JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 18, No. 2, April–June 2004

Study of Lennard–Jones Chains for Hydrocarbons

Jurij Avsec[*] and Milan Marčič[†]
University of Maribor, 2000 Maribor, Slovenia
and
Koichi Watanabe[‡]
Keio University, Yokohama 8522, Japan

A mathematical model is featured for computing equilibrium thermophysical properties of state in the fluid domain for pure hydrocarbons with the help of classical thermodynamics and statistical associating chain theories. We calculated thermodynamic properties for butane as an example of hydocarbon substances. To calculate the thermodynamic properties of a real fluid, the models based on Lennard–Jones intermolecular potential were applied. To calculate the thermodynamic properties of a real fluid with the help of classical thermodynamics we used the Tillner–Roth–Watanabe–Wagner (TRWW) equation of the Helmholtz type. We developed the mathematical model for the calculation of all equilibrium thermodynamic functions of state for pure hydrocarbons. The analytical results obtained using statistical thermodynamics are compared with the TRWW model and show relatively good agreement.

Nomenclature

A = free energy
A^* = reduced free energy
a_{ij} = coefficients for calculation of radial distribution function
C_p = molar heat capacity at constant pressure
C_V = molar heat capacity at constant volume
c_0 = velocity of sound
D = hard sphere diameter
d_i = exponent
f = number of degrees of freedom
G = free enthalpy
g_0 = hard sphere radial distribution function
g_{LJ} = Lennard–Jones radial distribution function
H = enthalpy
H_H = Hamiltonian
k = Boltzmann constant
M = molecular mass
m = number of segments
N = number of molecules in system, Lennard–Jones with influence of rotational contribution
p = pressure, momentum
R_m = universal gas constant
r = intermolecular distance
S = entropy
T = temperature
T^* = reduced temperature
t_i = exponent
U = internal energy
V = volume
v = specific volume
Z = partition function
α_I = exponent
β = Boltzmann factor
β_I = exponent
β_t = coefficient of thermal expansion
δ = inversed reduced volume
ε = Lennard–Jones parameter
ε_s = segment interaction parameter
η = packing factor
θ = characteristic temperature
μ_J = Joule–Thomson coefficient
ρ = density
ρ^* = reduced density
σ = Lennard–Jones parameter
σ_s = segment diameter
τ = inversed reduced temperature
χ = isothermal compressibility

Superscripts and Subscripts

assoc = association
c = critical condition
conf = configurational
el = influence of electron excitation
ir = internal rotation
nuc = influence of nuclear excitation
pot = potential energy
res = residual
rot = rotation
seg = segment
trans = translation
vib = vibration
0 = ground state

Introduction

In the engineering practice processes occurring in the liquid–gas region are of vital importance. To design devices for this field of activity, it is necessary to know the thermodynamic properties of state in a one- or two-phase environment for pure hydrocarbons and their mixtures.

In most cases the thermodynamic tables or diagrams of different empirical functions obtained from measurement are used (classical thermodynamics). Today, there are numerous equations of state (EOS) reported in the literature for describing the behavior of fluids: van der Waals EOS (VDW), Peng–Robinson (PR), Redlich–Kwong

---

Presented as Paper 2002-3339 at the AIAA/ASME 8th Joint Thermophysics and Heat Transfer Conference, 24–26 June 2002; received 17 January 2003; revision received 16 June 2003; accepted for publication 17 June 2003.

[*] Assistant Professor and Mechanical Engineer, P.O. Box 224, Department of Thermodynamics, Faculty of Mechanical Engineering, Smetanova 17. Member AIAA.

[†] Professor and Mechanical Engineer, P.O. Box 224, Department of Thermodynamics, Faculty of Mechanical Engineering, Smetanova 17.

[‡] Professor and Mechanical Engineer, Thermodynamics Laboratory, Department of System Design Engineering, Faculty of Science and Technology.

Table 1 Fundamental characteristics of various EOS obtained on the basis of classical thermodynamics

EOS	Number of constants used	Influence of polarity	Type
VDW	2	No	Pressure
RK	2	No	Pressure
PR	3	Yes	Pressure
BWR	8	No	Pressure
BWRSN	16	Yes	Pressure
MBWR	32	Yes	Pressure
JS	75–150	Yes	Helmholtz
TR	>200	Yes	Helmholtz
MW	>200	Yes	Helmholtz

(RK) EOS, Soave EOS, and so forth.[1] However, these equations have exhibited some noticeable defects, such as poor agreement with experimental data at moderate densities. On the other hand, we can use the complex EOS with many constants: Benedict–Webb–Rubin[1] (BWR) EOS, Lee–Kessler[1] EOS, Benedict–Webb–Rubin–Starling–Nishiumi[1] (BWRSN) EOS, modified BWR[1,2] (MBWR), Jacobsen–Stewart[3] (JS) EOS, Tillner–Roth–Watanabe–Wagner[4–8] (TRWW), and so forth. These equations are more complicated; however, they have no insight into the microstructure of matter and have poor agreement with experimental data outside interpolation limits.

The calculation of thermodynamic functions of state with the help of classical thermodynamics is a well-known topic and is not described in this paper. Table 1 shows only the fundamental characteristics of various EOS obtained by classical thermodynamics.

Statistical thermodynamics, on the other hand, calculates the properties of the state on the basis of molecular motions in a space and intramolecular interaction. The calculation of the thermodynamic functions of state is possible via many statistical theories. One of the most successful is the perturbation theory. Several EOS have been published that are based on perturbation theory.[9,10] The evolution of perturbation theory is well described in the literature by Barker and Henderson,[11] Münster,[12] Lucas,[13] and Gray and Gubbins.[14]

In this paper we developed the mathematical model of computing the equilibrium properties of state. We compared the deviation of the results from the TRWW model among various models for thermodynamic functions of state and also for their derivatives (i.e., enthalpy, pressure, entropy, isothermal compressibility, the coefficient of thermal expansion, the heat capacities, and the velocity of sound).

The results of the analysis are compared with the TRWW model obtained on the basis of classical thermodynamics and show a relatively good agreement, especially for real gases. Somewhat larger deviations can be found, however, in the region of real liquid due to the large influence of the attraction and repulsion forces, because the Lennard–Jones (LJ) potential is an approximation of the actual real intermolecular potential.

Computation of Thermodynamic Properties of State

To calculate thermodynamic functions of state we applied the canonical partition.[13] Utilizing the semiclassical formulation for the purpose of the canonical ensemble for the N indistinguishable molecules the partition function Z can be expressed as follows[12]:

$$Z = \frac{1}{N! h^{Nf}} \int \cdots \int \exp\left(-\frac{H_H}{kT}\right) \cdot \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \cdots \mathrm{d}\boldsymbol{r}_N \mathrm{d}\boldsymbol{p}_1 \mathrm{d}\boldsymbol{p}_2 \cdots \mathrm{d}\boldsymbol{p}_N \tag{1}$$

where f stands for the number of degrees of freedom of each individual molecule, H_H designates the Hamiltonian molecule system, vectors $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$ describe the positions of N molecules and $\boldsymbol{p}_1, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_N$ momenta, k is Boltzmann's constant, and h is Planck's constant. The canonical ensemble of partition functions for the system of N molecules can be expressed as follows[15]:

$$Z = Z_0 Z_{\mathrm{trans}} Z_{\mathrm{vib}} Z_{\mathrm{rot}} Z_{\mathrm{ir}} Z_{\mathrm{el}} Z_{\mathrm{nuc}} Z_{\mathrm{conf}} \tag{2}$$

Thus, the partition function Z is a product of terms of the ground state (0), translation, vibration, rotation, internal rotation, influence of electrons excitation, influence of nuclei excitation, and influence of the intermolecular potential energy.

Utilizing the canonical theory for computation the thermodynamic functions of state can be listed as follows.[12,13]

Pressure:

$$p = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T \tag{3a}$$

Internal energy:

$$U = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{3b}$$

Free energy:

$$A = -kT \cdot \ln Z \tag{3c}$$

Entropy:

$$S = k\left[\ln Z + T\left(\frac{\partial \ln Z}{\partial T}\right)_V\right] \tag{3d}$$

Free enthalpy:

$$G = -kT\left[\ln Z - V\left(\frac{\partial \ln Z}{\partial T}\right)_V\right] \tag{3e}$$

Enthalpy:

$$H = kT\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_V + V\left(\frac{\partial \ln Z}{\partial V}\right)_T\right] \tag{3f}$$

where T is temperature and V is the volume of the molecular system.

The computation of the individual terms of the partition function and their derivatives, except for the configurational integral, is dealt with in Refs. 13–15.

The various derivatives and expressions of the fundamental equations (3) have an important physical significance. This paper presents expressions that are very important for planning the energetic processes. The various derivatives also prove to be of physical interest.

Coefficient of thermal expansion:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{4}$$

Isothermal compressibility:

$$\chi = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{5}$$

Heat capacity at constant volume per mole:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \tag{6}$$

Heat capacity at constant pressure per mole:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = C_v + \frac{TV\beta^2}{\chi} \tag{7}$$

Velocity of sound:

$$\begin{aligned} c_0 &= \sqrt{-V^2 \frac{1}{M}\left(\frac{\partial p}{\partial V}\right)_s} \\ &= \sqrt{-V^2 \frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p \frac{1}{M} \Big/ \left(\frac{\partial V}{\partial T}\right)_p - \frac{C_p}{T}\left(\frac{\partial T}{\partial p}\right)_v} \end{aligned} \tag{8}$$

where M is molecular mass.

Joule–Thomson coefficient:

$$\mu_J = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] \tag{9}$$

Statistical Associating Fluid Theory[16–42]

Over the past 50 years, quite accurate models based on statistical thermodynamics have been developed for predicting thermodynamic properties of simple molecules. Simply, we refer to molecules for which the most important intermolecular forces are repulsion and dispersion with weak electrostatic forces due to dipoles, quadrupoles, and higher multipole moments. Many hydrocarbons, natural constituents, and simple organic and inorganic molecules fall within this category, but a lot of other components such as electrolytes, polar solvents, hydrogen-bonded fluids, polymers, liquid crystals, plasmas, and particularly mixtures do not belong to this group. The reason for this is that, for such fluids, important new intermolecular forces have become important: Coulombic forces, strong polar forces, complexing forces, the effects of association and chain formation and so on.

An important kind of these complex fluids consists of those that associate to form relatively long-lived dimers or higher n-mers. This kind of fluid includes hydrogen bonding, charge transfer, and others. The intermolecular forces involved are stronger than those due to dispersion or weak electrostatic interactions but are still weaker than forces due to chemical bonds.

In recent years thermodynamic theories based on statistical thermodynamics have been rapidly developed. Fluids with chain bonding and association have received much attention in recent years. Interest in these fluids is prompted by the fact that they cover a much wider range of real fluids than spherical ones. A good theory describing these fluids will be very beneficial in chemical engineering applications by reducing the number of parameters and making them more physically meaningful and more predictable. In technical practice energy processes are of vital importance. To calculate the thermodynamic properties of a real LJ fluid, the Liu–Li–Lu (LLL) EOS is based on simple perturbation theory and the statistical associating fluid theory (SAFT)-VR EOS for an LJ chain fluid. At the same time we have developed and applied a complex Tang–Lu (TL) analytical model with a new radial distribution function (RDF) based on simplified exponential approximation and expansion. The developed RDF was applied to the development of a new SAFT model. The presented model has been used to calculate several typical properties of LJ chains and associating LJ chains. This paper discusses for the first time the accuracy of presented models in real engineering practice.

The original derivation of SAFT models can be read in the literature.[40−43] The models require a comprehensive knowledge of graph theory to be fully understood. The residual Helmholtz energy consists of three terms, representing contributions from different intermolecular forces:

$$A^{\mathrm{res}} = A^{\mathrm{seg}} + A^{\mathrm{chain}} + A^{\mathrm{assoc}} \tag{10}$$

The first term, A^{seg}, represents segment–segment interactions. In this paper we represent segment–segment interactions through LJ interaction potential. Each segment is characterized by its diameter σ_s and segment interaction parameter ε_s, and each molecule is characterized with the number of segments, m.

The second term, A^{chain}, is the result of the presence of covalent chain-forming bonds between the LJ segments.

The third term, A^{assoc}, is the result of site–site interactions between segments, for example, hydrogen bonding. For the hydrocarbons the association term is not importance and will be neglected in our equations:

$$\begin{aligned} A^{\mathrm{res}} &= A^{\mathrm{seg}}(m\rho, T, \sigma_s, \varepsilon) + A^{\mathrm{chain}}(\rho, d, m) \\ &\quad + A^{\mathrm{assoc}}(\rho, T, d, \varepsilon^{\mathrm{AB}}, \kappa^{\mathrm{AB}}) \end{aligned} \tag{11}$$

where ρ is the molar density.

Liu–Li–Lu model[17]

The presented model is developed on the basis of SAFT and perturbation theory around a hard sphere with new coefficients by fitting reduced pressure and internal energy data from molecular simulation:

$$A^{\mathrm{seg}} = A^{\mathrm{hs}} + A^{\mathrm{pert}} \tag{12}$$

$$\frac{A^{\mathrm{hs}}}{R_m T} = m\frac{4\eta - 3\eta^2}{(1-\eta)^2}, \qquad A^{\mathrm{pert}} = m\frac{A^{(1)}}{T^*} + m\frac{A^{(2)}}{T^{*2}} \tag{13}$$

$$\frac{A^{(1)}}{R_m T} = \sum_{m=1}^{4} A_{1m}\left(\frac{\eta}{\tau}\right)^m, \qquad \frac{A^{(2)}}{R_m T} = \sum_{m=1}^{4} A_{2m}\left(\frac{\eta}{\tau}\right)^m \tag{14}$$

$$\tau = 0.7405, \qquad \eta = \frac{\pi\rho d_s^3}{6}m \tag{15}$$

The effective segment diameter d_s is determined on the basis of Barker perurbation theory. We use a function developed by Chapman et al.[27]:

$$d_s = \frac{1 + 0.2977T^*}{1 + 0.33163T^* + 0.0010477 + 0.025337[(m-1)/m]} \tag{16}$$

where

$$T^* = kT/\varepsilon \tag{17}$$

According to the Wertheim first-order thermodynamic perturbation theory, the contribution to free energy due to chain formation of the LJ system is expressed as

$$\frac{A^{\mathrm{chain}}}{NkT} = (1-m)\ln g^{\mathrm{LJ}}(\sigma) \tag{18}$$

Johnson et al.[20] gave a correlation result of the radial distribution function for LJ fluids dependent on reduced temperature and reduced density:

$$g^{\mathrm{LJ}}(\sigma_s) = 1 + \sum_{i=1}^{5}\sum_{j=1}^{5} a_{ij}(\rho^*)^i(T^*)^{1-j} \tag{19}$$

The coefficients a_{ij} are found in Ref. 20.

Tang–Lu Model[16]

The TL model is expressed as

$$\frac{A^{\mathrm{seg}}}{NkT} = m(a_0 + a_1 + a_2) \tag{20}$$

where a_0 represents the free energy of the hard sphere fluid and a_1 and a_2 are perturbed first- and second-order parts, respectively,

$$a_0 = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{21}$$

$$\begin{aligned} a_1 = &-\frac{12\eta\beta\varepsilon}{D^3}\left\{k_1\left[\frac{L(z_1D)}{z_1^2(1-\eta)^2Q(z_1D)} - \frac{1+z_1}{z_1^2}\right]\right. \\ &\left.- k_2\left[\frac{L(z_2D)}{z_2^2(1-\eta)^2Q(z_2D)} - \frac{1+z_2}{z_2^2}\right]\right\} \\ &+ 48\eta\beta\varepsilon\left[\frac{1}{9}\left(\frac{\sigma}{D}\right)^{12} - \frac{1}{3}\left(\frac{\sigma}{D}\right)^{6}\right] \\ &- 8\eta\beta\varepsilon g_0\left[\frac{1}{9}\left(\frac{\sigma}{D}\right)^{12} - \frac{1}{3}\left(\frac{\sigma}{D}\right)^{6} + \frac{2}{9}\left(\frac{\sigma}{D}\right)^{3}\right] \end{aligned} \tag{22}$$

$$\begin{aligned} a_2 = &-\frac{6\eta\beta^2\varepsilon^2}{D^3}\left[\frac{k_1^2}{2z_1Q^4(z_1D)} - \frac{k_2^2}{2z_2Q^4(z_2D)}\right. \\ &\left.- \frac{2k_1k_2}{(z_1+z_2)Q^2(z_1D)Q^2(z_2D)}\right] - 24\eta\beta^2\varepsilon^2\left[\frac{k_1/D}{Q^2(z_1D)}\right. \\ &\left.- \frac{k_2/D}{Q^2(z_2D)}\right] \times \left[\frac{1}{9}\left(\frac{\sigma}{D}\right)^{12} - \frac{1}{3}\left(\frac{\sigma}{D}\right)^{6} + \frac{2}{9}\left(\frac{\sigma}{D}\right)^{3}\right] \end{aligned} \tag{23}$$

$$\eta = \frac{\pi\rho d_s^3}{6}m \tag{24}$$

In this paper we used the simplified exponential (SEXP) approximation of an RDF. A SEXP approximation is proposed based on combination of the first-order mean spherical approximation (MSA) with the available exponential approximation, the SEXP approximation. This function is obtained analytically with help of a first-order solution of the MSA of RDF and is improved by SEXP[16]:

$$g^{\mathrm{SEXP}}(r) = g_0(r)\exp(g_1(r)) \tag{25}$$

The original exponential approximation was proposed independently by Anderson et al. in 1976 and by Stell in 1976 (see Ref. 16). The advantage of the SEXP approximation is that it yields much better RDF values around $r = \sigma$.

Classical Thermodynamics: TRWW Model

The TRWW EOS for pure hydrocarbons is given in terms of the dimensionless Helmholtz free energy function:

$$\frac{A}{R_m T} = \frac{A^{\mathrm{ig}}}{R_m T} + \frac{A^r}{R_m T} \tag{26}$$

In Eq. (26) A^{ig} is related to the free energy ideal gas function: A^r represents the residual part, which corrects the ideal-gas part to real fluid behavior; T represents the temperature; and R_m is the universal gas constant. The general structure of the ideal-gas and residual parts is written as

$$\frac{A^{\mathrm{ig}}}{R_m T} = \ln\delta + a_1^0 + a_2^0\tau + a_3^0 \ln\tau + \sum_{i=4}^{10} a_i \tau^{n_i} + \sum_{i=11}^{16} a_i \ln[1-\exp(-n_i\tau)], \qquad \left(\delta = \frac{V_c}{V}, \tau = \frac{T_c}{T}\right) \tag{27}$$

$$\frac{A^r}{R_m T} = \sum_{i=1}^{15} a_i \tau^{t_i}\delta^{d_i} + \sum_{i=16}^{45} a_i \tau^{t_i}\delta^{d_i}\exp(-\delta c_i) + \sum_{i=46}^{60} a_i \tau^{t_i}\delta^{d_i}\exp\left[-\alpha_i(\delta-\nu_i)^2 - \beta_i(\tau-\gamma_i)^2\right] \tag{28}$$

The EOS for the different refrigerants result from the use of coefficients a_i and different exponents t_i, d_i, e_i, α_i, and β_i. In Eqs. (27) and (28), δ and τ represent inverse reduced volume and inverse reduced temperature, respectively.

For the purpose of calculation of thermodynamic properties of hydrocarbons, we have selected the thermodynamic model recently published by Miyamoto and Watanabe (MW)[5–8] that covers a range of temperatures from the triple-point temperature to 600 K, pressures up to 100 MPa, and densities up to 741 $\mathrm{kg \cdot m^{-3}}$. The MW model contains more than 70 constants. At the present stage this model is one of the most accurate models for calculation of equilibrium thermodynamic properties for hydrocarbons in the gaseous and liquid state. The absolute deviations of experimental thermodynamic property data from the analytical model are mostly within ±1% (Refs. 5–8).

Results and Comparison with TRWW Model

The constants necessary for computations such as the characteristic rotation, electronic temperatures, and so on, are obtained from the literature.[43–46] The vibration constants are obtained in the National Institute of Standards and Technology Chemistry Web Book page.[§] The inertia moments are obtained analytically by applying the knowledge of the atomic structure of the molecule. Constants for LJ potential are obtained from the literature.[46] We carried out calculations for n-butane (C_4H_{10}), propane (C_3H_8), ethane (C_2H_6), and methane (CH_4). The most important data for calculation are presented in Table 2.

The comparison of our calculations with the TRWW model is presented in Figs. 1–24 and Tables 3–10.

Figures 1–20 show the relative deviation of the results for butane, propane, ethane, and methane in the saturated gas region between

Table 2 Important constants for analytical calculation

Parameter	n-Butane	Propane	Ethane	Methane
σ, σ_s, m	$3.87E{-10}$	$3.77E{-10}$	$3.756E{-10}$	$3.729E{-21}$
$\varepsilon, \varepsilon_s$, J	$3.84E{-21}$	$3.20E{-21}$	$2.954E{-21}$	$2.02E{-21}$
M, −	2.134	1.85	1.52	1.13

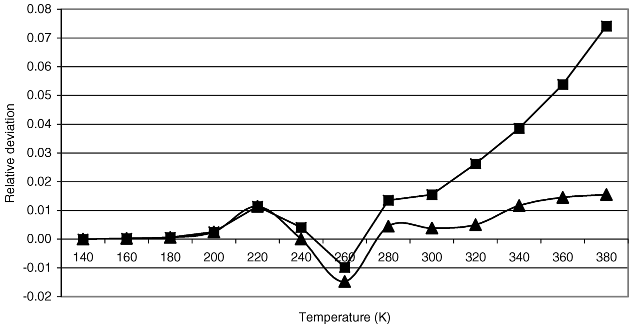

Fig. 1 Vapor pressure for *n*-butane: ▲, TL and ■, LLL.

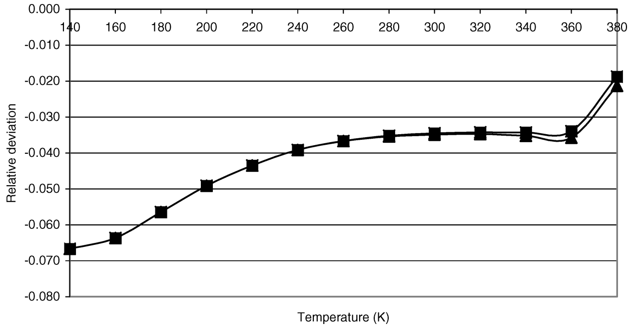

Fig. 2 Molar isocoric heat capacity for *n*-butane: ▲, TL and ■, LLL.

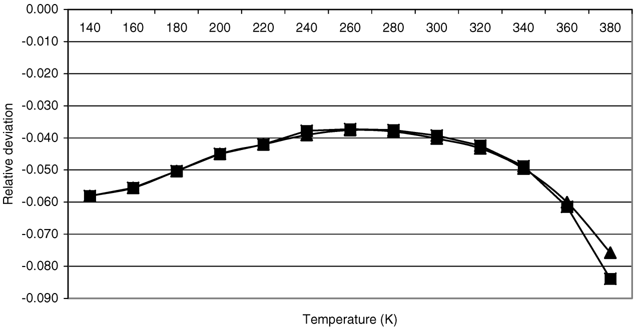

Fig. 3 Molar isobaric heat capacity for *n*-butane: ▲, TL and ■, LLL.

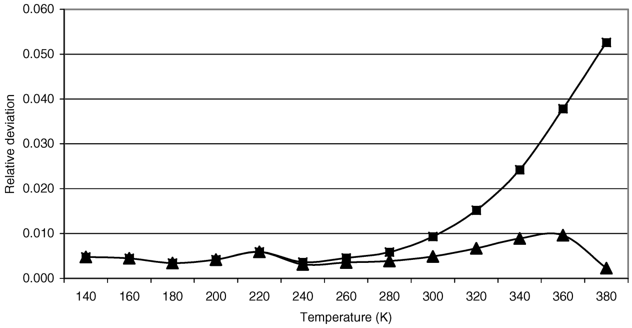

Fig. 4 Speed of sound for *n*-butane: ▲, TL and ■, LLL.

[§] http://webbook.nist.gov/chemistry/.

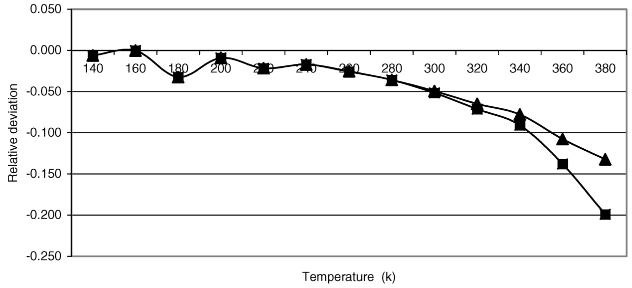

Fig. 5 Volumetric expansion coefficient for *n*-butane: ▲, TL and ■, LLL.

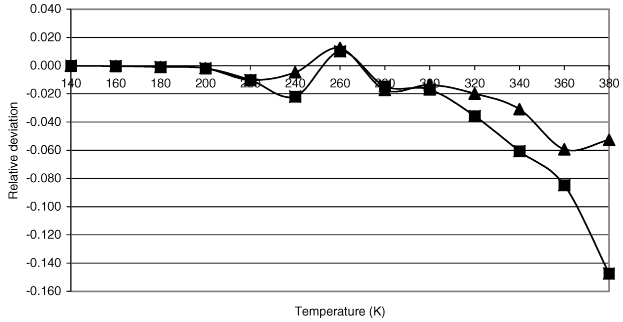

Fig. 6 Isothermal compressibility for *n*-butane: ▲, TL and ■, LLL.

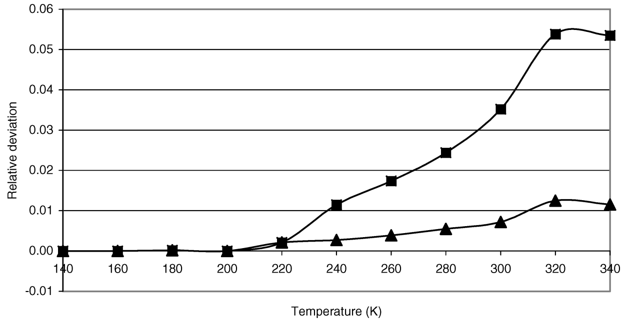

Fig. 7 Vapor pressure for propane: ▲, TL and ■, LLL.

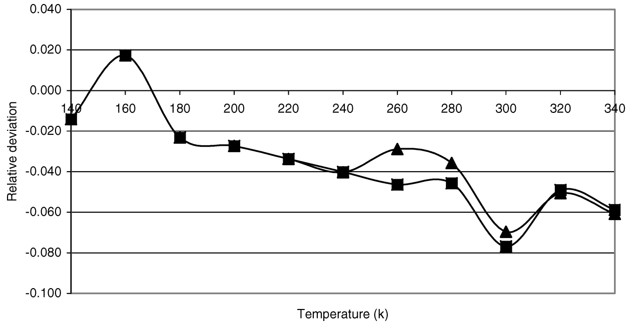

Fig. 8 Molar isochoric molar capacity heat for propane: ▲, TL and ■, LLL.

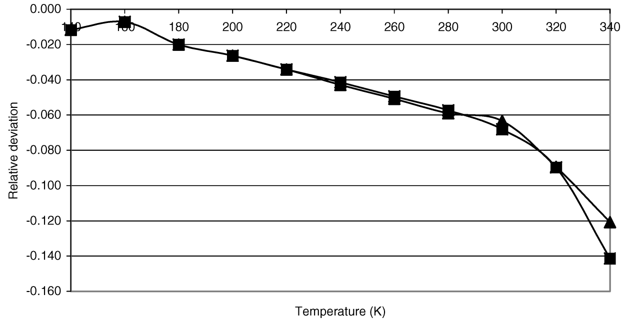

Fig. 9 Molar isobaric heat capacity for propane: ▲, TL and ■, LLL.

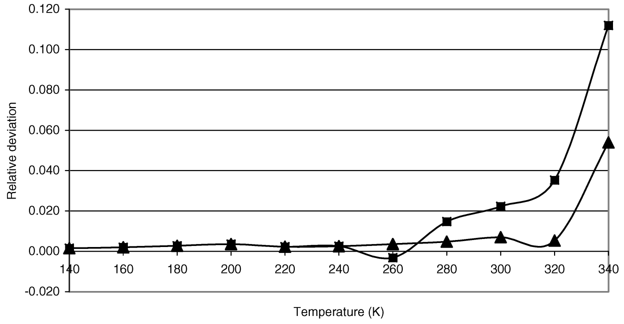

Fig. 10 Speed of sound for propane: ▲, TL and ■, LLL.

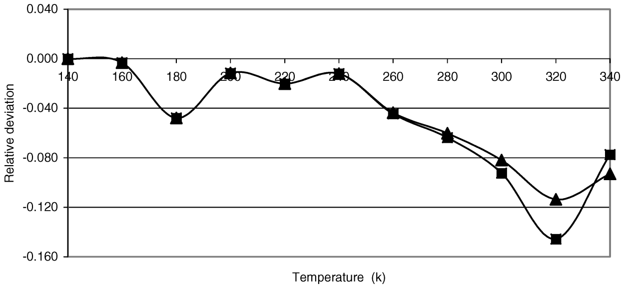

Fig. 11 Volumetric expansion coefficient for propane: ▲, TL and ■, LLL.

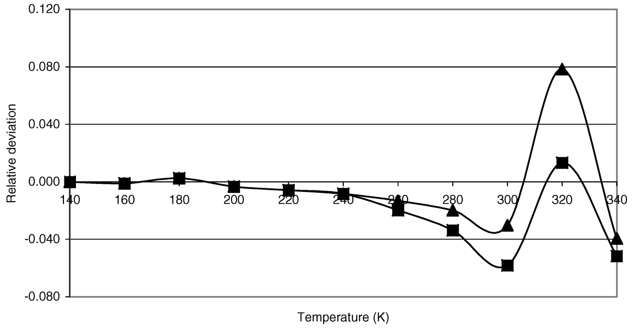

Fig. 12 Isothermal compressibility for propane: ▲, TL and ■, LLL.

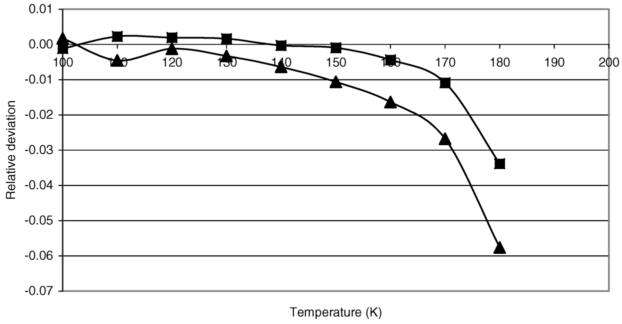

Fig. 13 Vapor pressure for methane: ▲, TL and ■, LLL.

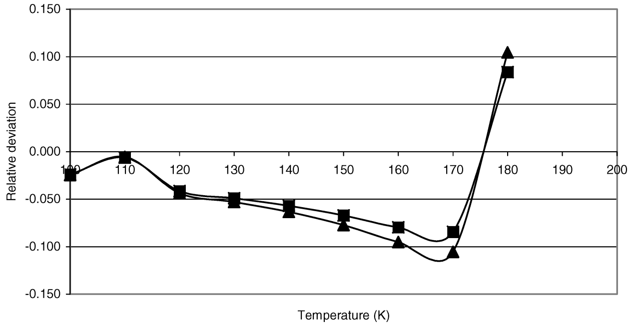

Fig. 14 Molar isobaric heat capacity for methane: ▲, TL and ■, LLL.

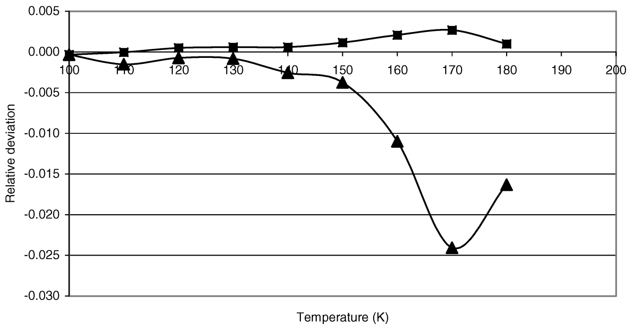

Fig. 15 Speed of sound for methane: ▲, TL and ■, LLL.

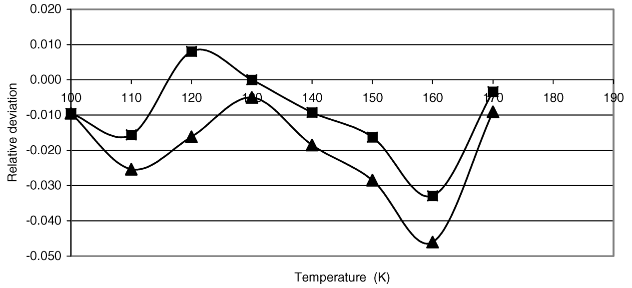

Fig. 16 Volumetric expansion coefficient for methane: ▲, TL and ■, LLL.

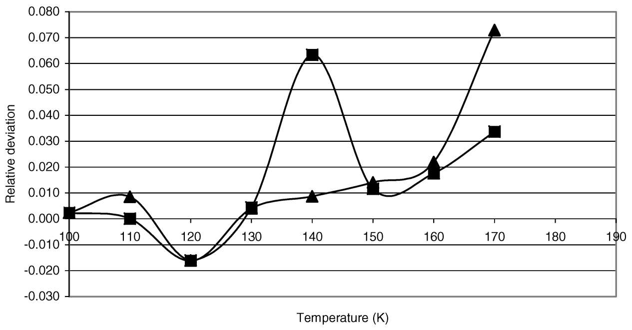

Fig. 17 Isothermal compressibility for methane: ▲, TL and ■, LLL.

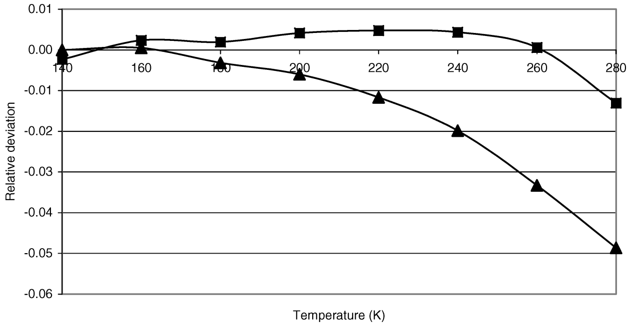

Fig. 18 Vapor pressure for ethane: ▲, TL and ■, LLL.

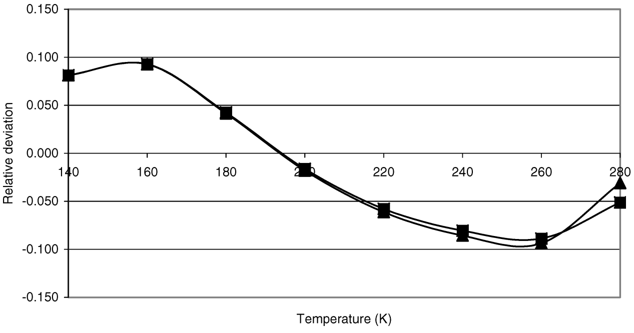

Fig. 19 Molar isobaric heat capacity for ethane: ▲, TL and ■, LLL.

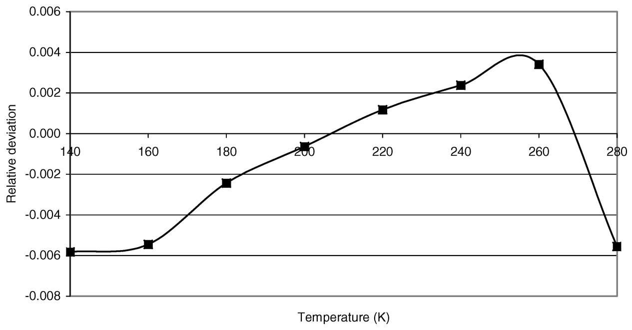

Fig. 20 Speed of sound for ethane: ■, LLL.

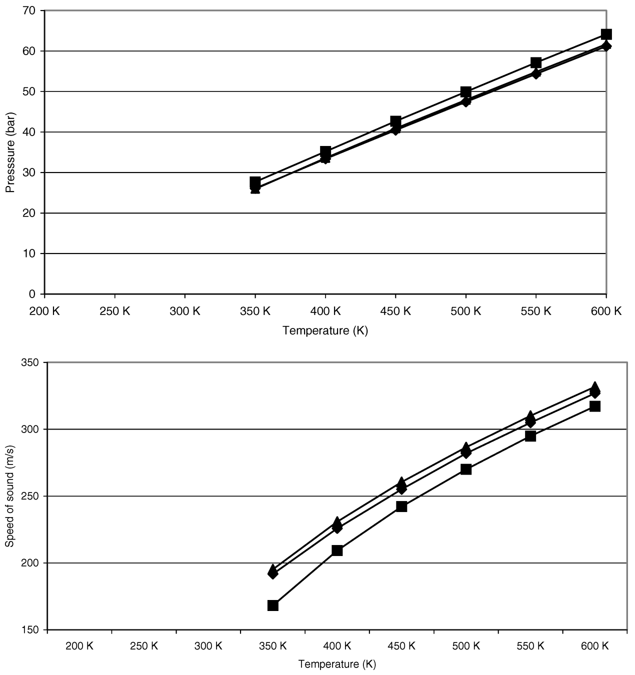

Fig. 21 Pressure and speed of sound for propane at $V = 0.74823$ m^3/kmol: ◆, TL; ■, LLL; and ▲, TRWW.

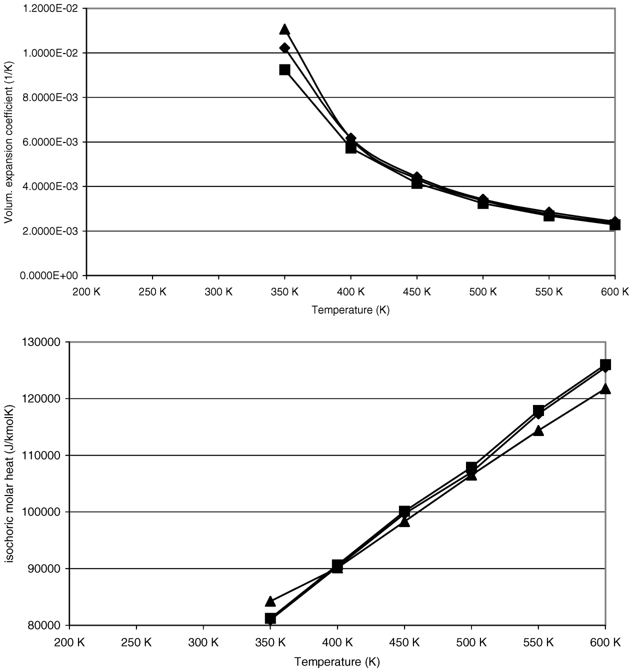

Fig. 22 Volumetric expansion coefficient and molar isochoric heat capacity for propane at $V = 0.74823$ m^3/kmol: ◆, TL; ■, LLL; and ▲, TRWW.

Table 3 Relative pressure deviation for propane

	$V = 81.604$ m^3/kmol		$V = 2.036$ m^3/kmol		$V = 0.74823$ m^3/kmol	
Temperature, K	TL	LLL	TL	LLL	TL	LLL
200	0.001689	0.003675	——	——	——	——
250	0.000277	0.001463	——	——	——	——
300	−0.00076	0.000887	0.009423	0.03749	——	——
350	−0.00115	0.000535	0.00161	0.021739	0.005167	0.068014
400	0.000172	0.000664	0.000474	0.01742	−0.00634	0.047837
450	0.000175	0.004545	0	0.015854	−0.00937	0.044221
500	−0.00529	−0.00525	−0.00026	0.029831	−0.00999	0.042167
550	0.000286	0.000643	$9.3E{-}05$	0.016374	−0.0095	0.041177
600	0.000196	0.00054	0.000548	0.016577	−0.00856	0.038932

Table 4 Relative speed of sound deviation for propane

	$V = 81.604$ m^3/kmol		$V = 2.036$ m^3/kmol		$V = 0.74823$ m^3/kmol	
Temperature, K	TL	LLL	TL	LLL	TL	LLL
200	0.041957	0.041957	——	——	——	——
250	0.00121	0.00121	——	——	——	——
300	0.000278	0.000676	0.006899	0.022282	——	——
350	$-3.7E{-}05$	0.000333	0.000579	0.01547	−0.01787	−0.13872
400	−0.00021	0.000139	−0.00102	0.012945	−0.02178	−0.09366
450	−0.00049	−0.00016	−0.00168	0.010917	−0.02099	−0.07088
500	−0.00207	−0.00207	−0.00292	0.006921	−0.01605	−0.05792
550	−0.00117	−0.00057	−0.00183	0.008708	−0.01677	−0.04902
600	−0.00092	−0.00063	−0.00159	0.007542	−0.0145	−0.04374

Table 5 Relative deviation for volumetric expansion coefficient for propane

	$V = 81.604$ m^3/kmol		$V = 2.036$ m^3/kmol		$V = 0.74823$ m^3/kmol	
Temperature, K	TL	LLL	TL	LLL	TL	LLL
200	−0.01231	−0.01231	——	——	——	——
250	−0.00205	−0.00181	——	——	——	——
300	−0.00009	−0.00038	−0.08427	−0.09574	——	——
350	0.00007	0.00007	−0.01521	−0.03068	−0.07653	−0.16454
400	0.00024	−0.00016	−0.00216	−0.02001	0.00431	−0.06942
450	0.00018	−0.00027	0.00275	−0.01712	0.02194	−0.04405
500	−0.00522	−0.00522	0.01891	0.02360	0.01628	−0.03720
550	−0.00005	−0.00060	0.00614	−0.01619	0.03178	−0.02838
600	0.00012	−0.00048	0.00657	−0.01638	0.03256	−0.02590

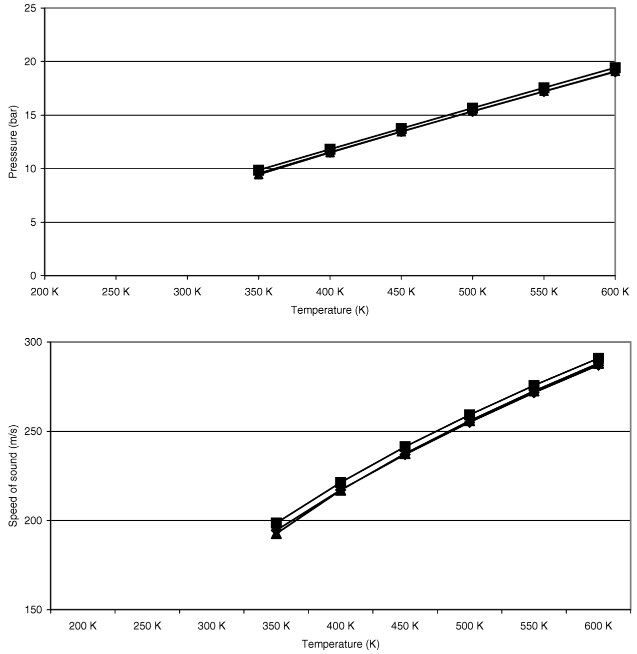

Fig. 23 Pressure and speed of sound for *n*-butane at $V = 2.4086$ m^3/kmol: ◆, TL; ■, LLL; and ▲, TRWW.

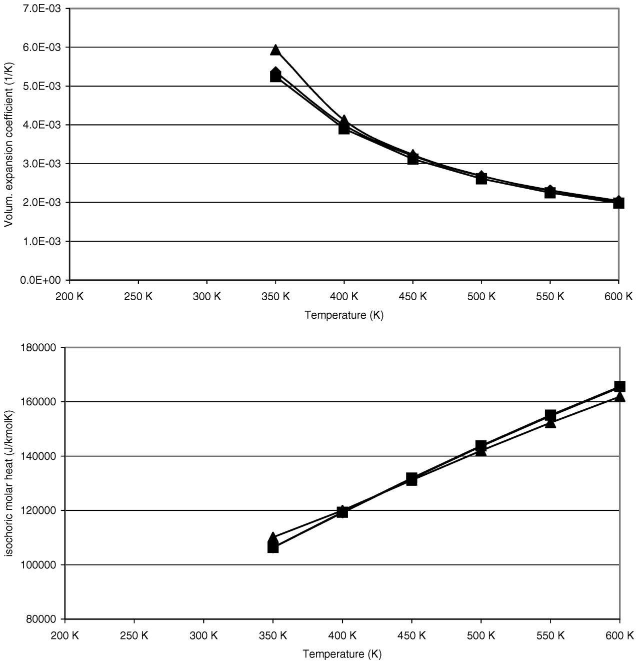

Fig. 24 Volumetric expansion coefficient and molar isochoric heat capacity for *n*-butane at $V = 2.4086$ m^3/kmol: ◆, TL; ■, LLL; and ▲, TRWW.

Table 6 Relative deviation for molar isochoric heat capacity for propane

	$V = 81.604\ \mathrm{m^3/kmol}$		$V = 2.036\ \mathrm{m^3/kmol}$		$V = 0.74823\ \mathrm{m^3/kmol}$	
Temperature, K	TL	LLL	TL	LLL	TL	LLL
200	−0.02733	−0.02836	——	——	——	——
250	−0.01523	−0.01505	——	——	——	——
300	−0.00618	−0.00618	−0.05183	−0.05086	——	——
350	0.002323	0.002323	−0.0037	−0.00243	−0.03878	−0.03581
400	0.009995	0.009995	0.00911	0.010598	0.002141	0.005802
450	0.016554	0.016554	0.016773	0.018328	0.013934	0.018104
500	0.006615	0.016202	0.008084	0.01379	0.004506	0.012955
550	0.027336	0.027336	0.02718	0.028945	0.025619	0.030865
600	0.030474	0.030474	0.03109	0.032744	0.030547	0.034653

Table 7 Relative pressure deviation for *n*-butane

	$V = 845.60\ \mathrm{m^3/kmol}$		$V = 8.9006\ \mathrm{m^3/kmol}$		$V = 2.4086\ \mathrm{m^3/kmol}$	
Temperature, K	TL	LLL	TL	LLL	TL	LLL
200	0.000663	0.001172	——	——	——	——
250	0.000448	0.000448	——	——	——	——
300	9.003393	0.000339	0.006202	0.01938	——	——
350	0.002915	0.002915	0.001942	0.010356	0.011653	0.044492
400	0	0.000509	0.000837	0.00725	0.002958	0.028184
450	−0.00068	0.000226	0.000393	0.005791	0.00052	0.022077
500	0.000183	0.000183	0.000351	0.005394	−0.00111	0.01973
550	0.000203	0.000203	0.000238	0.005394	−0.00163	0.019271
600	0.00022	0.00022	−0.00062	0.005721	−0.00147	0.018975

Table 8 Relative deviation for speed of sound for *n*-butane

	$V = 845.60\ \mathrm{m^3/kmol}$		$V = 8.9006\ \mathrm{m^3/kmol}$		$V = 2.4086\ \mathrm{m^3/kmol}$	
Temperature, K	TL	LLL	TL	LLL	TL	LLL
200	0.003075	0.003075	——	——	——	——
250	0.001661	0.001661	——	——	——	——
300	0.000878	0.000878	0.004948	0.009401	——	——
350	0.000215	0.000215	0.001804	0.006315	0.00997	0.03074
400	$-4E{-}05$	$-4E{-}05$	0.000335	0.005355	0.001061	0.020427
450	0	0	0.000157	0.004473	−0.00202	0.016086
500	−0.00033	−0.00033	$-7.4E{-}05$	0.004006	−0.00324	0.013173
550	−0.00021	−0.00021	−0.00042	0.003809	−0.00363	0.011409
600	−0.00033	−0.00033	−0.00037	0.003337	−0.00361	0.009579

Table 9 Relative deviation for volumetric expansion coefficient for *n*-butane

	$V = 845.60\ \mathrm{m^3/kmol}$		$V = 8.9006\ \mathrm{m^3/kmol}$		$V = 2.4086\ \mathrm{m^3/kmol}$	
Temperature, K	TL	LLL	TL	LLL	TL	LLL
200	−0.00436	−0.00436	——	——	——	——
250	−0.00117	−0.00117	——	——	——	——
300	−0.00024	−0.00024	−0.04811	−0.04969	——	——
350	−0.00091	−0.00021	−0.01371	−0.01719	−0.09575	−0.11615
400	−0.00020	−0.00020	−0.00437	−0.00926	−0.03083	−0.05388
450	0.00018	0.00018	−0.00826	−0.00338	−0.01018	−0.03493
500	0.00015	0.00015	−0.00101	−0.00654	−0.00067	−0.02714
550	0.00027	−0.00027	0.00093	−0.00627	0.00425	−0.02351
600	0.00018	0.00018	0.00102	−0.00692	0.00720	−0.02141

Table 10 Relative deviation for isochoric molar heat for *n*-butane

	$V = 845.60\ \mathrm{m^3/kmol}$		$V = 8.9006\ \mathrm{m^3/kmol}$		$V = 2.4086\ \mathrm{m^3/kmol}$	
Temperature, K	TL	LLL	TL	LLL	TL	LLL
200	−0.04943	−0.04943	——	——	——	——
250	−0.0287	−0.0287	——	——	——	——
300	−0.01477	−0.01477	−0.03486	−0.03454	——	——
350	−0.0057	−0.0057	−0.90107	−0.01075	−0.03504	−0.03413
400	0.001717	0.001717	−0.00043	0.000426	−0.0065	−0.00483
450	0.007529	0.007529	0.007183	0.007183	0.004347	0.005872
500	0.012325	0.012325	0.012568	0.012568	0.011268	0.012676
550	0.017409	0.017409	0.017106	0.017766	0.016615	0.018585
600	0.021308	0.021308	0.021522	0.021522	0.021064	0.022917

the analytical computation (LLL model and TL model) and the MW model obtained by classical thermodynamics. The relative deviation (RD) is defined by the following expression:

$$\mathrm{RD} = \frac{\mathrm{data_{ST}} - \mathrm{data_{MW}}}{\mathrm{data_{MW}}} \tag{29}$$

The results for all the models obtained by statistical thermodynamics show relatively good agreement. The computed vapor pressure, isothermal compressibility, molar isobaric heat capacity, and speed of sound were confirmed well for all models, and were obtained by statistical associating statistical thermodynamics. Somewhat larger deviations can be found in the region near the critical point due to the large influence of fluctuation theory and the singular behavior of some thermodynamic properties in the near-critical condition. The perturbation models on the basis of SAFT (TL and LLL) yield surprisingly good results. The models on the basis of SAFT give better results in comparison with models based on classical statistical thermodynamics, especially in high-temperature and high-pressure regions.

Figures 21 and 22 show a comparison among TL, LLL, and MW models for speed of sound, pressure, molar isochoric heat capacity, and volumetric coefficient of expansion. The figures are elaborated for propane for the real gas phase at $V = 0.74823$ m^3/kmol in the large temperature (200–600 K) and pressure field. The thermodynamic properties of state can be analyzed even better in Tables 3–6, which present the properties of state as a function of the relative error. All the thermodynamic properties are presented for temperatures (200–600 K) and molar volumes ($V = 81 - 0.78423$ m^3/kmol). The present model yields very good results as a whole, particularly for the high-temperature range. The results of the TL model are much better than those of the LLL model. A detailed analysis of relative deviations of the TL model shows the highest relative deviation for the lowest realistic value ranges, that is, in the lowest volume and temperature range. The highest deviations are 5.1% for pressure, 1.7% for speed of sound, 7.6% for volumetric coefficient of expansion, and 3.8% for molar isochoric heat capacity. The present analytical model yields very good results with much lower deviations in all other points. The analysis shows that multipole effects must be taken into account for the areas of very low factors of reality[31] to be able to expect full matching of results, even though the matching is even now very satisfactory. The review of analytical results in the temperature and pressure field for n-butane leads to almost identical conclusions (see Figs. 23 and 24 and Tables 7–10).

The present analysis provides a good basis for further upgrading this model,[47–49] allowing for the calculation of very accurate thermodynamic properties of state in the liquid and gas range as well as in super- and subcritical regions.

Conclusions

The paper presents the mathematical model on the basis of statistical associating chain theory for the calculation of thermodynamic functions of the state in the fluid region. The analytical results are compared with the TRWW model based on classical thermodynamics. The comparison of results between our analytical model and TRWW shows relatively good agreement. In our further research, we intend to extend the presented mathematical model to the calculation of mixtures and to include the theory of fluctuation in the vicinity of the critical point.

References

[1] Walas, S. M., *Phase Equilibria in Chemical Engineering*, Butterworths, Boston, 1984, Chap. 1.

[2] Younglove, B. A., and Ely, J. F., "Thermophysical Properties of Fluids. II. Methane, Ethane, Propane, Isobutane and Normal Butane," *Journal of Physical and Chemical Reference Data*, Vol. 16, No. 4, 1987, pp. 577–798.

[3] Jacobsen, R. T., Stewart, R. B., Jahangiri, M., and Penoncello, S. G., "A New Fundamental Equation for Thermodynamics Property Correlations," *Advances in Cryogenic Engineering*, Vol. 31, 1986, pp. 1161–1169.

[4] Tillner-Roth, R., "Die Thermodynamischen Eigenschaften von R152a, R134a und ihren Gemischen," Ph.D. Dissertation, Universität Hannover, Hannover, Germany, Feb. 1993.

[5] Miyamoto, H., and Watanabe, K., "A Thermodynamic Property Model for Fluid-Phase Propane," *International Journal of Thermophysics*, Vol. 21, No. 5, 2000, pp. 1045–1072.

[6] Miyamoto, H., and Watanabe, K., "A Thermodynamic Property Model for Fluid-Phase n-Butane," *International Journal of Thermophysics*, Vol. 22, No. 2, 2001, pp. 459–475.

[7] Miyamoto, H., and Watanabe, K., "A Thermodynamic Property Model for Fluid-Phase Isobutane," *International Journal of Thermophysics*, Vol. 23, No. 2, 2002, pp. 477–499.

[8] Miyamoto, H., and Watanabe, K., "Helmholtz-Type Equations of State for Binary and/or Ternary Hydrocarbon Mixtures of Propane, N-Butane, and Isobutane," *5th IIR Gustav Rorentzen Conference*, International Inst. of Refrigeration, Guangzhou, PRC, 2002.

[9] Barker, J. A., and Hendersom, D., "Perturbation Theory and Equation of State for Fluids II," *Journal of Chemical Physics*, Vol. 47, No. 11, 1967, pp. 4714–4721.

[10] Weeks, J. D., Chandler, D., and Anderson, H. C., "Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids," *Journal of Chemical Physics*, Vol. 54, No. 11, 1971, pp. 5237–5245.

[11] Barker, J. A., and Henderson, D., "What is Liquid," *Reviews of Modern Physics*, Vol. 48, 1976, pp. 587–671.

[12] Münster, A., *Statistical Thermodynamics*, Springer-Verlag, New York, 1974, Chaps. 4 and 5.

[13] Lucas, K., *Applied Statistical Thermodynamics*, Springer-Verlag, New York, 1992, Chaps. 1, 3, 5, and 6.

[14] Gray, C. G., and Gubbins, K. E., *Theory of Molecular Fluids*, Clarendon, Oxford, 1984, Chaps. 2–4.

[15] McClelland, B. J., *Statistical Thermodynamics*, Chapman and Hall, London, 1980, Chaps. 1–11.

[16] Tang, Y., and Lu, B. C.-Y., "A Study of Associating Lennard–Jones Chains by a New Reference Radial Distribution Function," *Fluid Phase Equilibria*, Vol. 171, No. 1, 2000, pp. 27–44.

[17] Liu, Z.-P., Li, Y.-G., and Lu, J.-F., "Comparison of Equation of State for Pure Lennard–Jones Fluids and Mixtures with Molecular Simulation," *Fluid Phase Equilibria*, Vol. 173, No. 1, 2000, pp. 189–209.

[18] Chapman, W. G., Gubbins, K. E., Jackson, G., and Radosz, M., "New Reference Equation of State for Associating Liquids," *Industrial and Engineering Chemistry Research*, Vol. 29, No. 8, 1990, pp. 1709–1721.

[19] Condo, P. D., and Radosz, M., "Equations of State for Polymers," *Fluid Phase Equilibria*, Vol. 117, No. 1, 1996, pp. 1–10.

[20] Johnson, J. K., and Gubbins, K. E., "Phase Equilibria for Associating Lennard–Jones Fluids from Theory and Simulation," *Molecular Physics*, Vol. 77, No. 6, 1992, pp. 1033–1053.

[21] Wei, Y. S., and Sadus, R. J., "Equations of State for the Calculation of Fluid-Phase Equilibria," *AIChE Journal*, Vol. 46, No. 1, 2000, pp. 169–196.

[22] Banaszak, M., Chen, C. K., and Radosz, M., "Copolymer SAFT Equation of State. Thermodynamic Perturbation Theory Extended to Heterobonded Chains," *Macromolecules*, Vol. 29, No. 20, 1996, pp. 6481–6486.

[23] Huang, S. H., and Radosz, M., "Equation of State for Small, Large, Polydisperze and Associating Molecules," *Industrial and Engineering Chemistry Research*, Vol. 29, No. 11, 1990, pp. 2284–2294.

[24] Davies, L. A., Gil-Villergas, A., and Jackson, G., "Describing the Properties of Chains of Segments Interacting via Soft-Core Potentials of Variable Range with the SAFT-VR Approach," *International Journal of Thermophysics*, Vol. 19, No. 3, 1998, pp. 675–686.

[25] Chapman, W. G., Jackson, G., and Gubbins, K. E., "Phase Equilibria of Associating Fluids," *Molecular Physics*, Vol. 65, No. 5, 1988, pp. 1057–1079.

[26] Huang, S. H., and Radosz, M., "Equation of State for Small, Large, Polydisperze and Association Molecules, Extension to Fluid Mixtures," *Industrial and Engineering Chemistry Research*, Vol. 30, No. 8, 1991, pp. 1994–2005.

[27] Chen, C.-K., Banaszak, M., and Radosz, M., "Statistical Associating Fluid Theory Equation of State with Lennard–Jones Reference Applied to Pure and Binary n-Alkane Systems," *Journal of Physical Chemistry B*, Vol. 102, No. 13, 1998, pp. 2427–2431.

[28] Jackson, G., Chapman, W. G., and Gubbins, K. E., "Phase Equilibria of Associating Fluids," *Molecular Physics*, Vol. 65, No. 1, 1988, pp. 1–31.

[29] Kiselev, S. B., and Ely, J. F., "Crossover SAFT Equation of State: Application for Normal Alkanes," *Industrial and Engineering Chemistry Research*, Vol. 38, No. 12, 1999, pp. 4993–5004.

[30] Müller, E. A., and Gubbins, K. E., "Molecular-Based Equations of State for Associating Fluids: A Review of SAFT and Related Approaches," *Industrial and Engineering Chemistry Research*, Vol. 40, No. 10, 2001, pp. 2193–2211.

[31] Adidharma, H., and Radosz, M., "Prototype of an Engineering Equation of State for Heterosegmented Polymers," *Industrial and Engineering Chemistry Research*, Vol. 37, No. 11, 1998, pp. 4453–4462.

[32] Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics," *Journal of Statistical Physics*, Vol. 35, Nos. 1–2, 1984, pp. 19–34.

[33] Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations," *Journal of Statistical Physics*, Vol. 35, Nos. 1–2, 1984, pp. 35–47.

[34] Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. III. Multiple Attraction Sites," *Journal of Statistical Physics*, Vol. 42, Nos. 3–4, 1986, pp. 459–477.

[35] Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization," *Journal of Statistical Physics*, Vol. 42, Nos. 3–4, 1986, pp. 477–493.

[36] Johnson, J. K., Müller, E. A., and Gubbins, K. E., "Equation of State for Lennard–Jones Chains," *Journal of Physical Chemistry*, Vol. 98, No. 25, 1994, pp. 6413–6419.

[37] Kraska, T., and Gubbins, K. E., "Phase Equilibria Calculations with a Modified SAFT Equation of State 1. Pure Alkanes, Alkanols and Water," *Industrial and Engineering Chemistry Research*, Vol. 35, No. 12, 1996, pp. 4727–4737.

[38] Kraska, T., and Gubbins, K. E., "Phase Equilibria Calculations with a Modified SAFT Equation of State 2. Binary Mixtures of n-Alkanes, 1-Alkanols and Water," *Industrial and Engineering Chemistry Research*, Vol. 35, No. 12, 1996, pp. 4738–4746.

[39] Sengers, J. V., Kayser, R. F., Peters, C. J., and White, H. J., "Equations of State for Fluids and Fluid Mixtures," *International Union of Pure and Applied Chemistry*, Elsevier, Amsterdam, 2000, Chaps. 3, 5, and 6.

[40] Tang, Y., Wang, Z., and Lu, B. C.-Y., "Thermodynamic Calculations of Linear Chain Molecules Using a SAFT Model," *Molecular Physics*, Vol. 99, No. 1, 2001, pp. 65–76.

[41] Pamies, J. C., and Vega, L. F., "Vapour-Liquid Equilibria and Critical Behavior of Heavy n-Alkanes Using Transferable Parameters from the Foft-SAFT Equation of State," *Industrial and Engineering Chemistry Research*, Vol. 40, No. 11, 2001, pp. 2532–2543.

[42] Avsec, J., and Marcic, M., "An Application of Statistical Chain Theories on HC and HFC Mixtures," AIAA Paper 2003-3916, June 2003.

[43] Bellamy, L. J., *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1980, Chap. 1.

[44] Herzberg, G., *Electronic Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, London, 1966, Chaps. 1–3.

[45] Herzberg, G., *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1984, Chap. 3.

[46] Hirschfelder, O. O., Curtiss, C. F., and Bird, R. B., *Molecular Theory of Gases and Liquids*, Wiley, London, 1954, pp. 1109–1181.

[47] Avsec, J., and Marčič, M., "Calculation of Elastic Modulus and Other Thermophysical Properties for Molecular Crystals," *Journal of Thermophysics and Heat Transfer*, Vol. 16, No. 3, 2002, pp. 463–468.

[48] Avsec, J., and Marčič, M., "Influence of Multipolar and Induction Interactions on the Speed of Sound," *Journal of Thermophysics and Heat Transfer*, Vol. 14, No. 4, 2000, pp. 496–503.

[49] Avsec, J., and Marčič, M., "Approach for Calculating Thermophysical Properties with the Help of Statistical Thermodynamics," *Journal of Thermophysics and Heat Transfer*, Vol. 16, No. 3, 2002, pp. 455–462.