

# Structure and property prediction of sub- and supercritical water

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## Abstract

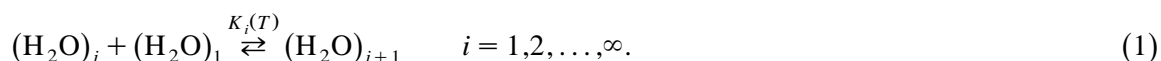
In this report two approaches are presented to predict the structure and PVT behavior of associating fluids with emphasis on water. One approach is the development of equations of state based on the analytic chain association theory (ACAT). An associating fluid is assumed to be a mixture of monomers, dimers, trimers, etc., for which the composition distribution is obtained. The resulting equations are simple enough to be used for PVT calculations. The second approach is the development of an effective Kihara pair potential for water which incorporates the hydrogen bonding using the ACAT. This potential function has been used in an analytical expression to predict the first shell of the radial distribution function (RDF) for water. The expression for RDF which was initially applied to simple potential energy functions, such as the Lennard–Jones and Kihara functions 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. The effective potential parameters 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. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Equation of state; Radial distribution function; Potential energy function; Association

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## 1. Introduction

The key feature of water molecules is the hydrogen bonding which refers to the formation of chemical aggregates or polymers. Nemethy and Scheraga [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 100 H<sub>2</sub>O molecules at room temperature. We have represented the association of water molecules due to hydrogen bonding with the following chain reaction [2]:



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The equilibrium constant of the above reaction can be expressed as

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

where  $x_i$  and  $\gamma_i$  are the mole fraction and activity coefficient of  $(\text{H}_2\text{O})_i$ , respectively, and  $\Gamma_i$  is the ratio of activity coefficients. For simplicity, we assume that all  $K_i$ 's and all  $\Gamma_i$ 's are the same, (i.e.  $K = K_1 = K_2 = \dots = K_i = \dots$  and  $\Gamma = \Gamma_1 = \Gamma_2 = \dots = \Gamma_i = \dots$ ). Let us define  $\kappa$  as the ratio of  $K/\Gamma$ ,

$$\kappa \equiv K/\Gamma = x_{i+1}/(x_i x_1) \quad i = 1, 2, \dots, \infty \quad (3)$$

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

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

Since the summation of all mole fractions is unity, then

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

Assuming  $\kappa x_1 < 1$ , the left side of Eq. (5) converges to give

$$x_1/(1 - \kappa x_1) = 1. \quad (6)$$

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

$$x_1 = 1/(1 - \kappa). \quad (7)$$

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.

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

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

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

$\chi_0$  is the normalizing factor and can be calculated by using Eq. (8).

$$\chi_0 = -(\ln \kappa x_1)/x_1 \quad (10)$$

If we substitute  $\chi_0$  and  $x_1$  into Eq. (9), we get the following result.

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

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.

$$a = \sum_i^{\infty} \sum_j^{\infty} x_i x_j a_{ij} = \sum_i^{\infty} \sum_j^{\infty} x_i x_j (a_i a_j)^{1/2} = \left( \sum_i^{\infty} x_i a_i^{1/2} \right)^2 \quad (12)$$

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

The above equations can be replaced with the following expressions:

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

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

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) and (16) and Eq. (17) into Eq. (14) and Eq. (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

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

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

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

The association constant appearing in the above equation is expressed as

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

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

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

where  $\alpha$  is a constant. Using Eqs. (23) and (24), the parameter  $\xi$  in Eq. (22) can be rewritten as

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

where  $\xi_0$  is defined as

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

Since  $\xi$  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 the true number of moles. To calculate molar volume from Eq. (27) we need to have pressure and temperature of the system.

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:

$$a_c = (27R^2 T_c^2) / (64P_c) \quad (28)$$

$$b_c = RT_c / (8P_c) \quad (29)$$

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 has been 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:

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

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 have been 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

Table 1

Absolute average deviation of vapor pressure and specific volume of water

EOS	$\xi_0$	$C_1$	AAD% in $P_{\text{sat}}$	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

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  $\xi_0$ . According to this table,  $C_1 = \pm\infty$  which implies that only the parameter  $\xi_0$  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 Section 3, another application of the analytic chain association theory (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:

$$\chi(I) = -[K/(1+K)]^I \ln[K/(1+K)]. \quad (31)$$

The association constant appearing in the above equation may be determined from Eq. (23). The most reliable values for  $\Delta H^\circ$  and  $\Delta S^\circ$  are those obtained using spectroscopic methods, such as Raman spectroscopy as reported by Walrafen et al. [5]:  $\Delta H^\circ = -22$  kJ/mol,  $\Delta S^\circ = -52 \sim$  J/mol K.

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 for the parameters of the Kihara potential which is a realistic potential function for water if the effect of hydrogen bonding is incorporated into its parameters:

$$\sigma^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \quad (32)$$

$$\varepsilon \sigma^3 = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \quad (33)$$

$$\delta^3 = \sum_i \sum_j x_i x_j \delta_{ij}^3 \quad (34)$$

where  $\sigma_{ij}$ ,  $\varepsilon_{ij}$  and  $\delta_{ij}$  are the Kihara parameters. 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:

$$\sigma^3 = \sum_i \sum_j x_i x_j [(\sigma_i^3 + \sigma_j^3)/2] = \sum_i x_i \sigma_i^3 \quad (35)$$

$$\delta^3 = \sum_i \sum_j x_i x_j [(\delta_i^3 + \delta_j^3)/2] = \sum_i x_i \delta_i^3 \quad (36)$$

$$\varepsilon \sigma^3 = \sum_i \sum_j x_i x_j (\varepsilon_i \varepsilon_j)^{1/2} [(\sigma_i^3 + \sigma_j^3)/2] = \sum_i (x_i \varepsilon_i^{1/2} \sigma_i^3) \sum_j x_j \varepsilon_j^{1/2} \quad (37)$$

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.

$$\sigma^3 = \int_0^\infty \chi(I) [\sigma(I)]^3 dI \quad (38)$$

$$\delta^3 = \int_0^\infty \chi(I) [\delta(I)]^3 dI \quad (39)$$

$$\varepsilon \sigma^3 = \int_0^\infty \chi(I) [\varepsilon(I)]^{1/2} [\sigma(I)]^3 dI \int_0^\infty \chi(I) [\varepsilon(I)]^{1/2} dI \quad (40)$$

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

$$[\sigma(I)]^3 = \sigma_1^3 I^{\xi_1} \quad (41)$$

$$[\delta(I)]^3 = \delta_1^3 I^{\xi_2} \quad (42)$$

$$[\varepsilon(I)]^{1/2} = \varepsilon_1^{1/2} I^{\xi_3} [1 + \xi_3(1/I - 1) + \xi_4(1 - I)] \quad (43)$$

where  $\sigma_1$ ,  $\delta_1$  and  $\varepsilon_1$  are the potential energy function parameters for the monomer and  $\xi_1$ ,  $\xi_2$ ,  $\xi_3$  and  $\xi_4$  are constants.

Substituting Eqs. (31), (38)–(40) into Eqs. (41)–(43), respectively, and integrating, we will have

$$\sigma = \sigma_1 [\Gamma(1 + \xi_1) \theta^{\xi_1}]^{1/3} \quad (44)$$

$$\delta = \delta_1 [\Gamma(1 + \xi_2) \theta^{\xi_2}]^{1/3} \quad (45)$$

$$\begin{aligned} \varepsilon = \varepsilon_1 \theta^{2\xi_3} & \left[ \Gamma(1 + \xi_1 + \xi_3) \Gamma(1 + \xi_3) / \Gamma(1 + \xi_1) \right] \{ 1 + \xi_3 / [(\xi_1 + \xi_3) \theta] - \xi_3 \\ & + \xi_4 [1 - (2 + \xi_1 + \xi_3) \theta] \} \{ 1 + 1/\theta - \xi_3 + \xi_4 [1 - (2 + \xi_3) \theta] \} \end{aligned} \quad (46)$$

where  $\Gamma$  is the gamma function and  $\theta \equiv -1/\ln[K/(1 + K)]$ .

In order to find the adjustable parameters in the above equations, we use these potential parameters in an analytical expression for the first shell of the radial distribution function (RDF) proposed by the authors [3] for simple potential energy functions such as the Lennard–Jones and Kihara potential function. Fig. 1 shows the variations of calculated values of Kihara parameters using the proposed

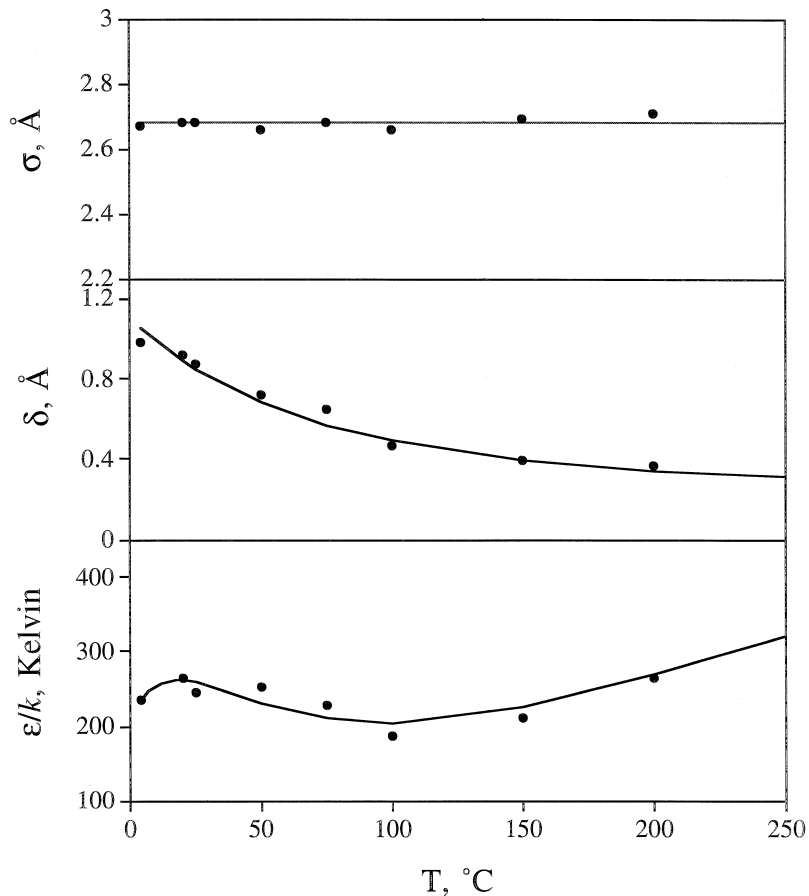


Fig. 1. Variations of the Kihara parameters for water with temperature using the proposed model for the first shell of RDF.

model for the first shell of RDF and the experimental data reported by Narten and Levy [6]. It can be inferred from this figure that  $\sigma$  does not practically change with temperature which implies that  $\xi_1$  in Eq. (44) is almost zero. The values of  $\delta_1$  and  $\xi_2$  are found to be 0.35 Å and 1.0. Consequently, Eqs. (44)–(46) reduce to

$$\sigma \approx \sigma_1 = 2.68 \text{ \AA} \quad (47)$$

$$\delta = 0.35\theta^{1/3} \quad (48)$$

$$\varepsilon = \varepsilon_1 \left\{ \theta^{\xi_3} \Gamma(1 + \xi_3) \left[ 1 + 1/\theta - \xi_3 + \xi_4 [1 - (2 + \xi_3)\theta] \right] \right\}^2 \quad (49)$$

where  $\varepsilon_1/k = 130 \text{ K}$ ,  $\xi_3 = 0.4$  and  $\xi_4 = 0.0036$ . 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 [6].

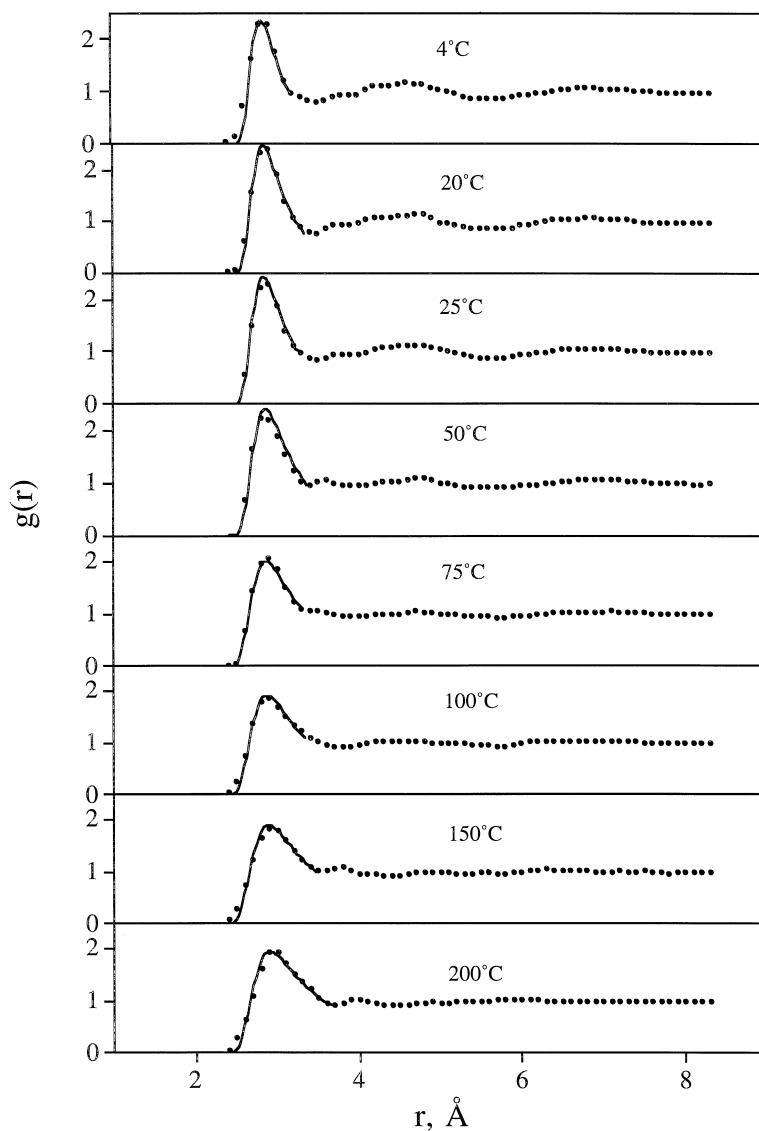


Fig. 2. Comparison of the proposed model for the first shell of the water RDF and the experimental data at various temperatures.

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  $T = 300^{\circ}\text{C}$ ,  $\rho = 0.72 \text{ g/cm}^3$  and  $T = 400^{\circ}\text{C}$ ,  $\rho = 0.66 \text{ g/cm}^3$  for which the experimental data [7] and molecular simulation data [8] are available. According to Fig. 3, there is a good general agreement between the proposed theory and the experimental and simulated data based on ST2 model as far as the location and height of the peak are concerned.

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  $170^{\circ}\text{C}$ , the first peak diminishes a

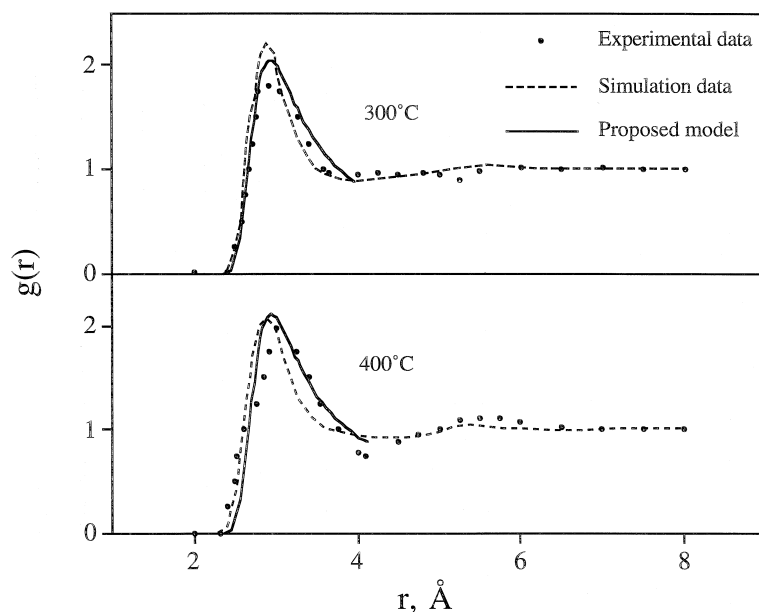


Fig. 3. Comparison of the predicted first shell of the water RDF with the experimental data and the molecular simulation results at near-critical and supercritical conditions.

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 [6–8] is also predicted by the proposed model.

#### 4. 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 nonassociating 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 RDF at very low densities. The calculated values of RDF compare well with subcritical experimental data and with simulation and experimental near-critical and supercritical data.

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