in terms of Z_{α} for species α . The numerical methods used and other computational details can be found in discussion of the Tramonto package in.^{S14–S17} Additional information concerning classical Density Functional Theory (cDFT) in general can be found in ^{S13,S18} and our specific approach to cDFT in.^{S14–S17}

S.3 Monovalent Ion Correlations

We performed additional BD simulations for the nanochannel system with a monovalent 1:1 electrolyte with the conditions that $\sigma = -6$ and $C_m = 2, 8, 10$ and $C_m = 4, 16, 20$. This allows us to make comparisons with the multivalent cases when changing either the total charge of the system or while keeping charge fixed and changing only the number of charge carriers for the counterions. We report the free energy for the nanoparticle position for constant number density in Figure S1. We report the ion-ion correlations and radial distribution function g(r) for ions in the bulk and near the wall in Figure S2 and S3. We discuss the g(r) analysis to distinguish these regions in Section S.4.

We find for all of the monovalent cases that there is no significant free energy minimum that forms for a preferred location for the nanoparticle within the channel, see Figure S1. This is in contrast to the free energy minima in comparable regimes seen in Figure 9. It is interesting to note that the case with $C_m = 10$ shows some free energy reduction as the nanoparticle approaches the wall but it is insignificant relative to k_BT . From observations of the simulation trajectory one can see again significant ion condensation on both the walls and the nanoparticle surface. A mechanism similar to that discussed in Section 4 may be at play but it appears the free energy gain is much reduced by the strength of the individual ion charges and entropic penalty associated with monovalent ions.



Figure S1: Free Energy of the Nanoparticle Position. Monovalent case with values $\sigma = -6$, and $C_m = 2, 4, 8, 10, 16, 20$.

We further explore the ion-ion correlations in the monovalent cases. We find that there are correlations between the individual counterions and coions as one may expect. However, in the bulk there is little to no coordination in the counterion-counterion or coion-coion interactions, see Figure S2. Near the walls, while we find there is little to no coordination in the counterion-counterion interactions there is some significant coordination in the coion-coion interactions, see Figure S3. From examination of the simulation trajectory of the system this appears to arise from the transient insertion of coions into the counterion-rich condensed layer near the walls. In contrast to the multivalent case we find for the monovalent electrolyte there are not significant ion clusters or other discrete ion structures that form in the bulk electrolyte.

Finally, cDFT calculations for monovalent electrolyte with $\sigma = -3$ and $C_m = 2, 4$ also show a monotonically increasing free energy as the nanoparticle nears the channel wall, in agreement with the simulations.



Figure S2: Ion Correlations in the Bulk. The RDF g(r) for ion-ion correlations in proximity to the wall for the monovalent case with $\sigma = -6$, and $C_m = 2, 4, 8, 10, 16, 20$.



Figure S3: Ion Correlations near the Wall. The RDF g(r) for ion-ion correlations in proximity to the wall for the monovalent case with $\sigma = -6$, and $C_m = 2, 4, 8, 10, 16, 20$.

S.4 Ion-Ion Correlation Analysis

We perform analysis of the radial distribution of the ions taking into account the proximity of the ions to wall vs the bulk regions and by choosing carefully a normalization taking into account accessible regions of ions. We split the channel into two sampling regions. The first corresponds to the wall case when the base ion is within the distance d < 1nm from the channel wall. The second is the bulk case when the base ion is a distance d > 1nm from the channel wall. In the confined channel geometry there are limited regions where ions are permitted given either the excluded volume of the wall or intrusion into the bulk or wall sampling region. We handle this by a careful normalization by accessible volume to obtain a radial distribution function g(r). We give details below with a schematic of our approach in Figure S4.

For a bulk system the radial distribution function can be sampled for a base ion by counting the number of ions within a spherical shell at radius r_k and thickness δr to obtain the normalized distribution function $\bar{g}(r_k) = H_k/V_kC_0$. The $V_k = \frac{4\pi}{3} (R_k^3 - r_k^3)$ is the volume of the spherical shell of thickness δr , $R_k = r_k + \delta r$, H_k is the histogram corresponding to the number of ions within the k^{th} spherical shell, and C_0 is a normalizing constant typically chosen to correspond to the bulk concentration.

Ion Radial Distribution Analysis



Figure S4: Ion Radial Distribution Analysis. To distinguish between the behaviors of the ions in the bulk vs near the channel wall in the condensed layer we perform regional sampling of a radial distribution function. To avoid issues with ions excluded from the wall domain or within other sampling region we perform our radial distribution analysis g(r) with probability conditioning on being within permissible regions. We normalize the distribution at a given radius by the accessible volume $V^{(1)}$ of the ions which correspond to spherical caps.

To obtain a more spatially refined description of the ions taking into account excluded regions we define the radial distribution function as $g(r_k) = \tilde{H}_k/\tilde{V}_k\tilde{C}_0$ where \tilde{H}_k for a given base ion is the histogram count for all permissible ions in the sampling region within the spherical shell of radius r_k and thickness δr and \tilde{C}_0 is a normalization based on the total concentration of ions. To obtain a radial density we use the volume \tilde{V}_k corresponding only to the part of the spherical shell that is within the permissible sampling region. This can be computed using the geometry of spherical caps to obtain $\tilde{V}_k = V^{(1)} = V_k - V^{(2)} - V^{(3)}$ where $V^{(2)} = \frac{\pi}{3} \left(A_k^2 \left(3R_k - A_k\right) - a_k^2 \left(3r_k - a_k\right)\right)$ and $V^{(3)} = \frac{\pi}{3} \left(B_k^2 \left(3R_k - B_k\right) - b_k^2 \left(3r_k - b_k\right)\right)$ are the volumes associated with the shell of a spherical cap of thickness δr .^{S19} We denote by $A_k = a_k + \delta r, B_k = b_k + \delta r, R_k = r + \delta r$, see Figure S4.

Our radial distribution function can be thought of as the conditional probability function for a pair of ions occupying the sample sampling region. Alternative methods have been considered in the literature such as sorting ions into z-slabs and sampling only in the xy-directions.^{S20,S21} Both approaches provide very similar information and allow for distinguishing between the behaviors of ions in the bulk region and behaviors of ions in the condensed layer near to the walls.

The approach we have introduced here allows for a unified observable that can transition from calculations involving sampling regions that are relatively narrow similar to z-slabs to intermediate and larger regions that yield results approaching the bulk radial distribution. By use of this radial distribution function, we are able to obtain a refined understanding of how the ion correlations change when in regions in the bulk of the nanochannel versus when an ion occupies the condensed ion layer near to the wall which exhibits a quasi-two dimensional behavior.

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