

# Critical properties of mixtures of alkanes from perturbation theory

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The critical properties of binary mixtures of linear and branched alkanes have been evaluated using 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 potential model. No adjustable parameters were used either for the pure compounds or for the binary mixtures. The aim of this work is to show which features of the critical properties of alkane mixtures can be obtained from a fully molecular based theory. It is shown that the main trends of the critical properties of alkane binary mixtures can be described qualitatively by the theory. © 1999 American Institute of Physics. [S0021-9606(99)51331-7]

## I. INTRODUCTION

The critical properties of pure alkanes and alkane mixtures are of interest from the practical and from the theoretical point of view. From the practical point of view, interest arises from the fact that alkanes are one of the main products of the oil industry. From a merely theoretical point of view, alkanes constitute a challenge for statistical thermodynamics theories, since, unlike simple rigid molecules, they have internal degrees of freedom which provide the molecule with a new feature: flexibility. In the last 20 years, the interest in molecules having internal flexibility has been increasing steadily. Simulation of flexible off-lattice molecules were pioneered by Ryckaert and Bellemans,<sup>1</sup> followed and expanded by Hall and co-workers,<sup>2,3</sup> received new oxygen with the development of the configurational bias method<sup>4,5</sup> and finally reached maturity with the extension of the Gibbs ensemble<sup>6</sup> method to long chains.<sup>7-9</sup> The structure of flexible molecules as described by the site-site correlation function was pioneered by Chandler *et al.*<sup>10</sup> with the development of the site-site Ornstein-Zernike equation (RISM), which was extended to polymers (after some further approximations) by Curro and Schweizer in the Polymer Reference Interaction site model (PRISM).<sup>11,12</sup> The equation of state of hard flexible molecules has been an area of renewed interest since the important work of Wertheim<sup>13</sup> and Chapman *et al.*<sup>14</sup> Taking the hard sphere fluid as a reference system and using Wertheim's theory of association, these authors were able to develop an equation of state for chains of hard tangent spheres. This equation of state has been extended successfully to other hard flexible models by Boublik *et al.*<sup>15</sup> and to hard alkane models (branched and linear) by ourselves.<sup>16,17</sup>

As we will focus our attention on alkane mixtures in what follows, it may prove interesting to give our perspective of the current situation concerning molecular studies of alkanes:

(1) Though there is still some room for improvement, good potential models have been developed within the united

atom approach, thus allowing for a simple but accurate description of the fluid phase. See for instance Refs. 8,18-22.

- (2) Good EOS are now available for hard alkane models.<sup>16,23,17</sup>
- (3) The structure of hard alkane models can be obtained in principle from integral equation theories formulated on a site-site basis.<sup>10-12</sup>
- (4) Vapor-liquid equilibrium can be obtained from computer simulations by using the Gibbs ensemble method.<sup>7,8</sup>

Points 1-3 suggest that perturbation theories can now be developed for alkanes (linear and branched) and results can be compared to experiment and to numerical simulations (point 4). Certainly, if one performs a good job for points 1-3 one could expect good agreement with experiment. However, point 3 is probably the most difficult, since it requires good results for the site-site correlation functions of linear and branched alkanes for each thermodynamic state.

The goal of this work is to analyze if a simple perturbation theory can describe at least qualitatively the critical lines of binary alkane mixtures. We shall combine a reasonable choice for the potential parameters of the model and a good EOS for the hard reference alkane model, with a very simple approximation for the structure of the reference fluid. In other words, we shall use the best methods we can for steps 1 and 2, whereas for step 3 we shall use the simplest rather than the best. We are not looking for the quantitative or semi-quantitative agreement with experiment that one could expect from a more rigorous theory (although hopefully the time for that does not appear now to be too far away). We are rather looking for a simple theory with a molecular basis and no adjustable parameters, able to describe the qualitative features of the critical lines of alkane mixtures. A more practical approach has been widely used, where a sound statistical mechanical theory for an idealized and simple flexible model such as the tangent sphere model is used to correlate experi-

mental data. The self-associating fluid theory (SAFT) for tangent spheres has been successfully used in this manner.<sup>24–28</sup> This kind of work is quite interesting, since it shows that the methods of statistical mechanics can be used by chemical engineers to correlate experimental data and to predict properties not available from experiment. However, it can not be considered as a strictly molecular approach, since the mapping of the tangent sphere model to the true model one aims to describe requires *a priori* experimental information of the system. The application of theories such as SAFT for realistic models with overlapping spheres and well defined bond and torsion angles is possible in principle, but it requires three and four body cavity functions, something that is far beyond present knowledge. We certainly believe that these two types of studies are complementary and both of them are needed.

In previous work we have proposed a simple perturbation theory for linear and branched alkanes.<sup>29,30</sup> This theory was able to explain on a simple basis some of the experimental features of the vapor–liquid equilibrium of alkanes. Just to mention two examples, the origin of the maximum in the critical density<sup>31,32</sup> and the effect of branching on the critical properties of different isomers have been described. In this work we extend this theory to alkane mixtures. Two particular aspects of alkane mixtures which are of interest are the critical lines and the excess properties. In this paper we focus on the critical lines and we leave the issue of the excess properties to the following paper.<sup>33</sup> The goal of this paper is to analyze if a simple perturbation theory can describe qualitatively the trends of the critical lines of binary mixtures of alkanes.

The scheme of the paper is as follows. In Sec. II the potential used in this work to model alkanes is presented. Section III describes the perturbation theory for mixtures of alkanes. The results of the theory are presented in Sec. IV, while a brief summary of our conclusions is given in Sec. V.

## II. POTENTIAL MODEL FOR ALKANES

The alkane (linear or branched) is modeled by means of the united atom approach, whereby each  $\text{CH}_n$  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  $\theta$  is set to the tetrahedral value, i.e.,  $\theta = 109.5^\circ$ . The torsional degrees of freedom are treated within the rotational isomeric state approximation (RIS), the details of which are explained elsewhere.<sup>34</sup> The site–site interaction (intra or intermolecular) is described by the Lennard-Jones (LJ) potential. The intramolecular energy is divided into short and long range contributions. The short range contribution accounts for the interaction between carbon atoms three bonds apart, described by the Ryckaert–Bellemans torsional potential;<sup>1</sup> whereas the long range contribution accounts for the interaction between carbon atoms separated by four or more bonds (see Ref. 30 for further details). The intra-molecular energy for a certain conformation is thus given by:

$$U_{\text{intra}} = U_{\text{intra}}^{\text{short}} + U_{\text{intra}}^{\text{long}} \\ = n_g E_1 + \sum_k \sum_l' 4 \varepsilon_{kl} \left( \left( \frac{\sigma_{kl}}{r_{kl}} \right)^{12} - \left( \frac{\sigma_{kl}}{r_{kl}} \right)^6 \right), \quad (1)$$

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<sup>23</sup> while 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:

$$U_{\text{inter}} = \sum_{k=1}^{n_1} \sum_{l=1}^{n_2} 4 \varepsilon_{kl} \left( \left( \frac{\sigma_{kl}}{r_{kl}} \right)^{12} - \left( \frac{\sigma_{kl}}{r_{kl}} \right)^6 \right), \quad (2)$$

where the summation is now over the  $n_1$  interaction sites of molecule 1 and the  $n_2$  interaction sites of molecule 2. 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).<sup>35</sup> Our choice for the parameters  $\sigma$  and  $\varepsilon$  corresponds to that used in our previous work on the critical properties of alkanes (parameter set II of Ref. 30), i.e.:  $\sigma/\text{Å} = 4.10, 3.95, 3.87, 3.73$  and  $\varepsilon/k_B = 93 \text{ K}, 67 \text{ K}, 37 \text{ K}, 12 \text{ K}$  for the  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$  and  $\text{C}$  groups, respectively. With these parameters we were able to describe qualitatively the critical properties of pure alkanes (linear and branched).

## III. PERTURBATION THEORY FOR ALKANE MIXTURES

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

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

The value  $\lambda = 0$  defines the reference system, while setting  $\lambda = 1$  we recover the original system. Each site–site LJ intermolecular interaction,  $u$ , is divided into a reference and a perturbation part following the Weeks–Chandler–Andersen criterion (WCA),<sup>36</sup> so that the reference potential  $u_0$  is given by:

$$u_0(r_{kl}) = 4 \varepsilon_{kl} \left( \left( \frac{\sigma_{kl}}{r_{kl}} \right)^{12} - \left( \frac{\sigma_{kl}}{r_{kl}} \right)^6 \right) + \varepsilon_{kl}, \\ r_{kl} < 2^{1/6} \sigma_{kl} \\ u_0(r_{kl}) = 0, \quad r_{kl} > 2^{1/6} \sigma_{kl}. \quad (4)$$

The perturbation part of the potential,  $u_1$ , is obtained from the condition  $u = u_0 + u_1$ . Note that the *intra-molecular interactions of our reference system are of LJ type*, whereas the intermolecular interactions are of the WCA type. This division of the potential guarantees that in the low density limit, the reference system has the same conformational population as the full system.

The Helmholtz free energy,  $A$ , is given by an ideal, an intra-molecular and an intermolecular contribution:

$$A = A_{\text{ideal}} + A_{\text{intra}}(\mathbf{Q}, \mathbf{W}) + A_{\text{inter}}(\mathbf{Q}, \mathbf{W}), \quad (5)$$

where  $\mathbf{Q}=(q_1, q_2, \dots, q_{M_1})$  is a vector whose components are the molar fractions of the  $M_1$  possible conformers of molecule 1 and  $\mathbf{W}=(w_1, w_2, \dots, w_{M_2})$  is a vector whose components are the molar fractions of the  $M_2$  possible conformers of molecule 2. Recall that within the RIS approximation, the number of possible conformers may be large but always finite. Let us now describe briefly each term. The ideal term is given by:

$$A_{\text{ideal}}/N = k_B T (x_1 \ln(\rho_1 \Lambda_1^3) + x_2 \ln(\rho_2 \Lambda_2^3) - 1), \quad (6)$$

where  $\rho_1$  and  $\rho_2$  are the number densities,  $\Lambda_1$  and  $\Lambda_2$  are the thermal wavelengths and  $x_1$  and  $x_2$  are the molar fractions of components 1 and 2, respectively;  $N$  is the total number of molecules in the system and  $k_B$  is the Boltzmann constant.

The intra-molecular term is given within the RIS approximation by:<sup>16,30</sup>

$$\begin{aligned} A_{\text{intra}}/N = & k_B T x_1 \left[ \sum_{i=1}^{M_1} q_i \ln(q_i) + \sum_{i=1}^{M_1} q_i n_{g,i} E_1 \right. \\ & \left. + \sum_{i=1}^{M_1} q_i U_{\text{intra},i}(\mathbf{LJ}) \right] \\ & + k_B T x_2 \left[ \sum_{i=1}^{M_2} w_i \ln(w_i) + \sum_{i=1}^{M_2} w_i n_{g,i} E_1 \right. \\ & \left. + \sum_{i=1}^{M_2} w_i U_{\text{intra},i}(\mathbf{LJ}) \right], \quad (7) \end{aligned}$$

where  $n_{g,i}$  is the number of gauche bonds of conformer  $i$  and  $U_{\text{intra},i}(\mathbf{LJ})$  is the intra-molecular LJ energy of conformer  $i$ .

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:

$$A_{\text{inter}}(x_1, x_2; \mathbf{Q}, \mathbf{W}) = A_0(x_1, x_2; \mathbf{Q}, \mathbf{W}) + A_1(x_1, x_2; \mathbf{Q}, \mathbf{W}), \quad (8)$$

where  $A_0(x_1, x_2; \mathbf{Q}, \mathbf{W})$  is the intermolecular free energy of the reference system mixture with composition defined by the molar fractions  $x_1$  and  $x_2$  and with a distribution of the conformational population defined by  $\mathbf{Q}$  for component 1 and by  $\mathbf{W}$  for component 2.  $A_1$  is the intermolecular free energy due to the perturbation potential which is given by the following equation:

$$\begin{aligned} \frac{A_1}{N} = & \frac{\rho}{2} \left[ \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j \sum_{k=1}^{n_i} \sum_{l=1}^{n_j} \varepsilon_{kl} \sigma_{kl}^3 \right. \\ & \left. \times \int u_1^*(r_{kl}^*) g_{0,kl}^{ij}(r_{kl}^*; \rho, x_1, x_2; \mathbf{Q}, \mathbf{W}) 4\pi r_{kl}^{*2} dr_{kl}^* \right], \quad (9) \end{aligned}$$

where  $\rho$  is the total number density and  $g_{0,kl}^{ij}(r; \rho, x_i, x_j; \mathbf{Q}, \mathbf{W})$  is the site-site correlation function between site  $k$  of molecule  $i$  and site  $l$  of molecule  $j$  of the reference system. Note that for a given temperature, this function depends explicitly on the composition of the system

through  $\rho$ ,  $x_1$  and  $x_2$  and parametrically through the conformational populations, given by  $\mathbf{Q}$ ,  $\mathbf{W}$ . 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. For a certain thermodynamic state, defined by its temperature, total density and molar fraction, the free energy of the system depends on the conformational population (i.e.,  $\mathbf{Q}, \mathbf{W}$ ) of components 1 and 2. The reader familiar with density functional theory (DFT)<sup>37,38</sup> would have probably realized that our treatment can be defined as a DFT for flexible molecules.<sup>39</sup> In fact, we are writing the free energy as a functional (a function in the RIS approximation) of the conformational population (which takes the role of the singlet correlation function). As in DFT, where the free energy functional is minimized with respect to the singlet correlation function, we should minimize the total free energy with respect to the conformational population for each thermodynamic state. In most of the cases, such a minimization is an overwhelming task and further approximations are required. We shall therefore assume that for a given temperature, the conformational population at zero density is valid for all densities and compositions. Whereas this approximation is unjustified in the more general case of an arbitrarily long polymer chain, where dramatic conformational changes are expected on going from the gas to the liquid phases, it has been shown that for the rather stiff and short alkane chains that are considered in this work the conformational changes are rather small.<sup>40</sup> When changes in conformational population with density are neglected, the intra-molecular term given by Eq. (7) depends only on temperature and composition. Consequently, it does not affect the vapor–liquid equilibrium (it does not contribute to the pressure and the contribution to the chemical potential is a constant which is identical in the liquid and the vapor phases). Within this approximation, the intra-molecular term may be neglected in the vapor–liquid equilibrium calculations.

Now, we shall describe the approximations used to get the structure and thermodynamics of the reference system. We shall identify the properties of the WCA reference system to those of a hard body system. A hard sphere will be assigned to each interaction site. The diameter of this hard interaction site will be given by the Barker–Henderson prescription<sup>41</sup> as implemented in Ref. 30. 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.<sup>16,23,42</sup> According to this equation, the free energy is given by:<sup>23</sup>

$$\begin{aligned} \frac{A_0}{N k_B T} = & (2\alpha_{\text{mixture}} - 1) \ln \left( \frac{2(1-y)^3}{(2-y)} \right) - (2\alpha_{\text{mixture}} - 2) \\ & \times \frac{1+y-0.5y^2}{(1-y)(1-0.5y)}. \quad (10) \end{aligned}$$

The magnitudes  $\alpha_{\text{mixture}}$  and  $y$  are defined as:<sup>16</sup>

$$\alpha_{\text{mixture}} = x_1 \bar{\alpha}_1 + x_2 \bar{\alpha}_2, \quad (11)$$

$$y = \rho V_{\text{mixture}} = \rho (x_1 \bar{V}_1 + x_2 \bar{V}_2), \quad (12)$$

where  $\alpha_{\text{mixture}}$  is the nonsphericity parameter of the mixture, given in terms of the nonsphericity parameters of components 1 and 2 (i.e.,  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$ ). The packing fraction,  $y$ , is given as the product of  $\rho$  and the average molecular volume, expressed as the molar fraction average of the molecular volumes of components 1 and 2 (i.e.,  $\bar{V}_1$  and  $\bar{V}_2$ ). The bar in Eqs. (11)–(12) recalls that the nonsphericity and volume of a given component is the average of these magnitudes over the conformational population of the molecule. For instance for  $\bar{\alpha}_1$  it holds:

$$\bar{\alpha}_1 = \sum_{i=1}^{M_1} q_i \alpha_i \quad (13)$$

with similar equations for  $\bar{\alpha}_2$ ,  $\bar{V}_1$  and  $\bar{V}_2$ . Note that, due to our choice of the conformer populations, Eq. (10) gives an approximation to 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 intra-molecular potential.

The values of  $\alpha_i$  needed in Eq. (13) are chosen to reproduce the second virial coefficient of the hard model assigned to conformer  $i$ . Convex body geometry (CBG) methodology as described in Refs. 17 and 29 is used to estimate the second virial coefficient of each conformer. Further details concerning the evaluation of  $\alpha_i$  are given elsewhere.<sup>17</sup> The methodology of Dodd and Theodorou<sup>43</sup> is used to determine the volume of conformer  $i$ .

Now we shall describe our implementation of the perturbation term  $A_1$ . Obviously, the evaluation of this term is difficult, since it requires for each temperature, density and composition the evaluation of all the site–site correlation functions of the reference system. In principle, by solving an integral equation such as RISM for each thermodynamic state one could get this information.<sup>10</sup> Certainly, this is the way to be followed if one is looking for quantitative results. However, in this paper we are rather looking for a qualitative description of the problem and a simplified treatment of the perturbation term is enough. We shall therefore use a mean field approximation. In a mean field theory, the contribution of the attractive forces to the free energy is linear in the number density. From Eq. (9), it can be seen that this is achieved when the radial distribution function is density independent:

$$g_{0,kl}^{ij}(r; \rho, x_i, x_j; \mathbf{Q}, \mathbf{W}) = f_{0,kl}^{ij}(r; x_i, x_j). \quad (14)$$

When such an approximation is invoked for  $g_{0,kl}$ , the integrals of Eq. (9) become constants (for a given temperature and composition) and the theory is said to be of “mean field” type. The type of mean field theory now depends on the choice of the function  $f_{0,kl}^{ij}$ . Let us mention two possibilities which we have used in previous work. The first one leads to a mean field theory which will be denoted as mean field 1 (MF1):

$$f_{0,kl}^{ij} = H(r - \sigma_{kl}). \quad (15)$$

In this approximation, all site–site correlation functions are approximated as Heaviside step functions. This approximation is “democratic” in the sense that it assigns the same

site–site correlation function to all type of sites and molecules. It was shown in Ref. 29 that the MF1 approximation is able to reproduce qualitatively the experimental maxima in the critical properties of  $n$ -alkanes. However, it was found later that this approximation fails completely in describing the effect of branching on the critical properties of alkanes.<sup>30</sup> Therefore, Eq. (15) does not seem to be appropriate for studying critical properties of branched alkane mixtures. This is not to say that Eq. (15) is useless. It will be shown in the next paper that MF1 does a very good job in predicting excess properties of  $n$ -alkane mixtures at high densities. However, for the purpose of studying critical properties, the following approximation (denoted as MF2) seems to be more appropriate:

$$f_{0,kl}^{ij} = g_{0,kl}^{ij}(r; \rho = 0). \quad (16)$$

The approximation given by Eq. (16) can be summarized in words saying that we approximate the site–site correlation function between site  $k$  of molecule  $i$  and site  $l$  of molecule  $j$  at any density and composition by its respective low density limits. This approximation has been used recently in Ref. 30 to correctly describe the critical properties of linear and branched alkanes. Equation (16) is not “democratic” in the sense that it assigns different correlation functions to different sites of the same molecule and to the same type of site (i.e.,  $\text{CH}_3$  or  $\text{CH}_2$ ) of different molecules. Equation (16) is exact in the zero density limit and introduces correctly the molecular geometry. Unless otherwise stated, all the results of this work were obtained with the MF2 approximation. In this way,  $A_1$  becomes a trivial linear function of the density, as is usual in mean field theories:

$$\frac{A_1}{N} = -\rho a_{\text{MF}}, \quad (17)$$

$$a_{\text{MF}} = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}, \quad (18)$$

where  $a_{\text{MF}}$  is the mean field constant of the mixture expressed in terms of the mean field constants,  $a_{ij}$  given by:

$$a_{ij} = -\frac{1}{2} \sum_{k=1}^{n_i} \sum_{l=1}^{n_j} \varepsilon_{kl} \sigma_{kl}^3 \int u_i^*(r_{kl}^*) g_{0,kl}^{ij}(r_{kl}^*; \rho = 0)^2 \times 4\pi r_{kl}^{*2} dr_{kl}^*. \quad (19)$$

The prime on  $g_{0,kl}^{ij}$  reminds of the fact that we are approximating the structure of the reference system by that of a hard body system. The zero density site–site correlation functions  $g_{0,kl}^{ij}$  of the hard body were evaluated as described in Appendix C of Ref. 17, (method 2). Since the dependence of  $g_{0,kl}^{ij}$  on temperature is weak, it was evaluated for a single temperature (close to the critical temperature) for each alkane and this value was used for all the temperatures (i.e., the mean field constants  $a_{11}$  and  $a_{22}$  were made temperature independent).

Finally, let us mention how the critical properties of the mixture can be obtained. From the perturbation theory described above, an analytical expression of the Helmholtz free energy as a function of temperature, reduced number density  $\rho^* = \rho \sigma_{\text{CH}_2}^3$  and composition is available, i.e.,  $A(T, \rho^*, x_1)$ . All what is needed is the knowledge of the mean field con-

TABLE I. van der Waals constants  $a_{11}$ ,  $a_{12}$  and  $a_{22}$  (in units of  $k_B \text{ \AA}^3$ ) as obtained from the MF2 approximation at  $T=298.15$  K and test of the van der Waals mixing rule.

| Component 1        | Component 2           | $a_{11}$ | $a_{22}$   | $a_{12}$   | $(a_{11}a_{22})^{1/2}$ |
|--------------------|-----------------------|----------|------------|------------|------------------------|
| <i>n</i> -hexane   | <i>n</i> -heptane     | 543 906. | 677 713.   | 607 183.   | 607 134.               |
| <i>n</i> -hexane   | <i>n</i> -octane      | 543 906. | 819 230.   | 670 060.   | 667 521.               |
| <i>n</i> -hexane   | <i>n</i> -decane      | 543 906. | 1 133 893. | 792 894.   | 785 322.               |
| <i>n</i> -hexane   | <i>n</i> -dodecane    | 543 906. | 1 473 070. | 909 179.   | 895 104.               |
| <i>n</i> -hexane   | <i>n</i> -tetradecane | 543 906. | 1 842 212. | 1 024 816. | 1 000 995.             |
| <i>n</i> -hexane   | <i>n</i> -hexadecane  | 543 906. | 2 242 724. | 1 132 489. | 1 104 460.             |
| 2,2-dimethylbutane | <i>n</i> -hexane      | 495 704. | 543 906.   | 520 012.   | 519 246.               |
| 2,3-dimethylbutane | <i>n</i> -hexane      | 506 325. | 543 906.   | 525 653.   | 524 779.               |
| 2-methylpentane    | <i>n</i> -hexane      | 523 505. | 543 906.   | 534 174.   | 533 608.               |
| 3-methylpentane    | <i>n</i> -hexane      | 519 919. | 543 906.   | 532 188.   | 531 777.               |
| pentane            | cyclohexane           | 423 434. | 478 069.   | 449 615.   | 449 923.               |
| cyclohexane        | 2,2-dimethylbutane    | 478 069. | 495 704.   | 486 493.   | 486 807.               |
| cyclohexane        | 2,3-dimethylbutane    | 478 069. | 506 325.   | 491 935.   | 491 994.               |
| cyclohexane        | 3-methylpentane       | 478 069. | 519 919.   | 498 827.   | 498 555.               |
| cyclohexane        | <i>n</i> -hexane      | 478 069. | 543 906.   | 510 966.   | 509 926.               |

stants  $a_{11}$ ,  $a_{12}$ ,  $a_{22}$  which are assumed to be temperature independent and of the molecular volumes and the nonsphericity parameters of components 1 and 2 which are temperature dependent. The critical line of a binary mixture can be then obtained from this analytical expression of the Helmholtz free energy by solving for each composition (i.e.,  $x_1$ ) the following system of equations:<sup>35,44</sup>

$$A_{v,x_1} A_{x_1,x_1} - (A_{v,x_1})^2 = 0, \quad (20)$$

$$A_{x_1,x_1} A_{v,v}^2 - A_{v,v} A_{v,x_1} A_{x_1,v} - 3A_{v,x_1} A_{v,v} A_{v,x_1} + 3A_{v,v} A_{v,x_1}^2 = 0, \quad (21)$$

where  $v$  is the molar volume and  $A_{(y_1, \dots, y_n)}$  stands for the  $n$  partial derivative of  $A$  with respect to the variables  $y_1, \dots, y_n$ . For each composition, the systems formed by Eqs. (20)–(21) is solved with respect to  $\rho^*$  and  $T$ , so that the critical density and temperature are obtained. The critical pressure is then obtained from the equation of state, through the well known relation:

$$Z = \frac{p}{\rho k_B T} = \rho \left( \frac{\partial A}{\partial \rho} \right)_{T, x_1} \frac{1}{N k_B T}. \quad (22)$$

The derivatives needed in Eqs. (20)–(21) were obtained by using the program of symbolic algebra MATHEMATICA.<sup>45</sup>

#### IV. RESULTS

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

Let us start by considering the mean field constants  $a_{11}$ ,  $a_{22}$ , and  $a_{12}$  of several binary mixtures. These  $a_{ij}$  were evaluated at a temperature of 298.15 K, from the exact values of the  $g_{0,kl}^{ij}$  in the zero density limit. In Table I, results are presented for several binary mixtures. As can be seen, the exact value of the cross mean field constant,  $a_{12}$ , can be estimated quite accurately from the geometric average of the mean field constants  $a_{11}$  and  $a_{22}$  of the pure components. As it is well known, in empirical EOS the geometric average is often used as an estimate of  $a_{12}$ .<sup>44</sup> Here, we simply notice

that this empirical rule is justified on a molecular level for alkane mixtures, at least when the structure is taken from the zero density limit. Given the good results obtained by the geometric average, in what follows  $a_{12}$  will be approximated by the geometric average of  $a_{11}$  and  $a_{22}$ .

Let us now present the results for the critical lines of several alkane mixtures. Each figure shows a set of critical lines of mixtures of a given alkane with several others. Unless otherwise stated, the graph in the left shows the experimental data,<sup>46</sup> while the one in the right shows the predictions from the theory. The scale is chosen such that the temperature and pressure are reduced by the corresponding experimental or theoretical values of the common alkane.

Let us start considering systems of a short  $n$ -alkane + longer  $n$ -alkanes. This is done in Fig. 1, where we present results for the systems propane+ $n$ -butane,  $n$ -pentane,  $n$ -hexane and  $n$ -octane. Note that, although quantitative agreement is not obtained, as expected from the use of the simple mean field approximation, the theory qualitatively describes the behavior of the set of critical lines. The existence of a maximum in the critical pressure which increases in magnitude as the difference in size between the alkanes increases is predicted correctly, although the magnitude of this maximum is underestimated.

Let us now consider the critical lines of a long  $n$ -alkane with mixtures of shorter linear alkanes. This is done in Fig.

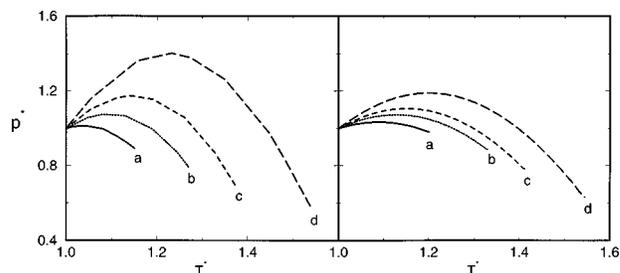


FIG. 1. Critical lines of propane+ $n$ -alkane mixtures. Left, experimental data; right, results from theory. (a) butane; (b) pentane; (c) hexane; (d) octane. Temperature and pressure reduced by the critical temperature and pressure of propane, respectively.

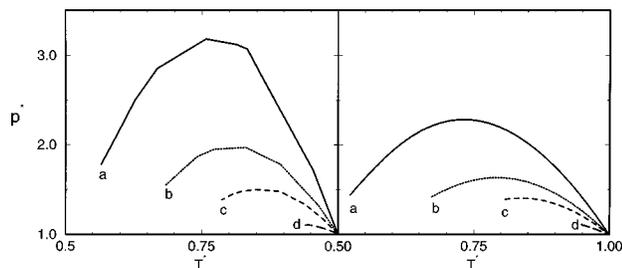


FIG. 2. Critical lines of *n*-heptane+*n*-alkane mixtures. Left, experimental data; right, results from theory. (a) ethane; (b) propane; (c) *n*-butane; (d) *n*-hexane. Temperature and pressure reduced by the critical temperature and pressure of *n*-heptane, respectively.

2, where we show the critical lines of *n*-heptane+ ethane, propane, *n*-butane and *n*-hexane. Again, the theory describes qualitatively the features of the critical lines, correctly predicting the existence of a maximum in the critical pressure for all but the *n*-heptane+*n*-hexane mixture. Once more, however, the magnitude of the maximum is underestimated by the theory.

Now let us show results for mixtures of a linear alkane with branched alkanes. This is done in Fig. 3 for mixtures of propane + hexane isomers. In this case, the critical pressures and temperatures of the pure hexane isomers are so similar that to observe the differences it has been necessary to concentrate in a small region of the  $pT$  surface. As the experimental data are scarce, the lines which connect them appear discontinuous. These lines are only a guide to the eye and must not be considered as a correlation of the critical data between available experimental points. Note that the theory is not only able to describe the appearance of a maximum for all the mixtures, but also the relative ordering of these maxima for the five mixtures considered. This is remarkable, since the critical properties of hexane isomers are very similar and the differences in the critical lines arise as a consequence of chemical details which the theory is qualitatively able to grasp. The theory does fail in one instance, however, as it predicts a slightly smaller critical temperature for pure 2-methylpentane than for pure 2,2-dimethylbutane. As a result of this, a crossover of the corresponding critical lines

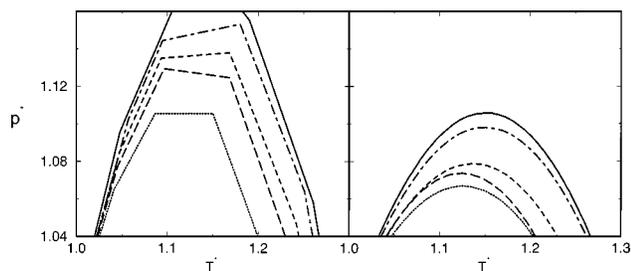


FIG. 3. Critical lines of mixtures of propane+hexane isomers. Left, experimental data (the lines joining the data are a guide to the eye); Right, results from theory. The mixtures, from top to bottom, belong to propane + *n*-hexane (full line), 3-methylpentane (dot-dashed line), 2,3-dimethylbutane (short-dashed line), 2-methylpentane (long-dashed line) and 2,2-dimethylbutane (dotted line) mixtures. Temperature and pressure reduced by the critical temperature and pressure of propane, respectively. Note that the theory incorrectly predicts a crossing over of the critical lines of 2-methylpentane and 2,2-dimethylbutane.

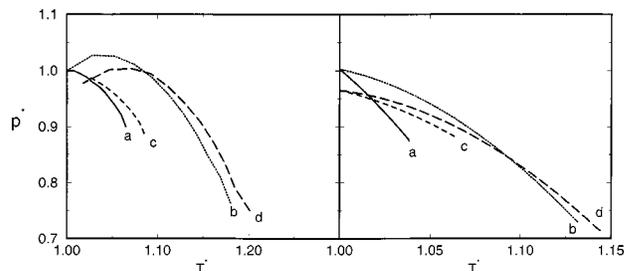


FIG. 4. Critical lines of mixtures of branched alkanes. Left, experimental data; Right, results from theory. (a) 2,2-dimethylbutane + 2,2-dimethylpentane; (b) 2,2-dimethylbutane+2,2-dimethylheptane; and (c) 2-methylpentane+2-methylhexane; (d) 2-methylpentane+2-methyloctane. Pressure and temperature reduced by the critical pressure and temperature of 2,2-dimethylbutane.

occurs (not observed in the figure). It is thus seen that the theory can be applied quite successfully to *n*-alkane mixtures but also to mixtures of *n*-alkane+branched alkanes. Let us now show an example of mixtures of two branched alkanes. This is done in Fig. 4, where results are presented for mixtures containing 2,2-dimethylbutane+2,2-dimethylpentane and 2,2-dimethylheptane (lines a and b) and 2-methylpentane +2-methylhexane and 2-methyloctane (lines c and d). In this case, the maximum in the critical pressures of lines b and d are not predicted (see below for an explanation), but several other features of the graphs are correctly described, e.g.: the crossing between lines a and c, between lines a and d and between lines b and d.

The results presented so far illustrate that the theory can describe qualitatively the critical lines of several alkane mixtures. Notice again that, given the potential model, there are no adjustable parameters whatsoever as the theory has a fully molecular origin.

Let us now analyze what happens for heavier *n*-alkane mixtures. In Fig. 5, the critical lines of mixtures of *n*-hexane + *n*-heptane, *n*-octane, *n*-decane and *n*-tetradecane are shown. The figure on the top shows the results of the theory, whereas the one below shows the experimental results. It is seen that, although the results for mixtures of *n*-hexane with *n*-heptane and *n*-octane are acceptable, the theory is far from predicting the pronounced maxima in the critical lines of the *n*-hexane + *n*-decane and *n*-tetradecane mixtures. Furthermore, the prediction for the critical temperature of the long *n*-alkanes relative to that of *n*-hexane is increasingly underestimated. Apparently, the theory deteriorates as the weight of the alkanes considered is increased. Note that, as has been shown elsewhere,<sup>30</sup> the theory predicts (absolute) critical temperatures which are always lower than the experimental ones. However, the ratio of the critical temperature of the long *n*-alkanes relative to that of *n*-hexane could be predicted correctly if *both were underestimated by the same factor*. Actually, for *n*-tetradecane this ratio is experimentally found to be 1.35, while the theory predicts a ratio of 1.25, which is significantly lower. As it will be shown, this disagreement can be traced to an increasing underestimation of the correlations as the chain length increases.

Let us first define  $I_{ki}(\rho)$  as the integral appearing in the first order perturbation term of Eq. (9), i.e.:

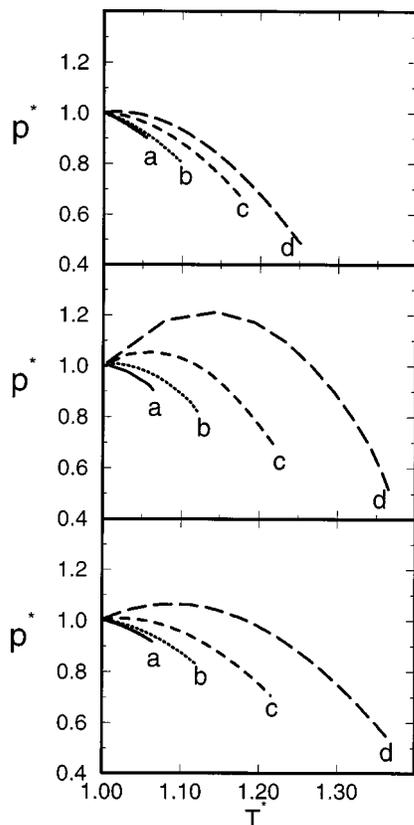


FIG. 5. Critical lines of *n*-hexane+*n*-alkane mixtures. Top, results from theory; center, experimental data; bottom, results from the theory with the van der Waals constants scaled so as to reproduce the experimental critical temperature of the pure components. (a) *n*-heptane; (b) *n*-octane; (c) *n*-decane; (d) *n*-tetradecane. Temperature and pressure reduced by the critical temperature and pressure of *n*-hexane, respectively.

$$I_{kl}(\rho) = \int u_1^*(r_{kl}^*) g'_{0,kl}(r_{kl}^*; \rho) 4\pi r_{kl}^{*2} dr_{kl}^*. \quad (23)$$

From its definition it is clear that  $I_{kl}(\rho)$  is negative. Moreover, it is found that it is a decreasing function of the density (except at very high densities where this trend is inverted). Let us now express the first order perturbation term of a pure substance in terms of  $I_{kl}(\rho)$ :

$$A_1/N = \frac{\rho}{2} \sum_{k=1}^n \sum_{l=1}^n \varepsilon_{kl} \sigma_{kl}^3 I_{kl}(\rho). \quad (24)$$

Whereas this relation is exact, the MF2 implementation of our theory requires  $I_{kl}(\rho)$  to be a constant equal to its value at zero density:

$$I_{kl}^{\text{MF2}}(\rho) \approx I_{kl}(\rho=0). \quad (25)$$

In order to know to what extent this is a good approximation for the calculation of critical properties, we would like to know how much does  $I_{kl}(\rho_c)$  differ relative to its value at zero density. Although the rigorous evaluation of this ratio for our model alkanes is far beyond the scope of this work, we can get further insight into the problem by considering the simple pearl necklace model. Recently, Chiew<sup>47,48</sup> proposed an integral equation which allows for the computation of  $g_{kl}$ . Moreover, the resulting average site-site correlation function,<sup>49,50</sup>  $g_{\text{average}}$ , has been solved

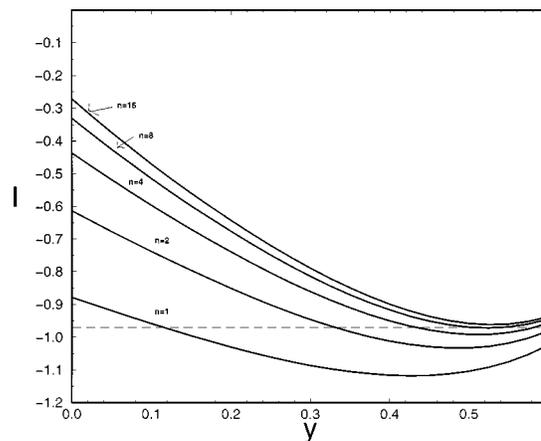


FIG. 6.  $I_{\text{average}}(\rho)$  for the pearl necklace model. The average site-site correlation function was obtained from Chiew's integral equation. Results are shown as a function of the volume fraction  $y$  for several chain lengths  $n = 1, 2, 4, 8, 16$ .

analytically in Laplace's space.<sup>51</sup> Therefore, an expression for  $g_{\text{average}}$  as a function of density and number of monomers can be obtained by performing an inverse Laplace transform. This allows us to calculate the average  $I_{kl}$  factor for the pearl necklace model as:

$$I_{\text{average}}(\rho) = \int u_1^*(r^*) g_{\text{average}}(\rho, n) 4\pi r^{*2} dr^*. \quad (26)$$

In Fig. 6, the value of  $I_{\text{average}}$  as a function of density for 1, 2, 4, 8, and 16 spheres is shown. From this figure, the following conclusions can be drawn:

- (1)  $I_{kl}$  is a decreasing function of the density (except at very high densities where this trend is inverted).
- (2) The absolute value of  $I_{\text{average}}$  at zero density decreases with the length of the chain. This is due to the fact that the correlation hole<sup>52</sup> which dominates the low density behavior of  $I_{\text{average}}$  increases with the length of the chain.
- (3) For sufficiently long chains (i.e.,  $n > 8$ ) and high densities (i.e.,  $y > 0.4$ )  $I_{kl}$  depends very weakly on chain length and density.

Now, in order to analyze how the predictions of the MF2 theory deteriorate with density and chain length, we plot in Fig. 7 the following function:

$$F(\rho) = I_{\text{average}}(\rho) / I_{\text{average}}(\rho=0). \quad (27)$$

The critical densities of the pearl necklace model as obtained from Gibbs ensemble simulations<sup>9,53-55</sup> have been also included. From this figure, it is clearly seen that the mean dispersive energy at the critical density, relative to that at zero density, increases with the chain length, even though the volume fraction at the critical point decreases slightly. Accordingly, the quality of the MF2 approximation deteriorates with chain length. Although strictly speaking these considerations concern the pearl necklace model, we believe they apply qualitatively to any chain molecule and thus explain the failure of our theory in predicting the critical lines of *n*-hexane+*n*-decane and *n*-tetradecane mixtures.

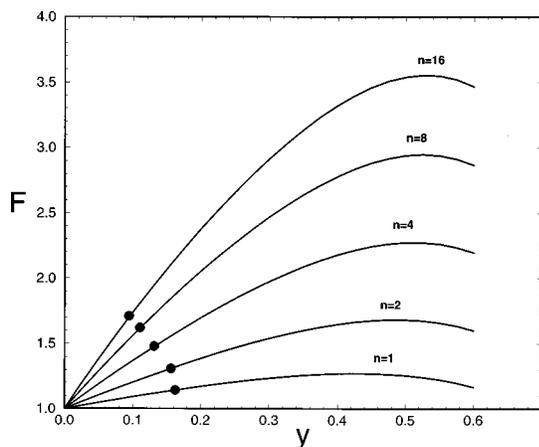


FIG. 7. Value of  $F_{\text{average}}$  [see Eq. (27) of the main text] for the pearl necklace model. Results are shown as a function of the volume fraction,  $y$  for several chain lengths  $n = 1, 2, 4, 8, 16$ .

That the mean field theory can be brought into closer agreement with experiment is shown in the bottom part of Fig. 5. In this figure, the van der Waals constants of the pure compounds were chosen to match the experimental critical temperatures. In doing so, we are somehow correcting for the underestimation of the dispersive energy. As can be seen, the agreement with experiment is now better and the curvature of the critical lines is increased.

Let us finish with another application of the perturbation theory proposed in this work. We shall analyze the problem of the distribution of a solute (an  $n$ -alkane) at infinite dilution between the vapor and liquid phases of a solvent (a lighter  $n$ -alkane) in the neighborhood of the critical point of the solvent. This problem has been studied experimentally recently.<sup>56</sup> The partition coefficient,  $K$ , which gives the ratio of the molar fraction of the heavy alkane in the vapor  $x_v$  and in the liquid phase  $x_l$  can be approximated (see Refs. 56, 57 for details) as:

$$RT \ln(K^0) = \lim_{x \rightarrow 0} RT \ln \left( \frac{x_v}{x_l} \right) = 2 \frac{\rho_{l1} - \rho_{c1}}{\rho_{c1}^2} \left( \frac{\partial p}{\partial x} \right)_{\rho, T}^c, \quad (28)$$

where  $\rho_{l1}$  and  $\rho_{c1}$  denote the orthobaric and critical densities of the pure solvent and the derivative is evaluated at the critical point of the solvent.<sup>56,57</sup> Note that all the properties appearing in Eq. (28) can be readily evaluated from the perturbation theory of this work. However, the partial derivative appearing in this equation can only be calculated from experiment by means of indirect methods.<sup>56</sup> In Fig. 8, the partition coefficient for binary mixtures of  $n$ -hexane (solvent) +  $n$ -decane,  $n$ -dodecane and  $n$ -tetradecane (solutes) are shown as obtained from experiment (left figure)<sup>56</sup> and from theory (right figure). In the implementation of the theory we used the van der Waals constants which match the critical temperatures of the pure compounds (the same that were used in the bottom of Fig. 5). As it can be seen, the theory predicts correctly the enrichment of the liquid phase in the solute as one moves away from the critical point of the solvent. Also, it is shown that the theory predicts a bigger enrichment of the liquid phase for the heaviest solute ( $n$ -tetradecane) than for the lightest one ( $n$ -decane). The results of this figure show

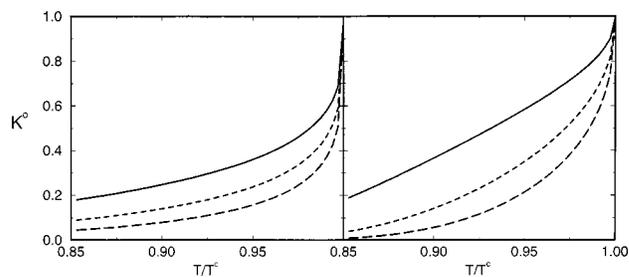


FIG. 8. Limiting partition coefficient of  $n$ -hexane+ $n$ -alkane mixtures in the vicinity of the critical point of  $n$ -hexane. Left, experimental data; Right, results from theory with the van der Waals constant adjusted to fit the experimental critical temperature. The lines belong to, from top to bottom,  $n$ -hexane +  $n$ -decane (full line), +  $n$ -dodecane (dashed line), +  $n$ -tetradecane (long-dashed line).

how the simple perturbation theory of this work can be useful in getting a qualitative understanding of some process involved in supercritical extraction.

## V. CONCLUSIONS

In this paper, the perturbation theory of linear and branched alkanes proposed previously<sup>30</sup> has been extended to mixtures. The theory has a full molecular origin and no adjustable parameters. Critical lines of  $n$ -alkane mixtures have been computed from the theory and compared to the experimental results. Since the theory is of mean field type, quantitative agreement with experiment cannot be expected. Even so, main trends found in the critical lines of alkane mixtures are correctly described. The performance of the theory deteriorates when increasing the molecular weight of the alkane. An explanation for that is proposed on the basis of the behavior of the pearl necklace model, for which there are approximate analytical expressions for the average site-site correlation function. Finally, it is shown that the theory is also useful in getting a qualitative idea of the distribution of an  $n$ -alkane solute in an  $n$ -alkane solvent in the proximities of the critical point of the latter. This shows that perturbation theory can be useful in understanding some phenomena associated with supercritical extraction. In the following paper, the possibilities of using a perturbation theory to predict excess properties of  $n$ -alkane mixtures is analyzed.

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