

A ROLE OF 3-BODY EFFECTS IN A DESCRIPTION OF THE CRITICAL BEHAVIOUR OF SIMPLE REAL FLUIDS

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The reasons for a necessity of taking into account 3-body interactions in a description of a behaviour of real fluid near the liquid-gas critical point are regarded.

The influence of 3-body forces on some properties of argon is estimated. Particularly, a way of taking into account 3-body interactions in the theory of liquid-gas critical point by the collective variables method is considered. The effects of 3-body forces on the structure functions of the reference system, as well as on the value of 3-rd virial coefficient and on the thermodynamical properties of some simple real system are investigated. Using the generalized mean field theory, the critical amplitudes for some thermodynamic functions of argon are calculated.

1. Introduction

An interest to the role of many-particle interactions is a characteristic feature of the phase transition theory in classical fluids at present time. As a rule, only three-particle interactions are concerned. It is known, that their influence may be rather important in the vicinity of the liquid-gas critical point. Hence, any quantitative theory describing the phenomenon of the phase separation should provide explicit or effective taking into account many-particle interactions. In the previous papers [1,2] we have proposed the foundations of the liquid-gas phase transition theory in the classical fluid basing on the collective variable method. It was managed to derive an expression for the fluid partition function functional, with coefficient functions explicitly defined using the structure functions of the reference system. All properties of the reference system are assumed to be known. The interparticle interaction both in initial and reference systems was supposed to be pair-wise. Such approach is quite true if one considers a narrow vicinity of the critical point on the thermodynamic surface. An interparticle potential here may be chosen in a way that allows to take into consideration interactions of higher than pair-wise orders. But it will depend on the temperature and particle density, so, one can not use the expressions obtained for the

certain thermodynamical functions, in a wide range of a temperature and density.

In this paper we will present some estimations, exposing an influence of 3-particles interactions on the properties of argon.

So, we consider the classical homogeneous system of N particles.

In general, the potential energy may be presented as a cluster sum (external field is supposed to be absent):

$$U_N = \sum_{N \geq i > j \geq 1} \sum U_2(r_{ij}) + \sum_{N \geq i > j > k \geq 1} \sum U_3(r_i, r_j, r_k) + \sum_{N \geq i > j > k > l \geq 1} \sum U_4(r_i, r_j, r_k, r_l) + \dots \quad (1.1)$$

An assumption about the pair-wise character of interparticle interactions being used in the most of modern statistical theories. One of the main arguments is sufficient concordance between theoretically calculated and experimentally obtained values. Usually, the parameters of the pair potential, for example, ε and σ for the Lennard-Jones potential, are determined from the experimental data. Perhaps, it compensates neglecting higher terms, and transforms the pair-wise potential into effective one, which well describes the properties of the system.

The equation of state and free energy in the mean field approximation one can write as [3]:

$$\begin{aligned} P - P_0 &= a\rho^\alpha, \\ \frac{U - U_0}{V} &= \frac{a\rho^\alpha}{\alpha - 1}, \end{aligned} \quad (1.2)$$

here P, V, ρ, U are pressure, volume, density and internal energy of the system; the letters with the subscript "0" are the same values, calculated in the pair-wise theory, a is a constant, and α characterises an order of the many-particles interactions ($\alpha = 3, 4, \dots$; if in (1.1) one limits himself only with two first terms, than $\alpha = 3$). From (1.2) it follows, that

$$\alpha = 1 + \frac{(P - P_0)V}{U - U_0} \quad (1.3)$$

In [3] formula (1.3) was used to calculate α from experimental data (see Table 1, where the values of α are presented for the temperature $\frac{k_B T}{\varepsilon} = 1.48$; r_m is a position of a minimum of the pair potential).

Table 1. The values of the parameter α [3], characterising an order of the many-particle interactions.

Density ρr_m^3	α	
	Xe	Kr
1.15	—	3.7
1.10	3.8	—
0.96	3.5	3.3
0.77	3.0	3.2
0.58	2.6	2.6

One can see that the difference between the real interaction and the pair-wise one essentially increases with the increase of a density.

The problem of taking into account three-particle interactions is an actual task of the modern statistical theory (see, for example [4-6]).

Three-particle non-additional potential was obtained for the first time in paper [8]:

$$U_3^{ABC} = C^{ABC} \frac{\Delta(\theta_A, \theta_B, \theta_C)}{R_{AB}^3 R_{AC}^3 R_{BC}^3} . \quad (1.4)$$

Here R_{AB}, R_{BC}, R_{AC} are the lengths of the sides of the triangle, formed by atoms A, B, C ; $\theta_A, \theta_B, \theta_C$ are the angles of the triangle, $\Delta(\theta_A, \theta_B, \theta_C)$ is geometric factor:

$$\Delta(\theta_A, \theta_B, \theta_C) = 1 + 3 \cos \theta_A \cos \theta_B \cos \theta_C . \quad (1.5)$$

Positive constant C^{ABC} is expressed by the oscillator forces and transition frequencies. A general expression for C^{ABC} is adduced in many papers (see, for example, [9]).

For identical atoms formula (1.4) has a form:

$$U_3 = \frac{9}{16} \bar{\omega} \alpha_p^3 \frac{\Delta(\theta_1, \theta_2, \theta_3)}{R_{12}^3 R_{23}^3 R_{13}^3} , \quad (1.6)$$

Here $\bar{\omega}$ is an average excite frequency of the molecules; α_p is the static dipole polarization.

A sign of 3-particle dispersion energy is determined by factor $\Delta(\theta_A, \theta_B, \theta_C)$.

An estimation of the relative significance of 3-particle Axilrod-Teller potential U_3 and pair-wise potential U_2 , the main part of which can be presented as $U_2 = -\frac{3}{4} \frac{I \alpha_p^2}{r^6}$, where I is the ionization energy, was carried out in papers [4-6]. There was shown, that

$$\frac{U_3}{U_2} \sim \alpha_p \rho_c \sim T_c^{1/2} .$$

This means that 3-body interaction is relatively more significant in fluids with high polarization and, hence, with higher critical temperature [6].

Other 3-body potentials are known besides widely-used long-range Axilrod-Teller potential, they are:

1. The long-range potential which includes all terms of the multipolar expansion up to the triple-quadrupole [10]:

$$U_3 = Z(DDD)W(DDD) + Z(DDQ)W(DDQ) + Z(DQQ)W(DQQ) + Z(QQQ)W(QQQ) , \quad (1.7)$$

The constants $Z(DDD), Z(DDQ), Z(DQQ), Z(QQQ)$ depend on the type of atoms. Values of Z for Kr is adduced in [10]. Functions $W(DDQ), W(DQQ), W(QQQ)$ describes interactions of two dipoles and one quadrupole, two quadrupoles and one dipole and three quadrupoles.

2. The short-range exponential potential plus the Axilrod-Teller triple-dipole potential [13]:

$$U_3 = \left[\frac{C^{ABC}}{r_{12}^3 r_{23}^3 r_{13}^3} - A \exp[-\alpha(r_{12} + r_{23} + r_{13})] \right] (1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3) , \quad (1.8)$$

here A, α are constants. For example, $A = 7.4866 \times 10^{-8} \text{ erg}$, $\alpha = 1.546 \times 10^{10} \text{ m}^{-1}$ for Kr .

2. The virial equation of state for Ar.

The virial equation of state expresses a deviation from ideal gas equation of state in the form of an infinite series:

$$\frac{PV}{Nk_B T} = 1 + B(T)\rho + C(T)\rho^2 + \dots \quad , \quad (2.1)$$

where $B(T), C(T), \dots$ are 2-nd, 3-nd, ... virial coefficients; $\rho = \frac{N}{V}$ is particle density.

The second virial coefficient accounts for the deviation from the ideal gas state caused by interactions of pairs of the molecules:

$$B(T) = -\frac{1}{2} \int f(r) d\vec{r} \quad , \quad (2.2)$$

here $f(r)$ is the Mayer function: $f(r) = e^{-\beta U_2(r)} - 1$.

The third virial coefficient is a sum of two terms:

$$C(T) = C_{add} + \Delta C \quad , \quad (2.3)$$

where C_{add} is an additive term connected with the pair potential only:

$$C_{add} = -\frac{1}{3} \int f(r) f(s) f(|\vec{r} - \vec{s}|) d\vec{r} d\vec{s} \quad , \quad (2.4)$$

and ΔC accounts both pair and three particle interactions:

$$\Delta C = -\frac{1}{3} \int \int [f(r) + 1][f(s) + 1][f(|\vec{r} - \vec{s}|) + 1] \left(e^{-\beta U_3(r,s)} - 1 \right) d\vec{r} d\vec{s} \quad . \quad (2.5)$$

The third virial coefficient can be easily enough measured experimentally and theoretically calculated and during many years is used for evaluation of 3-body effects [11]. The results of these and other papers indicate, that the value of ΔC may be up to 40% of the value of third virial coefficient calculated in the pair potential approximation, depending on temperature and density.

The results, presented in Fig. 1, clearly indicate, that both the third virial coefficient and its non-additive part are to be considered, especially at the densities close to critical one (0.531 gr/cm^3), and at higher.

3. Three-body interactions in the mean field theory.

The free energy of one-component system with pair-wise interaction in classical (Van-der-Waals) theory is [12]:

$$F = Nk_B T \ln \left(\frac{N\lambda^3}{e(V - Nb)} \right) - aN \left(\frac{N}{V} \right) \quad , \quad (3.1)$$

here $\lambda = h(2\pi mk_B T)^{-1/2}$ is the thermal de Broyl wavelength, h is the Plank constant, m is a mass of a particle, $e = 2.7182 \dots$, $b = 4\eta \frac{V}{N}$; $\eta = \frac{\pi}{6} \frac{N}{V} \sigma^3$ is a fraction density and σ is a diameter of a molecule.

$$a = -\frac{1}{2} \int \Phi(r) F_2(r) d\vec{r} \quad , \quad (3.2)$$

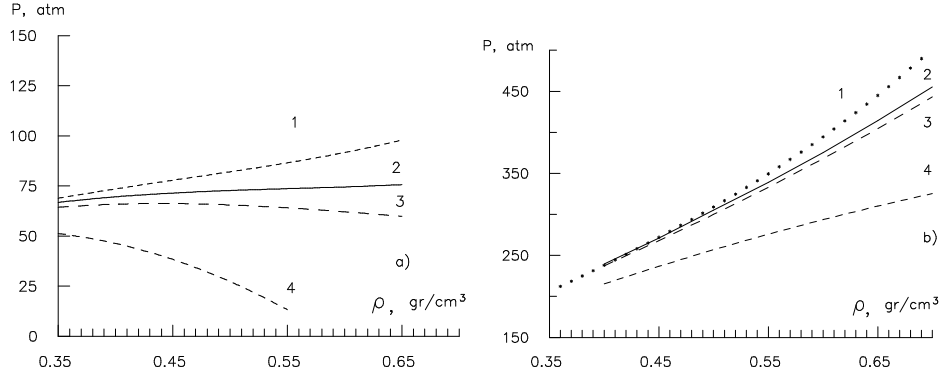


Figure 1. The isotherms of the virial equation of state for argon: a). $T = 170\text{K}$ b). $T = 300\text{K}$; curve 1 - the experimental values for the pressure; curve 2 - the isotherm of the equation (2.1) with taking into account the third virial coefficient; curve 3 - the isotherm of the equation (2.1) with taking into account the additive part of the third virial coefficient; curve 4 - the isotherm of the equation (2.1) with taking into account the second virial coefficient.

$F_2(r)$ is pair distribution function of the reference system.

Van der Waals theory leads to the following critical point parameters

$$\rho_c = \frac{1}{3b} \quad ; \quad k_B T_c = \frac{8a}{27b} \quad ; \quad P_c = \frac{a}{27b^2} \quad ; \quad (3.3)$$

Consideration 3-body interactions in the mean field theory leads to one more term in the expression for the free energy [5]:

$$F_3 = qN \left(\frac{N}{V} \right)^2 \quad , \quad (3.4)$$

here

$$q = \frac{1}{6} \int \int d\vec{r} d\vec{r}' U_3(r, r') F_3(\vec{r}, \vec{r}', \vec{r} - \vec{r}') \quad , \quad (3.5)$$

$F_3(r_{12}, r_{13}, r_{23})$ is 3-particle distribution function of the reference system.

Equation of state in the mean field theory with 3-body forces taken into account can be written as:

$$P = \frac{\rho k_B T}{1 - b\rho} - a\rho^2 + 2q\rho^3 \quad . \quad (3.6)$$

The critical point parameters can be determined and cast in form similar to (3.3), namely [5]:

$$\rho_c = \frac{1}{3b} \tilde{\rho}(x) \quad ; \quad k_B T_c = \frac{8a}{27b} \tilde{T}(x) \quad ; \quad P_c = \frac{a}{27b^2} \tilde{P}(x) \quad , \quad (3.7)$$

here

$$\tilde{\rho}(x) = \frac{3}{4} + \frac{3}{8x} [1 - (1 - \frac{4}{3}x + 4x^2)^{1/2}] \quad ,$$

$$\begin{aligned}\tilde{T}(x) &= \frac{9}{4}\tilde{\rho}(x)\left(1 - \frac{1}{3}\tilde{\rho}(x)\right)^2(1 - x\tilde{\rho}(x)) \quad , \\ \tilde{P}(x) &= \frac{8}{3}\frac{\tilde{\rho}(x)\tilde{T}(x)}{1 - \frac{1}{3}\tilde{\rho}(x)} - 3\tilde{\rho}^2(x) + 2x\tilde{\rho}^3(x) \quad .\end{aligned}\quad (3.8)$$

One can see from (3.7) and (3.8), that all thermodynamical properties of the system depends on the only parameter

$$x = \frac{q}{ab} \quad , \quad (3.9)$$

which may be supposed in the mean field theory as a value characterizing a relative contributions of two- and three-particles interactions.

It follows from calculation, that value of x is rather small (see Fig. 2).

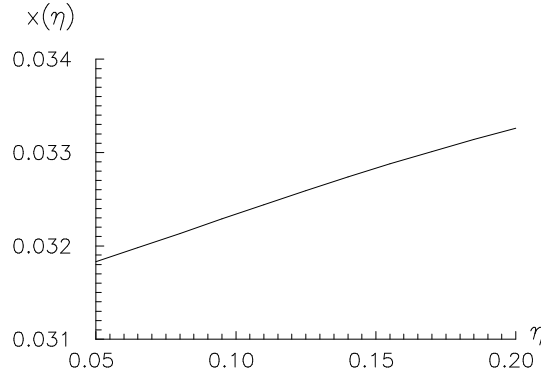


Figure 2. A dependence on a density of the parameter x , which characterizes the relative contribution of 3-body interactions.

In the case $x \ll 1$ the formulae for $\tilde{\rho}(x)$, $\tilde{T}(x)$, $\tilde{P}(x)$ can be expanded in powers of x . One obtains:

$$\begin{aligned}\tilde{\rho}(x) &\approx 1 - \frac{2}{3}x \quad , \\ \tilde{T}(x) &\approx 1 - x \quad , \\ \tilde{P}(x) &\approx 1 - 2x \quad .\end{aligned}\quad (3.10)$$

Plots for $\tilde{\rho}(x)$, $\tilde{T}(x)$, $\tilde{P}(x)$ are shown on Fig. 3.

To calculate an isotherm from equation of state (3.6) it is suitable to express the equation in terms of $\bar{P} = \frac{P}{P_c}$, $\bar{T} = \frac{T}{T_c}$, $\bar{\rho} = \frac{\rho}{\rho_c}$, where ρ_c , P_c , T_c are defined by (3.7). As a result the equation of state will be:

$$\bar{P} = \frac{\tilde{\rho}(x)\tilde{T}(x)}{\tilde{P}(x)} \frac{8\bar{\rho}\bar{T}}{3 - \bar{\rho}\tilde{\rho}(x)} - \frac{\tilde{\rho}^2(x)}{\tilde{P}(x)} 3\bar{\rho}^2 + \frac{2x\tilde{\rho}^3(x)}{\tilde{P}(x)} \bar{\rho}^3 \quad . \quad (3.11)$$

From (3.11) it follows, that considering 3-body forces leads to violation of the correspondent states law.

As $x > 0$, the contributions (see (3.11)) of two- and three-body interactions enter in equation of state with different signs, but including 3-body

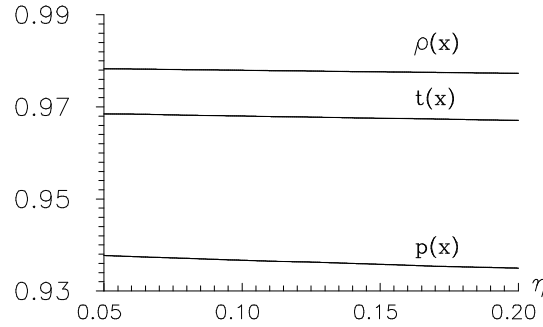


Figure 3. The related with 3-body interactions corrections (3.8) to the critical point parameters in the mean field theory.

forces causes an increase of the pressure, which adjusts with results of other papers.

In the mean field theory of the liquid-gas phase transition the pressure in one-component system can be written as [12]:

$$\frac{P}{P_c} = \sum_{m,n=0}^{\infty} \frac{1}{m!} \frac{1}{n!} P_{mn} (\Delta\rho)^m (\Delta T)^n \quad , \quad (3.12)$$

here $\Delta\rho = \frac{\rho - \rho_c}{\rho_c}$, $\Delta T = \frac{T - T_c}{T_c}$.

So, one can find connections between the coefficients of expansion for P_{mn} and critical amplitudes, and calculate the critical exponents for the thermodynamical functions.

The coexistence curve near the critical point is defined by the following asymptotic expression:

$$(\Delta\rho)_{l,v} = \pm A_\beta t^\beta + A_1 t + \dots \quad , \quad (3.13)$$

Here $t = -\Delta T$, β is the order parameter critical exponent, equal in the mean field theory to $1/2$, A_β is an amplitude of the order parameter, A_1 describes a slope of the coexistence curve.

Using (3.12), (3.13) and the Maxwell's rule, one can find a relationships between A_β , A_1 and P_{mn} [5]:

$$A_\beta = \left(\frac{6P_{11}}{P_{30}} \right)^{1/2} \quad ,$$

$$A_1 = \frac{P_{21}}{P_{30}} - \frac{3}{5} \frac{P_{11}P_{40}}{P_{30}^2} + \frac{4}{5} \frac{P_{11}}{P_{30}} \quad . \quad (3.14)$$

The values of A_β , A_1 are characteristic for the main field theory:

$$A_\beta = 2; \quad A_1 = \frac{2}{5} \quad .$$

Equation of state in presence of 3-body forces is adduced in (3.6), the values of coefficients P_{mn} are here functions of the parameter x [16], and for A_β

and A_1 one receives:

$$A_\beta = \frac{3 - \tilde{\rho}(x)}{\tilde{\rho}(x)} \left[\frac{\tilde{\rho}(x)(1 - x\tilde{\rho}(x))}{\tilde{\rho}(x)(1 - x\tilde{\rho}(x)) + 3x(1 - \frac{1}{3}\tilde{\rho}(x))^2} \right]^{1/2}, \quad (3.15)$$

$$A_1 = \frac{6}{5} \frac{(1 - \frac{1}{3}\tilde{\rho}(x))(1 - x\tilde{\rho}(x))}{\tilde{\rho}(x)[\tilde{\rho}(x)(1 - x\tilde{\rho}(x)) + 3x(1 - \frac{1}{3}\tilde{\rho}(x))^2]^2} [\tilde{\rho}(x)(1 - \frac{1}{2}\tilde{\rho}(x))(1 - x\tilde{\rho}(x)) + 3x(1 + \frac{1}{2}\tilde{\rho}(x))(1 - \frac{1}{3}\tilde{\rho}(x))^2].$$

When x is small, the formula (3.15) become essentially simpler:

$$A_\beta \approx 2 + \frac{2}{3}x + \dots, \quad A_1 \approx \frac{2}{5} + \frac{22}{15}x + \dots.$$

In the similar way one can calculate the amplitudes and critical exponents of other thermodynamical functions.

In part, a dependence of $P - P_c$ on $\rho - \rho_c$ on the critical isotherm $T = T_c$ has the following asymptotic form:

$$\Delta P = \text{sgn}(\rho - \rho_c) [D\Delta\rho^\delta + D_1\Delta\rho^{\delta + \frac{\Delta}{\beta}}], \quad T = T_c, \quad (3.16)$$

here $\Delta P = \frac{P - P_c}{P_c}$; δ is the critical isotherm exponent, Δ is the Wegner index; D, D_1 - the critical amplitudes.

Comparing (3.16) and (3.12), one can find:

$$\delta = 3, \quad \delta + \frac{\Delta}{\beta} = 4, \quad \Delta = \frac{1}{2},$$

$$D = \frac{1}{3!}P_{30}, \quad D_1 = \frac{1}{4!}P_{40}. \quad (3.17)$$

Using values of P_{mn} , one can calculate the critical amplitudes for the case 2-body forces only:

$$D = \frac{3}{2}, \quad D_1 = \frac{3}{4}, \quad (3.18)$$

and for the case of 2-body and 3-body forces taken into account:

$$D = \frac{2}{3}\tilde{\rho}(x) \frac{\tilde{\rho}(x)(1 - \tilde{\rho}(x)) + 3x(1 - \frac{1}{3}\tilde{\rho}(x))^2}{(1 - \frac{1}{3}\tilde{\rho}(x))^2[4(1 - x\tilde{\rho}(x))(1 - \frac{1}{2}\tilde{\rho}(x)) - 1]},$$

$$D_1 = \frac{2}{9} \frac{\tilde{\rho}^3(x)(1 - x\tilde{\rho}(x))}{(1 - \frac{1}{3}\tilde{\rho}(x))^3[4(1 - x\tilde{\rho}(x))(1 - \frac{1}{2}\tilde{\rho}(x)) - 1]}. \quad (3.19)$$

At small x , one obtains for D and D_1

$$D \approx \frac{3}{2}(1 - x), \quad D_1 \approx \frac{3}{4}(1 - \frac{10}{3}x).$$

Using the above results, we can also calculate a compressibility at the critical point, that is

$$Z_c = \frac{P_c}{\rho_c k_B T_c} \quad .$$

For the Van-der-Waals equation one has $Z_c = \frac{3}{8}$. Considering of the 3-body interactions leads to the following value of Z_c :

$$Z_c = \frac{3}{8} \frac{\tilde{P}(x)}{\tilde{\rho}(x)\tilde{T}(x)} = \frac{[\frac{1}{3}x\tilde{\rho}^2(x) - \frac{1}{3}\tilde{\rho}(x)(1+2x) + \frac{1}{2}]}{(1-x\tilde{\rho}(x))(1-\frac{1}{3}\tilde{\rho}(x))^2} \quad , \quad (3.20)$$

which at small x transforms to formula

$$Z_c \approx \frac{3}{8} - \frac{1}{8}x \quad .$$

From this expression it follows, that 3-body forces cause decreasing of Z_c . It satisfies with experimental data, according to which $Z_c < 0.375$ for all liquids.

4. Consideration 3-body interactions in the collective variables method.

Let us write down the first term in (1.1) as a sum:

$$\sum_{i<j} U_2(r_{ij}) = \sum_{i<j} \varphi(r_{ij}) + \sum_{i<j} \tilde{\Phi}(r_{ij}) \quad . \quad (4.1)$$

Here potential $\varphi(r)$ describes an interaction in the reference system and is supposed to be the short-range one, related mainly with repulsion. Potential $\tilde{\Phi}(r)$ describes the long-range attraction, which results in the phase transition. A calculation of the partition function is carried out in the expanded phase space, which includes a subspace of the cartesian coordinates and the collective variable subspace [1,2].

Let us introduce in the configuration integral

$$Q_N = \int e^{-\frac{1}{2}\beta \sum_{i \neq j} U(r_{ij})} (d\vec{r})^N = \int e^{-\frac{1}{2}\beta \sum_{i \neq j} \varphi(r_{ij}) - \frac{1}{2}\beta \sum_{i \neq j} \tilde{\Phi}(r_{ij})} (d\vec{r})^N \quad , \quad (4.2)$$

the point density operator $\hat{n}(\vec{r})$ and its Fourier-image $\hat{\rho}_{\vec{k}}$:

$$\hat{n}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \quad , \quad (4.3)$$

$$\hat{\rho}_{\vec{k}} = \hat{\rho}_{\vec{k}}^c - i\hat{\rho}_{\vec{k}}^s = \frac{1}{\sqrt{N}} \int \hat{n}(\vec{r}) e^{-i\vec{k}\vec{r}} d\vec{r} = \frac{1}{\sqrt{N}} \sum_i e^{-i\vec{k}\vec{r}_i} \quad ;$$

$$\hat{\rho}_{\vec{k}}^c = \frac{1}{\sqrt{N}} \sum_i \cos(\vec{k}\vec{r}_i); \quad \hat{\rho}_{\vec{k}}^s = \frac{1}{\sqrt{N}} \sum_i \sin(\vec{k}\vec{r}_i); \quad \hat{\rho}_0 = \sqrt{N} \quad .$$

Then Q_N can be presented in a form [1]:

$$Q_N = Q_0 \int \exp\{-i2\pi \sum_{\vec{k}} \omega_{\vec{k}} \rho_{\vec{k}} - \frac{1}{2} \sum_{\vec{k}} \alpha(k) \rho_{\vec{k}} \rho_{-\vec{k}} + \frac{1}{2} \sum_{\vec{k}} \alpha(k)\}$$

$$\exp\left\{\sum_{n \geq 1} \frac{(-i2\pi)^n}{n!} N^{1-\frac{n}{2}} \sum_{\vec{k}_1, \dots, \vec{k}_n} M_n(k_1, \dots, k_n) \omega_{\vec{k}_1} \cdots \omega_{\vec{k}_n}\right\} (d\rho_{\vec{k}})(d\omega_{\vec{k}}), \quad (4.4)$$

here

$$\alpha(k) = \frac{N}{V} \beta \Phi(k); \quad \Phi(k) = \frac{1}{V} \int \tilde{\Phi}(r) e^{-i\vec{k}\vec{r}} d\vec{r}, \quad (4.5)$$

$Q_0 = \int \exp[-\frac{1}{2}\beta \sum_{i \neq j} \varphi(r_{ij})] (d\vec{r})^N$ is the reference system partition function;

$M_n(k_1, \dots, k_n) = \langle \hat{\rho}_{\vec{k}_1}, \dots, \hat{\rho}_{\vec{k}_n} \rangle_c$ is the reference system n -order cumulant, related with thermodynamical and structure properties of the reference system. In part, $M_2(0) = \rho k_B \chi_T$ is the structure factor ($\rho = \frac{N}{V}$, χ_T is isothermal compressibility).

It was shown [1], that the interval of the wave vector values in the sum $\sum_{\vec{k}} \alpha(k) \rho_{\vec{k}} \rho_{-\vec{k}}$ may be limited to $[0, B]$, a point B is related with properties of the long-range potential. For the cummulants with a reduced dependence on wave vectors $M_n(k, 0) \equiv M_n(k, -k, 0, \dots, 0)$ there exists a recursion relation allowing to investigate their dependence on k :

$$M_{n+1}(k, 0) = M_n(0) \left[M_n(k, 0) + \rho \frac{\partial M_n(k, 0)}{\partial \rho} \right], \quad (4.6)$$

Here $M_n(0) \equiv M_n(k_1, \dots, k_n)$ at $k_1 = \dots = k_n = 0$.

A case when hard spheres with diameter σ are used as the reference system was regarded in details in papers [1,2].

The structure properties of the hard sphere system are well known, and for the cummulants one can derive explicit expressions. A main property of cummulants is here their weak dependence on the wave vector in the above mentioned interval $[0, B]$, that allows to neglect the dependence. Than the coefficients at products $\omega_{\vec{k}_1} \cdots \omega_{\vec{k}_n}$ in (4.4) become constant and depend in general only on the fraction density $\eta = \frac{N}{V} \frac{\pi \sigma^3}{6}$.

In such case in calculation of the partition function one can use the approach developed earlier for the Ising model [15].

It was shown, that at the critical point - a point of the 2-rd order phase transition there takes place:

$$M_3(0) = 0, \quad (4.7)$$

which allows to determine the critical density η_c . It was found

$$\eta_c = 0.130443... \quad (4.8)$$

A case, when the reference system is a system with more realistic potential was regarded in paper [14]. Such choice allows to avoid difficulties which arise in connection with taking into account long-wave modes of particle density fluctuations, with $k > B$, but solving of Ornstein-Zernike equation becomes here necessary. It was shown, that the method of calculation of the partition function developed for the hard spheres can be used here.

In present paper we regard a case, when the potential energy (1.1) besides pair-wise interaction contains also 3-particle ones.

The well-known analytical form of 3-particle potentials (1.6), (1.7), (1.8) makes here more suitable the approach, when 3-particle interactions are accounted in the reference system.

The Lennard-Jones potential is mostly used for 2-body forces and for 3-body forces - one of potentials (1.6) - (1.8). The most widespread method of calculation of distribution functions consists in the effective taking into account 3-body forces by adding to 2-body potential a term which depends on the temperature and density [13]:

$$\begin{aligned}\tilde{U}_2(r_{12}) &= U_2(r_{12}) + \bar{U}_2(r_{12}) \quad , \\ \bar{U}_2(r_{12}) &= \frac{\rho}{\beta} \int \left(e^{-\beta U_3(r_1, r_2, r_3)} - 1 \right) g_2(r_{31}) g_2(r_{32}) d\vec{r}_3 \quad .\end{aligned}\quad (4.9)$$

In paper [13] calculations of the equation of state, internal energy, compressibility, radial distribution function and the mean force potential were fulfilled for argon. It was shown, that contribution of the 3-body forces into the internal energy at the temperature below the critical temperature (100-120 K) can be about 15% depending on a density.

From the point of view of the above adduced scheme of derivation of the starting form for the partition function, the influence of 3-body forces on the structure factor and, in this way, on all cummulants in (4.4) is of a special interest. The series in exponent of the density measure in (4.4) consists generally of the infinite number of terms with coefficients M_n . It was shown earlier [2], that the qualitatively true description of the critical point can be received in " ω^4 " approximation for the density measure. For convergence of the integral it is necessary to have $M_4 < 0$. For the more, one could neglect the dependence of the cummulants on the wave vector, if the dependence is weak enough.

The calculations of the structure factor and radial distribution function were fulfilled in paper [13]. The dependence of the structure factor $S(k)$ on 3-body interaction is noted in the narrow interval near point $k = 0$. At small and mean densities $\eta < 0.28$ including 3-body interactions make results of calculation nearer to the experimental data on Kr. However, at $\eta > 0.28$ a deviation from the experimental data both for Ar and Kr is significant. The authors have concluded that or the Axilrod-Teller potential is here not appropriate, or consideration of still higher is necessary.

In paper [10] an influence of 3-body interactions on correlation functions and structure factor of Kr at low and high density was investigated. The 3-body Axilrod-Teller potential (1.6), the multipole potential (1.7) and the modified Axilrod-Teller potential (1.8) were applied. A method used in the paper allows to avoid solving the Ornstein-Zernike equation at low densities. At high densities the modified HNC approximation was applied, when the bridge-function

$$E(r) = [1 - l(r)]E_{HS}(r; d) + l(r)[-h(r) + \ln g(r)] \quad , \quad (4.10)$$

is expressed with a help of crossover function $l(r)$ and ensures the proper asymptotic of $C(r)$ at large and small distances. It is shown, that 3-body potentials (1.6), (1.7), (1.8) ensure at low densities good accordance with experimental data on $S(k)$ at $k \rightarrow 0$; some worse at finite k ($T = 297K$). At high densities ($\rho = 13.84 \text{ atom/nm}^3$) the values of $S(k)$ obtained by calculations deviate significantly from the experimental data, and any form of 3-body potentials, apparently, is an adequate one. 3-body interactions, in general, cause a displacement of the main peak of the structure factor to the region of smaller k and decrease the factor at $k \rightarrow 0$, comparing with its values without 3-body interactions. Such displacement is related with a character of 3-body forces which are effectively repulsive. As a function of

density, a coordinate of the first peak k_m increases because of decrease of the average interparticle density. So, a calculation of $S(k)$ and comparing of a position of the peak with the experimental data can provide the arguments concerning the necessity consideration of higher orders interactions.

In paper [4] was also investigated an influence of 3-body forces on Fourier-image of direct correlation function

$$C_k = \frac{1}{\rho} \left(1 - \frac{1}{S(k)} \right) . \quad (4.11)$$

It was established, that taking into account 3-body interactions provide good accordance with experiment at $k \sim 0$ excepting high densities ($\rho > 6 \text{ atom/nm}^3$), when a significant deviation appears. At mean values of $k \sim 6 \div 8 \text{ nm}^{-1}$ the influence is weaker, and it grows sharply again with increase of a density ($\rho \sim 12 \text{ atom/nm}^3$) at $k > 10 \text{ nm}^{-1}$.

Authors conclude that at high density including of another forces (4-body and higher) is necessary, namely, repulsive ones, that follows from the sign of the deviation of C_0 from its experimental value. Notice, that the critical density for Kr is about 6.55 atom/nm^3 .

An investigation of the phase equilibrium in Ar in presence of two- and three-body interactions was fulfilled in paper [7]. The Axilrod-Teller and Lennard-Jones potentials are used. Although the method of solving of the Ornstein-Zernike equation used in the paper does not allow to investigate the narrow vicinity of the critical point on the thermodynamical surface, an interpolation of the results shows, that by means of only 2-body potential it is impossible to obtain quantitative meanfull results, for example, for the equation of state. Including of 3-body forces essentially improves the results of calculations and brings them closer to the experimental data.

In this paper we present the calculations of the influence of 3-body forces on the coefficient functions of the configuration integral (4.4) - the reference system cummulants. As a full 2-body potential $U_2(r)$ (4.1) we use Lennard-Jones potential, with parameters $r_0 = 3.761 \text{ \AA}$, $\varepsilon/k_B = 119.8 \text{ K}$ for Ar.

The 2-body potential of the reference system was chosen in a way, that ensures $\tilde{\Phi}(r)$ to have the Fourier-image $\Phi(k)$, which have parabolic form and differs from zero only in narrow interval $k \in [0, B]$, $B = \frac{\pi}{r_0}$ [14].

The 3-body forces, in a form of the Axilrod-Teller potential (1.6), was effectively included into 2-body reference system potential according to expression (4.9). The Ornstein-Zernike equation was solved in HNC approximation by simple interactions, and 3-body forces have been averaged by the position of the third particle according to (4.9), with a help of the radial distribution function $g(r)$ obtained on each interaction.

In Fig. 4 the curves for the effective potential $\bar{U}_2(r)$ for a set of temperatures and densities are shown. One can see, that potential $\bar{U}_2(r)$ possesses the repulsive character and decreases both with a growth of a temperature and decreasing of a density, that corresponds to increasing of the mean interparticle distance, and is about 3 – 6% of the full potential $U_2(r)$ in a region of the potential well ($r \sim 3.7 \text{ \AA}$).

An influence of 3-body forces is essential at small values of k , but presents almost on the whole interval $[0, B]$ ($kr_0 \leq \pi$). A change of a value of the reference system structure factor - the cummulant $M_2(k)$ at $k \rightarrow 0$ due to 3-body forces is about $\sim 20\%$ (Fig.5).

In Gaussian approximation (neglecting terms of order ω^4 and higher),

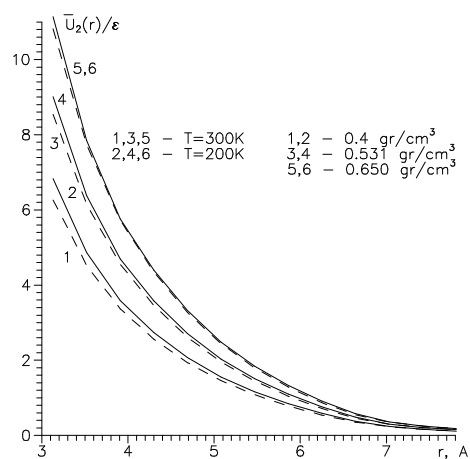


Figure 4. The effective pair-wise potential $\bar{U}_2(r)$ (4.9) for same values of density and temperature.

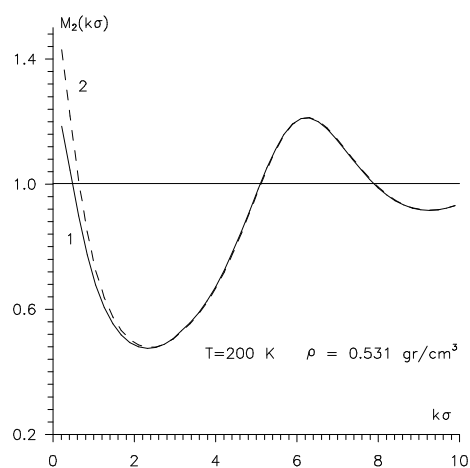


Figure 5. The influence of 3-body interactions on the structure factor of the reference system: 1 - taking into account 2- and 3-body interactions; 2 - taking into account 2-body interactions only.

the critical temperature corresponds to the condition $1 + \alpha(k)M_2(k) = 0$:

$$T_c = \frac{N}{V} \frac{|\Phi(0)|}{k_B} M_2(0) \quad , \quad (4.12)$$

It follows, that taking into account 3-body interactions can decrease a value the critical temperature by $\sim 20\%$. Let us notice, that approximately such value follows from the curves presented for the boundary of 2-phase region in paper [7].

In Fig. 6 an influence of 3-body forces on a direct correlation function of used in this paper realistic reference system for Ar is shown. The main effect consists in a displacement of the plot to the region of small values of the distance.

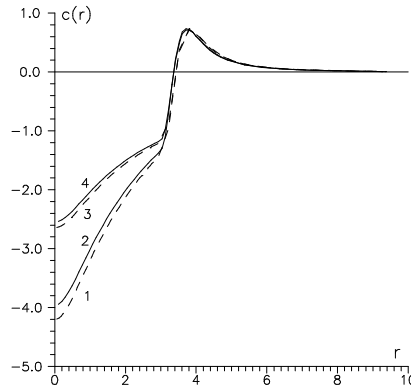


Figure 6. A direct correlation function of the realistic reference system for argon ($T=200\text{K}$): 1,2 - for the density 0.4 gr/cm^3 ; 3,4 - for the density 0.65 gr/cm^3 ; 1,3 - taking into account only 2-body interactions; 2,4 - taking into account 2- and 3-body interactions.

The essential for calculation the partition function by collective variable method [1] is a dependence of cummulant $M_3(k), M_4(k)$ on $k, k \in [0, B]$. When the above described realistic reference system is used, it is expedient by change of variables $\omega_{\vec{k}}, \rho_{\vec{k}}$, to transform the configuration integral Q_N into the form, which contains instead of cummulants M_3, M_4 in (4.4) another structure functions:

$$\bar{M}_3(k) = M_3(k, -k, 0) / (M_2(k))^{3/2} \quad ,$$

$$\bar{M}_4(k) = M_4(k, -k, 0, 0) / (M_2(k))^2 \quad .$$

One can see in Fig.7, that functions $\bar{M}_3(k), \bar{M}_4(k)$ conserve the main property of the of the cummulants M_3, M_4 - a weak dependence on wave vector at $k \leq B$. But a change in absolute values can be meanfull enough - about one and half times for $\bar{M}_4(k)$, and for $\bar{M}_3(k)$ even a sign can change. With a condition $\bar{M}_3(0) = 0$ a value of a critical density is related [2], therefore, it also will change.

Resuming let us notice, that although taking into account 3-body forces by including in the reference system demands rather long computer calculations, but another way of solution of this problem in the collective variable

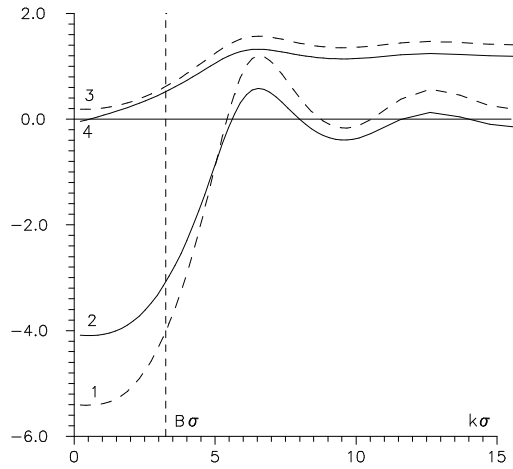


Figure 7. The influence of the 3-body interactions on the structure functions $\bar{M}_3(k)$ and $\bar{M}_4(k)$ of the reference system: 1,2 - $\bar{M}_4(k)$; 3,4 - $\bar{M}_3(k)$; Argon, $T = 200K, \rho = 0.531 \text{ gr/cm}^3$; 2,4 - taking into account 2- and 3-body interactions; 1,3 - taking into account 2-body interactions only.

method is, possibly, more complex task, if we will try to solve it on the level of accuracy, which may be reached by used in this paper treatment.

At the same time the above adduced estimations show, that quantitatively significant calculations for a set of the thermodynamical properties (a pressure, a structure factor at $k = 0$, the critical density) in the critical point vicinity can be received only with taking into account 3-body forces. Of course, it can partially provide the well-known effective 2-body potentials (Aziz-Slaman, Lennard-Jones, etc)

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ВРАХУВАННЯ ТРИЧАСТИНКОВИХ ВЗАЄМОДІЙ ПРИ ОПИСІ КРИТИЧНОЇ ПОВЕДІНКИ ПРОСТИХ РЕАЛЬНИХ РІДИН

I.M.Ідзик, В.О.Коломієць

Обґрунтовано необхідність врахування 3-частинкових взаємодій при описі поведінки реальних рідин поблизу критичної точки рідина-газ.

Запропоновано спосіб врахування 3-частинкових взаємодій в теорії критичної точки рідина-газ за методом колективних змінних, шляхом опису їх в системі відліку. Проаналізовано вплив 3-частинкових взаємодій на структурні функції системи відліку та на значення 3-го віріального коефіцієнта. В рамках узагальненої теорії середнього поля обчислені критичні амплітуди деяких термодинамічних функцій для аргону.