

# Modeling of Unit Operations by Molecular Simulations

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## Abstract

The behavior of separation columns can be simulated by molecular simulation, where the influence of all relevant elements of a separation stage is taken into account. In order to decrease the computational time the column is divided in separation stages, where the simulation of each stage is carried out on an individual computer and the number of stages can be set to any desired value. By performing a dimensional analysis the residence time of the molecules in the molecular simulation can be adjusted such that the simulated mass transfer corresponds to a macroscopic stage, i.e. the column simulation is also able to depict the influence of the residence time on the efficiency of separation stages.

## Introduction

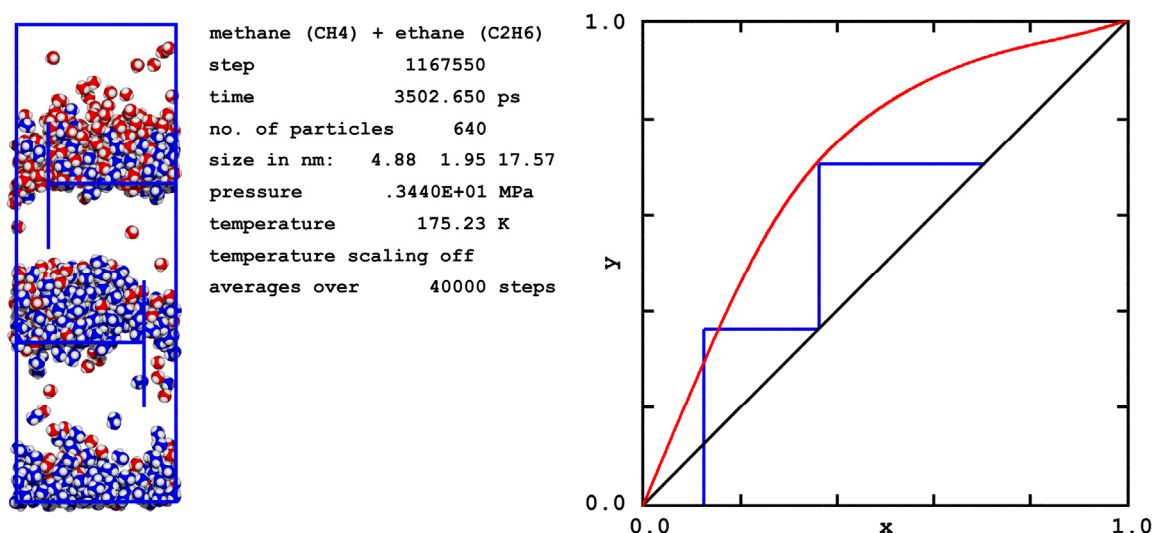
The properties and interactions of the molecules involved in chemical-engineering processes determine the behavior and thus the design of the used equipment. Nowadays it is still considered as impossible to bridge the length and time scales between molecules and technical equipment in only one or a few steps of model hierarchy. Nevertheless it is generally accepted that the major effects in chemical engineering facilities can be modeled just with equilibrium or rate-based approaches. These effects have their origin on molecular level and corresponding data can be obtained by only taking the vicinity of the interface into account, i.e. the simulation of a few hundred or thousand particles is sufficient.

In this work a simulation tool has been developed that is able to predict the behavior of entire separation columns based on molecular simulations. In principle any countercurrent separation equipment can be described, until today we focus on distillation and solvent extraction. The benefit of this approach is that the simulations are performed at the exact operating conditions, i.e. compositions, temperature, pressure and their gradients corresponding to the real apparatus. Thus it is not necessary to simulate data over the entire range of possible temperatures and compositions, where the data for the relevant conditions are then obtained afterwards by correlation or interpolation. Furthermore molecular simulations are able to predict multi-component effects of mass transfer as well as complex equilibrium data accurately and consistently.

## Modeling

In the molecular approach the column is depicted by consecutive separation stages, i.e. the simulation of one separation stage is performed for two flowing phases in contact. Hereby the outflow of one stage is directly the inflow of the next stage with respect to material flow, composition, and temperature. In order to implement this concept in a first step the code of a molecular-simulation program has been modified as to allow different compartments and boundaries between them to be accounted for in a simulation, i.e. specific boundary properties can be applied to molecules that cross a border. By using

different boundary properties all relevant elements of a separation process can be depicted on molecular level: partly penetrable walls simulate the behavior of sieve trays, heating and cooling regions are induced by influencing the molecular velocities or feed and product flows by inserting and removing particles from the simulation. In a first approach a counter flow had been induced by introducing gravity. It was already shown that with this setup the principle behavior of a distillation column can be simulated with less than a thousand particles [1]. The agreement with experimental data is excellent (Fig. 1). This approach has been refined and applied to solvent extraction.

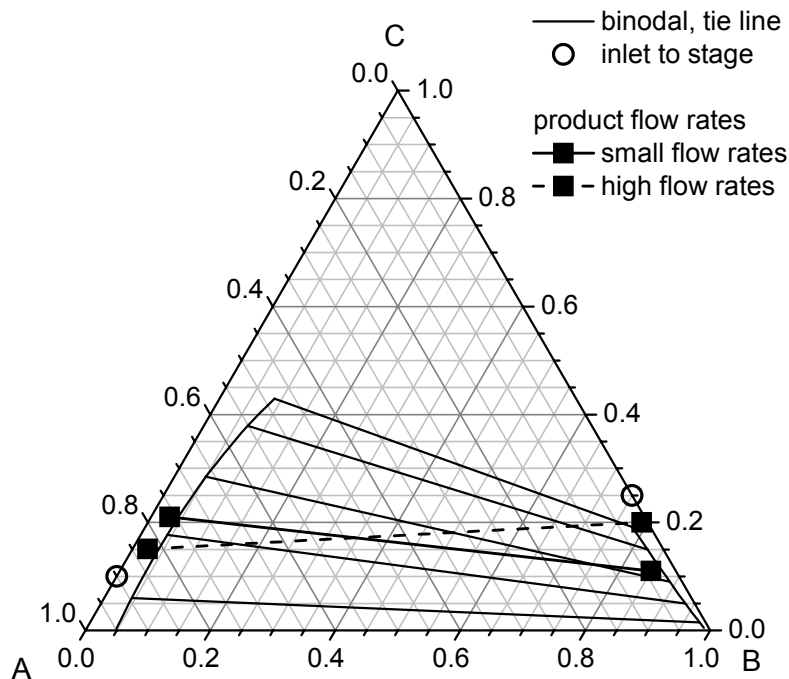


**Figure 1.** Snapshot of a distillation column simulated by molecular dynamics.

In order to make this method capable for liquid-liquid systems one has to be aware of the computational cost of the simulation presented in Fig. 1, which took about one week on a PC. Thus neither more particles, i.e. two liquid phases, nor more stages can be simulated with this method in reasonable simulation times. Therefore it is obvious that the method has to be parallelized. For that purpose the simulation cell has been cut into individual separation stages, where each stage can be simulated on an individual PC. By connecting the individual stages with their entering and leaving fluxes a separation column is depicted. The information that has to be exchanged between the stages, i.e. the PCs, doesn't have to include data regarding every individual molecule that left one stage but only overall data like the amount of substance, the composition or temperature of the flow rates are required. Additionally not after every simulation step the information has to be exchanged. It is sufficient to update the feed and product flows of every stage only after a few ten thousand steps. Thus the computational cost of the data exchange between the stages is negligible and the number of separation stages can be set to any desired value.

In the McCabe-Thiele plot on the right hand side of Fig. 1 one can see that the sieve trays of the column essentially behave as ideal separation stages, i.e. the products leaving one stage are in equilibrium. Due to the short length scales in the molecular simulation the residence time of the particles on one stage is too high, which means that equilibrium will be achieved. In order to simulate also the non-equilibrium character of separation stages on molecular level a dimensional analysis has been performed which provides the necessary residence time of the fluids in a molecular simulation that corresponds to a macroscopic separation stage.

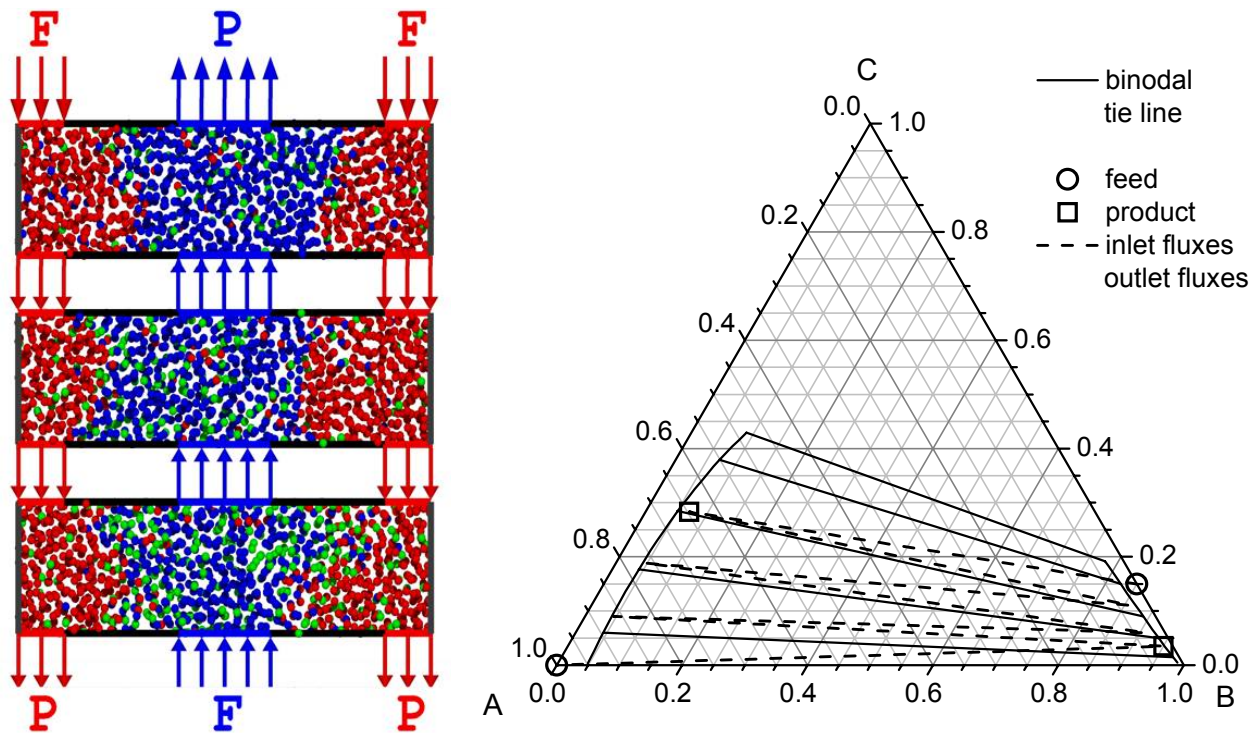
In the triangular diagram in Fig. 2 the compositions of the feed (open circles), the products in the case of high (solid line) and low residence times (dashed line) and the equilibrium data of a separation stage simulated on molecular level are shown. The equilibrium data were obtained in simulations where the feed and product flow rates were set to zero, i.e. for infinite residence times.



**Figure 2.** Compositions of streams leaving an extraction stage in the case of high (solid line) and low residence time (dashed line).

In both cases, short and long residence time, the A-rich product flow has a higher C concentration than the feed flow. Due to the finite residence time in both cases the products are not in equilibrium, i.e. their connecting line doesn't fall on a tie line. Fig. 2 also shows that increasing the flow rates (dashed line) leads to less C in the A-rich phase than in the case of low product flow rates (solid line), i.e. the product compositions are less equilibrated. Hence, with these molecular simulations it is possible to reproduce the influence of the residence time on the efficiency of a separation stage and the molecular simulation does not only depict adequately combined equilibrium stages like suggested by the McCabe-Thiele plot in Fig. 1.

In order to simulate an extraction column more than one separation stage has to be regarded. Therefore individual simulations as shown in Fig. 2 have to be connected, i.e. the outlet of one stage is the inlet of the consecutive stage and vice versa. In Fig. 3 a snapshot of such a simulation is presented. On the left hand side a schematic sketch of the column is shown, where the blue particles indicate component A, the red ones component B and green the transferred component C. The inlet and outlet streams are indicated by the arrows connecting the individual stages. On the right hand side the process is represented in the triangular diagram. The compositions of the feeds (F) are indicated by circles, the compositions of the products (P) by squares and the inlet and outlet fluxes connecting the individual stages by the dashed line.



**Figure 3.** Simulation of an extraction column on molecular level.

### Conclusion

The results in Figs. 1 and 3 demonstrate that a design of unit operations by molecular simulation is possible. To that end not all molecules in the column have to be regarded but only the relevant conditions have to be taken into account. This means that simulations that are performed in the vicinity of the interfacial region are sufficient to depict one separation stage. By connecting the inlet and outlet fluxes of the stages all relevant conditions are regarded that the particles pass in the column. But the simulations don't just behave like adequately connected equilibrium calculations. As can be seen in Fig. 3 the lines connecting the product compositions of one stage don't coincide with tie lines, i.e. the separation stages aren't ideal separation stages. They also include the non-equilibrium character of a stage, which can be either caused by multi-component effects of the mass transfer or by the finite residence time of the fluids on one stage. A dimensional analysis provides the necessary residence time of the fluids in the molecular simulation so that the mass transfer in the simulation corresponds to that of a macroscopic stage.

Currently we are comparing simulations with data from columns on pilot-plant scale. Also simulations with 20 and more stages are under way on a multi-CPU high-performance cluster.

### References

1. A. Pfennig, "Distillation Simulated on Molecular Level," *Mol. Sim.* **30**(6), 361-366 (2004).