Ensemble inequivalence in the elasticity of semiflexible polymers with reversible spontaneous curvature

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Previous work has shown that finite bistable or multistable polymer systems, away from the thermodynamic limit, may exhibit statistical ensemble inequivalence in their elastic response: the Gibbs and Helmholtz ensembles yield different force-deformation relations. In practice, this means that the measured elasticity depends on the experimental control protocol, e.g., fixed force versus fixed extension. Such behavior is known for polymers with reversible, locally fluctuating bending stiffness, as described by the reversible freely jointed chain (rFJC) [1,2], or the reversible wormlike chain (rWLC) [3,4]. Similar behavior has also been predicted for looping-linear and zipped-unzipped polymers [5]. Here, we identify a different mechanism for the same phenomenon: reversible spontaneous curvature.

We formulate a two-state modified wormlike chain (WLC) model in two dimensions, in which the polymer switches between an uncurved state and a curved state with spontaneous curvature. Reversible spontaneous curvature may arise through internal conformational changes, such as a helix–coil transition, or through external mechanisms such as ligand attachment/detachment or reversible hybridization. Two representative settings are studied: (i) a stretched polymer with either constant or sinusoidal spontaneous curvature and (ii) a grafted polymer subject to a bending torque applied at its free end.

For the stretching problem, we build on the force-extension relation from [6] for a polymer with a prescribed spontaneous curvature and extend it to a two-state description. The curved state is treated as an athermal curved branch, while thermal fluctuations are retained only in the uncurved branch to simplify our analytic calculations. Within a weak-bending approximation, this yields analytical partition functions in both Gibbs and Helmholtz ensembles and explicit expressions for the mean extension, the mean force, and the occupation probability of the curved state. For the bending torque problem, we introduce a coarse-grained effective Hamiltonian in terms of the tip angle and derive the corresponding Gibbs and Helmholtz partition functions, torque-angle relations, and state occupancies.

In the stretching setting, the theory predicts a crossover from a curvature-dominated regime at low force to an entropy-dominated regime at strong stretching, together with a progressive suppression of the probability of the curved state. In the bending torque setting, the two ensembles produce distinct torque-angle response curves, yielding ensemble inequivalence. Our results demonstrate that reversible spontaneous curvature alone is sufficient to induce ensemble inequivalence in semiflexible polymers, even in the absence of any difference in the value of bending stiffness between states. The theory provides an analytical framework for comparing single-polymer measurements on related systems performed under different control protocols.

References:

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