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Appendix. The calculation of tention exerted by the brush of linear polyelectrolyte chains at the grafting surface

Within the strong stretching approximation there is a universal relation between polymer density profile, $c_p(z)$, local stretching function, $E(z, z')$, of the chain with the end position at z' and normalized to unity distribution of the end segments, $g(z')$, as

$$c_p(z) = \frac{1}{s} \int_z^H \frac{g(z')dz'}{E(z, z')} \tag{31}$$

The stretching function $E(z, z')$ is given by

$$E(z, z') = a\sqrt{1 - \frac{\cos^2(\pi z'/2L)}{\cos^2(\pi z/2L)}}$$

and thus eq 31 can be used for obtaining the end segments distribution $g(z)$. By introducing new variables

$$\xi = \cos^2(\frac{\pi x'}{2L}) - \cos^2(\frac{\pi H}{2L})$$

$$\eta = \cos^2(\frac{\pi x}{2L}) - \cos^2(\frac{\pi H}{2L})$$

eq 31 can be reduced to a standard Abel's integral equation

$$\phi(\eta) = \int_0^\eta \frac{f(\xi)d\xi}{\sqrt{\eta - \xi}}$$

where

$$\phi(\eta) = \frac{\pi s}{2La^2} \frac{c_p(x(\eta))}{\cos(\frac{\pi x(\eta)}{2L})}$$

and

$$f(\xi) = \frac{g(x'(\xi))}{\sin\frac{\pi x'(\xi)}{L}}$$

with the soution

$$f(\xi) = \frac{1}{\pi}\Big(\frac{\phi(0)}{\sqrt{\xi}} + \int_0^\xi \frac{(d\phi(\eta)/d\eta)d\eta}{\sqrt{\xi-\eta}}\Big)$$

Hence the (normalized to unity) distribution of the end segments is given by

$$g(z) = \frac{sa}{2L}\sin(\frac{\pi z}{L})\Big(\frac{c_p(H)}{\cos(\frac{\pi H}{2L})\sqrt{\cos^2(\frac{\pi z}{2L}) - \cos^2(\frac{\pi H}{2L})}}$$
$$-\int_z^H dz' \frac{\sec(\frac{\pi z'}{2L})\frac{dc_p(z')}{dz'} + \frac{\pi}{2L}c_p(z')\tan(\frac{\pi z'}{2L})\sec(\frac{\pi z'}{2L})}{\sqrt{\cos^2(\frac{\pi z}{2L}) - \cos^2(\frac{\pi z'}{2L})}}\Big) \tag{32}$$

Tension exerted at the grafting surface, $z = 0$, by the chain with the end point localised at z'

$$\frac{f(z=0,z')a}{k_BT} = \frac{3}{2}\ln\frac{1+E(z=0,z')/a}{1-E(z=0,z')/a} \tag{33}$$

is expressed though the local stretching function

$$E(z=0,z')/a = \Big(\sqrt{1-\frac{\cos^2 \pi z'/2L}{\cos^2 \pi z/2L}}\Big)_{z=0} = \sin\frac{\pi z'}{2L} \tag{34}$$

By averaging tension given by eqs 33, 34 with respect to the position z' of the free chain end with the distribution function $g(z')$, given by eq 32, we obtain an expression for the average tension extered by the brush per unit area of the grafting surface

$$\frac{T(0)a}{k_BT} = \frac{3}{2s}\int_0^H g(z')\ln\Big(\frac{1+\sin\frac{\pi z'}{2L}}{1-\sin\frac{\pi z'}{2L}}\Big)dz' =$$

$$\frac{3a}{4L}\Big[\int_0^H \sin\frac{\pi z'}{L}\ln\Big(\frac{1+\sin\frac{\pi z'}{2L}}{1-\sin\frac{\pi z'}{2L}}\Big)\frac{c_p(H)}{\cos(\frac{\pi H}{2L})\sqrt{\cos^2(\frac{\pi z'}{2L}) - \cos^2\frac{\pi H}{2L}}}dz'$$
$$-\int_0^H dz'\sin\frac{\pi z'}{L}\ln\Big(\frac{1+\sin\frac{\pi z'}{2L}}{1-\sin\frac{\pi z'}{2L}}\Big)\int_{z'}^H dz\frac{(\frac{dc_p(z)}{dz})\sec(\frac{\pi z}{2L}) + (\frac{\pi}{2L})c_p(z)\tan(\frac{\pi z}{2L})\sec(\frac{\pi z}{2L})}{\cos^2(\frac{\pi z'}{2L}) - \cos^2(\frac{\pi z}{2L})}\Big] \tag{35}$$

After changing the order of integration in the second integral in eq 35 and using the relation

$$\int_0^b \ln\frac{1+y}{1-y}\frac{ydy}{\sqrt{b^2-y^2}} = \pi(1-\sqrt{1-b^2})$$

we obtain a general expression for $T(0)$

$$\frac{T(0)a}{k_BT} = 3a\Big[c_p(H)(\sec\frac{\pi H}{2L}-1)-$$

$$\int_0^H dz(1-\cos\frac{\pi z}{2L})\Big(\frac{dc_p(z)}{dz}\sec(\frac{\pi z}{2L})+\frac{\pi}{2L}c_p(z)\tan(\frac{\pi z}{2L})\sec(\frac{\pi z}{2L})\Big)\Big] \quad (36)$$

applicable at any shape of the polymer density profile $c_p(z)$, that is, at any type of interactions in the brush.

Consider now the brush of linear polyelectrolyte chains of length $L = na$ grafted with the density a^2/s to planar surface.

The electrostatic potential in the linear polyelectrolyte brush with finite extensibility is specified as

$$\psi_{in}(x) = \frac{U(x)}{\alpha k_BT} = \frac{3}{\alpha}\ln\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)} \quad (37)$$

By applying similar arguments as above, we find the polymer concentration profile

$$\alpha c_p(z) = \frac{3\pi}{16 l_B \alpha L^2}\sec^2(\frac{\pi z}{2L}) + \frac{1}{2\pi l_B \widetilde{\Lambda}^2}\left[\frac{\cos(\pi z/2L)}{\cos(\pi H/2L)}\right]^{\frac{3}{\alpha}} \quad (38)$$

where

$$\widetilde{\Lambda} = \frac{4}{3\pi}\frac{\alpha L}{\tan(\pi H/2L)} = \frac{H_0^2}{H}\frac{(\pi H/2L)}{\tan(\pi H/2L)} \quad (39)$$

Then eq 38 can be presented in the form

$$c_p(z) = \frac{1}{2\pi l_B \alpha H_0^2}\Big(\sec^2\frac{\pi z}{2L} + \frac{3}{2\alpha}\frac{\pi H}{2L}\left[\frac{\cos(\pi z/2L)}{\cos(\pi H/2L)}\right]^{\frac{3}{\alpha}}\Big) \quad (40)$$

and we find finite expression for the tension exerted to the unit area of the surface as

$$\frac{T(0)a}{k_BT} = \frac{3a}{4\pi l_B \alpha H_0^2}\Big[\tan^2(\frac{\pi H}{2L}) + \frac{\pi H}{2L}\tan(\frac{\pi H}{2L})\Big(\sec^{3/\alpha}(\frac{\pi H}{2L})-1\Big)\Big] \quad (41)$$