Correlation function formula for the intrinsic viscosity of dilute polymer solutions

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The correlation function formalism for the intrinsic viscosity of polymers is studied. A controversy concerning the correct force to use in the momentum flux is resolved. It is shown that when the diffusion equation is used in the full configuration space of polymer segments the forces entering the momentum flux are purely mechanical and there is no entropic contribution. A comparison is made with Kirkwood's theory of viscoelastic behavior. The correlation function expression we advocate is shown to yield the correct high frequency limiting behavior for the case of elastic dumbbells.

I. INTRODUCTION

In recent years several proposals[1-5] have been advanced for the appropriate time correlation function formula for the frequency-dependent intrinsic viscosity $[\eta(\omega)]$ of a dilute polymer solution,

$$[\eta(\omega)] = \frac{N_A}{M\eta_0 kT}\int_0^\infty \exp(-i\omega t)C(t)\,dt, \tag{1.1}$$

where N_A is Avogadro's number, M the polymer molecular weight, η_0 the solvent viscosity, k Boltzmann's constant, and T the absolute temperature. Here $C(t)$ is the equilibrium time correlation function of an appropriate stress tensor J_{xy},

$$C(t) = \langle J_{xy}(0)J_{xy}(t)\rangle. \tag{1.2}$$

The time evolution is governed by the internal forces between polymer segments, derivable from a potential of mean force, and by the Brownian motion of the segments due to interactions with the surrounding fluid. On the time scale of interest the Brownian motion is described by an equation of the Smoluchowski type in the configuration space of the polymer. In this context confusion has arisen concerning the correct expression for the flux J_{xy}. For a single polymer consisting of n beads at positions $\mathbf{R} \equiv (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ the flux is given by

$$J_{xy} = \sum_{j=1}^{n} y_j G_j^x, \tag{1.3}$$

where $\mathbf{G}_j$ is the force acting on bead j. Originally Stockmayer *et al.*[1] postulated, without derivation, that the force $\mathbf{G} \equiv (\mathbf{G}_1, \mathbf{G}_2, \ldots, \mathbf{G}_n)$ contains two contributions: one from the mechanical intramolecular interactions, and the other a diffusion force of entropic nature corresponding to the Brownian motion.

Later Bixon[3] adopted this expression within the framework of the Smoluchowski equation but included an additional momentum contribution to the flux. Recently Doi and Okano[4] claimed that the flux J_{xy} is purely mechanical and that the diffusion force must be omitted. They base their argument on a study of the Liouville equation of the polymer-solvent system. Assuming that one can distinguish between gross variables which vary slowly, and microscopic variables which vary on a fast time scale, they integrate over the latter using the Mori/Zwanzig projection operator[6,7] method. Doi and Okano[4] also claim that the limiting high-frequency viscosity cannot be obtained from the Brownian motion theory as described by the diffusion equation.

In an effort to settle the issue Yamakawa, Tanaka, and Stockmayer[5] have presented a more detailed analysis, also based on the projection operator method applied to the Liouville equation for the whole system. They show that on the slow time scale the probability distribution $P(\mathbf{R}, t)$ satisfies the Smoluchowski diffusion equation

$$\frac{\partial P(\mathbf{R}, t)}{\partial t} = \mathfrak{D}P(\mathbf{R}, t), \tag{1.4}$$

where the generalized diffusion operator $\mathfrak{D}$ is

$$\mathfrak{D} = \nabla_{\mathbf{R}}^T \cdot \mathbf{D} \cdot [\nabla_{\mathbf{R}} + \beta\nabla_{\mathbf{R}}U], \tag{1.5}$$

where $\beta = 1/kT$, the superscript T indicates transpose, and the diffusion tensor $\mathbf{D}$ is given by the $3n \times 3n$ matrix with elements

$$\mathbf{D}_{ij} = kT[\zeta_i^{-1}\delta_{ij}\mathbf{I} + \mathbf{T}_{ij}], \tag{1.6}$$

where ζ_i is the segment friction constant and $\mathbf{T}_{ij}$ the Oseen hydrodynamic interaction. Furthermore $U(\mathbf{R})$ is the potential of mean force between the polymer segments, from which the $3n$-dimensional force $\mathbf{K} \equiv (\mathbf{K}_1, \ldots, \mathbf{K}_n)$ is derived by

$$\mathbf{K} = -\nabla_{\mathbf{R}}U. \tag{1.7}$$

Yamakawa *et al.*[5] conclude that the correct expression for the flux is

$$\mathbf{J}(t) = \mathbf{J}_p(t) \tag{1.8}$$

with

$$\mathbf{J}_p(t) = \int \bar{\mathbf{J}}_p(t) G(\mathbf{R}\,|\,\mathbf{R}_0, t)\,d\mathbf{R}, \tag{1.9}$$

where $G(\mathbf{R}\,|\,\mathbf{R}_0, t)$ is the Green's function of the diffusion equation Eq. (1.4), and with the reduced flux $\bar{\mathbf{J}}_p(t)$ given by

$$\bar{\mathbf{J}}_p(t) = \mathbf{R}^T\mathbf{K} - kT\mathbf{R}^T\nabla_{\mathbf{R}}\ln G(\mathbf{R}\,|\,\mathbf{R}_0, t). \tag{1.10}$$

The first term in (1.10) is the mechanical force contribution mentioned before and the second term involves the diffusion force. Yamakawa *et al.*[5] claim that the limiting high-frequency viscosity follows naturally from the first term in Eq. (1.10), specifically from the bond-stretching part of the intramolecular potential energy. The second term in (1.10) is said to make the frequency-dependent contribution to the viscosity for rigid rods.

In contrast, Doi and Okano only have the mechanical term, from which they derive the frequency-dependent part of the viscosity, whereas according to these authors the limiting high-frequency viscosity cannot be found from the diffusion equation. They write the correlation function Eq. (1.2) as

$$C(t)=C_0\delta(t)+\langle \bar{J}_{xy}(0)\bar{J}_{xy}(t)\rangle, \qquad (1.11)$$

where the second term involves the reduced flux with mechanical contribution only, and the time evolution is calculated from the diffusion equation. The first term in Eq. (1.11) describes the variation of the correlation function on the fast time scale and gives the high frequency contribution to the intrinsic viscosity. The value of the constant C_0 is left undetermined in Doi and Okano's theory. As an example of their formalism they consider the rigid dumbbell model and explicitly calculate the second term in Eq. (1.11), obtaining a result agreeing with the traditional Kirkwood–Auer calculation for rigid rods, except for the absence of the limiting high-frequency viscosity, which is attributed to the first term in Eq. (1.11).

In this article we wish to clarify the issue by showing that both groups of authors in fact have the same starting point from which they come to misleading and ambiguous conclusions. The controversy about which force to use in Eq. (1.3) is easily settled by observing that, when accepting the derivation of Yamakawa *et al.* and their expression Eq. (1.10) for the flux, one finds that the diffusion force gives zero contribution. To show this we note that in Eq. (1.2) one needs the xy component of the flux, and substitution of this component of Eq. (1.10) in Eq. (1.9) gives zero after integration over the y coordinate. Thus instead of (1.10) one can use the reduced flux

$$\bar{\mathbf{J}}_p(t)=\mathbf{R}^T\mathbf{K} \qquad (1.12)$$

involving only the mechanical force. In the sequel we shall show that this expression for the flux yields both the frequency-dependent viscosity and the high-frequency limiting value correctly. Note that for the above argument it is essential that one is dealing with the full set of $3n$ Cartesian coordinates. Thus it must be applied before a further reduction of the diffusion equation to a smaller space by the introduction of rigid constraints. In our picture one deals with a purely mechanical system and "rigid" constraints correspond to strong restoring forces along certain directions in configuration space.

The flux employed by Doi and Okano[4] does not correspond to Eq. (1.12) but involves an average over the constrained coordinates. This flux, as noted by Yamakawa *et al.*,[5] is overly coarse grained and accordingly must be employed with caution in the correlation function formalism.

When the correct, mechanical expression for the flux Eq. (1.12) is introduced into Eq. (1.7) and use is made of Eqs. (1.8), (1.1), and (1.2) one finds, after certain mathematical simplifications, the correlation function expression for $[\eta(\omega)]$

$$[\eta(\omega)]=\frac{N_A\beta}{M\eta_0}\int_0^\infty \exp(-i\omega t)\times\langle(\mathbf{R}^T\mathbf{K})_{xy}[\exp(\mathfrak{D}^\dagger t)(\mathbf{R}^T\mathbf{K})_{xy}]\rangle\,dt, \qquad (1.13)$$

where

$$(\mathbf{R}^T\mathbf{K})_{xy}=\sum_{j=1}^{n} y_j K_j^x,$$

and where $\mathfrak{D}^\dagger$ is the adjoint of the diffusion operator Eq. (1.5),

$$\mathfrak{D}^\dagger=\nabla_{\mathbf{R}}^T\cdot\mathbf{D}\cdot\nabla_{\mathbf{R}}-\beta(\nabla_{\mathbf{R}}U)^T\cdot\mathbf{D}\cdot\nabla_{\mathbf{R}}, \qquad (1.14)$$

and the angular bracket denotes an average over the equilibrium distribution

$$P_{\text{eq}}(\mathbf{R})=\exp[-\beta U(\mathbf{R})]\Big/\!\int\exp[-\beta U(\mathbf{R}')]\,d\mathbf{R}', \qquad (1.15)$$

for which $\mathfrak{D}P_{\text{eq}}=0$. The expression Eq. (1.13) is identical to that proposed by Yamakawa *et al.* when account is taken of the vanishing of the diffusion force in Eq. (1.10). In the next section we show that the expression is also obtained, simply and directly, by application of linear response theory to the diffusion equation. Thus, once the diffusion equation is accepted as the basic equation valid on the time scale of interest, one has a well-defined expression for the frequency-dependent viscosity over a corresponding frequency range. This expression does include those contributions from the mechanical forces which correspond to rigid bonds in other treatments, e.g., the calculation for rigid rods by Kirkwood and Auer.[8] Such rigid constraints are introduced at the end of the calculation of the correlation function expression by letting appropriate force constants increase indefinitely.[2] This point of view is physically reasonable and mathematically simple, and completely consistent with the analysis of Yamakawa *et al.*[5]

Doi and Okano[4] perform the passage to the rigid limit in a different fashion, which we consider less transparent. However, our calculation of the frequency-dependent part of the viscosity is equivalent to theirs. The fact that Doi and Okano do not obtain the high frequency limiting viscosity results from an arbitrary decision to ignore processes on the time scale of the oscillations in the length of the dumbbell, rather than from any inherent limitation of their method.

In order to demonstrate that the correlation function expression Eq. (1.13) takes proper account of the rigid bonds we do an explicit calculation for rigid dumbbells in Sec. IV. To accomplish this calculation, consistent with the point of view we have adopted, the correlation function expression is first evaluated for an elastic dumbbell according to the Fraenkel model[9,10] where the potential between the two centers of friction is described by a harmonic potential with finite equilibrium separation l,

$$U(\mathbf{r}_1, \mathbf{r}_2) = \tfrac{1}{2}\kappa[\,|\mathbf{r}_1 - \mathbf{r}_2| - l\,]^2 . \tag{1.16}$$

Passage to the rigid dumbbell case is made after evaluation of the correlation function by letting $\kappa \to \infty$.

In Sec. III we compare the correlation function formalism with Kirkwood's theory of viscoelastic behavior, and show that both theories lead to the same result for the intrinsic viscosity, although starting from different premises. In our view the correlation function formalism is to be preferred.

II. LINEAR RESPONSE THEORY

In this section we demonstrate that direct application of linear response theory to the diffusion equation leads precisely to the simple correlation function expression for $[\eta(\omega)]$ displayed in Eq. (1.13). In such a calculation one evaluates the average of an appropriate stress tensor J_{xy} in linear response to an external flow perturbation $\mathbf{v}_0(\mathbf{r}, t)$ acting on each segment of the polymer. Before specifying the relevant observables in detail we develop the theory from a more general point of view.

In the presence of the external perturbation the diffusion equation Eq. (1.4) is modified to

$$\partial P(\mathbf{R}, t)/\partial t = [\mathfrak{D} + \mathcal{E}(t)]P(\mathbf{R}, t) , \tag{2.1}$$

where the linear operator $\mathcal{E}(t)$ corresponds to the external perturbation and may involve an explicit dependence on time. We write $P = P_{\text{eq}} + P_1$, where P_{eq} is the equilibrium distribution (1.15). To linear order in the perturbation

$$\begin{aligned}\partial P_1/\partial t &= \mathfrak{D}P_1 + \mathcal{E}(t)P_{\text{eq}} \\ &= \mathfrak{D}P_1 + A(\mathbf{R}, t)P_{\text{eq}} ,\end{aligned} \tag{2.2}$$

where $A(\mathbf{R}, t)$ is defined by the second equality and denotes the function that results from the operator $\mathcal{E}$ acting on P_{eq}. Assuming harmonic time dependence,

$$A(\mathbf{R}, t) = A(\mathbf{R}) \exp(i\omega t) , \tag{2.3}$$

and solving with the initial condition $P = P_{\text{eq}}$ at $t = -\infty$ one finds

$$\begin{aligned}P_1(\mathbf{R}, t) &= \int_{-\infty}^{t} \exp[\mathfrak{D}(t - t')](AP_{\text{eq}}\, e^{i\omega t'})\, dt' \\ &= e^{i\omega t} \int_0^{\infty} \exp[(-i\omega + \mathfrak{D})\tau](AP_{\text{eq}})\, d\tau .\end{aligned} \tag{2.4}$$

Using the identity

$$\mathfrak{D}(AP_{\text{eq}}) = P_{\text{eq}}\mathfrak{D}^{\dagger}A , \tag{2.5}$$

where $\mathfrak{D}^{\dagger}$ is the adjoint of the diffusion operator given by Eq. (1.14), one finds

$$P_1 = e^{i\omega t}\, P_{\text{eq}}(i\omega - \mathfrak{D}^{\dagger})^{-1}A . \tag{2.6}$$

Hence the average of an observable $B(\mathbf{R})$ in the stationary state $[P_{\text{eq}} + P_1]$ is

$$\langle B\rangle_t = \langle B\rangle_{\text{eq}} + e^{i\omega t}\langle B(i\omega - \mathfrak{D}^{\dagger})^{-1}A\rangle_{\text{eq}} , \tag{2.7}$$

where the averages on the right are over the equilibrium distribution P_{eq}. The linear response can therefore be expressed as the one-sided Fourier transform of an equilibrium time correlation function,

$$\langle B(i\omega - \mathfrak{D}^{\dagger})^{-1}A\rangle_{\text{eq}} = \int_0^{\infty} e^{-i\omega t}\langle BA(t)\rangle_{\text{eq}}\, dt , \tag{2.8}$$

where the time evolution of the observable A is given by the Heisenberg type equation

$$A(t) = \exp(\mathfrak{D}^{\dagger}t)A. \tag{2.9}$$

To conclude this formal discussion we note that

$$\int A\mathfrak{D}B\, d\mathbf{R} = \int B\mathfrak{D}^{\dagger}A\, d\mathbf{R} , \tag{2.10}$$

which expresses the adjoint relation between $\mathfrak{D}$ and $\mathfrak{D}^{\dagger}$.

We now turn to the specific observables of interest for the intrinsic viscosity. We consider a flow situation where the polymer center of resistance is at rest at the origin and the external flow is given by

$$\mathbf{v}_0(\mathbf{r}, \mathrm{t}) = g_0 y e^{i\omega t}\,\hat{\mathbf{i}} \quad . \tag{2.11}$$

Corresponding to this external flow the linear operator $\mathcal{E}(t)$ is

$$\mathcal{E}(t) = -\, e^{i\omega t}\, \mathbf{v}_0^T \cdot \nabla_{\mathbf{R}} \quad , \tag{2.12}$$

where the scalar product is between $3n$-component vectors. Hence from Eqs. (2.2) and (2.3) the observable $A(\mathrm{R})$ is given by

$$A(\mathrm{R}) = -\,\beta g_0 \sum_{j=1}^{n} y_j K_j^x \quad . \tag{2.13}$$

The intrinsic viscosity $[\eta(\omega)]$ is defined by

$$[\eta(\omega)]g_0 e^{i\omega t} = -\frac{N_{\mathrm{A}}}{M\eta_0}\,\langle J_{xy}\rangle_t \quad . \tag{2.14}$$

Comparing with Eq. (2.7) and identifying the dynamical observable B as

$$J_{xy} = \sum_{j=1}^{n} y_j K_j^x$$

one sees that Eq. (2.14) may be recast in the form

$$[\eta(\omega)] = \frac{N_{\mathrm{A}}\beta}{M\eta_0}\int_0^{\infty} e^{-i\omega\tau}\left\langle \sum_{i=1}^{n} y_i K_i^x \left[\exp(\mathfrak{D}^{\dagger}\tau)\sum_{j=1}^{n} y_j K_j^x\right]\right\rangle_{\text{eq}} d\tau \quad , \tag{2.15}$$

which is identical to Eq. (1.13).

Note that in this derivation the mechanical force K appears naturally in the observable A. The identification of the observable B as involving the mechanical force is less obvious, apart from a consideration of symmetry. The justification of the use of

$$J_{xy} = \sum_{j=1}^{n} y_j K_j^x$$

in Eq. (2.14) ultimately must be made on the basis of a separate analysis.

Before turning to the application of the correlation function expression Eq. (2.15) to the case of elastic dumbbells we compare the above formalism with a version of Kirkwood's theory.

III. COMPARISON WITH A VERSION OF KIRKWOOD'S METHOD

In 1949 Kirkwood[11] proposed a general theory of viscoelastic behavior which accounted for the observed rigidity modulus of polymer solutions. An important feature of his theory is the introduction of chain space, i.e., that subspace of the complete $3n$-dimensional configuration space of the polymer segments which is allowed by the rigid constraints of constant bond angle and constant bond length. The equivalent of the diffusion equation Eq. (1.4) is written in terms of the generalized curvilinear coordinates of chain space. The resulting formalism was applied by Kirkwood and Auer[8] to rigid rods and by Hearst[12] to wormlike chains.

We shall show that applying Kirkwood's method, but using the diffusion equation in the full cartesian configuration space, leads to exactly the same expression for the intrinsic viscosity as found in Eq. (2.15). This is worthy of note since in calculating the intrinsic viscosity Kirkwood employs Eq. (2.14) with a different expression for J_{xy} than the one we have used.

The diffusion equation Eq. (1.4) in the presence of an external flow disturbance can be written as

$$\partial P/\partial t + \nabla_{\mathrm{R}}^{T} \cdot (\mathbf{u}P) = 0 \;, \tag{3.1}$$

where $\mathbf{u}$ is an $3n$-component vector comprising the polymer segment velocities

$$\mathbf{u}_i = \mathbf{v}_i^0 - \sum_{\substack{j=1\\ j\neq i}}^{n} \mathbf{D}_{ij} \cdot [\nabla_j \ln P + \beta \nabla_j U] \;. \tag{3.2}$$

The forces $\mathbf{F} \equiv (\mathbf{F}_1, \ldots, \mathbf{F}_n)$ exerted on the fluid by the polymer segments are mutually related by the hydrodynamic interactions and are given by

$$\mathbf{F}_i + \zeta_i \sum_{j\neq i} \mathbf{T}_{ij} \cdot \mathbf{F}_j = \zeta_i(\mathbf{u}_i - \mathbf{v}_i{}^0) \;. \tag{3.3}$$

Recalling Eq. (1.6), expressing the diffusion tensor $\mathbf{D}_{ij}$ in terms of the Oseen tensor $\mathbf{T}_{ij}$, one finds from Eqs. (3.2) and (3.3)

$$\mathbf{F}_i = -\nabla_i U - kT \nabla_i \ln P(t) \;. \tag{3.4}$$

According to Kirkwood's prescription the nonequilibrium average on the rhs of Eq. (2.14) should be computed with the flux including the diffusion term,

$$J_{xy} = \sum_{i=1}^{n} y_i F_i^x \;;$$

thus

$$\langle J_{xy}\rangle_t = \int \sum_{i=1}^{n} y_i F_i^x P(t)\, d\mathrm{R} \;. \tag{3.5}$$

However, as pointed out by Kirkwood and Auer,[8] to linear terms in the shear rate it is legitimate to replace the nonequilibrium probability distribution $P(t)$ by the equilibrium distribution P_{eq}, since the "forces" $\mathbf{F}_i$ are proportional to the shear rate through the diffusion term involving $P(t)$ in Eq. (3.4). Thus to lowest order in the shear rate the Kirkwood procedure permits calculation of the nonequilibrium flux according to the expression

$$\langle J_{xy}\rangle_t = \sum_{i=1}^{n} \langle y_i F_i^x \rangle \;, \tag{3.6}$$

where the angular bracket without subscript t denotes an equilibrium average.

It is an easy matter to show that this expression for the flux, which involves a diffusion term, leads to the same autocorrelation function expression Eq. (2.15). Substituting $P = P_{\mathrm{eq}} + P_1$, where P_{eq} is given by Eq. (1.15), into Eq. (3.4) leads to

$$\mathbf{F}_i = -kT \nabla_i \ln[1 + (P_1/P_{\mathrm{eq}})] \;, \tag{3.7}$$

or, to linear terms in the external shear rate disturbance,

$$\mathbf{F}_i = -kT \nabla_i (P_1/P_{\mathrm{eq}}) \;. \tag{3.8}$$

Hence one finds after substitution of Eqs. (2.6) and (2.13) into (3.8) that Eq. (3.6) becomes

$$\langle J_{xy}\rangle_t = g_0 e^{i\omega t} \sum_{i=1}^{n} \left\langle \left\{ y_i \frac{\partial}{\partial x_i} \left[\frac{1}{i\omega - \mathfrak{D}^{\dagger}} \sum_{j=1}^{n} y_j K_j^x \right] \right\} \right\rangle \;. \tag{3.9}$$

After integration by parts and use of the defining equation for $[\eta(\omega)]$, Eq. (2.14), one sees that this procedure leads to an autocorrelation function expression for $[\eta(\omega)]$ which is identical to Eq. (2.15).

IV. EXPLICIT CALCULATION FOR DUMBBELLS

As an illustration of the evaluation of the correlation function formula Eq. (2.15) we consider the elastic dumbbell model[9,10] where the two centers of friction are bound by the harmonic potential Eq. (1.16). We emphasize that this calculation is put forward simply to demonstrate that careful evaluation of the autocorrelation function without "entropic terms" yields the correct answer.[9,10] Our treatment includes the effect of hydrodynamic interaction between the two centers of resistance and slightly generalizes the known result[13] for this case by letting the two beads have different friction constants. The effect of rigid constraints is studied by taking the limit $\kappa \to \infty$ at the end of the calculation.

The diffusion equation Eq. (1.4) for the dumbbell can be written

$$\begin{aligned} \frac{\partial P(\mathbf{r}_1, \mathbf{r}_2, t)}{\partial t} = {} & D_1 \nabla_1 \cdot [\nabla_1 P + \beta(\nabla_1 U)P] \\ & + D_2 \nabla_2 \cdot [\nabla_2 P + \beta(\nabla_2 U)P] \\ & + kT \nabla_1 \cdot \mathbf{T}_{12} \cdot [\nabla_2 P + \beta(\nabla_2 U)P] \\ & + kT \nabla_2 \cdot \mathbf{T}_{12} \cdot [\nabla_1 P + \beta(\nabla_1 U)P] \;, \end{aligned} \tag{4.1}$$

where $D_i = kT/\zeta_i$. In writing Eq. (2.11) we assumed that the center of resistance of the dumbbell with coordinates

$$\overline{\mathrm{R}} = [\zeta_1 \mathbf{r}_1 + \zeta_2 \mathbf{r}_2]/(\zeta_1 + \zeta_2) \tag{4.2}$$

is locally moving with the fluid. We consider a statistical ensemble of dumbbells with uniform distribution of centers, so that Eq. (4.1) reduces to an equation for the distribution of the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$,

$$\partial P(\mathbf{r}, t)/\partial t = \nabla \cdot \mathbf{D}_r \circ [\nabla P(\mathbf{r}, t) + \beta(\nabla U) P(\mathbf{r}, t)] \;, \tag{4.3}$$

where

$$\begin{aligned} \mathbf{D}_r &= (D_1 + D_2)\,\mathbf{I} - 2kT\,\mathbf{T}(\mathbf{r}) \\ &= (D_1 + D_2)\,\mathbf{I} - (kT/4\pi\eta_0 r)[\mathbf{I} + (\mathbf{r}\mathbf{r}/r^2)] \;, \end{aligned} \tag{4.4}$$

which is conveniently expressed as

$$\mathbf{D}_r = D\{\mathbf{1} - (h/r)[\mathbf{1} + (\mathbf{r}\,\mathbf{r}/r^2)]\}\,, \tag{4.5}$$

where $D = (D_1 + D_2)$ and $h = [kT/4\pi\eta_0(D_1 + D_2)]$ is the strength parameter for the hydrodynamic interaction; in the free draining limit $h = 0$. The adjoint operator $\mathfrak{D}^\dagger$ appearing in Eq. (2.15) is

$$\mathfrak{D}^\dagger = -\beta(\nabla U)\cdot\mathbf{D}_r\cdot\nabla + \nabla\cdot\mathbf{D}_r\cdot\nabla\,; \tag{4.6}$$

it has the property noted in Eq. (2.5), where $P_{\mathrm{eq}}(\mathbf{r}) \sim \exp[-\beta U(\mathbf{r})]$.

Moreover $\mathfrak{D}^\dagger$ is self-adjoint with respect to averages over the equilibrium distribution. This means that the eigenfunctions of $\mathfrak{D}^\dagger$, defined by

$$\mathfrak{D}^\dagger\phi_n(\mathbf{r}) = -\lambda_n\phi_n(\mathbf{r})\,, \tag{4.7}$$

obey the orthogonality condition

$$\int \phi_n^*(\mathbf{r})\,\phi_m(\mathbf{r})\,P_{\mathrm{eq}}(\mathbf{r})\,d\mathbf{r} = \delta_{nm}\,. \tag{4.8}$$

The flux for the dumbbell,

$$\begin{aligned} J_{xy} &= -y(\partial U/\partial x) = -(xy/r)\,U'(r) \\ &= -\kappa r(r-l)\sin^2\vartheta\,\sin\varphi\cos\varphi\,, \end{aligned} \tag{4.9}$$

may be expanded in terms of these eigenfunctions:

$$J_{xy} = \sum_{n=0}^{\infty} c_n\phi_n(\mathbf{r})\,, \tag{4.10}$$

and substituting into Eq. (2.15) one finds for the intrinsic viscosity

$$[\eta(\omega)] = \frac{N_A\beta}{M\eta_0}\sum_{n=0}^{\infty}\frac{|c_n|^2}{i\omega + \lambda_n}\,. \tag{4.11}$$

For spherically symmetric potentials $U(r)$ the operator $\mathfrak{D}^\dagger$ commutes with the rotation operator and it is sufficient to consider only eigenfunctions of the angular symmetry exhibited in the flux Eq. (4.9), i.e.,

$$\phi_n(\mathbf{r}) \sim \chi_n(r)\sin^2\vartheta\,\sin\varphi\cos\varphi\,. \tag{4.12}$$

The radial functions $\chi_n(r)$ obey the eigenfunction equation obtained from Eq. (4.6) by substituting the harmonic potential Eq. (1.16) and employing Eqs. (4.7) and (4.12):

$$\begin{aligned} D\Big[&-\beta\kappa(r-l)\left(1-\frac{2h}{r}\right)\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial}{\partial r}r^2\left(1-\frac{2h}{r}\right)\frac{\partial}{\partial r} \\ &-\frac{6}{r^2}\left(1-\frac{h}{r}\right)\Big]\chi_n(r) = -\lambda_n\chi_n(r)\,. \end{aligned} \tag{4.13}$$

The factor 6 arises in the last term on the lhs of Eq. (4.13) from the angular Laplacian in the operator $\mathfrak{D}^\dagger$, which contributes a value $l(l+1) = 6$, since the flux under consideration has the symmetry of a second order ($l = 2$) spherical harmonic. Accordingly $[\eta(\omega)]$ may be expressed as

$$[\eta(\omega)] = \frac{N_A\beta}{M\eta_0}\frac{1}{15}\sum_{n=0}^{\infty}\frac{d_n^2}{i\omega + \lambda_n} \tag{4.14}$$

where the eigenvalues λ_n are determined from Eq. (4.13), the coefficients from the relation

$$d_n = -\int_0^\infty [\kappa r(r-l)]\chi_n(r)P_{\mathrm{eq}}(r)\,dr\,, \tag{4.15}$$

and the factor $\frac{1}{15}$ arises from the angular average of $[\sin^2\theta\sin\varphi\cos\varphi]^2$. The eigenfunctions $\chi_n(r)$ are constructed to be normalized and orthogonal according to

$$\int_0^\infty \chi_m^*(r)\chi_n(r)r^2P_{\mathrm{eq}}(r)\,dr = \delta_{nm}\,. \tag{4.16}$$

The eigenvalues and eigenfunctions cannot be determined exactly for all κ and h. We are interested in obtaining a solution in the limit of a rigid dumbbell ($\kappa\to\infty$), so we transform to a variable

$$\xi = (r-l)(\kappa\beta)^{1/2} \tag{4.17}$$

that expresses the deviation of the oscillator separation from its equilibrium position. In terms of this variable the eigenfunction equation becomes

$$\begin{aligned} D\Big\{&\beta\kappa(1-2\alpha)L_0 + \frac{2}{l}(1-\alpha)(\beta\kappa)^{1/2}\frac{\partial}{\partial\xi} + \left[(\beta\kappa)^{1/2}\frac{2\alpha}{l} - \frac{4\alpha}{l^2}\right]L_0 \\ &-\frac{6}{l^2}(1-\alpha) + \mathcal{O}[(\beta\kappa)^{-1/2}]\Big\}\chi_n(r) = -\lambda_n\chi_n(r)\,, \end{aligned} \tag{4.18}$$

where we have written $\alpha = h/l$ ($\alpha \leqslant 3/8$), and where L_0 is the operator

$$L_0 = \frac{\partial^2}{\partial\xi^2} - \xi\frac{\partial}{\partial\xi}\,. \tag{4.19}$$

The symbol $\mathcal{O}[(\beta\kappa)^{-1/2}]$ indicates that terms of this order have been dropped; these terms are clearly negligibly small compared to those retained in the rigid rod limit.

In leading order in $\beta\kappa$ the operator $\mathfrak{D}^\dagger$ involves just the operator L_0 in the first term on the lhs of Eq. (4.18). To this order the eigenfunctions χ_n are given in terms of Hermite polynomials $H_n(x)$:

$$\chi_n(r) = (2^n n!)^{-1/2}H_n(\xi/\sqrt{2})\,, \tag{4.20}$$

and the associated eigenvalues are simply

$$\lambda_n = D\beta\kappa(1-2\alpha)n + \mathcal{O}[(\beta\kappa)^{1/2}]\,. \tag{4.21}$$

For $n = 0$ correction terms must be determined. However, for $n = 0$ the eigenfunction is a constant and the associated eigenvalue is easily determined from Eq. (4.18) to be

$$\lambda_0 = 6l^{-2}(1-\alpha) + \mathcal{O}[(\beta\kappa)^{-1/2}]\,. \tag{4.22}$$

Employing the eigenfunctions Eq. (4.20) the coefficients d_n, Eq. (4.15), are

$$\begin{aligned} d_0 &= -3\beta^{-1} + \beta^{-1}\mathcal{O}[(\beta\kappa)^{-1}]\,, \\ d_1 &= l\beta^{-1}(\beta\kappa)^{1/2} + \beta^{-1}\mathcal{O}[(\beta\kappa)^{-1/2}]\,, \\ d_n &= \beta^{-1}\mathcal{O}[(\beta\kappa)^{-(n-2)/2}] \quad n \geqslant 2\,. \end{aligned} \tag{4.23}$$

Substitution of these results into the expression for $[\eta(\omega)]$ Eq. (4.14) yields in the rigid dumbbell limit, i.e., to lowest order in κ^{-1},

$$[\eta(\omega)] = \frac{N_A}{15M\eta_0}\frac{l^2}{D(1-\alpha)\beta}\left[\frac{3/2}{1+i\omega\tau} + \frac{1-\alpha}{1-2\alpha}\right], \tag{4.24}$$

where we have defined the relaxation time

$$\tau^{-1} = 6D(1-\alpha)l^{-2}\,. \tag{4.25}$$

This result is exactly the result obtained by Fraenkel,[9,10] when we neglect the hydrodynamic interaction ($\alpha = 0$) and substitute $D = 2kT/\zeta$, as is the case for a symmetric dumbbell. The result also agrees with the result for symmetric dumbbells obtained by Kirkwood and Plock[14] in the absence of hydrodynamic interaction, and the result obtained by Bird and Warner[13] in the presence of hydrodynamic interaction. Both these calculations employ an entirely different method.

For the case of the Fraenkel dumbbell, the procedure of Doi and Okano[4] is to employ the coarse grained flux $\bar{J}_{xy}$ which in the notation of this section is

$$J_{xy} = \langle J_{xy} | \phi_0 \rangle \phi_0 \equiv C_0 \phi_0 , \qquad (4.26)$$

and proceed to the rigid limit $\kappa \to \infty$ before evaluating the correlation function. This procedure clearly eliminates the high frequency contribution and yields only the first term on the rhs of Eq. (4.24). Doi and Okano correctly recognize that a separate calculation of $[\eta(\omega)]$ is required. A correct procedure for computing this high frequency limit has been given by Nakajima, Doi, Okano, and Wada.[15]

Recently, Doi, Nakajima, and Wada[16] have extended the procedure of Refs. 4 and 15. These authors as well as those of Refs. 4 and 15 attempt to separate the flux into noninterfering (orthogonal) slow (unconstrained) and fast (constrained) contributions, a device that works admirably for the Fraenkel dumbbell. However for more complex systems, e.g., freely jointed chains, this separation may not be realized because of interaction between the constrained and unconstrained coordinates[17] that arises from the coupling of the center of mass and internal motions.

V. CONCLUDING REMARKS

We wish to emphasize that our exclusive concern in this paper is the proper use of the correlation function method for evaluating the intrinsic viscosity. In the correlation function method one has the choice of going to the limit of a constrained coordinate ($\kappa \to \infty$) either before[4,16] or after[15] evaluation of the correlation function. The former procedure requires a separate evaluation of the high frequency limit. The latter procedure which we address here does not require "entropic forces" and always yields the correct high and low frequency behavior.

There are however a number of other methods available for calculation of the intrinsic viscosity.[18] These methods, which rely on direct evaluation of the nonequilibrium flux $\langle J_{xy} \rangle_t$ [see Eqs. (2.14) and (3.5)], differ in their treatments of constraints. There are three possibilities: (a) elimination of constraints directly from the Lagrangian[19–21]; (b) retention of constrained coordinates in the diffusion equation but passage to the limit of a rigid constraint ($\kappa \to \infty$) prior to evaluation of $\langle J_{xy} \rangle_t$[22,23,16]; and (c) passage to the limit of a rigid constraint after evaluation of $\langle J_{xy} \rangle_t$, as is done for the case of a dumbbell in Refs. 9, 10, and 24. The advantage of these latter methods compared to the correlation function method is that they permit generalization to nonlinear response. We mention these other methods to stress to the reader that the correlation function approach is not the only alternative available.

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