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A new force–extension formula for stretched macromolecules and polymers based on the Ising model

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HIGHLIGHTS

- A new force–extension formula taking into account of external effects is derived using an idea from Ising model.
- This formula is fitted with experimental data with and without conformational changes, and shows a good agreement.
- A Monte Carlo simulation is used to demonstrate a possible theoretical extension for the present model.

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ABSTRACT

In this paper, we derive a new force–extension formula for stretched macromolecules and homogeneous polymer matrices. The Ising model arising from paramagnetism is employed, where the magnetic force is replaced by the external force, and the resistance energy is addressed in this model instead of the usual persistent length arising from the freely jointed chain and worm-like chain models. While the force–extension formula reveals the distinctive stretching features for stretched polymers, the resistance energy is found to increase almost linearly with the external force for our two polysaccharides stretching examples with and without ring conformational changes. In particular, a jump in the resistance energy which is caused by a conformational transition is investigated, and the gap between the jump determines the energy barrier between two conformational configurations. Our theoretical model matches well with experimental results undergoing no and single conformational transitions, and a Monte Carlo simulation has also been performed to ensure the correctness of the resistance energy. This technique might also be employed to determine the binding energy from other causes during molecular stretching and provide vital information for further theoretical investigations.

1. Introduction

Scanning electron microscope (SEM) [1], atomic force microscope (AFM) [2,3] and optical tweezers [4] are the three most powerful tools to probe the surface topology at micro and nano scales. In particular, for AFM, it can be used to scan non-conducting surfaces and therefore forms an indispensable tool for molecular and biological research. A force–extension curve for stretched bio-macromolecules could be obtained by scrutinizing the electronic signal generated by AFM, where Butt et al. [2] provide an excellent review on the force–extension measurements and theoretical treatments using AFM. Force–extension relation offers important mechanical information for stretched macromolecules and polymers. The freely

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jointed chain (FJC) model [5] and the worm-like chain (WLC) model [6,7] are the two most common and basic models for determining force–extension formula from stretching a macromolecule, and a good account for both models can be found in Storm and Nelson [5].

FJC model discretizes the molecule into unbendable and straight segments of length a which can be freely rotated around the joints between each segment. Assuming $\hat{\mathbf{t}}_\mathbf{i}$ be a unit orientation vector for each ith segment and an external force of strength F is applied on the $\hat{\mathbf{z}}$ direction, the energy functional for the molecular chain, E^{FJC} is given by

$$E^{EJC} = -\sum_{i=1}^{N}(Fa)\hat{\mathbf{t}}_\mathbf{i}\cdot\hat{\mathbf{z}},$$

where N denotes the total number of segments. Upon reducing its conformational entropy subject to the external force F, the force–extension formula becomes [5]

$$\left\langle\frac{Z}{L}\right\rangle = \coth\left(\frac{Fa}{k_BT}\right) - \frac{k_BT}{Fa}, \tag{1}$$

where k_B, T, Z and L denote the Boltzmann constant, the temperature, the total extension and the total contour length, respectively. We comment that Eq. (1) does not involve any external effects (apart from the external force) on the molecular stretching process. Recently, several attempts have been made to seek an exact solution using the FJC model with additional external effects [8,5] and such solutions could provide a sound mathematical grounding for incorporating ring conformational transitions, from which each segment can be easily scaled with a designated monomer length. On the other hand, the WLC model assumes macromolecule to be isotropic and homogeneous rod, and the energy functional, E^{WLC} is given by

$$E^{WLC} = \int_0^L \left\{\frac{A}{2}\left|\frac{\mathrm{d}\hat{\mathbf{t}}(\mathbf{s})}{\mathrm{d}s}\right|^2 - F\hat{\mathbf{t}}(\mathbf{s})\cdot\hat{\mathbf{z}}\right\}\mathrm{d}s,$$

where A, $\mathrm{d}s$ and $\hat{\mathbf{t}}(\mathbf{s})$ denote the bending stiffness of the chain, the length element and the unit tangential vector, respectively. Upon minimizing a partition function involving such energy functional, the interpolated force–extension formula becomes [9]

$$F = \frac{k_BT}{\ell_p}\left[\frac{1}{4}\left(1-\frac{Z}{L}+\frac{F}{A}\right)^{-2} + \frac{Z}{L} - \frac{F}{A} - \frac{1}{4}\right], \tag{2}$$

where ℓ_p denotes the persistence length of the chain. WLC model takes into account the bending resistance which is entirely ignored in the FJC model.

In this paper, we take the advantages of both models and describe the problem using a discrete model. We introduce the resistance energy for each monomer so that the individual chain's probability distribution and bending resistance due to external effects are considered. A new simple force–extension formula for such stretched macromolecules and polymers is also deduced using the idea of Ising model. The major contribution of the present paper is that the formula maps experimental data from the real space into the energy space so that any conformational and molecular transitions can be reflected by the changes in resistance energy.

The Ising model has successfully been used to describe the magnetization for paramagnets [10]. This model comprises discrete variables that represent the magnetic dipole moment of atomic spins that can be only taken in either spin up $(+1)$ or spin down (-1) states. Here, we employ the idea of the Ising model, however, an infinite rotational freedom for each monomer is considered. In addition, the external applied force, instead of the magnetic field, is used to overcome the resistance energy acting on each monomer at the thermal equilibrium. We comment that the resistance energy opposes the stretched molecules from being aligned in the same direction of the applied force. The current model deduces the resistance energy for stretched molecules upon fitting with experiential data, and the gap for the jump in the resistance energy corresponds well with the energy barrier for a conformational transition. Hence, the resistance energy provides vital information for the topological changes in molecular structure and the background interactions which are crucial for undertaking further theoretical studies using molecular dynamics simulations or Monte Carlo simulations.

In Section 2, basic theory is introduced, followed by experimental methods, numerical analysis and discussion in Section 3. The conclusion is made in the last section.

2. Theory

In this section, the theoretical basis is derived where a single macromolecule with N monomers is stretched by an external force in the z-direction (see Fig. 1 for details). The total extension, Z for a polymer could be written as

$$Z = N_+a + N_-a\langle\cos\theta\rangle = NaP(N_+) + Na\langle\cos\theta\rangle P(N_-) \tag{3}$$

where N_+, N_-, a, $\langle\cos\theta\rangle$, $P(N_+)$ and $P(N_-)$ denote the number of monomers which are pointing in the same direction as the external force in the z-direction, the number of monomers which offsets from the z-direction, the unit length of monomers,