INTERPRETATION OF SINGLE-MACROMOLECULE FORCE-EXTENSION CURVES USING A TWO-ELONGATION-STATE FEJC MODEL WITH NEAREST-NEIGHBOUR INTERACTIONS

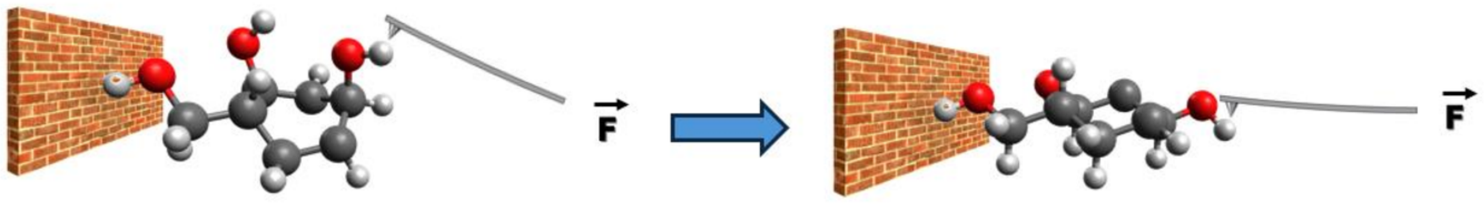
Javier Orradre[1], Pablo M. Blanco[2], Sergio Madurga[1], Maria I. Giannotti[1,3], Francesc Mas[1], Josep L. Garcés[2]

1. Department of Materials Science and Physical Chemistry & IQTC, Faculty of Chemistry, Universitat de Barcelona, Barcelona, Spain.
2. Department of Chemistry, Physics and Environmental and Soil Sciences & Agrotecnio, Universitat de Lleida, Lleida, Spain.
3. Institute for Bioengineering of Catalonia (IBEC), Nanoprobes & Nanoswitches group, Barcelona, Spain

j.orradre@ub.edu

Two-Elongation-State FEJC Model with NN interactions

Conformational changes in polymer chains can be induced by the application of an **external force**. These conformational changes arise either from the **rearrangement of the macromolecular backbone** (dihedral angles rotation, hydrogen bonding, supra-structures, etc.) or due to the **binding of external ligands** present in the surrounding media [1]. In this study we provide some exact results based on the freely elastically jointed chain (FEJC) model where the chain fragments interact at the nearest neighbour level.



Free energy in the two-elongation-state FEJC model

$$F(\{s_i, m_i\}) = -\sum_{i=1}^{N} f \cdot m_i\left[a_{i,0}(1-s_i) + a_{i,1}s_i\right] + \sum_{i=1}^{N} \mu\, s_i + \\ + \sum_{i=1}^{N-1} \varepsilon\, s_i s_{i+1} + \sum_{i=1}^{N}\left[\frac{k_0}{2}(a_{i,0}-a_0)^2(1-s_i) + \frac{k_1}{2}(a_{i,1}-a_1)^2 s_i\right]$$

Systems with **Short Range (SR) interactions** can be exactly solved using the **Transfer Matrix Method** [2,3], since the partition function can be expressed as **a linear recurrence relation:**

$$\Xi = \mathbf{v_i}\mathbf{T}^N\mathbf{v_f^T}$$

where the **transfer matrix T** relates the partition function of N sites/bonds to that of the $N-1$ sites/bonds in the following manner [4]

Site N

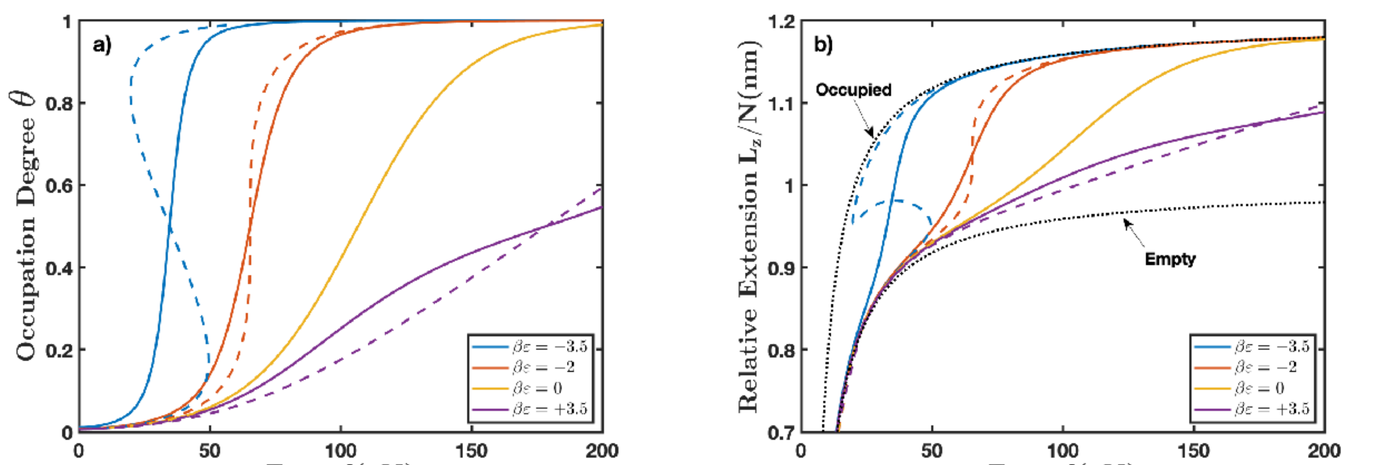
$$\mathbf{T} = \begin{array}{c} \text{Site } N-1 \\ \begin{matrix} \bigcirc \\ \bigcirc \end{matrix} \end{array} \begin{pmatrix} q_0 & q_1 z \\ q_0 & q_1 z u \end{pmatrix}$$

$$z = e^{-\beta\mu}$$

$$u = e^{-\beta\varepsilon}$$

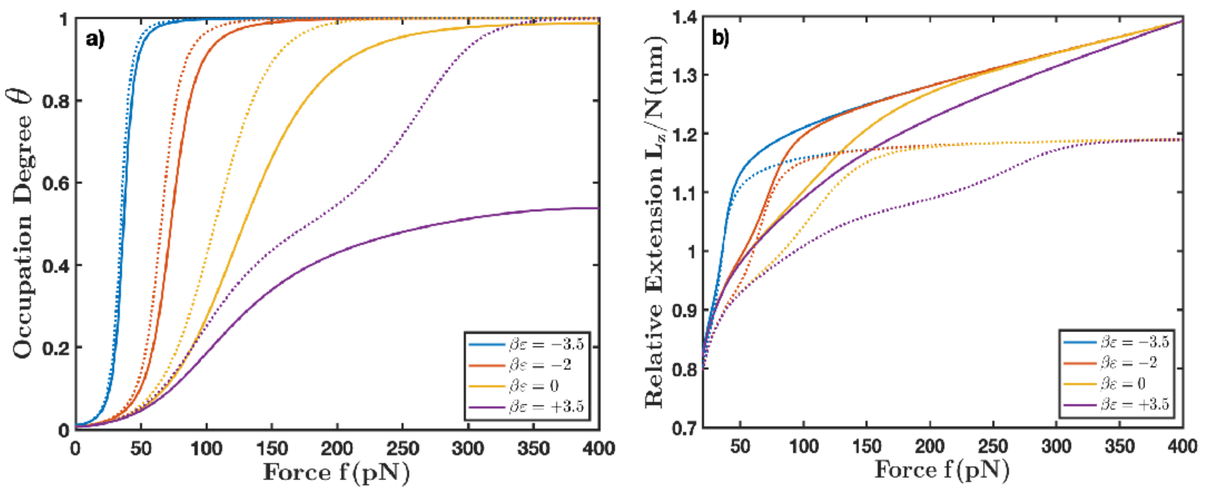
with q_0 and q_1 the partition functions of the empty and occupied sites/bonds respectively. without considering binding which is treated separately through z and u.

Comparison: Exact vs Mean-Field solution [5]

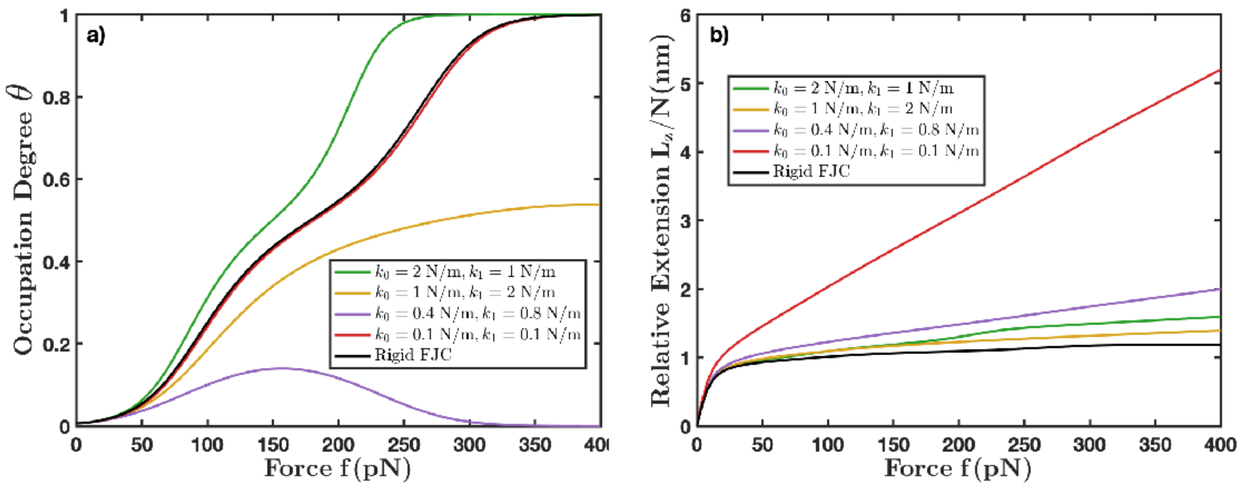


Elastic Regime

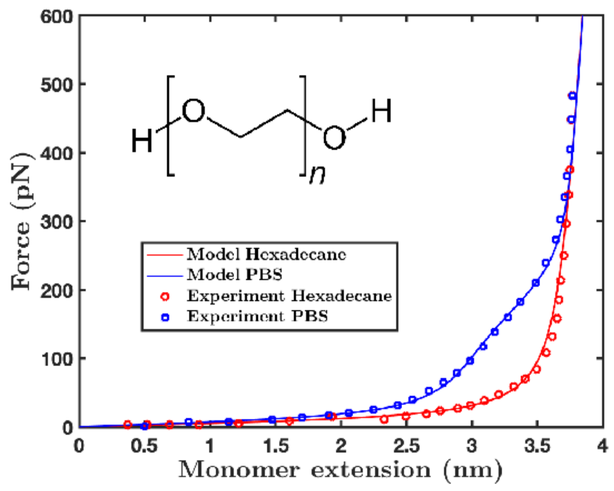
Comparison: Rigid vs Elastic Behaviour



Effect of the spring constants relation



Experimental Implementation



PEG: Poly(ethylene-glyclol)

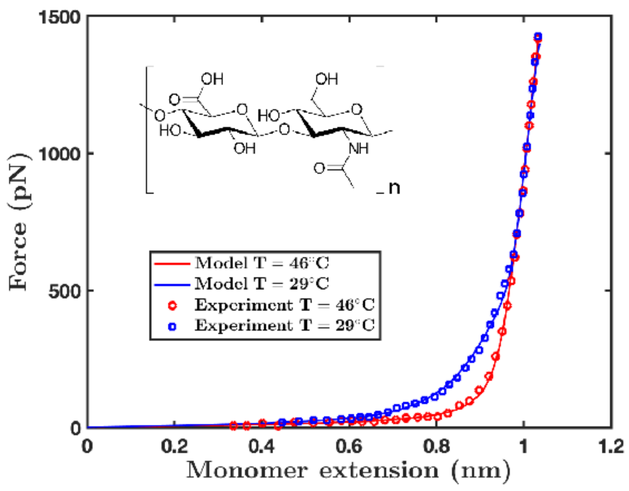
Poly(ethylene-glycol) is widely used in the chemical and medical industry due to its extensive variety of applications and low toxicity. **With hexadecane no hydrogen bonding is present** and only one type of fragment is considered [6].

PEG Data
- $\beta\mu = -5,5\ \mathrm{k_B T}$
- $\beta\varepsilon = 0\ \mathrm{k_B T}$
- $a_0 = 0,72\ \mathrm{nm}$
- $a_1 = 0,60\ \mathrm{nm}$

HA: Hyaluronic Acid

Hyaluronic Acid (HA) is a natural polysaccharide which acts as the cornerstone of many cosmetic and medical products. **At high temperature no hydrogen bonding is present** and only one type of fragment is considered [7].

HA Data
- $\beta\mu = -7\ \mathrm{k_B T}$
- $\beta\varepsilon = -2,3\ \mathrm{k_B T}$
- $a_0 = 0,60\ \mathrm{nm}$
- $a_1 = 0,49\ \mathrm{nm}$



Conclusions

- The two-elongation-state FEJC model is capable of describing conformational changes due to the arrengement of the macromolecule or due to ligand binding on the same footing.
- The transfer matrix methodology allows the introduction of NN interactions in an exact way, solving the unexpected behaviour of the mean-field solution from Radiom & Borkovec [5].
- The model shows almost a perfect fitting to the experimental data and provides inspiring information of the macromolecule mechanical behaviour. Also, the consideration of the FEJC fragment type allows a trustworthy description of the elastic regime.

Bibliografia

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