PHYSICAL KINETICS and TRANSFER PROCESSES in PHASE TRANSITIONS

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This monograph is based on the original works of the authors. It aims at revealing the necessity and efficiency of combining the kinetic and phenomenological approaches to study heat and mass transfer processes with phase transitions. On the basis of kinetic equations, mass transfer in channels and a model high-porous body is investigated taking into account physiochemical transformations on the walls. The focus is placed on the problems of heat and mass transfer with phase transitions in porous media and metals under the action of high concentrated energy sources. Mathematical statements of the likewise problems are different from traditional.

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FOREWORD

Processes of heat and mass transfer with phase transitions take an important place in such modern technologies as thermal treatment and drying of materials, welding of details, vacuum techniques, metallurgy, heat protection, laser and electron-beam treatment of materials, etc. Correct description of such processes, especially of high-rate ones and of the ones proceeding in non-equilibrium conditions, requires the use of the methods of physical kinetics. In certain cases here it is necessary to use a kinetic approach for describing transfer processes on the whole, whereas in other cases it should be used only for the formulation of the corresponding boundary conditions for phenomenological transfer equations. The kinetic examination refers, mainly, to mass transfer processes in a gaseous phase. At the same time, the issues, related to the kinetics proper of physicochemical transitions on surfaces (for instance, step mechanism of crystal bodies evaporation, the appearance and the growth of crystals, etc.), go beyond the framework of this book and are not examined here.

The problems of heat transfer with phase transitions for solid bodies in a heated gas flow (as well as during the injection and the suction of substance through a porous surface) should be regarded as conjugated [1], i.e. transfer equations in two media, for instance, an equation for a boundary layer in gas and a heat conduction equation for a solid body should be solved simultaneously. The most complicated issue during the mathematical formulation of such problems is a correct formulation of boundary conditions on a phase transition boundary.

A moving phase boundary is a discontinuity surface on which conjugation conditions, obtained from mass, momentum and energy conservation laws [2–4], should be set. However, to find a unique solution of this problem, additional conditions, the form of which depends on gas rarefaction degree and on non-equilibrium degree of phase transitions, should be formulated on this boundary. It turns out here, that such conditions are not always evident even in the case of a dense gas (for example, ordinary sticking conditions [5] can become unfeasible). To obtain similar additional conditions on gas-body interface the methods of kinetic theory of gases should be used.

Chapter 1 examines the problems of boundary conditions on a permeable phase boundary surface and their use during the examination of weakly non-equilibrium processes, for the description of which ordinary equations of viscous and heat conductive gas movement (the Navier-Stokes approximation) are used, while kinetic effects, appearing only in a thin layer near a gas-body surface, are taken into consideration in boundary conditions.

It should be noted, that in markedly non-equilibrium conditions the problem of studying heat and mass transfer during phase transitions becomes much more complicated. For these conditions transfer processes in a gaseous phase should be examined on the basis of the Boltzmann kinetic equation. Such an approach is used, for instance, in [6] to describe the evaporation of solid bodies into vacuum in a one-dimensional case, whereas paragraph 2.6 displays the examination results of high intensity gas escape into vacuum from an axiasymmetric hole during material evaporation from an inner surface.

An interesting situation appears during the description of mass transfer in porous bodies. The matter is, that the radii of pores (capillaries) can often be compared to a mean free path of molecules, so to examine evaporation (condensation) processes in pores even at a normal outer pressure, strictly speaking, it is also necessary to solve a kinetic equation with corresponding boundary conditions.

Real porous bodies have an extremely complicated structure, which makes mathematical description of heat and mass transfer processes in them very difficult. Various models of porous bodies are therefore widely used. Here we will use only two of them, i.e. a "dusty gas" globular model and a capillary model, since these are the models which are adjusted best of all to the use of the methods of kinetic theory of gases. In the first of the above models a highly porous body is simulated by a homogeneous system of stationary and chaotically located spheres of the same radius. Chapter 3 "Transfer Processes In High-Porous Media At Different Knudsen Numbers" provides a review of kinetic theories of transfer processes in dispersed and porous bodies. On the basis of the already mentioned "dusty gas" model a new approach to describe mass transfer during gas evaporation and filtration through a layer of a finite thickness has been suggested. In a one-component case simple expressions have been found for evaporation and filtration velocities, permeability coefficient and density jumps on a gas-porous medium boundary which depend on the Knudsen number and comparison has been made with the experimental results on the permeability of porous catalysts.

A capillary model (a system of parallel cylindrical capillaries) is the simplest one and it is widely used for describing heat and mass transfer during the drying of capillary-porous bodies, for heterogeneous catalysis and in thermal protection. Various asymptotic relations, for example, the Fick law and the Knudsen law for diffusion and the Poiseuille formula for hydrodynamic gas flow regime are widely used for calculating mass transfer in technological processes. One of the aims of solving the above-mentioned internal boundary problems of the kinetic theory of gases is to find the limits of the application of such relations. Besides, in many cases, to describe transfer processes in porous media (catalysis, separation of gas mixtures and drying) it is necessary to know the detailed structure of a gas flow in individual pores, i.e. internal boundary problems of the kinetic theory of gases acquire an independent significance. In the case of a free molecular flow, however, when a major role is played by collisions of molecules with walls, mass transfer in channels is examined taking into consideration adsorption and the presence of mobile adsorbed layers on the surface. A kinetic analysis here makes it possible to reject an assumption on the equilibrium between gas and adsorbed phases in each cross-section whereas such an assumption is characteristic for channels of infinite length. The calculation of mass transfer taking into consideration phase transitions on the walls of a non-isothermal channel shows, that the value and the sign of the temperature drop influence considerably the character of mass transfer since there may take place either a transition from evaporation to condensation or, on the contrary, a transition from condensation to evaporation. All these issues are examined in Chapters 2 and 4.

The knowledge of the kinetics of transfer processes inside pores is also required for the correct statement of the problems of heat and mass transfer with phase transitions in porous and capillary-porous bodies. During the thermal treatment of such media the phase transition boundary is moving into the depth of the material with a velocity depending on the nature of a vapor flow in a "dry" zone of a porous body. Differently speaking, the kinetics of mass transfer in pores determines the boundary conditions on the phase transition surface which is inside the body. In Chapter 5 "Problems of Heat and Mass Transfer with Phase Transitions in Porous Media" at first the known methods of describing heat and mass transfer during phase transitions in porous media are analyzed and then certain problems of the Stefan type with a mobile phase transition boundary inside a model porous body are examined. The expressions, obtained on the basis of the analysis of mass transfer kinetics during evaporation in a channel are used here for the movement velocity of the above boundary.

During the examination of the influence of high-concentration radiation (laser beam, electron beam) on materials it is necessary, in certain cases, to study the kinetics of photon and electron absorption in a substance, which makes it possible to define the form of a heat source. In particular, the analysis of the heat source form with the use of the numerically obtained spatial distribution of electron energy losses shows, that with an increase of the electron beam diameter the energy release maximum shifts from the surface to the depth of the material. This result, which cannot be obtained with the help of the known approximate models for the distribution of electron energy losses, gives an additional opportunity to explain the experimental fact, that a transition from a continuous mass removal to explosive boiling up is observed only at beam diameters, exceeding electron mean free path. The peculiarities of transfer processes during melting, surface and volume vapor formation in metals, related to the structure of the heat source, being formed in a sample, are examined in Chapter 6.

There are some additions and changes, introduced into this publication in comparison with the book in Russian. A greater number of works has been reviewed in Chapter 2 due to new research of intensive evaporation and condensation processes and a new paragraph has been added on high intensity gas escape from a hole during evaporation from an inner surface. Chapter 3 is new (with the exception of the part of para 3.2). A new paragraph has been added to Chapter 4 on a new phenomenon, i.e. on a lightinduced drift of molecules as applied to porous bodies. Certain changes have been introduced into the statement of the Stefan problem in porous bodies (Chapter 5). New paragraphs have been added to Chapter 6 about the influence of a high-current electron beam's proper magnetic field on electron absorption kinetics and about a possibility to strengthen the subsurface layer of a metal by an electron beam. Certain explanations and additions have also been introduced into some paragraphs of the book for a better understanding of the issues considered there. At the same time, certain materials, illustrating the use of the obtained boundary conditions, have been taken away from Chapter 1.

The bibliography has been considerably enlarged at the expense of new works on the problems under examination.

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CHAPTER

ONE

EXTERNAL PROBLEMS OF HEAT AND MASS TRANSFER IN A WEAKLY RAREFIED GAS ON PERMEABLE SURFACE

1.1 ELEMENTS OF KINETICS THEORY OF GASES†

For many problems of gasdynamics (as well as of heat and mass transfer), hydrodynamic description of gas flow is insufficient, i.e. it is insufficient to know only averaged quantities, such as gas density ρ, its velocity $\vec{v}$ and its temperature T. In such cases we have to solve the problem at molecular level, i.e. to search for the function of gas molecules distribution in velocities.

In gas molecules are separated by distances, much in excess of their dimensions, and they may fairly freely move relative to each other. The distance, which a molecule travels from one collision to another, is called a free path. Such a path is different for different molecules, as well as for the same molecule in various sections of its trajectory. That is why we introduce a notion of mean free path Λ, which allows one to clarify the essence of such transfer phenomena as viscosity, heat conduction and diffusion in gases. At that, transfer coefficients depend on a mean free path. If gas molecules are regarded as elastic spheres of fixed diameter d, then

$$\Lambda = \frac{1}{\sqrt{2}\sigma n} = \frac{1}{\sqrt{2}\pi d^2 n}$$

† For detailed study of kinetic theory and dynamics of rarefied gas books [7–12] can be recommended.

where $\sigma = \pi d^2$ is the cross-section of molecule collision, n is the number of particles per gas unit volume. For molecules, which are force field centers and which have an infinite radius of action, a notion of effective diameters, and, consequently, of effective cross-sections, is introduced.

The number of particles with coordinates and velocities, which at the time instant t are within the interval $d\vec{r}d\vec{\xi}$ near the point $(\vec{r}, \vec{\xi})$ of the six-dimensional phase space $(\vec{r} = (x_1, x_2, x_3), \vec{\xi} = (\xi_1, \xi_2, \xi_3))$ is equal to

$$dN = F(\vec{r}, \vec{\xi}, t)\, d\vec{r}d\vec{\xi}$$

where the function $F(\vec{r}, \vec{\xi}, t)$ is called the function of gas molecule distribution in velocities. Consideration is also given to the mass distribution function $f = mF$ (m is a molecular mass). Knowing f (or F), it is possible to determine the mean value of any function

$$\bar{\varphi} = \frac{\int \varphi f d\vec{\xi}}{\int f d\vec{\xi}} = \frac{1}{\rho}\int \varphi f d\vec{\xi}$$

The basic equation of the gas kinetic theory is the Boltzmann integro-differential equation for the distribution function f. When external forces are absent, it has the form

$$\frac{\partial f}{\partial t} + \vec{\xi}\frac{\partial f}{\partial \vec{r}} = \frac{1}{m}J(f) = \frac{1}{m}\int (f'f_1' - ff_1)\, g b db d\psi d\vec{\xi}_1 \tag{1.1}$$

where $f' = f'(t, \vec{r}, \vec{\xi}')$, $f_1 = f(t, \vec{r}, \vec{\xi}_1)$, $f_1' = f(t, \vec{r}, \vec{\xi}_1')$, $\vec{\xi}, \vec{\xi}'$ are the vectors of molecule velocity in a stationary coordinate system before and after a collision, respectively; $J(f)$ is the collision integral, which expresses the rate of the change in the distribution function due to collisions of molecules; g is the relative velocity of colliding molecules; b is the collision parameter; ψ is the angle, determining the spatial position of the collision plane.

In deriving equation (1.1) it is assumed that consideration can be confined to binary collisions, i.e. the collisions, in which only two molecules participate; that the distribution function does not change at the distances of the order of the interaction diameter and $f(t, \vec{r}_1, \vec{\xi}_1) = f(t, \vec{r}, \vec{\xi}_1)$; that the condition of molecular chaos is satisfied, i.e. probabilities of two colliding molecules being at the phase points $(\vec{r}, \vec{\xi})$ and $(\vec{r}_1, \vec{\xi}_1)$, respectively, are independent. The collision integral $J(f)$ takes on various forms depending on the nature of molecular force interaction during collisions. If the Boltzmann equations (1.1) is reduced to the dimensionless type [9], then the parameter $1/\mathrm{Kn}$ (where $\mathrm{Kn} = \Lambda/L$ is the Knudsen number, equal to the ratio of the mean free path of molecules Λ to the characteristic length L) appears before the collision integral $J(f)$. The Knudsen number, which characterizes the degree of gas rarefaction, plays an important role in the kinetic theory of gases. With its help the classification of rarefied gas flows is conducted. When $\mathrm{Kn} \gg 1$, there exists a free molecular flow, in which the main role is played by collisions of molecules with walls, whereas the collisions inside the flow can be ignored. The other extreme case Kn $\ll 1$ corresponds to the flow of weakly rarefied gas (the slip-flow), when for describing the gas movement it is sufficient to use the Navier-Stokes macroscopic equations, however, with the boundary conditions of slip and temperature jump. These conditions will be discussed in more detail in paragraph 1.2.

A widely known method for solving the Boltzmann equation (1.1) for small Kn numbers is the method of expansion in a small parameter ε = Kn, introduced for the first time by Gilbert and further developed in works by Enskog and Chapman. This expansion has the form

$$f(t, \vec{r}, \vec{\xi}) = \sum_{k=0}^{\infty} \varepsilon^k f^{(k)}(t, \vec{r}, \vec{\xi}) \tag{1.2}$$

Here

$$f^{(0)} = f_0 = \frac{\rho}{(2\pi RT)^{3/2}} \exp\left\{-\frac{(\vec{\xi} - \vec{v})^2}{2RT}\right\} \tag{1.3}$$

is the local Maxwell distribution function; $\vec{v}(\vec{r}, t) = \frac{1}{\rho}\int \vec{\xi} f d\vec{\xi}$ is the mean mass velocity of gas; $\rho = \int f d\vec{\xi}$ is the gas density; $T = \frac{2}{3\rho R}\int \frac{(\vec{\xi} - \vec{v})^2}{2} f d\vec{\xi}$ is the gas temperature. Confining ourselves to two terms of series (1.2), we will obtain†

$$f^{(1)} = f_0\left[1 + \frac{p_{ij}}{2pRT} u_i u_j - \frac{q_i u_i}{pRT}\left(1 - \frac{u^2}{5RT}\right)\right] \tag{1.4}$$

where $\vec{u} = \vec{\xi} - \vec{v}$ is the relative molecular velocity, while the tensor of viscous stresses p_{ij} and the heat flux q_i are equal ($i, j, k = 1, 2, 3$, δ_{ij} is the Kronecher's symbol):

$$p_{ij} = \int f u_i u_j d\vec{\xi} - p\delta_{ij} = -\mu\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\frac{\partial v_k}{\partial x_k}\right)$$

$$q_i = \int \frac{u_i u^2}{2} f d\vec{\xi} = -\lambda \frac{\partial T}{\partial x_i} \tag{1.5}$$

It should be noted, that in a zero approximation, when f is specified by expression (1.3), $p_{ij} = 0$, $q_i = 0$. Expressions (1.4), (1.5) correspond to the Navier-Stokes approxima-

† The summation is carried out by the repeated indexes.

tion. Leaving three terms of series (1.2), the distribution function in the Barnett approximation is obtained, etc.

From microscopic description of non-equilibrium state of gas with the help of the distribution function it is possible to proceed to a less detailed description by means of macroscopic hydrodynamic quantities ρ, $\vec{v}$, T, determined above. Multiplying both the left-hand and the right-hand sides of the Boltzmann equation (1.1) by 1, ξ_i, $\frac{1}{2}\xi^2$ respectively and integrating over the entire range of molecule velocity variation ($-\infty \le \xi_i \le \infty$) we obtain the continuity equation, the momentum conservation equation and the energy conservation equation. However, the equations, obtained with respect to ρ, $\vec{v}$, T, contain the quantities p_{ij} and q_j. To close the system of equations, it is necessary to make use of the additional relations between the quantities, which enter into the equations. In particular, in the Chapman-Enskog method for small Knudsen numbers these additional relations are found from approximation (1.3) for the distributional function $f^{(0)}$, (1.4), (1.5) for $f^{(1)}$, etc. As a result, familiar Euler, Navier-Stokes, Barnett equations are obtained. It should be noted, that similar conservation equations can also be obtained phenomenologically. However, the kinetic approach allows one not only to obtain hydrodynamic equations, but also to find the transfer coefficients (the viscosity μ, the thermal conductivity λ and the diffusion D coefficients), which enter into them.

A characteristic feature of the solution in the form of series (1.2) is the fact, that the distribution function in any point (t, $\vec{r}$) is completely determined by the hydrodynamic quantities ρ, $\vec{v}$, T in the same point. However, the values of these quantities at any time instant are found with the aid of macroscopic transfer equations by their initial value at the time instant $t = t_0$. Since hydrodynamic quantities represent integrals over $\vec{\xi}$ from the distribution function f, there exists an infinite set of initial distribution, which lead to the same initial values of the hydrodynamic quantities. That is why, generally speaking, the distribution function is not found in a unique manner, i.e. solution (1.2) cannot represent the general solution of the Boltzmann equation. At the same time, expansion (1.2) is reduced asymptotically to the solution of the Boltzmann equation when Kn $\to 0$ and at the increase of $t - t_0$, i.e. at the internal points of the flow region. However, near the boundaries and near the initial instant series (1.2) does not represent the solution to the Boltzmann equation. In connection with this there arises a question of the correct initial and boundary conditions, which the macroscopic Navier-Stokes, Barnett equations, etc., valid at the internal points of the flow, should satisfy. To obtain such conditions, it is necessary to study the structure of initial and boundary (Knudsen) layers [9].

Another method of the solution for kinetic equation (1.1), i.e. the method of moments should also be considered briefly. Grad [13] used the expansion of the distribution function f in a series by the Hermite polynomial[†]:

$$f = f_0 \sum_{n=0}^{\infty} \frac{1}{n!} a_i^{(n)} H_i^{(n)} = f_0 \Big[a^{(0)} H^{(0)} + a_i^{(1)} H_i^{(n)} +$$

[†] The summation is carried out by the repeated indexes.

$$+\frac{1}{2!}a_{ij}^{(2)}H_{ij}^{(2)}+\frac{1}{3!}a_{ijk}^{(3)}H_{ijk}^{(3)}+\ldots\Big] \tag{1.6}$$

where $a_i^{(n)}(\vec{r},t) = \frac{1}{\rho}\int fH_i^{(n)}d\vec{\xi}$ are the coefficients of expansion (1.6); $H_i^{(n)}(c_1, c_2, c_3)$ are the Hermite polynomials from three independent variables; $\vec{c} = \vec{u}/\sqrt{RT}$ is the dimensionless relative velocity of molecules (ρ and $\vec{v}$ are the moments of the zero and of the first order respectively). The moments of the second and of the third order from the distribution function are determined by the expressions

$$P_{ij}(\vec{r},t) = \int u_i u_j f d\vec{\xi} \qquad q_{ijk} = \frac{1}{2}\int u_i u_j u_k f d\vec{\xi}$$

By reducing the indexes the following tensors will be obtained:

$$P_{ii} = 3p \qquad q_{ijj} = q_i$$

Here $p_{ij} = P_{ij} - p\delta_{ij}$, where p is the pressure ($p_{ii} = 0$). The coefficients $a_i^{(n)}$ can be expressed by moments. In particular,

$$a^{(0)} = 1 \qquad a_i^{(1)} = 0 \qquad a_{ij}^{(2)} = p_{ij}/p \qquad a_{ijk}^{(3)} = q_{ijk}/p\sqrt{RT}$$

If expansion (1.6) is reduced to the three first terms and if from the system of moments, used here, only those are left, which have a clear physical sense ($\rho, v_i, T, p_{ij}, q_i$), then the so-called thirteen-moment approximation, coinciding in form with (1.4), is obtained. However, the thirteen-moment approximation for the distribution function f differs from approximation (1.4) in the fact, that in the Chapman-Enskog method the distribution function is completely determined by the hydrodynamic quantities ρ, $\vec{v}$, T. That is why the stress tensor p_{ij} and the heat flux q_i, which enter into the Navier-Stokes approximation (1.4), are expressed in terms of velocity components, density, temperature and their derivatives. This makes it possible to close the hydrodynamic system of the Navier-Stokes equations. In the method of moments (in particular, in the thirteen-moment approximation), the tensor of viscous stresses p_{ij} and the heat flux q_i are used as independent variables along with the hydrodynamic quantities ρ, $\vec{v}$, T. The system of macroscopic differential equations, corresponding to the thirteen-moment approximation, which is obtained by the multiplication of the Boltzmann equation into the respective Hermite polynomials and by integrating with respect to various velocities $\vec{\xi}$, contains the equations for p_{ij} and q_i and has the form

$$\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial x_r}(\rho v_r) = 0 \tag{1.7}$$

$$\frac{\partial v_i}{\partial t}+v_r\frac{\partial v_i}{\partial x_r}+\frac{1}{\rho}\frac{\partial P_{ir}}{\partial x_r} = 0 \tag{1.8}$$

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x_r}(v_r p) + \frac{2}{3} P_{ir}\frac{\partial v_i}{\partial x_r} + \frac{2}{3}\frac{\partial q_r}{\partial x_r} = 0 \tag{1.9}$$

$$\frac{\partial p_{ij}}{\partial t} + \frac{\partial}{\partial x_r}(v_r p_{ij}) + \frac{2}{5}\left(\frac{\partial q_i}{\partial x_j} + \frac{\partial q_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\frac{\delta q_r}{\partial x_r}\right) +$$

$$+ \; p_{ir}\frac{\partial v_j}{\partial x_r} + p_{jr}\frac{\partial v_i}{\partial x_r} - \frac{2}{3}\delta_{ij}p_{rs}\frac{\partial v_r}{\partial x_r} +$$

$$+ \; p\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\frac{\delta v_r}{\partial x_r}\right) + \frac{6}{m}B_1^{(2)}\rho p_{ij} = 0 \tag{1.10}$$

$$\frac{\partial q_i}{\partial t} + \frac{\partial}{\partial x_r}(v_r p_i) + \frac{7}{5}q_r\frac{\partial v_i}{\partial x_r} + \frac{2}{5}q_r\frac{\partial v_r}{\partial x_i} +$$

$$+ \frac{2}{5}q_i\frac{\partial v_r}{\partial x_r} + RT\frac{\partial p_{ir}}{\partial x_r} + \frac{7}{2}p_{ir}\frac{\partial}{\partial x_r}(RT) -$$

$$-\frac{p_{ir}}{\rho}\frac{\partial P_{rs}}{\partial x_s} + \frac{5}{2}p\frac{\partial}{\partial x_i}(RT) + \frac{4}{m}B_1^{(2)}\rho q_i = 0 \tag{1.11}$$

where $B_1^{(2)}$ is the value, depending on the law of molecule interaction [13]. The first three equations (1.7)–(1.9) are the usual conservation equations.

It should be noted, that the system of non-stationary equations (1.7)–(1.11) is of the hyperbolic type, whereas the Navier-Stokes equations are of the parabolic type. In the phenomenological linear theory of heat conduction hyperbolic equation [14] is often used

$$\rho c_v\frac{\partial T}{\partial t} + \tau_p\frac{\partial^2 T}{\partial t^2} = \lambda\frac{\partial^2 T}{\partial x^2} \tag{1.12}$$

When deriving this equation the relation for the heat flux q (at τ_p = const) is used instead of the Fourier law

$$q = -\lambda\frac{\partial T}{\partial x} - \tau_p\frac{\partial q}{\partial t} \tag{1.13}$$

where c_v is the specific heat capacity; τ_p is the time of the heat stress relaxation. The equation of the type (1.12) can be obtained from the general system of equations (1.7)–(1.11) with very considerable limitations, i.e. while considering a one-dimensional unsteady heat flux in the gas at rest ($v = 0$) at $p_{ij} = 0$. Then from (1.7)–(1.11) we have

$$\frac{\partial\rho}{\partial t} = \frac{\partial p}{\partial x} = 0 \qquad \frac{3}{2}R\rho\frac{\partial T}{\partial t} = -\frac{\partial q}{\partial x}$$

$$\frac{\partial q}{\partial t} + \frac{5}{2}pR\frac{\partial T}{\partial x} + \frac{4}{m}B_1^{(2)}\rho q = 0 \tag{1.14}$$

Further relations [13] will be used

$$\tau_c = \frac{m}{6B_1^{(2)}\rho} = \frac{\mu}{p} \qquad \lambda = \frac{15}{4}R\mu$$

$$\mu = \rho\Lambda\left(\frac{2RT}{\pi}\right)^{1/2} \tag{1.15}$$

for molecules as solid spheres.

The value τ_c has the dimension of time and in the order it coincides with the mean time between two successive collisions of the molecule τ, which in its turn can be determined as the ratio of the mean free path Λ to the mean thermal velocity of molecules $\bar{u}$:

$$\tau = \frac{1}{\nu} = \frac{\Lambda}{\bar{u}} = \rho\frac{\Lambda}{\int_0^\infty f_0 u\, 4\pi u^2 du} = \frac{\Lambda}{\sqrt{8RT/\pi}} \tag{1.16}$$

Here ν is the frequency of collisions. Then (1.14) can be written in the following form

$$q + \frac{3}{2}\tau_c\frac{\partial q}{\partial t} + \frac{15}{4}R\mu\frac{\partial T}{\partial x} = 0$$

or

$$q = -\lambda\frac{\partial T}{\partial x} - \frac{3}{2}\tau_c\frac{\partial q}{\partial t} \tag{1.17}$$

Thus, (1.17) in fact coincides with (1.13). However, non-one-dimensional heat flux causes the appearance of stresses ($p_{ij} \neq 0$) [13]. Transfer equations, taking into consideration the finite velocity of the substance propagation in porous bodies, will be treated in paragraph 5.1. For small Kn numbers, when the relaxation time τ_c is considerably less than the characteristic time of the problem and prehistory of the process is not essential, Navier-Stokes and Barnett approximations [9] can be obtained from thirteen-moment equations (1.7)–(1.11).

It should be noted, that, strictly speaking, the study of unsteady state of gas in terms of the times, comparable with the mean time between two successive collisions of molecules τ, should be conducted on the basis of the solution for the Cauchy problem for the Boltzmann equation with setting, at $t = 0$, of a certain initial distribution function, which is equivalent to specifying an infinite set of moments [15].

In the case of a mixture of gases of N of the components, not reacting with each other, N of the Boltzmann equations for N of the distribution function can be obtained [9]:

$$\frac{\partial f_r}{\partial t} + \vec{\xi}\frac{\partial f_r}{\partial \vec{r}} = \sum_{\nu=1}^{N} \frac{1}{m_\nu} J_{r\nu} \qquad r = 1, 2, \ldots, N \tag{1.18}$$

where

$$J_{r\nu} = \int \left[f_r(\vec{\xi}')f_\nu(\vec{\xi}_1') - f_r(\vec{\xi})f_\nu(\vec{\xi}_1) \right] g_{r\nu} b\,db\,d\psi\,d\vec{\xi}_1$$

The basic hydrodynamic quantities for a mixture of gases are defined in the following way:

the density of the t^{th} component of gas

$$\rho^{(r)} = \int f_r(\vec{\xi})\,d\vec{\xi} \tag{1.19}$$

the density of the mixture

$$\rho = \sum_{r=1}^{N} \rho^{(r)} \tag{1.20}$$

the mean velocity of the t^{th} component

$$\vec{v}^{(r)} = \frac{1}{\rho^{(r)}} \int \vec{\xi} f_r(\vec{\xi})\,d\vec{\xi} \tag{1.21}$$

the mean velocity of the mixture

$$\vec{v} = \frac{1}{\rho} \sum_{r=1}^{N} \rho^{(r)} \vec{v}^{(r)} \tag{1.22}$$

the diffusion velocity of the t^{th} component

$$\vec{V}^{(r)} = \frac{1}{\rho^{(r)}} \int (\vec{\xi} - \vec{v}) f_r\,d\vec{\xi} = \vec{v}^{(r)} - \vec{v} \tag{1.23}$$

the diffusion flux of the t^{th} component

$$\rho^{(r)}\vec{V}^{(r)} = \rho^{(r)}(\vec{v}^{(r)} - \vec{v}) \qquad \sum_{r=1}^{N} \rho^{(r)}\vec{V}^{(r)} = 0 \tag{1.24}$$

the individual temperature of the t^{th} component of gas

$$\frac{3}{2}kn^{(r)}T^{(r)} = \frac{3}{2}\rho^{(r)}R^{(r)}T^{(r)} = \frac{1}{2}\int u^2 f_r d\vec{\xi} \qquad (1.25)$$

(k is the Boltzmann constant, n is the number of particles in the gas volume unit);

the mean temperature of the mixture

$$\frac{3}{2}knT = \frac{3}{2}\rho RT = \frac{1}{2}\sum_{r=1}^{N}\int u^2 f_r d\vec{\xi} \qquad nT = \sum_{r=1}^{N} n^{(r)}T^{(r)} \qquad (1.26)$$

the partial tensor of the viscous stresses of the t^{th} component

$$p_{ij}^{(r)} = P_{ij}^{(r)} - p^{(r)}\delta_{ij} = \int\left(u_i u_j - \frac{1}{3}u^2\delta_{ij}\right)f_r d\vec{\xi} \qquad (1.27)$$

the tensor of viscous stresses of the mixture

$$p_{ij} = \sum_{r=1}^{N} p_{ij}^{(r)} \qquad p = \frac{1}{3}(P_{11} + P_{22} + P_{33}) \qquad (1.28)$$

the partial heat flux of the t^{th} component

$$q_i^{(r)} = \frac{1}{2}\int u_i u^2 f_r d\vec{\xi} \qquad (1.29)$$

the heat flux in the mixture

$$q_i = \sum_{r=1}^{N} q_i^{(r)} \qquad (1.30)$$

At the expansion of the distribution function f_r into a series by the Hermite polynomials there appears a situation, which does not take place in the case of a one-component gas. It is connected with the possibility of a certain arbitrariness in the choice of the local Maxwell distribution function, near which the expansion can be carried out. To determine the local Maxwell function either mean mass velocity of the mixture $\vec{v}$ and mean temperature T or mean velocities of individual components $\vec{v}^{(r)}$ and their temperatures $T^{(r)}$ can be used. For two weakly interacting subsystems, which slowly exchange energy (for example, electrons and ions, whose masses sharply differ), it is possible to speak of various temperatures of the subsystems and to use individual temperatures in the expansion. If mean velocity and mean temperature of the mixture are taken as the original quantities in the local Maxwell function, then, under the approximation, analogous to the thirteen-moment approximation for a one-component gas, the following relation can be obtained [16]:

$$f_r = \frac{\rho^{(r)}}{(2\pi R^{(r)}T)^{3/2}m}\left[1 + \frac{p_{ij}^{(r)}}{2p^{(r)}R^{(r)}T}u_iu_j - \frac{q_i^{(r)}u_i}{p^{(r)}R^{(r)}T}\left(1 - \frac{u^2}{5R^{(r)}T}\right) + \right.$$

$$\left. + \frac{u_iV_i^{(r)}}{2R^{(r)}T}\left(7 - \frac{u^2}{R^{(r)}T}\right)\right]\exp\left(-\frac{u^2}{2R^{(r)}T}\right) \tag{1.31}$$

To solve boundary problems of the kinetic theory of gases it is necessary to know the nature of interaction of gas molecules with the surface of a streamlined body, i.e. the distribution function of reflected molecules, which can be of quite a different character, compared to the distribution function of incident molecules. These two functions are connected with each other on the gas-body interface by a certain integral relationship [9], which contains the probability function $W(\vec{\xi}^-, \vec{\xi}^+)$ of the fact, that the molecule, incident on the surface at the velocity $\vec{\xi}^-$ at the interval $d\vec{\xi}^-$, is reflected from it with the velocity $\vec{\xi}^+$ at the interval $d\vec{\xi}^+$. The function $W(\vec{\xi}^-, \vec{\xi}^+)$ depends on many factors, such as physical and chemical properties of the surface, its temperature and the degree of its treatment. However, due to non-availability of reliable experimental data various approximate models of molecular interaction with the surface, containing the so-called accommodation coefficients, are used. For example, the coefficient of energy accommodation α_E and the coefficient of tangential momentum accommodation α_τ are determined by the expressions:

$$\alpha = \frac{E^- - E^+}{E^- - E_w} \quad \text{or} \quad E^+ = (1 - \alpha_E)\,E^- + \alpha_E E_w$$

$$\alpha_\tau = \frac{P_\tau^- - P_\tau^+}{P_\tau} \quad \text{or} \quad P_\tau^+ = (1 - \alpha_\tau)\,P_\tau^- \quad (P_{w\tau} = 0)$$

where E and P_τ are the absolute values of fluxes of energy and tangential momentum component, respectively. The indexes (–) and (+) refer, respectively, to the flows of incident and reflected molecules. The quantities E_w and $P_{w\tau}$ define the fluxes of energy and of the tangential momentum component, carried-over by molecules, emitted with the Maxwellian distribution, corresponding to the surface temperature T_w [8].

One of the most prevailing models suggests, that a fraction $(1 - \alpha_\tau)$ of the incident molecules is specular-reflected, whereas the remaining fraction α_τ is diffuse-reflected with the Maxwellian distribution. If, in this distribution, the temperature is equal to the wall temperature (the gas enters into the heat equilibrium with the wall), then $\alpha_E = \alpha_\tau = \alpha$ (the Maxwell model). The distribution function for the reflected molecules in this case has the form:

$$f^{+}(t,\vec{r},\vec{\xi}^{+}) = (1-\alpha)f^{-}(t,\vec{r},\vec{\xi}^{+}-2(\vec{\xi}^{+}\vec{n})\vec{n}) + \alpha\frac{\rho_w}{(2\pi RT_w)^{3/2}}\exp\left(-\frac{\xi^{+2}}{2RT_w}\right)$$

A more detailed description of molecular interaction with surfaces is given in paragraph 4.1.

1.2 THE BOUNDARY CONDITIONS OF JUMPS OF HYDRODYNAMIC QUANTITIES ON PERMEABLE SURFACES

As was noted in the last paragraph, the presentation of the distribution function in the form of series (1.2) asymptotically tends, when $\varepsilon \to 0$, to the solution of the Boltzmann equation at the inner points of the flow. However, in the near-wall layer of the thickness of the order of Λ (the Knudsen layer) expansion (1.2) is not valid. The molecules of gas pass through this layer, on the average, without collisions, and near the wall gas consists of the molecules, which departed from it, and of the molecules, which came from the layer at the distance Λ. As a result, one can observe, in particular, the phenomena of slip and temperature jump, i.e. the gas velocity near the wall is other than zero, whereas the temperature differs from the temperature of the wall. That is why for the Navier-Stokes equations, valid beyond the Knudsen layer, it is necessary to determine dummy macroscopic boundary conditions on the streamlined surface (Fig. 1), which would allow the solution of these equations, coinciding, beyond the Knudsen layer, with the solution of the Boltzmann equation for real kinetic conditions on the body surface [9]. Strictly speaking, the deduction of such boundary conditions should be based on the study of the Knudsen layer. However, certain assumptions, formulated by Maxwell, which allow one to obtain approximate dummy boundary conditions without the solution of the Boltzmann equation, are often used. According to one of the hypotheses, the distribution function for the molecules, incident on the wall, is the same, as that in the main flux, i.e. it does not change in the Knudsen layer. According to the second hypothesis gas molecules should be specular-reflected and diffuse-reflected from the surface.

In the present paragraph we will derive the approximate boundary conditions for the case, when the mixture of gases flows past a permeable surface, i.e. the surface, on

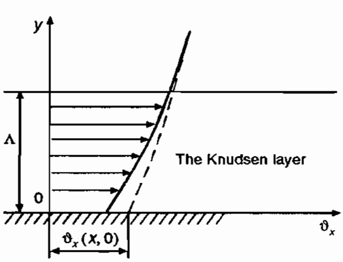

Figure 1 Diagram of the Knudsen layer near the surface of the streamlined body.

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