Intrinsic viscosity for Brownian particles of arbitrary shape

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Abstract. General expressions for the frequency-dependent Brownian contribution to the intrinsic viscosity of arbitrary-shaped particles have been derived from the Smoluchowski equation.

Dedicated to François Feuillebois on the occasion of his 65th birthday

1. Introduction
In physical chemistry, dynamic light scattering and viscosity measurements can provide information about structure of particles (such as e.g. fibrinogen) in colloidal suspensions [1]. Indeed, a change of the particle shape modifies its self-diffusion, and in general leads to a significant change of its intrinsic viscosity. For suspensions of arbitrary-shaped particles, the single-particle short-time self-diffusion coefficient and the high-frequency intrinsic viscosity can be easily derived from the existing theoretical framework, e.g. with the use of the bead model, and the multipole expansion of the Stokes equations [2]. However, as far as we know, the Brownian contribution to the intrinsic viscosity has been determined only for special types of shapes, such as axially symmetric particles [3, 4]. In this work, we theoretically derive general expressions for the frequency-dependent Brownian contribution to the intrinsic viscosity of arbitrary-shaped particles.

2. Problem
We start from reminding the basic equation, which describes motion of a single particle of arbitrary shape in the Stokes flow [5]. Assuming that there exist external force and torque $\mathbf{F}, \mathbf{T}$ exerted on the particle, and an ambient linear flow $\mathbf{v}_0$, we express the particle translational and rotational velocities, $\mathbf{U}$ and $\widetilde{\boldsymbol{\Omega}}$, and the stresslet $\mathbf{S}$, by the following relation [5],

$$\begin{bmatrix} \mathbf{U} - \mathbf{v}_0(\boldsymbol{R}) \\ \widetilde{\boldsymbol{\Omega}} - \boldsymbol{\omega}_0(\boldsymbol{R}) \\ -\mathbf{S} \end{bmatrix} = \begin{bmatrix} \boldsymbol{\mu}^{tt} & \boldsymbol{\mu}^{tr} & \boldsymbol{\mu}^{td} \\ \boldsymbol{\mu}^{rt} & \boldsymbol{\mu}^{rr} & \boldsymbol{\mu}^{rd} \\ \boldsymbol{\mu}^{dt} & \boldsymbol{\mu}^{dr} & \boldsymbol{\mu}^{dd} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{F} \\ \mathbf{T} \\ \mathbf{g}_0 \end{bmatrix}, \tag{1}$$

where $\boldsymbol{R}$ is the particle center, $\boldsymbol{\omega}_0 = \mathrm{rot}\,\mathbf{v}_0/2$ and $\mathbf{g}_0$ is the rate-of-strain tensor. The grand mobility matrix in the above equation consists of single-particle mobility tensors $\boldsymbol{\mu}$ with the corresponding upper indices, as indicated above.

We consider a spatially uniform suspension of the particle concentration $n = N/V$ with N being the number of suspended particles in volume V. The suspension is subjected to an oscillating shear flow $\mathbf{v}_0$ with the rate of strain

$$\mathbf{g}_0(t) = \mathbf{g}_{0\omega} \exp(-i\omega t). \tag{2}$$

Other quantities oscillate with the same frequency, and their amplitudes are denoted in a similar way, i.e. by adding the lower index ω.

In the presence of particles, the rate of strain (2) is modified. Introducing $\langle ... \rangle$ as the average with respect to the ensemble of particle positions and orientations, we write the amplitude of the effective rate of strain as $\langle \mathbf{g} \rangle_\omega$. For small-amplitude oscillations, the effective viscous part of the stress tensor amplitude $\langle \boldsymbol{\sigma} \rangle_\omega^v$ and the effective rate of strain amplitude $\langle \mathbf{g} \rangle_\omega$ are linearly related, with the coefficient equal to the effective viscosity $\eta_{\mathrm{eff}}(\omega)$,

$$\langle \boldsymbol{\sigma} \rangle_\omega^v = 2\eta_{\mathrm{eff}}(\omega) \langle \mathbf{g} \rangle_\omega . \tag{3}$$

Taking into account the results of the Chapter 2.5 from Ref. [5] one can write

$$\langle \boldsymbol{\sigma} \rangle_\omega^v = 2\eta_0 \langle \mathbf{g} \rangle_\omega - \langle \mathbf{S} \rangle_\omega \frac{N}{V}, \tag{4}$$

where $- \langle \mathbf{S} \rangle_\omega$ is the amplitude of average particle stresslet oscillations and η_0 is the solvent viscosity.

We consider low particle concentrations N/V, corresponding to low volume fractions $\phi = Nv/V$, where v is the particle volume, with no hydrodynamic interactions between the particles. In this case, the suspension effective viscosity can be written as

$$\eta_{\mathrm{eff}}(\omega) = \eta_0 \left(1 + [\eta]_\omega \phi + ... \right), \tag{5}$$

where the coefficient $[\eta]_\omega$ is called the intrinsic viscosity. Value of the intrinsic viscosity depends on a particle shape and its internal structure. In particular, for a hard sphere, $[\eta]_\omega = 5/2$. According to Eq. (5), we are interested to determine the linear dependence of the effective viscosity on volume fraction. Within this approximation, $\langle \mathbf{g} \rangle_\omega$ in Eqs. (3)-(4) can be replaced by $\mathbf{g}_{0\omega}$.

The intrinsic viscosity consists of two parts: the high-frequency contribution $[\eta]_\infty$ and the Brownian contribution $[\eta]_\omega^B$,

$$[\eta]_\omega = [\eta]_\infty + [\eta]_\omega^B . \tag{6}$$

The high-frequency contribution $[\eta]_\infty$ is obtained from Eqs. (3)-(4) as the average of $\mathbf{S}$ with respect to the equilibrium probability distribution; for an isotropic system, $\langle \mathbf{S} \rangle_\omega$ is proportional to $\mathbf{g}_{0\omega}$, with a scalar proportionality coefficient evaluated by the double contraction of both tensors. Therefore, according to Eq. (1),

$$[\eta]_\infty = \frac{\mu_{kllk}^{dd}}{10\eta_0 v}, \tag{7}$$

where $k, l = x, y, z$ denote the Cartesian indices of the matrix $\boldsymbol{\mu}^{dd}$, and the Einstein summation convention has been used.

3. The Smoluchowski equation

To evaluate $[\eta]_{\omega}^{B}$, we first need to introduce the probability distribution and the Smoluchowski equation. For a spatially uniform suspension, only the rotational motion contributes to the Brownian part of the effective viscosity $[\eta]_{\omega}^{B}$ [6]. The orientation of an anisotropic particle is given by the Euler angles $\widehat{\boldsymbol{\Omega}} = (\alpha, \beta, \gamma)$ which specify the orientation of the particle body-fixed axes with respect to the space-fixed axes. We use the notation proposed by Berne and Pecora in Ref. [7]. We denote the orientational probability distribution at time t by $P(\widehat{\boldsymbol{\Omega}}, t)$. It is normalized as

$$\int d\widehat{\boldsymbol{\Omega}} P(\widehat{\boldsymbol{\Omega}}, t) = 1, \tag{8}$$

with

$$\int d\widehat{\boldsymbol{\Omega}} \, ... = \int_{0}^{2\pi} d\alpha \int_{0}^{2\pi} d\gamma \int_{0}^{\pi} d\beta \sin\beta \, ... \tag{9}$$

Evolution of the probability distribution $P(\widehat{\boldsymbol{\Omega}}, t)$ is governed by the Smoluchowski equation,

$$\frac{\partial}{\partial t} P(\widehat{\boldsymbol{\Omega}}, t) = \mathcal{L}(\widehat{\boldsymbol{\Omega}}, t) P(\widehat{\boldsymbol{\Omega}}, t). \tag{10}$$

In the absence of an ambient flow, $\mathcal{L}(t) = \mathcal{L}_0$, with

$$\mathcal{L}_0 = -\mathbf{I} \cdot \mathbf{D}^r \cdot \mathbf{I} \tag{11}$$

where

$$\mathbf{D}^r = k_B T \, \boldsymbol{\mu}^{rr} \tag{12}$$

is the tensor of the rotational diffusion, and

$$\mathbf{I} = (I_x, I_y, I_z) \tag{13}$$

is the total angular momentum operator with components being the angular momentum operators about axes x, y, z stuck in the particles. If α_k is the angle of rotation around axis k then

$$I_k = -i \frac{\partial}{\partial \alpha_k}. \tag{14}$$

In the presence of an external flow,

$$\mathcal{L}(t) = \mathcal{L}_0 + \delta\mathcal{L}(t). \tag{15}$$

When the particle is located in a rate-of-strain field characterized by $\mathbf{g}_0(t)$,

$$\delta\mathcal{L}(t) = -i\mathbf{I} \cdot \boldsymbol{\mu}^{rd} \cdot \mathbf{g}_0(t), \tag{16}$$

where the contraction of $\boldsymbol{\mu}^{rd}$ and the strain tensor $\mathbf{g}_0(t)$ is performed with respect to two Cartesian indices.

4. Rotational Brownian contributions to the intrinsic viscosity

To find the Brownian contribution $[\eta]_{\omega}^{B}$ to the intrinsic viscosity (6), we must calculate the time-dependent averages, which appear in Eqs. (3)-(4). These averages are performed only over the angles,

$$\langle ... \rangle_t = \int d\widehat{\boldsymbol{\Omega}} \, P(\widehat{\boldsymbol{\Omega}}, t) \, ... \tag{17}$$

Within the linear response theory [8, 9], the solution of Eq. (10), with $\mathcal{L}(t)$ given by Eqs. (15)-(16), has the following form,

$$P(\widehat{\mathbf{\Omega}},t) \;=\; P_{eq}(\widehat{\mathbf{\Omega}}) + \int_{-\infty}^{t} dt' \exp[\mathcal{L}_0(t-t')]\delta\mathcal{L}(t')P_{eq}(\widehat{\mathbf{\Omega}}). \tag{18}$$

The contribution to the non-Brownian intrinsic viscosity, coming from averaging with the equilibrium distribution, P_{eq}, has been already described in Eq. (7). The Brownian contribution follows entirely from the averaging with respect to the non-equilibrium part of P.

In case of the Brownian rotation, the average stresslet is due to the Brownian torque,

$$-\langle \mathbf{S}^B \rangle_t = \langle \boldsymbol{\mu}^{dr} \cdot \mathbf{T}_{Br} \rangle_t, \tag{19}$$

with [5]

$$\mathbf{T}_{Br} = -ik_B T \, \mathbf{I} \ln P(\widehat{\mathbf{\Omega}},t). \tag{20}$$

The expression (19) may be transformed to

$$-\langle \mathbf{S}^B \rangle_t = k_B T \, \langle \mathbf{H} \rangle_t, \tag{21}$$

with

$$H_{ij} = iI_k \mu^{rd}_{kij}. \tag{22}$$

To obtain the above equation, we performed integration by parts in angles and took into account the antisymmetric property of the generalized mobility matrix elements with dr and rd indices, i.e.

$$\mu^{dr}_{ijk} = -\mu^{rd}_{kij}. \tag{23}$$

The symmetric and traceless tensor $\mathbf{H}$ can be derived from $\boldsymbol{\mu}^{rd}$ by the irreducible tensor analysis described in Ref. [10],

$$H_{ij} = \epsilon_{ikl}\mu^{rd}_{lkj} + \epsilon_{jkl}\mu^{rd}_{lki}. \tag{24}$$

Let us now consider an oscillating shear flow with the rate of strain, see Eq. (2), and assume that the amplitude $\mathbf{g}_{0\omega}$ is small. From Eq. (16) we calculate $\delta\mathcal{L}(t)$ and insert it into Eq. (18). Then, we obtain the following relation between the oscillation amplitudes $\langle \mathbf{S}^B \rangle_\omega$ and $\mathbf{g}_{0\omega}$,

$$-\langle S^B_{ij} \rangle_\omega = \left[\frac{k_B T}{8\pi^2} \int d\widehat{\mathbf{\Omega}} \; H_{ij}(\widehat{\mathbf{\Omega}}) \frac{1}{i\omega + \mathbf{I} \cdot \mathbf{D}^r \cdot \mathbf{I}} H_{kl}(\widehat{\mathbf{\Omega}}) \right] g_{0\omega,kl}, \tag{25}$$

where the Einstein summation convention has been used.

For the isotropic system, $\langle S^B_{ij} \rangle_\omega$ is proportional to $g_{0\omega,ij}$. It is convenient to write the scalar proportionality coefficient using the double contraction of both tensors. Taking into account Eqs. (3)-(4), we therefore write,

$$[\eta]^B_\omega = \frac{k_B T}{80\pi^2 v\eta_0} \int d\widehat{\mathbf{\Omega}} \; H_{ij}(\widehat{\mathbf{\Omega}}) \frac{1}{i\omega + \mathbf{I} \cdot \mathbf{D}^r \cdot \mathbf{I}} H_{ij}(\widehat{\mathbf{\Omega}}), \tag{26}$$

with contraction of the repeated indices.

To find the inverse operator in Eq. (26), we now choose the body-fixed frame in which the rotational diffusion tensor $\mathbf{D}^r$ is diagonal,

$$\mathbf{D}^r_{ij} \;=\; D_i\delta_{ij}, \quad \text{for } i,j = x,y,z. \tag{27}$$

In this frame, we consider the eigen-problem for the operator

$$\mathbf{I} \cdot \mathbf{D}^r \cdot \mathbf{I} = (D_x I_x^2 + D_y I_y^2 + D_z I_z^2), \tag{28}$$

and construct the eigen-solution [7, 11] as

$$(D_x I_x^2 + D_y I_y^2 + D_z I_z^2)\psi_{K,M}^{(J)}(\widehat{\mathbf{\Omega}}) = f_K^{(J)} \, \psi_{K,M}^{(J)}(\widehat{\mathbf{\Omega}}),$$
$$\text{for } J = 0, 1, 2, ... \text{ and } K, M = -J, -J+1, ..., J \tag{29}$$

The tensor $\mathbf{H}$ is symmetric and traceless; therefore, to invert the operator in Eq. (26), we need explicit expressions for $\psi_{K,M}^{(J)}$ and $f_K^{(J)}$ with $J = 2$ only. The functions $\psi_{K,M}^{(2)}$ form a complete orthonormal set in our space of the considered functions. In Ref. [7], the eigen-functions are given in terms of the normalized Wigner functions $C_{K,M}^{(2)}$,

$$\psi_{K,M}^{(2)}(\widehat{\mathbf{\Omega}}) = \sum_{m'} a_{K,m'} C_{m',M}^{(2)}(\widehat{\mathbf{\Omega}}). \tag{30}$$

The coefficients $a_{K,m'}$ are listed in table 1. They depend only on the rotational diffusion

Table 1. The coefficients $a_{K,m'}$.

$K \setminus m'$	-2	-1	0	1	2
-2	$-\frac{1}{\sqrt{2}}$	0	$-\frac{a}{\sqrt{2(a^2+b^2)}}$	0	$\frac{b}{\sqrt{2(a^2+b^2)}}$
-1	0	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0
0	0	0	$\frac{b}{\sqrt{a^2+b^2}}$	0	$\frac{a}{\sqrt{a^2+b^2}}$
1	0	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	0
2	$\frac{1}{\sqrt{2}}$	0	$-\frac{a}{\sqrt{2(a^2+b^2)}}$	0	$\frac{b}{\sqrt{2(a^2+b^2)}}$

coefficients, and are expressed in terms of the combinations,

$$a = \sqrt{3}(D_x - D_y), \tag{31}$$
$$b = 3(D_z - D) + 2\Delta, \tag{32}$$

with

$$D = \frac{1}{3}(D_x + D_y + D_z). \tag{33}$$

In Eq. (29), the eigen-values with $J = 2$ are given as,

$$f_2^{(2)} = 6D + 2\Delta, \tag{34}$$
$$f_0^{(2)} = 6D - 2\Delta, \tag{35}$$
$$f_1^{(2)} = 3(D_x + D), \tag{36}$$
$$f_{-1}^{(2)} = 3(D_y + D), \tag{37}$$
$$f_{-2}^{(2)} = 3(D_z + D), \tag{38}$$

where

$$\Delta = \left(D_x^2 + D_y^2 + D_z^2 - D_x D_y - D_x D_z - D_y D_z \right)^{1/2}. \tag{39}$$

In Eq. (38), the modes are listed taking into account that they split into two groups: the modes with the indices $K = 2, 0$ are similar to each other, and the same holds for the modes with $K = 1, -1, -2$. Therefore, we introduce new labels, and we denote $f_i = f_K^{(2)}$, with $i = 1, 2$ corresponding to $K = 2, 0$, and $i = 3, 4, 5$ corresponding to $K = 1, -1, -2$, respectively.

Taking into account the completeness of the eigenfunctions $\psi_{K,M}^{(2)}(\widehat{\boldsymbol{\Omega}})$, and using Appendix of Ref. [7], we obtain from Eq. (26) a simple expression for the Brownian intrinsic viscosity,

$$[\eta]_\omega^B = \frac{k_B T}{10 v \eta_0} \sum_{i=1}^{5} \frac{A_i}{i\omega + f_i}, \tag{40}$$

where $A_i = A_K^{(2)}$, with $i = 1, 2, 3, 4, 5$ corresponding to $K = 2, 0, 1, -1, -2$, respectively, and

$$A_K^{(2)} = \sum_{M=-2}^{2} \iint \frac{d\widehat{\boldsymbol{\Omega}}\, d\widehat{\boldsymbol{\Omega}}'}{8\pi^2} H_{ij}(\widehat{\boldsymbol{\Omega}}) \psi_{K,M}^{(2)*}(\widehat{\boldsymbol{\Omega}}) H_{ij}(\widehat{\boldsymbol{\Omega}}') \psi_{K,M}^{(2)}(\widehat{\boldsymbol{\Omega}}'). \tag{41}$$

To evaluate the above integrals, we express ψ in terms of the Wigner functions (see Eq. (30)), and then apply the expressions from Appendix of Ref. [7] for the rotational integrals of symmetric traceless tensors projected onto Wigner functions. Using this method, we calculate the coefficients A_i in Eq. (40). For $i = 3, 4, 5$, they depend only on the rotational-dipole mobility $\boldsymbol{\mu}^{rd}$,

$$A_3 = 2H_{yz}^2, \tag{42}$$

$$A_4 = 2H_{zx}^2, \tag{43}$$

$$A_5 = 2H_{xy}^2, \tag{44}$$

with the symmetric traceless tensor $H_{\alpha\beta}$ given by Eq. (24). Explicitly,

$$H_{yz} = \mu_{xzz}^{rd} - \mu_{zxz}^{rd} + \mu_{yxy}^{rd} - \mu_{xyy}^{rd}, \tag{45}$$

$$H_{zx} = \mu_{yxx}^{rd} - \mu_{xyx}^{rd} + \mu_{zyz}^{rd} - \mu_{yzz}^{rd}, \tag{46}$$

$$H_{xy} = \mu_{zyy}^{rd} - \mu_{yzy}^{rd} + \mu_{xzx}^{rd} - \mu_{zxx}^{rd}. \tag{47}$$

The coefficients A_i in Eq. (40), with $i = 1, 2$, depend on the rotational-dipole mobility and the rotational diffusion coefficients,

$$A_1 + A_2 = H_{xx}^2 + H_{yy}^2 + H_{zz}^2, \tag{48}$$

$$A_1 - A_2 = \frac{1}{\Delta} \left[\bar{c}_x D_x + \bar{c}_y D_y + \bar{c}_z D_z \right], \tag{49}$$

where

$$\bar{c}_x = -2H_{xx}^2 + H_{yy}^2 + H_{zz}^2, \tag{50}$$

$$\bar{c}_y = H_{xx}^2 - 2H_{yy}^2 + H_{zz}^2, \tag{51}$$

$$\bar{c}_z = H_{xx}^2 + H_{yy}^2 - 2H_{zz}^2, \tag{52}$$

and from Eq. (24),

$$H_{xx} = 2(\mu_{zyx}^{rd} - \mu_{yzx}^{rd}), \tag{53}$$

$$H_{yy} = 2(\mu_{xzy}^{rd} - \mu_{zxy}^{rd}), \tag{54}$$

$$H_{zz} = 2(\mu_{yxz}^{rd} - \mu_{xyz}^{rd}). \tag{55}$$

5. Conclusions

In this work, we have theoretically derived general frequency-dependent expressions for the Brownian contribution to the intrinsic viscosity of arbitrary-shaped particles, see Eq. (40). The intrinsic viscosity depends on single-particle rotational-rotational and rotational-dipole mobilities. The effect of Brownian rotations on dilute suspensions of rigid particles of arbitrary shape was studied in Ref. [12] by another method (rotation-matrix formalism), but with no explicit expressions for the intrinsic viscosity.

In the present work, performing the time-dependent analysis, we have evaluated the characteristic time scales which determine when the high-frequency or zero-frequency approximations to the intrinsic viscosity are adequate. In a next publication, we will explain how to use the expressions given here to calculate explicitly the Brownian intrinsic viscosity, and will perform computations for a few particle shapes of a given symmetry, relevant for practical applications.

Acknowledgments

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