

# Statistical Approach to Calculate Thermodynamic Properties for Propane<sup>1</sup>

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The paper describes a mathematical model to compute equilibrium thermodynamic properties in the fluid phase of pure hydrocarbons with the aid of classical thermodynamics and statistical associating chain theories. In the present paper thermodynamic properties for propane, as an example of hydrocarbon substances, are calculated. To calculate the thermodynamic properties of real fluids, models based on the Lennard–Jones intermolecular potential were applied. To calculate the thermodynamic properties of real fluids with the aid of classical thermodynamics, Miyamoto–Watanabe (MW) equations, developed in terms of the Helmholtz energy were used. Analytical results obtained by statistical thermodynamics are compared with the MW model and show relatively good agreement.

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**KEY WORDS:** chain theory; propane; SAFT model; statistical thermodynamics; thermodynamics.

## 1. INTRODUCTION

In engineering practice, processes occurring in liquid-gas regions are of vital importance. In order to design devices that operate in these regions, it is necessary to know the thermodynamic properties in single- and two-phase systems for pure hydrocarbons and their mixtures.

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**Table I.** Fundamental Characteristics of Various EOS Based On Classical Thermodynamics

EOS	Number of Constants	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

In most cases thermodynamic property tables or diagrams or different empirical functions obtained from measurements are used (classical thermodynamics). Today, there are numerous equations of state (EOS) reported in the literature for describing the behavior of fluids, e.g., Van der Waals EOS, Peng–Robinson EOS, Redlich–Kwong EOS, and Soave EOS [1]. However, these cubic equations exhibit some noticeable problems, such as poor agreement with experimental data at moderate densities. On the other hand, we can use complex equations of state with many parameters (Benedict–Webb–Rubin (BWR) EOS [1], Lee–Kessler EOS [1], Benedict–Webb–Rubin–Starling–Nishiumi EOS [1], modified BWR EOS [1,2], Jacobsen–Stewart (JS) EOS [3], Tillner–Roth et al. EOS [4], Miyamoto–Watanabe (MW) EOS [5,6],...etc). The calculation of thermodynamic functions of state with the aid of classical thermodynamics is well known and is not described in this paper. Table I shows 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 motion and intramolecular interactions. A good theory for these fluids will be very beneficial to chemical engineering applications by reducing the number of parameters and making them more physically meaningful and more predictable. In technical practice energy conversion processes are of vital importance. Calculation of the thermodynamic functions of state is possible by many statistical theories. One of the most successful approaches is perturbation theory. Several equations of state have been published that are based on perturbation theory [7,8]. The evolution of perturbation theory is well described in the literature by Barker and Henderson [9], Münster [10], Lucas [11], Gray and Gubbins [12], and McClelland [13].

In this paper we have developed expressions for models obtained on the basis of statistical associating fluid theory (SAFT) [14,15] (Tang–Lu (TL) model [16] and Liu–Li–Lu (LLL) model [17]). These models are based on the Lennard–Jones intermolecular potential function and the use of SAFT. The Lennard–Jones intermolecular potential is important for models for the study of simple fluids in single- and two-phase regions. It is widely used as a reference potential in perturbation theories for more complex potentials.

In the present paper we have developed a model for computation of the equilibrium properties of state. We have compared deviations of the results between various models for thermodynamic functions of state and also for their derivatives (enthalpy, pressure, entropy, isothermal compressibility, coefficient of thermal expansion, heat capacities, and speed of sound).

Results of the analysis are compared with the MW EOS obtained on the basis of classical thermodynamics and shows relatively good agreement, especially for real gases. Somewhat larger deviations are, however, found in the liquid region due to the large influence of attractive and repulsive forces, since the Lennard–Jones potential is an approximation of the actual real intermolecular potential.

## 2. COMPUTATION OF THERMODYNAMIC PROPERTIES OF STATE

To calculate thermodynamic functions of state, we applied the canonical partition function [11]. Utilizing the semi-classical formulation for the purpose of the canonical ensemble for  $N$  indistinguishable molecules, the partition function  $Z$  can be expressed as follows [11]:

$$Z = \frac{1}{N!h^{Nf}} \int \dots \int \exp\left(-\frac{H}{kT}\right) \cdot d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N d\vec{p}_1 d\vec{p}_2 \dots d\vec{p}_N \quad (1)$$

where  $f$  stands for the number of degrees of freedom of an individual molecule,  $H$  designates the Hamiltonian of the molecular system, vectors  $\vec{r}_1, \vec{r}_2 \dots \vec{r}_N$  describe the positions of  $N$  molecules and  $\vec{p}_1, \vec{p}_2 \dots \vec{p}_N$  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

$$Z = Z_0 Z_{\text{trans}} Z_{\text{vib}} Z_{\text{rot}} Z_{\text{ir}} Z_{\text{el}} Z_{\text{nuc}} Z_{\text{conf}} \quad (2)$$

Thus, the partition function  $Z$  is a product of terms of the ground state (0), translation (trans), vibration (vib), rotation (rot), internal rotation (ir),

influence of electrons excitation (el), influence of nuclei excitation (nuc), and influence of the intermolecular potential energy (conf).

Utilizing the canonical theory for computation, the thermodynamic functions of state can be defined as follows [10, 11]:

$$\begin{aligned}
 \text{Pressure } p_p &= kT \left( \frac{\partial \ln Z}{\partial T} \right)_V, \\
 \text{Internal energy } U &= kT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_V, \\
 \text{Helmholtz free energy } A &= -kT \ln Z, \\
 \text{Entropy } S &= k \left[ \ln Z + T \left( \frac{\partial \ln Z}{\partial T} \right)_V \right], \\
 \text{Gibbs free energy } G &= -kT \left[ \ln Z - V \left( \frac{\partial \ln Z}{\partial T} \right)_V \right], \\
 \text{Enthalpy } H_h &= kT \left[ T \left( \frac{\partial \ln Z}{\partial T} \right)_V + V \left( \frac{\partial \ln Z}{\partial T} \right)_V \right],
 \end{aligned} \tag{3}$$

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

Computation of the individual terms of the partition function and their derivatives except for the configurational integral is dealt with in the works of Lucas [11], Gray and Gubbins [12], and McClelland [13].

Various derivatives and expressions of the fundamental equations (Eq. (3)) have important physical significance. This paper presents expressions which are very important for designing energy-conversion processes [14]. Various derivatives also prove to be of physical interest:

$$\text{Coefficient of thermal expansion: } \beta_t = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p. \tag{4}$$

$$\text{Isothermal compressibility: } \chi = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T. \tag{5}$$

$$\text{Isochoric molar heat capacity: } C_v = \left( \frac{\partial U}{\partial T} \right)_V. \tag{6}$$

$$\text{Isobaric molar heat capacity: } C_p = \left( \frac{\partial H}{\partial T} \right)_p = C_v + \frac{TV\beta^2}{\chi}. \tag{7}$$

$$\begin{aligned}
 \text{Speed of sound: } c_0 &= \sqrt{-V^2 \frac{1}{M} \left( \frac{\partial p}{\partial V} \right)_s} \\
 &= \sqrt{-V^2 \frac{\frac{C_p}{T} \left( \frac{\partial T}{\partial V} \right)_p \frac{1}{M}}{\left( \frac{\partial V}{\partial T} \right)_p - \frac{C_p}{T} \left( \frac{\partial T}{\partial p} \right)_V}}, \tag{8}
 \end{aligned}$$

where  $M$  is the molar mass.

### 3. STATISTICAL ASSOCIATING FLUID THEORY (SAFT)

Over the last 50 years, accurate models on the basis of statistical thermodynamics have been developed for predicting the thermodynamic properties for simple molecules [15–40]. By simple we mean molecules for which the most important intermolecular forces are repulsive and dispersive 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 fall into this group. The reason for this is that, for such fluids, important new intermolecular forces play essential roles: Coulombic forces, strong polar forces, complexing forces, the effects of association and chain formation, etc.

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

In recent years thermodynamic theories based on statistical thermodynamics have been widely developed. Fluids with chain bonding [15–40] and association have received much attention. Interest in these fluids have been prompted by the fact that they cover a much wider range of real fluids than for spherical systems [15]. In Ref. 15 is explained in detail the advantage of SAFT models in comparison with classical statistical models over all fluid regions.

To calculate the thermodynamic properties of real Lennard–Jones (LJ) fluids, the LLL (revised Cotterman) equation of state based on simple perturbation theory and the SAFT-VR equation of state for LJ chain fluids, the complex TL analytical model with a new radial distribution function (RDF) based on simplified exponential approximation (SEXP) and perturbation expansion, were applied. The developed RDF has been applied to the development of a new SAFT model. The present model has been used to calculate several typical properties of LJ chains and associating LJ chains. This paper, for the first time, discusses the accuracy of these models to be used in real engineering practice.

The original derivation of SAFT models is shown in Wertheim papers [32–35]. They require a comprehensive knowledge of graph theory to be fully understood;

$$A^{\text{res}} = A^{\text{seg}} + A^{\text{chain}} + A^{\text{assoc}} \quad (9)$$

The residual Helmholtz energy consists of three terms representing contributions from different intermolecular forces. The first term  $A^{\text{seg}}$  represents segment–segment interactions. In the present paper segment–segment interactions are represented through the Lennard–Jones interaction potential. Each segment is characterized by its diameter  $\sigma_s$  and segment interaction parameter  $\varepsilon_s$ , and each molecule is characterized with the number of segments,  $m$ . The second term  $A^{\text{chain}}$  represents the presence of covalent chain-forming bonds between the LJ segments. The third term  $A^{\text{assoc}}$  is the result of site–site interactions between segments, for example, hydrogen bonding. For the hydrocarbons the association term is of no significance and will be neglected in our equations.

$$A^{\text{res}} = A^{\text{seg}}(m, \rho, T, \sigma_s, \varepsilon_s) + A^{\text{chain}}(\rho, d, m) + A^{\text{assoc}}(\rho, T, d, \varepsilon^{\text{AB}}, \kappa^{\text{AB}}) \quad (10)$$

where  $\rho$  is the molar density,  $T$  is the temperature,  $\varepsilon^{\text{AB}}$  is the association energy between two sites, and  $\kappa^{\text{AB}}$  is the volume interaction between two sites.

### 3.1. Liu–Li–Lu Model [17]

The present model is developed on the basis of SAFT and perturbation theory around hard spheres with new coefficients by fitting reduced pressure and internal energy data from molecular simulation.

$$A^{\text{seg}} = A^{\text{hs}} + A^{\text{pert}} \quad (11)$$

$$\frac{A^{\text{hs}}}{R_m T} = m \frac{4\eta - 3\eta^2}{(1 - \eta)^2}, \quad A^{\text{pert}} = m \frac{A^{(1)}}{T^*} + m \frac{A^{(2)}}{T^{*2}} \quad (12)$$

$$\frac{A^{(1)}}{R_m T} = \sum_{m=1}^4 A_{1m} \left(\frac{\eta}{\tau}\right)^m, \quad \frac{A^{(2)}}{R_m T} = \sum_{m=1}^4 A_{2m} \left(\frac{\eta}{\tau}\right)^m, \quad (13)$$

$$\tau = 0.7405, \quad \eta = \frac{\pi \rho d_s^3}{6} m, \quad (14)$$

The effective segment diameter  $d_s$  is determined on the basis of Barker perturbation theory. We use a function developed in the work of Chen et al. [27]:

$$d_s = \frac{1 + 0.2977T^*}{1 + 0.33163T^* + 0.0010477 + 0.025337 \frac{m-1}{m}} \quad (15)$$

where

$$T^* = \frac{kT}{\varepsilon} \text{ is the reduced temperature.} \quad (16)$$

According to Wertheim's first-order thermodynamic perturbation theory [32–35], the contribution to free energy due to chain formation of the LJ system is expressed as

$$\frac{A^{\text{chain}}}{NkT} = (1 - m) \ln g^{\text{LJ}}(\sigma) \quad (17)$$

Johnson et al. [20] gave a correlated result of the RDF for LJ fluids dependent on the reduced temperature and reduced density:

$$g^{\text{LJ}}(\sigma_s) = 1 + \sum_{i=1}^5 \sum_{j=1}^5 a_{ij} (\rho^*)^i (T^*)^{1-j} \quad (18)$$

With the use of the configurational free energy, we can calculate all configurational thermodynamic properties. We used derivations of all other expressions for calculation of thermophysical properties.

### 3.2. Tang–Lu Model [16]

The TL model uses as the intermolecular potential a new two-Yukawa potential function. This function is found to mimic very closely the Lennard–Jones potential. The TL analytical model calculates thermodynamic functions of state on the basis of a solution of the Ornstein–Zernike equation with the help of perturbation and SAFT theory. Comparisons with computer simulation data indicate that the expressions developed yield better results (pressure, internal energy, free energy) than classical statistical thermodynamics theory. The configurational segment free energy is given by

$$\frac{A^{\text{seg}}}{NkT} = m(a_0 + a_1 + a_2), \quad (19)$$

where  $a_0$  represents the reduced Helmholtz energy of the hard-sphere fluid, and  $a_1$  and  $a_2$  are perturbed first- and second-order parts as given below:

$$a_0 = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}, \quad (20)$$

$$a_1 = -\frac{12\eta\beta\varepsilon}{D^3} \left\{ k_1 \left[ \frac{L(z_1 D)}{z_1^2 (1-\eta)^2 Q(z_1 D)} - \frac{1+z_1}{z_1^2} \right] \right. \\ \left. - k_2 \left[ \frac{L(z_2 D)}{z_2^2 (1-\eta)^2 Q(z_2 D)} - \frac{1+z_2}{z_2^2} \right] \right\} \\ + 48\eta\beta\varepsilon \left[ \frac{1}{9} \left( \frac{\sigma}{D} \right)^{12} - \frac{1}{3} \left( \frac{\sigma}{D} \right)^6 \right] \\ - 8\eta\beta\varepsilon g_0 \left[ \frac{1}{9} \left( \frac{\sigma}{D} \right)^{12} - \frac{1}{3} \left( \frac{\sigma}{D} \right)^6 + \frac{2}{9} \left( \frac{\sigma}{D} \right)^3 \right] \quad (21)$$

$$a_2 = -\frac{6\eta\beta^2\varepsilon^2}{D^3} \left[ \frac{k_1^2}{2z_1 Q^4(z_1 D)} - \frac{k_2^2}{2z_2 Q^4(z_2 D)} \right. \\ \left. - \frac{2k_1 k_2}{(z_1+z_2) Q^2(z_1 D) Q^2(z_2 D)} \right] \\ - 24\eta\beta^2\varepsilon^2 \left[ \frac{k_1/D}{Q^2(z_1 D)} - \frac{k_2/D}{Q^2(z_2 D)} \right] \\ \times \left[ \frac{1}{9} \left( \frac{\sigma}{D} \right)^{12} - \frac{1}{3} \left( \frac{\sigma}{D} \right)^6 + \frac{2}{9} \left( \frac{\sigma}{D} \right)^3 \right] \quad (22)$$

$$k_1 = k_0 \exp[z_1(\sigma - D)], \quad k_2 = k_0 \exp[z_2(\sigma - D)], \\ Q(t) = \frac{S(t) + 12\eta L(t) \exp[-t]}{(1-\eta)^3 t^3}, \quad (23)$$

$$S(t) = (1-\eta)^2 t^3 + 6\eta(1-\eta)t^2 + 18\eta^2 t - 12\eta(1+2\eta), \quad (24)$$

$$g_0 = \frac{1+\eta/2}{(1-\eta)^2}, \quad L(t) = \left(1 + \frac{\eta}{2}\right)t + 1 + 2\eta, \quad \beta = \frac{1}{kT}, \quad (25)$$

$$k_0 = 2.1714\sigma, \quad z_1 = 2.9637/\sigma, \quad z_2 = 14.0167/\sigma. \quad (26)$$

$$\eta = \frac{\pi\rho d_s^3}{6} m \quad (27)$$

In Eqs. (21) and (22),  $\beta$  is the Boltzmann factor. In the present paper we used a SEXP of the RDF. This function is obtained analytically with a first-order solution of the mean spherical approximation of the RDF and improved by the SEXP [16].

$$g^{\text{SEXP}}(r) = g_0(r) \exp(g_1(r)) \quad (28)$$

Due to the very complex structure of Eq. (28) and almost the same behavior as Eq. (18), we have developed the needed derivatives for the RDF with the help of Eq. (18).



The contribution to free energy due to chain formation is calculated with the same model as presented in Eq. (17).

#### 4. CLASSICAL THERMODYNAMICS MW MODEL

For the purpose of comparison of the present statistical model with available analytical models, we have selected thermodynamic models for hydrocarbons recently published by Miyamoto and Watanabe [5,6] which cover a wide range of temperatures and pressures. For propane the model covers the range from the triple point temperature (85.48 K) to 623 K, at pressures up to 103 MPa and densities up to 741 kg·m<sup>-3</sup>. The MW model is one of the most accurate models for calculation of equilibrium thermodynamic properties for propane in the gaseous and liquid states. The absolute deviations of experimental thermodynamic property data from the analytical model are mostly within ±1% in pressure. The MW equations of state for pure hydrocarbons are given in terms of the dimensionless Helmholtz free energy,

$$\frac{A}{R_m T} = \frac{A^{\text{ig}}}{R_m T} + \frac{A^r}{R_m T} \quad (29)$$

In Eq. (29)  $A^{\text{ig}}$  represents the free-energy ideal-gas function, and  $A^r$  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 structures of the ideal-gas and residual parts are written as

$$\begin{aligned} \frac{A^{\text{ig}}}{R_m T} &= \ln \delta + a_1^0 + a_2^0 \tau + a_3^0 \ln \tau + \sum_{i=4}^{10} a_i \tau^{n_i} \\ &+ \sum_{i=11}^{16} a_i \ln(1 - \exp(-n_i \tau)), \quad \left( \delta = \frac{V_c}{V}, \tau = \frac{T_c}{T} \right) \end{aligned} \quad (30)$$

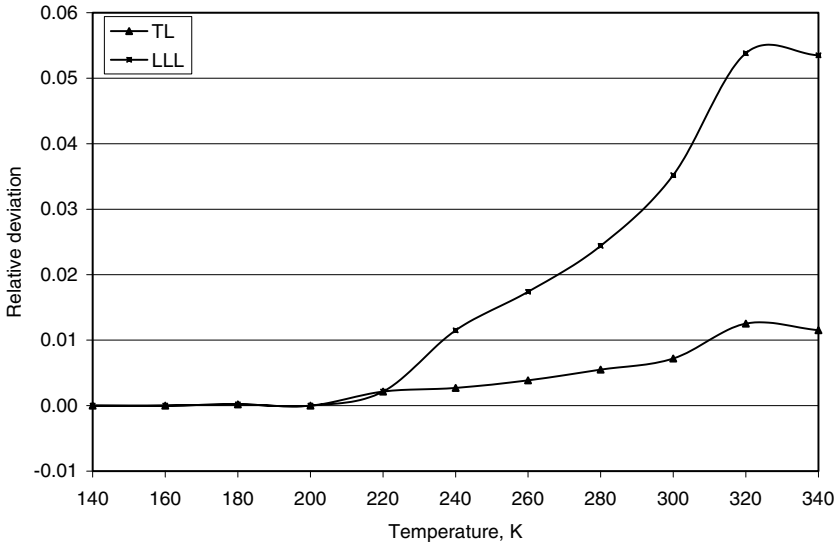
The coefficients  $\delta$  and  $\tau$  represent inverse reduced volume and inverse reduced temperature, respectively:

$$\begin{aligned} \frac{A^r}{R_m T} &= \sum_{i=1}^{15} a_i \tau^{t_i} \delta^{d_i} + \sum_{i=16}^{45} a_i \tau^{t_i} \delta^{d_i} \exp(-\delta c_i) \\ &+ \sum_{i=46}^{60} a_i \tau^{t_i} \delta^{d_i} \exp\left(-\alpha_i (\delta - v_i)^2 - \beta_i (\tau - \gamma_i)^2\right) \end{aligned} \quad (31)$$

The equations of state for different hydrocarbons require the use of different coefficients  $a_i$  and different exponents  $t_i$ ,  $d_i$ ,  $e_i$ ,  $\alpha_i$ , and  $\beta_i$ .

**Table II.** Important Constants for Analytical Calculation

propane	
$\sigma, \sigma_s$ (m)	$3.77 \times 10^{-10}$
$\varepsilon_s$ (J)	$3.20 \times 10^{-21}$
m (-)	1.85
M (kg/kmol)	44.08

**Fig. 1.** Deviations of the vapor pressure results from the models of this study and the MW model for propane.

## 5. RESULTS AND COMPARISONS WITH MW MODEL

The constants necessary for computation such as the characteristic rotation-, electronic-, etc. temperatures are obtained from data [10–12]. The vibration constants are obtained from the NIST Chemistry Web Book page. The inertia moments are obtained analytically by applying a knowledge of the atomic structure of the molecule. We carried out calculations for propane ( $C_3H_8$ ). The most important data for calculation are presented in Table II. Comparison of our calculations with the MW model are presented in Figs. 1–6.

Figures 1–6 show the relative deviations of the results for propane and in the saturated-gas region between the analytical computations (LLL

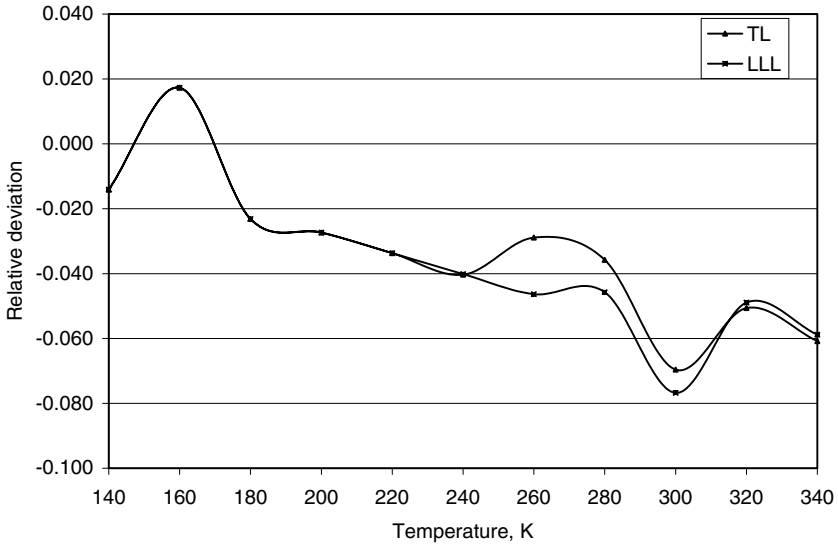


Fig. 2. Deviations of the isochoric molar heat capacity results from the models of this study and the MW model for propane.

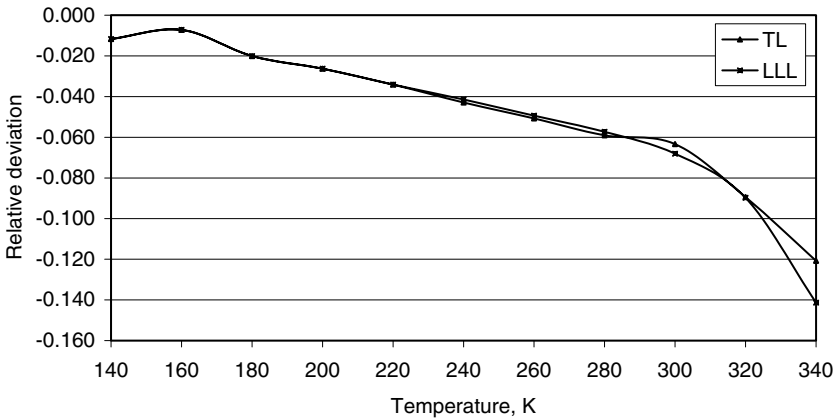
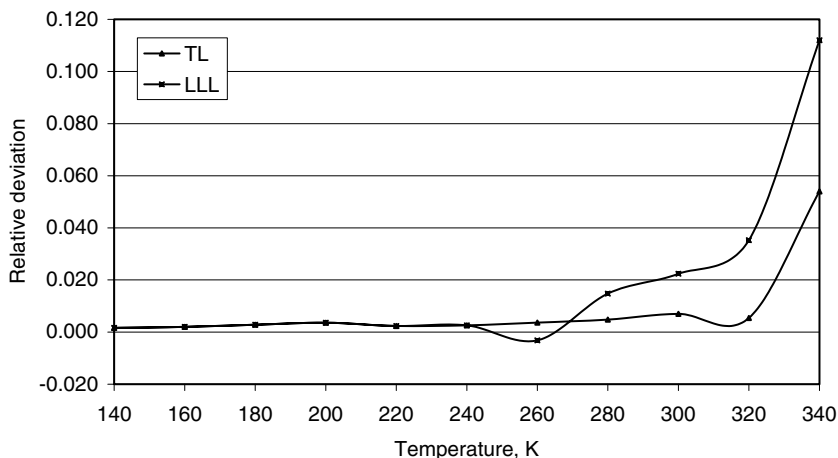


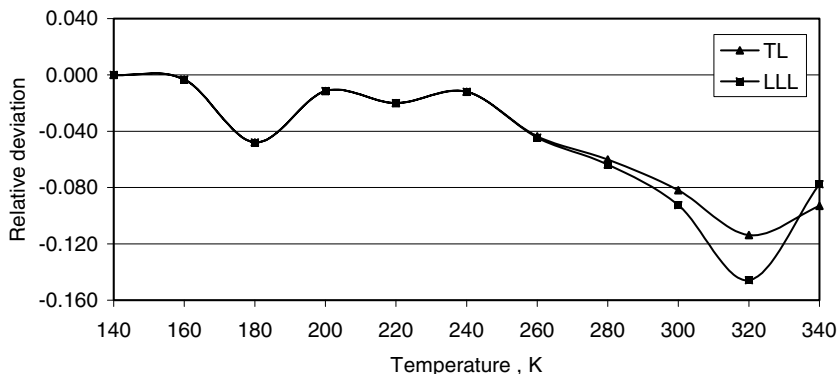
Fig. 3. Deviations of the isobaric molar heat capacity results from the models of this study and the MW model for propane.

and TL), and the MW model obtained by classical thermodynamics. The relative deviations are defined as follows:

$$\text{Relative deviation}(RD) = (\text{data}_{ST} - \text{data}_{MW}) / \text{data}_{MW} \quad (32)$$

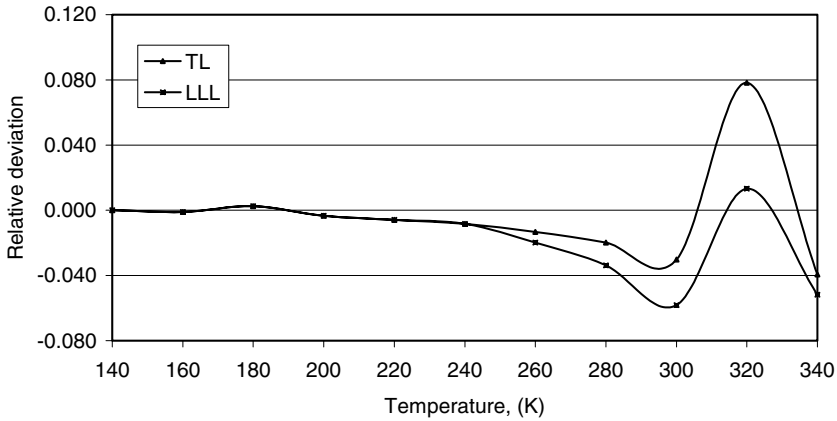


**Fig. 4.** Deviations of the speed of sound results from the models of this study and the MW model for propane.



**Fig. 5.** Deviations of the volumetric coefficient of expansion results from the models of this study and the MW model for propane.

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 in relatively good agreement for all models, obtained by associating statistical thermodynamics. Somewhat larger deviations can be found in the region near the critical point due to the large effect of fluctuation theory (Pelt and Sengers [41]) and the singular behavior of some thermodynamic



**Fig. 6.** Deviations of the isothermal compressibility results from the models of this study and the MW model for propane.

properties in the near-critical region. The perturbation models on the basis of SAFT theory (TL and LLL) yield surprisingly good results. The models on the basis of SAFT theory give better results in comparison with models on the basis of classical statistical thermodynamics, especially in high-temperature and high-pressure regions. The present model yields very good results as a whole, particularly the high-temperature range. The results of the complex TL model are much better than those of the LLL model.

Figures 7–11 show comparisons between TL and MW models for speed of sound, molar isochoric heat capacity, molar isobaric heat capacity, isothermal compressibility, and volumetric coefficient of expansion. The figures are displayed for propane for the real gas and liquid phases over extensive temperature (200–600 K) and pressure (1–50 bar) ranges. A detailed analysis of relative deviations of the TL model shows the highest relative deviations near the critical pressure and temperature where the presented model does not take into account the fluctuation theory of the critical point. The present analytical model yields very good results with much lower deviations at all other points. The analysis shows that multiple effects must be taken into account for the areas of very low compressibility factors in the liquid phase [14] so as to expect full matching of results, even though the matching is even now very satisfactory.

The present analysis provides a good basis for further upgrading of this model allowing the calculation of very accurate thermodynamic properties of state in liquid and gas phases as well as in super- and sub-critical regions.

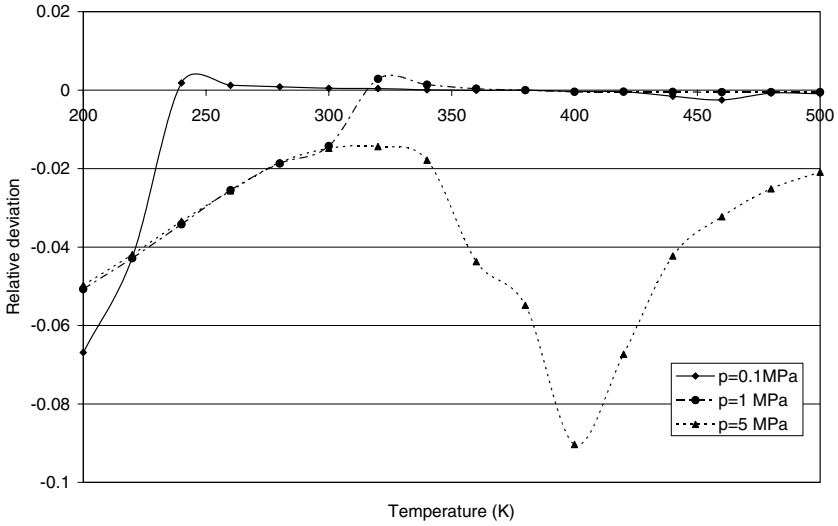


Fig. 7. Deviations of the speed of sound for propane in the fluid region obtained with the TL model compared with the MW model.

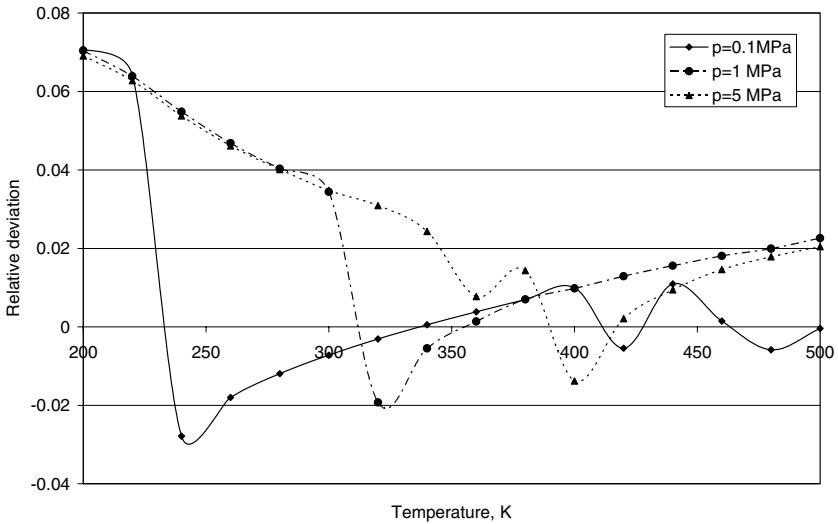


Fig. 8. Deviations of the isochoric molar heat capacity for propane in the fluid region obtained with the TL model compared with the MW model.

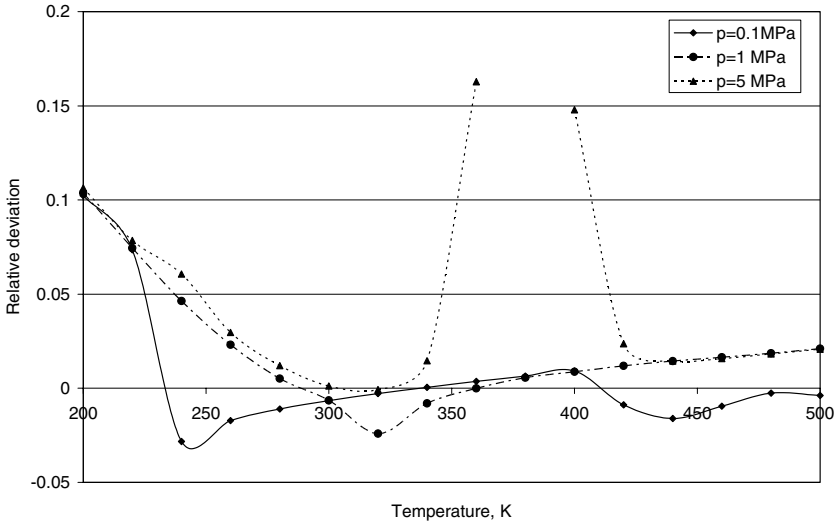


Fig. 9. Deviations of the isobaric molar heat capacity for propane in the fluid region obtained with the TL model compared with the MW model.

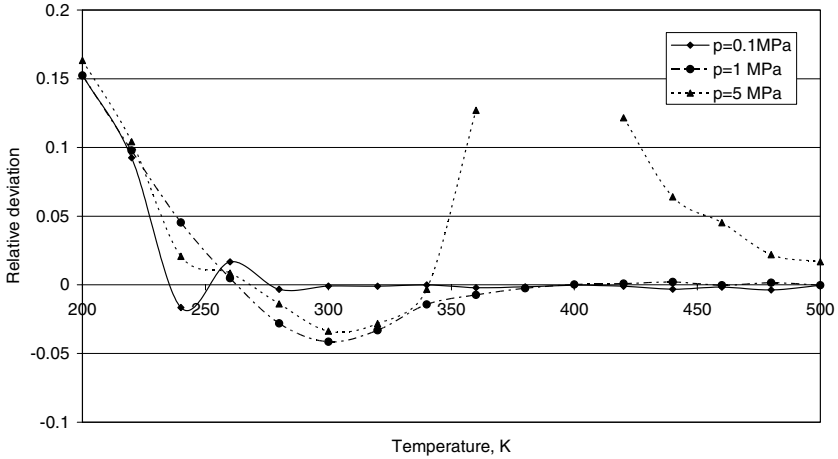


Fig. 10. Deviations of the volumetric coefficient of expansion for propane in the fluid region obtained with the TL model compared with the MW model.

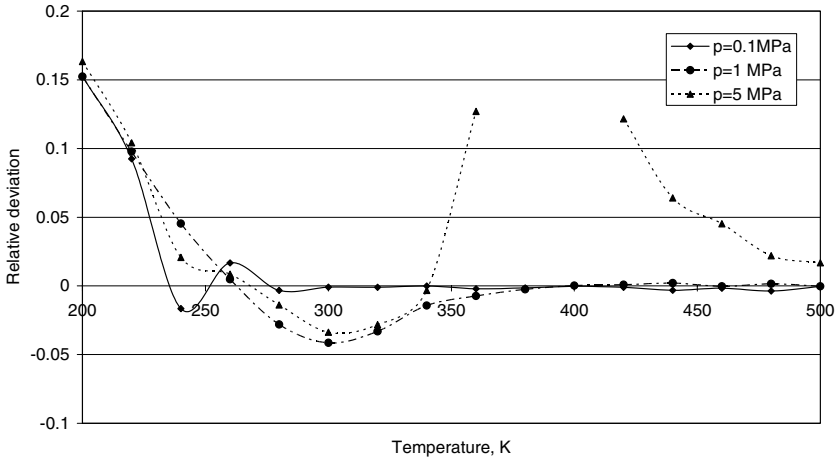


Fig. 11. Deviations of the isothermal compressibility for propane in the fluid region obtained with the TL model compared with the MW model.

## NOMENCLATURE

$A$	Helmholtz free energy
$a$	reduced Helmholtz energy
BWR	Benedict–Webb–Rubin
$c_0$	speed of sound
$C_p$	isobaric molar heat capacity
$C_V$	isochoric molar heat capacity
$f$	number of degrees of freedom
$G$	Gibbs free enthalpy
$g_0$	hard-sphere radial distribution function
EOS	equation of state
$H$	Hamiltonian
$H_h$	enthalpy
$k$	Boltzmann constant
LLL	Liu–Li–Lu
$m$	number of segments
$M$	molar mass
MW	Miyamoto–Watanabe
$N$	number of molecules in system
$p$	momentum
$p_p$	pressure
$R_m$	universal gas constant
$S$	entropy
SAFT	statistical associating fluid theory



SEXP	simplified exponential approximation
ST	statistical thermodynamics
$T$	temperature
$T^*$	reduced temperature
TL	Tang-Lu
$r$	intermolecular distance
$U$	internal energy
$v$	specific volume
$V$	volume
$Z$	partition function
$\beta$	Boltzmann factor
$\beta_T$	coefficient of thermal expansion
$\delta$	inverse reduced volume
$\varepsilon_s$	segment interaction parameter
$\varepsilon^{AB}$	association energy between two sites
$\eta$	packing factor
$\theta$	characteristic temperature
$\kappa^{AB}$	volume of interaction between two sites
$\rho$	density
$\rho^*$	reduced density
$\chi$	isothermal compressibility
$\sigma_s$	segment diameter

### Superscripts and Subscripts

0	ground state
assoc	association
c	critical state
chain	chain
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

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