Chain motion and viscoelasticity in highly entangled solutions of semiflexible rods

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Brownian dynamics simulations are used to study highly entangled solutions of semiflexible polymers. Bending fluctuations of semiflexible rods are significantly affected by entanglement only above a concentration $c^*$, where $c^* \sim 10^3 L^{-3}$ for chains of similar length $L$ and persistence length. For $c > c^*$, the tube radius $R_e$ approaches a dependence $R_e \propto c^{-3/5}$, and the linear viscoelastic response develops an elastic contribution that is absent for $c < c^*$. Experiments on isotropic solutions of $F$-actin span concentrations near $c^*$ for which the predicted asymptotic scaling of the plateau modulus $G \propto c^{1/3}$ is not yet valid.

Solutions of long polymers become entangled when the concentration or chain length exceeds a threshold. The nature of “entanglement” is obviously different, however, for random walks, rigid rods, and semiflexible threads. It has been proposed that solutions of semiflexible rods, of length $L$ less than or equal to their persistence length $L_p$, may exhibit two different levels of entanglement, in different concentration regimes $[1, 2, 3, 4]$ – a loosely-entangled regime, in which only rotations and transverse translations are hindered by collisions, and a tightly-entangled regime, in which transverse shape fluctuations are also strongly affected. The crossover between these two regimes is expected to be associated with a qualitative change in viscoelastic properties, due to the inability of a tightly-entangled solution to rapidly relax stress arising from transverse chain deformations. Clear experimental evidence of “tight” entanglement has been obtained only for so-called wormlike chains.

A modified tube model $[2, 3, 13]$ in which each chain undergoes reptation in a narrow wormlike tube. A scaling argument due to Odijk and Semenov $[1, 3, 4]$ predicts a tube radius $R_e \propto L_p (\rho L_p^2)^{-3/5}$ for $c \gg c^*$.

Our simulations use a novel algorithm that was designed to allow simulation of Brownian dynamics of arbitrarily thin but uncrossable wormlike threads. Each polymer is represented as a discretized chain of $N$ inextensible rods and $N + 1$ beads. A periodic cubic simulation cell is initially populated with a thermally equilibrated solution of wormlike chains, by a Monte Carlo growth algorithm. At each step of our dynamical simulation, a trial move is generated for a randomly chosen chain by taking one time step of the Brownian dynamics (BD) algorithm used in previous work on dilute solutions $[14, 15, 16]$. A trial move is rejected, however, if it would cause the chosen chain to cut through any other. Whether or not a move is accepted, another chain is then chosen at random, and the process is repeated. In this work, we use an algorithm for chains with anisotropic friction, with $\zeta_\parallel / \zeta_\perp = 1/2$ $[18]$, where $\zeta_\parallel$ and $\zeta_\perp$ are longitudinal and transverse friction coefficients, respectively. Details of the algorithm are presented elsewhere $[17, 18]$. Here, we present results for entangled solutions of chains with $L/L_p = 0.25 - 2.0$ and $N = 10 - 40$ rods at concentrations $c L_3 = 0 - 4000$. A $1\, \text{mg/ml}$ solution of (hypothetically) monodisperse $F$-actin filaments with $L = 8\, \mu\text{m}$ would have $c L_3 \approx 2500$.

To characterize the effect of entanglement upon bending fluctuations, we have calculated two measures of the transverse mean-squared displacement (MSD) vs. time for the middle bead of a polymer. The quantity $\langle \Delta d^2(t) \rangle$, shown in the main plot in Figure 1, is the variance of the distance $\Delta d(t)$ between the middle bead at time $t$ and the closest point on the contour of the same chain at an earlier time $t = 0$. The inset shows $\langle \Delta r_{m,\perp}^2(t) \rangle \equiv \langle |r_{m,\perp}(t) - r_{m,\perp}(0)|^2 \rangle$, in which $r_{m,\perp}(t)$ is the transverse component (transverse to the local chain tangent) of the displacement of the middle bead from the chain’s center of mass. The quantity $\langle \Delta r_{m,\perp}^2(t) \rangle$ is not sensitive to center-of-mass diffusion, but only to displacements arising from bending fluctuations, and so approaches a finite value at long times. At early times, both measures of transverse MSD increase as $t^{3/4}$, as predicted $[19]$. With increasing concentration, both quantities become suppressed over a range of intermediate times, indicating the formation of a tube.
If each chain were confined to a tube of well-defined radius $R_e$ over a wide range of intermediate times, $\langle \Delta d^2(t) \rangle$ would develop a plateau, with a plateau value $\langle \Delta d^2(t) \rangle \simeq 4R_c^2$. Here, $R_c^2$ is defined, as in Ref. [20], as the variance of the transverse displacement of the chain from the “center” of the tube (i.e., the average chain contour) in either of two transverse directions. A plateau could appear in $\langle \Delta d^2(t) \rangle$ even in the rigid rod limit, however, due to suppression of transverse center-of-mass motion. The suppression of $\langle \Delta r_{m,\perp}^2(t) \rangle$ at intermediate times, however, is evidence of hindered bending motion, and thus of tight entanglement. In fact, we never observe a clean plateau in either quantity. Instead, we see a crossover from $t^{5/4}$ growth at small $t$ to a much slower growth at intermediate times, which becomes flatter with increasing concentration and/or chain length (i.e., increasing $cL^3$), with a crossover time $\tau_e$ that decreases with increasing $c$. The suppression in $\langle \Delta r_{m,\perp}^2(t) \rangle$ is significant only for $cL^3 \gtrsim 500$, suggesting a crossover $c^{**} \simeq 500/L^3$ for $L = L_p$.

For $cL^3 = 1000$, our results for $\langle \Delta r_{m,\perp}^2(t) \rangle$ include both a plateau at intermediate times and an upturn at the end of this plateau. This upturn is mimicked very accurately by the results of a separate slithering-snake simulation of pure reptation of a wormlike chain (the red dashed line in the inset) [18]. Pure reptation yields a nonzero transverse MSD ($\langle \Delta r_{m,\perp}^2(t) \rangle$) at times less than the reptation time $\tau_{rep} = c_\perp L_{\perp}/(\pi^2 k_B T)$ because reptation occurs along a curved tube. $\langle \Delta d^2(t) \rangle$ is defined so as not to be affected by pure reptation, and shows a slightly broader plateau than $\langle \Delta r_{m,\perp}^2(t) \rangle$.

To quantify $\tau_e$ and $R_e$, we have collapsed our data for $\langle \Delta d^2(t) \rangle$ in a manner that assumes the existence of a scaling relationship $\langle \Delta d^2(t) \rangle = 4R_c^2 f(t/\tau_e)$. That is, we have chosen values for $R_e$ and an entanglement time $\tau_e$ for each set of parameters so as to collapse the data for many different values of $L/L_p$ and $cL^3$ onto a master curve of $\langle \Delta d^2(t) \rangle/(2R_c)^2$ vs. $t/\tau_e$. The resulting collapse is shown in Figure 2. We display separate master curves for chains with $N = 20$ and $N = 40$ because early time behavior is noticeably different for discrete chains with different numbers of rods. The collapse is excellent for solutions with $cL^3 \gtrsim 1000$. The horizontal dashed lines with $\langle \Delta d^2(t) \rangle/4R_c^2 = 1$ represent an assumed long time asymptote for hypothetical systems of much longer chains, from which we have extracted estimates of $R_e$.

Figure 3 shows results of the dimensionless tube radius $R_e/L_p$ vs. dimensionless concentration $\rho L_p^2$ for systems with $L/L_p = 0.5 - 2$. Dimensional analysis requires that the ratio $R_e/L_p$ be a function $R_e/L_p = f(\rho L_p^2/L_p L_p)$ of dimensionless length $L/L_p$ and dimensionless concentration $\rho L_p^2$ alone. In the tightly-entangled regime, however, we expect $R_e$ to become independent of $L$, implying that $R_e/L_p$ must approach a function of $\rho L_p^2$ alone for $c \gg c^{**}$. At high concentrations, our results for different values of $L/L_p$ do indeed approach a common asymptote, which is furthermore very accurately described by the predicted relation $R_e/L_p = \alpha(\rho L_p^2)^{-3/5}$, with $\alpha = 0.95$ (dashed black line). For each value of $L/L_p$, $R_e/L_p$ also exhibits small but systematic deviations from this asymptote at lower concentrations. This deviation is seen most clearly in the inset, in which we plot the ratio $R_e/[0.95\rho L_p(\rho L_p^2)^{-3/5}]$ vs. $\rho L_p^{c**}$, where we have taken $c^{**} = 500L_p^{1/2}L_n^{-7/2}$. The near collapse of the deviations from the asymptote for the stiffest 2 chains ($L/L_p = 0.25$ and 0.5) is consistent with the prediction that $c^{**} \propto L_p^{1/2}L_n^{-7/2}$ for $L \ll L_p$. [4]. The experimental values for $R_e$ in F-actin solutions (crosses) are the fluorescence microscopy results of Kit et al. [5, 6], as defined and presented previously in Ref. [20].

The crossover from loose- to tight-entanglement is expected
to cause a dramatic change in viscoelastic behavior. Detailed theories of linear viscoelasticity have been developed for the extreme limits of dilute solutions (c \ll c^*) \cite{14, 15} and of very tightly entangled solutions (c \gg c^*) \cite{13}. Both theories make use of a formal decomposition of the stress into curvature, orientational, and tension contributions \cite{4}, and a corresponding decomposition of the dynamic modulus G(t) (i.e., the response to an infinitesimal step strain) as a sum G(t) = G_{curv}(t) + G_{ort}(t) + G_{tens}(t). In both dilute and loosely-entangled solution, G_{curv}(t) and G_{tens}(t) are predicted to exhibit power law decays at very early times, but to decay exponentially at times greater than the relaxation time \tau_{\perp} = \beta \zeta \lambda L^3/(k_B T L_p) of the longest wavelength bending mode, where \beta = (4.74)^{-4}. For c < c^*, G(t) is thus dominated at t > \tau_{\perp} by a more slowly decaying orientational modulus G_{ort}(t) \approx (3/5)ck_B T e^{-t/\tau_{rod}}, where \tau_{rod} is a rotational diffusion time. In loosely-entangled solutions, the only predicted effect of entanglement is to increase \tau_{rod}, without significantly changing G_{curv}(t) or G_{tens}(t). The plateau of magnitude (3/5)ck_B T in G_{ort}(t), which is present even in dilute solution, reflects the free energy cost of partially aligning an initially random distribution of rod orientations. The crossover to tight entanglement, however, is expected to cause a plateau to appear in G_{curv}(t), with a plateau value G_{curv,0} that varies as \cite{4, 13, 21} G_{curv,0} \propto k_B T \rho^{7/5} L_p^{-1/5} for c \gg c^*.

We have “measured” G(t) and its components by simulating stress relaxation after a rapid, small amplitude uniaxial step extension of an initially cubic periodic unit cell. Stress is evaluated using the virial tensor, as in previous simulations of dilute solutions \cite{14, 15}. Measurements of G(t) in dilute solution by this method agree to within statistical errors with those obtained previously \cite{14, 15} from stress fluctuations in equilibrium.

In Figure 4 the main plot shows a non-dimensionalized sum [G_{ort}(t) + G_{curv}(t)]/(ck_B T) of the orientational and curvature moduli as a function of \rho L_p^2. Numbers in the legend are values of \rho L_p^2 = 250, 500, 1000. Inset: Corresponding tension stress G_{tens}(t)/(ck_B T) for systems with \rho L_p^2 = 0, 250, 500, 1000.

![FIG. 3: Non-dimensionalized tube radius vs. concentration. Numbers in the legend are values of L/L_p. Crosses are fluorescence microscopy results for F-actin \cite{3}, non-dimensionalized by L_p = \lambda T_{eff}. Inset: Deviation R_c^*/R_c^{(0)} from the asymptote vs. c/c^*+, where R_c^{(0)} \equiv 0.95L_p(\rho L_p^2)^{-3/5} corresponds to the dashed line in the main plot, and where c^*+ = 500L_p^{1/2} L^{-7/2}.

![FIG. 4: Non-dimensionalized sum [G_{ort}(t) + G_{curv}(t)]/(ck_B T) of the orientational and curvature moduli vs t/\tau_{rod} for L/L_p = 0.5. Numbers in the legend are values of cL_p^3. Dashed curves are fits, as discussed in the text. Black solid curves in both plots are theoretical predictions for dilute solutions \cite{15}. Inset: Corresponding tension stress G_{tens}(t)/(ck_B T) for systems with cL_p^3 = 0, 250, 500, 1000.}
The total plateau modulus $G_0$ in $G(t)$ is a sum $G_0 = (3/5)ck_BT + G_{\text{curv,0}}$, of orientational and curvature contributions. Figure 5 compares simulation results for $G_0$ and $G_{\text{curv,0}}$ to reported values of $G_0$ in entangled F-actin solutions [9, 10]. The results of Hinner et al. [8] were obtained by macroscopic rheological measurements, while those of Gardel et al. [10] were obtained from two-particle micro-rheology. Our results for $G_0$ agree well with the values of Hinner et al., and are well within the scatter of results reported in the recent literature. A fit of our results for $G_0$ to a power of $c$ yields $G_0/c \propto c^{0.7}$. It is clear from the simulation data, however, that the range of concentrations accessed in our simulations, and most of that studied experimentally, lies within about one decade of the beginning of a broad crossover to tightly entangled behavior, below which $G_{\text{curv}}(t)$ does not contribute to $G_0$. As a result of this proximity to $c^*$, $G_{\text{curv}}(t)$ dominates $G_0$ over much of this range, while the contribution $G_{\text{curv,0}}$ that is actually predicted to vary as $G_{\text{curv,0}}/c \propto c^{0.4}$ in the limit $c \gg c^*$ increases much more rapidly from nearly zero. The results suggest that the very rough agreement between the predicted asymptotic behavior of $G_{\text{curv,0}}$ for $c \gg c^*$ and measurements of $G_0$ in F-actin may be largely fortuitous.

The isotropic-nematic (IN) transition for rodlike polymers occurs at a concentration $c_{1N}L^3 \approx 4L/d$. Values of $L/d$ for available model systems with $L \lesssim L_p$ other than F-actin, such as Fd virus [22] ($L \approx 0.9 \mu m$, $L_p \sim 2 \mu m$, $d \sim 7$ nm) and rod-like poly(benzyl glutamate) [11] ($L_p \sim 0.15 \mu m$ and $d \sim 2$ nm) are all at least 10 times smaller than for F-actin, for which $L/d \sim 10^3$. The IN transition in systems with $L/d < 100$ occurs at concentrations $c_{1N}L^3 \lesssim 400$, at which $c < c^*$. Our rough estimate of $c^* \sim 500L_p^2L^{-7/2}$ for $L \lesssim L_p$ implies that a clear tightly-entangled isotropic regime for semiflexible rods can exist only in systems with $L/d \gtrsim 10^3$. This is consistent with the fact that a clear rheological signature of tight entanglement has been observed only in F-actin solutions.

Taken as a whole, our results both provide evidence for the correctness of a simple scaling theory for the asymptotic dependence of tube radius upon concentration in tightly-entangled solutions, and (equally importantly) clarify the limits of validity that theory, particularly as applied to rheology. It appears that bending fluctuations of rods with $L \sim L_p$ are significantly hindered by entanglement only under surprisingly stringent conditions.

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