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Viscoelasticity of a Single Semiflexible Polymer Chain

Tetsuya Hiraiwa and Takao Ohta*

Department of Physics, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

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ABSTRACT: We study the dynamic properties of a single semiflexible polymer chain based on the theory for the wormlike-chain model developed by Hallatschek et al. The linear viscoelastic response is investigated under oscillatory forces acting at the two chain ends. The complex compliance and complex modulus are obtained analytically as a function of the oscillation frequency ω. The real part of the complex compliance in the low frequency limit $\omega \to 0$ is consistent with the static result of Marko and Siggia whereas the imaginary part in the low frequency regime exhibits the power-law dependence $\omega^{1/2}$. On the other hand, these compliances decrease as $\omega^{-7/8}$ in the high frequency limit $\omega \to \infty$. This is consistent with the theoretical result obtained by Everaers et al. in a slightly different condition. A scaling argument is developed to get understanding of these novel results.

1. Introduction

The recent experimental advances in the manipulation of single molecules, such as optical tweezers and atomic force microscopy together with single-molecule fluorescence,[1−4] have enabled us to carry out mechanical and relaxational measurements in the nanoscale with piconewton sensitivity[5] in both equilibrium and nonequilibrium conditions. For example, static force-extension measurements of stretching of a single polymer chain have been carried out.[1,6−8] As a nonequilibrium dynamics, the viscoelastic properties have also been studied.[9−14] Such experiments have provided us with more accurate information on single molecules, which is difficult in bulk experiments because the data are smeared out due to the average taken over molecules and time. Therefore, these investigations lead to better understanding of the hierarchical structures of soft matter and the relationship between the molecular morphology and the functionality of biological molecules.[4,15]

One of the characteristic features of soft matter such as polymers or membranes is that they often possess several length scales. Even in a single polymer chain, if the chain is semiflexible, there are at least two length scales, i.e., the persistence length and the total chain length. In the several experiments of single polymer chains, the semiflexibility or the stiffness has been recognized as an important factor.[6,7,9] In fact, the wormlike-chain model, which is a model of a semiflexible polymer,[6,16,17] explains many experimental findings considerably better than the flexible polymer chain model[18] particularly in the situation such as the highly stretching limit in the force-extension measurement and the large wavenumber limit of the dynamic structure factor, and so on.[2,6,7,9,19,20] It is emphasized that the rigidity effect can be enhanced in the above two limits even for flexible polymers and, as a result, some discrepancy is often observed between experiments and the theory based on a purely flexible model.[20] Therefore, investigation of the dynamics incorporating the nonlinearity due to the stiffness is necessary not only for semiflexible polymers but also for weakly stiff polymers.

Despite the above fact as well as their fundamental interest in the field of mesoscopic physics and their importance for the material and biological application, semiflexible polymer chains have not been studied intensively especially for the dynamics because of the strong nonlinearity contained in the wormlike-chain model. Most of the theoretical studies of single polymers have been limited either to very flexible polymers or to rigid rods.[21] So far, computer simulations have been carried out for a stiff chain or a semiflexible chain.[22−25]

Static theories of a semiflexible polymer chain are summarized as follows. Marko and Siggia derived the static force-extension relation based on the wormlike-chain model.[6] Other statistical properties, such as the distribution function of the end-to-end distance, have also been investigated.[26−28] Improvement of the wormlike-chain model has been proposed to examine the static properties.[7,29]

On the other hand, as mentioned above, analytical approaches to nonequilibrium dynamics of a semiflexible single polymer chain are limited. Some of the previous works have employed an approximation of linearization for the inextensibility constraint.[30] This linearization neglects nonuniformity of the line tension along the chain and has been applied to stretched polymers.[19,31−33]

It is also mentioned that the scaling approach has been utilized for semiflexible polymer chains,[34−36] which was successful for flexible chains.[37−39] Everaers et al. have applied a scaling argument to the longitudinal fluctuation of a semiflexible filament.[35] In the short time limit, they have obtained a power law time-dependence with the exponent 7/8 and have confirmed this result by Brownian dynamics simulations of inextensible polymer chains. They consider the situation such that there is no pre-stretching force.

Morse and his co-workers have formulated a viscoelastic theory of semiflexible rods in dilute solution.[40−42] They employ the local compliance approximation based on the scale separation between the longitudinal mode and the transverse mode of a rod.[42] This approximation takes account of the nonuniformity of the line tension along a rod.

Recently, Hallatschek et al.[34,43] have developed the force-extension theory for the wormlike-chain dynamics without linearization of the inextensibility condition. They consider a weakly bend situation and use a multiscale perturbation method. This method can deal with a large-scale motion along a chain, which Hallatschek et al. call a tension propagation. The theory has been

*Corresponding author. E-mail: takao@scphys.kyoto-u.ac.jp.

applied to the relaxation of an elongated chain after removing or adding an external force.[34,44]

In the present paper, we develop the linear viscoelastic theory of a strongly prestretched single semiflexible polymer chain based on the method by Hallatschek et al.[34,43] We consider the situation such that an oscillatory force in addition to a constant force is applied to the two ends of a wormlike-chain and derive the analytic representation of the complex compliance and the complex modulus as a function of the oscillatory frequency. The preliminary results have been published in ref 45. It will be shown that the frequency dependence of the complex modulus is quite different from that of the Rouse model[39] and that the high frequency behavior is consistent with the result of Everaers et al.[35] We apply a scaling analysis to clarify the physical insight of the results.

The outline of the paper is as follows: In section 2, we present the dynamical model of the wormlike-chain and the linearized tension-propagation equation is derived based on the method by Hallatschek et al.[34,43] In section 3, the complex compliance and the complex modulus are derived analytically. In section 4, the compliance and the modulus in the Rouse dynamics are given for comparison. In section 5, the scaling approach is applied to both the weak-bending wormlike-chain dynamics and the Rouse dynamics. A summary and discussion are given in section 6.

2. Wormlike-Chain Model and the Response to the Oscillatory Force

Dynamics of the Wormlike-Chain Model. The effective Hamiltonian for a wormlike-chain is given by[16]

$$H_{WLC} = \frac{\kappa}{2}\int_0^L \mathrm{d}s \left|\frac{\partial^2 r}{\partial s^2}\right|^2 \tag{1}$$

with the constraint

$$|\boldsymbol{r}'(s,t)|^2 = 1 \tag{2}$$

where t denotes the time, s is the length along the chain from one end, L is the total length and $\boldsymbol{r}(s,t)$ represents the conformation of the chain. The positive constant κ is the bending rigidity. The prime indicates the derivative with respect to s. The constraint given by eq 2 can be incorporated into the Hamiltonian as

$$H_{WLC} = \frac{\kappa}{2}\int_0^L \mathrm{d}s \left|\frac{\partial^2 \boldsymbol{r}}{\partial s^2}\right|^2 + \frac{1}{2}\int_0^L \mathrm{d}s\, f(s,t)\left|\frac{\partial \boldsymbol{r}}{\partial s}\right|^2 \tag{3}$$

where $f(s,t)$ is the Lagrange multiplier for the constraint (eq 2) and is interpreted as the line-tension.

By assuming an overdamped motion, the stochastic equation of motion of a chain is given by

$$\zeta\frac{\partial \boldsymbol{r}(s,t)}{\partial t} = -\kappa \boldsymbol{r}'''' + (f(s,t)\boldsymbol{r}'(s,t))' + \boldsymbol{g}(s,t) + \boldsymbol{\xi}(s,t) \tag{4}$$

where the friction coefficient ζ is a 3×3 matrix with the components $\zeta_{ij}(i,j = x,y,z)$ and $\boldsymbol{g}(s,t)$ represents the external force. The random force $\boldsymbol{\xi}(s,t)$ obeys the Gaussian white statistics:

$$\langle \xi_i(s,t)\rangle = 0 \tag{5}$$

$$\langle \xi_i(s,t)\xi_j(s',t')\rangle = 2k_\mathrm{B}T\zeta_{ij}\delta(s-s')\delta(t-t') \tag{6}$$

with k_B the Boltzmann constant and T the absolute temperature. The equation of motion (eq 4) is the same as that employed by Liverpool.[46]

A remark is now in order. A stiff filament with an internal friction has been studied where the friction is supposed to arise from the internal conformation rearrangement of the filament with a finite radius.[47] It is emphasized here that we have not introduced such an additional friction in eq 4. As described below, the constraint given by eq 2 produces a strong nonlinear coupling between the longitudinal (parallel to the external force) and the transverse components of the conformation, which causes an energy dissipation whose magnitude is comparable with the typical elastic energy.

Weak Bending Approximation and Multiple Scale Analysis. Now we follow the theory developed by Hallatschek, Frey, and Kroy.[34,43] They consider the situation such that a chain is elongated by a force f applied to the ends. The smallness parameter is introduced as $\varepsilon \equiv k_BT/(\kappa f)^{1/2}$. That is, the elastic energy due to the external force is much larger than the thermal energy. The conformation vector $\boldsymbol{r}(s,t)$ is divided into two components. One is parallel to the elongation direction (along the x-axis) and the other is perpendicular to it, i.e., $\boldsymbol{r}(s,t) = (s - r_\parallel, \boldsymbol{r}_\perp)$. The basic approximation is the weak bending approximation such that $\boldsymbol{r}'_\perp(s,t)^2 = O(\varepsilon) \ll 1$. In this situation one has $r'_\parallel = (1/2)(\boldsymbol{r}'_\perp)^2 + O(\varepsilon^2)$. Hallatschek et al.[34,43] have introduced a concept of stored excess length defined by

$$\rho(s,t) = \frac{1}{2}(\boldsymbol{r}'_\perp)^2 \tag{7}$$

Since the parallel component of the end-to-end distance is given by $R_\parallel \equiv L - (r_\parallel(L) - r_\parallel(0))$, one obtains the relation

$$\langle \Delta R_\parallel\rangle(t) = -\int_0^L \langle\Delta\rho\rangle(s,t)\,\mathrm{d}s + o(\varepsilon) \tag{8}$$

where $\Delta R_\parallel$ and $\Delta\rho$ indicate the deviation from some reference state and < .. > means a statistical average.

The Langevin eq 4 is split into two equations for $r_\parallel(s,t)$ and $\boldsymbol{r}_\perp(s,t)$ with the scalar friction coefficients $\zeta_\parallel$ and $\zeta_\perp$ respectively. The equation of the transverse motion is given by[34,43]

$$\zeta_\perp\frac{\partial \boldsymbol{r}_\perp}{\partial t} = -\kappa \boldsymbol{r}''''_\perp + (f(s,t)\boldsymbol{r}'_\perp)' + \boldsymbol{g}_\perp + \boldsymbol{\xi}_\perp \tag{9}$$

where the external force $\boldsymbol{g}$ and the random force $\boldsymbol{\xi}$ have been divided into the longitudinal and transverse components as $\boldsymbol{g}(s,t) = (g_\parallel, \boldsymbol{g}_\perp)$ and $\boldsymbol{\xi}(s,t) = (\xi_\parallel, \boldsymbol{\xi}_\perp)$, respectively. Taking the first derivative with respect to s in the both sides of eq 4, equation of the longitudinal motion is obtained as[34,43]

$$\begin{aligned}\zeta_\parallel\frac{\partial r'_\parallel}{\partial t} &= +(\zeta_\parallel - \zeta_\perp)(\boldsymbol{r}'_\perp\cdot\partial_t\boldsymbol{r}_\perp)' - \kappa r'''''_\parallel - f''(s,t)\\ &\quad + (f(s,t)r'_\parallel)'' - g'_\parallel - \xi'_\parallel\end{aligned} \tag{10}$$

Note that the sign in front of $\xi_\parallel{}'$ is minus because of the relation $\boldsymbol{r} = (s - r_\parallel, \boldsymbol{r}_\perp)$. In these expressions, $o(\varepsilon^{1/2})$ terms and $o(\varepsilon^1)$ terms are neglected in eq 9 and eq 10, respectively. Hallatschek et al.[34,43] have solved this set of equations by a perturbation expansion together with the multiple scale analysis by introducing two scaled variables $s_s = s$ and $s_l = \varepsilon^{1/2}s$. Noting that the ratio of the relaxation rate of $r_\parallel$ to that of $\boldsymbol{r}_\perp$ is $O(\varepsilon^{-1/2})$, one may apply an adiabatic approximation for $r_\parallel$. Furthermore, the local equilibrium approximation is employed such that the degrees of freedom in the length scale s_s is relaxed for a given conformation for the larger scale s_l. In this way, one obtains the following set of equations[34,43]

$$-\frac{1}{k_B T}\langle\Delta\bar{\rho}(s,t)\rangle = \int_0^\infty \frac{dq}{\pi}\left\{\frac{1-\exp(-A(q,s,t))}{\kappa q^2 + f0} - \frac{2q^2}{\zeta_\perp}\int_0^t d\tilde{t}\exp(-A(q,s,t)+A(q,s,\tilde{t}))\right\} \quad (11)$$

and

$$\langle\Delta\bar{\rho}\rangle(s,t) = -\frac{1}{\zeta_{||}}\frac{\partial^2}{\partial s^2}F(s,t) \quad (12)$$

where q is the wavenumber representing modulations of the conformation $\mathbf{r}_\perp(s,t)$ and

$$F(s,t) = \int_0^t d\tilde{t} f(s,\tilde{t}) \quad (13)$$

$$A(q,s,t) = \frac{2q^2}{\zeta_\perp}(\kappa q^2 t + F(s,t)) \quad (14)$$

The quantity $\langle\Delta\bar{\rho}\rangle(s,t)$ is the bulk value of $\langle\Delta\rho\rangle(s,t)$. See ref 43 for details. We consider the situation such that the polymer chain is in a steady condition under a constant force f_0 applied at the ends until $t = 0$ and then another time dependent force $\Delta f(s,t)$ is switched on at $t=0$, i.e., $f(s,t)=f_0 + \Delta f(s,t)$ for $t > 0$. The time-integral of the force along the polymer chain is given by

$$F(s,t) = F_0(t) + \Delta F(s,t) \quad (15)$$

where $F_0(t) \equiv f_0 t$ and

$$\Delta F(s,t) = \int_0^t d\tilde{t}\,\Delta f(s,\tilde{t}) \quad (16)$$

The tangential vector at the chain ends is approximated to be parallel to the direction of the external force. This is justified in the weak bending limit.[43] (We shall return to this point in section 6).

Characteristic Length and Time. By comparing two terms in eq 3 and k_BT, one notes that there are three characteristic lengths

$$l_p = \frac{\kappa}{k_B T} \quad (17)$$

$$l_f = \frac{k_B T}{f} \quad (18)$$

$$\xi = \left(\frac{\kappa}{f}\right)^{1/2} \quad (19)$$

where l_p is the persistence length of the chain. In the linear response with respect to $\Delta f(s,t)$ as we study in the present paper, the constant force f_0 applying to the prestretched chain should be used for f. The total length of the chain L is also a characteristic length. The smallness parameter of the weak bending limit ε can be rewritten as

$$\varepsilon = \frac{\xi}{l_p} = \frac{l_f}{\xi} = \left(\frac{k_B T}{l_p f}\right)^{1/2} \quad (20)$$

This indicates that the magnitude of the characteristic lengths has a definite order for $\varepsilon \ll 1$ as

$$l_f \ll \xi \ll l_p \lesssim L \quad (21)$$

Hereafter we ignore the shortest one l_f.

Comparing each term in the Langevin equation (eq 4), one obtains the following characteristic times

$$\tau_1 = \frac{l^4\zeta_\perp}{\kappa} \quad (22)$$

$$\tau_2 = \frac{l^2\zeta_\perp}{f} \quad (23)$$

with l a length scale. Substituting $l = \xi$ into eq 23 yields

$$\tau_\xi = \frac{\kappa\zeta_\perp}{f^2} \quad (24)$$

This characteristic time corresponds to t_f introduced by Hallatschek et al.[34,43] Substituting $l = l_p$ into eq 22, one has[41]

$$\tau_p = \frac{{l_p}^3\zeta_\perp}{k_B T} = \frac{\kappa^3\zeta_\perp}{(k_B T)^4} \quad (25)$$

Note that this is the only characteristic time which contain neither f nor L.

Substituting the characteristic lengths $l = l_p$, l_f, ξ, and L into τ_1 defined by eq 22 and τ_2 by eq 23, one obtains several important characteristic times apart from τ_ξ and τ_p. The characteristic time τ_1 with $l = L$ gives us

$$\tau_L \equiv \frac{L^4\zeta_\perp}{\kappa} \quad (26)$$

which is the relaxation time for the longest bending mode. This is the same as $\tau_\perp$ defined by Shankar et al.,[42] where they have considered the rigid limit $L \ll l_p$. In the strong stretching limit studied in the present paper, we have to use τ_{fs} defined by eq 28 below rather than τ_L because τ_{fs} contains the force f_0 but τ_L does not. Substituting $l = \xi$ into τ_1 gives us τ_ξ defined by eq 24

$$\frac{\kappa\zeta_\perp}{f_0^2} = \tau_\xi \quad (27)$$

This fact implies that ξ is the characteristic length over which the relaxation time associated with the line tension becomes shorter than that associated with the bending rigidity. The characteristic time τ_2 with $l = L$ gives us

$$\tau_{fs} \equiv \frac{L^2\zeta_\perp}{f_0} \quad (28)$$

This is the longest time where the finiteness of the chain length L enters explicitly. Other times τ_1 and τ_2 with $l = l_f$ and τ_2 with $l = l_p$ have no relevance in the present paper in the sense that these quantities do not appear in the compliance and the modulus obtained theoretically and are unnecessary in the scaling theory described in the subsequent sections. It is noted that $\tau_{fs} \ll \tau_L$ from the relation given by eq 21. This implies again that we have to use the characteristic time τ_{fs}

rather than τ_L in the situation considered in the present paper.

Linearized Tension Dynamics. In this subsection, we focus our attention on the propagation of the line tension $f(s,t)$ or $F(s,t)$ based on the theory by Hallatschek et al.[34,43] This concept itself can also be applied to a flexible polymer chain.[48] From eqs 11 and 12, the tension propagation equation for $F(s,t)$ is obtained in a closed form and in terms of the dimensionless quantities as[34,43]

$$K\frac{\partial^2}{\partial\hat{s}^2}\hat{F}(\hat{s},\hat{t}) = \int_0^\infty d\hat{q}\left\{\frac{1-\exp(-\hat{A}(\hat{q},\hat{s},\hat{t}))}{\hat{q}^2+1} - 2\hat{q}^2\int_0^{\hat{t}} d\tilde{t}\exp(-\hat{A}(\hat{q},\hat{s},\hat{t})+\hat{A}(\hat{q},\hat{s},\tilde{t}))\right\} \quad (29)$$

where

$$\hat{q} = \xi q \quad (30)$$

$$\hat{s} = \varepsilon^{1/2}s\xi^{-1} \quad (31)$$

$$\hat{t} = t/\tau_\xi \quad (32)$$

The constant $K = \pi/\hat{\zeta}$ with $\hat{\zeta} \equiv \zeta_\parallel/\zeta_\perp$ is just a numerical factor. The total length L is now rescaled as $\hat{L} = \varepsilon^{1/2}L\xi^{-1}$. The scaled functions $\hat{A}$ and $\hat{F}$ are given respectively by

$$\hat{A}(\hat{q},\hat{s},\hat{t}) = 2\hat{q}^2(\hat{q}^2\hat{t} + \hat{F}(\hat{s},\hat{t})) \quad (33)$$

and

$$\hat{F}(\hat{s},\hat{t}) = \frac{\xi^2}{\kappa\tau_\xi}F(s,t) = \int_0^{\hat{t}} d\tilde{t}\,\frac{f(\xi\hat{s},\tau_\xi\hat{t})}{f_0} \quad (34)$$

We assume that $\Delta f(s,t)$ is sufficiently small keeping f_0 finite, i.e., $\Delta f(s,t) \ll f_0$ and hence $\Delta F(s,t) \ll f_0 t$, and apply the linearization approximation to eq 29. That is, substituting eq 15 into eq 29 and retaining the terms up to the first order of ΔF, one obtains

$$K\frac{\partial^2}{\partial\hat{s}^2}\Delta\hat{F} - \int_0^{\hat{t}} d\tilde{t}\,\Delta\hat{F}(\hat{s},\hat{t}-\tilde{t})M(\tilde{t}) = 0 \quad (35)$$

where the memory function $M(\hat{t})$ is given by

$$M(\hat{t}) \equiv -4\int_0^\infty d\hat{q}\left\{\hat{q}^4 e^{-2\hat{q}^2(\hat{q}^2+1)\hat{t}} - \frac{\hat{q}^2}{\hat{q}^2+1}\delta(\hat{t})\right\} \quad (36)$$

The asymptotic behavior is given by

$$M(\hat{t}) \sim \hat{t}^{-\beta}$$

with $\beta = 5/4$ for $\hat{t} \to 0$ and $\beta = 5/2$ for $\hat{t} \to \infty$.

Equation 35 is to be solved under the boundary conditions at $s = 0$ and $s = L$. In what follows, we consider the symmetric case that $\Delta F(0,t) = \Delta F(L,t) \equiv \Delta F(t)$. Applying the Laplace transformation with respect to t to eq 35, one obtains

$$K\frac{\partial^2}{\partial\hat{s}^2}\Delta\tilde{F}(\hat{s},z) - N(z)\Delta\tilde{F}(\hat{s},z) = 0 \quad (37)$$

where $\tilde{F}(\hat{s},z)$ denotes the Laplace transform of $\tilde{F}(\hat{s},t)$ and

$$N(z) \equiv -4\int_0^\infty d\hat{q}\left\{\frac{\hat{q}^4}{2\hat{q}^2(\hat{q}^2+1)+z} - \frac{1}{2}\frac{\hat{q}^2}{\hat{q}^2+1}\right\} \quad (38)$$

is the Laplace transform of $M(t)$. Note that the function $N(z)$ is positive when z is real and positive. The asymptotic form of $N(i\omega)$ is given as follows. For $\omega \to \infty$, one obtains from eq 38

$$\mathrm{Re}\,N(\pm i\omega\tau_\xi) = +2S_1(\omega\tau_\xi)^{1/4}$$

$$\mathrm{Im}\,N(\pm i\omega\tau_\xi) = +4S_2(\omega\tau_\xi)^{1/4} \quad (39)$$

with $S_1 = \int_0^\infty dq\,(4q^8+1)^{-1} \approx 0.863$ and $S_2 = \int_0^\infty dq\,q^4(4q^8+1)^{-1} \approx 0.179$. It is readily shown that the Taylor expansion of $N(z)$ around $z = 0$ breaks down. The correct expansion is obtained after some manipulation as

$$N(\pm i\omega\tau_\xi) = +2S_3(\omega\tau_\xi)^{3/2} \pm iS_4(\omega\tau_\xi)^1 \quad (40)$$

where $S_3 = \pi/8$ and $S_4 = \pi/4$.

We consider the case that the force $\Delta f(t)$ at the boundaries is oscillatory as $\Delta f(t) = f_A\sin(\omega t)$ with the amplitude f_A and the frequency ω. The scaled form of ΔF at the boundaries is given by

$$\Delta\hat{F}(\hat{t}) = (\omega\tau_\xi)^{-1}\frac{f_A}{f_0}[1-\cos(\omega\tau_\xi\hat{t})] \quad (41)$$

and the Laplace transform is given by

$$\Delta\tilde{F}(z) = \frac{f_A}{f_0}\frac{(\omega\tau_\xi)}{z[z^2+(\omega\tau_\xi)^2]} \quad (42)$$

The solution of eq 37 can be represented as

$$\Delta\tilde{F}(\hat{s},z) = \Delta\tilde{F}(z)\times\frac{\cos(\Gamma(z)(2\hat{s}-\hat{L}))}{\cos(\Gamma(z)\hat{L})} \quad (43)$$

where $\Gamma(z) = (N(z)/4K)^{1/2}$. One needs to evaluate the inverse Laplace transform of eq 43

$$\Delta\hat{F}(\hat{s},t) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\Delta\tilde{F}(z)\frac{\cos(\Gamma(z)(2\hat{s}-\hat{L}))}{\cos(\Gamma(z)\hat{L})}e^{zt}\,dz \quad (44)$$

which will be carried out in the next section.

3. Analytical Results

Now, we study the response of the end-to-end distance to the oscillatory force. The average end-to-end distance $\Delta R(t)$ which is a deviation from that of the prestretched state under the constant force f_0 is given by[34,43]

$$\Delta R(t) = -\int_0^L ds\,\langle\Delta\bar{\rho}\rangle(s,t) \quad (45)$$

$$= \frac{1}{\zeta_\parallel}\left\{\frac{\partial}{\partial s}F(s,t)|_{s=L} - \frac{\partial}{\partial s}F(s,t)|_{s=0}\right\} \quad (46)$$

Here, for simplicity, the statistical average of the end-to-end distance is represented as $\Delta R(t)$ without the brackets, the bar and the parallel mark. Substituting eq 44 into eq 46 together with eq 34, one obtains the time evolution of the average end-to-end distance under the given boundary condition.

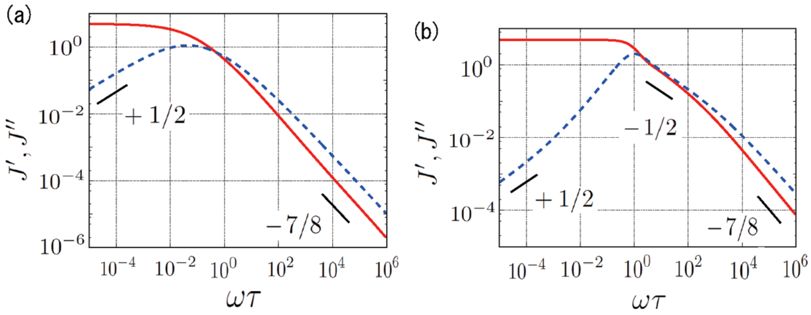

Figure 1. $\hat{J}'$ and $\hat{J}''$ as a function of $\omega\tau$ for $D = 1$ and (a) $\alpha = 1.0$ and (b) $\alpha = 100.0$. The full curve represents $\hat{J}'$ whereas the broken curve represents $\hat{J}''$. The characteristic time τ is defined by eq 55.

Since we are concerned with the asymptotic behavior $t \to +\infty$, we may consider only the poles on the imaginary axis $z = 0, \pm i\omega\tau_\xi$ in the integrand of eq 44 to carry out the inverse Laplace transform. The final result can be written as

$$\frac{\Delta R(t)}{L} = \frac{f_A}{f_0}[\hat{J}'(\omega)\sin(\omega t) - \hat{J}''(\omega)\cos(\omega t)] \quad (47)$$

The scaled complex compliance is given by

$$\hat{J}'(\omega) = \frac{2D}{\omega\tau}\mathrm{Im}(\overline{\Gamma}(i\omega\tau_\xi)\tanh(\overline{\Gamma}(i\omega\tau_\xi))) \quad (48)$$

$$\hat{J}''(\omega) = \frac{2D}{\omega\tau}\mathrm{Re}(\overline{\Gamma}(i\omega\tau_\xi)\tanh(\overline{\Gamma}(i\omega\tau_\xi))) \quad (49)$$

where

$$D \equiv \frac{1}{2\pi^2}\frac{k_BT}{\sqrt{f_0\kappa}} = \frac{\varepsilon}{2\pi^2} \quad (50)$$

and

$$\overline{\Gamma}(z) = \alpha N(z)^{1/2}/2$$

with the dimensionless constant

$$\alpha \equiv \frac{\hat{\xi}^{1/2}(k_BT)^{1/2}f_0^{1/4}L}{\pi^{1/2}\kappa^{3/4}} = \sqrt{\frac{\hat{\xi}}{\pi\varepsilon}}\frac{L}{l_p} \quad (51)$$

The scaled elastic modulus $\hat{G}'$ and the scaled loss modulus $\hat{G}''$ are obtained from $\hat{J}'$ and $\hat{J}''$ as follows

$$\hat{G}'(\omega) = \frac{\hat{J}'(\omega)}{\hat{J}'(\omega)^2 + \hat{J}''(\omega)^2} \quad (52)$$

$$\hat{G}''(\omega) = \frac{\hat{J}''(\omega)}{\hat{J}'(\omega)^2 + \hat{J}''(\omega)^2} \quad (53)$$

In the following, we introduce another characteristic time. The linearized eq 35 reduces to the simple diffusion equation by employing the Markov approximation

$$K\frac{\partial^2}{\partial\hat{s}^2}\Delta\hat{F}(\hat{s},\hat{t}) - \frac{\pi}{4}\frac{\partial}{\partial\hat{t}}\Delta\hat{F} = 0 \quad (54)$$

This implies that one may define a new relaxation time as the time scale of the slowest mode, just like the Rouse time in the continuous Rouse dynamics:

$$\tau \equiv \frac{k_BT\zeta_{||}L^2}{4\pi^2\kappa^{1/2}f_0^{3/2}} = \frac{\alpha^2}{4\pi}\tau_\xi \quad (55)$$

It is noted that the three parameters τ, τ_ξ, and α are not independent of each other. As will be shown below, the compliance and the modulus are plotted as a function of the scaled frequency $\omega\tau$ and the constant α is chosen as an independent parameter.

We examine the limiting behavior of $\hat{J}'$ and $\hat{J}''$. In the high frequency limit, substituting eq 39 into eqs 48 and 49 and after some manipulation, one obtains

$$\hat{J}'(\omega) \sim \frac{4S_1^{1/2}b(k_BT)^{1/2}f_0}{\pi^{1/2}\hat{\xi}^{1/2}\kappa^{5/8}\zeta_\perp^{7/8}L}\omega^{-7/8} \propto \kappa^{-5/8}(k_BT)^{+1/2}\omega^{-7/8},$$
$$\hat{J}''(\omega) \sim \frac{4S_1^{1/2}a(k_BT)^{1/2}f_0}{\pi^{1/2}\hat{\xi}^{1/2}\kappa^{5/8}\zeta_\perp^{7/8}L}\omega^{-7/8} \propto \kappa^{-5/8}(k_BT)^{+1/2}\omega^{-7/8} \quad (56)$$

and

$$\hat{J}'(\omega)/\hat{J}''(\omega) = b/a \approx 0.199 \quad (57)$$

where $a \approx 0.721$ and $b \approx 0.142$ are the positive solutions of $(a + bi)^2 = 1/2 + iS_2/S_1$. It should be noted from eq 56 that the unscaled complex compliance in the high frequency limit $J = L\hat{J}/f_0$ depends on neither L nor f_0.

In the low frequency regime, substituting eq 40 into eqs 48 and 49 and after some manipulation, one obtains

$$\hat{J}'(\omega) \sim \frac{1}{4}\frac{k_BT}{\sqrt{\kappa f_0}} \quad (58)$$

$$\hat{J}''(\omega) \sim \frac{k_BT\zeta_\perp^{1/2}}{4f_0^{3/2}}\omega^{+1/2} \propto \kappa^0(k_BT)^{+1}\omega^{+1/2} \quad (59)$$

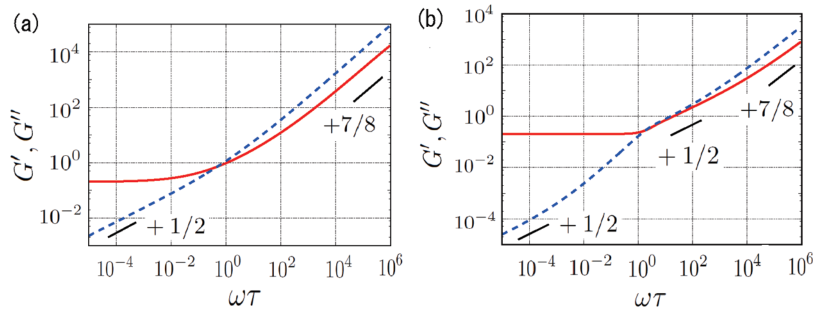

Figure 2. $\hat{G}'$ and $\hat{G}''$ as a function of $\omega\tau$ for $D = 1$ and (a) $\alpha = 1.0$ and (b) $\alpha = 100.0$. The full curve represents $\hat{G}'$ whereas the broken curve represents $\hat{G}''$.

Note that eq 58 is consistent with the result of Marko and Siggia for the static stress−strain relation[6]

$$\frac{R(f_0)}{L} = 1 - \frac{1}{2}\frac{k_BT}{\sqrt{\kappa f_0}} \tag{60}$$

which leads to

$$\frac{R(f_0(1+\delta))}{L} - \frac{R(f_0)}{L} = \frac{\delta}{4}\frac{k_BT}{\sqrt{\kappa f_0}} + O(\delta^2) \tag{61}$$

Parts a and b of Figure 1 display the compliances $\hat{J}'$ and $\hat{J}''$ for $\alpha = 1$ and $\alpha = 100$, respectively, as a function of the scaled frequency $\omega\tau$. As mentioned above, the compliances exhibit the fractional power law behavior for the high frequency whereas in the low frequency limit $\omega \to 0$, $\hat{J}'$ is consistent with the static result of the wormlike chain. The difference from the simple Maxwell-like elasticity is more evident for $\hat{G}'$ and $\hat{G}''$ as plotted for $\alpha = 1$ in Figure 2a and for $\alpha = 100$ in Figure 2b. Both $\hat{G}'$ and $\hat{G}''$ increase as $\omega^{7/8}$ for $\omega\tau_\xi \gg 1$. In the plot of Figure 1, parts a and b, we have put $D = 1$ for convenience although the value is actually small as defined by eq 50. This is not serious because the constant D is simply a multiplicative factor in the compliance (eqs 48 and 49).

It is noted that there is an intermediate region if $\tau \gg \tau_\xi$ or $\alpha \gg 1$. From the definition of α given by eq 51, this condition is realized in the situation that the total chain length L is much larger than $\varepsilon^{1/2} l_p = \xi^{1/2} l_p^{1/2}$. When this condition is satisfied, there is a finite frequency interval of the intermediate region; $1/\tau \ll \omega \ll 1/\tau_\xi$. For example, in both Figure 1b and Figure 2b, the interval $1 \ll \omega\tau \lesssim 10^2$ corresponds to this region. In this region, the asymptotic form of $N(z)$ is given by eq 40. Moreover, since

$$\overline{\Gamma}(i\omega\tau_\xi) = \alpha N(i\omega\tau_\xi)^{1/2}/2 \sim (i\omega\tau_\xi)^{1/2}$$

the imaginary part of $\overline{\Gamma}$ is so large that $\tan(\overline{\Gamma})$ is approximated by $+1$. By substituting eq 40 into eqs 48 and 49, the compliance becomes

$$\hat{J}'(\omega) \sim \omega^{-1/2} \frac{f_0^{1/4}(k_BT)^{1/2}}{\sqrt{2}L\zeta_\parallel^{1/2}\kappa^{1/4}}\left(1 - \frac{1}{2}(\omega\tau_\xi)^{1/2}\right)$$

$$\hat{J}''(\omega) \sim \omega^{-1/2} \frac{f_0^{1/4}(k_BT)^{1/2}}{\sqrt{2}L\zeta_\parallel^{1/2}\kappa^{1/4}}\left(1 + \frac{1}{2}(\omega\tau_\xi)^{1/2}\right) \tag{62}$$

which exhibits the $\omega^{-1/2}$ dependence in the intermediate region.

Figure 1 indicates that $\hat{J}''$ has a power law behavior $\omega^{1/2}$ for small values of $\omega\tau$. It is noted here that this behavior is restricted to the region that $\omega\tau_{fs} \gg 1$, where τ_{fs} is defined by eq 28. This is because the finite size effect of the chain length cannot be ignored for $\omega\tau_{fs} \lesssim 1$. The scale difference $\tau_{fs} \gg \tau$ is satisfied for $\varepsilon \ll 1$ and, hence, the region where the imaginary part of the complex compliance J'' obeys the power-law $\omega^{+1/2}$ appears in the low-frequency intermediate regime.

4. Comparison with Rouse Dynamics

In this section, following the paper by Khatri and McLeish,[39] we present the complex compliance for the Rouse model and compare it with the present result. The Rouse dynamics without internal friction is governed in the continuum limit by

$$\zeta\frac{\partial \boldsymbol{r}(n,t)}{\partial t} = k\frac{\partial^2 \boldsymbol{r}(n,t)}{\partial n^2} + \boldsymbol{f}(n,t) + \boldsymbol{\xi}(n,t) \tag{63}$$

where ζ is the friction coefficient and the argument n indicates the n-th monomer from one end, $\boldsymbol{r}(n)$ is the position vector of the nth monomer and k is the spring constant between a pair of adjacent two monomers. It is noted that the argument n and the number of monomer N are treated as real numbers in the continuum limit and satisfy $0 \le n \le N$. Both end points are subjected to the external forces which have the same amplitude but the opposite direction

$$\boldsymbol{f}(n,t) = \boldsymbol{f}(t)[\delta(n-N) - (n)] \tag{64}$$

The last term $\boldsymbol{\xi}(n,t)$ in eq 63 stands for the white Gaussian noises that satisfy the fluctuation−dissipation relation of the second kind

$$\langle \boldsymbol{\xi}(n,t)\boldsymbol{\xi}^\dagger(m,t')\rangle = 2k_BT\zeta\boldsymbol{I}\delta(n-m)\delta(t-t') \tag{65}$$

where $\boldsymbol{I}$ is the unit matrix and two adjacent matrices mean a tensor product.

We define the end-to-end distance as $\boldsymbol{R}(t) = \boldsymbol{r}(N,t) - \boldsymbol{r}(0,t)$ and the deviation as $\Delta\boldsymbol{R}(t) = \boldsymbol{R}(t) - \boldsymbol{R}(0)$. In the same way, the deviation of the external force is defined by $\Delta\boldsymbol{f}$. The complex compliance $J_R(\omega) = J'_R(\omega) + iJ''_R(\omega)$ is defined through the relation

$$\langle\widetilde{\Delta\boldsymbol{R}}\rangle(\omega) = J^*_R(\omega)\widetilde{\Delta\boldsymbol{f}}(\omega) \tag{66}$$

where the Fourier transformed function is indicated by the tilde and the asterisk means the complex conjugate and $J^*_R(\omega)$ is given by[39]

$$J^*_R(\omega) = \frac{2N}{\pi k}\frac{\tanh\left(\frac{\pi}{2}\sqrt{i\omega\tau_R}\right)}{\sqrt{i\omega\tau_R}} \tag{67}$$

where τ_R is the Rouse relaxation time defined by

$$\tau_R = \frac{N^2\zeta}{\pi^2 k} \tag{68}$$

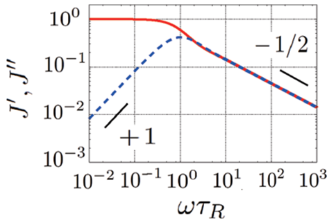

Figure 3. Complex compliance for the Rouse dynamics without internal friction. The full curve represents J'_R whereas the broken curve represents J''_R. The amplitude is normalized such that $J'_R = 1$ for $\omega \to 0$.

The complex compliance given by eq 67 is plotted in Figure 3, and the corresponding complex modulus G_R is plotted in Figure 4.

The limiting behavior is readily obtained. For $\omega \to \infty$, the complex compliance behaves as

$$J'_R(\omega) \propto \omega^{-1/2} \tag{69}$$

$$J''_R(\omega) \propto \omega^{-1/2} \tag{70}$$

and for $\omega \to 0$

$$J'_R(\omega) \to \text{const.} \tag{71}$$

$$J''_R(\omega) \propto \omega^{+1} \tag{72}$$

These exponents are distinctly different from those obtained in the previous section, $-^7/_8$ for both J' and J'' as $\omega \to \infty$ in eq 56 and the exponent $+^1/_2$ for J'' as $\omega \to 0$ in eq 59. The viscoelastic properties of the Rouse dynamics with internal friction have been investigated by Khatri and McLeish,[39] where the high frequency behavior is given by $J'_R \propto \omega^{-2}$ and $J''_R \propto \omega^{-1}$. These are again different from the present results.

5. Scaling Approach

In this section, we apply the scaling analysis to a semiflexible chain in order to get understanding of the behavior of complex compliances in the high and low frequency limits.

Scaling Form of $\Delta R(t)$. It should be noted that all the parameters are scaled out in eq 29. The parameters appear only through eq 34 for $F(s,t)$ and through the boundary condition which contains L scaled as $\hat{L} = \varepsilon^{1/2}L\xi^{-1}$. These facts together with eq 46 give us without ambiguity the following scaling form of ΔR;

$$\Delta R(t) = \varepsilon^{1/2}\xi^{-1}\tau_\xi f\zeta^{-1}Q(\varepsilon^{1/2}L\xi^{-1}, t/\tau_\xi) \tag{73}$$

where $Q(x,y)$ is an unknown function whose asymptotic form is to be determined.

Complex Compliance in the High Frequency Limit. The exponent $^7/_8$ exhibited by J' and J'' for $\omega \to \infty$ in eq 56 can be understood by the following scaling analysis. In the linear response regime where $f_A \ll f_0$, the dimensionless function Q in eq 73 should be proportional to f_A/f_0. In the high frequency limit, the effect of the external force is expected to be localized near the two ends and hence the compliance J should not depend on the chain length L. This leads us to the following form of the compliance

$$f_AJ(\omega) \sim \frac{f_A}{f}\varepsilon^{1/2}\xi^{-1}\tau_\xi f\zeta^{-1}(\omega\tau_\xi)^{-z} \tag{74}$$

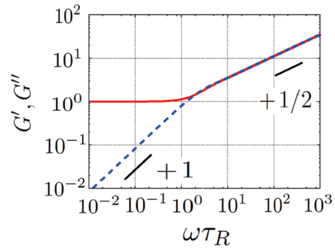

Figure 4. Complex modulus for the Rouse dynamics without internal friction. The full curve represents G'_R whereas the broken curve represents G''_R. The amplitude is normalized such that $G'_R = 1$ for $\omega \to 0$.

with an unknown exponent z. Substituting the definitions of ξ, ε and τ_ξ given, respectively, by eqs 19, 20, and 24 into eq 74 yields

$$f_AJ(\omega) \sim f_Af^{-7/4+2z}\kappa^{1/4-z}(k_BT)^{1/2}\zeta^{-z}\omega^{-z} \tag{75}$$

It should be noted that the compliance is independent of the line tension f in the high frequency limit. This is because the relaxation of the chain has the factor $\kappa q^4 + fq^2$ as can be seen from eq 4 and hence the term κq^4 is relevant in the high frequency limit (fq^2 is irrelevant). This requirement gives us

$$z = \frac{7}{8} \tag{76}$$

The scaling analysis in the Rouse dynamics is different from the above because of the absence of the local length scale, i.e., the persistence length l_p. The Rouse model has only one length scale, the root of the mean square end-to-end distance σ. When no external force is present, it is given by[21]

$$\sigma \sim \left(\frac{k_BT}{k}\right)^{1/2}N^{1/2} \tag{77}$$

Therefore, the dimensional analysis tells us that the deviation of the end-to-end distance should obey

$$\Delta R \sim \sigma\frac{\sigma f_A}{k_BT}\hat{J}(\omega\tau_R)e^{i\omega t} \tag{78}$$

with the external force

$$f(t) = f_Ae^{i\omega t} \tag{79}$$

Assuming that $\hat{J}$ has a power law behavior $\hat{J}(\omega\tau_R) \sim (\omega\tau_R)^{-z}$ as $\omega \to \infty$. The complex compliance is written as

$$f_AJ(\omega) \sim \sigma\frac{\sigma f_A}{k_BT}(\omega\tau_R)^{-z} \sim f_AN^{1-2z}\omega^{-z}k^{z-1}\zeta^{-z} \tag{80}$$

In the high frequency limit, the response is localized and the compliance should be independent of N so that the exponent is determined uniquely as $z = ^1/_2$ or

$$J(\omega) \propto \omega^{-1/2} \tag{81}$$

This is the argument given by Khatri et al.[39]

Complex Compliance in the Low Frequency Regime. The exponent $^1/_2$ exhibited by J'' for $\tau^{-1} \gg \omega \gg \tau_{fs}^{-1}$ obtained in eq 59 can be understood as follows. In the low frequency regime, the effect of the external force is extended almost uniformly to the whole chain. Therefore, one can require that

J is proportional to L so that

$$f_A J(\omega) = \frac{f_A}{f}\varepsilon^{1/2}\xi^{-1}\tau_\xi f\zeta^{-1}(\varepsilon^{1/2}L\xi^{-1})(\omega\tau_\xi)^z \qquad (82)$$

The real part J' is independent of the frequency for $\omega \to 0$ and hence $z = 0$ whereas the imaginary part J'' should be independent of κ for $\omega \to 0$. As mentioned above, the relaxation of the chain has the factor $\kappa q^4 + fq^2$ and hence κ is irrelevant in the low frequency regime. Therefore, substituting the definitions of ξ, ε and τ_ξ given, respectively, by eqs 19, 20, and 24 into eq 82, one obtains

$$z = \frac{1}{2} \qquad (83)$$

so that $J'' \propto k_B T\, \omega^{1/2}$. Note from eq 75 that J'' in the high frequency limit is proportional to $(k_B T)^{1/2}$ whereas it is proportional to $k_B T$ in the low frequency regime.

In contrast, the complex compliance in the Rouse dynamics is analytic in the $\omega \to 0$ limit. This fact is clear from eq 67 and should be compared with that of the wormlike-chain dynamics (eqs 48 and 49) where the function $N(z)$ in $\overline{\Gamma}(z)$ exhibits a nonanalyticity as eq 40.

6. Summary and Discussion

In summary, we have developed the analytical theory of the linear viscoelasticity of single semiflexible polymer chains and have obtained the complex compliance. In particular, it is found that the asymptotic behavior of the compliance obeys as $J', J'' \propto \omega^{-7/8}$ for $\omega \to \infty$ whereas $J'' \propto \omega^{+1/2}$ for $\omega\tau \ll 1$. These are different from the results of the Rouse dynamics. The constant of J' for $\omega = 0$ given by eq 58 is also different from that of a flexible chain.

The theory assumes weakness of the bending parameter $\varepsilon \ll 1$ which guarantees the scale separation.[34,42,43] This is due to the fact that the ratio of the characteristic length parallel to the stretched chain $l_\| \sim \Delta s$ to the characteristic length perpendicular to the chain $l_\perp \sim q^{-1}$ is given by

$$\frac{l_\perp}{l_\|} \sim \frac{q^{-1}}{\Delta s} \sim \varepsilon^{1/2}\frac{\hat{q}^{-1}}{\Delta\hat{s}} \ll 1 \qquad (84)$$

where the scaled forms given by eqs 30 and 31 have been used. It is emphasized that, for $\omega \to \infty$, the scale separation is valid without assuming the smallness of ε since $l_\| \propto \omega^{-1/8} \gg l_\perp \propto \omega^{-1/4}$. This is verified as follows. The characteristic value of $\hat{q}$ is estimated as $\hat{q} \sim \omega^{+1/4}$ from eq 38 with $z = i\omega$ for large values of ω. By using the relation $N(i\omega) \sim \omega^{1/4}$ and comparing the two terms in eq 37, the characteristic value of $\hat{s}$ is estimated as $\omega^{-1/8}$.

We make a remark about the boundary conditions and two related problems. We have assumed either $\mathbf{r}_\perp(s) = \mathbf{r}'_\perp(s) = 0$ or $\mathbf{r}'_\perp(s) = \mathbf{r}'''_\perp(s) = 0$ at $s = 0$ and L in deriving eq 11 from eqs 9 and 10.[34,43] Quite recently, other boundary conditions have been considered.[49] In any events, the effect of the boundary conditions is found to be negligible in eq 11 except for the extremely low frequency regime.

In the present theory, we are concerned with the compliance for much higher frequency. Here we discuss the lower limit of the frequency. We have introduced the Fourier transform with respect to the conformation s of a chain as eq 29 where the wavenumber q is a continuous real number. However, when the frequency of the modes is sufficiently small, the finiteness of the chain cannot be ignored and the discreteness of the wavenumber has to be taken into account. This actually occurs for $\omega\tau_{fs} \ll 1$ and the integral over the wavenumber in eq 29 has to be replaced by the summation. As a result, the nonanalyticity of the function $N(i\omega)$ at $\omega = 0$ disappears and the imaginary part J'' turns out not to be proportional to $\omega^{1/2}$ but to be proportional to ω.

We have assumed that the tangential vector of a chain at the ends is exactly parallel to the external force in the formulation of the line tension in section 2. However, if this is not the case, the clamped boundary condition for the line-tension is given by $f_{\text{actual}} = f\cos\theta$, where f denotes the magnitude of the external force and θ the angle between the tangential direction and the external force. In order to estimate the effect of the difference between the two directions, we approximate f_{actual} by an ensemble average $f_{\text{actual}} = \langle f\cos\theta\rangle$ and introduce the factor $\Delta \equiv f_{\text{actual}}/f$. Using the equilibrium distribution for θ for a rigid rod with the length l under the stretching external force, this factor is approximately given by $\Delta = 1/\tanh(lf/k_BT) - (k_BT)/(lf)$. Since l can be identified with the persistence length, which is the only characteristic length given by the bending rigidity and the thermal energy, one obtains $\Delta \sim 1 - (k_BT)/(l_pf) \approx 1$ because $\varepsilon = (k_BT)^{1/2}/(l_pf)^{1/2} \ll 1$. Thus, the effects of the perpendicular component of the external force are negligibly small in the weak bending situation.

Now we discuss the relation between the present results and those obtained by Hallatschek et al., who have considered the relaxation of the end-to-end distance after stepwise change of the external force.[34,44] They have predicted that both in the stretching case and in the release case the end-to-end distance behaves as

$$\langle \Delta R_\|(t)\rangle \propto f\kappa^{-5/8}(k_BT)^{-1/2}t^{7/8} \qquad (85)$$

where $t \ll t_f \sim \zeta\kappa f^{-2}$. The exponent $^7/_8$ is the same as that in the high-frequency limit given by eq 56. During a short time interval after the force change, its effect is localized near the chain ends, the length of which is small compared with both l_p given by eq 17 and ξ given by eq 19. This is the same as the localization of the effects of the oscillatory force at high frequency. In a more quantitative way, we can show that eq 85 is consistent with eq 56. The relaxation function $\psi(t)$ in the linear response theory is related to the response function $\phi(t)$ as $\phi(t) = -\mathrm{d}\psi(t)/\mathrm{d}t$. The complex compliance is the Fourier-Laplace transform of the response function and hence $J(\omega) = \psi(0) + i\omega\int_0^{+\infty}\mathrm{d}t\, e^{i\omega t}\psi(t)$. This gives us the relation $J(\omega) \sim \psi(1/\omega)$ and $\tilde{J}(\omega) = fJ/L \sim \langle\Delta R_\|(1/\omega)\rangle/L$.

In the intermediate time region $t_L \gg t \gg t_f$ where the crossover time t_L is defined through $l_\|(t_L) = L$, Hallatschek et al. have obtained[34,44]

$$\langle \Delta R_\|(t)\rangle \propto f^{3/4}\kappa^{-1/2}(k_BT)^{1/2}t^{3/4} \qquad (86)$$

for a pulling situation and

$$\langle \Delta R_\|(t)\rangle \propto f^{1/4}\kappa^{-1/4}(k_BT)^{1/2}t^{1/2} \qquad (87)$$

for a release situation. We have no results corresponding to eq 86 since this contains a nonlinear effect of the applied time-dependent force. On the other hand, the exponent $^1/_2$ in eq 87 corresponds to $\omega^{-1/2}$ in eq 62 in the present paper. Actually one can verify that not only the exponent but also the coefficient in eq 87 is consistent with our result. Note that the nonlinearity of the prestretching force is taken into consideration in the derivation of both eqs 62 and 87, which produces the factor $f^{1/4}$. In a release case, the force is removed at $t = 0$ and therefore no other nonlinearity is expected for $t \geq 0$. These two are the reasons why our result linearized around the prestretched state agrees with eq 87.

The power-law $\omega^{-7/8}$ or $t^{7/8}$ is consistent with the theoretical result by Everaers et al. for the longitudinal fluctuation $\langle\delta r_\|(t)^2\rangle$ of a semiflexible filament.[35] They consider a short polymer chain $l_p \gg$

L without the constant external force f_0. They confirm the power-law behavior $t^{7/8}$ by Brownian dynamics simulations. The agreement of our result and theirs is attributed to the fact that the background tension f_0 is irrelevant in the high-frequency regime, where the transverse dynamics is controlled by the bending rigidity.

Morse et al. have developed a theory for the complex modulus of semiflexible rods in dilute solution subjected to shear flow.[40−42] In their results, the asymptotic behavior of the complex modulus gives the power law $\omega^{3/4}$ in the high frequency limit. We emphasize that the exponent 3/4 can be understood by our scaling analysis. It is noted that, under shear flow, the whole chain segments are subjected to the shear stress. Therefore, one should assume $\Delta R \propto L^1$ in eq 73 rather than $\Delta R \propto L^0$. Hence, by the same procedure as in Section 5, one obtains

$$f_A J(\omega) \sim f_A \kappa^{-1/2-z} f_0^{-3/2+2z} L^1 (k_B T)^1 \zeta^{-z} \omega^{-z} \tag{88}$$

This expression should be independent of ξ (and hence f_0) because the modes with the wavelength much smaller than ξ are dominant in the high frequency limit . This requirement gives us $z = {}^3/_4$ and

$$f_A J(\omega) \sim f_A \kappa^{-5/4} L^1 (k_B T)^1 \zeta^{-3/4} \omega^{-3/4} \tag{89}$$

Since the compliance J is defined for a single chain under a stretching force acting at the ends of the chain, one needs a transformation of the quantity to compare it with the complex modulus under shear flow $G^*(\omega)$. First, we define the response per unit length of a chain $\overline{J}(\omega) \equiv J(\omega)/L$ and $\overline{G}(\omega) \equiv 1/\overline{J}(\omega)$. Since the shear stress for dilute solutions should be proportional to the force executed to the whole segments, one obtains;

$$G^*(\omega) \propto \overline{G}(\omega) \times L \sim \kappa^{5/4} L^1 (k_B T)^{-1} \zeta^{3/4} \omega^{3/4} \tag{90}$$

It is emphasized that all the exponents for κ, L, $k_B T$ and ω agree precisely with those obtained by Shankar et al.[42] In the above analysis, we have ignored the orientational stress under shear flow.[42] However, its effect is estimated to be much smaller than that of the tension stress in the high frequency limit.[42]

Finally we mention a theoretical study which produces the compliance proportional to $\omega^{-1/2}$. Caspi et al. have investigated the mean square displacement of a monomer of a prestressed semiflexible network[50] and have obtained

$$\langle \Delta h^2(x,t) \rangle \propto \frac{k_B T}{\nu^{1/2} \eta^{1/2}} t^{1/2} \tag{91}$$

where $h(x,t)$ denotes the undulation amplitude and $\Delta h(x,t) \equiv h(x,t) - h(x,0)$, ν the line tension, η the solvent viscosity and L the total chain length. Equation 91 holds in the time region $4\pi\eta\kappa/\nu^2 \ll t \ll \eta L^2/\nu$. Furthermore, they have shown that the effective time dependent friction $\zeta_e(t)$ satisfies the generalized Einstein relation

$$\frac{k_B T}{\zeta_e(t)} = \frac{\langle \Delta h^2(t) \rangle}{2t} \tag{92}$$

Combining eqs 91 and 92, one obtains the complex compliance ($J \propto t/\zeta_e(t)$)

$$J(\omega) \propto \nu^{-1/2} \eta^{-1/2} \omega^{-1/2} \tag{93}$$

Some experiments of semiflexible networks support the exponent ${}^1/_2$.[50,51] It is mentioned, however, that the physical origin of this result is different from our present result for semiflexible chain given by eq 62. The difference is obvious because the coefficient in eq 93 does not contain $k_B T$ whereas our expression eq 62 is proportional to $(k_B T)^{1/2}$.

Now we comment on the several effects which have not been considered in the present paper. The hydrodynamic effect has not been investigated quantitatively in a nonlinear wormlike-chain. Although it is expected to be not so strong in a strongly stretched semiflexible chain, the previous studies of the hydrodynamic effect in the linearized wormlike-chain dynamics[19,20,32,33] should be extended to the nonlinear theory in a general condition. The internal friction considered in the Rouse dynamics[39] should also be extended to the semiflexible chains. In addition, the helical wormlike-chain model, which contains the torsional energy, has been studied in dilute solutions.[27,53,54] This torsional effect may affect the viscoelastic properties of single polymer chains.

Before closing this article, we make an estimation of the characteristic times τ_ξ, τ and τ_{fs} defined by eqs 24, 55 and 28 respectively. The typical data for λ-DNA in an aqueous solution are as follows[34,55,56]

$$l_P \sim 50 \text{ nm}$$

$$L \sim 20\,\mu\text{m}$$

$$\zeta_\perp \sim 1.3 \times 10^{-3} \text{ Pa}\cdot\text{s} = 1.3 \times 10^{-3} \text{ pN}\cdot\text{s}/\mu\text{m}^2$$

For these values together with

$$\hat{\xi} \sim 1/2$$

for a rigid rod[21] and the room temperature $k_B T \sim 4.1$ pN·nm, and for the external force $f_0 \sim 10$ pN, the characteristic times are given by

$$\tau_\xi \sim 2.7 \times 10^{-9} \text{ s}$$

$$\tau \sim 6.0 \times 10^{-5} \text{ s} = 60\,\mu\text{s}$$

$$\tau_{fs} \sim 5.2 \times 10^{-2} \text{ s} = 52 \text{ ms}$$

and the dimensionless constant $\alpha \sim 5.3 \times 10^2$. We expect that the frequency of the order of 60 μs is accessible by improving the atomic force microscopy[14] and that the present predictions will be detected experimentally in the near future.

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