Supplement

The grand potential of the present model is expressed in eq.(2) of the manuscript as a functional of Helmholtz energy for density profile of certain species, in which the ideal gas contribution is written as

$$F^{id}\left[\{\rho_i\}\right]=k_BT\sum_i\int d\mathbf{r}\rho_i(\mathbf{r})\left[\ln\left(\rho_i(\mathbf{r})\lambda_i^3-1\right)\right] \tag{S1}$$

where λ_i is the de Broglie wavelengh. The direct Coulomb contribution is given by

$$F_C^{ex}\left[\{\rho_i\}\right]=\frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2\sum_{i,j}\frac{z_iz_je^2\rho_i(\mathbf{r}_1)\rho_j(\mathbf{r}_2)}{\varepsilon\varepsilon_0\left|\mathbf{r}_1-\mathbf{r}_2\right|} \tag{S2}$$

The excluded volume term, F_{hs}^{ex}, is calculated according to MFMT,

$$F_{hs}^{ex}=k_BT\int d\mathbf{r}\left[-n_0\ln(1-n_3)+\frac{n_1n_2-\mathbf{n}_{V1}\cdot\mathbf{n}_{V2}}{1-n_3}\right.$$
$$\left.+\frac{n_2^3\ln(1-n_3)-3n_2\mathbf{n}_{V2}\cdot\mathbf{n}_{V2}\ln(1-n_3)}{36\pi n_3^2}+\frac{n_2^3-3n_2\mathbf{n}_{V2}\cdot\mathbf{n}_{V2}}{36\pi n_3(1-n_3)^2}\right] \tag{S3}$$

where n_i, i = 0, 1, 2, 3 and n_{Vj} (j = 1, 2) are scalar and vector total weighted densities respectively. The detail definitions for the weighted densities are given in Ref.17. F_{ele}^{ex} is derived from a truncated second-order functional Taylor expansion around the corresponding bulk fluid, which is given by

$$F_{ele}^{ex}=F_{ele}^{ex}\left(\{\rho_i^b\}\right)+\sum_i\int d\mathbf{r}\frac{\delta F_{ele}^{ex}}{\delta\rho_i(\mathbf{r})}\Delta\rho_i(\mathbf{r})$$
$$+\frac{1}{2}\sum_{i,j}\iint d\mathbf{r}d\mathbf{r}'\frac{\delta^2F_{ele}^{ex}}{\delta\rho_i(\mathbf{r})\rho_j(\mathbf{r})}\Delta\rho_j(\mathbf{r})\Delta\rho_j(\mathbf{r}') \tag{S4}$$

where $\Delta\rho_i(\mathbf{r})=\rho_i(\mathbf{r})-\rho_i^b$, and $\{\rho_i^b\}$ is the bulk density of species i. The first-order and second-order direct correlation functions are defined as,

$$k_BT\Delta C_i^{(1)}(\mathbf{r})=-\delta F_{ele}^{ex}/\delta\rho_i(\mathbf{r}) \tag{S5}$$

$$k_BT\Delta C_{ij}^{(2)}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right)=-\delta^2F_{ele}^{ex}/\delta\rho_i(\mathbf{r})\delta\rho_j(\mathbf{r}') \tag{S6}$$

$\Delta C_{ij}^{(2)}(r)$ is obtained from the Ornstein–Zernike integral equation with the MSA [1,2],

$$\Delta C_{ij}^{(2)}=\frac{z_1z_2e^2}{\varepsilon\varepsilon_0}\left[\frac{2B}{d}-\left(\frac{B}{d}\right)^2s-\frac{1}{s}\right],\qquad s=\left|\mathbf{r}-\mathbf{r}'\right|\le d \tag{S7}$$

in which $B=\left[y^2+y-y(1+2y)^{1/2}\right]/y^2$, $y^2=\left(4\pi d^2/\varepsilon\varepsilon_0k_BT\right)\sum_i\rho_i^bz_i^2e^2$.

[1] Waisman, E. and J. L. Lebowitz., J. Chem. Phys., 1972, **56**(6): 3086.
[2] Waisman, E. and J. L. Lebowitz., J. Chem. Phys., 1972, **56**(6): 3093.