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Viscoelasticity of Concentrated Isotropic Solutions of Semiflexible Polymers. 1. Model and Stress Tensor

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ABSTRACT: The viscoelastic behavior of entangled solutions of semiflexible chains is discussed. After identifying the different possible regimes of concentration and chain length in such a solution, attention is focused on a "tightly-entangled" regime in which the polymer is confined to a tube of diameter less than its persistence length. A tube model analogous to the Doi−Edwards model is introduced to describe this regime. A general expression for the stress tensor of a solution of wormlike chains is derived, which may be applied to any concentration regime, and three intramolecular stress contributions are identified: a curvature contribution arising from forces that oppose transverse deformation or rotation of chain segments, a tension contribution arising from tangential forces that resist stretching or compression of the chain, and an orientational contribution that reduces in the appropriate limit to the Brownian stress of a rigid-rod solution. Intermolecular stress contributions are also calculated. A qualitative discussion is given of the high-frequency viscoelastic response of any solution of wormlike chains, which is dominated by the tension contribution and exhibits a characteristic power law dependence on frequency.

I. Introduction

Current understanding of the viscoelasticity of entangled polymer solutions[1−3] is based to a large extent upon the ideas contained in two models proposed by Doi and Edwards (DE) in 1978−9 to describe viscoelastic behavior in the two extreme cases of completely flexible[4] and completely rigid-rod polymers.[5] The DE model of flexible polymers, which was based upon deGennes' reptation model of polymer dynamics,[6] was, despite some well-documented failings,[7,8] the first qualitatively successful molecular model of such systems, and as such it has formed the starting point of most subsequent theoretical work on flexible backbone systems. Similarly, the DE model of semidilute rigid rod solutions[5] and the related Doi model[9,10] of liquid-crystalline solutions have together formed the starting point for most subsequent theoretical work on solutions of relatively rigid polymers such as those of interest here. There exists, however, a rather large class of persistent semiflexible polymers, in which the degree of backbone rigidity is intermediate between the extremes described by the two DE models and their progeny, but which remain stiff enough to form lyotropic liquid-crystalline solutions. Among these are[11−13] DNA, helical protein filaments such as actin, synthetic helical polypeptides such as poly(benzyl glutamate) (PBLG), cellulose and its derivatives, xanthan, various poly(*n*-alkyl isocyanates), and aromatic polyamides such as Kevlar. To accurately describe solutions of such polymers, it will presumably be necessary to develop models of viscoelasticity that explicitly take into account the semiflexible nature of the polymer backbone.

The degree of a polymer's backbone rigidity may be specified within the context of a wormlike chain model by the persistence length L_p of the chain, which is of order $L_p \simeq 10^2-10^5$ Å for the molecules of interest here, and, in the same class of systems, of order $10-10^3$ times the steric diameter d of the polymer. This model interpolates smoothly between the limit of rod-like polymers, with contour lengths L much less than L_p, and coil-like polymers, with $L \gg L_p$.

The degree to which the partial rigidity of a molecule will affect a solution's viscoelastic behavior will depend upon the ratio L/L_p, the solution concentration, and the length and time scales probed by experiment. In a dilute solution, fluctuation modes of the polymer with wavelengths $\lambda \gg L_p$ (where λ is measured along the polymer backbone) are presumably describable as Zimm modes of a Gaussian chain (though one with an enormous statistical segment length), while modes with wavelengths $\lambda \ll L_p$ are better described as bending modes of a nearly rigid chain. The low-frequency viscoelastic behavior of an entangled solution of long semiflexible chains, for which $L \gg L_p \gg d$, is expected to differ qualitatively from that of an entangled solution of flexible chains only if L_p exceeds the entanglement length of the solution, so that the relaxation of bending modes, with wavelengths $\lambda \lesssim L_p$, is impeded by entanglement with neighboring chains. The low-frequency behavior of a solution of more rod-like chains, with $L_p \gtrsim L \gg d$, is expected to differ qualitatively from that of an entangled solution of completely rigid rods only when the root mean square magnitude of the thermally excited transverse fluctuations of the chain (i.e., transverse to its end-to-end vector) become larger than the radius of the tube formed by neighboring chains, thus, again, impeding the relaxation of the bending modes.

These regimes in which relaxation of the polymers' bending modes is strongly impeded by the presence of other chains may be reasonably described by a reptation model in which the polymer is confined to a tube with a diameter D_e much less than its persistence length and in which the conformation of the tube is itself described by a wormlike chain model. Systems fitting this description are referred to in what follows as "tightly-entangled" solutions, by analogy to Semenov et al.'s[14] discussion of an analogous regime of "tight" gels in their study of gel electrophoresis and in contrast to the

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"loosely-entangled" regimes that the two DE models are intended to describe. In these regimes, the geometry of the tube may be characterized by specifying either a tube diameter D_e or a length L_e of order the contour distance between collisions of the polymer with the walls of the tube. The length L_e, which Odijk[15] referred to as the deflection length, will be referred to here as the entanglement length. The dependence of D_e and L_e upon L_p and concentration may be estimated by simple scaling arguments introduced by Odijk[15] and Semenov,[16] which are reviewed in section II. The Brownian motion of polymers in such tightly-entangled solutions has been discussed previously, using a tube model similar to that used here, by Odijk,[15] Doi,[17] and Semenov.[16]

The main purpose of this and parts 2 and 3 in this series[20] is to characterize the linear and nonlinear viscoelastic behavior of such solutions. In the context of studies of entangled solutions of actin filaments, two rather different pictures have been proposed for the physical origin of the elastic stress of tightly-entangled solutions by, respectively, MacKintosh et al.[18] and by Isambert and Maggs.[19] In both pictures, as here, it is assumed that the solution is tightly-entangled in the sense discussed above, and that D_e and L_e vary with concentration in the manner predicted by Semenov.

MacKintosh et al.[18] assume that the elastic stress arises primarily from the tangential tension that, by suppressing or enhancing the magnitude of undulation modes with a wavelength less than L_e, controls variations in the end-to-end distance of segments of length L_e. The resulting picture makes sense, however, only if it assumed that the polymer is somehow prevented from sliding tangentially along the tube in order to relax the resulting variations in chain tension within the time scales of interest, as could occur if the solution was cross-linked.

Isambert and Maggs[19] instead assume that, as in the DE model, a polymer in an un-cross-linked solution is free to slide tangentially along the tube, and thus cannot support such variations in tension over time scales on the order of the longest relaxation time in the problem, which is given by the time necessary for the entire polymer to disengage from the tube via reptation. As a result, Isambert and Maggs argued that the the longest lived components of the elastic stress will arise from the forces resisting transverse deformations of the tube conformation. Without actually formulating an expression for the resulting stress, Isambert and Maggs asserted (correctly) on heuristic grounds that the corresponding plateau modulus should be of order k_BT per entanglement length L_e of chain per unit volume of solution. As pointed out by Isambert and Maggs[19] and more pointedly by Maggs,[22] the distinction between the two mechanisms is in part a matter of time scales: experiments that probe time scales less than that required for relaxation of the chain tension will see a modulus dominated by the effects of tangential forces, while experiments that probe time scales long enough for tension to relax should see a smaller modulus that is dominated by the effects of transverse forces arising from the deformation of the tube.

The remainder of this paper is organized as follows: Section II contains a discussion of the different regimes of polymer concentration and chain length expected for solutions of semiflexible polymers and identifies the limits of the tightly-entangled regime of primary interest. In section III, a primitive chain model of a tightly-entangled solution is introduced in which, for specificity, the primitive (i.e., coarse-grained) chain is described as a discrete Kratky−Porod chain with link lengths on the order of the entanglement length. In section V, which draws on technical calculations presented in Appendices A and B, a rather general expression is presented for the stress tensor of an interacting solution of wormlike chains. Section VI is devoted to the construction of a more qualitative (i.e., scaling) description of high-frequency behavior, which predicts a power law of $G^*(\omega) \propto (i\omega)^{3/4}$ at very high frequencies. Section VII contains a brief summary of results.

The two companion papers in this series,[20] which will hereafter be referred to as "(II)" and "(III)" contain discussions of, respectively, the linear and nonlinear viscoelastic and optical behavior obtained from the model developed here. Occasional references to equations given in (II) will be denoted here by use of "II" as a prefix to the equation number; i.e., eq II.3 is eq 3 in (II). A brief summary of our results for linear viscoelastic response, as described in detail here and in (II), has been being published separately.[21]

II. Concentration Regimes

Consider a solution of M semiflexible polymers, each of fixed contour length L and hard-core diameter d. The conformation of chain α (with $\alpha = 1, ..., M$) may be described by specifying a position $\mathbf{r}_\alpha(s)$ as a function of contour length s, with $0 < s < L$. To describe the local orientation and curvature of the chain, we introduce tangent and curvature vectors

$$\mathbf{u}_\alpha(s) \equiv \partial\mathbf{r}_\alpha(s)/\partial s, \quad \mathbf{w}_\alpha(s) \equiv \partial\mathbf{u}_\alpha(s)/\partial s \tag{1}$$

The condition that the chain be locally inextensible is imposed by requiring that $|\mathbf{u}_\alpha(s)| = 1$. The variations of the tangent vector along each chain are controlled by a wormlike chain bending energy

$$U_{\mathrm{bend}} = {}^1\!/_2 TL_p \sum_\alpha \int_0^L \mathrm{d}s\ |\mathbf{w}_\alpha(s)|^2 \tag{2}$$

where L_p is a bending constant with dimensions of length, which is the persistence length of the chain. The Kuhn length l used by Semenov[16] and others to characterize the stiffness of the chain is given by $l = 2L_p$. Here and in what follows, temperature T is given in units of energy, thus implicitly setting $k_B = 1$.

The solution is assumed to contain M polymers in a volume V, yielding a number density $c = M/V$, and a polymer volume fraction $\phi = {}^1\!/_4\pi cLd^2$. For our purposes, the concentration of the solution is most conveniently specified by the density

$$\rho \equiv cL \tag{3}$$

of contour length per unit volume. This contour length density may be used to define a mesh size $L_m \equiv \rho^{-1/2}$, which, for $L_p \gg L_m$, is on the order of the average distance between neighboring strands of polymer.

The dynamics of a polymer within an entangled solution may be described by a reptation model, in which it is assumed that over short times each chain is trapped in a tube formed by the surrounding chains. In constructing such a model, it is useful to introduce as a phenomenological parameter a characteristic entanglement contour length L_e and assume that fluctuation (e.g., Rouse or undulation) modes of contour wave-

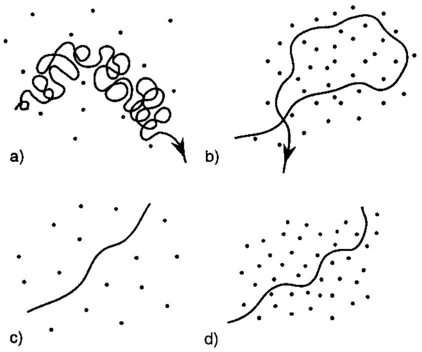

Figure 1. Schematic representation of a semiflexible chain within an entangled isotropic solution (with other chains represented by points) within (a) the loosely-entangled coil regime, in which $L \gg L_p$ but L_p is much less than the tube diameter D_e, (b) the tightly-entangled coil regime, where $L \gg L_p$ and $L_p \gg D_e$, (c) the loosely-entangled rod regime, where $L \ll L_p$ and where rotation of the rod is impeded by entanglement but fluctuations of the bending modes are not, and (d) the tightly-entangled rod regime, in which $L \ll L_p$ and in which both rotations and shape fluctuations are impeded by entanglement and thus relax only via reptation. Tightly-entangled solutions of coil-like and rod-like polymers have a similar local geometry and are both described here by a model based on a reptating wormlike primitive chain.

lengths $\lambda \ll L_e$ are essentially unaffected by entanglements and thus relax rapidly with decay times characteristic of an unentangled chain, but that modes with wavelengths $\lambda \gg L_e$ are constrained by entanglements and thus can relax only via reptation. The regimes of dynamical behavior of an entangled solution may thus be characterized in terms of the relative magnitudes of four length scales: the contour length L, the persistence length L_p, the entanglement length L_e (which depends upon both L_p and the mesh size L_m), and the chain diameter d.

A. Coil-like Limit: $L \gg L_p$. First, consider the case of long chains, with $L \gg L_p$, for which the equilibrium conformation is a random coil (in θ-solvent) with a radius of gyration R_g and a Kuhn length of order L_p. At concentrations above the overlap concentration

$$\rho^*_{\mathrm{coil}} \propto L/R_g^{\,3} \tag{4}$$

one expects to find two distinct isotropic entangled regimes and, at higher concentrations, a nematic liquid-crystalline phase:

(1) Loosely-Entangled Regime. At relatively low concentrations, for which $L_e \gg L_p$, a polymer within an entangled solutions may execute a random walk between entanglements or collisions with the walls of the suro unding tube, leaving the chain only "loosely" confined within the tube, as shown in Figure 1a. It is this regime that the DE model of flexible chains is intended to describe, since in this regime all slowly decaying contributions to the stress may be described using a stress tensor derived from the classical theory of rubber elasticity, which assumes that the chain executes a random walk between cross-links or entanglement points. The tube is assumed to have some diameter D_e, and the tube conformation may be modeled as a random walk of links of some link length $a \sim D_e$, each of which contains a contour length L_e of polymer. The contour density ρ may be approximated by the density $\rho \simeq L_e/D_e^3$ of polymer within a blob of size D_e and contour length L_e, where $D_e \propto [L_e L_p]^{1/2}$ if the polymer executes a random walk within the blob. This yields

$$L_e \propto L_p(\rho L_p^{\,2})^{-2}, \quad D_e \propto L_p(\rho L_p^{\,2})^{-1} \tag{5}$$

The requirement that $L_e \gg L_p$ is thus seen to be satisfied, in this simple treatment, only at concentrations less than a crossover concentration

$$\rho^{**}_{\mathrm{coil}} \propto 1/L_p^{\,2} \tag{6}$$

for which $L_p \sim L_e \sim L_m$.[24] Above this concentration, the solution becomes tightly-entangled, as discussed below.

(2) Tightly-Entangled Regime. This paper focuses instead upon the tightly-entangled regime in which $L_p \gg L_e$. In this regime, the polymer is confined to a weakly curved tube of a diameter $D_e \ll L_p$, so the polymer tangent $\mathbf{u}(s)$ can wander only slightly between entanglements, as shown in Figure 1b. To relate the diameter of the tube and the entanglement length, the entanglement length relevant to rheology is first identified with the "deflection length" introduced by Odijk,[15] which is the distance between collisions of the polymer with the walls of a confining tube. This yields a tube diameter $D_e \sim L_e^{3/2} L_p^{-1/2}$, given by the distance that a chain segment of length $L_e \ll L_p$ will wander in the plane perpendicular to its local orientation due to thermal fluctuations. A second relationship between D_e and L_e may then be obtained, following Semenov,[16] by requiring that the number of other polymers that pierce a cylinder of diameter D_e and length L_e should be of order 1, implying that $\rho L_e D_e \sim 1$. Together, these conditions yield an entanglement length and tube diameter

$$L_e \sim L_p(\rho L_p^{\,2})^{-2/5}, \quad D_e \sim L_p(\rho L_p^{\,2})^{-3/5} \tag{7}$$

Note that both L_e and D_e remain smaller than L_p, as assumed in the above discussion, only when $\rho L_p^2 \gg 1$, or, equivalently, when $\rho \gg \rho^{**}_{\mathrm{coil}}$.

(3) Liquid-Crystalline Phase. Further increasing the concentration must eventually lead to the creation of a nematic liquid-crystalline phase. According to Khokhlov and Semenov's[26] modification of the Onsager theory of rigid rods,[23] the formation of a biphasic region is expected to begin for long chains of diameter $d \ll L_p \ll L$ at a concentration

$$\rho_{\mathrm{nem}} \simeq 6.7/(L_p d) \tag{8}$$

where d is the effective steric chain diameter.

The fact that $\rho_{\mathrm{nem}}/\rho^{**}_{\mathrm{coil}} \propto L_p/d$ implies that the range of concentrations $\rho^{**}_{\mathrm{coil}} \ll \rho \ll \rho_{\mathrm{nem}}$ in which the solution is predicted to remain isotropic and tightly-entangled must become broad for sufficiently large values of the aspect ratio L_p/d, as shown in Figure 2. Recent experiments in which the motion of labeled chains of F-actin within an entangled solution was visualized by optical microscopy[25] (in isotropic solutions for which $L_p \sim L \sim 20\ \mu$m, $d \simeq 0.01\ \mu$m, and $\rho/\rho_{\mathrm{nem}} \sim 0.02-1.0$) give direct visual evidence of the confinement of the polymers to tubes of diameters $D_e \simeq (0.01-0.1)L_p$. Systems which exhibit a broad tightly-entangled isotropic regime might also be expected to remain tightly-entangled in the nematic phase, at least at concentrations sufficiently near ρ_{nem}, suggesting that the present analysis of a tightly-entangled isotropic solutions may constitute a prerequisite to the formulation of a sensible molecular theory for the rheology of lyotropic liquid-crystalline solutions of such polymers.

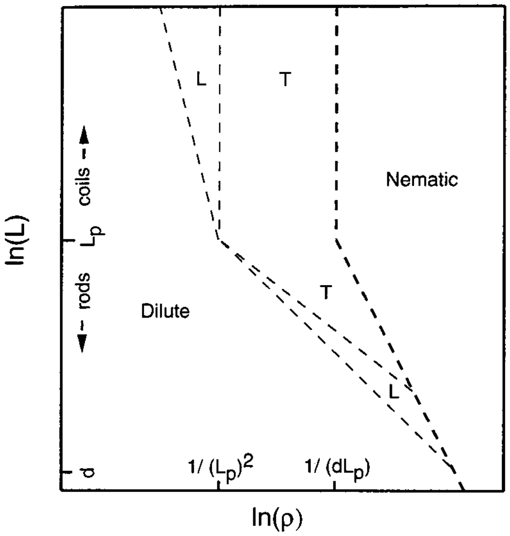

Figure 2. Schematic diagram of concentration and contour length regimes for solutions of semiflexible polymers, based on scaling arguments discussed in section II. *T* denotes the tightly-entangled regimes and *L* denotes the loosely entangled regimes of coil-like polymers, with $L > L_p$, and rod-like polymers, with $L < L_p$. The isotropic tightly-entangled coil-like regime is bounded below by a concentration $\rho^{**}_{\rm coil} \sim 1/L_p^2$ and above by the Khokhlov–Semenov isotropic–nematic transition concentration $\rho_{\rm nem} \sim 1/(dL_p)$. The isotropic tightly-entangled rod-like regime is bounded below by a concentration $\rho^{**}_{\rm rod} \sim L_p^{1/2}/L^{5/2}$, above which $L_e \lesssim L$, and is bounded above by the Onsager transition concentration $\rho_{\rm nem} \sim 1/(dL)$. The loosely-entangled coil-like and rod-like regimes are bounded below by the overlap concentrations $\rho^*_{\rm coil} \sim L/R_g^3$ and $\rho^*_{\rm rod} \sim 1/L^2$, respectively.

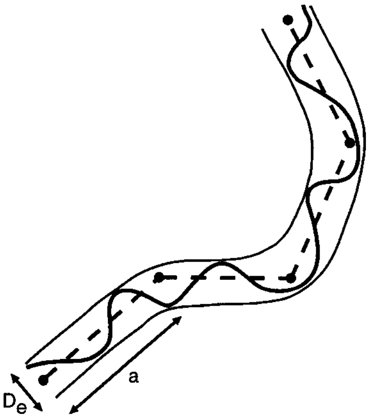

Figure 3. Schematic of relationship of actual chain contour, shown by thick line, the surrounding tube of diameter D_e, and the discrete representation of the primitive chain as a Kratky–Porod chain with links of length *a*, where $a \sim L_e$ is of order the distance between collisions of the polymer with the tube walls.

B. Rod-like Limit: $L \ll L_p$. Now consider the behavior of short, rod-like polymers, of length $L \lesssim L_p$. At concentrations less than an overlap concentration

$$\rho^*_{\rm rod} \sim 1/L^2 \tag{9}$$

solutions of such rods are dilute, since rods may rotate freely without colliding with other chains. At higher concentrations, two possible isotropic concentration regimes may be identified, which will again be described as loosely- and tightly-entangled, as well as a nematic phase at even higher concentrations:

(1) Loosely-Entangled Regime. At concentrations greater than $\rho^*_{\rm rod}$ but less than a crossover concentration

$$\rho^{**}_{\rm rod} \sim (L_p/L)^{1/2}\rho^*_{\rm rod} \tag{10}$$

rotation of the polymers is hindered by the presence of other polymers, but fluctuations of the polymers' bending modes are essentially unaffected, as shown in Figure 1c, since the root mean square transverse displacement $L^{3/2}/L_p^{1/2}$ of the chain due to the thermal fluctuations of such modes may be shown to be less than the tube diameter $1/(\rho L)$ introduced in the DE model of semidilute rigid rods.[5] The same criterion may be reached by noting that for $\rho < \rho^{**}_{\rm rod}$, *L* becomes shorter than the entanglement length L_e given in eq 7.

(2) Tightly-Entangled Regime. At concentrations $\rho \gtrsim \rho^{**}_{\rm rod}$, both the overall orientation and the shape of each chain become constrained by the presence of other chains, as shown in Figure 1d, so distortions of the polymers shape relax only via disengagement of the polymer by reptation. In this regime, the chain becomes longer than the entanglement length L_e given in eq 7, and so the polymer collides several times with the walls of the tube along its length, as a result of its partial flexibility. The local effect of entanglement upon the polymers bending modes is thus very similar in this regime to that found in the tightly-entangled coil-like regime, despite the differences in the global structure of the polymer contour. It has been predicted [15–17] that in this regime the mechanism of rotational diffusion suggested by DE[5] to describe solutions of rigid rods, which involves small rigid rotations of the chain within a tube formed by neighboring chains and yields a predicted rotational diffusivity that decreases rapidly with increasing concentration,[5,27] will be supplanted by a mechanism that makes use of the nonzero flexibility of the chain.[15–17] This latter mechanism yields a predicted rotational diffusivity that depends upon the persistence length L_p of the chain but that is nearly independent of concentration.

(3) Liquid-Crystalline Phase. The formation of a nematic liquid crystalline phase is expected to occur at a critical concentration

$$\rho_{\rm nem} \simeq 4.3/(Ld) \tag{11}$$

as originally predicted by Onsager.[23] Whether $\rho_{\rm nem}$ is greater than $\rho^{**}_{\rm rod}$ depends upon both the aspect ratio L/d and persistence length of the polymer, as well as upon the magnitude of the various unknown numerical prefactors implicit in the scaling arguments given here. At the level of such arguments, however, one finds that $\rho_{\rm nem} \gg \rho^{**}_{\rm rod}$, only if the chain is long or flexible enough so that $L_p \ll L^3/d^2$. A tightly-entangled but isotropic regime of rod-like polymers thus cannot be formed in the limit of completely rigid chains and should be most easily observed in systems with $L/d \gg 1$ but L/L_p not too small.

III. Primitive Chain Model

In this section, a coarse-grained model is introduced to describe low-frequency viscoelastic behavior of tightly-entangled solutions, which applies to both tightly-entangled coils and rods. As in the DE model of flexible polymers, stress relaxation is described in terms of the motion of coarse-grained (or "primitive") chain that is assumed to move only along its own contour. The main difference from the DE model is that, in the tightly-entangled regime, the primitive chain must be described as a semiflexible, rather than a freely-jointed, chain.

The conformation of the primitive chain will be described here, for specificity, by a discrete chain of $N + 1$ beads connected by N links, each representing a subchain containing a fixed contour length L_e of chain, with a preferred end-to-end distance a for each link, as shown in Figure 3. In the limit $L_e \ll L_p$ of interest here, a is only slightly less than L_e so that these two lengths may be treated as equal except in expressions (such as those describing stretching of a segment) that depend upon small differences in length. The numerical value of the link length is, as in the DE model, a phenomenological parameter, but is expected to vary with changes of ρ and L_p as predicted by eq 7.

The position of bead n on polymer α is specified by a vector $\mathbf{r}_\alpha(n)$. The lengths and orientations of the links connecting consecutive beads are described by variables

$$q_\alpha(n) \equiv |\mathbf{r}_\alpha(n) - \mathbf{r}_\alpha(\mathrm{n} - 1)|$$

$$\mathbf{u}_\alpha(n) \equiv (\mathbf{r}_\alpha(n) - \mathbf{r}_\alpha(n - 1))/q_\alpha(n) \tag{12}$$

The limit of interest here is the nearly-inextensible, weakly-curved limit in which $q_\alpha(n)$ fluctuates only very weakly around the preferred link length a and in which $|\mathbf{u}(n) - \mathbf{u}(n + 1)| \ll 1$. In this limit, the discrete analog of the curvature may be written as a difference

$$\mathbf{w}(n) \equiv (\mathbf{u}(n + 1) - \mathbf{u}(n))/a \tag{13}$$

In the same limit, it will also be possible for many purposes to adopt a continuous parametrization of the primitive chain, in which the bead position, unit tangent vector, and curvature are approximated, as in eqs 1 and 2, as continuous functions $\mathbf{r}_\alpha(s)$, $\mathbf{u}_\alpha(s) \equiv \partial\mathbf{r}_\alpha/\partial s$, and $\mathbf{w}_\alpha(s) = \partial\mathbf{u}_\alpha/\partial s$ of a contour length $s \equiv na$. Both the discrete and continuum representations of the primitive chain will be used in what follows, the choice being a matter of convenience.

The total potential energy U of the solutions is given by a sum of single-chain intramolecular potentials U_{intra}, which resist bending of the chain or stretching of the links, plus an intermolecular potential U_{inter}, which is given in an athermal solution by the excluded-volume potential appropriate to a system of locally cylindrical molecules with a hard-core diameter d. The intramolecular potential U_{intra} of a specified chain may be expressed by a sum $U_{\mathrm{intra}}= U_{\mathrm{const}} + U_{\mathrm{bend}}$ of a bond energy and a bending energy

$$U_{\mathrm{bond}} = \sum_{n=1}^{N} v(q(n))$$

$$U_{\mathrm{bend}} = {}^1\!/_2 T L_p a \sum_{n=1}^{N-1} |\mathbf{w}(n)|^2 \tag{14}$$

In the above, $v(q(n))$ is a two-body bond potential that is assumed to have a very sharp minimum at a preferred distance $q(n) = a$, whose functional form is otherwise immaterial.[30]

The statistical state of such a system is described by the normalized probability $\Psi(\{\mathbf{r}\})$ that the beads will be located at a specified set $\{\mathbf{r}\}$ of positions. In order to calculate the stress within the wormlike chain model, it will be sufficient to calculate two reduced probability distributions that are defined, for the discrete primitive chain, by

$$f(\mathbf{u},n) \equiv \langle \delta(\mathbf{u}(n) - \mathbf{u})\rangle \tag{15}$$

$$\mathbf{F}(\mathbf{u},n) \equiv \langle \mathbf{w}(n)\ \mathbf{w}(n)\ \delta(\bar{\mathbf{u}}(n) - \mathbf{u})\rangle \tag{16}$$

where $\bar{\mathbf{u}}(n) \equiv (\mathbf{u}(n + 1) + \mathbf{u}(n))/2$, and where $\langle\cdots\rangle \equiv \int \mathrm{d}\{\mathbf{r}\}\ \Psi(\{\mathbf{r}\}) \cdots$ denotes a nonequilibrium ensemble average. The function $f(\mathbf{u},n)$ is the probability that link n in a random chain will be oriented in a specified orientation $\mathbf{u}$. The ratio $\mathbf{F}(\mathbf{u},n)/f(\mathbf{u},n)$ is the conditional average of the tensor $\mathbf{w}(n)\ \mathbf{w}(n)$ averaged over the subset of chains for which $\bar{\mathbf{u}}(n)$ is oriented in the specified direction.

The thermal equilibrium values of f and $\mathbf{F}$ in an isotropic solution, which are independent of n, are given by

$$f(\mathbf{u},n) = 1/4\pi \tag{17}$$

$$\mathbf{F}(\mathbf{u},n) \simeq \frac{1}{L_p a}\mathbf{P}(\mathbf{u})\ f(\mathbf{u},n) \tag{18}$$

where $\mathbf{P}(\mathbf{u}) \equiv \boldsymbol{\delta} - \mathbf{u}\mathbf{u}$ is a tensor that projects onto the plane perpendicular to $\mathbf{u}$. Equation 17 requires that $f(\mathbf{u},n)$ be rotationally isotropic in equilibrium. Equation 18 is a statement of the fact that $\mathbf{w}$ is effectively constrained to a plane perpendicular to $\bar{\mathbf{u}}$, since in the continuum limit $\mathbf{w}(s)\cdot\mathbf{u}(s) = \partial|\mathbf{u}(s)|/\partial s = 0$, and that the fluctuations of $\mathbf{w}$ within that plane are characterized in equilibrium by a Gaussian distribution of values with a variance obtained by applying the equipartition theorem to joint n of U_{bend}. In an isotropic solution undergoing rapid tangential Brownian motion (i.e., reptation) the rapid destruction and creation of chain segments at the ends of the chain will be assumed to guarantee that the curvature (but not necessarily the orientation) of the chain is always equilibrated at the chain ends and thus that eq 18 always holds for $n = 1$ and $n = N - 1$. In what follows, we will also consider some partially equilibrated states in which the curvature is “locally-equilibrated” along all or part of the chain but in which the distribution of link distributions remains anisotropic, so that eq 18 holds for all or part of the chain but eq 17 does not.

If each link is taken to represent a fixed contour length L_e of chain, then the end-to-end distance $q(n)$ of each link must be assumed to be slightly extensible, since the link length can be changed slightly by changing the extent of the “wrinkling” of the polymer within the confining tube. For the same reason, the preferred value a of the link length will be slightly less than L_e. Changes in the link length are resisted by a tension $\mathcal{T}(n)$ whose value depends upon the link length $q(n)$, which diverges if $q(n)$ approaches the full contour length L_e of the subchain.

In our discussion of linear viscoelastic behavior in (II), it will be necessary only to consider the effect of very weak tangential compressions or extensions, for which $\mathcal{T}(n)$ may be approximated by a harmonic spring

$$\mathcal{T}(n) \simeq B\ (q(n) - a)/a \tag{19}$$

in which B is an effective single-chain extension modulus. The resulting tension must vanish at the ends of the chain. The dependence of the entropic modulus B of a confined chain upon the chain rigidity and entanglement length was estimated previously by MacKintosh et al.[18] by calculating how the end-to-end distance of a fixed length of chain depended upon the applied tension; they obtained a value on the order of

$$B \propto T{L_{\mathrm{p}}}^2/{L_{\mathrm{e}}}^3 \tag{20}$$

A calculation of B similar to that given by MacKintosh et al.[18] is included in Appendix B. It should be borne in mind that the parameter B is a linear modulus, useful only for calculating the linear viscoelastic properties, since the relationship between $q(n)$ and $\mathscr{T}(n)$ is strongly nonlinear in extension and is expected[18] to lead to a strongly strain hardening contribution to the macroscopic stress.

IV. Stress Tensor

The macroscopic stress is calculated here within the context of the standard Kramers–Kirkwood theory of viscoelasticity[1,2,28,29] by considering the forces exerted upon the beads of the primitive chain introduced above, assuming that the beads may be treated as "Stokeslets" (i.e., point centers of hydrodynamic resistance) in a solvent of viscosity η_{s}. The stress tensor of a solution subjected to a macroscopic fluid velocity $\mathbf{v}$ with a spatially homogeneous rate-of-deformation tensor $\kappa(t) \equiv (\nabla\mathbf{v})^{\dagger}$ is given in the Kramers–Kirkwood theory by a sum

$$\boldsymbol{\sigma} = \eta_{\mathrm{s}}\,(\kappa + \kappa^{\dagger}) + \boldsymbol{\sigma}_{\mathrm{p}} \tag{21}$$

where the polymer stress $\boldsymbol{\sigma}_{\mathrm{p}}$ of a system with total volume V is given by a sum

$$\boldsymbol{\sigma}_{\mathrm{p}} \equiv -\frac{1}{V}\sum_{\alpha,n}\langle \mathbf{f}_{\alpha}(n)\ \mathbf{r}_{\alpha}(n)\rangle \tag{22}$$

in which

$$\mathbf{f}_{\alpha}(n) \equiv -\frac{\partial}{\partial \mathbf{r}_{\alpha}(n)}[U + T\ln(\Psi)] \tag{23}$$

is an effective force $\mathbf{f}_{\alpha}(n)$ on bead n of chain α. Here and in Appendix A, various contributions to $\boldsymbol{\sigma}_{\mathrm{p}}$ are calculated using the principle of virtual work, which states that the linear variation in the dynamical free energy

$$A[\Psi] \equiv \int \mathrm{d}\{\mathbf{r}\}\ \Psi[U + T\ln(\Psi)] \tag{24}$$

under an infinitesimal affine displacement $\delta\mathbf{r}_{\alpha}(n) = \delta\epsilon\cdot\mathbf{r}_{\alpha}(n)$ of the positions of all beads within a system of total volume V may be expressed as a scalar product $\delta A = V\boldsymbol{\sigma}_{\mathrm{p}}{:}\delta\epsilon^{\dagger}$.

The polymer stress tensor may be divided into contributions

$$\boldsymbol{\sigma}_{\mathrm{p}} = \boldsymbol{\sigma}_{\mathrm{intra}} + \boldsymbol{\sigma}_{\mathrm{inter}} \tag{25}$$

arising from forces associated with, respectively, intramolecular and intermolecular (e.g., steric or Van der Waals) interactions, which are discussed separately below.

A. Intramolecular Stress. Below and in Appendix B, we give two complementary calculations of the intramolecular contribution to the stress, based upon slightly different representations of a tightly-entangled chain. Both are based upon the calculation presented in Appendix A, in which a general expression is derived for the intramolecular stress contribution $\boldsymbol{\sigma}_{\mathrm{intra}}$ of a system of discrete wormlike chains with an unspecified link length $a \ll L_{\mathrm{p}}$. Below, the intramolecular stress is calculated within the context of the primitive chain model introduced in the previous section, in which the polymer is replaced by a discrete coarse-grained chain with a link length similar to the entanglement length and in which the stress is calculated by applying the results of Appendix A to this coarse-grained chain. In Appendix B, the stress is instead calculated by applying the results of Appendix A to the actual continuous polymer contour (by taking the limit of vanishing link length), while taking into account the effects of confinement by literally requiring that the polymer fluctuate weakly about a smoother average contour. The two calculations are found to yield completely equivalent results but to have complementary virtues: The primitive chain model discussed below is technically less complex, while the more detailed tube model of Appendix B has one fewer free parameter, since it allows us to at least approximately express the two parameters L_{e} and B of the primitive chain model as functions of L_{p} and the tube diameter.

To calculate the intramolecular stress for the primitive chain model, we use the results of Appendix *A* to calculate the stress for a discrete chain of $N = L/L_{\mathrm{e}}$ links and a link length $a \simeq L_{\mathrm{e}}$. The resulting stress is conveniently expressed as a sum

$$\boldsymbol{\sigma}_{\mathrm{intra}} = \boldsymbol{\sigma}_{\mathrm{bend}} + \boldsymbol{\sigma}_{\mathrm{link}} + \boldsymbol{\sigma}_{\mathrm{tens}} - cT\boldsymbol{\delta} \tag{26}$$

where, in the weakly-curved, nearly-inextensible limit of interest, we find

$$\begin{aligned} \boldsymbol{\sigma}_{\mathrm{bend}} &\simeq cTL_{\mathrm{p}}a\sum_{n=1}^{N-1}\langle \mathbf{w}(n)\ \mathbf{w}(n) - \bar{\mathbf{u}}(n)\ \bar{\mathbf{u}}(n)|\mathbf{w}(n)|^2\rangle \\ \boldsymbol{\sigma}_{\mathrm{link}} &= 3cT\sum_{n=1}^{N}\langle \mathbf{u}(n)\ \mathbf{u}(n) - {}^{1}\!/_{3}\boldsymbol{\delta}\rangle \\ \boldsymbol{\sigma}_{\mathrm{tens}} &\simeq ca\sum_{n=1}^{N}\langle \mathscr{T}(n)\ \mathbf{u}(n)\ \mathbf{u}(n)\rangle \end{aligned} \tag{27}$$

Here,

$$\mathscr{T}(n) \equiv \frac{\partial}{\partial q(n)}[U + T\ln(\Psi)] \tag{28}$$

is a generalized force conjugate to the link length $q(n)$, which has a natural interpretation as the tension in link n. By construction, this tension vanishes in thermal equilibrium, where $\Psi(\{\mathbf{r}\}) \propto \epsilon^{-U(\{\mathbf{r}\})/T}$.

The stress contributions introduced in eq 26 are defined physically as follows:

(i) The stress $\boldsymbol{\sigma}_{\mathrm{bend}}$ is a purely mechanical contribution arising from bending forces, which is obtained by calculating the variation

$$\delta\langle U_{\mathrm{bend}}\rangle = V\boldsymbol{\sigma}_{\mathrm{bend}}{:}\delta\epsilon^{\dagger} \tag{29}$$

of the bending energy U_{bend} (which depends only upon the link orientations) under an affine deformation of bead positions.

(ii) The stress $\boldsymbol{\sigma}_{\mathrm{link}}$ is the contribution of the orientational entropy of the links, which is given by the corresponding variation

$$-T\delta S = V\boldsymbol{\sigma}_{\rm link}{:}\delta\boldsymbol{\epsilon}^{\dagger} \tag{30}$$

of the dynamic entropy

$$S \equiv -\int \mathrm{d}\{\mathbf{r}\}\ \Psi \ln(\Psi) \tag{31}$$

under a hypothetical change of the link orientations alone, in which the changes in orientation are equal to those obtained under a simple affine deformation of bead positions, as described in eq A1, with no corresponding changes in link lengths. The resulting expression for $\boldsymbol{\sigma}_{\rm link}$ is the same as that obtained for the orientational stress of a solution of either disconnected or (as in the DE model for the primitive chain) freely jointed rigid rods.

(iii) The stress $\boldsymbol{\sigma}_{\rm tens}$ is a contribution arising from the existence of a nonzero tension in one or more of links, which is obtained from the variation of the total dynamic free energy under a hypothetical change in the link lengths $q(n)$ alone, in which the link lengths are changed by amounts equal to those obtained in a simple affine deformation, as described by eq A2, with no corresponding changes of link orientations.

The contribution $-cT\boldsymbol{\delta}$ is the ideal solution osmotic pressure arising from the translational entropy of the molecule as a whole.

Some insight may be gained by considering the behavior of $\boldsymbol{\sigma}_{\rm intra}$ for a partially equilibrated state in which the chain curvature is everywhere locally equilibrated, so that eq 18 holds for all n, but in which the distribution of link orientations remains anisotropic, so that eq 17 does not. Physically, such a state would be found for times t after a step deformation of a solution of rod-like polymers such that t is longer than the time necessary for the polymer to disengage from its original tube, and thus equilibrate the curvature, but shorter than the time necessary for rotational diffusion to equilibrate the distribution of end-to-end orientations. By using eq 18 to evaluate moments of $\mathbf{w}$, eq 27 for $\boldsymbol{\sigma}_{\rm bend}$ may be reexpressed as a sum

$$\boldsymbol{\sigma}_{\rm bend} = -3cT\sum_{n=1}^{N-1}\langle \bar{\mathbf{u}}(n)\ \bar{\mathbf{u}}(n) - {}^{1}\!/_{3}\boldsymbol{\delta}\rangle \tag{32}$$

involving moments of $\bar{\mathbf{u}}(n)$ alone. Upon comparing this to eq 27 for $\boldsymbol{\sigma}_{\rm link}$, we find that, in the weakly curved limit in which we may take $\bar{\mathbf{u}}(n) \simeq \mathbf{u}(n)$, each term in eq 32 for $\boldsymbol{\sigma}_{\rm bend}$ cancels against a corresponding contribution to $\boldsymbol{\sigma}_{\rm link}$. The total contribution of any segment of a weakly curved chain to the quantity $\boldsymbol{\sigma}_{\rm bend} + \boldsymbol{\sigma}_{\rm link}$ is thus seen to vanish whenever the curvature is locally-equilibrated, even if the distribution of link orientations remains anisotropic.

A closer look reveals, however, that the cancellation of $\boldsymbol{\sigma}_{\rm bend}$ and $\boldsymbol{\sigma}_{\rm link}$ is not perfect even in this case, simply because there are N terms contributing to $\boldsymbol{\sigma}_{\rm link}$, corresponding to the N links in the chain, but only $N - 1$ terms contributing to $\boldsymbol{\sigma}_{\rm bend}$, corresponding to the $N - 1$ three-body contributions to $U_{\rm bend}$. As a result, we find that even in a state in which the curvature is everywhere locally-equilibrated and the tension everywhere zero, there can exist a residual stress

$$\boldsymbol{\sigma}_{\rm intra} \simeq {}^{3}\!/_{2}cT\langle \mathbf{u}(N)\ \mathbf{u}(N) + \mathbf{u}(1)\ \mathbf{u}(1) - {}^{2}\!/_{3}\boldsymbol{\delta}\rangle - cT\boldsymbol{\delta} \tag{33}$$

arising from the remaining orientational entropy of the chain ends (which yields the term in angle brackets) and from the translational entropy of the molecule as a whole (which yields the ideal gas contribution of $-cT\boldsymbol{\delta}$). In a system of rod-like polymers, for which $\mathbf{u}(1)$ and $\mathbf{u}(N)$ must be nearly parallel to each other and to the end-to-end vector, this residual stress reduces to the entropic elastic stress found previously for noninteracting solutions of rigid rods.[1,2,5,31] The rigid-rod result is thus recovered here as a limiting form obtained for rod-like chains whenever the curvature fluctuations of the chain are equilibrated.

Our final expression for $\boldsymbol{\sigma}_{\rm intra}$ is obtained by simply regrouping terms in eqs 26 and 27 in a manner motivated by the above observations about the local cancellation of $\boldsymbol{\sigma}_{\rm bend}$ and $\boldsymbol{\sigma}_{\rm link}$ in a state of local equilibrium and then taking the continuum limit (i.e., replacing the link number n by a contour length s), while taking care to retain the residual end contributions. The result may be expressed as a sum

$$\boldsymbol{\sigma}_{\rm intra} = \boldsymbol{\sigma}_{\rm curve} + \boldsymbol{\sigma}_{\rm orient} + \boldsymbol{\sigma}_{\rm tens} - cT\boldsymbol{\delta} \tag{34}$$

in which

$$\begin{aligned}\boldsymbol{\sigma}_{\rm curve} = {} & cTL_{\rm p}\int_0^L \mathrm{d}s\ \langle \mathbf{w}(s)\ \mathbf{w}(s) - \mathbf{u}(s)\ \mathbf{u}(s)|\mathbf{w}(s)|^2\rangle \\ & + \frac{cT}{a}\int_0^L \mathrm{d}s\ \langle 3\mathbf{u}(s)\ \mathbf{u}(s) - \boldsymbol{\delta}\rangle\end{aligned} \tag{35}$$

$$\boldsymbol{\sigma}_{\rm orient} = {}^{3}\!/_{2}cT\langle \mathbf{u}(0)\ \mathbf{u}(0) + \mathbf{u}(L)\ \mathbf{u}(L) - {}^{2}\!/_{3}\boldsymbol{\delta}\rangle \tag{36}$$

$$\boldsymbol{\sigma}_{\rm tens} = c\int_0^L \mathrm{d}s\ \langle \mathcal{T}(s)\ \mathbf{u}(s)\ \mathbf{u}(s)\rangle \tag{37}$$

Here, the curvature stress $\boldsymbol{\sigma}_{\rm curve}$ is a continuum expression for the stress arising from the deviation of $\mathbf{F}(\mathbf{u},s)$ from the local equilibrium value given by eq 18, due to the deformation of the distribution of tube conformations. By construction, the contribution of a segment of tube to $\boldsymbol{\sigma}_{\rm curve}$ vanishes if the curvature in that segment is locally-equilibrated. The orientational stress $\boldsymbol{\sigma}_{\rm orient}$ defined above is in general a residual stress arising from the orientational entropy of the chain ends, which reduces to the usual rigid-rod result only when the chains are rod-like. The tension stress $\boldsymbol{\sigma}_{\rm tens}$ in eq 37 is the continuum limit of the tension stress introduced in eq 27.

It is interesting to note how the above expression interpolates between those obtained previously for entangled solutions of completely-flexible and completely-rigid chains. We focus here upon the contributions of $\boldsymbol{\sigma}_{\rm curve}$ and $\boldsymbol{\sigma}_{\rm orient}$, which will be shown in (II) to dominate the low-frequency rheological behavior of entangled solutions.

In the limit of loosely-entangled or completely-flexible coils, the contribution $\boldsymbol{\sigma}_{\rm bend}$ in eq 26 may be taken to vanish, due to the vanishing of the elastic coefficient $L_{\rm p}$ that appears as a prefactor of $\boldsymbol{\sigma}_{\rm bend}$ in eq 27. For experiments involving time or frequency scales for which the tension $\mathcal{T}$ can relax, so that $\boldsymbol{\sigma}_{\rm tens}$ also vanishes, this leaves the intramolecular stress

$$\lim_{L_{\rm p}\ll a} \boldsymbol{\sigma}_{\rm intra} \simeq \boldsymbol{\sigma}_{\rm link} \tag{38}$$

used in the DE model, in which the primitive chain is described as a chain of freely-jointed links with a link length $a \gg L_{\rm p}$. For a polymer with given values of L

and L_p, one may envision a sequence of primitive chain models that continuously connects the loosely-entangled and tightly-entangled concentration regimes, in which the link length of the coarse-grained chain is taken to decrease and the strength of bending forces to increase with increasing concentration in a manner that keeps the radius of gyration of the primitive chain equal to that of the polymer. The presence of bending forces, which become large within the tightly-entangled regime, immediately destroys the statistical mechanical basis of the stress−optic relation. The main obstacle to the construction of such a generalized primitive chain model is the difficulty of predicting exactly how the entanglement length should vary through the crossover between these two concentration regimes.

In the opposite limit of rod-like chains, the standard expression for the elastic stress of solution of rigid rods is recovered from the contribution $\boldsymbol{\sigma}_{\text{orient}}$ to eq 34, which dominates whenever the curvature of the chain is equilibrated, so that $\boldsymbol{\sigma}_{\text{curve}}$ vanishes.

In Appendix B, we present an alternative calculation of $\boldsymbol{\sigma}_{\text{intra}}$ in which, instead of using a coarse-grained model, we calculate the stress by considering the forces acting on the actual polymer contour $\mathbf{r}(s)$ when the polymer is confined within a tube. To do wo, we assume that the polymer contour $\mathbf{r}(s)$ is confined to fluctuate weakly around a smooth average contour $\mathbf{r}_0(s)$ that defines the contour of the center-line of a tube. The unit tangent and curvature of this tube contour are denoted by $\mathbf{u}_0(s) \equiv \partial\mathbf{r}_0/\partial s$ and $\mathbf{w}_0(s) \equiv \partial\mathbf{u}_0/\partial s$, where s refers here to a distance measured along the tube contour. The transverse displacement of the polymer from the center-line of the tube is specified by a two-dimensional displacement $\mathbf{h}(s) = \mathbf{r}(s) - \mathbf{r}_0(s)$, for which $\mathbf{h}(s)\cdot\mathbf{u}_0(s) = 0$ and $\langle\mathbf{h}(s)\rangle = 0$. To describe the fluctuations of $\mathbf{h}(s)$, we assume that, in the weakly curved limit of interest, fluctuations of the Fourier mode amplitudes $\mathbf{h}(q) \equiv \int ds\, e^{iqs}\mathbf{h}(s)$ within a relatively straight segment of tube with overall orientation $\mathbf{u}$ may be parameterized by a function of the form

$$\langle\mathbf{h}(q)\,\mathbf{h}(-q)\rangle = \frac{T}{TL_p q^4 + \mathcal{T}q^2 + \gamma(q)}(\boldsymbol{\delta} - \mathbf{u}\mathbf{u}) \tag{39}$$

The denominator in the right-hand side (rhs) of the above may be interpreted as a spring constant for modes of wavenumber q, in which TL_pq^4 is a contribution arising from the polymer bending energy, $\mathcal{T}$ is the tension applied to the segment of interest, if any, and $\gamma(q)$ is a q-dependent spring constant arising from collisions with other polymers, which act to confine the polymer to a tube.

To obtain a formal expression for the $\boldsymbol{\sigma}_{\text{intra}}$ within this tube model, we simply average the microscopic expression for $\boldsymbol{\sigma}_{\text{intra}}$, which is obtained by applying the results of Appendix A to the continuous polymer contour, over the rapid transverse fluctuations of the chain, which are described by eq 39. This procedure yields an expression for the average contribution to $\boldsymbol{\sigma}_{\text{intra}}$ of a polymer confined to a tube with a known tube conformation $\mathbf{r}_0(s)$. The corresponding expression for $\boldsymbol{\sigma}_{\text{intra}}$, expressed as an average over the distribution of tube conformations, is found to be of a form exactly analogous to that given in eqs 35−37, but with the tangent and curvature vectors of the discrete coarse-grained chain that appear in eqs 35−37 everywhere replaced by the tangent and curvature vectors $\mathbf{u}_0(s)$ and $\mathbf{w}(s)$ of the continuous tube contour. The relevant expression for $\boldsymbol{\sigma}_{\text{curve}}$ is given in eq B11. The resulting values of the compression modulus B, the entanglement length L_e, and the tube diameter D_e may be expressed as Fourier integrals

$$\begin{aligned}
B &= \left\{\int\frac{dq}{2\pi}\,\frac{Tq^4}{[TL_pq^4 + \gamma(q)]^2}\right\}^{-1} \\
L_e &= \left\{\int\frac{dq}{2\pi}\,\frac{\gamma(q)}{TL_pq^4 + \gamma(q)}\right\}^{-1} \\
D_e &= 2\left\{\int\frac{dq}{2\pi}\,\frac{T}{TL_pq^4 + \gamma(q)}\right\}^{1/2}
\end{aligned} \tag{40}$$

where we have defined the tube diameter D_e, as a matter of convention, to be twice the standard deviation of either of the two Cartesian components of $\mathbf{h}(s)$, i.e., $D_e \equiv [2\langle|\mathbf{h}(s)|^2\rangle]^{1/2}$.

As discussed in Appendix B, the entanglement length L_e defined in eq 40 is found to enter the equations that describe the tube model in two ways that are exactly analogous to the ways in which the link length a enters the corresponding equations for the primitive chain model: (i) It appears explicitly in the analog of eq 35 for $\boldsymbol{\sigma}_{\text{curve}}$, given by eq B11, where the value of L_e given in eq 40 replaces the explicit factor of a that appears in second line of eq 35. (ii) It also appears in the analog of eq 18 for the variance of $\mathbf{w}(n)$ in a state of thermal equilibrium, given in eq B15, in which we find that the thermal equilibrium variance of the tube curvature $\mathbf{w}_0(s)$, averaged over segments of tube with a specified orientation $\mathbf{u}$, is given by an expression $\langle\mathbf{w}_0(s)\,\mathbf{w}_0(s)\rangle_{\text{eq}} \simeq (\boldsymbol{\delta} - \mathbf{u}\mathbf{u})/(L_pL_e)$, in which link length a that appears in eq 18 is again replaced by the value of L_e defined in eq 40. The physical content of a tube model with a given value of L_e is thus found to be completely equivalent to that of a discretized primitive chain model with the same value for a. The conceptual advantage of the tube model is that it allows us to derive the parameters appearing in either version of the model from a more microscopic description of the fluctuations of a confined polymer.

A simple quantitative approximation for B, L_e, and D_e may be obtained by approximating $\gamma(q)$ by a q-independent constant $\gamma(q) = TL_pq_e^4$, in which the parameter q_e is an inverse length of order $1/L_e$. This is equivalent to mimicking the forces confining the polymer to a tube by those produced by a local harmonic confinement potential $U_{\text{conf}} = {}^1\!/_2 TL_pq_e^4\int ds|\mathbf{h}(s)|^2$. Using this approximation in eq 40 yields $L_e = 2^{3/2}/q_e$, $B = 2^{7/2}TL_p^2q_e^3$, and $D_e = 2^{1/4}L_p^{-1/2}q_e^{-3/2}$, or, equivalently,

$$\begin{aligned}
B &= 16TL_pD_e^{-2} \\
L_e &= 2^{4/3}L_p^{1/3}D_e^{2/3}
\end{aligned} \tag{41}$$

The power law exponents in eq 41 agree with those given in eqs 7 and 20.

The characteristic free energy densities for the curvature and orientational stresses (as defined by, e.g., their contributions to the instantaneous elastic modulus $G(0)$ measured in response to an infinitesimal step strain) are given by the prefactors of

$$G_{\text{curve}} \sim \rho T/L_e, \quad G_{\text{orient}} \sim \rho T/L \tag{42}$$

in eqs 35 and 36, where we have assumed a value of $\langle\mathbf{w}\mathbf{w}\rangle \sim 1/(L_pL_e)$ to estimate G_{curve}. These estimated moduli correspond to, respectively, T times the number density ρ/L_e of entanglement links for $G_{\rm curve}$ and T times the number density ρ/L of chains for $G_{\rm orient}$. The estimate of $G_{\rm curve}$ in eq 42 is the same as that proposed by Isambert and Maggs[19] on heuristic grounds. Because we must have $L_e < L$ for the model considered here to be valid, the instantaneous orientational modulus is always much smaller than the instantaneous curvature modulus. The orientational stress can nonetheless play a significant role in the low-frequency rheology of systems for which $\boldsymbol{\sigma}_{\rm orient}$ decays much more slowly than $\boldsymbol{\sigma}_{\rm curve}$, as is found to be true for rod-like polymers. It therefore must be retained if the model is to recover rigid-rod behavior in the appropriate limit. The free energy scale for the tension stress induced by a step strain of magnitude $\delta\epsilon$ may be estimated by approximating $\mathcal{T} \simeq B\delta\epsilon$, yielding a corresponding contribution to the modulus of order

$$G_{\rm tens} \sim \rho B \sim \frac{\rho T}{L_e}\left(\frac{L_p}{L_e}\right)^2 \qquad (43)$$

as found previously by MacKintosh et al.[18] This contribution is much larger than either $G_{\rm curve}$ or $G_{\rm orient}$ but is found in (II) to decay much more rapidly than either of these contributions. As a result, the tension contribution is found to dominate the high-frequency linear viscoelastic response but to have relatively little effect upon the zero shear viscosity and other measures of low-frequency behavior.

B. Intermolecular Stress. The intermolecular stress contribution $\boldsymbol{\sigma}_{\rm inter}$ may be approximated in semidilute solution by applying the principle of virtual work to an interaction free energy functional of the form

$$A_{\rm inter} = {}^1\!/_2 VT\rho^2 \int d\mathbf{u} \int d\mathbf{u}'\, \bar{f}(\mathbf{u})\, \bar{f}(\mathbf{u}')\, \Theta(\mathbf{u},\mathbf{u}') \qquad (44)$$

in which

$$\bar{f}(\mathbf{u}) \equiv \frac{1}{L}\int_0^L ds\, f(\mathbf{u}, s) \qquad (45)$$

is the total link orientational distribution and in which $\Theta(\mathbf{u},\mathbf{u}')$ is an orientation-dependent effective interaction between chain segments with orientations $\mathbf{u}$ and $\mathbf{u}'$. In the case of an athermal semidilute solution of stiff molecules of steric diameter $d \ll L_p$ and $d \ll L$, the interaction is given by the excluded volume interaction

$$\Theta(\mathbf{u},\mathbf{u}') = 2d|\mathbf{u} \times \mathbf{u}'| \qquad (46)$$

calculated by Onsager[23] and applied to systems of semiflexible chains by Khokhlov and Semenov.[26]

The stress contribution $\boldsymbol{\sigma}_{\rm inter}(t)$ is obtained by calculating the change of $A_{\rm inter}$ induced by applying a constant deformation rate κ over an infinitesimal time δt, and setting

$$\delta A_{\rm inter} = V\boldsymbol{\sigma}_{\rm inter}{:}\kappa^{\dagger}\delta t \qquad (47)$$

The change of $A_{\rm inter}$ for a system of volume V that contains a fixed number of polymers is given by

$$\delta A_{\rm inter} = V\int d\mathbf{u}\, \mu(\mathbf{u})\, \delta(\rho f(\mathbf{u})) \qquad (48)$$

where

$$\mu(\mathbf{u}) \equiv \rho T \int d\mathbf{u}\, \Theta(\mathbf{u},\mathbf{u}')\, \bar{f}(\mathbf{u}') \qquad (49)$$

is an orientation-dependent chemical potential field for contour length.

To calculate the variation $\delta(\rho\bar{f}(\mathbf{u}))$, we may make use of the description of reptation dynamics given in Appendix B of (II). Setting $\delta(\rho\bar{f}(\mathbf{u})) = (\partial(\rho\bar{f}(\mathbf{u}))/\partial t)(\delta t)$ and using eq II.B7 for $\partial f/\partial t$, we obtain

$$\begin{aligned}\frac{\delta(\rho\bar{f}(\mathbf{u}))}{\partial t} &= -\frac{\partial}{\partial\mathbf{u}}\,(\boldsymbol{g}(\mathbf{u})\,\bar{f}(\mathbf{u})) + \kappa{:}(\mathbf{u}\mathbf{u} - \boldsymbol{\delta})\,\bar{f}(\mathbf{u}) \\ &\quad + \langle\delta(\mathbf{u}(L) - \mathbf{u})[\nu(L) - \nu(0)]\rangle \end{aligned} \qquad (50)$$

where $\partial/\partial\mathbf{u}$ denotes a gradient operator on the unit sphere, which has nonzero components only in the two directions perpendicular to $\mathbf{u}$, where $\nu(s)$ is a tangential velocity of the polymer relative to the tube and where the statistical equivalence of the two ends of the polymer has been assumed when writing the last term. Substituting eq 50 into eq 48, integrating the first term in 50 by parts, and using eq II.B5 for $\partial\bar{\nu}/\partial s$ yields a stress

$$\begin{aligned}\boldsymbol{\sigma}_{\rm inter} &= \rho\int d\mathbf{u}\, \bar{f}(\mathbf{u})\left\{\frac{\partial\mu(\mathbf{u})}{\partial\mathbf{u}}\,\mathbf{u} - \mu(\mathbf{u})\boldsymbol{\delta}\right\} \\ &\quad + \rho\int_0^L ds\, \langle\mathbf{u}(s)\,\mathbf{u}(s)\,[\,\mu(\mathbf{u}(s)) - \mu(\mathbf{u}(L))]\rangle \end{aligned} \qquad (51)$$

The first line of the right hand side is the intermolecular stress contribution obtained by Doi and co-workers[9,10] for the case of completely rigid rods. The second line, which arises from the effects of the tangential flow of the polymer along the tube, is seen to vanish in the limit of rigid rods, since it depends upon the difference between the orientations of links at different points along the chain.

The overall free energy scale of $\sigma_{\rm inter}$, as measured by its contribution to the instantaneous modulus $G(0)$, is given by the free energy density

$$G_{\rm inter} \sim A_{\rm inter}\,/\,V \sim T\rho^2 d \qquad (52)$$

where d may be taken to be the steric diameter of the polymer or, more generally, a corresponding measure of the magnitude of the anistropic interaction $\Theta(\mathbf{u},\mathbf{u}')$. In the limit of rod-like chains, with $L \ll L_p$ this free energy density becomes comparable to $G_{\rm orient}$, which is the slowest decaying contribution to the modulus in this limit, only at concentrations of order $\rho_{\rm nem}$, as found previously for solutions of true rigid rods. In the limit of coil-like chains, with $L \gg L_p$, $G_{\rm inter}$ is instead seen to remain smaller than $G_{\rm curve}$, which is the slowest decaying contribution in this limit, even at concentrations of order $\rho_{\rm nem}$. The intermolecular contribution to the low-frequency behavior of the complex modulus $G^*(\omega)$ (the effect of intermolecular stress upon high-frequency behavior can be shown to be negligible) is thus expected to become comparable to that of the intramolecular contribution at concentrations near $\rho_{\rm nem}$ in the limit of rod-like chains, as found previously for solutions of true rigid rods, but to remain negligible compared to the intramolecular curvature contribution at concentrations up to and (presumbably) above $\rho_{\rm nem}$ in the limit of coil-like chains. The intermolecular stress contribution is thus expected to play a much smaller role in determining the low-frequency viscoelasticity of systems of long semiflexible chains than that found for more rod-like polymers.

V. High-Frequency Viscoelasticity

The primitive chain model introduced in section III is designed only to describe rheological behavior measured at frequencies low enough or time scales long enough so that the observed stress is insensitive to the rapid transverse motions of the polymer within the tube. To describe higher frequencies, we now introduce a crude dynamical coarse-graining procedure, similar in spirit to the coarse-graining procedure used in section III to define the primitive chain model, in which the entanglement length will be replaced by a smaller dynamically determined coarse-graining length. This procedure yields qualitative description of viscoelasticity in the high-frequency regime in which the complex modulus becomes sensitive to the dynamics of transverse undulations of wavelength less than L_e.

First, we consider the dynamics of the short-wavelength transverse undulations of a polymer within a short segment of tube that is oriented in some direction $\mathbf{u}$. Since we focus here on very short-wavelength fluctuations, $\mathbf{u}$ may be regarded as a constant, and the contour of the polymer may be expressed as a sum

$$\mathbf{r}(s) = s\mathbf{u} + \mathbf{h}(s) \tag{53}$$

where $\mathbf{h}(s)\cdot\mathbf{u} = 0$. To describe fluctuations of $\mathbf{h}(s)$, we introduce the Fourier transform

$$\mathbf{h}(q) = \int \mathrm{d}s\, \mathrm{e}^{iqs}\, \mathbf{h}(s) \tag{54}$$

and express the potential energy for modes of wavenumber $q \gg L_e^{-1}$ (which do not feel the effects of confinement) as a bending energy

$$U_{\mathrm{bend}} = {}^{1}\!/_{2} T L_p \int \frac{\mathrm{d}q}{2\pi}\, q^4 |\mathbf{h}(q)|^2 \tag{55}$$

The corresponding Langevin equation for the mode amplitude $\mathbf{h}(q)$ is

$$\zeta_\perp \frac{\partial \mathbf{h}(q,t)}{\partial t} = -TL_p q^4 \mathbf{h}(q,t) + \mathbf{f}_\perp(q,t) \tag{56}$$

where $\zeta_\perp$ is a coefficient of friction for perpendicular motions and $\mathbf{f}_\perp$ is a corresponding random force. A q-independent friction coefficient may be used with reasonable accuracy because hydrodynamic interactions are known to lead to only a logarithmic dependence of $\zeta_\perp$ on q. This yields a relaxation frequency

$$\omega(q) = \frac{T}{\zeta_\perp} L_p q^4 \tag{57}$$

for undulations of wavenumber q.

The primitive chain model of section III is based upon a coarse-graining procedure in which all undulation modes of wavenumber $q \gtrsim L_e$ are assumed to remain equilibrated, and to thus make no contribution to the curvature stress, while contributing to the tension stress only by providing a thermally equilibrated reservoir of excess length. The model therefore cannot be used to describe phenomona involving variations of stress over time scales less than the relaxation time

$$\tau_e \sim \frac{\zeta_\perp}{T} \frac{L_e^{\,4}}{L_p} \tag{58}$$

of an undulation mode of wavenumber $q \sim L_e^{-1}$.

The relaxation of $\boldsymbol{\sigma}_{\mathrm{tens}}(t)$ and $\boldsymbol{\sigma}_{\mathrm{curve}}(t)$ over times scales $t \lesssim \tau_e$ may be described qualitatively by a generalization of this coarse-graining procedure. For specificity, we consider the relaxation of stress after a step deformation by an infinitesimal strain $\delta\epsilon$ at time $t = 0$ and describe the stress contributions by dynamical moduli $G_{\mathrm{curve}}(t)$ and $G_{\mathrm{tens}}(t)$, such that $\sigma_{\mathrm{curve}}(t) = G_{\mathrm{curve}}(t)\delta\epsilon$ (where the stress and strain may be treated as scalars rather than tensors for the present purpose). To estimate the values of the dynamic moduli at times $t \ll \tau_e$, we assume that, in this range of time scales, only those undulation modes with relaxation times $\omega^{-1}(q) \gtrsim t$, which have not had time to re-equilibrate, contribute directly to the curvature stress at time t and that only those modes with relaxation times $\omega(q)^{-1} \ll t$ can provide an effectively equilibrated reservoir of excess length that determines the magnitude of an effective extension modulus $B(t)$. By setting $\omega(L_c^{-1}(t)) \sim 1/t$, we define a dynamically determined coarse-graining length

$$L_c(t) \propto \left(\frac{TL_p}{\zeta_\perp} t\right)^{1/4} \tag{59}$$

which increases with time as $t^{1/4}$. To estimate the stress at time t, we will consistently replace the coarse-graining length L_e introduced in the primitive chain model by the length $L_c(t)$ defined above.

We first consider the tension stress, which is found to dominate at very high frequencies. Replacing L_e by $L_c(t)$ in eq 20 yields a time-dependent extension modulus

$$B(t) \sim \frac{TL_p^{\,2}}{(L_c(t))^3} \tag{60}$$

that decreases with time as

$$B(t) \propto t^{-3/4} \tag{61}$$

This modulus is intended to describe the initial decay of tension at times $t \lesssim \tau_e$, giving a tension $\mathcal{T}(s,t) \sim B(t)\delta\epsilon{:}\mathbf{u}(s)\,\mathbf{u}(s)$ at time t in segments with orientation $\mathbf{u}(s)$. The predicted divergence of $B(t)$ at $t = 0$ is a necessary consequence of the microsocopic inextensibility of the chain. An equivalent result for the temporal autocorrelation function for fluctuations in the end-to-end distance of a nearly straight semiflexible polymer, which is related to $B(t)$ by a fluctuation dissipation theorem, has recently been obtained by Granek[36] and by Gittes and MacKintosh.[37] Generalizing eq 43 for $G_{\mathrm{tens}}(t)$, by using eq 60 for $B(t)$, then yields a corresponding modulus

$$\lim_{t \ll \tau_e} G_{\mathrm{tens}}(t) \sim \rho B(t) \sim \frac{\rho T}{L_p}\left(\frac{T}{\zeta_\perp L_p^{\,3}} t\right)^{-3/4} \tag{62}$$

that also decays as $t^{-3/4}$. The corresponding complex frequency dependent modulus $G^*(\omega)$, which is defined in eq II.3, may be shown to vary with frequency ω as

$$\lim_{\omega \gg \tau_e^{-1}} G_{\mathrm{tens}}(\omega) \sim \frac{\rho T}{L_p}\left(i\omega \frac{\zeta_\perp L_p^{\,3}}{T}\right)^{3/4} \tag{63}$$

thus yielding storage and loss moduli $G'(\omega)$ and $G''(\omega)$ that both vary with frequency as $\omega^{3/4}$. This power law dependence on frequency is in essentially perfect agreement with that reported in several recent microrheological experiments on the high-frequency viscoelastic behavior of actin solutions.[32−34] A more quantitative treatment of the physics described above, which yields the same power law dependence, is given in subsection III.B of (II).

A corresponding expression for the curvature modulus may be obtained by replacing L_e by $L_c(t)$ in eq 42, yielding

$$\lim_{\omega \gg \tau_e^{-1}} G_{\text{curve}}(t) \sim \rho T/L_c(t) \sim \frac{\rho T}{L_p}\left(\frac{T}{\zeta_\perp L_p^{\;3}}\,t\right)^{-1/4} \tag{64}$$

and a corresponding complex modulus

$$\lim_{\omega \gg \tau_e^{-1}} G^*_{\text{curve}}(\omega) \sim \frac{\rho T}{L_p}\left(i\omega\,\frac{\zeta_\perp L_p^{\;3}}{T}\right)^{1/4} \tag{65}$$

that increases with frequency as $(i\omega)^{1/4}$. This estimate of $G^*_{\text{curve}}(\omega)$ is shown below to remain much smaller than $G^*_{\text{tens}}(\omega)$ throughout the high-frequency regime in which our argument remains valid. A result similar to eq 65 was obtained over 30 years ago by Harris and Hearst,[35] who considered a simplified Gaussian model of semiflexible chains in which the chains resists bending, but in which the distribution of link lengths actually remains Gaussian.

Because the above analysis describes the effect of modes of wavelength less than L_e, for which the effects of entanglement are irrelevant, it may be applied without modification to describe unentangled solutions of coil-like chains at all frequencies greater than a crossover frequency $\tau_p^{-1} \sim T/(\zeta_\perp L_p^3)$ on the order the relaxation frequency of a mode of wavelength L_p in an unentangled solution. At lower frequencies, where the modulus is dominated by the contribution of modes of wavelength greater than L_p, the viscoelastic response may instead be described by the Rouse or Zimm model of flexible chains. Comparison of eq 63 for $G^*_{\text{tens}}(\omega)$ to eq 65 for $G^*_{\text{curve}}(\omega)$ shows that $G^*_{\text{tens}}(\omega) \gtrsim G^*_{\text{curve}}(\omega)$ all $\omega \gtrsim \tau_p^{-1}$. In tightly-entangled solutions, the above analysis applies only to frequencies $\omega \gtrsim \tau_e^{-1}$, where $\tau_e \gg \tau_p$, implying that $G^*_{\text{tens}}(\omega) \gg G^*_{\text{curve}}(\omega)$ throughout the frequency regime of interest. The Harris−Hearst model, which gives $G^*(\omega) \propto (i\omega)^{1/4}$ at high frequencies, is thus found to miss the dominant contribution to the high-frequency modulus of a wormlike chain, which arises from the tangential forces that act to prevent local changes in contour length.

VI. Summary

A reptation model has been presented here for the behavior of tightly-entangled solutions of semiflexible chains, i.e., solutions in which the entanglement length is substantially less than the persistence length.

The scaling arguments given in section II indicate that, for long, thin chains with $L \gtrsim L_p \gg d$, isotropic solutions of this type should occur over a substantial range of concentrations $\rho^{**}_{\text{coil}} \ll \rho \ll \rho_{\text{nem}}$, where $\rho_{\text{nem}} \propto (L_p/d)\rho^{**}_{\text{coil}}$, and over a somewhat narrower range of concentrations for rod-like chains with $L_p \gtrsim L \gg d$. The discussion in section II was, however, carried out at the level of simple scaling arguments, in which all unknown numerical prefactors have been assumed to be numbers of order unity, and thus can show convincingly only that such an isotropic but tightly-entangled regime must necessarily occur in the limit $d \ll L_p$. The model used here is expected to be a reliable starting point for the description of actin solutions, for which $L_p/d \simeq 10^3$. How well it can describe somewhat less stiff model semiflexible polymers such as DNA or PBLG, for which $L_p/d \simeq 20-100$, remains a question for future work.

A general expression for the stress tensor of a solution of wormlike chains is derived in section IV, which may serve as a common starting point for the calculation of rheological properties in either the tightly-entangled isotropic regime emphasized here or, in the future, in the unentangled, loosely-entangled, and nematic regimes. The stress tensor is found to contain several physically distinct intramolecular components with disparate magnitudes, which will be shown in (II) to exhibit disparate decay times: a large rapidly decaying tension component, a smaller but much more slowly decaying curvature component, and an even smaller orientational component. The identification of an orientational component, which reduces in the rigid-rod limit to the Brownian stress of a solution of rods but which is found to depend in general on the orientation of the ends of the chain, allows us to understand how the model can interpolate smoothly between the limits of flexible and rod-like chains.

Comparison of the curvature and tension contributions showed that the tension contribution generally dominates the stress at high frequencies, though the meaning of “high” depends upon both the degree of entanglement and the chain length. Qualitative arguments are given to show that this tension contribution will vary with frequency as $G^*(\omega) \propto (i\omega)^{3/4}$ at high frequencies. This behavior is expected whenever the frequency dependence of the stress is controlled by the relaxation of unentangled bending modes of wavelength less than L_p and is the natural analog of the Rouse−Zimm spectra found when $G^*(\omega)$ is dominated by random-coil modes of wavelength greater than L_p.

Intermolecular stress contributions arising from steric interactions have also been considered. Upon comparing inter- and intramolecular contributions, it is found that for rod-like chains, with $L \ll L_p$, the intermolecular contribution can begin to have a signficant effect on low-frequency rheology of the isotropic phase at concentrations approaching ρ_{nem}, as found previously for solutions of true rigid rods, but that, for chains of length $L \gtrsim L_p$, the intramolecular curvature contribution will dominate the dynamic modulus at concentrations up to and presumbably above the critical concentration for the formation of a nematic phase. This observation, together with the observation that $\rho_{\text{nem}} \gg \rho^{**}$, suggests that the inclusion of curvature stress will be a necessary part of the development of a molecular model of the rheology of tightly-entangled nematic solutions.

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Appendix A: Intramolecular Stress

Here, we calculate the intramolecular contribution to $\boldsymbol{\sigma}_p$ for a discrete semiflexible chain, of the type introduced in section II to describe the primitive chain, but with an arbitrary preferred link length a. The calculation is based upon a calculation of the variation $\delta A = \boldsymbol{\sigma}{:}\delta\epsilon^{\dagger}$ of the dynamic free under an infinitesimal change $\delta\mathbf{r} = \delta\epsilon\cdot\mathbf{r}$ of all bead positions. Such a variation of bead positions leads to corresponding changes

$$\delta\mathbf{u}(n) = (\boldsymbol{\delta} - \mathbf{u}(n)\mathbf{u}(n))\cdot\delta\epsilon\cdot\mathbf{u}(n) \tag{A1}$$

$$\delta q(n) = q(n)\ \delta\epsilon{:}\mathbf{u}(n)\ \mathbf{u}(n) \tag{A2}$$

in the link orientations and link lengths. In what follows we calculate separately the three contributions $\boldsymbol{\sigma}_{\text{bend}}$, $\boldsymbol{\sigma}_{\text{link}}$, and $\boldsymbol{\sigma}_{\text{tens}}$ that appear in eqs 26 and 27, whose definitions are given in the text below eq 27.

To obtain the bending contribution defined in eq 29, we carry out a straightforward calculation of the variation of U_{bend} under an infinitesimal variation A1 of $\mathbf{u}(n)$. When expressed in terms of $\bar{\mathbf{u}}(n) \equiv (\mathbf{u}(n+1) + \mathbf{u}(n))/2$ and $\mathbf{w}(n) \equiv (\mathbf{u}(n+1) - \mathbf{u}(n))/a$, this yields

$$\boldsymbol{\sigma}_{\text{bend}} = cTL_{\text{p}}a\sum_{n=1}^{N-1}\langle\mathbf{w}\mathbf{w} - \bar{\mathbf{u}}\bar{\mathbf{u}}|\mathbf{w}|^{2} - {}^{1}/_{4}a^{2}\mathbf{w}\mathbf{w}|\mathbf{w}|^{2}\rangle$$

Only the first two terms on the right hand side yield a contribution on the order of T per segment in the weakly-curved limit of interest, in which $a/L_{\text{p}} \ll 1$ and $\langle|\mathbf{w}|^{2}\rangle \sim 1/(L_{\text{p}}a)$, while the third term yields a contribution of order $T(a/L_{\text{p}})$ per segment. Only the two dominant terms have been retained in eq 27. Use of some other expression for U_{bend}, of the general form $U_{\text{bend}} = (L_{\text{p}}/a)\Sigma_{n}\ f(\mathbf{u}(n+1)\cdot\mathbf{u}(n))$, with $df(x)/dx = -1$ for $x = 1$ (where eq 14 corresponds to use of a function $f(x) = 1 - x$), would generally lead to the appearance of further subdominant corrections to $\boldsymbol{\sigma}_{\text{bend}}$, the largest of which would be of the same order as the subdominant term in the above, without changing the dominant terms retained in eq 27.

The contribution $\boldsymbol{\sigma}_{\text{link}}$ defined in eq 30 may be obtained as follows: We first change variables to reexpress the single-chain probability distribution $\Psi(\{\mathbf{r}\})$ as a function

$$\Psi(\{\mathbf{r}\}) = \frac{1}{V}\Psi'(\{\mathbf{q}\}) \tag{A3}$$

of a new set of variables consisting of the position $\mathbf{r}(0)$ of the first bead on the chain (which is assumed to be randomly distributed) and of the N link vectors $\mathbf{q}(n) \equiv \mathbf{r}(n) - \mathbf{r}(n-1)$. We then calculate the change

$$\delta S = -\int \mathrm{d}\{\mathbf{q}\}\ \delta\Psi'\ \ln(\Psi') \tag{A4}$$

in S under a change $\delta\mathbf{q}(n) = q(n)\delta\mathbf{u}(n)$ of the orientations, but not the lengths, of each of the link vectors $\mathbf{q}(n)$. This variation gives rise to a change

$$\delta\Psi'(\{\mathbf{q}\}) = -\sum_{ni}\frac{\partial}{\partial\mathbf{q}(n)}\cdot(\delta\mathbf{q}(n)\Psi') \tag{A5}$$

in $\Psi'(\{\mathbf{q}\})$. Substituting $\delta\Psi'$ into eq A4 and integrating twice by parts yields an entropy change

$$\delta S = \int d\{\mathbf{q}\}\ \Psi'(\{\mathbf{q}\})\ \frac{\partial}{\partial\mathbf{q}(n)}\cdot(\delta\mathbf{q}(n)) \tag{A6}$$

Evaluating the divergence in the above then yields eq 27 for $\boldsymbol{\sigma}_{\text{link}}$.

The tension contribution $\boldsymbol{\sigma}_{\text{tens}}$ is obtained by calculating the variation

$$\delta A = \int \mathrm{d}\{\mathbf{q}\}\ [U + T\ln(\Psi')]\ \delta\Psi' \tag{A7}$$

in the case of a pure extension of each link length, with no change in orientation. Substitution of eq A5 for $\delta\Psi'$, with $\delta\mathbf{q}(n) = \delta q(n)\ \mathbf{u}(n)$, into eq A7 for δA, followed by an integration by parts, then yields eq 27 for $\boldsymbol{\sigma}_{\text{tens}}$.

Appendix B: Tube Model

In this appendix, we consider a more detailed model of a polymer confined within a tube, in which the stress is calculated from the forces exerted on a continuous polymer contour. We assume here that the actual contour of a polymer within a tightly-entangled solution (when viewed over time scales short enough for the tube to remain well-defined) fluctuates weakly about a smooth average contour $\mathbf{r}_{0}(s)$ that defines the tube contour. Throughout this appendix, s is the distance from the end of the tube measured along the tube contour $\mathbf{r}_{0}$, rather than the contour distance measured along the actual polymer. If we focus upon a short section of tube, of length $\Delta L \ll L_{\text{p}}$, we may parametrize both $\mathbf{r}$ and $\mathbf{r}_{0}$ as functions

$$\mathbf{r}(s) = \mathbf{u}s + \mathbf{r}_{\perp}(s) \tag{B1}$$

$$\mathbf{r}_{0}(s) = \mathbf{u}s + \mathbf{r}_{0\perp}(s) \tag{B2}$$

of the projected contour distance s, where $\mathbf{r}_{\perp}(s)$ and $\mathbf{r}_{0\perp}(s)$ are displacements in the plane perpendicular to a straight reference line with fixed unit tangent $\mathbf{u}$. The transverse displacement

$$\mathbf{h}(s) \simeq \mathbf{r}_{\perp}(s) - \mathbf{r}_{0\perp}(s) \tag{B3}$$

of the polymer from the center of the tube will be assumed to have a zero average, $\langle\mathbf{h}(s)\rangle = 0$, with fluctuations that are described by eq 39. Here and in what follows, we use $\langle\cdots\rangle$ to denote a conditional average of the field $\mathbf{h}(s)$ over conformations of a polymer with a specified tube conformation $\mathbf{r}_{0}$ and an overbar $\overline{\cdots}$ to refer to an average over an ensemble of tube conformations.

To calculate the parameter B introduced in eq 19, we introduce a dimensionless density $\phi(s)$

$$\phi \equiv \left\langle\sqrt{1 + \left|\frac{\partial\mathbf{h}}{\partial s}\right|^{2}}\right\rangle \tag{B4}$$

of polymer contour length per unit length of tube, such that $\phi(s) - 1$ is a measure of the density of excess contour length due to short-wavelength undulations. This density may be expressed in terms of the variables of the discrete primitive chain model as a ratio $\phi(s) \equiv L_{\text{e}}/q(s)$, and thus takes on a value $\phi_{\text{eq}} = L_{\text{e}}/a$ in thermal equilibrium. The linear extension modulus B is given by the derivative

$$B = \left[-\frac{1}{\phi}\frac{\partial\phi}{\partial\mathcal{T}}\bigg|_{\mathcal{T}=0}\right]^{-1} \tag{B5}$$

in which ϕ is regarded as a function of the applied tension $\mathcal{T}$. By expanding eq B4 to lowest order in $\partial\mathbf{h}/\partial s$, expanding in Fourier modes, and using eq 39 for $\langle\mathbf{h}(q)\ \mathbf{h}(-q)\rangle$, we find that

$$\phi \simeq 1 + \int \frac{\mathrm{d}q}{2\pi} \frac{Tq^2}{TL_\mathrm{p}q^4 + \mathcal{T}q^2 + \gamma(q)} \tag{B6}$$

Differentiating eq B6 with respect to $\mathcal{T}$ then yields eq 40 for B.

To determine a precise value for L_e within the same model, we calculate the curvature stress by applying the results of Appendix A to the continuous polymer contour, while again using eq 39 to relate the distribution of polymer conformations to the distribution of tube conformations, and assuming $\mathcal{T} = 0$.

Because the link contribution to $\boldsymbol{\sigma}_\mathrm{curve}$, which has been calculated in Appendix A for a discrete chain of beads and links, contains an explicit prefactor of the inverse link length $1/a$, we must first introduce a corresponding cutoff length into our continuous description of the chain. If we approximate the polymer contour by a discrete chain with a very small link length, $a \ll L_\mathrm{e}$, we may express $\mathbf{h}(s)$ by a discrete Fourier transform containing only modes with wavenumbers less than some cutoff wavenumber $\Lambda \propto 1/a$. In this representation, the inverse link length is given by the integral

$$\frac{1}{a} = \int_{|q|<\Lambda} \frac{\mathrm{d}q}{2\pi} \tag{B7}$$

which gives the number of independent mode amplitudes (i.e., independent vector degrees of freedom) per unit length of chain. None of our final results will depend upon the link length a, which will be taken to zero at the end of the calculation. The link length a must thus be distinguished in this model from the physical entanglement length L_e, which is instead determined by the magnitude of the fluctuations of $\mathbf{h}(s)$.

By substituting parametrization B1 of $\mathbf{r}_\perp$ and eq B7 for $1/a$ into eq 35 for $\boldsymbol{\sigma}_\mathrm{curve}$ and then expanding to harmonic order in the Fourier amplitudes of $\mathbf{r}_\perp$, we obtain a stress contribution

$$\frac{\boldsymbol{\sigma}_\mathrm{curve}}{\Delta L} = TL_\mathrm{p} \int_{|q|<\Lambda} \frac{\mathrm{d}q}{2\pi}\, q^4\, \overline{\langle \mathbf{r}_\perp(q)\,\mathbf{r}_\perp(-q) - \mathbf{uu}|\mathbf{r}_\perp(q)|^2\rangle} + 3T\left(\mathbf{uu} - \frac{1}{3}\boldsymbol{\delta}\right) \int_{|q|<\Lambda} \frac{\mathrm{d}q}{2\pi} \tag{B8}$$

from a segment of tube of length ΔL with average orientation $\mathbf{u}$. By expanding

$$\overline{\langle \mathbf{r}_\perp(q)\,\mathbf{r}_\perp(-q)\rangle} = \overline{\mathbf{r}_{0\perp}(q)\,\mathbf{r}_{0\perp}(-q)} + \langle \mathbf{h}(q)\,\mathbf{h}(-q)\rangle \tag{B9}$$

and using eq 39 for $\langle \mathbf{h}(q)\,\mathbf{h}(-q)\rangle$, we may then reexpress eq B8 as an average

$$\frac{\boldsymbol{\sigma}_\mathrm{curve}}{\Delta L} = TL_\mathrm{p}\int \frac{\mathrm{d}q}{2\pi}\, q^4 \overline{\langle \mathbf{r}_{0\perp}(q)\,\mathbf{r}_{0\perp}(-q) - \mathbf{uu}|\mathbf{r}_{0\perp}(q)|^2\rangle} + 3T\left(\mathbf{uu} - \frac{1}{3}\boldsymbol{\delta}\right) \int \frac{\mathrm{d}q}{2\pi} \frac{\gamma(q)}{TL_\mathrm{p}q^4 + \gamma(q)} \tag{B10}$$

involving only the distribution of tube conformations. The limits on the Fourier integrals in eq B10 may be taken to infinity because the integrals in eq B10 converge at large q, allowing us to take $\Lambda \to \infty$. Inverse Fourier transforming eq B8 then yields a stress contribution of the form

$$\boldsymbol{\sigma}_\mathrm{curve} = TL_\mathrm{p}\int \mathrm{d}s\, \overline{\langle \mathbf{w}_0\mathbf{w}_0 - \mathbf{uu}|\mathbf{w}_0|^2\rangle} + \frac{3T}{L_\mathrm{e}}\int \mathrm{d}s \left(\mathbf{uu} - \frac{1}{3}\boldsymbol{\delta}\right) \tag{B11}$$

in which $\mathbf{w}_0(s) \simeq \partial^2\mathbf{r}_{0\perp}(s)/\partial s^2$, and in which L_e is given by eq 40. This definition of L_e is chosen here so as to put eq B11 for $\boldsymbol{\sigma}_\mathrm{curve}$ in a form analogous to eq 35.

An alternative way of defining an entanglement length L_e is by constructing the analog of eq 18 for the variance of the curvature of the primitive chain in a state of thermal equilibrium, by calculating the corresponding equilibrium variance $\overline{\mathbf{w}_0(s)\,\mathbf{w}_0(s)}|_{\mathrm{eq},\mathbf{u}}$ of the tube curvature. Here and in the remainder of this appendix, we use the notation $\overline{\cdots}_{\mathrm{eq},\mathbf{u}}$ to denote an average over tube segments with a specified orientation $\mathbf{u}$, evaluated in a state of thermal equilibrium. We can determine the spectrum of transverse fluctuations of the tube contour $\mathbf{r}_0(s)$ by requiring that, in equilibrium, the actual polymer contour $\mathbf{r}(s)$ exhibits the undulation spectrum

$$\overline{\langle \mathbf{r}_\perp(q)\,\mathbf{r}_\perp(-q)\rangle}|_{\mathrm{eq},\mathbf{u}} \simeq \frac{1}{L_\mathrm{p}q^4}(\boldsymbol{\delta} - \mathbf{uu}) \tag{B12}$$

required by the equipartition theorem. By combining this requirement with eqs 39 and B9, it is straightforward to show that this spectrum of polymer fluctuations corresponds to a spectrum of tube contour fluctuations of the form

$$\overline{\mathbf{r}_{0\perp}(q)\,\mathbf{r}_{0\perp}(-q)}|_{\mathrm{eq},\mathbf{u}} \simeq \frac{1}{L_\mathrm{p}q^4}\frac{\gamma(q)}{TL_\mathrm{p}q^4 + \gamma(q)}(\boldsymbol{\delta} - \mathbf{uu}) \tag{B13}$$

Note that the rhs of eq B12 is similar to the rhs eq B11 for all q much less than the entanglement wavenumber q_e, for which $TL_\mathrm{p}q_\mathrm{e}^4 \equiv \gamma(q_\mathrm{e})$, but drops off much more rapidly with q for $q \gg q_\mathrm{e}$, reflecting a smoothing of the tube contour over distances less than q_e^{-1}. By expanding $\mathbf{w}_0(s)\,\mathbf{w}_0(s)$ in Fourier modes, we obtain

$$\overline{\mathbf{w}_0(s)\,\mathbf{w}_0(s)}|_{\mathrm{eq},\mathbf{u}} \simeq \int \frac{\mathrm{d}q}{2\pi}\, q^4 \overline{\mathbf{r}_{0\perp}(q)\,\mathbf{r}_{0\perp}(-q)}|_{\mathrm{eq},\mathbf{u}} \tag{B14}$$

or, after substiting eq B13 into eq B14,

$$\overline{\mathbf{w}_0(s)\,\mathbf{w}_0(s)}|_{\mathrm{eq},\mathbf{u}} \simeq \frac{1}{L_\mathrm{p}L_\mathrm{e}}(\boldsymbol{\delta} - \mathbf{uu}) \tag{B15}$$

where L_e is the entanglement length defined in eq 40. Equation B15 is the analog of eq 18, in which the link length a appearing in eq 18 has simply been replaced by L_e.

Because eqs B15 and B11 are completely analogous to eqs 18 and 35, it is easy to show, by repeating the reasoning applied to the discrete primitive chain in section III, that eq B11 will yield a vanishing curvature stress contribution for each possible value of $\mathbf{u}$ in a state of thermal equilibrium if and only if the values of L_e appearing in eqs B11 and B15 are identical. The above demonstration of the equivalence of these two possible ways of defining of L_e, which are obtained by comparing eq B11 to eq 35 or by comparing eq B15 to eq 18, is necessary to show that, in the tube model, as in the discrete primitive chain model, the curvature stress contribution of a tube segment vanishes whenever the variance of the curvature in that segment takes on its thermal equilibrium value.

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(30) Similarly, our choice of a functional form for U_{bend} in eq 14 is somewhat arbitrary, but ultimately immaterial: Any three-body potential of the general form $U_{\mathrm{bend}} = \sum_n (L_p/a) f(\mathbf{u}(n+1)\cdot\mathbf{u}(n))$ with the same behavior in the limit $|\mathbf{u}(n+1) - \mathbf{u}(n)| \ll 1$ would give identical results for $\boldsymbol{\sigma}_{\mathrm{bend}}$ in the weakly-curved, nearly-inextensible limit of interest, as discussed in Appendix A.

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