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Needs and Opportunities – Molecular Modeling Meets Polymer Process Modeling

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Summary: A non-exhaustive and somehow arbitrary review on actual trends and remaining challenges for a model based process development is given. An example how state of the art molecular modeling methods help to provide kinetic information is explained in some detail. A brief sketch of various methods providing thermodynamic information for engineering is given, and finally, recent concurrent coupling schemes of particle based simulation and computational fluid dynamics are highlighted.

Keywords: coarse graining; coupling schemes; molecular modeling; multiscale modeling; polymer process development

Introduction

The industrial production of synthetic polymers like polystyrene, PVC, PIB, polyacrylates, and many more started in the 1920ies and 30ies. Since then, production and development of properties, applications and volume is growing, and this trend goes on. Along with industrial production, the pioneering works of Staudinger, Mark, Flory and others laid the foundations of polymer physics. At the same time, young physicists in Göttingen, Copenhagen, Cambridge etc worked out quantum mechanics, the basis of all molecular theories. Of course, these developments of polymer science and quantum mechanics were completely independent of each other, and it could not be foreseen that they finally would meet. In 1929, PAM Dirac stated that "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation." [1] - This was the birth of quantum chemistry and later on molecular modeling. It was even later, in the 60ties of the last century, that Polymer Reaction Engineering became a discipline of its own. Meanwhile, molecular theories and methods can provide input for polymer reaction engineering, and this report will highlight a few examples. The report will start with a profile of model based process development to catch the needs and opportunities for in silico process developments followed by a review of Molecular Modeling methods for kinetics, thermodynamics and transport properties.

Model Based Process Development and Molecular Modeling

There is an ongoing demand for rational product design and manufacturing. Rational approaches require a deep understanding for the design of a new product, and a working process model for efficient upscale and production. A model-based process development and engineering can be applied in the very early stages for the evaluation of preliminary concepts for a new process or for designing the structure

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of a new product. Later in the work-flow, it facilitates the detailed and optimized layout of the final process, be it single units for optimized world-scale plants or multipurpose plants. The basic constituents of a process model comprise the kinetics, thermodynamics, transport properties and a model for the equipment. Molecular modeling can contribute to mechanistic understanding and provide data for kinetics, thermodynamics and transport properties. These basics may be supplemented by the quantitative description of the fluid dynamics and mixing behavior as well as of transfer processes for mass and energy, but this is beyond the molecular level. Obviously, the rational design of products and processes is still in the beginning. This review tries to give an overview what we can expect from present molecular modeling approaches to support process models. Is Molecular Modeling a way to gain deeper insight? How predictive is it? Does it deliver in time? Are models sufficiently complex to match reality? Having these questions in mind, the scope of molecular modeling tools is briefly outlined. An example how state of the art molecular modeling methods help to provide kinetic information is explained in some detail. A brief sketch of various methods providing thermodynamic information for engineering is given, and finally, recent concurrent coupling schemes of particle based simulation and computational fluid dynamics are highlighted.

Molecular Modeling Toolbox

Molecular modeling involves a mathematical description of systems of chemical species in chemical detail. The goal is to solve complex equations such as the Schrodinger equation for electronic and nuclear motion or Newton's equations of motion for interacting many particle systems which accurately describe natural phenomena. In a practical application of molecular modeling, mathematical equations or algorithms are devised to quantitatively describe the physical and chemical phenomena (e.g., energy states, structures, reactivity, positions and moments of atoms, order parameter etc) that occur in a particular system. Molecular modeling can be used to describe a diversity of chemical systems with a wide range of complexity. Polymers, for instance, consist of hundreds to millions of atoms, and the time scales range from picoseconds for molecular vibrations to seconds for stress relaxation processes. Consequently, a hierarchy of methods is available to address particular molecular systems and properties of interest. It should be noted that the communities working on the various levels are pretty diverse.

At the quantum molecular level (relevant to deliver reaction mechanisms and kinetic rate coefficients), chemical systems of hundreds of atoms can be modeled today, and highly accurate calculations are possible for up to 20 atoms. For applications in reaction engineering, usually high level methods are required.

Ab Initio Methods refer to a collection of approximations to solve the Schrödinger equation, as already envisioned by Dirac. They form a hierarchy of methods with increasing accuracy. Hartee-Fock (HF) is the starting point in most cases. This single-determinant wave function method is computationally cheap. However, it has the drawback that there is no ‘‘correlated movement’’ of the electrons any more – each electron only experiences the averaged potential of all other electrons. This leads to systematic errors that are not acceptable for calculations with chemical accuracy. Although Hartree-Fock energies are not accurate enough by themselves, almost all ‘‘higher correlated’’ methods are based on the Hartree-Fock reference wave function via an inclusion of further (excited-state) determinants into the ground state wave function. The current ‘‘gold standard’’ for validation are Coupled Cluster (CC) methods[2]. Benchmark calculations have clearly proven the reliability of coupled cluster methods, in particular of CCSD(T).

Density Functional Methods [3] are based on the theorem by Hohenberg and Kohn which states that the exact ground-state energy of any molecular system can be computed from the one-particle electron density. They introduce a one-particle functional that contains all manybody effects. With the knowledge of this functional, it would be possible to compute the exact ground-state energy. Although it has been shown that such a functional exists, its form is unknown. All current variants of functionals, that is, functionals within the local density approximation (LDA) or the generalized gradient approximation (GGA), meta-GGAs or hybrid functionals are guesses or approximations to this functional. The two very popular DFT-methods BP86 and B3LYP [4] represent a GGA-and a hybrid-GGA-functional, respectively. Practically, DFT is the working horse of quantum chemistry nowadays. It is a good compromise between accuracy and computational effort. All systems of interest up to approx. 1000 atoms can be calculated on the DFT level. The accuracy is usually not sufficient for quantitative predictions. Error bars cannot be given since errors are unpredictable. Systematic improvements, like perturbation theory as in the case of HF, are not possible since the Hamiltonian in DFT is approximated itself. Of the above-mentioned methods, only DFT is "affordable" for real chemical applications. In addition, methods for a quantum chemical treatment of molecules in the condensed phase (solvation effects) are also typically based on DFT calculations.

More approximate classical atomistic methods can handle systems up to millions of atoms, depending on the time scale. The atomistic or molecular scale encompasses a wide variety of computations, which are usually performed by Molecular Dynamics (MD) or Monte Carlo (MC) methods using classical atomistic or united atom force fields. Properties described at this scale might range from thermodynamic properties (critical points, pressures) to transport properties (mass and heat transfer) and phase equilibria. Using statistical mechanics, the results of atomistic or molecular scale calculations can then be applied to describe behavior at the mesoscopic and macroscopic scale (e.g., process or bulk properties). Excellent reviews on Molecular Dynamcis and Monte Carlo in the context of engineering applications have been recently published by Gubbins and Moore,[5] Maginn and Elliott,[6] and Theodorou.[7]

At the upper end, the mesoscale involves systems of billions or trillions of atoms which still manifest molecular effects. There are many potential applications of molecular modeling in chemical processes where predicting the characteristics and behavior of a system may be beneficial. By predicting system behavior, molecular modeling can potentially be used to improve the efficiency of existing operating systems as well as the design of new systems. It can help to shorten product and process development cycles, optimize processes to improve energy efficiency and environmental performance, and solve problems as they arise in plant operations. At the macroscale, materials behavior is described with continuum mechanical methods. Properties are fully linked to their morphologies on the micrometer level. Finally, bridging techniques (e.g. Coarse Graining) attempt to provide continuity and interface between the various scales, allowing the results of calculations at one scale to be used as input parameters to calculations at another scale. These techniques are particularly important for polymers because of the many time and length scales involved, but their development stage is yet far from being mature. Bridging is still on the research level and currently cannot be applied to day-to-day problems.

Molecular Modeling Contributions to Kinetics – Example on Free Radical Polymerization

Mathematical polymerization models are based on the underlying principles of chemistry and physics. From these principles, the individual concentrations of reactants and products, polymerization rates and polymer architecture are derived. The showcase task in industrial polymer reaction engineering is to identify the process that leads to the optimal combination of productivity and desired polymer properties. Productivity is codetermined by the overall reaction rate, while polymer architecture and, thus, polymer properties depend on reaction rates of the individual reactions, like transfer or cross-propagation in copolymerizations. Therefore, a detailed understanding of the kinetic scheme of a polymerization reaction and the knowledge of its kinetic coefficients is a prerequisite for a simultaneous optimization of capacity and polymer properties.[8,9]

An understanding of polymerization kinetics is never complete until all relevant model parameters are determined. Deducing reasonable values for the coefficients and parameters of a kinetic model from laboratory or plant data is one of the most critical and time-consuming (and therefore costly) steps for the successful development of a process model. Crucial model parameters are rate coefficients and thermodynamic parameters. Depending on the purpose of the model, further inputs, such as mass transfer coefficients, heat capacity, mixing effects, fluid dynamics, etc., may be needed. It goes without saying that some of these parameters are strongly dependent on process conditions.

In addition, determination of kinetic coefficients is complex because some observable effects are not caused by an isolated kinetic mechanism but result from several mechanisms affecting each other or are overlaid by physical phenomena (e.g., diffusion). Hence, it is not always possible to design experiments that allow for the unambiguous determination of all relevant kinetic parameters. A prominent example within free radical polymerization is the effect of backbiting,[10] that is, intramolecular H-transfer, on the obvious propagation rate. Backbiting leads to a steady state between differently reactive radicals and often the observed reaction rates are the averaged result caused by those different species. It thus appears highly desirable to have a computational method for deducing rate coefficients that overcomes the mentioned shortcomings. However, the fact that such an ab initio rate coefficient calculation is not a well-established method already shows that this task is rather complex. One main reason is that the prediction of kinetic parameters from calculations requires a high level of accuracy. This is a consequence of the fact that rate coefficients depend more or less exponentially on energetic and entropic barriers to be overcome. The Eyring equation relates thermodynamic functions of reacting species and transition states with chemical rate coefficients.[11,12] Its application to chemical reactions upon radical polymerization started around fifteen years ago. For the monomer ethylene, Radom et al. discuss, in their paper from 1995 [13] how an accurate theoretical description of propagation in gas-phase polymerization should be performed. According to them, key ingredients for a successful prediction of radical propagation rate coefficients are a careful choice/validation of the quantum chemical method for the energy calculation plus an entropy computation that takes into account the high degree of internal rotational flexibility in the gas phase transition state. To account for solvent effects, Thickett and Gilbert[14] applied the polarizable continuum model to the polymerization of acrylic acid in toluene and water; they obtained lower activation energy for the polar aqueous medium which is due to a better resonance stabilization of the transition state. Although a remarkably good agreement with experimental rate coefficients is reported in these papers, it is clear that such approaches will not be able to describe, for example, monomer concentration effects in aqueous solution polymerization. For a completely different chemistry (aqueous oxidation of hydroxylamine with nitric acid) Green et al.[15] describe the application of the COSMO-RS method, which allows for an explicit solvent description, to the computation of kinetic data. The latter approach was also chosen by Deglmann et al.[16] for the prediction of propagation rate coefficients in free radical solution polymerization of acrylates and acrylic acid. The methods reported so far all deal with "chemically controlled" reactions, that is, processes that require an energetic activation barrier to be overcome. "Diffusion-controlled" reactions that take place immediately as soon as two reactive sites encounter each other have to be treated by molecular simulation techniques, combined with a suitable description of bond breaking and creation. However, the accuracy of these approaches is insufficient for predictive modeling or the proper parameterization is extremely time consuming. At the moment, quantum chemical methods present the state of the art.

The correct computation of the total gas phase energies is crucial and finally determines the predictive power. The required chemical accuracy of 1 kcal/mol still is a challenge. CCSD(T)][2] can deliver this accuracy, but is limited to 20 atoms if appropriate basis sets are used. There is no hope that CCSD(T) can be applied to condensed phase at present. Thus, a combination of methods is required to provide quantitative results for kinetics in solvents.

Up to now, solvation effects are mostly treated with so called continuum models which place a single molecular species in media with a non-vacuum dielectric constant. A prominent example is the "polarizable continuum model" (PCM) which has been pioneered by Tomasi.[17] A special case of such continua around solvated molecules are environments with an infinite dielectric constant ($\varepsilon = \text{inf}$). This means placing the quantum chemically treated species in a perfectly screening medium, that is, an electric conductor. The corresponding method is known as the "conductor-like screening model" (COSMO) and has been developed by Klamt.[18] A quantum chemically computed surface charge density within the COSMO method also forms the basis for the more refined COSMO-RS[19] model (where RS indicates "real solvents"), in which mixtures of different solvent molecules are treated explicitly (via their electrostatic fingerprint) instead of approximating the environment by ε as the only input parameter. Due to the fairly good performance of COSMO-RS in engineering problems, it was decided to apply this method to chemical reactions in solution. As there are no fit parameters in COSMO-RS that depend on the specific chemical environment but (chemistry-independent) atomic radii, this solvation model should not only be applicable to stable molecules (intermediates) but also to transition states and short-lived radicals, for which it has not explicitly been developed, as experimental data in solution are scarce for such species. In Table 1, a representative example is

Table 1.

Comparison of relative behavior between experimental and computed free radical propagation rate coefficients kp for the polymerization of N-vinyl pyrrolidone, methacrylic acid and acrylic acid in aqueous solution at different monomer concentrations. Exp. Data taken from ref.[36–38]

NVP at 25 °C				MAA at 25 °C				AA at 20 °C			
NVP wt.-%	k_p (abs., exp.)[36] [$L \cdot mol^{-1} \cdot s^{-1}$]	k_p (rel., exp.)	k_p (rel., calc.)	MAA wt.-%	k_p (abs., exp.)[37] [$L \cdot mol^{-1} \cdot s^{-1}$]	k_p (rel., exp.)	k_p (rel., calc.)	AA wt.-%	k_p (abs., exp.)[38] [$L \cdot mol^{-1} \cdot s^{-1}$]	k_p (rel., exp.)	k_p (rel., calc.)
5	16 060	1	1	5	5 940	1	1	5	150 000	1	1
10	12 662	0.788	0.835	15	3 830	0.645	0.580	10	119 000	0.793	0.828
40	5 298	0.330	0.319	30	1930	0.325	0.2S6	20	83 400	0.556	0.587
70	3 032	0.189	0.141	45	1 320	0.222	0.155	40	60 300	0.402	0.326
90	176S	0.110	0.083	60	1000	0.168	0.091	60	44 000	0293	0.199
100	1013	0.063	0.064	100	574	0.097	0.031	100	20 100	0.134	0.090

given to show what level of information on kinetics can be obtained with state of the art quantum chemistry. It is well known from experiments that a transition from bulk polymerization to solution polymerization in solvents which are chemically similar to the monomer does not influence kp very much. The situation changes, however, if the solvent is water: for all (water-soluble) monomers, a strong increase of kp upon dilution in the aqueous medium is observed in experiments. This effect is reproduced quite well by the calculation, that is, the COSMO-RS description of solvation effects for intermediates and transition states is rather consistent.

Relative kp refers here to the maximal kp (either experimental or computational value) obtained for a dilution of 5% monomer in each system. A graphical representation of the results for N-vinylpyrrolidone (NVP) in Figure 2 shows the excellent agreement between theory and experiment. The results are also satisfying for MAA and AA. The agreement over the whole range of concentra-

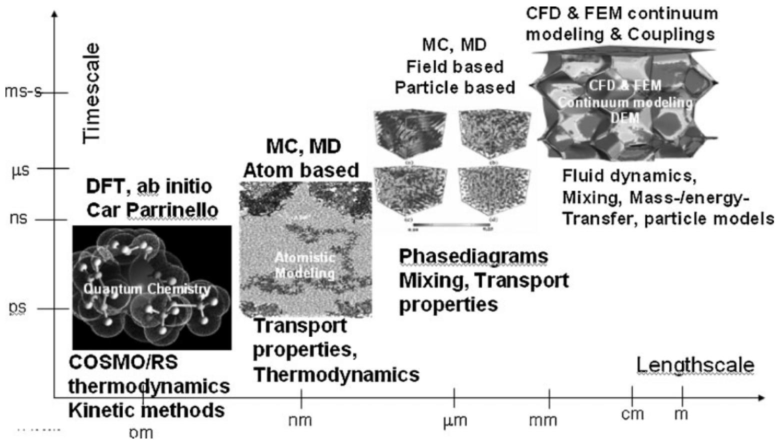

Figure 1.
time scales and length scales relevant for materials and process development.

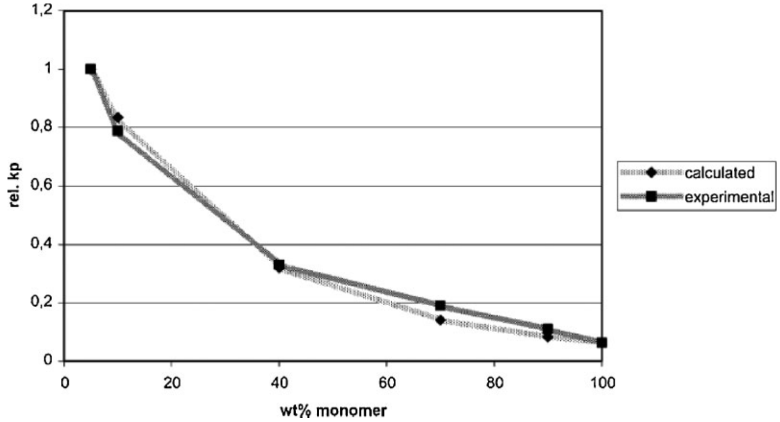

Figure 2.
Comparison of experimental and computed radical polymerization propagation relative rate coefficients of N-vinyl pyrrolidone in aqueous solution at different monomer concentrations.

tions is not as good as for NVP, which might be due to increasing carboxylic acid dimer formation with higher monomer concentration.

Molecular Modeling Contributions to Polymer Process Thermodynamics

When it comes to modeling of thermodynamics for process engineering, one clearly has to distinguish between modeling of chemicals (small molecules) and modeling of polymers. A number of well developed methods are at hand to compute data necessary for process engineering for small molecules. Groups like Hasse and Vrabec [20] have documented their success in prediction of thermophysical data in many publications and contests [21] showing that molecular modeling methods are a convenient and reliable tool for providing accurate data. Other approaches like the aforementioned COSMO-RS achieve similar accuracy.[22] The main advantage of these methods from an industrial perspective is that with little effort in time, it is possible to provide high quality data without the need of costly re-parameterization. A variety of chemical compounds can be modeled with these approaches.

With polymers, however, the situation is different, although there are attempts to modify COSMO for polymers.[23] The reason is the need for a proper treatment of entropy for molecules with a large number of conformations like polymers. From the viewpoint of statistical mechanics, the proper approach for this type of molecules is Molecular Dynamics (MD) and Monte Carlo (MC). Beautiful and remarkably accurate results have been published by groups like Theodorou,[24] de Pablo,[25] and many others proving that, provided a suitable force field is given,[26] deep chemical insight into complex systems can be obtained. Of course, these applications have required a widespread development of computer simulation methodology, and significant advances were possible through the invention of improved MC [27] and sampling techniques.[28]

For practical purposes, however, the key point is the non-availability of accurate force fields. When the situation is compared to biophysics where forcefields like OPLS,[29] CHARM[30] and others to name just a few are available and well parameterized for physiological conditions (298.15 K, normal pressure), there is a remarkable lack of general purpose force fields for polymer modeling with sufficient accuracy. One of the reasons is the large parameter space of polymer simulations. Polymers have to be simulated in solid state, melt and solution. The relevant temperature range is from say 200 K (T_g acrylates) to over 500 K (processing engineering plastics). Relevant pressures range from normal pressure to a few hundred bar (e.g. extrusion). No available force field can treat these different conditions with acceptable accuracy, and thus it is very likely that a project using simulation as a tool for enhanced product development will start with force field (atomistic and/or coarse grained) development and validation efforts. Another reason for the lack of a general purpose force field is the nature of the force fields itself. Typically, the non-bonding part is described by Lennard-Jones [31] types of interaction, although many others have been used and described.[32] It cannot be expected that a single set of parameters describes the situation in a melt with similar accuracy as in solution or with solids, and so on. To make things more complicated, the validation of force fields requires accurate data from experiment which are usually not at hand. The last and very important point that prohibits classical (atomistic or united atom) MD and MC as an engineering tool for polymer process engineering is the computational effort which makes the simulation of a realistic polymer system a project in the order of several months, and it can be more... To reduce computer time and reach relevant time scales, it is necessary to reduce the number of particles in the simulation, and, within MD, to increase the time step of the integration of Newton's equations. This leads to so called coarse grained techniques which have been developed both for MC and MD. In coarse graining, several atoms up to many monomer units are grouped together thus reducing the number of particles and, even more important for coarse grained MD, due to softer interaction potentials increasing the time steps and thus exploring larger time scales. The parameterization of these coarse grained potentials is often based on atomistic simulation of small model systems, and a variety of methods have been developed. The quality of the simulation again mainly depends on the quality of the parameterization, and remarkable accurate results even for complex phase diagrams can be obtained which have an enormous impact on product development due to insights into details of the chemical system. For instance, the phase diagram of hexadecane and CO_2 has been modeled by the Binder-group with a simple coarse grained model for CO_2 (one bead) and hexadecane (5 beads).[33] The Lorentz-Berthelot mixing rule [34] was applied with a single adjustable parameter for the binary interaction between CO_2 and hexadecane. A few years later, the same group published an improved method were the quadrupolar moment of CO_2 was taken into account.[35] This time, the Lorentz-Berthelot mixing parameter was set to unity, and the overall match of the phase diagram with experiment was satisfactory. The relevance of this approach is that knowledge of the pure component data was sufficient to describe the phase behavior of the mixture with satisfactory accuracy. It is much easier and cheaper to measure and thus calibrate and validate pure component data than it is for mixtures, which is an advantage for industrial usage. A further beneficial aspect of this approach is that the parameters which constitute the coarse grained model of the system of interest can be used as parameters in a variant of the SAFT equation of state (EOS), the TPT1-MSA of MacDowell et al.[39] The statistical associating fluid theory (SAFT), in its various flavors[40] based on Wertheim's ideas, has been gaining ground as an equation-of-state approach for a wide variety of fluid systems. In Wertheim's theory[41] of associating fluids a multi-density formalism is introduced in which the expansion of the free energy is expressed in terms of the densities of the various bonding states of the monomers. Wertheim developed the theory for the simplest model of associating fluids, namely hard spheres with 1, 2, or more bonding sites. Meanwhile, the method comes in many different flavors, and the aforementioned approach has the important advantage that the set of parameters chosen for the TPT1-MSA can be validated with the exact MC approach. After validation with exact MC at a few selected points, the complex phase diagram can be computed with the TPT1-MSA EOS. Due to their simplicity, accuracy (if properly parameterized) and low computational demands, EOS are at present the method of choice when thermodynamic information is required for polymer process modeling. Consequently, there are numerous ongoing activities to broaden the scope of applicability (initially developed for hard spheres, then parameterized for alkanes, now even applied to polyelectrolytes [38]) and to facilitate parameterization (e.g. group contribution SAFT [42]).

Transport Properties

The development of methods to model transport properties (diffusion, shear, viscosity etc) is a very active area which can be only briefly addressed here. For the computation of diffusion coefficients, methods ranging from free volume theory, atomistic molecular dynamics to coarse grained molecular dynamics are available which provide data with sufficient accuracy if properly parameterized. In particular with coarse grained MD, time scales are within reach that allow for prediction of diffusion of oligomers in realistic polymer melts.[43] With these methods, the design of polymers with specific barrier properties should be possible, although it has not been reported yet.

Recently, the coupling of many particle methods with Computational Fluid Dynamics (CFD) has been reported. Generally, CFD simulations are of great value for the detailed lay-out of reactors, apparatus, pipes etc. The simulation of integral properties like pressure-drop, power-input, shear-stress, dead-zones etc. but also of flow and mixing patterns is meanwhile state-of-the-art for homogeneous systems even for rather complicated geometries. The coupling of chemical kinetics and flow behavior is becoming more and more feasible.[44] For homogenous systems, also non-Newtonian shear-thinning fluids can be described, and meanwhile, visco-elastic solvers are available in open source packages like Open Foam. Multiphase simulations are not complicated for fundamental reasons, but computationally very demanding. With coupling schemes where particles are described by Discrete Element Methods (DEM), efficient models can be set up describing multi phase systems.[45] These concurrent coupling schemes show best that molecular modeling and engineering methods are really growing together.

Conclusion

Due to large progress in method development and computer hardware, meanwhile complex systems can be simulated in chemical detail. Quantitative results are still difficult to obtain, but match with experiment is coming closer. Quantum chemistry with suitable correction for solvent effects can help to complete complex reaction schemes and to provide rate coefficients for kinetic modeling. Equations of state (EOS) are helpful to provide thermodynamic data for polymer process modeling. Monte Carlo can be used to check the quality of parameters used in EOS. First coupling schemes for particle based DEM with CFD are available. Coarse grained methods help to study transport properties.

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