Integral Kinetic Equations for a Mixture of Gases with Internal Degrees of Freedom

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INTEGRAL kinetic equations for the theory of monatomic rarefied gases were derived in Ref. 1. A modification of these equations for the case in which a constant field of gravitational forces is present is given in Ref. 2.

The present paper investigates this problem in a considerably more general aspect than do Refs. 1 and 2; the form of integral kinetic equations is established for a mixture of monatomic gases in which chemical reactions may occur during motion and in which motion occurs in a constant external field of gravitational forces.

As in Refs. 1 and 2 it is assumed that only paired collisions of molecules are important for the motion of the gas. This excludes such chemical reactions from the investigation which may occur only for multiple (triple, etc.) collision of gaseous molecules. The equations that will be derived are not applicable to the investigation of the motion of gases in which reactions of this kind take place.

In addition, it is assumed that the gas particles formed during the chemical reactions are electrically neutral; the Coulomb interaction, which should be taken into consideration for charged gas particles, is neglected. This assumption means that the derived equations are not suitable for an investigation of the motion of gases in the presence of considerable ionization.

The notations from Refs. 1 and 2 are used, since the investigation concerns quantities which have the same physical meaning.

The state of the mixture of gases with internal degrees of freedom cannot be described by one distribution function $f(\bar{r}, \bar{u}, t)$ as was the case in Refs. 1 and 2 for the investigation of monatomic gases without internal degrees of freedom. Representation of the state of a mixture of gases with internal degrees of freedom requires a system of distribution functions.

First of all, one has gas particles of different kinds. The type of gas particle can be indicated with an index that assumes a certain finite number of values. In addition, gas particles of a certain kind can be in different energy states that can be denoted by a finite set of quantum numbers (indices), each of which may pass through a finite or denumerable sequence of values.* In general, one is concerned with a finite or denumerable aggregate of types and states of gas particles; in the following it is convenient to disregard the differences between the types of gas particles and their different energy states and consider only aggregate types of gases.

Let us then employ such a representation of the types of gas particles and enumerate with index i the types of particles in terms of the expanded concept. In such a case, the state of the gas can be described by a finite or denumerable set of distribution functions $f_1(\bar{r}, \bar{u}, t)$.

The object of the present paper is to construct a complete system of integral equations from which functions f_i can be derived.

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* The translational degrees of freedom are treated in the classical manner.

1. Probability of Free Motion

Let index i denote the type of gas in its expanded concept. The number dn^i of particles of the ith type, which have velocities from $d\omega$ and located in volume $d\Omega$, is given in terms of the corresponding distribution function $f_i(\bar{r}, \bar{u}, t)$ and equals

$$dn^i = f_i(\bar{r},\bar{u},t)d\omega d\Omega \tag{1}$$

We establish the equation for the probability of free motion during the time interval (τ,t) of a particle of the ith type.

If one is concerned with a gas in a constant external gravitational field, then the radius vector which determines the position of any kind of particle at moment $q(\tau < q < t)$ and the velocity of the particle can be written as follows:

$$\begin{aligned} \bar{r}_q &= \bar{r} - \bar{u}(t-q) + \bar{g}[(t-q)^2/2] \\ \bar{u}_q &= \bar{u} - \bar{g}(t-q) \end{aligned} \tag{2}$$

where $\bar{r}$ is the radius vector and $\bar{u}$ the velocity vector of the particle at moment t.

A particle of the ith kind may collide with a particle of any kind. Let σ_{ik} denote the collision cross section of particles of the ith and kth kinds. Obviously, $\sigma_{ik} = \sigma_{ki}$. Let at a time q a particle of the ith kind have a radius vector $\bar{r}_q$ and velocity $\bar{u}_q$. Then the probability ΔQ_{ik} that the ith particle will collide with any particle of the kth kind in an interval of time Δq is given by:

$$\Delta Q_{ik} = \Delta q \iiint_{-\infty}^{+\infty} |\bar{u}_q - \bar{u}'|\, \sigma(|\bar{u}_q - \bar{u}'|) f_k(\bar{r},\bar{u}',q)d\omega' \tag{3}$$

Correspondingly, the probability Π_{ik} of the event that the particle of the ith kind during the interval of time (τ,t) does not undergo a single collision with particles of the kth kind is expressed as follows:

$$\Pi_{ik}(\bar{r},\bar{u},t,\tau) = e^{-\int_\tau^t \left[\iiint_{-\infty}^{+\infty} |\bar{u}_q - \bar{u}'| \sigma_{ik}(|\bar{u}_q - \bar{u}'|) f_k(\bar{r}_q,\bar{u}',q)d\omega'\right]dq} \tag{4}$$

The probability Π_i of free motion of a particle of the ith kind, the position and velocity of which are determined by equalities (2), in the interval of time (τ,t) according to the theorem of probability multiplication, is given in the following terms:

$$\begin{aligned} \Pi_i(\bar{r},\bar{u},t,\tau) = \prod_k \Pi_{ik} = \exp\sum_k \Bigg\{ - \int_\tau^t \Bigg[\iiint_{-\infty}^{+\infty} |\bar{u} - \bar{g} \times \\ (t-q) - \bar{u}'| \times \sigma_{ik}(|\bar{u} - \bar{g}(t-q) - \bar{u}'|) \times \\ f_k(\bar{r} - \bar{u}(t-q) + \bar{g}\,[(t-q)^2/2],\bar{u}',q)d\omega' \Bigg] dq \Bigg\} \end{aligned} \tag{5}$$

2. Generation Functions Φ_i and $\tilde{\Phi}_i$ and Their Relation with Functions f_i and Π_i

Generalizing (1), we introduce internal generation functions Φ_i such that

$$dn_1{}^i = \Phi_i(\bar{r},\bar{u},t)d\Omega d\omega dt \tag{6}$$

gives the mathematical expectation of the number of particles of the ith kind generated in $d\Omega$ during the time dt which have the velocities from $d\omega$. Analogously, we introduce the limiting generation functions $\tilde{\Phi}_i$ such that quantity

$$dn_2^i = \tilde{\Phi}_i(\bar{r}_s,\bar{u},t)dSd\omega dt \tag{7}$$

gives the mathematical expectation of the number of particles of the ith kind generated on the surface element dS during the time dt which have the velocities from $d\omega$.

Repeating the conclusion given in Ref. 2 in relation to particles of the ith kind, one derives the relationship between the distribution function f_i and functions Φ_i and $\tilde{\Phi}_i$ in the following form:

$$f_i(\bar{r},\bar{u},t) = (1/|(u_s)_n|)\tilde{\Phi}_i(\bar{r}_s,\bar{u}_s,\tau_s)\Pi_i(\bar{r},\bar{u},t,\tau_s) + \int_{\tau_s}^{t} \Phi_i[\bar{r} - \bar{u}(t-\tau) + \bar{g}[(t-\tau)^2]/2]\,\bar{u} - \bar{g}\,(t-\tau),\tau] \times \Pi_i(\bar{r},\bar{u},t,\tau)d\tau \tag{8}$$

3. Collision Transformants and Their Relationship with the Generation Functions

The mathematical expectation of the number of collisions $dn_3^{k,l}$ of particles of the kth kind, which have velocities in $d\omega_1$, with particles of type 1, which have velocities in $d\omega_2$, during the time dt in volume $d\Omega$ is given in the following terms:

$$dn_3^{k,l} = \sigma_{k,l}(|\bar{u}_1 - \bar{u}_2|)\,|\bar{u}_1 - \bar{u}_2|\,f_k(\bar{r},\bar{u}_1,t)f_l(\bar{r},\bar{u}_2,t)d\omega_1 d\omega_2 d\Omega dt \tag{9}$$

We now introduce the internal collision transformants $T_{k,l}^i(\bar{u}_1, \bar{u}_2, \bar{u})$. Function $T_{k,l}^i(\bar{u}_1, \bar{u}_2, \bar{u})$ is called the internal collision transformant if

$$dn_4 = T_{kl,}{}^i(\bar{u}_1,\bar{u}_2,\bar{u})d\omega \tag{10}$$

gives the mathematical expectation of the number of particles of the ith kind which are generated as a result of a real collision of particles of the kth kind, which have velocity $\bar{u}_1$, with a particle of the kind l, which have velocity $\bar{u}_2$, which in such a case have velocities from $d\omega$.

Multiplication of (9) by (10) gives the mathematical expectation of the number of particles of the kind i with velocity from $d\omega$ in volume $d\Omega$, generated during time dt as a result of collisions of particles of the kind k, which have velocities $\bar{u}_1$, with particles of the kind l, which have velocities $\bar{u}_2$.

Integration of the obtained derivation over all $\bar{u}_1$ and $\bar{u}_2$ gives the number dn_{kl}^i of particles of the ith kind in volume $d\Omega$ with velocities from $d\omega$, formed as a result of collisions of particles of the kth kind with particles of kind l:

$$dn_{kl}^i = d\Omega d\omega dt \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int_{-\infty}^{+\infty} |\bar{u}_1 - \bar{u}_2|\,\sigma_{kl}\,(|\bar{u}_1 - \bar{u}_2|) \times f_k(\bar{r},\bar{u}_1,t)\,f_l(\bar{r},\bar{u}_2,t)\,T_{kl}^i(\bar{u}_1,\bar{u}_2,\bar{u})d\omega_1 d\omega_2 \tag{11}$$

Summation of Eq. (11) over all k and all l gives a double number dn_1^i of particles of the ith kind with velocities from $d\omega$ which are formed in volume $d\Omega$ during time dt as a result of all possible collisions of particles of different kinds among themselves. (The number is doubled because each type is repeated twice during the summation over k and l.) Hence

$$dn_1^i = \frac{1}{2}\,d\Omega d\omega dt \sum_k\sum_l \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int_{-\infty}^{+\infty} |\bar{u}_1 - \bar{u}_2|\,\sigma_{kl} \times (|\bar{u}_1 - \bar{u}_2|)f_k(\bar{r},\bar{u}_1,t)\,f_l(\bar{r},\bar{u}_2,t)\cdot T_{kl}^i(\bar{u}_1,\bar{u}_2,\bar{u})d\omega_1 d\omega_2 \tag{12}$$

Comparison of (6) and (12) for dn_1^i gives

$$\Phi_i(\bar{r},\bar{u},t) = \frac{1}{2}\sum_k\sum_l \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int_{-\infty}^{+\infty} |\bar{u}_1 - \bar{u}_2|\,\sigma_{kl} \times (|\bar{u}_1 - \bar{u}_2|)f_k(\bar{r},\bar{u}_1,t)\,f_l(\bar{r},\bar{u}_2,t)\,T_{kl}^i(\bar{u}_1,\bar{u}_2,\bar{u})d\omega_1 d\omega_2 \tag{13}$$

We now introduce the collision transformants $\tilde{T}_k^i(\bar{u}_1,\bar{n},\bar{u},\theta)$ which characterize the collision of particles with a fixed surface with the normal n and temperature θ:

$$dn_5 = \tilde{T}_k^i(\bar{u}_1,\bar{n},\bar{u},\theta)d\omega \tag{14}$$

gives the mathematical expectation of the number of particles of type i which are generated as a result of a real collision of particles of the kth kind, which have velocity $\bar{u}_1$, with the surface element dS with the normal n and the temperature θ and which have velocities from $d\omega$ after generation.

Multiplication of (14) by $f_k(\bar{r}_s,\bar{u}_1,t)/(\bar{u}_1)_n/dSdtd\omega_1$ gives the mathematical expectation of the number of particles of type i with velocities from $d\omega$ which are generated during the interval of time dt as a result of collisions with dS particles of the kth kind having velocities $\bar{u}_1$. Integration according to all velocities $\bar{u}_1$ which provide satisfaction of inequality $(\bar{u}_1)_n < 0$ and summation of the derived expressions over all k, that is, taking the collisions of gaseous particles of all kinds with element dS into account gives

$$dn_2^i = dSd\omega dt\sum_k \int\!\!\int\!\!\int_{(u_1)_n<0} |(u_1)_n|\,f_k(\bar{r}_s,\bar{u}_1,t)\tilde{T}_k^i(\bar{u}_1,\bar{n},\bar{u},\theta)d\omega_1 \tag{15}$$

Comparison of (7) and (15) for dn_2^i gives

$$\tilde{\Phi}_i(\bar{r}_s,\bar{u},t) = \sum_k \int\!\!\int\!\!\int_{(u_1)_n<0} |(\bar{u}_1)_n| f_k(\bar{r}_s,\bar{u}_1,t)\tilde{T}_k^i(\bar{u}_1,\bar{n},\bar{u},\theta)d\omega_1 \tag{16}$$

4. System of Equations

Equations (5, 8, 13, and 16) form a system of integral equations which should give functions f_i, Π_i, Φ_i, and $\tilde{\Phi}_i$. This system of equations is as follows:

$$f_i(\bar{r},\bar{u},t) = (1/|(u_s)_n|)\tilde{\Phi}_i(\bar{r}_s,\bar{u}_s,\tau_s)\Pi_i(\bar{r},\bar{u},t,\tau_s) + \int_{\tau_s}^{t} \Phi_i[\bar{r} - \bar{u}(t-\tau) + \bar{g}[(t-\tau)^2/2],\,\bar{u} - \bar{g}(t-\tau),\tau] \times \Pi_i(\bar{r},\bar{u},t,\tau)d\tau \tag{17}$$

$$\Pi_i(\bar{r},\bar{u},t,\tau) = \exp\sum_k \left\{-\int_\tau^t\left[\int\!\!\int\!\!\int_{-\infty}^{+\infty} |\bar{u} - \bar{g}(t-q) - \bar{u}'| \times \sigma_{ik}(|\bar{u} - \bar{g}(t-q) - \bar{u}'|)f_k(\bar{r} - \bar{u}(t-q) + \bar{g}[(t-q)^2/2],\,\bar{u}',q)d\omega'\right]dq\right\} \tag{18}$$

$$\Phi_i(\bar{r},\bar{u},t) = \frac{1}{2}\sum_k\sum_l \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int_{-\infty}^{+\infty} |\bar{u}_1 - \bar{u}_2|\,\sigma_{kl}(|\bar{u}_1 - \bar{u}_2|) \times f_k(\bar{r},\bar{u}_1,t)f_l(\bar{r},\bar{u}_2,t)\,T_{kl}^i(\bar{u}_1,\bar{u}_2,\bar{u})d\omega_1 d\omega_2 \tag{19}$$

$$\tilde{\Phi}_i(\bar{r}_s,\bar{u},t) = \sum_k \int\!\!\int\!\!\int_{(u_1)_n<0} |(u_1)_n| f_k(\bar{r}_s,\bar{u}_1,t)\tilde{T}_k^i\,(\bar{u}_1,\bar{n},\theta)d\omega_1 \tag{20}$$

As indicated in Refs. 1 and 2, functions Π_i, Φ_i, and $\tilde{\Phi}_i$ can be excluded from the system of Eqs. (17–20), and then a system of integral equations can be derived for the purpose of determining f_i. This system is as follows:

$$f_i = V_i(f_1,\ldots,f_k,\ldots) \tag{21}$$

where V_i are certain integral operators over functions f_i which can be readily written out.

If the system of Eq. (21) is solved, then functions Π_i, Φ_i, and $\tilde{\Phi}_i$ are calculated according to known f_i with the aid of (18–20).

5. Remarks

Some general remarks are made in conclusion.

First, if the differential operator

$$\frac{\partial}{\partial t} + u_1\frac{\partial}{\partial x_1} + u_2\frac{\partial}{\partial x_2} + u_3\frac{\partial}{\partial x_3} + g_1\frac{\partial}{\partial u_1} + g_2\frac{\partial}{\partial u_2} + g_3\frac{\partial}{\partial u_3} \tag{22}$$

affects both parts of (21), then the differential equations give the integro-differential equations that are a generalization of Boltzmann's equation, adapted to an investigation of gaseous mixtures of a variable chemical composition.

Second, for the particular case of a mixture of monatomic gases without internal degrees of freedom, located in a constant gravitational field, Eq. (22) indicates that they are satisfied if the following functions stand for the distribution functions:

$$f_i = a_i e^{-hm_i(u^2+2\chi)} \tag{23}$$

which corresponds to Boltzmann's distribution. In Eq. (23), m_i stands for the mass of the ith atom, χ the potential of the gravitational forces, and a_i certain constants.

Third, the method of sequential approximations can be used for solving (21) in a large number of cases.

References

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[2] Belova, A. V. and Vallander, S. V., "Integral kinetic equations of the theory of monatomic gases in the presence of an external field of gravitational forces," Vestn. Leningr. Univ., Ser. Mat., Mekh., i Astron. (Bull. Leningrad Univ., Math., Mech., Astron. Ser.), no. 7, issue 2, 75 (1961).

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Comments on "Role of Radiation in Modern Gasdynamics"

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THE paper by Zhigulev et al.,* together with the material referred to by the reviewer, provides a useful introduction to radiation and gasdynamics. However, the reader who is interested in current professional activities and in broad coverage of modern research in this field might do well to avail himself of the unique opportunity for study provided by a series of four separate colloquium proceedings, all of which have been published or will be published in 1963. This heavy concentration of activity reflects the fact that the astrophysicists, who have been active workers on radiation and gasdynamics for more than thirty years, have not yet relinquished it to the aerodynamicists—who have been rediscovering this field of applied science during the last few years. The four symposium publications are briefly described in the following paragraphs.

Colloquium on Radiation Transfer in Stellar Atmospheres, edited by C. de Jager and A. B. Underhill, J. Quant. Spectry. & Radiative Transfer **3**, 98–220 (1963). This journal issue contains papers on "Fundamental Problems of Radiative Transfer," "Transfer in Lines and Related Problems," and "Computer Techniques Useful for Radiative Transfer Problems."

Proceedings of the Symposium on Quantitative Spectroscopy and Applications in Space Science, edited by S. S. Penner and L. D. Kaplan (to be published in J. Quant. Spectry. & Radiative Transfer, December 1963). These proceedings will contain papers on quantitative spectroscopy (using electric arcs, atomic beams, and shock tubes), spectral line shapes, induced intensities, and solar, interstellar, Venerial, and cosmological problems in spectroscopy.

Proceedings of the Sixth AGARD Combustion and Propulsion Colloquium, Part II, Radiative Transfer in Flow Fields, edited by D. B. Olfe (to be published by Pergamon Press, Ltd., London, October 1963.) This book will contain six papers dealing primarily with the influence of radiative transfer on shock propagation and re-entry heat transfer, as well as selected contributions on basic spectroscopy, temperature measurements, and radiation cooling.

High Temperature in Aeronautics, edited by Carlo Ferrari (to be published by the Politecnico di Torino, Torino, Italy, October 1963). This volume contains surveys on re-entry heat transfer, the influence of radiative transfer on shock propagation, material problems, etc.

The AIAA community will have the opportunity of first-hand exposure at the Aerospace Science Conference, New York City, January 20–22, 1964, where one session will be devoted to "Radiation and Gasdynamics."

* Zhigulev, V. N., Romishevskii, Ye. A., and Vertushkin, V. K., "Role of radiation in modern gasdynamics" AIAA J. 1, 1473–1485 (1963).