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The Hydrodynamic Equations for Di-Atomic , Excited und Dissociated Gases  
as Approximations of the BOLTZMANN Equations Describing such Gases .

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## Introduction

There are two ways of finding the laws which describe the macroscopic behaviour of gas flows. The phenomenological method proceeds from experiments and takes the state variables, which describe the flow completely, from the experimental results. The simplest laws which connect these state variables are found by an Ansatz which puts each vector quantity (scalars or tensors) proportional to all possible vector quantities (scalars or tensors) that can be performed by the state variables. The proportional factors which enter into these relations are taken from the experiment, too. To these equations the equations for the conservation of mass, momentum and energy are added. The simplest equations which can be obtained in this way are the EULER equations and the NAVIER-STOKES equations for monoatomic gases.

On the other hand it should be possible to derive these equations from the microscopic structure of the gas. Thus the "material constants" in these equations should result from the properties of the molecules which form the gas.

Experience demonstrates that many phenomena in gases of low density can be described by BOLTZMANN's integro-differential equation. The properties of the gas to be described by this equation enter by the binary collision cross-sections of the gas molecules only. The BOLTZMANN equation describes more phenomena than the macroscopic hydrodynamic equations do. If one wants such hydrodynamic equations from the microscopic point of view one has to solve the BOLTZMANN equation under certain restrictions which one has to find from the experiment. This was done for two different methods by CHAPMAN-ENSKOG [1] and GRAD [2] for monoatomic gases. Both methods lead to the NAVIER-STOKES equations resp. to more complicated equations which represent a higher approximation but which belong likewise to the type of hydrodynamic equations.

The method of CHAPMAN-ENSKOG has been used by WANG CHANG and UHLENBECK to solve an extended BOLTZMANN equation for excited molecules. The same method has been used by M. HEIL [4, 5] for the solution of a BOLTZMANN equation for di-atomic, reacting gases. He had to restrict himself, however, to two limiting cases, chemical equi-

librium and nearly frozen chemical equilibrium . With respect to the internal degrees of freedom of the molecules equilibrium between internal and translational temperature was assumed , i. e. the exchange of internal energy and translational energy shall be easy .

GRAD's method was applied by KOLODNER [6] to a mixture of non-reacting molecules . H. HEIL [7] treated a gas of excited molecules by extending GRAD's method . One finds hydrodynamic equations which represent in the simplest approximation just the NAVIER-STOKES equations for excited molecules . This solution is identical to that of WANG CHANG and ULENBECK [3] using the method of CHAPMAN . Beyond it one can write down a higher approximation , which is , however , so complicated that it can be applied at best to rather special flow problems .

The here presented work treats the BOLTZMANN equations for di-atomic, excited and dissociated gases given by M. HEIL [4, 5] by a generalized GRAD method . Neither chemical equilibrium nor equilibrium between the internal and the translational degrees of freedom has to be assumed . The calculation of the proportional factors is straight-forward. To simplify the evaluation of the collision integrals given in the appendix additional assumptions about the collision cross-sections have to be made . In fact , PETZOLD [8] and GROßMANN [9] neglect an angle-dependence of the collision cross-sections .

Unfortunately there exists an uncertainty with respect to the calculated cross-sections . There are no experimentally measured dissociation cross-sections. The comparison by indirect methods [7] , [10] , i. e. the comparison of experimental and theoretical results for shock wave experiments shows a strong difference . The experimental results of BYRON [10] would lead to at least 100 times larger cross-sections than the theoretical calculations give . This discrepancy is yet unsolved .

The direct experimental measurement of flow "constants" as for instance viscosity etc. of a highly heated gas is also connected with great difficulties and errors . We hope that one day one succeeds in measuring or calculating these cross-sections sufficiently good to find then from the kinetic theory both the form of the hydrodynamic equations and the numerical values of the wanted flow constants .

§ I BOLTZMANN's collision equations

The gas may consist of atoms and di-atomic molecules belonging to these atoms . We restrict ourselves to the case of the atoms being in their ground state while the molecules may be in states of different internal energy  $\epsilon_i$  . In fact , at temperatures which make possible a noticeable dissociation , the lower electronic states of the atoms are excited . Therefore we should better say that we make the assumption that the state of the shell electrons is neglected in the transition probabilities which enter into the collision integrals . Contrary to that this excitation has to be considered in the specific energy of the atoms in the hydrodynamic equations . The BOLTZMANN function of the atoms gives the number of the atoms in the velocity- and position interval , the integration over the internal energy states has already been done . For the dissociation mechanism the oscillation- and rotation state is essential . Therefore we make a similar assumption for the electronic part of the excitation of the molecules . The internal energy  $\epsilon_i$  of the molecules describes then the rotation- and oscillation state or the oscillation state alone , only . The last assumption is unessential for the following considerations , we use it , however , for the numerical evaluation of the collision integrals by introducing of corresponding models for the calculation of the cross-sections (see for instance [8, 9]) .

The possibility of ionization of atoms and molecules is disregarded . This approximation is not too bad for oxygen and nitrogen up to temperatures of  $10\,000^\circ\text{K}$  because of the high ionization energies (see [11, 12]) . We assume that the internal excitation state of the molecules be given by the energy of the state only and that it is independent on additional quantum numbers as spin , for instance . It may at least be possible to introduce such averaged transition probabilities by averaging over the additional quantum states . The BOLTZMANN equations for this problem without external fields are given in [4, 5] . Here we state the result only , which may serve as starting point for the derivation of hydrodynamical equations .

We introduce BOLTZMANN's density functions  $f_1$  for atoms and  $f_{2i}$  for molecules in the state  $\epsilon_i$  . These functions be normalized to the particle number  $n$  per  $\text{cm}^3$  after integration over the velocities .

$$f_i = f_i(\vec{r}_1, \vec{r}, t) \quad , \quad f_{ai} = f_{ai}(\vec{R}_i, \vec{r}, t, \sigma_i) \quad (1)$$

with

$$\int_{-\infty}^{+\infty} f_i d\vec{p}_i = n_i(\vec{r}) = \text{number of atoms per cm}^3$$

$$\sum_i \int_{-\infty}^{+\infty} f_{ai} d\vec{p}_i = n_m(\vec{r}) = \text{number of molecules per cm}^3 .$$

The BOLTZMANN equations are given by

$$\begin{aligned} \frac{\partial f_i}{\partial t} + \vec{p}_i \frac{\partial f_i}{\partial \vec{r}} = & \int (f_i' f_i' - f_i \bar{f}_i) \sigma_{11} d\vec{p}_1' d\vec{p}_1' d\vec{p}_1' \\ & + \sum_{j,l} \int (f_i' f_{lj} - f_i f_{lj}) \sigma_{12} d\vec{p}_j' d\vec{p}_j' d\vec{p}_j' \\ & + 3 \int (f_i' f_{ij}' - k_1 f_i \bar{f}_i \bar{f}_i) \sigma_{111}' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' \\ & + 2 \sum_{j,k} \int (f_{ij}' f_{jk}' - k_1 f_i \bar{f}_i f_{ij}') \sigma_{112}' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' \\ & + \int (k_1 f_i' \bar{f}_i' \bar{f}_i' - f_i f_{ii}) \sigma_{111}'' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{\partial f_{ai}}{\partial t} + \vec{p}_i \frac{\partial f_{ai}}{\partial \vec{r}} = & \sum_{j,k,e} \int (f_{aj}' f_{jk}' - f_{ai} \bar{f}_{ie}) \sigma_{22} d\vec{p}_j' d\vec{p}_k' d\vec{p}_e' \\ & + \int (f_{aj}' f_i' - f_{ai} f_i) \sigma_{21} d\vec{p}_j' d\vec{p}_i' d\vec{p}_i' \\ & + 2 \int_{j,k} \int (k_1 f_i' \bar{f}_i' f_{ij}' - f_{ai} \bar{f}_{ie}) \sigma_{222}' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' \\ & + \int_{j,k} \int (f_{aj}' f_{jk}' - k_1 f_{ai} f_i \bar{f}_i) \sigma_{212}' d\vec{p}_j' d\vec{p}_k' d\vec{p}_i' d\vec{p}_i' \\ & + \int (k_1 f_i' \bar{f}_i' \bar{f}_i' - f_{ai} f_i) \sigma_{211}'' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' d\vec{p}_i' \end{aligned} \quad (3)$$

where we used the abbreviation  $\vec{F}_i' = \vec{F}_i(\vec{F}_i', \tau, t)$  etc.

The following symmetry relations exist between the transition probabilities :

$$\begin{aligned}
 \sigma_{11}(\vec{p}_1, \vec{p}_1' | \vec{p}_1, \vec{p}_1') &= \sigma_{11}(\vec{p}_1, \vec{p}_1' | \vec{p}_1, \vec{p}_1') \\
 \sigma_{12}(\vec{p}_1, \vec{p}_2, \epsilon_1 | \vec{p}_1' \vec{p}_2' \epsilon_1') &= \sigma_{12}(\vec{p}_1' \vec{p}_2' \epsilon_1' | \vec{p}_1 \vec{p}_2 \epsilon_1) \\
 \sigma_{12}^{(12)}(\vec{p}_1, \vec{p}_1', \vec{p}_2, \vec{p}_2' | \vec{p}_1' \vec{p}_2' \epsilon_1' | \vec{p}_1 \vec{p}_1' \vec{p}_2) &= k_1 \sigma_{12}^{(12)}(\vec{p}_1' \vec{p}_2' \epsilon_1' | \vec{p}_1 \vec{p}_1' \vec{p}_2) \\
 \sigma_{22}^{(12)}(\vec{p}_1, \vec{p}_1', \vec{p}_2, \epsilon_1 | \vec{p}_2' \epsilon_1' \vec{p}_2' \epsilon_1') &= k_1 \sigma_{22}^{(12)}(\vec{p}_2' \epsilon_1' \vec{p}_2' \epsilon_1' | \vec{p}_1 \vec{p}_1' \epsilon_1)
 \end{aligned}
 \tag{4}$$

with  $k_1 = \left(\frac{2h}{m_1}\right)^3$

$h =$  PLANCK's constant

$m_1 =$  atom mass

Moreover , the transition probabilities are invariant against permutation of particles of the same kind . Using the conservation of energy and momentum we can still perform part of the integrations in equations (2) , (3) . The result is that instead of the transition probabilities the usual differential cross-sections would appear in these equations . The symmetries of the collision cross-sections follow from the symmetries of the transition probabilities (4) . But they are more complicated . Therefore we keep the notation (2) , (3) and perform the integration later with the explicit evaluation of certain collision integrals .

§ 2 The momentum equations

To derive the momentum equations belonging to the system (2), (3) we introduce the following vector notation :

Let  $\vec{x}$  be a vector  $\vec{x} = (x_1, x_2, x_3)$ . Then we denote with  $\vec{x}^{(n)}$  a tensor of  $n^{\text{th}}$  degree with components  $(\vec{x}^{(n)})_{i_1 \dots i_n} = x_{i_1} x_{i_2} \dots x_{i_n}$ .  $x^2$  on the contrary denotes the scalar product  $x^2 = \sum_i x_i^2 = x_i \cdot x_i$ . We use the sum convention for double indices .

We define now the following rule for the multiplication of two tensors : The product of two tensors  $A^{(n)}$ ,  $B^{(m)}$  be the sum of all different products of the components  $A_{i_1 \dots i_n}^{(n)}$  and  $B_{j_1 \dots j_m}^{(m)}$  which are obtained by a permutation of the subscripts . We have for instance for the square of the unit tensor  $\vec{\delta}$  with the components  $\delta_{ij}$  :  $\delta_{ijk}^2 = \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}$ . Because of the symmetry of  $\vec{\delta}$  only these 3 given terms are different from one another . The product of two different , symmetrical tensors of second degree , however , has six terms .

The product  $\vec{x}^{(n)} \cdot \vec{x}^{(m)}$  consists of one term only :

$$(\vec{x}^{(n)} \cdot \vec{x}^{(m)})_{i_1 \dots i_n \dots i_{n+m}} = x_{i_1} \dots x_{i_n} \dots x_{i_{n+m}}$$

If there is no misunderstanding we omit the subscripts .

After these definitions we consider again the system (2), (3) . We use the following abbreviations for the right hand sides of (2), (3)

$$\frac{\partial f_1}{\partial t} + \vec{F}_1 \cdot \frac{\partial f_1}{\partial \vec{r}} = c_1 \quad (4)$$

$$\frac{\partial f_2}{\partial t} + \vec{F}_2 \cdot \frac{\partial f_2}{\partial \vec{r}} = c_{2i} \quad (5)$$

The equations (4), (5) can be replaced by an equivalent system of moment equations . For that we multiply (4) by  $(\vec{F}_1 - \vec{u})^n$  and integrate over  $\vec{F}_1$  while (5) is multiplied by  $(\vec{F}_2 - \vec{u})^n \cdot e_i^m$ , integrated over  $\vec{F}_2$  and summed up over  $i$  .  $\vec{u}$  is for the present an arbitrary function of  $\vec{r}$  which could be chosen differently for  $f_1$  and  $f_2$  . One finds , however , that the lowest order moment equations result in simple equations , which we can give a clear interpretation , if  $\vec{u}$  is chosen as the mean mass velocity . This velocity is defined below .

We define the following abbreviations for the moments of  $f$  resp. for the collision integrals :

$$N^{(n)} = \int f_1 (\vec{p}_1 - \vec{u})^n d\vec{p}_1 \quad (6)$$

$$M^{(n, m)} = \sum_i \int f_{2i} (\vec{p}_2 - \vec{u})^n \varepsilon_i^m d\vec{p}_2$$

$$C_{(1)}^{(n)} = \int c_1 (\vec{p}_1 - \vec{u})^n d\vec{p}_1 \quad (7)$$

$$C_2^{(n, m)} = \sum_i \int c_{2i} (\vec{p}_2 - \vec{u})^n \varepsilon_i^m d\vec{p}_2$$

The subscripts of the tensors  $N^{(n)}$ ,  $M^{(n, m)}$  etc. have been omitted which means that they can be chosen arbitrarily. If a tensor is written with one or more subscripts it means that these subscripts are fixed while the others can be arbitrary. In the following moment equations we give those subscripts only, over which one has to sum up. Thus we get the general moment equations of the system (4), (5) which can be written as follows :

$$\frac{D}{Dt} N^{(n)} + \frac{D\vec{u}}{Dt} N^{(n-1)} + \frac{\partial u_i}{\partial x_i} N^{(n)} + \frac{\partial}{\partial x_i} N_i^{(n+1)} + \frac{\partial \vec{u}}{\partial x_i} N_i^{(n)} = C_{(1)}^{(n)} \quad (8)$$

$$\frac{D}{Dt} M^{(n, m)} + \frac{D\vec{u}}{Dt} M^{(n-1, m)} + \frac{\partial u_i}{\partial x_i} M^{(n, m)} + \frac{\partial}{\partial x_i} M_i^{(n+1, m)} + \frac{\partial \vec{u}}{\partial x_i} M_i^{(n, m)} = C_2^{(n, m)} \quad (9)$$

$\frac{D}{Dt}$  represents the EULER-derivative

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u_i \frac{\partial}{\partial x_i} \quad (10)$$

The lowest order moments of  $N^{(n)}$  and  $M^{(n, m)}$  can be interpreted as mean velocity, pressure tensor, heat flow vector etc. Since only a hydrodynamic approximation of the collision equations is wanted, we will need later on these lowest order moments only. Therefore we want to introduce the following special notations of some moments :

$$\begin{aligned} \int f_1 d\vec{p}_1 &= n_1 \\ \sum_i \int f_{2i} d\vec{p}_2 &= n_2 \end{aligned} \quad (11)$$

$$\int (\vec{F}_1 - \vec{u}) f_1 d\vec{F}_1 = m_1 (\vec{u}_1 - \vec{u})$$

$$\sum_i \int (\vec{F}_2 - \vec{u}) f_{2i} d\vec{F}_2 = m_2 (\vec{u}_2 - \vec{u}) \quad (12)$$

$$\int (\vec{F}_1 - \vec{u})^2 f_1 d\vec{F}_1 = \frac{1}{m_1} P^{(1)}$$

$$\sum_i \int (\vec{F}_2 - \vec{u})^2 f_{2i} d\vec{F}_2 = \frac{1}{m_2} P^{(2)} \quad (13)$$

$$\int (\vec{F}_1 - \vec{u})^3 f_1 d\vec{F}_1 = \frac{1}{m_1} S^{(1)}$$

$$\sum_i \int (\vec{F}_2 - \vec{u})^3 f_{2i} d\vec{F}_2 = \frac{1}{m_2} S^{(2)} \quad (14)$$

$$\int (\vec{F}_1 - \vec{u})^4 f_1 d\vec{F}_1 = \frac{m_1}{m_1} Q^{(1)}$$

$$\sum_i \int (\vec{F}_2 - \vec{u})^4 f_{2i} d\vec{F}_2 = \frac{m_2}{m_2} Q^{(2)} \quad (15)$$

$$\sum_i \int \varepsilon_i f_{2i} d\vec{F}_2 = m_2 \bar{\varepsilon} \quad (16)$$

$$\sum_i \int \varepsilon_i (\vec{F}_2 - \vec{u}) f_{2i} d\vec{F}_2 = \vec{q} \quad (17)$$

$$\sum_i \int \varepsilon_i (\vec{F}_2 - \vec{u})^2 f_{2i} d\vec{F}_2 = m_2 R^{(2)} \quad (18)$$

$m_0 = 2m_1$  is the mass of a molecule . Additionally we define :  
the density by

$$\rho = m_1 n_1 + m_2 n_2 \quad (19)$$

the mean mass velocity  $\vec{h}$  by  $\rho \vec{h} = m_1 n_1 \vec{u}_1 + m_2 n_2 \vec{u}_2$  (20)

the total pressure tensor by  $\mathcal{P} = \mathcal{P}^{(1)} + \mathcal{P}^{(2)}$  (21)

the total heat flow resulting from the transfer of kinetic energy by

$$\frac{1}{2} \mathcal{S} = \frac{1}{2} (\mathcal{S}^{(1)} + \mathcal{S}^{(2)}) \quad (22)$$

the kinetic energy per unit volume by

$$E_{kin} = \frac{1}{2} (\mathcal{P}_{jj}^{(1)} + \mathcal{P}_{jj}^{(2)}) \quad (23)$$

the total energy per unit mass  $e$  by

$$\rho e = E_{kin} + n_2 \bar{\epsilon} + \rho \alpha \epsilon_D^* \quad (24)$$

the flow energy per unit mass  $e$  by

$$h = e + \frac{u^2}{2} \quad (25)$$

and the degree of dissociation by

$$\alpha = \frac{m_1 n_1}{\rho} \quad (26)$$

With the notations such as pressure tensor etc. we have already interpreted the corresponding kinetic moments as hydrodynamic state variables .

By addition of (8) , (9) we find for the lowest order moments the equations of conservation for mass , momentum and energy if one considers the vanishing of the sum of the right hand sides of (8) and (9) . We have with  $\mathcal{Y}_1 = \mathcal{Y}_1(\vec{p}_1 - \vec{u})$  and  $\mathcal{Y}_2 = \mathcal{Y}_2(\vec{p}_2 - \vec{u}, \epsilon_i)$  the following result :

$$\int C_1 \mathcal{Y}_1 d\vec{p}_1 + \int C_2 \mathcal{Y}_2 d\vec{p}_2 = 0 \quad (27)$$

if  $\mathcal{Y}_i$  are quantities the sum of which is a collision invariant . This holds for the number of the atoms at a collision , their total momentum and total energy . Thus we have for  $\mathcal{Y}_1, \mathcal{Y}_2$

$$\begin{aligned} \mathcal{Y}_1 &= m_1, \quad m_1 (\vec{p}_1 - \vec{u}), \quad \frac{m_1}{2} (\vec{p}_1 - \vec{u})^2 + \frac{\epsilon_D}{2} \\ \mathcal{Y}_2 &= m_2, \quad m_2 (\vec{p}_2 - \vec{u}), \quad \frac{m_2}{2} (\vec{p}_2 - \vec{u})^2 + \epsilon_i \end{aligned} \quad (28)$$

(27) can be proved by symmetrization of the collision integrals and is given in the appendix of reference [4] .

After these remarks one finds the following conservation equations :

$$\text{for } n = 0, m = 0, \quad \rho \frac{\partial f}{\partial t} + \frac{\partial(\rho u_i)}{\partial x_i} = 0 \quad (29)$$

$$\text{for } n = 1, m = 0, \quad \rho \frac{D\bar{u}}{Dt} + \frac{\partial}{\partial x_i} P_i = 0 \quad (30)$$

$$\text{for } \begin{matrix} n = 2, n = 0 \\ \text{and } m = 1 \end{matrix} \quad \rho \frac{D\epsilon}{Dt} + \frac{\partial}{\partial x_i} \left( \frac{1}{2} S_{ikk} + q_i + \rho \alpha E_D^* (\bar{u}_i - \bar{u})_i \right) + \frac{\partial u_k}{\partial x_i} P_{ki} = 0 \quad (31)$$

Equation (31) can be transformed into an equation for the flow energy

$$\rho \frac{Dh}{Dt} + \frac{\partial}{\partial x_i} \left( \frac{1}{2} S_{ikk} + q_i + \rho \alpha E_D^* (\bar{u}_i - \bar{u})_i + u_k P_{ki} \right) = 0 \quad (32)$$

Equations (29) - (32) differ from the corresponding equations for monoatomic gases by the fact that the energy and the heat flow contain an additional term which results from the internal energy of the molecules. The possibility of dissociation leads to an additional term in the total energy which is proportional to the dissociation energy. The total heat flow contains a term which results from the diffusion of atoms resp. molecules and a following recombination resp. dissociation.

Equations (29) - (31) represent no complete system. Here we want a "hydrodynamic approximation", i. e. the quantities  $P_{ij}, S_{ikk}, q_i$  shall be dependent on the state variables  $\rho, \bar{u}, e$  etc. of the flow only. Additionally to the variables contained in (29) - (31) the degree of dissociation  $\alpha$  and the internal energy  $n_2 \bar{\epsilon}$  resp. the internal "temperature" of the dissociating gas will appear as new hydrodynamic state variables, which give two more differential equations. With the help of additional assumptions the differential equations for  $P_{ij}, S_{ikk}, q_i$  etc. are simplified to functions depending on  $\rho, \bar{u}, e, \alpha, n_2 \bar{\epsilon}$  and their derivatives.

### § III A special Ansatz for the solution

A consideration of the orders of magnitude of the collision cross-sections for the different kinds of collisions show that for not too high temperatures the dissociation cross-sections are smaller than then the excitation cross-sections and both are considerably smaller than the cross-sections for the transfer of translation energy . This leads to the result that a gas , which is at an initial time in a "strong" non-equilibrium with respect to all degrees of freedom , will at first approach the equilibrium with respect to the degree of freedom of translation , after that the equilibrium of the internal degrees of freedom and finally the chemical equilibrium . By strong non-equilibrium we understand that also the higher order moments of the BOLTZMANN functions as for instance the quantities  $\mathcal{P}^{(n)}$  ,  $\int v^n$  etc. are independent state variables . However, one knows from experiments that this independence dies out rapidly with time . After a short time a flow represents a state which is "near" the equilibrium state . The time constant of a degree of freedom for approaching such a "quasi equilibrium" is the smaller the larger the cross-section of the corresponding collision type is .

Here we make the Ansatz that the particle numbers  $n_1$  of atoms and  $n_2$  of molecules are independent quantities , i. e. the degree of dissociation of the gas is an independent variable , the deviation from chemical equilibrium can be arbitrarily large .

The equilibrium distribution function for the atoms at a temperature  $\mathcal{T}$  is the MAXWELL-distribution . This distribution leads to the following Ansatz of a "local MAXWELL-distribution" given by

$$f_{01} = \frac{1}{(2\pi R_1 \mathcal{T})^{3/2}} e^{-\frac{(\vec{p} - \vec{u})^2}{2R_1 \mathcal{T}}}$$

The mean velocity of flow  $\vec{u}$  and the temperature  $\mathcal{T}$  may be a position- and time-dependent function . However , the gradients shall be so small that at the flow velocity  $\vec{u}$  the local equilibrium can take place . The natural extension of this Ansatz is an expansion round the local equilibrium . Because of the weight function  $e^{-\frac{(\vec{p} - \vec{u})^2}{2R_1 \mathcal{T}}}$  this leads to an expansion according to HERMITEAN polynomials of  $\frac{\vec{p} - \vec{u}}{(R_1 \mathcal{T})^{1/2}}$  . The coefficients of this expansion are functions of position and time . This Ansatz has been used for

monoatomic gases by GRAD [2] and gives hydrodynamic equations, if the series is cut off in a proper manner. Additional assumptions simplify GRAD's so-called "thirteen-moment-equations" to the NAVIER-STOKES-equations. In a second paper [13] GRAD deals with the polydimensional HERMITEAN polynomials. We give here only the form of the first polynomials. We introduce the non-dimensional atom velocity  $\vec{v}_1$ , by

$$\vec{v}_1 = \frac{\vec{v} - \vec{u}}{(R_1 \sigma)^{1/2}} \quad (33)$$

$R_1$  is the specific gas constant of the atoms given by  $R_1 = \frac{R_0}{M_1} = \frac{k}{m_1}$

$R_0$  = general gas constant

$M_1$  = atomic weight (34)

$k$  = BOLTZMANN constant

$\vec{u}$  be the mean mass-velocity defined by (20). Let us denote the HERMITEAN polynomials of  $n^{\text{th}}$  degree by  $\mathcal{H}^{(n)}$ . They are symmetric tensors of  $n^{\text{th}}$  degree. They are orthogonal with the weight factor  $e^{-v^2/2}$ . The normalization of the polynomials is chosen such that

$$\begin{aligned} \left(\frac{1}{2\pi}\right)^{3/2} \int_{-\infty}^{+\infty} e^{-v^2/2} \mathcal{H}_i^{(v)} \mathcal{H}_j^{(v)} d\vec{v}_1 &= 0 \quad \text{for } i \neq j \quad (35) \\ &= \delta_{ij}^v \quad \text{for } i = j \end{aligned}$$

holds.

The subscripts  $i_1, i_2, \dots, i_v$  resp.  $j_1, j_2, \dots, j_v$  were abbreviated by  $i$  resp.  $j$ .  $\delta_{ij}^v$  has to be formed according to the multiplication rule of § II, each  $\delta_{ij}^v$ , however, has a pair  $i, j$  of subscripts. This means that  $\delta_{ij}^v$  does not vanish only if the subscripts  $j_1, \dots, j_v$  are a permutation of the subscripts  $i_1, \dots, i_v$ .

The first HERMITEAN polynomials which we only need later on are given by

$$\begin{aligned}
 \mathcal{H}^{(0)} &= 1 \\
 \mathcal{H}_i^{(1)} &= v_i \\
 \mathcal{H}_{ij}^{(2)} &= v_i v_j - \delta_{ij} \\
 \mathcal{H}_{ijk}^{(3)} &= v_i v_j v_k - (v_i v_j v_k + v_j v_i v_k + v_k v_i v_j) \\
 \mathcal{H}_{ijkl}^{(4)} &= v_i v_j v_k v_l - (v_i v_j v_k v_l + v_j v_i v_k v_l + v_k v_i v_j v_l \\
 &\quad + v_l v_i v_j v_k + v_j v_l v_i v_k + v_k v_l v_i v_j) \\
 &\quad + (v_i v_j v_k v_l + v_j v_k v_i v_l + v_l v_i v_j v_k)
 \end{aligned} \tag{36}$$

The expansion of the distribution function  $f_1$  into HERMITEAN polynomials be given by

$$\begin{aligned}
 f_1 &= f_{10} \left( 1 + a_i^{(1)}(x,t) \mathcal{H}_i^{(1)} + \frac{a_{ij}^{(2)}}{2!} (x,t) \mathcal{H}_{ij}^{(2)} + \dots \right) \\
 &= f_{10} \sum_{\nu} \frac{a_{i\nu}^{(\nu)}}{\nu!} \mathcal{H}_{i\nu}^{(\nu)}
 \end{aligned} \tag{37}$$

with 
$$f_{10} = \frac{m_1}{(2\pi R_1 \sigma)^{3/2}} e^{-\sigma^2/2}$$

The factor  $\nu!$  has been introduced to express the quantities  $a_{i\nu}^{(\nu)}$  as simple moments of  $f_1$  without a numerical factor. Because of the symmetry of  $\mathcal{H}_{i\nu}^{(\nu)}$  against permutations of the subscripts  $i_\nu$  one has also to assume that the quantities  $a_{i\nu}^{(\nu)}$  are identical if they differ by a permutation of the  $i_\nu$  only. Thus one gets by multiplication of (37) with  $\mathcal{H}_{i\nu}^{(\nu)}$  and integration and using (35):

$$a_{i\nu}^{(\nu)}(x,t) = \frac{(R_1 \sigma)^{3/2}}{m_1} \int f_1 \mathcal{H}_{i\nu}^{(\nu)} d\vec{v} \tag{38}$$

$\sigma^2$  is a free parameter. It shall from now on be defined as the "translational temperature" of the atoms, i. e. it is given by the thermodynamic relation between temperature and mean kinetic energy of the atoms:

$$\frac{3}{2} m_1 k \sigma^2 = \frac{1}{2} P_{ii}^{(1)} \tag{39}$$

If we define additionally

$$P_{ii}^{(\nu)} = 3 p^{(\nu)} \tag{40}$$

we find the relation

$$n_1 k \bar{v} = p^{(1)} = n_1 m_1 R_1 \bar{v} \quad (41)$$

which is a defining equation for  $\bar{v}$ , but no equation of state. From (41) we get the corresponding relation for  $i_1^{(2)}$ :

$$i_1^{(2)}(x,t) = \frac{(R_1 \bar{v})^{3/2}}{n_1} \int f_1(\vec{v}, \vec{v} - \vec{v}) \vec{v} = \frac{2}{n_1} \left( \frac{p^{(1)}}{R_1 \bar{v}} - n_1 \right) \bar{v} \quad (42)$$

The second parameter, the mass-velocity  $\bar{u}$ , has to lead to another relation between the coefficients of the expansion if we apply its definition (20).

Before doing that let us consider the distribution functions  $f_{2i}$ . With respect to their dependence on the velocity  $\vec{v}_2$  we use the same expansion into HERMITEAN polynomials as we did for  $f_1$ . Additionally we assume that the "translation temperatur"  $\bar{v}$  is equal both for atoms and molecules. This means that the transition probabilities  $\sigma_{12}, \sigma_{21}$  are assumed to be so large that the kinetic energy can be assumed as being equally distributed over atoms and molecules. The time constant for approaching the equilibrium has the magnitude of a few collision times. It is easy to see this in the case  $\sigma_{11}$  of a monoatomic gas ([2] and § VI). There is no reason to assume that the order of magnitude of  $\sigma_{12}$  is essentially different from  $\sigma_{11}$  since in both cases the collision mechanism is hardly influenced by the internal structure of the colliding particles.

The HERMITEAN polynomials as functions of  $\vec{v}_2$

$$\vec{v}_2 = \frac{\vec{v} - \vec{u}}{(R_2 \bar{v})^{1/2}} \quad (43)$$

shall be denoted with  $K^{(v)}$ . According to our just made remarks the relation

$$n_2 k \bar{v} = p^{(2)} = \frac{1}{3} P_{JJ}^{(2)} = n_2 m_2 R_2 \bar{v} \quad (44)$$

shall hold.

Thus we get for the expansion of  $f_{2i}$ :

$$f_{2i} = f_{20i} \left( 1 + C_{K^{(1,i)}}^{(1,i)}(x,t, \varepsilon_i) K_K^{(1)} + C_{K^{(2,i)}}^{(2,i)}(x,t, \varepsilon_i) \frac{K_{KK}^{(2)}}{2!} + \dots \right) \quad (45)$$

Substituting the Ansatz for  $f_1$  and  $f_{2i}$  into the BOLTZMANN equations (2), (3) we get a system of partial differential equations for the coefficients  $a^{(v)}$  and  $c^{(v,i)}$  which is equivalent to the system (2), (3). We do not

give this system here since it will not be used later . Instead of this system the moment equations (8) , (9) will serve as a starting point .

The hitherto used Ansatz for  $f_i$  shall now be extended by an Ansatz for the coefficients  $C^{(v,i)}$  . If we disregard the fact that the numbers  $\varepsilon_i$  assume discrete values we can assume the quantities  $C^{(v,i)}$  and  $f_i$  to be functions of the continuous parameter  $\varepsilon$  . The absolute equilibrium distribution of the internal energy at a temperature  $\Theta$  is given by BOLTZMANN's e-distribution :

$$f_{20\varepsilon} = e^{-\frac{\varepsilon}{k\Theta}} \quad (46)$$

The expansion of the coefficients  $C^{(v)}(x,t,\varepsilon)$  into orthogonal functions of  $\varepsilon$  should be an expansion into LAGUERRE-functions of the non-dimensional parameter  $\frac{\varepsilon}{k\Theta}$  . We define

$$\eta = \frac{\varepsilon}{k\Theta} \quad (47)$$

The weight factor of the LAGUERRE-functions is  $e^{-\eta}$  , integration runs from 0 to  $\infty$  . This is also adapt to the energy-scale which we define in the following way : the energy of the molecules in their ground state be 0 , an atom in its ground state has half of the dissociation energy  $\frac{E_D}{2}$  . The first LAGUERRE polynomials are given by

$$\begin{aligned} L^{(0)} &= 1 \\ L^{(1)} &= 1 - \eta \\ L^{(2)} &= 1 - 2\eta + \frac{\eta^2}{2} \end{aligned} \quad (48)$$

The complete expansion of  $f_2(\varepsilon)$  would be if we assume a continuous dependence of  $f_2$  of the parameter  $\varepsilon$  :

$$f_{2\varepsilon} = f_{20} \sum_{v,m} \frac{\beta^{(v,m)}(x,t)}{\sqrt{v!}} K^{(v)}(\varepsilon) L^{(v)}(\eta) \quad (49)$$

with

$$f_{20} = \frac{1}{(2\pi R_2 \bar{v})^{3/2}} e^{-\frac{v_0^2}{2} - \eta} \quad (50)$$

The expansion (49) is correct if we have a continuous spectrum  $\varepsilon$  for one degree of freedom . However , a molecule has more than one internal degree of freedom . Thus the Ansatz (49) should be extended . In the case

of the three kinetic degrees of freedom this was done by the introduction of the 3-dimensional HERMITEAN polynomials . The fact that  $\xi_i$  takes discrete values shall be disregarded for the present . We can indeed , approximate the appearing sums sufficiently good by integrals in large parts of the spectrum . For the  $k^{\text{th}}$  degree of freedom the non-dimensional energy parameter be defined by

$$k_{\eta} = \frac{k_{\xi}}{k_{\Theta}} \quad (51)$$

It may be assumed that it makes sense to introduce a joint "internal temperature"  $\Theta$  . That means we assume different degrees of freedom of the same type of excitation . In the case of di-atomic molecules we have three types of excitation , the electronic excitation of the outer shell , the rotation- and oscillation excitation . These types are excited in a differently difficult manner . The excitation of the rotation states can be assumed to be in equilibrium with the translation temperature as we are in a region of high temperatures . However , the excitation of oscillations is much more difficult . The degrees of freedom of oscillation of di-atomic molecules are fully excited at some thousand<sup>o</sup>K , only . Thus one has to introduce at least for the degrees of freedom of the oscillation an internal temperature  $\Theta$  as being different from the translation temperature  $\mathcal{T}$  . We define this "internal temperature"  $\Theta$  by the relation between temperature and mean energy :

$$C_{\Theta} d\Theta = d(e_{\Theta}) \quad (52)$$

$C_{\Theta}$  becomes the specific heat at constant volume .  $e_{\Theta}$  is the specific energy of the corresponding type of excitation .

In the following we treat the equations as if there would exist one type of excitation with the internal temperature  $\Theta$  only . The extension to several types of excitation is possible . For this case the basic equations (2) , (3) had to be extended and we had to introduce a distribution function  $f_2$  which does not only depend on the total energy , but also on the distribution of the energy over the different types of excitation .

Let us consider again the expansion (49) . It can be extended by using (51) and making as Ansatz for each  $k_{\eta}$  the corresponding expansion . One gets a function  $f = f(\mathcal{T}, \frac{\mathcal{T}}{\Theta}, k_{\Sigma})$  which depends on the different

energy values belonging to the different degrees of freedom (this procedure is incorrect since because of quantum mechanical reasons the set  $\{ \epsilon_k \}$  of energy values belonging to the different degrees of freedom must not be measurable simultaneously . At this point one has to use a classical picture to understand the following Ansatz ) .

$$\tilde{f}_2 = \tilde{f}_{20} \sum_{\nu} \left( \sum_{m_1} \tilde{G}^{(\nu, m_1)} L^{(\nu, m_1)}(q_{m_1}) \dots \left( \sum_{m_k} \tilde{G}^{(\nu, m_k)} L^{(\nu, m_k)}(q_{m_k}) \right) \right) \frac{1}{\nu!} K^{(\nu)} \quad (53)$$

$$\tilde{f}_{20} = \left( \frac{m_2}{2\pi R_2} \right)^{3/2} e^{-v^2/2} e^{-\frac{1}{2}k_1^2 - \frac{1}{2}k_2^2 - \dots - \frac{1}{2}k_n^2} \quad (54)$$

One sees immediately that the Ansatz is useless in this form since the series (53) includes more information than  $f_2(\epsilon)$  which shall depend on the total energy  $\frac{1}{2}m_1 v^2 + \dots + k_n^2$  only . Thus the Ansatz (53) has to be "coarse grained" in a certain manner . Let us before again consider the expansion of  $f_1$  .

The solution of the system of infinitely many differential equations for  $\alpha^{(\nu)}$  and  $C^{(\nu, i)}$  which follows from the expansions (37) , (45) is as difficult as the solution of (2) , (3) . However , if one restricts to a special solution of (2) , (3) which shall describe a flow the distribution function of which is near the MAXWELLIAN distribution , one can make the system of differential equations finite by a cut-off of the expansion . Here we want to cut-off the series (37) , (45) for  $\nu > 3$  . This means that the higher coefficients of the expansion are considered to be vanishingly small . Thus we make the following approximation for a special solution :

$$\begin{aligned} \alpha^{(\nu)}(x, t) &= 0 & \text{for} & \quad \nu > 3 \\ C^{(\nu, i)}(x, t) &= 0 & \text{for} & \quad \nu > 3 \end{aligned} \quad (55)$$

This Ansatz seems to be a little arbitrary . That it makes sense with respect to the wanted hydrodynamic approximation can be seen if one expresses the first coefficients  $\alpha^{(\nu)}(x, t)$  by the moments (11) - (18) .

One finds

$$\alpha^{(\nu)}(x, t) = \left( \frac{R_1 \sigma}{m_1} \right)^{3/2} \int \mathcal{K}^{(\nu)} f_1 d\vec{\sigma}_1 = \frac{1}{m_1} \int \left( \frac{\vec{L}_1 - \vec{u}}{R_1 \sigma} \right)^{\nu} f_1 d\vec{\sigma}_1 = \frac{\vec{u}_1 - \vec{u}}{(R_1 \sigma)^{3/2}} \quad (56)$$

$$a^{(2)}(x,t) = \frac{(R_1 v)^{3/2}}{n_1} \int \mathcal{H}^{(2)} f_1 d\vec{v}_1 = \frac{p^{(2)}}{n_1 m_1 R_1 v} - \vec{\sigma} \quad (57)$$

$$a^{(3)}(x,t) = \frac{(R_1 v)^{3/2}}{n_1} \int \mathcal{H}^{(3)} f_1 d\vec{v}_1 = \frac{S^{(3)}}{n_1 m_1 (R_1 v)^{3/2}} - \left( \frac{\vec{u}_1 - \vec{u}}{(R_1 v)^{3/2}} \cdot \vec{\sigma} \right) \quad (58)$$

$$a^{(4)}(x,t) = \frac{(R_1 v)^{3/2}}{n_1} \int \mathcal{H}^{(4)} f_1 d\vec{v}_1 = \frac{Q^{(4)}}{m_1 (R_1 v)^2} - \left( \frac{p^{(4)}}{n_1 m_1 R_1 v} \vec{\sigma} \right) + \vec{\sigma} \quad (59)$$

To complete the system of conservation equations (29) - (31) one has to consider terms up to  $a^{(3)}$  of the expansion. If one also neglects  $a^{(2)}$  and  $a^{(4)}$  one assumes that also the heat flow  $\vec{S}_{ij}^{(2)}$  and the pressure tensor  $(p^{(4)} - \frac{1}{3} p_{jj}^{(4)} \vec{e}^2)$  are vanishingly small. Thus one gets EULER'S equations of the flow. If one is interested in equations which are of the type of the NAVIER-STOKES equations one has to take  $a^{(2)} \neq 0$  and  $a^{(3)} \neq 0$ .  $a^{(4)}$  contains the new moment  $Q^{(4)}$  which does not appear in the conservation equations. Thus it seems to be consequent to make the Ansatz  $a^{(v)} = 0$  for  $v > 3$ .

We get now

$$f_1 = f_{10} \left( 1 + a^{(1)} \mathcal{H}^{(1)} + \frac{a^{(2)}}{2!} \mathcal{H}^{(2)} + \frac{a^{(3)}}{3!} \mathcal{H}^{(3)} \right) \quad (60)$$

Now we have to ask for a similar cut-off of the expansion (53). One gets

$$k_{\vec{v}}^{(v,m)} = 0 \quad \text{for} \quad v+m > 3 \quad (61)$$

One has to notice only that linear terms in  $k_{\vec{v}}$  have the weight of quadratic terms in  $\vec{v}$ . Since one may assume that the translational temperature  $\bar{v}^2$  does not differ from the internal temperature  $\bar{\epsilon}$  by orders of magnitude, one has to assume for the mean values of  $v^2$  and  $\epsilon$ .

$$\bar{v}^2 \approx \bar{\epsilon}$$

This relation can be used to estimate the magnitude of the coefficients  $\tilde{c}^{(v,n)}$  and thus one finds (61)

The expansions (53) simplifies to

$$\begin{aligned} \tilde{f}_2 = & \tilde{f}_{20} \left[ 1 + (\tilde{c}^{(1,1)} L^{(1)}(\eta) + \tilde{c}^{(2,0)} L^{(2)}(\eta) + \dots + \tilde{c}^{(3,0)} L^{(3)}(\eta)) \right] + \\ & + \tilde{c}^{(1,0)} K^{(1)} + (\tilde{c}^{(1,1)} L^{(1)}(\eta) + \dots + \tilde{c}^{(2,1)} L^{(2)}(\eta)) K^{(1)} + \\ & + \frac{\tilde{c}^{(2,0)}}{2!} K^{(2)} + \frac{\tilde{c}^{(3,0)}}{3!} K^{(3)} \end{aligned} \quad (62)$$

with  $\tilde{g}^{(v, \mu)} = \sum_k k \tilde{g}_k^{(v, \mu)}$

Since  $f_2$  shall be dependent on the sum  $\gamma = \sum_k k \eta_k$  only, the Ansatz (62) is further coarse grained.

We put

$${}^1 \tilde{g}^{(0,1)} L^{(1)}(\eta) + \dots + k \tilde{g}^{(0,1)} L^{(1)}(k \eta) = \frac{1}{k} \tilde{g}^{(0,1)} \sum_k L^{(1)}(k \eta) \quad (63)$$

$${}^1 \tilde{g}^{(1,1)} L^{(1)}(\eta) + \dots + k \tilde{g}^{(1,1)} L^{(1)}(k \eta) = \frac{1}{k} \tilde{g}^{(1,1)} \sum_k L^{(1)}(k \eta) \quad (64)$$

$$\sum_k L^{(1)}(k \eta) \stackrel{\text{def}}{=} L(\eta) = K - \gamma \quad (65)$$

It follows

$$\begin{aligned} \tilde{f}_2 &= \tilde{f}_{20} \left( 1 + \tilde{g}^{(0,1)} \left( 1 - \frac{\gamma}{k} \right) + \tilde{g}^{(1,0)} K^{(1)} + \tilde{g}^{(1,1)} \left( 1 - \frac{\gamma}{k} \right) K^{(1)} \right) \\ &+ \frac{\tilde{g}^{(2,0)}}{2!} K^{(2)} + \frac{\tilde{g}^{(3,0)}}{3!} K^{(3)} \end{aligned} \quad (66)$$

Because of the orthogonality of the quantities  $L^{(v)}(k \eta)$  one obtains the quantities  $\tilde{g}^{(v, \mu)} = \sum_k \tilde{g}_k^{(v, \mu)}$  on the right hand side of (53) by multiplication with  $\sum_k L^{(v)}(k \eta) K^{(v)}$  and integration over all  $k \eta$  and  $\vec{v}$ . We get, for instance, for  $\tilde{g}^{(0,1)}$ ,  $\tilde{g}^{(1,1)}$  and  $\tilde{g}^{(v,0)}$  the relations

$$\tilde{g}^{(0,1)} = \frac{(R_2 \bar{v})^{3/2}}{n_2} \int_{-\infty}^{+\infty} \int_0^{+\infty} \tilde{f}_2(\xi, \dots, k \xi) \sum_k (1 - \frac{k \eta}{k}) d\vec{v} d\eta_1 \dots d\eta_n \quad (67)$$

$$\tilde{g}^{(1,1)} = \frac{(R_2 \bar{v})^{3/2}}{n_2} \int_{-\infty}^{+\infty} \int_0^{+\infty} \tilde{f}_2(\xi, \dots, k \xi) \sum_k (1 - \frac{k \eta}{k}) K^{(1)}(\vec{v}) d\vec{v} d\eta_1 \dots d\eta_n \quad (68)$$

$$\tilde{g}^{(v,0)} = \frac{(R_2 \bar{v})^{3/2}}{n_2} \int_{-\infty}^{+\infty} \int_0^{+\infty} \tilde{f}_2(\xi, \dots, k \xi) K^{(v)}(\vec{v}) d\vec{v} d\eta_1 \dots d\eta_n \quad (69)$$

We state that  $\tilde{g}^{(0,1)} = 0$ . To see this let us again consider (52), which defines  $\Theta$ . If a type of excitation is fully excited the specific heat belonging to it is equal to the number of degrees of freedom times the BOLTZMANN constant times the number of particles per unit mass. Then (52) can be replaced by

$$K \cdot k \Theta = \bar{\epsilon} \quad (70)$$

$\bar{\epsilon}$  is the mean energy per molecule of the considered type of excitation.

On the other hand we have

$$\frac{(R_2 v)^{3/2}}{n_2} \int_0^\infty \int_0^\infty \tilde{f}_2(\varepsilon) \frac{\int k_\eta d\vec{v} d\eta \dots d\eta}{\varepsilon} = \frac{\bar{\varepsilon}}{k\Theta} \quad (71)$$

Thus we find from (67), (70) and (71) our statement

$$\tilde{g}^{(0,1)} = 0 \quad (72)$$

(72) is equivalent to (42):  $a_{vv}^{(0)}(x,t) = 0$ , which was also a consequence of the definition of the temperature  $\bar{v}$ .

Hitherto we assumed that  $\varepsilon$  is a continuous parameter. The analogous Ansatz for (66) for a discrete energy parameter  $\varepsilon_i$  can be easily obtained from (66), (67), (68), (69) by replacing the integration over  $\varepsilon, \eta, \dots, \eta$  by summation over  $i$ . If some of the energy values  $\varepsilon_i$  are degenerated the sum will contain this energy value repeatedly. One gets

$$f_{2i} = f_{20i} \left( 1 + \beta^{(1)}(x,t) K^{(1)} + \beta^{(1,1)}(x,t) K^{(1)} \left( \varepsilon_i - \frac{\bar{\varepsilon}}{k\Theta} \right) \right. \\ \left. + \frac{\beta^{(2)}(x,t)}{2!} K^{(2)} + \frac{\beta^{(3)}(x,t)}{3!} K^{(3)} \right) \quad (73)$$

with  $f_{20i} = \frac{1}{(2\pi R_2 v)^{3/2}} \frac{1}{Z} \exp\left(-\varepsilon_i - \frac{v^2}{2}\right)_i$ ,  $Z = \sum_i e^{-\varepsilon_i}$  = partition sum.

For the coefficients  $\beta^{(v)}$  the following equations hold

$$\beta^{(1,1)} = \frac{(R_2 v)^{3/2}}{n_2} \frac{k\Theta}{\varepsilon} \frac{1}{i} \int f_{2i} K^{(1)} \left( \varepsilon_i - \frac{\bar{\varepsilon}}{k\Theta} \right) d\vec{v}_2 \quad (74)$$

$$\beta^{(v)} = \frac{(R_2 v)^{3/2}}{n_2} \sum_i \int f_{2i} K^{(v)} d\vec{v}_2 \quad (75)$$

Instead of using the LAGUERRE polynomials to find the Ansatz (73), (74), (75) one can make for  $f_{2i}$ , the Ansatz of a power series as follows:

$$f_{2i} = f_{20i} \left( C^{(0,0)} + C^{(1,0)} K^{(1)} + \frac{C^{(2,0)}}{2!} K^{(2)} + \frac{C^{(3,0)}}{3!} K^{(3)} + C^{(0,1)} \varepsilon_i + C^{(1,1)} \varepsilon_i K^{(1)} \right) \quad (73a)$$

By a multiplication of (73a) with  $K^{(v)}$ , integration and summation one gets certain relations for the coefficients  $C^{(v,m)}$ . According to that the Ansatz proves to be identically with (73), (74), (75) (see ref. [7]).

At first the simpler linear Ansatz in  $\varepsilon_i$  seems to be a little arbitrary. It is clear because of former considerations that terms with  $\varepsilon_i^2$  must not appear. However, from (73a) and the coefficient equations belonging to it one cannot see at once that it is indeed the corresponding Ansatz as in the

case of the Ansatz in HERMITEAN polynomials for the dependence of  $\eta_i$ .

The connection with the formerly defined moments for the quantities  $\rho^{(v)}$  follows by the relations :

$$\rho^{(1)} = \frac{(R_2 \bar{v})^{3/2}}{m_2} \sum_i \int f_{2i} K^{(1)} d\bar{v}_2 = \frac{\bar{u}_2 - \bar{u}}{(R_2 \bar{v})^{1/2}} \quad (76)$$

$$\rho^{(2)} = \frac{(R_2 \bar{v})^{3/2}}{m_2} \sum_i \int f_{2i} K^{(2)} d\bar{v}_2 = \frac{P^{(2)}}{m_2 m_2 R_2 \bar{v}} - \bar{J} \quad (77)$$

$$\rho^{(3)} = \frac{(R_2 \bar{v})^{3/2}}{m_2} \sum_i \int f_{2i} K^{(3)} d\bar{v}_2 = \frac{S^{(2)}}{m_2 m_2 (R_2 \bar{v})^{1/2}} - \frac{\bar{J} \cdot (\bar{u}_2 - \bar{u})}{(R_2 \bar{v})^{1/2}} \quad (78)$$

$$\rho^{(4)} = \frac{(R_2 \bar{v})^{3/2}}{m_2} \sum_i \int f_{2i} K^{(4)} d\bar{v}_2 = \frac{Q^{(2)}}{m_2 (R_2 \bar{v})^2} - \left( \frac{P^{(2)} \cdot \bar{J}}{m_2 m_2 R_2 \bar{v}} \right) + \bar{J}^2 \quad (79)$$

$$\rho^{(4,1)} = \frac{(R_1 \bar{v})^{3/2}}{m_2} \frac{k \Theta}{\bar{\epsilon}} \sum_i \int f_{2i} K^{(4)} \left( \eta_i - \frac{\bar{\epsilon}}{k \Theta} \right) d\bar{v}_2 = \bar{q} - \frac{\bar{u}_2 - \bar{u}}{m_2 \bar{\epsilon} (R_2 \bar{v})^{1/2}} \quad (80)$$

We make still a final approximation in the special Ansatz for  $f_1$  and  $f_{2i}$ .

In the conservation equations (2), (3) only the reduced tensors

$$S_{ijj}^{(v)} \stackrel{\text{def}}{=} S_i^{(v)}$$

of the heat flow appear. Thus the Ansatz for  $f_1$  and  $f_{2i}$  can still be simplified by assuming  $S_{ijk}^{(v)}$  to be diagonal.

Thus one has an Ansatz which contains just the minimum number of coefficients necessary to make the conservation equations to be a complete system of the appearing quantities.

Thus it shall hold :

$$S_{ijk}^{(v)} = \frac{1}{5} (S_i^{(v)} \delta_{jk} + S_j^{(v)} \delta_{ik} + S_k^{(v)} \delta_{ij}) \quad (81)$$

(81) is equivalent to the assumption that  $a^{(3)}$  and  $\beta^{(3)}$  are diagonal. Instead of the full HERMITEAN polynomials of third degree one can introduce reduced tensors  $\bar{\mathcal{H}}_i^{(3)}$  and  $\bar{K}_i^{(3)}$  by

$$\begin{aligned} \bar{\mathcal{H}}_i^{(3)} &= \mathcal{H}_{ijj}^{(3)} = v_{1i} (v_1^2 - 5) \\ \bar{K}_i^{(3)} &= K_{ijj}^{(3)} = v_{2i} (v_2^2 - 5) \end{aligned} \quad (82)$$

Replacing in (60) and (73) the terms  $\frac{a_{ijk}^{(3)}}{3!} \mathcal{H}_{ijk}^{(3)}$  and  $\frac{\beta_{ijk}^{(3)}}{3!} K_{ijk}^{(3)}$  by  $\bar{a}_i^{(3)} \bar{\mathcal{H}}_i^{(3)}$  and  $\bar{\beta}_i^{(3)} \bar{K}_i^{(3)}$  multiplying the new Ansatz with  $\bar{\mathcal{H}}_i^{(3)}$  resp.  $\bar{K}_i^{(3)}$  and integrating one finds

$$\frac{(R_1 v)^{3/2}}{n_1} \int f_1 \mathcal{H}_i^{(3)} d\vec{v}_1 = \bar{a}_k^{(3)} \int e^{-\frac{v^2}{2}} \mathcal{H}_k^{(3)} \mathcal{H}_i^{(3)} = 10 \bar{a}_i^{(3)} \quad (83)$$

resp.

$$\frac{(R_2 v)^{3/2}}{n_2} \sum_i \int f_{2i} \bar{K}_k^{(3)} d\vec{v} = 10 \bar{b}_k^{(3)} \quad (84)$$

To remove the numerical factor 10, we define new coefficients by

$$\begin{aligned} \bar{a}_i^{(3)} &= \frac{1}{10} \bar{a}_i^{(3)} \\ \bar{b}_i^{(3)} &= \frac{1}{10} \bar{b}_i^{(3)} \end{aligned} \quad (85)$$

Thus the final Ansatz for  $f_1$  and  $f_{2i}$  is given by

$$f_1 = \frac{n_1}{(2\pi R_1 v)^{3/2}} e^{-\frac{v^2}{2}} \left( 1 + a^{(1)} \mathcal{H}^{(1)} + \frac{a^{(2)}}{2!} \mathcal{H}^{(2)} + \frac{\bar{a}^{(3)}}{10} \mathcal{H}^{(3)} \right) \quad (86)$$

$$\begin{aligned} f_{2i} &= \frac{n_2}{(2\pi R_2 v)^{3/2}} \frac{1}{Z} \exp\left(-\frac{v^2}{2} - \eta_i\right) \left( 1 + b^{(1)} \left( \eta_i - \frac{\bar{\Sigma}}{k\Theta} \right) K^{(1)} \right. \\ &\quad \left. + b^{(2)} K^{(2)} + \frac{b^{(3)}}{2} K^{(3)} + \frac{b^{(3)}}{10} \bar{K}^{(3)} \right) \end{aligned} \quad (87)$$

$$\text{with } a^{(v)} = \frac{(R_1 v)^{3/2}}{n_1} \int f_1 \mathcal{H}^{(v)} d\vec{v}_1 \quad (88)$$

$$b^{(v)} = \frac{(R_2 v)^{3/2}}{n_2} \sum_i \int f_{2i} K^{(v)} d\vec{v}_2 \quad (89)$$

$$b^{(1,1)} = \frac{(R_2 v)^{3/2}}{n_2} \sum_i \int f_{2i} K^{(1)} \left( \eta_i - \frac{\bar{\Sigma}}{k\Theta} \right) d\vec{v}_2 \quad (90)$$

The new Ansatz (86), (87) is equivalent to (81), This can be easily seen for  $f_1$  by substituting (86) into (60). One finds

$$\begin{aligned} a_{ijk}^{(3)} &= \frac{(R_1 v)^{3/2}}{n_1} \int f_1 \mathcal{H}_{ijk}^{(3)} d\vec{v}_1 = \frac{\bar{a}_v}{10} \int e^{-\frac{v^2}{2}} \mathcal{H}_v^{(3)} \mathcal{H}_{ijk}^{(3)} d\vec{v}_1 \quad \left( \frac{1}{2\pi} \right)^{3/2} \\ &= \frac{1}{5} (\bar{a}_i \delta_{jk} + \bar{a}_j \delta_{ik} + \bar{a}_k \delta_{ij}) \end{aligned} \quad (91)$$

Comparing (91) with (58) we find that (91) is identical to (81).

The starting point of all further investigations shall be from now on the special Ansatz (86), (87).

§ IV The equations for the "hydrodynamical" moments

In this chapter the equations for  $\alpha^{(v)}$  and  $\beta^{(v)}$  resp. the corresponding moment equations shall be derived. The coefficients  $\alpha^{(v)}$  and  $\beta^{(v)}$  are linear combinations of certain moments (see equs. 56 - 59 and 76 - 80). Therefore it is unnecessary to start from equations for  $\alpha^{(v)}$  and  $\beta^{(v)}$  and to cut off this system according to the approximation (86), (87). It is better to use as starting point the simpler moment equations (8), (9). Substituting into these equations the approximation (86), (87), to calculate the right hand sides and considering the connection between the moments and  $\alpha^{(v)}$ ,  $\beta^{(v)}$  to introduce also on the left hand sides the corresponding approximations one gets equations which, by the underlying approximations, completely correspond to those for  $\alpha^{(v)}$ ,  $\beta^{(v)}$ . However, these are equations for moments which can be immediately interpreted by hydrodynamic state variables. In addition to the conservation equations (2), (3) they form a complete system of equations for the wanted hydrodynamic quantities.

This system is very complicated. For special cases only one can hope to find a solution. With the help of certain additional assumptions one gets essential simplifications. In the case of monoatomic gases the corresponding approximations lead to the ordinary NAVIER-STOKES equations.

Let us write down the complete moment equations. The right hand sides are abbreviated by  $\bar{c}^{(v)}$ , the bar shall denote that the approximation (86), (87) for  $f_1$  and  $f_{2i}$  shall be used. In § V follows the evaluation of the right hand sides by partly integration of the collision integrals.

The equation for the particle number  $n_1$  or the degree of dissociation follows from (8) for  $n = 0$ .  $n_2$  is then given by (29) and (19). We have

$$\frac{\partial}{\partial t} n_1 + \frac{\partial}{\partial x_i} (\bar{u}_1 n_1) = \bar{c}^{(0)}_{(1)} \quad (92)$$

Multiplication by  $\rho$ , and using (29) we get from (92) an equation for  $\alpha$  :

$$\rho \frac{D\alpha}{Dt} + \frac{\partial}{\partial x_i} (\rho \alpha (\bar{u}_1 - \bar{u})_i) = m \bar{c}^{(0)}_{(1)} \quad (93)$$

For  $n = 1$  we get the equation for the mean velocities of the atoms  $\bar{u}_1$ . Again, we do not need an equation for  $\bar{u}_2$ . Using (30) and (20) we find

$$\begin{aligned} & \frac{D}{Dt} (m_1(\bar{u}_1 - \bar{u})) + \frac{D\bar{u}}{Dt} m_1 + \frac{\partial u_i}{\partial x_k} m_1 (\bar{u}_1 - \bar{u}) \\ & + \frac{\partial}{\partial x_i} \left( \frac{1}{m_1} P_i^{(1)} \right) + \frac{\partial \bar{u}}{\partial x_i} m_1 (\bar{u}_1 - \bar{u}) i = \bar{C}_{(1)}^{(1)} \end{aligned} \quad (94)$$

or

$$\begin{aligned} & \frac{D}{Dt} [P\alpha(\bar{u}_1 - \bar{u})] + \frac{\partial u_i}{\partial x_i} [P\alpha(\bar{u}_1 - \bar{u})] \\ & + \frac{\partial P}{\partial x_i} [P\alpha(\bar{u}_1 - \bar{u}) i] + \frac{\partial P_i^{(1)}}{\partial x_i} - \alpha \frac{\partial P_i}{\partial x_i} = \bar{C}_{(1)}^{(1)} m_1 \end{aligned} \quad (95)$$

For  $n = 2$  and  $n = 3$  we have to form two moment equations since there are no supplementary conservation equations.

From (8) and (9) we get for  $n = 2$  and  $m = 0$ :

$$\begin{aligned} & \frac{D}{Dt} P_{ij} + \frac{\partial u_k}{\partial x_k} P_{ij} + \frac{\partial}{\partial x_k} S_{kij} + \frac{\partial u_i}{\partial x_k} P_{kj} + \frac{\partial u_j}{\partial x_k} P_{ki} \\ & = m_1 \bar{C}_{(1)}^{(2)} ij + m_2 \bar{C}_{(2)}^{(2)} ij \end{aligned} \quad (96)$$

For  $n = 2$  we get from (8) the equation for  $P^{(1)}$ :

$$\begin{aligned} & \frac{D}{Dt} P_{ij}^{(1)} - \left( \frac{1}{P} \frac{\partial P_k}{\partial x_k} m_1 m_1 (\bar{u}_1 - \bar{u}) \right) ij + \frac{\partial u_k}{\partial x_k} P_{ij}^{(1)} \\ & + \frac{\partial}{\partial x_k} S_{kij}^{(1)} + \left( \frac{\partial \bar{u}}{\partial x_k} P_k \right) ij = m_1 \bar{C}_{(1)}^{(3)} ij \end{aligned} \quad (97)$$

where we replaced  $\frac{D\bar{u}}{Dt}$  by using (30). Now we have to introduce into (96), (97) the approximation (81) for  $S_{ijk}^{(1)}$ . The result is given by

$$\begin{aligned} & \frac{D}{Dt} P_{ij} + \frac{\partial u_k}{\partial x_k} P_{ij} + \frac{1}{5} \left( \frac{\partial S_i}{\partial x_j} + \frac{\partial S_j}{\partial x_i} + \frac{\partial S_k}{\partial x_k} \delta_{ij} \right) \\ & + \left( \frac{\partial \bar{u}}{\partial x_k} P_k \right) ij = m_1 \bar{C}_{(1)}^{(2)} ij + m_2 \bar{C}_{(2)}^{(2)} ij \end{aligned} \quad (98)$$

$$\begin{aligned} & \frac{D}{Dt} P_{ij}^{(1)} - \left( \frac{\partial P_k}{\partial x_k} \alpha (\bar{u}_1 - \bar{u}) \right) ij + \frac{\partial u_k}{\partial x_k} P_{ij}^{(1)} \\ & + \frac{1}{5} \left( \frac{\partial S_i^{(1)}}{\partial x_j} + \frac{\partial S_j^{(1)}}{\partial x_i} + \frac{\partial S_k^{(1)}}{\partial x_k} \delta_{ij} \right) + \left( \frac{\partial \bar{u}}{\partial x_k} P_k^{(1)} \right) ij = m_2 \bar{C}_{(2)}^{(3)} ij \end{aligned} \quad (99)$$

For  $n = 2$ ,  $m = 0$  we find

$$\begin{aligned} & \frac{D}{Dt} S_{ijj} - \left( \frac{1}{P} \frac{\partial P_k}{\partial x_k} P \right) ij + \frac{\partial u_k}{\partial x_k} (n Q_{kij}) \\ & + 2 \frac{\partial u_j}{\partial x_k} S_{ijk} + \frac{\partial u_i}{\partial x_k} S_{kji} = m_1 \bar{C}_{(1)}^{(3)} ij + m_2 \bar{C}_{(2)}^{(3)} ij \end{aligned} \quad (100)$$

$$\begin{aligned} \frac{D}{dt} S_{ij}^{(1)} - \left( \frac{1}{\rho} \frac{\partial P_k}{\partial x_k} p^{(1)} \right)_{ij} + \frac{\partial u_k}{\partial x_k} S_{ij}^{(1)} + \frac{\partial}{\partial x_k} (m_1 Q_{ki}^{(1)}) \\ + \left( \frac{\partial u_i}{\partial x_k} S_k^{(1)} \right)_{ij} = m_1 \bar{C}_{(1)}^{(3)} \bar{C}_{(1)}^{(2)}_{ij} \end{aligned} \quad (101)$$

For  $S_{ijk}^{(1)}$  we use again the approximation (81). We can find an expression for  $Q$  resp.  $Q^{(1)}$  by putting  $Q^{(1)}$  and  $Q^{(2)}$  in (59), (79) equal to zero. Thus one finds an equation for  $Q^{(1)}$  and  $Q^{(2)}$  which corresponds (86).

We have

$$\begin{aligned} m_1 Q^{(1)} &= R_1 \sigma (p^{(1)} \vec{r}) - (R_1 \sigma)^2 m_1 n_1 \vec{r}^2 \\ &= R_1 \sigma [ (p^{(1)} \vec{r}) - p^{(1)} \vec{r}^2 ] \end{aligned} \quad (102)$$

$$m Q = m_1 Q^{(1)} + m_2 Q^{(2)} = \frac{R_1 \sigma}{2} [ (p + p^{(1)}) \vec{r} - (p + p^{(1)}) \vec{r}^2 ] \quad (103)$$

From (100) and (101) we find with (102), (103), (81) the following equations:

$$\begin{aligned} \frac{D}{dt} S_i - \frac{1}{\rho} \frac{\partial P_{ki}}{\partial x_k} P_{ij} - \frac{2}{\rho} \frac{\partial P_{ki}}{\partial x_k} P_{ji} + \frac{\partial u_k}{\partial x_k} S_i \\ + \frac{7}{5} \frac{\partial}{\partial x_k} (R_1 \sigma P_{ik} + R_1 \sigma P_{ik}^{(1)}) + \frac{2}{5} \left( \frac{\partial u_k}{\partial x_k} S_i + \frac{\partial u_k}{\partial x_i} S_k \right) \\ - \frac{\partial}{\partial x_i} (R_1 \sigma (p + p^{(1)})) + \frac{2}{5} \left( \frac{\partial u_k}{\partial x_k} S_i + \frac{\partial u_k}{\partial x_i} S_k \right) + \frac{7}{5} \frac{\partial u_i}{\partial x_k} S_k \\ = m_1 \bar{C}_{(1)}^{(3)}_{ij} + m_2 \bar{C}_{(2)}^{(3)}_{ij} \end{aligned} \quad (104)$$

$$\begin{aligned} \frac{D}{dt} S_i^{(1)} - \frac{1}{\rho} \frac{\partial P_{ki}}{\partial x_k} P_{ij}^{(1)} - \frac{2}{\rho} \frac{\partial P_{ki}}{\partial x_k} P_{ji}^{(1)} + \frac{\partial u_k}{\partial x_k} S_i^{(1)} + \frac{7}{5} \frac{\partial}{\partial x_k} (R_1 \sigma P_{ik}^{(1)}) \\ - \frac{2}{5} \frac{\partial}{\partial x_i} (R_1 \sigma p^{(1)}) + \frac{2}{5} \left( \frac{\partial u_k}{\partial x_k} S_i^{(1)} + \frac{\partial u_k}{\partial x_i} S_k^{(1)} \right) + \frac{7}{5} \frac{\partial u_i}{\partial x_k} S_k^{(1)} = \\ = m_1 \bar{C}_{1ikk}^{(3)} \end{aligned} \quad (105)$$

In order to have a complete differential system we have to add to these equations two equations of type (9) for  $m = 1$ , since in the energy equation (31) the quantities  $q_k$  and because of (24) also  $\bar{\epsilon}$  as part of  $\mathcal{C}$  appear. For  $m = 1$ ,  $n = 0$  resp.  $n = 1$  we find

$$\frac{D}{dt} (m_2 \bar{\epsilon}) + \frac{\partial u_k}{\partial x_k} (m_2 \bar{\epsilon}) + \frac{\partial q_k}{\partial x_k} = \bar{C}_{(1)}^{(2)} \quad (106)$$

$$\begin{aligned} \frac{D}{dt} q_i - \frac{1}{\rho} \frac{\partial P_{ki}}{\partial x_k} (m_2 \bar{\epsilon}) + \frac{\partial u_k}{\partial x_k} q_i + \frac{\partial (m_2 R_{ik})}{\partial x_k} + \frac{\partial u_i}{\partial x_k} q_k \\ = \bar{C}_{(1)}^{(2)} \end{aligned} \quad (107)$$

Again we have to substitute for  $R_{ik}$  an approximation according to the Ansatz for  $f_{2i}$ . One can obtain the wanted approximation for  $f_{2i}$  by two ways. The first one is to continue the series for  $\tilde{f}_2$  putting the coefficient  $\tilde{C}^{(1,2)}$  from  $K^{(1)} L^{(1)}$  equal to zero. On the other hand one finds the same result by multiplying the Ansatz (87) with  $(\vec{r} - \vec{w})^2 \vec{e}_i$  integrating and summing

this expression . Using the second way one gets :

$$\begin{aligned}
 m_2 R_{jk} &= \sum_i f_{zi} (\bar{g}_2 - \vec{u})_{jk} \varepsilon_i \alpha \bar{g}_2 \\
 &= R_2 \delta \sum_i f_{zi} (K^{(4)} + \vec{v})_{jk} \varepsilon_i \alpha \bar{g}_2 = R_2 \delta m_2 \bar{E} (G_{jk}^{(4)} + \vec{v}_{jk}) \\
 &= \bar{E} \rho_{jk}^{(4)} m_2^{-1} = m_2 \bar{E} (P_{jk} - P_{jk}^{(4)}) [\beta(1-\alpha)]^{-1}
 \end{aligned} \tag{108}$$

With (108) we find for (107) :

$$\begin{aligned}
 \frac{D}{Dt} q_i - \frac{1}{\rho} \frac{\partial P_{ki}}{\partial x_k} (m_2 \bar{E}) + \frac{\partial u_k}{\partial x_i} q_i + \frac{\partial}{\partial x_k} \left( \frac{m_2 \bar{E} (P_{ik} - P_{ik}^{(4)})}{\rho(1-\alpha)} \right) \\
 + \frac{\partial u_i}{\partial x_k} q_k = \bar{C} \begin{matrix} (1,1) \\ (2,i) \end{matrix}
 \end{aligned} \tag{109}$$

Equations (29) - (31) and (93), (95), (98), (99), (104), (105), (106), (109) are the wanted differential equations . Next we investigate the right hand sides  $\bar{C} \begin{matrix} (1) \\ (n) \end{matrix}$  of these equations .

§ V The collision integrals

The calculation of the collision integrals is somewhat laborious . Therefore we bring it in the appendix . Here we give the general way only . The collision integrals contain five different types of integrals corresponding to the five different transition probabilities  $\sigma$  . Each type is treated differently in the appendix . The following notation is used :

$$J_{\nu\mu}(\psi) = \int \psi (f'_\nu f'_\mu - f_\nu f_\mu) \sigma_{\nu\mu} d\vec{x} \quad (110)$$

$$J_{\nu\mu\rho}^{\alpha\beta}(\psi) = \int \psi (f_\alpha f'_\beta - k_1 f_\nu f_\mu \bar{f}_\rho) \sigma_{\nu\mu\rho}^{\alpha\beta} d\vec{x} \quad (111)$$

$\psi$  can be a function of the velocities  $\vec{p}_1$  ,  $\vec{p}_2$  and for the energy eigenvalues  $\epsilon_i$  .  $d\vec{x}$  means the product of all volume elements of the velocities which appear . The integral sign  $\int$  includes also summation if  $f_{ei}$  ,  $f_{ej}$  , etc. stand behind the integral sign . With this notation we get for the right hand sides of the moment equations the following expressions :

$$\bar{C}_{(1)}^{(0)} = 2 J_{11}^{12} (1) + 2 J_{112}^{22} (1) \quad (112)$$

$$\bar{C}_{(1)}^{(1)} = J_{12} (\vec{p}_1 - \vec{u}) + J_{11}^{(2)} (3(\vec{p}_1 - \vec{u}) + (\vec{p}_1' - \vec{u})) + 2 J_{112}^{22} (\vec{p}_1 - \vec{u}) \quad (113)$$

$$\bar{C}_{(1)}^{(2)} = J_{11} ((\vec{p}_1 - \vec{u})^2) + J_{12} ((\vec{p}_1 - \vec{u})^2) + J_{11}^{(2)} (3(\vec{p}_1 - \vec{u})^2 - (\vec{p}_1' - \vec{u})^2) + 2 J_{112}^{22} ((\vec{p}_1 - \vec{u})^2) \quad (114)$$

$$\bar{C}_{(1)}^{(4)} + 2 \bar{C}_{(2)}^{(4)} = J_{11} ((\vec{p}_1 - \vec{u})^4) + 2 J_{22} ((\vec{p}_2 - \vec{u})^4) + J_{12} ((\vec{p}_1 - \vec{u})^4 + 2(\vec{p}_1' - \vec{u})^2) + J_{11}^{(2)} (3(\vec{p}_1 - \vec{u})^4 - (\vec{p}_1' - \vec{u})^2 - 2(\vec{p}_2 - \vec{u})^2) + 2 J_{112}^{22} ((\vec{p}_1 - \vec{u})^4 + (-1)2(\vec{p}_2 - \vec{u})^2 + (\vec{p}_2' - \vec{u})^2) \quad (115)$$

$$\bar{C}_{(1)}^{(3)} = J_{11} ((\vec{p}_1 - \vec{u})^3) + J_{12} ((\vec{p}_1 - \vec{u})^3) + J_{11}^{(2)} (3(\vec{p}_1 - \vec{u})^3 - (\vec{p}_1' - \vec{u})^3) + 2 J_{112}^{22} ((\vec{p}_1 - \vec{u})^3) \quad (116)$$

$$\begin{aligned} \bar{C}_{(1)}^{(3)} + 2 \bar{C}_{(2)}^{(3)} &= J_{11} (\vec{F}_1 - \vec{u})^3 + 2 J_{22} (\vec{F}_2 - \vec{u})^3 + J_{22} (\vec{F}_1 - \vec{u})^3 + \dots \\ &+ 2 (\vec{F}_2 - \vec{u})^3 + J_{11}^{(2)} (3 (\vec{F}_1 - \vec{u})^3 - (\vec{F}_1' - \vec{u})^3 - 2 (\vec{F}_2' - \vec{u})^3) \\ &+ 2 J_{112}^{(2)} ((\vec{F}_1' - \vec{u})^3 - 2 (\vec{F}_2' - \vec{u})^3 + (\vec{F}_2 - \vec{u})^3) \end{aligned} \quad (117)$$

$$\bar{C}_{(2)}^{(0,1)} = J_{22} (\varepsilon_i) + J_{12} (\varepsilon_i) + J_{11}^{(2)} (-\varepsilon_j) + J_{112}^{(2)} (\varepsilon_i - 2\varepsilon_j) \quad (118)$$

$$\begin{aligned} C_{(2)}^{(1,1)} &= J_{22} (\varepsilon_i (\vec{F}_2 - \vec{u})) + J_{12} (\varepsilon_i (\vec{F}_2 - \vec{u})) \\ &+ J_{11}^{(2)} (-\varepsilon_j' (\vec{F}_2' - \vec{u})) + J_{112}^{(2)} (\varepsilon_i (\vec{F}_2 - \vec{u}) - \dots \\ &\dots - 2\varepsilon_j' (\vec{F}_2' - \vec{u})) \end{aligned} \quad (119)$$

Some integrals  $J$  vanish since the function  $\psi$ , belonging to it, is a collision invariant. We have, for instance,  $J_{11}(\gamma) = 0$ . Such integrals have already been omitted.

For the following calculation of the integrals it is better to introduce the center of gravity coordinates. The integrations over all variables can be performed with exception of the magnitudes of the relative velocities and the angles between the relative velocities.

To calculate the integrals  $J$  one has to substitute for  $f_1, f_{2i}$  the Ansatz (86), (87). As a result the different integrals  $J$  split up into a sum of integrals, which are multiplied by products of  $a^{(\nu)}$ ,  $\beta^{(\nu)}$ . Part of the integrals vanish because of reasons of symmetry such that in the right side of a moment equation not all products of  $a^{(\nu)}$ ,  $\beta^{(\nu)}$  appear. This can be seen easily in the center of gravity system. The transformation into center of gravity coordinates is given in the appendix. Some more approximations for the calculations of the integrals are introduced. As mentioned a substitution of (86), (87) into the collision integrals gives a sum of terms which do not contain  $a^{(\nu)}$ ,  $\beta^{(\nu)}$  or contain these quantities linearly, as double or triple product only. The additional approximation consists in neglecting all terms with double- or triple products. The reason for that is that we already used that  $a^{(\nu)}$ ,  $\beta^{(\nu)}$  have to be small compared to one. The higher products are then small of second resp. third order and are assumed to be

negligible compared to quantities of first order . The order of the neglected double products is discussed in reference [2] for monoatomic gases . For a special force law one can show that for (86) the higher products can indeed be neglected . This estimation and the argumentation with quantities being small of higher order may be the only argument here . A more exact discussion would become too complicated for the equations used in this paper .

Moreover , it is assumed that the translation temperature  $\mathcal{V}$  and the internal temperature  $\Theta$  do not differ very much . We introduce a mean temperature of the dissociating gas which is defined by

$$\begin{aligned} d(e) &= \alpha \left( \frac{3}{2} p + m_2 \bar{E} + \frac{m_1}{2} E_D \right) \\ &= \alpha \left( \frac{3}{2} (1+\alpha) R_2 \mathcal{V} + (1-\alpha) \int_0^{\Theta} c_{\Theta} d\Theta + \alpha E_D^* \right) \\ &= \frac{3}{2} (1+\alpha) R_2 d\mathcal{V} + (1-\alpha) c_{\Theta} d\Theta \\ &\quad + \left( \frac{3}{2} R_2 \mathcal{V} - \int_0^{\Theta} c_{\Theta} d\Theta + E_D^* \right) d\alpha \stackrel{\text{def}}{=} C_V dT + \alpha d\alpha \end{aligned} \quad (120)$$

$C_V$  is the specific heat of the mixture for  $\alpha = \text{const}$  , i. e. without reactions .

One has to connect  $T$  with the specific heat of the non-reacting mixture , since in the case of chemical non-equilibrium the degree of dissociation is a new free variable besides temperature . A change of the internal energy is possible both by changing temperature and degree of dissociation .

According to (120) we have

$$C_V = \frac{3}{2} (1+\alpha) R_2 + (1-\alpha) c_{\Theta} \quad (121)$$

$$\alpha = \frac{3}{2} R_2 T - \int_0^T c_{\Theta} d\Theta + E_D^* \quad (122)$$

$\Theta$  and  $\mathcal{V}$  shall not differ much , thus also  $T$  can only differ little from  $\Theta$  and  $\mathcal{V}$  . If one replaces in (120) for  $d\alpha = 0$  the differentials  $d\mathcal{V}$  ,  $d\Theta$  ,  $dT$  approximately by the finite differences  $\Theta - T_0$  ,  $\mathcal{V} - T_0$  ,  $T - T_0$  then from (120) follows the relation

$$\frac{3}{2} (1+\alpha) R_2 (\mathcal{V} - T) = (1-\alpha) c_{\Theta} (T - \Theta) \quad (123)$$

With the definitions

$$\begin{aligned} \Delta\Theta &= \frac{\Theta - T}{T} \\ \Delta\mathcal{V} &= \frac{\mathcal{V} - T}{T} \end{aligned} \quad (124)$$

we can rewrite (123) into

$$\Delta \bar{v} = -\frac{2}{3} \frac{(1-\alpha) C \Theta}{(1+\alpha) R_2} \Delta \Theta \quad (125)$$

Relation (125) is needed since the mean temperature  $T$  and the translational temperature  $\bar{v}$  or the inner temperature  $\Theta$  enter the final equations as temperature variables.

The approximations to be applied in the calculation of the collision integrals  $J$  make use of the assumption that  $\Delta \bar{v}$  and  $\Delta \Theta$  are assumed to be small compared to one. All quantities depending on  $\bar{v}$  and  $\Theta$  are expanded into  $\Delta \bar{v}$  and  $\Delta \Theta$  and those terms are retained only which contain  $\Delta \Theta$  and  $\Delta \bar{v}$  linear. Also neglected are all products with the small quantities  $\alpha^{(v)}$  and  $\beta^{(v)}$ .

These approximations are not necessary for the calculation of  $J_{11}$ ,  $J_{12}$ ,  $J_{22}$  but they reduce the calculations essentially for  $J_{11}^{12}$ ,  $J_{12}^{22}$ . Besides these advantages this approximation makes sense since (87) assumes that also the internal degrees of freedom are fully excited and that their distribution functions are nearly equilibrium distributions. For the oscillation this will be the case at some thousand degrees Kelvin only. Therefore the internal temperature must not be smaller by magnitudes than the translational temperature. The equations which one gets for letting  $\bar{v}$  and  $\Theta$  be arbitrarily different would not only be very complicated but physically wrong.

If the above used approximations are applied to a gas where an excitation without dissociation of the molecules is possible only <sup>one</sup> gets equations which derived WANG CHANG and UHLENBECK [3] by an application of the CHAPMAN-ENSKOG method. These equations follow as a special case of the here derived equations for  $\alpha = 0$ ,  $\sigma_{111}^{12} = \sigma_{112}^{22} = \sigma_{11} = \sigma_{12} = 0$

Summarizing the results found in the appendix one finds for the quantities  $\bar{C}_{(\mu)}^{(v)}$  the expressions below. The coefficients  $A_v$ ,  $B_v$  etc. consist of a larger number of special collision integrals. These coefficients are still functions of temperature, degree of dissociation and density  $\rho$ . The exact expressions for the different coefficients are given in appendix e)

$$\bar{C}_{(\mu)}^{(0)} = A_1(T, \alpha, \rho) (1 + a_1(T, \alpha, \rho) \Delta \bar{v} + a_2(T, \alpha, \rho) \Delta \Theta) \quad (126)$$

$$\bar{C}_{(1)v}^{(1)} = B_1(T, \alpha, p) a_v^{(1)} + B_2(T, \alpha, p) \beta_v^{(1)} + B_3(T, \alpha, p) \bar{a}_v^{(3)} + B_4(T, \alpha, p) \bar{\beta}_v^{(3)} + B_5(T, \alpha, p) \beta_v^{(1,1)} \quad (127)$$

$$\bar{C}_{(1)v\mu}^{(2)} = \delta_{v\mu} C_1(T, \alpha, p) (1 + \alpha_1(T, \alpha, p) \Delta \vartheta + \alpha_2(T, \alpha, p) \Delta \theta) + a_{v\mu}^{(2)} C_3(T, \alpha, p) + \beta_{v\mu}^{(2)} C_4(T, \alpha, p) \quad (128)$$

$$\bar{C}_{(1)v\mu}^{(2)} + 2 \bar{C}_{(2)v\mu}^{(2)} = \delta_{v\mu} D_1(T, \alpha, p) (1 + \alpha_1(T, \alpha, p) \Delta \vartheta + \alpha_2(T, \alpha, p) \Delta \theta) + a_{v\mu}^{(2)} D_3(T, \alpha, p) + \beta_{v\mu}^{(2)} D_4(T, \alpha, p) \quad (129)$$

$$\bar{C}_{(1)vkk}^{(3)} = E_1(T, \alpha, p) a_v^{(1)} + E_2(T, \alpha, p) \beta_v^{(1)} + E_3(T, \alpha, p) \bar{a}_v^{(3)} + E_4(T, \alpha, p) \bar{\beta}_v^{(3)} + E_5(T, \alpha, p) \bar{a}_v^{(3)} \quad (130)$$

$$\bar{C}_{(1)vkk}^{(3)} + 2 \bar{C}_{(2)vkk}^{(3)} = F_1(T, \alpha, p) + F_2(T, \alpha, p) \beta_v^{(1)} + F_3(T, \alpha, p) \bar{a}_v^{(3)} + F_4(T, \alpha, p) \bar{\beta}_v^{(3)} + F_5(T, \alpha, p) \beta_v^{(1,1)} \quad (131)$$

$$\bar{C}_{(2)}^{(0,1)} = -\frac{3}{2} m_1 D_1 (1 + \alpha_1 \Delta \vartheta + \alpha_2 \Delta \theta) - \frac{E D}{2} A_1 (1 + \alpha_1 \Delta \vartheta + \alpha_2 \Delta \theta) \quad (132)$$

$$\bar{C}_{(2)v}^{(1,1)} = G_1(T, \alpha, p) + G_2(T, \alpha, p) \beta_v^{(1)} + G_3(T, \alpha, p) a_v^{(3)} + G_4(T, \alpha, p) \beta_v^{(3)} + G_5(T, \alpha, p) \beta_v^{(1,1)} \quad (133)$$

For the case of chemical equilibrium one gets from  $\bar{C}_{(1)}^{(0)}$ , which represents the change of the degree of dissociation  $\alpha$  (equation 93), a relation between temperature and degree of dissociation. Before reaching dissociation equilibrium temperature equilibrium between internal and translational temperature will appear. From appendix e) one gets for  $\bar{C}_{(1)}^{(0)}$  for  $\Delta \vartheta = \Delta \theta = 0$

$$A_1(T, \mu, p) = (\bar{\beta} + \bar{\gamma}) (n_1 \bar{F}_1(T) + n_2 \bar{F}_2(T)) \quad (134)$$

To keep of flow in locally chemical equilibrium for all times the quantities  $A_1(T)$  and  $A_2(T)$  have to tend to infinite (at least the collision cross sections  $\sigma_{111}^{(2)}$  resp.  $\sigma_{112}^{(2)}$  have to become large).  $\bar{c}^{(0)}$  remains a finite quantity and gives according to (93) the change of the degree of dissociation (see references [4, 5]). Thus we find from (134)

$$\bar{\beta} = -\bar{\gamma} \quad (\bar{\beta} = \beta(T), \bar{\gamma} = \gamma(T))$$

Substituting the expressions for  $\bar{\beta}$  and  $\bar{\gamma}$  from appendix c), (A65), we find the known law of mass action :

$$\frac{n_1^2}{n_2} = \frac{2^{3/2} (2\pi R_1 T)^{3/2}}{Z \cdot \left(\frac{2h}{m_1}\right)^3} e^{-\frac{E_D}{kT}} \quad (135)$$

It replaces equation (93) in the case of chemical equilibrium .

§ VI The "NAVIER-STOKES" equations for  
a dissociating gas with internal degrees  
of freedom

The quantities  $\vec{u}_1 - \vec{u}$ ,  $P_{ij}$ ,  $P_{ij}^{(1)}$ ,  $S_i$ ,  $S_i^{(1)}$ ,  $\vec{q}$  which appear in the moment equations (95), (99), (98), (104), (105), (107) are treated as independent hydrodynamic state variables. It is known both from experiments and estimations for  $P_{ij} - p\delta_{ij}$  and  $S_i$  for monoatomic gases [2] that these quantities after times of the order of some mean free path times are functions of the variables  $\vec{u}$ ,  $\rho$ ,  $T$  only. This fact together with some additional approximations is used to simplify the given equation such that they correspond to the NAVIER-STOKES equations for monoatomic gases.

First we consider equations (98), (99) for  $P_{ij}$  and  $P_{ij}^{(1)}$ . We define tensors  $p_{ij}$  and  $p_{ij}^{(1)}$  by

$$p_{ij} = P_{ij} - p\delta_{ij}, \quad p_{ij}^{(1)} = P_{ij}^{(1)} - p^{(1)}\delta_{ij} \quad (136)$$

Addition of (98) and (99) gives equations for  $p$  and  $p^{(1)}$ :

$$\frac{D}{Dt} p + \frac{\partial u_k}{\partial x_k} p + \frac{1}{3} \frac{\partial s_k}{\partial x_k} + \frac{2}{3} \frac{\partial u_e}{\partial x_k} P_{ke} = \frac{1}{3} m_1 (\bar{C}_{(1)}^{(2)} + 2\bar{C}_{(2)}^{(2)}) e e \quad (137)$$

$$\begin{aligned} \frac{D}{Dt} p^{(1)} - \frac{2}{3} \alpha (\vec{u}_1 - \vec{u})_e \frac{\partial P_{ke}}{\partial x_k} + \frac{\partial u_k}{\partial x_k} p^{(1)} + \frac{1}{3} \frac{\partial S_k^{(1)}}{\partial x_k} \\ + \frac{2}{3} \frac{\partial \vec{u}_e}{\partial x_k} P_{ke}^{(1)} = \frac{1}{3} m_1 (\bar{C}_{(1)}^{(2)}) e e \end{aligned} \quad (138)$$

Multiplying of (137) with  $\delta_{ij}$  and subtracting it from (98) resp. (138) from (99) we get equations for  $p_{ij}$  and  $p_{ij}^{(1)}$ .

$$\begin{aligned} \frac{D}{Dt} P_{ij} + \frac{\partial u_k}{\partial x_k} P_{ij} + \frac{1}{5} \left( \frac{\partial S_i}{\partial x_j} + \frac{\partial S_j}{\partial x_i} - \frac{2}{3} \frac{\partial S_k}{\partial x_k} \delta_{ij} \right) \\ + \frac{\partial u_i}{\partial x_k} (P_{kj} + p\delta_{jk}) + \frac{\partial u_j}{\partial x_k} (P_{ki} + p\delta_{ki}) - \frac{2}{3} \frac{\partial u_e}{\partial x_k} (P_{ke} + p\delta_{ke}) \delta_{ij} \\ = m_1 (\alpha_{ij}^{(4)} D_3 + \beta_{ij}^{(4)} D_4) \end{aligned} \quad (139)$$

$$\begin{aligned} \frac{D}{Dt} P_{ij}^{(1)} + \frac{2}{3} \alpha (\vec{u}_1 - \vec{u})_e \frac{\partial (P_{ke} + p\delta_{ke})}{\partial x_k} \delta_{ij} - \alpha (\vec{u}_1 - \vec{u})_j \otimes \\ \otimes \frac{\partial (P_{ki} + p\delta_{ki})}{\partial x_k} - \alpha (\vec{u}_1 - \vec{u})_j \frac{\partial (P_{ki} + p\delta_{ki})}{\partial x_k} + \frac{\partial u_k}{\partial x_k} P_{ij}^{(1)} \\ + \frac{\partial u_i}{\partial x_k} (P_{jk}^{(1)} + p^{(1)}\delta_{jk}) + \frac{1}{5} \left( \frac{\partial S_i^{(1)}}{\partial x_j} + \frac{\partial S_j^{(1)}}{\partial x_i} - \frac{2}{3} \frac{\partial S_k^{(1)}}{\partial x_k} \delta_{ij} \right) \\ + \frac{\partial u_j}{\partial x_k} (P_{ik}^{(1)} + p^{(1)}\delta_{ik}) - \frac{2}{3} \frac{\partial u_e}{\partial x_k} (P_{ke}^{(1)} + p^{(1)}\delta_{ke}) \delta_{ij} = \\ m_1 (\alpha_{ij}^{(4)} C_3 + \beta_{ij}^{(4)} C_4) \end{aligned} \quad (140)$$

According to (57), (77), (39) and (44) the coefficients  $a_{ij}^{(2)}$  and  $b_{ij}^{(2)}$  are given by :

$$a_{ij}^{(2)} = \frac{p_{ij}^{(2)}}{p^{(2)}}, \quad b_{ij}^{(2)} = \frac{p_{ij}^{(2)}}{p^{(2)}} \quad (141)$$

Because of (21) we have between  $p_{ij}^{(1)}$ ,  $p_{ij}^{(2)}$  and  $p_{ij}$  resp.  $p^{(1)}$  the relations :

$$p_{ij} = p_{ij}^{(1)} + p_{ij}^{(2)}$$

$$p = p^{(1)} + p^{(2)} = (n_1 + n_2) R_1 \bar{v} m_1 = (1 + \alpha) \rho R_2 \bar{v} \quad (142)$$

Thus the right hand sides of (139) and (140) are given by

$$m_1 (a_{ij}^{(2)} D_3 + b_{ij}^{(2)} D_4) = \frac{1}{R_1 \bar{v}} (p_{ij}^{(1)} (\frac{D_3}{m_1} - \frac{D_4}{m_2}) + p_{ij} \frac{D_4}{m_2})$$

$$m_1 (a_{ij}^{(1)} C_3 + b_{ij}^{(1)} C_4) = \frac{1}{R_1 \bar{v}} (p_{ij}^{(1)} (\frac{C_3}{m_1} - \frac{C_4}{m_2}) + p_{ij} \frac{C_4}{m_2}) \quad (143)$$

Now we make three more approximations which are equivalent to certain restrictions on the flow .

1) The flow shall have the property that the gradients of the state variables are small quantities . This mean for instance that we can treat not too strong shock fronts by the following final equations only . Moreover we assume the quantities

$$\frac{p_{ij}}{p}, \quad \frac{p_{ij}^{(1)}}{p^{(1)}}, \quad \frac{S_i}{p(R_1 T)^{1/2}}, \quad \frac{S_i^{(1)}}{p^{(1)}(R_1 T)^{1/2}}, \quad \frac{q_k}{p(R_1 T)^{1/2}}, \quad \frac{\vec{u}_1 - \vec{u}}{u}$$

to be small of the same order . As a first approximation all products of small quantities being quantities small of second order , will be neglected .

2) The second approximation refers to the variation of the flow quantities in time .

For monoatomic gases and homogenous systems (139) reduces to

$$\frac{D}{Dt} p_{ij} = - \frac{1}{\tau} p_{ij}$$

In this case it can be shown by an estimate of the only collision integral (see ref. [2] that  $\tau$  is of the order of the mean free path time . Thus a disturbance of  $p_{ij}$  , will die out to zero within a few mean free path times . This estimation can be taken over here since the additional terms which come from dissociation collisions and excitation collisions will not remarkably change the times for the decay of the disturbances . In the flow variables

in the homogeneous case shall change slowly within the mean free path time, we can consider the solution of (139) approximately as a superposition of solutions of the following equation (145) which change strongly in time,

$$\frac{D}{Dt} P_{ij} = m_1 (a_{ij}^{(4)} D_3 + \beta_{ij}^{(4)} D_4) \quad (145)$$

and the stationary equation (146)

$$\begin{aligned} \frac{\partial u_k}{\partial x_k} P_{ij} + \frac{1}{5} \left( \frac{\partial S_i}{\partial x_j} + \frac{\partial S_j}{\partial x_i} - \frac{2}{3} \frac{\partial S_k}{\partial x_k} \delta_{ij} \right) + \frac{\partial \bar{u}_i}{\partial x_k} (P_{kj} + P_{jk}) \\ + \frac{\partial \bar{u}_j}{\partial x_k} (P_{ki} + P_{ik}) - \frac{2}{3} \frac{\partial \bar{u}_k}{\partial x_k} (P_{ke} + P_{ek}) \delta_{ij} = m_1 (a_{ij}^{(4)} D_3 + \beta_{ij}^{(4)} D_4) \end{aligned} \quad (146)$$

The solution of (145) is neglected because it dies out quickly.

The same estimation gives also a constant for dieing out of  $S_i$  which differs from  $\tau$  by a factor of order one only. Accordingly we neglect the derivations  $\frac{D}{Dt} S_i$  too.

The constant for the slowing down of heat flow  $\bar{q}$  can become larger than  $\tau$ . The excitation cross sections for that are strongly energy dependent and not well known. However, one can say that  $\bar{q}$  becomes small if the excitation cross sections are small (low temperatures). If  $\bar{q}$  can be compared with  $S_i^{(4)}$  the time constant will not be different by orders from that of  $S_i^{(4)}$ . Therefore we neglect the derivation of  $\bar{q}$  with respect to time, too.

We have still to consider the diffusion equation (95). For an estimate of the order of  $m_1 \bar{C}_{(1)}^{(4)}$  we consider a homogeneous system with  $S_i^{(4)}$  and  $q_i$  equal to zero. Equation (95) reads in this case

$$\frac{D}{Dt} (P_{\alpha}(\bar{u}_1 - \bar{u})) = m_1 \bar{C}_{(1)}^{(4)} \quad (147)$$

where  $\bar{C}_{(1)}^{(4)}$  contains the terms with  $a_{\nu}^{(4)}$  and  $\beta_{\nu}^{(4)}$  of  $\bar{C}_{(1)}^{(4)}$ , only. If one considers on the other hand a flow with  $\frac{D}{Dt} (P_{\alpha}(\bar{u}_1 - \bar{u})) = 0$  one gets from (95), neglecting products of small quantities according to 1), the following equation

$$\frac{\partial P_{ik}^{(4)}}{\partial x_i} - \alpha \frac{\partial P_{ik}}{\partial x_i} = \bar{C}_{(1)}^{(4)} \kappa m_1 \quad (148)$$

Neglecting the derivates of the quantities  $P_{ik}^{(4)}$  too (see 3), one finds

$$\frac{\partial P_{ik}^{(4)}}{\partial x_k} - \alpha \frac{\partial P_{ik}}{\partial x_k} = \bar{C}_{(1)}^{(4)} \kappa m_1 \quad (149)$$

(149) can be transformed into

$$\frac{\partial \frac{m_1}{m_1+m_2}}{\partial x_i} + \frac{\partial \ln p}{\partial x_i} \left( \frac{m_1}{m_1+m_2} - \frac{n_1 m_1}{p} \right) = \frac{m_1}{p} \bar{C}_{(1)}^{(1)}; \quad (150)$$

For a binary mixture without reactions and neglecting thermodiffusion (which corresponds in our approximation neglecting terms with  $\alpha^{(2)}$ ,  $\beta^{(3)}$ ,  $\alpha^{(3)}$  in  $\bar{C}_{(1)}^{(1)}$ ) the diffusion equation has the form (see [14])

$$\begin{aligned} \vec{u}_1 - \vec{u} &= - \frac{(m_1+m_2)^2}{m_1 p} \sum m_i D_{ij} d_j \\ d_j &= \frac{\partial \frac{m_j}{m_1+m_2}}{\partial r} + \frac{\partial \ln p}{\partial r} \left( \frac{m_j}{m_1+m_2} - \frac{n_j m_j}{p} \right) \end{aligned} \quad (151)$$

For a simple model calculated for an oxygen-nitrogen mixture by HANSEN [12] one gets

$$D = D_{12} = D_{21} \approx \frac{2\eta}{p} \quad (152)$$

where  $\eta$  is the coefficient of viscosity of the mixture.

$\eta$  depends again on the time  $\tau$  introduced in (144). If one simplifies (139) to the NAVIER-STOKES relation between  $\rho_{ij}$  and the gradient of  $\vec{u}$  by using the approximations 1) and 2), putting  $S_i = 0$  and

$$\rho_{ik}^{(1)} = c(T, \alpha) \rho_{ik}, \quad \text{one gets}$$

$$p\tau = \eta \quad (153)$$

and thus

$$D = \frac{2p\tau}{p} \quad (154)$$

Taking  $d_1 = d_2$  as a rough estimation one finds from (150), (151) and (154):

$$d_1 = d_2 = \frac{m_1}{p} \bar{C}_{(1)}^{(1)} = -p\alpha (\vec{u}_1 - \vec{u}) \frac{1}{p} \frac{4}{6(1+\alpha)^2} \quad (155)$$

According to this estimation we get from (147)

$$\frac{D}{Dt} (p\alpha (\vec{u}_1 - \vec{u})) \approx -\frac{1}{\tau} p\alpha (\vec{u}_1 - \vec{u}) \quad (156)$$

Thus  $\frac{D}{Dt} (p\alpha (\vec{u}_1 - \vec{u}))$  can be neglected, too.

3) The third approximation refers again to the local variation of the state variables. We require that the gradients of the quantities assumed to be small in 1) be small of second order. This approximation requires more than 1) and is not absolutely necessary. For special cases one can drop this approximation. The equations, resulting without this approximation become so complicated that they would be generally useless. They represent a higher

approximation than the NAVIER-STOKES equations do .

Substituting the approximations 1) , 2)<sup>and</sup> 3) and (143) into (139) , (140)

one gets the NAVIER-STOKES relations :

$$\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij} = \frac{(1+\alpha)\rho}{2} (P_{ij}^{(1)} (\frac{D_3}{m_1} - \frac{D_4}{m_2}) + P_{ij} \frac{D_4}{m_2}) \quad (157)$$

$$\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij} = \alpha \rho (P_{ij}^{(1)} (\frac{C_3}{m_1} - \frac{C_4}{m_2}) + P_{ij} \frac{C_4}{m_2}) \quad (158)$$

Solving these equations for  $P_{ij}$  resp.  $P_{ij}^{(1)}$  one gets

$$P_{ij} = -\mu (\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij}) \quad (159)$$

$$P_{ij}^{(1)} = -\mu_1 (\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij}) \quad (160)$$

with

$$\mu = \frac{1}{m_1} \frac{1-\alpha}{\alpha(1+\alpha)} \frac{\frac{1+\alpha}{2} ( \frac{1-\alpha}{2} D_3 - \alpha D_4 ) - \alpha ( \frac{1-\alpha}{2} C_3 - \alpha C_4 )}{D_4 ( \frac{1-\alpha}{2} C_3 - \alpha C_4 ) + C_4 ( \frac{1-\alpha}{2} D_3 - \alpha D_4 )} \quad (161)$$

and

$$\mu_1 = \frac{1}{m_1} \frac{1-\alpha}{1+\alpha} \frac{\alpha C_4 - \frac{1+\alpha}{2} D_4}{D_4 ( \frac{1-\alpha}{2} C_3 - \alpha C_4 ) + C_4 ( \frac{1-\alpha}{2} D_3 - \alpha D_4 )} \quad (162)$$

The second coefficient of viscosity seems to be missing. In fact gives the second coefficient of viscosity contributions to the diagonal part of  $P_{ij}$  only . Because of the special division of  $P_{ij}$  into  $p_{ij}$  and  $P$   $P_{ij}$  does not contain this contribution . The second coefficient of viscosity is responsible for a relaxation between the internal and translational temperature . This can be seen with the here used method of solution . Genrally one starts with a diagonal term  $p_0 = (1+\alpha)\rho R_2 T$  instead of  $p$  in a division of  $P_{ij}$  . This too must be done here , since  $T$  serves as "temperature" of the gas also for the calculation of all coefficients .

One obtains :

$$\begin{aligned} P &= p_0 (1 + \Delta \vartheta) & p_0 &= (n_1 + n_2) m_1 R_1 T \\ P^{(1)} &= p_0^{(1)} (1 + \Delta \vartheta) & p_0^{(1)} &= n_1 m_1 R_1 T \end{aligned} \quad (163)$$

For temperature equilibrium no second coefficient of viscosity appears. How far we can take the part  $p_0^{(1)} \Delta \vartheta$  of  $P^{(1)}$  as being proportional to the divergence of the flow viscosity will be discussed later when treating the equation

for the internal temperature. The equations for the heat flows  $S_i, S_i^{(1)}, q_i$  are simplified now by the approximations 1) - 3). Thus we find from (104), (105), (109)

$$-\frac{5p}{\rho} \frac{\partial p}{\partial x_i} + \frac{5}{2} \frac{\partial}{\partial x_i} (R_1 \bar{\nu} (p + p^{(1)})) = m_1 (\bar{C}_{(1)}^{(3)} + 2\bar{C}_{(2)}^{(3)})_{ij} \quad (164)$$

$$-\frac{5p^{(1)}}{\rho} \frac{\partial p}{\partial x_i} + 5 \frac{\partial (R_1 \bar{\nu} p^{(1)})}{\partial x_i} = m_1 \bar{C}_{(1)}^{(3)}_{ij} \quad (165)$$

$$-\frac{1}{\rho} \frac{\partial p}{\partial x_i} (m_2 \bar{\epsilon}) + \frac{1}{2} \frac{\partial}{\partial x_i} (R_1 \bar{\nu} m_2 \bar{\epsilon}) = \bar{C}_{(2)}^{(1,1)}_i \quad (166)$$

To these equations we have still to add the diffusion equation which we obtain from (95) using the mentioned approximations:

$$\frac{\partial p^{(1)}}{\partial x_i} - \alpha \frac{\partial p}{\partial x_i} = m_1 \bar{C}_{(1)}^{(1)}_i \quad (167)$$

The right sides of (164) - (167) contain terms with  $a^{(1)}, b^{(1)}, a^{(3)}, b^{(3)}$  and  $b^{(1,1)}$ . We replace the coefficients  $a^{(1)}, b^{(1)}$  by the hydrodynamic quantities  $\bar{u}, \bar{u}_1, \bar{J}, \bar{J}^{(1)}, \bar{q}$  using (20) - (22), (56), (58), (76), (78), (80). The following relation exists between  $\bar{u}, \bar{u}_1, \bar{u}_2$ :

$$\bar{u}_2 - \bar{u}_1 = -\frac{\alpha}{1-\alpha} (\bar{u}_1 - \bar{u}) \quad (168)$$

Since the coefficients  $a^{(1)}, b^{(1)}$  contain <sup>the</sup> differences  $\bar{u}_1 - \bar{u}, \bar{u}_2 - \bar{u}$  only we have instead of five variables  $a^{(1)}, b^{(1)}, a^{(3)}, b^{(3)}, b^{(1,1)}$  the four hydrodynamic variables  $\bar{u}_1 - \bar{u}, \bar{J}, \bar{J}^{(1)}, \bar{q}$  only. Therefore the four equations (164)-(167) can be resolved for these quantities.

If we express the right sides  $\bar{C}_{(\mu)}^{(\nu)}$  by the hydrodynamic variables we obtain for (164) - (167)

$$-\frac{5p}{\rho} \frac{\partial p}{\partial x_i} + \frac{5}{2} \frac{\partial (R_1 \bar{\nu} (p + p^{(1)}))}{\partial x_i} = \frac{m_1}{(R_1 \bar{\nu})^{1/2}} [(E_1 - 5E_3 - \frac{\alpha \sqrt{V}}{(1-\alpha)} (E_5 - 5E_4 - E_5))] \otimes \quad (169)$$

$$\otimes (\bar{u}_1 - \bar{u}) + \frac{\bar{J}^{(1)}}{\rho R_1 \bar{\nu}} \left( \frac{E_3}{\alpha} - \frac{E_4 + 2^{3/2}}{(1-\alpha)} \right) + \frac{\bar{J}^{(1) 3/2} E_4}{\rho R_1 \bar{\nu} (1-\alpha)} + \frac{\bar{q} \sqrt{V} E_5}{m_2 \bar{\epsilon}} \Big]$$

$$-\frac{5p^{(1)}}{\rho} \frac{\partial p}{\partial x_i} + 5 \frac{\partial (R_1 \bar{\nu} p^{(1)})}{\partial x_i} = \frac{m_1}{(R_1 \bar{\nu})^{1/2}} \left[ \frac{\bar{J}^{(1) 3/2} E_4}{\rho R_1 \bar{\nu} (1-\alpha)} + (E_1 - 5E_3 - \frac{\alpha \sqrt{V}}{(1-\alpha)} (E_4 - 5E_4 - E_5)) (\bar{u}_1 - \bar{u}) + \frac{\bar{q} \sqrt{V} E_5}{m_2 \bar{\epsilon}} + \frac{\bar{J}^{(1)}}{\rho R_1 \bar{\nu}} \left( \frac{E_3}{\alpha} - \frac{E_4 + 2^{3/2}}{(1-\alpha)} \right) \right] \quad (170)$$

$$-\frac{1}{\rho} \frac{\partial p}{\partial z} (m_2 \bar{\epsilon}) + \frac{1}{2} \frac{\partial}{\partial z} (R_1 \sigma m_2 \bar{\epsilon}) = \quad (171)$$

$$\begin{aligned} & \frac{1}{(R_1 \sigma)^{1/2}} \left[ (G_1 - 5G_3 - \frac{\alpha \sqrt{2}}{1-\alpha}) (G_2 - 5G_4 - G_5) (\vec{u}_1 - \vec{u}) \right. \\ & \quad \left. + \frac{\rho^{(1)}}{\rho R_1 \sigma} \left( \frac{G_3}{\alpha} - \frac{G_4 2^{3/2}}{1-\alpha} \right) + \frac{\rho^{3/2} G_4}{\rho R_1 \sigma (1-\alpha)} + \frac{\rho \sqrt{2} G_5}{m_2 \bar{\epsilon}} \right] \\ \frac{\partial p^{(1)}}{\partial z} - \alpha \frac{\partial p}{\partial z} &= \frac{m_2}{(R_1 \sigma)^{1/2}} \left[ (B_1 - 5B_3 - \frac{\alpha \sqrt{2}}{1-\alpha}) (B_2 - 5B_4 - B_5) (\vec{u}_1 - \vec{u}) \right. \\ & \quad \left. + \frac{\rho^{(1)}}{\rho R_1 \sigma} \left( \frac{B_3}{\alpha} - \frac{B_4 2^{3/2}}{1-\alpha} \right) + \frac{\rho^{3/2} B_4}{\rho R_1 \sigma (1-\alpha)} + \frac{\rho \sqrt{2} B_5}{m_2 \bar{\epsilon}} \right] \end{aligned} \quad (172)$$

From (169) - (172) we find the wanted NAVIER-STOKES relations .

Let us define

$$-\frac{5\rho}{\rho} \frac{\partial p}{\partial z} + \frac{5}{2} \frac{\partial}{\partial z} (R_1 \sigma (p + p^{(1)})) = \vec{f}_1$$

$$-\frac{5\rho^{(1)}}{\rho} \frac{\partial p}{\partial z} + 5 \frac{\partial}{\partial z} (R_1 \sigma p^{(1)}) = \vec{f}_2 \quad (173)$$

$$-\frac{1}{\rho} \frac{\partial p}{\partial z} (m_2 \bar{\epsilon}) + \frac{1}{2} \frac{\partial}{\partial z} (R_1 \sigma m_2 \bar{\epsilon}) = \vec{f}_3$$

$$\frac{\partial p^{(1)}}{\partial z} - \alpha \frac{\partial p}{\partial z} = \vec{f}_4$$

$$\frac{m_2}{(R_1 \sigma)^{1/2}} (F_1 - 5F_3 - \frac{\alpha \sqrt{2}}{1-\alpha}) (F_2 - 5F_4 - F_5) = g_{11} \quad (174)$$

$$\frac{m_2}{\rho (R_1 \sigma)^{3/2}} \left( \frac{F_3}{\alpha} - \frac{F_4 2^{3/2}}{1-\alpha} \right) = g_{12}, \quad \frac{m_2 2^{3/2} F_4}{\rho (R_1 \sigma)^{3/2} (1-\alpha)} = g_{13}$$

$$\frac{m_2}{\rho (R_1 \sigma)^{1/2}} \frac{\sqrt{2}}{m_2 \bar{\epsilon}} F_5 = g_{14}$$

Replacing in (174) the coefficients  $F_\nu$  by  $E_\nu$ ,  $G_\nu$ ,  $B_\nu$  we have

to replace  $g_{1\beta}$  by  $g_{2\beta}$ ,  $g_{3\beta}$ ,  $g_{4\beta}$

Thus we find for (169) - (172)

$$\vec{f}_\nu = g_{\nu 1} (\vec{u}_1 - \vec{u}) + g_{\nu 2} \vec{S}^{(1)} + g_{\nu 3} \vec{S} + g_{\nu 4} \vec{q} \quad (175)$$

Resolution of (175) gives

$$\begin{aligned}
 \vec{u}_1 - \vec{u} &= \Delta_{1V} \vec{f}_V \\
 \vec{f}^{(1)} &= \Delta_{2V} \vec{f}_V \\
 \vec{f} &= \Delta_{3V} \vec{f}_V \\
 \vec{q} &= \Delta_{4V} \vec{f}_V
 \end{aligned}
 \tag{176}$$

The coefficients  $\Delta_{\mu\nu}$  being functions of  $T$ ,  $p$  and  $\alpha$ . They can be calculated by KRAMER's rule

$$\begin{aligned}
 \Delta_{\mu\nu} &= (-1)^{(\mu+\nu)} \frac{\Delta^{(\mu,\nu)}}{\Delta} \\
 \Delta &= |g_{\mu\nu}|
 \end{aligned}
 \tag{177}$$

where  $\Delta^{(\mu,\nu)}$  represents the subdeterminant of  $\Delta$  by omitting the  $\nu^{\text{th}}$  row and the  $\mu^{\text{th}}$  column. The quantities  $\vec{f}_V$  can still be transformed, but generally they cannot be expressed by gradients of the temperatures  $\vartheta$ ,  $\Theta$ ,  $T$  and the degree of dissociation  $\alpha$ . This is possible for three special cases only: monoatomic gas, polyatomic gas the molecules of which can be excited and a non-reacting gas mixture. For the more general case it is useful to introduce:  $c_{kin} = \frac{3}{2} \frac{p}{\rho}$

the kinetic energy per unit mass  $\epsilon_{kin} = \frac{3}{2} \frac{p}{\rho}$  (178)

the energy of the internal degrees of freedom  $\epsilon^* = \frac{\bar{\epsilon}}{2m_1}$   
per unit mass

Moreover the gradient of an arbitrarily chosen concentration quantity appears.

Generally one chooses as concentration the particle number concentration of the atoms given by  $\frac{n_1}{n} = \frac{2\alpha}{(1+\alpha)}$ . Besides these defined quantities the gradient of pressure still appears in  $\vec{f}_V$ . These  $\vec{f}_V$  can be transformed now into:

$$\begin{aligned}
 \vec{f}_1 &= \frac{5}{4} (R_1 \vartheta)^2 p \left[ \alpha(1-\alpha) \frac{\partial \ln p}{\partial \vec{r}} + (1+3\alpha) \frac{\partial \ln \epsilon_{kin}}{\partial \vec{r}} + \alpha(1-3\alpha) \frac{\partial \ln \frac{2\alpha}{1+\alpha}}{\partial \vec{r}} \right] \\
 \vec{f}_2 &= \frac{5}{2} (R_1 \vartheta)^2 p \left[ \alpha(1-\alpha) \frac{\partial \ln p}{\partial \vec{r}} + 2\alpha \frac{\partial \ln \epsilon_{kin}}{\partial \vec{r}} + 2\alpha(1-\alpha) \frac{\partial \ln \left( \frac{2\alpha}{1+\alpha} \right)}{\partial \vec{r}} \right] \\
 \vec{f}_3 &= \frac{1}{2} (R_1 \vartheta)^2 p \epsilon^* \left[ \alpha(\alpha-1) \frac{\partial \ln p}{\partial \vec{r}} + (1-\alpha) \frac{\partial \ln \epsilon^*}{\partial \vec{r}} - 2\alpha \frac{\partial \ln \frac{2\alpha}{1+\alpha}}{\partial \vec{r}} \right] \\
 \vec{f}_4 &= \frac{1}{2} (R_1 \vartheta)^2 p \left[ \alpha(1-\alpha) \frac{\partial \ln p}{\partial \vec{r}} + 2\alpha \frac{\partial \ln \left( \frac{2\alpha}{1+\alpha} \right)}{\partial \vec{r}} \right]
 \end{aligned}
 \tag{179}$$

The solution (176) of the system (175) can be replaced by a form, using (179), which corresponds to the NAVIER-STOKES relations :

$$\vec{u}_1 - \vec{u} = -(1-\alpha) \frac{D_1 \rho}{2} \frac{\partial \ln \rho}{\partial \vec{r}} - D_1 \vartheta \frac{\partial \ln \epsilon_{kin}}{\partial \vec{r}} - D_1 \Theta \frac{\partial \ln \epsilon^*}{\partial \vec{r}} - (1+\alpha) D_{12} \frac{\partial \ln \left( \frac{\rho \alpha}{1+\alpha} \right)}{\partial \vec{r}} \quad (180)$$

$$\vec{J}^{(1)} = -\lambda_p^{(1)} \frac{\partial \ln \rho}{\partial \vec{r}} - \lambda_{\vartheta}^{(1)} \vartheta \frac{\partial \ln \epsilon_{kin}}{\partial \vec{r}} - \lambda_{\Theta}^{(1)} \Theta \frac{\partial \ln \epsilon^*}{\partial \vec{r}} - \lambda_{12}^{(1)} \frac{\partial \ln \left( \frac{\rho \alpha}{1+\alpha} \right)}{\partial \vec{r}} \quad (181)$$

$$\vec{J} = -\lambda_p \frac{\partial \ln \rho}{\partial \vec{r}} - \lambda_{\vartheta} \vartheta \frac{\partial \ln \epsilon_{kin}}{\partial \vec{r}} - \lambda_{\Theta} \Theta \frac{\partial \ln \epsilon^*}{\partial \vec{r}} - \lambda_{12} \frac{\partial \ln \left( \frac{\rho \alpha}{1+\alpha} \right)}{\partial \vec{r}} \quad (182)$$

$$\vec{q} = -\lambda_p^{(q)} \frac{\partial \ln \rho}{\partial \vec{r}} - \lambda_{\vartheta}^{(q)} \vartheta \frac{\partial \ln \epsilon_{kin}}{\partial \vec{r}} - \lambda_{\Theta}^{(q)} \Theta \frac{\partial \ln \epsilon^*}{\partial \vec{r}} - \lambda_{12}^{(q)} \frac{\partial \ln \left( \frac{\rho \alpha}{1+\alpha} \right)}{\partial \vec{r}} \quad (183)$$

$D_{12}$  is equal to the common binary coefficient of diffusion and the coefficients  $\lambda_{\vartheta}$  and  $\lambda_{\Theta}$  are the common coefficients of heat conductivity.

Not all of the coefficients used in (180) - (183) will have the same order. Experiments show that generally the coefficient of thermodiffusion can be neglected compared with the ordinary coefficient of diffusion. Thus we conjecture also  $D_1 \vartheta$  and  $D_1 \Theta$  being much smaller than  $D_{12}$ . An estimation of the different orders is possible but shall be not performed here.

According to (176), (179), (180) - (183) the coefficients  $D$  and  $\lambda$  are linear combinations of the quantities  $\Delta_{\mu\nu}$  with factors containing  $\alpha$ ,  $\vartheta$ ,  $\Theta$  and  $\rho$ .  $\vartheta$  and  $\Theta$  have to be replaced by  $T$  here since in an expansion around  $T$  terms with  $\Delta \Theta$  and  $\Delta \vartheta$  are multiplied by gradients and have thus to be considered as small quantities of second order (according to 1)). Both equation (181) for  $\vec{J}^{(1)}$  and equation (160) for  $\rho_i^{(1)}$  are superfluous since  $\vec{J}^{(1)}$  and  $\rho_i^{(1)}$  do not appear in the conservation equations and are moreover no state variables. We have still to consider (93) and (106) for  $\alpha$  and the internal energy  $n_2 \bar{\epsilon}$

$$\rho \frac{D\alpha}{Dt} + \frac{\partial}{\partial \vec{r}} \rho \alpha (\vec{u}_1 - \vec{u}) = m_1 A_1 (1 + a_1 \Delta \vartheta + a_2 \Delta \Theta) \quad (184)$$

$$\frac{D}{Dt} (n_2 \bar{\epsilon}) + \frac{\partial u_k}{\partial x_k} (n_2 \bar{\epsilon}) + \frac{\partial q_k}{\partial x_k} = -\frac{3}{2} m_1 D_1 (1 - d_1 \Delta \vartheta + d_2 \Delta \Theta) - \frac{\epsilon_D}{2} A (1 + a_1 \Delta \vartheta + a_2 \Delta \Theta) \quad (185)$$

We replace  $\Delta \bar{v}$  by  $\Delta \Theta$  using (125). With  $m_2 \bar{v} = (1-\alpha) \rho \bar{v}^*$  and using the equation of continuity we obtain

$$\rho \frac{D\alpha}{Dt} + \frac{\partial(\alpha \rho(\bar{u}_2 - \bar{u}^*))}{\partial x} = K_1 + K_2 \Delta \Theta \quad (186)$$

$$\rho \frac{D}{Dt} [(1-\alpha) \bar{v}^*] + \frac{\partial \bar{q}}{\partial x} = K_3 + K_4 \Delta \Theta \quad (187)$$

with

$$K_1 = m_1 A_1$$

$$K_2 = m_1 A_1 \left( a_2 - a_3 \frac{2}{3} \frac{(1-\alpha)}{(1+\alpha)} \frac{C\Theta}{R_2} \right)$$

$$K_3 = - \left( \frac{3}{2} m_1 D_1 + \frac{E_D}{2} A_1 \right) \quad (188)$$

$$K_4 = - \frac{3}{2} m_1 D_1 \left( d_2 - d_1 \frac{2}{3} \frac{(1-\alpha) C\Theta}{(1+\alpha) R_2} \right) - \frac{E_D}{2} A_1 \left( a_2 - a_3 \frac{2}{3} \frac{(1-\alpha)}{(1+\alpha)} \frac{C\Theta}{R_2} \right)$$

As we remarked above it is possible under certain additional assumptions that the part  $\rho \Delta \bar{v}$  of  $\rho$  can be described by a second coefficient of viscosity. To do this we simplify (187) further. With (186) and the relation between  $\bar{v}^*$  and  $\Theta$  we can write (187):

$$\rho(1-\alpha) C\Theta \frac{D\Theta}{Dt} + \bar{v}^* \frac{\partial(\alpha \rho(\bar{u}_2 - \bar{u}^*))}{\partial x} = K_3 + \bar{v}^* K_1 + (K_4 + \bar{v}^* K_2) \Delta \Theta \quad (189)$$

The aim is to transform (189) into an equation which contains  $\frac{D}{Dt} \Delta \Theta$

We have

$$\frac{D}{Dt} \Delta \Theta = \frac{1}{T} \frac{D(\Theta - T)}{Dt} - \frac{\Delta \Theta}{T} \frac{DT}{Dt} \quad (190)$$

In (31) we can replace the derivation of the energy by the derivations of temperature and degree of dissociation using (120). Using (186) for  $\frac{D}{Dt} \alpha$  the energy equation can be written:

$$\rho C_v \frac{DT}{Dt} - C_\alpha \frac{\partial(\alpha \rho(\bar{u}_2 - \bar{u}^*))}{\partial x} + \frac{\partial}{\partial x} \left( \frac{1}{2} \bar{v} + \bar{q} + \rho \alpha E_D^*(\bar{u}_1 - \bar{u}^*) \right) + \frac{\partial u_k}{\partial x_i} P_{ki} = - C_\alpha K_1 - C_\alpha K_2 \Delta \Theta \quad (191)$$

Combining (189) and (190) we obtain

$$\begin{aligned} & \rho \frac{D}{Dt} \Delta \theta + \left( \frac{\varepsilon^*}{(1-\alpha) c_{\theta}} + \frac{c_{\alpha}}{c_v} + \frac{\Delta \theta c_{\alpha}}{c_v} \right) \frac{1}{T} \frac{\partial \rho (\vec{u}_1 - \vec{u})}{\partial \vec{r}} + \frac{1}{T(1-\alpha) \theta} \frac{\partial \vec{q}}{\partial \vec{r}} \\ & - \frac{1}{T c_v} (1 + \Delta \theta) \frac{\partial}{\partial \vec{r}} \left( \frac{1}{2} \vec{J} + \vec{q} + \rho \alpha (\vec{u}_1 - \vec{u}) \varepsilon \vec{D} \right) - \frac{1}{T c_v} (1 + \Delta \theta) \frac{\partial u_k}{\partial x_k} P_k \\ & = \frac{1}{(1-\alpha) c_{\theta} T} [X_3 + \varepsilon^* X_1 + (X_4 + \varepsilon^* X_2) \Delta \theta] + \frac{c_{\alpha}}{T c_v} (1 + \Delta \theta) (X_1 + X_2 \Delta \theta) \\ & \stackrel{def}{=} X_5 + X_6 \Delta \theta + X_7 \Delta \theta^2 \end{aligned} \quad (192)$$

Assuming that the exchange between internal temperature and translational temperature is easy, i. e. assuming the excitation cross sections to be large, we can apply 2) here too and can neglect  $\frac{D}{Dt} \Delta \theta$ . Using the approximations 1) and 3) we obtain from (192)

$$-\frac{\rho \theta}{T c_v} \frac{\partial u_k}{\partial x_k} = X_5 + X_6 \Delta \theta \quad (193)$$

or with (125)

$$\rho_0 \Delta \vec{v} = -\alpha_0 \frac{\partial u_k}{\partial x_k} + \gamma \varepsilon_1 \quad (194)$$

where we used the abbreviations

$$\begin{aligned} \alpha_0 &= -\frac{2}{3} (1-\alpha)^2 c_{\theta}^2 T \rho_0 \frac{1}{c_v (X_4 + \varepsilon^* X_2) + \alpha c_{\theta} (1-\alpha) (X_1 + X_2)} \\ \alpha_1 &= -\frac{2}{3} (1-\alpha) c_{\theta} T \frac{c_{\alpha} (X_3 + \varepsilon^* X_2) + \alpha c_{\theta} (1-\alpha) X_1}{c_v (X_4 + \varepsilon^* X_2) + \alpha c_{\theta} (1-\alpha) (X_1 + X_2)} \end{aligned} \quad (195)$$

For an excited but non dissociated gas we have  $\varepsilon_1 = 0$  (see [7]).  $\varepsilon_0$  is the so-called second coefficient of viscosity. For the case that the exchange between excitation- and translational temperature is easy (194) replaces (187);

The here obtained equations can be generalized by dropping approximation 3). Instead of neglecting the gradients of the small quantities  $P_k$ ,  $\vec{J}$  we apply an iteration process. The equations obtained in this way are so complicated that they can be solved at best in special case.

§ VII Summary

In the proceeding chapters we derived a system of equations for the hydrodynamic state variables of a dissociating gas using a system of BOLTZMANN-equations. The approximations applied correspond to the NAVIER-STOKES equations for monoatomic gases. The resulting system of equations may be again summed up.

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho \vec{u})}{\partial \vec{r}} = 0 \quad (196)$$

$$\rho \frac{D\vec{u}}{Dt} + \frac{\partial \mathcal{P}}{\partial \vec{r}} = 0 \quad (197)$$

$$\rho \frac{De}{Dt} + \frac{\partial}{\partial \vec{r}} \left( \frac{1}{2} \vec{J} + \vec{q} + E_0^* \rho \alpha (\vec{u}_1 - \vec{u}) \right) + \frac{\partial u_k}{\partial x_k} \mathcal{P}_{ki} = 0 \quad (198)$$

$$\rho \frac{D\alpha}{Dt} + \frac{\partial}{\partial \vec{r}} (\rho \alpha (\vec{u}_1 - \vec{u})) = \mathcal{X}_1 + \mathcal{X}_2 \Delta \Theta \quad (199)$$

$$\rho \frac{D}{Dt} [(1-\alpha) \varepsilon^*] + \frac{\partial \vec{q}}{\partial \vec{r}} = \mathcal{X}_3 + \mathcal{X}_4 \Delta \Theta \quad (200)$$

$$P_{ij} = -\mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij} \right) \quad (201)$$

$$\vec{u}_1 - \vec{u} = \frac{-(1-\alpha^2)}{2} D_{1p} \frac{\partial \ln p}{\partial \vec{r}} - D_{1v} \frac{\partial \ln e_{kin}}{\partial \vec{r}} - D_{1\theta} \frac{\partial \ln e^*}{\partial \vec{r}} - (1-\alpha) D_{12} \frac{\partial \ln \frac{2\alpha}{(1+\alpha)}}{\partial \vec{r}} \quad (202)$$

$$\vec{J} = -\lambda_p \frac{\partial \ln p}{\partial \vec{r}} - \lambda_{v^*} \frac{\partial \ln e_{kin}}{\partial \vec{r}} - \lambda_{\theta} \frac{\partial \ln e^*}{\partial \vec{r}} - \lambda_{12} \frac{\partial \ln \frac{2\alpha}{(1+\alpha)}}{\partial \vec{r}} \quad (203)$$

$$\vec{q} = -\lambda_p^{(q)} \frac{\partial \ln p}{\partial \vec{r}} - \lambda_{v^*}^{(q)} \frac{\partial \ln e_{kin}}{\partial \vec{r}} - \lambda_{\theta}^{(q)} \frac{\partial \ln e^*}{\partial \vec{r}} - \lambda_{12}^{(q)} \frac{\partial \ln \frac{2\alpha}{(1+\alpha)}}{\partial \vec{r}} \quad (204)$$

$$e = e_{kin} + (1-\alpha) \varepsilon^* + \alpha E_0^* ; \varepsilon^* = \int_0^{\Theta} c_{\theta} \alpha \Theta$$

$$e_{kin} = \frac{3}{2} p ; p = p_0 (1 + \Delta \sigma) , p_0 = (1+\alpha) p_{R2} T \quad (205)$$

$$\Delta \sigma = \frac{2(1-\alpha) c_{\theta}}{3(1+\alpha) R_2} \Delta \Theta , P_{ij} = p_{ij} + p \nu_{ij}$$

For case of an easy excitation of the internal degrees of freedom we may replace (200) by

$$p_0 \Delta \vartheta = - \alpha_0 \frac{\partial u_k}{\partial x_k} + \alpha_1 \quad (206)$$

Generally the coefficients  $\kappa, \mu, \lambda, D, \alpha$  are functions of  $T, \alpha, \beta$ . The above system contains different special cases.

1) The monoatomic gas

$$\alpha = 1, \Theta = \vartheta = T, \sigma_{11} \neq 0, \text{ all other } \sigma = 0, \varepsilon^* - E_D^* = 0$$

Equations (199), (200), (202) and (205) become superfluous.

2) The polyatomic excited gas.

$$\alpha = 0, \Theta \neq \vartheta, \sigma_{22} \neq 0 \quad \text{all other } \sigma = 0, E_D^* = 0$$

Equations (199) and (202) become superfluous.

3) The mixture of non-reacting atoms and molecules

$$\alpha = \text{const}, \Theta \neq \vartheta, \sigma_{11}^{(2)} = \sigma_{12}^{(2)} = 0, E_D^* = 0$$

Equation (199) can be dropped.

4) Chemical reaction equilibrium.

In this case (199) has to be replaced by (135)



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