FUNDAMENTALS OF THE MODELING AND SIMULATION IN THE CHEMICAL INDUSTRY

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Abstract: *Direct Metal Laser Sintering[1] (DMLS) is a revolutionary technology that allows a production of fully functional metal parts directly from a 3D CAD data, eliminating the investment to production tools and technologies which brings considerable cost and time savings. Metal parts made by DMLS technology are fully comparable with casted or machined parts. A range of application of DMLS technologies is very wide – from prototypes, through short-run production to final products. Advantages of DMLS technology are arising along with complexity of parts – more complex geometry of parts (in terms of shape and occurrence of the detail) make DMLS technology even more economically effective.*

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1. Introduction

The modeling and simulation are a basic approach to quantifying processes and phenomena. They have become realistic as a result of the development of computing and applied mathematics. In the industry, the modeling and simulation offer a quantitative description of the kinetics of processes and systems for the purposes of their optimal design or control. In the industrial systems, the process models of the individual devices are known in advance, and system models offer quantitative descriptions of the systems (process systems engineering).

In the industry, quantification of systems can also be used for various other tasks. For example, in periodically operating systems, the optimal schedules of the apparatuses (machines) for conducting different processes (operations) of different duration and different sequence to obtain different substances (machined details) can be determined. In these cases, the mass service theory offers models that allow for optimal solutions.

The fundamentals of the modeling and simulation, as a part of human knowledge and science, are related to the combination of intuition and logic, that are in different scales in individual sciences [1, 2]. In mathematics, logic dominates intuition, where intuition is the axiom (unconditional truth that is not proof able), and logic is the theorem (the logical consequences of the axiom). In the natural sciences (physics, chemistry, biology), the logic/intuition ratio is maintained, but axioms are usually conditional (principles, postulates, laws). This ratio goes back to the humanities and reaches the extreme in religion.

The modeling and simulation offer quantitative (mathematical) descriptions that have different degrees of detail. The lowest level is the thermodynamic (non-equilibrium thermodynamics) that examines the volume of the phase (gas, liquid, solid). The next level is the hydrodynamic, which examines the elementary phase volumes (mechanics of continua), which are much smaller than the phase volumes, but much larger than the intermolecular volumes, i.e. the molecules are indistinguishable. The highest level is the molecular (the kinetic theory of the ideal gas).

The modeling and simulation of industrial processes has a wide application, so the processes in the chemical industry and related biotechnologies and heating technologies, will be discussed. The major part of these processes is the transfer of mass and heat as a result of phase or phase boundary reactions. By reaction, we will understand the creation or disappearance of a particular substance (or amount of heat) as a result of a chemical reaction in the phase or on the phase boundary, interphase mass transfer, adsorption on the phase boundary or a liquid-vapor-liquid phase transition. These reactions result in varying concentrations and temperatures in the phases, i. e. to a deviation from the thermodynamic equilibrium and as a result of the mass transfer and heat transfer to restore the thermodynamic equilibrium. The models of mass transfer and heat transfer are analogous and, therefore, the models of mass transfer in industrial processes will be presented.

2. Thermodynamic approximation

The reactions deviate the industrial systems from the thermodynamic equilibrium and the industrial processes for its recovery begin. The determining of the rate of these processes is a major problem in the industry, as it is the basis for their optimal design and control. This gives reason to use the thermodynamic laws of irreversible processes such as mathematical structures in the construction of the process models, described by extensive and intense variables (in the case of merging of two identical systems, the extensive variables double their values, while the intensive variables retain their values).

The kinetics of the irreversible processes use the mathematical structures resulting from Onsanger's "linearity principle" [3]. According to him, the mean values of the derivatives at the time of the extensive variables depend linearly on the mean deviations of the conjugated intensive variables from their equilibrium states (values). This principle is valid in the vicinity of the equilibrium, and proportionality coefficients are kinetic (rate) constants.

According to the principle of linearity, the mass derivative at time $J_0 = \dfrac{dm}{dt}$ [kg-mol.s^{-1}] depends linearly on the deviation from the thermodynamic equilibrium Δc [kg-mol.m^{-3}] of the concentration in two phase volumes or in one phase and the phase boundary, i.e.

$$J_0 = k_0 \Delta c, \qquad (1)$$

where k_0 [m^3.s^{-1}] is a proportionality coefficient.

Consider a system that contains two identical volumes in one phase $v_1 = v_2 = v$ [m^3]. The system contains a substance whose masses m_i [kg-mol] and concentrations $c_i = \dfrac{m_i}{v_i}$ [kg-mol.m-3] are different in two volumes, $i = 1, 2,$. The system is not in thermodynamic equilibrium. Let us assume for certainty $c_1 - c_2 > 0$, $i = 1, 2$. As a result, the mass of the substance starts to be transferred from volume v_1 to volume v_2 for to achieve the equilibrium. According to the principle of linearity, the mass transfer rate between the two volumes J_0 [kg-moll.s^{-1}] can be represented as:

$$J_0 = \frac{dm_1}{dt} = -\frac{dm_2}{dt} = k_0 (c_1 - c_2), \qquad (2)$$

where k_0 [kg-mol^{-1}.m^3.s^{-1}] is a proportionality coefficient. If we replace masses with concentrations $m_i = v_i c_i, i = 1, 2$, the mass transfer rate in one phase J [kg-mol.m^{-3}.s^{-1}] between two points with different concentrations is:

$$J = \frac{dc_1}{dt} = -\frac{dc_2}{dt} = k(c_1 - c_2), \qquad (3)$$

where k [s^{-1}] is a rate coefficient. This equation is capable of presenting the rate of interphase mass transfer in the case of adsorption or catalytic process, where c_1 is the concentration of the substance in the gas phase, while c_2 is the concentration of the substance in the gaseous portion of the solid (capillaries of the adsorbent or catalyst) phase.

In the cases, where the volumes $v_1 = v_2 = v$ are in different phases (for example, 1 is a gas phase and 2 is a liquid phase), the thermodynamic equilibrium law has the form $c_1 - \chi c_2 = 0$, i.e. this is the law of Henry and χ is the number of Henry. If $c_1 - \chi c_2 > 0$ the mass transfer is from phase 1 to phase 2 and the mass transfer rate between phases is:

$$J = k(c_1 - \chi c_2), \qquad (4)$$

where k [s-1] is the rate coefficient of the interfacial mass transfer.

On the surface between two phases, the thermodynamic equilibrium is immediately established, practically, i.e. $c_1^* - \chi c_2^* = 0$, where $c_i^*, i = 1, 2$, are the equilibrium concentrations on the phase boundary. Thus, the mass transfer rate can be expressed by mass transfer rate in two phases:

$$J = k_1(c_1 - c_1^*) = k_2(c_2^* - c_2), \qquad (5)$$

where $k_i, i = 1, 2$ [s^{-1}] are mass transfer rate coefficients.

The Onsanger principle of linearity represents the thermodynamic approximation of the mathematical description of the kinetics of irreversible processes, but it does not show the way to reach equilibrium, i.e. the mechanism of the process and as a result the rate coefficient, is not known. Obviously, this "thermodynamic level" does not allow a real quantitative description of the kinetics of irreversible processes in industry and the next level of detail of the description, the so-called "hydrodynamic level", should be used.

3. Hydrodynamic approximation

The processes in the chemical industry and related biotechnologies and heating technologies are realized in one-, two- and three-phase systems (gas-liquid-solid). They are a result from the reactions, i.e. processes of disappearance or creation of any substance. The reactions are associated with a particular phase and can be homogeneous (occurring in volume of the phase) or heterogeneous (occurring at the interface with another phase). Homogeneous reactions are usually chemical, while heterogeneous reactions may be chemical, catalytic and adsorption. Heterogeneous reaction is the interphase mass transfer too, where on the interphase boundary the substance disappears (created) in one phase and creates (disappears) in the other phase.

The volume reactions lead to different concentrations of the reagents in the phase volumes and as a result two mass transfer processes are realized – convective transfer (caused by the movement of the phases) and diffusion transfer (caused by the concentration gradients in the phases). The mass transfer models are a mass balance in the phases, where components are convective transfer, diffusion transfer and volume reactions (volume mass sources or sings). The surface reactions participate as mass sources or sings in the boundary conditions of the model equations. The

models of this complex process are possible to be created on the basis of the mass transfer theory as a main approach to quantitative description of the industrial processes.

The mass transfer theory combines the chemistry, physics and mathematics and builds its logical structures on three main "axioms":

1. The postulate of Stokes for the linear relationship between the stress and deformation rate, which is the basis of the Newtonian fluid dynamics models;

2. The first law of Fick for the linear relationship between the mass flow and the concentration gradient, which is the basis of the linear theory of the mass transfer;

3. The first law of Fourier for the linear relationship between the heat flux and the temperature gradient, which is the basis of the linear theories of the heat transfer.

These are the laws of the impulse, mass and energy transfer.

In Boltzmann's kinetic theory of the ideal gas, these axioms are replaced by the "elastic shock" axiom (in a shock between two molecules the direction and the velocity of the movement change, but the sum of their kinetic energies is retained, i.e. there is no loss of kinetic energy) and the rate coefficients are theoretically determined by the average velocity and the average free run of the molecules.

The contemporary mass transfer theory is based of diffusion boundary layer theory (Landau, Levich [4]). This approach substitutes (physically justified) elliptic partial differential equations with parabolic partial differential equations, which facilitates their mathematical solution and offers a mathematical description of physical processes with free (not predetermined) ends.

The diffusion boundary layer theory is developed in the cases of drops and bubbles (Levich, Krylov [5]), film flows (Levich, Krylov, Boyadjiev, Beshkov[6, 7]), non-linear mass transfer and hydrodynamic stability (Krylov, Boyadjiev, Babak [8, 9]).

The diffusion boundary theory is not applicable to the modeling of chemical, absorption, adsorption and catalytic processes in column apparatuses, which necessitated the creation of new type of convection-diffusion and average-concentration models (Chr. Boyadjiev, M. Doichinova, B. Boyadjiev, P. Popova-Krumova [10]). where the unknown interphase surface requires substitution of the surface reactions with equivalent volume reactions and the unknown velocity distribution with the average velocity and experimentally determined parameters.

The theory of mass transfer allows the construction of the process model if its physical mechanism is known. The model thus obtained allows for the identification of this mechanism, i.e. the determining of the significant physical effects and rejection of the insignificant, using the generalized analysis method [11].

4. Physical mechanism identification

The qualitative analysis of the models permits to be made the physical mechanism identification, using generalized variables [11], whereas characteristic (inherent) scales are used the maximal or average values of the variables. The introduction of the generalized variables leads to ddimensionless model. As a result the unity is the order of magnitude of all functions and their derivatives in the model, i.e. the effects of the physical and chemical phenomena (the contribution of the terms in the model), are determined by the orders of magnitude of the dimensionless parameters in the model. If all model equations are divided by the dimensionless parameter, which has the maximal order of magnitude, all terms in the model equations will be classified in three parts:

1. The parameter is unity or its order of magnitude is unity, i.e. this mathematical operator represents a main physical effect;

2. The parameter's order of magnitude is 10^{-1}, i.e. this mathematical operator represents a small physical effect;

3. The parameter's order of magnitude is $\leq 10^{-2}$, i.e. this mathematical operator represents a very small (negligible) physical effect and has to be neglected, because it is not possible to be measured experimentally.

After the physical mechanism identification the model contains a minimum number of parameters which must be determined experimentally.

5. Parameters identification

In general case, the identification of the parameters in the model is made by the minimization of the least squares function by the inverse identification problem solution [11]. The least squares function represents the sum of the squares of the differences between the calculated and the experimental values of the functions in the model and its minimum must be obtained with respect to the parameters in the model. This inverse identification problem is very often incorrect and needs special methods for the solutions [11].

6. Statistical analysis of the model adequacy

The stochastic nature of the errors during the experimental data determination leads to subsequent errors of the mode parameters. The model is adequate if the variance of the statistical error of the model does not exceed the variance of the statistical error of the experimental data, i. e. the accuracy of the functions calculation by the model is not less than the accuracy of the function experimental measurement [11].

7. Processes simulation

The process simulation uses the most common numerical methods of applied mathematics to solve model equations. For this purpose, commercial software is usually used. In many cases, however, it is necessary to introduce this software into specialized algorithms [10, 11].

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