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The Three-Parameter Corresponding States Principle

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A multiproperty approach for the evaluation of the existing three-parameter corresponding states principles (CSP) and calculation of the corresponding states parameter is presented. This technique is based on the assumption that contribution of the third parameter to the thermophysical properties is much smaller than the contributions of the first two parameters. The first two parameters are, generally, the molecular energy and length parameters, ϵ/k and σ (or critical temperature and volume, T_c and V_c). Based on the present multiproperty technique, several existing three-parameter CSPs are evaluated. It is demonstrated that the three-parameter CSP, which is based on the two- and three-body intermolecular potential parameters, effectively satisfies the requirements of this technique. The corresponding states parameters of several compounds, including normal alkane hydrocarbons (CH_4 to $C_{20}H_{42}$), for which proper thermophysical data are available, are calculated through the present technique, and they are reported here.

KEY WORDS: corresponding states principle; intermolecular potential parameters; thermophysical properties correlation; three-body forces.

1. INTRODUCTION

The corresponding states principle (CSP) is a useful tool for estimating thermophysical properties of a substance with a knowledge of the properties of a reference substance [1–3]. This principle provides us with practical methods of making predictions of properties of a substance under conditions where no experimental data may exist, and where no satisfactory theoretical treatment may be possible. The CSP for the thermodynamic properties was

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originally developed by Van der Waals [1, 2]. Later on, Kamerlingh Onnes [1, 3] presented the method of derivation of the CSP for transport properties. Generally, in the development of the CSP of simple pure substances, it is assumed [1] that (a) intermolecular energies are independent of density, (b) quantum effects may be ignored, and (c) the total intermolecular potential energy function of the molecules of the system consists of two-body interactions only, represented by

$$U_{\text{total}} = \sum_{j>i=1}^{N} u_{ij} = \epsilon \sum_{j>i=1}^{N} f(r_{ij}/\sigma) \tag{1}$$

where ϵ and σ are the potential parameters. Based on these assumptions, the reduced CSP relations for thermophysical properties of simple pure substances will be

$$\overline{V} = \overline{V}(\overline{T}, \overline{P}) \tag{2}$$

$$\overline{\mu} = \overline{\mu}(\overline{T}, \overline{P}) \tag{3}$$

$$\overline{K} = \overline{K}(\overline{T}, \overline{P}) \tag{4}$$

where $\overline{V} = V/N\sigma^3$ is the reduced volume, $\overline{\mu} = \mu\sigma^2/(m\epsilon)^{1/2}$ is the reduced viscosity, $\overline{K} = K\sigma^2(m/\epsilon)^{1/2}/k$ is the reduced thermal conductivity, $\overline{T} = kT/\epsilon$ is the reduced temperature, $\overline{P} = P\sigma^3/\epsilon$ is the reduced pressure, m is the molecular mass, and k is the Boltzmann constant. Since the reducing parameters in Eqs. (2)–(4) are ϵ and σ, these equations are called the two-parameter CSP relations of thermophysical properties. Instead of ϵ and σ, one may choose the critical temperature and volume (T_c and V_c) as the reducing parameters [1].

While the two-parameter CSP may be adequate for substances with simple molecules, it is not sufficient for other substances. This observation has brought about the idea of the three-parameter CSP in which a third parameter, in addition to ϵ and σ (or T_c and V_c), is also introduced [4–7]. In a number of the existing theories of the three-parameter CSP, the nature of the third parameter is based on empirical grounds [4–6]. Among these theories, the one due to Pitzer and coworkers [6] is widely used for thermophysical property calculation of polyatomic substances. In order to develop a three-parameter CSP theory based on statistical mechanics, one should consider an appropriate three-parameter potential energy function. There exist two possible routes for this. One is the assumption that the total potential energy function consists of only pairwise potentials with three parameters, i.e.,

$$U_{\text{total}} = \epsilon \sum_{j>i=1}^{N} f\left(\frac{r_{ij}}{\sigma}, \frac{\alpha}{\sigma}\right) \tag{5}$$

The second route is the assumption that the total potential energy function consists of the pair- and triplet-potentials, with the pair-potentials represented by a two-parameter functional form, and the triplet potential represented by a one-parameter functional form, i.e.,

$$\begin{aligned} U_{\text{total}} &= \sum_{j>i=1}^{N} u_{ij} + \sum_{k>j>i=1}^{N} w_{ijk} \\ &= \epsilon \sum_{j>i=1}^{N} f\left(\frac{r_{ij}}{\sigma}\right) + \alpha \sum_{k>j>i=1}^{N} f\left(\frac{r_{ij}}{\sigma}, \frac{r_{jk}}{\sigma}, \frac{r_{ki}}{\sigma}, \theta_i, \theta_j, \theta_k\right) \end{aligned} \tag{6}$$

where θ_i, θ_j, and θ_k are the angles of a triangle connecting the centers of mass of three molecules.

In the present report, a multithermophysical property technique is introduced, through which one may calculate the three corresponding states parameters of pure substances, provided that the CSP parameters of at least two reference substances are available. The underlying assumption of this technique is the understanding that the contribution of the third parameter (α) to the prediction of thermophysical properties is considerably smaller than the other two parameters (ϵ and σ or T_c and V_c). With the utilization of this technique we are able to calculate intermolecular pair- and triplet-potential energy parameters of the substances for which intermolecular potential energy parameters are not available.

2. THE THREE-PARAMETER CORRESPONDING STATES PRINCIPLE

According to the three-parameter CSP, one may replace the dimensionless relations (2)–(4) with

$$\bar{V} = \bar{V}(\bar{T}, \bar{P}, \bar{\alpha}) \tag{7}$$

$$\bar{\mu} = \bar{\mu}(\bar{T}, \bar{P}, \bar{\alpha}) \tag{8}$$

$$\bar{K} = \bar{K}(\bar{T}, \bar{P}, \bar{\alpha}) \tag{9}$$

where $\bar{\alpha}$ is the reduced third parameter. The success of application of the two-parameter CSP for simple substances and its partial success with complex substances (the fact that the gas phase properties of complex substances can be treated effectively by the two-parameter CSP) is an indication of the smaller role of α, as compared to ϵ and σ, in the thermophysical property prediction of complex substances. With this observation, one may expand Eqs. (7)–(9) around $\bar{\alpha}_0$ of a reference substance and derive

$$\bar{V}(\bar{T}, \bar{P}, \bar{\alpha}) = \bar{V}(\bar{T}, \bar{P}, \bar{\alpha}_0) + (\bar{\alpha} - \bar{\alpha}_0)\left[\frac{\partial \bar{V}(\bar{T}, \bar{P}, \bar{\alpha})}{\partial \bar{\alpha}}\right]_{\bar{\alpha}=\bar{\alpha}_0} \tag{10}$$

$$\bar{\mu}(\bar{T}, \bar{P}, \bar{\alpha}) = \bar{\mu}(\bar{T}, \bar{P}, \bar{\alpha}_0) + (\bar{\alpha} - \bar{\alpha}_0)\left[\frac{\partial \bar{\mu}(\bar{T}, \bar{P}, \bar{\alpha})}{\partial \bar{\alpha}}\right]_{\bar{\alpha}=\bar{\alpha}_0} \tag{11}$$

$$\bar{K}(\bar{T}, \bar{P}, \bar{\alpha}) = \bar{K}(\bar{T}, \bar{P}, \bar{\alpha}_0) + (\bar{\alpha} - \bar{\alpha}_0)\left[\frac{\partial \bar{K}(\bar{T}, \bar{P}, \bar{\alpha})}{\partial \bar{\alpha}}\right]_{\bar{\alpha}=\bar{\alpha}_0} \tag{12}$$

These truncations are valid as long as $(\bar{\alpha} - \bar{\alpha}_0)$ is small enough such that one can neglect the terms of the order of $(\bar{\alpha} - \bar{\alpha}_0)^2$ and higher.[2] In order to utilize the above CSP relations for thermophysical property calculation of substances from the properties of a reference substance (V_0, μ_0, K_0), we must transform them to the following forms:

$$\bar{V} = \bar{V}_0 + (\bar{\alpha} - \bar{\alpha}_0)\,\Delta\bar{V}_0 \tag{13}$$

$$\bar{\mu} = \bar{\mu}_0 + (\bar{\alpha} - \bar{\alpha}_0)\,\Delta\bar{\mu}_0 \tag{14}$$

$$\bar{K} = \bar{K}_0 + (\bar{\alpha} - \bar{\alpha}_0)\,\Delta\bar{K}_0 \tag{15}$$

For the right-hand sides of Eqs. (10)–(12) and (13) and (15) to be equivalents, respectively, the following corresponding states conditions should be satisfied:

$$\bar{T} = \bar{T}_0, \bar{P} = \bar{P}_0 \tag{16}$$

For calculation of $\Delta\bar{V}_0$, $\Delta\bar{\mu}_0$, and $\Delta\bar{K}_0$, we will need to utilize reduced properties of a second reference substance. Then from Eqs. (13)–(15), we will have

$$\Delta\bar{V}_0 = \frac{\bar{V}_* - \bar{V}_0}{\bar{\alpha}_* - \bar{\alpha}_0}, \quad \Delta\bar{\mu}_0 = \frac{\bar{\mu}_* - \bar{\mu}_0}{\bar{\alpha}_* - \bar{\alpha}_0}, \quad \Delta\bar{K}_0 = \frac{\bar{K}_* - \bar{K}_0}{\bar{\alpha}_* - \bar{\alpha}_0} \tag{17}$$

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[2] Equations (10)–(12) are similar to Pitzer's three-parameter CSP when $\bar{\alpha}$ is replaced by ω (the acentric factor) and $\bar{\alpha}_0$ is put equal to zero.

where the subscript $(*)$ denotes the properties of the second reference substance with $\bar{P}_0 = \bar{P}_*$, $\bar{T}_0 = \bar{T}_*$ as the corresponding conditions. With the use of Eqs. (13)–(17) and the following identities:

$$\frac{\bar{T}}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial \bar{T}}\right) = \frac{T}{V}\left(\frac{\partial V}{\partial T}\right) \tag{18}$$

$$\frac{\bar{T}}{\bar{\mu}}\left(\frac{\partial \bar{\mu}}{\partial \bar{T}}\right) = \frac{T}{\mu}\left(\frac{\partial \mu}{\partial T}\right) \tag{19}$$

$$\frac{\bar{T}}{\bar{K}}\left(\frac{\partial \bar{K}}{\partial \bar{T}}\right) = \frac{T}{K}\left(\frac{\partial K}{\partial T}\right) \tag{20}$$

we have developed a technique here that can be used for both construction and evaluation of the existing three-parameter CSPs. This technique will make it possible to evaluate the consistency of a three-parameter CSP in prediction of thermophysical properties. The major advantage of this technique is its application for calculation of CSP parameters of substances for which the parameters are not available. Since the importance of the three-parameter CSPs is most felt in the liquid state, the computations and consistency tests that are performed here are for liquids.

To construct this multiproperty technique, we need to consider either the zero-pressure liquid thermophysical property data or the data at saturation pressure. In the first case,

$$\bar{P} = \bar{P}_0 = \bar{P}_* = 0 \tag{21}$$

and in the second case,

$$\bar{P}(\bar{T}) = \bar{P}_0(\bar{T}_0) = \bar{P}_*(\bar{T}_*) \tag{22}$$

However, in both of the above cases, the pressure as an independent variable in Eqs. (13)–(20) will disappear. As a result, Eqs. (13)–(15) can be written as

$$1 + (\bar{\alpha} - \bar{\alpha}_0)\frac{\Delta \bar{V}_0(\bar{T}, \bar{\alpha}_0)}{\bar{V}_0(\bar{T}, \bar{\alpha}_0)} = \frac{V(T)}{V_0(T_0)}\left(\frac{\sigma_0}{\sigma}\right)^3 \tag{23}$$

$$1 + (\bar{\alpha} - \bar{\alpha}_0)\frac{\Delta \bar{\mu}_0(\bar{T}, \bar{\alpha}_0)}{\bar{\mu}_0(\bar{T}, \bar{\alpha}_0)} = \frac{\mu(T)}{\mu_0(T_0)}\left(\frac{\sigma}{\sigma_0}\right)^2\left(\frac{m_0\epsilon_0}{m\epsilon}\right)^{1/2} \tag{24}$$

$$1 + (\bar{\alpha} - \bar{\alpha}_0)\frac{\bar{K}_0(\bar{T}, \bar{\alpha}_0)}{\bar{K}_0(\bar{T}, \bar{\alpha}_0)} = \frac{K(T)}{K_0(T_0)}\left(\frac{\sigma}{\sigma_0}\right)^2\left(\frac{m\epsilon_0}{m_0\epsilon}\right)^{1/2} \tag{25}$$

Also, by replacing Eqs. (13)–(15) in Eqs. (18)–(20), and in the absence of pressure as an independent variable, we get

$$\frac{1 + (\bar{\alpha} - \bar{\alpha}_0)\dfrac{\partial \Delta \bar{V}_0(\bar{T}, \bar{\alpha}_0)}{\partial \bar{T}} \Bigg/ \dfrac{\partial \bar{V}_0(\bar{T}, \bar{\alpha}_0)}{\partial \bar{T}}}{1 + (\bar{\alpha} - \bar{\alpha}_0)\Delta \bar{V}_0(\bar{T}, \bar{\alpha}_0)/\bar{V}_0(\bar{T}, \bar{\alpha}_0)} = \left(\frac{T}{T_0}\right)\frac{V_0(T_0)}{V(T)}\,\frac{\partial V(T)/\partial T}{\partial V_0(T_0)/\partial T_0} \tag{26}$$

$$\frac{1 + (\bar{\alpha} - \bar{\alpha}_0)\dfrac{\partial \Delta \bar{\mu}_0(\bar{T}, \bar{\alpha}_0)}{\partial \bar{T}} \Bigg/ \dfrac{\partial \bar{\mu}_0(\bar{T}, \bar{\alpha}_0)}{\partial \bar{T}}}{1 + (\bar{\alpha} - \bar{\alpha}_0)\Delta \bar{\mu}_0(\bar{T}, \bar{\alpha}_0)/\bar{\mu}_0(\bar{T}, \bar{\alpha}_0)} = \left(\frac{T_0}{T}\right)\frac{\partial[\ln \mu(T)]/\partial(1/T)}{\partial[\ln \mu_0(T_0)]/\partial(1/T_0)} \tag{27}$$

$$\frac{1 + (\bar{\alpha} - \bar{\alpha}_0)\dfrac{\partial \Delta \bar{K}_0(\bar{T}, \bar{\alpha}_0)}{\partial \bar{T}} \Bigg/ \dfrac{\partial \bar{K}_0(\bar{T}, \bar{\alpha}_0)}{\partial \bar{T}}}{1 + (\bar{\alpha} - \bar{\alpha}_0)\Delta \bar{K}_0(\bar{T}, \bar{\alpha}_0)/\bar{K}_0(\bar{T}, \bar{\alpha}_0)} = \left(\frac{T}{T_0}\right)\frac{K_0(T_0)}{K(T)}\,\frac{\partial K(T)/\partial T}{\partial K_0(T_0)/\partial T_0} \tag{28}$$

Provided that pressure-independent thermophysical properties $V(T)$, $V_0(T_0)$, $V_*(T_*)$, $\mu(T)$, $\mu_0(T_0)$, $\mu_*(T_*)$, $K(T)$, $K_0(T_0)$, and $K_*(T_*)$ are available, and provided that the CSP parameters for the two reference substances (ϵ_0, σ_0, α_0, ϵ_*, σ_*, α_*) are known, the above equations may be used to calculate ϵ, σ, and α of another substance together with the corresponding state temperatures T and T_0. Since $\bar{T} = \bar{T}_0$, then

$$T/T_0 = \epsilon/\epsilon_0$$

This condition reduces the number of the above unknowns to four. As a result, we only need to use four out of the six equations (23)–(28) in order to find the values of ϵ, σ, α, T, and T_0. Since every two of the above equations, (23) and (26), (24) and (27), (25) and (28), are based on one kind of thermophysical data, we will need only two kinds of thermophysical data to calculate the unknowns. In the computations that are presented in this report all the possible combinations of every two thermophysical properties are used.

3. COMPUTATION AND DISCUSSION

In the technique presented above for the calculation of the corresponding states parameters, it is necessary to have empirical correlations for constant zero pressure (or saturation pressure) liquid thermophysical properties of the substances under consideration. The computations performed here are for a few substances for which sufficient thermophysical properties were at hand. They include nitrogen, oxygen, a few unsaturated hydrocarbons, and a large number of normal alkane hydrocarbons (CH_4 to $C_{20}H_{42}$). The liquid viscosity, molar volume, and thermal conductivity data of each substance used in this report are fitted to the following polynomials by the method of least squares:

$$V(T) = \sum_{i=0}^{m_1} A_i T^i \tag{29}$$

$$\ln [\mu(T)] = \sum_{i=0}^{m_2} B_i T^{-i} \tag{30}$$

$$K(T) = \sum_{i=0}^{m_3} C_i T^i \tag{31}$$

The number of terms in these power series are chosen such that the root-mean-square deviation between the data and the correlation is minimized. The literature sources for the thermophysical data of the substances that are investigated here are presented in Table I.[3] From correlations (29)–(31), one can derive reduced liquid properties as functions of reduced temperature. For example, for the first reference substance,

$$\overline{V}_0(\overline{T}, \overline{\alpha}_0) = \frac{1}{N\sigma_0^3} \sum_{i=0}^{m_1} [A_i(\epsilon_0/k)^i]\overline{T}^i \tag{32}$$

$$\ln [\overline{\mu}_0(\overline{T}, \overline{\alpha}_0)] = \frac{\sigma_0^2}{(m\epsilon_0)^{1/2}} \sum_{i=0}^{m_2} [B_i(\epsilon_0/k)^{-i}]\overline{T}^{-i} \tag{33}$$

$$\overline{K}_0(\overline{T}, \overline{\alpha}_0) = \frac{\sigma_0^2}{k}\left(\frac{m}{\epsilon_0}\right)^{1/2} \sum_{i=0}^{m_3} [C_i(\epsilon_0/k)^i]\overline{T}^i \tag{34}$$

Similar reduced relations can be derived for the second reference substance. For consistency tests and calculation of the corresponding states parameters,

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[3] Coefficients A_i, B_i, C_i for each liquid substance are not reported here due to limitations in the length of the paper. The authors can provide these data upon request.

Table I. Literature Sources for the Thermophysical Properties of Liquids Used in This Paper

	Volume data		Viscosity data		Thermal conductivity data	
Substance	State	Ref. no.	State	Ref. no.	State	Ref. no.
N_2	Sat. liq.	8	Sat. liq.	8	Sat. liq.	8
O_2	Sat. liq.	8	Sat. liq.	8	Sat. liq.	8
CO_2			Sat. liq.	9	Sat. liq.	9
C_2H_4	Liq. at 0 atm	10	Liq. at 0 atm	11		
C_6H_6	Liq. at 0 atm	12	Liq. at 0 atm	13		
CH_4	Liq. at 0 atm	14	Liq. at 0 atm	15		
	Sat. liq.	16	Sat. liq.	16	Sat. liq.	16
C_2H_6	Liq. at 0 atm	14	Liq. at 0 atm	14		
	Sat. liq.	17	Sat. liq.	17	Sat. liq.	9
C_3H_8	Liq. at 0 atm	14	Liq. at 0 atm	14		
	Sat. liq.	18	Sat. liq.	18	Sat. liq.	9
C_4H_{10} to $C_{10}H_{22}$	Liq. at 0 atm	14	Liq. at 0 atm	14	Sat. liq.	19
$C_{11}H_{24}$ to $C_{20}H_{42}$	Liq. at 0 atm	14	Liq. at 0 atm	14		

we must specify two reference substances for which pressure-independent thermophysical properties are known for a large range of temperature. Then with the assumption that corresponding states parameters for the reference substances are known, we attempt to derive the corresponding states parameters of other substances through the present technique. For the present calculations, ethane and propane are chosen as the two reference substances. The three-parameter CSPs investigated in this report are discussed as follows.

First, we consider Pitzer's three-parameter CSP [6], for which the parameters are T_c, V_c, and ω, and the acentric factor, which is defined by $\omega = -1 - \log(P/P_c)$ at $T/T_c = 0.7$. This CSP is widely used in the calculation of properties of substances by practicing scientists and engineers. The choice of the third parameter, ω, is based on purely empirical grounds.

Second, we consider the three-parameter CSP according to the Kihara pair-potential energy function [7]

$$\begin{aligned} u_{ij} &= 4\epsilon\left[\left(\frac{\sigma - 2a}{r_{ij} - 2a}\right)^{12} - \left(\frac{\sigma - 2a}{r_{ij} - 2a}\right)^{6}\right]; && \text{for } r_{ij} > 2a \\ u_{ij} &= \infty; && \text{for } r_{ij} < 2a \end{aligned} \tag{35}$$

where the third parameter consists of the hard-core molecular diameter a. The parameters of this potential function can generally be calculated from the gas-phase thermophysical properties with the use of the principles of statistical thermodynamics of gases (second virial coefficient) and the kinetic theory of dilute gases (collision integrals). A three-parameter CSP based on the Kihara potential parameters does not generally satisfy the truncated equations (10)–(12) or (13)–(15). This is because of the large value of $a^* - a_0^* = (a/\sigma) - (a_0/\sigma_0)$ for most of the molecules, which makes the terms of the order of $(a^* - a_0^*)^2$ and higher nonnegligible.

Third, we consider the three-parameter CSP in which the total potential energy function consists of the pair- and triplet-potentials. The pair-potential is represented by the Lennard-Jones two-parameter function

$$u_{ij} = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{36}$$

while the triplet-potential is represented by the Axilrod-Teller triple-dipole function [20], which contains one parameter ν, i.e.,

$$\omega_{ijk} = \nu(1 + 3\cos\theta_i \cos\theta_j \cos\theta_k)/(r_{ij}\, r_{jk}\, r_{ki})^3 \tag{37}$$

parameters ϵ and σ of the Lennard-Jones function can be calculated from the gas-phase thermophysical properties. Parameter ν can only be calculated from the third virial coefficient data. However, the following equation is being used for ν, which is based on quantum mechanical principles:

$$\nu = \frac{9}{16} I\alpha^3 \tag{38}$$

where I is the ionization potential and α is the polarizability of the molecules. In the case where the Lennard-Jones parameters are derived from the second virial coefficient data and for simple molecules, it is observed that this pair-potential can effectively represent the total intermolecular energy of interactions in calculating liquid thermodynamic properties. However, when the parameters of this potential are derived from a combination of thermophysical properties, then it would be a true pair-potential function. The computations reported here are based on the latter case. The Lennard-Jones potential parameters of the two reference substances chosen are based on the combination of the gas viscosity and the second virial coefficient data.

Application of the present technique for calculation of the Pitzer's CSP parameters of different substances was not successful. This is mainly due to the empirical nature of ω, the acentric factor, which does not necessarily satisfy truncated equations (10)–(12) or (13)–(15). The present technique is also applicable for calculation of the Kihara's CSP parameters of substances. This is due to the large values of $a^* - a_0^*$, which makes the terms of the order of $(a^* - a_0^*)^2$ and higher nonnegligible. However, application of the present technique for calculation of parameters of the Lennard-Jones and Axilrod-Teller potential functions, as the CSP parameters, has been success-

Table II. Comparison of σ, for Lennard-Jones (12–6) Potential Function Calculated by the Present Technique with the Values from the Literature

	σ (Å)			
		By present technique		
Compound	From literature	From volume & viscosity data	From volume & thermal conductivity data	From viscosity & thermal conductivity data
C_2H_6(ref.)	4.221[b]	4.221	4.221	4.221
C_3H_8 (ref.)	4.838[b]	4.838	4.838	4.838
N_2	3.694[a] 3.663[b]	3.865	3.772	3.934
O_2	3.433[c]	3.405	3.577	3.808
C_2H_4	4.433[a] 4.066[c] 4.200[b]	4.244	[f]	[f]
C_6H_6	8.443[a] 5.628[c] 4.776[b]	4.574	[f]	[f]
CH_4	4.010[a] 3.808[c] 3.697[d] 3.678[b]	3.824	3.515	4.212
n-C_4H_{10}	7.152[a] 5.869[c] 5.003[b]	[g]	5.153	5.006
n-C_5H_{12}	8.540[a] 6.099[c] 5.282[b]	5.399	5.484	5.467
n-C_6H_{14}	5.916[c]	5.499	5.809	5.914
n-C_7H_{16}	10.22[a] 5.715[b]	5.705	5.667	5.724
n-C_8H_{18}	10.21[e] 7.407[c]	6.028	6.394	[g]

[a] Ref. 21; based on the second virial coefficient data.
[b] Ref. 21; based on combined gas viscosity and second virial data.
[c] Ref. 22; based on gas viscosity data.
[d] Ref. 22; based on gas thermal conductivity data.
[e] Ref. 22; based on the second virial coefficient data.
[f] Calculations were not performed due to the lack of liquid thermal conductivity data.
[g] Calculations did not converge to a meaningful solution.

ful. In Table II, values of σ, and in Table III, values of ϵ/k for the Lennard-Jones potential function calculated by the present technique (with ethane and propane as the reference substances) using three different pairs of properties, are compared with the literature values of σ and ϵ/k. In Table IV, values of ν (third parameter of the CSP based on two- and three-body potential

Table III. Comparison of ϵ/k, for Lennard-Jones (12–6) Potential Function Calculated by the Present Technique with the Values from the Literature

	ϵ/k (K)			
		By present technique		
Compound	From literature	From volume & viscosity data	From volume & thermal conductivity data	From viscosity & thermal conductivity data
C_2H_6 (ref.)	274.5[b]	274.5	274.5	274.5
C_3H_8 (ref.)	299.9[b]	299.9	299.9	299.9
N_2	96.26[a] 96.96[b]	102.9	108.7	111.1
O_2	113.0[c]	129.6	137.3	137.2
C_2H_4	202.5[a] 230.[c] 219.0[b]	219.6	[f]	[f]
C_6H_6	247.5[a] 335.[c] 638.3[b]	516.6	[f]	[f]
CH_4	142.8[a] 140.[c] 156.7[d] 166.8[b]	147.8	177.6	163.4
n-C_4H_{10}	223.7[a] 208.[c] 398.9[b]	[g]	371.9	329.4
n-C_5H_{12}	217.6[a] 269.[c] 474.2[b]	383.8	368.9	365.9
n-C_6H_{14}	423.0[c]	440.1	377.3	390.6
n-C_7H_{16}	239.5[a] 621.2[b]	490.7	491.8	446.1
n-C_8H_{18}	260.0[e] 333.0[c]	537.8	403.6	[g]

[a] Ref. 21; based on the second virial coefficient data.
[b] Ref. 21; based on combined gas viscosity and second virial data.
[c] Ref. 22; based on gas viscosity data.
[d] Ref. 22; based on gas thermal conductivity data.
[e] Ref. 22; based on the second virial coefficient data.
[f] Calculations were not performed due to the lack of liquid thermal conductivity data.
[g] Calculations did not converge to a meaningful solution.

Table IV. Comparison of ν, the Coefficient of Triple-Dipole Potential Calculated by the Present Technique with the Values Calculated Using Eq. (38)[a]

	$\nu/k \times 10^{-4}$ ($Å^9 \cdot K$)			
		By present technique		
Compound	From Eq. (38)	From volume & viscosity data	From volume & thermal conductivity data	From viscosity & thermal conductivity data
C_2H_6 (ref.)	615.7	615.7	615.7	615.7
C_3H_8 (ref.)	1,838.5	1,838.5	1,838.5	1,838.5
N_2	53.1	68.5	78.6	122.9
O_2	30.3	40.0	52.1	115.3
C_2H_4	530.1	596.9	[b]	[b]
C_6H_6	4,899.7	3,604.1	[b]	[b]
CH_4	166.7	120.8	101.7	339.6
n-C_4H_{10}	4,031.2	[c]	4,486.6	2,495.2
n-C_5H_{12}	6,886.9	7,478.5	7,271.4	4,918.9
n-C_6H_{14}	11,269.3	12,226.0	9,179.9	7,222.9
n-C_7H_{16}	17,335.6	20,298.4	14,736.2	7,982.1
n-C_8H_{18}	24,892.0	39,868.0	27,995.0	[c]

[a] The ionization potential and polarizability of each compound are taken from ref. [23].
[b] Calculations were not performed due to the lack of liquid thermal conductivity data.
[c] Calculations did not converge to a meaningful solution.

Table V. Values of σ and ϵ/k for Lennard-Jones (12–6) Potential Function and ν for the Triple-Dipole Potential Function for Normal Alkanes Calculated Through the Present Technique Using Liquid Molar Volume and Liquid Viscosity Data

Compound	σ (Å)	ϵ/k (K)	$\nu/k \times 10^{-4}$ ($Å^9$ K)
n-C_9H_{20}	6.087	579.00	47,318
n-$C_{10}H_{22}$	6.125	560.2	49,891
n-$C_{11}H_{24}$	6.243	594.2	66,238
n-$C_{12}H_{26}$	6.315	620.0	82,124
n-$C_{13}H_{28}$	6.338	649.3	93,104
n-$C_{14}H_{30}$	6.547	679.3	135,450
n-$C_{15}H_{32}$	6.757	708.6	176,510
n-$C_{16}H_{34}$	7.034	760.9	261,840
n-$C_{17}H_{36}$	7.159	744.4	304,080
n-$C_{18}H_{38}$	7.255	765.7	353,490
n-$C_{19}H_{40}$	7.220	801.8	378,676
n-$C_{20}H_{42}$	7.413	828.8	483,170

functions) calculated by the present technique are compared with the values of ν from Eq. (38). Values of σ, ϵ/k, and ν as calculated by the present technique are in good agreement with the literature data. The small deviations in the predicted values of the CSP parameters by the present technique from the literature data could be due to (a) inaccuracies in the parameters of the reference substances; (b) inaccuracies in Eqs. (37) and (38), which are actually quantum mechanical approximations; (c) inaccuracies in the literature data and the thermophysical data used for this study. In Table V, values of σ, ϵ/k, and ν, respectively, of normal alkanes (n-C_9H_{20} to n-$C_{20}H_{42}$), as calculated by the present technique, are reported. Data for CH_4 to C_8H_{18} are reported in Tables II, III, and IV. The reasons for choosing normal alkanes in this study are two-fold: first, because sufficient liquid viscosity and liquid volume data are available for normal alkanes; and second, because we can make a systematic comparison of the predicted parameters as the number of carbon atoms in the chain increases. This comparative study is useful in the absence of any experimental data for long-chain hydrocarbons.

Based on the above observations, it seems that a three-parameter CSP that is constructed upon pair- and triplet-potential energy parameters is certain to satisfy the assumptions made in deriving Eqs. (12) and (13). The present technique also allows us to calculate pair- and triplet-potential parameters of substances for which these data are not available in the literature. This conclusion is especially significant due to the new developments in the equilibrium statistical thermodynamics of liquids, in which it is necessary to consider both the two- and three-body potential energy functions [24, 25]. Also, the liquid state data that are needed in utilizing the present technique for calculation of potential energy parameters of complex molecules are easier to produce in the laboratory than the gas-phase thermophysical data of complex and large molecules.

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