Calculation of Translational Friction and Intrinsic Viscosity. I. General Formulation for Arbitrarily Shaped Particles

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ABSTRACT A general method for calculating translational friction and intrinsic viscosity is developed through exploiting relations between hydrodynamics and electrostatics. An approximate relation $\xi = 6\pi\eta_0 C$ between the translational friction coefficient ξ of a particle (η_0: solvent viscosity) and its capacitance C was derived previously. This involved orientationally preaveraging the Oseen tensor, but the result was found to be very accurate. Based on preaveraging, we find that the intrinsic viscosity $[\eta]$ of a particle can be estimated from its polarizability α through $[\eta] = \frac{3}{4}\alpha + \frac{1}{4}V_p$, where V_p is the volume of the particle. Both the capacitance and the polarizability can be obtained in a single calculation using the boundary-element technique. An efficient approach is thus found for estimating $[\eta]$, a quantity that is very useful in practice because of its sensitivity to particle shape but is notoriously difficult to calculate. Illustrative calculations on ellipsoids, cylinders, and dumbbells demonstrate both the accuracy of the approximate relations and the efficiency of the present method.

INTRODUCTION

The intrinsic viscosity of a particle measures its contribution to the viscosity of the solution in which it is dissolved:

$$[\eta] = \lim_{c_p \to 0} \frac{\eta - \eta_0}{c_p \eta_0}, \qquad (1)$$

where η_0 and η are the viscosities of the solvent and solution, respectively, and c_p is the concentration of the particle. If c_p is measured by the number density, then $[\eta]$ has the unit of volume. It is well known that $[\eta]$ is very sensitive to particle shape (Cantor and Schimmel, 1980). In the case of a macromolecule, $[\eta]$ contains valuable information on its conformation. Unfortunately, it is also well known that the calculation of $[\eta]$ is difficult (Garcia de la Torre and Bloomfield, 1981). The few cases where $[\eta]$ has been obtained analytically are ellipsoids (Rallison, 1978; Haber and Brenner, 1984), long cylinders (Brenner, 1974), and dumbbells consisting of two identical spheres (Wakiya, 1971; Brenner, 1974). The purpose of this paper is to present a practical method for calculating the intrinsic viscosities of arbitrarily shaped rigid particles.

The solvent flow past a rigid particle satisfies the creeping motion equations (Happel and Brenner, 1965)

$$\eta_0 \nabla^2 \mathbf{v}(\mathbf{r}) - \nabla p(\mathbf{r}) = \mathbf{0}, \qquad (2a)$$

$$\nabla \cdot \mathbf{v}(\mathbf{r}) = 0, \qquad (2b)$$

where $\mathbf{v}(\mathbf{r})$ and $p(\mathbf{r})$ are the solvent velocity and pressure, respectively, at position $\mathbf{r}$. For an arbitrarily shaped particle, two numerical methods have been developed to solve these equations. They involve either dividing the surface of the particle into small elements (Youngren and Acrivos, 1975; Brune and Kim, 1993) or covering the surface of the particle with a shell of small beads (Swanson et al., 1978, 1980; Garcia de la Torre and Bloomfield, 1981; Garcia de la Torre et al., 1994). Although the solution of the creeping motion equations for one-particle geometry is time consuming, the calculation of the intrinsic viscosity is vastly more so because one has to first solve these equations for a large (infinite, in principle) number of particle orientations and then average the results (McCammon and Deutch, 1976; Garcia de la Torre and Bloomfield, 1981).

Our approach to the problem of calculating $[\eta]$ is devised by extending a relation between hydrodynamics and electrostatics recognized by Hubbard and Douglas (1993). The essential idea in relating these two branches of science is that the Green function $\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r})$ of the creeping motion equations, when orientationally averaged, reduces to the Green function $\gamma(\mathbf{r}' - \mathbf{r})$ of the Laplace equation, which governs the electrostatic potential. The hydrodynamic Green function $\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r})$ is just the Oseen tensor (Happel and Brenner, 1965)

$$\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r}) = \frac{1}{8\pi\eta_0 R}\left(\underset{\sim}{\mathbf{1}} + \frac{\mathbf{R}\mathbf{R}}{R^2}\right), \qquad (3)$$

where $\mathbf{R} = \mathbf{r}' - \mathbf{r}$ and $\underset{\sim}{\mathbf{1}}$ is the unity tensor. It satisfies the equation

$$\eta_0 \nabla^2 \underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r}) - \nabla \mathbf{Q}(\mathbf{r}' - \mathbf{r}) = -\underset{\sim}{\mathbf{1}}\delta(\mathbf{r}' - \mathbf{r}), \qquad (4)$$

where

$$\mathbf{Q}(\mathbf{r}' - \mathbf{r}) = -\frac{\mathbf{R}}{4\pi R^3}. \qquad (5)$$

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The orientational average of $\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r})$ is $T(\mathbf{r}' - \mathbf{r})\underset{\sim}{\mathbf{1}}$, where

$$T(\mathbf{r}' - \mathbf{r}) = \frac{1}{6\pi\eta_0 R} = \frac{2}{3\eta_0}\gamma(\mathbf{r}' - \mathbf{r}). \tag{6}$$

The electrostatic Green function is

$$\gamma(\mathbf{r}' - \mathbf{r}) = \frac{1}{4\pi R}, \tag{7}$$

which satisfies the equation

$$\nabla^2\gamma(\mathbf{r}' - \mathbf{r}) = -\delta(\mathbf{r}' - \mathbf{r}). \tag{8}$$

If $\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r})$ is replaced by its orientational average, Hubbard and Douglas (1993) showed that the translational friction coefficient ξ of a particle is related to its capacitance C through

$$\xi = 6\pi\eta_0 C. \tag{9}$$

This relation proves to be accurate to within 1% for many cases where analytical results are known and has been used to estimate translational friction coefficients in cases where analytical results are not available (Zhou et al., 1994). A study using the bead method by Garcia de la Torre et al. (1984) also showed that orientational preaveraging has only a minor effect in the calculation of translational properties.

Recently Douglas and Garboczi (1995) found a correlation between the intrinsic viscosity $[\eta]$ and another electrostatic quantity, namely the polarizability α. Based on direct comparison of $[\eta]$ and α in the cases of ellipsoids and dumbbells, they proposed the relation $[\eta] = 0.79\alpha$, which is accurate to within 5% for the cases examined. In the next section of this paper we will show that orientational averaging of the Oseen tensor leads to the relation

$$[\eta] = \tfrac{3}{4}\alpha. \tag{10}$$

To make the relation between $[\eta]$ and α exact for a sphere, we will propose adding a constant to Eq. 10, i.e.,

$$[\eta] = \tfrac{3}{4}\alpha + \tfrac{1}{4}V_{\mathrm{p}}, \tag{11}$$

where V_{p} is the volume of the particle. It will be demonstrated later that this relation is accurate to within about 3% for globular particles.

With Eqs. 9 and 11 at hand, we can estimate the translational friction coefficient and the intrinsic viscosity by calculating their electrostatic counterparts. It turns out that if the boundary-element technique (Zhou, 1993, 1994) is used to solve the electrostatic problems, both the capacitance and the polarizability can be obtained in a single calculation. This method is described in the section after the derivation of Eq. 10. For the sake of comparison, in the same section we also present a boundary-element solution for the translational friction coefficient and the intrinsic viscosity of a centrosymmetric particle. The accuracy of Eqs. 9 and 11 is then illustrated in the cases of ellipsoids, cylinders, and dumbbells. Conclusions are given at the end of the paper.

RELATIONS OF HYDRODYNAMICS AND ELECTROSTATICS

In this section we define the electrostatic quantities C and α and the hydrodynamic quantities ξ and $[\eta]$ and establish their relations. Although the relation between C and ξ, given by Eq. 9, has been derived previously by Hubbard and Douglas (1993), here we derive it again using a different procedure. An analogous procedure is then used to derive Eq. 10, the relation between α and $[\eta]$.

Electrostatics

Consider an arbitrarily shaped conducting particle, inside which the electric field is zero. The electrostatic potential $\varphi(\mathbf{r})$ outside the particle satisfies the Laplace equation

$$\nabla^2\varphi(\mathbf{r}) = 0. \tag{12}$$

Only cases where $\varphi(\mathbf{r})$ goes to zero at positions far away from the particle are of interest. Use of Green's theorem then leads to the following integral equation for the charge density $\sigma(\mathbf{r}') = -\nabla'\varphi(\mathbf{r}')\cdot\mathbf{n}'/4\pi$ on the surface S_{p} of the particle (Zhou, 1993)

$$\frac{1}{2}\varphi(\mathbf{r}) = \int_{S_{\mathrm{p}}} ds'[\gamma(\mathbf{r}' - \mathbf{r})4\pi\sigma(\mathbf{r}') + \varphi(\mathbf{r}')\nabla'\gamma(\mathbf{r}' - \mathbf{r})\cdot\mathbf{n}'], \quad \mathbf{r} \in S_{\mathrm{p}}, \tag{13}$$

where ds' and $\mathbf{n}'$ are the surface area element and outward unit normal vector at $\mathbf{r}'$, respectively, and ∇' is the gradient operator operating on $\mathbf{r}'$. If the surface potential takes the linear form

$$\varphi(\mathbf{r}) = g + \mathbf{h}\cdot\mathbf{r}, \quad \mathbf{r} \in S_{\mathrm{p}}, \tag{14}$$

where $\mathbf{h}$ is an arbitrary vector, then after evaluation of the second term on the right-hand side of Eq. 13 one finds

$$\int_{S_{\mathrm{p}}} ds'\gamma(\mathbf{r}' - \mathbf{r})[4\pi\sigma(\mathbf{r}') + \mathbf{h}\cdot\mathbf{n}'] = g + \mathbf{h}\cdot\mathbf{r}, \quad r \in S_{\mathrm{p}}. \tag{15}$$

The surface potential appropriate for defining the capacitance is given by Eq. 14 with $g = 1$ and vanishing $\mathbf{h}$. Consequently the surface charge density $\sigma_{\mathrm{c}}(\mathbf{r})$ in this case satisfies the equation

$$\int_{S_{\mathrm{p}}} ds'\gamma(\mathbf{r}' - \mathbf{r})4\pi\sigma_{\mathrm{c}}(\mathbf{r}') = 1, \quad \mathbf{r} \in S_{\mathrm{p}}. \tag{16}$$

The capacitance is given by the total charge:

$$C = \int_{S_p} ds\sigma_c(\mathbf{r}). \tag{17}$$

The polarizability of a conducting particle measures its response to an external electric field $\mathbf{E}$. For this case $\varphi(\mathbf{r})$ and $\sigma(\mathbf{r})$ in Eq. 13 represent the induced electrostatic potential and induced surface charge density, respectively. The boundary condition for $\varphi(\mathbf{r})$ is given by Eq. 14 with $g = 0$ and $\mathbf{h} = \mathbf{E}$. Consequently the net surface charge density $\sigma(\mathbf{r}) + \mathbf{E}\cdot\mathbf{n}/4\pi \equiv \sigma_p(\mathbf{r})$ satisfies the equation

$$\int_{S_p} ds'\gamma(\mathbf{r}' - \mathbf{r})4\pi\sigma_p(\mathbf{r}') = \mathbf{E}\cdot\mathbf{r}, \quad \mathbf{r} \in S_p. \tag{18a}$$

In addition, the total surface charge should vanish:

$$\int_{S_p} ds\sigma_p(\mathbf{r}) = 0. \tag{18b}$$

The dipole moment of the particle

$$\mathbf{m} = \int_{S_p} ds\mathbf{r}\sigma_p(\mathbf{r}) \tag{19}$$

can be related to the external field via

$$\mathbf{m} = \frac{1}{4\pi}\underset{\sim}{\boldsymbol{\alpha}}\cdot\mathbf{E}, \tag{20}$$

where $\underset{\sim}{\boldsymbol{\alpha}}$ is the polarizability tensor.

The dipole moment depends on the orientation of the particle (relative to the external field). If one has a dilute collection of identical but randomly oriented particles or a single particle that is undergoing unbiased rotational Brownain motion, then one is only interested in the average dipole moment $\langle\mathbf{m}\rangle_0$, where $\langle\cdots\rangle_0$ signifies averaging over a uniform distribution of orientation. To find $\langle\mathbf{m}\rangle_0$, let us attach a coordinate system ($\mathbf{e}_i$, i = 1, 2, and 3) to the particle. As the dot products $\mathbf{r}\cdot\mathbf{e}_i \equiv r_i$ are independent of orientation, the functions $\sigma_i(\mathbf{r})$ defined by

$$\int_{S_p} ds'\gamma(\mathbf{r}' - \mathbf{r})4\pi\sigma_i(\mathbf{r}') = r_i, \quad \mathbf{r} \in S_p, \tag{21}$$

should also be independent of orientation. Writing $\mathbf{r}$ as $r_1\mathbf{e}_1 + r_2\mathbf{e}_2 + r_3\mathbf{e}_3$, upon comparison of Eqs. 18a and 21 one finds

$$\sigma_p(\mathbf{r}) = [\sigma_1(\mathbf{r})\mathbf{e}_1 + \sigma_2(\mathbf{r})\mathbf{e}_2 + \sigma_3(\mathbf{r})\mathbf{e}_3]\cdot\mathbf{E}. \tag{22}$$

The average dipole moment can be found by inserting Eq. 22 into Eq. 19 and using

$$\langle\mathbf{e}_i\mathbf{e}_j\rangle_0 = \tfrac{1}{3}\delta_{ij}\underset{\sim}{\mathbf{1}}. \tag{23}$$

The result is

$$\langle\mathbf{m}\rangle_0 = \frac{1}{4\pi}\alpha\mathbf{E}, \tag{24}$$

where the orientationally averaged polarizability α is

$$\alpha = \frac{1}{3}\mathrm{Tr}(\underset{\sim}{\alpha}) = \frac{4\pi}{3}\int_{S_p} ds[r_1\sigma_1(\mathbf{r}) + r_2\sigma_2(\mathbf{r}) + r_3\sigma_3(\mathbf{r})]. \tag{25}$$

Hydrodynamics

In analogy to the foregoing derivation in electrostatics, we start our derivation in hydrodynamics with an integral equation satisfied by the surface stress force $\mathbf{f}(\mathbf{r}) = \mathbf{n}\cdot\underset{\sim}{\mathbf{\Pi}}(\mathbf{r}) = \mathbf{n}\cdot\{-p(\mathbf{r})\underset{\sim}{\mathbf{1}} + \eta_0[\nabla\mathbf{v}(\mathbf{r}) + (\nabla\mathbf{v}(\mathbf{r}))^T]\}$ (Ladyzhenskaya, 1963; Happel and Brenner, 1965; Youngren and Acrivos, 1975):

$$\frac{1}{2}\mathbf{v}(\mathbf{r}) = -\int_{S_p} ds'\left[\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r})\cdot\mathbf{f}(\mathbf{r}') + \mathbf{v}(\mathbf{r}')\cdot\frac{3\mathbf{RRR}}{4\pi R^5}\cdot\mathbf{n}'\right], \quad \mathbf{r} \in S_p. \tag{26}$$

It has been assumed that $\mathbf{v}(\mathbf{r})$ and $p(\mathbf{r})$ go to zero at positions far away from the particle. We will be interested in cases where the solvent velocity on the particle surface takes the linear form

$$\mathbf{v}(\mathbf{r}) = \mathbf{g} + \mathbf{h}\times\mathbf{r} - \underset{\sim}{\mathbf{s}}\cdot\mathbf{r}, \quad \mathbf{r} \in S_p, \tag{27}$$

where $\mathbf{g}$ and $\mathbf{h}$ are arbitrary vectors and $\underset{\sim}{\mathbf{s}}$ is a traceless symmetric tensor. For these cases one can manipulate the second term on the right-hand side of Eq. 26 and obtain

$$-\int_{S_p} ds'\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r})\cdot[\mathbf{f}(\mathbf{r}') + 2\eta_0\underset{\sim}{\mathbf{s}}\cdot\mathbf{n}'] = \mathbf{g} + \mathbf{h}\times\mathbf{r} - \underset{\sim}{\mathbf{s}}\cdot\mathbf{r}, \quad \mathbf{r} \in S_p. \tag{28}$$

For simplicity we will now restrict ourselves to centrosymmetric particles, i.e., those possessing three mutually perpendicular symmetry planes (and thus a center of symmetry). Some comments concerning noncentrosymmetric particles will be made at the end of this section.

The translational friction tensor $\underset{\sim}{\boldsymbol{\xi}}$ of a particle relates its velocity $\mathbf{U}$ to an external drag force $\mathbf{F}$ through

$$\mathbf{U} = \underset{\sim}{\boldsymbol{\xi}}^{-1}\cdot\mathbf{F}. \tag{29}$$

In this case the solvent velocity on the particle surface, according to the requirement of nonslip, is given by Eq. 27 with $\mathbf{g} = \mathbf{U}$ and vanishing $\mathbf{h}$ and $\underset{\sim}{\mathbf{s}}$. Consequently the surface stress force satisfies the equation

$$-\int_{S_p} ds'\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r})\cdot\mathbf{f}(\mathbf{r}') = \mathbf{U}, \quad \mathbf{r} \in S_p. \tag{30}$$

The external force balances the stress force exerted by the solvent on the particle, thus

$$\mathbf{F} = -\int_{S_p} ds\mathbf{f}(\mathbf{r}). \tag{31}$$

If one has a dilute collection of identical but randomly oriented particles or a single particle that is undergoing unbiased rotational Brownian motion, then one is only interested in the average velocity $\langle \mathbf{U} \rangle_0$. It can be easily shown that

$$\langle \mathbf{U} \rangle_0 = \xi^{-1}\mathbf{F}, \tag{32}$$

where the scalar friction coefficient ξ is given by

$$\xi^{-1} = \tfrac{1}{3}\,\mathrm{Tr}(\underset{\sim}{\xi}^{-1}). \tag{33}$$

If we replace the Oseen tensor in Eq. 30 by its orientational average (see Eq. 6), then the surface stress force satisfies the equation

$$-\frac{2}{3\eta_0}\int_{S_p} ds'\gamma(\mathbf{r}' - \mathbf{r})\mathbf{f}(\mathbf{r}') = \mathbf{U}, \quad \mathbf{r} \in S_p. \tag{34}$$

By comparing Eqs. 34 and 16, one finds

$$\mathbf{f}(\mathbf{r}) = -6\pi\eta_0\sigma_c(\mathbf{r})\mathbf{U}. \tag{35}$$

Upon integrating both sides of Eq. 35 over the particle surface, one obtains the expression for the translational friction coefficient ξ given by Eq. 9.

To define the intrinsic viscosity of a particle one considers the case where the particle is dissolved in a solvent that otherwise has the velocity

$$\mathbf{v}_0(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}_C) + \boldsymbol{\omega} \times \mathbf{r} + \underset{\sim}{\mathbf{s}} \cdot \mathbf{r}, \tag{36}$$

where $\mathbf{r}_C$ is a location to be specified, $\mathbf{r}$ is the position vector relative to $\mathbf{r}_C$, and the rate-of-shear tensor $\underset{\sim}{\mathbf{s}}$ is assumed to have a small magnitude. Now in Eq. 26 $\mathbf{v}(\mathbf{r})$ and $\mathbf{f}(\mathbf{r})$ represent the changes in solvent velocity and surface stress force, respectively, upon the addition of the particle. Let the translational and rotational velocities of the particle be $\mathbf{U}$ and $\boldsymbol{\Omega}$, respectively, and $\mathbf{r}_C$ be its center of symmetry; then the requirement of nonslip provides the boundary condition for $\mathbf{v}(\mathbf{r})$ as given by Eq. 27 with $\mathbf{g} = \mathbf{U} - \mathbf{v}_0(\mathbf{r}_C)$, $\mathbf{h} = \boldsymbol{\Omega} - \boldsymbol{\omega}$, and $\underset{\sim}{\mathbf{s}}$ identified with the shear. For a centrosymmetric particle, one has (Brenner, 1974; Haber and Brenner, 1984)

$$\mathbf{U} = \mathbf{v}_0(\mathbf{r}_C). \tag{37}$$

Consequently the net surface stress force $\mathbf{f}(\mathbf{r}) + 2\eta_0\underset{\sim}{\mathbf{s}} \cdot \mathbf{n} \equiv \mathbf{f}_v(\mathbf{r})$ satisfies the equation

$$-\int_{S_p} ds'\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r}) \cdot \mathbf{f}_v(\mathbf{r}') = (\boldsymbol{\Omega} - \boldsymbol{\omega}) \times \mathbf{r} - \underset{\sim}{\mathbf{s}} \cdot \mathbf{r}, \qquad \mathbf{r} \in S_p. \tag{38}$$

To be consistent with Eq. 37, the total force exerted on the particle by the solvent should vanish: $\int_{S_p} ds\mathbf{f}_v(\mathbf{r}) = \mathbf{0}$.

The rate of energy dissipation per unit volume in the absence of the particle is (Happel and Brenner, 1965)

$$W_0 = 2\eta_0\underset{\sim}{\mathbf{s}}:\underset{\sim}{\mathbf{s}}, \tag{39}$$

where the symbol ":" is defined by $\underset{\sim}{\mathbf{A}}:\underset{\sim}{\mathbf{B}} = \mathrm{Tr}(\underset{\sim}{\mathbf{A}} \cdot \underset{\sim}{\mathbf{B}})$. Suppose the rate of additional energy dissipation per unit volume due to a dilute suspension of the particle is δW, the intrinsic viscosity $[\eta]$ is defined in analogy to Eq. 38 as

$$\delta W = 2c_p\eta_0[\eta]\underset{\sim}{\mathbf{s}}:\underset{\sim}{\mathbf{s}}, \tag{40}$$

where c_p is the concentration of the particle. In Appendix A we derive the following expression for δW:

$$\delta W = c_p\langle \underset{\sim}{\mathbf{A}} \rangle_0:\underset{\sim}{\mathbf{s}}, \tag{41}$$

where

$$\underset{\sim}{\mathbf{A}} = \int_{S_p} ds\mathbf{r}\mathbf{f}_v(\mathbf{r}). \tag{42}$$

For a centrosymmetric particle the orientational averaging of $\underset{\sim}{\mathbf{A}}$ can be carried out analytically. Appendix A contains the details. The final result is

$$\begin{aligned}\langle \underset{\sim}{\mathbf{A}} \rangle_0 = \eta_0\Bigg[\frac{1+\lambda}{10}\int_{S_p} & ds(r_1g_{212} + r_2g_{112} + r_2g_{323} \\ & + r_3g_{223} + r_3g_{131} + r_1g_{331}) \\ + \frac{1-\lambda}{10}\int_{S_p} & ds(r_1g_{221} + r_2g_{121} + r_2g_{332} \\ & + r_3g_{232} + r_3g_{113} + r_1g_{313}) \\ - \frac{1}{15}\int_{S_p} & ds(r_1g_{122} + r_1g_{133} + r_2g_{233} \\ & + r_2g_{211} + r_3g_{311} + r_3g_{322}) \\ + \frac{2}{15}\int_{S_p} & ds(r_1g_{111} + r_2g_{222} + r_3g_{333})\Bigg]\underset{\sim}{\mathbf{s}},\end{aligned} \tag{43}$$

where λ is a constant given in Appendix A, and the functions $g_{jkl}(\mathbf{r})$ are defined by Eq. A14. This is a generalization of an earlier result by Yoshizaki and Yamakawa (1980) in the case of an axisymmetric particle (for which $\lambda = 0$) to an arbitrary centrosymmetric particle. In deriving Eq. 43, the axes $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ have been aligned with the three symmetry axes of the centrosymmetric particle.

If we replace the Oseen tensor in Eq. A14 by its orientational average (see Eq. 6), then $g_{jkl}(\mathbf{r})$ satisfy the equation

$$\frac{2}{3}\int_{S_p} ds'\gamma(\mathbf{r}' - \mathbf{r})g_{jkl}(\mathbf{r}') = \delta_{jk}r_l, \quad \mathbf{r} \in S_p. \tag{44}$$

By comparing Eqs. 21 and 44, one finds

$$g_{jkl}(\mathbf{r}) = 6\pi\delta_{jk}\sigma_l(\mathbf{r}). \tag{45}$$

Use of Eq. 45 in Eq. 43 leads to

$$\begin{aligned}\langle \underset{\sim}{\mathbf{A}} \rangle_0 &= 2\pi\eta_0\left[\int_{S_p} ds(r_1\sigma_1 + r_2\sigma_2 + r_3\sigma_3)\right]\underset{\sim}{\mathbf{s}} \\ &= 2\eta_0\left(\frac{3}{4}\alpha\right)\underset{\sim}{\mathbf{s}}.\end{aligned} \tag{46}$$

When this is inserted into Eq. 41 and compared with Eq. 40, we find that the expression for the intrinsic viscosity is given by Eq. 10.

The relations between translational friction and capacitance and between intrinsic viscosity and polarizability have been derived for centrosymmetric particles. For noncentrosymmetric particles, complications arise because of the coupling of translation, rotation, and shear. However, rigorous calculations of translational friction for highly irregular particles give results that differ by less than 3–4% from those obtained by neglecting translation-rotation coupling (Garcia Bernal and Garcia de la Torre, 1980; Wegener, 1981). In light of this finding, we expect that the relations between translational friction and capacitance and between intrinsic viscosity and polarizability derived for centrosymmetric particles should apply to arbitrarily shaped particles with essentially the same accuracy.

BOUNDARY-ELEMENT SOLUTION

The capacitance and polarizability of a particle can be obtained by solving integral equations on the particle surface (see Eqs. 16 and 21). A convenient way to solve these integral equations is to use the boundary-element technique. The basic idea is to discretize the particle surface into small elements so that the integral equations reduce to matrix equations. A detailed implementation of this technique has been given elsewhere (Zhou, 1993, 1994).

The boundary-element solution of the translational friction has a long history (Youngren and Acrivos, 1975; Brune and Kim, 1993). For the intrinsic viscosity, one encounters the difficulty of averaging calculation results over orientation. We showed in the last section that the orientational averaging can be carried out analytically for the case of centrosymmetric particles. The boundary-element solution of the intrinsic viscosity for this case thus becomes practical.

Below we outline the boundary-element solutions of the capacitance and polarizability for an arbitrarily shaped particle and the translational friction and intrinsic viscosity for a centrosymmetric particle.

Electrostatics

The surface charge densities $\sigma_c(\mathbf{r})$, required for calculating the capacitance, and $\sigma_i(\mathbf{r})$, $i = 1$, 2, and 3, required for calculating the polarizability, satisfy the integral equation (see Eqs. 16 and 21)

$$\int_{S_p} ds'\gamma(\mathbf{r}' - \mathbf{r})4\pi\sigma(\mathbf{r}') = h(\mathbf{r}), \quad \mathbf{r} \in S_p. \tag{47}$$

In particular, $\sigma_c(\mathbf{r}) = \sigma(\mathbf{r})$ if $h(\mathbf{r}) = 1$, and $\sigma_i(\mathbf{r}) = \sigma(\mathbf{r})$ if $h(\mathbf{r}) = \mathbf{r}\cdot\mathbf{e}_i = r_i$. To solve Eq. 47 one discretizes the surface S_p into small elements and assumes that $\sigma(\mathbf{r})$ and $h(\mathbf{r})$ are constant within each element. In matrix and vector forms, Eq. 47 reduces to

$$\mathscr{A}\cdot\mathscr{s} = \mathscr{h}. \tag{48}$$

Each element of the vector $\mathscr{s}$ is the assumed constant value of $\sigma(\mathbf{r})$ on a surface element, whereas each element of the vector $\mathscr{h}$ is the value of $h(\mathbf{r})$ at a particular position on a surface element. Let this position on the nth element be $\mathbf{r}_n$ (usually taken to be at or near the center of the element) and the total number of surface elements be N. Each element of the $N \times N$ matrix $\mathscr{A}$ is a surface integral, e.g.,

$$\mathscr{A}_{mn} = \int_{S_n} ds\frac{1}{|\mathbf{r} - \mathbf{r}_m|}, \tag{49}$$

where S_n denotes the nth surface element. Note that the indices i, j, k, and l refer to the axes of a coordinate system fixed in the particle and run from 1 to 3, whereas the indices n and m refer to the surface elements and run from 1 to N.

The vector $\mathscr{s}$ can be found by simply inverting the matrix $\mathscr{A}$. As those corresponding to both $\sigma_c(\mathbf{r})$ and $\sigma_i(\mathbf{r})$ involve the same matrix, they can be found by a single matrix inversion. Let these vectors be $\mathscr{s}^{(c)}$ and $\mathscr{s}^{(i)}$, respectively. According to Eq. 17, the capacitance is

$$C = \sum_n S_n\mathscr{s}_n^{(c)}. \tag{50}$$

In calculating the polarizability, one needs to make sure that the total charge is zero (see Eq. 18b). This can be achieved by subtracting the average value $\langle\mathscr{s}^{(i)}\rangle \equiv \Sigma_n S_n\mathscr{s}^{(i)}/S_p$ from each element of $\mathscr{s}^{(i)}$. Assuming that this has been done, the orientationally averaged polarizability is then (see Eq. 25)

$$\alpha = \frac{1}{3}\sum_{i=1}^{3}\left[4\pi \sum_{n} S_n r_{in} \mathscr{s}_n^{(i)}\right], \tag{51}$$

where $r_{in} \equiv \int_{S_n} ds r_i / S_n$ are the averages of r_i over the nth element. If $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are chosen to be the principal axes of the polarizability tensor $\underset{\sim}{\boldsymbol{\alpha}}$, then each term inside the square brackets of Eq. 50 is a principal component of $\underset{\sim}{\boldsymbol{\alpha}}$. In the case of a centrosymmetric particle the principal axes coincide with the three symmetry axes.

Hydrodynamics

In obtaining the boundary-element solution of the translational friction and intrinsic viscosity for a centrosymmetric particle, we will choose $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ to be along the symmetry axes and the origin to be at the center of symmetry. With such a choice, the principal components of the translational friction tensor $\underset{\sim}{\boldsymbol{\xi}}$ are given by (see Eqs. 29–32)

$$\xi_i = \eta_0 \int_{S_p} ds \mathbf{e}_i \cdot \mathbf{g}_i(\mathbf{r}), \tag{52}$$

where the functions $\mathbf{g}_i(\mathbf{r})$, $i = 1, 2$, and 3, are defined by

$$\int_{S_p} ds' \, \eta_0 \, \underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r}) \cdot \mathbf{g}_i(\mathbf{r}') = \mathbf{e}_i. \tag{53}$$

The scalar friction coefficient ξ is given by (see Eq. 33)

$$\xi^{-1} = 1/3(\xi_1^{-1} + \xi_2^{-1} + \xi_3^{-1}). \tag{54}$$

Both Eq. 53, satisfied by the just introduced $\mathbf{g}_i(\mathbf{r})$ functions, and Eq. A14, satisfied by the $\mathbf{g}_{kl}(\mathbf{r})$ functions which give the intrinsic viscosity, have the form

$$\int_{S_p} ds' \, \eta_0 \, \underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r}) \cdot \mathbf{g}(\mathbf{r}') = \mathbf{u}(\mathbf{r}). \tag{55}$$

In particular, $\mathbf{g}_i(\mathbf{r}) = \mathbf{g}(\mathbf{r})$ if $\mathbf{u}(\mathbf{r}) = \mathbf{e}_i$, and $\mathbf{g}_{kl}(\mathbf{r}) = \mathbf{g}(\mathbf{r})$ if $\mathbf{u}(\mathbf{r}) = \mathbf{e}_k r_l$. After discretizing the particle surface, Eq. 55 reduces to the matrix-vector form

$$\mathscr{B} \cdot \mathscr{g} = \mathscr{u}. \tag{56}$$

The $(3n - 3 + i)$th element of the vector $\mathscr{g}$ contains the ith component of $\mathbf{g}(\mathbf{r})$ on the nth surface element, and $\mathscr{u}_{3n-3+i} = \mathbf{e}_i \cdot \mathbf{u}(\mathbf{r}_n)$. The elements of the $3N \times 3N$ matrix $\mathscr{B}$ are given by

$$\mathscr{B}_{3m-3+i,3n-3+j} = \mathbf{e}_i \cdot \int_{S_n} ds \eta_0 \, \underset{\sim}{\mathbf{T}}(\mathbf{r} - \mathbf{r}_m) \cdot \mathbf{e}_j. \tag{57}$$

The vectors $\mathscr{g}^{(i)}$ and $\mathscr{g}^{(kl)}$ that correspond to $\mathbf{g}_i(\mathbf{r})$ and $\mathbf{g}_{kl}(\mathbf{r})$, respectively, can be obtained by inverting the same matrix $\mathscr{B}$. Then the principal components of $\underset{\sim}{\boldsymbol{\xi}}$ are given by (see Eq. 52)

$$\xi_i = \eta_0 \sum_n S_n \mathscr{g}_{3n-3+i}^{(i)} \tag{58}$$

and the intrinsic viscosity is given by (see Eqs. 40–43)

$$\begin{aligned}
[\eta] = {} & \frac{1+\lambda}{20} \sum_n S_n [r_{1n} \mathscr{g}_{3n-1}^{(12)} + r_{2n} \mathscr{g}_{3n-2}^{(12)} + r_{2n} \mathscr{g}_{3n}^{(23)} \\
& \qquad + r_{3n} \mathscr{g}_{3n-1}^{(23)} + r_{3n} \mathscr{g}_{3n-2}^{(31)} + r_{1n} \mathscr{g}_{3n}^{(31)}] \\
& + \frac{1-\lambda}{20} \sum_n S_n [r_{1n} \mathscr{g}_{3n-1}^{(21)} + r_{2n} \mathscr{g}_{3n-2}^{(21)} + r_{2n} \mathscr{g}_{3n}^{(32)} \\
& \qquad + r_{3n} \mathscr{g}_{3n-1}^{(32)} + r_{3n} \mathscr{g}_{3n-2}^{(13)} + r_{1n} \mathscr{g}_{3n}^{(13)}] \qquad (59) \\
& - \frac{1}{30} \sum_n S_n [r_{1n} \mathscr{g}_{3n-2}^{(22)} + r_{1n} \mathscr{g}_{3n-2}^{(33)} + r_{2n} \mathscr{g}_{3n-1}^{(33)} \\
& \qquad + r_{2n} \mathscr{g}_{3n-1}^{(11)} + r_{3n} \mathscr{g}_{3n}^{(11)} + r_{3n} \mathscr{g}_{3n}^{(22)}] \\
& + \frac{1}{15} \sum_n S_n [r_{1n} \mathscr{g}_{3n-2}^{(11)} + r_{2n} \mathscr{g}_{3n-1}^{(22)} + r_{3n} \mathscr{g}_{3n}^{(33)}].
\end{aligned}$$

In summary, for a centrosymmetric particle one can calculate the translational friction and the intrinsic viscosity by inverting a $3N \times 3N$ matrix and calculate the capacitance and the polarizability by inverting an $N \times N$ matrix. Upon going to an arbitrarily shaped particle, calculating the translational friction becomes a problem of inverting a $6N \times 6N$ matrix due to translation-rotation coupling, and calculating the intrinsic viscosity becomes an intractable problem because of the difficulty of averaging calculation results over orientation. On the other hand, calculating the capacitance and the polarizability is still a problem of inverting an $N \times N$ matrix. Equations 9 and 11 thus provide an efficient route for calculating the translational friction and the intrinsic viscosity.

ILLUSTRATIVE CALCULATIONS

We now use analytical results and numerical calculations to test the relations between the translational friction coefficient ξ and the capacitance C and between the intrinsic viscosity $[\eta]$ and the polarizability α. These relations were obtained by orientationally preaveraging the Oseen tensor. The preaveraging result for ξ, given by Eq. 9, has been shown to be very accurate (Hubbard and Douglas, 1993; Zhou et al., 1994). However, the analogous result for $[\eta]$, given by Eq. 10, is much less accurate. For example, in the case of a sphere, Eq. 9 is exact. On the other hand, the polarizability of a sphere is $\alpha = 3V_p$ and the intrinsic viscosity predicted by Eq. 10 is thus $[\eta] = 9V_p/4$, which differs from the exact result $[\eta] = 5V_p/2$ by 10%. We propose to add a constant to the right-hand side of Eq. 10 so that the resulting relation becomes empirically useful for globular particles. The constant is fixed by requiring that the relation is exact for a sphere. This leads to the relation given by Eq. 11.

Ellipsoids

Ellipsoids have been widely used as models of globular proteins. The main reason is that results for the hydrodynamic properties in this case are analytically known. Let $p = b/a$ be the axis ratio (b is the polar radius and a is the equatorial radius). The translational friction coefficient is (Perrin, 1936)

$$\xi = 6\pi\eta_0 a/pB, \tag{60}$$

where

$$\begin{aligned} B &= p^{-1}(p^2-1)^{-1/2}\cosh^{-1}p, && \text{when } p>1,\\ &= 1, && \text{when } p=1,\\ &= p^{-1}(1-p^2)^{-1/2}\cos^{-1}p, && \text{when } p<1. \end{aligned} \tag{61}$$

The capacitance of an ellipsoid is (Landau et al., 1984)

$$C = a/pB. \tag{62}$$

Combining Eqs. 60 and 62, one finds that the relation given by Eq. 9 between translational friction and capacitance is exact in the case of ellipsoids.

The intrinsic viscosity of an ellipsoid is (Brenner, 1974)

$$\begin{aligned} \frac{[\eta]}{V_p} = \frac{2}{5}(p^2-1)^2\bigg\{ & \frac{-(4p^2-1)B+2p^2+1}{3p^2(3B+2p^2-5)[(2p^2+1)B-3]} \\ & + \frac{14}{3p^2(3B+2p^2-5)} + \frac{2}{(p^2+1)(-3p^2B+p^2+2)} \\ & + \frac{p^2-1}{p^2(p^2+1)[(2p^2-1)B-1]}\bigg\}. \end{aligned} \tag{63}$$

The polarizability is (Landau et al., 1984)

$$\frac{\alpha}{V_p} = \frac{1}{3}(p^2-1)\left[\frac{4}{p^2(1-B)} + \frac{1}{p^2B-1}\right]. \tag{64}$$

The predicted values of intrinsic viscosity for $-5 < \ln p < 5$ using Eqs. 11 and 64 are plotted in Fig. 1 against the exact results from Eq. 63. They agree to within 2% for $1/4 \leq p \leq 4$. We will refer to particles with aspect ratios less than 4 as "globular."

Cylinders

Cylinders roughly represent DNA molecules. Except in certain limits (see below), analytical results are not available for hydrodynamic and electrostatic properties of cylinders. Thus numerical calculations have to be used.

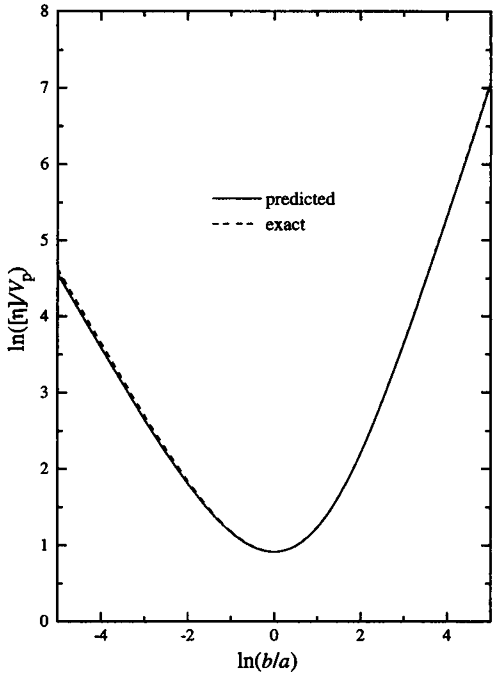

FIGURE 1 Comparison of exact results for the intrinsic viscosity of ellipsoids (*dashed curve*) and those predicted by Eq. 11 (*solid curve*).

Circular cylinders with flat ends

This class of cylinders is encountered most often. In the limit that the total length ($2L$) goes to zero, a flat-ended cylinder becomes a disk. The intrinsic viscosity and polarizability of a disk with radius a can be found from Eqs. 63 and 64, respectively, by taking the $p \to 0$ limit. The results are $[\eta] = 128a^3/45$ and $\alpha = 32a^3/9$, and consequently the prediction of Eq. 11 has an error of 6.25% for the limit $L \to 0$. The same error also occurs in the opposite limit $L \to \infty$ (here the cylinder becomes a needle). We are interested in the accuracy of Eqs. 9 and 11 in the case of

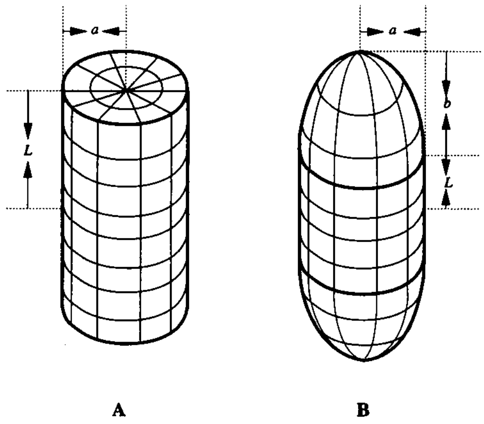

FIGURE 2 Surface discretization of cylinders. (*A*) Flat-ended cylinder. (*B*) Hemiellipsoidal-ended cylinder. The cylinder in *B* becomes a full ellipsoid when the length of the side ($2L$) is zero.

TABLE 1 Capacitance C, translation friction ξ, polarizability α, and intrinsic viscosity $[\eta]$ of flat-ended circular cylinders

L/a	C/a	$\xi/6\pi\eta_0 a$	$3\alpha/4V_p + 1/4$	$[\eta]/V_p$
¼	0.828	0.836	3.78	3.92
⅓	0.876	0.886	3.35	3.46
½	0.964	0.975	2.96	3.05
1	1.191	1.206	2.80	2.87
2	1.572	1.591	3.33	3.40
3	1.907	1.927	4.16	4.25
4	2.216	2.237	5.17	5.27

globular cylinders, for which the ratio L/a ranges from ¼ to 4.

The surface discretization of a flat-ended cylinder for calculations of C, α, ξ, and $[\eta]$ is shown in Fig. 2 *A*. The total length $2L$ is divided into $2N_L$ equal intervals and the range of the azimuthal angle, 0 to 2π, is divided into $2N_\pi$ equal intervals, so every surface element on the side of the cylinder has the same area $\pi aL/N_\pi N_L$. On the two ends, the range of the radius square, 0 to a^2, is divided into N_E equal intervals to ensure that the surface elements have the same area $\pi a^2/2N_\pi N_E$. The total number of elements is $N = (2N_L + 2N_E) \times 2N_\pi$. The calculated electrostatic and hydrodynamic properties for $1/4 \leq L/a \leq 4$ are listed in Table 1. Within this range of L/a, the predictions of Eq. 9 are accurate to within 1.3% and the predictions of Eq. 11 are accurate to within 3.6%. The results in Table 1 were obtained using the discretization parameters $N_L = 14$, $N_E = 10$, and $N_\pi = 15$ (a total of $N = 1440$ elements). The calculation of C and α for each L/a value took 62 s of cpu time on a Convex C3830 computer, and the calculation of ξ and $[\eta]$ for each L/a value took 27 min.

All of the digits given in Table 1 are accurate. This was confirmed by repeating the calculations of C and α using 4000 elements ($N_L = 24$, $N_E = 16$, and $N_\pi = 25$) and repeating the calculations of ξ and $[\eta]$ using 3200 elements ($N_L = 24$, $N_E = 16$, and $N_\pi = 20$). Furthermore, the values for α are in agreement with earlier results of Fixman (1981), and values for the longitudinal component of the translational friction tensor (data not shown) are in agreement with earlier results of Youngren and Acrivos (1975).

The translational friction coefficient of a flat-ended cylinder is sometimes compared to that of a torus, formed by bending the cylinder into a circle. Let the radius of the circle formed by the cylinder axis be b; then the corresponding circumference $2\pi b$ is identical to the cylinder length $2L$. Both the translational friction tensor and the capacitance of the torus are analytically solvable. The former has been tabulated by Goren and O'Neill (1980) for b/a between 1 and 100, and the latter is given by Lebedev et al. (1965) in terms of Legendre functions. This allows us to test Eq. 9 for the present case. At $b/a = 1$, $C/a = 1.742$ and $\xi/6\pi\eta_0 a = 1.744$, so Eq. 9 is almost exact. The error of Eq. 9 increases slowly as b/a increases and passes 1% at $b/a = 8$. Thus for a "globular" torus, Eq. 9 is very accurate. When $b/a = 4/\pi$ (corresponding to $L/a = 4$), $\xi/6\pi\eta_0 a$ is 1.937 for the torus but is 2.237 for the cylinder, so the torus diffuses faster than the cylinder at this aspect ratio. This is also true at $b/a = 100/\pi$ (i.e., $L/a = 100$), although the difference becomes smaller ($\xi/6\pi\eta_0 a$ is 18.3 for the torus but is 20.4 for the cylinder). In the limit $b/a \rightarrow \infty$, the capacitances of the torus and the cylinder are equal, given by $C/a = (L/a)/\ln(L/a)$. When this is used in Eq. 9, the predicted friction coefficient is the same as that obtained from Kirkwood's double-sum formula (Zwanzig, 1966). The prediction is exact for the cylinder but is low by 8.3% for the torus (Zwanzig, 1966). Consequently the torus diffuses more slowly than the cylinder when $b/a \rightarrow \infty$.

Circular cylinders with hemiellipsoidal ends

Yoshizaki and Yamakawa (1980) studied the hydrodynamics of this class of cylinders in detail. They found the translational friction and the intrinsic viscosity numerically. For convenience, we listed their results in Table 2 and will refer to them as YY. To utilize the YY results for checking the accuracy of Eqs. 9 and 11, we numerically calculated the capacitance and the polarizability for these hemiellipsoidal-ended cylinders. The surface discretization used is shown in Fig. 2 *B*. The side of the cylinder was treated in the same way as described earlier. To discretize the ends, the polar radius (denoted by b) of each hemiellipsoid was divided into N_E equal intervals. The surface elements on the ends have unequal areas (equal area cannot be achieved by a simple discretization scheme).

Our results for the capacitance and the polarizability, calculated using 4000 elements ($N_L = 16$, $N_E = 24$, and $N_\pi = 25$), are listed in Table 3. They have been used in Eqs. 9 and 11 to predict the translational friction and the intrinsic viscosity. For the translational friction, the difference between the predictions and YY values is within 2%. However, for the intrinsic viscosity the difference is as large as 9%. This is obviously a questionable result, as the error of Eq. 11 is only 6.25% even for extreme cases of cylinders.

TABLE 2 Translation friction ξ and intrinsic viscosity $[\eta]$ of hemiellipsoidal-ended circular cylinders found by Yoshizaki and Yamakawa (1980)

L/a	b/a	$\xi/6\pi\eta_0 a$	$[\eta]/V_p$
0.13	0.5	0.899	2.622
0.3	0.5	0.993	2.547
0.5	0.5	1.106	
0.17	0.63	0.964	2.525
0.37	0.63	1.066	2.563
0.63	0.63	1.198	2.741
0.2	0.8	1.033	2.502
0.46	0.8	1.156	2.602
0.8	0.8	1.319	2.875
0.26	1	1.124	2.556
0.6	1	1.277	2.758
1	1		3.131
0.34	1.26	1.239	2.713
0.74	1.26		3.019
1.24	1.26		3.588

TABLE 3 Capacitance *C*, translation friction ξ, polarizability α, and intrinsic viscosity $[\eta]$ of hemiellipsoidal-ended circular cylinders

L/a	b/a	C/a	$\xi/6\pi\eta_o a$	$3\alpha/4V_p + 1/4$	$[\eta]/V_p$
0.13	0.5	0.903	0.904	2.656	2.666
0.3	0.5	0.992	0.993	2.564	2.574
0.5	0.5	1.086	1.089	2.557	2.571
0.17	0.63	0.966	0.966	2.545	2.550
0.37	0.63	1.063	1.064	2.530	2.538
0.63	0.63	1.178	1.181	2.597	2.609
0.2	0.8	1.034	1.034	2.509	2.512
0.46	0.8	1.152	1.153	2.566	2.573
0.8	0.8	1.293	1.295	2.721	2.733
0.26	1	1.122	1.123	2.546	2.549
0.6	1	1.267	1.268	2.691	2.699
1	1	1.422	1.424	2.931	2.944
0.34	1.26	1.234	1.234	2.671	2.677
0.74	1.26	1.392	1.394	2.900	2.910
1.24	1.26	1.576	1.578	3.257	3.271

We thus made our own calculations of translational friction and intrinsic viscosity for hemiellipsoidal-ended cylinders. The results calculated using 1440 elements ($N_L = 14$, $N_E = 10$, and $N_\pi = 15$) are listed in Table 3. Now the errors of Eqs. 9 and 11 are found to be less than 0.3% and 0.6%, respectively. We conclude that the YY values are erroneous and our results confirm the accuracy of Eqs. 9 and 11.

At comparable aspect ratios, Eq. 11 is much more accurate for hemiellipsoidal-ended cylinders than for flat-ended cylinders. We can infer that for particles with sharp edges Eq. 11 will in general be less accurate.

Dumbbells

A dumbbell that consists of two spheres can be used as a model for a protein dimer or a protein consisting of two separate domains. The relation between the capacitance and the translational friction for dumbbells has been studied in detail (Hubbard and Douglas, 1993; Zhou et al., 1994), and Eq. 9 was found to be accurate to within 0.5% for two equal-radius spheres at various separations. We now consider the relation between the polarizability and the intrinsic viscosity.

TABLE 4 Polarizability α and intrinsic viscosity $[\eta]$ of dumbbells

u	L/a	$3\alpha/4V_p + 1/4$	$[\eta]/V_p$
0	1	3.4054	3.4496
0.2	1.0201	3.4530	3.4978
0.5	1.1276	3.7135	3.6748
1.0	1.5431	4.8184	4.8920
1.5	2.3524	7.5805	7.6785
2.0	3.7622	14.632	14.756
2.5	6.1323	33.142	33.309
3.0	10.068	82.452	82.690

Wakiya (1971) and Brenner (1974) calculated the intrinsic viscosity for dumbbells consisting of two equal-radius spheres at various separations. Their results are listed in Table 4 for the ratio L/a between 1 and 10.068, where a is the radius of the spheres and L is half of their center-to-center separation. For large L/a, the following asymptotic result can be derived from the work of Brenner (1974)

$$[\eta]/V_p = 3(L/a)^2/4 + 63(L/a)/160 + 3497/1280. \tag{65}$$

At $L/a = 10.068$, Eq. 65 gives $[\eta]/V_p = 82.715$, which is almost identical to the exact result $[\eta]/V_p = 82.690$. Thus Eq. 65 is essentially exact for $L/a > 10$.

The polarizability of a dumbbell can be found analytically by using bispherical coordinates (Lebedev et al., 1965; Lebedev, 1972; Douglas and Garboczi, 1995). The result is

$$\frac{\alpha}{V_p} = 2\sinh^3 u \sum_{n=0}^{\infty} \left[\frac{(2n+1)^2}{e^{(2n+1)u} - 1} + \frac{4n(n+1)}{e^{(2n+1)u} + 1} \right], \tag{66}$$

where $u = \cosh^{-1}(L/a)$. Predictions of the intrinsic viscosity for L/a between 1 and 10.068 by the use of Eq. 66 in Eq. 11 are listed in Table 4. The difference between predicted and exact values of the intrinsic viscosity is less than 1.5% in the range $1 < L/a < 10$. At higher L/a, the difference actually decreases. In the limit $L/a \to \infty$, $[\eta]/V_p = 3(L/a)^2/4$ and $\alpha/V_p = (L/a)^2$ and thus Eq. 11 becomes exact.

Analogous to the intrinsic viscosity, the rotational friction tensor also has some relation to the polarizability. This is discussed in Appendix B.

CONCLUSIONS

We have demonstrated the accuracy of the relations, given by Eqs. 9 and 11, between the translational friction and the capacitance and between the intrinsic viscosity and the polarizability. For ellipsoids, cylinders, and dumbbells with moderate aspect ratios, Eq. 9 is accurate to within about 1% and Eq. 11 is accurate to within about 3%. We expect the accuracy of the two relations to remain the same for arbitrarily shaped globular particles.

These two relations provide an efficient route for calculating the translational friction and the intrinsic viscosity. We showed that both the capacitance and the polarizability of an arbitrarily shaped particle can be found in a single calculation using the boundary-element technique. Direct calculation of the translational friction and the intrinsic friction for a centrosymmetric particle is possible but takes 27 times as long. For an arbitrarily shaped particle, the time needed to directly calculate the translational friction is increased by another eightfold, and the difficulty of averaging over orientation does not even allow a direct calculation of the intrinsic viscosity.

For macromolecules, which have detailed structures and complicated shapes, Eqs. 9 and 11 should prove especially useful. The case of globular proteins will be studied in detail in the following paper (Zhou, 1995).

APPENDIX A: ENERGY DISSIPATION AND INTRINSIC VISCOSITY

In this appendix, some results concerning the intrinsic viscosity of a centrosymmetric particle are derived. The derivation largely follows previous work by Brenner and collaborators. According to Brenner (1958), the rate of additional energy dissipation per unit volume due to a single particle dissolved in the solvent is

$$\delta w = -\frac{1}{V}\int_{S_p} ds\mathbf{f}_v(\mathbf{r})\cdot\mathbf{v}(\mathbf{r}), \qquad \text{(A1)}$$

where V is the volume of the solvent. The change in solvent velocity on the particle surface is given by $\mathbf{v}(\mathbf{r}) = (\mathbf{\Omega} - \boldsymbol{\omega}) \times \mathbf{r} - \underset{\sim}{s} \cdot \mathbf{r}$, consequently

$$\delta w = \frac{1}{V}[-\mathbf{L}\cdot(\mathbf{\Omega} - \boldsymbol{\omega}) + \underset{\sim}{A}:\underset{\sim}{s}], \qquad \text{(A2)}$$

where $\mathbf{L}$ is the torque exerted on the particle by the solvent,

$$\mathbf{L} = \int_{S_p} ds\mathbf{r} \times \mathbf{f}_v(\mathbf{r}), \qquad \text{(A3)}$$

and $\underset{\sim}{A}$ is the stresslet on the particle, given by Eq. 42.

If one has a suspension of particles that is dilute enough so that interactions among them are negligible, then the rate of additional energy dissipation per unit volume is

$$\delta W = c_p[-\langle\mathbf{L}\cdot(\mathbf{\Omega} - \boldsymbol{\omega})\rangle + \langle\underset{\sim}{A}\rangle:\underset{\sim}{s}], \qquad \text{(A4)}$$

where $\langle\cdots\rangle$ signifies averaging over an appropriate distribution of orientation, which we now specify following Haber and Brenner (1984). Let the orientation of a particle be $\boldsymbol{\phi}$; then its distribution $\rho(\boldsymbol{\phi})$ in the presence of the torque $\mathbf{L}$ should satisfy the equation

$$k_B\, T\, \nabla_{\phi} \ln \rho(\boldsymbol{\phi}) = \mathbf{L}, \qquad \text{(A5)}$$

where k_B is Boltzmann's constant and T is the temperature. In addition, as $d\boldsymbol{\phi}/dt = \mathbf{\Omega}$, $\rho(\boldsymbol{\phi})$ should satisfy the conservation equation

$$\nabla_{\phi}\cdot[\mathbf{\Omega}\rho(\boldsymbol{\phi})] = 0. \qquad \text{(A6)}$$

The torque $\mathbf{L}$ can be related to the rotational slip velocity $\mathbf{\Omega} - \boldsymbol{\omega}$ and the shear $\underset{\sim}{s}$ through

$$\mathbf{L} = -[\underset{\sim}{\zeta}\cdot(\mathbf{\Omega} - \boldsymbol{\omega}) - \underset{\sim}{\tau}:\underset{\sim}{s}], \qquad \text{(A7)}$$

where $\underset{\sim}{\zeta}$ is the rotational friction tensor and $\underset{\sim}{\tau}$ is the coupling tensor between rotation and shear. If $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are chosen as the three symmetry axes of the centrosymmetric particle, one has

$$\underset{\sim}{\zeta} = \zeta_1\mathbf{e}_1\mathbf{e}_1 + \zeta_2\mathbf{e}_2\mathbf{e}_2 + \zeta_3\mathbf{e}_3\mathbf{e}_3, \qquad \text{(A8a)}$$

$$\begin{aligned}\underset{\sim}{\tau} = {}& \tau_1\mathbf{e}_1(\mathbf{e}_2\mathbf{e}_3 + \mathbf{e}_3\mathbf{e}_2) + \tau_2\mathbf{e}_2(\mathbf{e}_3\mathbf{e}_1 + \mathbf{e}_1\mathbf{e}_3)\\ & + \tau_3\mathbf{e}_3(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1).\end{aligned} \qquad \text{(A8a)}$$

Combining Eqs. A5 and A7, one finds an expression for $\mathbf{\Omega}$ in terms of $\rho(\boldsymbol{\phi})$:

$$\mathbf{\Omega} = \boldsymbol{\omega} + \underset{\sim}{\zeta}^{-1}\cdot\underset{\sim}{\tau}:\underset{\sim}{s} - \mathrm{k_B T}\, \underset{\sim}{\zeta}^{-1}\cdot\nabla_{\phi} \ln \rho(\boldsymbol{\phi}). \qquad \text{(A9)}$$

Inserting this expression into Eq. A6, one finally arrives at the equation satisfied by $\rho(\boldsymbol{\phi})$:

$$k_BT\, \nabla_{\phi}\cdot\underset{\sim}{\zeta}^{-1}\cdot\nabla_{\phi}\rho(\boldsymbol{\phi}) = \nabla_{\phi}\cdot(\boldsymbol{\omega} + \underset{\sim}{\zeta}^{-1}\cdot\underset{\sim}{\tau}:\underset{\sim}{s})\rho(\boldsymbol{\phi}). \qquad \text{(A10)}$$

To obtain δW to the second order of the shear rate, one only needs $\rho(\boldsymbol{\phi})$ up to the first order. The solution, found by Haber and Brenner (1984), is

$$\rho(\boldsymbol{\phi}) = \rho_0(1 - \underset{\sim}{\kappa}:\underset{\sim}{s}), \qquad \text{(A11a)}$$

where

$$\rho_0 = \frac{1}{8\pi^2}, \qquad \text{(A11b)}$$

$$\underset{\sim}{\kappa} = \qquad \text{(A11c)}$$

$$\frac{(\tau_2\zeta_3 - \tau_3\zeta_2)\mathbf{e}_1\mathbf{e}_1 + (\tau_3\zeta_1 - \tau_1\zeta_3)\mathbf{e}_2\mathbf{e}_2 + (\tau_1\zeta_2 - \tau_2\zeta_1)\mathbf{e}_3\mathbf{e}_3}{k_BT(\zeta_1 + \zeta_2 + \zeta_3)}.$$

Now let us calculate the two terms of δW in Eq. A4 to the second order of the shear rate. The result for the first term is simple:

$$\langle\mathbf{L}\cdot(\mathbf{\Omega} - \boldsymbol{\omega})\rangle = 0. \qquad \text{(A12)}$$

This directly leads to Eq. 41. To prove Eq. A12, the expressions of $\mathbf{L}$ and $\mathbf{\Omega} - \boldsymbol{\omega}$ are needed. By inserting Eq. A11a into Eqs. A5 and A9, respectively, one finds

$$\begin{aligned}&(\zeta_1 + \zeta_2 + \zeta_3)\mathbf{L}\\ &= -\{[(\tau_2 + \tau_3)\zeta_1 - \tau_1(\zeta_2 + \zeta_3)]\mathbf{e}_1(\mathbf{e}_2\mathbf{e}_3 + \mathbf{e}_3\mathbf{e}_2) \qquad \text{(A13a)}\\ &\quad + [(\tau_3 + \tau_1)\zeta_2 - \tau_2(\zeta_3 + \zeta_1)]\mathbf{e}_2(\mathbf{e}_3\mathbf{e}_1 + \mathbf{e}_1\mathbf{e}_3)\\ &\quad + [(\tau_1 + \tau_2)\zeta_3 - \tau_3(\zeta_1 + \zeta_2)]\mathbf{e}_3(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1)\}:\underset{\sim}{s},\end{aligned}$$

$$\begin{aligned}&(\zeta_1 + \zeta_2 + \zeta_3)(\mathbf{\Omega} - \boldsymbol{\omega})\\ &\quad = (\tau_1 + \tau_2 + \tau_3)[\mathbf{e}_1(\mathbf{e}_2\mathbf{e}_3 + \mathbf{e}_3\mathbf{e}_2) \qquad \text{(A13b)}\\ &\qquad + \mathbf{e}_2(\mathbf{e}_3\mathbf{e}_1 + \mathbf{e}_1\mathbf{e}_3) + \mathbf{e}_3(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1)]:\underset{\sim}{s}.\end{aligned}$$

Note that for an axisymmetric particle, one has $\tau_1 = -\tau_2$ and $\tau_3 = 0$ (Haber and Brenner, 1984), and consequently $\mathbf{\Omega} - \boldsymbol{\omega} = \mathbf{0}$. This particular result has been found previously by Yoshizaki and Yamakawa (1980). For an arbitrary centrosymmetric particle, Eqs. A13a and A13b give

$$\begin{aligned}&\langle\mathbf{L}\cdot(\mathbf{\Omega} - \boldsymbol{\omega})\rangle\\ &\quad = \langle\mathbf{L}\cdot(\mathbf{\Omega} - \boldsymbol{\omega})\rangle_0\\ &\quad = \frac{\tau_1 + \tau_2 + \tau_3}{(\zeta_1 + \zeta_2 + \zeta_3)^2}[(\tau_2 + \tau_3)\zeta_1 - \tau_1(\zeta_2 + \zeta_3)\\ &\qquad + (\tau_3 + \tau_1)\zeta_2 - \tau_2(\zeta_3 + \zeta_1) + (\tau_1 + \tau_2)\zeta_3\\ &\qquad - \tau_3(\zeta_1 + \zeta_2)]\underset{\sim}{s}:\langle(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1)(\mathbf{e}_1\mathbf{e}_2 + \mathbf{e}_2\mathbf{e}_1)\rangle_0:\underset{\sim}{s},\end{aligned}$$

in which only terms up to the second order of the shear rate have been kept and the invariance of orientational average to ordered interchange of the orthonormal vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ has been used. The terms inside the square brackets obviously sum up to zero, and Eq. A12 is thus proved.

The orientational averaging of the stresslet **A**, which appears in the second term of δW, can be carried out analytically for centrosymmetric particles. In analogy to the manipulations in deriving the polarizability (Eqs. 21–25), we define the orientation-independent functions $g_{jkl}(\mathbf{r}) \equiv \mathbf{e}_j \cdot \mathbf{g}_{kl}(\mathbf{r})$ by

$$\int_{S_p} ds'\, \mathbf{e}_i \cdot \eta_0\, \underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r}) \cdot \sum_{j=1}^{3} \mathbf{e}_j g_{jkl}(\mathbf{r}') = \delta_{ik} r_l, \quad \mathbf{r} \in S_p, \tag{A14}$$

where $i, j, k, l = 1, 2,$ and 3. We want to express the net surface stress force $\mathbf{f}_v(\mathbf{r})$ in terms of $\mathbf{g}_{kl}(\mathbf{r})$. To this end one calculates the dot products of both sides of Eq. 38, the governing equation for $\mathbf{f}_v(\mathbf{r})$, with $\mathbf{e}_i$. For example, for $i = 1$ one finds

$$\int_{S_p} ds'\, \mathbf{e}_1 \cdot \eta_0\, \underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r}) \cdot \sum_{j=1}^{3} \mathbf{e}_j \mathbf{e}_j \cdot \mathbf{f}_v(\mathbf{r}')/\eta_0$$

$$= \lambda \mathbf{e}_1 \cdot \underset{\sim}{\mathbf{s}} \cdot (\mathbf{e}_2 r_2 - \mathbf{e}_3 r_3) + \mathbf{e}_1 \cdot \underset{\sim}{\mathbf{s}} \cdot \sum_{k=1}^{3} \mathbf{e}_k r_k, \qquad \mathbf{r} \in S_p, \tag{A15}$$

where $\lambda = 2(\tau_1 + \tau_2 + \tau_3)/(\zeta_1 + \zeta_2 + \zeta_3)$ and the expression for $\boldsymbol{\Omega} - \boldsymbol{\omega}$ given in Eq. A13b has been used. Comparison of Eqs. A14 and A15 leads to

$$\begin{aligned} \mathbf{f}_v(\mathbf{r})/\eta_0 = {} & [(1 + \lambda)\mathbf{g}_{12} + (1 - \lambda)\mathbf{g}_{21}]\mathbf{e}_1 \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_2 \\ & + [(1 + \lambda)\mathbf{g}_{23} + (1 - \lambda)\mathbf{g}_{32}]\mathbf{e}_2 \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_3 \\ & + [(1 + \lambda)\mathbf{g}_{31} + (1 - \lambda)\mathbf{g}_{13}]\mathbf{e}_3 \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_1 \\ & + \sum_{k=1}^{3} \mathbf{g}_{kk} \mathbf{e}_k \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_k. \end{aligned} \tag{A16}$$

By writing $\mathbf{r}\mathbf{f}_v$ as $\sum_{i,j=1}^{3} (r_i \mathbf{e}_j \cdot \mathbf{f}_v)\mathbf{e}_i\mathbf{e}_j$, one finds that $\underset{\sim}{\mathbf{A}} = \int_{S_p} ds \mathbf{r}\mathbf{f}$ is composed of terms that have the form $\int_{S_p} ds r_i g_{jkl} \mathbf{e}_i \mathbf{e}_k \cdot \mathbf{s} \cdot \mathbf{e}_l \mathbf{e}_k$. The problem of carrying out the orientational averaging of $\underset{\sim}{\mathbf{A}}$ thus reduces to the evaluation of $\langle \mathbf{e}_i \mathbf{e}_k \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_l \mathbf{e}_j \rangle_0$. From Haber and Brenner (1984), one obtains ($i \neq j$)

$$\langle \mathbf{e}_i \mathbf{e}_i \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_j \mathbf{e}_j \rangle_0 = \langle \mathbf{e}_i \mathbf{e}_j \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_i \mathbf{e}_j \rangle_0 = \frac{1}{10} \underset{\sim}{\mathbf{s}}, \tag{A17a}$$

$$\langle \mathbf{e}_i \mathbf{e}_j \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_j \mathbf{e}_i \rangle_0 = -\frac{1}{15} \underset{\sim}{\mathbf{s}}, \tag{A17b}$$

$$\langle \mathbf{e}_i \mathbf{e}_i \cdot \underset{\sim}{\mathbf{s}} \cdot \mathbf{e}_i \mathbf{e}_i \rangle_0 = \frac{2}{15} \underset{\sim}{\mathbf{s}}. \tag{A17c}$$

Terms with other combinations of indices vanish because $\mathbf{e}_1$, $\mathbf{e}_2$, or $\mathbf{e}_3$ appears an odd number of times. The final result for the orientationally averaged stresslet is given in Eq. 43.

APPENDIX B: ROTATIONAL FRICTION AND POLARIZABILITY

From the derivation of the relation between the intrinsic viscosity of a centrosymmetric particle and its polarizability, it becomes apparent that the rotational friction tensor $\underset{\sim}{\boldsymbol{\zeta}}$ can also be related to the polarizability tensor $\underset{\sim}{\boldsymbol{\alpha}}$ within the approximation of orientationally averaging the Oseen tensor. Here we derive this relation. We note that many years ago Riseman and Kirkwood (1949) recognized the relation between intrinsic viscosity and rotational friction for flexible molecules, where they found $\underset{\sim}{\boldsymbol{\zeta}} = \zeta \underset{\sim}{\mathbf{1}}$ and $\zeta = 4\eta_0[\eta]$.

For defining the rotational friction tensor, the solvent velocity on the particle surface, according to the requirement of nonslip, is given by Eq. 27 with $\mathbf{h} = \boldsymbol{\Omega}$, the rotational velocity of the particle, and vanishing **g** and $\underset{\sim}{\mathbf{s}}$. Consequently the surface stress force satisfies the equation

$$-\int_{S_p} ds'\, \underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r}) \cdot \mathbf{f}(\mathbf{r}') = \boldsymbol{\Omega} \times \mathbf{r}, \quad \mathbf{r} \in S_p. \tag{B1}$$

Replacing $\underset{\sim}{\mathbf{T}}(\mathbf{r}' - \mathbf{r})$ by its orientational average and writing **r** as $r_1\mathbf{e}_1 + r_2\mathbf{e}_2 + r_3\mathbf{e}_3$, one finds

$$\mathbf{f}(\mathbf{r}) = -6\pi\eta_0 \boldsymbol{\Omega} \times [\sigma_1(\mathbf{r})\mathbf{e}_1 + \sigma_2(\mathbf{r})\mathbf{e}_2 + \sigma_3(\mathbf{r})\mathbf{e}_3]. \tag{B2}$$

The resulting torque on the particle is

$$\mathbf{L} = \int_{S_p} ds \mathbf{r} \times \mathbf{f}(\mathbf{r}) = -[3\eta_0(3\alpha\underset{\sim}{\mathbf{1}} - \underset{\sim}{\boldsymbol{\alpha}})/2] \cdot \boldsymbol{\Omega}. \tag{B3}$$

Consequently

$$\underset{\sim}{\boldsymbol{\zeta}} = 3\eta_0(3\alpha\, \underset{\sim}{\mathbf{1}} - \underset{\sim}{\boldsymbol{\alpha}})/2 \equiv 3\eta_0\, \underset{\sim}{\boldsymbol{\beta}}. \tag{B4}$$

For an isotropic particle, $\underset{\sim}{\boldsymbol{\zeta}} = \zeta\underset{\sim}{\mathbf{1}}$ and $\underset{\sim}{\boldsymbol{\alpha}} = \alpha\underset{\sim}{\mathbf{1}}$, consequently Eq. B4 gives $\zeta = 3\eta_0\alpha$. When combined with another preaveraging result, $[\eta] = \frac{3}{4}\alpha$, this leads to the relation of Riseman and Kirkwood referred to in the beginning of this appendix.

We now check the accuracy of Eq. B4. For an ellipsoid, the longitudinal and transverse components of the rotational friction tensor are (Brenner, 1974)

$$\frac{\zeta_l}{\eta_0 V_p} = \frac{4(p^2 - 1)}{p^2(1 - B)}, \tag{B5a}$$

$$\frac{\zeta_t}{\eta_0 V_p} = \frac{4(p^4 - 1)}{p^2[(2p^2 - 1)B - 1]}. \tag{B5b}$$

The longitudinal and transverse components of the tensor $\underset{\sim}{\boldsymbol{\beta}}$ are (Landau et al., 1984)

$$\frac{\beta_l}{V_p} \equiv \frac{\alpha_t}{V} = \frac{2(p^2 - 1)}{p^2(1 - B)}, \tag{B6a}$$

$$\frac{\beta_t}{V_p} \equiv \frac{\alpha_l + \alpha_t}{2V_p} = \frac{p^2 - 1}{p^2}\left[\frac{1}{1 - B} + \frac{p^2}{2(p^2B - 1)}\right]. \tag{B6b}$$

Comparison of Eqs. B5a and B6a shows that

$$\zeta_l/\eta_0 = 2\beta_l. \tag{B7}$$

The numerical factor predicted by Eq. B4 is 3 instead of 2. For the transverse component, the ratio $\zeta_t/\eta_0\beta_t$ is 4 for both a disk ($p = 0$) and a needle ($p = \infty$) and decreases to a minimum of 2 for a sphere ($p = 1$).

We carried out numerical calculations for the rotational friction tensor of flat-ended cylinders, and results almost identical to those in the case of ellipsoids were found. Specifically, for the longitudinal component Eq. B7 again holds, and for the transverse component the ratio $\zeta_t/\eta_0\beta_t$ is 4 for both a disk ($L/a = 0$) and a needle ($L/a = \infty$) and decreases to a minimum close to 2 at $L/a \approx 1$.

For a dumbbell consisting of two equal-radius spheres (Brenner, 1974), the longitudinal component of the rotational friction tensor is

$$\frac{\zeta_l}{\eta_0 V_p} = 24 \sinh^3 u \sum_{n=1}^{\infty} \frac{n(n+1)}{e^{(2n+1)u} + 1}. \qquad \text{(B8)}$$

The transverse component has values of $\zeta_t/\eta_0 V_p$ = 11.220, 11.459, 11.710, 18.816, 34.741, 76.199, 185.916, and 479.556, respectively, at $u = \cosh^{-1}(L/a)$ = 0, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0. At large L/a, it is given by the asymptotic formula $\zeta_t/\eta_0 V_p = 9(L/a)^2/2 + 27(L/a)/16 + 849/128$, which is essentially exact for $L/a > 10$. The longitudinal and transverse components of the tensor are (Lebedev et al., 1965; Lebedev, 1972; Douglas and Garboczi, 1995)

$$\frac{\beta_l}{V_p} = 12 \sinh^3 u \sum_{n=1}^{\infty} \frac{n(n+1)}{e^{(2n+1)u} + 1}, \qquad \text{(B9a)}$$

$$\frac{\beta_t}{V_p} = 3 \sinh^3 u \sum_{n=0}^{\infty} \left[\frac{(2n+1)^2}{e^{(2n+1)u} - 1} + \frac{2n(n+1)}{e^{(2n+1)u} + 1} \right]. \qquad \text{(B9b)}$$

It is clear from Eqs. B8 and B9a that Eq. B7 again holds for the longitudinal component. For the transverse component, the ratio $\zeta_t/\eta_0\beta_t$ increases from 2.26 at $L/a = 1$ to 3 at $L/a = \infty$. (The value of ζ_t at $u = 0.5$ given by Brenner (1974) seems to be wrong. The resulting ratio $\zeta_t/\eta_0\beta_t$ is 2.11, which is less than the corresponding value of 2.26 at $u = 0$. The value of $[\eta]$ at $u = 0.5$ is probably also wrong (given in Table 4). At every value of u other than 0.5, the value of $[\eta]/V_p$ is slightly greater than the value of $3\alpha/4V_p + 1/4$, but at $u = 0.5$ this order is reversed.)

Based on the results in the cases of ellipsoids, cylinders, and dumbbells, we conjecture that Eq. B7 holds for the longitudinal component of the rotational friction tensor of any axisymmetric particle (possessing fore-aft symmetry). Furthermore, in the case of an arbitrary centrosymmetric particle, for which the principal axes of $\boldsymbol{\zeta}$ and $\boldsymbol{\beta}$ coincide, the ratios of the corresponding principal components are in the range $\zeta_i/\beta_i = (3 \pm 1)\eta_0$, i = 1, 2, and 3. The median value of $3\eta_0$ is predicted by orientationally averaging the Oseen tensor.

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