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Transport processes in dense gases

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A simple and direct procedure for evaluating the properties of dense gases has been attempted based on the BBGKY hierarchy of equations. The basic idea of Enskog, namely that increasing the density affects the behaviour of the assembly, mainly by reducing the specific volume and by providing a certain amount of shielding to molecular interactions, has been developed at length in this investigation. The decrease in specific volume allows one to approximate the three-particle distribution function in terms of one-particle and two-particle distribution functions. These distribution functions are expanded in terms of generalized Hermite polynomials to study small departures from equilibrium. In the simple Couette flow and one-dimensional heat flux problems, explicit expressions for viscosity and heat conductivity have been obtained. This enables one to study the variation of these with density and temperature. Numerical results are compared with experimental values for simple gases like argon, neon and helium. The values for the inverse-power-law forces behave monotonically and approach the Enskog curve. The Lennard–Jones potential shows, as density increases, an increase of viscosity and heat conductivity that is less rapid than for other power laws. The experimental values agree well for the force laws studied here, as seen from the figures.

1. INTRODUCTION

The classical theory of gases founded by Maxwell and Boltzmann has been extensively studied by Chapman and Enskog and explains the behaviour and properties of dilute gases in the density range of 10^{16} – 10^{18} particles/ml. and in the pressure range of 10^{-2} –1 atm (Chapman & Cowling 1939; Hirschfelder, Curtiss & Bird 1954). Critical analysis of the foundations of Maxwell–Boltzmann equation and Chapman–Enskog solution by Grad (1949), Uhlenbeck (1960) and others has established that the following assumptions were made tacitly: (i) The statistics of the assembly is adequately represented by the single particle distribution function so that the particles could move freely except for occasional encounters with other particles. (ii) The interaction between the particles is purely binary and takes place in a period of time much less than the duration of the mean free flight. So, the average volume of the inter-particle interaction is much smaller than the specific volume of the assembly. One important consequence of these basic assumptions is that the transport properties of the gases brought about by collisions are independent of the specific volume or the density of the gas. In dense gases as in combustion engines, operating at high temperature and pressure, considerable difference has been noticed from the classical values. In dense gases, the duration of mean free flight is comparable to the duration of collision itself so that complete randomness of the molecular

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velocities does not prevail. This necessitates the introduction of simultaneous distributions and single-particle distribution is inadequate to represent the basic statistics of the assembly. Moreover, the specific volume also becomes comparable to the interaction volume and hence the transport process and transport properties depend on the density as well.

The simple effect of increasing density is to make the probability of binary collisions smaller owing to the fact that the third molecule interferes and partly shields the target molecule. Based on this simple assumption, Enskog (1921) modified the probability of collisions and obtained the density variation of transport processes. Since the above argument is valid only so long as the increased density could be treated as a correction to collisions, the expressions obtained by Enskog are not valid for very dense gases. This has been borne out by experimental results (Waldman 1958), the discrepancy becoming marked when the density increases beyond 10 times the original atmospheric value. Moreover, the expressions of correction obtained by Enskog are independent of temperature and accordingly have restricted applicability.

Recently, based on BBGKY hierarchy of equations (Green 1952) for liquids, Cohen (1966), Green (1958), Mazo (1967), and others, have worked out theories of dense gases. Essentially, it depends on including the two-particle distribution functions f_{12} along with the one-particle distribution function f_1 to describe the statistics of the assembly. The first and second equations of the hierarchy are used to deduce transport equations and the transport coefficients. In all these approaches some approximate expression has to be used to express the three-particle distribution f_{123} in terms of the single particle and two-particle distributions. Following Bogoliubov (1962), in general, f_1 , f_{12} and f_{123} are expanded in a power series of the parameter which is the ratio of the interaction volume to the specific volume. Even though, theoretically one establishes the existence of transport equations, these approaches are extremely complicated owing to the fact that the distributions are expressed as functions and functional derivatives. Explicit simple expansions describing the transport process and transport equations are difficult to obtain.

A simple and straightforward method can be obtained as follows. The increase in density primarily affects the simple binary collisions and the most important molecular process then is the successive incomplete binary collisions. These are well represented by the introduction of the correlation function f_{12} : however, the evolution of f_1 and f_{12} depends on f_{123} . The specific volume of the gas decreases at the same time owing to increased density; consequently, f_{123} and higher order particle distributions evolve relatively very little, which suggests that one may approximate f_{123} from those appropriate to liquids having almost vanishing specific volume, such as Kirkwood superposition approximation (1946), or Tchen's quasilinear approximation (1959). Such an approximation, which does not take into account the details of three-particle collisions, is valid provided the density is high enough but not exceeding the limit when the mean free time becomes equal to the time scale of the

order of collision time itself. If σ denotes the effective molecular diameter and r_0 the range of molecular forces, we can express the above condition in the form

$$\frac{1}{r_0^3} \ll n \ll \frac{1}{r_0 \sigma^2}.$$

Another instance, where the basic assumptions of Maxwell–Boltzmann are violated, is in plasmas, especially at high temperatures and high densities. Because of the long-range Coulomb force, the volume of the Debye sphere is much greater than the specific volume and the collisions are no longer binary. For, under the conditions of relatively low density in plasmas, deflexion of a particle due to interaction with most others is small and the effect of different deflexions is as if they occurred simultaneously and successively and considered linearly; large repulsive deflexions are rarer. Since this is not possible at higher temperatures or densities, one must introduce correlation between particles. Since plasmas have at least two components, the mathematics becomes extremely complex and in this paper, we shall, for the sake of clarity, consider only one component gas and study gas mixtures separately.

Secondly, the primary object of this investigation is to study the transport processes and the transport properties of dense gases, we shall consider simple gases like argon, neon, and helium with inverse power law for molecular interaction and Lennard–Jones (6:12) potential. Also to simplify the analysis, we shall suppose that there are no external forces acting on the system. We shall adopt, for transport processes, Grad's (1949) procedure for solving the resulting kinetic equations. The advantage of this procedure is the explicit expression of the distribution function in terms of its macroscopic quantities and the direct evaluation of the transport equations in the neighbourhood of the thermodynamic equilibrium state. We have obtained explicit density and temperature-dependent expressions for the properties of simple assemblies and the results are compared with the experimental observations for helium, argon and neon in figures 1 and 2. These show reasonably good agreement justifying the present procedure.

2. FORMULATION AND BASIC EQUATIONS

Consider an assembly of N similar neutral particles contained in the volume V . If \mathbf{q} and \mathbf{p} denote the position and momentum of the particle and $f_1(1)$, $f_{12}(1, 2)$ and $f_{123}(1, 2, 3)$ denote 1, 2 and 3 particle distributions respectively, then the corresponding hierarchy of equations is given by

$$\frac{\partial f_1}{\partial t} = \frac{\partial H_1}{\partial \mathbf{q}_1} \frac{\partial f_1}{\partial \mathbf{p}_1} - \frac{\partial H_1}{\partial \mathbf{p}_1} \frac{\partial f_1}{\partial \mathbf{q}_1} + \frac{N-1}{V} \iint \frac{\partial \phi_{12}}{\partial \mathbf{q}_1} \frac{\partial f_{12}}{\partial \mathbf{p}_1} d\mathbf{q}_2 d\mathbf{p}_2 \quad (1)$$

$$\text{and} \quad \frac{\partial f_{12}}{\partial t} = \sum_{1 \leq i \leq 2} \left[\frac{\partial H_2}{\partial \mathbf{q}_i} \frac{\partial f_{12}}{\partial \mathbf{p}_i} - \frac{\partial H_2}{\partial \mathbf{p}_i} \frac{\partial f_{12}}{\partial \mathbf{q}_i} + \frac{N-2}{V} \iint \frac{\partial \phi_{i3}}{\partial \mathbf{q}_i} \frac{\partial f_{123}}{\partial \mathbf{p}_i} d\mathbf{q}_3 d\mathbf{p}_3 \right], \quad (2)$$

where the Hamiltonian H_i for i -particles in the absence of external forces is given by

$$H_i = \sum_{1 \leq j \leq i} \frac{1}{2m_j} \mathbf{p}_j^2 + \sum_{1 \leq j < k \leq i} \phi_{jk}. \quad (3)$$

In order to obtain a closed set of equations we shall use the approximation of Tchen for f_{123} given by

$$f_{123} = f_1(1)f_2(2, 3) + f_1(2)f_2(3, 1) + f_1(3)f_2(1, 2) - 2f_1(1)f_1(2)f_1(3). \quad (4)$$

Two restrictions imposed by the above approximation should be noted. By expressing f_{123} in terms of f_1 and f_{12} alone, the non-Markovian behaviour of the system is lost. This is not a very serious error since most of the observed phenomena in liquids require only pair correlation function and hence behave like a Markovian system. However, in the limiting case of vanishing specific volume, the Markovian processes are governed by Kirkwood's superposition principle.

$$f_{123} = \frac{f_2(1, 2)f_2(2, 3)}{f_1(2)}. \quad (5)$$

However, this is highly nonlinear in correlation functions and incorporates the large time effects of the evolution of the independent triple correlation. By neglecting this effect and assuming that the triple correlations decay faster, one obtains Tchen's approximation (4) which is quasilinear in double correlations. If one is interested in long time effect approximation (5) has to be considered. But limiting oneself to systems not far from thermodynamic equilibrium state, such as the transport processes, approximation (4) is more convenient to handle. Further, in order to have tractable kinetic equations, we shall use Bogoliubov's modified expression (Bogoliubov 1946) for the collisional contributions in (1) and (2). Bogoliubov's modification merely consists in the proper evaluation of the space integration in the collisional contribution

$$\iint \frac{\partial \phi_{12}}{\partial \mathbf{q}_2} \cdot \frac{\partial f_{12}}{\partial \mathbf{p}_2} d\mathbf{q}_2 d\mathbf{p}_2.$$

Since this is no more than the number of particles scattered per unit time from the unit phase element through molecular interactions, integration over space is equivalent to summing over all scattered particles over all impact parameters of collision. Hence, it reduces to an operator having the same form as the Boltzmann collision operator. Thus, we have the collisional terms

$$\frac{N-1}{V} \iint [f'_{12} - f_{12}] g_{12} b_{12} db_{12} d\epsilon_{12} d\mathbf{p}_2 \quad (1')$$

and
$$\frac{N-2}{V} \iint [f'_{123} - f_{123}] g_{i3} b_{i3} db_{i3} d\epsilon_{i3} d\mathbf{p}_3, \quad (2')$$

respectively in the notations of Chapman & Cowling (1939).

To facilitate the derivation of the transport equations, we non-dimensionalize the momentum with the help of local sound speed $a_i = [kT(\mathbf{q}_i)/m]^{1/2}$ so that the non-dimensional momentum is given by

$$\mathbf{P} = \frac{1}{(mkT)^{1/2}} \mathbf{p} = \frac{1}{ma} \mathbf{p}, \quad (6)$$

and the non-dimensional distribution functions by

$$F_1 = (ma_1)^{-3} f_1, \quad (7)$$

$$F_{12} = (m^2 a_1 a_2)^{-3} f_{12}, \quad (8)$$

$$F_{123} = (m^3 a_1 a_2 a_3)^{-3} f_{123}. \quad (9)$$

The equations satisfied by F_1 and F_{12} are then

$$\begin{aligned} \frac{\partial F_1}{\partial t} + a_1 \mathbf{P}_1 \frac{\partial F_1}{\partial \mathbf{q}_1} - 3 \left[\frac{\partial}{\partial t} (\ln a_1) + a_1 \mathbf{P}_1 \frac{\partial}{\partial \mathbf{q}_1} (\ln a_1) \right] F_1 \\ = \frac{(N-1)a_1}{V} \int (F'_{12} - F_{12}) \mathcal{G}_{12} b_{12} db_{12} d\epsilon_{12} d\mathbf{P}_2, \end{aligned} \quad (10)$$

and

$$\begin{aligned} \frac{\partial F_{12}}{\partial t} + \sum_{1 \leq i \leq 2} \left[a_i \mathbf{P}_i \frac{\partial F_{12}}{\partial \mathbf{q}_i} - \frac{1}{ma_i} \frac{\partial \phi_{12}}{\partial \mathbf{q}_i} \frac{\partial F_{12}}{\partial \mathbf{P}_i} - 3 \left\{ \frac{\partial}{\partial t} (\ln a_i) + a_i \mathbf{P}_i \frac{\partial}{\partial \mathbf{q}_i} (\ln a_i) \right\} F_{12} \right] \\ = \frac{(N-2)}{V} \sum_{1 \leq i \leq 2} a_i \int (F'_{123} - F_{123}) \mathcal{G}_{i3} b_{i3} db_{i3} d\epsilon_{i3} d\mathbf{P}_3, \end{aligned} \quad (11)$$

with the approximation (5) taking the form

$$F_{123} = F_1 F_{23} + F_2 F_{31} + F_3 F_{12} - 2F_1 F_2 F_3. \quad (12)$$

In order to obtain the transport equations, we introduce the kernel $\omega(\mathbf{P})$ in momentum space defined by

$$\omega(\mathbf{P}) = \frac{1}{(2\pi)^{3/2}} \exp[-\frac{1}{2}\mathbf{P}^2] \quad (13)$$

and expand F_1 and F_{12} in terms of the generalized Hermite polynomials $H^{(n)}(\mathbf{P})$ (Grad 1949):

$$F_1(\mathbf{q}_1, \mathbf{P}_1, t) = \omega(\mathbf{P}_1) \sum_n A^{(n)}(\mathbf{q}_1, t) H^{(n)}(\mathbf{P}_1), \quad (14)$$

and

$$F_{12}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{P}_1, \mathbf{P}_2, t) = \omega(\mathbf{P}_1) \omega(\mathbf{P}_2) \sum_m \sum_n B^{(m,n)}(\mathbf{q}_1, \mathbf{q}_2, t) H^{(m)}(\mathbf{P}_1) H^{(n)}(\mathbf{P}_2), \quad (15)$$

in the Cartesian tensor product notation. Using the orthogonality property of Hermite polynomials one has

$$\left. \begin{aligned} A^{(n)} &= \frac{1}{X^{(n)}} \int H^{(n)}(\mathbf{P}_1) F_1 d\mathbf{P}_1, \\ B^{(m,n)} &= \frac{1}{X^{(m)} X^{(n)}} \iint H^{(m)}(\mathbf{P}_1) H^{(n)}(\mathbf{P}_2) F_{12} d\mathbf{P}_1 d\mathbf{P}_2, \end{aligned} \right\} \quad (16)$$

where $X^{(r)} = r_1! r_2! r_3!$, (r) being the set of indices (r_1, r_2, r_3) in the directions 1, 2, 3 of $H^{(r)}$ such that $r_1 + r_2 + r_3 = r$. It is evident from the relations (16) that the coefficients $A^{(n)}$ and $B^{(m,n)}$ are nothing but linear combinations of the moments of distribution functions.

Multiplying the equation (10) by $H^{(r)}(\mathbf{P}_1)$ and integrating over the momentum space, we obtain the coefficient equation

$$\begin{aligned} X^{(r)} \frac{\partial}{\partial t} (A_1^{(r)}) + \frac{\partial}{\partial t} (\ln a_1) [r X^{(r)} A_1^{(r)} + 2\delta^{(2)} X^{(r-2)} A_1^{(r-2)}] \\ + a_1 \left\{ X_i^{(r+1)} \frac{\partial}{\partial q_{1i}} (A_{1i}^{(r+1)}) + \delta_i^{(2)} X^{(r-1)} \frac{\partial}{\partial q_{1i}} (A_1^{(r-1)}) \right. \\ + \frac{\partial}{\partial q_{1i}} (\ln a_1) [(r+1) X_i^{(r+1)} A_{1i}^{(r+1)} + 2\delta^{(2)} X^{(r-1)} A_1^{(r-1)} \\ \left. + (r-1) \delta_i^{(2)} X^{(r-1)} A_1^{(r-1)} + 2\delta_i^{(2)} \delta^{(2)} X^{(r-3)} A_1^{(r-3)} \right\} \\ = \frac{(N-1)a_1}{V} \sum_i \sum_n \langle l, n | r \rangle [A_1^{(l)} A_1^{(n)} - C^{(l, n)}]. \end{aligned} \quad (17)$$

Here the suffix 1 denotes the position and we have put

$$B^{(l, n)} = A^{(l)} A^{(n)} - C^{(l, n)} \quad (18)$$

and

$$\langle l, n | r \rangle = \iiint \omega(\mathbf{P}_1) \omega(\mathbf{P}_2) [H^{(l)}(\mathbf{P}'_1) H^{(n)}(\mathbf{P}'_2) - H^{(l)}(\mathbf{P}_1) H^{(n)}(\mathbf{P}_2)] H^{(r)}(\mathbf{P}_1) \mathcal{G}_{12} b_{12} db_{12} d\epsilon_{12} d\mathbf{P}_2 d\mathbf{P}_1. \quad (19)$$

Similarly, multiplying (11) by $H^{(r)}(\mathbf{P}_1) H^{(s)}(\mathbf{P}_2)$ and integrating an analogous equation for $B^{(r, s)}$ is obtained. Using the definition (18) and rearranging, the equation for $C^{(r, s)}$ reduces to

$$\begin{aligned} X^{(r)} X^{(s)} \frac{\partial}{\partial t} (C^{(r, s)}) + \frac{\partial}{\partial t} (\ln a_1) \{r X^{(r)} X^{(s)} C^{(r, s)} + 2\delta^{(2)} X^{(r-2)} X^{(s)} C^{(r-2, s)}\} \\ + \frac{\partial}{\partial t} (\ln a_2) \{s X^{(r)} X^{(s)} C^{(r, s)} + 2\delta^{(2)} X^{(r)} X^{(s-2)} C^{(r, s-2)}\} \\ + a_1 \left\{ X_i^{(r+1)} X^{(s)} \frac{\partial}{\partial q_{1i}} (C_i^{(r+1, s)}) + \delta_i^{(2)} X^{(r-1)} X^{(s)} \frac{\partial}{\partial q_{1i}} (C^{(r-1, s)}) \right. \\ + \frac{\partial}{\partial q_{1i}} (\ln a_1) [(r+1) X_i^{(r+1)} X^{(s)} C_i^{(r+1, s)} + 2\delta^{(2)} X^{(r-1)} X^{(s)} C^{(r-1, s)} \\ \left. + (r-1) \delta_i^{(2)} X^{(r-1)} X^{(s)} C^{(r-1, s)} + 2\delta_i^{(2)} \delta^{(2)} X^{(r-3)} X^{(s)} C^{(r-3, s)} \right\} \\ + a_2 \left\{ X^{(r)} X_i^{(s+1)} \frac{\partial}{\partial q_{2i}} (C_i^{(r, s+1)}) + \delta_i^{(2)} X^{(r)} X^{(s-1)} \frac{\partial}{\partial q_{2i}} (C^{(r, s-1)}) \right. \\ + \frac{\partial}{\partial q_{2i}} (\ln a_2) [(s+1) X^{(r)} X_i^{(s+1)} C_i^{(r, s+1)} + 2\delta^{(2)} X^{(r)} X^{(s-1)} C^{(r, s-1)} \\ \left. + (s-1) \delta_i^{(2)} X^{(r)} X^{(s-1)} C^{(r, s-1)} + 2\delta_i^{(2)} \delta^{(2)} X^{(r)} X^{(s-3)} C^{(r, s-2)} \right\} \\ + \frac{1}{ma_1} \frac{\partial \phi_{12}}{\partial q_{1i}} \delta_i^{(2)} X^{(r-1)} X^{(s)} C^{(r-1, s)} + \frac{1}{ma_2} \frac{\partial \phi_{12}}{\partial q_{2i}} \delta_i^{(2)} X^{(r)} X^{(s-1)} C^{(r, s-1)} \\ = \frac{(N-2)a_1}{V} X^{(s)} \sum_i \sum_n \langle l, n | r \rangle n_1^{l+n+s} [A_1^{(l)} C^{(s, n)} + A_1^{(n)} C^{(l, s)}] \\ + \frac{(N-2)a_2}{V} X^{(r)} \sum_l \sum_n \langle l, n | s \rangle n_2^{l+n+r} [A_2^{(l)} C^{(r, n)} + A_2^{(n)} C^{(l, r)}]. \end{aligned} \quad (20)$$

The most significant simplification of using Grad's procedure of representing the distribution function in terms of the Hermite polynomials, though complicated, is the explicit equations (17) and (20). Secondly, all the collisional effects of the assembly are presented through the integrals $\langle l, n|r \rangle$. Using the properties of collision terms, we can write (19) in simpler terms, useful for evaluation:

$$\langle l, n|r \rangle = \iiint \omega(\mathbf{P}_1) \omega(\mathbf{P}_2) [H^{(r)}(\mathbf{P}'_1) - H^{(r)}(\mathbf{P}_1)] \\ \times H^{(l)}(\mathbf{P}_1) H^{(n)}(\mathbf{P}_2) \mathcal{G}_{12} b_{12} db_{12} d\epsilon_{12} d\mathbf{P}_2 d\mathbf{P}_1, \quad (21)$$

$$= \sum \sum \sum \beta_{i_1 i_2} I_{i_1 i_2}, \quad (21a)$$

where β_{ijk} are constants and I_{ijk} is the integral

$$I_{ijk} = \pi^{\frac{1}{2}} \iint \exp(-\frac{1}{4}\mathcal{G}^2) \cos^i \theta \sin^j \theta \mathcal{G}^k b db d\mathcal{G}, \quad (21b)$$

where θ is the angle through which the relative velocity turns during an encounter with the impact parameter b . The appropriate coefficients β_{ijk} are given in the appendix and these integrals are evaluated numerically for inverse power law and for Lennard-Jones (6:12) potential.

In most of the physical situations of fluids, the important macrovariables, density, mean velocity, stresses and heat flux, adequately represent the phenomenon and higher order moments have a negligible part to play. The skewness and the deformation brought about in distribution functions by using these variables adequately take account of the macroscopic situation in the neighbourhood of thermodynamic equilibrium. So, we further truncate the infinite series (14) at $n = 3$ and (15) at $m + n = 3$. Similarly, the collisional terms in (17) and (20) are truncated at $l + n = 3$, so that one obtains a consistent system of equations for the moments up to order 3. Converting the moment equations (17) into equations for physical variables, one obtains the macroscopic equations:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial q_i} (n u_i) = 0, \quad (22)$$

$$\frac{1}{n} \frac{\partial}{\partial t} (n u_r) + \frac{1}{n} \frac{\partial}{\partial q_i} (n P_{ir}) = \frac{(N-1) a_1^2}{nV} \sum_l \sum_n \langle l, n|1 \rangle B^{(l,n)}, \quad (23)$$

$$\frac{1}{n} \frac{\partial}{\partial t} (n P_{rr}) + \frac{1}{n} \frac{\partial}{\partial q_i} (n S_{rsi}) = \frac{(N-1) a_1^3}{nV} \sum_l \sum_n \langle l, n|2 \rangle B^{(l,n)}, \quad (24)$$

$$\frac{1}{n} \frac{\partial}{\partial t} (n P_{rs}) + \frac{1}{n} \frac{\partial}{\partial q_i} (n S_{rsi}) = \frac{(N-1) a_1^3}{nV} \sum_l \sum_n \langle l, n|2 \rangle B^{(l,n)}, \quad (25)$$

$$\frac{1}{n} \frac{\partial}{\partial t} (n S_{rrr}) + \frac{1}{n} \frac{\partial}{\partial q_i} (n Q_{rrri}) = \frac{(N-1) a_1^4}{nV} \sum_l \sum_n \langle l, n|3 \rangle''' B^{(l,n)}, \quad (26)$$

$$\frac{1}{n} \frac{\partial}{\partial t} (n S_{rrs}) + \frac{1}{n} \frac{\partial}{\partial q_i} (n Q_{rrsi}) = \frac{(N-1) a_1^4}{nV} \sum_l \sum_n \langle l, n|3 \rangle'' B^{(l,n)}, \quad (27)$$

$$\text{and} \quad \frac{1}{n} \frac{1}{\partial t} (nS_{rst}) + \frac{1}{n} \frac{\partial}{\partial q_i} (nQ_{rsti}) = \frac{(N-1)a_1^4}{nV} \sum_l \sum_n \langle l, n|3 \rangle B^{(l,n)}, \quad (28)$$

$$\text{where} \quad \begin{aligned} \langle l, n|3 \rangle''' &= \langle l, n|3 \rangle + 3a_1^2 \langle l, n|1 \rangle, \\ \langle l, n|3 \rangle'' &= \langle l, n|3 \rangle + a_1^2 \langle l, n|1 \rangle. \end{aligned} \quad (29)$$

The equations (22) to (28), together with the correlation equation (20), determine completely the behaviour of the assembly in the non-equilibrium state. The left-hand side of (20) represents the change produced in the correlation during free streaming of the particles, while the right-hand side represents the production of correlations due to molecular interactions. For plasmas, consisting mainly of charged particles, the intense molecular interactions are of considerably less importance than the change produced due to streaming, while for the neutral gases, especially for studying the contribution to transport properties, the molecular interactions are more significant than streaming.

3. SOME SIMPLE APPLICATIONS

The important molecular transport properties are the viscosity, heat conductivity, diffusivity and electrical conductivity. By considering a simple two-dimensional Couette flow and one-dimensional heat flux flow one can obtain, following Grad, simple expression for viscosity and heat conductivity for a simple gas. However, diffusivity and electrical conductivity are essentially properties of gas mixtures and hence will not be considered here.

For a steady, two-dimensional flow in the absence of external forces, concentrating on the dependence of the stress term P_{12} on the rate of strain term

$$\frac{1}{2} \left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1} \right),$$

from (25) in the absence of correlation term we obtain

$$P_{12} = -\frac{2anV}{N-1} [\langle 2, 0|2 \rangle + \langle 0, 2|2 \rangle]^{-1} \left[\frac{1}{2} \left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1} \right) \right].$$

This is identical to the expression obtained by Grad, Chapman, and Enskog. Consequently, the coefficient of viscosity can be taken as

$$\eta = \frac{2anV}{N-1} [\langle 2, 0|2 \rangle + \langle 0, 2|2 \rangle]^{-1}. \quad (30)$$

Similarly, for the one-dimensional heat flux flow, in the absence of correlations, the relation between the heat flux and the temperature gradient reduces to result of Grad:

$$S_1 = -\frac{10anVk}{N-1} [\langle 3, 0|3 \rangle''' + \langle 0, 3|3 \rangle''' + \langle 3, 0|3 \rangle'' + \langle 0, 2|3 \rangle'']^{-1} \left(\frac{\partial T}{\partial x_1} \right),$$

so that the heat conduction coefficient is given by

$$\kappa = \frac{15anVk}{2(N-1)} [\langle 3, 0|3 \rangle''' + \langle 0, 3|3 \rangle''' + \langle 3, 0|3 \rangle'' + \langle 0, 3|3 \rangle'']^{-1}. \quad (31)$$

In the presence of correlations, eliminating the correlations produced by molecular interactions from the equations for physical variables, after rearranging and concentrating on the relation between P_{12} and e_{12} , we obtain as before,

$$P_{12} = -\bar{\eta}e_{12},$$

where

$$\bar{\eta} = \eta \left[1 + \frac{(\langle 0, 0|2\rangle + \langle 0, 0|2\rangle)^2}{\langle 2, 0|2\rangle + \langle 0, 2|2\rangle} \frac{1}{a^2} - \frac{(\langle 1, 1|2\rangle + \langle 1, 1|2\rangle)^2}{\langle 2, 0|2\rangle + \langle 0, 2|2\rangle} \frac{n}{a^4} + \frac{(\langle 2, 0|2\rangle + \langle 0, 2|2\rangle)^2}{\langle 2, 0|2\rangle + \langle 0, 2|2\rangle} \frac{n^2}{a^6} \right]^{-1}, \quad (32)$$

while similar expression for heat flux vector yields

$$S_1 = -\bar{\kappa} \frac{\partial T}{\partial x_1},$$

$$\text{with } \bar{\kappa} = \kappa \left[1 - \frac{(n/a^2)(\langle 1, 0|3\rangle + \langle 0, 1|3\rangle)^2 + (n/a^4)(\langle 0, 1|1\rangle + \langle 1, 0|1\rangle)^2}{\langle 3, 0|3\rangle''' + \langle 0, 3|3\rangle''' + \langle 3, 0|3\rangle'' + \langle 0, 3|3\rangle''} + \frac{(n^2/a^4)(\langle 1, 2|3\rangle + \langle 2, 1|3\rangle)^2 + (n^2/a^6)(\langle 1, 2|1\rangle + \langle 2, 1|1\rangle)^2}{\langle 3, 0|3\rangle''' + \langle 0, 3|3\rangle''' + \langle 3, 0|3\rangle'' + \langle 0, 3|3\rangle''} \right]^{-1}. \quad (33)$$

Once again, the Cartesian tensor product notation has been used to express these.

4. DISCUSSION OF THE RESULTS

Two important conclusions can be derived immediately from the form of the expressions (32) and (33). They are similar in structure to Enskog expressions for rigid spheres which are mainly of the form

$$\bar{\eta}_E = \eta[1 - \text{constant} \times n]^{-1}, \quad (34)$$

but in our case the constants being replaced by functions of temperature as well. The terms inside the bracket can thus be interpreted as depicting the shielding effect of the increasing density from the unshielded binary collisions. Secondly, at very high temperatures these corrections decrease. This might be expected since, keeping density fixed and increasing the temperature has the effect of increasing the mean molecular motion and decreasing the shielding effect.

Numerical calculations have been carried out for the case of intermolecular potentials of the inverse distance from and for Lennard-Jones potential. Keeping fixed temperature and varying the density, the results are compared against the Enskog expression for viscosity for rigid spheres, which is the limiting case of power law of force as the exponent tends to ∞ . From figure 1 it is evident that as the exponent of the power law increases, gradually the curves approach Enskog curve. At small increase in density, all power law exponents give almost the same result; but with increasing density, the power law curves vary much less rapidly than the Enskog curve. The behaviour of the heat conductivity (figure 2) is almost the same, even though numerically it varies a little more than the viscosity terms, thereby indicating an increase of Prandtl number. By properly scaling and superposing

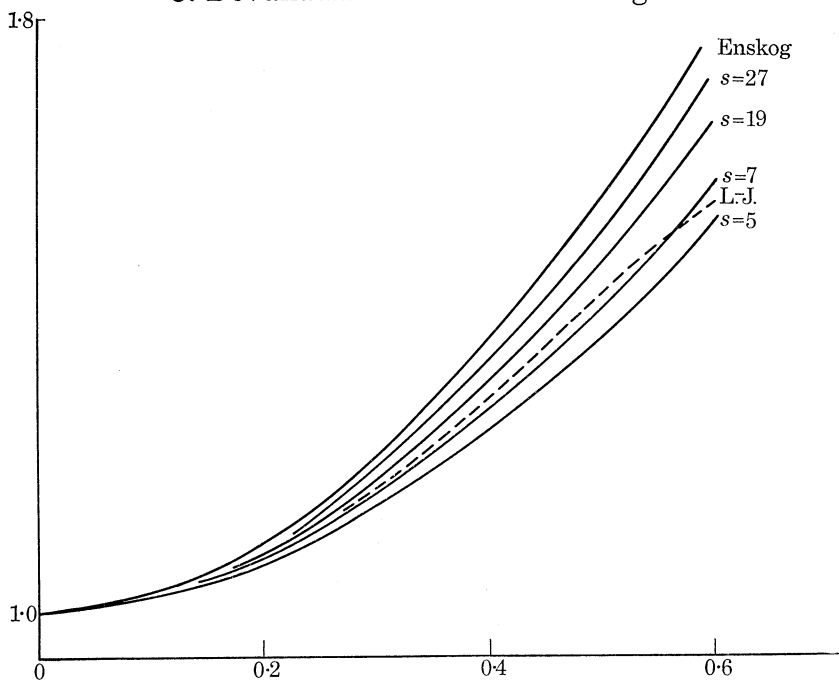


FIGURE 1

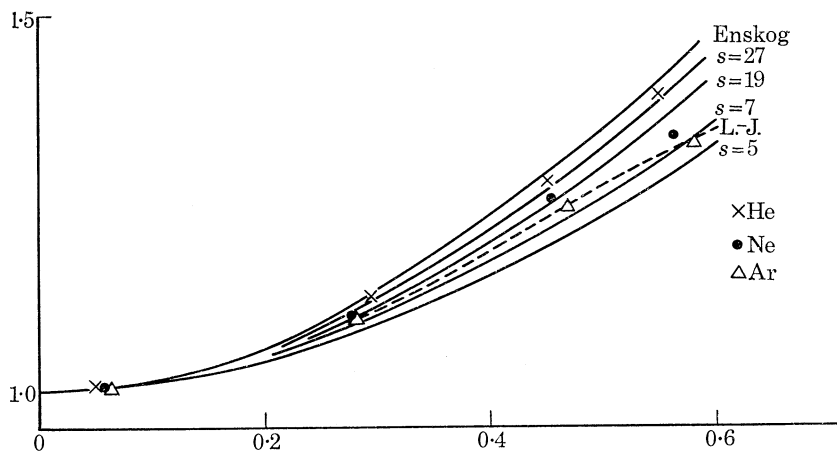


FIGURE 2

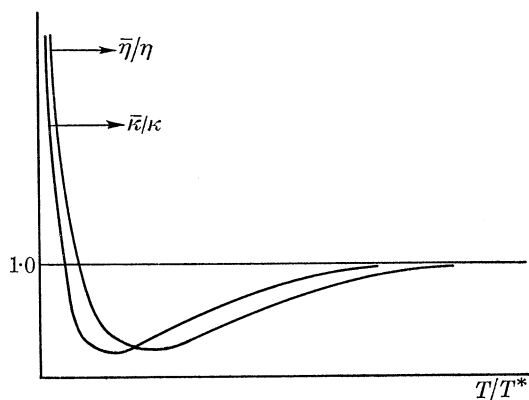


FIGURE 3

the experimental results (Waldmann 1958) on the same plot, we find better agreement with data than for the Enskog curve especially at higher densities.

In figure 3, with density kept constant, the typical variation of these correction factors for the power law exponent $s = 9$ with temperature is given. From the expressions (32) and (33), it is clear that as the temperature tends to zero, these correction factors become very large and show a behaviour, in general, of the form

$$1 - \frac{a}{T} + \frac{a^2 + b}{T^2},$$

where a and b are positive constants. Consequently, both $\bar{\eta}/\eta$ and $\bar{\kappa}/\kappa$ have a minimum below unity and approach the classical value at high temperatures. This behaviour is similar for all the force laws.

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APPENDIX. TABLE OF THE COEFFICIENTS β_{ijk} OF I_{ijk} IN EQUATION (21a)

	$I(2, 0, 5)$	$I(2, 0, 7)$	$I(2, 0, 9)$	$I(4, 0, 5)$	$I(4, 0, 7)$	$I(4, 0, 9)$	$I(6, 0, 5)$	$I(6, 0, 7)$	$I(6, 0, 9)$
$\langle 0, 1 1 \rangle$	$\frac{1}{6}$	—	—	—	—	—	—	—	—
$\langle 1, 0 1 \rangle$	$-\frac{1}{6}$	—	—	—	—	—	—	—	—
$\langle 0, 111 1 \rangle$	$-\frac{1}{4}$	$\frac{1}{40}$	—	—	—	—	—	—	—
$\langle 111, 0 1 \rangle$	$+\frac{1}{4}$	$\frac{1}{40}$	—	—	—	—	—	—	—
$\langle 0, 122 1 \rangle$	$-\frac{1}{12}$	$\frac{1}{120}$	—	—	—	—	—	—	—
$\langle 122, 0 1 \rangle$	$\frac{1}{12}$	$\frac{1}{120}$	—	—	—	—	—	—	—
$\langle 1, 11 1 \rangle$	$\frac{1}{3}$	$-\frac{1}{40}$	—	—	—	—	—	—	—
$\langle 11, 1 1 \rangle$	$-\frac{1}{3}$	$-\frac{1}{40}$	—	—	—	—	—	—	—
$\langle 1, 22 1 \rangle$	$\frac{1}{12}$	$-\frac{1}{120}$	—	—	—	—	—	—	—
$\langle 22, 1 1 \rangle$	$\frac{1}{12}$	$+\frac{1}{120}$	—	—	—	—	—	—	—
$\langle 2, 12 1 \rangle$	$\frac{1}{12}$	$-\frac{1}{120}$	—	—	—	—	—	—	—
$\langle 12, 2 1 \rangle$	$\frac{1}{12}$	$\frac{1}{120}$	—	—	—	—	—	—	—
$\langle 0, 11 11 \rangle$	$\frac{1}{3}$	$-\frac{1}{30}$	—	—	$\frac{1}{30}$	—	—	—	—
$\langle 11, 0 11 \rangle$	$-\frac{1}{3}$	$-\frac{1}{30}$	—	—	$\frac{1}{30}$	—	—	—	—
$\langle 0, 22 11 \rangle$	—	$\frac{1}{60}$	—	—	$-\frac{1}{60}$	—	—	—	—
$\langle 22, 0 11 \rangle$	—	$-\frac{1}{60}$	—	—	$\frac{1}{60}$	—	—	—	—
$\langle 1, 1 11 \rangle$	—	$\frac{1}{30}$	—	—	$-\frac{1}{30}$	—	—	—	—
$\langle 0, 12 12 \rangle$	$\frac{1}{6}$	$-\frac{1}{40}$	—	—	$\frac{1}{40}$	—	—	—	—
$\langle 12, 0 12 \rangle$	$-\frac{1}{6}$	$-\frac{1}{40}$	—	—	$\frac{1}{40}$	—	—	—	—
$\langle 1, 2 12 \rangle$	—	$\frac{1}{40}$	—	—	$-\frac{1}{40}$	—	—	—	—
$\langle 2, 1 12 \rangle$	—	$\frac{1}{40}$	—	—	$-\frac{1}{40}$	—	—	—	—
$\langle 0, 111 111 \rangle$	$\frac{27}{8}$	$-\frac{1}{40}$	$\frac{9}{1120}$	—	$\frac{32}{40}$	$-\frac{3}{280}$	—	$\frac{3}{8}$	$\frac{1}{140}$
$\langle 111, 0 111 \rangle$	$-\frac{27}{8}$	$-\frac{1}{40}$	$-\frac{9}{1120}$	—	$\frac{35}{40}$	$\frac{3}{280}$	—	$-\frac{3}{8}$	$-\frac{1}{140}$
$\langle 0, 221 111 \rangle$	$-\frac{1}{4}$	$-\frac{1}{20}$	$-\frac{81}{1120}$	—	$\frac{1}{40}$	$\frac{51}{224}$	—	—	$-\frac{17}{112}$
$\langle 221, 0 111 \rangle$	$\frac{1}{4}$	$-\frac{1}{20}$	$\frac{81}{1120}$	—	$\frac{1}{40}$	$-\frac{51}{224}$	—	—	$\frac{17}{112}$
$\langle 1, 11 111 \rangle$	$-\frac{5}{8}$	$\frac{1}{40}$	$-\frac{91}{1120}$	—	$-\frac{1}{20}$	$-\frac{23}{80}$	—	—	$-\frac{1}{140}$
$\langle 11, 1 111 \rangle$	$\frac{1}{8}$	$\frac{1}{40}$	$\frac{91}{1120}$	—	$\frac{1}{20}$	$-\frac{23}{80}$	—	—	$\frac{1}{140}$
$\langle 1, 22 111 \rangle$	$\frac{1}{8}$	$-\frac{5}{80}$	$-\frac{17}{1120}$	—	$\frac{1}{40}$	$\frac{39}{1120}$	—	—	$-\frac{13}{560}$
$\langle 22, 1 111 \rangle$	$-\frac{1}{8}$	$-\frac{1}{80}$	$\frac{17}{1120}$	—	$-\frac{1}{40}$	$-\frac{39}{1120}$	—	—	$\frac{13}{560}$
$\langle 2, 12 111 \rangle$	$-\frac{1}{8}$	—	$-\frac{17}{1120}$	—	$\frac{1}{40}$	$\frac{39}{1120}$	—	—	$-\frac{13}{560}$
$\langle 12, 2 111 \rangle$	$\frac{1}{8}$	$-\frac{2}{40}$	$\frac{17}{1120}$	—	$-\frac{1}{40}$	$-\frac{39}{1120}$	—	—	$\frac{13}{560}$
$\langle 0, 2 112 \rangle$	—	$\frac{1}{120}$	—	—	$\frac{23}{120}$	—	—	$-\frac{1}{10}$	—
$\langle 2, 0 112 \rangle$	—	$\frac{1}{120}$	—	—	$-\frac{25}{120}$	—	—	$\frac{1}{10}$	—
$\langle 0, 222 112 \rangle$	—	$\frac{3}{80}$	$\frac{17}{1120}$	—	$\frac{11}{40}$	$\frac{57}{1120}$	—	$-\frac{3}{20}$	$-\frac{11}{560}$
$\langle 222, 0 112 \rangle$	—	$-\frac{3}{80}$	$-\frac{17}{1120}$	—	$-\frac{13}{40}$	$-\frac{57}{1120}$	—	$\frac{3}{20}$	$\frac{11}{560}$
$\langle 0, 112 112 \rangle$	$-\frac{1}{40}$	$-\frac{17}{240}$	$\frac{13}{672}$	—	$\frac{1}{30}$	$\frac{43}{1120}$	—	$\frac{1}{20}$	$-\frac{19}{1680}$
$\langle 112, 0, 112 \rangle$	$\frac{1}{40}$	$-\frac{15}{240}$	$-\frac{13}{672}$	—	$\frac{1}{10}$	$-\frac{43}{1120}$	—	$-\frac{1}{20}$	$\frac{19}{1680}$
$\langle 0, 332 112 \rangle$	—	$\frac{1}{240}$	$-\frac{17}{3360}$	—	$-\frac{13}{120}$	$\frac{1}{112}$	—	$\frac{1}{20}$	$-\frac{1}{210}$
$\langle 332, 0 112 \rangle$	—	$-\frac{1}{240}$	$\frac{1}{336}$	—	$\frac{9}{120}$	$-\frac{1}{112}$	—	$-\frac{1}{20}$	$\frac{1}{210}$
$\langle 2, 22 112 \rangle$	—	$\frac{1}{120}$	$-\frac{17}{120}$	—	$\frac{73}{120}$	$-\frac{57}{1120}$	—	$-\frac{3}{20}$	$\frac{11}{560}$
$\langle 22, 2 112 \rangle$	—	$-\frac{3}{120}$	$\frac{17}{120}$	—	$-\frac{77}{120}$	$\frac{57}{1120}$	—	$\frac{3}{20}$	$-\frac{11}{560}$
$\langle 2, 11 112 \rangle$	$\frac{1}{12}$	$\frac{9}{120}$	$-\frac{11}{840}$	—	$\frac{4}{30}$	$-\frac{2}{35}$	—	$-\frac{1}{20}$	$\frac{1}{42}$
$\langle 11, 2 112 \rangle$	$-\frac{1}{12}$	$-\frac{11}{120}$	$\frac{11}{840}$	—	$-\frac{2}{30}$	$\frac{2}{35}$	—	$\frac{1}{20}$	$-\frac{1}{42}$
$\langle 1, 12 112 \rangle$	—	$\frac{5}{240}$	$-\frac{11}{840}$	—	$\frac{5}{60}$	$-\frac{4}{35}$	—	$-\frac{1}{60}$	$\frac{1}{42}$
$\langle 12, 1 112 \rangle$	—	$\frac{4}{240}$	$\frac{11}{840}$	—	$-\frac{7}{60}$	$\frac{4}{35}$	—	$\frac{1}{60}$	$-\frac{1}{42}$

APPENDIX (*cont.*)

	$I(2, 0, 5)$	$I(2, 0, 7)$	$I(2, 0, 2)$	$I(4, 0, 5)$	$I(4, 0, 7)$	$I(4, 0, 9)$	$I(6, 0, 5)$	$I(6, 0, 7)$	$I(6, 0, 9)$
$\langle 2, 33 112 \rangle$	—	$\frac{4}{240}$	$\frac{1}{3360}$	—	$\frac{21}{240}$	$-\frac{1}{112}$	—	$-\frac{1}{20}$	$\frac{1}{210}$
$\langle 33, 2 112 \rangle$	—	$\frac{2}{240}$	$-\frac{1}{3360}$	—	$-\frac{18}{240}$	$\frac{1}{112}$	—	$\frac{1}{20}$	$-\frac{1}{210}$
$\langle 3, 23 112 \rangle$	—	$\frac{2}{240}$	$\frac{1}{3360}$	—	$\frac{25}{240}$	$-\frac{1}{112}$	—	$-\frac{1}{20}$	$\frac{1}{210}$
$\langle 23, 3 112 \rangle$	—	—	$-\frac{1}{3360}$	—	$-\frac{20}{240}$	$\frac{1}{112}$	—	$\frac{1}{20}$	$-\frac{1}{210}$
$\langle 0, 123 123 \rangle$	$\frac{1}{8}$	$\frac{3}{40}$	$\frac{2}{1120}$	—	$\frac{3}{80}$	$-\frac{4}{1120}$	—	—	$\frac{1}{840}$
$\langle 123, 0 123 \rangle$	$-\frac{1}{8}$	$-\frac{3}{40}$	$-\frac{2}{1120}$	—	$\frac{1}{80}$	$\frac{4}{1120}$	—	—	$-\frac{1}{840}$
$\langle 1, 23 123 \rangle$	$\frac{1}{24}$	$\frac{3}{240}$	$-\frac{2}{1120}$	—	$\frac{2}{120}$	$\frac{3}{560}$	—	—	$-\frac{1}{840}$
$\langle 2, 31 123 \rangle$	$\frac{1}{24}$	$\frac{3}{240}$	$-\frac{2}{1120}$	—	$\frac{2}{120}$	$\frac{3}{560}$	—	—	$-\frac{1}{840}$
$\langle 3, 12 123 \rangle$	$\frac{1}{24}$	$\frac{3}{240}$	$-\frac{2}{1120}$	—	$\frac{2}{120}$	$\frac{3}{560}$	—	—	$-\frac{1}{840}$
$\langle 32, 1 123 \rangle$	$-\frac{1}{24}$	$\frac{1}{240}$	$\frac{2}{1120}$	—	$-\frac{1}{120}$	$-\frac{3}{560}$	—	—	$\frac{1}{840}$
$\langle 31, 2 123 \rangle$	$-\frac{1}{24}$	$\frac{1}{240}$	$\frac{2}{1120}$	—	$-\frac{1}{120}$	$-\frac{3}{560}$	—	—	$\frac{1}{840}$
$\langle 12, 3 123 \rangle$	$-\frac{1}{24}$	$\frac{1}{240}$	$\frac{2}{1120}$	—	$-\frac{1}{120}$	$-\frac{3}{560}$	—	—	$\frac{1}{840}$