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## Statistical mechanical theory of fluid mixtures

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### HIGHLIGHTS

- We present the statistical mechanical expressions of separation factor  $\alpha_{ij}$  and  $\gamma_i$ .
- The physical meaning of activity coefficient  $\gamma_i$  in the liquid phase is discussed.
- This model connects the classical thermodynamics with molecular simulation.
- It is reliable for VLE predictions of non-ideal mixtures and associating fluids.
- The model equations have good compatibility with classical thermodynamic equations.

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### ABSTRACT

A general statistical mechanical theory of fluid mixtures (liquid mixtures and gas mixtures) is developed based on the statistical mechanical expression of chemical potential of components in the grand canonical ensemble, which gives some new relationships between thermodynamic quantities (equilibrium ratio  $K_i$ , separation factor  $\alpha_{ij}$  and activity coefficient  $\gamma_i$ ) and ensemble average potential energy  $\bar{u}_i$  for one molecule. The statistical mechanical expressions of separation factor  $\alpha_{ij}$  and activity coefficient  $\gamma_i$  derived in this work make the fluid phase equilibrium calculations can be performed by molecular simulation simply and efficiently, or by the statistical thermodynamic approach (based on the saturated-vapor pressure of pure substance) that does not need microscopic intermolecular pair potential functions. The physical meaning of activity coefficient  $\gamma_i$  in the liquid phase is discussed in detail from a viewpoint of molecular thermodynamics. The calculated Vapor–Liquid Equilibrium (VLE) properties of argon–methane, methanol–water and *n*-hexane–benzene systems by this model fit well with experimental data in references, which indicates that this model is accurate and reliable in the prediction of VLE properties for small, large and strongly associating molecules; furthermore the statistical mechanical expressions of separation factor  $\alpha_{ij}$  and activity coefficient  $\gamma_i$  have good compatibility with classical thermodynamic equations and quantum mechanical COSMO–SAC approach.

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### 1. Introduction

The theory of fluid phase equilibrium is very important for the prediction of thermodynamic properties [1–5] at vapor–liquid equilibrium (VLE) and liquid–liquid equilibrium (LLE). The VLE and LLE data are essential for the design and optimization of the multi-component separation and purification industrial process of distillation and extraction [5]. Until now, there are two main groups of methods in fluid phase equilibrium calculations: classical thermodynamics [4–16] and molecular simulation [17–29]. The phase equilibrium calculations in classical thermodynamics are generally conducted by the equation of state (EOS) approach or by the activity coefficient method; and phase equilibrium is expressed in terms of vapor–liquid and liquid–liquid equilibrium ratio  $K$ -values [5], the  $K$ -values in turn is formulated in terms of fugacity  $f_i$  and

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**Nomenclature**

$E_i^{(t)}$	the mean molar potential energy change of component $i$ in phase transition
$h$	Planck's constant
$\Delta H_{vap,i}^{(o)}$	molar enthalpy of Vaporization of pure component $i$
$k$	Boltzmann's constant
$K_i$	equilibrium ratio of component $i$
$N_i$	the ensemble average molecular number of component $i$
$N_o$	Avogadro's constant
$P$	pressure
$R$	universal gas constant
$T$	temperature
$t_b$	boiling point
$\bar{u}_i$	the mean potential energy deserved by one molecule of component $i$
$U_{p,i}^{(L)}$	the mean molar potential energy of component $i$ in liquid mixture
$U_{p,i}^{(L,o)}$	the mean molar potential energy of pure liquid $i$ at system temperature and pressure
$V_m^{(\alpha)}$	molar volume of mixture in fluid phase $\alpha$
$V_{m,i}^{(o)}$	molar volume of pure liquid $i$ at system temperature and pressure
$V_m^{(V,o)}$	the molar vapor phase volume of pure component
$x_i$	liquid phase mole fraction of component $i$
$y_i$	vapor phase mole fraction of component $i$

**Greek letters**

$\mu_i$	chemical potential of component $i$
$\alpha_{ij}$	separation factor
$\gamma_i^{(\alpha)}$	activity coefficient of component $i$ in liquid phase $\alpha$

**Subscripts**

$j$	component index
$m$	molar

**Superscripts**

<i>calc.</i>	calculated
<i>expt.</i>	experimental
<i>mix.</i>	mixture
<i>o</i>	pure fluid
<i>L</i>	liquid phase
<i>V</i>	vapor phase

activity coefficient  $\gamma_i$ . In recent years, the Cubic Plus Association Equation of State (CPA EoS) [9,10] and Statistical Associating Fluid Theory (SAFT) [11–13] have made great success in the calculation of thermodynamic properties of associating fluids. The fugacity is usually computed by an equation of state (EOS) [4,5], which is easy to use with little computation effort; while the EOS approach only gives qualitative predictions especially at extreme high temperatures and pressures. In chemical engineering calculations, the activity coefficient  $\gamma_i$  is usually estimated by the Group-Contribution methods (such as ASOG [6], UNIQUAC [7] and UNIFAC [8]) or by the semi-theoretical quantum COSMO-based approach [14–16] reliably and quickly, which need experimental data fitted group-interaction parameters or empirical parameters. Molecular simulation techniques [17–29] allow direct calculation of phase equilibrium through the equality of chemical potential of each species in all phases at equilibrium ( $\mu_i^{(\alpha)} = \mu_i^{(\beta)}$ ), and make the prediction of thermodynamic properties possible especially at extreme high temperatures and pressures. The molecular simulation methodologies for fluid phase equilibria include Gibbs ensemble Monte Carlo [20], Kirkwood coupling method [21], Gibbs–Duhem integration [22–24], the Virtual Gibbs ensemble [25], integral equation method [26,27], NPT plus test particle method [28], etc., which make the molecular simulation a promising alternative to EOS models in VLE calculations; among these, the simplest and least demanding of computer resources are the methods based on Widom insertion [29]. The methods based on Widom insertion are applicable only in moderately dense fluids; at very high fluid densities, the insertion acceptance probability will be too low [29].

In this work, the statistical mechanical expressions of equilibrium ratio  $K_i$ , separation factor  $\alpha_{ij}$  and activity coefficient  $\gamma_i$  for fluid mixtures are derived; which connect the classical thermodynamics with molecular simulation, and provide a

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