Classical Theory of Transport Phenomena in Dilute Polyatomic Gases*

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A classical theory of transport phenomena in dilute gases of molecules possessing internal degrees of freedom is presented. It is shown that the existence of inverse collisions is unnecessary for the development of the theory. First-order formal expressions for the coefficients of thermal conductivity, shear viscosity, and bulk viscosity are given. In cases where the molecules make only elastic collisions the expressions found reduce to the well-known Chapman-Enskog results. The treatment is very similar to the semiclassical one of Wang Chang and Uhlenbeck, who treated the internal degrees of freedom quantum-mechanically and could thus use the fact that quantum inverse collisions exist. Their theory reduces to the present one in the classical limit.

I. INTRODUCTION

CHAPMAN and Enskog (CE)[1] have presented a classical theory of transport phenomena in dilute gases. They treated only molecules not possessing internal degrees of freedom, and the extension of the theory to eliminate this restriction has not yet been given. This state of affairs arises from the difficulty presented by the general nonexistence of "inverse collisions"[2] in classical mechanics. Certain special models have, nevertheless, been treated.[3–5] Furthermore, it was possible for Wang Chang and Uhlenbeck (WCU)[6] to present a semiclassical theory in which the internal degrees of freedom were treated quantum-mechanically. They took advantage of the existence of inverse collisions as guaranteed by quantum mechanics.

We expect the classical description of transport phenomena to be valid over a large temperature range for many molecules, in particular for heavy polyatomic molecules with nearly classical rotations. It, therefore, seems worthwhile to establish a classical theory, which is an extension of the CE theory and at the same time the classical limit of the WCU theory. That is the purpose of this paper. The results, first-order expressions for the coefficients of thermal conductivity, shear viscosity, and bulk viscosity, are presented in Sec. IV.[7] They are given in the usual classical collision parameter formalism, which in principle allows direct application of the theory, providing we can solve the classical scattering problem.

II. CLASSICAL BOLTZMANN EQUATION

We start with the task of determining under various physical conditions the form of the distribution function, $f(\mathbf{c},\Omega,\mathbf{r},t)\equiv f$, where $\mathbf{c}$ is the absolute linear velocity of the center of mass of the molecule, Ω represents the totality of coordinates and momenta about the center of mass for the classical internal degrees of freedom, $\mathbf{r}$ is the position vector to any point in the gas, and t is the time. This distribution is defined in such a way that $fd\mathbf{c}d\Omega d\mathbf{r}$ represents the number density of molecules contained in a velocity phase element $d\mathbf{c}$ about $\mathbf{c}$ with internal degrees of freedom in the phase element $d\Omega$ about Ω and in a volume element $d\mathbf{r}$ about $\mathbf{r}$ at a time t. By the customary arguments we get for the equation which f obeys for a dilute gas in which only binary collisions are important:

$$\frac{\partial f}{\partial t}+\mathbf{c}\cdot\frac{\partial f}{\partial \mathbf{r}}+\mathbf{F}\cdot\frac{\partial f}{\partial \mathbf{c}}=\int(f''f_1''-ff_1)gbdbd\varphi d\mathbf{c}_1d\Omega_1, \quad (1)$$

where $m\mathbf{F}$ is the total external force on the molecule, m being the mass of the molecule; g is the initial relative speed; b is a collision parameter specifying the magnitude of the initial orbital angular momentum; φ is an azimuthal angle about the direction of the initial relative velocity specifying the direction of the initial orbital angular momentum; and, as with f, $f(\mathbf{c}_1,\Omega_1,\mathbf{r},t)$ is written f_1, etc. The subscript 1 refers to the second molecule in the collision. The double-primed quantities refer to the initial conditions in the "corresponding collision"[2] which restores molecules to the state described by f. In the collision integral of (1) we are to think of the double-primed quantities as functions of the unprimed quantities, obtained in principle from the classical equations of motion. The coordinates and momenta of the two-molecule system are to be reckoned at some time before and after the collision when the molecular interaction is negligible, at "critical constellations" in the language of Tolman.[2] Since classical inverse collisions are known not to exist in general, we cannot make the usual symmetry arguments that allow replacement of the double-primed quantities by ones which refer to the final conditions in the "direct colli-

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[1] See S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, New York, 1952), second edition.

[2] R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, New York, 1938).

[3] J. H. Jeans, Trans. Roy. Soc. (London) **196**, 399 (1901).

[4] F. B. Pidduck, Proc. Roy. Soc. (London) **A101**, 101 (1922).

[5] C. F. Curtiss, J. Chem. Phys. **24**, 225 (1956).

[6] C. S. Wang Chang and G. E. Uhlenbeck, "Transport Phenomena in Polyatomic Molecules," Michigan University Engineering Research Institute Report CM-681, 1951 (unpublished). (Available on Interlibrary Loan from Michigan University Library.)

[7] Only simple gases will be treated for mathematical simplicity.

sion,"[2] which removes molecules from the state described by f. We must, therefore, look elsewhere for the apparatus to express solutions to the transport problem.

In (1) the classical Liouville theorem for a dynamical system of two colliding molecules[2] has been used. In collision parameter language, this is

$$g''b''db''d\varphi''d\mathbf{c}''d\mathbf{c}_1''d\Omega''d\Omega_1''=gbdbd\varphi d\mathbf{c}d\mathbf{c}_1d\Omega d\Omega_1.$$

Along with WCU, we have tacitly assumed that the external forces do not act on the internal degrees of freedom.[8]

III. EQUILIBRIUM SOLUTION

When there are no external forces, the $\mathbf{r}$-independent solution for $f\equiv f^{(0)}$ must satisfy

$$\frac{\partial f}{\partial t}=\int(f''f_1''-ff_1)gbdbd\varphi d\mathbf{c}_1d\Omega_1. \qquad (2)$$

If we now define H, a function of the time only, as

$$H\equiv\int f\ln f d\mathbf{c}d\Omega, \qquad (3)$$

it is not possible by simple manipulations of (2) and (3) to show that $dH/dt\leqslant 0$ in the usual way.[2] Instead we must appeal to the device of the "closed cycle of corresponding collisions" of Boltzmann, a chain of molecular collisions which has the property of repeating itself after a finite number of collisions. When one uses this concept, it can be shown that $dH/dt\leqslant 0$ and $dH/dt=0$ provided

$$f^{(0)}=n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\left[\int\exp\left(-\frac{E_\Omega}{kT}\right)d\Omega\right]^{-1}\times\exp\left[-\frac{1}{kT}\left(\frac{mC^2}{2}+E_\Omega\right)\right],$$

where n is the number density of molecules in the gas; k is the Boltzmann constant; T is the absolute temperature; $\mathbf{C}$ is the peculiar velocity, $\mathbf{c}-\mathbf{c}_0$, with $\mathbf{c}_0$ the streaming velocity of the gas as a whole; and E_Ω is the energy corresponding to the internal degrees of freedom. Along with WCU, we have neglected in $f^{(0)}$ any "summational invariants" other than the number of molecules, the linear momentum and the total energy. We might have included the total angular momentum as well. But although its inclusion may be mathematically more general, it does not necessarily lead to results of physical interest. For example, in Pidduck's "rough sphere" model its inclusion leads to a possible nonzero average rotational energy at equilibrium for each molecule. But it is more likely experimentally that we are interested in the equilibrium state in which the average is zero. Mathematically the treatment of this latter condition is equivalent to having neglected the total angular momentum summational invariant in the first place.

IV. NEAR-EQUILIBRIUM SOLUTION

Transport Phenomena

We may now proceed exactly along the lines of the WCU theory, in which the exchange of energy between the translational and the internal degrees of freedom takes place with ease. This is because it will not be possible in general for the "temperature" of the internal degrees of freedom to become very different from the "temperature" of the translational degrees of freedom. We might think of some process like the passage of a sound wave through the gas, exciting during each cycle classical rotations and translations for which we consider equilibration to take place fast enough that the local state of the gas may be described by a single temperature.

Thus, we may write in a way that is formally similar to WCU the general equation of change, the hydrodynamic equations, the various fluxes, the linearized Boltzmann integral equation, the integral conditions, the *Ansatz* for the first-order solution, etc. Along with WCU, we eventually obtain formal bracket expressions for the thermal conductivity λ, the shear viscosity η, and the bulk viscosity κ, as follows:

$$\lambda=\frac{2k^2T}{3m}[A\boldsymbol{\mathfrak{C}},A\boldsymbol{\mathfrak{C}}],$$
$$\eta=\frac{kT}{10}[B(\boldsymbol{\mathfrak{C}}\boldsymbol{\mathfrak{C}}-\tfrac{1}{3}\mathfrak{C}^2\mathbf{U}),B(\boldsymbol{\mathfrak{C}}\boldsymbol{\mathfrak{C}}-\tfrac{1}{3}\mathfrak{C}^2\mathbf{U})], \qquad (4)$$
$$\kappa=\frac{c_\Omega{}^2kT}{c_v{}^2}[D,D],$$

where c_Ω is the internal specific heat at constant volume per molecule, assumed temperature-independent; c_v is the total specific heat at constant volume per molecule, $\frac{3}{2}k+c_\Omega$; A, B, and D are unknown scalar functions of $\mathfrak{C}^2$, ϵ, n, and T, to be determined; $\mathbf{U}$ is the unit tensor; $\boldsymbol{\mathfrak{C}}\equiv(m/2kT)^{\frac{1}{2}}\mathbf{C}$; and $\epsilon\equiv E_\Omega/kT$. These bracket expressions may be written in the convenient form

$$[M,N]\equiv 2\int M\odot(N+N_1-N''-N_1'')d\tau, \qquad (5)$$

where

$$d\tau\equiv\tfrac{1}{2}\left(\frac{m}{2\pi kT}\right)^3\left(\int e^{-\epsilon}d\Omega\right)^{-2}\exp(-\mathfrak{C}^2-\mathfrak{C}_1{}^2-\epsilon-\epsilon_1)\times gbdbd\varphi d\mathbf{c}d\mathbf{c}_1d\Omega d\Omega_1 \qquad (6)$$

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[8] We have also shown, for example, how it is possible to formulate the effect of a uniform electric field on a gas of polar molecules [Ph.D. dissertation, Northwestern University, 1957 (unpublished)].

and $\odot$ signifies a simple product of two scalars, a scalar product of two vectors, or the trace of the product tensor, depending on the character of M and N. In (5) the double-primed quantities are still to be thought of as functions of the unprimed ones just as in (1).

At this point we must depart from the WCU treatment in that we shall be unable to make use of a convenient, but fortunately unnecessary, property of the bracket expressions which holds under the general existence of inverse collisions, namely,

$$[M,N]=[N,M]. \tag{7}$$

We shall, however, be able to retain the important result

$$[M,M]\geqslant 0. \tag{8}$$

Equation (8) is necessary because, consistent with the second law of thermodynamics, λ, η and κ, which are of this form, must be non-negative. To understand these points we digress from the present development to consider the properties of the bracket expressions.

Using the Liouville theorem and the principle of conservation of energy, we are permitted to write from (6)

$$d\tau''=d\tau. \tag{9}$$

Then (5) may be rewritten

$$[M,N]=2\int M\odot(N+N_1-N''-N_1'')d\tau'', \tag{10}$$

where the unprimed quantities are now thought of as functions of the double-primed quantities, obtained in principle from the classical equations of motion. Let now the final state of the direct collision of Sec. II be denoted by single-primed quantities. But the single-primed quantities through the equations of motion are exactly the same functions of the unprimed ones as the unprimed quantities are of the double-primed ones. Hence, (10) may be rewritten

$$[M,N]=2\int M'\odot(N'+N_1'-N-N_1)d\tau, \tag{11}$$

where the single-primed quantities are thought of as functions of the unprimed ones. This last manipulation may be looked upon as either a formal change of variables or a physical translation along the closed cycle of corresponding collisions of Sec. III. It should be noted that we have removed all reference to the corresponding collision and have now to deal with the direct collision. By symmetry, (11) may be rewritten

$$[M,N]=\int (M'+M_1')\odot(N'+N_1'-N-N_1)d\tau. \tag{12}$$

However, there appears to be no way open for us without the general existence of inverse collisions to write from (12) the expression from which (7) and (8) would follow, namely,

$$[M,N]=\tfrac{1}{2}\int (M'+M_1'-M-M_1)\odot(N'+N_1'-N-N_1)d\tau.$$

Thus, it is necessary to appeal elsewhere for the proofs of these relations. We again call upon the closed cycle of corresponding collisions.

Let us consider first the proof of (8). Let

$$\begin{gathered}M+M_1\equiv x_1,\\ M'+M_1'\equiv x_2,\\ \cdots\\ M''+M_1''\equiv x_s.\end{gathered}$$

Then translating along the closed cycle of corresponding collisions of length s, say, we could write s equal expressions for $[M,M]$ just as in (11):

$$\begin{aligned}[M,M]&=\int x_2\odot(x_2-x_1)d\tau\\ &=\int x_3\odot(x_3-x_2)d\tau'\\ &\cdots\\ &=\int x_1\odot(x_1-x_s)d\tau''.\end{aligned} \tag{13}$$

Here x_2 is a function of the variables of x_1, x_3 of the variables of x_2, etc. But by the connectivity of the chain we could always express the variables of x_i $(i=2,\cdots,s)$ in terms of those of x_1, and we could write by repeated application of (9)

$$d\tau=d\tau'=\cdots=d\tau''. \tag{9'}$$

We may then write, on combining (9′) and (13),

$$[M,M]=\frac{1}{s}\int[x_2\odot(x_2-x_1)+x_3\odot(x_3-x_2)+\cdots+x_1\odot(x_1-x_s)]d\tau. \tag{14}$$

But in all cases,

$$x_i\odot x_j=x_j\odot x_i,\quad i,j=1,\cdots,s.$$

Thus,

$$[M,M]=\frac{1}{2s}\int[(x_1-x_2)\odot(x_1-x_2)+(x_2-x_3)\odot(x_2-x_3)+\cdots+(x_s-x_1)\odot(x_s-x_1)]d\tau\geqslant 0$$

in all cases.

Let us consider in a similar way the possible proof of (7). Let

$$\begin{gathered}N+N_1\equiv y_1,\\ N'+N_1'\equiv y_2,\\ \cdots\\ N''+N_1''\equiv y_s.\end{gathered}$$

The two brackets $[M,N]$ and $[N,M]$ become, in a way similar to (14),

$$[M,N]=\frac{1}{s}\int[x_2\odot(y_2-y_1)+x_3\odot(y_3-y_2)+\cdots+x_1\odot(y_1-y_s)]d\tau,$$

$$[N,M]=\frac{1}{s}\int[y_2\odot(x_2-x_1)+y_3\odot(x_3-x_2)+\cdots+y_1\odot(x_1-x_s)]d\tau.$$

We see that the integrands would not in general be equal for $M\neq N$ except for $s=2$ for which case inverse collisions exist. If the integrands are not the same, it is not likely that we could show the integrals to be equal, although this, of course, constitutes no proof. At any rate it appears that in what follows we will have to distinguish between $[M,N]$ and $[N,M]$. This is the basic difference between the present treatment and that of WCU.

First approximations to (4) may now be found by breaking off double power-series expansions in $\mathfrak{C}^2-\frac{3}{2}$ and $\epsilon-c_\Omega/k$ after the first few terms. Along with WCU, we do not justify that such expansions would be convergent. Then, the uniform center-of-mass motion and the arbitrary direction of the initial relative velocity may be integrated out of the formulation. We obtain finally the transport coefficients in terms of a binary collision in the relative system as follows:

$$\lambda=\frac{3k^2T}{2m}\left(\frac{c_\Omega^2}{k^2}X-\frac{5c_\Omega}{2k}Y-\frac{5c_\Omega}{2k}\tilde{Y}+\frac{25}{4}Z\right)\bigg/(XZ-Y\tilde{Y}),$$

with

$$X=4\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}}\left(\int e^{-\epsilon}d\Omega\right)^{-2}\int\left[\gamma^4\sin^2\chi+\left(\gamma^2\cos^2\chi+\frac{25}{8}-\frac{15}{4}\gamma^2\right)\Delta\epsilon+\frac{11}{4}(\Delta\epsilon)^2\right]\exp(-\gamma^2-\epsilon_1-\epsilon_2)\gamma^3bdbd\varphi d\gamma d\Omega_1d\Omega_2,$$

$$Y=-5\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}}\left(\int e^{-\epsilon}d\Omega\right)^{-2}\int[(\tfrac{3}{2}-\gamma^2)\Delta\epsilon+(\Delta\epsilon)^2]\exp(-\gamma^2-\epsilon_1-\epsilon_2)\gamma^3bdbd\varphi d\gamma d\Omega_1d\Omega_2,$$

$$\tilde{Y}=-10\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}}\left(\int e^{-\epsilon}d\Omega\right)^{-2}\int\left(\epsilon_1'-\frac{c_\Omega}{k}\right)\Delta\epsilon\exp(-\gamma^2-\epsilon_1-\epsilon_2)\gamma^3bdbd\varphi d\gamma d\Omega_1d\Omega_2,$$

$$Z=4\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}}\left(\int e^{-\epsilon}d\Omega\right)^{-2}\int\left(\epsilon_1'-\frac{c_\Omega}{k}\right)[\tfrac{3}{2}\Delta\epsilon+\gamma'^2(\epsilon_1'-\epsilon_2')-\gamma\gamma'(\epsilon_1-\epsilon_2)\cos\chi]\exp(-\gamma^2-\epsilon_1-\epsilon_2)\gamma^3bdbd\varphi d\gamma d\Omega_1d\Omega_2;$$

$$\frac{1}{\eta}=\frac{8}{5(\pi mkT)^{\frac{1}{2}}}\left(\int e^{-\epsilon}d\Omega\right)^{-2}\int[\gamma^4\sin^2\chi-(\tfrac{2}{3}\gamma'^2+\gamma^2\sin^2\chi)\Delta\epsilon]\exp(-\gamma^2-\epsilon_1-\epsilon_2)\gamma^3bdbd\varphi d\gamma d\Omega_1d\Omega_2;$$

$$\frac{1}{\kappa}=\frac{4c_vk}{c_\Omega^2(\pi mkT)^{\frac{1}{2}}}\left(\int e^{-\epsilon}d\Omega\right)^{-2}\int\left[\left(3\epsilon_1'-\frac{3c_\Omega}{2k}-\gamma^2\frac{c_\Omega}{k}\right)\Delta\epsilon+\frac{c_\Omega}{k}(\Delta\epsilon)^2\right]\exp(-\gamma^2-\epsilon_1-\epsilon_2)\gamma^3bdbd\varphi d\gamma d\Omega_1d\Omega_2.$$

Here $\gamma^2\equiv(m/4kT)g^2$; χ is the scattering angle, the angle between the initial and final relative velocity vectors expressed as a function of the initial conditions; the primes denote quantities after collision which must be expressed as functions of the initial conditions; $\Delta\epsilon\equiv\epsilon_1'+\epsilon_2'-\epsilon_1-\epsilon_2=\gamma^2-\gamma'^2$; and the now more appropriate subscripts 1 and 2 represent the first and second molecules, respectively. Some of the expressions may be put into slightly different but necessarily equivalent forms by using one or the other of (11) and (12); in every case we have chosen the more concise form.

By putting $\gamma=\gamma'$ and $c_\Omega=0$,[9] we obtain the usual first approximations to the CE theory; *viz.*,

$$\lambda=\frac{15k}{4m}\eta,$$

$$\frac{1}{\eta}=\frac{16\pi}{5(\pi mkT)^{\frac{1}{2}}}\int\sin^2\chi\exp(-\gamma^2)\gamma^7bdbd\gamma,$$

$$\kappa=0.$$

This theory may then be regarded as the extension of the CE theory to treat molecules possessing internal degrees of freedom. It is also necessarily the classical limit of the WCU theory.[10] The emphasis now appears

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[9] It is necessary to set $c_\Omega=0$, since the elastic collisions do not allow the internal degrees of freedom to take up heat energy.

[10] See Sec. V.

to be on the difficulty of the solution of the classical-mechanical scattering problem for any assumed molecular model and not on the difficulty of the nonexistence of a general statistical mechanical theory.

Although we have not considered these matters in detail, we forsee little difficulty in extending the theory to mixtures so as to describe diffusion phenomena, nor in going to higher orders of approximation than the first.

V. RELATION BETWEEN THE CLASSICAL AND QUANTUM TRANSPORT THEORIES

As in the usual generalization of the classical CE results to those of quantum mechanics, in our formulation we formally replace $bdbd\varphi$ by $\sigma_{ij\to kl}(g,\chi,\varphi)d\omega$ and the integrals over the initial conditions by sums over the variety of now possible final states as well as over the initial states. $\sigma_{ij\to kl}(g,\chi,\varphi)$ is the differential scattering cross section for a transition in which the molecules are initially in internal states i and j and end up finally in internal states k and l, when the initial relative speed is g, the final azimuthal angle is φ, and the scattering angle is χ. The symbol i represents the totality of quantum numbers required for the specification of the initial internal state of the first molecule, j for the initial internal state of the second molecule, etc.; $d\omega$ is the element of solid angle about the direction in which the scattering occurs.

There remains one significant difference between our formally generalized results and those of WCU: inverse collisions will always exist in the quantum-mechanical formalism. Thus, we are allowed to perform the mathematical manipulations that give us (7). Although we have shown (7) to be unnecessary, it nevertheless proves convenient in expressing certain of the final results of WCU in more symmetrical forms. WCU could have calculated the bracket expressions just as we have, so that the results would have been formally the same. Since it essentially makes no difference which of the number of equivalent ways WCU use to calculate the bracket expressions, we may still regard the formally generalized theory as that of WCU.

There might appear to be yet some confusion, if we enquire into the nature of the quantum inverse collisions in the classical limit. That classical inverse collisions do not exist in general is well-known. A simple example of this which is often considered is the collision of a smooth rigid sphere with a rigid wedge of equal mass. The collision is shown schematically in Fig. 1. The bodies collide along the line connecting their centers of mass, and we shall assume them not to be rotating. A represents the initial state in which the wedge is at rest and the sphere is moving. B represents the final state in which the sphere is at rest and the wedge is moving. It is, of course, not possible to achieve the inverse collision which C and D represent.

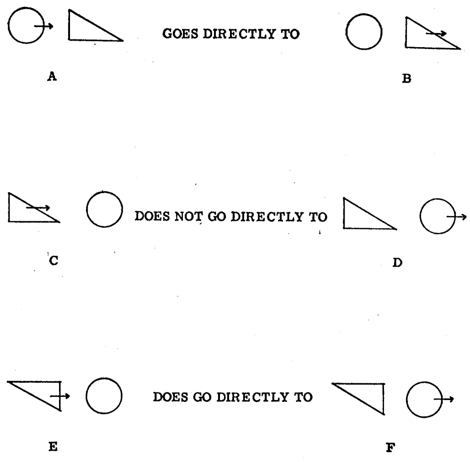

FIG. 1. Inverse collisions in classical and quantum mechanics. $A\to B$ represents a direct collision; $C\to D$ represents a classical inverse collision which cannot be directly achieved; $E\to F$ represents a quantum inverse collision which can be directly achieved.

If this is so, in what sense is it possible that quantum, or more precisely, semiclassical inverse collisions exist? For a quantum description of the collisions we would have to give up some of the precise knowledge of the system inherent in the classical description. Since we know exactly the spin angular momenta of both bodies, we must give up entirely any knowledge of the angular orientations of the bodies. Then, if the orientations are irrelevant, we have little trouble in constructing an inverse collision as shown in E and F. It is in this sense that inverse collisions for classical molecules exist in quantum mechanics.

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