

Brownian Motion in a Rotating Fluid: Diffusivity is a Function of the Rotation Rate

Gregory Ryskin

Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60208

(Received 3 November 1987)

The phenomenological relations between thermodynamic fluxes and forces are normally assumed to be invariant with respect to arbitrary motion of the frame of reference. We describe a breakdown of this invariance strong enough to be observable. It is shown that the diffusivity in a rotating fluid is anisotropic and also smaller in magnitude than in a fluid at rest in an inertial frame, giving rise to a diffusion analog of the Hall effect. For large Brownian particles (e.g., biological macromolecules) the diffusivity may decrease by 50% at the rotation speeds achievable in ultracentrifuges.

PACS numbers: 05.40.+j, 66.10.Cb

Consider diffusion of an initially concentrated distribution of solute in a quiescent liquid. The solution of this problem is well known (the "point source") and describes a monotonically expanding spherically symmetric "cloud" of the solute particles.

Now consider the same experiment in a body of fluid which is rapidly rotating as a whole, or, in other words, is at rest with respect to a rotating, noninertial frame of reference. Will there be any changes in the way the "cloud" expands? (We assume that the densities of the solute and the solvent are perfectly matched, so that there is no sedimentation due to the large centrifugal forces.) In other words, is diffusion influenced by the rigid-body rotation of the system?

Such an influence would, of course, be forbidden if one were to require that the phenomenological relations between thermodynamic fluxes and forces (often called "constitutive relations") be invariant with respect to arbitrary motion of the frame of reference. All of the established constitutive relations (Fourier's law for heat flux, Fick's law for diffusion flux, Navier-Stokes's law for viscous stress, etc.) satisfy this requirement, and it is normally imposed (often implicitly) when postulating a new one. Recently, however, it has been the subject of some controversy.¹

The above requirement is called differently by different authors, e.g., "principle of material frame indifference" (MFI), "Euclidean invariance," "objectivity," "frame invariance," "rheological invariance," "admissibility," "rotational invariance," "Poincaré invariance," etc. The "rational mechanics" school² presented it as a law of nature, and this point of view was for a while prevalent in rheology,³ but the situation is changing now.⁴ The main argument of the rational mechanics school, viz., that MFI is a consequence of the fact that the material behavior is independent of the motion of an observer, has been shown⁵ to be based on a misconception, which arose because of the vague language of definitions. (That argument is still very much in use, though—see, e.g., Ref. 6.) It has been pointed out by several workers⁷ that MFI cannot be exact, since the microscopic dynamics that gives rise to constitutive behav-

ior obeys Newton's second law, which is not frame indifferent. However, MFI can be a very good approximation, essentially because the macroscopic rotation is usually extremely slow on the time scale of the microscopic motion (which is often the molecular time scale). In fact, no violations of MFI have ever been observed experimentally, to the best of my knowledge.

In macroscopic physics, MFI is invariably used nowadays when formulating constitutive relations in viscoelasticity⁴ or for anisotropic fluids such as liquid crystals,⁸ or when constructing memory functions for irreversible processes in hydrodynamic media such as dielectric liquids or magnetic colloids,⁹ etc. Better understanding of the nature of MFI and of the circumstances under which it may break down is thus of considerable interest.

The question raised in the beginning of the Letter is also important in other contexts: If diffusion is influenced by the rigid-body rotation of the system, the theory of the ultracentrifuge, used in biochemistry and polymer science for the characterization of macromolecules, needs modification.

The answer to the above question is, in fact, positive: The viscous drag on a Brownian particle (and thus the diffusion coefficient according to the Einstein relation) is influenced by the rigid-body rotation of the system, as a result of the Coriolis force effect on the *fluid motion* caused by the particle's translation. The rest of the Letter explores the phenomenon in some detail; in particular, the dependence of the "cloud" expansion on the speed of rotation is calculated.

Consider diffusion in a dilute solution at uniform temperature, and assume the perfect matching of the specific volume, so that the pressure diffusion (i.e., sedimentation) is absent. The diffusion flux \mathbf{j} is then due to the concentration gradient alone, and is given by Fick's law (in arbitrary molar, mass, number units since the solution is dilute)

$$\mathbf{j} = -\mathbf{D} \cdot \text{grad}c,$$

where c is the concentration and \mathbf{D} is the diffusivity tensor.

In the absence of rotation, \mathbf{D} is an isotropic tensor and

can be written as $\mathbf{D} = D\mathbf{I}$, where \mathbf{I} is the identity tensor and D is the familiar scalar diffusion coefficient.

In a frame rotating with angular velocity $\boldsymbol{\Omega} \equiv \Omega \hat{\mathbf{k}}$ with respect to the inertial frame, the diffusivity is no longer isotropic and may depend on the magnitude and direction of $\boldsymbol{\Omega}$ (but not on the distance from the axis of rotation, since the effect is due to the Coriolis force alone). Let us write for this case

$$\mathbf{D} = D\mathbf{Q}, \tag{1}$$

where the dimensionless tensor \mathbf{Q} contains the effect of rotation and reduces to \mathbf{I} when $\Omega \rightarrow 0$.

\mathbf{Q} may depend on Ω only via some dimensionless group, and for Brownian diffusion in a liquid dimensional considerations suggest that this group must be $\Omega a^2 \rho / \eta$, where ρ and η are the density and viscosity of the liquid, and a is the (effective) radius of a diffusing particle. For notational convenience, in what follows we shall use as a parameter not this group itself, but its square root $\lambda \equiv (\Omega a^2 \rho / \eta)^{1/2}$. Thus we have

$$\mathbf{Q} = \mathbf{Q}(\lambda, \hat{\mathbf{k}}).$$

It is easy to see that the above dependence can be represented, without loss of generality, in the form

$$\mathbf{Q} = Q_I \mathbf{I} + Q_S \hat{\mathbf{k}} \otimes \hat{\mathbf{k}} + Q_A \mathbf{A},$$

where $A_{lm} = \epsilon_{lmn} \hat{k}_n$ and ϵ_{lmn} is the Levi-Civita alternating tensor. The scalar functions $Q_I(\lambda)$, $Q_S(\lambda)$, $Q_A(\lambda)$ must, of course, reduce to 1, 0, 0, respectively, when $\lambda \rightarrow 0$.

The component matrix of \mathbf{Q} takes an especially simple form in an orthonormal basis with one basis vector being $\hat{\mathbf{k}}$, e.g., in a Cartesian or cylindrical coordinate system where $\hat{\mathbf{k}}$ is the unit vector in the z direction

$$\mathbf{Q} = \begin{pmatrix} Q_I & Q_A & 0 \\ -Q_A & Q_I & 0 \\ 0 & 0 & Q_I + Q_S \end{pmatrix}.$$

Not surprisingly, the above form is reminiscent of the

form of thermal conductivity in some crystalline materials (see, e.g., Carslaw and Jaeger,¹⁰ p. 40). In the latter case, the antisymmetric part is often eliminated (i.e., Q_A is set equal to zero) by an appeal to the Onsager principle.¹¹ Our situation is different: In a rotating frame the Onsager principle can be written as¹²

$$Q_{ij}(\boldsymbol{\Omega}) = Q_{ji}(-\boldsymbol{\Omega}),$$

and is thus satisfied by \mathbf{Q} with arbitrary Q_A .

The diffusion flux can now be written as

$$\mathbf{j} = -D[Q_I \nabla c + Q_S (\hat{\mathbf{k}} \cdot \nabla c) \hat{\mathbf{k}} + Q_A (\nabla c) \times \hat{\mathbf{k}}].$$

Note that the last term in the above equation describes a diffusion analog of the Hall effect.

The diffusion equation follows in the form

$$\frac{\partial c}{\partial t} = D[Q_I \nabla^2 c + Q_S \nabla \cdot (\hat{\mathbf{k}} \cdot \nabla c) \hat{\mathbf{k}}].$$

In a Cartesian (or cylindrical) coordinate system with the z axis parallel to $\hat{\mathbf{k}}$, the last equation simplifies to

$$\frac{\partial c}{\partial t} = D \left[Q_I \nabla^2 c + Q_S \frac{\partial^2 c}{\partial z^2} \right],$$

and can be written as

$$\frac{\partial c}{\partial t} = D_{\perp} \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right] + D_{\parallel} \frac{\partial^2 c}{\partial z^2},$$

where $D_{\perp} \equiv Q_I D$; $D_{\parallel} \equiv (Q_I + Q_S) D$.

Thus, if $Q_S \neq 0$, the expanding "cloud" in the diffusion from a point source will not be spherically symmetric, but instead will have a shape of an ellipsoid of revolution, with its axis of symmetry parallel to the axis of rotation. The mathematical solution of this problem is easily obtained by rescaling of the coordinates and thus reducing the problem to the ordinary diffusion equation¹⁰; the final result for the concentration distribution is

$$c(\mathbf{r}, t) = \frac{M}{8\pi^{3/2} D_{\perp} D_{\parallel}^{1/2} (t - t_0)^{3/2}} \exp \left\{ -\frac{1}{4(t - t_0)} \left[\frac{(x - x_0)^2 + (y - y_0)^2}{D_{\perp}} + \frac{(z - z_0)^2}{D_{\parallel}} \right] \right\} \\ = \frac{M}{8\pi^{3/2} D_{\perp} D_{\parallel}^{1/2} (t - t_0)^{3/2}} \exp \left\{ -\frac{1}{4(t - t_0)} \left[\frac{(\mathbf{r} - \mathbf{r}_0)^2 - [\hat{\mathbf{k}} \cdot (\mathbf{r} - \mathbf{r}_0)]^2}{D_{\perp}} + \frac{[\hat{\mathbf{k}} \cdot (\mathbf{r} - \mathbf{r}_0)]^2}{D_{\parallel}} \right] \right\},$$

where M is the total amount of the diffusing substance. The propagator of a Brownian particle $\mathbf{G}(\mathbf{r}, t | \mathbf{r}_0, t_0)$ is obtained by putting $M = 1$ in the above expression.

This is about as far as we can go on the basis of symmetry alone.

As shown by Einstein¹³ in 1905, in the case of the Brownian diffusion in liquids the diffusion coefficient D is

related to the mobility of the diffusing particle b as $D = kTb$, where k is the Boltzman constant and T is the absolute temperature; the mobility is defined by the relation $\mathbf{U} = b\mathbf{F}$, where \mathbf{U} is the velocity of the steady motion of the particle through the liquid under the influence of the force \mathbf{F} . For a spherical particle of radius a , the

Stokes formula gives $b = 1/6\pi\eta a$.

The generalized form of the Einstein relation is

$$\mathbf{D} = kT\mathbf{B} = \frac{kT}{6\pi\eta a} \mathbf{R}^{-1}, \quad (2)$$

where the mobility tensor \mathbf{B} is defined by $\mathbf{U} = \mathbf{B} \cdot \mathbf{F}$, while \mathbf{R} is the dimensionless resistance tensor which determines the drag force \mathbf{F}_d

$$\mathbf{F}_d = -6\pi\eta a \mathbf{R} \cdot \mathbf{U}.$$

For a spherical particle of radius a , in the absence of rotation of the system, we have $\mathbf{R} = \mathbf{I}$. For a nonspherical particle \mathbf{R} is not isotropic, but since the orientations of the diffusing particles are random, we still have $\mathbf{D} = D\mathbf{I}$, and the *effective* radius of the particle is now inferred from the diffusion measurements as

$$a = \frac{kT}{6\pi\eta D}.$$

The effective (averaged over orientations) $\bar{\mathbf{R}}$ is again equal to \mathbf{I} if a is determined by the last expression.

If the fluid is now in rapid rotation as a whole, the mobility of a particle will change, and so will \mathbf{D} . From Eqs. (1) and (2) we see that $\mathbf{Q} = \mathbf{R}^{-1}$. Note that λ can be expressed as

$$\lambda = \frac{kT\rho^{1/2}\Omega^{1/2}}{6\pi\eta^{3/2}D},$$

so that the particle dimensions are eliminated.

It is clear that $\bar{\mathbf{R}}$ is equal to \mathbf{R} for a spherical particle, and so to complete the analysis we need a solution of the following problem: find the drag force on a spherical particle moving through a rotating fluid, i.e., find the correction to the Stokes law due to the rotation of the reference frame in which the fluid is at rest.

The solution of this problem is available in the fluid mechanics literature¹⁴; the result is

$$\mathbf{R} = \mathbf{I} + \lambda\Delta + O(\lambda^2), \quad (3)$$

where the component matrix of Δ in a basis whose third basis vector is \mathbf{k} has the form

$$\Delta = \begin{pmatrix} \frac{5}{7} & -\frac{3}{5} & 0 \\ \frac{3}{5} & \frac{5}{7} & 0 \\ 0 & 0 & \frac{4}{7} \end{pmatrix}.$$

Neglecting the $O(\lambda^2)$ term, one finally obtains

$$\begin{aligned} Q_I &= \frac{1 + 5\lambda/7}{(1 + 5\lambda/7)^2 + (3\lambda/5)^2}, \\ Q_S &= \frac{1}{1 + 4\lambda/7} - \frac{1 + 5\lambda/7}{(1 + 5\lambda/7)^2 + (3\lambda/5)^2}, \\ Q_A &= \frac{3\lambda/5}{(1 + 5\lambda/7)^2 + (3\lambda/5)^2}. \end{aligned} \quad (4)$$

Two remarks are in order:

(i) It was tacitly assumed in the derivation of (2) that $\mathbf{F} + \mathbf{F}_d = \mathbf{0}$. Strictly speaking, the total force on a spherical particle is not zero but equal to $\frac{3}{2}m(2\boldsymbol{\Omega} \times \mathbf{U})$, where m is the mass of the sphere, $2\boldsymbol{\Omega} \times \mathbf{U}$ is the Coriolis acceleration, and the factor $\frac{3}{2}$ is needed to account for the virtual mass effect (the densities of the fluid and of the particle being equal). However, this correction is obviously $O(\lambda^2)$ and therefore can be neglected together with the similar term in (3).

(ii) Strictly speaking, the expressions (4) are valid to $O(\lambda)$ only, and thus could be written as

$$Q_I \approx 1 - \frac{5}{7}\lambda, \quad Q_S \approx \frac{1}{7}\lambda, \quad Q_A \approx \frac{3}{5}\lambda, \quad (5)$$

which could also be obtained immediately by noting that to this order

$$\mathbf{Q} = (\mathbf{I} + \lambda\Delta)^{-1} \approx \mathbf{I} - \lambda\Delta.$$

I choose to use the form (4) since experience with small-parameter expansions like (3) in other contexts¹⁵ shows that they may provide results in reasonable agreement with experiment for values of the parameter much higher than one would generally expect. Thus, form (4) might be compared to data at values of λ or order 1, whereas (5) could not.

The described effect may be quite significant at the highest rotation speeds of commercially available centrifuges (Ω up to 10^4 s^{-1}). For a particle of radius $a = 5 \mu\text{m}$ at $\Omega = 10^4 \text{ s}^{-1}$ in water, or a similar low-viscosity liquid, we have $\lambda = 0.5$, and so the diffusivity may be reduced by about 30%. The anisotropy of diffusion should also be observable: for $\lambda = 0.5$, one finds that D_{\perp} is less than D_{\parallel} by about 10%.

Nevertheless, no experimental observations of the phenomenon appear to exist, which is not surprising since the question raised in the present work has not been asked before. In an experiment designed to check the present results, the perfect density matching would be desirable in order to avoid sedimentation. One way to achieve this would be to follow Cheng and Schachman,¹⁶ who used polystyrene latex particles as a solute and a mixture $\text{H}_2\text{O}-\text{D}_2\text{O}$ as a solvent. It would be necessary, however, to find materials that can be matched not only by densities but also by compressibilities, since the difference in the latter leads to the breakdown of the density matching in very high pressure gradients.¹⁶

It should be emphasized that the importance of the described effect is by no means limited to cases where sedimentation is absent: When sedimentation and diffusion occur simultaneously in a rotating fluid, both should be treated correctly, and this cannot be done (except for $\lambda \ll 1$) unless the described effect is taken into account.

Some puzzling anomalies have long been observed in the results of the ultracentrifugation analysis of large DNA molecules at high speeds; the current explanation of these is based on the idea of the distortion of the

shape of a macromolecule by flow.¹⁷ It is quite likely that these anomalies, at least in part, are due to the decrease of mobility and diffusivity in a rotating fluid: Large DNA molecules may have molecular weight of order 10^{11} , and contour length up to few centimeters; the radius of gyration of such giant molecules may easily reach values of order $10\ \mu\text{m}$ and higher.¹⁸

As mentioned before, invariance of the phenomenological relations between thermodynamic fluxes and forces with respect to arbitrary motion of the frame of reference (MFI) has been the subject of a considerable controversy. Examples of violation of this invariance have been derived from the kinetic theory of gases,⁷ but the predicted effects are much too small to be observed, while the validity of the derivation has been questioned by the advocates of MFI on the ground of the inherently approximate nature of the kinetic theory.¹⁹ The phenomenon described in the present work is thus of fundamental importance: It provides a clear example of the failure of the invariance, and the effect is so strong that it should be measurable. The physical origin of the effect is equally manifest: Note that $a^2\rho/\eta$ is the time scale of the microscopic motion (the relaxation time of the viscous flow around the Brownian particle), which may range from the extremely small values typical for molecular motion (when the particle is a small molecule itself) to values of order $10^{-3}\ \text{s}$ (for a large Brownian particle in a low-viscosity liquid). The parameter λ thus indicates how rapid the macroscopic rotation is on the time scale of the microscopic motion.

¹Proceedings of the Conference on Nonlinear Fluid Behavior, Boulder, Colorado, 1982, edited by H. J. M. Hanley [Physica (Amsterdam) **118A**, No. 1-3 (1983)], see especially the discussion, pp. 43-47; W. G. Hoover, B. Moran, R. M. More, and A. J. C. Ladd, Phys. Rev. A **24**, 2109 (1981); W. Band, Phys. Rev. A **29**, 2139 (1984); J. W. Dufty, Phys. Rev. A **30**, 622 (1984).

²C. Truesdell and W. Noll, *The Nonlinear Field Theories of Mechanics*, Handbuch der Physik, Vol. 3/3 (Springer-Verlag,

Berlin, 1965).

³R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, Vol. 1: Fluid Mechanics* (Wiley, New York, 1977); W. R. Schowalter, *Mechanics of Non-Newtonian Fluids* (Pergamon, Oxford, 1978).

⁴R. I. Tanner, *Engineering Rheology* (Clarendon, Oxford, 1985), pp. 53-55; R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, Vol. 1: Fluid Mechanics* (Wiley, New York, 1987), 2nd ed., pp. 482-483; R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions* (Butterworths, Boston, 1988), pp. 20-22, 63-66.

⁵G. Ryskin, Phys. Rev. A **32**, 1239 (1985), and **36**, 4526 (1987).

⁶G. A. Maugin, *Continuum Mechanics of Electromagnetic Solids* (North-Holland, Amsterdam, 1988), pp. 93-94.

⁷I. Müller, Arch. Rational Mech. Anal. **45**, 241 (1972); see also I. Müller, *Thermodynamics* (Pitman, Boston, 1985), pp. 145-148; D. G. B. Edelen and J. A. McLennan, Int. J. Eng. Sci. **11**, 813 (1973); P. G. de Gennes, Physica (Amsterdam) **118A**, 44 (1983); see also Refs. 1 and 5.

⁸F. M. Leslie, Adv. Liq. Cryst. **4**, 1 (1979).

⁹J. Hubbard and L. Onsager, J. Chem. Phys. **67**, 4850 (1977); J. B. Hubbard and P. J. Stiles, J. Chem. Phys. **84**, 6955 (1986).

¹⁰H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon, Oxford, 1959).

¹¹L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, Oxford, 1970), 2nd ed., p. 152.

¹²L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1980), 3rd ed., p. 367.

¹³A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1956).

¹⁴I. H. Herron, S. H. Davis, and F. P. Bretherton, J. Fluid Mech. **68**, 209 (1975).

¹⁵See, e.g., G. K. Batchelor, *An Introduction to Fluid Dynamics* (Cambridge Univ. Press, Cambridge, 1967), p. 234.

¹⁶P. Y. Cheng and H. K. Schachman, J. Am. Chem. Soc. **77**, 1498 (1955).

¹⁷D. Freifelder, *Physical Biochemistry* (Freeman, New York, 1982), 2nd ed., p. 384.

¹⁸See, e.g., Ref. 17, pp. 16-17, 486-488.

¹⁹C.-C. Wang, Arch. Rational Mech. Anal. **58**, 381 (1975); C. Truesdell, Meccanica **11**, 196 (1976); L. C. Woods, J. Fluid Mech. **136**, 423 (1983); C. Truesdell, *Rational Thermodynamics* (Springer-Verlag, New York, 1984), 2nd ed.