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Compressibility effects in the hydrodynamic theory of Brownian motion

By ROBERT ZWANZIG
Institute for Fluid Dynamics and Applied Mathematics, University of Maryland

AND MORDECHAI BIXON
University of Tel Aviv

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The velocity correlation function of a Brownian particle in a viscous compressible fluid is studied in the limit of very small compressibility. The main effect of compressibility is an initial rapid change of the particle mass from a real inertial mass to a virtual mass.

The purpose of this article is to clarify the role of compressibility in the hydrodynamic theory of Brownian motion.

When a spherical rigid body accelerates in an incompressible fluid, its mass m is augmented by an induced mass $\frac{1}{2}M$, where M is the mass of the displaced fluid. The body responds to an imposed force as if its mass were $m^* = m+\frac{1}{2}M$, and m^* is called the virtual mass of the body. In a real fluid with non-vanishing compressibility, no matter how small, the body responds as if its mass were m and not m^*. This lack of continuity in the limit of zero compressibility has led to much confusion in the hydrodynamic theory of Brownian motion. (The articles listed in the references provide a moderately complete history of the subject.)

We analyse here the effects of a very small but non-vanishing compressibility on the velocity correlation function of a Brownian particle. The velocity correlation function is defined as

$$A(t) = \langle v(0)\, v(t)\rangle, \tag{1}$$

where $v(t)$ is the component of particle velocity in some fixed direction at time t, and $\langle\ \rangle$ denotes an equilibrium ensemble average.

A brief summary of results will be given first, and then their justification will be discussed.

The velocity correlation function starts with the initial value given by equipartition, $A(0) = kT/m$, where k is the Boltzmann constant and T is the temperature. After a short time, $A(t)$ decays from kT/m to kT/m^*. The initial decay time is of order ma/m^*c, where a is the particle radius and c is the fluid sound velocity. The initial decay is due to acoustic damping of the particle velocity, and occurs even when the fluid is inviscid. In the absence of viscosity, $A(t)$ thereafter remains at kT/m^*. But when the fluid is viscous, the initial decay is followed by a much slower decay from kT/m^* to zero, just as if the fluid were incompressible. The main effect of compressibility is to produce the rapid initial drop from kT/m to kT/m^*. This behaviour was anticipated, on intuitive grounds, by several authors (Giterman & Gertsenshtein 1966; Berne 1972; Hynes 1972; Burgess 1973; Davis & Subramanian 1973).

The starting point for the analysis of the velocity correlation function is an equation provided by linear response theory,

$$\frac{dA(t)}{dt} = -\int_0^t ds K(s) A(t-s), \tag{2}$$

where $K(s)$ is a memory function, to be specified later. [Equations of this sort are discussed in useful reviews by Kubo (1966) and by Berne (1971).] This equation is solved easily by Laplace transforms. It is convenient to work in the complex frequency plane, so the Laplace transform of the memory function is defined as

$$\hat{K}(\omega) = \int_0^\infty dt\, e^{i\omega t} K(t). \tag{3}$$

On inverting the Laplace transform solution of this equation, one finds

$$A(t) = \frac{mA(0)}{2\pi}\int_{-\infty+i\epsilon}^{\infty+i\epsilon} d\omega \frac{e^{-i\omega t}}{-i\omega m + \hat{K}(\omega)}. \tag{4}$$

The contour of integration is above all singularities in the complex ω plane, and the resulting expression for $A(t)$ is valid for all $t \geqslant 0$.

The hydrodynamic theory of Brownian motion is based on a special approximation to $\hat{K}(\omega)$. Consider small amplitude oscillations of a sphere about a fixed point in a viscous compressible fluid, with frequency ω. The velocity of the sphere is $u(\omega)$, and the frictional force on the sphere is $F(\omega)$. The hydrodynamic friction coefficient $\zeta(\omega)$ is defined by

$$F(\omega) = -\zeta(\omega)\, u(\omega). \tag{5}$$

The fundamental assumption of the hydrodynamic theory of Brownian motion is

$$\hat{K}(\omega) \simeq \zeta(\omega). \tag{6}$$

We are not concerned here with the validity of this assumption, but only with its consequences. Recent articles by Bedeaux & Mazur (1974) and by Mazur & Bedeaux (1974) provide some theoretical justification for (6).

Frequency-dependent friction coefficients have been derived many times. The viscous incompressible fluid was treated first by Stokes in 1850, and his result may be found in various textbooks. The viscous compressible fluid was treated by Giterman & Gertsenshtein (1966; their result has a misprint); later and independently by Zwanzig & Bixon (1970; in a somewhat more general but less convenient form); by Chow & Hermans (1973*b*; this may be the most useful source – their expression for $\zeta(\omega)$ is correct and easy to use); and by Burgess (1973; with several misprints). The friction coefficient for an inviscid compressible fluid (where the damping is due to acoustic radiation) may be found in various textbooks, or by taking the limit of zero viscosity in the more general expression. We use here only the two limiting cases of an inviscid compressible fluid and a viscous incompressible fluid, so we do not write down the general expression.

The mathematical problem at hand is to take the known expression for $\zeta(\omega)$ for a viscous compressible fluid, put it into the denominator of (4), and then evaluate the contour integral. This procedure, while perfectly feasible in principle, is quite difficult in practice because of the branch-point structure of the integrand. When the compressibility is very small, however, there is a convenient separation of time scales, which makes an approximate evaluation practical.

One time scale,

$$t_c = a/c, \tag{7}$$

is determined by the time required for a sound wave to traverse a sphere radius. Another time scale,

$$t_v = a^2/\nu \tag{8}$$

(where ν is the kinematic viscosity of the fluid), is determined by the characteristic lifetime of a transverse wave. The ratio of these two time scales

$$t_v/t_c = ca/\nu \tag{9}$$

is the dimensionless number α. When α is much larger than unity, the fluid is 'almost incompressible'.

To evaluate the velocity correlation function on the shorter time scale, we introduce the scaled variables

$$\tau = t/t_c, \quad x = \omega t_c, \tag{10}$$

so that

$$A(t) = \frac{mA(0)}{2\pi}\int_{-\infty+i\epsilon}^{\infty+i\epsilon} dx \frac{e^{-ix\tau}}{-imx+t_c\zeta(x/t_c)}. \tag{11}$$

When α is very large, and τ is of the order of unity, we anticipate that interesting values of x are of order unity. Then the friction coefficient is approximately

$$\zeta(x/t_c) = \frac{M}{t_c}\frac{x(x+i)}{x^2+2ix-2}[1+O(\alpha^{-\frac{1}{2}})]. \tag{12}$$

The leading term is the friction coefficient for an inviscid compressible fluid. The remaining terms, of order $\alpha^{-\frac{1}{2}}$, will be neglected.

In this approximation, the contour integral may be evaluated by the Cauchy residue theorem. The integrand has three simple poles, located at

$$\left.\begin{aligned} x_0 &= 0, \\ x_1 &= -i\frac{m^*}{m}+\left[1-\frac{M^2}{4m^2}\right]^{\frac{1}{2}}, \\ x_2 &= -i\frac{m^*}{m}-\left[1-\frac{M^2}{4m^2}\right]^{\frac{1}{2}}. \end{aligned}\right\} \tag{13}$$

The residues are found easily, and the velocity correlation function is

$$\begin{aligned} A(t) = \frac{m}{m^*}A(0)&+\frac{M}{2m^*}A(0)\left\{\frac{1}{2}-\frac{im^*}{(4m^2-M^2)^{\frac{1}{2}}}\right\}e^{-ix_1t/t_c} \\ &+\frac{M}{2m^*}A(0)\left\{\frac{1}{2}+\frac{im^*}{(4m^2-M^2)^{\frac{1}{2}}}\right\}e^{-ix_2t/t_c}. \end{aligned} \tag{14}$$

This expression is valid for times of the order of t_c. It is continuous in the limit $t \to 0$, so there is no difficulty about assigning the initial value $A(0) = kT/m$. The poles x_1 and x_2 have negative imaginary parts. When $2m > M$, the contribution from these poles decays through exponentially damped oscillations. When $2m < M$, the oscillations are overdamped, and the decay is exponential. In either case, the contribution from these poles decays to zero, and only the contribution from x_0 remains. For times much longer than t_c but still small compared with t_v, the velocity correlation function takes on the value kT/m^*. In the complete absence of viscosity (so that $t_v \to \infty$), this result is exact.

To evaluate the velocity correlation function on the longer time scale, we introduce the scaled variables

$$\tau = t/t_v, \quad y = \omega t_v \tag{15}$$

so that

$$A(t) = \frac{kT}{2\pi}\int_{-\infty+i\epsilon}^{\infty+i\epsilon} dy \frac{e^{-iy\tau}}{-imy + t_v\zeta(y/t_v)}. \tag{16}$$

When α is very large and τ and y are of order unity, the friction coefficient is approximately

$$\zeta(y/t_v) \to \frac{9M}{2t_v}[1 - i(iy)^{\frac{1}{2}} - \tfrac{1}{9}iy](1 + O(\alpha^{-2})). \tag{17}$$

The leading term is the friction coefficient for a viscous incompressible fluid. The remaining terms, of order α^{-2}, will be neglected.

The resulting contour integral has been discussed by many authors, e.g. Case (1971), Hynes (1972) and Mazo (1973). At long times, it decays as $t^{-\frac{3}{2}}$. In the limit $t \to 0$, one finds the remarkable result that $A(t)$ approaches kT/m^*. This is, of course, entirely consistent with the short-time calculation just described. Large t on the time scale t_c are also small t on the time scale t_v. However, if we had restricted our attention to an incompressible fluid from the beginning, the time scale t_c would not have appeared anywhere. Then we would find an unphysical lack of continuity,

$$A(0) = kT/m, \quad A(0^+) = kT/m^*. \tag{18}$$

This is the source of confusion that was alluded to in the introduction. The confusion is eliminated by taking into account the effects of compressibility, and the resulting velocity correlation function is physically reasonable.

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