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Equations of state for associating fluids (based on the analytic chain association theory)

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Abstract

In this work, we report a method for the application of equations of state for associating fluids using the analytic chain association theory (ACAT). ACAT has been extensively used in thermodynamic calculations of properties of associating fluids. However, its utility in the development of analytic equations of state for associating fluids is not well recognized. We have demonstrated that the ACAT can be incorporated in the equations of state without the need for any additional approximations other than what is already in the theory. Using certain mathematical manipulations and simplifications which were not recognized in the past, it is now possible to produce analytic equations of state for associating fluids. The resulting equations are still simple enough to be used for PVT and other property calculations. When this theory is applied to cubic equations of state, the cubic nature of these equations is retained. In order to demonstrate the applicability of the theory, numerical work for density and vapor pressure calculations are performed over wide ranges of temperature and pressure.

Keywords: Equation of state; Theory of association

1. Introduction

The development of an accurate theory for associating fluids has been a challenging field of research in thermodynamics. The most common chemical effects encountered in the thermodynamics of associating fluids are due to the hydrogen bondings and charge transfers which link molecules as monomers to form dimers, trimers and other association species. As an example of associating fluids, Nemethy and Scheraga (1962), 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 H₂O molecules at room temperature.

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In the literature, there are different approaches to deal with associating fluids. The most common approach is just to apply the equations of state and mixing rules of non-associating fluids directly for property calculation of associating fluids without any regard to the differences in the molecular nature of the two categories of fluids. This may result in the successful correlation of a certain region of the phase diagram. However, extrapolations to other regions and to mixtures would require additional empirical correlations of the constants of the equation of state to the state variables (Benmekki and Mansoori, 1987).

Apparently, the oldest theoretical method to deal with associating fluids is the chemical theory of solution developed by Dolezalek (1908) which postulates the existence of distinct molecular species in solution. This theory accounts for both positive and negative deviations from ideality. However, the arbitrary way in deciding which species are present in solution is the major disadvantage of this theory.

Another approach for describing association is based on lattice theory which considers a liquid to be solid-like in character. Different equations of state based on lattice theory are known in chemical engineering and have been applied with varying degrees of success to polar fluids. The representation of liquid molecular structure by lattice theory is an oversimplification which is restricted to predict the basic qualitative features of fluid properties.

Theories of statistical mechanics have also been developed which account for the strong intermolecular forces within an associating fluid by using different potential models. Wertheim (1984) considers hydrogen bonding in the pair potential and obtains Helmholtz free energy of association based on perturbation theory.

Hamad and Mansoori (1990); Hamad et al. (1992), developed a fluctuation theory to calculate properties and phase equilibria of associating fluid mixtures based on the relations among the mixture correlation function integrals.

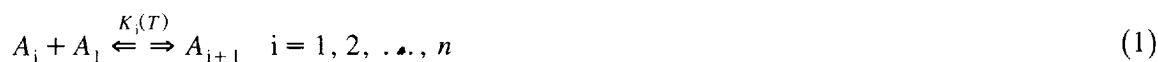
The other method incorporating association was proposed by Anderko (1992). It is based on the separation of physical and chemical contribution to compressibility factor. Panayiotou (1990) assumed that the partition function of an associating fluid is a product of a physical partition function and a chemical partition function.

Due to the formation of different molecular aggregates within an associating fluid, thermodynamic characterization of such fluids would be better represented through polydisperse thermodynamics which accounts for all possible associating species that constitute a polar fluid. The application of this theory to highly polar and hydrogen bonding compounds leads to a better knowledge of associating fluids (Al-Mutawa et al., 1993).

In what follows, we introduce a method for the development of equations of state of associating fluids applying ACAT which deals with equilibrium mixtures of associated species.

2. Extension of ACAT to equations of state

Association refers to formation of chemical aggregates or polymers because of loosely bonded chemical compounds. Association can be represented by reactions of the type (Anderko, 1992; Campbell, 1994)



Studies on the structure of most associating fluids show that each molecule is attached to another molecule through hydrogen bonding (Pimentel and McClellan, 1960).

The equilibrium constant of reaction (1) can be expressed as

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

where n is the limit of association, x_i and γ_i are the mole fraction and activity coefficient of A_i , respectively, and Γ_i is the ratio of activity coefficients. This equation is general enough to be applied to all possible classes of solutions and phases of matter. For simplicity we assume that all K_i s and all Γ_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 κ as the ratio of K/Γ ,

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

This equation is valid so long as the monomer is the prevailing species in the mixture (κ is small).

We may extend Eq. (3) to different i 's as follows

$$\begin{aligned} x_2 &= \kappa x_1^2 \\ x_3 &= \kappa x_2 x_1 = \kappa^2 x_1^3 \\ x_4 &= \kappa x_3 x_1 = \kappa^3 x_1^4 \\ &\vdots \\ &\vdots \\ x_{i+1} &= \kappa x_i x_1 = \kappa^i x_1^{i+1} \\ &\vdots \end{aligned} \quad (4)$$

Using the above system of equations, x_i s may be calculated provided that x_1 and κ are known.

Since summation of all mole fractions is unity, then

$$\begin{aligned} x_1 + \kappa x_1^2 + \kappa^2 x_1^3 + \dots + \kappa^i x_1^{i+1} + \dots &= 1 \\ \sum_{i=0}^n \kappa^i x_1^{i+1} &= 1 \end{aligned} \quad (5)$$

It may be shown that the series on the left side of Eq. 5 converge to

$$x_1 [1 - (\kappa x_1)^n] / (1 - \kappa x_1) = 1 \quad (6)$$

For an associating fluid 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 as proposed by Al-Mutawa et al. (1993). For the case where n is very large the summation in Eq. 5 can be replaced with an integral.

$$\int_0^n \chi(I) dI = 1 \quad (7)$$

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

$$\chi(I) = \chi_0 \kappa^I x_1^{I+1} \quad (8)$$

χ_0 is the normalizing factor and can be calculated using Eq. 7.

$$\chi_0 = -(\ln \kappa x_1) / \left\{ x_1 [1 - (\kappa x_1)^n] \right\} \quad (9)$$

If we substitute χ_0 in Eq. 8, we get the following result

$$\chi(I) = -(\kappa x_1)' (\ln \kappa x_1) / [1 - (\kappa x_1)^n] \quad (10)$$

We now illustrate the utility of the present theory in equations of state from statistical mechanical point of view. The configurational Helmholtz free energy is defined as

$$A_{\text{conf}} = -kT \ln Q_c \quad (11)$$

where k is the Boltzmann's constant, T is the absolute temperature, and Q_c is the configurational integral which can be represented by the following equation:

$$Q_c = \frac{1}{\prod_i N_i!} \int \dots \int e^{-\Phi/kT} dr_1 \dots dr_N \quad (12)$$

Here \mathbf{r} is position vector, Φ is the intermolecular potential energy function which, for the present case, is considered to be the sum of pair potentials.

$$\Phi = \sum_i \sum_j \Phi_{ij} \quad (13)$$

Using 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, Φ_{ij} can be represented as follows (Brown, 1957)

$$\Phi_{ij} = f_{ij} \Phi_{\infty} \left(r/h_{ij}^{1/3} \right) \quad (14)$$

where subscript (oo) denotes the reference fluid and the parameters f_{ij} and h_{ij} represent the molecular conformal energy and volume parameter, respectively. The mixture theory is considered very important in extending the applicability from pure fluids to fluid mixtures. Mansoori (1986) developed proper mixture theories which correctly utilize the conformal solution theory of statistical mechanics for discrete mixtures.

The combining rules for unlike-interaction potential parameters are usually expressed by the following expressions

$$f_{ij} = (1 - k_{ij})(f_{ii}f_{jj})^{1/2} \quad (15)$$

$$h_{ij} = \left[(h_i^{1/3} + h_j^{1/3}) / 2 \right]^3 \quad (16)$$

where k_{ij} is the binary coupling parameter of an unlike pair of molecules i and j , and is equal to zero between the same molecules (e.g. monomers vs. dimers of an associating fluid here).

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

$$f_m h_m = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \quad (17)$$

and

$$h_m = \sum_i \sum_j x_i x_j h_{ij} \quad (18)$$

Now we will demonstrate extension of these mixing rules to associating fluids and development of associating fluid equation of state. As an example this extension is first performed on the van der Waals equation of state (VDW EOS). However, the methodology introduced is applicable to all equations of state.

3. Application of theory to the van der Waals EOS

We now illustrate the utility of the ACAT by converting the van der Waals equation of state of non-associating fluids to the case of associating fluids. The residual configurational Helmholtz free energy based on the VDW EOS is

$$(A_{\text{conf}} - A_{\text{conf}}^{\circ})/RT = \ln[V/(V-b)] - a/(RTV) \quad (19)$$

where a and b are the equation of state parameters and A_{conf}° is the molar configurational Helmholtz free energy of the ideal gas, i.e.

$$A_{\text{conf}}^{\circ}/RT = \ln(N_A/V) - 1 + \sum_i x_i \ln x_i \quad (20)$$

N_A is Avogadro's number, x_i is the mole fraction, and R is the Universal gas constant.

As it will be shown later by using the ACAT to calculate parameters a and b of the VDW EOS for an associating fluid we will produce state dependent parameters, i.e., $a = a(T, V)$ and $b = b(T, V)$. Then in order to calculate other thermodynamic properties, one has to consider the state dependencies of these parameters. For example, given the configurational Helmholtz free energy by Eqs. (19) and (20), we can calculate the pressure by differentiation with respect to volume

$$P = -(\partial A/\partial V)_T = RT[1 - (\partial b/\partial V)_T]/(V-b) + [(\partial a/\partial V)_T V - a]/V^2 \quad (21)$$

The residual configurational internal energy can be determined by differentiating Eq. (19) with respect to temperature at constant volume, i.e.

$$(U_{\text{conf}} - U_{\text{conf}}^{\circ})/RT = -T(\partial b/\partial T)_V/(V-b) - a/(RTV) + (\partial a/\partial T)_V/RV \quad (22)$$

Then the residual configurational entropy is obtained by subtracting Eq. (20) from Eq. (22), i.e.

$$(S_{\text{conf}} - S_{\text{conf}}^{\circ})/R = -T(\partial b/\partial T)_V/(V-b) + (\partial a/\partial T)_V/RV - \ln[V/(V-b)] \quad (23)$$

Depending whether we ignore the coupling parameters between the associating species or we consider them we may formulate two different sets of expressions for equation of state parameters.

4. Case 1: When no coupling parameters are considered

Using the above conformal solution argument, 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 (Kwak and Mansoori, 1986).

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij} = \sum_i^n \sum_j^n x_i x_j (a_i a_j)^{1/2} = \left(\sum_i^n x_i a_i^{1/2} \right)^2 \quad (24)$$

and

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij} = \sum_i^n \sum_j^n x_i x_j (b_i + b_j)/2 = \sum_i^n x_i b_i \quad (25)$$

In deriving these equations, we have assumed that $a_{ij} = (a_i a_j)^{1/2}$ and $b_{ij} = (b_i + b_j)/2$. This is a simplifying assumption which also ignores the existence of coupling (unlike-interaction) parameters between associating species. Considering the number of associating species n to be very large ($n = \infty$), the above summations can be replaced with the following expressions

$$a = \left(\int_0^\infty \chi(I) [a(I)]^{1/2} dI \right)^2 \quad (26)$$

and

$$b = \int_0^\infty \chi(I) b(I) dI \quad (27)$$

For simplicity, we relate parameter $a(I)$ to be a linear function of distribution index I in the following form:

$$a(I)^{1/2} = a_0^{1/2} + a_1^{1/2} I \quad (28)$$

and since b is proportional to molecular volume, $b^{1/3}$ will be linearly proportional to molecular length of associating species, thus

$$b(I)^{1/3} = b_1^{1/3} I \quad (29)$$

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

Then the following relation will result from Eq. (6) for the case where n approaches infinity, since $\kappa x_1 < 1$.

$$x_1 = 1/(1 + \kappa) \quad (30)$$

Again for the case where n goes to infinity, by inserting Eq. (30) into Eq. (10), we get

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

Substituting Eqs. (28)–(30) into Eqs. (26) and (27), respectively, and integrating, we will have

$$a = \{a_0^{1/2} - a_1^{1/2}/\ln[\kappa/(1 + \kappa)]\}^2 \quad (32)$$

and

$$b = -6b_1/\{\ln[\kappa/(1 + \kappa)]\}^3 \quad (33)$$

The above two equations can be written in the following forms with respect to the critical properties:

$$a = a_c F(\xi) \tag{34}$$

and

$$b = b_c \xi^3 \tag{35}$$

where

$$\xi \equiv \ln[\kappa_c/(1 + \kappa_c)]/\ln[\kappa/(1 + \kappa)] \tag{36}$$

$$F(\xi) = [(C_1 + \xi)/(C_1 + 1)]^2 \tag{37}$$

and

$$C_1 \equiv -(a_0/a_1)^{1/2} \ln[\kappa_c/(1 + \kappa_c)] \tag{38}$$

5. Case 2: When coupling parameters are considered

In this case we assume the unlike interaction parameter a_{ij} is represented by $a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij})$ and therefore a can be determined as follows:

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij} = \sum_i^n \sum_j^n x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}) \tag{39}$$

For simplicity, for the parameter b_{ij} we use the same expression as in Case 1 which is $b_{ij} = (b_i + b_j)/2$.

We propose the following simple expression for the coupling parameter k_{ij} of associating species:

$$k_{ij} = k_0 (i - j)^2 \tag{40}$$

where k_0 is a constant representing the coupling parameter between r -mer and $(r + 1)$ -mer which we have assumed to be independent of r . For identical species ($i = j$), the coupling parameter becomes zero as it should be. Now by substituting Eq. (40) into Eq. (39) and assuming that $a(I)$ is a linear function of distribution index as shown by Eq. (28) we will get

$$a = a_c F(\xi) \tag{41}$$

Where, in this case,

$$\begin{aligned} F(\xi) = & \left\{ [a_0^{1/2} - a_1^{1/2} \xi / \ln[\kappa_c/(1 + \kappa_c)]]^2 - 2k_0 [a_0 \xi^2 / \{\ln[\kappa_c/(1 + \kappa_c)]\}]^2 \right. \\ & \left. - 4a_0^{1/2} a_1^{1/2} \xi^3 / \{\ln[\kappa_c/(1 + \kappa_c)]\}^3 + 2a_1 \xi^4 / \{\ln[\kappa_c/(1 + \kappa_c)]\}^4 \right\} \\ & / \left\{ [a_0^{1/2} - a_1^{1/2} / \ln[\kappa_c/(1 + \kappa_c)]]^2 - 2k_0 [a_0 / \{\ln[\kappa_c/(1 + \kappa_c)]\}]^2 \right. \\ & \left. - 4a_0^{1/2} a_1^{1/2} / \{\ln[\kappa_c/(1 + \kappa_c)]\}^3 + 2a_1 / \{\ln[\kappa_c/(1 + \kappa_c)]\}^4 \right\} \end{aligned} \tag{42}$$

Parameter ξ has the same definition as in Eq. (36),

$$\xi \equiv \ln[\kappa_c/(1 + \kappa_c)]/\ln[\kappa/(1 + \kappa)] \tag{43}$$

Parameter b will remain the same as in Case 1, i.e.,

$$b = b_c \xi^3 \quad (44)$$

6. State dependency of parameter ξ

In both of the above cases, parameter ξ appears as defined by Eq. (36) (or (43)). Since κ is a small number $\kappa \ll 1$, $\kappa/(1 + \kappa) \cong \kappa$, therefore, Eq. (36) (or (43)) can be approximated as

$$\xi = \ln \kappa_c / \ln \kappa \quad (45)$$

Replacing $\kappa = K/\Gamma$ into Eq. (45), we get

$$\xi = (\ln K_c - \ln \Gamma_c) / (\ln K - \ln \Gamma) \quad (46)$$

The association constant appearing in the above equation can be expressed as

$$\ln K = (T \Delta S^\circ - \Delta H^\circ) / (RT) \quad (47)$$

where the reference change of enthalpy ΔH° and entropy ΔS° 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.

$$\ln \Gamma = \alpha / (RT) \quad (48)$$

where α is a constant. It may be argued that Eq. (48) may be valid for liquid and not for vapor. However, considering the fact that there is much less association present in the vapor phase than the liquid, Eq. (48) could be a reasonable approximation for vapor and liquid. It should be pointed out that a better assumption will be to consider $\alpha = \alpha(V)$. This assumption may improve the predictions of the resulting equation of state, but it will make it more complicated and in the case of the VDW EOS, it will become a non-cubic equation, besides to the fact that there is no theoretical expression available for $\alpha(V)$ and any empirical assumption will introduce empirical adjustable parameters to be determined.

Then, using Eqs. (47) and (48), the parameter ξ in Eq. (46) can be rewritten as

$$\xi = T_r [1 - (\Delta H^\circ + \alpha) / (\Delta S^\circ T_c)] / [T_r - (\Delta H^\circ + \alpha) / (\Delta S^\circ T_c)] \quad (49)$$

T_r is the reduced temperature. By defining ξ_0 as

$$\xi_0 \equiv -(\Delta H^\circ + \alpha) / (\Delta S^\circ T_c) \quad (50)$$

then

$$\xi = T_r(1 + \xi_0) / (T_r + \xi_0) \quad (51)$$

Since ξ depends only on temperature, parameters a and b in Eqs. (34) (or (41)) and (35) will also be temperature dependent only. Therefore, we substitute a and b in Eq. (21) to obtain.

$$P = RT / (V - b_c \xi^3) - a_c F(\xi) / V^2 \quad (52)$$

In this equation, $F(\xi)$ for each case is defined by Eqs. (37) and (42). Eq. (52) constitute the associating fluids equation of state. The term V appearing in Eq. (52) is the true molar volume, and it is based on true number of moles. To calculate molar volume from Eq. (52) we need to have pressure and temperature of the system like any equation of state.

Since at the critical point ($\xi = 1$), the following 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:

$$a_c = (27R^2T_c^2)/(64P_c) \quad (53)$$

and

$$b_c = RT_c/(8P_c) \quad (54)$$

which are the same as the original VDW EOS.

7. Discussion

7.1. Extension to other equations of state

The theory proposed here can be extended to other equations of states by a similar method as it is reported above for the VDW EOS. For example, considering the Redlich–Kwong equation of state (RK EOS), $P = RT/(V - b_c) - a_c/[T^{0.5}V(V + b_c)]$, it can be shown that it takes the following form for associating fluids:

$$P = RT/(V - b_c \xi^3) - a_c F(\xi)/[T^{0.5}V(V + b_c \xi^3)] \quad (55)$$

Where a_c and b_c in this equation are the same as in the original RK EOS:

$$a_c = (0.42748R^2T_c^{2.5})/P_c \quad (56)$$

$$b_c = (0.08664RT_c)/P_c \quad (57)$$

In the calculations reported below we use, both, the van der Waals and Redlich–Kwong equations of state for associating and non-associating fluids.

7.2. Further simplifying assumptions for Case 2

In order to perform calculation, we need to examine $F(\xi)$ for both cases presented above.

In Case 1 where no coupling interaction is assumed, $F(\xi)$ takes a rather simple form as shown by Eq. (37). In this equation $F(\xi)$ has two unknown parameters (C_1 and ξ_0) to be determined.

In Case 2 where coupling interaction is considered, $F(\xi)$ takes a rather complicated form as shown by Eq. (42) which has four adjustable parameters (ξ_0, a_0, a_1, k_0) to be determined. In order to reduce the number of these adjustable parameters from four to two, similar to Case 1, we could make two different assumptions:

7.2.1. Case 2(i)

We may assume $a_0 = 0$ in Eq. (42), as a result of which we conclude the following two parameter equation for $F(\xi)$.

$$F(\xi) = \xi^2(1 + C_{2(i)}\xi^2)/(1 + C_{2(i)}) \quad (58)$$

where

$$C_{2(i)} \equiv -4k_0 / \{\ln[\kappa_c / (1 + \kappa_c)]\}^2 \quad (59)$$

and it is a constant. As a result the equation of state (VDW or RK) will have two adjustable parameters ($C_{2(i)}$ and ξ_0) as in Case 1.

7.2.2. Case 2(ii)

We may instead, assume $a_1 = 0$ in Eq. 42, as a result of which

$$F(\xi) = (1 + C_{2(ii)}\xi^2) / (1 + C_{2(ii)}) \quad (60)$$

where

$$C_{2(ii)} \equiv -2k_0 / \{\ln[\kappa_c / (1 + \kappa_c)]\}^2 \quad (61)$$

which is also a constant. As a result of this assumption the equation of state (VDW or RK) will have again two adjustable parameters ($C_{2(ii)}$ and ξ_0) as in Case 1 and Case 2(i).

8. Calculations and results

The calculations performed here are for Cases 1, 2(i) and 2(ii) reported above. Five different experimental isotherms (with reduced temperatures of 0.5, 0.7, 1.0, 1.5 and 2.0) for water (Haar et al., 1984) and four experimental isotherms (with reduced temperatures of 0.5, 0.7, 1.0, and 1.5) for ammonia (Haar and Gallagher, 1978) and methanol (Goodwin, 1987) are chosen for specific volume calculations which cover both vapor and liquid phases equally. Also 35 saturation data points (from triple point to critical point) are used for vapor pressure calculations of the above mentioned associating fluids.

In Table 1, absolute average percentage errors of vapor pressures ($E - P^{\text{sat}}$) and specific volumes ($E - V$) of three associating fluids (water, ammonia and methanol) and methane (as a non-associating reference fluid) are reported by using the original VDW EOS, $P = RT/(V - b_c) - a_c/V^2$, and RK EOS, $P = RT/(V - b_c) - a_c/[T^{0.5}V(V + b_c)]$. This table is to demonstrate the high errors of the van

Table 1

Absolute average percent error of vapor pressure and specific volume of associating fluids and methane for original VDW and RK EOSs

Component	EOS	$E - P^{\text{sat}}$	$E - V$
Water	VDW	2851.0	28.2
	RK	144.6	14.2
Ammonia	VDW	636.6	41.5
	RK	64.0	14.6
Methanol	VDW	34832.8	55.5
	RK	827.3	22.8
Methane	VDW	128.8	18.1
	RK	12.8	3.8

der Waals and Redlich–Kwong equations of state when they are applied for associating fluids compared to their much lower errors when they are used for a non-associating fluid like methane. In this and subsequent tables, $(E - P^{\text{sat}})$ and $(E - V)$ are defined by

$$E - P^{\text{sat}} = \frac{100}{n} \sum_{i=1}^n \left| \frac{P_{\text{exp}}^{\text{sat}} - P_{\text{cal}}^{\text{sat}}}{P_{\text{exp}}^{\text{sat}}} \right|_i \quad (62)$$

$$E - V = \frac{100}{n} \sum_{i=1}^n \left| \frac{V_{\text{exp}} - V_{\text{cal}}}{V_{\text{exp}}} \right|_i \quad (63)$$

where P^{sat} is the vapor pressure, V is the molar volume, E stands for error, exp stands for experimental data, cal stands for the calculated value, and n is the number of data points.

Table 2 shows values of the pairs of associating parameters (C_1 and ξ_0), ($C_{2(i)}$ and ξ_0), and ($C_{2(ii)}$ and ξ_0) corresponding to the associating forms of the VDW, $P = RT/(V - b_c \xi^3) - a_c F(\xi)/V^2$, and RK, $P = RT/(V - b_c \xi^3) - a_c F(\xi)/[T^{0.5}V(V + b_c \xi^3)]$, equations of state as obtained by optimizing specific volume of water, ammonia and methanol. This table also shows the absolute average percentage errors in vapor pressures and specific volumes based on the associating forms of the van der Waals and Redlich–Kwong equations of state. Also reported in this table are the same associating parameters as calculated for methane. Since the RK EOS is the best cubic equation of state for methane, associating parameters for this equation all become zero as a result of the above mentioned fit. However, the associating parameters for the VDW EOS when applied to methane are non-zero. This is because the VDW EOS is not the best cubic equation of state for methane and there is space for its improvement. One should not interpret this as the proof of the existence of association in methane.

According to Table 2, for Cases 1 and 2(ii) and for all the three associating fluids (water, ammonia, methanol), we conclude that $F(\xi) = 1$ [when $C_1 = \pm\infty$ in Case 1 or when $C_{2(ii)} = 0$ in Case 2(ii)]. This tells us that we probably need to consider only one parameter " ξ_0 " in the associating VDW and RK EOSs. For Case 2(i), where both of the parameters ($C_{2(i)}$ and ξ_0) are non-zero the fit to the data is not as good as Cases 1 and 2(ii).

In order to calculate the associating parameter ξ_0 from a particular reference point, we use the specific volumes of the associating fluids at the triple point in the liquid and vapor states. This is because we believe the association is very close to its maximum at the triple point. The second association parameter [C_1 in Case 1, $C_{2(i)}$ in Case 2 and $C_{2(ii)}$ in Case 2(ii)] may be assumed to be zero or $\pm\infty$. This generates six different cases to be studied for each associating fluid.

Table 3 shows the absolute average percentage errors of vapor pressures and specific volumes of associating fluids when the parameter ξ_0 is obtained based on setting the difference in error at the triple point-between that of methane and that of associating fluid equal to zero for the six situations where $C_1 = C_{2(i)} = C_{2(ii)} = 0$ and $C_1 = C_{2(i)} = C_{2(ii)} = \infty$. According to this table, parameter ξ_0 is now almost independent of the equation of state for each case and for each associating fluid. However, in the middle section of Table 3, when C_1 and $1/C_{2(ii)} = \pm\infty$, which corresponds to Cases 1 and 2(ii) of Table 2, parameter ξ_0 will be less sensitive to the equation of state and the percentage error in the vapor pressure predictions are less than the other cases reported in Table 3. However, the percentage errors for property calculations in this case are higher than in Table 2. One may ask whether there is any improvement in the description of the critical region. Since at the critical point, $\xi = 1$ and $F(\xi) = 1$, therefore the effect of the proposed theory diminishes in the critical region.

Table 2

Absolute average percent error of vapor pressure and specific volume of associating fluids and methane based on all data points

Case 1					
Component	EOS	ξ_0	C_1	$E - P^{\text{sat}}$	$E - V$
Water	VDW	0.297	$\pm \infty$	41.3	9.2
	RK	0.109	$\pm \infty$	29.6	5.1
Ammonia	VDW	0.251	$\pm \infty$	29.6	12.1
	RK	0.0825	$\pm \infty$	17.8	5.2
Methanol	VDW	0.3127	$\pm \infty$	84.5	17.0
	RK	0.116	$\pm \infty$	52.3	8.9
Methane	VDW *	0.287	0.716	15.0	13.9
	RK	0.0	0.0	12.8	3.8
Case 2(i)					
Component	EOS	ξ_0	$C_{2(i)}$	$E - P^{\text{sat}}$	$E - V$
Water	VDW	0.328	-0.538	32.5	9.6
	RK	0.1629	-0.4136	28.6	5.5
Ammonia	VDW	0.283	0.0	388.6	12.5
	RK	0.0814	-0.574	20.3	5.2
Methanol	VDW	0.3382	-0.346	980.4	17.2
	RK	0.1338	-0.2758	118.9	9.2
Methane	VDW	0.188	-0.535	10.6	14.6
	RK	0.0	0.0	12.8	3.8
Case 2(ii)					
Component	EOS	ξ_0	$C_{2(ii)}$	$E - P^{\text{sat}}$	$E - V$
Water	VDW	0.297	0.0	41.3	9.2
	RK	0.109	0.0	29.6	5.1
Ammonia	VDW	0.251	0.0	29.6	12.1
	RK	0.0825	0.0	17.8	5.2
Methanol	VDW	0.3127	0.0	84.5	17.0
	RK	0.116	0.0	52.3	8.9
Methane	VDW *	0.287	1.42	82.2	7.9
	RK	0.0	0.0	12.8	3.8

* If $C_1 = \infty$ (or $C_{2(ii)} = \infty$) and $\xi_0 = 0.240$, $E - P^{\text{sat}} = 21.8$, $E - V = 14.1$.

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 and other property calculations. Numerical calculations for density and vapor pressure are performed over wide ranges of temperature and pressure for water, ammonia, and methanol as the three representative associating fluids. 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. This means that the presented model takes care of association very well. The method proposed here is applicable to all equations of state, whether cubic or non-cubic and empirical

Table 3

Absolute average percent error of vapor pressure and specific volume of associating fluids when the parameter ξ_0 is obtained in such a way that the difference in error at the triple point between that of methane and that of associating fluid is set equal to zero

Component	EOS	ξ_0	$C_1, C_{2(i)}, 1/C_{2(ii)}$	$E - P^{sat}$	$E - V$
Water	VDW	0.0794	0.0	2110.1	21.0
	RK	0.0697	0.0	93.4	7.6
Ammonia	VDW	0.09345	0.0	530.1	27.4
	RK	0.08182	0.0	42.0	6.1
Methanol	VDW	0.08554	0.0	22184.1	39.7
	RK	0.0763	0.0	438.2	13.7
Component	EOS	ξ_0	$C_1, 1/C_{2(ii)}$	$E - P^{sat}$	$E - V$
Water	VDW	0.07139	$\pm \infty$	752.1	21.2
	RK	0.06422	$\pm \infty$	28.9	11.4
Ammonia	VDW	0.0817	$\pm \infty$	248.8	27.2
	RK	0.0735	$\pm \infty$	16.0	6.0
Methanol	VDW	0.07771	$\pm \infty$	4850.1	42.4
	RK	0.07099	$\pm \infty$	90.2	13.1
Component	EOS	ξ_0	$C_{2(i)}$	$E - P^{sat}$	$E - V$
Water	VDW	0.09328	$\pm \infty$	6869.8	21.9
	RK	0.07770	$\pm \infty$	365.5	8.2
Ammonia	VDW	0.11563	$\pm \infty$	1296.3	27.7
	RK	0.09492	$\pm \infty$	163.0	6.3
Methanol	VDW	0.09933	$\pm \infty$	107943.7	41.0
	RK	0.08434	$\pm \infty$	2864.8	14.5

or statistical mechanical. Applicability of the proposed model for associating fluid mixtures and strongly associating fluids still needs to be investigated.

9. List of symbols

- a equation of state parameter
- a_c equation of state parameter at critical point
- a_0 parameter defined by Eq. 28
- a_1 parameter defined by Eq. 28
- A Helmholtz free energy
- A_{conf} configurational Helmholtz free energy
- A_{conf}^o ideal gas configurational Helmholtz free energy
- b equation of state parameter
- b_c equation of state parameter at critical point
- b_1 equation of state parameter for the monomer
- C_1 quantity defined by Eq. 38
- $C_{2(i)}$ quantity defined by Eq. 59
- $C_{2(ii)}$ quantity defined by Eq. 61

$E - V$	Absolute average percent error of specific volume
$E - P^{\text{sat}}$	Absolute average percent error of vapor pressure
F	function defined by Eq. 37 or 42
f_{ij}	molecular conformal energy parameter
f_m	mixture molecular conformal energy parameter
h_{ij}	molecular conformal volume parameter
h_m	mixture molecular conformal volume parameter
I	distribution index
k	Boltzmann's constant
K	association equilibrium constant
k_{ij}	binary coupling parameter of an unlike pair of molecules i and j
k_0	coupling parameter between two consecutive associating species
n	number of associating species
N_A	Avogadro's number
P	pressure
P_c	critical pressure
Q_c	configurational integral
R	Universal gas constant
\mathbf{r}	position vector
S_{conf}	configurational entropy
S_{conf}°	ideal gas configurational entropy
T	absolute temperature
T_c	critical temperature
T_r	reduced temperature
U_{conf}	configurational internal energy
U_{conf}°	ideal gas configurational internal energy
V	molar volume
x_i	mole fraction of component i

9.1.1. Greek letters

α	parameter defined by Eq. 48
χ	composition distribution function
χ_0	normalizing factor in Eq. 8
γ_i	activity coefficient of component i
Γ_i	ratio of activity coefficients
ΔH^0	reference change of enthalpy association
ΔS^0	reference change of entropy of association
Φ	total intermolecular potential energy function
Φ_{ij}	pair potential
Φ_{00}	reference fluid pair potential
κ	ratio of mole fractions
κ_c	ratio of mole fractions at the critical point
ξ	quantity defined by Eq. 36
ξ_0	parameter defined by Eq. 50

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