

THERMOPHYSICAL PROPERTIES OF MATERIALS

Construction of a System of Kinetic Equations for a Nonideal Gas

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Abstract—For molecules interacting among each other with the potential having both repulsive and attractive components, a system of kinetic equations is derived using the Bogolyubov method, which takes into account the effect of forming bound states by molecules. This system implies all conservation laws and their corollaries that are invariant under the Galilean transformation. With consideration of the relaxation problem for the given system of kinetic equations, the H -theorem can be obtained. It is noted that the equation of state, which is derived in this case, coincides in form with the van der Waals equation of state.

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INTRODUCTION

It is known that N.N. Bogolyubov, by using asymptotic methods, derived the Boltzmann equation from the BBGKY system (the derivation can be found in [1]). In this method, the Boltzmann equation is obtained as an equation for determining a single-particle distribution function in the λ -scale, which is the zeroth-order term in the expansion of the BBGKY system with respect to the small parameter $\varepsilon = n_0 d^3$. Here n_0 is the typical density of gas molecules, $\lambda = \frac{1}{n_0 d^2}$ is the free

path of molecules in the gas, and $d \approx 10^{-8}$ cm is the size of a molecule (or atom). Usually as this quantity, the size is taken at which the intermolecular interaction potential is different from zero.

When a derivation of the Boltzmann equation is regarded, the potential with which molecules interact with each other is always assumed to be specified. Moreover, it is suggested that the gas molecules interact as point centers of repulsion. In reality, as is known, the potential of molecular interaction has both repulsive and attractive components; therefore, the Boltzmann equation is valid for an ideal rarefied gas [2], i.e., for a gas in which the averaged potential energy of attraction of molecules can be neglected in comparison with their mean kinetic energy. A gas in which this suggestion is not satisfied will be called a nonideal gas everywhere in this work.

There are many works in which attempts are made to take into account the corrections on the order of ε in the Boltzmann equation. The equations derived by this procedure are treated as kinetic equations for a dense gas. Already in [1], a procedure for taking into consideration the effect of shading of molecules is pro-

posed. A consecutive asymptotic procedure to account for terms on the order of ε is related to consideration of simultaneous collisions of three or more molecules, which leads to the appearance of divergent integrals in the procedure mentioned. In [3], this problem is solved using the principle of attenuation of correlations in the expression for multiparticle distribution functions. In [3], it is also noted that, in cases of allowance for corrections on the order of ε , the nonadditivity of the potential of interaction between molecules should be taken into consideration in the Liouville equation. The kinetic equation obtained in this case (it is given in [3]) is interpreted as the kinetic equation for a nonideal gas.

It should be noted that the introduced parameter ε is less than unity for almost all media (it is noted in [3] and earlier in [4]). For instance, for iron (Fe) whose density $\rho = 7.8$ g/cm³, $\varepsilon \cong 0.08$, which is more than ten times smaller than unity; for water, $\varepsilon \cong 0.02$. From this it can be concluded that a trend connected with the allowance for only effects of gas consolidation, will hardly lead to creation of kinetic equations describing the behavior of real media.

There are several works in which attempts are made to take into account the gas nonideality in the Boltzmann equation (the attractive component in the potential of molecule interaction). In [3], a fairly comprehensive overview of these works is given. One such trend is connected with the fact that the repulsive forces manifest themselves at short distances, whereas at greater distances, molecules attract each other. In [3], a method is proposed for building kinetic equations with allowance for far-ranging attractive forces based on the BBGKY chain. In [4], with construction of a kinetic equation, the potential of interaction

between molecules has been divided into two parts, one of which describes only repulsion, while another sets forth only attraction. Obtained in this way, kinetic equations are sufficiently complex for analytical or numerical study. Therefore, no significant results have been achieved in this direction. Most likely, a reason also is here that the lengths cannot be segregated at the micro level, at which only forces of attraction would be significant separately from forces of repulsion. In the kinetic theory, microscopic interaction potentials are used, the forces of repulsion and attraction of which are noticeable only at distances on the order of the molecule size.

A significant contribution to the understanding of problems associated with creating the kinetic theory of a nonideal gas was made by Yu.L. Klimontovich. He introduced [5] one more parameter of length characterizing the medium: $l = n_0^{-1/3}$. It is interpreted as the distance between molecules. Then, it follows from the above that $\frac{d}{l} = \varepsilon^{1/3}$, while the reciprocal of the Knudsen number, which stands in front of the collision integral in the Boltzmann equation, is $l/\lambda = \varepsilon^{2/3}$. This implies that the collision integral is a nonanalytic function of multiparticle distribution function; therefore, its expansion in integer powers of ε does not provide the correct allowance for effects associated with an increase in the medium density. In [5], Yu.L. Klimontovich has also indicated that the kinetic description of a nonideal gas requires using a two-particle distribution function, which, generally speaking, is understandable because the average potential energy of molecules will be expressed through the two-particle distribution function. In [6], he constructed an equation for the two-particle distribution function describing a nonideal gas. This has not made a noticeable resonance. Apparently, it occurred due to the fact that it was impossible to pass from this equation to the ideal gas.

An absolutely different approach to the problem was proposed by A.A. Vlasov [7]. He introduced the notion of the potential of the self-consistent field and constructed a kinetic equation for evolution of the distribution function located in this field. In [3], the information about the area of applicability of the approach of A.A. Vlasov is given, and it is also indicated that, at the present time, the representations of the collision integral as the sum of the Boltzmann integral, Vlasov's approach, and some other terms are used.

The most striking effect of the action of the forces of attraction between molecules is the formation of bound states by the molecules, the kinetic energy of which does not allow the action of forces of attraction to be overcome. If what is written in [3] is true, then the problem of taking into consideration the bound states is far from being solved, while the kinetic equations available, which take the indicated effect into

account, are too complicated for analytical and numerical studies.

In this work, a model is proposed that takes into account the nonideality of a rarefied gas caused namely by creation of bound states.

MODIFICATION OF THE BOLTZMANN EQUATION FOR TAKING THE GAS NONIDEALITY INTO ACCOUNT

Consider the derivation of the Boltzmann equation from the BBGKY hierarchy following the ideas available in [1, 2]. The first two equations of the above hierarchy have the following form:

$$\frac{\partial F_1}{\partial t} + \xi^i \frac{\partial F_1}{\partial x^i} = \frac{N-1}{m} \int \frac{\partial U}{\partial x^i} \frac{\partial F_2}{\partial \xi^i} d\Gamma, \quad (1)$$

$$\begin{aligned} \frac{\partial F_2}{\partial t} + \xi^i \frac{\partial F_2}{\partial x^i} + \xi_j^i \frac{\partial F_2}{\partial x_j^i} \\ - \frac{1}{m} \left(\frac{\partial U}{\partial x^i} \frac{\partial F_2}{\partial \xi^i} + \frac{\partial U}{\partial x_j^i} \frac{\partial F_2}{\partial \xi_j^i} \right) = J_3. \end{aligned} \quad (2)$$

Here, $F_1 = F(t, \mathbf{x}, \boldsymbol{\xi})$ and $F_2 = F(t, \mathbf{x}, \boldsymbol{\xi}, \mathbf{x}_1, \boldsymbol{\xi}_1)$ are the single-particle and two-particle distribution functions, respectively, normalized to unity; $U = U(|\mathbf{x}_1 - \mathbf{x}|)$ is the intermolecular interaction potential; $d\Gamma = d\mathbf{x}_1 d\boldsymbol{\xi}_1$. Entering the right-hand side of (2), the quantity J_3 is expressed through the three-particle distribution function $F_3 = F(t, \mathbf{x}, \boldsymbol{\xi}, \mathbf{x}_1, \boldsymbol{\xi}_1, \mathbf{x}_2, \boldsymbol{\xi}_2)$. The quantity N , appearing in the right-hand side of (1), arises during the corresponding integration of the Liouville equation over the phase space of the system of N molecules [2] and presents a number of particles in the system. While writing his equation, Boltzmann believed that the number of molecules in the system was so great that in the physically small volume $\Delta\Gamma = \Delta\mathbf{x}\Delta\boldsymbol{\xi}$, the true number of molecules can be assumed equal to their average number; i.e., he neglected the fluctuation of particles [8]. In [7], the issues connected with the indicated difference are considered more thoroughly. From the above in this work, it is believed that $N-1 \approx N = n_0 L^3$, where L is the characteristic size of the motion.

A specific feature of the BBGKY hierarchy is that it contains an infinite number of equations coupled to each other. Derivation of the Boltzmann equation is based on the fact that there are two scales of length: $d \approx 10^{-8}$ cm is the distance at which the intermolecular interaction potential reveals its action; $\lambda = \frac{1}{n_0 d^2}$ is the free path which, for the Boltzmann's gas, is a value on the order of unity. Since $\frac{d}{\lambda} = \varepsilon \ll 1$, then the application of asymptotic methods makes it possible to

break off the above-mentioned infinite chain of equations at the first step.

The right-hand side of (1) (a would-be collision integral), due to the fact that $\int_{\Sigma} \frac{\partial F_2}{\partial \xi_1^i} d\xi_1 = 0$, $i = 1, 2, 3$ (Σ is the velocity space), can be written as

$$J = \frac{N-1}{m} \int \frac{\partial U}{\partial x^i} \frac{\partial F_2}{\partial \xi_1^i} d\Gamma$$

$$= \frac{N-1}{m} \int \left(\frac{\partial U}{\partial x^i} \frac{\partial F_2}{\partial \xi_1^i} + \frac{\partial U}{\partial x_1^i} \frac{\partial F_2}{\partial \xi_1^i} \right) d\Gamma.$$

The analysis of Eq. (2) is conveniently performed in the variables $q = \frac{\mathbf{x} + \mathbf{x}_1}{2}$, $r = \mathbf{x}_1 - \mathbf{x}$, $\mathbf{w} = \frac{\xi_1 + \xi}{2}$, and $\mathbf{g} = \xi_1 - \xi$. Then

$$\frac{\partial}{\partial x_1^i} = \frac{1}{2} \frac{\partial}{\partial q_i} + \frac{\partial}{\partial r_i}, \quad \frac{\partial}{\partial x_i} = \frac{1}{2} \frac{\partial}{\partial q_i} - \frac{\partial}{\partial r_i},$$

$$\frac{\partial}{\partial \xi_1^i} = \frac{1}{2} \frac{\partial}{\partial w_i} + \frac{\partial}{\partial g_i}, \quad \frac{\partial}{\partial \xi_i} = \frac{1}{2} \frac{\partial}{\partial w_i} - \frac{\partial}{\partial g_i},$$

$$i = 1, 2, 3.$$

In the new variables, Eqs. (1) and (2) will have the following form:

$$\frac{\partial F_1}{\partial t} + \xi^i \frac{\partial F_1}{\partial x^i} = 2 \frac{n_0 L^3}{m} \int \frac{\partial U}{\partial r^i} \frac{\partial F_2}{\partial g^i} d\Gamma, \quad (3)$$

$$\frac{\partial F_2}{\partial t} + w^i \frac{\partial F_2}{\partial q^i} + g^i \frac{\partial F_2}{\partial r_i} - \frac{2}{m} \frac{\partial U}{\partial r^i} \frac{\partial F_2}{\partial g^i} = J_3.$$

We will suggest that, in the two-particle function, relative motion occurs on the scale d and in the time $t_d = t/O(\epsilon)$, while the motion of the center of mass takes place on the scale λ and in the time $t_\lambda = t$. Then, according to a formalism of the asymptotic procedure described in [9], $F_2 = F_2 \left(\frac{L}{\xi_0} t_\lambda, \frac{d}{\xi_0} t_d, L\mathbf{q}, d\mathbf{r}, \xi_0 \mathbf{w}, \xi_0 \mathbf{g} \right)$, where $t_\lambda, t_d, \mathbf{q}, \mathbf{r}, \mathbf{w}, \mathbf{g}$ are the dimensionless variables, $\xi_0 = \sqrt{\frac{2kT_0}{m}}$, T_0 is the typical value of temperature (on the order of the critical one). Substituting the expression for F_2 written above into the second equation of (3), we derive

$$\frac{\partial F_2}{\partial t_\lambda} + w^i \frac{\partial F_2}{\partial q^i} - J_3 \frac{L}{\xi_0 F_0^2} + \frac{1}{\text{Kn}\epsilon}$$

$$\times \left(\frac{\partial F_2}{\partial t_d} + g^i \frac{\partial F_2}{\partial r^i} - \chi \frac{\partial U}{\partial r^i} \frac{\partial F_2}{\partial g^i} \right) = 0, \quad (4)$$

where $\text{Kn} = \frac{\lambda}{L}$ is the Knudsen number, $\chi = \frac{U_0}{kT_0}$, U_0 is the typical value of the intermolecular interaction

potential, $F_0 = \frac{1}{(\xi_0 L)^3}$, and F_2 is the dimensionless value of the two-particle distribution function. If the F_2 expansions in the scales d and λ are introduced as $F_2^d = \bar{F}_2 + O(\epsilon) + \dots$ and $F_2^\lambda = \tilde{F}_2 + O(\epsilon) + \dots$, then in the first approximation for the two-particle function from (4), we have

$$\frac{\partial \bar{F}_2}{\partial t_d} + g^i \frac{\partial \bar{F}_2}{\partial r^i} - \chi \frac{\partial U}{\partial r^i} \frac{\partial \bar{F}_2}{\partial g^i} = 0, \quad (5)$$

$$\frac{\partial \tilde{F}_2}{\partial t_\lambda} + w^i \frac{\partial \tilde{F}_2}{\partial q^i} = J_3. \quad (6)$$

As has been already noted, the integrand on the right-hand side of (1) is nonzero inside the sphere of the radius on the order of d , whose center is placed at the center of mass of a molecule having velocity ξ ; therefore, J will depend upon the two-particle distribution function in the scale d and upon the variables \mathbf{r}, \mathbf{g} . Changing in the integration to the variables $\mathbf{r} = \mathbf{x}^1 - \mathbf{x}$, $\mathbf{g} = \xi^1 - \xi$, we derive that $J = n_0 d^2 F_0^2 \xi_0^2 L^3 U_0 \int_{\Omega} \int_D \frac{2}{m} \frac{\partial U}{\partial r^i} \frac{\partial F_2}{\partial g^i} d\mathbf{r} d\mathbf{g}$. Introduce the F_1 expansion

in the d scale, setting $F_1^d = F_1^d + O(\epsilon) + \dots$. Then $\frac{\partial F_1^d}{\partial t_d} + \xi^j \frac{\partial F_1^d}{\partial x_d^j} = O(\epsilon)$ (here $\mathbf{x}_d = \mathbf{x}/d$, $t_d = td/\xi_0$). From the relation obtained, it can be seen that, in the zeroth approximation, the single-particle distribution function does not change in the scale d (homogeneity principle [2]).

We make a change to dimensionless variables in (1) as follows: $F = F_0 F'$, $\xi = \xi_0 \xi'$, $\mathbf{x} = L\mathbf{x}_\lambda$, and $t = \frac{L}{\xi_0} t_\lambda$.

If for F_1 in the λ scale, we write $F_1^\lambda = \bar{F} + O(\epsilon) + \dots$, then, omitting the index λ in the dimensionless variables, for the zeroth-order term of the asymptotic expansion of the single-particle distribution function \bar{F} , we derive

$$\frac{\partial \bar{F}}{\partial t} + \xi^i \frac{\partial \bar{F}}{\partial x^i} = \frac{1}{\text{Kn}} \int_{\Omega} \int_D \chi \frac{\partial U}{\partial r^i} \frac{\partial \bar{F}_2}{\partial g^i} d\mathbf{r} d\mathbf{g}. \quad (7)$$

Here, Ω is the velocity space, while D is the coordinate space (the phase space Γ is $\Omega \times D$). It should be noted that, in the dimensional variables, a diameter of D will be on the order of d ; therefore, $D = \eta(\epsilon)\lambda$ can be put where $\eta(\epsilon)$ is such that $\lim_{\epsilon \rightarrow 0} \eta(\epsilon) = 0$. Then, in the dimensionless variables, $D = \eta(\epsilon)/\epsilon$.

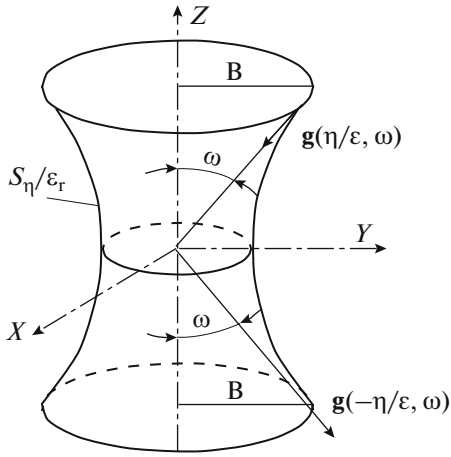


Fig. 1. To derivation of the Boltzmann equation.

The right-hand side of (7) depends on the time t in the λ scale. Since $\frac{\partial}{\partial t_d} = O(\epsilon) \frac{\partial}{\partial t}$, from (5) it follows that $\chi \frac{\partial U}{\partial r^i} \frac{\partial \bar{F}_2}{\partial g^i} = g^i \frac{\partial \bar{F}_2}{\partial r^i}$. Then for \bar{F} , we will have the following equation:

$$\frac{\partial \bar{F}}{\partial t} + \xi^i \frac{\partial \bar{F}}{\partial x^i} = \frac{1}{\text{Kn}} \int \int_{\Omega_D} g^i \frac{\partial \bar{F}_2}{\partial r^i} dr dg.$$

As has already been noted above, in deriving the Boltzmann equation, the intermolecular interaction potential is suggested to be repulsive in the form $U = U_0 \left(\frac{d}{r}\right)^s$, $s > 1$. In this case, projections of phase trajectories of the motion of colliding molecules (characteristics (5)) onto the D space are open and penetrate this space. Thus, \bar{F}_2 is represented by a continuous function in D together with its derivatives, while D is represented by a simply connected domain; therefore, with each fixed \mathbf{g} , the Gaussian theorem and the equation

$$\int \int_{\Omega_D} g^i \frac{\partial \bar{F}_2}{\partial r^i} dr dg = \int \int_{\Omega_{S_{\eta/\epsilon}}} (\mathbf{g} \cdot \mathbf{n}) \bar{F}_2 d\sigma dg \quad (8)$$

are applicable. Here, $S_{\eta/\epsilon}$ is the surface that bounds the domain D with a diameter of $\eta(\epsilon)/\epsilon$ and \mathbf{n} is the external normal to the surface defined above.

In the domain D , as in [2], we introduce a coordinate system linking its origin to a molecule moving at the velocity ξ , while the z axis will be directed opposite to the velocity \mathbf{g} . Consider trajectory (5), having with $z \rightarrow +\infty$, $\mathbf{g} = (-g, 0, 0)$ (here $g = |\mathbf{g}|$) and impact parameters b, θ . As $S_{\eta/\epsilon}$, we will take the surface created by rotation of these trajectory around the z axis and bound by the planes $z = \pm \eta(\epsilon)/\epsilon$.

This surface is depicted in Fig. 1. Along the trajectory, the velocity $\mathbf{g} = \mathbf{g}(z, \omega)$ varies in accordance with the conservation laws $\mu g b' \sin \omega r = C_1$ and $\frac{\mu}{2} g^2 + U(r) = C_2$, where $b'(\pm \eta/\epsilon) = r \sin \omega$, while r is the magnitude of the radius-vector of a trajectory point. At the side part of $S_{\eta/\epsilon}$, $(\mathbf{g} \cdot \mathbf{n}) = 0$ and $(\mathbf{g}(\eta/\epsilon, \omega) \mathbf{n}) = -(\mathbf{g}(-\eta/\epsilon, \omega) \mathbf{n}) \leq 0$. Therefore, we have for (8)

$$\begin{aligned} \int \int \int_{\Omega_{S_{\eta/\epsilon}}} (\mathbf{g} \cdot \mathbf{n}) \bar{F}_2 d\sigma dg &= \int \int \int_{\Omega} (\mathbf{g}(\eta/\epsilon, \omega) \cdot \mathbf{n}) \\ &\times (\bar{F}_2(t, \mathbf{x}, \mathbf{w} - (1/2)\mathbf{g}(-\eta/\epsilon, \omega), \mathbf{x} + \mathbf{r}, \mathbf{w} \\ &+ (1/2)\mathbf{g}(-\eta/\epsilon, \omega)) - \bar{F}_2(t, \mathbf{x}, \mathbf{w} - (1/2)\mathbf{g}(\eta/\epsilon, \omega), \\ &\mathbf{x} + \mathbf{r}, \mathbf{w} + (1/2)\mathbf{g}(\eta/\epsilon, \omega))) b db d\theta dg, \\ \mathbf{r} &= (\eta(\epsilon), 0, 0). \end{aligned}$$

Taking into account that in the λ scale, the hypothesis of molecular chaos ($\bar{F}_2(t, \mathbf{x}, \xi, \mathbf{x}_1, \xi_1) = \bar{F}(t, \mathbf{x}, \xi) \bar{F}(t, \mathbf{x}_1, \xi_1)$) holds, the passage to the limit with $\epsilon \rightarrow 0$ and a coupling procedure can be implemented in the last expression. For this purpose, according to [9], the condition $\lim_{\epsilon \rightarrow 0} \eta(\epsilon)/\epsilon = \infty$ has to be imposed on the function $\eta(\epsilon)$, introduced previously and defining the scale on which the intermolecular potential acts, and the intermediate variable $\mathbf{r}_\eta = \mathbf{r}_\lambda/\eta$ should be introduced. Following [9], we have $\lim_{\epsilon \rightarrow 0} (\bar{F}_2(t, \mathbf{x}, \mathbf{w} - (1/2)\mathbf{g}(\eta/\epsilon, \omega), \mathbf{x} + \mathbf{r}_\eta \eta, \mathbf{w} + (1/2)\mathbf{g}(\eta/\epsilon, \omega)) - \bar{F}(t, \mathbf{x}, \xi) \bar{F}(t, \mathbf{x}_1, \xi_1)) = 0$ and $\lim_{\epsilon \rightarrow 0} (\bar{F}_2(t, \mathbf{x}, (1/2)\mathbf{w} - \mathbf{g}(-\eta/\epsilon, \omega), \mathbf{x} + \mathbf{r}_\eta \eta, (1/2)\mathbf{w} + \mathbf{g}(-\eta/\epsilon, \omega)) - \bar{F}(t, \mathbf{x}, \xi) \bar{F}(t, \mathbf{x}_1, \xi_1)) = 0$.

From here, considering that $b'(\pm \eta/\epsilon) \rightarrow b$, $\mathbf{w} - (1/2)\mathbf{g}(+\infty, \omega) = \xi$, $\mathbf{w} + (1/2)\mathbf{g}(+\infty, \omega) = \xi_1$ are the velocities of molecules before the collision and after $\mathbf{w} - (1/2)\mathbf{g}(-\infty, \omega) = \xi$, $\mathbf{w} + (1/2)\mathbf{g}(-\infty, \omega) = \xi_1$, while $\lim_{\eta(\epsilon)/\epsilon \rightarrow \infty} |(\mathbf{g}(\eta/\epsilon, \theta) \cdot \mathbf{n})| = g$, we derive the equation for \bar{F} in the form

$$\begin{aligned} \frac{\partial \bar{F}}{\partial t} + \xi^i \frac{\partial \bar{F}}{\partial x^i} &= \frac{1}{\text{Kn}} \int \int_{\Omega} g (\bar{F}(t, \mathbf{x}, \xi) \\ &\times \bar{F}(t, \mathbf{x}, \xi_1) - \bar{F}(t, \mathbf{x}, \xi) \bar{F}(t, \mathbf{x}, \xi_1)) b db d\theta d\xi_1. \end{aligned} \quad (9)$$

In (9), from integration with respect to \mathbf{g} , we returned again to the integration with respect to ξ_1 . In (9) we return to the dimensional variables and from the function \bar{F} we pass to the usually used function $f = f(t, \mathbf{x}, \xi) = \bar{F}N$, then (9) will change to the well-known Boltzmann equation.

If, instead of the free path λ , the length scale $l = n_0^{-1/3}$ is introduced, then $\frac{1}{Kn} = \varepsilon^{2/3}/K$, where $K = l/L$. The last remark shows that the collision integral for Boltzmann's gas is a quantity on the order of $\varepsilon^{2/3}$ and should be taken into consideration since the expansion is performed in integer powers of ε .

As is evident, the Boltzmann equation is represented as an equation, which is satisfied by the function $\bar{F}(f)$ of the zeroth order in the asymptotic expansion in ε ; therefore, the recent attempts to "improve" the Boltzmann equation lie beyond the formalism of asymptotic methods.

In the above derivation of the Boltzmann equation, it is important that the coordinate space D can be presented to be woven of characteristics (5), which in the case of the exponential repulsive potential are open. However, for potentials that describe both attraction and repulsion, it is not so.

If, e.g., the Lennard–Jones potential $U(r) = U_0 \left(\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right)$ is taken, then particles for which $E = \frac{m}{4} g^2 + U(r) \leq 0$ cannot go off to infinity and will form closed trajectories. The presence of closed paths of the molecules in the case of real interaction potentials is known in the literature as creation of bound states. In the opinion of the authors of this work, the formation of bound states is the main effect that distinguishes an ideal gas from a nonideal one at the kinetic level. The next part will be dedicated to derivation of the Boltzmann-type equation taking into account the effect of forming bound states.

We suggest that the potential of interaction of molecules with each other is as follows:

$$U(r) = \begin{cases} +\infty, & 0 \leq r < d, \\ -U_0 \left(\frac{d}{r} \right)^4, & r \geq d. \end{cases} \quad (10)$$

Interaction potential (10) is a particular case of the Sutherland intermolecular potential

$$U(r) = \begin{cases} +\infty, & 0 \leq r < d \\ -U_0 \left(\frac{d}{r} \right)^m, & r \geq d \end{cases} \quad \text{with } m = 4.$$

According to (10), at distances smaller than d , molecules interact as solid spheres, and at larger distances, they are attracted as Maxwellian molecules. It should be noted that Eq. (10) is used rather frequently in various works.

For potential (10) in the phase space domain $\Omega_d := \left\{ \frac{E}{kT_0} = \frac{g^2}{2} - \frac{\chi}{r^4} \leq 0, r \geq 1 \right\}$ (in the dimensionless variables), phase trajectories (5) are closed and do not

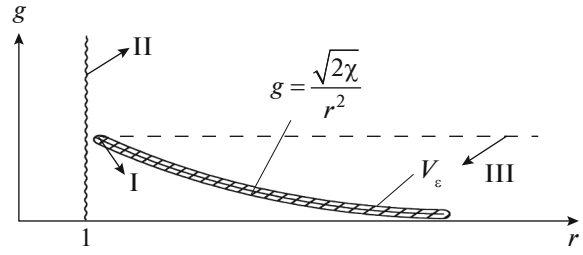


Fig. 2. Projection of the phase space $\Omega \times D$ onto the plane (r, g) .

go off to infinity. Since \bar{F}_2 is kept constant along characteristics (5), then on the surface γ , the equation of which is $\frac{g^2}{2} - \frac{\chi}{r^4} = 0$, \bar{F}_2 will be discontinuous because, for the distribution function \bar{F}_2 in the domain where trajectories are closed, the hypothesis of molecular chaos does not take place and the formal application of the Gauss theorem, which was used in deriving the Boltzmann equation, becomes unlawful.

Figure 2 depicts a projection of the dimensionless phase space onto the plane (r, g) , where $g = |\mathbf{g}|$, $r = |\mathbf{r}|$. The domain where $0 < r \leq 1$ is inaccessible to molecules; therefore, with $r = 1$, $(\mathbf{g} \cdot \mathbf{n}) = 0$. Domain I shown in Fig. 2, where $g \leq \frac{\sqrt{2\chi}}{r^2}$, corresponds to the projection of the phase space domain of bound states Ω_d . The function \bar{F}_2 in this domain will be denoted by \bar{F}_d . The trajectories of molecules in domains II and III are not closed; therefore, we will keep in them the old designation \bar{F}_2 for the two-particle function.

As previously, we will fix the coordinate space D to the molecule moving at the velocity $\boldsymbol{\xi}$, while the z axis will be directed opposite to $\mathbf{g} = \mathbf{g}(+\infty)$, then $D = D(\mathbf{g})$. The phase space in Fig. 2 is divided into three domains that are elementary relative to Ω , namely,

$$\begin{aligned} \Gamma_I &= \{0 \leq g \leq \sqrt{2\chi}\} \left\{ 1 \leq r \leq \frac{\sqrt{(2\chi)^{1/2}}}{g^{1/2}} \right\}, \\ \Gamma_{II} &= \{\sqrt{2\chi} \leq g < +\infty\} \{1 \leq r < +\infty\}, \\ \Gamma_{III} &= \{0 \leq g \leq \sqrt{2\chi}\} \left\{ \frac{\sqrt{(2\chi)^{1/2}}}{g^{1/2}} \leq r < +\infty \right\}. \end{aligned}$$

If we now apply the Gauss–Ostrogradsky theorem, then we will have the following. For Γ_I , we derive $J_I = \int_{g \leq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_1} (\mathbf{g} \cdot \mathbf{n}) \bar{F}_d d\sigma \right) + \int_{g \leq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_{rd}} (\mathbf{g} \cdot \mathbf{n}) \times \bar{F}_d d\sigma \right)$. For Γ_{II} , we have $J_{II} = \int_{g \geq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_{\infty}} (\mathbf{g} \cdot \mathbf{n}) \times \bar{F}_2 d\sigma \right) + \int_{g \geq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_1} (\mathbf{g} \cdot \mathbf{n}) \bar{F}_2 d\sigma \right)$, where the surface

depicted in Fig. 1, i.e., $S_{\eta/\epsilon}$, can be taken as S_∞ , while S_1 is the sphere of unit radius; for Γ_{III} , we have $J_{III} = \int_{g \leq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_{r_d}} (\mathbf{g} \cdot \mathbf{n}) \bar{F}_2 d\sigma \right) + \int_{g \leq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_\infty} (\mathbf{g} \cdot \mathbf{n}) \times \bar{F}_2 d\sigma \right)$, where S_{r_d} is the sphere of the radius $r_d = \sqrt{\frac{(2\chi)^{1/2}}{g}}$. Summing the above expressions, we derive $\int_{g \geq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_\infty} (\mathbf{g} \cdot \mathbf{n}) \bar{F}_2 d\sigma \right) + \int_{g \leq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_\infty} (\mathbf{g} \cdot \mathbf{n}) \times \bar{F}_2 d\sigma \right) = \int d\mathbf{g} \left(\oint_{S_\infty} (\mathbf{g} \cdot \mathbf{n}) \bar{F}_2 d\sigma \right) = J_B$, which is the usual Boltzmann integral of collisions. Since the surface S_∞ is everywhere crossed by the molecules, whose trajectories come to infinity and go off from there, then the integral written above can be reduced to the form obtained earlier. It is clear that $\int_{g \geq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_1} (\mathbf{g} \cdot \mathbf{n}) \bar{F}_2 d\sigma \right) + \int_{g \leq \sqrt{2\chi}} d\mathbf{g} \left(\oint_{S_1} (\mathbf{g} \cdot \mathbf{n}) \times \bar{F}_2 d\sigma \right) = 0$, since the molecules do not penetrate into the domain where $0 \leq r \leq 1$.

On the sphere of the radius $r = \sqrt{\frac{(2\chi)^{1/2}}{g}}$, the function \bar{F}_2 has a discontinuity: with $(\mathbf{g}\mathbf{n}) \leq 0$, the function \bar{F}_2 enters the domain of bound states; therefore, $\oint_{S_{r_d}} ((\mathbf{g} \cdot \mathbf{n}) \dots d\sigma = \frac{\sqrt{2\chi}}{2} \int_0^\pi \int_0^{2\pi} |\cos \omega| (\bar{F}_d - \bar{F}_2) \times \sin \omega d\omega d\theta$. From here, the procedure of deriving the Boltzmann equation in the case of allowance for bound states leads to the following equation:

$$\frac{\partial \bar{F}}{\partial t} + \xi^i \frac{\partial \bar{F}}{\partial x^i} = \frac{1}{\text{Kn}} (J_B - J_{\text{del}}), \quad (11)$$

where $J_{\text{del}} = \frac{\sqrt{2\chi}}{2} \int_{g \leq \sqrt{2\chi}} d\mathbf{g} \int_0^\pi \int_0^{2\pi} |\cos \omega| (\bar{F}_2 - \bar{F}_d) \sin \omega d\omega d\theta$. If in (11), $\chi \rightarrow 0$, then the usual Boltzmann equation is obtained, which is natural since $\chi = \frac{U_0}{kT_0} \ll 1$ is the condition of gas ideality.

The problem being solved above is an attempt to take bound states into account in the Boltzmann equation. In [3], it is noted that, apart from the bound states with $E \leq 0$, bound states with $E > 0$ may form. In [3], it is also noted that these states are metastable, since they disappear over time. The Boltzmann equation itself is derived on the time scale t_λ ; therefore, $\bar{F}_2(t, \mathbf{x}, \xi, \mathbf{x}_1, \xi_1) = \lim_{t_d \rightarrow +\infty} \bar{F}_2(t_d, \mathbf{x}, \xi, \mathbf{x}_1, \xi_1)$. This fact is substantiation of disregarding the metastable bound states in the above analysis. These states already will not be present on the time scale t_λ . The bound states with $E \leq 0$ remain, since they can be destroyed only

by collisions between three or more particles, which are not taken into account in the given approximation.

Coming from infinity to the boundary of the domain of bound states, the function \bar{F}_2 is constant along characteristics (5) and has the form $\bar{F}_2 = \Phi\left(\frac{g^2}{2} - \frac{\chi}{r^4}\right) = \Phi(0)$, since on the surface γ , $\frac{g^2}{2} - \frac{\chi}{r^4} = 0$. From here it follows that to the boundary of the domain of bound states, the function \bar{F}_2 comes with $g = 0$, because with $r \rightarrow +\infty$ (at infinity), only particles with $g = 0$ have zero energy. Suggesting that, in domain III, the hypothesis of molecular chaos takes place, we obtain that in the expression for J_{del} , $\bar{F}_2 = \bar{F}(t, \mathbf{x}, \xi) \bar{F}(t, \mathbf{x}, \xi_1)_{g=0} = \bar{F}^2(t, \mathbf{x}, \xi) = \bar{F}^2(t, \mathbf{x}, \mathbf{w})$. Then with allowance for creation of bound states, the equation for the dimensionless single-particle distribution function will have the following form: $\frac{\partial \bar{F}}{\partial t} + \xi^i \frac{\partial \bar{F}}{\partial x^i} =$

$$J_B - J_{\text{del}}.$$

If in (11) a change is made to the dimensional variables and to the distribution functions usually used, then the following equation will be derived:

$$\begin{aligned} \frac{\partial f}{\partial t} + \xi^i \frac{\partial f}{\partial x^i} &= J_B - J_{\text{del}}, \\ J_B &= \int d\xi_1 \left(\int_0^{+\infty} \int_0^{2\pi} g(f'f'_1 - ff_1) b db d\theta \right), \\ J_{\text{del}} &= d^2\chi_1 \int_{g \leq \sqrt{2\chi_1}} d\mathbf{g} \int_0^\pi \int_0^{2\pi} |\cos \omega| (\bar{f} - \bar{F}_d) \sin \omega d\omega d\theta, \\ \chi_1 &= \sqrt{\frac{U_0}{m}}, \quad \bar{f} = f^2(t, \mathbf{x}, \xi). \end{aligned} \quad (12)$$

It can also be noted that there is no difference in the form between the collision integral obtained and the collision integral of various modifications of the Boltzmann equation given in [3].

SYSTEM OF KINETIC EQUATIONS FOR A NONIDEAL GAS

As is evident, the expression for J_{del} depends on the two-particle distribution function \bar{F}_d . In the previous paragraph, the suggestion is made that, in domains II and III (see Fig. 2), bordering with the domain of bound states, the hypothesis of molecular chaos takes place; therefore, it is natural that $\bar{F}_2 = f \cdot f_{1g=0} = f^2(t, \mathbf{x}, \xi) = f^2(t, \mathbf{x}, \mathbf{w}) = \bar{f}$ (in this way, \bar{F}_2 entering J_{del} will be denoted). Molecules in the bound state, by the time instant t in the λ scale will cross multiply this domain itself (will endure a great number of colli-

sions); therefore, \bar{F}_d is suggested to take a quasi-canonical form, i.e.,

$$\bar{F}_d = f_0(t, \mathbf{q}, \mathbf{w}) \exp \left\{ -\frac{1}{k\varphi(t, \mathbf{q}, \mathbf{w})} \times \left(m \frac{g^2}{4} - U_0 \left(\frac{d}{r} \right)^4 \right) \right\}. \quad (13)$$

The functions $f_0 = f_0(t, \mathbf{q}, \mathbf{w})$ and $\varphi = \varphi(t, \mathbf{q}, \mathbf{w})$, appearing in (13), are functions in the λ scale. Since $\mathbf{x} = \mathbf{q} - \mathbf{r}/2 = \mathbf{q} + O(\varepsilon)$, then $f_0 = f_0(t, \mathbf{q}, \mathbf{w})$ and $\varphi = \varphi(t, \mathbf{q}, \mathbf{w})$ can be considered to be dependent on \mathbf{x} .

The task now is to derive the equations that determine the evolution of the functions f_0 and φ . For this purpose, we introduce the following functions:

$$s = s(t, \mathbf{q}, \mathbf{w}) = \iint_{\Omega_{\text{del}}} \bar{F}_d d\mathbf{r} d\mathbf{g}, \quad (14)$$

$$h = h(t, \mathbf{q}, \mathbf{w}) = \iint_{\Omega_{\text{del}}} \left(\frac{mg^2}{4} - U_0 \left(\frac{d}{r} \right)^4 \right) \bar{F}_d d\mathbf{r} d\mathbf{g} \leq 0,$$

where Ω_{del} is the phase space domain of bound states (domain I in Fig. 2); $s\Delta\mathbf{q}\Delta\mathbf{w}$ is the number of molecules in the bound state, the coordinates and velocities of which are located in the corresponding element of the phase space, while $h\Delta\mathbf{q}\Delta\mathbf{w}$ is their energy.

We derive specific expressions for the functions s and h (14). If during the integration with respect to \mathbf{g} and \mathbf{r} , we change to spherical variables, making in this case the substitution $r = dt$ (t is the dimensionless variable of integration), then we will obtain

$$s = 16\pi^2 d^3 f_0 \int_1^{+\infty} t^2 \exp \left\{ \frac{\bar{\chi}}{t^4} \right\} dt \int_0^{2\sqrt{U_0/m}} g^2 \times \exp \left(-m \frac{g^2}{4\varphi} \right) dg = 16\pi^2 d^3 f_0 (U_0/m)^{3/2} Z_s(\bar{\chi}), \quad (15)$$

$$\text{where } Z_s(\bar{\chi}) = \int_1^{+\infty} \left(1 + \frac{\bar{\chi}}{t^4} + \frac{\bar{\chi}^2}{2t^8} + \dots \right) \left(\frac{8}{3t^4} - \frac{8\bar{\chi}}{5t^8} + \frac{4\bar{\chi}^2}{7t^{12}} + \dots \right) dt = \frac{8}{9} + \frac{16}{105}\bar{\chi} + \frac{32}{11 \times 105}\bar{\chi}^2 + \dots, \bar{\chi} = \frac{U_0}{k\varphi}.$$

It is easy to see that the radius of convergence of the series is infinity. On performing a similar procedure for h , we obtain

$$h = -16\pi^2 d^3 f_0 U_0 (U_0/m)^{3/2} Z_h(\bar{\chi}), \quad (16)$$

$$Z_h(\bar{\chi}) = \frac{16}{105} + \frac{64}{55 \times 21}\bar{\chi} + \frac{64}{315 \times 15}\bar{\chi}^2 + \dots$$

In Eq. (11), as compared to the Boltzmann equation, there is the term J_{del} , defining the molecules, which due to collisions pass from the domain of molecular chaos to the domain of bound states. It is

clear that J_{del} will be a source term in the equation which determines the evolution of the function s . Therefore, the following equation is offered for this function: $\frac{Ds}{Dt} = J_{\text{del}}$, where $\frac{D}{Dt} = \frac{\partial}{\partial t} + w^i \frac{\partial}{\partial q^j} + a^j \frac{\partial}{\partial w^j}$ is the transport operator.

On averaging over the domain of bound states, we will derive equations for the averaged functions in the λ scale (the ideology developed in [10] is used).

We will set the scale value of \bar{F}_d to be $F_d^m = \frac{n_0^2}{\xi_0^6}$, while a typical value of s , according to (15), will be defined as $s_0 = \frac{n_0^2 d^3}{\xi_0^{3/2}} \chi^{3/2}$. The equation for s in the

dimensionless form is represented as $\chi^{3/2} \frac{Ds}{dt} = \frac{L}{d} J_{\text{del}}$ (here J_{del} is written in dimensionless form). It is worth noting that the concept of the free path of a molecule has a clear physical meaning when molecules interact as solid spheres. In the cases of other interaction potentials (especially those having a domain of attraction), the quantity $l = n_0^{-1/3}$, interpreted as the distance between molecules, is more natural [5]. If it is taken as the main scale value, then $\frac{L}{d} = \frac{Ll}{dl} = \frac{1}{K\varepsilon^{1/3}}$. Then for

the function s , we will have $\chi^{3/2} \frac{Ds}{dt} = \frac{1}{\varepsilon^{1/3} K} J_{\text{del}}$ or $\chi^{3/2} \varepsilon^{1/3} \frac{Ds}{dt} = J_{\text{del}}$. In the dimensionless form, the right-

hand side of the equation for f looks like $\varepsilon^{2/3} J_B + \varepsilon^{2/3} J_{\text{del}}$, and if the estimates obtained above are used, then its order will be $\varepsilon^{2/3} + \varepsilon \chi^{3/2}$. This implies that $J_B \approx J_{\text{del}}$, when $\varepsilon^{1/3} \chi^{3/2} \approx 1$ or $\chi \approx \varepsilon^{-2/9}$. From the estimates obtained, the conclusion can be drawn that, if $\chi < \varepsilon^{-2/9}$, then the gas can be considered as ideal and, for its description, the Boltzmann equation can be utilized. Otherwise, the nonideality should be taken into account in the appropriate kinetic equation.

The transport operator introduced above comprises an unknown quantity a^i , $i = 1, 2, 3$, which will be

$$\text{defined as } a^i = -\frac{U_0}{m} \frac{\partial}{\partial q^i} \int_V d\mathbf{x} \int_{\Omega} \left(\frac{d}{\mathbf{q} - \mathbf{x}} \right)^4 f(t, \mathbf{x}, \boldsymbol{\xi}) d\boldsymbol{\xi},$$

where V is the volume occupied by the gas. The latter means that while constructing a transport operator, we use the ideology of [7].

Consider in detail the expression derived. We assume that $\int_{\Omega} f d\boldsymbol{\xi} = n_f(\mathbf{x})$ is the density of molecules in the unbound state. The intermolecular potential is noticeably different from zero, if $\mathbf{q} \approx \mathbf{x}$ therefore, we will change to the new variables of integration:

$\mathbf{x} = \mathbf{q} - d\mathbf{t}$. Taking into account that $n_f(\mathbf{q} - \varepsilon\mathbf{t}) = n_f(\mathbf{q}) + O(\varepsilon)$, we obtain

$$\mathbf{a} = -\frac{U_0 d^3 \text{grad}(n_f)}{m} \int_V (1/t^4) d\mathbf{t}. \quad (17)$$

In (17), $V = V(\mathbf{t}) \Rightarrow V(\mathbf{x})$, where $V(\mathbf{x})$ is the domain enclosed between the sphere $|\mathbf{x}| = |\mathbf{q} + \mathbf{e}d|$ (\mathbf{e} is the normal to the sphere) and the piecewise smooth surface $S(\mathbf{x})$. This surface is the union of a finite number of smooth surfaces. For the external surface $S(\mathbf{x})$, we have $S(\mathbf{q} - \varepsilon\mathbf{t}) \approx S(\mathbf{q}) - \frac{\partial S}{\partial x_i} \varepsilon t_i$. This implies that $1 \leq |\mathbf{t}| \leq O(1/\varepsilon) \approx +\infty$ in the context of the given approximation. Then we obtain

$$\mathbf{a} = -\frac{4\pi U_0 d^3 \text{grad}(n_f)}{3m}. \quad (18)$$

Force term (17) in the equation for the function s , as compared with other terms, has the order of $O(\chi\varepsilon) = O(\varepsilon^{7/9})$ and, as the above analysis has shown, should be taken into account in this approach. Moreover, the allowance for the impact of the bound particles on each other will be natural, i.e., the definition of

a^i as $a^i = -\frac{U_0}{m} \frac{\partial}{\partial q^i} \int_V d\mathbf{x} \int_{\Omega} \left(\frac{d}{\mathbf{q} - \mathbf{x}}\right)^4 f(t, \mathbf{x}, \boldsymbol{\xi}) d\boldsymbol{\xi} - \frac{U_0}{m} \frac{\partial}{\partial q^i} \int_V d\mathbf{x} \int_{\Omega} \left(\frac{d}{\mathbf{q} - \mathbf{x}}\right)^4 s(t, \mathbf{x}, \boldsymbol{\xi}) d\mathbf{w}$. With respect to the first summand, the second summand has the order of $\varepsilon\chi^{3/2}$ and should be taken into consideration when the nonideality is accounted for. The second summand allows for the same simplification as the first one; therefore, we have for a^i the following expression:

$$\mathbf{a} = -\frac{4\pi U_0 d^3 \text{grad}(n)}{3m},$$

where $n = n_f + n_d$ is the total gas density and $n_d = \int s d\mathbf{w}$ is the density of particles in the bound state.

As a source term in the equation for h , we take the work that is done by intermolecular forces to transfer \bar{F}_2 to F_d through the curve γ (see Fig. 2). Select, as shown in Fig. 2, the domain $V_\varepsilon = \left\{ -\varepsilon \leq \frac{mg^2}{4} - U_0 \left(\frac{d}{r}\right)^4 \leq \varepsilon \right\}$. The power of intermolecular forces in the volume of this domain is written as

$$A_d = \lim_{\varepsilon \rightarrow 0} \int_{V_\varepsilon} \frac{\partial}{\partial r_i} \left(-U_0 \left(\frac{d}{r}\right)^4 \right) g_i \bar{F}_2 d\mathbf{r} d\mathbf{g}.$$

This expression can be transformed to the form

$$A_d = \lim_{\varepsilon \rightarrow 0} \int_{V_\varepsilon} \frac{\partial}{\partial r_i} \left(-U_0 \left(\frac{d}{r}\right)^4 g_i \bar{F}_2 \right) d\mathbf{r} d\mathbf{g} + \lim_{\varepsilon \rightarrow 0} \int_{V_\varepsilon} \left(-U_0 \left(\frac{d}{r}\right)^4 \right) g_i \frac{\partial \bar{F}_2}{\partial r_i} d\mathbf{r} d\mathbf{g} = I_1 + I_2.$$

We suggest that on the curve γ the derivative $\frac{\partial \bar{F}_2}{\partial r_i}$ has discontinuities of the first kind; i.e., it is limited. Then I_2 is zero, while $I_1 = -\chi_1 d^2 \int_{g \leq 2\chi_1} \frac{m}{4} g^2 d\mathbf{g} \times \int_0^{2\pi} \int_0^\pi |\cos \omega| (\bar{F} - f_0) \sin \omega d\omega d\theta$. The last formula has been obtained taking into account that one external normal V_ε is directed towards domain I and, for it, $(\mathbf{g} \cdot \mathbf{n}) \leq 0$, while another is directed towards domain II and $(\mathbf{g} \cdot \mathbf{n}) \geq 0$ in this case.

From the above, we have the following equation for h :

$$\frac{Dh}{Dt} = -\chi_1 \int_{g \leq 2\chi_1} \frac{m}{4} g^2 d\mathbf{g} \int_0^{2\pi} \int_0^\pi |\cos \omega| \times (\bar{F} - f_0) \sin \omega d\omega d\theta = A_d.$$

This approach leads to the closed system of kinetic equations if the equations for s and h are attached to the Boltzmann equation. This system of equations has the form

$$\begin{aligned} \frac{\partial f}{\partial t} + \xi^i \frac{\partial f}{\partial x^i} &= J_B - J_{\text{del}}, \quad \frac{Ds}{Dt} = J_{\text{del}}, \\ \frac{Dh}{Dt} &= A_d, \quad J_B = \int d\xi_1 \left(\int_0^{b} \int_0^{2\pi} g(f'f'_1 - ff_1) b db d\theta \right), \\ \frac{D}{Dt} &= \frac{\partial}{\partial t} + w^i \frac{\partial}{\partial x^i} + a^j \frac{\partial}{\partial w^j}, \quad J_{\text{del}} = \chi_1 d^2 \\ &\times \int_{g \leq 2\chi_1} d\mathbf{g} \left(\int_0^{2\pi} \int_0^\pi |\cos \omega| (\bar{F} - f) \sin \omega d\omega d\theta \right), \\ A_d &= -2\chi_1 d^2 \int_{g \leq 2\chi_1} \frac{m}{4} g^2 d\mathbf{g} \int_0^{2\pi} \int_0^\pi |\cos \omega| \\ &\times (\bar{F} - f_0) \sin \omega d\omega d\theta, \quad \mathbf{a} = -\frac{4\pi U_0 d^3 \text{grad}(n)}{3m}. \end{aligned} \quad (19)$$

The quantity J_{del} , which appeared in (19), is the number of molecules per unit time in the element of phase space $d\mathbf{x}d\boldsymbol{\xi}$, which have passed from a domain (II and III) of molecular chaos to the domain of bound states. It can easily be seen that J_{del} may have both positive and negative signs. In derivation of system (19), suggestions were made concerning the behavior of the two-particle distribution function on the boundary of the domain of bound states and in the

domain itself. All remaining suppositions were the same as in deriving the Boltzmann equation.

CONSERVATION LAWS

We introduce the following macroscopic functions:

$$n_f = \int f d\xi, \quad n_d = \int s d\mathbf{w}, \quad (20)$$

$n_f = n_f(t, \mathbf{x})$ was introduced above, while $n_d = n_d(t, \mathbf{x})$ is the density of molecules in the bound state. Since, according to (14), each pair of molecules forming the bound state is accounted for twice, then n_d from (20) will be the number of molecules in the bound state. Therefore, $n = n_f + n_d$ is the number density of gas molecules, while $\rho = mn$ is the gas density.

Define the vectors: $\mathbf{u} = \frac{1}{n}(\int \xi f d\xi + \int \mathbf{w} s d\mathbf{w})$, $\mathbf{c}_f = \xi - \mathbf{u}$, and $\mathbf{c}_d = \mathbf{w} - \mathbf{u}$. Then

$$\int \mathbf{c}_f f d\xi + \int \mathbf{c}_d s d\mathbf{w} = \int \xi f d\xi + \int \mathbf{w} s d\mathbf{w} - n\mathbf{u} = 0. \quad (21)$$

We integrate the first equation of (19) with respect to $d\xi$, and the second equation with respect to $d\mathbf{w}$ and sum. As a result, we derive a typical equation of conservation of the number of particles:

$$\frac{\partial n}{\partial t} + \frac{\partial(nu_i)}{\partial x_i} = 0, \quad i = 1, 2, 3. \quad (22)$$

We multiply the first equation of (19) by $m\xi^j$ and integrate it with respect to $d\xi$:

$$\begin{aligned} & \frac{\partial(\int m\xi^j f d\xi)}{\partial t} + \frac{\partial(\int m\xi^j \xi^i f d\xi)}{\partial x_i} \\ &= -d^2\chi_1 \int_{g \leq 2\chi_1} m\xi^j d\xi_1 d\xi_2 \int_0^{2\pi} \int_0^\pi |\cos \omega| (\bar{f} - \bar{F}_d) \\ & \times \sin \omega d\omega d\theta = -d^2\chi_1 \int_{g \leq 2\chi_1} \int_0^{2\pi} \int_0^\pi (\bar{f} - \bar{F}_d) \\ & \times R(\omega, \theta) m\xi_1^j d\omega d\theta d\xi_1 d\xi_2. \end{aligned}$$

The last equality is obtained with the substitution $\xi \rightleftharpoons \xi_1$ in the right-hand side of the integral. Taking also into account that $d\xi_1 d\xi_2 = d\mathbf{w} d\mathbf{g}$, the last equality can be rewritten in the form

$$\begin{aligned} & \frac{\partial(\int m\xi^j f d\xi)}{\partial t} + \frac{\partial(\int m\xi^j \xi^i f d\xi)}{\partial x_i} = -d^2\chi_1 \\ & \times \int_{g \leq \chi_1} \int_0^{2\pi} \int_0^\pi (\bar{f} - \bar{F}_d) R(\omega, \theta) m w^j d\omega d\theta d\mathbf{g} d\mathbf{w}. \end{aligned}$$

If now we multiply the second equation of (19) by $m w^j$, then integrate it with respect to $d\mathbf{w}$, and summa-

rize with the expression presented above, we will obtain

$$\begin{aligned} & m \left(\frac{\partial(\int \xi^j f d\xi)}{\partial t} + \frac{\partial(\int \xi^j \xi^i f d\xi)}{\partial x_i} \right. \\ & \left. + \frac{\partial(\int w^j s d\mathbf{w})}{\partial t} + \frac{\partial(\int w^j w^i s d\mathbf{w})}{\partial x_i} \right) - m n_d a^j = 0. \end{aligned}$$

Define the stress tensor P^{ij} in the following way:

$$P^{ij} = m \int c_f^i c_f^j f d\xi + m \int c_d^i c_d^j s d\mathbf{w}. \quad (23)$$

Taking into account (21) and (23), the law of conservation of momentum is written through the introduced macroparameters in the form

$$\frac{\partial(\rho u^j)}{\partial t} + \frac{\partial(\rho u^i u^j)}{\partial x_i} + \frac{\partial P^{ij}}{\partial x_i} - n_d a_j = 0, \quad j = 1, 2, 3. \quad (24)$$

According to (22), $u^j \left(\frac{\partial n}{\partial t} + \frac{\partial(nu_i)}{\partial x_i} \right) = 0$, $j = 1, 2, 3$ therefore, (24) can be transformed to the form

$$\rho \frac{\partial u^j}{\partial t} + \rho u^i \frac{\partial u^j}{\partial x_i} + \frac{\partial P^{ij}}{\partial x_i} - n a_j = 0, \quad j = 1, 2, 3. \quad (25)$$

Equation (25) is the form of momentum conservation equations that is invariant with respect to the Galilean transformation. This form is usually called the equations of motion.

In [11], based on general considerations, an attempt was made to define the pressure for a nonideal gas. Now, having the particular expressions for P^{ij} , the pressure for a nonideal gas can be defined in this way

$$3P = P^{11} + P^{22} + P^{33} = m \left(\int c_v^2 f d\xi + \int c_d^2 s d\mathbf{w} \right).$$

Multiply each equation of (25) by u^j and sum the expressions obtained; after which, we find

$$\begin{aligned} & \rho \frac{\partial(\mathbf{u}^2/2)}{\partial t} + \rho u^i \frac{\partial(\mathbf{u}^2/2)}{\partial x_i} + u^j \frac{\partial P^{ij}}{\partial x_i} \\ & - u^j n_d a_j = 0, \quad j, i = 1, 2, 3. \end{aligned} \quad (26)$$

Consider the quantity $W = \int m \frac{\xi^2}{2} f d\xi + \int \left(m \frac{\mathbf{w}^2}{2} s - \frac{1}{2} h \right) d\mathbf{w}$ that is the total energy per unit volume of gas. In order to derive the energy conservation law, we multiply the first equation of (19) by $m \frac{\xi^2}{2}$ and integrate over the whole space of velocities. In the right-hand part, the following will remain:

$$\begin{aligned}
& \int m \frac{\xi^2}{2} \int_{g \leq 2\chi_1} \int_0^{2\pi} \int_0^\pi (\bar{f} - \bar{f}_d) R(\omega, \theta) m \xi^j d\omega d\theta d\xi_1 d\xi \\
& = 1/2 \int m \frac{\xi^2 + \xi_1^2}{2} \int_{|\xi_1 - \xi| \leq 3\chi_1} \int_0^{2\pi} \int_0^\pi (\bar{f} - \bar{f}_d) R(\omega, \theta) \\
& \times d\omega d\theta d\xi_1 d\xi = 1/2 \int \int_{g \leq 2\chi_1} \int_0^{2\pi} \int_0^\pi \left(m \mathbf{w}^2 + m \frac{g^2}{4} \right) \\
& \times (\bar{f} - f_0) R(\omega, \theta) d\omega d\theta d\mathbf{w} dg.
\end{aligned}$$

It is easy to see that all similar operations for J_B yield zero. We multiply the second equation of (19) by $m \frac{\mathbf{w}^2}{2}$, and the third equation by $\frac{1}{2}$. Upon integration over the velocity space \mathbf{w} , we derive the energy conservation law ($n_d u_d^i = \int w^i s d\mathbf{w}$):

$$\begin{aligned}
& \frac{\partial}{\partial t} \left(\int m \frac{\xi^2}{2} f d\xi + \int \left(m \frac{\mathbf{w}^2}{2} s - \frac{1}{2} h \right) d\mathbf{w} \right) \\
& + \frac{\partial}{\partial x_i} \left(\int \xi^i m \frac{\xi^2}{2} f d\xi \right) \\
& + \int w^i \left(m \frac{\mathbf{w}^2}{2} s - \frac{1}{2} h \right) d\mathbf{w} - n_d u_d^i a_i = 0.
\end{aligned} \quad (27)$$

We introduce the following macroparameters:

$$\begin{aligned}
\frac{3}{2} nk T^* &= \int m \frac{\bar{c}_f^2}{2} f d\xi + \int \left(m \frac{\mathbf{c}_d^2}{2} s - \frac{1}{2} h \right) d\mathbf{w}, \\
\mathbf{Q} &= \int m \mathbf{c}_f \frac{\bar{c}_f^2}{2} f d\xi + \int \mathbf{c}_d \left(m \frac{\mathbf{c}_d^2}{2} s - \frac{1}{2} h \right) d\mathbf{w}.
\end{aligned} \quad (28)$$

The quantity T^* defined in (28) is an analog of the temperature of the nonideal gas, and \mathbf{Q} is the heat flux vector. With allowance for the quantities introduced above, the energy conservation law will take the following form:

$$\begin{aligned}
& \frac{\partial}{\partial t} \left(\frac{3}{2} nk T^* + \rho \mathbf{u}^2 / 2 \right) + \frac{\partial}{\partial x_i} \left(u^i \left(\frac{3}{2} nk T^* + \rho \mathbf{u}^2 / 2 \right) \right) \\
& + \frac{\partial (u_k P^{ki})}{\partial x_i} + \frac{\partial Q_i}{\partial x_i} - n_d u_d^i a_i = 0.
\end{aligned}$$

If, however, (22) and (26) are taken into account in the last equation, it will look like

$$\begin{aligned}
& \frac{3}{2} kn \left(\frac{\partial T^*}{\partial t} + u^i \frac{\partial T^*}{\partial x_i} \right) + P^{ki} \frac{\partial u_k}{\partial x_i} \\
& + \frac{\partial Q_i}{\partial x_i} - n(u_d^i - u^i) a_i = 0.
\end{aligned} \quad (29)$$

Equation (29) is the form of the energy conservation equation that is invariant relative to the Galilean transformation. In essence, (29) is the first law of ther-

modynamics for a nonideal gas that was derived from the kinetic theory.

The pressure of a nonideal gas introduced above is $P = nk T^* + \frac{1}{3} \int h d\mathbf{w}$, from which

$$\left(P - \frac{1}{3} \int h d\mathbf{w} \right) / n = k T^*. \quad (30)$$

If $1/n$ is identified with the volume occupied by the gas, while $-\frac{1}{3} \int h d\mathbf{w}$ is the identification of the potential energy of interaction of molecules, then (30) is the equation of state of a nonideal gas [11].

THE UNIFORM RELAXATION PROBLEM FOR A NONIDEAL GAS

As has already been noted above, with the change to the thermodynamics from the model considered, the first law follows. The other requirement imposed on kinetic models is that they should provide a transition of the system, described by them and located in the adiabatic shell, to the state of thermodynamic equilibrium (the zeroth law of thermodynamics). As is known, the satisfaction of the above requirements is verified for the uniform relaxation problem. This problem for the system of kinetic equations constructed above will have the following form:

$$\begin{aligned}
\frac{\partial f}{\partial t} &= \frac{d^2}{2} \int d\xi_1 \left(\int_0^{2\pi} \int_0^\pi g(f' f_1' - f f_1) b d\theta \right) \\
& - d^2 \chi_1 \int_{g \leq 2\chi_1} d\xi_1 \int_0^{2\pi} \int_0^\pi |\cos \omega| (\bar{f} - f_0) \sin \omega d\omega d\theta, \\
\frac{\partial s}{\partial t} &= d^2 \chi_1 \int_{g \leq 2\chi_1} d\mathbf{g} \int_0^{2\pi} \int_0^\pi |\cos \omega| (\bar{f} - f_0) \sin \omega d\omega d\theta, \\
\frac{\partial h}{\partial t} &= -\chi_1 d^2 \int_{g \leq 2\chi_1} \frac{m}{4} g^2 d\mathbf{g} \\
& \times \int_0^{2\pi} \int_0^\pi |\cos \omega| (\bar{f} - f_0) \sin \omega d\omega d\theta.
\end{aligned} \quad (31)$$

We recall that, in our case, $f = f(t, \xi)$, $s = s(t, \mathbf{w})$, and $h = h(t, \mathbf{w})$. In the second and third equations of (31), $\bar{f} - f_0$ depends on t and \mathbf{w} therefore, they can be transformed to the form

$$\frac{\partial s}{\partial t} = J/3, \quad \frac{\partial h}{\partial t} = -U_0 J/5,$$

where $J = 64\pi^2 \chi_1 d^2 \left(\frac{U_0}{m} \right)^{3/2} (\bar{f} - f_0)$.

From which $\frac{\partial}{\partial t} \left(\frac{3}{5} U_0 s + h \right) = 0$ and $\frac{3}{5} U_0 s + h = c =$
 $\text{const} = \frac{3}{5} U_0 s(0, \mathbf{w}) + h(0, \mathbf{w})$. If it is suggested that

$$\frac{3}{5} U_0 s(0, \mathbf{w}) + h(0, \mathbf{w}) = 0, \quad (32)$$

then we have $(3/5) U_0 s(t, \mathbf{w}) = -h(t, \mathbf{w})$. Then from (15) and (16), we obtain

$$\frac{h(t, \mathbf{w})}{s(t, \mathbf{w})} = -\frac{3}{5} U_0 = -U_0 \frac{Z_h(\bar{\chi})}{Z_s(\bar{\chi})}. \quad (33)$$

From (33) it follows that the introduced quantity φ is a constant. If φ is assigned a physical meaning, then it is the energy per molecule in the bound state. Then the result obtained is explained by the fact that the motion of molecules in the bound state occurs in the d scale, and their equilibrium state is achieved for a time interval that is significantly less than the time scale t_λ . Therefore, their energy per particle is determined only by the potential of their interaction between each other, which is an argument in favor of relation (32) (it is not excluded that formulas (15) and (16) should be determined by means of quantum mechanics). If in expressions for $Z_s(\bar{\chi})$ and $Z_h(\bar{\chi})$ (see (15), (16)), only terms of the first degree in $\bar{\chi}$ are left, then from (33), it can be obtained that $\bar{\chi} \approx -10$.

As is known, the zeroth law of thermodynamics for the Boltzmann gas follows from the H -theorem. Consider the H -theorem for the above constructed model of a nonideal gas.

Introduce $S(t, \mathbf{w}) = \int_{\Omega_{\text{del}}} \bar{F}_d \ln \bar{F}_d d\mathbf{r} d\mathbf{g}$. The quantity $H_d = \frac{k}{2} \int S(t, \mathbf{w}) d\mathbf{w}$ is the H -function of a unit volume for molecules in the bound state. Taking into account for \bar{F}_d representation (13), we derive that $S = \int_{\Omega_{\text{del}}} f_0 \times$
 $\exp \left\{ -\frac{\left(\frac{m}{4} g^2 - U(r) \right)}{k\varphi} \right\} \left(\ln f_0 - \frac{\left(\frac{m}{4} g^2 - U(r) \right)}{k\varphi} \right) d\mathbf{r} d\mathbf{g} =$
 $s \ln f_0 - \frac{h}{k\varphi}$.

We will apply to S the operator $\frac{\partial}{\partial t}$ defined in the second section and obtain $\frac{\partial S}{\partial t} = \ln f_0 \frac{\partial s}{\partial t} + s \frac{\partial \ln f_0}{\partial t} -$
 $\frac{1}{k\varphi} \frac{\partial h}{\partial t}$. From (14), we have

$$\frac{\partial s}{\partial t} = \int_{\Omega_{\text{del}}} f_0 \exp \left\{ -\frac{\left(\frac{m}{4} g^2 - U(r) \right)}{k\varphi} \right\} \times \frac{\partial \ln f_0}{\partial t} d\mathbf{r} d\mathbf{g} = s \frac{\partial \ln f_0}{\partial t}. \quad (34)$$

With allowance for (33) and (34), the expression for $\frac{\partial S}{\partial t}$ will take the following form:

$$\frac{\partial S}{\partial t} = \left(\ln f_0 + 1 + \frac{3U_0}{5k\varphi} \right) \frac{\partial s}{\partial t}.$$

On taking into consideration the equation for s , we derive

$$\frac{\partial S}{\partial t} = \int_{g \leq 2\chi_1} \int_0^{2\pi} \int_0^\pi \left(\ln f_0 + 1 + \frac{3U_0}{5k\varphi} \right) \times (\bar{f} - f_0) R(\omega, \theta) d\omega d\theta d\mathbf{g}. \quad (35)$$

The production of H -function per unit time in a unit volume for molecules in the bound state is naturally defined as

$$\dot{H}_d = \frac{k}{2} \int \frac{\partial S}{\partial t} d\mathbf{w} = \frac{k d^2}{2} \times \int_{g \leq 2\chi_1} \int_0^{2\pi} \int_0^\pi \left(\ln f_0 + 1 + \frac{3U_0}{5k\varphi} \right) \times (\bar{f} - f_0) R(\omega, \theta) d\omega d\theta d\mathbf{g} d\mathbf{w}.$$

The H -function of molecules in the unbound state will be defined as usual: $H_f = k \int k \int f \ln f e^{1/2 + \frac{3U_0}{10k\varphi}}$
 $d\xi d\xi_1$. In the case of uniform relaxation, when a distribution function depends only on time, we will have

$$\frac{\partial H_f}{\partial t} = \int \frac{\partial \left(f \ln f e^{1/2 + \frac{3U_0}{10k\varphi}} \right)}{\partial t} d\xi = \int \left(\ln f + 1/2 + \frac{3U_0}{10k\varphi} \right) \frac{\partial f}{\partial t} d\xi.$$

If we use the first equation of (19), then

$$\frac{\partial H_f}{\partial t} = \left(k d^2 / 2 \right) \int \int_0^{+\infty} \int_0^{2\pi} \int_0^\pi \ln \frac{ff_1}{f_1 f'} (f_1' f' - ff_1) \times b b b d \varepsilon d \xi_1 d \xi - \frac{k}{2} d^2 \int_{g \leq 2\chi_1} \int_0^{2\pi} \int_0^\pi \left(\ln f^2 + 1 + \frac{3U_0}{5k\varphi} \right) \times (f^2 - \bar{F}_d) R(\omega, \theta) d\omega d\theta d\mathbf{g} d\mathbf{w}.$$

This definition of the H -function in the above expression is connected with the fact that the H -function has to be defined in the situation when the interaction between molecules in the bound and unbound states takes place. While introducing the H -function for the mixture of chemically reacting gases [12] and in the case when a molecule had rotational degrees of freedom [13], the H -function has to be introduced as the sum of H -functions of different components with different weights.

Summing \dot{H}_d and $\frac{\partial H_f}{\partial t}$, we derive

$$\begin{aligned} \dot{H}_d + \frac{\partial H_f}{\partial t} = & (kd^2/2) \int_0^{+\infty} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \ln \frac{ff_1}{f_1'f'} (f_1'f' - ff_1) \\ & \times bdbd\epsilon d\xi_1 d\xi + \frac{k}{2} d^2 \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \ln \frac{f_0}{f} \\ & \times (\bar{f} - f_0) R(\omega, \theta) d\omega d\theta dg d\mathbf{w}. \end{aligned} \quad (36)$$

In derivation of (36), it is taken into consideration that $\ln f(t, \mathbf{x}, \boldsymbol{\xi}) = \frac{1}{2} \ln f^2(t, \mathbf{x}, \boldsymbol{\xi}) = \frac{1}{2} \ln \bar{f}$. It is easy to see that both summands in the right-hand side of (36) are less than or equal to zero. Then $\dot{H} = \dot{H}_d + \frac{\partial H_f}{\partial t} \leq 0$. The last inequality is an analog of the H -theorem for a nonideal gas.

Since for the kinetic model constructed above the H -theorem holds, then a solution to problem (31) with $t \rightarrow +\infty$ will go to the state with which $\dot{H} = \dot{H}_d + \frac{\partial H_f}{\partial t} = 0$. From this, it follows that $f_1'f' = ff_1$, $\bar{f} = f_0$. The first relation, as is known, is satisfied by

$$f = n_f \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left\{ -\frac{m}{2kT} \boldsymbol{\xi}^2 \right\}, \quad (37)$$

where n_f is the density of molecules in the free state, while T can be treated as their temperature. Since $\bar{f} = f_0$, then (37) implies

$$f_0 = f^2(\mathbf{w}) = n_f^2 \left(\frac{m}{2\pi kT} \right)^3 \exp \left\{ -\frac{m}{kT} \mathbf{w}^2 \right\}. \quad (38)$$

In the case of the relaxation problem, the conservation equations have the following form:

$$\begin{aligned} \frac{\partial n_f}{\partial t} + \frac{\partial n_d}{\partial t} = & 0, \quad \frac{\partial}{\partial t} \left(\int m \frac{\boldsymbol{\xi}^2}{2} f d\boldsymbol{\xi} \right) \\ & + \int \left(m \frac{\mathbf{w}^2}{2} s - \frac{1}{2} h \right) d\mathbf{w} = 0. \end{aligned} \quad (39)$$

According to the definitions given in (28), from (39), we have $n_f(t) + n_d(t) = n$, $n(t)T^*(t) = n\bar{T}^*$, where n and \bar{T}^* are the specified values of the density and the

thermodynamic temperature of the medium, respectively. Using (37) and (38), we obtain

$$\begin{aligned} n_f + rn_f^2 = n, \quad T(n_f + r/2n_f^2(1 + 3/5\tilde{\chi})) = n\bar{T}^*, \\ r = 2\sqrt{\pi}d^3\tilde{\chi}^{3/2}Z_s(\tilde{\chi}), \quad \tilde{\chi} = \frac{U_0}{T}. \end{aligned} \quad (40)$$

From relations (40), we can find $n_f(n, \bar{T}^*)$, $n_d = rn_f^2$, and $T(n, \bar{T}^*)$, so that the equilibrium state of a nonideal gas, as in the case of an ideal gas, is determined by the values of its density and temperature.

CONCLUSIONS

Consider equation of state (30), derived earlier for a nonideal gas. From (33) it follows that $-\frac{1}{3} \int h d\mathbf{w} = \frac{1}{5} U_0 \int s d\mathbf{w} = \frac{1}{5} n_d U_0$. It can be easily seen that $n_d \sim n_0^2 d^3 \chi^{3/2}$, where n_0 is the typical density of the medium. Believing $n_0^2 = \frac{1}{V^2}$, we obtain the equation of state in the form $\left(p + \frac{a}{V^2} \right) V = kT^*$, resembling the form of the van der Waals equation of state. Indeed, the classical van der Waals equation for a mole of the gas has the following form:

$$\left(p + \frac{a}{V^2} \right) (V - b) = RT,$$

where $b = \frac{N}{3} \frac{4\pi}{3} d^3$ [11]. According to [11], due to the action of forces of intermolecular repulsion, the gas molecules cannot move closer than a distance smaller than d , which is taken as the diameter of a molecule. Then in the van der Waals equation of state, the quantity $b = O(\epsilon)$ (here $\epsilon = n_0 d^3$). Since the derived system of kinetic equations represents a zeroth approximation in the asymptotic method, which is used in the work, then b is absent in the equation of state obtained from this system.

The fundamental difference between the derived equation of state from the classical van der Waals equation of state is that, in the equation written above, $a \sim d^3 \chi^{3/2} (T^*) = a(T^*)$ (terms on the order of $\chi^{3/2} \epsilon$, as was noted above, are preserved) depends on the temperature, whereas in the van der Waals equation of state, a is a constant.

In this work, a closed kinetic model is constructed that describes the behavior of a nonideal gas. The model includes all conservation laws and their corollaries, which are invariant with respect to the Galilean transformation. The H -theorem is also present. From the remark concerning the equation of state, we may hope that the derived kinetic model of a nonideal gas will reproduce its properties.

The model constructed is equivalent to the Boltzmann equation itself.

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