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Excess properties of mixtures of *n*-alkanes from perturbation theory

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Excess properties of binary mixtures of *n*-alkanes have been evaluated from perturbation theory. A good equation of state for the reference system mixture is combined with a simple approximation to the perturbation term and with a reasonable set of potential parameters to yield a qualitatively correct description of the trends of excess volumes and excess Gibbs energies of *n*-alkane mixtures without the need for any adjustable parameter. Moreover, the theory can be made quantitative by introducing two adjustable parameters for each temperature. These two parameters have a clear molecular origin and they could be removed if some of the approximations of the theory proposed here were replaced by a more rigorous evaluation. In this sense this paper is just a first step toward a fully molecular theory of excess properties of alkanes. Excess properties estimated from perturbation theory by using these two adjustable parameters are in excellent agreement with experiment and are clearly superior to those obtained from the classic FOV theory proposed by Flory, Orwoll and Vrij [J. Am. Chem. Soc. **86**, 3507, 3515 (1964)]. It is our view that the theory of this work is also conceptually superior to the FOV theory, since it rests on a more rigorous molecular basis. © *1999 American Institute of Physics.* [S0021-9606(99)51431-1]

I. INTRODUCTION

Experimental interest in the properties of alkane mixtures is probably due to the importance of alkanes within the oil industry. However, mixtures of alkanes constitute also an interesting challenge for liquid theories since long ago. The first important step toward an understanding of this type of mixtures was led by Prigogine's group in the fifties.[1] Prigogine and co-workers extended the cell theory developed by Lennard-Jones and Devonshire[2] for spherical molecules to the case of flexible molecules. Although this extension was at the cost of introducing the *ad hoc* parameter ''c'' which gives ''the number of translational degrees of freedom per monomer,'' it met considerable success. In the early sixties Freeman and Rowlinson[3] found fluid–fluid immiscibility in *n*-alkane mixtures with large differences in size. This finding was rather puzzling for the community of that time,[4–6] as it contradicted the old and well established principle ''like dissolve like.'' This surprise stimulated the theoretical research in *n*-alkane mixtures. Obviously an intermediate step to understand the immiscibility of *n*-alkane mixtures with large differences in size is to understand the excess properties of lighter *n*-alkane mixtures. Initial attempts to explain the behavior of *n*-alkane mixtures were done by Patterson[5] and Flory *et al.*,[7–10] though many other approaches were proposed later.[11–14] The treatment of Flory, Orwoll and Vrij[8] (hereinafter denoted as FOV) developed in the middle sixties can be considered as a modification of that of Prigogine. The repulsive forces are treated in a similar way but the attractive forces are treated within a mean field approximation. The FOV theory when applied to *n*-alkane mixtures yields results in excellent agreement with experiment. The theory contains a number of adjustable parameters for each substance and mixture which must be fitted to experimental data. In particular, the theory requires knowledge of the molar volume and some of its derivatives, such as the isothermal compressibility and thermal expansion coefficients.[9] Since experimental data of isothermal compressibilities and thermal expansion coefficients of pure alkanes were scarce at that time, a number of experimental groups undertook their determination. In particular, experimental determination of these coefficients was a very active area of research in our department over the sixties and seventies.[15–20] The FOV theory has become quite popular in describing excess properties of mixtures and its influence is quite large on experimental groups, engineering oriented groups and polymer research groups.[21,22]

A major achievement in the field of statistical mechanics of fluids occurred in 1967 when Barker and Henderson proposed a perturbation theory for spherical Lennard-Jones (LJ) systems.[23,24] The theory was both satisfactory from a quantitative point of view and from a conceptual point of view, since it was firmly based on statistical mechanics. A further improvement by Weeks, Chandler and Andersen[25] led the theory to even better quantitative results. In the seventies and eighties, perturbation theories were extended successfully to linear[26–29] and nonlinear rigid molecules.[30] However, the extension of perturbation theory to flexible molecules has not yet achieved the same degree of refinement. In some studies, flexible molecules are treated as linear rigid molecules[31] which is obviously a severe approximation. Other studies which fully account for flexibility have not been extended to molecules longer than *n*-butane.[32] Studies of perturbation theory of mixtures of flexible molecules are even more scarce than those of pure fluids. However, the progress performed in the last 15 years in the study of flexible molecules allows one to think that the time for development of perturbation theories for flexible molecules has now arrived.[33] In fact, for the pearl necklace model (a model of fully flexible tangent hard spheres) and its LJ version, quite good theories are now available which are both satisfactory from a quantitative and a conceptual point of view.[34–37] The same is true for pearl necklace-like mixtures.[38–42] Nevertheless, the situation is not yet fully satisfactory, since perturbation theories have not been implemented successfully to more realistic chain molecules with fixed bond angles, a torsional potential and contiguous overlapping monomers as is the case of *n*-alkanes.

Perturbation theory has a clear molecular origin, with well defined approximations and therefore it has become the favorite treatment adopted by the liquid state community, working mostly in physics, physical chemistry or even in chemical engineering. There are two reasons why the FOV theory is not popular among the theoretical liquid state community. First of all, the cell theory has been abandoned in liquid research state (although it is quite a good theory for solids[43–45]). Second, the parameter ''c'' of Prigogine has an obscure molecular origin. In fact, it cannot be derived from any theoretical treatment and remains a completely empirical parameter. Because of that, the FOV theory is not considered a useful tool by the liquid state community. On the other hand, experimentalist and polymer research groups still use the FOV theory because tractable perturbation theories have not been extended to realistic flexible molecules such as *n*-alkanes or real polymers, so that there is no theoretical alternative yielding results in quantitative agreement with experiment.

In the last years we have worked in the implementation of perturbation theory for alkane and alkane mixtures. The simple mean field approximation has been adopted. The results presented by the theory have not been quantitative but a number of qualitative features of alkane and alkane mixtures have been described correctly. In particular, the existence of a maximum[46–48] in the critical pressure and density,[49] the effect of branching[50,51] on the critical properties and the general shape of the critical lines of alkane mixtures[52] have been described by the theory. In this work we study the performance of this theory for describing excess properties of *n*-alkanes. Although our main aim is to show that with a simple and molecular based theory excess properties of alkanes can be described qualitatively, we shall also try to go one step further in the search for quantitative agreement. Our aim is to show that perturbation theory can be used successfully to describe quantitatively excess properties of alkane mixtures. In particular, it will be shown that perturbation theory is comparable in accuracy to the popular FOV theory in describing excess properties of alkanes. For that purpose, we shall fit some parameters of the theory to experimental data. One may argue that this leaves our treatment in the same empirical category as the FOV. However, it will be shown that since the theory has a clear molecular origin, the parameters required in our treatment have a clear molecular meaning and this is in contrast to the FOV theory. Moreover, the fitting can be eventually removed if some additional theoretical work is performed. This paper pretends to be a first step in the long range goal of showing that perturbation theories can be used to describe quantitatively the excess properties of mixtures of flexible molecules.

The scheme of the paper is as follows. In Sec. II the mean field perturbation theory used in this work is briefly described. In Sec. III, we show how to correct for the mean field by introducing a meaningful, temperature dependent parameter. The effect of conformational changes on excess properties is considered in Sec. IV. Section V is devoted to a discussion of the results obtained from the parametric form of our equation of state. Finally, in Sec. VI the conclusions to this work are presented.

II. A MEAN FIELD PERTURBATION THEORY FOR *n*-ALKANE MIXTURES

In the preceding paper, hereinafter denoted as paper I,[52] we presented a rather general approach to first order perturbation theory for flexible molecules. The reference system was accurately described by a modification of Wertheim's EOS, which has shown to give very reliable results for *n*-alkanes.[53–55] However, in order to make the theory simple, some approximations were made for the remaining intramolecular and perturbation contributions. Essentially, we ignored the effect of conformational changes on the equation of state and invoked the simple mean field approximation for the first order perturbation term. The implementation of the mean field approximation is not unique and we suggested two alternative possibilities. In the first version, hereinafter denoted as mean field 1 (MF1), the structure of the reference system as given by the site–site correlation functions was approximated by a Heaviside step function. In the second version, denoted as mean field 2 (MF2), the structure of the reference system was approximated by its zero density limit. As our main interest in this paper is to describe excess properties in the liquid regime, we expect the MF1 approach to be more appropriate and we will mainly consider this approach in what follows. The reader is referred to paper I for further details on the theory and on notation. Contrary to paper I, where we were mainly concerned with linear and branched alkanes of low molecular weight, in this work we will concentrate on linear *n*-alkanes that span the range from C_4 to C_{60}. We thus find it convenient to employ an alternative force field that very much resembles that used previously in order to describe the second virial coefficients of *n*-alkanes.[56,57] Moreover, recent computer simulations [58,59] using similar parameters obtained reasonable agreement with experiment for *n*-alkane liquids. We will use a single size parameter, $\sigma_{CH_3}=\sigma_{CH_2}=3.85$ Å and two strength parameters, $\epsilon_{CH_3}/k_B=104$ K, $\epsilon_{CH_2}/k_B=49.7$ K. Note that we have slightly modified the size parameter proposed previously,[57] from 3.923 Å to 3.85 Å (the change being less than 2%), because better agreement with experimental excess properties was achieved. Furthermore, this allows us to use the empirical fit to the nonsphericity parameter and to the molecular volume proposed by us in previous work.[49] Although the size parameter used in that work was $\sigma=3.923$ Å, we

TABLE I. Excess volumes (in cm^3/mol) for *n*-alkane mixtures as obtained from experiment and for the MF1 and MF1C versions of the perturbation theory. The temperature in Celsius is denoted as *t*.

Mixture	t	$V_{\rm exc}^{\rm MF1}$	$V_{\rm exc}^{\rm MF1C}$	$V_{\rm exc}^{\rm exp}$
C_6+C_{10}	20	−0.45	−0.24	−0.20
C_6+C_{12}	20	−0.70	−0.39	−0.31
C_6+C_{14}	25	−0.96	−0.54	−0.52
C_6+C_{16}	20	−1.08	−0.61	−0.49
$C_{10}+C_{16}$	20	−0.16	−0.09	−0.07
C_8+C_{16}	20	−0.42	−0.24	−0.19

find that simply rescaling the molecular volume of that fit by $(3.85/3.923)^3$ gives a very good estimate for the volume of our model. The differences with the potential parameters of the previous paper are mainly due to two reasons. In the first place, the parameters used in paper I were optimized to describe the properties of a very large set of both branched and linear alkanes. We found that the use of completely transferable potentials for such a set was at the cost of changing the Lennard-Jones parameters previously optimized for *n*-alkanes. Second, the optimization procedure is different, as the set used in paper I was optimized for use in the mean field theory proposed in that paper, while the parameters used here were optimized to predict experimental second virial coefficients of *n*-alkanes. We cannot expect *a priori* that the parameters used in the previous paper will give the best agreement with experiment when tested by means of simulation, as the theory includes several approximations which may have required to alter these. On the other hand, the set of parameters used in this paper are known to yield rather good predictions for the second virial coefficients and liquid vapor equilibrium of *n*-alkanes.[56,58,59]

Let us now compare the predictions of the MF1 theory for the above force field with experimental results. In Table I, experimental excess volumes for some *n*-alkane mixtures at $T=298.15$ K and atmospheric pressure[60–62] are compared with the MF1 theory.[63] As can be seen, the MF1 theory gives fair qualitative agreement, correctly predicting the sign and order of magnitude of the excess volume, even though the results are systematically overestimated by a factor of 2 or so. Other less evident trends are also predicted by the theory, namely, the increase of absolute value of the excess volume when the difference in size of the components increases (see lines 1 to 3 of Table I) and the decrease in excess volume as the size of the components increases at fixed size difference (compare lines 3 and 6 of Table I). It may appear somewhat surprising that the MF2 theory, which described the critical lines of alkane mixtures with relative success, completely fails in describing the excess volumes of the same mixtures (results not shown). In fact, predictions of this theory were wrong by a factor of 10 or more and we will no longer consider this version in what follows. These findings can be rationalized if one considers the following facts:

(1) The MF2 theory approximates the pair correlation function of the reference system by its low density limit. Since the packing fraction along the critical lines is not too high (i.e., $y\simeq 0.10$), the MF2 approximation turns to be rather reasonable for the purpose of describing critical lines. On the contrary, the excess properties we are considering refer to the liquid state, which typically has much higher packing fractions (i.e., $y>0.45$). At such high densities, the structure of the fluid is considerably modified relative to that in the low density limit and the MF2 approximation seems to be no longer valid.

(2) The MF1 theory approximates the contribution per site to the first order perturbation term (I_{kl}) to a constant which is independent of chain length and of density. As was shown in paper I (see Fig. 6) the average contribution per site to the first order perturbation term does not depend much either on density or on chain length and this is correctly described by MF1. On this basis, it can be stated that *perturbation theories which assign a density and chain length independent site–site correlation function will provide a qualitatively correct description of pure fluids and mixtures of linear chain molecules in the liquid state.*

(3) Although apparently quite crude, the Heaviside function is a reasonable approximation to the structure of a high density linear (not branched) chain fluid. That this is so can be seen for example in the paper of Martin and Siepmann,[64] where site–site correlation functions for *n*-alkanes in the liquid state are obtained from simulation and are seen to resemble a Heaviside step function rather closely. Further evidence arises from Fig. 6 of our previous paper. In this figure, the value of $I_{\rm average}$ for $n=1$ and $y=0$ is the mean dispersive energy felt by a monomer whose site–site correlation function is a Heaviside function (i.e., for hard spheres the low density limit is the Heaviside function). Comparing this value with that obtained for the mean dispersive energy of relatively long chain molecules at moderate liquid densities it can be seen that differences are not more than a 10% or so. Accordingly, the value of $I_{\rm average}$ adopted by the Heaviside function is not too far from its typical liquid value in chain molecules

Points 2 and 3 illustrate why MF1 gives qualitatively correct results for mixtures of chain molecules in the liquid state. However, to bring the theory into quantitative agreement with experiment it is necessary to go one step further.

III. CORRECTING FOR THE MEAN FIELD APPROACH

In accordance with point 2 of the previous discussion, the mean field integrals, I_{kl}, will be set to a constant independent of chain length, density and type of site. However, in order to correct for the deficiencies noted in point 3, we shall allow these constants to be slightly different from the value obtained assuming a Heaviside step function. By denoting the latter value as $I^{\rm MF1}$, the modified mean field integrals are now written as follows:

$$I_{kl}(y)=F_1(T)I^{\rm MF1}, \tag{1}$$

where $F_1(T)$ is a substance independent parameter which corrects for the lack of correlations introduced by the MF1 approximation. Since the Heaviside step function is not a bad description for the site–site correlation function in the liquid

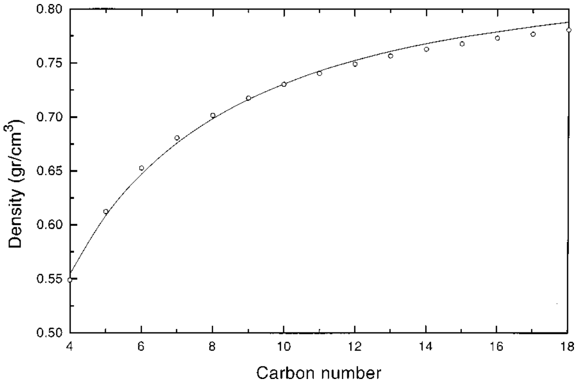

FIG. 1. Densities of *n*-alkanes (at $T = 298.15$ K and zero pressure) from C_4 up to C_{18} as obtained from experiment (symbols) and from the MF1C perturbation theory of this work (solid line). Experimental results were obtained by using Simha's equation of state (Ref. 74) with the parameters given in Ref. 75.

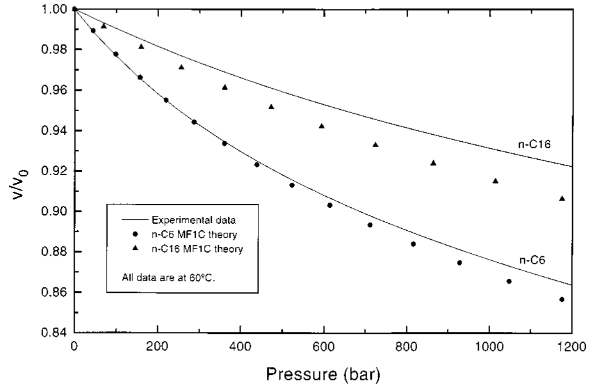

FIG. 2. Equation of state of *n*-hexane and *n*-hexadecane (density versus pressure) at 60 °C as obtained from the perturbation theory MF1C (symbols) and from experiment (lines). Experimental results were obtained using Simha's equation of state (Ref. 74) with the parameters reported in Ref. 75. The molar volume is denoted by v, and the molar volume at zero pressure is denoted as v_0.

state we expect the value of $F_1(T)$ to be close to one. To lead the theory to quantitative agreement with experiment, some experimental information must be introduced at this point. We shall fix the value of F_1 at each temperature by imposing the condition that the density of *n*-decane (C_{10}) at zero pressure as obtained from the theory matches the experimental orthobaric density. In this way, only one experimental data per temperature is needed and the temperature dependence of the F_1 parameter in the range 20–120 °C is well described by the simple relation $F_1 = (1.092\,630 - 0.000\,453t)^2$ (t is the Celsius temperature). Analysis of this fit shows that F_1 is everywhere close to one. This provides further evidence for the fact that the Heaviside step function is a fair approximation to the site–site correlation function of alkane liquids. The temperature dependence of F_1 reflects the decrease of correlations which follows from the decrease of the orthobaric densities as temperature increases.

Although we obtain the parameter F_1 fitting to experimental data, it must be pointed out that this parameter has a clear molecular origin. In future work this parameter can be calculated theoretically if site–site correlation functions are obtained from integral equations.[65,66] In this work, however, we will keep the theory as simple as possible while still retaining the molecular framework. Since both F_1 and I^{MF1} are density independent, our theory is still of the mean field type. Since it is closely related to the MF1 theory, this version of the theory which includes the parameter F_1 will be denoted hereinafter as MF1 corrected (MF1C).

Let us now present results for the MF1C theory. In Fig. 1, the experimental orthobaric densities of alkanes from C_4 to C_{18} at 298.15 K are compared with the theoretical predictions (zero pressure densities). As it can be seen, although we force F_1 to match the experimental density of C_{10}, the description of the experimental data of other *n*-alkanes not involved in the fitting is fairly good. This is easy to understand if one invokes again the hypothesis that site–site correlation functions become almost independent of chain length at high densities. The theory describes not only the zero pressure densities but also provides a fairly good description of the high density regime. In Fig. 2, the equation of state at high pressures of *n*-hexane and *n*-hexadecane at 60 °C as obtained from theory is compared with experimental data. The agreement between theory and experiment is fair. In Table I, experimental excess volumes are compared with MF1C, showing that the introduction of the fitting parameter considerably improves the predictions of the theory.

We have also tested the predictions of the theory for the chemical potentials and activity coefficients. Using the symmetric criterion, the activity coefficient of component 1, γ_1 can be obtained as:

$$\mu_1(T,P,x_1) - \mu_1^0(T,P) - k_B T \ln(x_1) = k_B T \ln(\gamma_1), \qquad (2)$$

where $\mu_1(T,P,x_1)$ is the chemical potential of component 1 in the mixture and $\mu_1^0(T,P)$ is the chemical potential of component 1 when $x_1 = 1$. The chemical potentials can be obtained by differentiating the Helmholtz free energy:

$$\left(\frac{\partial A/k_B T}{\partial N_1} \right)_{T,V,N_2} = \frac{\mu_1}{k_B T}. \qquad (3)$$

As the algebra required to obtain the chemical potential is involved, it is a good idea to check for thermodynamic consistency[67] using the expression:

$$\frac{G^{\mathrm{exc}}}{N k_B T} = x_1 \ln(\gamma_1) + x_2 \ln(\gamma_2). \qquad (4)$$

We have checked that our calculations indeed satisfied this equation.

In Table II, the activity coefficients of the lightest component (component 1) at infinite dilution as obtained from

TABLE II. Logarithm of the activity coefficient of component 1 at infinite dilution as obtained from MF1C and from experiment.

Mixture	t	$\ln(\gamma_{1,\infty}^{\mathrm{MF1C}})$	$\ln(\gamma_{1,\infty}^{\mathrm{exp}})$
$C_5 + C_{18}$	35	−0.089	−0.138
$C_6 + C_{16}$	40	−0.062	−0.094
$C_6 + C_{24}$	60	−0.218	−0.253
$C_7 + C_{24}$	60	−0.211	−0.207
$C_8 + C_{32}$	75	−0.330	−0.325

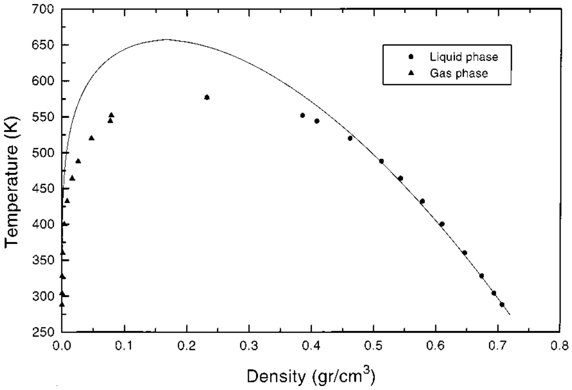

FIG. 3. Vapor–liquid equilibria for *n*-octane as obtained from the MF1C theory (solid line) and from experiment (symbols).

MF1C and from experiment (see Refs. 14,11,12 and references therein) for some selected *n*-alkane mixtures are presented. As it can be seen in Table II, the agreement between theory and experiment is satisfactory. Since activity coefficients and excess Gibbs energies are related through Eq. (4), good agreement for activity coefficients means also good agreement for excess Gibbs energies. In Fig. 3, the vapor–liquid equilibria coexistence densities of *n*-octane as obtained from MF1C and from experiment are shown (to apply the MF1C to temperatures higher than 120 °C we extrapolate to high temperatures the fit to F_1). As can be seen, the agreement between theory and simulation is quite good at low temperatures. The critical temperature is overestimated by about 15%.

We have thus shown that MF1C reproduces reasonably well the behavior of pure *n*-alkanes. In fact, theoretical predictions of the EOS of liquid *n*-alkanes at high pressures and of the vapor-liquid equilibria are satisfactory. The MF1C gives also good predictions for the excess volumes, excess Gibbs energies and activity coefficients. Taking into account that the potential model used to describe alkanes is realistic, the evaluation of the molecular volume is performed exactly,[68] the EOS for the reference repulsive system is quite good[54] and that the estimate of the first order perturbation term is both simple and theoretically sounded, the results presented so far illustrate that perturbation theories can do a quite good job for describing the properties of *n*-alkanes and *n*-alkane mixtures. However, there is still waiting an unpleasant surprise.

Enthalpies for the pure components and for the mixture can be calculated through derivatives of the Helmholtz free energy A:

$$\frac{H}{Nk_BT}=\frac{1}{T}\left(\frac{\partial A/Nk_BT}{\partial(1/T)}\right)_{V,N_1,N_2}+\rho\left(\frac{\partial A/Nk_BT}{\partial\rho}\right)_{T,N_1,N_2}$$

$$=\frac{U}{Nk_BT}+Z, \tag{5}$$

where Z is the compressibility factor, U is the internal energy and ρ is the number density. In Table III, the excess enthalpies as obtained from MF1C and from experiment are presented. The MF1C predicts correctly small values for the excess enthalpies of *n*-alkane mixtures. However, it is seen in Table III that the agreement is not quantitative. In particular, MF1C is unable to predict positive values of the excess enthalpies at low temperatures. The fact that the predictions of excess enthalpies are not quite good is striking, taking into account that all the other properties were correctly described. How can we solve this problem?

TABLE III. Excess enthalpies (in cal/mol) for *n*-alkane mixtures as obtained from experiment, from the MF1C perturbation theory, and from the MF1C theory once the intra-molecular term is included (MF1CI).

Mixture	t	$H_{\mathrm{exc}}^{\mathrm{MF1C}}$	$H_{\mathrm{exc}}^{\mathrm{MF1CI}}$	$H_{\mathrm{exc}}^{\mathrm{exp}}$
C_6+C_7	20	-0.26	0.29	0.22
C_6+C_{10}	20	-2	6	4
C_6+C_{12}	20	-3	12	11
C_6+C_{16}	20	-6	31	31
$C_{10}+C_{16}$	20	-1	10	10
C_8+C_{16}	20	-3	19	21

IV. THE EFFECT OF CONFORMATIONAL CHANGES

It is somewhat mysterious and surprising that a theory describing correctly the equation of state, coexistence properties, excess volumes and excess Gibbs energies does not perform well for excess enthalpies. What is going on?

Since at low temperatures excess enthalpies predicted by the theory are negative and experimental values are positive, a possible route to bring theory into agreement with experiment is to raise the enthalpy of the mixture. In a perturbation theory, A is obtained as a sum of A_0 and A_1. The term A_0 contributes mainly to the entropy of the system and very little to the internal energy, while the term A_1 contributes very little to the entropy of the system and significantly to the internal energy.[69] Taking this into account and comparing the first order perturbation expansion with the expression for the free energy in terms of entropic and energetic contributions,

$$A=A_1+A_0=U-TS, \tag{6}$$

we can approximately identify A_1 with U and A_0 with $-TS$. In a further step, we can consider that at zero pressure, the internal energy and the Helmholtz free energy are equivalent to the enthalpy and Gibbs free energy, respectively. Accordingly, we can bring the theoretical predictions of the enthalpy into closer agreement with experiment by raising the value of the internal energy of the mixture or, equivalently, by raising the first order perturbation term for the free energy of the mixture. This raise in A_1 can be justified if one assumes that site–site correlation functions between different species in the mixture are different from site–site correlations in the pure fluids (indeed, such changes have been observed in idealized polymer models in a recent study[70]). Actually, introducing a second parameter to account for these differences, we were able to bring excess enthalpies into close agreement with experiment. However, it follows from Eq. (6) that an increase in the internal energy of the mixture will result in an increase in its Helmholtz free energy. Thus, by introducing a second parameter we were able to improve the predictions for the excess enthalpy, but this was at the cost of spoiling the predictions for the Gibbs free energy. Orwoll and Flory[10] face a similar problem in the FOV theory. The way they solve the problem was to introduce a parameter to correct A_1 (i.e., Γ) so that good excess enthalpies were predicted and then to introduce a completely ad hoc entropic term (i.e., Γ_S) to recover good values of the Gibbs excess energies.

At this point it seems as if we had reached a dead end were we can no longer advance. However, there is a term to which we have paid very little attention, both in this work and in paper I. This is the intra-molecular term. We have been assuming all the time that conformational populations are only a function of temperature and depend neither on density nor in composition. However, it is reasonable to expect small but appreciable conformational changes when mixing two different alkanes. In fact, it has been shown previously that packing effects can change the fraction of gauche bonds by about 2%–5%.[55,71] These small changes may have a significant effect on excess enthalpies, however. Assume, as an example, that on mixing propane (rigid molecule) with *n*-pentane (flexible molecule) at equimolar composition, the population of gauche conformers increases in about 3%. The increase of the torsional energy per molecule is then given as the product of the number of torsional degrees of pentane, times the molar fraction of pentane, times the increase of gauche conformers, times the energy of a gauche bond, i.e.: $2\times 0.5\times 0.03\times 3302 J=99 J$. By taking a look at Table III, we can see that this is indeed a significant amount of energy compared to the typical values of the excess enthalpies, similar to the difference between our calculated enthalpies and the experimental data. Our working hypothesis is that the positive values of the excess enthalpies of alkanes at low temperatures are due to conformational changes (i.e., a small increase in the fraction of gauche bonds). Certainly, the rigorous evaluation of conformational changes within a perturbation theory is an overwhelming task. It would imply to provide expressions for A_0, A_1 and A_{intra} for each conformational population and to minimize the total free energy with respect to the population of conformers at each temperature and density. In previous work we have done that for repulsive models of short alkanes (i.e., up to *n*-octane).[71] However, extending this treatment to longer *n*-alkanes including attractive forces is at this point an almost impossible task. We shall try to approach the problem in a less rigorous way by invoking the following approximations:

(1) The energy of a given conformer depends mainly on the number of gauche conformers, so that the LJ intra-molecular contribution can be neglected. This is reasonable, because the torsional energies are usually much bigger than the nonlocal intra-molecular Lennard-Jones interactions.
(2) The torsional degrees of freedom are independent from each other.
(3) There are three rotational states[72] for each torsional degree of freedom (RIS approximation) which are denoted as trans (t), gauche$^+$, (g^+) and gauche$^-$ (g^-).

With these approximations, the expression for the intra-molecular free energy of the pure fluid reduces to:[55,71]

$$\frac{A_{\text{intra}}}{Nk_BT}=(n-3)\frac{a_{\text{intra}}}{k_BT}, \tag{7}$$

$$\begin{aligned}\frac{a_{\text{intra}}}{k_BT}&=\left[2x_{g^+}\frac{E_1}{k_BT}\right]-[-x_t\ln(x_t)-2x_{g^+}\ln(x_{g^+})]\\&=\left[\frac{u_{\text{intra}}}{k_BT}\right]-\left[\frac{s_{\text{intra}}}{k_B}\right],\end{aligned} \tag{8}$$

where a_{intra} is the contribution to the intra-molecular free energy per torsional degree of freedom, n the number of carbon atoms and $(n-3)$ is the number of torsional degrees of freedom of the molecule and x_t, x_{g^+} and x_{g^-} are the fraction of torsional degrees of freedom in the t, g^+ and g^- states, respectively, while E_1 is the energy difference between the gauche and trans states. In what follows, we will use a fixed value for this energy of 3302, 2 J/mol (i.e., 790 cal). These molar fractions satisfy the following constraints:

$$x_{g^+}=x_{g^-}, \tag{9}$$

$$x_t+x_{g^+}+x_{g^-}=1. \tag{10}$$

The way Eq. (8) has been written emphasizes the fact that the intra-molecular free energy per torsional degree of freedom can be split into an energetic [first square bracket on the right hand side of Eq. (8)] and an entropic term [second square bracket on the right hand side of Eq. (8)]. At zero density, the residual contributions to the free energy, A_0 and A_1, vanish and the fraction of trans bonds is obtained by minimizing the intra-molecular free energy. This amounts to solving the following equation [subject to the constraints given by Eqs. (9)–(10):

$$\left(\frac{\partial a_{\text{intra}}}{\partial x_{g^+}}\right)_{N,T}=0. \tag{11}$$

Solving Eq. (11) leads to the following result for the fraction of torsional degrees of freedom in the gauche$^+$ state:

$$x_{g^+}^{ig}=\exp\left(-\frac{E_1}{k_BT}\right)\Bigg/\left(1+2\exp\left(-\frac{E_1}{k_BT}\right)\right), \tag{12}$$

where the superscript ig recalls the fact that this is the population at zero density. We will assume from now on that the conformational populations *of the pure components are given by the ideal gas population along all the density range*. Although some conformational changes with density should be expected, this happens to be rather small.[64,73] Contribution of the intra-molecular term to other thermodynamic properties can be obtained by derivation of the function $A_{\text{intra}}[T,N,x_{g^+}(T,V,N)]$ with respect to T (internal energy), V (pressure) and N (chemical potential). As x_{g^+} is generally a function of T, V and N, the chain rule must be used. Furthermore, the following equality must be taken into account:

$$\left[\left(\frac{\partial A_{\text{intra}}}{\partial x_{g^+}}\right)_{N,T}\right]_{x_{g^+}^{ig},T}=0, \tag{13}$$

where the subscripts following the parenthesis indicate the quantities that should be kept constant when performing derivatives and the subscripts following the square brackets indicate the values of the variables at which the derivative must be evaluated. The contribution of the intra-molecular term to the thermodynamic properties of the pure alkanes are then given by:

$$Z_{\mathrm{intra}}=0, \tag{14}$$

$$\frac{U_{\mathrm{intra}}}{Nk_BT}=2(n-3)x_{g^+}^{ig}\frac{E_1}{k_BT}, \tag{15}$$

$$\frac{\mu_{\mathrm{intra}}}{k_BT}=\frac{A_{\mathrm{intra}}}{Nk_BT}, \tag{16}$$

where A_{intra}/Nk_BT is given by Eqs. (7)–(12).

Let us now focus on the treatment of the mixture. We shall assume that in the mixture the conformational population of components 1 and 2 is the same (i.e., the population of trans bonds in the mixture is the same for molecules of type 1 and type 2). With this approximation, A_{intra}/Nk_BT of the mixture is given by:

$$\frac{A_{\mathrm{intra}}}{Nk_BT}=x_1(n_1-3)\left[x_t\ln(x_t)+2x_{g^+}\ln(x_{g^+})+2x_{g^+}\frac{E_1}{k_BT}\right]+x_2(n_2-3)\left[x_t\ln(x_t)+2x_{g^+}\ln(x_{g^+})+2x_{g^+}\frac{E_1}{k_BT}\right]. \tag{17}$$

However, we shall allow the mixture to have conformational changes relative to the pure components. Accordingly, the conformational population in the mixture may be expressed in terms of the change with respect to the ideal gas population by the following empirical expression:

$$x_{g^+}=x_{g^+}^{ig}+\delta, \tag{18}$$

$$\delta=\frac{F_2(T)yx_1x_2(n_2-n_1)^2}{(x_1\overline{V_1}+x_2\overline{V_2})}, \tag{19}$$

where $\overline{V_1}$ and $\overline{V_2}$ denote the molecular volumes of components 1 and 2, respectively, and the volume fraction is given by $y=\rho V_{\mathrm{mixture}}$ [see Eq. (12) of the previous paper]. Note that when Eqs. (18)–(19) are used for the pure components, the ideal gas population is recovered. On the contrary, for a given mixture (i.e., n_2,n_1,V_2,V_1 fixed), Eq. (19) predicts that conformational changes will increase with increasing density. Also, for fixed y, x_1, x_2 and n_1 Eq. (19) predicts that conformational changes increase with n_2. The denominator of Eq. (19) accounts for the fact that for a certain difference in size (n_2-n_1), conformational changes should be smaller as the size of the chains increases (i.e., larger conformational changes are expected when mixing C_4 and C_8 than when mixing C_{100} and C_{104}). The parameter $F_2(T)$ is obtained for each temperature by fitting the experimental excess enthalpies of the C_6+C_{16} mixture. This second parameter of the theory shows a temperature dependence that can be described by the relation $F_2=0.000\,915\,97+0.007\,186\,94\exp(-t/47.4815)$ where, again, t is the celsius temperature and the fit has been performed in the range 20–120 °C.

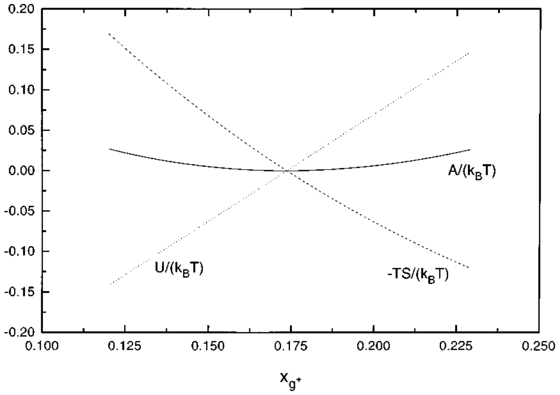

FIG. 4. The intra-molecular free energy a_{intra}/k_BT per torsional degree of freedom as function of the molar fraction of the $gauche^+$ state (x_g^+). The energy of the gauche state $E_1=3302$ J/mol (i.e., 790 cal) was used in the calculations which were performed for $T=300$ K. The zero of energy has been set at the minimum of the free energy curve. Values of the intra-molecular energy and entropy are also shown.

Once we have an explicit expression for the intra-molecular contribution to the free energy, $A_{\mathrm{intra}}[T,N_1,N_2,x_{g^+}(T,V,N_1,N_2)]$, the intra-molecular contribution to the remaining thermodynamic properties is obtained by using standard thermodynamic relations (and with the help of the chain rule):

$$Z_{\mathrm{intra}}=\rho\left[\left(\frac{\partial A_{\mathrm{intra}}/(Nk_BT)}{\partial x_{g^+}}\right)_{T,N_1,N_2}\right]_{x_{g^+},T,N_1,N_2}\left(\frac{\partial x_{g^+}}{\partial\rho}\right), \tag{20}$$

$$\frac{U_{\mathrm{intra}}}{Nk_BT}=\frac{E_1}{k_BT}2x_{g^+}(x_1(n_1-3)+x_2(n_2-3))-T\times\left[\left(\frac{\partial A_{\mathrm{intra}}/Nk_BT}{\partial x_{g^+}}\right)_{T,N_1,N_2}\right]_{x_{g^+},T,N_1,N_2}\left(\frac{\partial x_{g^+}}{\partial T}\right), \tag{21}$$

$$\frac{\mu_{1,\mathrm{intra}}}{k_BT}=(n_1-3)\left[x_t\ln(x_t)+2x_{g^+}\ln(x_{g^+})+2x_{g^+}\frac{E_1}{k_BT}\right]+(N_1(n_1-3)+N_2(n_2-3))\times\left[\left(\frac{\partial a_{\mathrm{intra}}/k_BT}{\partial x_{g^+}}\right)_{T,N_1,N_2}\right]_{x_{g^+}}\left(\frac{\partial x_{g^+}}{\partial N_1}\right). \tag{22}$$

In Fig. 4, the a_{intra}/k_BT term as a function of the number of gauche$^+$ bonds is shown. The minimum is found for the population of gauche$^+$ bonds given by Eq. (12). The zero of the Helmholtz free energy was set arbitrarily to its minimum. The energetic and the entropic terms of the intra-molecular contribution are also shown. As it can be seen, a change of 2% in the population of the gauche$^+$ population changes the free energy in about $10^{-4}\,k_BT$, whereas the change in internal energy is two orders of magnitude larger, $10^{-2}\,k_BT$. One can therefore expect that when the population of *gauche*$^+$ bonds is close to its ideal value, the derivative of the Helmholtz free energy with respect to x_{g^+} is very close to zero. This allows us to perform the following approximation:

$$\left[\left(\frac{\partial(A_{\mathrm{intra}}/(Nk_BT))}{\partial x_{g^+}}\right)_{T,N_1,N_2}\right]_{x_{g^+}} \simeq \left[\left(\frac{\partial(A_{\mathrm{intra}}/(Nk_BT))}{\partial x_{g^+}}\right)_{T,N_1,N_2}\right]_{x_{g^+}^{ig}} = 0. \tag{23}$$

The use of Eq. (23) simplifies considerably the resulting expressions for Eqs. (20)–(22) that now read as follows:

$$Z_{\mathrm{intra}} = 0, \tag{24}$$

$$\frac{U_{\mathrm{intra}}}{Nk_BT} = \frac{E_1}{k_BT}\, 2x_{g^+}(x_1(n_1-3)+x_2(n_2-3)), \tag{25}$$

$$\frac{\mu_{1,\mathrm{intra}}}{k_BT} = (n_1-3)\left[x_t \ln(x_t) + 2x_{g^+}\ln(x_{g^+}) + 2x_{g^+}\frac{E_1}{k_BT}\right]. \tag{26}$$

We shall include the intra-molecular contribution both to the properties of the pure substances through Eqs. (7)–(16) and to the mixture through Eqs. (24)–(26). This version of the theory, which involves adding the intra-molecular contributions to the MF1C theory will be denoted as MF1CI. Note that, neither the EOS of the pure fluid nor that of the mixture is modified by the addition of the intra-molecular term. Therefore, the excess volumes are not affected and are identical as those obtained by MF1C. On the contrary, both the chemical potential and Helmholtz free energy are changed. Despite this, properties such as the activity coefficients are affected only in a very small degree. For instance, the activity coefficients presented in Table II change in the third/fourth digital number once the intra-molecular term is included. It can be concluded that excess volumes and activity coefficients obtained from MF1CI are almost indistinguishable from those of the MF1C theory which were already presented in Tables I and II. However, the intra-molecular contribution has a significant contribution to the excess enthalpies, resulting in predictions that differ considerably from those given by the MF1C theory. In order to show this, excess enthalpies from the MF1CI theory are compared to experiment for some selected mixtures in Table III. As it can be seen, the agreement with experiment is now quite good.

The basic idea behind MF1CI is that the inclusion of the intra-molecular term brings a new internal energy and a new entropic term. A conformational change raises both the internal energy term and the entropic term (-TS), and this change is approximately equal for both magnitudes so that the Helmholtz free energy of the system changes in a very small amount. Consequently, the EOS and the chemical potential do not change much with conformational changes. However, conformational changes bring important changes in the intra-molecular contribution to the internal energy and in the intra-molecular contribution to the total entropy of the system.

Our final version of the theory is therefore a first order perturbation theory, with a molecular based force field, a good description of the reference system through the modified Wertheim EOS and a perturbation term evaluated within the MF1 approximation. Two additional factors are introduced to bring the theory to quantitative agreement, namely, F_1 which corrects for the use of the step function, and the F_2 factor which accounts for conformational changes in the *n*-alkane mixture.

V. RESULTS

In this section the results of the MF1CI theory will be presented for a number of mixtures. Some results were presented in Tables I–III and we shall proceed now to a more extensive comparison. In Table IV, excess properties for a number of *n*-alkane mixtures and temperatures are presented. For each mixture, experimental results, results from FOV theory and the results from the MF1CI perturbation theory of this work are presented. As can be seen, MF1CI yields excellent results for the prediction of excess properties.

In order to compare the performance of these two theories, we have defined the average deviation Δ as:

$$\Delta_X = \sqrt{\sum_{i=1}^{i=n_{\mathrm{data}}} (X_{\mathrm{exc},i} - X_{\mathrm{exc},i}^{\mathrm{exp}})^2 / n_{\mathrm{data}}}, \tag{27}$$

where n_{data} is the number of experimental data. By using the state points of Table IV where experimental and theoretical results from both MF1CI and FOV are given, the average deviations have been evaluated. The average deviations for the MF1CI perturbation theory are $\Delta_V = 0.10$ cm^3/mol for the excess volume and of $\Delta_H = 3.7$ cal/mol for the excess enthalpies. The corresponding deviations for the FOV theory are $\Delta_V = 0.11$ cm^3/mol for excess volume and $\Delta_H = 8.1$ cal/mol for excess enthalpies. As can be seen, the MF1CI theory yields results comparable in accuracy (or even better) to those presented by Flory *et al.*[10] This is remarkable since the only experimental data required in MF1CI are the densities of C_{10} and the excess enthalpies of the $C_6 + C_{16}$ mixture. In Flory's theory, the equation of state, compressibilities and thermal expansion coefficient of each pure alkane are needed in addition to two additional parameters (Γ and Γ_S) which are fitted to describe excess enthalpies and activity coefficients. The results of Table IV cover a wide range of temperatures and chain lengths so that it illustrates the utility of perturbation theory in a broad range of conditions.

In Fig. 5, the excess volumes for the *n*-octane + *n*-hexadecane mixture at several temperatures are shown. As seen, the MF1CI theory yields quite good results, describing the general shape of the excess volume curves. The minimum in the excess volume occurs for molar fractions richer in the lighter component (*n*-octane). In Fig. 6, excess enthalpies for the *n*-hexane + *n*-hexadecane mixture at different temperatures are presented. Again, the theory describes quite well the experimental data and it is able to predict the change in sign of the excess enthalpy with temperature.

In Table V, results for the activity coefficient of the shorter alkane at infinite dilution are presented for a number of mixtures. The agreement between MF1CI theory and experiment is reasonable. The value of Δ for the logarithm of the activity coefficient at infinite dilution obtained from MF1CI is of $\Delta_{\ln(\gamma_{1,\infty})} = 0.03$ to be compared with the value obtained from the FOV theory which is of $\Delta_{\ln(\gamma_{1,\infty})} = 0.03$.

TABLE IV. Excess volumes (in cm^3/mol) and enthalpies (in cal/mol) as obtained from experiment, from the MF1CI theory of this work and from the FOV theory.

			$V_{\mathrm{exc}}/(\mathrm{cm}^3/\mathrm{mol})$			$H_{exc}/(\mathrm{cal/mol})$		
Mixture	x_1	t	Exp	FOV	MF1CI	Exp	FOV	MF1CI
C_5+C_6	0.5	30	-		−0.07	**−0.72**		−0.29
C_5+C_{10}	0.5	20	**−0.42**		−0.52	**6**		8
C_5+C_{16}	0.5	20	**−0.82**		−1	**36**		37
C_6+C_7	0.5	20	-		−0.03	**0.22**		0.29
C_6+C_{10}	0.5	20	**−0.2**		−0.24	**4**	7	6
C_6+C_{12}	0.5	20	**−0.31**	−0.34	−0.39	**11**	12	12
	0.5	35	**−0.38**	−0.44	−0.47	-		7
C_6+C_{14}	0.5	25	**−0.52**		−0.54	-		18
C_6+C_{16}	0.5	20	**−0.49**	−0.56	−0.61	**31**	23	31
	0.5	30	**−0.58**	−0.65	−0.69	**23**	21	23
	0.5	40	**−0.69**	−0.76	−0.79	**16**	19	16
	0.5	51	**−0.82**	−0.9	−0.9	**9**	16	9
	0.5	60	**−0.97**	−1.05	−1.01	**4**	13	4
	0.5	76	-		−1.24	**−4**	7	−6
	0.5	100	-		−1.69	**−23**	−3	−19
C_6+C_{24}	0.5	51	**−1.19**	−1.34	−1.31	**33**	31	32
	0.5	60	-		−1.46	**22**	27	22
	0.5	76	-		−1.78	**6**	19	5
C_6+C_{36}	0.5	76	-		−2.22	**28**	33	37
C_7+C_{12}	0.5	25	**−0.17**	−0.23	−0.22	-		7
	0.5	35	**−0.2**	−0.26	−0.25		-	5
C_7+C_{16}	0.5	20	**−0.31**	−0.4	−0.38	**25**	16	25
	0.5	40	**−0.45**	−0.5	−0.49	-		14
	0.5	50	-		−0.56	**10**	13	9
	0.5	76	**−0.77**	−0.74	−0.76	-		−1
C_7+C_{24}	0.5	76	**−1.22**	−1.24	−1.22	-		9
C_7+C_{36}	0.5	76	**−1.56**	−1.77	−1.62	**31**	35	39
C_8+C_{16}	0.5	20	**−0.19**	−0.24	−0.24	**21**	12	19
	0.5	30	**−0.21**	−0.27	−0.27	-		15
	0.5	50	**−0.33**	−0.36	−0.35	-		8
	0.5	76	**−0.48**	−0.52	−0.48	-		1
	0.5	106	**−0.74**	−0.82	−0.69	-		−7
C_8+C_{24}	0.5	51	-		−0.64	**28**	21	28
	0.5	76	-		−0.86	**10**	16	10
	0.5	96	-		−1.08	**−1**	11	−1
	0.5	106	**−1.33**	−1.46	−1.22	**−6**	8	−6
C_8+C_{32}	0.5	76	-		−1.11	**23**	24	28
	0.5	96	**−1.49**	−1.61	−1.4		-	10
	0.5	106	**−1.7**	−1.86	−1.57	-		2
C_8+C_{36}	0.5	96	**−1.62**	−1.83	−1.53	-		18
	0.5	106	**−1.85**	−2.07	−1.72	-		9
C_9+C_{32}	0.5	96	**−1.14**	−1.19	−1.06	-		12
C_9+C_{36}	0.5	76	-		−0.94	**29**	26	38
	0.5	96	**−1.25**	−1.39	−1.18	-		20
	0.5	106	**−1.41**	−1.59	−1.32	-		12
	0.5	126	**−1.89**	−2.05	−1.65	-		−2
C_9+C_{62}	0.5	126	**−2.51**	−2.62	−2.75	-		93
$C_{10}+C_{16}$	0.5	20	**−0.07**	−0.1	−0.09	**10**	5	10
	0.5	30	**−0.09**	−0.1	−0.11	-		8
$C_{16}+C_{36}$	0.5	76	-		−0.22	**14**	9	22

VI. CONCLUSIONS

In this work a mean field perturbation theory for *n*-alkane mixtures is proposed. The theory uses potential parameters for *n*-alkanes which represent the current state of the art. The equation of state used for describing the reference *n*-alkane mixture (or pure fluid) is probably the most accurate proposed so far.[54] The evaluation of the perturbation term is performed by assuming that for a given temperature, site–site correlations of *n*-alkane liquids do not depend on chain length. For each temperature it is assumed that the contribution of each site–site interaction to the perturbation term is given by the product of a parameter denoted as F_1 and the value of the perturbation term evaluated from a Heaviside step function. The value of F_1 for each temperature is obtained by fitting the orthobaric density of C_{10}. This procedure provides good values of excess volumes and excess Gibbs energies for *n*-alkane mixtures. However, excess enthalpies do not agree so well with experiment. The as-

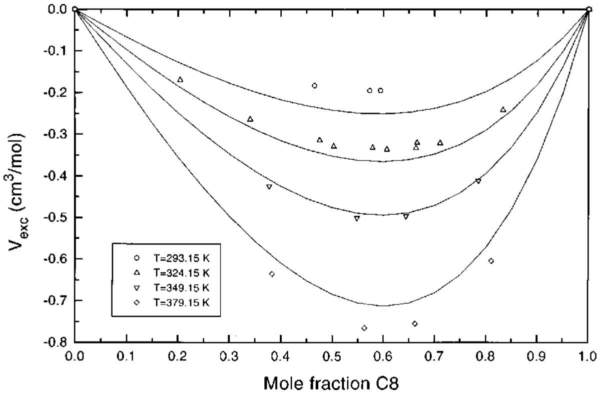

FIG. 5. Excess volume as a function of the molar fraction of *n*-octane for the *n*-octane + *n*-hexadecane mixture. Results from perturbation theory MF1CI (solid line) and from experiment (symbols) are presented for the following temperatures: $T=293.15$ K, $T=324.15$ K, $T=349.15$ K and $T=379.15$ K.

TABLE V. Logarithm of the activity coefficient of component 1 at infinite dilution for *n*-alkane mixtures as obtained from experiment, from the MF1CI theory of this work and from the FOV theory.

		$\ln(\gamma_{1,\infty})$		
Mixture	t	Exp	FOV	MF1CI
C_5+C_{16}	30	−0.088	−0.13	−0.049
C_5+C_{18}	35	−0.138	−0.173	−0.089
C_5+C_{24}	60	−0.274	−0.303	−0.211
C_6+C_{16}	20	−0.099	−0.11	−0.065
C_6+C_{16}	30	−0.101	−0.116	−0.063
C_6+C_{16}	40	−0.094	−0.11	−0.062
C_6+C_{16}	50	−0.11	−0.123	−0.06
C_6+C_{16}	60	−0.117	−0.123	−0.057
C_6+C_{18}	35	−0.131	−0.144	−0.101
C_6+C_{20}	40	−0.161	−0.191	−0.141
C_6+C_{22}	60	−0.219	−0.248	−0.177
C_6+C_{24}	60	−0.253	−0.292	−0.218
C_6+C_{28}	70	−0.309	−0.382	−0.293
C_7+C_{16}	30	−0.074	−0.085	−0.064
C_7+C_{18}	35	−0.113	−0.122	−0.099
C_7+C_{20}	40	−0.134	−0.154	−0.137
C_7+C_{24}	60	−0.207	−0.242	−0.211
C_7+C_{32}	75	−0.364	−0.413	−0.35
C_8+C_{18}	35	−0.09	−0.113	−0.09
C_8+C_{24}	60	−0.184	−0.222	−0.195
C_8+C_{32}	75	−0.325	−0.36	−0.33

sumption is made that conformational changes are responsible for this difference. Certainly, further work to clarify this point is needed. In particular, computer simulations may be quite useful. By including the intra-molecular contribution to the free energy and simplifying its formulation, it is then possible to obtain good predictions for excess enthalpies once conformational changes are permitted in the mixing process. A second parameter, F_2, is introduced into the theory, and it is obtained by fitting the excess enthalpy of the C_6+C_{16} mixture. The summary is that a perturbation theory with a molecular flavor is able to describe excess properties of *n*-alkanes with an accuracy similar to that obtained by the venerable FOV theory. The theory presented here can be considered only a first step. We hope it encourages further theoretical work in the area. In particular, it would be important to remove the parameters F_1 and F_2 by purely theoretical results. This could be done if: (i) Site–site correlation functions for *n*-alkanes could be evaluated from integral equations. The PRISM theory[65,66] would be a quite good candidate. (ii) Conformational changes were included in a self-consistent manner within the theory. To achieve this goal, further progress is needed in the simplification of the intra-molecular term (the number of possible conformers grows too fast so that the free energy minimization becomes a titanic task for alkanes longer than *n*-decane) and in describing the dependence of the A_0 and A_1 terms on the conformational populations. Steps (i) and (ii) represent in our opinion the energy barrier to be passed in order to get quantitative agreement with experiment from a fully molecular theory.

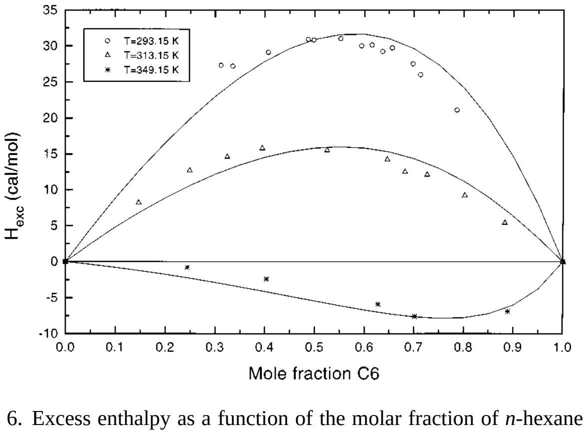

FIG. 6. Excess enthalpy as a function of the molar fraction of *n*-hexane for the *n*-hexane + *n*-hexadecane mixture. Results from the MF1CI version of the perturbation theory (solid lines) and from experiment (symbols) are presented for the following temperatures: $T=293.15$ K, $T=313.15$ K, and $T=349.15$ K.

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[1] I. Prigogine (with the collaboration of V. Mathot and A. Bellemans), *The Molecular Theory of Solutions* (North Holland, Amsterdam, 1957).
[2] J. E. Lennard-Jones and A. F. Devonshire, Proc. R. Soc. London, Ser. A **168**, 53 (1937).
[3] P. I. Freeman and J. S. Rowlinson, Polymer **1**, 20 (1960).
[4] G. Delmas, D. Patterson, and T. Somcynsky, J. Polym. Sci. **57**, 79 (1962).
[5] D. Patterson, Macromolecules **2**, 672 (1969).
[6] T. Somcynsky, Polym. Eng. Sci. **22**, 58 (1982).
[7] P. A. J. Flory, J. Am. Chem. Soc. **87**, 1833 (1964).
[8] P. A. J. Flory, R. A. Orwoll, and A. Vrij, J. Am. Chem. Soc. **86**, 3507, 3515 (1964).
[9] R. A. Orwoll and P. J. Flory, J. Am. Chem. Soc. **89**, 6814 (1967).
[10] R. A. Orwoll and P. J. Flory, J. Am. Chem. Soc. **89**, 6822 (1967).
[11] G. M. Janini and D. E. Martire, J. Chem. Soc., Faraday Trans. 2 **70**, 837 (1974).
[12] J. F. Parcher and K. S. Yun, J. Chromatogr. **99**, 193 (1974).
[13] E. Liebermann, Phys. Chem. Liq. **9**, 323 (1980).
[14] A. T. Rodriguez and D. Patterson, J. Chem. Soc., Faraday Trans. 2 **78**, 501 (1982).

[15] M. D. Peña and M. Benitez de Soto, Anales Real Soc. Espan. Fis. Quim. **61**, 1163 (1965).
[16] M. D. Peña and G. Tardajos, J. Chem. Thermodyn. **10**, 19 (1978).
[17] E. Aicart, G. Tardajos, and M. Dias Peña, J. Chem. Eng. Data **140**, 25 (1980).
[18] M. D. Peña and C. Menduiña, J. Chem. Thermodyn. **6**, 1097 (1974).
[19] M. D. Peña, G. Tardajos, R. L. Arenosa, and C. Menduiña, J. Chem. Thermodyn. **11**, 951 (1979).
[20] R. L. Arenosa, C. Menduiña, G. Tardajos, and M. D. Peña, J. Chem. Thermodyn. **11**, 159 (1979).
[21] T. M. Letcher and R. Baxter, S. Afr. J. Chem. **40**, 71 (1987).
[22] G. C. Benson, S. Murakami, V. T. Lam, and J. Singh, Can. J. Chem. **48**, 211 (1970).
[23] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).
[24] J. A. Barker and D. Henderson, J. Chem. Phys. **47**, 4714 (1967).
[25] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).
[26] M. Lombardero, J. L. F. Abascal, and S. Lago, Mol. Phys. **42**, 999 (1981).
[27] J. Fischer, J. Chem. Phys. **72**, 5371 (1980).
[28] D. B. McGuigan, M. Lupkowski, D. M. Paquet, and P. A. Monson, Mol. Phys. **67**, 33 (1989).
[29] T. Boublik, J. Chem. Phys. **87**, 1751 (1988).
[30] C. Vega and S. Lago, J. Chem. Phys. **94**, 310 (1991).
[31] T. Boublik, Mol. Phys. **95**, 363 (1998).
[32] C. Vega, S. Lago, and P. Padilla, J. Phys. Chem. **96**, 1900 (1992).
[33] J. Luettmer-Strathmann, J. A. Schoenhard, and J. E. G. Lipson, Macromolecules **31**, 9231 (1998).
[34] M. S. Wertheim, J. Chem. Phys. **87**, 7323 (1987).
[35] W. G. Chapman, G. Jackson, and K. E. Gubbins, Mol. Phys. **65**, 1057 (1988).
[36] J. K. Johnson, E. A. Muller, and K. E. Gubbins, J. Phys. Chem. **98**, 6413 (1994).
[37] R. O'Lenick and Y. C. Chiew, Mol. Phys. **85**, 257 (1995).
[38] Y. J. Sheng, A. Z. Panagiotopulos, and D. P. Tassios, AIChE. J. **41**, 2306 (1995).
[39] Y. J. Sheng, A. X. Panagiotopoulos, and S. K. Kumar, J. Chem. Phys. **103**, 10315 (1995).
[40] Y. Song, S. M. Lambert, and J. M. Prausnitz, Ind. Eng. Chem. Res. **33**, 1047 (1994).
[41] T. Hino, Y. Song, and J. M. Prausnitz, J. Polym. Sci., Part B: Polym. Phys. **34**, 1961 (1996).
[42] T. Hino, Y. Song, and J. M. Prausnitz, J. Polym. Sci., Part B: Polym. Phys. **34**, 1977 (1996).
[43] E. P. A. Paras, C. Vega, and P. A. Monson, Mol. Phys. **77**, 803 (1992).
[44] C. Vega and P. A. Monson, Mol. Phys. **85**, 413 (1995).
[45] C. Vega, F. Bresme, and J. L. F. Abascal, Phys. Rev. E **54**, 2746 (1996).
[46] R. I. Smith, Jr., A. S. Teja, and W. B. Kay, AIChE. J. **33**, 232 (1987).
[47] M. J. Anselme, M. Gude, and A. Teja, Fluid Phase Equilibria **57**, 317 (1990).
[48] E. D. Nikitin, High Temp. **36**, 305 (1998).
[49] C. Vega and L. G. MacDowell, Mol. Phys. **88**, 1575 (1996).
[50] L. G. MacDowell and C. Vega, J. Chem. Phys. **109**, 5670 (1998).
[51] L. G. MacDowell and C. Vega, J. Chem. Phys. **109**, 5681 (1998).
[52] L. G. MacDowell, C. Vega, and A. Lopez Rodriguez, J. Chem. Phys. **111**, 3183 (1999), preceding paper.
[53] T. Boublik, C. Vega, and M. D. Peña, J. Chem. Phys. **93**, 730 (1990).
[54] C. Vega, L. G. MacDowell, and P. Padilla, J. Chem. Phys. **104**, 701 (1996).
[55] C. Vega, S. Lago, and B. Garzon, J. Chem. Phys. **100**, 2182 (1994).
[56] A. Lopez Rodriguez, C. Vega, J. J. Freire, and S. Lago, Mol. Phys. **73**, 691 (1991).
[57] A. Lopez Rodriguez, C. Vega, J. J. Freire, and S. Lago, Mol. Phys. **80**, 1565 (1993).
[58] J. I. Siepmann, S. Karaborni, and B. Smit, Nature (London) **365**, 330 (1993).
[59] B. Smit, S. Karaborni, and J. I. Siepmann, J. Chem. Phys. **102**, 2126 (1995); erratum, *ibid.* **109**, 352 (1998).
[60] T. H. Holleman, Physica **29**, 585 (1963).
[61] T. H. Holleman, Physica **31**, 49 (1965).
[62] M. L. McGlashan and K. W. Morcum, Trans. Faraday Soc. **57**, 907 (1961).
[63] Theoretical results were obtained imposing zero pressure. The zero pressure densities obtained from the perturbation theory were determined numerically.
[64] M. G. Martin and J. I. Siepmann, 102, 2569 (1998).
[65] K. S. Schweizer and J. C. Curro, J. Chem. Phys. **89**, 3350 (1988).
[66] K. S. Schweizer and J. C. Curro, Adv. Chem. Phys. **88**, 1 (1997).
[67] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd Ed. (Butterworth, London, 1982).
[68] L. R. Dodd and D. N. Theodorou, Mol. Phys. **72**, 1313 (1991).
[69] H. C. Longuet-Higgins and B. Widom, Mol. Phys. **8**, 549 (1964).
[70] P. A. Tillman, D. E. Rottach, J. D. McCoy, S. J. Plimpton, and J. G. Curro, J. Chem. Phys. **109**, 806 (1998).
[71] P. Padilla and C. Vega, Mol. Phys. **84**, 435 (1995).
[72] J. P. Flory, *Statistical Mechanics of Chain Molecules* (Wiley, New York, 1969).
[73] N. G. Almarza, E. Enciso, and F. J. Bermejo, J. Chem. Phys. **96**, 4625 (1992).
[74] O. Olabisi and R. Simha, J. Appl. Polym. Sci. **21**, 149 (1977).
[75] S. K. Nath, J. D. McCoy, and J. G. Curro, Macromolecules **28**, 3275 (1995).