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Viscoelasticity of tightly entangled solutions of semiflexible polymers

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A molecular model is introduced to describe the linear viscoelasticity of tightly entangled solutions of semiflexible polymers. An expression for the stress of a solution of wormlike chains is derived, and a tube model is used to describe the effects of entanglement. Consideration of the Brownian dynamics of the polymer within its tube yields a dynamic modulus $G^{*}(\omega)\propto(i\omega)^{3/4}$ at high frequencies, in agreement with the results of recent microrheology experiments on actin solutions. [S1063-651X(98)52008-9]

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Current understanding of the viscoelasticity of polymer solutions is based to a large extent upon models that are designed to describe either completely flexible (Gaussian) or completely rigid-rod polymers [1]. There exists, however, a large class of semiflexible polymers, which typically form lyotropic liquid-crystalline phases at high enough concentrations [2], for which there exists no equally detailed molecular model of viscoelasticity. Among these are biopolymers, such as DNA, F-actin, and fibrin, as well as synthetic liquid-crystalline polymers such as Kevlar. For lack of a molecular model of partially flexible chains, experiments on both isotropic and nematic solutions of such polymers are often compared to models of rigid rods. The present paper provides a framework for the calculation of the various sources of elastic stress in solutions of semi-flexible polymers generally, and, motivated in part by recent experiments on actin solutions [3–7], presents a model of linear viscoelasticity in the tightly entangled regime [8–13] relevant to these experiments.

In what follows, we consider a solution of c wormlike chains per unit volume, each of contour length L, giving a density $\rho\equiv cL$ of contour length per unit volume and a mesh size $L_m\equiv\rho^{-1/2}$. The conformation of a single polymer is specified by a continuous contour $\mathbf{r}(s)$, where s is the contour distance from one chain end, and by corresponding tangent and curvature vectors $\mathbf{u}(s)\equiv\partial\mathbf{r}(s)/\partial s$ and $\mathbf{w}(s)\equiv\partial\mathbf{u}(s)/\partial s$. The chains are assumed to be inextensible, so that $|\mathbf{u}(s)|=1$ and $\mathbf{w}(s)\cdot\mathbf{u}(s)=0$, and to have a bending energy

$$U_{bend}=\tfrac{1}{2}TL_p\int_0^L ds|\mathbf{w}(s)|^2, \tag{1}$$

where T is the temperature in units of energy and L_p is the persistence length.

We consider, more specifically, a ''tightly-entangled'' solution in which $L_m\ll L_p$, and in which each polymer is confined to a tube of diameter $D_e\ll L_p$, as sketched in Fig. 1. In this regime, there exists a tangential correlation length $L_e\propto D_e^{2/3}L_p^{1/3}$, of order the distance between collisions of the polymer with the walls of the tube [8–10], such that only undulation modes of wavelength less than L_e can fluctuate freely. Simple scaling arguments [10] yield length scales $D_e\propto L_p(\rho L_p^2)^{-3/5}$ and $L_e\propto L_p(\rho L_p^2)^{-2/5}$.

To describe this regime we use the tube model, which is analogous to the Doi-Edwards (DE) model [1], in which (i) each polymer is confined to a weakly-curved tube, (ii) tangential motion of the polymer relative to the tube is resisted only by viscous forces, and (iii) the tube deforms affinely. To describe low-frequency viscoelasticity, we introduce a coarse-grained (or ''primitive'') chain. Because only undulation modes of wavelengths greater than L_e are constrained by entanglement, we may represent the coarse-grained chain as a chain of $N=L/L_e$ discrete links and $N+1$ beads, where each link represents a subchain of length L_e with a preferred end-to-end length a that is slightly less than L_e. This coarse-grained chain is assigned a bending energy

$$U_{bend}=\tfrac{1}{2}TL_pa\sum_{n=1}^{N-1}|\mathbf{w}(n)|^2, \tag{2}$$

where $\mathbf{w}(n)=[\mathbf{u}(n+1)-\mathbf{u}(n)]/a$ and $\mathbf{u}(n)$ is a unit vector parallel to link n. We will describe a bending joint of the

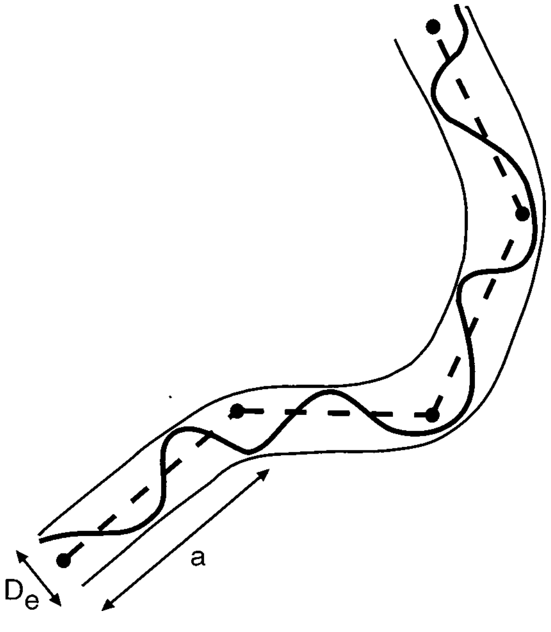

FIG. 1. Tube model for an entangled wormlike chain.

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primitive chain as being ''locally equilibrated'' if the conditional average of the tensor $\mathbf{w}(n)\mathbf{w}(n)$, averaged over chains with a specified orientation $\mathbf{u}$ for the vector $\overline{\mathbf{u}}(n)\equiv[\mathbf{u}(n+1)+\mathbf{u}(n)]/2$, takes on the value

$$\frac{\langle\mathbf{w}(n)\mathbf{w}(n)\,\delta(\overline{\mathbf{u}}(n)-\mathbf{u})\rangle}{\langle\,\delta(\overline{\mathbf{u}}(n)-\mathbf{u})\rangle}=\frac{1}{L_p a}(\boldsymbol{\delta}-\mathbf{uu}),\tag{3}$$

obtained by applying the equipartition theorem to joint n of U_{bend}, while constraining $\mathbf{w}(n)$ to be perpendicular to $\overline{\mathbf{u}}(n)$.

The links of this coarse-grained chain must also be taken to be slightly extensible, since the end-to-end distance $q(n)$ of a link may be changed slightly by changing the magnitude of transverse undulations of the polymer, without changing the true chain length. To describe this, we introduce a dimensionless density $\phi(n)\equiv L_e/q(n)$ of contour length per unit length of the primitive chain, with a thermal equilibrium value of $\phi_{eq}=L_e/a$. To calculate linear response, we may assume a linear relationship

$$\mathcal{T}(n)\simeq-B[\phi(n)-\phi_{eq}]/\phi_{eq}\tag{4}$$

between the tension $\mathcal{T}(n)$ and contour length density $\phi(n)$ in each link. The elastic modulus B has been calculated by MacKintosh, Janmey, and Kas [11], who obtained a value $B\propto TL_p^2/L_e^3$ by considering the effect of an applied static tension upon the undulations of a confined polymer.

A general expression for the intramolecular polymeric contribution to the stress of a solution of discretized wormlike chains may be obtained [1] by evaluating the sum $\boldsymbol{\sigma}=c\Sigma_{n=1}^{N+1}\langle\mathbf{r}(n)\mathbf{f}(n)\rangle$, where $\mathbf{r}(n)$ is the position of bead n of a randomly chosen chain, $\mathbf{f}(n)=\partial[U+T\ \ln(\Psi)]/\partial\mathbf{r}(n)$ is the force on bead n, $U(\{\mathbf{r}\})$ is the intramolecular potential energy, and $\Psi(\{\mathbf{r}\})$ is a single-chain probability distribution. After a straightforward calculation [13], and after taking the wormlike limit $a\ll L_p$, we obtain a stress of the form $\boldsymbol{\sigma}=\boldsymbol{\sigma}_{curve}+\boldsymbol{\sigma}_{orient}+\boldsymbol{\sigma}_{tens}-cT\boldsymbol{\delta}$, in which

$$\begin{aligned}\boldsymbol{\sigma}_{curve}\simeq{}&cTL_pa\sum_{n=1}^{N-1}\langle\mathbf{w}(n)\mathbf{w}(n)-\overline{\mathbf{u}}(n)\overline{\mathbf{u}}(n)|\mathbf{w}(n)|^2\rangle\\&+3cT\sum_{n=1}^{N-1}\langle\overline{\mathbf{u}}(n)\overline{\mathbf{u}}(n)-\tfrac{1}{3}\boldsymbol{\delta}\rangle,\end{aligned}\tag{5}$$

$$\boldsymbol{\sigma}_{orient}=3cT\langle\tfrac{1}{2}\mathbf{u}(1)\mathbf{u}(1)+\tfrac{1}{2}\mathbf{u}(N)\mathbf{u}(N)-\tfrac{1}{3}\boldsymbol{\delta}\rangle,\tag{6}$$

$$\boldsymbol{\sigma}_{tens}\simeq ca\sum_{n=1}^{N}\langle\mathcal{T}(n)\mathbf{u}(n)\mathbf{u}(n)\rangle.\tag{7}$$

The curvature stress $\boldsymbol{\sigma}_{curve}$ contains both purely mechanical bending energy contributions (in the first line) and entropic contributions (in the second line) arising from the orientational entropy of the links. It is easy to show, by evaluating Eq. (5) while assuming that Eq. (3) holds, that the total contribution to $\boldsymbol{\sigma}_{curve}$ from any bending joint exactly vanishes when the curvature in that joint is locally equilibrated. The orientational stress $\boldsymbol{\sigma}_{orient}$ is a residual contribution of the link orientational entropy from the two end links, which can persist even when Eq. (3) holds for all n, as might occur in a solution of rodlike chains ($L\ll L_p$) if the undulation modes were equilibrated but the distribution of chain orientations was not. This contribution is seen to reduce in this rodlike limit, in which $\mathbf{u}(1)\simeq\mathbf{u}(N)$, to the known result [1] for the elastic stress in a solution of rigid rods. The tension stress $\boldsymbol{\sigma}_{tens}$ arises from the link tension $\mathcal{T}(n)$.

Linear viscoelasticity is characterized by a dynamic modulus $G(t)$ that describes the decay of the stress tensor $\boldsymbol{\sigma}(t)=G(t)(\boldsymbol{\delta\epsilon}+\boldsymbol{\delta\epsilon}^{\dagger})$ after an infinitesimal step strain $\boldsymbol{\delta\epsilon}$ at $t=0$, or by the complex modulus $G^{*}_{tens}(\omega)\equiv i\omega\int_0^\infty dt\ e^{-i\omega t}G(t)=G'(\omega)+iG''(\omega)$. Both moduli may be expressed as sums $G=G_{curve}+G_{orient}+G_{tens}$ of moduli describing the decay of different stress contributions. In what follows, we switch to a continuous description of the chain in which $\mathbf{w}(s)$, $\mathbf{u}(s)$, and $\mathcal{T}(s)$ are treated as continuous functions of a distance $s=an$.

In tightly entangled solutions, $\boldsymbol{\sigma}_{curve}(t)$ and $\boldsymbol{\sigma}_{orient}(t)$ can decay only via reptation, i.e., by diffusion of the chain along its own contour, with a diffusivity $D_{rep}=T/(\zeta L)$, where ζ is a friction coefficient per unit length [1,8–10]. The semiflexible nature of the chain affects only the boundary conditions imposed at the ends of the tube [8–10], where we require the curvature to be locally equilibrated at all times. As a result of this boundary condition, segments of the tube that have been created at times after a step deformation at $t=0$ make no contribution to $G_{curve}(t)$, exactly as in the DE model [1]. We thus obtain a modulus

$$G_{curve}(t)=\frac{7}{5}\frac{\rho T}{L_e}\chi(t/\tau_{rep}),\tag{8}$$

with the same time dependence as that of the DE model, in which $\chi(t/\tau_{rep})\equiv\Sigma_{n\ odd}(8/\pi^2)e^{-n^2t/\tau_{rep}}$ is a function with an initial value $\chi(0)=1$ and a longest decay time $\tau_{rep}\equiv L^2/(\pi^2D_{rep})\propto L^3$ of order the time required for the chain to reptate a distance L [1]. The initial value of $G_{curve}(0)=\frac{7}{5}\rho T/L_e$, which is obtained from the curvature stress induced by an affine deformation of the tube [13], is of order T times the number density ρ/L_e of links, i.e., of order T per entanglement. If $L_e\propto\rho^{-2/5}$, then $G_{curve}(0)\propto\rho^{7/5}$, as proposed previously by Isambert and Maggs [12].

The orientational stress $\boldsymbol{\sigma}_{orient}(t)$ also decays by reptation, with a decay time given by time required to randomize the orientation of the chain ends. The initial value $G_{orient}(0)$ is of order T per chain, and so is smaller than $G_{curve}(0)$ by a factor of L_e/L. For $L\gg L_p$, $G_{orient}(t)$ also exhibits a decay time $\tau_{end}\sim L_p^2/D_{rep}$ of order the time required to diffuse a distance L_p, which is much smaller than τ_{rep}, and so $G_{orient}(t)\ll G_{curve}(t)$ for all t. For rodlike chains, with $L_p\gg L$, reptation is instead known to lead [8–10] to a diffusion of the end-to-end vector with a rotational diffusivity $D_{rot}\propto D_{rep}/(LL_p)$, yielding a relaxation time D_{rot}^{-1} that is much larger than τ_{rep}. In this limit, where $G_{orient}(t)$ can dominate $G(t)$ for large t, we find

$$\lim_{L\ll L_p}G_{orient}(t)\simeq\frac{3}{5}\frac{\rho T}{L}e^{-t/\tau_{rod}},\tag{9}$$

with $\tau_{rod}=6LL_p/D_{rep}$ [9,10].

The tension stress can instead decay by diffusion of excess length along the tube, as pointed out by Isambert and Maggs [12]. The contour length density $\phi(s,t)$ obeys a conservation equation $\partial\phi/\partial t=-\partial(\phi\overline{v})/\partial s$, where $\overline{v}(s,t)$ is a tangential velocity of the polymer relative to the tube. The tension $\mathcal{T}(s,t)$ is related to $\overline{v}(s,t)$ by a force balance $\zeta\overline{v}=\partial\mathcal{T}/\partial s$, and to ϕ by Eq. (4). Combining these relations yields a diffusion equation

$$\left(\frac{\partial}{\partial t}-D_{\phi}\frac{\partial^2}{\partial s^2}\right)\phi(s,t)=0, \tag{10}$$

with $D_{\phi}=B/\zeta$. The evolution of $\delta\phi(s,t)\equiv\phi(s,t)-\phi_{eq}$ at $t>0$ on a chain of known conformation (which may be taken to be stationary, since $D_{\phi}\gg D_{rep}$) is given by

$$\delta\phi(s,t)=-\phi_{eq}\int_0^L ds'\,G(s,s',t)\,\boldsymbol{\delta\epsilon}\mathbf{:}\mathbf{u}(s')\mathbf{u}(s'), \tag{11}$$

where $G(s,s',t)$ is the Greens function solution of Eq. (10), with $G(s,s',0)=\delta(s-s')$ and $G(s,s',t)=0$ for $s=0,L$, and where $\boldsymbol{\delta\epsilon}:\mathbf{uu}$ is the initial fractional extension of a segment with orientation $\mathbf{u}$ under affine deformation. After averaging Eq. (7) for $\boldsymbol{\sigma}_{tens}(t)$ over an equilibrium distribution of chain conformations, using Eq. (4) for $\mathcal{T}(s,t)$, we obtain

$$G_{tens}(t)=\tfrac{1}{15}\rho B\psi(t), \tag{12}$$

where $\psi(t)$ has an initial value $\psi(0)=1$, and

$$\psi(t)\equiv\int_0^L ds\int_0^L ds'\,G(s,s',t)e^{-3|s-s'|/L_p}. \tag{13}$$

To calculate $\psi(t)$, we have used the fact that $\langle S_{ij}(s)S_{kl}(s')\rangle=\frac{1}{15}e^{-3|s-s'|/L_p}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}-\frac{2}{3}\delta_{ij}\delta_{kl})$ in equilibrium, where $S_{ij}(s)\equiv u_i(s)u_j(s)-\frac{1}{3}\delta_{ij}$. For $L\ll L_p$, $\psi(t)$ decays almost exponentially with a decay time $\tau_{\phi L}=L^2/(\pi^2 D_{\phi})$ given by the time required for excess length to diffuse to the chain ends. For $L\gg L_p$, $\psi(t)\simeq 1$ for t less than the time $\tau_{\phi p}\equiv L_p^2/(9D_{\phi})$ required for excess length to diffuse a distance L_p, decays as $\psi(t)\propto t^{-1/2}$ for $\tau_{\phi p}\ll t\ll\tau_{\phi L}$, and decays as $\psi(t)\propto e^{-t/\tau_{\phi L}}$ for $t\gg\tau_{\phi L}$.

The three moduli G_{curve}, G_{orient}, and G_{tens} have widely disparate magnitudes and relaxation times. The tension modulus, with an initial value $G_{tens}(0)\propto TL_p^2/L_e^3$ and decay times $\tau_{\phi L}$ and/or $\tau_{\phi p}$, is both the largest and fastest decaying contribution, and dominates the high-frequency behavior of $G^*(\omega)$. The curvature modulus is smaller, with $G_{curve}(0)\propto\rho T/L_e$, and more slowly decaying, and dominates low-frequency behavior for chains with $L\gtrsim L_p$, leading to a broad elastic plateau in which $G'(\omega)\sim\rho T/L_e$. The modulus $G_{orient}(t)$ is smaller still, and is significant only for rodlike chains, for which it can lead to an additional entropic plateau with $G'(\omega)\simeq\rho T/L$ at still lower frequencies.

The model described above is limited to relatively low frequencies by the assumption (implicit in the use of a coarse-grained chain) that all undulation modes of wavelength less than L_e are equilibrated. To describe viscoelasticity at higher frequencies, we will assume (and later confirm) that $G^*(\omega)$ is dominated by $G^*_{tens}(\omega)$ at very high frequencies, due to the large free energy cost of tangential deformations. To extend our calculation of $G^*_{tens}(\omega)$, we generalize Eq. (4) by allowing for a frequency-dependent linear relationship, of the form

$$\hat{\mathcal{T}}(s,\omega)=\hat{B}(\omega)\,\delta\hat{\phi}(s,\omega)/\phi_{eq}, \tag{14}$$

between the temporal Fourier transforms (hereafter denoted by carets) of $\delta\phi(s,t)$ and $\mathcal{T}(s,t)$. Given an expression for the frequency-dependent modulus $\hat{B}(\omega)$ (which is calculated below by considering the response of a confined chain to an oscillating applied tension) we may recalculate $G^*_{tens}(\omega)$ by repeating the arguments leading to Eq. (12), again assuming that relaxation of $\phi(s,t)$ is driven by gradients in $\hat{\mathcal{T}}$, to obtain the generalization

$$G^*_{tens}(\omega)\simeq\tfrac{1}{15}\rho\hat{B}(\omega)\,\psi^*(\omega), \tag{15}$$

where $\psi^*(\omega)\equiv i\omega\int ds\int ds'\,\hat{G}(s,s',\omega)e^{-3|s-s|/L_p}$ and $\hat{G}(s,s',\omega)$ is the Green's function solution of the transformed diffusion equation $[i\omega-\hat{D}_{\phi}(\omega)(\partial^2/\partial s^2)]\hat{G}(s,s',\omega)=0$, with $\hat{D}_{\phi}(\omega)=\hat{B}(\omega)/\zeta$.

To calculate $\hat{B}(\omega)$, we consider a Langevin equation for the normal displacement $\mathbf{h}(s,t)$ of a polymer from a straight line representing the center of the tube, in the presence of a time-dependent tension $\mathcal{T}(t)$. The confinement to a tube may be approximated by adding a harmonic potential $U_{tube}=\frac{1}{2}TL_pq_e^4\int ds|\mathbf{h}(s)|^2$, with $q_e\sim 1/L_e$, to the bending energy $U_{bend}=\frac{1}{2}TL_p\int ds|\partial^2\mathbf{h}(s)/\partial s^2|^2$. After Fourier transforming with respect to s, this yields a Langevin equation

$$\zeta_{\perp}\frac{\partial\mathbf{h}(q,t)}{\partial t}=-[K(q)+\mathcal{T}(t)q^2]\mathbf{h}(q,t)+\boldsymbol{\eta}(q,t) \tag{16}$$

for the amplitude $\mathbf{h}(q,t)$ of a mode of wave number q, where $K(q)\equiv TL_p(q^4+q_e^4)$, $\zeta_{\perp}$ is a friction coefficient, and $\boldsymbol{\eta}(q,t)$ is a Langevin noise. The coarse-grained model fails for all $\omega\gtrsim\tau_e^{-1}$, where $\tau_e^{-1}\sim TL_pq_e^4/\zeta_{\perp}$ is the relaxation rate of a mode of wave number q_e.

By using Eq. (16) to calculate the linear response of the density $\phi\simeq 1+\frac{1}{2}\langle|\partial\mathbf{h}(s)/\partial s|^2\rangle$ to a sinusoidally oscillating tension $\mathcal{T}(t)$, we obtain the compliance $\hat{B}^{-1}(\omega)$. The calculation is straightforward [13], and yields

$$\hat{B}(\omega)=\left\{\int\frac{dq}{2\pi}\frac{T}{K(q)}\frac{q^4}{K(q)+(i/2)\zeta_{\perp}\omega}\right\}^{-1}. \tag{17}$$

For $\omega\ll\tau_e^{-1}$, Eq. (17) yields the static modulus $\hat{B}(\omega)\propto TL_p^2q_e^3$ found in Ref. [11]. For $\omega\gg\tau_e^{-1}$, it yields

$$\hat{B}(\omega)\simeq 2^{3/4}T^{1/4}L_p^{5/4}(i\omega\zeta_{\perp})^{3/4}. \tag{18}$$

Equation (18) is equivalent to results obtained in Refs. [14,15] for the dynamics of contour length fluctuations of a semiflexible rod. At very high ω, friction also becomes effective in suppressing slippage of the chain along the tube, which yields a relaxation function $\psi^*(\omega)\simeq 1$. This, combined with Eqs. (15) and (18) yields

$$G^*(\omega) \simeq \frac{2^{3/4}}{15} \rho T^{1/4} L_p^{5/4} (i\omega\zeta_\perp)^{3/4}. \tag{19}$$

Limiting form (19) for $G^*(\omega)$, which has been obtained independently in Ref. [15], depends only upon the dynamic response of a single unconfined chain, and so is expected to give the generic high-frequency response of solutions of wormlike chains, at any concentration. The predicted frequency dependence of $G^* \propto (i\omega)^{3/4}$ is in excellent agreement with that reported in several recent microrheological studies of F-actin solutions [5–7].

The high-frequency behavior found above may be explained qualitatively as follows: For a chain subjected to a tension oscillating with frequency $\omega \gg \tau_e^{-1}$, only undulation modes with q greater than a cutoff $q_c(\omega) \simeq (\omega\zeta_\perp / T L_p)^{1/4}$, with relaxation frequencies $K(q)/\zeta_\perp > \omega$, are able to respond adiabatically to variations in $\mathcal{T}(t)$, and to thus provide an effectively equilibrated reservoir of excess length. To estimate $\hat{B}(\omega)$, we thus assume that only these large-q modes contribute to the compliance $\hat{B}^{-1}(\omega)$, and so replace the cutoff wave number $q_e \sim 1/L_e$ appearing in the static modulus $\hat{B}(0) \sim T L_p^2 / L_e^3$ of Ref. [11] by the dynamic cutoff $q_c(\omega)$, thus giving $\hat{B}(\omega) \sim T L_p^2 q_c^3(\omega)$, which agrees with Eq. (18).

Using an analogous argument to estimate the high-frequency behavior of $G^*_{curve}(\omega)$, we may replace $1/L_e$ by $q_c(\omega)$ in Eq. (12) to obtain $G^*_{curve}(\omega) \sim \rho T q_c(\omega) \propto \omega^{1/4}$. This estimate of $G^*_{curve}(\omega)$ is much smaller than $G^*_{tens}(\omega)$ at any $\omega \gtrsim \tau_e^{-1}$, confirming that $G^*(\omega)$ is dominated by $G^*_{tens}(\omega)$ at high frequencies.

Figure 2 shows numerical results for $G^*(\omega)$, calculated using Eqs. (15) and (17) for $G^*_{tens}(\omega)$, for a solution with parameter values similar to those of a 1 mg/ml solution of F-actin. The calculation reproduces the main features found in experiments on such solutions [3,4,7], including a broad curvature-dominated elastic plateau with a storage modulus $G' \sim 1 - 10$ dyne/cm^2 [3,4,7], and a high-frequency tension-dominated regime with $G^*(\omega) \propto (i\omega)^{3/4}$ [5–7].

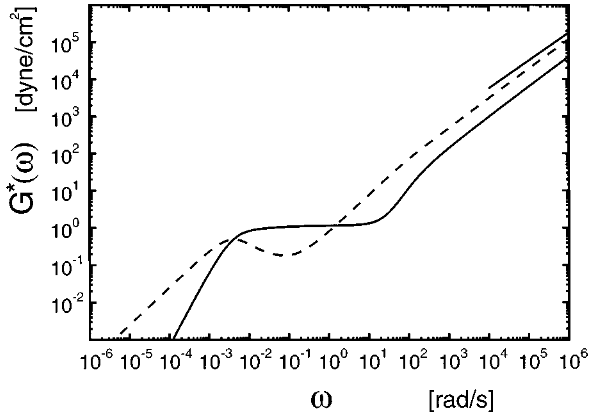

FIG. 2. Calculated moduli $G'(\omega)$ (solid line) and $G''(\omega)$ (dotted line) for $L = L_p = 17$ μm, $L_m = 0.16$ μm, $L_e = 2.0$ μm, $\hat{B}(0)/T = 6900$ μm^{-1}, $T = 293$ K, $\zeta_\perp = 2\zeta = 0.04$ Poise. The straight line has a slope of 3/4.

The above model should describe any sufficiently entangled isotropic solution of wormlike chains, and provides a starting point for understanding the viscoelasticity of such solutions complementary to that of rigid-rod [1] and fuzzy-cylinder [2] models. Equations (5)–(7) for the intramolecular stress are actually applicable to any solution of wormlike chains, and reduce in the appropriate limits to known results for rodlike and flexible chains, and so may provide a useful starting point for describing the effects of semiflexibility in other concentration regimes. The above high-frequency limiting form of $G^*(\omega)$, which is a result of tangential forces, is expected to be a generic feature of solutions of wormlike chains.

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