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Some Comments on Correlation-function Formulas for Polymer Intrinsic Viscosity

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COMMENT

Some comments on correlation-function formulas for polymer intrinsic viscosity*

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Recently Yamakawa, Tanaka, and Stockmayer (YTS)[1] gave a derivation of a correlation-function formula for the intrinsic viscosity of a polymer solution that had been offered earlier on intuitive grounds.[2] According to these authors, the intrinsic viscosity is proportional to the Laplace–Fourier transform of the autocorrelation function of a quantity $\bar{J}_p^{(xy)}$ which is an off-diagonal element of the stress tensor,

$$\bar{J}_p = R^T K - kT R^T \nabla_R \ln G(R \mid R^0; t) , \tag{1}$$

where the chain coordinates are symbolized by R and the forces K are derived from the intramolecular potential W of mean force,

$$K = -\nabla_R W . \tag{2}$$

The final term in Eq. (1) invokes the "entropic" or "diffusion" force as obtained from the Green's function $G(R \mid R^0; t)$ for the polymer diffusion operator defined in the full polymer coordinate space.

Unfortunately the work of YTS did not fully clarify the questions associated with the application of the correlation-function formalism. In fact, their final intrinsic viscosity formula based on Eq. (1), though technically correct, is overstated; for, as remarked in an accompanying paper by Felderhof, Deutch, and Titulaer (FDT),[3] a simple integration by parts reveals that the contribution of the entropic-force term to the correlation function of $\bar{J}_p^{(xy)}$ vanishes identically provided that a *complete* set of polymer coordinates is used. It is therefore unjust and meaningless to criticize[1] alternative formulations of intrinsic-viscosity theory because the entropic-force contribution is omitted.[4] The entire Newtonian intrinsic viscosity at any frequency can be found from the autocorrelation function of an off-diagonal element of $R^T K$. This latter assertion has been doubted[4] for the case of rigid polymer molecules; but if care is taken a complete result can be obtained. A convenient device[5] in such cases is to start with deformable bond lengths and angles, working in the full coordinate space, and then to let the appropriate force constants increase without limit at a convenient late stage of the calculation. An excellent testing ground for this procedure is the Fraenkel dumbbell,[6,7] with[3] or without hydrodynamic interaction, and one can choose either to derive the Green's function itself[3] or to evaluate the required moments.[8]

A more common theoretical approach to intrinsic viscosity[9–11] does not invoke correlation functions in the equilibrium ensemble but deals directly with the average value of $\bar{J}_p^{(xy)}$ in the perturbed, nonequilibrium ensemble; it is not restricted to Newtonian flow. An integration by parts for this case shows that in the full polymer coordinate space the entropic-force contribution to the intrinsic viscosity again vanishes identically, for both linear[3] and nonlinear response regimes; thus the entire effect is always proportional to the nonequilibrium average value of $x^T K_y$. This fact appears to have been known,[7,11] but it has not been universally recognized.

Since the entropic-force term vanishes, its retention is innocuous and at worst possibly uneconomical; yet Kirkwood and Auer,[12] Fraenkel,[6] and more recently Fixman and Kovac[13] have found this maneuver practically useful in dealing with rigid molecules or systems with constraints. A similar procedure can equally well be used[5] in the correlation–function method. The average force is related to the equilibrium distribution function $f_e(R)$ by $K = kT \nabla_R \ln f_e$, and therefore the stress tensor can always be written in the form

$$\bar{J}_p = -kT R^T \nabla_R \ln(G/f_e) \tag{3}$$

and correctly evaluated. In treating the free-draining rigid rod, Chikahisa and Stockmayer[5] actually performed a hybrid calculation, using Eq. (3) to evaluate the contribution from the angular coordinates (θ, ϕ) defining the orientation of the rod; but they then resorted to direct use of the $R^T K$ term for the contribution from the bond-stretching coordinates within the rod. Such a mixed procedure is likely to be confusing and is probably best avoided in future work.

In considering systems with constraints[14] one internally consistent procedure, mentioned above and discussed at length by FDT,[3] is to operate in the full coordinate space and introduce constraints at a late stage of calculation. There are, however, two other possible approaches, as pointed out to us by Fixman. In one of these methods[15–18] consideration is given to diffusion in only the subspace of unconstrained degrees of freedom, and the momenta conjugate to the constrained coordinates are ignored. In the other method[4,13,19–21] consideration of the full coordinate space is preserved, but constraints are introduced at an early stage of calculation. For this latter method, correlation function formulas also exist.[4,19,20] A general feature of these formulas is the appearance of a separate frequency-independent term, the limiting high-frequency intrinsic viscosity. This term can be obtained either with[13,19,20] or without[21] recourse to the polymer diffusion equation. Fixman and Kovac[13] did not work with time correlation

functions, but their result can be recast[8] into this form.

Finally, we must point to an erroneous formula given by YTS at an intermediate stage of their development. Their relation for the stress tensor in the polymer phase space, Eq. (41), contains a spurious term, $-R^T\zeta \cdot m^{-1}P$, which can be shown to lead to physically inadmissable results, [8,22] and we believe the correct formula is simply

$$\bar{J}_p = m^{-1}P^TP + R^TK . \qquad (4)$$

This and related questions will be discussed more fully at a later time.

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[1]H. Yamakawa, G. Tanaka, and W. H. Stockmayer, J. Chem. Phys. 61, 4535 (1974).
[2]W. H. Stockmayer, W. Gobush, Y. Chikahisa, and D. K. Carpenter, Chem. Soc. Faraday Discuss. 49, 182 (1970).
[3]B. U. Felderhof, J. M. Deutch, and U. M. Titulaer, J. Chem. Phys. 63, 740 (1975), this issue.
[4]M. Doi and K. Okano, Polymer J. 5, 216 (1973).
[5]Y. Chikahisa and W. H. Stockmayer, Rep. Prog. Polym. Phys. Jpn. 14, 79 (1971).
[6]G. K. Fraenkel, J. Chem. Phys. 20, 642 (1952).
[7]R. B. Bird, H. R. Warner, Jr., and D. C. Evans, Adv. Polym. Sci. 8, 1 (1971).
[8]G. Wilemski (unpublished calculations).
[9]J. G. Kirkwood and J. Riseman, J. Chem. Phys. 16, 565 (1948).
[10]H. Yamakawa, Modern Theory of Polymer Solutions (Harper and Row, New York, 1971), Chap. VI.
[11]M. Fixman, J. Chem. Phys. 42, 3831 (1965).
[12]J. G. Kirkwood and P. L. Auer, J. Chem. Phys. 19, 281 (1951).
[13]M. Fixman and J. Kovac, J. Chem. Phys. 61, 4939, 4950 (1974).
[14]M. Fixman, Proc. Natl. Acad. Sci. 71, 3050 (1974).
[15]H. A. Kramers, J. Chem. Phys. 14, 415 (1946).
[16]J. G. Kirkwood, Rec. Trav. Chim. 68, 648 (1949).
[17]O. Hassager, J. Chem. Phys. 60, 2111, 4001 (1974).
[18]C. F. Curtiss, R. B. Bird, and O. Hassager, WIS-TCI-507; to appear in Adv. Chem. Phys.
[19]J. J. Erpenbeck and J. G. Kirkwood, J. Chem. Phys. 29, 909 (1958); 38, 1023 (1963).
[20]K. Iwata, J. Chem. Phys. 54, 1570 (1971).
[21]M. Doi, H. Nakajima, and Y. Wada, submitted to Colloid Polym. Sci. (1975).
[22]U. M. Titulaer (unpublished calculations).

Comment on "Elastic continuum theory cutoffs and order in nematics and solids"

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Berreman[1] has recently calculated the magnitude of thermal fluctuations of the director in nematic liquid crystals. In particular, an equation was obtained in which the cutoffs in the spectrum of fluctuations could be expressed in terms of an order parameter S (defined as $1 - 3\langle n_x^2 \rangle$, where n_x is the component of the local director transverse to the mean direction of axial symmetry z):

$$\sum_{h,m,n=1}^{H,M,N} \frac{1}{K_{11}h^2 + K_{22}m^2 + K_{33}n^2} \approx \frac{\pi^2}{3k_BT}(1-S) . \qquad (1)$$

In this note we stress that the order parameter S in the above equation *must not be confused* with the usual nematic order parameter (also often called S) defined as the thermal average of the second Legendre polynomial, $\langle P_2(\cos\theta) \rangle$, where θ is the angle between the long axis of a given molecule and the local director. Whereas the S used in Eq. (1) is a measure of *director fluctuations* away from the mean symmetry axis, $\langle P_2 \rangle$ is a measure of the *nematic order with respect to the local director* and is defined without regard to fluctuations of the director. [2-4]

Berreman has apparently overlooked this distinction and has used experimentally measured values of $\langle P_2 \rangle$ for S in Eq. (1) in order to deduce approximate values of

$(HMNV)^{-1/3}$, where V is the molecular volume and H, M, and N are the cutoff wave vectors of the elastic continuum theory. This procedure is incorrect and, as a consequence, the numerical results and qualitative conclusions quoted for liquid crystals are not meaningful.

If we follow Berreman and identify S in Eq. (1) with $\langle P_2 \rangle$, then Eq. (1) predicts a definite temperature dependence for $\langle P_2 \rangle$ which can easily be tested using published data. In particular, since[5-7] $K_{ii} \propto \langle P_2 \rangle^2$, and H, M, N are expected to be temperature independent, Eq. (1) predicts

$$\langle P_2 \rangle^2 (1 - \langle P_2 \rangle) \propto T . \qquad (2)$$

In Fig. 1 we have plotted $\langle P_2 \rangle^2 (1 - \langle P_2 \rangle)$ as a function of temperature for four materials and for simple mean field theory. The figure clearly demonstrates that Eq. (2) is not obeyed.

It is interesting to note that, had Berreman calculated S from director fluctuation amplitudes which could in principle be measured in light scattering experiments[11] on the nematic phase, he could indeed have determined meaningful estimates of the quantity $(HMNV)^{-1/3}$ for nematics. Moreover, Eq. (1) further predicts that the quantity S defined by Berreman should have the temper-