
FREE ENERGY FUNCTIONAL EXPANSION AS THE GENERALIZED APPROACH TO THE EQUATION OF STATE OF DENSE FLUIDS

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A version of the thermodynamic perturbation theory based on a scaling transformation of the partition function has been applied to the statistical derivation of the equation of state in a high-pressure region. Two modifications of the equations of state have been obtained on the basis of the free energy functional perturbation series. The comparative analysis of the experimental *PVT*-data on the isothermal compression for the supercritical fluids of inert gases has been carried out.

1. Introduction

Despite the essential progress achieved during the last decades in the theoretical description of the equations of state (EOS) for dense fluids [1–4], the equation describing the thermodynamics in wide intervals of pressures and temperatures, including the stability boundaries, still remains to be solved. In our study, we have developed a version of the thermodynamic perturbation theory to elaborate EOS within the framework of a generalized approach. This approach can be extended to all kinds of low-molecular fluids which can be described by rotationally averaged intermolecular potentials similar to the potential of atomic fluids such as Ne, Ar, Kr, and Xe. This was illustrated in [5], where the thermodynamic properties of water are described by means of an averaged potential.

A version of perturbation theory was first applied to the problem involving the equation of state by Zwanzig [6]. He proposed to treat the attractive forces in a fluid as a perturbation of a hard-core potential. Then this idea was studied by Smith and Alder [7] and by Frisch *et al.*

[8]. Mc Quarrie and Katz [9] combined the technique of Zwanzig and Rowlinson [10] and derived the equation of state which was satisfactory in the high-temperature region. Later, Barker and Henderson [11] examined the convergence of the perturbation expansion in the case of a square-well potential and then devised a version [12] of perturbation theory, which combined the techniques of Zwanzig [6] for treating the attractive potential and Rowlinson [10] to deal with the softness of a repulsive potential. As a result, they obtained the equation of state, which was in good agreement with a simulation (Monte-Carlo and molecular dynamics) and experimental data for argon in the wide range of temperatures and densities. We also mention the review by Barker and Henderson [13], where some perturbation theories applied to liquids have been discussed.

The basic idea of perturbation theory is that the potential of a system can be presented as a sum of two terms

$$U(r) = U_0(r) + \Delta U(r), \quad (1)$$

where $U_0(r)$ is the potential energy of a reference system, and $\Delta U(r)$ is the perturbation. Following Bogoliubov [14], we use the scale transformation of the dynamic variables

$$\bar{r} \rightarrow q\bar{r}, \quad q^3 = \frac{V}{V_0} = \frac{\rho_0}{\rho}, \quad \rho_0 = \frac{N}{V_0}, \quad (2)$$

where q is a scale factor, V and ρ are volume and the density. We assume that a variation of the volume corresponds to the variation of the intermolecular potential,

considering the potential energy $U(r)$ of the system as a scale transformed function $U_0(r) \rightarrow U_0(qr)$ and the difference $\Delta U = U_0(qr) - U_0(r)$ as a perturbation; whereas, $q = 1$ or $V = V_0$ should be treated as the zero-order approximation. Therefore, the main distinction of our approach from the those referred above involves the assumption that a functional form of the perturbed potential is identical to the potential of the reference system. Thus, we consider the deviation of the potential of the more compressed system from the potential of the less compressed system as a perturbation. The scale transformation of the variable \bar{r} by q times is equivalent to the variation of the molecular size σ by q^{-1} times

$$\sigma = \sqrt[3]{\frac{V_0}{V}} \sigma. \quad (3)$$

Hereafter, we will discuss a development of perturbation theory realized on the basis of a functional Taylor expansion of the free energy and will present some results obtained by treating the derived EOS and by the comparison with experimental *PVT*-data.

2. Functional Expansion of the Free Energy

As is well known for a system of N particles enclosed in a volume V at a given temperature T (canonical ensemble), the partition function can be written as

$$Q(V_0) = \frac{1}{N!} \int_{V_0} \dots \int_{V_0} d\bar{r}_1 \dots d\bar{r}_N \exp \left[- \sum_{i < j} \varphi(r_{ij}) / (kT) \right], \quad (4)$$

where $d\bar{r}_1 \dots d\bar{r}_N$ denote the set of spatial coordinates of N particles, $r_{ij} = |\bar{r}_i - \bar{r}_j|$, $i, j = 1, \dots, N$, $\varphi(r_{ij})$ - intermolecular potential. We restrict ourselves to a system of particles interacting through central pair forces, for which the total potential energy can be written as a sum of pairwise additive terms, i.e.,

$$U(\bar{r}_1, \dots, \bar{r}_n) = \sum_{1 \leq i < j \leq N} \varphi(|\bar{r}_i - \bar{r}_j|). \quad (5)$$

For a dense system, we can use the mean field approximation

$$\langle U(\bar{r}_1, \dots, \bar{r}_n) \rangle = U(\langle \bar{r}_1, \dots, \bar{r}_n \rangle)$$

According to work [6], the free energy in the second approximation can be written as the average perturbed energy with a canonical distribution function in the reference state

$$F(V) = F_0 + \langle \Delta U \rangle_0 - \frac{1}{2kT} \left[\langle \Delta U^2 \rangle_0 - \langle \Delta U \rangle_0^2 \right], \quad (6)$$

where F_0 is the free energy of the reference system, and $\langle \dots \rangle_0$ means the ensemble average with a distribution function in the reference state. As was stated above, we use a scale transformation [14] in order to describe the increase of linear dimensions of the system. Then it is easy to rewrite the expression for the partition function (4) as follows:

$$Q(q) = q^{3N} \frac{1}{N!} \int_{V_0} \dots \int_{V_0} d\bar{r}_1 \dots d\bar{r}_N \exp \left[- \sum_{i < j} \varphi(qr_{ij}) / (kT) \right]. \quad (7)$$

Here, V_0 is the initial value of volume corresponding to the reference state on the isotherm. After the scale transformation (2), the expression for the free energy can be presented as

$$F(V) = F_0 - 3kT \left\{ N \ln q + \frac{1}{3} \ln Q(V_0) \right\}, \quad (8)$$

where $F_0 = -\frac{3kTN}{2} \ln \frac{MkT}{2\pi\hbar^2}$, and M is the mass of a molecule. Further, we analyze namely expression (8), rather than (6). Our procedure is to expand $F_V(V_0) = -kT \ln Q(V_0)$ in the functional Taylor series in $\Delta e(r_{ij}) = e(r_{ij}) - e_0(r_{ij}) = e^{-\frac{\varphi(qr_{ij})}{kT}} - e^{-\frac{\varphi(r_{ij})}{kT}}$. As a result, we obtain the exact expression

$$F_V(V_0) = F_0(V_0) + \sum_{i < j} \int d\bar{r}_i d\bar{r}_j \Delta e(\bar{r}_{ij}) \frac{\delta F(V_0)}{\delta e(\bar{r}_{ij})} + \frac{1}{2!} \sum_{\substack{i < j \\ e < m}} \int d\bar{r}_i d\bar{r}_j d\bar{r}_l d\bar{r}_m \Delta e(r_{ij}) \Delta e(r_{lm}) \times \frac{\delta^2 F(V_0)}{\delta e(r_{ij}) \delta e(r_{lm})}, \quad (9)$$

where $F_0(V_0)$ is the free energy of the reference thermodynamic state. This is the basic expansion for a future consideration of the EOS for gases and liquids. The functional derivatives in (9) can be expressed via partial distribution functions as follows:

$$\frac{\delta F(V_0)}{\delta e(r_{ij})} = -\frac{kT}{V_0^2} \exp \left[-\frac{\varphi(qr_{ij})}{kT} \right] g_2(\bar{r}_i, \bar{r}_j), \quad (10)$$

$$\frac{\delta^2 F(V_0)}{\delta e(r_{ij}) \delta e(r_{lm})} = -\frac{kT}{V_0^4} \exp\left[-\frac{\varphi(qr_{ij}) + \varphi(qr_{lm})}{kT}\right] \times \\ \times [g_4(\bar{r}_i, \bar{r}_j, \bar{r}_l, \bar{r}_m) - g_2(\bar{r}_i, \bar{r}_j) g_2(\bar{r}_l, \bar{r}_m)] \quad (11)$$

with the proviso that $\{i, j\} \neq \{l, m\}$. We restrict by the first-order term and represent, for the sake of convenience, (9) in the form

$$F_V(V_0) = \exp(\zeta \hat{\Lambda}) F(V_0), \quad (12)$$

where $\hat{\Lambda} = \sum_{i<j} \int d\bar{r}_i d\bar{r}_j \Delta e(r_{ij}) \frac{\delta}{\delta e(r_{ij})}$, and ζ is an auxiliary parameter introduced for indicating the powers of $\Delta e(r_{ij}) = e^{-\frac{\varphi(qr_{ij})}{kT}} - e^{-\frac{\varphi(r_{ij})}{kT}}$. In calculations, we set $\zeta = 1$. In general, expression (12) is inappropriate for specific calculations, but it is an important initial point for the resummation of series in the problem concerning the determination of the EOS of a dense fluid.

In the high-pressure region, Eq. (12) must be considered with regard for the smallness of the dimensionless parameter Δ , given by the relation $\Delta = \frac{V_0 - V}{V_0}$. The relation $\Delta \ll 1$ works properly in a wide pressure range, where the inequality $\rho kT \beta_T = \alpha \ll 1$ holds, where β_T is the isothermal compressibility. This statement follows from the approximate equality $\Delta \approx \frac{P_0 \alpha}{\rho kT} \frac{P - P_0}{P_0}$, which is accurate for dense fluids in a wide interval of pressures and temperatures, but far from the stability boundary points. For illustrative purposes, the values of parameter Δ in the certain ranges of pressures and temperatures are presented in Table 1 for various substances.

It should be noted that similar small parameters of the type $\frac{V_0 - V}{V}$ or $\frac{V_0 - V}{V_0}$ have been already proposed by Bridgman [15] and Slater [16] to describe the elastic properties of alkali metals. Indeed, one can see (Table 1) that Δ has a small value and varies weakly in fairly wide ranges of pressures and temperatures. In order to derive the equation of state of dense fluids, it is necessary to choose the initial (reference) value of V_0 in the region of thermodynamic variables, where the inequality $\Delta \ll 1$ holds.

3. Realistic Potentials

At first, we consider a system with pair potential written as the sum

$$\varphi(r) = \Phi(r) + \psi(r) \quad (13)$$

of a short-range function $\Phi(r)$ corresponding to repulsive forces and $\psi(r)$ corresponding to attractive forces.

The latter is smoother than $\Phi(r)$. For the attractive potential, we can use the function $\psi(r) \sim r^{-n}$, with $n = 6$ or 7 (the Lennard-Jones or Casimir–Polder potential model). Then the perturbation series (12) can be written as

$$F_V(V_0) = \exp(\zeta \hat{\Lambda}_\Phi + \xi \hat{\Lambda}_\psi) F(V_0), \quad (14)$$

where $\hat{\Lambda}_\Phi = \sum_{i<j} \int d\bar{r}_i d\bar{r}_j [e^{-\frac{\Phi(qr_{ij})}{kT}} - e^{-\frac{\Phi(r_{ij})}{kT}}] \frac{\delta}{\delta e(r_{ij})}$ is the operator that corresponds to the repulsive part of the potential. Since the attractive potential is a smooth function, the operator $\hat{\Lambda}_\psi = \sum_{i<j} \int d\bar{r}_i d\bar{r}_j [\psi(qr_{ij}) - \psi(r_{ij})] \frac{\delta}{\delta \psi(r_{ij})}$ is an expansion in the difference of $\Delta \psi(r_{ij}) = \psi(qr_{ij}) - \psi(r_{ij})$, and the parameter ξ has the same meaning as the parameter ζ . Then the expression for the first-order functional derivative can be given as

$$\frac{\delta F(V_0)}{\delta \psi(r_{ij})} = \frac{kT}{V^2} g_2(\bar{r}_i, \bar{r}_j). \quad (15)$$

At the calculation of functional derivatives, the condition $q = 1$ means that the distribution functions $g_2(\bar{r}_i, \bar{r}_j)$ depend on the value of V_0 on the isotherm and must be calculated in the reference state. Thus, we can now write the free energy as a series

$$F(V) = F_0 - 3NkT \ln q + F_0(V_0) + \frac{kT}{2} [\Omega + \Xi], \quad (16)$$

where

$$\Omega = -\sum_{i<j} \int d\bar{r}_i d\bar{r}_j \left[e^{-\frac{\Phi(qr_{ij})}{kT}} - e^{-\frac{\Phi(r_{ij})}{kT}} \right] \times \\ \times \frac{\exp\left[-\frac{\Phi(qr_{ij})}{kT}\right] g_2(\bar{r}_i, \bar{r}_j)}{V_0^2} \quad (17)$$

and

$$\Xi = \sum_{i<j} \int d\bar{r}_i d\bar{r}_j [\psi(qr_{ij}) - \psi(r_{ij})] \frac{g_2(\bar{r}_i, \bar{r}_j)}{V_0^2}. \quad (18)$$

Table 1. Values of the parameter Δ

Substance	Δ	Pressure	Temperature
neon			
argon	0.02 ÷ 0.04	50–700 MPa	100–400 K
krypton			
xenon			
nitrogen	0.02 ÷ 0.06	10–2200 MPa	120–900 K

For the homogeneous system, we omit the indices i and j and use $g_2(r)$ instead of $g_2(\bar{r}_i, \bar{r}_j)$. Differentiating series (16) with respect to V and using the approximate equality for the attractive part of the potential $\psi(qr) - \psi(r) \approx \frac{d\psi}{dr} \bar{r} \frac{\Delta}{3}$, which works properly at $\Delta \ll 1$, we obtain the expression for the pressure

$$P - P_0 = \frac{NkT\Delta V}{V} - \frac{\rho_0^2 V_0}{6V} \int_V g_2(r) \exp[\beta(-\Phi(qr) + \Phi(r))] \times \frac{d\Phi(qr)}{dr} r d\bar{r} + \frac{\rho_0^2}{6} \int_V g_2(r) \frac{d\Phi(qr)}{dr} r d\bar{r}. \quad (19)$$

It should be noted that the term with the attractive potential $\psi(r)$ implicitly appears in the expression for the pressure in the reference state

$$P_0 = \frac{NkT}{V_0} - \frac{\rho_0^2}{6} \int_V g_2(r) v_0(r) d\bar{r}, \quad (20)$$

where

$$v_0(r) = -\frac{d\phi(qr)}{dr} \bar{r} \Big|_{q=1} = -\nabla\phi(r) \bar{r} \quad (21)$$

is the virial of intermolecular forces in the reference state.

At the next stage, in order to evaluate the terms of Eq. (19), we should specify the functional form of the repulsive potential $\Phi(r)$. We assume that $\Phi(r)$ is a homogeneous function with the homogeneity exponent m , the Euler's theorem of homogeneous functions being applied to the potential function

$$\Phi(q\bar{r}_1, \dots, q\bar{r}_n) = q^{-m} \Phi(\bar{r}_1, \dots, \bar{r}_n). \quad (22)$$

For example, function (5) that describes the sum of pair potentials within the soft-sphere model takes the form

$$\Phi(r) = \varepsilon \left(\frac{\sigma}{r}\right)^m. \quad (23)$$

We may now rewrite Eq.(19) in the form

$$P - P_0 = \frac{NkT\Delta}{V} + [q^{-m} - 1] [B(T) + P_0] -$$

$$-q^{-m} \frac{\rho_0^2 V_0}{6V} \int_V g_2(r) e^{[\beta(-\Phi(qr) - q^3\Phi(r))]} e^{[\beta\Phi(qr)]} \times$$

$$\times \frac{d\Phi(r)}{dr} r d\bar{r}. \quad (24)$$

The parameter $B(T)$ is the difference between the cohesion and the ideal gas pressure in the reference state,

$$B(T) = -\frac{\rho_0^2}{6} \int_V g_2(r) \frac{d\Phi(r)}{dr} r d\bar{r} - P_0 = P_0^a - \frac{NkT}{V_0}, \quad (25)$$

P_0^a is the pressure corresponding to the repulsive forces in the reference state, and m is the homogeneity exponent, which does not depend on the thermodynamic variables within the framework of the statistical theory of liquids. Unfortunately, the situation is more complicated with regard for the integral term in (24). It is impossible to calculate this term in an explicit form using some model potentials and the approximate form of the function $g_2(r)$. Indeed, the shift of the first maximum of the radial distribution function by a few percent (2-3%) leads to the variation of pressure, i.e. the values of the integrals in (24), by two or three orders of magnitude [17]. However, some conclusions about the functional form of this term can be made under the assumption that, for a sufficiently steep repulsive potential, the function $e^{-\beta\Phi(r)}$ behaves as the Heaviside step function $\Theta(r - \sigma)$. In a similar way, $e^{-\beta\Phi(qr)}$ at $q \leq 1$ behaves as the function $\Theta(r - \sigma/q)$. Thus, their difference at $\Delta \ll 1$ is a function concentrated on the interval $[\sigma, \sigma/q]$ with the length that satisfies the relation $l = O(\Delta V) = O([1 - q])$. This yields the relation

$$\frac{\rho_0^2 V_0}{6V} \int_V g_2(r) e^{[\beta(-\Phi(qr) - q^3\Phi(r))]} e^{[\beta\Phi(qr)]} \frac{d\Phi(r)}{dr} \bar{r} dr = = D(T) (1 - q) + O(1 - q) \quad (26)$$

and the equation of state

$$P - P_0 = \frac{NkT\Delta}{V} + [q^{-m} - 1] [B(T) + P_0] -$$

$$-q^{-m} D(T) (1 - q). \quad (27)$$

The parameters $B(T)$, m , and $D(T)$ are constants on the isotherm and can be calculated as adjustable parameters. The analysis of the experimental PVT -data revealed that the term $q^{-m} D(T) (1 - q) \approx 0$ and, therefore, can be neglected in the PVT -data processing under the isothermal compression. Finally, we reduce Eq. (27) to the equation of state

$$P - P_0 = \frac{NkT\Delta}{V} + [q^{-m} - 1] [B(T) + P_0]. \quad (28)$$

Another modification of this equation has been derived, by assuming that the role of repulsive forces is dominant in the high-pressure region (where the isothermal compressibility β_{to} is small or $\Delta \ll 1$), and we use the realistic potential (13) without attractive part. So, we obtain

$$P = \frac{NkT}{V} + P_0^r(T) \left(\frac{V_0}{V} \right)^{\frac{m}{3}}, \quad (29)$$

where $P_0^r(T)$ is the pressure, which is caused by repulsive forces between molecules and is considered as an adjustable parameter. It should be noted that both Eqs. (28) and (29) can be obtained on the basis of the first-order perturbation series close to series (6) (Ref. [6]). We will outline briefly some steps in the derivation of Eq. (29) on the basis of expansion (6). By using a scaling transformation, the first-order approximation of series (6) will be rewritten as

$$F(V) - F(V_0) = 3NkT \ln q - \langle \Delta U_r \rangle, \quad (30)$$

where $F(V_0)$ is the free energy of a reference state, and ΔU_r is a perturbation of the repulsive potential. To differentiate the free energy with respect to the volume, it is necessary to express the potential function as a function of the volume, so we present a perturbation of the repulsive potential in the form

$$\langle \Delta U_r \rangle = \left\langle \frac{\partial U_r}{\partial \sigma} \Delta \sigma \right\rangle, \quad (31)$$

where σ is a molecular size, $\Delta \sigma = \frac{\sigma' - \sigma}{\sigma}$. Using (3), we can reduce $\Delta \sigma$ to the approximate equality $\Delta \sigma \approx \frac{1}{3} \Delta$ and write expression (31) as

$$\langle \Delta U_r \rangle = -\frac{\Delta}{3} \sum \langle \nabla U_r \cdot \mathbf{r} \rangle. \quad (32)$$

Having differentiated the free energy (30) with respect to V ,

$$P = \frac{NkT}{V} - \frac{1}{3V_0} \left[\sum \langle \nabla U_r \cdot \mathbf{r} \rangle \right], \quad (33)$$

and taking the virial theorem and the property of homogeneity for the potential function (22) into account, we obtain the equation of state in the form (29).

4. Analysis of Experimental Data

In order to obtain the values of adjustable parameters m , $B(T)$, and P_0^r under the isothermal compression, we

used the experimental PVT -data. As far as it was of interest to prove namely the extrapolation capabilities of the equations of state, the values of parameters m and P_r were considered as fitting constants. The analysis of the data with the use Eqs. (28) and (29) was carried out in two stages. At first, the parameters m , $B(T)$, and P_0^r were calculated at three reference points P_0 , P_1 , and P_2 (since P_0 is the pressure in the reference state, we choose any of those points for P_0 , where the isothermal compressibility became as small as desired or the parameter $\Delta \ll 1$; usually, it was equal to about 50 MPa). The values of the parameters obtained in this way were then substituted into Eq. (28) or Eq. (29) for the calculation of a volume on the isotherm and the comparison with experimental data.

The analysis carried out for supercritical fluids of inert gases (Figure) showed that EOS (28) and (29) can be used successfully. It turns out that both Eqs. (28) and (29) reveal good extrapolation properties in describing the isothermal compression in the range of the thermodynamic variables, where the isothermal compressibility is low, which corresponds to the pressure interval 50–1000 MPa and temperatures 200–700 K. For comparison, we used the experimental data from [1, 18].

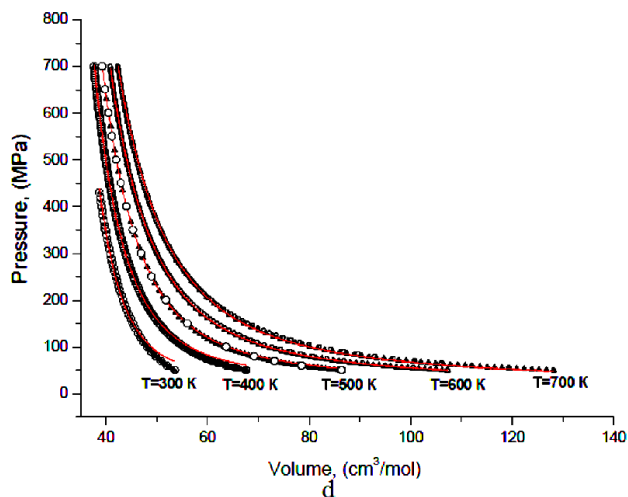
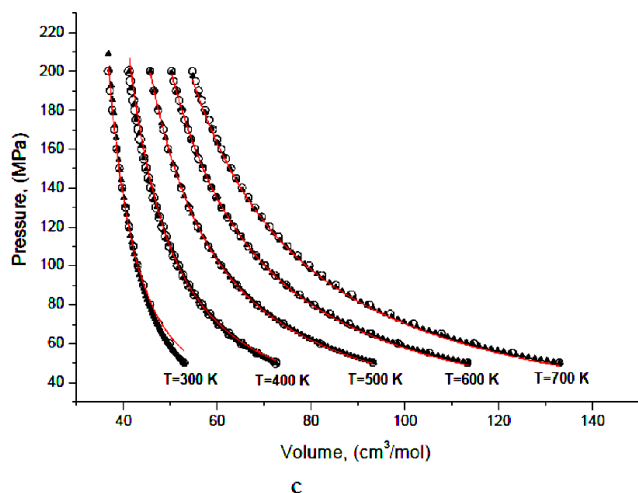
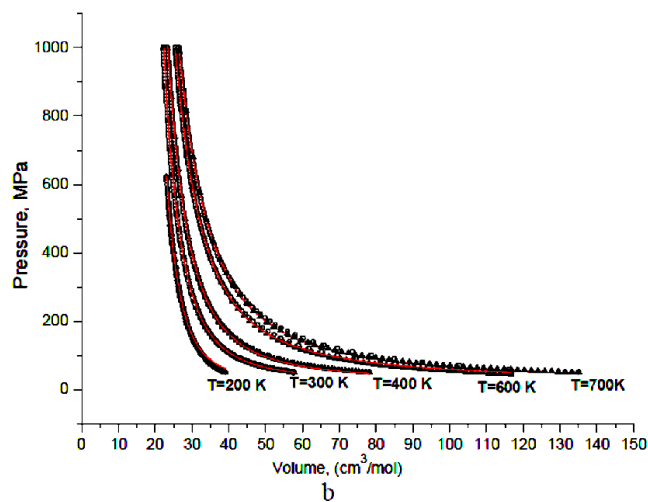
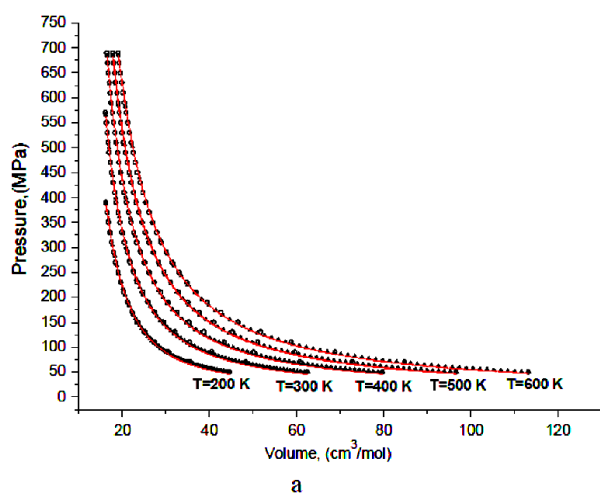
The values of adjustable parameters of EOS (29) are given in Table 2. For illustrative purpose, we present only the parameters of Eq. (29), so their values demonstrate a similar behavior.

5. Conclusion

Thus, the functional expansion of the free energy has given a possibility to obtain, at a certain choice of the parameter expansion, the equations of state for dense fluids ($\Delta \ll 1$). The question of special interest is the variation of the homogeneity parameter m with the temperature. This parameter can hypothetically be considered as a softness parameter within the framework of the soft sphere potential model. However, to verify this, the computer simulations of a series of isotherms with a

Table 2. Values of the parameters of Eq. (29) for supercritical fluids of inert gases on isotherms

Substance	Parameter	300 K	400 K	600 K	700 K
Ar	m	15.18	13.5	11.25	10.8
	$P_0^r(T)$ MPa	7.25	3.87	2.69	2.23
Kr	m	23.13	16.8	11.1	3.33
	$P_0^r(T)$ MPa	8.51	5.39	4.90	4.66
Xe	m	27.6	20.07	15.54	14.25
	$P_0^r(T)$ MPa	19.87	12.37	3.88	2.94



Analysis of the experimental PVT -data for supercritical fluids of inert gases: a – neon, b – argon, c – krypton, d – xenon, (○) – experiment; (▲) – Eq. (28); (line) – Eq. (29)

suitable choice of other parameters of the potential have to be performed. In connection with this, one should refer to a number of works [19–21], in which values of this parameter have been varied as $m = 4, 6, 9, 12, 15$, or to work [22], in which the value of softness parameter in the simulations ranged from 18 to the unusually high value of 288. This fact was noted earlier in [23], where the analysis of the temperature dependence of the second and third virial coefficients for argon, krypton, and xenon in view of the equation of state for these substances led to the conclusion that the repulsive potential can be presented in the form

$$\Phi(r) = \varepsilon \left(0.331 \left(\frac{r_m}{r} \right)^{28} + 2.072 \left(\frac{r_m}{r} \right)^{18} \right),$$

where r_m is the position of a minimum of the potential, and the values of softness parameters are 28 and 18. Specifically, this question has been already discussed in our previous articles [24–26], where a modification of the repulsive potential was proposed in the form of a power series

$$U(r) = 4\varepsilon \left[\left(\sigma_1 n^{1/3} \right)^{16} + \left(\sigma_2 n^{1/3} \right)^{21} + \left(\sigma_3 n^{1/3} \right)^{24} \right],$$

where, σ_1 , σ_2 , and σ_3 are effective intermolecular parameters, and $\langle r \rangle = n^{-1/3}$. This formula was derived on the basis of the analysis of statistical equations of state, the high-frequency asymptotics of a depolarized light scattering, and the processing of the temperature

dependences for one-particle contributions to the self-diffusion coefficient.

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ФУНКЦІОНАЛЬНИЙ РОЗКЛАД ВІЛЬНОЇ ЕНЕРГІЇ ЯК УЗАГАЛЬНЕНИЙ ПІДХІД ДО РІВНЯННЯ СТАНУ ГУСТИХ ФЛЮЇДІВ

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Резюме

Використано варіант термодинамічної теорії збурень, заснований на масштабному перетворенні статистичної суми, для отримання статистично обґрунтованого рівняння стану в області високих тисків. На основі функціонального розкладу вільної енергії отримано дві модифікації рівняння стану і проведено порівняльний аналіз їх кількісного опису експериментальних *PVT*-даних для суперкритичних флюїдів інертних газів.