

Longitudinal Relaxation of Initially Straight Flexible and Stiff Polymers

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The relaxation mechanism of an initially straight flexible or stiff polymer chain of length N in a viscous solvent is studied through Brownian dynamics simulations covering a broad range of time scales. After the short-time free diffusion, the chain's longitudinal reduction $R_{\parallel}^2(0) - R_{\parallel}^2 \sim Nt^{1/2}$ at early intermediate times is shown to constitute a universal behavior for any chain stiffness caused by a quasisteady $T \sim Nt^{-1/2}$ relaxation of tensions associated with the deforming action of the Brownian forces. Stiff chains with a persistence length $E \geq N$ are shown to exhibit a late intermediate-time longitudinal reduction $R_{\parallel}^2(0) - R_{\parallel}^2 \sim N^2 E^{-3/4} t^{1/4}$ associated with a $T \sim N^2 E^{-3/4} t^{-3/4}$ relaxation of tensions affected by the deforming Brownian and the restoring bending forces.

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The present study considers the conformational relaxation of a single flexible or stiff polymer chain from an initial straight configuration in a viscous solvent. This problem commonly arises when strong flows are turned off in both industrial and biological applications. The problem is also motivated by recent experiments with single DNA molecules relaxing after being fully extended by applied forces as well as by the recent development of microdevices involving stretched tethered biopolymers [1]. Our interest lies in understanding the relaxation mechanism for flexible and stiff polymers, and thus our results are applicable to a wide array of both synthetic polymers, such as polyacrylamides, Kevlar, and polyesters as well as biopolymers, such as DNA, actin filaments, microtubules, and rodlike viruses.

In recent years considerable progress has been made in understanding the properties of semiflexible polymers near equilibrium [2–5]. In this regime the transverse fluctuations of semiflexible polymers were found to scale as $t^{3/4}$, while the longitudinal fluctuations scale as $t^{7/8}$ [2,3]. With this study, we want to understand the relaxation mechanism of a specific problem far from equilibrium where a complete theory of the relaxation process is lacking. We show that the early longitudinal relaxation, being associated with a quasisteady relaxation of link tensions of a Brownian nature, is valid for any chain stiffness. Stiff chains are shown to exhibit a late longitudinal relaxation associated with the cumulative effect of the deforming Brownian forces and the restoring bending forces on the link tensions. The techniques we develop to understand the relaxation mechanism may be useful for a wide array of problems in polymer rheology.

To describe the polymer chain, Brownian dynamics simulations are employed based on a discretized version of the wormlike chain model described in our previous publication [5]. This method considers a bead-rod model with fixed bond lengths and ignores hydrodynamic interactions among beads as well as excluded-volume effects [6]. The polymer chain is modeled as $N_B = (N + 1)$ identical beads connected by N massless links of fixed length

b (which is used as the length unit). The position of bead i is denoted as \mathbf{X}_i , while the link vectors are given by $\mathbf{d}_i = \mathbf{X}_{i+1} - \mathbf{X}_i$. The polymer stiffness is accounted by a bending potential proportional to the square of the local curvature, $\phi^{\text{bend}} = \mathcal{E} \sum_{i=1}^{N-1} (1 - \mathbf{d}_i \cdot \mathbf{d}_{i+1}/b^2)$. The bending energy \mathcal{E} is related to the persistence length L_p via $\mathcal{E}/k_B T \equiv L_p/b$, where k_B is the Boltzmann constant. Assuming that the bead inertia is negligible, the following Langevin equation is obtained:

$$\zeta \frac{d\mathbf{X}_i}{dt} = \mathbf{F}_i^{\text{bend}} + \mathbf{F}_i^{\text{rand}} + \mathbf{F}_i^{\text{cor}} + \mathbf{F}_i^{\text{ten}}, \quad (1)$$

where the friction coefficient ζ is assumed to be uniform. $\mathbf{F}_i^{\text{bend}}$ and $\mathbf{F}_i^{\text{rand}}$ are the bending and the Brownian forces, respectively. The corrective potential force $\mathbf{F}_i^{\text{cor}}$ is added so that the equilibrium probability distribution of the chain configurations is Boltzmann [6]. The force $\mathbf{F}_i^{\text{ten}} = T_i \mathbf{d}_i - T_{i-1} \mathbf{d}_{i-1}$, where T_i is a constraining tension along the direction of each link \mathbf{d}_i , ensures the link inextensibility. The Brownian forces give rise to a microscopic time scale associated with the diffusive motion of one bead, $\tau_{\text{rand}} = \zeta b^2/k_B T$, which is used as the time unit. The computations were performed on multiprocessor computers provided by the National Center for Supercomputing Applications (NCSA) in Illinois.

To determine the chain's conformational evolution, we monitor the three eigenvalues of the chain's gyration tensor $\mathbf{G} = \sum_{i=1}^{N_B} (\mathbf{X}_i - \mathbf{X}_c)(\mathbf{X}_i - \mathbf{X}_c)/N_B$, where $\mathbf{X}_c = \sum_{i=1}^{N_B} \mathbf{X}_i/N_B$ is the center of mass of the chain. The first (largest) eigenvalue G_1 reveals the chain's length R_{\parallel} , while the other two eigenvalues G_2 and G_3 can be used to monitor the chain's width R_{\perp} . These configuration functions involve all the chain's length scales and thus the polymer relaxation can be determined over extended time scales by employing scaling laws [7].

The length reduction of an initially straight flexible polymer immediately after the chain is left to relax is shown in Fig. 1(a). This figure reveals that, until times $t \sim N^{-2}$, the chain's length reduction is

$$R_{\parallel}^2(0) - R_{\parallel}^2 \sim N^2 t \quad \text{or} \quad \Delta R_{\parallel} \equiv R_{\parallel}(0) - R_{\parallel} \sim N t. \quad (2)$$

This behavior results from the corresponding free diffusion in the transverse motion of each bead, i.e., $R_{\perp}^2 \sim d_{\perp}^2 \sim t$, where d_{\perp} is the transverse component of the link vectors [6,7]. Just after the chain is left to relax, the transverse component of the tension force on each bead scales as $F_{\perp}^{\text{ten}} \sim T d_{\perp} \sim N^2 t^{1/2}$, where $T \sim N^2$ are the tensions along the (nearly) straight chain, while the transverse component of the effective Brownian force on each bead scales as $F_{\perp}^{\text{rand}} \sim t^{-1/2}$ [6,7]. Thus at short times $t \ll N^{-2}$, $F_{\perp}^{\text{ten}} \ll F_{\perp}^{\text{rand}}$ and the beads show a free transverse diffusion $d_{\perp}^2 \sim t$. Because of the link inextensibility, the longitudinal length of each link is shortened as $b^2 - d_{\parallel}^2 = d_{\perp}^2 \sim t$, which results in a chain's length reduction $R_{\parallel}^2(0) - R_{\parallel}^2 \sim N^2 b^2 - N^2 d_{\parallel}^2 \sim N^2 t$.

At the transition times $\tau_{\text{ten}} \sim N^{-2}$ the transverse tension force on each bead balance the corresponding Brownian force, $F_{\perp}^{\text{ten}} \sim F_{\perp}^{\text{rand}} \sim N$, and the free diffusion of the beads is arrested. During intermediate times $N^{-2} \ll t \ll N^2$, the participation of the chain's different length scales results in a slower longitudinal reduction

$$R_{\parallel}^2(0) - R_{\parallel}^2 \sim N t^{1/2} \quad \text{or} \quad \Delta R_{\parallel} \sim t^{1/2}, \quad (3)$$

as depicted over eight time decades in Fig. 1(b). As shown in our earlier study [7], during these times the chain width grows as $R_{\perp} \sim N^{-1/4} t^{3/8}$; thus the configuration relaxation is anisotropic at intermediate times.

The length reduction of the polymer chain reveals the longitudinal component of the force acting on the entire chain,

$$F_{\parallel} \sim \zeta_{\text{ch}} \frac{d\Delta R_{\parallel}}{dt} \sim N t^{-1/2}, \quad (4)$$

where $\zeta_{\text{ch}} \sim N$ is the friction coefficient for the entire chain. This force is the tension force along the polymer chain, $F_{\parallel}^{\text{ten}} \sim T d_{\parallel} \sim N t^{-1/2}$, since the tensions during intermediate times relax as $T \sim N t^{-1/2}$ while the polymer chain is still practically straight, i.e., $d_{\parallel} \sim 1$ [6,8]. Thus the relaxation of a flexible chain is associated with the relaxation of tension forces from a magnitude of $O(N^2)$ at times $\tau_{\text{ten}} \sim N^{-2}$ to a magnitude $O(1)$ at times N^2 . The chain's length reduction and the corresponding longitudinal force satisfy the equipartition of energy, i.e., $F_{\parallel} \Delta R_{\parallel} \sim N k_B T$, which reveals that during intermediate times there exists a quasisteady equilibrium of the tension forces along the chain length.

For stiff polymer chains $E \geq N$ there is an additional force which affects the chain evolution, the bending force F^{bend} . Immediately after the chain is left to relax, the longitudinal bending force is negligible compared to the $O(N^2)$ strong longitudinal tension force. Thus, initially the chain's stiffness is expected to have a negligible effect on the longitudinal relaxation process; the bending forces should affect only the late behavior of the chain relaxation. Therefore, stiff chains are expected to show two intermediate-time behaviors. The same conclusion is derived if we consider the influence of the forces in the transverse direction which are responsible for the initiation of the polymer relaxation.

In particular, immediately after the chain is left to relax, the transverse Brownian force $F_{\perp}^{\text{rand}} \sim t^{-1/2}$ dominates the dynamics and the beads show a free sideways diffusion $d_{\perp}^2 \sim R_{\perp}^2 \sim t$, identical to that for the flexible chains. For long enough stiff chains, i.e., for $N \geq (E/N)$, the transverse tension force on each bead $F_{\perp}^{\text{ten}} \sim T d_{\perp} \sim N^2 t^{1/2}$ grows faster than the corresponding bending force $F_{\perp}^{\text{bend}} \sim E d_{\perp} \sim E t^{1/2}$. (The scaling for this force can be readily derived from the definition of the bending energy ϕ^{bend} .) For these chains, the transition from short to intermediate times occurs when F_{\perp}^{ten} on each bead balances F_{\perp}^{rand} at times $\tau_{\text{ten}} \sim N^{-2}$; the free diffusion is arrested and then the chain shows a slower transverse evolution $R_{\perp}^2 \sim N^{-1/3} t^{5/6}$, as seen in our earlier work [7]. However, for short enough stiff chains, i.e., for $N \leq (E/N)$, the transverse bending force F_{\perp}^{bend} on each bead balances first

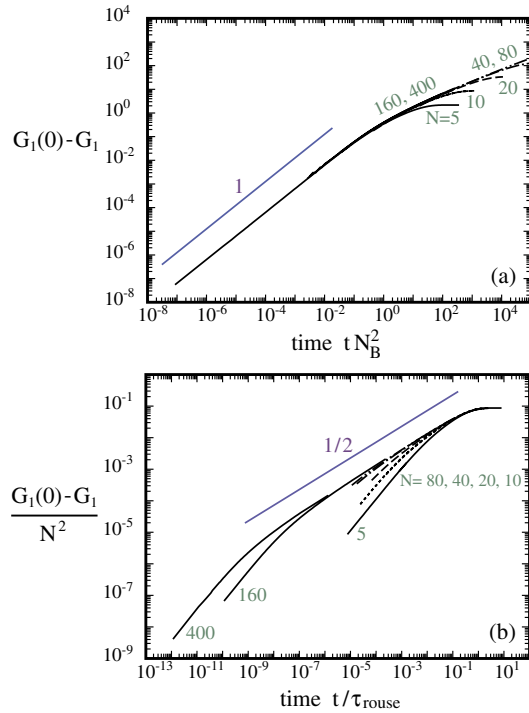


FIG. 1 (color online). Scaling law for the chain's length reduction $R_{\parallel}^2(0) - R_{\parallel}^2 \sim G_1(0) - G_1$ (where G_1 is the first eigenvalue of the gyration tensor) at (a) short times and (b) intermediate times for a completely flexible chain ($E = 0$). [Note that τ_{rouse} is the exact value of the time scale for the relaxation of the first normal mode of the Rouse model; for long chains $\tau_{\text{rouse}} = \tau_{\text{rand}} N^2 / (3\pi^2) \sim N^2$ [8].] Both laws were generated by employing chains with $N = 5, 10, 20, 40, 80, 160$, and 400.

F_{\perp}^{rand} at times $\tau_{\text{bend}} \sim E^{-1}$, i.e., the shortest time scale associated with the transverse fluctuations of two successive links due to the bending energy. Afterwards, these chains show a transverse evolution $R_{\perp}^2 \sim E^{-1/4} t^{3/4}$ until the end of the intermediate-time behavior at times $\tau_{\perp} \sim N^4/E$, i.e., the longest bending time scale associated with the entire polymer chain. Therefore, long stiff chains show two intermediate-time behaviors; by matching the two growing rates for R_{\perp}^2 , the transition from the early to the late intermediate-time behavior was also identified as the times $\tau_{\text{mid}} \sim N^4/E^3$ [7].

Based on the discussion above, after a long stiff chain is left to relax, its length is reduced as $R_{\parallel}^2(0) - R_{\parallel}^2 \sim N^2 t$ until times $\tau_{\text{ten}} \sim N^{-2}$; this reduction results from the transverse free diffusion of each bead and the link inextensibility as explained previously for flexible chains. [The corresponding figure is similar to Fig. 1(a) and has been omitted.] During the early intermediate times $\tau_{\text{ten}} \ll t \ll \tau_{\text{mid}}$, the chain's length reduction is identical to that for flexible chains, i.e., $R_{\parallel}^2(0) - R_{\parallel}^2 \sim N t^{1/2}$ or $\Delta R_{\parallel} = R_{\parallel}(0) - R_{\parallel} \sim t^{1/2}$, as shown in Fig. 2 for stiff chains with $E/N = 10$. Therefore, the dominant longitudinal force $F_{\parallel} \sim N t^{-1/2}$ is again derived from Eq. (4) above and is associated with the tensions necessary to ensure link inextensibility against the action of the deforming Brownian forces.

In the case of short stiff chains $N \leq (E/N)$, the initial length reduction due to the transverse free diffusion of each bead is again $R_{\parallel}^2(0) - R_{\parallel}^2 \sim N^2 t$; however, the short-time behavior is now extended up to $\tau_{\text{bend}} \sim E^{-1}$, as shown in Fig. 3(a). During the intermediate times $\tau_{\text{bend}} \ll t \ll \tau_{\perp}$ the chain's length reduction is slower as shown in Fig. 3(b) over seven time decades,

$$R_{\parallel}^2(0) - R_{\parallel}^2 \sim N^2 E^{-3/4} t^{1/4} \quad \text{or} \quad \Delta R_{\parallel} \sim N E^{-3/4} t^{1/4}. \quad (5)$$

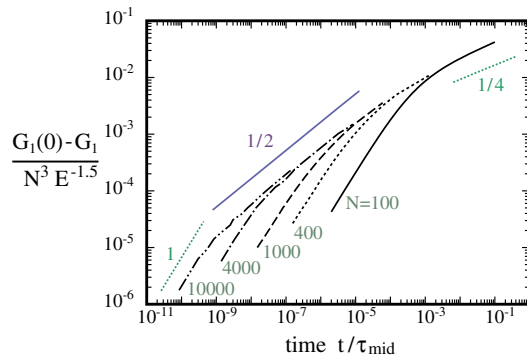


FIG. 2 (color online). Scaling law for the chain's length reduction $R_{\parallel}^2(0) - R_{\parallel}^2 \sim G_1(0) - G_1$ of long stiff chains with $E/N = 10$ at early intermediate times. The length reduction $G_1(0) - G_1$ has been scaled with its magnitude $N^3/E^{3/2}$ at the end of the early intermediate times, τ_{mid} . Also shown are the free diffusion at short times and the $t^{1/4}$ evolution at late intermediate times.

This behavior also constitutes the late intermediate-time behavior of long stiff chains for times $\tau_{\text{mid}} \ll t \ll \tau_{\perp}$.

The solvent friction resists the chain's length reduction and thus the longitudinal component of the dominant force acting on the polymer chain is given by

$$F_{\parallel} \sim \zeta_{\text{ch}} \frac{d\Delta R_{\parallel}}{dt} \sim N^2 E^{-3/4} t^{-3/4}. \quad (6)$$

This force should be the longitudinal tension force $F_{\parallel}^{\text{ten}} \sim T d_{\parallel} \sim T$ (since $d_{\parallel} \sim 1$), and thus during the late intermediate times the tensions should relax as $T \sim N^2 E^{-3/4} t^{-3/4}$. To verify our conclusion on the tension relaxation, we numerically determined the average tensions along the polymer chain and found the same scaling law behavior, as shown in Fig. 4(a). The dependence of the tensions on the chain stiffness E verifies our earlier conclusion that only during the late intermediate times the chain stiffness should affect the longitudinal relaxation.

Thus for both flexible and stiff chains, the entire polymer relaxation is caused by the relaxation of tensions. A completely straight chain has accumulated $T = O(N^2)$ tensions required to preserve the link length against the action of the deforming Brownian forces. This applies to both flexible and stiff chains since for a straight chain the bending forces are identically zero. For a flexible chain,

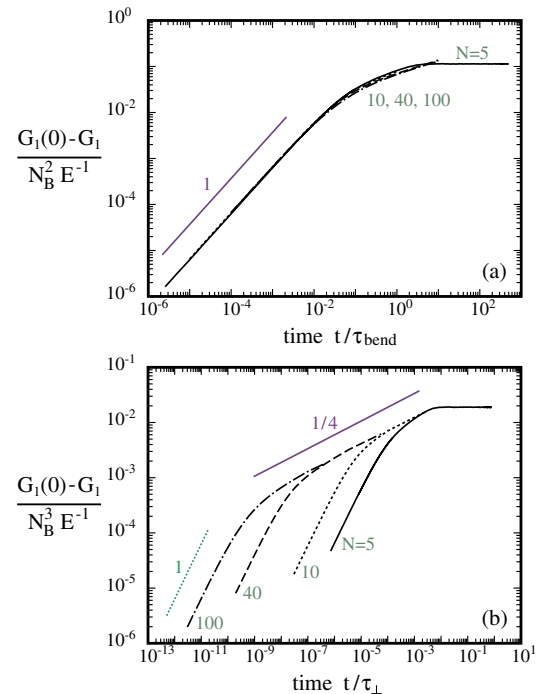


FIG. 3 (color online). Scaling law for the chain's length reduction $R_{\parallel}^2(0) - R_{\parallel}^2 \sim G_1(0) - G_1$ at (a) short times and (b) (late) intermediate times for stiff chains with $E/N = 10$. The curves were generated by employing chains with $N = 5, 10, 40, \text{ and } 100$.

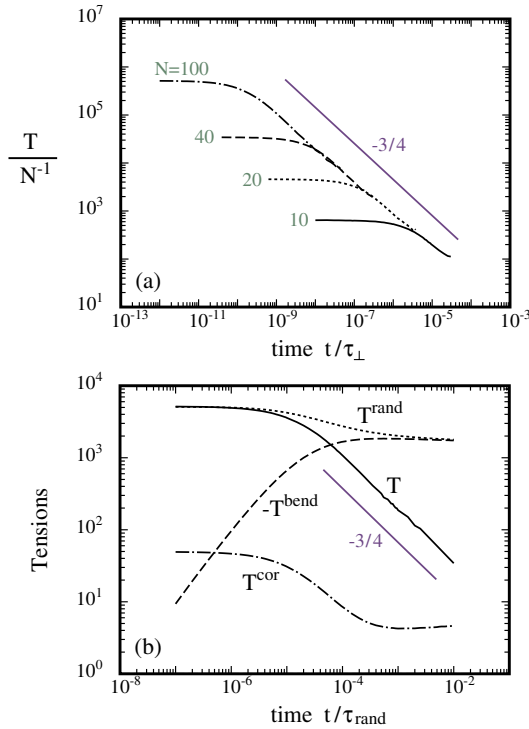


FIG. 4 (color online). Tension relaxation at the late intermediate times for stiff chains with $E/N = 10$. (a) Scaling law for the total tensions T . (b) Relaxation of the tension components for a chain with length $N = 100$. Each component represents the tensions required to preserve the link inextensibility against the action of the corresponding force appearing in (1) above.

the single intermediate-time behavior is associated with the tension relaxation due to the deforming Brownian forces. The same conclusion is valid for the early intermediate-time relaxation of stiff chains where the influence of the longitudinal bending forces is negligible due to the nearly straight chain configuration. For a stiff chain, at the transition times τ_{mid} the tension relaxation changes nature since afterwards it is affected by both Brownian and bending forces, as seen in Fig. 4(b). This figure reveals that the Brownian and bending forces have opposite effects on the link tensions: the former try to change the link length, while the latter try to preserve the link length. [Note that in Fig. 4(b) we plot $-T^{bend}$.] The component of the tensions which is associated with the (small) corrective potential force F_i^{cor} is negligible as expected. The cumulative effect of T^{rand} and T^{bend} produces a total tension T decaying as $t^{-3/4}$.

Therefore, the early intermediate-time behavior shown in Figs. 1(b) and 2 above is a *universal* behavior valid for any polymer chain with $0 \leq E \leq N^2$, i.e., from the completely flexible $E = 0$ up to the ultrastiff limit $E = N^2$. Ultrastiff chains $E \gg N^2$ (i.e., a stiffness regime we identified in our earlier work [5]) show $\tau_{bend} \ll \tau_{ten}$ and thus are expected to follow only one intermediate-time

behavior identical to late intermediate-time behavior of stiff chains shown in Fig. 3(b) above. Thus, the late intermediate-time behavior is valid for any stiff chain $E \geq N$.

We emphasize that it is the early longitudinal relaxation which constitutes a universal behavior for any chain stiffness, and not the corresponding transverse evolution which is affected by the bending forces. For a given length reduction $R_{\parallel}(0) - R_{\parallel}$, a flexible chain is more likely to relax transversely through shorter modes than a stiff chain; this results in a slower transverse growth for the flexible chain, $(R_{\perp}^2)_{flexible} \sim N^{-1/2}t^{3/4} \leq (R_{\perp}^2)_{stiff} \sim N^{-1/3}t^{5/6}$. Thus, polymer properties which depend on the chain's length R_{\parallel} should also show an early universal relaxation, while those depending on R_{\perp} should be affected by the chain stiffness.

The experience with the wormlike chain model suggests that the tensions always play a significant role in the polymer dynamics both near and far from equilibrium (e.g., [3,4,6] as well as the present study). Our methodology to determine the tensions and the tension components (which we establish in the current Letter) combined with our methodology to determine over extended time periods the chain's configuration evolution (which we established in our previous paper [7]) helps us understand the problem mechanism and physics, and furthermore the properties of the polymer solution. For example, during intermediate times we can prove that the polymer stress scales as $\sigma_{11} \sim R_{\parallel}F_{\parallel} \sim NF_{\parallel}$, where F_{\parallel} is given by (4) and (6), while the solution birefringence obeys the law $B(0) - B(t) \sim [R_{\parallel}^2(0) - R_{\parallel}^2]/N$, where $R_{\parallel}^2(0) - R_{\parallel}^2$ is given by (3) and (5) above [8,9]. Thus, we believe that these methodologies are well suited to study a wide array of problems in polymer dynamics.

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