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Thermodynamic Properties of Mixtures of Kihara Molecular Fluids from Perturbation Theory

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A perturbation theory for mixtures of molecules interacting through the Kihara potential is proposed. We show that the Kihara potential with the Lorentz–Berthelot combination rule to describe the crossed interaction is able to give very good results for the excess properties of different mixtures. The results obtained by using the Kihara model are comparable to or even better than those obtained with the more popular site–site model. We have applied the theory to several mixtures of hydrocarbons involving different geometries, such as methane + ethane, methane + propane, ethane + propane, methane + isobutane, ethane + isobutane, and propane + benzene. In all the cases the calculated excess properties agree very well with the experimental values. The theory can be applied to any nonpolar mixture without restriction of geometry and the calculations can be performed in a personal computer which make the theory well suited for practical applications.

I. Introduction

During the past years important advances have been made in the understanding of the thermodynamic behavior of molecular fluids from the basic principles of statistical thermodynamics.[1-3] Among the different developed methods in statistical thermodynamics to the study of molecular liquids, perturbation theories appear as a very successful approach since they are accurate and simple to use. Perturbation theories have been applied during the past decade to the study of nonpolar molecular fluids.[4-6] The molecular interaction has been generally modeled by the site–site potential, the Gaussian model, or the Kihara potential. The accuracy of the proposed perturbation theories has been tested by comparing the theoretical to the simulation results for the studied potential model. Their possibilities for practical applications have been verified by applying the theory to real nonpolar molecules. In our laboratory we have recently developed a perturbation theory for molecules interacting through the Kihara potential model.[7-10] We have recently applied with success this theory to molecules such as nitrogen, ethane, propane, isobutane, cyclopropane, ozone, and benzene. Vapor pressures, orthobaric densities, second virial coefficient, and equation of state (EOS) have been determined with great accuracy for these fluids.[11]

The next natural step is, therefore, to extend this theory to mixtures. This extension is important from a practical point of view since perturbation theories constitute an alternative way (with respect to semiempirical equations of state) of characterizing vapor–liquid equilibria at high pressures. The theory that we shall develop in this paper can be regarded as an extension to Kihara mixtures of the theory previously proposed for site–site mixtures by Fischer and Lago.[12] The first goal of this paper is to establish

such an extension and to show that the Kihara potential is not worse than the more popular site–site potential in the determination of excess properties of real mixtures. The second goal of the work is to compare the results of the proposed theory with those obtained by Boublik using his perturbation theory for Kihara mixtures.[13] Since both theories use the same potential model, any discrepancy between the results of the theories will be due to the approximations used. To decide which of these two theories is superior to the other it would be necessary to compare the results with simulation results of the model. Unfortunately, there is no such simulation yet. The third goal of the paper is to show how the theory can be applied with success to the determination of excess properties of hydrocarbons mixtures. The mixtures we shall study have different geometries and, therefore, constitute a severe test of the real possibilities of the theory for practical purposes.

II. Theory

The theory we shall present is very similar to that introduced by Fischer and Lago[12] for the site–site model. We shall extend it to molecular systems interacting through the Kihara potential model. In a few words we can consider both theories as extensions to molecular systems of the well-known perturbation theory proposed by Weeks, Chandler, and Andersen[14] (WCA) for simple liquids. We shall formulate the theory for binary mixtures, although the extension to a multicomponent mixture is straightforward. The Kihara potential between a molecule of type γ and another of type λ, where γ and λ stand for any of the two components of the mixture, either A or B, is given by[15]

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

where ϵ is the well depth of the potential, σ is a size parameter, and $\rho(r,\omega_1,\omega_2)$ is the shortest distance between the molecular cores. The shortest distance depends on the distance between the centers of mass r and on the orientation of molecules 1, ω_1, and 2, ω_2. For convenience we shall suppose that the orientational coordinates of molecule i, ω_i, are normalized to unit and we shall denote $\rho(r,\omega_1,\omega_2)$ simply as ρ. The molecular cores are chosen to reproduce the molecular shape. Within our formalism the molecular cores may or not be convex bodies. The full intermolecular po-

(1) Gray, C. G.; Gubbins, K. E. *Theory of Molecular Fluids*; Clarendon Press: Oxford, U.K., 1984; Vol. I.
(2) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: London, 1986.
(3) Lee, L. L. *Molecular Thermodynamics of Nonideal Fluids*; Butterworth: Stoneham, U.K., 1987.
(4) Fischer, J. *J. Chem. Phys.* **1980**, *72*, 5371.
(5) Lombardero, M.; Abascal, J. L. *Chem. Phys. Lett.* **1982**, *85*, 117.
(6) Boublik, T. *J. Chem. Phys.* **1987**, *87*, 1751.
(7) Padilla, P.; Lago, S. *Fluid Phase Equilib.* **1989**, *48*, 53.
(8) Vega, C.; Lago, S. *J. Chem. Phys.* **1991**, *94*, 310.
(9) Vega, C.; Lago, S. *Mol. Phys.* **1991**, *72*, 215.
(10) Padilla, P.; Lago, S.; Vega, C. *Mol. Phys.* **1991**, *74*, 161.
(11) Vega, C.; Lago, S.; Padilla, P. *J. Phys. Chem.*, following paper in this issue.
(12) Fischer, J.; Lago, S. *J. Chem. Phys.* **1983**, *78*, 5750.

(13) Boublik, T. *J. Phys. Chem.* **1988**, *92*, 2629.
(14) Weeks, J. D.; Chandler, D.; Andersen, H. C. *J. Chem. Phys.* **1971**, *54*, 5237.
(15) Kihara, T. *Adv. Chem. Phys.* **1975**, *33*, 51.

tential is divided into a reference u_0 and a perturbation part u_1 = $u - u_0$ according to the prescription of Mo and Gubbins.[16] This prescription incorporates all the repulsive forces into the reference system and treats all the attractive forces as the perturbation. Therefore, the Mo and Gubbins division when applied to the Kihara potential model yields for u_0:

$$u_0^{\gamma\lambda} = u^{\gamma\lambda} + \epsilon^{\gamma\lambda} \qquad \rho^{\gamma\lambda} < 2^{1/6}\sigma^{\gamma\lambda} \qquad (2)$$

$$u_0^{\gamma\lambda} = 0 \qquad \rho^{\gamma\lambda} > 2^{1/6}\sigma^{\gamma\lambda} \qquad (3)$$

The Helmholtz free energy of the full Kihara system is expanded about that of the reference system as in eq 5 of ref 11 but the expansion is now truncated at the first order term.

The structure of the anisotropic reference system as given by the pair correlation function $g_0(r,\omega_1,\omega_2)$ is obtained by using zero-order RAM theory[17] for the background correlation function $y_0(r,\omega_1,\omega_2)$ so that we get

$$g_0^{\gamma\lambda}(r_{12},\omega_1,\omega_2) = \exp(-\beta u_0^{\gamma\lambda}(r_{12},\omega_1,\omega_2))y_{RAM}^{\gamma\lambda}(r_{12}) \qquad (4)$$

The background correlation function of the spherical RAM mixture $y_{RAM}^{\gamma\lambda}(r)$ is obtained by solving the Ornstein-Zernike (OZ) equation and using the Percus-Yevick closure relation (PY). The RAM potential $\Phi_{RAM}^{\gamma\lambda}(R)$ for which the OZ equation is solved is given by

$$\exp(-\beta\Phi_{RAM}^{\gamma\lambda}(r_{12})) = \langle\exp(-\beta u_0^{\gamma\lambda}(r_{12},\omega_1,\omega_2))\rangle_g \qquad (5)$$

The Helmholtz free energy of the reference system is approximated to that of a hard bodies mixture. The diameters of the corresponding hard bodies to molecules A and B is obtained by setting to zero the BLIP integrals $B_{AA}(d_{AA})$ and $B_{BB}(d_{BB})$, respectively. The BLIP integrals $B_{\gamma\lambda}(d_{\gamma\lambda})$ are defined as

$$B_{\gamma\lambda} =$$
$$\int (\exp(-\beta u_H^{\gamma\lambda}) - \exp(-\beta u_0^{\gamma\lambda}))y_0^{\gamma\lambda}(r_{12},\omega_1,\omega_2) \, dr_{12} \, d\omega_1 \, d\omega_2 \qquad (6)$$

where $u_H^{\gamma\lambda} \equiv u_H^{\gamma\lambda}(1,2,d_{\gamma\lambda})$ represents the interaction between a pair of hard molecules whose diameter is $d_{\gamma\lambda}$. By setting $B_{AA}(d_{AA})$ and $B_{BB}(d_{BB})$ to zero we obtain d_{AA} and d_{BB}, respectively.[12] The crossed diameter d_{AB} is obtained assuming additive hard body diameters according to the expression:

$$d_{AB} = (d_{AA} + d_{BB})/2 \qquad (7)$$

In this way, according to the approximations contained in eqs 4-7 the residual Helmholtz free energy can be written as

$$A^{res}/NkT = A_H^{res}/NkT + nx_Ax_BB_{AB}(d_{AB}) + 2n\pi/kT \times$$
$$\sum_\gamma\sum_\lambda x_\gamma x_\lambda \int \langle u_1^{\gamma\lambda}(r_{12}\omega_1,\omega_2) \exp(-\beta u_0^{\gamma\lambda}(r_{12},\omega_1,\omega_2))\rangle y_{RAM}^{\gamma\lambda}(r)r^2 \, dr \qquad (8)$$

where n is the number density and x_A, x_B the mole fractions of the components A and B, respectively. Only the way to obtain A_H is left to complete the perturbation scheme. We shall get A_H from thermodynamic integration of the EOS of a hard body mixture according to the well-known expression

$$A_H^{res}/(NkT) = \int_0^n (Z_H - 1)/n' \, dn' \qquad (9)$$

where Z_H stands for the compressibility factor of the hard mixture. The way to obtain the equation of state of a hard body mixture should now be clarified. A possibility is to use an EOS for mixtures of hard convex bodies as for instance that proposed by Boublik[18]

$$Z_H = [1 + (3\alpha_1 - 2)\eta + (3\alpha_2 - 3\alpha_1 + 1)\eta^2 + (5\alpha_1 - 6\alpha_2)\eta^3]/(1 - \eta)^3 \qquad (10)$$

$$\eta = n\sum_\lambda x_\lambda V_{H,\lambda} \qquad (11)$$

$$\alpha_1 = (\sum_\lambda x_\lambda R_{H,\lambda})(\sum_\lambda x_\lambda S_{H,\lambda})/(3\sum_\lambda x_\lambda V_{H,\lambda}) \qquad (12)$$

$$\alpha_2 = (\sum_\lambda x_\lambda R_{H,\lambda}^2)(\sum_\lambda x_\lambda S_{H,\lambda})^2/(9(\sum_\lambda x_\lambda V_{H,\lambda})^2) \qquad (13)$$

where $R_{H,\lambda}$, $S_{H,\lambda}$, and $V_{H,\lambda}$ stand for the mean radius or curvature, the surface and the volume of the hard body of molecule λ, respectively. The mean radius of curvature $R_{H,\lambda}$ is defined only for convex bodies. For nonconvex bodies it is usual to take $R_{H,\lambda}$ as that of a closely related convex body.[19]

Another possibility to obtain Z_H which does not require the knowledge of $R_{H,\lambda}$ and $S_{H,\lambda}$ but that of the nonsphericity parameter α and the volume V has been recently proposed by Boublik.[20,21] The EOS has the form given by eq 10 but α_1 and α_2 are now given by

$$\alpha_1 = \sum_\gamma\sum_\lambda x_\gamma x_\lambda E_{\gamma\lambda}/\sum_\lambda x_\lambda V_{H,\lambda} \qquad (14)$$

$$E_{\gamma\lambda} = 0.5[(\alpha_\gamma V_{H,\gamma})^{1/3}(\alpha_\lambda V_{H,\lambda})^{2/3} + (\alpha_\lambda V_{H,\lambda})^{1/3}(\alpha_\gamma V_{H,\gamma})^{2/3}] \qquad (15)$$

$$\alpha_2 = [\sum_\lambda x_\lambda(\alpha_\lambda V_{H,\lambda})^{2/3}]^3/(\sum_\lambda x_\lambda V_{H,\lambda})^2 \qquad (16)$$

where the nonsphericity parameter of molecule λ, α_λ, is related to the second virial coefficient of the hard body $B_{H,\lambda}$ according to the expression proposed by Rigby[22] and used in eq 13 or ref 11.

Equations 1-16 constitute the perturbation scheme of this work. The orientational averages needed to use the theory can be easily performed by using the multidimensional integration method proposed by Conroy.[23] We typically use 4822 different orientations to obtain an orientational average at every distance between the centers of mass r. The solution of the OZ equation for the RAM potential is performed with the efficient algorithm proposed by Labik et al.[24] to solve integral equations. To give an idea of the computer time needed to get excess properties we shall indicate that, for a binary mixture at a given temperature, for five different compositions and 50 densities at every composition it takes about 24 h of CPU time in a personal computer, IBM PS/2 80-041.

Thermodynamic properties of liquids depend only very mildly on pressure at typical conditions of the low-pressure vapor-liquid equilibrium. It is usual then in statistical thermodynamic to evaluate the excess properties at zero pressure. Excess volume V^E, excess Gibbs free energy G^E, and excess free enthalpy are given by

$$V^E(x_A,x_B,T,p=0) =$$
$$V(x_A,x_B,T,p=0) - x_AV(1,0,T,p=0) - x_BV(0,1,T,p=0) \qquad (17)$$

$$H^E(x_A,x_B,T,p=0) =$$
$$U^{res}(x_A,x_B,T,p=0) - x_AU^{res}(1,0,T,p=0) - x_BU^{res}(0,1,T,p=0) \qquad (18)$$

$$G^E(x_A,x_B,T,p=0) = A^{res}(x_A,x_B,T,p=0) - x_AA^{res}(1,0,T,p=0) - x_BA^{res}(0,1,T,p=0) + \ln(n(x_A,x_B,T,p=0)) - x_A \ln(n(1,0,T,p=0)) - x_B \ln(n(0,1,T,p=0)) \qquad (19)$$

To determine the properties of a given mixture it is necessary not only to know the pair potential of the pure molecules u_{AA} and u_{BB} but also the crossed interaction u_{AB}. In this work we shall use the Lorentz-Berthelot rules (LB) which are given by the relations

$$\sigma^{AB} = (\sigma^{AA} + \sigma^{BB})/2 \qquad (20)$$

$$\epsilon^{AB} = \xi(\epsilon^{AA}\epsilon^{BB})^{1/2} \qquad (21)$$

when the parameter ξ takes the value unity.

(16) Mo, K. C.; Gubbins, K. E. *Chem. Phys. Lett.* **1974**, *27*, 144.
(17) Smith, W. R.; Nezbeda, I. *Adv. Chem. Ser.* **1983**, *204*, 235.

(18) Boublik, T. *Mol. Phys.* **1981**, *42*, 209.
(19) Boublik, T.; Nezbeda, I. *Collect. Czech. Chem. Commun.* **1986**, *51*, 2301.
(20) Boublik, T. *Collect. Czech. Chem. Commun.* **1983**, *48*, 192.
(21) Boublik, T. *Pure Appl. Chem.* **1989**, *61*, 993.
(22) Rigby, M. *Mol. Phys.* **1976**, *32*, 575.
(23) Conroy, H. *J. Chem. Phys.* **1967**, *47*, 5307.
(24) Labik, S.; Malijevsky, A.; Vonka, P. *Mol. Phys.* **1985**, *56*, 709.
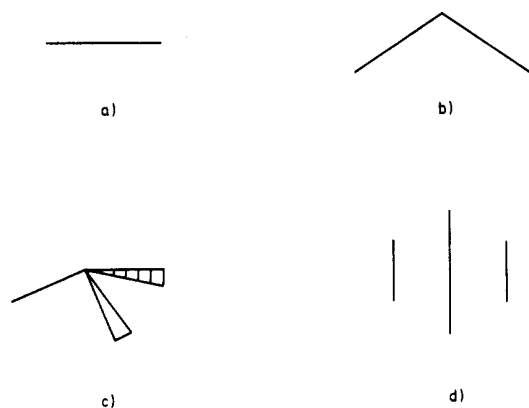
Figure 1. Geometry of the cores used in this work. Cores reduce to a point for Ar and methane and were not drawn. (a) Core for ethane, O_2, N_2; (b) core of propane; (c) core of isobutane; (d) core of benzene.

TABLE I: Potential Parameters of the Kihara Potential Proposed by Boublik[6] for Ar, N_2, and O_2[a]

molecule	$\sigma/\text{Å}$	$(\epsilon/k)/K$	L^*
Ar	3.400	116.80	0
O_2	2.954	141.04	0.3486
N_2	3.216	113.94	0.2892

[a] $L^* = l/\sigma$.

III. Results

In this work we shall apply the theory described in section II to several mixtures interacting through the Kihara potential. The core has to be previously defined for every molecule. For spherical molecules like Ar we take a point as the core so that the Kihara potential reduces to a spherical Lennard-Jones potential. For linear molecules like nitrogen or oxygen we take a linear rod as the core. For the different hydrocarbons we take the core as a set of rigid rods given by the carbon to carbon C–C bonds. Thus, for methane the core would be a point, for ethane a rod, for propane two connected rods in an angular geometry, and for isobutane three rods in a triangular pyramid configuration. For benzene we shall take three rods imitating a Dewar resonant electronic structure. All these cores are drawn in Figure 1.

The only previously proposed theories for Kihara mixtures have been developed by Boublik et al.[13,25] These theories are based on the formalism of convex bodies and can only be applied to molecules whose core is convex. In Table I we show the potential parameters proposed by Boublik[6] for argon, nitrogen, and oxygen. In Table II the excess properties for the mixtures Ar + N_2, Ar + O_2, and N_2 + O_2 are presented as evaluated from Boublik's perturbation theory and from the theory of this work. The results of both theories agree with each other. To decide which of these two theories is superior to the other it would be necessary to compare the theoretical results with excess properties evaluated from simulation from the same potential model. Unfortunately, there is no such simulation data yet. The theory of this work presents the advantage with respect to that proposed by Boublik that it gives a detailed information of the structure of the fluid as provided by the pair correlation function. Moreover, it lies on well-defined approximations allowing thus a systematic improvement and may be applied to convex and nonconvex models. Boublik's theory yields structural information through the average surface to surface correlation function which contains less information than $g(1,2)$. This average surface-to-surface correlation function is obtained in a semiempirical way and the use of that function restricts the application of the theory only to convex bodies. In spite of these drawbacks Boublik's theory presents the important advantage of numerical simplicity and speed when compared to the theory proposed in this work. In any case, the results of Table II look promising and seem to confirm the pos-

TABLE II: Excess Properties of Several Equimolar Binary Mixtures As Evaluated from Perturbation Theories Using Potential Parameters from Table I[a]

	V^E	H^E	G^E
Ar + N_2 (84 K)			
Boublik[b]	−0.13	26	31
this work	−0.22	41	30
experiment[c]	−0.18	51	34
Ar + O_2 (84 K)			
Boublik[b]	−0.03	−2	−3
this work	−0.02	−14	−7
experiment[c]	0.14	60	37
N_2 + O_2 (78 K)			
Boublik[b]	−0.24	55	50
this work	−0.21	54	40
experiment[c]	−0.25	60	40

[a] V^E in cm^3/mol, H^E in J/mol, and G^E in J/mol. Lorentz–Berthelot rule has been used in all the cases. [b] Reference 13. [c] Reference 32.

sibilities of both theories to determine excess properties of Kihara fluids.

Kihara potential, however, is less popular than other potential models as, for instance, the site–site model. It is a generalized belief that site–site model yields better results than the Kihara one as effective pair potential to describe the thermodynamic properties of pure liquids and their mixtures. In the past years, we have carried out several studies to show that this belief is at least questionable.[26,27] To gain more evidence on this point we shall compare the results obtained with the theory of section II and the Kihara potential model to those obtained by using a site–site potential and a perturbation theory[28,29] very similar to that described in section II. Since the theories used for the Kihara and the site–site potential are very similar the discrepancies with experimental data would arise fundamentally from deficiencies in the used potential as an effective pair potential. Such a comparison is shown in Table III. The Kihara potential yields results comparable to those obtained with the site–site model. In the case of the mixtures Ar + N_2 or N_2 + O_2 the results obtained with Kihara potential are slightly better than those from the site–site model. We conclude that Kihara potential model is not worse than the site–site one as an effective pair potential for mixtures.

The mixtures studied until now present in general simple geometries of the type spherical + linear, linear + linear. The only previously studied model of non linear mixtures by perturbation theory is that of spherical + tetrahedral made by Bohn et al.[30] for the site–site model. In this work we shall study by the first time mixtures involving more complicated geometries using perturbation theory with a nonspherical reference system. Thus, we shall study the mixtures methane + propane, ethane + propane, methane + isobutane, ethane + isobutane, and propane + benzene corresponding to the geometries spherical + angular, linear + angular, spherical + pyramidal, linear + pyramidal, and angular + hexagonal, respectively. We shall study all these mixtures using the Kihara potential and the cores shown in Figure 1. To describe the pair interaction between molecules of different type we shall use in all the cases the Lorentz–Berthelot combination rules (eqs 20 and 21 with $\xi = 1$). The used potential parameters are shown in Table IV. These parameters were obtained by fixing the value of $L^* = l/\sigma$ and the different angles between the rods of the core and selecting ϵ and σ in such a way that for a given temperature T the vapor pressure and orthobaric density evaluated from perturbation theories reproduce their corresponding experimental values.[11] The calculated excess properties along with the experimental values where available are shown in Table V. The agreement between theoretical and experimental values is very

(25) Lago, S.; Boublik, T. *Collect. Czech. Chem. Commun.* **1980**, *45*, 3051.

(26) Vega, C.; Frenkel, D. *Mol. Phys.* **1989**, *67*, 633.
(27) Vega, C.; Lago, S. *J. Chem. Phys.* **1990**, *93*, 8171.
(28) Bohn, M.; Lago, S.; Fischer, J.; Kohler, F. *Fluid Phase Equilib.* **1985**, *23*, 137.
(29) Bohn, M.; Fischer, J.; Kohler, F. *Fluid Phase Equilib.* **1986**, *31*, 233.
(30) Bohn, M.; Lustig, R.; Fischer, J.; Kohler, F. *Mol. Phys.* **1988**, *64*, 595.

TABLE III: Excess Properties of Several Equimolar Binary Mixtures As Evaluated in This Work for the Kihara Potential, and from a Similar Theory[29] for the Site-Site Model[a]

mixture	T/K	site-site			this work			experiment[b]		
		V^E	H^E	G^E	V^E	H^E	G^E	V^E	H^E	G^E
Ar + N_2	84	-0.19	19	26	-0.22	41	30	-0.18	51	34
Ar + O_2	84	-0.05	-14	-10	-0.02	-14	-7	0.14	60	37
N_2 + O_2	78	-0.22	54	52	-0.21	54	40	-0.25	60	40

[a] Units as in Table II. [b] Reference 32.

TABLE IV: Potential Parameters of Pure Substances As Obtained from the Counterpart for Pure Liquids of the Perturbation Theory of This Work[11]

	L^*	$(\epsilon/k)/K$	$\sigma/Å$
methane	0	149.92	3.7327
ethane	0.4123	305.75	3.5679
propane	0.4123	427.00	3.5587
isobutane	0.4123	506.82	3.5881
benzene	0.58	887.635	2.926

[a] $L^* = l/\sigma$ where l is the C-C distance. The C-C-C angle was taken as 109.5° for propane and isobutane and 120° for benzene.

good in all the cases taking into account the diversity of studies geometries. Boublik[13] has recently pointed out that Lorentz-Berthelot rules when applied to the Kihara potential yield better results of excess properties that when applied to the site-site model. The results of Table IV reinforce the idea that Lorentz-Berthelot combination rules works very well when applied to the Kihara potential, at least for the studied hydrocarbon mixtures, which have similar chemical constituting groups. It is also interesting to study the effect of the mixing parameter ξ of the Berthelot combination rule on the excess properties. In Table VI we show the results for the excess properties of three equimolecular mixtures at zero pressure, when $\xi = 1$ (LB) and when $\xi = 0.99$. A decrease of ξ of 1% causes noticeable changes in the excess properties. All the studied excess properties undergo an important increase when the parameter ξ decreases. We can then conclude that

$$\frac{\partial G^E}{\partial \xi} < 0; \quad \frac{\partial H^E}{\partial \xi} < 0; \quad \frac{\partial V^E}{\partial \xi} < 0 \qquad (22)$$

ξ lying near to 1.

This condition is fulfilled for the three studied mixtures which have different geometries. Thus, the conclusion supported by eq 22 seems to be independent of the geometry of the molecules of the mixture. Moreover, the behavior defined by eq 22 has been found for spherical Lennard-Jones mixtures[31] and for molecular site-site mixtures, too.[30] Therefore, eq 22 is satisfied for different potential models and for different geometries and seems to be a general conclusion for molecular systems without polar interactions. From the results of Table VI we can conclude that a decrease of ξ of about 1% causes an increase ranging from 60 to 90 J/mol for G^E, from 70 to 120 J/mol for H^E, and from 0.01 to 0.20 cm³/mol for V^E.

The theory in this work allows the determination of excess properties at different compositions. Thus, the behavior of the excess properties as a function of the composition for a given pressure and temperature can be studied. In Table VII some results for the excess properties of the mixtures methane + ethane, methane + propane, and ethane + propane for the compositions $x_1 = 0.25, 0.5,$ and 0.75 are shown. In general, a nonsymmetric behavior with respect to $x_1 = 0.5$ is found especially for H^E and G^E. V^E is more symmetric for these mixtures.

An interesting function which can be easily calculated from the theory of section II and is difficult to obtain from experiments is the radial distribution function between the centers of mass of
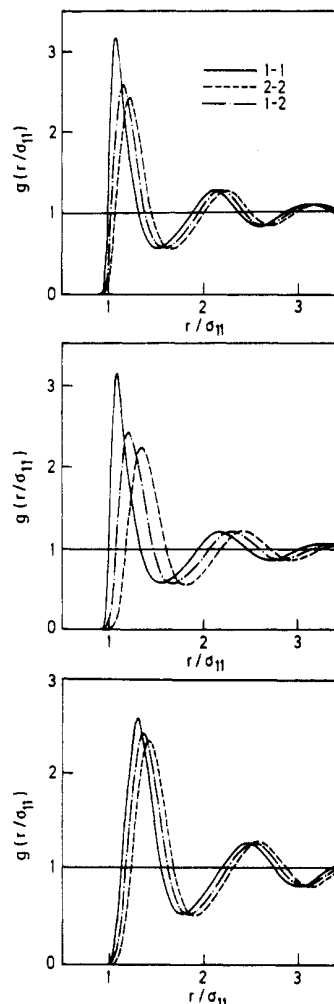

Figure 2. Radial distribution function as given by the theory of this work at $T = 112$ K, $p = 0$, $x_1 = 0.5$ for the mixtures: (a) methane + ethane; (b) methane + propane; (c) ethane + propane. Solid line, $g_{11}(r)$; dashed line, $g_{22}(r)$; dot-dashed line $g_{12}(r)$. σ_{11} is the size parameter (see text) of the first component of the mixture.

the molecules of the mixture. The radial distribution function measures the conditional probability of finding the center of mass of a molecule at a distance r from the center of mass of another molecule placed at the origin. In Figure 2 we show the radial distribution functions for the equimolecular mixtures of methane + ethane, methane + propane, and ethane + propane at zero pressure and $T = 112$ K.

In section II, two alternative ways to determine A_H (see eqs 9 and 10) differing in their definitions of α_1 and α_2 were introduced. The first option given by eqs 12 and 13 is convenient when the shape of the molecules of the mixture is close to that of a convex body and it is then a good approximation to take R_H of the nonconvex molecule as that f a similar convex model. When any of the molecules of the mixture has a nonconvex shape it may be more convenient to use eqs 14-16 to define α_1 and α_2. In Table VIII, the excess properties for two equimolecular mixtures containing a typical nonconvex angular molecule like propane are shown. The excess properties are very similar for these two routes

(31) Singer, J. V. L.; Singer, K. *Mol. Phys.* **1972**, *24*, 357.

(32) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworth: London, 1982.

(33) Hiza, M. J.; Haynes, W. M.; Parrish, W. R. *J. Chem. Thermodyn.* **1977**, *9*, 873.

TABLE V: Excess Properties of Several Binary Mixtures As Evaluated from the Perturbation Theory of Kihara Fluids of This Work and Potential Parameters from Table IV[a]

mixture	x_1	T/K	this work			experiment		
			V^E	H^E	G^E	V^E	H^E	G^E
methane + ethane	0.5	103.99	−0.38	67	104	−0.45[b]	74[b]	120.5[b]
methane + ethane	0.5	112	−0.49	71	112	−0.58[a]	68.6[b]	
methane + propane	0.5	90.68	−0.55	63	176	−0.51[b]		187[b]
methane + propane	0.5	112	−0.59	73	166	−0.84[b]	129.2[b]	
ethane + propane	0.5	105	0.19	61	8	−0.04[c]		
ethane + propane	0.5	125	0.09	18	1.6	−0.04[c]		
methane + isobutane	0.486	110	−0.63	−4	145	−0.80[c]		
ethane + isobutane	0.689	115	0.05	−19	−10	0.012[c]		
propane + benzene	0.50	310	−2.17	142	298			

[a] Units as in Table II. [b] Reference 32. [c] Reference 33.

TABLE VI: Excess Properties of Equimolecular Binary Mixtures and Different Crossed Interaction Parameter (Eqs 20 and 21)[a]

mixture	x_1	T/K	$\xi = 1$			$\xi = 0.99$		
			V^E	H^E	G^E	V^E	H^E	G^E
methane + ethane	0.5	103.99	−0.38	67	104	−0.34	137	163
methane + propane	0.5	90.68	−0.55	63	176	−0.37	180	244
ethane + propane	0.5	105	0.19	61	8	0.25	178	102

[a] Units as in Table II.

TABLE VII: As in Table V, for Three Different Compositions $x_1 = 0.25, 0.5, \text{and } 0.75$

mixture	x_1	T/K	this work		
			V^E	H^E	G^E
methane + ethane	0.25	103.99	−0.32	22	72
methane + ethane	0.5	103.99	−0.38	67	104
methane + ethane	0.75	103.99	−0.32	60	85
methane + propane	0.25	90.68	−0.38	21	114
methane + propane	0.5	90.68	−0.55	63	176
methane + propane	0.75	90.68	−0.48	74	153
ethane + propane	0.25	105	0.12	35	2
ethane + propane	0.5	105	0.19	61	8
ethane + propane	0.75	105	0.15	52	8

TABLE VIII: Excess Properties of Equimolecular Binary Mixtures Using the Two Different Treatments for the Equation of State (EOS) of the Reference System Defined in the Main Text

mixture	x_1	T/K	EOS mixtures[a]			EOS one fluid[b]		
			V^E	H^E	G^E	V^E	H^E	G^E
methane + propane	0.5	90.68	−0.55	63	176	−0.54	73	182
ethane + propane	0.5	105	0.19	61	7.8	0.18	63	7.5

[a] Equations 12 and 13. [b] Equations 14–16.

to get A_H. Equations 14–16 present, however, the advantage that they may be applied to nonconvex bodies since V_H and α are uniquely defined (see eq 13 of ref 11 for α definition) even for nonconvex models. However, eqs 12 and 13 need the arbitrary assignment of a convex body to the studied molecule so that R_H can be determined.

IV. Conclusions

In this work we have extended to mixtures the previously developed perturbation theory of Kihara fluids. We have shown that the excess properties determined from this theory and those obtained from Boublik's perturbation theory of Kihara mixtures are very close. This suggests that the accuracy of both theories is rather similar. A definitive test of the accuracy of both theories requires the comparison against simulation data, which were unavailable up to now. The calculated excess properties with the theory of this work, Kihara potential to model the pair interaction, and Lorentz–Berthelot combining rules agree very well with experimental results, provided that the interaction parameters of the pure fluids are obtained by fitting the calculated values of vapor pressure and orthobaric density coming from the counterpart of the theory for pure fluids[11] to experimental results. The agreement with experimental excess properties obtained from the perturbation theory of Kihara mixtures of this work is comparable to or even better than that obtained from a similar perturbation theory of site–site mixtures. This confirms, also for mixtures, our previous suggestion that the Kihara model is not worse than the site–site model as an effective pair potential to describe the thermodynamic behavior of pure fluids and their mixtures.

The presented theory can be easily be applied to mixtures of different geometries and we have got good results for the excess properties for several mixtures of hydrocarbons. The analysis of the change undergone by the excess properties due to a change in ξ (eq 21) leads us to the conclusion that a decrease of about 1% in ξ provokes an important increase of all the excess properties of Kihara mixtures.

The theory of this work can be applied to the determination of excess properties of molecular nonpolar mixtures at any value of T and p. This undoubtedly constitutes an important advantage over those semiempirical treatments which generally give only good results at low pressures close to the vapor–liquid saturation curve of the mixtures studied.