Cooperative Phenomena and the Decay of the Angular Momentum Correlation Function at Long Times*

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(Received 13 July 1970)

A hydrodynamic solution for the decay of the angular momentum of an initially moving volume element in an otherwise stationary, compressible, viscous fluid predicts a long time decay of the angular momentum autocorrelation function which behaves as $[\eta_s t/M\rho]^{-(d+2)/2}$ where η_s is the shear viscosity, $M\rho$ is the mass density, and d is the dimension of the system. This slow decay, which would not lead to the divergence of the rotational diffusion coefficient, or of the spin–rotation relaxation time, is caused by a vortex field which results from the interaction between a structured particle and host fluid. This result is analogous to the long time tail in the linear momentum autocorrelation function recently reported by Alder and Wainwright.

Previous studies of hard sphere fluids[1] show that the linear momentum autocorrelation function has a long positive tail indicating a surprising persistence of velocities. This effect was shown to be very dependent on the dimensionality of the sample; so much so in fact that the self-diffusion coefficient (which is the time integral of the correlation function) will diverge in two dimensions but not in three dimensions. This remarkable persistence of linear momentum can be attributed to a cooperative phenomenon in which a moving particle creates a vortex field in its neighborhood with which it continues to interact. It is well known from hydrodynamics that a vortex field will relax with a time constant which is inversely proportional to the kinematic viscosity. This time constant is much longer than the mean collision time in the fluid—hence the long time tail in the correlation function. Alder and Wainwright[1] have considered a hydrodynamic model in which a fluid is imagined to be at rest except that a small volume element of molecular size is given an initial velocity. The subsequent motion of the fluid is then calculated by direct numerical integration. This model gives nearly quantitative agreement with the results of molecular dynamics, and predicts a long time dependence of the momentum autocorrelation function which goes as $(\nu t)^{-d/2}$, where ν is the kinematic viscosity (η_s divided by the mass density, $M\rho$), and d is the dimensionality of the sample ($d=2$, 3 in two and three dimensions). This result has also been predicted by Zwanzig and Bixon[2] on the basis of a generalization of Stokes' law for the frictional force on a sphere moving in a viscous fluid. This theory has the advantage of predicting a short time negative region as well as the long time tail in the linear momentum autocorrelation function.

The question arises as to whether there exists corresponding persistence effects in other molecular properties. For example, in a liquid or a gas consisting of polyatomic molecules (structured molecules), an angular momentum can be associated with each molecule. This angular momentum can be decomposed into two parts: an orbital part **l** representing the angular momentum due to the motion of the molecular center of mass (c.m.) about some origin, and an intrinsic part, **s**, representing the angular momentum of the molecule about its own center of mass. It is this latter angular momentum which plays an important role in many physical processes. For example, in magnetic resonance experiments the spin–rotation relaxation time[3] is proportional to the Fourier component of the autocorrelation function of **s** at the Larmour frequency. In addition, from the Debye theory of rotational diffusion it can be shown[4] that the rotational diffusion coefficient is just the time integral of the autocorrelation function of **s**. Consequently, if there is a long time persistence of intrinsic angular momentum, these physical quantities may show dramatic effects.

In this paper we show that there is reason to expect a long time persistence of intrinsic angular momentum which depends on time as $(\nu t)^{-(2+d)/2}$, where ν is again the kinematic viscosity and d is the dimensionality of the system. Thus in two and three dimensions the long time tail behaves like $(\nu t)^{-2}$ and $(\nu t)^{-5/2}$ and the time integral of this tail behaves like $(\nu t)^{-1}$ and $(\nu t)^{-3/2}$. Thus both in two and three dimensions the spin–rotation relaxation time and the rotational diffusion coefficient converge. This is in marked contrast with the translational self-diffusion coefficient which is expected to diverge in two dimensions and converge in three dimensions.

A previous study[5,6] of gases and liquids containing structured molecules shows that if a molecule is given an initial intrinsic angular momentum, this angular momentum will on the average decay. Since the total angular momentum (orbital plus intrinsic) is conserved it follows that if the intrinsic angular momentum decays, the orbital angular momentum of the neighboring molecules must grow. This orbital angular momentum is simply a vortex field. Put more precisely, the intrinsic angular velocity of a molecule rapidly comes to equilibrium with a vortex field which it creates. The vortex field then decays (diffuses away) with a relaxation time again proportional to ν^{-1}. It is no wonder then that the intrinsic angular momentum persists for a long time. This occurs because the rate determining step in the long time relaxation of **s** is the dissipation of the vortex field which occurs on a hydrodynamic time scale.

THEORY

The calculation proceeds in two steps:

(1) The Navier–Stokes equation (transverse part) for a fluid containing structured molecules is solved for a fluid imagined to be at rest except that a small fluid element is given an initial linear and angular velocity. The initially moving volume element is made equal in size to the average volume per molecule. The subsequent decay of the linear and angular momentum fields is determined for times sufficiently long that

$$d\boldsymbol{\omega}_\perp(\mathbf{r},t)/dt \to 0$$

but shorter than times for which $d\mathbf{v}_\perp(\mathbf{r},t)/dt \to 0$.[7]

(2) The time correlation functions of the transverse velocity $\psi_\perp(\mathbf{r},t)=\langle \mathbf{v}_\perp(0,0)\cdot\mathbf{v}_\perp(\mathbf{r},t)\rangle$, and the transverse angular velocity $C_\perp(\mathbf{r},t)=\langle \boldsymbol{\omega}_\perp(0,0)\cdot\boldsymbol{\omega}_\perp(\mathbf{r},t)\rangle$ at the point $\mathbf{r}$ and time t are computed. Our problem is to determine that part of the transverse angular velocity correlation function which corresponds to the original molecule (fluid element). We now assume that even though the times are sufficiently long that

$$d\boldsymbol{\omega}_\perp(\mathbf{r},t)/dt \to 0,$$

the fluid element has not moved significantly from its initial position ($\mathbf{r}=0$). It follows then that the angular momentum autocorrelation function of the molecule for long times such that hydrodynamics is valid is just the integral of $C_\perp(\mathbf{r},t)$ over the volume of the original fluid element. This kind of procedure is necessary, for example, to obtain Zwanzig and Bixon's[2] result that $\psi_\perp(\mathbf{r},t)\propto t^{-3/2}$ is a consequence of ordinary hydrodynamics [we follow this up in Eq. (6)]. From Ref. 6, the relevant equations are

$$\begin{aligned}(\partial/\partial t)\mathbf{v}_\perp(\mathbf{r},t)&=(\nu+\nu_r)\nabla^2\mathbf{v}_\perp(\mathbf{r},t)+2\nu_r\nabla\times\boldsymbol{\omega}_\perp(\mathbf{r},t),\\ (\partial/\partial t)\omega_\perp(\mathbf{r},t)&=2(M/I)\nu_r[\nabla\times\mathbf{v}_\perp(\mathbf{r},t)-2\boldsymbol{\omega}_\perp(\mathbf{r},t)].\end{aligned} \tag{1}$$

Here $\mathbf{v}_\perp(\mathbf{r},t)$ and $\boldsymbol{\omega}_\perp(\mathbf{r},t)$ are the transverse velocity and the transverse intrinsic angular velocity fields. The constants ν, ν_r, M, and I are, respectively, the kinematic shear viscosity ($\eta_s/M\rho$), the kinematic rotational viscosity ($\eta_r/M\rho$), the mass and the moment of inertia ($\frac{1}{3}\mathrm{Tr}\mathbf{I}$) of a molecule.

In order to provide some insight into the behavior of the fluid we focus our attention on some simple properties of these equations. Let us assume for a moment that there are two separated times: a short time during which $[d\boldsymbol{\omega}_\perp(\mathbf{r},t)/dt]\to 0$ and a long time during which $[d\mathbf{v}_\perp(\mathbf{r},t)/dt]\to 0$. Thus for times sufficiently long, the second equation becomes

$$\boldsymbol{\omega}_\perp(\mathbf{r},t)=\tfrac{1}{2}[\nabla\times\mathbf{v}_\perp(\mathbf{r},t)]. \tag{2}$$

This time interval is one in which the intrinsic angular momentum of the molecule decays thereby producing vortex motion ($\nabla\times\mathbf{v}$). When Eq. (2) is substituted into Eq. (1) we also find that the transverse velocity obeys the equation

$$(\partial/\partial t)\mathbf{v}_\perp(\mathbf{r},t)=\nu\nabla^2\mathbf{v}_\perp(\mathbf{r},t). \tag{3}$$

This equation is identical to that of ordinary hydrodynamics where the angular momentum of the constituent molecules is totally ignored.

In order to solve Eq. (3) we must first determine an initial condition $\mathbf{v}_\perp(\mathbf{r},0)$ corresponding to our physical problem. Since we are trying to describe the velocity field at the space–time point $(\mathbf{r},t)$ caused by an initial situation in which the fluid is stationary except for a little volume element centered at the point $\mathbf{r}=0$, we take the initial condition as $\mathbf{v}_\perp(\mathbf{r},0)=\mathbf{v}_\perp\delta(r)$, where $\mathbf{v}$ is the velocity of this volume element. Thus as far as Eq. (3) is concerned it should be solved subject to the boundary condition

$$\mathbf{v}_\perp(\mathbf{r},0)=\mathbf{v}_\perp\delta(r), \tag{4}$$

where $\mathbf{v}_\perp$ is the initial transverse velocity of the fluid element. The solution of Eq. (4) subject to this initial value is the well known solution of the diffusion equation in a system with a point source,

$$\mathbf{v}_\perp(\mathbf{r},t)=\mathbf{v}_\perp[4\pi\nu t]^{-3/2}\exp(-r^2/4\nu t). \tag{5}$$

The time correlation function of the transverse velocity at the point $\mathbf{r}$ and at time t is $\psi_\perp(\mathbf{r},t)=\langle \mathbf{v}_\perp(0,0)\cdot\mathbf{v}_\perp(\mathbf{r},t)\rangle$. In order to determine the transverse velocity correlation function for the original molecule (fluid element), we make the assumption involved in the second step of the calculation, namely, that the fluid element has not moved significantly from its initial position ($\mathbf{r}=0$). If this assumption is made, then it follows that the velocity correlation function of the molecule for long times such that hydrodynamics is valid is simply the integral of $\psi_\perp(\mathbf{r},t)$ over the volume of the original fluid element; thus,

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle=\tfrac{2}{3}\langle v^2\rangle[4\pi\nu t]^{-3/2}. \tag{6}$$

Were we to repeat this calculation for hydrodynamics in two dimensions Eq. (5) would be a two dimensional Gaussian and thus Eq. (6) would behave as $(\nu t)^{-1}$. This is the result observed by Alder and Wainwright.[1]

In a completely analogous manner the transverse angular velocity correlation function

$$\begin{aligned}C_\perp(\mathbf{r},t)&=\langle \boldsymbol{\omega}_\perp(0,0)\cdot\boldsymbol{\omega}_\perp(\mathbf{r},t)\rangle\\ &=\tfrac{1}{4}\langle[\nabla\times\mathbf{v}_\perp(0,0)]\cdot[\nabla\times\mathbf{v}_\perp(\mathbf{r},t)]\rangle\end{aligned}$$

can be determined. We merely substitute Eq. (5) into Eq. (2) and the resulting equations into $C_\perp(\mathbf{r},t)$. Then

$$\begin{aligned}C_\perp(\mathbf{r},t)=&\tfrac{1}{4}[4\pi\nu t]^{-3/2}\\ &\times\langle[\mathbf{v}_\perp\times\nabla\delta(r)]\cdot[\mathbf{v}_\perp\times\nabla\exp(-r^2/4\nu t)]\rangle.\end{aligned}$$

From the well-known properties of the delta function

$$\begin{aligned}C_\perp(\mathbf{r},t)=&-[(4\pi\nu t)^{-3/2}/4]\\ &\times\langle\delta(r)[\mathbf{v}_\perp\times\nabla]^2\exp(-r^2/4\nu t)\rangle.\end{aligned}$$

The vector identity

$$[\mathbf{v}_\perp \times \nabla]^2 = v_\perp^2 \nabla^2 - (\mathbf{v}_\perp \cdot \nabla)^2$$

when substituted into the preceding equation yields

$$C_\perp(\mathbf{r}, t) = \tfrac{3}{2}\pi^{-3/2}(4\nu t)^{-5/2}\langle v_\perp^2 \delta(r)\, \exp(-r^2/4\nu t)\rangle.$$

When this is integrated over the initial volume element, it is found that the intrinsic angular momentum autocorrelation function has a long time tail

$$\langle \mathbf{s}(0)\cdot\mathbf{s}(t)\rangle \propto (\nu t)^{-5/2}. \tag{7}$$

If the same computation was performed for a two-dimensional system it would yield $(\nu t)^{-3/2}$.

This calculation can be carried through without making the assumptions that lead to Eqs. (2) and (3). The results are essentially the same.

CONCLUSIONS

The angular momentum autocorrelation function is thus expected to have a long time tail proportional to $(\nu t)^{-(d+2)/2}$. This persistence of intrinsic angular momentum is predicted on the basis of a hydrodynamic model in which a rotating molecule couples to the host fluid in such a way that it produces a vortex field. The subsequent decay of the angular momentum is then rate limited by the decay (diffusion) of this vortex field. This occurs very slowly thus accounting for the long time tail.

On the basis of this calculation we expect that the time integral of the angular momentum autocorrelation function (and thereby the spin–rotation relaxation time and the rotational diffusion coefficient) will have a pronounced dependence on the kinematic viscosity. The smaller the kinematic viscosity the larger will be the contribution of the tail to this integral. Since in gases the kinematic viscosity has a minimum at a certain density (pressure), we expect that this integral will have a maximum for those densities. Thus, the persistence of the angular momentum might show up as a maximum in the pressure dependence of either the spin–rotation relaxation rate or in the rotational diffusion coefficient. This would be the analogue of similar effects in the translational self diffusion coefficient of gases.[8]

Leontovich[9] has developed a phenomenological theory for rotational reorientation. If this model is studied from the same vantage point of the angular momentum, it can be shown that the orientation of a molecule relaxes on two time scales: a short time scale during which the orientation comes to equilibrium with local velocity gradients, and a much longer time scale during which these velocity gradients decay. We can show that the relaxation of the time correlation function $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ (where $\mathbf{u}$ is the orientation of the principal axis in a symmetric top molecule) has a long time tail which behaves like $(\nu t)^{-1/2}$ in three dimensions.

Our conclusions are based on a hydrodynamic model. It is well known that this model is not valid for distances and times of a molecular order. Our argument therefore is of a purely dimensional nature. It is consistent with the computer experiments of Alder and Wainwright on the long time behavior of hard sphere fluids.[1] For molecular fluids, our results are of interest since they predict long time persistence effects in the orientational motion of molecules, and should stimulate new experimental studies. Note that this procedure yields no information about short time behavior. A microscopic theory for the angular momentum autocorrelation function is desirable. Zwanzig and Bixon's treatment of linear momentum[2] provides a possible framework for such a theory.

It should be noted that even in our dimensional argument, it is implicitly assumed that the molecule remains very close to its initial position. We expect this assumption to be valid for times long compared to the rapid initial decay (typically $\sim 10^{-13}$ sec) of the angular momentum of a single molecule but short compared to the time it takes a molecule to diffuse a few molecular diameters (typically $\sim 10^{-10}$ sec). Thus, our theory predicts the $t^{-(d+2)/2}$ tail for the angular momentum correlation for these intermediate times.

We reiterate, this paper is to be regarded as conjectural.[10]

* Work supported by a grant from the National Science Foundation.

† Alfred P. Sloan Foundation Fellow.

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[10] *Note added in proof*: After this paper was submitted, an elegant formulation of the problem of asymptotic time behavior of the correlation function appeared in the literature: M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwan, Phys. Rev. Letters **25,** 1254 (1970); J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Letters **25,** 1257 (1970). Both of these papers were submitted about the same time as ours and both deal with similar hydrodynamic analysis of the single particle velocity autocorrelation function. We have recalculated our results using this new formulation. We arrive at essentially the same conclusions as before. In particular, the intrinsic angular momentum autocorrelation function has a long time tail given by Eq. (7). This modified version of the present paper will appear in the Proceedings of the I.U.P.A.P. Conference on Statistical Mechanics, March 29–April 2, 1971.