Derivation of a new cubic equation of state based on partition function for Polymers and Volatile Fluids

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Abstract: A three parameter cubic equation of state, EOS, is derived from statistical thermodynamic theoretical standpoint using partition function. In this work, generalized Van der Waals theory is used to establish a partition function that considers the effect of density on rotational and vibrational motions. Two universal functions of a reduced temperature were introduced to represent the effect of temperature on b and a; they were determined from the vapor pressures and the densities of saturated liquid and vapor of n-alkane and extended to molecular fluids and polymers.

Key-Words: Cubic equation of state, Partition function, Hard sphere, Hydrocarbons.

1 Introduction
Quantitative calculations in chemical process design require reliable estimates of thermodynamic properties. As discussed in numerous texts, an equation of state provides one possible tool for obtaining such properties for fluids. Most existing equation of states are applicable only to mixtures containing volatile fluids. However, several authors have presented EOS that can be used for fluids containing nonvolatile and large molecules. Equations of state provide useful tools for correlating and estimating thermodynamic properties of polymer solutions [18-19]. The EOS theory has successfully explained both lower-critical-solution-temperature (LCST) and upper-critical-solution-temperature (UCST) phenomena for polymer solutions, in contrast to the classical Flory-Huggins polymer-solution theory [24] that fails to describe LCST behavior at elevated temperatures. The equations of state published in the literature's are often complex and require molecular parameters that are not readily available. Recently cubic equations of state combined with activity coefficient models have been applied to correlate the phase equilibrium of large molecules and polymer solutions [20-21].

In this work we present a cubic equation of state in simple form and useful for both small and large molecules. We derive an EOS from the generalized V an der Waals partition function that considers the effect of density on rotational and vibrational motions [1-2]. We introduced, the new function for free volume expression, and the Soave-Redlich-K wong (SRK) [17] potential field in the partition function. We proposed critical compressibility factor taken as substance dependent and present a new method for calculating generalize pure component parameters.

2 Theoretical Derivation
The approach proposed in this study is based on the generalized V an der Waals partition function. Vera and Prausnitz [1] presented the following form of partition function.

\[ Q = \frac{1}{N!} \left[ \frac{V}{N} \right] \left[ \frac{V}{N} \right] \exp \left( \frac{-E}{kT} \right) \]  

(1)

The term \( \left( \frac{N!}{\left[ \frac{V}{N} \right]^2} \right) \) gives the translational contribution of an ideal gas to the partition function. The second and third bracketed terms account for the repulsive and attractive forces between molecules. The last term represents the contribution of the rotational and vibrational degrees of freedom. Equation of state is given by

\[ \ln \left( \frac{T}{N_A} \right) = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{\rho,N} \]  

(2)

We define the free volume term by the following form

\[ \frac{V_f}{V} = \left( 1 - (4 - m) \xi \right)^{\frac{4}{4-n}} \]  

(3)

In Eq (4) \( m \) and \( n \) are the repulsive-term parameters and packing fraction \( \xi \) is defined as [3]

\[ \xi = \frac{b}{4\nu} = \frac{bN}{4VN_A} \]  

(4)

We use the Soave-Redlich-K wong form for the potential field [7]
\[ E_c = \frac{-2a}{N} \ln \left(1 + \frac{Nb}{N} \right) \]  
\[ \text{(5)} \]

For small molecules (argon-like molecules), \(Q_{cv}\) depends only on temperature. However, for polyatomic molecule, this frequently made simplifying assumption is not valid [1] and \(Q_{cv}\) depends on density. By using Prigogine's procedure [2] we factor the contribution of the rotational and vibrational degrees of freedom into an internal part and external part

\[ Q_{v,i} = Q_{v,ext} (\text{int}) \times Q_{v,ext} (\text{ext}) \]  
\[ \text{(6)} \]

Where \(Q_{v,ext}\) depends only on temperature, but \(Q_{v,int}\) depends also on density. As discussed by Beret and Prausnitz [1], external part in Eq. (6) is represented by the following form

\[ Q_{v,ext} (\text{ext}) = \left( \frac{V}{V'} \right)^{-1} \]  
\[ \text{(7)} \]

Where \(3c\) is the total number of external degrees of freedom per molecule [3]. By substituting Eqs. (3), (5), and (7) into (1) the following cubic equation of state is obtained

\[ Z = \frac{V + (\lambda + \theta \varepsilon) \times b}{V + \lambda b} - \frac{a}{v(v + b)} \]  
\[ \text{(8)} \]

Where \(\lambda = (4 - m) / 4 \) \& \(\theta = (4 - m)/4(4 - n) \). The third parameter \(c\) extends the applicability of equation (9) to systems containing large molecules. For small and argon-like molecules \(C = 1\). Repulsive-term parameters \(m\) and \(n\) are approximates from the molecular dynamic calculations of hard-sphere fluids which are accurately represented by the Carnahan-Starling [8] and Hajipour-Eadalat [5] repulsive terms. By applying these terms to \(m\) and \(n\) in Eq. (8), the following result was obtained

\[ Z = \frac{v + (1.253 \times c - 0.401) \times b}{v - 0.401 \times b} - \frac{a}{RT \times (v + b)} \]  
\[ \text{(9)} \]

a, b and c in equations (10) are three adjustable parameters of equation.

3 Determination of pure-component parameters

To apply Eq. (9) to polymers as well as to volatile fluids, energy parameter \(a\) is determined from London's formula for dispersion forces [22], and volume parameter \(b\) is calculated using the van der Waals volume obtained from Bondi's method. Only parameter \(c\) is determined from PVT data.

To calculate parameter \(a\) and \(b\), we assume that: (1) a polymer molecule can be divided into equal segments; (2) the potential energy between two adjacent, nonbonded segments is given by London's dispersion formula; (3) the potential energy of the entire system is pairwise additive [6]; and (4) both \(a\) and \(b\) parameters are temperature-dependent. When a polymer molecule consists of \(r\) segments, molar volume \(v_r\) and parameters \(a, b, c\) of the polymer are related to those of the segment by

\[ a = r^3 \times a' = r^2 \times \left[ a' \times f_1(p') \right] \]
\[ b = r \times b' = r \times \left[ b' \times f_1(p') \right] \]
\[ c = r \times c' \]
\[ \text{(10)} \]

Where \(m\) represents segment basis and \(c\) designates a close-packed system. In Eq. (29), \(f_1(p')\) and \(f_2(p')\) are two universal functions and depends on reduced temperature which is the ratio of kinetic energy to potential energy per molecule

\[ \frac{p_r}{\varepsilon} = \frac{cK}{\varepsilon} \]  
\[ \text{(11)} \]

\(c\) is a potential-energy parameter per molecule. Parameter \(\varepsilon_m\) (per molecule) is related to potential-energy parameter \(\varepsilon'\) (per segment) by (Appendix A)

\[ \varepsilon = r \times \varepsilon' = \left( \frac{9}{16\pi} \right) \times \frac{r \times A'}{N_a} \times \frac{1}{V^2} \]  
\[ \text{(12)} \]

\(A'\) is molar polarization of the segment \((\text{cm}^3/\text{mol})\), \(I'\) is the first ionization potential of the segment \((\text{cm} \times \text{bar}^2/\text{mol})\), and \(V^0\) is the van der Waals volume of the segment \((\text{cm}^3/\text{mol})\).

We calculate \(b'\) from extrapolating \(b\) at zero temperature. Result show that \(V\) volume parameter \(b'\) is nearly proportional to the van der Waals volume. Figure 1 shows that, when \(b\) is determined from zero temperature, we obtain

\[ b' = r \times b' = 3.6303 \times V^0 \]  
\[ \text{(13)} \]

Equation (13) is used to calculate \(b\) for polymers. As in Eq. (13), \(V^0\) is obtained from Bondi's correlation.

![Fig.1 Relation between parameter b (cm^3/mol) and V (aroma-like molecules)]
As shown in Appendix A, parameter $a'$ in Eq. (10) is written as

$$a' = 0.2356 \times \frac{A^2 I}{V_w}$$  \hspace{1cm} (13)$$

Function $f_1(T)$ and $f_2(T)$ are expected to have a universal form for $n$-alkanes and for linear chain polymers such as polyethylene. These functions must meet two boundary conditions $f_1(P_t) \rightarrow 1$ & $f_2(P_t) \rightarrow 1$ as $P_t \rightarrow 0$, and $f_1(P_t) \rightarrow 0$ & $f_2(P_t) \rightarrow \text{constant} \times b'$ as $P_t \rightarrow \infty$. A simple and accurate function which satisfies these boundary conditions is

$$f(P_t) = \frac{\left(1 - A \cdot B P_t^cight)}{1 + C \times P_t^c \times D \times P_t^c + E \times P_t^c}$$  \hspace{1cm} (14)$$

For polymers, $a$ and $b$ are calculated from physical properties of the polymer's saturated monomer. The segment number $r$ is calculated from the number-average molecular weight $\bar{M}_n$ of the polymer. The van der Waals volume per polymer segment $v_w$ is obtained using the segment number $r$ and the van der Waals volume of the repeating unit $(v_w)_R$. In this work, only parameter $c'$ is estimated from polymer-density data.

### 3.1 Results for pure component

Table 1 shows the parameters $c$ and $r$ for $n$-alkanes, which were fitted to vapour-pressure and liquid density data. These parameters cover temperatures from $0.4 \leq T \leq 0.95$. Table 1 also shows comparisons between the experimental and calculated results from using the procedures of Sako et al [6, 9]. In a homologous series, the parameters $c$ and $r$ were found to be linear dependent on the number of carbon atoms per molecule. All needed physical properties, except the ionization potential for the $n$-alkanes higher than $n$-octane, could be obtained from literature [10, 15]. The ionization potential for $n$-alkanes from nonane up to $n$-dotriacontane are estimated via $I = 0.836161 + 1.10801 \times (2 + N_{\text{mol}})^{-1}$ that presented by Tork et al [9]. From the results in Table 1, it is clear that the accuracy of our model is better. The polyethylene LDPE and HDPE. Density data were taken from Danner and High [25]. The parameters $c' = c/r$ for the considered substances are given in Table 1. $c'$ decreases with increasing segment number. This behavior was already discussed by Patterson [26], who showed that the reduced temperature $\tilde{P}_t$ as a function of the segment number decreases rapidly and reaches a lower limit of $\tilde{P}_t$ as $r \rightarrow \infty$ in a homologous series. Hence, if the segment number increases $c'$ becomes independent of the segment number.
The thermodynamic property calculated using the new equation of state can be used to predict PVT and VLE for small and large molecules over a wide range of temperature and pressure. Pure component parameters have been determined for n-alkane series and 1-Alkenes, using vapor pressure data, and liquid density predictions of light and heavy hydrocarbons. The presented models significantly improve prediction of the liquid density and vapor pressure predictions of light and heavy hydrocarbons.

### 4 Conclusion

The new equation of state is based on partition function in which the rotational and vibrational degrees of freedom for small and large molecules are counted. New equation of state can be used to predict PVT and VLE for small molecules and polymer like molecules over a wide range of temperature and pressure. Pure component parameters have been determined for n-alkane series and 1-Alkenes, using vapor pressure data, saturated liquid volumes.

The thermodynamic property calculated using the new equation and the results are compared with the results obtained from the equations of states such as Sako-W - Prausnitz [6], Song-Lambert-Prausnitz[23]. It is indicated that the proposed equation has an acceptable performance for property predictions of pure fluids. The presented models significantly improve prediction of the liquid density and vapor pressure predictions of light and heavy hydrocarbons.

### 5 Appendix A: DERIVATION OF Eq. (13)

For Eq. (5) discussed previously in detail (Sako et al.) we can write

\[ a^* = -\frac{N_A k_B}{2} \frac{1}{\ln (1 + b^*/a^*)} E_0^* \]  

(17)

Where \( E_0^* \) is the potential field experienced by one segment in a close-packed system at volume per
segment $v^*$. From London's dispersion model for nonpolar molecules, the attractive potential energy between two simple, spherically symmetric molecules is (if the two molecules are similar [6])

$$E_0^* = -\frac{3}{4} \frac{\alpha^2 i}{r^6}$$

Where $r$ is the distance between the two molecules (In a close-packed system $r$ is equal to molecular diameter $d$). The attractive potential energy of a molecule with respect to all of the others is given by

$$E_0 = \frac{2\pi}{d^6} \left( -\frac{3}{4} \alpha^2 i \right) = -\frac{3}{4} \alpha^2 i z_s^{*} \frac{1}{d^6}$$

$Z$ is the coordination number of the molecule, $S_m$ is the packing constant. For Ionization potential and Molecular polarizability respectively. By combining these equations we obtain

$$E_0^* = -\frac{3}{4} \frac{3A}{4\pi N_A} \left( \frac{\frac{b^*}{N_A} z_s^{*} \frac{1}{d^6}}{\frac{2}{d^6}} \right)$$

And for segments

$$E_0^* = -\frac{27}{64\pi^2} \frac{A^2}{N_A} \left( \frac{z_s^{*} \frac{1}{d^6}}{\frac{2}{d^6}} \right)$$

Where $'$ denotes segment basis. For a face-centered-cubic lattice, $z'=12$ and $S_m=1.2045$. For a close-packed system, the fraction of space occupied by molecules of diameter $d$ is [6]

$$\frac{V_s}{V^*} = \left( \frac{\pi d^3}{6} \right) \left( \frac{\sqrt{2}}{d^3} \right) = 0.7405$$

As discussed above we calculate $b^*$ at zero temperature and apply to the segment, we obtain

$$b^* = 3.6303 \times V_s$$

Combining eqs. (17), (23)-(35) with the values for $z'$ and $S_m$ we obtain

$$a^* = 0.2356 \times \frac{A^2}{V_s}$$

References:


