

Excess Thermodynamic Properties of Chainlike Mixtures. 1. Predictions from the *Soft*–SAFT Equation of State and Molecular Simulation

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Monte Carlo simulation and theory are used to calculate excess thermodynamic properties of binary mixtures of Lennard-Jones chains. Chainlike molecules are formed by Lennard-Jones spherical sites that are tangentially bonded. This molecular model accounts explicitly for the most important microscopic features of real chainlike molecules, such as *n*-alkanes: repulsive and attractive forces between chemical groups and the connectivity of segments to make up the chain. A version of the statistical associating fluid theory, the so-called *Soft*–SAFT equation of state, is used to check the theory's ability to predict this kind of property. Predictions from the theory are directly compared to NPT Monte Carlo simulation results obtained in the present work. The influence of segment size, dispersive energy, and chain length on excess properties is studied using simulation and theory, and results are analyzed and discussed. The equation of state is then used to predict the general trends of some excess thermodynamic properties of real *n*-alkane binary mixtures, such as excess volumes and heats. In particular, the temperature and chain-length dependence of these properties is studied. The *Soft*–SAFT theory is found to be able to correctly describe the most important features of excess thermodynamic properties of *n*-alkane models.

1. Introduction

The knowledge of thermodynamic properties and phase equilibria of fluid systems, such as hydrocarbons and, in particular, *n*-alkanes, is central to chemical process design in the traditional chemical and oil industries. Applications include supercritical fluid extraction, chromatography, surfactancy, and development of separation and extraction processes.^{1–3} The extent to which real liquid mixtures deviate from ideality is best expressed through the use of thermodynamic excess properties, such as excess volumes, heats, and Gibbs free energies, at vapor pressures of less than a few bars.⁴ Nowadays, and from an experimental point of view, scientists tabulate the results of their measurements on the thermodynamic properties of nonideal mixtures in this form. Such data are used extensively in a wide variety of scientific and technical fields, including chemistry, spectroscopy, and chemical engineering. The optimum operation working conditions and design of chemical reactors, distillation columns, and other separation devices critically depend on the accuracy for predicting this kind of experimental information. From a theoretical point of view, the excess thermodynamic functions are also valuable information because classical equations of state and other advanced modeling techniques, such as those based on statistical mechanics, lead naturally to the prediction of theoretical values of excess properties.

Much experimental work about excess thermodynamic properties of binary mixtures of *n*-alkanes is found in the literature. These kinds of systems were extensively studied between 1950 and 1970 because of the industrial importance of such mixtures; the studies also were inspired by a desire to test the empirical principle of congruence put forward by Bronsted and Koefoed in 1946.^{4,5} The most accurate results are those of McGlashan and co-workers^{6–8} and measurements from other researchers.^{9–11}

Recently, precise values for all the principal excess functions have been published for *n*-hexane + *n*-decane, and + *n*-undecane.^{12,13}

Experimental data often are not available at all thermodynamic conditions of temperature and composition, and for all members of a given chemical family, such as *n*-alkanes. In addition, such data may be difficult and expensive to obtain experimentally in some cases. In this situation, an equation of state or any other theoretical approach is highly desirable.

Correlations and macroscopic equations traditionally used in the chemical industry do not correctly predict the thermodynamic behavior of complex fluid mixtures. Simple correlations, such as the Redlich–Kister equation,^{14–16} have parameters with no physical meaning; more sophisticated theories, such as UNIQUAC,¹⁷ NRTL,¹⁷ or DISQUAC,^{17,18} have little predictive power at thermodynamic conditions far away from those at which the parameters are fitted. In essence, this inability to predict is due to the fact that the microscopic features of real systems are not explicitly accounted for. In addition, these later theories cannot describe excess thermodynamic functions based on volumetric properties, such as the excess volume, because they are based on the assumption of a rigid lattice model.

Molecular-based theories constitute alternative methods that correctly describe the thermodynamics and phase behavior of complex systems. They are based on knowledge of the intermolecular interaction forces between the molecules that form the system. These forces depend on molecular parameters with physical meaning, such as molecular sizes and dispersive energies. Because they are microscopic, the forces do not depend on thermodynamic conditions, such as pressure, temperature, and composition. This leads to theories with high predictive power far away from conditions at which the molecular parameters are correlated.

Molecular methods can be classified in two different

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groups: molecular simulations and analytical theories.^{19,20} Molecular simulations can be used to determine whether a given intermolecular potential is suitable for describing different systems, as well as to test the accuracy of a theory.^{21,22} In this later use, molecular simulations constitute a valuable tool because they allow testing of the approximations made to obtain analytical molecular-based equations of state.^{21,22} Unfortunately, little work has been done in calculating excess functions for Lennard-Jones chainlike binary mixtures using molecular simulation. By the 1970s, McDonald^{23,24} and Singer and Singer²⁵ had performed a detailed study to understand the effect that molecular parameters, such as segment size and dispersive energy, of binary mixtures of Lennard-Jones spheres had on the principal excess functions. These later authors have shown that the Lorentz–Berthelot combining rules can predict negative values of all three major excess functions (V^E , H^E , G^E) for particular values of the molecular parameters. In general, G^E is more positive when the dispersive energy ratio $\epsilon_{12}/\epsilon_{11}$ is decreased; for molecules with equal dispersive energies, $\epsilon_{11} = \epsilon_{22}$, G^E becomes more negative with decreasing values of the σ_{12}/σ_{11} ratio.^{4,25} These authors found a similar behavior for the excess molar enthalpy and excess molar volume.^{4,25} More recently, Fotouh and Shukla^{26,27} have performed NPT molecular dynamic simulations to obtain all three major excess thermodynamic properties of binary and ternary mixtures of Lennard-Jones spheres. They have also considered two-center Lennard-Jones molecules and point quadrupolar interactions, and have studied the effect of the molecular elongation and quadrupole on excess properties. These authors have compared their simulation data with the van der Waals one-fluid theory and a new statistical mechanics perturbation theory developed by Fotouh and Shukla.²⁸ The authors found that both theories yield a reasonable description of simulation data, although the perturbation theory seems to be superior to the traditional van der Waals theory.

The statistical associating fluid theory (SAFT)^{29,30} is a molecular-based equation of state, originally developed from Wertheim's first-order perturbation theory for associating fluids^{31–36} by Jackson et al.,³⁷ Chapman et al.,³⁸ and Wertheim^{35,36} in the late 1980s. SAFT is specifically designed to deal with chainlike molecules, such as hydrocarbons, and associating substances, such as water and alcohols. The SAFT approach has since been used to predict the phase equilibria behavior of a wide variety of pure components and their mixtures, and nowadays is considered one of the most powerful predictive tools for the study of fluid phase equilibria.

The SAFT approach was first proposed and defined by Chapman et al.^{29,30} It means, in general, to combine a chain reference contribution with an associating perturbation term for the description of real fluids. SAFT was first applied as an equation of state for real fluids by Huang and Radosz.^{39,40} Subsequently, many variations have been made on the original approach. Here we will summarize only the most widely used versions in the literature that correctly describe the thermodynamics and phase equilibria behavior of real systems.

The simplest version of SAFT, SAFT–HS, developed by Jackson et al.³⁷ and Chapman et al.,³⁸ models the chains as hard-sphere segments tangentially bonded with attractive interactions described at the mean-field level of the van der Waals theory. Although this equation has been successfully applied for predicting the phase equilibria behavior of systems in which one or two components are strongly associated, such as alkane + water,⁴¹ refrigerant + hydrogen fluoride,⁴² and water +

alkylpolyoxyethylenes,^{43,44} it is not adequate for systems in which the dispersive interactions play a dominant role, such as alkanes.

Recently, Gil-Villegas et al.⁴⁵ and Galindo et al.⁴⁶ have proposed a new version of SAFT, called SAFT–VR, to deal with systems that have attractive potentials of variable range. This new approach can accurately predict the phase equilibria behavior of chain molecules formed by tangent segments with attractive interactions (modeled as square-well potentials), such as *n*-alkanes, perfluoroalkanes, and their mixtures,^{46–49} hydrogen fluoride + water,⁵⁰ refrigerant systems,⁵¹ hydrogen chloride + *n*-alkanes,⁵² reacting systems (formaldehyde + water),⁵³ and electrolyte solutions.⁵⁴ The advantage of SAFT–VR is the wide range of potentials that could be treated through it, such as Lennard-Jones⁵⁵ and Yukawa⁵⁶ systems.

Other versions of SAFT, specific to systems with intermolecular Lennard-Jones interactions, have been introduced and developed by several authors. Chapman and co-workers were the first to extend the SAFT approach to deal with associating Lennard-Jones spheres⁵⁷ and associating Lennard-Jones dimers.⁵⁸ Johnson and Gubbins⁵⁹ have used the SAFT equation to study pure diatomic Lennard-Jones molecules. Chapman and co-workers^{60,61} have also extended the SAFT theory accounting for both pure and binary mixtures of Lennard-Jones chains. Johnson et al.⁶² have proposed a new version of the SAFT equation for pure Lennard-Jones chains, using accurate simulation data for the pair radial distribution function. All the predictions presented in these later works^{57–62} have been tested against computer simulation. Kraska and Gubbins^{63,64} have extended the SAFT approach for Lennard-Jones systems including a specific Helmholtz free energy due to electrostatic contributions. These authors have applied the resulting equation to describe pure and binary mixtures of real *n*-alkanes and 1-alkanols, finding an excellent agreement with experimental data. A more recent version of SAFT, the so-called *Soft*–SAFT equation of state, specific to Lennard-Jones chains, has been applied by Blas and Vega, and extended to deal with mixtures of both homonuclear and heteronuclear Lennard-Jones chains.⁶⁵ This theory has proved to be highly accurate in predicting thermodynamic properties and phase equilibria behavior of both model and real hydrocarbon mixtures.^{65,66} In particular, this version of SAFT can predict the anomalous low critical pressure of methane with the *n*-alkane homologous series,⁶⁶ the transition from type I to type V phase behavior in the methane + *n*-alkane binary mixtures,⁶⁷ and the tricritical behavior of methane + pseudoalkane binary mixtures.^{68,69} The advantage of *Soft*–SAFT versus other simplified versions of SAFT, such as SAFT–HS or SAFT–VR, is that *Soft*–SAFT incorporates in the same term, namely, the Lennard-Jones contribution, both the attractive and dispersive forces between the segments that form the chain, instead of considering additional perturbation theories over the hard-sphere fluid to account for the attractive interactions.

Although the SAFT approach has been widely used to predict the phase equilibria of many different model and real systems, there is little work about the ability of SAFT in predicting other properties, such as excess thermodynamic functions. Recently, Filipe et al.^{70,71} have determined the thermodynamics of liquid mixtures of xenon with alkanes from an experimental point of view. These authors have obtained the total vapor pressure for liquid mixtures of xenon + ethane, + propane, + *n*-butane, and + isobutane at different temperatures and in the whole range of concentrations. Additionally, they have calculated all three major excess properties (V^E , H^E , G^E). The results have been interpreted using the SAFT–VR equation of state.^{45,46} This

theory can correctly predict the excess thermodynamic properties of these kinds of mixtures. MacDowell et al.⁷² have recently calculated the excess properties of binary mixtures of *n*-alkanes using a modified perturbation theory, based on the Wertheim's first-order perturbation theory. Using a reasonable set of parameters, they are able to yield a qualitative correct description of the main trends of excess volumes and excess Gibbs energies of *n*-alkane mixtures.

The aim of the present work is to calculate excess thermodynamic properties of binary mixtures of Lennard-Jones chains using Monte Carlo simulation and the *Soft*-SAFT molecular-based equation of state. The theoretical results obtained from the theory are compared to *exact* molecular simulation data. This allows us to check the accuracy of the equation of state for predicting excess functions. In particular, we have investigated the influence of segment size, dispersive energy, and chain length on excess properties, such as the excess volume, configurational internal energy, and heat.

Once the theory has proved to describe the excess thermodynamic behavior of model systems correctly, the equation can be used with confidence to predict some general trends of experimental excess functions of *n*-alkane mixtures of low molecular weight.⁴ In particular, excess volumes and heats increase very rapidly with the difference in chain length of both components.⁴ These magnitudes are negative and approximately quadratic. They also increase in magnitude as the temperature increases.⁴ Another interesting trend found in the experiments using these kinds of mixtures is the behavior of the excess heat, H^E , with the temperature and chain length of one of the components: this property is positive and quadratic at low temperatures and becomes negative at high temperatures. It crosses the axis $H^E = 0$ as a sigmoid curve, which has $H^E < 0$ for mixtures weak, and $H^E > 0$ for those strong in the longer component.⁴ The temperature at which $H^E(x_1 = 0.5) = 0$ increases with the difference between the chain lengths of the mixture.^{4,73-75}

To our knowledge, this is the first systematic comparison between excess thermodynamic properties of Lennard-Jones chainlike molecules obtained using the SAFT equation of state and molecular simulation.

The rest of the paper is organized as follows: in section 2 we present the most relevant features of the Lennard-Jones chain model and the *Soft*-SAFT equation of state. Molecular simulation details are described in section 3, followed by results and discussion in section 4. Finally, conclusions are presented in section 5.

2. Molecular Model and Equation of State

Homonuclear chain molecules of component *i* are modeled as *m* Lennard-Jones segments of equal diameter σ_{ii} , and the same dispersive energy ϵ_{ii} , bonded tangentially to form the chains, as shown in Figure 1. Intermolecular and intramolecular interactions between segments of different chains and the same chain are taken into account through the Lennard-Jones potential model

$$\phi(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (1)$$

where σ_{ij} and ϵ_{ij} are the segment size and the dispersive energy between segments *i* and *j*, respectively.

This model, previously used in the literature to accurately represent hydrocarbon molecules, accounts for the most important attribute of chain molecular architecture—that is, the bead

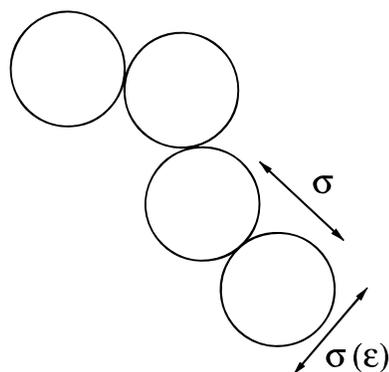


Figure 1. Schematic two-dimensional view of a homonuclear Lennard-Jones chain with four segments, diameter σ and dispersive energy ϵ .

connectivity—to represent topological constraints and internal flexibility, the excluded volume effects, and the attractions between different beads.^{39-41,66,67}

Care must be taken when using the tangent-sphere model and the SAFT approach to represent real *n*-alkanes. As is well-known from simulation studies,⁷⁶ the ratio of the critical temperatures between the tangent Lennard-Jones spheres formed by eight segments and the Lennard-Jones spheres is close to 2, whereas the ratio of *n*-octane to methane is close to 3. The number of spheres, or chain length, should not be identified with the number of carbon atoms of real *n*-alkanes when the tangent-sphere model is used within the SAFT approach. In this case, the chain length parameter is usually adjusted to give the best representation of the experimental data. This fact makes the *Soft*-SAFT equation, like other versions, a highly accurate theory for predicting the phase behavior of pure and binary mixtures of hydrocarbons, including the most important features of the critical properties of the *n*-alkane homologous series (see Blas and Vega^{66,67}).

Because the SAFT equation of state approach is widely used in the literature, we will explain here only the most important features of the *Soft*-SAFT equation of state for binary mixtures of Lennard-Jones chains.

The *Soft*-SAFT theory, like other versions of SAFT, is written in terms of the Helmholtz free energy, which can be expressed as a sum of different microscopic effects: the Lennard-Jones term, A^{LJ} , for the attractive and repulsive forces between the segments that form the molecules, and the chain contribution, A^{chain} , accounting for the connectivity of the chains.⁶⁵ The residual Helmholtz free energy of an *n*-component mixture of Lennard-Jones chains may be written as

$$\frac{A}{N_c k_B T} - \frac{A^{\text{ideal}}}{N_c k_B T} = \frac{A^{LJ}}{N_c k_B T} + \frac{A^{\text{chain}}}{N_c k_B T} \quad (2)$$

where N_c is the number of chain molecules in the system, k_B is Boltzmann's constant, and T is the temperature. Each individual contribution to the Helmholtz free energy of the system is explained separately here.

Ideal Term. The ideal Helmholtz free energy of an ideal mixture of chains can be written as follows:

$$A^{\text{ideal}} = N_c k_B T \left\{ \sum_{i=1}^n [x_i \ln(x_i \rho_c \Lambda_i^3)] - 1 \right\} \quad (3)$$

where $\rho_c = N_c/V$ is the chain density, x_i is the molar fraction of component *i*, V is the volume, and Λ is the thermal de Broglie wavelength. The segment density, ρ , is easily related to the chain density through

$$\rho = \left[\sum_{i=1}^n m_i x_i \right] \rho_c = \sum_{i=1}^n m_i \rho_i \quad (4)$$

where m_i is the chain length of species i , and ρ_i is the monomeric density of species i .

Lennard-Jones Reference Term. The reference term accounts for both the repulsive and the attractive interactions of the segments forming the chains. A^{LJ} is the Helmholtz free energy of a mixture of spherical Lennard-Jones sites. In this work we use the Lennard-Jones equation of state proposed by Johnson et al.,⁷⁷ although any other choice would be equally appropriate.^{78,79} This equation is an extended Benedict–Webb–Rubin equation of state that was fitted to simulation data for pure Lennard-Jones fluids over a broad range of temperatures and densities. Details of the simulations are reported elsewhere.⁷⁷

Chain Term. The contribution to the chain formation is accounted for in A^{chain} . This term was independently introduced by Wertheim,³⁵ and by Jackson et al.³⁷ and Chapman et al.³⁸ from the first-order perturbation theory for associating spherical molecules.^{31–34} For mixtures of Lennard-Jones chains with bond lengths equal to σ_{ii} , the diameter of the Lennard-Jones segments in species i , the final expression takes the form

$$A^{\text{chain}} = N_c k_B T \sum_{i=1}^n x_i (1 - m_i) \ln y_{\text{LJ}}^{(ii)}(\sigma_{ii}) \quad (5)$$

where $y_{\text{LJ}}^{(ii)}(\sigma_{ii})$ is the contact value of the cavity correlation function for spherical segments of species i in the Lennard-Jones reference fluid. $y_{\text{LJ}}^{(ii)}(\sigma_{ii})$ is easily related to the pair radial distribution function of the Lennard-Jones fluid, $g_{\text{LJ}}^{(ii)}(\sigma_{ii})$.

Extension to Mixtures. Because the Helmholtz free energy is calculated by adding different terms, in mixtures studies each of them should be expressed in terms of compositions. In the *Soft*–SAFT version, only the reference term needs to be extended to mixtures.⁶⁵ The ideal and chain contributions are valid for multicomponent systems; thus, they are readily applicable to mixtures. We use the van der Waals one-fluid theory (vdW-1f) to describe the A^{LJ} term of the mixture.¹⁹ In this theory, the residual Helmholtz free energy of the mixture is approximated by the residual Helmholtz free energy of a pure hypothetical fluid, with parameters σ_m and ϵ_m , calculated from

$$\sigma_m^3 = \frac{\sum_{i=1}^n \sum_{j=1}^n m_i m_j x_i x_j \sigma_{ij}^3}{\sum_{i=1}^n \sum_{j=1}^n m_i m_j x_i x_j} \quad (6)$$

$$\epsilon_m \sigma_m^3 = \frac{\sum_{i=1}^n \sum_{j=1}^n m_i m_j x_i x_j \epsilon_{ij} \sigma_{ij}^3}{\sum_{i=1}^n \sum_{j=1}^n m_i m_j x_i x_j} \quad (7)$$

where the mixing rules for a Lennard-Jones mixture have been expressed as functions of the molar fractions.

The chain term, A^{chain} , depends explicitly on composition, and no changes are needed for mixtures. To obtain the pair correlation function of a mixture of Lennard-Jones spheres, the same mixing rules (vdW-1f)¹⁹ as in previous works^{65–68} have been used. Results from Johnson et al.⁶² are used for the pair radial distribution function of the Lennard-Jones fluid. These

results are from extensive computer simulations fitted to an empirical function of the reduced temperature and density. Details of the simulations are reported elsewhere.^{62,77}

For the crossed interactions, the Lorentz–Berthelot combining rules are used.¹⁹

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (8)$$

$$\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2} \quad (9)$$

3. Monte Carlo Simulation Details

We have used the isothermal–isobaric (NPT) ensemble Monte Carlo simulation technique^{80,81} to study binary mixtures of Lennard-Jones chains described in the previous section. In particular, we have obtained the influence of several parameters, such as the segment size, dispersive energy, and chain length, on the excess volume, V^E , configurational internal energy, U^E , and enthalpy or heat, H^E . These excess properties are calculated in the usual way.⁴

All the simulations have been performed with different molecules of each type (except pure systems) and chain length, although N , the number of the total segments present in the system, was kept approximately constant and around 700 segments. At the start of the simulations, molecules are placed at random positions inside the simulation box and with random internal configurations.^{80,81}

The temperature, pressure, and number of molecules are specified a priori, allowing the volume, as well as the energy and the chemical potential to fluctuate. Attempts to reptate a molecule in a random manner and attempts to change the volume of the box are made to reach the internal and the mechanical equilibrium, respectively.⁸¹ The use of the reptation algorithm instead of other, more sophisticated simulation methods, such as the configurational bias Monte Carlo, is justified for systems in which short lengths and low densities are used.^{81–84}

We have used periodic boundary conditions and the minimum image convention. The calculation of the configurational energy is performed in the usual way, truncating the Lennard-Jones interactions at half the box size and adding the standard long-range corrections. The simulations are organized by cycles. Each cycle consists of N attempts to displace molecules and a volume change.^{80,81} An equilibrium period of at least 2×10^4 cycles is used. The equilibrium period is increased for the case of high densities. The total simulation length is around 10^5 cycles. Errors are estimated by dividing the simulation in blocks of 10^3 cycles, so as to obtain statistically independent block sequences, and calculating the standard errors of the mean.^{80,81} These conditions allow us to obtain results comparable with those corresponding to similar systems previously studied.^{65,85,86}

4. Results

We have performed NPT Monte Carlo simulations at $T^* = k_B T / \epsilon_{11} = 3.5$ and $P^* = P \sigma_{11}^3 / \epsilon_{11} = 1$. Note that we have reduced the pressure and temperature with respect to the molecular parameters of component 1. These thermodynamic states correspond to supercritical conditions for both components. Because the theory has proven to be highly accurate at different working conditions, we expect that the conclusions obtained here will be applicable to other thermodynamic states. At present, we are studying the behavior of these kinds of mixtures in liquid states for both components, where most experimental excess property data are obtained. This research will be the subject of a future work.⁸⁷

TABLE 1: NPT Ensemble Monte Carlo Simulation Results for Binary Mixtures of Lennard-Jones Dimers and Chains, at $T^* = 3.5$ and $P^* = 1$, with Equal Segment Sizes and Dispersive Energies, and Different Chain Lengths^a

m_2	x_1	ρ_c^*	$-U_c^*$
3	0.0	0.159(2)	7.128(9)
3	0.2	0.167(2)	6.5(1)
3	0.4	0.175(2)	5.93(7)
3	0.6	0.183(2)	5.31(6)
3	0.8	0.192(2)	4.71(6)
3	1.0	0.202(2)	4.13(4)
4	0.0	0.129(2)	10.2(2)
4	0.2	0.139(2)	8.9(2)
4	0.4	0.152(2)	7.75(7)
4	0.6	0.166(2)	6.56(8)
4	0.8	0.183(2)	5.34(8)
4	1.0	0.202(2)	4.13(4)
5	0.0	0.108(2)	13.3(2)
5	0.2	0.119(2)	11.5(2)
5	0.4	0.134(2)	9.6(2)
5	0.6	0.152(2)	7.8(1)
5	0.8	0.174(2)	5.94(8)
5	1.0	0.202(2)	4.13(4)

^a $m_1 = 2$ and m_2 is the chain length of the second component.

TABLE 2: NPT Ensemble Monte Carlo Simulation Results for Binary Mixtures of Lennard-Jones Chains, at $T^* = 3.5$ and $P^* = 1$, with Four Segments, Equal Segment Sizes, and Different Dispersive Energies

$\epsilon_{22}/\epsilon_{11}$	x_1	ρ_c^*	$-U_c^*$
0.6667	0.0	0.114(1)	5.37(7)
0.6667	0.2	0.116(1)	6.17(9)
0.6667	0.4	0.119(1)	7.06(8)
0.6667	0.6	0.122(1)	8.0(1)
0.6667	0.8	0.125(1)	9.1(1)
0.6667	1.0	0.129(2)	10.2(2)
0.5	0.0	0.1071(9)	3.43(5)
0.5	0.2	0.110(1)	4.43(6)
0.5	0.4	0.114(1)	5.62(6)
0.5	0.6	0.118(1)	6.9(1)
0.5	0.8	0.123(2)	8.4(2)
0.5	1.0	0.129(2)	10.2(2)
0.3333	0.0	0.1025(8)	1.75(2)
0.3333	0.2	0.1060(9)	2.9(4)
0.3333	0.4	0.110(1)	4.23(6)
0.3333	0.6	0.1152(9)	5.86(6)
0.3333	0.8	0.121(2)	7.8(1)
0.3333	1.0	0.129(2)	10.2(2)

We have obtained the reduced molecular density, $\rho_c^* = \rho_c \sigma_{11}^3$, where ρ_c is the molecular density, and the configurational internal energy, $U_c^* = \frac{U}{N_c \epsilon_{11}}$. Excess thermodynamic properties presented in this work are expressed in segment units and calculated in the usual way from results obtained from molecular simulation. Results obtained from molecular simulations are shown in Tables 1–3. Standard deviations in the tables are determined as described by Allen and Tildesley.⁸⁰ We have also applied the *Soft*–SAFT equation of state to verify the accuracy of this version of SAFT for predicting excess thermodynamic properties. In particular, we have studied the effect of the segment size and dispersive energy ratios, σ_{22}/σ_{11} and $\epsilon_{22}/\epsilon_{11}$, respectively, as well as the effect of chain length on excess volume, enthalpy, and internal energy. Once the theory demonstrated its ability to describe the excess functions of Lennard-Jones chains binary mixtures, we used it to predict excess properties of several chainlike mixtures at different conditions of temperature and composition.

Effect of Molecular Parameters on Excess Thermodynamic Properties. First we studied the influence of the chain

TABLE 3: NPT Ensemble Monte Carlo Simulation Results for Binary Mixtures of Lennard-Jones Chains, at $T^* = 3.5$ and $P^* = 1$, with Four Segments, Equal Dispersive Energies, and Different Segment Sizes

σ_{22}/σ_{11}	x_1	ρ_c^*	$-U_c^*$
0.8571	0.0	0.176(3)	8.8(2)
0.8571	0.2	0.165(3)	9.2(2)
0.8571	0.4	0.154(3)	9.4(2)
0.8571	0.6	0.145(2)	9.7(2)
0.8571	0.8	0.136(2)	9.9(2)
0.8571	1.0	0.129(2)	10.2(2)
0.75	0.0	0.221(4)	7.4(1)
0.75	0.2	0.197(4)	8.3(2)
0.75	0.4	0.174(3)	8.8(2)
0.75	0.6	0.156(2)	9.4(2)
0.75	0.8	0.142(2)	9.8(1)
0.75	1.0	0.129(2)	10.2(2)
0.6667	0.0	0.259(7)	6.2(2)
0.6667	0.2	0.224(6)	7.5(2)
0.6667	0.4	0.192(4)	8.5(2)
0.6667	0.6	0.165(2)	9.1(1)
0.6667	0.8	0.145(2)	9.7(2)
0.6667	1.0	0.129(2)	10.2(2)

length on the excess volume, configurational internal energy, and enthalpy. Figure 2 shows the excess volume of three Lennard-Jones binary mixtures at $T^* = 3.5$ and $P^* = 1$, versus the molecular composition of component 1. The first component of the mixture is a Lennard-Jones dimer and the second a Lennard-Jones chain made up of m_2 spherical segments. Solid lines represent the predictions from the *Soft*–SAFT equation of state, and symbols are the NPT Monte Carlo simulation results obtained for the same systems. As can be observed, the excess volumes of the systems studied are negative and approximately quadratic. This property, when plotted versus the composition, is often asymmetric, with the minimum shifted toward the more volatile component. The excess volume increases in magnitude as the chain length of the second component increases, as experiments indicate.⁴ The *Soft*–SAFT predictions obtained are also able to correctly describe the general trends observed experimentally for this kind of systems. An excellent agreement between theory and molecular simulation data is obtained in all cases and in the whole range of concentrations. Although the statistical errors of pure and binary mixture properties, such as density, configurational internal energy, and enthalpy, are around 1% of the average values (see Tables 1–3), relative statistical errors of excess properties are large because excess properties are obtained by subtracting quantities of the same order of magnitude.

We have also obtained the excess configurational internal energy of these mixtures, and results are shown in Figure 3. The solid lines are the predictions obtained from *Soft*–SAFT, and the different symbols correspond to NPT Monte Carlo simulation results. The excess internal energy is also a negative and quadratic function of the molecular composition. As in Figure 2, this excess property increases as the chain length of the second component is increased. Agreement between molecular simulations and theoretical predictions is excellent in all cases.

We have obtained the excess enthalpy or heat as a function of the molecular composition of component 1, using standard thermodynamic relationships and previous results. Figure 4 shows the comparison between simulation data, represented by the symbols, and theoretical predictions from *Soft*–SAFT, described by the solid lines. Both results predict a negative excess heat, and its magnitude increases with the chain length of the second component, as is observed experimentally for real

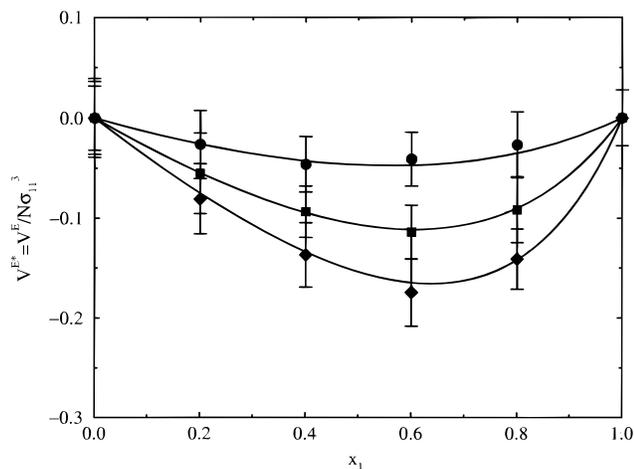


Figure 2. Excess volumes per segment, at $T^* = 3.5$ and $P^* = 1$, of three Lennard-Jones binary mixtures as functions of the molecular concentration of component 1. The first component is a dimer and the second is a Lennard-Jones chain with m_2 segments. Solid lines are the predictions from the *Soft*-SAFT equation of state, and symbols correspond to NPT Monte Carlo simulations for different chain lengths: $m_2 = 3$ (circles), 4 (squares), and 5 (diamonds).

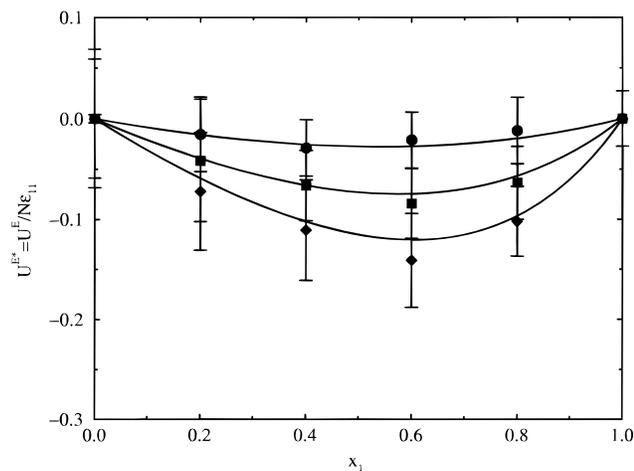


Figure 3. Excess configurational internal energies per segment of the same three mixtures presented in Figure 2. Legends are the same as in the previous figure.

short molecular chains.⁴ Agreement between theoretical results and NPT Monte Carlo simulation data is excellent in the whole range of concentrations.

The apparent singular behavior of the excess thermodynamic functions of short Lennard-Jones binary mixtures with different chain lengths presented here is a direct consequence of the liquid structure and packing arrangements in the mixture. This argument has recently been confirmed by measurements of the crossed second virial coefficients for the xenon + ethane binary mixture.⁸⁸ Xenon, in contrast to the anomalous behavior of methane, can be treated as the first member of the n -alkane series.^{70,71}

The behavior of two excess properties, namely the excess volume and heat, for different dispersive energy ratios is investigated for mixtures of chain molecules of length 4. Figure 5 shows the excess volume, as a function of the molecular composition of component 1, at $T^* = 3.5$ and $P^* = 1$, of Lennard-Jones binary mixtures with different dispersive energy ratios, $\epsilon_{22}/\epsilon_{11}$, and equal segment sizes. The solid lines are the predictions obtained from the *Soft*-SAFT equation of state, and the symbols correspond to different dispersive energy ratios,

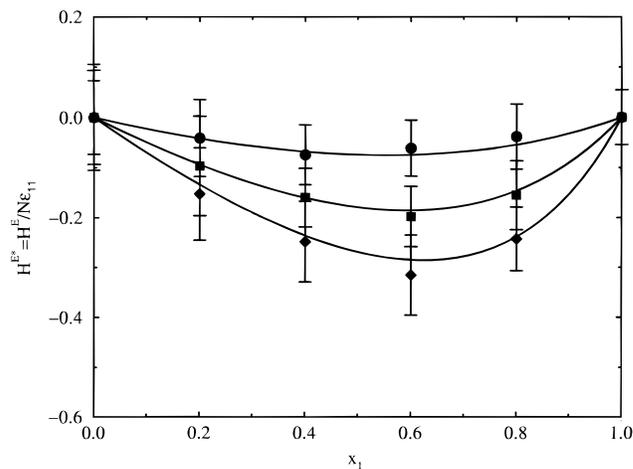


Figure 4. Excess heats per segment of the three Lennard-Jones binary mixtures presented in the previous figure. Legends are the same as in Figure 2.

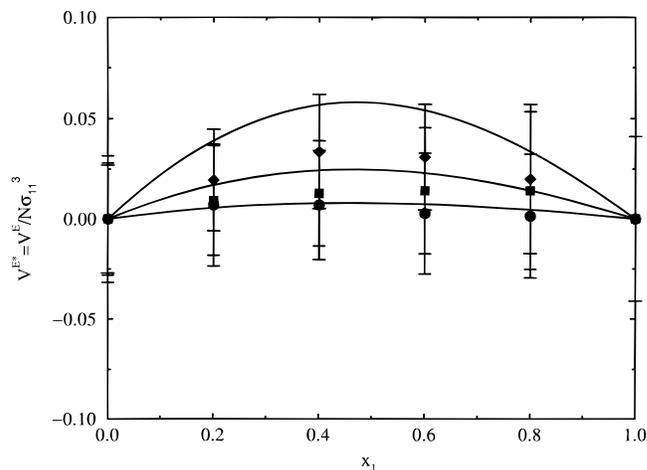


Figure 5. Excess volumes per segment, at $T^* = 3.5$ and $P^* = 1$, of three Lennard-Jones binary mixtures. Both components have the same chain length ($m_1 = m_2 = 4$) and segment size ($\sigma_{11} = \sigma_{22}$). Solid lines represent the predictions obtained from the *Soft*-SAFT approach, and symbols are the NPT simulations for different dispersive energy ratios: $\epsilon_{22}/\epsilon_{11} = 0.6667$ (circles), 0.5 (squares), and 0.3333 (diamonds).

$\epsilon_{22}/\epsilon_{11} = 0.6667$ (circles), 0.5 (squares), and 0.3333 (diamonds). Both approaches show that the excess volumes are positive and nearly quadratic. This magnitude increases when the dispersive energy ratio is decreased, as with previous molecular simulation results for spherical Lennard-Jones mixtures (see ref 25). The *Soft*-SAFT equation of state correctly describes the molecular simulation data for mixtures with dispersive energy ratios close to unity, but only in a qualitative way for highly asymmetric systems.

Figure 6 shows the excess heat behavior, as a function of x_1 , of the previous systems. Predictions from the *Soft*-SAFT theory (solid lines) and NPT Monte Carlo simulation results (symbols) give a positive and approximately quadratic excess heat in the whole range of compositions. Agreement between theoretical and molecular simulation data is excellent in all cases, although the differences between both results increase when the dispersive energy ratio is lowered. Singer and singer²⁵ have previously obtained this result using Monte Carlo simulation for binary mixtures of Lennard-Jones spheres. These authors have shown that the major excess thermodynamic properties become more positive with increasing values of the dispersive energy ratio, $\epsilon_{11}/\epsilon_{22}$. Our calculations confirm that these results are also valid

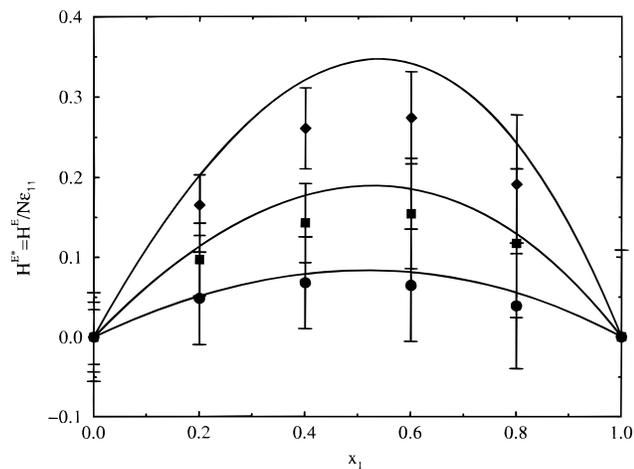


Figure 6. Excess heats per segment of the same three systems presented in the previous figure. Legends are the same as in Figure 5.

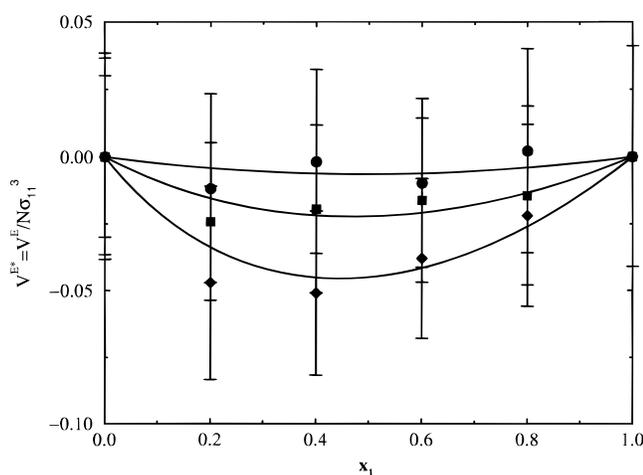


Figure 7. Excess volumes per segment, at $T^* = 3.5$ and $P^* = 1$, of three Lennard-Jones chain binary mixtures. Each component has the same chain length ($m_1 = m_2 = 4$) and dispersive energy $\epsilon_{11} = \epsilon_{22} = 1$. Solid lines are the predictions from the *Soft*-SAFT approach, and symbols represent the simulation results obtained in this work for different segment size ratios: $\sigma_{22}/\sigma_{11} = 0.8571$ (circles), 0.75 (squares), and 0.6667 (diamonds).

for short asymmetric Lennard-Jones chains.

Finally, we have also considered the dependence of the excess volume and heat on the segment size ratio of the mixture, σ_{22}/σ_{11} . Figure 7 shows the excess volume behavior of binary mixtures of Lennard-Jones chains made up by four segments, with the same dispersive energy and different segment size ratios. The excess enthalpies of these systems have also been studied, and the results are presented in Figure 8. In both cases, molecular simulation data (symbols) and theoretical results (solid lines) show that these two excess properties are negative and approximately quadratic in the whole range of compositions. Agreement between both results is excellent in all cases, showing the predicting power of the *Soft*-SAFT theoretical approach.

Effect of Temperature on Excess Functions of Lennard-Jones Chain Mixtures. Once the theory proved that it can correctly describe excess thermodynamic properties of Lennard-Jones chain binary mixtures, we applied the *Soft*-SAFT equation of state to predict some general trends of the excess volumes and heats of model *n*-alkanes of low and intermediate molecular weight. In particular, we have studied the influence

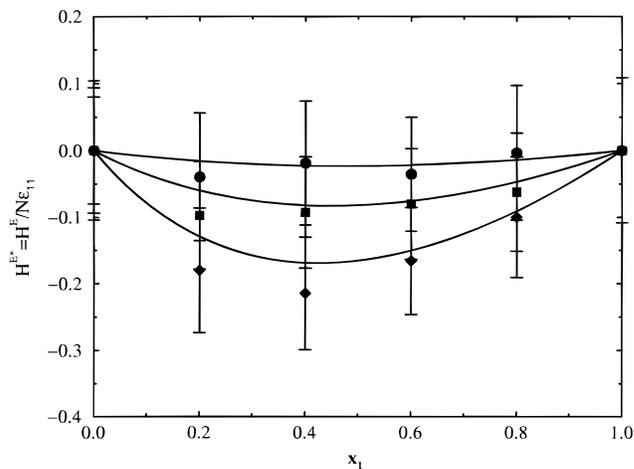


Figure 8. Excess heats per segment of the systems presented in the previous figure. Legends are the same as in Figure 7.

that the temperature and chain length of one of the components has on excess volumes and heats.

To capture the molecular characteristics of real *n*-alkanes, we have used the Lennard-Jones model and a set of transferable parameters for *n*-alkanes obtained in a previous work⁶⁶ to calculate the segment size and the dispersive energy of each component. This approach ensures that the molecular parameter ratios (σ_{22}/σ_{11} and $\epsilon_{22}/\epsilon_{11}$) selected here are approximately those corresponding to the interaction forces between real *n*-alkanes. We have fixed the number of beads per chain, and using the transferable parameters of Blas and Vega, we have calculated the segment size and dispersive energy ratios according to relationships 21–23 in ref 66. We have studied excess volumes and heats at different temperatures, and the reduced pressure, P^* , has been fixed equal to 0.002. These conditions are below the critical temperatures and pressures of the pure components. In fact, the working conditions studied here correspond to single-phase liquid states for the mixtures considered, mimicking the experimental thermodynamic coordinates at which excess properties are obtained.

Figure 9a,b shows the excess volumes and heats, respectively, of a binary mixture of Lennard-Jones chains, with chain lengths $m_1 = 3$ and $m_2 = 8$, at different temperatures and $P^* = 0.002$, predicted by the *Soft*-SAFT equation. The values of ($\sigma_{22}/\sigma_{11} = 1.0088$ and $\epsilon_{22}/\epsilon_{11} = 1.1198$) are obtained from the transferable parameters as explained above. As can be seen, the excess volumes are negative and approximately quadratic in the whole range of compositions, as experimental data indicate.⁴ The excess volume of the system becomes more negative when the temperature is increased. This behavior corresponds to that observed in real *n*-alkane binary mixtures.

We have also considered the effect of temperature on the excess heat of the mixture. Figure 9b shows H^E , as a function of x_1 , at the same pressure and temperatures studied in Figure 9a. As can be observed at low temperatures $H^E > 0$. When the temperature is increased, the excess heat becomes negative. At intermediate temperatures, $H^E(x_1)$ behaves as a sigmoid curve, with $H^E > 0$ for mixtures rich in the more volatile chain and $H^E < 0$ for those rich in the less volatile compound. These results show that the *Soft*-SAFT equation of state adequately predicts the general trends of real *n*-alkane binary mixtures.⁴

We have also investigated the behavior of the excess heat, at several temperatures and the same pressure ($P^* = 0.002$), of mixtures in which the second component has different chain lengths, keeping constant $m_1 = 3$. Figure 10a,b shows this

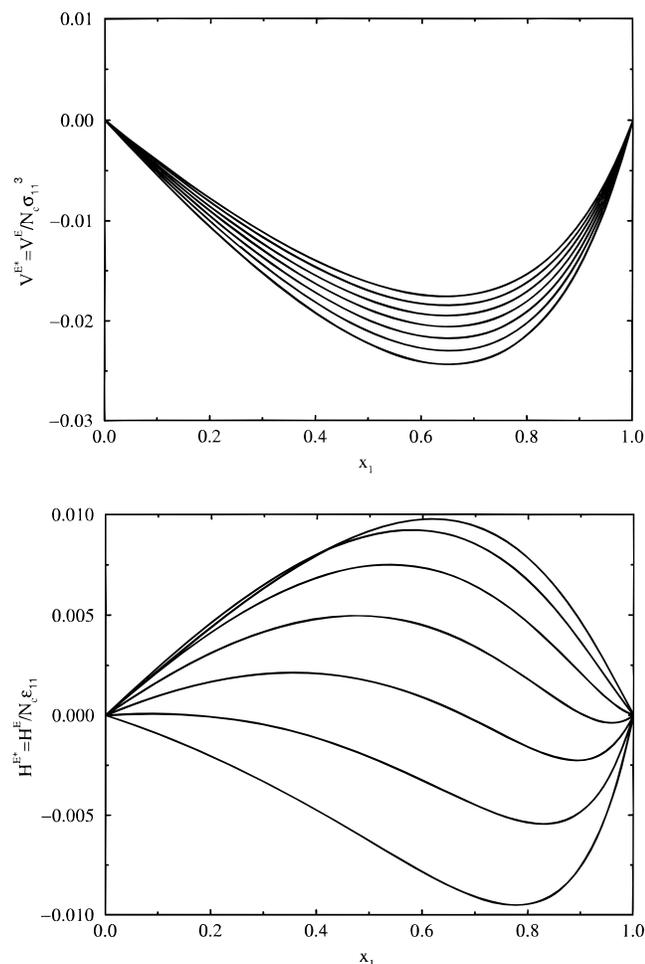


Figure 9. Excess volumes (a) and heats (b) of a binary mixture of Lennard-Jones with $m_1 = 3$ and $m_2 = 8$, at $P^* = 0.002$ and different temperatures; from bottom to top, $T^* = 1.12, 1.10, 1.08, 1.06, 1.04, 1.02$, and 1.0 . The segment size (σ_{22}/σ_{11}) and dispersive energy ($\epsilon_{22}/\epsilon_{11}$) ratios are chosen as indicated in the text.

property, as a function of composition, for binary mixtures with $m_2 = 10$ and $m_2 = 12$, respectively. These results indicate that the effect on $H^E(x_1)$ curves, due to the increase in chain length of one of the components, is to shift the excess heats curves toward higher temperatures, as experiments indicate.⁴ This confirms the behavior of the temperature at which $H^E(x_1 = 0.5) = 0$ with the chain length of one of the mixture components.

To highlight the predictions obtained from the *Soft*-SAFT theory, we have calculated the temperatures at which $H^E(x_1) = 0$ as functions of the molecular composition of component 1, at $P^* = 0.002$. Figure 11 shows the predictions from *Soft*-SAFT for three different binary mixtures of Lennard-Jones chains. As can be seen, the temperature at which $H^E(x_1) = 0$ increases when the chain length m_2 increases, keeping constant the composition of the mixture; for a given mixture, this temperature behaves as a decreasing function of composition of the more volatile compound. These results show that *Soft*-SAFT can qualitatively predict the behavior of excess thermodynamic properties observed experimentally for real *n*-alkane binary mixtures.^{4,73–75}

Conclusions

We have performed NPT Monte Carlo molecular simulations to obtain excess thermodynamic properties of binary mixtures of Lennard-Jones chains. The influence of several molecular

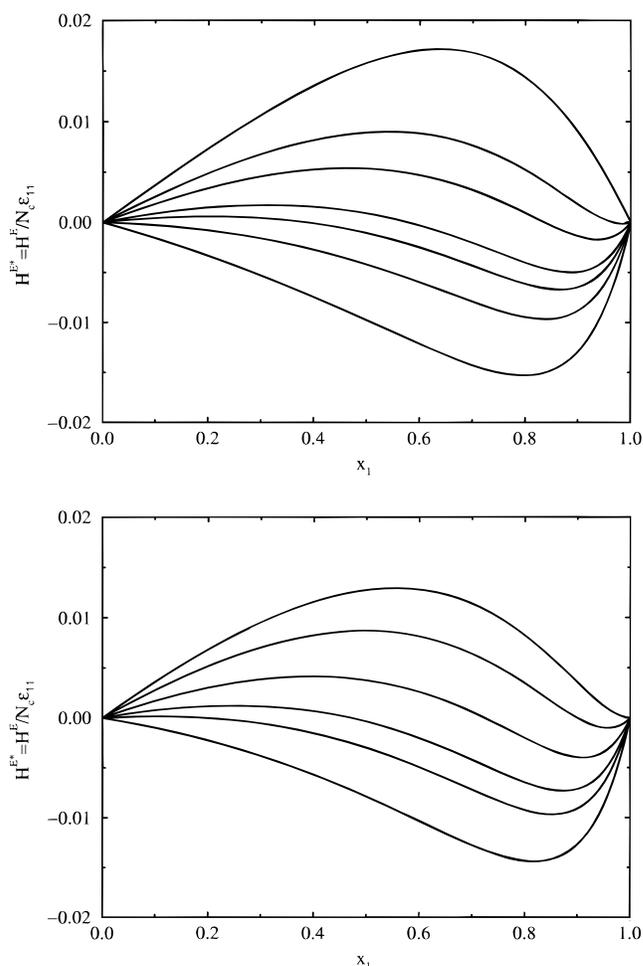


Figure 10. Excess heats of binary mixtures of Lennard-Jones chains with different chain lengths at $P^* = 0.002$ and several temperatures. (a) $m_1 = 3$ and $m_2 = 10$, from bottom to top, at $T^* = 1.14, 1.12, 1.108, 1.10, 1.08, 1.06$, and 1.0 ; (b) and $m_1 = 3$ and $m_2 = 12$, from bottom to top, at $T^* = 1.15, 1.134, 1.125, 1.11, 1.09$, and 1.07 . The segment size and dispersive energy ratios are obtained as in the previous figure.

parameters on the excess functions of these systems has been discussed in detail. The results obtained from molecular simulations have been used to check the accuracy of the *Soft*-SAFT equation of state in predicting these kinds of thermodynamic properties.

We have studied the influence of segment size, dispersive energy, and chain length on some excess functions of Lennard-Jones chains. Molecular simulations and theoretical results show that excess volumes, configurational internal energies, and heats are negative, in the whole range of compositions, for chain mixtures with the same segment size and dispersive energy but different chain lengths. The magnitude of the excess functions increases with the differences in the chain length of the components. We have also observed that these properties are positive when the dispersive energy is varied and negative when the segment size ratio is lower than unity, keeping constant the rest of the molecular parameters in each case. Results from both simulation and theory show that the magnitude of the excess properties increases with the asymmetry of the mixture. Agreement between the molecular simulation results and the theoretical predictions is excellent, although some deviations between the two are observed when the system is very asymmetric. NPT Monte Carlo simulation results obtained in this work are consistent with previous molecular simulation predictions for binary mixtures of Lennard-Jones spheres.

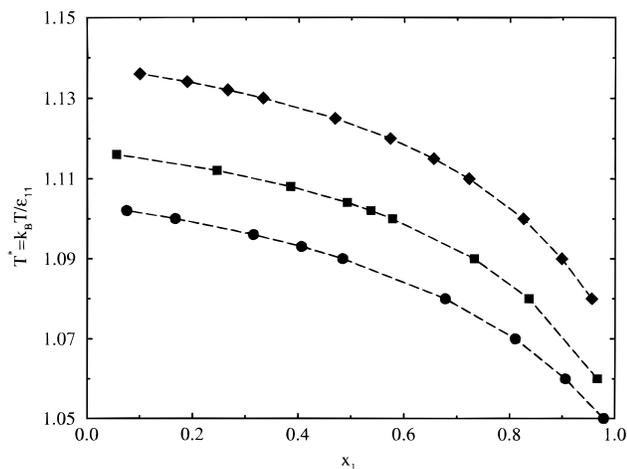


Figure 11. Temperatures, as functions of the molecular composition of component 1, at which $H^E(x_1) = 0$ and $P^* = 0.002$, predicted by the *Soft*-SAFT equation of state for three binary mixtures of Lennard-Jones chains with different chain lengths: circles [$(m_1 = 3) + (m_2 = 8)$], squares [$(m_1 = 3) + (m_2 = 10)$], and diamonds [$(m_1 = 3) + (m_2 = 12)$]. Dashed lines are included as guides to the eye.

This work proves that the *Soft*-SAFT equation of state is a valuable tool for predicting excess thermodynamic properties of Lennard-Jones chains with a wide range of chain lengths, segment sizes, and dispersive energy ratios. Once the theory proved its ability to predict these kinds of properties, we applied the equation to study the influence of temperature on excess volumes and heats of model *n*-alkane binary mixtures. In particular, the *Soft*-SAFT equation of state can predict the general trends of the thermodynamic behavior of real systems: negative excess volumes that increase in magnitude when temperature and differences in chain length are increased. It is also observed that the excess heat is positive and nearly quadratic at low temperatures, but becomes negative at high temperatures. At intermediate states, *Soft*-SAFT predicts sigmoid curves for the excess heats when plotted versus the composition of the mixture. Using these results, we have obtained the temperature at which the excess heat equals zero, in the whole range of molar fractions and for different chain lengths. Theoretical results indicate that the temperature decreases with composition, keeping constant the chain length, and increases with the chain length of one of the components at fixed composition.

Currently, we are applying the *Soft*-SAFT equation of state to predict excess thermodynamic properties of binary mixtures of real *n*-alkanes. Theoretical results will be compared to experimental data taken from the literature to test the theory's accuracy in predicting real excess functions. This work will be the subject of a future paper.⁸⁷

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