DERIVATION OF GRAD'S TYPE EQUATIONS AND STUDY OF THEIR RELAXATION PROPERTIES BY THE METHOD OF MAXIMIZATION OF ENTROPY

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Derivation of macroscopic equations is studied for nonequilibrium processes in a rarified gas by means of breaking the chain of momentum equations with the aid of maximum entropy distribution (Section 1). In the description of a monatomic gas, ten-momentum (Section 2) and thirteen-momentum (Section 3) approximations are utilized. It is shown that the method is easily generalized to the case of polyatomic (Section 4) and also degenerate (Section 5) gas.

For various nonequilibrium processes nonequilibrium expressions are found for entropy, rise of entropy and dissipation of energy, and also for mechanical energy of small perturbation .

By means of simple examples the difference between systems obtained and common systems of equations of the Navier-Stokes type is discussed (Section 6).

1. The Boltzmann equation which gives a microscopic description of the motion of a rarified gas, on one hand is quite complex for analysis and on the other contains information about the behavior of the system which is too detailed from a practical point of view [1]. Therefore, customarily a less refined description of the system is applied utilizing a finite number of macroscopic quantities. In various approximations of the Chapman-Enskog [2] method the density ρ , the velocity u_i and the energy E of the gas are selected as such macroscopic variables. Here viscous tensions σ_{ij} and the heat flux Q_i do not appear as independent variables but are connected through definite relationships with derivatives of functions u_i and E . In connection with this the Chapman-Enskog method is not capable by itself to describe the relaxation process as a result of which the mentioned relationships are established. Illustrative in this respect is Maxwell's example of relaxation of tensions in a homogeneous quiescent gas. Similar limitation of the Chapman-Enskog method becomes understandable if it is taken into consideration that nonequilibrium conditions in the relaxation process must be characterized in addition to ρ, u_i and E also by other independent quantities, for example by quantities σ_{ij} and Q_i, and perhaps also by higher moments of distribution function $f(\mathbf{x}, \mathbf{v}, t)$. Here additional moments must satisfy relaxation equations which are independent of conservation equations.

In order to obtain these equations it is natural to proceed from an infinite chain of Maxwell momentum equations

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = 0, \qquad \frac{\partial \rho u_i}{\partial t} + \frac{\partial (\rho u_i u_k + P_{ik})}{\partial x_k} = 0 \tag{1.1}$$

$$\frac{\partial (P_{ik} + \rho u_i u_k)}{\partial t} + \frac{\partial (\rho u_i u_k u_l + 2Q_{ikl} + P_{ik} u_l + P_{il} u_k + P_{kl} u_i)}{\partial x_l} = J_{ik} \qquad \text{etc.}$$

$$\left(P_{ik} = \int m (v_i - u_i)(v_k - u_k) f d\mathbf{v},\ Q_{ikl} = \int {}^1\!/\!_2 m (v_i - u_i)(v_k - u_k)(v_l - u_l) f d\mathbf{v}\right)$$

which are equivalent to Boltzmann equation.

Here J_{ik} designates the moment of the tensor $v_i v_k$ with resect to the collision integral. Macroscopic approximation of the chain (1.1) is achieved by breaking it by means of one or another statistical hypothesis with regard to the form of the distribution function.

If a certain number of selected moments is retained when the chain is broken, the higher moments should be expressed through the selected ones. This is achieved, as a rule, through the selection of distribution function which depends on the selected moments as parameters. Here the independent effect of higher moments on the development of the process is neglected.

This is Grad's approach. It utilizes the statistical hypothesis according to which the distribution function of molecules is represented by a finite section of a series in orthogonal Hermite functions where the number of terms corresponds to the number of selected moments in a given approximation.

Grad's method suffers from some deficiencies. Being tied to a certain orthogonal system of functions, it cannot be immediately generalized to a polyatomic or degenrate gas. In each new case a selection is required of an appropriate orthogonal system of functions and Grad's method does not provide a principle for such a selection.

A second deficiency of the method lies in the following circumstance. If the local entropy is computed by means of Grad's distribution as a function of selected moments, then it is not possible to obtain from Grad's equations as a consequence or corollary, equations of the type that would give a balance of this entropy. As a result of this it turns out impossible to prove the increase of Grad's total entropy with time for an isolated gas.

The statistical hypothesis examined below does not have the deficiencies mentioned but at the same time for monatomic gases shows little practical difference from Grad's. This hypothesis consists in that among all distributions with one and the same values of selected moments of a given approximation with maximum entropy is selected. On dehalf of this hypothesis the following purely heuristic considerations can be presented. The system of equations for selected moments is capable to describe reality with some degree of probability only in the case when the real distribution function varying according to the Boltzmann equation will be able to adjust itself at least approximately to the statistical hypothesis. This indicates that the characteristic time of change θ of an arbitrary distribution function is much smaller than the time interval Δt of the least noticeable change of selected moments. In the opposite case there would be no basis to assume that the distribution correspon s to any statistical hypothesis at all and it would have been necessary to utilize the Boltzmann equation, abstaining from macroscopic description. In the interval Δt the values of selected moments practically do not change, in addition to this for an isolated gas the total entropy increases with characteristic time θ ; therefore, because of the great difference between Δt and θ, it is possible to assume that towards the end of the interval of macroscopic time Δt, the entropy is able to grow to its maximum value which is compatible with practically constant values of selected moments in the interval Δt. Since limitations in the maximization of entropy have a local character (values of moments are given at each point in space occupied by the gas) a maximum of total entropy necessitates a maximum in local entropy at each point in space. The possibility of such a statistical hypothesis for the case of monatomic gas was pointed out in [4].

2. As a most lucid example serves Grad's second approximation in which the following ten moments are selected as "slow"

$$\rho = \int mf d\mathbf{v}, \qquad \rho u_i = \int m v_i f d\mathbf{v}, \qquad P_{ik} = \int m (v_i - u_i)(v_k - u_k) f d\mathbf{v} \quad (2.1)$$

Here m designates the mass of the molecule, P_{ik} designates the pressure tensor.

Utilization of only ten moments indicates that the effect of heat conductivity and, of course, the effect of higher moments are not considered.

The entropy maximum of a unit volume

$$\rho S = -k \int f \ln f \, d\mathbf{v} \quad (2.2)$$

where k is the Boltzmann constant, is readily obtained by means of Lagrange's multipliers with supplementary conditions (2.1). The maximum is reached for the function

$$f(\mathbf{x}, \mathbf{v}, t) = \frac{\rho}{m(2\pi)^{3/2}} \left(\frac{\rho^3}{\det \| P_{ik} \|} \right)^{1/2} \exp \left\{ -\frac{\rho}{2} P^{ik} (v_i - u_i)(v_k - u_k) \right\} \quad (2.3)$$

Here P^{ik} are matrix elements of the inverse of P_{ik}. Since $P_{ik} = p\delta_{ik} + \sigma_{ik}$, where $p = {}^1/_3 P_{ik}$ is the isotropic pressure, (2.3) converts to locally Maxwellian distribution for $\sigma_{ik} = 0$. If σ_{ik} is considered to be small and (2.3) is expanded in terms of σ_{ik} to the first order, the following function is obtained:

$$f_\Gamma(\mathbf{x}, \mathbf{v}, t) = \frac{\rho}{m} \frac{1}{(2\pi RT)^{3/2}} \exp\left(-\frac{(\mathbf{v} - \mathbf{u})^2}{2RT} \right) \left[1 + \frac{\sigma_{ik}}{2pRT} (v_i - u_i)(v_k - u_k) \right] \quad (2.4)$$

Here R is the gas constant and the temperature T is determined by Equation $p = \rho RT$.

Function (2.4) corresponds in accuracy to Grad's distribution for the second approximation. Thus, (2.3) improves Grad's function (2.4) only in the second order with respect to tensions. Breaking of chain (1.1) by means of (2.3) at ten moments gives the following system of equations

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = 0, \qquad \frac{\partial \rho u_i}{\partial t} + \frac{\partial (\rho u_i u_k + P_{ik})}{\partial x_k} = 0$$

$$\frac{\partial (P_{ik} + \rho u_i u_k)}{\partial t} + \frac{\partial (\rho u_i u_k u_l + P_{ik} u_l + P_{il} u_k + P_{kl} u_i)}{\partial x_l} = -\frac{p}{\mu} \sigma_{ik} \quad (2.5)$$

where μ is the coefficient of viscosity. System (2.5) coincides with the system of second approximation obtained by Grad's method. It is appropriate, however, to note that the moment of the tensor $v_i v_k$ with respect to the collision integral in the right-hand side of (2.5) has the indicated form strictly speaking only for Maxwellian molecules. For other models of molecules the right-hand side of (2.5) represents the first term of the expansion in terms of σ_{ik} for exact expression. For intermolecular force depending on a power of intermolecular distance $F \sim d^{-s}$ we can calculate by means of (2.3) a quadratic correction to the right-hand side of (2.5). This correction

$$\frac{s-5}{s-1}\frac{1}{21\mu}\left(\sigma_{jr}\sigma_{jr}\delta_{ik} - 3\sigma_{ij}\sigma_{jk}\right) \tag{2.6}$$

is two times greater than Grad's corrections computed by means of (2.4). Here the difference between (2.3) and (2.4) appears in the second order. This difference leads also to somewhat different boundary conditions of slippage. Utilizing considerations presented in [3] we can obtain with the aid of (2.3) the following boundary conditions of slippage:

$$\sigma_{1i} + \frac{2(1-\alpha)}{(1+\alpha)} u_i \left(\frac{\rho(p+\sigma_{11})}{2\pi}\right)^{1/2} = 0 \qquad (i = 2,\ 3) \tag{2.7}$$

It is assumed here that the normal to the surface element is directed along the x_1-axis in the positive direction, α is the fraction of mirror-reflected molecules, the remaining molecules are reflected diffusely. If in (2.7) the root is expanded to the first order with respect to σ_{11}, then Grad's conditions for the second approximation are obtained

$$\sigma_{1i} + \frac{2(1-\alpha)}{1+\alpha} u_i \left(\frac{\rho p}{2\pi}\right)^{1/2}\left(1 + \frac{\sigma_{11}}{2\rho}\right) = 0 \qquad (i = 2,\ 3) \tag{2.8}$$

Expansion (2.4) of function (2.3) was utilized in [5] to obtain conditions of slippage (2.8), here the author limited himself to the zero order, neglecting $\frac{1}{2}\sigma_{11}/p$.

From Equation (2.2) with the aid of (2.3) the expression of entropy is readily obtained through macroscopic parameters

$$S = -\,{}^5/_2 R \ln \rho + {}^1/_2 R \ln \det \|P_{ik}\| \tag{2.9}$$

At equilibrium $P_{ik} = p\delta_{ik}$ and (2.9) converts into the equilibrium expression for entropy. The change of entropy with time is examined by means of (2.5). Utilizing the relationship $d \ln \det \|P_{ik}\| = P^{ik} dP_{ik}$ the following is easy to obtain from (2.5) and (2.9)

$$\rho \frac{dS}{dt} = \frac{\partial \rho S}{\partial t} + \frac{\partial \rho S u_i}{\partial x_i} = \frac{R}{6}\frac{\rho p}{\mu}\left[P_{kk}P^{ll} - 9\right] \tag{2.10}$$

Let p_1, p_2 and p_3 be eigenvalues of the positively singular matrix P_{ik}. Then the components of the quantity P^{ik} will be p_1^{-1}, p_2^{-1} and p_3^{-1}.

From this

$$P_{kk}P^{ll} - 9 = (p_1 + p_2 + p_3)\left(\frac{1}{p_1} + \frac{1}{p_2} + \frac{1}{p_3}\right) - 9 =$$

$$= \left[\left(\frac{p_1}{p_2}\right)^{1/2} - \left(\frac{p_2}{p_1}\right)^{1/2}\right]^2 + \left[\left(\frac{p_1}{p_3}\right)^{1/2} - \left(\frac{p_3}{p_1}\right)^{1/2}\right]^2 + \left[\left(\frac{p_2}{p_3}\right)^{1/2} - \left(\frac{p_3}{p_2}\right)^{1/2}\right]^2$$

Therefore, the right-hand side of (2.10) is nonnegative and equalt to zero only if $P_{ik} = p\delta_{ik}$. If now (2.10) is integrated over the volume of the gas and if it is taken into account that $u_n = 0$ at the boundary, we obtain that the total entropy can only increase.

It is easy to see that just as in the derivation of (2.5) the thermal conductivity was not taken into account. In (2.10) the flow entropy term related to thermal conductivity is absent and the gas automatically turns out to be thermally isolated from surroundings.

It is not difficult to show that (2.9) is the only entropy corresponding to system (2.5). Speaking more precisely, if the following requirements are placed on $S(\rho, P_{ik})$:

a) as a consequence of (2.5) a balance (of the type (2.10)) is applicable which permits to establish the increase of total entropy;

b) in the equilibrium condition the expression for S converts into the known form for equilibrium entropy, then the function $S(\rho, P_{ik})$ coincides with (2.9). In fact, by virtue of (2.5)

$$\rho\frac{dS}{dt} = -\rho\left(2P_{kl}\frac{\partial S}{\partial P_{ik}} + P_{jk}\frac{\partial S}{\partial P_{jk}}\delta_{il} + \rho\frac{\partial S}{\partial \rho}\delta_{il}\right)\frac{\partial u_i}{\partial x_l} - \frac{\rho p\sigma_{jk}}{\mu}\frac{\partial S}{\partial P_{jk}} \qquad (2.11)$$

It is apparent that for given ρ and P_{ik} we can select u_i so that the integral of the right-hand side over the volume will have any sign, with the exception of the case when

$$2P_{kl}\frac{\partial S}{\partial P_{ik}} + P_{jk}\frac{\partial S}{\partial P_{jk}}\delta_{il} + \rho\frac{\partial S}{\partial \rho}\delta_{il} = 0 \qquad (2.12)$$

From (2.12) it is easy to obtain (taking first the trace of (2.12)) that

$$\frac{\partial S}{\partial P_{ik}} = -\frac{1}{5}\rho\frac{\partial S}{\partial \rho}P^{ik} \qquad (2.13)$$

From here

$$dS = -\frac{1}{5}\rho\frac{\partial S}{\partial \rho}\,d\,[\ln\det\|P_{ik}\| - 5\ln\rho], \qquad \text{or} \qquad S = F(\ln\det\|P_{ik}\| - 5\ln\rho)$$

Condition (b) now permits to determine the form of function F and to establish that S coincides with (2.9).

In this way only the hypothesis of maximum entropy gives the correct expression of entropy (2.9) uniquely corresponding to system (2.5). Expansion of (2.9) with respect to σ_{ik} to second order gives

$$S = -{}^5/_2R\ln\rho + {}^3/_2R\ln p - {}^1/_4R\sigma_{ik}\sigma_{ik}p^{-2} \qquad (2.14)$$

By means of (2.4), however, even the quadratic correction $(-\frac{1}{4}R\sigma_{ik}\sigma_{ik}p^{-2})$ to equilibrium entropy turns out incorrectly.

Expnding the right-hand side of (2.10) with respect to σ_{ik} near equilibrium, it is easy to obtain that the entropy increase in unit of volume is equal to $\frac{1}{2}\sigma_{ik}\sigma_{ik}/\mu T$ and the energy dissipation per unit volume is

$$\rho T\frac{dS}{dt} = \frac{\sigma_{ik}\sigma_{ik}}{2\mu} \qquad (2.15)$$

Small perturbations of the state at rest with density ρ_0 and pressure p_0 will be examined. Linearization of (2.5) gives

$$\frac{\partial\rho}{\partial t}+\rho_0\frac{\partial u_k}{\partial x_k}=0,\qquad \rho_0\frac{\partial u_i}{\partial t}+\frac{\partial p}{\partial x_i}+\frac{\partial\sigma_{ik}}{\partial x_k}=0 \tag{2.16}$$

$$\frac{\partial p}{\partial t}+\frac{5}{3}p_0\frac{\partial u_k}{\partial x_k}=0,\qquad \frac{\partial\sigma_{ik}}{\partial t}+p_0\left(\frac{\partial u_i}{\partial x_k}+\frac{\partial u_k}{\partial x_i}-\frac{2}{3}\delta_{ik}\frac{\partial u_l}{\partial x_l}\right)+\frac{p_0}{\mu}\sigma_{ik}=0$$

The second equation is multiplied by u_i, the third by $^3/_5 p/p_0$, and fourth by $\frac{1}{2}\sigma_{ik}/p_0$ and these equations are added. If the relationship $p = {}^5/_3 p_0\rho/\rho_0$ which is not violated by (2.16), is utilized, it is easy to obtain that

$$\frac{\partial}{\partial t}\left\{\frac{\rho_0\mathbf{u}^2}{2}+\frac{5}{6}\frac{p_0}{\rho_0^2}\rho^2+\frac{\sigma_{ik}\sigma_{ik}}{4p_0}\right\}+\frac{\partial\,(p\delta_{ik}+\sigma_{ik})\,u_i}{\partial x_k}+\frac{\sigma_{ik}\sigma_{ik}}{2\mu}=0 \tag{2.17}$$

The second term in (2.17) is the work of perturbation per unit time, the third term by virtue of (2.15) is the energy dissipation. Therefore the expression under the differential sign with respect to time should be identified with mechanical energy of perturbation so that (2.17) represents a balance of mechanical perturbation energy. The first two terms in the expression for mechanical energy are well known equilibrium energy terms of the sonic wave, the third member is energy which is due to nonequilibrium viscous process.

If the collision integral contains a large parameter, then μ can be formally considered a small parameter. Expanding the solution in series with respect to the small parameter, we obtain from (2.16) in the first approximation

$$\sigma_{ik}=-\mu\left(\frac{\partial u_i}{\partial x_k}+\frac{\partial u_k}{\partial x_i}-\frac{2}{3}\delta_{ik}\frac{\partial u_l}{\partial x_l}\right) \tag{2.18}$$

Entropy increase then converts into an expression which corresponds to thermodynamics of irreversible process

$$\rho\frac{dS}{dt}=\frac{\mu}{2T}\sum_{i,\,k}\left(\frac{\partial u_i}{\partial x_k}+\frac{\partial u_k}{\partial x_i}-\frac{2}{3}\delta_{ik}\frac{\partial u_l}{\partial x_l}\right)^2$$

3. In order to account for thermal conductivity it is necessary in addition to (2.1) to select also moments which correspond to heat flow

$$Q_i=\int\frac{m\,(v_i-u_i)\,(\mathbf{v}-\mathbf{u})^2}{2}\,f\,d\mathbf{v} \tag{3.1}$$

In the application of the presented method in this case some peculiarities arise. Traces of this peculiarity are already evident in Grad's distribution function for the 13-moment approximation

$$f=f_0\left\{1+\frac{\sigma_{ij}}{2pRT}(v_i-u_i)(v_j-u_j)-\frac{Q_i\,(v_i-u_i)}{pRT}\left[1-\frac{(\mathbf{v}-\mathbf{u})^2}{5RT}\right]\right\} \tag{3.2}$$

where f_0 is Maxwell's distribution. For sufficiently large v_i (with respect to modulus) the function (3.2) becomes negative. This circumstance apparently does not introduce substantial difficulties if Q_i are sufficiently small. The point is that for an isolated gas with the total energy H the velocity of molecules is limited: $\mathbf{v}^2\leqslant 2H/m$. In this region of velocities for sufficiently small Q_i, (3.2) will be positive. Outside of this region f_0 turns to be quite small so that negative values of f practically have no influence and Equation (3.2) can be used over infinite range of velocities. Maximization of entropy in the region $-(2H/m)^{1/2} \leqslant v_i \leqslant (2H/m)$ with supplementary conditions (2.1) and (3.1) leads to the function

$$f = c \exp\left[-\alpha_i (v_i - u_i)(\mathbf{v} - \mathbf{u})^2 - \beta (\mathbf{v} - \mathbf{u})^2 - \gamma_{ik} (v_i - u_i)(v_k - u_k)\right] \quad (3.3)$$

In utilizing (3.3) it is necessary to take into account the limitation of velocity since over the infinite range (3.3) cannot be integrated at all. For sufficiently small α_i and γ_{ik} we can expand (3.3) in the indicated region to first order with respect to these quantities and to utilize this expansion in the infinite range. If now α_i, β, γ_{ik} and c are related to the selected moments by means of (2.1) and (3.1), then Equation (3.2) is obtained. Grad's function (3.2), just as in the case of ten moments, in principle does not permit to compute even quadratic corrections to entropy. The advantage of (3.3) consists in the possibility to expand this expression to higher orders with respect to α_i and γ_{ik}. In this way it is possible to obtain the entropy for example to third order

$$S = -\frac{5}{2} R \ln \rho + \frac{3}{2} R \ln p - \frac{1}{4} R \frac{\sigma_{ik}\sigma_{ik}}{p^2} + \frac{1}{6} R \frac{\sigma_{ik}\sigma_{kl}\sigma_{li}}{p^3} - \\ - \frac{R}{5} \frac{\rho Q_i Q_i}{p^3} + \frac{9R}{25} \frac{\rho \sigma_{ik} Q_i Q_k}{p^4} \quad (3.4)$$

By virtue of 13-moment equations [3] the following balance for S is applicable with accuracy to second order:

$$\frac{\partial \rho S}{\partial t} + \frac{\partial\, \rho S u_i}{\partial x_i} + \frac{\partial}{\partial x_i}\left[\frac{Q_i}{T} - \frac{2}{5}\frac{\sigma_{il} Q_i}{pT}\right] = \frac{\sigma_{ik}\sigma_{jk}}{2\mu T} + \frac{Q_i Q_i}{\varkappa T^2} \quad (3.5)$$

where $\varkappa$ is the coefficient of thermal conductivity.

The balance for mechanical energy of small perturbation has in virtue of linearized 13-moment equations the form

$$\frac{\partial}{\partial t}\left\{\frac{\rho_0 \mathbf{u}^2}{2} + \frac{5}{6}\frac{p_0}{\rho_0^2}\rho^2 + \frac{3}{4p_0}\left[p - \frac{5}{3}\frac{p_0}{\rho_0}\rho\right]\left[p - \frac{1}{3}\frac{p_0}{\rho_0}\rho\right] + \frac{\sigma_{ik}\sigma_{ik}}{4p_0} + \frac{\rho_0}{5p^2_0} Q_i Q_i\right\} + \\ + \frac{\partial}{\partial x_j}\left\{u_i (p\delta_{ij} + \sigma_{ij}) + \frac{2}{5p_0}\sigma_{ij} Q_i + \frac{T}{T_0} Q_j\right\} + \frac{\sigma_{ij}\sigma_{ij}}{2\mu} + \frac{Q_i Q_i}{\varkappa T_0} = 0 \quad (3.6)$$

The term containing square brackets in the expression for mechanical energy is due to the fact that in the presence of thermal conductivity the nonadiabatic nature of the process in an element of gas appears already in the first order with respect to deviations.

4. To begin a study of a gas consisting of molecules with internal degrees of freedom, we examine at first the case of rough spherical molecules. If the process of second viscosity turns out to be determining, then in the number of selected moments it is necessary to include separately, for example, the translational energy

$$\rho = \int m f d\mathbf{v} d\boldsymbol{\omega}, \qquad \rho u_i = \int m v_i f d\mathbf{v} d\boldsymbol{\omega}$$

$$\rho E = \int [{}^1/_2 m (\mathbf{v} - \mathbf{u})^2 + {}^1/_2 I \boldsymbol{\omega}^2] f d\mathbf{v} d\boldsymbol{\omega}, \qquad \rho \Pi = \int {}^1/_2 m (\mathbf{v} - \mathbf{u})^2 f d\mathbf{v} d\boldsymbol{\omega} \quad (4.1)$$

Here $\boldsymbol{\omega}$ is the angular velocity of the molecule, I is its moment of inertia and Π is the translational part of energy. The entropy maximum for conditions (4.1) is achieved with the following function

$$f = \frac{\rho}{(2\pi)^3} m^{1/2} (I\alpha\beta)^{3/2} \exp\left[-\frac{m\alpha}{2}(\mathbf{v}-\mathbf{u})^2 - \frac{I\beta}{2}\omega^2\right]$$
$$\left(\alpha = \frac{3}{2m\Pi}, \quad \beta = \frac{3}{2m(E-\Pi)}\right) \tag{4.2}$$

Here the internal and translational degrees of freedom are at different temperatures which corresponds to the assumption expressed in [6]. Equations analogous to (4.1) and (4.2) can be readily written for any concrete form of internal degrees of freedom. In the general case it is convenient to introduce instead of E and Π, equilibrium pressure $p = (\gamma - 1)\rho E$ and a kinetic increment $\varepsilon = \rho\,[{}^2/_3\Pi - (\gamma - 1)E]$, where $\gamma = c_p / c_v$ is the adiabatic exponent for the given model of molecule. With the aid of the function of maximum entropy the chain of momentum equations which is obtained from the Boltzmann equation corresponding to the given model, is broken and this leads to a system of equations of relaxational gas dynamics

$$\frac{\partial\rho}{\partial t} + \frac{\partial\rho u_i}{\partial x_i} = 0, \qquad \rho\frac{\partial u_i}{\partial t} + \rho u_k\frac{\partial u_i}{\partial x_k} + \frac{\partial(p+\varepsilon)}{\partial x_i} = 0$$
$$\frac{\partial p}{\partial t} + \frac{\partial p u_i}{\partial x_i} + (\gamma - 1)(p+\varepsilon)\frac{\partial u_i}{\partial x_i} = 0 \tag{4.3}$$
$$\frac{\partial\varepsilon}{\partial t} + \frac{\partial\varepsilon u_i}{\partial x_i} + \left(\frac{5}{3} - \gamma\right)(p+\varepsilon)\frac{\partial u_i}{\partial x_i} + \frac{\varepsilon}{\tau} = 0$$

For the model of rough spheres $\gamma = {}^4/_3$ and the relaxation time τ can be computed exactly

$$\frac{1}{\tau} = \frac{32}{3}\frac{\sigma^2\sqrt{\pi}}{m}\frac{K}{(K+1)^2}\sqrt{\rho(p+\varepsilon)} \qquad \left(K = \frac{I}{m\sigma^2}\right) \tag{4.4}$$

Here σ is the diameter of the molecule. If near equilibrium ε is neglected in comparison to p, then (4.4) coincides with the expression obtained by Kohler [2]. For an arbitrary model of a molecule the calculation of τ in explicit form is difficult. For small ε, τ can be considered a function of ρ and p only and accounted for phenomenologically.

From the function of maximum entropy we can obtain the expression for entropy in terms of ρ, p and ε

$$S = \frac{3}{2}R\ln(p+\varepsilon) + \frac{5-3\gamma}{2(\gamma-1)}R\ln\left[p - \frac{3(\gamma-1)}{5-3\gamma}\varepsilon\right] - \frac{\gamma}{\gamma-1}R\ln\rho \tag{4.5}$$

From inequalities $0 < \Pi < E$ it follows that the expression under the logarithms are positive. Because of (4.3) the following entropy balance is applicable:

$$\frac{\partial\rho S}{\partial t} + \frac{\partial\rho S u_i}{\partial x_i} = \frac{R\rho\varepsilon^2}{\tau\,({}^5/_3 - \gamma)(p+\varepsilon)\,[p - 3\varepsilon(\gamma-1)/(5-3\gamma)]} \tag{4.6}$$

Just as in the case of the 10-moment equations we can verify that the entropy (4.5) uniquely corresponds to system (4.3). Linearization of (4.3) gives

$$\frac{\partial \rho}{\partial t} + \rho_0 \frac{\partial u_i}{\partial x_i} = 0, \qquad \rho_0 \frac{\partial u_i}{\partial t} + \frac{\partial (p+\varepsilon)}{\partial x_i} =$$

$$\frac{\partial p}{\partial t} + \gamma p_0 \frac{\partial u_i}{\partial x_i} = 0, \qquad \frac{\partial \varepsilon}{\partial t} + \left(\frac{5}{3} - \gamma\right) p_0 \frac{\partial u_i}{\partial x_i} + \frac{\varepsilon}{\tau_0} = 0 \tag{4.7}$$

If τ_0 is a small parameter then expanding the solution formally in series with respect to τ_0 we obtain in the first approximation the common relationship

$$\varepsilon = -\xi\, \partial u_i / \partial x_i \qquad (\xi = (^5/_3 - \gamma)\, p_0 \tau_0) \tag{4.8}$$

Here ξ is the coefficient of second viscosity.

Because of (4.6) the entropy increase per unit volume with accuracy to second order with respect to ε is equal to $\varepsilon^2/\xi T_0$, and energy dissipation is equal to ε^2/ξ. Multiplying the second equation of system (4.7) by u_i, the third by $p/\gamma p_0$, the fourth by $\varepsilon/(^5/_3 - \gamma)p_0$ and adding, we obtain the balance of mechanical energy of perturbation

$$\frac{\partial}{\partial t}\left[\frac{\rho_0 \mathbf{u}^2}{2} + \frac{\gamma p_0}{2\rho_0^2}\rho^2 + \frac{\varepsilon^2}{2(^5/_3 - \gamma)p_0}\right] + \frac{\partial (p+\varepsilon) u_i}{\partial x_i} + \frac{\varepsilon^2}{\xi} = 0 \tag{4.9}$$

In the case where τ_0 is the small parameter, i.e. the relationship (4.8) exists, Equation (4.9) converts to the usual balance of energy in a sound wave for the process of second viscosity.

In order to take into account processes of first and second viscosity simultaneously, it is necessary to introduce into (4.1) the following expression in place of $\rho\Pi$

$$P_{ik} = (p + \varepsilon)\,\delta_{ik} + \sigma_{ik} = \int m\,(v_i - u_i)(v_k - u_k)\, f d\mathbf{v} d\boldsymbol{\omega}$$

Here p is the pressure connected with energy E by an equilibrium relationship, ε is the kinetic increment due to second viscosity and σ_{ik} is the tension characterizing the process of first viscosity.

Maximizing the entropy and breaking the corresponding chain of momentum equations with the aid of the obtained distribution, we arrive at the system

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = 0, \qquad \rho \frac{\partial u_i}{\partial t} + \rho u_k \frac{\partial u_i}{\partial x_k} + \frac{\partial (p\delta_{ik} + \varepsilon\delta_{ik} + \sigma_{ik})}{\partial x_k} = 0$$

$$\frac{\partial p}{\partial t} + \frac{\partial p u_i}{\partial x_i} + (\gamma - 1)\left[(p+\varepsilon)\,\delta_{ik} + \sigma_{ik}\right]\frac{\partial u_i}{\partial x_k} = 0$$

$$\frac{\partial \sigma_{ik}}{\partial t} + \frac{\partial \sigma_{ik} u_l}{\partial x_l} + \sigma_{kl}\frac{\partial u_i}{\partial x_l} + \sigma_{il}\frac{\partial u_k}{\partial x_l} - \frac{2}{3}\delta_{ik}\sigma_{rs}\frac{\partial u_r}{\partial x_s} +$$

$$+ (p+\varepsilon)\left[\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} - \frac{2}{3}\delta_{ik}\frac{\partial u_l}{\partial x_l}\right] + \frac{p\sigma_{ik}}{\mu} = 0 \tag{4.10}$$

$$\frac{\partial \varepsilon}{\partial t} + \frac{\partial \varepsilon u_l}{\partial x_l} + \left(\frac{5}{3} - \gamma\right)\left[(p+\varepsilon)\,\delta_{ik} + \sigma_{ik}\right]\frac{\partial u_i}{\partial x_k} + \frac{1}{\xi}\left(\frac{5}{3} - \gamma\right) p\varepsilon = 0$$

In (4.10) moments with respect to collision integral are accounted for to the first order in ε and σ_{ik}. Phenomenological coefficients μ and ξ

are computed only in exceptional cases of molecular models. Entropy per unit mass corresponding to system (4.10) turns out to be equal to

$$S = \frac{R}{2}\ln\det\|P_{ik}\| + R\,\frac{5-3\gamma}{2(\gamma-1)}\ln\left[p-\frac{3(\gamma-1)}{5-3\gamma}\,\varepsilon\right] - \frac{R\gamma}{\gamma-1}\ln\rho \qquad (4.11)$$

From the system which is obtained by linearization of (4.10) it is easy to deduce the balance for mechanical energy of perturbation

$$\frac{\partial}{\partial t}\left[\frac{\rho_0\mathbf{u}^2}{2}+\frac{\gamma p_0}{2\rho_0^2}\,\rho^2+\frac{\sigma_{ik}\,\sigma_{ik}}{4p_0}+\frac{\varepsilon^2}{2\,(^5/_3-\gamma)^{l}p_0}\right]+$$
$$+\frac{\partial\,(p\delta_{ik}+\varepsilon\delta_{ik}+\sigma_{ik})\,u_i}{\partial x_k}+\frac{\sigma_{ik}\,\sigma_{ik}}{2\mu}+\frac{\varepsilon^2}{\xi}=0 \qquad (4.12)$$

To the usual expression of sound wave energy terms are added here which are due to nonequilibrium processes of first and second viscosity.

5. As an example of application of the method to a degenerate gas we will examine thermal conductivity of a simple lattice of dielectric. Let $\omega_{\mathbf{k}}^{l}$ (l = 1, 2, 3) be the dependence of characteristic frequencies of the crystal on the wave vector **k** for three values of polarization of displacement wave. If $n_{\mathbf{k}}^{l}$ is the number of phonons with the wave vector **k** and polarization l, energy and flow of heat are written in the form [7]

$$E = \sum_{l,\mathbf{k}}\langle n_{\mathbf{k}}^{l}\rangle\, h\omega_{\mathbf{k}}^{l} = \sum_{n} W(\ldots, n_{\mathbf{k}}^{l}, \ldots)\sum_{l,\mathbf{k}} n_{\mathbf{k}}^{l} h\omega_{\mathbf{k}}^{l}$$
$$Q_i = \sum_{l,\mathbf{k}}\langle n_{\mathbf{k}}^{l}\rangle\, h\omega_{\mathbf{k}}^{l}\frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_i} = \sum_{n} W(\ldots, n_{\mathbf{k}}^{l}, \ldots)\sum_{l,\mathbf{k}} n_{\mathbf{k}}^{l} h\omega_{\mathbf{k}}^{l}\frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_i} \qquad (5.1)$$

where $W(\ldots, n_{\mathbf{k}}^{l}, \ldots)$ is the probability of given distribution of phonon numbers, and $\langle n_{\mathbf{k}}^{l}\rangle$ is the average number of phonons. In (5.1) the summation over all $n_{\mathbf{k}}^{l}$ is carried out over integers from 0 to ∞ in accordance with Bose-Einstein statistics for phonons. Maximizing the entropy $-k\,\langle\ln W\rangle$ under conditions (5.1) we obtain

$$W(\ldots, n_{\mathbf{k}}^{l}, \ldots) = \prod_{n} C_{\mathbf{k}}^{l}\exp\left[-\left(\beta h\omega_{\mathbf{k}}^{l}+\sum_{i}\alpha_i h\omega_{\mathbf{k}}^{l}\frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_i}\right)n_{\mathbf{k}}^{l}\right] \qquad (5.2)$$

where β and α_i are Lagrange's multipliers, and $C_{\mathbf{k}}^{l}$ is a normalizing constant. It is evident from (5.2) that $n_{\mathbf{k}}^{l}$ are independent. Taking into consideration normalization of probability to one, it is easy to obtain from (5.2) that

$$\langle n_{\mathbf{k}}^{l}\rangle = \left[\exp\left(\beta h\omega_{\mathbf{k}}^{l}+\sum_{i}\alpha_i h\omega_{\mathbf{k}}^{l}\frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_i}\right)-1\right]^{-1} \qquad (5.3)$$

For $\alpha_i = 0$ this equation converts to Bose equilibrium distribution for phonons. In (5.3) quantities β and α_i are expressed with the aid of (5.1) through macroscopic parameters E and Q. From kinetic equation [7]

$$\frac{\partial\langle n_{\mathbf{k}}^{l}(\mathbf{x})\rangle}{\partial t}+\sum_{i=1}^{3}\frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_i}\frac{\partial\langle n_{\mathbf{k}}^{l}(\mathbf{x})\rangle}{\partial x_i} = J_{\mathbf{k}}^{l} \qquad (5.4)$$

where $J_{\mathbf{k}}^{l}$ is the "collision integral" of phonons due to nonharmonic members in the potential energy, impurities and other defects in crystal structure, follows the chain of equations

$$\frac{\partial E}{\partial t}+\frac{\partial Q_i}{\partial x_i}=0, \qquad \frac{\partial Q_i}{\partial t}+\frac{\partial T_{ij}}{\partial x_j}=L_j \qquad \text{etc.} \qquad (5.5)$$

Here

$$T_{ij}(\mathbf{x}) = \sum_{l\mathbf{k}} \hbar\omega_{\mathbf{k}}^{l} \frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_i} \frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_j} \langle n_{\mathbf{k}}^{l}(\mathbf{x})\rangle, \qquad L_i = \sum_{l,\mathbf{k}} \hbar\omega_{\mathbf{k}}^{l} \frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_i} J_{\mathbf{k}}^{l}$$

Cutting off system (5.5) is accomplished by means of (5.3). An explicit form of dependence of T_{ij} on E and Q_i can be obtained in some limiting cases. The heat flux will be considered small and only the linear approximation to the system will be written out. In addition we will limit ourselves to cases of low temperatures (large β). In this case only small frequencies $\omega_{\mathbf{k}}^{l}$ are important. Let

$$\theta_i^{l}(\mathbf{n}) = \lim_{\mathbf{k}\to 0} \frac{\partial\omega_{\mathbf{k}}^{l}}{\partial k_i}$$

where $\mathbf{k} \to 0$ in direction prescribed bu the unit vector $\mathbf{n}$. At low frequencies the number of oscillations in the solid angle $d\mathbf{n}$ of reciprocal space $\sim\omega^2$, i.e.

$$Z^{l}(\omega, \mathbf{n})\, d\mathbf{n} = a^{l}(\mathbf{n})\, \omega^2\, d\mathbf{n}$$

It is easy to show that then $T_{ij} = A_{ij}E$, where

$$A_{ij} = \sum_{l} \int \theta_i^{l}\theta_j^{l} a^{l} d\mathbf{n} \quad \Big(\sum_{l} \int a^{l} d\mathbf{n}\Big)^{-1} \tag{5.6}$$

The system of equations for thermal conductivity at low temperatures is written in the form

$$\frac{dE}{dt} + \operatorname{div}\mathbf{Q} = 0, \qquad \frac{\partial\mathbf{Q}}{\partial t} + A \operatorname{grad} E + c_v A \lambda^{-1}\mathbf{Q} = 0 \tag{5.7}$$

In (5.7) the thermal conductivity tensor λ is taken into account phenomenologically. According to (5.6) tensor A depends only on properties of the lattice. If the relaxation time is small (for definite frequencies of change in physical parameters), the term $\partial\mathbf{Q}/\partial t$ can be neglected so that

$$\mathbf{Q} = -c_v^{-1}\lambda \operatorname{grad} E = -\lambda \operatorname{grad} T \tag{5.8}$$

Therefore the first equation of system (5.7) transforms into the common equation of thermal conductivity in a solid. However at low temperatures cases may be encountered when the length of free path is great and it is necessary to use the complete system of equations (5.7).

Entropy S with accuracy to second order with respect to $\mathbf{Q}$ has the form

$$S = S_0(E) + \frac{1}{2}\frac{\partial^2 S_0}{\partial E^2}(A^{-1}\mathbf{Q}, \mathbf{Q}) = S_0 - \frac{1}{2c_v T}(A^{-1}\mathbf{Q}, \mathbf{Q}) \tag{5.9}$$

where $S_0(E)$ is the equilibrium entropy [7], A^{-1} is a tensor, reciprocal of A, the parantheses indicate scalar product. By virtue of (5.7) entropy balance (5.9) is applicable with accuracy to second order

$$\frac{\partial S}{\partial t} + \operatorname{div}\frac{\mathbf{Q}}{T} = \frac{1}{T^2}(\lambda^{-1}\mathbf{Q}, \mathbf{Q}) \tag{5.10}$$

If relationship (5.8) exists, then (5.10) transforms into the common entropy balance which is given by thermodynamics of irreversible processes for the case of thermal conductivity in a solid body.

6. The hypothesis examined has the character of a recipe and therefore definite conclusions cannot be drawn with respect to the region of applicability of equations obtained. Their value has to be judged by studying their properties. It was shown that these equations correspond to definite expressions for nonequilibrium entropy. The entropy balance resulting directly from these equations permits to compute energy dissipation. In the case of small perturbations the possiblity exists to determine the nonequilibrium expression of mechanical energy and to derive the equation for its balance.

In the low-frequency process when the time of relaxation can be considered small, equations and balances mentioned transform into known equations and balances corresponding to thermodynamics of irreversible processes. Therefore it is interesting to examine high-frequency processes:

A plane monochromatic wave satisfies system (4.7) if frequency ω and wave number k are related by the dispersion relation

$$k = \omega \sqrt{1 - i\omega\tau_0}\,(\gamma p_0 / \rho_0 - 5i\omega p_0\tau_0 / 3\rho_0)^{-1/2} \qquad (6.1)$$

From (6.1) it is evident that waves with high frequencies have a velocity which approaches $\sqrt{5/_3\, p_0 / \rho_0}$. This is a physically natural result since high frequency oscillations are not able to excite internal degrees of freedom and molecules appear here like rigid spheres. The usual equations for second viscosity which take into account (4.8) yield in this respect to system (4.7).

As another example we examine small fluctuations of a plate which confines a semi-infinite volume with gas in its own plane. In this case a decaying transverse wave propagates into the gas. Application of Navier-Stokes equations, as is well known [8], yields the following expression for the depth of penetration of a wave with frequency ω

$$\delta = \sqrt{2\mu / \rho_0\omega} \qquad (6.2)$$

Equation (6.2) shows that $\delta \to 0$ for $\omega \to \infty$, i.e. high frequencies are "pushed out" to the surface. For the given problem the following system is easily obtained from (2.16)

$$\rho_0 \frac{\partial u_1}{\partial t} + \frac{\partial \sigma_{12}}{\partial x_2} = 0, \qquad \frac{\partial \sigma_{12}}{\partial t} + p_0 \frac{\partial u_1}{\partial x_2} + \frac{p_0}{\mu}\sigma_{12} = 0 \qquad (6.3)$$

where subscript 1 designates direction of oscillation of the plate and 2 the direction normal to the plate. The dispersion relationship for system (6.3) connecting real ω with complex k has the form

$$p_0 k^2 = \rho_0\omega\,(\omega + ip_0 / \mu) \qquad (6.4)$$

From (6.4) it follows that

$$\delta = (\operatorname{Im} k)^{-1} \to 2\mu / \sqrt{\rho_0 p_0} \sim L \quad \text{for } \omega \to \infty \qquad (6.5)$$

where L is the length of free path. Qualitatively this result appears quite natural. In this fashion we see that even through equations of Grad's type describe the gas as a continuous medium they are capable of showing (at least qualitatively) effects which occur at distances of the order of the length of free path. An analogous comparison of system (5.7) and the usual Fourier equation can be made for the case of high frequency wave of thermal conductivity in a solid.

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