

Virial coefficients, thermodynamic properties, and fluid-fluid transition of nonadditive hard-sphere mixtures

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Different theoretical approaches for the thermodynamic properties and the equation of state for multicomponent mixtures of nonadditive hard spheres in d dimensions are presented in a unified way. These include the theory by Hamad, our previous formulation, the original MIX1 theory, a recently proposed modified MIX1 theory, as well as a nonlinear extension of the MIX1 theory proposed in this paper. Explicit expressions for the compressibility factor, Helmholtz free energy, and second, third, and fourth virial coefficients are provided. A comparison is carried out with recent Monte Carlo data for the virial coefficients of asymmetric mixtures and with available simulation data for the compressibility factor, the critical consolute point, and the liquid-liquid coexistence curves. The merits and limitations of each theory are pointed out. © 2010 American Institute of Physics. [doi:10.1063/1.3429600]

I. INTRODUCTION

Nonadditive hard spheres represent a versatile model to study various real physical systems. These include alloys, aqueous electrolyte solutions, molten salts, rare gas mixtures, and colloids. In these systems homocoordination and heterocoordination may be interpreted in terms of excluded volume effects due to nonadditivity of the repulsive (hard-core) part of the intermolecular potential and so, for instance, the occurrence of liquid-liquid demixing in real systems may be linked to a binary hard-sphere mixture with positive nonadditivity, while negative nonadditivity may be invoked to explain chemical short-range order in amorphous and liquid binary mixtures with preferred heterocoordination. On the theoretical side, prototype models of nonadditive hard-sphere mixtures, such as the Widom–Rowlinson model¹ or the Asakura–Oosawa model,² have been very useful to gain insight into interesting physical aspects, such as fluid-fluid phase transitions and the nature of depletion forces.

A few years ago, in a paper³ where a rather thorough review of the theoretical and simulation works on nonadditive hard-sphere mixtures was provided, we introduced an equation of state of multicomponent nonadditive hard-sphere mixtures in d dimensions. Such an equation of state results from a natural extension of the one we had earlier proposed for additive hard spheres,⁴ has an explicit (simple) density dependence, and by construction leads to the exact second and third virial coefficients. In the case of $d=3$, in the same paper we compared the predictions for the compressibility factor corresponding to our proposal with those of the proposal by Hamad,^{5–8} which shares some characteristics with

ours, and available simulation results for various binary mixtures.^{9–13} We also compared the predictions of the fourth and fifth virial coefficients arising from the above two theoretical proposals and the then available Monte Carlo results.^{14,15} The restriction in the comparison only to Hamad's approach was justified then by the fact that Hamad had already proved that his proposal was superior to other theories, including the so-called MIX1 theory originally due to Melnick and Sawford.¹⁶

Recently, Pellicane *et al.*¹⁷ reported new evaluations of the fourth virial coefficient of a binary nonadditive hard-sphere mixture covering a wide range of size ratios and values of the nonadditivity parameter. Also recently, Paricaud¹⁸ proposed a new equation of state for nonadditive hard-sphere mixtures, which is based on and corrects one of the deficiencies of the MIX1 theory, namely, the fact that MIX1 does not lead to the correct second virial coefficient. These two recent papers serve as a motivation for the present contribution. On the one hand, we want to see to what extent the conclusions drawn from the analysis carried out in Ref. 3 are still valid in view of the new available data. On the other hand, we will also introduce a (new) nonlinear extension of the MIX1 theory. As an extra bonus, we will write all the theoretical expressions in a unified language which will hopefully make the comparison much easier.

The paper is organized as follows. In order to make it self-contained, in Sec. II we provide the necessary background for the later development. Section III provides the explicit expressions for the contact values of the radial distribution functions, compressibility factors, Helmholtz free energies, and second, third, and fourth virial coefficients as given by the original MIX1 theory, Paricaud's modified MIX1 theory, Hamad's theory, and our earlier proposal. A nonlinear extension of the MIX1 theory is also introduced here. In Sec. IV we compare the numerical values of the composition-independent virial coefficients, compressibility

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