Structure and Property Prediction of Sub- and Super-Critical Water[1]

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ABSTRACT

In this report two approaches are presented to predict the structure and PVT behavior of associating fluids with emphasis on water. One approach is the development of equations of state based on the analytic chain association theory (ACAT). An associating fluid is assumed to be a mixture of monomer, dimer, trimer, etc., for which the composition distribution are obtained. The resulting equations are simple enough to be used for PVT calculations.

The second approach is the development of an analytical expression for the first shell of the radial distribution function (RDF). This expression satisfies the general functionality of the RDF with respect to intermolecular potential, temperature and density as well as all the limiting values of RDF at high temperature and dilute gas, and infinite separation. This model has initially been applied to simple potential energy functions, such as the Lennard-Jones and Kihara functions. The results have been reported to be in good agreement with the available computer simulation data of RDF for these fluid models and the experimental data for argon.

Finally, an effective Kihara pair potential is derived for water which incorporates the hydrogen bonding using the ACAT. The potential parameters of this model are determined to predict the first shell of the RDF data for water at various subcritical temperatures and densities. The predicted results for water at near critical and supercritical conditions are shown to be in agreement with the data obtained by neutron diffraction experiments and with the simulation data.

KEY WORDS: equation of state; radial distribution function; potential energy function; association.

1. INTRODUCTION

The key feature of water molecules is the hydrogen bonding which refers to the formation of chemical aggregates or polymers. Nemethy and Scherga [1], indicated through their studies on water structure that hydrogen bonding plays an important role in forming aggregates that can reach sizes of up to one hundred H_2O molecules at room temperature. We have represented the association of water molecules due to hydrogen bonding with the following chain reaction [2].

$$(H_2O)_i + (H_2O)_1 \overset{K_i(T)}{\longrightarrow} (H_2O)_{i+1} \qquad i=1,2,\ldots,\infty \qquad (1)$$

The equilibrium constant of the above reaction can be expressed as

$$K_i = [x_{i+1}/(x_i\, x_1)]\,[\gamma_{i+1}/(\gamma_i\, \gamma_1)] = [x_{i+1}/(x_i\, x_1)]\,\Gamma_i \qquad i=1,2,\ldots,\infty \qquad (2)$$

where x_i and γ_i are the mole fraction and activity coefficient of $(H_2O)_i$, respectively, and Γ_i is the ratio of activity coefficients. For simplicity, we assume that all K_i 's and all Γ_i's are the same, (i.e. $K=K_1=K_2=\ldots=K_i=\ldots$ and $\Gamma=\Gamma_1=\Gamma_2=\ldots=\Gamma_i=\ldots$). Let us define κ as the ratio of K/Γ,

$$\kappa \pounds K/\Gamma = x_{i+1}/(x_i\, x_1) \qquad i=1,2,\ldots,\infty \qquad (3)$$

We may extend Eq. (3) to different species as follows:

$$\begin{aligned} x_2 &= \kappa\, x_1^2 \\ x_3 &= \kappa\, x_2\, x_1 = \kappa^2\, x_1^3 \\ &\vdots \\ x_{i+1} &= \kappa\, x_i\, x_1 = \kappa^i\, x_1^{i+1} \\ &\vdots \end{aligned} \qquad (4)$$

Since the summation of all mole fractions is unity, then

$$\sum_{i=0}^{\infty} \kappa^i\, x_1^{i+1} = 1 \qquad (5)$$

Considering $\kappa\, x_1<1$, we may show that the series on the left side of Eq. (5) converge to

$$x_1/(1-\kappa\, x_1) = 1 \qquad (6)$$

Then the following relation will result for the composition of the monomer:

$$x_1 = 1/(1-\kappa) \tag{7}$$

Having a large number of associated components, compositions may be replaced with a composition distribution function $\chi(I)$ where I is the number of associated monomers. In this case, the summation in Eq. (5) can be replaced with an integral.

$$\int_0^\infty \chi(I)\, dI = 1 \tag{8}$$

where $\chi(I)$ is defined as follows:

$$\chi(I) = \chi_0\, \kappa^I\, x_1^{I+1} \tag{9}$$

χ_0 is the normalizing factor and can be calculated by using Eq. (8).

$$\chi_0 = -(\ln \kappa\, x_1)/\, x_1 \tag{10}$$

If we substitute χ_0 and x_1 into Eq. (9), we get the following result.

$$\chi(I) = -[\kappa/(1+\kappa)]^I \ln[\kappa/(1+\kappa)] \tag{11}$$

In what follows, we present a method for the development of equations of state of associating fluids applying the above composition distribution which is related to equilibrium mixtures of associated species. Moreover, this composition distribution will be used in obtaining the molecular potential function parameters. Having the potential energy function, we may be able to obtain the RDF applying a general analytical expression for the first shell of the RDF which was initially proposed by the authors [3] for simple potential energy functions, such as the Lennard-Jones and Kihara functions.

2. APPLICATION OF COMPOSITION DISTRIBUTION TO EQUATIONS OF STATE

The authors have used the composition distribution already developed in order to extend the equations of state parameters to associating fluids [2]. As an example this extension is first

performed on the van der Waals equation of state (VDW EOS). Since an associating fluid is a multicomponent mixture of different polymers, equation of state parameters “a” and “b” can be expressed by the following mixing rules.

$$a = \sum_{i}^{\infty}\sum_{j}^{\infty} x_i x_j a_{ij} = \sum_{i}^{\infty}\sum_{j}^{\infty} x_i x_j (a_i a_j)^{1/2} = (\sum_{i}^{\infty} x_i a_i^{1/2})^2 \quad (12)$$

$$b = \sum_{i}^{\infty}\sum_{j}^{\infty} x_i x_j b_{ij} = \sum_{i}^{\infty}\sum_{j}^{\infty} x_i x_j (b_i+b_j)/2 = \sum_{i}^{\infty} x_i b_i \quad (13)$$

The above equations can be replaced with the following expressions

$$a = (\int_0^{\infty} \chi(I)\,[a(I)]^{1/2}\,dI)^2 \quad (14)$$

$$b = \int_0^{\infty} \chi(I)\,b(I)\,dI \quad (15)$$

For simplicity, the parameter a(I) is considered to be a linear function of distribution index "I" in the following form, and since "b" is proportional to molecular volume, $b^{1/3}$ will be linearly proportional to molecular length of associating species, thus

$$a(I)^{1/2} = a_0^{1/2} + a_1^{1/2} I \quad (16)$$

$$b(I)^{1/3} = b_1^{1/3} I \quad (17)$$

where “b_1” is the equation of state parameter for the monomer.

Substituting Eqs. (11), (16) and (17) into Eqs. (14) and (15), respectively, and integrating, and then writing the resulting equations with respect to the critical properties, we get:

$$a = a_c F(\xi) \quad (18)$$

$$b = b_c \xi^3 \quad (19)$$

where

$$F(\xi) = [(C_1+\xi)/(C_1+1)]^2 \quad (20)$$

$$C_1 \text{ £ } - (a_0/a_1)^{1/2} \ln[\kappa_c/(1+\kappa_c)] \quad (21)$$

$$\xi = \ln \kappa_c / \ln \kappa = (\ln K_c - \ln \Gamma_c)/(\ln K - \ln \Gamma) \quad (22)$$

The association constant appearing in the above equation is expressed as

$$\ln K = (T\,\Delta S° - \Delta H°)/(RT) \quad (23)$$

where the reference change of enthalpy $\Delta H°$ and entropy $\Delta S°$ of association are independent of temperature. The activity coefficient ratio, Γ, is a function of temperature, pressure and mole fraction. For simplicity, we may assume Γ to be also independent of pressure and mole fraction, and have the following simple expression.

$$\ln \Gamma = \alpha / (RT) \quad (24)$$

where " α " is a constant. Using Eqs. (23) and (24), the parameter "ξ" in Eq. (22) can be rewritten as

$$\xi = T_r (1 + \xi_0)/(T_r + \xi_0) \quad (25)$$

where ξ_0 is defined as

$$\xi_0 \equiv - (\Delta H° + \alpha)/(\Delta S°\, T_c) \quad (26)$$

Since " ξ" depends only on temperature, parameters “a” and “b” will also be temperature dependent only. Therefore, the VDW EOS for associating fluids can be written as

$$P = RT/(V - b_c\, \xi^3) - a_c\, F(\xi)/V^2 \quad (27)$$

The term V appearing in this equation is the true molar volume, and it is based on true number of moles. To calculate molar volume from Eq. (27) we need to have pressure and temperature of the system like any equation of state.

Since at the critical point, the conditions $(\partial P/\partial V)_{T,cr} = (\partial^2 P/\partial V^2)_{T,cr} = 0$ have to be satisfied, then for the VDW EOS, we will have:

$$a_c = (27\, R^2\, T_c^2)/(64 P_c) \tag{28}$$

$$b_c = RT_c/(8P_c) \tag{29}$$

which are the same as the original VDW EOS.

The theory proposed here can be extended to other equations of state by a similar method as it is reported above for the VDW EOS. For example, considering the Redlich-Kwong equation of state (RK EOS), it can be shown that it takes the following form for associating fluids:

$$P = RT/(V-b_c\, \xi^3) - a_c\, F(\xi)\, /[T^{0.5}\, V(V+b_c\, \xi^3)] \tag{30}$$

where "a_c" and "b_c" in this equation are the same as in the original RK EOS.

In the calculations reported below, both the van der Waals and Redlich-Kwong equations of state were used for water. Five different experimental isotherms with reduced temperatures of 0.5, 0.7, 1.0, 1.5 and 2.0 [4] were chosen for specific volume calculations of water which cover both vapor and liquid phases equally. Also 35 saturation data points (from triple point to critical point) were used for vapor pressure calculations. Table 1 shows the absolute average deviations (AAD%) of vapor pressure and specific volume calculations of water based on the original VDW EOS and RK EOS and based on the improved equations applying the values of associating parameters C_1 and ξ_0. According to this table, $C_1 = \pm\infty$ which implies that only the parameter ξ_0 needs to be considered for water in the associating VDW and RK EOS's.

Another case of interest may be the case where the unlike interaction parameter "a_{ij}" is represented by $a_{ij} = (a_i a_j)^{1/2}\,(1-k_{ij})$ where k_{ij} is the coupling parameter of associating species. This case has been studied in detail in Ref. [2]. Calculations have also been reported for various associating fluids based on these two cases. It has been demonstrated that incorporating the proposed theory with equations of state will improve the properties calculations in all cases.

In the following section, another application of the ACAT and the corresponding composition distribution will be studied in order to obtain molecular potential function parameters for associating fluids.

3. APPLICATION OF COMPOSITION DISTRIBUTION TO POTENTIAL PARAMETERS

The composition distribution previously developed, may also be incorporated in the potential energy function. For simplicity, we assume that the associating species form an ideal solution, i.e. $\Gamma=1$ and according to Eq. (3), $\kappa = K$. Therefore, Eq. (11) has the following form.

$$\chi(I) = -[K/(1+K)]^{I} \ln [K/(1+K)] \tag{31}$$

The association constant appearing in the above equation may be determined from Eq. (23). The most reliable values for $\Delta H°$ and $\Delta S°$ are those obtained using spectroscopic methods, such as Raman spectroscopy as reported by Walrafen et al. [5]:

$\Delta H° = -22$ kJ/mole, $\Delta S° = -52$ J/mole K

Applying the conformal solution theory, which assumes that there exists a pure hypothetical fluid with the same properties as those of the mixture at the same density and temperature, the pair potential φ_{ij} can be represented as follows [6]:

$$\varphi_{ij} = \varepsilon_{ij}\, \varphi_{oo}\, (r/\sigma_{ij}) \tag{32}$$

where subscript (oo) denotes the reference fluid, r is the intermolecular distance and the parameters σ_{ij} and ε_{ij} represent the molecular diameter and energy parameter, respectively.

Among the statistical mechanical conformal solution theories of mixtures, one-fluid van der Waals theory is simple to use and accurate enough with the following form:

$$\sigma^3 = \sum_i \sum_j x_i x_j\, \sigma_{ij}^3 \tag{33}$$

$$\varepsilon\, \sigma^3 = \sum_i \sum_j x_i x_j\, \varepsilon_{ij}\, \sigma_{ij}^3 \tag{34}$$

$$\delta^3 = \sum_i \sum_j x_i x_j\, \delta_{ij}^3 \tag{35}$$

Applying the combining rules $\sigma_{ij}^3 = (\sigma_i^3 + \sigma_j^3)/2$, $\delta_{ij}^3 = (\delta_i^3 + \delta_j^3)/2$ and $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ for unlike-interaction potential parameters, we get the following expressions:

$$\sigma^3 = \sum_i \sum_j x_i x_j [(\sigma_i^3 + \sigma_j^3)/2] = \sum_i x_i \sigma_i^3 \tag{36}$$

$$\delta^3 = \sum_i \sum_j x_i x_j [(\delta_i^3 + \delta_j^3)/2] = \sum_i x_i \delta_i^3 \tag{37}$$

$$\varepsilon \sigma^3 = \sum_i \sum_j x_i x_j (\varepsilon_i \varepsilon_j)^{1/2} [(\sigma_i^3 + \sigma_j^3)/2] = \sum_i (x_i \varepsilon_i^{1/2} \sigma_i^3) \sum_j x_j \varepsilon_j^{1/2} \tag{38}$$

Considering the number of associating species to be very large, we can replace the above summations with integrals and the compositions with the composition distribution function.

$$\sigma^3 = \int_0^\infty \chi(I) [\sigma(I)]^3 \, dI \tag{39}$$

$$\delta^3 = \int_0^\infty \chi(I) [\delta(I)]^3 \, dI \tag{40}$$

$$\varepsilon \sigma^3 = \int_0^\infty \chi(I) [\varepsilon(I)]^{1/2} [\sigma(I)]^3 \, dI \int_0^\infty \chi(I) [\varepsilon(I)]^{1/2} \, dI \tag{41}$$

We relate parameters $[\sigma(I)]^3$, $[\delta(I)]^3$ and $[\varepsilon(I)]^{1/2}$ to be functions of distribution index "I".

$$[\sigma(I)]^3 = \sigma_1^3 \, I^{\xi_1} \tag{42}$$

$$[\delta(I)]^3 = \delta_1^3 \, I^{\xi_2} \tag{43}$$

$$[\varepsilon(I)]^{1/2} = \varepsilon_1^{1/2} \, I^{\xi_3} \, [1 + \xi_3 (1/I - 1) + \xi_4 (1 - I)] \tag{44}$$

where σ_1, δ_1 and ε_1 are the potential energy function parameters for the monomer and ξ_1, ξ_2, ξ_3 and ξ_4 are constants.

Substituting Eqs. (31) and (39)-(41) into Eqs. (42)-(44), respectively, and integrating, we will have

$$\sigma = \sigma_1 \, [\Gamma\,(1+\xi_1)\,\theta^{\xi_1}]^{1/3} \tag{45}$$

$$\delta = \delta_1 \, [\Gamma\,(1+\xi_2)\,\theta^{\xi_2}]^{1/3} \tag{46}$$

$$\varepsilon = \varepsilon_1\,\theta^{2\xi_3}\,[\Gamma\,(1+\xi_1+\xi_3)\,\Gamma\,(1+\xi_3)/\,\Gamma\,(1+\xi_1)]\,\{1+\xi_3/[(\xi_1+\xi_3)\,\theta]-\xi_3+\xi_4\,[1-(2+\xi_1+\xi_3)\,\theta]\}.$$

$$\{1+1/\theta-\xi_3+\xi_4\,[1-(2+\xi_3)\,\theta]\} \tag{47}$$

where Γ is the gamma function and θ £-1/ln [K /(1+K)].

At this point, we are going to use these potential parameters in an analytical expression for the first shell of the RDF proposed by the authors [3] for simple potential energy functions.

4. AN ANALYTIC EXPRESSION FOR THE FIRST SHELL

The radial distribution function of water is the most informative feature of its molecular structure. In general, two limiting conditions that the radial distribution function has to satisfy are the case of dilute gases in which the density approaches zero and the case of hard spheres where the temperature approaches infinity. The RDF of dilute gases can be derived from the statistical thermodynamics as

$$g_{dg}(y)=\exp\,[-\beta\,\varphi(y)] \tag{48}$$

where $g_{dg}(y)$ is the dilute gas RDF, y£r/σ, β£1/(k T) and k is the Boltzmann's constant. The authors [3] proposed the following functional form for the first shell of radial distribution function which satisfies these two limiting cases.

$$g(y)= m_1\, g_{hs}(1)\,\exp\,[-m_2\,\beta\,\varphi(x)]+(1-m_1)\,\exp\,[-m_2\,\beta\,\varphi(y)-c_1\,(y-d^*)] \quad \text{for } 0 \le y \le d^* \tag{49}$$

$$g(y)=m_1\, g_{hs}(x)+(1-m_1)\,\exp\,[-m_2\,\beta\,\varphi(y)-c_2\,(y-d^*)] \quad \text{for } d^* \le y < y_m \tag{50}$$

where x£r/d, d^*£d/σ, d is the location of maximum of RDF which in the case of hard sphere RDF corresponds to the hard core diameter, y_m is the minimum of the RDF after the first peak,

$g_{hs}(x)$ is the hard sphere RDF for which the Wertheim's analytical solution [7] of Percus-Yevick equation for the first shell of hard sphere radial distribution function has been utilized. Both Eqs. (49) and (50) converge to the the following simple equation at the maximum of the first peak of the RDF (at $y=d^*$).

$$g(d^*)=m_1\, g_{hs}(1)+(1-m_1)\exp[-m_2\,\beta\,\varphi(d^*)] \tag{51}$$

The parameters c_1 and c_2 appearing in Eqs. (49) and (50) must be determined from the fact that the g(y) has to be maximum at distance d^*, i.e. $[\partial g(y)/\partial y]_{y=d^*} = 0$.

$$c_1= -m_1 m_2\,\beta\,\varphi'(1)\, g_{hs}(1) / \{d^*(1-m_1)\exp[-m_2\,\beta\,\varphi(d^*)]\} -m_2\,\beta\,\varphi'(d^*) \tag{52}$$

$$c_2= m_1\, g'_{hs}(1) /\{d^*(1-m_1)\exp[-m_2\,\beta\,\varphi(d^*)]\} -m_2\,\beta\,\varphi'(d^*) \tag{53}$$

The parameters m_1, m_2 and d^* in the RDF equation are expressed as functions of the dimensionless temperature T^*£$k\,T/\varepsilon$, and dimensionless density ρ^*£ $\rho\sigma^3$ such that they satisfy the limiting conditions of RDF.

$$m_1= \exp[-4.93/(\rho^*\, T^*)] \tag{54}$$

$$m_2= \exp[0.68\,\rho^*\,(1-1/T^*)] \tag{55}$$

$$d^*=R_m \exp(-0.0483\,\rho^{*2}\, T^{*0.5}) \tag{56}$$

where R_m is the location of dilute gas RDF peak which can be calculated by solving the equation:

$$[\partial\varphi(y)/\partial y]_{y=R_m} = \varphi'(y=R_m) = 0 \tag{57}$$

According to Eq. (54), as the temperature approaches infinity, m_1 will approach unity. Therefore, we conclude that Eq. (50) approaches the limiting case of hard sphere RDF, g_{hs} for $y\geq d^*$ (or $x\geq 1$). For the case where the density is very low, according to Eqs. (52)-(56), $m_1=c_1=c_2=0$ and $m_2=1$. Hence Eqs. (49) and (50) reduce to Eq. (48), the dilute gas RDF.

The present model was tested versus the first shell RDF data for the Lennard-Jones and Kihara fluids and versus the experimental results for the argon. A good agreement was reported to be between the calculated RDF and the simulated and experimental data [3].

In the following section, the above expressions for the first shell of RDF are joined with the Kihara potential energy function whose parameters, in the case of water, has been found by using the ACAT and the conformal solution theory.

5. APPLICATION TO KIHARA POTENTIAL FUNCTION

The Kihara potential in which each molecule is assumed to have an impenetrable hard core of diameter δ accounts for the intermolecular forces of water provided that its parameters include the hydrogen bonding effects. In order to apply the preceding first-shell RDF model to Kihara potential, we derive the following expressions for $\varphi(y)$, $\varphi(x)$, $\varphi(d^*)$, $\varphi'(d^*)$, $\varphi'(1)$, and R_m.

$$\varphi(y)= 4\varepsilon \{[(1-\delta^*)/(y- \delta^*)]^{12} - [(1- \delta^*)/(y- \delta^*)]^6\} \tag{58}$$

$$\varphi(x)= 4\varepsilon \{[(1- \delta^*/d^*)/(x- \delta^*/d^*)]^{12} - [(1- \delta^*/d^*)/(x- \delta^*/d^*)]^6\} \tag{59}$$

$$\varphi(d^*)= 4\varepsilon \{[(1- \delta^*)/(d^*- \delta^*)]^{12} - [(1- \delta^*)/(d^*- \delta^*)]^6\} \tag{60}$$

$$\varphi'(d^*)= [-24\varepsilon/(d^*- \delta^*)] \{2 [(1- \delta^*)/(d^*- \delta^*)]^{12} - [(1- \delta^*)/(d^*- \delta^*)]^6\} \tag{61}$$

$$\varphi'(1)= -24\varepsilon/(1- \delta^*/d^*) \tag{62}$$

$$R_m= \delta^*+2^{1/6} (1- \delta^*) \tag{63}$$

where $\delta^*= \delta/\sigma$. Fig. 1 shows the variations of calculated values of Kihara parameters using the proposed model for the first shell of RDF and the experimental data reported by Narten and Levy [8]. It can be inferred from this figure that σ does not practically change with temperature

which implies that ξ_1 in Eq. (45) is almost zero. The values of δ_1 and ξ_2 are found to be 0.35 Å and 1.0. Consequently, Eqs. (45)-(47) reduce to

$$\sigma \approx \sigma_1 = 2.68 \text{ Å} \tag{64}$$

$$\delta = 0.35\ \theta^{1/3} \tag{65}$$

$$\varepsilon = \varepsilon_1 \{\theta^{\xi_3}\ \Gamma\ (1+ \xi_3)\ \{1+1/\theta - \xi_3 + \xi_4\ [1-(2+ \xi_3)\ \theta]\}\ \}^2 \tag{66}$$

where ε_1/k =130 K, ξ_3= 0.4 and ξ_4= 0.0036. Fig. 2 represents the calculated first shell of the RDF of water at various temperatures using the effective Kihara potential function for associating fluids. The curves have been compared with the experimental data for RDF at the same conditions determined by Narten and Levy [8].

In order to verify the validity of the proposed model for near critical and supercritical conditions, we have calculated the first shell of RDF for the conditions T=300˚C, ρ=0.72 g/cm^3 and T=400˚C, ρ =0.66 g/cm^3 for which the experimental data were reported by Postorino et al. [9] and the molecular simulation data based on ST2 model were reported by Chialvo and Cummings [10]. According to Fig. 3, there is a good general agreement between the proposed theory and the experimental and simulated data as far as the location and height of the peak are concerned. However, the bump on the left hand side of the first peak in the experimental data could not be reproduced with the proposed model. Chialvo and Cummings [10] believed that this bump was a false feature of the RDF of water introduced by the diffraction data analysis. Their molecular simulation model also failed to predict this bump.

One of the important features of the experimental RDF data of water was reported to be the fact that as the temperature is raised from ambient temperature to about 170˚C, the first peak diminishes a little in height, while by further increasing the temperature to supercritical region, there is a rise in the first peak again [9]. This peculiarity of water which can be considered in all experimental and simulated data [8-10] is also predicted by the proposed model.

Fig. 4 represents the variations of the first peak of RDF of water at reduced temperatures ($T_r=T/T_c=T^*/T_c^*$) of 0.5, 1.0 and 1.5 and reduced densities ($\rho_r=\rho/\rho_c=\rho^*/\rho_c^*$) of 0.5, 1.0 and 2.0, respectively. In order to compare the results obtained for water with the RDF of Lennard-Jones fluids, the corresponding RDF curves for Lennard-Jones fluids at the similar conditions have been plotted on the same figure. We have chosen the critical temperature and density of Lennard-Jones fluids [11,12] $T_c^*=1.31$ and $\rho_c^*=0.31$. The first peaks of Lennard-Jones fluids RDF are higher at subcritical and lower at supercritical conditions than those of water.

In order to investigate the sufficiency of the information for the first shell of RDF, the concept of the radius of influence has been utilized which was proposed by Mansoori and Ely [13] for the theory of local compositions. This concept is applied to calculate the distance at which the RDF could be truncated for determining the isothermal compressibility. In all cases studied, it is shown that the radius of truncation is located inside the first shell of RDF.

The isothermal compressibility, κ_T, can be calculated by applying the equation:

$$\kappa_T^* = 1/(\rho^* T^*) + (4\pi/T^*)\int_0^\infty [g(y) - 1]\, y^2\, dy \qquad (67)$$

where $\kappa_T^* £ \kappa_T\, \varepsilon/\sigma^3$. The integral in Eq. (67) can be written in the following form.

$$\int_0^\infty [g(y) - 1]\, y^2\, dy = \int_0^{R_\kappa} [g(y) - 1]\, y^2\, dy + \int_{R_\kappa}^\infty [g(y) - 1]\, y^2\, dy \qquad (68)$$

The radius of truncation of RDF, R_κ, is chosen such that the second integral disappears, i.e.

$$\int_{R_\kappa}^\infty [g(y) - 1]\, y^2\, dy = 0 \qquad (69)$$

In general, Eq. (69) has several roots for R_κ. However, we impose the constraint that R_κ has to be within the first shell of RDF. Therefore

$$\kappa_T^* = 1/(\rho^* T^*) + (4\pi/T^*)\int_0^{R_\kappa} [g(y) - 1]\, y^2\, dy \qquad (70)$$

Fig. 5 represents schematically the value of R_κ which gives rise to the equality of dashed areas above and below the horizontal axis to the right of R_κ. Since g(y) is a function of temperature and density, R_κ is also a function of temperature and density. Fig. 8 illustrates the variations of R_κ with the temperature for water at P_{sat}, 0.5 and 1 kbar. In order to obtain R_κ, we have utilized the experimental isothermal compressibility data reported by Helgeson and Kirkham [14]. According to Fig. 6, the radius of truncation of RDF is within the first shell for all the conditions reported.

6. CONCLUSION

We have demonstrated that the analytic chain association theory can be incorporated into equations of state. When this theory is applied to cubic equations of state, with certain assumptions the cubic nature of these equations can be retained. The resulting equations are simple enough to be used for PVT calculations. Numerical calculations for density and vapor pressure have been performed over wide ranges of temperature and pressure for water as one representative associating fluid. It can be observed that the results are greatly improved when applying the association theory and the error is in the order of magnitude of applying the equation to non-associating systems.

We have also derived an effective Kihara pair potential for water which incorporates the hydrogen bonding by using the ACAT and the conformal solution theory. The potential parameters have been obtained based on the first shell of RDF experimental data for water by using an analytical expression for the first shell of RDF previously proposed by the authors which satisfies the limiting cases of hard sphere radial distribution function at high temperatures and the dilute gas radial distribution function at very low densities. The calculated values of RDF compare well with sub-critical experimental data and with simulation and experimental near-critical and supercritical data.

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Table 1. Absolute average deviation of vapor pressure and specific volume of water.

EOS	ξ_0	C_1	AAD% in P_{sat}	AAD% in V
VDW (original)			2851.0	28.2
VDW (proposed theory)	0.297	$\pm\infty$	41.3	9.2
RK (original)			144.6	14.2
RK (proposed theory)	0.109	$\pm\infty$	29.6	5.1

Figure captions:

Fig. 1. Variations of the Kihara parameters for water with temperature using the proposed model for the first shell of RDF

Fig. 2. Comparison of the proposed model for the first shell of the water RDF and the experimental data at various temperatures.

Fig. 3. Comparison of the predicted first shell of the water RDF with the experimental data and the molecular simulation results at near critical and supercritical conditions.

Fig.4. Variations of the first peak of the water RDF and a Lennard-Jones fluid at different conditions.

Fig. 5. Radius of truncation R_κ for the isothermal compressibility integral $[g(y)-1]\, y^2$.

Fig. 6. Variations of the radius of truncation R_κ with temperature and density for water.

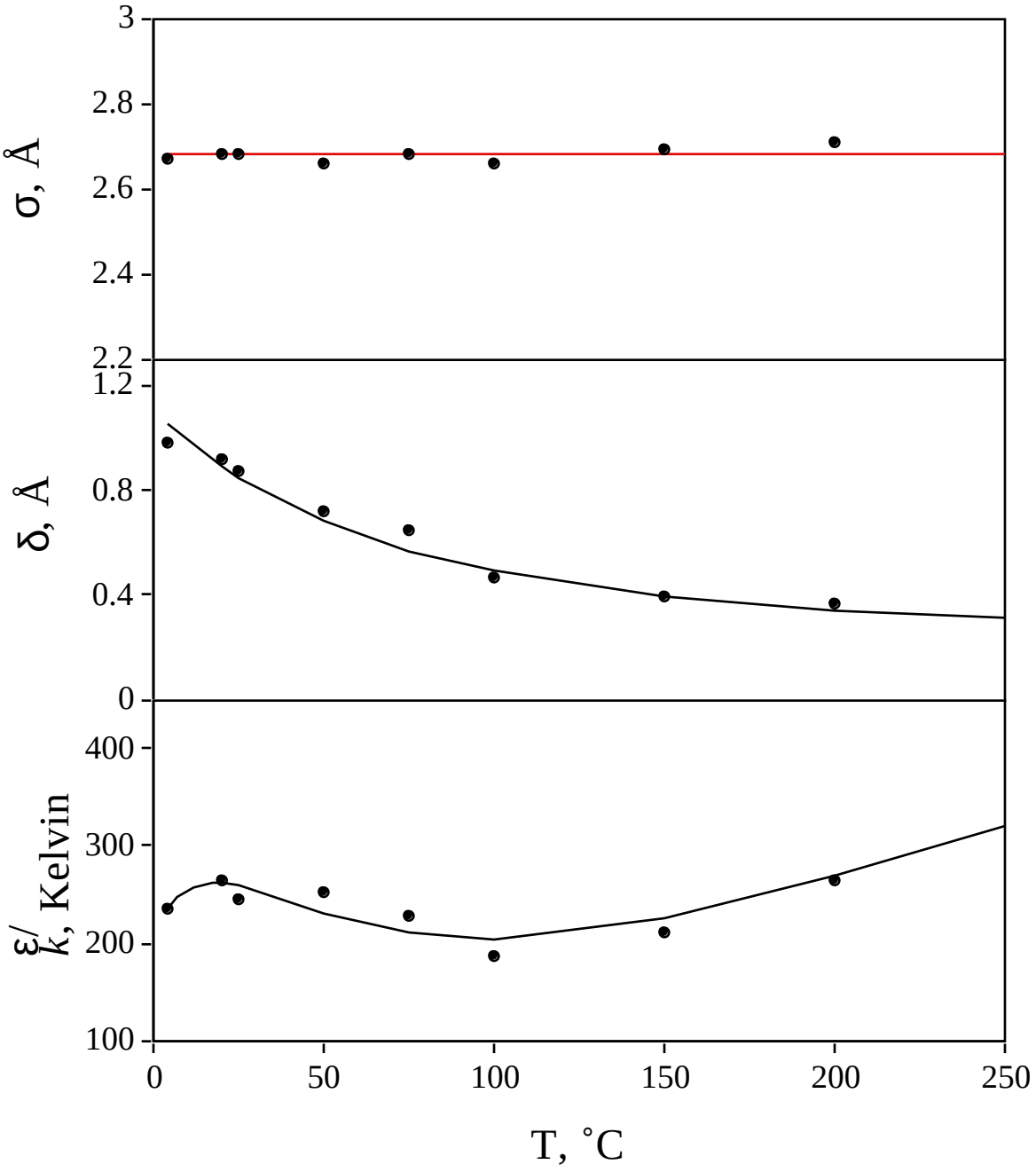
σ, Å
3
2.8
2.6
2.4
2.2
δ, Å
1.2
0.8
0.4
0
ε/k, Kelvin
400
300
200
100
0
50
100
150
200
250
T, ˚C

Fig. 1

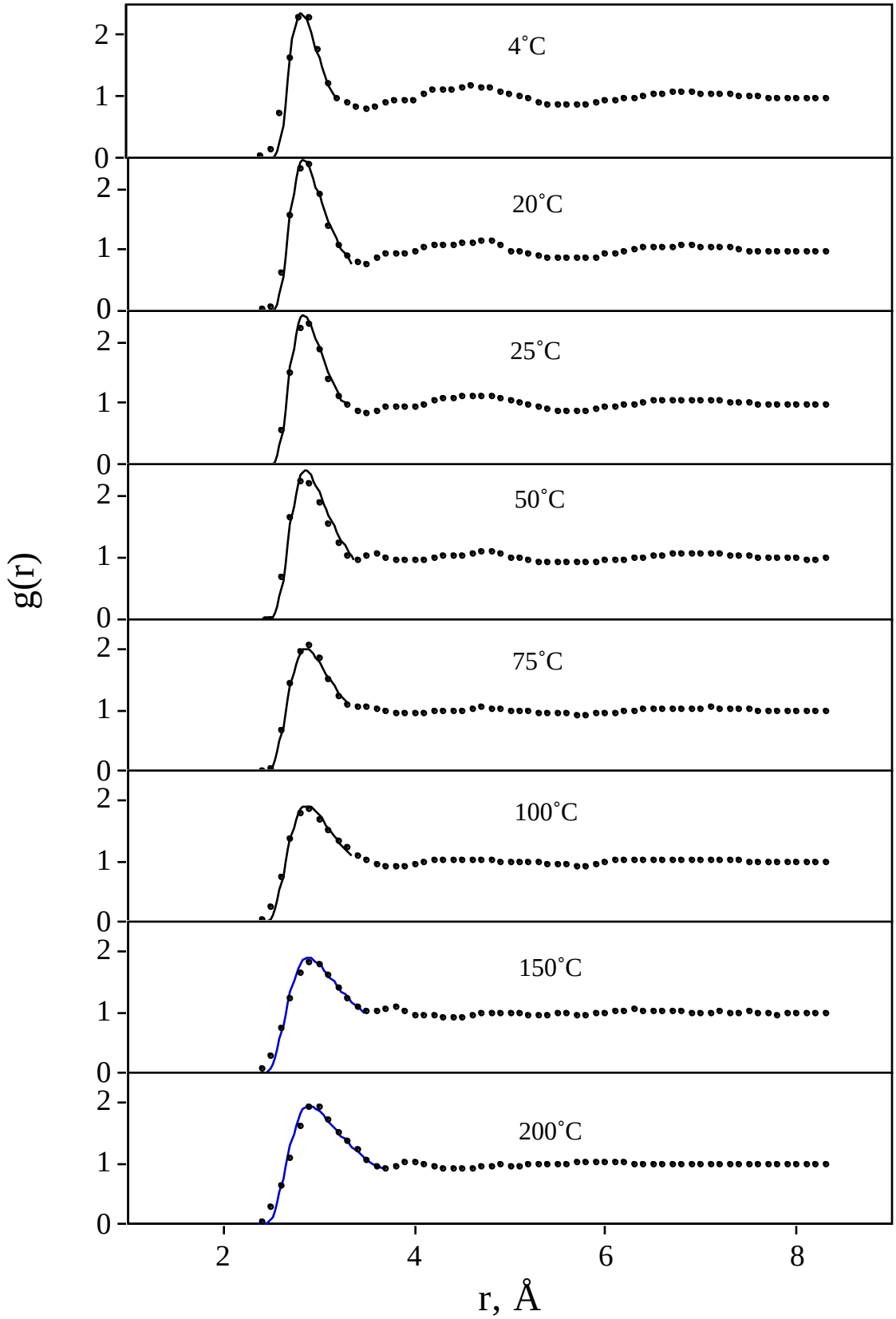

Fig. 2

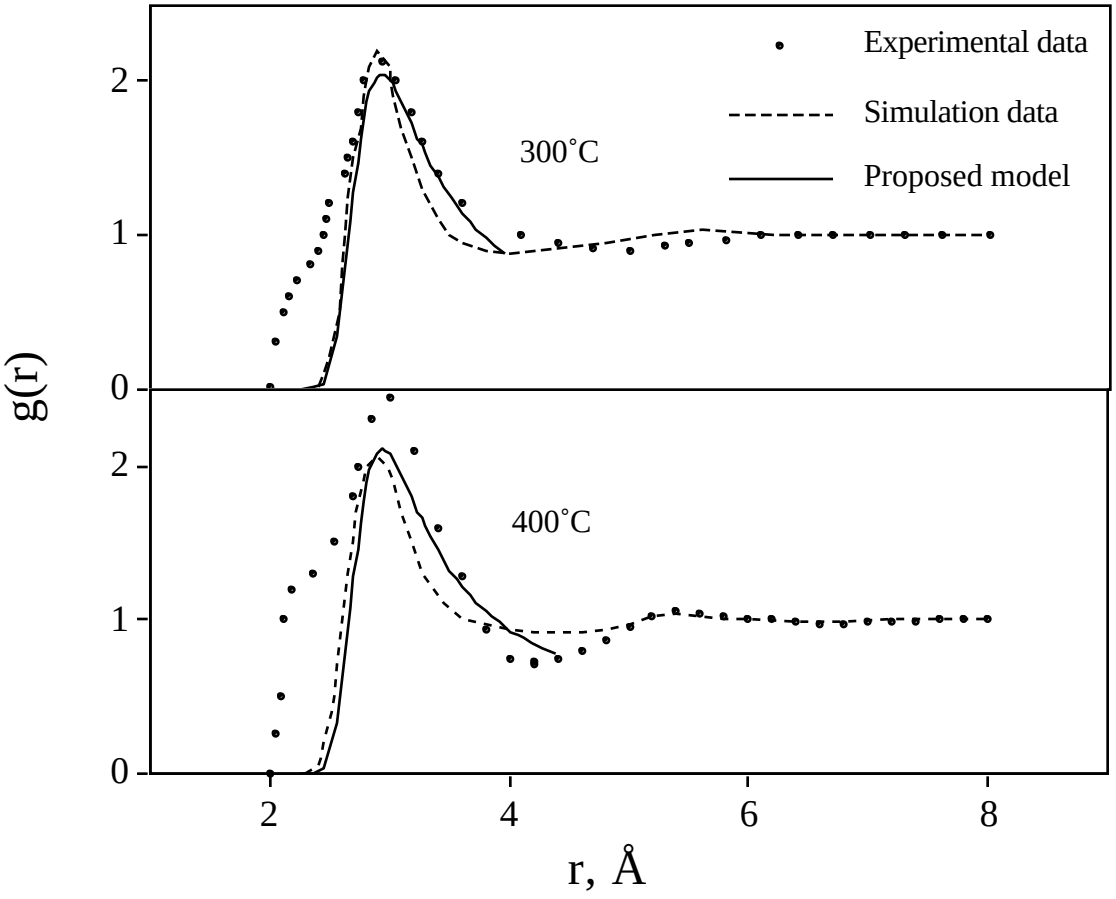
Experimental data
Simulation data
Proposed model
300˚C
400˚C
g(r)
r, Å
0
1
2
2
4
6
8

Fig. 3

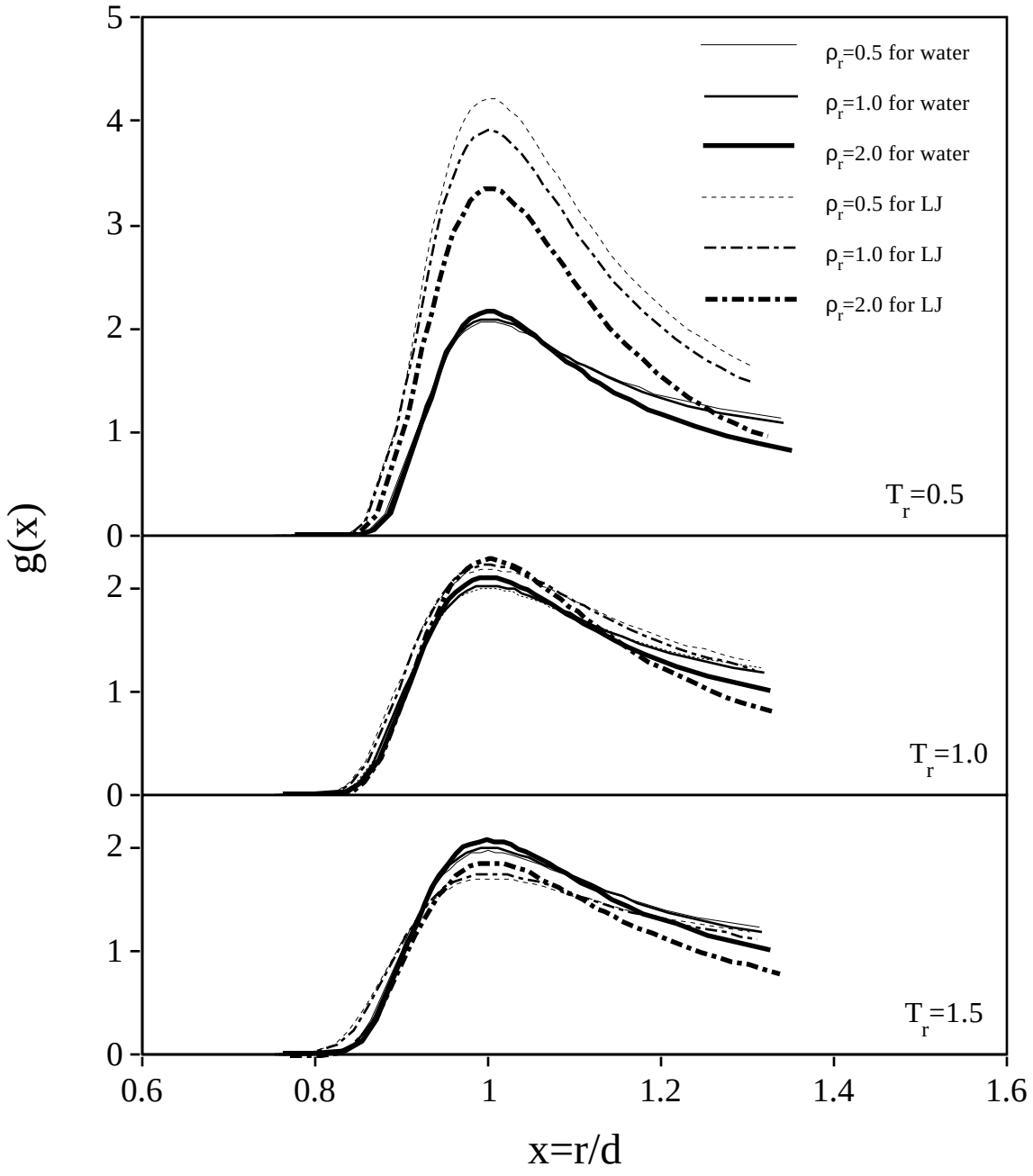
ρr=0.5 for water
ρr=1.0 for water
ρr=2.0 for water
ρr=0.5 for LJ
ρr=1.0 for LJ
ρr=2.0 for LJ
Tr=0.5
Tr=1.0
Tr=1.5
g(x)
x=r/d
0
1
2
3
4
5
0.6
0.8
1
1.2
1.4
1.6

Fig. 4

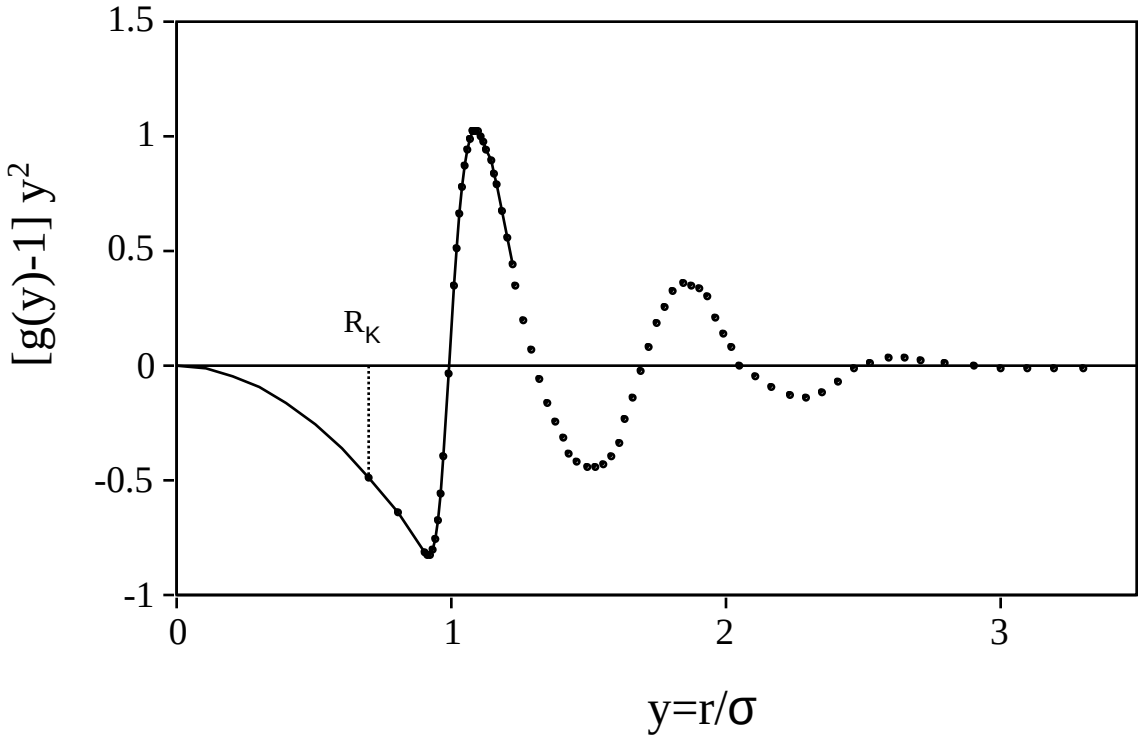

Fig. 5

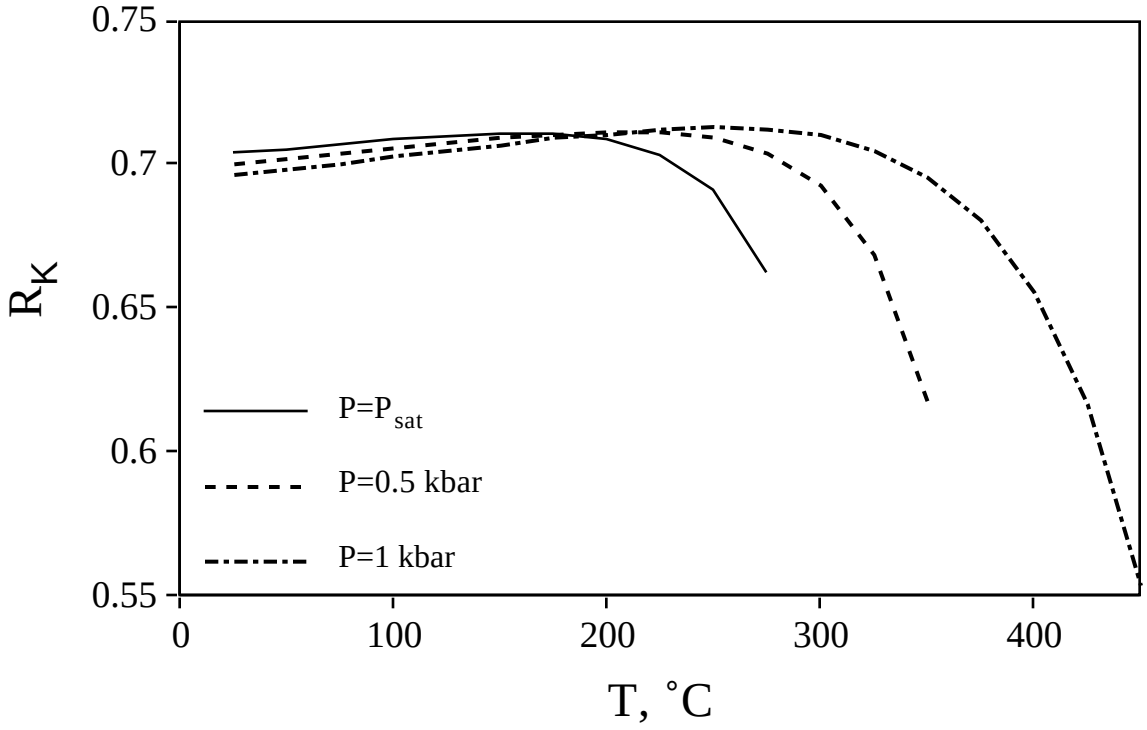

Fig. 6