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Statistical thermodynamics of chain molecular fluids: Equation of state parameters for PVT scaling and their group contributions

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STATISTICAL THERMODYNAMICS OF CHAIN MOLECULAR FLUIDS: EQUATION OF STATE PARAMETERS FOR *PVT* SCALING AND THEIR GROUP CONTRIBUTIONS

b y

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STATISTICAL THERMODYNAMICS OF CHAIN MOLECULAR FLUIDS: EQUATION OF STATE PARAMETERS FOR *PVT* SCALING AND THEIR GROUP CONTRIBUTIONS

Abstract

by

UGUR YAHSI

Extensive experimental studies of fluid hydrocarbons in the lubricating range of molar mass have been undertaken sometime ago by American Petroleum Institute Project 42, located in the Departments of Chemistry and Physics at Pennsylvania State University. In these studies systematic structural changes were introduced, so that the equation of state (e.o.s.) as well as the viscosities of linear paraffins, branched hydrocarbons, and various rings attached to *n*-alkanes tails are known. Hence this material became the basis for various semi-empirical or empirical structural correlations. We proceed here with the hole theory of Simha-Somcynsky (SS) which has proven quantitatively successful for low as well as high molar mass system and examine e.o.s. data. We demonstrate the success of the theory and obtain the characteristic volume (υ^*), energy (ε^*) and flexibility (c)

parameters as functions of chain-length for the different structures. For the short chains in question these represent averages over the terminal and internal units. By suitable generalization of the SS theory developed for physical mixtures we decompose these averages into the individual group contributions. The accuracy of the numerical procedures employed is tested by back computations.

Sometime ago A. Bondi developed structural rules for the computation of Van der Waals excluded group volumes. Interesting correlations between these and the above υ^* values, defined for a 6-12 potential, are obtained. In the same way we examine correlations between D. W. Van Krevelen's and P. J. Hoftyzer's cohesive group energies and ε^* values.

In name of Allah (God) Most Gracious and Most Merciful.

" And there is not a single thing but extols His Glory and Praise."

Al Qur'an 17:44

If every particle is not an official of God acting with His permission and under his authority, and if it is not undergoing change within His Knowledge and Power, then every particle must have infinite knowledge and limitless power, it must have eyes that see everything, a face that looks to all things.... Indeed, a particle despite being powerless and lifeless by carrying out its important duties consciously and raising mighty loads bears decisive witness to the existence of the Necessarily-Existent ***One****.*

From the Risale-i Nur Collections

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LIST OF SYMBOLS

$3c$	total number of external degrees of freedom of a molecular chain
ΔV_{max}	maximum error in volume
ΔV_{mean}	average error in volume
ΔV_{std}	standard deviation in volume
e.o.s.	equation of state
ε^* or $<\varepsilon^*>$	average characteristic interaction energy per segment or unit
ε_{ij}^*	interaction energy parameter between ith and jth species
E_o	total interaction energy of the lattice
E_{coh}	cohesive energy
F_{conf}	configurational free energy
$\tilde{F}$	reduced free energy
Φ_{ij}	interaction energy between ith and jth species
g	combinatorial factor
n	number of carbon atoms for a given molecule
N or N_s	total number of molecules
N_h	total number of holes
M_o	molecular mass per segment or unit
M_{rep}	molecular mass of the repeat unit of the n-mer
PVT	pressure-volume-temperature
P	pressure
P^*	characteristic pressure
$\tilde{P}$	reduced pressure
P_1	contact probability of finding a chain internal unit in an occupied cell
P_2	contact probability of finding a chain terminal unit in an occupied cell
P_i	contact probability of finding a chain ith unit in an occupied cell
q_z	total number of contact pairs

q_{iz}	number of intermolecular contact pairs of ith species
s	number of segments per molecule
s_r	number of segments per ring
T	temperature
T^*	characteristic temperature
$\tilde{T}$	reduced temperature
υ^* or $<\upsilon^*>$	average characteristic volume per segment or unit
υ_{ij}^*	repulsive volume parameter between ith and jth species
υ_f	free volume
V	volume
V_w	Van der Waals volume
V^*	characteristic volume
$\tilde{V}$	reduced volume
ω	cell volume
y	fraction of occupied sites
z	coordination number
Z_{conf}	configurational partition function
$< >$	mean value

Universal Constants

N_A	Avagadro number ($6.02\ 10^{23}$ mol^{-1})
R	Universal gas constant (8.314 J/mol·°K)
k	Boltzmann constant ($1.38\ 10^{-23}$ J/°K)

CHAPTER 1

Introduction

There are basic and practical motivations for the study of configurational thermodynamical properties of fluids or amorphous polymers in the melt and glassy state: first as a problem in the statistical mechanics of dense, disordered system and secondly, consider the response of these systems to changes in temperature and pressure in connection with polymer processing. Predictions, based where possible, on theory, thus are highly desirable. Considering all this and in particular the equation of state (e.o.s.) a number of empirical relationships have been developed since Van der Waals first developed a theoretically founded e.o.s.

In the area of *simple* fluids considerable progress has been made in recent years by analytical theories, based on the development of integro-differential equations for the positional distribution functions.[1] Solution of these required closure

approximations. There have also been computer simulations. The distribution function approach has gradually found its uses into the area of chain-molecular fluids. Its primary contribution so far has been the description of structure factors.

An alternative approach has been influenced by the realization of a short range order or a quasi-crystalline structure in liquids. This has let to development of cell theories, originated by Lennard-Jones and Devonshire[2] for rare gas type of fluids. This theory was then extended to fluids with chain-molecular constituents by Prigogine, Mathot and Trappeniers.[3] Applications of the theory to the equation of state of n-paraffins, other hydrocarbons and polymers have been offered.[4-6]

In the cell theory the reference unit, molecule or segment allowed to move, is subject to molecular interactions with its neighbors. However these neighbors are placed into average positions, defined by lattice sites. With these assumptions at hand, it is comparatively convenient to obtain the configurational free energy and thus the pressure from the equation

$$P \equiv kT \left(\frac{\partial \ln Z}{\partial V}\right)_T . \tag{1.1}$$

The cell theory, it turns out, generates too much order in the system. In an effort to improve on this situation while maintaining the comparative ease, provided by what is essentially a lattice model, one may introduce disorder in the form of lattice

vacancies or holes. In statistical theories of polymer solutions, lattice models have played a prominent role because they facilitated the formulation of combinatory factors in the partition function. Returning to the pure melt the hole theory of Simha-Somcynsky[7] has been quantitatively successful in providing an e.o.s. of one and multi-constituted systems. More recently it has been refined by Nies, Stroeks[8] and Xie[9] in an effort to improve the performance in dealing with phase equilibria in polymer solutions and mixtures.

This work is based on SS theory. Our work is focused on the aspects of a) testing of the theory in low molar mass fluids which moreover allow b) extraction of group parameters. The chapters are arranged as follows:

In Chapter 2, we review the cell theory and SS theory in the first section and then establish the decompositional polynomial equations for normal paraffins, branched hydrocarbons, single ring attached to an alkyl and two rings connected with a carbon chain in the second section.

In Chapter 3, we analyze the normal paraffins. The requisite degrees of freedom and parameters are determined and tested with experimental PVT data using the SS theory. We then decompose these average parameters of attraction energy and repulsion volume into the group contribution of the constituent units.

In Chapter 4, we analyze the branched hydrocarbons. The requisite degrees of freedom and other parameters are determined and tested with experimental PVT data using the SS theory. We decompose these into the contributions of the specific groups and then test these with the experimental PVT data using the theory.

In Chapter 5, we analyze the contributions of ring(s) attached to linear chain alkanes. First we deduce the corresponding quasi-segment of ring by a linear chain correspondence. With the guidance of decomposed values in Ch. 3 for linear chain, we compute the group contribution parameters of the segments of the rings.

In Chapter 6, we correlate the characteristic repulsion with the Van der Waals volume and total attractive interaction with cohesive energy given by Van Krevelen.

In Chapter 7, the dissertation is concluded and future work is suggested.

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CHAPTER 2

Theory

2.1 Theories of Polymer Liquids

2.1.1 Cell Model

The early great progress in the theory of liquids is given by the well-known van der Waals equation of state as follows

$$(P + a\, n^2/V^2)(V - nb) = nRT \qquad (2.1)$$

which describes not only imperfect gases but also the liquid phase.[1] Theory which seeks to take account of the short range order existing in liquids and highly compressed gases was formulated by Lennard-Jones and Devonshire (1937).[2] They

consider each molecule to be enclosed in a cell formed by its nearest neighbors and to move only in its cell under a definite potential field. A suitable average spherical symmetry and a specific close-packed structure then yield the cell potential. This is determined by an assumed pair potential to be of the 6-12 form, i.e:

$$\varepsilon(r) = A\, r^{-12} - B\, r^{-6} \qquad (2.2)$$

A particular simplification consists of replacing the cell by a square-well potential. It is first used by Lennard-Jones and Devonshire (LJD)(1937)[2] and then modified by Eyring and Hirschfelder (1937).[3] All this applies strictly to ensembles of small, spherically symmetrical molecules.

2.1.2 Prigogine Cell Model (PCM)

Prigogine et al.[4,5] extended the LJD cell model to chain molecular system (s-mer molecules) employing two different forms of potentials, harmonic oscillator and the square-well potential approximation to the Lennard-Jones potential. We will consider only the latter for our purposes.

The ensemble is represented by a quasi-crystalline lattice and with the coordination number "z" for their polymer system. Each site is occupied by a chain segment. This makes it possible in what follows to calculate the combinatory factor (see below). Before attempting to write the partition function explicitly, we separate as an assumption the contribution of internal and external degrees of freedom. Only the latter depend on the volume and are pertinent for the computation of configurational thermodynamic functions. In a rigid molecule there are only three translational and maximally three rotational external degrees of freedom.

The kind of chain molecules to be considered here possesses internal flexibility, i.e. internal rotations which generate additional external degrees of freedom because of the comparatively low rotational barriers. This is in contrast to the high frequency valance bond and valence angle deformational motions which may be treated as volume independent. The potential energy between two segments of the molecule is again assumed to be of the Lennard-Jones type:

$$\varepsilon(r) = \varepsilon^*[A(r^*/r)^{12} - 2B(r^*/r)^6]. \qquad (2.3)$$

where $A=1.011$ and $B=1.2045$ for a close packed hexagonal cell

geometry and with non-nearest neighbor contributions included.

We can write the configurational partition function for N s-mer molecules

$$Z = g\, f(T,V)^{3cN}\, exp(-\beta E_0) \tag{2.4}$$

where g is the combinatory factor, that is the number of distinguishable ways of placing the N chains on the lattice sites, $f(T,V)$ is a cell partition function with $3c$, the number of the external degrees of freedom as discussed above, and E_0 is the total lattice energy when each segment is placed on its site. Prigogine et al.[4,5] treated the s-mer molecule as a set of s point-centers and enclosed into the cells. Each such center experiences a potential field produced by the neighbor molecules. The potential energy of the lattice in accord with eq. 2.3 is assumed to be given by

$$E_0 = \frac{1}{2} N q_z \varepsilon^* [A(\upsilon^*/\upsilon)^4 - 2B(\upsilon^*/\upsilon)^2] \tag{2.5}$$

where q_z is the number of the first neighbor intermolecular pairs of the s-mer, viz.,

$$q_z = s(z-2)+2. \tag{2.6}$$

The number of external volume dependent degrees of freedom of an ideally flexible chain is given by

$$3c = 3s-(s-1)-(s-2) = s+3; \quad s>3 \tag{2.7}$$

where the second and third term on the right hand side account for the bond stretching and bond angle deformation respectively. For a monomer $s=1$, $3c=3$. In a real molecule we may have a perturbation of an internal rotation by the surrounding molecules and no fixed number $3c$ can be strictly be defined. The procedure adopted by Prigogine et al. is to make c a disposable parameter. The cell partition function, $f(V,T)$ in eq. 2.4, is related in the smoothed potential approximation, to the factor $(1-2^{-1/6}(\upsilon/\upsilon^*)^{-1/3})$ which does not explicitly depend on temperature. Here $2^{-1/6}$ arises from the cell geometry taken as a close packed hexagonal structure ($z=12$).

The equation of state follows from the free energy,

$$F = -kT\, lnZ \tag{2.8}$$

through

$$P = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{2.9}$$

With eq. 2.4 and the expression for $f(T,V)$ we can write the equation of state in the scaled form

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 2^{-1/6}} + \frac{2}{\tilde{T}}\left[\frac{A}{\tilde{V}^4} - \frac{B}{\tilde{V}^2}\right] \tag{2.10}$$

where the reduced variables $\tilde{V}=V/V^*$, $\tilde{T}=T/T^*$ and $\tilde{P}=P/P^*$ are defined by the characteristic parameters as

$$T^* = q_z \varepsilon^*/(ck), \quad V^* = M_0 \upsilon^*/N_A$$

$$\text{and} \qquad P^* = q_z \varepsilon^*/\upsilon^* \tag{2.11}$$

where M_0 is the segmental molecular mass, satisfying the relation:

$$(P^*V^*/T^*)M_0 = (c/s)R. \tag{2.12}$$

where R is the gas constant.

The scaling parameters P^*, V^* and T^* are to be obtained by a superposition of the scaled theoretical and experimental PVT surface. Hence, see eq. 2.10, the parameter c in this theory is absorbed in T^* and no specific assignment is required.

2.1.3 Simha-Somcynsky Hole Model (SS):

To increase the degree of disorder in the lattice model various authors have introduced vacancies. Simha and Somcynsky[6] modified the Prigogine theory in this sense and applied it to both chain molecules and small molecules.

In the hole theory, the occupied site fraction, y, is defined by

$$y = sN/(sN + N_h) \tag{2.13}$$

where N_h is the number of vacant sites. The scaled configurational partition function for N s-mer molecules has the following form in a generalization of eq. 2.4

$$Z_{conf} = g(N,y)[\upsilon_f(\tilde{V},y)]^{cN} exp[-E_0(\tilde{V},\tilde{T},y)/kT] \tag{2.14}$$

We discuss now each factor in eq. 2.14 below.

i. Combinatorial Factor, $g(N,y)$:

The combinatory factor arises from the mixing of sites either vacant or occupied by a chain segment. We make use of the simplest version in the solution theory of Flory[7] and Huggins[8] based on the lattice model, now applied to a mixture of holes and molecules.

We note that this theory and the expression to be employed make the assumption of random mixing. We revert to this point in subsequent Chapters. Retaining then for our purposes only the factor dependent on y and hence volume we have

$$g(N,y) \propto y^{-N}\,(1-y)^{-sN(1-y)/y}. \tag{2.15}$$

ii. The lattice Energy, E_0:

The appropriate modification of eq. 2.5 is

$$E_0 = \frac{1}{2} y N q_z \varepsilon^* [A(\upsilon^*/\omega)^4 - 2B(\upsilon^*/\omega)^2] \tag{2.16}$$

where υ^* and ε^* retain their previous definition as the characteristic repulsion volume and attractive energy per segment respectively, q_z, the number of nearest neighbor sites per chain is given by eq. 2.6, and ω ($=yV/(Ns)$) is the cell volume weighted by the occupied site fraction. The above interaction potential energy includes non-nearest neighbor contributions.

iii. Cell Partition Function (Free Volume), υ_f:

Simha and Somcynsky[6] proposed two cell partition functions. In I they averaged linearly the free lengths of solidlike and gaslike structures with the weight factors y and $1-y$ respectively, and in II corresponding free volumes. Various applications have shown the quantitative superiority of version I

and it has been adopted by these and other authors. The result is:

$$\upsilon_f = \upsilon^*\{y[(y\tilde{V})^{1/3} - 2^{-1/6}] + (1 - y)(y\tilde{V})^{1/3}\}^3. \qquad (2.17)$$

The first term in eq. 2.17 reduces for $y=1$ to the expression $f(V,T)$ of Prigogine.

Equations 2.15-2.17 yield the configurational Helmholtz free energy:

$$\begin{aligned} F_{conf} = \; & -kT\, lnZ_{conf} = \\ & NkT\, lny + kTsN[(1-y)/y]ln(1-y) - \\ & 3kTcN\{ln[(y\tilde{V})^{1/3} - y2^{-1/6}] + \tfrac{1}{3}\ln\upsilon^*\} + \\ & \tfrac{1}{2}yNq_z\,\varepsilon^*(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 2.409]. \end{aligned} \qquad (2.18)$$

The scaled pressure equation is given by

$$\tilde{P} = -(\partial\tilde{F}/\partial\tilde{V})_{\tilde{T}} = \tilde{P}[\tilde{V},\tilde{T};y(\tilde{V},\tilde{T})] \qquad (2.19)$$

The equation of state (e.o.s.) is

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = [1-2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1} + \frac{2y}{\tilde{T}}(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 1.2045]. \qquad (2.20)$$

To obtain the thermodynamically correct e.o.s. or other configurational equilibrium functions, the variable y must be explicitly obtained as a function of the variables of state. This is accomplished by solving the minimum condition on the free energy $(\partial\tilde{F}/\partial y)_{\tilde{V},\tilde{T},Cls} = 0$ with the result

$$\frac{s}{3c}\left[\frac{s-1}{s} + y^{-1}ln\,(1-y)\right] =$$

$$(1-\eta)^{-1}(\eta-1/3) + \frac{y}{6\tilde{T}}(y\tilde{V})^{-2}[2.409 - 3.033(y\tilde{V})^{-2}] \qquad (2.21)$$

where $\eta = 2^{-1/6}y(y\tilde{V})^{-1/3}$.

We note that y will depend explicitly on the chain length

and most importantly on the *flexibility* parameter c/s . Thus in contrast to the cell theory, a specific assignment or determination of this quantity is required.

Extensive comparisons of the theory and experiment have demonstrated the quantitative success of the former. The usual procedure employed for high polymers has been to make the assignment $3c/s=1$. Physically this amounts to replacing the actual chain by a chain with free internal rotations and, of course, with the actual physical properties. The alternative is discussed below. Equation 2.12 continues to be valid. The next problem then is the superposition of the theoretical and experimental surfaces as a test and to extract the numerical values of the scaling parameters. Numerical procedures were discussed by Hartmann, Simha and Berger.[9] Moreover these authors compared their results with those obtained by the simplifications described below. These consist essentially of extracting first V^* and T^* from atmospheric ($\tilde{P} \rightarrow 0$) data and then fitting elevated pressure data, to obtain P^*.

Simha, Wilson and Olabisi[10] showed that the coupled eqs. 2.20 and 2.21 can be well approximated by the following interpolation expression at atmospheric pressure:

$$ln\tilde{V} = A(S,C) + B(S,C)\ \tilde{T}^{3/2}. \qquad (2.22)$$

A and B are slowly varying functions of S and C. For an infinite S-mer, A=-0.1034 and B=23.835 in the range ($0.95<\tilde{V}<1.40$). Simha and Wilson[11] showed that predicted and measured volumes are in a very good agreement. McKinney and Simha[12] and Jain and Simha[13] compared satisfactorily eq. 2.22 with eqs. 2.20 and 2.21 for large and small s values. As shown by Hartmann et. al.[9] the agreement between experiment and theory is further improved if the simultaneous fit methods are employed. However here the simplification of the successive fits will be used. Equation 2.22 then provides as immediate test of the theory's numerical adequacy. If V^* and T^* are to be true constants of a particular system over a specified temperature range, then the experimental isobar should satisfy the equation:

$$lnV = C + D\,T^{3/2} \tag{2.23}$$

with C and D constants for a given molecular chain length. Moreover, the consistency of eqs. 2.22 and 2.23 yields the scaling parameters, viz.:

$$V^* = exp(C\text{-}A) \quad \text{and} \quad T^* = (B/D)^{2/3} \tag{2.24}$$

As stated earlier one method of application assumed on a priori value of the ratio c/s. The alternative is to stay with the n-mer rather than its replacement, the s-mer, and to consider c as a disposable parameter to be obtained by a best fit. We note that this requires recomputation of the A and B factors in eq. 2.22 by solving the coupled eqs. 2.20 and 2.21. Thus the segment mass M_0 in eq. 2.12 becomes the known mass of the chemical repeat unit. This is the procedure adopted in what follows when we are concerned with the characterization of the constituent groups of the molecule.

2.2 Decomposition of Average Volume and Energy Parameters into Group Contribution

2.2.1 Linear Chain Hydrocarbons

The hole theory formulated by Simha and Somcynsky[6] has been applied to the equation of state (PVT) of high and low molar mass melts, including n-paraffins, to copolymers and finally to multi-component systems. The theory operates with two parameters v^* and ε^*, accounting for intersegmental attractions and repulsions, and a quantity $3c$ as a measure of the volume-dependent degrees of freedom of the molecule. In physical mixtures, these parameters represent suitable compositional averages over self and cross-interactions. Provided information about the former has been obtained from studies of the individual constituents, the mixture then yields information about the latter.

Linear chain molecular systems of sufficiently large molar mass, but excluding copolymers, involve effectively a single type of structural units, and hence a single set of parameters. On the other hand, corresponding short chain lengths may be viewed as mixtures of terminal and interior units. The application of the equations shown in the preceding section then yields average

parameters. For fundamental reasons and predictive purposes however, it becomes of interest to decompose these averages and to derive individual group contributions to the PVT parameters. A beginning was made by comparing polyethylene and the series of n-paraffins.[14,15] A consistent analysis for certain alkanes and their mixtures was carried out by Zhou et al.[15] based on the mixture theory of Jain and Simha.[16] Good quantitative agreement is obtained. However in their analysis these authors adopt the device of an equivalent s-mer employed by SS, with $3c=s+3$. This does not allow for distinctive group contributions of terminal and internal units in a linear chain. Therefore we will employ the n-mer rather than s-mer procedure. In the placement of the different types of units and holes on the lattice sites we make the assumption of randomness.

Consider now a pair of normal paraffin chains consisting of $(n-2)$ CH_2 and 2 CH_3. Figure 1 shows the characteristic interaction energies and repulsion volumes of the individual elements. These are to be related to the average values $<\varepsilon>^*$ and $<v>^*$ obtained by treating the chain as if it was constituted by a single type of units.

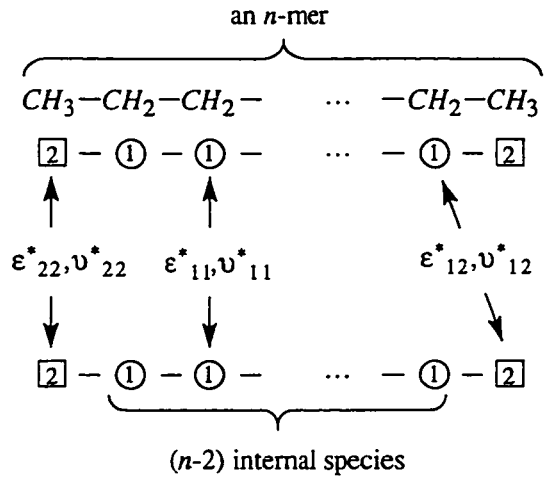


Figure 2.1. Scheme and definition of interaction parameters (ε^*_{ij} and υ^*_{ij}, i,j=1,2) in an n-mer; normal alkanes. The indices 1 and 2 refer to methylene and methyl respectively.

As illustrated in Fig. 2.1, the interaction energy and repulsive volume (ε^*_{ij} and υ^*_{ij} respectively) of a normal alkane are defined as:

ε^*_{11} and υ^*_{11} between a pair of internal units (CH_2-CH_2),

ε^*_{22} and υ^*_{22} between a pair of terminal units (CH_3-CH_3), and

ε^*_{12} and υ^*_{12} between an internal and a terminal unit (CH_2-CH_3).

We define the corresponding intermolecular contact numbers of each species as follows:

$q_{1z} = (n\text{-}2)(z\text{-}2)$: for the $(n\text{-}2)$ internal CH_2 units

and

$q_{2z} = 2(z\text{-}1)$: for the two terminal CH_3 units (2.25)

with the corresponding contact probabilities as follows:

$$P_1 = (n\text{-}2)(z\text{-}2)/(n(z\text{-}2)+2)$$

and

$$P_2 = 1\text{-}P_1 = 2(z\text{-}1)/(n(z\text{-}2)+2) \quad (2.26)$$

with $q_z=q_{1z}+q_{2z}=(n(z\text{-}2)+2)$, the total number of contact pairs. Indices 1 and 2 refer to internal and terminal species respectively.

The volume dependent factor in the interaction energy

between a (k,l)th pair equals, following the pattern of eqs. 2.5 and 2.16,

$$\Phi_{kl} = \varepsilon_{kl}^{*} [1.011(v_{kl}^{*}/\omega)^4 - 2.409(v_{kl}^{*}/\omega)^2], \quad (k,l=1,2) \tag{2.27}$$

These factors are weighted by the product of the respectively contact probabilities and the contact numbers. In this manner we obtain for the total lattice energy:

$$E_0 = \frac{1}{2} yN[q_{1z}(P_1\Phi_{11} + P_2\Phi_{12}) + q_{2z}(P_1\Phi_{12} + P_2\Phi_{22})]. \tag{2.28}$$

The first factor accounts for the fraction of occupied sites and coverts for double counting. The first two terms in the bracket represent contributions of species one interacting with 1 and 2 and the last two terms those of species two interacting with 1 and 2. On the other hand, in terms of averages $\langle\varepsilon\rangle^{*}$ and $\langle v\rangle^{*}$, E_0 is given by the following equation, as in eq. 2.26:

$$E_0 = \frac{1}{2} yNq_z \langle\varepsilon\rangle^{*}[1.011(\langle v\rangle^{*}/\omega)^4 - 2.409(\langle v\rangle^{*}/\omega)^2] \tag{2.29}$$

and equating the coefficients of the factors $1/\omega^4$ and $1/\omega^2$ yields a set of polynomial equations. These relate the characteristic parameters ε_{ki}^{*} and υ_{ki}^{*} to the averages $\langle\varepsilon\rangle^{*}$ and $\langle\upsilon\rangle^{*}$ and the chain length. The relations are:

$$(u+v)^2 \langle\varepsilon\rangle^{*}\langle\upsilon\rangle^{*2} =$$

$$u^2\ \varepsilon_{11}^{*}\upsilon_{11}^{*2} + v^2\ \varepsilon_{22}^{*}\upsilon_{22}^{*2} + 2uv\ \varepsilon_{12}^{*}\upsilon_{12}^{*2}$$

$$(u+v)^2 \langle\varepsilon\rangle^{*}\langle\upsilon\rangle^{*4} =$$

$$u^2\ \varepsilon_{11}^{*}\upsilon_{11}^{*4} + v^2\ \varepsilon_{22}^{*}\upsilon_{22}^{*4} + 2uv\ \varepsilon_{12}^{*}\upsilon_{12}^{*4} \qquad (2.30)$$

where

$$u=(n-2)(z-2) \quad \text{and} \quad v=2(z-1) \qquad (2.31)$$

2.2.2 Branched Hydrocarbons

In the previous section we have decomposed the linear chain molecule into the terminal and internal units. In the case of branched molecules with a single branch arm, we have an additional terminal methyl unit to the two terminal units of a linear chain, but we have also a branch point connecting a branch arm to a linear chain. Therefore, a single branch molecular chain

with n repeating carbon atoms consists of $(n\text{-}4)$ internal units (CH_2), 3 terminal units (CH_3) and a single branch point unit (CH) as shown in Fig. 2.2a. We will extend the decomposition of the linear chain to the branched chain.

As illustrated in Fig. 2.2b, the interaction energies and repulsion volumes of the branch point with internal, external and a second branch point are defined as:

ε^*_{33} and v^*_{33} between a pair of branch units $(CH\text{-}CH)$,

ε^*_{13} and v^*_{13} between an internal and a branch unit $(CH_2\text{-}CH)$,

and

ε^*_{23} and v^*_{23} between a terminal and a branch unit $(CH_3\text{-}CH)$.

The intermolecular contact numbers of each species are given below:

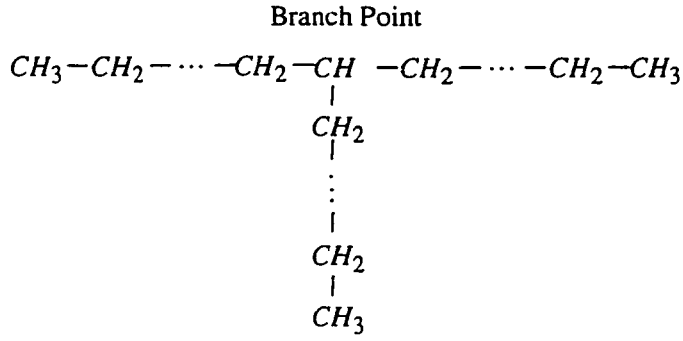
$q_{1z} = (n\text{-}4)(z\text{-}2)$: for the $(n\text{-}4)$ internal CH_2 units,

$q_{2z} = 3(z\text{-}1)$: for the three terminal CH_3 units

and

$q_{3z} = (z\text{-}3)$: for the branch point CH unit (2.32)

a)



b)

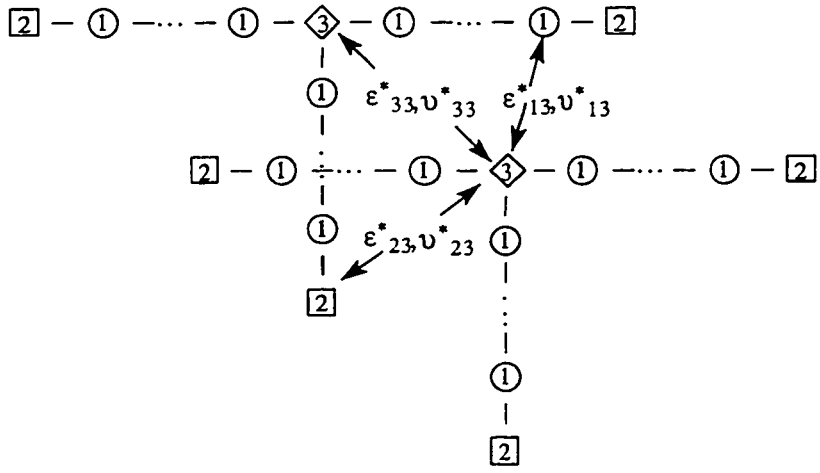


Figure 2.2.a) Chemical structure of a symmetric branched hydrocarbon. b) Scheme and definition of interaction parameters of a branch point (ε^*_{i3} and υ^*_{i3}, i=1,2 or 3) in addition to those of a normal alkane.

with the corresponding contact probabilities as follows:

$$P_1 = (n\text{-}4)(z\text{-}2)/(n(z\text{-}2)+2),$$

$$P_2 = 3(z\text{-}1)/(n(z\text{-}2)+2)$$

and

$$P_3 = 1\text{-}(P_1 + P_2) = (z\text{-}3)/(n(z\text{-}2)+2) \qquad (2.33)$$

where $q_z = q_{1z} + q_{2z} + q_{3z} = (n(z\text{-}2)+2)$, the total number of contact pairs. Indices 1,2 and 3 refer to internal, terminal and branch point species respectively.

The total energy of the system can be obtained by the same method as for the linear chain, with the modifications due to the additional terminal unit and to the presence of an additional species, that is the branch point. The total interaction energy of N branched chain molecules can then be expressed as follows

$$\begin{aligned} E_0 = \tfrac{1}{2} yN[& q_{1z}P_1\Phi_{11} + q_{2z}P_2\Phi_{22} + q_{3z}P_1\Phi_{33} \\ & + (q_{1z}P_2 + q_{2z}P_1)\Phi_{12} \\ & + (q_{1z}P_3 + q_{3z}P_1)\Phi_{13} \\ & + (q_{2z}P_3 + q_{3z}P_2)\Phi_{23}\,] \end{aligned} \qquad (2.34)$$

with again

$$\Phi_{kl} = \varepsilon^{*}_{kl}[1.011(\upsilon^{*}_{kl}/\omega)^4 - 2.409(\upsilon^{*}_{kl}/\omega)^2], \quad (k,l=1,2,3) \tag{2.35}$$

Comparing this expression of E_0 with the formula of the average interaction energies given as

$$E_0 = \frac{1}{2} y N q_z \langle\varepsilon\rangle^{*}[1.011(\langle\upsilon\rangle^{*}/\omega)^4 - 2.409(\langle\upsilon\rangle^{*}/\omega)^2] \tag{2.36}$$

and equating the coefficients of the terms in $1/\omega^4$ and $1/\omega^2$, we deduce a set of polynomial equations. These correlate the characteristic parameters $\langle\varepsilon\rangle^{*}$ and $\langle\upsilon\rangle^{*}$ with the characteristic parameters of the different types of species interaction in terms of the molecular chain-length parameter n. The analog of eq. 2.30 then is

$$(r+p+t)^2\langle\varepsilon\rangle^{*}\langle\upsilon\rangle^{*2} = r^2\,\varepsilon^{*}_{11}\,\upsilon^{*2}_{11} + p^2\,\varepsilon^{*}_{22}\,\upsilon^{*2}_{22} + t^2\,\varepsilon^{*}_{33}\,\upsilon^{*2}_{33}$$

$$+ 2rp\,\varepsilon^{*}_{12}\,\upsilon^{*2}_{12} + 2rt\,\varepsilon^{*}_{13}\,\upsilon^{*2}_{13} + 2pt\,\varepsilon^{*}_{23}\,\upsilon^{*2}_{23}$$

$$(r+p+t)^2\langle\varepsilon\rangle^{*}\langle\upsilon\rangle^{*4} = r^2\,\varepsilon^{*}_{11}\,\upsilon^{*4}_{11} + p^2\,\varepsilon^{*}_{22}\,\upsilon^{*4}_{22} + t^2\,\varepsilon^{*}_{33}\,\upsilon^{*4}_{33}$$

$$+ 2rp\,\varepsilon^{*}_{12}\,\upsilon^{*4}_{12} + 2rt\,\varepsilon^{*}_{13}\,\upsilon^{*4}_{13} + 2pt\,\varepsilon^{*}_{23}\,\upsilon^{*4}_{23} \tag{2.37}$$

where

$$r=(n\text{-}2)(z\text{-}4),\ p=3(z\text{-}1) \text{ and } t=(z\text{-}3) \tag{2.38}$$

2.2.3 A Ring Attached To An Alkane

In this section we are interested in contribution of a single ring. We consider only three different types of nonfused ring structures; phenyl, cyclohexyl, and cylopentyl. Each ring consists of corresponding s_r segments as shown in Fig. 2.3.

The definition of these segments remains open as will be discussed in the actual applications to follow.

As shown in Fig. 2.3, we have a ring divided into corresponding s_r segments and attached a normal alkane with (s-s_r-1) internal units and a single terminal unit. As illustrated in Fig. 2.3b, the attraction energy and the repulsive volume of ring segments with the same kind and internal and external species are defined as:

ε^*_{rr} and v^*_{rr} between a pair of ring segments,

ε^*_{1r} and v^*_{1r} between an internal (CH_2) unit and a ring segment, and

ε^*_{2r} and v^*_{2r} between a terminal (CH_3) unit and a ring segment.

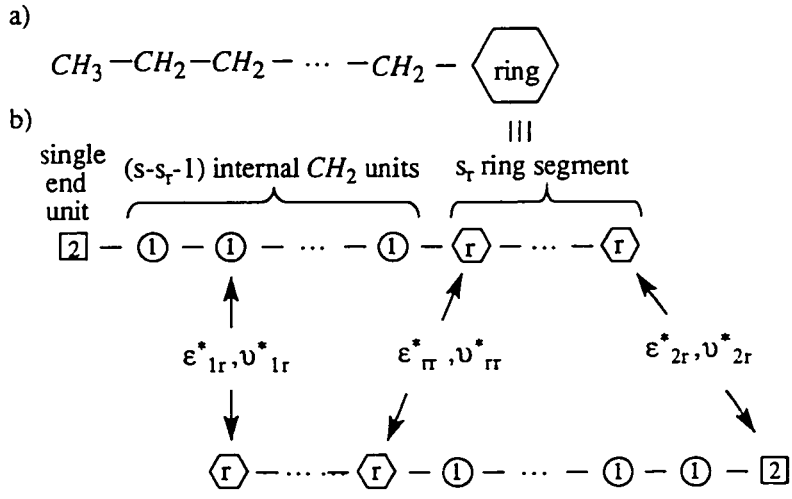


Figure 2.3.a) Chemical structure of a ring attached to a normal alkane chain. s is the total number of segments. b) Scheme and definition of interaction parameters (ε^*_{ir} and v^*_{ir}, i=1,2 and r) of ring segments in addition to those of a normal alkane.

The intermolecular contact numbers are given below:

$q_{1z} = (s\text{-}s_r\text{-}1)(z\text{-}2)$: for the $(s\text{-}s_r\text{-}1)$ internal CH_2 units,

$q_{2z} = (z\text{-}1)$: for the single terminal CH_3 units,

and

$$q_{rz} = s_r(z\text{-}2)+1 \quad \text{: for the } s_r \text{ ring segments} \tag{2.39}$$

with the corresponding contact probabilities as follows:

$$P_1 = (s\text{-}s_r\text{-}1)(z\text{-}2)/(s(z\text{-}2)+2),$$

$$P_2 = (z\text{-}1)/(s(z\text{-}2)+2),$$

and

$$P_r = 1\text{-}(P_1 + P_2) = (s_r(z\text{-}2)+1)/(s(z\text{-}2)+2) \tag{2.40}$$

where $q_z = q_{1z} + q_{2z} + q_{rz} = (s(z\text{-}2)+2)$ is the total number of contact pairs, and s is the total number of segments of the molecule. Indices 1,2 and r refer to internal, terminal and ring segment species respectively.

The total energy of the system can be obtained by the same method as for the simple linear chain, but with the additional contributions involving the ring segments. The total interaction energy of the N single ring attached chain molecule can then be expressed as follows

$$\begin{aligned} E_0 = \tfrac{1}{2} yN[& q_{1z}P_1\Phi_{11} + q_{2z}P_2\Phi_{22} + q_{rz}P_1\Phi_{rr} \\ & + (q_{1z}P_2 + q_{2z}P_1)\Phi_{12} \\ & + (q_{1z}P_r + q_{rz}P_1)\Phi_{1r} \\ & + (q_{2z}P_r + q_{rz}P_2)\Phi_{2r}\,] \end{aligned} \tag{2.41}$$

where again

$$\Phi_{kl} = \varepsilon^{*}_{kl}[1.011(\upsilon^{*}_{kl}/\omega)^4 - 2.409(\upsilon^{*}_{kl}/\omega)^2], \quad (k,l=1,2,r) \tag{2.42}$$

and comparing this expression of E_0 with the formula of the average interaction energies given as

$$E_0 = \frac{1}{2} yNq_z <\varepsilon>^{*}[1.011(<\upsilon>^{*}/\omega)^4 - 2.409(<\upsilon>^{*}/\omega)^2] \tag{2.43}$$

and equating the coefficients of the terms in $1/\omega^4$ and $1/\omega^2$, we deduce once more the polynomial equations which correlate the characteristic parameters $<\varepsilon>^{*}$ and $<\upsilon>^{*}$ with the characteristic parameters of the different types of species in terms of the molecular chainlength parameter s.

$$(u_r+v_r+t_r)^2<\varepsilon>^{*}<\upsilon>^{*2} = u_r^2\ \varepsilon^{*}_{11}\ \upsilon^{*2}_{11} + v_r^2\ \varepsilon^{*}_{22}\ \upsilon^{*2}_{22} + t_r^2\ \varepsilon^{*}_{rr}\ \upsilon^{*2}_{rr}$$

$$+ 2u_rv_r\varepsilon^{*}_{12}\ \upsilon^{*2}_{12} + 2u_rt_r\varepsilon^{*}_{1r}\ \upsilon^{*2}_{1r} + 2v_rt_r\varepsilon^{*}_{2r}\ \upsilon^{*2}_{2r}$$

$$(u_r+v_r+t_r)^2<\varepsilon>^{*}<\upsilon>^{*4} = u_r^2\ \varepsilon^{*}_{11}\ \upsilon^{*4}_{11} + v_r^2\ \varepsilon^{*}_{22}\ \upsilon^{*4}_{22} + t_r^2\ \varepsilon^{*}_{rr}\ \upsilon^{*4}_{rr}$$

$$+ 2u_rv_r\varepsilon^{*}_{12}\ \upsilon^{*4}_{12} + 2u_rt_r\ \varepsilon^{*}_{1r}\ \upsilon^{*4}_{1r} + 2v_rt_r\varepsilon^{*}_{2r}\ \upsilon^{*4}_{2r} \tag{2.44}$$

where

$$u_r=(s-s_r-1)(z-2),\ v_r=(z-1) \text{ and } t_r=s_r(z-2)+1. \qquad (2.45)$$

2. 2.4 Two Terminal Rings Attached To An Alkane

We consider two terminal rings attached to a normal alkane. As illustrated in Fig. 2.4, there are $(s-s_{r1}-s_{r2})$ internal methylene units sandwiched between two different types of rings divided into corresponding s_{r1} and s_{r2} segments each. There is no terminal methyl unit in this case.

The definitions in Fig. 2.4b simply extend the scheme of Fig. 2.3b. The intermolecular contact numbers are given below:

$q_{1z} = (s-s_{r1}-s_{r2})(z-2)$: for the $(s-s_{r1}-s_{r2})$ internal CH_2 units,

$q_{r1z} = s_{r1}(z-2)+1$: for s_{r1} ring segments,

and

$$q_{r2z} = s_{r2}(z-2)+1 \quad : \text{for } s_{r2} \text{ ring segments} \qquad (2.46)$$

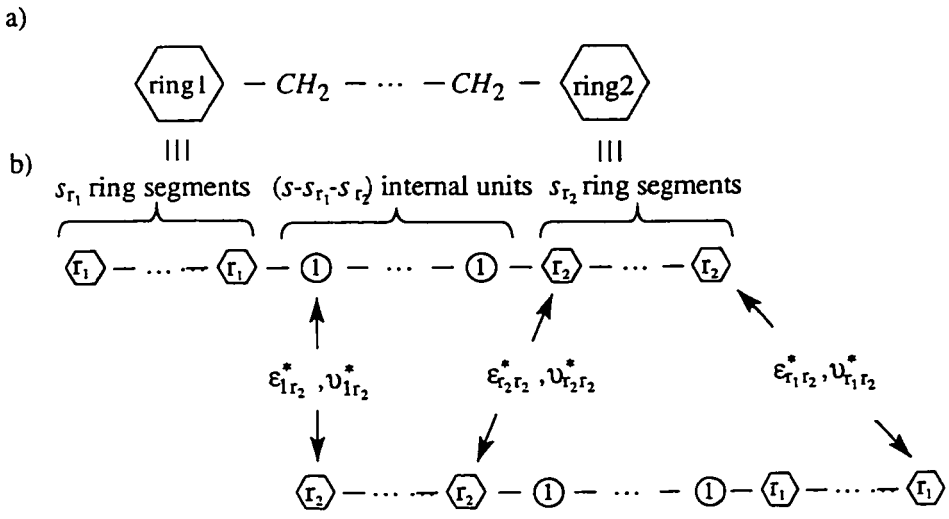


Figure 2.4.a) Chemical structure of two rings. s is the total number of segments, b) Scheme and definition of interaction parameters of ring segments in addition to those of a normal alkane. We omit the $\varepsilon^*_{1r_1}$ are $\upsilon^*_{1r_1}$ for reasons of clarity.

with the corresponding contact probabilities as follows:

$$P_1 = (s-s_{r1}-s_{r2})(z-2)/(s(z-2)+2)$$

$$P_{r1} = (s_{r1}(z-2)+1)/(s(z-2)+2),$$

and

$$P_{r2} = 1-P_{r1}-P_{r2} = (s_{r2}(z-2)+1)/(s(z-2)+2) \qquad (2.47)$$

where $q_z = q_{1z}+q_{r1z}+q_{r2z} = (s(z-2)+2)$ is the total number of contact pairs, and s is the total number of segments of the molecule.

Indices 1, r_1 and r_2 refer to internal, ring-1 and ring-2 segment species respectively.

The total energy of the system can be obtained by the same method as for the simple linear chain, but with the additional contributions involving two types of ring segments. The total interaction energy of the N chain molecule of interest can then be expressed as follows

$$E_0 = \frac{1}{2} yN[q_{1z}P_1\Phi_{11} + q_{r1z}P_{r1}\Phi_{r1\,r1} + q_{r2z}P_{r2}\Phi_{r2\,r2} + (q_{1z}P_{r1} + q_{r1z}P_1)\Phi_{1r1} + (q_{1z}P_{r2} + q_{r2z}P_1)\Phi_{1r2} + (q_{r1z}P_{r2} + q_{r2z}P_{r1})\Phi_{r1\,r2}] \qquad (2.48)$$

with again

$$\Phi_{kl} = \varepsilon^*_{kl}[1.011(\upsilon^*_{kl}/\omega)^4 - 2.409(\upsilon^*_{kl}/\omega)^2] \qquad (k,l=1,r_1 \text{ and } r_2) \qquad (2.49)$$

and comparing this expression of E_0 with the formula of the

average interaction energies given as

$$E_0 = \frac{1}{2} y N q_z \langle \varepsilon \rangle^* [1.011(\langle \upsilon \rangle^*/\omega)^4 - 2.409(\langle \upsilon \rangle^*/\omega)^2] \qquad (2.50)$$

and equating the coefficients of the terms in $1/\omega^4$ and $1/\omega^2$, we deduce the polynomial equations which correlate the characteristic parameters $\langle \varepsilon \rangle^*$ and $\langle \upsilon \rangle^*$ with the characteristic parameters of the different types of species interaction in terms of the molecular chain-length s.

$$(u'_r + t'_{r1} + t'_{r2})^2 \langle \varepsilon \rangle^* \langle \upsilon \rangle^{*2} =$$

$$u'^2_r \varepsilon^*_{11} \upsilon^{*2}_{11} + t'^2_{r1} \varepsilon^*_{r1r1} \upsilon^{*2}_{r1r1} + t'^2_{r2} \varepsilon^*_{r2r2} \upsilon^{*2}_{r2r2}$$

$$+ 2u'_r t'_{r1} \varepsilon^*_{1r1} \upsilon^{*2}_{1r1} + 2u'_r t'_{r2} \varepsilon^*_{1r2} \upsilon^{*2}_{1r2} + 2t'_{r1} t'_{r2} \varepsilon^*_{r1r2} \upsilon^{*2}_{r1r2}$$

$$(u'_r + t'_{r1} + t'_{r2})^2 \langle \varepsilon \rangle^* \langle \upsilon \rangle^{*4} =$$

$$u'^2_r \varepsilon^*_{11} \upsilon^{*4}_{11} + t'^2_{r1} \varepsilon^*_{r1r1} \upsilon^{*4}_{r1r1} + t'^2_{r2} \varepsilon^*_{r2r2} \upsilon^{*4}_{r2r2}$$

$$+ 2u'_r t'_{r1} \varepsilon^*_{1r1} \upsilon^{*4}_{1r1} + 2u'_r t'_{r2} \varepsilon^*_{1r2} \upsilon^{*4}_{1r2} + 2t'_{r1} t'_{r2} \varepsilon^*_{r1r2} \upsilon^{*4}_{r1r2} \qquad (2.51)$$

where

$$u'_r=(s-s_{r1}-s_{r2})(z-2),\quad t'_{r1}=s_{r1}(z-2)+1$$

$$\text{and}\qquad t'_{r2}=s_{r2}(z-2)+1. \tag{2.52}$$

In case there is no internal methylene unit with just two rings connected each other, s equals $s_{r1}+s_{r2}$ and the terms with u'_r become zero. If the two rings are identical, then s_{r1} equals s_{r2}.

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CHAPTER 3

Application to *n*-paraffins

3.1. Experimental Data Source

A number of years ago, extensive syntheses, PVT and viscosity measurements on hydrocarbon fluids and their mixtures were carried out at Pennsylvania State University under support by the American Petroleum Institute (API) Research Project 42.[1,2] Systematic structural variations, starting out with *n*-paraffins as the parent compounds, were generated. The results were presented in reports, theses and papers, of which we cite here Refs. 1 and 2. Earlier analyses of the data were formed and group contributions were obtained by Hadden and Simha[3] based on the cell theory of Prigogine, Trappeniers and Mathot.[4] These considerations provided a rationalization of empirical relations between volume, chain length, number of double bonds and rings.[5]

In view of the quantitative success of the SS theory, it becomes of interest to reexamine the extensive material provided by the API Project. We note again that this includes viscosity measurements and may allow correlation between equilibrium and transport processes, based on free volume arguments, as explored by Utracki.[6] Particularly for the n-paraffins, there exist other data over wider ranges of chain length. However, for reasons of internal consistency, the focus is to be on the API set.

In addition to and referring again to the earlier rationalization of empirical relations between volume and structure on the basis of cell theory, we now apply SS theory to this problem.

3.2 The External Degrees of Freedom, $3c$

For s-mer segmental system, the $(3c/s)$ ratio was adopted as unity for long chain molecules and $1+3/s$ for short chain molecules as discussed by Simha and Somcynsky[7] and reviewed by Simha[8] for the SS theory; see also Chapter 2.

Here we subdivide the linear chain into n segments corresponding to the number of carbon atoms. As discussed in the previous chapter, we treat the number $3c$ of effectively external degrees in the partition function as a disposable constant. It is determined by a best fit of the theory to experimental volumes

over the available range of temperatures and pressures. The corresponding scaling parameters are then obtained by the procedures described earlier.

Consider the experimental data of API[1] for linear paraffins $n\text{-}C_{12}$, $n\text{-}C_{15}$ and $n\text{-}C_{18}$ to estimate the necessary characteristic parameters as well as the external degrees of freedom. These compounds are the only API data with elevated pressure information which is necessary to determine the degrees of freedom. We make use of the experimental data in the range of temperature, $37.8<T(°C)<135$, from atmospheric pressure to 3445 bar. They are well-fitted for this broad temperature range at atmospheric pressure by eq. 2.23, with C and D values given in Table 3.2.

For given c and n values, the coupled eqs. 2.20 and 2.21 can be solved for y eliminating $\tilde{T}$, ending up with a $\tilde{V}$–$\tilde{T}$ relation. This relation can be cast in the form of eq. 2.22, yielding the A and B parameters. Fig. 3.1 shows this linear relation with the experimental points for each normal paraffin. Equations 2.24 yields V^* and T^*, and P^* follows from eq. 2.12. The final result of the iteration procedure and the corresponding average, maximum and standard (STD) deviations of volume prediction from experiment are seen in Table 3.1. Scaled compressibility factors as a function of scaled densities for a series of isotherms are shown in Figs. 3.2-3.4 for each normal paraffins respectively.

Table 3.3. Degrees of freedom of paraffins at n=12, 15 and 18 chain lengths with the corresponding volumetric deviation from theory. The values in parenthesis are given by the best fit eq. 3.1.

n	c	Aver. Error%	Max. Error%	STD %
12	1.86 (1.863)	0.31	0.70	0.48
15	2.08 (2.073)	0.15	0.42	0.23
18	2.28 (2.283)	0.14	0.47	0.21

The number c is a linear function of n, see Fig. 3.5. Thus decomposing the degrees of freedom into the contributions of internal and external units, we have

$$c = (n\text{-}2)c_i+2c_e \qquad 3.1$$

where the simple linear regression gives c_i=.070 and c_e=0.5815 through the data in Table 3.3 with the maximum deviation of ±%0.34. This implies that terminal effects remain significant up to quite high chain length. As for the deviations cited in Table 3.1 we note the definitions:

percentage mean error (Mean Err %):

$$\Delta V_i = 100 \cdot | V_{ith} - V_{iexp} | / V_{iexp},$$

$$\Delta V_{mean} = (1/N) \sum_i \Delta V_i,$$

percentage maximum error (Max Err %):

$$\Delta V_{max} = Max\ (\Delta V_i)$$

and *percentage standard deviation* (STD%):

$$\Delta V_{std} = 100 \cdot (1/N) \left(\sum_i (V_{ith} - V_{iexp})^2 \right)^{1/2}. \qquad 3.2$$

where V_{exp} is the experimental volume and V_{th} is the theoretically calculated volume, with the sums extended over all *i* indices, i.e. all available data. The deviations increase with pressure and temperature. Table 3.1 indicates that the percentage

error in the theory does not exceed 0.7% up to 3445 bar. At atmospheric pressure, the maximum error is less than 0.07%.

3.3 Extension to Alkanes of Different Chain Lengths with atmospheric pressure data, adopting the c - n relation, eq. 3.1.

The range of chain lengths in the previous section is narrow. It is desirable to make predictions at interpolated as well as extrapolated n-values. For this purpose equations for the parameters as functions of chain-length are required. We begin with the c quantity, expected to be a linear function of n, satisfying the relation in eq. 3.1. This relation would imply that terminal effects represented by the constant term continue to be significant up to quite high chain-lengths. The parenthesis in Table 3.1 shows the results of eq. 3.1.

The iteration procedures for c can be practically applied satisfactorily only in conjunction with elevated pressure data. On the other hand, we wish to predict by means of the theory volumetric data at other chain lengths and from the same source, where information at atmospheric pressure only is available. For this purpose we continue to employ eq. 3.1 and analyze data with twelve n-paraffins including our original set of n=12, 15, 18, intermediate, and larger chain-lengths. The results of the analysis appear in Table 3.2 together with the characteristic scaling

parameters and the C, D, A and B quantities. For each item pertaining to the scaling parameters, the derived quantities and the deviations there appear three entries. The first of these refer to the procedure just described, i.e. an analytical expression for $c(n)$ and a determination of V^* and T^* for each n-value. We conclude that eq. 3.1 and the determined parameters are satisfactory. The maximum error in volume does not exceed 0.09% at atmospheric pressure for the twelve paraffins and 1% up to 3445 bar elevated pressures for n=12, 15 and 18. The second entries in parentheses employ analytical expression for these latter quantities as well. These are

$$\upsilon^*(cc/mole) = 16.394 + 16.596/n \quad \text{and}$$

$$\varepsilon^*(^\circ K) = 138.39 + 232.23/n \qquad 3.3$$

We conclude that the use of eqs. 3.1 and 3.3 in the theory allows satisfactory predictions. The maximum error in volume does not exceed 0.30% at atmospheric pressure for the twelve paraffins and 0.93% at elevated pressures for n=12, 15 and 18. Moreover densities of elevated pressures can be compared. The adequacy of these expressions may be judged from Fig. 3.6 given by lines through black squares determined by the original calculation given in the first entries of Table 3.2. The open squares will be

explained below appeared in the third entries of Table 3.2.

The V^*, T^* and P^* parameters are also plotted with respect to $1/n$ in Fig. 3.7 as black squares. The best-fit curves are drawn through the data and the best-fit equations of these parameters are given below

$$V^*(cc/g) = 1.169 + 0.999\ (1/n)$$
$$10^{-4}\ T^*(^\circ K) = 1.8215 - 14.1847\ (1/n) + 56.9636\ (1/n)^2$$
$$10^{-4}\ P^*(bar) = 0.6926 + 0.9649\ (1/n) - 3.5115\ (1/n)^2. \quad (3.4)$$

Equation 3.4 is derived with the same source of data which is used to derive eq. 3.2; therefore, we do not test the consequence of eq. 3.4. Fig. 3.7 already shows the fit and reliability of eq. 3.4.

3.4 Decomposition of the average values of $<\varepsilon^*>$ and $<\upsilon^*>$ into the υ_{ij}^* and ε_{ij}^* contributions

With the averages $<\upsilon^*>$ and $<\varepsilon^*>$ obtained in the previous section at hand we are ready now to examine the group contributions of $CH_2$and CH_3, using the polynomial expression, eq. 2.30 derived in Ch. 2.2.1. There are three unknowns $\varepsilon_{ik}^*\upsilon_{ik}^{*2}$ and further three $\varepsilon_{ik}^*\upsilon_{ik}^{*4}$, with two equations for a given chain-length n. We have twelve n-values ($12 \le n \le 32$) and thus an overdetermined

set.

To solve this set we employ a *PseudoInverse* matrix method in Mathematica software, which optimizes the solution, that is, generates the least error. A code program to solve the set is included in Appendix A.

Using eq. 2.30 with eq. 2.31, and taking all the ε^* and υ^* data in Table 3.2 from n=12 to n=32, we derive the optimized six parameters characterizing n-paraffins of sufficiently high molar mass with the result on Table 3.4.

Table 3.4. Decomposed parameters of linear chain molecules. The indices 1 and 2 refer to methylene and methyl respectively.

υ^*_{11}=16.480 $cm^3\,mole^{-1}$	ε^*_{11}=136.16 ^oK
υ^*_{12}=17.908 $cm^3\,mole^{-1}$	ε^*_{12}=218.61 ^oK
υ^*_{22}=23.589 $cm^3\,mole^{-1}$	ε^*_{22}=234.36 ^oK

($\varepsilon^*_{ij}(^oK)$ is defined by ε^*_{ij}/k as unit, but we drop the Boltzmann k constant for convenience.)

We can now reverse the procedure and recompute the averages and hence calculate P^*, V^* and T^* (white squares in Fig. 3.7). Table 3.2 shows the results in the third parentheses from n=12 to n=32 chain lengths. The maximum error in volume does

not exceed 0.22% at atmospheric pressure for the twelve paraffins and 0.89% at elevated pressures for n=12, 15 and 18. Recalculated averages of υ^* and ε^* are plotted versus $1/n$ in Fig. 3.6. Reasonable agreement between the white squares and lines, eq. 3.3, is noted.

In examining these numbers one may think first of certain combination rules for *mixed* interactions seen in the literature. For example, the arithmetic mean length $\upsilon_{12}^*=[(\upsilon_{11}^{*1/3}+\upsilon_{22}^{*1/3})/2]^3$ and geometric mean $\varepsilon_{12}^* = (\varepsilon_{11}^*\varepsilon_{22}^*)^{1/2}$. The respective results are 19.823 and 178.64, deviating by 11% and 18% respectively from our results. Here we note that we made the assumption of randomness in the calculation of the combinatorial factor. This discrepancy suggests that more accurate result can be found by the non-randomness of the distribution of the methyl and methylene.

3.5 Infinity Chain Limiting Case; Polyethylene

The limits in eq. 3.3 for $n\to\infty$ are 138.39 and 16.394, to be compared with the (1,1) interactions 136.16 and 16.480, i.e. differences of 1.6 and 0.7% respectively. We will test the predictions of the PVT surface of polyethylene. We have experimental data for polyethylene given by Olabisi and Simha[9] in a temperature range from 142 °K to 200 °K and pressure range from atmospheric to 2,000 bar. The theoretical volume deviates

by 1.2% maximally and 0.54% on the average for the former and by 1.5% and 0.59% respectively for the latter. We also take the degrees of freedom as a disposable parameter and varying the value as we did for normal paraffins in Chapter 3.1, we end up with the best parameters tabulated in Table 3.5. The degrees of freedom is 0.085 with maximum 0.22% and average 0.086% corresponding least error in the predicted versus the experimental volume.

Above obtained parameters for polyethylene are compatible with those of Olabisi and Simha[9], given by 141.69 $^{\circ}K$ and 16.018 $cc/mole$ for ε^* and υ^* respectively. Equation 3.3 gives 138.39 $^{\circ}K$ and 16.394 $cc/mole$ at the limit respectively.

3.6 Comparison of the Characteristic Repulsion Volume with Van der Waals Volume

We also compare the decomposed values with the Van der Waals volume, V_w, of each species. Van Krevelen[10] and Bondi[11] calculated and summarized all the available data on the Van der Waals volume of each structural component. Their values of Van der Waals volume for methyl and methylene units are given by

$V_w(-CH_2-)$=10.23 cm^3/mole

$V_w(-CH_3)$=13.67 cm^3/mole.

The ratios of Van der Waals volume of methyl to methylene is 1.336. The ratio of characteristic volume of methyl to methylene is 1.431. And the ratios of characteristic volume to Van der Waals volume of methylene and methyl are

$$\upsilon_{11}^{*}/V_w(\text{-}CH_2\text{-})=1.61$$

$$\upsilon_{22}^{*}/V_w(\text{-}CH_3\ )=1.73.$$

This work is generalized to other compounds in Chapter 6. We will leave the discussion to that chapter.

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Table 3.1 List of the API Data[1,2] Normal Paraffins Employed with Temperature and Pressure Ranges.

PSU #	Hydro-carbon	Struc-ture	Empirical Formula	Molecular Weight	$T(°K)$ Range	Pressu re P_{max}[a]
528	n-Dodecane	n-C_{12}	$C_{12}H_{26}$	170.328	273-408	3445
529	n-Tridecane	n-C_{13}	$C_{13}H_{28}$	184.354	273-372	1
531	n-Tedradecane	n-C_{14}	$C_{14}H_{30}$	198.380	273-372	1
532	n-Pentadecane	n-C_{15}	$C_{15}H_{32}$	212.406	273-408	3445
534	n-Hexadecane	n-C_{16}	$C_{16}H_{34}$	226.432	273-372	1
535	n-Heptadecane	n-C_{17}	$C_{17}H_{36}$	240.458	273-372	1
537	n-Octadecane	n-C_{18}	$C_{18}H_{38}$	254.484	273-408	3445
540	n-Eicosane	n-C_{20}	$C_{20}H_{42}$	282.536	273-372	1
541	n-Tedracosane	n-C_{24}	$C_{24}H_{50}$	338.640	273-372	1
106	n-Hexacosane	n-C_{26}	$C_{26}H_{54}$	366.692	273-372	1
176	n-Octacosane	n-C_{28}	$C_{28}H_{58}$	394.744	273-372	1
197	n-Dotria-contane	n-C_{32}	$C_{32}H_{66}$	450.848	273-372	1

[a] Elevated Pressure is only avalible for n-C_{12}, n-C_{15} and n-C_{18} in the API Project 42.[1]

Table 3.2. Original[a], Equation[b] and Calculated[c] Characteristic Parameters of Linear Chain Hydrocarbons

n	12	13	14	15	16	17
$M_o(g)$	14.194	14.181	14.170	14.160	14.152	14.145
c [d]	1.86	1.93	2.00	2.07	2.14	2.21
C	0.09845	0.09976	0.09264	0.08701	0.08532	0.08275
D 10^5	3.7948	3.5767	3.5421	3.5042	3.4122	3.3516
$-A$	0.1258	0.1222	0.1227	0.1248	0.1226	0.1223
B	39.5906	39.8604	40.8490	42.1347	42.4148	43.1096
$V^*(cc/g)$	1.2513	1.2485	1.2403	1.2359	1.2311	1.2276
	(1.2524)	(1.2461)	(1.2406)	(1.2359)	(1.2317)	(1.2281)
	((1.2529))	((1.2463))	((1.2406))	((1.2357))	((1.2314))	((1.2277))
$T^*(°K)$	10287	10749	10997	11308	11561	11827
	(10330)	(10670)	(10987)	(11283)	(11559)	(11818)
	((10313))	((10664))	((10988))	((11288))	((11568))	((11829))
$P^*(bar)$	7465	7494	7432	7413	7379	7362
	(7501)	(7465)	(7435)	(7408)	(7385)	(7364)
	((7486))	((7459))	((7435))	((7413))	((7392))	((7373))
υ^*	17.761	17.705	17.575	17.501	17.423	17.364
(cc/mol)	(17.777)	(17.671)	(17.579)	(17.500)	(17.431)	(17.370)
	((17.784))	((17.673))	((17.579))	((17.498))	((17.427))	((17.366))
$\varepsilon^*(°K)$	156.83	157.17	154.89	153.99	152.72	151.97
	(157.75)	(156.26)	(154.98)	(153.87)	(152.91)	(152.05)
	((157.49))	((156.16))	((154.99))	((153.95))	((153.03))	((152.20))
At Atmospheric Pressure						
Ave.Err%	0.042	0.045	0.052	0.038	0.051	0.052
	(0.11)	(0.063)	(0.047)	(0.052)	(0.057)	(0.054)
	((0.037))	((0.046))	((0.046)	((0.040))	((0.052))	((0.054))
Max.Err%	0.084	0.072	0.070	0.074	0.069	0.068
	(0.16)	(0.14)	(0.10)	(0.11)	(0.11)	(0.11)
	((0.14))	((0.18))	((0.10))	((0.085))	((0.076))	((0.084))
STD%	0.068	0.074	0.073	0.060	0.075	0.074
	(0.16)	(0.11)	(0.082)	(0.089)	(0.090)	(0.088)
	((0.074))	((0.12))	((0.082))	((0.065))	((0.075))	((0.077))
At Elavated Pressure[e] (up to 3445 bar)						
Ave.Err%	0.31			0.16		
	(0.31)			(0.16)		
	((0.31))			((0.16))		
Max.Err%	1.00			0.57		
	(0.93)			(0.54)		
	((0.89))			((0.56))		
STD%	0.50			0.27		
	(0.47)			(0.27)		
	((0.48))			((0.27))		
$\tilde{V}$ range	1.04-1.21	1.03-1.15	1.03-1.15	1.03-1.18	1.03-1.13	1.02-1.13

[a] computed average values (without parenthesis) from the theory.

[b] calculated average values (in parenthesis) from the best fit equations 3.3

[c] calculated average values (in double parenthesis) from the polynomial equations 2.30 using the υ^*_{ij} and ε^*_{ij} pertinent universal parameters.

[d] the degrees of freedom are calculated from the equation 3.1: $c=0.07n+1.023$.

[e] only available data at elevated pressure (e.i. API PSU528, PSU532 and PSU537.)

Continued from Table 3.2

n	18	20	24	26	28	32
$M_o(g)$	14.138	14.127	14.110	14.104	14.0980	14.089
c	2.28	2.42	2.70	2.84	2.98	3.26
C	0.07816	0.07540	0.06907	0.06370	0.06303	0.06139
$D\ 10^5$	3.3176	3.2231	3.0972	3.0697	3.0168	2.9245
$-A$	0.1247	0.1228	0.1226	0.1230	0.1234	0.1228
B	44.3758	45.1681	47.3015	48.3353	49.2783	50.6053
$V^*(cc/g)$	1.2249	1.2192	1.2113	1.2053	1.2049	1.2023
	(1.2248)	(1.2192)	(1.2109)	(1.2077)	(1.2049)	(1.2004)
	((1.2244))	((1.2189))	((1.2108))	((1.2077))	((1.2051))	((1.2009))
$T^*(°K)$	12140	12523	13262	13535	13870	14413
	(12061)	(12506)	(13257)	(13577)	(13867)	(14373)
	((12073))	((12517))	((13260))	((13575))	((13858))	((14351))
$P^*(bar)$	7383	7315	7258	7231	7225	7208
	(7345)	(7314)	(7266)	(7247)	(7231)	(7205)
	((7355))	((7322))	((7268))	((7246))	((7226))	((7191))
υ^* $(cc/mole)$	17.318	17.223	17.091	16.999	16.987	16.939
	(17.316)	(17.224)	(17.086)	(17.032)	(16.987)	(16.913)
	((17.311))	((17.219))	((17.084))	((17.033))	((16.989))	((16.920))
$\varepsilon^*(°K)$	152.08	150.03	147.96	146.71	146.57	145.92
	(151.29)	(150.00)	(148.07)	(147.32)	(146.69)	(145.65)
	((151.45))	((150.14))	((148.11))	((147.30))	((146.59))	((145.42))
At Atmospheric Pressure						
Ave.Err%	0.050	0.051	0.053	0.052	0.050	0.029
	(0.16)	(0.051)	(0.061)	(0.096)	(0.052)	(0.081)
	((0.10))	((0.056))	((0.064))	((0.10))	((0.045))	((0.032))
Max.Err%	0.088	0.070	0.066	0.065	0.069	0.046
	(0.30)	(0.086)	(0.11)	(0.19)	(0.079)	(0.13)
	((0.22))	((0.088))	((0.12))	((0.19))	((0.085))	((0.069))
STD%	0.074	0.072	0.070	0.069	0.067	0.041
	(0.24)	(0.076)	(0.092)	(0.14)	(0.069)	(0.11)
	((0.16))	((0.080))	((0.10))	((0.15))	((0.071))	((0.053))
At Elavated Pressure (up to 3445 bar)						
Ave.Err%	0.19					
	(0.21)					
	((0.20))					
Max.Err%	0.56					
	(0.60)					
	((0.56))					
STD%	0.30					
	(0.32)					
	((0.31))					
$\tilde{V}$ range	1.02-1.17	1.02-1.12	1.01-1.11	1.01-1.11	1.01-1.11	1.00-1.10

Table 3.5. Original[a], Best-fit[b] and Pertinent[c] Characteristic Parameters of Polyethylene

	Polyethylene
$M_o(g)$	14.026
c/n	0.085
	(0.07)
	(0.07)
C	0.02899
$D\ 10^5$	2.4701
$-A$	0.1306
B	59.498
$V^*(cc/g)$	1.1730
	(1.1688)
	((1.1750))
$T^*(°K)$	17969
	(19770)
	((19451))
$P^*(bar)$	7719
	(7019)
	((6869))
υ^*	16.453
$(cc/mole)$	(16.394)
	((16.480))
$\varepsilon^*(°K)$	152.74
	(138.39)
	((136.16))
Pressure Range (1bar to 2000 bar)	
Temperature Range(142°K to 200°K)	
Ave.Err%	0.086
	(0.54)
	((0.59))
Max.Err%	0.22
	(1.16)
	((1.51))
STD%	0.12
	(0.79)
	((0.91))
$\tilde{V}$ range	1.07-1.14

a computed average values (without parenthesis) from the theory and c is taken disposable.

b extrapolated average values (in parenthesis) from the best fit equation, eq. 3.3, and the degrees of freedom, eq. 3.1, when n goes to infinity

c υ_{11}^* and ε_{11}^* pertinent universal parameters (in double parenthesis) derived from normal paraffins, see Table 3.4. The degrees of freedom are the same as above from the limiting case of eq. 3.1.

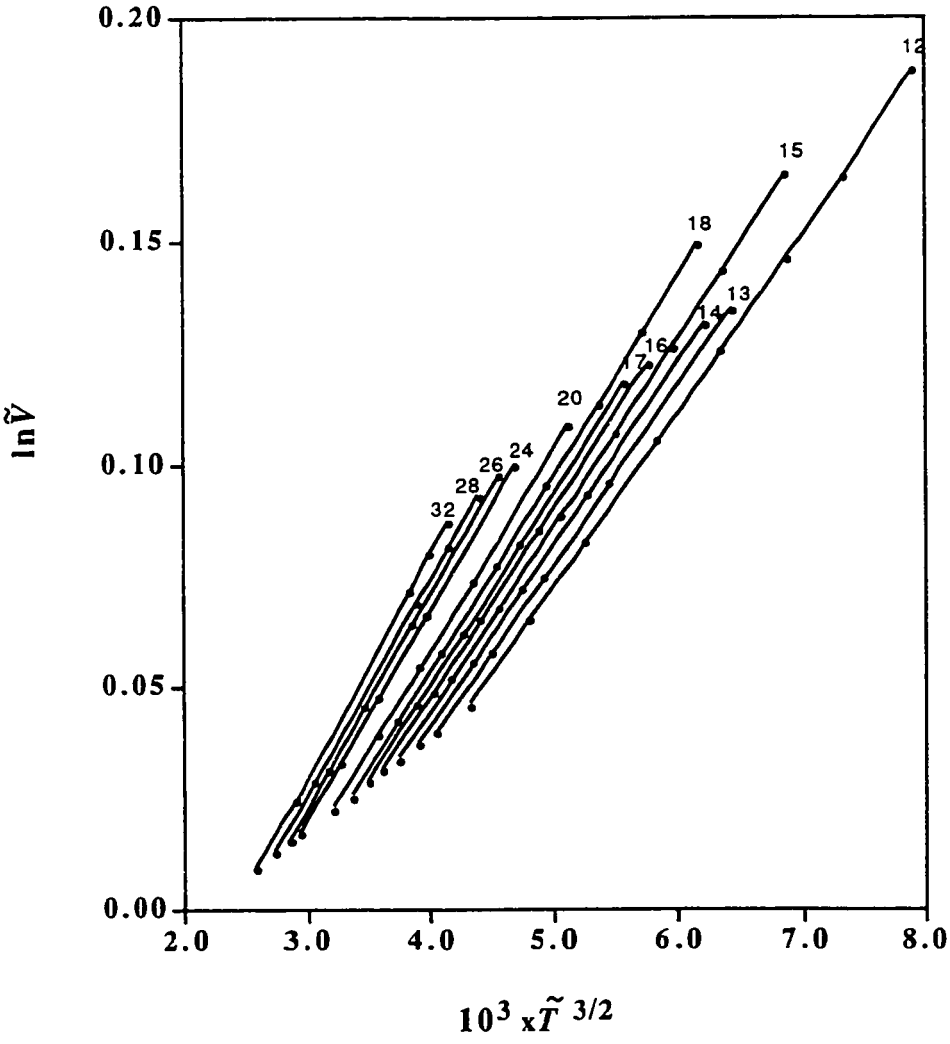


Figure 3.1. Comparison of theoretical (lines) and experimental (points) isobars at atmospheric pressure for a series of normal alkanes. The molecular chain length, *n*, is shown on the top of each line.

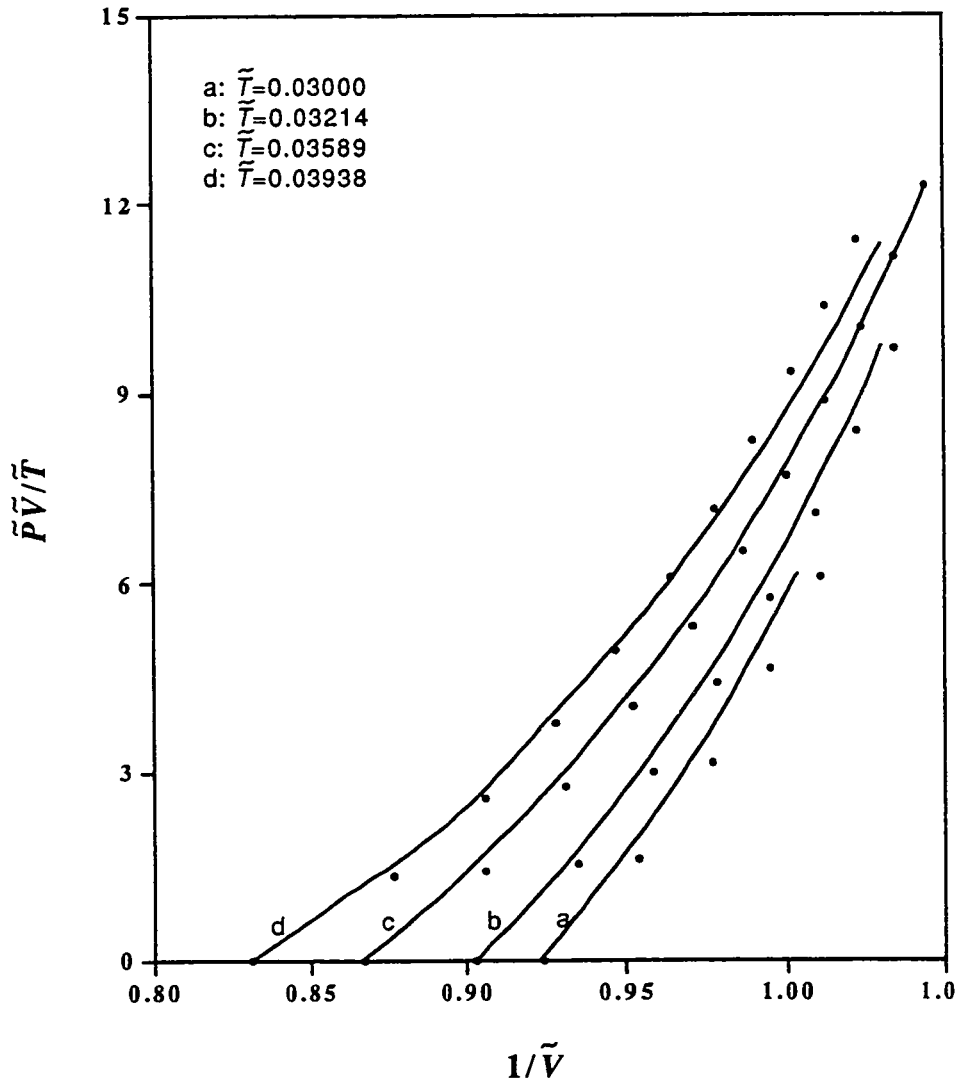


Figure 3.2. Scaled compressibility factor of normal dodecane as a function of scaled density: lines, theory and points, experimental.

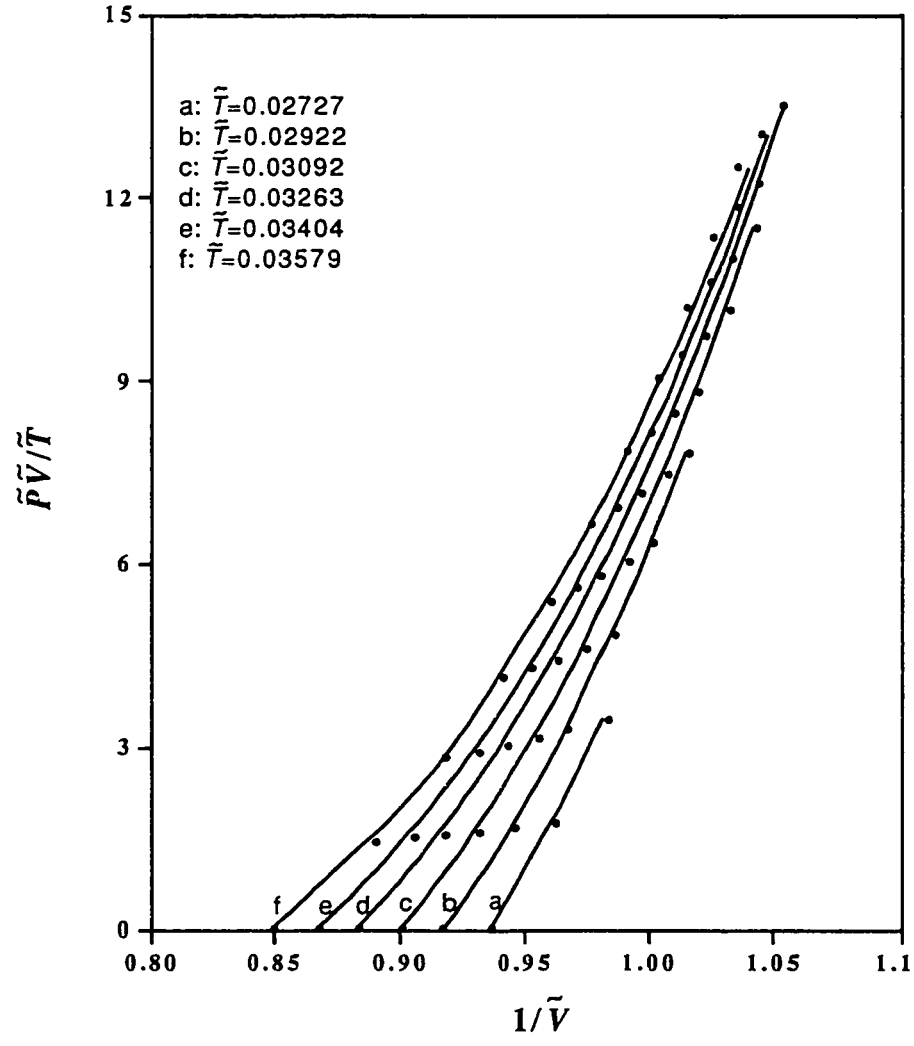


Figure 3.3. Scaled compressibility factor of normal pentadecane as a function of scaled density: lines, theory and points, experimental.

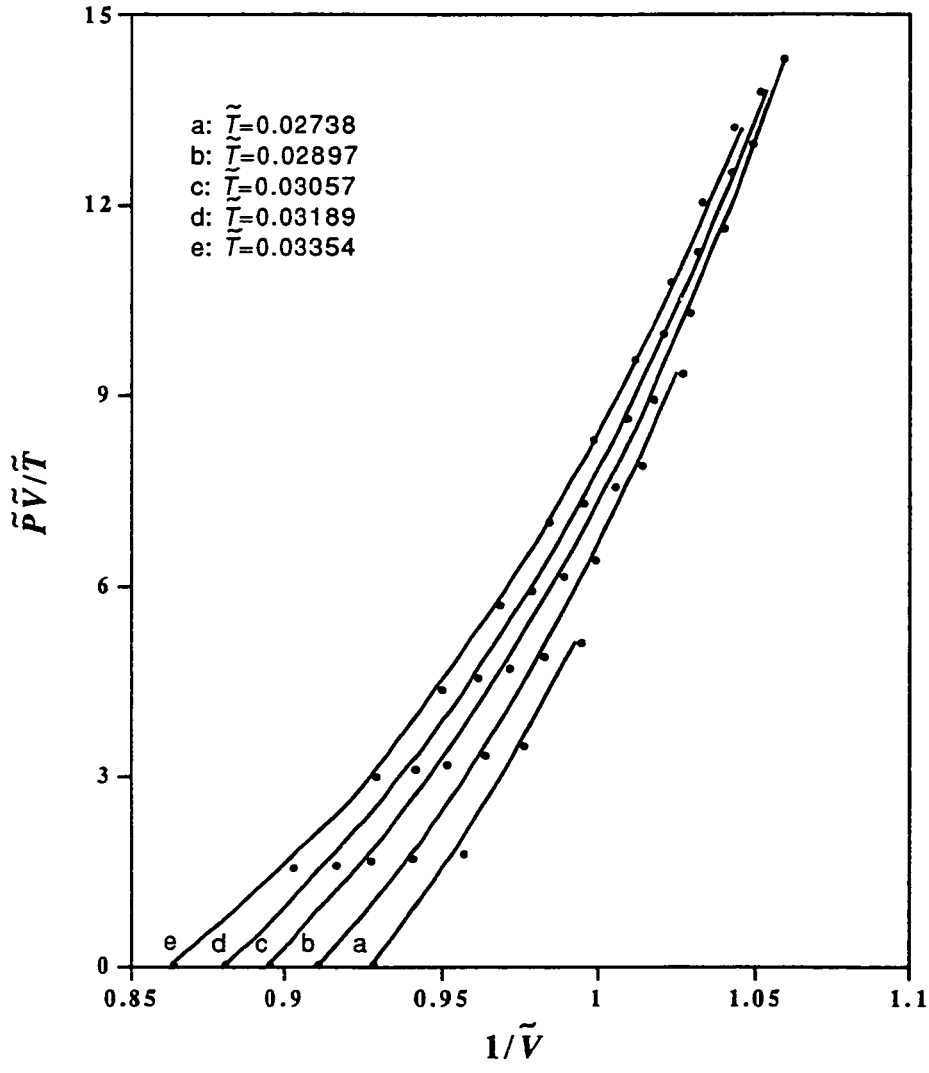


Figure 3.4. Scaled compressibility factor of normal octadecane as a function of scaled density: lines, theory and points, experimental.

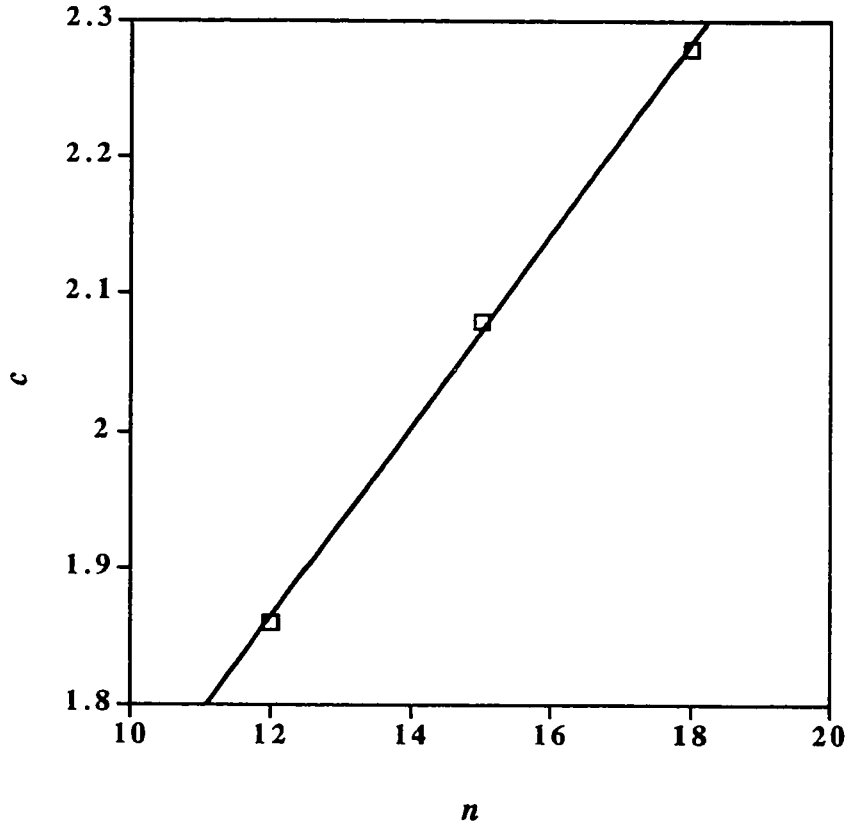


Figure 3.5. c, degrees of freedom, versus n, the number of repeat carbon units. White squares are the evaluated c values for normal C_{12}, C_{15}, and C_{18} hydrocarbons. The line is the best-fit linear relation through these values given by:

$$c=0.07n+1.023.$$

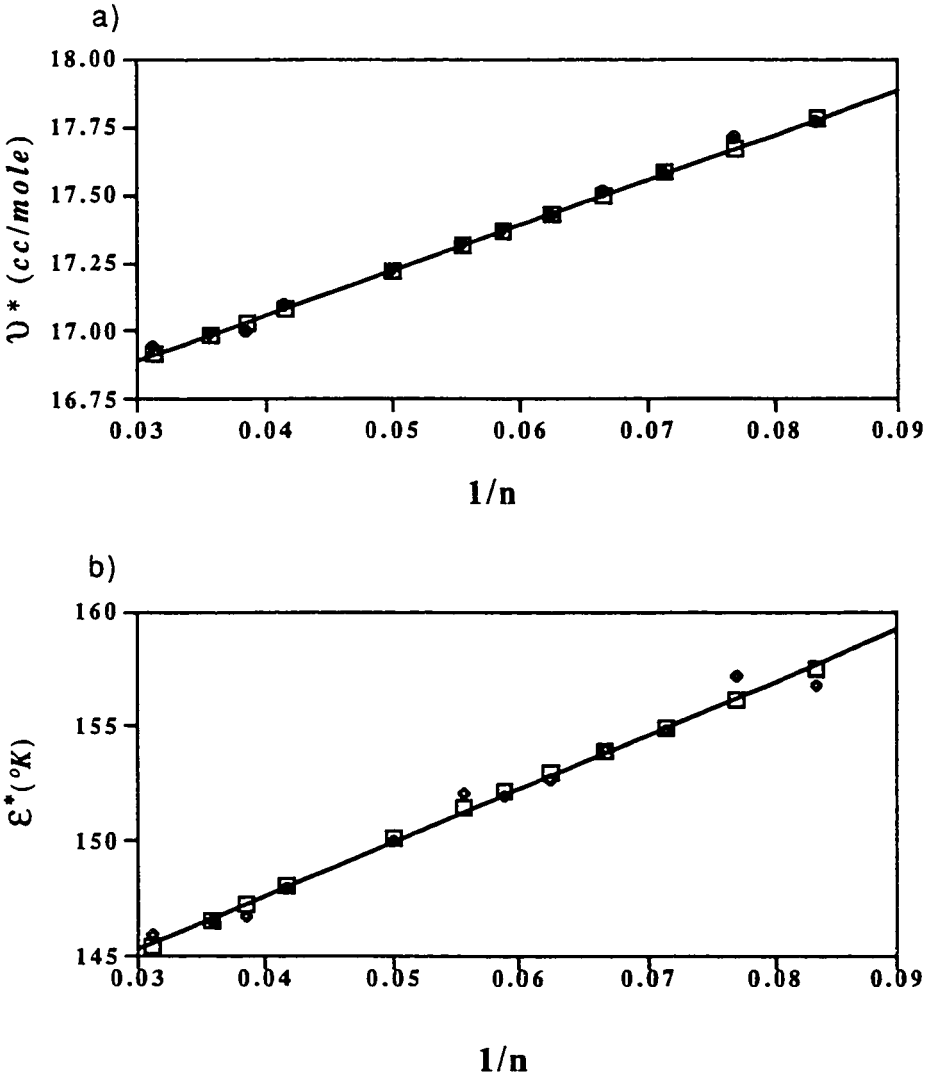


Figure 3.6. a) υ^* versus $1/n$, b) ε^* versus $1/n$. Lines are the best-fit equations on averages of υ^* and ε^*, eq. 3.3.

- ◆ calculated from the theory
- □ calculated from decomposed values of υ^*_{ij} and ε^*_{ij}

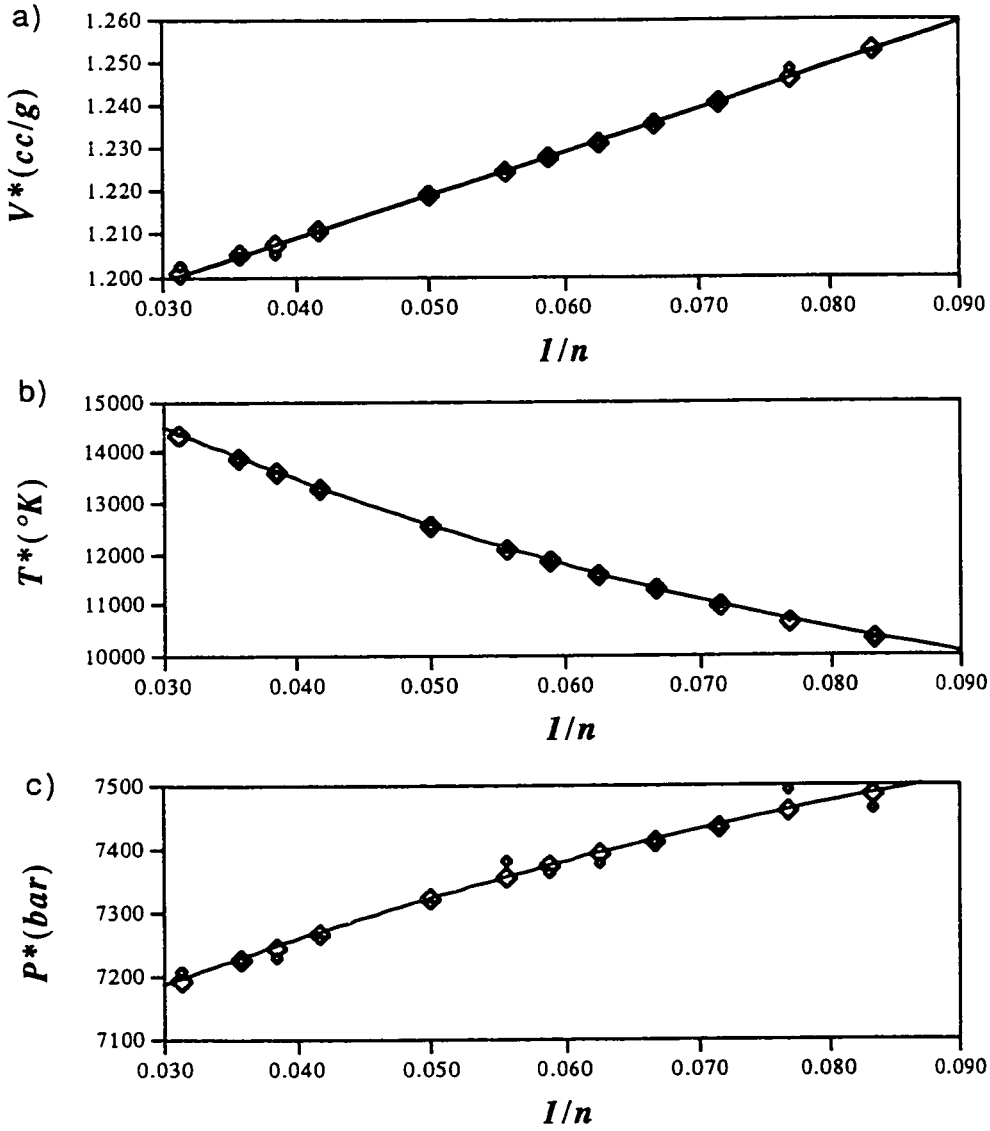


Figure 3.7. a) V^*, b) T^* and c) P^* versus $1/n$ for linear paraffins. Chain length ranges from 12 to 32.

◆ calculated from the theory

◇ calculated from the decomposed values of υ^*_{ij} and ε^*_{ij}

—— the line is the best fit curve, eq. 3.4, through theoretical values of parameters, black points.

CHAPTER 4

Application to Branched Hydrocarbons

4.1. Experimental Data and Comparison with Linear Paraffins

We employ the same source of experimental data for the branched as for the linear hydrocarbons. For four of the branched structures, namely $C_{19}H_{40}$, $C_{25}H_{52}$, $C_{31}H_{64}$, and $C_{38}H_{78}$ elevated pressure data[1,2] are available. We use these to evaluate the degrees of freedom of the branched hydrocarbons. The remainder of API data[2] at atmospheric pressure serves to evaluate the necessary characteristic parameters. Again these parameters are averages determined by dividing the branched molecule into n units, with n ranging from 10 to 50. All the branched hydrocarbons are tabulated in Table 4.1. We have chosen the symmetric structures with a single branch arm. For other and more complicated structures such as more than one branch arm and no symmetry, pressure data have not been obtained.

A comparison of volume data for linear and branched chain hydrocarbons is shown in Fig. 4.1 for three chain lengths. With increasing chain length and temperature, the differences between linear and branched hydrocarbon volumes decrease. At the highest available temperature for n=32, the difference in volume amounts to about 0.05%. This is about the corresponding deviation between theory and experiment at atmospheric pressure. The maximum difference in volume between linear and branched molecules is seen at the lowest temperature and chain-length. For n=13 at 273°K this amounts to 0.7% as seen in Fig. 4.1. This difference is sufficient to obtain new set of parameters for the branched species.

4.2 The Number of External Degrees of Freedom for Branched Hydrocarbons, $3c_b$

We make the same assumption as for n-paraffins, subdividing the chain into n repeating carbon units. The degrees of freedom of branched hydrocarbon will be determined as in the previous chapter for linear chain. That is, c is treated as an adjustable parameter, to minimize the difference between the theoretical and experimental PVT surfaces. Thus we employ the experimental API data[1] for branched hydrocarbons; $C_{19}H_{40}$, $C_{25}H_{32}$, $C_{31}H_{64}$, and $C_{38}H_{78}$. The experimental data are in the range of temperature, $37.8<T(°C)<135$, and extend from atmospheric

pressure to 3445 bar. The results and deviations in volume are tabulated in Table 4.2 below

Table 4.2. Degrees of freedom of branched hydrocarbons at n=19, 25, 31 and 38 chain lengths with the corresponding volumetric deviation from theory. The values in parenthesis are given by the best fit eq. 4.1.

n	c_b	Aver. Error%	Max. Error%	STD%
19	1.85 (1.905)	0.12	0.32	0.17
25	2.61 (2.511)	0.12	0.46	0.19
31	3.12 (3.117)	0.15	0.31	0.20
38	3.81 (3.824)	0.10	0.30	0.16

A plot of c_b, versus n, the number of carbon units, is shown in Fig. 2, together with the equation

$$c_b = 0.101n - 0.014 \pm 0.099, \qquad 19 < n < 38 \tag{4.1}$$

with maximal deviations of ±0.099 between the original c_b's and eq. 4.1. The resulting values of eq. 4.1 are included in parenthesis in Table 4.2. We will employ and test eq. 4.1 in next section for the interpolated and extrapolated branched hydrocarbons as well as those used to derive this equation in this section.

As seen from Table 4.2, the volumetric error in the theory does not exceed 0.46% up to 3445 bar pressure range. At atmospheric pressure, the maximum error is less than 0.06% (not shown in Table 4.2.)

4.3 Determination of Scaling Parameters for Chain-lengths from n=10 to n=50 Including Those Employed in Determining the Degrees of Freedom in the Previous Section.

This is to include the compounds used in the previous section. We obtain all the parameters for branched hydrocarbons from n=10 to n=50, including those employed in determining the degrees of freedom, by means of the procedures in Chapter 1. Those parameters determined are shown in Table 4.3. Figure 4.3 shows the validity of eq. 2.22. Deviations in volume is tabulated for each compound with the average and maximum errors evaluated by eq. 3.2. The maximum error is not more than 0.11% at atmospheric pressure and 1.04% at elevated pressure.

The best fit equations for the theoretical values of υ^* and ε^* of the branched hydrocarbons are given below as function of $1/n$

$$\upsilon^*(cc/mole) = 16.382 + 17.023/n$$
$$\varepsilon^*(^\circ K) = 158.49 - 485.80/n + 1302.1/n^2. \qquad (4.2)$$

These equations are tested and corresponding parameters and error in the theory are tabulated in Table 4.2 in parentheses. In Fig. 4.8, the original data (black squares) and the results of eq. 4.2 (curves) are displayed. The resulting maximum error does not exceed 0.18% at atmospheric and 1.04% at elevated pressure.

The V^*, T^* and P^* parameters are also plotted with respect to 1/n in Fig. 4.9 as black squares. The best-fit curves are drawn through the data and the best-fit equations of these parameters are given below

$$V^*(cc/g) = 1.169 + 1.024\ (1/n)$$
$$10^{-4}\ T^*(^\circ K) = 1.5617 - 4.2420\ (1/n) + 11.5356\ (1/n)^2$$
$$10^{-4}\ P^*(bar) = 0.8026 - 3.0516\ (1/n) + 7.9345\ (1/n)^2. \quad (4.3)$$

Equation 4.3 is derived with the same source of data which is used to derive eq. 4.2; therefore, we do not test the consequence of eq. 4.3. Figure 4.9 already shows the fit and reliability of eq. 4.3.

4.4 Comparison of ε^* and υ^* values of branched and linear chain

In Fig. 4.8 linear chain parameters υ^* and ε^* (white circles) are shown as functions of $1/n$ with branched ones for comparison

reason. In our range the υ^* parameters are situated approximately on the same line with at most a few percent deviation from each other. However the ε^* are surprisingly quite different. Moreover the dependencies on n differ. In the linear chain the average value of ε^* is decreasing with increasing chain-length because of the decreasing relative contribution of methyl units. But in the branched chain molecules although the same chain end should be operating, as seen on Fig. 4.8 the average value of ε^* is increasing with increasing n. The presence of the side-chain may produce shielding and non-random effects, which oppose the reduction observed in linear chains. This indicates that υ_{ij}^* and ε_{ij}^* values obtained for the latter will not be applicable, in our simplified treatment, which ignores the above effects.

4.5 Decomposition of the average values of $<\varepsilon^*>$ and $<\upsilon^*>$ into υ_{ij}^* and ε_{ij}^* for branched chain

We wish to decompose the average values of υ^* and ε^* of branched chains tabulated in Table 4.3 from n=10 to n=50 into υ_{ij}^* and ε_{ij}^* values (e. i., internal, CH_2, terminal, CH_3, and a branch point, CH, in a branched chain n-mer). We employ the polynomial equations eq. 2.37 with eq. 2.38 derived in Ch. 2.2.2 for branched chain molecules. These are two coupled equations with 12 unknown for the case of singly branched molecules.

There are some problems in the solution procedure arising from the structure of the polynomial equations. In eq. 2.37 the coefficient matrices of the polynomial equations have a degeneracy. That is, three terms have constant coefficients without a dependence on n and two terms have the identical n dependence, i.e. $r=(n-4)(z-4)$. To eliminate this degeneracy, we combine all the constant coefficient terms in one effective (2,3) interaction terms (i.e. ε^{*}_{23eff} and υ^{*}_{23eff}) and the n dependent coefficient terms together in ξ_x and ξ_y. Thus eq. 2.37 in a new form reads as follows

$$(r+p+t)^2 <\varepsilon^*><\upsilon^*>^2 = r^2\ \varepsilon^{*}_{11}\ \upsilon^{*2}_{11} + (p+t)^2\ \varepsilon^{*}_{23eff}\ \upsilon^{*2}_{23eff} + 2r\ \xi_x$$

$$(r+p+t)^2 <\varepsilon^*><\upsilon^*>^4 = r^2\ \varepsilon^{*}_{11}\ \upsilon^{*4}_{11} + (p+t)^2\ \varepsilon^{*}_{23eff}\ \upsilon^{*4}_{23eff} + 2r\ \xi_y \qquad (4.4)$$

where

$$(p+t)^2\ \varepsilon^{*}_{23eff}\ \upsilon^{*2}_{23eff} = p^2\ \varepsilon^{*}_{22}\ \upsilon^{*2}_{22} + t^2\ \varepsilon^{*}_{33}\ \upsilon^{*2}_{33} + 2pt\ \ \varepsilon^{*}_{23}\ \upsilon^{*2}_{23},$$

$$(p+t)^2\ \varepsilon^{*}_{23eff}\ \upsilon^{*4}_{23eff} = p^2\ \varepsilon^{*}_{22}\ \upsilon^{*4}_{22} + t^2\ \varepsilon^{*}_{33}\ \upsilon^{*4}_{33} + 2pt\ \ \varepsilon^{*}_{23}\ \upsilon^{*4}_{23},$$

$$\xi_x = p\ \varepsilon^{*}_{12}\ \upsilon^{*2}_{12} + t\ \varepsilon^{*}_{13}\ \upsilon^{*2}_{13},$$

$$\xi_y = p\ \varepsilon^*_{12}\ \upsilon^{*4}_{12} + t\ \varepsilon^*_{13}\ \upsilon^{*4}_{13},$$

and

$$r=(n-2)(z-4),\ p=3(z-1) \text{ and } t=(z-3)$$

Employing the chain length, n, from 10 to 50, and the resulting set is overdetermined. Employing the *PseudoInverse* Matrix method as in the solution of polynomial equations set for linear chain molecules (see Appendix A), we carry out fits to numerical data in left hand side of the polynomial equations, eq. 4.4, for branched molecules. The results are tabulated in Table 4.4 below.

Table 4.4. Decomposed parameters of branched chain molecules. The indices 1, 2 and 3 refer to methylene, methyl and the branch point respectively.

υ^*_{11}=16.377 *cc/mole*	ε^*_{11}=158.70 °K
υ^*_{23eff} = 20.024 *cc/mole*	ε^*_{23eff}=109.71 °K
ξ_x = 1.5594 10^6	ξ_y = 5.3651 10^8

We now reverse the procedure and recompute the averages and hence calculate P^*, V^* and T^*. Table 4.3 shows the results in

the third parentheses from n=10 to n=50 branched chain-lengths. The maximum error in volume does not exceed 0.17% at atmospheric pressure for the entire range of branched hydrocarbons considered and 1.03% at elevated pressures for n=19, 25, 31 and 38. Recalculated value of $\langle \upsilon^* \rangle$ and $\langle \varepsilon^* \rangle$ are plotted versus $1/n$ in Fig. 4.8. Reasonable agreement between the recomputed and original values of $\langle \upsilon^* \rangle$ and $\langle \varepsilon^* \rangle$ as function of n is seen. The maximum departures in Table 4.3 are 0.19% and 0.50% for $\langle \upsilon^* \rangle$ and $\langle \varepsilon^* \rangle$ respectively. Recalculated P^*, V^* and T^* parameters from $\langle \upsilon^* \rangle$ and $\langle \varepsilon^* \rangle$ are also shown in Fig. 4.9 as white squares. They are well-satisfactory.

References

1 R. W. Schiessler, J. A. Dixon , W. Webb, American Petroleum Institute Research Project 42 Report, 1955, The Pennsylvania State University, University Park, Pennsylvania.

2 W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Schiessler, J. Chem. Phy., 29, 727 (1958)

3 R. W. Schiessler(1947-1955), J. A. Dixon (1955-), W. Webb, American Petroleum Institute Research Project 42, 1940-1955, The Pennsylvania State University, University Park, Pennsylvania.

Table 4.1. List of the API Data[1,2] Branched Chain Hydrocarbons Employed with Temperature and Pressure Ranges

PSU #	Hydrocarbon	Structure	Empirical Formula	Molecular Weight	$T(°K)$ Range	Pressure* P_{max} (bar)
549	4-n-Propyl heptane	$C_3-\underset{\underset{C_3}{\vert}}{C}-C_3$	$C_{10}H_{22}$	142.276	273-372	1
546	5-n-Butyl-nonane	$C_4-\underset{\underset{C_4}{\vert}}{C}-C_4$	$C_{13}H_{28}$	184.354	273-372	1
500	7-n-Hexyl-tridecane	$C_6-\underset{\underset{C_6}{\vert}}{C}-C_6$	$C_{19}H_{40}$	268.510	273-408	3445
554	8-n-Hexyl-pentadecane	$C_7-\underset{\underset{C_6}{\vert}}{C}-C_7$	$C_{21}H_{44}$	296.562	273-372	1
163	9-n-Hexyl-heptadecane	$C_8-\underset{\underset{C_6}{\vert}}{C}-C_8$	$C_{23}H_{48}$	324.614	273-372	1
25	9-n-Octyl-heptadecane	$C_8-\underset{\underset{C_8}{\vert}}{C}-C_8$	$C_{25}H_{52}$	352.666	273-408	3445
63	9-n-Octyl-eicosane	$C_8-\underset{\underset{C_8}{\vert}}{C}-C_{11}$	$C_{28}H_{58}$	394.744	273-372	1
8	11-n-Decyl-heneicosane	$C_{10}-\underset{\underset{C_{10}}{\vert}}{C}-C_{10}$	$C_{31}H_{64}$	436.822	273-408	3445
7	11-n-Decyl-docosane	$C_{10}-\underset{\underset{C_{10}}{\vert}}{C}-C_{11}$	$C_{32}H_{66}$	450.848	273-372	1
107	11-n-Decyl-tetracosane	$C_{10}-\underset{\underset{C_{10}}{\vert}}{C}-C_{13}$	$C_{34}H_{70}$	478.900	273-372	1
133	13-n-Undecyl pentacosane	$C_{12}-\underset{\underset{C_{11}}{\vert}}{C}-C_{12}$	$C_{36}H_{74}$	506.952	273-372	1
134	13-n-Dodecyl-hexacosane	$C_{12}-\underset{\underset{C_{12}}{\vert}}{C}-C_{13}$	$C_{38}H_{78}$	535.004	273-408	3450
58	17-Mexadecyl tetratriaconta ne	$C_{16}-\underset{\underset{C_{17}}{\vert}}{C}-C_{16}$	$C_{50}H_{102}$	703.316	273-372	1

* Elevated pressure data is only avalible for branched C_{19}, C_{25}, C_{31} and C_{38} in the API Project 42.[1]

Table 4.3. Original[a] ,Equation[b] and Predicted[c] Characteristic Parameters of Branched Hydrocarbons

n	10	13	19	21	23	25
M_o(g)	14.228	14.181	14.132	14.122	14.114	14.107
cd	0.996	1.299	1.905	2.107	2.309	2.511
C	0.10256	0.08702	0.07339	0.07189	0.06883	0.06542
D 10^5	4.0756	3.7156	3.2901	3.1953	3.1367	3.0886
$-A$	0.1375	0.1329	0.1273	0.1268	0.1264	0.1248
B	57.6093	55.4926	53.0917	52.7907	52.5441	51.9742
V *(cc/g)	1.2713	1.2460	1.2222	1.2198	1.2156	1.2095
	(1.2711)	(1.2475)	(1.2226)	(1.2174)	(1.2132)	(1.2096)
	((1.2706))	((1.2478))	((1.2229))	((1.2176))	((1.2133))	((1.2097))
T *(°K)	12595	13066	13758	13975	14105	14148
	(12590)	(13091)	(13761)	(13916)	(14050)	(14165)
	((12589))	((13094))	((13760))	((13915))	((14048))	((14163))
P *(bar)	5767	6143	6640	6768	6862	6925
	(5765)	(6148)	(6639)	(6752)	(6849)	(6933)
	((5767))	((6148))	((6638))	((6751))	((6848))	((6932))
υ*(cc/g)	18.088	17.670	17.273	17.226	17.157	17.062
	(18.084)	(17.692)	(17.278)	(17.193)	(17.122)	(17.063)
	((18.078))	((17.696))	((17.282))	((17.196))	((17.124))	((17.064))
ε*(°K)	122.99	128.58	136.50	138.90	140.38	140.97
	(122.93)	(128.83)	(136.53)	(138.31)	(139.83)	(141.14)
	((122.93))	((128.86))	((136.53))	((138.30))	((139.82))	((141.13))
At Atmospheric Pressure						
Ave.Err%	0.061	0.040	0.054	0.052	0.043	0.063
	(0.064)	(0.041)	(0.050)	(0.098)	(0.11)	(0.066)
	((0.085))	((0.060))	((0.056))	((0.077))	((0.091))	((0.064))
Max.Err%	0.094	0.057	0.083	0.076	0.075	0.077
	(0.098)	(0.11)	(0.079)	(0.16)	(0.16)	(0.099)
	((0.13))	((0.13))	((0.11))	((0.14))	((0.15))	((0.085))
STD%	0.094	0.056	0.076	0.073	0.067	0.081
	(0.098)	(0.074)	(0.073)	(0.144)	(0.148)	(0.095)
	((0.129))	((0.095))	((0.087))	((0.122))	((0.132))	((0.086))
At Elavated Pressure[e] (up to 3445 bar)						
Ave.Err%			0.38			0.48
			(0.36)			(0.48)
			((0.34))			((0.47))
Max.Err%			0.74			1.04
			(0.72)			(1.04)
			((0.69))			((1.03))
STD%			0.52			0.63
			(0.49)			(0.63)
			((0.47))			((0.62))
V~ range	1.02-1.18	1.02-1.16	1.01-1.13	1.01-1.13	1.01-1.13	1.00-1.12

[a] computed average values (without parenthesis) from the theory.

[b] calculated average values (in parenthesis) using the best-fit equations 4.2.

[c] calculated average values (in double parenthesis) from the polynomial equations, eq. 4.3 using the defining parameters of decomposition.

[d] In given three calculations (a, b and c), the degrees of freedom is adopted from eq. 4.1 as c=0.101n-0.014.

[e] only API data at elavated pressure (PSU500, PSU25, PSU8 and PSU134.)

continuing from Table 4.3

n	28	31	32	34	36	38	50
$M_o(g)$	14.098	14.091	14.089	14.085	14.082	14.079	14.066
c	2.814	3.117	3.218	3.420	3.622	3.824	5.036
C	0.06103	0.05909	0.05705	0.05753	0.05661	0.05437	0.05002
$D\ 10^5$	3.0406	2.9763	2.9813	2.9214	2.9040	2.8972	2.7914
$-A$	0.1244	0.1241	0.1240	0.1239	0.1238	0.1236	0.1231
B	51.7349	51.5409	51.4850	51.3831	51.2920	51.2108	50.8623
$V^*(cc/g)$	1.2038	1.2011	1.1985	1.1989	1.1977	1.1948	1.1890
	(1.2051)	(1.2016)	(1.2005)	(1.1986)	(1.1969)	(1.1954)	(1.1888)
	((1.2051))	((1.2015))	((1.2004))	((1.1985))	((1.1968))	((1.1952))	((1.1886))
$T^*(°K)$	14252	14421	14394	14571	14612	14619	14918
	(14311)	(14431)	(14467)	(14533)	(14592)	(14646)	(14882)
	((14309))	(14431))	((14467))	((14533))	((14592))	((14646))	((14885))
$P^*(bar)$	7018	7123	7127	7216	7247	7271	7470
	(7038)	(7126)	(7152)	(7199)	(7242)	(7281)	(7453)
	((7038))	((7126))	((7152))	((7200))	((7243))	((7282))	((7456))
υ^*	16.971	16.924	16.886	16.887	16.866	16.822	16.725
$(cc/mole)$	(16.990)	(16.931)	(16.914)	(16.883)	(16.855)	(16.830)	(16.723)
	((16.990))	((16.930))	((16.913))	((16.881))	((16.853))	((16.828))	((16.719))
$\varepsilon^*(°K)$	142.22	144.07	143.85	145.71	146.20	146.34	149.66
	(142.80)	(144.18)	(144.58)	(145.33)	(146.00)	(146.61)	(149.30)
	((142.79))	((144.17))	((144.58))	((145.33))	((146.00))	((146.62))	((149.33))
At Atmospheric Pressure							
Ave.Err%	0.062	0.056	0.078	0.052	0.051	0.050	0.044
	(0.058)	(0.050)	(0.066)	(0.053)	(0.060)	(0.049)	(0.051)
	((0.057))	((0.052))	((0.067))	((0.052))	((0.064))	((0.053))	((0.046))
Max.Err%	0.106	0.092	0.109	0.079	0.091	0.085	0.089
	(0.11)	(0.11)	(0.18)	(0.10)	(0.12)	(0.090)	(0.12)
	((0.107))	((0.098))	((0.17))	((0.094))	((0.13))	((0.098))	((0.095))
STD%	0.086	0.078	0.10	0.075	0.077	0.073	0.070
	(0.090)	(0.076)	(0.11)	(0.076)	(0.092)	(0.075)	(0.076)
	((0.088))	((0.076))	((0.11))	((0.073))	((0.097))	((0.080))	((0.066))
At Elavated Pressure (up to 3445 bar)							
Ave.Err%		0.31				0.28	
		(0.28)				(0.26)	
		((0.29))				((0.27))	
Max.Err%		0.74				0.63	
		(0.71)				(0.59)	
		((0.72))				((0.61))	
STD%		0.44				0.38	
		(0.41)				(0.35)	
		((0.41))				((0.37))	
V~ range	1.00-1.12	1.00-1.12	1.00-1.12	1.00-1.12	1.00-1.12	1.00-1.12	1.00-1.12

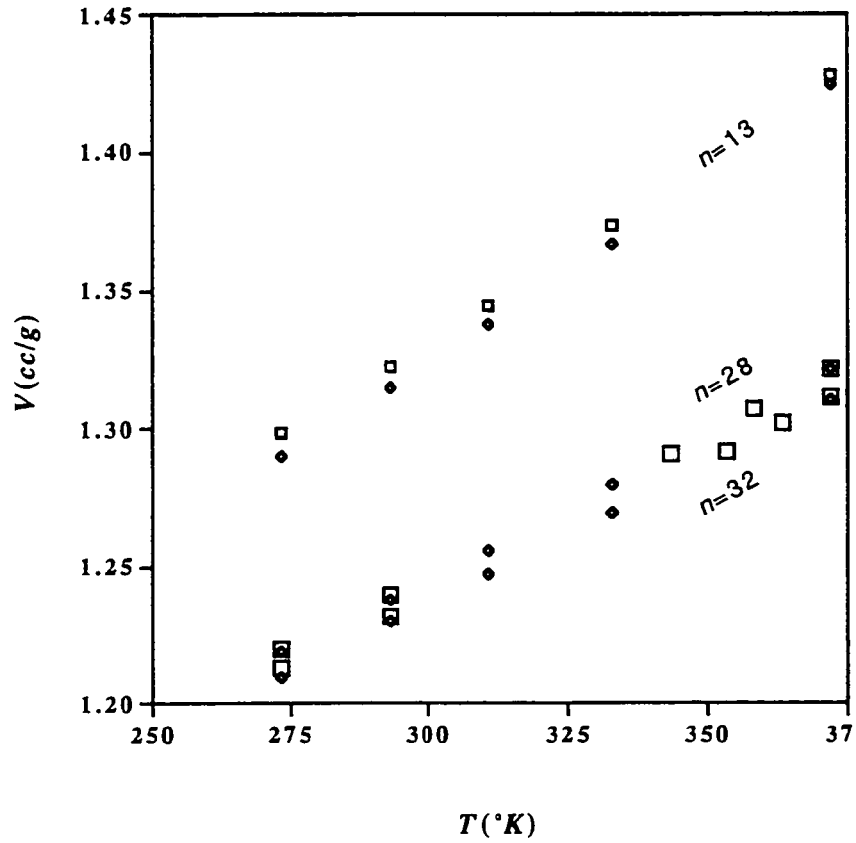


Figure 4.1. Comparison of experimental volume-temperature data at atmospheric pressure between linear and branched hydrocarbons of chain lengths n=13, 28 and 32. White squares: linear chains; black squares: branched chains.

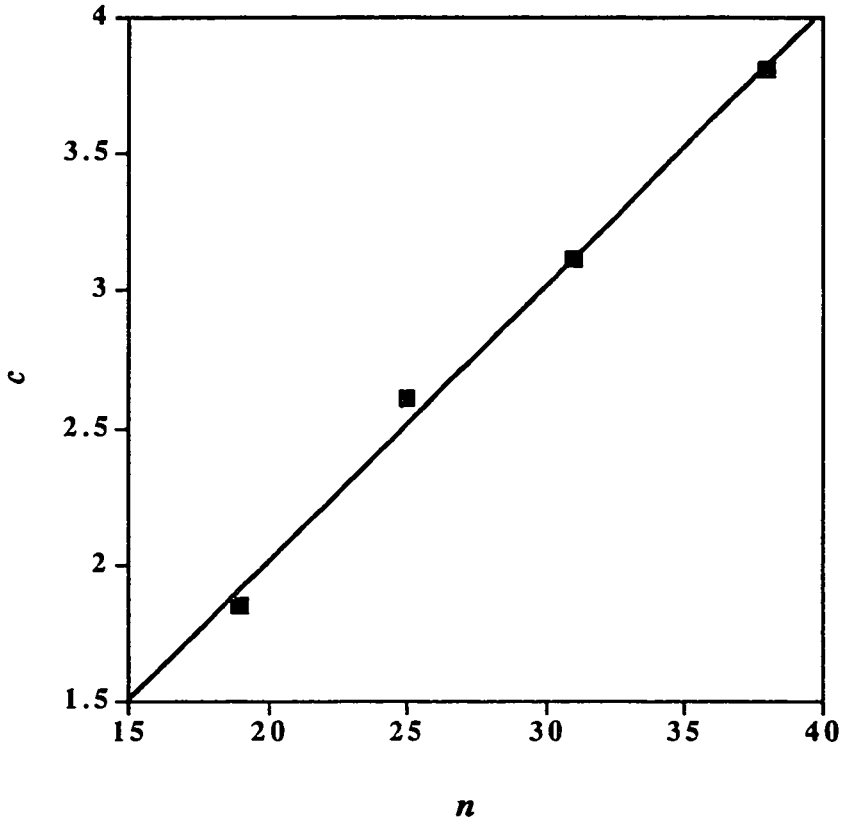


Figure 4.2. c, degrees of freedom, versus n, the number of repeating carbon unit. Black squares are the evaluated c values for branched C_{19}, C_{25}, C_{31}, and C_{38} hydrocarbons. The line is the best-fit linear relation through these values given by:

$$c=0.101n-0.014.$$

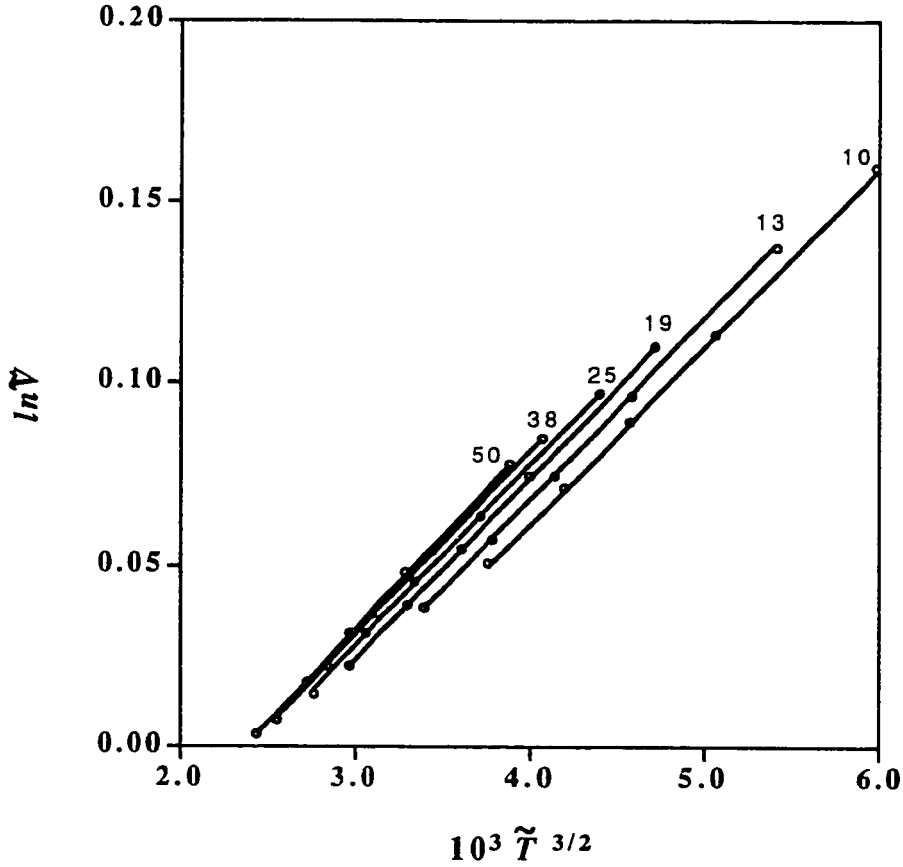


Figure 4.3. Comparison of theoretical (lines) and experimental (points) isobars at atmospheric pressure for a series of branched molecules. The molecular chain length, *n*, is shown on the top of each line.

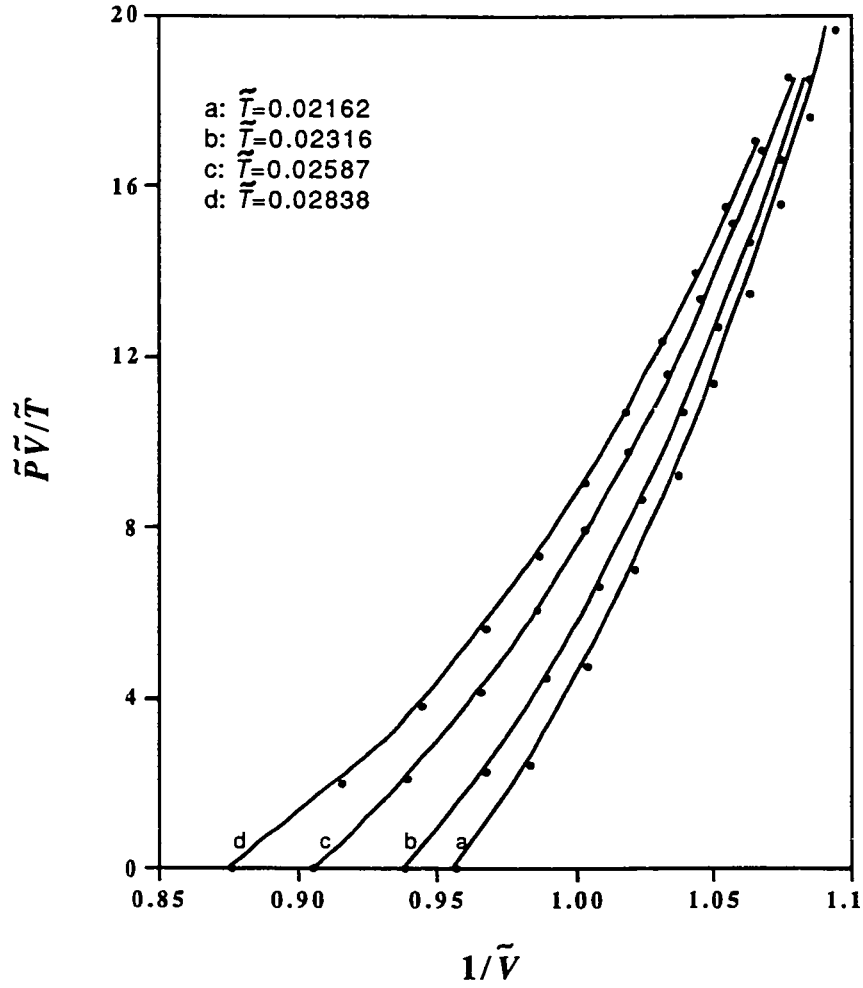


Figure 4.4. Scaled compressibility factor of 7-*n*-Hexyltridecane (n=19) as a function of scaled density: lines, theory and points, experimental.

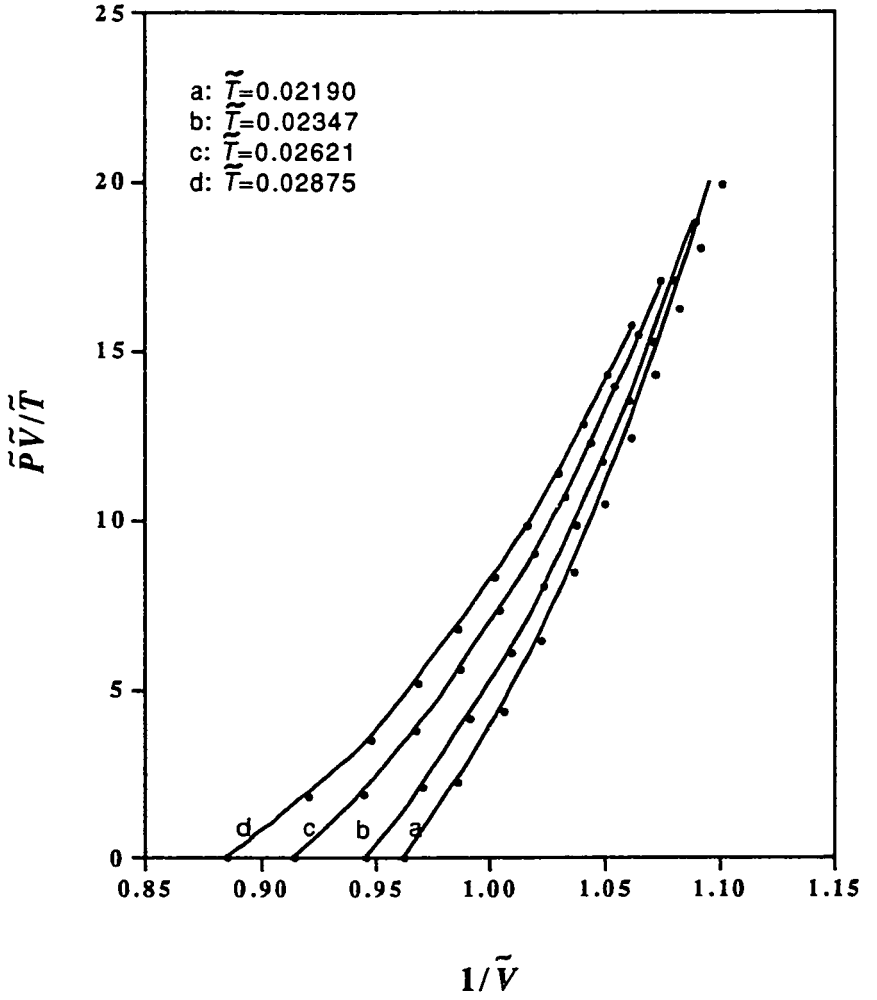


Figure 4.5. Scaled compressibility factor of 9-*n*-Octylheptadecane (*n*=25) as a function of scaled density: lines, theory and points, experimental.

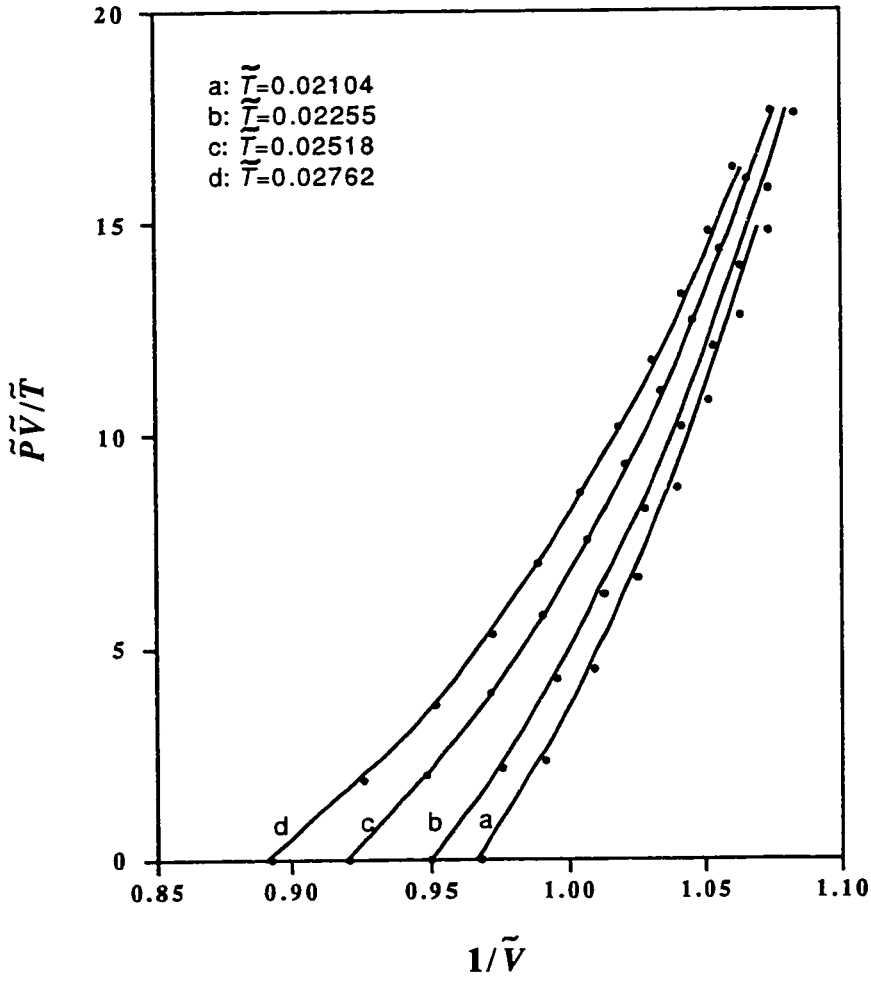


Figure 4.6. Scaled compressibility factor of 11-*n*-Decylheneicoane (n=31) as a function of scaled density: lines, theory and points, experimental.

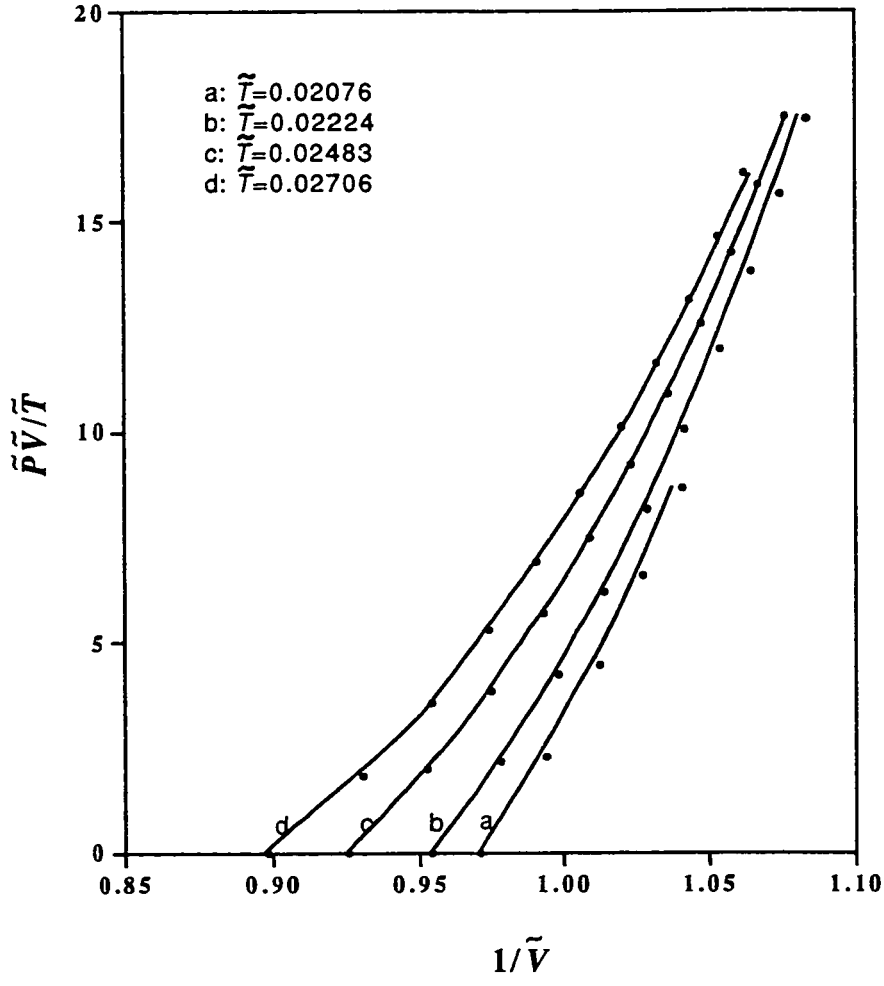
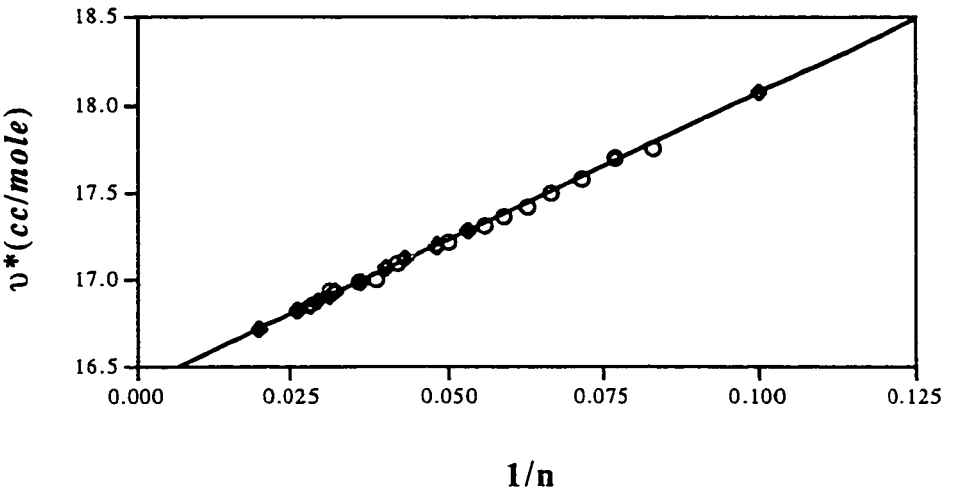


Figure 4.7. Scaled compressibility factor of 13-*n*-Dodecylhexacosane (n=38) as a function of scaled density: lines, theory and points, experimental.

a)



b)

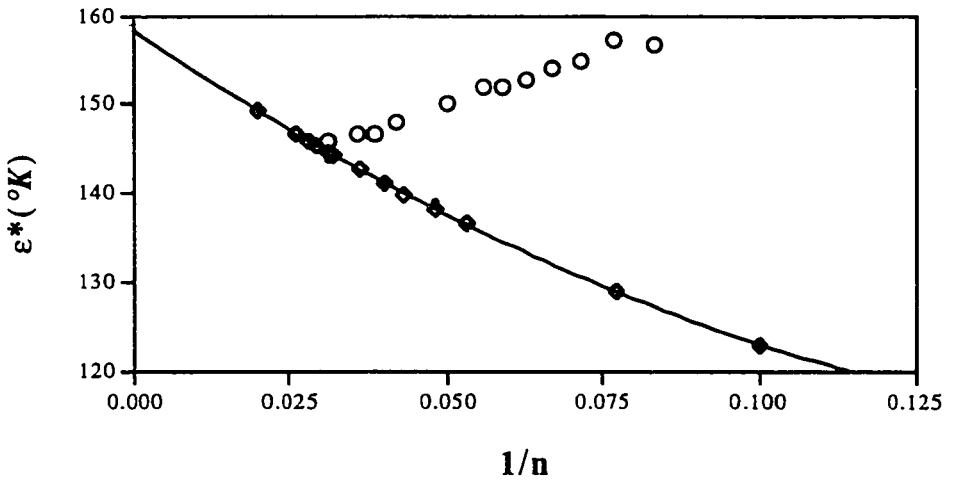


Figure 4.8. a) υ^* versus $1/n$ and b) ε^* versus $1/n$. Solid lines are the best-fit equations, eq. 4.2 through averages of υ^* and ε^*.

- • calculated from the theory
- ◇ calculated from the decomposed values of υ^*_{ij} and ε^*_{ij}
- o the theoretical parameters of linear paraffins; see Fig. 3.6

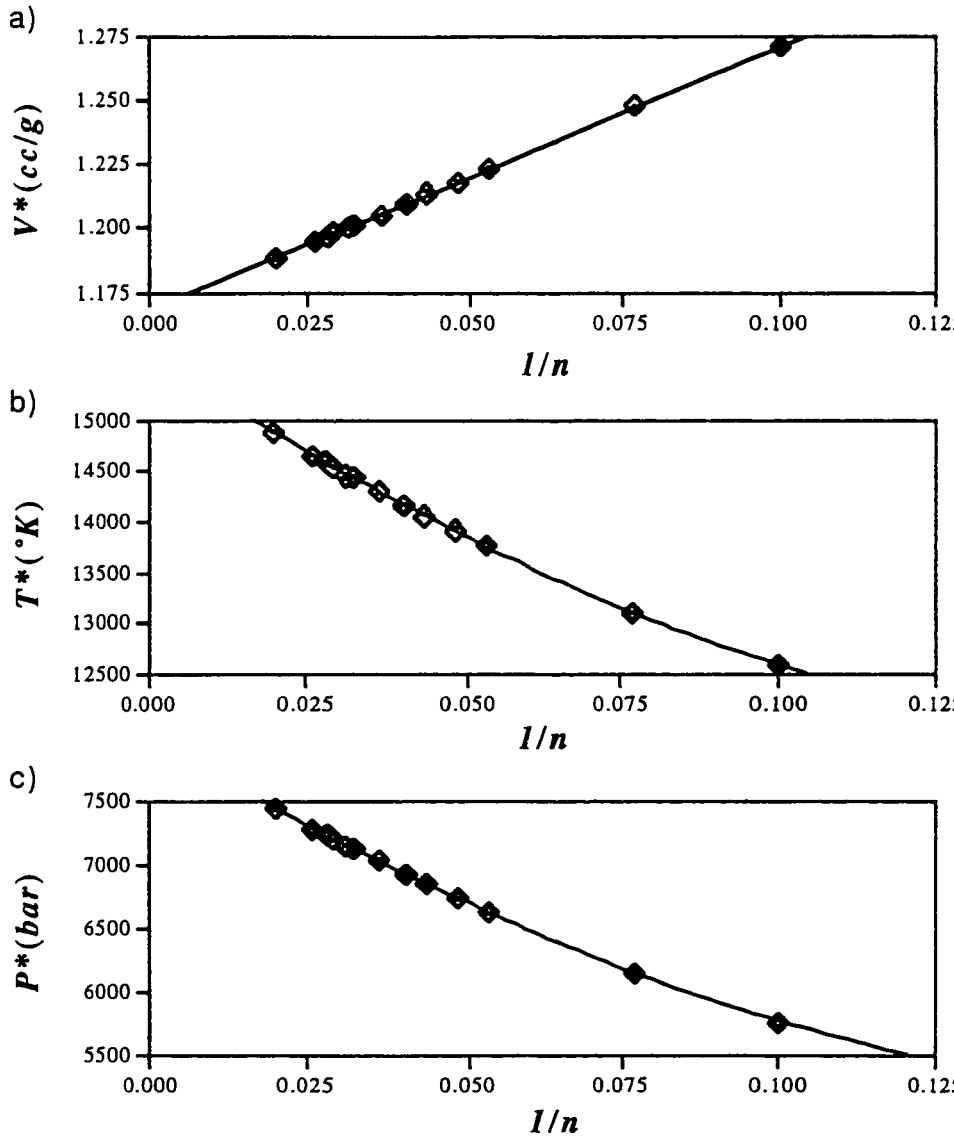


Figure 4.9. a) V^*, b) T^* and c) P^* versus $1/n$ for branched hydrocarbons. Chain length ranges from 10 to 50. The best fit curve on each plot is drawn through theoretical value of parameters, black points, given by eq. 4.3.

◆ calculated from the theory
◇ calculated from the decomposed values, Table 4.4.

CHAPTER 5

Application to Alkyl Substituted Rings

5.1 Experimental Data and Corresponding State

In this section we will analyze the contributions of ring structures attached to linear chain alkanes. The hydrocarbons employed and their structures are shown in Table 5.1, and the data are due to the project API 42[1] and refer to atmospheric pressure only. We are dealing with aromatic, saturated six or five membered rings and their combinations.

The analysis is to be guided by the analysis of *n* alkanes discussed in Chapter 3. There the segments into which the molecule was decomposed were identified with the chemical repeat unit, and placed on lattice sites.

In *n*-paraffins the size disparities between different groups are sufficiently small to be neglected. In the compounds of Table 5.1, this is no longer the case and the ring must be decomposed

into segments, particularly so in the case of unsaturated rings. Particular decomposition rules were given by Hadden and Simha[2]. Here however we proceed in a different manner. We will define a quasi-segment so that it corresponds to the same segmental volume as in the corresponding normal alkane. Hijmans[3] used a principle of corresponding states for normal alkanes from a phenomenological perspective to define the segment of the n-mer. This required shifts of V-T curves. We will use the same procedure to evaluate the quasi-segment for each ring, as related to a corresponding reference normal alkane. Consider then eq. 2.23, viz.,

$$lnV = C + D\ T^{3/2} \tag{5.1}$$

where C and D are constants for a given molecular chain-length. An identical relation is valid for the reference compound with the corresponding coefficients, C_{ref} and D_{ref}. This yields the following expressions for the volume and corresponding reference temperature ratios:

$$V/V_{ref}=exp(C-C_{ref}) \text{ and } T/T_{ref}=(D_{ref}/D)^{2/3} \tag{5.2}$$

where $V=s\upsilon_s$ and $V_{ref}=n\upsilon_n$. υ_s is the average segmental volume of the molecule and υ_n is the unit volume of the reference normal

alkane averaged over methyl and methylene units. Here we have replaced the actual molecule of interest by a model s-mer. Stipulating the equality of the segmental volumes, υ_s and υ_n at the respective temperatures, given by eq. 5.2, there follows

$$s/n=exp(C-C_{ref}) \quad \text{and} \quad T/T_{ref}=(D_{ref}/D)^{2/3}. \tag{5.3}$$

In Table 5.2, C, s/n and s values are tabulated for a few phenylalkanes. Using eq. 5.3 an average value of s_b for the benzene ring equal to about 4.7 is found. The same procedures are applied next to six and five membered saturated rings with the results exhibited in Tables 5.3 and 5.4 respectively. The average value of s_h is 5.3 for cyclohexyl (six membered saturated ring), and of s_p is 4.4 for cyclopentyl (five membered saturated ring). We note only slight fluctuations in these s values.

Finally to obtain the complete equation of state, the dependence of the c-parameter on chain length is required. Continuing with the *equivalent* chain model, we retain eq. 3.1, substituting the total chain length, s, of the molecule for n. With all this information in hand, all the characteristic parameters of the ring attached alkanes can be obtained, as shown in Tables 5.5-5.7 for phenyl, cyclohexyl and cyclopentyl alkanes respectively with either single or identical double ring terminals. Table 5.8

refers to unequal ring terminals. Figures 5.1-5.4 show the relation between scaled volumes and scaled temperatures in accord with eq. 2.22, together with the experimental points. The deviations between theory and experiment are seen as the first entries in the second parts of Tables 5.5-5.8. The max error is not larger than 0.098%, in a range of ninety nine degrees at atmospheric pressure. In the next section the decomposition into group contributions of rings will be discussed.

5.2 Decomposition of the average values of υ^* and ε^* into υ^*_{ir} and ε^*_{ir} contributions for rings

Accepting the known interaction parameters determined for normal alkanes in Table 3.4, we have to consider now the υ^*_{ir} and ε^*_{ir} (i=1, 2 and a segment of a ring such as b, h and p referring to the segment of phenyl, cyclohexyl and cyclopentyl rings respectively and $r= b, h$ and p) contributions, see eqs. 2.44 and 2.51. There are fourteen compounds with three different rings. That is, we have 24 unknowns with 28 equations and thus an overdetermined set. The combination of unknown can be found in Tables 4.9 and 4.10.

We solve the set for the decomposed values with the average υ^* and ε^* values tabulated on Tables 4.5-4.8 and with the decomposed values given in Table 3.4 evaluated in Ch. 3 for

normal paraffins. We employed the Pseudoinverse method in carrying out the best-fit solution of the polynomial equation set, eqs. 2.44 and 2.51. Tables 5.9 and 5.10 show the decomposed values of rings.

Table 5.9. Decomposed repulsive molar volume parameter of the ring segments. The indices *b* , *h* and *p* refer to the segment of phenyl, cyclohexyl and cyclopentyl rings respectively. Unit is *cc/mole*.

υ^*_{bb}=15.274	υ^*_{1b}=16.534	υ^*_{2b}=17.025
υ^*_{hh}=17.218	υ^*_{1h}=16.802	υ^*_{2h}=19.511
υ^*_{pp}=17.325	υ^*_{1p}=16.534	υ^*_{2p}=19.896
υ^*_{bh}=16.184	υ^*_{hp}=17.409	υ^*_{bp}=16.363

Table 5.10. Decomposed attractive interaction energy parameter of the ring segments. The indices *b* , *h* and *p* refer to the segment of phenyl, cyclohexyl and cyclopentyl rings respectively. Unit is *°K*.

ε^*_{bb}=189.91	ε^*_{1b}=182.68	ε^*_{2b}=132.44
ε^*_{hh}=182.81	ε^*_{1h}=166.10	ε^*_{2h}=207.40
ε^*_{pp}=188.15	ε^*_{1p}=162.64	ε^*_{2p}=268.21
ε^*_{bh}=186.67	ε^*_{hp}=192.03	ε^*_{bp}=190.05

We note that the above parameters refer to a single *equivalent* segment of the ring. Next we reverse the procedure and recompute the averages and hence P^*, V^* and T^*. All these parameters are shown as the second entries (in parentheses) of Tables 5.5-5.8. Comparisons between resulting theoretical and experimental volumes are also given in Tables 5.5-5.8. The observed maximum error, in volume does not exceed 0.13%, when the recomputed parameters υ^* and ε^* are employed.

5.3. Prediction of *PVT* surface of Alkylbenzenes at elevated pressure.

We will test the decomposed values derived in the previous section for the phenyl rings in the prediction of the *PVT* surface of some alkylbenzenes. We have butylbenzene, hexylbenzene, octylbenzene and nonylbenzene *PVT* data[4] in the range of temperature from 293 to 345 $^{\circ}K$ and of pressure from atmospheric to 400 *bar*. Our parameters are determined in the range of chain-lengths s=11.4 to s=24.7. We will then interpolate the parameters for octylbenzene and nonylbenzene, but extrapolate for butylbenzene and hexylbenzene. Employing the polynomial equation, eq. 2.44, with the decomposed parameters given in Tables 3.4, 5.9 and 5.10, we evaluate the parameters of interest. Using these parameters we compare the theoretical *PVT* surface with the experimental *PVT* data at the given temperature and pressure ranges. The maximum error in volume for

butylbenzene is 1.43%. It is at an extrapolated chain-length. But in the interpolated range, the maximum error in volume does not exceed 0.75% for the data. Table 5.11 shows all the parameters calculated and errors in volume.

References

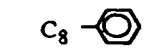
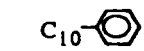
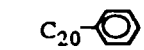
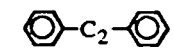
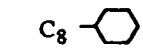
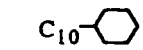
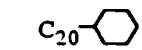
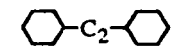
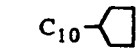
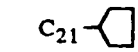
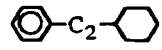
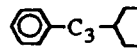
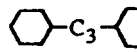
1 R. W. Schiessler(1947-1955), J. A. Dixon (1955-), W. Webb, *American Petroleum Institute Research Project 42*, 1940-1955, The Pennsylvania State University, University Park, Pennsylvania.

2 R. Simha and S. T. Hadden, *J. Chem. Phys.*, **25**, 702, (1956); S. T. Hadden and R. Simha, *ibid.*, **36**, 1104 (1962); *J. Chem. Eng. Data*, **7**, 444 (1962).

3 J. Hijmans, *Physica*, **27**, 433 (1961).

4 Honggang Zhou, Bernard Lagourette, Jacques Alliez and Pierre Xans, *Fluid Phase Equilibria*, **59**, 309 (1990).

Table 5.1. Ring Added Linear Chain Hydrocarbons of API Data* and Temperature Ranges at Atmospheric Pressure

PSU #	Hydrocarbon	Structure	Empirical Formula	Molecular Weight	$T(°K)$ Range
538	1-Phenyl-octane		$C_{14}H_{22}$	190.316	273-372
571	1-Phenyl-decane		$C_{16}H_{26}$	218.368	273-372
99	1-Phenyl-eicosane		$C_{26}H_{46}$	358.628	273-372
519	1,2-Diphenyl-ethane		$C_{14}H_{14}$	182.252	273-372
539	1-Cyclohexyl-octane		$C_{14}H_{28}$	196.364	273-372
572	1-Cyclohexyl-decane		$C_{16}H_{32}$	224.416	273-372
100	1-Cyclohexyl-eicosane		$C_{26}H_{52}$	364.676	273-372
520	1,2-Dicyclo-hexylethane		$C_{14}H_{26}$	194.348	273-372
573	1-Cyclopentyl decane		$C_{15}H_{30}$	210.390	273-372
117	1-Cyclopentyl heneicosane		$C_{26}H_{52}$	364.676	273-372
551	Bicyclopentyl		$C_{10}H_{18}$	138.244	273-372
521	1-Phenyl-2-cyclohexyl-ethane		$C_{14}H_{20}$	188.300	273-372
522	1-Phenyl-3-Cyclopentyl propane		$C_{14}H_{20}$	188.300	273-372
523	1-cyclohexyl-3-Cyclopentyl propane		$C_{14}H_{26}$	194.348	273-372

* All these data are available at atmospheric pressure in the API Project 42.[1]

Table 5.2. Corresponding segment for phenylalkanes compared with the same chain length of the normal paraffins. Entry below ring compound denotes reference compound.

PSU#	Structure	Empirical Formula	$10^2 xC$	$s/n = exp(C-C_r)$	s	s_b
538	C_8-⬡	$C_{14}H_{22}$	-0.887	0.904	12.66	4.6_6
531	*n*-C_{14}	$C_{14}H_{30}$	9.264		14	
571	C_{10}-⬡	$C_{16}H_{26}$	-0.017	0.918	14.69	4.6_9
534	*n*-C_{16}	$C_{16}H_{34}$	8.532		16	
99	C_{20}-⬡	$C_{26}H_{46}$	1.551	0.953	24.78	4.7_8
106	*n*-C_{26}	$C_{26}H_{54}$	6.370		26	
519	⬡-C_2-⬡	$C_{14}H_{14}$	-13.58	0.796	11.14	4.5_7
531	*n*-C_{14}	$C_{14}H_{30}$	9.264		14	
					Average s_b for ring ≡ 4.7	

Table 5.3. Corresponding segment for cyclohexylalkanes compared with the same length of the normal paraffins. Entry below ring compound denotes reference compound.

PSU#	Structure	Empirical Formula	$10^2 xC$	$s/n = exp(C\text{-}Cr)$	s	s_h
536	C_8-⬡	$C_{14}H_{28}$	4.159	0.950	13.30	5.3_0
531	*n*-C_{14}	$C_{14}H_{30}$	9.264		14	
572	C_{10}-⬡	$C_{16}H_{32}$	4.335	0.959	15.34	5.3_4
534	*n*-C_{16}	$C_{16}H_{34}$	8.532		16	
100	C_{20}-⬡	$C_{26}H_{52}$	3.805	0.975	25.35	5.3_5
106	*n*-C_{26}	$C_{26}H_{54}$	6.370		26	
520	⬡-C_2-⬡	$C_{14}H_{26}$	-1.533	0.898	12.57	5.2_9
531	*n*-C_{14}	$C_{14}H_{30}$	9.264		14	
					Average s_h for ring ≡	5.3

Table 5.4. Corresponding segment for cyclopentylalkanes compared with the same lenght of the normal paraffins. Entry below ring compound denotes reference compound.

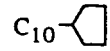
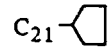
PSU#	Structure	Empirical Formula	$10^2 xC$	$s/n = exp(C\text{-}Cr)$	s	s_p
573	C_{10}- 	$C_{15}H_{30}$	4.777	0.962	14.43	4.4_3
532	*n*-C_{14}	$C_{15}H_{32}$	7.701		14	
117	C_{21}- 	$C_{26}H_{52}$	3.892	0.976	25.38	4.3_8
106	*n*-C_{26}	$C_{26}H_{54}$	6.370		26	
551		$C_{10}H_{18}$	-2.043	0.877	8.77	4.3_9
	n-C_{10}	$C_{10}H_{22}$	11.100		10	
				Average s_p for ring	≡	4.4

Table 5.5. Original[1] and Calculated[2] Characteristic Parameters of Phenylalkanes.

PSU #	PSU538	PSU571	PSU99	PSU519
$M_o(g)$	14.986	14.855	14.519	15.987
c	1.912	2.052	2.752	1.821
s	12.7	14.7	24.7	11.4
10^2C	-0.887	-0.017	1.551	-13.584
10^5D	3.256	3.113	2.827	2.927
$-A$	0.1198	0.1208	0.1226	0.1182
B	39.081	41.000	47.612	37.504
$V^*(cc/g)$	1.1174 (1.1183)	1.1282 (1.1270)	1.1481 (1.1484)	0.9825 (0.9825)
$T^*(°K)$	11295 (11307)	12015 (12000)	14155 (14158)	11798 (11798)
$P^*(bar)$	8444 (8446)	8321 (8319)	7866 (7866)	9975 (9975)
$\upsilon^*(cc/mole)$	16.745 (16.758)	16.759 (16.741)	16.670 (16.674)	15.707 (15.707)
$\varepsilon^*(°K)$	167.41 (167.59)	165.47 (165.26)	156.44 (156.48)	185.21 (185.21)
At Atmospheric Pressure				
Ave.Err%	0.038 (0.045)	0.043 (0.086)	0.047 (0.051)	0.055 (0.055)
Max.Err%	0.057 (0.091)	0.060 (0.13)	0.088 (0.10)	0.084 (0.084)
STD%	0.051 (0.070)	0.055 (0.12)	0.068 (0.069)	0.063 (0.063)
$\tilde{V}$ range	1.01-1.13	1.01-1.13	1.00-1.12	1.00-1.12

1 computed average values (without parenthesis) from the theory adopting $c=0.07n+1.023$ derived for the linear chain molecules.

2 calculated average values (in parenthesis) from the polynomial equation using the υ^*ij and ε^*ij parameters.

Table 5.6. Original[1] and Calculated[2] Characteristic Parameters of Cyclohexylalkanes

PSU #	PSU539	PSU572	PSU100	PSU520
$M_o(g)$	14.764	14.668	14.414	15.424
c	1.954	2.094	2.794	1.905
s	13.3	15.3	25.3	12.6
10^2C	4.159	4.335	3.805	-1.533
10^5D	3.266	3.123	2.902	2.985
$-A$	0.1201	0.1210	0.1227	0.1188
B	39.682	41.531	47.922	38.774
$V^*(cc/g)$	1.1755 (1.1771)	1.1787 (1.1764)	1.1744 (1.1748)	1.1091 (1.1091)
$T^*(°K)$	11385 (11437)	12094 (12022)	13971 (13988)	11905 (11905)
$P^*(bar)$	8013 (8039)	7960 (7929)	7578 (7585)	8748 (8748)
$\upsilon^*(cc/mole)$	17.355 (17.380)	17.289 (17.255)	16.928 (16.934)	17.107 (17.107)
$\varepsilon^*(°K)$	164.79 (165.54)	163.38 (162.42)	153.08 (153.26)	177.17 (177.17)
At Atmospheric Pressure				
Ave.Err%	0.058 (0.051)	0.041 (0.061)	0.042 (0.042)	0.064 (0.064)
Max.Err%	0.075 (0.094)	0.059 (0.097)	0.074 (0.075)	0.091 (0.091)
STD%	0.073 (0.070)	0.055 (0.085)	0.063 (0.064)	0.078 (0.078)
$\tilde{V}$ range	1.01-1.13	1.01-1.13	1.01-1.12	1.00 -1.12

1 computed average values (without parenthesis) from the theory adopting $c=0.07n+1.023$ derived from the linear chain molecules.

2 calculated average values (in parenthesis) from the polynomial equation using the υ^*_{ij} and ε^*_{ij} parameters.

Table 5.7. Original[1] and Calculated[2] Characteristic Parameters of Cyclopentylalkanes.

PSU #	PSU573	PSU117	PSU551
$M_0(g)$	14.610	14.357	15.710
c	2.031	2.801	1.639
s	14.4	25.4	8.8
10^2C	4.778	3.892	-2.043
10^5D	3.234	2.952	3.304
$-A$	0.1207	0.1227	0.1183
B	40.727	47.973	34.700
$V^*(cc/g)$	1.1834	1.1755	1.1028
	(1.1834)	(1.1755)	(1.1028)
$T^*(°K)$	11661	13823	10332
	(11661)	(13823)	(10332)
$P^*(bar)$	7909	7510	9235
	(7909)	(7510)	(9235)
$\upsilon^*(cc/mole)$	17.290	16.877	17.325
	(17.290)	(16.877)	(17.325)
$\varepsilon^*(°K)$	162.22	151.24	188.15
	(162.22)	(151.24)	(188.15)
At Atmospheric Pressure			
Ave.Err%	0.044	0.048	0.027
	(0.044)	(0.048)	(0.027)
Max.Err%	0.098	0.077	0.041
	(0.098)	(0.077)	(0.041)
STD%	0.069	0.065	0.034
	(0.069)	(0.065)	(0.034)
$\tilde{V}$ range	1.01-1.13	1.00-1.12	1.02-1.14

1 computed average values (without parenthesis) from the theory adopting $c=0.07n+1.023$ derived from the linear chain molecules.

2 calculated average values (in parenthesis) from the polynomial equation using the υ^*_{ij} and ε^*_{ij} parameters. We do not have overdetermined equations so that we end up with the same original value for these listed hydrocarbons.

Table 5.8. Original[1] and Calculated[2] Characteristic Parameters of Different Rings Attached.

PSU #	PSU521	PSU522	PSU523
$M_o(g)$	15.692	15.562	15.303
c	1.863	1.870	1.912
s	12.0	12.1	12.7
10^2C	-7.249	-6.380	-0.779
10^5D	2.967	2.984	2.983
$-A$	0.1185	0.1186	0.1189
B	38.151	38.257	38.875
$V^*(cc/g)$	1.0471 (1.0471)	1.0563 (1.0563)	1.1175 (1.1175)
$T^*(°K)$	11824 (11824)	11801 (11801)	11930 (11930)
$P^*(bar)$	9289 (9289)	9225 (9225)	8733 (8733)
$\upsilon^*(cc/mole)$	16.431 (16.431)	16.438 (16.438)	17.101 (17.101)
$\varepsilon^*(°K)$	180.56 (180.56)	179.41 (179.41)	176.82 (176.82)
At Atmospheric Pressure			
Ave.Err%	0.058 (0.058)	0.059 (0.059)	0.029 (0.029)
Max.Err%	0.082 (0.082)	0.111 (0.111)	0.050 (0.050)
STD%	0.067 (0.067)	0.073 (0.073)	0.038 (0.038)
$\tilde{V}$ range	0.93-1.05	0.93-1.05	1.00-1.12

1 computed average values (without parenthesis) from the theory adopting $c=0.07n+1.023$ derived from the linear chain molecules.

2 calculated average values (in parenthesis) from the polynomial equation using the υ^*_{ij} and ε^*_{ij} parameters. We do not have overdetermined equations so that we end up with the same original value for these listed hydrocarbons.

Table 5.11. Predicted[1] Characteristic Parameters and *PVT* surface of Phenylalkanes at Elevated Pressure.[2]

Molecule	Butylbenzene	Hexylbenzene	Octylbenzene	Nonylbenzene
Structure	C_4 	C_6 	C_8 	C_9 
Emprical Formula	$C_{10}H_{14}$	$C_{12}H_{18}$	$C_{14}H_{22}$	$C_{15}H_{24}$
$M_o(g)$	15.427	15.165	14.986	14.916
c	1.632	1.772	1.912	1.982
s	8.7	10.7	12.7	13.7
$V^*(cc/g)$	1.0880	1.1061	1.1183	1.1270
$T^*(°K)$	9331	10446	11307	11671
$P^*(bar)$	8671	8575	8446	8381
$\upsilon^*(cc/mole)$	16.784	16.774	16.758	16.749
$\varepsilon^*(°K)$	171.10	169.82	167.59	166.41
		At Elevated Pressure[2]		
Ave.Err%	1.11	0.90	0.16	0.58
Max.Err%	1.43	1.13	0.36	0.75
STD%	1.35	1.07	0.22	0.70

1 calculated average values from the polynomial equation, eq. 2.44 using the υ^*_{ij} and ε^*_{ij} parameters with $c=0.07n+1.023$ derived for the linear chain molecules. The segment of the phenyl ring is taken as $s_b=4.7$ derived in Table 5.2.

2 Pressure range is given from atmospheric to 400 bar. And temperature range is also given from 293 °*K* to 353 °*K*.

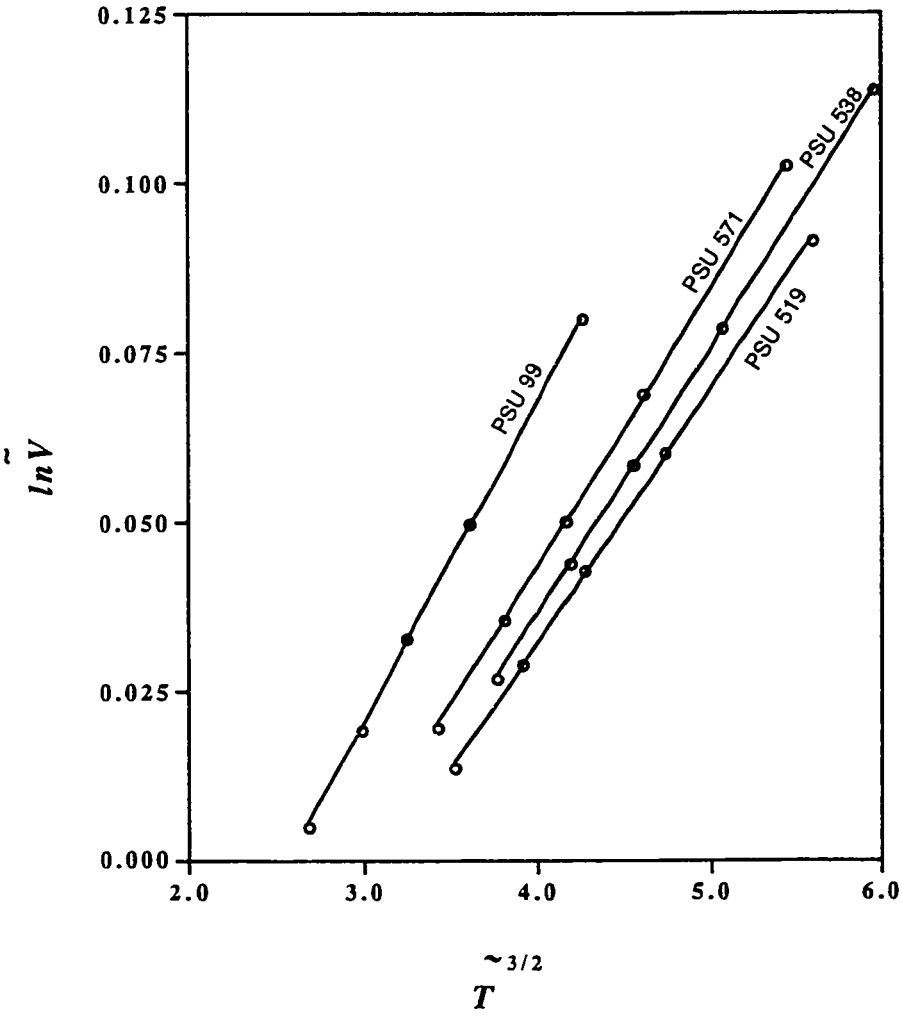


Figure 5.1. Comparison of theoretical (lines) and experimental (points) isobars at atmospheric pressure for a series of aromatic ring attached to a linear chain. PSU, the molecular identification number, is put on the each line (see Table 1.)

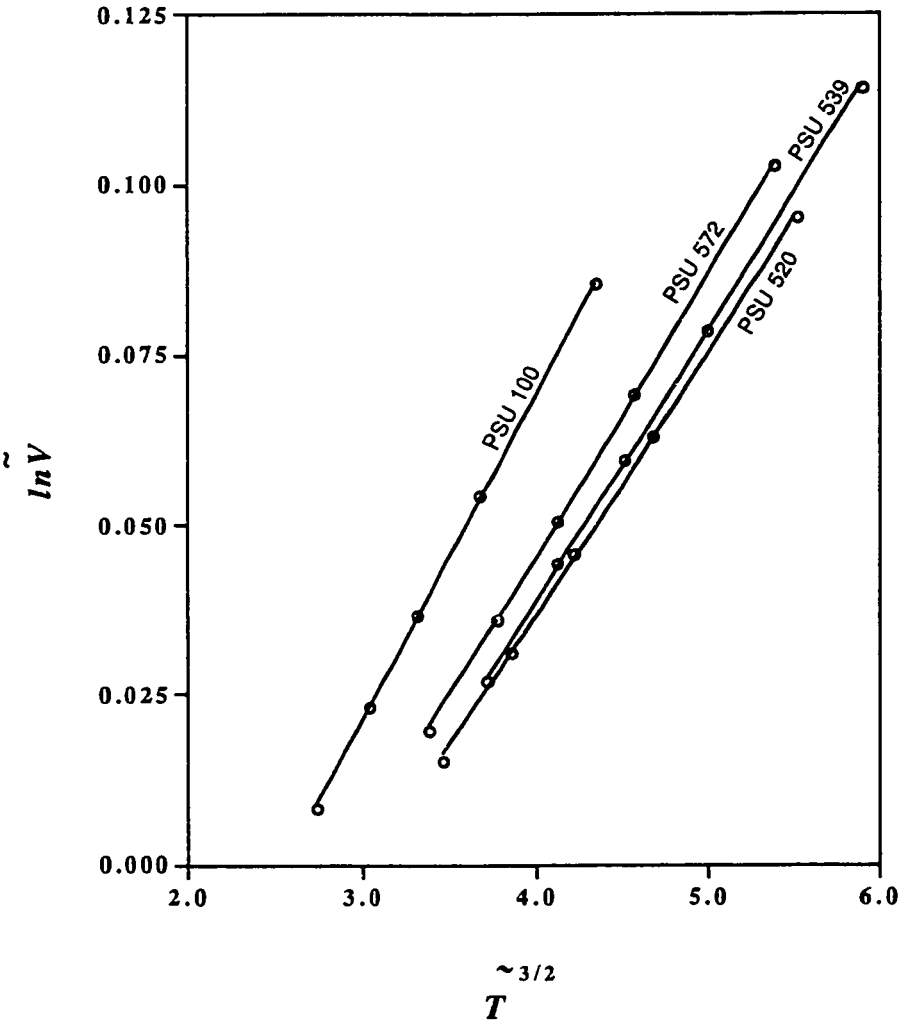


Figure 5.2. Comparison of theoretical (lines) and experimental (points) isobars at atmospheric pressure for a series of six members of cyclic ring attached to a linear chain. PSU, the molecular identification number, is put on the each line (see Table 1.)

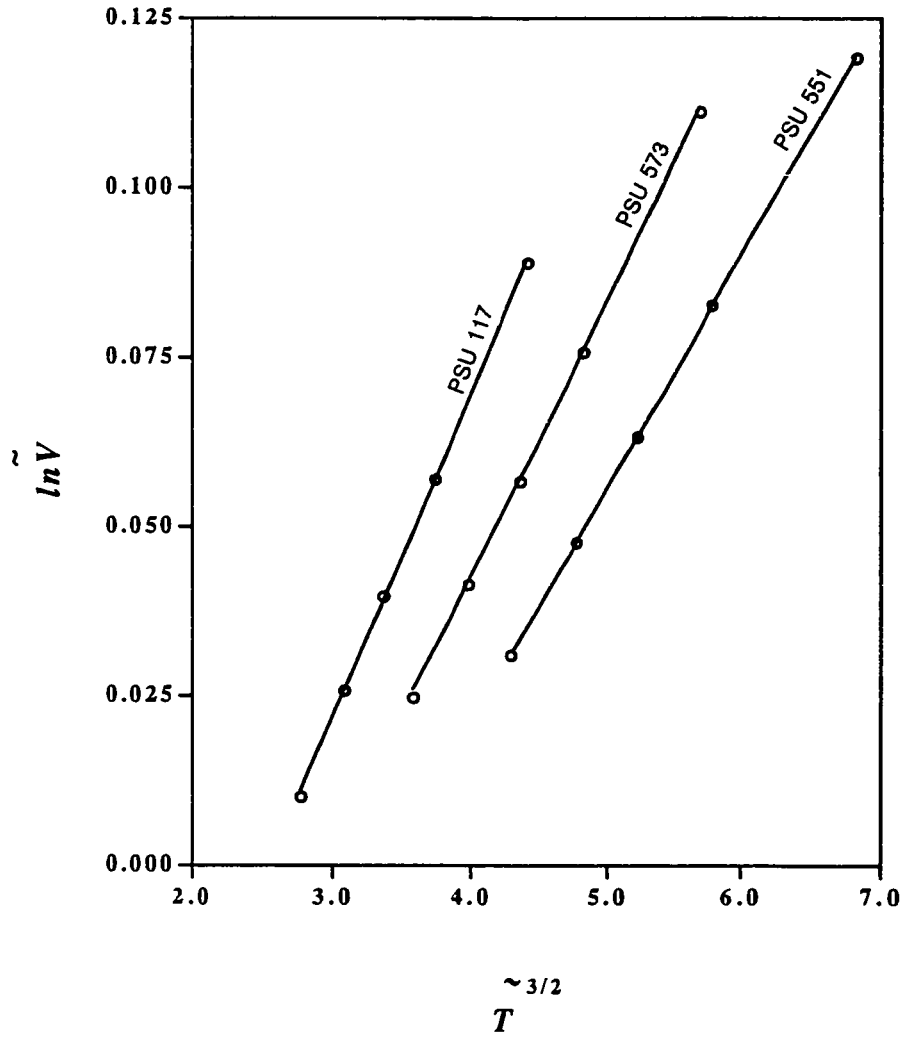


Figure 5.3. Comparison of theoretical (lines) and experimental (points) isobars at atmospheric pressure for a series of five members of cyclic ring (pentyl) attached to a linear chain. PSU, the molecular identification number, is put on the each line (see Table 1.)

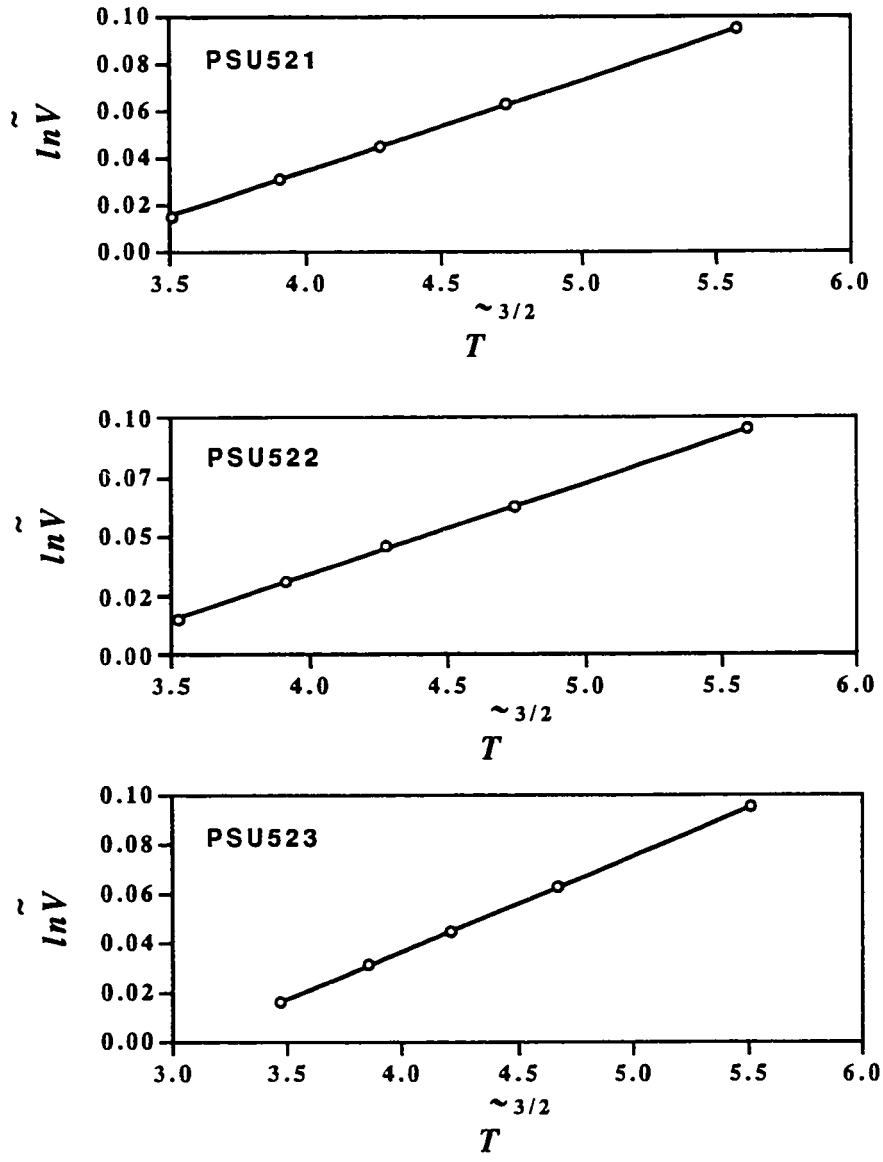


Figure 5.4. Comparison of theoretical (lines) and experimental (points) isobars at atmospheric pressure for two different terminated rings attached. PSU, the molecular identification number, is put on the each line (see Table 5.1.)

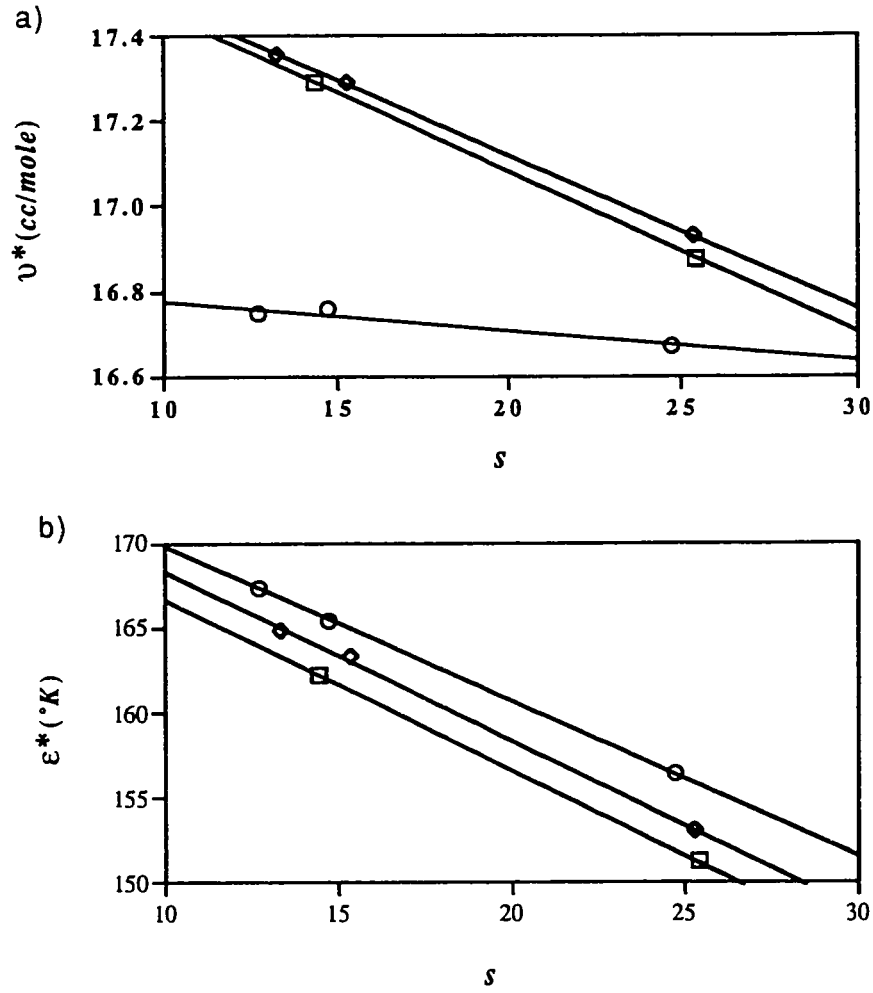


Figure 5.5. a)v^*(*cc/mole*) and b) ε^*(*°K*) versus *s* plot. Lines are the best-fit linear curves through the data available.

□ Cyclopentylalkanes
◇ Cyclohexylalkanes
○ Phenylalkanes

CHAPTER 6

Characteristic Repulsion and Attraction Parameters versus Van der Waals Volume and Cohesive Energy Respectively

6.1 Correlation between the repulsion and the Van der Waals Volumes

In this section we correlate the characteristic repulsion volume υ^* versus the Van der Waals volume, V_w. Van Krevelen[1] and Bondi[2] calculated and summarized a large number of data on the Van der Waals volume of constituent groups. Assuming additivity, V_w can be computed for the whole molecule.

6.1.1 Van der Waals volumes of Structural Units and Groups

The Van der Waals volume V_w of an atom is determined by the outer shell of the atom.[1] In case of two neutral atom or molecule without having any chemical interaction, their Van der Waals volumes will be determined by their closest distance, that is, the sum of their atomic Van der Waals volumes. If they react and combine in a new molecule, the Van der Waals volumes of combined molecules will be smaller than those of the composing atoms.

The Van der Waals volume of a particular unit or structure can be estimated by presuming that the impenetrable space occupied by the molecule is confined by the outer surface of a number of interpenetrating species.[1] To calculate the Van der Waals volume[2] of a molecule, the bond distance, the sum of the adjacent covalent atomic radii and the nonbonded contact radii (the Van der Waals radii) of constituent atoms, are necessary from experimental data. These radii are assumed to be constant. The method used is completely by means of solid geometry. Bondi[2] gives the detailed description of the calculation based on a diatomic molecule. Van Krevelen[1] gives the contribution of a given atom A with radius to the Van der Waals volume as below

$$V_{w.A} = N_A\left[\frac{4}{3}\pi R^3 - \sum \pi h_i^2\left(R - \frac{h_i}{3}\right)\right]$$

$$h_i = R - \frac{l_i}{2} - \frac{R^2}{2l_i} + \frac{r_i^2}{2l_i} \qquad (6.1)$$

where N_A is Avogadro's number, r_i is the Van der Waals radii of ith atom, and l_i is the covalent bond distance with the ith atom. The volume contribution eq. 6.1 of the atom depends on the geometry of the surrounding impenetrable atoms.

Bondi[2] calculated the Van der Waals volumes of some sixty structural groups. The Van der Waals volumes of the whole polymer or molecular chain is then approximated by the sum of the group contribution of the structural units or groups. Each structural group contains the contribution of the Van der Waals volume of the impenetrable atoms. In Table 6.1 we display the Van der Waals volumes of interest taken from Van Krevelen[1] and Bondi[2].

6.1.2 Characteristic Repulsion Volumes versus Van der Waals volumes

Characteristic repulsion volumes of interest are calculated in previous chapters as in Table 6.1. To obtain v_{II}^* (I refer to whole phenyl, cyclopentyl or cyclohexyl rings) for a ring, the values shown in Tables 9 and 10 in Chapter 5 are multiplied by the respective s_r-values. v_{ii}^* are plotted versus V_w in Fig. 6.1. The best-fit equation through these data points is a linear function, viz.:

$$v_{ii}^{*}=1.59V_w + 1.00 \pm 2.44. \qquad (6.2)$$

Table 6.1. Group contribution of Van der Waals and characteristic repulsion volumes for our structural units. The data in the parenthesis show the results of eq. 6.2.

Group	M_Q (g)	V_w (cc/mole)	v_{ii}^{*}(cc/mole)
Methylene	14.03	10.23	16.480 (17.266)
Methyl	15.03	13.67	23.589 (22.735)
Phenyl	77.10	45.85	71.788 (73.902)
Cyclopentyl	69.12	46.5	76.230 (74.935)
Cyclohexyl	83.15	56.8	91.255 (91.312)

The value (±2.44) in eq. 6.2 is the estimate of variance. Equation 6.2 yields the results shown in the parenthesis on Table 6.2. Maximum deviations from the original values are less than 5%.

We note that Simha and Carri[3] obtained for *n*-paraffins, benzene and carbontetrachloride a factor of 1.6 with a small intercept. The significance of this result is first to show a consistent correspondence between two quantities obtained by

such different operations; that is one by means of theory from measurements in the dense fluid, and the other from structural geometry and hard core atomic values. Second it makes it possible to estimate the scaling temperature and hence predict an atmospheric pressure isobar based on a single experimental point in the V-T plane.[3]

6.2 Correlation Between the Characteristic Attraction and Cohesive Energies

In this section we correlate the characteristic total attraction energy, $q_z\varepsilon^*/2$, versus cohesive energy, E_{coh}. Van Krevelen[1,4] tabulated contributions of cohesive energy of groups, including the cohesive energy of other authors. Assuming the additivity method, E_{coh} can be predicted for the whole molecule of interest.

6.2.1 Cohesive Energy

The cohesive energy is defined as the increase in internal energy of the molecule transformed from a condensed state into an ideal solution, e.i., all the intermolecular forces are eliminated.[1,4] For liquids of low molecular mass, the cohesive energy can be determined from the heat of vaporization below

$$E_{\text{coh}} = \Delta U_{\text{vap}} = \Delta H_{\text{vap}} - \text{p}\Delta V \approx \Delta H_{\text{vap}} - RT \qquad (6.3)$$

For liquids of low molecular mass, group additivity technique has been developed and used for many years. Cohesive energy of the whole polymer or molecular chain is then approximated by the sum of the group contribution of the structural units or groups. In Table 6.2 we display the cohesive energy of interest at room temperature taken from Van Krevelen.[1,4] Each structural group contains the contribution of the cohesive energy. We note that in the literature, unit of energy is used as Joule or calorie, but here the $^{\circ}K$ is used as unit of energy. It can be converted using the gas constant.

Table 6.2. Group contribution of the cohesive energy at $0^{\circ}K$ by Bondi and $298^{\circ}K$ by Van Krevelen for the structural units of interest. $R=8.314\ J/mol^{\circ}K$

Group	M_O (g)	$H_o^{\circ}(^{\circ}K)$	$E_{coh}(^{\circ}K)$
Methylene	14.03	763.77	503.97
Methyl	15.03	1270.15	1159.49
Phenyl	77.10	4938.66	3728.65
Cyclopentyl	69.12	4061.82	2836.18
Cyclohexyl	83.15	4595.86	3317.30

Using the cohesive energy of the structural units in Table 6.2, we can predict the cohesive energy of whole molecule by means of additivity functions. The accuracy of this method is

given by about 10%, which is within the limits of experimental accuracy.[4] We evaluated the cohesive energy of linear paraffins, branched hydrocarbons and rings with side chains shown in Table 6.3.

Characteristic total attraction energies of interest are also included in Table 6.3. A plot of total attraction energies versus cohesive energy of interest are shown in Fig. 6.2. The best-fit line through these data points is approximated with a neglected intercept, viz.,

$$\frac{q_z \cdot \varepsilon^* / 2}{E_{coh}} = 1.33.$$

References

1 D. W. Van Krevelen, *Properties of Polymers*, **Chs.4 and 7** in Part II, Third Edition, (Elsevier Science Publishing Company Inc., 1990).

2 A. Bondi, *Physical Properties of Molecular Crystals, Liquids, and Glasses*, **Chap.14**, (John Willey and Sons, Inc., 19?).

3 R. Simha and G. Carri, personal communication.

4 J. Bicerano (editor), *Computational Modeling of Polymers, Group Contribution Techniques*, **Chap. 1** by D. W. Van Krevelen, Marcel Dekker, Inc., 1992.

Table 6.3. Total attractive interaction, $q_z \varepsilon^*(^\circ K)$, and cohesive energy, $E_{coh}\ (^\circ K)$, by Van Krevelen. The unit of energy is $^\circ K$. Gas constant R=8.314$J/mol\ ^\circ K$ for unit conversion.

PSU #	$10^{-3} q_z \varepsilon^*(^\circ K)$	$10^{-3} E_{coh}(^\circ K)$
Linear Chain		
528	9.567	7.3587
529	10.373	7.8626
531	10.997	8.3666
532	11.703	8.8706
534	12.370	9.3745
535	13.069	9.8785
537	13.839	10.3825
540	15.153	11.3904
541	17.903	13.4063
106	19.219	14.4142
176	20.666	15.4222
197	23.493	17.4381
Branched Chain		
549	6.272	6.553
546	8.486	8.065
500	13.104	11.089
554	14.723	12.097
163	16.284	13.104
25	17.762	14.112
63	20.053	15.624
8	22.475	17.136
7	23.160	17.640
107	24.916	18.648
133	26.462	19.656
134	27.951	20.664
58	37.565	26.712

PSU #	$10^{-3} q_z \varepsilon^*(^\circ K)$	$10^{-3} E_{coh}(^\circ K)$
Cyclopentyl-alkanes		
573	11.842	8.531
117	19.359	14.075
551	8.467	5.672
Cyclohexyl-alkanes		
539	11.123	8.005
572	12.662	9.013
100	19.518	14.052
520	11.339	7.643
Phenyl-alkanes		
538	10.798	8.416
571	12.328	9.424
99	19.477	14.464
519	10.742	8.465

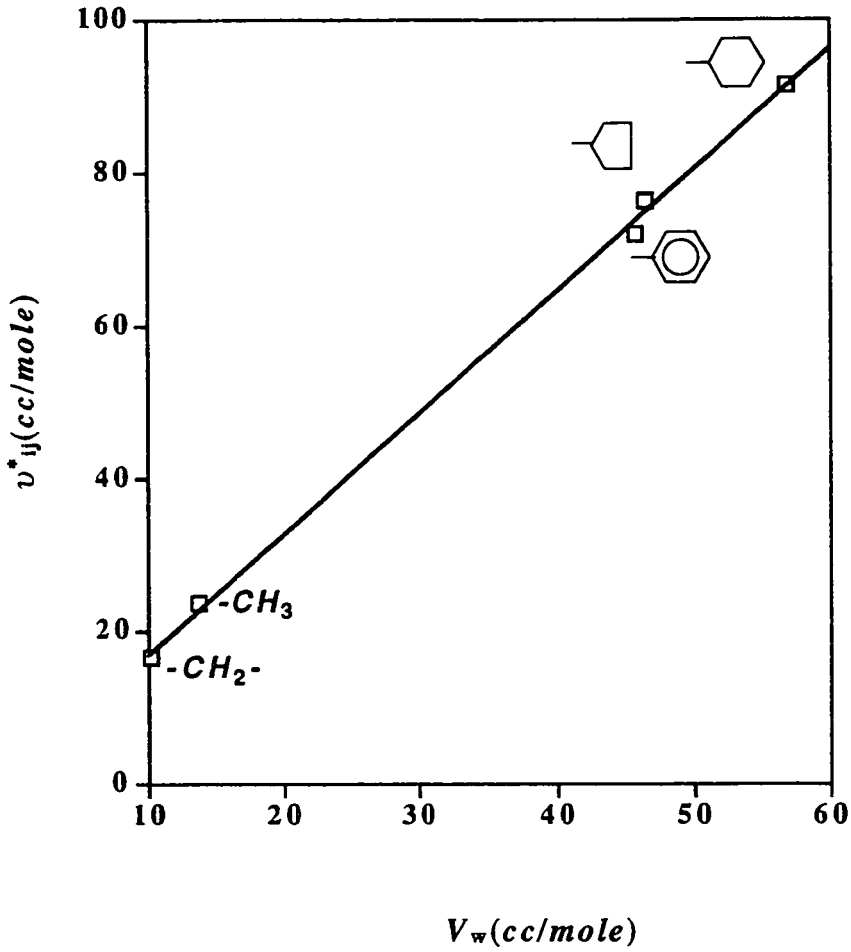


Figure 6.1. Characteristic repulsion versus van der Waals volumes (points) are plotted for the structural unit of methylene, methyl, phenyl, cyclopentyl and cyclohexyl. The best fit linear curve (line) is put through these data and corresponding equation is given by $\upsilon^*_{ij} = 1.59V_w + 1.00$.

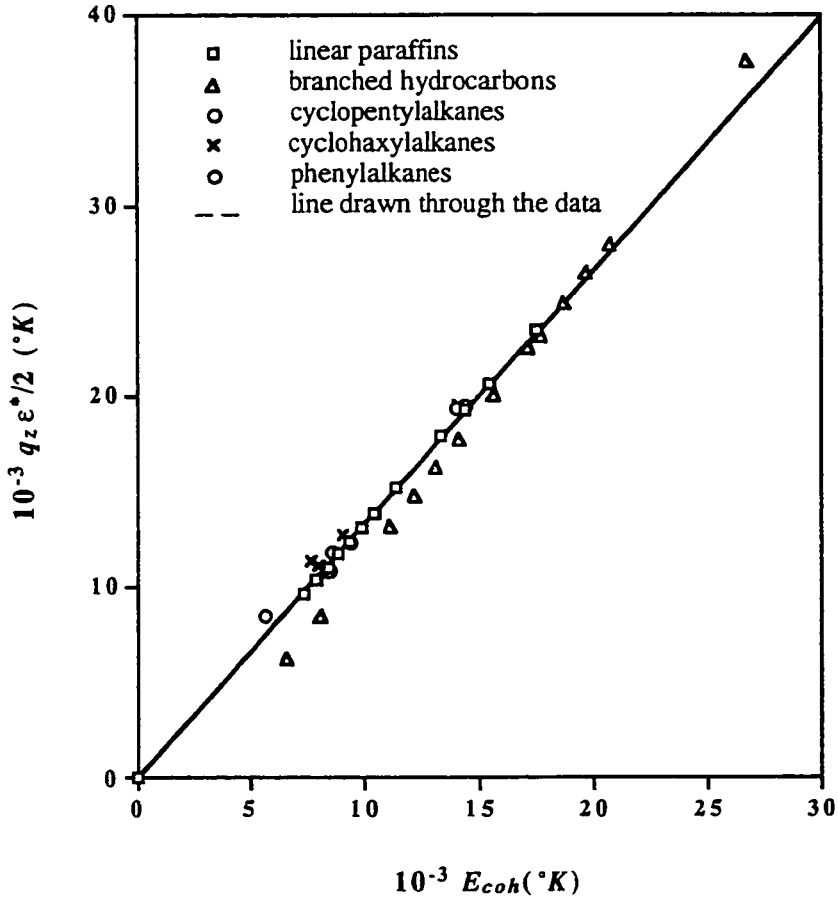


Figure 6.2. Total attractive interaction versus cohesive energy of chain molecules. Line is the best-fit equation with zero intercept below

$$10^{-3}\, q_z \varepsilon^*/2\ (°K) = 1.331 \times 10^{-3}\, E_{coh}(°K) - 0.016$$

CHAPTER 7

Conclusions and Future Work

7.1 Conclusions

The SS theory satisfies the PVT data and leads to the characteristic average parameters of interest. These parameters have been obtained for normal paraffins, branched chain molecules and ring attached alkyls. We are then able to obtain the characteristic group contributions of the constituent molecular units. For normal paraffins our schemes worked very well for the group contribution parameters of CH_2 and CH_3 of normal paraffins. However, for branched hydrocarbon, we had some difficulty in trying to solve the necessary polynomial equations, eq. 2.37, with the inclusion of the CH-CH interaction term between the branched molecules. Therefore, we dealt with a combination of the like and unlike interactions of CH_3 and CH as characteristic entities. In this manner satisfactory results were obtained. We worked on three kinds of rings, namely phenyl, cyclopentyl and cyclohexyl,

attached to alkyls. We subdivided each ring into segments with comparison of the normal paraffins. We then decomposed and calculated the group contributions of the segment of each ring. They are satisfactory. The correlation of theoretical group contributions of the repulsion volume with the empirical group contribution of Van der Waals volume is also established with reasonable agreement. The correlation between the total attractive interaction and cohesive energies is exhibited.

7.2 Future Work

In recent years the refinement and development of e.o.s. has been carried out by some authors[1] to obtain a more appropriate and precise theory for polymeric fluids. In our work of group contribution preference to certain species can be involved in the distribution of the interaction, Therefore the effect of nonrandomness can be introduced in the theory to refine the results and especially group contributions. On the other hand, degeneracy solving the polynomial equations of branched hydrocarbons will disappear with nonrandomness. Therefore, Gugenheim-Nies method[1,2] for nonrandomness has to be examined for our e.o.s. and polynomial equations.

This work might be extended to physical mixtures. Another aspect is the generalization to multicomponent fluids, using Simha and Jain[3] procedures.

Another extension is to correlation between hole fraction and viscosity. Utracki[4] showed such correlation for *n*-paraffins and for some mixtures.

References

1 E. Nies and H. Xie, *Macromolecules*, **26**, 1683 (1993)

2 E. A. Guggenheim, *Mixtures*, Oxford University Press, London 1952

3 L. A. Utracki, *The Canadian Journal of Chem. Eng.*, **61**, 753 (1983)

4 R. K. Jain and Robert Simha, *Macromolecules*, **13**, 1501 (1980)

APPENDIX A

Solution of rectangular matrix (overdetermined) using the PseudoInverse Method (Mathematica Code Program).

Here we solve the polynomial equation, eq. 2.30 for the group contribution of linear paraffins (ε^*_{ij} and υ^*_{ij}, i,j=1,2) using Mathematica. We put eq. 2.30 into a form:

$$a_x X_{11} + b_x X_{22} + c_x X_{12} = 1$$
$$a_y Y_{11} + b_y Y_{22} + c_y Y_{12} = 1 \qquad (A.1)$$

where

$$X_{ij} = \varepsilon^*_{ij} \upsilon^{*2}_{ij}, \qquad Y_{ij} = \varepsilon^*_{ij} \upsilon^{*4}_{ij} \quad (i,j=1,2),$$

and

$$a_x = (u^2/q_z^2)/X, \qquad a_y = (u^2/q_z^2)/Y$$
$$b_x = (v^2/q_z^2)/X, \qquad b_y = (v^2/q_z^2)/Y$$
$$c_x = (2u\ v/q_z^2)/X, \qquad c_y = (2u\ v/q_z^2)/Y$$
$$X = \varepsilon^* \upsilon^{*2} \quad \text{and} \quad Y = \varepsilon^* \upsilon^{*4}.$$

(*, n is chain-length and υ^s (=υ^*) and ε^s (=ε^*) are the respective average interaction energy and repulsion volume parameters for linear paraffins calculated from the theory, *)

```
U = { 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1};
n =  {12,13,14,15,16,17,18,20,24,26,28,32};

υ^s = {17.761,  17.705,  17.575,  17.501,
       17.423,  17.364,  17.318,  17.223,
       17.091,  16.999,  16.987,  16.939  };

ε^s =  {156.83,  157.17,  154.89  ,153.99,
        152.72,  151.97,  152.08,  150.03,
        147.96,  146.71,  146.57,  145.92  };

X = ε^s υ^s^2;     (*,   = ε* υ*2   ,*)
Y = ε^s υ^s^4;     (*,   = ε* υ*4   ,*)


z = 12;          (*, coordination number ,*)

u = (z-2)(n-2)

{100, 110, 120, 130, 140, 150, 160, 180, 220, 240, 260,300}


v = 2(z-1)U

{22, 22, 22, 22, 22, 22, 22, 22, 22, 22, 22, 22}


q_z = n(z-2)+2

{122, 132, 142, 152, 162, 172, 182, 202, 242, 262, 282,322}


a = u^2/q_z^2 ;
b = v^2/q_z^2 ;
c =2u*v/q_z^2 ;
```

(*, The coefficient matrix elements of eq. A.1.,*)

$a_x = a/X;\quad b_x = b/X;\quad c_x = c/X;$
$a_y = a/Y;\quad b_y = b/Y;\quad c_y = c/Y;$

(*, Solving the polynomial equation given above, eq. A.1, into X_{ij} and Y_{ij} (i,j=1,2). *)

X_{ij} = PseudoInverse[Transpose[{a_x, b_x, c_x}]].U

{36977.75, 130411.41, 70105.97}

Y_{ij} = PseudoInverse[Transpose[{a_y, b_y, c_y}]].U

{1.00427 10^7, 7.25686 10^7, 2.24823 10^7}

(*, Calculating the decomposed values of linear paraffins, υ^*_{ij} ($=\upsilon^s_{ij}$) and ε^*_{ij}($=\varepsilon^s_{ij}$). ,*)

N[υ^s_{ij} = Sqrt[Y_{ij}/X_{ij}], 5] (*, i,j=1,2 ,*)

{16.48, 23.589, 17.908}

N[ε^s_{ij} = X_{ij}/(υ^s_{ij}^2), 5] (*, i,j=1,2 ,*)

{136.15, 234.36, 218.61}

(*, We recalculate the average values of υ^*_b and ε^*_b using above decomposed values υ^*_{ij} and ε^*_{ij} to compare with the original average values.,*)

$\{X_{11}, X_{22}, X_{12}\} = X_{ij}$
$\{Y_{11}, Y_{22}, Y_{12}\} = Y_{ij}$

$X_b = a\ X_{11} + b\ X_{22} + c\ X_{12}$

{49809.4, 48775.4, 47895.2, 47136.8, 46476.7, 45897.,
45383.9,44516.2, 43225.7, 42732.9, 42312.1, 41631.4}

$Y_b = a\ Y_{11} + b\ Y_{22} + c\ Y_{12}$

{1.57533 10^7, 1.52349 10^7, 1.48008 10^7, 1.44322 10^7,
1.41156 10^7, 1.38408 10^7, 1.36001 10^7, 1.31988 10^7,
1.26155 10^7, 1.23972 10^7, 1.22127 10^7, 1.19182 10^7}

υ^s_b = Sqrt[Y_b / X_b]

{17.784, 17.673, 17.579, 17.498, 17.427, 17.366,
17.311, 17.219, 17.084, 17.033, 16.989, 16.920}

$\varepsilon^s_b = X_b / \upsilon^s_b \wedge 2$

{157.49, 156.16, 154.99, 153.95, 153.03, 152.20,
151.45, 150.14, 148.11, 147.30, 146.59, 145.42}

(*, Percentage deviation of the average values of $\upsilon^s{}_b$ $(=\upsilon^*{}_b)$ and $\varepsilon^s{}_b$ $(=\varepsilon^*{}_b)$ recalculated from the decomposed parameters above from the original average parameters of the theory, *)

$\mathrm{Dev}\upsilon^s = 100(\upsilon^s{}_b - \upsilon^s)/\upsilon^s$

{0.13, -0.18, 0.02, -0.02, 0.03, 0.01,
-0.04, -0.02, -0.04, 0.20, 0.01, -0.11}

$\mathrm{Dev}\varepsilon^s = 100(\varepsilon^s{}_b - \varepsilon^s)/\varepsilon^s$

{0.42, -0.64, 0.06, -0.02, 0.20, 0.15,
-0.42, 0.07, 0.10, 0.40, 0.02, -0.34}

APPENDIX B

Table B.1. Experimental and Scaled Volume and Temperature with Scaling Parameters and Error in Volume at Atmospheric Pressure for Paraffins (*n* from12 to 32). (*h*=1-*y*; hole fraction and volume in *cc/g* unit)

PSU528 $C_{12}H_{26}$

n = 12; *c* = 1.86; V^* = 1.2513 *cc/g*; T^* = 10287°*K*; P^* = 7464 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
9.77	273.16	2.6554	1.0475	1.3107	1.3096	+8.37
11.39	293.16	2.8498	1.0670	1.3351	1.3356	-3.66
12.87	310.94	3.0226	1.0854	1.3582	1.3587	-4.05
14.76	333.16	3.2386	1.1099	1.3888	1.3900	-8.44
16.45	352.56	3.4272	1.1328	1.4174	1.4180	-3.88
18.18	372.05	3.6167	1.1573	1.4481	1.4478	+1.95
19.64	388.16	3.7733	1.1787	1.4749	1.4745	+2.98
21.49	408.16	3.9677	1.2071	1.5104	1.5103	+0.60

Average Percentage Error in Volume : 4.24×10^{-2}
Percentage Standard Deviation in Volume : 6.80×10^{-2}

PSU529 $C_{13}H_{28}$

n = 13; *c* = 1.93; V^* = 1.2485 *cc/g*; T^* = 10749°*K*; P^* = 7494 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
9.22	273.16	2.5413	1.0403	1.2988	1.2989	-0.42
10.78	293.16	2.7273	1.0589	1.3220	1.3222	-1.47
12.20	310.94	2.8927	1.0764	1.3438	1.3448	-7.16
14.03	333.16	3.0994	1.0996	1.3729	1.3738	-6.85
17.33	372.05	3.4612	1.1444	1.4287	1.4278	+6.62

Average Percentage Error in Volume : 4.51×10^{-2}
Percentage Standard Deviation in Volume : 7.41×10^{-2}

PSU531 $C_{14}H_{30}$

n = 14; c = 2.00; V^* = 1.2403 *cc/g*; T^* = 10997°K; P^* = 7432 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
9.08	273.16	2.4839	1.0382	1.2877	1.2868	+7.04
10.63	293.16	2.6658	1.0565	1.3104	1.3108	-2.96
12.04	310.94	2.8275	1.0738	1.3318	1.3324	-4.42
13.85	333.16	3.0295	1.0967	1.3603	1.3611	-6.25
17.12	372.05	3.3832	1.1408	1.4150	1.4142	+5.52

Average Percentage Error in Volume : 5.23×10^{-2}
Percentage Standard Deviation in Volume : 7.28×10^{-2}

PSU532 $C_{15}H_{32}$

n = 15; c = 2.07; V^* = 1.2359 *cc/g*; T^* = 11308°K; P^* = 7413 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
8.82	273.16	2.4156	1.0347	1.2787	1.2778	+7.40
10.34	293.16	2.5925	1.0525	1.3008	1.3012	-3.02
11.72	310.94	2.7497	1.0693	1.3216	1.3224	-6.14
13.50	333.16	2.9462	1.0917	1.3492	1.3499	-5.28
15.09	352.56	3.1178	1.1124	1.3749	1.3751	-1.74
16.72	372.05	3.2902	1.1346	1.4022	1.4015	+5.26
18.09	388.16	3.4326	1.1539	1.4262	1.4263	-1.04
19.82	408.16	3.6095	1.1794	1.4576	1.4575	+0.58

Average Percentage Error in Volume : 3.81×10^{-2}
Percentage Standard Deviation in Volume : 5.97×10^{-2}

PSU534 $C_{16}H_{34}$

$n = 16$; $c = 2.14$; $V^* = 1.2311$ *cc/g*; $T^* = 11561$ °K; $P^* = 7379$ *bar*

$10^2 \times h$	T(°K)	$10^2 \times \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 \times$%Error
8.65	273.16	2.3628	1.0323	1.2709	1.2700	+6.74
10.15	293.16	2.5358	1.0498	1.2925	1.2925	-0.24
11.52	310.94	2.6896	1.0664	1.3128	1.3137	-6.66
13.28	333.16	2.8817	1.0883	1.3399	1.3405	-4.84
16.46	372.05	3.2181	1.1305	1.3918	1.3908	+6.90

Average Percentage Error in Volume : 5.07×10^{-2}
Percentage Standard Deviation in Volume : 7.54×10^{-2}

PSU535 $C_{17}H_{36}$

$n = 17$; $c = 2.21$; $V^* = 1.2276$ *cc/g*; $T^* = 11827$ °K; $P^* = 7362$ *bar*

$10^2 \times h$	T(°K)	$10^2 \times \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 \times$%Error
8.45	273.16	2.3096	1.0296	1.2639	1.2633	+5.13
9.93	293.16	2.4787	1.0468	1.2851	1.2853	-1.71
11.28	310.94	2.6291	1.0630	1.3050	1.3058	-6.29
13.01	333.16	2.8169	1.0845	1.3314	1.3323	-6.84
16.15	372.05	3.1458	1.1258	1.3821	1.3812	+6.23

Average Percentage Error in Volume : 5.24×10^{-2}
Percentage Standard Deviation in Volume : 7.37×10^{-2}

PSU537 $C_{18}H_{38}$

n = 18; c = 2.28; V^* = 1.2249 *cc/g*; T^* = 12140°K; P^* = 7383 *bar*

$10^2 \times h$	T(°K)	$10^2 \times \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 \times$%Error
8.17	273.16	2.2501	1.0260	1.2568	1.2557	+8.76
9.62	293.16	2.4148	1.0428	1.2773	1.2775	-1.46
10.94	310.94	2.5613	1.0586	1.2966	1.2974	-6.00
12.64	333.16	2.7443	1.0795	1.3222	1.3231	-6.59
14.16	352.56	2.9041	1.0989	1.3460	1.3468	-5.91
15.72	372.05	3.0647	1.1195	1.3713	1.3714	-0.69
17.03	388.16	3.1974	1.1375	1.3934	1.3941	-5.34
18.69	408.16	3.3621	1.1611	1.4223	1.4215	+5.37

Average Percentage Error in Volume : 5.01×10^{-2}
Percentage Standard Deviation in Volume : 7.41×10^{-2}

PSU540 $C_{20}H_{42}$

n = 20; c = 2.42; V^* = 1.2192 *cc/g*; T^* = 12523°K; P^* = 7315 *bar*

$10^2 \times h$	T(°K)	$10^2 \times \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 \times$%Error
7.98	273.16	2.1813	1.0233	1.2476	1.2467	+6.99
9.41	293.16	2.3410	1.0397	1.2676	1.2677	-0.90
10.71	310.94	2.4829	1.0551	1.2864	1.2872	-6.05
12.39	333.16	2.6604	1.0756	1.3114	1.3122	-6.09
15.42	372.05	2.9709	1.1149	1.3592	1.3585	+5.42

Average Percentage Error in Volume : 5.09×10^{-2}
Percentage Standard Deviation in Volume : 7.15×10^{-2}

PSU541 $C_{24}H_{50}$

n = 24; c = 2.7; V^* = 1.2113 *cc/g*; T^* = 13262°*K*; P^* = 7258 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.57	273.16	2.0597	1.0175	1.2325	1.2318	+5.81
8.94	293.16	2.2105	1.0332	1.2515	1.2519	-2.94
10.20	310.94	2.3446	1.0480	1.2694	1.2702	-6.10
11.83	333.16	2.5121	1.0676	1.2931	1.2940	-6.65
14.77	372.05	2.8054	1.1050	1.3385	1.3378	+5.12

Average Percentage Error in Volume : $5.32 x 10^{-2}$
Percentage Standard Deviation in Volume : $7.01 x 10^{-2}$

PSU106 $C_{26}H_{54}$

n = 26; c = 2.84; V^* = 1.2053 *cc/g*; T^* = 13535°*K*; P^* = 7231 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.45	273.16	2.0182	1.0159	1.2245	1.2237	+6.28
8.82	293.16	2.1659	1.0314	1.2432	1.2435	-2.71
10.07	310.94	2.2973	1.0460	1.2608	1.2615	-5.92
11.68	333.16	2.4615	1.0654	1.2841	1.2849	-6.49
14.60	372.05	2.7488	1.1023	1.3286	1.3280	+4.71

Average Percentage Error in Volume : $5.22 x 10^{-2}$
Percentage Standard Deviation in Volume : $6.85 x 10^{-2}$

PSU176 $C_{28}H_{58}$

$n = 28$; $c = 2.98$; $V^* = 1.2049$ *cc/g*; $T^* = 13870°K$; $P^* = 7225$ *bar*

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.24	273.16	1.9694	1.0132	1.2208	1.2201	+5.98
8.59	293.16	2.1136	1.0284	1.2391	1.2395	-3.21
12.13	343.16	2.4741	1.0705	1.2898	1.2907	-6.95
13.23	358.16	2.5823	1.0843	1.3065	1.3070	-3.94
14.27	372.05	2.6824	1.0977	1.3226	1.3219	+5.14

Average Percentage Error in Volume : 5.04×10^{-2}
Percentage Standard Deviation in Volume : 6.66×10^{-2}

PSU197 $C_{32}H_{66}$

$n = 32$; $c = 3.26$; $V^* = 1.2023$ *cc/g*; $T^* = 14413°K$; $P^* = 7208$ *bar*

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
6.95	273.16	1.8952	1.0094	1.2136	1.2132	+3.64
8.27	293.16	2.0340	1.0241	1.2313	1.2317	-3.26
12.44	353.16	2.4503	1.0737	1.2909	1.2913	-2.85
13.17	363.16	2.5197	1.0828	1.3019	1.3019	-0.04
13.82	372.05	2.5813	1.0912	1.3119	1.3113	+4.58

Average Percentage Error in Volume : 2.87×10^{-2}
Percentage Standard Deviation in Volume : 4.13×10^{-2}

Table B.2. Experimental and Scaled Volume and Temperature with Scaling Parameters and Error in Volume at Atmospheric Pressure for Branched Hydrocarbons (chain length, n from10 to 50). ($h = 1 - y$; hole fraction and volume in cc/g unit)

PSU549 $C_{10}H_{22}$

n = 10; c = 0.996; V^* = 1.2713 cc/g; T^* = 12595°K; P^* = 5767 bar

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	10^2x%Error
10.38	273.16	2.1687	1.0477	1.3319	1.3321	-1.54
12.12	293.16	2.3275	1.0686	1.3585	1.3598	-9.43
13.72	310.94	2.4686	1.0886	1.3840	1.3852	-9.25
15.78	333.16	2.6451	1.1156	1.4182	1.4188	-4.21
19.58	372.05	2.9538	1.1688	1.4859	1.4850	+5.89

Average Percentage Error in Volume : 6.06×10^{-2}
Percentage Standard Deviation in Volume : 9.43×10^{-2}

PSU546 $C_{13}H_{28}$

n = 13; c = 1.299; V^* = 1.2460 cc/g; T^* = 13066°K; P^* = 6143bar

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	10^2x%Error
9.34	273.16	2.0906	1.0358	1.2906	1.2902	+3.48
10.95	293.16	2.2436	1.0547	1.3141	1.3148	-4.59
12.42	310.94	2.3797	1.0726	1.3365	1.3373	-5.67
14.32	333.16	2.5498	1.0967	1.3664	1.3671	-4.53
17.78	372.05	2.8474	1.1435	1.4248	1.4245	+1.77

Average Percentage Error in Volume : 4.01×10^{-2}
Percentage Standard Deviation in Volume : 5.63×10^{-2}

PSU500 $C_{19}H_{40}$

n = 19; c = 1.905; V^* = 1.2222 *cc/g*; T^* = 13758 °*K*; P^* = 6640 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	10^2x%Error
8.09	273.16	1.9854	1.0217	1.2488	1.2481	+5.19
9.54	293.16	2.1308	1.0384	1.2691	1.2694	-2.19
10.87	310.94	2.2600	1.0541	1.2883	1.2893	-8.26
12.58	333.16	2.4215	1.0749	1.3138	1.3148	-7.39
15.69	372.05	2.7042	1.1151	1.3629	1.3624	+3.88

Average Percentage Error in Volume : 5.38×10^{-2}
Percentage Standard Deviation in Volume : 7.55×10^{-2}

PSU554 $C_{21}H_{44}$

n = 21; c = 2.107; V^* = 1.2198 *cc/g*; T^* = 13975 °*K*; P^* = 6768 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	10^2x%Error
7.75	273.16	1.9545	1.0180	1.2417	1.2408	+7.24
9.16	293.16	2.0976	1.0340	1.2613	1.2617	-2.86
10.45	310.94	2.2248	1.0492	1.2798	1.2807	-7.59
12.12	333.16	2.3838	1.0693	1.3043	1.3051	-6.51
15.14	372.05	2.6621	1.1079	1.3514	1.3512	+1.75

Average Percentage Error in Volume : 5.19×10^{-2}
Percentage Standard Deviation in Volume : 7.29×10^{-2}

PSU163 $C_{23}H_{48}$

$n = 23$; $c = 2.309$; $V^* = 1.2156$ *cc/g*; $T^* = 14105$ °K; $P^* = 6862$ *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.55	273.16	1.9366	1.0158	1.2348	1.2340	+6.63
8.94	293.16	2.0783	1.0315	1.2538	1.2538	+0.70
10.21	310.94	2.2044	1.0463	1.2718	1.2726	-5.96
11.84	333.16	2.3619	1.0659	1.2957	1.2967	-7.52
14.81	372.05	2.6377	1.1036	1.3415	1.3414	+0.83

Average Percentage Error in Volume : 4.33×10^{-2}
Percentage Standard Deviation in Volume : 6.65×10^{-2}

PSU25 $C_{25}H_{52}$

$n = 25$; $c = 2.511$; $V^* = 1.2095$ *cc/g*; $T^* = 14148$ °K; $P^* = 6925$ *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.47	273.16	1.9307	1.0149	1.2275	1.2267	+6.89
8.85	293.16	2.0720	1.0305	1.2463	1.2470	-5.62
10.10	310.94	2.1977	1.0451	1.2641	1.2650	-7.65
11.72	333.16	2.3548	1.0645	1.2876	1.2885	-7.18
14.67	372.05	2.6297	1.1018	1.3326	1.3321	+3.94

Average Percentage Error in Volume : 6.26×10^{-2}
Percentage Standard Deviation in Volume : 8.09×10^{-2}

PSU63 $C_{28}H_{58}$

$n = 28$; $c = 2.814$; $V^* = 1.2038$ *cc/g*; $T^* = 14252$°*K*; $P^* = 7018$ *bar*

$10^2 \times h$	T(°K)	$10^2 \times \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 \times$%Error
7.31	273.16	1.9165	1.0131	1.2196	1.2188	+6.89
8.66	293.16	2.0568	1.0284	1.2380	1.2382	-2.07
9.90	310.94	2.1816	1.0428	1.2553	1.2561	-6.68
11.50	333.16	2.3375	1.0618	1.2782	1.2796	-10.63
14.40	372.05	2.6104	1.0983	1.3221	1.3215	+4.59

Average Percentage Error in Volume : 6.17×10^{-2}
Percentage Standard Deviation in Volume : 8.59×10^{-2}

PSU8 $C_{31}H_{64}$

$n = 31$; $c = 3.117$; $V^* = 1.2011$ *cc/g*; $T^* = 14421$°*K*; $P^* = 7123$ *bar*

$10^2 \times h$	T(°K)	$10^2 \times \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 \times$%Error
7.07	273.16	1.8941	1.0106	1.2138	1.2129	+7.75
8.40	293.16	2.0328	1.0254	1.2317	1.2320	-2.58
9.61	310.94	2.1561	1.0395	1.2485	1.2492	-5.89
11.18	333.16	2.3102	1.0580	1.2708	1.2719	-9.22
14.02	372.05	2.5799	1.0935	1.3133	1.3130	+2.44

Average Percentage Error in Volume : 5.57×10^{-2}
Percentage Standard Deviation in Volume : 7.75×10^{-2}

PSU7 $C_{32}H_{66}$

$n = 32$; $c = 3.218$; $V^* = 1.1985$ *cc/g*; $T^* = 14394$°K; $P^* = 7127$ *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.10	273.16	1.8976	1.0109	1.2115	1.2102	+10.86
8.43	293.16	2.0366	1.0258	1.2294	1.2302	-6.21
9.65	310.94	2.1601	1.0398	1.2462	1.2473	-9.03
11.21	333.16	2.3145	1.0584	1.2685	1.2697	-9.19
14.06	372.05	2.5846	1.0939	1.3111	1.3106	+3.64

Average Percentage Error in Volume : 7.79×10^{-2}
Percentage Standard Deviation in Volume : 10.16×10^{-2}

PSU107 $C_{34}H_{70}$

$n = 34$; $c = 3.420$; $V^* = 1.1989$ *cc/g*; $T^* = 14571$°K; $P^* = 7216$ *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
6.87	273.16	1.8746	1.0084	1.2089	1.2080	+7.65
8.17	293.16	2.0119	1.0229	1.2264	1.2265	-1.24
9.37	310.94	2.1339	1.0366	1.2428	1.2438	-7.91
10.90	333.16	2.2864	1.0547	1.2645	1.2655	-7.69
13.69	372.05	2.5533	1.0893	1.3060	1.3058	+1.33

Average Percentage Error in Volume : 5.16×10^{-2}
Percentage Standard Deviation in Volume : 7.51×10^{-2}

PSU133 $C_{36}H_{74}$

$n = 36$; $c = 3.622$; $V^* = 1.1977$ *cc/g*; $T^* = 14612°K$; $P^* = 7247$ *bar*

$10^2 \times h$	$T(°K)$	$10^2 \times \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 \times$%Error
6.82	273.16	1.8694	1.0077	1.2070	1.2060	+8.22
8.11	293.16	2.0063	1.0222	1.2243	1.2243	-0.06
9.30	310.94	2.1279	1.0358	1.2406	1.2413	-6.05
10.82	333.16	2.2800	1.0538	1.2621	1.2633	-9.10
13.60	372.05	2.5461	1.0881	1.3032	1.3029	+2.20

Average Percentage Error in Volume : 5.13×10^{-2}
Percentage Standard Deviation in Volume : 7.68×10^{-2}

PSU134 $C_{38}H_{78}$

$n = 38$; $c = 3.824$; $V^* = 1.1948$ *cc/g*; $T^* = 14619°K$; $P^* = 7271$ *bar*

$10^2 \times h$	$T(°K)$	$10^2 \times \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 \times$%Error
6.80	273.16	1.8684	1.0076	1.2038	1.2029	+7.45
8.09	293.16	2.0052	1.0220	1.2211	1.2212	-0.79
9.27	310.94	2.1268	1.0355	1.2373	1.2381	-6.70
10.79	333.16	2.2788	1.0535	1.2587	1.2598	-8.47
13.56	372.05	2.5449	1.0877	1.2996	1.2994	+1.57

Average Percentage Error in Volume : 5.00×10^{-2}
Percentage Standard Deviation in Volume : 7.32×10^{-2}

PSU58 $C_{50}H_{102}$

$n = 50$; $c = 5.036$; $V^* = 1.1890\ cc/g$; $T^* = 14918°K$; $P^* = 7470\ bar$

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
6.42	273.16	1.8311	1.0034	1.1931	1.1920	+8.87
7.66	293.16	1.9650	1.0172	1.2095	1.2095	-0.12
8.80	310.94	2.0842	1.0302	1.2249	1.2255	-4.93
10.27	333.16	2.2331	1.0473	1.2453	1.2463	-7.96
12.94	372.05	2.4938	1.0799	1.2840	1.2840	+0.15

Average Percentage Error in Volume : $4.41 x 10^{-2}$
Percentage Standard Deviation in Volume : $7.03 x 10^{-2}$

Table B.3. Experimental and Scaled Volume and Temperature with Scaling Parameters and Error in Volume at Atmospheric Pressure for Phenyl Ring(s) with Alkanes. ($h=1-y$; hole fraction and volume in cc/g unit)

PSU538 $C_{14}H_{22}$

s = 12.7; c = 1.912; V^* = 1.1174 cc/g; T^* = 11295°K; P^* = 8444 bar

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	10^2x%Error
8.10	273.16	2.4185	1.0276	1.1482	1.1478	+3.37
9.54	293.16	2.5954	1.0443	1.1669	1.1675	-5.51
10.86	310.94	2.7528	1.0600	1.1845	1.1846	-0.64
12.55	333.16	2.9495	1.0809	1.2078	1.2085	-5.68
15.60	372.05	3.2938	1.1208	1.2524	1.2519	+3.91

Average Percentage Error in Volume : 3.82×10^{-2}
Percentage Standard Deviation in Volume : 5.06×10^{-2}

PSU571 $C_{16}H_{26}$

s = 14.7; c = 2.052; V^* = 1.1282 cc/g; T^* = 12015°K; P^* = 8321 bar

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	10^2x%Error
7.54	273.16	2.2736	1.0202	1.1510	1.1504	+5.74
8.92	293.16	2.4399	1.0360	1.1688	1.1690	-2.00
10.18	310.94	2.5878	1.0508	1.1856	1.1862	-5.72
11.80	333.16	2.7728	1.0705	1.2077	1.2085	-6.00
14.74	372.05	3.0965	1.1080	1.2501	1.2498	+1.91

Average Percentage Error in Volume : 4.27×10^{-2}
Percentage Standard Deviation in Volume : 5.54×10^{-2}

PSU99 $C_{26}H_{46}$

$s = 24.7$; $c = 2.752$; $V^* = 1.1481$ *cc/g*; $T^* = 14155°K$; $P^* = 7866$ *bar*

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
6.49	273.16	1.9299	1.0055	1.1544	1.1535	+7.80
7.75	293.16	2.0710	1.0195	1.1705	1.1704	+0.78
8.91	310.94	2.1966	1.0327	1.1856	1.1862	-5.09
10.39	333.16	2.3536	1.0501	1.2056	1.2067	-8.83
13.10	372.05	2.6283	1.0833	1.2437	1.2436	+0.95

Average Percentage Error in Volume : 4.69×10^{-2}
Percentage Standard Deviation in Volume : 6.83×10^{-2}

PSU519 $C_{14}H_{14}$

$s = 11.4$; $c = 1.821$; $V^* = 0.9825$ *cc/g*; $T^* = 11798°K$; $P^* = 9975$ *bar*

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
6.84	273.16	2.3154	1.0142	0.9964	0.9958	+6.13
8.15	293.16	2.4847	1.0290	1.0110	1.0111	-1.60
9.35	310.94	2.6354	1.0429	1.0246	1.0254	-8.00
10.88	333.16	2.8238	1.0612	1.0426	1.0435	-8.43
13.67	372.05	3.1534	1.0961	1.0769	1.0765	+3.56

Average Percentage Error in Volume : 5.54×10^{-2}
Percentage Standard Deviation in Volume : 6.31×10^{-2}

Table B.4. Experimental and Scaled Volume and Temperature with Scaling Parameters and Error in Volume at Atmospheric Pressure for Cyclohexyl Ring(s) with Alkanes. ($h = 1 - y$; hole fraction and volume in cc/g unit)

PSU539 $C_{14}H_{28}$

$s = 13.3$; $c = 1.954$; $V^* = 1.1755$ cc/g; $T^* = 11385°K$; $P^* = 8013$ bar

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
8.14	273.16	2.3991	1.0277	1.2081	1.2074	+5.61
9.59	293.16	2.5748	1.0445	1.2279	1.2287	-6.49
10.91	310.94	2.7310	1.0603	1.2464	1.2473	-7.46
12.61	333.16	2.9261	1.0813	1.2710	1.2716	-4.71
15.67	372.05	3.2677	1.1213	1.3181	1.3175	+4.58

Average Percentage Error in Volume : 5.77×10^{-2}
Percentage Standard Deviation in Volume : 7.33×10^{-2}

PSU572 $C_{16}H_{32}$

$s = 15.3$; $c = 2.094$; $V^* = 1.1787$ cc/g; $T^* = 12094°K$; $P^* = 7960$ bar

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.58	273.16	2.2586	1.0204	1.2027	1.2021	+5.37
8.96	293.16	2.4240	1.0362	1.2214	1.2216	-1.63
10.23	310.94	2.5710	1.0511	1.2390	1.2396	-5.32
11.86	333.16	2.7547	1.0708	1.2622	1.2629	-5.86
14.80	372.05	3.0763	1.1085	1.3066	1.3063	+2.15

Average Percentage Error in Volume : 4.06×10^{-2}
Percentage Standard Deviation in Volume : 5.51×10^{-2}

PSU100 $C_{26}H_{52}$

$s = 25.3$; $c = 2.794$; $V^* = 1.1744$ *cc/g*; $T^* = 13971\,°K$; $P^* = 7578$ *bar*

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
6.79	273.16	1.9552	1.0087	1.1846	1.1839	+635
8.08	293.16	2.0982	1.0231	1.2016	1.2016	-0.49
9.27	310.94	2.2255	1.0367	1.2176	1.2183	-6.29
10.79	333.16	2.3845	1.0548	1.2387	1.2396	-7.35
13.56	372.05	2.6629	1.0891	1.2790	1.2789	+0.75

Average Percentage Error in Volume : 4.25×10^{-2}
Percentage Standard Deviation in Volume : 6.32×10^{-2}

PSU520 $C_{14}H_{26}$

$s = 12.6$; $c = 1.905$; $V^* = 1.1091$ *cc/g*; $T^* = 11905\,°K$; $P^* = 8748$ *bar*

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.09	273.16	2.2947	1.0162	1.1270	1.1261	+8.07
8.42	293.16	2.4625	1.0313	1.1438	1.1442	-3.08
9.64	310.94	2.6119	1.0455	1.1596	1.1606	-9.07
11.20	333.16	2.7985	1.0643	1.1804	1.1812	-6.58
14.04	372.05	3.1252	1.1001	1.2201	1.2195	+4.98

Average Percentage Error in Volume : 6.35×10^{-2}
Percentage Standard Deviation in Volume : 7.78×10^{-2}

Table B.5. Experimental and Scaled Volume and Temperature with Scaling Parameters and Error in Volume at Atmospheric Pressure for Cyclopentyl Ring(s) with Alkanes. ($h=1-y$; hole fraction and volume in cc/g unit)

PSU573 $C_{15}H_{30}$

s = 14.4; c = 2.031; V^* = 1.1834 cc/g; T^* = 11661°K; P^* = 7909 bar

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
8.02	273.16	2.3424	1.0258	1.2139	1.2127	+9.78
9.45	293.16	2.5139	1.0423	1.2335	1.2332	+2.48
10.76	310.94	2.6663	1.0579	1.2519	1.2522	-2.00
12.44	333.16	2.8569	1.0786	1.2764	1.2765	-0.90
15.48	372.05	3.1904	1.1181	1.3231	1.3222	+6.88

Average Percentage Error in Volume : 4.41×10^{-2}
Percentage Standard Deviation in Volume : 6.94×10^{-2}

PSU117 $C_{26}H_{52}$

s = 25.4; c = 2.801; V^* = 1.1755 cc/g; T^* = 13823°K; P^* = 7510 bar

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
6.99	273.16	1.9762	1.0109	1.1883	1.1874	+7.71
8.30	293.16	2.1207	1.0256	1.2056	1.2060	-2.91
9.51	310.94	2.2493	1.0395	1.2220	1.2228	-6.70
11.06	333.16	2.4101	1.0579	1.2436	1.2442	-5.11
13.88	372.05	2.6914	1.0931	1.2849	1.2847	+1.57

Average Percentage Error in Volume : 4.80×10^{-2}
Percentage Standard Deviation in Volume : 6.45×10^{-2}

PSU551 $C_{10}H_{18}$

$s = 8.8$; $c = 1.639$; $V^* = 1.1028\ cc/g$; $T^* = 10332°K$; $P^* = 9235\ bar$

$10^2 x h$	$T(°K)$	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
8.20	273.16	2.6440	1.0316	1.1377	1.1373	+3.39
9.66	293.16	2.8374	1.0486	1.1564	1.1566	-1.64
10.99	310.94	3.0095	1.0646	1.1741	1.1745	-4.05
12.69	333.16	3.2245	1.0858	1.1974	1.1977	-2.68
15.77	372.05	3.6010	1.1264	1.2422	1.2419	+1.82

Average Percentage Error in Volume : 2.72×10^{-2}
Percentage Standard Deviation in Volume : 3.36×10^{-2}

Table B.6. Experimental and Scaled Volume and Temperature with Scaling Parameters and Error in Volume at Atmospheric Pressure for Unlike Rings Attached with Methylene Units. ($h=1-y$; hole fraction and volume in cc/g unit)

PSU521 $C_{14}H_{20}$

s = 12.0; c = 1.863; V^* = 1.0471 cc/g; T^* = 11824°K; P^* = 9289 bar

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.01	273.16	2.3103	1.0157	1.0635	1.0628	+6.62
8.33	293.16	2.4793	1.0307	1.0793	1.0797	-3.98
9.55	310.94	2.6296	1.0448	1.0940	1.0949	-8.17
11.11	333.16	2.8176	1.0635	1.1136	1.1143	-6.81
13.93	372.05	3.1465	1.0990	1.1508	1.1504	+3.65

Average Percentage Error in Volume : 5.85×10^{-2}
Percentage Standard Deviation in Volume : 6.68×10^{-2}

PSU522 $C_{14}H_{20}$

s = 12.1; c = 1.870; V^* = 1.0563 cc/g; T^* = 11801°K; P^* = 9225 bar

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.08	273.16	2.3148	1.0164	1.0736	1.0728	+7.06
8.41	293.16	2.4841	1.0315	1.0896	1.0899	-3.03
9.63	310.94	2.6348	1.0457	1.1046	1.1058	-11.05
11.20	333.16	2.8231	1.0645	1.1245	1.1250	-4.74
14.03	372.05	3.1526	1.1003	1.1623	1.1618	+3.56

Average Percentage Error in Volume : 5.89×10^{-2}
Percentage Standard Deviation in Volume : 7.25×10^{-2}

PSU523 $C_{14}H_{26}$

s = 12.7; c = 1.912; V^* = 1.1175 *cc/g*; T^* = 11930°*K*; P^* = 8733 *bar*

$10^2 x h$	T(°K)	$10^2 x \tilde{T}$	$\tilde{V}$	V_{theory}	V_{exp}	$10^2 x$%Error
7.08	273.16	2.2898	1.0160	1.1354	1.1351	+3.13
8.41	293.16	2.4572	1.0312	1.1523	1.1527	-3.66
9.63	310.94	2.6063	1.0454	1.1682	1.1688	-4.97
11.20	333.16	2.7925	1.0641	1.1892	1.1895	-2.65
14.03	372.05	3.1185	1.0999	1.2291	1.2291	+0.26

Average Percentage Error in Volume : $2.93 x 10^{-2}$
Percentage Standard Deviation in Volume : $3.85 x 10^{-2}$

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