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Stokes Laws for Ions in Solutions with Ion-Induced Inhomogeneity

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We present generalized Stokes relations for translational and rotational friction coefficients for spherical particles moving in a solvent with particle-induced inhomogeneous viscosity.

It often happens that microscopic phenomena can be surprisingly well treated in terms of macroscopic theories. A notable example is the application of Stokes laws, derived in the framework of continuum hydrodynamics, to the motion of particles of atomic dimension in solution. For translational motion one has

$$\vec{F} = -\xi \vec{U} \quad \xi = 6\pi\eta R \quad (1)$$

where \vec{F} is the force exerted on the particle moving with the translational velocity \vec{U} , R is the radius of the particle (which is assumed to be spherical), and η the viscosity of the solvent. For a rotational motion the similar relations hold:

$$\vec{M} = -\xi_R \vec{\Omega} \quad \xi_R = 8\pi\eta R^3 \quad (2)$$

Here \vec{M} is the torque exerted on the particle rotating with the angular velocity $\vec{\Omega}$. In the derivation of eqs 1 and 2, the solvent surrounding the particle was assumed to be homogeneous.

Whereas eqs 1 and 2 give close agreement with experimental data for neutral molecules, the agreement for charged ions is rather poor (see, e.g., refs 1-3 and references therein). This may be a

consequence of a local modification of the solvent structure near the surface of the charged particle due to strong electrostatic interaction with the solvent molecules. As a result, the solvent in the vicinity of the particle becomes locally inhomogeneous and nonisotropic. The simplest way to account for such local modification is to consider a fluid with a radial-dependent viscosity $\eta(r)$, where r is a distance from the center of the spherical particle. This model was first introduced by Wolynes,⁴ who suggested the following approximate relation for the translational friction coefficient:

$$\xi^{-1} = \int_R^\infty dr / (4\pi r^2 \eta(r)) \quad (3)$$

In the present study we derive exact results for translational and rotational friction coefficients⁵ in the framework in this model. Later a more thorough approach will take into account the effects

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(3) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworths: London, 1959.

(4) Wolynes, P. G. *Annu. Rev. Phys. Chem.* **1980**, *31*, 345.

(5) The rotation motion should be considered for charged molecules or ions with their hydration shells.

(1) Pau, P. C. F.; Berg, J. O.; McMillan, W. G. *J. Chem. Phys.* **1990**, *94*, 2671.

of electrical strain in the solvent, which lead to the so-called dielectrical friction.⁶⁻⁹ We shall first discuss the influence of viscosity inhomogeneity on the friction coefficients ξ and ξ_R and neglect the dielectrical friction. Thus we start from the Navier-Stokes equations for an incompressible fluid in the low Reynolds number limit, which are relevant in our case:

$$\rho \, d\vec{V}/dt = \vec{\nabla}\sigma = \vec{\nabla}(\eta \text{div} - pI) \quad (4)$$

$$dd_{ij} = \nabla_i V_j + \nabla_j V_i$$

Here σ is the stress tensor, P is the hydrostatic pressure, I is the unit tensor, and V_i and ∇_j are the components of the velocity field \vec{V} and operator $\vec{\nabla}$.

First, we consider the simpler case of rotational motion. The velocity \vec{V} field around a uniformly rotating sphere with angular velocity $\vec{\Omega}$ is azimuthal, i.e., $\vec{V} = \{V_r, V_\vartheta, V_\phi\} = \{0, 0, W\}$, where V_r, V_ϑ, V_ϕ are the components of the velocity field in the spherical coordinate system.

Therefore, it is sufficient to consider only the azimuthal component of the vector equation (4). Omitting all terms with $\partial/\partial\phi$ due to the axial symmetry of the problem, one obtains for a steady flow¹⁰

$$(1/r^2) \partial/\partial r (r^3 \sigma_{r\phi}) + (1/\sin \vartheta) \partial/\partial \vartheta ((\sin \vartheta) \sigma_{\vartheta\phi}) + (\text{ctg } \vartheta) \sigma_{\phi\phi} = 0 \quad (5)$$

It is not difficult to show that in the case of interest all diagonal components of the stress tensor are equal to $(-P)$, and the only nonzero off diagonal components are the following:¹¹

$$\sigma_{\phi r} = \sigma_{r\phi} = \eta(r)(\partial W/\partial r - W/r) \quad (6a)$$

$$\sigma_{\phi\vartheta} = \sigma_{\vartheta\phi} = \eta(r)(\partial W/\partial \vartheta - W \text{ctg } \vartheta)/r \quad (6b)$$

To solve eqs 5 and 6, we assume

$$W = \Omega f(r) \sin \vartheta \quad (7)$$

Note that the same $\sin \vartheta$ dependence for the azimuthal velocity is obtained for the homogeneous viscosity.¹⁰ From eqs 7 and 6 one can find

$$\sigma_{\phi\phi} = 0 \quad \sigma_{r\phi} = \Omega \eta(r)(df/dr - f/r) \sin \vartheta \quad (8)$$

Thus eq 5 yields

$$d/dr [\eta(r) r^3 (df/dr - f/r)] = 0 \quad (9)$$

The solution of eq 9 satisfying the stick boundary condition $f(R) = R$ has the form

$$f = r \left[\int_r^\infty \frac{dr}{r^4 \eta(r)} \right] \left[\int_R^\infty \frac{dr}{r^4 \eta(r)} \right]^{-1} \quad (10)$$

Using eqs 10 and 8, one can calculate the stress tensor components and then the torque M exerted on a rotating sphere. Finally we come to a fairly simple exact result: The generalized Stokes law for the rotational friction coefficient in a fluid with nonuniform viscosity is

$$\xi_R^{-1} = \frac{3}{8}\pi \int_R^\infty \frac{dr}{r^4 \eta(r)} \quad (11)$$

We emphasize that this result is valid for an arbitrary dependence $\eta = \eta(r)$ (since at $r \rightarrow \infty$ $\eta(r) \rightarrow \eta_0$, the bulk viscosity, the integral in eq 11 is convergent).

Now we turn to the translational motion. In this case the velocity field \vec{V} around a sphere moving with a velocity \vec{U} has two nonzero components: $\vec{V} = (u, v, 0)$. They may be written in terms of a stream function $\Psi(r, \vartheta)$:

$$u = \frac{1}{r^2 \sin \vartheta} \frac{\partial \Psi}{\partial \vartheta} \quad v = -\frac{1}{r \sin \vartheta} \frac{\partial \Psi}{\partial r} \quad (12)$$

When $\eta = \text{constant}$, the stream function $\Psi_0(r, \vartheta)$ and pressure around the particle $P_0(r, \vartheta)$ are known:

$$\Psi_0 = U f_0(r) \sin^2 \vartheta \quad P_0 = P_\infty - U \eta g_0(r) \cos \vartheta \quad (13a)$$

where

$$f_0(r) = r^2/2 + 4rR/4 + R^3/4r$$

$$g(r) = g_0(r) = \frac{3}{2}R/r^2 \quad (13b)$$

Here P_∞ is the pressure in the bulk of solvent. Let us suppose that in the fluid with inhomogeneous viscosity the stream function and pressure may be written in the same form, (13a), but with unknown functions $f(r)$ and $g(r)$.

Calculating the velocity components with the use of eq 12 and then components of the stress tensor,¹¹ we observe that the only nonzero components are

$$\sigma_{rr} = \eta(r)(\cos \vartheta)F(r) \quad F = g + 4 \, d(f/r^2)/dr \quad (14a)$$

$$\sigma_{\vartheta\vartheta} = \sigma_{\phi\phi} = \eta(r)(\cos \vartheta)G(r) \quad G = g - 2 \, d(f/r^2)/dr \quad (14b)$$

$$\sigma_{r\vartheta} = \eta(r)(\sin \vartheta)H(r) \quad H = -d^2(f/r)/dr^2 \quad (14c)$$

These stress tensor components should be substituted into the Navier-Stokes equations (4), which for steady flow may be written as follows:^{10,11}

$$(1/r) \partial/\partial r (r^2 \sigma_{rr}) + (1/\sin \vartheta) \partial/\partial \vartheta ((\sin \vartheta) \sigma_{r\vartheta}) - (\sigma_{\vartheta\vartheta} + \sigma_{\phi\phi}) = 0 \quad (15)$$

$$(1/r^2) \partial/\partial r (r^3 \sigma_{r\vartheta}) + (1/\sin \vartheta) \partial/\partial \vartheta ((\sin \vartheta) \sigma_{\vartheta\vartheta}) - (\text{ctg } \vartheta) \sigma_{\phi\phi} = 0 \quad (16)$$

After some rearrangements eqs 14-16 yield

$$d/dr [r^2 \eta(r)(F - 2H)] = 0 \quad (17)$$

$$d/dr [r^3 \eta(r)H] - \eta(r)r^2 G = 0 \quad (18)$$

(17) and (18) are coupled equations for functions $f(r)$ and $g(r)$. For stick boundary conditions we have at $r = R$

$$f = 0 \quad df/dr = 0 \quad r = R \quad (19)$$

and from the condition of the flow uniformity at infinity

$$f \rightarrow r^2/2 \quad g \rightarrow 0 \quad r \rightarrow \infty \quad (20)$$

From eq 17 it follows that

$$\eta(r)r^2(F - 2H) = \text{const} = A \quad (21)$$

For the force, exerted on the moving sphere by the surrounding fluid, we obtain

$$F = 2\pi R^2 \int_0^\pi \sin \vartheta \, d\vartheta (\sigma_{rr} \cos \vartheta - \sigma_{r\vartheta} \sin \vartheta)|_{r=R} = (4\pi/3)U[\eta(R)R^2(F(R) - 2H(R))] = -\frac{4}{3}\pi AU \quad (22)$$

Here in the last equality we use eq 21. Thus, we come to a simple form of generalized Stokes law, with $\xi = \frac{4}{3}\pi A$, where the constant A may be evaluated by solving eqs 17 and 18 with the use of the boundary conditions (19) and (20).

One can get an approximate result for the constant A without solving these equations. Note that eq 21 may be written in the form

$$\int_R^\infty [F(r) - 2H(r)] \, dr = A \int_R^\infty dr/(r^2 \eta(r)) \quad (23)$$

To evaluate the left-hand side of (23), one can use the definitions (14) for F and H :

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(10) Happel, J.; Brenner, H. *Low Reynolds Number Hydrodynamics*; Prentice-Hall: New York, 1965.

(11) The Navier-Stokes equations, written in the spherical coordinate system and corresponding expressions for stress tensor components may be found in ref 10.

$$\int_R^\infty [F(r) - 2H(r)] dr = \int_R^\infty g(r) dr + 4(f/r^2)|_R^\infty + 2 d(f/r)/dr|_R^\infty \quad (24)$$

Taking into account the boundary conditions (19) and (20), we obtain

$$\xi = \left[1 + \frac{1}{3} \int_R^\infty g(r) dr \right] \left[\int_R^\infty dr / 4\pi r^2 \eta(r) \right]^{-1} \quad (25)$$

In the approximation used in ref 4, $p = \text{const}$ and $g(r) = 0$, so (25) becomes the Wolynes result (3). For a homogeneous fluid eq 3 is reduced to the Stokes law for slip boundary conditions, i.e., $\xi = 4\pi\eta R$. On the other hand, one can use the approximation $g(r) = g_0(r)$, i.e., $P(r) = -3/2\eta(r) g_0(r)U$. This approximation leads to the result

$$\xi^{-1} = \int_R^\infty dr / 6\pi r^2 \eta(r) \quad (26)$$

For $\eta = \text{const}$ we derive the usual Stokes relation (1) for stick boundary conditions.

To estimate the validity of the approximate relation (26) we have solved eqs 17–20 exactly for the special, somewhat physically unrealistic, case of power-law-dependent viscosity $\eta(r) = \eta_0(R/r)^n$ with n on the interval $0 \leq n < 1$. The final result for the friction coefficient is as follows:

$$\xi = (2\pi/3)\eta_0 R [(1-n)(n+6)(N+1-n)/(N-1+n)] \quad (27)$$

with $N = (n^2 + 2n + 25)^{1/2}$. The approximate formula (26) for the power-law dependent viscosity becomes

$$\xi_{\text{apr}} = 6\pi\eta_0 R(1-n) \quad (28)$$

Comparison of the exact (27) and approximate (28) dependencies $\xi = \xi(n)$ shows that the approximate result (28) overestimates the exact one, but the difference is relatively small, $1 \geq \xi/\xi_{\text{apr}} \geq 7/9$.

Now let us briefly discuss the methods of calculation of the distance-dependent viscosity. To estimate $\eta(r)$, the authors of ref 2 used the values of orientational relaxation times τ_R of solvent molecules in the vicinity of an ion and in the bulk solvent. One can also take into account a local pressure enhancement in the vicinity of ions due to electrostriction. This causes a local change of the solvent viscosity, so that the dependence $\eta = \eta(r)$ may be

found from the known pressure dependence of the viscosity, i.e.

$$\eta(r) = \eta[P(r)] \quad (29)$$

Note that in addition to the electrostriction, the ion field can cause local orientation of the solvent molecules, which also changes the viscosity. We believe, however, that the change of the viscosity due to the latter effect is much smaller than due to the former provided the solvents molecules are not extremely aspherical.

For the linearized Navier–Stokes equations one should use in eq 29 the pressure distribution around an immovable ion. This may be evaluated by using thermodynamic relations.¹² If one neglects the fluid compressibility, one has

$$P(r)|_{r=0} = P_\infty + \frac{1}{2}E^2\rho_0 \partial/\partial\rho \mathcal{H}|_{\rho=\rho_0} \quad (30)$$

Here E is the electric field of the charged particle, ρ_0 the solvent density, $\mathcal{H} = (\epsilon - 1)/4\pi$ the solvent polarizability (ϵ is the dielectrical permittivity of the solvent), and P_∞ the pressure in the bulk solvent.

As pointed out above, the electric field causes electrostriction and dielectrical friction simultaneously. For rotational motion both these effects may be treated exactly.¹³ Using the approximation $\mathcal{H} \approx \text{const}$, we have found¹³

$$\xi_R^{-1} = \xi_{RS}^{-1} \int_1^\infty \frac{3 dx}{(1 + b^4/x^4)x^4\eta(P_\infty + P^*/x^4)/\eta_0} \quad (31)$$

Here $\xi_{RS} = 8\pi R^3\eta_0$ is the Stokes result for ξ_R , $\eta_0 = \eta(P_\infty)$, $b^4 = [(\epsilon - 1)/4\pi^2](a^3/R^3)(q^2/k_B T R)$, q the charge of the ion, R its radius, a the radius of the solvent molecule, and P^* the excess pressure at $r = R$, $P^* \approx b^4\lambda$, with $\lambda = (k_B T/2\pi a^3)$. To estimate the relative significance of dielectrical friction and increase of viscosity due to electrostriction, we use the expression

$$\eta(P_\infty + P^*/x^4)/\eta_0 \approx 1 + ((\eta'/\eta_0)\lambda)b^4/x^4 \quad (32)$$

where $\eta' = \partial\eta/\partial P|_{P=P_\infty}$. From eqs 32 and 31 one can see that the relative significance of these effects is defined by the value of the factor $(\eta'/\eta_0)\lambda = (\eta'/\eta_0)(k_B T/2\pi a^3)$. Therefore the influence of the dielectrical friction is less for high temperatures and for solvents with small molecules. Therefore, if the conditions $b \ll 1$, but $b^4(\eta'/\eta_0)(k_B T/2\pi a^3) \simeq 1$ hold, one can use the generalized Stokes relations (11) and (26) for the friction coefficients.

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