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Vapour–liquid equilibria of propane and n-alkane conformers

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The vapour–liquid equilibrium of an angular Kihara model of propane is obtained from a very accurate perturbation theory proposed recently. Gibbs ensemble simulations are performed in order to determine the vapour–liquid equilibrium of this model. A comparison of the theoretical and simulation results for the vapour–liquid equilibria shows excellent agreement. In addition it is demonstrated that a simple extrapolation procedure of the theoretical results yields reliable estimates of the critical properties. Vapour–liquid equilibria of n-butane and n-pentane conformers were obtained by the perturbation theory. *trans*- and *gauche*-Butane differ in their vapour–liquid equilibria and in their critical properties. However, they do not differ significantly in their second virial coefficient. The critical temperature of *gauche*-butane is higher than that of the *trans* conformer by about 6%. For the different conformers of n-pentane similar results are obtained. The conclusion is that the more spherical is a molecule or conformer the higher the reduced critical temperature. The more anisotropic conformers present larger deviations from the principle of corresponding states. The critical temperature of the all-*trans* and of the all-*gauche* conformers appear as a lower and upper bound of the critical temperature of the n-alkane. That suggests that a good description of the vapour–liquid equilibria of the n-alkane could be obtained if a representative conformer of the n-alkane system were chosen.

1. Introduction

It is fair to say that the vapour–liquid equilibria of linear molecules are now well understood. Perturbation theories [1–8], integral equations [9–12], and computer simulation [13–16] have illustrated the role played by molecular anisotropy and polar forces in the vapour–liquid equilibria of linear molecules. Considerable progress has also been made towards an understanding of the vapour–liquid equilibria of fluids consisting of nonlinear molecules [17–19]. However, our understanding of the vapour–liquid equilibria of flexible molecules is not as satisfactory, although some progress has been made with computer simulations [20, 21]. This is an important problem, since molecules with internal flexibility, for instance, n-alkanes, are of great importance for the chemical industry. The main difference between rigid and flexible molecules is that for the former it is possible to define the shape of the molecule whereas for the flexible models the molecule may adopt conformations with different shapes. Among the different theoretical tools available for studying flexible molecules, perturbation theories appear to be quite promising. In perturbation theories the equation of state and the structure of the reference system (usually incorporating the repulsive forces) are needed. A great deal of work has been devoted recently to studying hard flexible molecules. Extension of Wertheim's theory of association to flexible molecules [22, 23], density functional theory [24], integral equations [25] and, finally, modifications of the Flory–Huggins theory of polymers

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[26] have been developed. Furthermore, we have recently proposed a modification of Wertheim's theory that provides a very good description of the equation of state and virial coefficients of hard n-alkane models [27]. A comparison of the theory with simulation results for the equation of state and conformational equilibria of hard n-alkane models showed excellent agreement [28]. Therefore, good equations of state are now available for hard flexible models. This is an important intermediate step in the development of perturbation theories for flexible models. The next step in the area of flexible molecules is the incorporation of attractive forces, probably within a perturbation scheme. However, this is not without problems. In our treatment of hard n-alkanes [27] we regard the alkane as a multicomponent mixture in chemical equilibrium (i.e., all the components have the same chemical potential). When considering the chemical potential of each component, intramolecular energies (those arising from the torsional potential) and intermolecular forces are taken into account. The components of the mixture are just the conformers of the n-alkane, defined within the rotational isomeric state (RIS) approximation [29]. Within this theoretical framework, perturbation theories of mixtures are needed. The problem arises from the fact that, in the case of n-octane for instance, the system is regarded as a multicomponent mixture of 31 different conformers [27]. It is clear that developing a perturbation theory for such a mixture, in which each component presents a considerable anisotropy, appears now as a formidable problem.

In this work we take a less ambitious approach. We have recently proposed a perturbation theory (PT) for rigid molecules of any shape interacting through the Kihara potential [19]. Comparison with simulation revealed the main deficiency of the theory and an improved version of the theory was proposed [30]. This improved perturbation theory (IPT) has been applied to the determination of the vapour–liquid equilibria of linear Kihara models. Theoretical predictions of vapour–liquid equilibria were compared with simulation results obtained from Gibbs ensemble simulations and agreement was found to be excellent [13]. In this work the theory is applied to a nonlinear molecular model. A simple model of propane is considered. Theoretical predictions of the vapour–liquid equilibrium are compared with simulation results. The purpose now is to show that the theory is successful, not only for linear models but for nonlinear ones as well. Therefore, the vapour–liquid equilibria of the different conformers of n-alkane molecules, treated as pure substances, will be considered. The kind of questions we would like to ask are: does the vapour–liquid equilibrium of *gauche*-butane differ from that of *trans*-butane? Do they have a different critical temperature? The interest in answering these questions is twofold. First, the properties of real butane must be related to those of the two conformers constituting butane. For instance, in chemical engineering approaches, mixtures are commonly described using the equation of state of a pure fluid and the parameters are obtained from certain mixing rules. To apply this procedure to vapour–liquid equilibria the equation of state of each component must be known. Experimentally, it is not possible to isolate a fluid made up of only *trans*-butane or only *gauche*-butane molecules. Butane in nature is always a mixture of these two conformers. However, in theoretical treatments *trans*-butane and *gauche*-butane can be considered as pure fluids and the information required to apply the mixing rules can be obtained. Second, answering these questions may help one to assess how to simplify the formidable problem of the theoretical determination of the vapour–liquid equilibria of n-alkanes.

The scheme of this paper is as follows. In section 2 the perturbation theory applied in this work is briefly described and a method of obtaining critical properties from

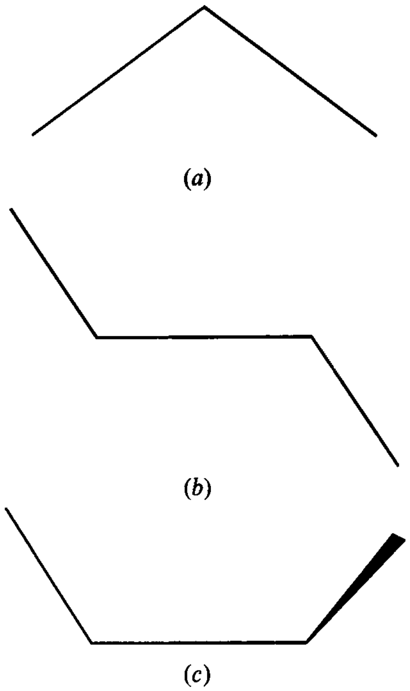


Figure 1. The cores used in this work for (*a*) propane, (*b*) *trans*-butane, and (*c*) *gauche*-butane. The angle between the bonds is 109·5°. In (*c*) the C–C bond on the right hand side is out of the plane of the paper.

perturbation theory treatments is proposed. In section 3 results of the theory for the vapour–liquid equilibria of propane and n-alkane conformers are given. In section 4 the main conclusions are presented.

2. Theory

To describe the interaction between a pair of molecules we use the Kihara potential [31]:

$$u = 4\epsilon[(\sigma/\rho)^{12} - (\sigma/\rho)^{6}], \tag{1}$$

where ϵ is the absolute value of the potential at the minimum, σ is the distance where the potential is zero and ρ is the shortest distance between the molecular cores. The cores used to describe propane, *trans*-butane and *gauche*-butane are shown in figure 1. The core is formed by rods defining the C–C bonds of the n-alkane. The internal angle between rods is set to 109·5°, and the bond length is given by $L^* = l/\sigma = 0{\cdot}4123$ where l is the C–C bond length. In order to evaluate the pair potential in equation (1) ρ must be calculated. In the case of propane we compute the shortest distance between each rod of molecule 1 and each rod of molecule 2. Since each molecule of propane is made up of two rods, we compute four shortest distances. The smallest among them defines the value of ρ in equation (1). For longer molecules we proceed in an analogous way. A very efficient algorithm for computing the shortest distance between a pair of rods is available [32].

In this work we use our improved perturbation theory. This IPT was proposed in [30] as an improvement over the theory described in [19]. Further details concerning the theory may be found in the appendix, and here we outline only the main features. In this IPT the pair potential is divided into a reference part, containing the repulsive forces, and a perturbation part, containing the attractive forces. Perturbation terms up to second order are considered. The reference system is related to a hard non-spherical body through the 'blip function' methodology [33]. The free energy of the hard body is obtained from the equation of state of hard non-spherical particles [34]. The structure of the reference system is approximated by zero-order reference averaged Mayer (RAM) function theory [35] for the background correlation function. The structure of the RAM system is obtained by solving the Percus–Yevick equation. Finally, an empirical correction is introduced into the first-order perturbation term. Except for the final (but crucial) empirical correction to A_1, IPT is just the extension to Kihara fluids of the perturbation theory proposed by Fischer [3].

IPT has been applied to the determination of the vapour–liquid equilibria of linear Kihara models. Comparison with Gibbs ensemble results was performed in [13]. This comparison showed that the IPT provides excellent predictions of coexistence densities and vapour pressures whenever T/T_c is less than 0·8, where T_c is the critical temperature of the model. However, at higher temperatures the agreement deteriorates. In fact, the critical temperature from IPT is too high by about 15%. A similar deviation has been found by other authors when using perturbation theories to estimate the critical temperature of several models [4, 6]. The reason for that failure is the mean-field character implicit in the perturbation treatment. In that respect it may be concluded that perturbation theories are not especially useful for an accurate determination of the critical point of a fluid. Rigorously speaking, the only way to overcome this situation is to improve the theoretical treatment around the critical region. However, if one is interested in an accurate estimate of the critical point based on PT results we shall show how a simple extrapolation procedure yields quite accurate results. We shall describe this procedure briefly.

The vapour–liquid equilibrium is obtained with IPT for temperatures satisfying $T/T_c < 0{\cdot}8$. The coexistence densities obtained in this way are fitted to the rectilinear diameters law [36], including a quadratic term in T:

$$(n_l^* + n_g^*)/2 = A + BT^* + CT^{*2}, \tag{2}$$

where n_l^* and n_g^* are the coexistence reduced number densities of the liquid and gas, respectively. The reduced density is defined as $n^* = n\sigma^3$, where n is the number density and $T^* = T/(\epsilon/k)$. The difference in the density between liquid and gas phases is fitted by assuming that the critical exponent $\beta = \frac{1}{3}$ [37] is valid even for temperatures relatively far from the critical point:

$$(n_l^* - n_g^*) = D(1 - T/T_c)^{1/3}. \tag{3}$$

By fitting the IPT vapour–liquid equilibrium results for $T/T_c < 0{\cdot}8$ to equations (2) and (3), the parameters A, B, C, D, T_c are determined. Therefore, an estimate of the critical point temperature and density is obtained from the fit of equations (2) and (3). Within the same spirit the theoretical vapour pressures for $T/T_c < 0{\cdot}8$ are fitted to the expression

$$\ln p^* = e_0 + e_1(1/T^*) + e_2(1/T^*)^2, \tag{4}$$

where $p^* = p/(\epsilon/\sigma^3)$ is the reduced vapour pressure for a given temperature. The use of equation (4) provides an estimate of the critical pressure. Note that equations (2) and (3) are commonly used in order to estimate the critical point from Gibbs ensemble data [38]. However, in this work we fit equations (2) and (3) by using coexistence data for $T/T_c < 0{\cdot}8$ whereas in the Gibbs ensemble methodology they are commonly fitted in the range $0{\cdot}8 < T/T_c < 1$. The procedure proposed here will be successful only if two conditions are satisfied simultaneously. The first is that IPT theory should describe correctly the vapour–liquid equilibria of the model for $T/T_c < 0{\cdot}8$. We know from previous work that this condition is indeed satisfied. The second condition is that the global shape of the vapour–liquid coexistence should be described by the critical exponent $\beta = \frac{1}{3}$. This is not obvious, since equation (3) holds rigorously only in the proximity of the critical point, and there is no *a priori* reason why it should hold far away from the critical point. This procedure for obtaining the vapour–liquid equilibrium for $T/T_c < 0{\cdot}8$ from IPT and then extrapolating to the critical point by using equations (2)–(4) will be denoted as IPTE. All theoretical results described in this work were obtained with IPTE.

3. Results

In table 1 the critical point properties of linear Kihara models obtained from IPTE are compared with those obtained from simulations. Agreement is quite good. The conclusion from the results of table 1 is that perturbation theory results (accurate at low temperatures) can be used to obtain a reasonable estimate of the critical point of a fluid. The success of IPTE methodology is due to the fact that equation (3) provides a very good description of the vapour–liquid envelope even far from the critical point. The reason for that is not known since equation (3) should hold only in the neighbourhood of the critical point. However, it is found that equation (3) fits the vapour–liquid equilibrium data of many real substances [39] and of many molecular models [40] quite well over the whole liquid range. For our purposes the main conclusion of the results presented in table 1 is that perturbation theory results can be used to obtain estimates of the critical point in quite good agreement with simulation.

Table 1. Critical properties of different Kihara models. Results are given in reduced units. Gibbs ensemble results are labelled as MC and critical estimates obtained from IPT plus the extrapolation scheme are labelled as IPTE. MC results of linear molecules are taken from [13]. The *trans* conformer is denoted as *t*, and the *gauche* conformer is denoted as *g*. The reduced length is defined as $L^* = l/\sigma$ where l is the length of the rod in the case of the linear models and the length of the bond for the n-alkane models.

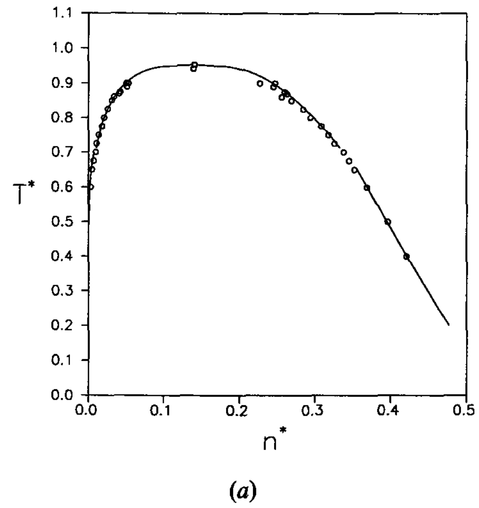
Model	L^*	Method	T_c^*	n_c^*	p_c^*
Linear	0·3	MC	1·114	0·219	0·073
Linear	0·3	IPTE	1·147	0·219	0·080
Linear	0·6	MC	1·000	0·161	0·051
Linear	0·6	IPTE	1·029	0·169	0·053
Linear	0·8	MC	0·952	0·140	0·038
Linear	0·8	IPTE	0·973	0·138	0·039
Propane	0·4123	MC	0·942	0·139	0·037
Propane	0·4123	IPTE	0·953	0·140	0·039
t Butane	0·4123	IPTE	0·894	0·110	0·029
g Butane	0·4123	IPTE	0·946	0·112	0·037
tt Pentane	0·4123	IPTE	0·859	0·0937	0·025
tg Pentane	0·4123	IPTE	0·885	0·0934	0·032
gg Pentane	0·4123	IPTE	0·952	0·0945	0·036

IPT theory was developed for molecules of any shape [19, 30]. However, so far it has been tested only in the case of linear Kihara models [13]. A check of the theory for a molecular nonlinear model seems interesting. For that purpose an angular model of propane interacting through the Kihara potential equation (1)) was chosen. The core is shown in figure 1. The vapour–liquid equilibrium for this model was obtained from IPTE. To assess the quality of the theoretical results Gibbs ensemble simulations were performed. Gibbs ensemble simulations allow a direct determination of the vapour–liquid equilibrium. The technique was proposed by Panagiotopoulos, and we refer the reader to [41] for a description of the methodology. Details of the Gibbs ensemble simulations performed in this work are similar to those of our previous studies [13, 14]. We used 512 molecules, 4000 cycles for equilibration and 6000 cycles for running averages. The pair potential was truncated at $r = 3\sigma$, where r is the distance between the centres of mass of the molecules, and long tail corrections to the thermodynamic properties were included according to the procedure of [42]. The code was checked by comparing internal energies and pressures at some selected points with those obtained in a previous molecular dynamics study of propane [42]. Excellent agreement between the two kinds of simulation was found. At low temperatures the application of the Gibbs ensemble technique failed. The reason for this failure is that the insertion of particles in the liquid becomes very difficult when the density is high. At low temperatures the vapour pressure is very small and therefore the orthobaric density is very close to the zero pressure density of the liquid. For $T^* = 0{\cdot}4$ and 0·5 we performed NVT Monte Carlo simulations and determined the density of the liquid at which the pressure becomes zero. A similar procedure was used in [13]. Results from Gibbs ensemble simulations are presented in table 2.

In figure 2(*a*) the coexistence densities obtained from simulation and from IPTE are shown. Figure 2(*b*) presents a similar comparison for vapour pressures. In both cases the agreement between theory and simulation is remarkably good. Critical points as obtained from simulation and from IPTE are compared in table 1. The

Table 2. Gibbs ensemble results of the vapour–liquid equilibria of a Kihara model of propane. The subscript g refers to gas phase results and subscript l to liquid phase results. Numbers in parentheses show the uncertainty of the simulation results: 0·3688(28) means 0·3688 ± 0·0028.

T^*	n_g^*	n_l^*	p_g^*	p_l^*
0·6	0.00311(11)	0.3688(28)	0·00175(6)	−0·015(22)
0·65	0·00467(19)	0·3522(46)	0·00282(11)	−0·014(24)
0·675	0·00695(46)	0·3450(43)	0·00421(25)	−0·013(20)
0·7	0·00946(35)	0·3376(41)	0·00580(22)	−0·003(16)
0·725	0·01040(85)	0·3255(32)	0·00656(51)	−0·013(19)
0·75	0·01333(58)	0·3173(65)	0·00844(34)	−0·005(21)
0·775	0·0187(12)	0·3089(47)	0·01157(63)	−0·002(15)
0·8	0·0212(14)	0·2943(66)	0·01332(71)	0·003(17)
0·825	0·0260(10)	0·2847(80)	0·01626(61)	0·008(15)
0·85	0·0313(12)	0·269(11)	0·01953(70)	0.013(19)
0·86	0·034(19)	0·256(13)	0·02092(86)	0·014(18)
0·87	0·0410(48)	0·263(14)	0·0238(18)	0·020(22)
0·875	0·0424(15)	0·260(12)	0·0246(11)	0·022(21)
0·89	0·0516(27)	0·245(15)	0·0284(17)	0·021(18)
0·9	0·0506(43)	0·227(15)	0·0289(17)	0·025(13)
0·9	0·0531(25)	0·247(19)	0·0295(14)	0·030(26)



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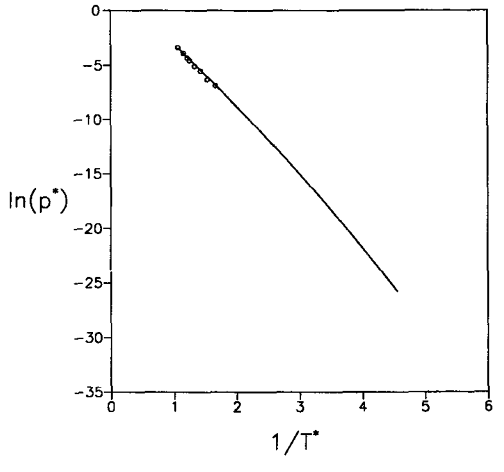
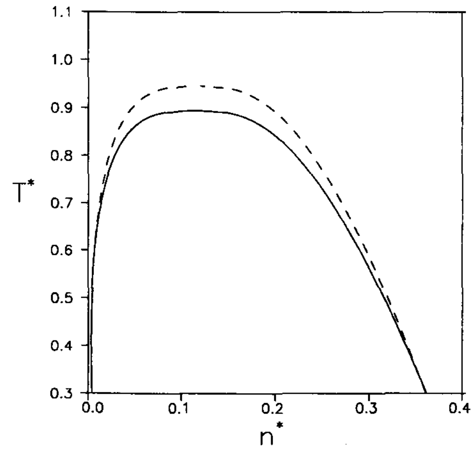


(*b*)

Figure 2. Vapour–liquid equilibrium of a Kihara model of propane as obtained from simulation (circles) and from perturbation theory with the extrapolation methodology explained in the main text (solid curve). (*a*) Coexistence densities. The critical point from IPTE is represented by an open square and from simulation by an open circle. The orthobaric densities at $T^* = 0{\cdot}4, 0{\cdot}5$ are the zero pressure densities as obtained from *NVT* simulations. (*b*) Vapour pressures. The highest value of $1/T^*$ corresponds to the triple point temperature of real propane.

agreement is again quite good. Two conclusions can be drawn immediately from these results. The first is that IPT works for angular molecules as well as it does for linear models. The second is that, although the critical temperature obtained directly from IPT is about 15% too high, when IPTE is used then very good estimates of the critical point and coexistence properties at high temperatures are obtained. In fact, IPTE overestimates the critical temperature by only 2%.

The results presented in figure 2 for propane suggest that IPTE will provide good results for the vapour–liquid equilibria of complicated molecules, as for instance the conformers of an n-alkane fluid. We have applied IPTE to determine the vapour–



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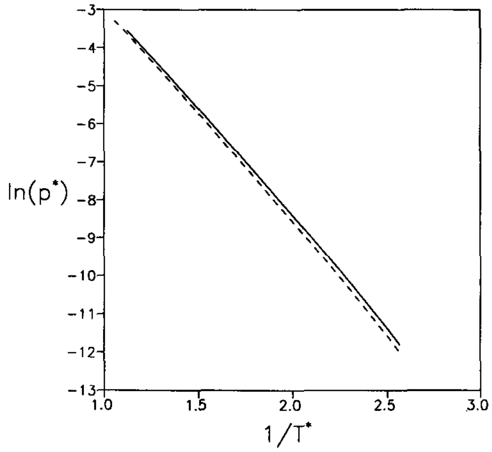


(*b*)

Figure 3. Vapour–liquid equilibria of n-butane conformers as obtained from IPTE: *trans*-butane (solid curve) and *gauche*-butane (dashed curve). Results are given in reduced units. (*a*) Coexistence densities. (*b*) Vapour pressures.

liquid equilibrium of *trans*-butane treated as a pure fluid. *trans*-Butane molecules interact through the Kihara potential of equation (1) and the core is illustrated in figure 1 (*b*). The same treatment was applied to *gauche*-butane treated as a pure fluid, and the core is shown in figure 1 (*c*). Vapour–liquid coexistence densities of *trans*- and *gauche*-butane are shown in figure 3 (*a*). The orthobaric density of *gauche*-butane at a given temperature is larger than that of *trans*-butane. However, at low temperatures the orthobaric densities of *trans*- and *gauche*-butane are almost identical. The vapour pressure of *trans*- and *gauche*-butane are shown in figure 3 (*b*). For a given temperarure *gauche*-butane has a lower vapour pressure than *trans*-butane. Differences in vapour pressures are smaller than those found for the coexistence densities.

The critical constants of *trans*- and *gauche*-butane are shown in table 1. The critical temperature of *gauche*-butane is higher than that of *trans*-butane, while the critical densities are almost identical. The critical pressure of *gauche*-butane is higher than that of *trans*-butane owing to its higher critical temperature. The questions raised in the introduction of this work are now answered. *trans*- and *gauche*-Butane differ in their vapour–liquid equilibria and in their critical point. Taking $\epsilon/k = 480$ K (which brings the reduced critical temperatures of butane conformers into reasonable agreement with the experimental critical temperature of butane [43]) as a reasonable estimate of ϵ for butane it may be concluded that the critical temperature of *trans*-butane is about 25 K lower than that of *gauche*-butane. The volumes of *trans*- and *gauche*-butane models are almost identical [27] (although slightly smaller for the *gauche* conformer). The difference in volume between the two conformers does not therefore explain differences observed in figure 3. Differences in properties arise from differences in shape between the two conformers. A measure of the anisotropy of a given molecule is given by the non-sphericity parameter α, defined as [44]

$$B_2^{\mathrm{H}}/V_{\mathrm{H}} = 1 + 3\alpha, \tag{5}$$

where B_2^{H} is the second virial coefficient of a hard molecule with the shape of the molecule and V_{H} its volume. *trans*-Butane has a larger value of α than *gauche*-butane. For tables showing the differences in volume and α of different hard n-alkane conformers see [27] (the hard models used there are slightly different from those of this work but the differences are very small). As a general rule, the more anisotropic is a molecule the lower is the reduced critical temperature T_{c}^*. This rule is in agreement with the decrease of T_{c}^* with L^* found in linear Kihara models, and with the lower critical temperature of *trans*-butane when compared with *gauche*-butane (see table 1). In figure 4 (*a*) a corresponding states plot of coexistence densities of butane conformers is presented. The larger anisotropy of the *trans* conformer (larger value of α) broadens the coexistence densities when represented in a corresponding states form. A corresponding states plot of the vapour pressures is shown in figure 4 (*b*). The slope of the vapour pressure curve of *trans*-butane is larger (in absolute terms) than that of *gauche*-butane. From our study of linear molecules [13] we know that molecular anisotropy increases the slope of the vapour pressure curve in a corresponding states plot. The results of figure 4 (*b*) are in agreement with this fact, because the anisotropy of *trans*-butane is larger than that of *gauche*-butane. The acentric factor [45] is related to the slope of the curves presented in figure 4 (*b*). It is clear from this figure that *trans*- and *gauche*-butane have a different acentric factor, being smaller for the *gauche* conformer. In chemical engineering applications the acentric factor is thought to be related to the anisotropy of the molecule [43, 45]. It is gratifying to find that our results assign a larger acentric factor to *trans*-butane in agreement with the intuitive idea that *trans*-butane is more anisotropic than the *gauche* conformer.

In order to check whether the conclusion obtained from the study of butane extend to longer n-alkanes we considered the case of n-pentane. Within the RIS approximation, n-pentane is made up of three different conformers: *trans-trans* (*tt*), *trans-gauche* (*tg*), and *gauche-gauche* (*gg*). The *gauche*$^+$-*gauche*$^-$ conformer was not considered since its population in n-pentane is very small due to the so-called 'pentane effect' [29]. Vapour–liquid equilibria of the three conformers of n-pentane obtained from the IPTE approach are shown in figure 5. Critical properties are presented in table 1. The highest critical temperature (see figure 5 (*a*) is that of the *gg* conformer and the lowest corresponds to the *tt* conformer. This is in agreement with the rule relating anisotropy to T_{c}^*. At low temperature orthobaric densities are almost the

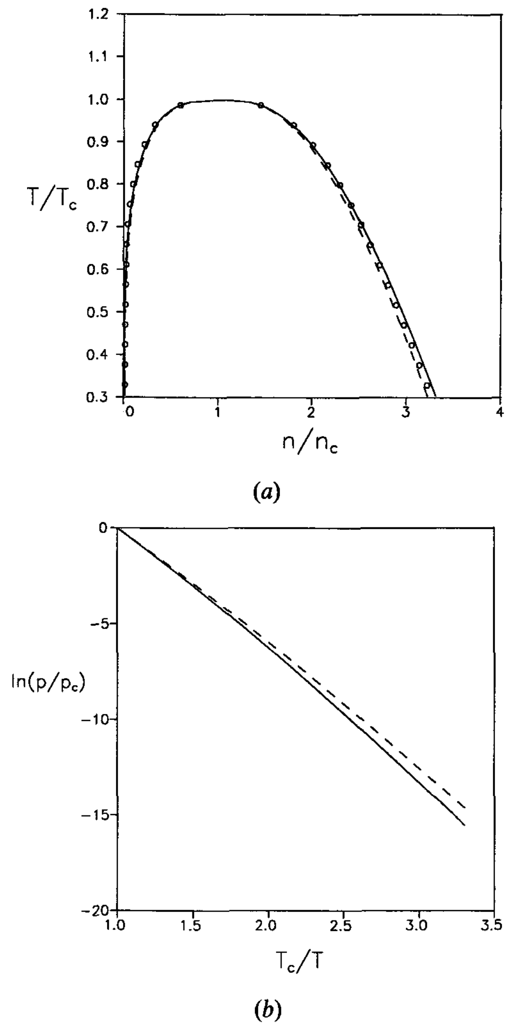
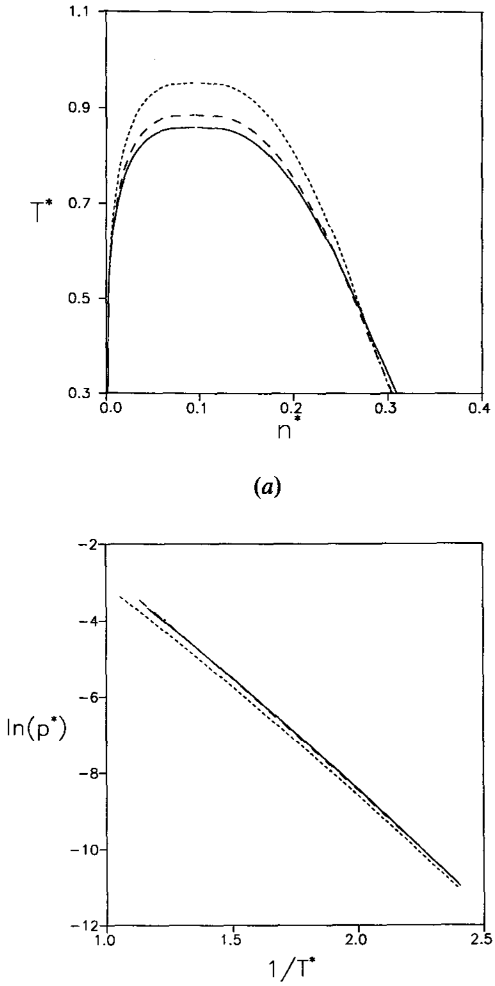


Figure 4. Corresponding states plot of the vapour–liquid equilibria of n-butane conformers as obtained from IPTE: *trans*-butane (solid curve) and *gauche*-butane (dashed curve). (*a*) Coexistence densities (symbols correspond to experimental data of butane [54]). (*b*) Vapour pressures.

same for all of the conformers. Taking $\epsilon/k = 523$ K as a reasonable estimate of ϵ for n-pentane (this approximately reproduces the experimental critical temperature of n-pentane [43]) then the critical temperatures of the *tt* and *gg* conformers differ by about 50 K. In figure 5 (*b*) vapour pressures of the three conformers of n-pentane are shown. For a given reduced temperature the vapour pressure of the *gg* conformer is lower than that of the *tg* and *tt* conformers. In figure 6 corresponding state plots of the coexistence densities and vapour pressures of the conformers of n-pentane are shown. The behaviour of the *tg* conformer is intermediate between that of the *tt* and *gg* conformers. This is expected since the anisotropy of the *tg* conformer is intermediate between those of the *tt* and *gg* conformers. In figure 6 (*b*) it can be seen that the largest slope (in absolute value) of the vapour pressure curve corresponds to the *tt* conformer and the smallest to the *gg* conformer. The difference in acentric



(*a*)

(*b*)

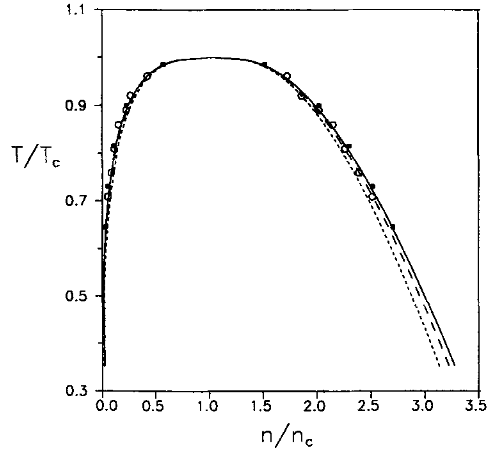
Figure 5. Vapour–liquid equilibria of the different conformers of n-pentane as obtained from IPTE: results for *tt* (solid curve), *tg* (dashed curve), *gg* (short dashed curve) conformers. (*a*) Coexistence densities in reduced units. (*b*) Vapour pressures.

factors between the *tt* and *gg* conformers calculated from our theoretical results is about 0·13. This is a significant difference taking into account that the experimental acentric factor found for n-pentane is about 0·25 [43].

Finally, we have considered differences in the second virial coefficient of n-alkane conformers. The second virial coefficient B_2 of a non-spherical molecule is given by

$$B_2 = -\tfrac{1}{2} \int [\langle \exp(-u(r, \omega_1, \omega_2)/(kT)) \rangle - 1] 4\pi r^2 \, dr, \tag{6}$$

where r is the distance between the centres of mass of the two molecules and ω_i denotes the set of angles which define the molecular orientation of molecule i. The pointed brackets in equation (6) stand for the geometrical average over all the relative orientations. In evaluating B_2 we used the Kihara potential with the cores shown in



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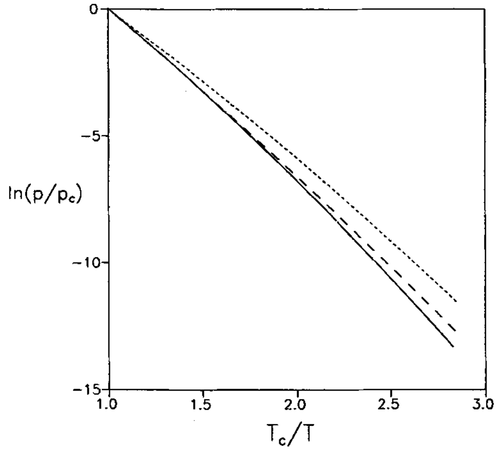

(*b*)

Figure 6. Corresponding states plot of the vapour–liquid equilibria of the different conformers of n-pentane as obtained from IPTE: results for *tt* (solid curve), *tg* (dashed curve), and *gg* (short dashed curve) conformers. (*a*) Coexistence densities. Open circles correspond to Gibbs ensemble simulation results of a site–site model of n-pentane [50]. Squares are experimental data for n-pentane [55]. (*b*) Vapour pressures.

figure 1. When the core is a convex body, equation (6) can be integrated analytically [46]. However, the cores used in this work (see figure 1) are not convex and equation (6) must be computed numerically. To obtain the average of the bracketed terms in equation (6) we used Conroy's method with 4822 different relative orientations [47]. The Simpson rule was used for integration over r. The estimated uncertainty of our calculations for B_2 is of about 1%. In table 3 the computed second virial coefficients of *trans*- and *gauche*-butane are shown. At low temperatures, B_2 of *trans*-butane is lower than that of *gauche*-butane. At high temperatures the opposite is true. Differences in B_2 between the two conformers of butane are small. In figure 7 the second virial coefficient of these two conformers is plotted, clearly showing that the two conformers present similar values of B_2. The Boyle temperature (the temperature

Table 3. Second virial coefficient B_2 of the *trans* (t) and *gauche* (g) conformers of n-butane. The second virial coefficient has been computed with the Kihara potential of equation (1) and the cores shown in figure 1. B_2 is given in σ^3 units.

	B_2	
T^*	t	g
0·4	−53·47	−51·81
0·6	−21·96	−21·30
0·8	−11·96	−11·61
1·0	−7·17	−6·97
1·4	−2·57	−2·51
1·6	−1·30	−1·28
1·8	−0·37	−0·38
2·0	0·35	0·32
2·2	0·91	0·86

where B_2 is zero) is almost the same for both conformers. We analysed B_2 for the n-pentane conformers and similar conclusions were drawn. We conclude that B_2 for the different conformers of an n-alkane are similar. The reason is that B_2 is given by an orientational average (see equation (6)) so that the differences in shape between conformers are lost after averaging. The fact that B_2 is similar for the different conformers of an n-alkane has an important consequence: the second virial coefficients of n-alkane models will not be very sensitive to changes in the torsional potential. The torsional potential defines the relative populations of each conformer in the gas phase. Different populations will result in similar values of the second virial coefficient

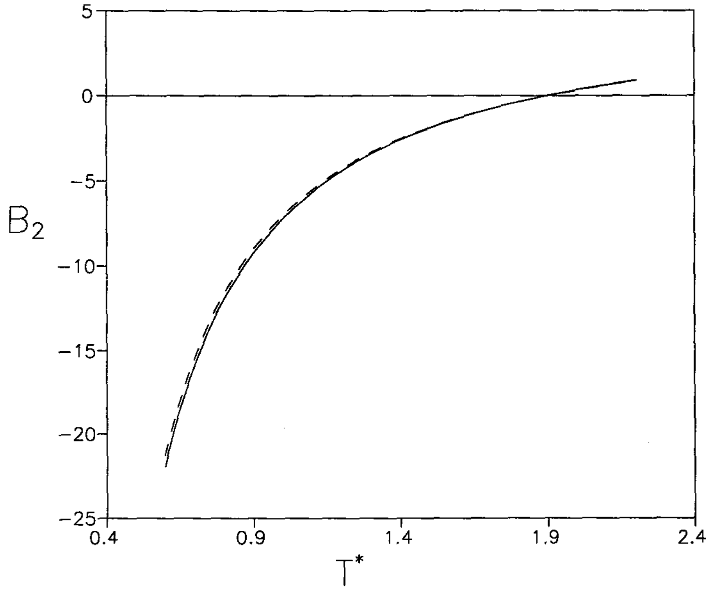

Figure 7. Second virial coefficient B_2 of n-butane conformers obtained from numerical integration of equation (6). Both conformers were modelled with the Kihara potential and the cores shown in figure 1. The results for B_2 are shown in σ^3 units. *trans*-Butane (solid curve), *gauche*-butane (dashed curve).

since the second virial coefficients of the different conformers are similar. The fact that the second virial coefficient of an n-alkane model is not very sensitive to changes in the torsional potential was noted before [48, 49]. The results in table 3 provide an explanation of this earlier finding.

So far we have focused on the differences in vapour–liquid equilibrium, critical constants and second virial coefficients of short n-alkane models. What can be expected for longer chains? Differences in α between the all-*trans* conformer (*tt* ... *ttt*) and the all-*gauche* conformer (*gg* ... *ggg*) are of about 0·05, 0·10, and 0·25 in the case of n-butane, n-pentane, and n-octane, respectively [27]. Consequently, the difference between T_c^* of the all-*gauche* and all-*trans* conformers will increase with the number of carbons of the n-alkane. It is also clear that the difference between these two conformers in corresponding states plots such as those presented in figures 4 and 6, will increase with the length of the chain. One could expect that properties of the n-alkane should be intermediate between those of these extreme conformers. For instance in figure 6 it is observed that the behaviour of the *tg* conformer is intermediate between that of the *tt* and *gg* conformers. That could open a new theoretical route for dealing with n-alkanes. It may be possible to choose a conformer for each n-alkane whose anisotropy is intermediate between that of the all-*trans* and the all-*gauche* conformers, and that approximately represents the behaviour of the real n-alkane. That being the case the formidable problem of developing a perturbation theory for a multicomponent system with a very large number of conformers could be replaced by the problem of developing a perturbation theory for a simple conformer representative of the 'average shape' of the n-alkane. In order to test this assumption, the vapour–liquid equilibria of the different conformers of the n-alkane, and the vapour–liquid equilibrium of the n-alkane (where all the conformers are present) should be compared. A good molecule where these ideas could be tested is n-pentane. According to our discussion the vapour–liquid equilibrium of n-pentane should be intermediate between that presented by the *tt* and *gg* conformers. If our assumption is correct, then the *tg* conformer could provide a good representation of the vapour–liquid equilibrium of n-pentane. Simulation results for a Kihara model of n-pentane, where the *tt*, *tg*, and *gg* conformers are present simultaneously in the liquid and gas are not yet available. However, quite recently Smit, Karaborni and Siepmann [50] have reported Gibbs ensemble results of a site–site model of n-pentane, where all the conformers appear in the coexistence phases. It is not possible to compare directly the results of the Kihara model with results of the site–site model since the pair potential is different. However, they can be compared in a corresponding states form. Such a comparison is shown in figure 6 (*a*). Vapour–liquid equilibria of the *tt*, *tg*, and *gg* conformers modelled with the Kihara model are shown. The vapour–liquid equilibria for those conformers are obtained from IPTE. Open circles correspond to the Gibbs ensemble simulation results of n-pentane modelled with the site–site potential obtained by Smit, Karaborni and Siepmann [50]. The interesting result of figure 6 (*a*) is that the simulation results for the n-pentane system are between these of the *tt* and *gg* conformers, and very close to those of the *tg* conformer. The filled squares in figure 6 (*a*) correspond to experimental results of the vapour–liquid equilibria of n-pentane. Again, the experimental data of n-pentane are close to the results obtained for the *tg* conformer. These results support our suggestion that the vapour–liquid equilibrium of an n-alkane can be described by choosing a representative conformer and taking it as a pure fluid. As another independent test, in figure 4 (*a*) experimental results of the vapour–liquid equilibria of n-butane are included in

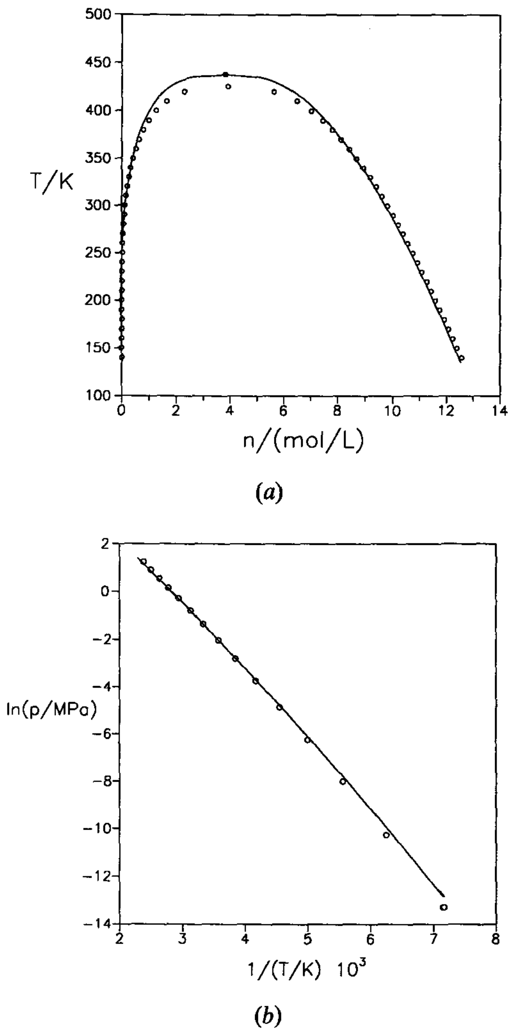

Figure 8. Vapour–liquid equilibria of n-butane as obtained from experiment [54] (symbols), and from IPTE (solid curve). For the IPTE approach, n-butane is modelled as the *trans* conformer interacting through the Kihara potential. Temperatures are given in K. (*a*) Coexistence densities in mol dm^{-3}. (*b*) Vapour pressures in MPa.

a corresponding states form. It is found that the experimental results for n-butane are intermediate between those for the *trans* and *gauche* conformers. For butane there is no intermediate conformer between the *trans* and the *gauche* forms (at least within the RIS approximation), but since experimental data are very close to the results of both conformers that suggests that a good description of n-butane may be obtained if it is modelled as a pure *trans* (or as pure *gauche*) fluid.

In figure 8 experimental results of the vapour–liquid equilibrium of n-butane are compared with the results of IPTE theory from this work for the *trans* conformer of n-butane interacting through the Kihara potential. The parameter ϵ and σ of the Kihara potential were obtained by fitting the orthobaric density and vapour pressure obtained from the theory at $T = 320$ K to the experimental results. The parameters obtained in this way are $\epsilon/k = 488{\cdot}98$ K and $\sigma = 3{\cdot}6378$ Å. The agreement between experiment and theory for the coexistence densities (figure 8 (*a*)) and vapour pressures (figure 8 (*b*)) is quite good from the triple point up to the critical point. The results of figure 8 show that the vapour–liquid equilibrium of n-butane can be described accurately by considering the vapour–liquid equilibria of only one of the conformers.

4. Conclusion

In this work our improved perturbation theory of Kihara fluids [30] has been tested for a nonlinear model. We have considered an angular model of propane. Gibbs ensemble simulations were performed in order to obtain the vapour–liquid equilibrium of this model. Perturbation theory provides very reliable predictions of vapour–liquid equilibrium for T/T_c less than 0·8 and breaks down for larger temperatures. We use an extrapolation procedure that allows an accurate estimate of the critical properties by using the low-temperature perturbation theory results. Thus, the coexistence properties obtained in this way in the range $T/T_c = 0{\cdot}8$–1 are also quite good. When perturbation theory results are used in this way, predictions of the vapour–liquid equilibrium agree quite well with the simulation results for all of the liquid range. The success of the theory for the model of propane suggests that the theory will be equally successful for treating other anisotropic models of nonlinear shape.

Following this approach we have considered the case of butane. The vapour–liquid equilibria of *trans*- and *gauche*-butane treated as pure fluids were obtained with the theory. *trans*- and *gauche*-butane differ in their vapour–liquid equilibria. The critical temperature of *gauche*-butane is larger than that of *trans*-butane by about 6%. However, differences in the second virial coefficient between these two conformers are small. We also obtained with the theory the vapour–liquid equilibria of the different conformers of n-pentane. The critical temperature of the *tt* conformer is much lower than that of the *gg* conformer. We conclude that when the anisotropy of the molecule, as given by the non-sphericity parameter α, increases, the reduced critical temperature decreases. The more anisotropic conformers present larger deviations from the principle of corresponding states, and this is shown in coexistence densities and vapour pressures.

The modelling of the n-alkane as a multicomponent system which can be treated by using perturbation theories of non-spherical mixtures constitutes a formidable problem. It would be quite useful if the problem could be simplified somewhat. Results of this work suggest that the vapour–liquid equilibrium of the n-alkane could be obtained from that of a representative conformer treated as a pure fluid. This representative conformer should present an anisotropy intermediate between that of the all-*trans* and that of the all-*gauche* conformers. This suggestion seems to be confirmed for n-butane and n-pentane. Experimental results for the vapour–liquid equilibria of n-butane fall in a corresponding states plot between those of the *trans* and *gauche* conformers. For n-pentane, the simulation results of Smit, Karaborni and Siepmann [50] for a site–site model fall very close to the theoretical results obtained for the *tg* conformer when plotted in a corresponding states form.

The idea of treating the n-alkane system as a pure fluid with a fixed shape is not new. In their study of the methane + n-pentane mixture, de Pablo *et al.* [20] explored the possibility of substituting the n-pentane molecule by a rigid model. Pavlicek and Boublik [51] have also described the behaviour of an n-alkane fluid by taking an equivalent spherocylinder. In this work it is shown that good results can be obtained for short n-alkanes by considering only one conformer. For longer chains it may be necessary to include several conformers (probably those with the largest population). That would still be useful since, for instance in the case of n-octane, the problem of the multicomponent system (31 different conformers) could be reduced to the problem of a few conformers.

Before finishing we would like to stress that the main conclusions of this work are not limited to Kihara models. We believe that they will hold also, at least qualitatively, for other potential models of n-alkanes. In support of this view is the fact that, for linear molecules, the trends of the vapour–liquid equilibria with changes in molecular elongation and/or polarity are similar, regardless of whether the Kihara or the multi-site model is chosen to describe the pair potential [13–16, 38].

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Appendix

This appendix presents the main details of the perturbation theory (PT) and of its improved version (IPT).

In PT the pair potential u is divided into a reference u_0 and a perturbation term u_1 according to the prescription first suggested by Mo and Gubbins [52]:

$$u_0(r, \omega_1, \omega_2) = u(r, \omega_1, \omega_2) - u_{\min}(\omega_1, \omega_2) \quad r < r_m, \tag{A 1}$$

$$u_0(r, \omega_1, \omega_2) = 0 \quad r > r_m, \tag{A 2}$$

where r_m is the distance between the centres of mass of the molecules at which the minimum in the pair potential appears for the relative orientation given by ω_1 and ω_2. The value of the potential at the minimum at a given relative orientation is denoted as $u_{\min}(\omega_1, \omega_2)$. According to equations (A 1) and (A 2), repulsive forces are incorporated into the reference system. The prescription of equations (A 1) and (A 2) may be considered as the extension to molecular fluids of the division of the potential first proposed for atomic fluids by Weeks, Chandler and Andersen [53].

When the prescription of equations (A 1) and (A 2) is applied to the Kihara potential (see equation (1) of the main text) then u_0 is given by

$$u_0(\rho) = u(\rho) + \epsilon \quad \rho < 2^{1/6}\sigma \tag{A 3}$$

$$u_0(\rho) = 0 \quad \rho > 2^{1/6}\sigma. \tag{A 4}$$

The perturbation potential u_1 is obtained as $u_1 = u - u_0$. The residual Helmholtz free energy of the Kihara fluid A is now expanded about the reference system to obtain up to second order:

$$\frac{A}{NkT} = \frac{A_0}{NkT} + \frac{A_1}{NkT} + \frac{A_2}{NkT}. \tag{A 5}$$

To evaluate the perturbation terms the structure of the reference system as given by the pair correlation $g_0(r, \omega_1, \omega_2)$ is needed. This function is approximated as

$$g_0(r, \omega_1, \omega_2) = \exp(-\beta u_0(r, \omega_1, \omega_2)) y_{\mathrm{RAM}}(r), \tag{A 6}$$

where $\beta = 1/kT$, and $y_{\mathrm{RAM}}(r)$ is the background correlation function of the spherical RAM potential $\phi_{\mathrm{RAM}}(r)$ which is defined as

$$\exp(-\beta \phi_{\mathrm{RAM}}(r)) = \langle \exp(-\beta u_0(r, \omega_1, \omega_2)) \rangle, \tag{A 7}$$

where the pointed brackets stand for unweighted orientational average. This orientational average is obtained numerically for a given value of r by using the Conroy integration method [47]. The background correlation function of the RAM potential $\phi_{\mathrm{RAM}}(r)$ is obtained by solving the Ornstein–Zernike equation with the Percus–Yevick closure.

The residual free energy of the reference system A_0 is taken as that of a corresponding hard body A_{H} whose diameter at every temperature and density is obtained by setting to zero the first order term of the blip expansion [33]:

$$\int (\exp(-\beta u_0) - \exp(-\beta u_{\mathrm{H}})) y_{\mathrm{RAM}}(r)\, \mathrm{d}r\, \mathrm{d}\omega_1\, \mathrm{d}\omega_2 = 0. \tag{A 8}$$

The term within the parentheses in equation (A 8) is denoted as the 'blip function'. The residual free energy of the hardbody A_{H} is obtained from integration of the equation of state of hard bodies proposed by Boublik [34]. Therefore, A_{H} is given by

$$\frac{A_{\mathrm{H}}}{\mathrm{NkT}} = \frac{y(c_1 + c_2 y)}{(1 - y)^2} + c_3 \ln(1 - y), \tag{A 9}$$

where the constants c_1, c_2, and c_3 are given by $c_1 = 6\alpha^2 - 2\alpha$, $c_2 = 1{\cdot}5\alpha(3 - 5\alpha)$ and $c_3 = 6\alpha^2 - 5\alpha - 1$. The non-sphericity parameter α is defined by equation (5). The packing fraction y is defined as

$$y = nV_{\mathrm{H}}, \tag{A 10}$$

where V_{H} is the volume of the equivalent hard body.

When the structure of the reference fluid is approximated by equation (A 6), the first order perturbation term A_1 is given by

$$A_1/N = 2n\pi \int_0^\infty \langle u_1 \exp(-\beta u_0) \rangle y_{\mathrm{RAM}}(r) r^2\, \mathrm{d}r. \tag{A 11}$$

The second order perturbation term A_2 is obtained from an extension to molecular systems [5] of the macroscopic compressibility equation. The final expression is then

$$\frac{A_2}{NkT} = -\frac{\pi n}{kT}\left(\frac{\partial n}{\partial p}\right)_0 \int \langle u_1^2 \exp(-\beta u_0) \rangle y_{\mathrm{RAM}}(r) r^2\, \mathrm{d}r \tag{A 12}$$

where $(\partial n/\partial p)_0$ is the isothermal compressibility of the reference system, which can be obtained easily from the equation of state of the reference system. Equations (A 1)–(A 12) constitute the perturbation theory which will be denoted as PT. This perturbation theory can be applied to any pair potential. Fischer, who first proposed this theory [3] (with some minor changes), applied it to a site–site diatomic model. Lustig [17] applied to propane and other nonlinear molecules interacting through site–site potentials, and finally we have applied it to Kihara models [19]. The main defect of the theory is the neglect of orientational structure in the background function of the reference system $y_0(r, \omega_1, \omega_2)$ which, within the context of the theory, is approximated by $y_{\mathrm{RAM}}(r)$. This is true for site–site models as well as for Kihara models. The neglect of orientational structure of the y_0 function results in an error in the evaluation of A_1 [19]. The error in A_1 increases with the anisotropy of the molecule [30], and it is expected to be important for the anisotropies of some of the conformers treated in this work. A correction for this PT theory is needed if accurate predictions (when compared with simulation) of vapour–liquid equilibrium are required. Such a correction has been obtained in the case of the Kihara model. For Kihara models we have compared A_1 as obtained from equation (A 11) with A_1 as obtained from simulations of the reference system. Deviations between theoretical (A_1^{theory} given by equation (A 11)) and simulation ($A_1^{\mathrm{simulation}}$) values were systematic and were fitted to the expression [30]

$$\Delta A_1 = 100\,\frac{A_1^{\mathrm{simulation}} - A_1^{\mathrm{theory}}}{A_1^{\mathrm{simulation}}} = (185{\cdot}52\alpha - 188{\cdot}42)(y - 0{\cdot}12). \qquad \text{(A 13)}$$

By solving equation (A 13) for $A_1^{\mathrm{simulation}}$, a very precise estimate of the first order perturbation term can be obtained by using the theoretical value A_1^{theory}. The PT described by equations (A 1)–(A 12) but with a corrected value of A_1 obtained through equation (A 13) is denoted as IPT. At the moment the IPT version of the theory is available only for Kihara models, since a correction term such as equation (A 13) has not yet been reported for site–site models. Therefore, although PT (equations (A 1)–(A 12)) can be applied in the same way to site–site or to Kihara models, the improved version of the theory (IPT) has been reported only for Kihara models. One of the difficulties in proposing an IPT version of the theory for site–site models is that simulations of the reference system are quite involved. The reason is that for every relative orientation it is necessary to calculate the distance r_m at which the global potential between a pair of molecules becomes repulsive, and this has to be done numerically. However, for Kihara models simulations of the reference system can be performed easily since the reference system is defined by the simple expressions equations (A 3) and (A 4). The fact that IPT is available for Kihara models whereas it is not yet available for site–site models motivated our choice of the Kihara potential in describing the interaction between n-alkane conformers.

The vapour–liquid equilibrium can be calculated from the theory by imposing the condition of equal pressure and chemical potential between the gas and the liquid phases. For low temperatures it is not necessary to apply perturbation theory to describe the gas since the second virial coefficient provides a simple and accurate description of the gas phase. Typically, the evaluation of the complete vapour–liquid equilibrium curve for a given model requires about 3 min CPU time on any standard workstation, so that the theory is not computationally demanding.

In addition to the perturbation scheme proposed by Fischer [3] which is used in this work (improved), other perturbation schemes have been proposed. For convex Kihara fluids, Boublik [5] has proposed a perturbation theory which is comparable in accuracy with IPT, although in principle it cannot be applied to non-convex Kihara models like those used in this work. For site–site potentials the perturbation scheme of [1, 2, 6] can be used also. In those papers the site–site potential is divided into a reference term and a perturbation term, and the structure of the reference system is obtained from the site–site Ornstein–Zernike equation. Good results of vapour–liquid equilibria were obtained for linear molecules with this scheme

[15], although its ability to describe coexistence properties in nonlinear molecules has not yet been tested.

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