

Hydrodynamic Theory of the Velocity Correlation Function*

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The velocity correlation function of an atom in a simple liquid is calculated using a frequency-dependent version of the Stokes-Einstein formula. Stokes's law for the frictional force on a moving sphere is generalized to arbitrary frequency, compressibility, and viscoelasticity, with arbitrary slip of the fluid on the surface of the sphere. This frequency-dependent friction coefficient is then used in a generalized Stokes-Einstein formula, and the velocity correlation function is found by Fourier inversion. By using physically reasonable values for viscoelastic parameters, good agreement is obtained with the velocity correlation function determined by Rahman using computer experiments.

INTRODUCTION

Rahman's determination¹ of the velocity correlation function in liquid argon, done by computer experiments, provides detailed information on dynamical processes in simple liquids. Many attempts² have been made to reproduce his results by purely theoretical arguments, with varying degrees of success. In this article, we present still another theoretical discussion of the velocity correlation function. Our calculation is based on hydrodynamics, and in particular, on a generalization of Stokes's law for the frictional force on a sphere moving in a viscous fluid continuum.

The possibility that a calculation of this kind might be reasonably valid for liquid argon occurred to us after learning about a recent investigation by Alder and Wainwright.³ Using computer experiments on a hard-sphere system, they observed hydrodynamic structure in the velocity field around a diffusing sphere.

Stokes's law was derived originally for the steady motion of a sphere in a viscous incompressible fluid. This was extended by Stokes and by Boussinesq to allow for motion with arbitrarily changing velocity. Our further generalization includes the effects of compressibility and viscoelasticity of the fluid.

In our treatment, the diffusing atom is a sphere of known radius and mass. (The radius is determined by the coefficient of self-diffusion.) The surrounding fluid is characterized by its density, sound velocity, shear and volume viscosities, and their associated relaxation times. The interaction between the atom and its environment is described by a hydrodynamic boundary condition.

In essence, our procedure is to derive a frequency-dependent version of the Stokes-Einstein formula, and from this, the frequency spectrum of the velocity correlation function. On Fourier inversion, the time dependence of the velocity correlation function is obtained.

By choosing reasonable values for the parameters listed above, we obtain good agreement with Rahman's numerical results. In particular, we find the first minimum in Rahman's curve, with the right depth and at the right position. The most serious discrepancy is at very short times: Our velocity correlation function has a cusp at zero time, while the correct one must be rounded. This is due to use of a boundary condition, rather than an intermolecular force, to describe the interaction of the atom with its surroundings. We find that the velocity correlation function becomes positive at very long times, and approaches 0 asymptotically with time as $1/t^{3/2}$. This agrees with conclusions obtained by Alder and Wainwright³ using dimensional arguments, and verified by them on the hard-sphere system. Our prediction cannot be checked against Rahman's results because of the time scales involved.

MOTIVATIONS

According to the Stokes-Einstein formula, the diffusion coefficient D of a spherical body of radius a in a fluid with viscosity η is given by

$$D = k_B T / 6\pi\eta a \quad (1a)$$

The absolute temperature is T , and k_B is Boltzmann's constant. This formula is derived with the boundary condition that the viscous fluid *sticks* perfectly to the surface of the sphere. If the fluid *slips* perfectly over the surface of the sphere, the corresponding formula is

$$D = k_B T / 4\pi\eta a \quad (1b)$$

The remarkable approximate validity of the Stokes-Einstein formula for bodies of molecular size is well known. By using experimental data for liquid argon at 90 K, the following atomic radii are found:

$$a(\text{stick}) = 1.17 \text{ \AA}; \quad a(\text{slip}) = 1.76 \text{ \AA}.$$

For liquid sodium at 373 K, the corresponding

numbers are

$$a(\text{stick}) = 0.94 \text{ \AA}; \quad a(\text{slip}) = 1.40 \text{ \AA}.$$

These radii are entirely reasonable, especially with the slipping boundary condition.

But the Stokes-Einstein formula is not exact for molecular diffusion. Inspection of the meager experimental data available suggests that the apparent radius is not independent of pressure and temperature.

Another reason for concern is that there is no Stokes's law in the conventional sense in a two-dimensional system. Here, the friction coefficient itself depends on the logarithm of the Reynold's number, and diverges in the limit of zero velocity.⁴

However, the *approximate* validity of this formula is so striking that we ought to take it seriously. It would be desirable to understand why it works so well, and how to improve its accuracy; but this is a difficult problem and little progress has been made.

So far we have discussed the Stokes-Einstein formula only for steady motion (or zero-frequency behavior). Since the Fourier transform of the velocity correlation function may be regarded as a frequency-dependent diffusion coefficient, the generalization of the Stokes-Einstein formula to arbitrary frequency is of interest. We present the generalization in this article, and we show that it is in good agreement with Rahman's computer experiments on liquid argon. Our results provide further evidence on the validity of the hydrodynamic approach to the theory of self-diffusion, although the more fundamental questions, why it works so well and how to improve it, remain unanswered.

STANDARD STOKES-EINSTEIN THEORY

A brief survey of the standard Stokes-Einstein theory will provide a useful introduction to our later discussion of the generalized frequency-dependent Stokes-Einstein formula. First, we outline the main steps in the derivation of Stokes's law, and then we show how the Stokes-Einstein formula follows.

The derivation of Stokes's law begins with the Navier-Stokes equations of hydrodynamics. These are equations of motion for the mass density $\rho(R, t)$ and the velocity field $\vec{v}(R, t)$ of the fluid,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \vec{v}, \quad (2)$$

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho \vec{v} \cdot \nabla \vec{v} = -\nabla P + \eta \nabla^2 \vec{v} + (\frac{1}{3}\eta + \eta_v) \nabla \nabla \cdot \vec{v}. \quad (3)$$

The coefficients of shear and volume viscosity are η and η_v , and P is the hydrodynamic pressure.

The first step is to linearize. In particular, the term $\vec{v} \cdot \nabla \vec{v}$ is omitted, and $\nabla \cdot \rho \vec{v}$ becomes $\rho_0 \nabla \cdot \vec{v}$,

where ρ_0 is the uniform equilibrium fluid density. Next, steady motion is assumed. This means that all time derivatives are set equal to 0. A special consequence is that the divergence of the velocity also vanishes, $\nabla \cdot \vec{v} = 0$, so that the fluid can be treated mathematically as incompressible. (Note that the fluid does not have to be physically incompressible; the derivation is equally valid for a gas.)

The sphere moves with uniform velocity \vec{U} . One boundary condition is that the fluid remains at rest infinitely far from the sphere. Another boundary condition is concerned with the behavior of the fluid at the surface of the sphere. Here two choices may be made. (One can in fact consider a continuous variation from one to the other, but we mention here only the two extreme cases.) In the limit that we refer to as "stick," the fluid adheres perfectly to the surface of the sphere, so that $\vec{v} = \vec{U}$ everywhere on the surface. In the other limit, referred to as "slip," the normal and tangential behavior of the fluid are specified separately. The normal component of the fluid velocity matches the normal component of the velocity of the sphere everywhere on the surface, $v_n = U_n$. This is a kinematic condition, and means that no fluid can enter or leave the sphere. The other part of the boundary condition for slip is that the fluid exerts no force tangentially on the sphere. If $\vec{\sigma}$ is the stress tensor at the surface, and \vec{a}_n and \vec{a}_t are unit vectors normal and tangential to the surface, this condition takes the form

$$\vec{a}_t \cdot \vec{\sigma} \cdot \vec{a}_n = 0.$$

The rest of the derivation involves solution of the linearized Navier-Stokes equations subject to these boundary conditions, calculation of the stress tensor on the surface, and integration over the surface to get the total frictional force. We pass over the details here.

The results of the derivation are the well-known formulas for the frictional force \vec{F} on the sphere,

$$\vec{F}(\text{stick}) = -6\pi\eta a \vec{U}, \quad \vec{F}(\text{slip}) = -4\pi\eta a \vec{U}. \quad (4)$$

To get the diffusion coefficient, Einstein argued that

$$D = k_B T / \zeta, \quad (5)$$

where ζ is the friction coefficient, either $6\pi\eta a$ or $4\pi\eta a$ in the Stokes's problem. In order to lead up to our later discussion, we give here a contemporary version of Einstein's argument.

The diffusion coefficient can be determined in general from the velocity correlation function

$$D = \int_0^\infty dt \langle U_x(0) U_x(t) \rangle, \quad (6)$$

where $U_x(t)$ is the velocity of the diffusing particle in the x direction at time t and $\langle \dots \rangle$ represents an equilibrium ensemble average.

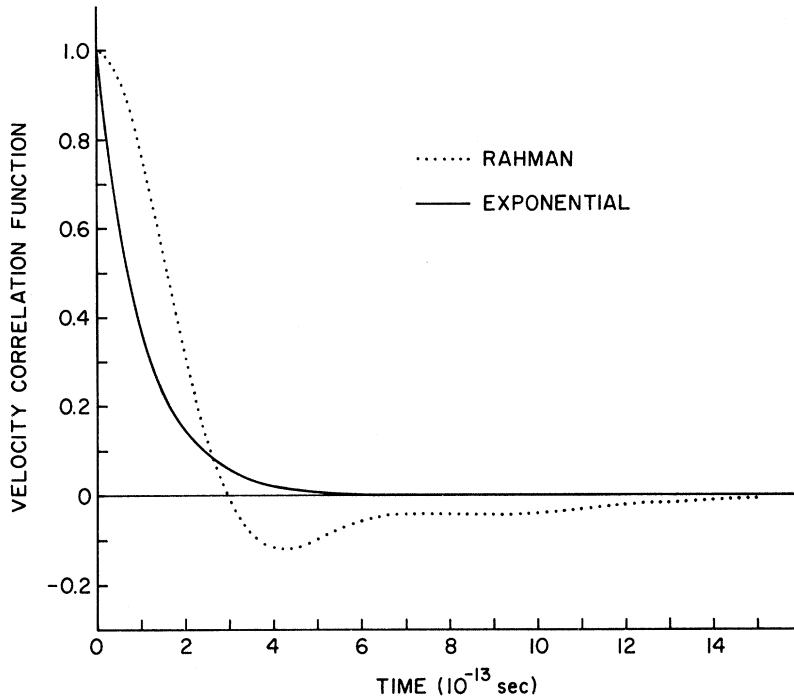


FIG. 1. Rahman's velocity correlation function (dotted curve) compared with exponential decay (solid curve). The exponential decay rate was determined by the diffusion coefficient. Both curves are normalized to unity at time $t=0$.

This average will be calculated in two stages. First, we average over an equilibrium distribution of initial states of the surrounding fluid, under the constraint that the initial velocity of the sphere is $\vec{U}(0)$; and then we average over an equilibrium distribution of initial velocities $\vec{U}(0)$. The equation of motion of the sphere is a Langevin equation in which the total force consists of a frictional force (given here by Stokes's law) and a randomly fluctuating force. The average of the random force over an equilibrium distribution of initial states of the fluid is 0. Let $\vec{V}(t; \vec{U}(0))$ denote the velocity of the sphere at t , averaged over the same distribution of initial states of the fluid. This depends parametrically on the given initial velocity $\vec{U}(0)$. Then the equation of motion of the *averaged* velocity \vec{V} is

$$m \frac{d\vec{V}}{dt} = -\zeta \vec{V}, \quad (7)$$

where m is the mass of the sphere and ζ is either of the friction coefficients mentioned above. The solution is

$$\vec{V}(t; \vec{U}(0)) = \vec{U}(0) e^{-\zeta t/m}. \quad (8)$$

We multiply this by the initial velocity $U_x(0)$ and do the final average over the initial velocities to find the correlation function

$$\langle U_x(0) U_x(t) \rangle = \langle (U_x(0))^2 \rangle e^{-\zeta t/m}. \quad (9)$$

On integrating over time, the diffusion coefficient becomes

$$D = \int_0^\infty dt \langle U_x^2 \rangle e^{-\zeta t/m} = \langle U_x^2 \rangle m / \zeta. \quad (10)$$

The equilibrium average of the square of the initial velocity is just $k_B T/m$, so that the result is the familiar Stokes-Einstein formula.

Note that in this argument the velocity correlation function decays exponentially in time. This is not observed in Rahman's computer experiments. The actual shape of his velocity correlation function is compared with the corresponding exponential decay in Fig. 1. The discrepancy suggests that a more detailed theory than the one just outlined must be developed.

FIRST GENERALIZATION OF THE STOKES-EINSTEIN THEORY

The standard Stokes-Einstein theory that has just been reviewed applies to steady motion only, and should be regarded as a zero-frequency theory. Generalizations to a theory for arbitrary frequencies can be made in several ways. The first generalization, to be discussed now, uses results already obtained by Stokes in 1851.

The basis of the first generalization is the observation that it is not consistent to use a friction coefficient derived with an assumption of steady motion in an equation of motion describing changes in velocity. Let us suppose that the velocity of the particle is an arbitrary function $\vec{U}(t)$ of time. This can be Fourier analyzed into frequency components \vec{U}_ω ,

$$\vec{U}(t) = \int_{-\infty}^{\infty} d\omega \vec{U}_{\omega} e^{-i\omega t} . \quad (11)$$

In the same way the frictional force $\vec{F}(t)$ has Fourier components \vec{F}_{ω} ,

$$\vec{F}(t) = \int_{-\infty}^{\infty} d\omega \vec{F}_{\omega} e^{-i\omega t} . \quad (12)$$

Because of the linearity of the hydrodynamic equations of motion, any Fourier component of the force is proportional to the corresponding Fourier component of the velocity,

$$\vec{F}_{\omega} = -\zeta(\omega)\vec{U}_{\omega} . \quad (13)$$

Stokes derived an expression for $\zeta(\omega)$ under the same conditions that were used for the zero-frequency theory: incompressibility and the stick boundary condition. It should be observed that now the assumption of incompressibility is a physically significant limitation, since it does not follow from an assumption of steady motion. Stokes's result is

$$\zeta(\omega) = 6\pi\eta a - 2\pi a^3 i\omega\rho/3 - 6\pi a^2 i(i\omega\rho\eta)^{1/2} . \quad (14)$$

The first term is the ordinary Stokes's friction, the second term is connected with the virtual mass of a sphere in an incompressible fluid, and the third term is related to the penetration depth of viscous unsteady flow around a sphere.

The corresponding expression for the time-dependent force $\vec{F}(t)$ was found by Boussinesq, and has been used, e. g., in treating the approach to steady motion of a sphere falling from rest in a viscous fluid.

The frequency-dependent friction coefficient derived with the slip boundary condition is

$$\zeta(\omega) = 4\pi\eta a - 2\pi a^3 \frac{1}{3} i\omega\rho - \frac{8\pi a^2 i(i\omega\rho\eta)^{1/2}}{3 + ai(i\omega\rho/\eta)^{1/2}} . \quad (15)$$

A derivation of the velocity correlation function, analogous to the one just described in connection with the zero-frequency theory, is easy to carry out. The results, with either boundary condition, do not agree at all well with Rahman's computer experiments.

The reason is that important physical effects have been left out. A consideration of characteristic time scales will suggest what has to be done. The time scale for diffusion is determined by the relaxation time m/ζ ; for liquid argon this is of the order of 10^{-13} sec. Thus we are concerned with frequencies of the order of 10^{13} Hz. These are also the time and frequency scales found in Rahman's work.

The sound velocity in liquid argon is of the order of 10^5 cm/sec. Then, the time required for a sound wave to propagate over an interatomic distance is also about 10^{-13} sec. This means that we should not

neglect sound propagation; important effects may arise from the compressibility of the liquid.

Finally, we note that for the short times or high frequencies of interest here, a liquid behaves *viscoelastically*.⁵ This behavior can be accounted for by using a complex frequency-dependent viscosity coefficient. A common approximation due to Maxwell, probably good enough for present purposes, is

$$\eta(\omega) = \eta_0/(1 - i\omega\tau) , \quad (16)$$

where τ is a viscoelastic relaxation time. It is known that this time is of the order of 10^{-13} sec for liquid argon.

Thus it seems obvious that both compressibility and viscoelasticity will contribute significantly to the structure of the velocity correlation function.

SECOND GENERALIZATION OF THE STOKES-EINSTEIN THEORY

This section contains a derivation of the generalized friction coefficient $\zeta(\omega)$, including the effects just mentioned. The derivation starts from the linearized Navier-Stokes equations,

$$\frac{\partial\rho}{\partial t} = -\rho_0\nabla\cdot\vec{v} , \quad (2')$$

$$\rho_0\frac{\partial\vec{v}}{\partial t} = -\nabla P + \eta\nabla^2\vec{v} + (\frac{1}{3}\eta + \eta_v)\nabla\nabla\cdot\vec{v} . \quad (3')$$

As in our earlier discussion, the arbitrary velocity of the moving sphere is expressed in terms of its Fourier components. Because of linearity, we may consider each Fourier component individually.

The excess density of the fluid is $\delta\rho = \rho - \rho_0$. This, and the velocity of the fluid, will vary periodically with frequency ω , so that we may write the Navier-Stokes equations in the form

$$-i\omega(\delta\rho)_{\omega} = -\rho_0\nabla\cdot\vec{v}_{\omega} , \quad (17)$$

$$-i\omega\rho_0\vec{v}_{\omega} = -\nabla P_{\omega} + \eta\nabla^2\vec{v}_{\omega} + (\frac{1}{3}\eta + \eta_v)\nabla\nabla\cdot\vec{v}_{\omega} . \quad (18)$$

It should be kept in mind that the two viscosity coefficients η and η_v are now regarded as complex functions of frequency.

The gradient of pressure is

$$\nabla P = \frac{\partial P}{\partial\rho}\nabla\rho = C^2\nabla\delta\rho , \quad (19)$$

where C is the sound velocity. [Normally Eq. (19) includes a gradient of temperature or entropy. At the frequencies of interest here the fluid is expected to behave isothermally, so that the extra gradient may be omitted. At lower frequencies, appropriate to the motion of a macroscopic sphere, the fluid is expected to behave isoentropically, and again the extra gradient may be omitted. In one case the sound velocity is isothermal, and in the other it

is adiabatic.]

On solving Eq. (17) for the excess density in terms of the velocity and substituting this into Eq. (18), we get

$$(\delta\rho)_\omega = \rho_0 \nabla \cdot \vec{v}_\omega / i\omega, \quad (20)$$

$$-i\omega\rho_0\vec{v}_\omega = -C^2(\rho_0/i\omega)\nabla\nabla \cdot \vec{v}_\omega + \eta\nabla^2\vec{v}_\omega + (\frac{1}{3}\eta + \eta_v)\nabla\nabla \cdot \vec{v}_\omega. \quad (21)$$

Equation (21) now contains only the fluid velocity.

For convenience we divide through by ρ_0 and then introduce the two kinematic viscosities

$$\nu_t = \eta/\rho_0, \quad \nu_l = (\frac{4}{3}\eta + \eta_v)/\rho_0. \quad (22)$$

Next, we multiply through by $i\omega$ and introduce two complex frequency-dependent sound velocities C_l and C_t ,

$$C_l^2 = C^2 - i\omega\nu_l, \quad C_t^2 = -i\omega\nu_t. \quad (23)$$

By means of a standard vector identity, we separate the Laplacian into its longitudinal and transverse parts. After all this, Eq. (21) becomes

$$\omega^2\vec{v}_\omega + C_l^2\nabla\nabla \cdot \vec{v}_\omega - C_t^2\nabla \times \nabla \times \vec{v}_\omega = 0. \quad (24)$$

Now the problem is to solve this vector Helmholtz equation with appropriate boundary conditions.

The sphere moves with velocity

$$\vec{U}(t) = \vec{U}_\omega e^{-i\omega t}. \quad (25)$$

Strictly speaking, the boundary conditions apply on the surface of the moving sphere; but as a result of linearization, we may safely use the boundary conditions on the surface of a stationary sphere, fixed at the origin. As was mentioned earlier, the boundary conditions have several parts. First, the fluid velocity vanishes at infinity. Second, the normal component of the relative velocity of sphere and fluid vanishes on the surface,

$$(\vec{v} - \vec{U}) \cdot \vec{a}_R = 0, \quad (26)$$

where \vec{a}_R is a unit vector normal to the surface of the sphere. The third condition is concerned with the degree of slip or stick at the surface. A commonly used assumption here is that the tangential component of the relative velocity of sphere and fluid is proportional to the tangential component of the force exerted on the sphere by the fluid. If \vec{a}_θ is a unit vector tangential to the surface of the sphere, and $\vec{\sigma}$ is the stress tensor, this proportionality is expressed as

$$\vec{a}_R \cdot \vec{\sigma} \cdot \vec{a}_\theta = (\beta/a)(\vec{v} - \vec{U}) \cdot \vec{a}_\theta, \quad (27)$$

where β is a coefficient of slip. Two extreme cases are $\beta = 0$, which corresponds to perfect slip, and

$\beta = \infty$, which corresponds to perfect stick. (In the latter case, if the force on the sphere is to remain finite, the tangential component of the relative velocity must vanish. Thus all components of \vec{v} and \vec{U} are identical.)

The stress tensor $\vec{\sigma}$ is

$$\vec{\sigma} = -P\vec{I} - (\frac{2}{3}\eta + \eta_v)\nabla \cdot \vec{v}\vec{I} + \eta(\nabla\vec{v} + \vec{v}\nabla). \quad (28)$$

The total force on the sphere is

$$\vec{F}_\omega = \oint d\Omega \vec{a}_R \cdot \vec{\sigma}. \quad (29)$$

On integration, any constant part of the pressure does not contribute to the surface integral, so that we can replace P by $C^2\delta\rho$. Also, Eq. (20) allows us to eliminate the pressure entirely, leaving

$$\vec{\sigma} = -[(\rho_0 C^2/i\omega) + \frac{2}{3}\eta + \eta_v]\nabla \cdot \vec{v}\vec{I} + \eta(\nabla\vec{v} + \vec{v}\nabla). \quad (30)$$

The viscosity coefficients are still complex functions of frequency.

Equation (24) is a vector Helmholtz equation with spherical boundary conditions, and can be solved easily by means of vector spherical harmonics. We follow the notation of Morse and Feshbach.⁶ In the solution, it is convenient to define two propagation constants

$$k_l^2 = \omega^2/C_l^2, \quad k_t^2 = \omega^2/C_t^2. \quad (31)$$

Then a general solution of the vector Helmholtz equation is any linear combination of the three vector harmonics \vec{L} , \vec{M} , and \vec{N} , which are given in terms of spherical Hankel functions $h_n(x)$ and spherical harmonics,

$$\begin{aligned} \vec{L}_{\sigma mn} &= k_l^{-1} \nabla [Y_{\sigma mn} h_n(k_l R)], \\ \vec{M}_{\sigma mn} &= \nabla \times [\vec{R} Y_{\sigma mn} h_n(k_l R)], \\ \vec{N}_{\sigma mn} &= k_t^{-1} \nabla \times \vec{M}_{\sigma mn}. \end{aligned} \quad (32)$$

Then the general solution takes the form

$$\vec{v} = \sum (A_L \vec{L} + A_M \vec{M} + A_N \vec{N}) U, \quad (33)$$

where A_L , A_M , and A_N are arbitrary constants.

In taking the square roots of Eq. (31) to get the propagation constants, we must choose signs so that e^{ikR} decays exponentially for large R . In this way, the boundary condition at infinity is satisfied automatically.

The direction of the velocity \vec{U} of the sphere is taken as the z axis for the spherical harmonics. By symmetry, we do not expect any components in the \vec{a}_θ direction in spherical coordinates. Thus, the \vec{M} contribution to the solution must vanish, or $A_M = 0$. In order to fit boundary conditions on the surface of the sphere, only the harmonics \vec{L}_{01} and \vec{N}_{01} can occur. So the most general solution satisfying the boundary conditions is

$$\vec{v} = (A_L \vec{L}_{01} + A_N \vec{N}_{01}) U, \quad (34)$$

where A_L and A_N remain to be determined.

For simplicity of notation, we denote the longitudinal and transverse Hankel functions by

$$h_{nt} = h_n(k_t R), \quad h_{nt} = h_n(k_t R). \quad (35)$$

Then, on applying the boundary conditions (26) and (27), we obtain

$$\begin{aligned} A_L &= (h_{2t})^{-1} A_N [h_{2t} - k_t a h_{1t} / (\beta + 2)], \\ A_N &= 3h_{2t} [h_{0t} h_{2t} + 2h_{0t} h_{2t} \\ &\quad + k_t a h_{1t} (2h_{2t} - h_{0t}) / (\beta + 2)]^{-1}. \end{aligned} \quad (36)$$

The force on the sphere is determined by Eq. (29). After integration over angles, we obtain the generalized friction coefficient

$$\begin{aligned} \zeta(\omega) &= [\eta k_t^2 / k_t^2 - 2\eta_v] (\frac{1}{3} 4\pi a) k_t a h_1(k_t a) A_L \\ &\quad + (\frac{1}{3} 4\pi a) 2\eta k_t a h_1(k_t a) A_N. \end{aligned} \quad (37)$$

This solves the problem of calculating Stokes's friction for arbitrary degree of slip, compressibility, and viscoelasticity.

The solution just obtained can be shown to reduce to previously known results in all the standard limiting cases, e.g., incompressibility (or infinite sound velocity), perfect slip or stick, and constant viscosity.

The relation between the velocity correlation function and the frequency-dependent friction coefficient can be found in several ways. The simplest is to use analogy with earlier results. In our discussion of the standard Stokes-Einstein theory, we found that the velocity correlation function decays exponentially. Thus the Fourier representation of the velocity correlation function is

$$\langle U_x(0) U_x(t) \rangle = \frac{2}{\pi} \operatorname{Re} \int_0^\infty d\omega \cos \omega t \frac{m \langle U_x^2 \rangle}{-i\omega m + \zeta}. \quad (38)$$

This suggests that the appropriate generalization is simply to replace the constant ζ by the frequency dependent $\zeta(\omega)$,

$$\langle U_x(0) U_x(t) \rangle = \frac{2}{\pi} \operatorname{Re} \int_0^\infty d\omega \cos \omega t \frac{m \langle U_x^2 \rangle}{-i\omega m + \zeta(\omega)}. \quad (39)$$

All subsequent calculations will be based on this formula.

It may be of some interest to note that the preceding result can be expressed also in a memory function form.⁷ The equation of motion of the velocity correlation function is

$$m \frac{d}{dt} \langle U_x(0) U_x(t) \rangle = - \int_0^t ds K(t-s) \langle U_x(0) U_x(s) \rangle, \quad (40)$$

where the memory kernel is related to the frequency-dependent friction coefficient by a one-sided Fourier transform,

$$\zeta(\omega) = \int_0^\infty dt K(t) e^{i\omega t}. \quad (41)$$

The memory-function approach is fully equivalent to the one followed here.

LIMITING BEHAVIOR

It is difficult to carry this calculation further because of the complexity of the formulas. However, some information can be extracted from limiting behavior.

The velocity correlation function is a cosine transform of a frequency spectrum. For very high frequencies, the spectrum is asymptotically

$$\operatorname{Re} [1 / -i\omega m + \zeta(\omega)] \sim (1/\omega^2) + \dots \quad (42)$$

In consequence, the short-time behavior of the velocity correlation function is

$$\langle U_x(0) U_x(t) \rangle \sim a - bt + \dots \quad (43)$$

Because the velocity correlation function is even in time, its graph has a *cusp* at $t=0$. Any correct molecular theory will predict instead a parabolic behavior at $t=0$. The reason for this discrepancy is that the present theory does not correctly describe the local interaction of the moving sphere with its environment. In a correct theory, this interaction is mediated by smooth intermolecular forces; in the present theory, the interaction is introduced by imposing a boundary condition at the surface of the sphere.

At very low frequencies, the frequency spectrum approaches

$$\operatorname{Re} [1 / -i\omega m + \zeta(\omega)] \sim a' - b' \sqrt{\omega} + \dots \quad (44)$$

The long-time behavior of the velocity correlation function is asymptotically

$$\langle U_x(0) U_x(t) \rangle \sim t^{-3/2} + \dots \quad (45)$$

It should be noted that this result is a consequence of ordinary hydrodynamics, and has nothing to do with compressibility or viscoelasticity. As has been observed already by Alder and Wainwright³ who used dimensional arguments, it is connected with the penetration depth of the velocity field due to unsteady motion of a sphere.

NUMERICAL RESULTS

To conclude this discussion we present a numerical comparison of results obtained from the hydrodynamic theory and results obtained by Rahman from computer experiments.⁸ Our procedure is to calculate the friction coefficient numerically for some reasonable set of parameters, and then to invert the Fourier transform numerically.

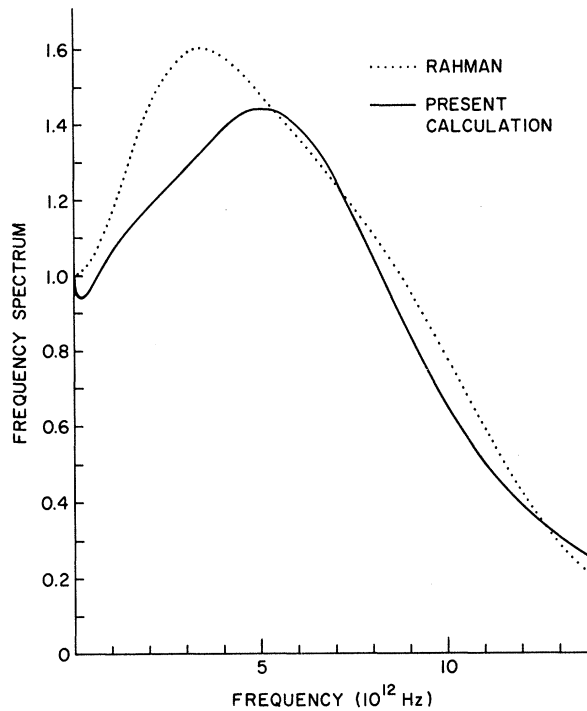


FIG. 2. Frequency spectrum of velocity correlation function, normalized to unity at zero frequency. Dotted curve is Rahman's data; solid curve is our calculation.

The mass of the sphere is set equal to the mass of a single argon atom. The radius of the sphere, appearing many places in $\zeta(\omega)$, is found from the temperature, diffusion coefficient, and shear viscosity.

The fluid is characterized by its sound velocity, diffusion coefficient, and viscoelastic behavior. For the latter, we use the Maxwell approximations

$$\eta(\omega) = \eta_0 / (1 - i\omega\tau), \quad \eta_l(\omega) = \eta_{l0} / (1 - i\omega\tau_l), \quad (46)$$

for both shear viscosity $\eta(\omega)$ and longitudinal viscosity $\eta_l(\omega)$. Thus, we have to know two zero-frequency viscosity coefficients and two relaxation times. (There does not seem to be any advantage at present in using a more detailed description of viscoelastic relaxation, e.g., with a distribution of relaxation times.)

The numerical calculations reported here were based on the following set of parameters:

Temperature T	= 76 K;
Density ρ	= 1.41 g/cc;
Diffusion coefficient D	= $1.63 \cdot 10^{-5}$ cm ² /s;
Sound velocity C	= $6 \cdot 10^4$ cm/s;
Shear viscosity η_0	= $2.8 \cdot 10^{-3}$ P;
Longitudinal viscosity η_{l0}	= $5.5 \cdot 10^{-3}$ P;
Shear relaxation time τ	= $2.0 \cdot 10^{-13}$ s;
Longitudinal relaxation time τ_l	= $1.8 \cdot 10^{-13}$ s;
Sphere radius a (slip)	= 1.83 Å;
Sphere radius a (stick)	= 1.22 Å.

T , ρ , and D are provided by the computer experiment on the velocity correlation function. The sound velocity was fixed by the long-wavelength limit of the liquid structure factor $S(k)$ obtained from the same computer experiment.

The viscoelastic parameters were found as follows. First, we selected values that appeared reasonable from an analysis by Ailawadi, Rahman, and Zwanzig⁹ of current-current correlation functions for the same system. Then we made small variations in these values in order to get a good fit of the first minimum in our velocity correlation function to the first minimum in Rahman's curve. We emphasize that our results are qualitatively insensitive to these variations; the parameters are all entirely reasonable ones. Order-of-magnitude changes in the parameters lead to substantially poorer agreement.

The frequency spectrum (with slip),

$$\sigma(\omega) = \text{Re}[k_B T / -i\omega m + \zeta(\omega)] \quad (47)$$

obtained with the above parameters is compared with Rahman's in Fig. 2. The dotted line is Rahman's curve; the solid line is ours.

Note in particular the small dip in our curve at very low frequency. If this were present in Rahman's computer experiment, it could not be seen because of the limited time scale available to him. This dip has an interesting practical consequence. Suppose that we are able to determine the spectrum only for frequencies larger than, e.g., 10^{12} Hz. Then we would not see the dip at all. On extrapolation to zero frequency, we would then estimate a diffusion coefficient that is about 10% smaller than the correct value. In other words, the very-long-time behavior of the velocity correlation function can contribute substantially to the diffusion coefficient. This observation was made also by Alder and Wainwright.³

The presence of the dip suggests that the correct self-diffusion coefficient in Rahman's computer experiment may be about 10% larger than the value used here. If we repeat our calculations with this revised value of D , the only significant change is that our frequency spectrum is raised everywhere by about 10%. The shape of the resulting velocity correlation function is essentially unchanged.

If all other parameters are kept the same and the sound velocity is increased substantially, e.g., by a factor of 3, this low-frequency dip is accentuated. Then the spectrum resembles qualitatively the spectrum of a velocity correlation function in a liquid metal.¹⁰

The results shown in Fig. 2 are for the slipping boundary condition. When this is replaced by the sticking boundary condition, and all parameters are kept the same, the spectrum is modified only

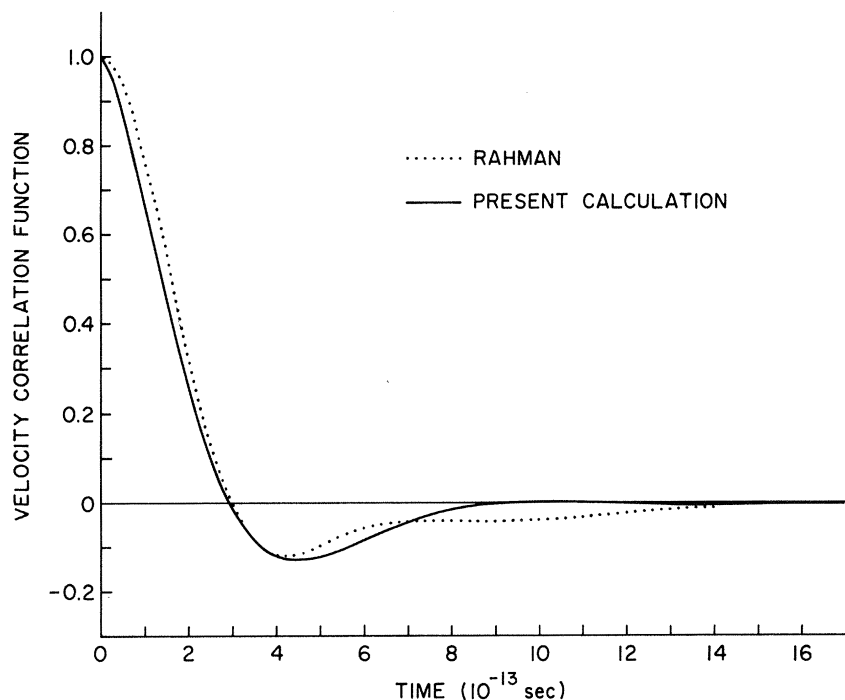


FIG. 3. Velocity correlation function, normalized to unity at zero time. Dotted curve is Rahman's data; solid line is our calculation.

slightly. The peak shifts to a frequency about 20% lower; at very high frequencies, the spectrum decreases more slowly. We feel that better results are obtained with slip, but the differences are small.

On Fourier inversion (performed numerically using the fast-Fourier-transform program), we obtain the velocity correlation functions shown in Fig. 3. Again the dotted line is Rahman's curve, and the solid one is ours. There are two main regions of discrepancy. One is at very short times,

where our curve shows a linear decay in time, rather than the correct parabolic decay. This is, as pointed out already, due to our use of a boundary condition instead of an intermolecular force to describe the interaction of the sphere with its environment. The other discrepancy is in the neighborhood of Rahman's second minimum. We suspect that this can be corrected by using a more detailed description of the viscoelastic relaxation of the fluid; but it does not seem to be worthwhile to do so at present.

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⁵See J. Frenkel, *Kinetic Theory of Liquid* (Oxford U.

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⁷See Berne, Boon, and Rice, Ref. 2.

⁸We are grateful to Dr. A. Rahman for providing the numerical data used here.

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¹⁰P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, New York, 1967). We are indebted to Dr. Egelstaff for calling to our attention to the possible relevance of our results to liquid metals.