Generalized hydrodynamics

Efforts to extend ordinary linear hydrodynamics to the microscopic scale have succeeded in predicting, under certain conditions, corrections to Stokes Law and the form of the neutron scattering function.

Berni J. Alder and W. Edward Alley

The object of generalized hydrodynamics is to extend from the macroscopic scale to the microscopic scale the domain in which ordinary hydrodynamics applies. With this extension, under well-defined conditions, we will then, among other things, be able to predict the momentum with which neutrons are scattered at various angles by the fluid; neutron scattering is one of the principal methods by which the dynamic structure of fluids is investigated experimentally.

Ordinary hydrodynamics is described by the Navier–Stokes equations, which contain the conservation laws of mass, momentum and energy, supplemented by the empirical constitutive relations that define the transport coefficients as the proportionality constants between the gradients of temperature and velocity and their corresponding fluxes. Generalized hydrodynamics retains the form of the Navier–Stokes equations (that is, the conservation laws and the constitutive relations), but the transport coefficients are allowed to depend on the range over which the gradients are applied and the duration over which they last. In this way, we introduce distance and time scales into ordinary hydrodynamics and are then able to go beyond the continuum approximation into the regime where the molecular structure of the fluid plays a role.

Such a theory should be exact on the molecular scale, provided one defines the generalized transport coefficients properly. However, there are two major restrictions on generalized hydrodynamics; both are also limitations on ordinary hydrodynamics. One is that the system be large compared to the mean free path, otherwise boundary effects and free-streaming (transport before the first collision) effects dominate the flow. Similarly, the time scale has to be longer than a few collisions per particle so that local equilibrium conditions prevail and so that again free streaming is not the major means of transport. The other restriction is that the gradients are not so steep that the linear relations defining the transport coefficients are violated. Thus, for example, generalized hydrodynamics is not able to deal with situations in which shocks occur, although it is able to describe sound waves, including their speed, their attenuation and their bandwidth, no matter what their wavelength and frequency, subject only to the limitations cited above.[1] Thus, the application of generalized hydrodynamics to any real situation is primarily a test of the validity of the linear approximation.

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Given such generalized transport coefficients, the question then becomes how to measure them and how to predict them theoretically. In principle, a measurement would be straightforward. For example, the generalized viscosity could be obtained from a standard viscometer, in which the fluid is confined in an annular space between two concentric cylinders, one of which executes rotational oscillations. The viscosity would then be measured by the damping of the oscillations as a function of the size of the annular space and the frequency of oscillation. This method is impractical, however, because the spatial and temporal dependence of the viscosity is not significant for an ordinary liquid unless the annular space is exceedingly small and the frequency of rotational oscillation is exceedingly high. Thus we have to consider theoretically when the ordinary hydrodynamic concept of a constant viscosity breaks down.

Continuum approximation

Until recently, the time scale relevant in hydrodynamics was thought to be vastly separated from the other two natural time scales in a liquid, namely the duration of a collision between molecules and the time between collisions (kinetic time scale). The duration of a collision depends somewhat on its definition and on the interatomic potential that describes the interaction between the molecules, but in general it is of the order of 10^{-15} sec. For hard spheres, with which we will deal here, a collision is instantaneous. The time between collisions for a typical liquid, such as water, is about 10^{-14} sec, and this is the time scale for which kinetic theory is relevant (see the article by E. G. D. Cohen, page 64). Kinetic theory has difficulty dealing with repeated collisions that lead to correlations with previous collision partners. These correlations are ignored in the simplest version of kinetic theory, which is based on the molecular chaos approximation. For short times (that is, a few collision times), these correlations can be neglected because recollisions with previous collision partners do not have time to occur.

The hydrodynamic time scale, on the other hand, was thought to be orders of magnitude greater than the kinetic time scale and completely decoupled from it. This belief was reexamined as a result of computer simulations that showed that in some instances ordinary hydrodynamics quantitatively applies down to times only an order of magnitude greater than the kinetic time scale, namely about 30 collision times or 10^{-13} sec. This result was first established through a quantitative explanation of the "long-time tail" of the velocity autocorrelation function at intermediate fluid densities by a hydrodynamic calculation.[2] The term "long-time tail" arises from the observation that the velocity of a particle is positively correlated with its initial velocity even after many hundreds of collisions. This persistence of correlations in velocity is described by a power-law decay in time. Before this observation, an exponential time dependence was expected because it was thought that after a sufficiently long time had elapsed, velocity correlations would die out and the molecular chaos approximation could be applied. Although the

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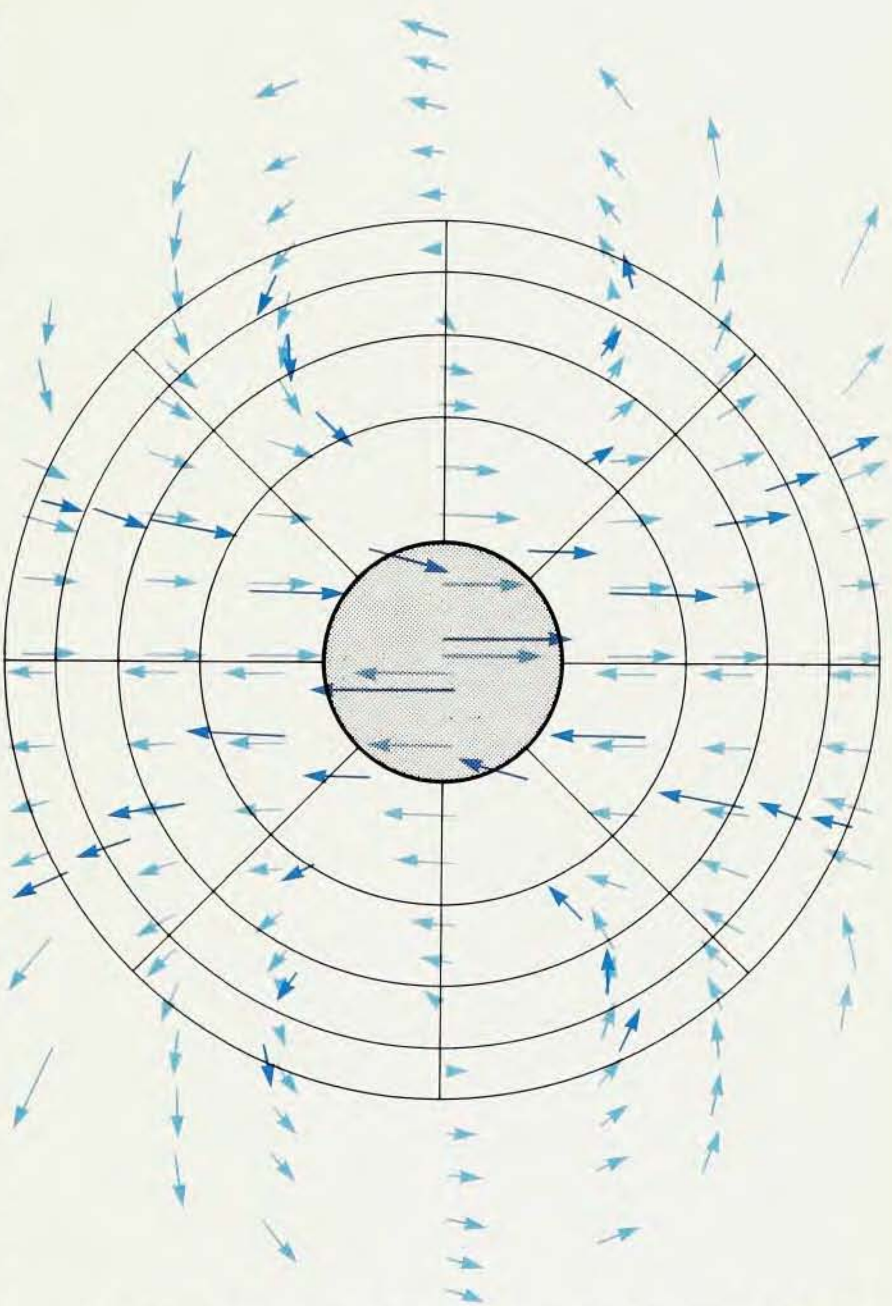
observations of the power-law decay led to a fundamental reexamination of the theory by which transport coefficients are calculated (a reexamination not yet completed), we believe that the primary significance of the long-time tail is that hydrodynamics applies at very short times and distances.

The hydrodynamic model by which the long-time tail was calculated treats the motion of a sphere with a given initial velocity through a continuum liquid (initially at rest, and characterized by a viscosity and compressibility). Over a hundred years ago, George Gabriel Stokes knew that this model leads to a long-time tail; however, no one dared to contemplate applying hydrodynamics to a sphere of the size of an atom. In figure 1 we show the correlated velocity field around an atom after about ten collisions according to computer simulation and the corresponding hydrodynamic calculation. In the computer simulation, usually referred to as molecular dynamics, the trajectory of each hard sphere is calculated by solving the simultaneous Newtonian equations of motion for all spheres. The atomistic and the fluid-dynamic calculations of the vortex are in quantitative agreement (as seen in figure 1) after the vortex has spread only over three molecular diameters after ten collisions. This vortex feeds the velocity of any particle back into itself via the medium and leads to the long-time correlations.

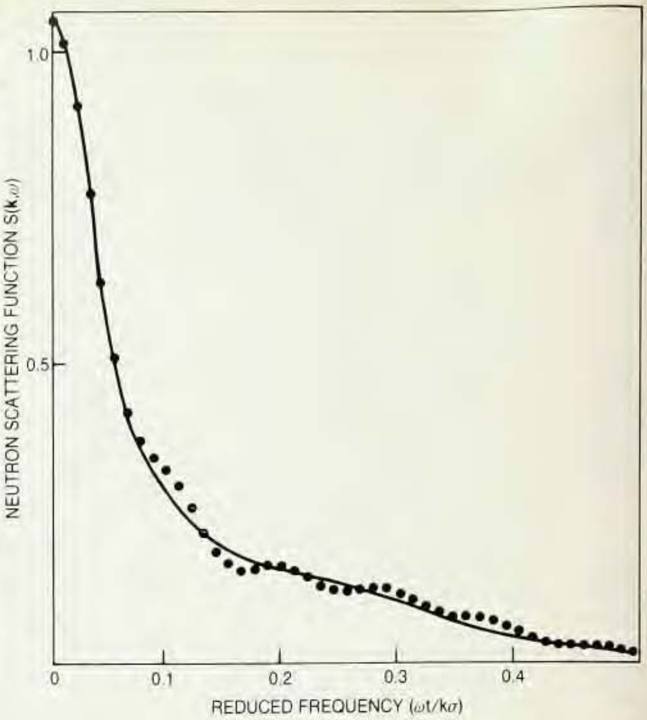
The distance scale of three molecular diameters to which ordinary hydrodynamics seems to apply in the above example is not surprising. It has been long known from the distribution of distances between particles in a liquid (determined by x-ray or neutron diffraction measurements) that only the first few neighboring shells can be identified by their above-average density. Beyond about three neighbors, the fluid can be considered a continuum characterized by its average density. These considerations indicate that conventional experimental measurements of transport coefficients cannot be extended into this regime to obtain the generalized transport coefficients. Instead, one must analyze the naturally occurring fluctuations in a liquid.



Velocity correlation between a central particle and its neighboring particles after the central particle has undergone about ten collisions. The size of the central particle is shown by the shaded circle and its velocity by the dark arrow near its center. The other dark arrows are of a size to indicate the velocity average (as obtained by molecular dynamics) of whatever neighboring particles are found in that section of space, shown at the center of the section. The dark arrows are to be compared with the light arrows, which are obtained from a hydrodynamic solution of the velocity field on a rectangular grid for the identical physical situation. Figure 1

Fluctuations

Fluctuations in a liquid occur at all wavelengths and frequency scales. Our task is to decompose the decay of the various fluctuations into wavelength- and frequency-dependent transport coefficients. To be sure, the fluctuations also have an amplitude, which should also be analyzed and which would lead to the determination of nonlinear transport coefficients. However, this task is much more complex and is just beginning (see the article by R. Bryon Bird and Charles F. Curtiss, page 36, and reference 3). We will, therefore, confine ourselves to small-amplitude fluctuations that can be described by the linear fluctuation–dissipation theory. The only fluctuations of this kind directly accessible to experiment are the density fluctuations revealed by x-ray or light-scattering experiments. The spectrum of these fluctuations is characterized by a central peak (called the Rayleigh peak) and two equally and oppositely spaced peaks (called the Brillouin peaks).



Neutron scattering function for a hard-sphere fluid at a density corresponding to a ratio of volume to close-packed volume, $V/V_0 = 1.6$, and a wavenumber $k = 0.76/\sigma$ (where σ is the hard-sphere diameter) versus angular frequency ω times the mean collision time t divided by $k\sigma$. The circles are the molecular dynamics results for 500 hard spheres and the solid line denotes wavelength-dependent hydrodynamics. Figure 2

Because the wavelength of light is roughly 1000 molecular diameters, one can accurately predict (as expected from the above considerations) with ordinary hydrodynamics the spectrum that will be obtained by means of light scattering. It is well known that the separation in frequency between the Rayleigh and Brillouin peaks is given by the product of the sound speed and the change in the wavenumber of the scattered light; the width of the Brillouin peaks is determined by the viscosity, while that of the Rayleigh peak is determined by a combination of transport processes involving the bulk viscosity and the thermal conductivity. If, on the other hand, the spectrum is determined by scattering neutrons with wavelength of the order of a molecular diameter, the Rayleigh and Brillouin peaks merge (see figure 2). Ordinary hydrodynamics does not correctly describe the spectrum, but generalized hydrodynamics should. In fact, we will use this spectrum to determine the generalized transport coefficients.

To determine all the generalized transport coefficients directly we must know not only the spectrum of the density fluctuations but also the spectra of the other conserved quantities, namely the energy and the transverse momentum. These spectra can readily be determined from molecular dynamics simulations. We shall illustrate the procedure for evaluating the generalized viscosity.

We choose to deal with the viscosity for two reasons. The first is that the methodology is simplest because the transverse momentum is decoupled from all the other transport processes, and yet the principle is the same as for all the other transport coefficients. Furthermore, in evaluating the other generalized transport coefficients, generalized thermodynamic properties—such as how the sound speed or the compressibility depend on wavelength—must also be known. This dependence can be experimentally determined from the separation in frequency of the Rayleigh and Brillouin peaks divided by the wavenumber. This ratio leads to a constant sound speed only at large wavelength. Of course, thermodynamic properties, being equilibrium properties, cannot depend on time or frequency.

The second reason for dealing with the viscosity is that its generalization allows us to deal with viscoelastic effects, which are the most important manifestation of the wavelength and frequency dependence of transport coefficients. The other transport coefficients are relatively insensitive to the structure of the liquid; their wavelength and frequency dependence can, therefore, be well predicted (for hard spheres) by kinetic theory under the molecular chaos approximation.

Generalized viscosity

The viscosity is defined through the constitutive law, which we write, for convenience, in Fourier space, that is referring to wavenumbers rather than positions:

$$\frac{\partial}{\partial t} J_k{}^T = -k^2 \nu J_k{}^T \qquad (1)$$

where k is the Fourier transform wavenumber variable, $J_k{}^T$ is the Fourier transform of the transverse momentum current, and ν is the kinematic viscosity (that is, the shear viscosity, η, divided by the density). The wavenumber and wavelength, λ, are reciprocally related to one another: $k = 2\pi/\lambda$. Equation 1 is of the well-known diffusion type. For a constant, positive viscosity, the equation can be integrated, yielding

$$J_k{}^T(t) = J_k{}^T(0)\,e^{-k^2\nu t} \qquad (2)$$

that is, an always positive, exponentially decaying transverse momentum current. However, as figure 3 illustrates, the transverse momentum current as determined by computer simulation agrees with this prediction only at long wavelengths (small wavenumber). At shorter wavelength, the ordinary hydrodynamic prediction breaks down, and the transverse momentum currents becomes negative (corresponding to shear-wave propagation). This is a manifestation of viscoelastic behavior, in which the medium on the average reverses the initial transverse momentum fluctuation, as it would if it were a solid. Thus we conclude that a hard-sphere fluid at sufficiently high density and sufficiently short wavelength can propagate shear waves.

To describe this negative region of the transverse momentum current (if, as we proposed, we insist on maintaining the form of the constitutive law) we can no longer keep the viscosity constant, but must make it depend on wavelength and frequency. In fact, the wavelength and frequency dependence of the viscosity is simply determined by inverting equation 1, using the numerically obtained transverse momentum current at several wavelengths. The result is shown in figure 4 for the zero-frequency case. We observe that the viscosity drops by an order of magnitude from its constant hydrodynamic value when the wavelength is equal to the nearest-neighbor distance, that is, when $k\sigma = 2\pi$. Furthermore, the wavelength dependence of the viscosity is weak beyond about three molecular diameters, that is for $k\sigma < 2$. This is consistent with previous discussions. As shown in figure 4, kinetic theory predicts the constant hydrodynamic viscosity rather poorly because it ignores collective effects. However, for wavelengths comparable to the diameter of a molecule, such spatial correlations can be neglected and the kinetic theory becomes quantitatively correct. An improvement on the kinetic theory that takes some of the collective effects into account,[4] called the mode-coupling theory, leads to considerably better agreement, as indicated in figure 4.

Stokes's Law

As an application of this generalized viscosity, we now discuss corrections to Stokes's law, describing the friction experienced by a sphere moving through a fluid when the sphere is of molecular dimensions. Stokes calculated the friction ξ of a macroscopic sphere of radius R moving through a fluid of viscosity η to be $\xi = 6\pi\eta R$, when "stick" boundary conditions (to be discussed later) apply. It has also been long known from measurements of the diffusion coefficient, D, either self-diffusion or diffusion of a foreign molecule in liquids, that Stokes's law makes a nearly correct quantitative prediction of the friction coefficient using the Einstein relation $\xi = k_B T/D$, where k_B is Boltzmann's constant and T is the absolute temperature, even though the conditions for which the Stokes–Einstein relations are derived are grossly violated. In the molecular diffusion process, as opposed to the macroscopic mdoel, the moving object is not large compared to the molecules of the fluid, nor is it much more massive. The latter condition is needed so that the momentum changes of the sphere are small on a collisional time scale, making linear hydrodynamics a valid approximation. Another problem is the relevance of a hydrodynamic boundary condition on a molecular scale.

To isolate the problem of how the friction coefficient depends on size, we determined the friction coefficient of an infinitely massive sphere immersed in a fluid of hard spheres. The use of elastic collision dynamics corresponds to "slip" boundary conditions. We calculated the friction coefficient from its defining expression as a force autocorrelation function by computer simulation and also using generalized hydrodynamics, as shown in figure 5. The generalized hydrodynamic calculation repeats that of Stokes except that the generalized viscosity is introduced in the empirical form

$$\eta(k)/\eta(0) = (1 + a^2k^2)^{-1} \qquad (3)$$

This equation fits the data given in figure 4 well at small values of k. The straight line in figure 5 is the theoretical prediction for the above form of the generalized viscosity, namely

$$\xi/4\pi\eta\sigma_{12} = 1 - a/\sigma_{12} \qquad (4)$$

where σ_{12} is the average diameter of the massive sphere and the solvent spheres. Had we fitted the generalized viscosity more accurately, we would have obtained, as expected, perfect agreement with the computed friction coefficient down to the smallest massive sphere investigated (one the same size as the solvent). The crucial fact is that the friction coefficient drops only by about 40% for a sphere of the size of the solvent relative to a much larger sphere. In other words, a, the characteristic length that has been introduced into hydrodynamics via the generalized viscosity, is of the order of the molecular size. For dense hard spheres, a/σ_{12} is even smaller than unity (it is 0.3) and this provides numerical evidence that ordinary hydrodynamics is applicable at near-molecular dimensions.

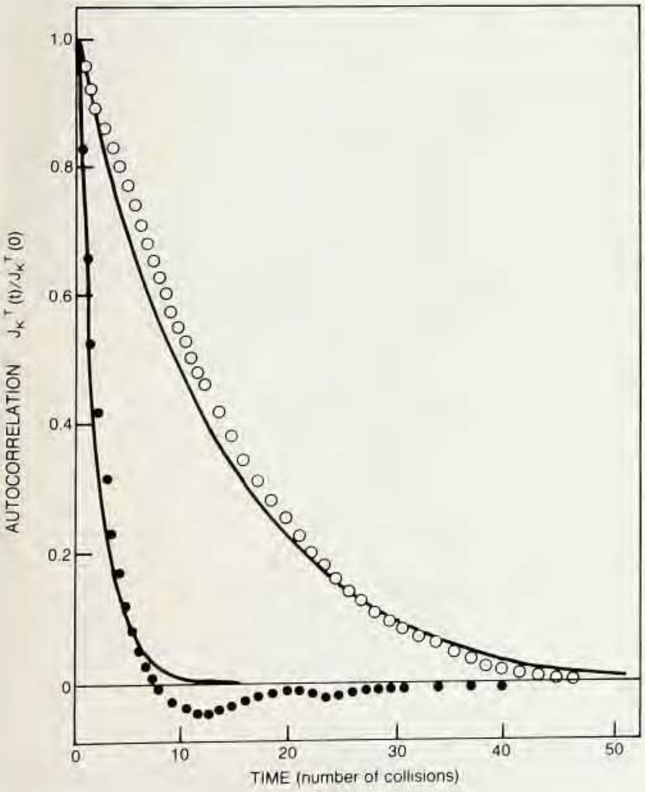
Boundary conditions

Solving the generalized hydrodynamic equations for a particular physical situation, such as the flow of a fluid through microscopic pores or the interpretation of picosecond spectroscopic experiments, is in general a difficult mathematical or numerical task because the introduction of wavelength- and frequency-dependent transport coefficients leads to a response that is non-local in both time and space. In other words, the fluid, through the generalized viscosity—expressed in real space and time variables, $\eta(\mathbf{r} - \mathbf{r}', t - t')$, as opposed to wavenumber and frequency variables, to make it more explicit—has acquired a "memory"—a signal generated at a location $\mathbf{r}'$ at a time t' has a delayed effect at a time t at another location $\mathbf{r}$. This delay reflects the fact that a fluid cannot respond instantaneously to a change induced by a fluctuation, because it takes time for atoms to rearrange themselves.

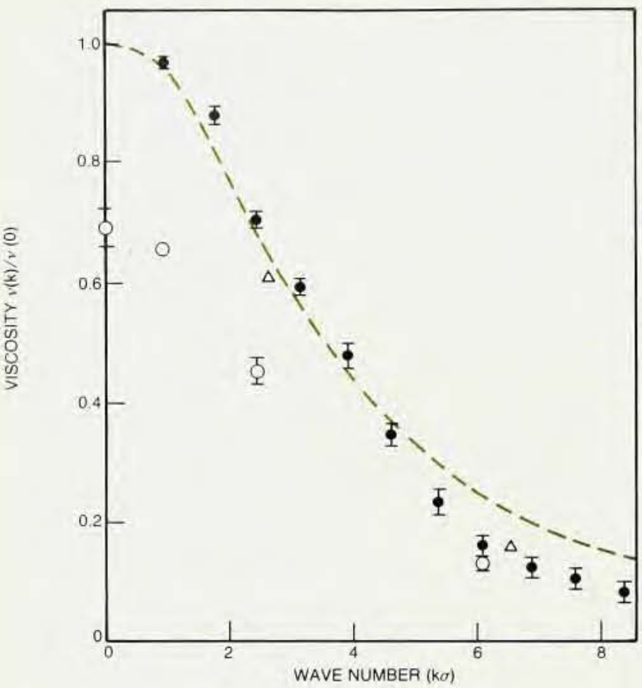
A further complication arises when one applies generalized hydrodynamics on a molecular scale in the specification of the appropriate boundary conditions. We require a molecular interpretation of the degree of "stickiness," which in the Stokes problem means how much of the incoming momentum of a solvent particle tangent to the surface of the massive object is randomized in the collision process. The extreme cases of slip and stick boundary conditions correspond to elastic and completely randomizing collisions, respectively, and lead to a 4π and a 6π numerical factor in Stokes's law. We were able to carry out a molecular dynamics simulation of the friction on an aggregate object which is, on the average, spherical. The infinitely massive object is made up of representative members of an ensemble of little spheres of the same size and number density as the solvent, frozen in position. The numerical factor in Stokes's law, as shown in figure 5, is found to be approximately 5π, which is between the limits given above. A detailed analysis of such simulations for how the momentum transfer depends on the surface roughness of objects relative to the wavelength of the fluctuations will have to be carried out before accurate macroscopic boundary conditions can be specified on a microscopic scale.

Nonlinear effects

We must also account for the nearly quantitative validity of Stokes's law in practical situations (for instance, diffusion in a mixture of liquids) even though the mass of the object is comparable to that of the solvent molecules. Under these circumstances, the momentum change of the objects is large in a typical collision and a linear theory is inapplicable. The nonlinear theory by which one might evaluate the mass corrections to Stokes's law has



Transverse current autocorrelation function (normalized) for a hard-sphere fluid at a density corresponding to $V/V_0 = 1.6$ and for wavenumbers $k\sigma = 0.76$ (open circle) and $k\sigma = 2.28$ (closed circle). The circles are the molecular dynamics calculation and the solid lines represent the corresponding wavelength-dependent hydrodynamics calculations. Figure 3



Normalized viscosity at zero frequency as a function of wavenumber at $V/V_0 = 1.6$. The molecular-dynamics results (closed circles) and the kinetic-theory results (open circles) are compared to the results of a mode-coupling calculation[4] (colored line). Error bars are indicated. The dashed curve represents an empirical low-wavenumber fit. Figure 4

not been satisfactorily worked out. Not only is the nonlinear theory difficult in itself, but an additional complication arises because the correction is apparently nonanalytic in the mass—that is, the corrections cannot be expressed in a power series of the ratio of the mass of the solvent molecule to that of the object. This is true for the same reason that all transport coefficients are nonanalytic in any of their dependences (such as on wavelength, frequency, temperature or density), namely, the existence of the long-time tail or long memory effects. Thus, equation 3, analytic in its wavelength dependence for the viscosity, cannot be strictly correct, even though it fits the data very well overall. Hence, typically, the nonanalytical contributions are quantitatively not very significant. As an example, the long-time tail for the velocity autocorrelation function has yet to be observed because the effects are so weak. Similarly, in spite of all these complications, we find empirically that the mass corrections to Stokes's law are small. Furthermore, the literature contains an amusing cancellation of errors that makes it appear that Stokes's law is nearly exact for a sphere of the same size and mass as the solvent molecules. Figure 5 shows that $\xi/4\pi\eta\sigma_{12} = 0.60$ for an infinitely massive sphere of the same size as the solvent ($\sigma_2/\sigma_{12} = 1$). Through a self-diffusion calculation it is easy to establish that $\xi/4\pi\eta\sigma_{12} = 0.52$ for the equal-mass sphere, so that the mass correction is only about 10%. If the radius of the object is now mistakenly used in the above formula instead of the diameter (doing this is valid only if the object is large compared to the solvent), the erroneous factor of 2 compensates for the deviations from Stokes's law.

Divergences

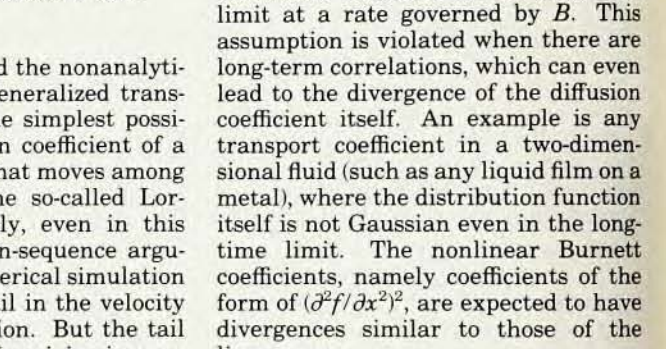
We have established the nonanalytical behavior of the generalized transport coefficients in the simplest possible case—the diffusion coefficient of a single point particle that moves among stationary objects, the so-called Lorentz gas. Surprisingly, even in this instance both collision-sequence arguments and direct numerical simulation predict a long-time tail in the velocity autocorrelation function. But the tail is not of hydrodynamic origin since no correlations can develop in the stationary medium. The long-lived velocity correlation again decays as a power law but with a negative coefficient, signifying a higher-than-random probability that the moving particle will return to its orgin. Specifically, the velocity autocorrelation function $\rho(t)$ of the point particle moving through randomly placed hard disks of radius R at low density decays as $-n^*/\pi t^2$, where n^* is the reduced density, NR^2/A, and A is the area of the system containing N scatterers. The divergence arises in the first linear Burnett coefficient whose autocorrelation functions can be shown by dimensional arguments and by numerical simulation to be of one higher power in time than that of the diffusion coefficient. Thus, the autocorrelation function behaves asymptotically as $1/t$ and the Burnett coefficient, which is the time integral of the autocorrelation function, diverges.[5]

The Burnett coefficient B measures the initial spatial or wavelength dependence of the diffusion coefficient D away from the hydrodynamic limit, and is defined through the correction to Fick's law of diffusion by

$$\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2} + B\,\frac{\partial^4 f}{\partial x^4} \qquad (5)$$

where f is the single-particle distribution function. If there are no long-term memory effects, then this distribution becomes a Gaussian in the long time limit at a rate governed by B. This assumption is violated when there are long-term correlations, which can even lead to the divergence of the diffusion coefficient itself. An example is any transport coefficient in a two-dimensional fluid (such as any liquid film on a metal), where the distribution function itself is not Gaussian even in the long-time limit. The nonlinear Burnett coefficients, namely coefficients of the form of $(\partial^2 f/\partial x^2)^2$, are expected to have divergences similar to those of the linear ones.

For the Lorentz gas, at the longest time that could be numerically investigated, the distribution function is far from being Gaussian. Because spatial correlation cannot develop in the Lor-



Friction coefficient ξ (relative to the slip Stokes's value ξ_H) as a function of particle size at $V/V_0 = 1.6$ for two different boundary conditions: slip (green) and aggregate (yellow) where σ_2 is the diameter of the fixed particle and σ_{12} the average diameter of the fixed and solvent particle. The green line gives the prediction of generalized hydrodynamics, and the yellow line represents an empirical extrapolation. Figure 5

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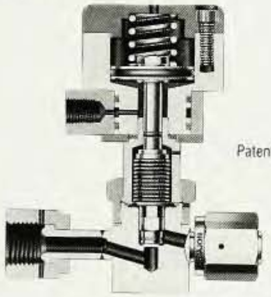

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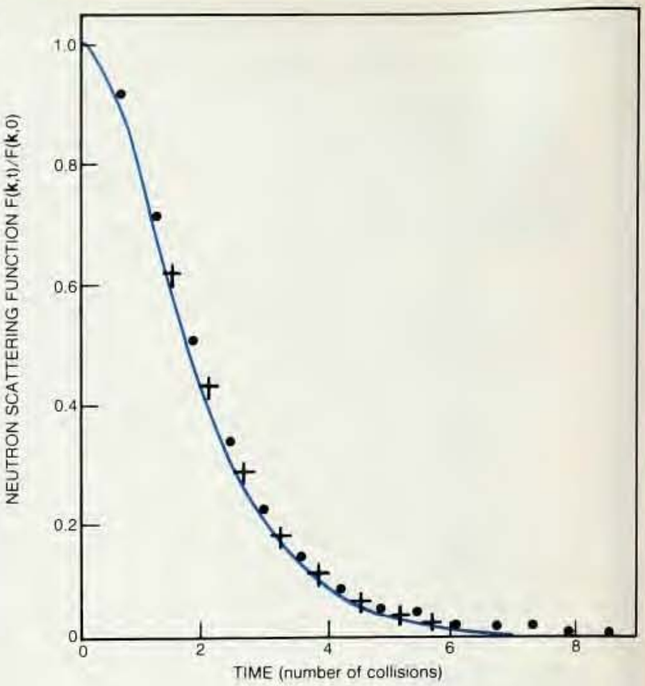
entz gas, long temporal correlation must account for the non-Gaussian approach to the Gaussian limit. Generalizing Fick's law by introducing a nonlocal (in time) memory function in the simplest possible way leads to a redefinition of the Burnett coefficient:

$$\frac{\partial f}{\partial t} = D \int_0^t \rho(t - t') \frac{\partial^2 f}{\partial x^2} dt' + B \int_0^t \rho(t - t') \frac{\partial^4 f}{\partial x^4} dt' \quad (6)$$

This equation leads not only to a well-behaved Burnett coefficient, but also to a quantitative prediction of the singlet distribution function at long times. Similarly, for a three-dimensional fluid, the diffusion coefficient exists and the Burnett coefficient diverges. However, the memory function that must be introduced to remove the divergence is nonlocal not only in time but in space as well. Its precise form is not yet firmly established.



Intermediate scattering function $F(\mathrm{k},t)$ normalized for a hard-sphere fluid at $V/V_0 = 1.6$ at a high reduced wavenumber $k\sigma = 25$ (closed circles), compared to kinetic theory (colored line) and wavelength-dependent hydrodynamics (crosses), as a function of time. Figure 6

Theory

The theoretical evaluation of the generalized transport coefficients presents formidable problems. From kinetic theory it is possible to predict the short-wavelength and short-time behavior of hard spheres at any density. For real potentials, which have attractive and repulsive features, only the low-density behavior is predictable. The long-time behavior is predictable on the basis of various theories, all basically of hydrodynamic origin, such as mode-coupling theory, graph-theoretical means, and renormalization techniques. The problem is that, although we have been able, through the analysis of linear fluctuation–dissipation, to formulate generally valid correlation-function expressions for the generalized transport coefficients (at any density and temperature and for any intermolecular potential), their evaluation still requires solution of the many-body problem. Through computer simulation, however, these expressions are readily evaluated. Their numerical evaluation presents a challenge to the theorists and permits testing their practical usefulness. There are alternative numerical simulation techniques to evaluate both the linear and nonlinear generalized transport coefficients that are more akin to real experiments wherein an external gradient is imposed (see the article by William G. Hoover, page 44). However, they suffer from having to deal with boundary effects that affect a significant number of the relatively small total number of particles that we can simulate, or from the necessity of imposing rather steep gradients compared to those in actual experiments. On the other hand, the fluctuations in an equilibrium system appear generally to be insensitive to the number of particles, as judged by studying systems of various sizes.

One interesting theoretical controversy in the long-time behavior of autocorrelation functions is worth some attention, since it has wider implications: the applicability of what is called "scaling" in predicting the long-time behavior in the Lorentz gas. The controversy arises in what is essentially the quantum version of the two-dimensional Lorentz gas, and concerns the question of whether a single electron moving through a stationary, randomly generated maze is localized at all temperatures and densities. On the basis of scaling, one can make a prediction of localization (Anderson localization)—namely, that the conductivity of liquid metal films vanishes.[6] Scaling implies that the decay of the correlation is universal, independent of the density of scatterers or the scattering law (that is, the intermolecular potential). In the classical case, that does not seem to be true. The asymptotic decay in the classical Lorentz gas, for example, depends on the type of scatterer, at least for the two cases examined in detail. One is the case of disks, the other of squares (which leads to the so-called Ehrenfest wind–tree model; see page 67). One could argue that for these singular potentials one might get unusual behavior. However, we also found[7] that for disks the exponent of the power-law decay is density dependent (that is, not universal), in contrast to the fluid, where it was density independent. One could argue that these numerical studies were not pursued to long enough times to be in the asymptotic region, although great efforts were made in that direction. It appears more likely, since in the Lorentz case no collective phenomenon is involved, that the decay is determined by topological or geometric considerations and, hence, that scaling is not applicable.

Neutron scattering function

Finally, we return to the prediction of the key time-dependent property, the neutron scattering function, $S(\mathbf{k},\omega)$, or equivalently its Fourier transform $F(\mathbf{k},t)$, called the intermediate scattering function. The function $S(\mathbf{k},\omega)$ plays the same central role in time-dependent phenomena that the equilibrium radial distribution function (determined by x-ray or neutron diffraction) does for equilibrium properties. To use generalized hydrodynamics to predict $S(\mathbf{k},\omega)$ would result in a tautology since $S(\mathbf{k},\omega)$ was used in determining the generalized transport coefficients. However, the significant question in time-dependent phenomena is whether we can predict the time evolution of a fluctuation given the equilibrium properties of the system. In the context of generalized hydrodynamics, this means determining how well $S(\mathbf{k},\omega)$ can be predicted, given the wavelength dependence of the thermodynamic properties and the transport coefficients.[8] If $S(\mathbf{k},\omega)$ cannot be predicted accurately, the hydrodynamic relaxation time is not long compared to the relaxation time of the individual transport coefficients or the dissipative relaxation time. Because the viscosity relaxes the slowest of all the transport coefficients, quantitative predictability implies that the hydrodynamic relaxation time $(\nu k^2)^{-1}$ is large compared to that of the stress–stress autocorrelation function. The slow decay of the stress–stress autocorrelation function over many collision times at liquid density can be ascribed to the slow readadjustment of the fluid structure at high density to an applied stress. The slow decay has been called the "molasses tail" to distinguish it from the hydrodynamically induced vortex tail of the velocity autocorrelation function.

The condition at liquid densities under which only wavelength-dependent properties are required to predict $S(\mathbf{k},\omega)$ accurately includes the entire wavelength spectrum except the portion corresponding to from 1 to 10 molecular diameters, as long as the wavelength is greater than one mean free path (typically $^1/_{10}$ the diameter of a particle). For dense gases, that is, for densities about half liquid densities, the wavelength-dependent hydrodynamic theory works over the entire wavelength region beyond the mean free path, because the molasses tail is absent. The absence of the molasses tail in the viscosity of liquids at short wavelength is also responsible for the initially surprising result that the theory is accurate for dense systems in the region of wavelengths between the diameter of the particle and the mean-free path. This result could have been expected, since no structural readjustment is necessary for such short wavelengths. The accuracy of the generalized hydrodynamic theory at short wavelength and at liquid density is demonstrated in figure 6. For wavelengths greater than 10 molecular diameters, ordinary hydrodynamics predicts $S(\mathbf{k},\omega)$ well, as shown in figure 2, while in the region between 1 and 10 molecular diameters only a viscoelastic description suffices.

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