

The influence of mechanical stretching on the properties of a weak polyelectrolyte

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Introduction

Weak polyelectrolytes are usually molecules with a certain degree of flexibility that can regulate their charge under the influence of external stimuli, such as electrostatic interactions with charged species, mechanical stress or variations in the ionic strength of the environment [1]. Due to this, the conformational degrees of freedom are strongly linked to ionization: if the protonatable groups change their charge, the electrostatic interactions of the molecule will suffer modifications, forcing the molecule to adopt new, more stable conformations.

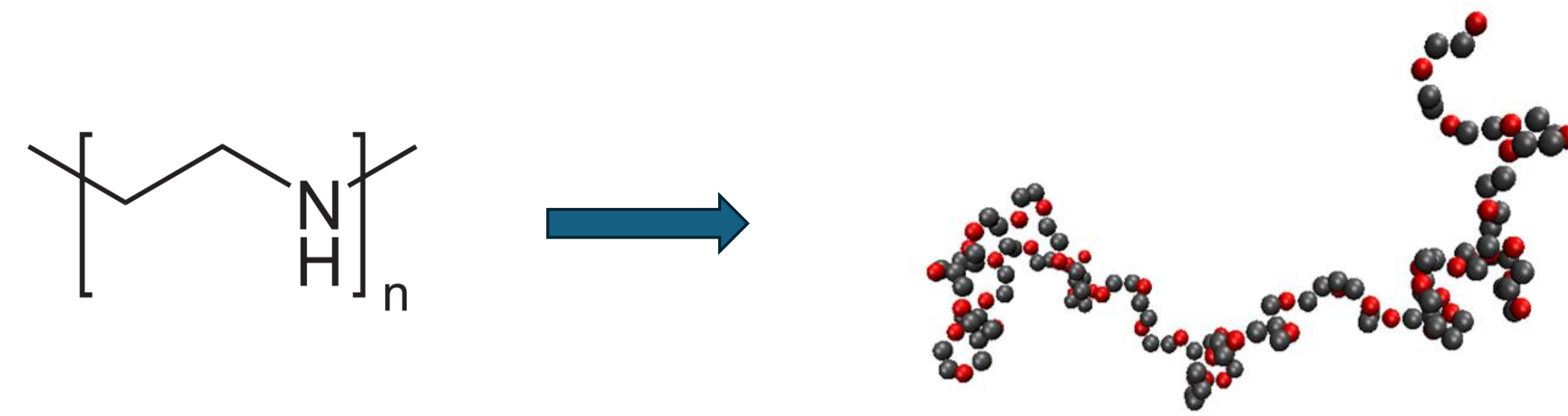
In this work, an effort has been made to understand the mechanical response of linear polyethyleneimine (LPEI) and how mechanical stretching is related to the charge regulation phenomenon through computational simulations [2], with sufficient simulation time to obtain significant results. Since the simulations of systems on long time scales are limited by the amount of computational resources, it is necessary to develop a coarse-grained model to reduce the degrees of freedom of the system.

The following objectives are highlighted:

- Generate coarse-grained models to simulate an ideal chain (FJC) and a freely rotating chain (FRC) of LPEI.
- Develop a computational protocol that allows to simulate the dynamic evolution of the system while the titration curves of the protonatable groups are performed.
- Compare the different properties of interest between models.

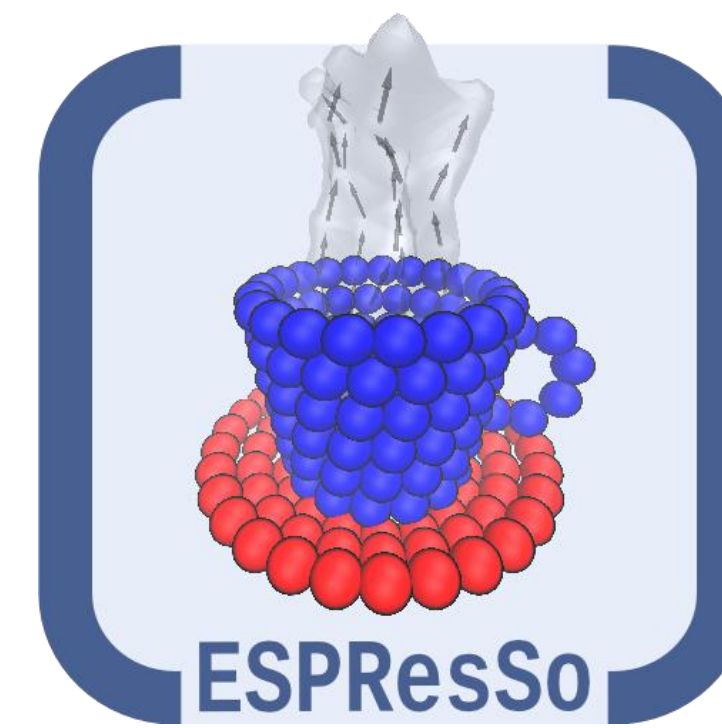
Computational methodology

Coarse-Grained model



A coarse-grained bead is incorporated per every group.

Computational simulations



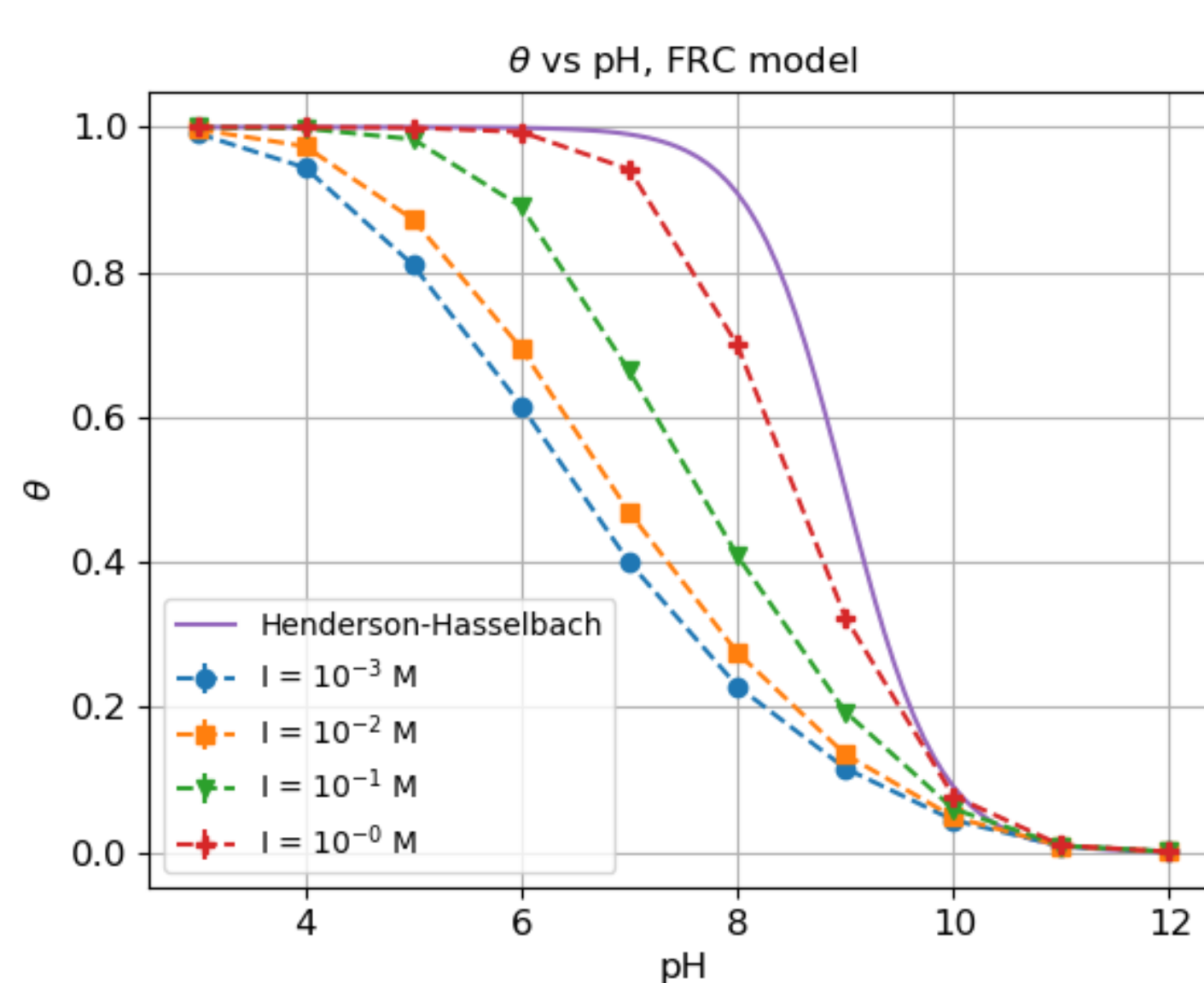
Two simulation approaches were implemented using Langevin dynamics combined with the constant pH method. The first simulates varying ionic strengths across 10 pH values without mechanical stretching. The second explores different stretching forces at a fixed ionic strength for 4 pH values, utilizing the ESPResSo software package [3].

During the simulation, various parameters are calculated, such as:

- Degree of protonation: $\theta = \frac{\langle N_+ \rangle}{N}$
- Elongation: $\frac{L_z}{L_c} = \frac{L_z}{N \cdot l} = \frac{L_z}{N \cdot l \cdot \cos((\pi - \alpha_0)/2)}$
- Radius of gyration: $R_g^2 = \frac{1}{2(N_b+1)^2} \sum_{i,j=1}^{N_b+1} \langle r_{ij}^2 \rangle$
- End-to-end distance: $\langle r^2 \rangle = \langle (\sum_{i=1}^{N_b} \vec{l}_i)^2 \rangle$

Results

Without mechanical stretching



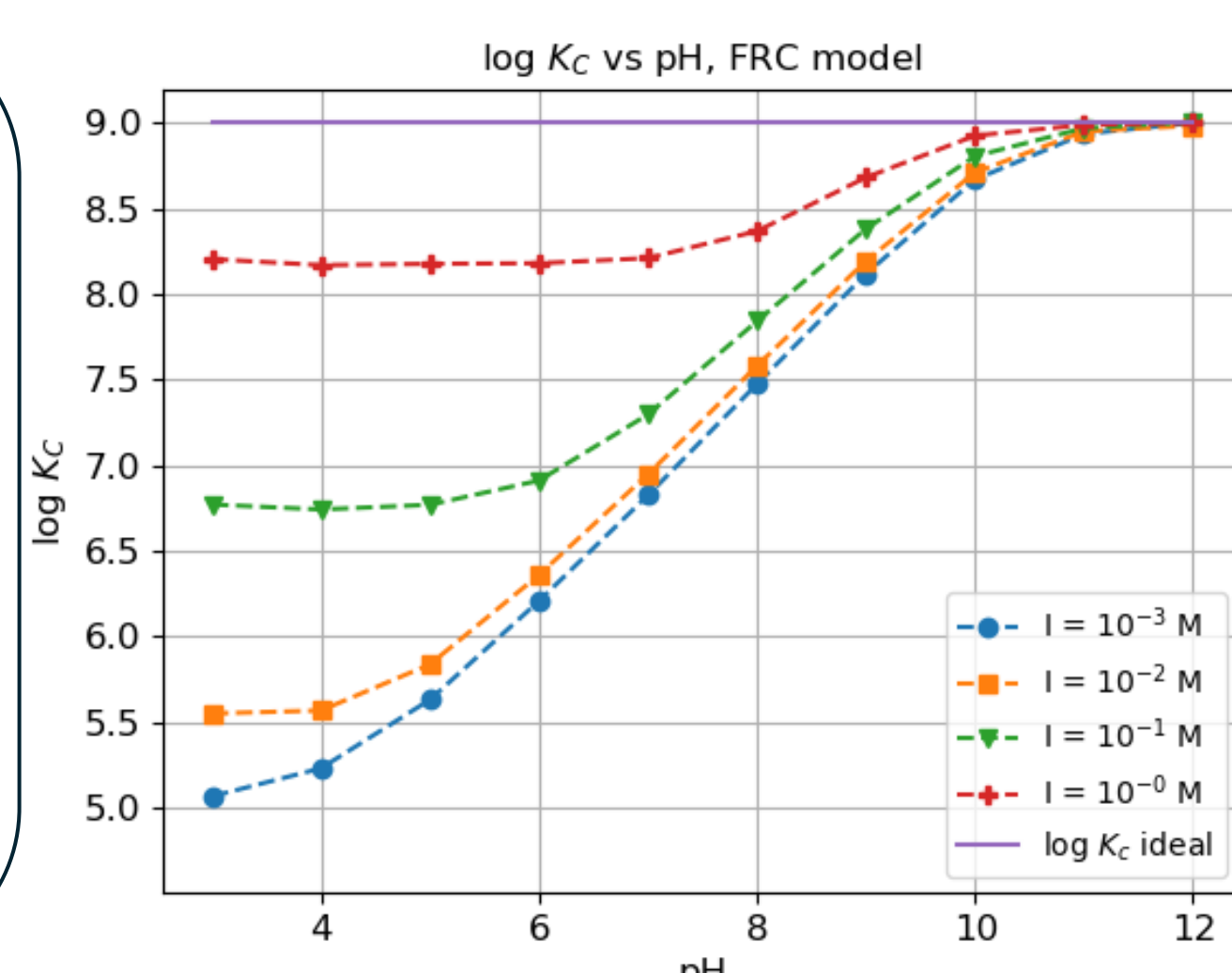
Degree of protonation with respect to pH at different ionic strengths. The Henderson-Hasselbach curve corresponds to:

$$\theta_{\text{ideal}} = \frac{1}{1 + 10^{\text{pH} - \text{p}K_a}}$$

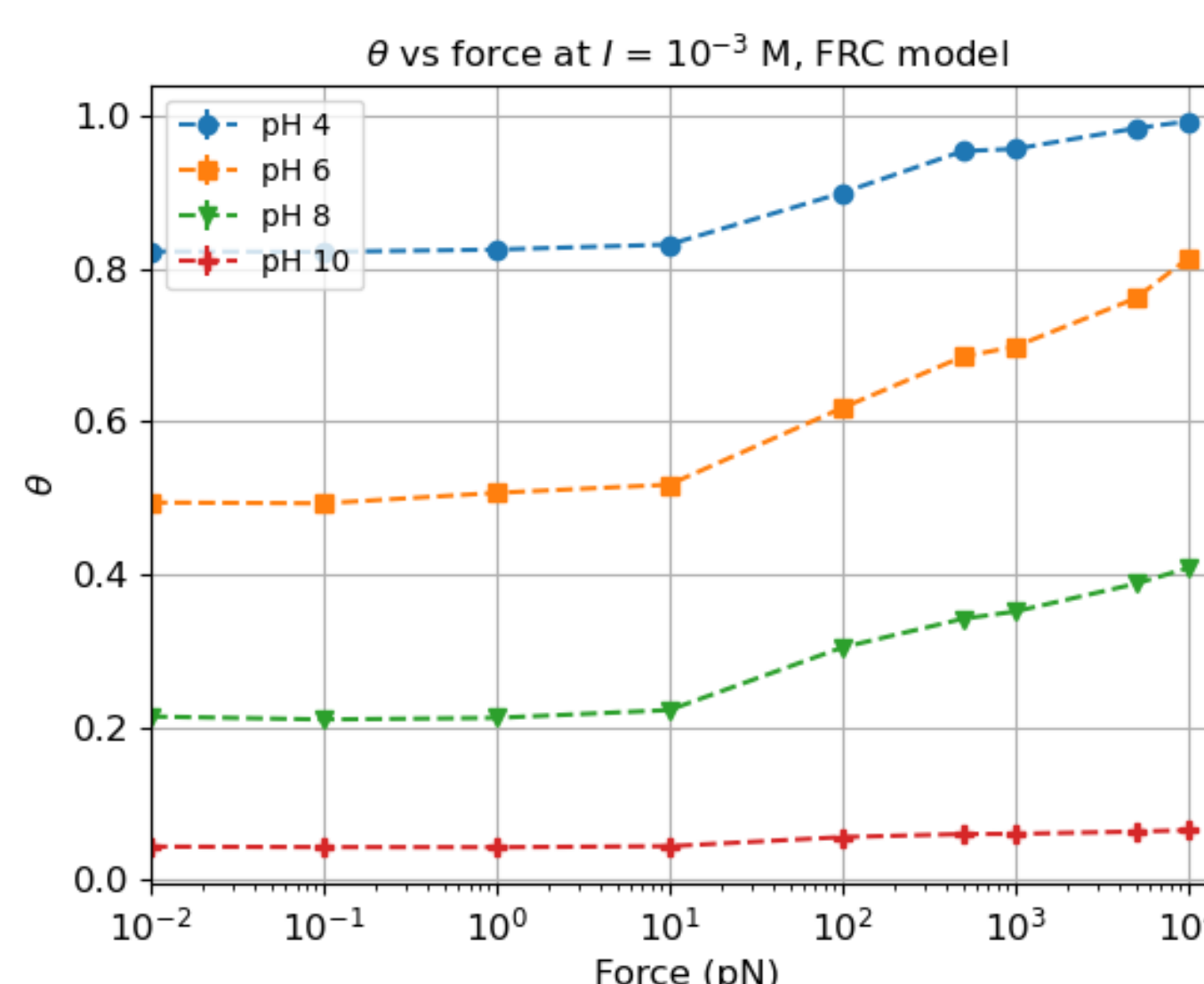
At greater ionic strengths, the results shift closer to ideal values due to the shielding of electrostatic repulsions.

Effective protonation constant of the system: $\log K_c = \text{pH} + \log\left(\frac{\theta}{1-\theta}\right)$

At lower pH values, the protonatable groups become ionized, increasing the work required to protonate the system due to electrostatic repulsions, resulting in lower values of K_c .



Under mechanical stretching

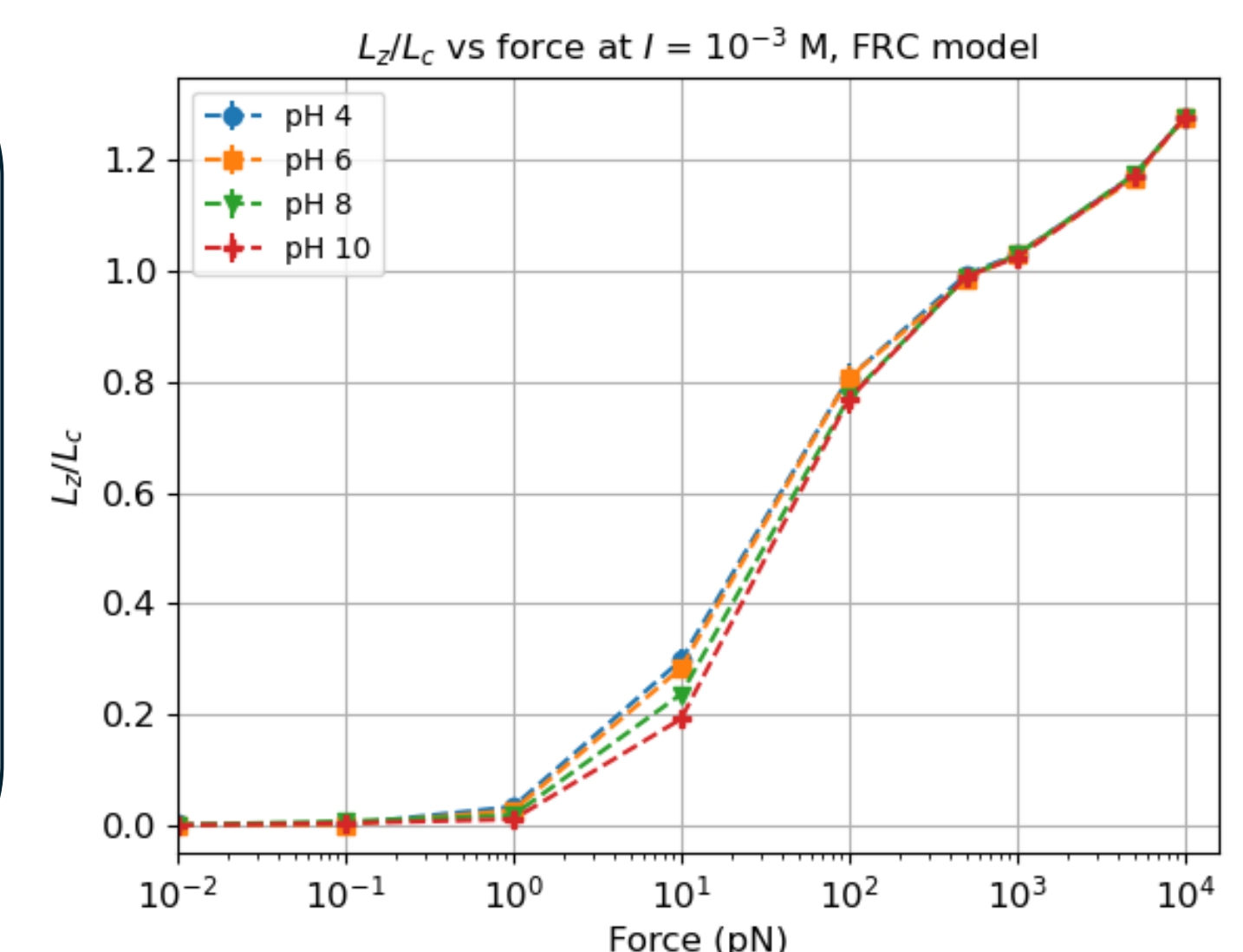


Degree of protonation with respect to applied force, with mechanical stretching forces between 10⁻² pN and 10⁴ pN.

It is observed how, as the stretching force is stronger, it is easier to protonate the system, since the charges will be further apart.

Elongation of the polymer in the direction of the force with respect to the applied force.

An interesting behaviour is observed. There is a coupling between conformational and protonation degrees of freedom between 1 pN and 100 pN.



Conclusions

- Overall, charge regulation is strongly linked to mechanical stretching, changes in the ionic strength of the environment, and changes in pH.
- When a stretching force is applied, the polyelectrolyte adopts more elongated conformations, reducing long-range repulsion and facilitating group protonation.
- A higher ionic strength of the environment implies more shielding in the protonatable groups, resulting in systems closer to ideal behaviour.

References

- [1]: Blanco. P.M., Narambuena. C.F., Madurga. S., Mas. F., Garcés. J.L., *Polymers*, **2023**, 15, 2680.
- [2]: Blanco. P.M., Madurga. S., Mas. F., Garcés. J.L., *Macromolecules*, **2019**, 52, 8017-8031.
- [3]: Weik. F., Weeber. R., Szuttor. K., Breitsprecher. K., de Graaf. J., Kuron. M., Landsgesell. J., Menke. H., Sean. D., Holm. C., *Eur. Phys. J. Spec. Top*, **2019**, 227, 1789-1816.