# EXACT SOLUTION FOR A FREELY JOINTED CHAIN POLYELECTROLYTE MODEL WITH UP TO NEXT NEAREST NEIGHBOUR INTERACTIONS


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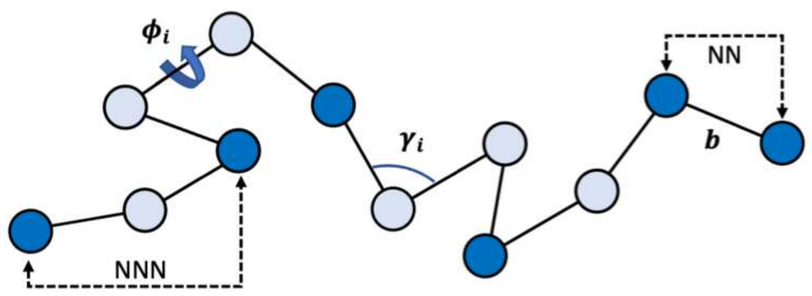
## Schematic representation

- The uncharged weak flexible polyelectrolyte behaves as a Freely Jointed Chain (random coil, $\gamma_i$ and $\phi_i$ can rotate freely) with rigid bonds of fixe length $b$.
- Electrostatic interaccions using the Debye Huckel potential only take place between nearest and next-nearest neighbouring sites.
- As an example we consider the case of a polybase, with association constant $k_i$.




$$R-NH-R+H^+ \rightleftharpoons R-(NH_2^+)-R$$

$$F(s,c)=\mu\sum_i s_i+\varepsilon_{\mathrm{n}}\sum_i s_i s_{i+1}+\sum_i \varepsilon_{\mathrm{nn}}(\gamma_{i+2})\, s_i s_{i+2}$$

## Finite Chain

The partition function of this PE model can be described in terms of the Transfer Matrix methodology due to the Short Range nature of its electrostatic interactions:

$$\Xi=\mathbf{v}_{\mathrm{i}}\tilde{\mathbf{T}}_{\mathrm{nn}}^{N}\mathbf{v}_{\mathrm{f}}^{\mathbf{T}}$$

where

$$\tilde{\mathbf{T}}_{\mathrm{nn}}=\begin{pmatrix}1&0&z&0\\1&0&z\tilde{u}_{\mathrm{nn}}&0\\0&1&0&z\tilde{u}_{\mathrm{n}}\\0&1&0&z\tilde{u}_{\mathrm{n}}\tilde{u}_{\mathrm{nn}}\end{pmatrix}\qquad \tilde{u}_{\mathrm{nn}}=\frac{1}{2}\int_0^{\pi}\exp\left(-\beta\varepsilon_{\mathrm{nn}}(\gamma)\right)\sin(\gamma)\,d\gamma$$

### Degree of ionization

The degree of ionization of the macromolecule is the average number of charged sites divided by the total amount of sites in the chain and weighted by the probability of being in a certain state $s$. Therefore, this quantity can be expressed in terms of the partition function as

$$\theta=\sum_s\theta(s)p(s)=\sum_s\left(\frac{\sum_i s_i}{N}\right)\frac{e^{-\beta F(s)}}{\Xi}=\frac{1}{N}\frac{\partial\ln\Xi}{\partial\ln z}$$

### End to end distance

The end to end distance can also be expressed in terms of the Transfer Matrix methodology and the partition function although the expression is much more complicated. Following geometric relations and using the formalism from Flory, it is possible to find that

$$\langle r^2\rangle=\left\langle\left(\sum_i\vec{b_i}\right)^2\right\rangle=\sum_i b^2+\sum_{i\neq j}\left\langle\vec{b_i}\cdot\vec{b_j}\right\rangle=\sum_i b^2+\sum_{i\neq j}\frac{1}{\Xi}\mathbf{v}_{\mathrm{i}}\left[\tilde{\mathbf{T}}_{\mathrm{nn}}^{(i+1)}\tilde{\mathbf{T}}_{\mathrm{cos}}^{(j-i)}\tilde{\mathbf{T}}_{\mathrm{nn}}^{(N-1-j)}\right]\mathbf{v}_{\mathrm{f}}^{\mathbf{T}}$$

where

$$\tilde{\mathbf{T}}_{\mathrm{cos}}=\begin{pmatrix}0&0&0&0\\0&0&z\langle\cos\gamma\rangle\,\tilde{u}_{\mathrm{nn}}&0\\0&0&0&0\\0&0&0&z\tilde{u}_{\mathrm{n}}\langle\cos\gamma\rangle\,\tilde{u}_{\mathrm{nn}}\end{pmatrix}\qquad \langle\cos\gamma\rangle\,\tilde{u}_{\mathrm{nn}}=-\frac{1}{2}\int_{-1}^{1}\cos\gamma\, e^{-\beta\varepsilon_{\mathrm{i,i+2}}(r(\gamma))}d\cos\gamma$$

$$\frac{\langle r^2\rangle}{(N-1)b^2}=1+\frac{2}{N-1}\sum_{i<j}\frac{1}{\Xi}\mathbf{v}_{\mathrm{i}}\left[\tilde{\mathbf{T}}_{\mathrm{nn}}^{(i+1)}\tilde{\mathbf{T}}_{\mathrm{cos}}^{(j-i)}\tilde{\mathbf{T}}_{\mathrm{nn}}^{(N-1-j)}\right]\mathbf{v}_{\mathrm{f}}^{\mathbf{T}}$$

## Infinite Chain

Considering the limit case in which the number of monomers $N\to\infty$, the previous equations adopt analytical expressions related with the direct $\boldsymbol{a}^{\mathbf{T}}$ and inverse $\mathbf{b}$ *eigenvectors* of the maximum *eigenvalue* ($\lambda_{\max}$) in the matrix $\tilde{\mathbf{T}}_{\mathbf{nn}}$. Then, the partition function and the characteristic properties (degree of ionization and end to end distance) stay

$$\Xi=\mathbf{v}_{\mathrm{i}}\tilde{\mathbf{T}}_{\mathrm{nn}}^{N}\mathbf{v}_{\mathrm{f}}^{\mathbf{T}}=\lambda_{max}^{N}\mathbf{v}_{\mathrm{i}}\mathbf{a}^{\mathbf{T}}\mathbf{b}\mathbf{v}_{\mathrm{f}}^{\mathbf{T}}$$

### Degree of ionization

$$\theta=\theta_c=\frac{\partial\ln\Xi}{\partial\ln z_c}=\frac{1}{\lambda_{max}}\mathbf{b}\frac{\partial\tilde{\mathbf{T}}_{\mathrm{nn}}}{\partial\ln z_c}\mathbf{a}^{\mathbf{T}}=\frac{1}{\lambda_{max}}\left[a_3\left(b_1z+b_2z\tilde{u}_{\mathrm{nn}}\right)+a_4\left(b_3z\tilde{u}_{\mathrm{n}}+b_4z\tilde{u}_{\mathrm{n}}\tilde{u}_{\mathrm{nn}}\right)\right]$$

### Interaction Functions

$$\varphi_{\bullet\bullet\circ}=(\varphi_{\bullet\bullet\circ})_c=\frac{1}{\lambda_{max}}\left[a_4b_3z\tilde{u}_{\mathrm{n}}\right]$$

$$\varphi_{\bullet\circ\bullet}=(\varphi_{\bullet\circ\bullet})_c=\frac{1}{\lambda_{max}}\left[a_3b_2z\tilde{u}_{\mathrm{nn}}\right]$$

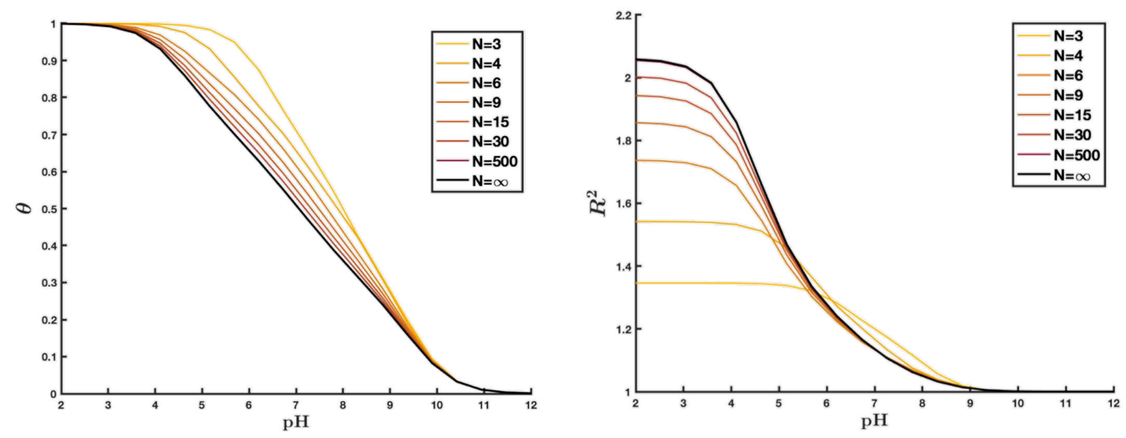
$$\xi_{\bullet\bullet\bullet}=(\xi_{\bullet\bullet\bullet})_c=\frac{1}{\lambda_{max}}\left[a_4b_4z\tilde{u}_{\mathrm{n}}\tilde{u}_{\mathrm{nn}}\right]$$

### End to end distance

$$\frac{\langle r^2\rangle}{(N-1)b^2}=1+2\langle\cos\gamma\rangle\left[\varphi_{\bullet\circ\bullet}+\frac{1}{1-\alpha}\xi_{\bullet\bullet\bullet}\right]\quad with\quad \alpha=\left(z\tilde{u}_{\mathrm{n}}\langle\cos\gamma\rangle\,\tilde{u}_{\mathrm{nn}}\right)/\lambda_{max}$$

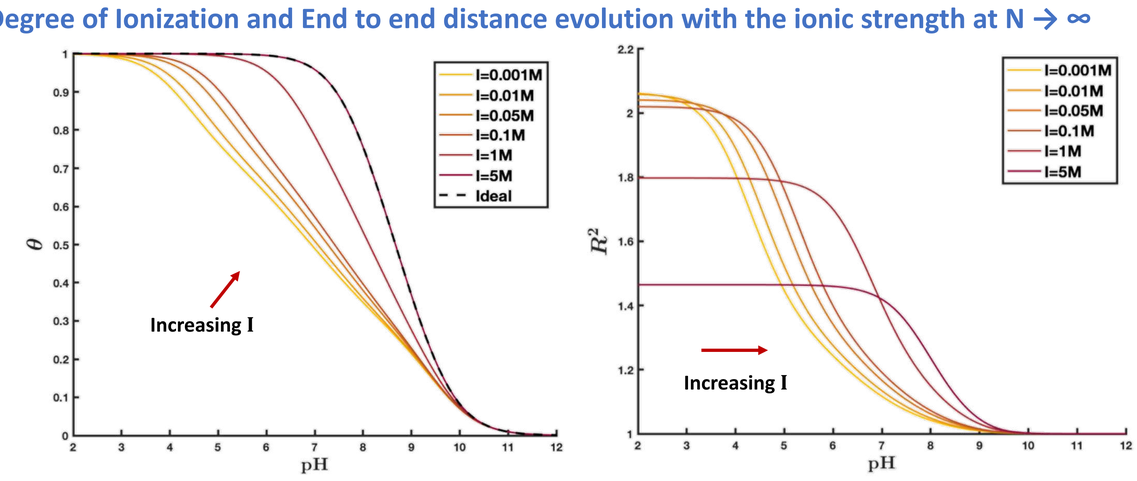
## Results

### Degree of Ionization and End to end distance evolution with the number of sites N at I=0.01M




- At high values of $N$, the behaviour of the finite chain is equivalent to that of the infite chain as expected.
- At low values of $N$ the chain tends to be more charged although it is proportionally less elongated in comparison to the freely jointed chain end to end distance.

### Degree of Ionization and End to end distance evolution with the ionic strength at N → ∞




- At high values of $I$, the electrostatic interactions become shielded and the ideal degree of ionization is recovered again.
- At low values of $I$ the chains extend more due to the electrostatic interactions as expected.

## Conclusions & Future Prospects

- ✓ The most interesting aspect of this model is that it allows excact expressions for the degree of ionization and the end to end distance.This expressions become analytic for the infinite case.
- ✓ There is a great confluence of the finite chain model to the infinite one for $N\approx 500$, meaning that at that point end effects are totally negligible. This information can be interesting at the design of simulation scales.
- ✓ Further research is being carried out in relation with ampholyte polelectrolytes and competition between proton binding and metal binding processes.

## Bibliography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