Supplementary information to "Coupling of charge regulation and conformational equilibria in linear weak polyelectrolytes: treatment of long range interactions *via* effective short-ranged and pH-dependent interaction parameters"

June 15, 2018

1 Matricial expression for the SBRIS partition function for a linear polyelectrolyte

Let us express the SBRIS partition function as

$$\Xi_{\mathrm{SBRIS}} = \sum_{s} \Xi_{\mathrm{rot}}(s) \tag{1}$$

where $\Xi_{\mathrm{rot}}(s)$ is the partition function for the molecule in a specific binding state $s = \{s_1, s_2, \cdots, s_N\}$. For simplicity, let us suppose that all the N-1 bonds hold two protonating sites at their ends.

The partition function for every 'frozen' binding configuration can then be expressed as a the RIS partition function but decorating the transfer matrices with suitable binding parameters. $\Xi_{\mathrm{rot}}(s)$ adopts the form [1, 2, 3]

$$\Xi_{\mathrm{rot}}(s) = \mathbf{p} \prod_{\mathrm{i}=1}^{N-1} \mathbf{U}_{\mathrm{i}}{}^{s_i s_{i+1}} \mathbf{q}^{\mathbf{T}} \tag{2}$$

In the simplest case $\mathbf{U}_{\mathrm{i}}^{00} = \mathbf{U}_{\mathrm{i}}^{10}$; $\mathbf{U}_{i}^{01} = z \cdot \mathbf{U}_{\mathrm{i}}$ and $\mathbf{U}_{\mathrm{c}}^{11} = z \cdot \mathbf{U}_i \mathbf{u}_i$ where $\mathbf{U}_i$ are the transfer matrices typical of the RIS model for a symmetric polymer

$$\mathbf{U_i} = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{pmatrix}_i \tag{3}$$

where z is the reduced activity of the site and $\mathbf{u}$ is a diagonal matrix containing the Boltzmann factors corresponding to the short range interactions between

charged sites

$$\mathbf{u}_i = \begin{pmatrix} u_t & 0 & 0 \\ 0 & u_g & 0 \\ 0 & 0 & u_g \end{pmatrix}_i \tag{4}$$

$-k_{\mathrm{B}}T \ln u_t$ and $-k_{\mathrm{B}}T \ln u_g$ represent the short range interaction energy between two sites separated by a bond in *trans* and *gauche* conformation, respectively. The next step is to calculate the sum in Eqn. (1), which can be done using the identity

$$\sum_s \left(\prod_{i=1}^{N-1} \mathbf{U}^{s_i s_{i+1}} \right) = (\mathbf{E}\,\mathbf{E}) \prod_{i=1}^{N-1} \begin{pmatrix} \mathbf{U}_i^{00} & \mathbf{U}_i^{01} \\ \mathbf{U}_i^{10} & \mathbf{U}_i^{11} \end{pmatrix} \begin{pmatrix} \mathbf{E} \\ \mathbf{E} \end{pmatrix} \tag{5}$$

where $\mathbf{E}$ is the 3×3 identity matrix. Combining Eqns. (5), (1) and (2), we obtain the SBRIS partition function.

$$\Xi_{\mathrm{SBRIS}} = \mathbf{s} \prod_{i=1}^{N-1} \begin{pmatrix} \mathbf{U}_i^{00} & \mathbf{U}_i^{01} \\ \mathbf{U}_i^{10} & \mathbf{U}_i^{11} \end{pmatrix} \mathbf{t}^{\mathbf{T}} \tag{6}$$

where $\mathbf{s} = (\mathbf{p}\,\mathbf{p})$ and $\mathbf{t} = (\mathbf{q}\,\mathbf{q})$. Note that the SBRIS partition function is obtained from the RIS partition function by replacing

$$\mathbf{U} \to \begin{pmatrix} \mathbf{U} & \mathbf{U}z \\ \mathbf{U} & \mathbf{U}\mathbf{u}z \end{pmatrix} \; ; \; \mathbf{p} \to (\mathbf{p}\,\mathbf{p}) \; ; \; \mathbf{q} \to (\mathbf{q}\,\mathbf{q})$$

It can be easily shown that if some of the matrices in Eqn. (2) does not depend on any index s_i, the proper substitution is

$$\mathbf{U} \to \begin{pmatrix} \mathbf{U} & \mathbf{0} \\ \mathbf{0} & \mathbf{U} \end{pmatrix} \tag{7}$$

which can be necessary for the transfer matrices corresponding to bonds which do not hold any ionizable site.

2 Calculation of the mean square distance between two nodes of the chain

The matrix summation trick used above can also be applied to calculate other physical quantities which become pH-dependent in the SBRIS approach. Let $f(c,s)$ be any quantity and $\langle f\,(c,s)\rangle$ its SBRIS thermal average. Then

$$\langle f\,(c)\rangle = \sum_{s,c} f\,(c)\,\frac{e^{-\beta F(s,c)}}{\Xi_{\mathrm{SBRIS}}} = \sum_s \pi\,(s)\,\left(\sum_c \frac{f(c) e^{-\beta F(s,c)}}{\Xi_{\mathrm{rot}}\,(s)} \right) = \sum_s \pi\,(s)\,\langle f\,(c,s)\rangle_c \tag{8}$$

where

$$\pi\,(s) = \frac{\Xi_{\mathrm{rot}}\,(s)}{\Xi_{\mathrm{SBRIS}}}$$

represents the probability of a protonation state s and $\langle f(c,s)\rangle_c$ is the average for that fixed protonation state. Note now that the quantity between brackets in Eqn. (8) represents a typical RIS average which can be calculated using the (conveniently decorated) transfer matrices $\mathbf{U}_{\mathrm{i}}{}^{s_i s_{i+1}}$. In particular, matricial expressions for the mean square distance between two nodes, k and l, of a linear chain are available [1, 4]. For a fixed ionization state, the result is

$$\left\langle d_{kl}^2 \right\rangle (s) = \frac{2}{\Xi_{\mathrm{rot}}(s)} \mathbf{p} \prod_{i=1}^{k} \mathbf{U}_{\mathrm{i}}{}^{s_i s_{i+1}} [\mathbf{E}\,\mathbf{0}\,\mathbf{0}\,\mathbf{0}\,\mathbf{0}] \prod_{r=k+1}^{l-k} \mathbf{G}_{\mathrm{r}}{}^{s_i s_{i+1}} \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{E} \end{bmatrix} \prod_{j=l+1}^{N-1} \mathbf{U}_{\mathrm{i}}{}^{s_i s_{i+1}} \mathbf{q} \tag{9}$$

where the matrices $\mathbf{G}$ are proper super-matrices which can be expressed in terms of the transfer matrices $\mathbf{U}_{\mathrm{i}}{}^{s_i s_{i+1}}$, the translation matrices and the bond vectors. The details and derivations are given in the Chapter 4 of the classical Flory's book [1] (see Eqn. 35). Introducing (9) in (8) and using the summation (5), $\left\langle d_{kl}^2 \right\rangle$ is calculated as a function of the pH.

3 Minimal symmetric polyelectrolyte model

The model used in this work to illustrate the LEIP method consists of a polyelectrolyte like the one in Fig. 2b. In this molecule the ionizable sites are separated by three bonds **a**, **b** and **c**. The structure is very similar to poly(oxyethylene) and the corresponding transfer matrices are given can be found in [1, 3]

$$\mathbf{U}_{\mathrm{a}} = \begin{pmatrix} 1 & \sigma_a & \sigma_a \\ 1 & \sigma_a\psi & \sigma_a\omega \\ 1 & \sigma_a\omega & \sigma_a\psi \end{pmatrix} ; \mathbf{U}_{\mathrm{b}} = \begin{pmatrix} 1 & \sigma_a & \sigma_a \\ 1 & \sigma_a\psi' & \sigma_a\omega' \\ 1 & \sigma_a\omega' & \sigma_a\psi' \end{pmatrix} ; \mathbf{U}_{\mathrm{c}} = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{pmatrix}$$

The conformational model here used can be obtained by taking $\sigma_a = 0$, which assures that the **a** and **b** bonds are always in the *trans* state, and $\omega = \psi = \omega' = \psi' = 1$, which means that the bonds of the deprotonated molecule are independent.

References

[1] Flory, P. L. *Statistical Mechanics of Chain Molecules*; John Wiley: New York, 1969.

[2] Garces, J. L. ; Koper, G. J. M.; Borkovec, M. Ion binding to polyelectrolytes. *J. Phys. Chem. B* **2006**, *110*, 10937-10950.

[3] Garcés, J. L.; Madurga, S.; Borkovec, M. Coupling of conformational and ionization equilibria in linear poly(ethylenimine): A study based on the site

binding/rotational isomeric state (SBRIS) model. *Phys. Chem. Chem. Phys.*, **2014**, *16*, 4626-4638.

[4] Flory P. J. ; Jernigan R. L. Second and fourth moments of chain molecules. *J. Chem. Phys.* **1965**, *42*, 3509-3519.