The H-theorem and equation of state for kinetic model of imperfect gas

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Abstract. In the offered article, having used earlier constructed kinetic model for imperfect gas, the equation of state for such gas which takes place which is able in a thermodynamic equilibrium is received and also expression for critical temperature as functions is received from an interaction potential between molecules.

1. Introduction

It is known that N.N. Bogolyubov, applying asymptotic methods, received Boltzmann’s equation from the BBGKY system (a conclusion can be found in the section ADDITION of the monograph [1]). In this method Boltzmann’s equation turns out as the equation for definition of the one-particle function of distribution in \( \lambda \)-scale, the BBGKY system which is a term of an order zero at decomposition in small parameter \( \varepsilon = n_0 d^3 \). It is accepted above that \( n_0 \), the reference density of molecules of gas, \( d \approx 10^{-8} \text{ sm} \), is molecular size (or atom). Usually take the size on which the potential of an intermolecular interaction is other than zero for this size, \( \lambda = \frac{1}{n_0 d^3} \) is a path length of molecules in gas.

When a conclusion of the equation of Boltzmann is considered, always the potential with which molecules interact among themselves is considered the given. And it is supposed that molecules of gas interact as the pointwise centers of a repulsion. In reality, as we know, the interaction potential of molecules has both the repelling, and attracting components therefore Boltzmann’s equation is fair for an ideal dilute gas (see [2]), i.e. for gas in which it is possible to neglect an average potential energy of an attraction of molecules in comparison with their average kinetic energy.

There are many works in which try to consider in Boltzmann’s equation of the amendment of an order \( \varepsilon \). The equations which are turning out in such procedure are treated as the kinetic equations for the dense gas. Already in [1] the procedure of accounting of effect of a shadowing of molecules is offered. The serial asymptotic procedure of accounting of terms of an order \( \varepsilon \) is bound to consideration of collisions of three and more numbers of molecules at the same time that leads to emergence in the made mention procedure of the dispersing integrals. In [3] this problem it is solved by means of use of the principle of easing of correlations at expression for multiparticle cumulative distribution functions.
It should be noted that injected parameter $\varepsilon$ less unit practically for all environments is higher (this fact is available in [3]). For example, for iron (Fe) whose density $\rho = 7.8 \, \text{g/cm}^3$, $\varepsilon \approx 0.08$ more, than is ten times less than unit (for water $\varepsilon \approx 0.02$). From this it is possible to draw a conclusion that the direction connected taking into account only effects of consolidation of gas will hardly lead to creation of the kinetic equations describing behavior of actual environments.

There is rather large number of works where try to consider not ideality of gas in Boltzmann’s equation (the attracting component in the potential of interaction of molecules). In [3] rather complete review of these works is given.

Noticeable contribution to comprehensions of problems, the bound to creation of the kinetic theory of imperfect gas were brought by Yu.L. Klimontovich. By it (see [4]) one more parameter of length characterizing the environment was injected. It is \( l = n_0^{1/3} \). It is treated as distance between molecules.

\[
\frac{d}{l} = \varepsilon^{1/3}
\]

Then, from above told follows that \( l = n_0^{1/3} \), and size, inverse is equal to Knudsen number which faces a collision integral in Boltzmann's equation \( 1/\lambda = \varepsilon^{2/3} \). From this it follows that the collision integral is nonanalytic function of multiparticle cumulative distribution functions therefore its decomposition on the whole degrees does not allow to consider correctly the effects bound to increase in density of the environment. Yu.L. Klimontovich in [4] also specified that for the kinetic description of imperfect gas it is necessary to use a two-particle cumulative distribution function that, generally speaking, is clear because the average potential energy of molecules will be expressed through a two-particle cumulative distribution function. It in [5] constructed the equation for the two-particle cumulative distribution function describing imperfect gas. It had no noticeable resonance. Probably because from this equation it was impossible to pass to ideal gas.

Absolutely other approach to a problem was offered by A.A. Vlasov ([6]). He entered a concept of capacity of the self-consistent field and constructed the kinetic equation for evolution of the cumulative distribution function which is in this field. In [3] data on area of applicability of approach of A.A. Vlasov are provided and also it is specified that now representations of a collision integral as the sums of boltsmanovsky integral, vlasovsky and still any terms are used.

The most relief effect of action of attractive forces between molecules is formations of the bound states those molecules which kinetic energy does not allow to overcome action of attractive forces. If to trust the author [3], then the problem of accounting of the bound states is still far from the decision, and the available kinetic equations considering the specified effect are too difficult for the analytical and numerical research.

In [7], the kinetic model considering effect of formation of the bound states was constructed. In this work the equilibrium equation of state received on the basis of this model is investigated.

2. The kinetic equation for imperfect gas

In [7] the kinetic model for imperfect gas was constructed. Imperfect gas authors called gas in which it is impossible to neglect a potential energy of interaction of molecules in comparison with their kinetic energy. In this case in a phase space $\Gamma = \Omega \times D$ where $\Omega$ - high-speed space of the relative velocities of the molecules $\vec{g} = \vec{z}_1 - \vec{z}_2$ and $D$ - the relative provisions $\vec{r} = \vec{x}_1 - \vec{x}_2$ areas of the bound states which are described by a ratio $\frac{m}{4} \vec{g}^2 + U(r) \leq 0$ where $U(r)$ is a potential of an intermolecular interaction are formed. In the assumption that the two-particle cumulative distribution function of the molecules which are in the bound state has a canonical distribution $\vec{F}_d = f_d(\vec{q}, \vec{w}) \cdot \exp\left\{ \frac{1}{k\varphi}(\varepsilon \frac{m}{2} \vec{q}^2 - U_0(\vec{g}^2)) \right\}$ For such gas, the following system of the kinetic equations was received:
\[
\frac{\tilde{c}_f}{\partial \tau} + \tilde{c}_f = J_a - J_{\text{det}}, \quad \frac{D_s}{\partial \tau} = J_{\text{det}}, \quad \frac{D_h}{\partial \tau} = \chi_i \int_{\mathcal{E}^{s=2}} \frac{m \bar{g}^2}{4} \int_0^{\tilde{g}} \cos \theta (\tilde{f}_a - f_a) \sin \omega \omega d \theta,
\]

\[
J_a = \int d \bar{g}_i \left[ \frac{1}{2} \left( g(f^{(r)}_i - f^{(c)}_i) \right) bdbd \theta \right], \quad \frac{D_s}{\partial \tau} = \frac{\partial}{\partial \tau} + w_i \frac{\partial}{\partial \bar{g}_i} + \alpha_i \frac{\partial}{\partial \omega_i}, \quad \bar{a} = \frac{-4 \pi U_{\text{det}}^3 \text{grad}(n)}{3 \bar{m}}, \quad \chi_i = \frac{\bar{U}_a}{m},
\]

\[
\mathcal{g} = \frac{\bar{g}_f + \bar{g}_i}{2}
\]

(1)

\[
J_{\text{det}} = \chi_i d^2 \int_{\mathcal{E}^{s=2}} d^2 \tilde{g} \left( \int_0^{\tilde{g}} \cos \theta (\tilde{f} - f) \sin \omega \omega d \theta \right), \quad f = f(t, \bar{x}, \bar{\xi}) \quad \text{- cumulative distribution function of molecules in the free state},
\]

\[
\tilde{f} = f^2(t, \bar{x}, \bar{\xi}) = f^2(t, \bar{w}, \bar{\xi}, \bar{x}); \quad s = s(t, \bar{q}, \bar{w}) = \int_{\Omega_{\text{det}}} \bar{F}_a d \bar{F} d \bar{\theta}, \quad h = h(t, \bar{q}, \bar{w}) = \int_{\Omega_{\text{det}}} \left( \frac{m \bar{g}^2}{4} + U(r) \right) \bar{F}_a d \bar{F} d \bar{\theta} \leq 0
\]

\[
\Omega_{\text{det}} \quad \text{- is an area of a phase space of molecules which are in the bound state; } \quad s \Delta q \Delta \bar{\omega} \quad \text{is a number of the molecules which are in the bound state whose coordinates and speeds are in the corresponding element of a phase space, and } \quad h \Delta \bar{q} \Delta \bar{\omega} \quad \text{- their energy.}
\]

Through the macro parameters entered above function \( f, s, h \) are expressed as follows:

\[
n(t, \bar{x}) = \int d \bar{g} \hat{\tilde{f}} + \int d \bar{w} \hat{s}, \quad n(t, \bar{x}) = \int d \bar{g} \hat{\tilde{f}} + \int d \bar{w} \hat{s} \quad \text{- numerical density gas; } \quad \hat{n} = \int \hat{\tilde{f}} d \bar{g} + \int \hat{s} d \bar{w} \quad \bar{u} \quad \text{- macroscopic speed of gas.}
\]

\[
P'' = m \hat{\tilde{c}}_i \hat{\tilde{c}}_j d \bar{\xi} + m \hat{\tilde{c}}_i \hat{\tilde{c}}_j \hat{s} d \bar{w}, \quad \hat{\tilde{c}}_j = \bar{\xi} - \bar{u}, \quad \hat{\tilde{c}}_d = \bar{w} - \bar{u}, \quad i, j = 1, 2, 3 \quad \text{ - stress tensor in imperfect gas.}
\]

Kinetic temperature is defined as follows:

\[
\frac{3}{2} nkT = \int \left( m \frac{\hat{\tilde{c}}^2}{2} \right) d \bar{g} + \int \left( (m \frac{\hat{\tilde{c}}^2}{2} - \frac{1}{2} h) d \bar{w} \right).
\]

Where \( k \) - Boltzmann constant. In [7] it is shown that from (1) all conservation laws follow.

\[
\frac{\partial n(t, \bar{x})}{\partial \tau} + \frac{\partial (nu_j)}{\partial \bar{x}_j} = 0, \quad mn \frac{\partial u}{\partial \tau} + mnu_i \frac{\partial u}{\partial \bar{x}_i} + \frac{\partial P_{ij}}{\partial \bar{x}_j} - na_j = 0, \quad i, j = 1, 2, 3, \quad n_i u_j = \int \bar{w} \hat{s} d \bar{w},
\]

\[
3 \frac{k n (\epsilon T + u \epsilon T)}{2} + P_{ij} \frac{\partial u}{\partial \bar{x}_i} + \frac{\partial Q_{ij}}{\partial \bar{x}_j} - n(u_i - u_j) a_i = 0, \quad Q = \int m \hat{\tilde{c}}_j \hat{s} d \bar{w} + \int \hat{\tilde{c}}_d (m \frac{\hat{\tilde{c}}^2}{2} - \frac{1}{2} h) d \bar{w}
\]

3. Equilibrium equation of state

As the concept of pressure for imperfect gas is entered also as well as for ideal -

\[
3P = P^{(1)} + P^{(2)} + P^{(3)} = m \left( \hat{\tilde{c}}_i d \bar{x} \hat{s} + \hat{\tilde{c}}_d \hat{s} \right). \quad \text{Then from determination of macroscopic sizes it is possible to receive the following ratio:}
\]

\[
(P - \frac{1}{3} \int \hat{\tilde{f}} d \bar{w}) = nkT
\]

(2)

The ratio (2) is a kinetic equation of state. In right members of the equations for \( s \) and \( h \) it is also possible to integrate on high speed space and in case in quality of mezhdu molekulyary potential the special case of potential of Sutherland was taken:

\[
U(r) = \begin{cases} +\infty, & 0 \leq r < d \\ -U_{0d} \left( \frac{r}{d} \right)^{4}, & r \geq d \end{cases}, \quad \text{to lead these equations to a look } \frac{D_s}{D_t} = J / 3, \quad \frac{D_h}{D_t} = -U_{0d} J / 5,
\]

\[
J = 64\pi^2 \chi d^2 \left( \frac{U_{0d}}{m} \right)^{\frac{3}{2}} (f - f_o)
\]

Then \( \frac{D}{D_t} \left( \frac{3}{5} U_{0d} + h \right) = 0 \rightarrow \frac{3}{5} U_{0d} + h = c = \text{cont} \). It is clear, that if
the number of particles of s an element of volume of a phase space is equal in the bound state to zero, then their energy is equal in the bound state to zero therefore s and h are always bound a ratio
\[ \frac{3}{5} U_s s(t, x, \bar{w}) + h(t, x, \bar{w}) = 0 \]
from where we have a ratio for definition: \( \varphi(t, x) = \varphi = \text{const} \)

\[ \frac{h(t, x, \bar{w})}{s(t, x, \bar{w})} = -\frac{3}{5} \frac{U_o}{Z_s(\bar{\gamma})} \frac{Z_s(\bar{\gamma})}{Z_s(\bar{\gamma})} = \frac{U_o}{k \varphi} \] [7]. In case of the homogeneous relaxation \( f = f(t, \bar{\gamma}) \) and \( s = s(t, \bar{w}) \). Respectively the system (1) will have the following appearance:

\[ \frac{\partial f}{\partial t} = \frac{d^2}{2} \int d\xi_k \left( \int_0^{2\pi} g(f_{\bar{\gamma}} - f_{\bar{\gamma}}) bdbd\theta - d^2 \chi \right) \int d\xi_k Z(\bar{\gamma}) \int \frac{g}{k \varphi} \cos \omega \left( f - f_{\bar{\gamma}} \right) \sin \omega d \omega d \theta \]

\[ \frac{\partial \varphi}{\partial t} = \frac{d^2}{2} \int d\chi \left( \int_0^{2\pi} g(f_{\bar{\gamma}} - f_{\bar{\gamma}}) bdbd\theta - \frac{3}{5} U_s s + h = 0 \right) \]

\[ S(t, \bar{w}) = \int F_{d} d\omega \ln F_{d} dtdw \]
\[ H_d = \frac{1}{2} \int S(t, \bar{w}) d\bar{w} \]

functions as:

\[ H_f = k \int f \ln f \frac{k \varphi}{2} \int d\omega d^2 \chi d \varphi, \]

\[ \frac{\partial H_f}{\partial t} = k \int d\omega d^2 \chi d \varphi \int f f_{\bar{\gamma}} - f_{\bar{\gamma}} bdbd\theta d\omega d\theta d \varphi + \frac{k}{2} \int d\omega d^2 \chi d \varphi \int f_{\bar{\gamma}} - f_{\bar{\gamma}} R(\alpha, \theta) d \alpha d \theta d \varphi \]

\[ \frac{\partial n_f}{\partial t} + \frac{\partial \varphi}{\partial t} = \frac{\partial n_f}{\partial t} = \frac{\partial n_f}{\partial t} - n = \text{const}, T = \text{const} \]

Using equilibrium values of required functions, we will receive that:

\[ n_f + m_f = n. \]

\[ T_f = \frac{1 + m_f \chi_{f}^{1/2}}{2} = T_f \]

The kinetic equation of state (2) if to write down it through equilibrium values of cumulative distribution functions will take the following form:

\[ (P + U_o m_f \chi_{f}^{1/2}) = k n T_f \].
\[ V = \frac{1}{n_f}. \] It makes sense of volume which occupies gas. The equation of state then will correspond as
\[
\left( P + \frac{U_0 V^{3/2}}{5} \right) \frac{V}{(1 + r_{X_f}^{3/2})} = kT \]
Boltzmann's equation is a term of an order zero at decomposition of BBGKY of a line-up in small parameter \( \varepsilon = nd^3 \). In [1] it is shown that not ideality of gas has to be considered when. If to write down an equation of state, assuming that \( \varepsilon X_f^{3/2} < 1 \), then it will take a form
\[
\left( P + \frac{U_0 V^{3/2}}{5} \right)(V - r_{X_f}^{3/2}) = kT \]
It is easy to see that this Van der Waals equation in which phenomenological parameters \( a \) and \( b \) also have concrete expressions through macroparameters of gas and a constant of an intermolecular interaction. Applying the procedure of receiving expression to critical temperature which is given in [8], we will receive that \( kT_{\text{crit}} = \frac{\pi^2}{135} U_0 \).

4. **Conclusion**

The assumption that \( \varepsilon X_f^{3/2} < 1 \), corresponds to the fact that approach to a critical state happens from gas, at the same time critical temperature is expressed through the reference value of an intermolecular interaction potential of molecules. In this kinetic model also other interaction potentials between molecules can be used, then in expression for critical temperature there will be other constant before \( U_0 \). To receive an isotherm for imperfect gas at any values of temperature, it is necessary to receive (2), proceeding from the decision (3) (a task about a relaxation) that in real the moment is been working on.

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