1
Process Engineering Methods and Microsystem Technology

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Abstract

The fundamentals of chemical engineering are presented with the aim of applications in microsystem technology, microfluidics, and transport processes in microstructures. After a general overview about both disciplines and common areas the concept of unit operations is briefly introduced. The balance equations are derived from statistical mechanics and applied to other relevant systems of process engineering together with the kinetic description of main transfer processes. Engineering tools like dimensional analysis, order of magnitude estimations, or lumped element modeling are explained, which are very helpful for dealing with complex nonlinear systems. Concluding this chapter, the benefits and limits of miniaturization of various unit operations and typical issues are explained that might serve as a plentiful source for the future development.

Keywords

Unit operations, balance equations, transport equations, engineering modeling, scaling process

1.1 Introduction *2*
1.2 Unit Operations and Beyond *5*
1.3 Balances and Transport Equations *9*
1.3.1 Statistical Mechanics and Boltzmann Equation *10*
1.3.2 Macroscopic Balance Equations *13*
1.3.3 The Mass Balance *14*
1.3.4 The Species Equation *14*
1.3.5 The Momentum Equation and Force Balance *15*
1.3.6 The Energy Balance *16*
1.3.7 The Entropy Equation and the Efficiency of a System *18*
1.3.8 Elementary Transport Processes and their Description *19*

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1.3.9 Additional Remarks to Balance Equations *21*
1.4 Calculation Methods and Simulation *21*
1.4.1 Physical Variables and Dimensional Analysis *22*
1.4.2 Similarity Laws and Scaling Laws *24*
1.4.3 Order of Magnitude *24*
1.4.4 Lumped Element Modeling *25*
1.4.5 Numerical Simulation and Analytical Modeling *26*
1.5 Miniaturization and its Application to Transport Processes *27*
1.5.1 Length *27*
1.5.2 Area *32*
1.5.3 Volume *38*
1.5.4 Other Topics *41*
1.6 Conclusions and Outlook *42*
References *42*

1.1
Introduction

Process technology and microsystem technology are both interdisciplinary engineering and natural science branches connecting physics, chemistry, biology, engineering arts, and management techniques to an enabling toolbox for various applications. Process engineering embraces orientating calculations for process and equipment design under general orientation, and system-orientated, cross-linked thinking. Process engineers are working in various areas ranging from the food industry through biotechnology to pharmaceutical products, from analytical and laboratory equipment through energy conversion to industrial chemistry for the production of millions of tons of chemicals [1, Chapter 1]. Chemical process engineering covers not only the design and implementation of chemical production and analytical processes but also deals with the equipment design, the appropriate materials, the fabrication, and operation of various chemical production processes. The aims of process technology are the economical and safe production of the desired products with the intended form and composition.

Microsystem technology, coming from information technology and miniaturization of data-processing devices, has now entered many fields in our daily life. Silicon chips and sensors can be found in cars, washing machines or smart cards with various functions. Besides the data-processing function, microsystems have taken over other tasks like sensing and analyzing, actuating or controlling larger systems. Microsystem engineering comprises besides engineering skills like design, simulation, or material knowledge also a deep physical and chemical knowledge for the fabrication and functional design issues. Also medical and biological skills are useful for the growing application fields for analysis, diagnostics, and therapeutics. A good overview about the state-of-the-art in microsystem technology is given in [2]. For the control and manipulation of still smaller systems, microsystem technology is a major link to nanotechnology [3, 4].

Figure 1.1 gives an impression of the wide field and complexity of both disciplines, but also illustrates the multiple interfaces and common fields. The fruitful ideas from both sides may inspire the further development in both disciplines and result in an enlargement of possibilities and applications for the innovation across the borderlines.

Chemistry in *miniaturized equipment* is an emerging discipline coming together from microsystem technology and from chemical engineering, but also an established discipline of chemical analytics. Starting at the end of the nineteenth century a group of researchers at the University of Delft around Behrens [4a] and at the Technical University of Graz around Prof. Emich and Prof. Pregl developed the chemical analysis of very small amounts of reagents. In 1900 Prof. Behrens wrote his book “Mikrochemische Technik” [4a] about micro chemical techniques. In 1911 Prof. Friedrich Emich published the textbook “Lehrbuch der Mikrochemie” [5] and Prof. Fritz Pregl was rewarded in 1923 by the Nobel price for his fundamental work in microchemical analysis. In the middle of the last century in nuclear science small structures were developed for the separation of isotopes, see [6]. From this work, among others, the LIGA technology emerges at German research institutes.

Dealing with very small geometrical structures is also a well-known area in process engineering. The adsorption technology and chemical reactions at catalytic surfaces are based on the flow and adhesion processes in nanoscale pores [7, Chapter 4]. Transformations and transfer processes on the molecular scale are called “micro processes” in contrast to a “macro process” where convection

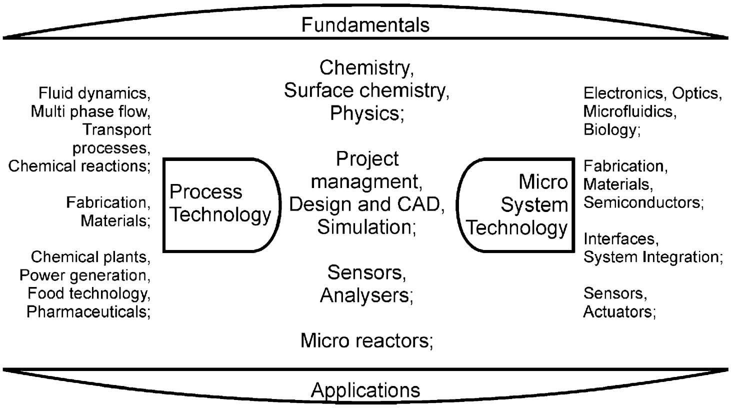

Fig. 1.1 Disciplines of process engineering and microsystem technology, differing and common overlapping areas (middle column). The lists are not complete and the future will certainly bring new applications and new common fields and applications.

plays the major role. Some typical length scales for process technology, chemistry and microtechnology are given in Fig. 1.2.

Figure 1.2 illustrates the different wording in process engineering, microsystem technology, and nanotechnology, especially the different meaning of "micro". The micropores in adsorption media are one characteristic example on the nanometer scale. Microstructured equipment has internal characteristic dimensions like channel diameter or gap height within the micrometer range. A clear definition of "micro" does not exist, but it is not necessarily required for all applications and areas.

In the process industry, there are several applications of structures with typical dimensions below 1 mm, like compact plate and fin heat exchangers or structured packings in separation columns for enhanced heat and mass transfer. This is often summarized under the key word of process intensification. However, the miniaturization of conventional technology is limited by two major restrictions: the fabrication possibilities for the small structures at reasonable costs and the increased fouling probability, the high danger of blocking, and total failure of these structures. The first restriction has been widened with the enhanced fabrication possibilities, but the risk of fouling and blocking is still there and should not be underestimated.

The elementary setup of microstructured and conventional equipment is similar and displayed in Fig. 1.3. Process plants consist of process units, which themselves are made of equipment like heat exchangers or vessels with internal structures. The basic geometrical elements of the internal structures in conven-

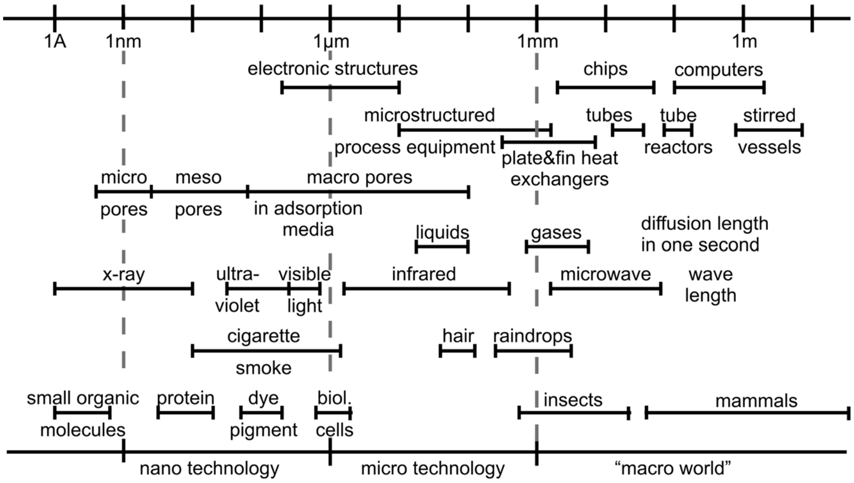

Fig. 1.2 Characteristic length of important processes and equipment in chemical engineering and microsystem technology. The top and bottom line indicate also the different wording of micro processes in the two disciplines, adopted from [8].

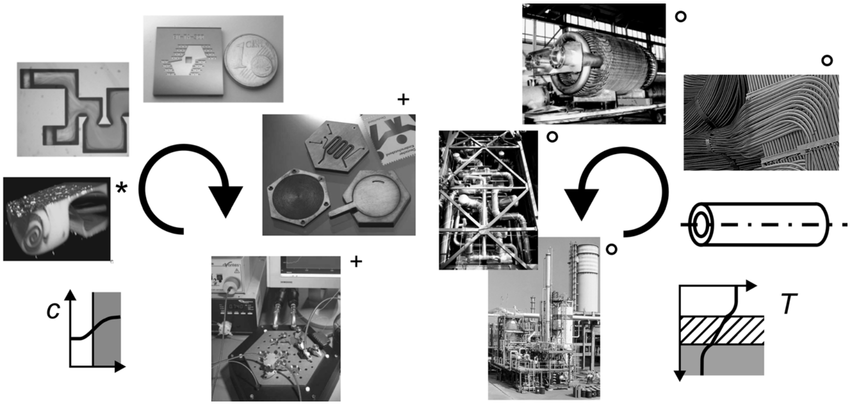

Fig. 1.3 Setup of microstructured and conventional equipment from single microstructures through combined elements to an entire plant. The principle of the active area can be applied in both cases (Sources: * from [9]; + courtesy of FhG-ICT, Pfinztal, Germany; o courtesy of Linde AG, Wiesbaden, Germany).

tional technology are the tube, the plate, and the film, on or in which the transport processes and transformations happen. The layout of process equipment and process steps follow this scheme from small elementary active areas ("micro process") over the process space of the device ("macro process") to the balancing of the complete process.

The parallel arrangement of microstructured channels or elements is called internal numbering-up, which is the most frequent way to increase the throughput of an apparatus. The parallelization of microstructured devices is called external numbering-up, applied to bypass the flow distribution problems within the equipment. A relatively new concept is the equal-up concept, the parallelization of similar effects [8]. The numbering-up and equal-up concepts facilitate the scale-up process from laboratory equipment to production equipment, but still have their own problems of flow distribution in manifolds, see Chapter 8.

1.2
Unit Operations and Beyond

The consecutive groups or steps in a process plant can frankly be named for many cases as

- pretreatment or conditioning of the incoming substances,
- transformation of the reagents in chemical, physical, or biological processes,
- separation of the received components, and
- purification and conditioning of the products, see Fig. 1.4.

The physical and chemical processes in the various steps may be the same or similar, like heat transfer or extraction. They are called *unit operations* that are playing a major role in the research and development of process engineering. The unit operations can be combined and connected in different forms. The concept of unit operation combines a macro process with the apparatus to a process unit. It allows us to treat all micro processes within the process space in the same manner and to derive scientifically based design rules and calculation instructions. For an entire process plant the unit operations are combined and switched in a proper way and integrated for efficient material and energy use. Besides the energy and mass flow integration the appropriate process control and automation determines the economical performance and safety of the plant. This gives a very complex picture of a chemical or process technology plant, which is illustrated in Fig. 1.4. For a proper design and operation of a plant, many disciplines have to work closely together.

The unit operations can be categorized into three major groups according the employed physical effects and major driving forces for combination or separation of substances: the mechanical, the electromagnetic, and the thermal unit operations (molecular driving forces) see Table 1.1. This list does not claim to be complete, especially the separation processes from analytics are only shown schematically. Probably in the next years further operations will be developed enabled by enhanced fabrication and integration possibilities. In adsorption of species or membrane separation, chemical processes may also be involved for mass-transfer processes in microstructures, see [11, Chapter 3]. The consequent treatment of unit operations allows the methodological design with help of the following principles. The *principle of continuity* of substances, phases, energy and momentum includes the preference of continuous processes opposite to batch processes. The *principle of balancing* of the relevant transport processes gives the energy, momentum, and mass fluxes in differential or black-box form. The *principle of scaling* and *similarity* of processes gives a calculation tool for transferring experimental, analytical, and numerical results to processes on different scales with the help of dimensionless numbers and groups.

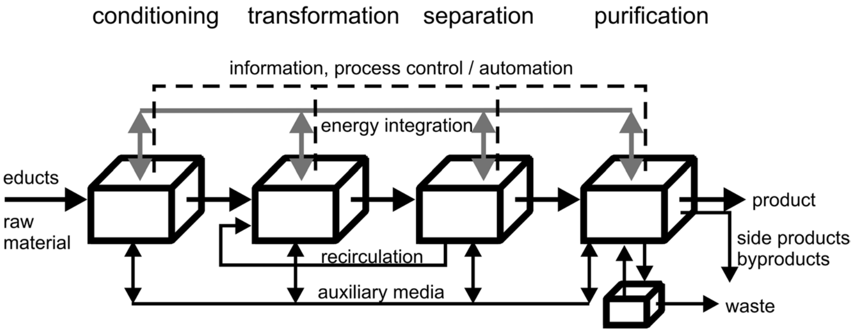

Fig. 1.4 Main process steps in a chemical production plant with pretreatment, conversion, separation, and purification of the products, adapted from [10]. The system integration includes the energy management, auxiliary media as well as information for the process control and automation.

Table 1.1 Main mixing and separation unit operations.

Unit operations	Molecular/thermal	Mechanical/ext. force	Electromagnetic
Mixing and aggregation Combination Control of segregation	diffusion$^{1)}$ dissolving$^{2)}$ extracting$^{2\,c)}$ desorption$^{2\,c)}$	spraying$^{2)}$ aeration$^{2)}$ stirring$^{2)}$ mixing$^{1,\,2)}$ dosing$^{1,\,2)}$	electrophoretic mixing$^{1)}$ mixing with magnetic beads$^{2)}$
Separation *Employed phases:* 1) single phase 2) multiple phase a) with own cophase b) own + additional cophase c) additional cophase	thermodiffusion$^{1)}$ countercurrent diffusion$^{1)}$ condensation$^{2\,a)}$ evaporation$^{2\,a)}$ crystallization$^{2\,a)}$ distillation/rectification$^{2\,a)}$ drying$^{2\,b)}$ absorption$^{2\,c)}$ adsorption$^{2\,c)}$ extraction$^{2\,c)}$ ion exchange$^{2\,c)}$ membrane processes	sedimentation$^{2)}$ cycloning$^{2)}$ centrifucation$^{2)}$ pressure diffusion$^{1,\,2)}$ (ultracentrifuge) filtration osmosis gas permeation classification sorting	eledcodeposition$^{2)}$ magnetodeposition$^{2)}$ electrofiltration electrodialysis electroosmosis electrophoresis magnetostriction

More detailed operation description and further reading in [10, 13–15]; additional thermal unit operations, which are closely related to the listed:

Condensation: partial condensation$^{2\,a)}$

Evaporation: flash evaporation$^{2\,a)}$, vacuum evaporation$^{2\,a)}$

Drying: freeze-drying$^{2\,a)}$, radiation drying$^{2\,a)}$, superheated steam drying$^{2\,a)}$

Distillation: outside/secondary steam distillation$^{2\,b)}$, molecular distillation$^{2\,a)}$, reactive distillation

Rectification: extractive rectification$^{2\,b)}$, azeotropic rectification$^{2\,b)}$

Absorption: chromatography, desorption

Membrane processes: permeation, pervaporation, dialysis, osmosis and reverse osmosis, micro- and ultrafiltration.

The *principle of an active area* indicates the platform of the driving forces in molecular and thermal processes. It provides a description for the transfer processes with linear correlations between the flux and the driving force, also called the kinetic approach [12, Chapter 1]. The processes act in basic geometrical elements like the vessel, the tube, a channel, pipe, pores, or plates, which are combined to form the process space in the chemical equipment. Within these elements the fluid itself forms geometrical elements like beads, drops, bubbles, films or thin layers, which determine the transfer processes and which are confined by the geometry, see Fig. 1.5. The three phases of a pure substance allow the following combinations for phase mixtures of a carrier fluid and a dissolved

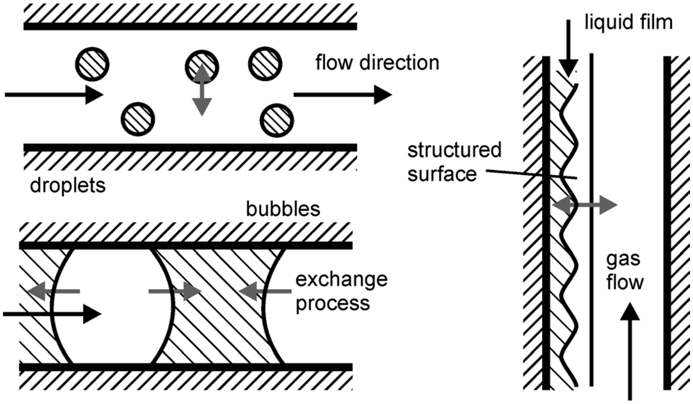

Fig. 1.5 Geometrical elements for transport processes between two phases: droplets, bubbles and a falling film on a structured surface.

phase: gas – gas, gas – liquid (droplets and aerosols), gas – solid (aerosols) and liquid – gas (bubbles and foam), liquid – liquid (miscible or immiscible, emulsion), and liquid – solid (suspension).

The *principle of technical enhancement* and *process intensification* compared to the natural driving forces gives the opportunity to control the transfer rates and state conditions in a way that is optimal for the desired results. The *principle of a selective phase* enormously enlarges the process space by adding a new component, which enforces a new equilibrium within a process (drying, extraction, stripping etc.). The *principle of flow guidance* in the equipment and process space (cocurrent, countercurrent, crosscurrent, mixed arrangement or recirculated flow) in addition with various switching possibilities (series, parallel, cascading) gives the basis for the effective exploitation of the existing driving force. The heuristic application of these principles can facilitate the system design and encourage the process engineering and microsystem engineering research and development [10].

Mixing can be treated as a major unit operation, which is fundamental for many other processes. Mixing can adopt many forms like homogenization, dispersing, or suspending; mixing can occur with or without chemical reactions, or as a precursor for chemical reactions, in combustion, or polymerization. A modern, general definition of mixing is the control of segregation, which describes the general role of mixing in process technology. The potential of microstructures in mixing processes, like the short diffusion length, a fast mixing or controlled flows, will be shown in various parts of this book.

A further major process step, the transport of fluids, is not listed in Table 1.1, but is partially included in the unit operation description. Active devices for fluid transport are pumps and compressors, which possess a wide variety of possibilities depending of the fluid, the viscosity, the required pressure increase, and the volume flow. Inside conventional equipment, field forces are employed for the fluid transport: a density or pressure difference, centrifugal or inertial forces. Additionally, capillary forces can be used for fluid transport due to the channel geometry and the surface characteristics of the material, see [16].

Chemical reactions are more heterogeneous than the above presented unit operations. There exist some segmentation proposals similar to the unit operations that follow physical or physicochemical aspects like heat release (exo-, endothermic), rate constants (fast, slow), kind of initiation (photo, electro, ...), or the component phases. Vauck and Müller [1] count up to 27 chemical reaction types, which can hardly be classified. The reactors, the equipment with chemical reactions inside, can be categorized with the help of the operation: batchwise within a vessel, stopped flow for many analytical applications, or continuous flow in a pipe, in a fixed or fluidized bed. The continuous-flow operation is the predominant mode for microstructured equipment due to the small hold up of media inside the reactor. A comprehensive overview of chemical reactions in microstructures is given in [17, Chapters 3 to 5], which describe 21 different reactor types with 23 gas-phase reactions, 36 different reactor types with 95 liquid-phase reactions, and 12 different reactor types with 28 gas-liquid reactions.

A large field of chemical reactions deals with catalytic transformations. In homogeneous catalysis, the catalyst acts in the same phase as the reagents. Examples are enzymatic reactions where the liquid catalyst enforces biological transformations. Hessel et al. [17, Chapter 3] count 24 reactor types for catalyst screening, which is a popular application for microstructured devices. The majority of catalytic reactions (>80%) are dealing with more than one phase, especially with solid or immobilized catalysts. In these reactions the mass transfer is the major limiting process. Fuel-cell reactors are summarized by Hessel et al. in [18, Chapter 2] with about 12 reactor types and 63 reactions.

At the end of this chapter, the scaling behavior of processes as well as the benefits and the potential for miniaturization is sketched for selected unit operations together with a more detailed description. The combination of the various units leads to a complex, hierarchic unit of processes and equipment that can show emerging abilities not possible within a single unit. The whole system is more than the sum of all elements. Hence, the concept of unit operations has its limits and should be complemented by a holistic integrated process design.

1.3
Balances and Transport Equations

The starting point of process engineering calculations and the design of process equipment are the conservation and balance equations of mass, species, momentum, and energy as well as the definition of the entropy. The conservation laws of mass (continuity equations) and energy (First Law of thermodynamics) hold in the scope of chemical processes dealt with in this book. They can be described by words in the following scheme:

$$\begin{bmatrix}\text{System change}\\ \text{with time}\end{bmatrix} = \begin{bmatrix}\text{Incoming}\\ \text{Flow}\end{bmatrix} - \begin{bmatrix}\text{Outgoing}\\ \text{Flow}\end{bmatrix} + \begin{bmatrix}\text{Source or}\\ \text{Sink}\end{bmatrix} \tag{1.1}$$

The source or sink of the flow property depends on the system and the parameter itself and is described later together with other possible simplifications.

1.3.1
Statistical Mechanics and Boltzmann Equation

Before introducing the balance equations of the various parameters, a short excursion to the molecular origin of these equations starts with the derivation of the Boltzmann transport equation for the thermodynamic equilibrium. In an ideal gas the molecules are regarded as hard spheres interacting only by very short hits with other molecules or with the boundary (wall, surface, or other limiting elements). It can be assumed that the probability of a molecule moving with the velocity w in a certain direction is equal for all three space coordinates, see also [19, p. 148]. This can be expressed by the constant ratio of the derivation of the probability distribution function (PDF) to the function $f(w)$ itself and the velocity component w,

$$\frac{f'(w)}{wf(w)} = \frac{\mathrm{d}\ln f(w)}{w\mathrm{d}w} = -2\gamma\,, \quad \Rightarrow \ \ln f(w) = c_i - \gamma \cdot w^2 \tag{1.2}$$

The integration constant is set to -2γ and determined with the kinetic energy of the molecules,

$$\gamma = \frac{M^*}{2kT} = \frac{M}{2R_\mathrm{m}T} \tag{1.3}$$

The integration constant c_i is determined by normalizing the sum of the probability to unity. The integration gives the probability distribution for one velocity component w, which stands for the other components as well.

$$f(w) = \left(\frac{M}{2\pi R_\mathrm{m} T}\right)^{\frac{1}{2}} \mathrm{e}^{-\frac{M}{2R_\mathrm{m}T}w^2} \tag{1.4}$$

The integration over a sphere of the three space coordinates gives the probability of the absolute velocity c, independent of the direction,

$$\varphi(c)\mathrm{d}c = 4\pi c^2 F(c)\mathrm{d}c \ \Rightarrow \ \varphi(c) = 4\pi c^2 \left(\frac{1}{2\pi RT}\right)^{\frac{3}{2}} \mathrm{e}^{-\frac{1}{2RT}c^2} \tag{1.5}$$

The most probable velocity of a molecule is determined by $c_\mathrm{mp} = \sqrt{2RT}$. The mean velocity from the kinetic energy is given by $\bar{w} = \sqrt{3RT}$. With the number of molecules in a unit volume N_A and the collision cross section of the spherical molecule $\pi\sigma^2$, the number of hits between the molecules and the mean time between these hits can be determined. Multiplied with the mean velocity, an estimation of the mean free path of a molecule, the average length between two collisions, can be derived:

$$\Lambda = \frac{kT}{\sqrt{2}\pi p \sigma^2} \ . \tag{1.6}$$

The mean free path divided by a characteristic length gives the dimensionless Knudsen number Kn, which is used later to estimate the influence of the molecular mobility on the fluid behavior inside microstructures, see Section 3.3. A closer look at the probability distribution f for the location $\vec{x} = \vec{x}\ (x, y, z)$ and the velocity space of a particle $\vec{w} = \vec{w}\,(u, v, w)$ varying with time gives a better image of the forces and energy distributions in an ideal gas. The integration of the PDF over the velocity space results in the number of particles in the control volume [20, p. 4],

$$\int f(t, \vec{x}, \vec{w})\mathrm{d}\vec{w} = N(t, \vec{x}) \tag{1.7}$$

The integration of the PDF over the velocity space, divided by the mass, results in the fluid density,

$$\rho = \frac{1}{m}\int f(t, \vec{x}, \vec{w})\mathrm{d}\vec{w} \tag{1.8}$$

The integration of a state variable multiplied by the PDF over the velocity space gives the mean value of this variable. The total derivative of the PDF in an external field (for example a gravitation field) is determined by the collisions of the molecules in a control volume, in detail, the current of gain and loss due to the molecule collisions,

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \vec{w}\cdot\frac{\partial f}{\partial \vec{x}} + \frac{F}{m}\,\frac{\partial f}{\partial \vec{w}} = J_{\mathrm{gain}} - J_{\mathrm{loss}} = \Delta J_{\mathrm{coll}} \tag{1.9}$$

This equation is called the Maxwell–Boltzmann transport equation, an integro-differential equation. The determination of the loss and gain current, the collision integral, and the construction of the PDF are the main problems in solving Eq. (1.9), see also [21, 22]. Regarding the collision of two molecules with the relative velocity w_{rel}, with the probability f and f_1 before and the probability f' and f'_1 after the collision, the integration over the volume element and the velocity space of both molecules after the collision determines the left side of Eq. (1.9), the collision integral, see [19, p. 263].

$$\Delta J_{\mathrm{coll}} = \int \frac{\sigma^2}{2}\,\vec{w}_{\mathrm{rel}}(f' f'_1 - f f_1)\mathrm{d}\vec{w}_1\,\mathrm{d}\vec{w}'\,\mathrm{d}\vec{w}'_1 \tag{1.10}$$

This collision term is also used and implemented in the numerical lattice methods, see [23]. The first moments of the PDF f_{J}, for which the collision term will vanish in the case of local equilibrium, are also called the collision invariants and will be used to yield the first solutions of Eq. (1.9). With these variables f_{J} the Boltzmann equation can be simplified to:

$$\frac{\partial}{\partial t}(\rho f_{\mathrm{J}}) + \frac{\partial}{\partial \vec{x}}(\rho f_{\mathrm{J}} \vec{w}) + \frac{\rho \vec{F}}{m} \frac{\partial f_{\mathrm{J}}}{\partial \vec{w}} = 0 \tag{1.11}$$

For $f_{\mathrm{J}} = 1$ the mass conservation equation is derived,

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \vec{w}) = 0 \tag{1.12}$$

For the velocity components $f_{\mathrm{J}} = u, v, w$, the momentum conservation equation for all three space coordinates is derived,

$$\rho\left(\frac{\partial \vec{w}}{\partial t} + \vec{w}\frac{\partial \vec{w}}{\partial \vec{x}}\right) + \frac{\partial p_{\mathrm{J}}}{\partial \vec{x}} + \operatorname{div}\left(\frac{\partial \vec{w}}{\partial \vec{x}}\right) - \frac{\rho \vec{F}}{m} = 0 \tag{1.13}$$

This equation is the basis for the Navier–Stokes equations of fluid dynamics. The collision invariant $f_{\mathrm{J}} = 1/2\ w^2$, which describes the continuity of the kinetic energy during the collision process, leads to the following equation,

$$\frac{\partial}{\partial t}\left(\frac{\rho}{2}\overline{\vec{w}^2}\right) + \frac{\partial}{\partial \vec{x}}\left(\frac{\rho}{2}\overline{\vec{w}^2\,\vec{w}}\right) + \frac{\rho \vec{F}}{m}\overline{\vec{w}} = 0 \tag{1.14}$$

With the following simplifications for the velocity mean values [19, p. 266]

$$\overline{\vec{w}^2} = \frac{3p}{\rho} + w^2 \quad \text{and} \quad \overline{\vec{w}^2\,\vec{w}} = \frac{2}{\rho}(-\lambda \operatorname{grad} T) \tag{1.15}$$

the energy conservation equation can be written as

$$\rho\frac{\partial \dot{q}}{\partial t} + \vec{w}\frac{\partial \dot{q}}{\partial \vec{x}} + \operatorname{div}(-\lambda \operatorname{grad} T) + p \operatorname{div} \vec{w} + \dot{e}_{\mathrm{q}} = 0 \tag{1.16}$$

where the term $\dot{e}_{\mathrm{q}}$ describes the shear and deformation tensors in the energy equation, which can be summarized with the viscous dissipation. A more detailed discussion on the energy equation is given in [19, p. 266]. Here, the illustration of the linkage between the microstate Boltzmann equation (1.9) and the macrostate balance Eqs. (1.12) to (1.16) is sufficient and gives a good insight for molecular processes. The macroscopic equations are valid, if enough molecules act together to receive a smoothed signal from the collisions ($N > 10^6$). A further and detailed discussion of special microeffects can be found in [24]. In Chapter 2 of this book the limits of continuity are treated in more detail.

1.3.2
Macroscopic Balance Equations

The macroscopic balance equations for process equipment can be formulated on various levels as shown in Fig. 1.6. The equipment level is the basic calculation niveau for plant design and layout. Elements of the equipment like tubes or trays can be balanced on the level of a differential length, which refers to the "micro process" description. The third and base level is represented by the differential element (here for all three dimensions with flow in the z-direction), which allows the continuum approach and the integration over the balance space. These three levels may take different forms regarding the relevant problem.

In Fig. 1.6 the balanced variables in a differential element are given by the parameter X, which stands for the mass, species, momentum, or energy. The general balance equation for a system and a differential element is written as:

$$\frac{\partial}{\partial t}X = X\mathrm{d}y\,\mathrm{d}x - \left(X\mathrm{d}y\mathrm{d}x + \frac{\partial}{\partial z}X\,\mathrm{d}z\,\mathrm{d}y\,\mathrm{d}x\right) \tag{1.17}$$

with X as the general balanced value.

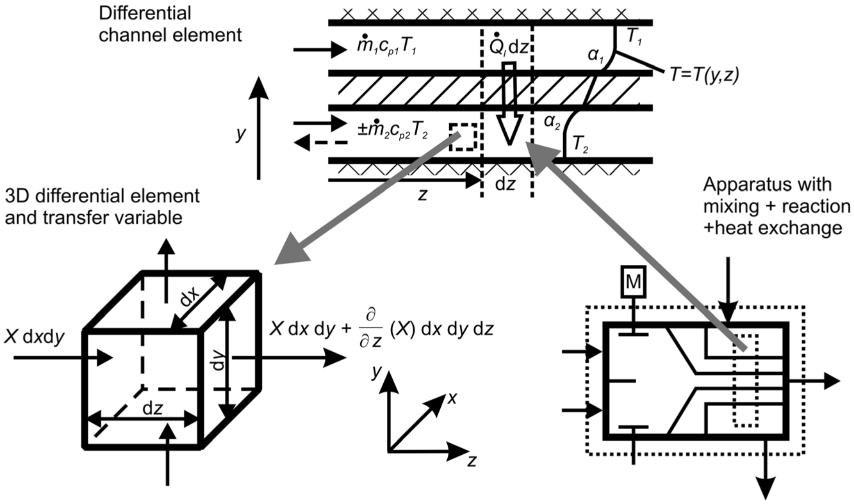

Fig. 1.6 Overview of the various balancing volumes in process engineering: 3D differential element for general calculations, 1D differential element depending on the geometry of the active area (channel, tube, plate, film, interface, see Fig. 1.5), and entire equipment for process balances (right).

1.3.3
The Mass Balance

Within the systems treated in this section no mass is generated or destroyed, hence no sink or source appears in the balance equation (1.1). The mass balance for a process element is written as

$$\sum m_{\text{in}} = \sum m_{\text{out}} - \sum m_{\text{conv}} = \text{const.} \tag{1.18}$$

For time-dependent mass flow rates, Eq. (1.8) can be written as

$$\frac{\partial m}{\partial t} = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} \tag{1.19}$$

In a one-dimensional differential element, the balanced value X is set to the density multiplied by the velocity. The balance equation (1.17) can accordingly be written as

$$\frac{\partial(\rho A)}{\partial t} = -\frac{\partial(\rho w A)}{\partial z} \tag{1.20}$$

For a constant cross section or for a cubic differential element the mass balance can be written as

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \vec{w}) = 0 \tag{1.21}$$

This equation is also known as the continuity equation [25, p. 2] and is one of the fundamental equations of fluid dynamics. For an incompressible fluid the continuity equation can be simplified to

$$\frac{\partial(\rho A)}{\partial t} = 0 = -\frac{\partial(\rho w A)}{\partial z} \tag{1.22}$$

This equation is also called the equation of continuity for the mass in a system. It will help to simplify other balance equations.

1.3.4
The Species Equation

If the fluid density is replaced by the concentration of the relevant species, the species balance of a system can be derived from the mass balance. For an arbitrary process volume this equation can be written as

$$\sum \dot{n}_{\text{in}} = \sum \dot{n}_{\text{out}} - \sum \dot{n}_{\text{conv}} = \text{const.} \tag{1.23}$$

The balance value X for a differential element is $X = \rho c_i w_i$ for the species formulation, which results in

$$\frac{\partial(\rho c_i A)}{\partial t} = -\frac{\partial(\rho c_i w A)}{\partial z} \ . \tag{1.24}$$

Considering chemical reactions [7, p. 297] in the balance space, a species source or sink must be added according the individual reaction rate r_i. For constant density and cross section of the channel the above equation can be rewritten

$$\frac{\partial c_i}{\partial t} = -\frac{\partial(c_i w)}{\partial z} + \sum_s \nu_{is} r_s \ . \tag{1.25}$$

The species transport over the boundary of the balance element is obtained by convection with the velocity w and additionally by diffusion. Hence, for a complete picture of the species transport, the diffusion term must be added to Eq. (1.25) and rewritten as

$$\frac{\partial c_i}{\partial t} = -\frac{\partial(c_i w)}{\partial z} + \frac{\partial(D_i \Delta c_i)}{\partial z} + \sum_s \nu_{is} r_s \ . \tag{1.26}$$

A closer look at the transport processes will be given in the next section as well as in Chapters 3 and 6 of this book.

1.3.5
The Momentum Equation and Force Balance

The momentum of a moving fluid can be expressed as the product of the mass and the flow velocity. The integral of the momentum over the volume results in a net force of the fluid on the volume boundary or on the equipment. In general, the momentum balance of a device can be written as

$$\sum J_{\text{in}} = \sum J_{\text{out}} - \sum J_{\text{loss}} = \text{const.} \tag{1.27}$$

The momentum loss can be interpreted as the viscous momentum loss, which is expressed as pressure loss along the channel or device flow. For a nonviscous fluid flow through an arbitrary channel with an external force, the momentum change can be expressed by the momentum, the pressure, and the gravity part:

$$\frac{\partial(mw)}{\partial t} = (\dot{m}w)_{\text{in}} - (\dot{m}w)_{\text{out}} + (pA_i)_{\text{in}} - (pA_i)_{\text{out}} + mg + F_{\text{z}} \tag{1.28}$$

For a one-dimensional differential channel element with viscous flow, the momentum balance can be written as

$$\frac{\partial(\rho A w)}{\partial t} = -\frac{\partial(\rho w A w)}{\partial z} - \frac{\partial(pA)}{\partial z} + p\frac{\partial A}{\partial z} - \tau L_c - \rho A g\ , \tag{1.29}$$

where L_c means the perimeter of the differential channel element. With the continuity equation (1.22), the above equation can be simplified to

$$\rho A\frac{\partial w}{\partial t} = -\rho w A\frac{\partial w}{\partial z} - A\frac{\partial p}{\partial z} - \tau L_c - \rho A g\,. \tag{1.30}$$

For constant density, nonviscous flow, and a cubic differential element for all three directions, the momentum balance can be written as

$$\frac{\partial \vec{w}}{\partial t} = -(\vec{w}\nabla)\vec{w} - \frac{\nabla p}{\rho} + \vec{g}\,. \tag{1.31}$$

This equation is also called the Euler equation for a nonviscous flow and is one of the basic equations of hydrodynamics [25, p. 4]. Additional forces in microflows may occur with surface effects in multiphase flow like bubbles and droplets, see also Chapters 4 and 5.

1.3.6
The Energy Balance

Energy can take various forms in process technology. But like the mass, the energy itself is conserved according the First Law of thermodynamics.

$$\sum \dot{E}_{\mathrm{in}} = \sum \dot{E}_{\mathrm{out}} - \sum \dot{E}_{\mathrm{loss}} = \mathrm{const.} \tag{1.32}$$

The energy loss takes into account that the energy conversion from one form into another is accompanied by natural losses. These losses are characterized by the entropy change during a process according the Second Law of thermodynamics. For a differential element, which describes the situation for heat transfer, the balanced value X can be set for the heat convection to $X = \rho w_i e_i$ in the z-direction and for the heat conduction to $X{=}q$ in the y-direction. This leads to the energy equation

$$\frac{\partial(\rho w_i)}{\partial t}e = -\frac{\partial(qA)}{\partial z}\ . \tag{1.33}$$

For a process device with mass flow, heat transfer over the boundary, and with technical work (for example mechanical work from an active mixer), and a chemical reaction, the energy equation is written as

$$\frac{\partial(me)}{\partial t} = (\dot{m}e)_{\mathrm{in}} - (\dot{m}e)_{\mathrm{out}} + (p\dot{V})_{\mathrm{in}} - (p\dot{V})_{\mathrm{out}} - p\frac{\partial V}{\partial t} + \dot{Q} + \dot{E}_{\mathrm{q}} + P\,. \tag{1.34}$$

In words: the energy change in a system with time consists of the energy flowing in and out, the volume flow in and out, the volume change inside the system, the heat flux over the boundary by convection, conduction, or radiation, the energy produced inside the system (for example from chemical reactions or flow dissipation), and on the very right-hand side the technical work brought into or produced by the system. This relatively complex equation can be simplified with the help of assumptions and simplifications regarding the actual system.

Considering a channel with a constant cross section, without chemical reactions, and technical work consumed or produced, the energy of the fluid can be expressed according the First Law with kinetic and potential energy

$$me = \rho A(u + w^2/2 + gz)\,. \tag{1.35}$$

The dissipated energy originates from the shear stress τ at the wall. With the First Fourier law $\dot{q} = -\lambda \dfrac{\partial T}{\partial z}$ for the conductive heat transfer, the energy equation can be written in the following form

$$\frac{\partial}{\partial t}\left(\rho\left(u + \frac{w^2}{2}\right)\right) = -\frac{\partial}{\partial z}\left(\rho w\left(u + \frac{w^2}{2}\right)\right) + \rho w g - \frac{\partial}{\partial z}(pw) - \frac{\partial}{\partial z}\left(\lambda\frac{\partial T}{\partial z}\right) - \frac{\partial}{\partial z}(\tau w) + \dot{w}\,, \tag{1.36}$$

the so-called Bernoulli equation for the energy balance in a channel flow. This complex equation (not taking into account other energy-transfer processes like radiation, technical work, or the chemical reactions) can be simplified by adjusting to the actual process.

For open systems and flow processes, the inner energy is replaced by the enthalpy $h = u + p/\rho$. For flow processes the total enthalpy $h_\mathrm{t} = u + p/\rho + \dfrac{w^2}{2} - gz$ is used with the kinetic and potential energy part [26, p. 66]. With the energy dissipation coming from the shear stress and the velocity gradient $\varepsilon = \dfrac{\partial}{\partial z}(\tau w)$ (here only the z-direction) the enthalpy form of the energy equation can be written as

$$\rho\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{\mathrm{d}p}{\mathrm{d}t} + \varepsilon - \nabla\dot{q}\,. \tag{1.37}$$

With the caloric equation of state, the correlation between the inner energy or enthalpy and the temperature

$$\mathrm{d}u = c_\mathrm{v}\mathrm{d}T\,;\ \mathrm{d}h = c_\mathrm{p}\mathrm{d}T\,, \tag{1.38}$$

the energy equation can be rewritten as

$$\rho c_\mathrm{p} \frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\mathrm{d}p}{\mathrm{d}t} + \varepsilon - \mathrm{div}\,(\lambda \,\mathrm{grad}\, T)\ . \tag{1.39}$$

The solution of this equation gives the temperature distribution for the actual process. Besides the conduction and convection, heat may also be transported by radiation, which is proportional to T^4 and the emission properties of a surface. Radiation heat transfer is not treated here; interested readers are referred to [27, Chapter 5]. A chemical reaction within the system touches not only the species equation but the reaction enthalpy has also to be considered in the energy balance due to the apparent heat consumption or release.

$$+\Delta H_\mathrm{R} = H_\mathrm{r} - H_\mathrm{p} \tag{1.40}$$

The net heat balance is calculated from the enthalpy of the reactants and the products, see also [28, p. 371].

1.3.7
The Entropy Equation and the Efficiency of a System

On dividing the reversible heat flux q by the temperature T a new state variable, the entropy s, is derived for further characterization of states and processes. With the thermodynamic correlations

$$\begin{aligned} \mathrm{d}s &= \frac{\mathrm{d}q}{T} = \frac{\mathrm{d}u + p\mathrm{d}v}{T}\ , \\ T\mathrm{d}s &= \mathrm{d}u + p\mathrm{d}v \\ &= \mathrm{d}h - v\mathrm{d}p\ , \end{aligned} \tag{1.41}$$

the entropy correlation can be derived from Eq. (1.37)

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\left\{\frac{\varepsilon}{\rho} - \frac{1}{\rho}\nabla\dot{q}\right\}\ . \tag{1.42}$$

The dissipation function ε is the friction loss per volume and time unit. The entropy production is a major indicator of the efficiency or effectiveness of the process. Generally, the efficiency of a process is described by the ratio of the profit to the effort put into the process. The effort for a process may come from the input like energy, pressure loss, or heat loss. Furthermore, the effort may be defined from the fabrication effort for the device, the used materials, the effort to maintain a correct operation, or reliability efforts. The profit from a process depends on the task. It may be the throughput, the energy transfer, the mixing intensity, or the conversion rate, selectivity or time-space yield of a chemical reactor. Due to the large variety of devices in micro process engineering, the application task is also very important. A mixing device for bioanalytical purposes possesses different specifications from a mixer for chemical reactions in the production. A micromixer for a fast chemical reaction may be inadequate for a slow reaction and lead to insufficient results. Therefore, the application of the device must be exactly specified and, hence, the effectiveness as well. These various applications may come from analysis systems (μTAS), from the lab-on-a-chip field, from process or material screening, from energy conversion, or from chemical production.

1.3.8
Elementary Transport Processes and their Description

The balance equations are derived from equilibrium states, which do not reflect the transport processes between the single states. If the gradients are not too high (valid in our case), the transport processes can be described with linear correlations and phenomenological coefficients. The entire change of a state variable is described by the transport processes of the conduction in the immobile phase (solids or resting fluids), of the convection in the fluid phase (gases and liquids), and by the generation or depletion in the control volume.

$$\begin{bmatrix}\text{Total flow}\\\text{density}\end{bmatrix}=\begin{bmatrix}\text{Conduction}\\\text{over the}\\\text{boundary}\end{bmatrix}+\begin{bmatrix}\text{Convection}\\\text{over the}\\\text{boundary}\end{bmatrix}+\begin{bmatrix}\text{Source}\\\text{or}\\\text{Sink}\end{bmatrix}\tag{1.43}$$

The transport correlations can be expressed in the fundamental form

$$J = L \cdot A \cdot X \tag{1.44}$$

In words: the flux (intensity) equals the intensity (transport coefficient) multiplied by the active area (cross section) and the driving force (parameter difference). The main transport phenomena in process engineering are given in Table 1.2 supplemented by the electrical transport. The geometrical situation of the flow, the temperature and concentration distribution at the channel wall is displayed in Fig. 1.7, left side.

Both single-phase transport as well as transport processes at interfaces often occur in process engineering. For the fluid/fluid exchange of mass, species and energy, there are several models to describe the transport process. The *two-film model* is one of the most common models, which gives good analytical results and shows a physical complete picture, see Fig. 1.7, right side.

For a liquid A and a fluid B, which may be gaseous or liquid with a low miscibility in A, the species transport equations may be written in the following form

$$\dot{n}_i^A = \beta_i^A A(c_{i,\mathrm{bulk}}^A - c_{i,\mathrm{interf}}^A) \tag{1.45}$$

$$\dot{n}_i^B = \beta_i^B A(c_{i,\mathrm{interf}}^B - c_{i,\mathrm{bulk}}^B) \tag{1.46}$$

Table 1.2 Transport mechanisms and transport properties.

Flow process	**Mass flow**	**Species**	**Momentum**	**Heat**	**Electrons**
Conduction	through porous membrane $\dot{m} = k\Delta p$	$\dot{n}_i = -DA\nabla c_i$	$\dot{J} = F = -\eta A\nabla w$	$\dot{Q} = -\lambda A\nabla T$ $= -a\rho c_p A\nabla T$	$I = \dot{E} = \frac{1}{R_{el}}\nabla U$
Convection	$\dot{m} = \rho Aw$	$\dot{n}_i = c_i Aw$	$\dot{J} = F = \frac{\rho}{2}Aw^2$	$\dot{Q} = \rho c_p TAw$	$P = U \cdot I$
Transfer flow	$\dot{m} = \rho Aw$	$\dot{n}_i = \beta A\Delta c_i$	$\dot{J} = F = \gamma A\Delta w$	$\dot{Q} = \alpha A\Delta T$	Flow of electrolytes [29]

Transfer coefficient $\beta = \frac{D}{\delta}$, m/s $\alpha = \frac{\lambda}{\delta}$, W/m^{2}K $\gamma = \frac{\eta}{\delta}$, kg/m^2 s,
with the boundary layer thickness δ

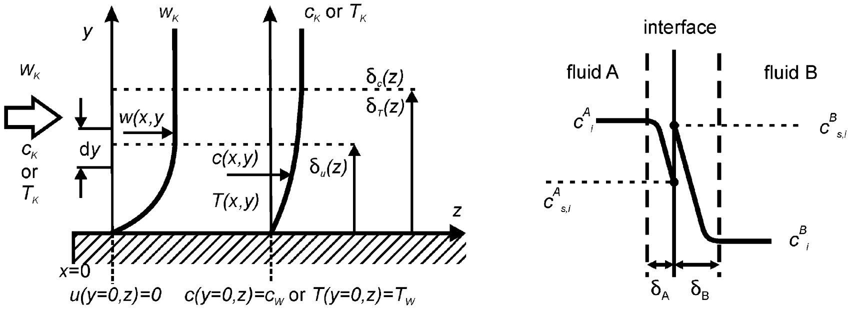

Fig. 1.7 Left: Transport process in a differential element in channel flow with velocity w, temperature T, and concentration c profiles at the wall; right: Two-film model with two different interface conditions [7, p. 93].

When fluid B is an ideal gas, the concentration can be replaced by the partial pressure and the ideal gas law can substitute the transfer coefficient. For the absorption of a gas into a liquid, Henry's law describes the solubility of the gas [30, p. 535]

$$p_{i,g} = H_i c_{i,i} \tag{1.47}$$

with the Henry coefficient H_i. For the evaporation or condensation of a binary mixture (distillation, rectification) the relation between the concentrations at the interface is described by the Raoult's law [30, p. 278]

$$p_i = p_t y_i = \pi_i x_i\,, \tag{1.48}$$

with the partial pressure p_i, the vapor concentration y_i, and the liquid concentration x_i. The concentration difference at the interface of emulsions can be described with the Nernst distribution for extraction applications [30, p. 634].

1.3.9
Additional Remarks to Balance Equations

In chemical engineering the values of the process parameters from the balance equations are often displayed in tables combined with process flow diagrams. This combined display gives a comprehensive overview and is the output from basic engineering design. The design and development of processes is described in Chapter 7 in more detail, which includes the usage of balance sheets, process flow diagrams, and pipe and instrumentation diagrams (PI diagram).

The rather complex balance equations can be simplified considering the actual process. In a steady process the time derivative vanishes $\partial/\partial t = 0$. In systems with high velocities, the convection transport is dominant compared to conductive and diffusive fluxes. For systems with dominant chemical reactions, only the change of substance has to be considered. Incompressible flow does not count for density changes. Also, simple pipe and channel flows without chemical reactions or technical work are often found in technical systems.

The limit of the continuity assumption is reached for the diffusivity in porous media [7, p. 74] and rarefied gas flow for Knudsen numbers Kn larger than 0.001 [2]. The linear transport coefficients are limited to moderate process conditions and low transport rates. The relaxation time of processes in liquids and gases under normal conditions is about 10^{-9} s, which gives an order of magnitude where the processes can be treated with linear correlations and transport coefficients. Faster processes are briefly mentioned in Chapter 3 and can be treated, for example, with the model of extended irreversible thermodynamics [31].

1.4
Calculation Methods and Simulation

Various steps of knowledge for technical processes exist: first the basics as a rough, but generally accurate interpretation of the observed phenomena, second, a detailed analysis, elaborated in the framework of measurement rules or empirical correlations that deliver a reliable solution for certain phenomena in the praxis, and third, as most exact knowledge, a theory that shows the physical background of the investigated process [1, Chapter 1]. Calculation for process engineering can be classified according to the knowledge and the needs of praxis to

- exact mathematical calculations with complete knowledge of the correlations and solutions of the differential equations (ideal case),
- calculation with simplified models, where the simplification grade determines the exactness (numerical simulations are always simplifications and approximations),
- inter- and extrapolation of experimental results,
- application of dimensional analysis and similarity theory for general laws and for scale up/down.

Besides the knowledge and application of mathematical and engineering tools, the accurate, critical judgment and interpretation of the results are essential for the reasonable and responsible work of an engineer. The main sources of errors in that process are:

- incomplete or erroneous information of states and behavior of technical systems. This plays an important role in complex systems, where emergent behavior cannot be predicted in an exact way;
- numerical procedures are always general approximation methods that only get close to the exact solution and possess an inherent error. These errors have to be estimated by the numerical code;
- the treatment of numbers by the programs and routines can lead to errors, for example by truncations that may influence the calculation of complex, iterative systems.

Hence, an approach from different sides, analytical and numerical calculations as well as experimental validation, will help in establishing a comprehensive treatment of microstructured devices.

1.4.1
Physical Variables and Dimensional Analysis

A numerical value and a related dimension define physical state variables. The dimension is the generalization of a physical parameter. For example, the mechanical theory can be explained with the help of three main dimensions: length (meter, L), mass (kilogram, M), and time (second, T). From these values derived units are the volume (M^3), the density (ML^{-3}), the velocity (LT^{-1}), or the acceleration (LT^{-2}). Other basic units are the temperature (Kelvin, Θ), the species amount (mol, N), or the electrical current (ampere, I). The following calculation rules are valid for the units:

$$\mathrm{L} + \mathrm{L} = \mathrm{L};\ \mathrm{LT}^{-1} - \mathrm{LT}^{-1} = \mathrm{LT}^{-1};\ \mathrm{L} \times \mathrm{L} = \mathrm{L}^2;\ \mathrm{L/T} = \mathrm{LT}^{-1};\ \mathrm{L/L} = 0 \qquad (1.49)$$

The important physical parameters of a process can be combined to dimensionless numbers. There are four ways to derive the dimensionless numbers from the problem description [32]:

1. dimensionless groups from the dimensionless differential equations, for example the Reynolds number Re from the dimensionless Navier–Stokes equations;
2. the fractional analysis of the important forces, of the energy currents and of the characteristic times, for example the ratio of the inertia force to the viscous force leads to the Re number;
3. the reduction of the variables by transformation to dimensionless variables, like the dimensionless time of unsteady heat conduction, which is also the Fourier number;
4. and with the *Π*-theorem of Buckingham applied on the set of important parameters describing the physical process.

A systematic procedure to derive dimensionless numbers is given by Wetzler [33], who lists about 400 numbers to describe various physical processes.

The Π-theorem of Buckingham says that every equation with correct dimensions can be written as a correlation of a complete set of dimensionless parameters.

$$f(x_1, x_2, \ldots x_n) = 0 \;\Rightarrow\; F(\Pi_1, \Pi_2, \ldots \Pi_\mathrm{s}) \tag{1.50}$$

The dimensionless numbers are the potential product of the physical variables

$$\Pi = x_1^{\mathrm{a}_1}\, x_2^{\mathrm{a}_2} \ldots x_n^{\mathrm{a}_\mathrm{n}} \tag{1.51}$$

The general procedure to set up the dimensionless numbers is to:

1. collect a list of the important physical variables x_i,
2. prepare the matrix of basic dimensions for the variables x_i,
3. draw the conditional equations for the exponents a_i,
4. select reasonably of one or more independent variables,
5. use known dimensionless numbers for first simplifications [32],
6. write down the potential equations,
7. determine the exponents with the help of experimental data, analytical, or numerical models.

The above-described procedure gives many possibilities of the dimensionless characterization. A few hints for simplification of dimensionless groups:

- let the interesting variable only appear in one number,
- use simple numbers (simplex) of similar variables from the beginning,
- systematic testing of various sets of numbers.

The dimensionless numbers give the following opportunities for the treatment of physical systems:

- processes are completely similar, if all of their corresponding dimensionless numbers are coinciding,
- if a process is described by several dimensionless numbers, each number is a function of the other numbers,
- to scale a parameter of a process from a test model to the real system, all other parameters should be varied and adjusted to keep the corresponding dimensionless numbers constant. If not all numbers can be kept constant, a partial similarity may be sufficient and an engineering approach with an error estimation has to be conducted to evaluate the scaling.

Based on the dimensionless numbers, the similarity of processes plays an important role in process engineering. The benefits of dimensionless numbers and groups are the possibility of scaling, the reduction of variables, the independence from the unit system (SI or British), and the similarity of processes with the same values for dimensionless numbers. One major drawback is their limited application range. The numbers and their combination are only valid for their model system they were defined for. For example, the Re number for pipe flow is somewhat different from the Re number of a flow over a plate, and should not be intermingled. Also the correlations between the dimensionless numbers are only valid for a certain range. The friction factor for laminar channel flow is inverse proportional to the Re number, which is not valid for turbulent channel flow ($Re > Re_{crit}$). The choice of the influence parameters has to be very cautious and adjusted to the existing problem. The dimensionless numbers do not give any new physical insight, but give a more structured description of the process.

1.4.2
Similarity Laws and Scaling Laws

The basic idea of the scaling is the insight that all physical rules are independent of the choice of the system of dimensions. The application of the scaling laws employs the following relations:
- geometric similarity of the systems;
- dynamic similarity of the systems, the relative values of temperature, pressure, velocity, and others in a system should be the same on both scales;
- boundary conditions should be the same, like constant temperature or zero velocity at the wall.

Miniaturization is assisted very much by the usage of dimensional analysis and the transfer of knowledge into the smaller dimensions. In microstructured equipment the so-called numbering-up process partly replaces the scale-up process, which describes the data transfer from model systems to real plant dimensions. Increasing the number of microstructured elements like channels, mixing elements, or heat-transfer plates in a device means an internal numbering-up. An external numbering-up is the parallel setup of some microstructured devices to a whole group. Both internal and external numbering-up are mainly limited by the appropriate fluid distribution to each element for a proper operation. This drawback can be overcome by a good design of the manifolds or by the equal-up method, where the microstructured elements are not fabricated on small devices like chips or platelets, but integrated on plates or tubes with appropriate fabrication technology, which are themselves also integrated into a whole apparatus [8]. The aim is to reach similar process conditions on different geometrical scales.

1.4.3
Order of Magnitude

To show scaling relations, the Trimmer brackets [2, Chapter 4] were introduced to give an overview about the consequences of a length variation. However, for more complex or coupled processes, this method needs a high effort for displaying the relations between length and other parameters. An alternative way to yield information about the order of magnitude for the relevant effects is the scale analysis described by Bejan [34]. Scale analysis goes beyond dimensional analysis and is a good supplement and a relatively facile method to gain information about the system behavior.

To estimate the order of magnitude for the quantities of interest, the governing equations like balances and the geometrical situation must be known. This has also to be done for the "exact" analysis and is the first step for an engineering analysis. The basic equations, often in the form of partial differential equations, are transformed into equations with geometrical and state parameters, for example a gradient is expressed as difference ratio:

$$\frac{\partial T}{\partial t} \rightarrow \frac{\Delta T}{t_c} \quad \text{or} \quad \frac{\partial^2 T}{\partial x^2} \rightarrow \frac{\Delta T}{L_c^2} \tag{1.52}$$

where t_c and L_c define the characteristic time and length, respectively, for the actual problem. With these simplifications, the governing equations are resolved for the interesting parameters like characteristic time or penetration depth. The relation between two dominant parameters can be found from one equation. If we have more than two relevant parameters, the following rules for estimation of the order of magnitude can be applied [34]:

- Summation: If $O(a) > O(b)$ and $c = a + b$, the order of c is $O(c) = O(a)$. If $O(a) = O(b)$ and $c = a + b$, the order of c is $O(c) \sim O(a) \sim O(b)$. The same holds for the difference and the negation.
- Product: For $c = a \cdot b$, the order of c is $O(c) = O(a) \cdot O(b)$.
- Ratio: For $c = a/b$, the order of c is $O(c) = O(a)/O(b)$.

According to Bejan [34], scale analysis is widely employed in heat transfer and one of the first steps in engineering analysis. It is easy to get a first impression and "house number" results without the effort of the "exact" analysis, which also depends on the model prerequisites.

1.4.4
Lumped Element Modeling

For complex systems and network arrangements, the analytical treatment is still possible, but the amount of elements cannot be handled in the traditional way. The numerical treatment of complex systems has advanced during the last decades, the treatment of complex and coupled systems is established, but nevertheless, the computational effort is extremely high to treat transport processes in a fluidic network, if even possible. From electronic engineering, systems with millions of individual, but analytically describable, elements are known that are treated with lumped element programs like P-Spice [35, 36]. The analogy of transport processes and the corresponding equations, see Table 1.2, helps to translate complex flow networks or heat-management problems into a mathematical description, which can be handled by electronic simulation programs. The individual processes of mass, species, heat and energy transfer have their equivalent process in the electrical current transport, like the resistance, the capacity (storage), and the inductivity (kinetic energy). The method is described in Chapter 8 of this volume. Other applications in microsystem technology can be found in [35, Chapter 6; 36, Chapter 12; 37, Chapter 4].

1.4.5
Numerical Simulation and Analytical Modeling

Basically, one can distinguish between continuum modeling of transport processes in microstructures [38, Chapter 4; 39, Chapter 2] and statistical methods like the Monte Carlo Methods DSMC [40, Chapter 10; 41, Chapters 7 and 8] or the lattice Boltzmann methods LBM [42, 43]. The tasks in process engineering demand the solution of the conservation and balance equation of convection, diffusion, and/or reaction problems in various geometries under certain boundary conditions, which means solving the partial differential equations on discrete domains. For the majority of problems this can be done with continuum models, described in the following.

The finite-element method (FEM) was initially derived from solving structure-mechanical problems using simple piecewise functions, but is also applied in fluid mechanics [44]. The finite-difference method (FD) generates approximations for the derivatives of the unknowns at each grid point with the help of truncated Taylor series expansions [45]. Originally developed as a special FD formulation, the finite-volume method (VOF) solves by an iterative method the algebraic equations, which have been derived from the integral equations governing the transport processes. Additionally, spectral methods approximate the unknowns with the help of truncated Fourier series or Chebychev polynomials on the entire domain [44].

In the context of process engineering, continuum modeling and analytical modeling are preferred to bridge the gap between micro processes, equipment transfer processes and complete process design. The analytical modeling of process engineering phenomena is based on physically partial founded models with adjustment parameters. A complete calculation comprises four working levels:
- physic level for the process principles of unit operations,
- equipment level of the process technical and mechanical,
- process structure for controlling and regulation programs of automation, and
- the validation level for economical calculations.

The risk and flexibility of the assumptions and simplifications of the model determine the system modeling. There has to be a compromise between the mathematical and physical exactness and the real technical complexity. The mathematical models have to be appropriate for the experimental test units or the real plant, from which the data are gathered.

1.5
Miniaturization and its Application to Transport Processes

The miniaturization of chemical equipment emphasizes mainly the length reduction of the main dimensions and simultaneously constant process conditions like pressure, temperature, or concentrations. In thermodynamics, these parameters are called intensive state variables, which are not changed by reducing the size of the system. The length reduction influences many aspects in process engineering that are treated in the following. This listing sheds light on the actual state of the art, but is hopefully just the beginning of a larger process of gaining knowledge and technical skills in an emerging field of new technology and application. The picture is certainly not complete, but shows the complexity of the interwoven fields and gives many hints and much advice for miniaturization aspects.

1.5.1
Length

Typical length scales in microelectronics, process technology, and other areas are shown in Fig. 1.2. With the decreasing length, the operation and efficiency of unit operations is affected in various ways, which is shown in the following.

Cyclone The density difference between dispersed particles and the surrounding fluid leads to a separation within a force field like centrifugal forces. They are generated in a rotating system like a centrifuge or a cyclone [46, Chapter 6].

In a mechanical centrifuge the acceleration scales proportional to the radius. Hence, a miniaturization will reduce the radial acceleration and therefore the separation factor. The cyclone is a mechanical separation process of dispersions of solid–gas or solid–liquid mixtures without moving parts. The separation of immiscible liquids with different densities is also possible, but other separation processes like settling, filtering, or coalescing are more effective, see [46, Chapter 6]. The separation factor z is defined as the ratio between the acceleration induced by the force field and the gravity g.

The vortex in a cyclone exhibits a high tangential velocity near the vortex center, which decreases with increasing radius r. The tangential velocity of a real viscous vortex, like an Hamel–Oseen vortex [47], scales with r^{-n}, where n ranges from 0.5 to 0.8 [46, Chapter 6]. The centrifugal acceleration is proportional to the square of the tangential velocity w_t divided by the radius r, which gives for the separation factor z.

$$z = \frac{w_\mathrm{t}^2}{rg} = \frac{\text{const.}}{r^2 g} \tag{1.53}$$

The separation factor increases with a smaller radius of the cyclone. Hence, small particles are more likely to be separated by smaller cyclones. In a feasibil-

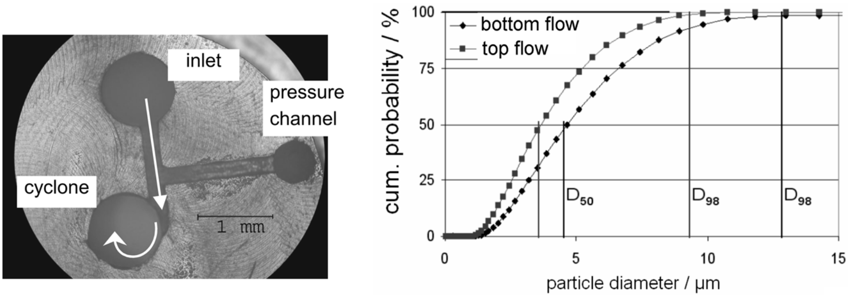

Fig. 1.8 Left: Cross section of the microcyclone with inlet and channel for pressure measurement; right: Cumulative probabilities of the particle diameter for the top and bottom flow of the cyclone, small particles are collected in the top flow.

ity study, Kockmann et al. [48] fabricated a microcyclone with an inner cyclone diameter of 1 mm from PMMA and separated an aqueous SiO_2 suspension (mean diameter $\sim 4.5\,\mu m$, particle density $\sim 2500\,kg/m^3$).

The suspension enters the cyclone hole tangentially. Driven by the centrifugal force the large particles flow to the outer radius; smaller particles are collected in the center and leave the cyclone through the top flow. The separation efficiency of one cyclone can be seen in Fig. 1.8 at the D_{98} value (9 µm and 13 µm for the top and bottom flow, respectively). A cascading of many microcyclones will give a higher separation factor but requires a higher pressure difference. The cyclone process can be extended to pressure diffusion, a coupled process described by the thermodynamics of irreversible processes, see Chapter 3, Section 4.

In two papers, Ookawara et al. [49, 50] presented the centrifugal separation of an aqueous suspension flow in curved rectangular channels ($200 \times 150\,\mu m$ cross section, 30° and 180° curves, 20 mm radius). With a pressure loss of about 200 Pa, the typical Dean numbers were between 30 and 45, which means Re numbers varied from 1400 to 2200. The experimental results and numerical evaluation by CFD simulation show a good separation of particles larger than 15 µm from the fluid. Contrary to centrifugal force, the Dean vortices push the particles inwards by friction forces and disturb the separation flow. Hence, a shorter bend may be more effective.

As part of the product catalogue of the German microchemtec project, two companies (Little Things Factory, Ilmenau [51], and mikroglas, Mainz) offer a microcyclone, which fits into their series of process equipment.

Molecular Distillation In molecular distillation and vacuum rectification, the gap width between the evaporating and condensing falling film plays a mayor role, where the mean free path of the molecules is larger than the distance between evaporating and condensing surfaces due to the low pressure. These processes usually separate liquid mixtures, which are thermally sensitive like vegetable oils, vitamins or fatty acids, see [52] for the historical development and [53, Chapter 4; 54, Chapter 10]. The Knudsen regime serves for a gentle thermal separation and low product degradation. A lower distance requires a lower process vacuum, less energy consumption, and will probably result in a higher product purity. The design length is limited by the film thickness of the often high viscous liquids (about 1 to 5 mm). Even though an application has not yet been reported, a falling film micro device under vacuum would be an interesting test object.

Flame Distance and Explosion Limits The typical dimension of microstructured equipment is just below the extinction length or quench distance of many fast reactions, which is about 1 mm. Veser [55] reports on a calm hydrogen oxidation with flame suppression in channels smaller than 500 μm. The author determined three different explosion limits for a stoichiometric H_2/O_2 mixture dependent on the pressure, temperature, and the channel diameter. The main mechanisms are thermal quenching by wall heat conduction and "radical" quenching by kinetic effects where the mean free path of the molecules is in the range of the channel dimensions.

Miesse and coworkers [56] observed small flame cells in flat microchannels. They regard the coupled heat and mass transfer and the reaction kinetics as a self-organized system that exhibits characteristic features like flame length or periodicity. For cold walls, the thermal quenching of the reaction is the dominant stopping mechanism for the combustion. They give three design rules for successful microburner layout and complete combustion. The wall material should not quench the radicals to keep the gas-phase reaction undisturbed. The thermal insulation must be sufficient to hold a high temperature for the combustion. The flow and temperature management must ensure a sufficient high bulk temperature and prevent a melting of the wall material.

For fuel-cell applications Hessel et al. [18, Chapter 2] show in a review that reactions with strong exo- or endothermic behavior and high-energy transfer, like explosive reactions, take profit from the high transfer rates in microchannels for precise temperature control.

Gradients d*X*/d*x* For constant differences of the process parameters like temperature, pressure, or concentration, a reduction of the transfer distance increases the gradient, the driving force for the transport processes. Therefore, the corresponding transfer flux is increased and the equilibrium state is reached much faster.

Not only are the main transport processes of mass, momentum, and energy increased by the high gradients, also many minor coupled processes become more important [57, Chapters 4 and 5]. The thermoelectric effect is exploited for sensing (thermocouple, no electrical current, NiCr-Ni 0.04 mV/K), for cooling (Peltier element) or for the generation of electrical energy (Seebeck element, about 0.5 mV/K). The generation of a species current with the help of a temperature gradient is called the Soret effect, the thermodiffusion. The Soret coefficient D' has an order of 10^{-12} to 10^{-14} m^2/s K for liquids and of 10^{-8} to 10^{-10} m^2/s K in gases [58, Chapter 13]. Mainly used for the separation of isotopes, the Clusius–Dickel column employs the thermodiffusion assisted by natural convection in a heated gap, and enhanced by cascading many of the columns. The species concentration gradient due to a pressure difference is called pressure diffusion, which was originally investigated also for isotope separation [6]. The fabrication of the separation nozzles for pressure diffusion combined with centrifugal forces is one of the birthplaces of microfluidic technology [59]. The exploitation of these processes is described more detailed in Chapter 3.

Thermal Insulation Length In small devices, the thermal insulation of devices with different temperatures is very difficult. One major problem of some modules in the "backbone system" (microchemtec, Germany [60]) was the thermal insulation of the different reactors with operating temperature from below 260 K to over 470 K. Technical polymers like PEEK ($\lambda = 0.25$ W/m K) can be used as the construction material for low temperature differences up to 100 K. For higher temperature differences or very short distances, multilayer superinsulation from cryogenic technology can help to overcome the difficulties [61, Chapter 7]. Although the multilayer insulations are very expensive and difficult to apply to complicated shapes, they offer the best performance of all technical insulations ($\lambda \sim 10^{-8}$ W/m K). The multilayer insulation consists of evacuated alternating layers of highly reflecting material (aluminum foil or copper foil) with low-conductivity spacers, like glass or polymers. Their extremely low thermal conductivity depends on the reduction of all three modes of heat transfer (radiation, gaseous and solid conduction) to a bare minimum by evacuation of the gaps. The low insulation of small elements is the main reason why Peterson et al. [62] give the size limits of small regenerative heat engines as a few millimeters. Small heat engines will suffer from an insufficient heat recovery in the regenerator and from the difficult buildup of the necessarily high temperature difference.

Characteristic Times The length scaling often goes along with a time scaling of the relevant processes. In general, the shorter the length, the shorter the characteristic time for transport processes will be, and the higher the frequencies of changes are. The diffusion of a species in a surrounding fluid is displaying this process. The mean path of a molecule or small particle in a surrounding fluid is given by the Einstein equation [63],

$$x^2 = 2Dt\,. \tag{1.54}$$

The typical diffusion length within one second is about 7 mm in gases (air) and about 70 µm in liquids like water. A similar conduction length can be derived from the basic balance equation for the momentum ($x_p = \sqrt{2\nu t}$) and the heat transfer ($x_q = \sqrt{2at}$). The characteristic time is proportional to the square of the length variation and the transport coefficient.

From unsteady heat transfer, the characteristic time for heating or cooling of a body is proportional to the temperature difference and the ratio of the heat capacity to the heat transfer with the environment,

$$t = \frac{m c_\mathrm{p}}{\alpha A} = \frac{\rho c_\mathrm{p} V}{\alpha A} \,. \tag{1.55}$$

In a similar manner, relaxation times of other unsteady processes can be estimated.

In process engineering, other characteristic times determine the process conditions. The channel length and the mean flow velocity determine the mean residence time $t_\mathrm{P} = l/w$ of a fluid element in the channel. With shorter length, also the residence time decreases. The residence time must be designed appropriately for the actual process. A very important characteristic time in process engineering belongs to the chemical reaction: Besides the concentration c and the reaction order m the reaction time scale depends mainly on the reaction rate constant $k\,(t_\mathrm{R} \propto 1/k)$. The reaction rate constant mainly depends on the temperature. Inside devices with short characteristic length and corresponding times like mixing or residence time, a slow reaction may be incomplete at the channel outlet. Fast reactions, on the other hand, take profit from the fast mixing and fast heat exchange. In particular, combined reactions with slower side-reactions will show a higher selectivity and higher yield in microstructured devices. Also, reactions with high energy demand or release are suitable for micro devices. The concentrations can be increased to intensify the reaction or new reaction paths can be addressed where fast mixing plays an important role. Within a chemical reactor, the three characteristic times of mixing t_M, of residence in the device t_P and of the chemical reaction t_R have to be adjusted to the entire process to yield an optimum result, see Chapter 6.

Free Convection The heat transfer due to free or natural convection is induced by the thermal expansion and density differences of a fluid under temperature gradient. The heat transfer between two plates with different temperatures and a gap width is characterized by the Grashoff number Gr, the ratio of the volume force to the viscous force,

$$\mathrm{Gr} = \frac{g \beta_\mathrm{p} s^3 (T_{w1} - T_{w2})}{\nu^2} \tag{1.56}$$

with the thermal expansion coefficient

$$\beta_\mathrm{p} = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{p=\mathrm{const.}} \tag{1.57}$$

Depending on the temperature difference between the walls and on the distance s between the walls, the fluid will circulate in the gap. A prominent example of natural convection is the Bénard convection in a horizontal layer, which is heated from below [58, Chapter 14]. If the layer or the gap is too thin, the viscous forces damp the convection and the heat is transferred solely by conduction. If the Rayleigh number Ra (=Gr Pr) is smaller than 3×10^8 the free convection flow is laminar and ruled by the viscous forces [27, Chapter 3; 34, Chapter 5]. For Ra numbers lower than 175, the heat-transfer augmentation by natural convection is smaller than 1%. In a gap filled with air or water, the influence of natural convection on the heat transfer is smaller than 1% for a gap width smaller than 8 cm or 4 cm, respectively. Therefore, natural convection may be neglected for most cases in micro process technology, but is the major cause of heat losses of equipment to the environment. For the measurement of an incline or acceleration, a sensing device developed by Billat et al. [64a] employs the temperature and flow field due to free convection around a heated wire.

1.5.2
Area

When miniaturizing the length, the area decreases proportional to the square of the length, L^2. The area plays a mayor role as a cross section for transport fluxes like mass or energy flow or as an active area, where processes take place. For a constant flow rate like fluid velocity, species transport, or heat exchange, the total amount of the quantity decreases proportional to L^2 with a smaller length scale. For a constant driving force, the area specific flux remains constant. The pressure loss in channel flow grows with smaller cross section, see Chapter 2, Section 5. The order of magnitude of the pressure loss increase depends on the variables, which remain constant.

With a constant absolute flux like energy transfer (in Watt), the specific flux dramatically increases [in W/m^2]. For example, the energy load in modern microelectronic devices increases with their performance improvement, which leads to heat loads of already above 100 W/cm^2 [64]. Finally, a small cross section of immersed bodies shows a small flow resistance, which appears in low settlement velocities and nearly Lagrangian particle behavior (massless particles).

High Specific Area for Transfer Processes Many transport processes take place at phase boundaries, which have the form of films, bubbles, or droplets in emulsions, dispersions, or foams. With a higher specific area and high gradients, the transport rates are increased and the equilibrium state is reached much faster. Temperature and concentration differences are homogenized much earlier, which plays a prominent role in mixing and heat transfer.

Considering the simple geometrical figure of a sphere, the specific surface-to-volume ratio a_v is inverse proportional to the characteristic length, $a_\text{v} \propto 6/L$. The smaller the channel structures, the larger grows the specific interface and therefore the active area for transport processes. This effect will be shown in the following for major separation unit operations, together with other specific miniaturization effects.

Filter and Membrane Processes The variety of membrane processes covers a broad area ranging from food technology through potable-water generation to blood and serum cleaning. A good overview of membrane types and specific application is given by Melin and Rautenbach [11]. Conventional membrane processes already work among others with hollow fibers with a diameter of 40 to 400 μm and a high specific surface up to 20 000 m^2/m^3 [10]. These hollow fibers reach a specific permeate volume flow (fluid passing through the membrane) of about 300 m^3/h per cubic meter equipment volume. Microstructured membranes from tantalum, palladium and its alloys are used for carbon monoxide cleanup in fuel-cell applications [18, Chapter 2].

A new field in membrane technology is covered by liquid membranes, where a liquid inside a porous structure absorbs components from one side and transfers them to the other side. They exhibit a good product selectivity, low pressure difference, and high transfer rates [11, Chapter 2]. Besides the appropriate material properties one crucial point is the protection of the enclosed liquid against the high pressure difference across the two membrane sides. The fabrication of the structures for liquid membranes can be assisted by microfabrication technology, but has not yet been reported.

Distillation and Rectification The separation of a liquid mixture with subsequent evaporation and condensation enriches the low boiling component in the vapor phase. This is the fundamental mechanism of distillation and rectification, the most frequently used separation technique in process technology [10, Chapter 7]. The coupled heat and mass transfer is performed in small laboratory equipment like the microdistillation apparatus, as well as in huge rectification towers like the 60-m high cryogenic rectification columns of air-separation units. A detailed treatment of the underlying transfer processes can be found in textbooks [30, 65] or concise handbooks [12].

Sowata and Kusakabe [66] demonstrated the vapor–liquid separation of a water-ethanol mixture on a chip (20×40 mm^2) with mixer-settler arrangement. Both streams come into contact in a Y-shaped mixer and the bubbly flow streams through a meandering channel. At the outlet, the two phases are separated by gravity in a separation chamber (8×8 mm^2). The experimental data indicate the equilibrium state for the gaseous phase and a liquid concentration of 0.65 mole fraction methanol, which means a stage efficiency of about 65% for the liquid side. A better mixing in the meandering channel may enhance the stage efficiency and lead to a better separation. Hence, a good mixing process enhances a separation process, too, due to the fast achievement of the thermodynamic equilibrium.

Fink and Hampe [67] presented a design study of a distillation column to illustrate the setup of an entire micro device. The experimental investigations show that a flow rate of about 20 ml/h has been realized with 2.5 theoretical separation stages. Even small temperature changes lead to operational disturbances and uncontrolled concentration changes [8, 60].

In our own design study [48], a distillation chip with various geometries was fabricated and tested by evaporation and condensation of a water-ethanol mix-

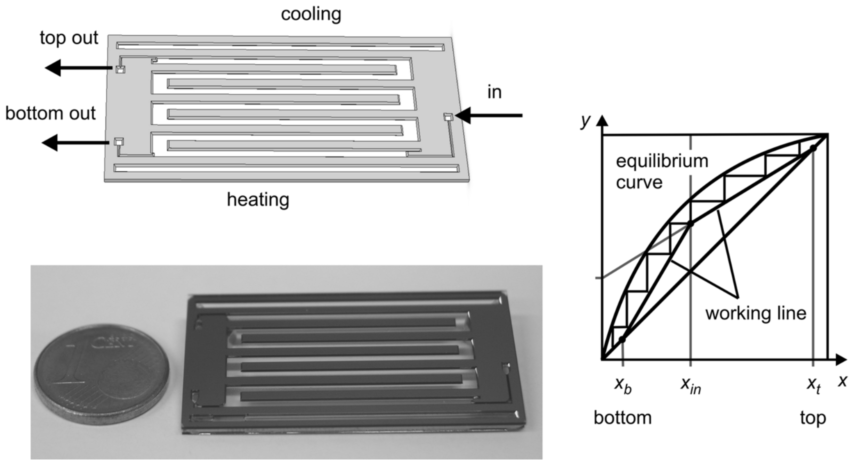

Fig. 1.9 Left top: Geometrical setup of a distillation/rectification chip ($20\times40\times1.6\ \mathrm{mm}^3$) made of a silicon wafer, anisotropic KOH etched and covered with two glass lids; bottom: image of a rectification chip with meandering separation channel; Right: McCobe-Thiele diagram stagewise operation of rectification process, see [69].

ture. The chip, with a meandering separation channel is made of an anisotropic KOH-etched silicon wafer covered with two Pyrex glass lids, see Fig. 1.9. From the heated side (hot water, 93°C) the mixture partly evaporates and condenses on the opposite side of the channel. The McCabe–Thiele diagram on the right side of Fig. 1.9 explains the stagewise operation of a rectification column. The operating line in the upper part of the diagram describes the enriching section of the separation column, where the low-boiling substance enriches in the vapor phase. A theoretical distillation stage or tray is described by the horizontal line for the condensation of the rising vapor and by the vertical line for the evaporation of liquid from the tray. In the ideal case of reaching an equilibrium state, the lines touch the equilibrium curve and give the number of theoretical trays. The graphical treatment of these operations is almost faster than analytical or numerical calculations and gives a better physical insight into the process.

The first experimental results show a low mass flow rate and a poor thermal insulation to the ambient. From the design study the following main issues have been identified:

- the fluid transport can not rely on gravity, other principles must be employed, i.e. capillary transport or external force fields like rotation [68];
- the contact between liquids of different concentration has to be avoided, which also limits the minimal size of the gaps for evaporation, condensation, and vapor flow;
- the fabrication of suitable geometries to guide the liquids and vapor currents is a crucial point. Besides the silicon techniques, alternative fabrication techniques like metal foil structuring should be investigated, see [8];

- an internal numbering-up may help to increase the volume flow, which is a considerable drawback of the actual devices.

These points are generally valid for multiphase flow transport problems and coupled heat and mass transfer. However, the potential of a high specific area provides a high transfer area and high exchange rate between the phases. A short distance between the phases and concentration differences allows a fast approach to the thermodynamic equilibrium and leads to smaller equipment, but low throughput and complex fluid management have to be considered.

Absorption and Desorption Similar to the rectification and the distillation process, absorption is a coupled heat and mass-transfer process, where a gaseous component is dissolved in the liquid phase [69]. Desorption or stripping is the opposite process, where a dissolved component is released from the liquid phase into the gaseous phase. The state changes and the stagewise operation is displayed in the operation diagram with the equilibrium line, given by Henry's law, and the operating lines for desorption and absorption, see Fig. 1.10.

The orientation of the operating line depends on the process conditions and is explained in [26, Chapter 1; 69]. In an absorption process a component of a gaseous mixture is step-wise received into a liquid, partially chemically bound in the liquid by additives. For successful operation, a high mass transfer between the phases leads to a fast establishment of the thermodynamic equilibrium. Prominent examples are the synthesis gas (syngas) cleaning in the chemical industry (CO_2 removal) or the CO_2 enrichment in water for sparkling water.

The opposite process of absorption, the stripping of a dissolved component from a liquid (toluene in water) was investigated by Cypes and Engstrom [70].

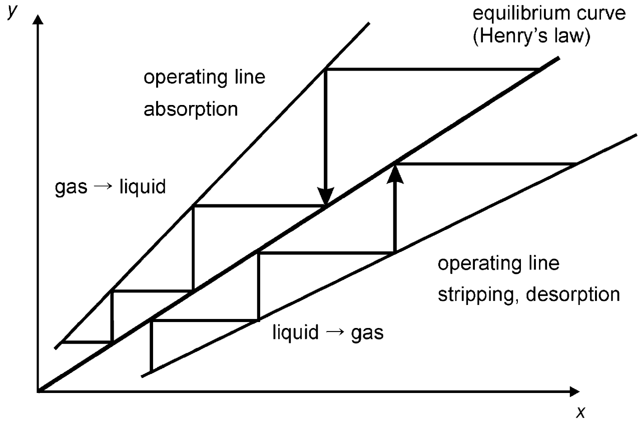

Fig. 1.10 Operation diagram for absorption and desorption/stripping, concentration of the key component in the gas phase y over the concentration in the liquid phase x. The display of the stagewise operation is similar to the McCabe-Thiele diagram for rectification, see Fig. 1.9.

The liquid mixture flowing in a silicon channel was treated with superheated steam entering from a second channel through a perforated wall. After leaving the channel the bubbly flow was separated in a chamber and analyzed. The comparison between a microfabricated stripping column and a conventional packed tower shows a transfer rate nearly an order of magnitude higher than conventional packed towers, indicating a high specific interface. This large interface enhances the convective mass-transfer process by reducing the diffusive length.

Both absorption and desorption integrated to a process cycle result in the absorption heat pump process [26, Chapter 6], or in the closed absorption and regeneration cycle to reuse the washing fluid. An absorption heat pump process with microstructured elements was presented by Ameel et al. [71] and Stenkamp and teGrotenhuis [72].

Extraction One can distinguish between liquid–liquid and liquid–solid extraction (leaching) [13, Chapter 15; 14, Chapter 1; 69, Chapter 3]. Extraction employs the different solubility of a component C within other components A and B. Often, the low solubility of component A in component C leads to a two-phase flow with mass transfer at the interface between the phases. The separation of the component B from A with the extracting agent C writes as follows:

$$(\mathrm{A}+\mathrm{B})+\mathrm{C} \Rightarrow \mathrm{A}+(\mathrm{B}+\mathrm{C})\,. \tag{1.58}$$

Many applications of extraction processes can be found in the pharmaceutical industry, for various foods and detergents, vitamins, or in the petrochemical industry. The Nernst distribution describes the equilibrium concentration between the three phases, see Fig. 1.11. Material properties can be found in the literature [14, Section 1.9; 69].

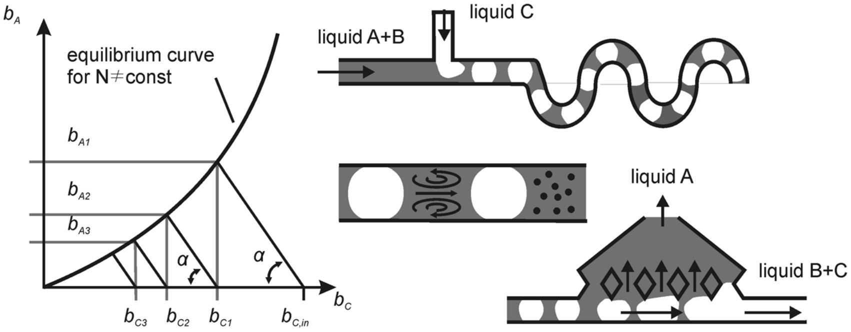

Fig. 1.11 Left: Loading of the component B b_A in A over the loading in C b_C; stepwise cross-flow extraction with four stages, equilibrium line is given by the Nernst distribution *N;* right:) geometrical examples of microcontacting equipment (adopted from [73, 74]), contacting and mixing in a serpentine channel, flow characteristics in the bubbly flow, and separation by geometry and surface properties using capillary forces.

Ehrfeld et al. [75] and Klemm et al. [8] describe the extraction process in microstructured equipment. Recently, Okubo et al. [76] presented the rapid extraction process on a chip. TeGrotenhuis et al. [77] developed micro devices for transport processes in solvent extraction. Kusakabe et al. [78] investigated the flow details and transport processes within a droplet in a micro contactor for solvent extraction. Their comparison with experimental data shows a good agreement for the extraction of ethyl acetate from n-hexane to water. Specific problems for solvent extraction are the fluid transport and phase separation after the mixing. In conventional equipment the driving forces for the fluid transport are the density difference and gravity, external pumps as well as capillary effects. In microstructures, the pressure-driven flow and capillary effects are the most predominant pumping mechanisms. A design study for microstructured extraction equipment is shown in Fig. 1.11 and 1.12.

The combination of microstructures with macro devices for fluid transport, for example, the mixer–settler chip with radial arrangement and the stepwise transport by a pump is displayed in Fig. 1.12. The general setup was adopted

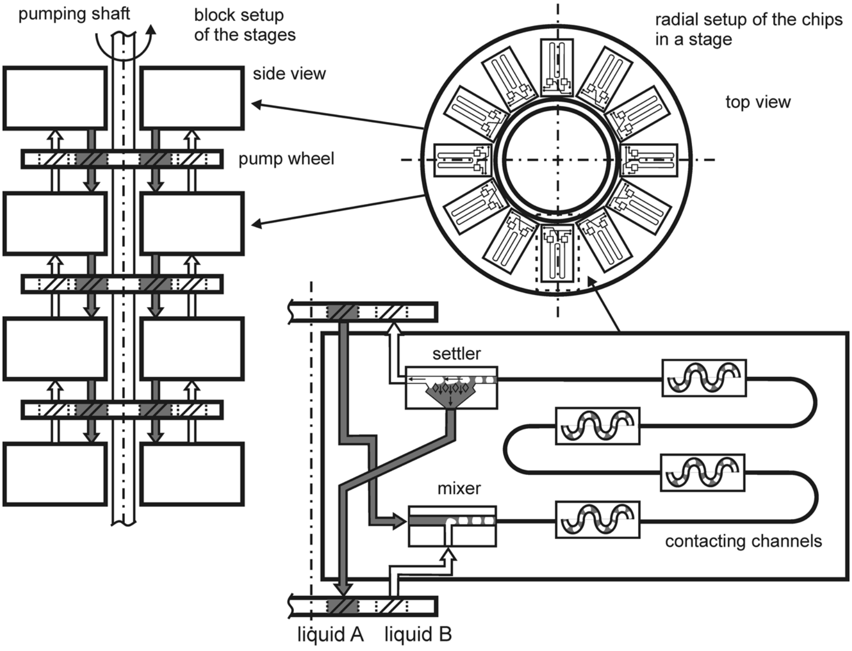

Fig. 1.12 Micro/macro integration of a mixer–settler extraction apparatus; bottom right: chip layout for contacting, mixing in a meandering channel and separation (settler) of a liquid–gas flow. The connections to further processing like the pump wheel are sketched, in the further layout, the fluids are guided perpendicular to the chip plane; top right: radial arrangement of different mixer-settler chips; left: side view of the chip blocks and intermittent pump wheels for fluid transport.

from conventional extraction equipment with rotating internals for mixing and fluid transport, like the Scheibel or the Kühni column, from Schlünder and Thuner [69, Chapter 3]. For the design and fabrication, the main effort has to be spent in the packing of the chips in the radial mount and in the sealing between the block and the pump wheel.

The integration of microstructures into macro equipment has to be carried out to use the benefits and opportunities of both fields and additional emergent effects. Hence, as guidelines for the next steps: Not only as small as useful for the designated application, but also as many microstructured devices as necessary for the actual process.

1.5.3
Volume

The volume scales with the cubic length L^3 and is directly connected over the material density with the mass. A low mass means low capacity of the elements (see Section 1.5.1, Characteristic Times) and corresponding high frequencies. A low volume in process equipment is useful for the handling of toxic and hazardous products, for expensive and valuable goods. With smaller plants a distributed onsite production is possibly a production at the point of use or point of care (in medicine or diagnostics). The production-on-demand of small amounts of chemicals is much easier and represents a flexible production [17, Chapter 1].

The high throughput screening is a valuable tool for catalysis research [18, Chapter 3] and chemical synthesis [79], but the extremely low volumes in microstructured equipment also affect other processes. With small devices with process conditions close to larger equipment, pilot plants can assist process development and process routes discovery with fast response on parameter variations and optimizing the equipment.

Adsorption The adsorption is the arrangement and attachment of volatile molecules to a solid, but porous surface from a gaseous or liquid phase. In conventional equipment porous pellets or beads provide the porous surface. The pellets are ordered in packed beds in larger vessels. Therefore, a miniaturization of the entire plant results in a low volume, which is quickly loaded and therefore negative for the amount of adsorbed species. Smaller pellets give a higher specific area per volume, but also increase the pressure loss of the flow through the bed.

The calculation and design procedure of the adsorption isotherm and the Knudsen regime for transport processes in pores is not treated here. Interested readers are referred to [13, Chapter 16; 30, Chapter 10; 46, Chapter 13; 65, Chapter 12]. In small pores the molecules are interacting more with the wall than with themselves. This process is described by Knudsen diffusion. For ideal gases the validity of this regime depends on the total pressure and the pore diameter.

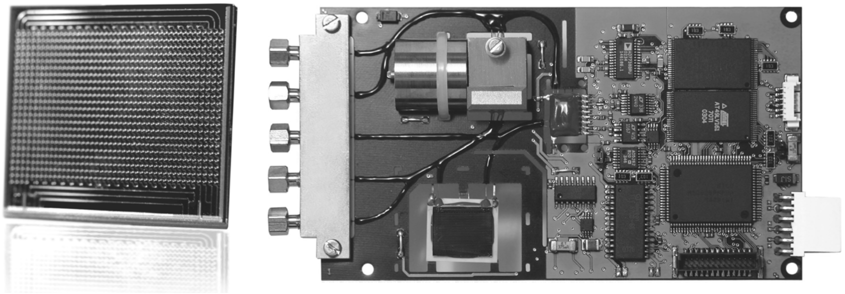

Fig. 1.13 Micro gas chromatograph. Left: separation column on a silicon chip, covered with a glass plate; right: IC plate and analytical equipment of the micro-GC, courtesy of SLS Microtechnology [80].

For analytical purposes the faster loading results in a fast response time of chromatographic analysis. The loading, detection and cleaning of the chromatographic separation column can be achieved in a very short time, compared to conventional systems. This allows a fast response to signal changes, which is very important for the proper control of modern chemical plants. The fabrication methods and the special system integration of microtechnology are very useful to enhance the performance, as has been demonstrated by Micro Gas Chromatography [80], see Fig. 1.13.

The chromatographic separation column is fabricated with a combined bulk and surface micromachined process on a silicon chip. The silicon-glass chip, on which this separation column with a separation channel length of 0.86 m and diameter of 60 μm is made, has a surface of 1 cm^2. This column is heated to 200 °C within 20 s, using an electric heating power of 5 W, and because of the low thermal capacity cools down to ambient temperature rapidly. This results in a measurement cycle faster than 60 s and a low carrier gas and electrical power consumption.

Pumping In general, microfluidic systems are typical for small flow rates and small holdups in the devices. This is also valid for micropumps, which have now a certain history of development and type variety [81]. Like conventional pumps, the micropumps can be classified into two different types, the displacement pumps with reciprocating or rotating elements, and the dynamic pumps using centrifugal, acoustic or electrical fields [82]. Due to the small dimensions, also the flow rate is small, but also small effects like electrohydrodynamic or magnetohydrodynamic effects can be employed. A pump is mainly characterized by the flow rate and the induced pressure difference for micro process applications. The frequency of displacement pumps is directly coupled with the flow rate up to a certain value, where sealing losses and dynamic effects like fluid acceleration are limiting and decrease the flow rate [81]. The flow rates of a micro diaphragm pump decrease linearly with increasing counterpressure due to the higher forces. Maximal flow rates of about 35 ml/min (0.78 kPa pressure difference) of air and 16 ml/min (4.9 kPa pressure difference) of water have been reported [82]. Flow oscillations caused by pumps are critical for the proper operation of microstructured devices like micro mixers or micro reactors and can be reduced by appropriate flow dampers.

Electro-osmosis employs the negative charge of the wall and corresponding positive charge of ions in the fluid. An external electrical field generates the motion of the counterions and therefore of the entire fluid in the capillary. The electro-osmotic effect decreases with increasing diameter of the channel, which have a characteristic dimension of about 1 μm. High pressure differences up to 2 MPa of water have been realized for low flow rates of 3.6 μm/min. High flow rates up to 33 ml/min have been measured that indicates that the main applications of electro-osmosis pumps are for dosing and analytical applications [82].

The rotating gear pump of HNP Mikrosysteme GmbH [83] belongs to the displacement pumps for dosing and pumping of liquids in analytical and production applications. The pumps, with an internal volume from 3 to 48 μl, deliver a flow rate up to 17 l/h against a counterpressure of 30 to 50 bar.

Fast Nucleation and Controlled Growth of Nanoparticles The small capacity and inertia with small system volume allows high change rates for heating, cooling, and mass transfer, see also Section 1.5.1 Characteristic Times. The fast mixing of two nearly saturated mixtures leads often to a high supersaturation of the mixture and particle generation, see Fig. 1.14, left side. The saturation S is measured with ratio of the partial pressure p_V to the saturation pressure p_S. In gaseous flow the particles (liquid or solid phase) are called aerosols, like fog in humid air. In liquid flow the particulate flow is called a suspension and is often combined with crystallization. Besides the exceeding of solubility limits in liquids, often also chemical reactions are involved in the precipitation process. Two solvable components in solution react to a third component with low solubility, which precipitates after the reaction.

The precipitation process is determined by the nucleation of the dissolved component and the following growth of the particles. A high supersaturation generates many nuclei in the mixture, see Fig. 1.14 right. The faster the mixing process, the more nuclei are formed. The homogeneous nucleation of the dissolved component is followed by the growth of the particles, which is determined by the mass transfer from the bulk to the nucleus.

Experimental investigations of the precipitation of barium sulfate in aqueous solution have shown that the particle size distribution strongly depends on the mixing intensity [86, 86a]. The investigated T-mixer has circular cross sections with an inlet diameter of 0.5 mm and an outlet diameter of 1 mm. The mean particle diameter decreases from about 200 nm for Re numbers of 255 to about 50 nm for a Re number of 6360. The authors set up a calculation model for the nucleation and growth of the particles depending on the flow regimes and interfacial energy within the T-mixer.

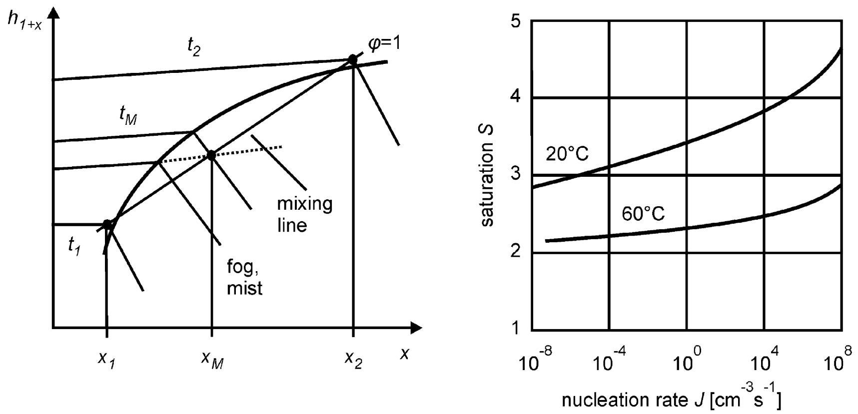

Fig. 1.14 Left: Saturation curve of a gas–vapor system, e.g. humid air system (fog generation); right: nucleation rate for the saturation at various temperatures [adopted from 84 and 85, Chapter Je].

In general, fast mixing in microstructures can be used for the production of nanoparticles in droplet flow, emulsions, and with fast chemical reactions and successful precipitation in bulk flow. The main problem is the sticking and adhesion of particles at the wall, see the fouling topic in Chapter 3, Section 4.

1.5.4
Other Topics

The microfabrication technology allows, under certain conditions, a cost-effective mass production and a dense integration of various elements. The integration of microstructured devices into the environment also needs conventional fabrication technologies and has to be considered during the device design. Many microfabrication techniques allow very complex geometries, a switching and a proper arrangement of various process steps.

The main drawbacks of microsystems for production applications and industrial use are the low mass flow rates and the sensibility to fouling and blocking. A high flow rate is achieved with internal and external numbering up. Fouling considerations can be found in Chapter 3.

Mechanical unit operations often include mechanical gears and motions with friction and wear that cause many problems in microsystems. Therefore, pure mechanical processes like pressing or crushing are not feasible and reasonable in micro process technology.

1.6
Conclusions and Outlook

Only a few physical principles and their potential for miniaturization have been demonstrated in this chapter. Schubert [87] gives a comprehensive collection of all known physical principles. Many of these principles are translated for design purposes by Koller [88] and illustrated by examples. This could be a starting point for further investigations. The aim should be the fruitful combination and connection between microsystem technology and process engineering.

The picture in this chapter and from the entire book is certainly not entirely complete, but is one of the first steps for a deeper understanding and a help for further applications of microsystem technology in process engineering and technology. Both sides can learn from each other and contribute to the progress. One motivation for process engineering can be summarized under the concept of process intensification. Additionally, processes in microstructured devices open new routes in mixing, transformation and separation with the help of system integration.

An emerging market is governed by a technology push from new possibilities and by a market pull from the consumer and application needs. In chemical technology and production a long-term business and complex production plants with decades of lifetime allow no easy change. The role of unit operations should be extended to integrated processes in microstructures to provide a comprehensive toolbox for treating various tasks from process engineering. Innovative reactor design adjusted to chemical reactions, optimized fluid flow, parallel and high throughput testing, new reaction routes, closer to the molecule and the transformation (time, rate, concentration) are the new applications of microstructured equipment in chemical industry, in energy conversion and fuel cells, and life science.

For the future research, many aspects need to be addressed like fluid flow and transport phenomena or two phase flow in capillary structures, like using small effects, fluctuations, surface effects and coupled processes, high throughput devices like mixers, premixers, reactors, heat exchangers, application of cost-effective fabrication technologies, and integrated processes like mixers with chemical reactions and heat exchangers. The integration of micro structures into macro equipment has to be carried out to use the benefits and opportunities of both fields and additional emergent effects.

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