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Gerald Wilemski

Missouri University of Science and Technology, wilemski@mst.edu

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Intrinsic viscosity of stiff dumbbells from time correlation functions*

Gerald Wilemski

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755
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The intrinsic viscosity of a suspension of stiff dumbbells is evaluated by a time correlation function method. The required moments of the internal coordinates are calculated directly from the diffusion equation, without explicit evaluation of the Green's function. For the rigid dumbbell, the correct high frequency limit is obtained, disposing of recent doubts over this possibility. The interplay of dumbbell stiffness and shearing frequency is also illustrated.

I. INTRODUCTION

Time correlation function methods (TCFM)¹ have previously been proposed²⁻⁸ for use in polymer dynamics. Several of these methods have been used to calculate the intrinsic viscosity of flexible⁴⁻⁷ and rigid^{6,9} chain polymers in solution. Although a correct result⁹ had been reported for the latter application, the adequacy of TCFM and diffusion equations for predicting limiting high frequency behavior has been questioned.⁶ Intertwined with these two disparate viewpoints was some confusion regarding the correct form of the stress tensor whose correlation function was to be calculated. Yamakawa, Tanaka, and Stockmayer¹⁰ attempted to resolve these difficulties, but it now appears that only very recently has this been accomplished.^{11,12} Much of the disagreement apparently arose because of misunderstanding over the different ways of handling constraints.¹³

In this article TCFM and a diffusion equation are used to calculate the Newtonian intrinsic viscosity of a suspension of free-draining stiff dumbbells. This problem has been considered before, both with^{6,9,11} and without¹⁴⁻¹⁶ TCFM. The present calculation differs from previous treatments in evaluating various moments of the internal coordinates of the dumbbell directly from the diffusion equation, avoiding entirely the somewhat lengthier procedure of explicitly calculating¹¹ the Green's function of the diffusion operator. A single relation for the intrinsic viscosity is obtained, valid at all frequencies through terms of order κ^{-1} , where κ is the spring force constant of the dumbbell. For a completely rigid dumbbell, direct passage to the limit $\kappa^{-1} \rightarrow 0$ yields the correct result at all frequencies, explicitly allaying the recent⁶ skepticism about TCFM. The results illustrate the interplay between the stiffness of the dumbbell and the frequency of the oscillating shear in determining the apparent rigidity of the particle in solution. Hydrodynamic interactions have been omitted for simplicity, but their inclusion in this case is not difficult.^{11,15}

II. EQUATIONS FOR THE FREE-DRAINING DUMBBELL

The dumbbell distribution function G satisfies the diffusion equation

$$\frac{\partial G}{\partial t} = \sum_{i=1,2} \frac{kT}{\zeta} \nabla_i \cdot [\nabla_i G - (kT)^{-1} \mathbf{K}_i G], \quad (2.1)$$

where ζ is the friction constant for a single particle and \mathbf{K}_i is the force on particle i

$$\mathbf{K}_i = -\nabla_i W. \quad (2.2)$$

For the potential of mean force W we make the same choice as Fraenkel.¹⁴ Thus,

$$W = (\kappa/2)(|\mathbf{r}_2 - \mathbf{r}_1| - b)^2, \quad (2.3)$$

where \mathbf{r}_i denotes the position vector of particle i , κ is the spring force constant, and b is the finite equilibrium length of the spring. Upon transforming into relative coordinates and rejecting any center of mass dependence, Eq. (2.1) becomes,

$$\partial G / \partial t = D \nabla \cdot (\nabla G - (kT)^{-1} \mathbf{K} G), \quad (2.4)$$

where

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, \quad (2.5)$$

$$D = 2kT/\zeta, \quad (2.6)$$

and

$$\mathbf{K} = -\kappa(r-b)\mathbf{r}/r. \quad (2.7)$$

In spherical coordinates Eq. (2.4) becomes

$$\begin{aligned} \frac{\partial G}{\partial t} = D r^{-2} \left(\frac{\partial}{\partial r} \right) \left[r^2 \left(\frac{\partial G}{\partial r} \right) + \kappa (kT)^{-1} r^2 (r-b) G \right] \\ + D r^{-2} M_{\theta, \phi} G, \end{aligned} \quad (2.8)$$

where

$$M_{\theta, \phi} G = (\sin \theta)^{-1} \left(\frac{\partial}{\partial \theta} \right) \left(\sin \theta \frac{\partial G}{\partial \theta} \right) + (\sin \theta)^{-2} \frac{\partial^2 G}{\partial \phi^2}. \quad (2.9)$$

The complex intrinsic viscosity $[\eta]$ is given by the expression^{10,11}

$$[\eta] = N_A (M \eta_0 kT)^{-1} \int_0^\infty C(t) e^{-i\omega t} dt, \quad (2.10)$$

where N_A is Avogadro's number, M is the dumbbell molecular weight, and η_0 is the solvent viscosity.

The time correlation function needed is the following^{11,12}:

$$C(t) = \langle J_{xy}(t) J_{xy}(0) \rangle_{\mathbf{e}_x}, \quad (2.11)$$

where

$$J_{xy}(t) = \int x K_y G d\mathbf{r}, \quad (2.12)$$

$$\langle (\dots) \rangle_{\text{eq}} = \int (\dots) f_{\text{eq}} d\mathbf{r}, \quad (2.13)$$

and

$$f_{\text{eq}} = n_0 \exp[-\kappa(r-b)^2/(2kT)]. \quad (2.14)$$

The normalization constant n_0 will be specified later. Here, J_{xy} has already been expressed in relative coordinates, and K_y is the y component of the force \mathbf{K} . In spherical coordinates Eq. (2.12) becomes

$$J_{xy}(t) = -\kappa \int r(r-b) \sin^2\theta \sin\phi \cos\phi G d\mathbf{r}. \quad (2.15)$$

III. CALCULATION OF MOMENTS

The moments of interest are defined as

$$\Delta^{(n)}(t) = \int (r-b)^n \sin^2\theta \sin\phi \cos\phi G d\mathbf{r} \quad (3.1)$$

and

$$R^{(n)}(t) = \int r^n \sin^2\theta \sin\phi \cos\phi G d\mathbf{r}. \quad (3.2)$$

Then, note that

$$J_{xy}(t) = -\kappa[\Delta^{(2)}(t) + b\Delta^{(1)}(t)]. \quad (3.3)$$

Upon multiplying Eq. (2.8) by $(r-b)^n$ and integrating, the following exact equations are obtained:

$$d\Delta^{(0)}/dt = -6DR^{(-2)}, \quad (3.4)$$

$$d\Delta^{(1)}/dt = -\tau_1^{-1}\Delta^{(1)} - 4DR^{(-1)} + 6DbR^{(-2)}, \quad (3.5)$$

$$d\Delta^{(2)}/dt = -2\tau_1^{-1}\Delta^{(2)} + 8DbR^{(-1)} - 6Db^2R^{(-2)}, \quad (3.6)$$

$$d\Delta^{(3)}/dt = -3\tau_1^{-1}\Delta^{(3)} + 6D\Delta^{(1)} + 6Db\Delta^{(0)} - 12Db^2R^{(-1)} + 6Db^3R^{(-2)}, \quad (3.7)$$

where

$$\tau_1 = kT/\kappa D. \quad (3.8)$$

In order to solve these equations for $\Delta^{(2)}$ and $\Delta^{(1)}$ a simple perturbation expansion is necessary. In the limit of very large κ , the dumbbell will perform small amplitude vibrations about the reference length b . Then r^{-1} and r^{-2} may be expanded in terms of the deviation, $\delta = r - b$. With these expansions, the moments $R^{(-1)}(t)$ and $R^{(-2)}(t)$ may in turn be expanded as

$$R^{(-1)} = b^{-1}\Delta^{(0)} - \epsilon_1 b^{-2}\Delta^{(1)} + \epsilon_2 b^{-3}\Delta^{(2)} - \epsilon_3 b^{-4}\Delta^{(3)} + \dots, \quad (3.9)$$

and

$$R^{(-2)} = b^{-2}\Delta^{(0)} - 2\epsilon_1 b^{-3}\Delta^{(1)} + 3\epsilon_2 b^{-4}\Delta^{(2)} - 4\epsilon_3 b^{-5}\Delta^{(3)} + \dots. \quad (3.10)$$

Here, parameters ϵ_i have been introduced in order to identify easily the terms arising in each order of the expansion in δ . For example, in order to display terms only through δ^2 , both ϵ_1 and ϵ_2 may be put equal to unity, and the higher $\epsilon_n (n \geq 3)$ set equal to zero. Equations (3.4)–(3.7) may be solved consistently through order δ^3 . Higher-order consistency would, of course, involve equations for higher moments.

After taking the Laplace transform of Eqs. (3.4)–(3.7) and performing the necessary algebra, one obtains the expressions for $\hat{\Delta}^{(1)}(s)$ and $\hat{\Delta}^{(2)}(s)$ which are displayed in Eqs. (A1)–(A2) of the Appendix. These equations in conjunction with Eqs. (2.10), (2.11), and (3.3) will yield the desired result. The final step is the calculation of the equilibrium averages. For large κ , the normalization constant n_0 of Eq. (2.13) is given as

$$n_0 = z_0(4\pi b^2)^{-1}[\kappa/(2\pi kT)]^{1/2}, \quad (3.11)$$

where

$$z_0 = 1/(1 + \gamma) \quad (3.12)$$

and

$$\gamma = kT/(b^2\kappa). \quad (3.13)$$

The averages which contribute terms of order κ^{-1} to $[\eta]$ are the following:

$$\langle \Delta^{(0)}(0)\Delta^{(1)}(0) \rangle_{\text{eq}} = 2b\gamma z_0/15, \quad (3.14)$$

$$\langle \Delta^{(1)}(0)\Delta^{(1)}(0) \rangle_{\text{eq}} = \langle \Delta^{(0)}(0)\Delta^{(2)}(0) \rangle_{\text{eq}} = b^2\gamma(1 + 3\gamma)z_0/15, \quad (3.15)$$

$$\langle \Delta^{(1)}(0)\Delta^{(2)}(0) \rangle_{\text{eq}} = 6b^3\gamma^2 z_0/15, \quad (3.16)$$

$$\langle \Delta^{(2)}(0)\Delta^{(2)}(0) \rangle_{\text{eq}} = 3b^4\gamma^2 z_0/15. \quad (3.17)$$

IV. THE INTRINSIC VISCOSITY

Upon combining Eqs. (2.10), (2.11), (3.3), (A1), and (A2) and displaying only terms which will contribute to order κ^{-1} , the following expression for $[\eta]$ may be obtained:

$$[\eta] = \frac{N_A \zeta b^2 z_0}{30M\eta_0} \left\{ \frac{1}{1 + i\omega\tau_1 + 6\gamma\nu_1\epsilon_1} + \frac{1}{1 + i\omega\tau} \left[\frac{1}{1 + i\omega\tau_1 + 6\gamma\nu_1\epsilon_1} + \frac{1/2}{1 + i\omega\tau_2 + 6\gamma\mu_1\epsilon_2} \right] + \gamma \left[[9 + (1 + i\omega\tau)^{-1}] \Omega_1(\omega) + [2\epsilon_1 + (4\epsilon_1 + 7\epsilon_2)(1 + i\omega\tau)^{-1} + (2\epsilon_1 - 3\epsilon_2)(1 + i\omega\tau)^{-2}] \Omega_2(\omega) \right] \right\}, \quad (4.1)$$

where

$$\tau_2 = \tau_1/2, \quad (4.2)$$

$$\tau = b^2/6D, \quad (4.3)$$

$$\Omega_1(\omega) = (1 + i\omega\tau_1)^{-1} + \frac{1}{2}(1 + i\omega\tau_2)^{-1}, \quad (4.4)$$

$$\Omega_2(\omega) = (1 + i\omega\tau_1)^{-1}(1 + i\omega\tau_2)^{-1}. \quad (4.5)$$

Note that ν_1 and μ_1 are defined in Eqs. (A9) and (A11)

of the Appendix.

Evidently the third-order expansion in δ has contributed no term of order κ^{-1} . Though no details are reported here, further analysis of the equations for higher moments shows that no other terms of order κ^{-1} will be generated. This statement is consistent with the value of $[\eta]$ at zero frequency. In general, for the free draining dumbbell at zero frequency¹⁷

$$[\eta]^0 = \frac{N_A \xi}{12M\eta_0} \langle \gamma^2 \rangle_{\bullet q}, \quad (4.6)$$

and for large κ , using Eq. (2.13) to evaluate $\langle \gamma^2 \rangle_{\bullet q}$ to order κ^{-1} ,

$$[\eta]^0 = \frac{N_A \xi b^2}{12M\eta_0} (1 + 5\gamma). \quad (4.7)$$

After setting $\omega = 0$ and expanding any remaining terms, Eq. (4.1) gives precisely this result.

The limit $\kappa \rightarrow \infty$ is easy to perform, and the expected result is obtained:

$$[\eta]_{rd} = \frac{N_A b^2 \xi}{30M\eta_0} \left\{ 1 + \frac{(3/2)}{1 + i\omega\tau} \right\}. \quad (4.8)$$

Thus, by means of TCFM the correct limiting high frequency behavior for a rigid dumbbell has been deduced. Upon further reflection there seems to be no *a priori* reason to doubt the fundamental accuracy of TCFM in this application. The conventional method,¹⁴⁻¹⁶ which does give the correct answer, requires the solution of the diffusion equation which is perturbed by an additional term representing the effect of the shearing flow. For small rates of shear (linear response) the dynamical behavior of this solution will be determined by the same relaxation modes found for the Green's function of the unperturbed equation. Thus, provided all constrained coordinates are treated properly, both methods should give identical results. From this point of view, the strategy of employing the Fraenkel model¹⁴ is quite satisfactory. Taking the limit $\kappa \rightarrow \infty$ is legitimate mathematically, and it is physically justifiable whenever experimental circumstances so warrant.

Particles in solution may appear rigid or nonrigid depending on the magnitude of the experimental probing frequency. This behavior is nicely illustrated by the set of calculations presented in Fig. 1. There, the real part of $[\eta]$, designated $[\eta]'$, is plotted as a function of frequency for four different values of κ . These values were chosen in order to make the ratio of the vibra-

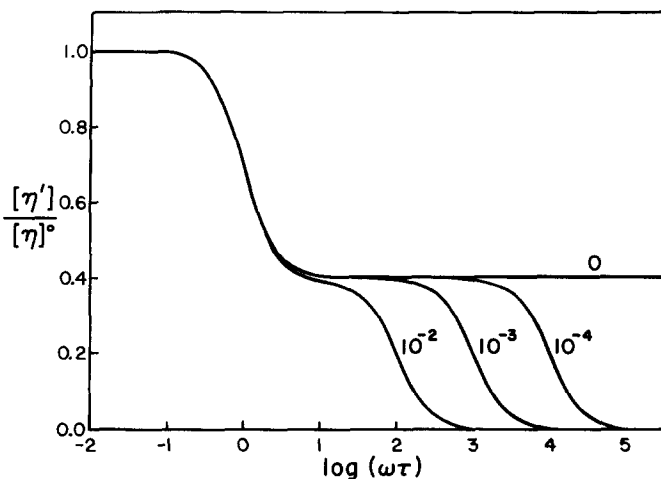


FIG. 1. Frequency dependence of $[\eta]'$ for dumbbells of varying stiffness. The curves were calculated for the indicated values of (τ_1/τ) . Note that stiffness increases as (τ_1/τ) decreases.

tional relaxation time τ_1 to the rotational relaxation time τ ,

$$\tau_1/\tau = 6\gamma, \quad (4.9)$$

become successively smaller, and ultimately zero ($\kappa \rightarrow \infty$). The four chosen values for τ_1/τ were 10^{-2} , 10^{-3} , 10^{-4} , and 0. For these choices the bracketed terms multiplied by κ^{-1} in Eq. (4.1) are negligibly small and may be omitted.

The three frequency ranges indicated by Fraenkel¹⁴ are apparent in Fig. 1. The initial decline attributable to the rotational motion of the dumbbell is followed by the plateau region characteristic of the rigid dumbbell. Last comes the decline in the highest frequency region. One sees clearly that as the force constant is increased the dumbbell responds to the oscillating shear like a rigid particle over successively larger ranges of frequency. In each case, though, for finite κ a frequency range is reached in which the vibrational modes of the stiff dumbbell can be excited. This leads to the final decline in viscosity since the dumbbell can now "follow" the oscillatory shear and reduce the frictional drag.

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APPENDIX

Through order δ^3 , Eqs. (3.4)–(3.7) may be solved for $\Delta^{(1)}(t)$ and $\Delta^{(2)}(t)$. The Laplace transforms (designated by $\hat{\Delta}$ and with s as the transform variable) of these quantities are given in the following expressions:

$$\begin{aligned} \hat{\Delta}^{(1)}(s) = & [\xi_1(1 - 36\gamma^2\rho\sigma)]^{-1} \{ \tau_1(1 + s\tau)^{-1}(b/3) \\ & \times (1 + 6\gamma\rho)\Delta^{(0)}(0) + \tau_1\Delta^{(1)}(0) \\ & + \tau_1 6\gamma\rho b^{-1}\Delta^{(2)}(0) - \tau_1 6\gamma b^{-2}\epsilon_3(\nu_2 + 12\gamma\mu_2\rho)\Delta^{(3)}(0) \} \end{aligned} \quad (A1)$$

$$\begin{aligned} \hat{\Delta}^{(2)}(s) = & [\xi_2(1 - 36\gamma^2\rho\sigma)]^{-1} \\ & \times \{ \tau_2(1 + s\tau)^{-1}(b^2/3)(1 + 6\gamma\sigma)\Delta^{(0)}(0) + \tau_2 6\gamma b\sigma\Delta^{(1)}(0) \\ & + \tau_2\Delta^{(2)}(0) - \tau_2 6\gamma b^{-1}\epsilon_3(2\mu_2 + 6\gamma\nu_2\sigma)\Delta^{(3)}(0) \}. \end{aligned} \quad (A2)$$

Here,

$$\tau = (6D)^{-1}b^2, \quad (A3)$$

$$\tau_n = (n\kappa D)^{-1}kT, \quad (A4)$$

and

$$\gamma = (b^2\kappa)^{-1}kT. \quad (A5)$$

Also,

$$\xi_1 = 1 + s\tau_1 + 6\gamma\nu\epsilon_1 + (6\gamma)^2\nu_2\epsilon_3, \quad (A6)$$

$$\xi_2 = 1 + s\tau_2 + 6\gamma\mu_1\epsilon_2 + (6\gamma)^2\mu_2\epsilon_3\epsilon_2, \quad (A7)$$

$$\xi_3 = 1 + s\tau_3 + 4\gamma, \quad (A8)$$

where

$$\nu_1 = \frac{2}{3} [2 - (1 + s\tau)^{-1}], \quad (A9)$$

$$\nu_2 = \frac{4}{9} [(\frac{5}{3}) - (1 + s\tau)^{-1}] \xi_3^{-1}, \quad (A10)$$

$$\mu_1 = \frac{1}{2} [(\frac{5}{3}) + (1 + s\tau)^{-1}], \quad (A11)$$

$$\mu_2 = -\frac{2}{3} [2 + (1 + s\tau)^{-1}] \xi_3^{-1}. \quad (\text{A12})$$

Next,

$$\rho = \rho_1 \epsilon_2 - 3\gamma\nu_2 \xi_2^{-1} \epsilon_3 \epsilon_2, \quad (\text{A13})$$

$$\sigma = \sigma_1 \epsilon_1 - 12\gamma\mu_2 \xi_1^{-1} \epsilon_3, \quad (\text{A14})$$

and finally

$$\rho_1 = \frac{1}{2} \left[\frac{7}{3} - (1 + s\tau)^{-1} \right] \xi_2^{-1}, \quad (\text{A15})$$

$$\sigma_1 = \frac{2}{3} [1 + (1 + s\tau)^{-1}] \xi_1^{-1}. \quad (\text{A16})$$

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