

Creation of the Set of Kinetic Equations for a Nonideal Gas near Critical Temperatures

A. M. Bishaev^a and V. A. Rykov^b

Presented by Academician Yu.G. Evtushenko July 2, 2014

Received July 8, 2014

Abstract—In this article, the derivation of the Boltzmann equation from BBK1Y of the chain is generalized for the case when the intermolecular interaction potential has both repulsive and attractive components. In this case, the application of the Bogolyubov method leads to situation when the term taking into account the transfer of molecules from the region where the hypothesis of the molecular chaos occurs into the region where molecules are arranged in a bound state is added to the usual collision integral. A two-particle distribution function of molecules in the bound state is assumed to be quasi-equilibrium with parameters depending on the variables that characterize the Boltzmann gas. Kinetic equations are written for these parameters performing the corresponding averaging over the region of bound states. Thus, this resulted in a closed set of kinetic equations describing nonideal gas. After introducing the corresponding macroparameters, all conservation laws and their consequences invariant relative to the Galileo transform follow from the corresponding set. The equation of state derived for such gas resembles the van der Waals equation by form. When considering the relaxation problem, the H-theorem is proven.

DOI: 10.1134/S1028335815010048

INTRODUCTION

It is known that N.N. Bogolyubov, when accepting asymptotic methods, derived the Boltzmann equation from the BBIGKY set (the derivation can be found in section ADDITION of monograph [1]). In this method, the Boltzmann equation is derived as the equation for determining the single-particle distribution function in λ scale, which is the zero-order term of the small-parameter expansion of the BBIGKY set $\varepsilon = n_0 d^3$, where n_0 is the characteristic density of gas molecules and $d \approx 10^{-8}$ cm is the molecule (or atom) size. Usually the size at which the intermolecular interaction potential is nonzero is accepted as this quantity, and $\lambda = \frac{1}{n_0 d^2}$ is the free-path length of molecules in the gas.

Monograph [2] contains a review and characteristics of studies in which corrections of order $\varepsilon = \frac{d}{\lambda}$ were

taken into account, as well as studies in which gas nonideality was taken into account. In this study, we construct the set of kinetic equations that takes into account the effect of formation of bound states by molecules.

1. MODIFICATION OF THE BOLTZMANN EQUATION TO TAKE ACCOUNT OF GAS NONIDEALITY

If we follow the scheme of the derivation of the Boltzmann equation described in [3], then in the zero approximation for single-particle function $\bar{F} = \bar{F}(t, \mathbf{x}, \xi)$ in λ scale and dimensionless form, we will derive the following equation:

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

$\bar{F}_2 = \bar{F}_2(t, \mathbf{q}, \mathbf{w}, \mathbf{r}, \mathbf{g})$ in (1) is the zero approximation of the two-particle distribution function in d scale. According to the formalism of the asymptotic method for \bar{F}_2 , we have the following equation:

$$\frac{\partial \bar{F}_2}{\partial t_d} + g^i \frac{\partial \bar{F}_2}{\partial r^i} - \chi \frac{\partial U}{\partial r^i} \frac{\partial \bar{F}_2}{\partial g^i} = 0, \quad (2)$$

where $\chi = \frac{U_0}{kT_0}$ and U_0 is the characteristic value of the intermolecular interaction potential. In Eq. (1),

^a Moscow Institute of Physics and Technology (State University), Institutskii per. 9, Dolgoprudnyi, Moscow oblast, 141700 Russia

^b Dorodnitsyn Computing Centre, Russian Academy of Sciences, ul. Vavilova 40, Moscow, 119991 Russia
e-mail: bishaev@bk.ru

$\mathbf{q} = \frac{\mathbf{x} + \mathbf{x}_1}{2}$ and $\mathbf{w} = \frac{\xi_1 + \xi}{2}$ are the position of the center of mass and its velocity of moving molecules having phase variables (\mathbf{x}, ξ) and (\mathbf{x}_1, ξ_1) , respectively; $\mathbf{r} = \mathbf{x}_1 - \mathbf{x}$, $\mathbf{g} = \xi_1 - \xi$, and $\text{Kn} = \frac{\lambda}{L}$ is the Knudsen number. The relation of dimensional variables with dimensionless ones was as follows: $\mathbf{x} = L\mathbf{x}'$, $\mathbf{q} = L\mathbf{q}'$, $\mathbf{r} = d\mathbf{r}'$, $\xi = \xi_0\xi'$, and $\mathbf{w} = \xi_0\mathbf{w}'$, $\mathbf{g} = \xi_0\mathbf{g}'$, $\xi_0 = \sqrt{\frac{2kT_0}{m}}$, where L is the characteristic flow size and T_0 is the scale value of the temperature near the critical one. It is important that the two-particle distribution function in d scale stands under the integral in the right side of (1) since the intermolecular interaction potential $U = U(|\mathbf{x}_1 - \mathbf{x}|) = U(r)$ noticeably differs from zero at distances of order d between molecules. This circumstance is associated with the fact that the diameter of the coordinate integration region in (1) D (Ω is the velocity space) in dimensional variables will be of order $\eta(\varepsilon)\lambda$, where $\eta(\varepsilon)$ is such that $\lim_{\varepsilon \rightarrow 0} \eta(\varepsilon) = 0$, while

$\lim_{\varepsilon \rightarrow 0} \frac{\eta(\varepsilon)}{\varepsilon} = \infty$. In dimensionless variables, this diameter will be $\frac{\eta(\varepsilon)}{\varepsilon}$.

When deriving the Boltzmann equation, the intermolecular interaction potential is assumed to be the repulsion potential having form $U = U_0\left(\frac{d}{r}\right)^s$, $s > 1$. In this case, the projections of phase trajectories of motion of colliding molecules (characteristics (2)) on space D are unclosed and penetrate this space as a whole. Thus, \bar{F}_2 is a continuous function in D along with its derivatives, while D is a simply connected region; therefore, the Gaussian theorem is applicable at each fixed \mathbf{g} and

$$\int_{\Omega D} g^i \frac{\partial \bar{F}_2}{\partial r^i} dr dg = \int_{\Omega S_{\eta/\varepsilon}} (\mathbf{gn}) \bar{F}_2 d\sigma dg,$$

where $S_{\eta/\varepsilon}$ is the surface limiting region D with diameter $\eta(\varepsilon)/\varepsilon$ and \mathbf{n} is the external normal to the above-defined surface. Properly selecting $S_{\eta/\varepsilon}$ and assuming that molecular chaos hypothesis $\bar{F}_2(t, \mathbf{x}, \xi, \mathbf{x}_1, \xi_1) = \bar{F}(t, \mathbf{x}, \xi)\bar{F}(t, \mathbf{x}_1, \xi_1)$ takes place in scale λ , we can perform the limiting transition at $\varepsilon \rightarrow 0$. Then, following the procedure of the method of splicing asymptotic expansions, we can derive the Boltzmann equation in the form

$$\frac{\partial \bar{F}}{\partial t} + \xi^i \frac{\partial \bar{F}}{\partial x^i} = \frac{1}{\text{Kn}} \int_{\Omega} \int_0^{+\infty} \int_0^\pi g(\bar{F}(t, \mathbf{x}, \xi)\bar{F}(t, \mathbf{x}, \tilde{\xi}) - \bar{F}(t, \mathbf{x}, \xi)\bar{F}(t, \mathbf{x}, \tilde{\xi}_1)) b db d\theta d\xi_1 = J_B.$$

In the last formula, $\tilde{\xi}$ and $\tilde{\xi}_1$ are the velocities that molecules colliding with velocities ξ and ξ_1 acquired.

For the above-presented derivation of the Boltzmann equation, it is on principle that coordinate space D can be presented as woven of characteristics (2), which are unclosed in the case of the power repulsion potential. However, this is not the case for potentials, which describe both attraction and repulsion of particles.

Particles with $E = \frac{m}{4}g^2 + U(r) < 0$, cannot go to infinity and will form closed trajectories. The presence of actual interaction potentials of molecules of closed trajectories is known in publications as the formation of bound states. The rest of this article will be devoted to the derivation of the Boltzmann-type equation taking into account the effect of the formation of bound states.

Let us assume that the interaction potential of molecules with each other is as follows:

$$U(r) = \begin{cases} +\infty, & 0 \leq r < d, \\ -U_0\left(\frac{d}{r}\right)^4, & r \geq d. \end{cases} \quad (3)$$

According to (3), molecules interact as rigid spheres at distances smaller than d and are attracted as the Maxwell molecules at distances larger than d . It should be noted that interaction potential (3) is rather often used in various studies.

For interaction potential (3) in the phase space region

$$\Omega_d := \left\{ \frac{E}{kT_0} = \frac{\mathbf{g}^2}{2} - \frac{\chi}{r^4} \leq 0, \quad r \geq 1 \right\}$$

(dimensionless variables are used) phase trajectories (2) are unclosed and do not pass to infinity. Since \bar{F}_2 is retained along characteristics (2), \bar{F}_2 will be discontinued on surface γ , the equation of which $\frac{\mathbf{g}^2}{2} - \frac{\chi}{r^4} = 0$, since the molecular chaos hypothesis is inapplicable for two-particle distribution function \bar{F}_2 in the region where trajectories are closed and the formal application of the Gaussian theorem becomes invalid. Performing corresponding division of D into elementary regions after applying the Gaussian theorem, we will find the equation for \bar{F} in the form

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

where

$$J_{del} = \int_{g \leq \sqrt{2\chi}} d\mathbf{g} \int_0^{\pi} \int_0^{2\pi} |\cos \omega| (\bar{F}_2 - \bar{F}_d) \sin \omega d\omega d\theta.$$

From infinity, where the molecular chaos hypothesis is applicable, function \bar{F}_2 comes to surface γ with zero energy; therefore, in the expression for J_{del}

$$\bar{F}_2 = \bar{F}(t, \mathbf{x}, \xi) \bar{F}(t, \mathbf{x}, \xi_1)_{g=0} = \bar{F}^2(t, \mathbf{x}, \xi) = \bar{F}^2(t, \mathbf{x}, \mathbf{w}).$$

When passing to dimensional variables and the distribution functions typically used, we should multiply

the above-derived equation by $\left(\frac{n_0}{\xi_0^3}\right) \frac{\xi_0}{L}$. Doing so, we

will derive $\frac{\partial f}{\partial t} + \xi^i \frac{\partial f}{\partial x^i} = J_B - J_{del}$,

$$J_B = \frac{d^2}{2} \int d\xi_1 \left(\int_0^{+\infty} \int_0^{2\pi} g(f'f'_1 - ff_1) b db d\theta \right),$$

$$J_{del} = d^2 \chi_1 \int_{|\xi^1 - \xi| \leq 2\chi_1} d\xi_1 \int_0^{2\pi} \int_0^{\pi} |\cos \omega| (\bar{f} - \bar{F}_d) \sin \omega d\omega d\theta,$$

$$\chi_1 = \sqrt{\frac{U_0}{m}}, \quad \bar{f} = f^2(t, \mathbf{x}, \xi).$$

It is mentioned in [2] that in addition to bound states with $E \leq 0$, bound states with $E > 0$ can form, as well as the fact that such states are metastable since they disappear with time. The Boltzmann equation itself is found in time scale t_λ ; therefore, metastable bound states are not taken into account in the above analysis. Molecules that are in the bound state will multiply intersect this region itself (undergo numerous collisions) by time instant t in λ scale; therefore, the authors assumed that \bar{F}_d , which figures in the derived equation, will take the quasi-canonical form

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

Functions $f_0 = f_0(t, \mathbf{q}, \mathbf{w})$ and $\varphi = \varphi(t, \mathbf{q}, \mathbf{w})$, which figure in (4), are functions in λ scale by essence. Since

$\mathbf{x} = \mathbf{q} - \frac{\mathbf{r}}{2} = \mathbf{q} + O(\varepsilon)$, then $f_0 = f_0(t, \mathbf{q}, \mathbf{w})$ and $\varphi = \varphi(t, \mathbf{q}, \mathbf{w})$ can be considered dependent on \mathbf{x} .

2. THE SET OF KINETIC EQUATIONS FOR A NONIDEAL GAS

To derive the equations that determine evolution of functions f_0 and φ , let us introduce the following functions:

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

$$h = h(t, \mathbf{q}, \mathbf{w}) = \iint_{\Omega_{del}} \left(\frac{mg^2}{4} - U_0 \left(\frac{d}{r} \right)^4 \right) \bar{F}_d d\mathbf{r} d\mathbf{g} \leq 0, \quad (5)$$

where Ω_{del} is the region of the phase space of bound states; $s\Delta\mathbf{q}\Delta\mathbf{w}$ is the number of molecules in the coupled state, the coordinates and velocities of which are arranged in the corresponding element of the phase space; and $h\Delta\mathbf{q}\Delta\mathbf{w}$ is their energy. Concrete expressions for functions s and h will be as follows: $s = RZ_s(\bar{\chi})$ and $h = RZ_h(\bar{\chi})$, where $Z_s(\bar{\chi})$ and $Z_h(\bar{\chi})$ are expressed in the form of convergent series with respect

to powers of $\bar{\chi} = \frac{U_0}{k\varphi}$, and $R = 16\pi^2 d^3 f_0 \left(\frac{U_0}{m} \right)^{3/2}$.

It is natural to accept previously determined J_{del} as the source term in the equation, which determines the evolution of function $s(t, \mathbf{x}, \mathbf{w})$; while the corresponding term in the equation for $h(t, \mathbf{x}, \mathbf{w})$ will be the work that is performed by intermolecular forces in order to transfer \bar{F}_2 into F_d through curve γ :

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

In this case, we have $\frac{Ds}{Dt} = J_{del}$ and $\frac{Dh}{Dt} = A_d$, where

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + w^i \frac{\partial}{\partial q^j} + a^j \frac{\partial}{\partial w^j}$$

is the transfer operator. If we use $l = n_0^{-1/3}$ instead of path length λ when reducing the equations to the dimensionless form (see [4]), then we can derive that $J_B \approx J_{del}$, when $\varepsilon^{1/3} \chi^{3/2} \approx 1$ or $\chi \approx \varepsilon^{-2/9}$. It follows from this evaluation that, when taking into account nonideality, χ will be rather large. Therefore, we defined

unknown quantity a^i , $i = 1, 2, 3$; in the transfer operator as $a^i = -\frac{\partial W}{m\partial q^i}$; where W is the potential of the force

field in which molecules move from Ω_{del} in λ scale. The latter means that when constructing transfer operators, the authors will use the ideology described in [5]. In this case, if we reject terms of order ε in

expression for W , we will derive $\bar{a} = \frac{4\pi U_0 d^3 \text{grad}(n)}{3m}$,

where $n = n_f + n_d$ is the total gas density, $n_d = \int s d\mathbf{w}$ is

the particle density in the bound state, and $n_f = \int f d\xi$ is the particle density in the free state. The above-described approach leads to a closed set of kinetic

equations if we attach equations for s and h to the Boltzmann equation. This set of equations is

$$\frac{\partial f}{\partial t} + \xi^i \frac{\partial f}{\partial x^i} = J_B - J_{del}, \quad \frac{Ds}{Dt} = J_{del}, \quad \frac{Dh}{Dt} = A_d, \quad (6)$$

where all operators and quantities were determined above.

3. CONSERVATION LAWS

Through the above-defined n_f and n_d , the numerical gas density $n = n_f + n_d$, while its mass density $\rho = mn$. Let us define vectors $\mathbf{u} = \frac{1}{n} \left(\int \xi f d\xi + \int \mathbf{w} s d\mathbf{w} \right)$, $\mathbf{c}_f = \xi - \mathbf{u}$, and $\mathbf{c}_d = \mathbf{w} - \mathbf{u}$. Then

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

We define the stress tensor in a nonideal gas as $P^{ij} = m \int c_f^i c_f^j f d\xi + m \int c_d^i c_d^j s d\mathbf{w}$ and pressure P as

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

Quantity

$$W = \int m \frac{\xi^2}{2} f d\xi + \int \left(m \frac{\mathbf{w}^2}{2} s - \frac{1}{2} h \right) d\mathbf{w}$$

is the total energy of the volume unit of the nonideal gas. Along with W , we also introduce quantities

$$\frac{3}{2} nkT^* = \int m \frac{c_f^2}{2} f d\xi + \int \left(m \frac{c_d^2}{2} s - \frac{1}{2} h \right) d\mathbf{w},$$

$$\mathbf{Q} = \int m c_f \frac{c_f^2}{2} f d\xi + \int c_d \left(m \frac{c_d^2}{2} s - \frac{1}{2} h \right) d\mathbf{w},$$

where T^* is the analog of the kinetic temperature of the nonideal gas, while \mathbf{Q} is the vector of the heat flux. Applying the procedure of the derivation of conservation laws developed for an ideal gas (see [3]) to (6) and herewith taking into account that $d\xi d\xi_1 = d\mathbf{w} d\mathbf{g}$, we will derive the divergent form of equations of conservation

$$\begin{aligned} \frac{\partial n}{\partial t} + \frac{\partial (n u_i)}{\partial x_i} &= 0, \quad i = 1, 2, 3, \\ m \left(\frac{\partial \left(\int \xi^j f d\xi \right)}{\partial t} + \frac{\partial \left(\int \xi^j \xi^i f d\xi \right)}{\partial x_i} \right) & \\ + \frac{\partial \left(\int w^j s d\mathbf{w} \right)}{\partial t} + \frac{\partial \left(\int w^j w^i s d\mathbf{w} \right)}{\partial x_i} &- mn_d a^j = 0, \end{aligned} \quad (7)$$

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

Using the known procedure, second and third equations (7) can be transformed to equations invariant relative to the Galileo transform. They are as follows:

$$\begin{aligned} \rho \frac{\partial u^j}{\partial t} + \rho u^i \frac{\partial u^j}{\partial x_i} + \frac{\partial P^{ij}}{\partial x_i} - n a_j &= 0, \quad j = 1, 2, 3, \\ \frac{3}{2} kn \left(\frac{\partial T^*}{\partial t} + u^i \frac{\partial T^*}{\partial x_i} \right) + P^{ki} \frac{\partial u_k}{\partial x_i} + \frac{\partial Q_i}{\partial x_i} & \\ - n(u_d^i - u^i) a_i &= 0. \end{aligned} \quad (8)$$

From the above-introduced macroscopic quantities, we can derive that

$$\frac{1}{n} \left(P - \frac{1}{3} \int h d\mathbf{w} \right) = kT^*. \quad (9)$$

By form, (9) resembles the van der Waals equation of state.

4. THE PROBLEM OF UNIFORM RELAXATION

In the case of the problem on uniform relaxation, set (6) takes the following form:

$$\frac{\partial f}{\partial t} = J_B - J_{del}, \quad \frac{\partial s}{\partial t} = J_{del}, \quad \frac{\partial h}{\partial t} = A_d. \quad (10)$$

In set (10), $\bar{f} - f_0$ depend on t and \mathbf{w} ; therefore, assuming that $\frac{3}{5} U_0 s(0, \mathbf{w}) + h(0, \mathbf{w}) = 0$, we can find that

$\frac{3}{5} U_0 s(t, \mathbf{w}) = -h(t, \mathbf{w})$. Then, taking into account the above-derived expressions for s and h , we will find $\frac{h(t, \mathbf{w})}{s(t, \mathbf{w})} = -\frac{3}{5} U_0$. From here, it follows that quantity φ introduced in Section 2 is constant. If we determine function H of the set as

$$H = \frac{k}{2} \int_{\Omega_{del}} \bar{F}_d \ln \bar{F}_d d\mathbf{r} d\mathbf{g} d\mathbf{w} + k \int f \ln \frac{f}{\exp \left(\frac{1}{2} + \frac{3U_0}{10k\varphi} \right)} d\xi,$$

then we derive that

$$\frac{\partial H}{\partial t} = \frac{kd^2}{2} \int_0^{+\infty} \int_0^{2\pi} \int \ln \frac{ff_1}{f_1'f'} (f_1'f' - ff_1) bdbd\varepsilon d\xi_1 d\xi_2$$

$$+ \frac{k}{2} d^2 \int_{g \leq \chi_1} \int_0^{\pi} \int_0^{2\pi} \ln \frac{f_0}{f} (\bar{f} - f_0) |\cos \omega| \sin \omega d\omega d\theta d\mathbf{g} d\mathbf{w} \leq 0.$$

From here, it follows that the solution of problem (10) at $t \rightarrow +\infty$ will attain the equilibrium state, at which $H = \text{const}$.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 13-01-00522.

REFERENCES

1. S. Chapman and T. Cowling, *Mathematical Theory of Nonequilibrium Gases* (Cambridge Univ., Cambridge, 1953).
2. V. Ya. Rudyak, *Statistic Theory of Nondissipative Processes in Gases and Fluids* (Nauka, Moscow, 1987) [in Russian].
3. M. N. Kogan, *Dynamics of a Rarefied Gas: Kinetic Theory* (Nauka, Moscow, 1967) [in Russian].
4. Yu. L. Klimontovich, *Statistical Physics* (Nauka, Moscow, 1982) [in Russian].
5. F. F. Vlasov, *Nonlocal Statistic Mechanics* (Nauka, Moscow, 1976) [in Russian].

Translated by N. Korovin