THERMOPHYSICAL PROPERTIES OF MATERIALS

Studying the Temperature Dependences of Thermodynamic Properties of Cesium Vapors Using the Three-Parameter Model Pair Interaction Potential

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Abstract—An analytical dependence between the critical temperature of the model system and the minimum of the interaction potential is obtained. It is shown that the law of corresponding states is fulfilled in the system with a three-parameter pair interaction potential, and the obtained thermodynamic properties of the system do not depend directly on the parameters of the potential, being the functions of a dimensionless combination of these parameters. Several thermodynamic properties of cesium vapor are calculated on the line of saturation and in a single-phase region. The results of the calculation are compared with the experimental data.

INTRODUCTION

Since the problem of establishing the relationship between the macroscopic properties of matter and its microscopic parameters is far from being resolved, it has not lost its relevance, having both applied and theoretical importance. In our paper [1], using the Gibbs method, several equilibrium thermodynamic properties were considered for the systems with the simplest pair interaction potentials, including repulsive ones. This work presents a further development of the studies of single-component systems with the aim of finding realistic potentials within the statistical approach [2]. In studying the thermodynamics of the system, it is desirable to obtain a theoretically sound equation of state in a closed form suitable for further applications. Obtaining such an equation within the approach under consideration has definite important restrictions when choosing the model interaction potential: this potential must be thermodynamically stable (non-catastrophic in terms of Ruelle [3]). In addition, the form of the potential must be similar to that for other realistic potentials, while its Fourier image must be simple enough to perform a straightforward analytical integration without any approximations. Since the procedure of the integration is exact, its impact should be excluded from the reasons which might cause deviations in the results of the calculation from the experimental data.

THE POTENTIAL OF INTERACTION AND EQUATION OF STATE

Among all model potentials satisfying the aforementioned restrictions, the most attractive one seems to have the form

$$v(r) = \frac{\exp(-ar)}{4\pi}\left(\frac{A}{r} - \frac{B}{2a}\right), \tag{1}$$

At a certain choice of parameters a, A, B this potential has a potential well and it is characterized by repulsion at small separations and attraction at large separations. On the whole, potential (1) has a short-range character and its repulsion is not very strong. The Fourier image of this potential is given by

$$\tilde{v}(k) = \frac{A}{k^2 + a^2} - \frac{B}{\left(k^2 + a^2\right)^2}, \quad \tilde{v}(0) = \frac{A}{a^2} - \frac{B}{a^4} = wd, \tag{2}$$

where $A > 0$, $B \geq 0$, $a > 0$, $w = A/a^2$, $d = 1 - \varepsilon$, $\varepsilon = B/Aa^2$.

Function (1) satisfies these restrictions under the condition

$$0 \leq \varepsilon < 1. \tag{3}$$

Since the Fourier image is positive provided (3), this guarantees that the thermodynamic limit exists [4].

Apart from the above-mentioned features, an important property of the potential (1) is that it has the analytical dependences of basic characteristics on the constituting parameters. So, the corresponding points of the zero, minimum, and the depth of the potential well are given by

$$R_0 = 2/a\varepsilon, \quad R_m = \left(1 + \sqrt{1 + 2\varepsilon}\right)\!/a\varepsilon, \tag{4}$$

$$v_m = v\left(R_m\right) = -\frac{Aa}{8\pi}\left(1 + \varepsilon - \sqrt{1 + 2\varepsilon}\right)$$
$$\times \exp\left(-\frac{1 + \sqrt{1 + 2\varepsilon}}{\varepsilon}\right). \tag{5}$$

In [1, 2] the theoretical prerequisites which lie at the foundation of our next calculations are given. As

was shown in these works, the configuration integral of the system of N particles occupying the volume V and interacting through the central pair potential $v(|r|)$ (with the Fourier image $\tilde{v}(k)$) is transformed to the Laplace integral. The obtained integral was then calculated using the saddle-point method and Gaussian approximation. The resulting Helmholtz free energy is given by

$$F = F_{\mathrm{id}} + \frac{n^2 V}{2}\tilde{v}(0)$$
$$+ \frac{V}{2\beta}\int_{\Omega}\frac{d^3k}{(2\pi)^3}\left[\ln\left(1 + n\beta\,\tilde{v}(k)\right) - n\beta\,\tilde{v}(k)\right], \tag{6}$$

where $\beta = 1/k_{\mathrm{B}}T$ is the inverse temperature, k_{B} is the Boltzmann constant, Ω is the definition range of the function $\tilde{v}(k)$, $F_{\mathrm{id}} = k_{\mathrm{B}}TN\ln\left(n\lambda^3\right)$ is the free energy of an ideal gas, $\lambda = h/\sqrt{2\pi m_0 k_{\mathrm{B}}T}$ is the de Broglie thermal wavelength, h is the Planck constant, and m_0 is the particle mass. As we can see from (6), among other forcing conditions applied to the form of the potential used, the condition of the Fourier decomposability is of great significance, since it restricts the class of the model potentials that can be studied within approximation (6). Since in this paper we use the basics of classical statistical mechanics, this also leads to restrictions on the range of applicability of the free energy approximation. Therefore, the calculations that are performed within the approach [1] in the range of very high temperatures, where the particle ionization occurs, cannot provide adequate results. In addition, one can expect that the proposed approach will be inconsistent in the range of high pressures, where the impact of many-particle forces on the properties of matter is significant. As a general rule, we can note an increasing agreement between the theory and experiment with increasing temperature and decreasing agreement otherwise. This rule is clearly illustrated by the calculations of the isobar specific heat using the model potentials [1].

It should be noted that at large k the asymptotics of the integrand function in (6) is $\ln\left(1 + n\beta\,\tilde{v}(k)\right) - n\beta\,\tilde{v}(k) \approx -(1/2)\times\times(n\beta\,\tilde{v}(k))^2$, and the corresponding integral converges if $\tilde{v}(k) \propto 1/k^{3/2}$, i.e., the degree exponent of k must be no less than 3/2. The Fourier image (2) naturally satisfies this condition.

Using (2), integration in (6) is performed in a spherical coordinate system. The resulting expression for the free energy takes the form

$$F = F_{id} + \frac{n^2 V}{2}wd + \frac{nV}{8\pi}Aa\left(1 + \frac{\varepsilon}{2}\right)$$
$$+ \frac{Va^2}{12\pi\beta}\left[2 - \left(Q(x)^3 - 3q(x)Q(x)\right)\right], \tag{7}$$

where $Q(x) = \sqrt{2 + x + 2q(x)}$, $q(x) = \sqrt{1 + xd}$, $x = n\beta w$. Then the corresponding equation of state is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{n}{\beta} + \frac{n^2 w}{2}d - \frac{a^3}{12\pi\beta}J(x), \tag{8}$$

where $J(x) = 2 - \left(Q^3(x) - 3q(x)Q(x)\right) - 3x\big(q(x)Q_1(x) + Q(x)q_1(x) - Q^2(x)Q_1(x)\big)$, and the functions $q_1(x) = d/2q(x)$, $Q_1(x) = \left(1 + 2q_1(x)\right)/2Q(x)$ are related with the derivatives of $q(x)$, $Q(x)$ with respect to n.

One of the ways of finding parameters in Eq. (1) that are used in further calculations of the properties of the substance is based on determination of the critical state

$$\begin{cases} \left(\partial P/\partial n\right)_c = 0, \\ \left(\partial^2 P/\partial n^2\right)_c = 0. \end{cases} \tag{9}$$

Hereafter the subscript 'c' marks the values corresponding to the critical point. In the case of Eq. (8), system (9) can be represented in the form

$$\begin{cases} \left(\dfrac{\partial P}{\partial n}\right)_c = k_{\mathrm{B}}T_c\left(q^2(x_c) + \dfrac{a^3 x_c^2}{4\pi n_c}J_1(x_c)\right) = 0, \\ \left(\dfrac{\partial^2 P}{\partial n^2}\right)_c = w\left(d + \dfrac{a^3 x_c}{4\pi n_c}J_1(x_c) + \dfrac{a^3 x_c^2}{4\pi n_c}J_2(x_c)\right) = 0, \end{cases} \tag{10}$$

where n_c, T_c are the experimental values of the critical density of particles and temperature,

$$J_1(x) = q(x)Q_2(x) + 2q_1(x)Q_1(x)$$
$$+ Q(x)q_2(x) - \left(2Q(x)Q_1^2(x) + Q^2(x)Q_2(x)\right);$$
$$J_2(x) = q(x)Q_3(x) + 3q_1(x)Q_2(x)$$
$$+ 3q_2(x)Q_1(x) + Q(x)q_3(x)$$
$$- \left(2Q_1^3(x) + 6Q(x)Q_1(x)Q_2(x) + Q^2(x)Q_3(x)\right);$$

The functions

$$q_2(x) = -\frac{d^2}{4q^3(x)}, \quad Q_2(x) = \frac{q_2(x) - Q_1^2(x)}{Q(x)}, \quad q_3(x) = \frac{3d^3}{8q^5(x)},$$
$$Q_3(x) = \frac{q_3(x) - 3Q_1(x)Q_2(x)}{Q(x)}$$

are correspondingly determined by the second and third derivatives of $q(x)$, $Q(x)$ with respect to n.

The system of equations (9) is nonlinear and has an exact analytical solution in the case of several potentials of the simplest form [1]. However, in the case of potential (1), obtaining an exact solution is impossible, while the numerical solution of (10) is considerably simpler when it reduces to a single equation with respect to the dimensionless variable $x_c = n_c\beta_c w$.

Dividing the first equation in (10) by the second one, we obtain

$$J_1(x_c, \varepsilon) + x_c q^2(x_c, \varepsilon)J_2(x_c, \varepsilon) = 0. \tag{11}$$

The functions $q(x_c, \varepsilon)$, $J_1(x_c, \varepsilon)$, $J_2(x_c, \varepsilon)$ in (11) are precisely identical to the functions in (11). The presence of the argument ε implies the dependence of the

solution x_c on ε. It should be noted that at $\varepsilon = 0 (B = 0)$ potential (1) reduces to the Yukawa potential, whereas Eq. (11) reduces in this limit case to the linear equation with the solution $x_c = 2$ [1].

The appearance of the phase transition in the system with repulsive interaction in approximation (6) is associated with the fact that Eq. (6) represents the result of summation from the contributions of all ring diagrams in the group expansion which describe the particle interaction with two neighboring particles [5].

Equation (11) was solved numerically. However, taking into account the asymptotics of x_c at $\varepsilon \to 0$ and $\varepsilon \to 1$, one can construct approximate expressions for x_c with various accuracy. For example, the uncertainty of the formula

$$x_c = (10 - 3c^3 - 2\varepsilon^4)/5(1 - \varepsilon), \qquad (12)$$

with respect to the exact numerical results does not exceed 1.8 % in the range [0, 1]. As can be shown analytically, at $\varepsilon = 1 (\tilde{v}(0) = 0)$, Eq. (11) has no solutions and the phase transition does not occur.

The calculation of parameters in Eq. (1) is performed according to the following scheme:

the root x_c of Eq. (11) is found for the value $\varepsilon \in (0;1)$, which sets in according to the experimental data;

using $x_c = n_c\beta_c w$, the value $w = x_c/n_c\beta_c = A/a^2$; is determined;

using the value of the screening parameter a, which is expressed through the first (or second) equation of (10), the values $A = a^2 w$ and $B = \varepsilon A a^2$ are consecutively calculated.

One can find the analytical relationships between the parameters R_0, R_m, v_m of potential (1) and the macroscopic characteristics of the system at the critical point. In doing this we need the value that is expressed from the first equation of (10):

$$a = \Psi(x_c) \sqrt[3]{n_c}, \qquad (13)$$

where $\Psi(x_c) = -\left(\dfrac{4\pi q^2(x_c)}{x_c^2 J_1(x_c)} \right)^{1/3} > 0$, since $J_1(x_c) < 0.$.

Substituting (13) in Eq. (4) for R_0 and R_m, we obtain

$$R_0 = \frac{2}{\varepsilon\Psi(x_c)} \frac{1}{\sqrt[3]{n_c}}, \quad R_m = \frac{1 + \sqrt{1+2\varepsilon}}{\varepsilon\Psi(x_c)} \frac{1}{\sqrt[3]{n_c}}.$$

Using (13) we find the product $Aa = \Psi^3(x_c) x_c k_B T_c$, substitute it in (5), and note that the depth of the potential well at a given ε is proportional to the critical temperature T_c

$$v_m = -\frac{\Psi^3(x_c) x_c}{8\pi} \left(1 + \varepsilon - \sqrt{1+2\varepsilon}\right)$$
$$\times \exp\left(-\frac{1 + \sqrt{1+2\varepsilon}}{\varepsilon}\right) k_B T_c = \kappa(\varepsilon) k_B T_c, \qquad (14)$$
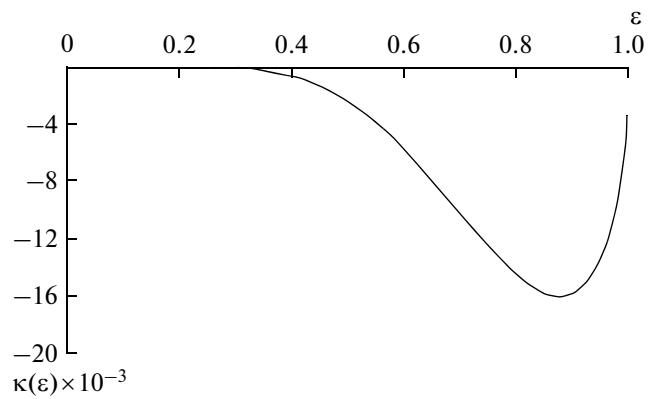
Fig. 1. Function $\kappa(\varepsilon)$.

Following Ulenbeck [6], "for all substances the value of this minimum is equal to $k_B T_c$ by the order of magnitude (more exactly it is close to $1.5 k_B T_c$)" Figure 1 compares the numerically calculated dependence $\kappa(\varepsilon)$, with the corresponding function obtained with the help of the approximate analytical expression (12) for $x_c(\varepsilon)$. As we see, both curves are indistinguishable on the scale used.

In the considered model, the absolute value of the numerical coefficient at $k_B T_c$ does not exceed the value $|\kappa_{min}| = 1.617 \times 10^{-2}$, which is reached at $\varepsilon \approx 0.88$.

The obtained parameters of the interaction potential allows one to rewrite the equation of state in the reduced variables $\Pi = P/P_c$, $\tau = T/T_c$, $\omega = n/n_c$

$$\Pi(\omega,\tau) = \frac{1}{Z_c}\left[\omega\tau + \frac{x_c d\omega^2}{2} - \frac{a^3\tau}{12\pi n_c} J(\omega,\tau) \right]. \qquad (15)$$

where $Z_c = P_c V_c / RT_c$, $J(\omega,\tau)$ is obtained from $J(x)$ when substituting $x = x_c \omega/\tau$.

Substituting in (15) the ratio a^3/n_c, being expressed from (13) yields

$$\Pi(\omega,\tau) = \frac{1}{Z_c}\left[\omega\tau + \frac{x_c d\omega^2}{2} - \tau\frac{\Psi^3(x_c)}{12\pi} J(\omega,\tau) \right]. \qquad (16)$$

The isotherms that are plotted at $\tau < 1$ using Eq. (16) have an S-shaped form that indicates the first kind of phase transition. Since Eq. (16) contains the root x_c of Eq. (11) depending on $\varepsilon = B/Aa^2$, the equation of state has a dimensionless combination of parameters in Eq. (1). It must be noted that the set of parameters A, a, B that determine the given value ε is not unique. In other words, the set of potentials with different sets A, a, B corresponds to the chosen value of ε. This fact can be interpreted as the manifestation of the law of corresponding states in the system with potential (1) at the single point ε, since the states in the model systems
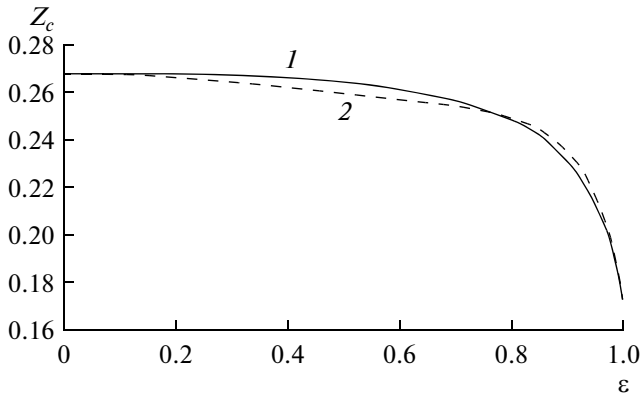
Fig. 2. Dependence of the critical compressibility $Z_c(\varepsilon)$: *1*, numerical calculation, Eq. (11); *2*, approximation (12).
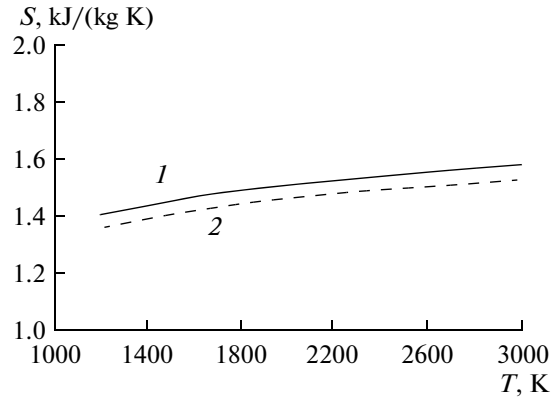

Fig. 3. Dependence $S(T)$ at the pressure $P = 6 \times 10^5$ Pa: *1*, experiment [9]; *2*, calculation, Eq. (18).

with the same value of ε will be described by the same equation of state.

As follows from Eq. (16), the compressibility factor Z_c is a function of only the single parameter ε ($x_c = x_c(\varepsilon)$) at the critical point and it is determined by the formula

$$Z_c = \frac{P_c V_c}{RT_c} = 1 + \frac{x_c d}{2} - \frac{\Psi^3(x_c)}{12\pi} J(1), \qquad (17)$$

where $J(1)$ is the value of the function $J(\omega, \tau)$ at $\omega = \tau = 1$.

Figure 2 shows the dependence of Z_c on ε at the critical point.

As follows from the analysis of the dependence $\kappa(\varepsilon)$,, which is shown in Fig. 1, two different values ε_1, ε_2 correspond to each value $\kappa(\varepsilon) \in (0, \kappa_{\min})$. Therefore, two potentials of type (1) exist at the fixed temperature T_c, and their minima coincide, as follows from (14). If, in addition, the critical densities n_{1c} and n_{2c} will be equal, the corresponding critical pressures will be different. This follows from the simple dependence $Z_c(\varepsilon)$, since $Z_c(\varepsilon_1) \neq Z_c(\varepsilon_2)$ and $P_{1c}/k_B T_c n_c \neq P_{2c}/k_B T_c n_c$. At the same time, the points of the zero and minima of the potentials will be different. In addition, given that $T_{1c} = T_{2c}$, $n_{1c} \neq n_{2c}$, the equality $P_{1c} = P_{2c}$ is not excluded.

THERMODYNAMIC PROPERTIES OF CESIUM VAPORS

According to the data of [7], the compressibility factor Z_c for alkaline metals changes at the critical point from $Z_c(\text{Li}) = 0.105$ to $Z_c(\text{Cs}) = 0.213$. Following [8], parameter Z_c lies in the limits $Z_c(\text{Li}) = 0.17 \pm 0.12$ for Li, and in the limits 0.25 ± 0.02 for Cs. As we can see from Fig. 2, the experimental values of Z_c prove to be in the interval of the calcu-

lated values (using Eq. (17)) from $Z_c^{\min} = 1/6 \approx 0.167$ at $\varepsilon \to 1$ to $Z_c^{\max} = 2 - \sqrt{3} \approx 0.268$ at $\varepsilon = 0$. Therefore, our attempt to calculate several thermodynamic characteristics of alkaline metals within the proposed statistical method seems to be helpful. For definiteness, we will consider Cs with the critical parameters $T_c = 2050$ K, $P_c = 11.7$ MPa, $\rho_c = 430\, \rho_c$ kg/m^3 ($n_c = 1.948 \times 10^{27}$ m^{-3}), and $Z_c = 0.212$ from the reference book [9], which contains quite extensive experimental information. The numerical solution to Eq. (17) at $Z_c(\text{Cs}) = 0.212$ yields $\varepsilon \approx 0.956$ ($x_c \approx 26.027$). According to the aforementioned algorithm, the corresponding values of the parameters which enter Eq. (1) are $a = 1.179 \times 10^9$ m^{-1}, $A = 5.258 \times 10^{-28}$ J m, $B = 6.991 \times 10^{-10}$ J/m.

Making use of Eqs. (7), (8), and the known thermodynamic relations, it is easy to find the expressions for the entropy, heat capacity, the velocity of sound, and other experimentally observed parameters. The problem of finding the temperature dependences of these values can be solved when determining the density of the substance. In the state corresponding to the one-phase region, $\Pi = P/P_c$, and $\tau = T/T_c$, the density ω is obtained from the numerical solution to the equation $\Pi(\omega, \tau) - \Pi = 0$.

The specific entropy, heat capacity, and the velocity of sound are computed and compared with experimental data for the cesium vapor (at a constant pressure) in [9]. The specific value X is related to the molar value X_M by the relationship $X = X_M/M$. The molar mass of Cs is $M = 0.1329$ kg/mol. Bearing in mind that $S_M = -(\partial F/\partial T)_V$, the molar entropy is then given by

$$S_M = S_{\text{id}} - \frac{R}{12\pi\omega} \Psi^3(x_c) J(\omega, \tau), \qquad (18)$$

where $S_{\text{id}} = R\left[\frac{5}{2} - \ln\left(\frac{\omega}{\tau^{3/2}} n_c \lambda_c\right)\right]$, $\lambda_c = h/\sqrt{2\pi m_0 k_B T_c}$, R is the universal gas constant. Figure 3 shows the tem-
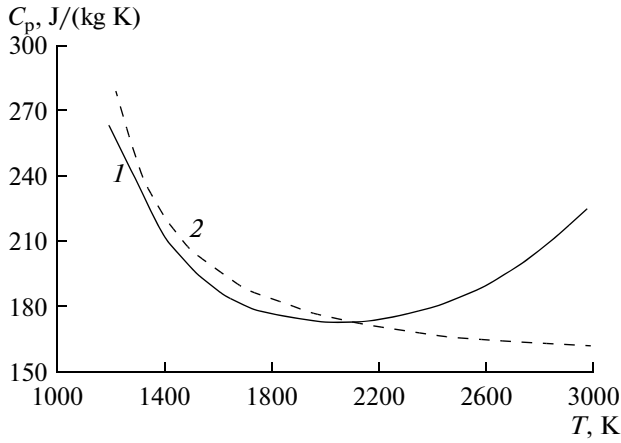
C_{p}, J/(kg K)

Fig. 4. Dependence $C_{\mathrm{p}}(T)$ at the pressure $P = 6 \times 10^5$ Pa: *1*, experiment [9]; *2*, calculation, Eq. (19).
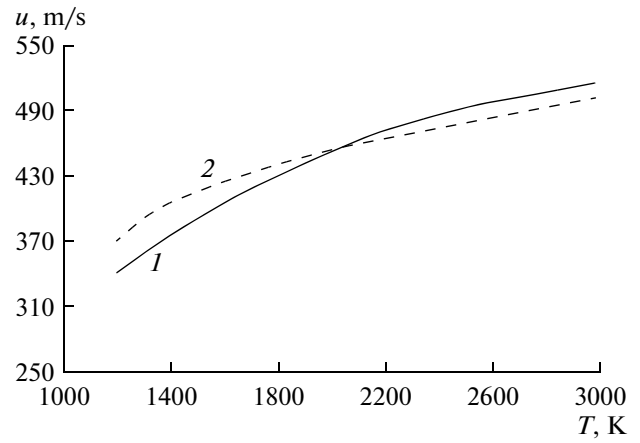
u, m/s

Fig. 5. Dependence $u(T)$ at the pressure $P = 6 \times 10^5$ Pa: *1*, experiment [9], *2*, calculation, Eq. (20).

perature dependence of specific entropy at a constant pressure $P = 6 \times 10^5$ Pa.

The molar isobar heat capacity is given by

$$C_P^M = C_V^M - T\frac{(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T},\qquad(19)$$

where

$$C_V^M = T\left(\frac{\partial S}{\partial T}\right)_V = C_V^{\mathrm{id}} - \frac{\Psi^3(x_c) R}{4\pi\omega}\left(\frac{x_c\omega}{\tau}\right)^2 J_1(\omega,\tau),$$

$$C_V^{\mathrm{id}} = \frac{3}{2}R,$$

$$\left(\frac{\partial P}{\partial T}\right)_V = k_{\mathrm{B}} n_c \omega$$

$$\times \left(1 - \frac{\Psi^3(x_c)}{12\pi\omega}\left[J(\omega,\tau) + 3\left(\frac{x_c\omega}{\tau}\right)^2 J_1(\omega,\tau)\right]\right),$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{\tau(n_c\omega)^2}{\beta_c N_{\mathrm{A}}}$$

$$\times \left(q^2(\omega,\tau) + \frac{\Psi^3(x_c)}{4\pi\omega}\left(\frac{x_c\omega}{\tau}\right)^2 J_1(\omega,\tau)\right),$$

N_{A} is the Avogadro constant, and $J_1(\omega,\tau)$ corresponds to $J_1(x)$, being expressed in reduced variables.

Figure 4 shows the calculated values of the specific isobar heat capacity obtained using Eq. (19) at $P = 6 \times 10^5$ Pa.

Comparing the dependences $S^{\mathrm{exp}}(T)$ and $S^{\mathrm{theor}}(T)$ in Fig. 3 shows that the absolute uncertainty for all the calculated points is nearly equal: $\Delta S = S^{\mathrm{exp}}(T) - S^{\mathrm{theor}}(T) \approx 48$ J/(kg K); i.e., each curve can be obtained from another one when shifting along the vertical axis by the value ΔS. We therefore could expect that the dependences $C_p^{\mathrm{exp}}(T)$ and $C_p^{\mathrm{theor}}(T)$ will also be analogous, since the heat capac-

ity is determined by the derivative $(\partial S/\partial T)_P$. However, as we can see from Fig. 4, the behavior of the corresponding dependences at $T > 2000$ K is qualitatively different. It should be noted that the calculated dependences of the isochoric capacity obtained by different authors [10] show both the dependences $C_V(T)$ which have a minimum on the temperature axis and those that monotonically decrease with increasing temperature.

Provided that the derivatives $(\partial P/\partial T)_V$, $(\partial P/\partial n)_T$ and C_V are given, one can obtain the velocity of the sound that is given by the formula [11]

$$u = v\sqrt{\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V^2 - \left(\frac{\partial P}{\partial V}\right)_T},\qquad(20)$$

where $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{n}{v}\left(\frac{\partial P}{\partial n}\right)_T$ is the derivative with respect to the specific volume $v = 1/\rho$, ρ being the density of the substance. Figure 5 shows the temperature dependence of the sound velocity.

It is worth noting that Eqs. (18)−(20) do not directly include parameters of the interaction potential. The entropy, heat capacity, and velocity of sound depend only on the dimensionless combination $\varepsilon = B/Aa^2$ of these parameters, which is a characteristic feature of the model three-parameter interaction potential (1). Other thermodynamic functions, such as, in particular, the internal energy and enthalpy, also have this feature within the range of validity of the statistical approach [1, 2, 12].

Calculations of the thermodynamic properties of cesium vapor on the line of saturation were carried out according to formulas (18)−(20). In this case, however, both the vapor and the liquid densities ω_1, ω_2 are determined from the conditions of equality of the pressures and chemical potentials

$$\begin{cases}\Pi(\omega_1,\tau) = \Pi(\omega_2,\tau);\\ \mu(\omega_1,\tau) = \mu(\omega_2,\tau),\end{cases}\qquad(21)$$

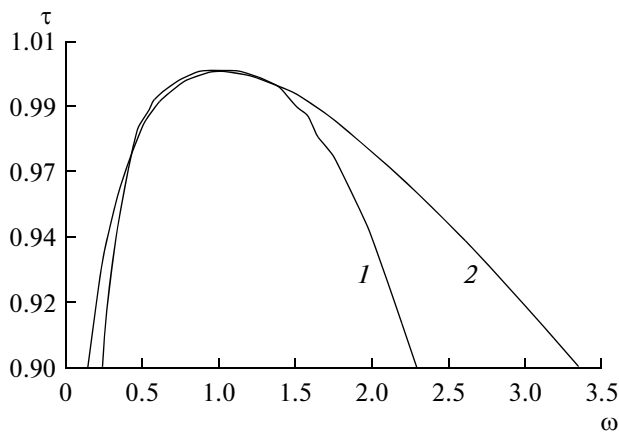**Fig. 6.** Saturation line: *1*, experiment [13]; *2*, solution of the system (21).
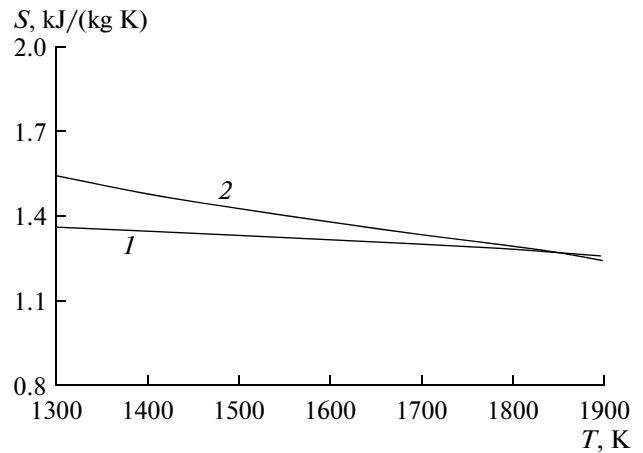

Fig. 7. Temperature dependence of entropy *S* on the line of saturation; *1*, experiment [14]; *2*, calculation, Eq. (18).
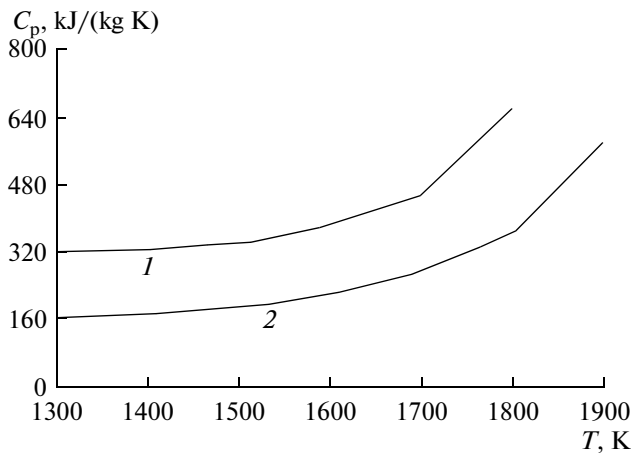

Fig. 8. Temperature dependence of the velocity of sound C_p on the line of saturation: *1*, experiment [14]; *2*, calculation, Eq. (19).
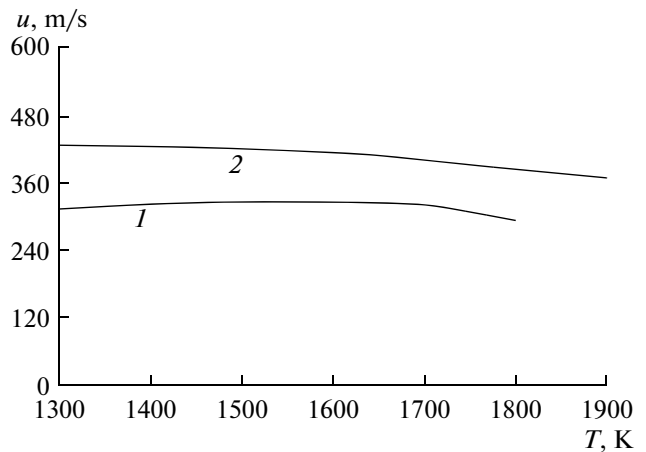

Fig. 9. Dependence of the sound velocity on temperature on the line of saturation; *1*, experiment [14], *2*, calculation, Eq. (20).

where

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$= \frac{\beta_c}{\tau}\left(\ln\left(n_c \omega \lambda^3\right) + \frac{x_c \omega d}{\tau} + \frac{x_c \Psi^3(x_c)}{8\pi\tau} \right.$$

$$\left. \times \left(1 + \frac{\varepsilon}{2} + \frac{Q(\omega,\tau)^2 - q(\omega,\tau) - d}{Q(\omega,\tau)} \right) \right)$$

is the chemical potential of the system and $q(\omega,\tau)$, and $Q(\omega,\tau)$ coincide with the functions $q(x), Q(x)$ in the reduced variables. System (21) does not explicitly contain any of the critical parameters or the parameters of the interaction potential, since the corresponding equations depend only on the dimensionless combina-

tion of parameters of the potential in the form $\varepsilon = B/Aa^2$. Hence, it follows that the solution ω_1, ω_2 provided that $\varepsilon = \text{const}$ depends only on τ, as is conditioned by the law of corresponding states. The numerical solution of (21) and experimental data [13] are compared in Fig. 6.

In Figs. 7–10 the dependences of entropy, isobar heat capacity, sound velocity, and compressibility factor $Z = PV/RT$ on temperature are shown. The experimental data were taken from [14]. Since the measurement data [14] are given with a temperature step of 100 K, while the values for C_p and for the sound velocity u at $T = 1900$ K are not presented, the experimental curves in Figs. 8 and 9 are somewhat shorter than the calculated ones.
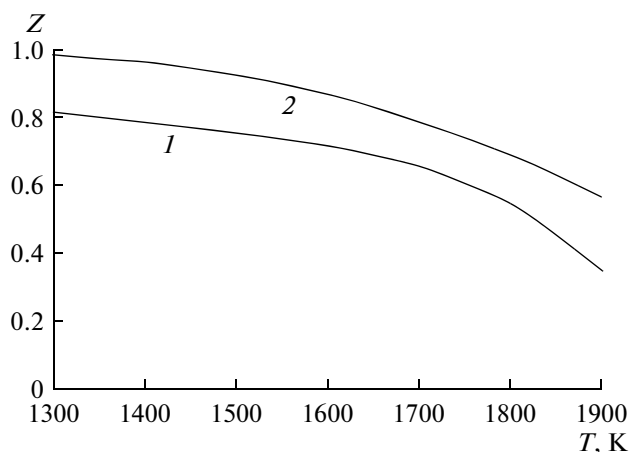
Fig. 10. Dependence of the compressibility factor Z on temperature on the line of saturation: *1*, experiment [14]; *2*, calculation according to the formula $Z = PV/RT$.

CONCLUSIONS

Using the Gaussian approximation for the free energy, it is established that in the system with the model three-parameter interaction potential the law of corresponding states is fulfilled provided that the parameters of the potential are combined into a single dimensionless parameter ε which takes a constant value.

Consideration of the thermodynamic properties of cesium vapor within the united approach provides a relatively simple analytical description of various thermodynamic parameters. The numerical calculations of these parameters, which are performed using the obtained formulas, show both qualitative and quantitative (in some cases) agreement with the experimental data. To increase the accuracy of the calculations, the use of oscillating potentials seems to be more effective.

As far as concerns the behavior of $C_P(T)$ at $T > 2000$ K, a possible reason for the qualitative discrepancy between the calculated and experimental data is likely related to the appearance of additional degrees of freedom owing to the dissociation of clusters with an increase in temperature. Another possible reason may be related to the contribution of an electron subsystem in $C_P(T)$. One may expect that adequate results for the heat capacity can be obtained if the calculations will be performed using a configuration integral for multicomponent systems. In conclusion, we want to underline that, when calculating the thermodynamic properties, information about the parameters of the interaction potentials is not necessary. The problem is solved when finding the value of ε corresponding to the compressibility factor Z_c, which is determined using the coordinates of one experimental point, the critical point of cesium.

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