ESTIMATION OF MULTICOMPONENT INTERFACIAL DENSITY PROFILES DIRECTLY FROM THE HELMHOLTZ FREE ENERGY SURFACE

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ABSTRACT

Interfacial properties such as surface or interfacial tension have recently acquired a renewed interest, particularly for multicomponent mixtures, as they are relevant for applications from oil and gas to emulsions and detergents. The density profiles of the species across coexisting phases may show preferential accumulation (adsorption), and this is directly related to the interfacial tension. Among other approaches, the gradient theory is perhaps one of the most widely accepted approaches, provided the interface density profiles as well as the influence parameters are known or can be estimated in a robust manner. Form a calculation perspective, it is in the estimation of the density profiles where the application of the method may run into several shortcomings that are not always easy to overcome, such as numerical convergence.

In this work, an alternative theory is presented, which allows for the independent calculation of the interfacial density profiles directly from the Helmholtz free energy surface. When two or more phases are in equilibrium, they share a common tangential hyperplane. The hypothetical path along which a dynamical interchange of species throughout their interfaces may take place must necessarily follow a minimal-energy path form one bulk phase to the other. Given a free energy model, this path is well defined and can be independently calculated, defining as well the density profiles throughout this path within the common interface. This idea is illustrated with some basic free energy calculation using common mixture models, and further illustrated and verified from Molecular Dynamics simulation (MD) results.

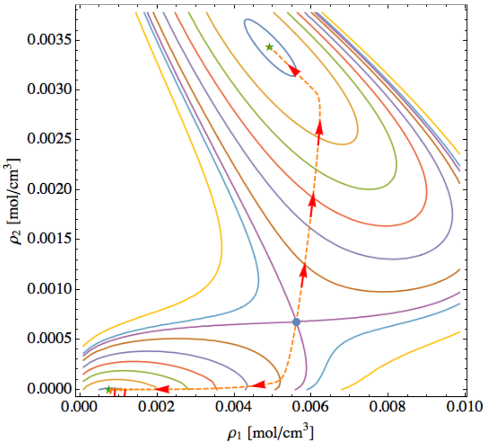


Figure 1: Minimum energy path between two coexisting phases.

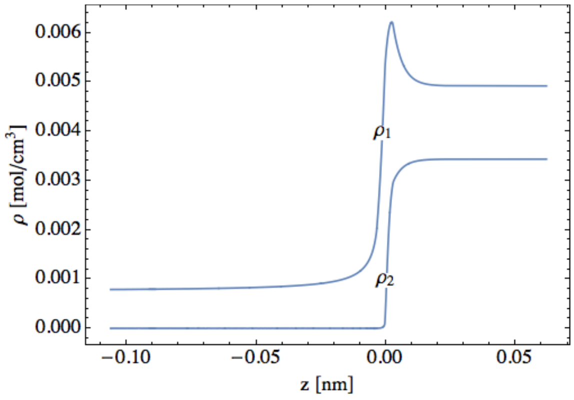
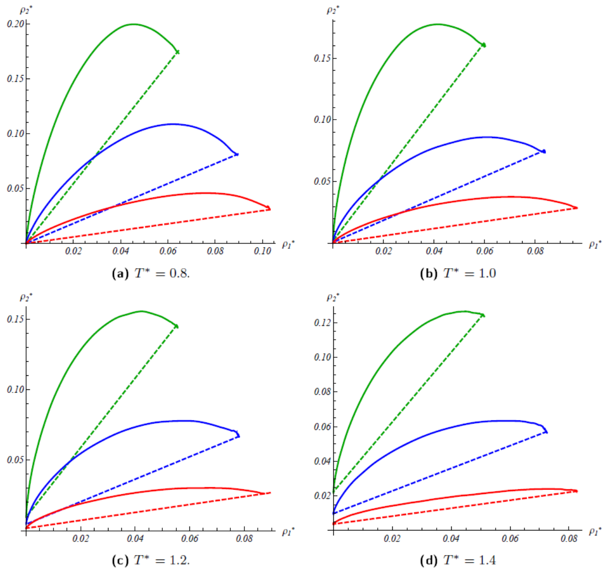


Figure 2: Resulting density profile projections.

Theory and MD Simulations

In principle, density profiles and surface tension can be explained with the density functional formalism. This, however, requires molecular and structural information that, at the present, can only be obtained by means of computer simulations. There exist several publications on interfacial properties and density profiles in binary and multicomponent mixtures, either in real fluids or Lennard-Jones (LJ) fluids, for example Miqueu's work on CO_2/hydrocarbons [1] and CH_4/water [2] mixtures, that of Georgiadis et al. [3] on a CO_2/water mixtures, and Makimura et al. in a CO_2/hexane/water mixture [4]; Lennard-Jones [5-7]; and more recently, linear-chain mixtures using the density functional theory (DFT) along with a SAFT model [8]. However, in none of the consulted works attention is paid to ρ_1–ρ_2 equilibrium diagrams (in binary mixtures). These kinds of diagrams are of special interest in the study of surface tension since a close relation between the density profiles obtained by means of free energy minimization (figures 1 and 2) and with molecular dynamics (Figure 3) was found.

Figure 1 shows a contour plot of the Helmholtz free energy density of the butane/ethane mixture obtained with the Peng-Robinson EoS in a ρ_1–ρ_2 diagram following the lowest ascendant path form one coexistence phase to the other, as defined by Quiñones-Cisneros [9, 10]. Vapour-liquid equilibrium (VLE) densities are defined by the two local minima (green stars) of the Helmholtz energy density, the blue point is the saddle point between the phases while the dashed orange curves represent the minimum energy path between the coexisting phases, which necessarily must go through the saddle point. From the MD results in Figure 3, on the other hand, the same qualitative features are reproduced an observed when similar diagrams are plotted. It is clear that when the thought the interfase the density profiles systematically deviates from the straight line (tie-line) that connects the two equilibrium points.



(a) $T^* = 0.8$. (b) $T^* = 1.0$ (c) $T^* = 1.2$. (d) $T^* = 1.4$

Figure 3: Vapour-liquid to ρ_1–ρ_2 equilibrium diagrams and density profile projections at constant temperature for LJ flexible chains: mixture of 8 and 2 element chains. Green lines, molar fraction $x_1 = 0.25$; blue lines, $x_1 = 0.5$; red lines $x_1 = 0.75$. Solid lines represent the density profiles of phase transition like those of Figure 4b, whereas the dashed lines are the tie-lines that connect the vapour-liquid equilibrium points. These figures are qualitatively similar to Figure 1.

The hypothesis is that, when the system passes through a phase transition, the components follow a set of states that, from state to state, represents the minimum energy or effort trajectory; in this case, such states are given by the arrowed curve (red arrows in Figure 1). In this sense, one of the main objectives of this work is to show, from a microscopic point of view, that the transition densities from one phase to another deviate from the tie-line, following a minimum effort path, and that such deviations yield the density profiles when projected through the interface, as in Figure 2.

In MD simulation, to investigate surface tension or density profiles, the usual approach is to set up a liquid film in a stable vapour-liquid equilibrium (Figure 4a) and then sample the relevant thermophysical properties in the surface regions [11, 12]. We performed canonical MD simulations of a vapour-liquid interface in three binary systems at the same conditions of temperature ($T^* = 0.8$, 1.0, 1.2 and 1.4 in reduced units) and molar composition ($x_1 = 0.25$, 0.50, 0.75). In the simulations we used a model of flexible linear tangent chains, where each chain consists of n particles (interaction sites) which interact via the Lennard-Jones potential with a “classical” cut-off radius $r_c^* = 2.5$.

$$U_{LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

$$\boldsymbol{F}_{LJ}(r_{ij}) = -\frac{48\varepsilon}{r_{ij}}\left[\frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{6} - \left(\frac{\sigma}{r_{ij}}\right)^{12}\right]\hat{\boldsymbol{r}}_{ij}$$

whereas the bonded particles interact through an harmonic potential

$$U_{\text{bond}}(r_{ij}) = \frac{1}{2}k(r_{ij} - l)^2$$

$$\boldsymbol{F}_{\text{bond}}(r_{ij}) = -k(r_{ij} - l)\hat{\boldsymbol{r}}_{ij}.$$

Thus, the total potential of the system is given by

$$U = U_{LJ} + U_{\text{bond}} = \sum_i \sum_{j>i} U_{LJ}(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_b U_{\text{bond}}(\boldsymbol{r}_i, \boldsymbol{r}_j),$$

where the index b in the second term means that the summation runs over the bonded particles i and j. The parameters σ and ε are those of argon; l and k are the bond length and the spring constant and correspond to those used by Johnson et al [13]. The studied binary mixtures were made from LJ flexible chains of 2 (C_2), 4 (C_4) and 8 (C_8) elements: C_4/C_2, C_8/C_2, and C_8/C_4. In our simulations cut-off corrections, due to cut-off radius, were not added since we were only interested in qualitative behaviour of density profiles of chain-like systems and in their ρ_1–ρ_2 diagrams representation (Figure 3), not the actual interfacial tension value.

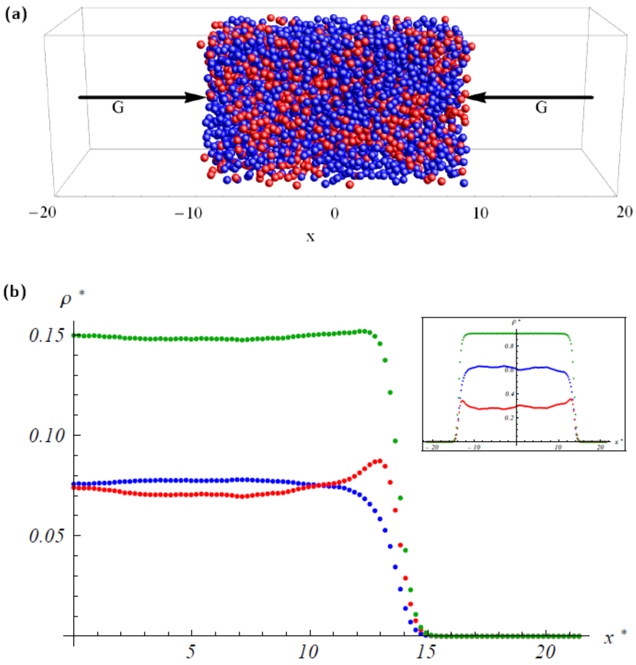


Figure 4: a) Snapshot of a Lennard-Jones fluid MD simulation. Construction of an interface made of 250 C_8 (blue) and 250 C_4 (red). The film force, **G**, takes the particles to the centre of the box to create the film and to stabilize the interface. Then the temperature is held constant and the **G** force released. b). The resulting equilibrium density profile. Molecular density of C_8 (blue), C_4 (red), and system global density (green) of Figure 4a. The upper right box shows the atomic densities of the system, molar fraction $x_1 = 0.50$. The adsorption is strongly dependent on the global composition of the system, especially on the ratio of atoms per chain in the components (4:1 for this system). Llovell et al [8] observed the same behaviour in C_3/C_1 and C_2/C_1 mixtures using Density Functional Theory.

CONCLUSIONS

We use molecular dynamics to obtain a set of equilibrium points in order to study ρ_1–ρ_2 diagrams. Figure 3 shows the equilibrium diagrams of a C_8/C_2 mixture at four temperatures. The dashed lines are the tie-lines whereas the solid lines are the density profiles throughout the interface (similar in Figure 4b). It can be seen that the qualitative shape of the diagrams are in good agreement with that obtained by following the minimum effort path of the

Helmholtz free energy (Figure 1) but in the latter the subscript 1 refers to the lightest component. Therefore, from the results obtained in this study, we infer that the density profiles do really minimize the energy in the phase transition and, plotted in ρ_1–ρ_2 diagrams, a minimum energy path in the vapour-liquid transition can be obtained which deviates more and more from the tie-line as temperature decrease, causing the lighter species to accumulate in the interfacial region. These results are of a general nature and can easily be extended to multicomponent mixtures.

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