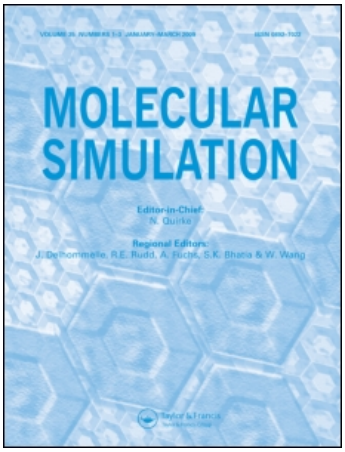


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# Distillation Simulated on Molecular Level

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# Distillation Simulated on Molecular Level

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**Different types of boundaries are introduced in molecular simulations to allow representation of a variety of walls. By suitable choice and combination of impenetrable walls, partly penetrable walls as well as heating and cooling boundaries, a distillation column was generated suitable for molecular simulations. With 640 molecules of a mixture of methane and ethane such a molecular distillation with three theoretical stages was run under total reflux. The introduction of gravity induced the cross-flow pattern across the sieve-trays. The result shows that molecular distillation behaves very much like distillation on technical scale.**

*Keywords*: Distillation column; Molecular stimulations; Moore's law; Impenetrable walls; Scale-up



## INTRODUCTION

It is generally accepted that it is out of the scope of molecular simulation to simulate technical equipment directly. Even on the fastest computers available with the most advanced algorithms at most some million molecules can be modelled for minute fractions of a second. Technical equipment, on the contrary, consists of the order of some $10^{23}$ molecules and reaching steady state may take several hours. The task of bridging this scale gap in time and space is generally approached by performing computer simulations on the molecular scale to determine individual properties of the mixtures of interest in a first step. Then models describing the mixture behavior are fitted to the data obtained from the computer experiment. With these models the description of the technical equipment is finally achieved [1,2].

At the same time, the computer power is continually increasing exponentially with respect to memory as well as computer speed. According to Moore's Law, it is generally assumed that both double roughly every 18 months. Simultaneously, the size of technical equipment is decreasing with the continuous development of micro-systems technology. Chemical plants can be built today with a content of substance of only a few millilitres and residence times of few seconds [3–5].

Thus the question arises of if the gap in time and spatial scale between molecular behavior and technical application cannot be bridged directly.

The fact that molecular simulation of phase equilibrium can be achieved with only some hundred molecules and that equilibration takes only a fraction of a nanosecond in such small systems can be regarded as a positive hint that this might indeed be possible. Also it is good engineering practice to scale-up equipment by quite significant factors. One way of scaling up can be understood, if it is recalled that it is possible to group the independent variables determining the behavior of a system as well as those which determine a process in dimensionless quantities like the Reynolds or the Sherwood number. If these dimensionless quantities can be kept constant in scaling up a process, the behavior of the scaled-up process can, in principle, be predicted quantitatively from an experiment on small scale. These arguments can, of course, be applied for scaling down a process as well.

For the scaling of thermal separation processes like distillation or extraction, an even simpler approach is generally followed: the concept of a theoretical stage is introduced. In a theoretical stage, equilibrium is

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assumed to be reached. Then the equipment, e.g. a distillation column, consists of several theoretical stages which are connected via the appropriate fluxes. Here the scaling concept is different from that via dimensionless quantities. In this picture, separation can be achieved by the mixture flowing through the equipment experiencing a specific succession of equilibria. If the order of these equilibria remains the same, scale-up can be performed quantitatively. This approach can directly be used for a scale-down to molecular level. If only the molecules pass through regions where they experience the appropriate equilibria in the correct order, the molecular system will behave like the technical process.

Of course, both approaches have their limitations. In scaling up with the help of dimensionless numbers the substances used in the small-scale process generally have to differ from those of the large-scale process in order to keep all dimensionless quantities constant simultaneously. This is, of course, a strong limitation for the design of thermal separation processes, since the equilibrium behavior is strongly influenced by the specific properties of the substances used. The scale-up based on theoretical stages describes the equilibria correctly but actually implies that the basic mass-transfer geometries behave comparably. Mass-transfer geometries are, for example bubbles in distillation or drops in solvent extraction. This implies that scaling becomes difficult, if the size of the equipment relative to that of the mass-transfer geometries decreases below a certain value. It is generally accepted that column diameters below around 50 mm are at least difficult to handle concerning the scale-up of experimental results.

Nevertheless, this work attempted to scale down a technical apparatus to molecular level. A distillation column was chosen, since experience with simulation of vapor–liquid equilibria is available and it appeared possible to generate the fluxes necessary between the theoretical stages with relatively simple means.

## SIMULATION DETAILS

In the simulations the conditions which are experienced by the molecules have to mimic those in a technical distillation column. These conditions are pressure, temperature, local concentrations, the gradients of these properties and of course, the interfaces present in the equipment. Thus a sequence of equilibrium stages had to be constructed between which the molecules are transferred via the appropriate fluxes. This made the introduction of "walls" in system necessary which divide the simulated region into different stages. These walls should display different behavior in principle to allow exchange between the stages. Also regions had to be defined where heat can be introduced into or withdrawn from the equipment locally to allow us to mimic reboiler and condensor. To enable the introduction of walls with different properties the system was divided into compartments where these compartments were chosen to be the basic cells which are usually introduced upon generating the starting configuration in a molecular system where each cell contains four molecules. During the simulations it is then checked at every time step if a border between two cells is crossed by a particle. If this is the case, it is looked up whether some specific properties are associated with the boundary between these individual cells, and if this is the case, appropriate measures are taken. The different cell boundaries considered are described in the following.

*Impenetrable walls:* To allow division of the simulated region into basic compartments a cell boundary can be defined through which no mass transfer can take place. This is achieved by reflecting the molecules from this boundary with respect to their centre of mass. It should be noted that the impenetrable boundary, like all other boundaries, does only act on the motion of the particles and only takes the centre of mass into account. The molecular interactions are not influenced by the properties of the boundaries.

*Partly penetrable walls:* To be able to simply generate a geometry resembling a sieve tray, walls were introduced that are partly penetrable in one direction. Thus for each particle crossing this boundary the direction of transfer is checked. In one direction, the particle is reflected like for impenetrable walls. In the other direction, a random number is generated and compared to the penetration probability. Only if the random number exceeds the penetration probability is the molecule reflected, otherwise no action takes place.

*Heating or cooling boundaries:* If a particle crosses a heating or cooling boundary its velocity is increased or decreased by a specified factor. This allows heating or cooling depending on the factor. If the velocity is increased, heat is introduced while heat is withdrawn if the velocity is reduced. The energy change is recorded and accumulated in a corresponding variable giving the local heat flux.

*Product-withdrawal boundary:* Whenever a molecule passes a product-withdrawal boundary, it is removed from the system with a specified probability which is again realized in comparison with a random number. The withdrawal is again recorded in a corresponding variable allowing us to determine product composition. The product withdrawal through several product-withdrawal boundaries

can be combined into one product stream. Several product streams can be defined.

*Feed boundary:* This type of boundary is probably the most disputable. If a particle crosses the feed boundary a new particle is inserted in the adjacent cell with a specified probability. The component is chosen according to a defined composition. Both the choices as well as the exact new position and the initial particle velocity are realized via random numbers, where the velocity is scaled with the temperature. Direct insertion of a new particle would result in the new particle being located unphysically close to some other particle already present in the system in many cases. Then the algorithm for solving the equations of motion would break down. Thus the particle is first introduced as a ghost particle which interacts with all other particles with a small fraction of its interaction energy, this fraction being chosen as $10^{-10}$ initially. This fraction is then doubled every time step until after roughly 30 time steps the particle is present with its full interaction energy.

All other boundaries do not show any effect in the simulation. The simulated region has periodic boundaries otherwise. It should also be noted that different properties can be attributed simultaneously to a cell boundary thus allowing a wide variety of properties. One problem with these boundaries is that molecules especially in condensed phases more or less vibrate in the cage formed by the nearest neighbors. This would result in a bias for those boundaries, which act on the particles with a specified probability. In order to reduce this bias the probability is only checked for the first intersection of the particle trajectory with the corresponding boundary. This is realized by setting a flag indicating that the intersection took place and may not be checked a second time in the course of additional vibrant molecular moves. This flag is then reset explicitly when another type of boundary—the corresponding reset boundary—is crossed.

With these boundaries a distillation column can be built as depicted in Fig. 1 with three stages in this example. Here some additional features need to be explained. Of course, in a distillation column the head of the column is colder than its bottom. Thus the periodic boundary conditions would lead to the cold head being in direct contact with the hot bottom leading to a short circuit for the heat. Since this is not desired an additional empty insulating layer separated by impenetrable walls is introduced. Since then the molecules in the liquid at the bottom are in direct contact with an impenetrable wall at which there are no other molecules on the other side, their structure strongly deviates from that of the unperturbed liquid and appears solid like. To avoid this, an additional heat-bath layer is introduced which contains a certain number of molecules at some intermediate

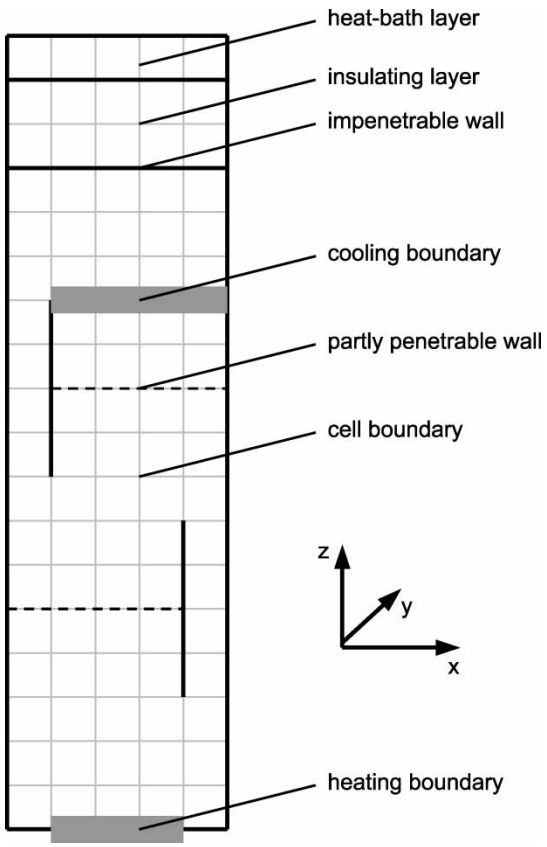


FIGURE 1 Structure of boundaries for simulation of sieve-tray distillation column.

density, which introduce some momentum from below, breaking this structure. Here this layer is introduced at the top of the column merely for optical reasons, since due to the periodic boundary conditions its effect is identical to being introduced directly below the bottom.

In order to facilitate evaluation of the results, some additional book-keeping possibilities were introduced which allow us e.g. to monitor the composition in some cells to be able to construct a McCabe–Thiele diagram. Also profiles of temperature, overall as well as partial densities and mole fractions are generated. The averaging is realized with rolling averages of a large number of simulation steps, 40,000 in the case presented.

It should be noted that the computational effort for taking these boundaries into account can be handled, since most of the computer time is spent for evaluating the intermolecular forces. The time for evaluating if a particle has crossed a boundary scales only proportional to the number of particles which is generally less than that for evaluating the forces which generally scales between linear and quadratic.

By the geometry shown in Fig. 1 the upward flow can easily be realized since the liquid at the bottom is evaporated and the vapor then moves upward through the column until the head of the column is reached. There the vapor is condensed by the cooling

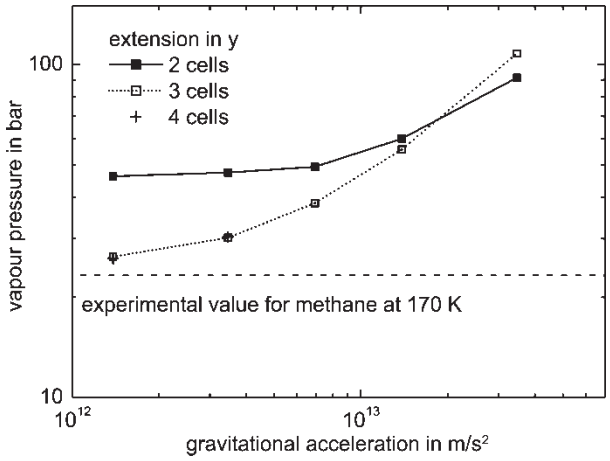


FIGURE 2 Vapor pressure of methane as function of gravity and system depth.

boundaries. But how then can the downward flow be realized? This is achieved by introducing gravitation. The gravitational acceleration is adjusted not to influence the equilibrium but large enough to supply enough driving force to effectively induce a flow across the trays and through the downcomers of the column. To find an acceptable choice, various simulations have been performed for methane where the virial pressures of a two-phase system have been evaluated in a closed box generated with the same computer code. The results are shown in Fig. 2. It can be clearly seen that the gravitational acceleration of $10^{12}\,m/s^2$ would lead to unbiased results. At the same time, it is obvious that an extension in $y$-direction of three cells corresponding to 2.6 nm in the simulation would be sufficient to depict a quasi infinitely extended system. With this introduction of gravity it turned out that it is possible to create the appropriate counter-current flow characteristic for distillation where the trays are actually passed in a cross-flow fashion.

## RESULTS AND DISCUSSION

The simulations were performed based on an NVE ensemble with mdmixt routines from the CCP5 library [6]. These routines have been modified severely to include the book-keeping of the particles crossing boundaries as well as including a neighbor list to improve the speed of the program for simulations with many particles. Additionally, output is written to an intermediate file with information which is then used to generate input for raytracing with POV-Ray [7] to obtain virtual 3D images. These images are then combined to movies with Adobe Premiere [8]. This visualization turned out to be necessary to efficiently improve the design of the different boundaries, since the behavior of the molecules can be best evaluated if their motion can be directly observed.

A first distillation simulation was performed with a laptop with AMD Athlon processor, 1.15 GHz and took slightly more than a week. Starting point of the simulation was a column which was completely filled with an equimolar mixture of methane and ethane with a density in the two-phase region which can be regarded essentially as the worst possible starting point. Methane was depicted as a 5-centre and ethane as an 8-centre Lennard–Jones molecule where the molecular parameters are those supplied in the example files of the CCP5 routines. From the starting point, phase separation on the trays took place, the counter-current flow started and after roughly 3 ns, a stable concentration profile had been reached. The final result after 3.5 ns is shown in Fig. 3. It can be clearly seen that the behavior is essentially that expected from the concept of theoretical stages. Equilibrium is reached on all trays. Since the compositions on the trays are fluctuating, it will happen that the compositions lie slightly above the equilibrium curve in the McCabe–Thiele diagram. This can also be seen in Fig. 3. Thus, it has been shown that the behavior of molecular distillation closely resembles that of a technical column.

Of course, time to reach steady state can be strongly reduced by choosing a better starting point. Most of the time for reaching steady state was spent for reaching the final composition profile like that in technical equipment. Reason for this is that exchange between the phases and thus, equilibration on a tray is much faster than convective exchange between the trays. To improve the starting point it is, for example, possible to start with preliminary vapor–liquid equilibrium simulations which take only a few hours. From these equilibrium data a first estimate of the concentration profiles can be generated by ordinary engineering approaches. If this concentration profile is initialized in the column at the start, reaching steady state will be greatly enhanced. This discussion also shows that diffusion on the trays is much faster than convection due to the small size of the equipment. As a result, concentration gradients on the trays may be minimized. Also effects that reduce tray efficiency in technical equipment can not occur, e.g. the formation of bubbles that rise past the liquid too fast to leave enough time for completion of mass transfer. Thus in the molecular distillation shown, the major mass transfer through the liquid on the tray is diffusive in nature and tray efficiency approaches 100%.

Further work will now focus on studying the details of distillation behavior. For example, it is known from experiments that aqueous systems behave very differently from organic systems especially for water-rich mixtures. One reason is the steepness of the equilibrium curve in

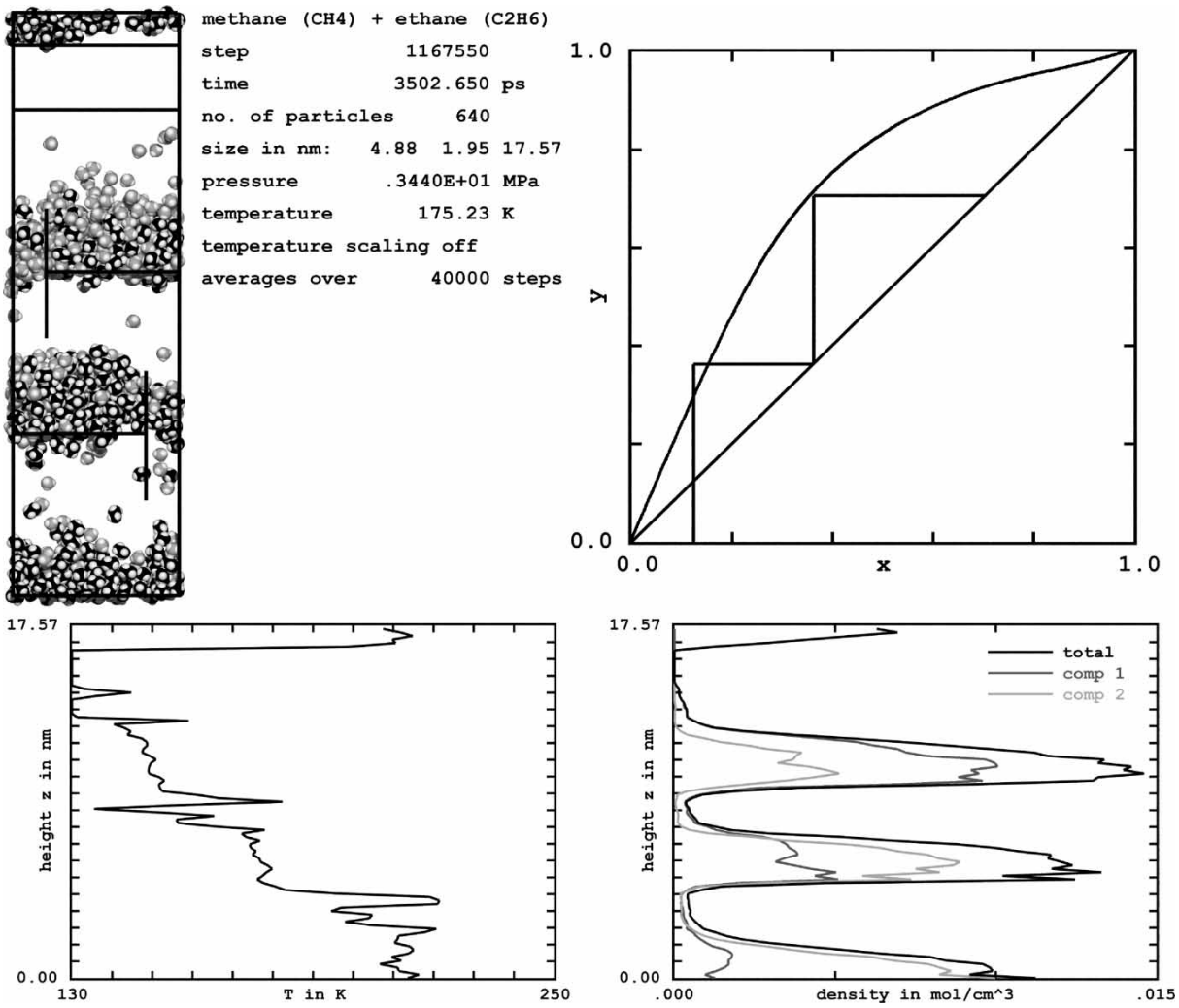


FIGURE 3 Molecular distillation column under total reflux as shown in the output POV-Ray image. Besides the column and some numerical data, a McCabe–Thiele diagram as well as temperature and density profiles are shown. Data for the equilibrium are taken from Ref. [9].



the McCabe–Thiele diagram. In the literature other reasons are discussed, one being the nature of the interface between liquid and vapor under mass transfer conditions. Since measurements of the behavior of the interface are today impossible in a distillation column, computer simulations on molecular level will be performed to evaluate the interfacial properties. These results will supplement a corresponding ongoing project with pilot-plant scale experiments.

## CONCLUSION

In this work it has been shown that distillation on molecular level can be simulated if appropriate boundaries are introduced in the system.

From the discussion of the boundaries introduced it is obvious that simulations are not limited to total reflux. Since the introduction of a feed as well as the withdrawal of product streams is possible, realization of finite reflux ratios is possible as well. It should also be noted that in principle, other thermal separation processes can be modeled as well. In most cases, the density difference between the phases is not as favorable as in distillation to induce counter-current flow.

Nevertheless one has to bear in mind that computer power will steadily increase further in the future. If it is assumed that the speed will increase continually as it has done at least during the last 30 years, a simulation like that shown in Fig. 3 will take less than a minute on an ordinary laptop in roughly 20 years and is thus in the scope of actual personal experience of many researchers of today. If more powerful computers are considered this situation will be reached significantly earlier. Thus it can be envisaged that design of distillation columns will be done by simulation on molecular level in the not too distant future. This development will be supported

by today's efforts to build better general molecular models for the description of real substances.

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