

# Phase and Interface behavior along three-phase line in type-III Lennard-Jones mixture. A comparative study between Gradient Theory and Molecular Dynamics

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A rational guide able to qualitatively predict the effect of added components on the thermo-physical properties of fluid mixtures plays a relevant role in pursuing the purpose of screening adequate solvents. 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. Theoretical Equation of State (EoS) models<sup>1-3</sup> 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. In addition, in previous contributions we have demonstrated<sup>4,5</sup> that the global phase diagram (GPD) calculated from theoretically based EoSs is effective for designing molecular simulation experiments involving different types of phase behavior<sup>6</sup>.

In this contribution two complementary methods, namely Molecular Dynamics simulations (MD) and Square Gradient Theory (SGT) have been used for describing the interfacial region, thus allowing predicting both the macroscopic and molecular details of mixtures exhibiting three-phase equilibrium. SGT calculations rely on the prediction of the GLLE by means of the equa-

tion of state developed by Johnson *et al.*<sup>1</sup> (JZG-EoS). MD simulations are then performed in the canonical ensemble using a Lennard-Jones potential field in order to confirm the presence of the coexisting phases and their accompanying interface. In order to perform a consistent comparison between both methodologies, the molecular parameters of this type of mixture were defined from the GPD of equal size Lennard-Jones mixtures. For all conditions explored in this work, this type-III mixture shows a three-phase equilibrium composed by a bulk immiscible liquid phase ( $L_1$ ) and a bulk gas phase ( $G$ ) separated by a second immiscible liquid phase ( $L_2$ ).

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