Quasi-elastic scattering by semiflexible rings*

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Quasi-elastic scattering by semiflexible rings is discussed with a modified version of an earlier theory due to Soda and Berg. The modified theory automatically yields correct results in the highly flexible Gaussian limit, but is found to be erroneous at very high degrees of stiffness. For moderate degrees of stiffness, the results obtained for the first cumulant should be reliable.

(Keywords: quasi-elastic light scattering; semiflexible rings; first cumulant; chain stiffness)

INTRODUCTION

The conformation and dynamics of semiflexible polymeric rings have been of interest ever since the recognition of circular DNA. In the past few years this interest has been augmented by the appearance of various synthetic macrocycles, including cyclopoly(dimethylsiloxanes) and cyclopoly(styrenes)[1–4]. In the present paper we discuss some aspects of quasi-elastic light (or neutron) scattering by such rings, augmenting and modifying a previous theoretical presentation by one of us[5]. We concentrate mainly on low scattering vectors and moderate degrees of chain stiffness. Hydrodynamic interactions are, as before[5], described at the pre-averaged level. Excluded-volume effects are neglected.

The translational diffusion and intrinsic viscosity of semiflexible rings have been treated by Fujii and Yamakawa[6].

MODIFIED SODA–BERG MODEL

The previous model[5] built on an earlier treatment of free-draining semiflexible rings by Berg[7], who adapted the open-chain theory of Harris and Hearst (HH)[8,9] to the cyclic case. Hereinafter we refer to it as the SB (for 'Soda–Berg') model. The main purpose of that work was to introduce the hydrodynamic interactions, and to display the form of the results for the case of a continuous ring or chain.

A basic deficiency of the HH model is that it fails to preserve a constant contour length of the chain. This was well known to its creators, and is thoroughly discussed elsewhere by one of us[10]. Each bond in the chain is constrained to have a fixed mean-square length, but fluctuations about this value still occur. The practical advantage of the quadratic condition is of course that the effective potential energy is still Gaussian, permitting the construction of a set of normal coordinates; indeed, Simon[11] pointed out that the HH model is equivalent to a bead-and-spring construction with Gaussian springs between second as well as nearest neighbours. For a ring of N beads and N bonds, the model is therefore described by Langevin equations (or equivalent diffusion equations) in $3N$ dimensions. Rigorous constraints to produce constant bond lengths (and perhaps also bond angles) would require much more difficult formalisms such as those of Fixman and Kovac[12] or of Titulaer and Deutch[13], and these are not contemplated here.

Our modification of the original SB model[5] is merely to alter numerical factors in several of the working equations. In constructing his theory, Berg[7] contended that the intended constraint of each of the N bond lengths to a constant value would reduce the number of degrees of freedom to $2N$, and he used this figure in applying the fluctuation–dissipation theorem. (This argument was *not* made by HH.) The Berg option was used in the original SB theory[5]. From a purely practical point of view, it is unacceptable because it fails to reproduce the known[14] relations for Gaussian chains in the limit of high flexibility. When the total number of degrees of freedom is taken as $3N$ (as in the present paper), the correct high-flexibility limit is obtained. However, even after this change, the behaviour of the model in the rigid-ring limit (Appendix C) fails to match the known exact results[15].

More fundamentally, the same basic question regarding constrained coordinates has often been discussed previously, for example by Fixman[16] and Helfand[17]. Since physical bonds are never perfectly rigid, each bond coordinate naturally shares in the equipartition of kinetic energy. This is seen very clearly, for example, in the presentation of Titulaer and Deutch[13]. It is also evident for the physical SB model, since after the imposition of the constraints on the second moments there are still $3N$ variable coordinates described by Langevin equations, and N of these describe bond stretching (of Gaussian springs). With more realistic stiff-chain models[10,12,13], these degrees of freedom would

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still exist, but they would be described by very different dynamical equations.

Thus far in the literature, models of the HH type have almost always been developed in terms of Langevin equations. Passage to the related Fokker–Planck equation was avoided, and of course is not necessary; but if the usual path to the diffusion limit is followed (Appendix A) the kinetic energy problem is automatically avoided and answered correctly. With augmentation of the kinetic energy by a factor of 3/2, the various SB equations[5,7] can now be further investigated. It is only necessary to multiply the thermal energy $k_B T$ by 3/2 wherever this occurs.

When the present work was started, we had hoped to adapt to rings a tractable and rather accurate approximate treatment of the statistics of worm-like chains due to Koyama[18] and already used successfully[19] for the open-chain light-scattering problem. However, the Koyama method requires an expression for the fourth moments of the inter-bead distances; this is of course well known for the Kratky–Porod worm-like open chain[20,21], but so far we have been unable to derive (or find in the literature) its counterpart for a worm-like ring.

Since the HH model has been shown to give rather good results for low-q scattering by open chains no shorter than a few persistence lengths[19], we consider that our modified SB theory should have a similar range of applicability.

In view of the fact that the HH and SB models place constraints directly on the second moments of bond lengths, we should expect to obtain rather good predictions of mean-square radii of gyration. For low stiffness, this was already verified by Berg, who found only small departures of the calculated mean-square radii $\langle S^2 \rangle$ from values predicted for a worm-like ring by Fujii and Yamakawa[6]. It is not difficult to extend Berg's calculations numerically, and we find that his expression for $\langle S^2 \rangle$ agrees well (though not perfectly), over the whole range of stiffness, with the virtually exact expression given by Shimada and Yamakawa[22]. This reinforces the statement of Berg, on physical grounds, that his formalism for rings is more successful than the Harris–Hearst theory for open chains. However, evaluation of the particle scattering factor $P(q)$ in the rigid-ring limit shows (Appendix C) that the model fails rather badly to match the details of the ring conformation, even though in this limit it gives the correct mean-square radius of gyration.

QUASI-ELASTIC SCATTERING AND FIRST CUMULANT

The equations to be displayed differ from corresponding ones by Soda[5] or Berg[7] only in certain numerical factors. In referring to one of their equations we shall use a corresponding prefix Sa or Bg. We work, except in Appendix A, entirely in the continuous-ring limit.

The dynamic structure factor is (Sa65):

$$S(q, t) = 2L\alpha^2 \exp(-q^2 Dt) \int_0^{L/2} \mathrm{d}s\, c(q, s, t)$$

with a modified form of (Sa64):

$$\ln c(q, s, t) = -\sum_{n=1}^{\infty} (2k_B T q^2 / L\lambda_n) \times [1 - \cos(2\pi sn/L) \exp(-t/\tau_n)] \quad (1)$$

Here $q = (4\pi/\lambda)\sin(\theta/2)$, the magnitude of the scattering vector; α is excess polarizability per unit length; L is contour length; and D is the translational diffusion coefficient. The quantities λ_n and τ_n are eigenvalue and relaxation time of the nth normal mode. For the continuous ring, the former is given by (Sa36):

$$\lambda_n = \varepsilon(2\pi n/L)^4 + \kappa(2\pi n/L)^2$$

and the latter by (Sa33):

$$\tau_n = \zeta_n/\lambda_n$$

with

$$\zeta_n = 3\pi\eta_0 \Big/ \int_0^{L/2} \mathrm{d}s\, K(s) \cos(2\pi ns/L) \quad \text{(Sa50)}$$

The elastic bending constant ε is related to the persistence length, not by (Bg25) but by:

$$\varepsilon = 3k_B T/4\lambda \quad (2)$$

which is the original relation of HH[8], where λ = Kuhn length. The other force constant κ, formally introduced via the constraints on the mean-square bond lengths, is in effect a bond-stretching force constant. It is to be found from a modified form of (Bg28) or (Sa38), which reads:

$$2(\kappa\varepsilon)^{1/2}/3k_B T = \coth(\kappa L^2/4\varepsilon)^{1/2} - (4\varepsilon/\kappa L^2)^{1/2} \quad (3)$$

Thus from equations (2) and (3) the eigenvalues λ_n of (Sa36) can be constructed for any L and λ. Finally, the function $K(s)$ to be used in equation (Sa50) for the friction factors ζ_n is that presented by Fujii and Yamakawa[6], with different analytical expressions for the cases of weak or strong bending moduli.

With the above expressions one can generate modified numerical results comparable to those displayed in the earlier SB theory[5]. Here, however, we restrict our attention to the first cumulant and especially to its behaviour at low values of q, as exemplified by the coefficient C in the relation:

$$-[\mathrm{d} \ln S(q, t)/\mathrm{d}t]_{t=0} = \Gamma = q^2 D(1 + Cq^2\langle S^2 \rangle + \cdots) \quad (4)$$

We use equations (Sa66)–(Sa70), appropriately modified, to obtain:

$$C\langle S^2 \rangle = 2(k_B^2 T^2/DL^2) \sum_{n=1}^{N/2} \zeta_n^{-1} \lambda_n^{-1} \quad (5)$$

Further, appropriate modification of (Bg30) and (Bg37) gives:

$$\langle S^2 \rangle = 6(k_B T/L) \sum_{n=1}^{N/2} \lambda_n^{-1} \quad (6)$$

so that finally we get:

$$C = (k_B T/3DL) \sum_n \zeta_n^{-1} \lambda_n^{-1} \Big/ \sum_n \lambda_n^{-1} \quad (7)$$

We can now evaluate C numerically from the above result together with (Sa36) and (Sa50) given above, plus the recipe for the translational diffusion coefficient (Sa52):

$$D = (k_B T/3\pi\eta_0 L) \int_0^{L/2} K(s)\, \mathrm{d}s \quad \text{(Sa52)}$$

and the Fujii–Yamakawa[6] expressions for $K(s)$. The broken curve III of *Figure 1* exhibits the result of such a calculation, where the logarithmically scaled abscissa is the number λL of Kuhn lengths. For comparison, the

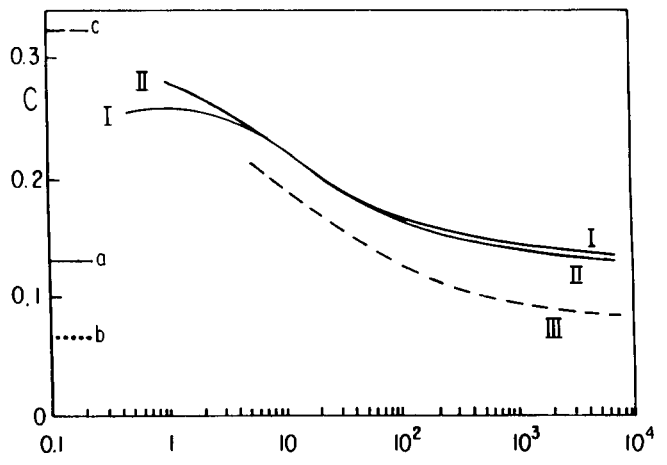

Figure 1 Coefficient C in first cumulant, equation (4), for semiflexible structures as a function of the number λL of Kuhn lengths: curve I, open chain, Koyama model; curve II, open chain, Hearst–Beals–Harris model; curve III, ring, modified SB model (present paper). Rigid limits are shown for: a, rigid rod; b, rigid ring; c, rigid ring according to modified SB model

full curves I and II represent the published calculations[19] for semiflexible linear chains, also with pre-averaged hydrodynamic interactions, based on the Koyama[18] interpolation and on the Hearst–Beals–Harris[9] model, respectively. For all three curves, the ratio of the chain diameter d to its Kuhn length $1/\lambda$ is kept at $\lambda d = 0.003$. The Gaussian limits of curves I (or II) and III at very large λL are 2/15 and 1/12, respectively. Thus, the ratio C(ring)/C(open) starts at 5/8 for very flexible chains, grows to a value of about 0.9 at $\lambda L \sim 10$, and ultimately drops to 1/2 for the rigid limit[15]. This is the chief new result of this paper.

The C value of 1/12 for Gaussian rings ($\lambda L \gg 1$) was previously derived by Burchard and Schmidt[14] by direct application of the Akcasu–Gurol[23] formula. In Appendix B we show that the same result follows from equation (7). Without modification, the original SB theory would lead to $C = 1/18$.

At greater degrees of stiffness than $\lambda L \simeq 1$ we cannot expect the present theory to be very reliable, as was indeed also true for the open-chain calculation[19] based on HH or Koyama models. The rigid-ring limit of the present theory can be evaluated exactly (Appendix C). It is found that, although the correct radius of gyration is obtained, the details of the particle scattering factor are quite different from the proper ones, and the value of C is 1/3 instead of the exact value 1/15.

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APPENDIX A

Diffusion equation for SB model

The Kirkwood diffusion equation for motion of a polymer molecule in solution is well known[21]. We write it in the form (for a discrete ring of N beads):

$$\partial\Psi/\partial t = \nabla^{\mathrm{T}} \cdot (k_{\mathrm{B}}T/f)\boldsymbol{H}[\nabla\Psi + (\Psi/k_{\mathrm{B}}T)\nabla V] \quad \text{(A1)}$$

where $\Psi(R, t)$ is the distribution function; R is a column matrix of N bead coordinates $\boldsymbol{r}_j$; V is the potential of mean force among the beads; and $\boldsymbol{H}$ is the $N \times N$ hydrodynamic-interaction matrix, which in its pre-averaged form has the elements:

$$H_{jl} = \delta_{jl} + (1-\delta_{jl})(f/6\pi\eta_0)\langle|\boldsymbol{r}_j - \boldsymbol{r}_l|^{-1}\rangle \quad \text{(A2)}$$

or

$$H_{jl} = \delta_{jl} + (1-\delta_{jl})(f/6\pi\eta_0)K(s) \quad \text{(A3)}$$

in the symbolism of Fujii and Yamakawa[6]. Here f is the bead friction coefficient and η_0 the solvent viscosity.

For the discrete SB ring the potential is given by equation (Sa6), which in matrix form is:

$$2V = \varepsilon_0 \boldsymbol{R}^{\mathrm{T}}\boldsymbol{A}\boldsymbol{A}\boldsymbol{R} + \kappa_0 \boldsymbol{R}^{\mathrm{T}}\boldsymbol{A}\boldsymbol{R} \quad \text{(A4)}$$

where the Töplitz matrix A has the elements:

$$A_{kl} = 2\delta_{kl} - \delta_{k,l+1} - \delta_{k+1,l} \qquad \delta_{k,l+N} = \delta_{kl} \quad \text{(A5)}$$

The diffusion equation in this case is thus:

$$\partial\Psi/\partial t = \nabla^{\mathrm{T}} \cdot (k_{\mathrm{B}}T/f)\boldsymbol{H}[\nabla\Psi + (\Psi/k_{\mathrm{B}}T)(\varepsilon_0\boldsymbol{A}\boldsymbol{A}\boldsymbol{R} + \kappa_0\boldsymbol{A}\boldsymbol{R})] \quad \text{(A6)}$$

Note that our A is not the matrix of Soda[5] but the more common Rouse connectivity matrix[21]. If we now introduce Fourier coordinates (which for the ring are

necessarily normal coordinates) following equations (Sa19) through (Sa30), and then use these relations in equation (A6), the diffusion equation becomes:

$$\partial\Psi/\partial t = \sum_{n=0} (k_B T/b\zeta_n)(\partial/\partial \boldsymbol{q}_n)\cdot[(\partial\Psi/\partial \boldsymbol{q}_n + (\Psi/k_B T)b\lambda_n \boldsymbol{q}_n] \tag{A7}$$

with the symbols defined as in ref. 5. Appropriate integrations over this equation yield equations (Sa31)–(Sa33) for the normal-coordinate correlation functions, but the equilibrium values are not given by equation (Sa34), but by:

$$\langle|\boldsymbol{q}_n^2|\rangle = 3k_B T/b\lambda_n \tag{A8}$$

Conversion of all results to the continuous-ring limit proceeds exactly as in ref. 5.

We call attention here to the basic similarity between our model and the 'optimum Rouse–Zimm model' described by Bixon and Zwanzig[24]. Examination of their equation (48) for semiflexible chains and transcription to the case of a ring shows that the effective potential of our equation (A4) is of the same form as theirs. However, their ratio of coefficients of the two terms is not related to the persistence length in the same way as ε_0/κ_0 in the SB model.

APPENDIX B

Flexible Gaussian limit

Here we evaluate C for very flexible rings, setting $\varepsilon = 0$. Then from equation (Sa36) we have:

$$\lambda_n = 4\kappa(n\pi/L)^2 \tag{B1}$$

Also in this limit:

$$K(s) = (6L/\pi)^{1/2} s^{-1/2}(1-s)^{-1/2} \tag{B2}$$

Thus from equations (7) and (Sa52) we get:

$$C = \frac{\sum_{n\geq 1} n^{-2} \int_0^{L/2} s^{-1/2}(L-s)^{-1/2}\cos(2\pi ns/L)\,\mathrm{d}s}{3\sum_{n\geq 1} n^{-2} \int_0^{L/2} s^{-1/2}(L-s)^{-1/2}\,\mathrm{d}s} \tag{B3}$$

Now the required sums are[25]:

$$\sum_{n=1}^{\infty} n^{-2} = \pi^2/6$$

$$\sum_{n=1}^{\infty} n^{-2}\cos(2\pi ns/L) = (\pi^2/6)[1-6(s/L)+6(s/L)^2]$$

so that

$$C = \frac{\int_0^{1/2}[x^{-1/2}(1-x)^{-1/2} - 6x^{1/2}(1-x)^{1/2}]\,\mathrm{d}x}{3\int_0^{1/2} x^{-1/2}(1-x)^{-1/2}\,\mathrm{d}x} = 1/12 \tag{B4}$$

in agreement with the calculation of Burchard and Schmidt[14] via the Akcasu–Gurol[23] formula.

APPENDIX C

Rigid-ring limit

Near the rigid limit, the solution of equation (3) is given by a modified equation (Bg44) as:

$$\kappa = -(3k_B T/\lambda L^2)(\pi^2 - 2\lambda L + \cdots) \tag{C1}$$

which upon substitution in (Sa36) along with equation (2) gives the eigenvalues:

$$\lambda_n/12k_B T = (\pi^4/\lambda L^4)(n^4 - n^2) + 2\pi^2 n^2/L^3 \tag{C2}$$

Thus, in the limit $\lambda L \to 0$ we have:

$$\begin{aligned} \lambda_1 &= 24\pi^2 k_B T/L^3 \\ \lambda_n &\to \infty \qquad (n>1) \end{aligned} \tag{C3}$$

and we are left, as we should be, with just the three rotational degrees of freedom, albeit with spherical symmetry. Hence, for rigid rings, equations (1) and (Sa65) give:

$$S(q,t) = 2L\alpha^2 \exp(-q^2 Dt)\int_0^{L/2} \mathrm{d}s \exp\{-(q^2L^2/12\pi^2) \times [1-\exp(-t/\tau_1)\cos(2\pi s/L)]\} \tag{C4}$$

With changes of variable:

$$\begin{aligned} z &\equiv q^2L^2/12\pi^2 = q^2\langle S^2\rangle/3 \\ z' &= z\exp(-t/\tau_1) \\ v &= 2\pi s/L \end{aligned} \tag{C5}$$

this becomes:

$$S(q,t) = L^2\alpha^2 \exp(-q^2Dt)\exp(-z)\cdot\pi^{-1}\int_0^{\pi} \exp(z'\cos v)\,\mathrm{d}v$$

$$= L^2\alpha^2 \exp(-q^2Dt)\exp(-z)I_0(z') \tag{C6}$$

where I_0 is a Bessel function of zero order; $I_0(z') = J_0(\mathrm{i}z')$.

The corresponding particle scattering factor is:

$$P(q) \equiv S(q,0)/S(0,0) = \exp(-z)I_0(z) \tag{C7}$$

This function is shown as the broken curve in *Figure 2* in the form of a Holtzer plot, $uP(q)$ against u, where $u^2 \equiv q^2\langle S^2\rangle = 3z$. The full curve in the figure is computed from the exact relation[26] for such a ring:

$$P(q) = \int_0^{\pi/2} J_0^2(qr\sin\beta)\sin\beta\,\mathrm{d}\beta \tag{C8}$$

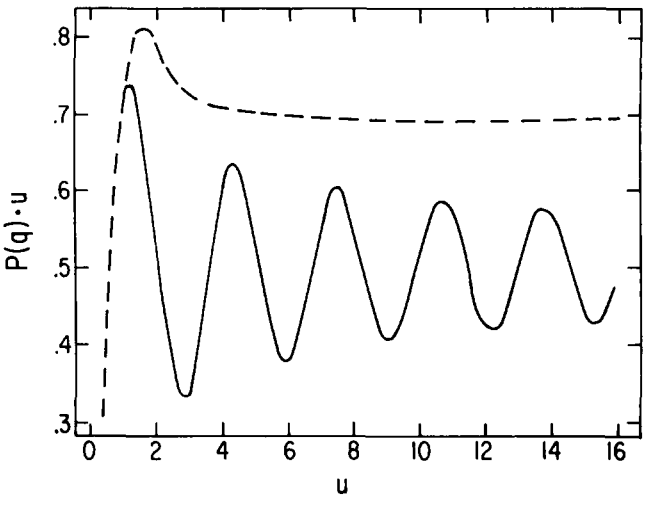

Figure 2 Holtzer plot, $uP(q)$ against u, where q=scattering vector, $u^2 = q^2\langle S^2\rangle$: full curve, exact; broken curve, SB model

where J_0 is a Bessel function. Although the curves match at low angles (which they must, since Berg obtained the correct mean-square radius of gyration), they deviate greatly at higher angles. The absence of oscillations in the curve for (C7) clearly points to a geometry very different from that of a rigid planar ring.

The dynamic behaviour predicted by (C6) also deviates considerably from that of a rigid ring. The first cumulant is found to be:

$$\Gamma = q^2 D + [zI_1(z)/\tau_1 I_0(z)] + \cdots \quad \text{(C9)}$$

where I_1 is also a common Bessel function. To find the relaxation time τ_1 for the model, we need equation (3) and (Sa50):

$$\zeta_1 = 3\pi\eta_0 \Big/ \int_0^{L/2} \cos(2\pi s/L) K(s)\, ds$$

For the rigid ring, Fujii and Yamakawa[6] use:

$$K(s) = (\pi/L)[\sin^2(\pi s/L) + (\pi d/2L)^2]^{-1/2} \quad \text{(C10)}$$

For thin rings, $d/L \ll 1$, neglect of all but the leading term in the integral leads to:

$$\zeta_1 = 3\pi\eta_0/\ln(L/d) \quad \text{(C11)}$$

and hence to

$$\tau_1 = \eta_0 L^3/8\pi k_B T \ln(L/d) \quad \text{(C12)}$$

This number is 3/2 times the correct result (with pre-averaged hydrodynamic interactions) for a rigid ring[27,28] and twice that obtained from their 'optimized Rouse–Zimm theory' by Bixon and Zwanzig[24].

The translational diffusion coefficient, from equation (Sa52), is:

$$D = (k_B T/3\pi\eta_0 L) \ln(L/d) \quad \text{(C13)}$$

Substitution of (C12) and (C13) into (C9) then produces:

$$C = 1/3 \quad \text{(C14)}$$

which is in wide disagreement with the correct value[15] of only 1/15 for rigid rings with pre-averaged hydrodynamics. This discrepancy reinforces our belief that the modified SB model, like its HH ancestor, is most useful for small or moderate degrees of chain stiffness.