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Rotatory Brownian motion of a rigid dumbbell

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The frictional torque on a dumbbell rotating with time-dependent angular velocity is calculated from the hydrodynamic interaction between the two ends of the dumbbell. This leads to the correlation function for the random torque in rotatory Brownian motion. Although the motion of each dumbbell end has the characteristics of a translational motion, the correlation function at large times decays like $t^{-\frac{3}{2}}$, as in the case of a solid sphere. The correlation function may be calculated for the limiting case of very small angular displacements. The results for displacements of arbitrary magnitude are the same provided that terms quadratic in the angular velocity are negligible.

1. Introduction

The autocorrelation function $G(t)$ for the random force on a particle in translational motion under stationary conditions is known (Case 1971) to be related to the friction coefficient for this particle by the fluctuation dissipation theorem

$$G(\omega)/2kT = \mathscr{R}\{B(\omega)\}. \tag{1}$$

Here $G(\omega)$ and $B(\omega)$ are Fourier time transforms, i.e.

$$G(t) = \int_{-\infty}^{\infty} G(\omega)\exp(-i\omega t)\,d\omega; \tag{2}$$

$B(\omega)$ is defined by the statement that $-B(\omega)\,u(\omega)$ is the Fourier transform of the systematic force on the particle when it has a time-dependent velocity $u(t)$. From early hydrodynamic studies (see, for example, Oseen 1927, p. 132) it is known that the frictional force on a sphere of radius a moving through a Newtonian liquid with velocity $u(t)$ is

$$B_{0p}\,u(t) = \zeta u + \alpha\pi^{-\frac{1}{2}}\int_{-\infty}^{t} d\tau(t-\tau)^{-\frac{1}{2}}\,du/d\tau + \tfrac{1}{2}m_0\,du/dt, \tag{3}$$

which means that
$$B(\omega) = \zeta + \alpha(-i\omega)^{\frac{1}{2}} - \tfrac{1}{2}m_0\,i\omega. \tag{4}$$

Here
$$\zeta = 6\pi\eta a, \quad \alpha = \zeta a\nu^{-\frac{1}{2}}, \quad m_0 = \tfrac{4}{3}\pi a^3\rho, \tag{5}$$

where η is the viscosity, ρ the density and $\nu = \eta/\rho$ is the kinematic viscosity of the liquid. In the last section use will be made of the notation

$$\pi^{-\frac{1}{2}}\int_{-\infty}^{t} d\tau(t-\tau)^{-\frac{1}{2}}\,d/d\tau = d^{\frac{1}{2}}/dt^{\frac{1}{2}}; \tag{6}$$

cf. Kowalewski (1930, p. 35). The validity of (6) is confirmed by the Fourier transform: if the operation on the left-hand side is performed twice, the result in Fourier space is a multiplication by $-i\omega$, which corresponds to the operation d/dt.

The results quoted thus far are based on the linearized Navier–Stokes equations. The function $G(\omega)$ is known explicitly from work of Chow & Hermans (1972*a*) and shows that $G(t)$ for large t is proportional to $t^{-\frac{3}{2}}$.

Likewise, the autocorrelation function $Q(t)$ for the random torque on a particle in rotatory Brownian motion is related to the rotational friction by the relation given by Chow (1973):

$$Q(\omega)/2kT = \mathscr{R}\{N(\omega)/\Omega(\omega)\}, \tag{7}$$

where $N(\omega)$ is the Fourier time transform of the systematic torque when the particle rotates with time-dependent angular velocity $\Omega(t)$. On the basis of $N(\omega)$ for solid spherical particles Berne (1972) has shown, by a series expansion in powers of $\omega^{\frac{1}{2}}$, that $Q(t)$ at large times is proportional to $t^{-\frac{5}{2}}$. Berne's calculation concerned the autocorrelation function for the rotational velocity rather than the random torque, but these functions are related to each other and have similar asymptotic behaviour at large times.

The problem considered in the present work is the rotational Brownian motion of a rigid dumbbell: two spheres of radius a are connected by a rigid rod of length $2L$; the friction on the spheres is supposed to be given by (3), while the frictional force on the rod connecting these spheres is considered to be negligible. This model is representative of rod-shaped particles in general (Kirkwood 1956).

The motion of each of the beads at the ends of the dumbbell has all the characteristics of translatory motion. It will be shown, however, that the asymptotic behaviour of $Q(t)$ for large times is of the type $t^{-\frac{5}{2}}$ and not $t^{-\frac{3}{2}}$. The treatment is based on the linearized Navier–Stokes equations. As shown by Chow (1973), for particles with this symmetry there is no coupling between translatory and rotatory motion or between different components of the rotation. For this reason it is permissible to restrict our considerations to rotation in a fixed plane about a fixed centre. The frictional torque will be calculated from the forces on the two beads, taking into account the hydrodynamic interaction between them. To estimate this hydrodynamic interaction, use is made of Oseen's results for the velocity produced by point forces.

The motivation for this work is twofold. In the first place, the terms in (3) which are due to the inertia of the liquid play a role in all transport properties of polymer solutions (viscosity, flow birefringence, etc.). For example, as shown in a forthcoming paper, the contribution of the inertia terms to the intrinsic viscosity of elastic dumbbells in a steady shear flow may be as large as 20 % when the viscosity of the solvent is low. Similar effects are to be expected in solutions of rigid rod-like molecules, and these effects will be particularly pronounced in dynamic measurements at high frequencies (acoustical birefringence, dielectric loss), not only for rod-like particles but also for random coils.

In the second place, a comparison of the rotational Brownian motion of rods with that of spheres is of interest in connexion with work by Berne (1972) and by Chow (1973). In particular, we hope to stimulate work on the fundamental question raised at the end of the next section: is the asymptotic behaviour of the correlation functions at large times due primarily to the flow field at large distances and, if so, will it be affected by the nonlinear terms in the hydrodynamic equations?

2. Hydrodynamic interaction for small angular displacements

General expressions for the velocity produced by a time-dependent force at a time-dependent position have been developed by Szu & Hermans (1973). They will be used in the next section. For the moment we observe that the relaxation time for the autocorrelation of rotational velocity is of order m/ζ, where m is the mass of a bead and $\zeta = 6\pi\eta a$ is the friction coefficient for steady translational motion of the bead. For most particles of coloidal or molecular dimensions, the total angular displacement during the relaxation time remains quite small, so that the hydrodynamic interaction is essentially that between two beads at fixed positions. It will be shown in the next section that the result obtained remains valid for arbitrarily large angular displacements if we consistently neglect all effects proportional to the second (or higher) power of the angular velocity. Such neglect is consistent with the linearization of the hydrodynamic equations.

The procedure followed is similar to that discussed by Chow & Hermans (1972*b*) when considering the hydrodynamic interaction of two particles in translatory Brownian motion, where the positions of these particles remain essentially stationary during the relaxation time. Let the rotation take place in the x, y plane and suppose that the beads are at positions $(L, 0)$ and $(-L, 0)$. Let $-Y_1(t)$ and $-Y_2(t)$ be the forces in the y direction exerted on the liquid by the first and the second bead respectively. As shown by Burgers (1938), the force $-Y_2$ produces at the position of bead 1 a velocity with y component

$$v_1(t) = -SY_2 = -(8\pi\eta)^{-1}\int_{-\infty}^{t} d\tau\, Y_2(\tau)\,(\nabla^2 - \partial^2/\partial y^2)\,\psi(t-\tau), \tag{8}$$

where $$\psi(t) = 2(\nu/\pi)^{\frac{1}{2}}\, r^{-1}\int_0^r d\lambda\, t^{-\frac{1}{2}}[1-\exp(-\lambda^2/4\nu t)]. \tag{9}$$

∇^2 represents the three-dimensional Laplace operator and operates with respect to the distance $r = r(x, y, z)$ between the two beads.

If $u_1(t) = L\Omega(t)$ is the velocity of bead 1, it is clear that its velocity relative to its immediate surroundings is $u_1 - v_1$ and consequently

$$Y_1(t) = -B_{0p}[u_1(t) - v_1(t)]. \tag{10}$$

The same relation applies to Y_2, u_2 and v_2, and since $u_2 = -u_1$ ($= -u$ say) for all time, it is clear from the equations given that at all times $Y_2 = -Y_1 = -Y$ and $v_2 = -v_1 = -v$. Taking Fourier time transforms we find

$$v(\omega) = S(\omega)\, Y(\omega), \quad Y(\omega) = -B(\omega)\,[u(\omega) - v(\omega)]. \tag{11}$$

Here $S(\omega)$ is the Fourier transform of the operator S, and may be found from that of ψ if, after performing the operation $\nabla^2 - \partial^2/\partial y^2$, we substitute $x = 2L$, $y = 0$ and $z = 0$ in the final result. This gives

$$S(\omega) = (32\pi i\rho\omega L^3)^{-1}[1-(1+2\kappa L+4\kappa^2L^2)\exp(-2\kappa L)], \tag{12}$$

where

$$\kappa = (-i\omega/\nu)^{\frac{1}{2}}. \tag{13}$$

By eliminating $v(\omega)$ from (11), it is found that

$$Y(\omega) = -B(\omega)\,u(\omega)\,[1-B(\omega)\,S(\omega)]^{-1},$$

which means that the frictional torque on the dumbbell is

$$N(\omega) = L^2B(\omega)\,\Omega(\omega)\,[1-B(\omega)\,S(\omega)]^{-1}. \tag{14}$$

Expanding the frictional factor in powers of $\omega^{\frac{1}{2}}$ we find

$$\frac{N(\omega)}{\Omega(\omega)} = \frac{\zeta L^2}{(1-\beta)^2}\left\{1-\beta-\left(\frac{a}{L}\right)\left(\frac{9}{8}-\frac{8a}{9L}\right)\frac{L^2}{\nu}i\omega+\frac{a}{L}\left(\frac{4}{5}-\frac{7a^2}{9L^2}\right)\frac{L^3(1+i)}{\nu(2\nu)^{\frac{1}{2}}}\omega^{\frac{3}{2}}+O(\omega^2)\right\}, \tag{15}$$

where use is made of the abbreviation

$$\beta = \zeta/(16\pi\eta L) = 3a/8L. \tag{16}$$

There is no term proportional to $\omega^{\frac{1}{2}}$ in (15). The ω term is pure imaginary and therefore does not contribute to $Q(\omega)$ in (7). The real part of the $\omega^{\frac{3}{2}}$ term, which corresponds to $t^{-\frac{5}{2}}$ behaviour at large times, is

$$\frac{\zeta L^2}{(1-\beta^2)^2}\frac{a}{L}\left(\frac{4}{5}-\frac{7}{9}\frac{a^2}{L^2}\right)\frac{L^3\omega^{\frac{3}{2}}}{\nu(2\nu)^{\frac{1}{2}}}. \tag{17}$$

This becomes $10{\cdot}6\rho a^2L^4\nu^{-\frac{1}{2}}$ when $L \gg a$, and $0{\cdot}76\rho L^6\nu^{-\frac{1}{2}}$ in the limit $a = L$. The corresponding coefficient in Landau & Lifshitz (1959, p. 97) for a solid sphere of radius R is $5{\cdot}92\rho R^6\nu^{-\frac{1}{2}}$.

The fact that the asymptotic behaviour at large times has the characteristics of rotational rather than translational Brownian motion suggests that this is related to the fluid flow at relatively large distances from the particle. However, it is well known (Oseen 1927, p. 166) that the flow at large distances is not accurately described by linearized hydrodynamics. This raises the question as to the extent to which the behaviour at large times may be affected by the nonlinear, convective, terms in the Navier–Stokes equations. No attempt is made here to find an answer to this difficult question.

3. Solution for arbitrary angular displacements

Szu & Hermans (1973) express the velocity at a point $\mathbf{r}$ produced by a time-dependent force $\mathbf{F}(t)$ acting at a time-dependent position $\mathbf{h}$ in the form of a series, which is written here as follows:

$$\mathbf{v}(t) = (8\pi\eta)^{-1}\sum_{n=0}^{\infty}[d^{\frac{1}{2}n}/d(\nu t)^{\frac{1}{2}n}]\{\alpha_n s^{n-1}\mathbf{F}+\beta_n s^{n-3}(\mathbf{F}.\mathbf{s})\,\mathbf{s}\}, \tag{18}$$

where $\mathbf{s} = \mathbf{r} - \mathbf{h}$ and $s = |\mathbf{s}|$; α_n and β_n are numerical coefficients: $\alpha_0 = 1$, $\beta_0 = 1$; $\alpha_1 = -\frac{4}{3}$, $\beta_1 = 0$; $\alpha_2 = \frac{3}{4}$, $\beta_2 = -\frac{1}{4}$; $\alpha_3 = -\frac{4}{15}$, $\beta_3 = \frac{2}{15}$, etc. The operation d^n/dt^n for a half-integer n is defined by a generalization of (6):

$$d^{\frac{1}{2}(2n-1)}/dt^{\frac{1}{2}(2n-1)} = \pi^{-\frac{1}{2}} \int_{-\infty}^{t} d\tau (t-\tau)^{-\frac{1}{2}} d^n/d\tau^n. \tag{19}$$

In (18) we let $\mathbf{v}$ be the velocity produced at the position of bead 1 by the force which bead 2 exerts on the liquid. As explained in the preceding section, this force is equal to that which the liquid exerts on bead 1, and this is related to $\mathbf{v}$ by the equation

$$-\mathbf{F} = \zeta(\mathbf{u}-\mathbf{v}) + \alpha\pi^{-\frac{1}{2}} d^{\frac{1}{2}}(\mathbf{u}-\mathbf{v})/dt^{\frac{1}{2}} + \tfrac{1}{2}m_0\, d(\mathbf{u}-\mathbf{v})/dt. \tag{20}$$

Here $\mathbf{u}$ is the velocity of bead 1, i.e.

$$\mathbf{u}(t) = L\Omega(t)\, \mathbf{e}_\phi(t), \tag{21}$$

where $\mathbf{e}_\phi$ is the unit vector in the azimuthal direction at the position of bead 1. We find $\mathbf{F}$ (and thus the torque) as a function of $\mathbf{u}$ by eliminating $\mathbf{v}$ from (18) and (20).

Equation (20) is a vector equation which can be immediately Fourier transformed, but (18) contains a mixture of both components of F, and its Fourier transform is not trivial. It is not difficult to show, however, that (18) is simplified considerably if we restrict ourselves to terms that are linear in Ω.

Suppose that we define the orientation of the dumbbell at a time τ by the angle $\phi(\tau)$ it makes with some fixed reference axis. Then, as explained by Szu & Hermans (1973), the vector $\mathbf{s}$ is a function of the angle ϕ. The differentiation of a product $s(\phi)\,F$ with respect to time gives

$$d(sF)/dt = s\, dF/dt + (ds/d\phi)\, \Omega F,$$

because $d\phi/dt = \Omega$. In this result, ΩF is of order Ω^2 and will therefore be omitted. It is easily verified that the same reasoning applies to any order of differentiation, whether integer or non-integer. For example,

$$\pi^{\frac{1}{2}} d^{\frac{1}{2}}(sF)/dt^{\frac{1}{2}} = \int_{-\infty}^{t} d\tau (t-\tau)^{-\frac{1}{2}} f(sF)/d\tau$$
$$= \int_{-\infty}^{t} d\tau (t-\tau)^{-\frac{1}{2}} [s_\tau\, dF/d\tau + (ds/d\phi)_\tau\, \Omega_\tau\, F_\tau],$$

where, again, the last term is of order Ω^2. We follow this procedure consistently and remember that $\mathbf{s}$, at time t, is equal to $2L\mathbf{e}_r(t)$, where $\mathbf{e}_r$ is the unit vector in the radial direction at the position of bead 1. It is then easily verified that (18) leads to

$$v_r = (8\pi\eta)^{-1} \sum_{n=0}^{\infty} (2L)^{n-1} (\alpha_n + \beta_n)\, d^{\frac{1}{2}n} F_r/dt^{\frac{1}{2}n} + O(\Omega^2),$$

$$v_\phi = (8\pi\eta)^{-1} \sum_{n=0}^{\infty} (2L)^{n-1} \alpha_n\, d^{\frac{1}{2}n} F_\phi/dt^{\frac{1}{2}n} + O(\Omega^2),$$

where the subscripts r and ϕ denote radial and tangential components, respectively. Combining this result with (20), and remembering that $\mathbf{u}$ has no radial component, it follows that F_r and v_r are zero for all time, or, rather, are of order Ω^2. The equations for F_ϕ and v_ϕ can easily be solved. This leads to a result that is identical to that found in the preceding section, where it was assumed that the angular displacements remain small.

In other words, the only appreciable contributions to the fluid flow at the position of bead 1 result from motions in which bead 2 occupies the angular position ϕ_1 just opposite bead 1. With hindsight, it is not difficult to see why this must be so: in principle, all previous positions ϕ different from ϕ_1 have an effect on the hydrodynamic flow at time t, but the time it takes the dumbbell to change its orientation from ϕ to ϕ_1 becomes larger as Ω becomes smaller, so that the effect of such previous positions on the liquid flow at time t becomes negligible, of order Ω^2.

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REFERENCES

BERNE, B. J. 1972 Hydrodynamic theory of the angular velocity autocorrelation function. *J. Chem. Phys.* **56**, 2164–2168.

BURGERS, J. M. 1938 On the motion of small particles of elongated form in a viscous liquid. *2nd Rep. on Viscosity & Plasticity, N.H. Uitgev. Mij, Amsterdam.*

CASE, K. M. 1971 Velocity fluctuations of a body in a fluid. *Phys. Fluids*, **14**, 2091–2095.

CHOW, T. S. 1973 Simultaneous translational and rotational Brownian movement of particles of arbitrary shape. *Phys. Fluids*, **16**, 31–34.

CHOW, T. S. & HERMANS, J. J. 1972*a* Effect of inertia on the Brownian motion of rigid particles in a viscous fluid. *J. Chem. Phys.* **56**, 3150–3154.

CHOW, T. S. & HERMANS, J. J. 1972*b* On the hydrodynamic interaction of two Brownian particles in a viscous, inert fluid. *Kolloid-Z. u. Z. Polymere*, **250**, 404–409.

KIRKWOOD, J. G. 1956 Non-Newtonian viscoelastic properties of rod-like macromolecules in solution. *J. Chem. Phys.* **24**, 665–669.

KOWALEWSKI, G. 1930 *Integralgleichungen.* Berlin: Walter de Gruyter.

LANDAU, L. D. & LIFSHITZ, E. M. 1959 *Fluid Mechanics.* Addison-Wesley.

OSEEN, C. W. 1927 *Hydrodynamik.* Leipzig: Akademische Verlagsgesellschaft.

SZU, S. C. & HERMANS, J. J. 1973 *J. Polymer Phys.* **11**, 1941–1948.