# THE KINETIC THEORY OF A POLYATOMIC GAS

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Using a method which employs an expansion of the molecular distribution function in a series in generalized orthogonal polynomials, we obtain relaxation equations and relations transfer for a simple polyatomic gas in a 17-moment approximation. We find expressions for the slipping velocity and the temperature jump in a polyatomic gas near a solid plane wall. The results obtained are valid both in the case of an "easy" and in the case of a "slow" exchange of energy between the translational and the internal degrees of freedom of the molecules.

## 1. INTRODUCTION

THE development of a formal kinetic theory of polyatomic gases [1-3] is usually based upon a generalized Chapman-Enskog method which is widely used in the theory of a monatomic gas.[4] In the framework of such a generalization one explains the occurrence of second (volume) viscosity, and also of an additional contribution to the thermal conductivity connected with taking into account the internal degrees of freedom of the molecules (modified Eucken correction).

It is well known that the Chapman-Enskog method is not able to describe processes which involve essentially relaxation and as a result of which one establishes time-independent linear relations between fluxes and the gradients of thermodynamic quantities. This deficiency becomes particularly marked in the case of a polyatomic gas when apart from the characteristic relaxation time $\tau$ describing the establishment of equilibrium with respect to the translational degrees of freedom there occurs in the problem yet another parameter: the characteristic time $\tau_E$ of exchange of energy between the translational and internal degrees of freedom. In fact, a consistent generalization of the Chapman-Enskog method is possible only in the case when $\tau_E \sim \tau$ and the appearance in the pressure tensor of a term with the volume viscosity which is proportional to the divergence of the velocity corresponds just to this case of so-called "easy" energy exchange.[1] When the exchange is "slow" ($\tau_E \gg \tau$), when $\tau_E$ may be of the same order of magnitude as the characteristic time $\tau_L$ of the problem, the linear relation by means of which one introduces the volume viscosity coefficient loses its validity and the corresponding term in the pressure tensor can be found only from the relaxation equations for the translational and internal energies of the gas.

Below we propose an alternative approach to a theory of transfer phenomena in a polyatomic gas which is based upon the use of an expansion of distribution functions in series in generalized orthogonal polynomials. The character of the expansion and the kind of polynomials are uniquely determined by the choice of the weight function (zeroth approximation) of a local single-temperature Maxwell-Boltzmann distribution in the velocities and the discrete internal states of the molecules. The relaxation equations and the transfer relations turn out to be in that case the natural consequences of the moment equations obtained from the kinetic equations. The results obtained are valid both in the case of "easy" and in the case of "slow" energy exchange between the translational and internal degrees of freedom of the molecules under the condition that the deviations of the energies corresponding to them from their equilibrium values are small.

The method used in this paper is essentially a generalization of Grad's method[5] for the case of a polyatomic gas. The 17-moment equations obtained here can find an application, as could the 13-moment equations of Grad's, in problems about the dispersion of sound and the structure of a weak shock wave in a polyatomic gas, for the analysis of a flow with slipping, and so on. As an example we consider in this paper the derivation of boundary conditions (slipping velocity and temperature jump) for a polyatomic gas at a non-absorbing plane surface.

## 2. EXPANSION OF THE DISTRIBUTION FUNCTION AND MOMENT EQUATIONS

We shall describe the polyatomic gas through a distribution function $f_i = f(v, E_i, r, t)$ where $v$ is the velocity of a molecule, and $E_i$ the energy of the i-th quantum state. If apart from other degrees of freedom in the gas the rotational degrees of freedom are excited, the assumption that $f_i$ depends only on $E_i$ is, strictly speaking, connected with the assumption that the density matrix for the internal states is independent of the orientation of the angular momentum vector $M$ of the molecule. A paper by Kagan and Afanas'ev[6] was the first to note the necessity to take into account the dependence of the distribution function on the orientation of $M$ and $v$. They also made numerical estimates of the influence of this factor on the kinetic coefficients for the sphero-cylinder model. In [7,8] the results of [6] were taken into account for calculating transfer coefficients for a model of "rough" and "charged" spheres. Bearing in mind that taking this into account (when there are no external forces) leads only to small corrections in the transfer coefficients we shall consider the problem in the usual formulation, used in [1,2].

We define the macroscopic parameters of the gas: the density n, the velocity u and the temperature T by means of the relations

$$n = \sum_i \int f_i d\mathbf{v} = \sum_i \int f_i^{(0)} d\mathbf{v}, \tag{1}$$

$$nu = \sum_i \int v f_i \, dv = \sum_i \int v f_i^{(0)} \, dv,$$

$$nE(T) = \sum_i \int (\tfrac{1}{2}mc^2 + E_i) f_i \, dv = \sum_i \int (\tfrac{1}{2}mc^2 + E_i) f_i^{(0)} \, dv.$$

Here $c = v - u$, $m$ is the molecular mass. The quantities (1) are given in the same way both by $f_i$ and by the "zeroth approximation" function $f_i^{(0)}$ for which we choose the local Maxwell-Boltzmann distribution of the form

$$f_i^{(0)} = n(m / 2\pi kT)^{3/2} Q^{-1} \exp[-(\tfrac{1}{2}mc^2 + E_i)/kT],$$

$$Q = \sum_i \exp(-E_i/kT). \tag{2}$$

In addition to (1) we introduce definitions for the average energies and heat currents corresponding to the translational and internal degrees of freedom of the molecules:

$$nE^{tr} = \sum_i \int \frac{m}{2} c^2 f_i \, dv, \quad nE^{int} = \sum_i \int E_i f_i \, dv,$$

$$q^{tr} = \sum_i \int \frac{m}{2} c^2 c f_i \, dv, \quad q^{int} = \sum_i \int E_i c f_i \, dv. \tag{3}$$

In accordance with (1)

$$nE^{tr} + nE^{int} = nE(T) = nE_0^{tr} + nE_0^{int}, \tag{4}$$

where

$$E_0^{tr} = \tfrac{3}{2}kT, \quad E_0^{int} = \langle\varepsilon\rangle kT,$$

$$\langle\varepsilon\rangle = Q^{-1} \sum_i \varepsilon_i \exp(-\varepsilon_i), \quad \varepsilon_i = E_i/kT,$$

We define also the total pressure tensor

$$P_{rs} = m \sum_i \int c_r c_s f_i \, dv = P\delta_{rs} + \pi_{rs}, \tag{5}$$

where

$$P = \tfrac{2}{3}nE^{tr}, \quad \pi_{rs} = m \sum_i \int (c_r c_s - \tfrac{1}{3}c^2\delta_{rs}) f_i \, dv. \tag{6}$$

We note that in contradistinction to the monatomic gas $P$ in our case is not the same as the usual statistical pressure $p = \tfrac{2}{3}nE_0^{tr}$, since $E^{tr} \neq E_0^{tr}$. The distribution function $f_i$ can be expanded in a series in generalized orthogonal polynomials. In [9] it was shown that when we use an expansion in the molecular velocity space the form of the polynomials is completely determined by the choice of the "zeroth approximation" distribution function. If we choose as the weight function a local Maxwell distribution the Hermite tensor polynomials used by Grad,[5] occur automatically in the expansion. When there is an additional Boltzmann factor $Q^{-1} \exp(-\varepsilon_i)$ in $f_i^{(0)}$ it is convenient to write the expansion for $f_i$ as a double series in the irreducible Hermite polynomials $H_{r_1 \ldots r_{m+n}}^{mn}(\xi)$ of [10], where $\xi = c\sqrt{(m/kT)}$ and the polynomials $P^{(a)}(\varepsilon_i)$ defined as[1] —

$$P^{(0)} = 1, \quad P^{(1)} = \varepsilon_i - \langle\varepsilon\rangle,$$

$$P^{(q)} = \varepsilon_i P^{(q-1)} - \sum_{s=0}^{q-1} \langle\varepsilon_i P^{(q-1)} P^{(s)}\rangle P^{(s)}/\langle P^{(s)2}\rangle \tag{7}$$

($\langle \ldots \rangle$ denotes averaging over the Boltzmann distribution). The corresponding expansion has the form

$$f_i = f_i^{(0)} \sum_{m,n,q=0}^{\infty} \frac{(2m+1)!(m+n)!}{n!(m!)^2(2m+2n+1)!} a_{r_1 \ldots r_{m+n}}^{mnq} H_{r_1 \ldots r_{m+n}}^{mn}(\xi) P^{(q)}(\varepsilon_i). \tag{8}$$

The expansion coefficients $a^{mnq}$ are, in agreement with the orthogonality conditions for the polynomials, determined from the relations

$$na_{r_1 \ldots r_{m+n}}^{mnq} \langle P^{(q)2}\rangle = \sum_i \int f_i H_{r_1 \ldots r_{m+n}}^{mn}(\xi) P^{(q)}(\varepsilon_i) \, dv. \tag{9}$$

Multiplying the kinetic equation for the polyatomic gas [2] by $H_{r_1 \ldots r_{m+n}}^{mn}(\xi) P^{(q)}(\varepsilon_i)$, integrating over the velocities and summing over $i$, we are led to an infinite set of differential equations for the coefficients $a^{mnq}$ and the parameters $n$, $u$, and $T$.

We shall look for a solution of the kinetic equation, limiting ourselves to a finite number of terms in the series (8) in such a way that the corresponding coefficients $a^{mnq}$ in (9) can be expressed in terms of the quantities (3) and (5) which have a clear physical meaning. To do this we retain in the expansion terms containing the products of the polynomials $H^{mn}$ by $P^{(0)} = 1$, for $m, n = 0, 1$, and $m = 2, n = 0$ and also the products of $H^{mn}$ by $P^{(1)} = \varepsilon_i - \langle\varepsilon_i\rangle$ for $m = 0, 1$ and $n = 0$. The distribution function in the approximation considered has the form

$$f_i = f_i^{(0)} \left\{ 1 + \frac{1}{3}\frac{\Delta E^{tr}}{kT}\left[ (\xi^2 - 3) + \frac{3k}{c^{int}}(\varepsilon_i - \langle\varepsilon\rangle) \right] \right.$$
$$+ \frac{m}{2kT}\frac{\pi_{rs}}{\rho}\left(\xi_r\xi_s - \frac{1}{3}\xi^2\delta_{rs}\right) + \frac{1}{5\rho}\left(\frac{m}{kT}\right)^{3/2} q^{tr}\xi(\xi^2 - 5)$$
$$\left. + \frac{k}{\rho c^{int}}\left(\frac{m}{kT}\right)^{3/2} q^{int}\xi(\varepsilon_i - \langle\varepsilon\rangle) \right\}, \tag{10}$$

where

$$\rho = mn, \quad c^{int} = (\partial E_0^{int}/\partial T)_v = k[\langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2].$$

In using (10) the parameters determining the state of the gas are the quantities $\rho$, $u$, $T$, $\Delta E^{tr} = E^{tr} - E_0^{tr}$, $\pi_{rs}$, $q^{tr}$ and $q^{int}$. (The approximation corresponding to them can be called the "17-moment approximation".) The closed system of equations for these quantities can be written in the form

$$\frac{d\rho}{dt} + \rho\frac{\partial u_l}{\partial x_l} = 0, \quad \rho\frac{du_r}{dt} + \frac{\partial P_{rs}}{\partial x_s} = 0,$$

$$nc_v\frac{dT}{dt} + P_{rs}\frac{\partial u_r}{\partial x_s} + \frac{\partial q_l}{\partial x_l} = 0; \tag{11}$$

$$n\frac{d\Delta E^{tr}}{dt} + \frac{c^{int}}{c_v}P_{rs}\frac{\partial u_r}{\partial x_s} + \frac{c^{int}}{c_v}\frac{\partial q_l^{tr}}{\partial x_l} - \frac{3}{2}\frac{k}{c_v}\frac{\partial q_l^{int}}{\partial x_l} = \frac{kT}{2}R^{010}, \tag{12}$$

$$\frac{d\pi_{rs}}{dt} + 2\left\{\pi_{rl}\frac{\partial u_s}{\partial x_l}\right\} + \pi_{rs}\frac{\partial u_l}{\partial x_l} + \frac{4}{5}\left\{\frac{\partial q_r^{tr}}{\partial x_s}\right\} + 2P\varepsilon_{rs} = kTR_{rs}^{200}, \tag{13}$$

$$\frac{dq_r^{tr}}{dt} + \frac{7}{5}q_s^{tr}\frac{\partial u_r}{\partial x_s} + \frac{2}{5}q_s^{tr}\frac{\partial u_s}{\partial x_r} + \frac{7}{5}q_r^{tr}\frac{\partial u_l}{\partial x_l} + \frac{7}{2}\frac{k}{m}\pi_{rs}\frac{\partial T}{\partial x_s}$$
$$+ \frac{kT}{m}\frac{\partial\pi_{rs}}{\partial x_s} + \frac{5}{3}\frac{kTn}{m}\frac{\partial\Delta E^{tr}}{\partial x_r} + \frac{5}{3}\frac{\Delta E^{tr}}{m}\frac{\partial nkT}{\partial x_r} -$$
$$- \frac{5}{3}\frac{\Delta E^{tr}}{m}\frac{\partial P_{rs}}{\partial x_s} - \frac{\pi_{rs}}{\rho}\frac{\partial P_{sl}}{\partial x_s} + \frac{5}{2}\frac{k}{m}P\frac{\partial T}{\partial x_r} = \frac{m}{2}\left(\frac{kT}{m}\right)^{3/2}R_r^{110}, \tag{14}$$

$$\frac{dq_r^{int}}{dt} + q_s^{int}\frac{\partial u_r}{\partial x_s} + q_r^{int}\frac{\partial u_l}{\partial x_l} + \frac{c^{int}}{m}\pi_{rs}\frac{\partial T}{\partial x_s}$$
$$+ \frac{kTn}{m}\frac{\partial\Delta E^{int}}{\partial x_r} + \frac{\Delta E^{int}}{m}\frac{\partial nkT}{\partial x_r} - \frac{\Delta E^{int}}{m}\frac{\partial P_{rs}}{\partial x_s}$$
$$+ \frac{c^{int}}{m}P\frac{\partial T}{\partial x_r} = m\left(\frac{kT}{m}\right)^{3/2}R_r^{t01}. \tag{15}$$

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[1] The polynomials (7) are easily obtained as the result of orthogonalization of $1, \varepsilon_i, \varepsilon_i^2, \ldots$, successively, with the weight function $Q^{-1}\exp(-\varepsilon_i)$. The first two polynomials of (7) were (together with Sonine polynomials) used in [1] in the generalization of the Chapman-Enskog method (see also [11]).

Here $c_V = \frac{3}{2}k + c^{int}$ and we have used the notation

$$d/dt = \partial/\partial t + u_l\,\partial/\partial x_l, \qquad \{A_{rs}\} = \frac{1}{2}(A_{rs} + A_{sr})$$
$$-\frac{1}{3}\delta_{rs}A_{ll}, \qquad \varepsilon_{rs} = \{\partial u_r/\partial x_s\}.$$

On the right-hand sides of Eqs. (12) to (15) occur the "moments with respect to the collision integral"

$$R^{mnq}_{r_1\ldots r_{m+n}} = \sum_{ijkl} \int [H^{mn}_{r_1\ldots r_{m+n}}(\boldsymbol{\xi}')P^{(q)}(\varepsilon_k)$$

$$- H^{mn}_{r_1\ldots r_{m+n}}(\boldsymbol{\xi})P^{(q)}(\varepsilon_i)]f_if_{j1}I_{ij}{}^{kl}\sin\chi\,d\chi\,d\varphi\,dv\,dv_1. \qquad (16)$$

Here $I^{kl}_{ij}(\mathbf{g}\rightarrow\mathbf{g}',\chi,\varphi)$ us the differential scattering cross section for the process $(\mathbf{g}\rightarrow\mathbf{g}';ij\rightarrow kl)$, where $\mathbf{g}$ is the relative velocity of the colliding particles (the prime refers to values determined after the collision); i, j and k, $l$ are the quantum states of the molecules before and after the collision, respectively, $\chi$ and $\varphi$ are the polar and azimuthal angles describing the orientation of $\mathbf{g}'$ relative to $\mathbf{g}$.

After substituting the expansion (10) for $f_i$ into (16) the quantities $R^{mnq}$ can be expressed in terms of the appropriate moments. As in the case of the monatomic gas it is convenient for the evaluation of the $R^{mnq}$ from the variables $v$ and $v_1$ to the variables $\mathbf{G}$ and $\mathbf{g}$ in the center of mass system of the colliding molecules. Since the $I^{kl}_{ij}$ are independent of $\mathbf{G}$ the integration over $\mathbf{G}$ can be done explicitly. A number of new terms appear since $\mathbf{g}' \neq \mathbf{g}$. The approximation chosen by us describes a state of the gas which does not deviate much from the equilibrium state so that the terms quadratic in the moments can be neglected in the expressions for the $R^{mnq}$ compared with the linear terms. The final results can be written in the form

$$R^{010} = -\frac{8}{3}(c_V/c^{int})n^2\Omega_E\Delta E^{tr}/kT, \qquad (17)$$

$$R^{200}_{rs} = -\frac{8}{5}n^2\Omega_\eta\pi_{rs}/p, \qquad (18)$$

$$\left(\frac{kT}{m}\right)^{1/2}R^{110}_r = -\frac{32}{15}n^2\left(\Omega_\eta + \frac{25}{24}\Omega_E\right)\frac{q_r^{tr}}{p} + \frac{10}{3}\frac{k}{c^{int}}n^2\Omega_E\frac{q_r^{int}}{p}, \quad (19)$$

$$\left(\frac{kT}{m}\right)^{1/2}R^{101}_r = \frac{2}{3}n^2\Omega_E\frac{q_r^{tr}}{p} - \frac{8}{3}n^2\left(\Omega_D + \frac{k}{c^{int}}\Omega_E\right)\frac{q_r^{int}}{p}. \qquad (20)$$

Here $p = nkT$ and we have introduced the quantities

$$\Omega_E = (kT/\pi m)^{1/2}\sum\int d\Omega(\Delta\varepsilon)^2,$$

$$\Omega_\eta = (kT/\pi m)^{1/2}\sum\int d\Omega[\gamma^2(\gamma^2 - \gamma'^2\cos^2\chi) - \frac{1}{6}(\Delta\varepsilon)^2],$$

$$(c^{int}/k)\Omega_D = (kT/\pi m)^{1/2}\sum\int d\Omega\{(\varepsilon_i - \langle\varepsilon\rangle)[(\varepsilon_i - \varepsilon_j)\gamma^2$$

$$- (\varepsilon_k - \varepsilon_l)\gamma\gamma'\cos\chi]\}, \qquad (21)$$

where

$$\gamma = (m/4kT)^{1/2}g, \qquad \gamma'^2 = \gamma^2 - \Delta\varepsilon, \qquad \Delta\varepsilon = \varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j$$

and $\sum\int d\Omega$ indicates an integral operator acting upon the function F as follows

$$\sum\int d\Omega F = Q^{-2}\sum_{ijkl}\int_0^\infty d\gamma\int_0^{2\pi}d\varphi\int_0^\pi d\chi$$

$$\times [F\gamma^3\exp(-\gamma^2 - \varepsilon_i - \varepsilon_j)I_{ij}{}^{kl}\sin\chi]. \qquad (22)$$

## 3. RELAXATION EQUATIONS AND TRANSFER RELATIONS

It is convenient to rewrite the right-hand sides of Eqs. (11) to (15) introducing the appropriate relaxation times. The meaning of those is elucidated when we

consider the behavior of the gas in the particular case when $\rho$, $\mathbf{u}$, and T are constant and the other moments depend solely on the time. Equations (11) to (15) reduce then to the following ones:

$$\partial\Delta E^{tr}/\partial t = -(2c_V/3k)\tau_E^{-1}\Delta E^{tr},$$

$$\partial\pi_{rs}/\partial t = -\tau_\eta^{-1}\pi_{rs},$$

$$\partial q^{tr}/\partial t = -\frac{2}{3}[\tau_\eta^{-1} + \frac{5}{6}(c^{int}/k)\tau_E^{-1}]q^{tr} + \frac{5}{6}\tau_E^{-1}q^{int},$$

$$\partial q^{int}/\partial t = -[\tau_D^{-1} + \frac{1}{2}\tau_E^{-1}]q^{int} + \frac{1}{3}(c^{int}/k)\tau_E^{-1}q^{tr}. \qquad (23)$$

Here

$$\tau_E^{-1} = (2k/c^{int})n\Omega_E, \qquad \tau_\eta^{-1} = \frac{8}{5}n\Omega_\eta,$$

$$\tau_D^{-1} = \frac{8}{3}n\Omega_D. \qquad (24)$$

Writing $P_{rs}$ from (5) in the form

$$P_{rs} = (p + \frac{2}{3}n\Delta E^{tr})\delta_{rs} + \pi_{rs}, \qquad (25)$$

we note that the off-diagonal components of the pressure tensor and the non-equilibrium corrections to the diagonal terms decrease exponentially with time with decrements $\tau_\eta^{-1}$ and $(2c_V/3k)\tau_E^{-1}$, respectively. In the case of a slow exchange of energy $\tau_E \gg \tau_\eta$, i.e., $\pi_{rs}$ is damped appreciably faster than $\Delta E^{tr}$. The relaxation of the heat current $\mathbf{q} = \mathbf{q}^{tr} + \mathbf{q}^{int}$ is in the general case described by a linear combination of exponents with damping decrements determined by the values of the characteristic equation of the system of coupled equations for $\mathbf{q}^{tr}$ and $\mathbf{q}^{int}$. For a slow energy exchange the cross terms on the right-hand sides of the equations for $\mathbf{q}^{tr}$ and $\mathbf{q}^{int}$ can be neglected and the relaxation of the heat current $\mathbf{q}$ is described by the expression

$$\mathbf{q}(t) \simeq \mathbf{q}^{tr}(0)\exp[-\frac{2}{3}(t/\tau_\eta)] + \mathbf{q}^{int}(0)\exp[-\frac{2}{3}(\eta/\rho D)(t/\tau_\eta)],$$

where we have used the relation[2] $\tau_D^{-1} = (\eta/\rho D)\tau_\eta^{-1}$ for $\tau_E \gg \tau_\eta$. (Here $\eta$ and D are the viscosity and self-diffusion coefficients of the gas.)

We consider now the case of slowly changing gas flows. When the conditions

$$\lambda \ll L, \qquad \tau \ll \tau_L, \qquad (26)$$

are satisfied, where L and $\tau_L$ are characteristic linear and time scales for the change in the macroscopic parameters of the gas, $\lambda$ and $\tau$ the mean free path and mean free flight time of the molecules, one can on the left-hand sides of Eqs. (13) to (15) neglect the derivatives $d\pi_{rs}/dt$, $dq^{tr}/dt$, $dq^{int}/dt$ and the non-linear terms, as $\tau \sim \tau_\eta \sim \tau_D$ and $\lambda \sim (kT/m)^{1/2}\tau_\eta$. In the case of easy energy exchange we have additionally $\tau_E \sim \tau_\eta$ and this enables us to neglect also in Eq. (12) the derivative $d\Delta^{tr}/dt$. As a result we are led to the relations

$$(c^{int}/c_V)p\,\mathrm{div}\,\mathbf{u} + (c^{int}/c_V)\,\mathrm{div}\,\mathbf{q}^{tr} - \frac{3}{2}(k/c_V)\,\mathrm{div}\,\mathbf{q}^{int}$$
$$= -\frac{2}{3}(c_V/k)\tau_E^{-1}n\Delta E^{tr}, \qquad (27)$$

$$2p\varepsilon_{rs} + \frac{4}{5}\{\partial q_r^{tr}/\partial x_s\} = -\tau_\eta^{-1}\pi_{rs}, \qquad (28)$$

$$\frac{5}{2}(k/m)p\,\partial T/\partial x_r + \frac{5}{3}(p/m)\partial\Delta E^{tr}/\partial x_r + (kT/m)\partial\pi_{rs}/\partial x_s$$
$$= -\frac{2}{3}[\tau_\eta^{-1} + \frac{5}{6}(c^{int}/k)\tau_E^{-1}]q_r^{tr} + \frac{5}{6}\tau_E^{-1}q_r^{int}, \qquad (29)$$

$$(c^{int}/m)p\,\partial T/\partial x_r + (p/m)\partial\Delta E^{tr}/\partial x_r$$
$$= -(\tau_D^{-1} + \frac{1}{2}\tau_E^{-1})q_r^{int} + \frac{1}{3}(c^{int}/k)\tau_E^{-1}q_r^{tr}. \qquad (30)$$

In the left-hand sides of (27) to (30) we have left the terms with derivatives of $\mathbf{q}^{tr}$, $\mathbf{q}^{int}$, $\pi_{rs}$, and $\Delta E^{tr}$. Some of those may have non-vanishing values, e.g., when we consider inhomogeneous problems (different longitudinal and transverse scales for changes in the macroscopic quantities). In most case, however, these

terms can be dropped and Eqs. (27) to (30) lead to the usual linear transfer relations:

$$^2/_3 n \Delta E^{\mathrm{tr}} = -\zeta \operatorname{div} \mathbf{u}, \qquad \pi_{rs} = -2\eta \varepsilon_{rs}, \qquad \mathbf{q} = -\lambda \operatorname{grad} T \quad (31)$$

with viscosity and thermal conductivity coefficients

$$\eta = p\tau_\eta, \qquad \zeta = (c^{\mathrm{int}}k / c_V{}^2)p\tau_E, \qquad \lambda = \lambda^{\mathrm{tr}} + \lambda^{\mathrm{int}},$$

$$\frac{\lambda^{\mathrm{tr}} m}{\eta} = \frac{15}{4} k \left\{ 1 - \frac{\alpha}{3} \frac{c^{\mathrm{int}}}{k} \left( \frac{5}{2} - \beta \right) \Big/ \left[ 1 + \frac{\alpha}{2} \left( \frac{5}{3} \frac{c^{\mathrm{int}}}{k} + \beta \right) \right] \right\},$$

$$\frac{\lambda^{\mathrm{int}} m}{\eta} = \beta c^{\mathrm{int}} \left\{ 1 + \frac{\alpha}{2} \left( \frac{5}{2} - \beta \right) \Big/ \left[ 1 + \frac{\alpha}{2} \left( \frac{5}{3} \frac{c^{\mathrm{int}}}{k} + \beta \right) \right] \right\}, \quad (32)$$

where

$$\alpha = \tau_\eta / \tau_E, \qquad \beta = \tau_D / \tau_\eta.$$

The expressions obtained are the same as the results of [2].

The equations (28) to (30) and the expressions for the viscosity coefficient $\eta$ and the thermal conductivity $\lambda$ following from them retain their meaning also in the case of slow exchange of energy between the translational and internal degrees of freedom. In particular, when $\alpha \to 0$

$$\lambda = \left( \frac{15}{4} k + \frac{\rho D}{\eta} c^{\mathrm{int}} \right) \frac{\eta}{m}, \quad (33)$$

which corresponds to the introduction of the modified Eucken correction in [4]. However, the volume viscosity coefficient $\zeta$ can no longer be introduced simply, as when $\tau_E \gg \tau_\eta$ it is necessary to use apart from Eq. (27) the more complete relaxation Eq. (12). Dropping in it the derivatives of $q^{\mathrm{tr}}$ and $q^{\mathrm{int}}$ and neglecting non-linear terms, we have

$$d\Delta E^{\mathrm{tr}} / dt + (c^{\mathrm{int}} / c_V) kT \operatorname{div} \mathbf{u} = -^2/_3 (c_V / k) \tau_E{}^{-1} \Delta E^{\mathrm{tr}}. \quad (34)$$

## 4. TWO-TEMPERATURE RELAXATION

In the case when inelastic collisions in the gas are relatively rare, the scheme, described in the foregoing, of expansion in generalized polynomials can easily be developed by choosing the zeroth approximation to $f_i$ in the form of a product of two equilibrium distributions in the velocities and the internal states of the molecules, determined respectively at the temperatures $T^{\mathrm{tr}}$ and $T^{\mathrm{int}}$, i.e.,

$$f_i^{(0)} = n \left( \frac{m}{2\pi k T^{\mathrm{tr}}} \right)^{3/2} Q^{-1}(T^{\mathrm{int}}) \exp \left( -\frac{mc^2}{2kT^{\mathrm{tr}}} - \frac{E_i}{kT^{\mathrm{int}}} \right). \quad (35)$$

It is then natural to assume that not only the total energy E of the gas, but also separately each of its constituents $E^{\mathrm{tr}}$ and $E^{\mathrm{int}}$ are determined in the same way both through $f_i$ and through $f_i^{(0)}$ by virtue of which

$$E^{\mathrm{tr}} = E_0{}^{\mathrm{tr}} = {}^3/_2 kT^{\mathrm{tr}}, \qquad E^{\mathrm{int}} = E_0{}^{\mathrm{int}} = \langle \varepsilon \rangle kT^{\mathrm{int}} \quad (36)$$

In such an approach the quantities n, u, $T^{\mathrm{tr}}$, and $T^{\mathrm{int}}$ which occur in the weight function and $\pi_{rs}$, $q^{\mathrm{tr}}$ and $q^{\mathrm{int}}$ which appear in the expansion serve as the moments which are of interest to us. The moment equations corresponding to them lead when conditions (26) are satisfied to linear relations for $\pi_{rs}$ and $q$. By virtue of condition (36), however, the pressure tensor is defined as $P_{rs} = nkT^{\mathrm{tr}}\delta_{rs} + \pi_{rs}$ and does not contain explicitly a term with the volume viscosity. Instead of this the complete set of equations includes in it relaxation equations for $T^{\mathrm{tr}}$ and $T^{\mathrm{int}}$. It is useful to establish a connection between these equations and

Eq. (34) obtained in the previous section.

As we are only interested in the relaxation of the energy, we can for the sake of simplicity put $\pi_{rs}$, $q^{\mathrm{tr}}$, and $q^{\mathrm{int}}$ equal to zero. In that case, the expansion for $f_i$ is the same as $f_i^{(0)}$. Expanding (35) in a series in the small differences $(T^{\mathrm{tr}} - T)/T$ and $(T^{\mathrm{int}} - T)/T$ which corresponds to the assumption used earlier that the deviations of the translational and internal energies from their equilibrium values at a temperature T are small, and neglecting quadratic terms, we find

$$f_i = n(m / 2\pi kT)^{3/2} Q^{-1}(T) \exp \left[ -(^1/_2 mc^2 + E_i) / kT \right]$$
$$\times [1 + {}^1/_2 (\xi^2 - 3)(T^{\mathrm{tr}} - T) / T + (\varepsilon_i - \langle \varepsilon \rangle)(T^{\mathrm{int}} - T) / T]. \quad (37)$$

One notes easily that the expansions (37) and (10) are the same, if we put

$$\Delta E^{\mathrm{tr}} = {}^3/_2 k(T^{\mathrm{tr}} - T), \qquad \Delta E^{\mathrm{int}} = -\Delta E^{\mathrm{tr}} = c^{\mathrm{int}}(T^{\mathrm{int}} - T). \quad (38)$$

If we use (38) and Eqs. (11) for T Eq. (34) transforms then to

$$dE^{\mathrm{int}} / dt = -\tau_E{}^{-1} c^{\mathrm{int}}(T^{\mathrm{int}} - T^{\mathrm{tr}}). \quad (39)$$

Equation (39) is the same as the usual relaxation equation for the internal energy of a gas which is used in the theory of two-temperature relaxation. [12,13]

## 5. SLIPPING VELOCITY AND TEMPERATURE JUMP AT A WALL

We shall use the results obtained earlier to derive the boundary conditions in the case of a plane flow of a polyatomic gas near a surface x = 0 (the x-axis is directed along the external normal to the surface, the y-axis in the direction of the flow). When describing the state of the gas in the immediate vicinity of the wall it is convenient to introduce distribution functions $f_i^-(\mathbf{v}, E_i, \mathbf{r}, t)$ and $f_i^+(\mathbf{v}, E_i, \mathbf{r}, t)$ corresponding to incident and reflected molecules in such a way that

$$f(\mathbf{v}, E_i, \mathbf{r}, t) = f^+(\mathbf{v}, E_i, \mathbf{r}, t) + f^-(\mathbf{v}, E_i, \mathbf{r}, t),$$
$$f^+(\mathbf{v}, E_i, \mathbf{r}, t) = 0 \text{ when } v_x < 0, \quad f^-(\mathbf{v}, E_i, \mathbf{r}, t) = 0 \text{ when } v_x > 0.$$

As kinetic boundary condition we take that part of the incident molecules is reflected specularly (without a change in the distribution in the internal states of the molecules) and that the other part is initially adsorbed by the wall and afterwards emitted with a Maxwell-Boltzmann distribution with the temperature $T_0$ of the wall, i.e.,

$$f^+(v_x, v_y, v_z, E_i) = (1 - a)f^-(-v_x, v_y, v_z, E_i)$$
$$+ \varkappa \exp \left[ -(^1/_2 mv^2 + E_i) / kT_0 \right]. \quad (40)$$

The coefficients $\kappa$ and $a$ are connected with the condition that there is no build-up of molecules at the wall, i.e., with the condition $u_x = 0$. In a rigorous approach we should give each of them an index i as the reflexion coefficients can, in principle, depend on the internal states of the molecules which interact with the surface. However, it then turns out to be practically impossible to express the macroscopic boundary conditions in terms of the usual parameters of the polyatomic gas which are obtained by averaging over all states of the molecules. Assuming thus for the sake of simplicity that $a$ and $\kappa$ are independent of i, multiplying (40) by $v_x$ and using the expansion (10) for $f_i$ we are after integrating over v and summing over i led to the condition

$$\varkappa = an\left(\frac{m}{2\pi k}\right)^{3/2}\frac{T^{1/2}}{T_0{}^2}\left(1+\frac{1}{3}\frac{\Delta E^{tr}}{kT}+\frac{\pi_{xx}}{2p}\right).$$

The relations for the slipping velocity and the temperature jump are found from the condition that the tangential component of the momentum current and the normal component of the energy current vanish at the wall. Multiplying (40) successively by $c_x c_y$ and $\frac{1}{2}mc^2 + E_i$ and using (10) we have after the appropriate integration and summation

$$\frac{2-a}{a}\frac{\pi_{xy}}{p}+\frac{1}{5}\left(\frac{2m}{\pi kT}\right)^{1/2}\frac{q_y{}^{tr}}{p}+\left(\frac{2m}{\pi kT}\right)^{1/2}u_y\left(1+\frac{1}{3}\frac{\Delta E^{tr}}{kT}+\frac{\pi_{xx}}{2p}\right)=0,$$

$$\frac{2-a}{a}\left(\frac{\pi m}{8kT}\right)^{1/2}\frac{q_x}{p}+\frac{1}{6}\frac{\Delta E^{tr}}{kT}+\frac{\pi_{xx}}{4p}+\left(1+\frac{1}{3}\frac{\Delta E^{tr}}{kT}+\frac{\pi_{xx}}{2p}\right)$$

$$\times\left[1-\frac{T_0}{T}+\frac{1}{2}\frac{E_0{}^{int}(T)-E_0{}^{int}(T_0)}{kT}-\frac{mu_y{}^2}{4kT}\right]=0. \qquad (41)$$

Substituting into (41) the relations (31) for $\pi_{xy}$, $\pi_{xx}$, $\Delta E^{tr}$, and $q_x$, and also $q_y{}^{tr}=-\lambda^{tr}\,\partial T/\partial y$ and neglecting terms quadratic in the gradients we are led to the formulae

$$u_y|_{x=0}=\frac{2-a}{a}\frac{\pi\bar{v}}{4}\frac{\eta}{p}\frac{\partial u_y}{\partial x}+\frac{1}{5}\frac{\lambda^{tr}}{p}\frac{\partial T}{\partial y}, \qquad (42)$$

$$\left(1+\frac{c^{int}}{2k}\right)\Delta T|_{x=0}=\frac{2-a}{a}\frac{\lambda}{nk\bar{v}}\frac{\partial T}{\partial x}+\frac{(\zeta+\,{}^2/_3\eta)}{4nk}\frac{\partial u_y}{\partial y}. \qquad (43)$$

Here $\Delta T = T - T_0$, $\bar{v} = \sqrt{(8kT/\pi m)}$. When changing to (43) we used the expansion

$$E_0{}^{int}(T)=E_0{}^{int}(T_0)+\left(\frac{\partial E_0{}^{int}}{\partial T}\right)_{T_0}\Delta T+\ldots=E_0{}^{int}(T_0)+c^{int}\Delta T+\ldots$$

The first term in (42) has the same form as in the case of a monatomic gas. It is interesting, however, that the second term describing the "thermal slip" depends solely on the translational part of the heat conductivity, $\lambda^{tr}$.

Bearing in mind that $c^{int} = c_V - \frac{3}{2}k$, and introducing $\gamma = c_p/c_V$ the expression (43) for the temperature jump can be transformed to

$$\Delta T|_{x=0}=\frac{2-a}{a}\frac{4}{\gamma+1}\frac{\lambda}{nc_V\bar{v}}\frac{\partial T}{\partial x}+\frac{\zeta+\,{}^2/_3\eta}{nc_V(\gamma+1)}\frac{\partial u_y}{\partial y}. \qquad (44)$$

The first term of this expression is the same as the result given in Kennard's book,[14] which was obtained from elementary considerations assuming that the flow of molecules of a polyatomic gas incident upon a wall carries along an energy

$$E^-=\frac{n\bar{v}}{4}\left(\frac{4}{3}\cdot\frac{3}{2}kT+c^{int}T\right)+\frac{1}{2}\lambda\frac{\partial T}{\partial x},$$

where the factor $\frac{4}{3}$ is introduced to take into account the correlation between the translational energy and the molecular velocity.

[1] C. S. Wang and G. E. Uhlenbeck, Report CM-681, University of Michigan Publication, 1951 (see also [12]).

[2] C. S. Wang, G. E. Uhlenbeck, and J. de Boer, Studies in Stat. Mech. 2, 243 (1964).

[3] N. Taxman, Phys. Rev. 110, 1235 (1958).

[4] S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases, Cambridge University Press, 1939.

[5] H. Grad, Comm. Pure and Appl. Math. 2, 331 (1949); see also Mekhanika 4, 71 (1952); 5, 61 (1952).

[6] Yu. Kagan and A. M. Afanas'ev, Zh. Eksp. Teor. Fiz. 41, 1536 (1961) [Sov. Phys.-JETP 14, 1096 (1962)].

[7] D. W. Condiff, W. K. Lu, and J. S. Dahler, J. Chem. Phys. 42, 3445 (1965).

[8] S. I. Sandler and J. S. Dahler, J. Chem. Phys. 43, 1750 (1965).

[9] D. Mintzer, Phys. Fluids 8, 1076 (1965).

[10] H. Grad, Phys. Fluids 6, 147 (1963); see also Nekotorye voprosy kineticheskoi teorii gazov (Some Problems in the Kinetic Theory of Gases) Mir, 1965.

[11] L. Waldmann and E. Trübenbacher, Zs. Naturf. 17a, 363 (1962).

[12] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, 1954.

[13] B. V. Egorov, V. N. Zhigulev, and V. M. Kuznetsov, Dokl. Akad. Nauk SSSR 164, 1249 (1965) [Sov. Phys.-Dokl. 10, 885 (1966)].

[14] E. H. Kennard, Kinetic Theory of Gases, McGraw-Hill, 1938.