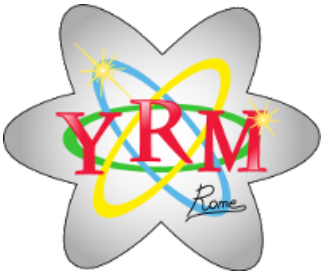

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Gibbs and Helmholtz ensembles for flexible and semiflexible polymers with elastic bonds

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Stretching experiments on arbitrarily long single molecules opened the way for studying the statistical mechanics of small systems. In many cases in which the thermodynamic limit is not satisfied, different macroscopic boundary conditions, corresponding to different statistical mechanics ensembles, yield different macroscopic force-displacement curves, or constitutive equations. We formulate analytical expressions to quantitatively evaluate the difference between the behaviour of the Helmholtz and the Gibbs ensembles for a wide range of polymer models of biological relevance, including generalization of the freely jointed chain model and of the worm like chain model with extensible bonds.

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