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"

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

Let us express the SBRIS partition function as

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

where $\Xi_{\mathrm{rot}}\left(s\right)$ 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. $\Xi_{\mathrm{rot}}\left(s\right)$ adopts the form [1, 2, 3]

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

In the simplest case $\mathbf{U}_i^{00} = \mathbf{U}_i^{10}$; $\mathbf{U}_i^{01} = z \cdot \mathbf{U}_i$ 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

$$\mathbf{u}_i = \begin{pmatrix} u_{\mathrm{t}} & 0 & 0 \\ 0 & u_{\mathrm{g}} & 0 \\ 0 & 0 & u_{\mathrm{g}} \end{pmatrix}_i \tag{4}$$

$-k_{\mathrm{B}}T \ln u_{\mathrm{t}}$ and $-k_{\mathrm{B}}T \ln u_{\mathrm{g}}$ 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

$$\mathbf{U} \to \begin{pmatrix} \mathbf{U} & \mathbf{U}z \\ \mathbf{U} & \mathbf{U}\mathbf{u}z \end{pmatrix} \; ; \; \mathbf{p} \to (\mathbf{p}\,\mathbf{p}) \; ; \mathbf{q} \to (\mathbf{q}\,\mathbf{q}) \tag{7}$$

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

$$\mathbf{U} \to \begin{pmatrix} \mathbf{U} & \mathbf{0} \\ \mathbf{0} & \mathbf{U} \end{pmatrix} \tag{8}$$

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

$$\langle f\,(s, c)\rangle = \sum_{s,c} f\,(s, c)\, \frac{e^{-\beta F(s,c)}}{\Xi_{\mathrm{SBRIS}}} = \sum_s \pi\,(s) \left(\sum_c \frac{f(s, c) e^{-\beta F(s,c)}}{\Xi_{\mathrm{rot}}\,(s)} \right) = \sum_s \pi\,(s)\, \langle f\,(c, s)\rangle_c \tag{9}$$

where

$$\pi\,(s) = \frac{\Xi_{\mathrm{rot}}\,(s)}{\Xi_{\mathrm{SBRIS}}} \tag{10}$$

represents the probability of a protonation state s and $\langle f\left(c,s\right)\rangle_c$ is the average for that fixed protonation state. Note now that the quantity between brackets in Eqn. (9) represents a typical RIS average which can be calculated using the (conveniently decorated) transfer matrices $\mathbf{U}_i{}^{s_i s_{i+1}}$. 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

$$\left\langle d_{kl}^2\right\rangle(s)=\frac{2}{\Xi_{\mathrm{rot}}\left(s\right)}\,\mathbf{p}\prod_{i=1}^{k}\mathbf{U}_{\mathrm{i}}{}^{s_i s_{i+1}}\left[\mathbf{E\,0\,0\,0\,0}\right]\prod_{r=k+1}^{l}\mathbf{G}_{\mathrm{r}}{}^{s_i s_{i+1}}\begin{bmatrix}\mathbf{0}\\\mathbf{0}\\\mathbf{0}\\\mathbf{0}\\\mathbf{E}\end{bmatrix}\prod_{j=l+1}^{N-1}\mathbf{U}_{\mathrm{j}}{}^{s_j s_{j+1}}\mathbf{q} \tag{11}$$

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 (11) in (9) 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 the one of 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

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