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First cumulant of the dynamic structure factor for rigid rings†

Klaus Huber and Walter H. Stockmayer
Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, USA
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The first cumulant of the dynamic structure factor is evaluated for rigid ring polymers. The results, together with those for flexible polymers, suggest that a careful experimental intercomparison of rings and open-chain polymers at low magnitudes of the scattering vector could serve to assess the degree of validity of the preaveraging approximation for the hydrodynamic interactions.

(Keywords: dynamic light scattering; first cumulant; rigid rings; hydrodynamic interactions)

The aim of this short paper is to fill a gap in our knowledge about the rigid circular limit of polymeric ring molecules, namely the first cumulant of the dynamic structure factor. The static structure factor of such rigid rings was calculated by Oster and Riley[1] and Burchard[2]. First calculations on the dynamics of circular rings were published by Tchen[3] in 1954. He derived the translational friction coefficients of circles and half-rings. Using Tchen's results in the limit of an infinitely large number N of friction centres, Zwanzig[4] showed that Kirkwood's general theory[5] of irreversible processes in polymer solutions yields only an approximate value for the mean translational diffusion coefficient D, differing by a factor 11/12 from Tchen's exact result. Finally, Paul and Mazo[6,7] and later Yamakawa and Yamaki[8] calculated translational and rotational diffusion coefficients which are valid for all N.

Our starting point is the derivation of the Fourier-transformed density distribution $\rho(q)$ for a continuous circle:

$$\rho(q) = (1/4\pi^3) \int \delta(\mathbf{s}-\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{s}) \mathrm{d}s \tag{1}$$

where $\mathbf{q}$ is the scattering vector, of magnitude $q = (4\pi/\lambda)\sin(\theta/2)$, and the vector $\mathbf{r}$ connects the centre of the ring to all points along the contour of the ring. With $\mathbf{q}$ in the laboratory-fixed coordinate system, we have:

$$\mathbf{q}\cdot\mathbf{r} = qr \sin\beta \sin\gamma \tag{2}$$

Here, r is the radius of the ring and β and γ are Eulerian angles[9], the former describing the polar angle and the latter the rotation about the symmetry axis. Integration of equation (1) yields:

$$\rho(q) = (1/2\pi^2) J_0(qr\sin\beta) \tag{3}$$

with J_0 the Bessel function of zeroth order. This density distribution is related to the particle scattering function $P(q)$ by:

$$P(q) = \langle \rho^*(q)\rho(q) \rangle \tag{4}$$

The brackets stand for equilibrium average over all orientations of the ring in the laboratoy-fixed coordinate system. Equation (4) together with equation (3) finally leads to the known[1] expression:

$$P(q) = \int_0^{\pi/2} J_0^2(qr\sin\beta)\sin\beta\,\mathrm{d}\beta \tag{5}$$

It is perhaps worth mentioning that this expression is equivalent[10] to

$$P(q) = (1/2qr) \int_0^{2qr} J_0(t)\,\mathrm{d}t \tag{6}$$

Having $\rho(q)$ available, we may use the equation of Akcasu and Gurol[11],

$$\Omega(q) = \frac{\langle \rho^*(q) L \rho(q) \rangle}{\langle \rho^*(q)\rho(q) \rangle} \tag{7}$$

to derive the angular dependence of the first cumulant. The translational-plus-rotational diffusion operator is:

$$L = -\nabla \underset{\sim}{D} \nabla + L_{\mathrm{rot}} \tag{8}$$

where

$$-\nabla \underset{\sim}{D} \nabla = -[D + (3\cos^2\beta - 1)\Delta/2]\nabla^2 \tag{9a}$$

with $D \equiv (D_\perp + 2D_\parallel)/3$ and $\Delta \equiv 2(D_\perp - D_\parallel)/3$. The Laplacian ∇^2 refers to the translation of the centre of mass and $D_\perp$, $D_\parallel$ are translational diffusion coefficients perpendicular and parallel to the plane of the ring. Since $\rho(q)$ does not depend on γ or the third Euler angle, the relevant rotational diffusion operator is simply:

$$L_{\mathrm{rot}} = -\Theta_\parallel \frac{1}{\sin\beta} \frac{\partial}{\partial\beta} \sin\beta \frac{\partial}{\partial\beta} \tag{9b}$$

where $\Theta_\parallel$ is the rotational diffusion coefficient about an axis in the plane of the ring.

Equations (3), (4), (5) and (9) provide the relationships required to calculate $\Omega(q)$ according to equation (7). Pursuing this procedure, we obtain the following expression:

$$\Omega(q) = q^2 D + q^2 \Delta \frac{I_1}{P(q)} + \Theta_\parallel \frac{2qrI_2 - 3qrI_3 - q^2r^2(I_4 - I_5)}{P(q)} \tag{10}$$

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† Dedicated with admiration and affection to Manfred Gordon on his 70th birthday.

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The terms I_1, I_2, I_3, I_4 and I_5 are integrals of products of Bessel functions, which can be represented as hypogeometric series[10,12]:

$$I_1=\int_0^{\pi/2}(\sin\beta-(3/2)\sin^3\beta)J_0^2(qr\sin\beta)\,\mathrm{d}\beta$$
$$=\frac{\sqrt{\pi}}{2}\sum_{k=0}^{\infty}(-1)^k\frac{(2k)!\,(qr/2)^{2k}}{(k!)^3\Gamma(k+3/2)}$$
$$-\frac{\sqrt{\pi}\,3}{4}\sum_{k=0}^{\infty}(-1)^k\frac{(2k)!\,(k+1)!\,(qr/2)^{2k}}{(k!)^4\Gamma(k+5/2)}\qquad(11a)$$

$$I_2=\int_0^{\pi/2}J_0(qr\sin\beta)J_1(qr\sin\beta)\,\mathrm{d}\beta$$
$$=\frac{qr}{2}\sum_{k=0}^{\infty}(-1)^k\frac{k!\,(qr)^{2k}}{[(k+1)!]^2}\qquad(11b)$$

$$I_3=\int_0^{\pi/2}J_0(qr\sin\beta)J_1(qr\sin\beta)\sin^2\beta\,\mathrm{d}\beta$$
$$=qr\sum_{k=0}^{\infty}(-1)^k\frac{(qr)^{2k}}{(2k+3)(k+1)!}\qquad(11c)$$

$$I_4=\int_0^{\pi/2}J_0(qr\sin\beta)J_2(qr\sin\beta)\sin\beta\,\mathrm{d}\beta$$
$$=\frac{(qr)^2}{4}\sum_{k=0}^{\infty}(-1)^k\frac{(qr)^{2k}}{k!\,(k+2)^2(2k+3)}\qquad(11d)$$

$$I_5=\int_0^{\pi/2}J_0(qr\sin\beta)J_2(qr\sin\beta)\sin^3\beta\,\mathrm{d}\beta$$
$$=2(qr)^2\sum_{k=0}^{\infty}(-1)^k\frac{(qr)^{2k}}{k!\,(k+2)(2k+5)(2k+3)}\qquad(11e)$$

The symbol Γ in equations (11) represents the gamma function.

In real scattering experiments, the range of the product $\langle S^2\rangle q^2$, where $\langle S^2\rangle$ is the mean square radius of gyration, is often fairly small, either because the molecules are small or the wavelength of the scattered radiation is large, or both. The first cumulant then can be expanded in powers of $\langle S^2\rangle q^2$,

$$(\Omega/q^2)=D(1+C\langle S^2\rangle q^2+\ldots)\qquad(12)$$

The coefficient C in equation (12) depends on the spatial structure of the scattering molecule, and its theoretical value for a given structure is also influenced by the excluded-volume interactions and by the formula used for the hydrodynamic interactions amongst the parts of the molecule. These interactions, according to the Oseen formula introduced into polymer theory by Kirkwood[5], depend for a given pair of chain elements on both the separation and orientation of the pair. For most applications it has been found necessary (or at least highly desirable) to produce a great simplification[5] by averaging the hydrodynamic interactions at the start over the equilibrium distribution of separations and orientations. The Akcasu–Gurol formula[11], equation (7), happily allows explicit calculations without the preaveraging step, as well as with it; and the resulting values of C are indeed different in the two cases. Thus, in principle, accurate determinations of C might be used to probe the validity of the chosen hydrodynamic description. This is a worthy objective, since it is not obvious that macroscopic hydrodynamics should apply with high accuracy at the molecular level. Existing scattering data on C for linear flexible chains seem to favour the full non-preaveraged Oseen formulation over the preaveraged approximation, provided that adequate attention is paid to the coarse-graining necessarily produced in the correlation equipment[17]. However, at higher q-values, in the so-called intermediate q region, it appears[18] at present that the preaveraged formula may actually be superior. More work on this question is clearly needed, and our calculations on ring molecules suggest some additional types of experiment.

Table 1 C-coefficients (equation 12) for linear and cyclic polymers

	Hydrodynamic interactions	C	Reference
Rigid rod	pa	2/15	16
	n-pa	1/30	
Gaussian coil	pa	2/15	15
	n-pa	13/75	
Rigid ring	pa	1/15	This work
	n-pa	7/165	
Gaussian ring	pa	1/12	14
	n-pa	2/15	

In *Table 1* we have summarized the existing calculations of C for rings and open linear macromolecules. Using the diffusion coefficient of Paul and Mazo[6,7] for rigid rings of small thickness in the full Oseen approximation, we find $C=7/165$, while the preaveraged diffusion coefficients[13] yield $C=1/15$. We call attention to several features revealed in *Table 1*.

(1) The values of C for the rigid molecules, both rod and ring, are considerably greater with the preaveraging approximation than if the full fluctuating Oseen formula is used. This is largely due to the fact that the asymmetry Δ in the translational diffusion coefficient is negative but is without effect in the preaveraged case since $(3\cos^2\beta-1)$ averages to zero.

(2) In the flexible Gaussian limit the preaveraged values of C are smaller than the full Oseen values. Since both distances and orientations are involved in the averaging process here, it is harder to give an intuitive reason in this case.

(3) In *both* flexible and rigid limits, the ratio C(ring)/C(open chain) is significantly greater in the fluctuating case than the preaveraged one; the difference is about 23% in the flexible Gaussian limit and rises to over 150% as the rigidity increases. Thus careful experiments on rings and chains of any rigidity could furnish criteria for judging the validity of the preaveraging approximation.

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