Supporting Information for:

Self-Consistent Field Theory Study of Solvation Effect in Polyelectrolyte Solutions: Beyond Poisson-Boltzmann Model

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1. Effect of the Ion Volume on Phase Behaviors

The effect of the ion volume on the phase behaviors was studied. The $v_\pm$ has a less marked effect on the order parameter profiles (Figure S1-a) and charge density distributions (Figure S1-b) when the $v_\pm$ is smaller. Only when the $v_\pm$ becomes much larger, does obvious difference appear. For the charge density distributions, the main difference was found in the domain they dislike. Therefore, the treatment of $v_\pm$ as 0 can approximate the cases of small ions well.

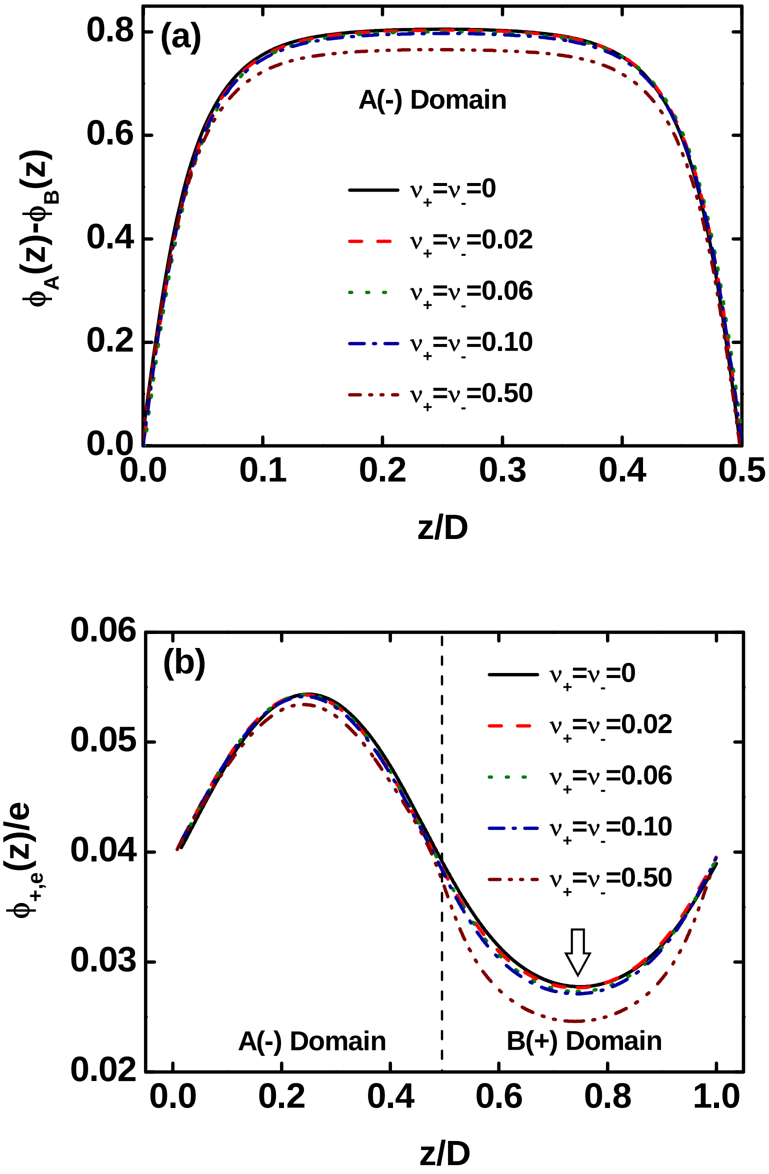

Figure S1. (a) Order parameter profiles $\phi_A(z)-\phi_B(z)$ and (b) charge density profiles $\phi_{+,e}(z)/e$ of the positive counterions as a function of the direction z/D along the lamellar normal for the salt-free solutions of the diblock polyampholytes. The parameters are α=0.1, p=0.6, $\chi_{A+}=\chi_{B-}=0$, $\chi_{A-}=\chi_{B+}=\chi_{+-}=0.3$, and $\chi_{S-}=\chi_{S+}=0$. In (b), the arrow indicates the place where the main difference appears.

2. Effect of the Magnitude of Dipole Moment on ODT

The effect of the magnitude of dipolar moment on order-disorder transition (ODT) of diblock polyampholyte solutions was studied. As shown in Figure S2, the $\chi_{ODT}N$, *i.e.*, the interaction strength at which order-disorder transition occurs, decreases as the magnitude of dipolar moment increases. This effect becomes more pronounced for the diblock polyampholyte solutions with larger α. Note that when the magnitude of dipolar moment is larger, the $\chi_{ODT}N$ approaches that of the neutral diblock copolymer solutions, implying that the charged objects are almost screened. From this result, we learned that the diblock polyampholyte solutions with higher magnitude of dipole moment can be microphase-separated at higher temperature, *i.e.*, lower χN.

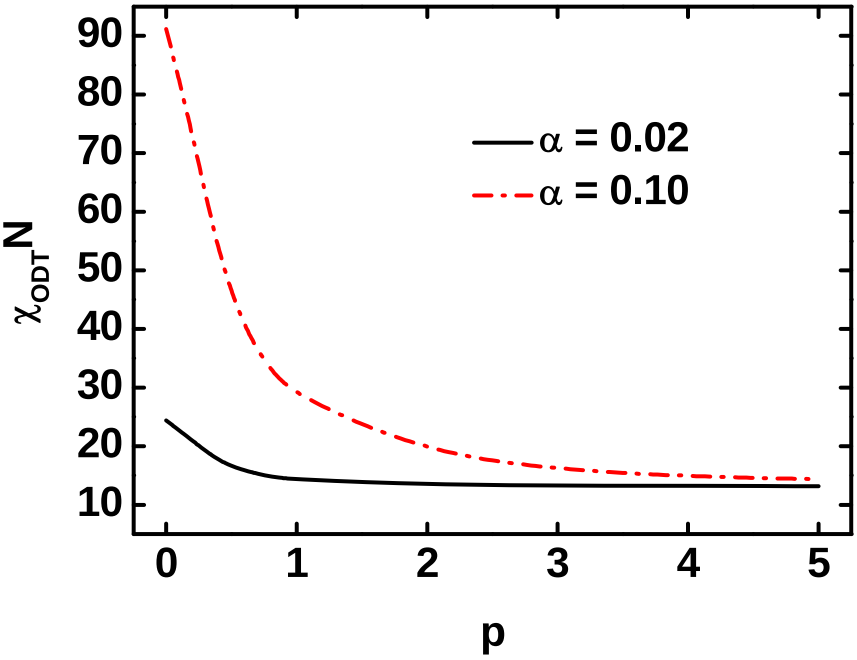

Figure S2. Plots of ODT properties as a function of the magnitude of the dipole moment *p*. The $\chi_{ODT}N$ is the interaction strength at which the order-disorder transition occurs.

3. Connection between Our Method and the SCFT Involving Only a Volume Fraction Weighted Dielectric Constant and No Explicit Ion-Dipole Interaction

For the convenience of description, we first denoted our method as SCFT_1. In addition, we denoted the SCFT method with no explicit ion-dipole interaction but a varying dielectric constant as SCFT_2. In SCFT_2, the dielectric constant is spatially varying, and depends on the volume fractions of the different species, *i.e.*, $\varepsilon(\mathbf{r})=\sum_j \phi_j(\mathbf{r})\varepsilon_j$. In what follows, we aim to build the relationship between the SCFT_1 and SCFT_2.

In the SCFT_2, we assumed the dielectric constant of solvent as $\varepsilon_{S,2}=\varepsilon_S+\Delta\varepsilon$, where the ε_S corresponds to the dielectric constant in the SCFT_1 and the $\Delta\varepsilon$ can be considered as an increment due to ion-dipole interactions between the ions and solvents. Therefore, the choice of $\varepsilon_{S,2}$ to be $\varepsilon_S+\Delta\varepsilon$ implies that the ion-dipole interactions are implicitly included in the SCFT_2. In the SCFT_2, the free energy is (more information for deriving the SCFT_2 can be referred to the work carried out by Fredrickson *et al.*[20])

$$\begin{aligned}\frac{\beta NF}{\rho_0 V}=\frac{1}{V}\int d\mathbf{r}\Bigg\{&\frac{1}{2}\sum_{\substack{j,j'\\ j\neq j'}}\chi_{jj'}N\phi_j(\mathbf{r})\phi_{j'}(\mathbf{r})-N\sum_{k=A,B}\omega_k(\mathbf{r})\phi_k(\mathbf{r})-N\left(\omega_S(\mathbf{r})-\frac{\Delta\varepsilon|\nabla\varphi(\mathbf{r})|^2}{8\pi\rho_0\beta}\right)\phi_S(\mathbf{r})\\ &-\frac{N\varepsilon(\mathbf{r})}{8\pi\rho_0\beta}|\nabla\varphi(\mathbf{r})|^2-\phi_S(\mathbf{r})\frac{N\Delta\varepsilon}{8\pi\rho_0\beta}|\nabla\varphi(\mathbf{r})|^2+N\xi(\mathbf{r})\left[\sum_j\phi_j(\mathbf{r})-1\right]\Bigg\}\\ &-c_p\,ln\left(\frac{Q_P}{V}\right)-Nc_{\pm}\,ln\left(\frac{Q_{\pm}}{V}\right)-Nc_S\,ln\left(\frac{Q_S}{V}\right)\end{aligned}\qquad\text{(S1)}$$

Here, the variables are identical to those in SCFT_1, except for the partition function Q_S of a single solvent and the Q_S-related ϕ_S. The Q_S is given as

$$Q_S=\int d\mathbf{r}\,exp\left[-\omega_S(\mathbf{r})+\frac{\Delta\varepsilon}{8\pi\rho_0\beta}|\nabla\varphi(\mathbf{r})|^2\right]\qquad\text{(S2)}$$

Extremizing the free energy with $\varphi(\mathbf{r})$ gives rise to the Poisson-Boltzmann equation

$$-\nabla\cdot\left\{\left[\frac{N\varepsilon(\mathbf{r})}{4\pi\rho_0\beta}+\frac{\phi_S(\mathbf{r})N\Delta\varepsilon}{4\pi\rho_0\beta}\right]\nabla\varphi(\mathbf{r})\right\}=N\phi_e(\mathbf{r}) \tag{S3}$$

Here, we have assumed that the $\Delta\varepsilon$ is independent of $\varphi(\mathbf{r})$, or else additional terms should be included. This is a Poisson-Boltzmann equation that usually appears in the SCFT_2, since $\frac{N\varepsilon(\mathbf{r})}{4\pi\rho_0\beta}+\frac{\phi_S(\mathbf{r})N\Delta\varepsilon}{4\pi\rho_0\beta}=\frac{N}{4\pi\rho_0\beta}\left[\phi_A(\mathbf{r})\varepsilon_A+\phi_B(\mathbf{r})\varepsilon_B+\phi_S(\mathbf{r})\varepsilon_{S,2}\right]$. Here, the volume of ions was ignored. To make the SCFT_1 and SCFT_2 completely equivalent, following condition should be satisfied. This condition was obtained by setting the Eq. S2 and 16 and Eq. S3 and 25 to be identical, respectively.

$$\frac{N\Delta\varepsilon}{8\pi\rho_0\beta}=N\,ln\left(\frac{sinh\left(p\left|\nabla\varphi(\mathbf{r})\right|\right)}{p\left|\nabla\varphi(\mathbf{r})\right|}\right)\Big/\left|\nabla\varphi(\mathbf{r})\right|^2=\frac{Np}{2\left|\nabla\varphi(\mathbf{r})\right|}\boldsymbol{L}\left(p\left|\nabla\varphi(\mathbf{r})\right|\right) \tag{S4}$$

The Eq. S4 can be transformed into

$$f(x)=ln\left(\frac{sinh(x)}{x}\right)-\frac{x}{2}\boldsymbol{L}(x)=0 \tag{S5}$$

where $x=p\left|\nabla\varphi(\mathbf{r})\right|$ is no less than zero. This equation can only be satisfied in the limit of $p\left|\nabla\varphi(\mathbf{r})\right|\to 0$. In this limit, $\frac{N\Delta\varepsilon(\mathbf{r})}{8\pi\rho_0\beta}$ is a constant $\frac{Np^2}{6}$, and therefore the assumption that the $\Delta\varepsilon$ is independent of $\varphi(\mathbf{r})$ is automatically satisfied. When the value of $p\left|\nabla\varphi(\mathbf{r})\right|$ is higher, the Eq. S5 can no longer be approximately satisfied. (Note $\left|f(x)\right|<10^{-3}$ when $p\left|\nabla\varphi(\mathbf{r})\right|<0.6$.) This means that the SCFT_1 and SCFT_2 can only be commutatively used in the weak-coupling limit (weak polyelectrolyte systems).