ON THE EQUATIONS OF NONEQUILIBRIUM GAS FLOWS

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Introduction

In investigating the flow of a relaxing gas with internal degrees of freedom it is customary to use phenomenological equations for the macroscopic quantities, including the second viscosity, the heat conduction due to internal energy transport, and the internal energy itself. In a relaxing medium the internal energy is not a function of temperature, but depends on the process and is determined by the probabilities of energy transfer between molecules during collisions. For the internal energy of the gas it is usual to employ a so-called relaxation equation of the type

$$\frac{d\varepsilon}{dt} = \frac{\varepsilon - \varepsilon^{(0)}(T)}{\tau(T, p)}$$

where d/dt is the substantive derivative, $\varepsilon^{(0)}(T)$ is the value of the internal energy in the equilibrium state, and τ is the relaxation time.

In reality, however, expressions of this type are valid only if very special assumptions are made concerning the nature of energy transfer between molecules. Moreover, in the general case it is usually impossible to write a single equation for the internal energy. The derivation of rigorous equations must be based on a kinetic analysis.

A number of authors have attempted to derive from the Boltzmann equation macroscopic equations describing the motion of a gas with the internal degrees of freedom taken into account. In [1] the problem was formulated and the limiting cases of very fast and very slow transitions – from translational energy to internal energy of the molecules – discussed. This treatment (unfortunately, known to the author only in the form of a very brief discussion of the results in [2]) has formed the basis of all subsequent attempts.

In [3] the influence of vibrational degrees of freedom on the coefficients of viscosity and heat conductivity was studied for the case where the time to establish equilibrium between vibrational and translational degrees of freedom is much less than the characteristic time of the process. In [4] Zhigulev considered the case of flows with vibrational relaxation on the assumption that the probability of vibrational energy transfer between molecules during collisions is of the same order as the probabilities of transfer of translational energy. In [5], which appeared after this paper had been prepared for the press, Vallander and Nagnibeda investigated the equations for a gas with internal degrees of freedom on the assumption that the gas is always in equilibrium with respect to translational velocities. The contents of [5] are closely related to §4 of this paper, the subject of which is the general case of a gas with an arbitrary number of relaxation times. It is shown, in particular, that in the general case the diagonal terms of the stress tensor contain, in addition to the pressure $p = RT\rho$, another term that is independent of the gradients. Then the temperature entering into the equation is not equal to the mean translational energy of the molecules.

§1. Following [1], we shall consider the translational motions of the gas molecules in classical terms and the internal degrees of freedom in terms of quantum mechanics. Molecules in the quantum state ν (with internal energy E^{ν}) will be regarded as a gas of the ν-th kind, so that the gas represents a mixture of gases differing in their quantum states. The state ν may be defined by one or more quantum numbers characterizing the excitation of rotational, vibrational or electronic levels of the molecules.

Let $f_{\nu}(t, x, \xi^{\nu})$ be the velocity distribution function for molecules in the ν-th state (of the ν-th kind). Then Boltzmann's equation may be written in the form:

$$\frac{df_{\nu}}{dt} = \frac{\partial f_{\nu}}{\partial t} + \xi_i \frac{\partial f_{\nu}}{\partial x_i} = \sum_{\mu k l} \int [f_k f_l - f_{\mu} f_{\nu}] \, P_{\nu\mu}{}^{kl} (\xi^{\nu}, \xi^{\mu}, \xi^{k}, \xi^{l}) \, g_{\nu\mu} d\xi^{k} d\xi^{l} d\xi^{\mu} \tag{1.1}$$

$$g_{\nu\mu} = | \xi^{\mu} - \xi^{\nu} | \qquad (\nu = 1, \ldots, N; \; \mu = 1, \ldots, N; \; k = 1, \ldots, N; \; l = 1, \ldots, N)$$

where $P_{\nu\mu}^{kl}(\xi^{\nu}, \xi^{\mu}, \xi^{k}, \xi^{l})$ is the probability (collision cross section) that as a result of a collision between molecules in states ν and μ with velocities ξ^{ν} and ξ^{μ}, respectively, the molecule ν goes over into the state k and acquires a velocity ξ^{k}, while the μ-molecule goes over into the state l and acquires a velocity ξ^{l}. The distribution functions are normalized so that

$$n^{\nu}(t, \mathbf{x}) = \int f_{\nu} d\xi^{\nu} \tag{1.2}$$

where n^{ν} is the number of particles in state ν in unit volume.

The mean velocity of the ν-th component of the gas

$$\mathbf{u}^{\nu} = \frac{1}{n^{\nu}} \int \xi^{\nu} f_{\nu} d\xi^{\nu} . \tag{1. 3}$$

Since the masses of all the molecules are the same, the macroscopic velocity of the gas as a whole

$$u = \frac{1}{n} \sum_{\nu} n^{\nu} u^{\nu} \qquad \left(n = \sum_{\nu} n^{\nu}\right) \tag{1. 4}$$

where n is the total number of molecules in unit volume. Multiplying each of Eqs. (1. 1) by 1, ξ_i^{ν}, and $(1/2)m\xi^{\nu 2} + E^{\nu}$ in turn, integrating with respect to ξ^{ν}, and summing the equations with respect to ν, we get the following conservation equation:

Conservation of number of particles

$$\frac{\partial n}{\partial t} + \frac{\partial n u_r}{\partial x_r} = 0 . \tag{1. 5}$$

Conservation of momentum

$$\left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial x_r}\right) u_i + \frac{1}{nm} \frac{\partial}{\partial x_i} P_{ij} = 0 . \tag{1. 6}$$

Conservation of energy

$$n\left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial x_r}\right)\left(\frac{3}{2} kT + \varepsilon\right) = -\frac{\partial q_r}{\partial x_r} - P_{ir} \frac{\partial u_i}{\partial x_r} \tag{1. 7}$$

where

$$P_{ij} = \sum_{\nu} m \int c_i^{\nu} c_j^{\nu} f_{\nu} d\xi^{\nu} \qquad (c_i^{\nu} = \xi_i^{\nu} - u_i) \tag{1. 8}$$

$$q_r = \sum_{\nu} \int c_r^{\nu} \left(\frac{m c^{\nu 2}}{2} + E^{\nu}\right) f_{\nu} d\xi \tag{1. 9}$$

$$\frac{3}{2} kT = \frac{1}{n} \sum_{\nu} \frac{m c^{\nu 2}}{2} \int f_{\nu} d\xi^{\nu} \tag{1. 10}$$

$$\varepsilon = \frac{1}{n} \sum_{\nu} E^{\nu} n^{\nu} . \tag{1. 11}$$

The right sides of the equations vanish, since the total number of particles, their momentum and energy do not change during collisions. Thus, we have five equations with 14 unknowns: n, u_i, q_i, P_{ij}, and ε (the tensor P_{ij} is symmetrical and T can be expressed in terms of P_{ij}).

§2. Before proceeding to derive the missing relations, we shall describe a method, more convenient for our purpose, of expanding solutions of the Boltzmann equation with respect to a small parameter. Let us write Boltzmann's equation for a monatomic gas in the form:

$$\frac{df}{dt} = \frac{1}{\varepsilon} J = \frac{1}{\varepsilon} \int_{1} (f_1' f' - f f_1) g P_{\nu\nu}^{\nu\nu} (\xi, \xi_1, \xi', \xi_1') d\xi_1 d\xi' d\xi_1' \tag{2. 1}$$

where the same letters denote dimensionless functions referred to their characteristic values; then the parameter ε is equal to the ratio of the mean time between collisions to the characteristic time of the process, i. e., to the Knudsen number.

Integrating (2. 1) over the trajectory of the particles with velocity ξ, we have

$$f(t, x_0 + \xi(t - t_0), \xi) - f(t_0, x_0, \xi) = \frac{1}{\varepsilon} \int_{t_0}^{t} J(s, x_0 + \xi(s - t_0), \xi) ds . \tag{2. 2}$$

Let $\tau = t - t_0$ be of the order of ε. If over the length of the free path or in the time $\tau = O(\varepsilon)$ the distribution function changes so slowly (i. e., if $\varepsilon \ll 1$) that the changes may be neglected, then the distribution function must satisfy the condition

$$\int_0^t J(s)\,ds = 0, \qquad J(t) = 0\,. \tag{2. 3}$$

The second equation (2. 3) is known to be satisfied by a local Maxwell distribution. Thus, the assumption that the change in the distribution function over the free path is negligibly small requires a locally equilibrium velocity distribution.

Let the variation of the distribution function over the free path be small, so that it can be represented in the form

$$f(t_0+\tau,\ x_0+\xi\tau,\ \xi) = f(t_0,\ x_0,\ \xi) + \left.\frac{df}{dt}\right|_{\tau=0}\tau + \frac{1}{2}\left.\frac{d^2f}{dt^2}\right|_{\tau=0}\tau^2 + \ldots\,. \tag{2. 4}$$

If we keep two terms of this expansion, then at each point of the flow the distribution function must be close to Maxwellian, i. e.,

$$f(t,\ x,\ \xi) = f^{(0)}(t,\ x,\ \xi)\,[1+\varphi(t,\ x,\ \xi)] \qquad \left(f^{(0)} = n\left[\frac{m}{2kT\pi}\right]^{3/2}\exp\frac{-mc^2}{2kT}\right) \tag{2. 5}$$

where $f^{(0)}$ is Maxwell's distribution and φ is a small component. Substituting (2. 5) in (2. 2), we get:

$$\begin{aligned} \left.\frac{df^{(0)}}{dt}\right|_{\tau=0}\tau + \left.\frac{df^{(0)}\varphi}{dt}\right|_{\tau=0}\tau &= \frac{1}{\varepsilon}\int_{t_0}^{t_0+\tau}[J^{(1)}(f,\ \varphi) + J^{(2)}(\varphi,\ \varphi)]\,ds\,, \\ J^{(1)}(f,\ \varphi) &= \int f^{(0)}f_1^{(0)}(\varphi_1' + \varphi' - \varphi_1 - \varphi)\,gP_{vv}^{vv}(\xi,\ \xi_1,\ \xi',\ \xi_1')\,d\xi_1 d\xi_1' d\xi'\,, \\ J^{(2)}(\varphi,\ \varphi) &= \int f^{(0)}f_1^{(0)}(\varphi_1'\varphi' - \varphi\varphi_1)\,gP_{vv}^{vv}(\xi,\ \xi_1,\ \xi',\ \xi_1')\,d\xi_1 d\xi_1' d\xi'\,. \end{aligned} \tag{2. 6}$$

From (2. 6) it is clear that the function φ must be of the order of ε, so that, neglecting quantities of the order of ε^2, at any point x at any moment of time we must have

$$\varepsilon\frac{df^{(0)}}{dt} = J^{(1)}(f,\ \varphi)\,, \tag{2. 7}$$

the standard integral equation for finding φ. The process may be continued so as to yield higher-order corrections.

Conditions (2. 3) and (2. 7) presuppose that the distribution function changes little over the free path or between collisions. If the distribution function changes by a full order, then there are no supplementary conditions and it is necessary to solve the Boltzmann equation (2. 1) itself.

Note that in order to construct a solution we only require the existence of the derivatives over the trajectory of the molecules d/dt, whereas the partial derivatives $\partial/\partial t$ and $\partial/\partial x$ may not exist.

§3. Boltzmann's equations (1. 1) may also be written in dimensionless form:

$$\frac{\partial f_v}{dt} = \frac{1}{\varepsilon_1}\sum_{\mu kl}{}^{(1)}{}_v + \frac{1}{\varepsilon_2}\sum_{\mu kl}{}^{(2)}{}_v + \frac{1}{\varepsilon_3}\sum_{\mu kl}{}^{(3)}{}_v + \ldots \tag{3. 1}$$

where the sums $\Sigma_\nu{}^{(1)}$, $\Sigma_\nu{}^{(2)}$, etc. combine terms with coefficients ε_i^{-1} of the same order. The value of the parameters ε_i is determined by the transition probabilities $P_{\nu\mu}{}^{kl}$.

Usually the highest probability is that of transfer of translational energy from particle to particle without change in internal energy. We shall assume that ε_i and $\Sigma_\nu{}^{(1)}$ relate to such transitions.

Then follow the probabilities of transfer between translational and rotational energy, resonance exchange of vibrational quanta (without conversion of vibrational into translational energy), transfer between translational and vibrational energy, etc. Since the probability of excitation of molecular rotations falls with increase in temperature, while the probability of exciting vibrations increases, at temperatures of the order of 2. 5 -3. 0 · 10^4 °K these probabilities are of the same order [6]. It is possible to get cases of "meshing" and other processes as, for example, transfer between vibration and rotation, simultaneous excitation of vibrational and electronic levels, vibration and dissociation, etc. However, in order not to complicate the picture, we shall disregard collisions with change in the number of particles.

We shall assume that there are certain "nonmeshing" processes or combinations of processes, so that we can form the sums in (3. 1) with $\varepsilon_1 \ll \varepsilon_2 \ll \varepsilon_3$, and so on. Each of these groups is characterized by its mean relaxation time $\theta_i =$

$= \varepsilon_1\theta$, where θ is the characteristic time of the process. As in the preceding section, we integrate (3. 1); we have

$$f_\nu(t_0 + \tau, \mathbf{x} + \xi\tau, \xi) - f_\nu(t_0, \mathbf{x}, \xi) = \frac{1}{\varepsilon_1}\int_{t_0}^{t+\tau} \Sigma_\nu^{(1)} ds + \frac{1}{\varepsilon_2}\int_{t_0}^{t_0+\tau} \Sigma_\nu^{(2)} ds + \ldots . \qquad (3.2)$$

Putting $\tau = O(\varepsilon_1)$ and analyzing the nature of the variation of the distribution function during this time, we can derive supplementary conditions analogous to (2. 3) and (2. 7).

§4. Let, for example, the flow be such that $\varepsilon_1 \ll \varepsilon_2 \sim 1 \ll \varepsilon_3$, and let the changes in the distribution function over the free path (or during time θ_1) be negligible. Putting $\tau = O(\varepsilon_1)$ in (3. 2), we get $\Sigma_\nu^{(1)} = 0$, and hence

$$f_\nu^{(0)} = n^\nu \left(\frac{m}{2k\pi T}\right)^{3/2} \exp\left\{-\frac{m}{2kT} c^{\nu 2}\right\}, \qquad (4.1)$$

i. e., the translational degrees of freedom are in equilibrium at the translational temperature T. In this case there is no diffusion of the ν-components, since $u_r^\nu = u_r$. After substitution of the distribution function (4. 1) in P_{ij} and q_i the conservation equations assume the form:

$$\begin{gathered}\frac{\partial n}{\partial t} + \frac{\partial n u_r}{\partial x_r} = 0, \qquad \left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial x_r}\right) u_i = -\frac{1}{mn}\frac{\partial p}{\partial x_i}, \\ \left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial x_r}\right)\left(\frac{3}{2}kT + \varepsilon\right) = -kT\frac{\partial u_r}{\partial x_r}, \qquad p = knT.\end{gathered} \qquad (4.2)$$

The system of six equations (4. 2) is not closed, since, apart from the ordinary hydrodynamic variables n, u_r, p, and T, it contains the internal energy, to determine which it is necessary to know all the n^ν. In order to find the latter, we integrate Eqs. (1. 1) with respect to ξ^ν, substituting for f_ν on the right side the equilibrium function with respect to translational velocities $f_\nu^{(0)}$.

Then, since $\Sigma_\nu^{(1)} = 0$, we get the following system of semi-macroscopic equations (the term $\Sigma_\nu^{(3)}$ is neglected):

$$\frac{\partial n^\nu}{\partial t} + \frac{\partial u_r n^\nu}{\partial x_r} = \frac{1}{\varepsilon_2}\sum_{\mu k l}{}^{(2)} \left(n^k n^l a_{kl}^{\nu\mu} - n^\nu n^\mu a_{\nu\mu}^{kl}\right) \qquad (4.3)$$

where

$$a_{\nu\mu}^{kl} = \frac{1}{n^\nu n^\mu}\int f_\nu^{(0)} f_\mu^{(0)} P_{\nu\mu}^{kl}(\xi^\nu, \xi^\mu, \xi^k, \xi^l)\, g_{\nu\mu}\, d\xi^k d\xi^l d\xi^\mu d\xi^\nu$$

is the velocity-averaged probability of transition of ν- and μ-molecules to the states k and l, respectively, upon collision.

Obviously, the coefficients a depend only on the translational temperature T. Thus, equilibrium of the gas with respect to translational degrees of freedom makes it possible to deal with less detailed information on the transition probabilities* in order to find n^ν (we need to know only the integral probabilities a rather than the differential probabilities P). Since the occupation numbers of the levels n^ν change by a full order during the relaxation time θ_2, assuming ($\varepsilon_1 \sim 1$), in the general case it is necessary to solve system (4. 2) simultaneously with system (4. 3), i. e., the process of taking into account the internal degrees of freedom can not be reduced to adding to system (4. 2) a single additional equation for the internal energy ε.

At the same time, in special cases with definite properties of the transition probabilities the system of nonlinear equations (4. 3) can be simplified or even reduced to a single equation for the internal energy or the temperature of the internal degrees of freedom.

Consider, for example, a gas in which the transition probabilities have the following properties [7]. The highest probability is that of transitions with a unit change in quantum number, i. e., transitions of the form $a_{\nu\mu}^{(\nu+1)\mu} = a_\nu^{(\nu+1)}$. The probability of deactivation is exp (ΔE^ν/kT) times greater than the probability of excitation of a level, i. e.,

$$a_\nu^{\nu-1} = a_{\nu-1}^\nu \exp(\Delta E^\nu / kT), \text{ where } \Delta E^\nu = E^\nu - E^{\nu-1} .$$

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* It is possible to deal with even less detailed information on the transition probabilities after summing the terms on the right side of (4. 3):

$$\frac{\partial n^\nu}{\partial t} + \frac{\partial u_r n^\nu}{\partial x_r} = \sum_{kl} n^k n^l a_{kl}^\nu - \sum_\mu n^\nu n^\mu a_{\nu\mu} \qquad \left(a_{kl}^\nu = \sum_\mu a_{kl}^{\nu\mu},\ a_{\nu\mu} = \sum_{kl} a_{\nu\mu}^{kl}\right).$$

This assumption follows from the principle of detailed equilibrium. Further, let $a_\nu^{\nu-1} = \nu a_1^\circ$. We shall also assume that the levels E^ν are distributed as in an harmonic oscillator, i. e., $E^\nu = \nu h\omega$, where ω is the frequency. Then, neglecting transitions with changes of two or more in the quantum number, we get:

$$\frac{\partial n^\nu}{\partial t} + \frac{\partial n^\nu u_r}{\partial x_r} = \sum_\mu \left[\nu n^\mu a_1^\circ \left(n^{\nu-1} \exp\left(\frac{-h\omega}{kT}\right) - n^\nu\right) + (\nu+1)\, n^\mu a_1^\circ \left(n^{\nu+1} - n^\nu \exp\left(\frac{-h\omega}{kT}\right)\right)\right].$$

Summing with respect to μ and bearing in mind that $\sum_\mu n^\mu = n$, we have:

$$\frac{\partial n^\nu}{\partial t} + \frac{\partial n^\nu u_r}{\partial x_r} = n a_0^1 \left[\nu n^{\nu-1} \exp\left(-\frac{h\omega}{kT}\right) - \nu n^\nu + (\nu+1)\, n^{\nu+1} - (\nu+1)\, n^\nu \exp\left(-\frac{h\omega}{kT}\right)\right]. \qquad (4.\,4)$$

Multiplying each of equations (4. 4) by $E^\nu = \nu h\omega$, and summing with respect to ν, we get:

$$\left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial x_r}\right) \varepsilon = n a_0{}^1 \left(1 - \exp\left(-\frac{h\omega}{kT}\right)\right) \left(\varepsilon^{(0)}(T) - \varepsilon\right)$$
$$\varepsilon^{(0)}(T) = h\omega\, (\exp h\omega / kT - 1)^{-1} \qquad (4.\,5)$$

where $\varepsilon^{(0)}(T)$ is the equilibrium energy of the oscillator system at temperature T. Thus, in this case Eq. (4. 5) closes system (4. 2).

In [7] it was shown that resonance transitions of vibrational quanta have higher probability than transitions between vibrational and translational energy. In this case the vibrational degrees of freedom come into equilibrium at a certain vibrational temperature T_k not equal to T [4].

Let θ_2 be the relaxation time of the resonance transitions and θ_3 the relaxation time for energy transfer between translation and vibration, and let $\varepsilon_1 \leq \varepsilon_2 \leq \varepsilon_3$.

There are three possible cases. If the characteristic time of the process is small compared with θ_2, i. e., $\varepsilon_2 \gg 1$, then the flow is frozen.

If $\varepsilon_2 \sim 1$ and $\varepsilon_2 \ll \varepsilon_3$, then energy transfer between translation and vibration may be neglected, and the motion of the gas is described by system (4. 2). In the sums on the right sides of Eqs. (4. 3) there remain only the terms with resonance transitions. Obviously, in this case we have

$$\left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial x_r}\right) \varepsilon = 0$$

since for such transitions there is no change in the mean internal energy of the molecules.

Finally, if $\varepsilon_2 \ll \varepsilon_3 \sim 1$, then, putting $\tau \sim \varepsilon_1$ in (3. 2) and assuming that in this time or over the corresponding distances changes in the distribution function may be neglected, we get:

$$\frac{1}{\varepsilon_1} \int_{t_0}^{t_0+\tau} \Sigma_\nu{}^{(1)} dt + \frac{1}{\varepsilon_2} \int_{t_0}^{t_0+\tau} \Sigma_\nu{}^{(2)} dt = 0 \ .$$

The solution of this equation is the function

$$f_\nu{}^{(0)} = n \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\frac{-mc^{\nu 2}}{2} \exp\frac{-E^\nu}{kT_k} \Big/ \sum_\nu \exp\frac{-E^\nu}{kT_k} \ . \qquad (4.\,6)$$

Multiplying (1. 1) by E^ν, integrating with respect to ξ^ν, substituting distribution (4. 6) on the right side instead of f, and adding the equations, we get:

$$\left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial_r}\right) \varepsilon = n \sum_{\nu\mu kl}^{(3)} \frac{E^\nu}{[\Sigma \exp(-E^\nu / kT_k)]^2} \left[a_{kl}^{\nu\mu} \exp\left(-\frac{E^k + E^l}{kT_k}\right) - \right.$$
$$\left. - a_{\nu\mu}^{kl} \exp\left(-\frac{E^\nu + E^\mu}{kT_k}\right)\right] . \qquad (4.\,7)$$

Since in the equilibrium state ε is uniquely related to T_k, Eq. (4. 7) closes system (4. 2).

In accordance with [7], the assumptions made in deriving (4. 5) hold true for $a_{kl}^{\nu\mu}$. If we again regard the molecules as oscillators with energy $E_\nu = \nu h\omega$, then formula (4. 5), in which ε now has the equilibrium (at T_k) value

$$\varepsilon = h\omega \left(\exp \frac{h\omega}{kT_k} - 1\right)^{-1}$$

also holds.

As might be expected, the presence of resonance transitions has no effect on the form of the system of macroscopic equations when system (4. 2) can be closed with a single equation for the internal energy [in our case Eq. (4. 5)], since resonance transitions do not alter the internal energy of the gas.

Finally, let us consider the common situation when one type (denoted by ε_2) of internal energy (e. g. , rotational) is in equilibrium with the translational degrees of freedom (i. e. , $\varepsilon_2 \ll 1$), whereas the relaxation time for another type (denoted by ε_3) of internal energy (e. g. , vibrational) is of the same order as the characteristic time of the process*, i.e., $\varepsilon_3 \sim 1$. Each ν-state may be regarded as a superposition of the ν_2- and ν_3-states corresponding to the first and second types of internal energy. We shall apply the term ν_3-gas to a gas consisting of molecules with internal energy of the second type in the ν_3-state and in an arbitrary state ν_2. In this case the distribution function assumes the form:

$$f_\nu^{(0)} = n^{\nu_3} \left(\frac{m}{2\pi kT}\right)^{3/2} \exp \left(\frac{-m}{2kT} c^{\nu 2}\right) \exp \frac{-E^{\nu_2}}{kT} \left(\sum_{\nu_2} \exp \frac{-E^{\nu_2}}{kT}\right)^{-1} \tag{4. 8}$$

where

$$n^{\nu_3} = \sum_{\nu_2} \int f_\nu^{(0)} d\xi^\nu \ .$$

The mean internal energy

$$\varepsilon = \varepsilon_2^{(0)} (T) + \frac{1}{n} \sum_{\nu_3} n^{\nu_3} E^{\nu_3} \qquad \varepsilon_2^{(0)} (T) = \sum_{\nu_2} E^{\nu_2} \exp \frac{-E^{\nu_2}}{kT} \left[\sum_{\nu_2} \exp \frac{-E^{\nu_2}}{kT}\right]^{-1} . \tag{4. 9}$$

Integrating (1. 1) with respect to ξ^ν and summing the equations with respect to all the ν_2 corresponding to a single ν_3, while bearing in mind that

$$\sum_\nu = \sum_{\nu_2} \sum_{\nu_3} , \qquad n^\nu = n^{\nu_3} \exp \frac{-E^{\nu_2}}{kT} \left(\sum_{\nu_2} \exp \frac{-E^{\nu_2}}{kT}\right)^{-1}$$

we get:

$$\begin{aligned} \frac{\partial n^{\nu_3}}{\partial t} + \frac{\partial u_r n^{\nu_3}}{\partial x_r} = \left(\sum_{\nu_2} \exp \frac{-E^{\nu_2}}{kT}\right)^{-2} \sum_{\nu_2 \mu k l} \Bigg(a_{kl}^{\nu\mu} n^{k_3} n^{l_3} \exp \left(-\frac{E^{k_2} + E^{l_2}}{kT}\right) - \\ - a_{\nu\mu}^{kl} n^{\nu_3} n^{\mu_3} \exp \left(-\frac{E^{\nu_2} + E^{\mu_2}}{kT}\right)\Bigg) \ . \end{aligned} \tag{4. 10}$$

Summing the right sides of Eqs. (4. 10) with respect to ν_2, μ_2, k_2, and l_2, we get Eqs. (4. 3) in which the subscripts ν, μ, k, and l must be replaced by ν_3, μ_3, k_3, and l_3, respectively, where

$$a_{\nu_3 \mu_3}^{k_3 l_3} = \left(\sum_{\nu_2} \exp \frac{-E^{\nu_2}}{kT}\right)^{-2} \sum_{\nu_2 \mu_2 k_2 l_2} a_{\nu_2 \nu_3 \mu_2 \mu_3}^{k_2 n_3 l_2 l_3} \exp \left(-\frac{E^{\nu_2} + E^{\mu_2}}{kT}\right) .$$

This system can be reduced to a single equation for ε only if the transition probabilities have special properties, e. g. , those assumed in deriving (4. 5) or (4. 7).

§5. In the preceding section it was assumed that the distribution function does not change during a time (or over a length) of order ε_1. We shall now consider a flow in which it is impossible to neglect such changes in the distribution function. At the same time, these changes will be assumed to be so small that the distribution function can be represented in the form:

$$f (t_0 + \tau, \mathbf{x}, \xi) = f (t_0, \mathbf{x} - \xi\tau, \xi) + df/dt \,|_{\tau=0} \tau \ . \tag{5. 1}$$

Here, as above, there may be a wide variety of possible relations between the characteristic relaxation times and the characteristic time of the process. Below we consider some of these. Other cases may be treated analogously.

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* All that follows remains valid if there is not one mode for which $\varepsilon_2 \ll \varepsilon_3$, but several modes with $\varepsilon_i \ll \varepsilon_3$.

Let us consider first of all the case where all $\varepsilon_i \ll 1$ and during the time (over the length) of the least of them, ε_1, the change in the distribution function is given by (5. 1). This case is discussed in relation to vibrational relaxation in [3]. Putting $\tau \sim \varepsilon_1$ in (3. 2), we get in the first approximation:

$$\sum_i \frac{1}{\varepsilon_i} \Sigma_\nu^{(i)} = 0 . \tag{5. 2}$$

Obviously, the solution of these equations is the distribution function corresponding to equilibrium between the translational and internal energy

$$f_\nu^{(0)} = n \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\frac{-mc^{\nu 2}}{2kT} e^{-E^\nu/kT} \left[\sum_\nu \exp\frac{-E^\nu}{kT}\right]^{-1} . \tag{5.3}$$

If we take into account small changes over a length of the order of ε_1, the distribution function must be only slightly different from (5. 3), i. e.,

$$f_\nu = f_\nu^{(0)}(1 + \varphi_\nu) . \tag{5. 4}$$

Substituting (5. 4) in (3. 2) for $\tau \sim \varepsilon_1$ and discarding terms of order ε_1^2, by analogy with (2. 7) we get the linear integral equations

$$\frac{df_\nu^0}{dt} = \frac{1}{\varepsilon_1} \sum_\nu^{(1)} J_{\nu\mu kl}^{(1)}(f, \varphi) + \frac{1}{\varepsilon_2} \sum_\nu^{(2)} J_{\nu\mu kl}^{(1)}(f_1\varphi) + \dots \tag{5. 5}$$

where

$$J_{\nu\mu kl}^{(1)}(f, \varphi) = \int f_\nu^{(0)} f_\mu^{(0)} (\varphi_k + \varphi_l - \varphi_\nu - \varphi_\mu) P_{\nu\mu}^{kl} g_{\nu\mu} d\xi^k \, d\xi^l \, d\xi^\mu .$$

Substituting the function (5. 3) on the left of (5. 5), we get:

$$\begin{aligned} \frac{df_\nu^{(0)}}{dt} = f_\nu^{(0)} \Bigg\{ &\left(\frac{m}{2kT} c^{\nu 2} - \frac{5}{2} + \frac{E^\nu - \varepsilon^{(0)}(T)}{kT}\right) c_r^\nu \frac{\partial \ln T}{\partial x_r} + \frac{m}{kT}\left(c_r^\nu c_i^\nu - \frac{1}{3}\delta_{ri} c^{\nu 2}\right)\frac{\partial u_i}{\partial x_r} + \\ &+ \left[\frac{1}{3}\frac{m}{kT} c^{\nu 2} - 1 - k\left(\frac{m}{2kT} c^{\nu 2} - \frac{3}{2} + \frac{E^\nu - \varepsilon^{(0)}(T)}{kT}\right)\left(\frac{3}{2}k + \frac{d\varepsilon^{(0)}(\tau)}{dT}\right)^{-1}\right] \frac{\partial u_r}{\partial x_r} . \end{aligned} \tag{5. 6}$$

Here the partial derivatives with respect to t have been eliminated with the aid of Euler's equations (4. 2), and $\varepsilon^{(0)}(T)$ is the equilibrium value of the mean internal energy:

$$\varepsilon^{(0)}(T) = \sum_\nu E^\nu \exp\left(\frac{-E^\nu}{kT}\right) \Big/ \sum_\nu \exp\frac{-E^\nu}{kT} .$$

It is easy to verify that zero is an eigenvalue of Eqs. (5. 5), and that the functions $\psi_i = 1,\ \xi_i^\nu,\ {}^1\!/\!_2 m\xi^{\nu 2} + E^\nu$ are eigenfunctions. For the existence of a solution of the nonhomogeneous equations it is necessary that

$$\sum_\nu \int \psi_i(\xi^\nu) \frac{df_\nu^{(0)}}{dt} d\xi^\nu = 0 .$$

Since the eigenfunctions coincide with the invariants by which the Boltzmann equations were multiplied in deriving the Euler equations (4. 2), used in obtaining expressions (5. 6), these conditions are fulfilled. The form of the left side of Eqs. (5. 5) makes it possible to seek a solution in the form:

$$\varphi_\nu = -A_k^\nu \frac{\partial \ln T}{\partial x_k} - B_{lk}^\nu \frac{\partial u_l}{\partial x_k} - D^\nu \frac{\partial u_l}{\partial x_l} + \alpha^* + \beta_r^* \xi_r^\nu + \gamma^*\left(\frac{m\xi^{\nu 2}}{2} + E^\nu\right) \tag{5. 7. 1}$$

or

$$\varphi_\nu = -A_k^\nu \frac{\partial \ln T}{\partial x_k} - B_{lk}^\nu \frac{\partial u_l}{\partial x_k} + \alpha + \beta_r c_r^\nu + \gamma\left(\frac{mc^{\nu 2}}{2} + E^\nu\right) \tag{5. 7. 2}$$

where A_k^ν, B_{lk}^ν, and D^ν are functions of c_i^ν, T, and E^ν.

By an analysis analogous to that carried out in [8] it can be shown that

$$A_k^\nu = c_r^\nu A^\nu, \qquad B_{lk}^\nu = \left(c_l^\nu c_k^\nu - \frac{1}{3}\delta_{lk} c^{\nu 2}\right) B^\nu, \qquad D^\nu = D^\nu \tag{5. 8}$$

where A^ν, B^ν, and D^ν are functions of c^ν, T, and E^ν. The constants α, β_r, and γ (or α^*, β_r^*, and γ^*) can be subjected to the conditions

$$\sum_\nu \int f_\nu{}^0 \varphi_\nu \, d\xi^\nu = 0, \qquad \sum_\nu \int \xi^\nu f_\nu{}^{(0)} \varphi_\nu \, d\xi^\nu = 0, \quad \sum_\nu \int \left(\frac{mc^{\nu 2}}{2} + E^\nu \right) f_\nu{}^{(0)} \varphi_\nu \, d\xi^\nu = 0 . \tag{5. 9}$$

Then

$$\sum_\nu \int f_\nu \, d\xi^\nu = \sum_\nu \int f_\nu{}^{(0)} \, d\xi^\nu = n, \sum_\nu \int \xi^\nu f_\nu \, d\xi^\nu = \sum_\nu \int f_\nu{}^{(0)} \xi^\nu \, d\xi^\nu = nu$$

$$\sum_\nu \int \left(\frac{mc^{\nu 2}}{2} + E^\nu \right) f_\nu \, d\xi^\nu = \sum_\nu \int \left(\frac{mc^{\nu 2}}{2} + E^\nu \right) f_\nu^{(0)} \, d\xi^\nu = n \left[\frac{3}{2} kT + \varepsilon^{(0)} \left(T \right) \right] . \tag{5. 10}$$

It should be noted that with these conditions the temperature T is not equal to the temperature determined by (1. 10). Instead of the last condition (5. 10), it is possible to require that the temperature be determined by (1. 10), i. e., be a measure only of the translational energy of the molecules. In this case, however, the expression for the internal energy will be more complicated.

Substituting (5. 7. 1) in (5. 5) and equating the terms associated with the same derivatives of the macroscopic quantities, we get integral equations for A^ν, B^ν, and D^ν, for whose solution it is necessary to know the specific law of interaction between molecules and the distribution of the molecules over the energy levels, together with all the transition probabilities. However, certain qualitative conclusions may be drawn directly from the form of the solutions of the equations, without actually solving them.

On substituting (5. 4) in (1. 7) on the left side, as a consequence of conditions (5. 9), instead of ε we can put the equilibrium function $\varepsilon^{(0)}(T)$ defined by (5. 6). After substitution of (5. 4), the stress tensor P_{ij} and the heat flux vector q_i may be expressed in terms of n, u_i, and T, so that the system (1. 5)-(1. 7) is closed.

From the first and third of conditions (5. 9), after substitution of (5. 7. 2), it follows that α and γ may be expressed in terms of $\partial u_r/\partial x_r$, and from the second condition that β_r is proportional to $\partial \ln T/\partial x_r$. Therefore these quantities may be included in $A_r{}^\nu$ and D^ν, respectively, without changing their essential form. Then the solution has the form (5. 7. 1), where α, β_r, and γ are equal to zero. Substituting these solutions in the definition of the tensor P_{ij} and the vector q_i, we have

$$\begin{aligned} P_{ir} &= \sum_r m \int c_i{}^\nu c_r{}^\nu f_\nu \, d\xi^\nu = m \sum_\nu \int c_i{}^\nu c_r{}^\nu f_\nu{}^{(0)} \, d\xi\nu + m \sum_\nu \int c_i{}^\nu c_r{}^\nu f_\nu{}^{(0)} \times \\ &\times \varphi_\nu \, d\xi^\nu = kTn\delta_{ir} - \mu \left[\left(\frac{\partial u_i}{\partial x_r} + \frac{\partial u_r}{\partial x_i} \right) - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ir} \right] - \zeta \frac{\partial u_k}{\partial x_k} \delta_{ir} , \\ q_i{}^{(1)} &= \sum_\nu m \int c_i{}^\nu \frac{c^{\nu 2}}{2} f_\nu \, d\xi^\nu = \sum_\nu m \int c_i{}^\nu \frac{c^{\nu 2}}{2} f_\nu{}^{(0)} \varphi_\nu \, d\xi^\nu = - \lambda_1 \frac{\partial T}{\partial x_i} \\ q_i{}^{(2)} &= \sum_\nu \int c_i{}^\nu E^\nu f_\nu \, d\xi^\nu = \sum_\nu E^\nu \int c_i{}^\nu f_\nu{}^{(0)} \varphi_\nu \, d\xi^\nu = - \lambda_2 \frac{\partial T}{\partial x_i} \end{aligned} \tag{5. 11}$$

where

$$\begin{aligned} \mu &= \frac{m}{15} \sum_\nu \int B^\nu c^{\nu_4} f_\nu{}^{(0)} \, d\xi^\nu, \qquad \zeta = m \sum_\nu \frac{1}{3} \int D^\nu c^{\nu_2} f_\nu{}^{(0)} \, d\xi^\nu \\ \lambda_1 &= \frac{m}{6T} \sum_\nu \int A^\nu c^{\nu_4} f_\nu{}^{(0)} \, d\xi^\nu, \qquad \lambda_2 = \frac{1}{3T} \sum_\nu E^\nu \int A^\nu c^{\nu_2} f_\nu{}^{(0)} \, d\xi^\nu \quad . \end{aligned} \tag{5. 12}$$

The shear viscosity μ depends on the internal energy only via the transition probabilities (B^ν is not expressed directly in terms of E^ν). The volume viscosity ζ is directly linked with the internal energy, since E^ν and $d\varepsilon^{(0)}/dT$ form part of the left side of the integral equation for D^ν. The quantities A^ν, and hence the heat conductivity λ_1, can be represented in the form of two components, one of which depends directly on E^ν, while the other depends on E^ν only via the transition probabilities [this is easily seen from (5. 6)].

Let us now consider the general case where, together with those already considered ($\varepsilon_i \ll 1$, $i \leq n - 1$), we have one more form of internal energy with a relaxation time of the order of the characteristic time of the process, i. e., $\varepsilon_n \sim 1$.

For simplicity, we shall consider three characteristic times, so that $\varepsilon_1 \leq \varepsilon_2 \ll \varepsilon_3 \sim 1$. This does not affect the generality of the treatment, since all $\varepsilon_i \neq \varepsilon_1$ or ε_n may be included in ε_2.

As in the analogous case considered in §4, each ν-state is characterized by two quantum numbers ν_2 and ν_3. Again as in §4 [formula (4. 8)], in the zeroth approximation we have

$$f_\nu^{(0)} = n^{\nu_3}\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\left(\frac{m}{2kT}c^2 + \frac{E^{\nu_2}}{kT}\right)\right] \Big/ \sum_{\nu_2} \exp\frac{-E^{\nu_2}}{kT} \quad . \tag{5. 13}$$

Representing the distribution function, as before, in the form (5. 4), we get the equations for φ_ν

$$\left(\frac{d}{dt} - \frac{1}{\varepsilon_3}\Sigma_\nu^{(3)}\right) f_\nu^{(0)} = \frac{1}{\varepsilon_1}\sum_\nu^{(1)} J^{(1)} + \frac{1}{\varepsilon_2}\sum_\nu^{(2)} J^{(2)} \quad , \tag{5. 14}$$

where the notation is the same as in (5. 5). It should be borne in mind, however, that φ_ν and φ_k now relate to one state ν_3, and φ_μ and φ_l, in the general case, to another state ν_3, since by assumption $\Sigma_\nu^{(1)}$ and $\Sigma_\nu^{(2)}$ do not include transitions between ν_3-energy and other forms of excitation.

Hence it follows that $\varphi_\nu = \alpha_{\nu_3}$, where α_{ν_3}, is some constant depending on ν_3 and the macroscopic flow parameters and the solution of the homogeneous equation. Therefore, in our case, there are not five eigenfunctions as before, but $(N_{\nu_3} + 4)$ functions $\psi_i = \alpha_{\nu_3}$, ξ_i^ν, $m\xi^{\nu_2}/2 + E^\nu$; N_{ν_3} is the number of ν_3-states.

After elimination of the partial derivatives with respect to t of n, u_i, and T with the aid of Euler's equations (4. 2) and the derivatives of n^{ν_3} with the aid of equations (4. 3), in which ν, μ, k, and l must be replaced by ν_3, μ_3, k_3, and l_3 (see §4), the left side of (5. 14) may be written in the form:

$$\begin{aligned}\frac{df_\nu^{(0)}}{dt} - \frac{1}{m}\Sigma_\nu^{(3)}(f_\nu^{(0)}) = f_\nu^{(0)} \Bigg\{&\left(\frac{m}{2kT}c^{\nu 2} - \frac{5}{2} + \frac{E^{\nu_2} - \varepsilon_2^{(0)}(T)}{kT}\right)\frac{\partial \ln T}{\partial x_r} c_r^\nu + \\ &+ \frac{m}{kT}\left(c_i^\nu c_r^\nu - \frac{1}{3}\delta_{ir}c^{\nu 2}\right)\frac{\partial u_i}{\partial x_r} + \Bigg[\frac{1}{3}\frac{m}{kT}c^{\nu 2} - 1 - \\ &- k\left(\frac{m}{2kT}c^{\nu 2} - \frac{3}{2} + \frac{E^{\nu_2} - \varepsilon_2^{(0)}(T)}{kT}\right)\left(\frac{3}{2}k + \frac{d\varepsilon_2^{(0)}}{dT}\right)^{-1}\Bigg]\frac{\partial u_r}{\partial x_r} + \\ &+ c_r^\nu \frac{\partial \ln n^{\nu_3}/n}{\partial x_r} + \frac{1}{n^{\nu_3}}\Sigma_{\nu_3}^{(3)}(a) - \\ - \left(\frac{m}{2kT}c^{\nu 2} - \frac{3}{2} + \frac{E^{\nu_2} - \varepsilon_2^{(0)}}{kT}\right)&\sum_{\nu_3} E^{\nu_3}\Sigma_{\nu_3}^{(3)}(a)\left[nT\left(\frac{3}{2}k + \frac{d\varepsilon_2^{(0)}}{dt}\right)\right]^{-1}\Bigg\} - \Sigma_\nu^{(3)}(f_\nu^{(0)}) ,\end{aligned} \tag{5. 15}$$

where, for brevity, $\Sigma_{\nu_3}^{(3)}(a)$ denotes the sum on the right side of an equation of type (4. 3) for n^{ν_3} (see §4); $\Sigma_\nu^{(3)}(f_\nu^{(0)})$ denotes $\Sigma_\nu^{(3)}$ in Eq. (1. 1), with $f_\nu^{(0)}$ substituted for f_ν.

In Eqs. (4. 2) the internal energy is determined from Eq. (4. 9). The form of the left side of (5. 14) makes it possible to represent the solution of this equation as follows:

$$\begin{aligned}\varphi_\nu = &- A^\nu \frac{\partial \ln T}{\partial x_k} c_k^\nu - \left(c_k^\nu c_l^\nu - \frac{1}{3}\delta_{kl}c^{\nu 2}\right)\frac{\partial u_l}{\partial x_k} - D^\nu \frac{\partial u_l}{\partial x_l} + \\ &+ \sum_\nu F_{\nu_3}^{\ \nu}\frac{\partial \ln n^{\nu_3}/n}{\partial x_k} c_k^\nu + G^\nu + \alpha_{\nu_3} + \beta_k c_k^\nu + \gamma\left(\frac{mc^{\nu 2}}{2} + E^\nu\right).\end{aligned} \tag{5. 16}$$

The functions A, B, D, F, and G depend on T, the energy equations, and the composition of the mixture of ν_3-gases, i. e., on all n^{ν_3} and the velocity of the molecules c^ν. The quantities α, β, and γ do not depend on the velocity c^ν. The constants of integration α_{ν_3}, β_k, and γ do not depend on the velocity c_ν. The constants of integration α_{ν_3} a_k, and γ can be determined by imposing the conditions

$$\sum_{\nu_3}\int f_\nu^{(0)}\varphi^\nu d\xi^\nu = 0, \qquad \sum_\nu\int \xi^\nu f^{(0)}\varphi^\nu d\xi^\nu = 0, \qquad \sum_\nu\int\left(\frac{mc^{\nu 2}}{2} + E^\nu\right) f^{(0)}\varphi^\nu d\xi^\nu = 0 .$$

Then

$$\sum_{\nu_3}\int f_\nu d\xi^\nu = \sum_{\nu_2}\int f_\nu^{(0)} d\xi^\nu = n^{\nu_3}, \quad \sum_\nu\int \xi^\nu f_\nu d\xi^\nu = \sum_\nu\int \xi^\nu f_\nu^{(0)} d\xi^\nu = nu$$

$$\begin{aligned}\sum_\nu\int\left(\frac{mc^{\nu_2}}{2} + E^\nu\right) f_\nu d\xi^\nu &= \sum_\nu\int\left(\frac{mc^{\nu 2}}{2} + E^\nu\right) f_\nu^{(0)} d\xi^\nu = \\ &= n\left(\frac{3}{2}kT + \varepsilon_2^{(0)}(T) + \frac{1}{n}\sum_{\nu_3} E^{\nu_3} n^{\nu_3}\right) \quad .\end{aligned}$$

Therefore the general conservation equations (1. 5)-(1. 7) retain their form, and only the expressions for P_{ij} and q_i change. As compared with the preceding case, the expression for the heat flux contains an additional term, depending on the diffusion of the ν_3-components of the gas and proportional to

$$\sum_{\nu_3} \frac{\partial}{\partial x_k} \ln \frac{n^{\nu_3}}{n}$$

and the expression for the diagonal components of the stress tensor a term not containing velocity gradients (this term appears since, in the general case, $G^{\nu} \neq 0$). As equilibrium is approached, this term tends to zero. Note that, as above, the quantity T in the macroscopic equations is not the same as the temperature determined from (1. 10). However, system (1. 5)-(1. 7) is not closed, since, apart from the macroscopic variables n, u_i, and T, these equations also contain N_3 unknowns n^{ν_3}

In order to derive the equations for n^{ν_3}, we integrate (1. 1) with respect to ξ^{ν} and sum over all ν_2 corresponding to a given ν_3-state; we have

$$\frac{\partial n^{\nu_3}}{\partial t} + \frac{\partial}{\partial x_r} \sum_{\nu_2} n^{\nu} u_r^{\nu} = \sum_{\nu_2} \int \Sigma_{\nu}^{(3)} d\xi^{\nu} . \tag{5. 17}$$

The sums $\Sigma_{\nu}^{(1)}$ and $\Sigma_{\nu}^{(2)}$ drop out, since the exchange of translational and ν_2-energy does not affect the number of molecules in the ν_3-state. We transform the sum on the left side of the equation:

$$\sum_{\nu_2} n^{\nu} u_r^{\nu} = \sum_{\nu_2} \int \xi_r^{\nu} f_{\nu} d\xi^{\nu} = \sum_{\nu_2} \left(\int c_r^{\nu} f_{\nu} d\xi^{\nu} + u_r \int f_{\nu} d\xi^{\nu} \right) = \sum_{\nu_2} \int c_r^{\nu} f_{\nu}^{(0)} \varphi_{\nu} d\xi^{\nu} + u_r n^{\nu_3} . \tag{5. 18}$$

Substituting φ_{ν} from (5. 16), we find

$$\sum_{\nu_2} n^{\nu} u_r^{\nu} = u_r n^{\nu_3} + L^{\nu_3} \frac{\partial T}{\partial x_r} + \sum_{\nu_3} M^{\nu_3} \frac{\partial}{\partial x_v} \left(\frac{n^{\nu_3}}{n} \right) , \tag{5. 19}$$

where L^{ν_3} and M^{ν_3} depend on T, the energy levels, and the local composition of the mixture of ν_3-gases. The right side of (5. 17) may be rewritten:

$$\begin{aligned} &\sum_{\nu_2 \mu k l}^{(3)} \int (f_k f_l - f_{\mu} f_{\nu}) P_{\nu\mu}^{kl} g_{\nu\mu} d\xi^k d\xi^l d\xi^{\mu} d\xi^{\nu} = \\ &= \sum_{\nu_2 \mu k l}^{(3)} \int [f_k^{(0)} f_l^{(0)} (1 + \varphi_k + \varphi_l) - f_{\nu}^{(0)} f_{\mu}^{(0)} (1 + \varphi_{\nu} + \varphi_{\mu})] P_{\nu\mu}^{kl} g_{\nu\mu} d\xi^k d\xi^l d\xi^{\mu} d\xi^{\nu} = \\ &= \sum_{\nu_2 \mu k l}^{(3)} \left[n^{k_3} n^{l_3} \left(b_{kl}^{\nu\mu} + d_{kl}^{\nu\mu} \frac{\partial u_r}{\partial x_r} \right) \exp\left(-\frac{E^{k_2} + E^{l_2}}{kT} \right) - \right. \\ &\left. - n^{\nu_3} n^{\mu_3} \left(b_{\nu\mu}^{kl} + d_{\nu\mu}^{kl} \frac{\partial u_r}{\partial x_r} \right) \exp\left(-\frac{E^{\nu_2} + E^{\mu_2}}{kT} \right) \right] . \end{aligned}$$

In integrating allowance was made for the fact that the transition probabilities may not depend on the orientation and are functions of the relative velocity of the colliding molecules. The coefficients $b_{kl}^{\nu\mu}$ differ from the corresponding $a_{kl}^{\nu\mu}$ in (4. 10), since they include a contribution from the functions G^{ν}. Summing with respect to ν_2 in the last expression, we finally get a system of semi-macroscopic equations for n^{ν_3}:

$$\begin{aligned} &\frac{\partial n^{\nu_3}}{\partial t} + \frac{\partial u_r n^{\nu_3}}{\partial x_r} + \frac{\partial}{\partial x_r} \left[L_j^{\nu_3} \frac{\partial T}{\partial x_j} + \sum_{\nu_3} M_j^{\nu_3} \frac{\partial}{\partial x_j} \left(\frac{n^{\nu_3}}{n} \right) \right] = \\ &= \sum_{\mu_3 k_3 l_3} \left[n^{k_3} n^{l_3} \left(b_{k_3 l_3}^{\nu_3 \mu_3} + d_{k_3 l_3}^{\nu_3 \mu_3} \frac{\partial u_r}{\partial x_r} \right) - n^{\nu_3} n^{\mu_3} \left(b_{\nu_3 \mu_3}^{k_3 l_3} + d_{\nu_3 \mu_3}^{k_3 l_3} \frac{\partial u_r}{\partial x_r} \right) \right] . \end{aligned} \tag{5. 20}$$

These equations close system (1. 5)-(1. 7) with the above-mentioned values of ε, q_i, and P_{ij}.

System (5. 20) may be further simplified if special assumptions are made about the transition probabilities. If the ν_3-states characterize vibrational levels, then, as shown above, resonance transitions of vibrational quanta may be more probable than transitions between vibrational and translational energy. In this case the resonance transition probabilities may be either of the same order as or different from the transition probabilities for translational, rotational, or other forms of energy, but greater than the probability of transition between translational and vibrational energy.

Then, relating relaxation transitions to ε_2-transitions, the distribution functions may be written in the form (cf. §4):

$$f_{\nu} = f_{\nu}^{(0)} (1 + \varphi_{\nu}) , \tag{5. 21}$$

$$f_\nu^{(0)} = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m}{2kT}c^{\nu 2} - \frac{E^{\nu_2}}{kT} - \frac{E^{\nu_3}}{kT_k}\right)\left(\sum_{\nu_3} \exp\frac{-E^{\nu_3}}{kT_k} \sum_{\nu_2} \exp\frac{-E^{\nu_2}}{kT}\right)^{-1} . \qquad \begin{matrix}(5.21)\\ \text{(cont'd)}\end{matrix}$$

Apart from $\Sigma_\nu^{(1)}$ and $\Sigma_\nu^{(2)}$, the right side of (5. 14) also contains a sum representing resonance transitions. The left side of this equation may be written in the form:

$$\begin{aligned} \frac{df_\nu^{(0)}}{dt} - \frac{1}{\varepsilon_3}\Sigma_\nu^{(3)}(f_\nu^{(0)}) = f_\nu^{(0)} \Bigg\{ & \left(\frac{m}{2kT}c^{\nu 2} - \frac{5}{2} + \frac{E^{\nu 2} - \varepsilon_2^{(0)}}{kT}\right)\frac{\partial \ln T}{\partial x_r} c_r^\nu + \\ & + \frac{m}{kT}\left(c_i^\nu c_r^\nu - \frac{1}{3}\delta_{ir} c^{\nu_2}\right)\frac{\partial u_i}{\partial x_r} + \left[\frac{1}{3}\frac{m}{kT}c^{\nu 2} - 1 - k\left(\frac{m}{2kT}c^{\nu 2} - \frac{3}{2} + \frac{E^{\nu_2} - \varepsilon_2^{(0)}}{kT}\right)\right] \times \\ & \times \left(\frac{3}{2}k + \frac{d\varepsilon_1^{(0)}}{dt}\right)^{-1}\frac{\partial u_r}{\partial x_r} + \frac{E^{\nu_3} - \varepsilon_k^{(0)}}{kT_k^2}\frac{\partial T_k}{\partial x_r} c_r^\nu + \left(\frac{E^{\nu_3} - \varepsilon_k^{(0)}}{kT_k^2}\frac{dT_k}{d\varepsilon_k^{(0)}} - \right. \\ & \left. - \left(\frac{m}{2kT}c^{\nu 2} - \frac{3}{2} + \frac{E^{\nu_2} - \varepsilon_2^{(0)}}{kT}\right)\left[nT\left(\frac{3}{2}k + \frac{d\varepsilon_2^{(0)}}{dT}\right)\right]^{-1}\right)\left[\sum_{\nu_3} E_\nu^{\nu_3}\Sigma^{(3)}(a)\right]\Bigg\} - \Sigma_\nu^{(3)}(f_\nu^{(0)}) . \end{aligned} \qquad (5.22)$$

Here the expression in square brackets stands for the right side of Eq. (4. 10) where all the ν, μ, k, and l must be replaced by ν_3, μ_3, k_3, and l_3.

From (5. 22) it is clear that, with the above-mentioned changes, the solution of (5. 14) differs in principle from solution (5. 16) only in respect of the presence of a term proportional to $\partial T_k/\partial x$ and the absence of a term proportional to $\partial n^{\nu_3}/\partial x_r$.

In the given case the number of arbitrary constants in the solution diminishes, since for arbitrary α_3 the functions $\varphi_\nu = \alpha_{\nu_3}$ are not a solution of the homogeneous equation including relaxation transitions. The solution will be $\varphi_\nu = \alpha_{\nu_3} = \sigma E^{\nu_3}$, since in relaxation transitions the ν_3-energy of the colliding molecules is conserved. Therefore the general solution of the homogeneous equation has the form:

$$\varphi_\nu = \alpha + \beta_k c_k^\nu + \gamma\left({}^1\!/_2 m c^{\nu_2} + E^\nu\right) + \sigma E^{\nu 3} .$$

The presence of six arbitrary constants makes it possible to impose six conditions on φ_ν, so that

$$\sum_\nu \int f^\nu d\xi^\nu = \sum_\nu \int f_\nu^{(0)} d\xi^\nu = n \quad \sum_\nu \int \xi^\nu f_\nu d\xi^\nu = \sum_\nu \int \xi^\nu f_\nu^0 d\xi^\nu = nu$$

$$\sum_\nu \int \left(\frac{mc^{\nu 2}}{2} + E^\nu\right) f_\nu d\xi^\nu = \sum_\nu \int \left(\frac{mc^{\nu 2}}{2} + E^\nu\right) f_\nu^{(0)} d\xi^\nu = n\left[\frac{3}{2}kT + \varepsilon_2^{(0)}\ (T) + \varepsilon_k^{(0)}(T_k)\right)\Big]$$

$$\sum_{\nu_3} E^{\nu_3} \sum_{\nu_2} \int f_\nu d\xi^\nu = \sum_{\nu_3} E^{\nu_3} \sum_{\nu_2} \int f_\nu^{(0)} d\xi^\nu = n\varepsilon_k^{(0)}(T_k)$$

where

$$\varepsilon_k^{(0)} = \sum_{\nu_3} E^{\nu_3} \exp\frac{-E^{\nu_3}}{kT_k}\left(\sum_{\nu_3} \exp\frac{-E^{\nu_3}}{kT_k}\right)^{-1} .$$

Here, as above, the temperature T is not equal to the mean translational energy of the molecules. Obviously, Eqs. (1. 5)-(1. 7) retain the same form as before. Only the form of the quantities P_{ij}, q, and ε changes. In accordance with the conditions just formulated $\varepsilon = {}^3\!/_2 kT + \varepsilon_2^{(0)}T + \varepsilon_k^{(0)}(T_k)$. The expression for q, as already mentioned, contains a term proportional to $\partial T_k/\partial x_r$. The expression for the tensor P_{ij} remains formally the same as in the preceding case.

This system is not closed, since it contains two temperatures T and T_k. Multiplying Eqs. (1. 1) by E^{ν_3}, integrating with respect to ξ^ν, and adding, as with (5. 20), we get:

$$n\left(\frac{\partial}{\partial t} + u_r\frac{\partial}{\partial x_r}\right)\varepsilon_k^{(0)} + \frac{\partial}{\partial x_r}\left(L\frac{\partial T}{\partial x_r} + M\frac{\partial T_k}{\partial x_r}\right) = b + d\frac{\partial u_r}{\partial x_r} \qquad (5.23)$$

where b and d depend on n, T, and T_k. Together with (1. 5)-(1. 7), Eq. (5. 23) forms a closed system for determining the six unknowns n, u_r, T, and T_k.

The above represents only the form of the equations of hydrodynamics for a relaxing gas with the internal degrees of freedom taken into account. Finding the coefficients entering into these equations involves a great deal of work in determining the transition probabilities and solving the kinetic integral equations.

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