Equation of state for water in the small compressibility region

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We derive the equation of state for supercritical fluids in the framework of the Sutherland and Katz potential models using the free energy perturbation expansion. The derived equation of state quantitatively agrees with experimental data on isothermal compression of water in the high pressure region. It establishes an explicit relationship between the thermodynamic experimental data and the parameters of the molecular potential. This can be used in calibration protocols for simulation forcefields for the high pressure regions.

1. Introduction

Deriving the equation of state (EoS) for water in a wide range of pressure and temperature remains a challenging open problem, especially in the high pressure region. In the recent papers [1-4] devoted to the water EoS this problem was solved by fitting multiparameter formulae with such a large number of adjustable parameters that it approaches the number of experimental points. These methods are not based on reliable statistical mechanic foundations and the applicability of these EoS is restricted. If the functional form of the EoS and their parameters are applicable to other substance or solutions is an open question.

In comparison with the majority of one-component liquids, water reveals many unusual properties in its normal and supercooled states. The analysis of the diffusion peak of quasi-elastic incoherent neutron scattering and kinematic shear viscosity of water has shown that the global H-bond network disintegrates into an ensemble of weakly interacting clusters: dimers, trimers, tetramers etc [9,10,11,12,13]. It was also shown [14] that in the supercritical region the properties of water are determined by the averaged spherically symmetrical potential. Therefore, it is reasonable to use for

water in the high pressure region such well-known models as Lennard-Jones, Buckingham, Sutherland or Katz potentials.

In this paper we derive the EoS for a supercritical fluid within the framework of the Sutherland or Katz potentials. In our previous work []we used a new version of the thermodynamic perturbation theory (TPT) originally proposed by Sysoev []. The main feature of the proposed TPT is in the assumption that the functional form of the perturbed potential is identical to the potential of the reference system and, therefore, the deviation of the potential of the more compressed system from the potential of the less compressed system is considered as the perturbation. On this basis the concept of a reference thermodynamic state has been developed. A functional expansion of the free energy gave the possibility to derive, at a certain choice of the parameter expansion, two EoS modifications within the framework of a realistic and a "soft" sphere potential models. As it was shown in [] these EoS correctly described the isothermal compression for supercritical fluids of inert gases.

Following [], we here use the free energy perturbation expansion

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

where $\Delta e(r_{ij}) = e(r_{ij}) - e_0(r_{ij}) = e^{-\frac{\varphi(qr_{ij})}{kT}} - e^{-\frac{\varphi(r_{ij})}{kT}}$, $\phi\left(qr_{ij}\right)$ is the potential of the perturbed system and q is a scale factor, $\overline{r} \to q\overline{r}, q = \sqrt[3]{\frac{V}{V_0}}$.

Equation (1) can be transformed into the expression for pressure (the details are given in []):

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

This expression was obtained within the framework of a realistic potential model that can be presented in the general form

$$\varphi(r) = \Phi(r) + \psi(r), \qquad\qquad\qquad\qquad\qquad\qquad\qquad (3)$$

where $\Phi(r)$ is the repulsive part of the potential and $\psi(r)$ is its attractive part.

2. The equation of state within the framework of Sutherland and Katz potential models

In the case of short-range potentials the expression for pressure can be rewritten in the form

$$P = \frac{NkT}{V} - \frac{\rho_0^2 V_0}{6V} \int_V g_2(r) f(r) \upsilon(r) d\bar{r} - \frac{\rho_0^2 V_0}{6V} \int_V g_2(r) \upsilon_0(r) d\bar{r}, \tag{4}$$

where $f(r) = e^{[\beta(-\varphi(qr)-\varphi(r))]} - 1$, $\upsilon(r) = -\bar{\nabla}\varphi(qr)\bar{r}$ is the virial of intermolecular forces and $\upsilon_0(r) = -\bar{\nabla}\varphi(qr)\bar{r}\big|_{q=1} = -\bar{\nabla}\varphi(r)\bar{r}$ is the virial of intermolecular forces in the reference state. Taking into account the expression for pressure in the reference state

$$P_0 = \frac{NkT}{V_0} - \frac{\rho_0^2}{6} \int_V g_2(r) \upsilon_0(r) d\bar{r}. \tag{5}$$

We rewrite (4) as

$$P = \frac{V_0 P_0}{V} - \frac{\rho_0^2 V_0}{6V} \int_V g_2(r) f(r) \upsilon(r) d\bar{r} - \frac{\rho_0^2 V_0}{6V} \int_V g_2(r) \Delta\upsilon(r) d\bar{r}. \tag{6}$$

Eq.(6) can be expressed in the terms of $\Pi = \dfrac{P - P_0}{P_0}$ or $\Delta = \dfrac{V_0 - V}{V_0}$, using of the approximate equality $\dfrac{V_0}{V} \approx 1 + \Delta$

$$\Pi = \Delta + (1 + \Delta)(L + K), \tag{7}$$

where

$$L = -\frac{\rho_0^2}{6P_0} \int_V g_2(r) f(r) \upsilon(r) d\bar{r}, \tag{8}$$

$$K = -\frac{\rho_0^2}{6P_0} \int_V g_2(r) \Delta\upsilon(r) d\bar{r}. \tag{9}$$

Now the problem of deriving EoS reduces to the evaluation of the integrals (8) and (9). We first consider the Sutherland potential

$$\varphi(r) = \begin{cases} \infty, & r < d_0 \\ -cr^{-m}, & r > d_0, \end{cases} \tag{10}$$

d_0 is the molecular diameter and the potential well depth ε is defined by $\varepsilon = \dfrac{c}{d_0^m}$. Then $\varphi(qr)$ is written as

$$\varphi(qr) = \begin{cases} \infty, & r < d_0 \\ -c\left(\dfrac{V_0}{V}\right)^{m/3} r^{-m}, & r > d_0, \end{cases} \tag{11}$$

where $d = \sqrt[3]{\dfrac{V_0}{V}}\,d_0$. We calculate the singular force $-\dfrac{d\varphi(r)}{dr}$ following [18] and obtain

$$\upsilon(\bar{r}) = -kT\delta(r-d)r + cm\left(\dfrac{V_0}{V}\right)^{m/3} r^{-m}\Theta(r-d), \tag{12}$$

$$\Delta\upsilon(\bar{r}) = -kT\left[\delta(r-d) - \delta(r-d_0)\right]r + cmr^{-m}\left[\left(\dfrac{V_0}{V}\right)^{m/3}\Theta(r-d) - \Theta(r-d_0)\right], \tag{13}$$

$\delta(r-d)$ is the Dirac delta function and $\Theta(r-d)$ is the Heaviside step function. The expression for L takes the form

$$L = -\dfrac{2\pi\rho_0^2}{3P_0}\left[-kTg_2(d)f(r\downarrow d)d^3 + cm\left(\dfrac{V_0}{V}\right)^{m/3}\int_d^\infty g_2(r)r^{-m+2}f(r)dr\right], \tag{14}$$

in which $f(r\downarrow d) = \lim\limits_{r\to d+0} f(r)$ [18]. The integral in (14) can be evaluated if we assume $g_2(r) \approx e^{-\beta\varphi(r)}$, then in view of $\dfrac{V_0}{V} \approx 1 + \Delta$ we have

$$cm\left(\dfrac{V_0}{V}\right)^{m/3}\int_d^\infty g_2(r)r^{-m+2}f(r)d = (-\beta)^{(3-m)/m}c^{3/m}\left[\left(\dfrac{V_0}{V}\right)^{2m/3}\gamma(x,y) - \left(\dfrac{V_0}{V}\right)^{m/3}\gamma\left(x, y\left(\dfrac{V}{V_0}\right)^{m/3}\right)\right]. \tag{15}$$

Here $\gamma(x,y)$ is the upper incomplete gamma function with $x = \dfrac{m-3}{\beta}$, $y = -\dfrac{\beta c}{d_0^m}$.

Using the same assumptions for the integral (9) we obtain

$$K = \dfrac{2\pi\rho_0^2}{3P_0}\left[kT\left[g_2(d)d^3 - g_2(r\downarrow d_0)d^3\right] - (-\beta)^{(3-m)/m}c^{3/m}\left[\left(\dfrac{V_0}{V}\right)^{2m/3}\gamma\left(x, y\left(\dfrac{V}{V_0}\right)^{m/3}\right) - \gamma(x,y)\right]\right], \tag{16}$$

where $g_2(r\downarrow d_0) = \lim\limits_{r\to d+0} g_2(r)$. Taking into account the smallness of the parameter Δ, we can expand $g_2(d)$ at a point d_0 using the Taylor series

$$g_2(d) \approx g_2(r\downarrow d_0)\left[1 + C(T)\Delta\right], \tag{17}$$

where $C(T) = \dfrac{d_0}{3} \dfrac{\partial \ln g(r)}{\partial r}\bigg|_{r \to d_0+0}$ is the function of the reference state. Since in the $\Delta \ll 1$

approximation $f(r \downarrow d) = \exp\left(\dfrac{\beta cm\Delta}{3d_0^m}\right) - 1$ and $\dfrac{\Delta}{\Pi} \ll 1$. In the case of small

compressibility Eq.(7) takes the form

$$P = P_0 + \left[B(T) + P_0\right] \cdot \left[\left(e^{\frac{\Delta}{A(T)\cdot T}} - 1\right)\left[1 + \Delta\left(2 + C(T)\right)\right] - \left(1 + C(T)\right)\Delta + 2\left(1 + C(T)\right)\Delta^2\right] + \Gamma, (18)$$

Γ is the term which comprises the incomplete gamma function

$$\Gamma = \dfrac{2\pi\rho_0^2}{3P_0}\left[(-\beta)^{(3-m)/m} c^{3/m}\left[\left(\dfrac{V_0}{V}\right)^{2m/3} - 1\right]\gamma(x,y)\right]. \tag{19}$$

For the Sutherland model it is expressed through the second virial coefficient $B_2(T)$:

$$\Gamma = \dfrac{kT\rho_0}{P_0}\left[\left(\dfrac{V_0}{V}\right)^{2m/3} - 1\right]\left[B_2(T) + \dfrac{2\pi d_0^3}{3}\right]. \tag{20}$$ The

experimental data for some dense fluids (water, argon, neon, krypton) show that this

term can be neglected at the condition $\Pi \approx 10^3$ with the accuracy of 1%. There is a

wide range of values of thermodynamic variables where the isothermal

compressibility is low ($\Delta \ll 1$) corresponding to the pressure interval 100 – 2200

MPa. The term $2(1 + C(T))\Delta^2$ can also be ignored with the same accuracy. Finally, we

arrive at the equation of state in the framework of the Sutherland model:

$$P = P_0 + \left[B(T) + P_0\right] \cdot \left[\left(e^{\frac{\Delta}{A(T)\cdot T}} - 1\right)\left[1 + \Delta(2 + C(T)\right] - \Delta\left(1 + C(T)\right)\right]. \tag{21}$$

The expression (21) is a three-constant equation of state with the adjustable

parameters $B(T)$, $C(T)$ and $A(T)$. The parameter $B(T)$ depends on temperature. It is

related to the pressure caused by attractive forces

$$B(T) = \dfrac{2\pi\rho_0^2}{3_0} kTg_2(r \downarrow d_0)d_0^3 - P_0 = P_0^r - P_0 = P_0^a - \dfrac{NkT}{V_0}, \tag{22}$$

Where P_0^r is the pressure caused by the repulsive forces in the reference state and P_0^a

is the part of pressure due to the attractive forces. The parameter $A(T)$, within the

framework of the Sutherland model, is expressed by the formula

$$A(T) = \frac{3 \cdot d_0^{\,m} \cdot k}{mc}.$$

(23)

If we use the Katz potential model

$$\Phi(\bar{r}) = \begin{cases} \infty, & r < d_0 \\ -\dfrac{aR_0^3}{4\pi} e^{-rR_0}, & r > d_0 \end{cases},$$

(24)

where R_0 is the interaction radius of the attractive forces, $\dfrac{aR_0^3}{4\pi}$ is the interaction constant, Eq.(21) retains its functional form, but the parameter $A(T)$ is defined by the formula

$$A(T) = \frac{12 \cdot \pi d_0^{\,m} \exp\left(R_0 d_0\right) \cdot k}{d_0 R_0^4 a}.$$

(25)

The parameters $B(T)$ and $C(T)$ are defined in a similar way.

3. Experimental PVT data analysis

We used the technique from the previous paper [] to process the PVT data and evaluate the EoS parameters. It turns out that Eq.(21) yields good agreement with the experimental PVT data under the extrapolation to the high pressure region. The results of the comparison are presented in Fig. 1.
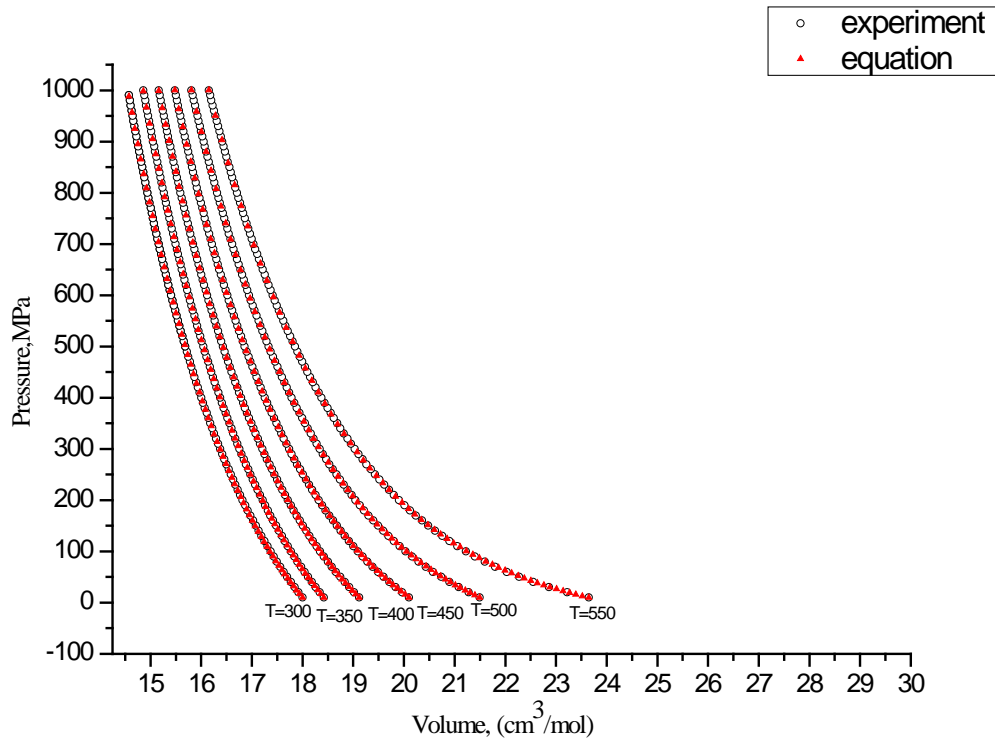
Fig.1. The experimental and theoretical PVT data for supercriticlal water.

Table 1. The values of the EoS parameters.

T,K	300	350	400	450	500	550
$B(T)$, MPa						
$C(T)$						
$A(T)$, K^{-1}	0,0042	0,0037	0,0032	0,0027	0,0024	0,002

Of special interest is the values of the parameter $A(T)$ because it is related to the parameters of the potential, formulae (23), (25) for the Sutherland and Katz models. On the basis of (23) we evaluated the values of the potential well depth ε at a fixed value $m = 12$ common-used in the Lennard-Jones model (Tab.2).

Table 2. The values of ε (Sutherland potential) at $m=12$ in the temperature interval 300-550K.

T,K	300	350	400	450	500	550
ε, J$\cdot 10^3$/mole	0,493	0,562	0,650	0,769	0,866	1,038

If we fix the value of $\varepsilon = 0{,}650$ kJ/mole, which corresponds to the SPC/E model [], we obtain the variation of the softness parameter m with temperature. In general, fixating ε at the values for well-known potential models, such as ,[] , [] , [], leads to the variation of the softness parameter m with temperature within the framework of the Sutherland potential.

4. Conclusion

The approach developed on the basis of the free energy perturbation expansion and a new version of TPT resulted in some universality (generalisation) for the EoS statistical foundation of low weight molecular supercritical fluids. The concept of the thermodynamic reference state implies that an initial state (P_0 , V_0) on the isotherm corresponds to the reference system with unperturbed potential and every subsequent point on the isotherm (P_1,V_2),… (P_n,V_n) corresponds to the system with the perturbed potential at isothermal compression of the system. This modification of TPT allowed obtaining the EoS which exhibits good results under the extrapolation to the high pressure region. Most importantly, it establishes a relationship between the parameters of the model potential and the thermodynamic properties of substances. This relationship gives estimations for the values of the parameter ε (Tab. 2). Interestingly, the values are of the same order of magnitude as the values of many well known water models (SPC/E,). However, the temperature dependence of ε in this region of thermodynamic variables remains to be explained. Nevertheless, this data can be used as additional information for calibrating potential parameters used in simulations.

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