Thermodynamic Properties of Nonpolar Molecular Fluids of Different Geometries from Perturbation Theory

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A perturbation theory for molecular nonpolar fluids is proposed. Intermolecular interactions are modeled by the Kihara potential. The potential parameters are obtained by fitting the theoretical vapor pressure and bubble density at a given temperature to the corresponding experimental values. We have studied several fluids involving different geometries as ethane, 2-butyne, propane, ozone, cyclopropane, isobutane, and benzene. The calculations have been performed with a personal computer and good results were found for vapor pressures, bubble densities, enthalpy of vaporization, and equation of state for all the substances studied. The theory is, therefore, suitable for practical applications.

I. Introduction

Advances in statistical mechanics during the 1960s and 1970s allow us to determine with great accuracy thermodynamic properties of simple liquids.[1,2] Thus, for noble gases, Malijevsky et al.[3] have shown that it is possible to determine their thermodynamic behavior from theoretical grounds. The high accuracy of the results makes them useful for practical applications. For molecular liquids, important progress has been made during the last decade, especially on integral equations and perturbation theories although the quality of the results is not comparable to that of simple liquids yet.[4] Perturbation theory[1,4,5] appears as the best candidate for practical applications since it is both accurate and fast from a computational point of view. Accurate perturbation theories are now available for several kinds of molecular fluids such as spherical or quasi-spherical polar fluids[4,6] and for anisotropic nonpolar fluids interacting through a site–site potential model.[7–9] The site–site potential model presents, however, the important disadvantage of a quadratic increase of the number of interactions between a pair of molecules as the number of sites per molecule grows. Therefore, the computational time required for calculations increases quadratically with the molecular complexity and that prevents an easy extension of the theories to complex molecules.

In 1951, Kihara[10] proposed a pair potential which only depends on the shortest distance ρ between the molecular cores. The cores are chosen to reproduce the molecular shape. Thus, in this model the pair interaction is described by only one interaction regardless of the molecular complexity. Although the time required for the evaluation of ρ increases slightly with the molecular complexity this increase is far from being quadratic. Hence, the interest of using Kihara potential as an effective pair potential for complex molecules. The simulation studies performed for the Kihara model in our laboratory,[11–13] either by Monte Carlo (MC) or by molecular dynamics (MD), have shown that it is easy to carry out simulations of these models and that Kihara potential constitutes a good effective pair potential for the liquid phase. The obtained results were not worse than those obtained with the more popular site–site model. Simulation studies yield exact results for the

studied model but they are computationally expensive. Therefore, for practical applications, it is important to develop less demanding theoretical approaches. Thus, we have recently extended the perturbation theory proposed by Fischer for the site–site model, first to Kihara linear models[14] and then to Kihara angular models.[15] Moreover, the extended theory has already provided excellent results for the vapor–liquid equilibrium of propane.[15] The goal of this work is to show that good results can be also obtained for the equation of state and the vapor–liquid equilibrium of nonpolar fluids of *any molecular geometry* by using the perturbation theory for the Kihara model. The advantage of our method when compared to empirical or semiempirical methods of studying the liquid state is that it is well defined on theoretical grounds, allowing systematic improvement. On the other hand, although the programming effort is still considerable, calculations can be carried out in a personal computer. The perturbation theory we shall present is limited to nonpolar (without important dipole or quadrupole moment) and nonflexible fluids. For polar and flexible fluids an additional theoretical effort within statistical thermodynamics is still necessary. The theory, however, can be still applied to a wide variety of fluids. We shall apply it to ethane, propane, cyclopropane, 2-butyne, isobutane, and benzene.

The scheme of the paper is as follows. In section II we shall describe the perturbation theory we shall use. Section III is devoted to the obtained results and section IV gives the conclusions of the work.

II. Theory

The perturbation theory we shall use is quite close to that formulated in the ref 15. We shall give here the main features of the theory and how it can be extended to any geometry and refer to the reader to ref 15 for a more detailed discussion. The interaction potential is assumed pairwise additive and the pair interaction as proposed by Kihara[10] is given by

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

where ϵ is the well depth of the potential, σ is a size parameter, and ρ is the shortest distance between the cores. The molecular cores are represented by a set of rods arranged to reproduce approximately the molecular shape. Then ρ will be obtained as

$$\rho = \text{minimum } \{\rho_{ij}\} \qquad (2)$$

where $\{\rho_{ij}\}$ stands for the set of shortest distances between the rod labeled as i of molecule 1 and rod labeled as j of molecule 2. Efficient algorithms for the evaluation of ρ_{ij} are given elsewhere.[16–18] We shall split the full potential into a reference system u_0 and a perturbation part u_1 according to the Weeks–Chandler–Andersen theory[19] (WCA), that is, by including all the

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repulsive forces into the reference system. The reference system is thus defined as[14,20]

$$u_0 = u(r_{12}, \omega_1, \omega_2) + \epsilon \qquad \rho < 2^{1/6}\sigma \qquad (3)$$

$$u_0 = 0 \qquad \rho > 2^{1/6}\sigma \qquad (4)$$

The perturbation term u_1 is obtained as $u_1 = u - u_0$. By expanding the residual part of the Helmholtz free energy of the Kihara system about that of the reference system one gets up to second order

$$\frac{A^{res}}{NkT} = \frac{A_0^{res}}{NkT} + \frac{A_1}{NkT} + \frac{A_2}{NkT} + \dots \qquad (5)$$

Now the following approximations are made:

1. The structure of the reference system, given by the pair correlation function $g_0(1,2)$, is approximated by[21]

$$g_0(r_{12}, \omega_1, \omega_2) = \exp(-\beta u_0(r_{12}, \omega_1, \omega_2))y_{RAM}(r_{12}) \qquad (6)$$

where $y_{RAM}(r)$ is the background function of the spherical RAM system. The potential of the RAM system $\Phi_{RAM}(r)$ is defined by

$$\exp(-\beta\Phi_{RAM}(r_{12})) = \langle \exp(-\beta u_0(r_{12}, \omega_1, \omega_2)) \rangle_g \qquad (7)$$

where the subscript g stands for unweighted orientational average. At every temperature and density $y_{RAM}(r)$ is obtained by solving the Ornstein–Zernike equation (OZ) with the Percus–Yevick[22] (PY) closure for the potential $\Phi_{RAM}(r)$.

2. The residual free energy of the reference system is obtained by equating to that of a hard equivalent system. The equivalent hard system is a hard body obtained by keeping constant the lengths of all the rods of the core and with a hard diameter given by

$$n/2 \int \langle \exp(-\beta u_0) - \exp(-\beta u_H(d_H)) \rangle_g y_{RAM}(r)r^2 \, dr = 0 \qquad (8)$$

where n is the number density. By choosing the diameter of the hard body d_H according to eq 8 the first term of the BLIP expansion of the reference system about the hard system vanishes.[1,7,15] A_H^{res} is evaluated from thermodynamic integration of the equation of state of hard bodies proposed by Boublik. A_H^{res} can be then written as[15,23]

$$A_H^{res}/NkT = \frac{\eta(c_1 + c_2\eta)}{(1 - \eta)^2} + c_3 \ln(1 - \eta) \qquad (9)$$

where the constants c_1–c_3 are given by

$$c_1 = 6\alpha^2 - 2\alpha \qquad (10)$$

$$c_2 = (-15\alpha^2 + 9\alpha)/2 \qquad (11)$$

$$c_3 = 6\alpha^2 - 5\alpha - 1 \qquad (12)$$

The nonsphericity parameter[24] α and the packing fraction η are defined by

$$B_2/V_H = (1 + 3\alpha) \qquad (13)$$

$$\eta = nV_H \qquad (14)$$

where B_{2H} and V_H are the second virial coefficient and the volume of the hard body, respectively.

3. With the approximation to $g_0(1,2)$ given by eq 6 the first order perturbation term A_1 is written as

$$A_1/N = 2 n\pi \int_0^\infty \langle u_1 \exp(-\beta u_0) \rangle_g y_{RAM}(r_{12})r_{12}^2 \, dr_{12} \qquad (15)$$

4. The second-order perturbation term A_2 is obtained from an extension to molecular systems of the macroscopic compressibility approximation proposed by Barker and Henderson. A_2 is then given by[15,25]

$$A_2/NkT =$$

$$\frac{-\pi n}{kT}\left(\frac{\partial n}{\partial p}\right)_0 \int_0^\infty \langle u_1^2 \exp(-\beta u_0) \rangle_g y_{RAM}(r_{12})r_{12}^2 \, dr_{12} \qquad (16)$$

where $(\partial n/\partial p)_0$ stands for the variation of density with pressure at constant temperature of the reference system. $(\partial n/\partial p)_0$ can be easily obtained from the equation of state of hard bodies of Boublik.

Steps 1–4 constitute the perturbation scheme of this work. The value of A^{res} is then obtained for any wished temperature or density. The pressure can be calculated from the thermodynamic relation

$$Z = 1 + \left(\frac{\partial(A^{res}/NkT)}{\partial n^*}\right)_T n^* \qquad (17)$$

where $n^* = n\sigma^3$.

Liquid–vapor equilibrium can be studied by treating the liquid with perturbation theory and the gas with the second virial coefficient B_2. It is a good approximation to describe the gas behavior with B_2 provided that $T/T_c < 0.8$, where T_c is the critical temperature of the fluid studied. The bubble density n_l and the density of the gas n_g at coexistence at a given temperature can be calculated by solving the nonlinear system of equations:

$$n_l Z_l = (1 + B_2 n_g)n_g \qquad (18)$$

$$A_l^{res}/NkT + Z_l + \ln(n_l) = B_2 n_g + (1 + B_2 n_g) + \ln(n_g) \qquad (19)$$

Once the densities of liquid and gas at coexistence are known, the enthalpy of vaporization H_v can be evaluated from the relations

$$H_v = H_g - H_l = (U_g^{res} - U_l^{res}) + p_v\left(\frac{1}{n_g} - \frac{1}{n_l}\right) \qquad (20)$$

$$U_g^{res} = - nkT^2\left(\frac{dB_2(T)}{dT}\right) \qquad (21)$$

The residual internal energy of the liquid U_l^{res} can be estimated by assuming that the structure of the reference system is very close to that of the full potential (a good approximation at high densities) from the relation:[14,15]

$$U_l^{res}/N = 2\pi n \int \langle u \exp(-\beta u_0) \rangle_g y_{RAM}(r_{12})r_{12}^2 \, dr_{12} \qquad (22)$$

All the orientational averages ($\langle \ \rangle_g$) of the theory are evaluated using Conroy[26] multidimensional integration method with 3022 orientations for every value of r. The evaluation of these averages typically requires between 4 and 9 h depending on the molecular complexity in a personal computer IBM PS/2 80041 with an INTEL 80387 mathematical coprocessor. In this time the orientational averages can be evaluated at eight different temperatures. The resolution of the OZ equation is performed with the efficient algorithm proposed by Labik et al.[27] and requires about 15 s at a given temperature and density in the same computer. The evaluation of the vapor–liquid equilibrium consumes only a few seconds. Therefore, the speed of the computation of the equilibrium properties depends mainly on the speed of evaluation of the orientational averages.

An appropriate description of the molecular shape is very important to achieve good results for vapor–liquid equilibrium and for the equation of state (EOS). Consequently, the choice of the molecular core must be done with care. In this work, ethane, 2-butyne, ozone, propane, cyclopropane, isobutane, and benzene are studied. The used cores are shown in Figure 1. So, to reproduce correctly the linear geometry of ethane and 2-butyne their cores are taken as a rod (Figure 1a). Two fused rods forming

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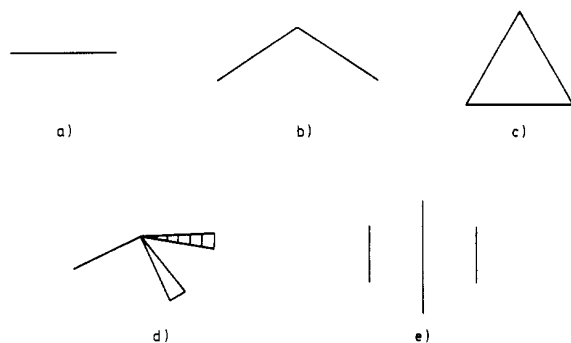(22) Percus, J. K.; Yevick, G. J. *Phys. Rev.* **1958**, *110*, 1.

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Figure 1. Molecular cores used in this work. The values of the length of the rods L^* and of the internal angles λ for each substance are shown in Table I. (a) Core for ethane and 2-butyne. (b) Core of propane and ozone. (c) Core of cyclopropane. (d) Core of isobutane. (e) Core of benzene.

an angle equal to the experimental O–O–O angle and C–C–C angle are taken for ozone and propane, respectively (Figure 1b). An equilateral triangle corresponding to the geometry of the three atoms of carbon is taken for cyclopropane (Figure 1c) and a triangular pyramid for isobutane (Figure 1d). Finally, for benzene we shall take three unconnected rods arranged in such a way that the extremes of the rods form a regular hexagon (see Figure 1e).

Once we have explained the theory and the choice has been made for the molecular cores it is necessary to specify the potential parameters we shall use for every compound. In principle, the problem of the determination of the potential parameters is exclusively a quantum-mechanics problem.[28,29] Unfortunately, there is not at the moment accurate ab initio pair potentials for the molecules we study in this work. Moreover, to determine with high precision the thermodynamic properties in the liquid state it is necessary not only to know the pair potential but the three-body potential too. Malijevsky et al. have shown that in the case of noble gases the contribution of three-body forces to the internal energy is of about 5% and much higher to the pressure.[3] The usage of ab initio two and three-body potentials for molecular systems is at the moment a dream. A way of avoiding partially this problem is to conceive the pair potential as an effective pair potential rather than the true pair potential. The effective pair potential will include in an averaged fashion the three-body effects. Within this perspective it seems legitimate to determine the potential parameters by fitting a calculated property to its experimental value in the liquid range. To that purpose we shall follow the procedure already used in refs 9 and 30. We shall fix from the beginning the molecular geometry. That means that all the angles of the model and the value of L^* = l/σ, where l is the length of the rods of the core, will be fixed. In the case of benzene l stands for the length of the outer rods. Once the molecular geometry is fixed (L^*, and angles), the values of σ and ϵ should be determined. At that point, the knowledge of the experimental bubble density and of the vapor pressure at a given temperature T_{exp} is needed. We shall proceed then in the following way:

(a) The vapor–liquid equilibrium is studied at several reduced temperatures T^* = $T/(\epsilon/k)$. The reduced bubble density n^*_l and the reduced vapor pressure p^* = $p/(kT/\sigma^3)$ for every value of T^* are then obtained.

(b) A trial value of ϵ is chosen and the corresponding T^*_{exp} is obtained.

(c) n^*_l and p^* are evaluated at T^*_{exp} with the data of step a.

(d) Bringing together n^*_l to the experimental bubble density and p^* to the experimental vapor pressure, two values of σ are obtained, one arising from the density correspondence and another

TABLE I: Potential Parameters Used in This Work

substance	L^*	λ/deg	σ/Å	(ϵ/k)/K
ethane	0.4123		3.5679	305.75
2-butyne	1.10		3.3465	653.57
propane	0.4123	109.5	3.5587	427
ozone	0.38	116	2.838	328.41
cyclopropane	0.50	60	3.2939	452.65
isobutane	0.4123	109.5	3.5881	506.82
benzene	0.58		2.926	887.64

TABLE II: Vapor–Liquid Equilibrium of Ethane[a]

Vapor Pressures

T/K	p^{exp}/MPa	p^{PT}/MPa
90.348	1.13×10^{-6}	2.22×10^{-6}
100	1.1×10^{-5}	1.87×10^{-5}
120	3.5×10^{-4}	5.12×10^{-4}
150	9.7×10^{-3}	1.07×10^{-2}
180	0.079	0.077
210	0.334	0.319
230	0.700	0.650
240	0.967	0.888

Bubble Densities

T/K	n^{exp}/(mol/L)	n^{PT}/(mol/L)
90.348	21.68	21.82
100	21.34	21.44
120	20.60	20.63
150	19.47	19.45
180	18.28	18.29
210	16.97	17.11
230	16.04	16.25
240	15.46	15.80

Dew Densities

90.348	1.51×10^{-6}	2.96×10^{-6}
100	1.33×10^{-5}	2.25×10^{-5}
120	3.56×10^{-4}	5.13×10^{-4}
150	7.84×10^{-3}	8.70×10^{-3}
180	5.45×10^{-2}	5.17×10^{-2}
210	0.209	0.196
230	0.425	0.382
240	0.585	0.516

[a] PT = perturbation theory with the potential parameters of Table I. Experimental data from ref 32.

from the pressure correspondence.

(e) If these two values of σ are identical then ϵ and σ are taken as the potential parameters. If the two values of σ are different then we return to the step b with a different trial ϵ.

In the next section the results obtained with the perturbation theory presented here for different fluids are shown.

III. Results

The parameters obtained from the procedure described in the previous section are shown in Table I for ethane, 2-butyne, ozone, propane, cyclopropane, isobutane, and benzene. For ethane, propane, and isobutane we have chosen L^* = 0.4123 which is the optimum value of L^* for propane as obtained from MD studies.[13] As the chemical bonds are similar for these three substances, the same value of L^* is taken for all of them. Furthermore, the values of σ obtained for these three hydrocarbons are also similar as in the previous assumption. The final value of the length of the rod l = $L^*\sigma$ is about 1.47 Å which is close to the experimental C–C bond length of 1.54 Å. The values of L^* assumed for ozone, benzene, and 2-butyne were estimated from the molecular geometry considering the experimental bond length and the approximate sizes of the constituting groups. In the most of cases the length of the rods is close to the experimental bond lengths.[31]

Table II contains the results for the vapor–liquid equilibrium of ethane obtained from the theory of this work along with experimental data.[32] The studied range of temperatures runs from

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TABLE III: Second Virial Coefficient B_2 of Ethane As Obtained from Experiment[33] and As Given by the Kihara Potential with the Potential Parameters of Table I

T/K	$B_2^{exp}/(cm^3/mol)$	$B_2/(cm^3/mol)$
210	-370 ± 5	-343
240	-283 ± 3	-267

TABLE IV: Vaporization Enthalpy of Ethane Determined from Perturbation Theory (PT) and from Experiment^a (Ref 32)

T/K	$H_v^{exp}/(kJ/mol)$	$H_v^{PT}/(kJ/mol)$
100	17.66	16.61
120	16.92	16.00
140	16.26	15.39
160	15.58	14.79
180	14.86	14.17
200	14.05	13.57
220	13.09	12.67
240	11.90	12.13

^{a} The potential parameters used are shown in Table I.

TABLE V: As Table II but for Cyclopropane^a

Vapor Pressures

T/K	p^{exp}/MPa	p^{PT}/MPa
193.15	7.42×10^{-3}	8.92×10^{-3}
213.15	2.64×10^{-2}	2.91×10^{-2}
233.15	4.52×10^{-2}	7.77×10^{-2}
243.15	0.114	0.118
273.15		0.345
293.15	0.631	0.621
313.15	1.065	1.04
333.15	1.682	1.63

Bubble Densities

T/K	$n^{exp}/(mol/L)$	$n^{PT}/(mol/L)$
193.15	17.47	17.56
213.15	16.92	17.08
233.15	16.36	16.55
243.15	16.09	16.27
273.15		15.48
293.15	14.87	14.91
313.15	14.15	14.31
333.15	13.31	13.67

Dew Densities

T/K	$n^{exp}/(mol/L)$	$n^{PT}/(mol/L)$
193.15		5.58×10^{-3}
213.15		1.66×10^{-2}
233.15		4.10×10^{-2}
243.15		6.05×10^{-2}
273.15		0.163
293.15	0.314	0.283
313.15	0.484	0.464
333.15	0.775	0.736

^{a} Experimental data from refs 38–40.

the triple point ($T_t = 90.348$ K) to $T = 240$ K (the critical temperature is 305.42 K). The results for the vapor pressure can be considered as satisfactory taking into account that the vapor pressure runs over six orders of magnitude in the studied range of temperatures. The calculated liquid and gas coexistence densities agree also well with the experimental data.

In Table III the calculated values of $B_2(T)$ along with the experimental values[33] are shown. The calculated values of B_2 are larger than the experimental ones. This also holds for the rest of the fluids studied in this work. The explanation of this discrepancy is that when the pair potential parameters are determined from liquid side properties (as we are indeed doing) we get an effective pair potential rather than the authentic pair potential. The net contribution of three-body forces to the internal energy is positive and therefore the values of ϵ of the effective pair po-

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TABLE VI: As Table II but for 2-Butyne^a

Vapor Pressures

T/K	p^{exp}/MPa	p^{PT}/MPa
240.90	6.12×10^{-3}	7.55×10^{-3}
260	1.78×10^{-2}	1.97×10^{-2}
280	4.55×10^{-2}	4.57×10^{-2}
290	6.88×10^{-2}	6.56×10^{-2}
300	0.101	0.093
320	0.200	0.172
340	0.367	0.295
390	1.187	0.892

Bubble Densities

T/K	$n^{exp}/(mol/L)$	$n^{PT}/(mol/L)$
240.90	13.74	13.83
260	13.40	13.43
280	13.03	13.03
290	12.84	12.83
300	12.64	12.63
320	12.24	12.23
340	11.83	11.82
390	10.76	10.78

^{a} Experimental vapor pressures are from ref 41 and experimental bubble densities from ref 42.

TABLE VII: As Table II but for Ozone^a

Bubble Densities

T/K	$n^{PT}/(mol/L)$	$n^{exp}/(mol/L)$
77.75	33.78	33.62*
90.15	32.92	32.73*
110	31.57	
130	30.27	
161.25	28.29	28.29
180	27.11	
190	26.47	
200	25.84	

^{a} Experimental data from ref 31 of the main text. The experimental densities with asterisk correspond to the given temperature and to the pressure of 0.1013 MPa.
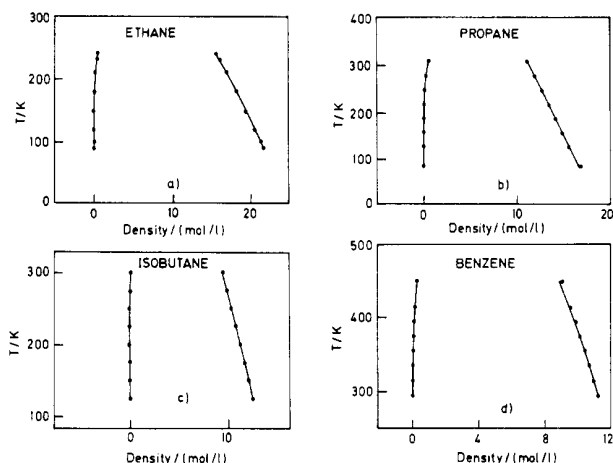

Figure 2. Bubble and dew densities at coexistence for ethane, propane, isobutane, and benzene as obtained from the perturbation theory of this work (solid line) and from experiment (dots).

tential are usually smaller than those of the true pair potential. Thus, the reduced temperature obtained with this ϵ is larger than the reduced temperature obtained with the true well depth and, therefore, B_2 is also larger. In Table IV the enthalpy of vaporization as obtained from theory and from experiment is shown. The agreement is now slightly worse here although it is still reasonable.

The vapor–liquid equilibrium of cyclopropane is illustrated in Table V. Again the results can be considered as satisfactory. The quality of the results is very good given the high anisotropy of this molecule and comparable to that obtained by Lustig[9] with

TABLE VIII: As Table II but for Benzene[a]

Vapor Pressures

T/K	p^{exp}/MPa	p^{PT}/MPa
295	1.10×10^{-2}	1.15×10^{-2}
315	2.63×10^{-2}	2.82×10^{-2}
335	5.57×10^{-2}	5.74×10^{-2}
355	0.107	0.106
375	0.189	0.183
395	0.313	0.298
415	0.491	0.461
450	1.07	0.908

Bubble Densities

T/K	$n^{exp}/(mol/L)$	$n^{PT}/(mol/L)$
295	11.23	11.19
315	10.95	10.92
335	10.67	10.66
355	10.39	10.40
375	10.10	10.13
395	9.79	9.87
415	9.47	9.59
450	8.87	9.11

Dew Densities

295	4.50×10^{-3}	4.73×10^{-3}
315	1.02×10^{-2}	1.09×10^{-2}
335	2.05×10^{-2}	2.12×10^{-2}
355	3.75×10^{-2}	3.75×10^{-2}
375	6.41×10^{-2}	6.23×10^{-2}
395	0.103	0.099
415	0.159	0.150
450	0.311	0.297

[a] Experimental data from ref 43.

the site–site model. In Table VI the results obtained for 2-butyne are presented. Table VII contains the bubble densities of ozone from theory and experiment. We have also evaluated its second virial coefficient for three temperatures, $T = 90.15$, 161, and 200 K yielding the values $B_2 = -1652, -388, -250 \, cm^3/mol$, respectively. To our knowledge there is no reported values of B_2 for ozone. In Table VIII the vapor–liquid equilibrium data for benzene are presented. In spite of the larger complexity of this molecule when compared to the previously studied substances, the agreement remains again satisfactory.

In Figure 2 the coexistence densities for ethane, propane, isobutane, and benzene from theory and from experiment are displayed. This figure summarizes the picture of the vapor–liquid equilibria obtained from the perturbation theory of this work. It can be concluded that perturbation theory provides a correct prediction of vapor–liquid equilibrium of nonpolar anisotropic fluids.

The results presented above prove the predictive power of the theory for determining coexisting properties. The only required information, involved in the determination of the potential parameters is the knowledge of vapor pressure and bubble density at a given temperature. Once the parameters are determined, the quality of the results holds in a wide range of temperatures, provided that the molecular shape is correctly taken into account within the model. Now the quality of the results can be globally analyzed. To that purpose we shall define the average deviation Δ as

$$\Delta = \frac{100}{n} \sum_{i=1}^{n} \frac{|X^i_{calc} - X^i_{expt}|}{X^i_{expt}} \qquad (23)$$

In Table IX the values of Δ for the different studied substances and for several properties are listed. The bubble densities have an average accuracy of about 0.5%. Vapor pressures and vaporization enthalpy are determined within an accuracy of about 5%. The second virial coefficient shows a typical error of about 8% due to the impossibility of describing simultaneously liquid and gas phases with effective pair potentials. The errors of the theory presented here are comparable to those obtained from empirical or semiempirical equations of state. Thus, Peng–

TABLE IX: Values of Δ (See Eq 23) for the Second Virial Coefficient B_2, Enthalpy of Vaporization H_V, the Logarithm of the Vapor Pressure in MPa ln (p_v), and the Bubble Density $n^{[a]}$

	ΔB_2	ΔH_v	Δ ln (p_v)	Δn	$\Delta T/K$
propane	4.0	5.5	1.7	1.0	225
ethane	6.5	4.4	6.1	0.7	150
ozone	*	*	*	0.3	90
cyclopropane	11.0	1.3	3.8	1.1	140
isobutane	7.8	5.3	5.6	0.5	175
benzene	15	5.6	2.8	0.7	155
2-butyne	1.1	8.9	6.2	0.2	150
average	7.6	5.2	4.4	0.6	155

[a] ΔT is the range of temperature in which the substance has been studied. An asterisk means that experimental data are not available.
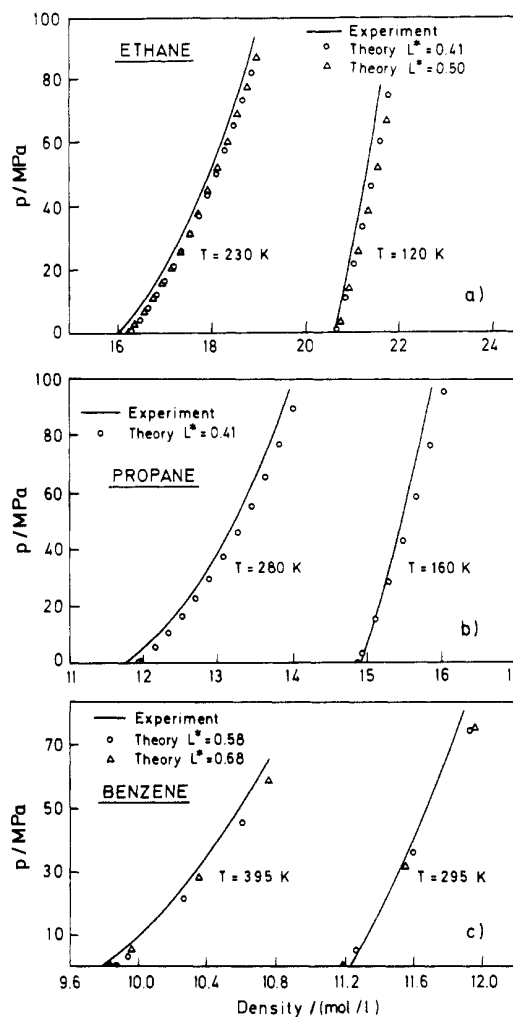

Figure 3. Pressure as a function of the density for two selected isotherms. Experimental data (solid line) and perturbation theory (circles). (a) Ethane; (b) propane; (c) benzene.

Robinson[34] equation of state yields errors of about 2% in vapor pressure and of about 8% in bubble densities.[35] The average accuracy of Soave–Redlich–Kwong[36] equation of state is of about 2% for vapor pressure and of 15% for bubble densities.[35] Taking into account these results the quality of the results summarized in Table IX is very good. In the case of ethane, 2-butyne, and benzene we believe that the inclusion of a molecular quadrupole in the potential model would lead to an improvement of the results. Unfortunately, there are not at the moment good perturbation theories for polar nonspherical fluids which enable one to evaluate

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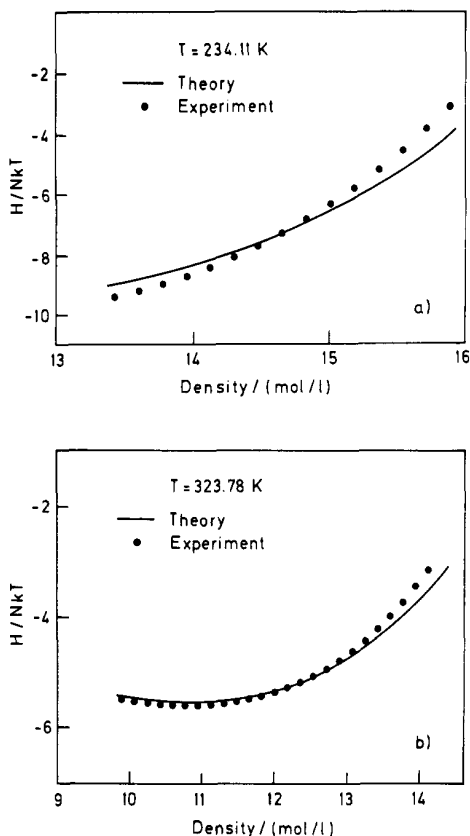(36) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.

Figure 4. Residual enthalpy H of propane as a function of the density for two selected temperatures as obtained from theory (solid line) and from experiment (dots) (a) $T = 234.11$ K; (b) $T = 323.78$ K.

correctly the contribution of the quadrupole to thermodynamic properties.

The perturbation theory proposed in the present work not only allows the determination of vapor–liquid equilibrium but also of the equation of state and of the rest of thermodynamic properties. Figure 3 shows the pressure as a function of the density for two different isotherms. The results correspond to ethane, propane and benzene. The description of the equation of state for these three substances is very good even at high pressures. The slope of the isotherms of Figure 3 is very sensitive to the molecular anisotropy. The nonsphericity parameter α defined in eq 13 gives an idea of the molecular anisotropy. The inclusion of the molecular shape appears then as necessary for an accurate evaluation of pressure in a wide range of temperatures and densities. In the theory of this work the molecular geometry is included in the model from the beginning because we choose the core as close as possible to the real shape of the molecule. In semiempirical cubic EOS the anisotropy is commonly introduced through the acentric factor.[37] The reduction of the shape of the molecule to a simple

factor, although useful because of its simplicity leads necessarily to errors in semiempirical theories when wide regions of the phase diagram are considered.

Perturbation theory provides residual Helmholtz free energy A as a primary property. Entropy, enthalpy, internal energy, Gibbs free energy, and EOS can be easily evaluated from A by using well-known thermodynamic relations. As an example we show in Figure 4 the residual enthalpy H of propane as a function of the density for two isotherms. At every temperature the smallest density corresponds to the bubble density. As we can see, the results for H also are good.

IV. Conclusions

The theory presented in this paper for molecules interacting through Kihara potential yields a satisfactory description of vapor–liquid equilibrium, equation of state, and thermodynamic properties of molecular liquids. The theory can be applied without restrictions of geometry and the only condition is that the molecule is basically nonpolar. For the studied substances, ethane, 2-butyne, propane, ozone, cyclopropane, isobutane, and benzene, good results in a wide range of temperatures for all the cases are found. The only required experimental information is the bubble density and vapor pressure at a given temperature as well as the molecular geometry.

The calculations can be performed with a personal computer. The quality of the results is comparable to or even better than those from empirical equations of state commonly used in chemical engineering. The theory of this work presents the advantage when compared to these empirical treatments that it is based on well-defined grounds and it allows its systematic improvement.

For molecules with important dipole or quadrupole moment it is still necessary to develop new theoretical approaches, and this problem is receiving at present much attention within statistical mechanics.

The development of perturbation theories for pure fluids is of great interest by itself. Nevertheless, the most of technical applications deals with mixtures and, therefore, the evaluation of their thermodynamic properties is a very challenging task. The extension of the present theory to mixtures will be shown in a later paper.[44]

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