

A Green function approach to shear viscosity coefficient

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Abstract. Modified transport equations are derived from Kadanoff and Baym kinetic equations, suitable for the study of thermal transport coefficients. These equations include the Hartree average energy term which has been ignored in the previous studies of thermal transport coefficients. They are linearised and the successive perturbation method is employed to solve them. The solutions are applied to shear viscosity coefficient of gases and the results are compared with the recent experimental measurements for several complex and simple gases. The potential assumed is a hard core one with a perturbation tail. The agreements are particularly good for gases with low molecular weight and in the high temperature range. For complex molecules even in the low temperature range, the agreement is better than the previous calculations. The formula derived yields the explicit temperature dependence of the viscosity coefficient.

Keywords. Green function; viscosity coefficient; Hartree energy.

1. Introduction

The equation-of-motion method using the Kadanoff and Baym kinetic equations (K and B equations) (Kadanoff and Baym 1963) for double time Green functions for the study of transport coefficients has attracted considerable interest in recent years (Fujita 1966 a, b, 1971; Hall 1975). This is because by this method one can develop transport equations, which include all orders of perturbations beyond the limits of dilute systems and the kinetic effects, which are ignored in ordinary Boltzmann equation.

The additional information contained in these equations consequently leads to further difficulties in solving them. An exact solution is a remote possibility even for the ordinary Boltzmann equation. In K and B equations one cannot even apply the usual Chapman-Enskog method. Therefore, a perturbation solution to these equations was presented in an earlier paper (Wagh 1978). This method which is successful for transport coefficients in the presence of external fields, cannot be applied for thermal transport coefficients. This is because the structure of the linearised thermal transport equations is such that all the dependent variables appear under integral signs and basically the equation requires an inversion of the integral equation. In this paper, modified transport equations are derived from K and B equations, which avoid such difficulties and are particularly suitable for the study of thermal transport coefficients.

These equations are still 'generalised Boltzmann equations' because they include all orders of perturbations and are applicable to denser systems. They can be directly

applied to make a connection to the Gibbsian equilibrium statistical mechanical approach, from the point of view of non-equilibrium statistical mechanics. Such a connection is possible only for dilute systems through conventional Boltzmann equation. For denser systems recently a connection between the equilibrium and non-equilibrium statistical mechanics has been presented by Eu (1979). Our approach is independent of any assumptions required by the method of Eu, and the equilibrium condition derived from our equations yields the results of cluster expansions of the equilibrium partition function.

The additional information contained in the K and B equations in terms of the Hartree average energy and the kinetic effect terms, in no way creates any difficulty in solving these equations, if the perturbation method of solution is used. Thus the effect of these two terms on transport coefficients may be studied directly. The significance of Hartree term has already been well studied in plasmas through the Vlasov equation (Jancel and Kahan 1963). In the problem of static transport coefficients, this term is not included in the basic transport (Boltzmann) equation itself and hence does not appear in earlier literature, where extensive comparison of the experimental results has been done with the solution of such equations (Hirschfelder *et al* 1964; Hogervorst 1971). However, our formalism clearly brings out the importance of this term. The usual procedure to calculate a transport coefficient is to solve the appropriate Boltzmann equation by Chapman-Enskog method (Chapman *et al* 1970). This involves the evaluation of a universal potential dependent collision integral. This is done by applying numerical computational methods. The method has been extensively applied to study the transport properties of inert and polar gases (Hogervorst 1971; McRury *et al* 1976). Recently however, Kestin *et al* (1972) presented a law of corresponding states, which has been applied to several gaseous hydrocarbons. Wang Chang and Uhlenbeck (1951) on the other hand, presented a formalism to include internal degrees of freedom for complex structures which was later modified by Taxman (1958). Extensive numerical calculations have been carried out by Evans and Watts (1976) and are applied to Benzene. All these calculations however fail to give a closed relation for viscosity. Our formalism leads one to such a closed relation which is applicable over a wide temperature range.

The formalism presented here uses the K and B kinetic equation to obtain a modified transport equation. The equation is solved by a perturbation technique. It is then applied to the shear viscosity of several gases and is compared with the calculations mentioned above. The potential we assume is a hard core part corrected by a perturbative tail. We show that even such potential presents agreements better than the earlier cases.

Finally in the process, the temperature dependence of the shear viscosity is given by a simple formula. In fact one of the major advantages of the perturbation method of solution is that it yields simple solutions to even complicated non-linear integro-differential equations. This has been exploited in the calculations presented here.

For the sake of basic definitions and the kinetic equations to be used, in § 2, a brief account of the generalised Boltzmann equation is given and then the modified transport equations are obtained from the K and B kinetic equations. These equations are linearised in § 3 and in the process an equilibrium condition is derived which has perturbation solutions resulting in linked cluster expansion of

equilibrium statistical mechanics. The linearised transport equations are solved in the second order of perturbation to study the temperature dependence of shear viscosity in the next two sections. This is applied to study the high temperature viscosity data for several gases in § 6 conclusions are then drawn.

2. Transport equations

We consider a spinless quantum imperfect gas obeying Maxwell-Boltzmann statistics, described by the Hamiltonian in second quantization given by

$$\begin{aligned}
 H \equiv & \sum_j \int d\mathbf{p} a^{\dagger(j)}(\mathbf{p}) h_0^{(j)}(\mathbf{p}) a^{(j)}(\mathbf{p}) \\
 & + \lambda \sum_{j>k} \int \dots \int \prod_{i=1}^4 d\mathbf{p}_i a^{\dagger(j)}(\mathbf{p}_1) a^{\dagger(k)}(\mathbf{p}_2) V(1234) a^{(k)}(\mathbf{p}_4) a^{(j)}(\mathbf{p}_3),
 \end{aligned}
 \tag{1}$$

where $h_0^{(j)}$ is the kinetic energy of the j th particle, $V(1234)$ is given by

$$V(1234) = v(\mathbf{p}_1 - \mathbf{p}_3) \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_3 - \mathbf{p}_4).
 \tag{2}$$

Here $v(\mathbf{p})$ is the Fourier transform of the potential $V(\mathbf{r})$ of the mutual interaction between the particles, $a^{(j)}(\mathbf{p})$ and $a^{\dagger(k)}(\mathbf{p})$ are the annihilation and creation operators of the j th and k th particle respectively satisfying the usual commutation relations for the distinguishable particles. λ is a coupling constant and the summation runs over all the particles.

The partial green functions are defined by

$$g^<(1, 2) \equiv -i \text{Tr} \left\{ \sum_j \rho a^{\dagger(j)}(2) a^{(j)}(1) \right\} = g^<(\mathbf{p}_1 t_1, \mathbf{p}_2 t_2),
 \tag{3}$$

$$g^>(1, 2) \equiv -i \text{Tr} \left\{ \sum_j \rho a^{(j)}(1) a^{\dagger(j)}(2) \right\} = g^>(\mathbf{p}_2 t_2, \mathbf{p}_1 t_1).
 \tag{4}$$

Here ρ is the density operator to be specified at the initial time $t = -\infty$.

It has been shown (Kadanoff and Baym 1963), that the partial Green functions given by (3) and (4) satisfy four kinetic equations known as Kadanoff and Baym kinetic equations. One can obtain the generalized Boltzmann equation from them (Kadanoff and Baym, 1963, page 110), which includes all orders of perturbations and the kinetic effects through the terms given by poisson brackets. Further the energy ω is considered to be an independent variable. This fact is of particular importance to us as shall be seen later.

In the steady state *viz.* as $T \rightarrow \infty$ for a homogeneous system, one can immediately write the equilibrium condition from the generalized Boltzmann equation as (Lodder *et al* 1972; Kadanoff and Baym 1963, pages 121-122)

$$G_{\text{eq}}^>(\mathbf{p} \omega) \sum_{\text{eq}}^<(\mathbf{p} \omega) = G_{\text{eq}}^<(\mathbf{p} \omega) \sum_{\text{eq}}^>(\mathbf{p} \omega)
 \tag{5}$$

The solution of this equation for distinguishable particles in the Born collision approximation is as given by (Kadanoff and Baym 1963, equation (10-6) and the paragraph following it)

$$G_{\text{eq}}^>(\mathbf{p}, \omega) = 2\pi \delta\left(\omega - \frac{p^2}{2m}\right), \quad (6)$$

$$G_{\text{eq}}^<(\mathbf{p}, \omega) = \exp(\alpha - \beta\omega) G_{\text{eq}}^>(\mathbf{p}, \omega). \quad (7)$$

This solution in fact is an equilibrium distribution of free particle ensemble. It is natural to expect that the equilibrium distribution of interacting particles will contain terms involving the potential in the energy ω . Unfortunately these terms cannot be obtained from (5), no matter what order of perturbation the self-energy parts are expanded to. They will cancel each other term by term without yielding any details of the interaction. Besides the generalised Boltzmann equation given by Kadanoff and Baym assumes that the disturbances in the system such as various gradients and the applied fields vary slowly in space and time. As the linear transport processes occur in this situation, the equation is the most suitable for the study of transport coefficients. However, the information contained in the equation is not easy to extract, particularly if spatial gradients occur. These being limitations of the generalised Boltzmann equation, we turn to modified transport equations, obtained under the same physical situation of slowly varying disturbances.

Adding Kadanoff and Baym kinetic equations for partial Green functions, changing the variables according to the following prescription *viz.*

$$t_1 - t_2 = t, \quad \frac{t_1 + t_2}{2} = T \quad (8)$$

$$\frac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2) = \mathbf{p}, \quad \mathbf{p}_1 + \mathbf{p}_2 = \mathbf{k} \quad (9)$$

$$f(1, 2) = F(\mathbf{p}, t, \mathbf{k}, T) \quad (10)$$

Fourier transforming and ignoring all space and time derivatives beyond the first order, one obtains

$$\left[\omega - \frac{p^2}{2m} - U(\mathbf{R}, T)\right] G^<(\mathbf{p}, \omega, \mathbf{R}, T) = \Phi^<(\mathbf{p}, \omega, \mathbf{R}, T), \quad (11)$$

where

$$\begin{aligned} \Phi^<(\mathbf{p}, \omega, \mathbf{R}, T) &= \frac{1}{2} \cdot \frac{1}{2\pi} P \int \frac{d\omega'}{\omega' - \omega} \\ &\left[\sum^>(\mathbf{p}, \omega', \mathbf{R}, T) G^<(\mathbf{p}, \omega, \mathbf{R}, T) + G^>(\mathbf{p}, \omega', \mathbf{R}, T) \sum^<(\mathbf{p}, \omega, \mathbf{R}, T) \right] \\ &+ \frac{1}{2} \left\{ \left[G^<(\mathbf{p}, \omega, \mathbf{R}, T), \sum^>(\mathbf{p}, \omega, \mathbf{R}, T) \right] \right. \\ &\left. - \left[G^>(\mathbf{p}, \omega, \mathbf{R}, T), \sum^<(\mathbf{p}, \omega, \mathbf{R}, T) \right] \right\}, \quad (12) \end{aligned}$$

where P denotes the principal value. The terms in the curly brackets on the right side of (12) are the generalized poisson brackets defined by

$$[X, Y] = \frac{\partial X}{\partial \omega} \cdot \frac{\partial Y}{\partial T} - \frac{\partial X}{\partial T} \cdot \frac{\partial Y}{\partial \omega} - \nabla_{\mathbf{p}} \cdot \nabla_{\mathbf{R}} Y + \nabla_{\mathbf{R}} X \cdot \nabla_{\mathbf{p}} Y. \quad (13)$$

Equation (11) along with (12) is a non-linear but Markoffian integro-differential equation for $G^<$ in Wigner space. Due to its time derivatives, Boltzmann equation seems to be very suitable for the study of evolution of the system, (11) is more appropriate for the study of equilibrium properties. As shown earlier (Wagh 1978), while the Boltzmann equation has a perturbation solution to the problems of transport due to external field, (11) is particularly suitable for the study of thermal transport coefficients. The latter point will be amplified in later sections. In the next section the equation will be used to study the equilibrium properties of the system.

To complete the analysis, one may follow the procedure for $G^>$ also. The new transport equations for $G^>(\mathbf{p}, \omega, \mathbf{R}, T)$ is

$$\left[\omega - \frac{p^2}{2m} - U(\mathbf{R}, T) \right] G^>(\mathbf{p}, \omega, \mathbf{R}, T) = P \int \frac{d\omega'}{2\pi} \cdot \frac{1}{\omega' - \omega} \\ \times \left[\sum^>(\mathbf{p}, \omega, \mathbf{R}, T) G^>(\mathbf{p}, \omega', \mathbf{R}, T) + \sum^>(\mathbf{p}, \omega', \mathbf{R}, T) G^>(\mathbf{p}, \omega, \mathbf{R}, T) \right]. \quad (14)$$

3. The equilibrium condition and the linear transport equation

For a system in thermodynamic equilibrium, each of the functions in (11) becomes independent of the macroscopic time T and \mathbf{R} . Thus one may write an equilibrium condition as

$$\left[\omega - \frac{p^2}{2m} - U_{\text{eq}} \right] G_{\text{eq}}^<(\mathbf{p}, \omega) = \Phi_{\text{eq}}^<(\mathbf{p}, \omega), \quad (15)$$

where

$$\Phi_{\text{eq}}^<(\mathbf{p}, \omega) = \frac{1}{2} P \int \frac{d\omega'}{2\pi} \cdot \frac{1}{\omega' - \omega} \left[\sum_{\text{eq}}^>(\mathbf{p}, \omega') G_{\text{eq}}^<(\mathbf{p}, \omega) \right. \\ \left. + G_{\text{eq}}^>(\mathbf{p}, \omega') \sum_{\text{eq}}^<(\mathbf{p}, \omega) \right]. \quad (16)$$

Going one step ahead, in the steady state, since all the functions will not explicitly depend on time and the part of the Green function, G_L , which is responsible for a

linear transport phenomenon is the one linear to the corresponding gradient, we may write the linearized transport equations as

$$\left[\omega - \frac{p^2}{2m} - U \right] G_L^<(\mathbf{p}, \omega, \mathbf{R}) = \Phi_L^<(\mathbf{p}, \omega, \mathbf{R}) + K_L(\mathbf{p}, \omega, \mathbf{R}), \quad (17)$$

and

$$\left[\omega - \frac{p^2}{2m} - U \right] G_L^>(\mathbf{p}, \omega, \mathbf{R}) = \Phi_L^>(\mathbf{p}, \omega, \mathbf{R}). \quad (18)$$

Here $\Phi_L^>$ and K_L are given in terms of the equilibrium and linear parts of the self energy $\sum_{\text{eq}}^>$, $\sum_L^>$ respectively by

$$\begin{aligned} \Phi_L^>(\mathbf{p}, \omega, \mathbf{R}) = & \frac{1}{2} \cdot \frac{1}{2\pi} P \int \frac{d\omega'}{\omega' - \omega} \left[\sum_{\text{eq}}^>(\mathbf{p}, \omega', \mathbf{R}) G_L^>(\mathbf{p}, \omega, \mathbf{R}) \right. \\ & + \sum_L^>(\mathbf{p}, \omega', \mathbf{R}) G_{\text{eq}}^>(\mathbf{p}, \omega, \mathbf{R}) + G_{\text{eq}}^>(\mathbf{p}, \omega', \mathbf{R}) \sum_L^>(\mathbf{p}, \omega, \mathbf{R}) \\ & \left. + G_L^>(\mathbf{p}, \omega', \mathbf{R}) \sum_{\text{eq}}^>(\mathbf{p}, \omega, \mathbf{R}) \right], \quad (19) \end{aligned}$$

and

$$\begin{aligned} K_L(\mathbf{p}, \omega, \mathbf{R}) = & \frac{1}{2} \left\{ \left[G_L^<(\mathbf{p}, \omega, \mathbf{R}), \sum_{\text{eq}}^>(\mathbf{p}, \omega, \mathbf{R}) \right] \right. \\ & + \left[G_{\text{eq}}^<(\mathbf{p}, \omega, \mathbf{R}), \sum_L^>(\mathbf{p}, \omega, \mathbf{R}) \right] - \left[G_L^>(\mathbf{p}, \omega, \mathbf{R}), \sum_{\text{eq}}^<(\mathbf{p}, \omega, \mathbf{R}) \right] \\ & \left. - \left[G_{\text{eq}}^>(\mathbf{p}, \omega, \mathbf{R}), \sum_L^<(\mathbf{p}, \omega, \mathbf{R}) \right] \right\}. \quad (20) \end{aligned}$$

One can now apply a perturbation expansion to $\Phi_{\text{eq}}^<$ using the connected diagram expansion. This yields $G_{\text{eq}}^<(\mathbf{p}, \omega)$ in various orders of perturbation. For example, for free particles we have

$$\left(\omega - \frac{p^2}{2m} \right) G_{\text{eq}}^{(0)<}(\mathbf{p}, \omega) = 0, \quad (21)$$

which yields a solution after comparing with (7), for all \mathbf{p} and ω as

$$G_{\text{eq}}^{(0)<}(\mathbf{p}, \omega) = 2\pi \exp(\alpha - \beta\omega) \delta\left(\omega - \frac{p^2}{2m}\right). \quad (22)$$

The higher orders of solution can be obtained if one notes that the energy ω of a particle has to be different from the free particle energy ($p^2/2m$). Due to the complexity involved in $\Phi_{\text{eq}}^<(\mathbf{p}, \omega)$ the solution of (15) is not possible without any proper simplifying assumption. Writing for

$$\Phi_{\text{eq}}^<(\mathbf{p}, \omega) = \phi^<(\mathbf{p}) G_{\text{eq}}^<(\mathbf{p}, \omega), \quad (23)$$

and rearranging the terms in (15), one may obtain

$$[\omega - E(\mathbf{p})] G_{\text{eq}}^<(\mathbf{p}, \omega) = 0, \quad (24)$$

where

$$E(\mathbf{p}) = \frac{p^2}{2m} + \phi(\mathbf{p}) = \frac{p^2}{2m} + (-U_{\text{eq}} - \phi^<(\mathbf{p})), \quad (25)$$

$\phi(\mathbf{p})$ represents the energy due to the interactions and is expandable in a perturbation expansion. Equation (24) has a solution

$$G_{\text{eq}}^<(\mathbf{p}, \omega) = 2\pi \delta(\omega - E(\mathbf{p})) \exp(\alpha - \beta\omega), \quad (26)$$

in analogy with (22). However to find the exact expression for the terms in the perturbation expansion of $\phi(p)$ one may substitute (26) in (15) and after integration with respect to ω obtain upto λ^2 order.

$$\begin{aligned} & [\phi(\mathbf{p}) - U_{\text{eq}}] \exp \left[\alpha - \beta \left(\frac{p^2}{2m} + \phi(\mathbf{p}) \right) \right] \\ &= \left(-\frac{\beta}{2} \right) \lambda^2 \int \int \int d\mathbf{p}' d\bar{\mathbf{p}} d\bar{\mathbf{p}}' \delta(\mathbf{p} + \mathbf{p}' - \bar{\mathbf{p}} - \bar{\mathbf{p}}') \\ & \times |v(\mathbf{p} - \bar{\mathbf{p}})|^2 \exp \left[2\alpha - \beta \left(\frac{p^2}{2m} + \frac{p'^2}{2m} \right) \right]. \end{aligned} \quad (27)$$

When $\phi(\mathbf{p})$ is expanded in a perturbation series

$$\phi(\mathbf{p}) = \sum_n \lambda^n \phi_n(\mathbf{p}), \quad (28)$$

and (27) yields, up to λ^2 order of perturbation

$$\lambda \phi_1(\mathbf{p}) = U_{\text{eq}}, \quad (29)$$

where

$$U_{\text{eq}} = \lambda n v(0) = \lambda n \bar{V} = \lambda n \int d\mathbf{r} V(\mathbf{r}), \quad (30)$$

and n is the particle density,

$$\phi_2(\mathbf{p}) = \left(-\frac{\beta}{2}\right) n \int d\mathbf{k} |v(\mathbf{k})|^2 - \beta (n \bar{V})^2. \quad (31)$$

The result (30) has been derived by Kadanoff and Baym (1963). U_{eq} as represented here is the average energy of each particle due to Vlasov field. ϕ_2 is the reduction in internal energy due to binary collisions. One may proceed with this analysis to the higher orders of λ .

The results (30) and (31) can also be obtained from the cluster expansion of the equilibrium partition function of an imperfect gas. However, we have obtained it from a non-equilibrium approach and our method extended to higher orders would establish the equilibrium thermodynamics as a limiting case of non-equilibrium process for even denser systems.

4. The shear viscosity coefficient (η)

The shear viscosity coefficient may either be studied by the kinetic equations or by the correlation function formula. (Fujita 1966b; Isihara 1971). We shall use the linearized transport equation (17) alongwith the correlation function formula derived in the appendix, to study the shear viscosity coefficient.

In the case of shear viscosity, the current tensor σ is given by (Isihara 1971; Fujita 1966b)

$$\sigma(\mathbf{r}, T) = \text{Tr} \left\{ \frac{1}{\Omega} \hat{\mathbf{J}} n(T) \right\}, \quad (32)$$

where $n(T)$ is the one body density operator, the matrix elements of which are related to $g^<(1, 2)$ by

$$\frac{L}{\Omega} \xrightarrow{\Omega \rightarrow \infty} \frac{(2\pi)^3}{\Omega} \frac{L}{t_2 \rightarrow t_1} i g^<(1, 2) = n_{12}(t_1). \quad (33)$$

The current σ consists of two parts (Isihara 1971, page 370) and (Fujita 1966b); σ_1 corresponds to the momentum transfer and σ_2 corresponds to the potential drag. Correspondingly η may be divided as

$$\eta = \eta_1 + \eta_2. \quad (34)$$

In the steady state ($T \rightarrow \infty$), the current tensor is related to the velocity gradient \mathbf{q} by

$$\sigma = 2\mathbf{q} \eta. \quad (35)$$

For a flow restricted to $x - y$ plane one obtains

$$\sigma_{1xy}(T) = \frac{1}{\Omega} \int d\mathbf{p} \frac{P_x P_y}{m} \int d\omega G^<(\mathbf{p}, \omega, T), \quad (36)$$

where we are working in a frame of reference in which the average velocity of the flow is zero.

Following the methodology described in (Lodder *et al* 1972) to obtain the asymptotic behaviour of $\sigma_{xy}(T)$, we equate the residues of the Laplace transforms of both the sides of (36) at a simple pole $Z = 0$. This yields

$$2q_{xy} \eta_1 = \frac{1}{\Omega} \int d\mathbf{p} \frac{P_x P_y}{m} \int d\omega G_L^<(\mathbf{p} \omega), \tag{37}$$

where $G_L^<(\mathbf{p} \omega)$ is the residue of $G_L^<(\mathbf{p} \omega, z)$ at $z = 0$. This residue may be obtained by solving (17).

A similar analysis follows for σ_2 also. We simply quote the result.

$$2q_{xy} \eta_2 = \frac{1}{\Omega} \int \dots \int d\mathbf{p} d\mathbf{p}' d\bar{\mathbf{p}} d\bar{\mathbf{p}}' \tilde{J}_{2xy}(\mathbf{p} \mathbf{p}' \bar{\mathbf{p}} \bar{\mathbf{p}}') \times \int G_{2L}(\mathbf{p} \mathbf{p}' \bar{\mathbf{p}} \bar{\mathbf{p}}', \omega) d\omega, \tag{38}$$

where J_{2xy} is Fourier transform of the potential drag term as given in (Fujita 1966b).

5. A perturbation expansion of shear viscosity

To solve the generalised transport equations similar to (17) a perturbation method was presented earlier (Wagh 1978). It consists of expanding the unknown Green function in the transport equation in a perturbation series and then obtaining the higher order terms in terms of the known lower order. Applying this to (17), the first few orders may immediately be written as follows:

$$G_L^< = \frac{UG_{L0}^<}{\left(\omega - \frac{p^2}{2m} - U\right)} + \frac{\Phi_{L0}^< + K_{L0}}{\left(\omega - \frac{p^2}{2m} - U\right)} + \frac{\Phi_{L1}^< + K_{L1}}{\left(\omega - \frac{p^2}{2m} - U\right)} + \dots \tag{39}$$

For the evaluation of η_1 , $G_{L0}^<$ is given by

$$G_{L0}^< = G_L^{<(0)} = \left(p_x \frac{\partial}{\partial p_y} + p_y \frac{\partial}{\partial p_x}\right) G_{\text{eq}}^<(\mathbf{p} \omega), \tag{40}$$

and may further be simplified as

$$G_{L0}^< = (-2\pi\beta) (2q_{xy}) \frac{p_x p_y}{m} \delta\left(\omega - \frac{p^2}{2m}\right) \exp\left[\alpha - \beta \frac{p^2}{2m}\right]. \tag{41}$$

$\Phi_{Li}^<$ and K_{Li} are obtained in terms of the lower order Green functions, such that each term is still of the i th order. Accordingly when η_1 is expanded in a perturbation

series $\sum_{i=0}^{\infty} \eta_1^{(i)}$ and the expansion (39) is used in the formula (37), we obtain

$$\eta_1^{(0)} = \beta \int d\mathbf{p} \frac{p_x^2 p_y^2}{m^2} \exp \left[\alpha - \beta \frac{p^2}{2m} \right]. \quad (42)$$

The next term is given by

$$\begin{aligned} \eta_1^{(1)} = & \int d\mathbf{p} p_x^2 p_y^2 \exp \left[\alpha - \beta \frac{p^2}{2m} \right] \frac{\exp \alpha}{4\pi nV} \int d\mathbf{k} \frac{|V(\mathbf{k})|^2}{k} \\ & + \frac{\pi\beta}{nV} \int d\mathbf{p} \frac{p_x^2 - p_y^2}{m} \exp \left[2\alpha - \beta \frac{p^2}{2m} \right] \int d\mathbf{k} \frac{|V(\mathbf{k})|^2}{k}. \end{aligned} \quad (43)$$

Thus the problem is reduced to the evaluation of integrals. One may proceed in a similar manner to evaluate any other higher order terms in the viscosity.

A perturbation expansion of $G_L^<$ and hence that of η_1 is evident from (39). The first term is of the order λ^0 , the next one of the order λ^1 and so on.

6. Applications to gases and conclusions

When the treatment given in the last two sections is applied to practical situations, many terms contribute negligibly small and the formulation is simplified. The kinetic effect term given by the second term on the right side of (43) is one order higher in density than the first term for the same order of perturbation. Hence for dilute systems, this will be neglected. (However, this term becomes an important one when one considers the density expansion of the viscosity coefficient. This will be demonstrated in a separate publication.) Same would be the case for higher order terms in the expansion of the collision terms.

A major difference between earlier treatment and the one presented here is the existence of the Hartree term U . In the studies of static transport coefficients, this term has not been included before, though its importance in plasma physics is well-known through the Vlasov equation.

It is well established that the interaction potential between the molecules can be considered to be a result of a hard core part and a weak potential. The exact form of such potentials is a wide field of investigation. Some of the popular forms are the ones involving two or more parameters (Evans and Watts 1976; Mason and Rice 1954; Neufeld and Aziz 1973). Molecular dynamics method also have been tried to fit the experimental data (Keller 1957; Monchick *et al* 1965). But none of these methods prescribes a unique form of potential applicable to all gases.

This has rendered the calculation of the transport coefficient as being mere calculation of collision integrals which are functions of the potentials, which requires a *priori* knowledge of the potentials. In practice, however, in simpler applications, one is interested in problems such as the temperature dependence of the transport coefficient without going into details of the potentials. Here such a requirement is dealt with.

Explicit temperature dependence of the shear viscosity coefficient in terms of two parameters which depend on the potential are derived.

We assume an interaction potential, having a hard core part up to $r = \sigma$ and then a perturbation part $V(r)$ beyond. The Fourier transform may be defined for the tail part as

$$v(\mathbf{k}) = \frac{1}{(2\pi)^3} \int_{\sigma}^{\infty} \mathbf{dr} V(r) \exp(i \mathbf{k} \cdot \mathbf{r}). \quad (44)$$

The inverse transform of this tail part of the potential, naturally, is zero (for $r < \sigma$). We use this part-potential for calculating the perturbation terms only and in $G_L^{<(0)}$, we use the rigid sphere density to involve the hard core part.

In terms of this (42) and (43), without the kinetic effects term, yield

$$\eta_1 = n_0 k_B T \left[1 + \left(\frac{m}{16\pi k_B} \right)^{1/2} \frac{1}{V T^{1/2}} \int \mathbf{dk} \frac{|v(\mathbf{k})|^2}{k} \right], \quad (45)$$

where, we have substituted for

$$e^a = n_0 (2\pi m k_B T)^{-3/2}, \quad (46)$$

with n_0 being the rigid-sphere particle density given by

$$n_0 = \frac{1}{\pi \sigma^2 v}. \quad (47)$$

v the average velocity of the rigid-sphere particles, is given by

$$v = \sqrt{\frac{8 k_B T}{\pi m}}. \quad (48)$$

Substitution of these in (45) yields

$$\eta_1 = a \sqrt{T} + b, \quad (49)$$

where

$$a = \frac{1}{\sigma^2} \sqrt{\frac{k_B m}{\pi}}, \quad (50)$$

and

$$b = \frac{a}{V} \left(\frac{m}{16\pi k_B} \right)^{1/2} \int \mathbf{dk} \frac{|v(\mathbf{k})|^2}{k}. \quad (51)$$

Equation (49) yields an explicit temperature dependence of the viscosity coefficient. Since all the details of the potential are embedded in the constant b , the formula is general enough to be applied to molecules with simple as well as complex structures and non-spherical potentials. In polar molecule problems the potential often used is Stockmayer potential which is a superposition of Lennard-Jones potential and the angular dependent dipole term (Hirschfelder *et al* 1964). In the case of non-polar gases one usually uses the Lennard-Jones (6-12) potential. Both these potentials indicate a hard core repulsive part and also an attractive term. Therefore, one may be justified in adopting the potential assumed above for both of the cases.

Here the formula has been applied to (i) inert gases at high temperature, (ii) polar gases at high temperatures, and (iii) complex organic molecules. Whenever possible, the formula has been tested in two different ranges, *i.e.* a low temperature range up to 1000° K and high temperature range from 1000° K to 2000° K, the percentage error between the calculated and observed viscosities are shown graphically. The results of the agreements can be summarised as follows:

6.1 Inert gases

The agreement of the formula (49) with viscosity at high temperatures between 1000° K to 2000° K is very good yielding not more than 1% error in any case. The agreement at lower temperatures is comparatively poor yielding a larger error. This is due to the slowly converging perturbation series. Thus for better agreements, higher order terms to include $\eta_1^{(2)}$ etc. are necessary.

6.2 Polar gases

Again the agreements at high temperatures are very good with no more than 1% error. The term in the viscosity arising out of the perturbation potential is not limited to only spherically symmetric potentials, hence agreement is not surprising.

The agreement for hydrogen at low temperatures between 100° K to 140° K is poor. This is due to the quantum effects dominating in that region.

6.3 Organic gases

It is evident from figure 1 that the agreement of (49) is better than the one shown by the Law of Corresponding States, except for butane which is heavy, where the agreement is poorer than the latter. This is due to the large mass number of the gas which converges the perturbation series slowly (McRury *et al* 1976).

6.4 Benzene

The transport properties of benzene have been investigated (Wang Chang and Uhlenbeck 1951) in detail by applying Taxman's and Wang Chang and Uhlenbeck (wcu) formalism. These theories take into account the internal degrees of freedom of the atoms.

It is interesting to see from figure 2 that the formalism presented here gives an agreement better than the previous calculations especially at higher temperatures. This is in spite of the heaviness of benzene molecules. Thus one may say that our formalism

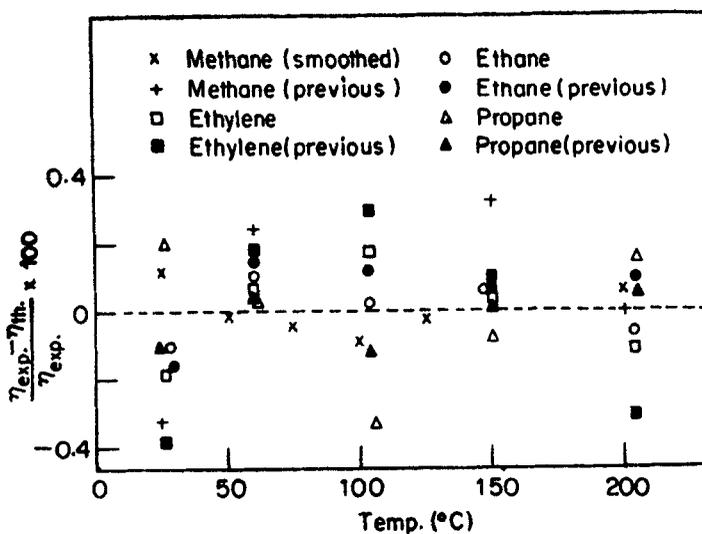


Figure 1. Comparison of the results of formula (49) with experimental results and the law of corresponding states for organic gases.

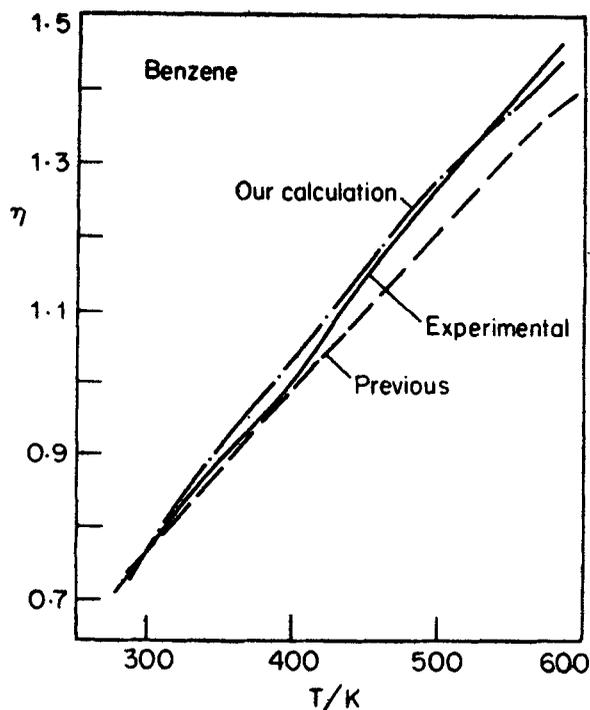


Figure 2. The present calculations of the viscosity of benzene are compared with experimental results and calculations done using Taxman's (1958) formalism.

agrees fairly well with the experimental results over a wide temperature range and for a wide range of gases. However a direct comparison with the prevalent theoretical methods of calculation of thermal transport coefficients, for example using Boltzmann

Table 1. Calculated viscosities are compared with best fitting experiments for inert and polar gases.

Gas	Temperature (°K)	Viscosity (Poise)	Calc. Visc. (Poise)	% Error	Ref.
Hydrogen Mol. wt. 2.000 $a = 0.7301 \times 10^{-6} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.342 \times 10^{-5} \text{ Poise}$ Standard Error = 0.1866×10^{-6}	100	0.4210E-05	0.3881E-05	0.7811E 01	
	120	0.4810E-05	0.4578E-05	0.4823E 01	
	140	0.5350E-05	0.5219E-05	0.2451E 01	
	160	0.5850E-05	0.5815E-05	0.5925E 00	
	180	0.6340E-05	0.6376E-05	-0.5609E 00	
	200	0.6810E-05	0.6905E-05	-0.1401E 01	
	220	0.7270E-05	0.7409E-05	-0.1917E 01	
	240	0.7710E-05	0.7891E-05	-0.2347E 01	
	260	0.8140E-05	0.8353E-05	-0.2614E 01	
	280	0.8560E-05	0.8797E-05	-0.2771E 01	
	300	0.8760E-05	0.9226E-05	-0.2969E 01	
	400	0.1127E-04	0.1118E-04	0.7775E 00	
	500	0.1305E-04	0.1291E-04	0.1104E 01	
800	0.1744E-04	0.1723E-04	0.1199E 01		
Hydrogen Mol. wt. = 2.00 $a = 0.9839 \times 10^{-6} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.1073 \times 10^{-4} \text{ Poise}$ Standard Error = 0.5437×10^{-7}	1987	0.3320E-04	0.3313E-04	0.2048E 00	
	1102	0.2202E-04	0.2194E-04	0.3845E 00	
	1152	0.2273E-04	0.2267E-04	0.2723E 00	
	1201	0.2342E-04	0.2337E-04	0.2095E 00	
	1251	0.2407E-04	0.2407E-04	-0.1463E-01	
	1300	0.2473E-04	0.2475E-04	-0.7497E-01	
	1349	0.2538E-04	0.2541E-04	-0.1220E 00	
	1399	0.2606E-04	0.2607E-04	-0.5601E-01	
	1447	0.2671E-04	0.2670E-04	0.3509E-01	
	1497	0.2731E-04	0.2734E-04	-0.1164E 00	
	1543	0.2783E-04	0.2792E-04	-0.3316E 00	
	1592	0.2845E-04	0.2853E-04	-0.2854E 00	
	1641	0.2909E-04	0.2913E-04	-0.1402E 00	
	1690	0.2967E-04	0.2972E-04	-0.1736E 00	
	1740	0.3026E-04	0.3032E-04	-0.1834E 00	
	1789	0.3086E-04	0.3089E-04	-0.9530E-01	
	1839	0.3150E-04	0.3147E-04	0.1049E 00	
1888	0.3205E-04	0.3203E-04	0.7678E-01		
1937	0.3267E-04	0.3258E-04	0.2857E 00		
1977	0.3309E-04	0.3302E-04	0.2070E 00		
Helium Mol. wt. = 4.000 $a = 0.1785 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.1099 \times 10^{-4} \text{ Poise}$ Standard Error = 0.1824×10^{-6}	293	0.1950E-04	0.1958E-04	-0.3913E 00	
	373	0.2350E-04	0.2349E-04	0.5796E-01	
	474	0.2794E-04	0.2788E-04	0.2315E 00	
	566	0.3159E-04	0.3148E-04	0.3475E 00	
	673	0.3543E-04	0.3532E-04	0.3066E 00	
	793	0.3894E-04	0.3928E-04	-0.8763E 00	
	799	0.3913E-04	0.3947E-04	-0.8716E 00	
	800	0.3952E-04	0.3950E-04	0.4393E-01	
	803	0.3989E-04	0.3960E-04	0.7339E 00	
	926	0.4340E-04	0.4333E-04	0.1523E 00	
	948	0.4407E-04	0.4398E-04	0.2146E 00	

(Guevara *et al* 1969 and ref. therein)

(Dawe and Smith 1970)

Table 1. (Contd.)

Gas	Temperature (°K)	Viscosity (Poise)	Calc. Visc. (Poise)	% Error	Ref.
Helium Mol. wt. = 4.000 $a = 0.2323 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.2785 \times 10^{-4} \text{ Poise}$ Standard Error = 0.4897×10^{-6}	1100	0.4985E-04	0.4920E-04	0.1307E 01	(Guevara <i>et al</i> (1969))
	1150	0.5137E-04	0.5093E-04	0.8567E 00	
	1200	0.5137E-04	0.5262E-04	-0.2442E 01	
	1250	0.5305E-04	0.5428E-04	-0.2306E 01	
	1300	0.5627E-04	0.5591E-04	0.6392E 00	
	1350	0.5782E-04	0.5751E-04	0.5432E 00	
	1400	0.5935E-04	0.5907E-04	0.4681E 00	
	1450	0.6074E-04	0.6061E-04	0.2128E 00	
	1500	0.6241E-04	0.6212E-04	0.4598E 00	
	1550	0.6363E-04	0.6361E-04	0.3101E-01	
	1600	0.6524E-04	0.6507E-04	0.2548E 00	
	1650	0.6667E-04	0.6651E-04	0.2333E 04	
	1700	0.6795E-04	0.6793E-04	0.2416E-01	
	1750	0.6942E-04	0.6933E-04	0.1268E 00	
	1800	0.7078E-04	0.7071E-04	0.9817E-01	
1850	0.7216E-04	0.7207E-04	0.1247E 00		
1900	0.7313E-04	0.7341E-04	-0.3847E 00		
1950	0.7447E-04	0.7473E-04	-0.3559E 00		
Neon Mol. wt. = 20.183 $a = 0.2673 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.1487 \times 10^{-4} \text{ Poise}$ Standard Error = 0.237×10^{-6}	293	0.3127E-04	0.3090E-04	0.1172E 01	(Dawe and Smith 1970)
	373	0.3680E-04	0.3676E-04	0.1146E 00	
	474	0.4306E-04	0.4333E-04	-0.6246E 00	
	566	0.4847E-04	0.4873E-04	-0.5288E 00	
	673	0.5416E-04	0.5448E-04	-0.5858E 00	
	800	0.6098E-04	0.6074E-04	0.3976E 00	
	801	0.6066E-04	0.6078E-04	-0.2057E 00	
	803	0.6082E-04	0.6088E-04	-0.9724E-01	
	804	0.6098E-04	0.6093E-04	0.8808E-01	
	948	0.6776E-04	0.6743E-04	0.4807E 00	
Neon Mol. wt. = 20.183 $a = 0.3013 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.2401 \times 10^{-4} \text{ Poise}$ Standard Error = 0.3017×10^{-6}	1100	0.7542E-04	0.7593E-04	-0.6740E 00	(Guevara and Stensland 1971)
	1150	0.7777E-04	0.7817E-04	-0.5199E 00	
	1200	0.8039E-04	0.8037E-04	0.2236E-01	
	1250	0.8228E-04	0.8252E-04	-0.2971E 00	
	1300	0.8462E-04	0.8463E-04	-0.1677E-01	
	1350	0.8696E-04	0.8670E-04	0.2947E 00	
	1400	0.8900E-04	0.8874E-04	0.2974E 00	
	1450	0.9105E-04	0.9073E-04	0.3505E 00	
	1500	0.9312E-04	0.9269E-04	0.4592E 00	
	1550	0.9494E-04	0.9462E-04	0.3356E 00	
	1600	0.9653E-04	0.9652E-04	0.1073E-01	
	1650	0.9847E-04	0.9839E-04	0.8293E-01	
	1700	0.1004E-04	0.1002E-04	0.1703E 00	
	1750	0.1024E-04	0.1020E-04	0.3489E 00	
	1800	0.1040E-04	0.1038E-03	0.1627E 00	
	1850	0.1056E-03	0.1056E-03	0.5553E-02	
1900	0.1070E-03	0.1073E-03	-0.3120E 00		
1950	0.1087E-04	0.1091E-03	-0.3227E 00		
2000	0.1102E-03	0.1107E-03	-0.4954E 00		

Table 1. (Contd.)

Gas	Temperature (°K)	Viscosity (Poise)	Calc. Visc. (Poise)	% Error	Ref.
Nitrogen Mol. wt. = 28.01399 $a = 0.1623 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.1021 \times 10^{-4} \text{ Poise}$ Standard Error = 0.1845×10^{-6}	293	0.1757E-04	0.1758E-04	-0.4058E-01	(Dawe and Smith 1970)
	373	0.2117E-04	0.2113E-04	0.1810E 00	
	474	0.2518E-04	0.2512E-04	0.2321E 00	
	566	0.2846E-04	0.2840E-04	0.2154E 00	
	673	0.3192E-04	0.3189E-04	0.9223E-01	
	793	0.3509E-04	0.3549E-04	-0.1141E 01	
	799	0.3532E-04	0.3566E-04	-0.9710E 00	
	800	0.3561E-04	0.3569E-04	-0.2294E 00	
	803	0.3595E-04	0.3578E-04	0.4794E 00	
	804	0.3588E-04	0.3581E-04	0.2055E 00	
	926	0.3936E-04	0.3917E-04	0.4712E 00	
	948	0.3997E-04	0.3976E-04	0.5309E 00	
Nitrogen Mol. wt. = 28.01399 $a = 0.1778 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.1457 \times 10^{-4} \text{ Poise}$ Standard Error = 0.6578×10^{-7}	1100	0.4437E-04	0.4439E-04	-0.4752E-01	(Guevara et al 1969)
	1150	0.4567E-04	0.4572E-04	-0.1013E 00	
	1220	0.4703E-04	0.4701E-04	0.3629E-01	
	1250	0.4828E-04	0.4828E-04	-0.5908E-02	
	1300	0.4951E-04	0.4953E-04	-0.3568E-01	
	1350	0.5087E-04	0.5075E-04	0.2384E-00	
	1400	0.5203E-04	0.5195E-04	0.1588E 00	
	1450	0.5321E-04	0.5312E-04	0.1602E 00	
	1500	0.5425E-04	0.5428E-04	-0.5929E-01	
	1550	0.5527E-04	0.5542E-04	-0.2719E 00	
	1600	0.5647E-04	0.5654E-04	-0.1244E 00	
	1650	0.5758E-04	0.5764E-04	-0.1091E 00	
	1700	0.5869E-04	0.5873E-04	-0.6613E-01	
	1750	0.5976E-04	0.5980E-04	-0.6519E-01	
	1800	0.6084E-04	0.6085E-04	-0.2291E-01	
	1850	0.6196E-04	0.6189E-04	0.1060E-00	
1900	0.6293E-04	0.6292E-04	0.1459E -01		
1950	0.6401E-04	0.6393E-04	0.1190E 00		
Argon Mol. wt. = 39.95 $a = 0.2262 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.163 \times 10^{-4} \text{ Poise}$ Standard Error = 0.6404×10^{-6}	293	0.2231E-04	0.2244E-04	-0.5682E 00	(Guevara et al 1969)
	373	0.2724E-04	0.2739E-04	-0.5547E 00	
	474	0.3277E-04	0.3295E-04	-0.5558E 00	
	566	0.3741E-04	0.3752E-04	-0.2936E 00	
	673	0.4433E-04	0.4239E-04	0.4384E 01	
	793	0.4676E-04	0.4740E-04	-0.1378E 01	
	799	0.4730E-04	0.4764E-04	-0.7288E 00	
	800	0.4739E-04	0.4768E-04	-0.6219E 00	
	803	0.4772E-04	0.4780E-04	-0.1773E 00	
	926	0.5243E-04	0.5254E-04	-0.2082E 00	
	948	0.5346E-04	0.5335E-04	0.2019E 00	

Table 1. (Contd.)

Gas	Temperature (°K)	Viscosity (Poise)	Calc. Visc. (Poise)	% Error	Ref.
Argon Mol. wt. = 39.95 $a = 0.2548 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.2397 \times 10^{-4} \text{ Poise}$ Standard Error = 0.6437×10^{-6}	1100	0.6034E-04	0.6052E-04	-0.2956E 00	(Guevara <i>et al</i> 1969)
	1200	0.6420E-04	0.6428E-04	-0.1174E 00	
	1250	0.6590E-04	0.6610E-04	-0.2962E 00	
	1300	0.6756E-04	0.6788E-04	-0.4721E 00	
	1350	0.6945E-04	0.6963E-04	-0.2573E 00	
	1150	0.6220E-04	0.6242E-04	-0.3494E 00	
	1400	0.7113E-04	0.7135E-04	-0.3041E 00	
	1450	0.7275E-04	0.7303E-04	-0.3898E 00	
	1500	0.7439E-04	0.7469E-04	-0.4058E 00	
	1550	0.7735E-04	0.7632E-04	0.1328E 01	
	1600	0.7883E-04	0.7793E-04	0.1145E 01	
	1650	0.8039E-04	0.7951E-04	0.1098E 01	
	1700	0.8198E-04	0.8106E-04	0.1117E 01	
	1750	0.8345E-04	0.8260E-04	0.1022E 01	
	1850	0.8485E-04	0.8560E-04	-0.8839E 00	
	1900	0.8614E-04	0.8707E-04	-0.1021E 01	
	1950	0.8756E-04	0.8852E-04	-0.1099E 01	
Oxygen Mol. wt. = 31.9988 $a = 0.1972 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.1364 \times 10^{-4} \text{ Poise}$ Standard Error = 0.1416×10^{-6}	321	0.2188E-04	0.2169E-04	0.8502E 00	(Clifford <i>et al</i> 1975)
	417	0.2647E-04	0.2663E-04	-0.6161E 00	
	515	0.3101E-04	0.3112E-04	-0.3430E 00	
	612	0.3508E-04	0.3515E-04	-0.1994E 00	
	772	0.4136E-04	0.4116E-04	0.4875E 00	
	911	0.4584E-04	0.4589E-04	-0.1045E 00	
	Oxygen Mol. wt. = 31.9988 $a = 0.2171 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.1998 \times 10^{-4} \text{ Poise}$ Standard Error = 0.734×10^{-7}	1060	0.5069E-04	0.5073E-04	
1211		0.5570E-04	0.5559E-04	0.1893E 00	
1300		0.5826E-04	0.5832E-04	-0.1071E 00	
Krypton Mol. wt. = 83.7999 $a = 0.2879 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.2665 \times 10^{-4} \text{ Poise}$ Standard Error = 0.1805×10^{-6}		293	0.2285E-04	0.2264E-04	0.9069E 00
	300	0.2338E-04	0.2321E-04	0.7224E 00	
	400	0.3084E-04	0.3092E-04	-0.2749E 00	
	500	0.3752E-04	0.3772E-04	-0.5348E 00	
	600	0.4364E-04	0.4386E-04	-0.5146E 00	
	700	0.4934E-04	0.4951E-04	-0.3536E 00	
	800	0.5471E-04	0.5477E-04	-0.1157E 00	
	900	0.5980E-04	0.5971E-04	0.1463E 00	
	1000	0.6467E-04	0.6438E-04	0.4421E 00	
	Krypton Mol. wt. = 83.7999 $a = 0.2966 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.2816 \times 10^{-4} \text{ Poise}$ Standard Error = 0.8328×10^{-6}	1100	0.7020E-05	0.7021E-05	-0.1947E-01
1200		0.7470E-05	0.7459E-05	0.1498E 00	
1300		0.7870E-05	0.7878E-05	-0.1065E 00	
1400		0.8270E-05	0.8282E-05	-0.1463E 00	
1500		0.8680E-05	0.8672E-05	0.9634E-01	
1600		0.9050E-05	0.9048E-05	0.1771E-01	

Table 1. (Contd.)

Gas	Temperature (°K)	Viscosity (Poise)	Calc. Visc. (Poise)	% Error	Ref.	
Xenon Mol. wt. = 131.2999 $a = 0.2862 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.2632 \times 10^{-4} \text{ Poise}$ Standard Error = 0.1447×10^{-6}	293	0.2284E-04	0.2268E-04	0.6787E 00	(Dawe and Smith 1970)	
	300	0.2337E-04	0.2325E-04	0.5135E 00		
	400	0.3082E-04	0.3092E-04	-0.3206E 00		
	500	0.3750E-04	0.3768E-04	-0.4669E 00		
	600	0.4361E-04	0.4378E-04	-0.3973E 00		
	700	0.4931E-04	0.4940E-04	-0.1831E 00		
	800	0.5467E-04	0.5463E-04	0.7581E-01		
	900	0.5976E-04	0.5954E-04	0.3698E 00		
	Xenon Mol. wt. = 131.2999 $a = 0.3087 \times 10^{-5} \frac{\text{Poise}}{\text{deg}^{1/2}}$ $b = -0.3309 \times 10^{-4} \text{ Poise}$ Standard Error = 0.6055×10^{-7}	1500	0.8649E-04	0.8648E-04		0.1163E-01
		1600	0.9049E-04	0.9040E-04		0.9813E 01
1000		0.6463E-04	0.6454E-04	0.1404E 00		
1100		0.6930E-04	0.6930E-04	-0.6069E-02		
1200		0.7380E-04	0.7386E-04	-0.7731E-01		
1300		0.7816E-04	0.7822E-04	-0.8173E-01		
1400		0.8238E-04	0.8442E-04	-0.5545E-01		

equation, is not possible. A simple reason is that the Boltzmann equation method uses an explicit calculation of collision integrals and does not use a perturbation type of solution as is done here. Therefore there is no one to one correspondence between the terms obtained here and terms obtained in the Boltzmann collision integrals. Our method uses a many-body theory in which the many body effects are seen through terms like Hartree energy ($n\bar{V}$) and brings out the effect of this term in a manner of softening process as in (45). The second term on the right side of (45) describes a second order perturbation effect reduced by the Hartree energy. It is *not* an exact equivalent of collision integral appearing in the Boltzmann equation. Boltzmann equation method is an exact method in its own way. Our method is more useful when one wishes to study the explicit temperature dependence. Since our method involves directly the many body effects, it should find better applications when one considers the denser gases, particularly in the case of density expansion of the transport coefficients. This we shall consider in a separate publication.

The modified transport equations presented here are very general and are applicable to both equilibrium and non-equilibrium problems of statistical physics. The equilibrium condition (15) alongwith (31) could very well be utilized for the cluster expansion of the distribution function by following the successive perturbation expansion of both sides of the equilibrium condition, as it is done here for the viscosity equation.

This is the first time that K and B kinetic equations involving two time Green functions have been used in actual evaluation of the transport coefficients. The dependence of shear viscosity coefficient on Hartree term is explicitly demonstrated. The equations coupled with the perturbation method of solutions, yield a transport coefficient parametrically dependent on the temperature.

The following conclusions may be drawn regarding its applicability:

- (i) The equation is equally valid for spherical as well as non-spherical molecules.
- (ii) It is better applicable for molecules with small molecular weight and in the higher temperature range.
- (iii) The agreement of the formula with experiment for even heavier gas like benzene seems to be better than several rigorous theories such as Taxman's (1958) and WCU (Wang Chang and Uhlenbeck 1951).

Appendix

Here an equivalence between the correlation function method (CF method) and the transport equation method presented in the text here, is outlined. This is with the view to enable one to use the CF formula in conjunction with the transport equations (17) and (18), for the evaluation of a transport coefficient.

The CF formula for the static coefficient of shear viscosity (Isihara 1971), (Fujita 1966b) is given by

$$\eta = \frac{1}{\Omega} \int_0^{\infty} d\tau \text{Tr} \left\{ \int_0^{\beta} d\beta_1 J_{xy}(-i\beta_1) J_{xy}(\tau) \right\}, \tag{52}$$

where the current tensor $J_{xy}(t)$ in Heisenberg picture is given by

$$J_{xy}(t) = \exp(itH) J_{xy} \exp(-itH). \tag{53}$$

The formula may be modified into a convenient form (Wagh 1975)

$$\eta = L \lim_{s \rightarrow 0} \frac{\partial}{\partial S} \int_0^{\infty} dt \frac{1}{\Omega} \text{Tr} \{ \rho^* J_{xy}(t) \}, \tag{54}$$

where

$$\rho^* = \frac{\exp[aN - \beta H^*]}{\text{Tr}_x \{ \exp[aN - \beta H^*] \}}, \tag{55}$$

with

$$H^* = H - J_{xy} s, \tag{56}$$

S in (56) is a c-number.

For the sake of simplicity, we shall consider only the momentum transfer part of the viscosity η_1 . From (54) it can be shown that

$$\eta_1 = L \lim_{s \rightarrow 0} \frac{\partial}{\partial s} \int d\mathbf{p} \frac{p_x p_y}{m} i \int_0^{\infty} dT \frac{1}{\Omega} \int d\omega G^{* <}(\mathbf{p}, \omega, T), \tag{57}$$

where $G^{* <}$ is defined by replacing ρ by ρ^* . We shall now develop a transport equation for $G^{* <}$. A knowledge of $G^{* <}$ from such an equation will enable one to calculate η_1 from (57).

$G^{* <}(\mathbf{p}, \omega, \mathbf{R}, T)$ is given by

$$G^{* <}(\mathbf{p}, \omega, \mathbf{R}, T) = i \int_{-\infty}^{\infty} dt \exp(i\omega t) G^{* <}(\mathbf{p}, t, \mathbf{R}, T). \quad (58)$$

An integration by parts on the right side of (58) yields

$$\omega G^{* <}(\mathbf{p}, \omega, \mathbf{R}, T) = - \int_{-\infty}^{+\infty} dt \exp(i\omega t) \frac{\partial G^{* <}}{\partial t}(\mathbf{p}, t, \mathbf{R}, T), \quad (59)$$

where we note that $G^{* <}(t)$ is zero for large values of t .

Following the procedure of deriving the kinetic equation for $G^{* <}(t, T)$ given in the text, (Kadanoff and Baym 1963; Fujita 1966 a, b), we obtain,

$$\begin{aligned} i \frac{\partial G^{* <}}{\partial t} - \left[\frac{p^2}{2m} + U^*(\mathbf{R}, T) \right] G^{* <}(\mathbf{p}, t, \mathbf{R}, T) \\ = \Phi^{* <}(\mathbf{p}, t, \mathbf{R}, T) + K^*(\mathbf{p}, t, \mathbf{R}, T). \end{aligned} \quad (60)$$

Combining (59) and (60) we obtain the transport equation

$$\begin{aligned} \left[\omega - \frac{p^2}{2m} - U^*(\mathbf{R}, T) \right] G^{* <}(\mathbf{p}, \omega, \mathbf{R}, T) = \Phi^{* <}(\mathbf{p}, \omega, \mathbf{R}, T) \\ + K^*(\mathbf{p}, \omega, \mathbf{R}, T). \end{aligned} \quad (61)$$

This is the basic transport equation. Its equivalence with (17) may be established by following a procedure presented by Wagh (1975) in connection with the electrical conductivity. Equation (61) may be solved using the perturbation method and the viscosity coefficient may be obtained using (57).

The procedure outlined here may be generalized for the study of η_2 by CF method. Since it is beyond the scope of application of the present theory, it is not presented here.

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