Dartmouth College

Dartmouth Digital Commons

Excluded-Volume Effect on Quasi-Elastic Light Scattering by Flexible Macromolecules

Genzo Tanaka
Dartmouth College

Walter H. Stockmayer
Dartmouth College

Excluded-volume effect on quasi-elastic light scattering by flexible macromolecules

(polymer dynamics/dynamic structure factor/diffusion)

GENZO TANAKA* AND WALTER H. STOCKMAYER†

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Contributed by W. H. Stockmayer, July 14, 1982

ABSTRACT   First-order perturbation expressions are developed for the first cumulant (initial time derivative) of the dynamic structure factor observable by photon-correlation measurements of the light scattered by flexible chain molecules in solution. A dimensionless coefficient C, which measures the initial departure of the first cumulant from proportionality to the square of the scattering vector, is found to be only slightly altered by excluded-volume effects.

Quasi-elastic light scattering (QELS) offers a powerful method for the characterization of macromolecules in solution (1). With modern photon-correlation methods, the dynamic structure factor $S(q,t)$ can be measured with quite high precision, and in most cases an accurate value of the first cumulant (initial time derivative) of the dynamic structure factor can be obtained (2, 3). By invocation of the known properties (4) of the usual polymer diffusion equation, Akcasu and Gurol (5) showed that the first cumulant can be expressed as an equilibrium average:

$$[-d \ln S(q,t)/dt]_{t=0} \equiv \Gamma = \sum_{j}^{N} \sum_{k}^{N} \langle\langle \mathbf{q}\cdot\mathbf{D}_{jk}\cdot\mathbf{q}\rangle\rangle / N^2 P(q), \quad [1]$$

where $\mathbf{q}$ is the scattering vector with a magnitude

$$q = (4\pi/\lambda)\sin(\theta/2),$$

involving the scattering angle θ and the wavelength λ in the solvent medium; t is time. The denominator of Eq. 1 is the well-known (5) equilibrium particle scattering factor:

$$N^2 P(q) = \sum_{j}^{N} \sum_{k}^{N} \langle \exp(i\mathbf{q}\cdot\mathbf{R}_{jk}) \rangle, \quad [2]$$

where $\mathbf{R}_{jk}$ is the vector between structural elements j and k. The numerator of Eq. 1 requires a knowledge of the diffusion tensor $\mathbf{D}_{jk}$. In most applications, this is given the form applied to polymer problems by Kirkwood and Riseman (6), which reads

$$\mathbf{D}_{jk}/k_B T = \delta_{jk} \zeta^{-1} \mathbf{1}$$
$$+ (1 - \delta_{jk})(8\pi\eta_0 R_{jk})^{-1}(1 + R_{jk}^{-2} \mathbf{R}_{jk}\mathbf{R}_{jk}). \quad [3]$$

In this formula, k_B is the Boltzmann constant, T is absolute temperature, ζ is the friction coefficient of a chain element, η_0 is the solvent viscosity, and $R_{jk} = |\mathbf{R}_{jk}|$. The Akcasu–Gurol recipe, Eq. 1, has been applied to a number of different polymer models (5, 7–11), and it has been shown (10, 11) how such calculations can aid in the estimation of branching and polydispersity in polymer samples, provided that excluded volume effects can be neglected.

In most polymer solutions, excluded volume effects on chain-length-dependent properties must be taken into account (12).

Supplementing previous work on the excluded volume effect in QELS, we offer here a rigorous first-order perturbation treatment, using well-established methods. Our results indicate that the estimation of branching or polydispersity from QELS will not be seriously affected by excluded-volume interactions.

General formulation

It is convenient to implement the averaging process of Eq. 1 in two stages: first, an average over orientations of $\mathbf{R}_{jk}$ with respect to $\mathbf{q}$, and then the average over magnitudes R_{jk}. After the first stage, we have

$$\Gamma/q^2 = (Nk_B T/\zeta)\left[1 + (\zeta/4\pi\eta_0)q \sum_{j\neq k}^{N}\sum^{N} \langle f(qR_{jk})\rangle\right] / N^2 P(q) \quad [4]$$

where

$$f(x) \equiv (x^{-2} - x^{-4})\sin x + x^{-3}\cos x. \quad [5]$$

For complete evaluation of Γ, an explicit expression for the equilibrium probability density of R_{jk} is needed. However, experimental results for conventional QELS are frequently confined to rather low q values, such that $q^2\langle S^2\rangle \ll 1$, and a moment expansion is then useful. Retaining only the first two terms in the series expansions of the functions of R_{jk}, we have

$$\Gamma/q^2 = D(1 + Cu^2 + \ldots); \quad u^2 \equiv q^2\langle S^2\rangle, \quad [6]$$

with

$$D = \lim_{q\to 0}(\Gamma/q^2) = k_B T[(N\zeta)^{-1} + (3\pi\eta_0)^{-1}\langle S^{-1}\rangle] \quad [7]$$

and

$$C = \lim_{q\to 0}\langle S^2\rangle^{-1} d \ln(\Gamma/q^2)/d(q^2)$$
$$= \frac{1}{3} - (k_B T/15\pi\eta_0)\langle S\rangle D^{-1}\langle S^2\rangle^{-1}. \quad [8]$$

In the last two expressions we have introduced average moments:

$$\langle S^p\rangle \equiv (2N^2)^{-1} \sum_{j\neq k}^{N}\sum^{N} \langle R_{jk}^p\rangle. \quad [9]$$

For $p = 2$, Eq. 9 reduces to the well-known definition of the mean square radius. Only even integral values of p appear in the conventional particle scattering function $P(q)$.

The right-hand side of Eq. 7 gives exactly a famous equation for the translational diffusion coefficient due to Kirkwood (13). This equation does not properly take account of coupling be-

---

Abbreviation: QELS, quasi-elastic light scattering.
* Present address: Michigan Molecular Institute, Midland, MI 48640.
† To whom reprint requests should be addressed.

tween internal and translational motions, and thus is strictly true for the model only at zero time. This shortcoming has been discussed theoretically (14, 15). Experimentally, numerous QELS experiments on polystyrene in θ solvents indicate (16) that the Kirkwood formula overestimates the observable D by about 15%; and for poly(methylmethacrylate) the discrepancy is even greater (17). Some of the approximations implied by the Kirkwood result can be avoided (14, 18), but it is possible that the underlying Oseen interaction of Eq. 3 is itself inadequate. In the absence of alternative formulations, we may hope that the *relative* effects of excluded volume can be adequately treated with eqs. 1 and 3.

An attractive aspect of the Akcasu–Gurol formula is that the full fluctuating form of the Oseen hydrodynamic interaction, as in Eq. 3, can be used directly in Eq. 1 for simple molecular models. This is in contrast to theoretical treatments of solution viscosity, where preaveraging of D_{jk} has almost always been introduced to avoid early-stage intractability. Since this maneuver may be desirable for sufficiently complicated molecular structures even in the light-scattering problem (10, 11), we also present some results using it here. In this approximation,

$$\Gamma_{pre}/q^2 = (Nk_BT/\zeta)$$

$$\left[1 + (\zeta/6\pi\eta_0)\sum_{j\neq k}\sum \langle \sin(qR_{jk})/qR_{jk}\rangle\langle R_{jk}^{-1}\rangle\right]\bigg/ N^2P(q). \quad [10]$$

The resulting diffusion coefficient is again that of Eq. 7, but the higher odd moments are different, Eq. 9 being replaced by

$$\langle S^{2r-1}\rangle_{pre} = (2N^2)^{-1}\sum_{j\neq k}\sum \langle R_{jk}^{-1}\rangle\langle R_{jk}^{2r}\rangle, \quad [11]$$

so that we now have

$$C_{pre} = \tfrac{1}{3} - (k_BT/18\pi\eta_0)\langle S\rangle_{pre}D^{-1}\langle S^2\rangle^{-1}. \quad [12]$$

Linear Gaussian chains with excluded volume

The customary model will be used: a chain of N identical Gaussian springs connecting $N + 1$ identical spherical centers of friction ("segments"), plus an excluded-volume potential that is a sum of short-range interactions between all pairs of nonadjacent segments. Long chains are assumed ($N \gg 1$).

We first consider low scattering angles, for which $u \ll 1$. Omitting the first (free-draining) term on the right-hand side of eq. 7, which is negligible for long chains, we obtain the diffusion coefficient

$$D = D_0 \alpha_f^{-1}; \quad D_0 = 4k_BT/9\pi^{3/2}\eta_0 \langle S^2\rangle_0^{1/2}. \quad [13]$$

The expansion factor for the "Stokes radius" of the coil is defined by

$$\alpha_f \equiv \langle S^{-1}\rangle_0/\langle S^{-1}\rangle \quad [14]$$

where the zero subscript denotes an unperturbed Gaussian value. The above value of D_0 was obtained by Kirkwood and Riseman in 1948 (6), and the first-order perturbation treatment of the expansion factor α_f was also given many years ago (19). Treatments of α_f for larger excluded volume effects, for which first-order perturbation theory is inadequate, are offered by Benmouna and Akcasu (20), by Weill and des Cloizeaux (21), by Akcasu *et al.* (22), and by Tanaka (23).

In a similar way, the coefficient C can be expressed as

$$C = \tfrac{1}{3} - \tfrac{4}{25}\alpha_1\alpha_f\alpha_2^{-2} \quad [15]$$

with

$$\alpha_1 \equiv \langle S\rangle/\langle S\rangle_0; \quad \alpha_2^2 \equiv \langle S^2\rangle/\langle S^2\rangle_0. \quad [16]$$

Here α_2 will be recognized as the expansion factor for the root-mean-square radius of gyration, more commonly symbolized as α_S.

Following the standard procedure (12), we have evaluated the first-order expansion factor for the odd moments $\langle S^{2r-1}\rangle$, with results given in the *Appendix*. From the result for $r = 0$ we find

$$D/D_0 = \alpha_f^{-1} = D_0(1 - 0.60927z + \ldots), \quad [17]$$

which checks the calculation of Stockmayer and Albrecht (19). Here z is the familiar (12) excluded-volume parameter

$$z \equiv \beta N^2(4\pi\langle S^2\rangle_0)^{-3/2}, \quad [18]$$

in which β represents the binary intersegment cluster integral or effective excluded volume per pair of segments.

From Eqs. 15 and 16,

$$C = \tfrac{13}{75} + (8.56 \times 10^{-5})z + \ldots \quad [19]$$

$$= 0.173(1 + 0.000494z + \ldots).$$

It was earlier conjectured (10, 11) that the excluded volume effect on C should be small, simply because C is a dimensionless quantity that is a ratio of different moments of the segment distribution function.

With preaveraged hydrodynamic interactions, the result is

$$C_{pre} = \tfrac{2}{15} + 0.0683z + \ldots \quad [20]$$

$$= 0.133(1 + 0.512z + \ldots),$$

showing a markedly greater excluded volume effect than Eq. 19. This is evidently due to the different weightings of configurations demanded by Eqs. 9 and 11, respectively. With present experimental capabilities, the coefficient C cannot be measured with high precision, and it therefore seems less than promising as a means for distinguishing between the full fluctuating and the preaveraged forms of hydrodynamic interaction. In our view, the result of Eq. 19 is physically the more reliable, and leads us to the conclusion that quite generally C should not be much influenced by the excluded volume effect. This coefficient is, however, quite sensitive to branching and polydispersity (10, 11).

For large scattering angles,[‡] with $u \gg 1$, we can also evaluate the first cumulant straightforwardly from Eqs. 4 and 5 to first order in the excluded volume parameter. Neglecting the free-draining terms from the start, we have

$$\Gamma/q^3 = (k_BT/4\pi\eta_0)\sum_{j\neq k}^{N}\sum^{N} \langle f(qR_{jk})\rangle/N^2P(q), \quad [21]$$

which finally leads to

$$\Gamma/q^3 = (k_BT/16\eta_0)[1 + 2\pi^{-1/2}(\pi^2 - 8)zu_0^{-1} + \ldots] \quad [22]$$

$$= (k_BT/16\eta_0)(1 + 2.11\,zu_0^{-1} + \ldots).$$

Although we have not evaluated any higher-order terms, simple consideration of the expression for the distribution function of R_{jk} shows that for $u \gg 1$ the coefficient of z^n in the series for Γ is proportional to u_0^{-n}. Hence, according to the model, $\Gamma\eta_0/k_BTq^3$ is a universal function of zu_0^{-1}. It is to be observed that the variable zu_0^{-1} is independent of molecular weight but does depend on solvent power.

[‡] Some authors would term the results that follow characteristic of an *intermediate* scattering region because by discarding the free-draining term we have implicitly excluded wave vectors so large that $1/q$ is of the order of a bond length, such as might be observed in neutron scattering experiments.

Chemistry: Tanaka and Stockmayer

Proc. Natl. Acad. Sci. USA 79 (1982)   6403

The preaveraging method gives, for high u,

$$\Gamma_{pre}/q^3 = (k_B T/6\pi\eta_0)[1 + (\pi^{3/2} + 2\pi^{1/2}$$
$$- 4\pi^{1/2}\ln 2 + 4\pi^{-1/2})zu_0^{-1} + ...] \qquad [23]$$
$$= (0.053 \, k_B T/\eta_0)(1 + 6.46zu_0^{-1} + ...).$$

The unperturbed leading term is not very far from the correct value of Eq. 22, but the excluded-volume correction is over 3 times too big.

The linear terms in zu_0^{-1} of Eqs. 22 and 23 are affected only by interactions between pairs of elements j and k that are not too far apart along the chain contour, such that $|j - k| \ll N$. Thus, as argued by Burchard *et al.* (10) for the unperturbed case, these results are quite general for any flexible macromolecule, irrespective of detailed topological features such as branches or rings.

An estimated exponent from Eq. 22 is

$$d \ln\Gamma/d \ln q = 3 - 2.11zu_0^{-1} + ... \qquad [24]$$

Early discussions of this exponent produced varied points of view: Dubois-Violette and deGennes (24) proposed a value of $8/3$; Silbey and Deutch (25) subsequently suggested $16/5$; but deGennes (26) later concluded that the limiting exponent at high q is exactly 3, independent of the presence or absence of excluded-volume effects. This conclusion is in full agreement with eq. 24, because u_0 is proportional to q. It was also reached by Benmouna and Akcasu (20, 27).

According to Eq. 22 the value of Γ/q^3 tends to the limiting value $k_B T/16\eta_0$ at high q—i.e., small zu_0^{-1}—independent of excluded volume, and this is also true to any higher order of the two-parameter perturbation theory. A similar conclusion was earlier reached by Benmouna and Akcasu (27) on the basis of the "blob" model of excluded volume effects. These authors also calculated Γ/q^3 at intermediate q values, which cannot be accomplished with first-order perturbation theory.[§] Their results produce an interesting prediction: in sufficiently good solvents, Γ/q^3 as a function of q may linger at a plateau value of 0.0789 $k_B T/\eta_0$ before finally descending to the universal limit $k_B T/16\eta_0$ discussed above. Some experimental results (29) appear at least partly to support this prediction. More recently, however, the calculation has been repeated by T. P. Lodge, C. C. Han, and A. Z. Akcasu (personal communication) with the improved, modified blob model (22), and in this case the intermediate plateau is far less distinct. This problem (and also the behavior of C) might be studied for large excluded volumes by means of Monte Carlo simulation of self-avoiding lattice chains.

Appendix

The first-order perturbation theory (12) when applied to $\langle S^{2r-1} \rangle$ gives

$$\langle S^{2r-1} \rangle = \langle S^{2r-1} \rangle_0 (1 + K_{2r-1}z - ...), \qquad [A1]$$

where the unperturbed value is

$$\langle S^{2r-1} \rangle_0 = [8 \cdot (r!)/\pi^{1/2}(2r + 1)(2r + 3)](4\langle S^2 \rangle_0)^{r-1/2} \qquad [A2]$$

and the coefficient K_{2r-1} is

$$K_{2r-1} = -4 + \frac{(2r + 3)!!}{2^{r+2}[(r + 2)!]} \pi \left\{ 2r + 5 \right.$$

$$\left. - \frac{4r^2 + 7r - 1}{2^{2r+3}(r + 1)(r + 2)} - 4\ln(3/2) - \sum_{n=0}^{r+1} [1/2^{2n+1}(n + 1)] \right\}. \qquad [A3]$$

Details of this derivation are omitted, for they are straightforward though tedious.

For $r = 0$,

$$K_{-1} = -4 + \pi[27/16 - 3/2\ln(3/2)] = -0.6092717 ... \qquad [A4]$$

which recovers an early result (19). In the text we also need

$$K_1 = -4 + \pi[255/128 - 5/4\ln(3/2)] = 0.66638 ... \qquad [A5]$$

The preaveraged value, $K_1^{(p)}$ is

$$K_1^{(p)} = 484/63 - \pi[85/64 + 5/2\ln(3/2)] = 0.325596 ..., \qquad [A6]$$

which is only half that of Eq. A5. Evidently the excluded volume effects on $\langle R_{jk}^{-1} \rangle$ and $\langle R_{jk}^2 \rangle$, which both appear in Eq. 11, neutralize each other to a considerable extent.

1. Berne, B. J. & Pecora, R. (1976) *Dynamic Light Scattering* (Wiley, New York).
2. Pusey, P. N. (1979) in *Light Scattering in Liquids and Macromolecular Solutions*, eds. Degiorgio, V., Corti, M. & Giglio, M. (Plenum, New York), pp. 1–29.
3. Akcasu, A. Z., Benmouna, M. & Han, C. C. (1980) *Polymer* 21, 866–890.
4. Fixman, M. (1965) *J. Chem. Phys.* 42, 3831–3837.
5. Akcasu, A. Z. & Gurol, H. (1976) *J. Polym. Sci. Polym. Phys. Ed.* 14, 1–10.
6. Kirkwood, J. G. & Riseman, J. (1948) *J. Chem. Phys.* 16, 565–573.
7. Akcasu, A. Z. & Higgins, J. S. (1977) *J. Polym. Sci. Polym. Phys. Ed.* 15, 1745–1756.
8. Burchard, W. (1978) *Macromolecules* 11, 455–459.
9. Schmidt, M. & Burchard, W. (1978) *Macromolecules* 11, 460–465.
10. Burchard, W., Schmidt, M. & Stockmayer, W. H. (1980) *Macromolecules* 13, 580–587.
11. Burchard, W., Schmidt, M. & Stockmayer, W. H. (1980) *Macromolecules* 13, 1265–1272.
12. Yamakawa, H. (1971) *Modern Theory of Polymer Solutions* (Harper & Row, New York).
13. Kirkwood, J. G. (1954) *J. Polym. Sci.* 12, 1–14.
14. Fixman, M. (1981) *Macromolecules* 14, 1710–1717.
15. Schurr, J. M. (1981) *J. Chem. Phys.* 74, 1428–1430.
16. Schmidt, M. & Burchard, W. (1981) *Macromolecules* 14, 210–211.
17. ter Meer, H.-U., Burchard, W. & Wunderlich, W. (1980) *Coll. Polym. Sci.* 258, 675–684.
18. Zimm, B. H. (1980) *Macromolecules* 13, 592–602.
19. Stockmayer, W. H. & Albrecht, A. C. (1958) *J. Polym. Sci.* 32, 215–219.
20. Benmouna, M. & Akcasu, A. Z. (1978) *Macromolecules* 11, 1187–1192.
21. Weill, G. & des Cloizeaux, J. (1979) *J. Phys. (Paris)* 40, 99–104.
22. Akcasu, A. Z., Benmouna, M. & Alkhafaji, S. (1981) *Macromolecules* 14, 147–150.
23. Tanaka, G. (1982) *Macromolecules* 15, 1028–1031.
24. Dubois-Violette, E. & deGennes, P. G. (1967) *Physics* 3, 181–198.
25. Silbey, R. & Deutch, J. M. (1972) *J. Chem. Phys.* 57, 5010–5011.
26. DeGennes, P. G. (1976) *Macromolecules* 9, 594–598.
27. Benmouna, M. & Akcasu, A. Z. (1980) *Macromolecules* 13, 409–414.
28. Miyaki, Y., Einaga, Y. & Fujita, H. (1978) *Macromolecules* 11, 1180–1186.
29. Han, C. C. & Akcasu, A. Z. (1981) *Macromolecules* 14, 1080–1084.

§ In good solvents the perturbation parameter is too large. For example, from the data of Miyaki *et al.* (28) on polystyrene in benzene at 25°C we estimate that zu_0^{-1} is about 1.5 for green light at a scattering angle of 15°.