Reports of the Academy of Sciences of the USSR

PHYSICS

1969

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1969. Volume 186, No. 6

UDC 536.71

PHYSICS

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JUSTIFICATION OF THE FORM OF AN EQUATION OF STATE REPRESENTED THROUGH ELEMENTARY FUNCTIONS

(Presented by Academician V. A. Kirillin on 10 XII 1968)

In recent years, an equation of state of a real gas represented through so-called elementary functions has been effectively used ([1–3]):

$$Z = \frac{pV}{RT} = \alpha_0(\omega) + \alpha_1(\omega)\vartheta + \beta(\omega)\psi(\vartheta) + \gamma(\omega)\varphi(\vartheta) + \dots, \tag{1}$$

where $\alpha_0(\omega), \alpha_1(\omega), \beta(\omega), \gamma(\omega), \dots$ are polynomials in the reduced density $\omega = V_{\text{cr}}/V$, and $\psi(\vartheta), \varphi(\vartheta), \dots$ are polynomials in $\vartheta = T_{\text{cr}}/T$. Equation (1) describes experimental thermal data with high accuracy over a wide range of temperatures and densities and, as a consequence, correctly represents caloric data. The number of temperature functions $\psi(\vartheta), \varphi(\vartheta) \dots$, as a rule, does not exceed two, which has made it possible to develop a fairly simple and reliable method for determining elementary functions ([3]), which is also successfully implemented on electronic digital computers ([4]).

The form of the equation of state (1) was obtained on the basis of an analysis of the configuration of the thermodynamic surface of a real gas; however, a proper justification of this equation from the standpoint of statistical physics has so far been lacking.

We shall show that equation (1) follows naturally from the theoretically justified equation of state of J. Mayer ([5]) and N. N. Bogolyubov ([6]), which has the form

$$\frac{pV}{RT} = 1 - \sum_{n \geqslant 1} \frac{n}{n+1} \left(\frac{N}{V}\right)^n \beta_n. \tag{2}$$

Here N is the number of particles in the volume V,

$$\beta_n = \frac{1}{n}\int_V \dots \int_V \sum \prod \left\{\exp\left[-\frac{U(r_{ij})}{kT}\right] - 1\right\} d\tau_1 \dots d\tau_n \tag{3}$$

are irreducible integrals whose dependence on temperature is determined by the form of the potential energy of pair interaction of molecules. Denoting by V_d the region of integration corresponding to repulsive forces, the expression for β_n may be written as the sum of two integrals

$$\beta_n = \frac{1}{n}\int_{V_d} \dots \int_{V_d} \sum \prod f_{ij} d\tau_1 \dots d\tau_n +$$

$$+\frac{1}{n}\int_{V-V_d} \dots \int_{V-V_d} \sum \prod f_{ij} d\tau_1 \dots d\tau_n, \tag{4}$$

where $f_{ij} = \exp[-U(r_{ij})/KT] - 1$. The first integral $\beta_n^{(1)}$ in expression (4) is independent of temperature, since for the region V_d, where the distance between molecules $r < d$, $kT \ll U(r_{ij})$. The integral over the region $V - V_d$, corresponding to attractive forces, can be written in the form ([7−9])

$$\beta_n^{(2)} = \sum_{m\geqslant 1} \frac{\alpha_{n,m}}{(kT)^m}, \tag{5}$$

where $\alpha_{n,m}$ are coefficients of the form

$$\alpha_{n,m} = \frac{1}{n}\int \dots \int \sum_{\nu_{ij}} \prod_{n+1\geq i>j\geq 1} \frac{[-U(r_{ij})]^{\nu_{ij}}}{\nu_{ij}!} d\tau_1 \dots d\tau_n, \tag{6}$$

$$\sum \nu_{ij} = m.$$

From (2)–(6) it follows that

$$\frac{pV}{RT} = 1 - \sum_{n\geq 1} \frac{n}{n+1}\left(\frac{N}{V}\right)^n \left[\beta_n^{(1)} + \sum_{m\geq 1} \frac{\alpha_{n,m}}{(kT)^m}\right]. \tag{7}$$

Let us transform the preceding equation to the coordinates $Z,\ \omega,\ \vartheta$, separating out the part linear with respect to ϑ:

$$Z = 1 - \sum_{n\geq 1} \frac{n}{n+1}\left(\frac{N}{V_{\text{cr}}}\right)^n \beta_n^{(1)}\omega^n - \sum_{n\geq 1} \frac{n}{n+1}\left(\frac{N}{V_{\text{cr}}}\right)^n \frac{\alpha_{n,1}}{kT_{\text{cr}}}\omega^n\vartheta - \sum_{n\geq 1}\sum_{m\geq 2} \frac{n}{n+1}\left(\frac{N}{V_{\text{cr}}}\right)^n \frac{\alpha_{n,m}}{(kT_{\text{cr}})^m}\omega^n\vartheta^m. \tag{8}$$

Denote

$$1-\sum_{n\geq 1}\frac{n}{n+1}\left(\frac{N}{V_{\text{cr}}}\right)^{n}\beta_n^{(1)}\omega^n=\alpha_0(\omega), \tag{9}$$

$$-\sum_{n\geq 1}\frac{n}{n+1}\left(\frac{N}{V_{\text{cr}}}\right)^{n}\frac{\alpha_{n,1}}{kT_{\text{cr}}}\omega^n=\alpha_1(\omega). \tag{10}$$

Represent the coefficients of the part of equation (8) curvilinear in ϑ in the form

$$-\frac{n}{n+1}\left(\frac{N}{V_{\text{cr}}}\right)^{n}\frac{\alpha_{n,m}}{(kT_{\text{cr}})^m}=\sum_i b_i c_{im}. \tag{11}$$

For brevity denoting

$$-\frac{n}{n+1}\left(\frac{N}{V_{\text{cr}}}\right)^{n}\frac{\alpha_{n,m}}{(kT_{\text{cr}})^m}=A_{n,m}, \tag{12}$$

for some fixed $n=n_k$ we obtain from (11)

$$A_{n_k,m}=\sum_i b_{in_k}c_{im}, \tag{13}$$

or, what is the same,

$$A_m=\sum_i b_i c_{im} \qquad (m=2,3,\dots,q). \tag{14}$$

Let us consider (14) as a system of equations linear with respect to the unknowns b_i. This system is consistent if and only if the rank of the matrix C, composed of the coefficients c_{im}, is equal to the rank of the augmented matrix A, obtained by adjoining to the matrix C the free terms A_m. However, it may turn out that, despite the possibility of an arbitrary choice of the quantities c_{im}, the condition stated above for $i<q-1$ is not fulfilled for all systems of the form (14), since they contain one and the same matrix C and different right-hand sides. In this case it is necessary, in the corresponding systems, to relate a certain number of the quantities $A_{n,m}$ by a linear dependence.

Let the matrix C have rank r. If its first r rows are linearly independent, then each of the remaining $m-r$ rows will be their linear combination, and then the corresponding values A_m must be linear combinations of the first r values A_m:

$$A_{m_s}=a_{s1}A_1+a_{s2}A_2+\dots+a_{sr}A_r \qquad (m_s>r). \tag{15}$$

From (12) and (6) it follows that condition (15) is fulfilled, since the latter represents a linear relation between the integrand expressions of one-dimensional integrals $a_{n_k,m}$.

From the formally mathematical point of view one could write the system (11) for fixed m and carry out analogous arguments; however, in this case the relations (15) are not satisfied.

Taking into account (9)–(11), one can write equation (8) in the form

$$Z = \alpha_0(\omega) + \alpha_1(\omega)\vartheta + \sum_{i\geq 1}\sum_{n\geq 1}\sum_{m\geq 2} b_{in}c_{im}\omega^n\vartheta^m, \tag{16}$$

which is nothing other than an equation represented by elementary functions.

Consequently, from equation (2), without any assumptions, the equation of state (1) can be obtained, where the constants b_{in} and c_{im} have, respectively, the meaning of the coefficients of the volume and temperature functions. From relation (11) it is obvious that the transition from (2) to (1) is not unique, i.e., to a single equation of state in the form (2) there corresponds a set of equations in the form (1). This circumstance is reflected in the invariance of equation (1) with respect to linear transformations of elementary functions, which is widely used in practice ([3]).

Let us note that the maximum value of the summation index n in (2) and (16) is determined by the greatest possible number of molecules in the groups forming a real gas. This value may be estimated from the following considerations ([5]). The integrand expression of each of the terms making up the irreducible integral β_n is the product of functions f_{ij}. The latter attain a maximum when the distance r_{ij} between molecules corresponds to the minimum of the potential energy $U(r_{ij})$. At low temperatures the maximum values of f_{ij} are large, and the greatest part of the integral β_n is determined by those terms into which the product of a large number of functions f_{ij} enters. There is, however, an upper limit equal to 12 functions that can simultaneously have values close to the maximum. Thus, at low temperatures the principal contribution to β_n is due to terms containing approximately 12 functions f_{ij} per molecule. As the temperature increases, the functions f_{ij} decrease, and an ever greater contribution to β_n is made by terms with a small number of f_{ij} in the product.

The theoretical premises for deriving equation (2) are such that, strictly speaking, it is valid in the region of small and moderate densities. Nevertheless, the equation (1) following from it has been successfully applied to describe experimental data in the interval $\omega = 0$—3. This is explained not only by the selection, in equation (1), of coefficients from experimental data, but also by the fact that rejection of the hypothesis of additivity of the energy of intermolecular interaction, adopted by J. Mayer, apparently will not lead to a fundamental change in the form of the equation of state.

In conclusion we note that the equation of state of a real gas obtained in ([10]) in the form

$$Z = \alpha_0(\omega) + \alpha_1(\omega)\vartheta + \sum_{i\geq 1} \beta_i(\omega)\psi^i(\vartheta), \tag{17}$$

where $\alpha_0(\omega)$, $\alpha_1(\omega)$, $\beta_i(\omega)$ are polynomials in the reduced density, and $\psi(\vartheta)$ is a polynomial in ϑ, appearing in different powers i, contradicts the Mayer–Bogoliubov equation (2). On comparing equations (17) and (8), taking into account the notation (9) and (10), the coincidence of the parts linear in ϑ is obvious. For the coincidence of the curvilinear parts it is necessary to satisfy the equality

$$-\frac{n}{n+1}\left(\frac{N}{V}\right)^n \sum_{m\geq 2} \frac{\alpha_{n,m}}{(kT\ )^m}\vartheta^m = \sum_{i\geq 1} b_{in}\left(\sum_{m\geq 2} c_m\vartheta^m\right)^i. \tag{18}$$

The latter is satisfied in the unique case $i = 1$. For $i > 1$ from

it follows from (18) that $a_{n,m}$ depends on temperature. For example, for $i = 2$

$$-\frac{n}{n+1}\left(\frac{N}{V_{\text{cr}}}\right)^n \sum_{m\geq 2} \frac{a_{n,m}}{(kT_{\text{cr}})^m} = b_{1n}\sum_{m\geq 2} c_m + b_{2n}\sum_{m,l\geq 2} c_m c_l \vartheta^l, \tag{19}$$

whereas $a_{n,m}$, according to (6), is not a function of temperature.

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Received
9 XII 1968

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Note: Figure translations are in progress. See original paper for figures.