Notes

First Cumulant of the Dynamic Structure Factor for Rigid Rods and Semiflexible Chains

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Recently, Wilcoxon and Schurr[1] and Maeda and Fujime[2] have derived expressions for the first cumulant $\Gamma(q)$ of the dynamic structure factor for rigid rod molecules, valid for all magnitudes q of the scattering vector, and with proper attention to anisotropy of translational diffusion. The two results agree numerically but were left in the form of summations or series expansions. One of our objects in this note is to exhibit a more compact closed form, which is equivalent to resumming the series. For semiflexible macromolecules, no completely general results for the first cumulant are yet available, but one of the analytically more tractable models, which gives surprisingly good results, is the so-called "sliding rod" model introduced by Benmouna, Akcasu, and Daoud.[3] Again, the authors presented their result in series form, and here we can also offer a closed form, obtained by going from a discrete set of points to a continuous limit. The closed expressions, aside from questions of taste, may be handier for the fitting of experimental data.

Following the Maeda–Fujime approach,[2] we show that $D_{\rm app}(q) = \Gamma(q)/q^2$ can be written in a more compact "analytical" form. Our starting point is the definition[4]

$$\Gamma(q) = \frac{\langle \rho^*(q)\ell\rho(q)\rangle}{\langle \rho^*(q)\rho(q)\rangle} \quad (1)$$

where the continuous density for a rod is given by

$$\rho(q) = e^{i\mathbf{q}\cdot\mathbf{R}} j_0\left(\frac{qL}{2}\mu\right) \quad (2)$$

μ is the cosine of the angle between $\mathbf{q}$ and the rod direction and $\mathbf{R}$ denotes the position of the center of mass. The dynamical operator ℓ can be separated into a translational part $-\nabla_{\mathbf{R}}\mathbf{D}_T\nabla_{\mathbf{R}}$ and a rotational part $-\theta I^2$, where $\mathbf{D}_{\rm T}$ is the translational diffusion tensor with transverse and longitudiual components $D_\perp$ and $D_\parallel$, θ is the rotatory diffusion coefficient, and I^2 is the angular momentum operator. It is straightforward to obtain

$$D_{\rm app}(q) = D + \Delta\frac{\int_0^1 {\rm d}\mu\left(\frac{3}{2}\mu^2 - 1\right)j_0^2\left(\frac{qL}{2}\mu\right)}{\int_0^1 {\rm d}\mu\, j_0^2\left(\frac{qL}{2}\mu\right)} + \frac{\theta L^2}{4}\frac{\int_0^1 {\rm d}\mu\,(1-\mu^2)j_1^2\left(\frac{qL}{2}\mu\right)}{\int_0^1 {\rm d}\mu\, j_0^2\left(\frac{qL}{2}\mu\right)} \quad (3)$$

where D is the average diffusion coefficient $D = (2D_\perp + D_\parallel)/3$, $\Delta = 2(D_\parallel - D_\perp)/3$ represents anisotropy, and $j_n(x)$ is the spherical Bessel function. The μ integrations in eq 3 can be performed and yield the result

$$D_{\rm app}(q) = D + \Delta\frac{I_2(qL)}{I_1(qL)} + \frac{\theta L^2}{4}\frac{I_3(qL)}{I_1(qL)} \quad (4a)$$

with

$$I_1(qL) = \frac{2}{qL}\left[\frac{\cos(qL) - 1}{qL} + {\rm Si}\,(qL)\right] \quad (4b)$$

$$I_2(qL) = -\frac{I_1(qL)}{2} + \frac{3}{q^2L^2}\left[1 - \frac{\sin(qL)}{qL}\right] \quad (4c)$$

$$I_3(qL) = -\frac{4}{q^2L^2}\cos^2\left(\frac{qL}{2}\right) + \frac{2}{3qL}{\rm Si}\,(qL) - \frac{16}{3q^4L^4}\sin^2\left(\frac{qL}{2}\right) + \frac{8}{3q^3L^3}\sin(qL) + \frac{8}{3q^2L^2}\cos(qL) - \frac{8}{q^3L^3}\left[\frac{qL}{4} + \frac{\sin(qL)}{4} - \frac{2}{qL}\sin^2\left(\frac{qL}{2}\right)\right] \quad (4d)$$

The large qL limit of eq 4a is

$$\lim_{qL\to\infty} D_{\rm app}(q) = D - \frac{\Delta}{2} + \frac{\theta L^2}{12} \quad (5)$$

In the sliding rod model,[3] the chain behaves as a rigid rod for lengths smaller than a characteristic length l (which is a measure of stiffness), whereas longer lengths follow Gaussian statistics. The continuous limit of the first cumulant which can also be written as[4]

$$\Gamma(q) = \frac{\sum_{i,j}\langle \mathbf{q}\cdot\mathbf{D}(\mathbf{R}_{ij})\cdot\mathbf{q}e^{i\mathbf{q}\cdot\mathbf{R}_{ij}}\rangle}{\sum_{i,j}\langle e^{i\mathbf{q}\cdot\mathbf{R}_{ij}}\rangle} \quad (6)$$

is taken in eq 12 of ref 3 to yield

$$\Gamma(q) = \frac{q^2\frac{k_{\rm B}T}{\zeta n} + q^3\frac{k_{\rm B}T}{\eta_0}F(q)}{S(q)} \quad (7)$$

with

$$S(q) = \frac{2}{ql}\left[{\rm Si}\,(ql) + \frac{\cos(ql) - 1}{qL}\right] + \frac{12}{q^2l^2}[e^{-q^2l^2/6} - e^{-q^2Ll/6}] - \frac{72}{q^4Ll^3}\left[\gamma\left(2,\frac{q^2Ll}{6}\right) - \gamma\left(2,\frac{q^2l^2}{6}\right)\right] \quad (8)$$

In Figure 1 we compare $(q^2l^2/4)S(q)$ vs. $ql/2$ for an infinitely long sliding rod chain with similar results for wormlike chains given by des Cloizeaux[5] and Koyama.[6] Note that these authors define the structure factor differently and that in this infinite chain limit the characteristic length l can be identified as the Kratky–Porod wormlike chain statistical Kuhn length.[7] Note also that the oscillations in curve 1 are an artifact of the sliding rod model for which the chain goes from a rigid rod to a

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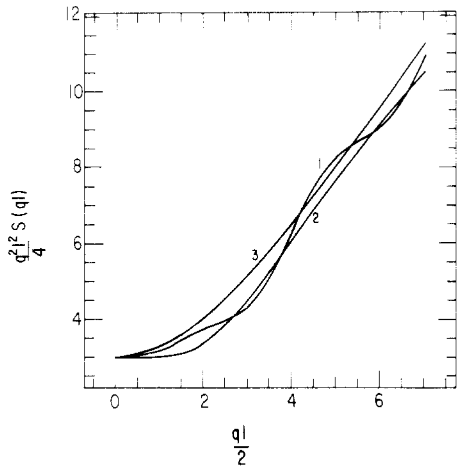

Figure 1. Variation of $(q^2l^2/4)/S(q)$ vs. $ql/2$ for an infinite semiflexible chain as given (1) by the sliding rod model, (2) by Koyama, and (3) by des Cloizeaux.

Gaussian coil discontinuously. When the hydrodynamic interaction is preaveraged

$$F(q) = \frac{1}{3\pi ql}\left[1 - \frac{\sin(ql)}{ql} + \text{Ci}(ql) - \text{Ci}(qd) - \frac{\text{Si}(ql)}{qL}\right] + \frac{2}{\pi\pi^{1/2}q^2l^2}\left[\gamma\left(\frac{3}{2},\frac{q^2Ll}{6}\right) - \gamma\left(\frac{1}{2},\frac{q^2l^2}{6}\right)\right] - \frac{12}{\pi\pi^{1/2}q^4Ll^3}\left[\gamma\left(\frac{3}{2},\frac{q^2Ll}{6}\right) - \gamma\left(\frac{3}{2},\frac{q^2l^2}{6}\right)\right] \quad (9)$$

In these expressions, the sine integral, cosine integral, and the incomplete γ function have been used:

$$\text{Si}(x) = \int_0^x dt\,\frac{\sin t}{t}; \qquad \text{Ci}(x) = -\int_x^\infty dt\,\frac{\cos t}{t}$$

$$\gamma(m,x) = \int_0^x dt\, e^{-t}t^{m-1}$$

Also a cutoff hydrodynamic thickness d associated with the chain has been introduced to avoid a singularity in $F(q)$ at zero contour length. The rigid rod limit of the apparent diffusion coefficient $D_{app}(q) = \Gamma(q)/q^2$ is obtained for $l = L$ as

$$D_{app}(q) = \left(D_0 + 2D_0\left[1 - \frac{\sin(qL)}{ql} + \text{Ci}(qL) - \text{Ci}(qd) - \frac{\text{Si}(qL)}{qL}\right]\right)\Big/\left(\frac{2}{qL}\left[\text{Si}(qL) + \frac{\cos(qL) - 1}{qL}\right]\right) \quad (10)$$

where $D_0 = k_BT/\zeta N$. Equations 10 and 4a have the same small qL limit

$$\lim_{q\to 0} D_{app}(q) = D_0 + 2D_0[\ln(L/d) - 1] \quad (11)$$

if both the free-draining and nondraining values are considered to define D as $D = D_0 + 2D_0[\ln(L/d) - 1]$. Note that when the length of the rod becomes large, eq 10 becomes

$$\lim_{qL\to\infty} D_{app}(q) = D_0\frac{qL}{\pi} + 2D_0\left[0.423 + \ln\left(\frac{1}{qd}\right)\right]\frac{qL}{\pi} \quad (12)$$

where the expansion $\lim_{qd\to 0}\text{Ci}(qd) \simeq 0.577 + \ln(qd)$ has been used. Equation 12 is different from eq 5. In eq 12, $D_{app}(q)$ increases linearly with qL for a fixed D whereas in eq 5 it reaches a plateau value at large qL. As pointed out before,[8,9] this discrepancy comes from the fact that eq 6 uses the full configuration space whereas eq 1 includes rigid constrainsts at the outset. For example, eq 6 gives for freely jointed chains[10] the same limit at large q as for flexible chains. We therefore conclude that the sliding rod model, as originally presented, i.e., based on eq 6, is valid for semiflexible chains with a small degree of stiffness, i.e., close to flexible coils.

For nonpreaveraged hydrodynamic interaction, the analysis is more involved but tractable to a point. For simplicity we present the infinitely long chain result only:

$$F(q) = \frac{1}{3\pi ql}\left[1 - \frac{\sin(ql)}{ql} + \text{Ci}(ql) - \text{Ci}(qd)\right] + \frac{2}{3\pi q^3l^3}\left[\frac{\sin(ql)}{ql} - \cos(ql)\right] + \frac{3}{\pi\pi^{1/2}q^2l^2}\int_0^1 dz\,\frac{z^2}{(1-z^2)^{1/2}}\left[\Gamma\left(\frac{1}{2}\right) - \gamma\left(\frac{1}{2},\frac{q^2l^2}{6}(1-z^2)\right)\right] + \frac{3}{\pi\pi^{1/2}q^2l^2}\left(\frac{6}{q^2l^2}\right)^{1/2}\left[\int_0^1 dz\, e^{(-q^2l^2/6)(1-z^2)} - 1\right] \quad (13)$$

The remaining integrations over the variable z would have to be performed numerically.

Using this continuous limit of the sliding rod model, Stockmayer and Hammouda have estimated[11] corrections to the first cumulant due to a small degree of stiffness ($l \simeq 20$ Å for polystyrene); these corrections have been found to be small.

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References and Notes

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Dielectric Normal Mode Process in Solutions of Polychloroprene

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In our recent papers,[1,2] we reported that bulk *cis*-polyisoprene (*cis*-PI) exhibits dielectric relaxation due to

