Dynamic Properties of an Extended Polymer in Solution

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Extended polymers are relevant in a variety of situations ranging from the classic coil-stretch problem to recent single molecule polymer experiments with DNA. We present theoretical calculations and computer simulations of the dynamic properties of extended single polymers. We discuss the effects of tension and hydrodynamics on τ, the fundamental relaxation time of the polymer, and find that tension dominates the behavior of τ. Furthermore, the symmetry breaking caused by extending the polymer "splits" τ, leading to distinct longitudinal and transverse relaxation times. Our results are in agreement with recent experiments, and we discuss implications for the coil-stretch transition. [S0031-9007(99)09004-3]

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Extended polymers play an important role in many rheological problems: Under shear or strain forces, polymers will extend. A classic example is the coil-stretch transition, in which polymers in a strain flow will undergo a phase transition from a coiled state to a highly stretched state when the strain rate exceeds a critical value [1]. The physics of this transition depend crucially on the relationship between hydrodynamic and entropic forces as a polymer is extended. Recent experiments with single molecules of DNA [2,3] have revealed its importance in a context outside biology—as a model system for studying polymer dynamics. When DNA is partially extended, one can use optical microscopy to image the internal modes of the polymer and study the normal mode structure. However, to analyze the results completely requires a detailed theory of the effects of extension.

Here we calculate the fundamental relaxation time of a polymer as a function of its extension. The effects of nonlinear force curves and changing hydrodynamic interactions are incorporated in the theory. We have performed computer simulations of an extended polymer, the results of which are in agreement with the theory. The theoretical predictions are compared with the single molecule DNA data of Ref. [2], and their implications for the coil-stretch transition are discussed.

Earlier theoretical studies of the dynamics of extended polymers [4,5] have made use of the blob model [6]. However, the blob model gives an incorrect prediction of polymer forces, which limits its applicability. For example, experiments with the synthetic polymer dextran have demonstrated that the force is best described by a modified freely jointed chain model [7]. We show below that a proper understanding of the forces of an extended polymer is crucial in predicting the dynamics. In the case of DNA, its stiffness precludes the application of blobs since the assumption $fb/k_BT \ll 1$ is not generally met, where f is the force extending the polymer, b is the Kuhn length, k_B is the Boltzmann constant, and T is the temperature. Other authors have considered the subtleties of extending polyelectrolyte polymers with flows and electric fields, but their primary results do not concern the dynamics of the polymer [8,9].

Polymer dynamics are usually considered within the context of the Zimm and Rouse models [10]. The Rouse model describes the polymer as a series of beads connected with Hookean springs and can be solved by decomposing the polymer's motion into a set of linear normal modes. In many practical situations, the behavior of the polymer is dominated by the fundamental mode. The relaxation time of the fundamental mode is given by $\tau_R = \zeta_R/k$, where ζ_R is the friction coefficient of the polymer and k is the spring constant. However, an accurate description of the motion of an isolated polymer in a solvent accurately requires inclusion of the effects of hydrodynamic interactions. Unfortunately, this couples the equations of motion in a nonlinear fashion and cannot be solved exactly. The Zimm model linearizes the equations of motion by "preaveraging" the hydrodynamic coupling tensor, that is, averaging it over the equilibrium distribution of polymer configurations. This restores the normal mode structure and gives the fundamental mode $\tau_Z = \zeta_Z/k$; $\zeta_Z = 1/H_{11}$ is the reciprocal first eigenvalue of the preaveraged hydrodynamic tensor $\mathbf{H}$. To understand how τ changes with extension, both ζ and k must be analyzed. Since ζ_R does not change as a function of extension, the Rouse model allows one to separate the effects of tension from those of hydrodynamics.

Although polymers act as linear springs for small extensions, their finite length causes the force to become nonlinear as the polymer is extended farther. If the polymer is at equilibrium, the fluctuations of the end points will be small and the force can be expanded in a Taylor series. Thus the Rouse equations of motion do not change as a function of extension; only the value of the spring constant varies.

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The anisotropy caused by extending a polymer introduces two distinct relaxation times, one each for the transverse and longitudinal dimensions. Consider the fluctuations of the end points of a polymer under constant traction. Their motion will be a sum of all the relaxation modes but will be dominated by the fundamental. In the longitudinal direction, for an average extension E, the force $F(E)$ is parallel to this direction, and for small changes in the extension δx, $F(E + \delta x) \approx F(E) + (dF/dx)|_E \delta x$. Thus the force required for a longitudinal displacement δx from equilibrium is linear with effective spring constant $k_\parallel = (dF/dx)|_E$. In the transverse direction one can calculate the restoring force if the polymer is displaced at its end point by a small amount δy. By simple vector algebra, the force $f(\delta y)$ to displace the end point δy is $f(\delta y) = (\delta y/\sqrt{E^2 + \delta y^2}) F(\sqrt{E^2 + \delta y^2})$, and by expanding to first order in δy, $f(\delta y) = [F(E)/E]\delta y$. Thus the spring constant in the transverse direction is $k_\perp = F(E)/E$. We note that the transverse and longitudinal spring constants are identical when the force is linear as is the case for small extensions. This is required by symmetry: when the polymer is coiled, it is isotropic and there should be a single relaxation time. When the polymer is extended, the symmetry is broken, and the nonlinear forces create distinct transverse and longitudinal relaxation times:

$$\tau_\parallel = \frac{\zeta}{k_\parallel} = \frac{\zeta}{(dF/dx)|_E} \qquad \tau_\perp = \frac{\zeta}{k_\perp} = \zeta \frac{E}{F(E)}. \tag{1}$$

Force versus extension curves have been calculated and measured experimentally on single polymers. For a simple freely jointed chain $F(x) = (k_B T/b)\mathcal{L}^{-1}(x/L)$, where the Langevin function $\mathcal{L}(\alpha) = \coth(\alpha) - (1/\alpha)$, k_B is the Boltzmann constant, T is the temperature, b is the Kuhn length of the polymer, and L is the length of the polymer [11]. For a wormlike chain such as DNA, the force is typically approximated by the function $F(x) = (2k_B T/b)[\frac{1}{4}(1 - x/L)^{-2} - \frac{1}{4} + x/L]$ [12]. These formulas for $F(x)$ can be used with Eq. (1) to calculate the relaxation times as a function of extension for the Rouse model (Figs. 1 and 3).

We now turn to the Zimm model. In order to incorporate the effects of hydrodynamic interactions, one must calculate the preaveraged hydrodynamic tensor as a function of extension. The exact form of the hydrodynamic tensor is $\mathbf{H}(\mathbf{r}) = (1/8\pi\eta r)(\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}})$, where $\mathbf{r}$ is the vector connecting the interacting points. For a coiled polymer, the preaveraging has been calculated: $\mathbf{H}(n - m) \approx (1/\sqrt{6\pi^3}|n - m|^{0.5}\eta b)\mathbf{I}$, where n and m index beads in the polymer [10]. For moderate extensions, we expect this description to remain valid on short length scales, i.e., when $|n - m|$ is small. For long length scales and high extensions, the beads align along the longitudinal axis, and $|\mathbf{R}_n - \mathbf{R}_m| \approx |n - m|$, so that if the polymer is extended along the x axis, $\mathbf{H}(n - m) \approx (1/|n - m|\eta b)(\mathbf{I} + \hat{x}\hat{x})$. For a fixed extension there is a crossover length scale $b\Delta$ between the two regimes which is determined by the spatial distribution of the polymer in the transverse direction and is analogous to the Pincus blob size. Thus $\mathbf{H}$ can be approximated as

$$\mathbf{H}(n - m) \approx \begin{cases} \dfrac{1}{\sqrt{6\pi^3}|n - m|^{0.5}\eta b}\,\mathbf{I} & |n-m| < \Delta^2, \\ \dfrac{\delta}{|n - m|^{1.0}\eta b}\,(\mathbf{I} + \hat{x}\hat{x}) & |n-m| > \Delta^2. \end{cases} \tag{2}$$

Δ depends on extension and is a dimensionless measure of the root mean square distribution of the polymer in the transverse direction, while δ is chosen to continuously join the curves. The longitudinal and transverse axes are distinguished by a prefactor of order unity. A crude estimate of Δ is obtained by treating the polymer as an N step random walk which can be decomposed into transverse and longitudinal directions, where $N = L/b$. Approximately $N\varepsilon$ steps will be longitudinal, where $\varepsilon = E/L$ is the fractional extension of the polymer. Thus the transverse random walk has $N(1 - \varepsilon)$ steps and radius of gyration $\Delta \approx \sqrt{N(1 - \varepsilon)}$. Then $b\Delta$ is the root mean square displacement of the polymer in the transverse direction, $b\Delta^2$ is approximately the length of polymer needed to achieve this displacement, and as required, $\Delta^2(L) = 0$ and $\Delta^2(0) = N$.

$H_{11}(E)$ can be calculated by using the sine basis as an approximation of the normal mode decomposition of an

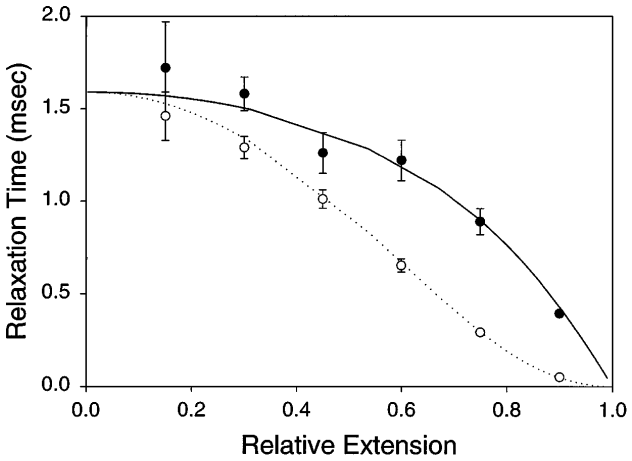

FIG. 1. Relaxation times for a Rouse polymer as a function of end-to-end extension. Theoretical predictions for the transverse (solid line) and longitudinal (dotted line) relaxation times of a freely jointed chain are compared to the results of the simulations (closed and open circles, respectively). Hydrodynamic interactions are not included in this case. The data points are derived from single exponential fits to the autocorrelation function of the first sine mode (see text for details). Each autocorrelation function was calculated with 3 sec of data. The relative extension is a dimensionless variable computed by normalizing the end-to-end extension by the total length of the polymer.

extended polymer. It has been shown experimentally that the error introduced by this approximation is small, on the order of 5% [2]. Then

$$\frac{1}{\zeta_Z} = H_{11} = \frac{1}{N^2}\int_0^N\int_0^N H(n-m)\sin\left(\frac{m\pi}{N}\right)\sin\left(\frac{n\pi}{N}\right)dm\,dn\,. \tag{3}$$

Numerical evaluation of Eq. (3) for various values of Δ shows that ζ_Z increases by only 20% as the polymer is extended from a coil to 90% extension. Thus, the hydrodynamic interactions have a much smaller influence on the fundamental relaxation time than the tension, which can change τ by more than an order of magnitude. The net effect is to lead to a reduction of the relaxation time with extension.

We performed computer simulations of a freely jointed chain in order to test these predictions. The simulations used chains of 21 beads of radius 10 nm connected by 20 massless rods; each bead moved freely within the constraint that the rod was rigid and of constant length 50 nm. The beads were subject to randomly fluctuating Brownian forces at temperature 300 K, and the constraints were enforced with Langrange multipliers. For each time step of the simulation, the beads moved simultaneously while constraint forces were iteratively computed [13]. The end beads were held fixed at an extension E. The polymer was started in an arbitrary configuration and allowed to thermalize for more than 10τ. In order to calculate the transverse relaxation time at each extension, the sine transform was calculated. The autocorrelation of the lowest sine mode was fit with an exponential, yielding τ. This closely follows the experimental data analysis from Ref. [2] and gives a direct measurement of τ. For the longitudinal relaxation times, the same procedure was followed.

The simulation does not include hydrodynamic interactions, and thus gives τ_R as a function of extension for a freely jointed chain. Figure 1 shows the simulation results compared to the theory, with no adjusted parameters. The relaxation times clearly decrease as a function of extension, and the extension symmetry breaking does introduce a difference between the longitudinal and transverse relaxation times. The agreement between the simulation and analytic model is good, and we conclude that for a Rouse polymer, the dominant cause of the decreasing relaxation time with extension is simply the nonlinear spring force.

The data from the simulations was also used to compute the preaveraged hydrodynamic tensor $\mathbf{H}(n-m)$. Computing the largest eigenvalue of $\mathbf{H}(n-m)$ effectively gives a measurement of ζ_Z, from which τ_Z can be computed. The values of ζ_Z derived from the simulation vary only slightly over a large range of extensions, consistent with Eq. (2). Figure 22 shows a comparison between the analytic model and the preaveraged values computed from the simulation. A similar result is expected for the wormlike chain, since the gross spatial polymer distribution is similar. The simulations thus agree with the calculations that τ will decrease with extension.

These predictions can also be tested with experimental data from DNA, which has been shown to behave like a wormlike chain. Figure 3 shows the relaxation times measured in Ref. [2] compared to the theoretical τ_Z, where the force constant $k_\perp$ for the wormlike chain curve and the preaveraged ζ_Z from Eqs. (2) and (3) were used. The agreement is good, except at the highest extension. In fact, tension dominates τ to the extent that the agreement is equally good if the hydrodynamics corrections are neglected.

These results have important implications for the coil-stretch transition. The relaxation time of the polymer plays an important role in the coil-stretch transition since the critical strain rate is of the order of the reciprocal of the relaxation time. It has been suggested that hydrodynamic effects will change dramatically for a highly stretched chain, leading to Rouse-like dynamic behavior [1]. Furthermore, it was suggested that this would be the dominant influence for the relaxation time, leading to increased relaxation times at higher extensions. Such an effect would cause hysteresis in the coil-stretch transition—the critical strain rate to extend a polymer would be greater than the rate to relax the polymer [1,4]. It is true that for a fixed extension if hydrodynamic interactions are

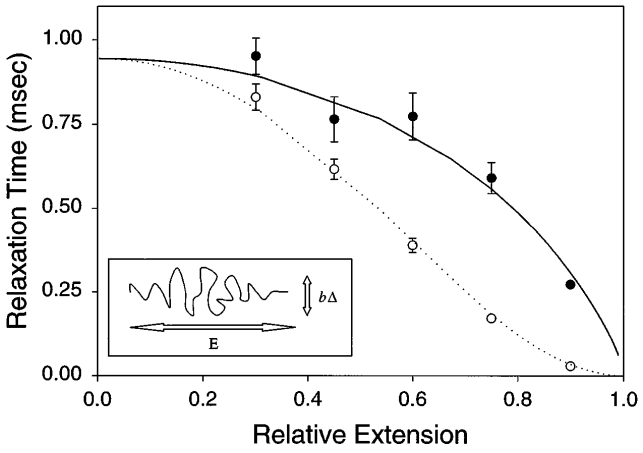

FIG. 2. Relaxation time as a function of extension, including preaveraged hydrodynamics. The theoretical model (solid line: transverse relaxation time; dotted line: longitudinal relaxation time) is compared to simulation results (closed circles: longitudinal relaxation time; open circles: transverse relaxation times). The simulation results were used to calculate the preaveraged hydrodynamics tensor as a function of extension. This tensor was used with the Rouse matrix in order to numerically compute the slowest relaxation time. Incorporating hydrodynamics leads to generally shorter relaxation times. Inset: drawing showing the role of Δ in Eq. (2). Hydrodynamics will dominate on length scales less than $b\Delta$ and will be less pronounced on longer length scales.

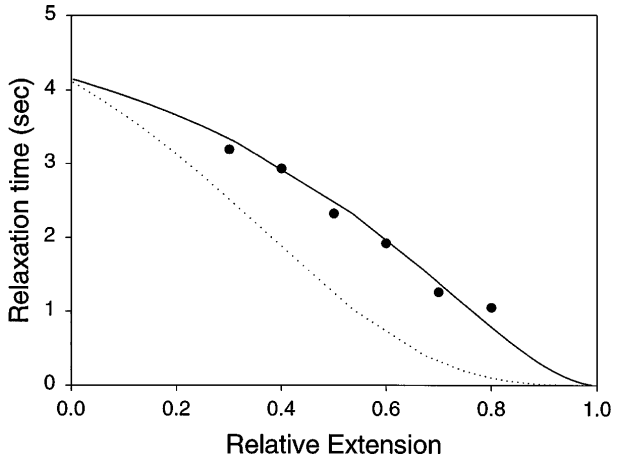

FIG. 3. Comparison of theory with experiment. Theoretical predictions for the transverse relaxation time of a wormlike chain (solid line) are compared to recent experimental results with single molecules of DNA from Ref. [2] (closed circles). Also shown is the predicted longitudinal relaxation time (dotted line). The theoretical calculation uses the relaxation times from Eq. (1), where ζ is replaced with the Zimm friction coefficient ζ_Z calcluated from Eqs. (2) and (3).

switched "off," the relaxation time increases. However, as the extension is varied the relaxation time is affected more by the changing tension than by the changing hydrodynamics. Thus the notion that extended polymers have longer relaxation times is inconsistent with our calculations and simulations, and with experiments with single molecules of DNA. We conclude that hysteresis most likely exists only in the highly idealized case of an infinite length polymer.

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