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Azeotrope Prediction by Monte Carlo Molecular Simulation

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This article presents a methodology for checking the existence of the azeotrope and computing its composition, density, and pressure at a given temperature by integrating chemical engineering insights with molecular simulation principles. Liquid-vapor equilibrium points are computed by molecular simulations using the Gibbs ensemble Monte Carlo (GEMC) method at constant volume. The appearance of the azeotropic point is marked by a shift of the equilibrium constant from one side of the unity to the other. After each GEMC simulation, an identity change move is derived in the grand canonical ensemble to progress towards the azeotrope along the equilibrium curve. The effectiveness of the proposed methodology is successfully tested for several binary Lennard-Jones mixtures reported in the literature.

Keywords Azeotrope; Lennard-jones fluid; Molecular simulation

Introduction

Phase equilibrium is a key physicochemical property for assessing the design feasibility of major separation processes driven by phase chemical potential differences, such as liquid-liquid extraction or distillation. For the case of distillation, for example, the prediction of the azeotrope and its composition is indispensable for proper design and operation of the separation unit (Widagdo and Seider, 1996; Kiva et al., 2003, Rodriguez-Donis et al., 2002, 2009a, 2009b). Towards this end, either the experimental data (Gmehling et al., 1994) or model predictions can be utilized. Among predictive models, the following approaches are widely reported in the literature:

- Homotopy continuation (Fidkowski et al., 1993; Eckert and Kubicek, 1996; Wasylkiewicz et al., 1999) or global optimization methods (Harding et al., 1997) attempt exhaustive azeotrope searches.
- Simpler methods based on successive phase equilibrium calculations coupled to phase stability assessment have also been implemented (Teja and Rowlinson, 1973; Chapman and Goodwin, 1993).

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- Residue curve exploration that ends at singular points of a multicomponent system is another way of finding azeotropes. These, together with the pure component vertexes, are singular points (Kiva et al., 2003; Doherty and Perkins, 1979; Gerbaud et al., 2006).

Many thermodynamic models with binary interaction parameters have been proposed to predict the phase behavior of nonideal mixtures. Their accuracy, however, depends on the mixture type and operating conditions (Missen, 2005, 2006). Moreover, in many emerging fields like ionic liquids, molecules of biological interest are poorly represented with existing models owing to the dependence of the models on temperature, pressure, and specific binary interaction parameters. Note that binary interaction parameters are regressed from experimental data: For a n -component mixture, $n(n - 1)/2$ parameter pairs are required, a challenge when experimental data are missing.

By the 1980s, the molecular simulation technique emerged by providing an accurate set of tools to exactly evaluate bulk thermodynamic properties of systems. It has since then established itself as a central element of research in chemical engineering thermodynamics to investigate energetic interaction-based phenomena (Allen and Tildesley, 2000; Frenkel and Smit, 2002). Molecular simulation basically samples the configuration of a molecular system using two different methods, namely the molecular dynamics (MD) and the Monte Carlo (MC) (De Pablo and Escobedo, 2002). Each method has some strengths as well as limitations (Bopp et al., 2008). The resulting molecular system can represent a homogeneous continuum when periodic boundary conditions are used (Allen and Tildesley, 2000). Following are different methodologies reported in the literature for azeotropic calculations:

- Azeotropy was observed for the first time in the work of Fincham et al. (1986, 1987) who performed MD calculations to study the mixture $\text{CO}_2/\text{C}_2\text{H}_6$ described with a diatomic Lennard-Jones model (Scalise et al., 1989).
- Direct computation of azeotropes has also been done successfully using the Gibbs Duhem integration (GDI) method (Kofke, 1993). This method uses the Clapeyron equation to provide the coexistence information but does not require particle exchange moves to ensure chemical potential equilibrium (Pandit and Kofke, 1999).
- Histogram-reweighting Monte Carlo simulation in the grand canonical ensemble was recently employed by Pottof and Bernard-Brunel (2009). In their work, the azeotropic coordinate of the binary mixture (ethane + perfluoroethane) was described by transferable united-atom force fields based on Mie potentials (a generalization of the classical Lennard-Jones 12-6 potential with a variant repulsive exponent). The agreement with experimental data was satisfactory only when binary interaction parameters were introduced. Earlier, using the same method but without fitting the binary interaction parameters, Stubbs et al. (2004) overestimated the azeotropic pressure of an acetone-hexane mixture, while the azeotropic composition was correctly estimated.
- More recently, azeotrope location was accurately predicted without any empirical binary interaction parameters or readjustment for acetone-hexane and propanal-pentane binary mixtures using Monte Carlo simulations in the bubble point pseudo-ensemble (Ferrando et al., 2010).
- However, the common route to finding azeotrope remains a posteriori identification of the vapor-liquid equilibrium (VLE) data, as in the recent compilation of 267 binary mixture VLE calculations by molecular simulation with the grand equilibrium method (Vrabec et al., 2009).

- The Gibbs ensemble Monte Carlo (GEMC) method proposed by Panagiotopoulos (Panagiotopoulos, 1987; Panagiotopoulos et al., 1988) for computing the phase equilibria has also been used to locate the azeotrope by Li et al. (2010), who studied the shift of the azeotropic point for binary Lennard-Jones mixtures confined in a slit-like pore.

However, even with the GEMC method, which has now become an integral part of several commercial simulation packages, azeotrope composition calculation is done a posteriori, for example, from a graphical vapor molar fraction y -liquid molar fraction x representation. Therefore, there is a need for a method suitable to assess a priori and directly the existence of an azeotrope and compute its composition, temperature, and pressure.

In order to promote molecular simulation tools for computing properties of interest in chemical engineering (Theodorou, 2010), an alternative approach to compute azeotropes by molecular simulation is presented here. This is based on the GEMC method coupled with a particular Monte Carlo move, called the swap move, which allows changing the identity of one particle by another present in the system. The idea was previously applied by Teja and Rowlinson (1973), who calculated homogeneous azeotropes of binary mixtures using an equation of state. Their approach was to fix temperature and vary composition and volume until thermodynamic equilibrium conditions were satisfied. In the method proposed here, the swap move is used to initialize successive GEMC simulations at imposed global volume in an iterative process, until the azeotrope conditions are matched. Within the process, equilibrium constant properties for azeotropic mixtures are exploited. For model validation, the popular Lennard-Jones model fluid is used. The proposed methodology could nevertheless be adapted to a more realistic force field as well.

The article first briefly presents both the Gibbs ensemble Monte Carlo (GEMC) and the grand canonical (GC) ensemble. The Monte Carlo swap move is introduced next. Properties of azeotropic binary conditions are then reviewed. The efficacy of the proposed methodology is tested against five different Lennard-Jones mixtures. Results show good agreement with previously reported simulation studies. The detailed algorithm of our method is presented in the appendix.

Gibbs Ensemble Monte Carlo (GEMC)

The Gibbs ensemble Monte Carlo method developed by Panagiotopoulos in 1987 enables direct simulations of phase equilibrium in fluids (Panagiotopoulos, 1987; Panagiotopoulos et al., 1988). Gibbs ensemble simulations are performed in the NVT statistical ensemble on two separate microscopic regions, each within periodic boundary conditions. The thermodynamic requirement for phase coexistence is that each region should be in internal equilibrium, and that temperature, pressure, and the chemical potential of all components should be the same in both regions.

System temperature T in Monte Carlo simulations is set constant. The remaining three conditions are satisfied by performing three types of Monte Carlo moves: (i) displacement of particles within each region, while keeping the total number of particles N constant, to satisfy internal equilibrium; (ii) fluctuations in the volume of the two regions, while keeping the total volume V constant, to satisfy equality of pressures; and (iii) transfers of particles between regions to satisfy equality of chemical potentials of all components. The acceptance of each move is done according to

the metropolis algorithm, enabling determination of probability densities that satisfy the microscopic reversibility of the system (Allen and Tildesley, 2000; Frenkel and Smit, 2002; Panagiotopoulos et al., 1988).

When applied to real fluids, the method has been frequently used in combination with the configurational bias sampling technique to improve the sampling of system configurations and compute phase diagrams of a large number of fluids (Frenkel and Smit, 2002).

The Swap Move

Among the usual statistical thermodynamic ensembles, the grand canonical (GC) ensemble (μVT) sets constant the chemical potential of each compound present in the system along with the volume and the temperature. This enables changing the number of particles (N) in the system during the simulation. As a result, the classical trial moves for this ensemble are: (i) displacement, (ii) insertion, and (iii) removal of particles.

In order to optimize the simulation time and move easily from one configuration to another without changing the position of particles in the system, the insertion and removal trial moves are replaced by just one move named the ‘‘swap move’’: particles are neither created nor destroyed; only the identity of different particles is shifted. The total number of particles is kept constant, but the composition of the system is modified.

This idea was first introduced by both Panagiotopoulos et al. (1988) to perform the exchange moves between boxes in the GEMC method and Kofke and Glandt (1988) in their comprehensive work about molecular simulation of multicomponent equilibria in the semi-grand canonical ensemble. It has also been employed by Cracknell et al. (1993) and Lachet et al. (1997) for simulating the adsorption of different mixtures.

In a metropolis algorithm, the swap move from a particle of type (B) into a particle of type (A) is accepted with probability:

$$p_{\text{swap}} = \min\left(1, \left(\frac{N_B}{N_A + 1}\right) \times \left(\frac{q_A}{q_B}\right) \times \exp(-\beta(\Delta E + (\mu_B - \mu_A)))\right) \quad (1)$$

where q_i is the molecular partition function of particles of type (i), $\beta = \frac{1}{kT}$ is the Boltzmann coefficient with T the absolute temperature and k the Boltzmann constant, ΔE is the energy difference between the old and the new system configuration, and μ_i is the chemical potential of particle of type (i).

We can notice that this move is the combination of the insertion and destruction moves in the GC Monte Carlo ensemble and that its probability acceptance is the product of the corresponding insertion and destruction probabilities.

Indeed, insertion of a particle of type (A) in the GC ensemble is characterized by the acceptance probability (McQuarrie, 1976):

$$p_{\text{insertion}} = \min\left(1, \left(\frac{q_A}{N_A + 1}\right) \times \exp(-\beta(\Delta E - \mu_A))\right) \quad (2)$$

While the removal of a particle of type B, in this instance, is accepted with a probability:

$$p_{\text{destruction}} = \min\left(1, \left(\frac{N_B}{q_B}\right) \times \exp(-\beta(\Delta E + \mu_B))\right) \quad (3)$$

So, it is obvious from Equations (1)–(3) that:

$$P_{\text{swap}} = P_{\text{insertion}} \times P_{\text{destruction}} \quad (4)$$

Azeotrope Properties

Azeotrope occurrence expresses a nonideal thermodynamic behavior of the mixture. Such behavior translates into a positive (minimum boiling temperature azeotrope) or a negative (maximum boiling temperature azeotrope) deviation from Raoult's law. This law describes the liquid-vapor equilibrium relation between an ideal liquid phase composition and a perfect gas phase composition (see Figure 1; Shulgin et al. (2001)). The azeotropic condition states that compositions of the vapor phase

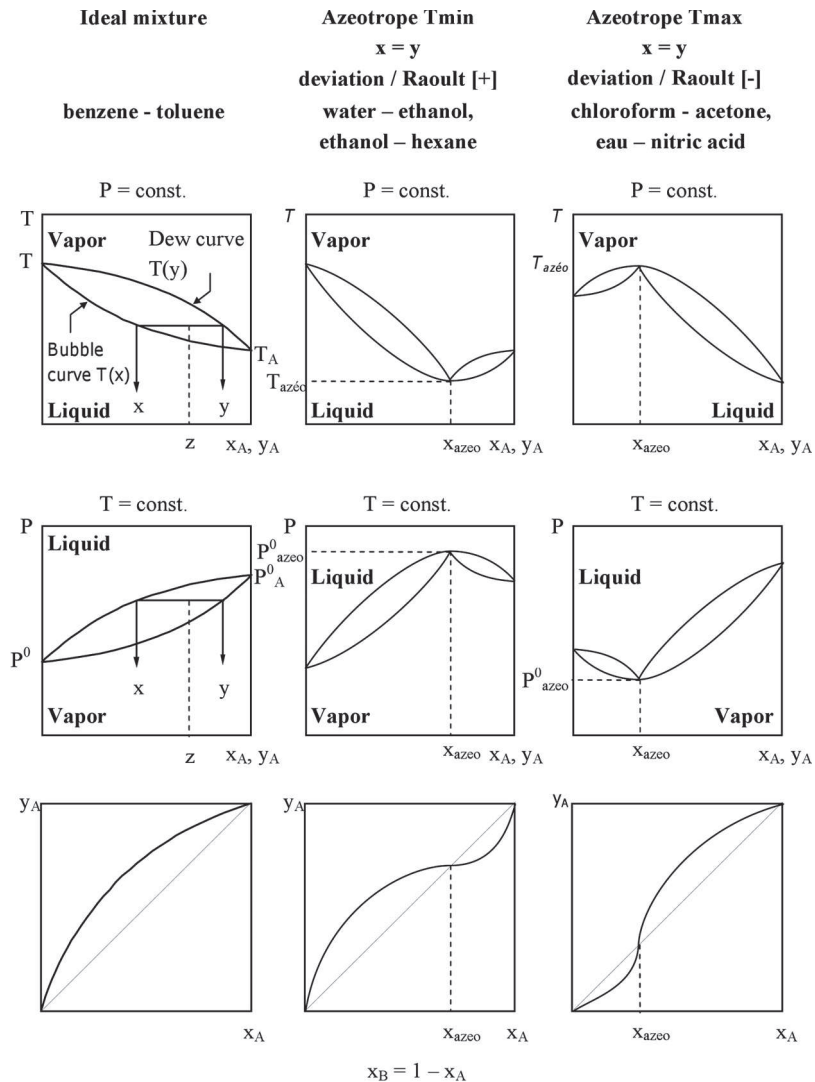


Figure 1. Schematic representation for the phase boundary of a binary mixture A-B.

and of the overall liquid phases are equal. If more than one liquid phase is concerned, the azeotrope is called heterogeneous, a case that is not dealt with in this article. In addition to composition equality, two other thermodynamic conditions occur: (i) phase equilibrium (equality of temperature, pressure, and chemical potential) and (ii) mole fractions of the components in each phase must sum to unity and must be positive.

Phase equilibrium between two phases can be expressed for a binary mixture A-B with the introduction of the equilibrium constant K_A , which is defined as the ratio of the liquid phase composition x and vapor phase composition y :

$$y_A = K_A \cdot x_A \quad (5)$$

$$y_A = 1 - y_B \quad \text{and} \quad x_A = 1 - x_B \quad (6)$$

Assuming, as in Figure 1, that component A is more volatile than B, one notices that:

- At the azeotropic point $K_A = 1$.
- Before the azeotropic point composition $K_A > 1$ for a minimum boiling temperature azeotrope and $K_A < 1$ for a maximum boiling temperature azeotrope.
- After the azeotropic point composition $K_A < 1$ for a minimum boiling temperature azeotrope and $K_A > 1$ for a maximum boiling temperature azeotrope.

This thermodynamic insight is exploited below for a quick check whether a mixture displays an azeotrope or not:

- If [$K_A > 1$ near $x_A \gg 0$] and [$K_A < 1$ near $x_A \gg 1$] then there exists a minimum boiling temperature azeotrope.
- If [$K_A < 1$ near $x_A \gg 0$] and [$K_A > 1$ near $x_A \gg 1$] then there exists a maximum boiling temperature azeotrope.
- If [$K_A > 1$ or $K_A < 1$] for the whole x_A molar fraction range, then no azeotrope exists.

Such a test is not valid for the rare cases of double azeotropy (Shulgin et al., 2001).

Model Validation

Computational Details

The method proposed in this work is detailed in the appendix. Five Lennard-Jones fluid mixtures taken from earlier work of both Panagiotopoulos et al. (1988) and Pandit and Kofke (1999) was tested. The corresponding parameters are given in Table I, along with their a priori azeotropic features that we intend to check.

A typical simulation involves a total number of $N = 800$ particles. The two initial boxes contain respectively 390 particles of type A with 10 particles of type B (which corresponds to $Z_H^0 = 0.975$) and 10 particles of type A with 390 particles of type B ($Z_L^0 = 0.025$).

The initial configuration in each box is a face-centered cubic lattice with initial densities giving rise to a vapor-liquid equilibrium. The choice of suitable initial densities is done by a small number of short exploratory calculations of the coexisting phases when no information is available on the phase behavior of the fluid. The

Table I. Lennard-Jones mixtures' potential parameters

Mixture	ϵ_{11}	ϵ_{12}	ϵ_{22}	σ_{11}	σ_{12}	σ_{22}	Azeotrope
I	1.000	0.900	1.000	1.000	1.050	1.150	Yes
II	1.000	1.000	1.000	1.000	0.885	0.769	No
III	1.000	0.750	1.000	1.000	1.000	1.000	Yes
IV	1.000	0.773	0.597	1.000	0.884	0.768	No
V	1.000	0.900	1.000	1.000	1.050	1.000	Yes

usual long-range correction is considered in calculating the energy described by a usual Lennard-Jones 6–12 potential (Allen and Tildesley, 2000) with a cutoff equal to the half box length.

Three types of Monte Carlo moves were performed during the GEMC simulations: (i) random displacement of particles within each region, (ii) an equal and opposite change in the volume of the two regions, and (iii) random transfers of particles between regions. The typical occurrences for the various types of moves were taken equal to 49.75% for translations, 0.50% for volume changes, and 49.75% for transfers.

After an equilibration period of approximately 10^6 steps, properties of the two regions converge to stable values quite different from the initial conditions. More than 5×10^6 configurations were generated for each simulation run, and control plots were used to check satisfactory convergence.

First Step: Fast Azeotrope Search

Table II displays results for the first step/quick check of azeotrope existence. Subscript numbers follow the notation for uncertainty values used in molecular

Table II. Results of the first step to check the existence of homogeneous azeotropes for the mixtures studied

1st Step		ρ^*_{liq}	ρ^*_{vap}	P^*_{liq}	P^*_{vap}	x_A	y_A	K_A
Mixture I	Z_L^0	0.4212 ₁₇	0.0307 ₁₆	0.0301 ₂₃	0.0311 ₇	0.0228 ₁	0.0570 ₂₅	>1
	$T^* = 1.10$	Z_H^0	0.6326 ₁₉	0.0557 ₁₅	0.0477 ₃₀	0.0456 ₁₀	0.9780 ₂	0.9605 ₁₁
Mixture II	Z_L^0	1.3020 ₄₇	0.1503 ₇₁	0.1285 ₇₇	0.1230 ₃₅	0.0291 ₄	0.0141 ₈	<1
	$T^* = 1.15$	Z_H^0	0.6148 ₂₈	0.0753 ₇	0.0576 ₃₅	0.0607 ₅	0.9783 ₂	0.9707 ₃
Mixture III	Z_L^0	0.5966 ₂₀	0.0689 ₁₇	0.0582 ₃₀	0.0590 ₉	0.0147 ₃	0.0639 ₂₀	>1
	$T^* = 1.15$	Z_H^0	0.5963 ₃₂	0.0729 ₂₅	0.0670 ₂₈	0.0606 ₁₂	0.9853 ₂	0.9388 ₁₆
Mixture IV	Z_L^0	1.1466 ₇₄	0.2025 ₄₉	0.1198 ₄₁	0.1039 ₁₆	0.0508 ₈	0.0040 ₁	<1
	$T^* = 0.75$	Z_H^0	0.6038 ₃₃	0.0652 ₁₄	0.0586 ₄₇	0.0559 ₈	0.9848 ₁	0.9351 ₁₁
Mixture V	Z_L^0	0.6356 ₂₅	0.0485 ₁₀	0.0414 ₃₀	0.0415 ₇	0.9800 ₄	0.9611 ₁₁	<1
	$T^* = 1.10$	Z_H^0	0.6298 ₂₁	0.3238 ₇	0.0206 ₄₃	0.0131 ₂₅	0.0205 ₆	0.0289 ₅

$Z_H^0 = 0.025$ and $Z_L^0 = 0.975$.

Subscript numbers follow the notation for uncertainty values (for example, 0.4212₁₇ means 0.4212 ± 0.0017).

* = reduced units (Frenkel and Smit, 2002).

simulation ($0.4212_{17} = 0.4212 \pm 0.0017$). Among the five mixtures, the first, third, and fifth exhibit homogeneous azeotropes in perfect agreement with the literature (Table I). As indicated by their Lennard-Jones parameters in Table I, the third and fifth mixtures are both symmetric and their azeotropic coordinates should be found during the second step at $x = y = 0.50$. Afterwards, step 2 is applied only to the third mixture (mixture III). In addition, a previous study of Pandit and Kofke (1999) has shown that the mixture I azeotrope point lies around $x = y = 0.70$.

In Table II, for mixture III, the densities and pressure match for both Z_H and Z_L , whereas this is not the case for mixture V, which is symmetric like mixture III. But this trend is merely fortuitous because even though the initial compositions of Z_H and Z_L are symmetric with respect to the pure components, the Gibbs Ensemble Monte Carlo simulations are not expected to give necessary rise to the same phase split as observed for mixture III.

The pressure is determined by applying the virial equation. As can be seen in Table II (and later in Tables III and IV), the pressures of the vapor and liquid regions at equilibrium generally agree to within their corresponding standard deviations, which reflects the convergence of simulations. Nevertheless, as already observed in the literature (Panagiotopoulos, 1987), the vapor box pressure fluctuates less than the liquid box where high densities submit particles to larger constraints, especially when transferring a particle from the low density box to the high density box. As a consequence, the standard errors for the pressure on the vapor region are significantly lower and can thus be more conveniently identified as the equilibrium pressure at the corresponding temperature.

However, the observation that the equilibrium conditions have been fulfilled within the statistical error is not always sufficient. It is suitable, therefore, to use graphical analysis to examine the data variation during each simulation.

Finally, the equilibrium molar fractions x_A and y_A bracket the initial feed composition as in any flash calculation that leads to phase equilibrium.

Second Step: Azeotrope Composition Localization

Tables III and IV give the simulation details for all points generated along the exploration process using the second step iterative methodology. For mixture I, the results are reported on the equilibrium curve (see Figure 2) along with those obtained by Pandit and Kofke (1999). They show the consistency of the proposed methodology.

As seen in Figure 2, the methodology based on the proposed search algorithm takes advantage of chemical engineering insights provided by the equilibrium constant values to reach the vicinity of the azeotrope in a few steps. Figure 2 also shows that the azeotrope is approached at the fourth iteration and that the three following iterations only narrow the composition window until the phase compositions are identical within statistical uncertainty (0.7009_{13} for the liquid and 0.7008_{61} for the vapor). The azeotrope composition is thus found to be 0.701_6 , in very good agreement with the azeotrope composition of 0.704_5 found by Pandit and Kofke (1999), assumed here as the average composition between the reported compositions of the two phases (0.6982 for the liquid and 0.7094 for the vapor).

For mixture III, Panagiotopoulos et al. (1988) did not perform any simulation near the azeotrope and drew a “guiding dashed line” that reached an azeotrope pressure $P^* = 0.1030$. Our computations (Table IV) show that the azeotrope composition

Table III. Simulation results for mixture I

Mixture I		ρ^*_{liq}	ρ^*_{vap}	P^*_{liq}	P^*_{vap}	x_A	y_A	K_A
Z = 0		0.4204 ₁₁	0.0325 ₁₁		0.0292 ₆	1	1	1
Z = 1		0.6431 ₁₃	0.0530 ₈		0.0442 ₄	1	1	1
$Z_L^0 = 0.025$		0.4212 ₁₇	0.0307 ₁₆	0.0301 ₂₃	0.0311 ₇	0.0228 ₁	0.0570 ₂₅	>1
$Z_H^0 = 0.975$		0.6326 ₁₉	0.0557 ₁₅	0.0477 ₃₀	0.0456 ₁₀	0.9780 ₂	0.9605 ₁₁	<1
Z1	$Z_L^0 = 0.025$	0.4473 ₁₃	0.0479 ₁₇	0.0426 ₂₀	0.0389 ₈	0.1982 ₄	0.3342 ₅₇	>1
0.2120	$Z_H^0 = 0.975$							
Z2	$Z_L^1 = 0.212$	0.5815 ₃₁	0.0596 ₁₂	0.0514 ₅₇	0.0484 ₇	0.8415 ₁₆	0.8198 ₇₀	<1
0.8386	$Z_H^1 = 0.975$							
Z3	$Z_L^2 = 0.212$	0.5243 ₁₀	0.0573 ₁₇	0.0506 ₂₀	0.0485 ₈	0.6303 ₉	0.6678 ₄₈	>1
0.6386	$Z_H^2 = 0.837$							
Z4	$Z_L^3 = 0.639$	0.5469 ₃₃	0.0603 ₂₅	0.0534 ₂₉	0.0487 ₁₁	0.7214 ₁₂	0.7141 ₅₆	<1
0.7163	$Z_H^3 = 0.837$							
Z5	$Z_L^4 = 0.639$	0.5297 ₁₀	0.5928 ₁₃	0.0502 ₁₇	0.0485 ₇	0.6526 ₉	0.6813 ₄₆	>1
0.6441	$Z_H^4 = 0.716$							
Z6	$Z_L^5 = 0.644$	0.5284 ₃₈	0.0605 ₁₈	0.0499 ₅₅	0.0486 ₉	0.6521 ₁₂	0.6983 ₅₈	>1
0.6489	$Z_H^5 = 0.716$							
Z7	$Z_L^6 = 0.649$	0.5433 ₁₂	0.0606 ₂₀	0.0506 ₁₈	0.0489 ₁₀	0.7009 ₁₃	0.7008 ₆₁	≈ 1
0.7032	$Z_H^6 = 0.716$							

Subscript numbers follow the notation for uncertainty values (for example, 0.4204₁₁ means 0.4204 ± 0.0011).

Table IV. Simulation results for mixture III

Mixture III		ρ^*_{liq}	ρ^*_{vap}	P^*_{liq}	P^*_{vap}	x_A	y_A	K_A
Z = 1		0.6070 ₁₉	0.0703 ₂₆		0.0582 ₁₃	1	1	1
Z _L = 0.025		0.5966 ₂₀	0.0689 ₁₇	0.0582 ₃₀	0.0590 ₉	0.0147 ₃	0.0639 ₂₀	>1
Z _H = 0.975		0.5963 ₃₂	0.0729 ₂₅	0.0670 ₂₈	0.0606 ₁₂	0.9853 ₂	0.9388 ₁₆	<1
Z1	Z _L ¹ = 0.025	0.5351 ₅₈	0.1213 ₄₆	0.0899 ₄₀	0.0873 ₁₅	0.1618 ₃₈	0.3251 ₄₅	>1
0.2250	Z _H ¹ = 0.975							
Z2	Z _L ² = 0.225	0.4130 ₆₅	0.1584 ₄₄	0.1045 ₂₁	0.1048 ₇	0.4095 ₅₂	0.4453 ₄₇	>1
0.4250	Z _H ² = 0.975							
Z3	Z _L ³ = 0.425	0.5831 ₂₀	0.0800 ₁₅	0.0620 ₃₅	0.0664 ₈	0.9549 ₆	0.8436 ₃₀	<1
0.9298	Z _H ³ = 0.975							
Z4	Z _L ⁴ = 0.425	0.5528 ₃₀	0.1116 ₆	0.0837 ₂₉	0.0836 ₂	0.8777 ₁₆	0.7242 ₂₈	<1
0.8239	Z _H ⁴ = 0.929							
Z5	Z _L ⁵ = 0.425	0.4363 ₈₀	0.1338 ₃₁	0.0974 ₁₉	0.0959 ₁₁	0.6770 ₃₆	0.5847 ₅₅	<1
0.6423	Z _H ⁵ = 0.824							
Z6	Z _L ⁶ = 0.425	0.3407 ₇₀	0.1691 ₃₂	0.1056 ₃₁	0.1043 ₁₀	0.5477 ₅₄	0.5155 ₆₁	<1
0.5361	Z _H ⁶ = 0.642							
Z7	Z _L ⁷ = 0.425	0.3438 ₁₃₇	0.1681 ₆₇	0.1104 ₂₅	0.1038 ₁₁	0.4679 ₆₄	0.5036 ₆₅	>1
0.4893	Z _H ⁷ = 0.536							
Z8	Z _L ⁸ = 0.489	0.4014 ₁₃₆	0.1771 ₃₁	0.1093 ₂₈	0.1044 ₉	0.5228 ₅₄	0.5129 ₃₉	<1
0.5175	Z _H ⁸ = 0.536							
Z9	Z _L ⁹ = 0.489	0.3981 ₁₄₀	0.1816 ₃₆	0.1100 ₁₈	0.1043 ₈	0.5068 ₈₆	0.5050 ₅₀	≤1
0.5111	Z _H ⁹ = 0.517							
Z10	Z _L ¹⁰ = 0.489	0.2658 ₄₄	0.1819 ₅₉	0.1099 ₁₃	0.1064 ₁₂	0.5051 ₃₂	0.5086 ₆₃	≈1
0.4998	Z _H ¹⁰ = 0.511							

Subscript numbers follow the notation for uncertainty values (for example, 0.6070₁₉ means 0.6070 ± 0.0019).

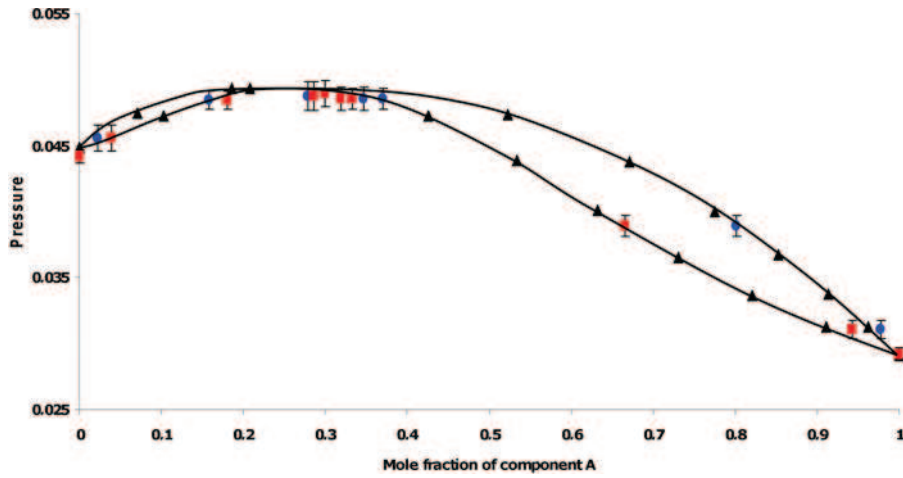


Figure 2. Liquid-vapor coexistence curve for mixture I at $T = 1.10$; our results (circles and squares for liquid and vapor phases respectively) are compared to constant pressure Gibbs simulations obtained by Pandit and Kofke (1999) (triangles). (Figure provided in color online.)

Table V. Comparison between our results and previous works

	Composition			Pressure		
	This work	Previous work	Error (%)	This work	Previous work	Error (%)
Mixture I	0.7008	0.7038 ^a	0.43	0.0489	0.0498 ^a	1.84
Mixture III	0.5068	0.5000 ^b	1.35	0.1064	0.1030 ^b	3.20

^aPandit and Kofke (1999).

^bPanagiotopoulos et al. (1988).

is correctly found at $x = 0.507_5$. The equilibrium pressure of the azeotrope ($P = 0.1064_{12}$) is higher than the guessed value by Panagiotopoulos et al. (1988). Comparison between our results and those published in the literature is summarized in Table V for mixture I and mixture III. The relative error is calculated for the property X (either the pressure or composition) as:

$$Error (\%) = \frac{|X_{cal}^{This\ work} - X_{cal}^{previous}|}{X_{cal}^{This\ work}} \quad (7)$$

The accuracy of our results could be improved by increasing the number of particles or by increasing the number of MC simulation steps.

Conclusions

A molecular simulation based–method was proposed for finding the azeotrope and computing its composition, pressure, and density at an initially given temperature.

These properties are usually computed by chemical engineers using macroscopic thermodynamic models like equations of state or activity coefficient models.

In this study, these macroscopic models are replaced by a set of molecular simulations in the Gibbs ensemble at constant volume combined to swap Monte Carlo moves, developed within the grand canonical ensemble formalism. The swap move enables changing the identity of particles in the simulation boxes and thus progressing towards the azeotrope along the equilibrium curve.

The proposed methodology combines chemical engineering insights together with molecular simulation principles. First, it checks for azeotrope existence by exploiting the variation of the equilibrium constant at each extremity of the equilibrium curve. Then, it computes the azeotrope coordinates by successive simulations in the Gibbs ensemble. The method has been successfully applied for different Lennard-Jones binary mixtures.

Compared with other molecular simulation techniques able to predict azeotropes (such as the bubble point pseudo-ensemble, the histogram reweighting method, or the grand equilibrium method), the proposed method allows immediately checking the azeotrope existence, while the remaining techniques require the exploration of the entire phase diagram to reach this point. In addition, thanks to the swap move, the computational time necessary to detect and localize the azeotrope could be significantly reduced.

However, the proposed method suffers from some deficiencies:

1. The initialization step proposed here does not allow the detection of an azeotropic point whose coordinates are closer than 0.025 mole fraction unit from the pure components. Relaxing this hypothesis requires using large initial boxes so as to get a sufficient number of each component in them.
2. The swap moves are applied to the final configuration obtained by the GEMC calculations and not to the most stable one. One could alternatively select the most stable configuration of the GEMC simulation before performing these moves.
3. When performing identity change move calculations, whether the chemical potential remains constant was not checked a posteriori. This may induce a small error that is readily compensated because the GEMC calculation run afterwards resets to constant the chemical potential.

Deficiencies 2 and 3 stress that successive simulations do not exactly progress along the equilibrium curves. Nevertheless, the final azeotropic point reached is accurately determined by the last GEMC calculation.

Further work is intended to implement the following algorithm for poly-atomic systems. For such mixtures, a more efficient algorithm than the branch and bound search may be used.

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Appendix: Algorithm Description

The proposed algorithm (see Figure 3) is composed of two steps (from here we drop the subscripts related to the component of the binary mixture by considering $x = x_A$).

1. The first step exploits the behavior of the equilibrium constant K , as described above, to check the existence of an azeotrope. It consists in running two GEMC simulations at constant volume with molar fraction Z near the pure components; for example, for $Z_H^0 = 0.975$ and $Z_L^0 = 0.025$, the subscripts H and L stand

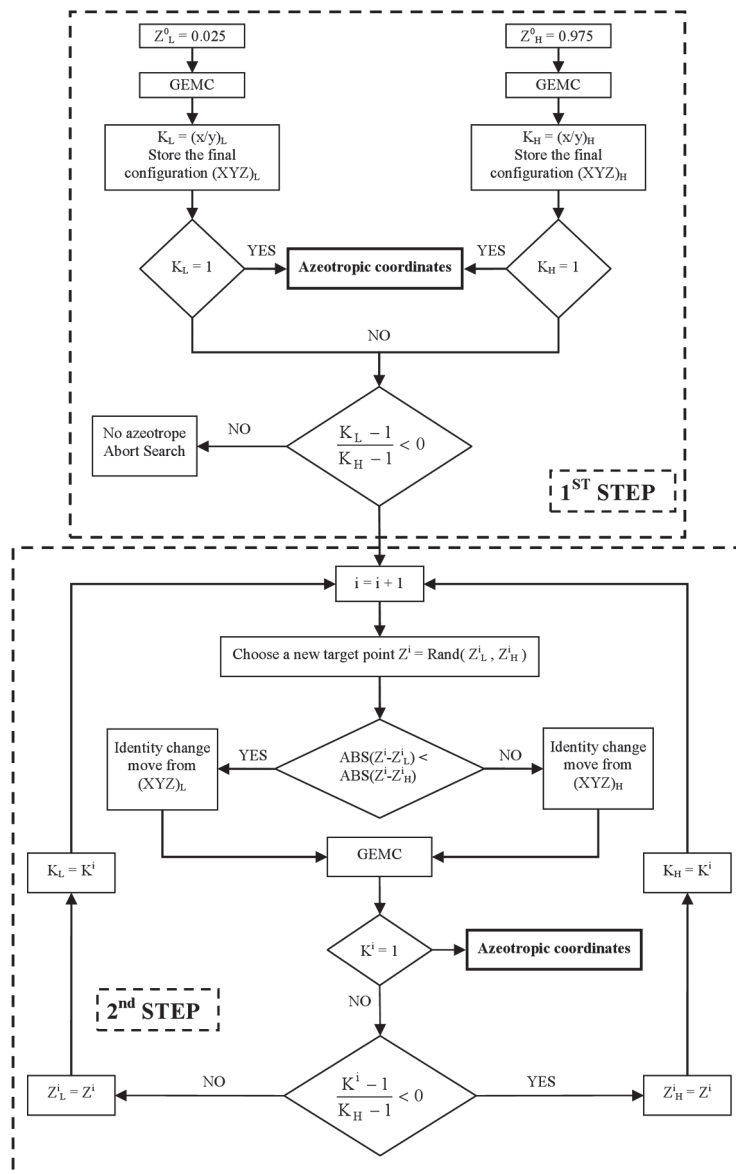


Figure 3. Algorithm for finding binary mixture A-B azeotropes.

respectively for high and low content in volatile component. Densities of the initial configuration boxes should be chosen to give rise to a liquid-vapor equilibrium.

The resulting molar fractions x^0 and y^0 in equilibrium are averaged over all the configurations, typically several millions, and the equilibrium constants K_H and K_L are calculated:

- If K_H and K_L are equal to 1.00 within statistical uncertainty, the azeotrope has been found and $x_{az} = y_{az} = Z$.
 - Otherwise, K_H and K_L are compared to unity applying the criteria described above to determine whether an azeotrope exists or not. If yes, the iteration counter is set to $i = 1$.
2. If the azeotropic point exists, the second step calculates its coordinates using swap moves to change the composition and to progress along the boiling-dew equilibrium curves towards the azeotrope as follows:
- A random coordinate Z^i is pulled out between Z_H^i and Z_L^i compositions.
 - A configuration of global composition Z^i is built by successive swap moves from the box with the closest composition, either Z_H^i or Z_L^i .^{*} Note that these swap moves are not intended to sample any statistical ensemble but simply to provide a convenient initialization for the next simulation.
 - Using the resulting configuration as the initial state of the system, a phase equilibrium calculation is performed in the Gibbs ensemble at constant volume.
 - The equilibrium constant K^i is evaluated:
 - If K^i is equal to unity within statistical uncertainty, the azeotrope composition is found ($x_{az} = y_{az} = Z^i$).
 - Else, a new step 2 is prepared on a narrower composition interval as the Z^i composition replaces either Z_H^i or Z_L^i composition, depending on whether $(K^i - 1)$ has the same sign as $(K_H^i - 1)$ or $(K_L^i - 1)$:
 - if $(K^i - 1)$ has the same sign as $(K_H^i - 1)$ then $Z_H^{i+1} = Z^i$ and $Z_L^{i+1} = Z_L^i$.
 - if $(K^i - 1)$ has the same sign as $(K_L^i - 1)$ then $Z_H^{i+1} = Z_H^i$ and $Z_L^{i+1} = Z^i$.

Nomenclature

E	total energy of the system
K	equilibrium constant
k	Boltzmann constant
N	number of particles
P	pressure
p	acceptance probability of the move
q	molecular partition function
T	absolute temperature
V	volume
XYZ	Cartesian coordinate
x	liquid composition
y	vapor composition
Z	mixture composition

^{*}In practice, to ensure an efficient convergence of the algorithm, the first steps are bounded to a maximum value, so that $Z = \min(\text{Rand}(Z_H, Z_L); Z_L(\text{or } Z_H) \pm \Delta Z_{max})$. ΔZ_{max} is taken here equal to 0.20.

Greek Letters

β	Boltzmann coefficient
ε	Lennard-Jones energy parameter
μ	chemical potential
σ	Lennard-Jones size parameter

Subscripts

A	component A
az	azeotropic point
B	component B
H	high
i	type of molecule
L	low
*	reduced unit

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