Evaluation of a Molecular-Dynamic Based Method for the Direct Simulation of a Distillation Column on Atomistic Scale

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Aachen, March 2015
To my grandmother (in memoriam), my mother and sister
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Abstract

Mass and energy balances, as well system-specific empirical and semi-empirical correlations, usually build the backbone of any established software used by chemical engineers in the simulation of unit operations. Such approaches, though relying on a robust methodology, are sometimes hindered by their own strong dependence on the availability of system-specific experimental information. An alternative to overcome such drawbacks is offered for instance by MDSTAGE, a molecular-dynamic-based approach for the description of unit operations in atomistic scale, as proposed by Pfennig (2004) and Babic (2011). In this approach, a finite number of molecules is simulated in atomistic scale under constraints resembling the macroscopic state of the investigated unit operation. Using specific molecular potentials in the description of the species involved in the investigation and mimicking macroscopic conditions directly in the atomistic scale, thermodynamic and transport properties of the system are eventually obtained in MDSTAGE, from the system itself, by means of its dynamical evolution in time. In the present work, the application of MDSTAGE to the simulation of thermal separation processes will be investigated. MDSTAGE is evaluated as a tool for the description of the stationary operation of a NORMAG distillation column. Experimental data obtained with the investigated equipment is used to validate the predicted results of the simulation tool.
Kurzfassung

1 Introduction

Over the past ten decades, chemical engineering has evolved from a unit operation-rooted discipline to an engineering field closely bounded to pure and natural sciences (Grossmann and Westerberg, 2000). Along the last forty years, molecular simulations have become a valuable tool for chemical engineers, supporting the investigation of theoretical and practical problems (Maginn, 2009) and within the next twenty years are set to achieve the same level of importance that computational fluid dynamics has today in industry (Todd, 2010). Ventures like the Industrial Fluid Properties Simulation Challenge (IFPSC) exemplify the efforts towards improvement of more reliable theories, modelling methods, intermolecular force fields and simulation algorithms in order to establish the atomistic approach as a standard industrial tool for modelling and predictive purposes (Maginn, 2010). Within this frame of increasing importance of atomistic investigations to chemical engineering, this work examines the plausibility of the direct investigation of the stationary operation of a distillation column on atomistic scale in terms of molecular methodology.

Traditionally in chemical engineering, the description of unit operations is subject to a classical macroscopic approach dependent on the availability of equilibrium and transport data of the investigated system. Such methods are widely established in the current industrial practice and build the foundations of standard simulation packages as in case of Aspen Plus®.

However, if on one hand these methods accurately describe the operation of the investigated equipment, their strong reliance on empirical and semi-empirical information regularly hinders the possibility of the immediate use of their benefits, when investigating non-ordinary chemical systems with sparse information about their physical and chemical properties. Determination and mathematical modelling of equilibrium and transport properties are fields of investigation still demanding huge efforts in order to cope with industry demands (Bardow, 2004; Kontogeorgis and Folas, 2010) and consume, solely in their calculations and interpolations, roughly 75 percent of the written code in algorithms of standard simulation tools (Fermeglia et al., 2003).
Atomistic simulations, on the other hand, have proven their concrete potential as an alternative methodology in the determination and prediction of physical and chemical quantities, where equilibrium and transports properties are directly derived from calculations based on the molecular interactions of the involved species. Allowing the description of a huge variety of substances and mixtures, this approach has offered a straightforward path in the study of mass-transfer rates, bulk and interface properties of phenomena described on molecular levels. Up to now, it has been shown that, with the aid of accurate molecular models and an assessable number of molecules, this approach is able to produce information of high quality comparable even to empirical databases (Vrabec, 2006; Guevara-Carrion et al., 2008; Kulschewiski and Pleiss, 2013).

A further field of application of atomistic methodologies is found in so-called multi-scale modelling, where the predictive power of the atomistic approach is refined by coupling of the calculations with other investigative approaches (Nielsen et al., 2010; Lei and Leng, 2012). In spite of the continued efforts to bridge atomistic approaches to higher scales, a direct application of its features in the description of continuum phenomena, as in the case of unit operations, has long been regarded as an unviable path due to the high computational costs it would demand and the evident discrepancy in the time and length scales characterizing both scales. Pfennig (2004) however described the operation of a distillation column of atomistic proportions with 640 molecules which pioneeringly proved, with exceptional results, that the direct description of macroscopic phenomena, within an atomistic approach, was in fact possible. By mimicking the operational condition of the equipment on an atomistic scale, a three-staged distillation column was simulated in terms of a molecular dynamical approach, producing excellent agreement between the generated results and the available experimental equilibrium data for the investigated system. Later, Babic (2011) proposed an alternative generic methodology for a stagewise investigation of unit operations on atomistic scale also in terms of a molecular-dynamics based algorithm, which resolved some numerical constraints and extended the application possibilities of this approach. MDSTAGE, the extended approach established in his work, eventually allowed the description of an arbitrary number of fluid separation processes and operational conditions on the molecular scale.
In this work, the predictive potential of MDSTAGE is investigated by examination of its suitability in the reproduction of empirical data obtained in the operation of a real distillation column. For this purpose, a NORMAG distillation column has been assembled and operated. Empirical information describing the stationary operation of the equipment has been gathered and establishes the reference data set used in the evaluation of the results predicted by MDSTAGE in the process simulation.

In the following chapters, the fundamentals, development and results accomplished in this work are reported. Initially, besides a summary of the current state of the art regarding the treated subject, chapter 2 provides an overview of the fundamental concepts building the scope of the work. Chapter 3 focuses on the description of the simulation tool as much as on the approach and methodology used in simulations of the distillation column in atomistic scale. A description of the equipment used and procedures applied in the acquisition of the experimental data are outlined in chapter 4. In chapter 5, the results achieved in this work are summarized, evaluated and discussed.
2. State of the art

The purpose of this work is the evaluation of a simulation method for the direct description of a distillation column on a molecular scale. In order to better understand the resemblances between the scale-bridging approach used here and standard multiscale methods, this chapter summarizes the background of the current state of the art and the theoretical concepts behind their methodological formulations. First, a review on the hierarchical frame of approaches for modelling of phenomena is outlined. After locating the evaluated method within this hierarchical frame, a survey of its fundamentals and ordinary applications is carried out. In the subsequent section, a review of available approaches for molecular simulation of unit operations is presented. In the last part of the chapter, the main concepts of the simulated equipment are briefly reviewed.

2.1 Characteristic scales of modelling

Pragmatically, in the mathematical modelling of a phenomenon, a hierarchy of time and length determine the approach through which it should be dealt with. Figure 1 presents five levels of description proposed by Gubbins (2010) as methodological approaches recurrently found in literature: the electronic, semi-empirical, atomistic, mesoscale and continuum scales.

![Figure 2.1: Hierarchical levels for phenomena modelling based on their temporal and length outreach (Gubbins, 2010).](image-url)
In the electronic level, the most rigorous one, no input of experimental data is required, i.e. the knowledge of the atomic species involved in the phenomenon suffices (Jensen, 1999; Cramer, 2002). This method is usually applied whenever the rearrangement of electrons and/or other fundamental particles lie in the focus of the study and provides results with accuracy in the order of 0.1-1 kcal/mol in energy (Sholl and Steckel, 2009). One level higher, in the semi-empirical approach, only valence electrons are taken into account. Compared to the electronic level, the description of larger systems as biomolecules and nanostructured materials is already possible here (Gubbins, 2010).

The atomistic approach allows the simulation of systems comprising thousands or millions of atoms over time intervals ranging from one to one hundred nanoseconds. On this level, electronic detailing is usually neglected. Monte Carlo (MC) and Molecular dynamic (MD) simulations are the best known examples of this approach (Allen and Tildesley, 1987; Frenkel and Smith, 2002). Practical use of these methods is found in the simulation of phase transitions, phase equilibrium, prediction of phase properties and transport phenomena.

In the mesoscale level, hindrances due to the molecular size and time scales are surmounted by a coarse-grained approach. Characteristic in this approach are the clustering of groups of atoms in the description of molecules and the usual representation of the system by means of fields instead of particles (Gubbins, 2010). A drawback of the simplifications of the coarse-grained method is the loss of detailing and calculation rigor, what justifies its use as a qualitative tool in the description and evaluation of phenomena.

Finally, in the continuum level, physical properties are treated as field variables, i.e. holding specific and well-defined values at any position of the investigated system. This approach is based on macroscopic conservation laws and currently builds, in chemical engineering, the base of almost all available process simulation software. Conservation equations for diffusion (Fick’s law), fluid flow (Newton’s law) and energy (Fourrier’s law) are, together with kinetic and thermodynamic relations, the fundamental equations solved in this approach (Bird et al., 2007). In spite of that, one
of its major limitations is the explicit and extensive dependence on phenomenological coefficients which, in general, have to be obtained either through empirical or semi-empirical methodologies.

In a historical retrospect, engineering sciences exhibit a traditional attempt to couple those aforementioned scales. Depending on the applied strategy, the so-called multiscale approaches may be classified as serial or concurrent methods. Serial methods, also known as many-scale methods, use information from calculations at smaller scales as input for lower resolution (larger scale) calculations; such is the case when constructing potential force fields from quantum information or determining kinetic rates using data from molecular dynamics (Abraham et al., 1998; Paschek and Krishna, 2001; Tabacchi et al., 2002). On the other hand, the concurrent, or hybrid, methodologies directly combine and simulate different levels of description within a single calculation (Hu and Yang, 2008; Krevekidis and Samaey, 2009, Tozzini, 2010).

Regarding the extension of its results, the simulating approach used in this work resembles a hybrid methodology. However, as explained in upcoming sections of this chapter, instead of splitting and describing a system into domains with different scales, the evaluated method here employs the direct emulation of larger scales into smaller ones. Before explaining the details and specificities of the applied method, a concise overview of the core definitions and current applications of molecular dynamics as a chemical-engineering tool are summarized in the next section. It is worth noting that an extensive description of the fundamentals of molecular dynamics is not the intent of the following section; additional information regarding definitions, methods, and specific applications is to be found in standard literature on this theme (Allen and Tildesley, 1987; Frenkel and Smith, 2002; Rapaport, 2004)

### 2.2 Molecular dynamics as a chemical-engineering tool

In classic molecular dynamics, bulk properties of an infinite medium are obtained as time averages of a virtual ensemble composed of a finite number of particles fenced in a virtual simulation space and subject to a set of predefined constraints. The dynamic evolution of such ensembles is fully described by its Hamilton function, $H$, a
The mathematical expression of the whole energy of the system which is written in terms of the momentum, \( \vec{p}_i \), and spatial coordinates, \( \vec{q}_i \), of its particles, and expressed as the summation of the total kinetic and potential energies over all its particles:

\[
H = E_{\text{kin}}(\vec{p}_1, \ldots, \vec{p}_N) + U(\vec{q}_1, \ldots, \vec{q}_N) = H(\vec{p}_1, \ldots, \vec{p}_N, \vec{q}_1, \ldots, \vec{q}_N)
\] (2.1)

The description of the system by means of a classical mechanical approach (i.e. where the movement of single particles is described by the solution of their Newtonian equations of motion) inherits the assumption that quantum effects are negligible. In other words, that the mean intermolecular distance is larger than the thermal de Broglie wavelength of the system:

\[
\left( \frac{V}{N} \right)^{1/3} \gg \Lambda = \frac{h}{\sqrt[3]{3mk_BT}}
\] (2.2)

In equation 2.2, \( V \) stands for the volume of the system, \( N \) for the number of molecules, \( \Lambda \) for the thermal de Broglie wavelength of the system, \( h \) for the Planck constant, \( m \) for the mass of a molecule, \( k_B \) for the Boltzmann constant and \( T \) for the temperature of the system.

The resultant force, \( \vec{F}_i \), acting on a particle, \( i \), described in terms of the Hamiltonian of the system, the mass and acceleration of the element \( i \) can also be expressed in terms of a summation of the negative derivatives of a field potential acting between element \( i \) and its neighbor particles:

\[
\vec{F}_i = -\nabla u_i = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\partial u_{ij}}{\partial r_{ij}}
\] (2.3)

The choice of an intermolecular potential depends on the approach used in the modeling of the intermolecular interactions. A detailed report of the currently available potential functions and their specificities has been summarized by Guevara-Carrion et al. (2011). The application of equation 2.3 to an \( N \)-body system leads to the mathematical core of molecular dynamical algorithms: a \( 3N \) second-order system of
coupled differential equations which, due to its restricted possibilities for analytic solution, demands a numerical approach in order to be solved.


Molecular dynamics is now an important predictive tool for engineers, offering not only the applications availability at present but also potential for expansion in the future (Maginn, 2010). Currently, predictions of vapour pressures and vapour-liquid equilibrium (Vahid et al, 2008, Vrabec et al, 2009a,b), liquid densities (Bomont, 2008; Kulschewski and Pleiss, 2013), self-diffusivities (Liu et al, 1998; Wei-Zhong et al, 2008), and viscosities (Hess, 2002; Kang et al, 2012), with accuracies ranging from one to ten percent, are already standard examples of the successful use of its predictive power. However, in spite of its robustness and generality, time scales of standard molecular-dynamics simulations are still decisively shorter than those observed in experimental practice. Such difference leads to inadequacy in the description of long time-scale phenomena. Long simulations describe, at best, only some hundreds of nanoseconds. Even using available acceleration techniques, many orders of magnitude would still need to be bridged in order to achieve, through a classical approach, some micro- or milliseconds in the simulations (Voter et al, 2002). This discrepancy is frequently a major reason why some macroscopic investigations, as in the case of kinetic phenomena, still remain excluded from the standard scopes of molecular dynamics (West et al, 2007). Nonetheless, a growing number of
investigations have been reported where such scale issues have been successfully overcome.

Investigating the Poiseuille flow within a molecular-dynamic simulation, Li et al. (1998) proposed a reflecting particle method which used a fictitious sectional membrane in the simulation space in order to induce a net translational movement in the system. The membrane, acting as a filter, allowed particles to cross only in one direction; this reflected those trying to cross from the other side under statistical conditions. Compared to similar approaches on flow induction such as the gravitation method (Koplik et al., 1989) or the reservoir method (Sun and Ebner, 1992), Li’s method featured no addition of artificial forces or generation of biased flow dynamics. Comparable examples of molecular dynamics applied in the direct simulation of nanoscale phenomena have further been given by Koplik et al. (1988), Thompson and Robbins (1989), Koplik and Banavar (1995 a,b) and Thompson and Troian (1997).

Omleyan (2009) reported a multiple time-scale algorithm focusing on the optimization of time and computational efforts in molecular-dynamic simulations. The fundamentals of his approach remounted to the work of Streett, Tildesley and Saville (1978) who, by splitting the concept of neighbor lists into ranks of primary and secondary importance and using different time increments for each one of them, stated a path for increasing temporal extension of simulations. Though not necessarily blending scales, multiple time-step approaches extended the horizon of possibilities of molecular dynamics by stretching their investigated time slot. Swindoll and Haile (1984), Teleman and Jösson (1986), Tuckermann et al. (1990,1991a,b) and Forester and Smith (1994) report similar investigative approaches.

In order to expand the temporal limitation of molecular dynamic investigations on kinetic controlled phenomena, Faradjian and Elber (2004) proposed the milestoning method where the transition between two configurations is described in terms of intermediate steps bridging the initial and final states within a discrete phase space. In general, this approach holds the advantage of facilitating parallelization, reduction of time costs and suitability for dealing with transitions between states separated by
free energy barriers. An example of the milestoning methodology is given by West et al. (2007) in the study of stereo transitions of a solvated peptide.

Aiming for a serial approach, Elliott et al. (2007) proposed a molecular-dynamic tool for the prediction of equilibrium and transport properties in the simulation of chemical processes. Their method was based on discontinuous molecular-dynamics simulation and thermodynamic perturbation theory (Barker and Henderson, 1967). Facilitating the adaptation of thermodynamic theories and higher algorithmic efficiency were, according to the authors, the reason for the use of discontinuous potentials. Approximations of vapor pressures and vapor-liquid equilibrium exhibited average deviations of 10% while approximations of viscosity, diffusivity, thermal conductivity were obtained with deviations of 15%.

Despite the aforementioned efforts in extending the time and length scales of molecular-dynamic simulations, these methods still remain limited within the boundaries of a single approach: the atomistic scale. As already mentioned, a coupling of scales and therefore the expansion of the application fields of molecular dynamics is achievable through the use of hybrid approaches. The main idea behind these methods is the recognition that, under small time and length scales, complex phenomena take place only in discrete and specific regions of the investigated domain. In these cases, a slight and strategically chosen sub-domain of the problem is modelled through a finer approach, while the rest of the domain is described using a coarser numerical approximation (Praprotinik et al, 2005; Ensing et al, 2007; Heyden and Truhlar, 2008).

In a hybrid approach, the investigated regions are connected by means of intermediate (healing) regions, where information is smoothly adapted across the existing boundaries. If in one direction information has to be progressively coarsened as the system bulks up, then in the other, information must literally be created as the description of the system becomes finer in detail. The restoration of information from blurred values, also known as reverse mapping, is the major challenge to the method’s effectiveness (Ensing and Nielsen, 2010) and remains, according to Pablo and Curtin (2007), a persistent challenge in these methodologies.
Abraham et al. (1998) used molecular dynamics in a hybrid approach in the investigation of brittle fractures in silicon slabs. In their study, quantum-mechanical calculation, molecular dynamics and finite elements were coupled in order to simultaneously describe the electronic, atomistic and continuum evolution of crystalline fractures. Investigations of micro- and nano-fluid flow in the vicinity of rigid walls were also performed in the works of O’Connel and Thompson (1995); Buscalioni and Convey (2003) and Nie et al. (2004) used a hybrid coupling of molecular dynamics and the solution of the Navier-Stokes equations in order to generate velocity, stress-field and streamlines profiles of studied geometries. Gu and Zhang (2006) presented an advantageous concurrent multiscale method combining molecular dynamics with a mesh free description of the continuum scale which, in the investigation of structural deformations of materials, yielded highly accurate predictions compared to similar finite element approaches.

An extensive amount of information regarding advantages, methods and applications of hybrid methodologies can be found in literature (Maroudas, 2000; Curtin and Miller, 2003; Weinan et al., 2003; Liu et al., 2004; Park and Liu, 2004; Weinan et al. 2007; Nielsen et al., 2010). Due to the multitude of targeted applications, conceptual frameworks and/or available background however, a comparative overview of their similarities can be problematic. In order to overcome these technical barriers, Miller and Tadmor (2007, 2009) reported an extensive review of standard hybrid approaches currently found in scientific publications, highlighting their assets and suitability.

Whether in a single or multiscale approach using a serial or a concurrent methodology, the aforementioned references exemplify the wide variety of uses and possibilities available to chemical engineering through the use molecular dynamics. From the engineering point of view, just as in fluid mechanics where empirical practice and analytical theories gradually cleared space for numerical solutions, this technique is already replacing traditional methods of physical-property estimation (Maginn, 2010). Nevertheless, when considering the simulation of large-scale phenomena, one still has to face the sobering restrictions of its length and temporal limitations. Klein and Shinoda (2008) remark that in spite of the growth of computer power as predicted by Moore’s Law brute force computation alone is both an
insufficient and inefficient way to handle scale problems and foresee the development of new methods and algorithms as a key to future progress in the simulations of large-scale phenomena in molecular dynamics.

2.3 The direct simulation of separation processes based on molecular simulations

The many applications of molecular dynamics in chemical engineering reported in the last section still reveal an intrinsic tendency when it comes to its applications. Generally, even as a part of hybrid approaches, molecular dynamics remain solely restrained to the description of the atomistic portion of the phenomena under investigation. Though not necessarily a discrepancy, due to its natural atomistic foundation, this tendency unveils however an established practice that tends to sort out of the scope of molecular dynamics any speculation around the investigation of higher scale phenomena. If numerical costs frequently justify the limitations of atomistic methods in the investigation of high-levelled phenomena, revisited applications of these techniques have already shown concrete alternatives to overcome some of the scale-bridging problems in molecular-dynamical approaches (Pfennig, 2004; Babic and Pfennig, 2006).

Back in 2004, Pfennig (2004) showed the viability of simulating unit operations directly in atomistic scale using a molecular-dynamic based method. His approach was based on mimicking on atomistic level the of real conditions experienced by molecules in a technical equipment, especially in terms of pressure, temperature, local concentrations, their gradients, and also internal structures. In order to achieve his task, the concepts of virtual walls and modular construction of the simulation space were introduced in the classic method of molecular dynamics. These new concepts allowed him to tailor the simulation space and the emulation of characteristics of real equipment into an atomistic space. Figure 2.2 depicts his results of a 3.5ns long simulation of a three-staged distillation column with a mixture of methane and ethane. In this simulation, methane was described as a 5-centre and ethane as an 8-centre Lennard-Jones molecule. In the left side of figure 2.2 on the three stages of the distillation module the liquid and vapor phases are straightforward to recognize, while in the right side of the figure a McCabe-Thiele diagram of the
process shows the concentration along the stages compared with equilibrium data from literature (Knapp et al, 1989). In this simulation, the descending liquid flow was included by means of an extra gravitational field.

Figure 2.2: Distillation simulated in molecular level (Pfennig, 2004).

Despite the already exceptional agreement between the simulated and experimental data reported in the work of Pfennig (2004), Babic (2011) recognized hindering aspects for its further application. Babic (2011) realized that the use of an artificial gravitational field to induce flow within the simulation space was not an appropriate method when simulating different phases with similar densities as in the case of liquid-liquid extraction. He also recognized that the algorithm could not afford the discrete subdivision of the simulation space in real stages. In fact, it could only resemble them through an ad hoc structuring of its virtual space. Babic therefore proposed a thorough restructuration of the algorithm such that arbitrary fluid-separation processes could be described using a freely chosen number of separation stages. In his approach, each simulation space represents a single separation stage and the mass transfer between consecutive stages is realized by streams connecting them. The amount and composition of species leaving or entering a specific stage is characterizes these streams. According to Babic, in comparison to the former approach, the use of stream flows helps along the investigation of kinetic effects within the operation of the simulated process.
In his work, Babic settled the fundamentals of his approach and evaluated its assumptions using multi-component systems of species described by 1-centre Lennard-Jones potentials. Figure 2.3 depicts the simulation of a three-staged liquid-liquid extraction module reported in his work. In this simulation a species C is extracted from a phase B into a phase A. The left side of figure 2.3 shows the single stages and their connecting streams while on the right side, the stationary operation is represented as a ternary diagram. In this diagram, the working lines connecting entering- and leaving streams slightly deviate from their proximal binodals showing that in the stationary state the simulated stages did not operate in equilibrium. Rather, it operated in a kinetic-controlled condition where the amount of flow directly influenced the extension of mass transfer in each stage.

![Figure 2.3: Liquid-liquid extraction simulated in molecular level (Babic, 2011).](image)

Both investigations show that direct molecular-dynamic simulation of unit operations is indeed possible. Nonetheless, up to this point, no attempt has been made in order to directly evaluate this approach using empirical information of equipment obtained under realistic operational conditions. Therefore, in the present work, the stationary operation of a distillation column is atomistically simulated and its results directly compared to empirical data obtained in a technical scale distillation column. In this investigation, the approach proposed by Babic (2011) is once again applied to a ternary system, composed this time of a mixture of hydrocarbons represented by multi-centre Lennard-Jones molecules.
2.4 Distillation

Compared to standard modeling approaches, the nature of the atomistic method used in this work offers a fundamentally new view in the investigation of distillation columns. Pragmatically, a choice between two main paths of description, namely the equilibrium and the rate-based models, always had to be made prior to any further consideration. While the former works around the concept of efficiencies for a stage or equipment, the latter has been developed explicitly to account for the influences of interphasic mass-transfer rates within a stage (Taylor and Krishna, 1993).

The equilibrium-stage model is a plain alternative in the description of separation equipment. Characteristic of such pragmatic approach is the postulation that streams leaving a separation stage are in equilibrium with each other. The mathematical description in this approach generates a set of equations also known as MESH-equations. MESH is an acronym of the balance equations necessary to the modeling procedure, namely: mass balances, equilibrium relationships, summation equations and heat (or energy) balances (Taylor, Krishna and Kooijman, 2003).

Depending on the level of accuracy desired in this modeling, a very complex set of equations may be achieved. However, in order to avoid mathematical problems with its solution, some simplifications are usually taken into account to ensure the simplicity while not sacrificing accuracy of the model. The most commonly found assumptions in literature state that in a stage liquid and vapor are ideally mixed, dragging effects are neglected, and pressure and temperature are uniform (Roffel et al, 2000). Whilst this approach may generate a very robust set of differential-algebraic equations with straightforward computational implementation on the one hand (Elgue et al, 2004), it carries on the other hand a primary flawed assumption. In the real world, streams leaving a separation stage are not in equilibrium. The degree of separation in a stage depends in fact on the mass transfer between phases and this subsequently depends on the extent to which the streams in a real stage depart from equilibrium.

In order to circumvent this false assumption, the concept of efficiency is introduced in this modeling approach. Efficiency measures how close to equilibrium a stage or
equipment operates. Depending on the application and type of equipment, different definitions for efficiency are available in the modeling of distillation columns (Murphree, 1925; Hausen, 1953; Holland, 1975 and Standart, 1965, 1971; Holland & McMahon, 1970; Medina et al., 1978, 1979; King 1980; Lockett 1986 and Seader, 1989). In the case of packed columns, an analogous approach is made through the HETS (height equivalent to a theoretical stage) approach. In multi-component mixtures, these efficiencies may vary from tray to tray and even from component to component (Taylor et al., 2003). Such weaknesses of the equilibrium-stage model have led to the development of a new descriptive approach for separation processes, which unveiled their real nature of mass-transfer-rate-governed processes. These new methods have been labeled as non-equilibrium stage models, or rate-based methods.

Similarly to the former approach, the mathematical set of equations describing the rate-based models is also known under an acronym: MERSHQ, which stands for the material and energy balances, rate (mass and heat transfer), summation, hydraulic and equilibrium equations. Despite some similarities, the main difference between both approaches is the way in which conservation and equilibrium equations are applied. A practical difference is also the fact that the equilibrium condition relating to outgoing streams, as in the former case, no longer applies. In fact, this condition holds only in the vicinity of the interfacial region.

As a general class of description, the non-equilibrium approach bounds a high number of models which are differentiated based on the way in which the hydrodynamic and mass-transfer processes are described. Comparatively, however, all these models demand the description of mass and energy transfers at the vapor-liquid interface and therefore also require knowledge of interfacial quantities such as temperature and composition. Wherever possible assumptions of interphasic thermal and chemical equilibrium are made in order to drop such dependencies and promote the mathematical simplification of the model.

Currently, rate-based models find a large field of application in the description of packed columns, strong non ideal systems, systems with trace elements and equipment with unknown efficiency. Due to its approach on mass and energy
transfer, this methodology has ultimately turned into a tool for diagnosis of operating and design problems of separation equipment (Taylor et al., 2003). Due to a high demand for very specific information on the equipment and physical properties, the excellence of rate-based models is sometimes constrained by its high dependence on accurate empirical correlations that need to be available for the regarded material system and separation equipment.
3 Conceptual and methodological basis of simulations

In the previous chapter, a literature review highlighted the fundamentals on the simulation of unit operations in molecular scale. As mentioned in section 2.3, the current approaches used for this will now be reviewed in detail, offering more concrete insights on the structure and functionalities of MDSTAGE, the simulation tool used in this work. In the upcoming sections, an overview of the structure, algorithm and facilities of MDSTAGE is presented, focusing both on its concept and main functionality i.e. the tailoring of the simulation space. Finally, a discussion regarding the application of the tool and the execution of simulations is carried out.

3.1 Fundamentals of MDSTAGE

Conceptually, MDSTAGE can be traced back to the MDMULP algorithm, an open-source code provided by the computational collaboration project CCP5, a British organization for the development, maintenance and supply of large-scale scientific software (Smith, 1982). Essentially, MDMULP is a molecular dynamics code for the simulation of polyatomic molecular liquid mixtures incorporating long-range interaction of electrostatic point multipoles via the Ewald-summation approach in microcanonical and canonical ensembles. Translational and rotational motions of rigid molecules are described using the leap-frog algorithm and quaternion parameters respectively.

The leap-frog algorithm is a variation of the basic Verlet algorithm (Smith, 1982), based on the positions, $\vec{r}_i$, velocities, $\vec{v}_i$, and accelerations, $\vec{a}_i$, of molecules. Trajectories and velocities of a molecule $i$ are determined from:

$$\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \delta t \vec{v}_i \left( t + \frac{\delta t}{2} \right)$$ (3.1)

$$\vec{v}_i \left( t + \frac{\delta t}{2} \right) = \vec{v}_i \left( t - \frac{\delta t}{2} \right) + \delta \vec{a}_i(t)$$ (3.2)
while current velocities, \( \mathbf{\dot{v}_i} \), at a time \( t \) are given by:

\[
\mathbf{\dot{v}_i}(t) = \frac{1}{2} \left( \mathbf{\dot{v}_i}\left(t + \frac{\Delta t}{2}\right) + \mathbf{\dot{v}_i}\left(t - \frac{\Delta t}{2}\right) \right)
\]  

(3.2)

Quaternions (Q) are a special case of versors, an algebraic parametric expression of rotations, defined by a set of four scalars:

\[
Q = [q_0, q_1, q_2, q_3]
\]

(3.3)

satisfying the constraint:

\[
q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1
\]

(3.3)

Due to their straightforward mathematical properties and simplified notation, quaternions are frequently used in classical molecular dynamics in order to represent the orientation of rigid molecules subject to rotation. In these cases the rotation matrix, \( A \), of a rigid molecule (Smith, 1982) is defined as:

\[
A = \begin{pmatrix}
\cos \phi \cos \psi & -\sin \phi \cos \theta \sin \psi & \sin \phi \cos \psi + \cos \phi \cos \theta \sin \psi & \sin \theta \sin \psi \\
-\cos \phi \sin \psi & -\sin \phi \cos \theta \cos \psi & -\sin \phi \sin \psi + \cos \phi \cos \theta \sin \psi & \sin \theta \cos \psi \\
\sin \phi \sin \theta & -\cos \phi \sin \theta & -\cos \phi \sin \theta & \cos \theta
\end{pmatrix}
\]

(3.4)

which becomes:

\[
A = \begin{pmatrix}
q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2q_1q_2 - 2q_0q_3 & 2q_1q_3 - 2q_0q_2 \\
2q_1q_2 - 2q_0q_3 & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2q_2q_3 - 2q_0q_1 \\
2q_1q_3 - 2q_0q_2 & 2q_2q_3 - 2q_0q_1 & q_0^2 - q_1^2 - q_2^2 - q_3^2
\end{pmatrix}
\]

(3.5)
where the values of the scalars $q_0$, $q_1$, $q_2$ and $q_3$ are given by:

\[
q_0 = \cos \frac{\theta}{2} \cos \left( \frac{\phi + \psi}{2} \right) \\
q_1 = \sin \frac{\theta}{2} \cos \left( \frac{\phi - \psi}{2} \right) \\
q_2 = \sin \frac{\theta}{2} \sin \left( \frac{\phi - \psi}{2} \right) \\
q_3 = \cos \frac{\theta}{2} \sin \left( \frac{\phi + \psi}{2} \right)
\]

(3.6)

In equations 3.4 and 3.6, $\phi$, $\theta$ and $\psi$ represent the rotational Euler angles of the body-fixed axis vectors of a rigid molecule related to a space-fixed frame (Smith, 1982). For further information regarding the specificities of MDMULP the reader is suggested to visit the repository website of CCP5 (CCP5, 2012).

On its way to MDSTAGE, the algorithm of MDMULP has undergone fundamental adaptations in order to accomplish the simulation of unit operations in atomistic scale. Essentially, these adjustments led to a tool capable of mimicking macroscopic characteristics of unit operations on the atomistic scale such as physical boundaries and flows of mass and energy. As already mentioned in the previous chapter Babic (2011) established the fundamentals of such approach and accomplished the necessary adjustments on the original code and came up with an alternative for investigating continuum-scale phenomena by directly introducing them into an atomistic level.

Basically, the core idea in MDSTAGE evolved into the reconsideration of the molecular-dynamics concept of simulation space. As illustrated in figure 3.1, in the classical molecular dynamic approach a simulation space defines a virtual region where the simulated molecules are allowed to interact with each other under the constraints of the considered ensemble. This approach leads however to problems describing macroscopic systems since either a finite number of molecules or limitation due to boundaries are effects not present in the bulk of macroscopic media. A solution to this problem is provided by the application of the concept of periodic
boundary conditions (PBC) (Born and von Karman, 1912), where the simulation space is replicated throughout space building an infinite lattice of its own copies. Figure 3.2 illustrates the concept of periodic boundary conditions.

**Figure 3.1:** Classical concept of a simulation space and its virtual boundaries for a hypothetical binary system.

**Figure 3.2:** A three-dimensional representation of periodic boundary conditions for the simulation space in figure 3.1.
As molecules move in the central simulation space of figure 3.2 during a simulation, their periodic duplicates in the neighboring boxes move the same way. Therefore, if a molecule leaves the central box in a specific direction, another one will enter the space from the direct opposite side. In this manner, there exists no wall at the boundary of the central simulation space and its structure simply forms a convenient reference system to relate the coordinates of the simulated molecules (Smith, 1982).

At the beginning of any molecular dynamical simulation, molecules need to be placed inside the simulation space. Regarding the stability of the system at these initial moments, a random distribution of molecules over the simulation space is not necessarily a good choice. It brings the risk of molecules lying extremely close to each other or, in extreme cases, even overlapping. An elegant solution for this task is given by the use of unit cells in the simulation space. In molecular dynamics, a unit cell is the smallest divisible unit of the simulation space, allowing the allocation of molecules within it and carrying geometrical information about the disposition of the molecules at the beginning of the simulation. The use of unit cells permits the ordered distribution of molecules following strict allocation constraints and, in terms of the final structure, allows the generation of a diverse number of isotropic patterns. As in the case of the simulation space, there exists no walls at the boundaries of a unit cell. Its structure is solely a virtual frame supporting the allocation of molecules in the simulation space. As in its predecessor, MDMULP, the unit cell in MDSTAGE is a cubic element with four sites for allocation of molecules. Figure 3.3 illustrates the structure of a unit cell in MDSTAGE showing these locations.

![Figure 3.3: MDSTAGE unit cell and the four allocation sites for molecules.](image)
When put together, the unit cells shown in figure 3.3 create an ordered distribution of molecules resembling a face-centered cubic lattice. As sketched in figure 3.4, for a simulation space with 8 unit cells, this spatial distribution is the initial state of any investigated system in simulations of MDSTAGE.

![Figure 3.4: A simulation space with eight unit cells featuring a face-centred cubic distribution of molecules at the beginning of a simulation.](image)

As thus far defined, the simulation space only delimitates the dimensions of the investigated system. Under these circumstances the implementation of constraints resembling macroscopic characteristics of unit operations is a hardly feasible task. Pfennig (2004) proposed an alternative concept for the assembling of a simulation space based on a modular approach, which offered a viable way for mirroring characteristics of the continuum scale in the atomistic one. The main idea behind this concept was the use of elementary building blocks, to which macroscopic characteristics could be attributed. In MDSTAGE, the unit cell was chosen as structure to represent this elementary building block. Figure 3.5 illustrates the primary difference between the classical and the MDSTAGE approaches in the definition of the simulation space.
The attribution of macroscopic characteristics on the unit cells in MDSTAGE – i.e. the elementary building blocks of the simulation space – follow the same concept proposed by Pfennig (2004), which uses the structure of the unit cells as a frame for the assignment of specific characteristics.

As sketched in figure 3.5.b, the walls of the unit cells delimit plane sections within the simulation space. These plane sections, illustrated in figure 3.6, are the places chosen by Pfennig (2004) in which macroscopic characteristics are addressed. In a simulation, where no properties are attributed to the plane sections of the unit cells, the molecules move freely over the entire simulation space, crossing all possible plane sections without any interference. In this case, there exists no differences between the classical and the MDSTAGE definitions of a simulation space. On the other hand, as soon as a generic property $X$ is attributed to a specific plane section of a unit cell, the trajectories of the simulated molecules becomes subjected to that constraint. In the case that a molecule reaches or crosses this plane section, its trajectory and properties will be changed in accordance with the addressed characteristic. A simple example of the dynamic between molecules and plane sections assigned with a property is the simple case of mimicking an impenetrable wall within the simulation space. If a specific plane section is set to act as an impenetrable wall, any molecule $i$, after hitting the wall, would have its velocity vector $\vec{v}_i$ redefined to $\vec{v}^{\text{new}}_i$ i.e. the molecule will continue moving, but now in the
opposite direction in reference to the motion before the collision. Further information regarding other possibilities for translation of macroscopic characteristics on the atomistic scale is given later, when specific functionalities of MDSTAGE are discussed.

Together with the possibility of tailoring the simulation space, MDSTAGE features a further particular aspect regarding its simulation methodology, namely the possibility of employing a stagewise approach in the description of unit operations. In the specific case of separation processes standardly described by a series of single stages, MDSTAGE allows the division of the investigation into simulations of each separation stage, allocating to each one of them its own simulation space. In order to recover the dynamic of the operation as a whole, these single simulation spaces are then interconnected by mass and energy flows between them. Such possibility supports the coupling between the molecular information, intrinsic to the approach, and the actual dynamics of the separation process. It allows the investigated material system to wander over the different stages of the equipment and therefore derive predictions on the performance of the examined operation based on the local and global thermodynamic conditions within the investigated equipment.

Compared to a standard (i.e. one-staged molecular-dynamics simulation), the splitting of the simulation of a unit operation into a finite number of N singles stages
directly means increasing the computational costs of the simulation by N times. Since the computational costs are directly proportional to the square of the number of simulated molecules in a single stage alone, the costs of a multi-staged simulation may rapidly rise to unfeasible limits depending on the number of simulated stages and their dimensions. In order to overcome this impediment, MDSTAGE also offers the possibility of distributing the simulation of the N stages over a network of processors, as in the case of a PC cluster connected via local area network (LAN). Therefore, instead of concentrating the simulation costs on only a single processor, the simulation of each stage can be assigned to a specific processor, reducing the simulation costs once again to those demanded in standard molecular-dynamics simulations.

In practice, stages of a unit operation continuously exchange mass and heat flows along any investigated process. For this reason, when simulating a unit operation in MDSTAGE, the splitting of the stages over a net of processors must also cope with the interaction between them in order to recover the dynamics of the process as a whole. Therefore, each simulated stage must regularly exchange information with its adjacent neighbors regarding material and energy transfer between them. This approach, exemplified in the simulation of a distillation column with the splitting of the single stages, is sketched in figure 3.7. The left side of figure 3.7 depicts the operation of a distillation column with trays. In the aforementioned splitting approach, each one of these trays are simulated in a single simulation space (figure 3.7-middle) and distributed over a cluster of PCs or a local area network (figure 3.7-right), which also permit the communication between them in order to exchange information about material and energy transfer between two adjacent stages. This approach also offers a benefit in the simulation of unit operations using systems with sparse information about their transport and equilibrium properties, which could eventually be directly deduced from the dynamical behavior of the system within the investigated equipment.
3.2 Utilities and structure of MDSTAGE

As previously mentioned, this work tackles the simulation of the stationary operation of a distillation column in terms of a mimicking approach on atomistic scale. In order to ensure a minimal level of resemblance between the simulated scales, the employed simulation tool had to ensure the description of those macroscopic characteristics ordinarily found in the simulated conditions of the investigated equipment into the atomistic level. A plot of such characteristics is illustrated in figure 3.8, where a generic stationary operation of a distillation column is sketched.

Figure 3.8 depicts a group of representative quantities through which the operation of a distillation column may be described. On the left side, the arrangement of mass and heat flows along the equipment is illustrated while on the right side, the demands for a single stage are outlined. Regarding conservative quantities, figure 3.8 states the necessity of MDSTAGE to cope with the transcription of mass and energy flows on an atomistic scale capable of representing, on one hand, mass streams such as feeds ($F$), distillates ($D$), side- ($S$) and bottom ($B$) products with their respective compositions (as implied on the right-side single-stage sketch of figure 3.8), and on
the other, the supply and withdraw of heat (Q) as in the case of a boiler and condenser respectively. Structural characteristics of the simulated equipment are also supposed to be transcribed by MDSTAGE in the simulation space on the atomistic scale.

![Diagram of distillation column](image)

**Figure 3.8**: Representative quantities in the description of the stationary operation of a distillation column

The concrete implementation of these requirements in the atomistic scale was accomplished through the aforementioned modular approach used in the definition of the simulation space. As previously mentioned, the plane segments defined by the boundaries of the unit cells in a simulation space were used to assign specific macroscopic properties. These properties act on the simulated molecules whenever a molecule crosses or contacts one of the assigned plane segments in the simulation space. A set of six basic properties in MDSTAGE build a group of fundamental properties supporting the transcription of the macroscopic scale into the atomistic one. These properties, illustrated in figure 3.9 and assembled on an ad hoc basis by Babic (2011), will now be explained.
3.2.1 Assignment of no specific property

The ordinary case in the assignment of properties on the segment planes of a unit cell is depicted in figure 3.9(a), where no special characteristic is in fact addressed. If a simulated element contacts or crosses this plane, its simulation path remains undisturbed. If in a simulation space of MDSTAGE this property was assigned to every plane of each unit cell, the final result would correspond to the classical definition of simulation space, as illustrated in figure 3.5(a).

3.2.2 Assignment of impenetrable walls

Walls, physical barriers or generic internal structures are described in MDSTAGE by a property illustrated in figure 3.9(b), which defines an impenetrable boundary within the simulation space. Simulated molecules coming in contact with this plane are, in terms of their center of mass, elastically reflected in the opposite direction of their trajectories.
Regarding a bi-dimensional case of a molecule $i$ moving along the x-y plane of a simulation space with velocity $\vec{v}_i = (v_{i,x}, v_{i,y})$, the new coordinate $\vec{r}_i^{\text{new}} = (x_i^{\text{new}}, y_i^{\text{new}})$ of the molecule after a time step $\Delta t$ is given by:

$$
\vec{r}_i^{\text{new}} = \vec{r}_i^{\text{old}} + \vec{v}_i \Delta t
$$

(3.7)

If, as illustrated in figure 3.10, the molecule reaches an impenetrable wall in the time step $\Delta t$, its new position $\vec{r}_i^{\text{new}}$ as given in equation 3.7 is no longer correct. In fact, the elastic reflection undergone by the molecule after hitting the barrier has to be taken into account and a corrected position $\vec{r}_i^{\text{new}^*}$ must be calculated.

![Figure 3.10: Impenetrable wall assigned to a plane segment in the simulation space of MDSTAGE.](image)

This new corrected position is also dependent on the distance between the molecule and the wall right before the hit. A factor $f_{\text{hit}}$ defined by:

$$
f_{\text{hit}} = 1 - \frac{\vec{r}_i^{\text{old}} - \vec{r}_i^{\text{wall}}}{\vec{r}_i^{\text{old}} - \vec{r}_i^{\text{new}^*}}
$$

(3.8)

defines the fraction of the trajectory of the molecule subject to correction proportional to the distance between the molecule and the wall before the impact. Therefore, the corrected new position of the molecule is obtained by:
A further aspect of this type of event is that after the collision the component of the velocity vector of the molecule $i$ corresponding to the plane, where the impenetrable wall was assigned, has its value multiplied by the scalar -1 in order to account for the change in the direction of the trajectory of the molecule. In the case depicted in figure 3.10, the new velocity vector of the molecule $i$ is given by:

$$
\vec{v}_{i} = (v_{i,x},-v_{i,y})
$$

(3.10)

### 3.2.3 Assignment of partially penetrable walls

Sieve trays, membranes and any other partially penetrable artefact are described in MDSTAGE with partially penetrable walls, as depicted in figure 3.9(c). In this case, the crossing of the boundary is accomplished, or not, in accordance with the result of a stochastic evaluation made for each molecule after it hits the wall. As illustrated in figure 3.11, in the assignment of this property a probability $p_{wall}$ lying between zero and one has to be additionally defined. This factor stands for the probability of a molecule crossing the plane segment and provides a decision criterion whenever a simulated molecule reaches the boundary. Usually the definition of the parameter $p_{wall}$ is proportional to the free area available in the simulated tray, membrane, perforated wall, etc.

![Figure 3.11: Partially penetrable wall assigned to a plane segment in the simulation space of MDSTAGE.](image)
Whether a molecule crosses a plane segment assigned as a partially penetrable wall or not depends on the value of a random number \( \zeta \) generated in the stochastic evaluation, which defines the further trajectory of the molecule.

Assuming:

\[
\zeta \leq p_{wall} \quad (3.11)
\]

the molecule will cross the plane segment and its new position, according to figure 3.11 and calculated with equation 3.7, will be \( \vec{r}_{i}^{new} \). On the other hand, when:

\[
\zeta > p_{wall} \quad (3.12)
\]

the assigned plane segment behaves as an impenetrable wall and the new position and velocity of the molecule, represented by \( \vec{r}_{i}^{new} \) is given by equations 3.9 and 3.10 respectively.

### 3.2.4 Assignment of heating and cooling walls

Heating and cooling elements perform the supply and withdraw of thermal energy in macroscopic scale. In the case of a distillation column, boilers and condensers are responsible for such tasks. In the atomistic scale, thermal energy is directly coupled with the kinetic energy of the simulated molecules and heating or cooling process are, therefore, velocity-scaling mechanisms as depicted in figure 3.11.

**Figure 3.11:** Heating/cooling wall assigned to a plane segment in the simulation space of MDSTAGE.
This boundary rescales the translational velocity of any molecule contacting or crossing it by a predefined factor $f_{\text{heat}}$, according to:

$$v_i^{\text{new}} = f_{\text{heat}}v_i^{\text{old}}$$

(3.13)

Per definition, the factor $f_{\text{heat}}$ is supposed to have a positive value. If $f_{\text{heat}}$ is greater than unity it increases the velocity of the element and induces, therefore, the heating of the system. Analogously, $f_{\text{heat}}$ values smaller than unity induce a cooling process in the investigated system.

In investigations of liquid or gas media on atomistic scale, a phenomenon easy to track is the random trajectories of the simulated molecules within the simulation space. This phenomenon, also known as pedesis or Brownian motion, is the result of a series of random collisions of a molecule with its pairs in the direct neighborhood, leading a molecule to follow an apparently arbitrary trajectory. A consequence of this phenomenon in the approach followed by MDSTAGE is that a molecule, which has just reached or crossed a plane segment assigned with a property, could bounce backwards after a series of collisions with other molecules and reencounter the plane segment just previously hit. This could seriously compromise the effectiveness of the properties assigned to a segment plane: for example the case of a partially penetrable wall, where any molecule hitting the same plane segment in sequence would eventually come to cross it, or the case of a heating wall, where a molecule could become indiscriminately overheated after colliding in series with the assigned plane segment. In order to avoid these problems in the investigations of MDSTAGE, each molecule hitting such plane segments is flagged in order to control and inhibit the repeated actuation of the plane segment on the same molecule. After a molecule has been flagged, there are two possible ways to reset it. In the first case, the flag is automatic removed when the molecule has reached a distance $L = \left(\frac{4}{\rho N_A}\right)^{1/3}$, equivalent to the length of the side of a unit cell in relation to the referred segment plane. In this definition of $L$, $\rho$ stands for the density of the system while $N_A$ for the Avogadro number. The second possible way to reset the flag is the use of an extra type of plane assigned with this characteristic, as depicted in figure 3.12. Although
not corresponding to any macroscopic characteristic illustrated in figure 3.9, MDSTAGE offers this alternative in the assembling of the simulation space.

![Flag resetting wall assigned to a plane segment in the simulation space of MDSTAGE.](image)

**Figure 3.12**: Flag resetting wall assigned to a plane segment in the simulation space of MDSTAGE.

### 3.2.5 Assignment of product and feed walls

As sketched in figure 3.8, under real operational conditions mass flows and material exchange between stages exemplify probably one of the most meaningful characteristics describing a unit operation. MDSTAGE transcribes these effects in the atomistic scale with product and feed boundaries shown in figures 3.9(e) and 3.9(f).

In MDSTAGE, any product wall determines an amount of molecules supposed to be withdrawn from the investigated system. In a time \( t \) after the beginning of the simulation, the total number of molecules supposed to be removed from the simulation space \( N_{rem}^{ref} \) is given by:

\[
N_{rem}^{ref} = \int_{0}^{t} N_{rem}^{ref}(t) dt
\]  

(3.14)

In equation 3.14 \( N_{rem}^{ref} \) is the reference rate of molecules supposed to be removed from the system per time step. The number of molecules supposed to be removed in a specific time step \( t_1 \) is given by:
where $N_{\text{rem}}^{\text{real}}$ stands for the number of molecules in fact removed from the simulation space up to the time $t_1$. Regarding the nature of each of the aforementioned quantities, one notices that, while $N_{\text{rem}}^{\text{real}}$ is defined as an integer, $N_{\text{rem}}^{\text{ref}}$, $N_{\text{rem}}^{\text{now}}$ and $N_{\text{rem}}^{\text{now}}$ are variables described by real numbers. Furthermore, the value of $N_{\text{rem}}^{\text{now}}$ (i.e. the current demand on the removal of molecules) indirectly offers a decision criterion by the event of a molecule crossing or contacting this type of boundary. Three cases need to be regarded in the evaluation of $N_{\text{rem}}^{\text{now}}$:

(i) $0 < N_{\text{rem}}^{\text{now}} < 1$

When the amount of molecules to be removed lies between zero and one (i.e. defining a hypothetical situation where only a fraction of a molecule had to be removed), the decision as to whether or not to proceed with the task is made with the aid of a random number $\zeta$ also lying between zero and one. The molecule will be removed from the simulation space if:

$$\zeta \leq N_{\text{rem}}^{\text{now}}$$

and remains in it otherwise. Molecules rejected by this criterion are also flagged in order to avoid a consecutive removal event, due to collisions with other molecules in the vicinity of the boundary.

(ii) $N_{\text{rem}}^{\text{now}} > 1$

This case denotes a favorable condition for the removal of a molecule, whereby the number of molecules withdrawn from the simulation space up to the time step $t_1$ is smaller than its analogous expected value. However, the molecule will only be
removed from the system if it has not been flagged by a product boundary in the previous steps of the simulation. If that is the case, the molecule remains in the system.

(iii) \( N_{rem}^{now} < 0 \)

This condition is verified when the number of molecules removed from the system is greater than the value expected at that time. In this case, no molecule hitting the product boundary is removed from the simulation space.

In the simulation of multicomponent systems, the type of component removed from the system by a product boundary is not defined by the boundary itself. In fact, it is a result of the local dynamics and composition near the assigned boundary, which determine what type of molecule hits the plane segment assigned with a product boundary. The ratio between the number of molecules of species \( i \) and the total number of molecules removed by the product wall returns the composition of the species \( i \) in that specific product stream.

Compared to the removal of molecules, their insertion in the simulation space is a procedure following quite a similar routine. At a time \( t \) after the beginning of the simulation the total number of molecules \( N_{add}^{ref} \) supposed to have been inserted in the simulation space is given by:

\[
N_{add}^{ref} = \int_{0}^{t} N_{add}^{ref}(t) dt
\]

(3.17)

where the number \( N_{add}^{ref} \) is the reference rate of molecules inserted per time. The difference:

\[
N_{add}^{now} = N_{add}^{ref} - N_{add}^{real}
\]

(3.18)
determines the amount of molecules to be inserted at a specific time $t_1$.

In equation 3.18, $N^{\text{real}}_{\text{add}}$ stands for the total number of molecules in fact added in the system at the time $t_1$ and $N^{\text{now}}_{\text{add}}$ establishes with the aid of the aforementioned random number $\zeta$ the decision criterion for the insertion of a molecule in the simulation space. Three situations have to be considered in this case:

(i) $0 < N^{\text{now}}_{\text{add}} < 1$

In this case, the condition:

$$\zeta \leq N^{\text{now}}_{\text{rem}}$$ (3.19)

is tested. In positive cases, a molecule is inserted in the simulation space and in negative cases, nothing happens.

(ii) $N^{\text{now}}_{\text{add}} > 1$

In this case, where the number of molecules inserted in the simulation space is smaller than the expected value $N^{\text{ref}}_{\text{add}}$, a new molecule is directly inserted in the system.

(iii) $N^{\text{now}}_{\text{add}} < 0$

Here, when the number of already inserted molecules is greater than the reference value for that specific time, no molecule is inserted.

A further aspect to be considered when inserting molecules in a simulation space is the method in which these molecules are supposed to be added without excessively disturbing the simulated system. In order to smoothly insert a new molecule, a
favorable local energetic condition is supposed to be available near the feed boundary. Because molecules in a simulation space will not spontaneously provide space for the insertion of a new molecule, this free place must be achieved by the new molecule itself. In an ideal scenario, a molecule would be slowly inserted in the simulation space directly from outside of it. This is however not a viable strategy since, due to the periodic boundary conditions, the concept of “outside” is not applicable to a simulation space as shown figure 3.2. A solution for this issue was proposed by Babic (2011) with the use of ghost particles as precursors of a new molecule in the insertion routine.

Ghost particles are fictive copies of those molecules present in the simulation space. The effect of their potential on real molecules is a function of the distance separating the ghost particles from the feed boundary. In order to insert one molecule in the simulation space, two equivalent ghost particles are required. These ghost particles, as sketched in figure 3.13, converge perpendicularly towards the feed boundary and merge into each other, generating a new molecule after reaching this assigned boundary. Up to the merging of the two ghost particles, no real molecule exists at the feed boundary. The effects of the potentials of the ghost particles at this place, however, gradually increase as if a seed of a new molecule had been placed and steadily grew at the assigned plane segment while the ghost particles move towards it. To insert a new molecule, two ghost particles are placed at a distance equivalent to two unit cells in relation to the feed boundary. This initial distance is chosen in order to avoid abrupt changes in the potential field around the feed wall. As long as it is greater than the mean intermolecular distance in the system, this initial distance in relation to the feed boundary ensures that potential disturbances generated by the new molecule will grow smoothly from a negligible value up to that equivalent to a whole new molecule.

This process of inserting a new molecule in the simulation space is schematically depicted in three steps in figure 3.13. Figure 3.13(a) shows two ghost particles approaching the feed boundary, where the seed of a new molecule continuously grows upon their approach. In figure 3.13(b), the two ghost particles are now closer to the feed boundary. The effects of the new molecule seed on the potential field in its neighborhood gradually increases. As the potential of a new molecule emerges at
the feed boundary, real molecules surrounding that location start to reallocate themselves, automatically creating free space to accommodate the new molecule. Figure 3.13(c) shows the final step of the process, when the two ghost cells have reached the feed boundary and merged with one another generating a new molecule.

**Figure 3.13**: Insertion of a new molecule in the simulation space of MDSTAGE using the ghost particle approach.

MDSTAGE also offers a further feature in the assembling of the simulation space, namely the possibility of combining different properties on the same plane segment. Combinations of different properties on one plane segment is necessary whenever the use of a single property does not adequately represent a macroscopic characteristic of a unit operation in its totality. A simple example of such a case is the atomistic scale mimicking of a heating element in the interior of a distillation column. Heating elements are physical artefacts located in the boiler of distillation columns that provides energy, to the fluid in the equipment in the form of heat. In order to properly describe such an element, the use of a heating wall as described in section 3.2.4 would not be sufficient so long as the assignment of this property does not alter any characteristic regarding the penetrability of the wall. Since heating elements, as any other physical artefact, impose a real barrier to the translational movement of any molecule in their proximity, the plane segments of the unit cells representing this macroscopic element should not only affect the velocities of the molecules (i.e. transferring energy (heat) to the system) but simultaneously act as impenetrable walls, as illustrated in figure 3.14. In the current approach of MDSTAGE, any combination of properties is possible although the choice of the properties to be combined is, as already mentioned, a matter of what macroscopic artefact the plane segments of the unit cells are supposed to represent.
Figure 3.14: Combination of an impenetrable and a heating wall on a same plane segment of a unit cell in MDSTAGE.

Last but not least, a final difference in the approaches of MDMULP and MDSTAGE regarding the definition of the simulation space must be observed. In its premises, MDMULP was a code meant to strictly describe the behavior of pure liquids or liquid mixtures. In practice, this meant that the simulation space investigated in the simulations of MDMULP was supposed to be completely filled with molecules in order to resemble the bulk of such media. As previously illustrated in figure 3.3, the distribution of molecules in the simulation space of MDSTAGE, as in MDMULP, is accomplished with the aid of unit cells. Each unit cell carries four molecules and together, in the case of full-filled space, they build a face-centered lattice of molecules at the beginning of the simulation. In MDSTAGE, however, it is also possible to choose how the simulation space will be initially filled. Besides the aforementioned tailoring of the plane segments of unit cells by the assignment of macroscopic properties, it is also possible in MDSTAGE to specify whether or not a unit cell will be filled with its four molecules. This feature extends the assembling possibilities of MDSTAGE, enabling for instance the investigation of systems demanding spatial tailoring of molecules distributed in the simulation space.
3.2.6 The algorithm of MDSTAGE

The original algorithm of MDMULP also had to be adapted in order to implement the aforementioned features of MDSTAGE. In MDMULP, a standard algorithm for molecular dynamics simulations integrates the Newton equation of motion for an n-body system following a simply structured sequence of commands over the simulation. Basically, the structure of the algorithm of MDMULP lies in six basic steps:

(i) Initialization of the simulation space by assignment of initial position and velocities for each molecule.
(ii) Evaluation of forces acting on each molecule according to the applied intermolecular potential.
(iii) Evaluation of the acceleration acting on each molecule by means of the Newton equation of motion.
(iv) Actualization of velocities and positions of each molecule according to the chosen integration method; in the case of the leap-frog algorithm, using equations 3.1 – 3.3.
(v) Evaluation of properties of the system.
(vi) Return to (ii) or finish the simulation.

In MDSTAGE, the implementation of the features necessary to the simulation of unit operations in molecular scale demanded a formal restructuring of the standard algorithm of MDMULP. The new algorithm, sketched in figure 3.15, will now be reviewed in detail.

Initially, the configuration of the investigated system must be defined. Information regarding the dimensions of the simulation space, the number of simulated molecules, the physical conditions of the system at the beginning of the simulation, the numerical parameters of the simulation and the architecture of the simulation space are specified. The molecules are distributed in the simulation space according to the tailoring approach chosen for the investigation, as discussed in section 3.1. Their initial velocities are assigned according to equipartition theorem which relates
the kinetic energy of each molecule to the desired average temperature of the system at time zero.

After setting up the basic definitions of the system and the simulation, the program enters into its main loop where the main adaptations from MDMULP into MDSTAGE have been conducted. At first, the forces $\vec{F}$ acting on the molecules are calculated according to an intermolecular potential $\partial \tilde{G}(\vec{r}_{ij})$ used to describe their interactions. Short- and long-range intermolecular interactions contribute to force $\vec{F} = -\vec{r}_{ij}(\partial \tilde{G} / \partial \vec{r}_{ij})$ acting on a molecule. In MDSTAGE, the short-range interactions between two molecules $i$ and $j$ are described by the standard Lennard-Jones potential:

$$\tilde{G}(\vec{r}_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{\vec{r}_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{\vec{r}_{ij}} \right)^{6} \right]$$ (3.20)

In equation 3.20, $\epsilon$ and $\sigma$ are component specific parameters describing energy and size contributions respectively. When necessary, Long range contributions describing the interactions between electrostatically charged molecules are described with the aid of the Ewald summation approach. Given their fundamental character, an elaborate explanation on the specificities of the Lennard-Jones potential or the Ewald summation method is not included in the scope of this work. Detailed information about these themes can be found in any standard book of molecular dynamical techniques (Allen and Tildesley, 1987; Frenkel and Smith, 2002).

In sequence to this step, after solving the Newton’s equation of motion, new spatial coordinates of the molecules are calculated. These new coordinates are obtained according to the leap-frog algorithm, as described in equations 3.1-3.3. Before proceeding to the evaluation of the physical properties of the system, the molecules are checked in order to determine whether or not they have crossed any plane segment assigned with a specific property. In positive cases, the properties of the plane segment are assigned on the molecule according to the procedures discussed in sections 3.2.1-5.
Numerically, this evaluation produces an extra computational cost directly coupled with the total number of simulated molecules, N. However, compared to the costs generated in the force calculation step (which are proportional to N^2) and considering the possibility of allocating the simulation over different processors as discussed in section 3.1, the viability of such evaluation is still affordable. After defining the new conditions of the system, the evaluation of specific properties is performed. These procedures are then repeated within the main loop of the program until the algorithm reaches the maximal number of simulated steps, as predefined at the beginning of the simulation.
4 Experimental Methods

As already set out in prior chapters, this work aims to evaluate the quality of the results for the stationary simulation of a distillation column predicted by means of an atomistic modelling approach. In order to accomplish this evaluation using a technical distillation column assembled for this purpose, numerical results of a simulated system are to be compared against a set of previously acquired experimental data. In the upcoming sections of this chapter, a report on the acquisition of the experimental information used in this work is summarized. Following an initial description of the experimental setup, focused on the equipment and test systems used, the procedures for preparation and conducting of experiments are reported. Finally, after a short discussion on the analytical methodology applied in their characterization, a summary of the evaluated experimental data set is provided.

4.1 The equipment

In order to acquire a set of experimental data on the stationary operation of a distillation column, a pilot-plant unit was assembled and brought to operation. Figure 4.1 sketches the body and internal structures of the DN50, vacuum-jacketed, mirror-glassed, five-staged bubble-cap tray QVF-NORMAG distillation column (manufactured by De Dietrich Process systems).

Figure 4.1: QVF-NORMAG column: Layout (a) and stage internal geometry (b).
As illustrated in figures 4.2, 4.3 and 4.4, the QVF-NORMAG distillation column has an internal diameter of 52.4mm. In each of its five stages, the rising vapor enters a stage through a 20mm high and 18mm wide cylindrical vapor pass covered by a 35mm high bubble cap. The vapor phase enters the vapor chamber of the current stage passing through 2.5 mm x 5 mm rectangular vents located at the base of the bubble cap. These vents, which remain immersed in liquid phase during the operation of the column, promote the mixing of liquid and vapor phases and therefore the exchange of species between them. The liquid phase flowing downwards enters a stage by a 38.6 mm long and 10.5 wide cylindrical liquid downcomer. It subsequently moves along the space circumscribing the bubble cap until reaching the next liquid downcomer leading to the stage bellow. In order to provide a minimal holdup of liquid on the stage, a 9 mm high and 10.5 mm wide weir dams the liquid flow in the tray. As long as entrance and exit of the liquid phase are located side by side, shortcuts are avoided by a wall separating both regions.

Figure 4.2: Constructive sketch of the internals of a stage featuring the bubble cap, vents, separating wall, weir and vapor pass.
Figure 4.3: Constructive sketch of the bubble cap and its vents.

Figure 4.4: Constructive sketch of a tray featuring the vapor pass, weir, separation wall and the liquid downcomer.
On top of the five stages of the NORMAG column, as illustrated in figure 4.5, a 33 mm high and 18 mm wide cylindrical vapor pass sealed to a 13 mm high and 32 mm wide glass crown builds the sixth tray of the column. This sixth tray does not count as a separation stage. In fact, its purpose is to limit the volume of the vapor chamber of the fifth stage in order to ensure its geometrical similarity in relation to the other stages.

![Figure 4.5: Constructive sketch of the sixth tray of the NORMAG column.](image)

As sketched in figure 4.6, in each stage of the NORMAG column two ports give direct access to the weir and vapor chamber regions and allow the sampling of liquid and temperature measurements respectively. Heat loss along the body of the column was diminished with the aid of a vacuum jacket and external mirrored walls.
Figure 4.6: Constructive sketch of the NORMAG distillation column featuring its vacuum jacket and access ports.

The body of the NORMAG column is connected to a 5.5 liters boiler vessel and to a condenser module, as sketched in figure 4.7. Two purge valves are connected to the bottom of the boiler vessel in order to facilitate the withdrawal of fluids from the equipment. A buffer vessel, adapted to the head of the column, connects the equipment to a vacuum pump used in the drying steps of the cleaning routines. Temperature in the boiler is adjusted using a 230V/740W glass immersion heater (QVF Engineering). Tap-water was used as the cooling medium in the condenser.
Along the body of the NORMAG column, measurement and control of temperatures were carried out by an IBP-controller running the 1.01 version of LAS-KONTI (a controlling software provided by Bayer AG). Four-wired PT100, calibrated with a TP 28 200S thermoblock (SIKA), were used in the equipment as temperature sensors. Regulation of temperature in the boiler was achieved through a PID controller with constants $K_p=160$, $K_i=40$ and $K_d=15$, determined with the Ziegler-Nichols method (Ziegler and Nichols, 1993). Figure 4.8 illustrates the assembled pilot-plant unit housed in a metallic frame in the test hall of the department and the used IBP-controller unit.
Figure 4.8: Distillation pilot-plant unit (a) and IBP controlling unit (b).
4.2 Material systems

In order to eventually evaluate the performance of MDSTAGE in the description of a stationary operation of a distillation column, a reliable set of experimental data had to be obtained. This level of quality was ensured in this work by means of a two-step approach in the acquisition of experimental information. While the initial step aimed at the standardization and optimization of the experimental methodology, the second one, using the aforementioned procedures, focused on the acquisition of the experimental information necessary to the evaluation of the simulation results.

Two distinct chemical systems were used in this methodology. The binary standard test system chlorobenzene/ethylbenzene was used to evaluate the performance of the NORMAG distillation column, while distillation runs of the ternary test system cyclohexane, n-heptane and iso-octane provided the experimental information necessary to the later investigation of MDSTAGE.

The binary standard test system chlorobenzene/ethylbenzene was chosen out of a list of twelve standard test systems recommended by Onken (1990) for investigation of distillation columns. The reasons for choosing this system were:

- Both chemicals and their mixtures presented appreciable chemical stability against air, humidity and light
- Distinguishing physical properties of the species like densities and refraction indexes ensured the possibility to application of straightforward analytical methodologies in the quantification of samples
- The standard test system chlorobenzene/ethylbenzene also provided a high number of theoretical stages available to measurement in the distillation runs, due to values of relative volatility nearing unity along the whole range of compositions of their mixtures.

A summary of the physical properties and hazard information about the standard test system chlorobenzene/ethylbenzene is given in table 4.1.
Table 4.1: Physical properties of the standard test system chlorobenzene and ethylbenzene

<table>
<thead>
<tr>
<th>Properties</th>
<th>Chlorobenzene</th>
<th>Ethylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS</td>
<td>-</td>
<td>108-90-7</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>$\text{C}_6\text{H}_5\text{Cl}$</td>
<td>$\text{C}<em>8\text{H}</em>{10}$</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>g/mol</td>
<td>112.56</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm$^3$</td>
<td>1.11</td>
</tr>
<tr>
<td>Melting point</td>
<td>°C</td>
<td>-45.0</td>
</tr>
<tr>
<td>Boiling point</td>
<td>°C</td>
<td>131.0</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>29.0</td>
</tr>
<tr>
<td>Vapour pressure [20°C]</td>
<td>hPa</td>
<td>11.7</td>
</tr>
<tr>
<td>Refraction index</td>
<td>-</td>
<td>1.5246</td>
</tr>
<tr>
<td>Occupational exposure limit</td>
<td>mg/m$^3$</td>
<td>47.00</td>
</tr>
<tr>
<td>R-Phrases</td>
<td>-</td>
<td>R10,R20,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R51/53</td>
</tr>
<tr>
<td>S-Phrases</td>
<td>-</td>
<td>S24/25,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S61</td>
</tr>
</tbody>
</table>

In the case of the ternary test system cyclohexane, n-heptane and isooctane, limitations on the numerical approach, chemical properties of the single species and thermodynamic and transport properties of the mixture were the main guidelines used in the choice of the components.

The molecular sizes of species set an upper limit in the choice of chemicals due to its direct correlation with the numerical costs of molecular simulations, when these, as in this work, are based on a functional-group approach for the description of species. Volatility and normal boiling points of single components and their mixtures constrained practical aspects of the experiments, due to operative limitations of the equipment used. Highly volatile species or those showing unusually high normal boiling points were deliberately avoided in the definition of the investigated system, due to safety concerns and technical drawbacks of the apparatus. Chemical stability and mutual affinity of the species was also regarded, in order to avoid the generation
of unstable or azeotropic systems. From all the evaluated components, the system cyclohexane, n-heptane and isoctane completely fulfilled the aforementioned technical prerequisites. The thermodynamic and transport characteristics of the mixtures of cyclohexane, n-heptane and isoctane also provided further supporting aspects for the choice of this set as the test system of this work.

Dealing with the distillation of ternary mixtures, residue- and distillation-curve maps offer a straightforward way to oversee the efficiency of the separation process (Stichlmair, Fair, 1998). Per definition, residue curves describe the changes in the liquid concentration in the still of an open distillation unit; distillation curves depict, on the other hand, the path followed by the composition profile of a rectification column, where all stages operate under equilibrium conditions i.e. the composition increment between two consecutive stages resembles the length of an equilibrium step for an investigated system. Supporting the investigation rectification experiments in this work, distillation-curve maps are used as guidelines in the evaluation of the collected experimental data. Figure 4.9 presents the distillation-curve map for the ternary system cyclohexane, n-heptane and isoctane calculated with the UNIQUAC method, as reported in appendix 7.1, and parameters from the Aspen Plus® simulation package.

Figure 4.9 illustrates the pattern of the distillation lines for the system cyclohexane, n-heptane and isoctane. The absence of converging regions, either in the middle of the map or in the middle of the binary segments, stands to a well-behaved system without immiscible regions or azeotropic compositions. The distilled composition in any series of single-staged distillations lying on one of the distillation curves of figure 4.9 will naturally head towards an enrichment of the volatile component of the system i.e. towards the cyclohexene-rich region of the map. With a slight curvature near the low cyclohexane region, all distillation curves for the cyclohexane, n-heptane and isoctane system are well-behaved functions of the composition of the system.
Mass transport effects also granted supporting arguments for the choice of cyclohexane, n-heptane and isooctane as the test system for this work. Concentration gradients of these species in their liquid mixtures are able to induce diffusion cross-effects in mass-transfer processes. A diffusion cross-effect is the influence of the composition gradient of a species \( j \) on the diffusion or mass transfer of a species \( i \). In distillation processes these phenomena directly affect the separation efficiency and therefore the performance of the equipment. Compared to the standard magnitude of diffusivities in multicomponent liquid mixtures (\(10^{-9} \text{ m}^2/\text{s}\)), these effects should only be neglected in cases where the off-diagonal terms of the matrix of diffusivities, \( D_{ij,i\neq j} \), fulfill the condition \( D_{ij,i\neq j} \ll 10^{-9} \text{ m}^2/\text{s} \) (Taylor, Krishna, 1993). The values of the off-diagonal Maxwell-Stefan diffusivities, \( D_{ij,i\neq j} \), calculated for the system cyclohexane, n-heptane and isooctane with the correlation proposed by Kooijiman and Taylor (1991), listed in appendix 7.2 are illustrated in figure 4.10. The graphic in figure 4.10 sketches the strong dependence of the diffusivities \( D_{ij,i\neq j} \) on the composition of the system cyclohexane, n-heptane and iso-octane.
isoctane. It shows, for this specific case, the non-fulfilment of the aforementioned condition and indicates that the influence of cross-diffusion effects on the performance of the equipment should indeed be taken in account.

The influence of diffusion cross-effects on the performance of distillation columns is in general not easily accounted for in the mathematical investigation of the operation and considerably increases the levels of complexity of the applied models. Although not representing an off-the-shelf option in industrial practice, complex modelling approaches like the rate-based model, as explained in chapter two, remain a unique option in cases where such effects may no longer be discarded. The possibility of examining the performance of MDSTAGE on the investigation of a system with such effects was also a supporting argument for the choice of cyclohexane, n-heptane and isoctane as the test system for this work. A summary of physical properties and hazard information about this system is given in table 4.2.

![Figure 4.10: Off-diagonal diffusion coefficients, \( D_{ij} \), for a liquid mixture of cyclohexane (1), n-heptane (2) and isoctane (3).](image-url)
Table 4.2: Physical properties of the test system cyclohexane, n-heptane and iso-octane

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>CAS</td>
<td>-</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>-</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>°C</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
</tr>
<tr>
<td>Vapour pressure [20°C]</td>
<td>hPa</td>
</tr>
<tr>
<td>Occupational exposure limit</td>
<td>mg/m³</td>
</tr>
<tr>
<td>R-Phrases</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>S-Phrases</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All chemical species used in this work had analytical quality with levels of purity higher than 99%. While chlorobenzene, ethylbenzene, n-heptane and iso-octane were provided by Merck®, cyclohexane was provided from Emplura®.

4.3 Experimental procedure

Acquisition of experimental information in the NORMAG distillation unit demanded a methodical preparation of the equipment as well as strict routines of collection and analysis of the samples. The core concepts of the cleaning, preparation and sampling procedures of the distillation unit detailed in this section were defined after standard praxis and know-how won and documented in the department over time (Lerlertwanich, 2003; Sotillo Gómez, 2004; Betz, 2005). In the forthcoming
paragraphs, a concise overview of these procedures is offered where their main steps are addressed and explained. Ultimately, a brief discussion about the analytical methodology applied in the discrimination of the samples is also outlined.

The cleaning and preparation procedures of the equipment comprised a washing and a drying step. Initially, any residual liquid from previous distillation runs was drained out of the column. Thereafter, the inner equipment was washed from the top to the bottom with bi-distilled water, three times in a row. The boiling vessel was subsequently filled with bi-distilled water and the column was brought to operation. A run of two hours in stationary conditions was carried out. Ultimately, after cooling down, the equipment was drained out once again. The same washing procedure was then repeated but replacing the bi-distilled water with acetone (provided by Merck® with analytical quality and levels of purity higher than 99%). At the end of this step, after draining the acetone out of the equipment, the unit was connected by the head of the column, over a buffer vessel, to a vacuum pump. Ensuring that all valves in the equipment remained opened, the distillation unit was dried overnight under vacuum. At the end of the cleaning procedure, the equipment was ready for use. The boiler was filled with the test system and the column was started up. In order to ensure stationary conditions at the sampling time, the equipment operated continuously over three hours without disturbances before any sample collection. All the experiments were performed under total reflux.

Liquid samples were collected with a sampling set made of a 5ml Luer Lock syringe, a PTFE valve, a needle (Ø: 1mm) and a Luer Lock plug, as illustrated in figure 4.11. The PTFE valves permitted the manipulation of the syringes independently of the operation of the equipment and the Luer lock plugs allowed the preservation of samples in the syringes in the meantime between collection and storage. Five of these sets were used, one for each stage of the column. These were assembled in the distillation column using a tailored external holder, depicted in figure 4.12. The needles were fixed to the sampling ports of the column with laboratory screw joints (BOLA, Grünsfeld Germany), as shown in Figure 4.13.

Figure 4.12: External holder to sampling sets.

Similarly to the rest of equipment, the syringes, valves and needles used in the collection of samples also demanded their own preparation steps. Initially they were internally washed with bi-distilled water and acetone (technical quality), repeating each step three times. The pieces were dried in sequence, firstly by flowing nitrogen (2-3 bars) through their internals and then in an oven for one hour under temperatures ranging from 40 to 45 °C.

Extra attention has also to be paid in order to avoid corruption of the collected data. During an experiment, along the transient operation of the column, small amounts of liquid could get into the needles, build a dead volume, and therefore corrupt the samples. To avoid this, an extra preparation step was carried out in the needles and syringes during the transient operation of the equipment. By disjoining the sampling syringes from the holder and connecting the valves to disposable syringes, air was repeatedly blown through the PTFE valves and needles. Altogether circa 10 ml were blown through them, three times in sequence. Afterwards all PTFE valves were closed and rejoined to the sampling syringes, remaining sealed until the scheduled sampling time after the stationary state of operation had been reached.

At the sampling time, all probes had to be simultaneously collected in order to minimize the perturbation of the already established hydrodynamic profile inside the equipment. Abrupt local changes in the head pressure of a single stage - as in the case of serial collection of probes – could lead to undesired mixing effects and consequent corruption of the collected data. Therefore, setting one person per stage, 5 ml samples were synchronously collected after an acoustic signal over the following 20 seconds. Thereupon, after sealing all PTFE valves, the syringes were loosened from the distillation unit, closed with the Luer Lock plugs and set down to be cooled to 6°C in a laboratory refrigerator FKEX 5000 (Liebherr). The cooled samples were then transferred to sealed crimp cap glasses, stored and kept under refrigeration for maximal 36 hours up to their analysis.

The analytical methods applied in the discrimination of the samples were chosen according to the physicochemical characteristics of the investigated systems. The observable difference in the densities of the single species of the binary standard test
system (chlorobenzene - ethylbenzene), used in the first part of the experimental work, allowed the use of this quantity as a measuring factor in the determination of the composition of the collected samples. In the second part of the experimental work, however, the discrimination of the species of the ternary system was based on the results of a gas-chromatographic analysis of the collected samples. Specific information about the applied analytical methods and the equipment used is given in appendix 7.3.

4.4 Experimental data

The following paragraphs report the experimental data set collected in this work as described in the aforementioned sections. The results, gathered for both investigated systems, are presented and discussed.

4.4.1 Acquisition of experimental data of a binary system for evaluation of the performance of the NORMAG distillation column

As previously outlined, experiments with the binary standard test system chlorobenzene / ethylbenzene aimed to investigate the performance of the NORMAG distillation column and establish the experimental methodologies applied in this work. Parallel to that, as a guiding parameter to the quality of the results, the performance of the equipment was also investigated. It is worth noting that both goals were not independent from each other, for only through excelling the experimental methodology, as described in the former sections, could the equipment be brought to its optimal efficiency. In the distillation of binary systems, previous investigations with the NORMAG column (Lerlerwanich, 2003; Sotillo Gómez, 2004; Betz, 2005) have examined the performance of the equipment evaluating its Murphree stage efficiency ($\eta$) (Treyball, 1980):

$$\eta_{Murphre,n} = \frac{y_{i,n} - x_{i,n}}{y^* - x_{i,n}}$$

(4.1)
and obtained values of mean Murphree stage efficiency ($\eta$) ranging between 0.43 and 0.73. The Murphree stage efficiency measures the efficiency of the separation in one stage, in respect to an ideal one. In equation 4.1, $x_{i,n}$ stands for the composition of the species $i$ in stage $n$ and $y_{i,n}$ for the composition of the same species in the vapor phase of the stage. The superscript * over the vapor composition $y$ denotes an ideal value, in equilibrium with the composition $x_{i,n}$.

To optimize the experimental routines, several trials were carried out striving towards a column composition profile that could reproduce those previously mentioned values of the equipment stage efficiency. After diverse runs, using the standard test system, both goals were successfully achieved. Table 4.1 reproduces a composition profile obtained along the equipment for a measurement with experimental procedures already optimized. The vapor compositions, in equilibrium with the liquid samples, were calculated using the UNIQUAC model, reported in appendix 7.1, with parameters from the Aspen Plus® simulation package. In order to compare these results with those obtained by Lerlertwanich (2003), Sotillo Gómez (2004) and Betz (2005), the mean value of the Murphree stage efficiencies was calculated. The single and mean values of the Murphree stage efficiency, given in the fourth column of table 4.3, confirmed the accomplishment of the objectives of this block of the work.

Table 4.3: Measured compositions and efficiencies over the column stages for a test with the binary system chlorobenzene-ethylbenzene.

<table>
<thead>
<tr>
<th>Stage</th>
<th>$x_{\text{chlorobenzene}}$</th>
<th>$y^{*}_{\text{chlorobenzene}}$</th>
<th>$\eta$ Murphree</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.419</td>
<td>0.448</td>
<td>0.66</td>
</tr>
<tr>
<td>4</td>
<td>0.403</td>
<td>0.432</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>0.387</td>
<td>0.414</td>
<td>0.59</td>
</tr>
<tr>
<td>2</td>
<td>0.369</td>
<td>0.395</td>
<td>0.69</td>
</tr>
<tr>
<td>1</td>
<td>0.360</td>
<td>0.385</td>
<td>0.37</td>
</tr>
<tr>
<td>Mean Efficiency ($\eta$)</td>
<td></td>
<td></td>
<td>0.57</td>
</tr>
</tbody>
</table>
4.4.2 Acquisition of experimental data of a ternary system for evaluation of simulation results

In the second part of experimental data acquisition, a specific distillation curve of the system cyclohexane, n-heptane and isoctane was investigated. The selection of one of the curves in the distillation curve map of the system was based on general aspects of the map as well on the influences of the cross-diffusivity effects of one species over the others.

As previously shown in figure 4.9, composition profiles obtained in the distillation of any mixture of cyclohexane, n-heptane and isoctane would lie along segments of distillation curves joining the cyclohexane vertex and the opposite base of the ternary diagram of the system. Except in the case of distilling mixtures with mean compositions lying at the very bottom of the ternary diagram, where distillation curves presented a characteristic curvature, any composition profile obtained in the distillation of ternary mixtures of the investigated system would standardly stretch itself towards the same direction in the ternary diagram. Therefore, the relative location of a distillation curve within the ternary diagram of the system did not constrain the selection criteria for choosing one of them for investigation. The relevant role played in the selection of a distillation curve was eventually carried by the expected influence of cross-diffusivities, $D_{ij}$, on the system. As illustrated in figure 4.10, the isoctane-poor region on the ternary diagram of the system is characterized by a higher variation of the absolute values of the cross-diffusivities relative to each other. According to Cussler (1976) and Taylor and Krishna (1993), such accentuated variation characterizes this zone as one, where the influences of cross-diffusive phenomena over diffusion and mass transfer effects are to be expected and therefore, in terms of testing the potential of the capabilities of MDSTAGE, are an interesting region for examination. Based on this and as outlined in figure 4.14, the right side of the ternary diagram of the system was chosen for the experimental investigations of this work.
Figure 4.14: Region in the ternary diagram of the system cyclohexane, n-heptane and iso-octane investigated in this work.

Over the ternary diagram, two distinct trends characterized the general shape of the distillation curves: a continuous segment crossing the ternary diagram monotonically towards the cyclohexane vertex and a smoothly curved segment at the base of the diagram. In the scope of this work, distillation experiments were carried out in both trend-zones following the experimental methodology described in previous sections of this chapter. For each zone, a previously prepared 20L reserve solution, stored in polyethylene canisters, ensured the supply of a common system in each one of the single distillation runs. Standardly, four liters of the solution were used in each run. The solutions were prepared with the aid of digital scales from OHAUS (Models Adventure Pro and Pioneer, with readabilities of 0.01g and 0.0001g respectively). The final composition of both reserve solutions obtained by gas-chromatographic analysis, as described in appendix 7.3, is depicted in figure 4.15. The experimental results obtained in multiple distillation runs of the two reserve solutions are presented in figure 4.16.
Figure 4.15: Final compositions of the two reserve solutions used in the distillation runs at the upper (a) and lower (b) trend-zones of the distillation curves.
Figure 4.16: Experimental data obtained from multiple runs on the upper (a) and lower (b) trend-zones of the distillation curves.
In figure 4.16, the composition profiles along the five stages of the NORMAG distillation column obtained in different experimental runs are reported together with the initial mean composition of the reserve solutions in both investigated trend-zones. The information presented in figure 4.16.a, describing the investigation of the continuous central segment of the distillation curves, exhibited well-behaved profiles, showed good reproducibility within the three presented runs, matched the expected tendency of the distillation curves in this trend-zone and, in relation to the initial composition of the reserve solution, showed the enrichment on cyclohexane along the stages of the column. The same, however, cannot be told about the results shown in figure 4.16.b.

Compared to the results presented in figure 4.16.a, the experimental investigation of the lower trend-zone of the distillation curves, reported in figure 4.16.b, produced results markedly more distinct. The lack of similarity among the four presented profiles is one of the first aspects immediately noticed when observing the results of this trend-zone. The composition profiles obtained in the lower trend-zone of the distillation curves did not show the same level of reproducibility as their previous pairs, despite stretching themselves along a common direction, similar to that predicted by an adjacent distillation curve. A second distinctive characteristic of the results in this region is the relative location of the initial composition of the reserve solution in relation to the measured composition profiles. In contrast to the upper region, the composition of the reserve solution lies approximately in the middle of the observed results. Despite the initial thought that such an unusual pattern is indicative of methodological or analytical failure during the experiments, an investigation of its plausibility was made and led to a supporting explanation of the results.

Assuming that, for the investigated system, the hexane vertex would represent the top of the ternary diagram, the lower trend-zone of the distillation curves would be located at the very bottom of the diagram. In addition to that and as already shown in table 4.2, cyclohexane is also the most volatile species present in the ternary system. Under these circumstances, by the investigation of the lower trend-zone, not only must the fact that small traces of cyclohexane available in the solution initially fed into the equipment be taken into account, but also its favored tendency to leave the boiler vessel due to its higher fugacity.
In order to evaluate the extension of cyclohexane separation at the boiler vessel of the NORMAG column, a material sample was collected at the boiler during the stationary distillation of a solution specific to investigate the lower trend-zone of the distillation columns. The acquisition of this sample followed the same procedures reported in section 4.3, using the sampling sets depicted in figures 4.11 and 4.13. The gas-chromatographic analysis of this sample revealed no traces of cyclohexane to be found in the boiler vessel during the stationary operation of the distillation column. Practically it showed that, under the investigated conditions, all the cyclohexane was in fact to be found in the body of the column and that its distribution over the stages of the column would therefore be more sensitive not only to the stationary thermic and hydrodynamic conditions of the equipment but also to perturbations of it during the sampling time. This observation eventually explained, on the one hand, the relative location of the initial composition of the reserve solution and on the other the singular shape of each one of the observed profiles.

The experimental results presented in figure 4.16 build the experimental base of information available for the evaluation of MDSTAGE. In the scope of this work, regarding the applied approach of the investigation, the focus of such an evaluation lies explicitly on the capacity of the simulation tool to reproduce patterns experimentally observed and not on the exact reproduction of absolute values dependent on specific conditions in each one of the data sets. Based on this, there would be no reason to evaluate single distillation runs presented in figures 4.16.a and 4.16.b claiming thereby to evaluate general aspects of MDSTAGE. Taking into account that, specific to each of the investigated trend-zones, all composition profiles in figure 4.16 were obtained by distillation of separate portions of the same reserve solution, the averaged measured compositions in each one of the stages turns out in this case to be a valid technique of data treatment in order to emphasize the data tendencies in each of the investigated zones. These new average profiles for both investigated regions are sketched in figure 4.17
Figure 4.17: Average composition profiles for the upper (a) and lower (b) trend-zones of the distillation curves.
In figure 4.17.a, the average composition profile in the upper trend-zone, resembling the information in figure 4.16.a, also exhibited a well behaved shape and matched the tendency of the adjacent distillation curve as well. Accordingly, the average profile at the lower trend-zone of the distillation curves depicted in figure 4.17.b, despite its smoother shape, still resembles the lack of reproducibility of the original data. In addition to the average composition profiles in figure 4.17, their adjacent distillation curves also display the composition increments expected in each stage, assuming they would per definition operate with a Murphree stage-efficiency equaling unity, as defined in equation 4.1. The ideal increments in each distillation curve were calculated using the UNIQUAC model, with parameters reported in appendix 7.1. Compared to the ideal increments in the distillation curves, the extent of separation in each one of the stages of the average profiles directly reveals deviations from the assumption of unit stage-efficiency. These deviations, mirroring the imperfect operation of real distillation columns, provide however an excellent set of conditions for the evaluation of MDSTAGE, under which the simulation tool would be demanded to cope not only with the thermodynamic aspects of the unit operation but also with the dynamic phenomena related to it. A summary with the actual Murphree stage-efficiency for all species in each one of the stages in figures 4.17.a and 4.17.b is provided in appendix 7.4.
5 Evaluation and discussion of simulations with MDSTAGE

Having reported in the previous chapters the theoretical and experimental backgrounds necessary to the present investigation, an evaluation of the functionalities of MDSTAGE will now be presented and discussed. Heading towards the main goal of this work, general and specific aspects of MDSTAGE will be examined. While on a general level of inspection, the simulation tool will be evaluated as a standard algorithm for molecular-dynamic simulations, the focus, on the specific level of examination, will be laid on the competence of the code to reproduce general macroscopic characteristics of real-world processes and the operation of a NORMAG distillation column based on the experimental results reported in chapter four.

5.1 Initial examination of the functionalities of MDSTAGE

Conceived to evaluate the possibility of the direct simulation of unit operations on the molecular level, MDSTAGE inevitably expanded the scope of ordinary molecular-dynamic simulations. Through its modular assembling of the simulation space and the mimicking of macroscopic phenomena, MDSTAGE settled an original and general approach of investigation to molecular and macroscopic phenomena. In order to evaluate primary functionalities of the algorithm, two case studies will be initially reported. These studies focused on the examination of fundamental aspects of the simulation tool – i.e. its numeric stability and main capabilities of the code. At first, in order to evaluate MDSTAGE as a standard tool for molecular-dynamic simulations, the prediction of the vapor-liquid equilibrium of a simple substance is examined. Next in order, evaluating the tailoring of the simulation space provided by MDSTAGE, an investigation of diffusion along a diffusion path is carried out.
5.1.1 Molecular-dynamic investigation of the vapor-liquid equilibrium of one-center Lennard-Jones (1CLJ) Argon molecules

Knowledge of the vapor-liquid equilibria (VLE) of pure substances and their mixtures is an ordinary demand in the work of chemical engineers (Vahid et al. 2008). Tough providing an excellent set of correlation tools, conventional methods for the calculation of VLE, such as equations of state and G^E models, frequently lack on predictive power due to an insufficient physical foundation of their approaches (Vrabec et al. 2001). Therefore, VLE predictions for specific multi-component systems remain further on a demanding field of investigations (Vrabec et al. 2009a,b; Domínguez et al. 2013; Nala et al. 2013; Nandi et al. 2013).

On the other hand, as previously observed in chapter two, molecular simulations have opened a new path to the acquisition of such information, where thermodynamic predictions are directly derived from correlations between the investigated phenomena and its origins in the realm of molecular interactions. Regarding the molecular investigation of pure substances, some systems have become established standard references after the extensive research invested in them. An example of such a substance is argon, which appears pragmatically as a standard example in reference literatures regarding the fundamentals of molecular simulation (Allen and Tildesley 1987; Todd 2010). Resting upon this fact, the prediction of the vapor-liquid equilibrium for argon has been chosen as the initial task on the examination of the functionalities of MDSTAGE. Direct comparison against empirical information obtained in literature will evaluate the quality of the predictions made by MDSTAGE.

VLE investigations reported by Trokhymchuck and Alejandre (1999), Mecke et al. (2001) and Inzoli et al. (2010) have guided and shaped the methodological approach of this section. In their reports, VLE conditions have been examined within a single simulation space through investigation of a stable liquid film in simultaneous and dynamical equilibrium with a vapor phase. Molecules have been initially allocated in the central section of an orthogonal parallelepiped-shaped simulation space, in order to provide favorable conditions for the establishment of the liquid-vapor equilibrium along the stationary period of the simulation. Except for the central section of the
simulation space, no molecule has been allocated in the remaining volumes of the simulation space. Figure 5.1 illustrates the three layered configuration of the simulation space generated by in approach at the beginning of the simulation: a central section, allocating the molecules for the simulation, and two neighboring empty sections along the longitudinal axis of the simulation space. Periodic boundary conditions (PBC) were applied throughout the simulation space. The allocation of the molecules in the central section of simulation space was based on the same concept of elementary unit cells, as reported in chapter three.

Figure 5.1: Profile of the initial configuration of the simulation space by the VLE investigations of Trokhymchuck and Alejandre (1999), Mecke et a.l, (2001) and Inzoli et al. (2010).

With parameters reported in table 5.1, argon molecules were described in this investigation by the one-center Lennard-Jones (1CLJ) molecular potential reported by Vrabec et al. (2001). Experimental data corroborating the conditions investigated in this subchapter were reported by Din (1956) and, providing VLE-information within the temperature range of 90.00K and 137.64 K, cover a considerable extension of VLE-conditions. A summary of these data are reported in appendix 7.5.
Table 5.1: Lennard-Jones parameters used in the investigation of the VLE of Argon

<table>
<thead>
<tr>
<th>Component</th>
<th>( \sigma ) [nm]</th>
<th>( \epsilon/k_B ) [K]</th>
<th>( M ) [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>0.33952</td>
<td>116.79</td>
<td>39.95</td>
</tr>
</tbody>
</table>

Along the stationary period of the simulations, the number of unit cells defining the dimensions of the simulation space and the initial central section of molecules directly influenced the establishment of a stable dynamic between the liquid and vapor phases. Width, height and depth of the simulation space as well the number of molecules initially filling its central section were therefore the subject of a previous investigation in order to specify an appropriate geometry, which suited the scope of the investigation. Concluding this initial examination, a set of 10, 10 and 18 unit cells defining the x, y and z axis of the simulation space proved to be an appropriate geometry against the scopes of the current VLE investigation. Simulations with 2400 argon molecules were able to generate a stable liquid film along the whole simulation and defined therefore the number of molecules used in the simulations of this section. As already observed, these 2400 molecules were initially positioned in the middle section of the simulation space following the allocation procedures reported in chapter three. The central section of the simulation space accommodating these molecules occupied 10, 10 and 6 unit cells along the x, y and z axis respectively. Figure 5.2 sketches the dimensions of the simulation space used in the simulations of this section.

VLE simulations in this section were performed under microcanonic conditions – i.e. under a constant number of elements, volume and total energy of the system. In further agreement with the reports of Trokhymchuck and Alejandre (1999) and Mecke et al. (2001) 130000 steps were simulated with a timestep of 3.0 fs. Scaling of temperature took place every 200 steps along the first 50000 steps of the simulation. A general overview of the main setup of the simulations of this section is summarized in Table 5.2. The results obtained in the investigations of the VLE of Argon are depicted by figures 5.3 through 5.7.
Figure 5.2: Sketch of a simulation cell used in the investigation of the vapor-liquid equilibrium of argon.

Table 5.2: Simulation parameters in the investigation of the VLE of Argon

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions of the simulation space in unit cells [x,y,z]</td>
<td>[10,10,18]</td>
</tr>
<tr>
<td>Number of molecules in simulation space</td>
<td>2400</td>
</tr>
<tr>
<td>Time step</td>
<td>3 fs</td>
</tr>
<tr>
<td>Number of simulated steps</td>
<td>130000</td>
</tr>
<tr>
<td>Number of simulated steps in equilibration phase</td>
<td>50000</td>
</tr>
<tr>
<td>Number of simulated steps in evaluation phase</td>
<td>80000</td>
</tr>
</tbody>
</table>

For neither feed- nor product-streams have been assembled on the structure of the simulation space, periodic boundary conditions ensured the conservation of the number of simulated molecules. Fixed geometry also guaranteed the invariability of the internal volume of the simulation space. As reported in table 5.2, relaxation of the initial conditions took place over the initial 50000 steps of the simulation, providing
the necessary time for establishment of a stationary dynamics within the molecules of the simulation space. Figures 5.3 and 5.4 illustrate respectively the evolution of the total energy and temperatures of the simulated systems over the whole extension of the simulations. In specific, figure 5.3 authenticates the microcanonic constraint regarding the stability of the internal energy of a simulated system. Fluctuations on the quantities depicted in figures 5.3 and 5.4 correlate with the characteristic dynamical equilibrium between liquid and vapor phases established along the progress of the simulations. Reporting an acceptable level of agreement between empirical and simulated quantities for each simulated condition, figures 5.5 and 5.6 depict the predictions generated with MDSTAGE for liquid- and vapor densities as well their respective saturation pressures. Reference values for densities and saturation pressures used in the evaluation of results were reported by Din (1956) and are listed in appendix 7.5.

Figure 5.3: Total energy of the simulated systems in the investigation of the VLE of argon
Figure 5.4: Temperatures of the simulated systems in the investigation of the VLE of argon

Figure 5.5: Vapor-liquid phase diagram for argon generated by molecular dynamic simulations with MDSTAGE.
Figure 5.6: Saturation pressure of argon simulated by MDSTAGE.

Under VLE conditions, the closer a system with constant amount of material approaches its critical conditions, the smaller will be the amount of molecules building the liquid film in equilibrium with the vapor phase is (Walas 1985). Besides well-behaved systems with defined and stable liquid films in the middle of the simulation space, the results reported in this section did also depict the aforementioned restraints of a closed system- i.e. the temperature-conditioned shrinking of the liquid film within the simulation space. Density profiles along the z-axis of the simulation space of figure 5.2, evaluated over the last 80000 steps of the simulation, are presented in figure 5.7. Recalling that all the simulations were performed with fixed number of molecules (2400), the density profiles depicted in figure 5.7, illustrating the temperature-conditioned shrinking of the liquid phase, confirm the expectations towards the behavior of the examined systems.
Figure 5.7: Stationary density profiles along the simulation space for the simulated conditions

With the results of the VLE investigation of argon reported in this section, the primary aims of the MDSTAGE evaluation were successfully achieved. In terms of the fundamental characteristics of the algorithm, the accomplished reproduction of selected conditions from an experimental data set ensured the preservation of its basic functionalities as standard software for molecular-dynamic simulations.

5.1.2 Molecular dynamic investigation of characteristic curvatures in composition profiles of ternary liquid mixtures along diffusion paths

Continuing the evaluation of the general properties of MDSTAGE, extra properties of the algorithm are now added to the simulations in order to further examine core features of the tool. In this section, in order to evaluate diffusion patterns of a generic ternary system along a diffusion path, the performance and effectiveness of the tailored assembling of the simulation space and the implementation of macroscopic effects on molecular scale are put under scrutiny. This evaluation is based on a previous study carried out by Schott (2005), who examining diffusion-induced
interfacial instabilities in liquid-liquid extraction systems reported a correlation between the investigated phenomena and the establishment of local characteristic composition profiles. Here, using a MDSTAGE-based approach of investigation, the repeatability of Schott’s results on molecular scale is going to be examined. In order to optimally situate the reader on the main scope of this section, a summary of Schott’s selected results is provided next.

**Diffusion-induced interfacial instabilities in liquid-liquid extraction systems**

Depending on the involved species, the presence of composition gradients in the bulk of ternary liquid mixtures may frequently lead to curved composition profiles within the compositions bounding the examined system (Taylor and Krishna 1993). By triggering instabilities in the interfacial region of a biphasic system (Schott 2005) and therefore affecting the rate of interphasic mass transfer (Henschke and Pfennig 1999), this phenomenon plays an important role in the study of liquid-liquid extraction. Figure 5.8 illustrate this argument the results reported by Schott and Pfennig (2004) in the investigation of composition profiles along a diffusion path for biphasic liquid systems. Outlined in this figure, two composition gradients, nearing the interphasic limit, lay in the homogeneous region. In both cases, a curved composition profile is established between the ends of the composition gradients. However, while one of the profiles stretches wholly in the homogeneous zone, the other crosses the boundaries of the biphasic region. The last case exemplifies the triggering mechanism of nano-drop formation and interfacial instabilities as investigated by Schott (2005) in his work: Once a specific stability limit has been passed while holding one of the boundaries of the composition gradient constant, the resulting composition profile steps irredeemably into the two phase region, causing therefore a local phase separation of the previously homogenous system.

In his work, Schott (2005) primarily examined and modelled the occurrence of such instabilities in biphasic liquid mixtures. Schott’s approach towards the explanation of the phenomena followed both experimental and theoretical paths. His theoretical investigations were fundamentally based on comparisons between classical methods of description: Fick and Maxwell-Steffan theories and molecular approaches of description based on Monte-Carlo simulations. Now, using the molecular-dynamic
approach of MDSTAGE, the same investigation is revisited intending to simultaneously evaluate the capacity of the algorithm in reproducing Schott’s observations and also consolidate the predictive potential of the tool.

Figure 5.8: Characteristic curvatures in composition profiles along a diffusion path for a specific ternary liquid mixture, Schott and Pfennig (2004).

The MDSTAGE approach

The initial task in the MDSTAGE approach was the definition a reliable set of molecular-dynamic parameters resembling the theoretical system investigated by Schott (2005) in his Monte-Carlo simulations. As already reported, intermolecular interactions are described in MDSTAGE with the aid of the geometry-, $\sigma$, and energy parameters, $\varepsilon$ of the Lennard-Jones potential. In the lattice-based methodology of Schott (2005), however, interactions between two molecules were described by a single energy parameter, $\Omega_{i,j}$, characterizing the amount energy necessary to the exchange of their positions within the simulated lattice. The values of the parameters $\Omega_{i,j}$ reported by Schott are given in table 5.3.
Table 5.3: Interaction energies for the theoretical ternary system with species A, B and C, as reported by Schott (2005).

<table>
<thead>
<tr>
<th>Interaction energy</th>
<th>[J/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w_{A,B}$</td>
<td>0</td>
</tr>
<tr>
<td>$w_{A,C}$</td>
<td>-1995</td>
</tr>
<tr>
<td>$w_{B,C}$</td>
<td>2993</td>
</tr>
</tbody>
</table>

In the MDSTAGE-approach, equivalent values for the Lennard-Jones energy parameters, $\varepsilon$, were the first quantities derived for the investigation. The starting point for the determination of these values was a direct correlation between the lattice interaction energies, $\Omega_{i,j}$, and the Lennard-Jones energy parameters, $\varepsilon$, for 1CLJ-molecules, reported by Schott (2005):

$$\Omega_{i,j} = \varepsilon_{i,j} + \varepsilon_{j,i} - \varepsilon_{i,i} - \varepsilon_{j,j}$$  \hspace{1cm} (5.1)

Recalling that $\varepsilon_{i,j} = \varepsilon_{j,i}$ and using the set of $\Omega_{i,j}$ given in table 5.3, equation 5.1 defines a system of three equations with six unknown variables. In order to solve this set of equations, three independent equations relating the values of $\varepsilon_{i,j}$, $\varepsilon_{i,i}$ and $\varepsilon_{j,j}$ had to be added to the system. The Lorentz-Berthelot mixing rules for the energy parameter of the Lennard-Jones potential (Allen and Tildeslay, 1987) provided the missing correlations:

$$\varepsilon_{i,j} = \eta_{i,j} \sqrt{\varepsilon_{i,i} \varepsilon_{j,j}}$$  \hspace{1cm} (5.2)

Although adding three independent correlations between the values of $\varepsilon_{i,j}$, $\varepsilon_{i,i}$ and $\varepsilon_{j,j}$, the Lorentz-Berthelot mixing rule also brings three new variables in the system, namely the mixing parameters $\eta_{i,j}$. The Lorentz-Berthelot mixing coefficient $\eta_{i,j}$ for the Lennard-Jones energy parameter $\varepsilon$ scales the interaction energy between
molecules adjusting the molecular potential between them. In general, \( \eta_{i,j} \) equals unity in two distinct cases: when \( i = j \), or in systems with isotropic intermolecular interactions. In other cases, \( \eta_{i,j} \) deviates from unity both with positive or negative increments (Allen and Tildeslay 1987). Data-fitting is the commonly applied methodology to the definition of the optimal values of \( \eta_{i,j} \) to be used for any specific system (Vrabec et al. 2009). In this section, this approach is however not applicable due to the theoretical character of the investigated system. A set of ad hoc values for \( \eta_{i,j} \) were therefore defined and used in the examination with MDSTAGE. The specification of values for \( \eta_{i,j} \) followed guidelines, which minimally resembled the fundamental characteristics of the system investigated by Schott (2005). The guidelines for the specification of values were given by Taylor and Krishna (1993) who related the general occurrence of the characteristic composition profiles examined by Schott (2005) to deviations of the investigated liquid system from the concept of an ideal liquid mixture – i.e. a liquid mixture obeying Raoult’s law. Deviations from an ideal liquid mixture are standardly evoked by the anisotropy of molecular geometries and intermolecular interactions among the molecules of the investigated liquid system. In this section, the choice of values for \( \eta_{i,j} \) was based on the composition gradients and region of the A-B-C ternary diagram investigated.

Diffusion processes are consequence of chemical-potential gradients driving the mass transfer phenomenon. In this section, the driving force for the examined diffusion processes is provided by a composition gradient of the species across the ends of the diffusion path. While component-specific quantities have not been yet defined, the choice of the species defining this composition gradient is not bounded to any constraint. Components A and B have been therefore chosen to be under the influence of a composition gradient along the examined diffusion path. Under no influence of an own composition gradient, component C is also impacted by the diffusion of the species A and B due to cross-diffusion effects, which eventually also contribute to deviations of the system from an ideal-mixture behaviour (Taylor and Krishna, 1993). Enhancing cross-diffusion effects and thereby providing the missing parameters of equation 5.2, anisotropic intermolecular interactions between component C and species A and B have been ensured by deviation of their mixing-
factors $\eta_{i,j}$ from unit, as reported in table 5.4. In the present examination, $\eta_{A,C}$ and $\eta_{B,C}$ were assigned with 0.5 and 1.8, respectively, in order to place in the simulated system a higher chemical affinity between B and C-molecules.

Table 5.4: Mixing-rule parameters, $\eta_{i,j}$, for the examined ternary system.

<table>
<thead>
<tr>
<th>$\eta_{i,j}$</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_{A,B}$</td>
<td>1.0</td>
</tr>
<tr>
<td>$\eta_{A,C}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\eta_{B,C}$</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Inserting the aforementioned values of $\eta_{i,j}$ into equations 5.2 and 5.1, the energy parameters $\epsilon_{i,i}$ of the Lennard-Jones potential for species A, B, and C were calculated and are reported in table 5.5.

Table 5.5: Calculated energy parameters, $\epsilon_i$, of the Lennard-Jones potential for the theoretical species A, B and C.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_i [K]$</td>
<td>189.02</td>
<td>189.02</td>
<td>281.75</td>
</tr>
</tbody>
</table>

Geometry parameters $\sigma_i$ for the species A, B and C were obtained with the aid of a linear correlation between $\epsilon_i$ and $\sigma_i$ based on data for 1CLJ molecular models provided by Bretsznajder (1971), see appendix 7.6:

$$\sigma_i [Å] = C_1 \cdot \epsilon_i [K] + C_2$$

(5.3)
Constants $C_1$ and $C_2$, in equation 5.3, are reported in table 5.6. Geometry parameters $\sigma_i$ obtained with equation 5.3 for the examined ternary system are reported in table 5.7.

Table 5.6: Parameters for the $\sigma(\varepsilon)$ correlation in equation 5.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$ [Å/K]</td>
<td>0.0081</td>
</tr>
<tr>
<td>$C_2$ [Å]</td>
<td>2.7412</td>
</tr>
</tbody>
</table>

Table 5.7: Geometry parameters, $\sigma_i$, for the Lennard-Jones potential of species A, B and C.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_i$ [nm]</td>
<td>0.427</td>
<td>0.427</td>
<td>0.502</td>
</tr>
</tbody>
</table>

Different molecular masses also directly affect the specific velocities of diffusion components in a multi-component liquid mixture and contribute further to the non-idealities of the system. On account of this, molar masses of 100 and 80 g/mol were proportionally assigned to each one of the examined species according to their geometry parameters $\sigma_i$. Together, these molecular parameters fulfill the aforementioned specifications for the occurrence of curved composition profiles along diffusion paths and characterize the aimed ternary system of 1CLJ components with anisotropic distribution of masses, size and intermolecular interactions.

In terms of the geometry of the simulation space, the concept of diffusion paths (Taylor and Krishna 1993) determined the approach used in the assembling of the simulated conditions. Again, in order to investigate the diffusion of species subject to an intermittent gradient of compositions, an orthogonal parallelepiped-shaped simulation space was defined as standard geometry for the simulations with MDSTAGE. Figure 5.9 depicts the strategy used to establish and maintain the gradient of compositions necessary to induce the diffusion of species along the longitudinal axis of the simulation space -i.e. assembling of feed and product streams at the ends of the simulation space. In order to restrain the diffusive motion of the
molecules within the simulation space, impenetrable walls were assigned to faces of the unit cells building boundaries in the system. All the other unit cells – i.e. those within the core of the simulation space and those assigned with feed or product streams at the ends of the diffusion path – were standardly defined with penetrable walls. The initial condition defined for the simulations of this subchapter is illustrated in figure 5.10: a linear profile bridging the compositions of the upper and lower feed-streams in the A-poor region of the ternary diagram. In this examination, the C-poor region of the ternary diagram was chosen for the possibility of creating a strong gradient of compositions relative to the species A and B. In order to reduce the simulation costs of investigations using MDSTAGE, Babic suggests the heuristic use of an initial configuration of the simulation space nearing a stable state of the examined system (Babic, 2011). Based on it, the use of a linear profile linking the compositions at the ends of the diffusion path was favoured over the use of a simulation space with a single isotropic composition at the beginning of the simulation. The use of a linear composition profile not only ensures simplicity for the initial condition of the simulation but also approximates the system to the investigated composition patterns – i.e. curved profiles of composition linking the extremities of the diffusion path.

Figure 5.9: Sketch of the simulation cell used in the investigation of characteristic composition profiles along a diffusion path.
As in the VLE study of argon, the dimensions of the simulation space sketched in figure 5.9 were also defined in order to optimally achieve the goals of the current investigation. For this task, a battery of test-simulations of the investigated system was carried out in order to determine the optimal dimension of the simulation space. This initial investigation showed that the investigation of stationary composition profiles along diffusion paths could be performed without detriments using 640 molecules enclosed in a simulation space with 4, 4 and 10 unit cells along the x, y and z axis respectively. Resembling the conditions investigated by Schott (2005), all simulations were performed at constant temperature (333.15 K) and covered $3 \times 10^6$ steps with a pace of 0.3 fs. For each examination, the results analysed were averaged over the last $1 \times 10^6$ steps of the simulations. A summary of the setup of the simulations is reported in table 5.8. Different rates of insertion and removal of molecules have been examined in order to co-evaluate their effects on the composition profiles of the species along the diffusion path. Meaningful results generated with flow rates of 200, 400 and 600 molecules/ns assembled at the ends of the diffusion paths, are reported in figure 5.11.
Table 5.8: Simulation parameters in the investigation of composition profiles along diffusion paths

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions of the simulation space in unit cells [x,y,z]</td>
<td>[4,4,10]</td>
</tr>
<tr>
<td>Composition of the upper feed stream [A,B,C]</td>
<td>[0.2,0.6,0.2]</td>
</tr>
<tr>
<td>Composition of the lower feed stream [A,B,C]</td>
<td>[0.2,0.2,0.6]</td>
</tr>
<tr>
<td>Number of molecules in simulation space</td>
<td>640</td>
</tr>
<tr>
<td>Time step</td>
<td>0.3 fs</td>
</tr>
<tr>
<td>Number of simulated steps</td>
<td>$3 \times 10^6$</td>
</tr>
<tr>
<td>Number of steps under temperature scaling</td>
<td>$3 \times 10^6$</td>
</tr>
<tr>
<td>Number of simulated steps in equilibration phase</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>Number of simulated steps in evaluation phase</td>
<td>$1 \times 10^6$</td>
</tr>
</tbody>
</table>

Figure 5.11: Stationary composition profiles obtained with MDSAGE for diffusion paths with a permanent gradient of composition

Characteristic curvatures have been observed for those stationary composition profiles established in the simulations with flow rates of 400 and 600 molecules/ns. In both profiles, an evident bend towards the C-rich region of the diagram supported the initial goal of the investigation in this section – i.e. the reproduction on a
molecular level of the establishment of characteristic composition profiles within diffusion processes of non-ideal systems, as previously reported by Schott (2005).

In the examined ternary system, component C has, among the other simulated species, both the highest mass and the highest Lennard-Jones size parameter, \( \sigma \). The combination of these two factors directly relates to the increment of its residence time and its eventual enrichment observed in both conditions in the middle of the simulated cell. The general shape of the composition profiles reported in figure 5.11 also correlates with the amount of flow applied at the ends of the diffusion path. Increase of the applied flow-rate stretches the observed composition profiles towards the length of the diffusion path. Such correlation is in fact an illustration of the balance between two effects characterizing the dynamics of the system: On one side, the generation of a continuous profile stretching along the diffusion path in consequence the composition gradient produced by high amounts of flow and, on the other side, mixing effects, which at lower amounts of flow dominate the dynamic evolution of the system and gradually convert it into a mixture of isotropic composition.

Illustrating the maintenance of the defined flow rates along the whole extension of the simulations, figure 5.12 depicts exemplarily for the examination with 600 molecules/ns the absolute amount of molecules leaving and entering the simulation space as a function of time. Similar curves for the examinations with 200 and 400 molecules/ns are reported in appendix 7.7. All curves depict well-behaved systems, with single flow rates continuously dampening towards those pre-defined values and reaching the desired amounts right after the first \( 1 \times 10^6 \) steps of simulation. Well-established tendencies are therefore verified throughout the whole evaluation steps of all three simulations.
Figure 5.12: Flow rates for feed and product streams generated by MDSTAGE in a simulation set for 600 molecules/ns.

General and component-specific material balances conducted within the simulation space were used to confirm the achievement of stationary conditions along the evaluation steps of the simulation, where the composition profiles reported in figure 5.11 were produced. These quantities, measuring the general and component-specific rate of material accumulation in the simulation space, are defined by:

$$\dot{N}_{net} = \sum_{j=1}^{N} v_j \cdot \dot{n}_j$$  \hspace{1cm} (5.4)

$$\dot{N}_{i,net} = \sum_{j=1}^{N} v_j \cdot \dot{n}_{i,j}$$  \hspace{1cm} (5.5)

In equations 5.4 and 5.5, the quantity $\dot{N}$ represents the net rate of accumulation of material within the simulation space at a specific time step of the simulation; $\dot{n}_j$ the rate by which molecules are carried into the simulation space by a specific stream $j$; the pre-factor $v_j$ is an integer constant, which assigns positive signs to material
flows entering the system and negative signs otherwise; and index \( i \) in equation 5.4 counts over the species present in the simulated system. In MDSTAGE simulations, where feed- and product streams are used, non-zero values of the variable \( \dot{N} \) characterize non-stationary conditions of the simulated system. Under these conditions, discrepancies between the absolute amounts of molecules inserted and removed from the simulation space generate momentary tendencies of growth or shrinkage of the system. In simulations where molecules are allowed to move freely within the simulation space and are occasionally removed after crossing a boundary assigned with a product stream property, such grow- and shrink tendencies are supposed to be observed throughout the whole course of the simulation. Eventually, after relaxation from the initial conditions and attainment of a stable system, these tendencies are supposed to dampen towards zero (in cases where stationary conditions are aimed) or otherwise any other finite quantity. For the simulations depicted in figure 5.11, the dynamic behavior of the general rate of material change, \( \dot{N} \), inside the simulation space is reported in figure 5.13. Specific net rates of material change, \( \dot{N}_i \), inside the simulation space are reported exemplarily for the component C in figure 5.14. Similar diagrams for components A and B are reported in appendix 7.7.

All curves depicted in the diagrams 5.13 and 5.14 illustrate the expected dampening of the net rate of accumulation of material inside the simulation space. While figure 5.13 illustrates the absolute rate of variation in the number of molecules in each simulate system, figure 5.14 and its pairs in appendix 7.7 illustrate the related component-specific rate of variation for all three flow-conditions investigated in this section. In all diagrams, high valued net flow-rates characterize the beginning of the simulations. These characteristic magnitudes verified at the beginning of the simulations are in fact the simple reflex of negligible amounts of time simulated by the algorithm, which, when accounted for, significantly increase the molecule/time ratio describing the flow rates entering or leaving the system. Following the equilibration steps of the system, i.e. along the last \( 1 \times 10^6 \) simulated steps, all net flow-rates dampened towards zero. This, as already explained, indicates the establishment and conservation of a stationary condition within the simulation space, which ultimately corroborates the composition profiles previously reported in figure 5.11.
Figure 5.13: Net flow rates for feed and product streams generated by MDSTAGE in simulations set for 200, 400 and 600 molecules/ns.

Figure 5.14: Component-specific net flow rates for species C in simulations with 200, 400 and 600 molecules/ns.
5.2 Molecular-dynamic simulation of the stationary operation of a NORMAG distillation column

After previous investigations of fundamental concepts and general features of the MDSTAGE algorithm, the main goal in this work is now examined. In this section, using the experimental data sets describing the stationary operation of a NORMAG distillation column reported in chapter four, the possibility of their reproduction on a molecular scale with aid of MDSTAGE is evaluated.

5.2.1 Molecular parameters

Before any proper examination on the ability of MDSTAGE to accomplish the here stated task, a prior discussion on the molecular-dynamic description of the simulated species has to be addressed. As in all other molecular-dynamic investigations performed in this work, an essential requisite to the generation of meaningful results is the availability of appropriate molecular models describing the species involved in the examined phenomena. Though, as reported in chapter two, one may nowadays effortlessly find an extensive literature devoted to the definition and optimization of molecular parameters and intermolecular potentials, the number of papers dealing with system-specific parameters, especially in the case of ternary or multi-component systems, represents however only a small percentage of this totality. Now, a set of system-specific Lennard-Jones parameters is also demanded in order to provide MDSTAGE the necessary means to appropriately describe the chemical system distilled within the NORMAG distillation column, i.e. cyclohexane, heptane and isoctane molecules. Ideally, a system-specific set of molecular models would conveniently fulfill the necessities related to the present investigation. Since the very beginning of this work, however, the development or optimization of a system-specific set of molecular parameters was not included in the main scope of this examination. For this task, a profitable trade-off between accuracy and specificity of the system-specific molecular parameters demanded by MDSTAGE is offered by transferable functional group parameters. These potentials, instead of providing component-specific molecular parameters, reassigns the intermolecular potential of a component to the cumulative effect of discrete contributions from functional groups present in the molecule, e.g. methyl (-CH₃), methylene (-CH₂), etc. Moreover, this approach also
holds benefit on the existence of extensive collections of parameters, covering a wide range of chemical families, and the fact that group-specific parameters reported in independent studies, though not exactly identical, exhibit quantitative resemblance of their values (Mountain and Brown 1985; Martin and Siepmann 1998; Chen et al. 2001; Wick et al. 2000; Liu et al. 2011). A summary of the reference group-potential parameters used in this work is reported in table 5.9.

Table 5.9: Reference of transferable Lennard-Jones parameters for hydrocarbons

<table>
<thead>
<tr>
<th>Component</th>
<th>(\sigma) [nm]</th>
<th>(\epsilon/k_B) [K]</th>
<th>M [g/mol]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3) (sp(_3)) - n-alkanes</td>
<td>0.376</td>
<td>92.61</td>
<td>15.0</td>
<td>[a]</td>
</tr>
<tr>
<td>CH(_2) (sp(_3)) - n-alkanes</td>
<td>0.396</td>
<td>48.02</td>
<td>14.0</td>
<td>[a]</td>
</tr>
<tr>
<td>CH(_2) (sp(_3)) - ciclohexane</td>
<td>0.396</td>
<td>57.12</td>
<td>14.0</td>
<td>[a]</td>
</tr>
<tr>
<td>CH (sp(_3)) - n-alkanes</td>
<td>0.465</td>
<td>10.00</td>
<td>13.0</td>
<td>[b]</td>
</tr>
<tr>
<td>C (sp(_3)) - n-alkanes</td>
<td>0.444</td>
<td>13.20</td>
<td>12.0</td>
<td>[c]</td>
</tr>
</tbody>
</table>


In order to ensure a minimal level of resemblance between the ternary system simulated by MDSTAGE and the one distilled in the NORMAG column, an adjustment of the parameters was carried out before any concrete investigation with MDSTAGE. In this procedure, through the optimization of a predefined objective function, all energy parameters, \(\epsilon\), of the functional groups in table 5.9, were rescaled by a common correction factor, \(\zeta\) (Allen and Tildesley 1987; Vrabec, Huang and Hasse 2009a):

\[
\tilde{\epsilon}_{\text{new}} = \zeta \cdot \tilde{\epsilon}_{\text{old}}
\]  

The choice of rescaling the energy parameters of the functional groups, \(\epsilon\), instead of the geometry parameters, \(\sigma\), listed in table 5.9 was due to the direct influence of \(\epsilon\) on the magnitude of the interaction between the functional groups present in the system. In the current investigation, VLE simulations have been carried out to determine an optimal value of the constant \(\zeta\) in equation 5.6. Due to lack of specific experimental information describing the VLE of the ternary system cyclohexane, heptane and isoctane, VLE simulations of a binary mixture of cyclohexane and heptane have been investigated. For the optimization of the energy parameters of the molecular
models listed in table 5.9, simulations of binary mixtures were favored over simulations of the VLE of pure components in order to simultaneously account mixture effects of the values of the values of the correction factor $\xi$. These simulations followed the same methodology as those previously carried out in the VLE investigation of argon reported in section 5.1.1 and had, as reference VLE data reported by Gmehling, Onken and Arlt (1980). A list with the characteristic conditions of these simulations is given in table 5.10.

Table 5.10: Simulation parameters in the investigation of the correction factor, $\xi$

<table>
<thead>
<tr>
<th>Dimensions of the simulation space in unit cells [x,y,z]</th>
<th>[8,8,18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of molecules in simulation space</td>
<td>1536</td>
</tr>
<tr>
<td>Number of Cyclohexane molecules in the simulation space</td>
<td>940</td>
</tr>
<tr>
<td>Number of Isooctane molecules in the simulation space</td>
<td>596</td>
</tr>
<tr>
<td>Time step</td>
<td>1 fs</td>
</tr>
<tr>
<td>Number of simulated steps</td>
<td>250000</td>
</tr>
<tr>
<td>Number of simulated steps in equilibration phase</td>
<td>200000</td>
</tr>
<tr>
<td>Number of simulated steps in evaluation phase</td>
<td>50000</td>
</tr>
</tbody>
</table>

The objective function, $f(\xi)$, minimized in the optimization of the factor $\xi$, 

$$f(\xi) = |p_{\text{sim}} - p_n|$$

(5.4)

described the deviation from the system pressure, $p_{\text{sim}}$, simulated by MDSTAGE to the reference value of pressure, $p_n$, under normal conditions, 0.1 MPa. Normal pressure was chosen as reference for his examination in order to resemble conditions under which the experiments of chapter four were carried out and also due to the available information on the VLE for cyclohexane and heptane provided by Gmehling, Onken and Arlt, (1980). Figure 5.15 reports the correlation observed between the pressure of the simulated systems and the values of the potential correction factor $\xi$. 

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Figure 5.15: Correlation between simulated pressures and the correction factor, $\xi$, on VLE simulations of cyclohexane and heptane.

Within the range of investigated values of the factor $\xi$, the results reported in figure 5.15 indicate a linear dependence between the pressure of the simulated system and the values of $\xi$. Assuming the validity of this proposition, the linear correlation between these two quantities, given by:

$$\xi(p) = -0.0337 \cdot \frac{P}{[\text{MPa}]} + 1.1557,$$  \hspace{1cm} (5.5)

returns, at normal conditions of pressure, a correction factor of 1.1522. In order to control the efficiency of the correction-factor, a proofing VLE simulation of the binary system cyclohexane and heptane, using the optimized value of $\xi$, was carried out. Results of this simulation are reported in figure 5.16 and table 5.11.
Figure 5.16: Density profile along the z axis of the simulation space for the VLE simulation of Cyclohexane and Heptane using the optimized value of the correction factor, $\zeta$.

Table 5.11: Reference and simulated values in the examination of the correction factor $\zeta$.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Reference value</th>
<th>Simulated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure [MPa]</td>
<td>0.10</td>
<td>0.097</td>
</tr>
<tr>
<td>Temperature [K]</td>
<td>360.65</td>
<td>358.3</td>
</tr>
<tr>
<td>Liquid composition $x_{\text{Cyc.}}$</td>
<td>0.5545</td>
<td>0.5833</td>
</tr>
<tr>
<td>Vapor composition $y_{\text{Cyc.}}$</td>
<td>0.6693</td>
<td>0.6757</td>
</tr>
</tbody>
</table>

In addition to stable liquid and vapor phases within the evaluation period of the simulation, as depicted in figure 5.16, table 5.11 reports a noticeable agreement between the reference and simulated values of system properties produced by MDSTAGE in the VLE-simulation of the cyclohexane-heptane mixture. On the other hand, a modest overestimation of the compositions of both liquid- and vapor phases indicate also a slightly negative deviation of the Raoul’s Law added to the system through the correction-factor $\zeta$ obtained with equation 5.5. Within the scope of the current examination, given the extension of the discrepancies between reference and
simulated values of compositions, effects of the correction-factor $\xi$ on the the VLE predictions for the investigated system are assumed to be negligible. The new set of Lennard-Jones parameters adjusted by the factor $\xi$ is given in table 5.12. Geometrical coordinates of the functional groups describing rigid molecules of the investigated species were provided by input-files of the COSMO-RS® package for quantum based thermodynamic calculations (Klamt 1995). A list with the coordinates of the functional groups for each component is given in appendix 7.8.

Table 5.12: Adjusted set of Lennard-Jones transferable group-parameters

<table>
<thead>
<tr>
<th>Component</th>
<th>$\sigma$ [nm]</th>
<th>$\epsilon/k_B$ [K]</th>
<th>$M$ [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ (sp3) - n-alkanes</td>
<td>0.376</td>
<td>106.71</td>
<td>15.0</td>
</tr>
<tr>
<td>CH$_2$ (sp3) - n-alkanes</td>
<td>0.396</td>
<td>55.33</td>
<td>14.0</td>
</tr>
<tr>
<td>CH$_2$ (sp3) - ciclohexane</td>
<td>0.396</td>
<td>65.82</td>
<td>14.0</td>
</tr>
<tr>
<td>CH (sp3) - n-alkanes</td>
<td>0.465</td>
<td>11.52</td>
<td>13.0</td>
</tr>
<tr>
<td>C (sp3) - n-alkanes</td>
<td>0.444</td>
<td>13.20</td>
<td>12.0</td>
</tr>
</tbody>
</table>

5.2.2 Specifications of the simulation space and simulated conditions

By the approach used to describe the operation of the NORMAG distillation column with MDSTAGE, each simulation space depicted a single separation stage of the equipment and virtually specified a simulation knot within the local network of personal computers where the simulations were run. Furthermore, each simulation space also interacted via feed- and product streams with its adjacent knots in order to reproduce on a molecular scale the material exchange between the stages of the NORMAG distillation column. Figure 5.17 sketches the general aspects of a simulation space specifically tailored for the simulations of the NORMAG distillation column on a molecular scale. Since each separation stage of the NORMAG distillation column is characterized by a dynamic interplay between vapour- and liquid phases, the approach used for description of the vapour- and liquid phases coexisting in the simulation space was that proposed by Trokhymchuck and Alejandre (1999), Mecke et al. (2001) and Inzoli et al. (2010). In this approach, as already mentioned in section 5.1.1, a liquid layer is generated and held under dynamical equilibrium with the vapor phase inside the simulation space. By this
virtue, as previously sketched in figure 5.1, molecules were initially allocated in the central section of an orthogonal parallelepiped-shaped simulation space and, except for this central section, all the remaining volumes of the simulation space initiate the simulation without molecules in it. Figure 5.17 also indicates the localization of the four material streams presented in each simulation space, depicting the streams of liquid and vapor phase both entering and exiting the simulation space. In order to correctly depict the operation of the separation stage, resembling the internal geometry of the NORMAG column discussed in chapter 4, extra attention was paid to the relative allocation of the material streams in the walls of the simulation space. As sketched in figure 5.17, the vapor phase leaving the simulation space has been withdrawn directly from one of the z-axis extremities of the simulation space which, due to periodic boundary condition, matches the geometrical bulk of the simulated vapor phase. Similarly, the liquid phase leaving the simulation space has been withdrawn from the middle of the simulation space, where the simulated liquid film of molecules was expected to be found after relaxation of the system. Material streams entering the simulation space had their entrances also set in the middle of the simulation space, thereby intending to enhance mixing effects and the material transfer between vapor and liquid phases. Except for the feed- and product streams depicted in figure 5.17, no other property has been assigned to the unit cells building simulation space. All other unit cells had therefore standard penetrable walls in order to ensure the preservation of the periodic boundary conditions and subsequently minimize boundary or interface effects within the simulated system.
5.2.3 Initial configurations in the simulations of the NORMAG distillation column by MDSTAGE

As in section 5.1.1, the dimensions of the simulation spaces simulated by MDSTAGE had to be previously specified in order to ensure the establishment of a system with stable liquid- and vapor phases in it. As two distinct regions in the ternary diagram of cyclohexane, heptane and isooctane are investigated in this section, two distinct geometries were specified. Essentially, as illustrated in figure 4.16, the two regions of the investigated ternary diagram differ from each other on the amount of cyclohexane available in the system. While the cyclohexane composition lies between 0.1 and 0.5 for one set of experimental data, the composition for the same component lies in the other between 0.0025 and 0.010. The main effect of the difference on the amount of cyclohexane in both data sets was eventually observed on the final dimensions of the simulation spaces assembled in investigations of each region. In order to determine appropriate numbers of molecules and dimensions of the simulation-spaces necessary in each examination, pre-evaluative simulations for each investigated
region were carried out. While, for the cyclohexane-rich region of the ternary diagram, 576 molecules provided a stable simulation space, 1200 molecules were necessary to ensure a stable system within the examined conditions of the cyclohexane-poor region of the ternary diagram. Regarding the geometric configuration of the simulation spaces, 6, 4 and 18 unit cells distributed along the x-, y- and z-axis determined a viable geometry for simulations in the cyclohexane-rich region of the ternary diagram, while 6, 5 and 30 unit cells, along the x-, y- and z-axis respectively, provided the aimed stability of the system on the cyclohexane-poor region.

In order to minimize the computational costs of the investigations in this section, the heuristics suggested by Babic (2011) are once again applied – i.e. the initial configuration of each examined system was defined so that it neared a stable or relaxed state of system. Here, in order to approximate the initial configuration of the simulation spaces to the stationary condition of their correspondent stages in the distillation column, the initial composition profile along the stages of the simulated equipment will already resemble the aimed stationary condition measured in the NORMAG column. In this arrangement, the time-consuming step associated with the establishment of a characteristic composition profile out of a homogeneous system is eliminated, providing more time to the core of the examination of this section, i.e. to check the ability of MDSTAGE to reproduce and sustain the stationary operation of the NORMAG column on molecular scale. For the examined ternary system, figure 5.18 sketches the initial configuration of the simulation spaces used in the investigations of the cyclohexane-rich and -poor regions of its ternary diagram.
Last but not least, the amount of material exchanged between the stages simulated by MDSTAGE also had to be specified. Despite their compositions being ultimately defined by the prevailing conditions observed in each one of the simulation spaces, the net amount of molecules leaving or entering these simulated stages is an arbitrary quantity independently defined by the user of the algorithm. Though arbitrary, the specification of these quantities should at least follow directions to provide further resemblance between simulated and real phenomenon. In the special case of the simulation of the NORMAG column on molecular scale, these guidelines were already suggested by Babic (2011) based on the dimensional analysis of the
operation. Concerning systems where interphasic material transfer is influenced both by viscous and diffusive effects, Babic (2011) proposed the dimensionless quantity \( \Pi \) as a link between the macroscopic level of the investigated phenomenon and the correspondent molecular system depicted by MDSTAGE:

\[
\Pi = \frac{A^2 \cdot n^2 \cdot D}{\dot{F} \cdot L},
\]

where, \( A \) represents the free-area available for interphasic material transfer in \( m^2 \), \( n \) the volume-specific amount of material in the system, \( D \) a characteristic diffusion coefficient of the examined species, \( \dot{F} \) the material flow through the system and \( L \) the holdup. Table 5.13 exemplifies the calculation of the demanded amount of flow in the simulation space defined for the cyclohexane-poor region of the ternary diagram.

| Table 5.13: Exemplary prediction of the demanded flow-rate in a molecular-dynamic simulation of the NORMAG column by MDSTAGE using a simulation space with \([x=6. y=5. z=30]\) unit cells, 1200 molecules and liquid phase as reference: |
|-----------------|-----------------|-----------------|
| Quantity        | NORMAG          | MDSTAGE         |
| \( A \) \( m^2 \) | 0.075 \( \text{Lockett (1986)} \) | 3.21x10^{-17} \( [a] \) |
| \( n \) \( \text{mol/m}^3 \) | 6569.79 \( \text{Yaws (2008)} \) | 6569.79 \( \text{Yaws (2008)} \) |
| \( D \) \( m^2/s \) | 10^{-10} \( \text{Taylor and Krishna (1993)} \) | 10^{-10} \( \text{Taylor and Krishna (1993)} \) |
| \( \dot{F} \) \( \text{mol/s} \) | 0.0197 \( [b] \) | \( X \) |
| \( L \) \( \text{mol} \) | 1.97 \( \text{Lockett (1986)} \) | 1.99x10^{-21} \( [c] \) |

\[
X = 3.562 \times 10^{-12} \frac{\text{mol}}{s} = 2144 \frac{\text{molecules}}{ns}
\]

[a] Based on the geometry of the simulation space, [b] Volumetric rate measured in the equipment, [c] Based on the number of simulated molecules.
With material rates of circa $2 \times 10^3$ molecules/ns, the implementation of such requirement faced both conceptual and practical impediments. Taking into account the 576 and 1200 molecules per simulation space respectively used by MDSTAGE along the investigations of the cyclohexane-rich and -poor regions of the ternary diagram, flow-rates of $2 \times 10^3$ molecules/ns not only restrain the residence time of molecules but also impair the split of components between liquid and vapor phases in each simulated stage. Concerning single stages of separation equipment, short residence time characterizes systems where flow related effects mainly dictate the dynamics of the operation; in other words, where diffusion-related phenomena such as interphasic mass transfer do not have enough time to take place.

Aside from the previous considerations, a second and more practical instance also hampered the implementation of the desired flow-rate condition. It was not possible to reproduce the required amount of material exchange between the simulated stages on the molecular level. In fact, only a small fraction of the required flow-rate could be accomplished in practice by the algorithm of MDSTAGE. Material streams assembled on simulation-spaces along test-simulations for the implementation of feed- and product streams were incapable of reaching material rates higher than 300 molecules/ns. Reasons for this limitation are best comprehended by recalling the multi-centered approach used in the molecular description of the species present in the investigated ternary system. As stated in chapter three, the insertion and removal of molecules performed by MDSTAGE does not occur independently from the conditions prevalent in the simulated system. For instance, in order to insert a molecule into the simulation space, energy and density conditions in the vicinity of the feed-boundary have to be favorable, i.e. enough free space has to exist or be created in order to accommodate the new molecule. While the insertion of one center Lennard-Jones molecules do not portray a troublesome task due to the modest amount of space needed for the procedure, the insertion of the examined multi-centered hydrocarbon molecules, depicting up to eight rigidly-bounded centers, faces, for similar reasons, greater hindrance in order to maintain a similar pace. Observation of the dimensionless number $\Pi$ in equation 5.6 shows that the increase of the simulated amount of molecules, $n$, inside the simulation space could favorably reduce the required amount of flow rates on the molecular scale. However, in order to achieve a fair compromise between holdup and flow-rates, it would lead to the
simulation of systems prohibitively defined with, at least, ten times more molecules than those previously specified. Recalling that the computational costs of molecular-dynamic simulations increase directly with the number of simulated sites within the simulation space, the costs for simulating systems with species having on average seven molecular sites would be impractically higher than those verified in the already challenging old setup. For simulations carried out in a local network of personal computers, as in those performed in this work, the unfeasibility of such investigations is indisputable. Therefore, given the aforementioned arguments, the outlook of the examination was partially restricted and the molecular simulations of NORMAG distillation column were performed with the maximal flow-rates currently attainable with MDSTAGE. A summary of the general conditions for the simulations in both regions of the investigated ternary diagram is given in table 5.14.

Table 5.14: Simulation parameters in the investigation of the cyclohexane-rich (I) and cyclohexane-poor (II) region of the ternary diagram of the examined system

<table>
<thead>
<tr>
<th>Region of the ternary diagram</th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions of the simulation space in unit cells [x,y,z]</td>
<td>[6,4,18]</td>
<td>[6,5,30]</td>
</tr>
<tr>
<td>Number of molecules in simulation space</td>
<td>576</td>
<td>1200</td>
</tr>
<tr>
<td>Material flow-rate of liquid- and vapor streams [molecules/ns]</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Time step</td>
<td>1fs</td>
<td>1fs</td>
</tr>
<tr>
<td>Number of simulated steps</td>
<td>7.0 x10⁶</td>
<td>8.0x10⁶</td>
</tr>
<tr>
<td>Number of steps under temperature scaling</td>
<td>7.0 x10⁶</td>
<td>8.0x10⁶</td>
</tr>
<tr>
<td>Number of simulated steps in equilibration phase</td>
<td>4.5 x10⁶</td>
<td>5.0x10⁶</td>
</tr>
<tr>
<td>Number of simulated steps in evaluation phase</td>
<td>2.5 x10⁶</td>
<td>3.0x10⁶</td>
</tr>
</tbody>
</table>
5.2.4 Simulation results

Cyclohexane-rich region of the investigated ternary diagram

The results of the MDSTAGE simulation for the operation of the NORMAG distillation column on the cyclohexane-rich region of the ternary diagram of the system cyclohexane, heptane and isoctane are reported in figures 5.19 through 5.23. Figure 5.19 illustrates the stationary compositions established over the simulated stages along the evaluation phase of the simulation. For the composition profiles reported in this diagram, remarkable agreement between experimental and simulated data is observed. These results demonstrate the ability of MDSTAGE to satisfactorily reproduce not only the experimentally observed pattern of compositions within the stages of the NORMAG column (i.e. following the expected directions of the distillation curves of the system), but also the breadth of separation of the most volatile component, cyclohexane, across the stages.

![Diagram showing stationary composition profiles in simulated stages](image)

Figure 5.19: Stationary composition profile in each simulated stage of the cyclohexane-rich region.
A quantitative evaluation of the results reported in figure 5.19 is provided in diagram 5.20. In this chart, the component-specific experimental Murphree stage-efficiency:

$$\eta_{i,n} = \frac{y_{i,n} - x_{i,n}}{y^* - x_{i,n}},$$  \hspace{1cm} (5.7)

for each component $i$ of the investigated system in each one of the five stages, $n$, of the NORMAG column are graphically compared to their simulated counterparts. In equation 5.7, $x_{i,n}$ stands for the composition of the species $i$ in stage $n$ and $y^*_{i,n}$ for the composition of the same species in the vapor phase of the stage. The superscript * over the vapor composition $y$ denotes an ideal value, in equilibrium with the composition $x_{i,n}$. The equilibrium data necessary for these calculations has been obtained with the UNIQUAC model, reported in appendix 7.1. For the simulated composition profile of figure 5.19, a table with the numeric values of the calculated efficiencies is given in table 5.15.

For cyclohexane, except on the first and fourth stages where separation efficiencies have been respectively over- and underestimated with a maximal deviation of 26%, all other experimental efficiencies have been reproduced with accuracies of at least 90%. For heptane and isooctane, in general, the simulated separation efficiencies showed accurate results for heptane and a variable accuracy for isooctane. For both species, the separation efficiency on the first stage was overestimated. Reasons for this are the relative separation between the compositions of the first and second stages simulated by MDSTAGE. Observing the compositions of the first and second stages reported in figure 5.19, one notices that while the composition in the first stage is slightly underestimated in terms of cyclohexane and heptane, the composition on the second one is slightly overestimated. Regarding isooctane, the overestimated separation efficiency in stage one comes from a minor rightwards shift of its composition relative to the correspondent experimental value. For isooctane, the explanation applies to the other simulated stages. Figure 5.19 shows that the experimental composition profile stretches along a distillation curve where the general isooctane composition modestly changes between the first and the fifth stage. As a consequence of this, as observed in figure 5.20, any left- or right-deviation of the simulated compositions relative to this guiding distillation curve produces a significant impact in the values of the isooctane-specific stage efficiency.
Table 5.15: Simulated compositions and Murphree stage efficiencies on the cyclohexane-rich region of the investigated ternary system.

<table>
<thead>
<tr>
<th>Stage</th>
<th>$X_{\text{Cyclohexane}}$</th>
<th>$Y_{\text{Cyclohexane}}$</th>
<th>$Y_{\text{Murphree}}$</th>
<th>$X_{\text{Heptane}}$</th>
<th>$Y_{\text{Heptane}}$</th>
<th>$Y_{\text{Murphree}}$</th>
<th>$X_{\text{Isooctane}}$</th>
<th>$Y_{\text{Isooctane}}$</th>
<th>$Y_{\text{Murphree}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.174</td>
<td>0.243</td>
<td>0.81</td>
<td>0.690</td>
<td>0.633</td>
<td>0.80</td>
<td>0.136</td>
<td>0.125</td>
<td>0.88</td>
</tr>
<tr>
<td>2</td>
<td>0.230</td>
<td>0.315</td>
<td>0.74</td>
<td>0.644</td>
<td>0.572</td>
<td>0.82</td>
<td>0.126</td>
<td>0.113</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>0.293</td>
<td>0.395</td>
<td>0.58</td>
<td>0.586</td>
<td>0.500</td>
<td>0.50</td>
<td>0.121</td>
<td>0.105</td>
<td>0.99</td>
</tr>
<tr>
<td>4</td>
<td>0.362</td>
<td>0.465</td>
<td>0.52</td>
<td>0.543</td>
<td>0.447</td>
<td>0.56</td>
<td>0.105</td>
<td>0.088</td>
<td>0.38</td>
</tr>
<tr>
<td>5</td>
<td>0.411</td>
<td>0.532</td>
<td>0.65</td>
<td>0.490</td>
<td>0.387</td>
<td>0.57</td>
<td>0.099</td>
<td>0.081</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Mean Efficiency ($\eta$): 0.66

![Component-specific Murphree stage efficiencies](image)

Figure 5.20: Compared component-specific Murphree stage efficiencies on the cyclohexane-rich region of the investigated system.
With flow-rates of 300 molecules/ns, each simulation space renewed its internal material at least 3.65 times at the end of the $7.0 \times 10^6$ steps simulated in the cyclohexane-rich region of the ternary diagram. After these 3.65 cycles of material renovation, any scattering tendency of the simulation results relative to the initial conditions of the system should be already noticeable along the composition profile generated by MDSTAGE. The absence of such tendencies corroborates therefore the quality of the results.

Examining the stationary operation of the simulated stages, figures 5.21 through 5.23 provide information on the stability of the systems. Figure 5.21 depicts the stationary density profiles averaged for each stage along the last $2.5 \times 10^6$ steps of the simulation. The well-behaved liquid film established in each stage in the middle of the simulation space not only confirm the suitability of the specified dimensions of the simulated system, holdup and amount of material flow but also the relative positioning of the material streams on the simulation space. Figures 5.22 and 5.23 report the stability of the material flows between the simulated stages and the preservation of stationary conditions in terms of general- and component-specific net rates of accumulation as previously defined in equations 5.4 and 5.5. While figure 5.22 shows by means of the exiting liquid flow-streams of each stage the attainment and preservation of the desired amount of material flow, figures 5.23 depict exemplarily for cyclohexane its net flow within the simulation space. Similar diagrams for other material-streams as well for the heptane- and isoctane net flow-rates are reported in appendix 7.9. These diagrams confirm the stationary operation of the simulated stages during the evaluation period of the simulation showing that no continuous accumulation or loss of material has taken place along the course of the simulation.
Figure 5.21: Density profiles along the z-axis of the simulation space for each stage in the investigation of the cyclohexane-rich region of the examined ternary diagram.

Figure 5.22: Exiting liquid flows in each simulated stage of the cyclohexane-rich region.
Figure 5.23: Net flow of cyclohexane in each simulated stage of the cyclohexane-rich region.
Cyclohexane-poor region of the investigated ternary diagram

As previously reported for the cyclohexane-rich region, the results of the MDSTAGE simulation for the operation of the NORMAG distillation column on the cyclohexane-poor region of the investigated ternary diagram are now summarized in figures 5.24 through 5.28. Figure 5.24 reports the stationary composition profile established over the simulated stages along the last $3 \times 10^6$ steps of the simulation by MDSTAGE. This diagram shows that despite the unusual pattern displayed by the experimental data set, which stretches itself over two different distillation curves, MDSTAGE was again able to reproduce the operation of the examined equipment on a molecular scale. The fact that the investigated region of the ternary diagram was mainly characterized by an expressive scarcity of cyclohexane did not play any major role on the results produced by MDSTAGE. In each stage, only minor deviations are observed on the simulated results relative to the experimental ones. A quantitative evaluation of the quality of the simulated results is provided by table 5.16 and figure 5.25.

![Stationary composition profile in each simulated stage of the cyclohexane-poor region.](image)

Figure 5.24: Stationary composition profile in each simulated stage of the cyclohexane-poor region.
Figures 5.25 report the experimental Murphree stage efficiencies, $\eta_i$, as in equation 5.7, for each component simulated by MDSTAGE. Similar to the previous section, the values of the efficiencies have been calculated with the aid of the UNIQUAC model and are listed in appendix 7.9. Figure 5.25 is characterized by remarkable variations in the values of the reported component-specific stage efficiencies. Recalling the extraordinary location of the experimental data set examined in this section, it is easy to understand the deviations observed in these diagrams. Given the extremely small traces of cyclohexane needed to be reproduced by MDSTAGE, any slight increase or decrease in the discrete number of these depicted molecules was directly reflected in effective changes in the compositions of this species. Though varying sometimes only the fourth decimal place of the cyclohexane composition, these changes did impact, for instance, the prediction of equilibrium data used in the calculation of the separation efficiencies. As confirmed by the composition and efficiency data reported in table 5.16, such variations were the reason for the unexpectedly high deviation of simulated cyclohexane separation efficiency relative to the experimental reference values in the first stage. Along the other stages, illustrating an average accuracy of 15% the reported cyclohexane separation efficiency resembles the results obtained for the cyclohexane-rich region of the examined ternary diagram. As observed in the previous section for the isooctane compositions, a remark must also be made regarding the compositions of heptane in the cyclohexane-poor region of the investigated ternary diagram. Observing figure 5.24, one notices that within the investigated experimental data-set from the lower to the top stage, heptane compositions display an absolute variation of 0.003. In other words, due to its slightly variable values, it facilitates deviations of the simulated efficiencies in relation to the experimental data. Another characteristic aspect of the heptane-specific stage efficiencies are the small values observed in the first and second stages, both in the experimental and simulated values. This, however, is explained by the left-shift of the experimental composition profile observed after the third stage in figure 5.24. This shift practically sets the data describing the two initial stages and those describing the third, fourth and fifth stages lying over two different distillation curves, as indicated in figure 5.24 and therefore shrinks the values of the heptane-specific separation efficiencies in the two first stages. No anomalous behavior was observed for the isooctane stage-efficiencies, which with average accuracies of 14% relative to the experimental data, satisfactorily reproduced the experimental data set.
Table 5.16: Simulated compositions and Murphree stage efficiencies on the cyclohexane-poor region of the investigated ternary system.

<table>
<thead>
<tr>
<th>Stage</th>
<th>$X_{\text{Cyclohexane}}$</th>
<th>$Y_{\text{Cyclohexane}}$</th>
<th>$\eta_{\text{Murphree}}$</th>
<th>$\chi_{\text{Heptane}}$</th>
<th>$Y_{\text{Heptane}}$</th>
<th>$\eta_{\text{Murphree}}$</th>
<th>$\chi_{\text{Isooctane}}$</th>
<th>$Y_{\text{Isooctane}}$</th>
<th>$\eta_{\text{Murphree}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0020</td>
<td>0.0029</td>
<td>1.46</td>
<td>0.7972</td>
<td>0.7998</td>
<td>0.31</td>
<td>0.2008</td>
<td>0.1971</td>
<td>0.59</td>
</tr>
<tr>
<td>2</td>
<td>0.0034</td>
<td>0.0049</td>
<td>0.93</td>
<td>0.7980</td>
<td>0.8001</td>
<td>0.24</td>
<td>0.1986</td>
<td>0.1949</td>
<td>0.53</td>
</tr>
<tr>
<td>3</td>
<td>0.0048</td>
<td>0.0071</td>
<td>0.75</td>
<td>0.7985</td>
<td>0.8000</td>
<td>0.73</td>
<td>0.1967</td>
<td>0.1928</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>0.0065</td>
<td>0.0095</td>
<td>0.57</td>
<td>0.7996</td>
<td>0.8005</td>
<td>0.58</td>
<td>0.1939</td>
<td>0.1900</td>
<td>0.56</td>
</tr>
<tr>
<td>5</td>
<td>0.0082</td>
<td>0.0120</td>
<td>0.69</td>
<td>0.8001</td>
<td>0.8007</td>
<td>0.71</td>
<td>0.1917</td>
<td>0.1873</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Mean Efficiency ($\eta$) 0.88 0.52 0.61

Figure 5.25: Compared component-specific Murphree stage efficiencies for on the cyclohexane-rich region of the investigated system.
With 1200 molecules in each simulation space and flow-rates of 300 molecules/ns, 8.0 x 10^6 steps of simulation provided 2 cycles of material renovation for the stages simulated on the cyclohexane-poor region of the ternary diagram. Given the extraordinary range of compositions examined in this section, these 2 cycles is in fact a suboptimal value, for it only provides conditions for the observation of coarse deviations of the system relative to the initial conditions of the simulation. Longer simulations, with 3 or more cycles of material renovation, would optimally describe the fully relaxed system. Unfortunately, these simulations were not possible within the timeframe of this work.

Finally, inspecting general aspects of the simulated conditions, figures 5.26 through 5.28 report the analysis of the stability of the system on the cyclohexane-poor region of the ternary diagram. As in the previous section, figure 5.26 illustrate the density profile along the z-axis of the simulation spaces averaged over the last 3 x 10^6 steps of the simulation. Here, as before, a well-established liquid film in the middle of the simulated spaces indicates the suitability of the general conditions setup for this investigation. The amount of flow streams and their relative positioning impaired in no form the maintenance of a stable system. Figures 5.27 and 5.28 illustrate the sustenance of the defined flow rates and the accomplishment of stationary operation for each simulated stage in terms of the exiting liquid-streams and cyclohexane-specific net rates of accumulation respectively. Similar diagrams for other material-streams as well for heptane and isoctane net flow-rates are reported in appendix 7.9. For both investigated regions of the examined ternary diagram, the average composition of the material streams in each stage obtained along the evaluation period of the simulations is reported in appendix 7.10.
Figure 5.26: Density profiles along the z-axis of the simulation space for each stage in the investigation of the cyclohexane-poor region of the examined ternary diagram.

Figure 5.27: Exiting liquid flows in each simulated stage of the cyclohexane-poor region.
Heptane-specific net-rate of molecules in simulation space, $\eta_{Hep}$ [molecules/ns]

Figure 5.28: Net flow of cyclohexane in each simulated stage of the cyclohexane-poor region.
5.3 Conclusion

In this chapter, three distinct investigations performed with the aid of MDSTAGE were reported. Along these examinations, the molecular-dynamic based algorithm of MDSTAGE was evaluated both in terms of its standard capabilities and its main distinctive feature – i.e. the mirroring of macroscopic characteristics of industrial processes and unit operations directly in the molecular level.

In terms of the general characteristics of the simulation tool, the accurate results initially obtained in the investigation of the vapour-liquid equilibria of argon ensured the preservation of the molecular-dynamic algorithm building the core structure of MDSTAGE. Concerning the capacity of the algorithm to reproduce and cope with specificities on the examination of arbitrary phenomena, the second block of investigations, focusing on the molecular-dynamic examination of stationary composition profiles along diffusion paths, delivered meaningful results reflecting the generic concept of the application of MDSTAGE. The reproduction of characteristic curved composition profiles previously investigated by Schott (2005), using a completely different approach of simulation, demonstrated not only the ability of the simulation tool to specifically tailor the simulation space according to generic demands of assembling but also its capacity to predict kinetic-dependent phenomena involved in the establishment of the investigated profiles of composition. Last but not least, the direct simulation of the stationary operation of a distillation column on a molecular scale fulfilled the ultimate goal of this work. The successful reproduction of the distillation of a ternary system of hydrocarbons by means of a molecular-dynamic approach corroborated the predictions of Pfennig (2004) and Babic (2011) regarding the plausibility and viability of this task. Through the adequate reproduction of compositions and efficiencies along the simulated stages of the column, the results of the simulation of the operation of the NORMAG distillation column by MDSTAGE reinforced once again for both sets of experimental data investigated in this work the ability of the algorithm to reproduce kinetic-dependent phenomena.
6 Summary

Since the late 80’s, when the first direct simulations of phase equilibria for simple molecules were reported (Panagiotopoulos, 1987), atomistic simulations have opened to chemical engineers a whole new field of possibilities regarding the modelling and prediction of physical-chemical properties of pure substances and their mixtures. The optimization of these techniques has continuously and progressively fostered the understanding of macroscopic phenomena and practical engineering problems in terms of their atomic and molecular characteristics (Pablo and Escobedo, 2004). In spite of this, many chances behind the direct mirroring of macroscopic phenomena on molecular and atomistic levels of investigation have steadily overlooked due to a rather misconceived incompatibility between both approaches of investigation.

In this work, an alternative methodology for the investigation of macroscopic phenomena and simulation of unit operations in molecular scale has been presented and evaluated. Using the molecular-dynamic based algorithm of MDSTAGE (Pfennig, 2004; Babic and Pfennig, 2006; Babic, 2011), general macroscopic phenomena and the stationary operation of a distillation column were reproduced in tailored atomistic spaces and simulated in a local area network of personal computers.

Compared to standard algorithms for atomistic simulations, the tailoring of the simulated conditions built one of the main differentials of MDSTAGE. Based on a modular approach, it offers the possibility to a generic specification of the simulated environment, allowing therefore the mimicry on molecular scale of macroscopic features commonly observed in industrial praxis, namely feed- and product streams, heat- and cooling walls, impenetrable and partially penetrable walls. Through the investigations reported in this work, three distinct instances of application of MDSTAGE have been examined. These investigations evaluated both the standard and specific aspects of the algorithm.

Concerning the core functionalities of MDSTAGE as a standard tool for molecular-dynamic simulations, the vapour-liquid behaviour of Argon has been successfully predicted and compared to experimental data. These simulations demonstrated the stability of the core algorithm of MDSTAGE and showed that, despite the continuous
adaptations of its code in order to mimic macroscopic characteristics on molecular scale, MDSTAGE has preserved the functionality of a standard tool for molecular-dynamic simulations.

The algorithm’s flexibility to manage and investigate general conditions of macroscopic phenomena was verified by the reproduction of results previously obtained by Schott (2005) for the establishment of characteristic stationary composition profiles along diffusion paths in the bulk of ternary liquid mixtures. These results not only exemplified the possibilities offered by the algorithm for the tailoring of the simulated space but also endorsed one of the primary hypothesis investigated in this work: the viability for predicting with MDSTAGE kinetic related phenomena based essentially on the molecular characteristic of the species involved in the molecular-dynamic simulation of the system.

Finally, the capacity of MDSTAGE to reproduce the stationary operation of separation equipments was examined through the simulation of a distillation process directly on molecular level. A ternary mixture of hydrocarbons, namely Cyclohexane, Heptane and Isooctane, was used as test system for this task. Results from the molecular simulation of the distillation process were evaluated through direct comparison to experimental data acquired in a bubble-cap tray NORMAG distillation column specifically assembled and used for this purpose. The successful reproduction on molecular scale of the operation of a NORMAG distillation column and the correct prediction of its performance in two distinct regions of the ternary diagram of the chemical system reinforced significantly the validity of the simulation approach evaluated in this work. It illustrated the capacity of MDSTAGE to simulate on molecular level the operation of a separation stage of a distillation column and its dynamic interplay with neighbouring stages. In this work, separation of species along the stages of the distillation column has been successfully simulated in terms of component-specific molecular parameters and dynamic exchange of material between neighbouring separation stages based on the concept of feed- and product streams brought by MDSTAGE to the classical approach molecular-dynamic investigations. Accomplishment of all the aforementioned results within a local area network of personal computers, also demonstrated the independence of MDSTAGE
to clusters of super computers, where standard molecular-dynamic simulations are as classically carried out.

Concisely, this work aimed and performed the evaluation of MDSTAGE, a molecular-dynamic based tool for the direct simulation of unit operations on molecular scale. The validity and viability of its concept came under the scrutiny of an experimental based examination. Results reported in this work not only corroborated the hypothesis of direct depiction of macroscopic phenomena and unit operations on molecular level (Pfennig, 2004 and Babic, 2011) but also reinforced the plausibility of such investigations.
APPENDIX

APPENDIX 7.1: UNIQUAC model

Equations of the UNIQUAC model used in calculations of vapour-liquid equilibrium

\[
\ln \gamma_i = \ln \gamma_{i,\text{comb}} + \ln \gamma_{i,\text{res}}
\]

\[
\ln \gamma_{i,\text{comb}} = \ln \frac{q_i}{x_i} + \frac{z}{2} q_i \ln \frac{\varphi_i}{x_i} + l_i - \frac{q_i}{x_i} \sum_{i=1}^{N} x_i l_i
\]

\[
\ln \gamma_{i,\text{res}} = q_i \left[ 1 - \ln \left( \sum_{j=1}^{N} \psi_{i,j} \tau_{j,i} \right) - \sum_{j=1}^{N} \frac{\psi_{j,i} \tau_{j,i}}{\sum_{k=1}^{N} \psi_{k,j} \tau_{k,j}} \right]
\]

\[
l_i = \frac{z}{2} \left( r_i - q_i \right) \left( r_i - 1 \right)
\]

\[
\tau_{j,i} = \exp \left( -\frac{a_{j,i}}{RT} \right)
\]

UNIQUAC parameters for the ternary system cyclohexane, heptane and isooctane

**Table 7.1.1:** Definition indexes and general information of the investigated system

<table>
<thead>
<tr>
<th>Index i</th>
<th>Component</th>
<th>CAS</th>
<th>(q_i)</th>
<th>(r_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexane</td>
<td>110-82-7</td>
<td>3.2400</td>
<td>4.0464</td>
</tr>
<tr>
<td>2</td>
<td>Heptane</td>
<td>142-82-5</td>
<td>4.3960</td>
<td>147.47</td>
</tr>
<tr>
<td>3</td>
<td>Isooctane</td>
<td>540-84-1</td>
<td>5.0080</td>
<td>166.08</td>
</tr>
</tbody>
</table>

Coordination factor:

\(Z=10\)

**Table 7.1.2:** Energy parameter \(a_{ji} \text{[cal/mol]}:\)

<table>
<thead>
<tr>
<th></th>
<th>(a_{12})</th>
<th>(a_{13})</th>
<th>(a_{23})</th>
<th>(a_{31})</th>
<th>(a_{32})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_{12})</td>
<td>145.368</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_{21})</td>
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<td></td>
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<td>(a_{23})</td>
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<td>(a_{31})</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(a_{32})</td>
<td></td>
<td></td>
<td>-17.490</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_{32})</td>
<td></td>
<td></td>
<td></td>
<td>19.134</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 7.2: Maxwell-Stefan diffusion coefficients in multi-component liquid systems


\[ D_{ij} = \left( D_{ij}^{0} \right)^{\frac{1+x_j-x_i}{2}} \left( D_{ji}^{0} \right)^{\frac{1+x_i-x_j}{2}} \]

- Maxwell-Stefan diffusion coefficients at infinite dilution (Siddiqi. Lucas. 1986)

\[ D_{ij}^{0} = 9.89 \times 10^{-8} \mu_j^{-0.907} V_i^{-0.45} V_j^{0.265} T \]
APPENDIX 7.3

Analytic methods

Along distillation experiments, liquid samples are in general the easiest and straightforward way to collect and discriminate information regarding the efficiency of a distillation column. Depending on each one of the investigated chemical-systems, a suitable analytical method was chosen in order to provide reliable quantification of compositions in the liquid-samples collected in the NORMAG distillation column. As reported in chapter 4, two chemical systems were examined within the scope of this work: While, chlorbenzene and ethylbenzene were initially used along the standardization of the experimental procedures; cyclohexane, heptane and iso-octane defined the work-system along the acquisition of data for evaluation of MDSTAGE.

Physical-chemical characteristics of the examined systems, as reported in chapter 4, oriented the selection of appropriate analytic methodologies. For the binary system, chlorbenzene and ethylbenzene, the density of the liquid samples collected was the parameter used for the quantification of the compositions of the collected samples. For the ternary system, cyclohexane, heptane and iso-octane, gas-chromatography provided the necessary measurements of composition.

The equipments necessary for the analysis were in both cases available in the department. Measurements of liquid densities were carried out with a density and sound analyser DAS48 from PAAR and a system-specific calibration curve obtained with the same equipment. Figure 7.3.1 and 7.3.2 illustrate the DAS48 - density and sound analyser – and the calibration curve used in the examination of the binary system chlorbenzene and ethylbenzene respectively. In the analysis of samples from ternary mixtures, a gas-chromatograph from Siemens, SICHROMAT-I, depicted in figure 7.3.3, was applied.
Figure 7.3.1: Density and sound analyser DAS48 (PAAR)

![Density and sound analyser DAS48](image)

Figure 7.3.2: Calibration curve for the binary system chlorbenzene-ethylbenzene

![ Calibration curve](image)

Chlorobenzene (1) / Ethylbenzene (2)
Temperature: 20°C
17.06.2011

$X_1$, Chlorobenzene molar fraction
$\rho$, Density [g/cm$^3$]

$X_1 = 12.452\rho - 44.109\rho^2 + 54.674\rho^3 - 22.361$

$1^{st}$ Measurement
$2^{nd}$ Measurement
$3^{rd}$ Measurement
Calibration curve

Experimental Data [GESTIS Data Bank]
All samples evaluated in the SiCHROMAT1 were prepared in toluene (Emplura, minimal purity: 99.9%). Toluene was chosen as carrying medium due to its high volatility, which ensured a very short residence time within the chromatographic column and therefore no interference on the peaks of the investigated components.

Using the SiCHROMAT1, an internal-standard was used in order avoid data-scattering due to variations in the amount of sample analysed by the equipment or its response between different runs. In the internal-standard method is an extra and constant amount of a reference substance is added to samples and calibration standards. The internal reference is expected to be similar but not identical to the targeted species and also produce an unambiguous response on the chromatographic detector. In the chromatogram, the mass fraction of an examined component will be proportional to the ratio of the area under its own peak relative to the area under the peak of the internal standard (Gottwald, 1995). In this work, n-hexane (Merck, minimal purity: 99%) was used as internal standard.

Samples and calibration standards for the SiCHROMAT1 were prepared with an analytical scale from OHAUS (Pioneer, with readability of 0.0001g). Calibration-standards with specific mass fractions of the targeted substances and the internal-
standard were prepared with cyclohexane (Emplura, minimal purity: 99%), n-heptane (Merck, minimal purity: 99%), isooctane (Merck. minimal purity: 99%), hexane and toluene.

Before any gas-chromatographic measurement, composition ranges of the calibration-standards were defined according to the sensibility of the equipment’s detector and samples were extra diluted, in order to avoid peaks of compositions going out of range. Using an analytical scale 0.5g of the experimental sample and 0.5g of n-hexane (internal standard) were added to 9.0g of toluene. In sequence 0.5g of this mixture was diluted in 9.5g of toluene. This final mixture was stored and sealed in crimp-cap glasses and sent to analysis. In the SiCHROMAT1, an Optima-TG column (Macherey-Nagel) was used with Helium as eluent. Table 7.3.1 summarizes its main characteristics and the standard setup of the equipment. Calibration-curves and calibration-parameters for cyclohexane. n-heptane and isooctane are shown in figures 7.3.4 through 7.3.6, respectively.

Table 7.3.1: Optima-TG Characteristics and equipment setup

<table>
<thead>
<tr>
<th>Column</th>
<th>Optima-TG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Dimethylpolysiloxan</td>
</tr>
<tr>
<td>Film thickness</td>
<td>0.1 μm</td>
</tr>
<tr>
<td>Column length</td>
<td>25 m</td>
</tr>
<tr>
<td>Column internal diameter</td>
<td>0.32 mm</td>
</tr>
<tr>
<td>Number of injections</td>
<td>3</td>
</tr>
<tr>
<td>Injection volume</td>
<td>0.20 μl</td>
</tr>
<tr>
<td>Column flow</td>
<td>1 ml/min</td>
</tr>
<tr>
<td>Oven temperature</td>
<td>35 °C</td>
</tr>
<tr>
<td>Split flow</td>
<td>47 ml/min</td>
</tr>
<tr>
<td>Split ratio</td>
<td>1:47</td>
</tr>
<tr>
<td>Detector</td>
<td>Flame ionization Detector</td>
</tr>
<tr>
<td>Injection temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>Detector Temperature</td>
<td>250 °C</td>
</tr>
</tbody>
</table>
0.23 w.% n-Hexane as internal standard for the GC-Analysis of:
0.22 - 1.70 w.% Cyclohexane in Toluene

Figure 7.3.4: Calibration curve for Cyclohexane

0.23 w.% n-Hexane als innerer Standard für die GC-Analyse von:
0.22 - 1.76 w.% n-Heptane in Toluene

Figure 7.3.5: Calibration curve for n-Heptane
Optima 1-TG

$p=0.28 \text{ bar}$

Split: 1:47

Injection temperature: 250°C

Detector temperature: 250°C

Oven temperature: 35°C

Injection volume: 0.2 µl

Calibration standards
g = a₁ * x + a₂ * x²

Values for: $a₁ = 0.89862$ $a₂ = 0.09768$

Error for: $a₁ = \pm 0.02555$ $a₂ = \pm 0.01864$

$0.23 \text{ w.\% } n$-Hexane as internal standard for the GC-Analysis of:

0.23 - 1.70 w.\% Iso-Octane in Toluene

Figure 7.3.6: Calibration curve for Isooctane
### APPENDIX 7.4: Experimental data obtained along the stationary operation of the NORMAG distillation column

#### Table 7.4.1: Measured compositions and efficiencies over the column stages for the investigated ternary system Cyclohexane, Heptane and Isooctane.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Data set I: Cyclohexane-rich region</th>
<th>Data set II: Cyclohexane-deficient region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_{\text{Cyclohexane}}$</td>
<td>$Y_{\text{Cyclohexane}}$</td>
</tr>
<tr>
<td>1</td>
<td>0.185</td>
<td>0.258</td>
</tr>
<tr>
<td>2</td>
<td>0.225</td>
<td>0.309</td>
</tr>
<tr>
<td>3</td>
<td>0.287</td>
<td>0.387</td>
</tr>
<tr>
<td>4</td>
<td>0.343</td>
<td>0.455</td>
</tr>
<tr>
<td>5</td>
<td>0.422</td>
<td>0.544</td>
</tr>
</tbody>
</table>

#### Table 7.4.2: Estimated compositions and efficiencies over the column stages for the investigated ternary system Cyclohexane, Heptane and Isooctane.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Data set I: Cyclohexane-rich region</th>
<th>Data set II: Cyclohexane-deficient region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_{\text{Cyclohexane}}$</td>
<td>$Y_{\text{Cyclohexane}}$</td>
</tr>
<tr>
<td>1</td>
<td>0.00235</td>
<td>0.00344</td>
</tr>
<tr>
<td>2</td>
<td>0.00597</td>
<td>0.00651</td>
</tr>
<tr>
<td>3</td>
<td>0.001235</td>
<td>0.001873</td>
</tr>
<tr>
<td>4</td>
<td>0.00845</td>
<td>0.00845</td>
</tr>
<tr>
<td>5</td>
<td>0.001235</td>
<td>0.001873</td>
</tr>
</tbody>
</table>
APPENDIX 7.5: Molecular models and empirical information used in the examination steps of MDSTAGE

Table 7.5.1: Lennard-Jones Parameters for Argon

<table>
<thead>
<tr>
<th>Component</th>
<th>( \sigma ) [nm]</th>
<th>( \varepsilon/k_B ) [K]</th>
<th>M [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.33952</td>
<td>116.79</td>
<td>39.95</td>
</tr>
</tbody>
</table>

Table 7.5.2: Vapor-liquid equilibrium data for Argon by Din (1956)

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Pressure [MPa]</th>
<th>Liquid Density [g/cm(^3)]</th>
<th>Vapour Density [g/cm(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.00</td>
<td>0.1199</td>
<td>1.3768</td>
<td>0.0079</td>
</tr>
<tr>
<td>97.76</td>
<td>0.2939</td>
<td>1.3359</td>
<td>0.0143</td>
</tr>
<tr>
<td>111.92</td>
<td>0.7879</td>
<td>1.2399</td>
<td>0.0361</td>
</tr>
<tr>
<td>122.39</td>
<td>1.3783</td>
<td>1.1462</td>
<td>0.0672</td>
</tr>
<tr>
<td>132.95</td>
<td>2.2803</td>
<td>1.0261</td>
<td>0.1227</td>
</tr>
<tr>
<td>137.64</td>
<td>2.8185</td>
<td>0.9628</td>
<td>0.1596</td>
</tr>
</tbody>
</table>
APPENDIX 7.6: Correlation between the values of the geometry, $\sigma$, and energy, $\epsilon$, for 1CLJ models based on parameters reported by Bretsznajder (1971)

\[ \sigma [Å] = C_1 \cdot \epsilon [K] + C_2 \]

Table 7.6.1: Parameters of the Bretsznajder (1971) correlation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$ [Å/K]</td>
<td>0.0081</td>
</tr>
<tr>
<td>$C_2$ [Å]</td>
<td>2.7412</td>
</tr>
</tbody>
</table>

Figure 7.6.1: Data set for the correlation between the values of the geometry, $\sigma$, and energy, $\epsilon$, parameters of the Lennard-Jones potential for 1CLJ molecular models.
APPENDIX 7.7: Material streams in the MDSTAGE simulations of section 5.1.2

Figure 7.7.1: Flow rates for feed and product streams generated by MDSTAGE in a simulation set for 200 molecules/ns.

Figure 7.7.2: Flow rates for feed and product streams generated by MDSTAGE in a simulation set for 400 molecules/ns.
Figure 7.7.3: Component-specific net flow-rates for species B in simulations with 200, 400 and 600 molecules/ns.

Figure 7.7.4: Component-specific net flow-rates for species A in simulations with 200, 400 and 600 molecules/ns.
APPENDIX 7.8: COSMO®-coordinates for the functional groups of the rigid molecules of Cyclohexane, Heptane and Isooctane

Table 7.8.1: COSMO®-coordinates for functional groups of Cyclohexane

<table>
<thead>
<tr>
<th>Site index</th>
<th>Mass</th>
<th>X [nm]</th>
<th>Y [nm]</th>
<th>Z [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.000</td>
<td>0.087683</td>
<td>-0.117635</td>
<td>0.023094</td>
</tr>
<tr>
<td>2</td>
<td>14.000</td>
<td>0.145725</td>
<td>0.017113</td>
<td>-0.023095</td>
</tr>
<tr>
<td>3</td>
<td>14.000</td>
<td>0.058037</td>
<td>0.134755</td>
<td>0.023093</td>
</tr>
<tr>
<td>4</td>
<td>14.000</td>
<td>-0.087684</td>
<td>0.117636</td>
<td>-0.023094</td>
</tr>
<tr>
<td>5</td>
<td>14.000</td>
<td>-0.145726</td>
<td>-0.017114</td>
<td>0.023095</td>
</tr>
<tr>
<td>6</td>
<td>14.000</td>
<td>-0.058037</td>
<td>-0.134755</td>
<td>-0.023093</td>
</tr>
</tbody>
</table>

Table 7.8.2: COSMO®-coordinates for functional groups of Heptane

<table>
<thead>
<tr>
<th>Site index</th>
<th>Mass</th>
<th>X [nm]</th>
<th>Y [nm]</th>
<th>Z [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.000</td>
<td>-0.384741</td>
<td>0.035860</td>
<td>-3.50570 x10^{-35}</td>
</tr>
<tr>
<td>2</td>
<td>14.000</td>
<td>-0.256968</td>
<td>-0.049002</td>
<td>6.31054 x10^{-35}</td>
</tr>
<tr>
<td>3</td>
<td>14.000</td>
<td>-0.128463</td>
<td>0.035013</td>
<td>-1.37279 x10^{-35}</td>
</tr>
<tr>
<td>4</td>
<td>14.000</td>
<td>-1.147x10^{-7}</td>
<td>-0.048987</td>
<td>-5.8400 x10^{-6}</td>
</tr>
<tr>
<td>5</td>
<td>14.000</td>
<td>0.128463</td>
<td>0.035013</td>
<td>1.87473 x10^{-35}</td>
</tr>
<tr>
<td>6</td>
<td>14.000</td>
<td>0.256968</td>
<td>-0.049002</td>
<td>-5.78157 x10^{-35}</td>
</tr>
<tr>
<td>7</td>
<td>15.000</td>
<td>0.384741</td>
<td>0.035859</td>
<td>2.97019 x10^{-35}</td>
</tr>
</tbody>
</table>

Table 7.8.3: COSMO®-coordinates for functional groups of Isooctane

<table>
<thead>
<tr>
<th>Site index</th>
<th>Mass</th>
<th>X [nm]</th>
<th>Y [nm]</th>
<th>Z [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.000</td>
<td>-0.111202654</td>
<td>-0.143634782</td>
<td>-0.106084014</td>
</tr>
<tr>
<td>2</td>
<td>12.000</td>
<td>0.000669335</td>
<td>-0.120054125</td>
<td>-0.002475665</td>
</tr>
<tr>
<td>3</td>
<td>14.000</td>
<td>0.068116553</td>
<td>0.018076166</td>
<td>-0.026288636</td>
</tr>
<tr>
<td>4</td>
<td>13.000</td>
<td>-0.018610503</td>
<td>0.145096292</td>
<td>-0.004262339</td>
</tr>
<tr>
<td>5</td>
<td>15.000</td>
<td>0.005602071</td>
<td>0.248311033</td>
<td>-0.115843262</td>
</tr>
<tr>
<td>6</td>
<td>15.000</td>
<td>-0.058081191</td>
<td>-0.130987911</td>
<td>0.139671642</td>
</tr>
<tr>
<td>7</td>
<td>15.000</td>
<td>0.006446715</td>
<td>0.209221331</td>
<td>0.133367627</td>
</tr>
<tr>
<td>8</td>
<td>15.000</td>
<td>0.108428432</td>
<td>-0.229096646</td>
<td>-0.020332587</td>
</tr>
</tbody>
</table>
APPENDIX 7.9: Material streams in the MDSTAGE simulations of section 5.2

Figure 7.9.1: Flow-rates for feed and product streams in each simulated stage of the cyclohexane-rich region.
Figure 7.9.2: Net flow of species in each simulated stage of the cyclohexane-rich region.

Figure 7.9.3: Net flow of heptane in each simulated stage of the cyclohexane-rich region.
Figure 7.9.4: Net flow of isooctane in each simulated stage of the cyclohexane-rich region.
Figure 7.9.5: Flow-rates for feed and product streams in each simulated stage of the cyclohexane-poor region.
Figure 7.9.6: Net flow of species in each simulated stage of the cyclohexane-poor region.

Figure 7.9.7: Net flow of cyclohexane in each simulated stage of the cyclohexane-poor region.
Figure 7.9.8: Net flow of isooctane in each simulated stage of the cyclohexane-poor region.
APPENDIX 7.10: Simulated flow compositions

Figure 7.10.1: Flow compositions in the investigation of the cyclohexane-rich region.

Figure 7.10.2: Flow compositions in the investigation of the cyclohexane-poor region.

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