Self-Organized Polyelectrolyte End-Grafted Layers Under Nanoconfinement

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1. **Minimization of the free energy functional, numerical implementation and molecular model.**

The minimization of the free energy functional, numerical implementation and molecular model have been described in detail in the Supporting Information of our previous work[1] and, therefore, we refer the reader to this publication. The only difference between the molecular theory presented in our previous work and that used here is the presence of an opposite wall in the two-wall system (Figure 1B in the main text). The opposite wall has two consequences for the theory: i) there is a contribution to the free energy arising from the hydrophobic attractions between polyelectrolyte segments and the opposing wall (last term of equation 6 in the main text) and ii) the chains in the set of randomly generated conformations required by the theory should not only be self-avoiding and avoid overlapping with the grafting wall (as required for the one-wall system), but they also should avoid overlapping with the opposing wall. Upon minimization of the free energy functional, the segment-opposing wall interaction energy gives rise to an additional term in the Boltzmann factor of the probability of each polyelectrolyte conformation, *i.e.* the term $\beta\varepsilon_{wall}g_{wall}(\mathbf{r})$ in eq. 10 of the main text.

2. **Derivation of the two-phase free energy functional for a neutral polymer, eq. 6 in the main text.**

We assume that the system can be split into two phases, a solution phase (without polymer segments) and a polymer phase, with an average polymer volume fraction ϕ_P^{mean}. We start by considering the free-energy functional given by eq. 6 in the main text, for the specific case of a neutral polymer layer,

$$\beta F = \int \rho_w(\mathbf{r})\left(\ln(\rho_w(\mathbf{r})v_w)-1\right)d\mathbf{r} + \sum_j^{N_p}\sum_\alpha P_p(j,\alpha)\ln(P_p(j,\alpha))$$
$$+\iint \frac{\beta\varepsilon}{2}g(|\mathbf{r}-\mathbf{r'}|)\langle\phi_p(\mathbf{r})\rangle\langle\phi_p(\mathbf{r'})\rangle d\mathbf{r}d\mathbf{r'}$$

(S1)

Note that we neglected the translational entropy of the ions, which, for a neutral system, is much smaller than that of the solvent. We have also dropped the electrostatic and chemical

equilibrium contributions to the free energy, which are constant for the neutral polymer system. We split each of the integrals in eq. (S1) into the regions corresponding to the solution and the polymer phases. The first term (entropy of the solvent) yields:

$$\int \rho_w(\mathbf{r})\left(\ln(\rho_w(\mathbf{r})v_w)-1\right)d\mathbf{r} \sim \frac{V^{sol}}{v_w} + \frac{V^{pol}}{v_w}\left(1-\phi_P\right)\left(\ln\left(1-\phi_P\right)-1\right) \tag{S2}$$

where V^{sol} and V^{pol} are the volumes of the polymer and solvent phases, respectively. In deriving eq. (S2), we have used the incompressibility constraint in the polymer phase, $\phi_P^{mean} + v_w\rho_w^{mean} = 1$. Eq. (S2) can be further simplified by the fact that the total volume of the system ($V^{sol} + V^{pol}$) is constant and thus it can be dropped from the free energy. Using this condition yields:

$$\int \rho_w(\mathbf{r})\left(\ln(\rho_w(\mathbf{r})v_w)-1\right)d\mathbf{r} \sim \frac{V^{pol}}{v_w}\left(\left(1-\phi_P\right)\ln\left(1-\phi_P\right)+\phi_P\right) \tag{S3}$$

In order to approximate the third term of eq. (S1), we divide the polymer phase in a surface region of thickness $\sim a$ (the polymer segment length), surface $\sim S$ (the interfacial area) and volume $\sim aS$, and a deep (bulk) region of volume $V^{pol} - aS$. This approach yields:

$$\iint \frac{\beta\varepsilon}{2}g(|\mathbf{r}-\mathbf{r}'|)\langle\phi_P(\mathbf{r})\rangle\langle\phi_P(\mathbf{r}')\rangle d\mathbf{r}d\mathbf{r}' \sim$$
$$+\left(V^{pol}-Sa\right)\frac{\beta\varepsilon g}{2}\left(\phi_P\right)^2 + \frac{1}{2}\left(Sa\right)\frac{\beta\varepsilon g}{2}\left(\phi_P\right)^2 \tag{S4}$$

The first and second terms in the right hand side (rhs) of eq. (S4) corresponds to the deep and surface regions, respectively. The factor g is a constant that depends on the function $g(|\mathbf{r}\text{-}\mathbf{r}'|)$. The factor one half in front of the second term in the rhs of eq. (S4) accounts for the fact that the number of segments that interact with a segment in the surface region is (on average) half the number segments that interact with a segment in the deep region. Eq. (S4) can be rearranged as:

$$\iint \frac{\beta\varepsilon}{2}g(|\mathbf{r}-\mathbf{r}'|)\langle\phi_P(\mathbf{r})\rangle\langle\phi_P(\mathbf{r}')\rangle d\mathbf{r}d\mathbf{r}' \sim V^{pol}\frac{\beta\varepsilon g}{2}\left(\phi_P\right)^2 - \frac{1}{2}\left(Sa\right)\frac{\beta\varepsilon g}{2}\left(\phi_P\right)^2 \tag{S5}$$

The first term in the rhs of eq. (S5) is the cohesive energy of the polymer phase, while the second term plays the role of a surface tension (*i.e.* an enthalpic penalty for increasing the area of the polymer-solution interface). Combining eqs. (S3) and (S5) yields

$$\beta F = \frac{V^{pol}}{v_w}\left[\left(1-\phi_P\right)\ln\left(1-\phi_P\right)+\phi_P\right]+V^{pol}\frac{\beta\varepsilon\phi_P^2 g}{2}$$
$$-S\frac{\beta\varepsilon\phi_P^2 ga}{4}+\sum_{j}^{N_p}\sum_{\alpha}P_p(j,\alpha)\ln(P_p(j,\alpha)) \tag{S6}$$

We express eq. (S6) in terms of the surface coverage of the system rather than the volume of the polymer phase, by replacing $V^{pol} = \sigma_P A N v_P/\phi_P$ (where A is the grafting area) into eq. (S6). We also divide eq. (S6) by A to obtain a free energy density (free energy per unit area). Finally, we neglect the last term in eq. (S6) because, as explained in the text, the conformational entropy of the chains is expected to be much smaller than the cohesive and osmotic-pressure energies. The resulting equation, eq. (S7), is equal to eq. 1 in the main text.

$$\frac{\beta F}{A} = \frac{N\sigma_p v_p}{\phi_p v_w}\left[\left(1-\phi_P\right)\ln\left(1-\phi_P\right)+\phi_P\right]+\frac{\beta\varepsilon N\sigma_p v_p\phi_P g}{2}-\frac{S}{A}\frac{\beta\varepsilon\phi_P^2 ga}{4} \tag{S7}$$

3. **Analysis of the competition between osmotic pressure and cohesive energy in eq. (S7).**

We consider the competition between the first and second terms of eq. (S7), namely, we aim to minimize the functional

$$\frac{\beta F}{A} = \frac{N\sigma_p v_p}{\phi_p v_w}\left[\left(1-\phi_P\right)\ln\left(1-\phi_P\right)+\phi_P\right]+\frac{\beta\varepsilon N\sigma_p v_p\phi_P g}{2} \tag{S8}$$

with respect to ϕ_P at fixed surface density of polymer chains (constant σ_P). Functional minimization of (S8) with respect to ϕ_P yields:

$$\frac{\ln\left(1-\phi_p^{opt}\right)+\phi_p}{\left(\phi_p^{opt}\right)^2}-\frac{\beta\varepsilon g v_w v_p}{2}=0 \tag{S9}$$

Applying the limit $\phi_P{}^{opt} \to 0$ to eq. (S9), we obtain $\varepsilon_C = -\left(\beta g v_w v_p\right)^{-1}$ which we divide by eq. (S9) to obtain,

$$\frac{\varepsilon_c}{\varepsilon} = -\frac{1}{2}\frac{\left(\phi_p^{opt}\right)^2}{\ln\left(1-\phi_p^{opt}\right)+\phi_p^{opt}} \tag{S10}$$

which shows that for a given value of $\varepsilon_C/\varepsilon$, there is an optimal volume fraction of the polymer, $\phi_P{}^{opt}$ in the polymer-rich phase. While this is an approximation, eq. (S10) captures the dominant effect of ε on $\phi_P{}^{opt}$ and the fact that $\phi_P{}^{opt}$ is a monotonically decreasing function of $\varepsilon_C/\varepsilon$ (the stronger the segment-segment attractions, the denser the polymer phase).

4. Determination of the interfacial free energy for the homogeneous brush, micelles and stripes.

Since we neglected the conformational entropy of the polymers in our derivation of eq. (S7), there is no penalty for the chains in the periphery of an aggregate to stretch towards its center in order to locate segments where the polymer density is highest. In other words, within the approximations made there is no cost in stretching the chains and, therefore, we can assume that the aggregates will have a size determined by the length of a fully stretched polymer chain, ~ Na (where N and a are the chain and segment lengths, respectively). Let us consider, therefore, a square unit cell of side Na and area $A = (Na)^2$ The surface area, S, of a micelle, a stripe and a homogeneous brush in this cell are $2\pi R^2$, $NaR\pi$ and $\left(Na\right)^2$, respectively, where R is the radius of the micelle or stripe. The volumes of the polymer phase for a micelle, a stripe and a homogeneous brush in the unit cell are $\left(2/3\right)\pi R^3$, $\left(1/2\right)\pi R^2 Na$ and $h\left(Na\right)^2$, respectively, where h is the thickness of the homogenous brush. The volume can also be expressed in terms of the number of segments as

$$V^{pol} = \frac{\sigma_p \left(Na\right)^2 N v_p}{\phi_P^{opt}} \tag{S11}$$

Combining the geometric expressions for the surface areas and volumes of the different morphologies with eq. (S11) provides an expression for the surface area, S, which we introduce

in the surface energy, βF_{surf} (given by the third term in eq. (S7)). Finally, we normalize the surface energy of the micelles and stripes to that of the homogenous brush to get equations 3 and 4 in the main text:

$$\frac{\beta F_{surf}^{M}}{\beta F_{surf}^{HB}} = 2\pi \left(\frac{3}{2\pi} \right)^{2/3} \left(\frac{v_p \sigma_p}{a\phi_P^{opt}} \right)^{2/3} \tag{S12}$$

$$\frac{\beta F_{surf}^{S}}{\beta F_{surf}^{HB}} = \pi \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{v_p \sigma_p}{a\phi_P^{opt}} \right)^{1/2} \tag{S13}$$

References

1.   Tagliazucchi, M.; de la Cruz, M. O.; Szleifer, I., Self-Organization of Grafted Polyelectrolyte Layers Via the Coupling of Chemical Equilibrium and Physical Interactions. Proc. Natl. Acad. Sci. U.S.A. 2010, 107, 5300-5305.