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FROM SITE-SITE COMPUTER SIMULATIONS:
PURE HYDROCARBONS AND BINARY MIXTURES
CONTAINING METHANE**

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ABSTRACT

Densities and enthalpies of vaporization for several alkanes have been calculated by dividing the molecules into sites (or groups) and then using Monte-Carlo simulation with site-site Lennard-Jones potential functions. The properties of uniphase systems have been determined from simulations in the isobaric-isothermal ensemble. The properties of saturated (two-phase) systems have been computed by simulations in the Gibbs ensemble. The intermolecular potential functions used in these simulations are similar to those presented by Jorgensen et al. However, to cover an appreciable range of external conditions, the characteristic energy ϵ used here is a linear function of site density. Site-site potential functions provide the microscopic analog of group-contribution methods for estimation of thermodynamic properties. Good agreement with experiment is achieved for several pure hydrocarbons and for a few binary mixtures containing methane.

INTRODUCTION

Accurate estimates of the thermodynamic properties of fluids, including phase equilibria, are of importance for a variety of applications, ranging from the design of chemical processes to the analysis of geological formations under the earth's crust. In the absence of experimental data, the thermodynamic properties of pure fluids and mixtures can be estimated by group-contribution methods (Reid et al., 1987). While such methods can often achieve semi-quantitative predictions, they have some severe limitations, especially for mixtures, because they are often used in conjunction with oversimplified analytical equations of

state or activity-coefficient models. An inherent shortcoming of empirical group-contribution methods resides in their inability to distinguish between isomers (e.g. *n*-butane and isobutane); further, for flexible molecules, these empirical methods do not take into account molecular configurations which may depend on composition as well as temperature and density. This work reports some initial studies toward estimating quantitatively the thermodynamic properties (including phase equilibria) of real polyatomic fluids by molecular simulation. In this work we are concerned with hydrocarbons and with methane-hydrocarbon mixtures.

For simple fluids, such as the noble gases, spherically symmetric potentials are adequate for calculating thermodynamic properties. Polyatomic fluids are more adequately described by multicenter (site-site) intermolecular potentials; if interaction sites are assigned to specific chemical groups of a molecule, and if the corresponding site-site parameters are transferable from one molecule to another, then the intermolecular potential functions used to describe such fluids can provide the microscopic analog of conventional macroscopic group-contribution methods.

When a functional form for intermolecular interactions is established, calculation of macroscopic equilibrium properties requires either an analytic theory of fluids or simulation by computer. In this work, equilibrium properties of uniphase systems are obtained from Monte-Carlo simulations in the isobaric-isothermal *NPT* ensemble (Allen et al., 1987). Vapor-liquid equilibrium properties are obtained by Monte-Carlo simulations in the Gibbs ensemble (Panagiotopoulos et al., 1988).

The so-called Gibbs-ensemble simulation method (Panagiotopoulos et al., 1988) has provided a useful procedure for phase-equilibrium calculations. Because molecular simulations in the Gibbs-ensemble avoid the need for extensive iterative calculations, phase equilibria can now be simulated much more easily.

Simulations in the Gibbs ensemble have been carried out for a variety of systems, including fluids in small pores and membrane equilibria. Most of these studies, however, have been carried out for monatomic fluids (Panagiotopoulos et al., 1989).

Recently, we have presented some results of Gibbs-ensemble simulations for polyatomic fluids (De Pablo et al., 1989). The fluids analyzed in that study were lower alkanes; each methyl group (with its corresponding hydrogen atoms) was replaced by a distinct interaction site. That study, however, was limited to methane, ethane, propane and water.

In this work, we present a systematic study of phase equilibria for alkanes by molecular simulation. The fluids discussed in this work include chains of up to six carbon atoms (e.g. *n*-hexane). The intermolecular potentials used here are slight modifications of those presented by Jorgensen et al. (1984). In the first section of this work we briefly describe these intermolecular potential functions and some details concerning the computer simulations. In the second section, we show results of Monte-Carlo simulations in the *NPT* ensemble. The first and second section follow the procedure described by Jorgensen (1984). However, significant modifications have been made which enable the calculation of single-

phase properties over a wider range of density. In the third section we discuss results of Gibbs-ensemble simulations of pure alkanes, cyclopentane, cyclohexane and benzene. In the fourth section, we present results for a few binary mixtures at elevated pressures.

POTENTIAL-ENERGY CALCULATION

Effective Potential-Energy Functions

An alkane molecule is divided into sites according to its number of carbon atoms. The total potential energy is given by:

$$U(r_1, r_2, \dots, r_n) = \sum_{k < l < n} \sum u_2(r_k, r_l) + \sum_{k < l < m < n} \sum u_3(r_l, r_k, r_m) + \dots \quad (1)$$

where r_k is the coordinate vector of interaction site k , n is the total number of sites in the system, u_2 is the pair-interaction potential-energy function and u_3 is the three-body potential-energy function.

The total potential energy may be approximated as a sum of effective pair interactions over all pairs of sites (k, l):

$$U(r_1, r_2, \dots, r_n) = \sum_{k < l < n} \sum u_2^{eff}(r_k, r_l) \quad (2)$$

Three-body and higher multibody terms are included in the effective pair potential-energy function. Since these multibody terms are more important at liquid-like densities than at low (vapor) densities, the effective potential-energy function may show some dependence on density and temperature.

Intermolecular Potential-Energy Functions

For alkanes, we assume that interactions between sites of different molecules are of the Lennard-Jones (LJ) type. The multicenter intermolecular potential energy between two identical molecules i and j , each having m interaction sites, is calculated from:

$$u_{ij}^{eff}(r_i, r_j) = \sum_k^m \sum_l^m 4\epsilon_{ij}^{kl} \left[\left(\frac{\sigma_{ij}^{kl}}{r_{ij}^{kl}} \right)^{12} - \left(\frac{\sigma_{ij}^{kl}}{r_{ij}^{kl}} \right)^6 \right] \quad (3)$$

where k and l correspond to interaction sites located on molecules i and j , respectively. (The kl 's in Equation (3) are indices, not exponents).

The intermolecular potential functions used here are based on the work of Jorgensen et al.(1984). These functions are generally referred to as OPLS functions, an acronym for optimized potentials for liquid simulations. Table A.1 of the Appendix gives standard geometric parameters required for representing the hydrocarbons studied here.

While, in principle, every atom of a hydrocarbon molecule could be considered explicitly, in the OPLS formalism, hydrogen atoms are taken into account implicitly, as an integral part of a functional group or site. Jorgensen et al. (1984) reported site parameters that were adjusted by fitting experimental liquid densities and enthalpies of vaporization at the normal boiling point or at 25°C for a variety of hydrocarbons. These are recalled in the Appendix (Table A.2).

In their original work, Jorgensen et al. (1984) used geometric-mean combining rules to calculate cross-interaction parameters for functional groups of a different nature; the LJ parameters for the interaction between sites k and l are given by

$$\epsilon^{kl} = (\epsilon^k \epsilon^l)^{1/2} \quad (4a)$$

$$\sigma^{kl} = (\sigma^k \sigma^l)^{1/2} \quad (4b)$$

In this work, we also use a geometric-mean combining rule for the energy parameter (ϵ). However, for the size parameter we use an arithmetic-mean combining rule, i.e.

$$\sigma^{kl} = \frac{\sigma^k + \sigma^l}{2} \quad (5)$$

Equation (5) is exact for mixtures of hard spheres, a common starting point for analytical work (Hansen et al., 1986). Further, the results of recent Gibbs-ensemble simulations of mixtures of methane and ethane (Panagiotopoulos et al., 1989) indicate that Equation (5) is superior to Equation (4b).

The parameters shown in Table A.2 (Appendix) were developed in conjunction with Equations (4a) and (4b). Since our aim is to study mixtures of alkanes under an interaction-site formalism, we have readjusted some of these parameters, using Equation (5) instead of Equation (4b), toward improving agreement with experiment for mixtures.

The work of Jorgensen et al. (1984) indicates that site-site Lennard-Jones parameters are slightly density-dependent. Although, in principle, intermolecular potentials should not depend on density, the Lennard-Jones potential-energy functions used here describe "effective" pair-interactions which take into account neglected multi-body interactions. Because higher-order interactions are more important at higher densities, the effective pair-potential-energy functions are density-dependent. In this work, site-site-energy parameters (ϵ 's) vary linearly with site-density. This density dependence improves significantly agreement with experiment. To represent thermodynamic properties of liquids over an appreciable density range, we use for every site k - site k potential:

$$\frac{\epsilon^{kk}}{k_b} = A_{kk} \rho_{site} (\sigma^{kk})^3 + B_{kk} \quad (6)$$

where ρ_{site} = molar density of sites and σ^{kk} = Lennard-Jones size parameter for the k - k

interaction. The site-specific constants A_{kk} and B_{kk} are given in Table 4.

For example, when butane's density is 0.45 g/cm^3 ($\rho_{site} = 0.031 \text{ mol/cm}^3$), ϵ/k_b for $\text{CH}_3 - \text{CH}_3$ is 88.3 K . When the density is 0.61 g/cm^3 ($\rho_{site} = 0.042 \text{ mol/cm}^3$), ϵ/k_b for $\text{CH}_3 - \text{CH}_3$ is 99.8 K . At very low densities, results are not sensitive to the value of ϵ .

For site k - site l interactions, ϵ^{kl} is given by Equation (4a).

Intramolecular Potential-Energy Functions

In addition to contributions from intermolecular interactions, the potential energy of an alkane can also have contributions from intramolecular interactions. For non-cyclic alkanes, the latter are given by torsional potentials for rotations around carbon-carbon bonds, and by Lennard-Jones interactions between sites located on the same molecule but separated by more than three bonds.

Jorgensen et al. (1984) have also reported torsional potential functions for isolated alkanes. These functions are Fourier series, with coefficients V_i adjusted to fit the results of molecular-mechanics calculations:

$$u_{tor}(\phi_p) = V_0 + \frac{1}{2}V_1(1 + \cos \phi_p) + \frac{1}{2}V_2(1 - \cos 2\phi_p) + \frac{1}{2}V_3(1 + \cos 3\phi_p) \quad (7)$$

where ϕ_p is the dihedral angle for rotation around a carbon-carbon bond (p). Table A.3 of the Appendix gives the coefficients V_i for Equation (7).

Interaction sites separated by more than three bonds (as the CH_3 groups in n -pentane) interact through a Lennard-Jones potential.

The intramolecular potential for an alkane molecule (i) is calculated according to:

$$u_i(\Phi) = \sum_p u_{tor}(\phi_p) + \sum_{k'} \sum_{l'} 4\epsilon_{k'l'} \left(\left(\frac{\sigma_{k'l'}}{r_{k'l'}} \right)^{12} - \frac{\sigma_{k'l'}}{r_{k'l'}} \right)^6 \quad (8)$$

where the sum for rotational contributions to the energy extends over all those carbon-carbon bonds for which rotations are possible, and where the prime on the indices for the sums over non-bonded contributions indicates that these sums extend over all pairs of sites on molecule (i) separated by more than three bonds.

Total Potential Energy

For a system containing N molecules, the total potential energy is calculated by summing all inter- and intramolecular interactions according to

$$E_{pot} = \sum_i^N \sum_{j < i}^N j u_{ij}^{eff}(r_i, r_j) + \sum_i^N u_i(\phi) \quad (9)$$

Jorgensen et al.[1] calculate molar enthalpies of vaporization according to

$$\Delta H_{vap} = E_{intra}(gas) - [E_{inter}(liq) + E_{intra}(liq)] + P[v(gas) - v(liq)] \quad (10)$$

where subscripts *inter* and *intra* denote intermolecular and intramolecular molar energies, respectively; the molar volume is designated by v and P is the saturation pressure. Several approximations are implicit in Equation (10). First, it assumes that, at constant temperature, the sum of kinetic and vibrational energies is the same for liquid and vapor states. Second, it neglects contributions to the vapor-phase energy arising from intermolecular interactions; while this assumption is justified for very low vapor-phase densities, it is not valid for intermediate densities. For the vapor phase, Jorgensen et al. obtain E_{intra} from a simulation for an isolated molecule.

Following Jorgensen et al. (1984), for low-density vapors (ideal-gas behavior) we calculate the molar enthalpy of vaporization according to

$$\Delta H_{vap} = E_{intra}(gas) - E_{pot}(liq) + RT \quad (11)$$

where the molar volume of the liquid has been assumed to be much smaller than that of the equilibrium vapor and where the ideal-gas law is assumed to hold. Here, for very low vapor densities, we obtain E_{intra} from a Monte-Carlo simulation of 10 molecules in a highly dilute gas.

For intermediate-density vapors, the molar enthalpy of vaporization at temperature T is calculated according to

$$\Delta H_{vap} = E_{pot}(gas) - E_{pot}(liq) + P[v(gas) - v(liq)] \quad (12)$$

where E_{pot} is given by Equation (9). Gibbs-ensemble simulations yield the vapor and liquid orthobaric densities (and internal energies). For low to intermediate vapor densities, the pressure required for Equation (12) can be calculated by the ideal-gas law or by a virial expansion truncated after the second term. For simplicity, in this work we always use the ideal-gas law.

MONTE-CARLO SIMULATIONS

NPT Simulations

For the fluids studied here, isothermal-isobaric Monte-Carlo simulations with Metropolis sampling (Allen et al., 1987) were carried out on systems of 150 to 350 molecules in a cubic box. The periodic boundary conditions affect the simulation results if the size of the

box is too small compared to the correlation length in the fluid. The number of molecules considered is therefore chosen depending on the density of the phase simulated, so as to minimize these size effects. All simulations consisted of $5 \cdot 10^5$ particle-displacement steps for equilibration, followed by 10^6 additional steps for averaging. Volume changes were attempted after cycles of 500 particle-displacement steps. Depending on the temperature, the magnitudes of particle and volume displacement attempts were adjusted in such a way that roughly 50% of these moves were successful.

For *n*-butane and *n*-pentane, following the suggestion of Jorgensen et al. (1984), we use umbrella sampling over chopped rotational barriers.

The cyclohexane molecule is fixed into the chair conformation; its intramolecular energy is considered constant. The model used for the benzene molecule is a hexagon with fixed side lengths equal to the aromatic C-C bond length. Its intramolecular energy is also considered constant.

Intermolecular interactions were truncated according to a spherical cutoff (Allen et al., 1987). In all cases, the radius for cutoff was slightly smaller than half the average edge of the simulation box. Corrections to the potential energy arising from truncations to intermolecular interactions were incorporated into the simulations according to

$$E_{cut} = 2\pi N \sum_k^m \sum_l^m \int_{r_c}^{\infty} \rho r^2 g_{kl}(r) u_{ij}^{eff}(r) dr \quad (13)$$

where N is the number of molecules included in the simulation, m is the number of sites, r equals $r_i - r_j$, u_{ij}^{eff} is the site-site potential (see Equation (3)), ρ is the number density of the fluid, r_c is the cutoff radius, and $g_{kl}(r)$ is the radial distribution function for sites k and l , assumed to be unity beyond the cutoff.

Gibbs-Ensemble Simulations

Pure Fluids

Simulations in the Gibbs ensemble (Panagiotopoulos et al., 1988) were carried out in systems of 250 to 400 molecules. The procedure followed for these simulations was essentially identical to that followed for the *NPT* simulations; however, in addition to particle and volume displacements, Gibbs-ensemble simulations require particle exchanges between coexisting phases.

When this study was undertaken, it was not clear if the random insertion of a relatively long alkane molecule (e.g. *n*-pentane) into a dense liquid phase, consisting of similar molecules, would be possible. Dickman and Hall (1988), for example, have carried out grand-canonical simulations of athermal chain molecules and have found that for chains of four or more beads, successful insertions are extremely unlikely. For multicenter LJ fluids,

we have observed that successful molecule exchanges between coexisting phases are indeed difficult, particularly for cyclohexane at low temperatures (25°C). However, we have found that, for a large enough number of exchange trials, a sufficient fraction of these trials is successful; good statistics can therefore be achieved in a few hours computer time using an IBM 3090.

The initial configurations for Gibbs-ensemble simulations (i.e. the number of particles and the number density of coexisting phases) are chosen such that, during the simulation, the volumes of the liquid and vapor phases are large enough not to affect the results. A series of exchange trials is performed at the end of each cycle, immediately after a volume-change attempt. Depending on the temperature, the total number of exchange trials per cycle is adjusted such that not more than two or three particles are exchanged per cycle. Because saturated liquid density falls with rising temperature, the acceptance ratio for particle exchange increases with temperature, facilitating the calculation of phase equilibria at high temperatures, as reported in Table 3.

Mixtures

Gibbs-ensemble simulations for binary mixtures were carried out at constant pressure for systems of 200 to 450 molecules, depending on the densities. The simulation procedure for mixtures is identical to that for pure components, except that after choosing at random which of the coexisting phases is to receive a molecule, it is decided with a fixed probability which species is to be transferred; this probability is adjusted such that the number of successful transfers for both species is roughly the same. Finally, to obtain good statistics, the number of exchange trials for a simulation run is such that at least a few thousand are accepted.

RESULTS AND DISCUSSION

NPT Simulations

NPT simulations of several pure liquid hydrocarbons were carried out at constant temperature and at various pressures and compared with experimental data. The parameters reported by Jorgensen (1984) were used as a starting point. Some of the group-size parameters (σ 's) have been slightly modified (with respect to the OPLS parameters of Jorgensen et al., 1984) in accord with Equation (5) instead of Equation (4b). Further, NPT simulations at various densities were carried out for the hydrocarbons studied and the parameters were readjusted. Quantitative agreement is achieved when the energy parameter ϵ is site-density dependent. The site-density is defined as the total molar number of LJ-sites per cubic centimeter. Similar calculations at constant density and at various temperatures and pressures suggest that the temperature dependence of the effective potential functions is negligible.

Table 1 gives the parameters proposed in this work.

Table 1 - Coefficients for Density Dependence of Site-Site Energy Parameters for Hydrocarbons				
site	$\epsilon/k_b = A \rho_{sites} \sigma^3 + B$		σ (Å)	site-density range (mol/cm ³)
	A(K)	B(K)		
C	13.223	1.23	3.800	0.040-0.042
CH	8.278	18.80	3.850	0.038-0.045
CH ₂ (C ₂)	4.954	44.36	3.905	0.025-0.055
CH ₃ (C ₁)	10.359	83.80	3.775	0.036-0.043
CH ₃ (C ₂)	17.446	56.11	3.905	0.025-0.045
CH ₃ (C ₃)	7.020	65.63	3.930	0.038-0.045
CH ₃ (C ₄)	11.503	44.55	3.980	0.040-0.042
CH ₄	1.254	145.50	3.730	0.005-0.025
CH(arom.)	0.000	52.87	3.715	0.060-0.070

For a variety of alkanes, Table 2 shows calculated results for density and enthalpy of vaporization obtained from NPT simulations and the corresponding experimental values. These results were calculated with the parameters in Table 1.

Table 2 - Simulated and Experimental Near-Saturated Liquid Densities and Enthalpies of Vaporization for Hydrocarbon Liquids

liquid	$T(^{\circ}C)$	ρ (g/cm^3)		$-E_{pot}$ (kcal/mol)	ΔH_{vap} (kcal/mol)	
		(sim)	(exp)		(sim)	(exp)
methane	-161.49	0.421 $\pm$ .002	0.424	1.73 $\pm$ .03	1.95 $\pm$ .03	1.96
ethane	-173.00	0.642 $\pm$ .002	0.644	4.05 $\pm$ .03	4.25 $\pm$ .03	4.19
ethane	-88.63	0.548 $\pm$ .002	0.546	3.18 $\pm$ .03	3.55 $\pm$ .03	3.52
propane	-42.07	0.556 $\pm$ .004	0.581	3.71 $\pm$ .04	4.17 $\pm$ .04	4.49
<i>n</i> -butane	-42.07	0.641 $\pm$ .006	0.645	5.04 $\pm$ .06	5.86 $\pm$ .06	5.82
<i>n</i> -butane	25.00	0.574 $\pm$ .006	0.572	3.84 $\pm$ .06	5.08 $\pm$ .06	5.04
<i>n</i> -pentane	25.00	0.634 $\pm$ .006	0.621	4.63 $\pm$ .06	6.45 $\pm$ .06	6.32
<i>n</i> -hexane	25.00	0.663 $\pm$ .004	0.655	5.85 $\pm$ .07	7.59 $\pm$ .07	7.54
isobutane	-60.00	0.643 $\pm$ .006	0.645	5.20 $\pm$ .06	5.62 $\pm$ .06	5.59
isobutane	-11.42	0.590 $\pm$ .006	0.594	4.53 $\pm$ .06	5.05 $\pm$ .06	5.04
isobutane	25.00	0.552 $\pm$ .006	0.551	4.07 $\pm$ .06	4.61 $\pm$ .06	4.58
neopentane	9.50	0.601 $\pm$ .006	0.602	4.89 $\pm$ .06	5.45 $\pm$ .06	5.44
neopentane	25.00	0.585 $\pm$ .006	0.585	4.67 $\pm$ .06	5.26 $\pm$ .06	5.21
cyclopentane	-10.00	0.772 $\pm$ .006	0.774	6.71 $\pm$ .06	7.23 $\pm$ .06	7.18
cyclopentane	25.00	0.743 $\pm$ .006	0.740	6.27 $\pm$ .06	6.86 $\pm$ .06	6.82
cyclopentane	40.00	0.724 $\pm$ .006	0.726	6.00 $\pm$ .06	6.62 $\pm$ .06	6.65
cyclohexane	25.00	0.778 $\pm$ .004	0.774	9.43 $\pm$ .06	7.94 $\pm$ .06	7.86

All computer codes used for this work were developed at the University of California, Berkeley. To verify these codes, we have tried to duplicate most of the simulations reported by Jorgensen et al., (1984). While the results presented here are, in general, in good agreement with those of Jorgensen et al., we have found some small deviations for propane, isobutane, and neopentane at 25°C. The discrepancies for these liquids can be explained by their normal boiling points, which are well below 25°C; at 25°C and 1 atm, these fluids are in the vapor state. Since Jorgensen et al. appear to have carried out their simulations at 1 atm and 25°C, and since they report liquid-like densities, we assume that the systems simulated by these authors were in a hypothetical state.

Because of the site-density dependence assigned to the ϵ 's, agreement with experiment has been improved significantly and extended to a wider range of densities relative to the results presented earlier by Jorgensen et al.(1984). Satisfactory agreement between experimental and simulated densities was also achieved at high pressures for methane (800 atm) and butane (300 atm). However, experimental enthalpies of vaporization are not available at these pressures and therefore, the results were not included in Table 2.

Gibbs-Ensemble Simulations

The results presented here show that the multicenter potential functions used by Jorgensen (1984), modified as explained above, can successfully be applied to vapor-liquid equilibrium calculations. Table 3 shows calculated values of orthobaric densities from Gibbs-ensemble simulations of alkanes, using the site parameters determined by single-phase simulations. Since the densities of the vapor phase are small, the value of the energy parameter ϵ used for the vapor phase energy calculations has no noticeable influence. Therefore, for simplicity, we use the same values of epsilon for the liquid and the vapor phases. Table 3 also shows corresponding experimental values.

The last column of Table 3 indicates the percentage of particle-exchange trials that are successful. For example, for *n*-butane at 25°C, out of a million exchange trials, only about 200 are successful.

Table 3 - Orthobaric Densities of Saturated Alkanes from Monte-Carlo Simulations in the Gibbs Ensemble						
fluid	<i>T</i> (°C)	ρ_l (g/cm ³)		ρ_v (g/cm ³)		successful insertions %
		(sim)	(exp)	(sim)	(exp)	
ethane	-88.8	0.557 ±.006	0.544	0.0021 ±.0004	0.0020	0.01
ethane	-58.6	0.515 ±.006	0.504	0.0072 ±.0004	0.0074	0.05
ethane	-39.1	0.477 ±.006	0.476	0.0014 ±.0004	0.0014	0.02
propane	-42.1	0.558 ±.005	0.581	0.0034 ±.0003	0.0024	0.02
propane	25.0	0.460 ±.007	0.497	0.0023 ±.0004	0.020	0.05
<i>n</i> -butane	50.0	0.538 ±.006	0.542	0.012 ±.002	0.012	0.04
<i>n</i> -pentane	100.0	0.551 ±.007	0.538	0.016 ±.003	0.016	0.04
isobutane	37.7	0.530 ±.008	0.536	0.0114 ±.001	0.0128	0.02
neopentane	37.7	0.578 ±.008	0.569	0.006 ±.0008	0.007	0.01
cyclopentane	100.0	0.671 ±.007	0.665	0.009 ±.002	0.009	0.08
cyclohexane	100.0	0.697 ±.007	0.700	0.006 ±.001	0.005	0.06
benzene	77.0	0.819 ±.009	0.827	0.002 ±.0005	0.002	0.08

Phase Equilibria for Mixtures

Gibbs-ensemble calculations were performed for the methane-*n*-pentane, methane-benzene and methane-cyclohexane systems. These systems were chosen first, because phase-equilibrium data are available over a wide range of temperature, and second, because these three mixtures exhibit retrograde condensation which often cannot be well predicted by conventional equations of state.

Given an estimate of the site density of the liquid phase, the epsilon values required for the different sites present in the mixture are calculated through the linear functions given in Table 1. These values can be then be more precisely fixed by using the density results of the simulation; these most depend on the sigma values.

Figure 1 shows a pressure-density and a pressure-composition diagram at 104.4 °C for the methane-*n*-pentane system. The results are also given in Tables 4 and 5. The pressure-composition diagram for the methane-cyclohexane system at 137.8°C is shown in Figure 2. Tables 6 and 7 report the results obtained for the methane-cyclohexane system at 137.8°C and for the methane-benzene system at 227°C, respectively. The square symbols show estimated value and standart deviation of simulations in the Gibbs ensemble. The solid circles represents experimental data. For the pressures studied here, agreement with experiment is remarkable for the two first systems. For the methane-benzene system, however, the Lennard-Jones multicenter potential model does not represent the coexistence curve. Since the calculated vapor-composition curve crosses the experimental curve, the deficiency of the model is not merely due to inadequate parameters, but to the form of the molecular model.

**Table 4 - Methane (1) - n-Pentane (2) Densities from
Monte-Carlo Simulations in the Gibbs Ensemble at 104.4 °C**

<i>P</i> (atm)	ρ_l (g/cm ³)		ρ_v (g/cm ³)		N methane	N pentane
	(sim)	(exp)	(sim)	(exp)		
13.60	0.0074±.0002	0.0074	0.0005 ±.00005	0.0005	20	280
25.24	0.0075±.0002	0.0076	0.0010 ±.00005	0.0010	50	240
40.82	0.0077±.0001	0.0078	0.0015 ±.00008	0.0015	80	220
54.44	0.0080±.0001	0.0080	0.0021 ±.00009	0.0020	120	240
68.05	0.0081±.0002	0.0081	0.0025 ±.0001	0.0026	140	220
85.06	0.0082±.0001	0.0083	0.0033 ±.0001	0.0034	180	210
102.07	0.0082±.0002	0.0084	0.0040 ±.0003	0.0042	200	200

Table 5 - Methane (1) - n-Pentane (2) Vapor-Liquid Equilibria from Monte-Carlo Simulations in the Gibbs Ensemble at 104.4 °C						
P (atm)	x ₁		y ₁		successful insertions (%)	
	(sim)	(exp)	(sim)	(exp)	methane	pentane
13.61	0.030 ±.0	0.030	0.472 ±.0	0.472	4.0	0.2
25.24	0.094 ±.012	0.087	0.711 ±.028	0.685	5.0	0.2
40.82	0.137 ±.007	0.143	0.775 ±.015	0.757	6.0	0.3
54.44	0.193 ±.007	0.198	0.808 ±.009	0.788	6.0	0.3
68.05	0.252 ±.009	0.251	0.805 ±.014	0.798	7.6	0.6
85.06	0.310 ±.030	0.340	0.808 ±.024	0.801	7.5	0.5
102.07	0.395 ±.014	0.382	0.811 ±.034	0.794	10.0	0.1

x = mole fraction in liquid

y = mole fraction in vapor

Table 6 - Methane (1) - Cyclohexane (2) Vapor-Liquid Equilibria from Monte-Carlo Simulations in the Gibbs Ensemble at 137.8 °C						
P (atm)	x ₁		y ₁		successful insertions (%)	
	(sim)	(exp)	(sim)	(exp)	methane	cyclohexane
13.61	0.040±.017	0.025	0.727 ±.020	0.652	3.0	0.10
27.22	0.053±.007	0.060	0.815 ±.022	0.799	3.6	0.10
40.84	0.098±.016	0.095	0.833 ±.018	0.846	3.4	0.09
54.45	0.115±.007	0.129	0.858 ±.011	0.871	3.0	0.08
68.06	0.157±.015	0.163	0.908 ±.017	0.885	3.8	0.16
85.08	0.225±.020	0.205	0.910 ±.015	0.894	3.3	0.14
102.09	0.250±.014	0.247	0.909 ±.015	0.897	3.6	0.16
119.11	0.277±.007	0.289	0.906 ±.012	0.896	5.0	0.22

Table 7 - Methane (1) - Benzene (2) Vapor-Liquid Equilibria from Monte-Carlo Simulations in the Gibbs Ensemble at 228.0 °C						
P (atm)	x_1		y_1		succesful insertions (%)	
	(sim)	(exp)	(sim)	(exp)	methane	benzene
50.58	0.072±.007	0.065	0.459 ±.033	0.448	8.5	1.1
72.03	0.117±.009	0.114	0.578 ±.047	0.533	12.1	2.2
100.26	0.180±.012	0.181	0.603 ±.045	0.571	10.9	1.7
125.39	0.243±.010	0.246	0.600 ±.050	0.556	13.6	2.2
134.92	0.262±.023	0.284	0.610 ±.045	0.542	12.9	1.9
143.70	0.315±.016	0.324	0.491 ±.021	0.515	14.8	2.4

Comparison of the Flexible Multisite Model to Simpler Models

Simulations of the methane-*n*-pentane system at 104.4 °C were also performed using three simple molecular models for *n*-pentane molecules: Lennard-Jones spheres, ellipsoids interacting through a Lennard-Jones potential function, rigid molecules with a fixed unique conformation. The results were compared to the experimental data as well as to the flexible multicenter potential model calculations. The Gibbs-ensemble method used is the same as that described earlier.

Spherical Model

The *n*-pentane molecule is described by a single Lennard-Jones site. The energy and size parameters are derived from critical density ρ_c and critical temperature T_c using $k_b \frac{T_c}{\epsilon} = 1.31$ and $\rho_c \sigma^3 = 0.31$ as estimates for the reduced critical properties of the three-dimensional LJ fluid (Panagiotopoulos, 1987, Smit et al., 1989). The parameters are $\frac{\epsilon}{k_b} = 358.5 \text{ K}$ and $\sigma = 5.27 \text{ Å}$.

The results are presented in Tables 8 and 9 and plotted on Figure 3. Simulations yield satisfactory agreement with the experimental densities, confirming the value chosen for size parameter σ . The discrepancies between calculated and experimental compositions are significant, pointing out the inadequacies of the spherical model. Any adjustment of the energy parameter ϵ provides only a translation of the vapor pressure-composition curve, without significantly correcting the curvature.

Table 8 - Methane (1) - n-Pentane (2) Densities from Monte-Carlo Simulations in the Gibbs Ensemble Using a Spherical Model for n-Pentane at 104.4 °C

P (atm)	ρ_l (g/cm ³)		ρ_v (g/cm ³)		N	
	(sim)	(exp)	(sim)	(exp)	methane	pentane
25.24	0.0078±.0002	0.0076	0.0010 ±.0001	0.0010	50	240
40.82	0.0080±.0003	0.0078	0.0016 ±.0002	0.0015	80	220
54.44	0.0080±.0003	0.0080	0.0020 ±.0002	0.0020	120	240
68.05	0.0083±.0002	0.0081	0.0027 ±.0002	0.0026	140	220
85.06	0.0077±.0003	0.0083	0.0037 ±.0005	0.0034	180	210

Table 9 - Methane (1) - n-Pentane (2) Vapor-Liquid Equilibria from Monte-Carlo Simulations in the Gibbs Ensemble Using a Spherical Model for n-Pentane at 104.4 °C

P (atm)	x_1		y_1		successful insertions (%)	
	(sim)	(exp)	(sim)	(exp)	methane	pentane
25.24	0.100 ±.005	0.087	0.546 ±.045	0.685	9.7	1.4
40.82	0.151 ±.010	0.143	0.614 ±.044	0.757	8.2	1.2
54.44	0.231 ±.015	0.198	0.683 ±.042	0.788	11.6	2.3
68.05	0.298 ±.010	0.251	0.714 ±.027	0.798	12.1	2.4
85.06	0.457 ±.016	0.340	0.751 ±.054	0.801	13.3	2.8

Ellipsoid Model

The ellipsoid used to describe the *n*-pentane molecule has the same volume as that of the sphere considered above. It is described in terms of the Lennard-Jones potential by a single energy parameter ϵ and two geometric parameters σ_1 and σ_2 . The size parameter σ entering in the potential energy function is a function of σ_1 , σ_2 and the relative orientation of the interacting molecules *i* and *j*.

$$u_{ij}^{eff}(r_i, r_j) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (14)$$

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2} \quad (14a)$$

$$\sigma^{ij} = \frac{\sigma^i + \sigma^j}{2} \quad (14b)$$

where, if i refers to a n -pentane molecule,

$$\sigma_i = \sigma_1 \cos \theta + \sigma_2 \sin \theta \quad (14c)$$

θ is the angle between the r_{ij} position vector and the main axis of the n -pentane ellipsoid.

The length-to-width ratio of the ellipsoid ($\frac{\sigma_1}{\sigma_2}$) is chosen so as to equal the geometric length-to-width ratio of the trans-trans conformation. The parameters used are:

$\frac{\epsilon}{k_b} = 358.5 \text{ K}$, $\sigma_1 = 6.434 \text{ \AA}$ and $\sigma_2 = 4.770 \text{ \AA}$. The results are presented in Tables 10 and 11 and plotted on Figure 4. For the density, agreement with experiment is satisfactory over the whole pressure range; this confirms the adequacy of the values chosen for size parameters σ_1 and σ_2 . The methane mole fraction in the gas, however, is underpredicted when compared to experimental data and when compared to multicenter potential computation results. Better agreement can be reached by increasing slightly the energy parameter of the ellipsoid. Such adjustment, however, deprives the method from its predictive power. Further, it is likely that the ellipsoid model would be unsuitable for chains longer than pentane.

**Table 10 - Methane (1) - n-Pentane (2) Densities from
Monte-Carlo Simulations in the Gibbs Ensemble
Using an Ellipsoid Model for n-Pentane at 104.4 °C**

P (atm)	ρ_l (g/cm ³)		ρ_v (g/cm ³)		N methane	N pentane
	(sim)	(exp)	(sim)	(exp)		
25.24	0.0073±.0002	0.0076	0.0010 ±.0002	0.0010	50	240
40.82	0.0079±.0002	0.0078	0.0014 ±.0002	0.0015	80	220
54.44	0.0079±.0003	0.0080	0.0019 ±.0003	0.0020	120	240
68.05	0.0083±.0002	0.0081	0.0027 ±.0004	0.0026	140	220
85.06	0.0083±.0002	0.0083	0.0031 ±.0002	0.0034	180	210
102.07	0.0088±.0003	0.0084	0.0042 ±.0004	0.0042	200	200

**Table 11 - Methane (1) - n-Pentane (2) Vapor-Liquid Equilibria from
Monte-Carlo Simulations in the Gibbs Ensemble
Using an Ellipsoid Model for n-Pentane at 104.4 °C**

<i>P</i> (atm)	<i>x</i> ₁		<i>y</i> ₁		successful insertions (%)	
	(sim)	(exp)	(sim)	(exp)	methane	pentane
25.24	0.107 ±.006	0.087	0.631 ±.058	0.685	9.4	1.5
40.82	0.154 ±.010	0.143	0.713 ±.037	0.757	8.7	1.2
54.44	0.223 ±.010	0.198	0.730 ±.040	0.788	8.6	1.2
68.05	0.281 ±.010	0.251	0.756 ±.023	0.798	10.1	1.6
85.06	0.317 ±.016	0.340	0.760 ±.034	0.801	10.3	1.6
102.07	0.403 ±.015	0.382	0.767 ±.035	0.794	10.0	1.4

Rigid Molecular Model

The pentane molecule was described with the same multicenter potential, but the two rotational degrees of freedom (around C-C bounds) were removed. Using simulations with the flexible-multicenter molecular model, the distribution of t-t, t-g, g+g+ and g-g+ conformations had been determined in the liquid and in the vapor phase of the methane-*n*-pentane mixture at 104.4 °C. (Here t stands for trans and g stands for gauche.) Because the t-t conformation is that most frequently (> 80%) adopted by the *n*-pentane molecules under these conditions, we fix the *n*-pentane molecules in this conformation. The calculated results are compared to experimental data in Tables 12 and 13.

Table 12 - Methane (1) - n-Pentane (2) Densities from Monte-Carlo Simulations in the Gibbs Ensemble With Rigid Trans-Trans n-Pentane Molecules at 104.4 °C						
<i>P</i> (atm)	ρ_l (g/cm ³)		ρ_v (g/cm ³)		N methane	N pentane
	(sim)	(exp)	(sim)	(exp)		
13.61	0.0074±.0002	0.0074	0.0007 ±.0001	0.0005	20	280
40.82	0.0076±.0002	0.0078	0.0013 ±.0001	0.0015	80	220
68.05	0.0080±.0002	0.0081	0.0025 ±.0002	0.0026	140	220
102.07	0.0085±.0002	0.0084	0.0038 ±.0004	0.0042	200	200

Table 13 - Methane (1) - n-Pentane (2) Vapor-Liquid Equilibria from Monte-Carlo Simulations in the Gibbs Ensemble with Rigid Trans-Trans n-Pentane Molecules at 104.4 °C						
<i>P</i> (atm)	x_1		y_1		successful insertions (%)	
	(sim)	(exp)	(sim)	(exp)	methane	pentane
13.61	0.039 ±.004	0.030	0.532 ±.03	0.472	4.8	0.2
40.82	0.162 ±.012	0.143	0.802 ±.02	0.757	6.9	0.5
54.44	0.238 ±.011	0.251	0.833 ±.02	0.798	7.9	0.6
68.05	0.353 ±.010	0.382	0.863 ±.02	0.794	7.3	0.5

Figure 5 shows that, upon restricting conformations of *n*-pentane, slightly lower simulated densities are obtained for the liquid phase. The volume of the rigid t-t *n*-pentane molecule is larger than that of the flexible molecule averaged over all conformations. The simulated composition coexistence curve overpredicts the methane content of the vapor.

However, if the *n*-pentane molecules are allowed to adopt t-t, t-g and g+g+ conformations with probabilities determined from the simulations with the flexible model (the g+g- population is negligibly small under these conditions), the densities and compositions of the vapor and liquid phases are predicted in good agreement with experiment.

CONCLUSION

The multicenter Lennard-Jones potential, with a linear site-density dependence of the epsilon parameters, permits representation of liquid densities and enthalpies of vaporization

of some lower alkanes over a wide range of temperature. When the site-site parameters are adjusted to optimize the fit of the densities and enthalpies of vaporization of these lower alkanes, good predictions are obtained for the properties of *n*-pentane, *n*-hexane and cyclohexane.

Gibbs-ensemble simulations can be used to calculate vapor-liquid equilibria for moderately long molecules. While the transfer of particles between coexisting phases becomes increasingly difficult at low temperatures, for the systems and conditions studied here, a few thousand successful transfers can be achieved in 5-8 hours (real computer time) on an IBM 3090. Corresponding time on a Cray supercomputer is 1-3 hours.

Phase-equilibrium Monte-Carlo simulations for methane-hydrocarbon mixtures can yield orthobaric compositions in good agreement with experiment. Under certain conditions of pressure and temperature, the mixtures studied here (methane/*n*-pentane, methane/cyclohexane and methane/benzene) exhibit retrograde condensation. It appears that, with care, Monte-Carlo simulations can represent the retrograde properties of the first two mixtures. Upon comparing the results using the multicenter Lennard-Jones potential with those based on simpler models, it appears that it is necessary to give attention to the configurational degrees of freedom of the alkane molecules (i.e. torsion about C-C bonds) to predict liquid-vapor equilibrium compositions. This comparison suggests that the retrograde effect can be represented with a simple ellipsoid model for the *n*-pentane molecule, indicating that this effect may be mostly due to the non-sphericity of the *n*-pentane molecule. However, for larger paraffins, we anticipate that successful calculations will require that consideration be given to the effect of molecular conformation.

Only simple alkanes and benzene have been studied here; therefore this work provides only a small first step towards building a more complete data bank, similar to those available for conventional group-contribution methods such as UNIFAC. The results obtained here suggest that it may be worthwhile to consider a concerted effort toward constructing a large site-site-potential data base obtained from readily available phase-equilibrium data. While computer requirements are as yet very high, it is likely that developments in computer hardware and software will reduce this requirement substantially within a five or ten years.

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Literature Cited

Allen M.P., and Tildesley D.J., 1987. *Computer Simulation of Liquids*, Clarendon Press, Oxford.

De Pablo J.J., and J.M. Prausnitz, 1989. "Phase Equilibria for Fluid Mixtures from Monte-Carlo Simulation," *Fluid Phase Eq.*, 53, 177.

Dickman R., and C.K. Hall, 1988. "High Density Monte Carlo Simulations of Chain Molecules: Bulk Equation of State and Density Profile Near Walls," *J.Chem.Phys.*, 89, 3168.

Hansen J.P., and I.R. McDonald, 1986. *Theory of Simple Liquids*, 2nd. edtn., Academic Press.

Jorgensen W.L., J.D. Madura, and C.J. Swenson, 1984. "Optimized Intermolecular Potential Functions for Liquid Hydrocarbons," *J.Am.Chem.Soc.*, 106, 6638.

Panagiotopoulos A.Z., 1987. "Direct Determination of Phase Coexistence Properties of Fluids by Monte-Carlo Simulation in a new Ensemble", *Mol.Phys.*, 61, 813.

Panagiotopoulos A.Z., N. Quirke, M. Stapleton, and D.J. Tildesley, 1988. "Phase Equilibria by Simulation in the Gibbs Ensemble," *Mol.Phys.* 63, 527.

Panagiotopoulos A.Z., and M.R. Stapleton, 1989. "The Gibbs Method for Molecular-Based Computer Simulations of Phase Equilibria," *Fluid Phase Eq.*, 53, 133.

Reid R.C., J.M. Prausnitz, and B. Poling, 1987. *The Properties of Gases and Liquids*, 4th edtn., McGraw Hill.

Smit B., De Smeth Ph., Frenkel D., 1989. "Computer Simulations in the Gibbs Ensemble", *Mol.Phys.*, 68, 931.

APPENDIX

Geometric and Potential-Function Parameters

Table A.1 - Standart Geometric Parameters for Hydrocarbons†			
bond lengths (Å)		bond angles (deg)	
C4 - C4	1.53	C-C4-C	112
C3 = C3	1.34		
C3 - C3 ††	1.397	C-C3-C	120

† Following Jorgensen et al.(1984), C4 and C3 are sp^3 and sp^2 carbons, respectively.

†† Aromatic CC bond.

Table A.2 - Optimized Lennard-Jones Parameters for Hydrocarbons†			
site	example	σ (Å)	$\frac{\epsilon}{k_b}$ (K)
CH ₄	methane	3.730	148.0
CH ₃ (C ₁)††	ethane	3.775	104.2
CH ₃ (C ₂)††	n-butane	3.905	88.1
CH ₃ (C ₃)††	isobutane	3.910	80.6
CH ₃ (C ₄)††	neopentane	3.960	73.0
CH ₂ (sp^3)	n-butane	3.905	59.4
CH ₂ (sp^2)	1-butene	3.850	70.5
CH (sp^3)	isobutane	3.850	40.3
CH (arom.)	benzene	3.750	55.4
C (sp^3)	neopentane	3.800	52.9

† From Jorgensen et al. (1984).

†† (C_i) indicates that the number of non-hydrogen attachments of the adjacent carbon atom is equal to i.

Table A.3 - Fourier Coefficients for Intramolecular Rotational Potential Functions†				
molecule	V_0	V_1	V_2	V_3
1-butene	1.363	0.343	-0.436	-1.121
isopentane	2.713	1.526	0.533	-3.453
n-butane	0	1.522	-0.315	3.207
other <i>n</i> -alkanes	0	1.411	-0.271	3.145

† From Jorgensen et al.(1984). The units are kcal/mol.

FIGURE

CAPTIONS

- 1 Simulated and Experimental Pressure-Density and Pressure-Composition Coexistence Curves for the Methane-*n*-Pentane System at 104.4°C
- 2 Simulated and Experimental Pressure-Composition Coexistence Curve for the Methane-Cyclohexane System at 137.8°C
- 3 Simulated and Experimental Pressure-Density and Pressure-Composition Coexistence Curves for the Methane-*n*-Pentane System at 104.4°C with *n*-Pentane Molecules as LJ-Spheres
- 4 Simulated and Experimental Pressure-Density and Pressure-Composition Coexistence Curves for the Methane-*n*-Pentane System at 104.4°C with *n*-Pentane Molecules as Ellipsoids
- 5 Simulated and Experimental Pressure-Density and Pressure-Composition Coexistence Curves for the Methane-*n*-Pentane System at 104.4°C with Rigid (trans-trans Conformation) *n*-Pentane

Fig. 1 : Simulated and Experimental Pressure-Density and Pressure-Composition Coexistence Curves for the Methane-n-Pentane System at 104.4°C

Fig. 2 : Simulated and Experimental Pressure-Composition
Coexistence Curve for the Methane-Cyclohexane System at 137.8 °C

Fig. 3 : Simulated and Experimental Pressure-Density and Pressure-Composition Coexistence Curves for the Methane-n-Pentane System at 104.4°C with Pentane Molecules as LJ-Spheres

Fig. 4 : Simulated and Experimental Pressure-Density and Pressure-Composition Coexistence Curves for the Methane-n-Pentane System at 104.4°C with Pentane Molecules as Ellipsoids

Fig. 5 : Simulated and Experimental Pressure-Density and Pressure-Composition Coexistence Curves for the Methane-n-Pentane System at 104.4°C with Rigid (trans-trans Conformation) Pentane

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