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# Modelling and Computer Simulations of Large Chemical Systems

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**Abstract.** The methodology of mathematical modelling and computer simulations for large chemical systems is outlined. It is demonstrated with some examples from the author's group that this methodology can provide answers where theoretical methods are limited and/or experiments cannot be performed. Some perspectives are given for overcoming the time and size limitation of standard simulation techniques.

## 1. Modelling and Simulations

During the last years, a third methodological category between theory and experiment has been established in science and technology. This is the methodology of mathematical modelling and computer simulations (MODSIM technology). Simulations can provide answers, where theory with its analytical methods is limited (examples are nonlinear dynamics and chaos research), but also in those cases where experiments cannot be performed because of technical difficulties or economical reasons. The interplay between theory, experiment and simulation is schematically shown in Fig. 1.

The large progress of MODSIM technology during the last couple of years is drastically influenced by the development of computer hardware technologies. Today, supercomputers are available with a computational speed at the edge of one teraflop (1 teraflop = 1,000,000,000,000 floating point operations per second) and a memory capacity which is nearly unlimited. On the other hand, high end graphical workstations are available for the interactive visualization of complex information which allows a very fast man-machine communication and thus forms the basis for interactive simulations.

What does the term MODSIM really mean? The answer to this question is sim-

ple, at least in principle (see Fig. 2). The basis forms in any case a model scenario: the real world (microscopic or macroscopic) is transformed into a virtual world of mathematical object (points, rigid bodies, distributions *etc.*) with well-defined interrelations. The transfer of the real world to model scenarios is termed modelling. The simulation is then the numerical solution of equations, which mimic the behaviour of the system. For many applications it is desirable for a scientist to interfere with the virtual reality of model objects. This is done *via* fast computer graphics visualization and interactive manipulation of the scenario. The visualization may

help to gain qualitative insights in order to modify the model scenarios while interactive manipulations allow for directly controlling the model scenario: parameters can be changed 'on the fly' (see Fig. 2). The aim of numerical simulations is testing the model scenarios (by comparing the calculated data with real experiments) or predicting unknown properties of real matter on one side and establishing correlations between model scenarios of different complexity (see Fig. 2) on the other side.

## 2. Simulation of Large Chemical Systems

The term large chemical system is used here to describe a system which contains a large number of atomic particles (some  $10^4$  up to Avogadro's number). This can be a macroscopic system (characterized by extensive and intensive thermodynamic or kinetic variables) but also a biological polymer like a protein. In the following, only those simulations are considered that are based upon a microscopic model scenario, *i.e.*, we do not deal with thermodynamic, fluid dynamic, or kinetic scenarios which are frequently used in chemical engineering.

There are two basic technologies commonly in use for the computer simulations based on microscopic models, the Monte Carlo (MC) method and the molecular dynamics (MD) simulation technique. In the MC scheme, a representative sample

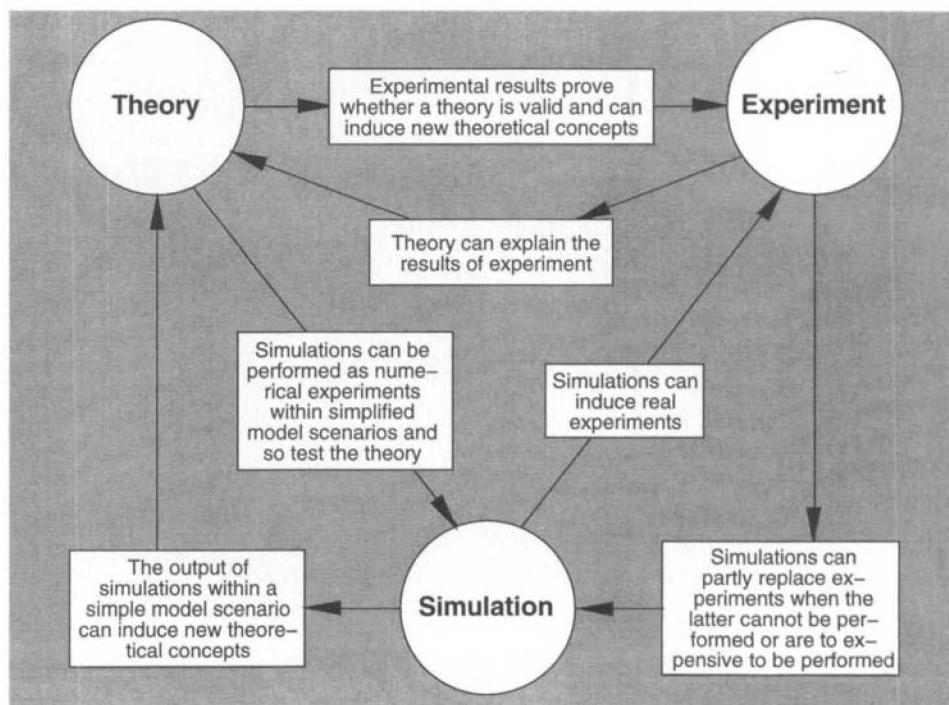


Fig. 1. The interplay of theory, experiment and simulation in science

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of different configurations of the model ensemble is constructed by a random procedure. This sample is then used for the calculation of averages and correlation functions. The latter can then be related to the results of microscopic and macroscopic measurements (see Fig. 2). In the MD procedure, the time evolution of a small number of initial configurations is calculated numerically on the basis of classical or quantum mechanical laws within a discrete propagation scheme. Macroscopically observable quantities are obtained as time averages. Many characteristic properties (atomistic force fields, periodic boundary conditions *etc.*) and limitations (system size, time scale, convergence of numerical procedures *etc.*) are very similar for both techniques; we, therefore, restrict the further discussion to MD simulations. The basic ideas and technologies of MD simulations are reflected in many reviews and books on this subject (see [1–4] and references given therein) and are not reviewed here again. The application of the method to proteins and other biomolecules [1][5] in the 1970s has led to its widespread use throughout the theoretical and experimental chemical communities. In almost all cases, the simulation results have been obtained using a standard MD procedure: predictions can be made directly from the output of the simulation based on a microscopic model scenario (with highest complexity level  $N$ , see Fig.

2) for both, the real microscopic and the macroscopic world. Standard MD simulations can be successfully performed for large chemical systems when these systems are periodic. This is demonstrated in the next section with the calculation of elastic properties of cellulose. For nonperiodic systems, the size of microscopic model scenarios being tractable by standard MD simulations can be up to some  $10^5$  atoms, reaching time scales of several nanoseconds. This is shown exemplarily in Sect. 4. Size and time scale can be increased when simplified models are used [1]. This is demonstrated in Sect. 5 and 6 for the simulation of phase transitions in liquid crystals and transport properties in zeolites.

### 3. Structural and Elastic Properties of Cellulose

For periodic systems (crystals), standard MD techniques can be very powerful tools for establishing correlations between microscopic structure and macroscopic properties of matter. This has been demonstrated recently for cellulose [6]. Structures and elastic properties (*Young's* moduli) of the different phases of cellulose I and II have been studied on the basis of MD simulations using a new force field for carbohydrates [7]. The structural results for all phases as well as the *Young's*

moduli for cellulose I and cellulose II with parallel chain arrangement are in very good agreement with experimental data, whereas the calculated *Young's* modulus for cellulose II (with antiparallel chains) does not match the experimental error margin. These results lead to the conclusion that cellulose II, as resulting from the mercerization, is arranged in parallel chains. Microscopically, the transition from phase I to II can then easily be explained as a rearrangement of the exocyclic torsional angles.

### 4. MD Simulations of Phospholipid Bilayers in Contact with Water

An example for the application of standard MD technique to large chemical systems which are nonperiodic is the simulation of biological membranes in contact with water.

The first available force fields for biomolecules were developed for the simulation of proteins [5]. *Schlenkrich et al.* [8] extended this microscopic model scenario with parameters for phospholipids. Extensive use of quantum-chemical calculations was necessary for this parametrization. Additionally, information from microscopic experiments were included.

First standard MD simulations of phospholipid crystals were performed in order to show the capability of the extended

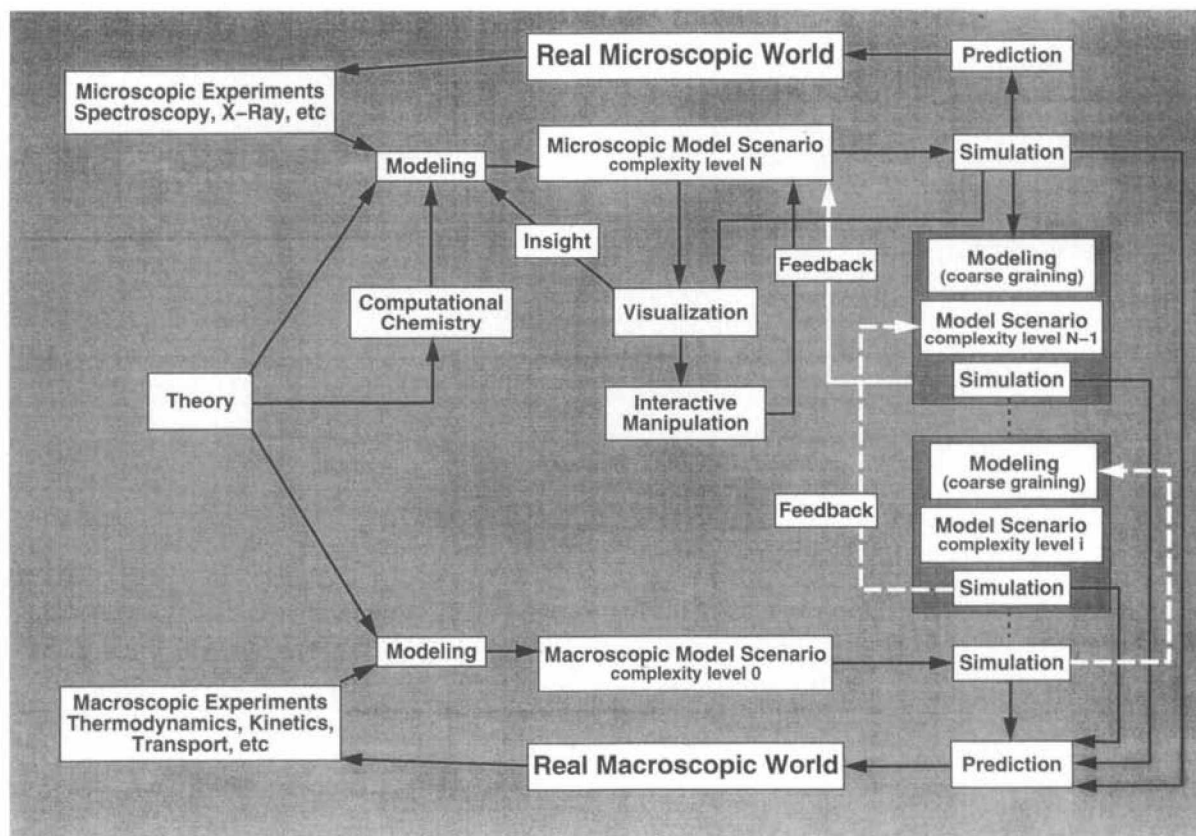


Fig. 2. Simulation pathways (explanation see text)

force field. The results showed that it is reliable for standard MD simulations of phospholipids in large aggregates [8][9].

For the bilayer MD simulation, a modified crystal structure was used as initial configuration. A water box with 2112 molecules was set on top of the bilayer. Constant temperature (320 K) and constant pressure (1 bar) conditions were applied. The system equilibrates rapidly and after 150 ps the area per head group remains constant at  $47 \text{ \AA}^2$  over a period of 100 ps. This value is in good agreement with experimental values [10]. The same is true for the average tilt angle of the lipid tails [9].

The model scenario described above for a phospholipid bilayer interfacing with water was successfully applied recently by several groups. All these works have in common that the numerical effort for the MD simulation is enormously high – the cost for our calculation exceed 1 million US Dollars (calculated on an academic cost level). This demonstrates that, for large systems, the standard techniques (*e.g.* simulation on the basis of a microscopic scenario in order to predict properties in macroscopic equilibrium) are very inefficient even if the capacities of modern computer technology are increased by several orders of magnitude.

### 5. Simulations of Liquid Crystals Consisting of Semiflexible Molecules

One way to overcome the time and size barriers of standard techniques is to choose simplified model scenarios, *i.e.* those with reduced complexity. Up to now, there are only a few attempts [11–13] to generate simplified model scenarios from the simulation results of high-complexity models (see Fig. 2) in a systematic way. In many cases, the simplified models are constructed with *ad hoc* assumptions. An example may demonstrate this.

The growing number of applications of polymeric liquid crystals of low molecular mass in the areas of electro-optics and high-performance materials has led to an enhanced interest in the relation between the molecular structure and the liquid crystalline state. The study of a large number of experimentally available data allows only limited qualitative predictions of the stability and the structure of liquid crystalline phases. A number of standard MD simulations have been carried out [14–16] using an all-atom representation for liquid crystalline materials of low molecular mass. Within the limits of today's computer power, however, the high cost of these

simulations make the systematic investigation of the state function of such 'realistic' model systems unfeasible. Hence, less complex molecular models have been used in MD and MC computer simulations, taking into account only some of the molecular properties [17].

This is shown in a recent study [18]. A simple steric model of so-called rfr (rigid-flexible-rigid) molecules was developed. It consists of two rigid spherocylindrical fragments linked by a flexible alkyl chain. MD simulations of 128 model molecules were carried out in a periodic box, and the influence of density and alkyl chain length on the molecular order and the self-diffusion was studied. Different liquid crystalline phases were found which are stable on the time scale of the simulations. In agreement with experimental results, the nematic order parameters and the stability of the phase, as indicated by the location of the isotropic/liquid crystalline phase show an odd-even effect with respect to the number of methylene groups in the alkyl chain. A separation of rigid and flexible fragments is observed leading to smectic liquid crystalline phases.

### 6. Xenon Diffusion in Zeolites

A rigorous use of standard MD simulation results for the generation of simplified model scenarios was recently presented by Mosell *et al.* [13]. In their work, the diffusion of Xe in zeolite NaY at low temperatures was investigated by MD simulations of individual trajectories started at the cage-to-cage boundary. Transmission coefficients are obtained from the normalized reactive-flux correlation function. Recrossings of the cage-to-cage boundary by Xe atoms at very low temperatures are attributed to instantaneous shifts of the maximum of the potential energy along the diffusion path. At higher temperatures, recrossings occur mainly because of the slow energy transfer from Xe to the zeolite lattice, enabling Xe atoms to pass several energy barriers during one activation period. These jump events to distant minima are investigated by the introduction of an absorbing boundary that surrounds the two supercages located on either side of the central cage-to-cage boundary. The absorbing-boundary function, defined as the percentage of trajectories that has reached the absorbing boundary as a function of time, contains a 'plateau', which confirms that the diffusion process may be divided into separate jump events. An absorbing-boundary factor, describing the percentage of trajectories that

reached the absorbing boundary during the original jump event, is obtained from the absorbing-boundary function in the same way as the transmission coefficient is obtained from the normalized reactive-flux correlation function. The diffusion coefficient for Xe in zeolite NaY at infinite dilution was calculated at low temperatures within a hopping model based upon cage-to-cage migration only. Diffusion is modelled therein as a sequence of jump events that may consist of several barrier passages. The number of jump events is calculated from transition-state theory using the potential of mean force. The potential of mean force is more or less independent of temperature. In the conversion of the jump rate to the diffusion coefficient, dynamical corrections are taken into account. The mean number of barrier passages per jump event increases significantly when the temperature is raised. In the range from 140 to 210 K, the diffusion coefficients obtained from the hopping model are in excellent agreement with corresponding data from conventional MD simulations [19].

### 7. Conclusion and Perspectives

A wide field of simulation strategies was shortly reviewed and some examples from the group of the author have been presented in order to draw a frame around the topic modelling and simulation of large chemical systems. It has been shown that the standard simulation techniques (based upon microscopic model scenarios, see Fig. 2) imply strong limitations for the size of the system and the time scale. Size and time scale can be increased when simplified models are used. Most of the simplifications follow *ad hoc* assumption. There are only a few attempts to develop simplified model scenarios in a systematic manner from the simulation results based on scenarios with higher complexity. At present, there are no technologies available (to the author's best knowledge) to implement a feedback control from a simulation in a model scenario of lower level to one of higher level of complexity (see Fig. 2, white arrows). A feedback control in MD and MC simulations could have the following structure:

- i) MD or MC simulation based on a microscopic model scenario (complexity level N).
- ii) Generation of a model scenario of lower complexity level N-1 with coarse-graining strategies.
- iii) Simulation based on this scenario in order to obtain large amplitude chang-

es in the chemical system (phase transitions, reactions *etc.*).

iv) Backtransformation to level N, *i.e.* generation of a new initial configuration. Details which have been lost by step *ii*) have to be restored.

v) Simulation based on N-level scenario in order to relax the system.

It has been demonstrated very recently in MD and MC simulations of polycarbonates [11][12] that such a strategy can, indeed, be realized and that it can be very effective in order to overcome the limitations mentioned above.

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## Molecular Photovoltaic Devices Mimic Photosynthesis

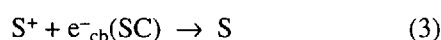
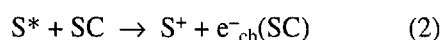
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**Abstract.** Photoinduced charge-transfer processes involving molecules adsorbed at interfaces are a fascinating topic which is presently attracting wide attention. Our investigations have focused on the identification of the factors that control the dynamics of such processes. The goal is to design molecular electronic devices that achieve efficient light-induced charge separation. Applications of similar systems in photochromic and electrochromic devices appear also feasible.

### Dynamics of Charge-Transfer Processes Involving Molecular Sensitizers

Photoinduced interfacial charge transfer between a discrete molecular excited state and a continuum of acceptor levels in a solid is the simplest photochemical surface reaction. Besides its fundamental interest, research in this field is strongly motivated by a large number of practical applications. This process is indeed the

basis of redox photosensitization of wide band gap semiconductors and is involved in most of the photographic and xerographic processes as well as in the photochemical solar energy conversion [1][2].



Charge injection (Eqn. 2) competes kinetically with the decay of the sensitizer's excited state. Hence, for dyes that are characterized by emission lifetimes as short as 1 ns, an ultrafast interfacial electron transfer rate is required to provide high injection yields. Back electron-transfer from the conduction band of the solid to the dye's oxidized state  $S^+$  (Eqn. 3) is equally important for photochemical conversion, since its rate controls the efficiency of the overall charge separation [3][4].

Mesoscopic transparent thin films (4–10  $\mu\text{m}$  thick) supported by a glass substrate and colloidal dispersions, both constituted of nanocrystalline particles (~20 nm diameter) of  $\text{TiO}_2$  anatase semiconductor (band gap  $\approx 3.2$  eV), are employed. These provide substrate material characterized by a very large effective surface area. Dye molecules carrying carboxylic or phosphonic anchoring groups, or a catechol moiety, are grafted onto the acidic

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