

# Liquid-liquid phase equilibria and interfacial properties of the tetrahydrofuran + methane mixture from molecular dynamics simulation

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Clathrate hydrates are nonstoichiometric inclusion solid compounds in which small guest molecules are enclathrated in voids left by a periodic network of water molecules [1]. Research on gas hydrates has been motivated to a great extent lately by the huge amount of methane that has been identified in hydrate deposits, either in the sea floor or in permafrost frozen substances. This fact makes hydrates a key future energetic source, whose exploitation represents a technical challenge of first magnitude [2, 3].

Additives of hydrates are an important class of substances that when are mixed with gas hydrates are able to shift the hydrate coexistence curves to different thermodynamic conditions of temperature and pressure [1]. Tetrahydrofuran or simply THF, a cyclic ether widely used as solvent in many industrial processes, is one of the most important and well-known thermodynamic hydrate promoters. In particular, THF is able to reduce the equilibrium pressure dramatically and it make it possible to treat gas hydrates under mild pressure conditions [4].

From a theoretical modelling point of view, computer simulation offers insight into atomic level phenomena that are not observable from an experimental points of view, providing unique and invaluable information about the underlying physicochemical principles governing hydrate behaviour, including thermophysical properties, phase equilibria, and interfacial properties [5]. The long-term goal of this work is to use molecular models to predict the phase equilibrium of THF hydrates and hydrates of mixtures of THF with methane. Since fluid-fluid interfacial properties, and particularly surface tension, are one of the most sensitive properties to subtle differences in molecular details, we analyse some molecular models of THF to critically assess the ability of them in predicting the interfacial behaviour of this mixture.

In this work, we determine the phase equilibria and interfacial properties of the tetrahydrofuran + methane binary mixture at different extreme thermodynamic conditions. Tetrahydrofuran (THF) is modelled using the united-atom approach. In particular, we use two different models: (a) the original TraPPE model proposed by Keasler *et al.* [6], and (b) an approximated model, based on the Keasler's model, in which the molecules are planar, rigid, and bending and torsional degrees of freedom are frozen, i.e., we consider that the equilibrium bond angles are fixed and the molecules have no torsional degrees of freedom [7].

We have performed molecular dynamics simulations in the canonical ensemble and determined the vapour-liquid interfacial tension evaluating the normal and tangential components of the pressure tensor along the simulation box. In addition to the surface tension, we have also obtained density profiles, coexistence densities (see Figure 1), pressure-composition phase diagrams, and interfacial thickness as

functions of pressure. Since no experimental data is available in the literature at the moment, theoretical predictions obtained from molecular dynamics simulation are compared with predictions from the Statistical Associating Theory for potentials of Variable Range (SAFT-VR) [8].

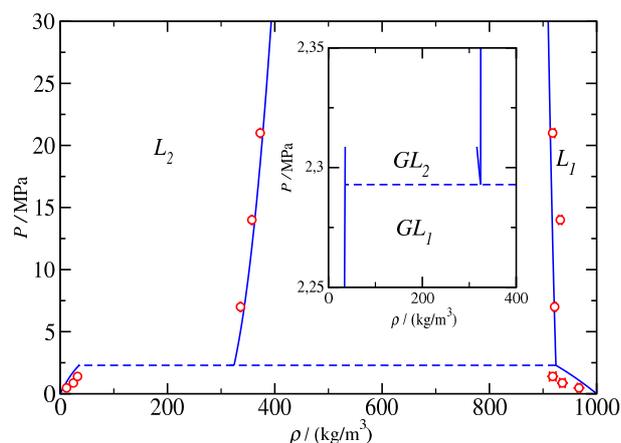


Figure 1: Pressure-density projection of the phase diagram of the THF + CH<sub>4</sub> binary mixture at 170 K. Curves represent the predictions from the SAFT-VR approach and symbols are the results from molecular dynamics simulation. Continuous curves correspond to liquid-liquid (high-pressure) and vapour-liquid (low-pressure) coexistence and discontinuous line to the three-phase line.

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