

## THE KINETIC THEORY OF GASES IN DISPERSED MEDIA\*

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A generalization of the kinetic theory of gases to non-uniform and non-equilibrium systems is given, and this is used to construct a kinetic theory of dispersed media.

The equations of motion of uniform liquids and gases were first obtained using Newton's dynamic equations at the beginning of the eighteenth century, when liquids and gases were regarded as continuous media, which filled the space completely /1/. At that time the idea of a molecular structure of materials was quite vague. These equations were later extended, without any proper basis, to the motion of non-uniform gaseous mixtures and liquids. It was assumed that non-uniform flows could be regarded as interpenetrating multicomponent systems, in which the elementary volumes contained approximately the same number of molecules of the same kind. However, it was later found that these generalizations were limited, and it was necessary to introduce empirical corrections, connected with the diffusion velocities and thermal fluxes. It was not clear in that case to what extent one could make use of the initial equations of motion. Only the methods of the kinetic theory of gases /2/ enabled one to introduce the necessary clarity into what had been essentially uncertain for a long time.

We will show below that the applicability of the assumption of the mutual penetration of different components of a gas in a gaseous mixture is confined to small diffusion velocities and systems which are in a state close to thermodynamic equilibrium /3/. These systems can be described by the initial equations of hydrodynamics. It is also shown that Boltzmann's kinetic theory can describe multicomponent gaseous systems, which are fairly far from a state of thermodynamic equilibrium, when the diffusion velocities and thermal fluxes may be considerable. The fundamental equations of motion, obtained for these cases, differ considerably from the classical equations of hydrodynamics /4/.

The first attempts to describe non-uniform disperse media, which were made at the middle of the present century, also without any proper basis, and to describe non-uniform gaseous mixtures, were based on the use of the classical mechanics of continuous mutually penetrating media and employed the additional concept of multivelocity interpenetrating continua /5/. Later, the methods of the kinetic theory of gases in combination with classical methods of aeromechanics were applied to disperse systems in a number of papers /6/. Investigations in which the conclusions of the kinetic theory of gases were applied directly to describe only individual characteristics of disperse media were widely used abroad /7/. Note that even the partial use of the methods of kinetic theory enabled the development of the theory of disperse media to progress. The kinetic theory of gases will also be used below to construct a theory of non-uniform dispersed media.

The kinetic theory of gases was extended by Boltzmann to describe gaseous mixtures. For a gaseous mixture consisting of  $M$  components we will have  $M$  distribution functions  $f_s(\mathbf{r}, \mathbf{u}, t)$  ( $s = 1, 2, \dots, M$ ), which will satisfy the following system of kinetic equations:

$$\frac{df_s}{dt} = \sum_{i=1}^M J(f_s, f_i) \quad (1)$$

Hence, for each component of the mixture we can obtain five, generally speaking, different mean parameters of the flow

$$n_s = \int f_s du, \quad \mathbf{V}^s = \frac{1}{n_s} \int \mathbf{u} f_s du, \quad 3kT_s = \frac{1}{n_s} \int m_s (\mathbf{u} - \mathbf{V}^s)^2 f_s du$$

The mean-mass parameters of the flow for the whole mixture have the form

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$$\rho_0 = \sum_{s=1}^M \rho_s, \quad U_0 = \frac{1}{\rho_0} \sum_{s=1}^M \rho_s V^s, \quad T_0 = \frac{1}{\rho_0} \sum_{s=1}^M \rho_s T_s \quad (2)$$

The diffusion parameters of the flow (the densities, velocities, and the temperatures) are

$$\Delta_s = \rho_0 - \rho_s, \quad W^s = U_0 - V^s, \quad \tau_s = T_0 - T_s \quad (3)$$

Hence, it is clear that to describe an  $M$ -component gaseous mixture we have  $5(2M + 1)$  averaged parameters.

When solving the system of kinetic Eqs. (1) by the Chapman-Enskog method we obtain systems of aerohydrodynamic equations for the mean-mass parameters of the flow.

In the zeroth approximation we obtain Euler's system of equations. The diffusion velocities are zero.

In the first approximation we obtain the system of Navier-Stokes equations. The diffusion velocities are small, do not influence the motion of the mixture as a whole, and are given by the equations

$$W^s = \frac{n^s}{n_s \rho} \sum_{\tau \neq s} m_\tau D_{s\tau} d_\tau - \frac{1}{m_s n_s} D_s^T \text{grad} \ln T$$

$$d_\tau = \text{grad} \frac{n_\tau}{n} + \left( \frac{n_\tau}{n} - \frac{n_\tau m_\tau}{\rho} \right) \text{grad} \ln P, \quad n = \sum_{s=1}^M n_s$$

In the second approximation we obtain the Barnett system of equations /8/. The diffusion velocities are now not small

$$W_\alpha^s = W_{\alpha(1)}^s + \zeta_1 \frac{\partial T_s}{\partial r_\alpha} \text{div} V^s + \dots$$

and have a considerable effect on the motion of the gaseous mixture as a whole

$$P_{\alpha\beta}^{(2)} = P \delta_{\alpha\beta} - \mu \varepsilon_{\alpha\beta} - \sum_{\tau=1}^M \rho_\tau W_\alpha^\tau W_\beta^\tau + \dots$$

(The second approximation was investigated in /9/ at the author's suggestion.)

The above expressions also contain a number of other Barnett and diffusion terms, which are omitted here for simplicity.

As can be seen, the use of the Chapman-Enskog method in the second approximation to describe gaseous mixtures indicates that the diffusion velocities occurring in the system affect the motion of the mixture as a whole and change the system of equations of motion. However, it is extremely difficult in this approximation to determine them in explicit form. Prigozhin /10/ first pointed out the limitations of this method: the first approximation of the Chapman-Enskog method does not enable one to advance any further than the linear thermodynamics of irreversible processes, i.e., processes which only depart slightly from the state of equilibrium.

In practice, we would expect more from Boltzmann's kinetic theory. To investigate these possibilities another method of solving the system of kinetic Eqs. (1) was developed in /3/ in the hope of describing processes which differ considerably from a state of thermodynamic equilibrium. In this method, system (1) is written in the form

$$\frac{df_s}{dt} = \sum_{\tau \neq s} J(f_s, f_\tau) + \frac{1}{\varepsilon} J(f_s, f_s)$$

In the zeroth approximation  $J(f_s^{(0)}, f_s^{(0)}) = 0$ , and the partial distribution functions of the zeroth approximation will have the form

$$f_s^{(0)} = n_s \left( \frac{m_s}{2\pi k T_s} \right)^{3/2} \exp \left[ - \frac{m_s (u - V^s)^2}{2k T_s} \right]$$

where  $V^s$  and  $T_s$  may differ for different components of the mixture. Then the partial parameters will satisfy the following system of hydrodynamic equations of the zeroth approximation:

$$-\frac{\partial \rho_s}{\partial t} + \frac{\partial}{\partial r_\alpha} (\rho_s V_\alpha^s) = 0 \quad (4)$$

$$\begin{aligned} \frac{\partial V_\alpha^s}{\partial t} + V_\beta^s \frac{\partial V_\alpha^s}{\partial r_\beta} + \frac{1}{\rho_s} \frac{\partial P_s}{\partial r_\alpha} &= \frac{16}{3\rho_s} \sum_{\tau \neq s} \frac{\rho_s \rho_\tau}{m_s + m_\tau} \Omega_{st}^{(1,1)} (V_\alpha^\tau - V_\alpha^s) \\ \frac{\partial T_s}{\partial t} + V_\alpha^s \frac{\partial T_s}{\partial r_\alpha} + \frac{2}{3} T_s \frac{\partial V_\alpha^s}{\partial r_\alpha} &= \frac{32}{9kn_s} \sum_{\tau \neq s} \frac{\rho_s \rho_\tau}{m_s + m_\tau} \Omega_{st}^{(1,1)} \frac{T_s}{m_s} \times \\ &\left( \frac{T_s}{m_s} + \frac{T_\tau}{m_\tau} \right)^{-1} \left[ \frac{3}{2} \frac{m_s}{m_s + m_\tau} \left( \frac{T_\tau}{T_s} - 1 \right) \times \right. \\ &\left. \left( \frac{2kT_s}{m_s} + \frac{2kT_\tau}{m_\tau} \right) + (V^\tau - V^s)^2 \right] \end{aligned}$$

The right-hand sides of the equations of conservation of momentum and energy of system (4) are identical with the equations of the first approximation, in which, for simplicity, we have omitted the viscous terms, and have only retained terms which take into account the interaction between the individual components of the gaseous mixture, which leads to equalization of the temperatures and the flow velocities.

Hence, we can now determine the averaged partial parameters for each component of the mixture ( $\rho_s, V^s, T_s$ ) taking their interaction into account, and we can then determine both the mean-mass parameters of the whole mixture and the diffusion velocities and temperatures, using relations (2) and (3).

The successes achieved by the dynamic theory when investigating gaseous mixtures indicate, without any doubt, that it is worth using this powerful method to construct a kinetic theory of dispersed media.

However, the history was somewhat different. In 1941 when investigating the superconductivity of liquid helium, Landau /11/ suggested considering it in the form of a mixture of two continuous interpenetrating media (in the static sense) namely, a normal and a superconducting flow of a quantum liquid. Despite Landau's warning that this approach is no more than a method of giving a graphical description, the revived representation in quantum mechanics of the mutual penetration of different media (in the static sense) has again been used in a number of papers on the dynamic theory when constructing the classical mechanics of considerably non-uniform heterogeneous media, which is in clear contradiction with the molecular structure of the material. These representations are reflected fairly fully in the monograph /5/. The equations of the mechanics of heterogeneous media, obtained on the basis of these representations, contain a considerable number of unknown functions and constants, defining the transfer coefficients of each component of the medium, and also coefficients representing the interaction between these components. These unknown constants are determined in this paper using quite arbitrary assumptions regarding the cellular structure of the medium, the operation of averaging etc.

As already mentioned, in a number of papers (/6/ etc.) the theory of disperse media has been based on a combination of the methods of kinetic theory and the methods of classical aerodynamics. Disperse particles are considered in the form of solid inclusions which interact with one another as elastic spheres. The effect of the carrying medium on the behaviour of the disperse particles was estimated by the methods of classical aerodynamics in the Stokes approximation. This combination of the methods of kinetic theory, which describe the behaviour of particles at the microlevel, with the methods of classical aerodynamics, which describe the flow of particles at the macrolevel, cannot be regarded as in any way satisfactory, since in the first case the behaviour of the dispersed particle is random, whereas in the second case it is uniquely determined by the Stokes force.

The methods developed in /7/ etc. have become widely used. Here, exact expressions, obtained in the kinetic theory of gaseous mixtures, in particular, expressions for the diffusion velocities, were used to determine the diffusion flows in disperse media, consisting of disperse particles of large dimensions ("macromolecules") and a carrying medium consisting of the molecules of an ordinary gas.

It follows from the above that the successive use of the methods of kinetic theory, in the same way as in the theory of gaseous mixtures, should enable a theory of dispersed media to be constructed.

We will first consider a two-component highly rarefied dispersed medium consisting of molecules of a certain gas and solid particles of spherical shape of much greater size. We can always choose the parameters of this gaseous medium and the dispersed phase so that the probability of triple collisions in such a system is extremely small. In six-dimensional phase space in an element of volume  $\Delta\tau$  we have the following equations for the number of particles of gas and the dispersed phase:

$$df_1 = f_1(\mathbf{r}, \mathbf{u}, t) \Delta\tau, \quad df_2 = f_2(\mathbf{r}, \mathbf{u}, t) \Delta\tau$$

If we assume that all the interaction between the molecules of the gas, the particles of the dispersed phase, and also between the molecules and the particles occurs in accordance with the laws of elastic collision, we obtain from the corresponding Liouville equations for

the whole system

$$\frac{df_1}{dt} = J(f_1, f_1) + J(f_1, f_2), \quad \frac{df_2}{dt} = J(f_2, f_1) + J(f_2, f_2) \quad (5)$$

In the first equation of system (5) the first term takes into account the interaction between the gas molecules, while the second takes into account the collisions between the spherical particles of the dispersed phase and the gas molecules. Since, according to our assumptions, the particles of the dispersed phase are much larger than the particles of gas, in a fairly rarefied medium the particles of the gas will change their parameters on each collision and this integral was not small. In the second equation the first term on the right-hand side describes the interaction between the particles of the mixture and the gaseous medium. It is well-known that in macroscopic mechanics in the Stokes approximation a definite force will act on the particles. However, there is no basis for a microscopic random force to be changed by the averaged Stokes force. This integral could then be simplified and reduce to corresponding terms of the Fokker-Plank equation. However, there is also no basis for this operation.

As can be seen, to a first approximation, there is no basis for simplifying the system of Eqs. (5) considered. However, it can be written in the following form, which is identical in form with system (1):

$$\frac{df_s}{dt} = \sum_{\tau=1}^M \int (f_s' f_{\tau}' - f_s f_{\tau}) g_{s\tau} b db de du_{\mathbf{v}}$$

The solution of the system of Eqs. (1) by the method described in /3/ leads to a system of aerodynamic equations, whose form is also identical with the system of aerodynamic Eqs. (4), in which we put

$$\Omega_{s\tau}^{(l,n)} = \sqrt{2\pi k \left( \frac{T_s}{m_s} + \frac{T_{\tau}}{m_{\tau}} \right)} \iiint \exp(-g_{s\tau}^2) g_{s\tau}^{2n+3} (1 - \cos^l \chi) dg$$

When  $T_s = T_{\tau}$ , these integrals are identical with those derived in /2/.

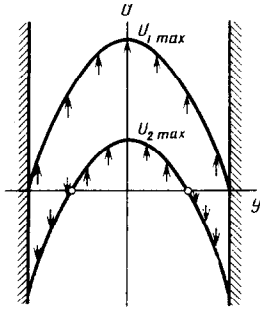
The fact that the system of equations for a dispersed medium is identical in form with the system of equations for gaseous mixtures, confirms the correctness of the method described in /7/, which has become widely used abroad.

As can be seen, an intense exchange of angular momentum and energy takes place between the particles of the gas and the dispersed impurity; the terms which take this exchange into account are written on the right-hand sides of the corresponding equations of system (4). It is important to note that explicit expressions for the terms which take into account the exchange of angular momentum and energy between the carrier medium and the particles of the dispersed phase occur in system (4). We particularly emphasize that explicit expressions have been obtained not only for the structure of the interaction terms, but also explicit expressions for the coefficients in front of these terms.

We made a number of important assumptions when deriving the system of kinetic equations for a dispersed medium, the solution of which was reduced to the aerodynamic Eqs. (4). The most important of these is the assumption that the medium considered is highly rarefied. Hence, for fairly rarefied systems, the coefficients defining the interactions, obtained above, can be assumed to be reliably defined. However, fairly dense dispersed systems are extremely important when solving many problems. It is obviously extremely difficult to construct a theory of the motion of dense dispersed systems. However, on the basis of experience in generalizing the kinetic theory of rarefied gaseous mixtures to dense gases /12/, we can make the following assertions: the general structure of the terms of the equations of motion on transferring from rarefied gaseous mixtures to dense mixtures, does not change; when there is a considerable increase in the density the transfer coefficients change, but not, apparently, to a great extent. On the basis of this it seems likely that for dense dispersed systems the system of equations will remain largely unchanged.

To determine the transfer coefficients we can use the experience of the founders of hydro-aerodynamics, who determined the coefficient of viscosity in Navier-Stokes equations experimentally, using the approximate Stokes solution for the slow motion of a sphere.

We will therefore consider the simplest model of the motion of a dispersed medium, which is at the same time the simplest model of a boiling layer, which is of considerable practical importance. We will assume that there is a gaseous medium and a finely dispersed catalyst in an infinitely long vertical tube. In the system of coordinates shown in the figure, the system of Eqs. (4) for the slow motion of the medium has the form



$$\begin{aligned} \frac{d^2 u_1}{dy^2} + \frac{d_{12}}{\mu_1} (u_2 - u_1) &= \frac{1}{\mu_1} \left( \frac{\partial P_1}{\partial x} + \rho_1 g \right) \\ \frac{d^2 u_2}{dy^2} + \frac{d_{12}}{\mu_2} (u_1 - u_2) &= \frac{1}{\mu_2} \left( \frac{\partial P_2}{\partial x} + \rho_2 g \right); \\ d_{12} &= \frac{n_1 n_2 k T}{n D_{12}} \end{aligned} \quad (6)$$

The coefficient  $D_{12}$  can be expressed directly in terms of Chapman-Cowling integrals, and represents the degree of inter-component interaction.

For the gaseous medium we will use the adhesion condition  $u_1(\pm h) = 0$ . For a finely dispersed catalyst we will use the condition that the flow rate of the catalyst along the length of the tube is constant

$$\int_{-h}^h u_2(y) dy = \text{const} = 0$$

The solution of the system of ordinary differential Eqs.(6) can be written in the form /13/

$$\begin{aligned} u_1(y) &= \frac{1}{2(\mu_1 + \mu_2)} \left( \frac{\partial P}{\partial x} + \rho g \right) (y^2 - h^2) \\ u_2(y) &= \frac{1}{2(\mu_1 + \mu_2)} \left( \frac{\partial P}{\partial x} + \rho g \right) \left( y^2 - \frac{h^2}{3} \right) \\ P &= P_1 + P_2, \quad \rho = \rho_1 + \rho_2 \end{aligned}$$

The figure shows the flow of gas and dispersed particles in a channel in which there is strong interaction between the gas and the particles. As can be seen, the velocity distribution in the gas is similar to Poiseuille flow. At the same time, the dispersed medium in the core of the flow moves together with the carrying medium, while on the walls of the channel it moves in the opposite direction. This flow pattern of a dispersed medium in a channel is confirmed by experiment.

The accurate solution obtained can be expressed in terms of the macroscopic parameters of the medium, such as  $\rho_1, \rho_2, P_1, P_2$ , and also in terms of the three parameters  $\mu_1, \mu_2, d_{12}$  defined by the microstructure of the medium. For rarefied dispersed media these three parameters can be calculated from the above expressions. However, as already pointed out, there is no absolute guarantee that these three parameters will correctly describe dense dispersed media. The explicit expressions obtained above for the two velocity distribution functions enables one, from their values at individual points of the flow, to determine the two constants at certain points of the flow.

If the carrying medium is, for example, water, one of the coefficients will be known. There are two others:  $\mu_2$  the coefficient of viscosity of the dispersed phase, and  $d_{12}$  - the coefficient of interphase interaction; they can be found, for example, from the values of  $u_{2\text{max}}$  when  $y = 0$ , and  $u_2$  when  $y = \pm h$ . As can be seen, only from the data of systematic experimental research, using the exact solutions of system (6), can one determine the unknown coefficients  $\mu_2$  and  $d_{12}$  for dense dispersed media. It then becomes possible to compare the data of kinetic theory for extremely rarefied dispersed media with experimental results. In this case, obviously, for large densities, experiment should introduce corrections to the theory of dense dispersed media.

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## ON THE STABILITY OF THE STEADY-STATE MOTIONS OF SYSTEMS WITH QUASICYCLIC COORDINATES\*

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The stability of the steady-state motions of a system with quasicyclic coordinates under the action of potential and dissipative forces and also forces which depend on the quasicyclic velocities is investigated. The results are applied to the problem of the stability of the steady-state plane-parallel motions of a rotor on a shaft which is set up in elasticated bearings with a non-linear reaction /1/.

The stability of the stationary motions and relative equilibria of systems with a single cyclic (quasicyclic) coordinate has previously been investigated /2/ from a common point of view. The question of the stability of the stationary motions of systems with quasicyclic coordinates under the action of constant and dissipative forces has been considered in /3/. The results obtained in /2/ have been generalized /4/ to systems with several cyclic (quasicyclic) coordinates and, additionally, a third regime of uniform motions, which includes the regime considered in /3/, has also been investigated.

1. Let us consider a holonomic mechanical system which is characterized by a Lagrange function  $L = L(q_i, \dot{q}_i, \varphi_j)$ , where  $q_i$  ( $i = 1, \dots, k$ ),  $\varphi_j$  ( $j = k + 1, \dots, n$ ) are generalized coordinates and  $\dot{q}_i \equiv dq_i/dt$ ,  $\dot{\varphi}_j \equiv d\varphi_j/dt$  are the generalized velocities of the system and, moreover, the function  $L$  is explicitly independent of the coordinates  $\varphi_j$  and the time  $t$ . Such a system with cyclic coordinates  $\varphi_j$  may execute stationary motions

$$q_i = q_{i0}, \quad \dot{q}_i = 0; \quad \dot{\varphi}_j = \omega_j, \quad \varphi_j = \omega_j t + \varphi_{j0} \quad (1.1)$$

in which the positional coordinates  $q_i$  and the cyclic velocities  $\dot{\varphi}_j$  remain constant over the whole time of the motion. At the same time the constants  $\omega_j$  are either specified arbitrarily within certain limits and the constants  $q_{i0}$  are determined from the equations

$$\partial L / \partial q_i = 0 \quad (1.2)$$

in which it follows to put  $\dot{q}_i = 0$ ,  $\dot{\varphi}_j = \omega_j$  or  $q_{i0}$  and  $\omega_j$  are determined from Eqs. (1.2) and the first integrals of the equations of motion

$$\partial L / \partial \dot{\varphi}_j = c_j \quad (1.3)$$

in which follows to put  $\dot{q}_i = 0$ ;  $c_j$  are arbitrary constants of integration. Here and everywhere subsequently

$$i, l = 1, \dots, k; \quad j, s = k + 1, \dots, n.$$