# Intramolecular micellization and nanopatterning in pH- and thermo-responsive molecular brushes

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# 1 Details of the box-like model

Let's ascribe index i = 1, 2, 3 to planar, cylindrical and spherical brush, respectively, and assume that the chains in spherical or cylindrical brushes are end-grafted to a small spherical or thin cylindrical core, respectively. The grafting density is characterized by

$$\sigma_i = \begin{cases} 1/s, & i = 1\\ 1/(2\pi l), & i = 2\\ p/(4\pi), & i = 3 \end{cases}$$
(1)

where s is area per chain in a planar brush, l is axial distance per chain in a cylindrical brush, p is the number of arms in the star (spherical brush). The average polymer concentration (volume fraction) in the brush is equal to

$$c = \sigma_i \frac{iN}{R^i},\tag{2}$$

where *N* is the number of monomer units per chain and *R* is the chain extension, which (assuming Gaussian elasticity and uniform extension of the chains) gives rise to **conformational entropy loss** 

$$F_{\rm conf} = \frac{3R^2}{2N}.$$
(3)

Here and below all energy values are expressed in  $k_{\rm B}T$  units and the monomer unit size (the lattice site) is taken as a unit length. The brush free energy is a function of polymer concentration *c* and can be presented as a sum of three terms

$$F(c) = F_{\text{conf}}(c) + F_{\text{int}}(c) + F_{\text{ionic}}(c).$$
(4)

The second term is the contribution of non-electrostatic interactions

$$F_{\rm int}(c) = N(vc + wc^2),\tag{5}$$

where v and w are the second and third virial coefficients. The third term represents the **ionic contribution**.

• We define this term using the local electroneutrallity approximation (LEA). In other words, we assume that the local concentration of charged monomers in the brush is equal to excess local concentration of counterions

$$c_{-}(r) + \alpha c(r) = c_{+}(r),$$
 (6)

where  $\alpha c(r)$  is the local concentration of negatively charged polymer with ionization degree  $\alpha$ ,  $c_{-}(r)$  and  $c_{+}(r)$  are the local concentrations of all negatively (Cl<sup>-</sup>,OH<sup>-</sup>) and positively (Na<sup>+</sup>,H<sup>+</sup>) charged ions, respectively.

In the bulk phase LEA condition implicates equality of salt ions concentration

$$c_{b+} = c_{b-} = c_{bs}.$$
 (7)

Let us consider the brush made of quenched (strong) polyelectrolyte first. Then we will cover the brush from annealed (weak) PE. The density of the brush free energy can be written as the sum of the difference in ion concentrations in a bulk and in the polymer solution (the osmotic pressure) and the mixing entropy of the components

$$f = c_{b+} + c_{b-} - c_{+} - c_{-} + c_{+} \ln \frac{c_{+}}{c_{b+}} + c_{-} \ln \frac{c_{-}}{c_{b-}}.$$
(8)

Taking into account LEA equation 6, we rewrite expression for free energy density (equation 8) to

$$f = 2c_{\rm bs} - \alpha c - 2c_{-} + \alpha c \ln \frac{c_{-} + \alpha c}{c_{\rm bs}} + c_{-} \ln \frac{c_{-} (c_{-} + \alpha c)}{c_{\rm bs}^2}.$$
(9)

The minimization of the free energy density with respect to  $c_{-}$ 

$$\frac{\partial f}{\partial c_{-}} = \ln \frac{c_{-}(c_{-} + \alpha c)}{c_{\rm bs}^2} = 0 \tag{10}$$

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gives a following equation, which is a relation of co- and countr-ions in the intramolecular volum and in the surrounding solution or so-called Donnan's rule:

$$\frac{c_{-}}{c_{\rm bs}} = \frac{c_{\rm bs}}{(c_{-} + \alpha c)}.\tag{11}$$

Solving quadratic equation ( $c_{-}^2 + \alpha cc_{-} - c_{bs}^2 = 0$ ) with respect to  $c_{-}$  we get a following equation for  $c_{-}$ 

$$c_{-} = c_{\rm bs} \left[ \sqrt{\left(\frac{\alpha c}{2c_{\rm bs}}\right)^2 + 1} - \frac{\alpha c}{2c_{\rm bs}} \right]. \tag{12}$$

A substitution of  $c_{-}$  expression 12 into equation 9 of the free energy density and an assuming of the expression Arsh = ln  $\left(x + \sqrt{1 + x^2}\right)$  give

$$f = -2c_{\rm bs}\left(\sqrt{\left(\frac{\alpha c}{2c_{\rm bs}}\right)^2 + 1} - 1\right) + \alpha c \operatorname{Arsh}\left(\frac{\alpha c}{2c_{\rm bs}}\right).$$
(13)

Next we recalculate this expression of the free energy density into the free energy *via*  $F = \frac{N}{c}f$  and taking into account that  $c_{bs}$  is the concentration either Na<sup>+</sup> or Cl<sup>-</sup> ions in the bulk, while the concentration of all salt ions in the bulk is  $c_s = 2c_{bs}$ .

The **ionic contribution** to the free energy for a **strong PE** is

$$F_{\text{ionic}} = N \left\{ \alpha \operatorname{Arsh}\left(\frac{\alpha c}{c_{s}}\right) - \frac{c_{s}}{c} \left( \sqrt{1 + \left(\frac{\alpha c}{c_{s}}\right)^{2}} - 1 \right) \right\}.$$
(14)

We can carry out the similar procedure for the case of annealed polyelectrolyte. Here, we have to bear in mind that the average ionization degree  $\alpha$  is not a constant, but a function of pH value. As a result, the free energy density of weak PE includes three extra terms corresponded to the mixing entropy of ionized and nonionized polymer segments, protonated water molecules as well as contribution of the dissociation reaction (with reaction constant *K*):

$$f = c_{b+} + c_{b-} - c_{+} - c_{-} + c_{+} \ln \frac{c_{+}}{c_{b+}} + c_{-} \ln \frac{c_{-}}{c_{b-}} + c_{-} \left( \alpha \ln \alpha + (1-\alpha) \ln (1-\alpha) - \alpha \ln \frac{K}{C_{bH^{+}}} \right).$$
(15)

We use equation 6 and equation 7 to rewrite expression for free energy density (equation 15) to

$$f = 2c_{\rm bs} - \alpha c - 2c_{-} + \alpha c \ln \frac{c_{-} + \alpha c}{c_{\rm bs}} + c_{-} \ln \frac{c_{-} (c_{-} + \alpha c)}{c_{\rm bs}^{2}} + c_{-} \left( \alpha \ln \alpha + (1 - \alpha) \ln (1 - \alpha) - \alpha \ln \frac{K}{C_{\rm bH^{+}}} \right).$$
(16)

The minimization of the free energy density with respect to  $\alpha$ 

$$\frac{\partial f}{\partial \alpha} = c \left( \ln \frac{c_- + \alpha c}{c_{\rm bs}} + \ln \alpha - \ln \left( 1 - \alpha \right) - \alpha \ln \frac{K}{C_{\rm bH^+}} \right) = 0$$
(17)

gives a following relation between average ionization degree  $\alpha$  and ionization degree in a bulk  $\alpha_{\rm b}$ 

$$\frac{\alpha}{1-\alpha}\frac{C_{\rm bH^+}}{K} = \frac{c_{\rm bs}}{c_- + \alpha c},\tag{18}$$

where the bulk ionization degree  $\alpha_b$  can be determined by pH and pK values via  $\alpha_b = (1 + 10^{pK-pH})^{-1}$ .

The minimization of the free energy density with respect to  $c_{-}$  gives us the same equation for concentration of ions  $c_{-}$  as in the case of strong PE. Now we substitute equation 12 to equation 18.

The dependence of the average ionization degree  $\alpha$  on the average polymer concentration *c* via the local ionization equilibrium condition representes as

$$\frac{\alpha}{1-\alpha}\frac{1-\alpha_{\rm b}}{\alpha_{\rm b}} = \sqrt{\left(\frac{\alpha c}{2c_{\rm bs}}\right)^2 + 1} - \frac{\alpha c}{2c_{\rm bs}}.$$
(19)

A substitution of  $c_{-}$  expression 12 and the local ionization equilibrium condition equation 19 into equation 16 of the free energy density gives

$$f = -2c_{\rm bs}\left(\sqrt{\left(\frac{\alpha c}{2c_{\rm bs}}\right)^2 + 1} - 1\right) + c\ln\left(1 - \alpha\right). \tag{20}$$

Therefore, the ionic contribution to the free energy for a weak PE is

$$F_{\text{ionic}} = N \left\{ \ln\left(1 - \alpha\right) - \frac{c_{\text{s}}}{c} \left( \sqrt{1 + \left(\frac{\alpha c}{c_{\text{s}}}\right)^2} - 1 \right) \right\}.$$
(21)

As a result, we have following equations for the free energy of the brush Strong PEs:

$$F = \frac{3}{2} \left( \frac{\sigma_i i}{c} \right)^{2/i} N^{(2-i)/i} + N(vc + wc^2) + N\left\{ \alpha \operatorname{Arsh}\left( \frac{\alpha c}{c_{\rm s}} \right) - \frac{c_{\rm s}}{c} \left( \sqrt{1 + \left( \frac{\alpha c}{c_{\rm s}} \right)^2} - 1 \right) \right\}.$$
(22)

Weak PEs:

$$F = \frac{3}{2} \left( \frac{\sigma_i i}{c} \right)^{2/i} N^{(2-i)/i} + N(vc + wc^2) + N\left\{ \ln\left(1 - \alpha\right) - \frac{c_s}{c} \left( \sqrt{1 + \left(\frac{\alpha c}{c_s}\right)^2 - 1} \right) \right\}.$$
(23)

In order to find the average polymer concentration c and the average ionization degree  $\alpha$ , we have to derive these equations with respect to c taking into account the local ionization equilibrium condition (equation 19).

Let us start with derivative of the ionic term for both strong and weak PE cases  $\frac{dF_{ionic}}{dc}$ . Strong PE:

$$\frac{\mathrm{d}F_{\mathrm{ionic}}}{\mathrm{d}c} = \frac{Nc_{\mathrm{s}}}{c^2} \left( \sqrt{1 + \left(\frac{\alpha c}{c_{\mathrm{s}}}\right)^2 - 1} \right) \tag{24}$$

Weak PE:

$$\frac{\mathrm{d}F_{\mathrm{ionic}}}{\mathrm{d}c} = \frac{\partial F_{\mathrm{ionic}}}{\partial c} + \frac{\partial F_{\mathrm{ionic}}}{\partial \alpha} \frac{\partial \alpha}{\partial c},\tag{25}$$

where

$$\frac{\partial F_{\text{ionic}}}{\partial c} = -\frac{Nc_{\text{s}}}{c^2} + \frac{Nc_{\text{s}}}{c^2} \sqrt{1 + \left(\frac{\alpha c}{c_{\text{s}}}\right)^2} - \frac{N\alpha^2}{c_{\text{s}} \sqrt{1 + \left(\frac{\alpha c}{c_{\text{s}}}\right)^2}}$$
(26)

$$\frac{\partial F_{\text{ionic}}}{\partial \alpha} = -\frac{N}{1-\alpha} - \frac{\alpha c N}{c_{\text{s}} \sqrt{1 + \left(\frac{\alpha c}{c_{\text{s}}}\right)^2}}$$
(27)

$$\frac{\partial \alpha}{\partial c} = -\frac{\alpha^2}{c_s} \frac{(1-\alpha)}{c_s \sqrt{1 + \left(\frac{\alpha c}{c_s}\right)^2 + \alpha c - \alpha^2 c}}$$
(28)

$$\frac{\mathrm{d}F_{\mathrm{ionic}}}{\mathrm{d}c} = N \frac{c_{\mathrm{s}}}{c^2} \left( \sqrt{1 + \left(\frac{\alpha c}{c_{\mathrm{s}}}\right)^2 - 1} \right) \tag{29}$$

Therefore,  $\frac{dF_{\text{ionic}}}{dc}$  is the same for strong and weak PE.

So, the derivative of the free energy with respect to *c* gives

$$\frac{\mathrm{d}F}{\mathrm{d}c} = 0 = -\frac{3\sigma_i^{2/i}i^{(2-i)/i}N^{(2-i)/i}}{c^{(2+i)/i}} + N(\nu + 2wc) + \frac{Nc_s}{c^2} \left(\sqrt{1 + \left(\frac{\alpha c}{c_s}\right)^2 - 1}\right).$$
(30)

For a neutral polymer brush ( $\alpha = 0$ ) in the theta-solvent ( $\nu = 0$ ) the equilibrium polymer concentration c can be calculated from equation 30

$$\frac{3\sigma_i^{2/i}i^{(2-i)/i}N^{(2-i)/i}}{c_{\theta}^{(2+i)/i}} = 2wc_{\theta}N$$
(31)

as a following

$$c_{\theta} = \left(\frac{3\sigma_i^{2/i}i^{(2-i)/i}N^{2(1-i)/i}}{2w}\right)^{i/2(1+i)}.$$
(32)

For example, for spherical geometry  $i = 3 = \sigma_3 = \frac{p}{4\pi}$ :  $c_{\theta} = \frac{3^{1/4}p^{1/4}}{2^{7/8}w^{3/8}\pi^{1/4}N^{1/2}}$ . Thus, we have the following equation for equilibrium polymer concentration *c* for both quenched and annealed polyelectrolyte brushes:

$$-\frac{c_{\theta}^{2(1+i)/i}}{c^{(i+2)/i}} + \frac{v}{2w} + c + \frac{c_{s}}{2wc^{2}} \left( \sqrt{1 + \left(\frac{\alpha c}{c_{s}}\right)^{2}} - 1 \right) = 0.$$
(33)

For the particular case of the cylindrical brush, i = 2, it will have a following form

$$-\frac{c_{\theta}^{3}}{c^{2}} + \frac{v}{2w} + c + \frac{c_{s}}{2wc^{2}} \left[ \sqrt{1 + \left(\frac{\alpha c}{c_{s}}\right)^{2}} - 1 \right] = 0$$
(34)

with

$$c_{\theta} = \left(\frac{3}{4\pi w l N}\right)^{1/3}.$$
(35)

#### Calculation of the fraction of collapsed polymer 2



(c)  $c_s = 8.96 \cdot 10^{-3} \text{ M}$ 

Figure 1 The contours of polymer density gradient for system with pH - pK = 1,  $\chi = 1.5$  and at different salinity.

To estimate amount of collapsed polymer in the brush we calculate the gradient of polymer density and plot only the area where its absolute value is bigger than 0.2 ( $|\nabla \phi| > 0.2$ ), see Figure 1. The presence of this region indicates the existence of collapsed phase and

defines its boundary, therefore we can estimate the fraction of collapsed matter  $\lambda$ . We calculate the fraction of collapsed polymer by the equation  $\lambda = \frac{\Theta_{\varphi>0.5}}{\Theta}$ , where  $\Theta$  is the total amount of polymer and  $\Theta_{\varphi>0.5}$  is the amount of polymer in the area of high density,  $\varphi > 0.5$ .

# 3 Results of the box-like model: Effect of pH on ionization and dimensions of the molecular brush

In the paper in Figure2 and 3 we compare results of the analytical theory and results obtained from SF-SCF calculations at different solvent quality parameter  $\chi = 1.0$  and  $\chi = 1.5$ , respectively. The reason is a position of the brush rapid swollen-collapsed transition in the range of pH - pK values. Both methods show approximately the same pH - pK values, when the jumps occur. Here, in Figure2 (right column) we present the results of the analytical theory at  $\chi = 1.5$ , where one can see that jump-wise transitions take place at different values of pH - pK.



**Figure 2** Dependencies of (a) the reduced size of the brush  $R/R_{\theta}$ , (c) the reduced polymer concentration  $c/c_{\theta}$  and (e) the ionization degree  $\alpha$  on pH – pK difference for  $\chi = 1.0$  (left column)  $\chi = 1.5$  (right column). Thin solid black curve is the ideal titration curve.

## 4 Comparison results of the box-like model with SF-SCF at theta-conditions

In Figure3 we compare results of the box-like model with results of SF-SCF at theta-conditions. In Figure3b one can see good agreement of both methods for the ionization degree  $\alpha$  dependence on pH – pK value. Howether, there is a big difference in values of the reduced size of the brush  $R/R_{\theta}$  (Figure3a) between two methods. The reason of that is a difference in the conformational energy term. In the box-like model we use a Gaussian approximation, that allows chains to stretch too much. Whereas the SF-SCF method implements finit extensibility. So, making a correction to the conformational term of the free energy in the box-like model can lead to better agreement. For example, using an analytical formula accounting for the finit extensibility of chains<sup>1</sup>.

## Reference

1 B. Miao, T.A. Vilgis, S. Poggendorf, S. Gabriele, Effect of finite extensibility on the equilibrium chain size, Macromol. Theory Simul., 19 (7) (2010), pp. 414-420



**Figure 3** Dependencies of (a) the reduced size of the brush  $R/R_{\theta}$  and (b) the ionization degree  $\alpha$  on pH – pK difference for  $\chi = 0.5$  obtained from the analytical theory — dashed curves and from the SF-SCF — empty markers. Thin solid black curve is the ideal titration curve.