Supporting Information:

Dynamic Adsorption of Ions into Like-Charged Nano-space: A Dynamic Density Functional Theory Study

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Numerical Calculation Details of the DDFT Differential Equation

In this appendix, the numerical calculation details of the DDFT differential equations are provided.

Local mean electrostatic potential

The local mean electrostatic potential can be obtained by solving the modified Poisson equation. In slab symmetry, the Poisson equation reads:

$$\frac{d}{dz}\left(\frac{d\psi\left(z,t\right)}{dz}\right)=-\frac{e}{\varepsilon_0\varepsilon_r}\sum_i Z_i\rho_i\left(z,t\right). \tag{A1}$$

where *i* refers to the ion species. Along the *z* direction, we integrate eq.(A1), yielding:

$$\begin{aligned}&\int_0^z d\left(\frac{d\psi\left(z,t\right)}{dz}\right)=-\frac{e}{\varepsilon_0\varepsilon_r}\int_0^z\sum_i Z_i\rho_i\left(z,t\right)dz\\&\left(\frac{d\psi\left(z,t\right)}{dz}\right)\Bigg|_{z=z}-\left(\frac{d\psi\left(z,t\right)}{dz}\right)\Bigg|_{z=0}=-\frac{e}{\varepsilon_0\varepsilon_r}\int_0^z\sum_i Z_i\rho_i\left(z,t\right)dz\end{aligned}. \tag{A2}$$

We set $-\frac{d\psi\left(z,t\right)}{dz}\Big|_{z=0}$ = *C*, and then eq.(A2) follows:

$$\left(\frac{d\psi\left(z,t\right)}{dz}\right)\Bigg|_{z=z}+C=-\frac{e}{\varepsilon_0\varepsilon_r}\int_0^z\sum_i Z_i\rho_i\left(z,t\right)dz\ . \tag{A3}$$

Further integration of eq.(A3) gives:

$$\begin{aligned}&\int_0^Z d\psi\left(z,t\right)+\int_0^Z C\,dz=-\frac{e}{\varepsilon_0\varepsilon_r}\int_0^z\left[\int_0^{z'}\sum_i Z_i\rho_i\left(z,t\right)dz\right]dz'\\&\psi\left(z,t\right)\Big|_{z=z}-\psi\left(z,t\right)\Big|_{z=0}+Cz=-\frac{e}{\varepsilon_0\varepsilon_r}\int_0^z\left[\int_0^{z'}\sum_i Z_i\rho_i\left(z,t\right)dz\right]dz'\end{aligned}. \tag{A4}$$

By setting $f\left(z',t\right)=\int_0^{z'}\sum_i Z_i\rho_i\left(z,t\right)dz$, eq.(A4) can be simplified as:

$$\psi\left(z,t\right)-\psi\left(0,t\right)+Cz=-\frac{e}{\varepsilon_0\varepsilon_r}\int_0^z f\left(z',t\right)dz'\ . \tag{A5}$$

With partial integration on the right part of eq.(A5), we have:

$$
\begin{aligned}
-\frac{e}{\varepsilon_0\varepsilon_r}\int_0^z f(z',t)dz' &= -\frac{e}{\varepsilon_0\varepsilon_r}\left\{f(z',t)z'\Big|_0^z - \int_0^z z'df(z',t)\right\} \\
&= -\frac{e}{\varepsilon_0\varepsilon_r}\left\{f(z,t)z - \int_0^z z'\sum_i Z_i\rho_i(z',t)dz'\right\} \\
&= -\frac{e}{\varepsilon_0\varepsilon_r}\left\{z\int_0^z \sum_i Z_i\rho_i(z,t)dz - \int_0^z z'\sum_i Z_i\rho_i(z',t)dz'\right\} \\
&= -\frac{e}{\varepsilon_0\varepsilon_r}\int_0^z (z-z')\sum_i Z_i\rho_i(z',t)dz'
\end{aligned}
\qquad \text{(A6)}
$$

The substitution of the above equation into eq.(A5) finally gives:

$$
\psi(z,t) = \psi(0,t) - Cz - \frac{e}{\varepsilon_0\varepsilon_r}\left\{\int_0^z (z-z')\sum_i Z_i\rho_i(z',t)\,dz'\right\}, \qquad \text{(A7)}
$$

where the constant C can be obtained by combining with the boundary condition eq.(4):

$$
CH = -\psi(H,t) + \psi(0,t) - \frac{e}{\varepsilon_0\varepsilon_r}\left\{\int_0^H (H-z')\sum_i Z_i\rho_i(z',t)\,dz'\right\}. \qquad \text{(A8)}
$$

Algorithm and computational details for solving the DDFT differential equation

With the help of center difference method, the gradient of local chemical potential reads:

$$
\mathbf{U}_i\left[\left\{\rho_i\left(\mathrm{z}_j,t\right)\right\},t\right] = \frac{\rho_i\left(\mathrm{z}_{j+0.5},t\right)\frac{\partial}{\partial z}\left[\mu_i\left(\mathrm{z}_{j+0.5},t\right)\right] - \rho_i\left(\mathrm{z}_{j-0.5},t\right)\frac{\partial}{\partial z}\left[\mu_i\left(\mathrm{z}_{j-0.5},t\right)\right]}{\Delta z}. \qquad \text{(A9)}
$$

A further application of center difference method on the gradient of chemical potential gives:

$$
\mathbf{U}_i\left[\left\{\rho_i\left(\mathrm{z}_j,t\right)\right\},t\right] = \left\{
\begin{array}{l}
\dfrac{\rho_i\left(\mathrm{z}_{j+1},t\right)+\rho_i\left(\mathrm{z}_j,t\right)}{2}\times\dfrac{\mu_i\left(\mathrm{z}_{j+1},t\right)-\mu_i\left(\mathrm{z}_j,t\right)}{\Delta z} \\
-\dfrac{\rho_i\left(\mathrm{z}_j,t\right)+\rho_i\left(\mathrm{z}_{j-1},t\right)}{2}\times\dfrac{\mu_i\left(\mathrm{z}_j,t\right)-\mu_i\left(\mathrm{z}_{j-1},t\right)}{\Delta z}
\end{array}
\right\} / \Delta z. \qquad \text{(A10)}
$$

When $j=1$ and $j=H/\Delta z$, the ionic density and chemical potential is given by the boundary equations (5)-(6)

With the help of $\mathbf{U}_i\left[\left\{\rho_i\left(\mathrm{z}_j,t\right)\right\},t\right]$ determined above, equation (7) can be integrated with Adams-Bashforth (AB) algorithm to give the new local density. Specifically, the second-order AB algorithm and the fourth-order AB algorithm are combined in order to accelerate the numerical calculation process. For the first four time steps, the second-order AB algorithm is utilized, and thereafter the fourth-order AB algorithm is applied.

The second-order AB algorithm reads:

$$\rho_i\left(z,t_{k+1}\right)=\rho_i^*\left(z,t_k\right)+\frac{\Delta t}{2}\left[3\mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_k\right)\right\},t_k\right]-\mathbf{U}_i\left[\left\{\rho_i\left(z,t_{k-1}\right)\right\},t_{k-1}\right]\right], \tag{A11}$$

and the fourth-order AB algorithm reads:

$$\rho_i\left(z,t_{k+1}\right)=\rho_i^*\left(z,t_k\right)+\frac{\Delta t}{24}\times\begin{bmatrix}55\\ \text{-59}\\ 37\\ \text{-9}\end{bmatrix}\begin{bmatrix}\mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_k\right)\right\},t_k\right]\\ \mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_{k-1}\right)\right\},t_{k-1}\right]\\ \mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_{k-2}\right)\right\},t_{k-2}\right]\\ \mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_{k-3}\right)\right\},t_{k-3}\right]\end{bmatrix}. \tag{A12}$$

The intermediate local density $\rho_i^*\left(z,t_k\right)$ is determined by the Adams-Moulton (AM) algorithm. Similarly, the second-order AM algorithm and the fourth-order AM algorithm are combined. For the first four time steps, the second-order AM algorithm is utilized, and thereafter the fourth-order AM algorithm is applied.

The second-order AM algorithm reads:

$$\rho_i^*\left(z,t_{k+1}\right)=\rho_i^*\left(z,t_k\right)+\frac{\Delta t}{2}\left[\mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_{k+1}\right)\right\},t_{k+1}\right]+\mathbf{U}_i\left[\left\{\rho_i\left(z,t_k\right)\right\},t_k\right]\right], \tag{A13}$$

and the fourth-order AM algorithm reads:

$$\rho_i^*\left(z,t_{k+1}\right)=\rho_i^*\left(z,t_k\right)+\frac{\Delta t}{24}\times\begin{bmatrix}9\\ 19\\ \text{-5}\\ 1\end{bmatrix}\begin{bmatrix}\mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_{k+1}\right)\right\},t_{k+1}\right]\\ \mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_k\right)\right\},t_k\right]\\ \mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_{k-1}\right)\right\},t_{k-1}\right]\\ \mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_{k-2}\right)\right\},t_{k-2}\right]\end{bmatrix}. \tag{A14}$$

The gradient of chemical potential $\mathbf{U}_i\left[\left\{\rho_i^\alpha\left(z,t_{k+1}\right)\right\},t_{k+1}\right]$ is computed by using another intermediate local density $\rho_i^\alpha\left(z,t_{k+1}\right)$, which is calculated by combining the prediction of

$\rho_i(z,t_{k+1})$ from the AB algorithm and $\rho_i^*(z,t_{k+1})$ from the AM algorithm.

$$\begin{cases} \rho_i^{\alpha}(z,t_{k+1}) = \rho_i^*(z,t_{k+1}) \times \alpha + \rho_i(z,t_{k+1}) \times (1-\alpha) \ , \ \text{iter} = 1 \\ \rho_i^{\alpha}(z,t_{k+1}) = \rho_i^*(z,t_{k+1}) \times \alpha + \rho_i^{\alpha}(z,t_{k+1}) \times (1-\alpha) \ , \ \text{iter} > 1 \end{cases} . \tag{A15}$$

Here α is the relaxation factor, we take α =0.4 during the calculation.