A SELF-CONSISTENT TECHNIQUE FOR THE CONSTRUCTION AND EVALUATION OF THE THREE-PARAMETER CORRESPONDING STATES PRINCIPLES

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Abstract A self-consistent approach for the evaluation of the existing three-parameter corresponding states principles of non-polar fluids and the calculation of the corresponding states parameters is presented. This self consistent approach is based upon the assumption that the contribution of the third parameter to the thermophysical properties is much smaller than the contributions of the first two parameters which are generally the molecular energy and length parameters, ε/k and σ. Based on this self-consistent approach several existing three-parameter corresponding states principles of non-polar fluids are evaluated. It is shown that the three-parameter corresponding states principle based on the two-and three-body intermolecular potential parameters effectively satisfies the requirements of the present self-consistent technique. The corresponding states principle parameters of normal hydrocarbons are calculated through the present technique and they are reported here.

Key Words Self-Consistent Technique, Three-Parameter Corresponding States Principles., Lennard Jones (n-m), Triple Interac-tion, Reduced Temperature and Pressure, Potential Function.

چکیده نظریه ای موزون برای ارزیابی اصل حالات متناظر با سه پارامتر برای سیالات غیرقطبی و طریقه محاسبه پارامترهای حالات متناظر ارائه گردیده است. این دیدگاه موزون با توجه به این حقیقت که سهم مشارکت پارامتر سوم در تعیین خواص فیزیکی بسیار کوچکتر از دو پارامتر انرژی و بعد مولکولی یعنیε/k و σ می باشد بنا گردیده است. بر اساس این نظریه چندین اصل حالات متناظر با سه پارامتر که برای سیالات غیر قطبی موجود می باشد مورد آزمایش قرار گرفته است. اصل حالات متناظر که متشکل از دو و سه پارامتر پتانسیل بین مولکولی بوجود آمده باشد بطور مؤثری نیاز این تکنیک موزون را برطرف می نماید. سه پارامتر اصل حالات متناظر ئیدروکربن های نرمال با این روش تعیین و گزارش گردیده اند.

INTRODUCTION

The corresponding states principle (C.S.P.) has proved to be of great value in chemical engineering practice for the correlation and prediction of, not only the thermodynamic properties, but also in the correlation and prediction of the transport properties of substances [1]. Arguments of C.S.P. provide practical methods for making use of measured thermodynamic or transport properties of one reference substance under conditions where no experimental data may exist and where no satisfactory theoretical treatment may be possible.

Since the classical deduction of the theory of C.S.P. by Vander Waals by means of his equation of state, modern statistical mechanical theories have proven the theory rigorously without reliance on any particular form of equation of state but strictly from the consideration of molecular intractions. The theory of C.S.P. is expressed by the generalized potential function as follows [2]:

$$\varepsilon / \varepsilon_0 = f(r/\sigma_i) \qquad (1)$$

where ε_0 and σ_i are an energy and a distance

characteristic of the potential energy, respectively and f is a function which is the same for all molecules which obey the law of corresponding states. Derivation of Equation 1 presupposes that the molecular force fields are spherically symmetrical and therefore the theory of C.S.P. based on Equation 1 is limited to simple molecules whose energies of rateration can be adequately described in terms of a function using only two parameters. Since only two independent molecular parameters are involved in the above derivation, this is called two-parameter corresponding state theory. While there are satisfactory relations available for two-parameter potential function, f, such as the Lennard-Jones (n-m) potential function:

$$\varepsilon/\varepsilon_0 = \frac{n}{(n-m)}\left(\frac{n}{m}\right)^{\frac{m}{n-m}}\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right] \qquad (2)$$

there is no satisfactory functional form available at the present time for the three-parameter potential function, but it is believed that the leading term in the triple interaction potential is the Axilord and Teller [3,4] form which, for a pure substance, the third parameter υ is in the following form:

$$\upsilon = \frac{9}{16} I \alpha^3 \qquad (3)$$

where I is the ionization potential and α is the polarizability of a molecule of the substance under consideration.

Based on two-parameter C.S.P., the following reduced relationships for the thermodynamic and transport properties of simple substances can be derived.

$$\bar{V} = \bar{V}(\bar{T}, \bar{P}) = \frac{V}{N\sigma^3} \qquad (4)$$

$$\bar{D} = \bar{D}(\bar{T}, \bar{V}) = \bar{D}(k/\varepsilon, \sigma^3/\varepsilon) = \frac{D}{\sigma}(m/\varepsilon) \qquad (5)$$

$$\bar{K} = K(m/4)^{1/2}.\frac{\sigma^2}{k} \qquad (6)$$

where $\bar{T} = \frac{kT}{\varepsilon}$ and $\bar{P} = \frac{P\sigma^3}{\varepsilon}$ are reduced temperature and pressure, respectively.

Extensive computations and research on the two-parameter corresponding states principle [5-8] have indicated that this principle, while it may be adequate for the C.S.P. treatment of the thermophysical properties of substances with simple non-polar spherical molecules, it is unsatisfactory for the C.S.P. treatment of non-polar substances with non-spherical molecules. This observation has motivated investigators to present a third parameter in the C.S.P. treatment of non-polar substances with complicated molecules and as a result the development of the three-parameter corresponding states principle.

In the development of three-parameter C.S.P.'s, the choice for the first two parameters are always molecular energy and size parameters, ε and σ(or critical temperature and volume, T_c and V_c), while the choice for the third parameter has been rather arbitrary. The choice for the third parameter may be based on either empirical or statistical mechanical grounds.

A number of three-parameter C.S.P.'s have been suggested by different investigators in which the choice for the third parameters has been based on empirical grounds [9-11]. Between these three-parameters C.S.P.'s, the one due to Pitzer and his colleagues [11] has been more successful and applicable in the C.S.P. treatment of polyatomic non-polar fluids. According to Pitzer [12] the thermodynamic and transport properties of non-polar substances with complicated molecules can be generalized in the reduced form by the application of T_c, V_c and ω as the corresponding states parameters, where ω is called the acentric factor and it is defined by the followng relation:

$$\omega = -(\text{Log } P^s/P_c)_{Tr=0.7} - 1 \qquad (7)$$

In order to develop a three-parameter C.S.P consistent with the principles of classical statistical

mechanics one should choose three parameters from the intermolecular potential parameters as the corresponding states parameters.

In three-parameter theory of C.S.P., Equation 1 still applies but the generalized function f is now different for each class. The class must be designated by some third parameter.

From the above presentation and discussion on the available three-parameter C.S.P.'s, it is evident that always the choices for the first two corresponding states parameters are clearly the energy parameter ε and the length parameter σ, appearing in the two-body interaction potential energy (or T_c and V_c which, in a sense, are proportional to ε/k and $N_0\sigma^3$, respectively). The choice of the third parameter has been different for different cases which are presented above, and also the computation of the third parameter has been rather difficult or impossible due to the lack of proper molecular or macroscopic data. As a result, the choice and the computation of the third parameter in the three-parameter C.S.P.'s have alwalys been the principle barrier in the extensive application of this principle in chemical engineering practice.

In the present work a self-consistent technique is introduced through which one can calculate the three corresponding states parameters of pure substances with a knowledge of the C.S.P. parameters of two reference substances. This technique is self-consistent in the sense that it satisfies the consistency conditions on which the thermophysical properties are bound.

THE SELF-CONSISTENT TECHNIQUE FOR COMPUTATION OF C.S.P. PARAMETERS

According to the three-parameter C.S.P. the thermophysical of pure, non-polar, substances are defined as

$$\overline{X}= \overline{X}(\overline{T}, \overline{P}, \overline{\alpha}) \qquad (8)$$

For the computation and evaluation of the three C.S.P. parameters by the present technique one should have in hand, at least, two different zero-pressure thermophysical property data of a substance with the unknown C.S.P. parameters and the same kind of zero-pressure data for two reference substances for which the C.S.P. parameters are known. In the present report the zero-pressure liquid specific volumes and the zero-pressure liquid viscosities are chosen as the two required thermophysical property data for the computation of the C.S.P. parameters of normal alkane hydrocarbons and methane and neo-pentane are chosen as the two required reference substances.

At zero-pressure condition, Equation 8 can be written in the following form:

$$\overline{X}= \overline{X}(\overline{T}, \overline{\alpha}) \qquad (9)$$

for

$$\overline{P} = P = 0.$$

Generally, the zero-pressure liquid thermophysical properties data can be generated by the linear extrapolation of the low-pressure liquid data to zero pressure. By the consideration of Equation 9 the following relations can be written between the properties of the substance with the unknown C.S.P. parameters and one of the reference substances with the known C.S.P. parameters both at zero-pressure condition.

$$\frac{\overline{X}(\overline{T}, \overline{\alpha})}{\overline{X}_0(\overline{T}_0, \alpha_0)} = \frac{X(T)}{X_0(T_0)} \cdot \frac{Q_0}{Q} \qquad (10)$$

where

$$\frac{\overline{T}}{\overline{T}_0} = \left(\frac{\varepsilon_0}{\varepsilon}\right) \cdot \left(\frac{T}{T_0}\right) \qquad (11)$$

and Q and Q_0 are coefficients depending on the potential function parameter of the physical property and it is given in Table 1. In the above relations, X(T),

and $X_0(T_0)$ are the zero-pressure empirical correlations of two substances as functions of absolute temperatures T and T_0.

The success of the two-parameter C.S.P. in the case of simple fluids and the partial success of this principle in the case of complex fluids is an indication of the smaller role of the third parameter $\bar{\alpha}$ in the three-parameter C.S.P. treatment of the thermophysical properties of substances as compared to the roles of the first two parameters ε/k and σ. One may expand Equation 9 in the following form:

$$\bar{X}(T,\bar{\alpha}) = \bar{X}(\bar{T},\bar{\alpha}_0) + (\bar{\alpha}-\bar{\alpha}_0)\left(\frac{\partial \bar{X}}{\partial \bar{\alpha}}\right)_{\bar{\alpha}=\bar{\alpha}_0} \qquad (12)$$

The above relations are valid as long as $(\bar{\alpha}-\bar{\alpha}_0)$ is small enough such that one can neglect the higher terms expansion. Now if we define

$$X_1 \equiv \left(\frac{\partial \bar{X}}{\partial \bar{\alpha}}\right)_{\bar{\alpha}=\bar{\alpha}_0} \qquad (13)$$

by replacing Equation 12 into Equation 10 we get the followng relation:

$$\frac{\bar{X}(\bar{T},\bar{\alpha})}{\bar{X}_0(\bar{T},\bar{\alpha}_0)} = \frac{\bar{X}(\bar{T},\bar{\alpha}_0) + (\bar{\alpha}-\bar{\alpha}_0)X_1(\bar{T},\bar{\alpha}_0)}{\bar{X}_0(\bar{T},\bar{\alpha}_0)} = \frac{X(T)}{X_0(T_0)} \cdot \frac{Q_0}{Q} \qquad (14)$$

It should be again mentioned that the above relations hold as long as the absolute pressure is equal to zero. In order to simplify the above equation, we choose $\bar{T}$ and $\bar{T}_0$ such that $\bar{T} = \bar{T}_0$, that is

$$\left(\frac{T}{T_0}\right)\cdot\left(\frac{\varepsilon_0}{\varepsilon}\right) = 1.$$

When $\bar{T} = \bar{T}_0$ the following equality wil hold:

$$\bar{X}(\bar{T},\bar{\alpha}_0) = \bar{X}_0(\bar{T}_0,\bar{\alpha}_0)$$

and

$$X_1(\bar{T},\bar{\alpha}_0) = X_{10}(\bar{T}_0,\bar{\alpha}_0)$$

and as a result Equation 10, will simplify to the following relation:

$$1 + (\bar{\alpha}-\bar{\alpha}_0)\frac{X_{10}(\bar{T}_0,\bar{\alpha})}{\bar{X}_0(\bar{T}_0,\bar{\alpha}_0)} = \frac{X(T)}{X_0(T_0)}\cdot\frac{Q_0}{Q} \qquad (15)$$

With the knowledge of the values of T_0 and T (for which $\bar{T} = \bar{T}_0$) one should have available the values Q, Q_0 and $\bar{\alpha}_0$ of the reference system in hand and also the empirical correlations for X(T), $X_0(T_0)$, $\bar{X}_0(\bar{T}_0,\bar{\alpha}_0)$, $X_{10}(T_0,\bar{\alpha}_0)$, should be available. The empirical correlations for X(T) and $X_0(T_0)$ can be obtained by the correlation of the isobaric (zero pressure) data of molar physical property of the substances under consideration. Since $\bar{\alpha}_0$ is a constant, we do not need to know the functional dependence of $\bar{X}_0$ and X_{10}, on $\bar{\alpha}_0$ in the present computations, and it is enough to have available the functional relation between these variables and $\bar{T}_0$ only. With the availability of the empirical correlations for $X_0(T_0)$ the functional relation for $\bar{X}_0(\bar{T}_0)$ will be as follows:

$$\bar{X}_0(\bar{T}_0,\bar{\alpha}_0) = \frac{X_0(k\bar{T}_0/\varepsilon_0,\ \varepsilon_0/k)}{Q_0} = \frac{X_0(\bar{T}_0,\ \varepsilon_0/k)}{Q_0} \qquad (16)$$

Similarly, with the availability of the empirical correlations for $X_{02}(T_{02})$ for the second reference substance, we will be able to derive the relations for $\bar{X}_{02}(\bar{T}_{02})$. For obtaining the functional form for $\bar{X}_0(\bar{T}_0)$ we use the following relation:

$$\bar{X}_0(\bar{T}_0,\bar{\alpha}_0) = \frac{\bar{X}_{01}(\bar{T}_0,\bar{\alpha}_0) - \bar{X}_{02}(\bar{T}_0,\bar{\alpha}_{02})}{\bar{\alpha}_0 - \bar{\alpha}_{02}} \qquad (17)$$

By the knowledge of the empirical correlations for X (T), $X_0(T_0)$, $X_0(\bar{T}_0)\,\bar{X}_0(\bar{T}_0,\bar{\alpha}_0)$ and

$X_{10}(\bar{T}_0, \bar{\alpha}_0)$, as presented above, and the knowledge of T and T_0 (for which $\bar{T} = \bar{T}_0$) one will be able to use Equation 15, in order to calculate the values of $\varepsilon/\varepsilon_0$, σ/σ_0, and $\bar{\alpha} - \bar{\alpha}_0$ for the choice of T and T_0 (for which $\bar{T} = \bar{T}_0$) the following method may be used.

For the computation of T and T_0 for which $\bar{T} = \bar{T}_0$, one can use the following identities:

$$\frac{\bar{T}}{\bar{X}} \cdot \left(\frac{\partial \bar{X}}{\partial \bar{T}}\right) = \frac{T}{X} \cdot \left(\frac{\partial X}{\partial T}\right) \qquad (18)$$

by writing the above identities, once for the substance with the unknown C.S.P. parameters and once for one of the reference substances (with the known C.S.P. parameters), and dividing the relations of the former by the relations of the latter, one will derive the following relations:

$$\frac{\bar{X}_0(\bar{T}_0, \bar{\alpha}_0)}{\bar{X}(\bar{T}_0, \bar{\alpha})} \cdot \frac{\dfrac{\partial \bar{X}(\bar{T}_0, \bar{\alpha})}{\partial T_0}}{\dfrac{\partial \bar{X}_0(\bar{T}_0, \bar{\alpha}_0)}{\partial \bar{T}_0}} = \left(\frac{T}{T_0}\right) \cdot \frac{X_0(T_0)}{X(T)} \cdot \frac{\dfrac{\partial X(T)}{\partial T}}{\dfrac{\partial X_0(T_0)}{\partial T_0}} \qquad (19)$$

by substituting Equations 12 for $\bar{X}(\bar{T}_0, \bar{\alpha})$ in the above equation, we get the following relation:

$$\frac{1 + (\bar{\alpha} - \bar{\alpha}_0) \cdot \dfrac{\partial \bar{X}_0(T, \bar{X}_0)}{\partial \bar{T}_0}}{1 + (\bar{\alpha} - \bar{\alpha}_0) \cdot X_0(\bar{T}_0, \bar{\alpha}_0)} = \left(\frac{T}{T_0}\right) \left(\frac{X_0(T_0)}{X(T)}\right) \cdot \frac{\dfrac{\partial X(T)}{\partial T}}{\dfrac{\partial X_0(T_0)}{\partial T_0}} \qquad (20)$$

The above equation can be joined with Equation 15 in order to calculate $\varepsilon/\varepsilon_0$, σ/σ_0, $\bar{\alpha} - \bar{\alpha}_0$, and T, T_0 for which $\bar{T} = \bar{T}_0$.

In the technique which is presented above for the calculation of the three parameters of a three- parameter C.S.P. it is necessary to have empirical correlations for the zero-pressure liquid molar volumes and zero-pressure liquid molar viscosities (or any other two properties) of the substances under consideration as functions of temperature. The substances of interest at the present time are normal alkane hydrocarbons. With the choice of normal alkanes, we will be able to compare the results of the present calculations with the already available corresponding states parameters of these substances, and we will be able, also, to observe the effect of the increase in the size of the molecules (from one homolog to the other) on the versatility of the present technique. For liquid normal alkanes the low-pressure liquid molar volume and viscosity data are available [13]. These data for liquid normal alkanes are extrapolated to zero-pressure and the resulting zero-pressure data are fitted to the follwoing polynomials for each hydrocarbon by the method of linear least squares

$$X(T) = \sum_{i=o}^{m} A_i T^i \qquad (21)$$

The number of terms of the above power series are chosen for which there are minimum root-mean-square deviations between the data and the correlations. In Tables 2 and 3 the values of coefficients A_i and B_i appearing in correlations (21) for normal alkanes from CH_4 to $C_{20}H_{42}$ are reported. Also reported in these tables are the percentage root-mean-square (R.M.S.) deviations, percentage maximum errors and the number of data points for each property of the hydrocarbons under consideration. As it is shown in these tables, the percentage R.M.S.'s and the percentage maximum errors of the correlations with respect to the experimental data are quite small and as a result the correlations are quite accurate for the temperature ranges under consideration. It is also shown in these tables that the maximum number of terms necessary in order to achieve the best correlations for the properties considered do not exceed four for the hydrocarbons considered.

RESULTS AND DISCUSSION

The present self-consistent technique allows us to compute the corresponding states parameters of substances based on any three-parameter C.S.P. provided that the parameters for two reference substances are already available. It should be pointed out that the present technique is valid as long as the contribution of the third parameter to the thermophysical properties is smaller than the contributions of the first two parameters.

The present self-consistent technique is utilized here in order to compute the corresponding states parameters of the normal alkane hydrocarbons (from CH_4 upto n-$C_{20}H_{42}$) for the different three-parameter C.S.P.'s presented above. In the computations performed here methane, CH_4, and neo-pentane, $C(CH_3)_4$, are chosen as the two required reference substances for which the corresponding states parameters are assumed to be known based on every C.S.P. and these parameters are reported in Table 4.

In Table 5 values of V_{cn}/V_{cl}, T_{cn}/T_{cl} and $\omega_n-\omega_l$ as calculated by the present technique (with methane as the first reference substance and neo-pentane as the second reference substance) are compared with the values calculated by Pitzer's technique and reported in Reference 14. Subscript *n* in this table and the other tables which will follow standards for the normal alkane hydrocarbon with *n* carbon atoms. Table 4 indicates that the present technique is not applicable for the prediction of the parameters of the Pitzer's three-parameter C.S.P. This is mainly because $\omega_n-\omega_l$ is not small enough such that one can neglect the terms of the order $(\omega_n-\omega_l)^2$ and higher in the expansions of the thermophysical properties with respect to $(\omega_n-\omega_l)$ as shown by Equation 9. This observation is negating the understanding that generally the thermophysical properties of polyatomic fluids could be represented to the first order with respect to ω, by the following equation:

$$X = X_{\omega=0} + \omega\left(\frac{\partial X}{\partial \omega}\right)_{\omega=0}$$

In Table 6, values of σ_n/σ_1, $\varepsilon_n/\varepsilon_1$, α_n^*- α_1^* for Kihara potential as calculated by the present technique (with methane as the first and neo-pentane as the second reference system) are compared with the values calculated based on the second virial coefficient data. Table 6 indicates that the present technique is not applicable for the prediction of the parameters of the Kihara three-parameter C.S.P., due to largeness of a_n^*-a_1^*, and as a result the invalidity of trucated expansions (9) for this corresponding states principle.

In Table 8, values of σ_n/σ_1, $\varepsilon_n/\varepsilon_1$ and υ_n as calculated by the present technique (with methane and neo-pentane as the reference systems) are compared with the reported values of σ_n/σ_1 and $\varepsilon_n/\varepsilon_1$ in the literature and the values of υ_n as calculated through Equation 4 and reported in Table 7, respectively. The reported values of σ_n/σ_1 and $\varepsilon_n/\varepsilon_1$ are for the Lennard-Jones (12-6) potential function and they are based on both the second virial coefficient and gas viscosity data. The values of σ and ε chosen for the two reference substances, methane and neo-pentane, are based on the gas viscosity data [15]. Table 7 indicates that the parameters of the C.S.P. based on the two-and three-body potential functions can be calcualted satisfactorily by the present technique. The small deviations of the predicted results from the known values of C.S.P. parameters in Table 7 could be due to, i) inaccuracies in the second virial coefficient and viscosity data for the case of $\varepsilon_n/\varepsilon_1$ and σ_n/σ_1, ii) inaccuracies in Equation 4 which are in reality approximations based on quantum mechanics, or iii) inaccuracies in the accepted values of the corresponding states parameters for the reference substances, methane and neo-pentane. Practically, the present self-consistent technique is applicable for the predication of the three corresponding states parameters of substances (based on the two- and three-body

potential functions) provided that the corresponding states parameters for the reference substances are known. In Table 9 the values of σ_n/σ_1 and $\varepsilon_n/\varepsilon_1$, for the Lennard-Jones (12-6) potential function, and υ_n^*, for Axilord-Teller three-body potential function, for normal alkanes (CH_4 to n-$C_{20}H_{42}$) as calculated by the present technique are tabulated. The experimental and calculated values of σ_n/σ_1, $\varepsilon_n/\varepsilon_1$ and υ_n are also reported on Figures 1, 2 and 3, respectively. Also reported on Figures 1 and 2 are the values of σ_n/σ_1 and $\varepsilon_n/\varepsilon_1$ as calculated through the corresponding states theory of polysegmented molecules developed by Hermsen and Prausnitz[16].

Based on the above observations it is clear that the present self-consistent technique enables us to compute the potential parameters of two-and three-body potential functions of the substances for which these potential parameters are not available. This is

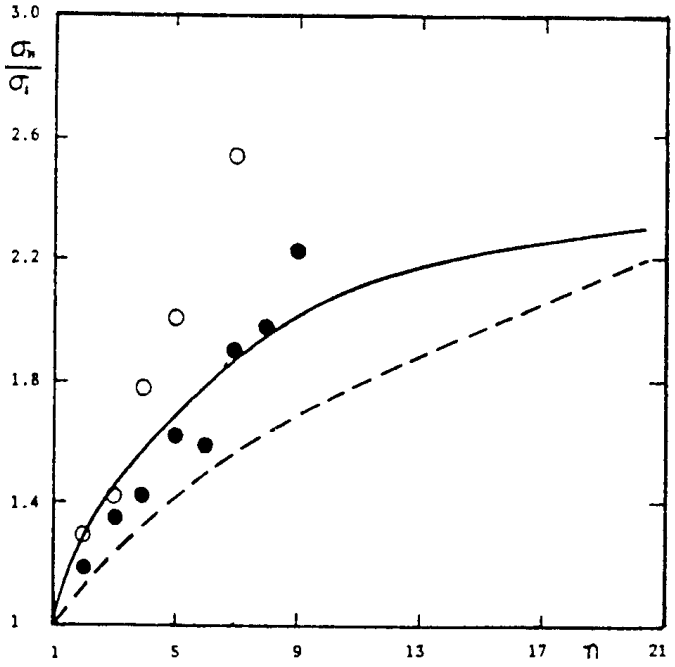

Figure 1. Values of σ_n/σ_1, the ratio of Lennard-Jones (12-6) parameters of normal alkanes with *n* carbon atoms to that of methane, versus *n*, the number of carbond atoms in the normal alkanes. The dashed line is the result of the corresponding states principle of the polysegmented molecules developed by Hermsen and Prausmitz[16]. The solid line is the result of the present self-consistent technique. The solid circles are the values based on the gas viscosity data and the open circles are the values based on the second virial coefficient data.

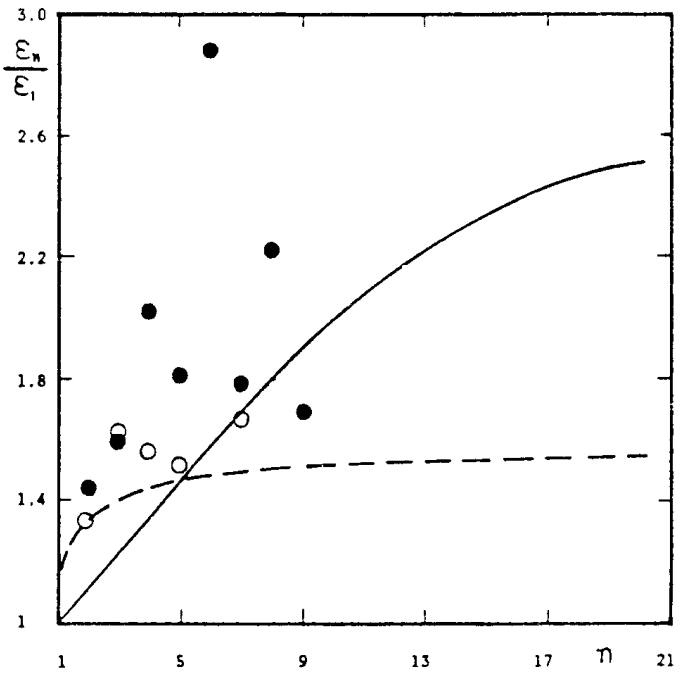

Figure 2. Values of $\varepsilon_n/\varepsilon_1$, the ratio of Lennard-Jones (12-6) energy parameters of normal alkanes with *n* carbon atoms to that of methane, versus *n*, the number of carbon atoms in the normal alkanes. The dashed line is the result of the corresponding states principle of the polysegmented molecules developed by Hermsen and Prausmitz[16]. The solid line is the result of the present self-consistent technique. The solid circles are the values based on the gas viscosity data and the open circles are the values based on the second virial coefficient data.

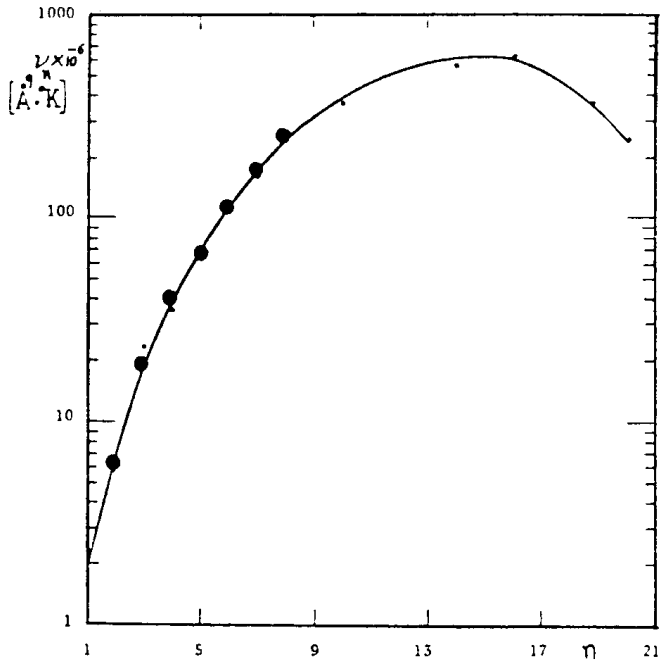

Figure 3. Values of υ_n the Axilord-Teller intermolecular potential energy parameter of normal alkanes with *n* carbon atoms versus *n*, the number of carbon atoms in the normal alkanes. The solid circles are the values calculated through Equation 3 and the solid line is the result of the present self-consistent technique.

specifically significant due to the new developments in the perturbation equations of state of fluids in which both the two and three-body potential functions are considered [21]. Also the abundance of zero pressure thermophysical property data for different polyatomic nonpolar fluids makes it possible to compute readily these corresponding states parameters through the present self-consistent technique.

NOMENCLATURE

a	Kihara potential spherical core radius
A_i	Coefficients in Equation 44
B_i	Coefficients in Equation 45
D	Self-diffusion coefficient
I	Molecular ionization potential
k	Boltzmann constant
K	Thermal conductivity
m	Molecular mass, coefficient in Equation 16
n	Coefficient in Equation 16
N	Number of molecules
P	Pressure
r	Intermolecular distance
T	Temperature

Greek Symbols

α	Molecular polarizability
$\bar{\alpha} = \omega$	for Pitzer three-parameter C.S.P.
$\bar{\alpha}=a^*=\frac{a}{(\sigma-a)}$	for Kihara three-parameter C.S.P.
$\bar{\alpha} = \upsilon^* = \frac{\upsilon}{\sigma^9\,\varepsilon}$	for Axillord-Teller potential function
μ	Viscosity
υ	Axillord-Teller intermolecular energy parameter
σ	Pair-intermolecular length parameter
ω	Accentric factor

Subscripts

c	Critical
i	Molecule i, ith order term
n	Number of carbon atoms in a normal alkane
01	First reference fluid
02	Second reference fluid
-	Dimensionless
=	Dimensionless derivative
*	Dimensionless

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TABLE 1

Transport Proerty	Q	Q_0
$\bar{D}$	$\sigma(\frac{\varepsilon}{m})^{\frac{1}{2}}$	$\sigma_0(\frac{\varepsilon_0}{m})^{\frac{1}{2}}$
$\bar{\mu}$	$\frac{(m\varepsilon)^{\frac{1}{2}}}{\sigma}$	$\frac{(m_0\varepsilon_0)^{\frac{1}{2}}}{\sigma_0}$
$\bar{K}$	$(\frac{\varepsilon}{m})^{\frac{1}{2}}.\frac{1}{k\sigma^2}$	$(\frac{\varepsilon_0}{m_0})^{\frac{1}{2}}.\frac{1}{k_0\sigma_0}$
$\bar{P}$	$\frac{\varepsilon}{\sigma^3}$	$\frac{\varepsilon_0}{\sigma_0^3}$
$\bar{V}$	$N\sigma^3$	$N_0\sigma_0^3$

TABLE 2. A_i- Coefficients Appearing in the Correlation of Zero-Pressure Liquid Specific Volumes of Hydrocarbons with Respect to Temperature as Shown by Equation 21

Compound	A_0	$A_1\times 10$	$A_2\times 10^4$	$A_3\times 10^6$	$A_4\times 10^8$	%R.M.S.	%Maximum Error	Number of Data Points
CH_4	30.80	-0.025	5.859	0.000	0.000	0.001	0.019	9
C_2H_6	-80.23	31.51	-255.1	67.26	0.000	0.031	0.311	19
C_3H_8	52.96	1.001	-2.637	1.121	0.000	0.001	0.014	39
n-C_4H_{10}	106.1	-7.417	62.80	-20.33	2.493	0.001	0.012	30
n-C_5H_{12}	72.94	2.067	-5.500	1.106	0.014	0.001	0.474	31
n-C_6H_{14}	84.63	2.409	-6.679	1.295	0.000	0.002	0.150	31
n-C_7H_{16}	98.98	2.248	-5.032	0.981	0.000	0.000	0.012	35
n-C_8H_{18}	15.28	-3.578	26.63	-6.328	61.08	0.000	0.092	34
n-C_9H_{20}	111.8	3.702	-8.563	1.245	0.000	0.000	0.111	21
n-$C_{10}H_{22}$	173.2	-2.437	21.23	-4.910	46.51	0.000	0.048	21
n-$C_{11}H_{24}$	124.7	5.072	-11.62	1.493	0.000	0.000	0.147	24
n-$C_{12}H_{26}$	115.4	7.041	-16.60	1.921	0.000	0.001	0.512	24
n-$C_{13}H_{28}$	333.0	-15.23	73.73	-14.00	1.033	0.000	0.279	26
n-$C_{14}H_{30}$	132.4	7.823	-17.51	1.934	0.000	0.001	0.368	25
n-$C_{15}H_{32}$	310.6	-8.747	44.47	-8.091	59.47	0.000	0.210	27
n-$C_{16}H_{34}$	165.8	7.271	-14.91	1.654	0.000	0.000	0.336	28
n-$C_{17}H_{36}$	362.0	-10.46	49.00	-8.322	57.18	0.000	0.224	29
n-$C_{18}H_{38}$	506.8	-23.24	95.48	-15.62	99.32	0.001	0.603	31
n-$C_{19}H_{40}$	530.1	-23.94	97.59	-15.80	99.29	0.001	0.495	32
n-$C_{20}H_{42}$	536.5	-22.98	93.76	-15.05	94.00	0.000	0.449	33

TABLE 3. B_i- Coefficients Appearing in the Correlation of Zero-Presure Liquid Viscosities of Hydrocarbons with Respect to Temperature as Shown by Equation 21

Compound	B_0	$B_1 \times 10^{-3}$	$B_2 \times 10^{5}$	$B_3 \times 10^{7}$	$B_4 \times 10^{9}$	%R.M.S.	%Maximum Error	Number of Data Points
CH_4	-2.896	-0.061	0.163	0.000	0.000	0.001	0.002	6
C_2H_6	-5.437	1.083	-0.995	0.446	0.000	0.057	0.005	19
C_3H_8	-5.692	1.621	-2.229	1.803	-0.493	0.014	0.006	31
n-C_4H_{10}	-5.106	1.344	-1.295	0.715	0.000	0.001	0.004	19
n-C_5H_{12}	-6.012	2.446	-4.940	5.667	-2.097	0.007	0.005	34
n-C_6H_{14}	-5.289	1.911	-2.955	2.619	0.000	0.017	0.009	34
n-C_7H_{16}	-5.418	2.149	-3.600	3.523	0.000	0.004	0.003	34
n-C_8H_{18}	-16.01	14.28	-54.19	96.30	-62.47	0.070	0.262	37
n-C_9H_{20}	-5.911	2.824	-5.630	6.286	0.000	0.005	0.004	42
n-$C_{10}H_{22}$	-8.934	6.796	-24.15	44.57	-28.51	0.005	0.002	42
n-$C_{11}H_{24}$	-6.422	3.567	-8.161	9.873	0.000	0.004	0.006	45
n-$C_{12}H_{26}$	-9.543	8.069	-31.38	62.56	-43.50	0.014	0.004	46
n-$C_{13}H_{28}$	-6.934	4.353	-11.07	14.11	0.000	0.007	0.011	49
n-$C_{14}H_{30}$	-7.077	4.635	-12.23	15.98	0.000	0.020	0.009	51
n-$C_{15}H_{32}$	-7.446	5.147	-14.18	18.75	0.000	0.013	0.087	53
n-$C_{16}H_{34}$	-7.126	4.938	-13.68	18.78	0.000	0.006	0.002	54
n-$C_{17}H_{36}$	-13.00	12.90	-48.23	67.25	0.000	0.135	0.244	57
n-$C_{18}H_{38}$	-7.084	5.116	-14.68	21.03	0.000	0.014	0.021	57
n-$C_{19}H_{40}$	-10.55	11.21	-53.40	128.2	-108.4	0.018	0.010	59
n-$C_{20}H_{42}$	-9.323	9.258	-41.38	96.13	-76.23	0.009	0.029	62

TABLE 4. Corresponding States Parameters of Methane and Neo-Pentane

Methane	Neo-pentane
Pitzer Corresponding States Parameters[14]	
V_c = 99.5 (cc/g-mole) T_c = 190.7 (°k) ω= 0.013	V_c = 303.0 (cc/g-mole) T_c = 433.8 (°k) ω= 0.195
Kihara Corresponding States Parameters [14]	
σ= 3.565 (Å) ε/k= 227.13 (°K) $a^* = \frac{a}{\sigma - a} = 0.283$	σ= 5.762 (Å) ε/k= 557.75 (°K) $a^* = \frac{a}{\sigma - a} = 0.551$
Two-and Three-Body Corresponding States Parameters	
Lennard-Jones (12-6) Potential Parameters [15]	
σ= 3.774 ε/k= 143.81	σ= 6.520 ε/k= 183.02
Three-Body Potential Parameter (See Table 7)	
υ = 166.72 x10^4 (Å. °K)	υ = 6982.0 x 10^4 (Å.°K)

TABLE 5. Values of V_{cn}/V_{c1}, T_{cn}/T_{c1}, and $\omega_n-\omega_1$ Reported in Reference 14 as Compared with the Results of the Calculations Based on the Present Self-Consistent Approach

Compound	V_{cn}/V_{c1}		T_{cn}/T_{c1}		$\omega_n-\omega_1$	
	Reference 14	Presen technique	Reference 14	Present technique	Reference 14	Present technique
CH_4	1.000	1.000	1.000	1.000	0.000	0.000
C_2H_6	1.487	*	1.601	*	0.092	*
C_3H_8	2.010	*	1.940	*	0.139	*
n-C_4H_{10}	2.563	4.213	2.230	3.988	0.188	0.513
n-C_5H_{12}	3.126	5.792	2.464	4.238	0.239	0.594
n-C_6H_{14}	3.698	6.268	2.666	5.932	0.277	0.651
n-C_7H_{16}	4.281	7.011	2.833	6.172	0.339	0.783

*Calculations did not converge to a meaningful solution

TABLE 6. Values of σ_n/σ_1, $\varepsilon_n/\varepsilon_1$, and $a^*_n-a^*_1$ for the Kihara Potential Reported in the Literature as Compared with the Calculations Based on the Present Self-Consistent Approach

Compound	σ_n/σ_1		$\varepsilon_n/\varepsilon_1$		$a^*_n-a^*_1$	
	Reference 18	Present technique	Reference 18	Present technique	Reference 18	Present technique
CH_4	1.0000	1.0000	1.0000	1.0000	0.000	0.000
C_2H_6	0.9829	1.6731	2.1868	2.7672	0.076	0.699
C_3H_8	1.2934	2.3681	2.2097	3.5530	0.187	0.927
n-C_4H_{10}	1.3231	2.7831	3.0870	3.6941	0.378	1.143
n-C_5H_{12}	1.4107	3.0141	3.6887	4.1046	0.535	1.536
n-C_7H_{16}	1.2477	**	5.4502	**	0.373	**

$$a^*_n - a^*_1 = \frac{a_n}{\sigma_n - a_n} - \frac{a_1}{\sigma_n - a_1}$$

**Calculations did not converge to a meaningful solution

TABLE 7. Values of υ, the Coefficient of Triple-Dipole Potential Calculated through Equation 3

Compound	$\alpha \times 10^{24}$ (cm^3/mole) (Reference 19)	I (ev) (Reference 19)	$\upsilon \times 10^4$ (Å . °K)
CH_4	2.699	12.99	166.72
C_2H_6	4.326	11.65	615.68
C_3H_8	6.31	11.21	1838.5
n-C_4H_{10}	8.30	10.80	4031.2
n-C_5H_{12}	10.00	10.55	6886.9
n-C_6H_{14}	11.81	10.48	11269.
n-C_7H_{16}	13.69	10.35	17335.
n-C_8H_{18}	15.50	10.24	24892.

Table 8. Values of σ_n/σ_l and $\varepsilon_n/\varepsilon_l$ for the Lennard-Jones (12-6) Potential Function and υ_n of the Triple-Dipole Potential Function Calculated by the Present Self-Consistent Technique as Compared with the Experimental Data

Compound	σ_n/σ_l		$\varepsilon_n/\varepsilon_l$		$\upsilon \times 10^{-4}$ (Å . °K)	
	experimental	present technique	experimental	present technique	experimental (d)	present technique
CH_4	1.0000	1.000[e]	1.000	1.000[e]	166.72	166.72[e]
C_2H_6	1.187[a] 1.302[b]	1.310	1.449[a] 1.359[b]	1.135	615.68	570.65
C_3H_8	1.361[a] 1.424[b]	1.451	1.599[a] 1.633[b]	1.236	1838.5	2312.3
n-C_4H_{10}	1.415[a] 1.783[b]	1.572	2.154[a] 1.566[b]	1.369	4031.2	3568.0
n-C_5H_{12}	1.617[a] 2.130[b]	1.679	1.813[a] 1.524[b]	1.479	6886.9	6907.8
n-C_6H_{14}	1.566[c]	1.780	2.872[c]	1.581	11269.	11967.
n-C_7H_{16}	1.893[a] 2.549[b]	1.852	1.785[a] 1.676[b]	1.680	17335.	16402.
n-C_8H_{18}	1.974[c]	1.938	2.225[c]	1.810	24892.	26013.
n-C_9H_{20}	2.238[c]	2.051	1.669[c]	1.892		35050.

a) Based on the gas viscosity data (Reference 15)
b) Based on the second virial coefficient data (Reference 15)
c) Based on the gas viscosity data (Reference 20)
d) Taken from Table 7
e) Pre-assumed values

Table 9. Values of σ_n/σ_1 and $\varepsilon_n/\varepsilon_1$ for the Lennard-Jones (12-6) Potential Function and $(\upsilon^*_n - \upsilon^*_1)$ for the Triple-Dipole Potential Function Calculated through the Present Self-Consistent Approach for Normal Alkane Hydrocarbonds

Compound	σ_n/σ_1	$\varepsilon_n/\varepsilon_1$	$\upsilon^*_n - \upsilon^*_1$
CH_4	1.000	1.000	0.0000
C_2H_6	1.310	1.135	-0.0531
C_3H_8	1.451	1.236	-0.0427
n-C_4H_{10}	1.572	1.369	-0.0530
n-C_5H_{12}	1.679	1.479	-0.0532
n-C_6H_{14}	1.780	1.581	-0.0541
n-C_7H_{16}	1.852	1.680	-0.0561
n-C_8H_{18}	1.938	1.810	-0.0565
n-C_9H_{20}	2.051	1.892	-0.0606
n-$C_{10}H_{22}$	2.062	1.941	-0.0610
n-$C_{11}H_{24}$	2.101	2.078	-0.0620
n-$C_{12}H_{26}$	2.148	2.142	-0.0626
n-$C_{13}H_{28}$	2.180	2.201	-0.0635
n-$C_{14}H_{30}$	2.201	2.275	-0.0648
n-$C_{15}H_{32}$	2.220	2.322	-0.0651
n-$C_{16}H_{34}$	2.242	2.381	-0.0661
n-$C_{17}H_{36}$	2.256	2.401	-0.0675
n-$C_{18}H_{38}$	2.271	2.405	-0.0681
n-$C_{19}H_{40}$	2.280	2.481	-0.0696
n-$C_{20}H_{42}$	2.289	2.520	-0.0720

$\upsilon^*_n - \upsilon^*_1 = \upsilon_n / \sigma_n^9 \ \varepsilon_n - \upsilon_1 / \sigma_1^9 \varepsilon_1$