Straightening of Thermal Fluctuations in Semi-Flexible Polymers by Applied Tension

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We investigate the propagation of a suddenly applied tension along a thermally excited semi-flexible polymer using analytical approximations, scaling arguments and numerical simulation. This problem is inherently non-linear. We find sub-diffusive propagation with a dynamical exponent of 1/4. By generalizing the internal elasticity, we show that tense strings exhibit qualitatively different tension profiles and propagation with an exponent of 1/2.

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Characteristic for soft matter systems such as polymers or membranes is the often subtle interplay between energy and entropy [1,2]. Thermal motion determines the conformations of these systems crucially. For instance, the typical end-to-end distance even of a semi-flexible polymer (let alone a Gaussian polymer) is much smaller than its contour length. Likewise for vesicles, thermal fluctuations can store a significant part of the "true" surface area. From the perspective of the projected length or area, this part is hidden. For vesicles or membranes, the hidden area can be pulled out without stretching the true area by application of a localized force such as the suction pressure in a micropipet [3] or the action of optical tweezers [4]. For polymers, recent advances in experimental techniques using magnetic beads, optical tweezers or flow fields made feasible detailed experimental studies of the conformations of single long molecules [5–10]). With these techniques it has become possible to measure the force-extension curve for these soft systems and to compare them with theoretical predictions [11–15]. These studies focus on the equilibrium conformations under the action of a *stationary* force.

The purpose of this letter is to investigate the *dynamics* of the straightening of initial thermal fluctuations. The approach to the stationary state takes time because these objects are immersed in a viscous medium (usually water) [16]. Since we are interested in the principle mechanism, we will simplify the system as much as possible still retaining what we believe to be the salient features. Thus we will study the straightening for a one-dimensional semiflexible chain confined to a two dimensional world [17]. The unwinding of a Gaussian polymer in a homogeneous flow is the only other system so far for which the dynamical approach to the new equilibrium has been studied using scaling arguments [12]. In contrast to this work, the conformation of our chains are dominated by bending modes. Also, we will consider the case of pulling one end holding the other end fixed, unlike the free-end situation in a homogeneous flow considered in [11,12]. Our main observations are that tension spreads slowly in a long chain, with a scaling law depending on the elastic character. We give numerical results along with simple scaling arguments to explain them.

Model: To make the calculation tractable we will neglect the thermal fluctuations in our dynamics: their only role is to prepare a rough initial state at time $t = 0$, in which the total contour length per unit of projected real-space length is greater than one. We also assume that at $t > 0$ the bending stiffness κ is negligible compared to the applied force $\mathbf{f}$; the only role of κ is then to set the initial roughness of the contour (see below).

Let us write the shape of a "polymer" confined to 2d as $\mathbf{r}(s) = (x(s), y(s))$ along its arc length $0 \le s \le L$. We fix the right end to $\mathbf{r}(L) = \mathbf{0}$. At the left end, a force $\mathbf{f} = -f\hat{\mathbf{x}}$ pulls in the $-x$ direction.

The total energy is then given by

$$F \equiv -\mathbf{f}\ \mathbf{r}(L) + \frac{1}{2}\int_0^L ds\gamma(s)\dot{\mathbf{r}}(s)^2 \qquad (1)$$

where dots denote derivatives with respect to arc length. The Lagrange multiplier $\gamma(s)$, which can be interpreted as the local tension, is necessary to preserve the arc length constraint $\dot{\mathbf{r}}(s)^2 = 1$ which arises from the inextensibility of the polymer [18]. We assume local isotropic dissipation and ignore long range hydrodynamic interactions. The equation of motion is then

$$\Gamma^{-1}\partial_t \mathbf{r} = -\delta F/\delta \mathbf{r} = \partial_s(\gamma\dot{\mathbf{r}}) + (\mathbf{f} + \gamma\dot{\mathbf{r}})\delta(s) \qquad (2)$$

where Γ is an inverse friction coefficient.

There is no explicit equation of motion for the Lagrange multiplier γ. This quantity has to be determined from

$$(1/2\Gamma)\partial_t \dot{\mathbf{r}}^2 = \dot{\mathbf{r}}\partial_s^2(\gamma\dot{\mathbf{r}}) = \ddot{\gamma} - \gamma\ddot{\mathbf{r}}^2 = 0. \qquad (3)$$

At any time t, this relation for γ is a second order differential equation which requires for its solution two boundary conditions. The first, at $s = 0$, is

$$\gamma(0) = f \qquad (4)$$

The fixed boundary condition at $s = L$ requires $(1/\Gamma)\partial_t \mathbf{r}(L) = \dot{\gamma}(L)\dot{\mathbf{r}}(L) + \gamma(L)\ddot{\mathbf{r}}(L) = 0$. This relation implies both

$$\dot{\gamma}(L) = 0 \qquad (5)$$

and $\ddot{\mathbf{r}}(L) = 0$ because $\dot{\mathbf{r}}\ddot{\mathbf{r}} = 0$. The tension profile $\gamma(s)$ can thus be calculated for any instantaneous conformation. This profile can then be put into the equation of motion for $\mathbf{r}$ which can then be integrated one time step.

Linear theory: Even for our simplified model, the coupled non-linear equations (2) and (3) cannot be solved analytically. Let us consider first the linearized problem, which will fail in an instructive way. Choose a single mode initial conformation of the form $y(s, t = 0) = a_q^0 \sin qs$. Note that $x(s)$ follows once we specify $y(s)$ because of the arclength constraint.

Ignoring the non-linear term, the equation for the tension becomes $\ddot{\gamma} = 0$ which leads with the boundary conditions to the flat profile $\gamma(s) = f$. Thus the tension spreads instantaneously in this approximation. In the linearized equation of motion for y, the modes decouple and one obtains the usual relaxation form, $a_q(t) = a_q^0 e^{-\Gamma f q^2 t}$.

The failure of the linear theory can be seen clearly by looking at the first correction term. Writing $\gamma(s) = f + \gamma_1(s)$, we have $\ddot{\gamma}_1(s) = f\ddot{\mathbf{r}}^2$, which implies for the single mode configuration $\gamma_1(L) \sim -L^2 f |a_q^0|^2 q^4$. This is less than the lowest order term f only if $L \ll 1/q^2|a_q^0|$. Thus depending on the wave-length and the amplitude of the initial conformation, there is a maximal chain length over which the linearized theory can be applied. For any longer chain, the problem becomes inherently non-linear.

Simulations: To gain insight into the non-linear problem, we simulated a discretized version of the equations of motion. The initial conformation is written as $y(s, 0) = \sum_q a_q^0 \sin qs$ with $q = n\pi/L, n \geq 1$. This choice guarantees that $y(0, 0) = y(L, 0) = 0$. For simplicity, we also restrict $y(0, t) = 0$ for all times so that the left endpoint moves only horizontally.

The small initial amplitudes are chosen from a Gaussian distribution with width

$$\langle |a_q^0|^2 \rangle = T/\kappa L q^4, \tag{6}$$

where T is temperature in units of energy and κ is the bending stiffness.

In Fig.1, we show ten snapshots of the configuration and the corresponding tension profiles. The tension spreads inward, decreasing the amplitudes in this range. For a quantitative analysis, we define a penetration length $\xi(t)$ over which the tension has already spread. For concreteness we will define ξ as the point where $\gamma(\xi) = f/2$. The initial value and the time evolution of this penetration length depends on the initial conformation. Averaging 50 runs, we find the power law

$$\langle \xi(t) \rangle \sim t^z \tag{7}$$

where the dynamic exponent $z = 0.24 \pm 0.01$. We will now show how this empirical scaling law follows from a simple physical picture.

Scaling argument I: An exact solution of the non-linear equations of motions looks impossible. Good insight, however, can be gained from the structure of the equation for the tension profile (3). Since $\ddot{\gamma}$ has the same sign as γ, the two boundary conditions (4) and (5) imply that $\gamma(s)$ is positive, monotonically decreasing and convex. We will now seek an approximate effective equation for the time development of γ. For uniform tension the modes decay as $a_q(t) = \exp(-\Gamma\gamma q^2 t) a_q^0$. Since this says that the short-wavelength modes decay the fastest, we will make the "adiabatic" Ansatz that γ varies slowly in space compared to the wavelengths $2\pi/q$ of the relevant modes; thus we write $y(s, t) = \sum_q a_q(s, t) \sin qs$ and regard a_q as slowly-varying functions of arclength s and of time: $a_q(s, t) = \exp(-\Gamma\gamma(s, t) q^2 t) a_q^0$. Using eq. (6), the average time-dependent local curvature then can be approximated as

$$\langle \ddot{y}(s, t)^2 \rangle = \sum_q \frac{T}{\kappa L q^4} q^4 \exp(-2\Gamma\gamma(s, t) q^2 t). \tag{8}$$

Written in this form, the curvature $< \ddot{y}(s, t)^2 >$ depends only implicitly on the arc length s via the function $\gamma(s, t)$. With this simplification, Eq. (3) for the unknown time dependent tension acquires the simple form

$$\ddot{\gamma}(s) = \gamma \sum_q \frac{T}{\kappa L q^4} q^4 \exp(-2\Gamma\gamma(s) q^2 t) \equiv -\frac{\partial V(\gamma)}{\partial \gamma}. \tag{9}$$

The equation for the tension profile has thus become a simple mechanical equation for the one-dimensional motion of a particle with unit mass in a potential $V(\gamma)$ where γ plays the role of position and the original spatial variable s plays the role of time. The original time t becomes a mere parameter. The potential exhibits two regimes,

$$V(\gamma) \approx \begin{cases} -\gamma^2, & \gamma \ll \gamma_c \\ -\dfrac{T}{\kappa(\Gamma t)^{1/2}} \gamma^{3/2}, & \gamma \gg \gamma_c \end{cases} \tag{10}$$

separated by a cross-over tension $\gamma_c \equiv 1/\Gamma q_m^2 t$. Here, q_m is a high momentum cut-off for the q-modes.

The particle starts with "initial" condition $\gamma(0) = f$ and has to reach zero velocity at "time" $s = L$ because of $\dot{\gamma}(L) = 0$. In the limit $L \to \infty$, it then follows that the particle has zero total energy from which we obtain the initial condition $\dot{\gamma}(0) = -2(V(f))^{1/2} < 0$. Identifying $\dot{\gamma}(0)$ with $-f/\xi(t)$, we obtain $\xi(t) \sim (\kappa/T)^{1/2}(\Gamma f t)^{1/4}$ in good agreement with our numerical simulation. Even though a *transversal* perturbation also propagates a distance $\sim t^{1/4}$ as it follows easily from linear response theory [19], our case of the non-linear response to a *longitudinal* force is fundamentally different as it is also obvious from the non-linear dependence of ξ from the applied force f.

For a rough estimate of the relevant scales, let us ignore all factors of order unity. For the friction coefficient Γ we can take the inverse of the bulk viscosity η, so $\Gamma = 1/\eta = 100\text{cm}^3/\text{erg sec}$. A typical weak force is

$f = 0.1$ pN [6]. For DNA, $\kappa/T \simeq 100$nm [6] and thus $\xi(t) \simeq 1\mu\text{m}(t/\text{sec})^{1/4}$. For actin, $\kappa/T \simeq 10\mu$m [20], so $\xi(t) \simeq 10\mu\text{m}(t/\text{sec})^{1/4}$. Neglecting the contribution of the bending elasticity to the straightening is admissible if the characteristic time $t_b \sim \eta\xi^4/\kappa$ it takes for a bending mode on scale ξ to relax is larger than the time it takes to straighten the length ξ. This criterion holds if $f > T^2/\kappa$ which is fulfilled for the numbers given above for actin. Thus, the dynamics of straightening in biopolymers should be accessible to video microscopy techniques.

Generalization: In the analysis above we took the initial chain configuration to be governed by bending modes. Another case of interest is when a floppy chain is initially under tension, and the tension is suddenly increased at time zero. To cover both cases let us replace the sample for the initial amplitudes in Eq. (6) by $\langle|a_q^0|^2\rangle = \mathcal{A}^{3-2b}/Lq^{2b}$, where $\mathcal{A}$ has the dimension of a length. Then the case $b = 2$, where $\mathcal{A} = \kappa/T$, was discussed above, while $b = 1$ (where $\mathcal{A} = T/\Sigma$) corresponds to a string with tension Σ.

Our scaling argument can be repeated for general $b > 1/2$. One finds the effective potential $V(\gamma) \sim -\mathcal{A}^{3-2b}(\Gamma f t)^{(2b-5)/2}\gamma^{b-1/2}$ for $\gamma \gg \gamma_c$. This potential leads to a penetration length $\xi(t) \simeq t^{(5-2b)/4}$.

We have studied the case $b = 1$ numerically. Here we find a dynamical exponent $z = 0.50 \pm 0.01$ clearly different from the prediction $z = 3/4$ which would follow from the above scaling argument.

What went wrong? Closer inspection of the tension profiles indicates a qualitative difference between the tense string $b = 1$ and the semi-flexible $b = 2$ cases. For the string, the 10 snapshots shown in Fig. 2 and the corresponding tension profiles reveal that the tension profile is not exponential but rather decays quite linearly over a long region, and the moving boundary of this region remains sharply defined. Intuitively the difference stems from the fact that more of the initial excess length is in short-wavelength modes in the tense string case. Since these modes are damped the fastest, the string straightens immediately when it feels the tension, and so most of the resistance to straightening comes from pulling a straight string through a viscous medium, which gives a linear tension profile. The straight region ends at a point controlled by the total length pulled so far. In the semirigid case, most of the excess length is initially in long-wavelength modes, which decay slowly. The tension propagates forward before the string has a chance to straighten, and so its front is not so well-defined.

Scaling argument II: We can turn these words into another simple scaling argument. We separate the string into two parts. In the left, straightened, part of length $\xi(t)$, we assume that all fluctuations have already been pulled out. Then the tension profile becomes $\gamma(s) = f - \dot\gamma(L)s$. In the right, unperturbed, part, pulling has not yet had a significant effect. Thus the tension profile for $s > \xi(t)$ is exponential, $\gamma(s) = \gamma(\xi(t))\exp(-(s - \xi(t))/\xi_{init})$, with a *time-independent* penetration length $\xi_{init} \equiv (1/\ddot{\mathbf{r}}^2)^{1/2}$ as given by the initial configuration. Matching the two profiles so that $\dot\gamma$ is continuous at $s = \xi(t)$, we obtain $\gamma(\xi(t)) = f/(1+\xi(t)/\xi_{init}) \simeq f\xi_{init}/\xi(t)$. The rate $d\xi(t)/dt$ with which the straightened regime grows is proportional to the force $\gamma(\xi(t))$ with which this regime "pulls" at the left end of the unperturbed regime. We thus obtain $d\xi(t)/dt \sim \gamma(\xi(t)) \sim f\xi_{init}/\xi(t)$. This equation is readily solved to give $\xi(t) \sim (ft)^{1/2}$. This "diffusive" behavior indeed corresponds to our simulation results for $b = 1$. We can easily understand it in terms of the intuitive picture sketched above: the total friction on the straight segment is proportional to its length $\xi(t)$, and so the string velocity is $v \sim \xi^{-1}$. Letting α be the initial excess contour length divided by L, conservation of string says that the front velocity is $\dot\xi = v/\alpha \sim \xi^{-1}$. Solving this equation then reproduces $\xi \sim \sqrt{t}$.

In Fig.3, we show the numerically determined exponents for various values of b. We have strong numerical evidence that $z = 1/2$ for $b \leq 1$ and $z < 1/2$ for $b > 1$. This plot shows that the two scaling theories yield upper limits to this exponent.

Conclusion: We have seen how thermal fluctuations, together with a viscous surrounding medium, impede the transmission of a suddenly imposed tension in a polymer. As we pointed out, this phenomenon is inherently nonlinear. In a model neglecting stochastic noise, simulations show that the tension propagation in a stiff chain is subdiffusive with an exponent 1/4. We showed how this law also follows from a simple self-consistent scaling theory. We also generalized both the model and the scaling theory to the case of chains with arbitrary initial elasticity. For tense strings, the spreading becomes diffusive, in the sense that the tension is nonnegligible in a region of size $\sim \sqrt{t}$. The application of these ideas to the case of suddenly-pulled membranes [4] will be addressed in future work.

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FIG. 1. (top) 10 subsequent snapshots of conformations $(x(s), y(s))$ of a semi-flexible chain ($b = 2$) with total chain length 250. The snapshots are taken at equidistant times. The inset shows how two adjacent bends are straightened. (bottom) Corresponding tension profiles as a function of the arc length.

FIG. 2. Same as Fig.1 for a string (b=1).

FIG. 3. Dynamical exponent z as a function of b. Error bars have the size of the symbols. The lines refer to the two scaling estimates.

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