

# Thermodynamic Properties of One-Component Systems with Pair Two-Parameter Interaction Potentials

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**Abstract**—One-component systems with the simplest pair model interparticle interaction potentials are considered. The equations of state are obtained, and the relationship between the critical parameters of each system and the parameters of the interaction potentials is established. The lines of the phase equilibrium are constructed, and the values of isobaric heat capacity are found in a wide temperature and pressure interval (with maxima in the supercritical region). The obtained results are compared with the experimental data.

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## INTRODUCTION

The establishment of the relationship between the macroscopic properties of the material and its microscopic parameters is one of the primary problems of statistical mechanics. The consequent solution of this problem can be performed within the Gibbs approach. The prospects of the elaboration of the microscopic theory of the equilibrium thermodynamic properties of materials in a wide temperature interval including the critical point (CP) can be related to [1]. In this work, the configuration integral (CI) of a classical one-component system with the pair interparticle potentials  $v(r)$ , allowing the Fourier decomposition is presented as a product of the same terms and is calculated by means of the Weil theorem. The idea of the factorization of the integrand was developed in [2], in which the CI for the considered systems was calculated by the saddle-point method.

In the pair-additive approximation, the CI of a system of  $N$  particles in a volume  $V$  is

$$Z = \int_V \dots \prod_{l=1}^N \frac{d^3 \mathbf{R}_l}{V^N} \exp \left( -\frac{\beta}{2} \sum_{\substack{l \neq l' \\ l, l'=1}} v(|\mathbf{R}_l - \mathbf{R}_{l'}|) \right) \quad (1)$$

and it allows the determination of the contribution of the interparticle interactions to the free Helmholtz energy  $F = -k_B T \ln Z + F_{id}$ . Here  $\beta = 1/k_B T$ ,  $T$  – is the temperature,  $k_B$  is the Boltzmann constant,  $R_l$  are atomic coordinates,  $F_{id} = Nk_B T \ln(n\lambda^3)$  is the free energy of the ideal gas,  $\lambda = h/\sqrt{2\pi m k_B T}$  is the thermal de Broglie wavelength,  $h$  is the Planck constant,  $m$  is the particle mass, and  $n = N/V$ .

It is supposed that pair potential can be expanded in a Fourier series

$$v(r) = \frac{1}{V} \sum_{\mathbf{k} \in \Omega} \tilde{v}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{r}), \quad (2)$$

$$\tilde{v}(\mathbf{k}) = \int_V v(\mathbf{r}) \exp(-i\mathbf{k}\mathbf{r}) d^3 \mathbf{r},$$

where  $\Omega$  (a set of wave vectors  $\mathbf{k}$ ) is a definitional domain of the Fourier image  $\tilde{v}(\mathbf{k})$ . The  $\tilde{v}(\mathbf{k})$  function is real and depends on the module of the modulus of the vector  $\mathbf{k}$ , since the potential is central  $v(r)$ . Let us consider that  $v(\mathbf{k}) > 0$ . In this case, the potential is stable and the system has a thermodynamic limit [3].

Let us express now the total potential energy of the system in terms of  $\tilde{v}(\mathbf{k})$ :

$$W = \frac{1}{2} \sum_{\substack{l, l'=1 \\ l \neq l'}} v(|\mathbf{R}_l - \mathbf{R}_{l'}|) \quad (3)$$

$$= \frac{N}{2} (n\tilde{v}(0) - v(0)) + \frac{1}{2V} \sum_{\mathbf{k} \in \Omega} \tilde{v}(\mathbf{k}) (C^2(\mathbf{k}) + S^2(\mathbf{k})).$$

Here

$$C(\mathbf{k}) = \sum_{l=1}^N \cos(\mathbf{k}\mathbf{R}_l),$$

$$S(\mathbf{k}) = \sum_{l=1}^N \sin(\mathbf{k}\mathbf{R}_l).$$

The constant  $v(0)$  is introduced to compensate the terms with  $l = l'$ . In the summation over  $\mathbf{k}$  a term with  $\mathbf{k} = 0$  is singled out in the right-hand part of (3) as the term  $Nn\tilde{v}(0)/2$ .

By substituting (3) into (1), we obtain the expression for the CI as

$$Z = C \int_V \dots \int_V \prod_{l=1}^N \frac{d^D \mathbf{R}_l}{V^N} \times \exp \left( -\frac{\beta}{V} \sum_{\mathbf{k} \in \Omega/2} \tilde{v}(k) [C^2(\mathbf{k}) + S^2(\mathbf{k})] \right), \quad (4)$$

where  $C = \exp(N\beta(v(0) - n\tilde{v}(0))/2)$ .

By means of the Stratonovich–Habbard transformation based on the Poisson integral, let us write

$$\exp(-b^2/4a) = \sqrt{\alpha/\pi} \int_{-\infty}^{+\infty} \exp(-ax^2 \pm ibx) dx, \quad (5)$$

$\alpha > 0$ .

By performing the transformation (5) separately for each multiplicand in the right-hand part of (4), we come to the following presentation for the CI:

$$Z = \int_V \dots \int_V \prod_{l=1}^N \frac{d^3 \mathbf{R}_l}{V^N} \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \prod_{\mathbf{k} \in \Omega/2} \frac{dx(\mathbf{k}) dy(\mathbf{k}) N}{4\pi n\beta \tilde{v}(k)} \times \exp \left( -\sum_{\mathbf{k} \in \Omega/2} \frac{V[x^2(\mathbf{k}) + y^2(\mathbf{k})]}{4\beta \tilde{v}(k)} \right) \times \exp \left( -i \sum_{\mathbf{k} \in \Omega/2} [C(\mathbf{k})x(\mathbf{k}) + S(\mathbf{k})y(\mathbf{k})] \right). \quad (6)$$

Only the last exponent in this expression depends on the coordinates of the particles. By changing the integration order in (6), let us select the integral

$$F_N = \int_V \dots \int_V \prod_{l=1}^N \frac{d^3 \mathbf{R}_l}{V^N} \exp \left( -i \sum_{\mathbf{k} \in \Omega/2} [C(\mathbf{k})x(\mathbf{k}) + S(\mathbf{k})y(\mathbf{k})] \right).$$

Taking into account that  $C(\mathbf{k})$  and  $S(\mathbf{k})$  are sums over the coordinates of the particles, there appears the possibility of the factorization  $F_N$ , i.e., the presentations as a product of  $N$  terms  $F_N = F_1^N$ :

$$F_1 = \int_V \frac{d^3 \mathbf{R}}{V} \exp \left( -i \sum_{\mathbf{k} \in \Omega/2} (x(\mathbf{k}) \cos(\mathbf{kR}) + y(\mathbf{k}) \sin(\mathbf{kR})) \right).$$

After the substitution of  $F_1$  and  $F_N$  in (6), we come to the expression

$$Z = C \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \prod_{\mathbf{k} \in \Omega/2} \frac{dx(\mathbf{k}) dy(\mathbf{k}) N}{4\pi n\beta \tilde{v}(k)} \exp \left( -NG(\dots, x(\mathbf{k}), y(\mathbf{k}), \dots) \right), \quad (7)$$

where  $G(\dots, x(\mathbf{k}), y(\mathbf{k}), \dots) = \sum_{\mathbf{k} \in \Omega/2} \frac{x^2(\mathbf{k}) + y^2(\mathbf{k})}{4n\beta \tilde{v}(k)} - \ln F_1$ ;

$x(\mathbf{k}), y(\mathbf{k})$  are the additional variables of the Stratonovich–Habbard transformation. The presence of the large parameter  $N$  allows us to calculate integral (7) by the saddle-point method. The expansion of the function  $G$  in the vicinity of the stationary point  $x(\mathbf{k}) = 0, y(\mathbf{k}) = 0$  with the accuracy of up to quadratic terms is

$$G \cong \frac{1}{4} \sum_{\mathbf{k} \in \Omega/2} \left[ \frac{1}{n\beta \tilde{v}(k)} + 1 \right] (x^2(\mathbf{k}) + y^2(\mathbf{k})). \quad (8)$$

It is seen that, at rather high temperatures, i.e., at  $n\beta \max_{\mathbf{k} \in \Omega} |\tilde{v}(k)| \ll 1$ , it is possible to ignore the unity in the square brackets of (8), and then the case of the ideal gas  $Z = 1$  occurs.

Let us substitute (8) in (7) and obtain Gauss integrals

$$Z = C \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \prod_{\mathbf{k} \in \Omega/2} \frac{dx(\mathbf{k}) dy(\mathbf{k}) N}{4\pi n\beta \tilde{v}(k)} \times \exp \left[ -\frac{N}{4} \sum_{\mathbf{k} \in \Omega/2} \left( \frac{1}{n\beta \tilde{v}(k)} + 1 \right) (x^2(\mathbf{k}) + y^2(\mathbf{k})) \right].$$

By integrating over the variables  $x(\mathbf{k}), y(\mathbf{k})$ , we find

$$Z = C \prod_{\mathbf{k} \in \Omega/2} \frac{1}{1 + n\beta \tilde{v}(k)}.$$

Thence after changing the summation over  $\mathbf{k}$  by integration with formula  $\sum_{\mathbf{k} \in \Omega} \dots = V \int_{\Omega} \frac{d^3 \mathbf{k}}{(2\pi)^3} \dots$  taken into

account and analogously  $\prod_{\mathbf{k} \in \Omega} \dots = \exp \left( V \int_{\Omega} \frac{d^3 \mathbf{k}}{(2\pi)^3} \dots \right)$ , we obtain

$$F = -\frac{1}{\beta} \ln Z = F_{id} - \frac{N}{2} (v(0) - n\tilde{v}(0)) + \frac{V}{2\beta} \int_{\Omega} \frac{d^3 k}{(2\pi)^3} \ln(1 + n\beta \tilde{v}(k)). \quad (9)$$

This formula coincides with the result obtained by D.N. Zubarev [4].

For potentials unlimited in zero, the singularity  $v(0) = \infty$  is compensated by the divergence of the integral over  $k$  in the right-hand part of (9). At  $|\mathbf{k}| \rightarrow \infty$  the Fourier image  $\tilde{v}(k)$  decreases, approaching zero. Then at large  $k$  values  $\ln(1 + n\beta \tilde{v}(k)) \approx n\beta \tilde{v}(k)$ , and since  $\int_{\Omega} \frac{d^3 k}{(2\pi)^3} n\beta \tilde{v}(k) = n\beta v(0) = \infty$ , the integral

$\int_{\Omega} \frac{d^3 k}{(2\pi)^3} \ln(1 + n\beta \tilde{v}(k))$  also diverges. Therefore, the addition of the term  $-n\beta \tilde{v}(k)$  to the integrand in (9)

$$F = F_{id} + \frac{N^2}{2V} \tilde{v}(0) + \frac{V}{2\beta} \int_{\Omega} \frac{d^3 k}{(2\pi)^3} [\ln(1 + n\beta \tilde{v}(k)) - n\beta \tilde{v}(k)] \quad (10)$$

allows us to eliminate the divergence of the integral at large  $k$ . In addition, note that at large  $k$  the function

$\ln(1 + n\beta\tilde{v}(k)) - n\beta\tilde{v}(k) \approx -(1/2)(n\beta\tilde{v}(k))^2$ , Therefore, the convergence of the integral is provided if  $\tilde{v}(k) \propto 1/k^{3/2}$ , i.e., the index  $k$  should be larger than  $3/2$ . This condition is satisfied by all model potentials considered in this work.

The thermodynamic functions were calculated by standard methods of thermodynamics from the Helmholtz free energy. Thus, the equation of state and the chemical potential of the model system are

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = P_{id} + \frac{n^2 w}{2} - \frac{1}{2\beta} \int_{\Omega} \frac{d^3 k}{(2\pi)^3} \left[ \ln(1 + n\beta\tilde{v}(k)) - \frac{n\beta\tilde{v}(k)}{1 + n\beta\tilde{v}(k)} \right], \quad (11)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu_{id} + nw + \frac{1}{2} \int_{\Omega} \frac{d^3 k}{(2\pi)^3} \frac{n\beta\tilde{v}^2(k)}{1 + n\beta\tilde{v}(k)}, \quad (12)$$

where the notation  $w = \tilde{v}(0)$  is introduced.

### MODEL POTENTIALS

The interparticle forces are not directly measured in the experiment, and the real interatomic potentials are unknown. However, one of the approximations, which can be used for any liquids when calculating their thermodynamic characteristics, consists in the assumption that the properties of liquids are mainly determined by the sharply increasing repulsion part of the interaction potential [5]. This assumption is supported, for example, by [6] on the numerical simulation of liquid, in which the obtained results were in agreement with the experimental data for real liquids. Therefore, to simplify the calculations, let us at first take into account only the repulsion forces, and represent the form of the interaction potential  $v(r)$  by the monotonically decreasing positive functions of  $r$  with the corresponding Fourier images

$$v(r) = A \exp(-ar)/4\pi r, \quad \tilde{v}(k) = A/(k^2 + a^2), \quad (13)$$

$$v(r) = A \exp(-ar)/8\pi a, \quad \tilde{v}(k) = A/(k^2 + a^2)^2. \quad (14)$$

In addition, the alternating potential with the potential wells and attraction part is of interest; it at least qualitatively corresponds to the potentials used for the description of the behavior of liquid metals [7]

$$v(r) = \frac{A}{4\pi a^2} \frac{\exp(-ar/\sqrt{2})}{r} \sin\left(\frac{ar}{\sqrt{2}}\right), \quad (15)$$

$$\tilde{v}(k) = A/(k^4 + a^4),$$

where  $a > 0$ ,  $A > 0$  are the parameters of the potential  $v(r)$ . When calculating the integrals (2), which determine the Fourier image of the interaction potential, it is convenient to transform to the spherical coordinate system by directing the  $OZ$  axis along the vector  $\mathbf{k}$ . The use in the calculations of simple two-parameter potentials (13)–(15) and their Fourier images simplifies the

analytical solution of the problem; however, as could be expected, it does not lead to the loss of main properties of the model systems characteristic for real liquids.

### EQUATION OF STATE AND CRITICAL POINT

As a result of calculation of the integral over  $k$  in the right-hand part of (11) with Fourier images (13)–(15), we obtain equations of state corresponding to the order of the introduction of the interatomic potentials:

$$P = \frac{n}{\beta} + \frac{n^2 w}{2} - \frac{a^3}{12\pi\beta} \left[ 1 - q(x) \left( 1 - \frac{x}{2} \right) \right], \quad w = A/a^2; \quad (16)$$

$$P = \frac{n}{\beta} + \frac{n^2 w}{2} - \frac{a^3}{6\pi\beta} \left[ 1 - \frac{1}{\sqrt{2}} Q(x) + \frac{x}{4\sqrt{2}Q(x)} \right], \quad (17)$$

$$w = A/a^4;$$

$$P = \frac{n}{\beta} + \frac{n^2 w}{2} - \frac{a^3}{6\pi\sqrt{2}\beta} \left[ \frac{3 + q^2(x)}{4\sqrt{q(x)}} - 1 \right], \quad w = A/a^4, \quad (18)$$

where  $q(x) = \sqrt{1+x}$ ,  $x = n\beta w$ ,  $Q(x) = \sqrt{1+\sqrt{1+x}} = \sqrt{1+q(x)}$ .

To give the microscopic description of different thermodynamic properties of the material, it is necessary to know the numeric values of the  $a$  and  $A$  parameters of the interaction potentials. These values can be found by any method, which allows one to establish the dependences between the  $a$  and  $A$  parameters and the quantities measured in the experiment. One such method, which requires minimal experimental information, is related to the solution of the system of equations determining the critical state of the material

$$\begin{cases} (\partial P/\partial n)_T = 0, \\ (\partial^2 P/\partial n^2)_T = 0. \end{cases} \quad (19)$$

With the substitution of functions (13)–(15), this system of equations is in each case reduced to the linear or quadratic equation with respect to the dimensionless quantity  $x_c = n_c \beta_c w > 0$ . In the case of the potential (13), system (19) is

$$\begin{cases} \left(\frac{\partial P}{\partial n}\right)_T = k_b T_c \left[ q^2(x_c) - \frac{a^3 n_c (\beta_c w)^2}{16\pi q(x_c)} \right] = 0, \\ \left(\frac{\partial^2 P}{\partial n^2}\right)_T = \beta_c w \left[ 1 - \frac{a^3 \beta_c w (1 + q^2(x_c))}{32\pi q^3(x_c)} \right] = 0. \end{cases} \quad (20)$$

By dividing the second equation of system (20) by the first one, we obtain the equation with respect to  $x_c$

$$2x_c - q^2(x_c) = 1.$$

Thence we find that  $x_c = 2$ . After substituting this value in the second equation of (20) we obtain  $\beta_c = 24\pi\sqrt{3}/a^3 w$ , and since  $x_c = n_c \beta_c w = 2$ , then  $n_c = a^3/12\pi\sqrt{3}$ .

Let us write the solutions of system (19) in the same order, in which the model potentials and corresponding equations of state are presented

$$a = (12\pi\sqrt{3}n_c)^{1/3}, \quad A = a^2 x_c / n_c \beta_c, \quad (21)$$

$$x_c = n_c \beta_c w = 2;$$

$$a = (32\pi\sqrt{2}Kn_c/x_c)^{1/3}, \quad A = a^4 x_c / n_c \beta_c, \quad x_c \approx 1.061, \quad (22)$$

$$K = \frac{(q(x_c)Q(x_c))^3}{x_c} \approx 10.600;$$

$$a = (50\pi\sqrt{2}n_c(9/5)^{9/4})^{1/3}, \quad A = a^4 x_c / n_c \beta_c, \quad (23)$$

$$x_c = n_c \beta_c w = 4/5.$$

It is clear that, to find  $a$  and  $A$ , it is sufficient to use experimental values of the critical density  $n_c$  and temperature  $T_c$ .

To check the validity of the theoretical conclusions and their quantitative agreement with the experimental data, argon is chosen here with the critical parameters  $\rho_c = 531 \text{ kg/m}^3$ ,  $T_c = 150.86 \text{ K}$  [8]. The  $a$  and  $A$  values calculated according to formulas (21)–(23) are given in the table of parameters of the interaction potentials (13)–(15). The values of the critical pressure calculated for the model systems from the experimental  $n_c$  and  $T_c$  values for argon are given in the last column of the table.

The plot of the oscillating potential (15) for the parameters found for argon is given in Fig. 1. The form of the potential curve leaves no doubt that this plot is applicable for the description of the properties of simple liquids.

Using the critical values  $n_c$ ,  $T_c$ , and  $P_c$ , let us present equations of state (16)–(18) in the reduced variables  $\tau = T/T_c$ ,  $\omega = n/n_c$ , and  $\pi = P/P_c$

$$\pi(\omega, \tau) = \frac{1}{Z_c} \left( \tau\omega + \frac{x_c\omega^2}{2} - \tau\sqrt{3} \left[ 1 - \sqrt{1 + \frac{x_c\omega}{\tau} \left( 1 - \frac{x_c\omega}{2\tau} \right)} \right] \right), \quad (24)$$

$$Z_c \approx 0.268;$$

$$\pi(\omega, \tau) = \frac{1}{Z_c} \left( \tau\omega + \frac{x_c\omega^2}{2} - \frac{16\sqrt{2}}{3} \left( \frac{K}{x_c} \right) \times \tau \left[ 1 - \frac{1}{\sqrt{2}} Y(\omega, \tau) + \frac{x_c\omega}{4\sqrt{2}\tau Y(\omega, \tau)} \right] \right), \quad (25)$$

$$Z_c \approx 0.277;$$

$$\pi(\omega, \tau) = \frac{1}{Z_c} \left( \tau\omega + \frac{x_c\omega^2}{2} - 27 \left( \frac{9}{5} \right)^{1/4} \tau \left[ \frac{1 + x_c\omega/4\tau}{(1 + x_c\omega/\tau)^{1/4}} - 1 \right] \right), \quad (26)$$

$$Z_c \approx 0.274;$$

where  $Y(\omega, \tau) = \sqrt{1 + \sqrt{1 + x_c\omega/\tau}}$ . The parameters  $v(r)$ , do not enter equations of state in the reduced form,

Parameters of the interaction potentials

Potential	$a, 1/\text{m}$	$A$	$P_c, \text{MPa}$
(13)	$8.0807 \times 10^9$	$3.3662 \times 10^{-29}, \text{J/m}$	4.5099
(14)	$2.2554 \times 10^{10}$	$7.0798 \times 10^{-8}, \text{J/m}$	4.6570
(15)	$1.8887 \times 10^{10}$	$2.6236 \times 10^{-8}, \text{J/m}$	4.6099

which agrees with the law of the corresponding states for the two-parameter potentials [9]. Isotherms built according to these equations at  $\tau < 1$  have characteristic van der Waals loops indicating the liquid–gas phase transition, and at  $\tau > 1$ , saddle points. Minima corresponding to the Boyle points, which form the curve of the same name, are observed in the isotherms in the coordinates  $\pi - \pi\phi$  in a certain temperature interval  $\tau$ . At the definite temperature  $\tau_B = T_B/T_c$  (Boyle temperature), this curve has a region close to horizontal.

Note that the appearance of condensation in the system with the Yukawa repulsion potential was established in the theory of reduced group decomposition [10] and the Monte Carlo method [11]. In addition, phase transitions in the systems with repulsion were considered in [12–15]; in particular, a model describing condensation was proposed in [12].

### LINES OF THE PHASE EQUILIBRIUM

A traditional approach when building the lines of the equilibrium is the solution of the system of equations

$$\begin{cases} \pi(\omega_1, \tau) = \pi(\omega_2, \tau), \\ \mu(\omega_1, \tau) = \mu(\omega_2, \tau), \end{cases} \quad (27)$$

which expresses the conditions of the equilibrium of the coexisting phases with the densities  $\omega_1$  and  $\omega_2$ . Avoiding writing the systems of type (27) for each case

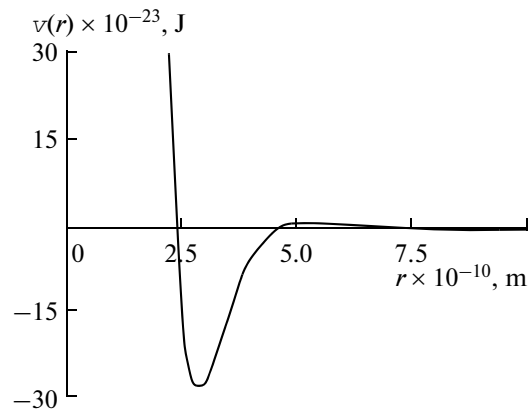
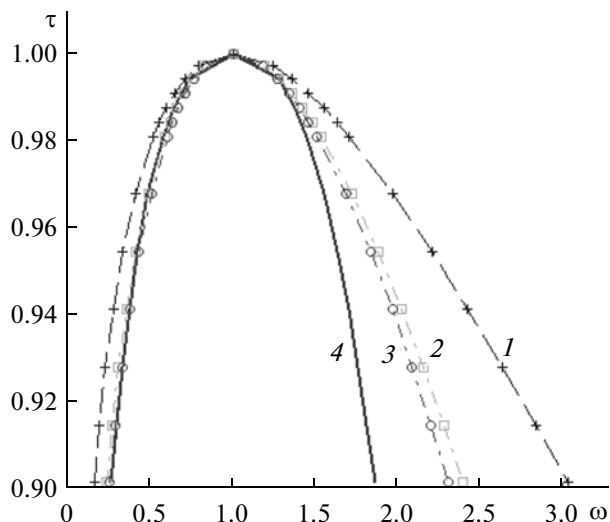


Fig. 1. Oscillating potential (15).



**Fig. 2.** Lines of the phase equilibrium in the reduced coordinates  $\tau = T/T_c$ ,  $\omega = n/n_c$ : 1—for the Yukawa potential (13); 2—for the exponential potential (14); 3—for the oscillating potential (15); 4—line for argon according to data of tables [8].

and keeping the specified sequence of the presentation of results, we give here only the expressions for the chemical potentials obtained upon the integration of (12) and used for the calculation of  $\omega_1$  and  $\omega_2$ :

$$\mu = \frac{\tau}{\beta_c} \left( \ln(n_c \omega \lambda^3) + \frac{x_c \omega}{\tau} + \frac{3\sqrt{3}}{\tau} \left( 1 - \sqrt{1 + \frac{x_c \omega}{\tau}} \right) \right),$$

$$\mu = \frac{\tau}{\beta_c} \left( \ln(n_c \omega \lambda^3) + \frac{x_c \omega}{\tau} - \frac{2\sqrt{2}}{\tau} K \left( 1 - \frac{\sqrt{2}}{Y(\omega, \tau)} \right) \right),$$

$$\mu = \frac{\tau}{\beta_c} \left( \ln(n_c \omega \lambda^3) + \frac{x_c \omega}{\tau} - \frac{5}{2\tau} \left( \frac{9}{5} \right)^{9/4} \left( 1 - \frac{2}{(1 + x_c \omega / \tau)^{1/4}} \right) \right).$$

Searching for the analytical solution of system (27) in the closed form is exceedingly complicated. However, it is possible to present the phase densities sums of several terms of the series expansion of powers of the small parameter  $\theta = \tau - 1$  in analogy with [16]. In this case, the error of the solution increases with distance from CP. Therefore, the numerical solution of the system is preferable.

Note that potential parameters do not enter the equations of system (27). Therefore, the solutions—reduced phase densities for different materials as functions of the reduced temperature—depend only on the type of interaction potential and not on its parameters; i.e., for different materials described by the potentials of one type, the lines of the phase equilibrium coincide. The results of the numerical calculations of the densities of the coexisting phases are given in Fig. 2 as lines 1–3.

Obviously, the gas branches of the lines of equilibrium for potentials (14) and (15) almost coincide with the experimental curve in the interval of reduced tem-

peratures  $\tau = 0.9-1$ . For liquid branches, satisfactory agreement of models (14) and (15) with experimental data is observed in a narrower temperature interval:  $\tau = 0.98-1$ . It was shown in [17] that, in the system with the Yukawa potential, the critical index of the line of the equilibrium is one-third, and the metastability boundary is determined by the cubic equation in  $\omega$  [2].

## HEAT CAPACITY

Multiple experimental results indicate that, in the supercritical region ( $T > T_c$ ), the temperature dependences of the isobaric heat capacity  $C_p$  and  $(\partial V / \partial T)_p$  on the isobars in the one-component systems have final maxima [18]. This interesting phenomenon is observed in the considered models as well, which differ from each other in quantitative agreement with the experimental data.

The main problem when determining  $C_p$  and  $(\partial V / \partial T)_p$  is reduced to the solution of the equation

$$\pi(\omega, \tau) - \pi = 0 \quad (28)$$

with respect to the reduced density  $\omega$  at the given temperature  $\tau$  and pressure  $\pi$ . The analytical solution of this equation would have allowed one to easily build the curves  $C_p(T)$  and  $(\partial V / \partial T)_p$  to find the points of the maxima of these functions. However, the form of equation (28) in the cases (24)–(26) does not allow one to solve it analytically, and it requires the application of numerical methods.

The solutions  $\omega$  of nonlinear equation (28) are found for the values  $\pi$  and  $\tau$  corresponding to the experimental  $P$  and  $T$ , taken from tables on heat capacity [8]. Then the derivative  $(\partial V / \partial T)_p$  on isobars and the isobaric molar heat capacity  $C_p^M$  are easily calculated according to the formulas

$$\left( \frac{\partial V}{\partial T} \right)_p = - \frac{\beta_c R}{n_c} \frac{\partial \pi / \partial \tau}{\partial \pi / \partial \omega},$$

$$C_p^M = C_v^M - \tau R \frac{(\partial \pi / \partial \tau)_\omega^2}{(\partial \pi / \partial \omega)_\tau},$$

$$C_v^M = -T \frac{\partial^2 F}{\partial T^2} = C_v^{\text{id}} + \frac{R}{2n} \int_{\Omega} \frac{d^3 k}{(2\pi)^3} \left( \frac{n\beta \tilde{v}(k)}{1 + n\beta \tilde{v}(k)} \right)^2,$$

where  $C_v^{\text{id}} = 3R/2$ ,  $R$  is the universal gas constant.

The relationship between the molar and specific heat capacities, as is well known, is established by the relation

$$C_p^{\text{sp}} = C_p^M / M.$$

Therefore, the individuality of the specific heat capacity of the material within each of the models of the two-parameter potentials is determined only by the molar mass of the material  $M$ .

The models with potentials (14) and (15) are the most attractive of the three discussed models for liq-

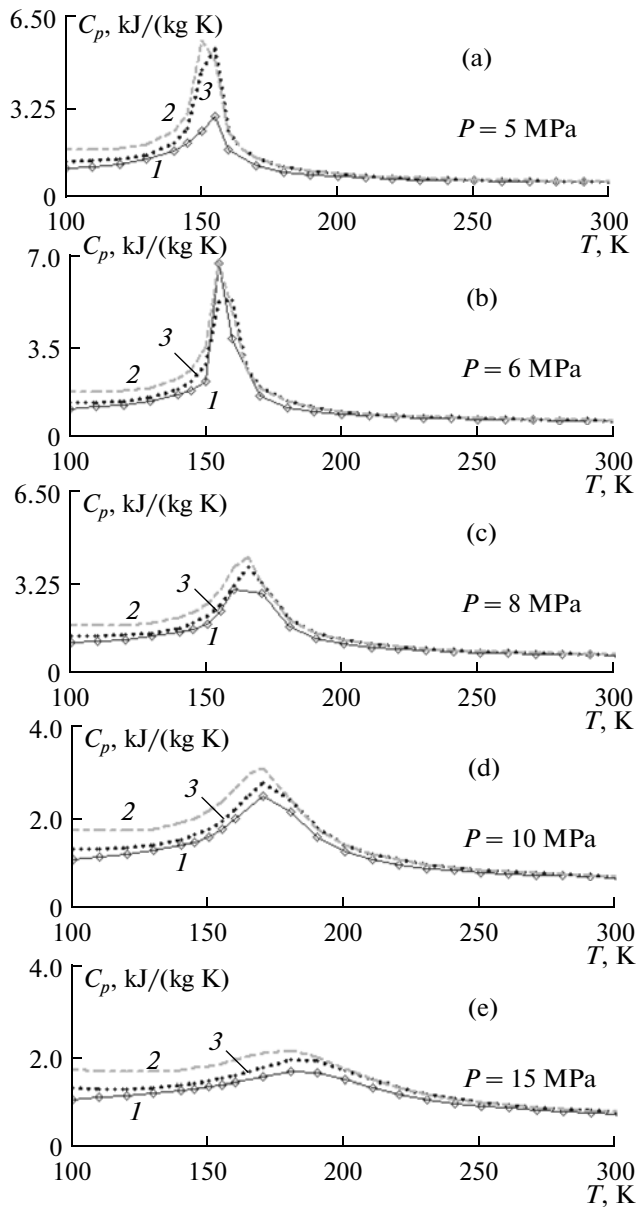


Fig. 3. Temperature dependences of the isobaric heat capacity for argon at different pressures: 1—according to data of [8]; 2—calculation with the exponential potential (14); 3—calculation with the oscillating potential (15).

uid, since they give the best agreement with the measurement data. The model with the Yukawa potential (13) shows only the qualitative features of the behavior of the system in the supercritical region.

The results of calculation of the specific heat capacity  $C_p$  in the models with the potential (14) and (15) for argon and experimental  $C_p$  values [8] are given in Fig. 3. The points of the  $C_p$  maxima are displaced to the right on the temperature axis with the increase in pressure. The highest maximum is observed at the pressure  $P = 6$  MPa (Fig. 3b). However, if the pressures  $P = 5, 6, 8, 10,$  and  $15$  MPa  $C_p(T)$  are calculated with

the increment reduced to at least 0.5 K (the minimum increment in the table of experimental values for argon [8] is 5 K), then, except for the shift of the points of  $C_p$  maxima to the right, it is possible to find the monotonic decrease in the maxima themselves with pressure, and the maxima become less pointed. This decrease is confirmed by measurements [19]. The lines of the  $C_p$  and  $(\partial V/\partial T)_p$  maxima on isobars plotted in the  $P$ – $T$  coordinates do not coincide, but they have a general origin in CP. Such a picture is completely confirmed by the conclusions of dispersoidological theory [20], and analogous conclusions were made in [21]. All lines are related to the presence of the inflections on isotherms; i.e., the  $C_p(T)$  and  $(\partial V/\partial T)_p$  extrema are determined by the extrema of the derivative  $(\partial P/\partial V)_T$ .

## CONCLUSIONS

It was established that, in the one-component systems with the considered model two-parameter potentials, the liquid–gas phase transition takes place. The exact solutions of the system of equations determining CP were found. The lines of the phase equilibrium and the temperature dependences  $C_p(T)$  were plotted at different pressures. It was shown that the phase densities and molar isobaric heat capacity calculated for a definite potential do not depend on its parameters.

Although the performed calculations allow comparison with experimental data, considerable discrepancies were observed, which could be due to several factors:

- imperfection of the form of the model interaction potential;
- means of determination of the parameters of the interaction potential (here only  $n_c$  and  $T_c$  were used for the calculation of the  $a$  and  $A$  parameters);
- approximate character of the expression for the free energy obtained in [2];
- taking into account the effect of the many-body interactions.

If the specification of the quadratic approximation for the free energy has some prospects, the problem related to taking into account even three-body interactions in the general form is far from being solved within the proposed approach. However, it is possible to indicate the direction in which the theory should develop for the adequate description of the experimental data.

This direction consists in the study of the effect of the “real” potentials on thermodynamics of the system, including multiparameter potential and, especially, linear combinations formed of simple potentials (the efficiency of such an approach was demonstrated, for example, in [22]). The use of potentials with several parameters can require more complete informa-

tion about the thermodynamic state of the material (not only in CP). In addition, since the parameters of the potential calibrated on one property can lead to the unsatisfactory description of other properties, the procedure of averaging the parameters found for several measured values cannot be excluded. Finally, it is possible to consider potentials with the solid core taking into account their cutting in zero, as well as the elaboration of the perturbation theory in which simple potentials can be used as the zero approximation for "real" ones. One such attempt at using perturbation theory for the description of CP was made in [23].

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#### APPENDIX

Expression (10) for the free energy was obtained in the quadratic approximation of the saddle-point method. Let us show that the integral

$$I = \int_{\Omega} \frac{d^3k}{(2\pi)^3} [\ln(1 + n\beta\tilde{v}(k)) - n\beta\tilde{v}(k)],$$

which determines the Helmholtz free energy  $F$  for the Yukawa potential singular in zero, converges. Each of the integrals (from the logarithmic term and the second term) diverges due to the overly slow decrease in the integrands at  $k \rightarrow \infty$ .

Let us transfer to the spherical coordinates in the space of wave vectors and consider the integral within a sphere  $|k| \leq K$ :

$$\begin{aligned} & \frac{1}{2\pi^2} \left[ \int_0^K dk k^2 \ln \left( \frac{k^2 + b^2}{k^2 + a^2} \right) - n\beta A \int_0^K dk \frac{k^2}{k^2 + a^2} \right] \\ &= \frac{1}{2\pi^2} \left[ \frac{k^3}{3} \ln \left( \frac{k^2 + b^2}{k^2 + a^2} \right) \Big|_0^K - \frac{2}{3} \int_0^K \frac{k^4 (a^2 - b^2) dk}{(k^2 + a^2)(k^2 + b^2)} \right. \\ & \quad \left. - n\beta A \left( \int_0^K dk - a^2 \int_0^K \frac{dk}{k^2 + a^2} \right) \right], \end{aligned}$$

where  $b^2 = a^2 + n\beta A$ .

Now we perform the limiting transition  $K \rightarrow \infty$ . At large  $K$  values, the first term in the last formula has following asymptotics:

$$\begin{aligned} L_1 &= \frac{k^3}{3} \ln \left( \frac{k^2 + b^2}{k^2 + a^2} \right) = \frac{k^3}{3} \left( \ln \left( 1 + \frac{b^2}{k^2} \right) - \ln \left( 1 + \frac{a^2}{k^2} \right) \right) \\ &= \frac{k^3}{3} \left( \left( \frac{b}{k} \right)^2 - \frac{1}{2} \left( \frac{b}{k} \right)^4 + \dots - \left( \frac{a}{k} \right)^2 + \frac{1}{2} \left( \frac{a}{k} \right)^4 + \dots \right) \\ &= \frac{k}{3} n\beta A - \frac{b^4 - a^4}{6k} + \dots \end{aligned}$$

The second term in the right-hand part  $I$  is transformed to

$$\begin{aligned} L_2 &= \frac{2}{3} \int_0^K \frac{k^4 (a^2 - b^2) dk}{(k^2 + a^2)(k^2 + b^2)} \\ &= \frac{2a^2}{3} \left[ \int_0^K dk - a^2 \int_0^K \frac{dk}{k^2 + a^2} \right] - \frac{2b^2}{3} \left[ \int_0^K dk - b^2 \int_0^K \frac{dk}{k^2 + b^2} \right] \\ &= -\frac{2}{3} n\beta A \int_0^K dk - \frac{\pi}{3} (a^3 - b^3). \end{aligned}$$

By substituting  $L_1$  and  $L_2$  in  $I$ , we obtain

$$\begin{aligned} I &= \frac{1}{2\pi^2} \lim_{K \rightarrow \infty} \left[ \left( \frac{K}{3} n\beta A - \frac{b^4 - a^4}{6K} \right) + \frac{2}{3} n\beta A \int_0^K dk \right. \\ & \quad \left. + \frac{\pi(a^3 - b^3)}{3} - n\beta A \left( \int_0^K dk - \frac{\pi a}{2} \right) \right] \\ &= \frac{1}{2\pi} \left[ \frac{a^3 - b^3}{3} + \frac{n\beta A a}{2} \right]. \end{aligned}$$

Thus, the problem of the convergence of the integral  $I$  in the case of potentials singular in zero does not exist.

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