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Generalized Peng–Robinson equation of state with pair potential parameters for liquid *n*-alkanes

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Abstract

Peng–Robinson EOS is generalized with pair potential parameters for the PVT relation of liquid *n*-alkanes C_1 to C_{30}, C_{32}, and C_{36} with the saturated vapors for temperatures near the normal boiling point to the critical point. The EOS is reduced with the Lennard–Jones pair potential depth parameter ε and the characteristic length d, which is determined with the pair potential parameters ε and σ. Two reduced parameters in the EOS, $\hat{a} = a/(N_A^2 \varepsilon d^3)$ and $\hat{b} = b/(N_A d^3)$, where N_A is Avogadro number, are in the corresponding states with reduced temperature, $\hat{T} = kT/\varepsilon$. The pair potential parameters ε and σ are expressed by universal functions of temperature reduced with critical temperature, $T_r = T/T_c$. The values of the coefficients in the functions are specific to each alkane. The vapor pressure and the liquid molar volume calculated with the EOS agreed to the observed ones with the root mean square deviation of 2.21% and 0.63%, respectively, better than those from the modified PR-EOS in the literature. The coefficients and the powers in the universal functions for ε and σ are expressed by generalized functions of acentric factor ω, where the calculated vapor pressure and liquid molar volume agreed well to the observed ones with the root mean square deviation of 4.16% and 1.57%, respectively.

Keywords: Equation of state; Corresponding states correlation; Liquid alkane; Pair potential

1. Introduction

An equation of state (EOS) describes fluid state and is one of the important tools to calculate the PVT relation and the vapor–liquid equilibrium. Although cubic EOSs based on the van der Waals equation, Peng–Robinson [1] and Soave–Redlich–Kwong [2] equations, are derived empirically, they are often used for industrial calculation, because they can be solved analytically and reproduce experimental results for simple fluids.

For complex fluids, long chain-like molecule liquids or associated liquids, factors related to the molecular shape and association should be considered. Many improved cubic EOSs based on PR or SRK equations have been proposed, which have temperature-dependent parameters *a* and *b* [3] or translated volume parameter *c* [4,5]. *a* and *b* are the functions of temperature and acentric factor, the coefficients in which are compound specific or universal constants, and *c* is the function of P_c, T_c and z_c. The improved EOSs reproduced the vapor pressure of the complex fluids over large temperature range but did not well the liquid densities near critical point.

Crossover EOSs [6–9] have been proposed to describe both the region far from the critical point and the critical region, which incorporated critical scaling laws near the critical point and improved the PVT relation for simple alkanes. However the equations and the calculation procedure are rather difficult for industrial use.

The aim of this work is to develop a generalized EOS for the PVT relation both in the regions far from the critical point and the critical region with a single set of parameters for *n*-alkanes C_1 to C_{36}. The excess Helmholtz free energy of alkane is expanded around that of a reference fluid, the intermolecular potential of which is expressed by the sum of a hard sphere potential and the same attractive potential as that of the alkane, with the difference between the core repulsive potentials. The hard sphere diameter is chosen as the characteristic length *d* such that the Helmholtz free energy of the alkane is equal to that of the reference. The PR EOS is reduced with the pair potential depth parameter ε and the characteristic length *d*. The reduced EOS parameters

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$\hat{a} = a/(N_A^2 d^3 \varepsilon)$ and $\hat{b} = b/(N_A d^3)$ and the characteristic length d are expressed by the universal functions of reduced temperature $\hat{T} = kT/\varepsilon$. ε and the other pair potential parameter σ are expressed by the functions of reduced temperature $T_r = T/T_c$. The coefficients in the functions are given by compound specific values or by the functions of acentric factor ω. The generalized EOS reproduce the vapor pressure and the liquid density under the saturated vapor well both far from the critical region and the critical region.

2. Generalized EOS

2.1. Intermolecular potential and characteristic length

The intermolecular potential between molecules 1 and 2 of a fluid is to be given by Lennard–Jones 12-6 potential:

$$v(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

where ε and σ are the intermolecular potential parameters and r is the distance between molecules 1 and 2.

The intermolecular potential of the fluid of interest $v(r)$ is separated into a repulsive part $v^0(r)$ and an attractive part $w(r)$ with WCA method [10]:

$$v(r) = v^0(r) + w(r) \tag{2}$$

$$v^0(r) = \begin{cases} v(r) + \varepsilon & r \le r_m = 2^{1/6}\sigma \\ 0 & r > r_m \end{cases} \tag{3}$$

$$w(r) = \begin{cases} -\varepsilon & r \le r_m \\ v(r) & r > r_m \end{cases} \tag{4}$$

The intermolecular potential for a reference fluid $v^{ref}(r)$ is made up of a hard sphere potential $v^{hs}(r)$ and the attractive potential $w(r)$:

$$v^{ref}(r) = v^{hs}(r) + w(r) \tag{5}$$

$$v^{hs}(r) = \begin{cases} \infty & r \le d \\ 0 & r > d \end{cases} \tag{6}$$

The excess Helmholtz free energy of a fluid of interest, an alkane, is projected on that of a reference fluid that has a hard sphere repulsive potential and the same attractive potential as that of the alkane. The hard sphere diameter d, which is the characteristic length, is chosen such that the Helmholtz energy of the alkane is equal to that of the reference and is evaluated from the perturbation expansion of the excess Helmholtz free energy in the method of Harada et al. [11]. When d is chosen such that Eq. (7) holds, the excess free energy of the alkane is equal to that of the reference, Eq. (8) (see Appendix A):

$$\frac{d^3}{3} = \int_d^{\infty} [\exp(\beta v^0) - 1] r^2 \, dr \tag{7}$$

$$\hat{A}^{ex} = \beta A^{ex} = \beta A^{ex^{ref}} = \hat{A}^{ex^{ref}} \tag{8}$$

Eq. (8) shows that the alkane and the reference fluid are in the corresponding states. The thermodynamic properties derived from the Helmholtz energy are in the corresponding states in the reference fluid and the alkane when they are reduced with the characteristic length d and the attractive potential depth ε because the Helmholtz energy of the alkane is equal to that of the reference.

The d value depends on the repulsive potential $v^0(r)$, Eq. (3) or the pair potential $v(r)$, Eq. (1) and is numerically calculated from Eq. (7). The resultant values are fitted by the function (9):

$$\frac{d}{\sigma} = 0.9573 + 5.020 \times 10^{-2} \ln\left(\frac{\varepsilon}{kT}\right) - 5.157 \times 10^{-3}\left(\frac{\varepsilon}{kT}\right) \tag{9}$$

Strictly speaking, the d value depends on the density because the radial distribution function depends on the density. This minor density dependency of d is not included in Eq. (9).

2.2. Generalized EOS

The alkanes are in the corresponding states when the thermodynamic variables are reduced with the characteristic length d and the potential depth ε as mentioned in the last section. The reduced pressure $\hat{P}$ derived from the reduced Helmholtz energy is given by Eq. (10):

$$\hat{P} \equiv \frac{Pd^3}{\varepsilon} = -\hat{T}\left(\frac{\partial \hat{A}}{\partial \hat{v}}\right)_{\hat{T}} \tag{10}$$

where

$$\hat{v} \equiv \frac{v}{N_A d^3} \tag{11}$$

$$\hat{T} \equiv \frac{kT}{\varepsilon} \tag{12}$$

Eq. (10) means that the reduced pressure is a function of the reduced volume and temperature. Thus the Peng–Robinson EOS is reduced with d and ε to be expressed by

$$\hat{P} = \frac{\hat{T}}{\hat{v} - \hat{b}} - \frac{\hat{a}}{\hat{v}^2 + 2\hat{b}\hat{v} - \hat{b}^2} \tag{13}$$

where

$$\hat{a} \equiv \frac{a}{N_A^2 \varepsilon d^3} \tag{14}$$

$$\hat{b} \equiv \frac{b}{N_A d^3} \tag{15}$$

and $\hat{P}$, $\hat{v}$, and $\hat{T}$ are given by Eqs. (10)–(12).

To obtain general functions for the reduced EOS parameters $\hat{a}$ and $\hat{b}$, the values of the parameters a and b of a standard fluid are needed in large temperature region. Propane was chosen as the standard fluid because it has the largest temperature region under the liquid vapor equilibrium in the alkanes in this work. The values of a and b of propane are evaluated at temperatures between the normal boiling point