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Vapor–liquid equilibria of linear and branched alkanes from perturbation theory

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The vapor–liquid equilibrium properties of linear and branched alkanes with up to eight carbon atoms have been determined by means of a simple perturbation theory. An accurate equation of state for the reference system is combined with a mean field treatment of the perturbation term, along with a reasonable set of potential parameters. Experimental trends of the critical properties of alkanes are described qualitatively by the theory. In particular, the maximum in the critical pressure and density of linear alkanes as a function of the number of carbon atoms is reproduced and explained on a simple basis. The effect of branching on the critical properties is considered and it is found that the decrease in the critical temperature with branching is correctly predicted. With a few exceptions for some substances, other general trends in critical pressure and density are predicted and explained. The effect of branching on the principle of corresponding states is also studied, in particular on the coexistence densities and vapor pressures. It is found that branching reduces the slope of the vapor pressure curve and makes the coexistence curve narrower when these magnitudes are represented in a corresponding states plot. It is shown that a simple mean field theory is able to describe qualitatively the variation in the critical properties of linear and branched alkanes. © *1998 American Institute of Physics.* [S0021-9606(98)50337-6]

I. INTRODUCTION

The critical properties of alkanes have received attention during the last years.[1] Experimentally a maximum in the critical density of *n*-alkanes when plotted as a function of the number of carbon atoms[2,3] has been found. This was quite surprising, as it was previously believed that the critical density of alkanes reached an asymptotic finite value.[4] Further experimental work, and even computer simulations,[5,6] seem to confirm the existence of this maximum.

The effect of branching on the critical properties of alkanes is another interesting issue. It is well known that branching generally provokes a decrease in the boiling point, or conversely, in the critical temperature. This is well documented and a number of General Chemistry[7] and Organic Chemistry[8] textbooks have proposed a simple explanation for this fact. Some recent Gibbs ensemble simulations[9,10] dealing with the effect of branching on the critical properties have also appeared.

Theoretically, the problem of the vapor–liquid equilibrium of alkanes has been considered less often. Some work by Prigogine's group[11] as well as by Flory[12] and Patterson[13] was pioneering in the area. However, it seems clear that after the great progress in the statistical mechanics of flexible systems performed during the seventies and eighties, the problem can and probably should be undertaken and reformulated in a new language.

From a theoretical point of view, the main contributions that made the problem of the vapor–liquid equilibrium of alkanes affordable are, in our opinion, the development of (i) perturbation theories for molecular fluids,[14–21] (ii) good equations of state (EOS) for hard flexible chains,[22–24] (iii) the development of potential parameters describing the interaction between alkane molecules,[6,25–29] and finally, (iv) integral equations to obtain the structure of flexible molecules for either short[30] or long chains.[31,32] It is clear that much effort is now focused on this area and great progress can be expected in the incoming years.

In this work we have a not so ambitious goal. Our aim is to show that with a good EOS for the reference system and a reasonable set of potential parameters, some of the properties of alkanes can be understood even with a simple mean field first order perturbation theory. We will analyze how much can be extracted from this simple treatment. Obviously, we are not searching for a quantitative agreement but rather for a qualitative description.

A first step in this direction was performed in a previous paper.[33] In fact, the conditions for the appearance of maxima in the critical properties of chain molecules were clearly identified. However, our previous work[33] was not fully satisfactory in two respects.

Owing to our ignorance on the second virial coefficient of hard branched alkanes, required as input for the reference part of the perturbation theory, only linear chains were considered. This gap has been fulfilled in the preceding paper[34] (hereinafter referred to as paper I) and we can now attempt this problem. Second, the mean field we proposed was estimated in a rather simple manner which did not consider the topological details of the molecule. In a general sense, the mean field approximation considers the structure of the reference system at any density as that of the zero density limit. For spherical particles, this limit is a Heaviside step function, such that the pair correlation function is zero for distances

TABLE I. Lennard-Jones parameters for the two models used in this work. Model I uses the potential parameters proposed by Poncela *et al.*, while Model II uses the parameters proposed in this work. The different σ are given in Å and the ϵ are given in units of k_B.

Model	σ_{CH_4}	σ_{CH_3}	σ_{CH_2}	σ_{CH}	σ_{C}	ε_{CH_4}	ε_{CH_3}	ε_{CH_2}	ε_{CH}	ε_{C}
I	4.10	4.02	3.72	3.36	2.44	140 K	96 K	57 K	36 K	9 K
II	4.10	4.10	3.95	3.87	3.73	140 K	93 K	67 K	37 K	12 K

less than σ and unity otherwise.[35] In our previous work on alkanes,[33] the site–site correlation functions of the molecules were approximated in this manner. Clearly, this does not correspond to the rigorous mean field treatment. In fact, the zero density limit of the site–site correlation function is not a Heaviside function even for the relatively simple diatomic fluid[36,37] and the same occurs for the more complicated models of alkane molecules. In this work, we present a perturbation theory which implements the mean field approximation exactly. We want to analyze whether such a theory is able to describe qualitatively the vapor–liquid equilibrium of short, linear and branched alkanes.

The scheme of this paper is as follows. In Sec. II, the potential model is described. Section III is devoted to the formulation of the perturbation theory. In Sec. IV, the results are presented. Finally, the main conclusions of this work are given in Sec. V.

II. MODEL

As in paper I, the alkane is modeled by means of the united atom approach, where each CH$_n$ group is described by an interaction site located on the position of the carbon atom. The carbon–carbon bond distance is taken as $l=1.53$ Å, while the C–C–C bond angle θ is set to the tetrahedral value, i.e., $\theta=109.5$ degrees. Certainly, the experimental bond angle is not exactly tetrahedral but depends on the length of the chain and on branching so that it may differ slightly for different bonds and alkanes. However, to make calculations relatively simple we have ignored this complication, as we do not expect the results to be severely distorted by such approximation. The torsional degrees of freedom are treated within the rotational isomeric state approximation (RIS), the details of which are explained elsewhere.[34,38]

The intramolecular energy is divided into short and long range contributions as explained in paper I, with the difference that long range interactions are considered to start from atoms separated by four or more bonds and that they are no longer hard sphere interactions but Lennard-Jones (LJ) interactions. The intramolecular energy for a certain conformation is thus given by:

$$U_{\mathrm{intra}}=U_{\mathrm{intra}}^{\mathrm{short}}+U_{\mathrm{intra}}^{\mathrm{long}}=n_g E_1+\sum_k \sum_l{}' \, 4\varepsilon_{kl}((\sigma_{kl}/r_{kl})^{12} -(\sigma_{kl}/r_{kl})^{6}), \tag{1}$$

where E_1 is a temperature dependent torsional energy which ensures that the RIS approximation gives the same conformational populations as the chosen continuous torsional potential,[39] which is taken to be the familiar Ryckaert–Bellemans potential.[40] The prime indicates that the double sum is constrained to those pairs of carbon atoms four or more bonds apart.

The intermolecular energy between two molecules is given by:

$$U_{\mathrm{inter}}=\sum_{k=1}^{N}\sum_{l=1}^{N} 4\varepsilon_{kl}((\sigma_{kl}/r_{kl})^{12}-(\sigma_{kl}/r_{kl})^{6}), \tag{2}$$

where the summation is now over the N interaction sites of each molecule. The same set of Lennard-Jones parameters are used for intramolecular and intermolecular interactions. The values of the Lennard-Jones interactions between chemically different groups are obtained from the Lorentz–Berthelot rule (LB).[41]

Concerning the values of the parameters σ and ε, several choices are possible. Initially, we have adopted the set of parameters proposed by Poncela, Rubio and Freire.[29] These parameters are able to fit the second virial coefficients of a number of linear and branched alkanes. The fact that second virial coefficient calculations may help in the search of potential parameters was already illustrated by Lopez-Rodriguez *et al.* for n-alkanes.[26,27,42] The parameters thus obtained were able to describe correctly the second virial coefficients and when modified slightly were even able to describe the critical properties of n-alkanes as obtained from Gibbs ensemble simulations.[5,6] The parameters used by Poncela, Rubio and Freire[29] are presented in Table I. The model described by this set of parameters will be named Model I from now on.

III. PERTURBATION THEORY

The total energy of the system will be divided into a reference and a perturbation part:

$$U=U_{\mathrm{intra}}+U_{\mathrm{inter}}=U_{\mathrm{intra}}+(U_0+\lambda U_1). \tag{3}$$

The value $\lambda=0$ defines the reference system, while setting $\lambda=1$ we recover the original system. Each LJ intermolecular interaction, u, will be divided into a reference and perturbation part following the Weeks–Chandler–Andersen criterion (WCA),[15] so that the reference potential u_0 is given by:

$$\begin{aligned} u_0(r_{kl})&=4\varepsilon_{kl}((\sigma_{kl}/r_{kl})^{12}-(\sigma_{kl}/r_{kl})^{6})+\varepsilon_{kl} \quad r_{kl}<2^{1/6}\sigma_{kl},\\ u_0(r_{kl})&=0 \quad r_{kl}>2^{1/6}\sigma_{kl}. \end{aligned} \tag{4}$$

The perturbation part of the potential u_1 is obtained from the condition $u=u_0+u_1$. Note that the *intramolecular interactions of our reference system are of LJ type,* whereas intermolecular interactions are of the WCA type. This may appear somewhat unusual but we believe it is a very useful way of implementing perturbation theories for flexible chains. In fact, this division of the potential guarantees that the reference system has the same conformational population as the full system at zero density.

The Helmholtz free energy A is given by an ideal, an intramolecular and an intermolecular contribution:

$$A=A_{\mathrm{ideal}}+A_{\mathrm{intra}}(\mathbf{X})+A_{\mathrm{inter}}(\mathbf{X}), \tag{5}$$

where $\mathbf{X}=(x_1,x_2,..,x_q)$ is a vector whose components are the molar fractions of the q conformers of the system (the number of possible conformers, q, may be large but it remains finite within the RIS approximation). Let us now describe briefly each term.

The ideal term is given by:

$$A_{\mathrm{ideal}}/N_{\mathrm{mol}}=k_BT(\ln(\rho\Lambda^3)-1), \tag{6}$$

where ρ is the number density, N_{mol} is the number of molecules in the system, k_B is the Boltzmann constant and Λ is the thermal wavelength. Without loss of generality, we shall assign Λ to equal the value of σ of the CH_2 group (i.e., σ_{CH_2}).

The intramolecular term is given within the RIS approximation by:[39,43]

$$A_{\mathrm{intra}}/N_{\mathrm{mol}}=k_BT\sum_{i=1}^{i=q} x_i \ln(x_i)+\sum_{i=1}^{i=q} x_i n_{g,i}E_1 +\sum_{i=1}^{i=q} x_i U_{\mathrm{intra},i}(\mathrm{LJ}), \tag{7}$$

where $n_{g,i}$ is the number of gauche bonds, $U_{\mathrm{intra},i}(\mathrm{LJ})$ is the intramolecular LJ energy of conformer i and q is the number of possible conformers of the molecule. The use of the A_{intra} term is not new and was already introduced in previous work.[39,43,44]

First order perturbation theory will be applied so that the excess free energy of the system interacting through the original potential is expanded about that of the reference system up to first order. In this way, the intermolecular contribution is split into a reference and a perturbation part:

$$A_{\mathrm{inter}}(\mathbf{X})=A_0(\mathbf{X})+A_1(\mathbf{X}), \tag{8}$$

where $A_0(\mathbf{X})$ is the intermolecular free energy of the reference system when the population of conformers is given by the actual population of the full system, $\mathbf{X}$, and $A_1(\mathbf{X})$ is the intermolecular free energy due to the perturbation potential.

The latter contribution is given by the following equation:

$$\frac{A_1}{N_{\mathrm{mol}}}=\frac{\rho}{2}\sum_{k=1}^{N}\sum_{l=1}^{N} \varepsilon_{kl}\sigma_{kl}^3\int u_1^*(r_{kl}^*)g_{0,kl}(r_{kl}^*,\mathbf{X})4\pi r_{kl}^{*2}dr_{kl}^*, \tag{9}$$

where $g_{0,kl}(r,\mathbf{X})$ is the site–site correlation function between sites k and l of the reference system and the asterisks denote reduced units, i.e., $r_{kl}^*=r_{kl}/\sigma_{kl}$ and $u_{1,kl}^*=u_1/\epsilon_{kl}$.

Substitution of Eqs. (6)–(9) into Eq. (5) yields an expression for the free energy which resembles that given by many density functional theories (DFT). In these treatments, the free energy of the system is divided into a noninteracting part (which depends only on the singlet correlation function and in our case includes the ideal and intramolecular terms) and an interaction part. The free energy functional is minimized with respect to the singlet correlation function (i.e., the set of $\mathbf{X}$). Although DFT is usually applied to nonhomogeneous fluids and in liquid crystal theories,[45,46] the fact that perturbation theories of flexible molecules can be regarded as a version of DFT is not new and was proposed by Enciso *et al.* previously.[47] Here we only notice that once the functional of the free energy has been written in terms of $\mathbf{X}$, the conformational population for a given density and temperature should be obtained by minimizing Eqs. (5)–(9) with respect to $\mathbf{X}$. Examples of this minimization for hard alkanes were performed in previous work.[39,43]

Actually, the minimization of Eqs. (5)–(9) with respect to $\mathbf{X}$ for each density and temperature is an overwhelming task for all but the simplest cases and further approximations are required. Fortunately, for short flexible chains it is well known that density effects on the conformational population are small.[48,49] In fact, the conformational changes of vapor and liquid coexisting phases of n-alkanes have been found to vary no more than a few percent for n-alkanes smaller than n-octane.[50] We shall therefore assume that for a given temperature, the conformational population at zero density is valid for all densities. When changes in conformational population with density are neglected, the intramolecular term given by Eq. (7) is a constant for a given temperature and does not affect the vapor–liquid equilibrium.

Even with this approximation, the perturbation theory is as yet incomplete, as we still need to know the structure and thermodynamics of the reference system. This requires a further approximation, which consists in assigning an effective hard body to the reference system. In a previous paper,[51] it was shown that mapping the WCA repulsive interaction sites into hard spheres with diameter given by the Barker–Henderson prescription[14] gave excellent results. In that paper, however, only one kind of interaction site was considered, so that the diameter of the effective hard sphere, d, was simply given as $d/\sigma=d_{\mathrm{BH}}(T/(\epsilon/k_B))$ where the subindex BH recalls the use of the Barker–Henderson prescription. In this work, each type of site may eventually interact with any other, so that the choice of the reduced energy (ϵ) to use in the preceding equation remains ambiguous. The choice we have taken is to reduce the temperature by means of an energy parameter that corresponds to the interaction of the given site with the ''average'' site of the molecule. In the context of the Lorentz–Berthelot rule, this means that the energy parameter used to reduce the temperature of site k, ζ_k, is given by:

$$\zeta_k=\left(\varepsilon_k\frac{1}{N}\sum_{l=1}^{N}\varepsilon_l\right)^{1/2}. \tag{10}$$

Therefore for each interaction site the diameter of the associated hard sphere d_k is given by $d_k/\sigma_k=d_{\mathrm{BH}}(T/(\zeta_k/k_B))$. Strictly speaking, however, the effective diameters of each site should be considered as additional variational parameters in Eq. (5).

Having assigned an effective hard body to the reference system, the thermodynamics is then calculated by means of the modified Wertheim equation, which has been shown to give excellent results for hard n-alkanes.[39,43,51] According to this equation, the free energy is given by:[51]

$$\frac{A_0}{N_{\mathrm{mol}} k_B T} = (2\overline{\alpha}-1)\ln\left(\frac{2(1-y)^3}{(2-y)}\right) - (2\overline{\alpha}-2)\frac{1+y-0.5y^2}{(1-y)(1-0.5y)}, \tag{11}$$

where $\overline{\alpha}$ is the nonsphericity parameter of the molecule and the packing fraction, y, is given as the product of the number density, ρ, and the average molecular volume, $\overline{V}$. Let us just mention that the modified Wertheim equation is obtained from Wertheim's equation[22,23] by simply imposing it to yield the true second virial coefficient of the fluid. More details may be found elsewhere.[39,43,51]

Now, since we regard the system as a multicomponent mixture of rotational isomers, $\overline{\alpha}$ and $\overline{V}$ are obtained as a conformational average:

$$\overline{\alpha} = \sum_{i=1}^{q} x_i \alpha_i, \tag{12}$$

$$\overline{V} = \sum_{i=1}^{q} x_i V_i. \tag{13}$$

In this way, it is seen that Eq. (11) gives the configurational free energy of a system with WCA repulsive intermolecular interactions which is forced to have the conformational population of an ideal gas of molecules with the LJ intramolecular potential. The values of α_i needed in Eq. (12) should be chosen so as to exactly reproduce the second virial coefficient of the conformers considered. Rather than making this time consuming calculation for each alkane, we will use the estimate given by the convex body geometry (CBG) methodology described in the preceding paper, which was seen to be very accurate. This allows for a fast implementation of the theory, since the evaluation of $\overline{\alpha}$ in this way requires only a few seconds in a workstation.

Now, both $\overline{\alpha}$ and $\overline{V}$ are temperature dependent, as a consequence of the temperature dependence of both the conformational population and the diameter of the effective hard body. In order to reduce the computational cost of the theory, these parameters are calculated only for three temperatures and are then fitted to a second order polynomial in the temperature. Details of the calculation of the nonsphericity and volume of the molecules for each temperature are given in paper I.[34]

The structure of the reference system is taken within the mean field approximation as that of the effective hard body at zero density. In this way, A_1 becomes a trivial linear function of the density, as is usual in mean field theories:

$$\frac{A_1}{N_{\mathrm{mol}}} = \rho \frac{a_{\mathrm{vdw}}}{2} \sum_{k=1}^{N} \sum_{l=1}^{N} \varepsilon_{kl} \sigma_{kl}^3 M_{kl}. \tag{14}$$

In the above equation, a_{vdw} is the van der Waals constant for a Lennard-Jones fluid[35] and M_{ij} are "mean field factors," given as the ratio of the van der Waals site–site constants to the van der Waals constant for a spherical Lennard-Jones molecule:

$$M_{kl} = \frac{\int_{d_{kl}^*}^{\infty} u_1^*(r_{kl}^*) g'_{o,kl}(r_{kl}^*, \mathbf{X}) 4\pi r_{kl}^{*2} dr_{kl}^*}{\int_1^{\infty} u_1^*(r^*) 4\pi r^{*2} dr^*} = \frac{\int_{d_{kl}^*}^{\infty} u_1^*(r_{kl}^*) g'_{o,kl}(r_{kl}^*, \mathbf{X}) 4\pi r_{kl}^{*2} dr_{kl}^*}{a_{\mathrm{vdw}}}, \tag{15}$$

where $g'_{o,kl}$ is the site–site correlation function of the hard body system at zero density and $d_{kl}^* = (d_k + d_l)/(\sigma_k + \sigma_l)$.

In practice, only five types of interaction sites will be considered (i.e., CH_4, CH_3, CH_2, CH and C), so that defining n_{kl} as the number of interactions of sites of type k with sites of type l, the sum in Eq. (14) may be finally expressed in the following manner:

$$\frac{A_1}{N_{\mathrm{mol}}} = \rho \frac{a_{\mathrm{vdw}}}{2} \sum_{k=1}^{5} \sum_{l=1}^{5} n_{kl} \varepsilon_{kl} \sigma_{kl}^3 \overline{M}_{kl}, \tag{16}$$

where it is clear that k and l denote the kind of site (i.e., the values $k = 1,2,3,4,5$ represent the CH_4, CH_3, CH_2, CH and C groups, respectively) and $\overline{M}_{kl}$ is an average mean field factor for all the kl interactions of that kind in the molecule.

The zero density site–site correlation function, $g'_{o,ij}$ of the hard body was evaluated as described in Appendix C of paper I. We used method II. Typically, we randomly selected 100 pairs of conformers from a sample of 300 conformers and averaged over 4280 orientations for each site–site distance and pair of conformers. The calculation of $g'_{o,ij}$ is time consuming. We have therefore evaluated the correlations at a single temperature for each alkane (recall that the dependence on temperature appears through the hard body diameter and through the conformational population). This temperature was chosen to be close to the predicted critical temperature. We have observed, however, that the mean field factors remain almost unchanged in a range of about 100 K.

IV. RESULTS

In this section, the main results of this work are shown and discussed.

Let us start by presenting the values of $\overline{M}_{kl}$ for Model I, as shown in Table I. This is done in Table II (numbers in parenthesis) for alkanes with up to six carbon atoms. Inspection of this table shows that bonding of a carbon atom with other carbon atoms greatly reduces the mean dispersive energy felt by that atom. This is seen by comparing mean field factors for CH_3–CH_3, CH_2–CH_2, CH–CH and C–C interactions, or simply by comparing to the mean field factor of a nonbonded Lennard-Jones interaction, which is equal to 1 [note that for CH_4 the mean field factor is not exactly one due to the fact that d_{kl}^* in Eq. (15) is not exactly one for the chosen temperature]. This decrease in $\overline{M}_{kl}$ for high order carbons is a natural consequence of the reduction of the con-

TABLE II. Average mean field factors multiplied by 100. Numbers in parenthesis correspond to data for Model I, while the others correspond to Model II. The entry for methane corresponds to CH_4–CH_4 interactions.

	Alkane	Average mean field factors, $\overline{M}_{kl}$									
	site k	CH_3				CH_2			CH		C
	site l	CH_3	CH_2	CH	C	CH_2	CH	C	CH	C	C
1	methane	98 (98)									
2	ethane	84 (83)									
3	propane	75 (76)	70 (68)			65 (61)					
4	2-methylpropane	66 (65)		58 (51)					49 (36)		
5	*n*-butane	70 (72)	64 (62)			57 (53)					
6	2,2-dimethylpropane	58 (57)			47 (29)						35 (10)
7	2-methylbutane	62 (62)	56 (54)	53 (46)		50 (46)	47 (39)		43 (31)		
8	pentane	68 (70)	60 (59)			51 (48)					
9	2,2-dimethylbutane	55 (55)	50 (47)		43 (26)	45 (40)		38 (21)			31 (9)
10	2,3-dimethylbutane	56 (56)		47 (41)					38 (27)		
11	2-methylpentane	60 (62)	52 (50)	51 (45)		43 (40)	42 (35)		41 (30)		
12	3-methylpentane	59 (60)	53 (51)	48 (42)		46 (43)	42 (34)		37 (27)		
13	*n*-hexane	66 (68)	57 (56)			48 (45)					

tact value of the site–site correlation functions. Note also that the mean field factors for crossed interactions seem to be well described by the simple prescription:

$$\overline{M}_{kl}=(\overline{M}_{kk}+\overline{M}_{ll})/2. \tag{17}$$

Once the geometrical parameters of the reference system are calculated (see paper I) and the mean field factors are known, the critical properties of the fluid may be determined by setting to zero the first and second derivatives of the pressure with respect to the volume, at constant temperature.

In Fig. 1, the experimental critical temperatures[52–54] for a number of alkanes with up to eight carbon atoms are compared to those of Model I, as predicted from our theory. For each group of isomers, the experimental critical temperature of a given alkane in that group is plotted in order of decreasing temperature, and the corresponding prediction from the theory is plotted for the same value of the abscissa. In order to identify to what particular alkane corresponds each integer number in the x axis, Table III shows a list of the alkanes considered, together with the substance index used to represent it in Fig. 1.

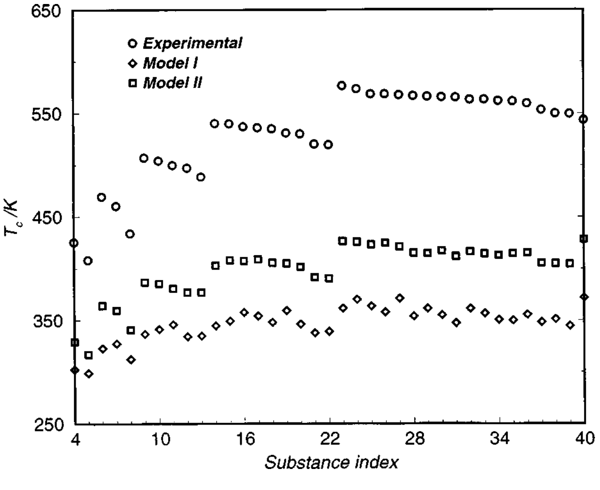

FIG. 1. Critical temperature of alkanes with up to eight carbon atoms, as obtained from experiment (Refs. 52–54) and from the theory of this work for Model I and Model II. Each alkane is represented by an integer number along the x axis which is shown in the third column of Table III.

A quantitative agreement between theory and experiment is not possible, since we are using the mean field approximation. Theoretical critical temperatures are lower than experimental ones, as usual in mean field theories, where correlations are underestimated. Let us mention that in our previous work,[33] where the site–site correlation functions were crudely approximated as Heaviside step functions, the critical temperatures of long chains were overestimated, showing that this incorrect treatment of the mean field may actually overestimate the correlations. Indeed, we have observed that such a simple treatment would completely fail in the description of the critical properties of branched alkanes, even though it may successfully predict several trends of linear alkanes, as shown in Ref. 33.

However, despite the use of the exact mean field, the results presented in Fig. 1 for Model I are not fully satisfactory. Experimental trends in the critical temperature do not seem to be correctly described by the theory when the parameters of Model I are used. Although we may not rule out the possibility of a failure of the theory, the discrepancies could arise from the use of an inadequate force field. We have therefore proposed a new set of Lennard-Jones parameters, presented in Table I and hereinafter denoted as Model II. The values of ε are relatively similar in both Models (I and II), but the decrease in σ on going from the CH_n to the C group is less pronounced in the new set. The average mean field factors needed to implement the theory for this model are presented in Table II.

In Fig. 1 the critical temperatures predicted by the theory for Model II are presented. As can be seen, for this potential model the theory captures the main trends of the variations of the critical temperatures in alkanes. Similar plots for the critical molar volume and pressure are shown in Figs. 2 and 3. The substance index used to represent each alkane along the x axis of Fig. 2 and Fig. 3 is shown in Table III. For the

TABLE III. List of the alkanes considered together with their corresponding substance index. For each of the critical properties, T_c, V_c and p_c, the table shows the substance index assigned to a given alkane in the corresponding figure. The notation R,S denotes the absolute configuration of the asymmetric carbon atoms.

		Order index		
	Alkane	T_c (Fig. 1)	V_c (Fig. 2)	p_c (Fig. 3)
1	methane	1	1	1
2	ethane	2	2	2
3	propane	3	3	3
4	2-methylpropane	5	4	5
5	*n*-butane	4	5	4
6	2,2-dimethylpropane	8	8	8
7	2-methylbutane	7	6	6
8	pentane	6	7	7
9	2,2-dimethylbutane	13	12	11
10	2,3-dimethylbutane	11	13	9
11	2-methylpentane	12	10	12
12	3-methylpentane	10	11	10
13	*n*-hexane	9	9	13
14	2,2,3-trimethylbutane	19	21	14
15	2,2-dimethylpentane	21	17	19
16	3,3-dimethylpentane	17	19	15
17	2,3-dimethylpentane(R)	16	22	16
18	2,4-dimethylpentane	22	16	20
19	2-methylhexane	20	15	22
20	3-methylhexane	18	20	18
21	3-ethylpentane	14	18	17
22	*n*-heptane	15	14	21
23	2,2,3,3-tetramethylbutane	27	34	23
24	2,2,3-trimethylpentane(S)	32	40	27
25	2,3,3-trimethylpentane	24	35	24
26	2,2,4-trimethylpentane	40	30	33
27	2,2-dimethylhexane	39	26	37
28	3,3-dimethylhexane	34	39	30
29	3-ethyl,3-metilpentane	23	36	25
30	2,3,4-trimethylpentane	29	33	26
31	2,3-dimethylhexane	33	29	31
32	3-ethyl,2-methylpentane	28	38	28
33	3,4-dimethylhexane(S,R)	25	31	29
34	2,4-dimethylhexane(S)	37	28	34
35	2,5-dimethylhexane(S,R)	38	25	38
36	2-methylheptane	36	24	40
37	3-methylheptane(R)	30	32	35
38	4-methylheptane	35	27	36
39	3-ethylhexane(R)	31	37	32
40	*n*-octane	26	23	39

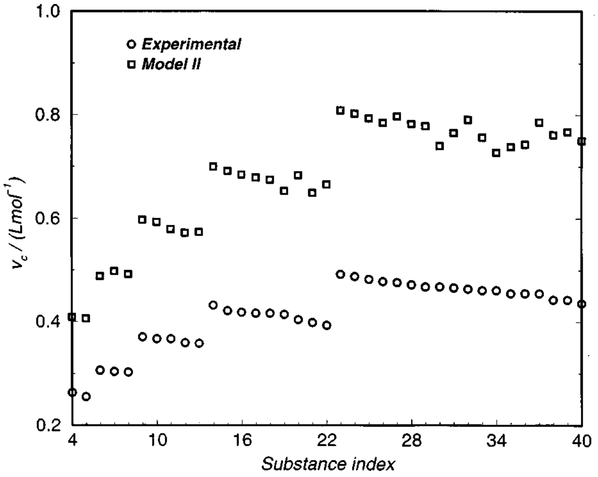

FIG. 2. Critical molar volume of alkanes with up to eight carbon atoms, as obtained from experiment (Refs. 52–54) and from the theory of this work for Model II. Each alkane is represented by an integer number along the *x* axis which is shown in the fourth column of Table III.

critical volume, agreement is not so good as for the critical temperature but still main trends with branching and length of the chain are described correctly. For the critical pressure the theory works quite well and trends of the experimental results are described correctly. Overall, the results presented in Figs. 1–3 for Model II can be considered as satisfactory. We must admit, however, that the theory is not always able to order exactly the critical values for a family of isomers. This would require a theory capable of predicting differences of less than 5% in the critical properties, a point which is beyond our possibilities as a consequence of (1) our ignorance on the exact force field of each molecule, (2) the description of the structure by a simple mean field term and (3) the truncation of the perturbation expansion. We do believe, however, that this is the first time that a theoretical treatment is able to describe qualitatively trends in the critical properties of alkanes.

A more detailed comparison of the experimental and theoretical critical properties of alkanes is presented in Table IV for the isomers with six carbon atoms (i.e., C_6H_{14}). To illustrate that the theory can also be applied to cyclic alkanes, results are also presented for cyclohexane (i.e., C_6H_{12}). Our treatment of cyclohexane is a straightforward extension of that described for other alkanes. This molecule is known to have two preferred conformations, known as chair and boat. However, the population of the chair configuration largely exceeds that of the boat configuration, as it is considerably more stable.[8] We have therefore chosen to describe cyclohexane as a single chair conformer.

As it can be seen in Table IV, quantitative agreement between theory and experiment is not good due to the mean field approximation. However, the theory describes correctly in most of the cases the ordering of the critical properties.

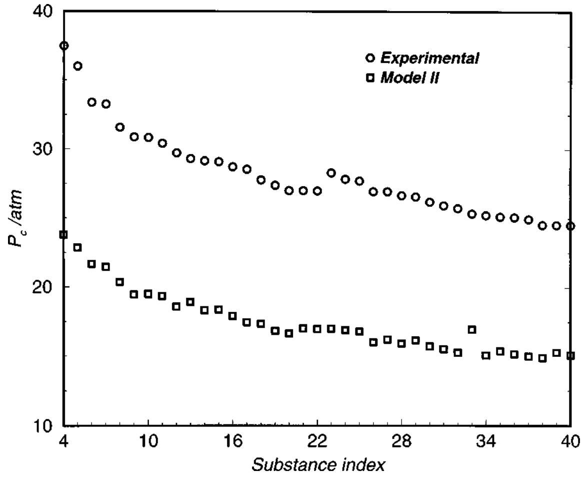

FIG. 3. Critical pressure of alkanes with up to eight carbon atoms, as obtained from experiment (Refs. 52–54) and from the theory of this work for Model II. Each alkane is represented by an integer number along the *x* axis which is shown in the fifth column of Table III.

TABLE IV. Critical properties of hexane isomers and of cyclohexane as obtained from experiment and from the mean field theory of this work with the potential parameters of Model II. Values of the mean interaction energy, E, as given by the double sum of Eq. (18) for some isomers are also presented. E' was obtained as E, but with the $\overline{M_{kl}}$ factors in Eq. (18) set to one. In the evaluation of E, ϵ was given in units of k_B, and σ in Å.

Alkane	Experiment T_c/K	Theory	$E'/10^4$	$E/10^4$
cyclohexane	553.50	471.06	14.86	8.52
n-hexane	507.40	386.85	17.41	9.48
3-methylpentane	504.40	385.51	17.23	9.07
2-3,dimethylbutane	499.93	380.86	17.05	8.83
2-methylpentane	497.45	377.09	17.23	9.12
2-2,dimethylbutane	488.73	377.04	16.77	8.70
	V_c/(Lmol^{-1})			
n-hexane	0.370	0.597		
2-methylpentane	0.367	0.593		
3-methylpentane	0.367	0.579		
2-2,dimethylbutane	0.359	0.572		
2-3,dimethylbutane	0.358	0.574		
cyclohexane	0.308	0.452		
	p_c/at			
cyclohexane	40.18	30.71		
2-3,dimethylbutane	30.86	19.46		
3-methylpentane	30.83	19.50		
2-2,dimethylbutane	30.40	19.35		
2-methylpentane	29.71	18.59		
n-hexane	29.30	18.92		

Also, the very high critical temperature of cyclohexane when compared to that of n-hexane is described correctly.

An advantage of this simple theory with respect to more sophisticated methods such as Gibbs ensemble simulations is that it allows for a rationalization of the results, which can be explained in terms of well defined, physically meaningful parameters. By solving Eq. (5) for the critical point in a similar manner as in Ref. 33, it can be shown that the critical temperature is given by the following equation:

$$T_c = \frac{F[\overline{\alpha}]a_{\mathrm{vdw}}}{\overline{V}} \sum_{k=1}^{5} \sum_{l=1}^{5} n_{kl}\varepsilon_{kl}\sigma_{kl}^3\overline{M_{kl}} = \frac{F[\overline{\alpha}]a_{\mathrm{vdw}}E}{\overline{V}}, \tag{18}$$

where $F[\overline{\alpha}]$ is a decreasing function of $\overline{\alpha}$ whose exact form is irrelevant for the discussion.

In this way, we are able to attribute the trends observed in the critical temperature to the competition between three different properties of the molecule, namely, the nonsphericity, $\overline{\alpha}$, the molecular volume, $\overline{V}$ and the mean dispersive energy, E.

In paper I, it is shown that for a given number of carbon atoms, branching provokes a decrease in $\overline{\alpha}$, so that this factor alone will result in an increase of T_c.

Equation (18) shows that T_c is an inverse function of the molecular volume. The effect of branching on this property, however, is hard to determine, as it depends dramatically on the chosen values of σ. When all type of sites (CH_3, CH_2...) have the same diameter, branching reduces slightly the molecular volume. However, with the choice of sigmas of Model I, the molecular volume increases substantially with branching, due to the relatively big volume of CH_3 sites compared with that of CH_2 and CH. On the other hand, with the sigmas of Model II branching increases only slightly the molecular volume of alkane molecules, in agreement with estimates of the molecular volume by other methods.[53] Therefore, both Models (I and II) predict an increase of the molecular volume with branching and according to Eq. (18) that will provoke a decrease in the critical temperature.

The third factor affecting the critical temperature is the mean dispersive energy as given by the double sum of Eq. (18) and denoted as E. Each term of the double sum contains two factors. The first one, $\epsilon_{kl}(\sigma_{kl})^3$, accounts for changes in the average interaction energy between a pair of molecules, regardless of steric effects. The second factor is the average mean field factor $\overline{M_{kl}}$ which accounts for steric hindrance. To see the effect of each factor we present in Table IV the value of E (fifth column) and the value that E would adopt if all average mean field factors $\overline{M_{kl}}$ were set to unity (fourth column). By analyzing the fourth column of Table IV (i.e., E') it can be seen that branching reduces the average interaction energy between a pair of molecules. For instance, by comparing n-hexane and 3-methyl pentane it can be seen how the replacement of two CH_2 groups by a CH_3 and a CH group reduces the average interaction energy between pairs of molecules by 1%. This is due to the low values of ϵ and σ for highly substituted carbons. When the steric hindrance i.e., $\overline{M_{kl}}$ is included (see fifth column of Table IV) it can be seen that the average interaction energy of 3-methyl pentane is about 4% lower than that of n-hexane. This additional 3% reduction in the interaction energy of the branched alkane is due to the low values that take the average mean field factors in branched alkanes (see Table II). Such a decrease in the average mean field factor is a consequence of the so called correlation hole,[31,32,55] which may be seen to increase considerably in branched molecules. To illustrate the meaning of the correlation hole, the site–site correlation functions for CH_3–CH_3 and CH–CH groups of 2-methyl propane at zero density are shown in Fig. 4. As it can be seen, the contact value of the correlation functions decreases on going from

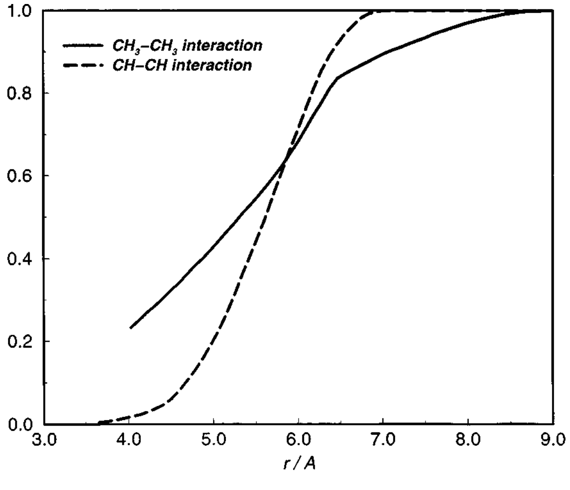

FIG. 4. Site–site correlation functions at zero density for 2-methyl propane (Model II) obtained from numerical integration. We present results for the CH_3–CH_3 and CH–CH correlation functions.

primary to tertiary carbons, due to the increasing steric hindrance that increasingly branched carbons present for contacts. It is thus clear that branching greatly diminishes the average dispersive energy felt by the interaction sites as a consequence of both smaller potential wells and greater correlation holes. This results in a decrease of the critical temperature.

It is thus seen that our theory allows to identify the factors that determine the experimental T_c. Our arguments are in contrast with the naive explanation presented in some textbooks,[7,8] where emphasis is made solely on the last point of the previous discussion (the correlation hole). Here it is shown that the total effect is a compromise between several factors and the moderate decrease of critical temperatures with branching is a consequence of this compromise. The three factors affecting Eq. (18) ($\overline{\alpha}$,$\overline{V}$ and the mean interaction energy, E) should be considered when discussing the effect of branching on the critical temperature. When these three factors are considered simultaneously as in our theory, it may be eventually found that the effect of a small nonsphericity is greater than that of the mean dispersive energy. Indeed, our theory predicts that such a behavior appears for highly branched isomers of the octane series, leading to a higher critical temperature for the branched alkane than for the corresponding n-alkane, in agreement with experiment.

Let us now focus on the critical molar volume, V_c, which may be expressed in terms of the molecular volume and the packing fraction at the critical point, y_c:

$$V_c=\frac{\overline{V}}{y_c[\overline{\alpha}]}. \tag{19}$$

According to our theory, y_c may be shown to be a steeply decreasing function of $\overline{\alpha}$. This means that the decrease in $\overline{\alpha}$ which follows from branching has the effect of increasing y_c, resulting in a decrease of V_c. On the other hand, the molecular volume seems to increase slightly with branching, as explained above. The actual V_c results from a delicate balance between two opposite trends, although experimental data show that the $\overline{\alpha}$ dependence is more important, since in most cases, V_c seems to decrease with branching.

Once differences in the absolute values of the critical properties have been presented and analyzed, let us now analyze these differences in a corresponding states sense.

A corresponding states plot of the coexistence liquid densities of three hexane isomers, n-hexane, 2-methyl pentane and 2,2-dimethyl pentane is shown in Fig. 5 for both theory and experiment. As it can be seen, the trend toward narrower coexistence curves for branched molecules is correctly predicted by the theory. Such a trend is a consequence of the decrease of $\overline{\alpha}$, which is known to affect the shape of the coexistence curve. In fact, for linear fluids (2CLJ or Kihara) it has been shown that as the anisotropy of the molecule increases, the vapor–liquid envelope becomes broader.[18,56,57] Here, the same effect is observed, and it is seen that the more anisotropic the molecule (as given by $\overline{\alpha}$), the broader the envelope. For the same substances, a Clausius–Clapeyron corresponding states plot of the vapor pressure curve (not shown) predicted a decrease of the absolute values of the slope with branching, in agreement with experiment.

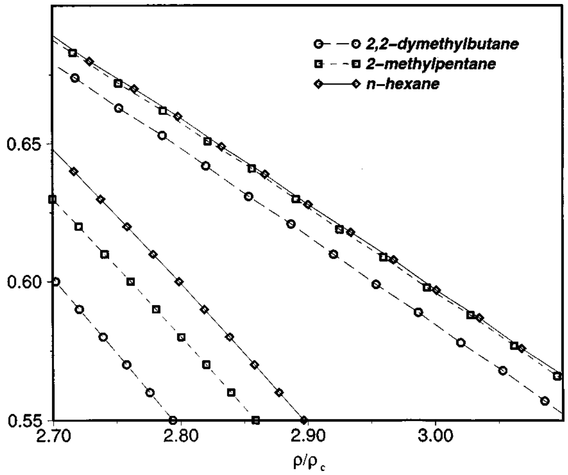

FIG. 5. Corresponding states plot of the liquid coexistence densities of n-hexane, 2-methyl pentane and 2,2-dimethyl butane as obtained from experiment (symbols in the lower part of the plot) and the perturbation theory of this work for Model II (symbols in the upper part of the plot).

In Figs. 6–8, the experimental critical properties of n-alkanes are compared with the predictions from our theory for Model II. It is obvious that our mean field treatment reproduces the maxima found experimentally in the critical density and critical pressure. Not only is the existence of the maxima correctly described, but their location as well. To our knowledge this is the first time that a theory reproduces correctly these trends. Recall that a few years ago, it was thought that there was no maximum in the critical density of alkanes but that it reached an asymptotic value.[4] The origin of these maxima was explained in detail in a previous paper[33] and will not be reproduced here. Let us just mention that the appearance of the maxima requires overlapping between the constituting monomer units. In addition, it is required that there be not too large end monomer–middle

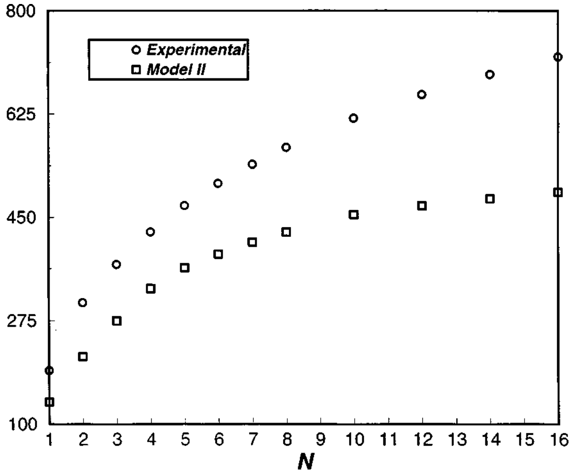

FIG. 6. The critical temperature of linear n-alkanes with up to eight carbon atoms as obtained from experiment (Refs. 52–54) (open circle) and from the perturbation theory of this work for Model II (open squares).

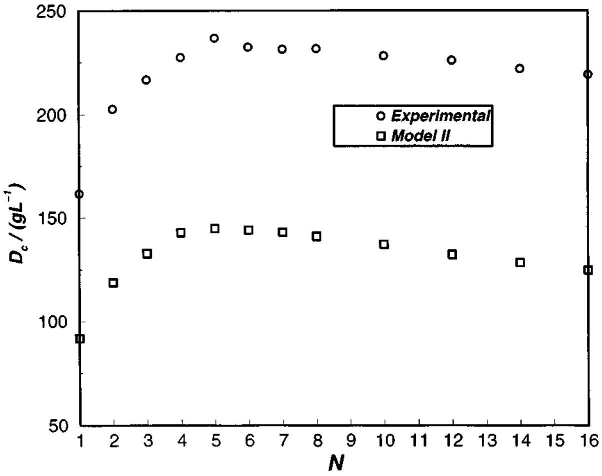

FIG. 7. The critical density D_c (in gL^{-1}) of linear n-alkanes with up to eight carbon atoms as obtained from experiment (Refs. 52–54) (open circle) and from the perturbation theory of this work for Model II (open squares).

monomer differences in either mass for the critical density or interaction energy for the critical pressure.

V. CONCLUSIONS

In this work, a mean field first order perturbation theory is proposed for alkanes. A modified version of Wertheim's EOS, obtained by imposing the true second virial coefficient of the hard body, is used to describe the reference system. The perturbation contribution is obtained from site–site correlation functions evaluated in the limit of zero density.

A set of Lennard-Jones parameters recently proposed in the literature is used to describe the force field of the alkanes. It is found that this set does not give satisfactory predictions for the critical temperatures of alkanes. A modified set of parameters has been proposed which considerably improves the results, yielding a qualitative description of the critical properties of both branched and linear alkanes. For the case of linear alkanes in particular, the theory is able to reproduce qualitatively the existence and position of maxima in the critical density and pressure, when plotted as a function of the number of carbon atoms.

The effect of branching on the critical temperature and density is analyzed in detail. It is found that the decrease in the critical temperature with branching may be attributed to an important decrease in the intensity of the dispersive forces and a slight increase in the molecular volume, although the influence of these two factors is somewhat mitigated by the decrease of the nonsphericity, which acts on the opposite direction. In fact, highly branched alkanes may have higher critical temperatures than the corresponding n-alkane due to the important decrease in $\overline{\alpha}$. On the other hand, the decrease in the critical molar volume with branching may be attributed to an increase in the critical packing fraction, which is usually more important than the increase in the molecular volume.

The principle of corresponding states in isomers is also analyzed. It is found that linear alkanes present larger deviations from the principle of corresponding states (for both vapor pressures and coexistence densities) than branched alkanes. This is explained on the basis of the smaller nonsphericity of the latter.

The theory of this work is able to describe a number of features of the vapor–liquid equilibrium of alkanes on a simple basis. To our knowledge, this is the first attempt to explain these features from a first principles theory. Certainly, an understanding of the critical properties of linear and branched alkanes in the light of Statistical Thermodynamics is by far more difficult that the naive picture provided in elementary text books of Organic and Physical Chemistry. In this paper, some of the key elements are presented. Obviously, further work is needed to get quantitative agreement between theory and experiment. In particular, the mean field approximation should be replaced by a better description of the structure of the reference system. Progress on this line can be anticipated.

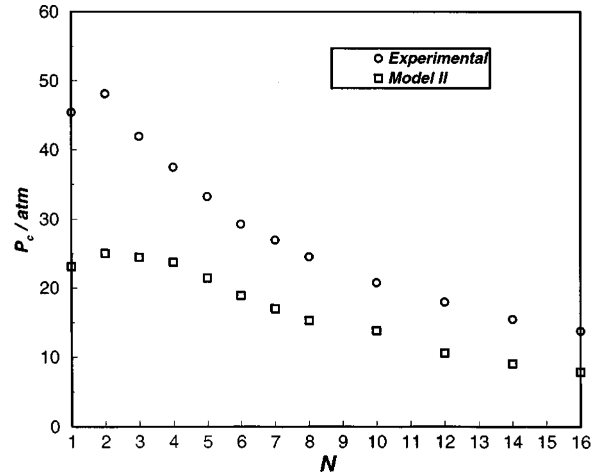

FIG. 8. The critical pressure of linear n-alkanes with up to eight carbon atoms as obtained from experiment (Refs. 52–54) (open circle) and from the perturbation theory of this work for Model II (open squares).

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