Mean Relaxation Rate of the Dynamic Structure Factor of the Rouse Chain

Themis Matsoukas

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

Received June 23, 2006; Revised Manuscript Received July 13, 2006

ABSTRACT: We study the internal autocorrelation function of a Gaussian coil in the free-drainage limit for chains of finite length that are much larger than the size of the monomer and obtain an exact analytic expression for the mean decay rate over the entire qR_G range, where q is the scattering vector and R_G is the radius of gyration of the coil. The mean decay rate approaches $30\pi/\tau_1$ at the low q limit, where τ_1 is the characteristic time of the first mode, and has the predicted q^4 scaling when $qR_G \gg 1$. At long times, the autocorrelation function decays as a single exponential with rate $2/\tau_1$ but the transition from multiexponential decay at short times to single-exponential decay at long times is very much dependent on the scattering vector.

1. Introduction

When light is scattered from flexible macromolecules, the autocorrelation function carries contributions from center-of-mass motion as well as from internal relaxation modes associated with the "breathing" dynamics of the coil. Under proper conditions both contributions can be observed experimentally by quasielastic light scattering (QELS). The simplest model of coil dynamics is the Rouse chain in the free draining limit. While more advanced treatments of hydrodynamics are available,[1,2] the Rouse chain provides a relative simple interpretation of internal coil dynamics and has been often used to interpret QELS experiments from dilute polymer systems.[3−11] The autocorrelation function for the Rouse chain in the free drainage limit was formulated by Pecora[12] using normal-mode analysis. Pecora further showed that the result can be expressed as a series of exponential terms with decay rates that are multiples of a characteristic time, τ_1, corresponding to the first normal mode of the chain.[13] The slowest decay rate in this series is $2/\tau_1$; accordingly, the autocorrelation function at long times decays as a single exponential from which the relaxation time, τ_1, can be obtained. This formulation has provided the basis for the experimental investigations of coil dynamics by a two-exponential method: one exponential term (the slowest) that arises from the translational motion of the coil, and a second one that arises from the slowest inter-coil relation process.[7] In refinements of this method, additional internal modes are resolved using multiexponetial analysis.[6,10,11,14]

This approach focuses attention to the *long-time* limit of the autocorrelation function: it starts with a single-exponential representation based on the slowest decay rate and progressively refines the approximation by including faster relaxation times. On the other hand, the initial decay of the autocorrelation function, expressed by the first cumulant, carries the effect of all relaxation rates. Thus, by focusing on short times, one is not required to adopt approximations. Unfortunately, while the first cumulant is easily measured experimentally, its interpretation in terms of coil dynamics is not straightforward. For large coils, the relaxation rates form an infinite, discrete, spectrum of higher multiples of the first normal relaxation rate,[11] and no simple expressions are available to guide analysis. In the high-q regime, where q is the scattering vector, scaling arguments show that the first cumulant scales as q^x with $x = 4$, if hydrodynamic interactions are neglected, and $x = 3$, when the preaveraged Oseen tensor is used.[1,15,16] Akcasu and co-workers formulated expressions for the first cumulant over the entire q range for various types of coils (open chains and rings), both in the free drainage limit and with hydrodynamics included.[2] These expressions are given as summations over the number of beads in the chain and produce simple results only in the limit of large scattering vectors. The lack of simple relations for the short-time behavior of the autocorrelation, and for the first cumulant in particular, has left experimentalists with little choice but to rely on the analysis of the long-time behavior of the autocorrelation function, even though the experimental window where such analysis is valid is indeed narrow.[2,7]

In this paper, we derive an analytic expression for the first cumulant based on the autocorrelation function obtained by Pecora.[13] We examine its asymptotic behavior in the low- and high-q limits and compare the results to the asymptotic expressions predicted by scaling theory. We further examine the behavior of the autocorrelation function in the limit $\tau \to \infty$ and corroborate the findings by numerical calculation of the autocorrelation function. The paper is organized as follows: in section 2, we review Pecora's result for the autocorrelation function, derive the first cumulant, and perform an analysis of the autocorrelation function in the limit $\tau \to \infty$. In section 3, we present numerical calculations and discuss the physical significance of our findings.

2. Theory

2.1. Autocorrelation Function. The theory of dynamic light scattering from Gaussian coils in the free-drainage limit was developed by Pecora[12,13,17] and is briefly reviewed here. The polymer is treated as a sequence of $N + 1$ freely joined beads connected by N springs, each with equilibrium length b. For large N, the radius of gyration, R_G, is

$$R_G{}^2 = Nb^2/6 \qquad (1)$$

In the free drainage limit, hydrodynamic interactions among adjacent beads are ignored and the dynamics of the coil are represented by a set of normal modes and their associated time constants, $\tau_k = k^2\tau_1$, $k = 1 \cdots N$, where τ_1 is the time scale of the first normal mode:

10.1021/ma061411o CCC: $33.50
Published on Web 08/16/2006

$$\tau_1 = \frac{2R_G^{\,2}}{\pi^2 D} \tag{2}$$

Here, D, is the translational diffusion coefficient of the coil, which in the Rouse limit is expressed as

$$D = \frac{D_m}{N} = \frac{kT}{6\zeta}\frac{b^2}{R_G^{\,2}} \tag{3}$$

where $D_m = kT/\zeta$ is the diffusion coefficient of the monomer in the chain, and ζ is the friction factor of the monomer.

The autocorrelation function, $S_{coil}(q,\tau)$, of the light (electric field) scattered by the coil in the limit of infinite dilution is

$$S_{coil}(q,\tau) = \exp(-q^2 D\tau) S(q,\tau) \tag{4}$$

where q is the scattering vector length. The first exponential term on the right-hand side is the contribution of center-of-mass diffusion while $S(q,\tau)$ arises from the internal motion of the macromolecule, i.e., of segmental motion relative to the center of mass. Center-of-mass diffusion and internal motion make multiplicative contributions to the autocorrelation function that can be separated. Since our interest is in the internal relaxation modes, we remove the center-of-mass contribution and focus on the internal part, $S(q,\tau)$, which we simply call the autocorrelation function. For the Rouse chain, this function is given by

$$S(q,\tau) = \left\langle \exp\left[-\frac{2(qR_G)^2}{\pi^2} A_{ij}(\tau)\right]\right\rangle \tag{5}$$

with the angular brackets used as shorthand notation for double summation over i, $j = 0 \cdots N$, followed by division by N^2. The parameters A_{ij} and R_{ij} are given by

$$A_{ij}(\tau) = \sum_{k=1}^{N} \frac{R_{ik}^{\,2} + R_{jk}^{\,2} - 2R_{ik}R_{jk}e^{-k_2\tau/\tau_1}}{k^2} \tag{6}$$

and

$$R_{ik} = \begin{cases} (-1)^{(k+1)/2}\cos(ik\pi/N) & k \text{ odd;} \\ (-1)^{k/2}\cos(ik\pi/N) & k \text{ even} \end{cases} \tag{7}$$

Equation 5 is the dynamic structure factor of the discrete chain and is exact for all N (though it involves the minor approximation $(N + 1)/N \approx 1$). We are interested in the limit $N \to \infty$ at constant R_G, or, equivalently, $N \to \infty$, $b \to 0$, at constant Nb^2. In this limit the chain becomes a continuous, finite-size string of freely joined beads and summations in i, j, revert to integrals in $x = i/N$, $y = j/N$. Even as the chain becomes continuous, the characteristic relaxation time in eq 2 is finite and the spectrum of characteristic times remains discrete. We note that the limit $N \to \infty$ with no restriction on R_G, as was done in Akcasu et al.,[2] corresponds to the scaling limit $qR_G \gg 1$. By contrast, the limit adopted here produces results that are valid in the entire qR_G region. With $N \to \infty$, the dynamic structure factor at $\tau = 0$ and $\tau = \infty$ is obtained from eqs 5−7 by performing the summations in i, j, and k:[13]

$$S_0 = \frac{2}{(qR_G)^4}[e^{-(qR_G)^2} - 1 + (qR_G)^2] \tag{8}$$

$$S_\infty = \frac{\pi}{(qR_G)^2}\exp\left[-\frac{(qR_G)^2}{6}\right]\left[\operatorname{erf}\frac{qR_G}{2}\right]^2 \tag{9}$$

The factors S_0 and S_∞ give the maximum value and the baseline, respectively, of the autocorrelation function. We further recognize S_0 as the classical (static) scattering function of the Gaussian coil, first obtained by Debye independently of the dynamic model adopted here.

2.2. First Cumulant. We now wish to obtain an expression for the first cumulant of the autocorrelation function, which is defined as[19]

$$K_1 = -\frac{d(\ln(S - S_\infty))}{d\tau}\Big|_{\tau=0} = -\frac{S_0'}{S_0 - S_\infty} \tag{10}$$

where S_0' is the derivative of $S(q,\tau)$, evaluated at $\tau = 0$. From eq 5, this derivative is

$$S_0' = -z\langle A_{ij}'(0)\exp(-zA_{ij}(0))\rangle \tag{11}$$

with

$$z = \frac{2(qR_G)^2}{\pi^2} \tag{12}$$

and $A_{ij}'(0)$ is the derivative of A_{ij} with respect to τ at $\tau = 0$. Following Pecora, we write

$$A_{ij}(0) = \sum_{k=1}^{N}\frac{(R_{ik} - R_{jk})^2}{k^2} = \frac{\pi^2}{2}\frac{|i - j|}{N} \tag{13}$$

The first equality follows from eq 6 by setting $\tau = 0$; the second equality is obtained by replacing upper limit in the summation over k by infinity, an approximation that is exact in the limit $N \to \infty$. From eq 6, the derivative, $A_{ij}'(0)$, is

$$A_{ij}'(0) = \frac{2}{\tau_1}\sum_{k=1}^{N} R_{ik}R_{jk} \tag{14}$$

The summation that appears in the right-hand side of eq 14 is derived in the appendix, and leads to the following result

$$\sum_{k=1}^{N} R_{ik}R_{jk} = \begin{cases} N(1 + \delta_{i0} + \delta_{i,N})/2, & i = j \\ 0, & i \neq j \text{ and } i - j \text{ even} \\ -1, & i \neq j \text{ and } i - j \text{ odd} \end{cases} \tag{15}$$

where δ_{mn} is Kronecker's δ. Next, we insert eqs 13−15, into eq 11 and perform the summations in i, j. The calculation, whose details are also shown in the appendix, leads to the rather simple result

$$S_0' = -z^2(1 - S_0) \tag{16}$$

Finally, combining eq 16 with eq 12 and eq 10 we obtain the first cumulant in the form

$$K_1 = \frac{2(qR_G)^2}{\pi^2\tau_1} \cdot \frac{1 - S_0}{S_0 - S_\infty} \tag{17}$$

CDV

with S_0, S_∞ given by eqs 8 and 9, respectively. This is the main result of this work: an exact analytic equation for the first cumulant, valid for continuous chains over the entire range $0 < qR_G < \infty$. Next, we examine the behavior of eq 17 in the limits of low and high q.

Low q Limit: $qR_G \ll 1$. Expanding the right-hand side of eq 17 in power series in qR_G about $qR_G = 0$, we find

$$K_1 = \frac{30}{\pi^2\tau_1}\left[1 + \frac{85}{630}(qR_G)^2 + \cdots\right] \quad (18)$$

In the limit $qR_G = 0$, therefore

$$K_1|_{qR_G=0} = \frac{30}{\pi^2\tau_1} \quad (19)$$

An alternative expression for the low-q limit is in the form

$$K_1|_{qR_G=0} = 15\frac{D}{R_G^{\ 2}} = 15\Omega_0 \quad (20)$$

where $\Omega_0 = D/R_G^2$ is the fundamental relaxation rate of the coil, corresponding to the inverse time for the chain to diffuse through a distance equal to its radius of gyration.

High-q Limit. In this regime, we obtain the following dependencies:

$$S_\infty \ll S_0 \approx \frac{2}{(qR_G)^2} \ll 1 \quad (21)$$

These lead to

$$K_1|_{qR_G=\infty} = \frac{(qR_G)^4}{\pi^2\tau_1} \quad (22)$$

Thus, we recover the q^4 dependence predicted by scaling.

2.3. Autocorrelation Function in the Limit $\tau \to \infty$. Unfortunately, the second cumulant cannot be calculated by the same method: if the second derivative of S at $\tau = 0$ is calculated first, the subsequent summations in i, j, k, diverge in the limit $N \to \infty$. If the summations are computed first and the derivative afterward, the behavior at $\tau = 0$ is proper; however, we were not able to resolve the summations with arbitrary τ. In light of this difficulty we seek additional insight in the behavior of the autocorrelation function in the limit $\tau \to \infty$ by examining the difference, $S - S_\infty$. Beginning with eq 5 we have

$$S - S_\infty = \langle \exp(-zA_{ij}^\infty)(\exp(-z\Delta A_{ij}) - 1)\rangle \quad (23)$$

where A_{ij}^∞ is A_{ij} at $\tau \to \infty$ and

$$\Delta A_{ij} = A_{ij} - A_{ij}^\infty = -2\sum_{k=1}^{N}\frac{R_{ik}R_{jk}}{k^2}e^{-k^2\tau/\tau_1} \quad (24)$$

Linearization of the exponential term in eq 23 gives

$$\exp(-z\Delta A_{ij}) - 1 = -z\Delta A_{ij} + \frac{z^2}{2}\Delta A_{ij}^{\ 2} + O[e^{-3\tau/\tau_1}] \quad (25)$$

thus eq 23 becomes

$$S - S_\infty = -z\langle e^{-zA_{ij}^\infty}\Delta A_{ij}\rangle + \frac{z^2}{2}\langle e^{-zA_{ij}^\infty}\Delta A_{ij}^{\ 2}\rangle + O[e^{-3\tau/\tau_1}] \quad (26)$$

Next we expand ΔA_{ij} and ΔA_{ij}^2 in $k = 1\cdots N$ and retain only the term $k = 1$, which corresponds to the slowest decay term in each of the expansions. With this, eq 26 leads to

$$S - S_\infty = 2ze^{-\tau/\tau_1}\langle R_{i1}R_{j1}e^{-zA_{ij}^\infty}\rangle + 2z^2e^{-2\tau/\tau_1}\langle R_{i1}^2R_{j1}^2e^{-zA_{ij}^\infty}\rangle + O[e^{-3\tau/\tau_1}] \quad (27)$$

We recall from Pecora the following asymptotic expression for A_{ij}^∞:

$$A_{ij}^\infty = \sum_{k=1}^{N}\frac{R_{ik}^{\ 2} + R_{jk}^{\ 2}}{k^2} = \frac{\pi^2}{2}\left(\frac{2}{3} - \frac{i+j}{N} + \frac{i^2+j^2}{N^2}\right) \quad (28)$$

whose right-hand side is valid for $N \to \infty$. Using the above result, the first ensemble average on the right-hand side of eq 27 gives

$$\left\langle e^{-z_\infty A_{ij}}\cos\frac{i\pi}{N}\cos\frac{j\pi}{N}\right\rangle = \int_0^1\int_0^1 \cos(\pi x) \times \cos(\pi y)\, e^{-z(\pi^2/2)((2/3)-x-y+x^2+y^2)}\, dx\, dy = 0 \quad (29)$$

in which the summations in i, j, have been replaced by integrals in $x = i/N$, $y = j/N$, and whose right-hand side evaluates to 0. Thus, eq 27 produces

$$S - S_\infty = 2z^2e^{-2\tau/\tau_1}\int_0^1\int_0^1 \cos^2(\pi x) \times \cos^2(\pi y)\, e^{-z(\pi^2/2)((2/3)-x-y+x^2+y^2)}dx\, dy + O[e^{-3\tau/\tau_1}] \quad (30)$$

Evaluating the integral, the result can be expressed as

$$S - S_\infty = e^{-2\tau/\tau_1}\Delta S_0 + O[e^{-3\tau/\tau_1}] \quad (31)$$

where

$$\Delta S_0 = \frac{z}{4\pi}\exp\left(-\frac{\pi^2 z}{12} - \frac{4}{z}\right)\left[\mathrm{erf}\left(\frac{\pi z - 4i}{2\sqrt{2z}}\right) + \mathrm{erf}\left(\frac{\pi z + 4i}{2\sqrt{2z}}\right) - 2e^{2/z}\mathrm{erf}\left(\frac{\pi\sqrt{z}}{2\sqrt{2}}\right)\right]^2 \quad (32)$$

in which, $\mathrm{erf}(a + ib)$ is the error function with a complex argument. Thus, we have recovered Pecora's result, namely, that the slowest relaxation rate in the autocorrelation function is $2/\tau_1$. Additionally, in eq 31, we have obtained a closed expression for the asymptotic tail of the autocorrelation function at long times.[21]

3. Discussion

The first cumulant from eq 17 is plotted as a function of qR_G in Figure 1. The low-q and high-q asymptotes are also shown, calculated from eqs 19 and 22, respectively. The cumulant demonstrates the expected power-law behavior, with exponent 0 in the low-q regime, and 4 in the high-q regime. The asymptotes calculated from eqs 19 and 22 are in excellent agreement with the computed cumulant. We further note that the transition between the two regimes is quite rapid, as demonstrated by the fact that eq 17 follows the asymptotic lines closely, except in the crossover region $0.5 \lesssim qR_G \lesssim 4$. The intersection of the asymptotes is at $qR_G = 2.34$, a point which may be considered as the nominal boundary between the low- and high-q regimes. With a realistic chain model, the first cumulant at sufficiently high-q must level off at a value corresponding to the diffusivity of the monomeric unit, produc-

CDV

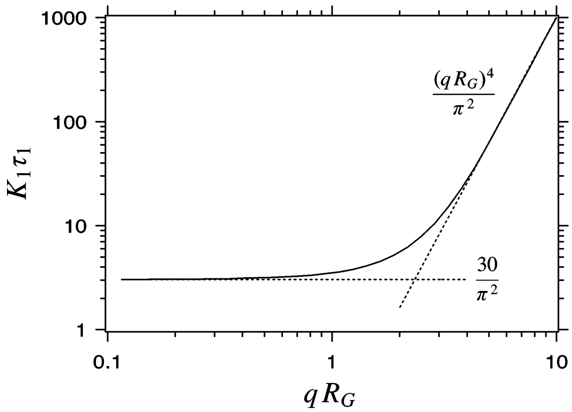

Figure 1. Mean decay rate of the internal autocorrelation as a function of qR_G.

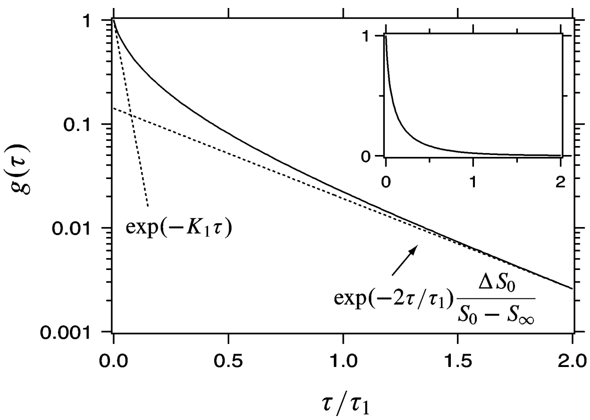

Figure 2. Normalized autocorrelation function for $qR_G = 4$. The limiting slopes are calculated using the following parameters obtained from equations in the text: $K_1 = 27.6095\tau_1$, $S_0 = 0.11719$, $S_\infty = 0.013516$, and $\Delta S_0 = 0.01461$.

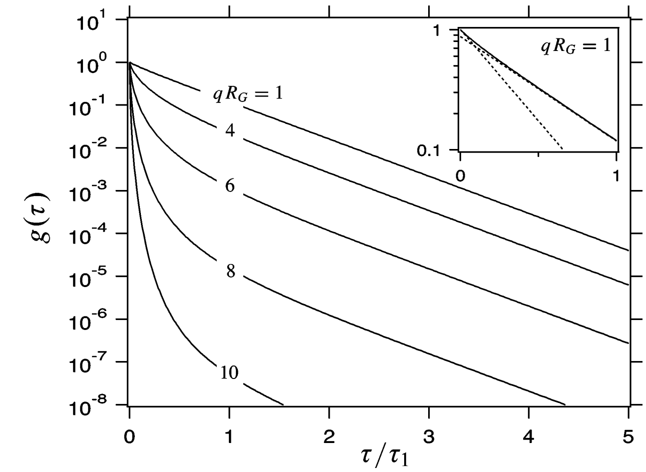

Figure 3. Autocorrelation functions for $qR_G = 1$, 4, 6, 8, and 10. Inset shows an expanded view of the autocorrelation function at $qR_G = 1$ with the initial and long-time slopes drawn. Autocorrelation functions at $qR_G < 1$ are nearly indistinguishable from that at $qR_G = 1$.

ing an overall S-shaped form in the graph of K_1 vs q, as was shown in calculations from chains with finite number of monomers.[2] This transition is not captured by the present model because the diffusivity of the monomer, $D_m = D/N$, goes to 0 as $N \to \infty$.

The low- and high-q asymptotes are power-law functions with exponents 0 and 4, respectively, in full agreement with the exponents obtained via scaling arguments.[1,20] By the same arguments, the first cumulant in the high-q regime must be independent of the size of the chain. Despite appearance to the contrary, eq 22 is indeed independent of the radius of gyration. Recalling eqs 2 and 3, we obtain $\tau_1 = 12\zeta R_G^4/\pi^2 b^2 kT$, and thus eq 22 becomes

$$K_1|_{qR_G=\infty} = \frac{kTb^2q^4}{12\zeta} \tag{33}$$

which is indeed devoid of all information pertaining to the size of the coil. The above is precisely the result reported by Akcasu et al.,[2] who obtained this expression by considering the first cumulant of a closed chain in the limit $N \to \infty$, since closed and open chains in this limit behave indistinguishably. We are not aware of any previous reports of the low-q limit result obtain here.

Figure 2 shows the autocorrelation function for $qR_G = 4$ calculated from eq 5 with $N = 40$ (additional numerical details for this calculation are given in Appendix A.3). Also shown is the initial slope based on the first cumulant ($K_1 = 27.61/\tau_1$), and the long-time asymptote calculated from eq 32. The transition from slope $-K_1$ at $\tau = 0$ to slope $-2/\tau_1$ at long times is seen clearly. We also notice that the autocorrelation function at short τ deviates substantially from single-exponential behavior, as demonstrated by the fact that it decays much more slowly than one would predict on the basis of the first cumulant.

In Figure 3, we plot the autocorrelation function at $qR_G = 1$, 4, 6, 8, and 10. In all cases the long-time tail is exponential with decay rate $2/\tau_1$; by contrast, the behavior at low τ is strongly dependent on qR_G. These features can be understood by recalling that dynamic light scattering probes dynamic behavior at length scales of the order $\sim 2\pi/q$. At large q, the scattering length is much smaller than the length of the chain and thus is capable of probing the faster dynamics associated with the smaller segments of the chain whose combined effect gives rise to strong nonexponential decay near $\tau = 0$. The long time decay rate is still $2/\tau_1$ but this behavior becomes increasingly obscured by the contribution of the fast modes and its onset is delayed until longer times. In the low-q limit, the probing length is much larger than the chain itself. In this regime, the slowest decay rate is the dominating feature and the autocorrelation function appears to be single exponential with decay rate $2/\tau_1$. Even so, the initial slope approaches $K_1 \approx 30/\pi^2\tau_1 \approx 3/\tau_1$, not $2/\tau_1$, but the autocorrelation function reaches its long-time asymptote very quickly, thus obscuring this faster initial decay and giving the impression of a single exponential throughout. This behavior is demonstrated in the inset graph in Figure 3, which shows an expanded view of the autocorrelation function for $qR_G = 1$. In this case, the initial slope is $-K_1\tau_1 = -3.5$, compared to -2 at long times. Such behavior is counter-intuitive as one would have expected that the first cumulant goes over to $2/\tau_1$ when the autocorrelation is dominated by the slowest decay rate. This would indeed be the case if the autocorrelation function were the sum of a finite number of exponential terms. In the limit of the continuous chain, $N \to \infty$, there is an infinite number of modes with progressively shorter decay rates. Their combined contribution to the first cumulant represents not merely a nonzero correction, but one that amounts to about 50% of the slowest decay rate. In the limit $qR_G \to 0$ this behavior is largely a mathematical curiosity that remains inaccessible to experiment. Nonetheless, in comparing experimental measurements of the first cumulant to the predictions of eq 17 one should be aware of the discrepancies at the low-q limit.

4. Conclusions

We have obtained an analytic expression for the first cumulant of a Gaussian coil in the free-drainage limit. The asymptotic expressions for the first cumulant are given by $K_1 = 30/\pi^2\tau_1$ in the low-q limit, and $K_1 = (qR_G)^4/\pi^2\tau_1$ at the high-q limit. These asymptotes have power-law dependence on qR_G with exponents that are in compliance with scaling theory. We have further demonstrated that long-time decay toward the baseline is exponential in time with decay rate $2/\tau_1$, as Pecora showed, but this decay rate dominates the autocorrelation function only at long times. We further find that the first cumulant is always larger than $2/\tau_1$, though this value is experimentally inaccessible at very low qR_G. The transition to the long-time asymptote depends on the value of qR_G: in the high-q regime this transition takes place at very long times and the autocorrelation function is dominated by the dynamics of the faster modes; in the low-q region the transition occurs too close to $\tau = 0$ to allow accurate experimental observation and the autocorrelation function appears as a single exponential.

These results may be used to place the experimental investigations of internal relaxation modes into perspective. For $qR_G \gtrsim 1$, the autocorrelation function is dominated by the slowest relaxation decay rate and Pecora's methodology, which neglects the faster relaxation modes, is appropriate. In principle, this methodology remains valid as qR_G is decreased further but in practice, this region becomes increasingly more inaccessible as the signal is dominated by the diffusional motion of the center of mass. Above $qR_G \approx 6$, the autocorrelation function drops to noise levels before the slow mode can make a strong presence. This region requires a multiexponential treatment. In general, above $qR_G \approx 1$ enough curvature is present at short τ to allow the experimental determination of the first cumulant.

Appendix

A.1. Evaluation of $\sum_k R_{ik}R_{jk}$. In this section we calculate the summation $\sum_k R_{ik}R_{jk}$, which is required in the derivation of S_0'. First, we can easily show

$$R_{ik}R_{jk} = \frac{1}{2}\left[\cos\frac{k\pi(i-j)}{N} + \cos\frac{k\pi(i+j)}{N}\right] \tag{34}$$

for all k, even or odd. Next we recall the trigonometric identity (see ref 22, p 109)

$$\sum_{k=1}^{N}\cos ka = \frac{\sin\left(N+\frac{1}{2}\right)a}{2\sin\frac{a}{2}} - \frac{1}{2} \tag{35}$$

For the sum of $R_{ik}R_{jk}$ over k, we now have

$$\sum_{k=1}^{N}R_{ik}R_{jk} = \frac{1}{2}\left[\sum_{k=1}^{N}\cos ka_+ + \sum_{k=1}^{N}\cos ka_-\right] \tag{36}$$

with

$$a_\pm = \frac{\pi(i \pm j)}{N} \tag{37}$$

Using eq 35 with $a_\pm$ from above, we find

$$\sum_{k=1}^{N}\cos ka_\pm = \pm\frac{1}{2} - \frac{1}{2} = \begin{cases}0, & i \pm j \text{ even}\\ -1, & i \pm j \text{ odd}\end{cases} \tag{38}$$

with the result on the far right obtained by noting that the $\pm$ sign is selected if $i \pm j$ is even/odd. The summation in eq 36 then becomes

$$\sum_{k=1}^{N}R_{ik}R_{jk} = \begin{cases}0, & i-j \text{ even}\\ -1, & i-j \text{ odd}\end{cases} \tag{39}$$

where we took into account the fact that $i + j$ and $i - j$ are even, or odd, simultaneously. The case $i = j$ must be derived separately by setting $i = j$ in eq 36 and performing the summation. We find

$$\sum_{k=1}^{N}R_{ik}R_{jk} = \frac{1}{2}\sum_{k=1}^{N}\left[1 + \cos\frac{2k\pi i}{N}\right] = \frac{N}{2} \tag{40}$$

provided that $i \neq N$ and $i \neq 0$. The last cases to consider then are $i = j = N$ and $i = j = 0$, both of which are easily shown to give

$$\sum_{k=1}^{N}R_{Nk}R_{Nk} = N \tag{41}$$

The final result can be summarized as follows:

$$\sum_{k=1}^{N}R_{ik}R_{jk} \equiv h_{ij} = \begin{cases}N(1+\delta_{i0}+\delta_{iN})/2, & i = j,\\ 0, & i \neq j \text{ and } i-j \text{ even},\\ -1, & i \neq j \text{ and } i-j \text{ odd}\end{cases} \tag{42}$$

which is eq 15 of the text.

A.2. Evaluation of S_0'. Using $A_{ij}(0)$ from eq 13 and $A_{ij}'(0)$ from eq 14, eq 11 becomes

$$S_0' = -\frac{z}{N^2}\sum_i\sum_j h_{ij}F_{ij} \tag{43}$$

with h_{ij} from eq 42 and

$$F_{ij} = \exp\left[-\frac{z\pi 2|i-j|}{2N}\right] \tag{44}$$

We notice that F_{ij} has the same value along any row parallel to the diagonal, $i = j$, and is symmetric about the diagonal. In total there are $N + 1$ diagonal elements ($|i - j| = 0$), and $2(N + 2 - 2l)$ off-diagonal elements with $|i - j| = 2l - 1$, $l = 1, 2, \cdots N/2$. Along the diagonal ($|i - j| = 0$) we have $F_{ij} = 1$, $h_{ij} = N/2$, except for the first and last elements for which $h_{ij} = N$. The contribution of the diagonal to the double summation is

$$\frac{\sum_{\text{diag}}}{N^2} = \frac{1}{N^2}\left(N + \sum_{i=0}^{N}\frac{N}{2}\right) = \frac{1}{2} + O\left[\frac{1}{N}\right] \tag{45}$$

For the off-diagonal element $|i - j| = 2l - 1$, $l = 1 \cdots N/2$, we have $h_{ij} = -1$ and $F_{ij} = \exp[-z(2l - 1)/N]$. There are $2(N + 2 - 2l)$ such elements and their contribution to the double summation is

$$\frac{\sum_{\text{offdiag}}}{N^2} = \frac{1}{N^2}\sum_{l=1}^{N/2}(-1)(2)(N+2-2l)\exp\left[-z\pi^2\frac{2l-1}{2N}\right] \tag{46}$$

CDV

In the limit of large N the summation is well approximated by the integral using $y = l/N$; with $a = z\pi^2/2 = (qR_G)^2$, eq 46 gives

$$\frac{\sum_{\text{offdiag}}}{N^2} = -2\int_0^{1/2}(1-2y)e^{-2ay}\,dy = -\frac{e^{-a} - 1 + a}{a^2} = -\frac{S_0}{2} \tag{47}$$

where we have recognized in the right-hand side the scattering function of the coil from eq 8. The simplicity of this result suggests an alternative calculation of the off-diagonal sum. The summation of $\exp(-z|i-j|/N)$ over all i, j, gives the total intensity scattered by the coil;[13] the term, $\sum_{\text{offdiag}}$, is the same summation but only over every other diagonal row. For large N, skipping half of the diagonal rows amounts to obtaining half the value of the full sum, leading immediately to the right-hand side of eq 47.

Finally, combining the sum of the diagonal and off-diagonal terms we obtain

$$\frac{\sum_i \sum_j h_{ij} F_{ij}}{N^2} = \frac{1 - S_0}{2} \tag{48}$$

With this result and in combination with eq 43 we obtain eq 16 of the text.

A.3. Numerical Calculation of $S(q, \tau)$. Numerical calculations of the autocorrelation function were based on eq 5 with $A_{ij}(\tau)$ given by eq 6. Specifically, we calculate the quantity $G = S - S_\infty$ in eq 23, which gives the autocorrelation function with the baseline subtracted. Notice that this baseline is calculated consistently with the finite number of springs, N, and not by eq 9 which is valid for $N \to \infty$. The calculation is computationally demanding because it involves three summations (in i, j, and k) and the computational time scales as N^3. While it may possible to treat the summations as integrals when $N \to \infty$, we have opted for a brute-force calculation based on eq 5. Some computational savings can be achieved by recognizing that A_{ij} is symmetric in i, j; thus, only one subdiagonal summation needs to be considered. The calculations shown in the text were performed using $N = 40$. To assess the accuracy of this calculation we compute the autocorrelation function with N varying from 5 to 80 and calculate the error in the computed maximum at $\tau = 0$:

$$\text{error} = \left|\frac{G_N(0)}{S_0 - S_\infty} - 1\right| \tag{49}$$

$G_N(0)$ is the computed autocorrelation function at $\tau = 0$ for a given N, and S_0, S_∞ are given by eqs 8 and 9, respectively, corresponding to $N \to \infty$. In the limit $N \to \infty$, this error goes to zero. Figure 4 shows this error as a function of N. Also shown is the CPU time on a Powerbook G5 (1.5 GHz) using Mathematic 5.2. The convergence is nearly power-law in N with exponent −1.2 while CPU time increases as $N^{3.8}$. With $N = 40$ the error in eq 49 as 12% and the calculation takes about 12 min, as opposed to nearly 3 h with $N = 80$ and corresponding error of 5.6%. As the purpose of the computations was illustrative, $N = 40$ was considered a reasonable compromise between accuracy and computational time.

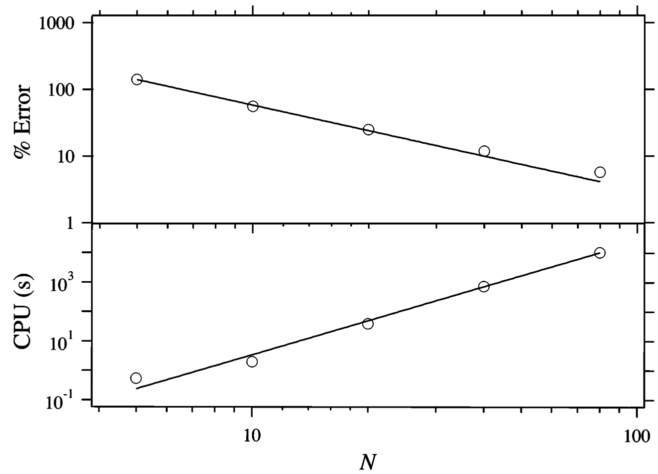

Figure 4. Percent error according to eq 49 and CPU time as a function of N.

References and Notes

(1) Schaefer, D. W.; Han, C. C. Quasielastic light scattering from dilute and semidilute polymer solutions. *Dynamic Light Scattering*; Plenum Press: New York, 1985; Chapter 5, p 181.
(2) Akcasu, A. Z.; Benmouna, M.; Han, C. C. *Polymer* **1980**, *21*, 866.
(3) Ellis, A. R.; Schaller, J. K.; McKiernan, M. L.; Selser, J. C. *J. Chem. Phys.* **1990**, *92*, 5731.
(4) Nicolai, T.; Brown, W.; Johnsen, R. *Macromolecules* **1989**, *22*, 2795.
(5) Reed, T. F.; Frederick, J. E. *Macromolecules* **1971**, *4*, 72.
(6) Sorlie, S. S.; Pecora, R. *Macromolecules* **1988**, *21*, 1437.
(7) Huang, W. N.; Frederick, J. E. *Macromolecules* **1974**, *7*, 34.
(8) Nishio, I.; Swislow, G.; Sun, S. T.; Tanaka, T. *Nature* **1982**, *300*, 243.
(9) Schaller, J. K.; Devanand, K.; Selser, J. C. *J. Chem. Phys.* **1993**, *98*, 1597.
(10) Pecora, R. *Science* **1991**, *251*, 893.
(11) Seils, J.; Pecora, R. *Macromolecules* **1992**, *25*, 350.
(12) Pecora, R. *J. Chem. Phys.* **1965**, *43*, 1562.
(13) Pecora, R. *J. Chem. Phys.* **1968**, *49*, 1032.
(14) Liu, H.; Gapinski, J.; Skibinska, L.; Patkowski, A.; Pecora, R. *J. Chem. Phys.* **2000**, *113*, 6001.
(15) de Gennes, P. E. *Physics* **1967**, *3*, 37.
(16) DuBois-Violette, E.; de Gennes, P.-E. *Physics* **1967**, *3*, 181.
(17) Berne, J. B.; Pecora, R. *Dynamic Light Scattering*; New York, Dover, 2000.
(18) Debye, P. In *Light Scattering from Dilute Polymer Solutions*; McIntyre, D., Gormick, F., Eds.; Gordon and Breach: New York, 1964.
(19) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(20) deGennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(21) Our expansion is essentially the same as Pecora's[13] except for the fact that we retain only the leading exponential term and obtain an explicit form for the preexponential factor. Our ΔS_0 corresponds to Pecora's factor, $P_2(x)$, which, however, is given in terms of other auxiliary functions ($P_1(x, k = 2)$ and $P_0(x)$, in Pecora's nomenclature).
(22) Spiegel, M. R. *Mathematical Outline Series*. Shaum's Outline Series; McGraw-Hill: New York, 1968.

MA061411O