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Dynamic scattering of semirigid macromolecules

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The polarized (VV) and depolarized (VH) dynamic light scattering functions of dilute solutions of semirigid macromolecules are calculated assuming that the scattering wave vector $\underline{q}$ is high compared to the chain Kuhn segment l: $ql \gg 1$. The terminal relaxation rate is $\Gamma \propto q^{8/3}$. Dynamics of both uniaxial and biaxial wormlike macromolecules (filaments) are considered. Biaxial macromolecules are characterized by two persistence lengths proportional to elastic constants for bending in two perpendicular directions (easy and hard bending). We showed that biaxiality may result in a significant broadening of the relaxation spectrum. A nonmonotonous q dependence of the depolarized scattering intensity is predicted. Analyzing the short-time behavior of the dynamic structure factor for $t \ll 1/\Gamma$, we show that it is characterized by two additional characteristic times: $t_\perp \propto q^{-4}$ and $t_\parallel \propto q^{-8}$ reflecting the transverse and the longitudinal dynamics of polymer chains. The longitudinal motions (along the chain contour) increase the initial relaxation rate of the structure factor by a factor of 2. The longitudinal contribution to the dynamic structure factor is significant even for $t \gg t_\parallel$.

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I. INTRODUCTION

Rigid macromolecules[1] consist of stiff, nearly rodlike fragments. They constitute an extensive class of materials including fibrillar polymers, alpha-helical polypeptides, aromatic polyamides, etc. Many biological polymers are either rigid (double-strand DNA, actin) or are able to form rigid filament self-assembling structures like peptide fibrils and fibers [1] or wormlike surfactant micelles [2]. Rigid macromolecules tend to form liquid-crystalline structures in solution [3] showing remarkable mechanical and optical properties.

Dynamics of semirigid macromolecules have recently attracted much attention, both experimental and theoretical [4,5,8–13]. If the solution is dilute enough or if the length scale of interest is short enough, then the interactions between macromolecules can be neglected, so it is enough to consider a single isolated macromolecule. It is this regime that we focus on in the present paper studying relaxations of short-scale concentration fluctuations in solutions of wormlike semirigid macromolecules. These relaxations define, in particular, the dynamic structure factor $S(q,t)$ analyzed in the paper.

The aim is twofold. First, we consider $S(q,t)$ for classical semirigid macromolecules characterized by single persistence length $l/2$. This problem was rather extensively studied theoretically recently [9–13], and a number of important points have been made. In particular, it was shown that long-time behavior of $S(q,t)$ for $q \gg 1/l$ is $S(q,t) \propto \exp(-\text{const}\, q^2 t^{3/4})$ [9,10]. There is no consensus, however, concerning the short-time behavior of $S(q,t)$: while some authors [9] find a linear short-time relaxation and calculate the initial decay rate, others obtain a nonlinear short-time decay [13]. Another issue concerns the relative contributions of transverse and longitudinal macromolecular motions to the structure factor relaxation. While earlier studies [9–11] neglected the longitudinal motions (along the chain contour), a more recent paper [13] shows that these dynamics are important. While this qualitative point is confirmed in the present study, we have to criticize Ref. [13]. In our opinion the approach they take to treat the longitudinal dynamics is not entirely correct. Moreover, Ref. [13] unfortunately suffer from errors (misprints) obscuring certain key equations. These defects affect even the results related to the transverse dynamics, so it would be fair to say that a reliable expression for $S(q,t)$ valid in the whole time range was missing. We try to eliminate this gap.

Second, we consider the dynamic structure factor and dynamic *light* scattering (both polarized and depolarized) of semirigid macromolecules focusing on the generic case when the chain cross section is biaxial. We consider the effects of both the anisotropic dielectric polarizability and the anisotropic bending rigidity of polymer chains (which are therefore characterized by two different persistence lengths [14–16]).

II. RELAXATION OF SHORT-SCALE CONCENTRATION FLUCTUATIONS

Isotropic solutions of semirigid macromolecules are normally rather dilute so that short-scale dynamics of their fragments are nearly unaffected by the presence of surrounding chains.[2] Hence the dilute regime is relevant here, i.e., isolated chains. More specifically, we consider a semirigid macromolecule with Kuhn segment l and effective diameter $d \ll l$. We consider wormlike polymers, i.e., persistence flexibility model due to Kratky and Porod [17] which is realistic for most stiff macromolecules. The model assumes that the tangential unit vector $\underline{n}$ varies continuously along the chain contour, i.e., a continuous function $\underline{n}(s)$, where s is the curvilinear coordinate along the chain contour. The orientation correlation function is

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[1] Often called *semiflexible* to distinguish them from flexible polymers on the one hand and from rodlike molecules on the other hand. However, we tend to use here the word *semirigid* instead.

[2] We use *chain* as a shortcut for *macromolecule*.

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$$\langle \underline{n}(s)\cdot\underline{n}(s')\rangle = e^{-2|s-s'|/l}, \tag{1}$$

where $l/2$ is the persistence length.

Concentration fluctuations in the solution may be characterized by the structure factor (the scattering function)

$$S(q,t) = \frac{1}{L}\int_0^L ds'\,ds''\langle e^{i\underline{q}\cdot(\underline{r}(s',t)-\underline{r}(s'',0))}\rangle, \tag{2}$$

where $\underline{q}$ is the fluctuation wave vector, L is the chain contour length, and $\underline{r}(s,t)$ is the position of the chain contour at time t. We consider short-scale fluctuations assuming that $\lambda = 2\pi/q \ll l$ (also that $L \gg \lambda$). In this regime the static structure factor $S_0(q) \equiv S(q,0)$ is nearly unaffected by the chain flexibility [18]

$$S_0(q) \simeq \int_{-\infty}^{\infty} ds \int \frac{d^2n}{4\pi} e^{isq\cdot n} = \int_{-\infty}^{\infty} \frac{\sin(qs)}{qs} ds = \frac{\pi}{q}. \tag{3}$$

Turning to relaxation of the coherent structure factor we note that it is the dynamics of short (nearly rodlike) chain fragments that are relevant. Hence we may consider a separate short fragment of length $\Lambda \ll l$. Its longitudinal and transverse diffusivities are $D_\parallel = k_BT/\nu_\parallel$ and $D_\perp = k_BT/\nu_\perp$, where k_BT is the thermal energy, and $\nu_\parallel, \nu_\perp$ are the corresponding friction constants. In the logarithmic approximation these constants are [19]

$$\nu_\parallel \simeq \frac{2\pi\eta_s\Lambda}{\ln(\Lambda/d)}, \qquad \nu_\perp \simeq 2\nu_\parallel, \tag{4}$$

where η_s is the solvent viscosity. The fragment, being nearly a straight rod, may bend slightly due to thermal fluctuations. The typical bend angle is $\theta \sim \sqrt{\Lambda/l}$ as implied in Eq. (1). The typical amplitude of transverse fluctuations of the fragment (with fixed position and orientation of one end) is then

$$\xi \sim \Lambda\theta \sim \Lambda^{3/2} l^{-1/2}, \tag{5}$$

i.e.,

$$\Lambda \sim l^{1/3}\xi^{2/3}. \tag{6}$$

When the fragment is incorporated in a long chain, its longitudinal motion is strongly suppressed [12]. However, its transverse motion is not suppressed if the transverse displacement does not exceed ξ. The time of transverse ξ displacement is then $t(\xi) \sim \frac{\xi^2}{D_\perp(\Lambda)}$, where Λ is related to ξ [Eq. (6)], so

$$t(\xi) \sim \tau_0 \frac{(\xi/l)^{8/3}}{\ln\left(\frac{l}{d}(\xi/l)^{2/3}\right)}, \tag{7}$$

where $\tau_0 = \frac{\eta_s l^3}{k_BT}$ is the characteristic relaxation time of a Kuhn segment l, i.e., the disorientation time.

Obviously a displacement on $\xi \sim 1/q$ is just enough for a concentration fluctuation to relax considerably. Hence the characteristic relaxation rate $\Gamma(q) \sim \frac{1}{t(1/q)}$ follows:

$$\Gamma(q) \sim \frac{1}{\tau_0}(ql)^{8/3}\ln\left(\frac{l}{(ql)^{2/3}d}\right). \tag{8}$$

Note that $\Gamma\tau_0 \gg 1$ since $ql \gg 1$. Equation (8) agrees with the results obtained in Refs. [9–11,13]. Note that in the dilute regime considered here the screening length ξ_h defined in Ref. [9] is replaced with

$$\Lambda^* \sim \frac{l}{(ql)^{2/3}}, \tag{9}$$

where the dynamic correlation length Λ^* is the length of a chain fragment that moves cooperatively (in the transverse direction) during the relaxation time $t(1/q)$.

In order to proceed quantitatively we consider an extremely short (hence straight) chain fragment and introduce local Cartesian coordinates (y_1, y_2, x) with x axis parallel to the fragment at $t=0$. The transverse displacement of the fragment is a $2d$ vector, $\underline{\xi} = \underline{y}(t) - \underline{y}(0)$, where $\underline{y} = (y_1, y_2)$, $\underline{\xi} = (\xi_1, \xi_2)$. The variables ξ_1, ξ_2 are both Gaussian and independent. A detailed quantitative analysis (see Appendix A) shows that $\langle \xi_1^2\rangle = \langle \xi_2^2\rangle = K(t)$ for relevant times $t \ll \tau_0$,

$$K(t) \simeq Cl^2\left(\ln\frac{\Lambda^*}{d}\right)^{3/4}\left(\frac{t}{\tau_0}\right)^{3/4}, \tag{10}$$

where $C = \frac{2^{5/4}\Gamma(1/4)}{3\pi(4\pi)^{3/4}} \approx 0.137$, and $\Lambda^* = \Lambda^*(t)$ is defined in Appendix A below Eq. (A8). The logarithmic-factor in Eq. (7) results from the hydrodynamic interactions that renormalize the transverse friction constant [see Eq. (A8)]. As this factor just weakly depends on Λ^*, the latter may be replaced by its typical value defined in Eq. (9) for $t \sim t(1/q)$.

The correlation function $K(t)$ was calculated in Ref. [9]. Equation (10) obviously agrees with the scaling equation (7).

Now we briefly outline the way to calculate the dynamic structure factor for $t \gtrsim 1/\Gamma(q)$. The expression in the exponent in Eq. (2) may be approximated as

$$\underline{q}\cdot(\underline{r}(s',t) - \underline{r}(s'',0)) \simeq q_1\xi_1 + q_2\xi_2 + q_3 s, \tag{11}$$

where $s = s' - s''$, $\xi_j = y_j(s',t) - y_j(s',0)$, $j = 1,2$. Here we take into account that $x(s',t) - x(s'',0) \simeq s$ and that $\tilde{y} \equiv |\underline{y}(s',0) - \underline{y}(s'',0)| \ll \xi$. Both conditions are valid since the relevant ξ and s are $\xi \sim 1/q$ and $s \sim 1/q$ [see the last integral in Eq. (3): the contribution coming from $s \gg 1/q$ is negligible there]. Hence the fragment (s', s'') is nearly straight and $\tilde{y} \sim s^{3/2}l^{-1/2} \sim q^{-3/2}l^{-1/2}$, i.e., $\tilde{y} \ll 1/q$ since $lq \gg 1$. Performing the averaging over the Gaussian ξ_1, ξ_2 we get

$$\langle e^{i\underline{q}\cdot(\underline{r}(s',t)-\underline{r}(s'',0))}\rangle \simeq e^{iq_3 s} e^{-0.5K(t)(q_1^2+q_2^2)}.$$

Hence

$$S(q,t) \simeq \int_{-\infty}^{\infty} ds \int \frac{d^2u}{4\pi} e^{iqsu_3} e^{-0.5K(t)q^2(1-u_3^2)} = \frac{\pi}{q} e^{-0.5K(t)q^2}, \tag{12}$$

where $\underline{u} = \underline{q}/q$ and u_3 is the projection of $\underline{u}$ onto the main chain axis x. The last equation may be written as

$$S(q,t) \simeq S_0(q)e^{-(\Gamma(q)t)^{3/4}}, \quad t \gg t_\perp, \tag{13}$$

where

$$\Gamma(q) \simeq \frac{C'}{\tau_0}(ql)^{8/3}\ln\frac{\Lambda^*}{d}, \tag{14}$$

and $t_\perp$ is defined by the condition $\xi \sim \tilde{y}$ [see Eq. (B1)]. Equations (13) and (14) are in agreement with the scaling result [Eq. (8)], and with the previously obtained results [9,10]. Here $C' = (C/2)^{4/3} = \frac{2^{1/3}}{4\pi}\left(\frac{\Gamma(1/4)}{3\pi}\right)^{4/3} \approx 0.02805$.

The complete time dependence of $S(q,t)$ is more difficult to obtain. The corresponding rather technically involved analysis is outlined in the Appendixes A–C. The main results are summarized below.

(1) Both transverse and longitudinal chain fluctuations contribute to the structure factor decay for $t \ll 1/\Gamma(q)$. The corresponding characteristic time scales are [see Eqs. (B1) and (C22)] $t_\perp \sim \frac{\eta_s}{lq^4}$ for transverse and $t_\parallel \sim \frac{\eta_s}{l^5q^8}$ for longitudinal fluctuations; $t_\perp/t_\parallel \sim (ql)^4 \gg 1$. The time scale $t_\perp$ was obtained in Ref. [9]; the second time $t_\parallel$ was identified more recently [13]; both time scales also follow from the scaling analysis given in Ref. [12]. Note, however, that the time behavior of the (coherent) dynamic structure factor for $t \lesssim t_\perp$ summarized below is different from the earlier predictions [9,13].

(2) We obtained analytical expressions defining the whole time dependence of $S(q,t)$ for $ql \gg 1$ [see Eq. (C24)] as follows:

$$S(q,t) \simeq S_0(q)\exp(-F_\perp(q,t) - F_\parallel(q,t)),$$

where $F_\perp(q,t)$ and $F_\parallel(q,t)$ are due to transverse and longitudinal macromolecular motions, respectively,

$$F_\perp(q,t) = \frac{2}{\pi lq}I(t/t_\perp), \quad F_\parallel(q,t) = \frac{q^3t}{3\pi\zeta_\parallel}\theta(t/t_\parallel). \tag{15}$$

The functions $I(\cdot)$ and $\theta(\cdot)$ are defined in Eqs. (B8) and (C23), and

$$t_\perp \simeq \frac{2\zeta_\perp(\Lambda^*)}{lq^4}, \quad t_\parallel \simeq \frac{4\zeta_\parallel^4}{\zeta_\perp(\Lambda_\perp)^3 l^5 q^8},$$

$$\zeta_\perp(\Lambda) = \frac{4\pi\eta_s}{k_BT\ln(\Lambda/d)}, \quad \zeta_\parallel = \frac{2\pi\eta_s}{k_BT\ln(q^{-1}/d)}. \tag{16}$$

Here $\zeta_\perp$ and $\zeta_\parallel$ are the effective friction constants per unit length for transverse and longitudinal fluctuations, respectively [see Eqs. (A8) and (C8)], and

$$\Lambda_\perp \sim \left(\frac{lt}{\zeta_\perp}\right)^{1/4}, \quad \Lambda^* \sim \begin{cases} 1/q, & t \lesssim t_\perp \\ \Lambda_\perp, & t \gtrsim t_\perp. \end{cases}$$

Note that both $t_\perp$ and $t_\parallel$ are slightly (logarithmically) time dependent as the length scales Λ^*, $\Lambda_\perp$ involved in the definition of $\zeta_\perp$ are not constant.

(3) For $t \ll t_\perp$ the ratio of the two contributions to the structure factor variation (longitudinal and transverse) is a universal function of $t/t_\parallel$ as follows:

$$\frac{F_\parallel(q,t)}{F_\perp(q,t)} \simeq \theta(t/t_\parallel). \tag{17}$$

In particular,

$$\frac{F_\parallel(q,t)}{F_\perp(q,t)} \sim \frac{\zeta_\parallel^{1/4}}{l^{5/4}}q^{-2}t^{-1/4} \quad \text{for } t_\parallel \ll t \ll t_\perp. \tag{18}$$

Note that time dependence of $\frac{F_\parallel(q,t)}{F_\perp(q,t)}$ is very weak (see Fig. 2).

(4) Both types of fluctuations (transverse and longitudinal) contribute nearly equally to the initial decay rate $\gamma(q) = -\frac{\partial \ln S(q,t)}{\partial t}\Big|_{t=0}$,

$$\gamma(q) \simeq \frac{4}{3\pi\zeta_\perp}q^3 \simeq \frac{1}{3\pi^2}\frac{k_BT}{\eta_s}q^3\ln\left(\frac{1}{qd}\right). \tag{19}$$

The predicted initial slope is therefore twice higher than that predicted in Ref. [9] where the effect of longitudinal fluctuations was not taken into account.

It is remarkable that Eq. (19) can also be obtained in an entirely different way, using the general expression for the initial decay rate [19] as follows:

$$\gamma(q) \simeq \frac{k_BT}{S_0(q)}\int\frac{d^3q}{(2\pi)^3}S_0(q')\underline{\underline{H}}(\underline{q}'+\underline{q}):\underline{q}\underline{q}, \tag{20}$$

where $H_{\alpha\beta}(q) = \frac{\delta_{\alpha\beta}-q_\alpha q_\beta}{\eta_s q^2}$ is the Oseen tensor and α,β refer to Cartesian coordinates (we neglect the hydrodynamic screening due to surrounding chains). Equation (20) can be simplified as

$$\gamma(q) = \frac{k_BTq^2}{2\eta_s S_0(q)}\int_d^\infty rg(r)\mathcal{H}(qr)dr, \tag{21}$$

where $g(r) = \int S_0(q)e^{i\underline{q}\cdot\underline{r}}\frac{d^3q}{(2\pi)^3}$ is the real-space correlation function defining the distribution of units around an arbitrary unit fixed at the origin, and

$$\mathcal{H}(x) = \left(1 - \frac{d^2}{dx^2}\right)\frac{\sin x}{x} = \frac{2\sin x}{x}\left(1 - \frac{1}{x^2}\right) + \frac{2\cos x}{x^2}.$$

Note that $\mathcal{H}(x)$ provides an effective long-range cutoff at $r \sim 1/q$ in the integral, Eq. (21). The short-range (ultraviolet) cutoff is set at the chain thickness d (the Oseen tensor is not applicable for $r \lesssim d$: the hydrodynamic interactions at these length scales are defined by the local chain structure). For semiflexible chains

$$g(r) \simeq \frac{2}{4\pi r^2}, \quad r \ll l.$$

Using this $g(r)$ in Eq. (21) we recover Eq. (19) within the logarithmic approximation.

(5) A more precise expression for the initial slope including a constant C along with the logarithmic factor reads

$$\gamma(q) \simeq \frac{1}{3\pi^2}\frac{k_BT}{\eta_s}q^3\left[C + \ln\left(\frac{1}{qd}\right)\right]. \tag{22}$$

The constant C can be calculated using continuous fluid dynamics assuming, say, that the macromolecule is locally a

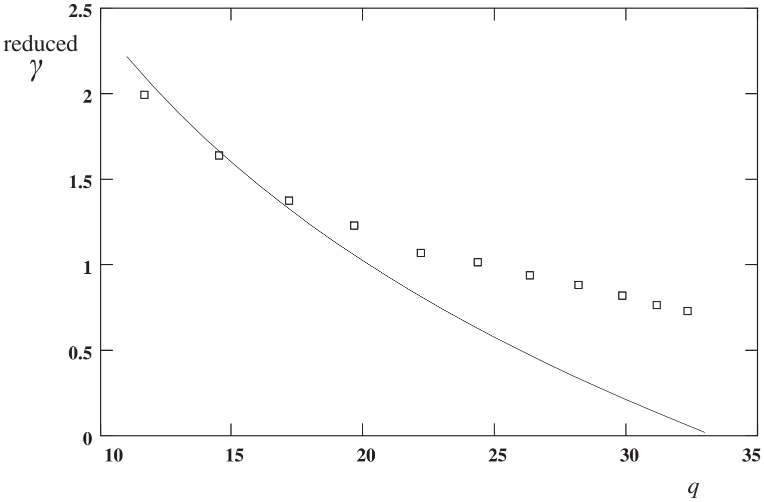

FIG. 1. The dependence of the reduced initial slope, $\gamma(q)6\pi^2\eta_s/(k_BTq^3)$, on the scattering wave vector q (in $1/\mu$m) for P_{11}-4 fibrils at 0.63 mM. Empty squares: experimental data [5]; solid line: Eq. (22) with $C=0$ and $d=30$ nm.

cylinder of well-defined diameter d. However, it is not obvious if the classical hydrodynamics is applicable down to the scales $\sim d$. The crucial point is that C depends on the boundary conditions at the cylinder surface. Typically, $d\sim 10$ nm (see, e.g., Ref. [5]). It is not clear if the fluid slip at the solid surface can be neglected for lateral length scales ~ 10 nm [6,7]. We therefore tend to treat C as an unknown constant. (Note that an analogous constant$=5/6$ in Eq. (3.4) of Ref. [9] was not precisely calculated but rather estimated there: $5/6$ can be replaced by anything ~ 1 in this equation.)

Equation (22) is compared in Fig. 1 with experimental data for peptide fibrils in water [5]. The unknown constant C in Eq. (22) is set to $C=0$; the fibril thickness is $d=30$ nm. A reasonable agreement can be observed at low q. At higher q the experimental γ is higher than the predicted. This is natural for 2 reasons: (1) the theory is not applicable for high q since the condition $qd \ll 1$ is violated there; (2) the time $t_\parallel$ strongly decreases with q and may well become shorter than the experimental resolution at high q.

III. MACROMOLECULES WITH ANISOTROPIC CROSS SECTION AND RIGIDITY

So far we assumed that macromolecules are filaments with isotropic circular cross section. We are now in a position to consider a more general case when the cross section is anisotropic, e.g., rectangular. The relevant examples are ribbonlike polymers, self-assembling tapelike structures, and fibrils [14–16,20,21]. The obvious consequence of the cross-section anisotropy is a difference between elastic energies for bending along shorter and longer sides of the cross section (sides 1 and 2), leading to two different persistence lengths $l_{p2}>l_{p1}$. The corresponding transverse displacements are also different [compare with Eq. (10)] as follows:

$$\langle \xi_j^2\rangle = K_j(t) \simeq C\left(\frac{k_BT}{\eta_s}\ln\frac{\Lambda_j^*}{d}\right)^{3/4}(2l_{pj})^{-1/4}t^{3/4}, \quad j=1,2, \tag{23}$$

where $\Lambda_j^* \sim l_{pj}^{1/3}q^{-2/3}$ [see Eq. (9)]. The generalization of Eq. (12) valid for $t \gg t_\perp$ then reads

$$S(q,t) \simeq \int_{-\infty}^{\infty} ds \int \frac{d^2u}{4\pi} e^{iqsu_3} e^{-1/2q^2[K_1(t)u_1^2+K_2(t)u_2^2]}.$$

Evaluating the integrals

$$S(q,t) \simeq S_0(q)\exp\left(-\frac{1}{4}q^2[K_1(t)+K_2(t)]\right)I_0\left(\frac{1}{4}q^2[K_1(t) - K_2(t)]\right), \tag{24}$$

where I_0 is a Bessel function. If the anisotropy is strong, $l_{p2} \gg l_{p1}$, then $K_1 \gg K_2$ and the relaxation spectrum is wide covering the range between Γ_1 and $\Gamma_2 \ll \Gamma_1$, where the characteristic relaxation rates are [see Eq. (14)]

$$\Gamma_j \simeq C'\frac{k_BT}{\eta_s}(2l_{pj})^{-1/3}q^{8/3}\ln\frac{\Lambda_j^*}{d}, \quad j=1,2.$$

Then $S(q,t)$ shows the following asymptotic behavior:

$$S(q,t) \propto \frac{1}{t^{3/8}}\exp[-(\Gamma_2 t)^{3/4}], \quad t>1/\Gamma_1, \tag{25}$$

i.e., $S(q,t)$ follows a power-law decay ($t^{-3/8}$) for $1/\Gamma_1 < t < 1/\Gamma_2$ and a stretched exponential decay ($\ln S \propto -t^{3/4}$) with the slower rate Γ_2 for $t>1/\Gamma_2$.

The theory may be applied to analyze the dynamic light scattering data.[3] The polarized (VV) dynamic light scattering intensity is related to the time correlation function of the VV component of dielectric polarizability (we omit the constant prefactor for simplicity) as follows:

$$I_{VV}(q,t) = \langle \varkappa_{VV}(\underline{q},0)\varkappa_{VV}(-\underline{q},t)\rangle_c, \tag{26}$$

where $\underline{q}$ is the scattering vector, $\kappa_{\alpha\beta}$ is the dielectric polarizability tensor (α,β refer to components in a fixed Cartesian frame), and "V" stands for vertical direction.

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[3] Provided that l is longer than the wavelength of light which is not unrealistic [4,5].

$$\varkappa_{\alpha\beta}(\underline{q},t) = \sum_{chains}\int_0^L ds\,\gamma_{\alpha\beta}(s)e^{i\underline{q}\cdot\underline{r}(s,t)}, \tag{27}$$

where the summation involves all chains in the system, and $\gamma_{\alpha\beta}(s)$ is the excess polarizability tensor per unit chain length (by "excess" we mean "in contrast to the isotropic solvent").

$$\gamma_{\alpha\beta} = \gamma_1 n_{1\alpha}n_{1\beta} + \gamma_2 n_{2\alpha}n_{2\beta} + \gamma_3 n_\alpha n_\beta,$$

where γ_3, γ_1, and γ_2 are the excess polarizabilities along the main chain direction $\underline{n}$, along the shorter side of the chain cross section (unit vector $\underline{n}_1$), and along its longer side ($\underline{n}_2$), respectively. In the general case $\gamma_1 \neq \gamma_2$, hence there are three contributions to $\gamma_{\alpha\beta}$,

$$\gamma_{\alpha\beta} = \gamma_0\delta_{\alpha\beta} + \gamma' n_\alpha n_\beta + \gamma''(n_{2\alpha}n_{2\beta} - n_{1\alpha}n_{1\beta}), \tag{28}$$

where $\gamma_0=(\gamma_1+\gamma_2)/2$, $\gamma'=\gamma_3-(\gamma_1+\gamma_2)/2$, $\gamma''=(\gamma_2-\gamma_1)/2$. Here the first term is isotropic, the second term is uniaxial, and the third term is affected by the chain rotation around its main axis.

On substitution of Eq. (27) in Eq. (26) we get

$$I_{VV} = \frac{c_L}{L}\int \langle \gamma_{VV}(s',t)\gamma_{VV}(s'',0)e^{i\underline{q}\cdot[\underline{r}(s',t)-\underline{r}(s'',0)]}\rangle ds'ds'', \tag{29}$$

where c_L is the average "length" concentration (total length of all macromolecules per unit volume). Using Eq. (11) and neglecting the difference between $\gamma_{VV}(s',0)$ and $\gamma_{VV}(s'',0)$ as the typical $|s'-s''|$ is small as explained just after Eq. (11), we obtain

$$I_{VV} \simeq c_L\int_{-\infty}^{\infty}\langle \gamma_{VV}(t)\gamma_{VV}(0)e^{i(q_3 s+q_1\xi_1+q_2\xi_2)}\rangle ds, \tag{30}$$

where $\gamma_{VV}(t)\gamma_{VV}(0) \equiv \gamma_{VV}(s',t)\gamma_{VV}(s',0)$. Next we note that $\gamma_{\alpha\beta}$ depends only on the orientation of the fragment, hence its time dependence is slow: $\gamma_{VV}(t) \simeq \gamma_{VV}(0)$ since the time scale of interest $[1/\Gamma(q)]$ is much shorter than the disorientation time τ_0. Integrating over s in Eq. (30) we get

$$I_{VV} \simeq 2\pi c_L\langle(\gamma_{VV}(0))^2\delta(q_3)e^{iq_1\xi_1+iq_2\xi_2}\rangle. \tag{31}$$

It is convenient to specify a fixed Cartesian frame with the z axis vertical and the y axis parallel to the scattering vector $\underline{q}$. Then $q_3 \equiv \underline{q}\cdot\underline{n} = qn_y$ and $\delta(q_3)=\frac{1}{q}\delta(n_y)$, hence $\underline{n}$ must be parallel to the xz plane. Let θ be the angle between $\underline{n}$ and vertical z axis, and φ, the angle between $\underline{n}_1$ and the y axis, so that $q_1=q\cos\varphi$, $q_2=q\sin\varphi$. By virtue of Eq. (28) we get

$$\gamma_{VV} = \gamma_0 + \gamma'\cos^2\theta + \gamma''\sin^2\theta\cos 2\varphi. \tag{32}$$

Performing the averaging in Eq. (31) we get [using also Eqs. (23)]

$$I_{VV} \simeq \frac{c_L}{4\pi q}\int_0^{2\pi}d\theta\int_0^{2\pi}d\varphi\,\gamma_{VV}^2\exp\left[-\frac{q^2}{2}[\cos^2\varphi K_1(t) + \sin^2\varphi K_2(t)]\right]. \tag{33}$$

Using Eq. (32) we finally obtain

$$I_{VV}(q,t) \simeq \frac{\pi}{q}c_L\exp\left[-\frac{q^2}{4}[K_1(t)+K_2(t)]\right]G\left(\frac{q^2}{4}[K_1(t) - K_2(t)]\right),$$

$$G(\alpha) \equiv \left(\gamma_0^2 + \gamma_0\gamma' + \frac{3}{8}\gamma'^2\right)I_0(\alpha) + \left(\frac{1}{2}\gamma_0 + \frac{1}{8}\gamma'\right)\gamma'' I_1(\alpha) + \frac{3}{8}\gamma''^2 I_1'(\alpha), \tag{34}$$

where $I_1'(\alpha) \equiv \frac{d}{d\alpha}I_1(\alpha)$. So I_{VV} is proportional to the dynamic structure factor $S(q,t)$, [Eq. (24)], only if $\gamma''=0$, i.e., if the dielectric polarizability is uniaxial. Otherwise the time behavior of the scattering intensity is more complicated although not dramatically different from $S(q,t)$. The spectrum of relaxation times is concentrated in the range between $1/\Gamma_1(q)$ and $1/\Gamma_2(q)$. The spectrum is wide if elastic anisotropy of filaments is strong, i.e., if $l_{p2} \gg l_{p1}$.

Let us now turn to the *depolarized* light scattering. The depolarized intensity is related to the *VH* component of the dielectric polarizability of the medium as follows:

$$I_{VH} = \langle\varkappa_{VH}(\underline{q},0)\varkappa_{VH}(-\underline{q},t)\rangle_c,$$

where "*H*" stands for the horizontal direction perpendicular to the wave vector of the scattered light. The standard scattering geometry implies that the angle between $\underline{H}$ and $\underline{q}$ is $\theta_s/2$, where θ_s is the scattering angle ($q=2q_0\sin\frac{\theta_s}{2}$, where q_0 is the wave vector of the incident beam). Hence, recalling that the z axis is vertical and the y axis is parallel to $\underline{q}$,

$$\underline{H} = \left(\sin\frac{\theta_s}{2},\cos\frac{\theta_s}{2},0\right), \quad \underline{V} = (0,0,1).$$

Using the angles θ and φ defined after Eq. (31) we get [compare with Eq. (32)]

$$\gamma_{VH} = \sin\theta\left\{\gamma'\cos\theta\sin\frac{\theta_s}{2} + \gamma''\left(\sin 2\varphi\cos\frac{\theta_s}{2} - \cos\theta\cos 2\varphi\sin\frac{\theta_s}{2}\right)\right\}.$$

The *VH* correlation function can be written in analogy with Eq. (33) as

$$I_{VH} \simeq \frac{c_L}{4\pi q}\int_0^{2\pi}d\theta\int_0^{2\pi}d\varphi\,\gamma_{VH}^2\exp\left[-\frac{q^2}{2}[\cos^2\varphi K_1(t) + \sin^2\varphi K_2(t)]\right]. \tag{35}$$

Evaluating the integrals we get

$$I_{VH}(q,t) \simeq c_L\frac{\pi}{q}\exp\left[-\frac{q^2}{4}[K_1(t)+K_2(t)]\right]\left[G_1(\alpha) + \left(\sin\frac{\theta_s}{2}\right)^2 G_2(\alpha)\right], \tag{36}$$

where

$$\alpha \equiv \frac{q^2}{4}[K_1(t) - K_2(t)],$$

$$G_1(\alpha) \equiv \frac{1}{2}\gamma''^2[I_0(\alpha) - I_1'(\alpha)] = \frac{1}{2}\gamma''^2\frac{1}{\alpha}I_1(\alpha),$$

$$G_2(\alpha) \equiv \frac{1}{8}[(\gamma'^2 - 4\gamma''^2)I_0(\alpha) + 2\gamma'\gamma'' I_1(\alpha) + 5\gamma''^2 I_1'(\alpha)].$$

Note that I_{VH} does not depend on the isotropic polarizability γ_0 as it should be. Like I_{VV}, the depolarized scattering function is characterized by a broad spectrum of relaxation times if $l_{p2} \gg l_{p1}$.

We are now in a position to discuss the main results of this section, the *VV* and *VH* scattering functions defined in Eqs. (34) and (36). Let us first consider dielectrically axisymmetric molecules: $\gamma''=0$. In this case both polarized and depolarized scattering functions are proportional to the dynamic structure factor $S(q,t)$ [Eq. (24)] as follows:

$$I_{VV}(q,t) \simeq c_L\left(\gamma_0^2 + \gamma_0\gamma' + \frac{3}{8}\gamma'^2\right)S(q,t),$$

$$I_{VH}(q,t) \simeq c_L\frac{\gamma'^2}{8}\sin^2\frac{\theta_s}{2}S(q,t). \qquad (37)$$

Hence the relaxation spectrum $\rho(\Gamma)$ is the same for both scattering geometries;

$$S(q,t) = \int \rho(\Gamma)e^{-\Gamma t}\frac{d\Gamma}{\Gamma}.$$

Equation (25) implies that $\rho(\Gamma) \propto \Gamma^{3/8}$ for $\Gamma_2(q) \lesssim \Gamma \lesssim \Gamma_1(q)$.

However, the wave-vector dependencies of the static intensities are different as follows:

$$I_{VV}(q,0) \propto \frac{1}{q}, \quad I_{VH}(q,0) \propto q$$

(recall that all these results are valid if $ql \gg 1$). The depolarization degree $\Delta = \frac{I_{VH}(q,t)}{I_{VV}(q,t)}$ depends on the scattering angle θ_s, but it does not depend on t.

$$\Delta \simeq \frac{\gamma'^2}{8\gamma_0^2 + 8\gamma_0\gamma' + 3\gamma'^2}\sin^2\frac{\theta_s}{2}. \qquad (38)$$

Thus $\Delta \propto q^2$ since $q \propto \sin\frac{\theta_s}{2}$. The depolarization degree is obviously bounded: $0 \leqslant \Delta \leqslant 1$ ($\Delta=1$ only for $\theta_s=\pi$ and $\gamma'=-2\gamma_0$).

Let us now consider the general case $\gamma'' \neq 0$, i.e., the biaxial dielectric polarizability tensor of chain fragments. Then the static intensities are

$$I_{VV}(q,0) \propto \frac{1}{q}, \quad I_{VH}(q,0) \propto \frac{q}{q_m} + A\frac{q_m}{q}, \qquad (39)$$

where $q_m=2q_0$ is the maximum scattering vector and $A = \frac{2}{(\gamma'/\gamma'')^2 - 1.5}$. The experimental dependence $I_{VH}(q)$ shown in Fig. 7 in Ref. [4] is in qualitative agreement with the second Eq. (39) with $A \sim 1$.

The static depolarization degree is

$$\Delta = \frac{I_{VH}(q,0)}{I_{VV}(q,0)} \simeq C_1 + C_2\sin^2\frac{\theta_s}{2},$$

where

$$C_1 = \frac{4\gamma''^2}{4(2\gamma_0 + \gamma')^2 + 2\gamma'^2 + 3\gamma''^2},$$

$$C_2 = \frac{2\gamma'^2 - 3\gamma''^2}{4(2\gamma_0 + \gamma')^2 + 2\gamma'^2 + 3\gamma''^2}.$$

Hence Δ may either increase (if $|\gamma''| < \sqrt{2/3}|\gamma'|$) or decrease (if $|\gamma''| > \sqrt{2/3}|\gamma'|$) with θ_s. The depolarized scattering function can be written as $I_{VH}(q,t) = \frac{1}{q}A_1(tq^{8/3}) + qA_2(tq^{8/3})$. The relaxation spectra (ρ_1 and ρ_2) of the two relaxation functions (A_1 and A_2) are different.

$$\rho_1(\Gamma) \propto \Gamma^{9/8}, \quad \rho_2(\Gamma) \propto \Gamma^{3/8}, \quad \Gamma_2(q) \lesssim \Gamma \lesssim \Gamma_1(q).$$

Hence the fast mode (Γ_1) contribution in the depolarized scattering function is more pronounced for smaller q's (as q decreases the relaxation spectrum of I_{VH} tends to $\rho_1(\Gamma)$, i.e., the slow mode is suppressed). The slow mode (Γ_2) contribution is enhanced at high q. Note that we disregard fast processes with relaxation times $\sim t_\perp$, $t_\parallel$ in this section, i.e., the theory is restricted to $t \gg t_\perp$.

IV. TWIST MODE

Let us consider the most important conjecture that was not stated explicitly yet. So far we totally neglected a rotation of the macromolecule around its main axis. Of course we mean rotation of chain fragments rather than of the whole chain, i.e., a twist motion. At first sight it seems that the twist dynamics is fast. In fact, let $\varphi=\varphi(s)$ be the angle of an extra rotation of the chain cross section at the position s with respect to its equilibrium orientation. The corresponding twist energy is

$$F_{twist} = \frac{k_{twist}}{2}\int\left(\frac{d\varphi}{ds}\right)^2 ds.$$

The twist angle of a fragment $(s', s'+s)$ of length s is $\varphi = \varphi(s'+s) - \varphi(s')$; its mean-square value is then $\langle\varphi^2\rangle = s/l_{p3}$, where $l_{p3} = k_{twist}/k_BT$ is the third (twist) persistence length. The typical twist angle is then $\varphi \sim \sqrt{s/l_{p3}}$. The angle φ may also be treated as the typical angle of rotation of the fragment with fixed ends (which are not allowed to rotate) around its main axis. The corresponding rotation diffusion constant is

$$D_{rot} \sim \frac{k_BT}{\pi\eta_s s d^2}$$

(the right-hand side is the exact result for a circular cylinder). The rotation time is

$$t \sim \varphi^2/D_{rot} \sim \eta_s d^2 \varphi^4 l_{p3}/(k_B T), \tag{40}$$

where we used the relation $s \sim \varphi^2 l_{p3}$. Equation (40) implies that the typical angle of twist rotation during time t is $\varphi(t) \sim \left(\frac{k_B T t}{\eta_s d^2 l_{p3}}\right)^{1/4}$.[4]

Let us assume that all persistence lengths are comparable: $l/2 = l_{p1} \sim l_{p2} \sim l_{p3}$. For the typical scattering relaxation time $t \sim 1/\Gamma(q)$, where $\Gamma(q)$ is defined in Eq. (14), we get

$$\varphi \sim (q d^{3/4} l^{1/4})^{-2/3},$$

i.e., a large angle of rotation $\varphi > 1$, if $1/q > d^{3/4} l^{1/4}$ which is likely to be the case (this regime is compatible with the condition $q \gg 1/l$). Hence the twist mode is fast: its relaxation time is defined in Eq. (40) with $\varphi \sim 1$,

$$t_{twist} \sim \frac{\eta_s}{k_B T} l_{p3} d^2 \sim \tau_0 \left(\frac{d}{l}\right)^2. \tag{41}$$

Note that the twist mode contributes to dynamic light scattering if $\gamma'' \neq 0$.

Now we arrive at the central point of the discussion. We claim that the simple description of the twist mode presented above is *not* valid if the chain rigidity is anisotropic, i.e., if $l_{p1} \neq l_{p2}$. The twist mode is much slower in this case: its characteristic time is of the order of τ_0 (Kuhn segment disorientation time). In fact, Eqs. (40) and (41) are perfectly valid if the chain trajectory is a straight line. However, it is typically not a straight line due to thermal fluctuations. Let us assume first that $t_{twist} \ll \tau_0$, so that during the twist relaxation the orientation and trajectory of a fragment of length l are roughly fixed. In this case the twist and bend energies are coupled: if a chain fragment was originally bent in the easy direction (involving l_{p1} elasticity), then after a rotation on $\varphi = \pi/2$ it will be bent in the hard direction (l_{p2}), hence a higher bending energy by a factor l_{p2}/l_{p1}. The above statement is true provided that the fragment does not have enough time to bend in a different direction, i.e., if its conformation relaxation time t_{conf} is longer than t_{twist}. The energy increase per fragment is then of the order $\epsilon_1 = k_B T \frac{l_{p2} - l_{p1}}{l_{p1}} \sim k_B T$ since its typical elastic energy is $\sim k_B T$ [here we assume that $(l_{p2} - l_{p1})/l_{p1} \sim 1$]. Now the conformation relaxation time of a fragment of length Λ is defined in Eqs. (6) and (7),

$$t_{conf} \sim \tau_0 \left(\frac{\Lambda}{l}\right)^4,$$

where we have omitted the logarithmic factor. The condition $t_{conf} \sim t_{twist}$ implies then that $\Lambda \sim l \left(\frac{t_{twist}}{\tau_0}\right)^{1/4}$. A $\varphi = \pi/2$ rotation is a cooperative process necessarily involving a whole persistence segment of length $l_{p3} \sim l$. The number of unrelaxed fragments per l_{p3} is $n \sim l/\Lambda$, hence the typical free energy increase on $\pi/2$ rotation is

$$\Delta F \sim n \epsilon_1 \sim \left(\frac{\tau_0}{t_{twist}}\right)^{1/4} k_B T.$$

Obviously the rotation is allowed only if $\Delta F \lesssim k_B T$, i.e., if $t_{twist} \gtrsim \tau_0$. As the rotation time cannot be much longer than τ_0, we conclude that $t_{twist} \sim \tau_0$. Hence the twist relaxation may be neglected for scattering with $q \gg 1/l$ as the relevant relaxation time is much shorter than τ_0: $1/\Gamma(q) \ll \tau_0$ [see Eq. (14)].

To resume, we showed that orientational relaxation does not contribute to the scattering of semirigid chains (for $ql \gg 1$) if their bending rigidity is anisotropic. The only situation when a rotation around the main chain axis (the twist mode) may be observed by light scattering is when the chain bending rigidity is (nearly) isotropic, but its dielectric polarizability is anisotropic in the plane perpendicular to the main axis. In this very special situation a twist relaxation mode with the q-independent rate defined in Eq. (41) is predicted.

V. DISCUSSION AND CONCLUSIONS

We calculated both the polarized (VV) and depolarized (VH) scattering functions for dilute solutions of semirigid macromolecules whose persistence length is longer than $1/q$, where q is the scattering vector.

(1) In all the cases the *terminal* relaxation rate Γ is proportional to $q^{8/3}$ (apart from a logarithmic correction), i.e., it shows a stronger than diffusive ($\Gamma \propto q^2$) q dependence. In the case of macromolecules with isotropic rigidity the relaxation is stretched exponentially: both VV and VH scattering functions are proportional to $S(q,t) \propto \exp(-\text{const}\, q^2 t^{3/4})$ [see Eq. (37)] in agreement with the earlier results for the dynamic structure factor [9,10].

(2) For dielectrically axisymmetric macromolecules the depolarization degree $\Delta = \frac{I_{VH}}{I_{VV}}$ is a linear increasing function of q^2, and it does not depend on time [see Eq. (38)]. Δ may take any value between 0 and 1 depending on dielectric anisotropy of chains and on the polymer/solvent dielectric contrast.

(3) For macromolecules with a dielectrically anisotropic cross section, the degree Δ may either decrease or increase with q depending on the degree of dielectric biaxiality γ''/γ'; Δ is bound between 0 and 4/3. The depolarized intensity I_{VH} is decreasing with q in the small q regime; I_{VH} increases for larger q if $|\gamma''/\gamma'| < \sqrt{2/3}$ [see Eq. (39)]. This behavior is in agreement with experimental data [4].

(4) The theory was also generalized to account for anisotropic rigidity of macromolecules characterized by two persistence lengths l_{p1} and l_{p2}. A broad relaxation spectrum with relaxation rates between $\Gamma_1(q)$ and $\Gamma_2(q)$ is predicted if the anisotropy is strong: $l_{p2} \gg l_{p1}$; $\Gamma_1/\Gamma_2 = (l_{p2}/l_{p1})^{1/3}$. The fast mode contribution to the depolarized intensity increases at low q; the slow VH mode is more pronounced at high q.

These results are hinged on the prediction that macromolecular rotation around its main chain axis is significantly hindered if $l_{p1} \neq l_{p2}$ (see Sec. IV). This prediction is valid if macromolecules do not show an intrinsic helical structure, or if their helical pitch P is much longer than $1/q$. More pre-

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[4] $\varphi \propto t^{1/4}$ shows the same time dependence as the typical short-scale displacement of a monomer in a Rouse chain [22].

cisely, the rotation of twisted chains is hindered for time scales $t \lesssim \tau(P)$, where $\tau(P)$ is defined in Eq. (7) with $\xi = \xi(P) \sim P^{3/2} l^{-1/2}$ [see Eq. (5) where Λ is replaced by P]. Consequently, the predicted effects of anisotropic elasticity (in particular, that of two distinct relaxation modes) are valid if $\tau(P) \gtrsim 1/\Gamma(q)$, which is equivalent to $\xi(P) \gtrsim 1/q$, i.e., $P \gtrsim \frac{l^{1/3}}{q^{2/3}}$. The predicted slowdown of the chain rotation (of the twist motion = "spinning" chain motion) is distinct from, but is reminiscent of the torsional drag enhancement effect in free DNA [24]. The difference is that in the DNA case the slowdown effect is due to *intrinsic* (natural) chain bends (caused by the heterogeneity of the DNA primary structure) [24], while in the present paper the effect is due to *anisotropic* thermal bends.

(5) For the special case when the rigidity is isotropic, but the dielectric polarizability tensor is biaxial, we predict an additional *twist mode* relevant for the depolarized scattering. The twist mode is fast; its relaxation rate is q independent and is inversely proportional to l_{p3}, the twist persistence length [see Eq. (41)].

(6) Turning to the short-time behavior of the dynamic structure factor $S(q,t)$ for $t \ll 1/\Gamma$, we elucidate the importance of both transverse and longitudinal fluctuations (along the main chain axis). Thus $S(q,t)$ is characterized by two "short" characteristic times: $t_\perp \simeq \frac{2\zeta_\perp}{lq^4}$ and $t_\parallel \simeq \frac{\zeta_\perp}{4l^5 q^8}$ [the friction constant $\zeta_\perp$ is defined in Eq. (A8)]. We found that

$$\frac{\partial \ln S(q,t)}{\partial t} \simeq \begin{cases} -\dfrac{2q^3}{3\pi\zeta_\perp}, & t_\parallel \ll t \ll t_\perp \\ -\dfrac{4q^3}{3\pi\zeta_\perp}, & t \ll t_\parallel . \end{cases}$$

The predicted initial decay rate $\gamma(q) = -\frac{\partial \ln S(q,t)}{\partial t}\big|_{t=0}$ is $\gamma(q) \simeq \frac{1}{3\pi^2}\frac{k_B T}{\eta_s} q^3 \ln\left(\frac{1}{qd}\right)$ [see Eq. (19)]; it is in agreement with experimental findings [5]. The obtained theoretical $\gamma(q)$ differs from the results of Refs. [9,13]. The difference with Ref. [9] is roughly by a factor of 2: $\gamma(q)$ was underestimated in Ref. [9] as they assumed that longitudinal fluctuations are totally suppressed for semirigid polymers which is not the case, in particular, at short times [12].

(7) The disagreement with the results of Ref. [13] invites a longer comment. It was found [13] that $-\frac{\partial \ln S(q,t)}{\partial t}$ changes logarithmically with t at short times, so the initial rate just does not exist. Noting that this result contradicts the well-known general expression for the initial decay rate derived, for example, in the textbook by Doi and Edwards [19], the authors of Ref. [13] claim that this general expression is not applicable to semiflexible polymers. They write concerning the general derivation: "The key step in the proof is a (functional) integration by parts of a correlation function. This requires the vanishing of this correlation function at the ultraviolet cutoff ($q \to \infty$)." This argument does not convince us. The relevant integration by parts in Ref. [19] is performed in real space, where no short-ranged singularities are involved (the wave vector q is not relevant for this integration). Moreover, the general expression for the initial rate [Eq. (4.100) in Ref. [19] which is equivalent to Eq. (20)] can be alternatively derived using the fluctuation-dissipation theorem [23] (which is general and can be applied also to semiflexible polymers). The alternative derivation of Eq. (20) is direct and it does not involve any integration by parts. Thus, the general equation (20) must be valid even for semiflexible polymers.

It is remarkable that our result for $\gamma(q)$ [Eq. (19)], agrees with the general expression for the initial rate (see the end of Sec. II). Note also that the difference between this result and the short-time behavior of the coherent dynamic structure factor obtained in Ref. [13] is not likely to be due to any ultraviolet (short-range) cutoff. The relevant short length scale is obviously the chain thickness d (denoted as a in the previous work); this cutoff is used both in the present paper and in Ref. [13] [see Eq. (54) there]. The difference has to do with the *long-range* cutoff which is $\sim 1/q$ as shown in the present paper (and in Ref. [9]). This long-range cutoff was mistakenly set to $l_\perp(t)$ (for transverse dynamics) and $l_\parallel(t)$ (for longitudinal dynamics) in Ref. [13]. Interestingly, the long-range cutoff is automatically accounted for in Eq. (21) which is equivalent to the general Eq. (20): the cutoff at $r \sim 1/q$ is provided by the function $\mathcal{H}$.

(8) To further illustrate the effect of longitudinal fluctuations, we represent the dynamic structure factor for $t \ll 1/\Gamma(q)$ as

$$S(q,t) \simeq S_0(q) - \Delta S_\perp(q,t) - \Delta S_\parallel(q,t),$$

where $\Delta S_\perp$ and $\Delta S_\parallel$ are due to transverse and longitudinal chain dynamics, respectively. The ratio $\Delta S_\parallel(q,t)/\Delta S_\perp(q,t) \simeq \theta(t/t_\parallel)$ is close to 1 at very short times and it decays very slowly: θ decreases by a factor of 3 when $t/t_\parallel$ spans 6 orders of magnitude changing from 10^{-3} to 10^3 (see Fig. 2).

Asymptotically, for $t_\perp \gg t \gg t_\parallel$ the ratio $\Delta S_\parallel / \Delta S_\perp \propto t^{-1/4}$. This behavior is also in disagreement with the results of Ref. [13]. In our view, the discrepancy originates from an incorrect treatment of the longitudinal dynamics in Ref. [13]. Deriving their key equation (25) for the correlation function $J_\parallel(s,t)$ [denoted as $H(s,t)$ in the present paper], they introduced an approximation: the longitudinal displacement $r_\parallel$ is averaged with respect to the transverse noise $\eta_\perp$. Therefore, according to this scheme, $r_\parallel$ is induced by the longitudinal noise $\eta_\parallel$ alone, so that $r_\parallel \equiv 0$ if $\eta_\parallel \equiv 0$. It is obvious, however, that $\eta_\perp$ must give rise to longitudinal fluctuations even in the absence of $\eta_\parallel$ (longitudinal fluctuations are necessarily coupled with transverse fluctuations induced by $\eta_\perp$). The simpler approach outlined in Appendix C here does not involve that sort of approximation. There are unfortunately other issues in the theory of Ref. [13]. For example, Eq. (25) there does not follow from Eq. (50) (as claimed in that paper).[5]

ACKNOWLEDGMENTS

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[5] This can be easily seen by doing inverse Fourier transform of $J_\parallel(s,t)$ defined in Eq. (25) and comparing the result with the integrand in Eq. (50).

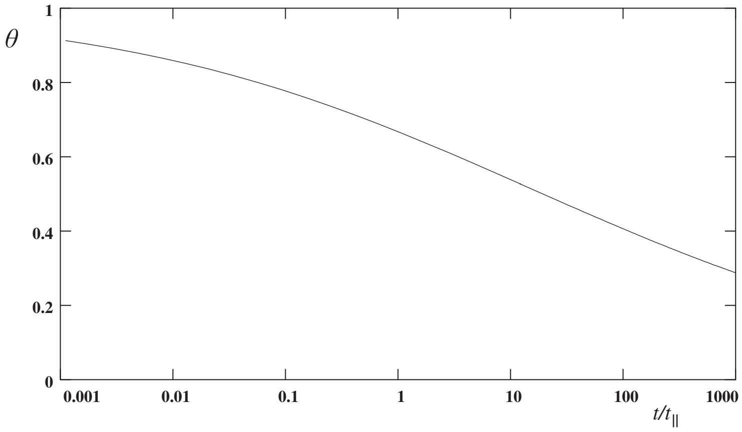

FIG. 2. The function $\theta(t/t_{\|})$ defined in Eq. (C23).

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APPENDIX A: TRANSVERSE DYNAMICAL CORRELATION FUNCTIONS OF SEMIRIGID CHAIN

Consider a chain fragment which is nearly parallel to the x axis (the fragment length $\ll l$). Its trajectory $\underline{r}(s)$ can be alternatively represented by the function $\underline{y}(x)$, where $\underline{y}=(y_1,y_2)\equiv\underline{r}_\perp$ is the projection of $\underline{r}$ onto the y_1y_2 plane $\perp$ to the x axis. The Kratky-Porod bending energy is

$$\mathcal{F}\simeq\frac{\varkappa}{2}\int\left(\frac{\partial^2\underline{y}}{\partial x^2}\right)^2 dx, \tag{A1}$$

where $\varkappa=l/2$ is the bending modulus (the thermal energy k_BT is considered as the energy unit). Equation (A1) is valid since

$$\left|\frac{\partial\underline{y}}{\partial x}\right|\ll 1. \tag{A2}$$

The latter condition also ensures that the contour length $s\simeq x$.

It is convenient to formally consider an infinite chain (rather than a short fragment). In order to satisfy the condition (A2) we introduce a weak attraction to the x axis adding the energy term

$$\frac{w}{2}\int\underline{y}^2dx \tag{A3}$$

to the bending energy $\mathcal{F}$. (Integration from $-\infty$ to ∞ is always assumed in all the Appendixes where the limits are not shown explicitly.) The chain is strongly oriented if

$$l_w=(\varkappa/w)^{1/4}\ll l. \tag{A4}$$

On the other hand, the term (A3) does not affect the short-scale chain dynamics for longitudinal length scales $\Lambda\ll l_w$. Both conditions can be satisfied since $\Lambda\ll l$. For that reason and in order to simplify the theory we formally set $w=0$ in all the equations below.

Note that $\mathcal{F}$ is quadratic in y_1 and y_2 which fluctuate independently. It is therefore enough to consider fluctuations of $y_1=y(x)$. It is convenient to define a quasicontinuous Fourier transform of $y(x)$ as follows:

$$y(x)=\frac{\epsilon}{2\pi}\sum_k y_ke^{ikx},\quad y_k=\int y(x)e^{-ikx}dx, \tag{A5}$$

where $k=n\epsilon$, $n=0,\pm1,\pm2\ldots$, and $\epsilon\to0$. The relevant part of the bending energy is

$$\mathcal{F}_1=\frac{\varkappa}{2}\frac{\epsilon}{2\pi}\sum_k k^4y_ky_{-k}.$$

Hence

$$\langle y_ky_{-k}\rangle=\frac{2\pi}{\epsilon}\frac{1}{\varkappa k^4}. \tag{A6}$$

Turning to the dynamics of the transverse fluctuations $y_1=y(x,t)$, we write the linear master equation

$$\zeta_\perp\frac{\partial y}{\partial t}=-\frac{\delta\mathcal{F}}{\delta y}+\phi, \tag{A7}$$

where

$$\zeta_\perp\simeq4\pi\eta_s/\ln(\Lambda^*/d) \tag{A8}$$

is the transverse friction constant per unit chain length in the logarithmic approximation [compare with Eq. (4)], $\frac{\delta\mathcal{F}}{\delta y}$ is the variational derivative, and $\phi=\phi(x,t)$ is the stochastic (white-noise) force in the y_1 direction. Λ^* is the cooperativity segment length defining an effective cutoff for hydrodynamic interactions [see below Eqs. (B9) and (B10)]. Note that in the general case Λ^* is $\sim1/k$.

Rewriting Eq. (A7) in terms of the Fourier transform $y_k=y_k(t)$,

$$\zeta_\perp\frac{\partial y_k}{\partial t}=-\varkappa k^4y_k+\phi_k, \tag{A9}$$

and defining $C_k(t)\equiv\frac{\epsilon}{2\pi}\langle y_k(t)y_{-k}(0)\rangle$ we find

$$\zeta_\perp\frac{\partial C_k}{\partial t}=-\varkappa k^4C_k.$$

Taking into account that Eq. (A6) defines $C_k(0)=\frac{1}{\varkappa k^4}$ we obtain

$$C_k(t)\equiv\frac{\epsilon}{2\pi}\langle y_k(t)y_{-k}(0)\rangle=\frac{1}{\varkappa k^4}e^{-\varkappa k^4t/\zeta_\perp}. \tag{A10}$$

The mean-square displacement $K(t)=\langle[y(0,t)-y(0,0)]^2\rangle$ can be represented in terms of C_k: $K(t)=2\frac{\epsilon}{2\pi}\Sigma_k[C_k(0)-C_k(t)]$, i.e.,

$$K(t)=\frac{1}{\pi}\int dk\frac{1}{\varkappa k^4}(1-e^{-\varkappa k^4 t/\zeta_\perp}). \tag{A11}$$

Doing the last integral yields Eq. (10):

$$K(t)=\frac{2}{3\pi}\Gamma(1/4)\varkappa^{-1/4}(t/\zeta_\perp)^{3/4}. \tag{A12}$$

APPENDIX B: SHORT-TIME SCATTERING FUNCTION: TRANSVERSE DYNAMICS

Turning to short-time behavior of the scattering function $S(q,t)$, we note that Eq. (13) is valid if $K(t)\gg\tilde{y}^2$, where $\tilde{y}\sim(1/q)^{3/2}l^{-1/2}$ is the typical amplitude of transverse fluctuations of a segment of length $\Lambda\sim 1/q$ [$\tilde{y}$ is defined by the right-hand side of Eq. (5)]. Thus we get the condition $t\gg t_\perp$ with

$$t_\perp=\frac{\zeta_\perp}{\varkappa q^4}. \tag{B1}$$

For $t\lesssim t_\perp$ the transverse displacement $\Delta y=y(x,t)-y(x,0)$ of a chain fragment is much smaller than the relevant "scattering" length: $\Delta y\ll 1/q$. Averaging the integrand in Eq. (2) over all orientations of q yields

$$S(q,t)=2\int_0^\infty\left\langle\frac{\sin(qR)}{qR}\right\rangle ds, \tag{B2}$$

where $R=|\underline{r}(s',t)-\underline{r}(s'',0)|$; in what follows we set $s''=0$, $s'=s$, i.e., the origin of the curvilinear coordinate s is set at an arbitrary macromolecular unit that was referred to as s''. As $q|R-s|\ll 1$, the integrand can be approximated as

$$\left\langle\frac{\sin(qR)}{qR}\right\rangle\simeq\frac{\sin(qs)}{qs}+\langle R-s\rangle\frac{\partial}{\partial s}\frac{\sin(qs)}{qs}. \tag{B3}$$

Neglecting longitudinal fluctuations

$$R^2\simeq s^2+D_y, \tag{B4}$$

where $D_y=D_y(s,t)=[\underline{y}(s,t)-\underline{y}(0,0)]^2$, so

$$\langle R-s\rangle\simeq\frac{1}{2s}\langle D_y\rangle. \tag{B5}$$

Using the above equations we obtain

$$\Delta S_\perp(q,t)\equiv S(q,t)-S(q,0)\simeq\int h(s,t)\frac{1}{2s}\frac{\partial}{\partial s}\frac{\sin(qs)}{qs}ds, \tag{B6}$$

where

$$h(s,t)=\langle D_y(s,t)-D_y(s,0)\rangle=-2\langle 2y(0,0)[y(s,t)-y(s,0)]\rangle. \tag{B7}$$

Here $y\equiv y_1$, and the contribution of y_2 is accounted for by the additional factor 2 in Eq. (B7) (note also that $\langle y(s,t)^2\rangle=\langle y(s,0)^2\rangle$). Using Eqs. (A5) and (A10), we find

$$\Delta S_\perp(q,t)\simeq 4\int_0^\infty ds\frac{1}{s}\frac{\partial}{\partial s}\frac{\sin(qs)}{qs}\int\frac{dk}{2\pi}e^{iks}\frac{1}{\varkappa k^4}(1-e^{-\varkappa k^4 t/\zeta_\perp}).$$

After some algebra we get

$$\Delta S_\perp(q,t)\simeq-\frac{1}{\varkappa q^2}I(t/t_\perp),$$

where $t_\perp$ is defined in Eq. (B1) and

$$I(z)=\int_0^1\frac{1-x^2}{x^4}(1-e^{-zx^4})dx. \tag{B8}$$

The function $I(z)$ shows the following asymptotics:

$$I(z)\simeq\begin{cases}(2/3)z, & z\ll 1\\ (1/3)\Gamma(1/4)z^{3/4}, & z\gg 1.\end{cases}$$

For $t\lesssim t_\perp$ the dominant contribution to $\Delta S_\perp(q,t)$ comes from the region $k\sim q$ corresponding to the longitudinal length

$$\Lambda^*\sim 1/k\sim 1/q,\quad t\lesssim t_\perp. \tag{B9}$$

For longer times, the corresponding typical length scale $\Lambda^*\sim 1/k$ is [compare with Eqs. (6) and (7)]

$$\Lambda^*\sim\frac{1}{q}\left(\frac{t}{t_\perp}\right)^{1/4}\sim\left(\frac{\varkappa t}{\zeta_\perp}\right)^{1/4},\quad t\gtrsim t_\perp. \tag{B10}$$

Note that $\Delta S_\perp(q,t)/S(q,0)\ll 1$ for $t\ll 1/\Gamma(q)$ [see Eq. (14)]. Therefore the scattering function can be represented in this time range as

$$S(q,t)\simeq S(q,0)e^{-F_\perp(q,t)}, \tag{B11}$$

where $S(q,0)\simeq\frac{\pi}{q}$ and

$$F_\perp(q,t)\simeq\frac{1}{\pi\varkappa q}I\left(\frac{\varkappa}{\zeta_\perp}q^4t\right). \tag{B12}$$

For $t\gg t_\perp$, Eq. (B11) agrees with Eq. (13) as it should do. Therefore Eqs. (B11) and (B12) are applicable for any t rather than only for $t\ll 1/\Gamma(q)$, so the time-dependence of the dynamic structure factor for $ql\gg 1$ is defined by Eqs. (B11), (B12), and (B8).

In particular, for short times $t\ll t_\perp$, we find $S(q,t)\simeq S(q,0)e^{-\gamma_\perp(q)t}$, where the initial slope $\gamma_\perp(q)$ is

$$\gamma_\perp(q)\simeq\frac{2}{3\pi\zeta_\perp}q^3=\frac{1}{6\pi^2}\frac{k_BT}{\eta_s}\ln\left(\frac{1}{qd}\right)q^3. \tag{B13}$$

The dynamic structure factor was analyzed for the same model in Ref. [9], where they obtained the long-time behavior of $S(q,t)$ for $t\gg t_\perp$ [see Eq. (2.18) in Ref. [9]], its short-time behavior [see Eq. (2.16) there], and the initial slope [see Eq. (3.4) there]. The long-time behavior of $S(q,t)$ and the initial slope obtained in this Appendix agrees with the previous results of Ref. [9] (within the logarithmic approximation for $\zeta_\perp$). On the other hand, the short-time behavior obtained in Ref. [9] disagrees both with their initial slope and with Eq. (B11) written above. It appears that their Eq. (2.16) is incorrect: it comes as a result of an improper evaluation of the sum in their Eq. (2.9) (they mistakenly neglected the nondiagonal terms in this sum). Note that the long-time behavior of $S(q,t)$ and the initial slope were obtained [9] using different methods, while a single approach is used in this Appendix.

More importantly, all results in this Appendix are obtained neglecting the effect of longitudinal displacements of chain elements. This is justified for long times, however, it is inappropriate for short enough t. In particular, the longitudinal motions do contribute to the initial slope. The corresponding effects are analyzed in Appendix C.

APPENDIX C: LONGITUDINAL DYNAMICS

Consider $x(s,t)$, the x coordinate of point s on the chain at time t. Obviously $\langle x(s,t)-x(0,t)\rangle=\alpha s$, where $\alpha\simeq 1$ if condition (A4) is satisfied. It is convenient to use $\tilde{s}=\alpha s$ instead of s; "tilde" above "s" is omitted in what follows to simplify notation. Thus $\langle x(s,t)\rangle = s$ (an irrelevant constant term is omitted). The longitudinal displacement from the mean position is $X(s,t)\equiv x(s,t)-s$, $\langle X\rangle=0$. Then Eq. (B4) must be replaced by $R^2=[x(s,t)-x(0,0)]^2+D_y=[s+X(x,t)-X(0,0)]^2+D_y$. Therefore

$$R-s\simeq X(s,t)-X(0,0)+\frac{1}{2s}D_y,$$

so Eq. (B5) stays valid: the longitudinal motions do not contribute to the right-hand side of Eq. (B3). A contribution can be found, however, in the quadratic approximation in $R-s$ as follows:

$$\left\langle\frac{\sin(qR)}{qR}\right\rangle\simeq\frac{\sin(qs)}{qs}+\langle R-s\rangle\frac{\partial}{\partial s}\frac{\sin(qs)}{qs}+\frac{1}{2}\langle(R-s)^2\rangle\frac{\partial^2}{\partial s^2}\frac{\sin(qs)}{qs}. \tag{C1}$$

The last term was neglected before because the effect of transverse motions is dominated by the term linear in $R-s$. Therefore, if the quadratic term is important at all, it must be due to longitudinal fluctuations, hence we may neglect the transverse contribution D_y in $(R-s)^2$ as follows:

$$(R-s)^2\simeq[X(s,t)-X(0,0)]^2.$$

The corresponding "longitudinal" contribution $\Delta S_\parallel$ to $S(q,t)-S(q,0)$ generated by the last term in Eq. (C1) is

$$\Delta S_\parallel(s,t)\simeq\frac{1}{2}\int H(s,t)\frac{\partial^2}{\partial s^2}\frac{\sin(qs)}{qs}ds, \tag{C2}$$

where

$$\begin{aligned}H(s,t)&=\langle[X(s,t)-X(0,0)]^2\rangle-\langle[X(s,0)-X(0,0)]^2\rangle\\&=-2[\mathcal{G}(s,t)-\mathcal{G}(s,0)],\end{aligned}$$

$$\mathcal{G}(s,t)=\langle X(s,t)X(0,0)\rangle \tag{C3}$$

In order to find $\mathcal{G}(s,t)$ we use the fluctuation-dissipation theorem [23].

$$\mathcal{G}(s,t)=\int_t^\infty\kappa(s,t')dt',\quad t>0, \tag{C4}$$

where $\kappa(s,t)$ is the dynamic susceptibility defining a linear response of the chain at time t to a weak external longitudinal force f applied to it at time 0:

$$\langle X(s,t)\rangle=\int ds'dt'\kappa(s-s',t-t')f(s',t').$$

Here $f(s,t)ds$ is the force applied to the element ds at time t; $\kappa(s,t)=0$ for $t<0$. It is sufficient to consider harmonic time dependence: $f(s,t)=f(s)e^{i\omega t}$. Then

$$X_k=\varkappa_k(i\omega)f_k, \tag{C5}$$

where $X_k=\int X(s,t)e^{-iks}ds$, f_k is defined analogously, and

$$\kappa_k(i\omega)=\int ds\int_0^\infty dt\kappa(s,t)e^{-iks-i\omega t}.$$

Using Eq. (C4) one finds

$$\int_0^\infty[\mathcal{G}(s,t)-\mathcal{G}(s,0)]e^{-pt}dt=-\int\frac{\kappa_k(p)}{p}e^{iks}\frac{dk}{2\pi}. \tag{C6}$$

The external force induces line tension $\mathcal{T}(s,t)=\mathcal{T}(s)e^{i\omega t}$ along the chain. The force balance for an element ds reads

$$f-\zeta_\parallel\frac{\partial X}{\partial t}+\frac{\partial\mathcal{T}}{\partial s}=0, \tag{C7}$$

where $-\zeta_\parallel\frac{\partial X}{\partial t}$ is the hydrodynamic friction force per unit length; the inertial effects are neglected. Here $\zeta_\parallel$ is the friction constant (per unit chain length) for longitudinal displacements

$$\zeta_\parallel\simeq\frac{2\pi\eta_s}{\ln(\Lambda^{**}/d)}\simeq\frac{2\pi\eta_s}{\ln(q^{-1}/d)} \tag{C8}$$

[compare with Eqs. (A8) and (4)]. The long-range cutoff length Λ^{**} in the denominator is $\sim 1/k$, where k is the wave number along the chain contour involved in Eq. (C5); this cutoff length is $\Lambda^{**}\sim q^{-1}$ since it is longitudinal fluctuations with $k\sim 1/|s|\sim q$ that provide a dominant contribution to $\Delta S_\parallel$ in the integrals [Eqs. (C19) and (C20)] ($|s|=|s'-s''|$ is the contour distance between two correlated units).

The tension $\mathcal{T}$ directly affects the transverse coordinates $\underline{y}(s,t)$ which in turn define $X(s,t)=x(s,t)-s$ via the relation

$$(ds/\alpha)^2=dx^2+(d\underline{y})^2,$$

giving rise to

$$\frac{dX}{ds}\simeq\text{const}-\frac{1}{2}\left(\frac{d\underline{y}}{ds}\right)^2, \tag{C9}$$

where const$=1/\alpha-1$ is a small irrelevant constant.

The effect of $\mathcal{T}$ on $\underline{y}(s,t)$ is transmitted by the transverse force $\mathcal{T}\frac{\partial^2\underline{y}}{\partial s^2}$. Including this force in the dynamic equation (A9) results in

$$\zeta_\perp \frac{\partial y_k}{\partial t} = -\varkappa k^4 y_k - \mathcal{T} k^2 y_k + \phi_k, \tag{C10}$$

where $y=y_1$ is one of the two transverse components. It is assumed here that $\mathcal{T}$ is uniform. This approximation is valid since the typical length-scale $\Lambda_\parallel$ associated with a variation of $\mathcal{T}$ is much longer than the typical length scale $\Lambda_\perp$ characterizing transverse fluctuations $y(s,t)$; the condition $\Lambda_\parallel \gg \Lambda_\perp$ is justified below [see Eq. (C18) and the note after Eq. (C23)]. Defining

$$\mathcal{C}_k(t) \equiv \frac{\epsilon}{2\pi}\langle y_k(t) y_{-k}(t)\rangle, \tag{C11}$$

and using Eq. (C10) we find

$$\zeta_\perp \frac{\partial \mathcal{C}_k(t)}{\partial t} = -2(\varkappa k^4 + \mathcal{T}k^2)\mathcal{C}_k + B_k, \tag{C12}$$

where $B_k \propto \langle \phi_k^2 \rangle$ is related to the random force ϕ and does not depend on $\mathcal{T}$. Therefore B_k can be obtained by formally setting $\mathcal{T}=0$ and simultaneously setting $\mathcal{C}_k(t)=C_k(0)=\frac{1}{\varkappa k^4}$ [see Eq. (A10)] in Eq. (C12): $B_k=2$. Considering $\mathcal{T} \propto e^{i\omega t}$ as a perturbation we find

$$\mathcal{C}_k(t) \simeq \frac{1}{\varkappa k^4} + \beta_k \mathcal{T}(t), \quad \beta_k = -\frac{2}{\varkappa k^2}\frac{1}{2\varkappa k^4 + i\zeta_\perp \omega}. \tag{C13}$$

Rewriting Eq. (C9) in terms of Fourier components

$$\left\langle \frac{dX}{ds} \right\rangle = \text{const} - \frac{1}{2} 2 \int \frac{dk}{2\pi} k^2 \frac{\epsilon}{2\pi}\langle y_k(t) y_{-k}(t)\rangle,$$

where the additional factor 2 accounts for equivalent contributions of two transverse components. On using the definition, Eq. (C11), and Eq. (C13), one finds

$$m \equiv \left\langle \frac{dX}{ds} \right\rangle \simeq b\mathcal{T}, \tag{C14}$$

where

$$b = -\int \frac{dk}{2\pi} k^2 \beta_k = (2p\zeta_\perp)^{-3/4}\varkappa^{-5/4}, \tag{C15}$$

and $p \equiv i\omega$. Note that the lion's share of the integral in Eq. (C15) comes from the region $k \sim \left(\frac{\zeta_\perp \omega}{\varkappa}\right)^{1/4}$ corresponding to the length

$$\Lambda_\perp \sim 1/k \sim \left(\frac{\varkappa t}{\zeta_\perp}\right)^{1/4}, \tag{C16}$$

since $\omega \sim 1/t$ [compare with Eq. (B10)].

Rewriting Eqs. (C7) and (C14) in terms of Fourier components: $f_k - i\omega\zeta_\parallel X_k + ik\mathcal{T}_k = 0$, $ikX_k = b\mathcal{T}_k$, solving them for X_k and comparing the result with Eq. (C5), we find

$$\kappa_k(p) = \frac{1}{p\zeta_\parallel + k^2/b} = \frac{1}{p\zeta_\parallel}\frac{1}{1+[k/(\mu p^{1/8})]^2}, \quad \mu \equiv \frac{\zeta_\parallel^{1/2}}{2^{3/8}\zeta_\perp^{3/8}\varkappa^{5/8}}. \tag{C17}$$

The characteristic k involved in Eq. (C17) is obviously $\sim \mu p^{1/8}$; the corresponding characteristic length scale (with $p \sim 1/t$) is

$$\Lambda_\parallel \sim t^{1/8}/\mu \sim \frac{t^{1/8}\varkappa^{5/8}}{\zeta_\perp^{1/8}}.$$

Note that $\Lambda_\parallel \sim \sqrt{l\Lambda_\perp}$, therefore

$$\Lambda_\parallel \gg \Lambda_\perp, \tag{C18}$$

as long as $\Lambda_\perp \ll l$. The latter condition is true since the longest relaxation time $t \sim 1/\Gamma(q)$ is much shorter than τ_0: $t \ll \tau_0 \sim \eta_s l^3$ [the terminal decay rate $\Gamma(q) \gg 1/\tau_0$ for $ql \gg 1$, see Eq. (8)]. The two length scales, $\Lambda_\perp(t)$ for transverse fluctuations, and $\Lambda_\parallel(t)$ for longitudinal fluctuations were identified in Ref. [12].

Defining Laplace transform

$$\Delta S_\parallel(q,p) \equiv \int_0^\infty \Delta S_\parallel(q,t)e^{-pt}dt,$$

and using Eqs. (C2), (C3), and (C6) we obtain

$$\Delta S_\parallel(q,p) \simeq \int ds \int \frac{dk}{2\pi}\frac{\kappa_k(p)}{p}e^{iks}\frac{\partial^2}{\partial s^2}\frac{\sin(qs)}{qs}. \tag{C19}$$

After integration it reduces to

$$\Delta S_\parallel(q,p) \simeq -\frac{1}{qp}\int_0^q k^2 \kappa_k(p)dk = \frac{(\mu p^{1/8})^3}{qp^2\zeta_\parallel}\left(\tan^{-1}\frac{q}{\mu p^{1/8}} - \frac{q}{\mu p^{1/8}}\right). \tag{C20}$$

Doing the inverse Laplace transform we get

$$\Delta S_\parallel(q,t) = -S(q,0)F_\parallel(q,t),$$

where $S(q,0)$ is defined in Eq. (3) and

$$F_\parallel(q,t) \simeq \frac{q^3 t}{3\pi\zeta_\parallel}\theta(t/t_\parallel). \tag{C21}$$

Here

$$t_\parallel = \left(\frac{\mu}{q}\right)^8 \simeq \frac{4\zeta_\parallel^4}{\zeta_\perp^3 l^5 q^8} \tag{C22}$$

is the characteristic longitudinal time, and

$$\theta(x) = \sum_{n=0}^{\infty}\frac{3}{2n+3}\frac{(-1)^n}{\Gamma(2+n/4)}x^{n/4} \tag{C23}$$

is the dimensionless function of the reduced time.

Note that the characteristic range of hydrodynamic interactions for longitudinal fluctuations involved in Eqs. (C19) and (C20) is $\Lambda^{**} \sim 1/k \sim 1/q$ (it is the region $k \sim q$ that provides the lion's share of the integrals in these equations). Therefore the long-range cutoff in the logarithmic factor involved in Eq. (C8) defining $\zeta_{\parallel}$ is $\Lambda^{**}\sim 1/q$. As for the cooperativity segment length defining effective cutoff for hydrodynamic interactions between transverse fluctuations, it is defined in Eq. (C16). Therefore $\zeta_{\perp}$ in Eqs. (C17), (C22), and (C21) is defined in Eq. (A8) where Λ^{*} must be replaced by $\Lambda_{\perp}$ [Eq. (16)]. Note, however, that $\Delta S_{\parallel}$ is nearly independent of $\zeta_{\perp}$ for short times $t \ll t_{\parallel}$. Note also that Eq. (C20) is valid if the "longitudinal" length $1/k \sim 1/q$ is much longer than the "transverse" length $\Lambda_{\perp}$: $1/q \gg \Lambda_{\perp}$, i.e., for $t \ll t_{\perp}$.

Equation (C23) is useful for $x \lesssim 10$; for $x \gtrsim 10$ the function $\theta(\cdot)$ is defined by the asymptotic expansion

$$\theta(x) \simeq \frac{3}{\Gamma(7/4)}x^{-1/4} - \frac{3\pi}{2\Gamma(13/8)}x^{-3/8} + \sum_{n=0}^{\infty}\frac{3}{2n+1}\frac{(-1)^{n}}{\Gamma(3/2-n/4)}x^{-n/4-1/2}.$$

Thus $\theta(0)=1$, $\theta(x)\simeq\frac{3}{\Gamma(7/4)}x^{-1/4}$ for $x\gg 1$.

On taking into account the effects of both transverse and longitudinal fluctuations the dynamic structure factor becomes

$$S(q,t) \simeq S(q,0)e^{-F_{\perp}(q,t)-F_{\parallel}(q,t)}, \tag{C24}$$

where $F_{\perp}(q,t)$ and $F_{\parallel}(q,t)$ are defined in Eqs. (B11) and (C21), respectively. In particular, the initial slope

$$\gamma(q) = -\left.\frac{\partial \ln S(q,t)}{\partial t}\right|_{t=0} \simeq \frac{4}{3\pi\zeta_{\perp}}q^{3}, \tag{C25}$$

i.e., the transverse and longitudinal modes contribute nearly equally to the initial decay of the structure factor.

The functions $F_{\perp}(q,t)$ and $F_{\parallel}(q,t)$ involve essentially different characteristic times [see Eqs. (B1) and (C22)]: $t_{\perp} \gg t_{\parallel}$ as $ql \gg 1$. For $t \ll t_{\perp}$ the relative contribution of longitudinal motions is

$$\frac{F_{\parallel}(q,t)}{F_{\perp}(q,t)} \simeq \theta(t/t_{\parallel}). \tag{C26}$$

The function $\theta(t/t_{\parallel})$ is shown in Fig. 2. It is clear that although θ must tend to 0 as $t/t_{\parallel}\to\infty$, the decay is very slow: $\theta \approx 0.3$ for $t/t_{\parallel}=1000$.

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