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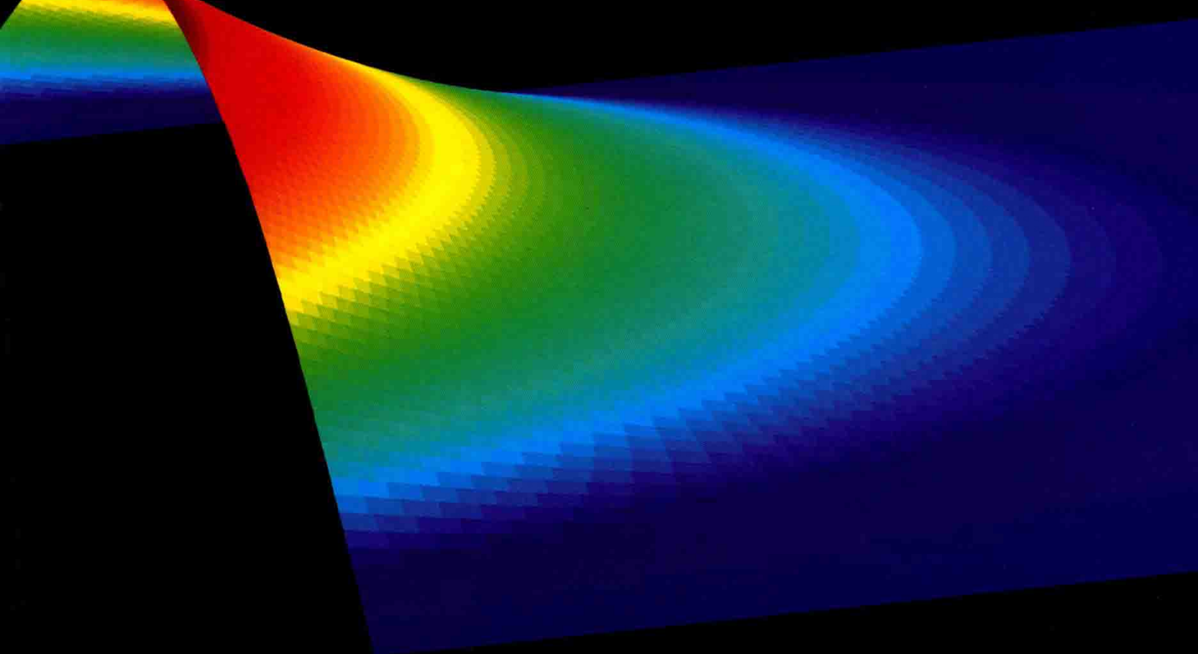

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Mathematical Modeling in Chemical Engineering

A solid introduction to mathematical modeling for a range of chemical engineering applications, covering model formulation, simplification, and validation. It explains how to describe a physical/chemical reality in mathematical language and how to select the type and degree of sophistication for a model. Model reduction and approximate methods are presented, including dimensional analysis, time constant analysis, and asymptotic methods. An overview of solution methods for typical classes of models is given. As final steps in model building, parameter estimation and model validation, and assessment are discussed. The reader is given hands-on experience of formulating new models, reducing the models, and validating the models.

The authors assume a knowledge of basic chemical engineering, in particular transport phenomena, as well as basic mathematics, statistics, and programming. The accompanying problems, tutorials, and projects include model formulation at different levels, analysis, parameter estimation, and numerical solution.

Anders Rasmuson is a Professor in Chemical Engineering at Chalmers University of Technology, Gothenburg, Sweden. He obtained his Ph.D. in chemical engineering at the Royal Institute of Technology, Stockholm, in 1978. His research has focused on mathematical modeling combined with experimental work in many areas of chemical engineering, for example particulate processes, multiphase flows and transport phenomena, mixing, and separation processes.

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Preface

The aim of this textbook is to give the reader insight and skill in the formulation, construction, simplification, evaluation/interpretation, and use of mathematical models in chemical engineering. It is *not* a book about the solution of mathematical models, even though an overview of solution methods for typical classes of models is given.

Models of different types and complexities find more and more use in chemical engineering, e.g. for the design, scale-up/down, optimization, and operation of reactors, separators, and heat exchangers. Mathematical models are also used in the planning and evaluation of experiments and for developing mechanistic understanding of complex systems. Examples include balance models in differential or integral form, and algebraic models, such as equilibrium models.

The book includes model formulation, i.e. how to describe a physical/chemical reality in mathematical language, and how to choose the type and degree of sophistication of a model. It is emphasized that this is an iterative procedure where models are gradually refined or rejected in confrontation with experiments. Model reduction and approximate methods, such as dimensional analysis, time constant analysis, and asymptotic methods, are treated. An overview of solution methods for typical classes of models is given. Parameter estimation and model validation and assessment, as final steps, in model building are discussed. The question "What model should be used for a given situation?" is answered.

The book is accompanied by problems, tutorials, and projects. The projects include model formulation at different levels, analysis, parameter estimation, and numerical solution.

The book is aimed at chemical engineering students, and a basic knowledge of chemical engineering, in particular transport phenomena, will be assumed. Basic mathematics, statistics, and programming skills are also required.

Using the book (course) the reader should be able to construct, solve, and apply mathematical models for chemical engineering problems. In particular:

- construct models using balances on differential or macroscopic control volumes for momentum, heat, mass, and numbers (population balances);
- construct models by simplification of general model equations;

- understand and use methods for model simplification;
- understand differences between models;
- understand and use numerical solution methods;
- understand and perform parameter estimation;
- use model assessment techniques to be able to judge if a model is good enough.

Contents

1 Introduction

In this introductory chapter the use of mathematical models in chemical engineering is motivated and examples are given. The general modeling procedure is described, and some important tools that are covered in greater detail later in the book are outlined.

1.1 Why do mathematical modeling?

Mathematical modeling has always been an important activity in science and engineering. The formulation of qualitative questions about an observed phenomenon as mathematical problems was the motivation for and an integral part of the development of mathematics from the very beginning.

Although problem solving has been practiced for a very long time, the use of mathematics as a very effective tool in problem solving has gained prominence in the last 50 years, mainly due to rapid developments in computing. Computational power is particularly important in modeling chemical engineering systems, as the physical and chemical laws governing these processes are complex. Besides heat, mass, and momentum transfer, these processes may also include chemical reactions, reaction heat, adsorption, desorption, phase transition, multiphase flow, etc. This makes modeling challenging but also necessary to understand complex interactions.

All models are abstractions of real systems and processes. Nevertheless, they serve as tools for engineers and scientists to develop an understanding of important systems and processes using mathematical equations. In a chemical engineering context, mathematical modeling is a prerequisite for:

- design and scale-up;
- process control;
- optimization;
- mechanistic understanding;
- evaluation/planning of experiments;
- trouble shooting and diagnostics;
- determining quantities that cannot be measured directly;
- simulation instead of costly experiments in the development lab;
- feasibility studies to determine potential before building prototype equipment or devices.

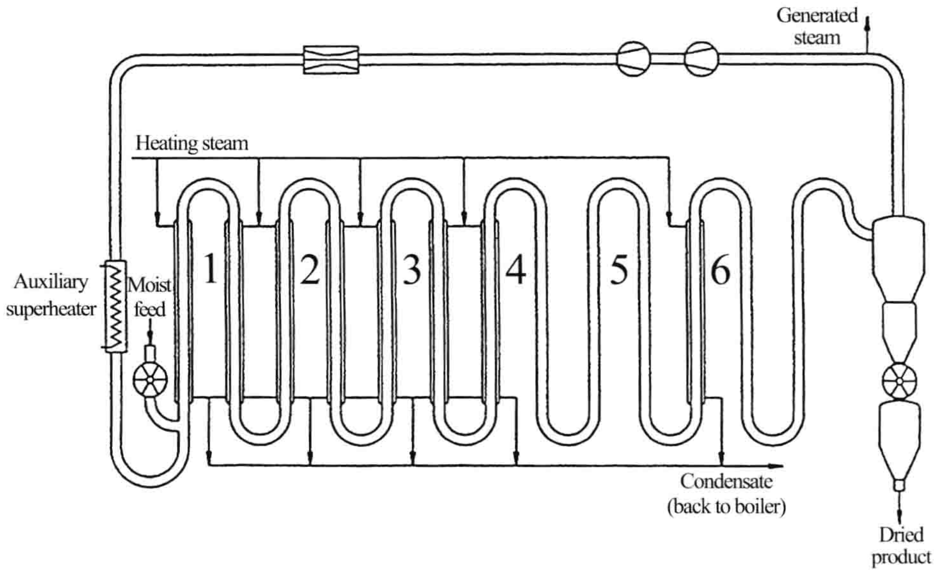

Figure 1.1. Pilot dryer, Example 1.1.

A typical problem in chemical engineering concerns scale-up from laboratory to full-scale equipment. To be able to scale-up with some certainty, the fundamental mechanisms have to be evaluated and formulated in mathematical terms. This involves careful experimental work in close connection to the theoretical development.

There are no modeling recipes that guarantee successful results. However, the development of new models always requires both an understanding of the physical/chemical principles controlling a process and the skills for making appropriate simplifying assumptions. Models will never be anything other than simplified representations of real processes, but as long as the essential mechanisms are included the model predictions can be accurate. Chapter 3 therefore provides information on how to formulate mathematical models correctly and Chapter 5 teaches the reader how to simplify the models.

Let us now look at two examples and discuss the mechanisms that control these systems. We do this without going into the details of the formulation or numerical solution. After reading this book, the reader is encouraged to refer back to these two case studies and read how these modeling problems were solved.

Example 1.1 Design of a pneumatic conveying dryer

A mathematical model of a pneumatic conveying dryer, Figure 1.1, has been developed (Fyhr, C. and Rasmuson, A., *AIChE J.* **42**, 2491–2502, 1996; **43**, 2889–2902, 1997) and validated against experimental results in a pilot dryer.

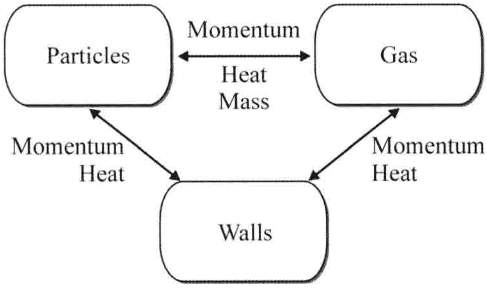

Figure 1.2. Interactions between particles, steam, and walls.

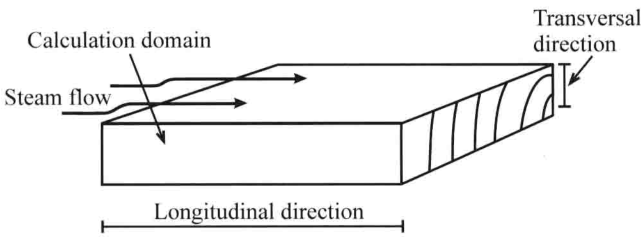

Figure 1.3. Wood chip.

The dryer essentially consists of a long tube in which the material is conveyed by, in our case, superheated steam. The aim of the modeling task was to develop a tool that could be used for design and rating purposes.

Inside the tubes, the single particles, conveying steam, and walls interact in a complex manner, as illustrated in Figure 1.2. The gas and particles exchange heat and mass due to drying, and momentum in order to convey the particles. The gas and walls exchange momentum by wall friction, as well as heat by convection. The single particles and walls also exchange momentum by wall friction, and heat by radiation from the walls. The single particle is, in this case, a wood chip shaped as depicted in Figure 1.3.

The chip is rectangular, which leads to problems in determining exchange coefficients. The particles also flow in a disordered manner through the dryer. The drying rate is controlled by external heat transfer as long as the surface is kept wet. As the surface dries out, the drying rate decreases and becomes a function of both the external and internal characteristics of the drying medium and single particle. The insertion of cold material into the dryer leads to the condensation of steam on the wood chip surface, which, initially, increases the moisture content of the wood chip. The pressure drop at the outlet leads to flashing, which, in contrast, reduces the moisture content.

The mechanisms that occur between the particles and the steam, as well as the mechanisms inside the wood chip, are thus complex, and a detailed understanding is necessary. How would you go about modeling this problem? Models for these complex processes have been developed in the cited articles by Fyhr and Rasmuson.

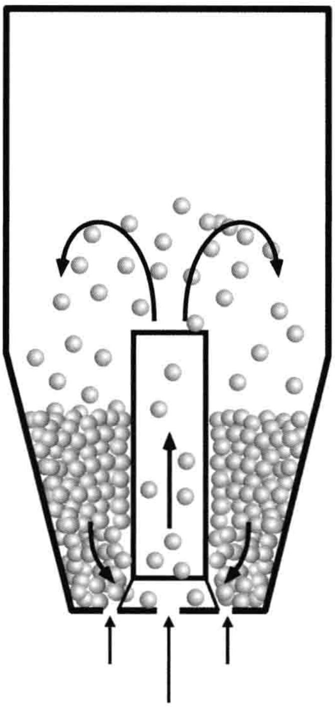

Figure 1.4. Schematic of a Wurster bed, Example 1.2.

Example 1.2 Design and optimization of a Wurster bed coater
In the second example, a mathematical model of a Wurster bed coater, Figure 1.4, has been developed (Karlsson, S., Rasmuson, A., van Wachen, B., and Niklasson Bjorn, I., *AIChE J.* **55**, 2578–2590, 2009; Karlsson, S., Rasmuson, A., Niklasson Bjorn, I., and Schantz, S., *Powder Tech.* **207**, 245–256, 2011) and validated against experimental results.

Coating is a common process step in the chemical, agricultural, pharmaceutical, and food industries. Coating of solid particles is used for the sustained release of active components, for protection of the core from external conditions, for masking taste or odours, and for easier powder handling. For example, several applications in particular are used for coating in the pharmaceutical industry, for both aesthetic and functional purposes.

The Wurster process is a type of spouted bed with a draft tube and fluidization flow around the jet (Figure 1.4). The jet consists of a spray nozzle that injects air and droplets of the coating liquid into the bed. The droplets hit and wet the particles concurrently in the inlet to the draft tube. The particles are transported upwards through the tube, decelerate in the expansion chamber, and fall down to the dense region of particles outside the tube. During the upward movement and the deceleration, the particles are dried by the warm air, and a thin coating layer starts to form on the particle surface. From the dense region the particles are transported again into the Wurster tube, where the droplets again hit the particles, and the circulation motion in the bed is repeated. The particles are circulated until a sufficiently thick layer of coating material has been built up around them.

The final coating properties, such as film thickness distribution, depend not only on the coating material, but also on the process equipment and the operating conditions during film formation. The spray rate, temperature, and moisture content are operating parameters that influence the final coating and which can be controlled in the process. The drying rate and the subsequent film formation are highly dependent on the flow field of the gas and the particles in the equipment. Local temperatures in the equipment are also known to be critical for the film formation; different temperatures may change the properties of the coating layer. Temperature is also important for moisture equilibrium, and influences the drying rate.

Several processes take place simultaneously at the single-particle level during the coating phase. These are: the atomization of the coating solution, transport of the droplets formed to the particle, adhesion of the droplets to the particle surface, surface wetting, and film formation and drying. These processes are repeated for each applied film layer, i.e. continuously repeated for each circulation through the Wurster bed.

Consequently, the mechanisms that occur at the microscopic and macroscopic levels are complex and include a high degree of interaction. The aim of the modeling task is to develop a tool that can be used for design and optimization. What models do you think best describe the mechanisms in this process?

1.2 The modeling procedure

In undergraduate textbooks, models are often presented in their final, neat and elegant form. In reality there are many steps, choices, and iterative processes that a modeler goes through in reaching a satisfactory model. Each step in the modeling process requires an understanding of a variety of concepts and techniques blended with a combination of critical and creative thinking, intuition and foresight, and decision making. This makes model building both a science and an art.

Model building comprises different steps, as shown in Figure 1.5. As seen here, model develpoment is an iterative process of hypotheses formulation, validation, and refinement.

Figure 1.5 also gives an outline of this process. Conceptual and mathematical model formulation are treated further in Chapters 3–5; solution methods are discussed in Chapter 6; and finally parameter estimation and model validation are discussed in Chapter 7.

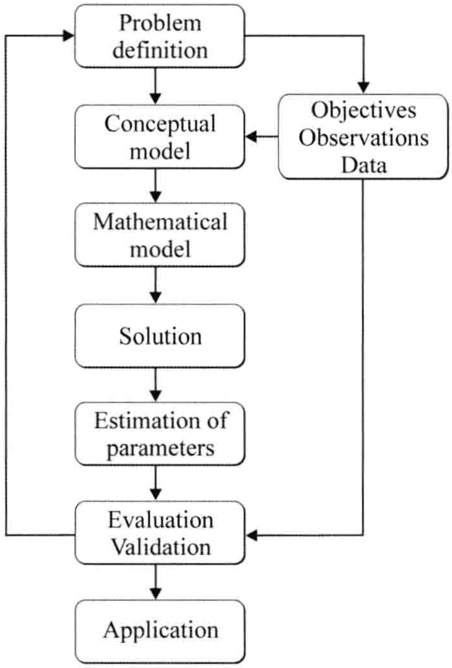

Figure 1.5. The different steps in model development.

Step 1: Problem definition

The first step in the mathematical model development is to define the problem. This involves stating clear goals for the modeling, including the various elements that pertain to the problem and its solution.

Consider the following questions:

What is the objective (i.e. what questions should the model be able to answer)?
What resolution is needed?
What degree of accuracy is required?

Step 2: Formulation of conceptual model (Chapter 3)

When formulating the conceptual model, decisions must be made on what hypothesis and which assumptions to use. The first task is to collect data and experience about the subject to be modeled. The main challenges are in identifying the underlying mechanisms and governing physical/chemical principles of the problem. The development of a conceptual model involves idealization, and there will always be a tradeoff between model generality and precision.

Step 3: Formulation of mathematical model (Chapters 3–5)

Each important quantity is represented by a suitable mathematical entity, e.g. a variable, a function, a graph, etc.

What are the variables (dependent, independent, parameters)? The distinction between dependent and independent variables is that the independent variable is the one being changed, x, and the dependent variable, y, is the observed variable caused by this change, e.g. $y = x^3$. Parameters represent physical quantities that characterize the system and model such as density, thermal conductivity, viscosity, reaction rate constants, or activation energies. Parameters are not necessarily constants, and can be described as functions of the dependent (or independent) variables, e.g. heat capacity $c_p(T)$ and density $\rho(p, T)$.

What are the constraints? Are there limitations on the possible values of a variable? For example, concentrations are always positive.

What boundary conditions, i.e. the relations valid at the boundaries of the system, are suitable to use?

What initial conditions, i.e. conditions valid at the start-up of a time-dependent process, exist?

Each relationship is represented by an equation, inequality, or other suitable mathematical relation.

Step 4: Solution of the mathematical problem (Chapter 6)

Check the validity of individual mathematical relationships, and whether the relationships are mutually consistent.

Consider the analytical versus the numerical solution. Analytical solutions are only possible for special situations; essentially the problem has to be linear. Most often, a numerical solution is the only option; luckily the cost of computers is low and models can run in parallel on computer clusters if necessary.

Verify the mathematical solution, i.e. ensure that you have solved the equations correctly. This step involves checking your solution against previously known results (analytical/numerical), simplified limiting cases, etc.

Step 5: Estimation of parameters (Chapter 7)

The parameters of the system must be evaluated and the appropriate values must be used in the model. Some parameters can be obtained independently of the mathematical model. They may be of a basic character, like the gravitation constant, or it may be possible to determine them by independent measurements, like, for instance, solubility data from solubility experiments. However, it is usually not possible to evaluate all the parameters from specific experiments, and many of them have to be estimated by taking results from the whole (or a similar system), and then using parameter-fitting techniques to determine which set of parameter values makes the model best fit the experimental results. For example, a complex reaction may involve ten or more kinetic constants. These constants can be estimated by fitting a model to results from a laboratory reactor. Once the parameter values have been determined, they can be incorporated into a model of a plant-scale reactor.

Step 6: Evaluation/validation (Chapter 7)

A key step in mathematical modeling is experimental validation. Ideally the validation should be made using independent experimental results, i.e. not the same set as used