

# Prediction of fluid-phase behavior of symmetrical binary Yukawa fluids using transition matrix Monte Carlo

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## ABSTRACT

Binary fluid mixtures display a wide array of fluid phase behavior ranging from simple vapor-liquid equilibrium diagrams to more complicated topology like azeotropy and heteroazeotropy. As a first step towards understanding the phenomena of equilibrium of binary molecular systems, the properties of binary monoatomic fluids have been studied in this work. An additional simplification made in this work is that of a symmetrical binary system where all similar molecules interact via the hard-core Yukawa (HCY) potential,  $u(r)$ , while the dissimilar molecules interact via a potential,  $\delta u(r)$  where  $\delta$  is a scalar parameter. The value of  $\delta$  here is 0.75, which leads to the dissimilar molecules showing a tendency to dislike one another and the resulting phase diagram is such that the mixing-demixing line intersects the vapor-liquid equilibrium curve away from the vapor-liquid critical point. The effect of the variable potential range parameter of the HCY potential on the topology of the phase diagrams is investigated using grand canonical transition matrix Monte Carlo simulations and the conditions of temperature and pressure at which the system exhibits azeotropy and heteroazeotropy are ascertained. We find that the densities of the mixtures, as predicted by our simulation at equimolar concentrations, are in close agreement with the self-consistent Ornstein-Zernike approximation results of Schöll-Paschinger and co-workers.

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## 1. Introduction

Knowledge and understanding of fluid phase behavior is important from an industrial perspective as this enables the design and optimization of various separation processes. The phase diagrams of complex mixtures such as colloidal suspensions, micellar and protein solutions, and simple charged fluid mixtures are very rich and characterized by multiple coexistence lines [1]. Binary fluid mixtures display a wide range of phase diagram topology ranging from simple vapor-liquid equilibrium to more complicated topology like azeotropy and liquid-liquid equilibrium depending upon the interactions between the different species present in the mixture. This is primarily due to the fact that there is an additional degree of freedom in the form of the number of molecules of the second species and the result is a more complex phase behavior than observed in single component systems. Different phase diagrams arise due to the nature of the interactions at molecular level between similar and dissimilar species such as the range and the

strength of these interactions. Hence, a study of such binary systems at a molecular level is important as it reveals the molecular-level intricacies involved in the observed phase behavior. As a first step towards understanding the complex fluid phase behavior exhibited by binary molecular systems, we have studied the relatively simple monoatomic binary systems with none of the complicated internal molecular parameters. An additional simplification adopted in this paper is that of a symmetrical binary fluid (SBF) where additional complications are eliminated by assuming that the relative size and the strength of interactions of molecules belonging to similar species are identical while the strength of interactions between molecules of dissimilar species differ, thereby generating a symmetric phase diagram. Theoretical investigations and molecular simulations of SBFs have revealed a wide repertoire of correlations between macroscopic phenomena and molecular interactions. One of the first studies in this field was conducted by van Konynenburg and Scott [2] in their landmark paper on the investigation of critical lines and phase diagrams for binary van der Waals fluids. In the paper [2], eight types of phase diagram topologies have been deduced on the basis of mean field van der Waals' equation of state and van der Waals' mixing rules for the

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parameters in the van der Waals' equation of state. Dieters and Pegg [3] have studied binary fluid mixtures using the Redlich-Kwong equation of state and quadratic mixing rules. Kraska and Deiters [4] have further extended this study using the Carnahan-Starling-Redlich-Kwong equation of state. With the advancement of liquid state theory, researchers have been able to discern the interplay of various forcefield parameters as well as the imposed thermodynamic fields on the phase behavior topology of various binary systems. Anisimov et al. [5] were able to calculate the thermodynamic and transport properties of binary fluid mixtures near critical points by mapping three physical field variables to the two scaling field variables of Ising-like systems. Walker and Vause [6] explained the closed loop behavior in two component systems using a lattice model of fluid mixtures. For the specific case of a SBF, other phase diagram topologies appear which pave the way for a more generic description of phase diagram topologies and their dependence upon the intermolecular potential energy parameters. Wilding et al. [7] employed mean-field calculations and multi-canonical Monte Carlo simulations to determine the phase diagrams of the square-well SBF at different values of the force field parameters and under different thermodynamic conditions. Their results revealed that there are three different types of phase diagram topologies depending on the value of  $\delta$ , the ratio by which the interaction between molecules of dissimilar species differ from that between molecules of similar species. Different values of  $\delta$  dictate the location of the consolute end points (CEP) of the liquid-liquid equilibria. The CEP is the point at which the mixing-demixing transition line or  $\lambda$ -line intersects the vapor-liquid phase envelope. If this line intersects the liquid-vapor equilibrium curve at a point far away from the critical point, then the phase diagram changes from vapor-liquid equilibrium (VLE) azeotropic behavior to a vapor-liquid-liquid equilibrium (VLE) heteroazeotropic behavior. In case the demixing line intersects the vapor-liquid equilibrium curve close to the critical point, there occurs a coupling between the composition and the density fluctuations close to the vicinity of the both the liquid-liquid and liquid-vapor critical points; and the result is a common tricritical point, a point where three phases (the vapor and the demixed liquid phases) simultaneously become critical. A third kind of phase diagram topology is also seen where the vapor occurs in equilibrium with a single liquid phase terminating at the critical point and the single liquid phase exists in equilibrium with two demixed liquid phases albeit at a different density, with all the coexisting phases terminating at a tricritical point.

Theoretical investigations of binary mixtures interacting via the hard-core Yukawa (HCY) potential have been extensively carried out by researchers worldwide using the mean spherical approximation (MSA) and hyper-netted chain (HNC) liquid state theories [8–14]. Caccamo et al. [1] have determined the phase diagrams of binary mixtures of symmetrical HCY fluids with values of the interaction strength ratio,  $\delta = 0.7$  and  $\delta = 0.9$ , using Gibbs ensemble Monte Carlo (GEMC) simulations, semi-grand canonical Monte Carlo simulations and modified HNC liquid state theory. At  $\delta = 0.7$ , the authors have determined that a cross-over occurs from VLE at low densities to liquid-liquid equilibrium (LLE) at high densities at the critical end point of the mixture, consistent with other studies in literature on fluids interacting via different potential models [2,15]. Binary symmetric fluid mixtures interacting via the HCY potential have also been investigated by Schöll-Paschinger et al. [16] using both simulation and theory. The theoretical approach applied SCOZA which is a solution to the Ornstein-Zernike (OZ) equation with a mean spherical approximation (MSA) type closure which takes into account thermodynamic state functions that have been determined using thermodynamic self-consistency. Grand-canonical Monte Carlo (GCMC) simulations have been used to

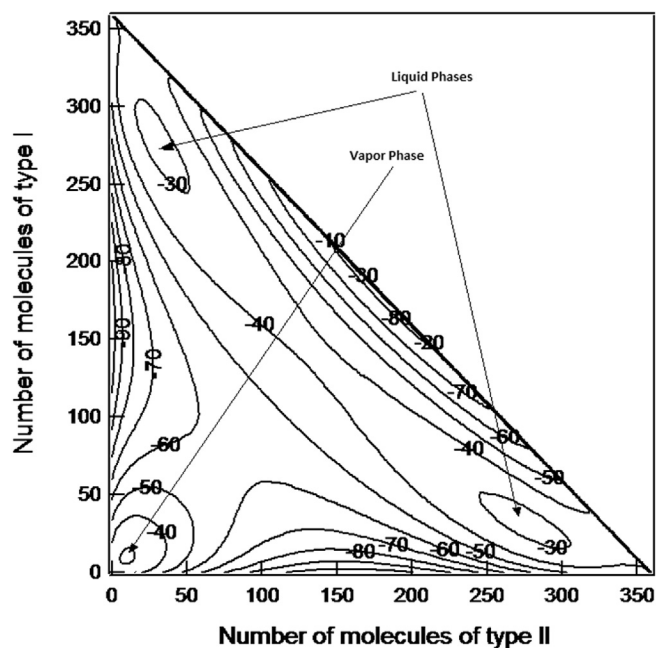


Fig. 1. Contour plot of the logarithm of the probability distributions for  $\kappa\sigma = 1.8$  at a reduced temperature ( $kT/\epsilon$ ) of 0.90 in a cubic volume with box length  $= 7.5\sigma$ . The plot represents data at values of the chemical potentials such that the values of the volumes under the three peaks enclosed by the contour line  $= -30$  are equal. This corresponds to the heteroazeotropic point in Fig. 4(a).

confirm the accuracy of the theoretical calculations. The presence of the three types of phase diagrams was confirmed by both the theory and subsequent simulations. In a later publication [17], Schöll-Paschinger and Kahl have reported the presence of a fourth type of topology which occurs when the  $\lambda$ -line intersects the vapor-liquid coexistence curve at a density lower than that corresponding to the VLE critical point which leads to the presence of a demixed liquid-demixed liquid critical point. All the studies mentioned above have been completed for a highly symmetrical case where

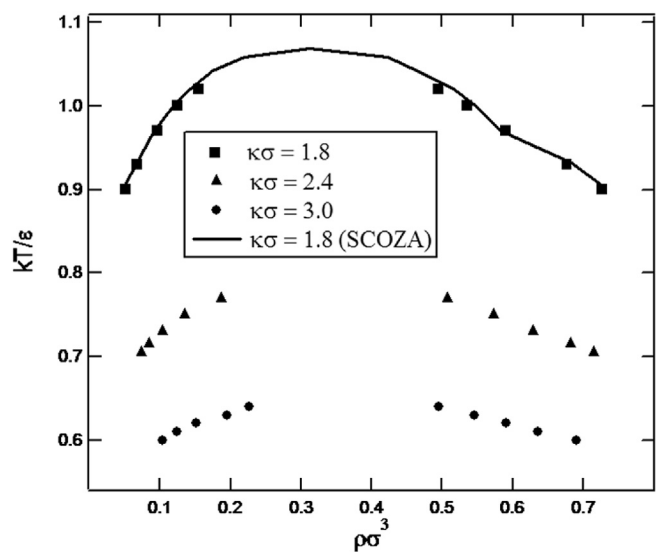


Fig. 2. Plot of reduced temperature ( $kT/\epsilon$ ) vs. the liquid and vapor phase reduced densities ( $\rho\sigma^3$ ) at azeotropic/heteroazeotropic points for three different values of  $\kappa\sigma$  (1.8, 2.4 and 3.0). The solid line is the result obtained for  $\kappa\sigma = 1.8$  using SCOZA analysis by Schöll-Paschinger et al. [16].

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