## **Supporting Information**

# Simulations of 3-Arm Polyelectrolyte Star Brushes under External Electric Fields

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## I. Methodological details

The polymers were created as a coarse-grained bead-spring model without explicit twist or bending potential; that is, the bonds are freely rotating and freely jointed within the limits set by excluded volume interactions with nearby monomers. All particles including neutral monomers, the charged monomers and counterions interact with each other through the Lennard-Jones (LJ) potential:

$$U_{LJ}\left(\mathbf{r}_{ij}\right) = \begin{cases} 4\varepsilon \left[ \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} + \frac{1}{4} \right] & r_{ij} \leq \sqrt[6]{2}\sigma \\ 0 & r_{ij} > \sqrt[6]{2}\sigma \end{cases}$$
(11)

where  $\sigma$  represents the nominal diameter of each particle and  $\varepsilon$  defines the Lennard-Jones energy unit.Because the main focus of this work is on the electrostatic interaction in the brush system under external electric fields, the hydrophobic effect of neutral monomers was not considered.

The connectivity between neighboring monomers i, j in a same polymer chain

is maintained by the finitely extensible nonlinear elastic (FENE) bond potential:

$$U_{FENE}(r_{ij}) = -\frac{1}{2} k R_0^2 \ln \left(1 - \frac{r_{ij}^2}{R_0^2}\right)$$
(I2)

where  $R_0 = 1.5\sigma$  and the spring constant k was set to  $k = 30.0 \varepsilon/\sigma^2$ , which was well tested in earlier studies. For uncharged and relaxed polymers, this parameter set leads to an average bond length of  $r_{av} = 0.97\sigma$ .

Both walls were modeled as a 12/6 Lennard-Jones wall potential:

$$U_{wall}(z) = \begin{cases} 4\varepsilon \left[ \left(\frac{\sigma}{z}\right)^{12} - \left(\frac{\sigma}{z}\right)^{6} + \frac{1}{4} \right] & z \le z_{c} \\ 0 & z > z_{c} \end{cases}$$
(I3)

where z is the distance between a particle and the neighboring wall. The cutoff distance  $z_c$  was set to  $z_c = 2^{1/6} \sigma$  to only keep the repulsive interaction.

The long-range Coulomb potential between any two charged particles  $q_i e$  and  $q_j e$  is:

$$U_{Coul}\left(r_{ij}\right) = k_B T \frac{\left(\lambda_B / \sigma\right) q_i q_j}{\left(r_{ij} / \sigma\right)}$$
(I4)

where  $k_B T$  represents thermal energy and  $\lambda_B$  denotes Bjerrum length  $\lambda_B = e^2/(4\pi\varepsilon_0\varepsilon_r k_B T)$  (*e* stands for an elementary charge,  $\varepsilon_0$ ,  $\varepsilon_r$  are the vacuum permittivity and the dielectric constant of the medium, respectively). The long-range Coulomb interaction was calculated using the Smooth Particle Mesh Ewald method (SPME). Because the periodic condition is broken in z the direction for the present star-polymer brush system, the Ewald sum was calculated in an extended system which periodically repeats the original slab system in the z direction with the insertion of an empty space between them. The empty space has twice the volume of the

original slab system in this study. Furthermore, a correction term is added to the Coulomb potential. Therefore the total potential energy of the star-polyelectrolyte brush system is given by

$$U_{\text{total}} = U_{LJ} + U_{FENE} + U_{wall} + U_{coul} \tag{15}$$

The external electric field  $\stackrel{!}{E}$  was applied along the z direction perpendicular to the two parallel walls. The motion of particle *i* with mass  $m_i$  at position  $r_i(t)$  is described by Langevin equation:

$$m_i \frac{d^2 r_i}{dt^2} = -\zeta_i \frac{dr_i}{dt} - \nabla_i U_{total} + q_i eE + \eta_i$$
(16)

where  $\zeta_i$  is the friction coefficient which couples the particle to a heat bath,  $\eta_i$  represents the random force acting on the particle and obeys the fluctuationdissipation theorem. In the above equation,  $q_i$  denotes the charge valence of the particle ( $q_i = 0$  for neutral monomers,  $q_i = -1$  for charged monomers and  $q_i = +1$  for counterions). All particles possess the same mass *m* and diameter  $\sigma$ . The temperature of the system is  $k_BT = 1.2\varepsilon$  with  $\varepsilon$  denoting the amplitude of LJ potential, and the friction coefficient  $\zeta = 1.0m\tau^{-1}$  with the time unit  $\tau = \sigma(m/\varepsilon)^{1/2}$ . The computer codes for Langevin Dynamics simulations were written in Fortran and are available with the link <u>https://github.com/wangshaoyun/MD\_Brushes</u>.

#### II. Additional Figures from Simulations



Figure S1. A snapshot of a row of the 3-arm polyelectrolyte brushes under a stretching electric





Figure S2. Brush center-of-mass height as a function of grafting density at different strengths of

the external electric field for the neutral-stem PE brushes.



**Figure S3.** A comparison of the fraction of grafted chains in the up- state  $R_{up}$  and the population weight of grafted chains with their branching points above the mean height  $H_{bp}$  in response to external electric fields for the neutral-stem brushes at  $\sigma_g^* = 0.003$ . The red line corresponds to  $R_{up}$ . Please Note that  $R_{area}$ , which denotes the population weight of grafted chains with their branching points above the mean height of the branching point of all grafted chains  $H_{bp}$ , was obtained from the distribution of the branching points shown **Figure 4**.



Figure S4. Probability distributions of the angle  $\alpha_{\text{branch}}$  formed by the two vectors connecting the branching point and the two free ends on the branches in each molecule at different strength of external electric fields. The grafting density is  $\sigma_g^* = 0.003$ .



Figure S5. Probability distributions of the angle  $\alpha_{end}$  formed by the vector linking the two free ends of the two branches in each molecule with respect to the grafting substrate at different strength of external electric fields. The grafting density is  $\sigma_g^* = 0.003$ .



Figure S6. Probability distributions of the free terminal monomers under different strengths of external electric fields for the neutral-stem PE brushes at  $\sigma_g^* = 0.003$ .



**Figure S7.** Probability distributions of the charged monomers (**a**) and counterions (b) under different external electric fields for the neutral-stem brushes at low grafting density ( $\sigma_g^* = 0.003$ ).

#### III. Analytical Self-consistent Field Theory



**Figure S8.** A schematic diagram of the Y-shaped neutral-stem brushes with two-layered structure adopted in the approximate analytical model.

Inside each of the two sub-layers, the electric potential is related to the spatial distribution of net charge via Poisson equation with mobile counter-ions following the Boltzmann distribution:

$$\frac{d^2 \psi_{in}^I(z)}{dz^2} = -4\pi\lambda_B \left[ C_m^I(z) - C_-(z=H)e^{\psi_{in}^I(z)} \right]$$
(III-1)

$$\frac{d^{2}\psi_{in}^{II}(z)}{dz^{2}} = -4\pi\lambda_{B} \left[ C_{m}^{II}(z) - C_{-}(z=H)e^{\psi_{in}^{II}(z)} \right]$$
(III-2)

where  $C_m^I$ ,  $C_m^{II}$  denote the monomer densities in the lower and upper sub-layers, respectively;  $C_-(z = H)$  is the counter-ion density at the top edge of the brush. Using the following two normalization conditions of monomer density profiles inside the two sub-layers

$$\int_{0}^{H_{1}} C_{m}^{I}(z) dz = \sigma_{g} n (1 - \beta) (f - 1)$$
(III-3)

$$\int_{H_1}^{H} C_m^{II}(z) dz = \sigma_g n \beta (f-1)$$
(III-4)

equations (III-1) and (III-2) can be integrated respectively with respect to z over the intervals  $[0, H_1]$  and  $[H_1, H]$ , affording

$$\sigma_{g}n(1-\beta)(f-1) - \frac{2na}{k}C_{-}(H)\frac{\sin[kH_{1}/(2na)] - \sin^{3}[kH_{1}/(2na)]/3}{\cos^{3}[kH_{1}/(2na)]\cos^{3}[\pi H_{2}/(2na)]}$$
(III-5)  
$$= \frac{3k}{8\pi na\lambda_{B}}\tan\left(\frac{kH_{1}}{2na}\right)$$
$$\sigma_{g}n\beta(f-1) - \frac{2na}{\pi}C_{-}(H)\frac{\sin[\pi H_{2}/(2na)] - \sin^{3}[\pi H_{2}/(2na)]/3}{\cos^{3}[\pi H_{2}/(2na)]}$$
(III-6)  
$$= \frac{3}{8na\lambda_{B}}\tan\left(\frac{\pi H_{2}}{2na}\right)$$

The net (uncompensated) charge of the brush is

$$Q_{net} = \int_{H}^{\infty} C_{-}^{out}(z) dz = \sigma_{g} n(f-1) - \int_{0}^{H_{1}} C_{-}^{I}(z) dz - \int_{H_{1}}^{H} C_{-}^{II}(z) dz$$
(III-7)

where  $C_{-}^{out}(z)$  is the counter-ion distribution above the brush.  $Q_{net}$  is just the sum of the right hand sides of eqs. (III-5) and (III-6), so

$$Q_{net} = \frac{3k}{8\pi na\lambda_B} \tan\left(\frac{kH_1}{2na}\right) + \frac{3}{8na\lambda_B} \tan\left[\frac{\pi H_2}{2na}\right]$$
(III-8)

Taking advantage of the fact that the equilibrium distribution of counter-ions outside the brush should coincide with that for counter-ions near a planar charged surface with charge density of  $Q_{net}$ , the distribution of counter-ions outside the brush is

$$C_{-}^{out}\left(z\right) = \frac{1}{2\pi\lambda_{B}} \frac{1}{\left(z - H + b\right)^{2}}$$
(III-9)

With Gouy-Chapman length  $b = 1/(2\pi\lambda_B Q_{net})$ . Therefore, we find

$$C_{-}(z=H) = C_{-}^{out}(z=H) = \frac{1}{2\pi\lambda_{B}b^{2}} = 2\pi\lambda_{B}Q_{net}^{2}$$
(III-10)

The formula for the force balance at the boundary between the two sub-layers is

derived next

$$P(z = H_1)\beta\sigma_g a^2 = C_-(z = H_1)a^3 = C_-(H)e^{\psi(H_1)}a^3$$
(III-11)

The above equation states that the tension force is balanced by the osmotic pressure of counter-ions at the boundary between the sub-layers, and the dimensionless tension force has been derived by Zhulina, et. al. (Zhulina, E. B.; Amoskov, V. M.; Polotsky, A. A.; Birshtein, T. M. *Polymer* **2014**, *55*, 5160)

$$P(H_1) = \frac{3}{2} \ln \left[ \frac{\tan(k/2) + \tan(kH_1/(2na))}{\tan(k/2) - \tan(kH_1/(2na))} \right]$$
(III-12)

After some simple algebra, eqs. (III-5), (III-6) and (III-11) can be simplified as eqs. (9), (10) and (11) in the main text. Eliminating the common factor  $\zeta\beta$  from both eqs. (10) and (11) leads to

$$\frac{3}{2} \left[ \frac{k}{\pi} \tan(kh_1) + \tan(\pi h_2) \right]^2 \frac{\left[ \sin(\pi h_2) - \sin^3(\pi h_2)/3 \right]}{\cos^3(\pi h_2)} + \tan(\pi h_2)$$

$$= \frac{\pi}{2} (f-1) \frac{\left[ (k/\pi) \tan(kh_1) + \tan(\pi h_2) \right]^2}{\cos^3(\pi h_2) \ln\left\{ \tan(k/2) + \tan(kh_1) \right] / \left[ \tan(k/2) - \tan(kh_1) \right] \right\}}$$
(III-13)

which relates  $h_1$  to  $h_2$ . Adding up eqs. (9) and (10) yields

$$\left[\frac{k}{\pi}\tan(kh_{1}) + \tan(\pi h_{2})\right] \begin{cases} 1 + \frac{3}{2} \left[\frac{k}{\pi}\tan(kh_{1}) + \tan(\pi h_{2})\right] g \\ \left[\frac{\pi}{k}\frac{\sin(kh_{1}) - \sin^{3}(kh_{1})/3}{\cos^{3}(kh_{1})\cos^{3}(\pi h_{2})} + \frac{\sin(\pi h_{2}) - \sin^{3}(\pi h_{2})/3}{\cos^{3}(\pi h_{2})}\right] \end{cases} (III-$$
$$= (f-1)\zeta$$

14)

which relates  $\zeta$  to  $h_1$  and  $h_2$ .

Equations (9), (10) and (11) were solved numerically as follows. First, for a given  $h_2$ , equation (III-13) was used to numerically obtain the corresponding  $h_1$ . Next, for the pair of  $h_1$  and  $h_2$ , equation (III-14) was used to get the corresponding  $\zeta$ . Finally,

 $\beta$  was obtained through equation (11).

It can be seen from Eq. (III-13) that in the case of  $h_2 \rightarrow 1/2$ , the first term on the LHS of the equation dominates over the second one, so that the second term can be neglected. In this case, analytical expression relating  $h_1$  to  $h_2$  can be obtained:

$$h_{1} = \frac{1}{k} \arctan\left\{ \tan\left(\frac{k}{2}\right) \frac{\exp\left[\pi (f-1)/(3\sin(\pi h_{2}) - \sin^{3}(\pi h_{2}))\right] - 1}{\exp\left[\pi (f-1)/(3\sin(\pi h_{2}) - \sin^{3}(\pi h_{2}))\right] + 1} \right\}$$
(III-15)