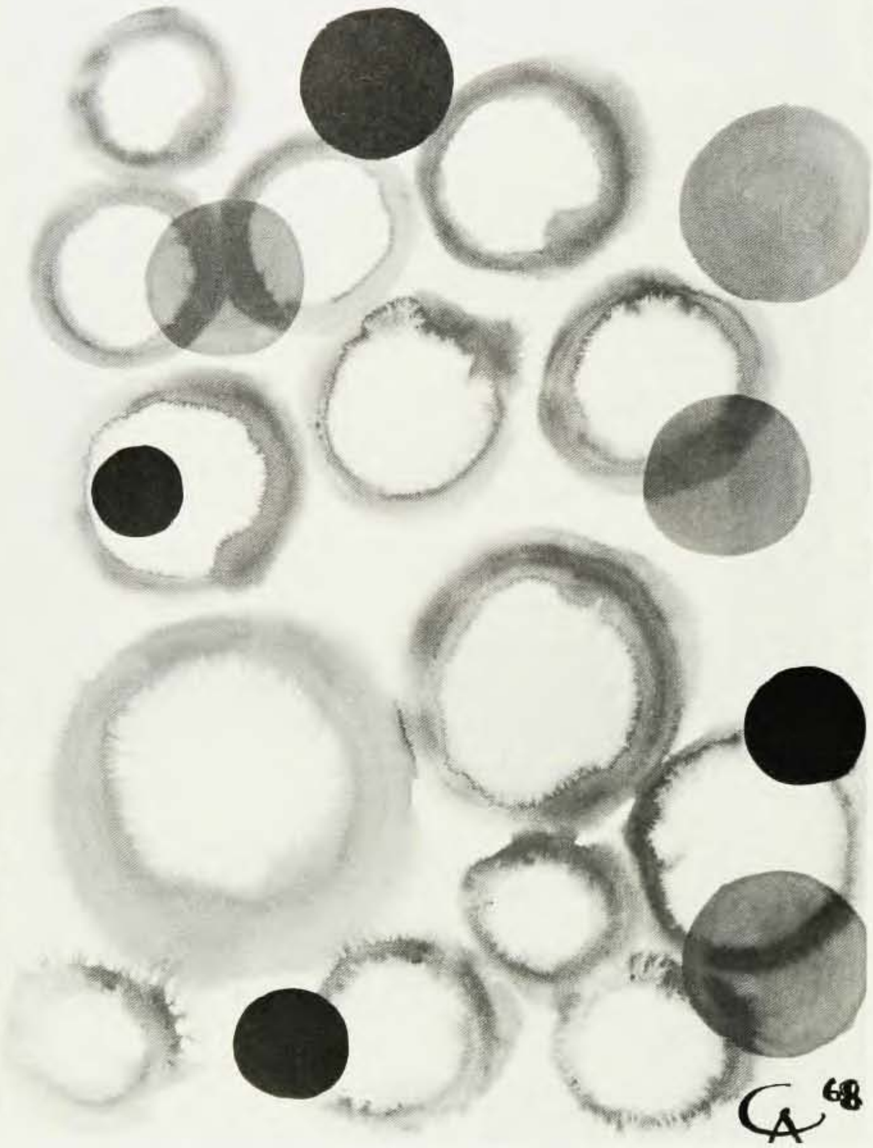


ALEXANDER CALDER/COURTESY SOTHEBY PARKE-BERNET. EPA

The kinetic theory of fluids—an introduction

E. G. D. Cohen

The main concern of kinetic theory over the last 35 years has been to understand the properties of dense gases and liquids in terms of the interactions and motions of the molecules. For dilute gases, the Boltzmann equation has provided a basis for a kinetic description of nonequilibrium properties, and although there are still many unresolved questions, there is little doubt that this equation is the correct starting point for an understanding of dilute gases. In spite of numerous efforts, no one has yet succeeded in deriving a comparable equation for dense gases or liquids. Several generalizations to higher densities of the Boltzmann equation have been found, and many interesting and unexpected results have been discovered, but something we could call a systematic and complete theory has so far eluded us. I want to emphasize that this article does not pretend in any way to be a survey of kinetic theory. I shall only try to sketch a few of the most striking developments in the kinetic theory of dense fluids to give an idea of what has been achieved so far.[1] It will become clear then that a dense fluid behaves in many respects quite differently from what one would expect on the basis of the properties of dilute gases as known from the Boltzmann equation.

Dilute gas

The description of a dilute gas, where only binary collisions between molecules occur, is based on the computation of the distribution function of the velocities, which for nonequilibrium states, changes as collisions redistribute the velocities of the particles. The distribution function for equilibrium states is the Maxwell velocity distribution. For nonequilibrium states, where the distribution function deviates from the Maxwellian one, a basic problem is to determine whether all initially non-Maxwellian distributions approach the Maxwell function, and if so, how? Boltzmann solved the first problem—whether systems approach equilibrium—in 1872 with his "*H* theorem." Sydney Chapman and David Enskog partially solved the second problem—how systems approach equilibrium—by showing that for sufficiently large times the approach is described by the hydrodynamic equations. In doing so, they were able to obtain explicit expressions for the thermodynamic and transport coefficients in these equations in terms of the intermolecular forces.[2] I will restrict myself here to

0031-9228 / 84 / 0100 64-09 / $01.00 © 1984 American Institute of Physics

Correlations in the positions and velocities of the particles in a dense fluid make it difficult to model their hydrodynamic behavior in the way that the Boltzmann equation models the behavior of dilute gases.

classical gases with (pairwise additive) spherically symmetric intermolecular potentials.

To make this discussion more precise, let me write down the Boltzmann equation in the following general form:

$$\frac{\partial f(\mathbf{r}_1,\mathbf{v}_1,t)}{\partial t} = -\mathbf{v}_1\cdot\frac{\partial f(\mathbf{r}_1,\mathbf{v}_1,t)}{\partial \mathbf{r}_1} + J(f,f) \qquad (1)$$

Here $f(\mathbf{r}_1,\mathbf{v}_1,t)$ is the average number of particles at position $\mathbf{r}_1$ with a velocity $\mathbf{v}_1$ at time t. The "streaming" term $-\mathbf{v}_1\cdot\partial f/\partial\mathbf{r}_1$ results from the fact that the molecules at $\mathbf{r}_1$ change their position because they have a finite velocity $\mathbf{v}_1$, while the collision term $J(f,f)$ is due to the change in the molecular velocity $\mathbf{v}_1$ at $\mathbf{r}_1$ due to binary (two-particle) collisions. The precise form of $J(f,f)$ is unimportant here. I only remark that $J(f,f)$ involves the collision dynamics of two particles in infinite space (one does not consider the effect of boundaries here) as well as a statistical assumption about the average number of binary collisions in the gas. This is the assumption of molecular chaos, that is, the complete absence of correlations—either in position or in velocity—of two particles that are going to collide. As a consequence, $J(f,f)$ contains only products of two single-particle distribution functions, such as $f(\mathbf{r}_1,\mathbf{v}_1,t)f(\mathbf{r}_1,\mathbf{v}_2,t)$. The main problem of the kinetic theory of dense fluids is to take into account the correlations that do exist in non-dilute fluids.

The assumption of molecular chaos in $J(f,f)$ lies at the heart of Boltzmann's H-theorem, which assured that any initial $f(\mathbf{r},\mathbf{v},0)$ approaches the Maxwell distribution function $f_M(v)$:

$$f_M(v) = n(m/2\pi k_B T)^{3/2}e^{-mv^2/2k_BT} \qquad (2)$$

Here n is the number density, m the mass of the molecule, k_B Boltzmann's constant and T the absolute temperature.

The Chapman-Enskog method. Chapman and Enskog established the connection with hydrodynamics by obtaining a special solution of the Boltzmann equation for times much larger than the mean free time between two successive collisions. Because each particle has then undergone many collisions, a local Maxwell velocity distribution $f_l(\mathbf{r},\mathbf{v},t)$ will have established itself, at least to a first approximation. For a fluid at rest, $f_l(\mathbf{r},\mathbf{v},t)$ has the form given by equation 2, but with the density n and temperature T now functions of $\mathbf{r}$ and t. Chapman and Enskog then considered the effects of gradients in n and T and obtained from the Boltzmann equation sets of hydrodynamic equations valid for increasing values of the gradients. In fact, the analysis gives (in a fluid at rest) an expansion in terms of powers of the relative variation of the temperature over the mean free path length. Because the macroscopic parameters generally vary only very slowly over the mean free path, the expansion parameter is small. The equations one finds from this expansion are, to first order, the Euler equations for an ideal fluid; to second order, the Navier–Stokes equations for a viscous fluid; to third order, the so-called Burnett equations, and so forth. Most importantly, the expansion leads to explicit expressions for the transport coefficients: the thermal conductivity $\lambda_0(T)$ and the shear viscosity $\eta_0(T)$ in the Navier–Stokes equations. While both are independent of the density n—an old result of kinetic theory already known to Maxwell—they depend via the intermolecular potential in a complicated way on the temperature T. This temperature dependence, when evaluated for realistic intermolecular potentials, agrees well with experiment.[3]

Generalizing the Boltzmann equation

The main reason for the restriction to low densities in the Boltzmann equation is the assumption of molecular chaos—the absence of all correlations between the two colliding molecules. That is, instead of containing products of pairs of distribution functions f, the collision term should really contain the pair-distribution function $f_2(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2,t)$, which gives the average number density of pairs of molecules one of which is at $\mathbf{r}_1$ with velocity $\mathbf{v}_1$, while the other is at $\mathbf{r}_2$ with velocity $\mathbf{v}_2$ at time t. While f_2 contains all correlations between the molecules at $\mathbf{r}_1$ and $\mathbf{r}_2$, the products that occur in equation 1 do not: They neglect not only all correlations in position—and even ignore the difference in position between the two molecules by setting $\mathbf{r}_2$ and $\mathbf{r}_1$ equal—but also those in velocity. The main task, therefore, of a kinetic theory of dense fluids is the determination of the pair-correlation function G_2, defined by:

$$G_2(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2,t) = f_2(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2,t) - f(\mathbf{r}_1,\mathbf{v}_1,t)\,f(\mathbf{r}_2,\mathbf{v}_2,t) \qquad (3)$$

(Because of the additivity of the intermolecular potentials, it turns out that here we need not consider higher-order correlation functions.) For simplicity and also because most results have been obtained for this case, I shall consider mainly the special case that the molecules behave like hard impenetrable spheres of diameter σ. Many of the results obtained hold, however, for more general interparticle potentials of finite range σ. The restriction to hard spheres is made mainly because of the great complexity of the theory. The results obtained on the basis of this model should be viewed with caution if it is to be applied to real fluids: The temperature dependence of all physical quantities will certainly be different from that obtained for hard spheres; however, the density dependence, in which we are mostly interested here, is expected to be similar. Clearly, an extension of the present results to more realistic intermolecular potentials is highly desirable.

In the case of hard spheres in the kinetic equation for f, only those configurations are relevant in which the molecules are in contact: $|\mathbf{r}_1 - \mathbf{r}_2| = \sigma$. To elucidate the nature of position and velocity correlations, it is useful first to consider the case of thermal equilibrium.

Position correlations. In thermal equilibrium, there are no velocity correlations and the distribution of the velocities is always Maxwellian, so that

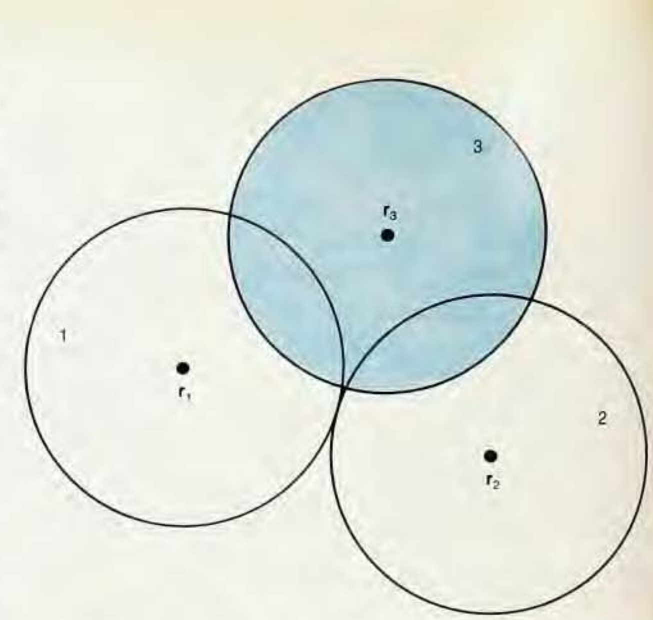
$$G_2^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2,t) = G^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2)\,f_M(v_1)f_M(v_2) \qquad (4)$$

Correlations in position arise because hard spheres cannot penetrate each other. The simplest such correlation occurs when the presence of a third particle, 3, prevents particles 1 and 2, considered in equation (4), to be at the positions $\mathbf{r}_1$ and $\mathbf{r}_2$. (See the diagram on page 66.) This volume exclusion gives rise to a contribution to the two-

---

E. G. D. Cohen is professor of physics at Rockefeller University in New York City

Position correlations. The presence of hard sphere 3 prevents the hard spheres 1 and 2 to be at r_1 and r_2 when 3 overlaps with both 1 and 2. For 1 and 2 at contact, the volume of all configurations of 3 that overlap with both 1 and 2 is finite and equals $5\pi\sigma^3/12$, if σ is the diameter of the hard spheres.



particle correlation function. The contribution is proportional to the number density of the "third" particles and to the volume of all the positions $\mathbf{r}_3$ in which the third particle overlaps both particles at positions $\mathbf{r}_1$ and $\mathbf{r}_2$. This volume is obviously finite; for hard spheres the resulting contribution to G^{eq} is $(^5/_{12})n\pi\sigma^3$.

As the density increases, more and more particles are successively involved, and one can obtain a power series or virial expansion of G^{eq} in powers of n; the coefficients in this series are known up to n^5. In general, these excluded-volume corrections extend over distances of the order of the range σ of the intermolecular forces.

The *same* excluded-volume corrections will also be present in a gas not in equilibrium. If one takes only those into account, and also the difference in position of the two colliding particles, one obtains a kinetic equation for a dense gas of hard spheres that Enskog had already found[1,2] in the 1920s. This equation is, of course, only a first step in the generalization of the Boltzmann equation to higher densities. So far it has not been extended to realistic intermolecular potentials. Nevertheless, it has been very useful for describing the density dependence of transport coefficients of dense fluids in practice.

Velocity correlations. Before discussing velocity correlations in nonequilibrium fluids, I remark that velocity correlations are, of course, also created by collisions in fluids in thermal equilibrium. The created correlations are, however, again destroyed through collisions in such a way that the Maxwell velocity distribution function is maintained. This is not true in nonequilibrium fluids, where due to the presence of gradients (in density or temperature, say), velocity correlations do exist and contribute to G_2.

In general, the velocity correlations are much more subtle and numerically much smaller than the position correlations I discussed above. Velocity correlations can arise from the fact that the two particles 1 and 2 at $\mathbf{r}_1$ and $\mathbf{r}_2$ may have collided before and upon meeting again at $\mathbf{r}_1$ and $\mathbf{r}_2$ "recognize each other." The simplest correlation in velocity occurs when a third particle makes the two particles 1 and 2 collide again at **A**, after their previous collision at **B**. (See sketch on page 68.) Again, the number of such collision events will be proportional to the number density n of the third particles at $\mathbf{r}_3$ as well as the volume in phase space, of those values of $\mathbf{r}_3$ and $\mathbf{v}_3$ that lead to a recollision of particles 1 and 2 (at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ with velocities $\mathbf{v}_1$ and $\mathbf{v}_2$, respectively) at time t. Because this volume of third-particle phases is finite, the total number of such recollision events is finite, and one can add a finite correction term to the collision term in equation 1 to obtain a generalized Boltzmann equation for a gas in infinite space that contains all the contributions of binary as well as ternary collisions. Assuming that particles 1, 2 and 3 were uncorrelated before the first collision between the particles 1 and 2 took place at **B**—which is a generalization of the assumption of molecular chaos made in the Boltzmann equation—one can write down such a correction term $K(f,f,f)$ explicitly. No H-theorem has been proved for the generalized Boltzmann equation that is obtained when this three-particle collision term added to the two-particle term $J(f,f)$ in equation 1.

Nicolai Bogolubov, Melville Green, I and many others[2,4] in the years after 1945 tried to continue in this way and considered velocity correlations between the particles 1 and 2 at $\mathbf{r}_1$ and $\mathbf{r}_2$ due to previous collisions with two particles. (See the middle diagram in the figure on page 68.) Because two intermediate particles are now involved, the contribution of this type of velocity correlation to G_2 is proportional to n^2 and to the volume of that part of the combined phase space of these two particles that leads to a recollision of the particles 1 and 2 at $\mathbf{r}_1$ and $\mathbf{r}_2$ with velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ at time t. However, as was discovered[2] around 1965, a difficulty presents itself in that this volume is *not* finite, but diverges logarithmically as $\log L/\sigma$, where L is the distance between the first and the second collision of the particles 1 and 2. In the infinite systems we consider here, this distance, of course, has no upper limit. Therefore, there is no finite term of the form $L(f,f,f,f)$ on the right-hand side of equation 1. These considerations show that, in contrast with the case of a fluid in thermal equilibrium, velocity correlations in a nonequilibrium fluid introduce long-range correlations between the particles that prevent a systematic generalization of the Boltzmann equation to higher densities. In fact, recollisions of the particles 1 and 2 at $\mathbf{r}_1$ and $\mathbf{r}_2$, of the type considered in the figure on page 68, mediated by $2,3,\ldots m$ particles would lead to terms on the right-hand side of the Boltzmann equation that diverge as $(L/\sigma)^{m-1}$ as L becomes infinite. The box on the Ehrenfest wind–tree model,[5] on the opposite page, describes a simple situation for which the divergence can be discussed in an elementary way.

As I pointed out before, these divergences are due to the fact that there is no limitation of the distance L between the two successive collisions of the particles 1 and 2. This is, in turn, a direct consequence of the fact that all the particles involved in the recollision events discussed above can have unlimited free paths, on which they move undisturbed by collisions with other particles. In a real gas, however, a particle can move on the average undisturbed only over a mean free path l. This means that in the divergent "individual particle" expansion considered above, a cutoff, due to all the other particles in the gas, is necessary and missing; this cutoff is effectively at the mean free path. Although we believe that we have a systematic procedure to remove successively all divergences,[4] so far only divergence-free three- and four-particle terms have been obtained explicitly.[6]

As we shall see below, the mean-free-path cutoff may not suffice to guarantee finite coefficients in the density expansions of the transport coefficients. Long-time tails in time correlation functions may also lead to divergences.

This mean-free-path cutoff replaces the divergence as $\log L/\sigma$ (with $L \to \infty$) in the four-particle collision term $L(f,f,f,f)$ with a finite contribution that behaves as $\log l/\sigma$. Because the mean free path is proportional to 1/$n\sigma^2$, the contribution is proportional to log $(n\sigma^3)$. The corresponding density expansion for the transport coefficients—for the thermal conductivity λ, for instance—then has the form

$$\begin{aligned}\lambda(n,T) = \lambda_0(T) &+ (n\sigma^3)\,\lambda_1(T) \\ &+ (n\sigma^3)^2 \log(n\sigma^3)\,\lambda_2'(T) \\ &+ (n\sigma^3)^2\lambda_2(T) + \dots \end{aligned} \tag{5}$$

One has a similar series for the viscosity η. The terms λ_0 (and η_0) are those obtained from the Boltzmann equation. Soon Takh Choh and George E. Uhlenbeck found[2,4] explicit expressions for $\lambda_1(T)$ and $\eta_1(T)$ for repulsive intermolecular forces. These have so far been evaluated only for hard spheres by Jan V. Sengers and his collaborators.[7] Sengers's computations show that 95% of the contributions to λ_1 and η_1 come from just the position correlations that are already contained in the Enskog theory; they thus confirm the dominance of position over velocity correlations that I mentioned earlier. (One should bear in mind, though, that realistic molecular potentials may yield different results.)

Behzad Kamgar-Parsi and Sengers[8] as well as Y. Kan and J. Robert Dorfman[7] have computed the coefficient $\lambda_2'(T)$ and the corresponding coefficient $\eta_2'(T)$ for a gas of hard spheres. Because these coefficients are extremely small, experiments have not yet been able to demonstrate convincingly the logarithmic density dependence of the transport coefficients for real gases.[9] Computer simulations, however, seem to confirm[2,10] this dependence. Even for hard spheres very little is known about the coefficient $\lambda_2(T)$ in the expansion 5, and virtually nothing is known about the higher-order terms.

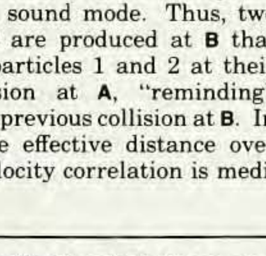
Long-time tails

The velocity correlations in a nonequilibrium fluid, which I discussed above, are related to sequences of individual-particle collisions that effectively stretch out over distances of the order of a few mean free paths. These correlations were relevant for gases of sufficiently low densities that density expansions could be used. The velocity correlations I will now discuss are different in that they are present in fluids of arbitrarily high densities.[2] They extend over much longer distances and are mediated by collective phenomena—what could be called kinetic sound modes, and so forth. These modes are the kinetic analogs in the phase space of **r** and **v** of the usual hydrodynamic modes in **r**-space. (See the box on hydrodynamic modes.) For brevity I shall drop the adjective "kinetic" when referring to these modes, but it should be understood that in the context of kinetic theory "hydrodynamic modes" always refers to "kinetic hydrodynamic modes."

A velocity correlation mediated by two sound modes is illustrated in figure 2c. The velocity correlation created in the first collision of the particles 1 and 2 at **B** can propagate over a distance L via two (kinetic) sound modes to the positions $\mathbf{r}_1$ and $\mathbf{r}_2$ where the second collision (at **A**) between these particles occurs. One could think of this propagation of a velocity correlation in the following way. The first collision of the particles 1 and 2 at **B** causes a local density disturbance where each particle creates a sound mode. Thus, two sound modes are produced at **B** that "meet" the particles 1 and 2 at their second collision at **A**, "reminding" them of their previous collision at **B**. In this case, the effective distance over which the velocity correlation is mediated is not the mean free path l, but the extinction length of the two sound modes, which is much larger than l. If Γ is the sound damping coefficient, the amplitude of each of the two sound modes that originates around **B** has been reduced by $e^{-\Gamma k^2 \tau}$ at **A**, where k is the wavenumber of each of the sound modes and τ the time the sound modes take to traverse the distance L. The total effect of all pairs of sound modes with wavevectors **k** that produce a velocity correlation at **A** due to a previous collision is then an integral of the amplitude-reduction factor over all wavevectors **k** and all travel times τ larger than a minimum cutoff time, $\tau_{\min}$ (which in turn is much larger than the mean free time of the molecules). This contribution to G_2 then gets added to the collision integral in the Boltzmann equation and leads in turn to a correction to f and ultimately to a

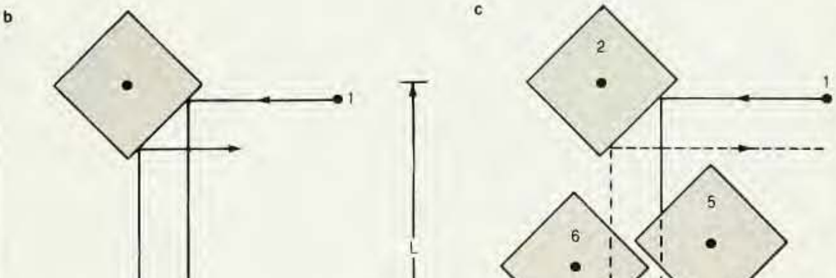
The Ehrenfest wind–tree model

Paul Ehrenfest considered the motion of point particles ("wind") through an array of infinitely heavy obstacles ("trees"). The wind particles all move with constant speed. The trees are squares, all oriented the same way—diagonally along the x–y directions; they all have the same diameter σ and are are randomly distributed through the x–y plane. If a point particle starts out in one of the four directions along the $\pm x$ or $\pm y$ axes, it will always move in one of these four directions, due to the perfect orientational alignment of all the squares. The analogs in this model of the three- and four-particle collisions in the figure on page 68 are sketched below.



In figure **a** the (wind) particle 1 collides twice with tree 2, once at **A** and once at **B**, with an intermediate collision with tree 3. If we keep point **A** fixed, then there is clearly a finite range of positions for the tree 3 that permits such a sequence of collisions. In figure **b** the wind particle collides with three trees. Then the range of positions for particles 3 and 4 for a fixed point **A**, diverges linearly—as L/σ, where L characterizes the distance between **A** and trees 3 and 4. In the three-dimensional case of identical spheres, an analogous argument leads to a logarithmic divergence, as mentioned in the text. This illustrates that the nature of the divergence depends on the dimension of space as well as on the nature of the interparticle potential.

The divergence is removed by a mean-free-path cutoff generated by intervening trees, such as those shown in **c**, that will deflect particle 1 from its free path between trees 2 and 3 or 2 and 4.



contribution to the transport coefficients that is proportional to

$$\int_{\tau_{\min}}^{\infty} \mathrm{d}\tau\,(2\Gamma\tau)^{-d/2}$$

when space has d dimensions.

Now according to ideas of Lars Onsager, particularly as worked out by M. S. Green and Ryogo Kubo,[11] each transport coefficient can be written in the form of an integral over an associated equilibrium correlation function $C(\tau)$ between microscopic currents. The transport coefficients obtained on the basis of these so-called time-correlation-function expressions have been shown to be identical to those obtained from the distribution functions, which I discussed earlier, up to terms of order $(n\sigma^3)^2\log(n\sigma^3)$. For the thermal conductivity λ, for instance, one has in terms of the time correlation function $C_\lambda(\tau)$ an expression of the form:

$$\lambda = \frac{1}{k_{\mathrm{B}}T^2}\int_0^{\infty}\mathrm{d}\tau\,C_\lambda(\tau)$$
$$= \frac{1}{k_{\mathrm{B}}T^2V}\int_0^{\infty}\mathrm{d}\tau\,\langle j_\lambda(\mathbf{r},0)\,j_\lambda(\mathbf{r},\tau)\rangle_{\mathrm{eq}} \quad (6)$$

Here V is the volume of the fluid and $j_\lambda(\mathbf{r},\tau)$ is the microscopic heat current at the position $\mathbf{r}$ at time τ. The precise form of $j_\lambda(\mathbf{r},\tau)$ is not needed here, suffice it to say that $j_\lambda(\mathbf{r},\tau)$ depends on the positions and velocities of all the particles in the fluid. Because the average, taken over an equilibrium ensemble, is translation invariant, $C_\lambda(\tau)$ is independent of $\mathbf{r}$ and only depends on τ. Without going into the derivation of equation 6, one can perhaps see the connection between C_λ and λ for the simple case of a dilute gas. In equilibrium the average of the current $\langle j_\lambda(\mathbf{r},\tau)\rangle_{\mathrm{eq}}$ must vanish for all $\mathbf{r}$ and τ, so that $j_\lambda(\mathbf{r},0)$ can also be considered as the fluctuation of the local heat current at $\mathbf{r}$. Assuming then that such a fluctuation on the average decays exponentially,

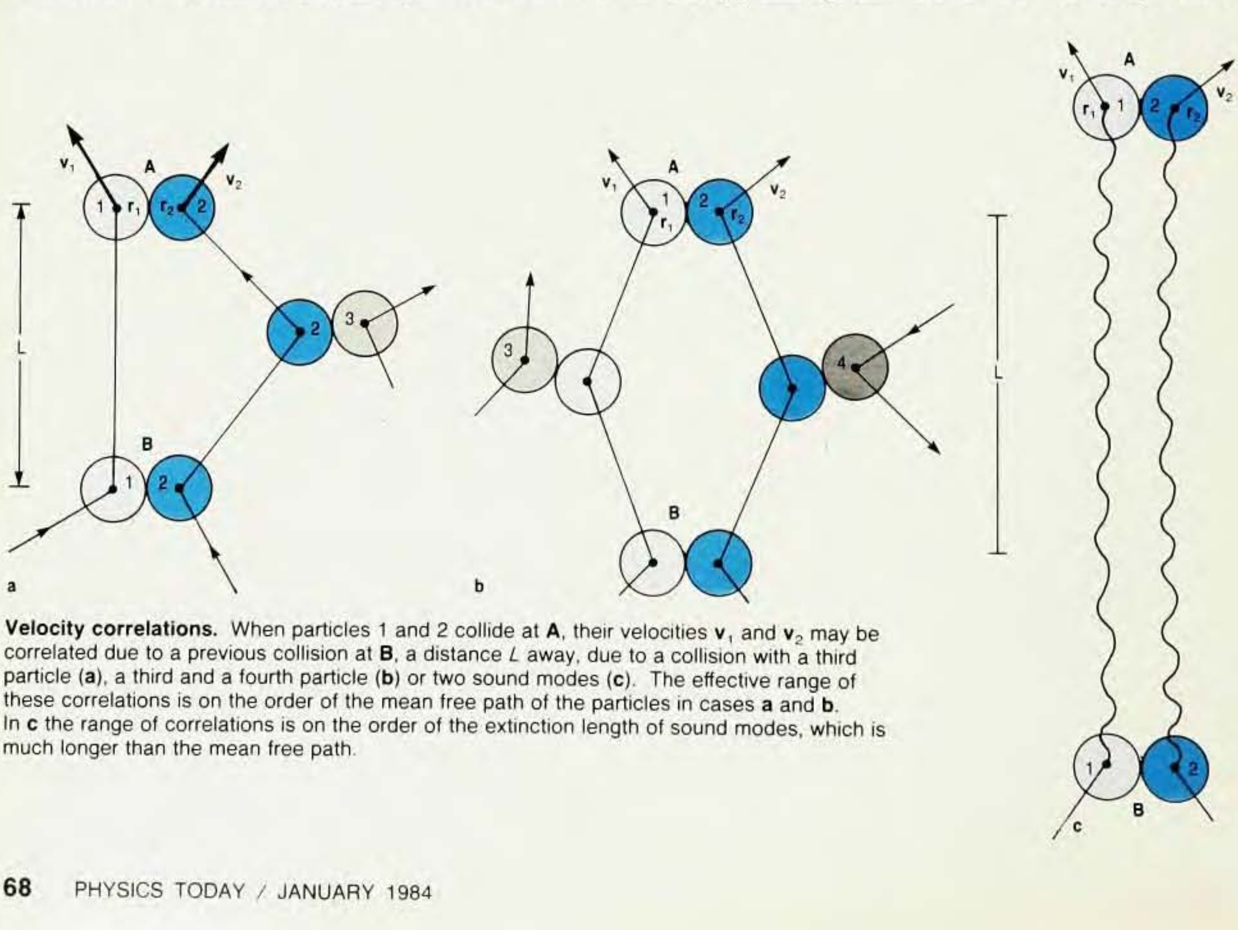
$$j_\lambda(\mathbf{r},\tau) = j_\lambda(\mathbf{r},0)\mathrm{e}^{-a\tau/\lambda_0}$$

where a is a constant and λ_0 is the thermal conductivity for a dilute gas as given by the Boltzmann equation. It is then easy to see that a result of the form of equation 6 holds in this case.

One of the consequences of the long-range correlations discussed here is that such an exponential decay of the current fluctuations is no longer true for a dense fluid. In fact, the considerations given above imply that, in general, the time correlation functions that determine the transport coefficients will have a slow time decay proportional to $1/\tau^{d/2}$, or a "long time tail."[12] In particular, for $C_\lambda(\tau)$ one finds[13] for times τ much larger than the mean free time

$$C_\lambda(\tau) = \frac{(k_{\mathrm{B}}T)^2}{(4\pi\tau)^{d/2}}\left[\left(\frac{1}{2\Gamma}\right)^{3/2}\frac{c^2}{d} + \left(\frac{1}{\nu+D_T}\right)^{3/2}Tc_p\left(\frac{d-1}{d}\right)\right] \quad (7)$$

(in d dimensions). Here c is the adiabatic velocity of sound, c_p the specific heat per unit mass at constant pressure, ν is the kinematic viscosity η/ρ and D_T the thermal diffusivity $\lambda/\rho c_p$. The two terms in the brackets on the right-hand side are due to the contributions of correlations mediated by pairs of hydrodynamic modes: the first term by two sound modes, the second term by a viscous and a heat mode respectively. Of the various types of hydrodynamic modes—sound modes, viscous modes and heat modes—only the pair combinations appearing in equation 7 occur; this fact is related to the particular character of each of these modes. To lowest order in the density, the thermodynamic properties c and c_p can be replaced by their ideal-gas values and the transport properties Γ, η and λ by their Boltzmann values. The resulting expression for C_λ leads with equation 6 to a contribution of order $(n\sigma^3)^2$ to $\lambda(n,T)$; that is, C_λ first contributes to the coefficient $\lambda_2(T)$ in the density expansion (equation 5) for $\lambda(n,T)$. The appearance of the full transport coefficients in equation 7 might appear contradictory, in view of equation 6. For a discussion of this point, I must refer readers to the literature.[14] For moderately dense gases, good agreement exists for C_λ and C_η between theory and computer simulations. On the basis of this, it is estimated that the long-time tails can contribute appreciably (up to 30%) to the transport coefficients for real fluids. However, no results are available for realistic intermolecular potentials to confirm this. For very dense gases, large discrepancies have been found[15] between the theoretical and computer results that



Velocity correlations. When particles 1 and 2 collide at **A**, their velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ may be correlated due to a previous collision at **B**, a distance L away, due to a collision with a third particle (**a**), a third and a fourth particle (**b**) or two sound modes (**c**). The effective range of these correlations is on the order of the mean free path of the particles in cases **a** and **b**. In **c** the range of correlations is on the order of the extinction length of sound modes, which is much longer than the mean free path.

amount to two orders of magnitude. The origin of this large disagreement is not yet understood.

The existence of long-time tails was first discovered by Berni Alder and Thomas Wainwright by computer simulations and studied extensively by them and others.[12] This is one example of the extremely fruitful and stimulating cooperation that exists between kinetic theory and computer simulations, to which I shall refer again later. If the long-time tails give the true asymptotic behavior of the time-correlation functions $C(\tau)$, they imply that finite transport coefficients do not exist in two dimensions, because the integral in equation 6 then diverges logarithmically. Nor, as one can show, do the Burnett and higher-order hydrodynamic equations have finite transport coefficients. In other words, except for a dilute gas—described by the Boltzmann equation—the hydrodynamic equations beyond the Navier–Stokes equations do not seem to exist. A direct observation of the long-time tails, other than by computer simulation, appears to be very difficult. I will describe a possible indirect verification below. Another effect of the long-time tails is an anomalous dispersion of sound in fluids; recent neutron scattering experiments of liquid argon[16] may have verified this prediction. The fact that *pairs* of hydrodynamic modes contribute to the transport coefficients, as exemplified by equation 7, is called mode coupling. Mode coupling in the sense used here was first introducted to explain the anomalies of the transport coefficients near the gas–liquid critical point.[17] From this article it will become clear that mode coupling plays a much wider role in nonequilibrium fluids than near a critical point alone.

Stationary states

So far we have neglected the effects of boundaries, treating the fluid as if it had infinite extent. In recent years, some work has been done on the kinetic theory of a fluid in a stationary state taking the effects of boundaries into account. To be specific, I will discuss the Rayleigh–Bénard cell (see the box on page 72), where a fluid in a container is heated from below, so that a fixed temperature difference ΔT is maintained across the fluid. If we wish to consider time-independent states, we must exclude too-large values of ΔT, because for large ΔT the system always exhibits time-dependent behavior.

I return to the case of a dilute gas, for which we can already discuss this problem. The first question one can ask is one already posed[18] by Ehrenfest: Is there a generalization of the H-theorem in that—at least for not too-large ΔT—any initial state approaches a unique stationary state, determined by the boundary conditions? Once we have established whether the system approaches a stationary state, we can ask, what is its nature?

Hydrodynamic modes and fluctuations

Hydrodynamic modes appear as the eigenmodes of the Navier–Stokes equations, linearized around equilibrium. Because there are five equations, relating to the conservation of mass (continuity equation), momentum (three equation of motion) and energy (energy equation), there are five types of eigenmodes. These eigenmodes have, for given wavevector **k**, the following eigenvalues up to order k^2:

mode	number	eigenvalue
sound	2	$\pm ic\mathbf{k} + \Gamma k^2$
viscous	2	νk^2
heat	1	$D_T k^2$

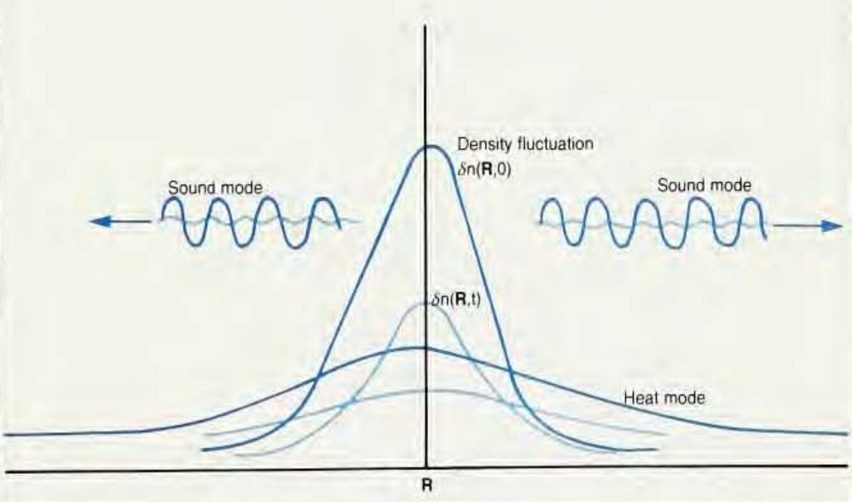
The two sound modes are propagating modes that are damped. They are combinations of oscillations in pressure and longitudinal momentum, that is, momentum in the direction of propagation **k**. Their propagation velocity is c and their damping constant Γ. The remaining modes are purely damped and do not propagate. The two viscous modes describe the diffusion of momentum in the two directions perpendicular to the wavevector **k**; the damping constant is the kinematic viscosity ν. The heat mode describes the isotropic diffusion of entropy (heat); the damping constant is D_T, the thermal diffusivity.

A density fluctuation $\delta n(\mathbf{R},0)$, that is, a deviation from the average density at **R** at time $t=0$, will in general decay through three types of hydrodynamic modes: two sound modes and a heat mode. The excess pressure and heat created due to a density fluctuations at **R**, disappear via sound modes propagating in opposite directions and heat diffusion, with all wavevectors **k**. After a time t a smaller density fluctuation $\delta n(\mathbf{R},t)$ results.

The sketch illustrates the decay of an excess density $\delta n(\mathbf{R},0)$ at **R**. Only two sound modes and one heat mode of a particular wavevector are shown. The density fluctuation, the heat mode and the two sound modes are shown at time $t=0$ (color) and at t (light color). Each sound mode contributes in the light scattering of the fluid to a Brillouin line.

Similarly, a velocity fluctuation $\delta\mathbf{u}(\mathbf{R},0)$ at **R** at time $t=0$ in general decays through two sound modes and two viscous modes, with all wavevectors **k**. After a time t a smaller velocity fluctuation $\delta\mathbf{u}(\mathbf{R},t)$ results.

The kinetic hydrodynamic modes are generalizations to phase space—that is **r**,**v** space—of the hydrodynamic modes we just discussed in **r** space. A binary collision can then be seen as a local disturbance of the density in **r**,**v** space that decays in time through the kinetic analogs of the hydrodynamic modes discussed above. Thus, the kinetic sound modes are damped propagating modes just as the usual sound modes are. For the case of a dilute gas these kinetic hydrodynamic modes can be found for the linearized Boltzmann equation, which can be derived from equation 1 by linearizing around the Maxwell distribution function 2. The eigenvalues of the kinetic hydrodynamic modes are the same as those of the usual hydrodynamic modes, given in the table above.



In the context of the kinetic theory, no answer has been given to Ehrenfest's question. However, something is known about the nature of the final states the system can approach. For the Rayleigh–Bénard cell, the final state depends upon the dimensionless Rayleigh number,

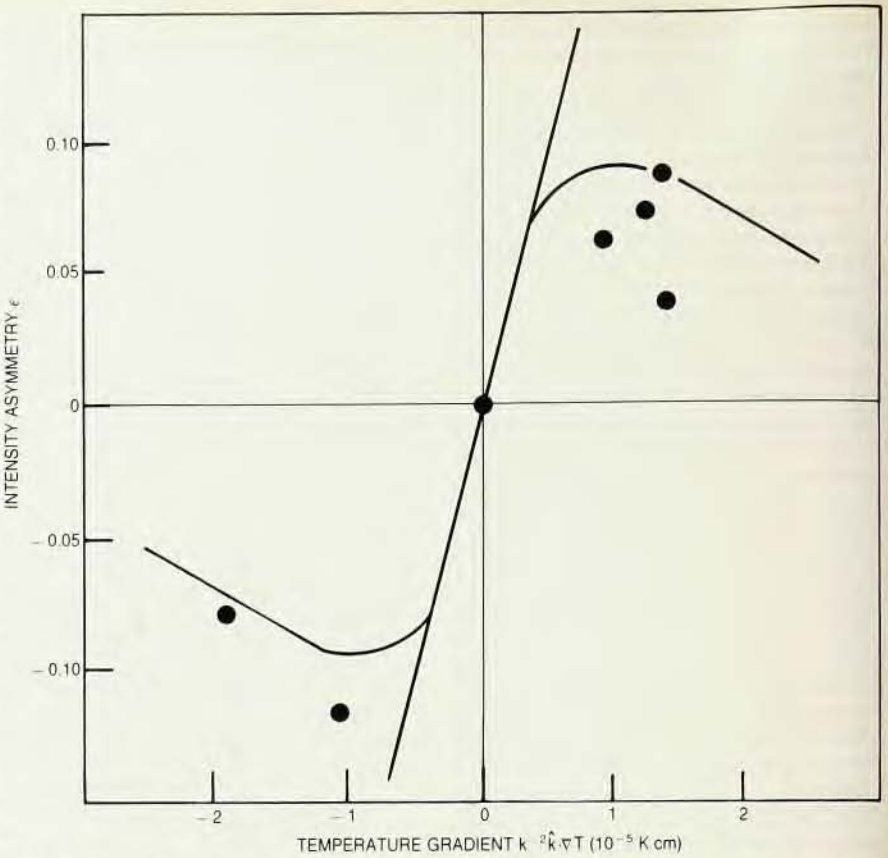
$$\mathscr{R} = (\alpha g \Delta T/\nu D_T)L^3$$

where α is the coefficient of thermal expansion of the fluid, ν is kinematic viscosity, and D_T the thermal diffusivity; g is the acceleration of gravity, ΔT

is the temperature difference between the lower and upper plates of the cell and L is the height of the cell. For small values of $\mathscr{R}$ the stationary state is that of a fluid at rest, with heat transport purely by conduction. When the Rayleigh number is raised above some critical value $\mathscr{R}_c$ the stable state becomes one with convection, initially with very regular flow patterns. As $\mathscr{R}$ is increased further, more and more complicated convection patterns appear, until the behavior becomes entirely chaotic.[19]

From kinetic theory we can only say something about the behavior below or near (just below or just above) $\mathscr{R}_c$. So far, only the distribution function f and some aspects of the pair-correlation function G_2 have been studied. As we will see again, contrary to fluids in equilibrium, dynamic events have to be considered explicitly in discussing correlations in a nonequilibrium fluid, in this case, a fluid in a stationary state.

Far from instability. When $\mathscr{R}$ is much less than $\mathscr{R}_c$, explicit calculations show that the influence of gravity and the walls can be ignored.[20,21] Then the Chapman–Enskog solution of the Boltzmann equation can be used, with the simplication that f is independent of t, since the fluid is stationary. The pair correlation function $G_2^{ss}(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_1,\mathbf{v}_2)$ is also independent of time and contains position correlations of exactly the same nature as those described before for G_2^{eq} and which extend over distances on the order of the range of the forces σ. In addition, however, velocity correlations—as discussed above for $G_2(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,v_2,t)$—occur. Here we are particularly interested in velocity correlations generated by mode coupling, that is, by pairs of hydrodynamic modes. However, now we are not interested in these correlations for configurations where the particles 1 and 2 are touching as before, but for configurations where these particles are widely separated—by distances much larger than the size of the particles. In fact, we are interested in correlations that extend over distances of the order of the wavelength of visible light; such correlations can be detected by light scattering, thus providing the possibility of a direct confirmation of mode-coupling effects in nonequilibrium fluids. (See the box on the Rayleigh–Bénard cell, page 72.)



Change in intensity in the Brillouin lines of light scattered by water in a Rayleigh–Bénard cell. The graph shows the ratio ϵ of the difference to the sum of the intensities of the two lines as a function of the temperature gradient. In the experiments (results indicated by dots) the cell is heated from below or above to change the sign of the temperature gradient. The straight line shows the results of a linear theory for the steady-state correlation function (equation 9 of the text). The curved line refers to a generalization of the theory for large temperature gradients.

Integrating $G_2^{ss}(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_2,\mathbf{v}_2)$ over velocities, we obtain a function $G^{ss}(\mathbf{r}_1,\mathbf{r}_2)$, which is nothing else than the correlation function for the number density fluctuations at $\mathbf{r}_1$ and $\mathbf{r}_2$ in the fluid:

$$G^{ss}(\mathbf{r}_1,\mathbf{r}_2) = \langle \delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)\rangle_{ss} \qquad (8)$$

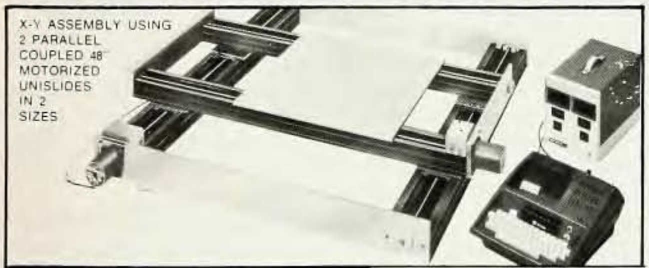
Here $\delta n(\mathbf{r})$ is the fluctuation of the number density at $\mathbf{r}$, that is, the deviation of the actual from the mean number density of particles at $\mathbf{r}$. The average in equation 8 is taken over the stationary state. Because density fluctuations cause light scattering, the mode-coupling contributions to the correlation function G^{ss} ultimately influence the intensity of the scattered light. Specifically, the intensity of the light scattered by the fluid is given by the Fourier transform of G^{ss}, the so-called static scattering function $S(\mathbf{R},\mathbf{k})$. Here the position $\mathbf{R}$ is the average of $\mathbf{r}_1$ and $\mathbf{r}_2$ in equation 8, and $\mathbf{k}$ is the wavevector determined by the momentum transfer from the fluid to the light. (The Fourier integral is over the relative coordinate $\mathbf{r}_1 - \mathbf{r}_2$.) Then, for small temperature gradients, the effect in $S(\mathbf{R},\mathbf{k})$ of the contribution of pairs of sound modes of wavevector $\mathbf{k}$ to G^{ss} manifests itself in an increase in the intensity of one and a decrease in the intensity of the other Brillouin line in the scattered light, by an amount[20]

$$\Delta S(\mathbf{R},\mathbf{k}) = \frac{c}{2\Gamma k^2 T}\,\hat{k}\cdot\nabla T \qquad (9)$$

Here c and Γ are both taken at $\mathbf{R}$ and $\hat{k}$ is a unit vector in the direction of $\mathbf{k}$. In so far as this change in intensity has been derived from kinetic theory, c and Γ refer to a dilute gas. The relation remains valid, however, for arbitrary fluid densities. A generalization of equation 9 to large temperature gradients and applied to water is in reasonable agreement with experiment.[20] (See the graph above.) I note that the appearance of 2Γ in both equations 7 and 9 illustrates the connection between the mode-coupling effects that contribute to the long-time tails and the transport coefficients on the one hand and the light scattering in a stationary state on the other hand. In fact, by carrying out, in the discussion above equation 6, the integral over τ instead of over $\mathbf{k}$, one sees that the contribution of pairs of sound waves of fixed wavenumber $\mathbf{k}$ to the long-time tail of C_λ and therefore to the transport coefficient λ itself, is proportional to $1/(2\Gamma k^2)$.

Fluids near instability. When $\mathscr{R}$ is in the neighborhood of $\mathscr{R}_c$, we must explicitly take into account gravity and the boundaries of the container in the Boltzmann equation for the computation of f as well as for the calculation of G_2^{ss}. The behavior of the fluid as far as its macroscopic properties is concerned can be derived from f; the more micro-

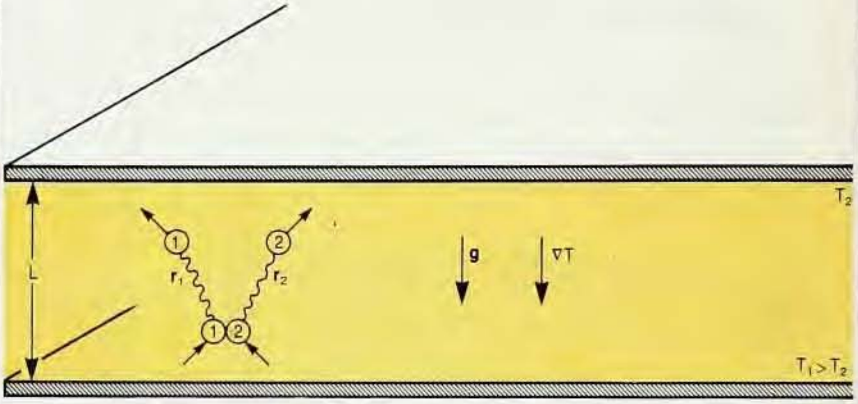

IL 700A RESEARCH RADIOMETER
4.25
PORTABLE



The Rayleigh-Bénard cell

The cell consists of a container, usually rectangular in shape, with horizontal dimension much greater than its height. One establishes a vertical temperature gradient by heating, for instance, the bottom of the cell ($\mathrm{d}T/\mathrm{d}z$ positive). For small gradients the fluid is at rest and the heat flow is by pure conduction. At sufficiently large temperature gradients, when the dimensionless Rayleigh number exceeds some critical value, the fluid becomes unstable, and convection sets in. The instability is caused by the tendency of the warmer and lighter fluid to rise but is suppressed by viscosity and heat conduction.

A correlation of the velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ of the particles 1 and 2 at $\mathbf{r}_1$ and $\mathbf{r}_2$ exists for interparticle distances $|\mathbf{r}_1 - \mathbf{r}_2|$ much larger than the range of interparticle forces. This correlation is established by two sound modes originating in a previous collision of particles 1 and 2 at point **B**, where a different temperature prevails. (See the drawing.) If $|\mathbf{r}_1 - \mathbf{r}_2|$ is of the order of the wavelength of visible light, the velocity correlation can be detected by light scattering.



scopic behavior, in particular that of the fluctuations, follows from G_2^{ss} or $G^{\mathrm{ss}}(\mathbf{r}_1\mathbf{r}_2)$. A kinetic calculation shows[21] that G^{ss} near $\mathscr{R}_c$ behaves as $\mathrm{e}^{-\kappa r}/\sqrt{r}$ with $\kappa \rightarrow 0$ as $\mathscr{R} \rightarrow \mathscr{R}_c$ and for separations $r = |\mathbf{r}_1 - \mathbf{r}_2|$ between the molecules much larger than the cell size L. At $\mathscr{R}_c$ then, the correlations have a very long range, decaying only as $1/\sqrt{r}$, and extend over much longer distances than the separation L of the heated walls of the container. These very-long-range correlations are again due to essentially the *same* pairs of hydrodynamic modes that also contribute to the intensity change ΔS of the Brillouin lines and the long-time tails of the transport correlation functions. Because their range extends over millimeters or more, these correlations could in principle be detected by microwave scattering. The behavior of the fluid for $\mathscr{R}$ near $\mathscr{R}_c$ is similar to that near the gas–liquid critical point, as described by Ornstein and Frits Zernike in 1914. There, also, long-range correlation functions occur, but they can be detected, in fact seen with the naked eye, because their range is of the order of the wavelength of visible light 10^{-4} cm rather than 10^{-1} cm.

Fluids far from equilibrium. Over the last five years a large number of computer simulations of very dense fluids with spherically symmetric intermolecular forces and periodic boundary conditions under extreme conditions of shear stress have been carried out. In fact, the shear rates are of such magnitude that the local velocity in the fluid varies significantly over the range of the intermolecular forces σ; nevertheless, the fluid is in a stable stationary state with a homogeneous shear rate. It appears that under these extreme conditions the fluid exhibits a behavior similar to that of polymeric fluids. Denis Evans, Howard Hanley and Siegfried Hess discuss this work in their article on page 26. I will here mention only that, first, a generalized thermodynamic description appears still to be possible, on condition that the shear rate γ is introduced as an additional thermodynamic variable; and second, the shear viscosity η depends on the shear rate and can be represented by the expression:

$$\eta(\gamma) = \eta(0) - \eta_1\gamma^{1/2}$$

This behavior can be qualitatively understood on the basis of mode-coupling and involves essentially the *same* pairs of hydrodynamic modes that lead to the long-time tails. One can obtain this behavior of the shear viscosity by assuming that in the case of very strong gradients there is an extra damping of the hydrodynamic modes proportional to the gradients present. Thus, for instance, one replaces the sound-wave damping coefficient Γk^2 by $\Gamma k^2 + b\gamma$ (b is a constant); an analysis like that given for the mode-coupling contribution to the thermal conductivity gives the expected behavior. Although the correct γ-dependence of η is obtained in this way, it is not clear that the simple linear assumption used can be applied under these extreme conditions. In fact, the theory gives values of η_1 that are two orders of magnitude smaller than those found by computer simulation. This is similar to the case of the long-time-tail contribution to C_λ and C_η mentioned above, where discrepancies of a similar magnitude between mode-coupling theory and computer simulations were found for very dense fluids. The origin of these discrepancies is still unclear.

The fact that $C_\eta(t)$, as given by equation 7, varies as $t^{-3/2}$ in three dimensions implies, through a Fourier transform, a frequency dependence of the viscosity that behaves as $\omega^{1/2}$ for small ω. An interesting argument, based on the principle of objectivity used in polymer fluids, has been given[22] for a connection between the $\gamma^{1/2}$ and $\omega^{1/2}$ dependence of η.

Unanswered questions

Of the many questions explicitly stated or implicitly contained in the above discussion of the kinetic theory of dense fluids, I would like to repeat the most important ones, thus emphasizing again the unfinished nature of the kinetic theory of dense fluids.

- What can one prove about the approach to equilibrium of a dense gas? In particular, can any statement be made when the ternary collision term $K(f,f,f)$ is added to the binary collision term $J(f,f)$ on the right-hand side of the Boltzmann equation?
- Can one prove some analog of the *H*-theorem for a dilute gas in a stationary state with fixed boundary conditions?
- Is the long-time tail—that is, the $t^{-d/2}$ behavior—the true asymptotic behavior in d dimensions of the time correlation functions related to the transport coefficients?
- Can one prove, for a dense fluid in three dimensions, the existence of the transport coefficients and that they are positive, and can one determine the density dependence of these coefficients? Is this dependence of the general form $n^r(\log n)^s$ (r, s integers) or do other density dependences occur?
- What is the nature of the discrepancy at very high densities or very high stresses between the magnitude of the mode-coupling contributions to the transport coefficients and the computer-simulation results?

* * *

The author is indebted to J. Robert Dorfman, Theodore R. Kirkpatrick and George E. Uhlenbeck for helpful comments and suggestions.

References

1. E. G. D. Cohen, Physica **118A**, 17 (1983).
2. J. R. Dorfman, H. van Beijeren, in *Statistical Mechanics B*, B. J. Berne, ed. Plenum, New York (1977), page 65; J. R. Dorfman, Physica **106A**, 77 (1981).
3. B. Najafi, E. A. Mason, J. Kestin, Physica **119A**, 387 (1983).
4. E. G. D. Cohen, in *Fundamental Problems in Statistical Mechanics I*, E. G. D. Cohen, ed. North-Holland, Amsterdam (1962) page 110; volume II (1968), page 228.
5. E. H. Hauge, E. G. D. Cohen, J. Math. Phys. **10**, 397 (1969); E. H. Hauge, in *Sitges Intern. School Statistical Mechanics* **31**, G. Kizczenow, J. Marro, eds., Springer-Verlag, New York (1974), page 338.
6. J. R. Dorfman, E. G. D. Cohen, Int, Journal. Quant. Chem. **16**, 63 (1982).
7. J. V. Sengers, D. T. Gillespie, J. J. Perez-Esandi, Physica **90A**, 365 (1978).
8. B. Kamgar-Parsi, J. V. Sengers, *Proc. 8th Symp. Thermophysical Properties*, Vol. I, J. V. Sengers, ed. Amer. Soc. Chem. Eng. (1982) 166.
9. J. Kestin, O. Korfali, J. V. Sengers, B. Kamgar-Parsi, Physica **106A**, 415 (1981).
10. C. Bruin, Phys. Rev. Lett. **29**, 1670 (1972); Physica **72**, 261 (1974).
11. R. Zwanzig, Annu. Rev. Phys. Chem. **16**, 67 (1965); W. A. Steele, in *Transport Phenomena in Fluids*, H. J. M. Hanley, ed., Dekker, New York (1969) 209.
12. J. J. Erpenbeck, W. W. Wood, Phys. Rev. **A26**, 1648 (1982); Y. Pomeau, P. Résibois, Phys. Rep. **19C**, 64 (1975).
13. M. H. Ernst, E. H. Hauge, J. M. J. van Leeuwen, J. Stat. Phys. **15**, 7 (1975).
14. J. R. Dorfman, E. G. D. Cohen, Phys. Rev. **A6**, 788 (1972).
15. J. J. Erpenbeck, W. W. Wood, J. Stat. Phys. **24**, 455 (1981).
16. I. M. de Schepper, P. Verkerk, A. A. van Well, L. A. de Graaf, Phys. Rev. Lett. **50**, 974 (1983).
17. K. Kawasaki, in *Phase Transitions and Critical Phenomena*, C. Domb, M. S. Green, eds. Academic, New York (1976) page 166.
18. P. Ehrenfest, T. Ehrenfest, *Conceptual Foundations of the Statistical Approach in Mechanics*, Cornell U. P., Ithaca, N.Y. (1959) 103.
19. S. Chandresakkar, *Hydrodynamic and Hydromagnetic Stability*, Dover, New York (1961), page 9; F. H. Busse, in *Hydrodynamic Instabilities and the Transition to Turbulence*, H. L. Swinney, J. P. Gollub, eds. Springer-Verlag, New York (1981) page 97.
20. T. R. Kirkpatrick, E. G. D. Cohen, J. R. Dorfman, Phys. Rev. **A26**, 972, 995 (1982); D. Beysens, Physica **118A**, 255 (1983).
21. T. R. Kirkpatrick, E. G. D. Cohen, Phys. Lett. **88A**, 44 (1982); and in *Statistical Physics and Chaos in Fusion Plasmas*, C. W. Horton, L. E. Reichl, eds., Wiley, New York (1984).
22. R. Zwanzig, Proc. Natl. Acad. Sci. USA **78**, 3296 (1981). ☐

MATH/PROTRAN

IMSL's Natural Resource
for
Mathematical Problem Solving

Mathematical problem solving can be involved and time consuming, but it doesn't have to be. MATH/PROTRAN, one of IMSL's Natural Resources, is a powerful system for the professional who expects a straightforward approach to problem solving.

You don't need any programming knowledge to use this remarkable system. In a surprisingly short time, MATH/PROTRAN is at your command. Convenient "help" files provide on-line reference, and the system automatically checks your statements for errors.

MATH/PROTRAN lets you define problems naturally, in a few simple statements — and gives you effective solutions to problems involving interpolation and data smoothing; integration and differentiation; eigenvalues and eigenvectors; differential, linear and nonlinear equations; as well as other mathematical procedures.

If you're currently solving problems using FORTRAN, you'll appreciate the ability to combine FORTRAN and PROTRAN statements for tailored problem solving. This added measure of flexibility sets MATH/PROTRAN apart from other systems of its kind.

The IMSL PROTRAN problem-solving systems are compatible with most Control Data, Data General, Digital Equipment and IBM computer environments.

Copyright © 1984 IMSL, Inc., Houston, Texas

MATH/PROTRAN is a member of the PROTRAN family of problem-solving systems for statistics, linear programming and mathematics. These systems use accurate, reliable numerical techniques to give you the consistently dependable results you have come to expect from IMSL, a world leader in affordable technical software.

MATH/PROTRAN is the natural resource for a wide variety of mathematical applications. And the low subscription rate makes this powerful system extremely affordable, even if only one person in your organization uses it.

To find out more about MATH/PROTRAN, contact:
IMSL, NBC Building, 7500 Bellaire Boulevard, Houston, Texas 77036, or call, toll-free, 1-800-222-IMSL.
In Texas, call (713) 772-1927.

Please send complete technical information about MATH/PROTRAN,

Name
Dept. Title
Organization
Address
City State Zip
Area Code / Phone

IMSL
Problem-Solving Software Systems

Circle number 30 on Reader Service Card