

Hydrodynamic friction of arbitrarily shaped Brownian particles

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We present a simple and accurate method of estimating the translational hydrodynamic friction on rigid Brownian particles of arbitrary shape. The Brownian friction coefficient f takes the form $f=6\pi\eta C_\Omega$, where C_Ω is mathematically equivalent to the electrostatic capacitance of the particle Ω in units where the capacity of a sphere equals its radius. This formula is particularly useful for particles consisting of a few globular subunits, for which slender body approximations are not very accurate.

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A classical problem of surprising difficulty in low-Reynolds-number hydrodynamics, and one that has become increasingly important in chemical engineering, polymer science, and biophysics, is the determination of the viscous drag on bodies of arbitrary shape [1]. Analytical calculations of the friction coefficient can be performed for only a limited number of shapes (see below) and calculations for bodies of complex shape have required approximation. Such calculations are greatly facilitated by an angular averaging of the Oseen tensor [2,3], and this approximation, along with others [3], was introduced by Kirkwood and Riseman (KR) in their classical treatment of dilute polymer solutions [2]. A stochastically tumbling Brownian particle experiences all orientations giving rise to an averaged translational scalar friction coefficient. The angular average approximation [1] involved in the KR calculation of the particle friction presumes that all orientations are equally probable. This approximation also arises in Ferrel's "mode-coupling" theory of critical slowing down in binary mixtures and de Gennes's theory of the cooperative diffusion coefficient of semidilute polymer solutions, and the reader is referred to these papers for a discussion of this averaging [2]. We adopt this idealized average for the description of the scalar translational friction and we follow the logical consequences of this *assumption* in relation to exactly known theoretical results and available experimental data for bodies of various shapes. We emphasize that our calculations *strictly avoid* the slender body and configurational preaveraging approximations, which are also implicit in the general "preaveraging" approximation of KR [1].

We start by considering the Oseen tensor [1] describing a point hydrodynamic source,

$$T_\Omega = \frac{1}{8\pi\eta} \frac{1}{|r-r_\Omega|} \left[I + \frac{(r-r_\Omega)(r-r_\Omega)}{|r-r_\Omega|^2} \right], \quad (1)$$

where r and r_Ω are two points in the fluid, η is the fluid viscosity, and I is the identity tensor. Now imagine forming a rigid, closed "hull" by stretching a piecewise smooth skin over the fluid-accessible surface of the

Brownian particle. Choose the origin inside this hull, take r_Ω as a point on the hull, and construct the isotropic angular average (AA) of T_Ω , corresponding heuristically to the *physical averaging* of the Brownian motion process,

$$\langle T_\Omega \rangle = \frac{1}{6\pi\eta} \frac{1}{|r-r_\Omega|} I. \quad (2)$$

We then observe that $\langle T_\Omega \rangle$ is the free-space Green's function for the Laplacian operator. Based on this observation we introduce a "momentum flux tensor" $U(r, r_\Omega)$ by

$$\sigma_\Omega(r_\Omega) \langle T_\Omega \rangle = U_\Omega(r, r_\Omega), \quad (3)$$

where σ_Ω is a scalar function specified below. The surface integral of U_Ω defines a "stress potential" ϕ :

$$\oint_\Omega U_\Omega(r, r_\Omega) = \frac{1}{6\pi\eta} \phi(r) I = \oint_\Omega \sigma_\Omega(r_\Omega) \langle T_\Omega \rangle, \quad (4)$$

which also satisfies Laplace's equation by linear superposition, and this implies that σ_Ω is constrained to be a "surface charge density" or in the hydrodynamic analog a "momentum flux density."

The crucial step is the construction of the AA hydrodynamic stress tensor S from the symmetrized product of the gradient of the stress potential and the AA rigid-body velocity u_Ω . This procedure must ensure not only that linear and angular momentum are conserved, but that the associated drag force is collinear to the average velocity u_Ω (Brownian symmetry). These conditions are satisfied if S takes the form

$$S = 6\pi\eta \{ (\nabla\phi)(u_\Omega) + (u_\Omega)(\nabla\phi) - (\nabla\phi) \cdot (u_\Omega) I \}. \quad (5)$$

The Navier-Stokes equation for steady flow then becomes

$$\nabla \cdot S = (6\pi\eta) u_\Omega \nabla^2 \phi = 0, \quad (6)$$

$$\phi = \begin{cases} 1 & \text{on } \Omega, \\ 0 & \text{at } \infty, \end{cases}$$

where the fluid is assumed to be undisturbed at infinity,

and the AA flow field is simply $u(r) = \phi(r)u_\Omega$. Equation (6) implicitly assumes a hydrodynamic “stick” boundary condition and that the particle is perfectly rigid. It should be noted that the AA approximation is expected to yield accurate values only for the scalar friction. The actual stress tensor and flow field are much more complex functions than those considered in this paper.

The drag force F may now be obtained as

$$F = 6\pi\eta \oint_{\Omega} \{ (\nabla\phi)(u_\Omega \cdot n_\Omega) + u_\Omega(\nabla\phi \cdot n_\Omega) - (\nabla\phi) \cdot (u_\Omega n_\Omega) \}, \quad (7)$$

where n_Ω is a unit normal on Ω pointing into the fluid. Since

$$-\nabla\phi|_{r=r_\Omega} = \sigma_\Omega n_\Omega, \quad (8)$$

Eq. (7) reduces to the simple form

$$F = -6\pi\eta u_\Omega \oint_{\Omega} \sigma_\Omega(r_\Omega), \quad (9)$$

where u_Ω is the velocity of a rigid Brownian particle averaged over all equally probable orientations with respect to a given driving force ($-F$).

Equations (6), (8), and (9) define an AA translational friction coefficient f :

$$f = 6\pi\eta C_\Omega, \quad (10)$$

where C_Ω is mathematically equivalent to the electrostatic capacitance of Ω ; i.e., the total charge on the conducting “hull” Ω , which is maintained at unit potential with respect to infinity. The main point is that C_Ω is generally much easier to calculate than the components of the friction tensor for bodies of arbitrary shape. Consider, for instance, the following examples.

Case (1). The capacity of an ellipsoid is well known [4],

$$C_\Omega = 2 \left[\int_0^\infty [(a^2 + \theta)(b^2 + \theta)(c^2 + \theta)]^{-1/2} d\theta \right]^{-1}, \quad (11)$$

where a , b , and c are the lengths of the three semi-axes. Combination of Eq. (11) with Eq. (10) gives an estimate of the friction on an ellipsoid. For the degenerate case in which two semi-axes are identical, Eqs. (10) and (11) reduce to the *exact* Perrin formulas for the average translational friction on prolate and oblate ellipsoids, and Eq. (11) holds more generally for triaxial ellipsoids [5].

Case (2). Two identical spheres separated by a fixed distance (see Table I) [6–8] can be likewise treated. Analytic calculation of the capacitance of two spheres at arbitrary separation is a classical but nontrivial mathematical problem, and tables of the capacity of two spheres are available [6]. A combination of these results with Eq. (10) is given in Table I, and good agreement is exhibited at all separations.

For comparison we note that the original KR approximation for “touching” spheres leads to an error of over 4%, and only slight improvement (error remains larger than 4%) is obtained by including the Rotne-Prager correction to the leading point-source Oseen-tensor hydrodynamic interaction [9]. These errors for arrays of spheres apparently accumulate at a rate of about 2.5%

TABLE I. Ratio of the AA friction on a pair of identical spheres to twice the friction on an isolated sphere, where a is the radius and l is the separation distance. The third column presents this same ratio for the capacitances. An experimental value of 0.691 has been observed for the dimensionless friction of touching spheres $l/a = 2$ [8,9].

l/a	$f(O \cdots O)/2f(O)^a$	$C(O \cdots O)/2C(O)^b$
2	0.6961	0.6931... = ln2
4	0.8027	0.8026
6	0.8578	0.8577
10	0.9092	0.9093
∞	1.000	1.000

^aReferences [7,9].

^bReference [6].

per pair of touching particles in the array [9], so it is evident that the point-source approximation can lead to rather appreciable errors. Swanson, Teller, and de Haën have conjectured that the friction of an arbitrarily shaped body can be calculated by covering the body with an *infinite array* of hydrodynamic sources interacting through the Rotne-Prager tensor [9]. Numerical calculations for these hydrodynamic source arrays distributed on two spheres support their conjecture. However, these “shell-model” calculations “require so much computer time that the method is not generally practical” [9]. Our calculation scheme avoids the point-source approximation altogether and the advantage of this approach is demonstrated by the results of Table I.

Case (3). Analytic calculations of the friction for right circular cylinders (“rods”) and circular tori (“rings”) based on the KR slender body approximation lead to rather inaccurate estimates of the friction for short rods or small rings. This point has been made before by Goren and O’Neill [10], in a comparison of their exact hydrodynamic calculations for a ring of finite cross section to the slender body calculations for a ring [11]. Tirado and de la Torre [12] compare numerical “shell-model” calculations and experimental data for rods to slender body calculations for rods. There is still no exact analytic calculation for the friction on a rod. The worst case for the slender body theory corresponds to a ring whose inner radius vanishes (“doughnut”) [10]. The capacity of a ring and the special case of doughnut are well known [13], so that the prediction of Eq. (10) can be compared to the analytic results of Goren and O’Neill for the friction of a doughnut [10],

$$\begin{aligned} C(\text{doughnut})/C(O^*) &= 0.871, \\ f(\text{doughnut})/f(O^*) &= 0.872, \end{aligned} \quad (12)$$

where O^* refers to the smallest sphere that encloses the doughnut. The exact calculation of the doughnut friction involves an infinite series of transcendental functions whose numerical determination could be responsible for the small discrepancy in Eq. (12). At any rate, the capacity estimate of the friction [Eq. (10)] is very accurate. It is also a simple matter to estimate the friction on a short rod based on Eq. (10) to compare with the best numerical [9] and experimental estimates [14] of the friction. The

Smythe approximation for the capacity of a rod equals [15]

$$C(\text{rod})/C(O) = (2^{4/3} 3^{-1/3} / \pi) \lambda^{-1/3} (1 + 0.869 \lambda^{0.76}), \quad 0 < \lambda < 8 \quad (13)$$

where $C(O)$ denotes the capacity of a sphere whose volume is the same as the cylinder and the rod aspect ratio λ is defined in Table II. Equation (10) gives excellent agreement with previous estimates of the rod friction in Table II and Eq. (13) is exact in the disk limit $\lambda \rightarrow 0$. This disk limit result is well known as a limit of the ellipsoid.

Case (4). The friction on a cube [16,17], tetrahedron [17,18], and octahedron [16,17], for which there are no previous analytic estimates of the friction, is also readily estimated from Eq. (10),

$$\begin{aligned} C(\text{cube})/C(O) &= 1.06, \quad f(\text{cube})/f(O) = 1.08(\text{expt}), \\ C(\text{tet})/C(O) &= 1.17, \quad f(\text{tet})/f(O) = 1.18(\text{expt}), \quad (14) \\ C(\text{oct})/C(O) &= 1.06, \quad f(\text{oct})/f(O) = 1.07(\text{expt}), \end{aligned}$$

where O refers to the equal volume sphere and where the scalar friction coefficients were determined from experiments with macroscopic models. The capacities of many other shaped bodies (lens, spindle, inverted prolate ellipsoid, and inverted oblate spheroid) are known exactly, but hydrodynamic data and theoretical calculations for these cases are lacking for comparison.

Case (5). The friction f_{\perp} associated with the motion of flat bodies of arbitrary shape normal to their surface is given by [19]

$$f_{\perp} = 8\pi\eta C_{\Omega} \quad (15)$$

From Eqs. (10) and (15), the two principal components of the friction in the plane of Ω are related in the AA approximated by

$$\frac{1}{6\pi\eta C_{\Omega}} = \frac{1}{3} \left[\frac{1}{f_1} + \frac{1}{f_2} + \frac{1}{8\pi\eta C_{\Omega}} \right] \quad (16)$$

For symmetric ($f_1 = f_2$) and highly asymmetric bodies ($f_2 \gg f_1$), we can solve Eq. (16) for the components of the friction tensor.

Case (6). A useful estimate for the capacitance, and by

TABLE II. Ratios of capacitances and friction coefficients of short circular cylinders to those of equal volume spheres, where λ is the ratio of cylinder length to cross-section diameter. Capacitance ratios were calculated from Eq. (13).

λ	$C(\text{cyl})/C(O)$	$f(\text{cyl,expt})/f(O)^a$	$f(\text{cyl,num})/f(O)^b$
$\frac{1}{4}$	1.15	1.16	
$\frac{1}{2}$	1.06	1.08	1.07
1	1.04	1.05	1.05
2	1.09	1.10	1.10
3	1.16	1.17	
4	1.22	1.23	1.23

^aReference [14].

^bReference [9].

Eq. (10), the hydrodynamic friction of convex but nonslender “globular” bodies is given by Russel’s approximation [6]

$$C_{\Omega} = (A_{\Omega}/4\pi)^{1/2}, \quad (17)$$

where A_{Ω} is the surface area of Ω . The estimate of friction based on Eqs. (10) and (17) was introduced phenomenologically by Pastor and Karplus [20,21].

Case (7). Generalization of the AA friction to d dimensions is straightforward and f for a sphere of radius R is obtained as

$$\begin{aligned} f(O) &= [d/(d-1)]H(d)R^{d-2}\eta, \\ H(d) &= 4\pi^{d/2}[\Gamma(d/2-1)]^{-1}, \quad d > 2 \end{aligned} \quad (18)$$

where Γ is the gamma function. This agrees with Brenner’s exact result for d dimensions [22]. For a d_{\parallel} -dimensional flat disk of radius R embedded in d -dimensional space ($d > 2$) we have the new result

$$\begin{aligned} f(\text{disk}) &= [d/(d-1)]A(d_{\parallel},d)H(d)R^{d-2}\eta, \\ A(d_{\parallel},d) &= \Gamma(d_{\parallel}/2)/[\Gamma(\epsilon)\Gamma(d/2)], \\ \epsilon &= (2+d_{\parallel}-d)/2, \quad \epsilon > 0. \end{aligned} \quad (19)$$

Observe that $A \rightarrow 0$ at the critical dimension at which $\epsilon \rightarrow 0+$. For random coils d_{\parallel} corresponds to a fractal dimension of 2 and thus the critical dimension is $d = 4$. The capacitance of any bounded plane set or set of Hausdorff dimension $d_H = 2$ vanishes above four dimensions. For rods ($d_{\parallel} = 1$) the critical dimension is $d = 3$ and we obtain the usual log corrections from the Perrin formula in the limit of long rods. Calculation of the capacitance of a random coil leads to the *same* integral equation encountered in the Kirkwood-Riseman theory of polymeric friction. This important case will be discussed elsewhere.

The connection between hydrodynamic friction and capacitance is easily extended to collections of bodies of arbitrary shape. Consider, for instance, the Brownian motion of a body Ω in the presence of fixed obstacles. The AA f_{Ω} is then determined by C_{Ω} in the presence of grounded ($\phi = 0$) conductors. Note that f_{Ω} , which defines a scalar diffusion coefficient obtained by averaging over all directions of motion with equal probability, now depends on the position and orientation of Ω with respect to the fixed obstacles.

As a final point, we note that C_{Ω} can be determined by the average volume V_t of the “Wiener sausage” (a region of space in which the center moves along a fixed Wiener trajectory) swept out at time t by Ω as it undergoes Brownian motion, where it is understood that self-intersections do not contribute to the volume [23]:

$$\begin{aligned} \lim_{t \rightarrow \infty} \frac{V_t}{t} &= C_{\Omega}^* + 4(2\pi)^{-3/2}(C_{\Omega}^*)^2 t^{-1/2} + \dots, \\ C_{\Omega}^* &= 2\pi C_{\Omega}. \end{aligned} \quad (20)$$

Thus, the AA momentum flux from Ω is analogous to a course-grained collision frequency in the kinetic theory of gases, the difference between the two models residing in

the assumptions of Brownian versus piecewise rectilinear motion. Note that if Ω is not a sphere, the cross-sectional area of the Wiener sausage fluctuates along its length. In particular, for needle-shaped bodies the shape fluctuations vary from thin tubes to flat ribbons and self-intersections are negligible. This disappearance of self-intersections reflects the absence of hydrodynamic

screening in highly extended bodies. Shape fluctuations should tend to be less extreme for bodies of high symmetry and in fact the capacity of a body of a given volume is minimized for a sphere [24]. Distortion of a body away from a more symmetric shape should generally increase the friction [17]. An investigation of which symmetry elements most affect friction would be interesting.

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