

## EQUATION OF STATE MOLECULAR PARAMETERS FOR A THEORY OF PURE $r$ -MER FLUIDS IN THE LIQUID PHASE

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### ABSTRACT

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Equation of state parameters for a theory of pure  $r$ -mers (Costas and Sanctuary, 1981) are presented for sixty common substances. The equation of state is tested for its ability to reproduce and predict thermodynamic data in the liquid phase. The theory has only two adjustable parameters:  $v^*$ , the close-packed volume of the  $r$ -mer, and  $\epsilon^* = z\epsilon/2$ , where  $\epsilon$  is the nonbonded mer–mer attractive interaction energy and  $z$  is the lattice coordination number, set to be a constant equal to 12. The number of  $r$ -mers per molecule,  $r$ , is also fixed for a given liquid to be equal to the number of atoms in the molecule other than hydrogen. The fitting procedure is fast and simple. The adjustment only involves the use of widely available density data. Comparisons between experimental and calculated first- and second-order thermodynamic properties are shown for several substances. A comparison with the equation of state due to Jain and Simha (1981) for  $PVT$  data for  $n$ -dodecane is presented. The theory qualifies as a useful tool, especially in engineering applications, for estimating thermodynamic properties in the liquid phase.

### INTRODUCTION

One of the major goals of physical chemistry is the calculation of the thermodynamic properties of fluids from a few molecular parameters. The development of equations of state with good levels of predictive ability has been the subject of numerous studies (for a recent review, see Chao and Robinson, 1979). Since the description of phase equilibria is of fundamental importance in the design of diffusional separation processes and for many other practical purposes, it has received a great deal of attention. Recent examples of such efforts are those due to Mollerup (1980), who used a corresponding-states approach, to Kleintjens (1983), who improved the mean-field two-component lattice-gas model, and to Gmehling et al. (1982), who reviewed and extended the UNIFAC group contribution method.

Recently, using a nearest-neighbor lattice model and the Guggenheim (1944) approximation to the partition function, we presented (Costas and Sanctuary, 1981; Costas et al., 1981) a new equation of state for pure  $r$ -mers. The theory is an extension of the Sanchez–Lacombe theory (1976), in that the large-coordination-number ( $z$ ) limit is not taken. The theory works well except in the critical region. In particular, a liquid–vapor transition is obtained. These characteristics, i.e., the finite  $z$  feature and the prediction of a phase transition, allowed Zuckermann et al. (1982) to combine our model with a “ten-state” model (Pink et al., 1980; Caillé et al., 1980) which describes the conformational states of the acyl chains of lipid molecules, to predict successfully gel–fluid and fluid–vapor phase boundaries for lipid monolayers.

Although perhaps the most appealing feature of Sanchez–Lacombe theory and our extension is its ability to undergo a continuous phase transition, in this work we have chosen to concentrate on the liquid phase only. Our main interest is to test the theory concerning its ability to reproduce and predict thermodynamic data for common substances in the liquid phase. The next section presents a brief recapitulation of the equation of state and its molecular parameters. The determination of the molecular parameters for sixty different substances is then discussed. Finally, we give a comparison between experimental data and theoretical predictions for various thermodynamic properties for a number of substances. Also in this section, we present a comparison between the results obtained through the equation of state for an  $n$ -paraffin fluid due to Jain and Simha (1981) and the predictions of our equation of state.

#### RECAPITULATION OF THE EQUATION OF STATE

The Gibbs free energy and the partition function are given in the isothermic–isobaric ensemble by

$$G = -kT \ln Z(T, P) \quad (1)$$

where

$$Z(T, P) = \sum_{E, V} \Omega(E, V, N) \exp[-(E + PV)/kT] \quad (2)$$

For a system of  $N$  molecules, each of which occupies  $r$  sites, with  $N_0$  vacant sites or holes ( $N_s = rN + N_0$ ) and coordination number  $z$ , the number of configurations available to the system for a given potential energy  $E$  and volume  $V$  is

$$\Omega(E, V, N) = (w/f)^N (1/f_0)^{N_0} (f_{NB})^{(z/2)N_q} \quad (3)$$

where  $f$  is the packing fraction of the lattice, given by  $f = rN/N_s$  ( $0 \leq f \leq 1$ ), and the fraction of vacant sites or holes is given by  $f_0 = 1 - f$ . In this model, therefore, the free volume is taken into account by assuming the presence of holes. In eqn. (3),  $(z/2)N_q$  is the total number of nonbonded pairs in the system, while  $f_{\text{NB}}$  is the fraction of nonbonded pairs in the system (that is, the hole-hole, hole-mer and nonbonded mer-mer pairs). This fraction is given by

$$f_{\text{NB}} = 1 - \phi f \quad (4)$$

with

$$\phi = (2/z)(1 - 1/r) \quad (5)$$

being the ratio of the fraction of bonded  $r$ -mer pairs to the fraction of sites occupied by  $r$ -mers. As such,  $f_{\text{NB}}$  gives a measure of the external degrees of freedom of the  $r$ -mers (Costas and Sanctuary, 1981). As  $f_{\text{NB}}$  decreases, the external degrees of freedom of the  $r$ -mers decrease. Finally, in eqn. (3), for a given lattice coordination number and number of monomers per  $r$ -mer ( $r$ ),  $w$  is a constant given by

$$w = z(z-1)^{r-2}r/2 \quad (6)$$

Sanchez and Lacombe (1976) used the  $z \rightarrow \infty$  limit of eqn. (3) to derive their equation of state. This choice implies that they approximate  $\phi$  to be zero (eqn. (5)) and  $f_{\text{NB}}$  to be unity (eqn. (4)). Previously, we have discussed in detail (Costas and Sanctuary, 1981) the consequences of such approximations. Using the full Guggenheim form, eqn. (3), the reduced free energy is obtained as

$$\begin{aligned} \tilde{G} = G/Nr\epsilon^* = & -\tilde{\rho}(1-\phi)^2/(1-\phi\tilde{\rho}) + \tilde{P}\tilde{\nu} + \tilde{T}\{(1/r)\ln(\tilde{\rho}/w) \\ & + (\tilde{\nu}-1)\ln(1-\tilde{\rho}) - (z/2)[(1-\phi\tilde{\rho})/\tilde{\rho}]\ln(1-\phi\tilde{\rho})\} \end{aligned} \quad (7)$$

Minimization of eqn. (7) with respect to  $f$  gives the equation of state:

$$[\tilde{\rho}(1-\phi)/(1-\phi\tilde{\rho})]^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) - (z/2)\ln(1-\phi\tilde{\rho})] = 0 \quad (8)$$

The reduced state variables in eqns. (7) and (8) are as follows:

$$\begin{aligned} \tilde{T} = T/T^* & & T^* = \epsilon^*/k \\ \tilde{P} = P/P^* & & P^* = \epsilon^*rN/V^* \\ f = \tilde{\rho} = 1/\tilde{\nu} = V^*/V & & f_0 = 1 - f = 1 - \tilde{\rho} \end{aligned} \quad (9)$$

where  $V^*$  is the molar close-packed volume of  $N$   $r$ -mers, equal to  $Nr\nu^*$ , with  $\nu^*$  the close-packed volume of a single mer ( $\nu^*$  is also the volume of a lattice site, and so a hole also has a volume equal to  $\nu^*$ ). In eqn. (9),  $\epsilon^* = z\epsilon/2$ , where  $\epsilon$  is an attractive interaction energy between two neighboring lattice

sites occupied by molecules, but not linked by a molecular bond (the hole-hole, hole-mer and bonded mer-mer interaction energies are considered equal to zero). When eqn. (8) is used a liquid-vapor transition is predicted. A numerical technique (Conte and de Boor, 1972) such as a fixed-point iteration method can be used to show this. From eqn. (8), the equation

$$\tilde{\rho} = h(\tilde{\rho}) = 1 - \exp\left\{-\frac{1}{\tilde{T}}\left[\left[\tilde{\rho}(1-\phi)/(1-\phi\tilde{\rho})\right]^2 + \tilde{P}\right] + (z/2) \ln(1-\phi\tilde{\rho})\right\} \quad (10)$$

defines the value of  $\tilde{\rho}$  at a given  $(T, P)$  which minimizes the free energy. In general, eqn. (10) has three solutions: the lowest and highest values of  $\tilde{\rho}$  correspond to minima in the Gibbs function, while the intermediate solution corresponds to a maximum in  $G$ . Since at a given pressure and temperature two minima appear, the lower free-energy minimum corresponds to a stable state, the higher being a metastable one. At a given pressure, there is a unique temperature such that the two free-energy minima are equal. This set of temperatures and pressures defines the coexisting liquid-vapor line, i.e., the model undergoes a liquid-vapor transition. In this way, in a  $P$  versus  $T$  diagram, eqn. (10) provides three regions: (i) stable liquid only, (ii) stable vapor only (in both cases eqn. (10) has only one solution), and (iii) metastable region.

#### DETERMINATION OF MOLECULAR PARAMETERS

At a given temperature and pressure, use of eqn. (10) to find the solution of the equation of state, eqn. (8), requires a knowledge of the quantities  $r$ ,  $z$ ,  $\epsilon^*$  and  $\nu^*$ . Sanchez and Lacombe (1976), having taken the limit  $z \rightarrow \infty$  in eqn. (3), obtained an equation of state independent of  $z$ . Being interested mainly in the liquid-vapor phase transition, they fitted their three parameters ( $\epsilon^*$ ,  $\nu^*$  and  $r$ ) to give the best fit to saturated-vapor-pressure data in the usual least-squares sense. As discussed earlier (Costas and Sanctuary, 1981), using the large  $z$  limit does not account for the fact that a molecule in the liquid state has a nearest-neighbor structure and hence a finite number of nearest neighbors. Also, having  $r$  acting as an adjustable parameter is to us an unappealing feature, since specific molecules have  $r$  values which are in disagreement with the philosophy implicit in the assumption of a lattice, i.e., that a molecule with  $r$  atoms (other than hydrogen) must occupy  $r$  sites. We have, thus, decided to remove  $r$  as an adjustable parameter and set it equal to the number of atoms, other than hydrogen, in the molecule. On the other hand, we find that the values of  $\epsilon^*$  and  $\nu^*$  (as well as the solution of the equation of state, eqn. (8)) obtained using the procedure described below are

practically insensitive to changes in  $z$  between the values 8 and 14; hence, we have chosen to fix  $z$  equal to 12, which is the average value (Tompa, 1956) generally accepted. Having, then, the parameters  $z = 12$  and  $r$  fixed for a given liquid, our equation of state has only two adjustable parameters, i.e.,  $\epsilon^*$  and  $\nu^*$ .

Since, as mentioned in the introduction, we are interested in thermodynamic properties in the liquid state, and the density is the most widely available datum for many liquids, we have fitted  $\epsilon^*$  and  $\nu^*$  using solely density data. The fitting procedure is as follows. We define an error function  $E'$  by

$$E' = \sum_{i=1}^n (\rho_i^{\text{exp.}} - \rho_i^{\text{calc.}})^2 \quad (11)$$

where  $n$  is the number of experimental density data points ( $\rho_i^{\text{exp.}}$ ) used and  $\rho_i^{\text{calc.}} = M\bar{\rho}/r\nu^*$  ( $M$  = molecular weight) the calculated density obtained by solving the equation of state, eqn. (8), at the corresponding  $T$  and  $P$ . At a given  $T$  and  $P$  the solution of the equation of state can be found using the form shown in eqn. (10). Here, an initial value for  $\bar{\rho}$  is needed (0.99 is a good choice), and then an iteration of the form  $\bar{\rho}_j = h(\bar{\rho}_{j-1})$  ( $j = 1, 2, \dots$ ) is performed until the difference  $\bar{\rho}_j - \bar{\rho}_{j-1}$  is less than or equal to a given threshold value (we have used  $1 \times 10^{-7}$ ). The values of the molecular parameters  $\epsilon^*$  and  $\nu^*$  that minimize eqn. (11) were thus found using an IMSL FORTRAN subroutine (ZXMIN) that finds the minimum of a function of  $N$  variables using a quasi-Newton method (Fletcher, 1972). Although this fitting procedure is not unique, its justification is that the resulting computer algorithm is fast and stable.

Table 1 lists the sixty different substances for which the above procedure was used to determine the characteristic parameters. For the majority of the substances, we used liquid density data at atmospheric pressure and variable temperature. For some liquids, as indicated in Table 1, experimental densities at pressures other than atmospheric were included in the fitting process. References to the experimental densities are given in Table 1.

Figure 1 shows the variation of the molecular parameters with the number of atoms ( $r$ ) other than hydrogen, for some of the substances listed in Table 1. Where there are few or no experimental data available for the fitting process, Fig. 1 may be used to estimate the required parameters. The linear behavior of the close-packed volume per molecule ( $r\nu^*$ ) and of the energy per molecule in the absence of holes ( $r\epsilon^*$ ) with  $r$  suggests that these parameters relate to molecular properties and are not merely adjustable constants. Similar behavior, i.e., linearity of molecular parameters with carbon number, was found by Donohue and Prausnitz (1978) using a perturbed-hard-chain theory for pure fluids applied to hydrocarbons.

TABLE 1  
Molecular parameters

Substance <sup>a</sup>	$r^b$	$\epsilon^*$ (kcal mol <sup>-1</sup> )	$\nu^*$ (cm <sup>3</sup> mol <sup>-1</sup> )	Substance	$r$	$\epsilon^*$ (kcal mol <sup>-1</sup> )	$\nu^*$ (cm <sup>3</sup> mol <sup>-1</sup> )
Methane	1	0.721	35.829	Methylcyclohexane	7	1.096	16.400
Ethane	2	0.782	23.641	Ethylcyclohexane	8	1.118	16.165
Propane	3	0.793	20.748	<i>n</i> -Propylcyclohexane	9	1.116	16.081
Butane	4	0.885	19.813	Ethene	2	0.700	21.278
Pentane	5	1.007	19.725	Propene	3	0.821	19.549
2-Methylbutane	5	0.986	19.743	1-Butene	4	0.925	18.950
2,2-Dimethylpropane	5	0.939	20.132	1-Hexene	6	1.048	18.348
Hexane <sup>c</sup>	6	1.057	19.257	1-Decene	10	1.078	17.092
2-Methylpentane	6	1.030	19.218	Benzene	6	1.106	13.295
3-Methylpentane	6	1.034	18.923	Toluene	7	1.130	13.782
2,2-Dimethylbutane	6	1.016	19.240	Ethylbenzene	8	1.126	13.927
2,3-Dimethylbutane	6	1.036	19.014	<i>n</i> -Propylbenzene	9	1.134	14.157
Heptane	7	1.027	18.398	<i>o</i> -Xylene	8	1.152	13.804
2-Methylhexane	7	1.037	18.611	<i>m</i> -Xylene	8	1.138	14.013
2,3-Dimethylpentane	7	1.045	18.222	<i>p</i> -Xylene	8	1.138	14.072

Octane	8	1.031	17.972	Naphthalene	10	1.372	12.015
3-Methylheptane	8	1.051	18.013	1-Methylnaphthalene	11	1.300	11.974
2,4-Dimethylhexane	8	1.039	18.085	2-Methylnaphthalene	11	1.276	12.116
2,2,4-Trimethylpentane	8	1.039	18.307	1,2-Dimethylnaphthalene	12	1.223	11.936
Nonane	9	1.042	17.687	1,6-Dimethylnaphthalene	12	1.246	12.172
Decane <sup>c</sup>	10	1.055	17.483	2,3-Dithiabutane	4	1.212	19.283
Dodecane <sup>c</sup>	12	1.083	17.203	3,4-Dithiahexane	6	1.152	18.641
Tetradecane <sup>c</sup>	14	1.106	16.911	4,5-Dithiaoctane	8	1.128	17.823
Hexadecane <sup>c</sup>	16	1.099	16.723	5,6-Dithiadecane	10	1.128	17.370
Eicosane	20	1.697	26.893	Methanol <sup>c,d</sup>	2	1.377	18.389
Cyclopentane	5	1.052	16.440	Ethanol <sup>c,d</sup>	3	1.266	17.672
Methylcyclopentane	6	1.037	16.431	1-Propanol <sup>c,d</sup>	4	1.223	17.048
Ethylcyclopentane	7	1.048	16.216	1-Pentanol <sup>c,d</sup>	6	1.187	16.525
Propylcyclopentane	8	1.055	16.117	1-Octanol <sup>d</sup>	9	1.154	16.084
Cyclohexane	6	1.097	16.129	Water	3	2.488	5.971

<sup>a</sup> All liquid densities at atmospheric pressure for adjusting  $\epsilon^*$  and  $\nu^*$  taken from API (1953) unless otherwise indicated.

<sup>b</sup> Not adjusted;  $r$  is a constant equal to the number of atoms other than hydrogen.

<sup>c</sup> Some liquid densities at  $P \neq 1$  atm. were also used for the adjustment: hexane, Stewart et al. (1954); decane, dodecane, tetradecane and hexadecane, Snyder and Winnick (1970); methanol, ethanol, 1-propanol and 1-pentanol, Sahli et al. (1976).

<sup>d</sup> Liquid densities at  $P = 1$  atm.: alcohols, Wilhoit and Zwolinski (1973); water, Riddick and Bunger (1970).

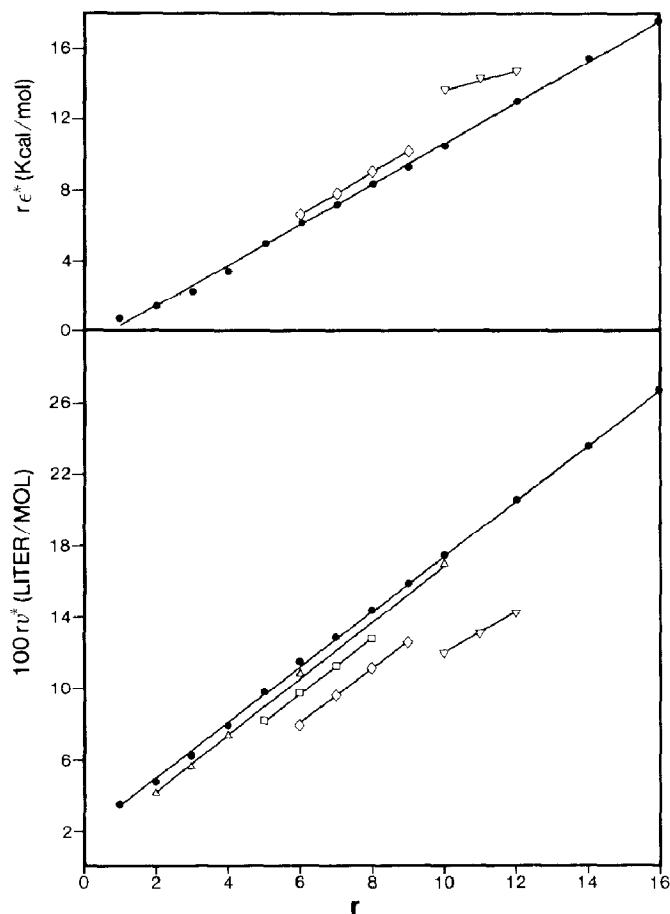


Fig. 1. Variation of molecular parameters with number of atoms in molecule ( $r$ ) other than hydrogen: ●,  $n$ -alkanes; Δ, alkenes; □, cyclopentane and derivatives; ◇, benzene and derivatives; ∇, naphthalene and derivatives.

#### CALCULATION OF THERMODYNAMIC PROPERTIES AND COMPARISON WITH EXPERIMENT

In this section we compare calculated and experimental values for first- and second-order thermodynamic properties. A first-order property is related to a first derivative on the Gibbs free energy and a second-order property is related to a second derivative. Figure 2 shows the volumetric behavior of  $n$ -hexane in the liquid phase. The calculated molar volume is given by  $V = r\nu^*/\bar{\rho}$ , where  $\bar{\rho}$  is the solution of eqn. (10) at given  $T$  and  $P$ . The calculated values are in fairly good agreement with experiment. It is worth noting that although the fitting procedure for  $\epsilon^*$  and  $\nu^*$  for  $n$ -hexane included only four density values at pressures other than atmospheric



(between 30°C and 50°C and at 14–27 atm.), the calculated molar volumes at high pressures and temperatures are in very good agreement with experiment (within 2.5% at 204°C and 544 atm.).

Table 2 lists experimental and calculated values for other first-order thermodynamic properties of six aromatic compounds: the heat of vaporization at the boiling temperature, and the liquid density and cohesive energy density (c.e.d.) at 25°C. The heat of vaporization is calculated using

$$\begin{aligned}\Delta H_{\text{vap}} &= H_G - H_L = (E + PV)_G - (E + PU)_L \\ &= r\epsilon^*(\tilde{\rho}_L - \tilde{\rho}_G) + r\nu^*P(1/\tilde{\rho}_G - 1/\tilde{\rho}_L)\end{aligned}\quad (12)$$

where  $\tilde{\rho}_G$  and  $\tilde{\rho}_L$  are the solutions of eqn. (10) for the gas and liquid at given  $T$  and  $P$ . Initial values for  $\tilde{\rho}$  of 0.99 and 0.0 for the iterative process in eqn. (10) converge after some iteration and are identified as  $\tilde{\rho}_L$  and  $\tilde{\rho}_G$ , respectively. The c.e.d. is simply the ratio  $\Delta H_{\text{vap}}(25^\circ\text{C})/V_L$ , where  $\Delta H_{\text{vap}}(25^\circ\text{C})$  was calculated using eqn. (12) at the experimental saturation pressure, and  $V_L = r\nu^*/\tilde{\rho}_L$ . Table 2 shows that while the calculated densities at 25°C are in very good agreement with experiment, the  $\Delta H_{\text{vap}}$  values at the boiling temperature and the c.e.d.'s at 25°C are in error by 8–15% (except for benzene, where the error is slightly higher). These errors probably arise because the calculations of  $\Delta H_{\text{vap}}$  and c.e.d. involve the calculation of a vapor density at conditions that are far away from the conditions at which

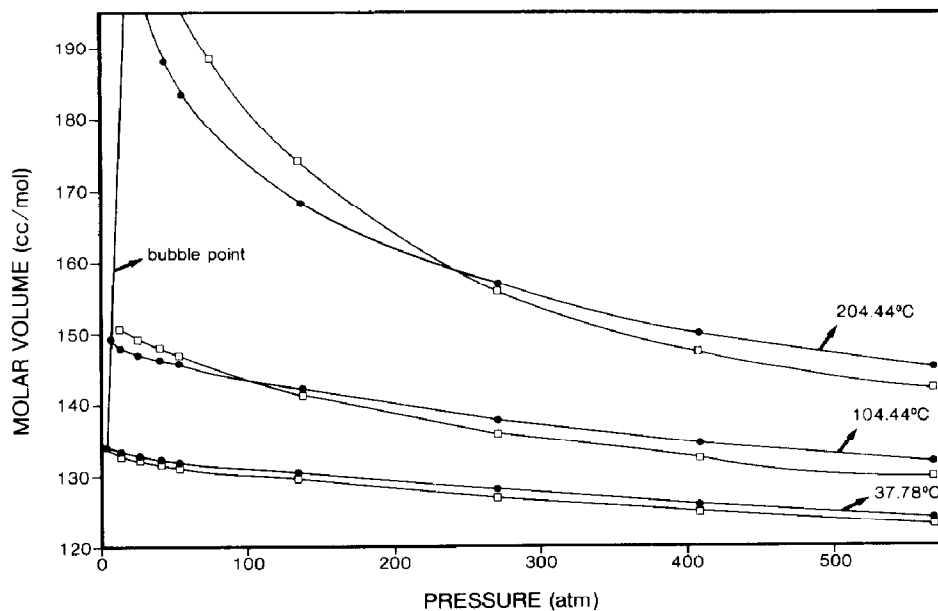


Fig. 2. Volumetric behavior of *n*-hexane: comparison between experimental (●) and calculated (□) values (experimental data from Stewart et al. (1954)).

TABLE 2

Comparison of experimental and calculated values for heat of vaporization at boiling point ( $T_b$ ), and liquid density and cohesive energy density (c.e.d.) at 25°C for six aromatic compounds<sup>a</sup>

Substance	$T_b$ (°C)	$\Delta H_{\text{vap}}(T_b)$ (kcal mol <sup>-1</sup> )			$\rho_L$ (25°C) (g cm <sup>-3</sup> )			c.e.d. (25°C) (cal cm <sup>-3</sup> )		
		Exp.	Theor.	Error(%)	Exp.	Theor.	Error(%)	Exp.	Theor.	Error(%)
<i>o</i> -Xylene	144.41	8.80	7.93	-11.0	0.87596	0.87616	-0.02	85.65	74.50	-13.0
<i>m</i> -Xylene	139.10	8.69	7.84	-9.8	0.85990	0.86018	+0.03	82.57	72.05	-12.7
<i>p</i> -Xylene	138.35	8.60	7.85	-8.7	0.85669	0.85657	-0.01	81.72	71.71	-12.2
Ethylbenzene	136.18	8.50	7.74	-9.8	0.86264	0.86286	+0.03	82.05	71.33	-13.1
Toluene	110.63	7.93	7.09	-10.6	0.86231	0.86280	+0.06	84.98	72.63	-14.5
Benzene	80.10	7.35	6.15	-16.0	0.87370	0.87414	+0.05	90.48	73.05	-19.2

<sup>a</sup> All experimental data taken from Riddick and Bunger (1970). Experimental saturation pressures for c.e.d. calculations taken from Reid et al. (1977).

liquid density data were used to fit the molecular parameters  $\epsilon^*$  and  $\nu^*$ .

Second-order thermodynamic properties can be derived from the equation of state, eqn. (8). The thermal expansion coefficient  $\alpha$  and the isothermal compressibility  $\beta$  are given by

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P = - \frac{1}{T^*} \left. \frac{\partial \ln \tilde{p}}{\partial \tilde{T}} \right|_P \quad (13a)$$

$$\beta = - \frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T = \frac{1}{P^*} \left. \frac{\partial \ln \tilde{p}}{\partial \tilde{P}} \right|_T \quad (14a)$$

$$\alpha T = \tilde{\alpha} \tilde{T} = \left[ (1 - \phi)^2 + \tilde{P}(\tilde{\nu} - \phi)^2 \right] / \left\{ \tilde{T}(\tilde{\nu} - \phi) \left[ (1 - \phi)/(\tilde{\nu} - 1) + 1/r \right] - 2(1 - \phi)^2 \tilde{\nu}/(\tilde{\nu} - \phi) \right\} \quad (13b)$$

$$\beta P = \tilde{\beta} \tilde{P} = \tilde{P}(\tilde{\nu} - \phi)^2 / \left\{ \tilde{T}(\tilde{\nu} - \phi) \left[ (1 - \phi)/(\tilde{\nu} - 1) + 1/r \right] - 2(1 - \phi)^2 \tilde{\nu}/(\tilde{\nu} - \phi) \right\} \quad (14b)$$

Figure 3 compares the calculated (using eqn. (13b)) and experimental values for the thermal expansion coefficients of two linear alkanes as functions of temperature. Table 3 shows experimental and calculated (using

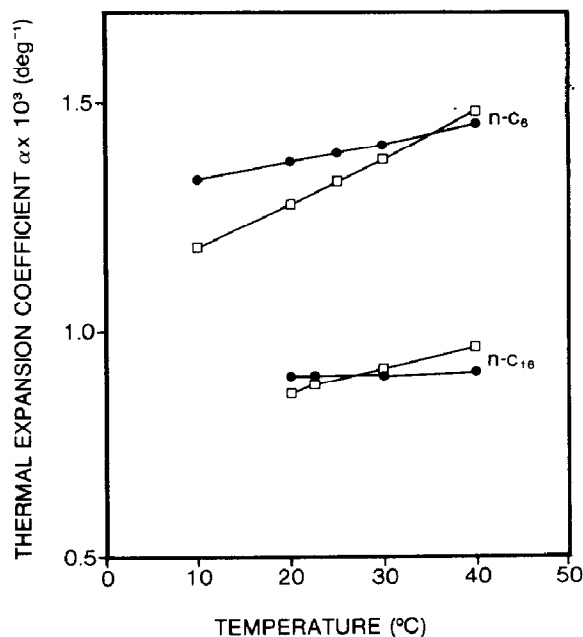


Fig. 3. Experimental (●) and calculated (□) thermal expansion coefficients for *n*-hexane and *n*-hexadecane (experimental data from Orwoll and Flory (1967)).

eqn. (14b)) values for the isothermal compressibility of *n*-decane at 25 °C as a function of pressure. In both cases, the comparison between experiment and theory shows that the theory is capable of predicting with fair accuracy second-order thermodynamic quantities which are usually difficult to estimate, and which are used by some other theories (Flory et al., 1964) as input values for parameter fitting.

Jain and Simha (1981) reported a complete equation of state for an *n*-paraffin fluid. They used a quasi-lattice model with sites occupied either by whole molecules, by chain segments or by vacancies (Simha, 1977). Their equation of state is easy to use and gives accurate *PVT* results for any *n*-paraffin melt between  $n = 6$  and  $n = 17$ . Since our model also allows vacancies or holes in the lattice, a comparison between the two equations of state is pertinent. Figure 4 shows the volumetric behavior of *n*-dodecane in the liquid phase together with the results calculated using the two equations of state. While the calculations using the Jain and Simha equation involve the use of five parameters ( $s$ ,  $A$ ,  $B$ ,  $C$  and  $D$ ), the use of eqn. (10) requires only the two parameters listed in Table 1 for *n*-dodecane. It can be seen that the results from eqn. (10) are in fairly good agreement with the experimental values. Nevertheless, at higher pressures (not shown in Fig. 4), eqn. (10) starts to deviate from the experimental values. Here again, as in the case of the volumetric behavior of *n*-hexane, it is worth noting that  $\epsilon^*$  and  $\nu^*$  for *n*-dodecane were fitted to densities at atmospheric pressure and to four density points at higher pressures (up to 68 atm.).

Overall, considering that the theory (a) only has two adjustable parameters ( $\epsilon^*$  and  $\nu^*$ ), (b) requires only a few density values to adjust  $\epsilon^*$  and  $\nu^*$ , and (c) requires simple fitting and calculation procedures for thermodynamic properties, it should qualify as a useful tool for estimating either first- or second-order thermodynamic properties in the liquid phase as frequently required in engineering work.

TABLE 3

Comparison of experimental and calculated values for the isothermal compressibility  $\beta$  of *n*-decane at 25 °C as a function of pressure<sup>a</sup>

$P$ (atm.)	$10^4 \times \beta$ (atm. <sup>-1</sup> )		
	Exp.	Theor.	Error(%)
272.11	0.84	0.94	11.9
340.14	0.79	0.83	5.1
408.16	0.75	0.75	0.0
476.19	0.72	0.67	-6.9

<sup>a</sup> All experimental data taken from Snyder and Winnick (1970).

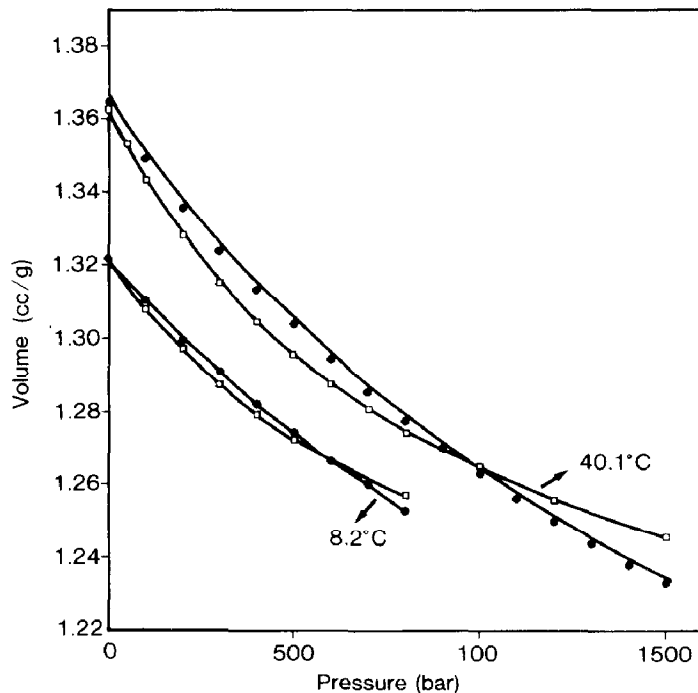


Fig. 4. Volumetric behavior of *n*-dodecane: comparison between experimental results (●) and values calculated using eqn. (10) (□) and Jain and Simha equation of state (lines through full symbols) (experimental data from Landau and Würflinger (1980)).

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