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Quasi-Elastic Light Scattering by Semiflexible Chains

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ABSTRACT: Quasi-elastic scattering at low scattering angles is calculated and compared for several approximate models of semiflexible chains: wormlike chain, Hearst–Beals–Harris model, weakly bending rod, sliding-rod model. From these results a curve is synthesized for predicting the coefficient *C*, which describes the initial angular dependence of the first cumulant, over the entire range from rigid rod to Gaussian coil.

1. Introduction

The dynamical behavior of semiflexible long-chain molecules in solution is of interest for its own sake and also because it offers opportunities for molecular characterization of some important natural and synthetic polymers. An accurate theory of such behavior is intrinsically difficult because it presents a nonseparable many-body problem. In the field of quasi-elastic light scattering (QELS), one may hope to achieve some understanding by focusing attention on the first cumulant of the dynamic structure factor, which can be expressed[1] as an equilibrium ensemble average in coordinate space. This hope, however, is not easily realized because the internal molecular relaxation times grow shorter and shorter as the rigidity of the molecule increases. If some of these times become sufficiently short compared to the time-resolution capability of the photon correlation device, the corresponding contributions to the observable first cumulant may fall below the true theoretical value and in extreme cases may be entirely absent on the experimental time scale.[2] In the latter limit the stiff degrees of freedom may be omitted from the theory at the start (as in the usual treatment of rigid rods[3,4]), or appropriate constraints may be imposed[5] on the relevant diffusion tensor; but for semiflexible chains, in the "crossover" domain between flexible coils and rigid rods, no such maneuver is available. In the present paper we describe some attempts to improve our still very incomplete understanding of this situation.

Fujime[6,7] some time ago discussed QELS from semiflexible chains with the aid of the Harris–Hearst[8] dynamical model. He recognized that this model does not give a good representation of rotational motions near the rigid-rod limit and made adjustments to overcome this difficulty. His equations have been used by Kubota and Chu[9] to discuss their measurements on solutions of a poly(*n*-alkyl isocyanate). However, the Fujime calculation is restricted to the case of hydrodynamic free draining, which is not a physically realistic model for dilute polymer solutions.

More recently, Benmouna, Akcasu, and Daoud[10] calculated the first cumulant for an ingenious "sliding-rod" model, definable for any degree of chain stiffness, but their results are not practically applicable near the rod limit because they did not take account of the previously mentioned shortening of the internal relaxation times.

The plan of the present paper is as follows. After reviewing the basic Akcasu–Gurol (AG) relation[1] for the first cumulant, we apply this in unmodified form to the wormlike chain with full or preaveraged hydrodynamic interaction, expecting the results to be useful at least for modest degrees of chain stiffness. Next we discuss the dynamic structure factor of Harris–Hearst chains with strong preaveraged hydrodynamic interaction, using the results of Hearst, Beals, and Harris.[11] Then we approximately treat slightly bending rods with the aid of recent studies by Hagerman and Zimm[12] and by Rallison and Leal;[13] finally we attempt to synthesize an optimum practical recipe from the various results obtained. Excluded-volume effects are neglected, and attention is confined to low scattering vectors, where the relevant and interesting experiments are to be found. Polydisperse systems are not specifically considered.

2. First Cumulant

For low scattering-vector magnitudes $q = (4\pi/\lambda)\sin(\theta/2)$ (where λ is wavelength and θ scattering angle), the first cumulant Γ of the dynamic structure factor $S(q,t)$ may be written

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

where D is the translational diffusion coefficient and $\langle S^2\rangle$ is the mean square radius of gyration. Good theories of D and $\langle S^2\rangle$ are available,[14,15] and so we concentrate on the numerical coefficient C, which is, as will be seen, sensitive to chain stiffness. This coefficient has been previously shown[16] to depend on polydispersity, on branching, and on the nature of the hydrodynamic interactions. Fortunately the effect of excluded volume on this coefficient is small.[17]

The AG formula is based on the standard Kirkwood diffusion equation for a chain molecule.[14] It has been

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discussed frequently[16,18] and its derivation[1] need not be recalled here. We write it in the form appropriate to a continuous chain:

$$\Gamma(q) = \int_0^L \mathrm{d}s\,(L - s)\phi^{\mathrm{Q}}(q,s) \Big/ \int_0^L \mathrm{d}s\,(L - s)\phi^{\mathrm{I}}(q,s) \qquad (2)$$

where L is the contour length of the entire chain and s is the contour length of a portion thereof. The integrations go over all pairs of scattering points in the molecule and involve two different pair scattering functions. The dynamic function, in the hydrodynamic nondraining limit, which is of interest for large molecules in dilute solution, is

$$\phi^{\mathrm{Q}}(q,s) = \int_0^\infty F^{\mathrm{Q}}(qR)W(R,s)\,\mathrm{d}^3\mathbf{R} \qquad (3)$$

with

$$F^{\mathrm{Q}}(z) = (q^3 k_{\mathrm{B}}T/4\pi\eta_0)(z^{-2}\sin z + z^{-3}\cos z - z^{-4}\sin z) \qquad (4)$$

Here, η_0 is solvent viscosity, $k_{\mathrm{B}}T$ is thermal energy, and $z \equiv qR$, where R is the magnitude of the vector $\mathbf{R}$ joining two points on the chain separated by a contour length s. The probability density for R is $W(R,s)$.

The static scattering function appearing in the denominator of eq 2 is

$$\phi^{\mathrm{I}}(q,s) = \int_0^\infty z^{-1}\sin z\,W(R,s)\,\mathrm{d}^3\mathbf{R} \qquad (5)$$

As we are interested mainly in low scattering vectors, it is often useful to use appropriate expanded forms.[17] Developing $F^{\mathrm{Q}}(z)$ of eq 4 in powers of z and retaining the first several, we eventually find the coefficient C to be given[17] by

$$C = (1/3) - (\langle S\rangle/5\langle S^{-1}\rangle\langle S^2\rangle) \qquad (6)$$

with the definition

$$\langle S^p\rangle \equiv L^{-2}\int_0^L \mathrm{d}s\,(L - s)\langle R(s)^p\rangle \qquad (7)$$

where

$$\langle R(s)^p\rangle \equiv \int_0^\infty R^p W(R,s)\,\mathrm{d}^3\mathbf{R} \qquad (8)$$

In this notation the translational diffusion coefficient is

$$D = (k_{\mathrm{B}}T/3\pi\eta_0)\langle S^{-1}\rangle \qquad (9)$$

and $1/\langle S^{-1}\rangle$ is seen to be twice the commonly defined "hydrodynamic radius" of the chain.

Equations 4 and 6 correspond to the nonpreaveraged (tensorial, fluctuating) form of the Oseen hydrodynamic interactions.[14] For comparison with other model calculations and with experimental results, it is also customary to consider the preaveraged scalar form of these interactions. This corresponds to replacing eq 3 and 4 by

$$\phi^{\mathrm{Q}}_{\mathrm{pre}}(q,s) = \phi^{\mathrm{I}}(q,s)(q^3 k_{\mathrm{B}}T/6\pi\eta_0)\int_0^\infty z^{-1}W(R,s)\,\mathrm{d}^3\mathbf{R} \qquad (3')$$

3. Wormlike Chain

The worm model of Kratky and Porod has long served[14] as a useful representation of the conformational properties of semiflexible chains and in its complete form describes equilibrium behavior over the full range from rigid rod to Gaussian coil. The lower even moments of the distribution function are well-known;[14] for example

$$\langle R^2\rangle/l^2 = y - (1 - e^{-2y})/2 \qquad (10a)$$

$$\langle R^4\rangle/l^4 = (5y^2/3) - (26y/9) - (1 - e^{-6y})/54 + 2(1 - e^{-2y}) - ye^{-2y} \qquad (10b)$$

In these equations, $l = 2P$, where P is the persistence length and l is the "Kuhn length", and $y = s/l$, where s is again the contour length of the segment considered. (In many papers and reference works[14] the Kuhn length is written $1/\lambda$.) Corresponding to eq 10 the mean square radius of gyration of the chain is given[14,19] by

$$\langle S^2\rangle = (Ll/6) - (l^2/4) + (l^3/4L) - (l^4/8L^2)(1 - e^{-2L/l}) \qquad (11)$$

A tractable expression for the complete $W(R,s)$ of a wormlike chain is not yet available. Near the coil limit the asymptotic expansion of Daniels[20] and its second-order extension[21] are valuable, but we are interested in the entire range of chain stiffness from coil to rod, and so have found it more useful to apply an accurate approximation due to Koyama.[22] Building on an earlier treatment by Ptitsyn and Eizner,[23] Koyama represented the characteristic function of $W(R,s)$ as a hybrid of those for rod and coil and obtained the formula

$$4\pi R^2 W(R,s) = (R/2AB\pi^{1/2}) \times \{\exp[-(R - B)^2/4A^2] - \exp[-(R + B)^2/4A^2]\} \qquad (12a)$$

where

$$A^2 \equiv \langle R^2\rangle(1 - \eta)/6 \qquad (12b)$$

$$B^2 \equiv \eta\langle R^2\rangle \qquad (12c)$$

$$2\eta^2 \equiv 5 - 3\langle R^4\rangle\langle R^2\rangle^{-2} \qquad (12d)$$

The Koyama formula automatically reproduces eq 10 and 11 exactly and gives the known higher even moments to within several percent.[22] It is, of course, completely correct in the rod and coil limits.

Substitution of eq 12 into eq 2–4 presents double integrals which we were able to treat only numerically, and they were evaluated with the Dartmouth IMSL program DCADRE. For low q, i.e., evaluation of C by eq 6–8, we easily have the analytical results

$$\langle R(s)^{-1}\rangle = B^{-1}\,\mathrm{erf}\,(B/2A) \qquad (13a)$$

$$\langle R(s)\rangle = (B + 2A^2B^{-1})\,\mathrm{erf}\,(B/2A) + 2A\pi^{-1/2}\exp(-B^2/4A^2) \qquad (13b)$$

Subsequent integration by eq 7 along the chain contour was done numerically.

The numerator of eq 2 contains a familiar divergence; except in the Gaussian limit, the integrand behaves as s^{-1} at small s. To cope with this hurdle it is customary to impose[14,24] a nonzero lower limit b or, as we found convenient, to replace[14] s^{-1} in this one term by $((b^2/4) + s^2)^{-1/2}$. The parameter b in either case acts like an effective hydrodynamic diameter of the chain and can be given appropriate numerical values in applications.

The first cumulant was calculated from eq 2–9 for varying degrees of chain stiffness. We find our translational diffusion coefficients to be in good agreement with the Yamakawa–Fujii figures,[15] thus increasing confidence in Koyama's approximation. The calculated values of C, for large values of L/b, are plotted in Figure 1 against the logarithm of the ratio L/l; the full nonpreaveraged hydrodynamic interactions give curve I and the preaveraged form leads to curve II. The Gaussian limits of these curves at very high L/l are $13/75 = 0.1733$ and $2/15 = 0.1333$, respectively.

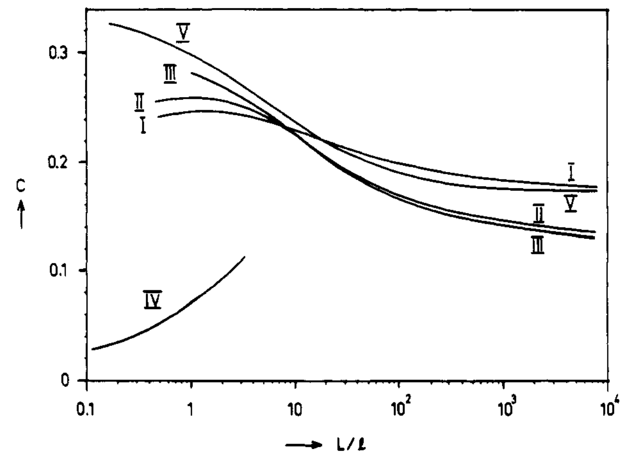

Figure 1. Slope C as a function of the reduced length L/l for various models as described in the text. Curve I: wormlike chain, nonpreaveraged hydrodynamic interaction; curve II: wormlike chain, preaveraged hydrodynamic interaction; curve III: Hearst–Beals–Harris model, preaveraged hydrodynamic interaction; curve IV: weakly bending rod, nonpreaveraged hydrodynamic interaction; curve V: sliding-rod model, nonpreaveraged hydrodynamic interaction. The reduced chain diameter is kept constant at $b/l = 0.003$.

It should be mentioned at this point that experimental results for flexible chains have been interpreted[25,26] to indicate that the *pre*averaged hydrodynamic interactions actually give a better representation of the q dependence of the first cumulant than the full Oseen form. However, there are indications[27,28] that this result does not represent the calculated initial value of C, because of the finite time resolution of correlators and that an appropriately extrapolated zero-time value of C is in better accord with the nonpreaveraged calculation.

4. Hearst–Beals–Harris Model

As mentioned earlier, a calculation of the complete dynamic structure factor $S(q,t)$ for the free-draining Harris–Hearst model has already been given by Fujime.[6,7] Here we treat the corresponding nondraining (but preaveraged) model of Hearst, Beals, and Harris[11] (HBH), using their published eigenvalues plus many additional ones kindly communicated to us by Professor Hearst.[29]

The Harris–Hearst model introduces chain stiffness in an incomplete way. The backbone potential energy is not that of a Gaussian chain, but it is still separable in Cartesian coordinates (the reason for its tractability) and is thus incapable of attaining a realistic rigid-rod limit. Indeed, Simon[30] has shown that the model can be generated from a Gaussian chain by incorporating additional Gaussian springs between second- and third-neighbor beads. Nevertheless, the model has afforded some valuable insights into semiflexible chain dynamics and should not be dismissed too lightly.

Our motivation for using the HBH model came from the fact that a complete dynamic structure factor $S(q,t)$ can be calculated from the known eigenfunctions and eigenvalues. Thus it was hoped that direct account could be taken of the rapid damping of stiff coordinates. The HBH eigenvalues[11,29] are evaluated to first order of perturbation; i.e., the eigenfunctions of the diffusion operator are taken to be those of free-draining (but of course not Gaussian) chains. First-order theory gives very good results[31,32] for Gaussian chains and is thus expected to be quite reliable here.

The expression for $S(q,t)$ can be directly transcribed from the papers of Fujime[6,7] or indeed from the Pecora[33] expression for the Rouse or Zimm model (or presumably for any model yielding to a normal-coordinate separation). For a continuous chain, the expression is

$$S(q,t) = \exp(-q^2Dt)\int_0^L\int_0^L \mathrm{d}s\,\mathrm{d}s'\exp\{-q^2\sum_{k=1}\langle\mu_k{}^2\rangle A_k(t)\} \tag{14}$$

where

$$A_k(t) = Q_k(s)^2 + Q_k(s')^2 - 2Q_k(s)Q_k(s')\exp(-t/\tau_k) \tag{15}$$

As stated above, the eigenfunctions $Q_k(s)$ and amplitude factors $\langle\mu_k{}^2\rangle$ are taken as those of free-draining Harris–Hearst molecules, but the relaxation times τ_k are for HBH chains (i.e., with strong hydrodynamic interactions). The expressions for these quantities may be found in the original papers.[6,7,11] They are not reproduced here, because we were unable to realize the hope expressed above. Probably because the rigidity of the model is exercised only in three separate and uncoordinated dimensions, the distribution of relaxation times and amplitudes does not approach that for real stiff rods, and we could not unambiguously identify a cutoff mode number above which the calculated contributions to the first cumulant could be discarded as too fast to contribute to experimental observations. The calculated full value of the coefficient C for the HBH model can be brought into comparison with the wormlike chain by matching the mean square end-to-end lengths. When this is done, we obtain curve III of Figure 1, which is not very different from curve II for the preaveraged wormlike chain.

5. Weakly Bending Rods

We now consider small departures from the behavior of a rigid rod, again concentrating on the coefficient C. Since a strictly rigid thin rod has only five degrees of freedom, we take the point of view that we can discuss the effects of very small flexibility by concentrating on just these degrees of freedom, supposing that the third rotation (about the long principal axis) and the various twisting, bending, and stretching motions will all be sufficiently rapid or stiff to justify their neglect for the present purpose. (A discussion of the twisting and bending motions of DNA has been given by Barkley and Zimm.[34])

Pecora's original solution of the polarized scattering problem for rigid rods[3,4] did not allow for translation–rotation coupling. The latter effect for rods has been discussed by various authors, perhaps most recently by Rallison and Leal,[13] who cite earlier work. We modify their results for strictly rigid rods to take account of some bending, and the coefficient C is found (cf. Appendix I) to be

$$C = (L^2\Theta/90D)(A_4/A_2) - (2\mu/15)(A_4/A_2) - (2\mu^2D/5L^2\Theta)(1 - A_4)/A_2 \tag{16}$$

where Θ is the rotatory diffusion coefficient, D is the mean translational diffusion coefficient, and μ measures the anisotropy in translational diffusion:

$$D = (D_\parallel + 2D_\perp)/3 \tag{17a}$$

$$\mu = 2(D_\parallel - D_\perp)/3D \tag{17b}$$

Here, $D_\parallel$ and $D_\perp$ are diffusion coefficients for migration parallel and perpendicular to the rod axis. The factors A_2 and A_4, given in eq A5, are flexibility factors which reduce to unity for stiff rods. For very long thin rods, the relations $\mu = {}^1/_2$ and $L^2\Theta/D = 9$ are well-known,[13,14] and these lead with eq 16 to $C = 1/30$, considerably below the value of 1/10 corresponding to Pecora's solution (which can be recovered when $\mu = 0$) and very much smaller than a figure of 1/3 which would result from applying the AG recipe to a full $3N$-coordinate space for a long rod containing N scattering elements.

For rigid rods our eq 16 appears to be consistent with the formula for the first cumulant given by Wilcoxon and Schurr,[35] who derived it by a quite different route. We can also check eq 16 against their experimental data for tobacco mosaic virus. Taking $L = 3000$ Å, $b = 180$ Å, and $\mu = 0.28$ (the latter from ref 35) and applying Broersma's expressions[36] for translational and rotational diffusion, we find $L^2\Theta/D = 6.3$ and then obtain $C = 0.033$, negligibly different from the limiting value 1/30. Our attempt to evaluate the initial slope in Figure 1 of the Wilcoxon–Schurr paper gives $C = 0.044 \pm 0.01$ but, as the curve has a sigmoid shape and corresponds to a single concentration and a single-exponential fit, the agreement may be all that could have been expected.

Now to implement eq 16 for slightly flexible rods, we take the translational diffusion coefficient D from the wormlike chain formula of Yamakawa and Fujii[15] near the rod limit, which for large L/b and vanishing b/l reads

$$3\pi\eta_0 LD/k_BT = \ln\,(L/b) + 0.3863 + 0.1667(L/l) + \ldots \quad (18)$$

For short rods with nonnegligible thickness additional terms exist[15] and have been incorporated into our numerical program.

The relevant rotatory diffusion coefficient, for motion about a short principal axis through the center of resistance, is taken from the recent Monte Carlo calculations of Hagerman and Zimm,[12] who did not preaverage hydrodynamic interactions and whose results may be summarized in the form

$$\Theta = \Theta_{\text{rod}}f(x) \quad (19)$$

where Θ_{rod} is the rotatory diffusion coefficient for a stiff rod, given by Broersma's expression[36] (compare Riseman and Kirkwood[24]):

$$\pi\eta_0 L^3\Theta_{\text{rod}}/3k_BT = \sigma - 1.57 + 7(\sigma^{-1} - 0.28)^2 \quad (20)$$

$$\sigma \equiv \ln 2L/b$$

The flexibility factor $f(x)$ is evaluated from

$$1/f(x) = (1.0120 - 2.4813x + 3.3703x^2 - 1.9177x^3) \times (1 - 0.6469x + 1.153x^2 - 0.9893x^3) \quad (21)$$

where

$$x \equiv L/10P = L/5l$$

Finally, the diffusional anisotropy μ is estimated from the formula

$$2\mu \cong 1 - 0.5(5x)^{1/4} \quad (22)$$

which is briefly discussed in Appendix I and which is of course restricted to small values of x. With eq 16, 18, 19, and 22 we then find the curve marked IV in Figure 1.

6. Interpolation and Discussion

In the preceding sections we have described four different calculations of C: (I) wormlike chain, nonpreaveraged hydrodynamic interactions; (II) wormlike chain, preaveraged hydrodynamic interactions; (III) Hearst–Beals–Harris chain, preaveraged hydrodynamic interactions; and (IV) weakly bending rod, nonpreaveraged hydrodynamic interaction. To these we add curve V, corresponding to the sliding-rod model of Benmouna, Akcasu, and Daoud.[10] The transcription of their equations to our purpose is outlined in Appendix II.

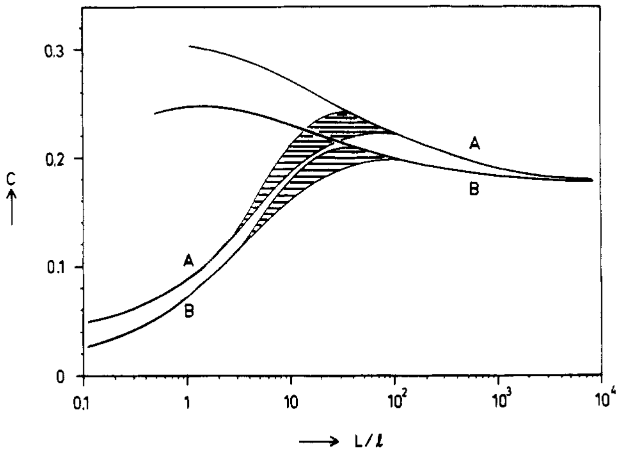

Figure 2. Slope C as a function of L/l. Curve B is based on the calculations of Figure 1. Curve A is calculated in similar fashion, but with $L/b = 10^6$ = constant for all L/l.

The nonpreaveraged wormlike chain is presumed to be the most reliable model at high values of L/l, and of course the weakly bending rod is the best model at very low L/l. The crossover between curves I and IV cannot be predicted accurately without detailed consideration of the full time dependence of $S(q,t)$. We estimate intuitively that the reduction of C by elimination of contributions from very rapid stiff local motions should become appreciable in the range $50 > L/l > 5$. On this arbitrary basis, we interpolate between curves I and IV and construct Figure 2. The shaded area indicates both the uncertainty of our construction and the fact that the experimentally derived value of C is itself dependent on the sampling time of the time-correlation equipment.[26,27] As will be discussed elsewhere, the experimental data of Kubota and Chu[9] for poly(hexyl isocyanates) are in reasonable accord with our prediction.

We thus leave the present study at an obviously incomplete stage, and it seems clear that a full dynamical theory for long semiflexible chains will require much greater effort. We have made some related Brownian dynamics calculations for stiff dumbbells and will report on these later.

It might be recalled that another way of reducing stiffness from the rod limit is to incorporate one or more flexible hinges. A recent paper of Zero and Pecora[37] treats QELS of a once-broken rod with a hinge of restricted angular range.

Finally, at a referee's suggestion we point out that all the complications due to optical anisotropy of the scattering elements[4,38] are ignored in the present treatment, and indeed these are not contemplated in the derivation of the AG relation. Dynamic light scattering by optically anisotropic rigid rods has been discussed by Maeda and Saito.[39]

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Appendix I. Slightly Bending Rod with Translational Anisotropy

The results of Rallison and Leal[13] for rigid rods are given with the translational diffusion coefficients expressed in units of ΘL^2, where Θ is the rotatory diffusion coefficient and L is the rod length. When their expression is transcribed to conventional form and corrected for several misprints,[41] the dynamic structure factor is

$$S(q,t) = \exp(-q^2Dt) \times \{a_0 \exp(+q^4\mu^2D^2t/30\Theta) + a_2 \exp(-6\Theta t) \exp(-2q^2\mu Dt/7)\} \tag{A1}$$

correct to terms of $\mathcal{O}(q^4L^4)$, where

$$D = (D_\parallel + 2D_\perp)/3$$

$$\mu = 2(D_\parallel - D_\perp)/3D \tag{A2}$$

Here, $D_\parallel$ and $D_\perp$ are components of the translational diffusion coefficient in directions parallel and perpendicular to the rod axis. With inclusion of all terms of $\mathcal{O}(q^4L^4)$, the coefficients are[41]

$$a_0 = 1 - (q^2L^2/36) + (13q^4L^4/32400) + (q^4L^2\mu D/540\Theta) - (q^4\mu^2D^2/180\Theta^2)$$

$$a_2 = (q^4L^4/6480) - (q^4L^2\mu D/540\Theta) + (q^4\mu^2D^2/180\Theta^2) \tag{A3}$$

When the anisotropy μ vanishes, the classical result of Pecora[3,4] is recovered.

In essaying an extension of the above expressions to weakly bending rods, we first ensure that the static structure factor $S(q,0)$ agrees with that for a wormlike chain. From eq 2, 5, and 10 we find

$$S(q,0) = 1 - (q^2L^2/36)A_2 + (q^4L^4/1800)A_4 + \ldots \tag{A4}$$

with

$$A_2 = 2u^{-1} - 3u^{-2} + 3u^{-3} - 3u^{-4}[1 - \exp(-2u)]/2 = 1 - (2u/5) + (2u^2/15) - (4u^3/105) + \ldots$$

$$A_4 = (25/6u^2) - (130/9u^3) + (535/18u^4) - (1010/27u^5) + (7285/324u^6) + (5/324u^6)\exp(-6u) - (45/2u^6)\exp(-2u) - (15/2u^5)\exp(-2u) = 1 - (20u/21) + (29u^2/42) - (28u^3/63) + \ldots \tag{A5}$$

$$u \equiv L/l$$

In the absence of detailed model calculations for the dynamics, we simply elect to apply the factor A_2 to each term of $\mathcal{O}(q^2)$ and the factor A_4 to each term of $\mathcal{O}(q^4)$ in eq A3. From eq A1 the first cumulant then turns out to be

$$\Gamma/q^2D = 1 + (q^2L^2/1080)(L^2\Theta/D)A_4 - (\mu q^2L^2/90)A_4 - (\mu^2q^2D/30\Theta)(1 - A_4) + \ldots \tag{A6}$$

where A_4 is given in eq A5. Since the mean square radius of gyration is

$$\langle S^2\rangle = A_2(L^2/12) \tag{A7}$$

we are led to the result for the coefficient C given as eq 16 of the main text.

It remains to consider the effect of flexibility on the asymmetry factor μ, and we are content with an estimate based on Hearst's[40] approximate calculation of the principal axes of a wormlike chain. From axial ratios so obtained we roughly fit the translational anisotropy by the formula

$$2\mu \cong 1 - 0.5(L/l)^{1/4} \quad \text{(small } L/l) \tag{A8}$$

which also appears as eq 22 of the main text.

Appendix II. Sliding-Rod Model[10]

The chain consists of N bonds, each of length b, so that its contour length is $L = Nb$. Within the chain, sequences of up to n bonds behave as rigid rods, and longer sequences follow Gaussian statistics. When $n = N$, the entire molecule is thus a rigid rod, and when n is small it is a Gaussian coil. It is straightforward to expand the equations of Benmouna, Akcasu, and Daoud[10] for this model to obtain the following results.

Writing $n/N = f$, with limits $N^{-1} \leq f \leq 1$, we find the mean square radius of gyration to be

$$\langle S^2\rangle = (L^2/12)(2f - 2f^3 + f^4) \tag{A9}$$

By comparing this equation with eq 11, we can establish the relation between the parameter f of this model and the ratio L/l of the more realistic wormlike chain.

With omission of terms of $\mathcal{O}(N^{-1})$, the diffusion coefficient is

$$D = (k_BT/3\pi\eta_0L)\{\ln(fN) - f + (8/3\pi)^{1/2}(2f^{-1/2} - 3 + f)\} \tag{A10}$$

and the coefficient C is

$$C = (1/3) - (k_BTLH/3\pi\eta_0D\langle S^2\rangle) \tag{A11}$$

with

$$H = (3f^2 - 2f^3 - 3N^{-2})/30 + 8(2f^{1/2} - 5f^2 + 3f^3)/75(6\pi)^{1/2} \tag{A12}$$

At the rigid-rod limit, $f = 1$, eq A10 gives the expected diffusion coefficient, but eq A11 does not agree with eq 16 because the former contains contributions from stiff coordinates. Curve V of Figure 1 has been constructed from the relations given above.

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(41) As pointed out to us by Dr. K. Kubota, the first exponential within the curly brackets of eq A1 was printed with an incorrect minus sign. Also, in the expression for a_0 a factor 13 is missing from the third term and is now correctly displayed in eq A3.

Universality of the Stockmayer Distribution[†]

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ABSTRACT: The molecular distribution function for random *f*-functional polycondensates was derived by Stockmayer in 1943 and has since found wide applications. He used a brilliant variational argument, in which the consideration of motion of model particles in space was not required. Recently, several groups have tried to refine the argument and then to generalize the model in terms of a spatial version of statistical mechanics. Although we are concerned with liquid systems, in which only vibrational modes are usually taken to generate the equation of state, successful generalizations of the Stockmayer distribution have been based on partition functions using explicitly only translational or only rotational motions of the particles! A fundamental explanation of such statistical equivalence of mechanical models generally requires an invariance principle, based on group symmetries. This is here applied, and the useful role of the rotational version (among equivalent spatial or nonspatial versions) is shown to lie in the ease with which it harmonizes with current visualizations of chemical kinetics and of configurational processes in polymer science. The mean-field treatment absorbs any detectable excluded-volume correction in its adjustable parameter (the free energy change in forming a bond). The modern approach to gelation via bond-percolation models on multidimensional lattices does not raise new philosophical issues but is shown to involve seriously faulty molecular (cluster) distributions for gelling systems, to which such models should not be applied.

1. Introduction

Stockmayer[1] published the formula for the equilibrium weight fraction distribution $w(x)$ of a random *f*-functional polycondensation (RFFP) system only 2 years after this new model had been presented to polymer science by Flory:[2]

$$w(x) = [(fx - x)!f/(x - 1)!(fx - 2x + 2)!]p^{x-1}(1 - p)^{fx-2x+2} \quad (1)$$

Here, $w(x)$ is the weight fraction of x-mer, f the functionality of the repeating unit, and p the equilibrium fractional conversion. This result and its implications have aroused tremendous interest and elicited applications in fields including not merely gelation but vapor/liquid equilibria,[3,4] the structure of water in solutions in hydrocarbons,[5] and, recently, immunology.[6,7]

Many authors have been stimulated to generalize the theory in various directions, especially toward dynamics. Whittle's[8] stochastic formulation accounts for compositional fluctuations, while Donoghue and Gibbs[9] succeeded in averaging over fluctuations in *finite* systems. Recently, Stockmayer himself, with Burchard and Schmidt,[10] used advanced techniques for harmonizing the characterization of the molecular architecture of randomly branched systems with their dynamic molecular behavior in terms of diffusion coefficients, first cumulants, hydrodynamic mean square radii, etc. The elimination of the preaveraging approximation for the Oseen tensor was a specially welcome feature.

Yet when Stockmayer originally derived eq 1, he did not define a mechanical model from which statistical properties could be calculated by analyzing particle motions in space. Instead, he employed brilliant intuitive shortcuts, avoiding the need to mention space or motions in his paper.[1] His analysis is amply confirmed by experiments, apart from minor amendments whose need was already indicated by Flory and to whose theoretical developments Stockmayer contributed, e.g., in his paper with Jacobson[11] on ring-chain competition for the case $f = 2$. Most confirmations,[12] but not all,[13] were concerned with kinetic (irreversible) gelation, to which eq 1 also applies.[1,7] Authors who have tried later to deepen the statistical-mechanical analysis by cutting out the intuitive shortcuts include Gordon and Judd,[14] C. Cohen et al.,[15] and R. J. Cohen and Benedek.[16] Of these, the last-cited paper does not introduce space or motion either; its analysis does not go beyond Stockmayer's in the direction of interest here. Gordon and Judd use the rotational partition functions of the molecules and remark that the "translational factor of the partition functions are not relevant to condensed polymer systems and are omitted". Cohen et al.,[15] on the other hand, assign to their particles translational motion and no others. Meanwhile textbooks of statistical mechanics typically asserted[17] that "translational and rotational terms disappear in the partition function and are replaced by vibrational terms" in the liquid state (in which RFFP is carried out). Accordingly, a fundamental explanation is required.

In conformity with the practice followed from nuclear physics to cosmology, I propose to define as *fundamental* an explanation which establishes an invariance principle on the basis of group symmetries, in order to demonstrate

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[†] To Stocky, with high regards, for his 70th birthday.

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