Dedication: To George Uhlenbeck, magister ludi.

ENTROPY in Nonequilibrium Statistical Mechanics

Statistical mechanics aims at deriving from first principles an entropy theorem that guarantees approach to thermodynamic equilibrium. The theory for dilute gases initiated by Boltzmann and formalized by Bogolyubov has been recently completed. But efforts to include the three-particle interactions in gases that are dense encounter intense difficulties.

by Arnold H. Kritz and Guido Sandri

SINCE ANCIENT TIMES describing the behavior of macroscopic matter in terms of dynamic principles that govern its microscopic constituents has fascinated physicists. Foundations of the modern understanding were laid by Ludwig Boltzmann in the latter part of the 19th century.[1] From physical arguments concerning the probable number of binary collisions (the Stosszahlansatz based on the principle of molecular chaos), Boltzmann deduced a "kinetic" equation satisfied by the probability distribution function.

The underlying theme of *nonequilibrium* statistical mechanics is to understand how macroscopic systems approach thermodynamic equilibrium. Boltzmann brilliantly opened the investigation by demonstrating by way of his H theorem that the molecular velocity-distribution function for a dilute gas ultimately approaches the Maxwellian distribution; thus he established an entropy principle. He based his demonstration on deep physical arguments but not on the exact dynamics of constituent particles.

In attempting to establish Boltzmann's equation as a consequence of particle dynamics, Nikolai N. Bogolyubov has developed a systematic expansion in which Boltzmann's equation is the lowest-order result. Bogolyubov's expansion, in conjunction with establishment of the class of correlations that allows for a kinetic description of the gas, yields the link that was missing in Boltzmann's theory between dynamics and the entropy principle. But paradoxically higher-order terms in Bogolyubov's expansion fail to yield an entropy principle, thereby reopening the problem of understanding approach to thermodynamic equilibrium.

The efforts that have been made toward resolution of this paradox have, in turn, produced a number of fascinating problems. The solution of the three-body problem for the simple case of hard spheres prompts current attempts to solve the N-body hard-sphere problem. Success in the study of simple interaction laws (step-function potentials) suggests the study of a kinetic description of realistic gases (that is, gases with an attractive part in their potential). The relationship established between the Liouville equation and Krook's relaxation equation stimulates interest in understanding the spectrum of linearized collision operators. In recent studies of higher-order kinetic theory, it has become apparent that density dependence of

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transport coefficients is not analytic. The precise form of this density dependence is not established for realistic gases.

Boltzmann and Bogolyubov theory

Boltzmann's kinetic equation predicts the behavior of the probability distribution function $f(\mathbf{x}, \mathbf{v}, t)$ for a particle with position $\mathbf{x}$ and velocity $\mathbf{v}$. It expresses the rate of change of the number of particles in an infinitesimal region of phase space as the flow of particles into this region due to their motion in a force field plus the net rate at which particles are scattered into this region by collisions. The kinetic equation can be written as

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \mathbf{F} \cdot \nabla_v f = A[f] \qquad (1)$$

The vector $\mathbf{F}$ represents the external force per unit mass, and $A[f]$ denotes the time rate of change of the distribution function due to collisions. Boltzmann's argument yields for the collisional rate of change of the distribution function produced by two-body interactions among point particles the famous result

$$A[f]_1 = \int\int [f'(1)f'(2) - f(1)f(2)\, g\sigma d\Omega d\mathbf{v}_2 \qquad (2)$$

With Boltzmann's kinetic equation (the combination of equations 1 and 2), it has been possible to explain most of the known features of the steady-state behavior of dilute gases, for example, the transport properties. Moreover, by means of Boltzmann's equation, entirely new phenomena have been predicted. For example, thermal diffusion, used during World War II in the separation of the fissionable ^{235}U from its abundant isotope ^{238}U, was predicted in 1911 by David Enskog.

A most important consequence of Boltzmann's kinetic theory is that it introduced a basic conceptual clarification of irreversibility.[2] Physically realizable macroscopic systems relax to thermodynamic equilibrium although individual particles satisfy time-reversible equations of motion. Boltzmann obtained from his kinetic theory a specific form of the entropy principle known as the " H theorem." (If the symbol "H" is read as (capital) eta, the initial letter of entropy, and not as capital h, the connection of the H theorem with entropy increase is more readily noted.)

$$\partial H / \partial t \leq 0 \qquad (3)$$

where

$$H \equiv \int f \log f d\mathbf{v} \qquad (4)$$

Equation 3 implies for a spatially homogeneous gas that the single-particle velocity-distribution function relaxes to the unique stationary solution of the kinetic equation, namely, the Maxwellian velocity distribution. Because the beautiful theory of Boltzmann was based on physical arguments regarding only two-body collisions and not obtained from the dynamical laws of motion for all the gas particles, a famous and important controversy resulted concerning the validity of the kinetic equation. This controversy helped place Boltzmann's theory in proper perspective: The theory represents the behavior of dilute gases.[3]

In 1940 Bogolyubov[4] broke new ground by establishing Boltzmann's equation for a nearly spatially homogeneous and isolated gas as the lowest-order term in a systematic expansion of the Liouville equation

$$\frac{\partial F_N}{\partial t} + [H_N, F_N]_{\mathrm{PB}} = 0 \qquad (5)$$

The second term represents the Poisson bracket of the N-body Hamiltonian with the N-body phase-space distribution function, F_N. Equation 5 compactly summarizes the time-reversible equations of motion for all the constituent particles. The gist of Bogolyubov's derivation of the Boltzmann equation is the observation that the joint probability distribution function for two bodies changes very rapidly during a collision (because of the drastic change in the two momenta) although the single-particle velocity-distribution function changes appreciably only on a much longer time scale, of the order of the mean free time between collisions. Exploiting this observation, Bogolyubov assumed that the two-body distribution becomes rapidly "synchronized" to the single-particle distribution in the sense that the time dependence of the two-body distribution function can be expressed in terms of the single-particle distribution function. Bogolyubov further assumed that the distribution function for any number of particles varies with time only through the single-particle distribution function ("functional assumption"). As the initial condition on the distributions, Bogolyubov imposed molecular chaos. The latter restriction has since been removed as you will see later in the section on multiple time scales.

Since Boltzmann's theory accounts for only two-body interactions, it is clear that an understanding of macroscopic properties that depend on three-body interactions cannot be obtained without going beyond Boltzmann's theory. Bogolyubov's analysis opened a major and most promising program since, by calculating to sufficiently high order, one should be able, in principle, to determine any macroscopic property of neutral gases or plasmas. George Uhlenbeck played a major role in giving momentum to the advancement of this program.[5] The transport coefficients are macroscopic properties of considerable physical importance since they fulfill a basic role in determining the space and time dependence of density, temperature and flow velocity. For a gas in which only two-body interactions are operative, Boltzmann's theory implies that the transport coefficients satisfy "Maxwell's law": The transport coefficients are density independent.[6] For dilute gases this result is experimentally verified. To describe transport properties in "dense" gases ($p \geqq 5$ atm, $T \approx 300°\mathrm{K}$) and gases in which chemical transmutations occur, three-body interactions are essential. For example, the understanding of dense monatomic gases requires knowledge of the bulk viscosity coefficient.[7] This transport coefficient for monatomic gases as deduced from the Boltzmann equation (which includes only binary collisions) vanishes identically. With regard to macroscopic properties of reacting gases, one can verify that even the simplest dissociation of a diatomic molecule requires a three-body collision to satisfy the conservation laws of energy and momentum. A similar argument applies to the association of two atoms into a diatomic molecule.

It was found in 1961 that the higher-order terms in Bogolyubov's expansion generally contain divergent integrals. Moreover these terms do not fulfill Boltzmann's entropy principle, the H theorem.[8] Consequently, Bogolyubov's method, in spite of providing conceptual progress over Boltzmann's approach, does not yield a fully satisfactory theory of irreversibility. Forms of the entropy principle that generalize Boltzmann's H theorem have been studied.[9] It is an open question whether these generalizations can resolve some of the difficulties associated with Bogolyubov's method.

In what follows we first present an example that demonstrates the failure of Bogolyubov's scheme. Paths that have been suggested to avoid these difficulties are then indicated. Special emphasis is given to the recently developed multiple-time-scale approach. Finally, there is a discussion of research in progress of which the aim is to carry to completion the basic program of nonequilibrium statistical mechanics, namely, that of obtaining a general description of the evolution of macroscopic systems that satisfies an appropriate entropy principle, thereby restoring the insight introduced into irreversibility by Boltzmann's H theorem.

Failure of Bogolyubov theory

Gradients in density, flow velocity and temperature result in transport of particles, momentum and energy. A transport coefficient can be expressed as a time average of statistical correlations among fluxes corresponding to the transport property considered. For example, the diffusion coefficient for a particle with velocity v is given by

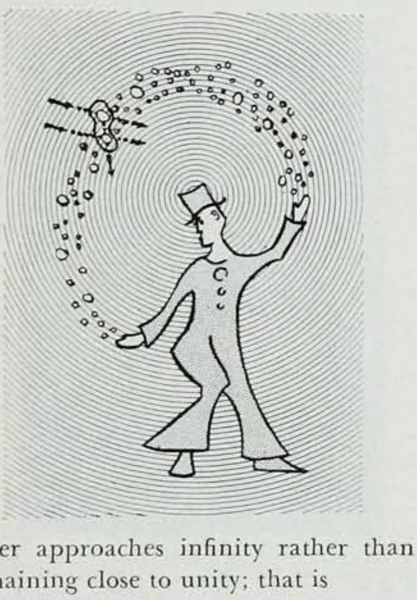
$$D = \int_0^\infty dt < \mathrm{v}(0) \cdot \mathrm{v}(t) > \qquad (6)$$

Relationships between the transport coefficients and the appropriate correlation functions, such as given in equation 6, are known as "fluctuation-dissipation" theorems.[10] Determination of the correlation functions is accomplished with kinetic theory. Thus analytic calculation of transport properties is ultimately dependent on establishment of a "physically correct" kinetic (or master) equation with an appropriate entropy principle.[11]

As a result of the convergence difficulties, the transport coefficients cannot be properly evaluated within Bogolyubov's theory.[12] For example, when Bogolyubov's technique is used to construct the kinetic equation, equation 6 yields, for fixed scattering centers, the following result for the diffusion coefficient correct to first order

$$D^{(0)} + (nd^s)\, D^{(1)} = A_s d \left(\frac{kT}{m}\right)^{1/2} (\lim_{z\to 0} |\log z\,|)^{-1} \quad (7)$$

(d is the particle diameter; n the particle density; s the dimension of the space, and A_s a numerical constant). Clearly, equation 7 implies that the ratio of the lowest-order coefficient to the result correct to first



order approaches infinity rather than remaining close to unity; that is

$$\frac{D^{(0)}}{D^{(0)} + (nd^s)\, D^{(1)}} \rightarrow \infty \qquad (8)$$

Equation 8 indicates that expansion of the diffusion coefficient in powers of the dilution parameter nd^s cannot be adequate since addition of higher-order terms does not produce correct density dependence.

Thus, Bogolyubov's method for systematizing kinetic theory yields divergent results for nonequilibrium density-dependent effects in neutral gases. It is natural to ask whether this result is peculiar to neutral gases. Bogolyubov's theory is of sufficient scope to describe ionized gases (plasmas). In fact, one of its major triumphs is that it yields a kinetic equation that properly accounts for Debye shielding.[4, 13] It has been proven that this theory yields divergent results for plasma properties when calculations are extended beyond the lowest order in the plasma parameter $(1/n\lambda_D{}^3)$.[8, 14] Difficulties implied by equation 8 are therefore not confined to neutral gases. Dramatic forms of these infinities also occur when Bogolyubov's method is applied to derive the master equation, that is, the irreversible equation for the distribution of all particle momenta.[15] It must be concluded that the divergences which arise in Bogolyubov's scheme prevent rigorous establishment of an entropy principle (and, consequently, of a physically correct kinetic equation) thereby depriving Bogolyubov's irreversibility theory of its logical foundations.

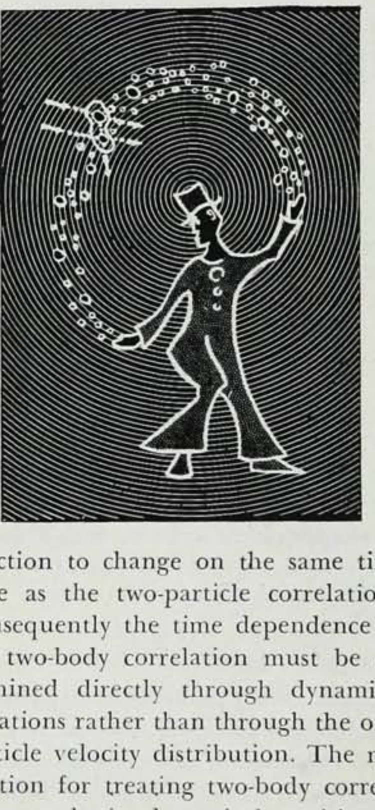
Physical basis for failure

A major reason for divergences in Bogolyubov's method of calculation can be understood as follows.[8] The lowest-order kinetic equation (the Boltzmann equation) takes into account the probable effect of collisions between two particles. The corrections to the Boltzmann equation require the calculation of interactions among three or more bodies. Three-body interactions include both "long-range" and "short-range" successive binary collisions. Short-range three-body interactions are those in which a particle that has already undergone a binary collision collides with a third particle at a distance short compared to the mean free path whereas long-range interactions are those in which the collision with the third particle occurs at a distance comparable with the mean free path.

If we call r_0 the range of the intermolecular potential, the mean duration of a binary collision is approximately $r_0/(kT/m)^{1/2}$ ($\sim 10^{-12}$ sec for an inert gas at standard conditions). In general the mean free time is the much longer time $\lambda/(kT/m)^{1/2}$ where $\lambda \approx 1/nr_0{}^2$ is the mean free path. The mean free time is about 10^{-9} sec, that is, 1000 times the duration of one collision. In figure 1 we show an interaction involving three particles that undergo two successive binary collisions. Due to energy and momentum balance, the successive collisions generate three-body correlations over the time interval $t_f - t_1$. The distinction between short- and long-range correlations corresponds to the time interval Δt. Three-particle correlations are "genuine" short-range correlations if Δt is of order of magnitude $r_0/(kT/m)^{1/2}$ whereas we have long range correlations if Δt is of the order of magnitude of $\lambda/(kT/m)^{1/2}$. In Bogolyubov's method, three-body interactions erroneously include long-range successive binary collisions. These collisions give rise to three-particle correlations with *macroscopic* correlation lengths, of the order of the mean free path. This type of collision has already been taken into account in the lower-order binary-collision term (Boltzmann) and should not be counted again. In Bogolyubov's method, however, these completed successive two-body collisions with long-range correlations are recounted in each of the higher orders giving rise to divergent integrals. By exploiting the physical argument given above, two approaches that ultimately may be related have been suggested to remedy the defects in Bogolyubov's expansion: (1) to sum the troublesome successive binary collisions to all orders and (2) to treat the two-particle distribution dynamically on the same footing as the one-particle distribution (closely related to the concept of closure).

The first approach emphasizes the singular nature of Bogolyubov's expansion. It is based on the observation that summing the most singular terms of a series often yields physically meaningful results. This idea has been used extensively in reproducing the main results of Bogolyubov's method by a perturbation technique.[16, 17] The method of "summing the most singular contributions" is applied in a natural way to the three-body problem by summing successive binary collisions to all orders. This process yields, for two-dimensional models, transport coefficients that have a logarithmic density dependence.[12] Full results for three-dimensional analysis are not yet available. Furthermore, it has been possible formally to sum the entire series by obtaining an explicit expression for the nth order term in Bogolyubov's expansion.[15, 18] However, it has not yet been established how to incorporate this summation process into a theory of irreversibility (with an appropriate entropy principle) that includes *all* three-body collisions.

The second approach emphasizes that the difficulty in Bogolyubov's expansion arises from correlations with an excessively long range. This approach requires that the two-body correlation function be treated as a fundamental variable, on the same footing as the one-particle distribution function. This approach has been used to calculate plasma conductivity for plasmas subjected to rapidly oscillating fields.[19] With rapidly oscillating fields, Bogolyubov's functional assumption becomes invalid since the impressed field can cause changes in the particle momenta on a time scale comparable to the collision time, thus causing the one-particle distribution



function to change on the same time scale as the two-particle correlations. Consequently the time dependence of the two-body correlation must be determined directly through dynamical equations rather than through the one-particle velocity distribution. The motivation for treating two-body correlations as basic dynamical entities in the absence of external fields is also based on a physical analysis of the pertinent time and space scales. To understand the physics of the distinct time scales that occur in a gas, the "multiple time-space scale expansion" technique has been developed.[8, 20] This technique has yielded important results in its own right, and we shall discuss it in more detail in the next section. The main conclusion concerning the two-particle correlation functions is that these subsist only for times comparable to the mean free time and become disrupted by collisions with a third body only for longer times. Even though complete results are not yet available, this approach is very promising in that primarily the "genuine"-short-range part of the correlations contributes to the correction to the Boltzmann equation.

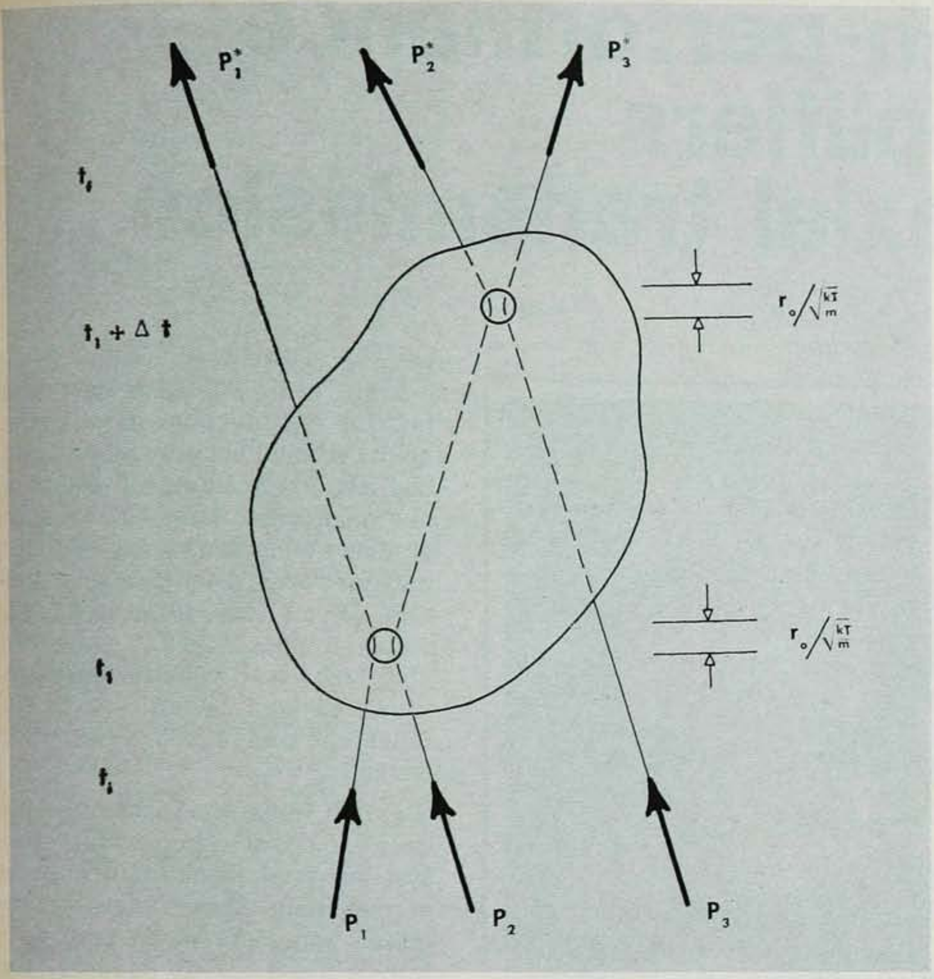
Multiple time scales

In view of the wide difference between the duration of one collision and the mean free time between collisions ($r_0/(kT/m)^{1/2} \ll \lambda/(kT/m)^{1/2}$) it is desirable to separate in the mathematical analysis phenomena that occur on the two time scales. The basic idea of the multiple-time-scale method is to use the chain rule of differentiation to express the time derivative of a function in terms of successively slower time scales

$$\frac{\partial\lambda(\tau_n = \epsilon^n t)}{\partial t} = \frac{\partial\lambda(\tau_n)}{\partial\tau_0} + \epsilon\frac{\partial\lambda(\tau_n)}{\partial\tau_1} + \epsilon^2\frac{\partial\lambda(\tau_n)}{\partial\tau_2} + 0(\epsilon^3) \qquad (9)$$

The fast time scale τ_0 is measured for neutral gases in units of the duration of one collision and, for fully ionized gases, in units of the inverse plasma frequency. The slower time scale τ_1 is measured in units of the mean free time. We shall discuss the meaning of the τ_2 scale at the end of this section.

It can be shown that the formulas of Bogolyubov correspond to the multiple-time-scale formulas in the limit as τ_0 approaches infinity. This result establishes a satisfactory link between Bogolyubov's systematic expansion and the descriptions of irreversibility due to John Kirkwood[21] and to Marshall Rosenbluth and Norman Rostoker.[13] By not taking τ_0 to infinity at the outset of the calculation, the multiple-time-scale technique yields the behavior of transients that occur in a gas prior to establishment of the fully developed kinetic regime, that is, the gaseous regime described by the single-particle distribution function. (In the same spirit, calculation of transients that occur prior to establishment of the hydrodynamic regime has been



THREE-BODY COLLISION consists of two successive binary collisions. Short-range correlations involve total collision times that are comparable with duration of binary collisions. Long-range ones involve collision times that are of the order of mean free time particles spend between collisions. —FIG. 1

carried out with this method by James McCune and his colleagues.[20]) The condition the correlation functions must satisfy, if a kinetic equation is to hold at all, has been established with multiple time scales when the collisions produce small momentum transfer.[22] The condition is that there should not be too many pairs of particles with vanishing relative velocity. Such pairs give a "beam" structure to the gas and slow down the approach to equilibrium. The determination of the class of correlations that are "kinetic" (that is, that guarantee that a kinetic equation holds) establishes from first principles the meaning and limitations of the idea of molecular chaos. Thus calculation of kinetic conditions completes the program initiated by Bogolyubov for deriving lowest-order kinetic theory on purely dynamical grounds.

We now pursue the implications of the multiple-time-scale expansion for higher-order kinetic theory by examining evolution of the single-particle distribution on the slower time scales $(\tau_n \equiv \epsilon^n t)$. On the τ_1 time scale, that is, within a few mean free times, the one-particle velocity distribution in a homogeneous gas becomes Maxwellian. On slower time scales one does not expect further time dependence of the one-particle distribution function. (It should be emphasized that fluctuations about equilibrium that occur over times comparable to Poincaré's recursion time are not pertinent to the present problem since the Poincaré recursion time is made infinite by letting the particle number and volume tend to infinity with the mean density held constant.)

The physical analysis of the pertinent time scales leads naturally to the condition of closure, that is, to the requirement that the single-particle distribution function be constant over time scales long compared with the mean free time. By setting the rate of change of the one-particle velocity distribution function, evaluated for large τ_1, equal to zero on all slower time scales, conditions are imposed on the higher-order contributions to the two- and three-body distribution functions. This leads to a dynamical treatment in which the two-particle correlations subsist on distances of the order of one mean free path only. A "weak H theorem" can then be shown to hold. This form of the H theorem is called "weak" because it requires restrictions on the rate of change of the single-particle distribution and on its moments. The consistency of the closure process to all orders has been proven only for the special case in which the interaction energy between particles is small compared to the thermal energy.[23] Also analysis of the strong short-range interaction is well under way.[24] An interesting series of investigations that may be considered as the ionized-gas version of the closure procedure concerns establishment of a completely convergent kinetic equation for a fully ionized Lorentz gas.[25] This theory accounts automatically for short-range interactions, for interactions with small momentum transfer and for the Debye shielding of distant encounters. The failure in Bogolyubov's theory to provide an entropy principle can be clarified by the multiple-time-scale analysis. On the fast time scale $(\tau_0 = t\,(kT/m)^{1/2}/r_0)$ the system is reversible. The approach to thermal equilibrium should be described in lowest order on the next time scale by a decay of the form

$$\exp(-\tau_1) = \exp(-\epsilon t) \qquad (10)$$

where the decay time is of the order of a mean free time $(\tau_1 = t(kT/m)^{1/2}/\lambda)$. This behavior is borne out by the Boltzmann equation. The correction to lowest-order decay appears on the $\tau_2 = \epsilon^2 t$ scale and should be of the "normal" type

$$\exp(-\tau_1) \times \exp(-\tau_2) \qquad (11)$$

The normal behavior corresponds to saying that the relaxation time $1/\epsilon$ is corrected to $1/(\epsilon + \epsilon^2)$. The presence of completed successive binary collisions in Bogolyubov's expansion,

however, leads to an "abnormal" behavior of the type

$$\exp(-\tau_1) + \exp(-\tau_2) \qquad (12)$$

The abnormal behavior corresponds to a time variation that continues well beyond the (lowest-order) relaxation time $1/\epsilon$. Bogolyubov's functional assumption, which leads to the "abnormal" evolution, prevents a satisfactory construction of the entropy principle. Use of multiple time scales in conjunction with the method of extension[8] provides a promising departure from this impasse.

It is interesting to note that there is a deep analogy between deriving irreversible equations from Liouville's theorem and deducing behavior of decaying nuclear or atomic states from the Schrödinger equation. The multiple-time-scale approach has clarified this important problem.[26]

Prospects for a complete theory

The convergence difficulties of Bogolyubov's method, which we described above, are only partially resolved by proposals previously considered. A complete theory of irreversibility that includes all types of three-body interactions is not provided by these techniques.

Therefore major steps must be taken to obtain such a complete theory and to predict with certainty transport properties when three-body interactions are important. In particular, the calculational methods that have been dominated by Bogolyubov's theory must be substantially improved. With such improvements it should be possible to determine accurately density dependence of transport coefficients and kinetic collision integrals. We believe that multiple-time-scale theory provides a promising approach in this direction.

Bogolyubov's technique yields formally the effects of three-body collisions on the transport coefficients. But, in giving a general (formal) solution, Bogolyubov imposes an asymptotic behavior on the distribution functions ("functional assumption") that, in view of the convergence difficulties, contradicts the three-body dynamics. In sharp contrast the multiple-time-scale technique (or more generally, the technique of extension) avoids this pitfall of Bogolyubov's method.[27] This technique does not impose a priori an asymptotic behavior on the distribution function. Instead, to determine the behavior of the distribution functions, the specific form of the particle trajectories is required. Since knowledge of the trajectories yields information concerning the transport of momentum and energy, requiring this knowledge is physically reasonable. Note that the successful calculation of transport coefficients for low-density gases is based on the Boltzmann equation, which contains detailed information on two-body trajectories. In higher-order theory it is essential to determine the three-body trajectories.

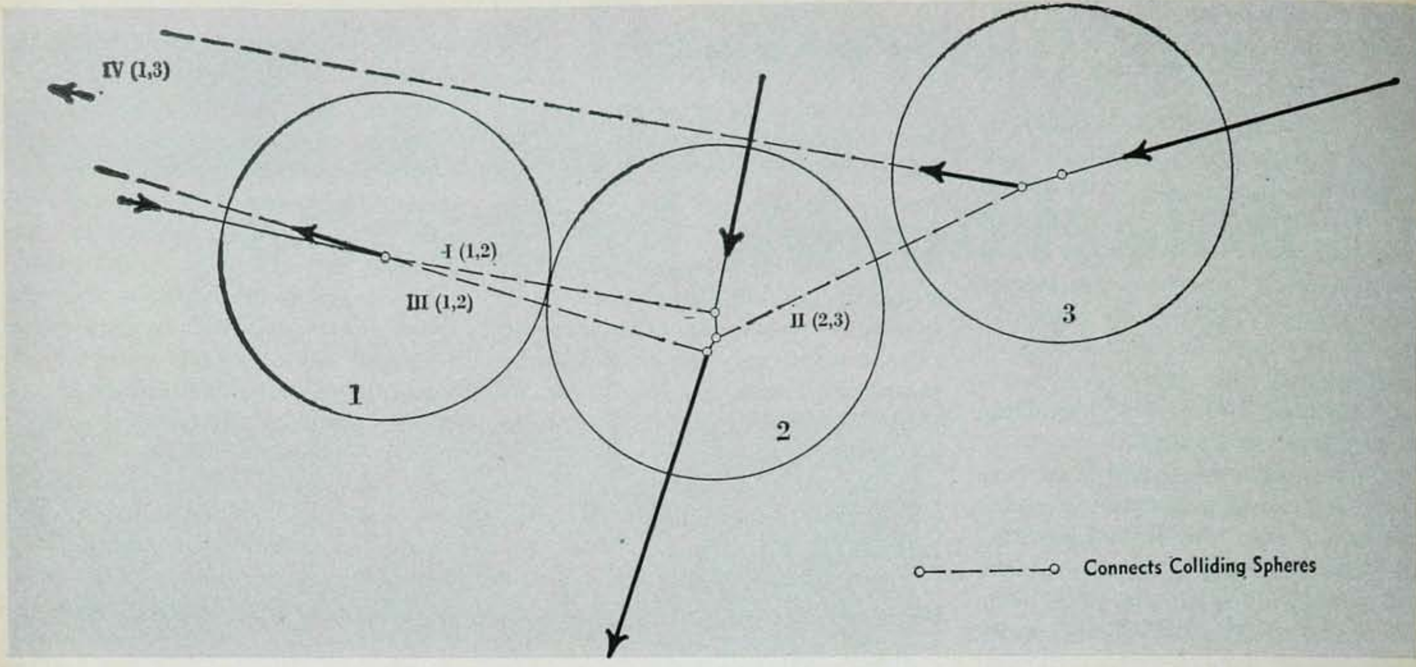
Types of collisions among three hard spheres (of equal masses and radii) have been categorized.[28] The analysis gives full details of phase-space behavior required by statistical mechanics. In particular, the boundaries of the phase-space regions in which 1, 2, 3, and 4 (!) successive binary collisions occur have been determined (see figure 2). Furthermore, it has been demonstrated that five successive binary collisions among three bodies are impossible. It has been proven, in fact, that the only collision chains that are possible among three hard spheres (of equal masses and radii) labeled 1, 2, and 3 are those listed in the following table. The symbol (i,j) represents a collision between particle i and particle j.

Single collision
(1,2)
Two successive collisions
(1,2) – (2,3)
Three successive collisions
(1,2) – (2,3) – (1,2)
(1,2) – (2,3) – (1,3)
Four successive collisions
(1,2) – (2,3) – (1,2) – (1,3)

It must be noted that time-reversed collision chains are also allowed. For example, the chain (1,3) – (1,2) – (2,3) – (1,2) is equivalent to the four-collision sequence given in the table. The reader is urged to experiment with three pennies on a smooth surface. With some practice he can generate the allowed collision chains. In Bogolyubov's expansion, not only were the precise domains for the particle-collision chains not employed, but some types of collisions, (for example, four successive collisions) were altogether omitted. The successful solution of the three-body problem has inspired an interesting program, establishment of trajectories for N hard spheres. Solution of this problem would constitute the first nontrivial model for nonequilibrium statistical mechanics. For hard spheres, the trajectories are sectionally straight lines. This enormous simplification over the gravitational problem is responsible for the solubility of the three-body problem and might permit solution of the N-body problem. The anslysis carried toward this end, however, indicates that the problem is a difficult one.[29]

To obtain a kinetic equation that yields density-dependent transport coefficients, it is very desirable to avoid the singularities associated with the hard-sphere interaction. These singularities correspond to an infinite potential jump at the boundary of the sphere. This jump yields for the force a delta function multiplied by an infinite coefficient. For finite-depth potentials, although the force remains a delta function, the coefficient is finite; consequently, the integrals required for calculating transport properties are more readily treated. It is desirable, therefore, to solve the dynamical problem corresponding to such an interparticle potential. Inclusion of finite-depth potentials is also of interest since it provides the basis for obtaining the kinetic equation for realistic gases whose particles interact through potentials that contain an attractive part. The kinetic equation for such realistic gases has not been rigorously established. An attractive part in the potential law is essential if consideration is to be given to association and dissociation in a neutral gas and ionization and recombination in a plasma.

We have seen that description of the evolution of a gas in terms of collisions among only a few particles meets with severe difficulties. Instead of considering only two-particle collisions in lowest order and three-body interactions in first order, it is natural to consider small departures from equilibrium in lowest order and to allow larger departures in higher order. With this point of view, an alternative approach to the problem of irreversibility has been established[30]



FOUR-COLLISION SEQUENCE: (1,2) – (2,3) – (1,2) – (1,3). Spheres are shown at instant of first collision. Velocities indicated are initial ones and those after third collision. Trajectory data were obtained from a computer experiment by Roger Sullivan. First three collisions (I, II and III) are shown and fourth (IV) occurs at approximately nine body diameters from location shown. Sphere 1 is stationary between collisions that are numbered I and III. —FIG. 2

through the derivation (subject to appropriate conditions) of the Jeans-Krook kinetic equation[31] from the Liouville equation. Thus, it has been shown that the Jeans-Krook equation is not subject to the limitation that only binary collisions are considered. In fact, the following relaxation equation has been shown to hold for a wide class of systems as a consequence of the master equations[32]

$$\partial\Delta/\partial t = -(1/\mathcal{T})\Delta \qquad (13)$$

The function Δ is the *departure* of the single-particle velocity-distribution function from its equilibrium value M. The operator $1/\mathcal{T}$ is a linear operator defined and discussed in detail in reference 30. Equation 13 implies that the state of the gas near equilibrium is a superposition of exponential decays. The entropy principle in this formulation of kinetic theory requires that $1/\mathcal{T}$ have only *positive* eigenvalues. Consequently, it is of major interest to study the spectrum of $1/\mathcal{T}$. It has been demonstrated that *if* a gap in the spectrum of $1/\mathcal{T}$ exists, that is, if $\mathcal{T}$ possesses a dominant eigenvalue, an expansion in the small parameter $\mathcal{T}$(next to dominant)/$\mathcal{T}$(dominant) is possible. Clearly this procedure can be extended to the case in which there is a clustering of eigenvalues about a dominant one. The spectrum of $\mathcal{T}$ need not be completely discrete.[33] Analysis of the pertinent time scales shows that in the first stage of the relaxation a transient behavior is exhibited by Δ which corresponds to the "small" relaxation times. When these transients subside, lowest-order theory yields the Jeans-Krook kinetic equation (which satisfies the Boltzmann H theorem)

$$\partial f/\partial t = (M - f)/\tau\,(\text{dominant}) \qquad (14)$$

where M is the equilibrium or steady-state distribution function. The familiar mean free time has been identified with the dominant eigenvalue of the operator $1/\mathcal{T}$. Although equation 14 can be obtained by linearizing the Boltzmann equation (equations 1 and 2), the derivation of equation 14 directly from the Liouville equation has established the validity of the Jeans-Krook kinetic equation for a class of systems for which the Boltzmann equation is inadequate. Knowledge of the transport properties of real gases results from study of the eigenvalues of the relaxation operator $1/\mathcal{T}$.[34] When a few relaxation times are dominant, analysis of transport coefficients is substantially simplified. By describing the transport coefficients in terms of a limited number of relaxation times, a phenomenological analysis of the transport properties of real gases is feasible.[35] Moreover, this analysis should yield information concerning the spectrum of $\mathcal{T}$. The Jeans-Krook equation described above yields the time evolution of the single-particle *momentum* distribution. The special choice of the degrees of freedom (particle position and momentum) employed in the above derivation is not essential. A simple relaxation equation can be based on any choice of degrees of freedom, some of which may be collective. In recent studies of Fermi liquids, the relaxation equation for the distribution of collective coördinates has been employed.[36]

All the problems in nonequilibrium statistical mechanics are ultimately related to the quest for the correct form of the entropy principle. Much effort is being devoted to the solution of these problems. We hope that, thanks to these efforts, a satisfactory description of the approach towards equilibrium, including an appropriate entropy principle, will be achieved in the near future. □

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