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"An Accurate Characterization of Complex Fluid Mixtures. A Collaborative Approach Based on Molecular Simulations and the Statistical Associating Fluid Theory"

Tesis para optar al grado de Doctor en Ciencias de la Ingeniería con Mención en Ingeniería Química

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Abstract

A rational guide able to qualitatively predict the thermo-physical properties in terms of state variables (*i.e.* temperature, pressure, composition) becomes relevant in various technological applications. As part of a global approach where theory and Molecular Simulations (MS) collaborate in characterizing phase and interface behaviors, it has been well established the need of a unequivocal guidance for estimating initial guesses of conditions able to generate stable MS experiments devoted to predict specific phenomena, where due to extreme conditions, experimental measurements have a limited capability to accurately predict all the properties of complex fluids. Molecular based Equation of State (EoS) models and MS provide key pieces of such an approach since, on the one hand, they are closely related in terms of the underlying molecular model -*i.e.* the force potential field- and, on the other hand, they directly depend on the interactions exerted by unlike molecules, so we claim in this thesis that an approach based on Global Phase Diagrams (GDP) -*i.e.* a parametric map where phase behaviors may be delimited in terms of molecular parameters- is useful to rationally guide molecular simulations. The present collaboration scheme used in this work, between molecular simulations and theoretical predictions shown to be effective and successful in bringing together different pieces of information for the purpose of: (a) analyzing the coherency of experimental results and theoretical predictions and (b) understanding the phase and interfacial behavior of the characterized mixtures. In this thesis, a novel elements correlation for the influence parameters in pure fluids is introduced. The proposed model is based on the van der Waals square gradient theory (SGT) and elegantly combines the SAFT-VR Mie EoS, the corresponding states principia for parameter determination and scaling arguments applied to MS data. The results are expressed in terms of the reduced energy, size and range of the Mie potential; hence the application to real fluids relies on mapping these properties to critical constants. The only input parameters needed are the critical temperature, the acentric factor and the liquid density of the fluid at a reference temperature. The GPD of equal-size Lennard-Jones mixtures has been used to define the molecular parameters of binary and ternary mixtures. Particularly for binary mixtures regions have been identified on the GPD in which density inversion phenomena has a direct relationship with the distortion of the density profiles. The exploration along the three-phase line for the ternary mixture shows good agreement between SGT and MS. Particularly, we observed the specific influence of a third component in the phase and interface behavior. Using the results and the experience gained with idealized force fields (Lennard-Jones), we develop a collaboration scheme for integrating both theory and molecular simulations in a unified approach, capable to predict phase behavior and properties of complex molecules. In such an approach, we calculate phase equilibrium and thermo-physical properties of real mixtures by considering molecular simulations of realistic force and Coarse-Grained (CG) force fields. Of particular interest for this latter application are the mixtures of liquids pressurized by supercritical gases (CO_2 and N_2) and H_2O+CO_2+hydrocarbons mixtures.