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EQUATION OF STATE OF A DENSE GAS IN A QUASICLASSICAL APPROXIMATION

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We obtain an equation of state for a dense monatomic gas involving the first quantum correction for thermodynamic functions.

The equilibrium theory of a classical fluid that has been intensively developed in recent years enables us at present to quantitatively describe the thermodynamic properties of a liquid and a dense gas consisting of monatomic particles that interact additively [1-4]. Further progress in fluid theory is related to the consideration of quantum and nonadditive effects, and also to the nonspherical nature of complex molecules.

The influence of small quantum effects on the thermodynamic properties of a fluid is studied in [5-8]. In [5-7] equations are used that require knowledge of the binary correlation function (or some integral of it) [6-7] of a classical system which is calculated by methods of molecular dynamics or the Monte Carlo method. The necessary calculations are carried out only for the Lennard-Jones potential (12-6) which does not adequately describe the intermolecular interaction and, in addition, does so only for low temperatures (referred to the characteristic energy of interaction), which conditions the application of these equations only for neon and argon [5-7].

The equation obtained by perturbation theory [8] is also valid for high temperatures. It has little accuracy, however, which is possibly due to the unsuccessful choice of the intermolecular potential. Another inadequacy in the equation obtained in [8] is the necessity of integrating a binary correlation function for the distribution of solid spheres that is given in table form for each temperature and density. Since we must solve an interpolation problem to obtain thermodynamic functions at a fixed pressure, this equation is practically inapplicable for engine ring calculations.

1. Presentation of the Quantum Correction for the Equation of State at High Temperature

At temperatures for which we can disregard the nonadditive interactions (shown by the example of three-particle interactions) of the monatomic sphericosymmetric neutral particles [9, 10], the free energy of the system of N particles contained in volume V takes the following form with accuracy up to the first nonzero quantum correction [11]:

$$F = F_{\mathrm{cl}} + \frac{h^2 (\rho N_{\mathrm{A}})^2 V}{24\pi mkT} \int_0^\infty g(R)\, \nabla^2 u(R)\, R^2 dR = F_{\mathrm{cl}} + F_{\mathrm{qu}}. \tag{1}$$

Here g(R) = exp [−u(R)/kT]y(R) is the radial function of the classical system of particles that interact additively with the force −du(R)/dR.

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Let L(R) = exp [$-u(R)/kT]\nabla^2 u(R)R/kT$, and then

$$F_{qu}=\frac{h^2(\rho N_A)^2V}{24\pi m}\int\limits_0^\infty L(R)\,y(R)\,RdR=\frac{h^2(\rho N_A)^2V}{24\pi m}F_1. \quad (2)$$

As shown by Henderson and his colleagues [12, 13], if the forces of interatomic repulsion are sufficiently large (for example, if the potential is stable and regular [14], all the realistic potentials characterizing the interaction among the neutral molecules satisfy these conditions), then the following approximation is valid for the function L(R):

$$L(R)\simeq\delta(R-c). \quad (3)$$

By substituting (3) into the expression for F_{qu}, we obtain

$$F_{qu}=\frac{h^2(\rho N_A)^2V}{24\pi m}S(T)\,y(c)\,c. \quad (4)$$

The quantity S(T) is determined from condition (3) ($c > 0$),

$$S(T)=\int\limits_0^\infty L(R)\,dR. \quad (5)$$

Equation (4), which yields part of the first quantum correction for the free energy of the fluid, is not closed, since diameter c remains undetermined.

2. The Kim Method

Kim [15] expands L(R) in series in derivatives of a delta-function. After expanding y(R)R in Taylor series [15] in the neighborhood of c, we have

$$F_1=\sum_{n=0}^\infty\frac{d^n[Ry(R)]}{n!\,dR^n}\bigg|_{R=c}\int\limits_0^\infty L(R)(R-c)^n\,dR, \quad (6)$$

where c is still not determined. The zero approximation ($n = 0$) for F_{qu} (6) agrees with the approximation of Henderson [4]. After we set one of the terms of series (6) equal to zero, we can determine diameter c_{n+1} [which, generally speaking, is not equal to c for the arbitrary potential u(R)].

In particular, we require that the first term ($n = 1$) of series (6) equal zero [requiring the agreement of the free energy of the system of particles interacting with the potential u(R) and of the system of solid spheres with diameter c_2] and thus we obtain

$$c_2=\int\limits_0^\infty L(R)\,RdR\Big/\int\limits_0^\infty L(R)\,dR. \quad (7)$$

The Kim method leads to a closed equation of state; however, if function y(R)R has more than six arbitrary constants in R, then integral (6) is expanded. The exact form of function y(R) is unknown [1, 3]; in the Perkus–Ievik approximation it is a polynomial of the third degree in R, and in contrast to the nonrelativistic classical case, series (6) converges in this approximation, although its leading terms are not necessarily small.

The convergence occurs more quickly if we apply the Kim method only to the repulsing part of the intermolecular potential [16]. We represent the intermolecular potential as a sum of the potentials corresponding to the repulsion and attraction forces:

$$u(R)=u_a(R)+u_r(R),$$
$$u_r(R)=\begin{cases}u(R), & R\leqslant\sigma',\\ 0, & R>\sigma',\end{cases}\qquad u_a(R)=\begin{cases}0, & R\leqslant\sigma',\\ u(R), & R>\sigma',\end{cases} \quad (8)$$

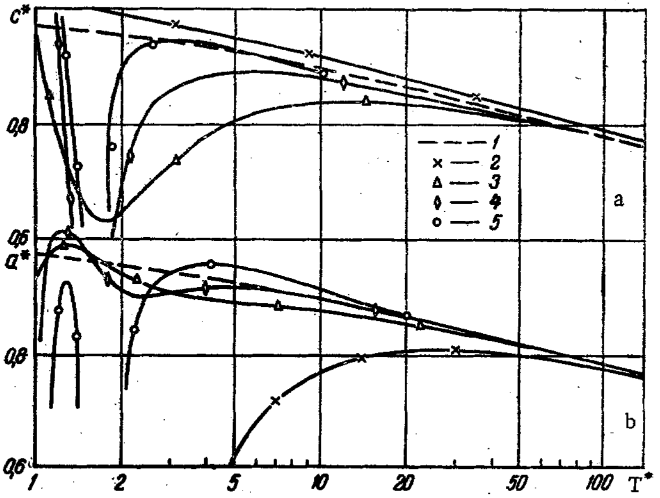

Fig. 1. Dependence of the effective diameter of solid spheres on reduced temperature: a) for a semiclassical case; b) for a classical case. 1) Calculation according to Eq. (18). The effective diameters are determined by virial coefficients and their first quantum corrections for the Lennard-Jones potential (12-6); 2,3,4,5) second, third, fourth, and fifth virial coefficients, respectively.

where σ' is a still undetermined parameter of division. Thus, for F_1 we obtain ($\alpha_n = d^n[xy\cdot(x)]/dx^n|_{x=1}$)

$$F_1 = \sum_{n=0}^{\infty} \frac{\alpha_n}{n!\,c^n}\left[\int_0^{\infty} L_r(R)(R-c)^n\,dR + \int_0^{\infty} L_a(R)(R-c)^n\,dR\right] =$$

$$= \sum_{n=0}^{\infty} \frac{\alpha_n}{n!\,c^n}\left[\int_0^{\sigma'} L(R)(R-c)^n\,dR + \int_{\sigma'}^{\infty} L(R)(R-c)^n\,dR\right] = \sum_{n=0}^{\infty} \frac{\alpha_n}{n!\,c^n}(J_{1,n}+J_{2,n}). \qquad (9)$$

The subscripts r and a in function L(R) denote that the function is taken for the potentials $u_r(R)$ and $u_a(R)$. We now determine σ' from the condition that in zero approximation the interaction is determined exclusively by the repulsing part of the potential, i.e.,

$$J_{2,0} = \int_{\sigma'}^{\infty} L(R)\,dR = 0, \qquad (10)$$

and c is determined from the condition that in the zero approximation ($J_{1,1} = 0$) the quantum correction for the free energy of the solid sphere system with diameter c_2' agrees with the real system:

$$c_2' = \int_0^{\sigma'} L(R)\,R\,dR \Big/ \int_0^{\sigma'} L(R)\,dR. \qquad (11)$$

As the numerical calculations show, $\sigma' \simeq r_m$, where r_m is the coordinate of the minimum potential. At the limit $\sigma' \to \infty$ (the step potential of repulsion), Eq. (11) transforms to the Kim result (7).

If in Eq. (9), as in the classical case [16], we limit ourselves to inclusion of the forces of attraction in the quantum correction for only the second virial coefficient (the term $J_{2,1}$), then the quasiclassical part of the equation of state is represented as

$$F_1 = y(c_2')\,c_2' \int_0^{\sigma'} L(R)\,dR + \int_{\sigma'}^{\infty} L(R)\,R\,dR. \qquad (12)$$

Here we take into account that the terms $J_{1,n}$, $n > 1$ are considerably less than $J_{1,0}$ and $J_{1,1} = 0$ because of (11).

3. Correct Choice of the Diameter of the Solid Spheres

We study an alternative choice of diameter c in Eq. (4). A part of the first quantum correction can be written in the equation of state in virial form [17]

$$\left.\frac{P}{\rho R_0 T}\right|_{\mathrm{qu}} = \Lambda^{*2}\sum_{j=2}^{\infty} B^*_{1,j}(T^*)\,(\rho b_0)^{j-1}, \tag{13}$$

where $\Lambda^* = h/(m\varepsilon)^{1/2}/\sigma$ is a de Bura parameter; ε and σ are parameters of the analytic intermolecular potential $u(R)$; $u(\sigma) = 0$, $\varepsilon = |u(r_m)|$, $b_0 = {}^2/_3\pi N_A\sigma^3$; $T^* = kT/\varepsilon$ is the reduced temperature.

The virial series for the solid spheres with diameter c^* (4) ($c^* = c/\sigma$) is

$$\left.\frac{P}{\rho R_0 T}\right|_{\mathrm{qu.sol.sph}} = \frac{\Lambda^{*2}S^*(T^*)}{(4\pi)^2 T^*}\sum_{j=2}^{\infty}(j-1)\,b^*_j\, c^{*(3j-5)}(\rho b_0)^{j-1}, \tag{14}$$

where $S^*(T^*)$ is the function introduced by Eq. (5) in dimensionless form. After setting equal the coefficients of series (13) and (14) having equal powers, we obtain the equations of the temperature dependence for the diameter of the solid spheres $c_j^*(T^*)$ for each virial coefficient:

$$B^*_{1,j}(T^*) = \frac{(j-1)\,S^*(T^*)\,b^*_j\,c_j^{*(3j-5)}}{(4\pi)^2 T^*}. \tag{15}$$

The dependence of c_j^* on the reduced temperature is shown in Fig. 1a. In our calculations we use the data for the first quantum correction for the virial coefficients of the Lennard-Jones potential (12-6) from [17, 18].

The equivalency condition of Eqs. (2) and (4) (it is assumed that expansions (13) and (14) converge correctly; see [14]) is as follows:

$$c^*_j(T^*) = c^*_k(T^*);\quad j,\ k = 2,\ 3,\ \ldots\ . \tag{16}$$

As we see from Fig. 1a, this condition is satisfied for the leading virial coefficients $T^* \gtrsim 15$, because at high temperatures the repulsion forces for many-particle collisions are dominating, and so the exact satisfaction of condition (16) increases with an increase of the temperature and of the virial coefficient.

The effect of the attraction forces on the first quantum correction for the second virial coefficient is considerable in the entire temperature range, and condition (16) is only satisfied asymptotically for $c_2^*(T^*)$.

We note that the behavior of functions $c_j^*(T^*)$ is completely equivalent (Fig. 1b) to the temperature dependence of the classical diameters of the solid spheres $a_j^*(T^*)$ [19] that are defined by the equations

$$B^*_j(T^*) = b^*_j\, a_j^{*3(j-1)};\quad j = 2,\ 3,\ \ldots\ . \tag{17}$$

At high temperature, $a_j^*(T^*)$ agrees with the diameter calculated according to the Barker–Henderson formula [20]

$$a^* = \frac{a}{\sigma} = -\frac{1}{\sigma kT}\int_0^{\sigma}\exp\left[-\frac{u(R)}{kT}\right]\frac{du(R)}{dR}\,R\,dR, \tag{18}$$

presented in Fig. 1. The diameters c_j^* and a_j^*, starting from $j = 3$, converge when the temperature and the number of the virial coefficient increase; they agree if $u(R)$ is a step potential of repulsion [12].

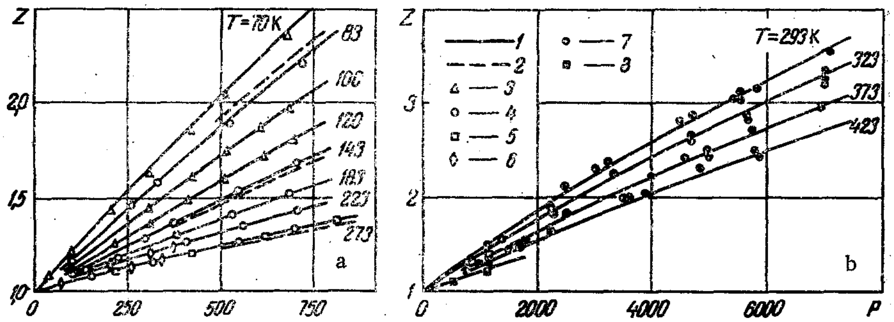

Fig. 2. Dependence of the compressibility coefficient for helium at low (a) and high (b) temperatures on pressure, bars: 1) calculation according to Eq. (21); 2) according to classical equation (20); experimental data: 3) according to [23]; 4) according to [24-26]; 5) according to [27]; 6) according to [28]; 7) according to [29] (unsmoothed data).

We can sometimes interpret $a^*(T^*)$ [16] as the "effective" diameter of the solid spheres, though we cannot call $c^*(T^*)$ the "quasiclassically effective" diameter, since this assumes the validity of the equation $c^*(T^*) = a^*(T^*) + 2^{-3/2}\lambda$ [21], where $\lambda = h/(2\pi mkT)^{1/2}$ is the heat wavelength. Actually, as we see from Fig. 1, $c_j^*(T^*) < a_j^*(T^*)$ for $j > 2$.

The equation for the diameter of the solid spheres that is determined from the first quantum correction for the second virial coefficient

$$c_2^* = (4\pi)^2 T^* B_{1,2}^*(T^*)/S^*(T^*) \tag{19}$$

is equivalent to the dimensionless equation for c_2 (7). Thus the fluid compressibility and all the virial coefficients calculated by the diameter of the solid spheres that is obtained according to the Kim method [15] will be excessive. The diameter c_2' that is determined by (11) yields even more excessive results.

4. The Equation of State

The classical equation of state for high temperatures can be approximated by the equation of state of the solid spheres with diameter a that depends on the temperature, with the inclusion of the attraction forces into the second virial coefficient taken into account [16, 19]:

$$Z_{\mathrm{cl}} = Z_{\mathrm{cl.sol.sph}}(\eta) - 4\eta + B_2^*\rho b_0, \tag{20}$$

$\eta = \pi\rho N_A a^3/6$, where a is given by Eq. (18).

As we already noted, the diameters of the solid spheres $c_j^*(T^*)$, $j > 2$ agree with $a_j^*(T^*)$ for high temperatures, so in our calculations we can assume that $c_j^*(T^*) = a^*(T^*)$, $j > 2$. Thus,

$$Z = Z_{\mathrm{cl}} + \Lambda^{*2}\left\{\frac{S^*(T^*)}{(4\pi a^*)^2 T^*}\left[Z_{\mathrm{cl.sol.sph}}(\eta)\,\eta\frac{(5\eta^3-5\eta^2+4)}{1-\eta} - 4\eta\right] + B_{1,2}^*\rho b_0\right\}, \tag{21}$$

where we use the equation of state for $Z_{\mathrm{cl.sol.sph}}(\eta)$ that was obtained in [16].

The equation of state (21) is used to calculate the compressibility coefficient for helium in a broad range of temperatures and pressures. It is known that the Lennard-Jones potential (12-16) is inadequate for helium (see [22]). Thus the temperature dependence of the force constants is assumed in the study. This dependence is found from the agreement of the data on the second virial coefficient with the viscosity of the helium [22]; within the margins of error for determining the force constants the dependence is described by the equations

$$\begin{aligned} \sigma &= 2.5912 - 4.1511\cdot 10^{-5}\cdot T, \\ \varepsilon/k &= 10.500 - 2.5863\cdot 10^{-3}\cdot T. \end{aligned} \tag{22}$$

The calculated and the experimental values [23-29] of the compressibility coefficient for helium are compared in Fig. 2a, b. The calculated values are somewhat excessive for temperatures less than 100°C, a fact explained by the approximation of the third virial coefficient by the virial coefficient for the system of solid spheres (see Fig. 1b) and also by the neglect of the second quantum correction for the equation of state. The data in [29] (Fig. 2b) for measurably high pressures are excessive in comparison with both the calculated and experimental data of [27] that are confirmed by experiments recently conducted [30].

The values for the compressibility coefficient of helium calculated according to Eq. (21) agree well with the data extrapolated from the semiempirical equation in [31]; for high pressures the discrepancies do not exceed the errors of extrapolation. However, Eq. (21) yields the thermodynamic functions of helium more exactly, since it does not contain the empirically determined diameters of the solid spheres [31].

Equation (21) is inexact for pressures that considerably exceed those studied (hundreds of kilobars and megabars). This is related to the incorrect determination (for ultrahigh pressures) of $\alpha^*(T^*)$ by Eq. (18) [32].

NOTATION

Z, compressibility coefficient; T, absolute temperature, °C; P, pressure, bars; ρ, molar density, mole/m^3; R_0, universal gas constant; B_j^*, $B_{1,j}^*$, reduced j-th virial coefficient and its first quantum correction; N_A, Avogadro's number; k, Boltzmann constant; h, Planck constant; m, molecular weight, kg; σ, ε/k, parameters of intermolecular potential, 10^{-10} m and °K b_j^*, reduced j-th virial coefficient for the potential of solid spheres.

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