| s | is the longitudinal coordinate; |
| :--- | :--- |
| $\varphi$ | is the angle between stream axis and horizontal; |
| $\rho$ | is the density; |
| $\eta$ | is the viscosity; |
| G | is the shear modulus; |
| $\theta$ | is the relaxation time; |
| $\alpha$ | is the surface tension of liquid; |
| $\mathrm{f}=\pi a^{2}$ | is the stream radius; |
| $\Pi=2 \pi a$ | is the stream area; |
| u | is the perimeter of stream cross section; |
| $\mathrm{Q}=\mathrm{uf}, \mathrm{M}=$ | is the liquid velocity in stream; |
| $\rho \mathrm{uF}$ | are the volumetric and mass flow rates; |
| T | is the longitudinal tension in stream; |
| c | is the solution concentration; |
| $\dot{\gamma}$ | is the shear rate; |
| $\lambda$ | is the degree of elongation of element of liquid; |
| g | is the acceleration of gravity. |

## LITERATURE CITED

1. S. Middleman, Flow of High Polymers, Wiley-Interscience (1968).
2. A. I. Leonov and A. N. Prokunin, "Spinability phenomenon for elasticoviscous liquids," Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 5 (1973).

## THEORY OF EQUATION OF STATE FOR REAL GASES

1. 

V. A. Bubnov

UDC 536.711

An equation of state for real gases is derived by using correlation relations between the components of the thermal velocity.
§1. Correlation of Velocities and Multiple Collisions
in Phase Space
The principles of mechanics were extensively used for molecular-kinetic interpretation of the properties of gases in the works of Professor Clausius at Bonn. He succeeded in setting up the famous equation known as the virial equation. In modern molecular physics, it is written in the form

$$
\begin{equation*}
p v=\frac{2}{3} K-\frac{1}{3} \sum_{i} \mathbf{r}_{i}-\frac{\partial \Phi\left(\mathbf{r}_{i}\right)}{\partial r_{i}} \tag{1}
\end{equation*}
$$

We recall that the product pv is interpreted here as the virial of the external forces acting on a gas enclosed in a given volume. The quantity K expresses the kinetic energy resulting from motion of the particles in the gaseous system. The second term on the right side of Eq. (1) expresses the virial for the internal forces.

Two phase spaces are introduced for the derivation of an equation of state from Eq. (1). The first is a velocity phase space, the coordinates of which are the three components $\xi, \eta$, and $\zeta$ of the thermal velocity vector. The quantities $(\partial \Phi / \partial r) n_{x},(\partial \Phi / \partial r) n_{y}$, and $(\partial \Phi / \partial r) n_{z}$ are taken as the coordinates of the second phase space.

Machine-Building Institute, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 34, No. 3, pp. 519-528, March, 1978. Original article submitted February 8, 1977.

The distribution of points in the first phase space usually obeys the Maxwell law, i.e., the LaplaceGauss law generalized to the three-dimensional case under the condition there are no correlation relations between the statistical quantities $\xi, \eta$, and $\zeta$. The second phase space involves quantities characterizing the positions of the molecules and a binary distribution function which is determined from the law of large numbers is introduced as its characteristic. For the derivation of the equation of state, it is now merely a matter of performing mathematical calculations depending on some interaction law. These calculations entail great mathematical difficulty associated with the calculation of the virial coefficients, but from the viewpoint of comparison between theory and experiment, the results obtained in this way cannot be considered satisfactory (for example, see [1]).

The statistics of latent elementary phenomena can be constructed in various ways. For example, why is it customary to assume the absence of correlations between the statistical quantities $\xi, \eta$, and $\zeta$ in velocity phase space? This is a more or less probable hypothesis. On the other hand, nonholonomic constraints may operate within the statistical system which do not permit an arbitrary change in the velocities of atoms or molecules. These nonholonomic constraints are equivalent to the presence of so-called gyroscopic forces in a system which may produce correlation between the components of molecular thermal velocity [2].

We previously established a distribution function for the thermal velocities of atoms or molecules where the velocity phase space lacks spherical symmetry [3]. It has the form

$$
\begin{aligned}
f= & A \exp \left[-\frac{1}{2}\left(\frac{R_{11}}{R} \cdot \frac{\xi^{2}}{\sigma_{1}^{2}}+\frac{R_{22}}{R} \cdot \frac{\eta^{2}}{\sigma_{2}^{2}}+\frac{R_{33}}{R} \cdot \frac{\zeta^{2}}{\sigma_{3}^{2}}+\right.\right. \\
& \left.\left.+\frac{2 R_{12}}{R} \cdot \frac{\xi \eta}{\sigma_{1} \sigma_{2}}+\frac{2 R_{13}}{R} \cdot \frac{\xi \zeta}{\sigma_{1} \sigma_{3}}+\frac{2 R_{23}}{R} \frac{\eta \zeta}{\sigma_{2} \sigma_{3}}\right)\right] .
\end{aligned}
$$

We assume the standard deviations, $\sigma_{1}, \sigma_{2}$, and $\sigma_{3}$ expressed through a certain quantity $\sigma$, the significance of which will be shown later, in the following manner:

$$
\sigma_{1}=\sqrt{\frac{R_{11}}{R}} \sigma, \quad \sigma_{2}=\sqrt{\frac{R_{22}}{R}} \sigma, \quad \sigma_{3}=\sqrt{\frac{R_{33}}{R}} \sigma .
$$

We now write the expression for the distribution function in the form

$$
\begin{equation*}
f=A \exp \left[-\frac{1}{2 \sigma^{2}}\left(\xi^{2}+\eta^{2}+\zeta^{2}+\frac{2 R_{12}}{\sqrt{R_{11} R_{2}}} \xi \eta+\frac{2 R_{13}}{\sqrt{R_{11} R_{33}}} \xi \zeta+\frac{2 R_{23}}{\sqrt{R_{22} R_{33}}} \eta \zeta\right)\right] . \tag{2}
\end{equation*}
$$

We consider isotropic correlation. Then the minors of the correlation determinant have the form

$$
R_{11}=R_{22}=R_{33}=1-r^{2} ; \quad R_{12}=R_{13}=R_{23}=-r(1-r) .
$$

Using this, we rewrite Eq.(2) in the form

$$
\begin{equation*}
f=A \exp \left\{-\frac{1}{2 \sigma^{2}}\left[\xi^{2}+\eta^{2}+\zeta^{2}-2 n(\xi \eta+\eta \zeta+\xi \zeta)\right]\right\}, \tag{3}
\end{equation*}
$$

where $n$ is defined in the following manner,

$$
\begin{equation*}
n=\frac{r}{1+r} . \tag{4}
\end{equation*}
$$

It is easy to bring the quadratic form (3) to a canonical form [4]. Then

$$
\begin{equation*}
f=A \exp \left[-\frac{1}{2 \sigma^{2}}\left(s_{1} \xi^{2}+s_{2} \eta^{2}+s_{3}^{2} 5^{2}\right)\right] \tag{5}
\end{equation*}
$$

where $s_{1}=1-2 n, s_{2}=1+n, s_{3}=1+n$. It is easy to see that $s_{1}=s_{2}=s_{3}=1$ if $r=0$ and the distribution function (5) is converted into a Maxwellian distribution with the latter being a special case.

The constant A in Eq. (5) is determined from the normalization condition and for calculation of the mean square thermal velocity $\left(c^{2}=\bar{\xi}^{2}+\bar{\eta}^{2}+\bar{\zeta}^{2}\right)$, it is necessary to transform to spherical coordinates; after performing well-known calculations we obtain

$$
\begin{equation*}
\overline{c^{2}}=\frac{3(1-n) \sigma^{2}}{(1+n)(1-2 n)}=3 \Psi(n) \sigma^{2} . \tag{6}
\end{equation*}
$$

For our case, the mean kinetic energy of translational molecular motion is

$$
K=\frac{1}{2} \sum_{i} m_{i} v_{i}^{2}=\frac{N m \overline{c^{2}}}{2}=\frac{3}{2} N m \sigma^{2} \Psi(n) .
$$

The quantity $\sigma$ can be related to the temperature through the Boltzmann postulate

$$
N m \sigma^{2}=R T
$$

Equation (1) now takes the form

$$
p v=\Psi(n) R T-\frac{1}{3} \sum_{i} \mathbf{r}_{i} \frac{\partial \Phi\left(\mathbf{r}_{i}\right)}{\partial r_{i}}
$$

In the above equation, we separate out the compressibility factor

$$
\begin{equation*}
\frac{p v}{R T}=\Psi(n)+F(\rho, T) \tag{7}
\end{equation*}
$$

The function $F(\rho, T)$ takes into account the contribution to the compressibility factor from the virial for the intermolecular forces. We first consider a state of the compressed gases such that the function $F(\rho, T)$ can be assumed small. In that case, we rewrite the equation of state in the form

$$
\begin{equation*}
\frac{p v}{R T}=\Psi(n) \tag{8}
\end{equation*}
$$

To make our derivation more convincing, we carry out the following check. For moderately high pressures, Hirshfelder recommends the following equation of state:

$$
\frac{p v}{R T}=1+\frac{B(T)}{v}+0.625\left(\frac{b}{v}\right)^{2}+0.2869\left(\frac{b}{v}\right)^{3}+0.1928\left(\frac{b}{v}\right)^{4}
$$

Here $\mathrm{B}(\mathrm{T})$ is the second virial coefficient, and $a$ and $b$ are the usual Van der Waals constants. This equation was obtained under the assumption the internal energy of the gas depended linearly on density and the molecules resembled hard, noninteracting spheres at sufficiently high temperatures. This equation has many good features. Thus, by means of it, the change in the Joule-Thomson coefficient with pressure is described rather well.

In the Hirshfelder equation, we replace the ratio $b / v$ by a quantity proportional to $n$; i.e., we set $b / v=$ an, and we represent the ratio $B(T) / v$ in the following manner:

$$
\frac{B(T)}{v}=\frac{A b}{v}=A \alpha n .
$$

The Hirshfelder equation then takes the form

$$
\frac{p v}{R T}=1+A \alpha n+0.625 \alpha^{2} n^{2}+0.2869 \alpha^{3} n^{3}+0.1928 \alpha^{4} n^{4}
$$

Now the right side of this equation is some function of the correlation coefficient which we denote by $\chi(n)$. The two functions $\Psi(n)$ and $X(n)$ can be superimposed on one another. In order to carry out this operation, it is necessary to calculate the constants $A$ and $\alpha$ of the function $\chi(n)$ from two points of the function $\Psi(n)$. They turned out to be $\alpha=2.76$ and $A=-0.264$. After this, the two functions were superimposed (Table 1). As is clear from the table, both functions are in reasonably good approximation.

Since triple and quadruple molecular collisions were considered in the derivation of the Hirshfelder equation, the matching of the functions $\chi(n)$ and $\Psi(n)$ leads one to think the introduction of correlation distribution functions is equivalent to these collisions. This is also understandable logically. Correlation is introduced in statistical entities when their change is constrained by any conditions. The tendency toward separate calculation of triple, quadruple, etc. collisions of molecules is essentially equivalent to the imposition of certain conditions on change in thermal velocities. The very fact that these collisions are selected implicitly assumes some constraint on free motion of the molecules. It is therefore not surprising that both functions $\Psi(n)$ and $X(n)$ are reasonably good approximations of one another.

TABLE 1. Comparison of the Functions $\chi(n)$ and $\Psi(n)$

| $n$ | $\chi(n)$ | $\Psi(n)$ | $n$ | $\chi(n)$ | $\Psi(n)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0,15 | 1,0239 | 1,0559 | 0,30 | 1,4634 | 1,3461 |
| 0,20 | 1,1109 | 1,1111 | 0,35 | 1,7548 | 1,6050 |
| 0,25 | 1,2533 | 1,2000 | 0,40 | 2,1429 | 2,1428 |

## 82. Kinematics of Statistical Motions

The French geometer Charles expounded the geometric principles of duality in detail in [5]. In his opinion, only custom with respect to the views of the ancients and the successes of Varignon and Newton, who replaced motion by forces, created a rational mechanics and thereby reinforced the conviction that the theory of mechanical motions must rest on the primary concept of the point as an element of space. At the same time, this can lead to a one-sided manifestation of natural phenomena. They made force force the dominant and primary concept in mechanics and the concept of a pair a derivative concept not equivalent to the concept of a force.

However from an analysis of the characteristics of the motion of a free rigid body, it is easy to confirm that rotational and translational motions enter in completely equivalent fashion in the overall motion of the body. Therefore, it was not difficult for Charles to show how it was necessary to construct a mechanical system in which another principle would prevail in place of the $D^{\prime}$ Alembert principle where rotational motion would play the same role as translational motion plays in the establishment of the D'Alembert principle. To do this, it is necessary to replace translational motions by rotational motions as far as motion of the body is concerned, and to replace points by planes as far as the body itself is concerned, as is done in higher geometry.

It is obvious that the new system does not nullify the old. Both systems are parallel and we must use them in accordance with the problem formulated. For our construction, however, it is not the operative side that is important but the principle itself. Indeed, if the principle of duality permits mutual interchange of translational motions with the rotational motions and vice versa, this principle must be preserved in statistical motions also; i.e., we have the right to assign preference to translational motions over rotational motions and vice versa. This means that the statistical quantities characterizing translational motion must somehow depend on the statistical quanties characterizing rotational motion and vice versa. Their independent existence is a direct negation of the possibility of describing a statistical state in accordance with the principle of duality.

In a three-dimensional problem it is necessary to have three pairs of statistical quantities, namely, $u_{1 p}, u_{1 r}$ as the first pair, $u_{2 p}, u_{2 r}$ as the second pair, and $u_{3 p}, u_{3 r}$ as the third pair.

In accordance with the principle of duality, the theory of statistical motions must be constructed so that rotational motions enter equivalently with translational motions. In other words, the description of a statistical state of a system must be based either on rotational motions or on translational motions. This means that the statistical features must be intercorrelated so that translational and rotational motions enter equivalently. Such a correlation can exist under conditions where the relation

$$
\begin{equation*}
\bar{u}_{i p}=f\left(u_{j r}, u_{k r}\right) ; \quad \bar{u}_{i r}=\varphi\left(u_{j p}, u_{k p}\right) \tag{9}
\end{equation*}
$$

occurs. In mathematical statistics, these functions are called regression lines. In the simplest case, these lines can be considered straight lines. We then have in place of Eqs. (9)

$$
\left.\begin{array}{l}
\bar{u}_{1 p}=a_{21} u_{2 r}+a_{31} u_{3 r}  \tag{10}\\
\bar{u}_{2 p}=a_{12} u_{1 r}+a_{32} u_{3 r} \\
\bar{u}_{3 p}=a_{13} u_{1 r}+a_{23} u_{2 r}
\end{array}\right\}
$$

For isotropic correlation we have the identity $a_{i j}=a_{\mathrm{ji}}$. Nothing is changed if the results of the preceding section are interpreted from the views put forward. It will be seen below that with such an interpretation an opportunity is provided for theoretically establishing a connection between the correlation coefficient and the density of a compressed gas or liquid.
A. relation between the parameters $a_{\mathrm{ij}}$ and the correlation coefficient was established by Edzhvors [6]. In the case of isotropic correlation, it takes the form

$$
\begin{align*}
& a_{21}=\frac{\sigma_{2}}{\sigma_{1}} \frac{r}{r+1}=n \frac{\sigma_{2}}{\sigma_{1}} \\
& a_{31}=\frac{\sigma_{3}}{\sigma_{1}} \frac{r}{r+1}=n \frac{\sigma_{3}}{\sigma_{1}} \\
& a_{32}=\frac{\sigma_{3}}{\sigma_{2}} \frac{r}{r+1}=n \frac{\sigma_{3}}{\sigma_{2}}
\end{align*}
$$

For this same case, we use the previously established equations and show that

$$
\sigma_{1}=\sigma_{2}=\sigma_{3}=\frac{1+r}{(1-r)(1+2 r)} \sigma
$$

We now rewrite Eqs. (11) in the form

$$
\begin{equation*}
a_{21}=a_{31}=a_{32}=n \tag{12}
\end{equation*}
$$

We then square Eqs. (10) and take their average. We then have

$$
\begin{align*}
& \overline{u_{1 p}^{2}}=a_{21}^{2} \overline{u_{2 r}^{2}}+a_{31} \overline{u_{3 r}^{2}}, \\
& \overline{u_{2 p}^{2}}=a_{12}^{2} \overline{u_{1 r}^{2}}+a_{32}^{2} \overline{u_{3 r}^{2}}  \tag{13}\\
& \overline{u_{3 p}^{2}}=a_{13}^{2} \overline{u_{1 r}^{2}}+a_{23}^{2} \overline{u_{2 r}^{2}} .
\end{align*}
$$

It is assumed $\bar{u}_{i r}=0$ since they are essentially central values. We use the notation

$$
\begin{aligned}
& \overline{u_{p}^{2}}=\overline{u_{1 p}^{2}}+\overline{u_{2 p}^{2}}+\overline{u_{3 p}^{2}} \\
& \overline{u_{r}^{2}}=\overline{u_{1 r}^{2}}+\overline{u_{2 r}^{2}}+\overline{u_{3 r}^{2}}
\end{aligned}
$$

Using Eqs. (13) we then obtain

$$
\overline{u_{p}^{2}}=\left(a_{12}^{2}+a_{13}^{2}+a_{23}^{2}\right) \overline{u_{r}^{2}}-\left(a_{23}^{2} \overline{u_{1 r}^{2}}+a_{13}^{2} \overline{u_{2 r}^{2}}+a_{12}^{2} \overline{u_{3 r}^{2}}\right)
$$

In addition, we set

$$
\overline{u_{1 r}^{2}}=\overline{u_{2 r}^{2}}=\overline{u_{3 r}^{2}}=\frac{1}{3} \overline{u_{r}^{2}}
$$

Then the next to last equation is transformed to the following:

$$
\overline{u_{p}^{2}}=\frac{2}{3} \overline{u_{r}^{2}}\left(a_{32}^{2}+a_{13}^{2}+a_{23}^{2}\right)
$$

If the quantities $a_{\mathrm{ij}}^{2}$ are replaced by their values expressed in terms of the correlation coefficient, we then have

$$
\overline{u_{p}^{2}}=2 \overline{u_{r}^{2}} n^{2}
$$

This leads to

$$
\begin{equation*}
n=\sqrt{\frac{\overline{u_{p}^{2}}}{2 \overline{u_{r}^{2}}}} \tag{14}
\end{equation*}
$$

The product $\bar{u}_{p}^{2} \mathrm{~m} / 2$ (we denote this by $\tau_{\mathrm{p}}$ ) can be treated as the kinetic energy of translational motions. The product $\bar{u}_{r}^{2} \mathrm{~m} / 2$ (we denote this by $\tau_{r}$ ) can be identified with molecular kinetic energy acquired by rotating around an axis located on a moving polhode.

In this regard, we recall the following definitions of translational and rotational velocities. The instantaneous angular velocity around an axis lying on a moving polhode multiplied by the radius of curvature yields the velocity corresponding to the rotation of the body. The instantaneous angular velocity of a plane figure around a pole lying on a stationary polhode multiplied by the radius of curvature of the polhode yields the translational velocity of the body.

Considering what has been said, we rewrite Eq. (14) in the form

$$
\begin{equation*}
n=\sqrt{\frac{\tau_{p}}{2 \tau_{r}}} \tag{15}
\end{equation*}
$$

If the molecules move in a force field the potential $U$ of which has a degree of uniformity $k$, the following relation holds in an unbounded medium for the average kinetic energy of translational motion,

$$
\bar{\tau}=\frac{k}{2} U .
$$

As the potential of the forces maintaining translational motion, we assume an attractive potential, the degree of uniformity of which is generally accepted to be 6 .

If the energy $\bar{\tau}$ is identified with the energy $\tau_{p}$, Eq. (15) can be rewritten in the form

$$
n=\frac{1}{d^{3}} \sqrt{\frac{3}{2} \cdot \frac{a}{\tau_{r}}}, \quad \bar{\tau}=3 \frac{a}{d^{6}} .
$$

It is obvious that the relation $m / d^{3}=\rho$ will have the significance of a density which agrees with the density of the gas or liquid. We now represent the formula for the definition of $n$ in the following manner:

$$
\begin{equation*}
n=\frac{\rho}{m} \sqrt{\frac{3 a}{2 \tau_{r}}} \tag{16}
\end{equation*}
$$

The resultant expression is reduced to a more interesting form. Nothing prevents us from expressing the energy $\tau_{r}$ through the attractive potential having selected an appropriate distance, which we denote by $d_{0}$. In this case, the last equation is rewritten in the form

$$
n=\sqrt{\frac{3}{2}} \cdot \frac{d_{0}^{3}}{m} \rho
$$

However, the ratio $\mathrm{m} / \mathrm{d}_{0}^{3}$ has the sense of a density, which we denote by $\rho_{0}$. We then have

$$
\begin{equation*}
n=\sqrt{\frac{3}{2}} \cdot \frac{\rho}{\rho_{0}} \tag{17}
\end{equation*}
$$

The quantity $\rho_{0}$ generally depends on the density of the gas. In first approximation, we can set $\rho_{0}=\sqrt{\rho\left(a_{1}+a_{2} \rho\right)}$. Then, to a certain approximation, Eq. (17) takes the form

$$
\begin{equation*}
\frac{r}{1+r}=n=\sqrt{\rho}\left(A_{1}+A_{2} 0\right) \tag{18}
\end{equation*}
$$

Thus, the arguments offered show what physical state it is necessary to assume in order to explain the empirically determined Eq. (18). It is obvious that the constants $A_{1}$ and $A_{2}$ depend on the volume occupied by a molecule if the intermolecular distance becomes such that the attractive potential force balances the rotational energy of a molecule around an axis lying on a moving polhode.

The question arises as to whether such a conceivable state of the medium exists. This state is a singular state among other possible states. In nature, singular states of thermal motion in matter are found precisely at the critical point.

We assume that the state specified above is realized at the critical point. Then the coefficients $A_{1}$ and $A_{2}$ must be proportional to the corrected specific volume at the critical point. But, as experiment shows, that last is proportional to the ratio between critical temperature and critical pressure. From what has been said we have the right to assume

$$
\begin{equation*}
A_{1}=a_{1}+b_{1} \frac{T_{c}}{p_{c}} ; \quad A_{2}=a_{2}+b_{2} \frac{T_{\mathrm{c}}}{p_{\mathrm{c}}} \tag{19}
\end{equation*}
$$

It is impossible to calculate the constants appearing here; it is necessary to select them on the basis of an analysis of experimental data. Further, the success of the theory will lie in the universality of these constants; i.e., they should remain constant for several different materials.

We shall show below that the following empirical formulas possess this property:

$$
\left.\begin{array}{l}
A_{1}=0.8096 \cdot 10^{-2}+0.4481 \cdot 10^{-2} \frac{T_{c}}{p_{c}}  \tag{20}\\
A_{2}=0.9924 \cdot 10^{-5}-0,5481 \cdot 10^{-5} \frac{T_{c}}{p_{c}}
\end{array}\right\}
$$

Returning to Eq. (7), we rewrite it in the form

$$
\begin{equation*}
\frac{p u}{R T}=\Psi(n)-B \rho . \tag{21}
\end{equation*}
$$

Here the virial for intermolecular forces is represented by only a single term and the correlation coefficient is independent of temperature according to Eqs. (18) and (20). The temperature dependence of the compressibility factor, according to Eq. (21), will be determined entirely by the function $\mathrm{B}(\mathrm{T})$, which should be found by approximation to experimental data. If the ratio $T_{c} / p_{c}$ is known, the function $\bar{\Psi}$ is calculated as a function of density according to Eqs. (6), (18), and (20), and only the single experimental constant B remains in Eq. (21).

## 83. Derivation of Correlation Distribution Function

## from Gibbs' Distribution

We assume the molecules are of finite size. Then the motion of each molecule can be divided into translational motion of the center of mass and rotation around the latter. Consequently, the expression for the kinetic energy of a molecule has the form

$$
\begin{equation*}
K=\frac{m}{2}\left(\xi^{2}+\eta^{2}+\zeta^{2}\right)+\frac{1}{2}\left(I_{1} \omega_{x}^{2}+I_{2} \omega_{y}^{2}+I_{3} \omega_{z}^{2}\right) . \tag{22}
\end{equation*}
$$

In statistical mechanics, it is customary to assume that the angular velocities $\xi, \eta$, and $\zeta$ of translational motion do not depend on the angular velocities $\omega_{\mathrm{x}}, \omega_{\mathrm{y}}$, and $\omega_{\mathrm{z}}$ of rotational motion. However, this assertion contradicts the geometric principle of duality mentioned above. More than that, types of mechanical motions exist where this coupling is simply obvious. For example, if a body participates in screw motion along some axis, the translational velocity of the body along this axis is expressed through the angular velocity of rotational motion in the following manner:

$$
\begin{equation*}
\xi=\frac{h}{2 \pi} \omega_{x}, \tag{23}
\end{equation*}
$$

where $h$ is the pitch of the screw which generally can be a function of time. Another example occurs when a disk of radius $R$ rolls along a plane without slipping. In this case the condition of rolling without slipping reduces to the fact that the path traversed by a point along the arc of the circumference is equal to the displacement along the plane over which rolling occurs and this leads to the following relation [7]:

$$
\begin{equation*}
\xi=R \omega_{x} . \tag{24}
\end{equation*}
$$

Equations (23) and (24) represent particular cases of nonintegrable, nonholonomic constraints imposed on a mechanical system and which reduce its degrees of freedom.

If the gas is in equilibrium motion and the molecules collide in accordance with the laws for noncentral collision, the molecules will acquire rotational velocities in addition to translational velocities. Since the rotational velocities are a consequence of the translational velocities nonholonomic constraints of the following form can occur:

$$
\frac{\xi}{\omega_{x}}=h_{1}, \quad \frac{\eta}{\omega_{y}}=h_{2}, \quad \frac{\zeta}{\omega_{z}}=h_{3} .
$$

Now Eq. (22) can be rewritten in the form

$$
\begin{equation*}
K=\frac{1}{2 m}\left[\left(1+\alpha_{1}\right) p_{x}^{2}+\left(1+\alpha_{2}\right) p_{y}^{2}+\left(1+\alpha_{3}\right) p_{2}^{2}\right] \tag{25}
\end{equation*}
$$

in which the translational velocity was replaced by the moments $\mathrm{p}_{\mathrm{x}}=\mathrm{m} \xi, \mathrm{p}_{\mathrm{y}}=\mathrm{m} \eta, \mathrm{p}_{\mathrm{z}}=\mathrm{m} \zeta$, and the additional notation

$$
\begin{equation*}
\alpha_{1}=\frac{I_{1}}{m h_{1}^{2}}, \quad \alpha_{2}=\frac{I_{2}}{m h_{2}^{2}}, \quad \alpha_{3}=\frac{I_{3}}{m h_{3}^{2}} . \tag{26}
\end{equation*}
$$

introduced. Using the Gibbs formula, we determine the probability of finding a molecule in a volume element of the six-dimensional phase space [8]

$$
\begin{equation*}
d W=A_{1} e^{-\frac{E}{k T}} d x d y d z d p_{x} d p_{y} d p_{z} \tag{27}
\end{equation*}
$$

We assume that the molecule has no potential energy. Then the total energy $E$ of the molecule is equal to its kinetic energy K and after integration over the coordinates of phase space, Eq. (27) can be rewritten as

$$
d W-A e^{-\frac{K}{k T}} d p_{x} d \rho_{y} d p_{z}
$$

Now, using Eq. (25), we return to the equation for the probability density

$$
f=A \exp \left\{-\frac{1}{2 m k T}\left\{\left(1+\alpha_{1}\right) p_{x}^{2}+\left(1+\alpha_{2}\right) p_{y}^{2}+\left(1+\alpha_{3}\right) p_{z}^{2}\right]\right\}
$$

or after transformation from momenta to velocities we have

$$
\begin{equation*}
f=A \exp \left\{-\frac{m}{2 k T}\left[\left(1+\alpha_{1}\right) \xi^{2}+\left(1+\alpha_{2}\right) \eta^{2}+\left(1+\alpha_{3}\right) \zeta^{2}\right]\right\} \tag{28}
\end{equation*}
$$

Equation (28) transforms into a Maxwellian velocity distribution if $\alpha_{1}=\alpha_{2}=\alpha_{3}=0$, which is equivalent to a zero value for the molecular moments of inertia $I_{1}, I_{2}$, and $I_{3}$ along the principal inertial axes.

Equation (28) agrees in form with Eq. (5). Consequently, it also represents the canonical form of the correlation distribution function (2). In comparing Eqs. (28) and (5), we express the parameters $\alpha_{1}, \alpha_{2}$, and $\alpha_{3}$ through the correlation coefficient $r$ in the following manner:

$$
\alpha_{1}=-\frac{2 r}{1+r}, \quad \alpha_{2}=\alpha_{3}=\frac{r}{1+r}
$$

## NOTATION

| p | is the pressure; |
| :--- | :--- |
| v | is the specific volume; |
| $\mathrm{r}_{\mathbf{i}}$ | is the radius vector for position of molecule; |
| $\dot{\xi}, \eta, \zeta$ | are the components of thermal velocity vector; |
| $\mathbf{r}$ | is the correlation coefficient; |
| m | is the molecular mass; |
| R | is the universal gas constant; |
| N | is Avogadro's number. |

## LITERATURE CITED

1. J. Hirshfelder, C. Curtiss, and C. Bird, Molecular Theory of Gases and Liquids, Wiley-Interscience (1954).
2. A. S. Predvoditelev, Inzh.-Fiz. Zh., 5, No. 8 (1962).
3. V. A. Bubnov, Inzh.-Fiz. Zh., 26, No. 2 (1974).
4. V. A. Bubnov, Int. J. Heat Mass Transfer, 19, 174 (1976).
5. Charles, Historical Review of the Origin and Development of Geometric Methods [Russian translation], Moscow (1883).
6. E. E. Slutskii, Correlation Theory and Elements of the Theory of Distribution Curves [in Russian], Kiev (1912).
7. A. A. Eichenwald, Theoretical Physics [Russian translation], Part III, Moscow (1934).
8. V. F. Nozdrev and A. A. Senkevich, Course in Statistical Physics [in Russian], Moscow (1969).
