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TRANSPORT PHENOMENA IN POLYATOMIC GASES

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TRANSPORT PHENOMENA IN POLYATOMIC GASES

I. INTRODUCTION

For polyatomic gases, because of the existence of internal energy states, one may expect that the transport coefficients will be given by expressions different from those for monoatomic gases. Furthermore, one expects a new constant, the relaxation time, which is a measure of the time required for the establishment of equilibrium between the translational and the internal energy states when the former is changed by some process. The effect of the relaxation time makes itself felt through various physical phenomena, most notably the dispersion and absorption of sound during its passage through a polyatomic gas. In fact, the effect of the relaxation time was first suggested by Lorentz¹ in 1881, in a paper entitled "Les Equations du Mouvement des Gaz, et la Propagation du Son suivant la Théorie cinétique des Gaz". Since then this effect has been seen experimentally, and many theoretical papers have been published on the theory of dispersion of sound in polyatomic gases².

In an earlier report³ we have given general expressions for the transport coefficients when the passage of energy from the translational

¹ H. A. Lorentz, Arch. neerl. 16, 1, 1881. See, for instance, Lorentz Collected Papers' Vol. VI.

² For a comprehensive summary on this and related topics, see W. T. Richards, Rev. Mod. Phys. 11, 36, 1939.

³ C. S. Wang Chang and G. E. Uhlenbeck. On the Transport Phenomena in Rarefied Gases. CM-443, Feb. 20, 1948, UMH-3-F.

to the internal degrees of freedom is not difficult. We will report here a calculation from the opposite approximation, namely, when the probability of the transfer of energy from the translational to the internal degrees of freedom is very small. In this way, a more clear-cut definition of the relaxation time is obtained, which ties in very well with the existing more or less phenomenological theories on this matter.

As before, our starting point is the Boltzmann equation for the distribution function, f^* . The state of a molecule is determined by its translational as well as internal states. Classically one could take, for instance, a nonspherical molecular model, or some very queer kind of spherical models like the rough sphere or the loaded sphere where rotational states can be excited. The orientation of each molecule is then specified by its Eulerian angles. The linear and angular velocities after collision can easily be expressed in terms of those before collision and some collision parameters. But in trying to work out the problem one meets with the difficulty which arises from the general nonexistence of the restituting collisions, except for very special models. In order to avoid this difficulty we choose to treat the problem semiquantum-mechanically. For the translational motion the classical description is retained, but for the internal motion we consider the molecules as being able to exist in different internal energy states.

The distribution function, f , we define as the number of molecules per cubic centimeter at the time, t , having coordinates lying between \vec{r} and $\vec{r} + d\vec{r}$ and velocities between \vec{v} and $\vec{v} + d\vec{v}$ and internal energy states E_i , where i stands for all the quantum numbers of the internal energy states.

* A partial list of the symbols used in this report is given in the appendix.

$$f_i = f(t, \vec{r}, \vec{s}, E_i). \quad *$$

When there are no outside forces acting on the internal motion, the Boltzmann equation is

$$\frac{\partial f_i}{\partial t} + \sum_{\alpha} \dot{r}_{\alpha} \frac{\partial f_i}{\partial r_{\alpha}} + F_{\alpha} \frac{\partial f_i}{\partial s_{\alpha}} = \frac{\partial f_i}{\partial t}, \quad (1)$$

where the right hand side is the change of f due to collisions:

$$\frac{\partial f_i}{\partial t} = \sum_j \sum_k \sum_l \int_{-\infty}^{+\infty} \int_0^{2\pi} \int_0^{\pi} d\vec{s}' \int_0^{2\pi} d\psi \int_0^{\pi} d\alpha \sin \alpha \cdot \quad (2)$$

$$g I_{ij}^{kl}(g, \alpha, \psi) (f'_k f'_l - f_i f_j).$$

The quantity $I_{ij}^{kl}(g, \alpha, \psi)$ is the differential collision cross section for the collision of particles in states i and j which after collision become states k and l ; \vec{g} and \vec{g}' are the relative velocities before and after collision, respectively; and α, ψ specify the orientation of \vec{g}' with respect to \vec{g} . One has

$$g I_{ij}^{kl} = g' I_{kl}^{ij}. \quad (3)$$

This relation is really the reason why the semiquantum-mechanical treatment is simpler than the purely classical description. The general transport

* In general, we write $f'_{ik} = f(t, \vec{r}, \vec{s}'_i, E_k)$.

equation of Boltzmann for a quantity $\bar{\Phi}(t, \vec{r}, \vec{c}, E_i)$ is obtained by multiplying Eq (1) by $\bar{\Phi}$, integrating over all velocities and summing over all internal energy states. A generally more useful equation is obtained when $\bar{\Phi}$ is expressed in terms of t, \vec{r}, E_i , and the molecular velocity $\vec{c} = \vec{c} - \vec{c}_0$, where \vec{c}_0 is the streaming velocity of the gas,

$$\begin{aligned} & \frac{Dn\bar{\Phi}}{Dt} + n\bar{\Phi} \frac{\partial f_{\alpha\alpha}}{\partial t_{\alpha}} + \frac{\partial}{\partial t_{\alpha}} n\bar{\Phi} C_{\alpha} - \\ & - n \left\{ \frac{D\bar{\Phi}}{Dt} + C_{\alpha} \frac{\partial \bar{\Phi}}{\partial r_{\alpha}} + \left(F_{\alpha} - \frac{Df_{\alpha\alpha}}{Dt} \right) \frac{\partial \bar{\Phi}}{\partial C_{\alpha}} - \frac{\partial \bar{\Phi}}{\partial C_{\alpha}} C_{\beta} \frac{\partial f_{\alpha\alpha}}{\partial r_{\beta}} \right\} \quad (4) \\ & = \sum_i \iiint d\vec{c} \bar{\Phi}(t, \vec{r}, \vec{c}, E_i) \frac{df_i}{dt} \end{aligned}$$

Here n is the number density, $\frac{D}{Dt}$, the mobile differential operator defined as

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + f_{\alpha\alpha} \frac{\partial}{\partial r_{\alpha}},$$

and

$$n\bar{\Phi} = \sum_i \iiint d\vec{c} f_i \bar{\Phi}(t, \vec{r}, \vec{c}, E_i).$$

There are of course the usual three conservation theorems: the number density, the linear momentum, and the total energy—translational plus internal.

The five summational invariants are

$$\Phi = 1$$

$$\Phi = m \xi_i \quad \text{or}$$

$$i = 1, 2, 3$$

$$= m C_i = m (\xi_i - \xi_{oi})$$

$$\Phi = \frac{1}{2} m C^2 + E_j,$$

where m is the mass of the gas molecule. These quantities, when put into Eq (4), lead to the general hydrodynamical equations

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho \xi_{\alpha}}{\partial x_{\alpha}} = 0$$

$$\frac{\partial \rho i_{\alpha}}{\partial x_{\alpha}} - \rho \left(F_i - \frac{D \xi_{oi}}{Dt} \right) = 0 \quad (5)$$

$$\frac{DU}{Dt} + \frac{m}{\rho} \frac{\partial (q_{tr})_{\alpha}}{\partial x_{\alpha}} + \frac{m}{\rho} \frac{\partial (q_{int})_{\alpha}}{\partial x_{\alpha}} + \frac{m}{\rho} p_{\alpha\beta} \frac{\partial \xi_{\alpha}}{\partial x_{\beta}} = 0$$

ρ is the density of the gas, and the other symbols are:

$$p_{ij} = ij \text{ component of the pressure tensor} = \overline{m C_i C_j}$$

$$(q_{tr})_i = i\text{th component of the translational heat-flux vector}$$

$$= \frac{m}{2} \overline{C^2 C_i}$$

$$(q_{int})_i = i\text{th component of the internal heat-flux vector} = \overline{E_j C_i}$$

$$U = \text{total energy} = \frac{m}{2} \overline{C^2} + E_j = U_{tr} + U_{int}.$$

For simplicity, we will limit ourselves in the following treatment to the case where there is only one mode of internal motion. The generalization to several modes is straight forward.

II. TRANSPORT COEFFICIENTS WHEN THE EXCHANGE BETWEEN THE TRANSLATIONAL AND THE INTERNAL ENERGIES IS NOT DIFFICULT ———

THE ENSKOG-CHAPMAN EXPANSION

When the exchange of translational and internal energies is easy, the internal temperature will follow the translational temperature closely. To the zeroth approximation the state of the gas can be described by one temperature. To find the transport coefficients one expands f and hence all the average values obtainable from f by series expansions in a parameter θ :

$$f = \sum_{n=0}^{\infty} \theta^{n-1} f^{(n)} \quad (6)$$

$$Q = \sum_{n=0}^{\infty} \theta^{n-1} Q^{(n)},$$

where Q is any of the average values p_{ij} , $(q_{tr})_i$, $(q_{int})_i$, U_{tr} and U_{int} . Substituting these expansions into Eqs (1) and (5), eliminating the time derivatives of the quantities ρ , \vec{v}_0 , and U by Eqs (5), and equating the coefficients of each power of θ equal to zero, one finds that the lowest-order equation is

$$\iiint_{-\infty}^{+\infty} d\vec{s}_i \int_0^{2\pi} d\psi \int_0^{\pi} d\alpha \sin\alpha g I_{ij}^{kl}(g, \alpha, \psi) (f_k^{(0)} f_l^{(0)} - f_i^{(0)} f_j^{(0)}) = 0, \quad (7)$$

the solution of which is

$$f_i^{(0)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{\sum_s e^{-E_s/kT}} e^{-\frac{1}{kT} \left(\frac{1}{2} m \vec{c}^2 + E_i \right)} \quad (8)$$

The identification of n , \vec{c}_0 , and T as the number density, the streaming velocity, and the temperature of the gas respectively, imposes certain conditions on the $f^{(n)}$'s. These conditions are satisfied by requiring that

$$\sum_i \int d\vec{s} \vec{s} f^{(n)} = 0 \quad (1)$$

$$\sum_i \int d\vec{s} \vec{s} \vec{s} f^{(n)} = 0 \quad (2) \quad (9)$$

$$\sum_i \int d\vec{s} \left(\frac{1}{2} m \vec{c}^2 + E_i \right) f^{(n)} = 0$$

for all $n > 0$.

The next-order equation is an integral equation for $f_i^{(1)}$.

Writing

$$f_i^{(1)} = f_i^{(0)} \phi_i^{(1)}$$

and after a calculation quite analogous to the case of the monoatomic gas⁴, one finds:

⁴ Chapman and Cowling, The Mathematical Theory of Nonuniform Gases, Chapter VII.

$$\begin{aligned}
 n^2 I(\phi_i^{(0)}) = & -f_i^{(0)} \left\{ \sqrt{\frac{2kT}{m}} (b^2 - \frac{5}{2}) b_\alpha \frac{\partial \log T}{\partial r_\alpha} \right. \\
 & + \sqrt{\frac{2kT}{m}} (\varepsilon_i - \varepsilon_{int}) b_\alpha \frac{\partial \log T}{\partial r_\alpha} + 2 (b_\alpha b_\beta - \frac{b^2}{3} \delta_{\alpha\beta}) \frac{\partial \xi_{\alpha\beta}}{\partial r_\beta} \\
 & \left. + \frac{\beta}{C_v} \left(\frac{2}{3} b^2 - \frac{k}{\beta} \varepsilon_i + \frac{k}{\beta} \varepsilon_{int} - 1 \right) \frac{\partial \xi_{\alpha\alpha}}{\partial r_\alpha} \right\} ; \quad (10)
 \end{aligned}$$

β is the specific heat for the internal motion, and C_v is the total specific heat at constant volume. We have introduced dimensionless quantities:

$$b^2 = \frac{m}{2kT} C^2, \quad \varepsilon_i = \frac{E_i}{kT}, \quad \varepsilon_{int} = \frac{U_{int}}{kT} = \frac{\bar{E}_i}{kT}.$$

I is an isotropic linear operator, defined by

$$n^2 I(\phi_i^{(0)}) = \sum_{j,k,l} \iiint d\vec{r}_i \iint d\vec{r}_j d\vec{r}_k d\vec{r}_l g I_{ij}^{kl} (g, \alpha, \psi) f_i^{(0)} f_j^{(0)} (\phi_i + \phi_j - \phi_k - \phi_l).$$

Eq (10) differs from the corresponding equation for a monoatomic gas in that there are two additional terms on the right-hand side. It will be seen that these terms are the transport of internal energy and the relaxation-time terms. The first two terms on the right-hand side of Eq (10) can be combined into one, but since they have distinct physical meanings we prefer to keep them separated.

As in the case of monoatomic gas, one can write as Ansatz for solution

$$\begin{aligned}
 \phi_i^{(0)} = & -\frac{1}{n} \sqrt{\frac{2kT}{m}} (A_{tr})_\alpha \frac{\partial \log T}{\partial r_\alpha} - \frac{1}{n} \sqrt{\frac{2kT}{m}} (A_{int})_\alpha \frac{\partial \log T}{\partial r_\alpha} \\
 & - \frac{1}{n} B_{\alpha\beta} \frac{\partial \xi_{\alpha\beta}}{\partial r_\beta} - \frac{1}{n} \frac{\beta}{C_v} D \frac{\partial \xi_{\alpha\alpha}}{\partial r_\alpha}, \quad (11)
 \end{aligned}$$

where $(A_{tr})_k$ and $(A_{int})_k$ are vectors, B_{jk} is a tensor of the second rank, and D is a scalar. Since I is an isotropic linear operator which changes an isotropic tensor, vector, and scalar⁵ into another isotropic tensor, vector, and scalar, respectively, it follows that

$$(A_{tr})_k = A_{tr} (b, \varepsilon_i) b_k$$

$$(A_{int})_k = A_{int} (b, \varepsilon_i) b_k$$

$$B_{jk} = B(b, \varepsilon_i) (b_j b_k - \frac{b^2}{3} \delta_{jk})$$

and

$$D = D(b, \varepsilon_i).$$

The integral Eq (10) can now be separated into four component equations,

$$nI((A_{tr})_k) = (b^2 - \frac{5}{2}) b_k f^{(0)}$$

$$nI((A_{int})_k) = (\varepsilon_i - \varepsilon_{int}) b_k f^{(0)}$$

$$nI(B_{jk}) = 2(b_j b_k - \frac{b^2}{3} \delta_{jk}) f^{(0)}$$

$$nI(D) = (\frac{2}{3} b^2 - \frac{k\varepsilon_i}{\beta} + \frac{k}{\beta} \varepsilon_{int} - 1) f^{(0)}.$$

(12)

⁵ H. P. Robertson, Proc. Camb. Phil. Soc. 36, II, 209, 1940.

Eqs (12) are nonhomogeneous integral equations. The integrability conditions are that the nonhomogeneous part must be orthogonal to the solutions of the homogeneous equation, namely, 1 , $m\vec{C}$, and $\frac{1}{2}mC^2 + E_i$. It is easily verified that all these integrability conditions are satisfied for the component equations. Thus, our problem reduces to finding the four scalar functions A_{tr} , A_{int} , B , and D , which satisfy Eqs (12). However, the requirements, Eqs (9), impose some auxiliary conditions on these functions. Aside from those automatically satisfied, the auxiliary conditions are:

$$\sum_i \int d\vec{s} f^{(0)} D = 0$$

$$\sum_i \int d\vec{s} C^2 f^{(0)} A_{tr} = 0$$

(13)

$$\sum_i \int d\vec{s} C^2 f^{(0)} A_{int} = 0$$

$$\sum_i \int d\vec{s} (C^2 + E_i) f^{(0)} D = 0$$

Before actually solving for these scalar functions, one can find formal expressions for the heat-flux vectors and the pressure tensor.

They are

$$(q_{tr})_k^{(0)} = -\frac{2k^2 T}{3m} [(A_{tr})_\alpha, (A_{tr} + A_{int})_\alpha] \frac{\partial T}{\partial r_k} \quad (14a)$$

$$\equiv -\lambda_{tr} \frac{\partial T}{\partial r_k}$$

$$\begin{aligned}
 (q_{int})_k^{(1)} &= -\frac{2kT}{3m} [(A_{int})_\alpha, (A_{tr} + A_{int})_\alpha] \frac{\partial T}{\partial r_k} \\
 &\equiv -\lambda_{int} \frac{\partial T}{\partial r_k}
 \end{aligned}
 \tag{14b}$$

$$\begin{aligned}
 p_{ij}^{(1)} &= -\frac{kT}{10} [B_{\beta\gamma}, B_{\beta\gamma}] \left(\frac{\partial \xi_{0i}}{\partial r_j} + \frac{\partial \xi_{0j}}{\partial r_i} - \frac{2}{3} \delta_{ij} \frac{\partial \xi_{0\alpha}}{\partial r_\alpha} \right) \\
 &\quad - \frac{2kT\beta}{3n C_{v,i}} \int d\vec{\xi} (b^2 - \frac{3}{2}) f^{(1)} D \delta_{ij} \frac{\partial \xi_{0\alpha}}{\partial r_\alpha}
 \end{aligned}
 \tag{14c}$$

The bracket symbol is defined as

$$[A, B] = \sum_i \int d\vec{\xi} A(b, \epsilon_i) I(B(b, \epsilon_i)),
 \tag{15}$$

which has the properties:

$$1) \quad [A, B] = [B, A]$$

because of Eq (3), and

$$2) \quad [A, A] \geq 0.$$

To this order of approximation one can write the sum of the two heat-flux vectors into one simple term

$$q_k^{(1)} = (q_{tr})_k^{(1)} + (q_{int})_k^{(1)} = -(\lambda_{tr} + \lambda_{int}) \frac{\partial T}{\partial r_k},$$

where

$$\lambda_{tr} + \lambda_{int} = \frac{2k^2T}{3m} [(A_{tr} + A_{int})_\alpha, (A_{tr} + A_{int})_\alpha] \cong 0.$$

The first term in the expression for the pressure tensor is the ordinary viscosity term with

$$\mu = \frac{kT}{10} [B_{\alpha\beta}, B_{\alpha\beta}].$$

The second term is new. It is proportional to the scalar $\frac{\partial \xi_{\alpha\alpha}}{\partial T_\alpha}$; the proportionality factor can be interpreted as the dilatation viscosity coefficient⁶. To see more clearly the meaning of this term and its relation with the relaxation time we now calculate the first-order correction to the translational and rotational energies:

$$\begin{aligned} \overline{\frac{1}{2} m C^2}^{(1)} &= \frac{1}{n} \sum_i \int d\vec{\xi} \frac{1}{2} m C^2 f_i^{(1)} \\ &= -\frac{\beta k T}{n^2 C_v} \sum_i \int d\vec{\xi} \left(C^2 - \frac{3}{2} \right) f_i^{(0)} D \frac{\partial \xi_{\alpha\alpha}}{\partial T_\alpha} \end{aligned}$$

$$\begin{aligned} \overline{E_i}^{(1)} &= \frac{1}{n} \sum_i \int d\vec{\xi} E_i f_i^{(1)} \\ &= -\frac{\beta k T}{n^2 C_v} \sum_i \int d\vec{\xi} (E_i - E_{int}) f_i^{(0)} D \frac{\partial \xi_{\alpha\alpha}}{\partial T_\alpha}. \end{aligned}$$

The corresponding temperature corrections are:

⁶ L. Tisza, Phys. Rev. 61, 531, 1942.

$$T_{tr}^{(1)} = \frac{1}{\frac{3k}{2}} \frac{1}{2} m C^2 \quad (1)$$

$$T_{int}^{(1)} = \frac{1}{\beta} \overline{E_i}^{(1)}$$

The second equation is only an approximation. The dependence of β on T has been neglected. This is all right when $T_{int}^{(1)}$ is small, which is consistent with our approximation calculation. The difference between the temperature corrections is the quantity of interest. It is the difference between the temperature of the translational and the internal states of motion, due to the dilation. One gets

$$\begin{aligned} T_{tr}^{(1)} - T_{int}^{(1)} &= -\frac{\beta T}{n^2 C_v} \sum_i \int d\vec{s} \left(\frac{2}{3} \beta^2 - 1 \right) f^{(1)} \mathcal{D} \frac{\partial \mathcal{S}_{\alpha}}{\partial r_{\alpha}} + \\ &+ \frac{kT}{n^2 C_v} \sum_i \int d\vec{s} (\epsilon_i - \epsilon_{int}) f^{(1)} \mathcal{D} \frac{\partial \mathcal{S}_{\alpha}}{\partial r_{\alpha}} \\ &= -\frac{\beta T}{n^2 C_v} \sum_i \int d\vec{s} \left(\frac{2}{3} \beta^2 - 1 - \frac{k\epsilon_i}{\beta} + \frac{k\epsilon_{int}}{\beta} \right) f^{(1)} \mathcal{D} \frac{\partial \mathcal{S}_{\alpha}}{\partial r_{\alpha}} \\ &= -\frac{\beta T}{n^2 C_v} [D, D] \frac{\partial \mathcal{S}_{\alpha}}{\partial r_{\alpha}}, \end{aligned}$$

where $[D, D]$ is positive. The quantity $\frac{1}{n} [D, D]$ has the dimension of time. Other conditions remaining constant, the smaller the value of $\frac{1}{n} [D, D]$, the smaller the temperature difference, or the deviation of the internal energy from the equilibrium value. Thus it can be interpreted

as a relaxation time. We will, however, define the relaxation time τ^* by

$$\tau = \frac{\beta}{nA} [D, D]. \quad (16)$$

The requirement (9c) states that

$$\frac{1}{2} m C^2 + E_i^{(1)} = 0.$$

The above equation together with the equation giving $T_{tr}^{(1)} - T_{int}^{(1)}$, namely

$$\frac{2}{3A} \frac{1}{2} m C^2 - \frac{1}{\beta} E_i^{(1)} = -\frac{\beta T}{m C_v} [D, D] \frac{\partial \xi_{\alpha\alpha}}{\partial T_{\alpha}}$$

leads to

$$\begin{aligned} \frac{1}{2} m C^2 &= -\frac{3k\beta}{2C_v} \frac{\beta T}{m C_v} [D, D] \frac{\partial \xi_{\alpha\alpha}}{\partial T_{\alpha}} \\ &= -\frac{\beta k T}{n^2 C_v} \sum_i \int d\vec{s} \left(\ell^2 - \frac{3}{2} \right) f^{(1)} D \frac{\partial \xi_{\alpha\alpha}}{\partial T_{\alpha}}. \end{aligned}$$

Thus

$$\begin{aligned} P_{ij}^{(1)} &= -\frac{kT}{10} [B_{\alpha\beta}, B_{\alpha\beta}] \left(\frac{\partial \xi_{\alpha i}}{\partial r_j} + \frac{\partial \xi_{\alpha j}}{\partial r_i} - \frac{2}{3} \delta_{ij} \frac{\partial \xi_{\alpha\alpha}}{\partial r_j} \right) \\ &\quad - \frac{\beta k T}{C_v^2} [D, D] \delta_{ij} \frac{\partial \xi_{\alpha\alpha}}{\partial T_{\alpha}}. \end{aligned}$$

* We have altered the definition of τ from that given in our former report, see ref. (2); so that τ will have the same meaning as the relaxation time to be defined in Sec. III.

Or,

$$p_{ij}^{(1)} = -\mu \left(\frac{\partial \xi_{0i}}{\partial r_j} + \frac{\partial \xi_{0j}}{\partial r_i} - \frac{2}{3} \delta_{ij} \frac{\partial \xi_{0\alpha}}{\partial r_\alpha} \right) - \kappa \delta_{ij} \frac{\partial \xi_{0\alpha}}{\partial r_\alpha}; \quad (17)$$

where

$$\mu = \frac{kT}{10} [B_{\alpha\beta}, B_{\alpha\beta}]$$

$$\kappa = \frac{\beta^2 kT}{C_v^2} [D, D],$$

both being positive. κ is to be interpreted as the dilatation-viscosity coefficient. It is due to the finite time required for the internal motion to reach equilibrium with the translational motion.

To this order of approximation, the generalization to the case where there are more than one internal modes of motion is clear. One gets for each additional mode of motion a new heat-conduction coefficient. The dilatation-viscosity coefficient is then a sum of the dilatation viscosity coefficients of the individual modes of motion.

$$\kappa = \sum_l \kappa_l = \frac{\pi k^2 T}{C_v^2} \sum_l \beta_l \tau_l$$

where τ_l is the relaxation time for the l th mode of motion and β_l is the corresponding specific heat.

The evaluation of the transport coefficients which reduces now to the evaluation of the square bracket follows the same line as given by Chapman⁴. All the formal proofs go through as given there. The present case is slightly more complicated because of the additional variable \mathcal{E}_i , but one still can make power series expansions in terms of θ^2 and \mathcal{E}_i .

We will give, as an example, the evaluation of $\mathcal{Z} = \frac{\beta}{nk} [D, D]$ to the lowest order in this expansion.

D satisfies the integral equation

$$nI(D) = \left(\frac{2}{3} b^2 - \frac{k\epsilon_i}{\beta} + \frac{k\epsilon_{int}}{\beta} - 1 \right) f^{(0)},$$

and the auxiliary conditions

$$\int_0^1 d\mathcal{E}^2 f^{(0)} D = 0$$

$$\int_0^1 d\mathcal{E}^2 (b^2 + \epsilon_i) f^{(0)} D = 0$$

We develop D into a double series in the complete sets of orthogonal

functions $u_k(b^2), v_j(\epsilon_i)$

$$D(b^2, \epsilon_i) = \sum_{k,j} d_{k,j} u_k(b^2) v_j(\epsilon_i).$$

These series will be chosen to be of the forms

$$u_k = \sum_{m=0}^k a_m^{(k)} b^{2m}$$

$$v_j = \sum_{m=0}^j b_m^{(j)} \epsilon_i^m$$

with $u_0 = v_0 = 1$ and weight factors, $b^2 e^{-b^2}$ and $e^{-\epsilon_i}$, respectively. This choice determines the u's and the v's uniquely. For instance,

$$u_1 = \frac{3}{2} - b^2, \quad v_1 = \epsilon_{int} - \epsilon_i.$$

The first auxiliary condition requires that $d_{\infty} = 0$, and the second puts a restriction on d_{01} and d_{10} ,

$$\sum_i \int d\vec{x} \left(\beta^2 - \frac{3}{2} + \epsilon_i - \epsilon_{int} \right) (d_{01} v_i + d_{10} u_i) f^{(0)} = 0$$

or,

$$d_{01} = -\frac{3k}{2\beta} d_{10}.$$

Up to the order $k + j = 1$,

$$\begin{aligned} \tau &= \frac{\beta}{nk} [D, D] = \frac{\beta}{nk} [d_{01} v_i + d_{10} u_i, d_{01} v_i + d_{10} u_i] \\ &= \frac{\beta}{nk} \left\{ d_{01}^2 [v_i, v_i] + 2 d_{01} d_{10} [v_i, u_i] + d_{10}^2 [u_i, u_i] \right\}. \end{aligned}$$

From the laws of conservation of the number density and the total energy, one finds that

$$I(u_i + v_i) = 0.$$

By multiplying by u_1 and v_1 , respectively, integrating over all velocities and summing over all the internal states i , we obtain:

$$[u_i, u_i] = -[u_i, v_i] = [v_i, v_i],$$

so that

$$\tau = \frac{\beta}{nk} (d_{01} - d_{10})^2 [u_i, u_i].$$

One has to find d_{01} next. The integral equation is, to this order of approximation,

$$\eta I(d_{01} v_1 + d_{10} u_1) = \left(\frac{2}{3} b^2 - 1 - \frac{k\epsilon_i}{\beta} + \frac{k\epsilon_{int}}{\beta} \right) f^{(0)},$$

$$\begin{aligned} \sum_i \int d\vec{s} u_i I(d_{01} v_1 + d_{10} u_1) &= \\ &= \frac{4\pi}{\eta} \sum_i \int d\vec{s} s^2 \left(\frac{3}{2} - b^2 \right) \left(\frac{2}{3} b^2 - 1 - \frac{k\epsilon_i}{\beta} + \frac{k\epsilon_{int}}{\beta} \right) f^{(0)} \\ &= -1, \end{aligned}$$

or

$$d_{01} [v_1, u_1] + d_{10} [u_1, u_1] = -1.$$

Similarly,

$$d_{01} [v_1, v_1] + d_{10} [v_1, u_1] = 1.$$

These two equations are identical on account of the relations between the square brackets. This shows also that the restriction on d_{01} and d_{10} is consistent with the theory. With the help of this relation, we find

$$d_{10} = -\frac{\beta}{\frac{3k}{2} + \beta} \frac{1}{[u_1, u_1]} = -\frac{\beta}{C_{01}} \frac{1}{[u_1, u_1]},$$

and

$$\begin{aligned} \tau &= \frac{\beta}{\pi k} \left(\frac{\frac{3k}{2} + \beta}{C_r} \right)^2 \frac{1}{[u_1, u_1]^2} [u_1, u_1] \\ &= \frac{\beta}{\pi k [u_1, u_1]}, \end{aligned}$$

where

$$\begin{aligned} [u_1, u_1] &= \sum_i \sum_j \sum_k \sum_l \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} d\vec{s}^i (\frac{3}{2} - C^2) f_i^{(0)} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} d\vec{s}^j f_j^{(0)} \\ &\quad \int_0^{2\pi} d\psi \int_0^\pi dd \sin \alpha g I_{ij}^{kl}(g, \alpha, \psi) \Delta(C^2 - \frac{3}{2}), \end{aligned}$$

$\Delta(\phi)$ being defined as

$$\Delta(\phi) = \phi'_{kl} + \phi'_{lk} - \phi_i - \phi_j$$

Similarly one finds

$$[B_{\alpha\beta}, B_{\beta\alpha}] = \frac{25}{[b_{\alpha} b_{\beta} - \frac{6}{3} \delta_{\alpha\beta}, b_{\alpha} b_{\beta} - \frac{6}{3} \delta_{\alpha\beta}]},$$

and

$$[(A_{tr})_{\alpha}, (A_{tr} + A_{int})_{\alpha}] = -\frac{15}{4} \frac{(-\frac{15}{4} b_{0101} + \frac{3\beta}{2k} b_{1001})}{b_{1010} b_{0101} - b_{1001}^2}$$

$$[(A_{int})_{\alpha}, (A_{tr} + A_{int})_{\alpha}] = -\frac{3\beta}{2k} \frac{(-\frac{3\beta}{2k} b_{1010} + \frac{15}{4} b_{1001})}{b_{1010} b_{0101} - b_{1001}^2},$$

where the b's are the following square brackets:

$$b_{10,10} = [(\bar{b}^2 - \frac{5}{2}) b_{\alpha}, (\bar{b}^2 - \frac{5}{2}) b_{\alpha}]$$

$$b_{10,01} = [(\bar{b}^2 - \frac{5}{2}) b_{\alpha}, (\epsilon_i - \epsilon_{int}) b_{\alpha}]$$

$$b_{01,01} = [(\epsilon_i - \epsilon_{int}) b_{\alpha}, (\epsilon_i - \epsilon_{int}) b_{\alpha}] .$$

Each of the square brackets is an eight-fold integral and four-fold sum. Five of the integrals can be carried out without any specific assumption as to the intermolecular forces. The expressions for μ , λ_{tr} , λ_{int} , χ , and ζ are:

$$\frac{1}{\mu} = \frac{\delta}{5\sqrt{\pi m k T}} \frac{1}{(\sum_i e^{-\epsilon_i})^2} \sum_i \sum_j \sum_k \sum_l e^{-\epsilon_i - \epsilon_j} \times$$

$$\times \int_0^{2\pi} d\psi \int_0^{\pi} d\alpha \sin\alpha \int_0^{\infty} dg g^3 e^{-g^2} I_{ij}^{kl}(\sqrt{\epsilon} g, \alpha, \psi) \times \quad (18)$$

$$\times [g^4 \sin^2 \alpha + \frac{2}{3} g^2 \Delta \epsilon (1 - \frac{2}{3} \sin^2 \alpha)] ,$$

$$\lambda_{tr} = \frac{\alpha k^2 T}{3m} \left(-\frac{15}{4}\right) \frac{-\frac{15}{2} b_{01,01} + \frac{3\delta}{2k} b_{10,01}}{b_{10,10} b_{01,01} - b_{10,01}^2} , \quad (19a)$$

$$\lambda_{int} = \frac{2k^2T}{3m} \left(-\frac{3B}{2k} \right) \frac{-\frac{3B}{2k} b_{10,10} + \frac{15}{4} b_{10,01}}{b_{10,10} b_{01,01} - b_{10,01}^2} \quad (19b)$$

where the b's are the following expressions:

$$b_{10,10} = 4\sqrt{\frac{kT}{\pi m}} \frac{1}{\left(\sum_s e^{-\epsilon_s}\right)^2} \sum_{ijkl} e^{-\epsilon_i - \epsilon_j} \times \\ \times \int_0^{2\pi} d\psi \int_0^\pi d\alpha \sin\alpha \int_0^\infty dg g^3 e^{-g^2} I_{ij}^{kl}(\sqrt{2}g, \alpha, \psi) \times \\ \times (g^2 \sin^2\alpha + g^2 \Delta\epsilon \left(\frac{2}{3} + \cos^2\alpha\right))$$

$$b_{10,01} = \frac{5\sqrt{kT}}{2\sqrt{\pi m}} \frac{1}{\left(\sum_s e^{-\epsilon_s}\right)^2} \sum_{ijkl} (\Delta\epsilon)^2 e^{-\epsilon_i - \epsilon_j} \times \\ \times \int_0^{2\pi} d\psi \int_0^\pi d\alpha \sin\alpha \int_0^\infty dg g^3 e^{-g^2} I_{ij}^{kl}(\sqrt{2}g, \alpha, \psi)$$

$$b_{01,01} = \frac{1}{2}\sqrt{\frac{kT}{\pi m}} \frac{1}{\left(\sum_s e^{-\epsilon_s}\right)^2} \sum_{ijkl} e^{-\epsilon_i - \epsilon_j} \times \\ \times \int_0^{2\pi} d\psi \int_0^\pi d\alpha \sin\alpha \int_0^\infty dg g^3 e^{-g^2} I_{ij}^{kl}(\sqrt{2}g, \alpha, \psi) \times \\ \times \left\{ 3(\Delta\epsilon)^2 + 2 \left[(\epsilon_i - \epsilon_j) \vec{g} - (\epsilon_k - \epsilon_l) \vec{g}' \right] \right\}$$

$$\Delta\epsilon = \epsilon_k + \epsilon_l - \epsilon_i - \epsilon_j$$

$$g'^2 = g^2 - \Delta\epsilon$$

$$\frac{1}{\pi} = \frac{2Cr^2}{\rho^2 \sqrt{\pi m k T}} \frac{1}{\left(\sum_s e^{-\epsilon_s}\right)^2} \sum_{ijkl} (\Delta \epsilon)^2 e^{-\epsilon_i - \epsilon_j} \times \quad (20)$$

$$\times \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \alpha \int_0^\infty dg g^3 e^{-g^2} I_{ij}^{kl}(\sqrt{2}g, \alpha, \phi),$$

$$\frac{1}{\pi} = 2\eta\beta \sqrt{\frac{kT}{\pi m}} \frac{1}{\left(\sum_s e^{-\epsilon_s}\right)^2} \sum_{ijkl} (\Delta \epsilon)^2 e^{-\epsilon_i - \epsilon_j} \times \quad (21)$$

$$\times \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \alpha \int_0^\infty dg g^3 e^{-g^2} I_{ij}^{kl}(\sqrt{2}g, \alpha, \phi).$$

III. TRANSPORT COEFFICIENTS WHEN THE EXCHANGE BETWEEN THE TRANSLATIONAL AND THE INTERNAL ENERGIES IS DIFFICULT

In this case we proceed slightly differently. Because of the slowness of energy exchange, there will, in general, be two different temperatures, the translational temperature T_{tr} and the internal temperature, T_{int} , where T_{int} may or may not be equal to T_{tr} . To allow for the description of this fact, we employ a partial perturbation calculation. We assume that the inelastic collision cross section is much smaller than the elastic collision cross section, and write

$$I = I_{el} + \theta'^2 I_{inel},$$

where I_{el} and I_{inel} are the elastic and inelastic collision cross sections, respectively, and θ' is a parameter to indicate the order of magnitude.

We will take θ' of the same order as θ , and after the sorting out of the

successive orders we will put as usual $\theta = \theta' = 1$. The expansion of f , and consequently of all the average values, remains as given in Eqs (6). Making substitutions as before, the lowest-order equation (coefficient of θ^{-1}) is

$$\sum_{j,k,l} \int \dots \int d\vec{s}_j d\psi d\alpha d\mu d\alpha g I_{kl}(g, \alpha, \psi) (f_k^{(n)} f_l^{(n)} - f_i^{(n)} f_j^{(n)}) = 0 \quad (22)$$

Eq (22) differs from Eq (7) only in that the collision cross section I_{ij}^{kl} is replaced by I_{el} . (Here, for short, we have omitted the indices indicating the internal energy states.) It is this replacement which allows for the possible existence of different temperatures for the translational and internal motion, respectively. The solution of Eq (22) is

$$f_i^{(0)} = n \left(\frac{m}{2\pi k T_{tr}} \right)^{3/2} e^{-\frac{mC^2}{2kT_{tr}}} F(E_i) ,$$

where $F(E_i)$ is arbitrary since the dependence of $f^{(0)}$ on the internal energy state is not determined by Eq (22). However, it seems most natural to choose for $F(E_i)$ also the local Maxwell-Boltzmann distribution but with a temperature T_{int} which may or may not be the same as T_{tr} . Thus, we take

$$f_i^{(0)} = n \left(\frac{1}{2\pi k T_{tr}} \right)^{3/2} \frac{1}{\int e^{-E_s/kT_{int}}} e^{-\frac{mC^2}{2kT_{tr}} - \frac{E_i}{kT_{int}}} \quad (23)$$

The conditions to be imposed on $f^{(n)}$ for the identification of n, \vec{s}_0, T_{tr} , and T_{int} as the number density, the streaming velocity, the translational, and the internal temperatures, respectively, are satisfied if

$$\sum_i \int d\vec{s} f_i^{(n)} = 0$$

$$\sum_i \int d\vec{s} \vec{s} f_i^{(n)} = 0$$

$$\sum_i \int d\vec{s} C^2 f_i^{(n)} = 0$$

$$\sum_i \int d\vec{s} E_i f_i^{(n)} = 0$$

(24)

for all $n > 0$. These are to be compared with Eqs (9).

The first-order equation (coefficient of θ^0 and θ'^0) is

$$\frac{\partial f_i^{(0)}}{\partial t} + \sum_\alpha \frac{\partial f_i^{(0)}}{\partial r_\alpha} = \sum_j \sum_k \sum_l \int d\vec{s} d\psi d\alpha d\alpha' g I_{ell}(g, \alpha, \psi) \times$$

$$\times (f_k^{(0)} f_{il}^{(0)} + f_k^{(0)} f_{il}^{(0)} - f_i^{(0)} f_{kj}^{(0)} - f_i^{(0)} f_{kj}^{(0)}).$$

(25)

Contrary to the case considered in Sec. II, the hydrodynamical equations are not enough to eliminate the time derivatives. There are six quantities, n , \vec{s}_0 , T_{tr} , and T_{int} , defining the state of the gas, but there are only five hydrodynamical equations. However, there is one additional equation of special physical significance which one can derive from $f^{(0)}$. This equation describes how the internal temperature (or the translational temperature) varies with time. It can be looked upon as an equation supplementary to the hydrodynamical equations. Inserting E_1 (or $\frac{1}{2} mC^2$) for Φ in Eq (4), keeping terms up to the zeroth order in θ and θ' , one finds:

$$\begin{aligned} \beta(T_{int}) \frac{DT_{int}}{Dt} + \frac{\gamma}{\rho} \frac{(\partial \rho_{int})_{\alpha}}{\partial t_{\alpha}} &= \sum_{i,j,k,l} \int \dots \int d\vec{s} d\vec{s}' d\psi d\alpha d\mu d\chi g I_{el}(g, \alpha, \psi) \times \\ &\times E_i (f_k^{(1)} f_l^{(1)} + f_k^{(1)'} f_l^{(1)'} - f_i^{(0)} f_j^{(0)} - f_i^{(0)'} f_j^{(0)'}) \\ &= \sum_{i,j,k,l} \int \dots \int d\vec{s} d\vec{s}' d\psi d\alpha d\mu d\chi g I_{el}(g, \alpha, \psi) \times \\ &\times E_i f_i^{(0)} f_j^{(0)} (\phi_k^{(1)} + \phi_{il}^{(1)} - \phi_i^{(0)} - \phi_{ij}^{(0)}), \end{aligned}$$

where we have again put $f^{(1)} = f^{(0)} \phi^{(1)}$. The second term on the left hand side of the above equation is zero because $(q_{int})_i^{(0)} = 0$.

$$\beta \frac{DT_{int}}{Dt} = [E_i, \phi_i^{(1)}]_{el}$$

the subscript el meaning that the total differential collision cross section is to be replaced by the elastic differential collision cross section. On account of the first property of the bracket symbol, and since the collision is to be limited to elastic ones only, it follows that

$$\frac{DT_{int}}{Dt} = 0. \quad (26)$$

The equation for $\phi_i^{(1)}$, which takes the place of Eq (10), is:

$$\begin{aligned} n^2 I_{el}(\phi_i^{(1)}) &= -f^{(0)} \left\{ \sqrt{\frac{2kT_{int}}{m}} (b^2 - \frac{5}{3}) b_{\alpha} \frac{\partial \log T_{int}}{\partial t_{\alpha}} + \right. \\ &\left. + \sqrt{\frac{2kT_{int}}{m}} (\epsilon_i - \epsilon_{int}) b_{\alpha} \frac{\partial \log T_{int}}{\partial t_{\alpha}} + 2(b_{\alpha} b_{\beta} - \frac{b^2}{3} \delta_{\alpha\beta}) \frac{\partial \log \alpha}{\partial t_{\beta}} \right\}, \end{aligned} \quad (27)$$

where $\varepsilon_1 = E_1/kT_{int}$ and $\varepsilon_{int} = \bar{\varepsilon}_1$. The Ansatz for solution is

$$\phi^{(0)} = -\frac{1}{\eta} \sqrt{\frac{2kT_{tr}}{m}} (A_{tr})_{\alpha} \frac{\partial \log T_{tr}}{\partial r_{\alpha}} - \frac{1}{\eta} \sqrt{\frac{2kT_{tr}}{m}} (A_{int})_{\alpha} \frac{\partial \log T_{int}}{\partial r_{\alpha}} - \frac{1}{\eta} B_{\alpha\beta} \frac{\partial \log}{\partial r_{\beta}}. \quad (28)$$

The main difference between Eq (27) and Eq (10) is that in the operator I, the elastic differential collision cross section takes the place of the total collision cross section. The expressions for the heat-flux vectors and the pressure tensor are:

$$\begin{aligned} (q_{tr})_j^{(1)} &= -\frac{2kT_{tr}}{3m} [(A_{tr})_{\alpha}, (A_{tr})_{\alpha}] \frac{\partial T_{tr}}{\partial r_j} - \frac{2kT_{tr}^2}{3mT_{int}} [(A_{tr})_{\alpha}, (A_{int})_{\alpha}] \frac{\partial T_{int}}{\partial r_j} \\ (q_{int})^{(1)} &= -\frac{2k^2T_{tr}}{3m} [(A_{tr})_{\alpha}, (A_{int})_{\alpha}] \frac{\partial T_{tr}}{\partial r_j} - \frac{2k^2T_{tr}}{3m} [(A_{int})_{\alpha}, (A_{int})_{\alpha}] \frac{\partial T_{int}}{\partial r_j} \end{aligned} \quad (29)$$

$$P_{ij}^{(1)} = -\frac{kT_{tr}}{10} [B_{\alpha\beta}, B_{\alpha\beta}] \left(\frac{\partial \log}{\partial r_j} + \frac{\partial \log}{\partial r_i} - \frac{2}{3} \delta_{ij} \frac{\partial \log}{\partial r_{\alpha}} \right).$$

The pressure tensor differs from Eq (14c) in that there is no term due to the relaxation time. Following the same argument as used in the derivation of Eq (25), one finds, to this order of approximation, the equation supplementary to the hydrodynamical equations:

$$\begin{aligned} \beta \frac{\partial T_{int}}{\partial t} + \frac{\eta}{\rho} \frac{\partial (q_{int})_{\alpha}}{\partial r_{\alpha}} &= \sum_{i,j,k,l} \int \dots \int d\vec{s} d\vec{s}_1 d\varphi d\alpha \sin \alpha g I_{int}(g, \alpha, \varphi) \times \\ &\times E_i (f_k^{(1)} f_l^{(1)} - f_i^{(0)} f_j^{(0)}). \end{aligned}$$

In the above equation, I_{inel} can be replaced by I_{ij}^{kl} because the elastic collisions give no contribution to the integral. Making use of the conservation of the total energy, one writes for the equation supplementary to the hydrodynamical equations:

$$\beta \frac{DT_{int}}{Dt} + \frac{m}{\rho} \frac{\partial (q_{int})_{\alpha}}{\partial x_{\alpha}} = -\frac{m}{2} \sum_i \sum_j \sum_k \sum_l \int \dots \int d\vec{s}^1 d\vec{s}_i^1 d\psi d\alpha d\alpha' d\alpha'' \times$$

$$\times g I_{ij}^{kl}(g, \alpha, \psi) C^2 (f_k^{(0)} f_l^{(0)} - f_i^{(0)} f_j^{(0)}) \quad (30)$$

From Eq (30), one derives an expression for the relaxation time.

When T_{tr} and T_{int} do not differ too much, as is in the case of the passage of sound waves through a gas, to a first approximation in $(T_{tr} - T_{int})/T_{tr}$ one finds:

$$(f_k^{(0)} f_l^{(0)} - f_i^{(0)} f_j^{(0)}) = f_i^{(0)} f_j^{(0)} \frac{m}{2kT_{tr}} (C_1'^2 + C_1''^2 - C^2 - C_1^2) \frac{T_{tr} - T_{int}}{T_{tr}},$$

where everywhere except in the factor $T_{tr} - T_{int}$, T_{int} is to be replaced by T_{tr} . The equation for $\frac{DT_{int}}{Dt}$ is then:

$$\beta \frac{DT_{int}}{Dt} + \frac{m}{\rho} \frac{\partial (q_{int})_{\alpha}}{\partial x_{\alpha}} = \frac{m^2}{4mkT_{tr}} (T_{tr} - T_{int}) \times$$

$$\times \sum_i \sum_j \sum_k \sum_l \int \dots \int d\vec{s}^1 d\vec{s}_i^1 d\psi d\alpha d\alpha' d\alpha'' \times g I_{ij}^{kl}(g, \alpha, \psi) \times$$

$$\times f_i^{(0)} f_j^{(0)} (C_1'^2 + C_1''^2 - C^2 - C_1^2) C^2.$$

We define:

$$\frac{1}{\tau} = -\frac{m^2}{4mk\beta T_H^2} \sum_{i,j,k,l} \int \int d\vec{s}^{\perp} d\vec{s}_i^{\perp} d\psi d\alpha \sin\alpha g I_{ij}^{kl}(g, \alpha, \psi) \times$$

$$\times f_i^{(0)} f_j^{(0)} c^2 (c'^2 + c_i'^2 - c^2 - c_i'^2),$$

$$\frac{1}{\tau} = +\frac{m^2}{16mk\beta T_H^2} \sum_i \sum_j \sum_k \sum_l \int \int d\vec{s}^{\perp} d\vec{s}_i^{\perp} d\psi d\alpha \sin\alpha \times$$

$$\times g I_{ij}^{kl}(g, \alpha, \psi) f_i^{(0)} f_j^{(0)} (c'^2 + c_i'^2 - c^2 - c_i'^2)^2, \quad (31)$$

and the equation for T_{int} becomes:

$$\beta \frac{DT_{int}}{Dt} + \frac{m}{\rho} \frac{\partial (q_{int})_{\alpha}}{\partial t_{\alpha}} = \frac{\beta(T_H - T_{int})}{\tau}, \quad (32)$$

where τ is always positive. From Eq (32) it is seen that Eq (31) is a sensible definition for τ . Apart from the heat-conduction term, Eq (32) says that the total time rate of change of the internal energy is equal to the deviation of the instantaneous internal energy from its equilibrium value divided by the relaxation time. One can easily verify that Eq (31) is the same as the first approximation value for τ obtained in the previous section, Eq (16).

In Eqs (29), both $(q_{tr})_j^{(1)}$ and $(q_{int})_j^{(1)}$ are the sum of two terms, proportional to the gradient of the translational and of the

internal temperature, respectively. The first-order approximation for the solution of the integral equations for $(A_{tr})_j$ and $(A_{int})_j$ gives, however, the value zero for the bracket expression $[(A_{tr})_\alpha, (A_{int})_\alpha]$. Thus

$$(g_{tr})_j^{(1)} = -\lambda_{tr} \frac{\partial T_{tr}}{\partial r_j}$$

$$(g_{int})_j^{(1)} = -\lambda_{int} \frac{\partial T_{int}}{\partial r_j} \quad (33)$$

$$p_{ij}^{(1)} = -\mu \left[\frac{\partial \rho_i}{\partial r_j} + \frac{\partial \rho_j}{\partial r_i} - \frac{2}{3} \delta_{ij} \frac{\partial \rho_\alpha}{\partial r_\alpha} \right].$$

The constants λ_{tr} , λ_{int} , and μ can be deduced from the expressions we obtained before, Eqs (18) and (19), by remembering that in the operator I, the collision cross section is the elastic collision cross section, so that $\Delta E_1 = \Delta C^2 = 0$. We find

$$\frac{1}{\mu} = \frac{8}{5\sqrt{\pi m k T}} \frac{1}{(\sum_s e^{-\epsilon_s})^2} \sum_i \sum_j \sum_k \sum_l e^{-\epsilon_i - \epsilon_j} \int d\psi \int d\alpha \sin^3 \alpha x$$

$$x \int d g g' e^{-g^2} I_{el}(\sqrt{2}g, \alpha, \psi) \quad (34a)$$

$$\frac{1}{\lambda_{tr}} = \frac{32}{75\sqrt{\pi m k^3 T}} \frac{1}{(\sum_s e^{-\epsilon_s})^2} \sum_i \sum_j \sum_k \sum_l e^{-\epsilon_i - \epsilon_j} x$$

$$x \int d\psi \int d\alpha \mu u^3 \alpha \int d g g' e^{-g^2} I_{el}(\sqrt{5}g, \alpha, \psi) \quad (34b)$$

$$\frac{1}{\lambda_{int}} = \frac{3}{8\beta\sqrt{\pi m kT}} \frac{k/\beta}{(\sum e^{-\epsilon_s})^2} \sum_i \sum_j \sum_k \sum_l e^{-\epsilon_i - \epsilon_j} \epsilon_i (\epsilon_i - \epsilon_j) \times \int d\psi \int d\alpha \sin\alpha \int d\beta \beta^5 e^{-\beta^2} I_{el}(\sqrt{\epsilon_j}, \alpha, \psi). \quad (34c)$$

The relaxation time, τ , given by Eq (31) can also be written as

$$\frac{1}{\tau} = \frac{2\pi k}{\beta} \frac{\sqrt{kT}}{\pi m} \frac{1}{(\sum e^{-\epsilon_s})^2} \sum_i \sum_j \sum_k \sum_l e^{-\epsilon_i - \epsilon_j} (\Delta \epsilon_i)^2 \times \int d\psi \int d\alpha \sin\alpha \int d\beta \beta^3 e^{-\beta^2} I_{ij}^{kl}(\sqrt{\epsilon_j}, \alpha, \psi). \quad (34d)$$

In Eq (34d), the differential cross section appearing under the integral sign should really be I_{inel} ; we have replaced it by I_{ij}^{kl} because the presence of the factor $(\Delta \epsilon_i)^2$ makes the contribution due to the added term zero. It is to be noted that the same integral appears in both Eq (34a) and Eq (34b), so that

$$\frac{\lambda_{tr}}{\mu} = \frac{15k}{4}$$

as for monoatomic gases.

The generalization to cases where there are more than one internal mode of motion is again very simple. There will be $n + 1$ temperatures, where n is the number of internal modes of motion. Besides the five hydrodynamical equations, there will be n supplementary equations giving the total time rate of change of these internal temperatures. There will also be n relaxation times.

IV. DISPERSION OF SOUND AND THE CONNECTION OF THE PRESENT THEORY WITH THE EXISTING MORE OR LESS PHENOMENOLOGICAL THEORIES

A. Dispersion of Sound

The one-dimensional hydrodynamical equations for a small disturbance have the same form for the case considered in Sec. II as for the case of a monoatomic gas. The only differences are: 1) the heat-conduction coefficient is now replaced by the sum of the heat-conduction coefficients for the translational and the internal motion, and 2) the viscosity coefficient is replaced by $\mu + \frac{3\chi}{4}$, where χ is the so-called dilatation-viscosity coefficient. Up to the first approximation in the Chapman-Enskog development, the velocity of sound remains the same as the velocity of sound at zero frequency, V_0 . The absorption coefficient is given by:

$$\frac{\gamma^2}{\rho V_0^3} \left\{ \left(\frac{4\mu}{3} + \chi \right) + \frac{mk}{C_p C_v} (\lambda_{tr} + \lambda_{int}) \right\},$$

where γ is the frequency of sound and C_p is the specific heat at constant pressure. We do not get the characteristic dispersion curve for a polyatomic gas for this case because we have started with one temperature, and our expansion extends only to values of frequencies such that $\gamma \tau$ is small. In this treatment, the effects of heat conduction and viscosity are assumed to begin in the same frequency range as the effect of the energy transfer between translational and internal degrees of freedom, so that these effects cannot be separated from each other.

The corresponding hydrodynamical equations for the case considered in Sec. III are:

$$\frac{\partial p}{\partial t} + \rho \frac{\partial \xi_0}{\partial x} = 0 \quad (35a)$$

$$\frac{\partial \xi_0}{\partial t} - \frac{4}{3} \frac{\mu}{\rho} \frac{\partial^2 \xi_0}{\partial x^2} = -\frac{1}{\rho} \frac{\partial p}{\partial x} \quad (35b)$$

$$\frac{3k}{2} \frac{\partial T_H}{\partial t} + \beta \frac{\partial T_{int}}{\partial t} = -\frac{m}{\rho} n k T_H \frac{\partial \xi_0}{\partial x} + \quad (35c)$$

$$+ \frac{m \lambda T_H}{\rho} \frac{\partial^2 T_H}{\partial x^2} + \frac{m \lambda_{int}}{\rho} \frac{\partial^2 T_{int}}{\partial x^2} ,$$

where ξ_0 is the streaming velocity in the x-direction, and p is the static pressure. To this set we add the supplementary equation:

$$\rho \frac{\partial T_{int}}{\partial t} = \frac{m \lambda_{int}}{\rho} \frac{\partial^2 T_{int}}{\partial x^2} + \frac{\beta}{T_H} (T_H - T_{int}) . \quad (36)$$

Eqs (35) and (36) are the same as the equations of Herzfeld and Rice⁷ except that Eq (35c) is the sum of the third and the fourth equations of Herzfeld and Rice, and that their relaxation time is $3k/2\beta$ times our relaxation time.

From Eqs (35) and (36) one can again derive expressions for the velocity and the absorption coefficient of sound. However, to see more clearly the effect of the relaxation time in polyatomic gases, we drop the viscosity and the heat conduction terms which amounts to assuming

⁷ K. F. Herzfeld and E. O. Rice, Phys. Rev. 31, 691, 1928.

that all absorption and dispersion effects are due to the slow transfer of energy from the translational to the internal degrees of freedom. For the passage of sound of frequency ν and wave number l , one obtains from Eqs (35) and (36), by dropping μ and λ :

$$-C_p C_v \frac{\frac{l^2 V_0^2}{\nu^2} - 1}{1 - \frac{C_v}{k} \left(\frac{l^2 V_0^2}{\nu^2} - 1 \right)} = \frac{i\beta k \nu}{1 + i\beta \nu}$$

From the above equation, it follows that for extremely high and low frequencies:

a) $\nu \ll 1$:

There is no absorption

$$V = \sqrt{\frac{C_p}{C_v} \frac{m}{k}} = V_0 \quad \text{the velocity of sound at zero frequency:}$$

b) $\nu \gg 1$:

There is no absorption

$$V = \sqrt{\frac{C_p - \beta}{C_v - \beta} \frac{m}{k}} \quad \text{the velocity of sound when the internal state is not excited.}$$

Between these two asymptotic values the velocity of sound increases monotonically with the frequency.

B. Application to the Rough-Sphere Model

For a rough, but perfectly elastic, spherical model, Pidduck⁸ has calculated the viscosity and the two heat-conduction coefficients.

⁸ F. B. Pidduck, Proc. Roy. Soc. A, 101, 101, 1922.

Because of the way the temperature was defined, no relaxation time was found. From our calculation, however, one obtains a relaxation time.

By the word "rough" is meant that "when two molecules collide, the two spheres grip each other without slipping; first each sphere is strained by the other, and then the strain energy is reconverted into kinetic energy of translation and rotation, no energy being lost; the effect is that the relative velocity of the spheres at their point of impact is reversed by the impact". The expressions for μ and the two λ 's as given by Pidduck and also derivable from our expressions, Eqs (18), (19a), and (19b) are:

$$\mu = \frac{15}{80^2} \sqrt{\frac{mKT}{\pi}} \frac{(1+K)^2}{6+13K} \quad (37a)$$

$$\lambda_{tr} = \frac{225 (1+2K)(1+K)^3}{160^2 (12+75K+101K^2+102K^3)} \sqrt{\frac{K^3 T}{\pi m}} \quad (37b)$$

$$\lambda_{int} = \frac{9(3+19K)(1+K)^2}{40^2 (12+75K+101K^2+102K^3)} \sqrt{\frac{K^3 T}{\pi m}}, \quad (37c)$$

where σ is the diameter of the molecule and

$$K = \frac{4I}{m\sigma^2},$$

I , being the moment of inertia; K measures the ease with which the energy goes from the translational to the internal states and which depends on

the mass distribution of the sphere. $K = 0$ corresponds to complete concentration of the mass at the center of the sphere, so that for $K = 0$, the inelastic collision cross section is zero.

For a rough sphere, the linear and angular velocities of the molecules after collision are restricted by the conservation of the angular momentum and the reversal of the relative velocity of the points of the spheres which come into contact, in addition to the other five conservation theorems. The former we will take into account by a special form of the collision cross section. Let $\vec{\omega}$ be the angular velocity, and \vec{k} be the unit vector in the direction of the line from the center of the second molecule to that of the first. We write:

$$I(g, \alpha, \psi) = \frac{\sigma^2}{4} \delta \left\{ \sqrt{\frac{I}{2kT}} (\vec{\omega}_1 + \vec{\omega}_2 - \vec{\omega}'_1 - \vec{\omega}'_2) - \frac{m\sigma}{2} \sqrt{\frac{1}{2IkT}} \vec{k} \times (\vec{g} - \vec{g}') \right\} \times$$

$$\times \delta \left\{ \sqrt{\frac{m}{2kT}} (\vec{g} + \vec{g}' - \frac{\sigma}{2} \vec{k} \times [\vec{\omega}_1 + \vec{\omega}_2 + \vec{\omega}'_1 + \vec{\omega}'_2]) \right\},$$

where the first δ -function is a dimensionless expression stating the conservation of the angular momentum, while the second δ -function expresses the reversal of the relative velocity of the points in contact due to collision. Inserting this expression for I in the following equation,

$$\frac{1}{\tau} = \frac{m^2}{8nk_B T^2} \sum_i \sum_j \sum_k \sum_l \int \int d\vec{s}_1 d\vec{s}_2 d\psi d\alpha \sin \alpha g I_{ij}^{kl}(g, \alpha, \psi) \times$$

$$\times f_i^{(0)} f_j^{(0)} (c_1^2 + c_2^2) (c_1^2 + c_2^2 - c_1'^2 - c_2'^2),$$

replacing the summations by integrations over the angular velocities $\vec{\omega}$'s, and making the proper change of normalization of f one finds:

$$\frac{1}{\tau} = \frac{\pi m^2}{12k^2T^2} \left(\frac{m}{2\pi kT}\right)^3 \left(\frac{I}{2\pi kT}\right)^3 \left(\frac{I}{2kT}\right)^3 \frac{\sigma^2}{4} \int \dots \int_{20 \text{ fold integral}} d\vec{\omega}_1 d\vec{\omega}_2 d\vec{\omega}'_1 d\vec{\omega}'_2 d\vec{g}_1 d\vec{g}'_2 \times$$

$$\times d\vec{g}'_1 d\vec{g}'_2 \times g e^{-\frac{m}{2kT}(G_1^2 + G_2^2) - \frac{I}{2kT}(\omega_1^2 + \omega_2^2)} (G_1^2 + G_2^2)(G_1^2 + G_2^2 - G_1'^2 - G_2'^2) \times$$

$$\delta \left\{ \sqrt{\frac{I}{2kT}} (\vec{\omega}_1 + \vec{\omega}_2 - \vec{\omega}'_1 - \vec{\omega}'_2) - \frac{m\sigma}{2} \sqrt{\frac{1}{2IkT}} \vec{k} \times (\vec{g}'_1 - \vec{g}'_2) \right\} \times$$

$$\times \delta \left\{ \sqrt{\frac{m}{2kT}} (\vec{g}'_1 + \vec{g}'_2 - \frac{\sigma}{2} \vec{k} \times [\vec{\omega}_1 + \vec{\omega}_2 - \vec{\omega}'_1 - \vec{\omega}'_2]) \right\}.$$

All the integrals involved are simple; the evaluation yields:

$$\frac{1}{\tau} = \frac{16\pi\sigma^2 K}{3(1+K)^2} \sqrt{\frac{\pi kT}{m}} \quad (38)$$

For this model, the relaxation time can also be calculated by simple kinetic methods. One calculates $\frac{dU_{tr}}{dt}$, the time rate of change of translational energy, which is $m/2n$ times the time rate of change of the average value of C^2 . The latter is equal to the total number of collisions per second multiplied by the change of C^2 by each collision, or $(C_1^2 + C_2^2 - C_1'^2 - C_2'^2)_{av}$. In this way, $\frac{dU_{tr}}{dt}$ is found to be proportional to $U_{tr} - U_{int}$. Identifying the proportionality constant as $1/\tau$, as is consistent with our definition,

$$\frac{dU_{tr}}{dt} = \frac{U_{int} - U_{eq}^*}{\tau} = - \frac{dU_{int}}{dt},$$

we obtained an expression which agrees with Eq (38). An estimate of the numerical value of τ shows that $\tau = \infty$ for $K = 0$, as is to be expected, and that τ decreases monotonically to $\sim 10^{-10}$ second for $K = 2/3$, corresponding to the complete concentration of the mass on the surface of the sphere.

C. The Eucken Constant

By a simple mean free-path argument Eucken⁹ reached the conclusion that:

$$\mathcal{E} = \frac{\lambda}{\mu C_v} = \frac{\gamma}{\gamma - 5} \quad (39)$$

when there is no correlation between the velocity of the molecule and the amount of the internal energy carried in the heat-transport process. In Eq (39), \mathcal{E} is the Eucken constant, and γ is the ratio C_p/C_v . $\mathcal{E} = 2.5$, 1.9, and 1.75, respectively, for $\gamma = 5/3$, monoatomic gas, $\gamma = 7/5$, diatomic gas with no vibrational states, and $\gamma = 4/3$, rigid triatomic gas like the rough spheres.

Without a knowledge of the collision cross section we cannot calculate μ and λ . But we can make two estimates of the value of the

* U_{eq} is the energy if the internal motion is in equilibrium with the translational motion. It is equal to U_{tr} in this example.

⁹ A. Eucken, Phys. Zeits. 14, 324, 1913. Eucken's formula is $\mathcal{E} = \frac{1}{C_v} (K_{tr} C_{tr} + K_{rot} C_{rot} + K_{vib} C_{vib})$. $K_{tr} = 2.5$, $K_{rot} = 1$, and $K_{vib} = 1$ to 1.5, depending on the molecular structure. $K_{vib} = 1$ if there is no correlation between the velocity of the molecule and the amount of vibrational energy carried.

Eucken constant from the results obtained so far.

For a rough sphere, it follows from Eqs (37) that

$$\mathcal{E} = \frac{1}{10} \frac{(6+13K)(37+151K+50K^2)}{12+75K+101K^2+102K^3}$$

$$= \begin{cases} 1.71 & \text{for } K = \frac{2}{3} \\ 1.85 & \text{for } K = 0 \end{cases}$$

From the expressions we obtained in Sec. III, a rough estimate of \mathcal{E} can also be reached. As has been remarked before $\lambda_{tr}/\mu = 15k/4$. If we now assume that the elastic cross section is independent of the states i, j of the molecules, and write

$$I_1 = \int_0^{2\pi} d\psi \int_0^\pi d\alpha \sin^3 \alpha \int_0^\infty dg g^7 e^{-g^2} I_{inel}(g, \alpha, \psi)$$

$$I_2 = \int_0^{2\pi} d\psi \int_0^\pi d\alpha \sin \alpha \int_0^\infty dg g^5 e^{-g^2} I_{inel}(g, \alpha, \psi);$$

then:

$$\mu = \frac{5}{8} \frac{\sqrt{\pi m k T}}{I_1}$$

$$\lambda_{tr} = \frac{75}{32} \frac{\sqrt{\pi m k T}}{I_1}$$

$$\lambda_{int} = \frac{3}{8} \frac{\beta \sqrt{\pi m k T}}{I_2}$$

$$\mathcal{E} = \frac{\frac{15}{4}k + \frac{3}{5}\beta \frac{I_1}{I_2}}{\frac{3}{2}k + \beta}$$

\mathcal{E} is temperature dependent through β . For very low temperatures, $\beta = 0$

$$\mathcal{E} = \frac{5}{2},$$

the value for monoatomic gases. For very high temperatures, the internal motion is completely excited, β is independent of T. Assuming that the elastic collisions can be described by the elastic sphere model so that

$$I(g, \alpha, \psi) = \frac{\sigma^2}{4},$$

one obtains:

$$\mathcal{E} = \frac{15k + \frac{24}{5}\beta}{2(3k + 2\beta)} = \frac{1}{4} \left(\frac{24}{5} \gamma - 3 \right) \quad (40)$$

$$= \begin{cases} 1.98 & \text{for rigid diatomic molecule} \\ 1.85 & \text{for rigid triatomic molecule, also} \\ & \text{the rough sphere} \end{cases}$$

D. Derivation from Eq (34d) of the Landau-Teller Expression for the Relaxation Time \mathcal{C} for Vibrational Degrees of Freedom¹⁰

For the case of the transfer of translational into vibrational energy (which is the most interesting and most often occurring case), Landau and Teller have given a derivation of the relaxation time, based on the following simplifying assumptions:

¹⁰ L. Landau and E. Teller, Phys. Zeit. d. Sowjetunion 10, 34, 1936.

- 1) The vibrations are harmonic.
- 2) The interaction between the molecules are, aside from the radial part, proportional to the normal coordinates of the oscillators.
- 3) First-order perturbation calculation is sufficient.
- 4) The translation motion can be separated off completely from the vibrational motion, so that the differential cross section has the form:

$$I_{ij}^{kl}(g, \alpha, \psi) = I(g, \alpha, \psi) T_{ij}^{kl},$$

where T_{ij}^{kl} is the transition probability from the states i, j to the states k, l . From assumptions 1), 2), and 3) it follows that

$$T_{ij}^{kl} = T_{ij} \delta_{ik} \delta_{jl} + T_{01} [(i+1) \delta_{k,i+1} \delta_{j,l} + (j+1) \delta_{l,j+1} \delta_{i,k}] +$$

$$+ T_{10} [i \delta_{k,i-1} \delta_{j,l} + j \delta_{l,j-1} \delta_{i,k}],$$

T_{01} being the transition probability for a molecule from the state 0 to the state 1, while T_{10} is that for the reverse process. We will now show how with these assumptions the Landau-Teller derivation fits in with our consideration.

$$\frac{1}{\sigma} = \frac{2\pi n k \sqrt{kT}}{\beta \sqrt{\pi m}} \frac{1}{(\sum_s e^{-\epsilon_s})^2} \sum_{i,j,k,l} (\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l)^2 e^{-\epsilon_i - \epsilon_j} \times$$

$$\times \int_0^{2\pi} d\psi \int_0^\pi d\alpha d\mu d\nu \int_0^\infty dg g^3 e^{-g^2} I(g, \alpha, \psi) \times$$

$$\times \left\{ T_{01} \left[(i+1) \delta_{k,i+1} \delta_{j,l} + (j+1) \delta_{l,j+1} \delta_{ik} \right] + T_{10} \left[i \delta_{k,i} \delta_{j,l} + j \delta_{l,j} \delta_{ik} \right] \right\}.$$

It can easily be seen that the collision frequency, F , is:

$$F = 8n \sqrt{\frac{kT}{\pi m}} \int d\psi \int d\alpha \int d\beta \int d\gamma g^3 e^{-g^2} I(\sqrt{2}g, \alpha, \psi);$$

thus

$$\frac{1}{\tau} = \frac{F}{4\beta} \frac{k}{\left(\sum_i e^{-\epsilon_i}\right)} \left(\frac{kV}{kT}\right)^2 \cdot 2 \sum_i e^{-\frac{ikV}{kT}} [T_{01}(i+1) + T_{10}i].$$

But $T_{01} = T_{10} e^{-kV/kT}$, hence,

$$\frac{1}{\tau} = FT_{10} \frac{k}{\beta} \left(\frac{kV}{kT}\right)^2 \frac{\sum_i i e^{-\frac{ikV}{kT}}}{\sum_i e^{-\frac{ikV}{kT}}}$$

Making use of the summation formulas:

$$\sum_i e^{-\frac{ikV}{kT}} = \frac{1}{1 - e^{-\frac{kV}{kT}}}$$

$$\sum_i i e^{-\frac{ikV}{kT}} = \frac{e^{-\frac{kV}{kT}}}{\left(1 - e^{-\frac{kV}{kT}}\right)^2},$$

and

$$\beta = \frac{dU_{\text{int}}}{dt} = \frac{h\nu^2}{kT^2} \frac{e^{-\frac{h\nu}{kT}}}{(1 - e^{-\frac{h\nu}{kT}})^2},$$

one obtains:

$$\frac{1}{\beta} = F(T_{10} - T_{01}), \quad (41)$$

where FT_{10} is the number of collisions per second in which molecules in internal states 1 are deexcited into the ground states 0, and FT_{01} is the number of collisions per second in which molecules in internal states 0 are excited into the states 1. Eq (41) is also the expression obtained by Landau and Teller. In fact, one can show that from the above assumption one finds that $\frac{dU_{\text{int}}}{dt}$ is proportional to $U_{\text{eq}} - U_{\text{int}}$, with the proportionality constant given by Eq (41). Let n_j be the number of molecules per cc in the state j . The equation of change can then be written as

$$\frac{dn_j}{dt} = F [T_{j+1,j} n_{j+1} + T_{j-1,j} n_{j-1} - (T_{j,j+1} + T_{j,j-1}) n_j].$$

By using the relationships among the $T_{l,m}$'s and the summation formulas, one obtains

$$\begin{aligned} \frac{dU_{\text{int}}}{dt} &= h\nu \sum_j j \frac{dn_j}{dt} \\ &= F [-h\nu T_{10} \sum_j (j+1) n_{j+1} + h\nu T_{01} \sum_j (j+1) n_j] \\ &= F T_{10} [-U_{\text{int}} (1 - e^{-\frac{h\nu}{kT}}) + n h\nu e^{-\frac{h\nu}{kT}}], \end{aligned}$$

where $U_{int} = kT \sum_j j n_j$. For equilibrium the average energy is

$$U_{eq} = kT \left(\sum_j j n_j \right)_{eq} = \frac{n kT e^{-\frac{kT}{T}}}{1 - e^{-\frac{kT}{T}}}$$

so that

$$\frac{dU_{int}}{dt} = F T_0 \left(1 - e^{-\frac{kT}{T}} \right) (U_{eq} - U_{int}) = \frac{U_{eq} - U_{int}}{\tau}$$

if τ is given by Eq (41). Thus our definition of the relaxation time is the same as that of Landau and Teller.

APPENDIX

Partial List of Symbols Used

- \vec{c} molecular velocity
- \hat{c} dimensionless molecular velocity
- c_p specific heat at constant pressure
- c_v specific heat at constant volume
- E_i energy of the internal state, the subscript i stands for all quantum numbers of the internal energy states
- \mathcal{E} Eucken constant
- f distribution function $f(t, \vec{r}, \vec{c}, E_i)$
- $f^{(n)}$ n th order term of f in the present development
- F collision frequency
- \vec{g} relative velocity of the colliding molecules before collision; g without the vector sign means its absolute value
- \vec{g}' relative velocity of the colliding molecules after collision
- I moment of inertia
- I_{ij}^{kl} differential collision cross section for the collision of particles in states i, j , which after collision become states k, l .
- I_{el} elastic differential collision cross section
- I_{inel} inelastic differential collision cross section
- \vec{k} unit vector in the direction of the line from the center of the second molecule to that of the first
- $K = 4I/m\sigma^2$, dimensionless quantity measuring the ease with which the energy goes from the translational to the internal states
- $p_{ij} = \overline{m c_i c_j}$, i, j component of the pressure tensor
- $\vec{q}_{tr} = m\overline{c^2 \vec{c}}/2$, the translational heat-flux vector

- $\vec{q}_{int} = \overline{E_i C}$, the internal heat-flux vector
- T temperature of the gas
- T_{tr} translational temperature
- T_{int} internal temperature
- T_{ij}^{kl} transition probability from the states i, j to the states k, l
- T_{ik} transition probability for a molecule from the state i to the state k
- $U_{tr} = \overline{mC^2/2}$, translational energy
- $U_{int} = \overline{E_i}$, internal energy
- $U = U_{tr} + U_{int}$, total energy
- U_{eq} internal energy if the internal motion is in equilibrium with the translational motion
- V velocity of sound
- V_0 velocity of sound at zero frequency
- β specific heat for the internal degree of freedom
- β_l specific heat for the l th internal degree of freedom
- ϵ_i energy of the internal state i measured in units kT or kT_{int}
- ϵ_{int} average internal energy measured in units kT or kT_{int}
- θ Chapman-Enskog expansion parameter
- θ' order of magnitude parameter for the inelastic collision cross section
- α dilatation-viscosity coefficient
- α_l dilatation-viscosity coefficient corresponding to the l th internal degree of freedom
- λ heat-conduction coefficient
- λ_{tr} translational heat-conduction coefficient
- λ_{int} internal heat-conduction coefficient

- μ viscosity coefficient
- ν frequency of the harmonic oscillator in the vibrational motion
- \vec{v} velocity of a molecule
- \vec{v}_0 streaming velocity
- σ diameter of molecule
- τ relaxation time
- τ_ℓ relaxation time belonging to the ℓ th internal motion
- Φ any function of the coordinates, velocities, and internal states of a molecule, in particular, the summational invariants at collisions
- $\phi^{(1)}$ defined by $f^{(1)} = f^{(0)} \phi^{(1)}$
- $\vec{\omega}$ angular velocity of a molecule

