

Insights into the Mass Transfer through Vapor-Liquid Interfaces from Molecular Dynamics Simulations

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Properties of vapor-liquid interfaces are believed to influence the mass transfer across the interface – especially the enrichment of components at the interface [1,2]. To study the influence of the enrichment on the mass transfer, two simulation methods based on non-equilibrium molecular dynamics simulation (NEMD) were developed by our group [3,4]. The first method establishes a stationary mass flux across vapor-liquid interfaces, and the second method investigates the transient mass flux of a low-boiling component through an interface into a liquid phase. For the stationary method, averaging is carried out using the classical block averaging method. In the non-stationary method, averaging is carried out using the replica method. The benefits and drawbacks of the two methods will be discussed in detail in this contribution.

The non-stationary method was found to be significantly more robust and insightful compared to the stationary method.

After testing, the non-stationary method was applied in systematic studies for elucidating the influence of interfacial properties, i.e. enrichment, surface tension, thickness etc., on the mass transfer through the vapor-liquid interface [5]. Therefore, binary Lennard-Jones model systems were considered, for which phase equilibrium bulk and interfacial properties [6,7] as well as bulk phase transport properties are well known [8,9]. The influence of the temperature, the (bulk phase) composition, and the mixture type on the interfacial mass transfer effects was thereby studied. Five binary systems were considered. It is shown that the differences in transport properties of the bulk phases alone cannot account for the findings of the NEMD simulations. Hence, the differences in the mass flux are attributed to interfacial effects. Furthermore, it was observed, that the particles entering the liquid phase through an interface may be repelled from the interface. In some cases, even a net negative mass flux back into the vapor phase is observed due to the repelling of particles from the interface. This repelling of particles significantly depends on the nature of the interface, i.e. its surface tension and interfacial thickness. Moreover, preliminary results for the mass transfer through vapor-liquid interfaces in a real substance system will be presented, namely for water + CO₂.

References

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