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Direct Modeling of Unit Operations on Molecular Level

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Abstract

The behavior of a sieve-tray distillation column with three trays at total reflux has been simulated on molecular level until steady state was reached. Sieve trays were created by introducing partly permeable boundaries in the system. The heating at the bottom and the cooling at the top of the column were achieved by influencing the molecular velocities in the corresponding regions of the column. The results show that it is possible to mimic the behavior of distillation columns directly based on molecular simulations.

Keywords: molecular simulation, unit operation, distillation.

1. The Goal

The behavior of technical equipment is determined by the properties and interactions of the molecules that are involved in the process. Thus it is finally these molecular properties, which determine the technical equipment design in chemical-engineering equipment. It is generally regarded as impossible to bridge the difference in length and time scale between molecular description and technical equipment in a single step. Thus a common approach is to introduce several steps of model hierarchy in between, e.g. describing mass transfer in a single phase and at interfaces as well as describing single drops or bubbles, the behavior of which is then accounted for to describe the entire equipment.

Simultaneously it is known that the major effects in unit operations can be described by equilibrium and rate-based approaches, which again have their basis on molecular level. As a result, in depicting the behavior of technical equipment it appears sufficient to describe the path of the components involved through various steps of conditions. These conditions refer to pressure, temperature, concentrations and gradients of these properties as well as interfaces. Information on the behavior of the substances as a function of these conditions can be obtained from molecular simulations with some hundred or at most some thousand molecules, which are easily feasible today.

Thus the goal of this work is to develop a simulation tool which is on the one hand based on molecular simulations and which on the other is capable of performing simulations of entire unit operations. Here, as a first step, the feasibility of this approach is shown for a simple example.

2. Advantage of the molecular approach

If unit operations are simulated based on molecular behavior a big advantage is that fully predictive calculations will become possible in the future. Based on quantum-chemical methods it is already today possible to obtain information which allows to determine thermodynamic data e.g. via the COSMO approach by Klamt (1995) and co-

workers. Different groups today try to transfer similar methods to the development of models necessary for molecular simulations.

3. Simulation

As a first step a demonstrator has been realized based on the molecular-dynamics code MDMIXT of the CCP5 library of the SERC Daresbury Laboratory (CCP5, 2005). This code has been thoroughly redesigned and modified as to allow different compartments and boundaries between them to be accounted for in a simulation. The size of the basic compartments between which the different boundaries can be defined are the elementary cells of the simulation which contain 4 molecules each. The boundaries are defined in two dimensions while in the third dimension the molecules can move freely with periodic boundary conditions. In general all boundaries between the elementary cells are assumed to have no effect unless specific conditions are defined.

Thus the molecules are simulated as they move through the system based on solving the equations of motion, where the molecules are depicted as multi-centre Lennard-Jones particles. Typically a time step for integrating the equation of motion of 10^{-15} s to $3*10^{-15}$ s is used, depending on the strength of the interactions. At each time step it is checked whether a molecule has passed a specific boundary between the basic cells. If this is the case the conditions specified for the boundary are applied to the molecule.

The major boundaries accounted for are as follows:

impenetrable walls

The molecules are reflected from the impenetrable walls with respect to their center of mass.

partly penetrable walls

To mimic the behavior of sieve trays in a column, partly penetrable walls have been defined through which the molecules can only pass in one direction with a specified probability. This probability corresponds to the fraction of the open area of the sieve tray. It is realized by comparing the probability with a random number for each instance a molecule tries to pass the boundary. If the molecule does not pass the boundary it is reflected.

heating or cooling boundaries

Molecules that pass a heating or cooling boundary have their velocity changed by a certain amount which can be specified. Since molecular velocity directly corresponds to temperature this boundary acts as a heating or cooling boundary.

Also feed as well as removal boundaries have been introduced to be able to describe a distillation column with finite reflux ratio. These boundaries modifying the amount of substance in the system are implemented but have not been used in the simulations below, since here total reflux is assumed in the first simulations for simplicity. Different properties of a boundary can be specified simultaneously for each individual boundary present in the system. Thus e.g. an impenetrable wall at the bottom of the column can simultaneously be a heating boundary. This allows a wide variety of behavior and geometries to be depicted.

The simulation is based on an NVE ensemble, where the number of particles, the volume and the energy of the system are specified. To adjust the starting temperature the velocities of the molecules are scaled to the desired temperature during initial simulation steps. The potential function is evaluated based on periodic boundary conditions in all three spatial directions. A cut-off radius of half the box length of 0.976 nm has been used.

Evaluation of the simulation results has been integrated into the program. As a function of column height the profiles of partial and overall density as well as temperature are determined. Additionally the compositions on the trays are evaluated by selecting appropriate compartments above and below the trays, which can be unequivocally attributed to the liquid or the vapor phase respectively. Averaging of the results occurs over a specified number of steps, e.g. 40000 in the simulation presented below. This averaging is realized as pseudo-rolling average. To avoid storing 40000 individual values of the property to be averaged e.g. only the last up to 1000 values are stored individually. For time steps before this only the averages over the 1000 steps are stored, e.g. a total of 40 such averaged values, thus information dating back over roughly 40000 steps is collected. The pseudo-rolling average is then obtained from the last up to 1000 individual values, the 39 averages over 1000 steps before that, and the appropriate fraction of the average over 1000 steps before these 39 values. Thus the information on the current simulation step is accounted for individually, whereas the information on the steps dating back 40000 steps is taken into account only on an averaged basis.

The boundaries described above have been used to describe a distillation column with three trays as shown in Fig. 1. A heating region was added at the bottom and a cooling area at the top by influencing the molecular velocities, which represent local temperature. The trays were represented by partly penetrable walls, which mimic the behavior of sieve trays.

In this column the molecules are moving from bottom to top induced by the heating at the bottom and the partly penetrable boundaries of the trays. To ensure a molecular motion of the liquid in the opposite direction, gravitation was included on a level where the transport and equilibrium properties of the mixture are not significantly affected. This leads to a counter flow of liquid, which closely mimics the behavior in a technical equipment with cross flow on each tray.

Nevertheless gravitation has to be set to a value much higher than on the earth surface, since the potential of gravitation introduced takes relatively small values due to the small height of only 15 nm of the entire simulated system. Here a value of 2.8×10^{13} m/s^2 was chosen. Only by choosing such a high value the gravitational potential has any effect as compared to the potential of molecular interaction.

In separate simulations the influence of gravitation as well as of the size of the system have been investigated. The corresponding simulations were performed for a system of pure methane, which was set up in a way that a two-phase system corresponding to a vapor-liquid equilibrium resulted. The vapor pressure has been evaluated in these simulations. The results show that the value of gravity as well as the system size in y-direction have a significant influence on the vapor pressure. The values chosen in the simulation shown below have a certain effect on the results which is accepted for this first simulations of the demonstrator, especially since the simulations with pure methane show that already slightly reduced values of gravity lead to strongly improved results. Both of these parameters also have a strong influence on the simulation time required to achieve steady-state results. Since the initial starting configuration chosen representing homogeneous distribution of the molecules of all species throughout the entire system is the most inefficient choice it is expected that improving this starting configuration can significantly speed up the simulation. Thus current activities are directed at choosing and manipulating the composition along the apparatus in a systematic way with the goal to reach steady state significantly faster.

To visualize the results of the simulation, output files were generated, which can be used by the ray-tracing tool POV-Ray (2005). With POV-Ray realistic pictures of the molecules in the distillation column can be generated and can be linked together to

obtain digital movies with appropriate tools. This way it is also possible to generate movies for teaching purposes visualizing the molecular behavior at different conditions also including interfaces. Such movies, which are suitable for visualizing the different states of matter as well as the molecular mobility e.g. in lectures on physical chemistry or thermodynamics, can be supplied by the authors upon request. Additionally an efficient output to screen is generated which can also be switched off and which can be updated e.g. every 1000 time steps. This output is very helpful for setting up the appropriate boundaries, since their effect can directly be seen. Also this output can be stored as individual frames which then can be combined to result in a movie. Thirdly a file format is generated which allows viewing the molecular motion inside a CAVE in 3D-projection. This application has been developed in collaboration with the virtual reality group of the Center for Computing & Communication of RWTH Aachen University.

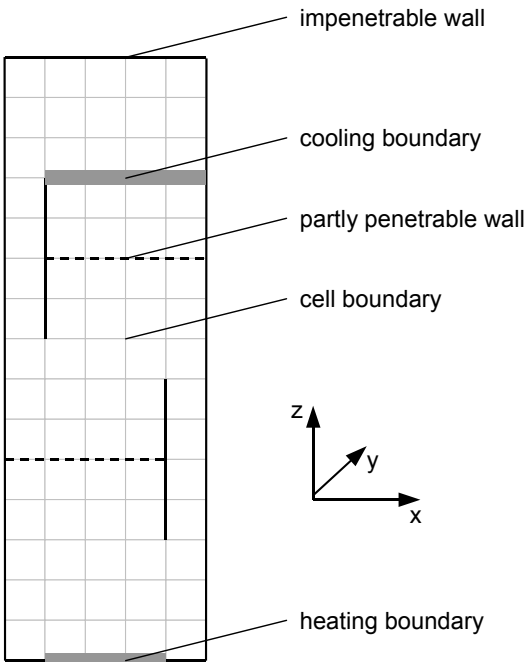

Fig. 1: Representation of a distillation column on molecular level

4. Results

Based on this configuration a simulation was performed for the column with three trays with a permeability of 60 % as shown in Fig. 1. The size of an elementary cell was 0.976 nm, the size of the system in y-direction was two elementary cells. A mixture of methane + ethane was simulated with as little as 600 molecules in the column. This is roughly the minimum required to obtain results that are only slightly influenced by the finiteness of the system. The starting condition was a uniform distribution of molecules in the entire column. Due to this starting configuration, which can be regarded as worst case, steady state was reached after simulation of 3.5 ns. The simulations were

performed on a laptop computer with pentium-III processor and 1.13 GHz. The simulation took roughly 9 days.

The result after reaching steady state is shown in Fig. 2. The top left diagram depicts the final state of the column together with some numeric output. To the top right the McCabe-Thiele diagram is plotted where the equilibrium line was generated from data taken from Knapp et al. (1982). It can be seen that the simulations generate sieve trays, which approximately correspond to theoretical stages. The equilibrium line is intersected because the concentrations are fluctuating properties in the simulation. The reason for reaching ideal equilibrium behavior with the trays is the small size of the system, where diffusion on each tray is much faster than the convective flow. Since in reality sieve trays have an efficiency considerably less than unity, future work will be directed at increasing the flow rates to generate states on the trays which are farther away from equilibrium. This will simultaneously lead to faster simulations, since higher flow rates directly correspond to shorter times for reaching steady state.

In the lower part of Fig. 2 temperature and density profiles are shown along the column. Temperature decreases from bottom to top of the column as expected. Also the partial density of methane increases in the same direction while that of ethane decreases. It can be seen that relatively strong statistical fluctuations occur in the vapor phase while the values for the liquid phase are much more stable on all trays. The reason for this is the higher number of molecules over which the averaging is performed in the liquid due to its higher density.

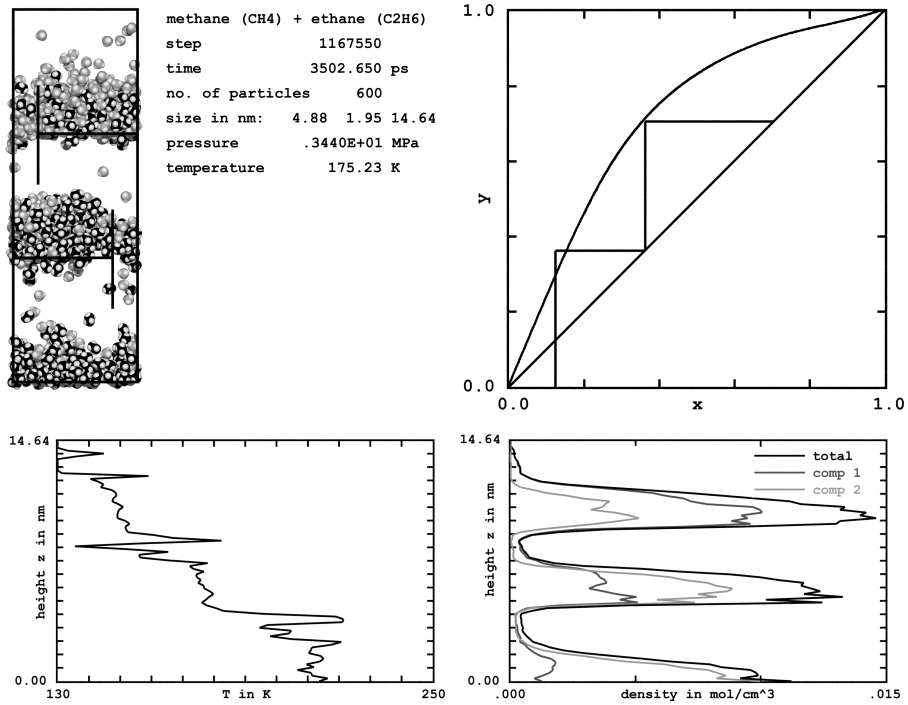

Fig. 2: Result of a direct molecular simulation of a distillation column at total reflux.

5. Conclusions

Overall the results of this simulation show that a distillation column can be simulated in principle with as few as 1000 molecules. The agreement with e.g. experimental equilibrium information is excellent.

This approach will now be extended to allow simulation also of other unit operations, e.g. solvent extraction and to take the rate-determining steps into account more appropriately. By increasing the flow rates the computational effort will be decreased, since steady state can be reached faster. Simultaneously the non-equilibrium character of the processes taking place inside technical equipment can be described more realistically. Additionally the results of the first simulation steps can be used to adjust the composition profile along the column. This will also lead to a much faster approach to steady state.

References

CCP5, 2005, http://www.ccp5.ac.uk/, programm library at: http://www.ccp5.ac.uk/librar.shtml, November 14, 2005

A. Klamt, 1995, Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena, J. Phys. Chem. 99, 2224-2235

H. Knapp, R. Döring, L. Oellrich, U. Plöcker, J. M. Prausnitz, 1982, Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances. Dechema Chemistry Data Series, Vol. VI, Dechema, Frankfurt

POV-Ray, 2005, http://www.povray.org/, November 14, 2005