Excess Thermodynamic Properties of Chainlike Mixtures. II. Self-Associating Systems. Predictions from the Soft-SAFT Theory and Molecular Simulation

Felipe J. Blas
Departamento de Física Aplicada,
Escuela Politécnica Superior, Universidad de Huelva, 21819 La Rábida, Huelva (SPAIN)
E-mail: Felipe.Jimenez@dfaie.uhu.es, FAX: +34 959 017304

The excess thermodynamic behaviour of self-associating binary mixtures of chainlike molecules is studied using a modified statistical associating fluid theory, the so-called *Soft*-SAFT equation of state. The chainlike molecules are described as Lennard-Jones spherical segments tangentially bonded together. The associating Lennard-Jones chains are modelled considering additional embedded off-centre square-well bonding sites. This model, which accounts for explicitly the most important microscopic features of real non-associating and associating chainlike molecules, such as repulsive and attractive forces between chemical groups, the connectivity of the segments to form the chains and the specific interactions (association), is also solved using the Monte Carlo molecular simulation technique. Comparison between theoretical predictions and simulation results for selected mixtures are made in order to assess the adequacy of the theory in predicting excess properties. Agreement between simulation and *Soft*-SAFT predictions indicates that the theory is able to provide a good description of the major excess properties. The theory is also used to study the effect of the molecular parameters on the excess properties of self-associating binary mixtures, with particular emphasis on the effect of association (including the bonding energy and number of associating sites) and chain length. The thermodynamic behaviour of these systems is governed by a delicate interplay between two important effects: the bond breaking of the structure formed by the associating molecules and the interstitial accommodation of the non-associating chains within the branched multimeric structure of the associating fluid. The theory is able to explain qualitatively the most salient features of the excess properties in real systems, including positive, negative and sigmoidal shape behaviour. After an in depth analysis of the effect of the association and chain length, we apply the *Soft*-SAFT theory by making some quantitative comparisons with experimental excess volumes for n-alkane + 1-alcohol binary mixtures.

1 Introduction

The accurate knowledge of the thermodynamic and phase behaviour of complex fluid systems, such as chainlike and associating substances and their mixtures, is central to the chemical process design in the traditional chemical and oil industries, including supercritical extraction, surfactancy and development of separation and extraction processes.[1–3] A great advance in the field of the equations of state has been made in last years, motivated partially by the industrial interest, and also by the rapid development of modern molecular theories. These approaches provide a realistic description of the free energy of the system, as they are able to make quantitative predictions for the phase behaviour of complex systems (see the book of Sengers *et al.*[4] for a recent review). Most of the thermodynamic studies undertaken during last years concentrate in obtaining the phase equilibria, including the high-pressure phase behaviour and the critical properties, of systems of industrial interest. However, descriptions of the excess thermodynamic properties of these mixtures, such as excess volume, V^E, heat, H^E, and Gibbs free energy, G^E, are less common. In this work we examine the excess properties of self-associating binary mixtures of chainlike systems, in which only one of the components can associate. The excess functions constitute the usual way to express the extent to which real liquid mixtures deviate from ideality.[5] These properties are used extensively in a wide variety of scientific and technical fields, including chemistry, spectroscopy and chemical engineering. From a theoretical point of view, the excess functions are also a valuable information since equations of state, particularly those based in statistical mechanics, lead naturally to the prediction of excess properties. Since they are more sensitive than phase equilibria to the molecular details, the prediction of the excess properties provides an excellent way to check if theoretical approaches are suitable for describing accurately the behaviour of a given system.

The simplest homologous series of real self-associating binary mixtures of chainlike fluids is the n-alkane + 1-alcohol series. Since we concentrate in modelling the excess properties of mixtures having the same molecular features (chainlike shape and self-association), it is important to review the most relevant experimental studies that have been undertaken for these systems. The excess properties, an in particular the excess volume of n-alkane + 1-alcohol binary mixtures, have been studied many times.[6–13] However, none of these investigations has been sufficiently systematic and extensive. For instance, Stavely and Spice[6] have obtained the excess volume of the n-heptane + 1-alcohol series, from ethanol up to 1-decanol at $293.15K$ and for mole fractions of 1-alcohol from 0.0005 to 0.035; Brown *et al.*[9] have also studied a large series of mixtures (n-hexane + 1-alcohol binary mixtures, from ethanol up to 1-octanol), but their measurements concentrated only in equimolar compositions. Stokes and co-workers[14] have also studied a number of mixtures containing primary, secondary and tertiary alcohols with a great variety of second compounds, with n-alkanes among them. Christensen *et al.*[15] studied the excess heat of n-decane + 1-hexanol, although they did not performed a systematic investigation of this property. Similarly, other authors have obtained the excess volume of several binary mixtures n-alkane + 1-alcohol,[16–20] although none of them have performed a systematic study of the behaviour with the composition and molecular weight of both components. The first systematic investigation of the excess volume and heat of the n-alkane + 1-alcohol homologous series have been undertaken by Benson and co-workers.[21–26] This group has measured the excess volume of a great number of such mixtures: n-heptane + methanol,[21] +ethanol,[21,25] + propanol,[21,25] + 1-butanol,[21,25] + 1-pentanol,[22,25] + 1-hexanol,[22,25] + 1-octanol,[22] + 1-decanol,[22] and + 1-dodecanol;[26] 1-hexanol + n-pentane,[23] + n-hexane,[23] + n-heptane,[22,25] + n-octane,[23] and + n-decane;[23] and 1-decanol + n-pentane,[24] + n-hexane,[24] + n-heptane,[22] + n-octane,[24]+ n-decane,[24] and + n-hexadecane.[24] They have also measured the excess heat of n-decane +, n-octane +, n-heptane +, n-hexane +, and n-pentane + 1-decanol binary mixtures.[27] Their experimental results show that the excess volume exhibits positive and negative values, and sigmoidal shape (positive values for mole fraction of n-alkane close to 1 and negative values for mixtures rich in 1-alcohols) depending on the molecular weight of the components. Essentially, the excess volume is positive when the chain length of the n-alkane is longer than that corresponding to the 1-alcohol, negative in the opposite situation, and exhibits a sigmoidal shape when both components have approximately the same number of carbon atoms. This behaviour has been explained by Benson and co-workers[28] in terms of a macroscopic model that accounts for the most salient effects that occur in the system: bond breaking of the structure formed by the 1-alcohol molecules and interstitial accommodation of the n-alkane molecules within the branched multimeric structure of the 1-alcohol fluid. In 1990s, other research groups have undertaken a systematic investigation of the excess volume and heat of such mixtures. Heintz and co-workers have measured both excess properties for mixtures of n-octane, n-decane and n-dodecane with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol,[29] and n-hexane + methanol, + ethanol and 1-hexanol, n-decane + 1-butanol and n-hexadecane + ethanol.[30] They have also used the extended real associated solution (ERAS) model[31,32] to describe the excess behaviour of these systems. More recently, two different groups have re-examined the excess properties of the n-alkane + 1-alcohol binary mixtures.[33] In some of these works the ERAS model has also been used to model the excess properties of such systems. For a recent review on this subject see the work of Piñeiro *et al.*[34]

To predict the thermodynamic properties of self-associating binary mixtures of Lennard-Jones chains, two important features must be incorporated at an early stage, namely, the extensive association in pure associating molecules and mixtures with molecular chains, and the non-spherical (chain-like) nature of both components. These two molecular characteristics cause anisotropies in the molecular interactions, and are responsible for large non-idealities in the mixtures. Simple correlation equations, such as this proposed by Redlich and Kister,[35] contain a number of adjustable parameters with no physical meaning. There exist several well established equations, such as UNIQUAC,[36,37] NRTL[37,38] or DISQUAC,[39] for describing excess properties of multicomponent fluid mixtures. These equations are based on the quasi-chemical approach introduced by Guggenheim,[40] which postulates that nonidealities in fluids could be assigned to the existence of nonrandom mixing at the molecular level. Such theories, although can account for accurately the excess properties of a great number of fluid mixtures at thermodynamic conditions well below their critical points, are not of practical use over the whole fluid range or for very large molecules. This is especially true for complex fluid mixtures, which usually have specific interactions that have not been accounted for explicitly in its original formulation. In addition, excess properties based on volumetric magnitudes, such as the excess volume, can not be described by these models since they are based on the assumption of a grid lattice model. In these cases, a suitable equation of state must be used in order to calculate volumetric properties. There exist other type of non-molecular based models that successfully avoid this limitation. This is the case of the extended real associated solution (ERAS) model introduced by Funke *et al.*[31,32] This theory, which combines the extended version of the Kretschner-Wiebe associated solution model with the equation of state of Flory,[41] is able to predict simultaneously volumetric and non-volumetric excess properties, such as excess heat H^E, volume V^E and Gibbs free energy G^E of self- and cross-associating binary mixtures. A similar approach has been also proposed by Treszczanowicz and Benson[27] for describing binary mixtures containing molecules that can associate. This model combines the Flory-Huggins athermal mixture theory,[41] which accounts for the dispersive interactions, with the athermal associated mixture model of the Mecke-Kempter type, accounting for the association. This approach is able to describe correctly the excess volume of n-alkane + 1-alcohol binary mixtures with different molecular weights. Both models, the ERAS and that proposed by Treszczanowicz and Benson, suffer from the same inherent defects. They use the equation of state of Flory, that contains the parameter κ_{12}. There is no unambiguous relationship with a truly molecular parameter, which means that is usually treated as an empirical adjustable parameter. Another inconvenient of these approaches, common to models based on the chemical theory for association, is that a description of each type of equilibrium process must be specified *a priori*, together with the temperature and density dependence of the corresponding equilibrium constants.

Recently, molecular-based approaches have been introduced as alternative methods that describe correctly the thermodynamics and phase behaviour of complex systems. They are based on a knowledge of the intermolecular interaction forces between the molecules that form the system. The interactions are defined in terms of molecular parameters with physical meaning, which are state-independent. This leads to theories with wide predictive capabilities, especially far away from thermodynamic conditions at which the molecular parameters are correlated.

Molecular methods can be classified in two different types: molecular simulations and analytical theories.[42,43] Molecular simulations can be used to check if a given intermolecular potential is suitable for describing different systems, as well as to test the accuracy of a theory.[44,45] In this later use, molecular simulations constitute a valuable tool because allow to test the approximations made to obtain analytical molecular-based equations of state.[44,45] This also includes the calculation of excess thermodynamic properties. However, some excess properties obtained using molecular simulation may not be reliable because the thermodynamic properties of each component, as well as those corresponding to the mixtures, are determined separately. Therefore, it may occur a cancellation or magnification of errors. Special care should be taken for the calculation of the excess free energy. As it is well known, the free energy is probably the most difficult magnitude to calculate from molecular simulation.[46,47] One of the most reliable routes to evaluate the free energy is based on the coupling parameter charging approach introduced by Kirkwood.[48] McDonald[49,50] and Singer and Singer[51] were the first to use the coupling parameter method in context of Monte Carlo simulation, although the original version required the values of the free energies of the pure components. The method has been improved and used in late 1980s and the 90s by several authors.[52] Nowadays, this method constitutes a highly accurate molecular simulation procedure in obtaining the excess free energies of a great variety of systems. Unfortunately, little work has been done in calculating excess functions for Lennard-Jones chainlike binary mixtures using molecular simulation. McDonald[49,50] and Singer and Singer[51] have performed a detailed study to understand the effect of molecular parameters, such as the segment size and dispersive energy, of binary mixtures of Lennard-Jones spheres 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.[5,51] More recently, Fotouh and Shukla[53,54] have performed isothermal-isobaric or 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 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,[55] founding that both theories yield a reasonable description of the simulation data, although the perturbation theory seems to be superior than the traditional van der Waals theory. In a previous work,[56] we have performed NpT Monte Carlo simulations and applied the *Soft*-SAFT theory to calculate the excess volume and heat of binary mixtures of Lennard-Jones chains. The effect of the molecular parameters (the segment size and dispersive energy ratios, and the chain length) on the excess functions have also been studied. On the other hand, analytical theories have extensively been developed and used to predict the thermodynamic and phase behaviour of complex systems. A number of molecular-based theories account for explicitly the non-spherical shape of molecules. Beret and Prausnitz[57] developed the perturbed hard chain theory (PHCT) in order to include molecular motions due to rotational and vibrational degrees of freedom of the chain. The original PHCT, however, contains a rather cumbersome representation of the attractive interactions derived from a perturbation expansion for square-well molecules.

Later, Kim *et al.*[58] introduced the simpler attractive term of Lee *et al.*[59] in the development of the simplified perturbed hard chain theory (SPHCT). The theory incorporates non-sphericity using Prigogine's concept of $3c$ equivalent translational degrees of freedom for the chain. Unfortunately, there is no unambiguous relationship between the parameter c and the actual molecular shape, which means that it is usually treated as an empirical adjustable parameter. The PHCT and SPHCT were extended to describe anisotropic multipolar interactions, as in the perturbed anisotropic chain theory (PACT).[60] There have been several attempts to include the effect of association. Most of them are based on the premise that the associations can be treated as chemical reactions. This approach, which was introduced originally by Dolezalek,[61] has been extensively used in a variety of ways. Heidemann and Prausnitz[62] have combined the chemical approach with an equation of state for non-associating substances. This approach was followed by Ikonomou and Donohue[63] with the perturbed anisotropic chain theory (PACT) equation of state, which has been used as the physical part to obtain the associating PACT (APACT). The APACT approach, and others based on the chemical theory of association, suffer from the same defects than the chemical association models, being the most important of them the strongly dependence with the number and type of reactions considered.

The statistical associating fluid theory (SAFT)[64,65] is also a molecular-based equation of state, originally developed from Wertheim's first-order thermodynamic perturbation theory for associating[66] and chain fluids.[67–70] The SAFT approach has since been used to predict the phase behaviour of a wide variety of pure components and their mixtures, and nowadays is considered as one of the most powerful predictive tools for the study of fluid phase equilibria. Many modifications following the general framework have also been presented. In general, it combines a chain reference contribution with an associating perturbation term for the description of complex chain and associating fluids. A variation of the original SAFT was first applied by Huang and Radosz[71,72] to successfully correlate the phase behaviour of a large number of pure fluids and mixtures. After this, there have been many variations on the original approach. For a detail description of the different versions of SAFT existing in the literature, we strongly recommend the excellent reviews of Müller and Gubbins.[73,74] Here we only summary the most commonly used versions of the approach, with special emphasis on those related with Lennard-Jones systems, and some recent new developments.

The simplest version of SAFT, SAFT-HS, developed by Jackson *et al.*[67] and Chapman *et al.*,[68] models the chains as hard-sphere segments tangentially bonded with attractive dispersion interactions described at the mean-field level of van der Waals. Recently, SAFT-HS has been extended to deal with branched chain fluids (SAFT-B) using first- and second-order thermodynamic perturbation theory of Wertheim.[75] Although the SAFT-HS theory has been successfully applied for predicting the phase behaviour of systems in which one or two components are strongly associated,[76–79] it is not adequate for systems where the dispersive interactions play a dominant role, such as alkanes. Gil-Villegas *et al.*[80] and Galindo *et al.*[81] have proposed the SAFT-VR equation of state to deal with systems with attractive potentials of variable range. This new approach is able to accurately predict the phase equilibria of a number of fluids and mixtures modelled as chain molecules formed by tangent square-well segments,[82–87] and it has been extended to study electrolyte[88,89] and polymer fluids.[90] The advantage of SAFT-VR is the wide range of potentials that could be treated through it, such as Lennard-Jones[91] and Yukawa[92] systems. More recently, Sadowski and co-workers[93,94] have developed the so-called Perturbed-Chain SAFT by applying the perturbation theory of Barker and Henderson with a hard-chain reference fluid, instead of the usual monomer reference system. The theory, which is in good agreement with simulation data of square-well chains,[93] is found to give an accurate description of the phase equilibria of a wide number of real substances and their mixtures.[94]

Other versions of SAFT, specific for systems with intermolecular Lennard-Jones interactions (including non-associating and associating chains), have been introduced and developed by a number of authors.[95–106] A more recent version of SAFT, the so-called

Soft-SAFT equation of state, specific for Lennard-Jones chains, has been applied by Blas and Vega, and extended to deal with mixtures of both, homonuclear and heteronuclear Lennard-Jones chains.[107] This theory, which has proved to be highly accurate in predicting the thermodynamic properties and phase behaviour of both, model and real hydrocarbons mixtures,[107–110] has been extended to account for the formation of mixtures of Lennard-Jones chains using a dimer reference fluid (*Soft*-SAFT-D).[111] Pàmies and Vega[112] have also proposed a new set of transferable parameters for the *Soft*-SAFT version to predict the phase equilibria of the n-alkanes and their mixtures.

The *Soft*-SAFT theory represents the implementation of the SAFT approach for Lennard-Jones molecules using the Johnson *et al.*'s Helmholtz free energy for the reference fluid,[113] the Johnson *et al.*'s correlation for the pair radial distribution function,[100] and the Müller and Gubbins' correlation for the association volume.[101] It is possible to implement SAFT for Lennard-Jones molecules using different parametrizations or theories for the distribution function. For instance, the SAFT-VR approach, which represents a general theory for attractive potentials of variable range, can be used to describe Lennard-Jones molecules using different reference, chain and association contributions. Tang *et al.*,[114] in a recent paper, have proposed a new version of the SAFT approach for Lennard-Jones molecules based on the analytical solution of the Ornstein-Zernike equation from Tang and Lu,[115] leading to the availability of analytical expressions for both, the Helmholtz free energy and the radial distribution function (as a function of the intermolecular distance, and not only valid for the contact length) of the spherical Lennard-Jones fluids.

More recently, there have been new applications and developments related to the formalism of Wertheim. McCabe *et al.*[116] have applied the SAFT-VR approach to study the fluid phase behaviour of binary mixtures of xenon and the lighter perfluoro-n-alkanes. Agreement between theoretical predictions and experimental data is excellent in all cases. This work provides another example of the alkane-like behaviour of xenon. Benzaghou *et al.*[117] have used the original SAFT to obtained new molecular parameters to describe the

n-alkane series. These authors have also extended the approach to describe moderately branched alkanes, alkenes and ring compounds. The SAFT results show an acceptable accuracy when they are compared with experimental data. New theoretical developments of the Wertheim's approach have been recently presented. Vega and MacDowell[118] have extended the Wertheim's theory to deal with hard-sphere chain molecules in the solid phase, and a study of the vapour-liquid interface and surface tension of associating and chain fluids determined using a local density functional theory that reduces to the SAFT-HS Helmholtz free energy in the bulk limit (SAFT-DFT).[120,121] More recently, and as the generalisation of the work of Vega and MacDowell,[118] Vega and co-workers[119] have extended the approach of Wertheim to deal with Lennard-Jones freely-jointed chains in the solid, liquid and gas phases, for chainlike molecules formed by 2, 4 and 8 Lennard-Jones segments.

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.*[122,123] have determined the vapour pressure and all three major excess properties (V^E,H^E,G^E) of liquid mixtures of xenon with several alkanes from an experimental point of view. The results have been interpreted using the SAFT-VR equation of state.[80,81] This theory is able to correctly predict the excess thermodynamic properties of this kind of mixtures. MacDowell *et al.*[124] have recently calculated the excess properties of binary mixtures of n-alkanes using a modified perturbation theory, based on Wertheim's first-order thermodynamic 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 free energies of n-alkane mixtures.

It becomes clear from the ensuing discussion that it is now possible to use the SAFT approach for describing the excess thermodynamic properties of self-associating binary mixtures of chainlike molecules. The goals of this work are threefold. First, to use the

Soft-SAFT theory to predict the excess behaviour of some self-associating binary mixtures of Lennard-Jones chains and compare the theoretical calculations with new molecular simulation results presented here. This allows to check the accuracy of the equation of state in predicting excess functions. Second, and once the theory has proved to describe correctly the excess properties obtained from simulation, use the theory to study the effect of different molecular parameters, such as the association (bonding energy and number of associating sites) and chain length. Third, to highlight the strengths of the *Soft*-SAFT approach by making some quantitative comparisons with experimental excess volumes for n-alkane + 1-alcohol binary mixtures. In a previous paper,[56] we have studied the excess properties, V^E and H^E, of non-associating binary mixtures of Lennard-Jones chains. Now we extend the previous work by considering self-associating binary mixtures of Lennard-Jones chains using the *Soft*-SAFT theory. The effect of the association and the chain length of such fluids is also considered.

To our knowledge, this is the first systematic comparison between the predictions of the excess thermodynamic properties of self-associating binary mixtures of Lennard-Jones chains from 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 theory, molecular simulation details are described in section 3, followed by results and discussion in next section. Finally, conclusions are presented in section 5.

2 Molecular model and theory

We consider in this work self-associating binary mixtures of homonuclear Lennard-Jones chains. This means that association is possible only between molecules of one of the components, in this case component 2. Both non-associating and associating chains of component i are modelled as m_i Lennard-Jones segments of equal diameter σ_{ii}, and dispersive energy ϵ_{ii}, bonded tangentially to form the chains, as shown in figure 1. Intermolecular and intramolecular interactions between the segments are taken into account through the Lennard-Jones potential model

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

where σ_{ij} and ϵ_{ij} are the segment size and the dispersive energy between segments i and j, respectively. Care must be taken by calling σ as the diameter of the segment size since, strictly speaking, the Lennard-Jones potential model represents a point core described by a potential energy given by equation (1). The segment size, σ, only defines the positive part of the potential, and not its repulsive contribution.

The associating molecules (component 2) are described considering additional embedded off-centre spherical bonding sites, which are modelled as square-well sites of diameter $\sigma_{AB,22}^{HB} = 0.2\sigma_{22}$ and placed at a distance $b_{AB,22}^{HB} = 0.4\sigma_{22}$ from the center of the Lennard-Jones core, to be tangential to the Lennard-Jones sphere (see figure 1) . The association potential between two given associating sites A and B located in two molecules of type 2 is written as

$$\phi_{AB,22}^{HB}(r_{AB}) = \begin{cases} -\epsilon_{AB,22}^{HB} & \text{if } r_{AB} \leq \sigma_{AB,22}^{HB} \\ 0 & \text{otherwise} \end{cases} \tag{2}$$

where $\epsilon_{AB,22}^{HB}$ is the depth of the energy well and r_{AB} is the AB site-site distance. Obviously, the molecules are considered bonded when r_{AB} is smaller than $\sigma_{AB,22}^{HB}$.

This model, previously used in the literature to represent accurately hydrocarbon molecules, accounts for the most important attributes of the chain molecular architecture, that is, the bead connectivity, to represent topological constraints and internal flexibility, the excluded volume effects, the attractions between different beads, and the specific interactions (hydrogen bonding).[71,72,80,108,109]

Since the SAFT approach has widely been used in the literature we will explain here only the most important features of the *Soft*-SAFT theory. Although in this work we concentrate only on self-associating mixtures, we summarise the general equations of the theory, valid for both non-associating and associating mixtures of Lennard-Jones chains. For further details, we recommend the reviews of Müller and Gubbins.[73,74]

The *Soft*-SAFT theory, as other versions of SAFT, is written in terms of the Helmholtz free energy, that 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, the chain contribution, A^{chain}, accounting for the connectivity of the chains, and the association contribution A^{assoc}, for the specific interactions.[107] The residual Helmholtz free energy of a n-component mixture of associating Lennard-Jones chains may by written as

$$\frac{A}{N_c k_B T} - \frac{A^{ideal}}{N_c k_B T} = \frac{A^{LJ}}{N_c k_B T} + \frac{A^{chain}}{N_c k_B T} + \frac{A^{assoc}}{N_c k_B T} \tag{3}$$

where N_c is the number of chain molecules in the system, k_B is the Boltzmann 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 in the following way[42]

$$A^{ideal} = N_c k_B T \left\{ \sum_{i=1}^{n} \left[x_i \ln(x_i \rho_c \Lambda_i^3) \right] - 1 \right\} \tag{4}$$

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

$$\rho = \left[\sum_{i=1}^{n} m_i x_i\right] \rho_c = \sum_{i=1}^{n} m_i \rho_i \tag{5}$$

with ρ_i the monomeric density of species i.

Lennard-Jones reference term

The reference term accounts for both the repulsive and attractive interactions of the segments forming the chains. A^{LJ} is the Helmholtz free energy of a mixture of spherical Lennard-Jones molecules. In this work we use the Lennard-Jones equation of state proposed by Johnson *et al.*[113] 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.[113] It is also possible to use an alternative Helmholtz free energy in the reference contribution, such as that proposed by Tang and Lu,[115] which is based on the solution of the Ornstein-Zernike equation, and provides an analytical equation for this term.

Chain term

The Helmholtz free energy due to the formation of binary mixtures of Lennard-Jones chains, A^{chain}, with bond lengths equal to σ_{11} and σ_{22}, the diameters of the Lennard-Jones segments of species 1 and 2, respectively, is written as[99,107]

$$A^{chain} = N_c k_B T \sum_{i=1}^{n} x_i (1 - m_i) \ln y_{ii}^{LJ}(\sigma_{ii}) \tag{6}$$

where $y_{ii}^{LJ}(\sigma_{ii})$ is the contact value of the cavity correlation function for spherical segments of species i in the Lennard-Jones reference fluid. $y_{ii}^{LJ}(\sigma_{ii})$ is easily related to the pair radial distribution function of the Lennard-Jones fluid, $g_{ii}^{LJ}(\sigma_{ii})$. The radial distribution function used here is given by the Johnson *et al.*'s correlation,[100] although the distribution function proposed by Tang and Lu[115] can also be appropriate (see also the recent work of Tang *et* *al.*[114]).

Association term

Finally, A^{assoc} is the Helmholtz free energy contribution due to the association. This term is expressed as a sum over all the association sites and components of the mixture[66]

$$A^{assoc} = N_c k_B T \sum_{i=1}^{N} x_i \left[\sum_{A \in \Gamma^{(i)}} \left(\ln X_A^{(i)} - \frac{X_A^{(i)}}{2} \right) + \frac{1}{2} n(\Gamma^{(i)}) \right] \tag{7}$$

where $n(\Gamma^{(i)})$ is the total number of associating sites of molecules i. $X_A^{(i)}$, the fraction of molecules i not bonded at site A, may be written as a mass-action equation[66,76]

$$X_A^{(i)} = \frac{1}{1 + \sum\limits_{j=1}^{N} x_j \rho_j \sum\limits_{B \in \Gamma^{(j)}} X_B^{(j)} \Delta_{AB}^{(ij)}} \tag{8}$$

All the non-zero site-site interactions should be defined *a priori* in order to solve eq. (8). $\Delta_{AB}^{(ij)}$ involves an weighted integral over all the orientations and an integration over all separations of molecules 1 and 2, defined as[95,107]

$$\Delta_{AB}^{(ij)} = \int g_{ij}^{LJ}(12) f_{ij}^{AB}(12) d(12) \tag{9}$$

where g_{ij}^{LJ} is the pair radial distribution function of the reference fluid, $f_{ij}^{AB} = \exp(\epsilon_{AB,ij}^{HB}/k_B T) - 1$ is the Mayer function of the association potential, and $d(12)$ denotes an unweighted average over all orientations and an integration over all separations between molecules 1 and 2.

The integration of eq. (9) is not straightforward, since the pair radial distribution function is not readily available. We have replaced the pair radial distribution function of the Lennard-Jones chain fluid by the pair radial distribution function of the Lennard-Jones segment fluid, evaluated at the same temperature and segment density. The choice of this approximation and its validity has been discussed previously.[96,105–107] In order to accurately calculate the integral (9), the expression from Müller and Gubbins[101] for the particular position of the association site inside the Lennard-Jones sphere has been used (see figure 1). As in the case of the chain contribution, the analytical radial distribution function proposed by Tang and Lu[115] for the Lennard-Jones spherical fluid can also be used in equation (9).

Extension to mixtures

Since the Helmholtz free energy is calculated by adding different contributions, each of them should be expressed in terms of compositions for mixtures studies. In the *Soft*-SAFT version, only the reference term needs to be extended to mixtures.[107] The ideal and chain contributions are valid for multicomponent systems; thus, 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.[42] 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

$$\sigma_m^3 = \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} m_i m_j x_i x_j \sigma_{ij}^3}{\sum_{i=1}^{n}\sum_{j=1}^{n} m_i m_j x_i x_j} \tag{10}$$

$$\epsilon_m \sigma_m^3 = \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} m_i m_j x_i x_j \epsilon_{ij} \sigma_{ij}^3}{\sum_{i=1}^{n}\sum_{j=1}^{n} m_i m_j x_i x_j} \tag{11}$$

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

The chain and association terms, A^{chain} and A^{assoc}, depend 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)[42] have been used, as in previous works.[56,107–110] Results from Johnson *et al.*[100] and Müller and Gubbins[101] are used for the pair radial distribution function of the Lennard-Jones fluid from extensive computer simulations fitted to an empirical function of the reduced temperature and density. Details of the simulations are reported elsewhere.[100,113]

For the crossed interactions, the Lorentz-Berthelot combining rules are used[42]

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{12}$$

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \tag{13}$$

In a mixture all parameters are reduced relative to one of the components, component 1 in our case, so that the reduced dimensionless magnitudes are defined in the following way: temperature, $T^* = k_B T/\epsilon_{11}$, pressure, $p^* = p\sigma_{11}^3/\epsilon_{11}$, molecular density, $\rho_c^* = \rho_c\sigma_{11}^3$, internal configurational energy, $U_c^* = U/N_c\epsilon_{11}$, enthalpy, $H_c^* = H/N_c\epsilon_{11}$, excess volume per segment, $V^{E*} = V^E/N\sigma_{11}^3$, excess internal energy per segment, $U^{E*} = U^E/N\sigma_{11}^3$, and excess heat per segment, $H^{E*} = H^E/N\sigma_{11}^3$.

3 Monte Carlo simulation details

We have used the isothermal-isobaric (*NpT*) ensemble Monte Carlo simulation technique[46,47] to study self-associating binary mixtures of Lennard-Jones chains, in which the component 1 is a non-associating molecule and component 2 is an associating chain with one square-well bonding site, as described in the previous section. In particular, we have obtained the influence of the chain length of the associating substance (component 2) 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.[5]

All the simulations have been performed with different molecules of each type (except pure systems) and chain length, although N, the total number of segments, is 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.[46,47]

The temperature, pressure and number of molecules are specified *a priori*, allowing the volume to fluctuate, as well as the energy and the chemical potential. 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 mechanical equilibrium, respectively.[47] The use of the reptation algorithm, instead other more sophisticated simulation methods, such as the configurational bias Monte Carlo, is justified for systems in which short lengths and low densities are considered.[47,125–127]

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 in N attempts to displace molecules and a volume change.[46,47] An equilibrium period of at least 5.10^4 cycles is used. The equilibrium period is increased for high densities. The total simulation length has been between 2.10^5 and 5.10^5 cycles, depending on the system studied . 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.[46,47] These conditions allow to obtain results comparable with those corresponding to similar systems previously studied.[105–107]

4 Results

We apply the *Soft*-SAFT equation of state outlined in section 2 to study some excess thermodynamic properties of self-associating binary mixtures of Lennard-Jones fluids. In order to assess the accuracy of the theory, first we compare the theoretical predictions from the equation of state *versus* molecular simulation results performed in this work for selected self-associating binary mixtures. After this, and once the theory has proved to predict correctly the excess thermodynamic behaviour, we use the equation to calculate the excess functions of self-associating spherical molecules with one and two associating sites, and investigate the effect of association. We also discuss the effect of the chain length of both components (non-associating and associating) on the excess properties. Predictions corresponding to the excess volume of n-alkane + 1-alcohol binary mixtures are also compared with experimental data.

4.1 Comparison with molecular simulation

We have performed NpT Monte Carlo simulations at $T^* = 3.5$ and $p^* = 1.0$. These thermodynamic conditions correspond to supercritical states for all the substances considered here. Because the theory is able to describe accurately the thermodynamic behaviour over a wide range of working conditions, we expect that the conclusions obtained in this section will be applicable to other thermodynamic states, such as those where most experimental excess properties are measured. We have obtained the reduced molecular density, ρ_c^*, and the configurational internal energy, U_c^*, of several self-associating binary mixtures. In this section we concentrate in mixtures for which the first component (a non-associating chain molecule) is formed by three Lennard-Jones segments ($m_1 = 3$) and the second component (associating fluid with one square-well bonding site A) has four, five and six segments ($m_2 = 4$, 5, and 6). The bonding energy of the second component is kept constant and equal to $\epsilon_{AA,22}^{HB*} = 30\epsilon_{22}$. The rest of molecular parameters, segment size and dispersive energy, are chosen to be equal between unlike components.

The excess thermodynamic properties presented in this work are expressed in segment units and calculated in the usual way from simulation data. Results obtained from molecular simulation are shown in table 1. Standard deviations are determined as described by Allan and Tildesley.[46] The relative statistical errors of excess properties are large because these functions are obtained by subtracting quantities of the same order of magnitude. This feature, which has been observed in a previous work,[56] is enlarged in the present study since we deal now with associating systems, where fluctuations are larger. Due to that we do not show bar errors in figures corresponding to excess properties. However, standard deviations obtained from simulation fall within the usual order of magnitude.

To illustrate the last point, we consider first the influence of the chain length of the self-associating substance (component 2) on the density of the mixture. Figure 2 shows the molecular density of three self-associating mixtures at $T^* = 3.5$ and $p^* = 1.0$ *versus* the molecular composition of component 1. As can be observed, the density of the mixture increases as the composition of the non-associating component is increased. At fixed molar composition, the density decreases as the chain length of the self-associating substance is increased. Agreement between molecular simulation data and theoretical predictions is excellent in all the mixtures considered here and in the whole range of compositions. The statistical error of the density of pure substances and binary mixtures are around 1% of the average values, as can been seen in figure 2 and table 1. We have also checked this point for the rest of mixture properties.

The excess functions of the mixtures have been obtained from the theory and molecular simulation using the standard thermodynamic relationships. Figure 3 shows the excess volume of the three self-associating binary mixtures at the same thermodynamic conditions. This property is negative and approximately quadratic in all cases. As can be seen, the excess volume is asymmetric, with the minimum shifted toward the more volatile component, and it increases in absolute value as the difference in chain length increases. The *Soft*-SAFT equation of state provides a good description of the excess volume in all cases and in the whole range of concentrations. Since in this section we are interesting mainly in the adequacy of the theory in predicting this kind of properties, we postpone the origin of the physical behaviour exhibited by these systems to section 4.3, where we discuss widely this point.

We have also obtained the excess configurational internal energy of these mixtures, and results are shown in figure 4. This excess function exhibits different behaviours depending on the chain length of the second component: for mixtures with an associating chain formed by four segments, U^E is positive in the whole range of concentrations; when the chain length of the second component is increased, the excess configurational internal energy behaves as a sigmoidal curve, being positive for mixtures rich in the non-associating component and negative for those rich in the associating substance; finally, when the chain length is increased further ($m_2 = 6$), the excess energy becomes negative at all the mixture concentrations. As can be seen, the theory is able to describe accurately the simulation data in all cases.

Finally, we have calculated the excess heat from the excess volume and configurational internal energy using the standard thermodynamic relationships. Figure 5 shows the comparison between simulation data and theoretical predictions. As can be seen, the excess heat behaves qualitatively in the same way as the excess configurational internal energy when the composition and the chain length of the second component are varied. In summary, the *Soft*-SAFT equation of state is able to describe correctly the excess properties of self-associating binary mixtures of Lennard-Jones chains, finding a good agreement with molecular simulation data.

4.2 Study of the effect of association on excess properties

In this section we first consider the effect of association, i. e., the association energy and the number of bonding sites. In order to study only the effect of association on excess properties, we have considered binary mixtures in which both components are spherical ($m_1 = m_2 = 1$), with the same molecular volume ($\sigma_{11} = \sigma_{22}$) and dispersive energy ($\epsilon_{11} = \epsilon_{22}$), thus eliminating the dependence of the excess functions with the segment size and dispersive energy ratios, as well as with the molecular size.

Figure 6 shows the excess volume and heat of self-associating binary mixtures of

Lennard-Jones spheres, in which the second component has only one bonding site for different values of the association energy. Only AA bonding is allowed so that only dimerization is possible. As can be seen, the excess volume is approximately zero but still positive, in the whole range of concentrations for the smallest associating energy $\epsilon_{AA,22}^{HB*} = 5$. When the bonding energy is increased ($\epsilon_{AA,22}^{HB*} = 10$), an increasing of the excess volume is observed for all compositions of the mixture. As the association well depth of the sites is further increased, $\epsilon_{AA,22}^{HB*} = 15$, the excess volume exhibits a sigmoidal shape, being positive for mixtures rich in the non-associating substance (component 1), and negative for those rich in the associating component. Finally, for higher values of the association energy, $\epsilon_{AA,22}^{HB*} = 20$ and 25, the excess volume becomes negative for all compositions. It is difficult to understand the excess volume and its behaviour in terms of the molecular properties since contributions to V^E due to the dispersive (van der Waals type) and specific (association) interactions are of the same order of magnitude, varying with the composition of the mixture as well.[21,28] However, and from a very simplified point of view, one can says that a positive excess volume implies an expansion of the volume mixture (with respect to that of the pure components) due to unfavourable or repulsive interactions; a negative V^E corresponds to a contraction of the mixture volume due to attractive or favourable interactions. Under this perspective, the excess volume of self-associating binary mixtures is governed by two different mechanisms: (1) a *bonding or association contribution*, that produces a positive excess volume due essentially to the bond breaking of the structure formed by the associating molecules; and (2) a *packing contribution* which produces a negative contribution to the excess volume due to the interstitial accommodation of the non-associating chains within the branched structure formed by the component 2. This later contribution also exists in mixtures of non-associating Lennard-Jones chains of different chain lengths. This system exhibits more negative excess volumes as the difference in chain length between both components increases.[21,28,56]

For low values of the association energy ($\epsilon_{AA,22}^{HB*} = 5$ and 10) the excess volume is positive in the whole range of compositions due to the site-site association breaking which dominates over the packing effect. Essentially, to accommodate a non-associating molecule in the mixture is necessary to break a certain number of bonds. As the bonding energy is increased, the number of associated molecules increases and the packing contribution balances the bonding contribution. This means that although the non-associating molecules continuously break the bonds formed in the system, a great number of molecules of component 1 are able to accommodate within the intersticial structure formed by the component 2. For association values sufficiently high, $\epsilon_{AA,22}^{HB*} = 20$ and 25, the packing contribution dominates the behaviour of the excess volume for all compositions ($V^E > 0$). For intermediate values, $\epsilon_{AA,22}^{HB*} = 15$, the sigmoid shape of the excess volume curves results from a shifting imbalance between relatively large positive and negative contributions. As can be seen, for mixtures rich in the associating component the excess volume is dominated by the packing contribution, while for mixtures rich in the non-associating component the excess volume becomes positive, indicating that the bonding contribution due to the bond breaking dominates over the packing contribution. We have also obtained the excess heat for the same system and thermodynamic conditions. As can be seen in figure 6b, a similar behaviour for this property is found when the association energy is varied, from $\epsilon_{AA,22}^{HB*} = 5$ to $\epsilon_{AA,22}^{HB*} = 25$. Mixtures with low bonding energies exhibit positive excess heats. As the association strength is increased, H^E shows sigmoidal behaviour ($\epsilon_{AA,22}^{HB*} = 20$), and negative values for the largest bonding energy considered ($\epsilon_{AA,22}^{HB*} = 25$).

We next proceed to investigate the excess properties of self-associating mixtures of spherical fluids with two anisotropic bonding sites (see figure 1). In this case the bonding sites, denoted by A and B, are only allowed to form AB bonds (no AA or BB association is considered). We have chosen the same thermodynamic conditions and bonding energy values for these systems. As can be seen in figure 7a, the excess volume exhibits a similar behaviour than that observed for mixtures in which the associating component has only one bonding site: for low association energy values the excess volume is positive, and for high values the excess function is negative in the whole range of concentrations. For intermediate values of $\epsilon_{AB,22}^{HB*}$, the excess volume exhibits a sigmoidal shape when is plotted *versus* the composition of the mixture, indicating a balance between the bonding and packing contributions, which depend on the concentration of the mixture. An important difference between the behaviour exhibited by this system and those corresponding to mixtures with only one bonding site can be observed: for systems with two bonding sites A and B, the magnitude of the excess volume is larger than the corresponding one to associating systems with one bonding site. This is due to a higher degree of association and the possibility of forming aggregates in the second system. A similar behaviour is also observed for the excess heat, as can be seen in figure 7b: positive values for low bonding energies, sigmoidal shape for intermediate values, and negative for high association energies.

In summary, the main effect of molecular association on the excess properties of self-associating Lennard-Jones spherical fluids is to increase the excess volume and heat for low values of the association energy. For intermediate values of the bonding strength, the excess properties exhibit a sigmoidal shape. Finally, for strong association energies, the excess properties are negative for all compositions. The effect of including additional bonding sites in the associating component (two instead of one) is to increase the absolute values of the excess properties, although the same qualitative behaviour is observed in both cases.

4.3 Effect of the chain length on excess properties

We consider now self-associating binary mixtures of Lennard-Jones chains, in which the second component (associating substance) has two A and B bonding sites. As in the previous section, only AB association is allowed. We first analyze the effect of the chain length of the associating substance on the excess properties. To do that, we consider self-associating binary mixtures in which the first component is a Lennard-Jones dimer and the second one is an associating chain formed by one, two, three and four spherical Lennard-Jones segments. The segment size and dispersive energy of the Lennard-Jones spheres of both components are equal ($\sigma_{11} = \sigma_{22}$ and $\epsilon_{11} = \epsilon_{22}$). The association energy is kept constant and equal to $\epsilon_{AB,22}^{HB*} = 15$, and the other geometrical parameters that characterise the square-well bonding sites are the same than those used in the previous sections (see figure 1). We have chosen this value for $\epsilon_{AB,22}^{HB*}$ since corresponds to a bonding energy similar to that found for real 1-alcohols.[108] Figure 8 shows the excess volume and heat of such mixtures. As can be seen in figure 8a, the excess volume has different signs as the chain length of the second component is increased: for mixtures with $m_2 = 1$ the excess volume is positive in the whole range of concentrations. As the chain length is increased ($m_2 = 2$ and 3), the excess volume becomes sigmoidal, being positive for mixtures rich in the non-associating component and negative for those rich in the component 2 (see also the inset of figure 8a). Finally, for mixtures with associating chains formed by 4 segments ($m_2 = 4$), the excess volume becomes negative in the whole range of concentrations. A similar behaviour is also observed for the excess heat (see figure 8b), although with a slight difference, the range of chain length values of the associating component at which the excess function changes its sign: H^E is positive for mixtures with $m_1 = 1$ and 2, and exhibits a sigmoidal shape when $m_2 = 3$ and 4. This behaviour, which is also observed in n-alkane + 1-alcohol binary mixtures,[21,28] can be explained in terms of the molecular parameters of the theory and taking into account the two main effects that govern the mixture properties of these systems, i. e., the bonding and packing contributions (see previous section). When the chain length of the associating component is shorter than that corresponding to the non-associating substance, it exists a disruption of the associating multimers through the breaking of associating bonds, due essentially to the impossibility for interstitial accommodation of the non-associating molecules. However, as the chain length of the associating molecules is increased, the capability for interstitial accommodation increases. On the other hand, as the difference in chain length between both components is increased, the negative (packing) contribution to the excess properties becomes more important. This effect, related with the interstitial accommodation, is also observed in binary mixtures of non-associating Lennard-Jones chains.[56] The same effects account for the decrease of the positive lobe of the V^E curves in figure 8 with increasing the chain length of the associating molecule, and its disappearance for sufficiently large molecules.

We now analyze the effect of the chain length of the non-associating component. We consider self-associating binary mixtures in which the second component is an associating Lennard-Jones dimer and the first one is a non-associating molecule formed by one, two, three and four Lennard-Jones spherical segments. The segment size and dispersive energy of the segments are chosen to be equal. The association energy is also kept constant and with the same value, $\epsilon_{AB,22}^{HB*} = 15$. Figure 9a shows the excess volume for different chain lengths of the non-associating molecule. For mixtures with $m_1 = 1$ the excess volume is negative in the whole range of compositions. As the chain length is increased, $m_1 = 2$, the excess volume behaves as a sigmoid curve, being positive for mixtures rich in the non-associating component, and negative at high molar fractions of the associating component. Finally, for mixtures with longer associating molecules, $m_1 = 3$ and 4, the excess volume is positive at all concentrations. Figure 9b shows the analogous curves corresponding to the excess heat of this kind of systems, which exhibit the same qualitatively behaviour: for mixtures with $m_1 = 1$ the excess heat has a sigmoid shape, while for longer chains, $m_1 = 2, 3$ and 4, the excess enthalpy is positive in the whole range of compositions. As in the previous set of systems, the behaviour observed in figure 9 can be explained as the resultant of the contributions from two opposing effects, namely, the bonding and packing contributions. We have also investigated the excess properties of self-associating Lennard-Jones chains formed by different chain lengths. Figure 10 shows a table where the signs of the excess volume and heat for mixtures of non-associating + associating chains formed by one, two, three and four segments are presented. As can be seen, when the chain length of the associating molecule is larger than that corresponding to the non-associating substance, the excess properties are negative since the packing contribution dominates over the bonding contribution. Contrary, excess properties are positive for mixtures in which the associating molecule is shorter than the non-associating component. For similar chain lengths, a strong competition effect between the bonding and packing contributions exists. Since this effect results from a shifting imbalance between relatively large positive and negative contributions which are sensitive to the lengths of the components and composition, a sigmoidal shape is observed for both excess properties. These results are able to explain qualitatively the experimental excess properties of n-alkane + 1-alcohol homologous series.[21–28]

In order to corroborate the existence of two oppositive contributions (bonding and packing), we analyze in deep detail the effect of the association energy on the excess properties, and particulary on the excess volume, for self-associating binary mixtures of Lennard-Jones chains with different chain lengths. The segment size and dispersive energy ratios are keep constants and equal to one. We consider initially a binary mixture of non-associating Lennard-Jones chains with different chain lengths, in particular, molecules formed by two and three segments, and study the effect of including two bonding sites for varying degrees of association. When $\epsilon_{AB,22}^{HB*}$ is equal to zero, the excess volume of the mixture is negative at all proportions.[56] Since the segments forming both components have the same segment size and dispersive energy, the only reason for which the mixture exhibits negative V^E is due to the interstitial accommodation of the molecules and changes of the free volume.[56] Figure 11a shows the excess volume of the mixture when two bonding sites, for different association energies, are incorporated to the longest molecule, $m_2 = 3$. We have also plotted the fraction of the associating molecules that exist in the mixture as monomers (figure 11b). As can be seen, for the lowest bonding energy, $\epsilon_{AB,22}^{HB*} = 5$, the excess volume does not change substantially, although its value is slightly higher. For $\epsilon_{AB,22}^{HB*} = 10$ an increasing of the excess volume is observed, especially for mixtures rich in the non-associating component. This is consistent with the rapid increasing of monomers in the mixture for molar compositions higher than 0.8 shown in figure 11b. As the association energy is further increased, $\epsilon_{AB,22}^{HB*} = 15$ and 20, the excess volume becomes negative at all concentrations (except for the case $\epsilon_{AB,22}^{HB*} = 15$ and molar concentrations between 0.94 and 1, where the excess volume is positive), which is consistent with the existence a great degree of association in the mixture (see figure 11b) over practically the whole range of concentrations. Since there is not bond breaking in the system, the non-associating molecules are easily accommodated in the interstitial positions within the branched structure of the associating molecule multimers.

We have also considered the opposite procedure, this is, to include two bonding sites for different association energy values in the shortest molecule formed by two Lennard-Jones spheres. Figure 12 shows the excess volume (12a) and the fraction of monomers corresponding to the associating substance (12b). As can be seen in figure 12a, the effect of increasing the association energy of the shortest component is to increase monotonically the excess volume, which becomes positive for $\epsilon_{AB,22}^{HB*}$ values between 8 and 9. This behaviour is consistent with the fraction of monomer curves shown in figure 12b. The main differences between this behaviour and that shown in figure 11b are mainly two: first, the degree of association in the current system is much lower than the corresponding one shown in figure 11; second, the slope of the curve for the fraction of monomers is much sharper, without the plateau for molar fractions between 0 and 0.8. This shows clearly that in the current case does not exist a competition effect between the bond breaking and the interstitial accommodation, since the non-associating component is longer than the associating chainlike fluid.

In summary, the excess behaviour of self-associating binary mixtures of Lennard-Jones chains is governed by a delicate interplay between the bond breaking and the interstitial accommodation of the non-associating chains within the branched multimeric structure of the associating fluid. This produces positive, negative and sigmoidal behaviour depending on the chain length and composition of the mixture.

4.4 Preliminary comparison with experiment

The models and theory described in the previous sections have widely been used to examine the phase equilibria of a great number of real systems, including n-alkanes and 1-alcohols (see the detailed reviews by Müller and Gubbins[73,74]). As mentioned in the introduction, the excess volume of n-alkane + 1-alcohol binary mixtures exhibit a rich behaviour which critically depends on the relative chain lengths of components:[21–28] when the n-alkane is much longer than the 1-alcohol, the mixture exhibits positive excess volumes; contrary, when the molecular weight of the 1-alcohol is higher than the corresponding to the n-alkane, the excess volume is negative; for n-alkane and 1-alcohol molecules formed by a similar number of carbon atoms, the excess volume exhibits sigmoidal behaviour, being positive for mixtures rich in n-alkane and negative for those rich in 1-alcohol.[21–28]

We use the *Soft*-SAFT equation of state to examine the excess properties (particularly the excess volume) of two binary mixtures: n-heptane(1) + 1-propanol(2) and n-pentane(1) + 1-propanol(2). As in previous works,[108] the n-alkane molecules are modelled as m Lennard-Jones spherical sites, with diameter σ and dispersive energy ϵ, tangentially bonded to form the chain. The non-spherical (chain-like) shape of 1-propanol is accounted for using the same model. Additionally, we place two square-well off-centre associating sites to model the hydrogen bonding interactions between 1-propanol molecules. The two hydrogen sites account for the two electron lone pairs and the hydrogen atom of the OH group.[108] The values of the molecular parameters are presented in table 2. This set of parameters were obtained by fitting them to the experimental saturated liquid density and by equating the chemical potential in both phases.[108]

The calculation of the mixture thermodynamic properties also requires the determination of a number of cross or unlike parameters. The segment size and dispersive energy between unlike components, σ_{12} and ϵ_{12}, are expressed using the generalised Lorentz-Berthelot combining rules

$$\sigma_{12} = \eta \frac{\sigma_{11} + \sigma_{22}}{2} \tag{14}$$

$$\epsilon_{12} = \xi \sqrt{\epsilon_{11} \epsilon_{22}} \tag{15}$$

where η and ξ are two adjustable parameters that describe the departure of the system from the Lorentz and Berthelot combining rules, respectively. These two unlike adjustable parameters are determined by fitting to the experimental excess volume at dilute concentrations of the n-alkane (see table 3).

A preliminary comparison of the *Soft*-SAFT predictions with the experimental values of the excess volume of n-heptane(1) + and n-pentane(1) + 1-propanol(2) is shown in figure 13. The excess volume is positive for the first mixture since the bonding contribution dominates over the packing effect. The n-heptane molecules disrupt the hydrogen bonds between 1-propanol species, and they are not able to accommodate within the branched network of the 1-propanol molecules due essentially to steric effects. However, as the chain length of the n-alkane is decreased (n-pentane), the packing contribution compensates the bonding effect. This is only true for compositions below $x_1 < 0.5$. For $x_1 > 0.5$, a large proportion of n-pentane molecules can not be accommodated within the intersticial positions of the 1-propanol branched network, resulting a positive excess volume of the system. As can be seen, the agreement between theoretical predictions and experimental data for both binary mixtures is excellent in the whole range of compositions, especially for the case of the n-heptane(1) + 1-propanol(2) system. It is important to note that the molecular parameters of pure components have been obtained correlating the vapour-liquid phase behaviour of n-heptane, n-pentane and 1-propanol, and only experimental excess volume data corresponding to $x_1 < 0.1$ has been used to correlate the unlike molecular parameters. It is very pleasing to see that the SAFT approach is able to reproduce the change in shape of the excess volume of n-alkane + 1-alcohol binary mixtures. A more systematic investigation of the excess properties of n-alkane + 1-alcohol binary mixtures will be undertaken in a future work.

5 Conclusions

The *Soft*-SAFT theory has been used to obtain the excess thermodynamic properties of self-associating binary mixtures of Lennard-Jones chains. To check the adequacy of the theory in predicting the excess behaviour of the molecular model, we have performed NpT Monte Carlo simulations of selected systems and obtained the excess volume, internal configuration energy and heat. In particular, we have considered binary systems in which the chain length of the associating component is varied. Agreement between theoretical predictions and simulation data is excellent in all cases and in the whole range of compositions.

We apply the theory to study the effect of several molecular parameters on the excess properties of such systems. In this paper we have focused on the effect of association and chain length on the excess volume and heat. The main effect of association is found to be strongly dependent on the bonding energy of the self-associating spherical compounds. For low values of the bonding energy, the excess properties are positive in the whole range of concentrations; at intermediate values of the bonding strength, the excess functions exhibit a sigmoidal shape, being positive for mixtures rich in the non-associating component and negative for those rich in the associating molecule; finally, for high association energies, the excess properties are negative at all compositions. The effect of including additional bonding sites, which has also been investigated, is to increase the absolute values of the excess properties, although the same qualitative behaviour is obtained. The effect of the chain length on the excess properties, which causes strong deviations from ideality, has also been considered including in the Helmoholtz free energy of the system the contribution due to the chain formation. An increase in the chain length of the non-associating component produces an increase of the excess volume and heat functions, being both properties positive in the whole range of compositions. Contrarily, an increase of the chain length of the associating compound produces a decreasing of the excess properties, being both of them negative at all compositions. However, when the chain length of both components is similar, the excess properties exhibit a sigmoidal shape. The behaviour observed can be explained in terms of two opposite contributions to the total excess functions: an bonding positive contribution due to the bond breaking and a packgin negative contribution due to the accommodation of the non-associating molecules within the interstitial branched multimeric structure of the associating fluid. Since both contributions are critically sensitive to the lengths of the components and composition, positive, negative and sigmoidal shape excess properties are observed.

Finally, a preliminary comparison with experiment is presented. The *Soft*-SAFT theory is used to predict the excess volume of n-pentane +, and n-heptane + 1-propanol binary mixtures. The theoretical predictions provide a good description of the experimental data, indicating that the SAFT approach contains the essential physics to describe the most salient features of the excess properties of self-associating binary mixtures of non-spherical molecules. In a future work we plan to use the SAFT theory to investigate the excess volumes and heats of n-alkane + 1-alcohol binary mixtures. Comparison with experimental data will also be considered.

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Table 1. NPT ensemble Monte Carlo simulation results for self-associating binary mixtures of Lennard-Jones chains at $T^* = 3.5$ an $P^* = 1$. ρ_c^* is the mixture density, U_c^* the configurational internal energy and X_A the fraction of monomers. The diameter and dispersive energy of both components are the same. The first component is a Lennard-Jones trimer and the second one has m_2 segments.

m_2	x_1	ρ_c^*	$-U_c^*$	X_A
4	0.0	0.1296(2)	12.6(9)	0.81(4)
4	0.2	0.1352(2)	11.3(3)	0.84(3)
4	0.4	0.1405(3)	9.9(3)	0.87(3)
4	0.6	0.1467(3)	8.9(2)	0.91(4)
4	0.8	0.1153(2)	7.9(2)	0.95(5)
4	1.0	0.2159(7)	7.14(3)	1.0
5	0.0	0.110(3)	15.6(6)	0.83(3)
5	0.2	0.117(2)	13.7(5)	0.84(4)
5	0.4	0.125(2)	11.9(4)	0.88(4)
5	0.6	0.135(2)	10.1(2)	0.91(4)
5	0.8	0.146(2)	8.5(2)	0.95(5)
5	1.0	0.1588(7)	7.14(4)	1.0
6	0.0	0.094(2)	18.5(6)	0.83(4)
6	0.2	0.102(2)	15.9(4)	0.87(4)
6	0.4	0.112(2)	13.6(4)	0.88(3)
6	0.6	0.125(2)	11.3(3)	0.91(4)
6	0.8	0.139(1)	9.1(1)	0.94(5)
6	1.0	0.1588(7)	7.14(4)	1.0

Table 2. Optimised parameters for the models of n-pentane, n-heptane and 1-propanol taken from Blas and Vega.[108]

Substance	σ/Å	(ϵ/k_B)/K	m	(ϵ^{HB}/k_B)/K	K^{HB}/σ^3
n-pentane	3.778	232.973	2.699	-	-
n-heptane	3.697	240.125	3.726	-	-
1-propanol	3.683	247.833	2.160	3355.03	46.2413

Table 3. Optimised unlike binary parameters for the mixture models of n-pentane(1) + 1-propanol(2) and n-heptane(1) + 1-propanol(2). ξ and η are determined by fiiting to the experimental excess volume at dilute concentrations of the n-alkane (see the text for further details).

Mixture	ξ	η
n-pentane(1) + 1-propanol(2)	1.008081860	1.00480039
n-heptane(1) + 1-propanol(2)	0.973343039	1.00467009

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Figure 1. Models for: (a) a spherical associating molecule with one bonding site; (b) a spherical associating molecule with two bonding sites; (c) a non-associating chainlike molecule; and (d) an associating chainlike molecule with two bonding sites. A number of off-centre square-well bonding sites are placed on Lennard-Jones spheres of diameter σ and dispersive energy ϵ. The sites are placed at a distance $b^{HB} = 0.4\sigma$ and have a range $\sigma^{HB} = 0.2\sigma$. The two different types of sites are depicted as white and gray; only white-gray bonding is allowed. The white and gray sites interact with an associating energy ϵ^{HB} when the site-site distance is less than σ^{HB}.

Figure 2. Mixture density *versus* composition of non-associating(1) + associating(2) binary mixtures of Lennard-Jones chains at $T^* = 3.5$ and $p^* = 1.0$. The diameter and dispersive energy of both components are the same. The chain length of component 1 is $m_1 = 3$ and $m_2 = 4$ (circles), 5 (squares) and 6 (diamonds). In all cases $\epsilon^{HB*}_{AA,22} = 30\epsilon_{22}$. The curves represent the predictions from the *Soft*-SAFT theory and symbols correspond to the simulation data.

Figure 3. Excess volume per segment of non-associating(1) + associating(2) binary mixtures of Lennard-Jones chains at $T^* = 3.5$ and $p^* = 1.0$. The diameter and dispersive energy of both components are the same. The chain length of component 1 is $m_1 = 3$ and $m_2 = 4$ (circles), 5 (squares) and 6 (diamonds). In all cases $\epsilon^{HB*}_{AA,22} = 30\epsilon_{22}$. The curves correspond to the *Soft*-SAFT predictions and symbols represent the simulation data.

Figure 4. Excess configurational internal energy per segment of non-associating(1) + associating(2) binary mixtures of Lennard-Jones chains at $T^* = 3.5$ and $p^* = 1.0$. The curves and symbols represent the same values as in figure 3.

Figure 5. Excess heat per segment of non-associating(1) + associating(2) binary mix-

tures of Lennard-Jones chains at $T^* = 3.5$ and $p^* = 1.0$. The curves and symbols represent the same values as in figure 3.

Figure 6. Excess volume (a) and heat (b) per segment of non-associating(1) + associating(2) binary mixtures of Lennard-Jones spheres with one bonding site for different values of the association energy: $\epsilon_{AA,22}^{HB*} = 5$ (continuous curve), 10 (dotted curve), 15 (dashed curve), 20 (long-dashed curve) and 25 (dot-dashed curve). The diameter and dispersive energy of both components are the same. In all cases $T^* = 1.0$ and $p^* = 0.03$.

Figure 7. Excess volume (a) and heat (b) per segment of non-associating(1) + associating(2) binary mixtures of Lennard-Jones spheres with two bonding sites for different values of the association energy: $\epsilon_{AA,22}^{HB*} = 5$ (continuous curve), 10 (dotted curve), 15 (dashed curve), 20 (long-dashed curve) and 25 (dot-dashed curve). The diameter and dispersive energy of both components are the same. In all cases $T^* = 1.0$ and $p^* = 0.03$.

Figure 8. Excess volume (a) and heat (b) per segment of non-associating(1) + associating(2) binary mixtures of Lennard-Jones chains with two bonding sites for different values of the chain length of the second component: $m_2 = 1$ (continuous curve), 2 (dotted curve), 3 (dashed curve) and 4 (long-dashed curve). The diameter and dispersive energy of the segments of both components are the same. The chain length of component 1 is $m_1 = 2$. In all cases $T^* = 1.0$, $p^* = 0.03$, and $\epsilon_{AB,22}^{HB*} = 15$. The insets also show the excess volume (a) and heat (b) for dilute concentrations of the associating component.

Figure 9. Excess volume (a) and heat (b) per segment of non-associating(1) + associating(2) binary mixtures of Lennard-Jones chains with two associating sites for different values of the chain length of the first component: $m_1 = 1$ (continuous curve), 2 (dotted curve), 3 (dashed curve) and 4 (long-dashed curve). The diameter and dispersive energy of the segments of both components are the same. The chain length of component 2 is $m_2 = 2$. In all cases $T^* = 1.0$, $p^* = 0.03$, and $\epsilon_{AB,22}^{HB*} = 15$. The insets also show the excess

volume (a) and heat (b) for dilute concentrations of the associating component.

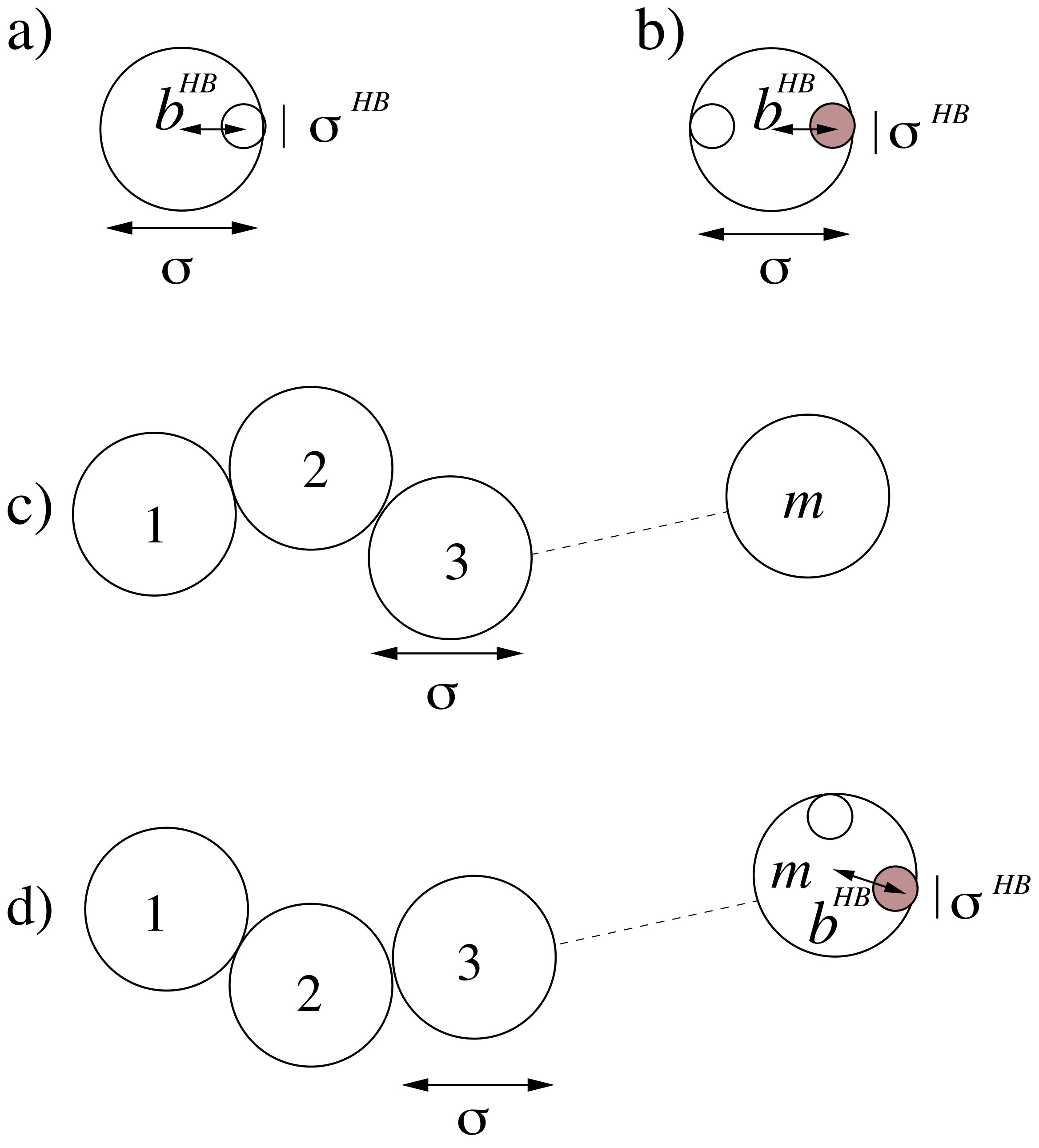
Figure 10. Summary of the predictions of the excess volume and heat from the *Soft*-SAFT theory for self-associating binary mixtures of Lennard-Jones chains with two bonding sites for $m_1 = 1, 2, 3$ and 4, and $m_2 = 1, 2, 3$ and 4. The + means that the excess property is positive in the whole range of concentrations, − that is negative at all compositions and S that the excess function exhibits a sigmoidal behaviour. In all cases $\sigma_{11} = \sigma_{22}$, $\epsilon_{11} = \epsilon_{22}$, $T^* = 3.5$, $p^* = 1.0$ and $\epsilon^{HB*}_{AB,22} = 15$.

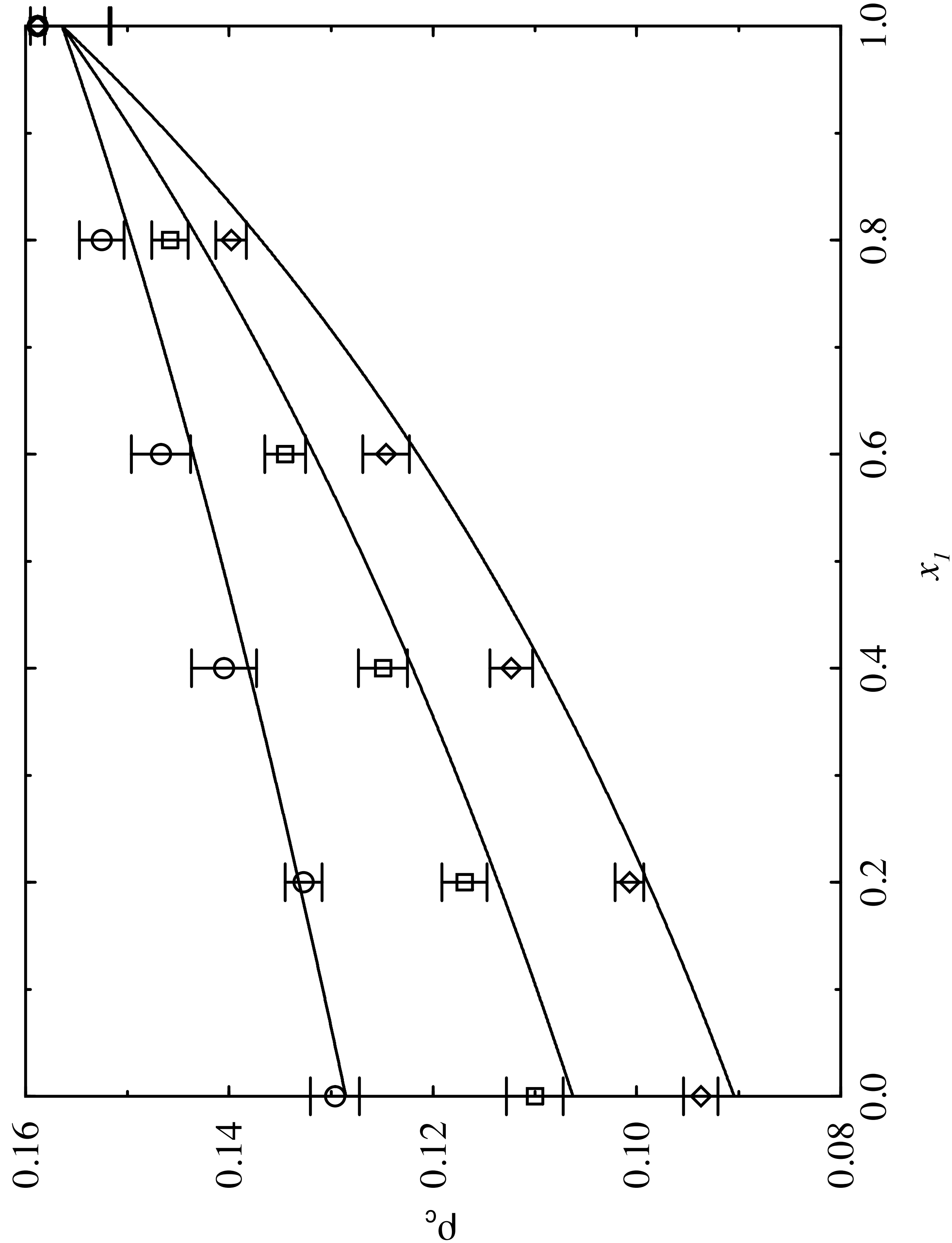
Figure 11. Excess volume per segment (a) and fraction of monomers (b) of non-associating(1) + associating(2) binary mixtures of Lennard-Jones dimers ($m_1 = 2$) and trimers ($m_2 = 3$) with two bonding sites for different values of the association energy: $\epsilon^{HB*}_{AB,22} = 0$ (continuous curve), 5 (dotted curve), 10 (dashed curve), 15 (long-dashed curve) and 20 (dot-dashed curve). The diameter and dispersive energy of the segments of both components are the same. In all cases $T^* = 1.0$ and $p^* = 0.03$. The inset of (a) represents the excess volume for dilute concentrations of the associating component.

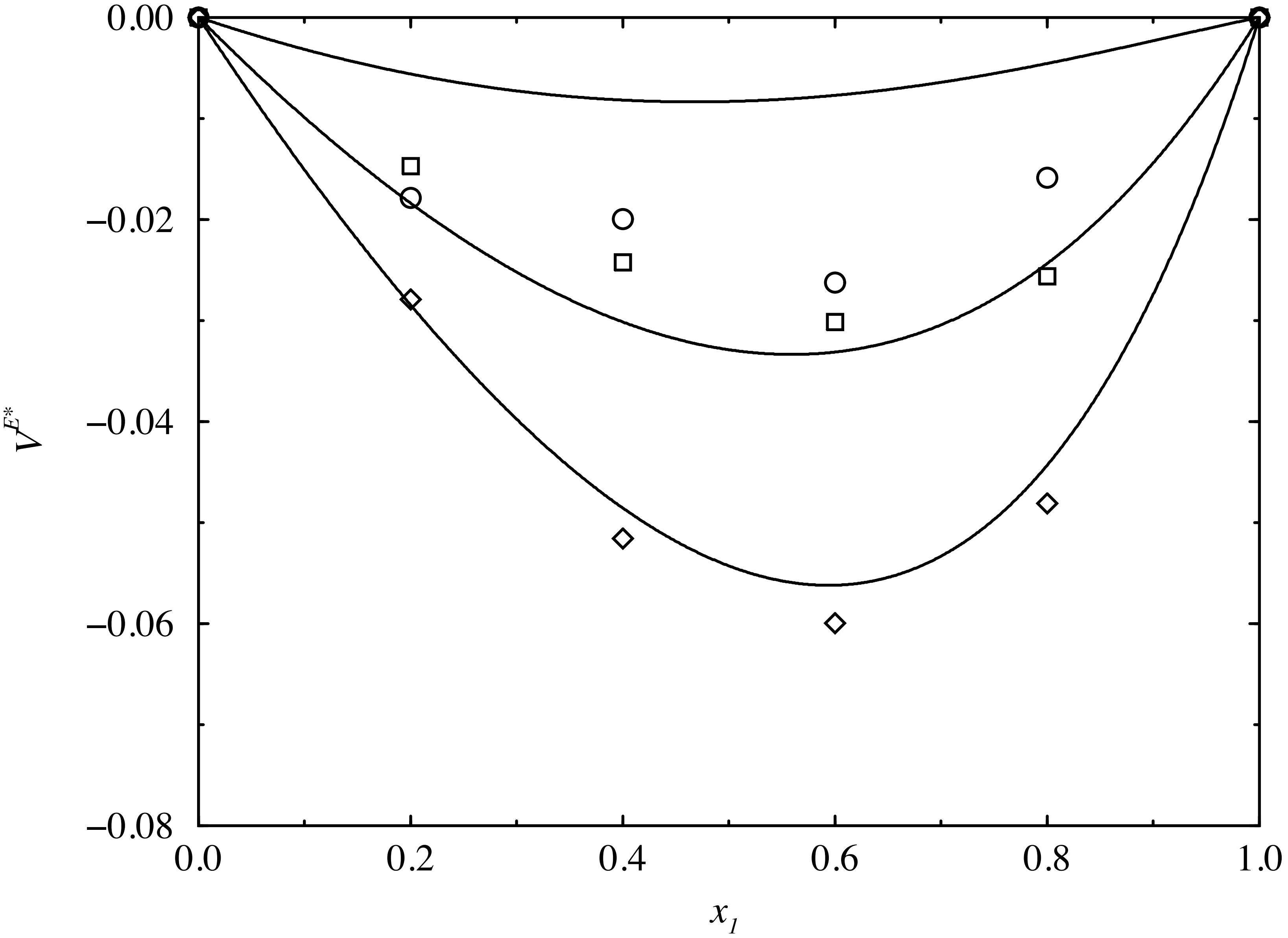
Figure 12. Excess volume per segment (a) and fraction of monomers (b) of non-associating(1) + associating(2) binary mixtures of Lennard-Jones trimers ($m_1 = 3$) and dimers ($m_2 = 2$) with two bonding sites for different values of the association energy: $\epsilon^{HB*}_{AB,22} = 0$ (continuous curve), 5 (dotted curve), 7 (dashed curve), 8 (long-dashed curve) and 9 (dot-dashed curve). The diameter and dispersive energy of the segments of both components are the same. In all cases $T^* = 1.0$ and $p^* = 0.03$. The inset of (a) represents the excess volume for dilute concentrations of the associating component.

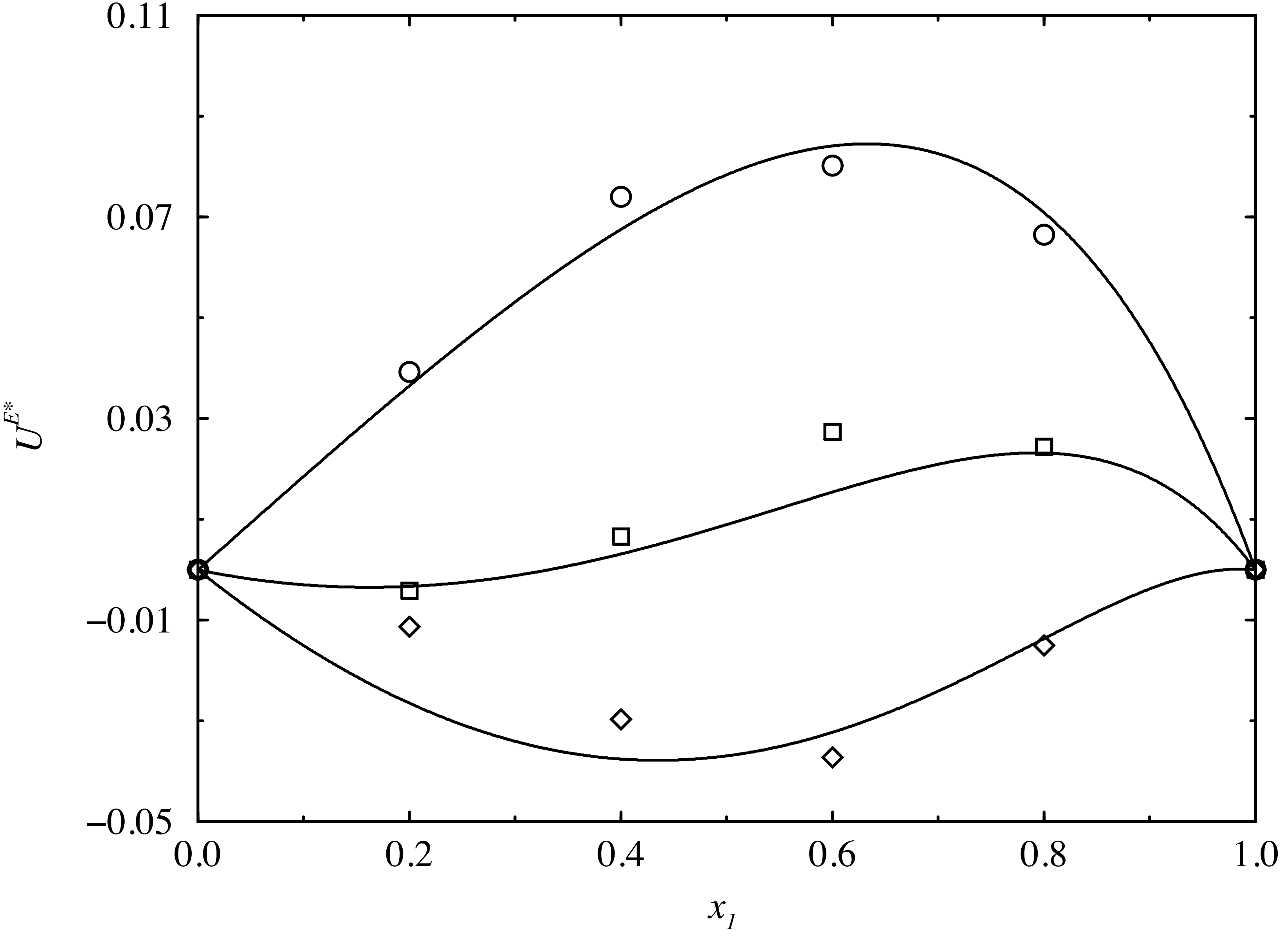
Figure 13. Excess volume of n-alkane + 1-alcohol binary mixtures at $T = 298.15$K and $p = 0.101325$MPa. The symbols represent the experimental data taken from the literature for n-heptane(1) + 1-propanol(2)[21] (circles) and n-pentane(1) + 1-propanol(2)[33] (squares), and continuous curves correspond to the *Soft*-SAFT predictions with the set

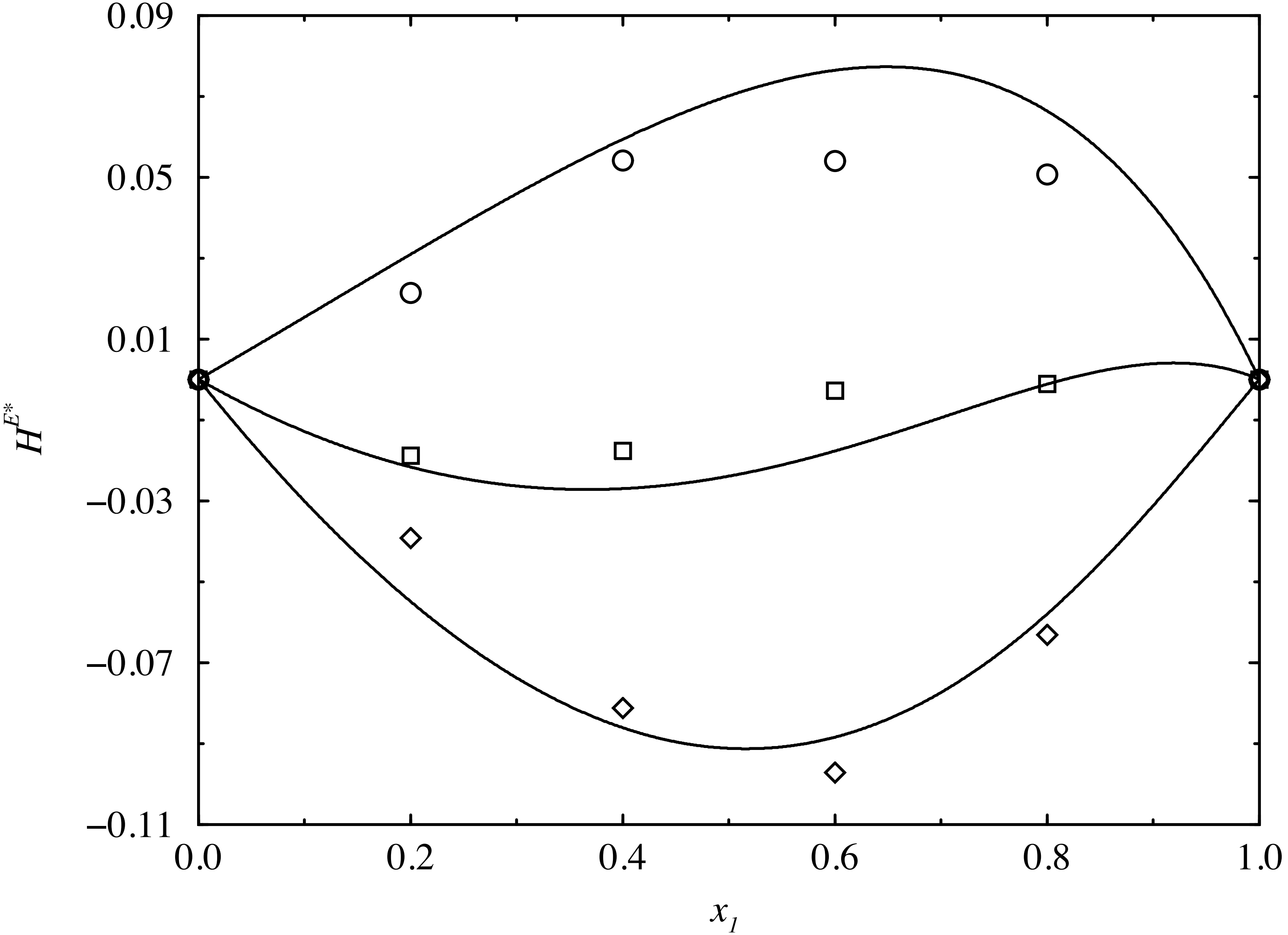
of parameters taken from Blas and Vega[108] (see table 2) and unlike mixture parameters shown in table 3.

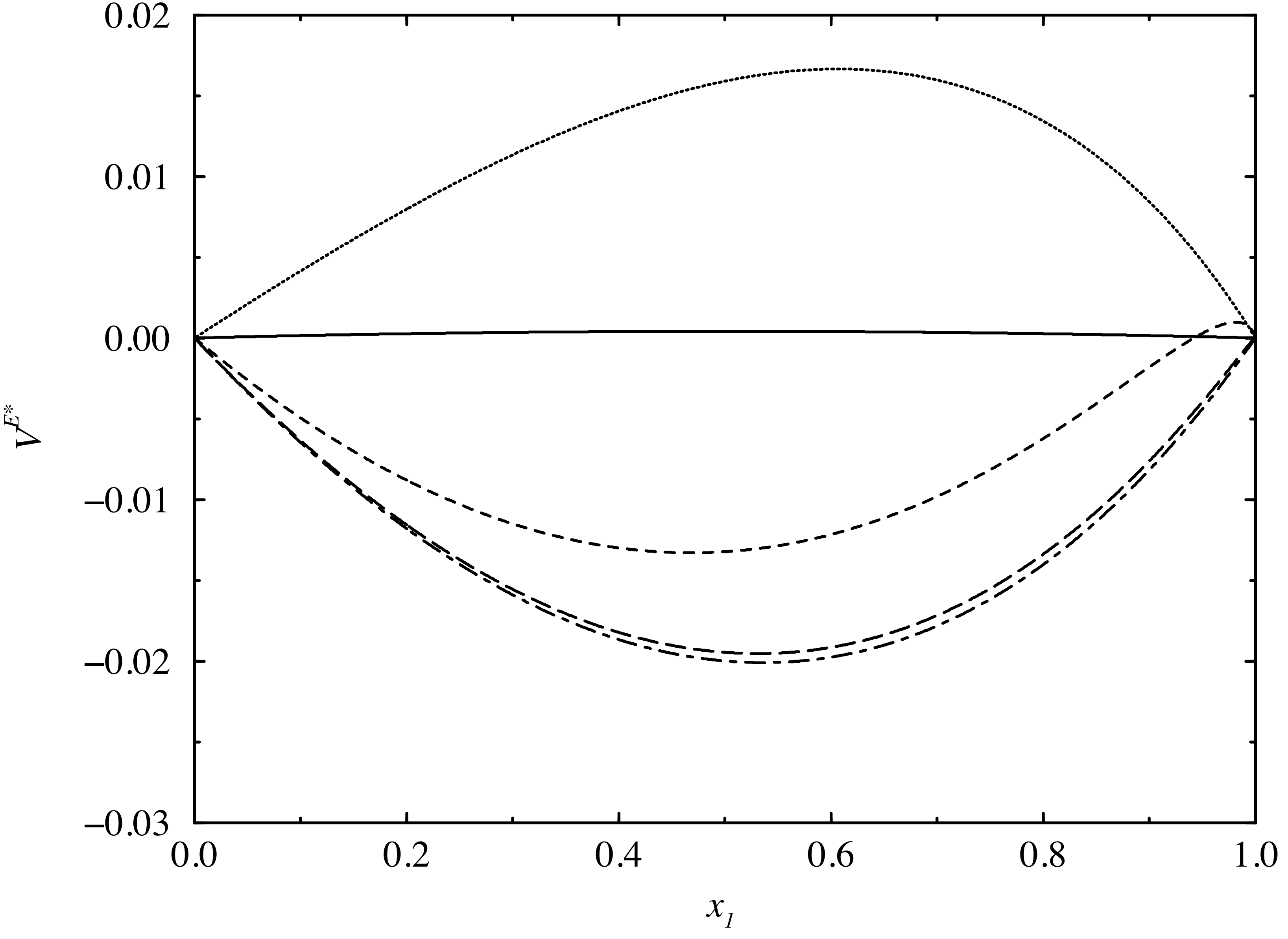

a)
b^{HB}
σ^{HB}
σ
b)
b^{HB}
σ^{HB}
σ
c)
1
2
3
m
σ
d)
1
2
3
m
b^{HB}
σ^{HB}
σ

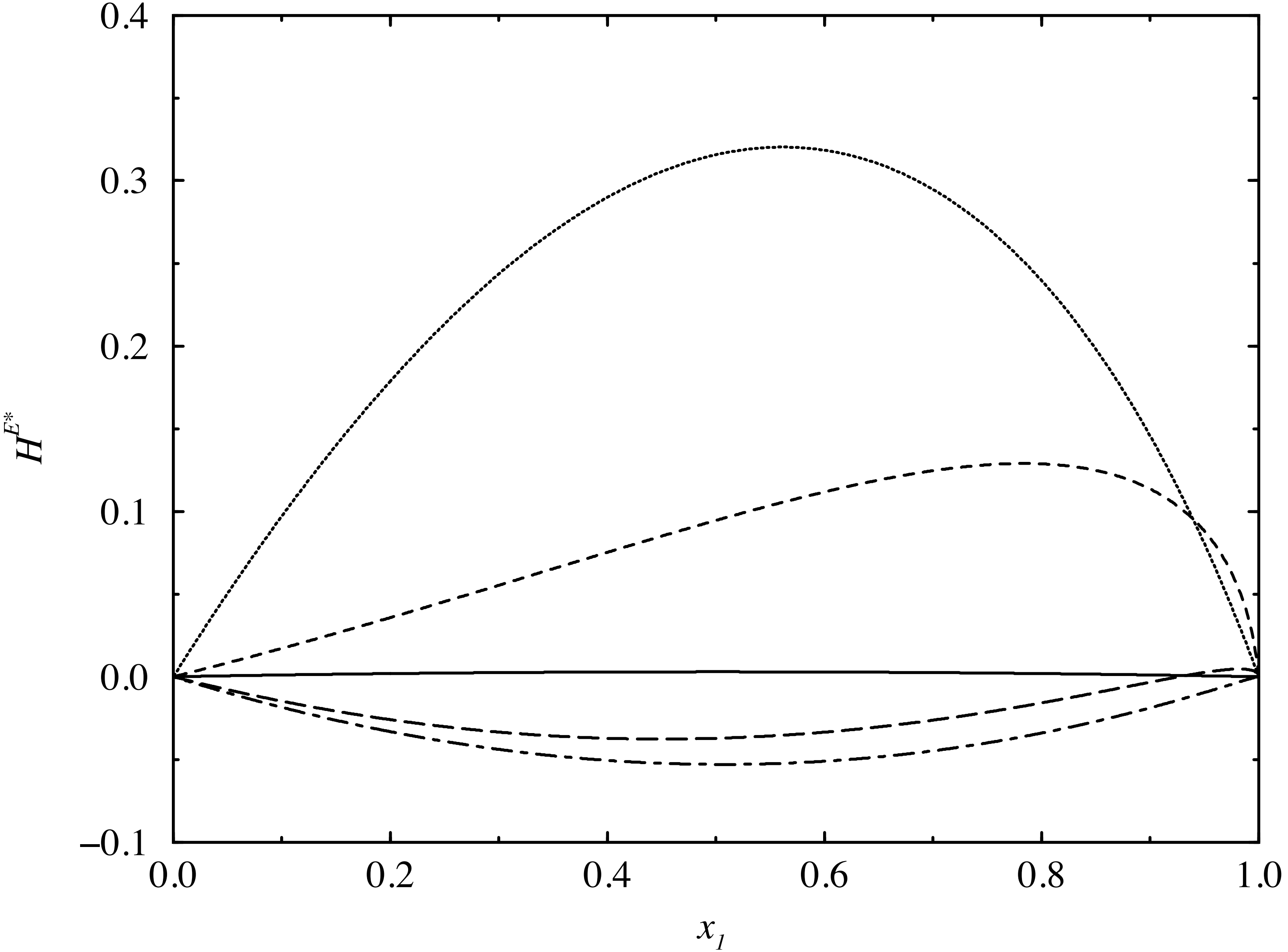

0.16
0.14
0.12
0.10
0.08
ρ_c^*
0.0
0.2
0.4
0.6
0.8
1.0
x_1

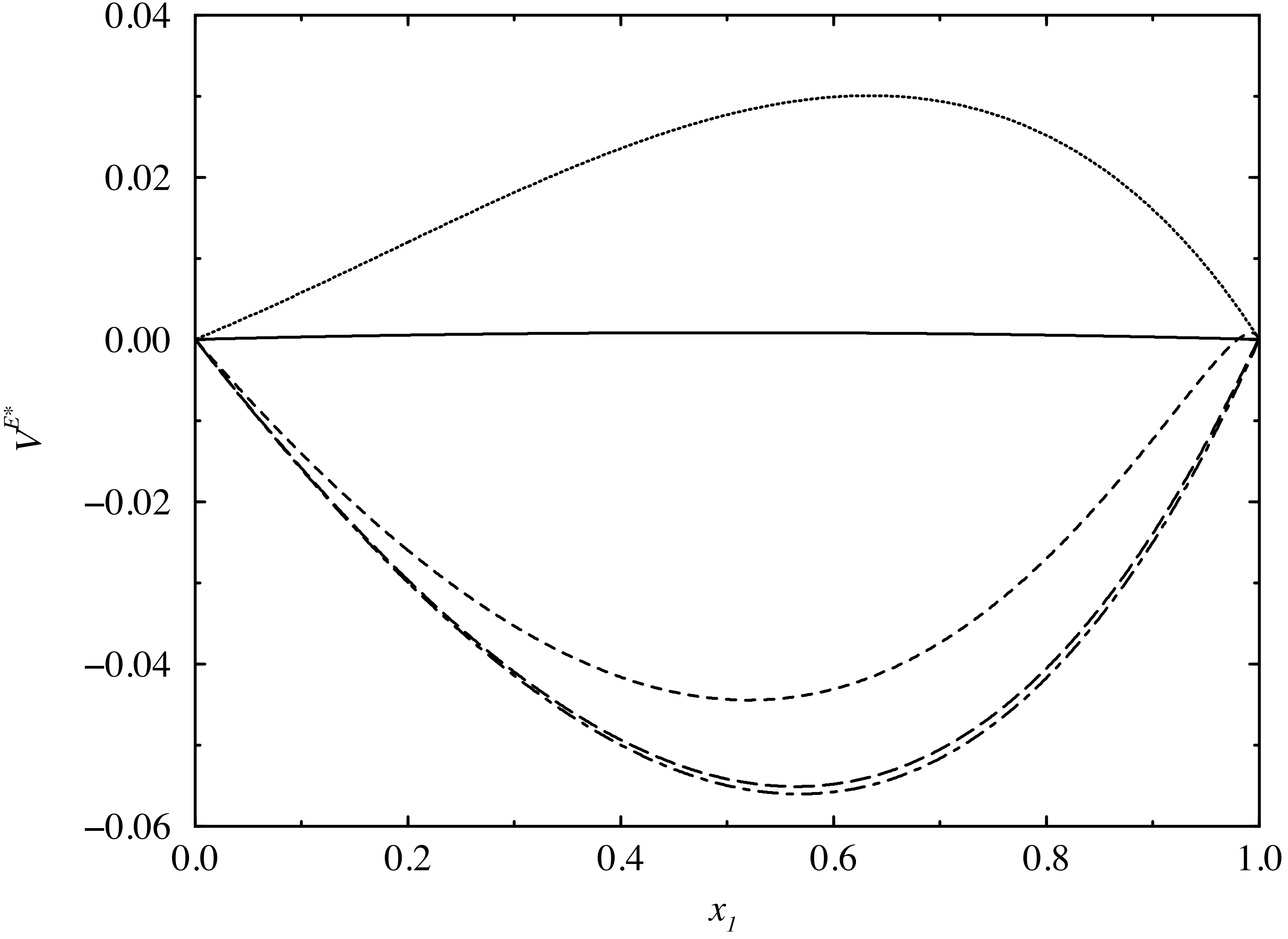

0.00
−0.02
−0.04
−0.06
−0.08
V^{E*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1

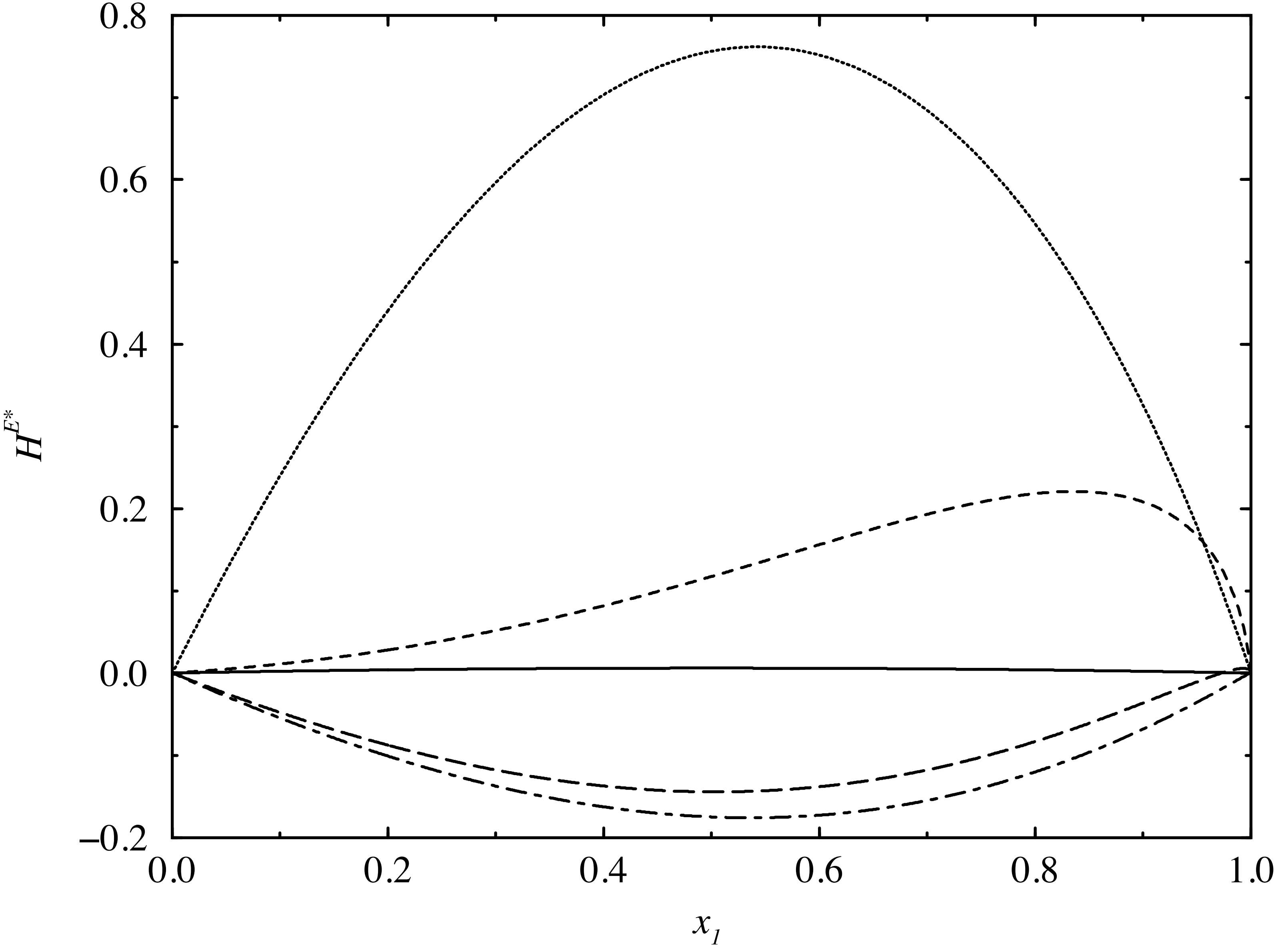

0.11
0.07
0.03
−0.01
−0.05
U^{E*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1

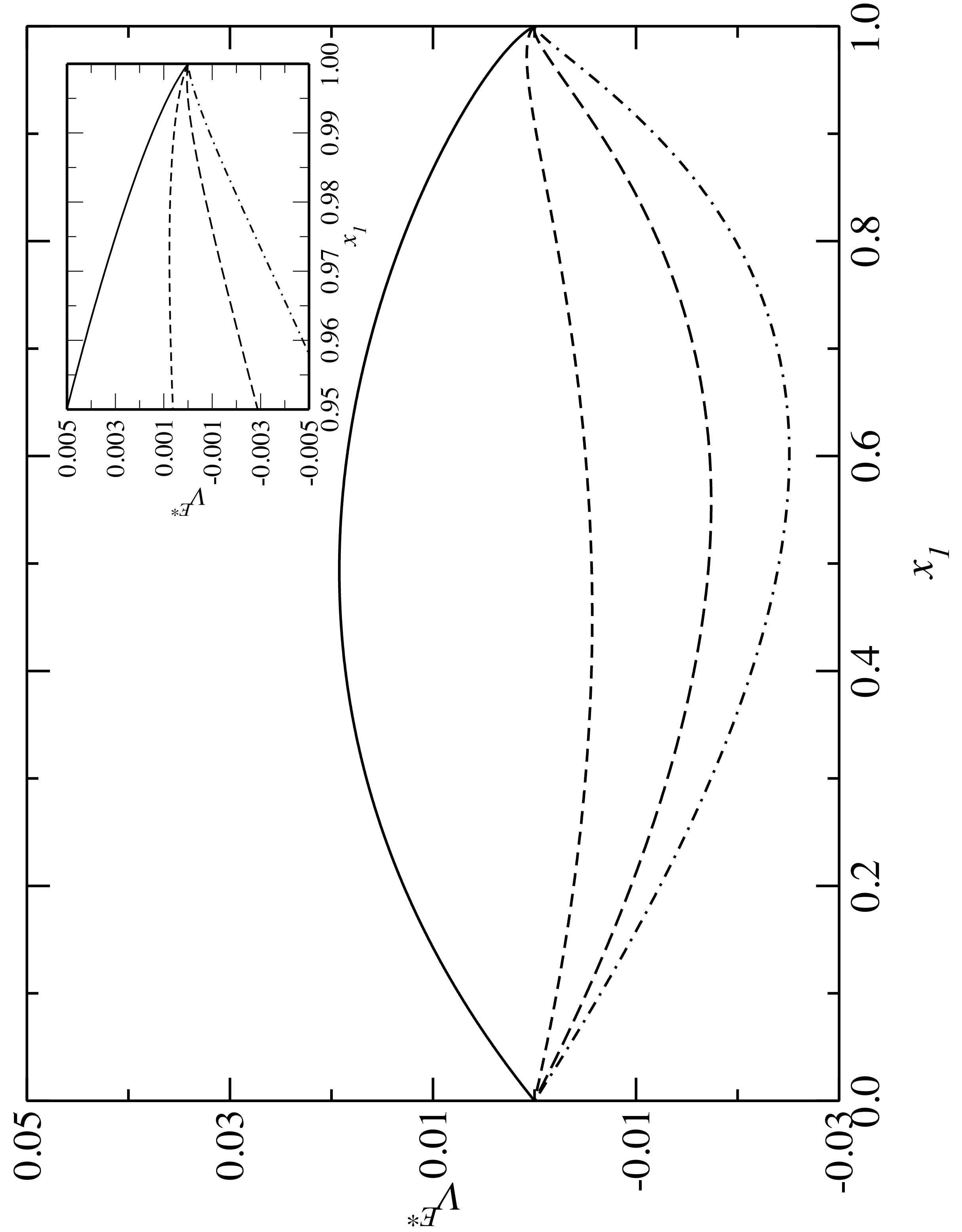

0.09
0.05
0.01
−0.03
−0.07
−0.11
H^{E*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1


0.02
0.01
0.00
−0.01
−0.02
−0.03
V^{E^*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1

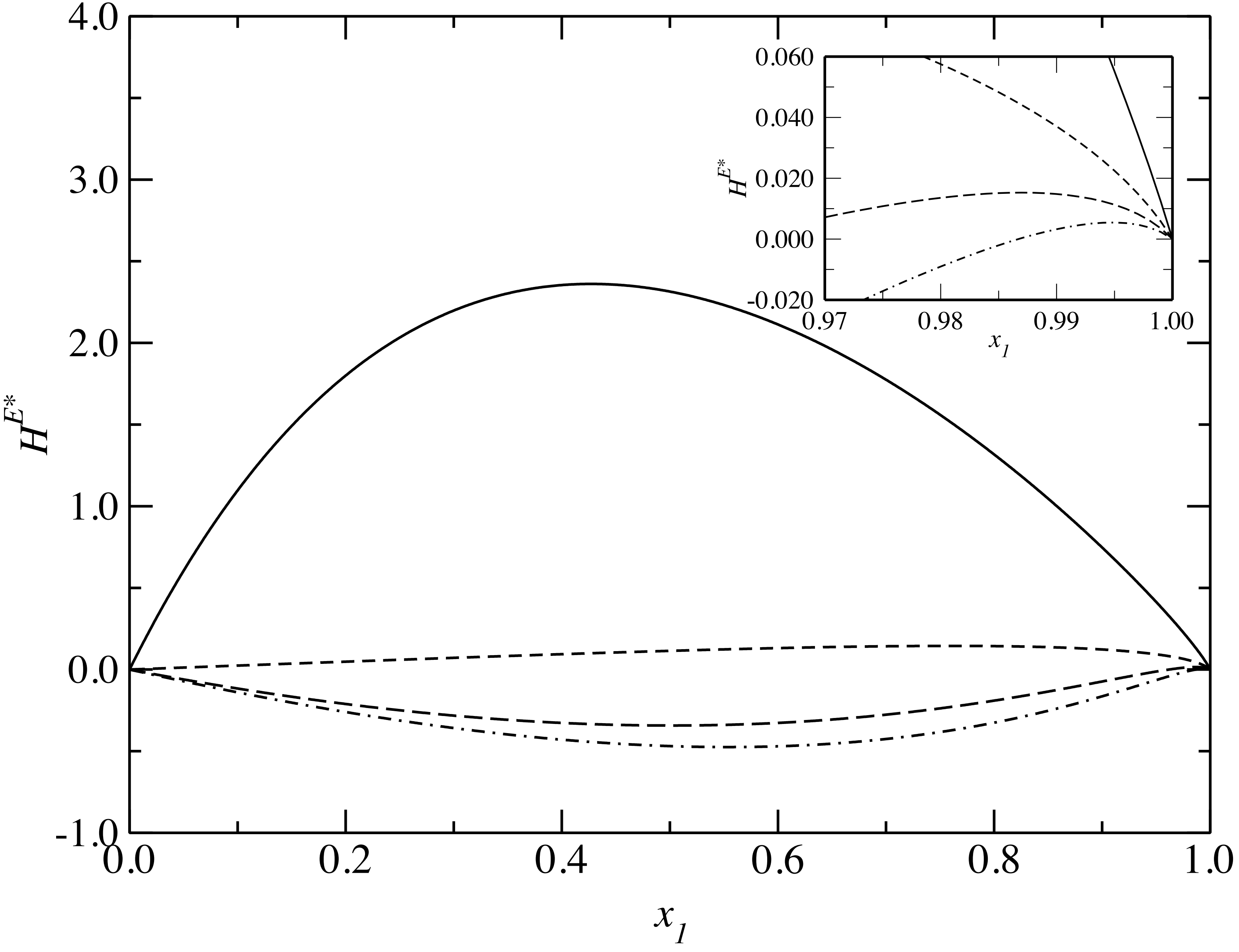

0.4
0.3
0.2
0.1
0.0
−0.1
H^{E*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1

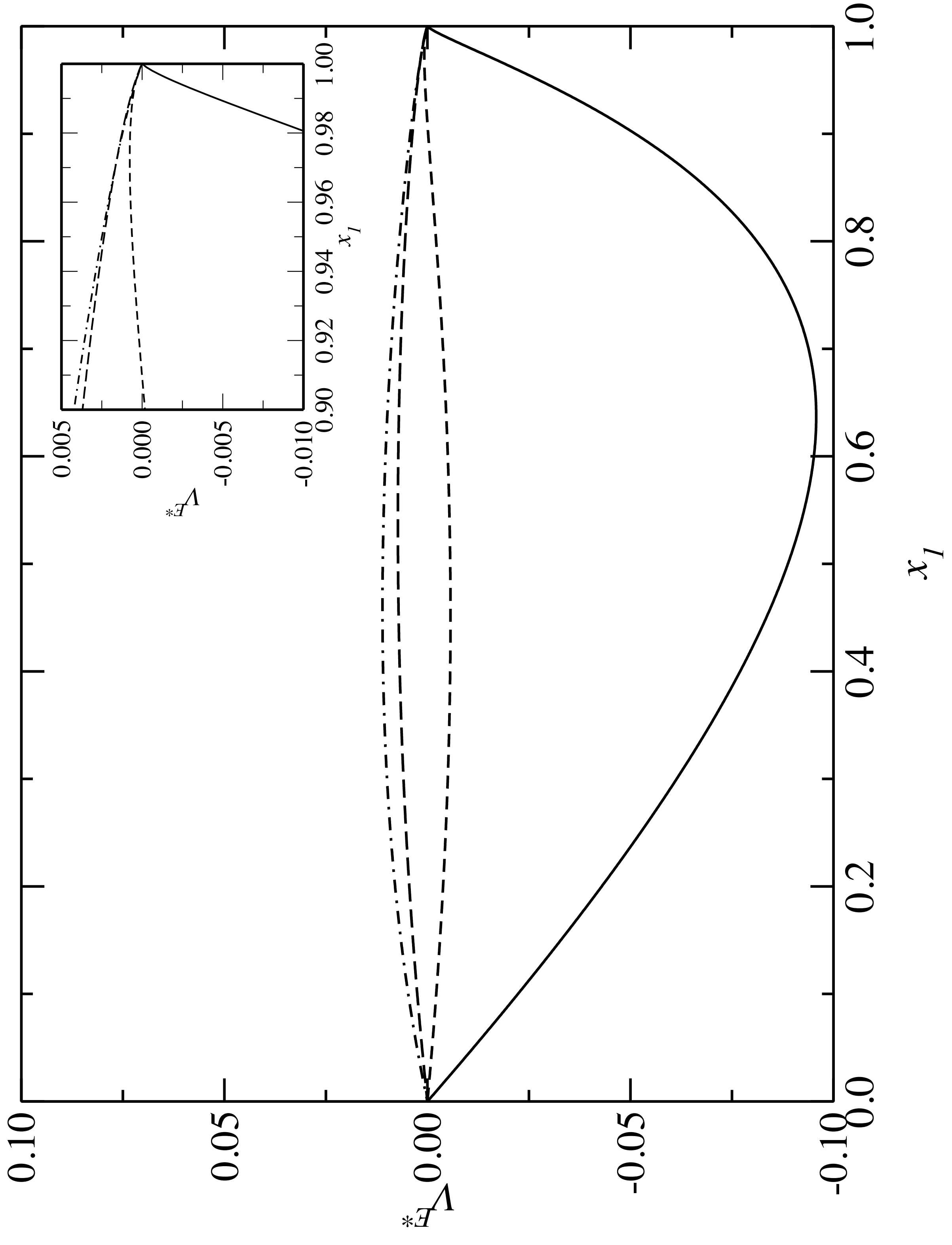

0.04
0.02
0.00
−0.02
−0.04
−0.06
V^{E*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1


H^{E^*}
0.8
0.6
0.4
0.2
0.0
−0.2
0.0
0.2
0.4
0.6
0.8
1.0
x_1

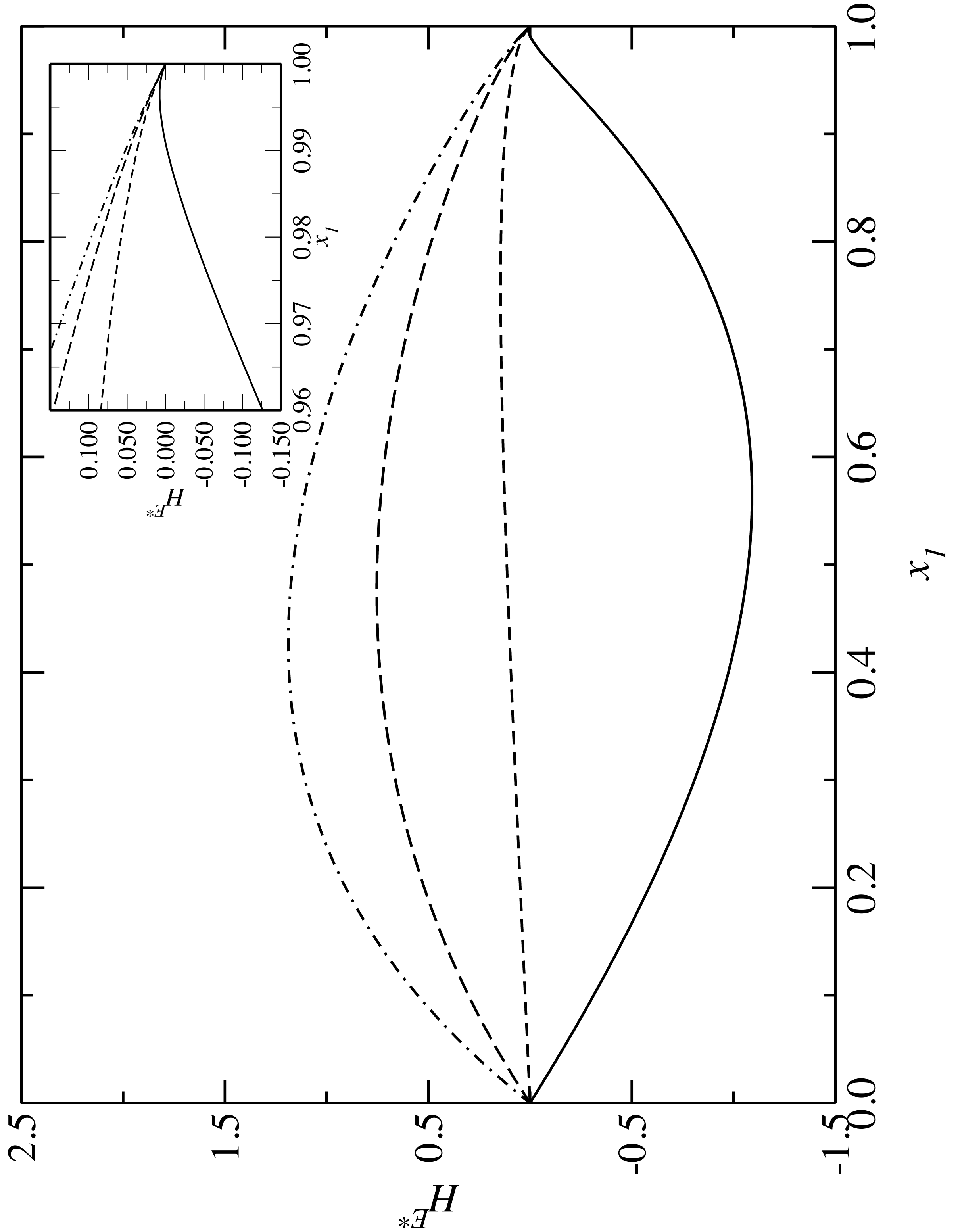


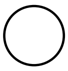
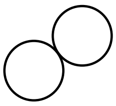
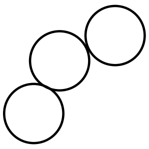
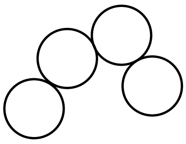
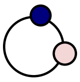
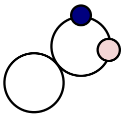
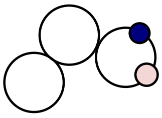
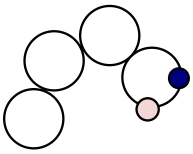
V_E^*
0.05
0.03
0.01
-0.01
-0.03
0.0
0.2
0.4
0.6
0.8
1.0
x_1
V_E^*
0.005
0.003
0.001
-0.001
-0.003
-0.005
0.95
0.96
0.97
0.98
0.99
1.00
x_1

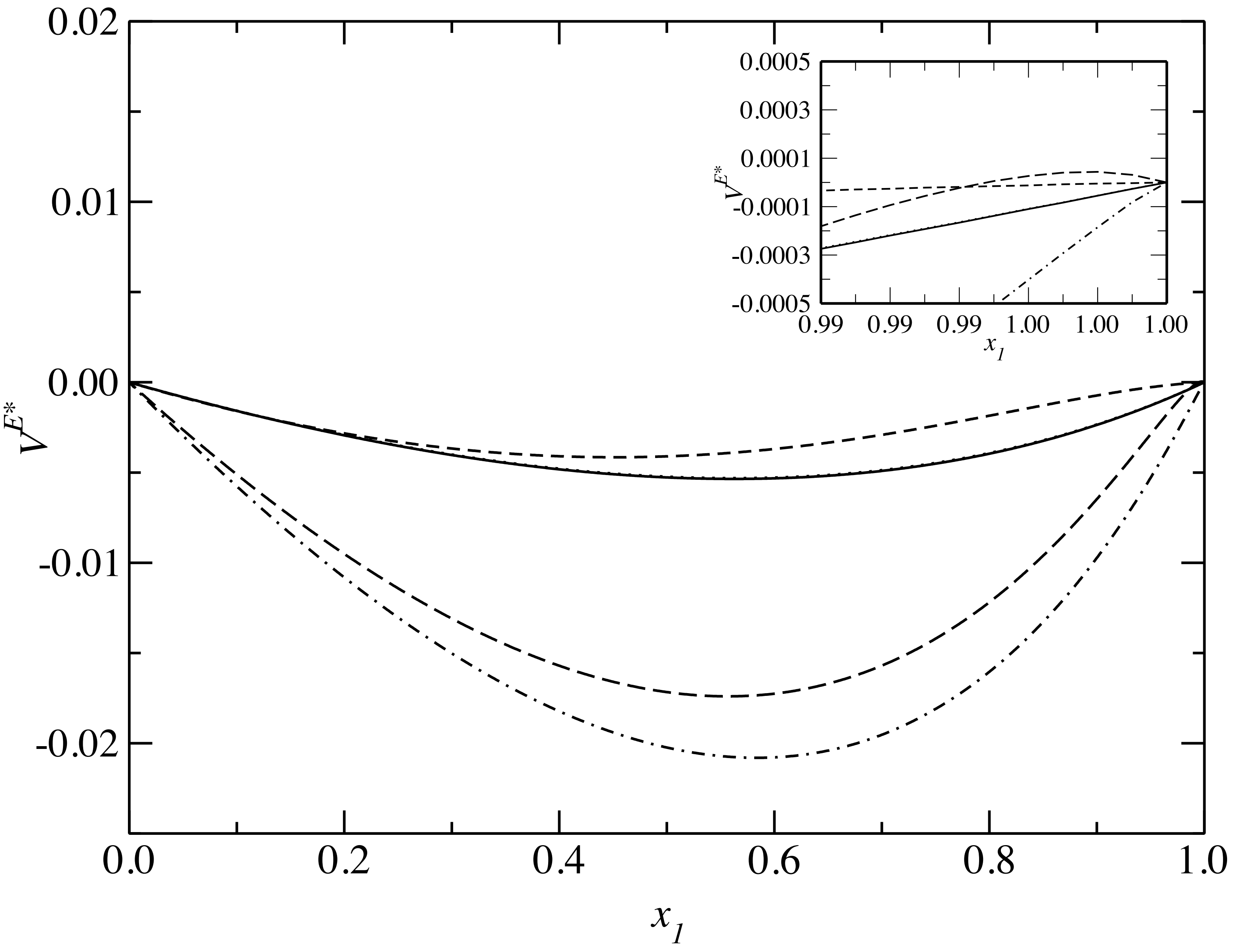

4.0
3.0
2.0
1.0
0.0
-1.0
H^{E*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1
0.060
0.040
0.020
0.000
-0.020
H^{E*}
0.97
0.98
0.99
1.00
x_1



V_E^*
x_1
0.10
0.05
0.00
-0.05
-0.10
0.0
0.2
0.4
0.6
0.8
1.0
0.005
0.000
-0.005
-0.010
0.90
0.92
0.94
0.96
0.98
1.00


H^{E*}
2.5
1.5
0.5
-0.5
-1.5
0.0
0.2
0.4
0.6
0.8
1.0
x_1
H^{E*}
0.100
0.050
0.000
-0.050
-0.100
-0.150
0.96
0.97
0.98
0.99
1.00
x_1

V^E/H^E				
	$S/+$	$+/+$	$+/+$	$+/+$
	$-/S$	$S/+$	$+/+$	$+/+$
	$-/S$	S/S	$S/+$	$+/+$
	$-/-$	$-/S$	S/S	$S/+$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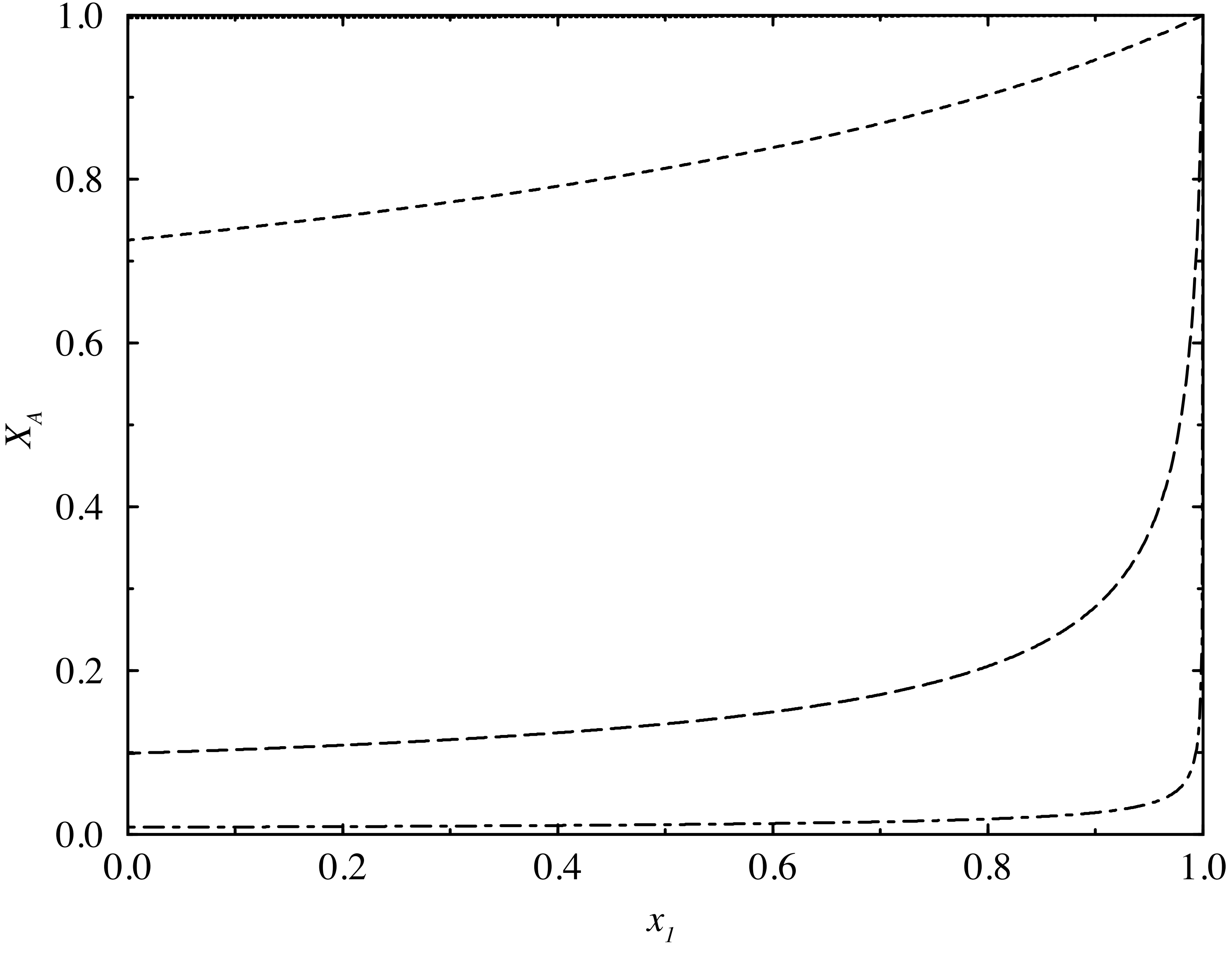
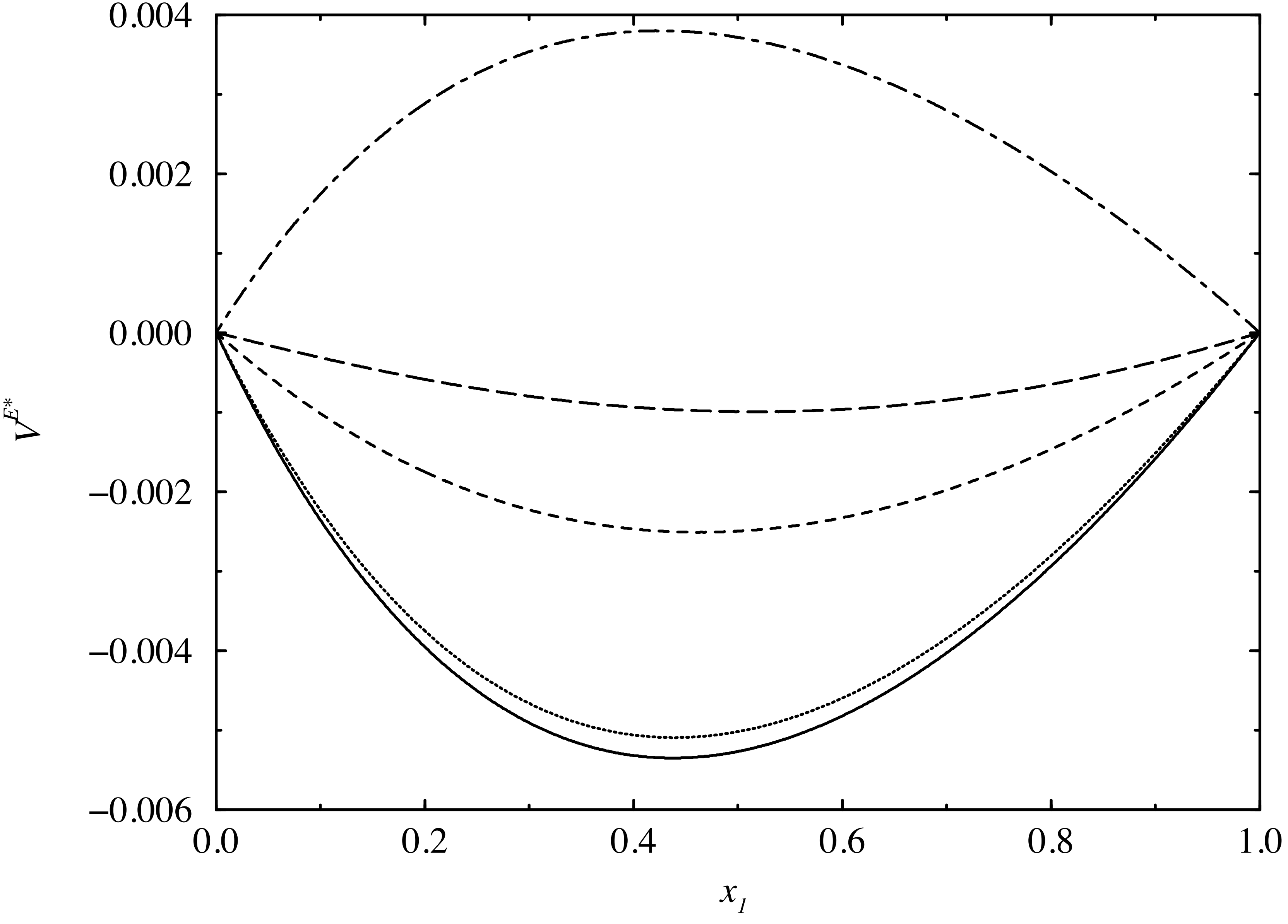
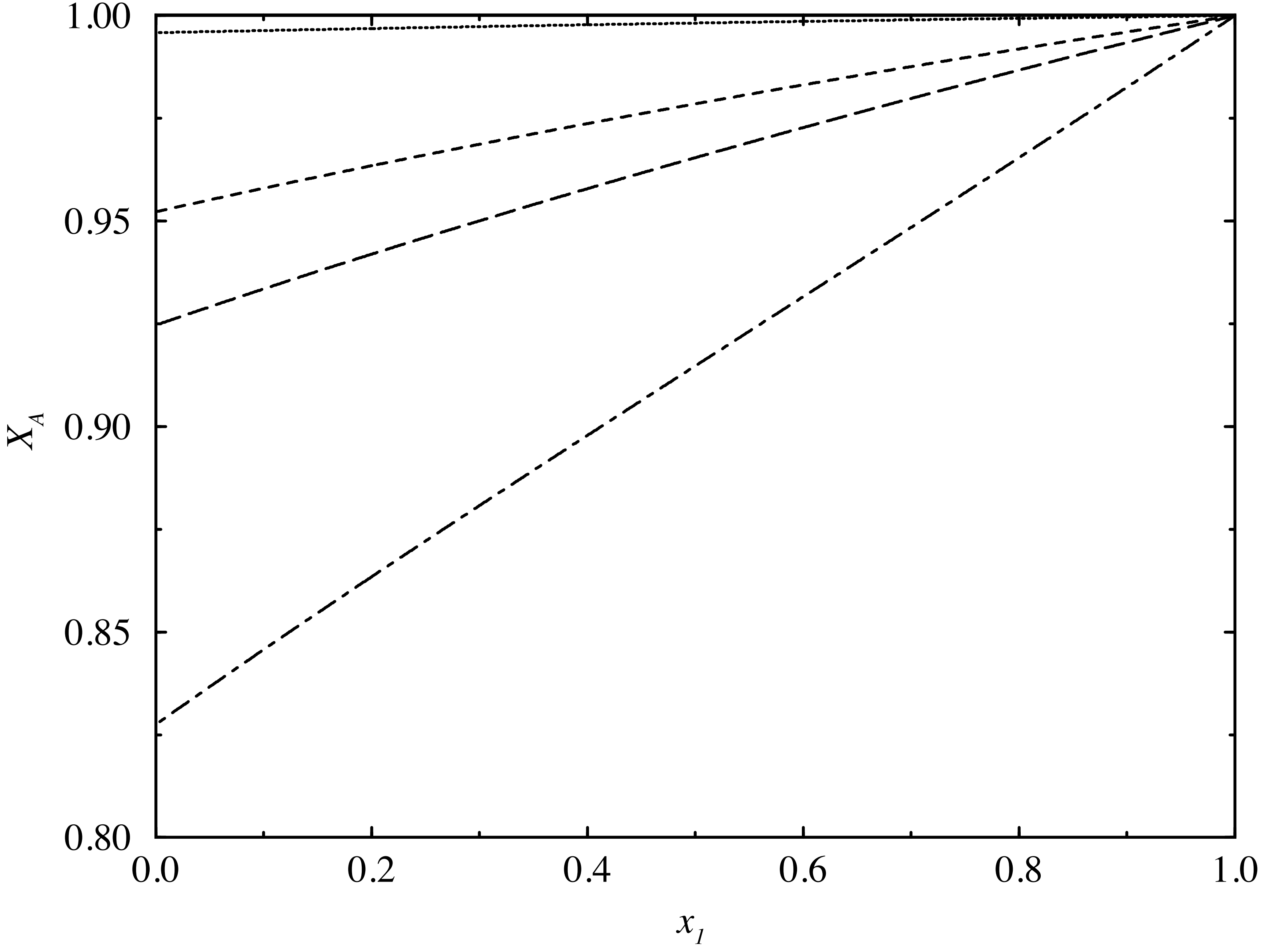
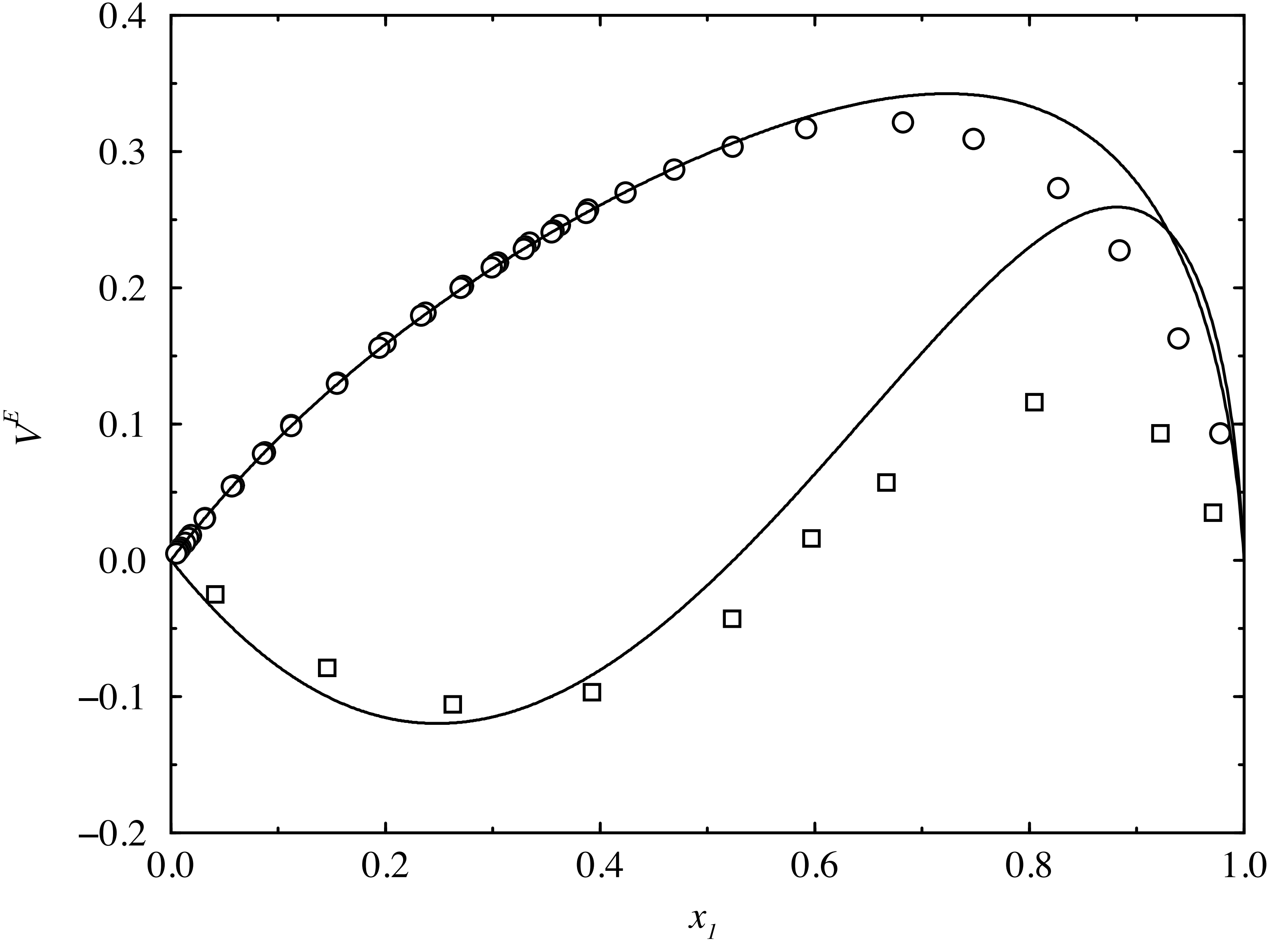
0.01
0.00
-0.01
-0.02
V^{E*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1
0.0005
0.0003
0.0001
-0.0001
-0.0003
-0.0005
V^{E*}
0.99
0.99
0.99
1.00
1.00
1.00
x_1


X_A
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
x_1


0.004
0.002
0.000
−0.002
−0.004
−0.006
V^{E*}
0.0
0.2
0.4
0.6
0.8
1.0
x_1


1.00
0.95
0.90
0.85
0.80
X_A
0.0
0.2
0.4
0.6
0.8
1.0
x_1


0.4
0.3
0.2
0.1
0.0
−0.1
−0.2
V^E
0.0
0.2
0.4
0.6
0.8
1.0
x_1