Exact model for conformational transitions in macromolecules under mechanical stretching

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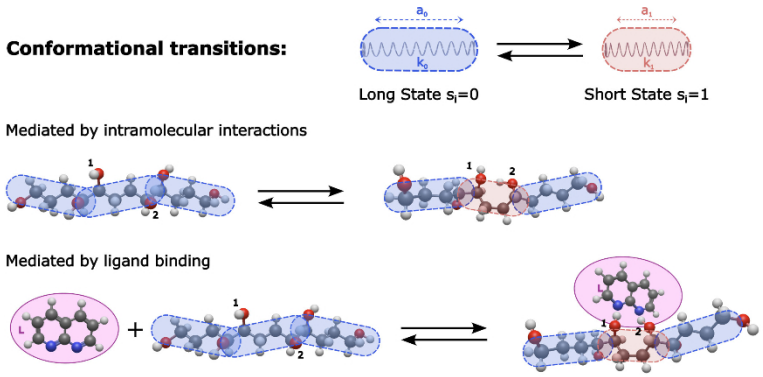
Conformational transitions are central to explain the mechanical properties of macromolecules and biopolymers. However, standard polymer models such as the freely jointed chain and worm-like chain neglect internal conformational degrees of freedom, limiting their ability to capture force-induced structural changes.
Here [1], we present an exact statistical-mechanical solution of a minimal two-state model within the elastic freely jointed chain (EFJC) framework [2]. Each segment can adopt two conformations with different Kuhn lengths and elastic constants, coupled through nearest-neighbor interactions that account for cooperativity (*cf* . Fig. 1). Using transfer-matrix methods, we obtain closed analytical expressions for the force–extension relation and state populations, ensuring thermodynamic consistency and avoiding the spurious phase transitions of mean-field approaches.
The model quantitatively reproduces experimental force-extension curves across different systems. Poly(ethylene glycol) displays non-cooperative behavior, hyaluronic acid exhibits a temperature-dependent transition with negative cooperativity, and DNA overstretching shows strong positive cooperativity. These results demonstrate that the framework captures a wide range of experimentally observed responses within a unified description.
We further identify the mechanisms underlying force-induced transitions, which arise from differences in Kuhn lengths, elastic constants, or their combination. The formalism can be extended to multistate systems, enabling the description of ligand–receptor interactions and competitive binding under mechanical load.

Keywords:
polymers, mechanical stretching, polymer theoretical modelling, single molecule experiments, AFM.



Two-state EFJC model: chain segments switch between conformations with different lengths and stiffness, including cooperative interactions.

References:

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