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 Lenard-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.

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1. Introduction

An equation of state (EOS) describes fluid state and is one of 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 [6,7,8,9] 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 an attractive potential, 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 $\hat{a} = a/(N_A^2 d^3 \varepsilon)$ 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.

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

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].

$$v(r) = v^0(r) + w(r) \qquad (2)$$

$$v^0(r) = v(r) + \varepsilon, \qquad r \leq r_m = 2^{1/6}\sigma$$

$$= 0, \qquad r > r_m \qquad (3)$$

$$w(r) = -\varepsilon, \qquad r \leq r_m$$

$$= v(r), \qquad r > r_m \qquad (4)$$

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 $w(r)$.

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

$$v^{hs}(r) = \infty, \qquad r \le d$$

$$= 0, \qquad r > d \qquad (6)$$

The hard sphere diameter of the reference d, which is the characteristic length, 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 fluid of interest is equal to that of the reference, Eq. (8) (See Appendix A).

$$d^3/3 = \int_d^\infty [\exp(\beta v^0) - 1] r^2 dr \qquad (7)$$

$$\hat{A}^{ex} = \beta A^{ex} = \beta A^{ex\,ref} = \hat{A}^{ex\,ref} \qquad (8)$$

Eq. (8) shows a simple thermodynamic equation expressing the law of corresponding states.

The d value is numerically calculated from Eq. (7) and the resultant values are fitted by the function (9).

$$d/\sigma = 0.9573 + 5.020 \times 10^{-2} \ln(\varepsilon/kT) - 5.157 \times 10^{-3} (\varepsilon/kT) \qquad (9)$$

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 Peng-Robinson EOS is reduced with the pair potential depth ε and the characteristic length d.

$$\hat{P} = \frac{\hat{T}}{\hat{v} - \hat{b}} - \frac{\hat{a}}{\hat{v}^2 + 2\hat{b}\hat{v} - \hat{b}^2} \qquad (10)$$

where $\qquad \hat{P} \equiv Pd^3/\varepsilon \qquad (11)$

$$\hat{v} \equiv v/(N_A d^3) \qquad (12)$$

$$\hat{T} \equiv kT/\varepsilon \qquad (13)$$

$$\hat{a} \equiv a/(N_A^2 \varepsilon d^3) \qquad (14)$$

$$\hat{b} \equiv b/(N_A d^3) \qquad (15)$$

Propane is taken as the standard fluid because it has large reduced temperature region in the liquid vapor equilibrium. The values of a and b of propane are determined at temperatures between the normal boiling point and the critical temperature such that Eq. (10) with the values of $\varepsilon = 3.507 \times 10^{-21}$ J and $\sigma = 5.061 \times 10^{-10}$ m in the literature [12] reproduces the observed vapor pressure and liquid volume under the phase equilibrium [13]. $\hat{a}$ and $\hat{b}$ of propane are expressed by the functions of the reduced temperature $\hat{T}_r$, Eqs. (16) and (17), which are used for other alkanes as universal functions.

$$\hat{a} = \hat{a}_{PR} f_c(\hat{T}_r; \hat{T}_{ar}) + [13.82 - 1.824\hat{T}_r - 1.738\exp(\hat{T}_r)][1 - f_c(\hat{T}_r; \hat{T}_{ar})] \qquad (16)$$

$$\hat{b} = \hat{b}_{PR} f_c(\hat{T}_r; \hat{T}_{br}) + [0.7489 + 0.9151\hat{T}_r - 0.1531\exp(1.699\hat{T}_r)][1 - f_c(\hat{T}_r; \hat{T}_{br})] \qquad (17)$$

where
$$f_c(\hat{T}_r; \hat{T}_{ir}) = \frac{\hat{T}_{ir}}{\hat{T}_{ir} + 1 - \hat{T}_r}, \quad i = a, b \qquad (18)$$

$$\hat{T}_r \equiv \frac{\hat{T}}{\hat{T}_c} = \frac{kT/\varepsilon}{kT_c/\varepsilon_c} \qquad (19)$$

f_c is a correction function so that $\hat{a}$ and $\hat{b}$ approach $\hat{a}_{PR}$ and $\hat{b}_{PR}$, respectively, when $\hat{T}_r$ approaches unity. $\hat{T}_{ar} = 1.4218 \times 10^{-3}$ and $\hat{T}_{br} = 1.8891 \times 10^{-3}$ are correction constants for $\hat{a}$ and $\hat{b}$, respectively. $\hat{a}_{PR} \equiv a_{PR}/(N_A^2 \varepsilon_c d_c^3)$ and $\hat{b}_{PR} \equiv b_{PR}/(N_A d_c^3)$ are the reduced Peng-Robinson EOS parameters, where $a_{PR} = 0.45724(RT_c)^2/P_c$ and $b_{PR} = 0.07780RT_c/P_c$ are derived from the conditions that the Peng-Robinson EOS has to satisfy at the critical point. ε_c and d_c are the parameters at the critical point.

The values of the potential parameters ε and σ for the other alkanes are determined at temperatures between the normal boiling point and the critical temperature such that the

observed vapor pressure and liquid volume under the phase equilibrium [13] are reproduced with Eq. (10). The values of ε and σ for propane are reevaluated such that the vapor pressure and liquid molar volume calculated from Eq. (10) are improved at the temperatures. ε and σ can be expressed by the universal functions of reduced temperature T_r, Eqs. (20) and (21), respectively, which are similar to the functions of Twu et al.[3]

$$\varepsilon/\varepsilon_c = T_r{}^{L_\varepsilon} \exp[M_\varepsilon(1 - T_r{}^{N_\varepsilon})] \tag{20}$$

$$\sigma/\sigma_c = T_r{}^{L_\sigma} \exp[M_\sigma(1 - T_r{}^{N_\sigma})] \tag{21}$$

where ε_c and σ_c can be expressed by the following functions of T_c and P_c.

$$\varepsilon_c = 4.7225 \times 10^{-23} + 9.0292 \times 10^{-24} T_c + 8.2817 \times 10^{-28} T_c^2 \tag{22}$$

$$\ln \sigma_c = -18.389 + 0.32323 \ln (T_c / P_c) \tag{23}$$

L_ε, M_ε, N_ε, L_σ, M_σ and N_σ are compound specific shown in Table 1.

It is useful that those parameters are expressed by functions of a parameter in available. In this work they are given by the following functions of acentric factor ω, the values of which are available in the literature [13].

$$L_\varepsilon = -2.9642 \times 10^{-2} - 8.2347 \times 10^{-2} \ln (0.16479 + \omega) - 0.30801\omega \tag{24}$$

$$M_\varepsilon = 8.8756 \times 10^{-2} + 7.5051 \times 10^{-2} \ln (0.25548 + \omega) \tag{25}$$

$$N_\varepsilon = 0.89979 + 4.2746\omega \tag{26}$$

$$L_\sigma = -1.0567 \times 10^{-2} + 5.7621 \times 10^{-2}\omega - 6.4470 \times 10^{-3} \omega^2 \tag{27}$$

$$M_\sigma = -2.7600 \times 10^{-2} + 1.1146 \times 10^{-6}\omega + 4.8328 \times 10^{-2} \exp (-2.6857\omega) \tag{28}$$

$$N_\sigma = 5.6888 \tag{29}$$

Since N_σ in Table 1 does not show any significant dependence on ω, it is expressed by a constant value as Eq. (29).

The generalized EOS (10) has eight parameters T_c, P_c, L_ε, M_ε, N_ε, L_σ, M_σ and N_σ or three parameters T_c, P_c and ω when Eqs. (24) to (29) are used. Although Eq. (10) needs

the values of T_c, P_c and ω, they are available in many literatures.

3. Results and Discussion

The generalized EOS (10) with the equality of vapor and liquid fugacities gives the vapor pressure and saturated liquid volume of n-alkanes C_1 to C_{30}, C_{32}, and C_{36} near the normal boiling temperature to the critical temperature with the help of Eq. (9) and Eqs. (16) to (23) with the values of T_c, P_c, L_ε, M_ε, N_ε, L_σ, M_σ and N_σ or with the help of Eq. (9) and Eqs. (16) to (29) with the values of T_c, P_c and ω. The root mean square deviations (RMSD) of the calculated properties from the observed ones are shown in Table 2.

The results of two improved PR EOS, PR EOS with a generalized alpha function by Twu et al. (GAPR) [3] and volume translated PR EOS by Ahler and Gmehling (VTPR) [4, 5] are also shown in the table. Twu et al. proposed the generalized alpha function to describe the vapor pressure of n-alkane C_1 to C_{20} near the triple point to the critical point. The parameter in PR EOS a is expressed by $a(T) = \alpha(T)a(T_c)$ where alpha function $\alpha(T) = T_r^{N(M-1)}\exp[L(1-T_r^{NM})]$. The parameters L, M, and N are specific to each alkane or universal constants. The parameter in PR EOS b is given by the critical point conditions. The RMSD for C_1 to C_{20} with the use of the compound specific parameter values [3] are shown in Table 2. Ahler and Gmehling proposed VTPR to describe the saturated liquid density of inorganic and organic compounds [4] and showed the translation parameter c specific to n-alkanes C_1 to C_{10} [5]. Thus the results for C_1 to C_{10} are shown for the comparison. The RMSD for the alkanes including the heavier alkanes with the values of L_ε, M_ε, N_ε, L_σ, M_σ and N_σ in this work (this work a in the table) is better than those of GAPR and VTPR for the lighter alkanes. That with the functions for L_ε, M_ε, N_ε, L_σ, M_σ and N_σ in this work (this work b in the table) is also better than those

of GAPR and VTPR.

Figures 1 and 2 show the vapor pressure and the liquid molar volume, respectively, of representative n-alkanes C_1, C_3, C_6, C_{10}, C_{15}, C_{21}, C_{28} and C_{36}. The symbols are the observed values [13], the solid lines are the values calculated from the EOS (10) with the values of L_ε, M_ε, N_ε, L_σ, M_σ and N_σ for C_1 to C_{36}, the broken lines are those from GAPR for C_1 to C_{15} and the dotted lines are those from VTPR for C_1 to C_{10}. The vapor pressure calculated in this work agrees well to the observed ones. The vapor pressures from GAPR and from VTPR also agree well for almost all the alkanes, although they show slight deviations from the observed ones for C_6 and C_{15}. The liquid volume calculated in this work agree with the observed one well, while those from GAPR and VTPR show some deviations.

Figures 3 and 4 show the vapor pressure and liquid molar volume observed [13] and calculated with the functions for L_ε, M_ε, N_ε, L_σ, M_σ and N_σ, Eqs.(24) to (29). The calculated values agree to the observed ones as well as in Figures 1 and 2, although the liquid volume for C_1, C_6, C_{10}, and C_{15} show slight deviations from the observed ones.

The reason of the excellent results in this work is thought to be as follows: Equation (8) means that the system interested is projected onto the reference system that has simple hard sphere and attractive potentials. The hard sphere diameter d is determined such that the Helmholtz free energy of the interested system is equal to that of the reference one and the attractive potential depth of the interested system ε is equal to that of the reference. The EOS reduced by d and ε of the interested system and that of the simple reference system are in the corresponding states. Thus the EOS can produce the excellent results of the vapor pressure and the liquid molar volume under vapor-liquid equilibrium.

It is important that the EOS is reduced by the characteristic length d that is the hard

sphere diameter of the simple reference system. When the EOS was reduced by the pair potential size parameter σ instead of d, where of course σ and another potential parameter ε depended on temperature and were evaluated such that the observed vapor pressure and liquid volume were reproduced, the results were worth than those when d was used. Also when the not-reduced parameters a and b were expressed by universal functions with compound specific coefficients, the results were worth than those when $\hat{a}$ and $\hat{b}$ were used.

The results of the heavier alkanes C_{21} to C_{30}, C_{32} and C_{36} are little worse than those of the lighter alkanes C_1 to C_{20}. It is thought that the effect of the higher perturbation terms that are neglected in the derivation of Eq. (8) might become larger for the heavier alkanes.

4. Conclusion

Peng-Robinson EOS was generalized with the depth of the pair potential ε and the characteristic length d for n-alkanes C_1 to C_{30}, C_{32}, and C_{36} near the normal boiling point to the critical point. The characteristic length d is the hard sphere diameter of a reference system, the pair potential of which is comprised of the hard sphere and attractive potentials and the Helmholtz free energy of which is equal to that of the system of interest. d is given by the function of reduced temperature $\hat{T}=kT/\varepsilon$ and the molecular size of the pair potential σ. The parameters in the generalized EOS $\hat{a}$ and $\hat{b}$ are expressed by the universal functions of reduced temperature $\hat{T}_r = \hat{T}/\hat{T}_c = (kT/\varepsilon)/(kT_c/\varepsilon_c)$. The pair potential parameters ε and σ are given by the functions of reduced temperature $T_r=T/T_c$, the coefficients in which L_ε, M_ε, N_ε, L_σ, M_σ and N_σ are compound specific or are given by the functions of acentric factor ω. In the former case eight parameters T_c, P_c, L_ε, M_ε, N_ε, L_σ, M_σ and N_σ are needed for the generalized PR-EOS

and three parameters T_c, P_c, and ω are needed in the latter case. The generalized EOS with the parameters L_ε, M_ε, N_ε, L_σ, M_σ and N_σ reproduced the observed vapor pressure and liquid molar volume excellently and that with the functions of ω reproduced them well.

Appendix A

The reduced excess Helmholtz free energy of a system is expressed in terms of diagrams [14]. Diagram is an expression of infinite series expansion for partition function, distribution function, configurational integral, and thermodynamic properties with the use of dot and bond, where dot means the position or the space integral of a molecule and bond does the interaction between molecules.

$-\hat{A}^{ex} = -\beta A^{ex}$ = [sum of all simple irreducible diagrams composed of two or more black density circles and f bonds] = [+ + + + ….] (A1)

Here the dot is a black density circle which means the space integral of a molecule and the segment line is an f bond defined by Eq. (A2) which means the interaction between two molecules.

$$f = \exp(-\beta v) - 1 \qquad\qquad (A2)$$

The f bond is separated into f^{ref} bond for the reference system and f^b bond which was called the blip function by Andersen et al. [15] The f^b bond is nonzero only in a small range of the molecular separation.

$$f = f^{ref} + f^b \qquad\qquad (A3)$$

$$f^{ref} = \exp(-\beta v^{ref}) - 1 \qquad\qquad (A4)$$

Introduction of Eq. (A3) into Eq. (A1) yields

$-\beta A^{ex} = -\beta A^{ex\,ref} + [$ + + + + ….] +

[higher order perturbation terms with respect to f^b] (A5)

where the dotted bond represents the f^b bond. If the second square-bracketed terms of higher orders are neglected and the characteristic length d is chosen such that the sum of the diagrams involving only one f^b bond vanishes, the excess free energy is expressed by Eq. (A6).

$$\hat{A}^{ex} = \beta A^{ex} = \beta A^{ex\,ref} = \hat{A}^{ex\,ref} \tag{A6}$$

The radial distribution function for molecules 1 and 2, the positions of which are r_1 and r_2, is expanded by a series of diagrams [14].

$$g(1,2) = [\,\underset{1}{\circ}\!\!=\!\!\underset{2}{\circ}\,]\ast[\ \underset{1\quad 2}{\triangle}\ +\ \underset{1\quad 2}{\square}\ +\ \underset{1\quad 2}{\boxtimes}\ +\ \underset{1\quad 2}{\boxtimes}\ +\ \underset{1\quad 2}{\boxtimes}\ +\ \ldots\ ]\tag{A7}$$

where the open circle is a white circle which means the position of a molecule and $=$ is an e bond defined by $\exp(-\beta v)$, the interaction between two molecules.

The characteristic length d is determined such that the first bracketed term in Eq. (A5) vanishes. From the first bracketed term in Eq. (A5) and Eq. (A7), d value is given implicitly as

$$\int g_{ij}\exp(\beta v_{ij})f^b{}_{ij}\,d\vec{r} = 0 \tag{A8}$$

where

$$f^b{}_{ij} = \exp(-\beta v_{ij}) - \exp(-\beta v_{ij}{}^{ref}) \tag{A9}$$

Eq. (A8) has the blip function which is effectively nonzero only in the vicinity of $r = d$. On the contrary, $g(r)$ is not sensitive to r in this range and it may be assumed that $g(r)$ is constant irrespective of r. This assumption and the introduction of Eq.(A9) into Eq.(A8) with the help of Eqs.(2) to (6) yield

$$\int \{1 - \exp[\beta(v_{ij} - v_{ij}{}^{ref})]\}d\vec{r} = 0 \tag{A10}$$

Since the pair potential v_{ij} and $v_{ij}{}^{ref}$ are expressed by Eqs.(2) to (6) and depend only on distance r, Eq.(A10) is changed to Eq.(A11).

$$\int_0^\infty 4\pi r^2 \{1 - \exp[\beta(v^{(0)}(r) - v^{hs}(r))]\}dr = 0 \qquad (A11)$$

Substitution of Eq.(6) into Eq.(A11) gives

$$\int_0^d r^2 dr + \int_d^\infty r^2 \{1 - \exp[\beta v^{(0)}(r)]dr = 0 \qquad (A12)$$

Integration of the first term in the right hand side of Eq.(A12) yields

$$d^3/3 = \int_d^\infty [\exp(\beta v^0) - 1]r^2 dr \qquad (A13)$$

5. List of symbols

A Helmholtz free energy

a EOS parameter related to attractive potential

b EOS parameter related to exclusive volume

c EOS translated volume parameter

d characteristic length = hard sphere diameter

f Mayer f bond

f^b f^b bond (blip function)

f_c correction function for EOS parameters a and b

g radial distribution function

k Boltzmann's constant

L parameter for generalized function of potential parameters ε and σ

M parameter for generalized function of potential parameters ε and σ

N_A Avogadro number

N parameter for generalized function of potential parameters ε and σ

P vapor pressure

r separation distance

r_m separation distance at which intermolecular potential takes the minimum value

T absolute temperature

T_{ar}	correction constant
T_{br}	correction constant
V	molar volume
v	intermolecular potential
w	attractive potential
z	compressibility factor

5.1. Greek letters

β	reciprocal temperature ($=1/kT$)
ε	intermolecular potential parameter
σ	intermolecular potential parameter
ω	acentric factor

5.2. Subscript

c	critical temperature
i, j	molecule
PR	Peng-Robinson EOS
r	reduced by critical parameter

5.3. Superscripts

ex	excess
hs	hard sphere
ref	reference
$^\wedge$	reduced form
0	repulsive potential

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Figure captions

Figure 1. Vapor pressure for representative n-alkanes C_1, C_3, C_6, C_{10}, C_{15}, C_{21}, C_{28} and C_{36}. Symbols: observed values [13]. Solid lines: this work calculated with the values of L_ε, M_ε, N_ε, L_σ, M_σ and N_σ for C_1 to C_{36}. Broken lines: GAPR for C_1 to C_{15}. Dotted lines: VTPR for C_1 to C_{10}.

Figure 2. Liquid molar volume for representative n-alkanes C_1, C_3, C_6, C_{10}, C_{15}, C_{21}, C_{28} and C_{36}. Solid lines: this work calculated with the values of L_ε, M_ε, N_ε, L_σ, M_σ and N_σ for C_1 to C_{36}. Broken lines: GAPR for C_1 to C_{15}. Dotted lines: VTPR for C_1 to C_{10}. Symbols are observed values [13] and are the same as in Figure 1.

Figure 3. Vapor pressure calculated with the functions for L_ε, M_ε, N_ε, L_σ, M_σ and N_σ for representative n-alkanes C_1, C_3, C_6, C_{10}, C_{15}, C_{21}, C_{28} and C_{36} (solid lines). Symbols are observed values [13] and are the same as in Figure 1.

Figure 4. Liquid molar volume calculated with the functions for L_ε, M_ε, N_ε, L_σ, M_σ and N_σ for representative n-alkanes C_1, C_3, C_6, C_{10}, C_{15}, C_{21}, C_{28} and C_{36} (solid lines). Symbols are observed values [13] and are the same as in Figure 1.

Table 1. Parameters in generalized functions for potential parameters ε and σ of n-alkanes L_ε, M_ε, N_ε, L_σ, M_σ and N_σ.

Compound	$L_\varepsilon \times 10^2$	$M_\varepsilon \times 10^2$	N_ε	$L_\sigma \times 10^3$	$M_\sigma \times 10^3$	N_σ
Methane	10.966	-0.4522	20.778	-9.9049	10.417	13.339
Ethane	5.1506	1.5030	1.1583	-4.6721	6.8887	20.969
Propane	3.7577	6.9051	0.7354	0.0085539	6.8949	15.000
n-Butane	-0.11779	3.1557	1.8806	0.71238	5.2740	15.000
n-Pentane	-5.2369	1.3420	5.9397	2.2654	1.5571	10.000
n-Hexane	-8.9418	1.3205	9.8606	2.5854	-2.7333	10.000
n-Heptane	-8.0194	4.7491	2.7730	3.5299	-8.2399	3.6288
n-Octane	-10.028	5.4598	3.1097	0.95952	-14.201	4.3327
n-Nonane	-13.031	5.3108	3.3609	7.2954	-12.362	8.2478
n-Decane	-14.049	6.8188	3.1653	6.0645	-18.376	4.4669
n-Undecane	-18.368	5.1956	4.3117	12.347	-17.888	7.1807
n-Dodecane	-19.434	6.3221	4.0267	14.710	-19.002	7.0645
n-Tridecane	-19.736	8.5139	3.1866	22.642	-20.856	6.8987
n-Tetradecane	-21.649	8.2053	3.5026	26.851	-23.018	13.539
n-Pentadecane	-20.693	11.015	2.9703	29.866	-23.420	14.378
n-Hexadecane	-25.183	8.5289	3.7699	32.717	-24.199	16.190
n-Heptadecane	-23.958	11.549	3.2052	33.278	-22.822	16.118
n-Octadecane	-25.550	11.808	3.3827	34.661	-24.535	15.162
n-Nonadecane	-29.253	10.309	4.0126	38.411	-24.051	15.513
n-Eicosane	-30.795	10.614	4.4184	41.319	-22.131	16.588
n-Heneicosane	-33.174	10.081	4.9787	41.339	-23.567	9.4640
n-Decosane	-37.073	8.3894	6.9438	38.541	-28.084	10.819

n-Tricosane	-36.830	10.419	5.0113	45.221	-23.411	10.822
n-Tetracosane	-36.354	11.901	4.7079	46.865	-23.130	8.1682
n-Pentacosane	-38.811	11.241	5.4739	42.532	-25.668	7.9753
n-Hexacosane	-37.408	13.782	4.5702	59.055	-18.474	8.5633
n-Heptacosane	-32.840	19.668	3.4347	60.244	-16.734	8.3945
n-Octacosane	-43.802	11.613	6.3930	51.775	-23.850	10.633
n-Nonacosane	-47.892	9.9469	9.0406	43.069	-29.482	7.4113
n-Triacontane	-49.424	10.133	9.0590	54.436	-24.072	10.042
n-Dotriacontane	-51.470	10.781	8.1591	39.540	-43.639	2.3538
n-Hexatriacontane	-57.780	10.854	11.959	54.648	-28.240	3.0000

Table 2. Root mean square deviations (RMSD) [%] of vapor pressure P and liquid molar volume v^l of n-alkanes. RMSD for vapor pressure is evaluated in $\log_{10} p$.

compound	this work a[1]		this work b[2]		GAPR[3]		VTPR[4]	
	P	v^l	P	v^l	P	v^l	P	v^l
C_1	0.401	0.200	2.02	1.72	0.369	8.74	0.637	4.71
C_2	0.548	0.161	0.452	0.626	0.778	6.51	1.98	4.08
C_3	1.03	0.209	1.01	0.622	1.23	5.11	0.956	4.32
C_4	1.08	0.223	3.46	1.30	0.605	4.38	5.26	4.33
C_5	2.46	0.625	2.06	1.34	5.40	4.18	9.50	4.64
C_6	2.14	0.248	5.78	1.25	2.49	4.01	14.4	4.83
C_7	1.06	0.225	2.40	1.11	8.15	5.09	4.63	5.00
C_8	0.871	0.273	2.86	1.04	1.77	6.47	1.94	5.39
C_9	1.12	0.308	0.877	1.06	13.7	7.63	10.7	5.17
C_{10}	0.976	0.269	1.80	0.853	1.52	8.37	4.13	4.94
C_{11}	1.14	0.339	3.97	0.688	2.87	9.82	-	-
C_{12}	1.21	0.341	2.01	0.661	1.18	10.7	-	-
C_{13}	1.37	0.319	3.66	0.972	16.4	12.5	-	-
C_{14}	1.45	0.515	6.53	2.48	9.54	14.5	-	-
C_{15}	1.56	0.526	3.46	2.48	13.5	15.5	-	-
C_{16}	1.82	0.560	8.14	2.79	7.09	16.4	-	-
C_{17}	1.81	0.519	3.30	1.98	13.0	15.6	-	-
C_{18}	1.89	0.574	3.32	2.22	2.66	17.1	-	-
C_{19}	1.99	0.561	4.40	2.19	8.68	17.6	-	-
C_{20}	2.31	0.526	2.47	1.63	6.29	17.7	-	-

C_{21}	2.43	0.498	2.89	1.25	-	-	-	-
C_{22}	2.59	0.673	5.55	2.24	-	-	-	-
C_{23}	2.53	0.490	3.32	1.08	-	-	-	-
C_{24}	2.95	0.620	4.65	1.03	-	-	-	-
C_{25}	2.58	0.762	2.63	0.956	-	-	-	-
C_{26}	2.55	0.706	4.83	1.19	-	-	-	-
C_{27}	3.20	0.700	5.94	1.47	-	-	-	-
C_{28}	2.67	0.988	3.55	1.31	-	-	-	-
C_{29}	2.58	1.03	3.63	1.42	-	-	-	-
C_{30}	2.95	1.02	3.84	1.47	-	-	-	-
C_{32}	2.90	1.29	3.74	1.66	-	-	-	-
C_{36}	5.83	1.41	9.27	2.27	-	-	-	-
av. C_1-C_{20}	1.43	0.382	3.72	1.61	7.75	11.5	7.00[5]	4.76[5]
av. C_{21}-C_{36}	3.11	0.890	4.78	1.51	-	-	-	-
av. C_1-C_{36}	2.21	0.627	4.16	1.57	-	-	-	-

1) Compound specific values are used for L_ε, M_ε, N_ε, L_σ, M_σ and N_σ.

2) Generalized functions of acentric factor are used for L_ε, M_ε, N_ε, L_σ, M_σ and N_σ.

3) Generalized alpha function PR-EOS by Tew et al. [3]

4) Volume translated PR-EOS by Ahler and Gmehling [5].

5) RMSD averaged for C_1-C_{10}.