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In-plane force–extension response of a polymer confined to a surface

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ABSTRACT

The force–extension response of synthetic polymers and biomolecules governs properties such as bulk elasticity of rubbery materials and the behavior of DNA and several filamentous proteins. In several cases, such as DNA adsorbed on a plasma membrane, or polymers adsorbed onto a hard material, the molecule is confined to two dimensions as it extends under external forces (e.g., due to applied electric field). However, the force response in two dimensions is relatively poorly-studied. In this paper, we present closed-form analytical expressions for the two-dimensional force–extension response of a freely-jointed chain under force control. Our principal results relate end-to-end distance to total force under two modes of stretching: (i) when force is applied only to the free end of the chain, and (ii) when the applied force is distributed uniformly throughout the chain. In both cases, we further propose explicit approximate expressions for force in terms of extension. Analytical results have been verified by Brownian dynamics simulation. We also show that the distributed force model agrees well with experimental measurements of stretching surface-adsorbed DNA by an electric field.

1. Introduction

It is well known that the elastic and viscoelastic behavior of polymers derives from the force–displacement response of individual macromolecules [1]. Systems where elastic stretching of macromolecules occurs in three-dimensional (3D) settings are common and well-studied. Systems where polymer molecules are confined to a surface are important but less frequent and, perhaps for this reason, there are far fewer studies of stretching a molecule in two-dimensions.

For biological macromolecules such as DNA and polypeptides, the mechanical behavior of individual molecules plays an important physiological role. For this reason, numerous experimental studies have examined the 3D stretching of macromolecules via the use of atomic force microscopy and optical or magnetic tweezers [2–4], electrophoretic stretching of DNA in uniform electric fields or flow [5,6], stretching of DNA under alternating current field [7,8], hydrodynamic focusing of multiple streams, and the effect of velocity gradient created by hydrodynamic flow in contracting and expanding channels [9,10]. To complement the experimental findings that assess the 3D stretching of a polymer, many theoretical models [11–15] have been developed and computer simulations conducted using molecular dynamics and Monte Carlo approaches [11,12,16,17]. Models range in complexity from the simple freely-jointed chain (FJC) and worm-like chain (WLC) [12,16,17], to all-atom representations in molecular dynamics [18]. Simpler models, such as the FJC and WLC, are particularly useful for interpretation and quantification of experiments by providing explicit closed-form relationships between force and extension of the molecule. For

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example, it is well-known that the stretching of the freely jointed chain under force control is governed by the Langevin function [16,17], and a similar approximate force–extension relationship is available for the worm-like chain [12]. Similarly, exact expressions relating force required to peel an FJC or a WLC from a substrate have been obtained [19–21]. However, much less work has been conducted on either analytical or the numerical aspects of stretching a chain-like molecule in 2D.

While long polymers with moderate or weak binding to a surface usually adsorb as brushes, there are several cases of relatively short polymers with sufficiently strong adsorption to result in essentially 2D conformations. For example, 2D stretching of polymers occurs in systems such as polymers confined to the air–water interface [22] and combing of molecules via a meniscus alignment technique [23,24]. In micro and nanofluidic systems, the transport of biopolymers such as DNA, RNA, and peptides has led to advances in gene and restriction mapping [25–29]. The stretching of biopolymers that are strongly adsorbed on a surface with one end fixed is often observed in systems involving separation of biomolecules via nanopillars and nanochannels [30–35].

Brownian dynamics simulations and partially directed walk models [36–38] have been used to study the pulling of surface-adsorbed polymeric molecules parallel to the surface. These studies show that external forces applied parallel to the molecule enhance the stiffness of the molecule, favoring its adsorption to the surface. In a study by Maier et al., the 2D stretching response of DNA to an external electric field was investigated by tethering one end of the molecule and confining the entire molecule to the surface of a cationic lipid membrane [39]. In a recent study, Manca et al., reported results for the stretching of a chain-like molecule due to a point and distributed forces both in 2D and 3D [40,41].

The principal results we present in this paper are simple, closed-form expressions, obtained from a direct and transparent derivation, relating extension to force experienced by a freely jointed chain confined to a planar surface. In addition, we provide approximate inverse expressions for the force-stretch relationship that are often needed in practice, complement our analytical results by Brownian dynamics simulations, and validate the 2D results for distributed applied force by comparison to experimental data. We expect that these results will be helpful to experimentalists for analyzing 2D stretching experiments.

2. Methods

To complement and verify our analytical results, we conducted Brownian Dynamics simulations of freely jointed chains in 3D and confined to a flat 2D surface, with and without self-avoidance. We used a program described previously elsewhere [42]; here we provide only a brief account. The freely jointed chain comprises N identical nodes connected by $N-1$ links. The vector form of the governing Brownian dynamics equation for bead i at position $\boldsymbol{r}_i = (x_i, y_i, z_i)$ is written in terms of the viscous damping constant, ξ_i (kg/s), a random force, $\boldsymbol{f}_i^{\,r}$ (N), and the potential energy of the system as a function of coordinates of each link E [43]:

$$0 = -\xi_i \frac{d\boldsymbol{r}_i}{dt} + \boldsymbol{f}_i^{\,r}(t) - \nabla E_i(\boldsymbol{r_i}) \tag{1}$$

The potential energy includes (i) possible repulsion between beads to model self-avoidance, (ii) attractive interaction with a surface to model adsorption, and (iii) constraints to enforce fixed bond length. One end was immobilized on a surface and force was applied either to the other end or to all other beads. Force was applied either out-of-plane, in a direction normal to the surface, to model 3D stretching, or in-plane, to model 2D stretching.

When modeling 2D stretching, we included an adsorption potential in the model that was sufficiently strong to ensure that all beads were strongly adsorbed and their motion confined to a frictionless surface. An adhesion free energy of 12 k_BT per Kuhn length of the molecule was chosen based on our previous work representative of single-stranded DNA (ssDNA) as adequate for strong adsorption on a surface such as graphite [19,42].

3. Results and discussion

3.1. Force–displacement response of a freely jointed chain in 2D

The Langevin function relates average stretch of a freely jointed chain to applied force, f. This relationship is derived under constraints of fixed force and temperature. A similar approach in 2D also yields closed form results. Consider the Helmholtz free energy of the externally loaded FJC:

$$A = U - TS - fl \tag{2}$$

where $l = \sum_{i=1}^{N} l_i = \sum_{i=1}^{N} b\cos\theta_i$ is the end-to-end distance of the chain, with b the Kuhn length, i.e., the distance between nodes (Fig. 1). Combining Eq. (2) with the fundamental equation for energy:

$$dU = -pdV + TdS + fdl \tag{3}$$

we have:

$$\begin{aligned} dA &= -SdT - pdV - ldf \\ l &= -\frac{\partial A}{\partial f}\bigg|_{T,V} = -\frac{\partial}{\partial f}(-k_BT\ln\, Z) \end{aligned} \tag{4}$$

where Z is the partition function for the FJC molecule. We need to consider only the conformational part of the partition function, since it is assumed that only orientation of the segments depends on force [17]. The conformational partition function Z_C is:

$$Z_C = \int w\ \exp(fl/k_BT)d\mathbf{q} \tag{5}$$

where the integral is over all degrees of freedom that define the conformation of the molecule, and w is the density of states. For stretching of a FJC in 3D by a point force (pf) applied at the free end of a molecule, the extension-force relationship, which results from Eqs. (4) and (5), is well-known [17]:

$$L_{pf,3D} = \coth(F) - \frac{1}{F} \equiv \mathcal{L}_{pf,3D}(F) \tag{6}$$