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Dynamic Light Scattering from Flexible Ring Macromolecules

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ABSTRACT: The molecular dynamic form factor for the Rouse–Zimm free-draining Gaussian ring is calculated in a form which facilitates comparison with experimental scattering data. The relative contributions of the pure translation mode and various internal modes are given. At zero time, the dynamic form factor reduces to the well-known Casassa result for the static form factor. The differences in the dynamic form factors of linear and circular free-draining Gaussian chains are discussed.

I. Introduction

Ring-shaped macromolecules are of considerable theoretical interest since models for the dynamics of flexible and semiflexible polymers can be substantially simplified for circular closed chains.[1,2] Circular chains are equivalent to periodic linear chains[3] in the sense that they can be regarded as linear chains without end effects, making solutions for the dynamics of circular molecules valuable as reference solutions for linear chains. Moreover, understanding the dynamics of rings is crucial in answering one of the long-standing problems in polymer physics as to whether and/or to what extent polymer chains might reptate in concentrated solutions.[4]

The discovery of circular DNA[5] suggests a biological function of these species which has not yet become clear. It has also led to the analytical problem of distinguishing circular from linear molecules, which has motivated a number of theoretical[6–9] and, very recently, also Brownian dynamics simulation studies[10,11] on the hydrodynamic properties of circular chains. It has become clear from these studies that the difference between translation or sedimentation of circular and linear chains is only moderate whereas a pronounced effect on the internal motions should be expected if the ring-shaped macromolecule is compared to its linear counterpart. These findings indicate that viscosity and dynamic light scattering techniques would be suitable techniques to study the dynamic differences between circular and linear molecules.

In this study we focus on the molecular dynamic form factor which is experimentally accessible by photon correlation spectroscopy and, for larger scattering vector lengths, perhaps also by neutron spin–echo techniques. The dynamic form factor for linear free-draining Gaussian polymers ("the free-draining Rouse–Zimm model") has been calculated by Pecora.[12] Although various expressions for the dynamic form factor of circular chains have been given in the literature,[2,13–15] none has been given in a convenient analytical form which makes it possible to evaluate the contributions of the different relaxation modes to the form factor. In such a form, comparison with experimental dynamic light scattering intensity correlation functions is easily accomplished.[16,17]

II. Theory

Rouse–Zimm Model for Rings. The Rouse–Zimm model *in the free-draining limit describes the motion of* a completely flexible Gaussian chain consisting of N beads and, in the case of the circular chain, of N springs, each with root-mean-square length b. The forces driving the motion are an entropic force linear in the distance between next neighbor beads, a frictional force on each bead which is proportional to the velocity of the bead, and a random force exerted on each bead by the surrounding solvent.

Pecora[12] has calculated the dynamic form factor $S(q,t)$ for the linear chain as a function of the square of the normalized scattering vector x in the limit of large N where

$$x \equiv q^2 R_G^{\ 2} \tag{1}$$

and q and R_G are, respectively, the scattering vector length and the root-mean-square radius of gyration of the chain. Following his approach, $S(q,t)$ for the circular chain can also be obtained. From eq 8 of ref 12, $S(q,t)$ is given in terms of normal-mode parameters

$$S(q,t) = \exp(-D_0 q^2 t) N^{-2} \sum\sum \exp[-(1/6)q^2\{\sum \mu_k^{\ 2}[Q_{ik}^{\ 2} + Q_{jk}^{\ 2} - 2Q_{ik}Q_{jk}\exp(-t/\tau_k)]\}] \tag{2}$$

Here D_0 is the translational diffusion coefficient of the chain and μ_k^2 the mean-squared equilibrium length of the kth normal mode which may be shown to be

$$\mu_k^{\ 2} = Nb^2/2\pi^2k^2 \tag{3}$$

The Q_{ik}s are the Fourier coefficients which transform the normal coordinates to laboratory bead coordinates. In the case of the circular chain they have been given by, among others, Akcasu, Benmouna, and Han[14] and Soda:[2]

$$Q_{ik} = (1/N)^{1/2} \exp[(-i)2\pi ki/N] \tag{4}$$

Finally τ_k is the relaxation time of the kth normal mode and is given in terms of measurable quantities as

$$\tau_k = R_G^{\ 2}/k^2\pi^2 D_0 \tag{5}$$

Substituting the expression for the mean-square radius of gyration for Gaussian circular chains

$$R_G^{\ 2} = (1/12)Nb^2 \tag{6}$$

(which, it should be noted, is half that for the corresponding linear chain) and defining for convenience

$$R_{ik} \equiv Q_{ik}/(1/N)^{1/2} \tag{7}$$

we find that expansion of the first exponential of the time-dependent factor of the k sum in eq 2 yields

$$P(x,t) = \exp(-D_0 q^2 t) \sum_{M=0}^{\infty} P_M(x,t) \tag{8}$$

where

$$P_M(x,t) = N^{-2}\sum_{i=0}^{N}\sum_{j=0}^{N}\exp[-(x/\pi^2)\sum_{k=1}^{N}k^{-2}(R_{ik}^{\ 2} + R_{jk}^{\ 2})] \times (M!)^{-1}\{(2x/\pi^2)\sum_{k=1}^{N}(R_{ik}R_{jk})/k^2 \exp(-t/\tau_k)\}^M \quad (9)$$

The first term in the expansion, $\exp(-D_0q^2t)P_0(x)$, is a pure translational diffusion contribution to the correlation function. Its relative contribution to the scattered light intensity is given as a function of x by $P_0(x)$. With eq 4 the k sum simplifies to

$$\sum_{k=1}^{N}\frac{1}{\pi^2k^2}(R_{ik}^{\ 2} + R_{jk}^{\ 2}) = \frac{1}{3} \quad (10)$$

Substituting eq 10 into eq 9, we obtain

$$P_0 = \exp[-(1/3)x] \quad (11)$$

Equation 11 was previously obtained by Akcasu, Benmouna, and Han.[14]

The total contributions to the scattered light of the other $P_M(x)$ terms are obtained by setting $t = 0$ in eq 9 and replacing the double sums over segments i and j by integrations. This gives for the first six terms

$$P_M(x) = a_Mx^M\exp[-(1/3)x] \quad (12)$$

where

$$a_1 = 0$$

$$a_2 = 1/90$$

$$a_3 = 1/2835$$

$$a_4 = 1/22680$$

$$a_5 = 1/1122660$$

$$a_6 = 53/525404880$$

It follows that the next important term after diffusion is the P_2 term, as is the case for the linear molecule. To calculate the contribution of the slowest internal relaxation time to P_2, we note that

$$P_2(x,t) = N^{-2}\exp[-(1/3)x]2x^2\sum_{kk'}\sum_{i=0}^{N}\sum_{j=0}^{N}F \times \frac{\cos\left(\dfrac{2\pi k|i-j|}{N}\right)}{\pi^2k^2}\frac{\cos\left(\dfrac{2\pi k'|i-j|}{N}\right)}{\pi^2k'^2}\exp(-t/(\tau_k + \tau_{k'}) \quad (13)$$

where $F = 1$ or $F = 2$ when $k = k'$ or $k \neq k'$. The double sum over the segments i and j can be replaced by a single sum since it only depends on the difference of i and j. Replacing the sum by an integral and dropping terms of order $1/N$, we finally get

$$P_2(x,t) = N^{-1}\exp[-(1/3)x]2x^2\sum_{kk'}\int_{a=1}^{N}2(N-a)F \times \frac{\cos\left(\dfrac{2\pi ka}{N}\right)}{\pi^2k^2}\frac{\cos\left(\dfrac{2\pi k'a}{N}\right)}{\pi^2k'^2}\exp(-t/\tau_k + \tau_{k'})\,\mathrm{d}a \quad (14)$$

where $a \equiv |i-j|$. Using the well-known trigonometric identities

$$\cos^2\left(\frac{2\pi ka}{N}\right) = \frac{1}{2}\left(1 + \cos\left(\frac{4\pi ka}{N}\right)\right)$$

and

$$\cos\left(\frac{2\pi ka}{N}\right)\cos\left(\frac{2\pi k'a}{N}\right) = \cos\left(\frac{2\pi a(k-k')}{N}\right) + \cos\left(\frac{2\pi a(k+k')}{N}\right)$$

we get for $k = k' = 1$ the contribution of the longest internal mode

$$P_{211}(x) = \exp[-(1/3)x]\frac{x^2}{\pi^4}\exp(-t/(2\tau_1)) \quad (15)$$

Using eq 5, we find that the next modes are

$$P_{222}(x) = \exp[-(1/3)x]\frac{x^2}{16\pi^4}\exp(-t/(8\tau_1)) \quad (16)$$

$$P_{233}(x) = \exp[-(1/3)x]\frac{x^2}{81\pi^4}\exp(-t/(18\tau_1)) \quad (17)$$

All $P_{2kk'}$ with $k \neq k'$ are 0.

These calculations can easily be extended for the $P_{3kk'k''}(x)$ terms which can be shown to be zero. It turns out that the terms contributing to the various P_M with odd M amplitudes equal to 0 if only the leading terms which are independent of N are considered. The neglected terms with magnitudes of order $1/N$, which are insignificant for the contributions of individual modes, however, add up to give a nonvanishing contribution to the scattered light given by the coefficients a_3, a_5, etc. From an experimental point of view they do not contribute to the correlation function since most of them are high-frequency low-contribution modes which would generally be outside the time range of a photon correlation spectroscopy experiment.

The total integrated intensity may also be obtained by setting $t = 0$ in eq 2 which yields

$$P(x) = N^{-2}\sum_{i=0}^{N}\sum_{j=0}^{N} \times \exp\left(-\frac{2x}{\pi^2}\sum_{k=1}^{N}\frac{1}{k^2} - \sum_{k=1}^{N}\frac{\cos\left(\dfrac{2\pi k(j-i)}{N}\right)}{k^2}\right) \quad (18)$$

Expanding the k sums to infinity yields well-known sums which are tabulated[18] and lead to the result

$$P(x) = N^{-2}\sum_{i=0}^{N}\sum_{j=0}^{N}\exp\left(-2x\left(\frac{|j-i|}{N} - \frac{|j-i|^2}{N^2}\right)\right) \quad (19)$$

Again the double sum can be replaced by a single sum dropping terms of order $1/N$ which yields

$$P(x) = N^{-1}\sum_{a=1}^{N-1}\exp\left(-2x\left(\frac{a}{N} - \frac{a^2}{N^2}\right)\right) \quad (20)$$

where, as before, $a \equiv |i-j|$.

Replacing the summation by an integration, we finally obtain

$$P(x) = 2^{1/2}x^{-1/2}\exp[-(1/2)x]\int_0^{(x/2)^{1/2}}\exp(z^2)\,\mathrm{d}z \quad (21)$$

which is exactly the same as obtained by Casassa for Gaussian rings.[6]

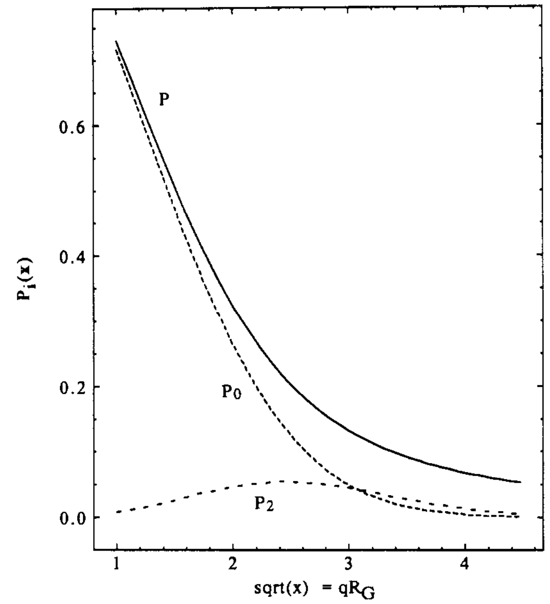

Figure 1. Relative intensities of scattered light from Gaussian rings. The figure shows the total scattered intensity $P(x)$ calculated from the Casassa equation, eq 21; the intensities of the pure translational contribution $P_0(x)$ and the sum of all $P_2(x)$ terms calculated from eqs 11 and 12.

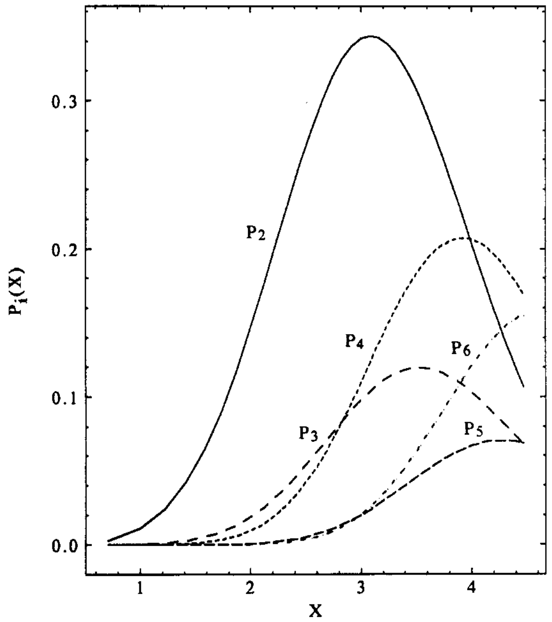

Figure 2. Relative intensities of scattered light from Gaussian rings for the sum of the P_2 to P_6 terms.

III. Numerical Calculations and Discussion

Figure 1 shows the contributions of the translational and the sum of all P_2 terms to the total scattered light intensity $P(x)$ as a function of the reduced scattering vector x. P_2 was obtained by eq 12 and numerically by eq 9 setting $t = 0$ for a chain with 250 segments. The curves are indistinguishable, showing the utility of the expansion in eq 12. Since P_2 is dominated by $P_{211} = 91\%$, Figure 1 represents as well the relative contributions of the pure translational and longest internal relaxation frequencies to the correlation function for various scattering vectors. Similar calculations were performed for other terms up to P_6 which are displayed in Figure 2. The odd terms contribute much less to the scattered light intensity integrated over all scattering vectors as the even terms. For instance, the area under P_4 and even P_6 is larger than under P_3. We mentioned already that the leading terms are in fact zero for the odd terms and the scattered light is produced by a huge number of fast relaxing modes with very small amplitudes that would be difficult if not impossible to detect in an experiment. To compare correlation functions for flexible Gaussian rings with experimental ones, it should therefore be sufficient to keep only those low frequencies which are connected to the even terms in eq 8.

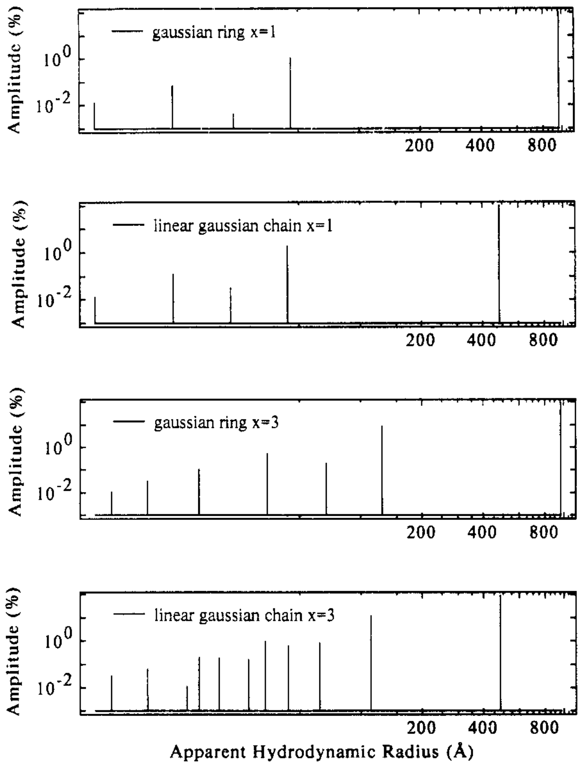

Figure 3. Relaxation time spectra of Gaussian chains. The relaxation times are expressed in units of the apparent hydrodynamic radius $R_h \equiv \tau q^2 kT/6\pi\eta$. They are calculated for a translational diffusion coefficient. $D_0 = 4.46 \times 10^{-10}$ m^2/s and a root-mean-square radius of gyration $R_G = 104$ nm in water at a temperature of 20 °C for the linear chain, parameters corresponding to those for a 2311 base pair DNA.[16,17] The scattering angles are 30° and 58° at a wavelength of 488 nm. The D_0 of the circular chain reduces to 2.23×10^{-10} m^2/s, keeping R_G constant. The translational relaxation time is included in all relaxation modes. The displayed relaxation times contribute 99.96%, 99.92%, 98.94%, and 99.13%, (from top to bottom respectively), to the total scattered light intensity.

The most pronounced differences in the form factors for circular and linear flexible Gaussian chains arise from the factor of 2 smaller mean-square radius of gyration for the circular chain, eq 6. This leads to a factor of 4 faster internal motions and a lower contribution of the internal modes to the correlation function for circular chains. Since the translational diffusion coefficients of circular and linear molecules, on the other hand, are rather similar (for the free-draining model they are, in fact, the same), the internal modes are more separated in time from the pure translational mode in the case of circles. Thus, we conclude that the experimental separation of internal modes from the translational diffusion would be easier for circular chains than for linear ones. This behavior becomes obvious if one compares the frequency spectrum of a linear Gaussian chain with total length L with that of a circular one which has twice the contour length of the former. This, in principle, means comparing them at the same x. For the free-draining Rouse–Zimm model the internal relaxation times for both chains are in this case exactly the same whereas the translational diffusion time for the circular chain should be twice as long as for the linear one. This can be seen by comparing eq 5 with the analogous equation for the linear case which reads

$$\tau_m = 2R_G^{\,1}/\pi^2 m^2 D_0^{\,1} \tag{22}$$

Setting $R_G = R_G^1$ and $D_0^1 = 2D_0$ yields $\tau_m = \tau_k$.

The difference in the dynamic form factors of linear and circular chains is not only a question of different length scales expressed by R_G. This can be demonstrated again by comparing both form factors at the same x. Such a comparison has been done in Figure 3, where the amplitudes and positions of the dominant relaxation frequencies are plotted for circular and linear free-draining Rouse–Zimm chains at two different x. Note that the displayed relaxation times contribute in all cases to about 99% of the total scattered light intensity, indicating that no major relaxation time has been overlooked. The larger separation of the translational relaxation time from internal modes in the case of the circular chain is also nicely demonstrated. Other differences between circular and linear Gaussian chains that should also be noted are the slightly lower contribution of internal modes to the spectrum for the circular chains and the lower density of these modes. The last finding results from the already mentioned negligible amplitudes of the odd-numbered modes which are therefore not displayed in the spectrum.

IV. Conclusion

The dynamic form factors for radiation scattered from Gaussian rings have been calculated in a way that makes comparison with dynamic light scattering experiments convenient.[16,17] The contribution of all internal relaxation times to the intensity of the scattered light can be expressed by very simple analytical expressions. The differences from linear Gaussian chains have been worked out and discussed in detail. With the developed analytical expressions the calculation of the spectral distribution of scattered light including hydrodynamic interaction should be straightforward. For this purpose the free-draining solution could serve as a reference solution for a perturbation approach which has been used earlier for linear Gaussian chains.[19,20]

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