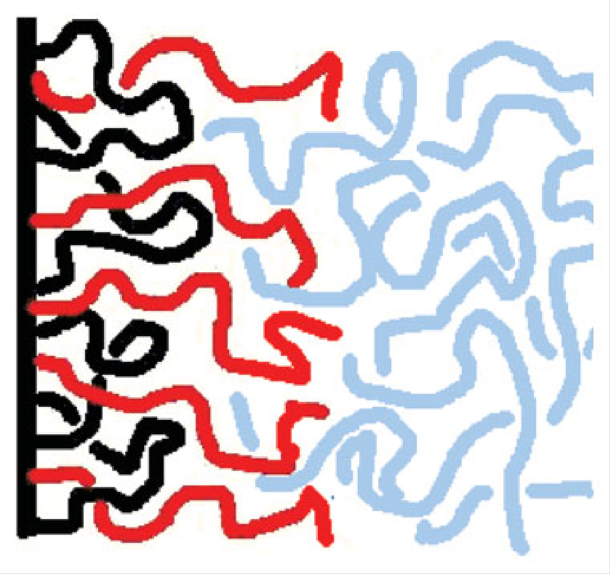
Review: In the context of a few characteristic examples, the perspectives of computational materials science for polymeric systems are being discussed. The examples chosen cover the range from atomistic/quantum models to coarse grained bead spring polymer models.



Cartoon of the average chain conformations near the surface. Since the chains are relatively short and only the chain ends adsorb, there is no entanglement network, which would otherwise enhance the bulk adhesion to the surface. Black lines represent chains with both chain ends stuck to the surface, red lines represent chains with only one chain end stuck to the surface and the other in the bulk, and blue lines represent chains in the bulk.[29]

Computer Simulations for Macromolecular Science

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Introduction

Macromolecules, or in the most simple version chain molecules of a given length posed and still pose a significant challenge to theoretical physics and chemistry. The computational materials science emerging from this is a growing and exciting field of science. Despite remarkable progress over many years, which is well documented in many research papers and several reviews, only (few) rather simple limiting cases are really well understood in (all) detail.[1–7] E.g. the very basic problem of the chain excluded volume can be solved approximately and it is well known that the isolated chain in good solvent is expanded, while in a melt of identical other chains the average conformation is that of a random walk. While this problem was and is mostly discussed in terms of simple lattice walks or bead spring chains in simulations, continuous paths in space are used in analytic theory.[8,9] This leads to the general scaling behavior. However a precise and controllable approach to go beyond that and to deal with specific chemical systems and to describe also the ''prefactors'' or the local packing as well, is still lacking.[1] This somehow, on a very elementary level, explains the range of questions one faces, when dealing with macromolecular systems. Since most of these current models can only be treated in a rather approximative manner, it is not surprising at all that computer modelling plays an increasingly important role. Since the very early days of computer simulations scientists addressed the by now classical problems of polymer theory by these new methods. The first papers date back about 50 years. Already in 1955, two years after the invention of Monte Carlo Simulations, Rosenbluth and Rosenbluth in a seminal paper recognized and tried to overcome the attrition problem when generating self avoiding walks (SAWs).[6,10] This problem occurs, when on a lattice with coordination number q randomly walks are grown. For an N-step SAW the number of possible conformations on a lattice is $Z \propto N^{\gamma-1} q_{eff}^{N}$, with γ being a so called critical exponent and $q_{eff} < q-1$ an effective coordination number. Since the walks are generated out of $(q-1)^N$ random walks, the success rate of generating SAWs, $O((q_{eff}/(q-1))^N)$, vanishes exponentially. Such a difficulty is of such a fundamental nature, that it cannot simply be solved by faster computers. To overcome this problem a number of

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approaches has been developed. The first ideas were to look several steps ahead, then only take the allowed walks and correct for the statistical bias, which is introduced by such a choice. This method was called inversely restricted sampling by Rosenbluth and Rosenbluth. Sometimes it is also called biased sampling or in more recent versions for dense systems, configurationally biased Monte Carlo (CBMC).[3,6,11,12] Thus these old ideas still are used in rather modern investigations. Alternatively many other sampling methods have been invented and are widely used nowadays. In the low concentration, dilute solution regime probably the pivot algorithm is the most effective one.[13] This, as well as the dimerization approach by Alexandrovizc[14] and Suzuki[15] start out from given conformations and introduce global changes or recombinations of pieces. In combination with local move methods they can be used for continuum models or even chemically detailed models as well. With increasing density the combinations of various methods such as local bead motion, slithering snake algorithms as well as chain breaking/recombining methods are nowadays employed.[16] However to properly equilibrate a long chain polymer melt without knowing the average chain conformation is still a challenging problem. This is of course a precondition for many studies both, for statics and dynamics. Nevertheless due to the steady progress via improved models, improved algorithms and faster computers, polymer modelling became an indispensable scientific method in modern polymer material science. Our relatively clear view on the dynamics of short and long chain polymer melts, i.e. the transition from Rouse to reptation dynamics as well as our improved understanding of rubber elasticity clearly is significantly, if not mostly due to recent results obtained by computer simulations. After a number of smaller studies using lattice Monte Carlo, continuous space Monte Carlo, as well as Brownian dynamics (BD) simulations to study the dynamics of a polymer melt, it was in 1988 that the first large scale molecular dynamics simulation of Kremer and Grest clearly demonstrated the crossover from Rouse like dynamics for shorter chains to reptation like dynamics for longer chains.[17,18] This was the first local motion analysis which showed this and at that time came earlier than the first neutron spin echo data confirming reptation on a molecular level. This success was possible due to an optimized choice of a simple computationally very efficient model together with highly optimized, at that time vectorized programs. In a similar manner the studies on phase separations of incompatible polymers, on the structure of block copolymers etc. rely on the powerful combination of experiment, computer simulation and analytic theory.[19] For charged systems (polyelectrolytes, colloids and hybrid systems thereof) the role of simulations is even more central.[20,21] Analytic theories can only in a very approximative way account for the long range electrostatic interaction, especially when it comes to the point that charge fluctuations are relevant. On the other hand the experiments also face characteristic problems. For biopolymers, which in most cases are monodisperse, it is difficult to have the necessary amount of material at hand. On the other hand, for conventional synthetic systems, e.g. polydispersity still is a crucial problem in comparison to any theory. Here, simulations currently are the only tool to perform ''experiments'' under fully controlled conditions. In general simulations as the ones mentioned above, are an important and sometimes the only bridge between analytic theories and experiment. Analytic theories typically deal with idealized models,

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Kurt Kremer studied physics at the University of Cologne. In 1983 he received his PhD in theoretical physics from the University of Cologne under the supervision of Prof. Binder at the National Research Center KFA Jülich, already working on soft matter. After spending another year at Jülich as scientific staff he moved for a post doctoral stay to Exxon Research and Engineering Co., Annandale, New Jersey, USA, where he worked with Drs. Grest, Pincus, and others. In 1985 he came back to Germany becoming a member of Prof. Binder's group at the University of Mainz as an Assistant Professor of theoretical physics. There he got his Habilitation in 1988. After another seven years at the solid state laboratory of the KFA Jülich he joined the Max Planck Institute for Polymer Research in September 1995 as a Director heading the Theory Group. He spent several extended visits as visiting professor/scientist at Exxon Research and Engineering Co., UC Santa Barbara, and University of Minnesota. In spring 1995 he stayed as a visiting scientists for three months at the central research department of the Bayer AG, Leverkusen. Prof. Kremer was awarded the "George T. Piercy Distinguished Professorship of Chemical Engineering and Materials Science" of the University of Minnesota, Minneapolis, in 1991, the "Walter Schottky Preis der Deutschen Physikalischen Gesellschaft" in 1992, and was the Whitby Lecturer of the Akron University in 1999. His research mainly employs various computer simulation techniques to a variety of different problems in the general area of soft matter science. Specific current research areas of his group include: computational physics methods/applications, computational chemistry methods/applications, statistical mechanics of soft matter (polymers, colloids, membranes), polymer networks, polyelectrolytes, liquid crystalline polymers, semiflexible polymers, structure property relation of polymeric materials, multiscale description of macromolecular materials.

meaning that the specific chemical structure is reduced to the very essential parameters, such as connectivity, topology, excluded volume etc. To understand a specific chemical system this certainly is not sufficient. Therefore, parallel to the work mentioned above, there is also a tradition of work dealing with models, which incorporate as many chemical details as possible.[5] Some include all atoms explicitly, others incorporate the hydrogens into the carbons they are bound to (united atoms model). The potentials for the bond lengths, angles and torsions are deduced from quantum chemical calculations. The non-bonded potentials here actually are often more a problem than the bonded ones. They typically are derived from comparison to experiments on low molecular weight components, such as the heat of evaporation etc. Once this is done one actually performs a classical simulation in a regime, where in principle one would have to do quantum calculations (the deBroglie wave length of hydrogen at 300 K is around 1 Å, just the relevant length scale of these calculations).[22] However, keeping this in mind, force field simulations of atomistic models have been very successful in determining many properties of macromolecules. Since time scales are short (much shorter than for coarse grained generic models) only small local conformational relaxations can be studied. A set of simulations which marked one of the very first big successes of atomistic polymer simulations is the amorphous cell work of Theodorou and Suter in 1985.[23,24] They studied the local conformations and the mechanical response to stress of a polyisoprene glass by simulations. They were the first to reproduce experimental values of e.g. the elastic constants to an accuracy, which was exceptional for that time. The trick they used was to grow one ‘‘very’’ long chain and fold it back into the ‘‘amorphous’’ cell via periodic boundary conditions. By that they were able to reach densities close to the experimental ones, as well as reasonable configurations resulting in the big success for the mechanical properties. This also for the first time allowed for the attempt to give a molecular interpretation for certain specific relaxation mechanisms. This ansatz is still frequently used and incorporated in a number of commercial packages. Currently atomistic simulations find a very wide application, especially in the field of biomolecules. It is a very useful approach in situations where the global conformations of the macromolecules do not change significantly while the interesting phenomena occur. Besides looking at a specific conformation of a biomolecule, another example is the diffusion of small molecules through a polymer matrix. For most problems in macromolecular chemistry and physics this is however not sufficient. Stress relaxation in a melt for instance is directly related to conformational relaxation on length scales of the order of the size of the whole macromolecule. To understand those phenomena quantitatively one has to connect approaches on very different length and especially time scales. Let me illustrate this for again a rather simple example. The viscosity η of a polymer melt can be written as $\eta = AN^x$. A is a chemistry and temperature dependent prefactor which stems form the local interaction of the beads on an Å scale. N is the chain length and x is a universal exponent, which turns out to be around $x \simeq 3.4$ in the reptation regime for all known polymers.[18] To change the viscosity one can vary A by manipulating the beads or by simply changing the temperatures. E.g. reducing the temperature from 500 K to 480 K for polycarbonate increases the viscosity by a factor of 10. To reach the same one can stick to $T = 500$ K but double N since $2^{3.4} \simeq 10$. This illustrates that both views are equally important.

In the following this will be explained in a little more detail and some recent examples will be given for macromolecules in solution as well as for dense systems.

Scale Considerations (cf. Figure 1)

Depending on the question under consideration specific methods have to be employed. For all problems involving excited states or chemical reactions quantum mechanics has to be considered explicitly either by extended quantum chemical calculations or more recently ab initio density functional theory, the Car-Parrinello (CPMD) approach.[25] Both have their strengths and weaknesses, however they developed into very powerful tools. Beyond that classical force field calculations play an important role.[5] A combination of both, so called embedded methods, is under development at several places and has already been implemented in a few cases. Force field simulations, where all or most atoms are included explicitly, are needed in all cases, where local properties are crucial such as specific relaxations, motion of groups or penetrants etc. The next steps are more simple bead spring polymer simulations or lattice Monte Carlo. They have been and are employed to study generic properties of polymers, as they show up typically in power laws of the polymerization index N. The simplest is the radius of gyration $R_G \propto N^\nu$ $\nu = 1/2$ in a melt and $\nu \approx 3/5$ in a dilute good solvent as mentioned before. This is however not restricted to static properties, but also includes dynamic quantities such as the diffusion constant $D(N) \propto N^{-x}$, $x = 1$ for a melt for short chains (Rouse regime) and $x \approx 2$ for long chains (reptation, directly related to the viscosity mentioned before). On an even more coarse grained level self consistent field methods or soft-sphere models are employed and beyond that macroscopic methods, such as finite element calculations are used.

In the following, three examples will shortly be discussed.

First an example of a recent dual scale simulation, namely a study of the selective adsorption of chain fragments onto a metal surface will be reviewed, while this study combines atomistic as well as coarse grained simulations. The other two examples employ one characteristic regime only, however go into more detail. The first one is a

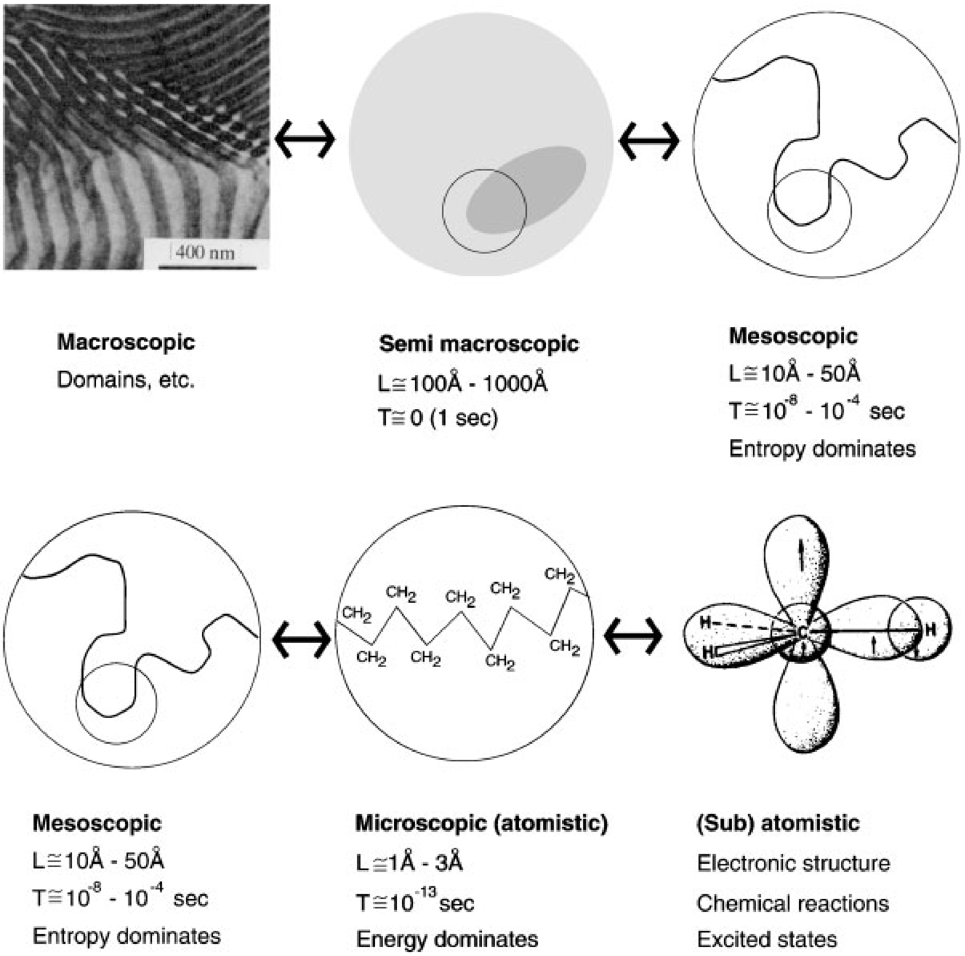

Figure 1. Polymers exhibit phenomena on many length scales (from entire devices down to electrons) and associated time scales (from years to femtoseconds). Starting from the top left side, one can observe the overall morphology of a polymer material. Looking a little bit more closely, e.g. by marking a chain in a melt or dense solution of otherwise identical chains, the individual polymer can be observed only as a very pale shadow. A typical spatial extension of the shadow is given by the overall coil diameter, as indicated. The characteristic time for this picture to change can vary dramatically depending on chain length and temperature, starting at about 10^{-4} s for short chains and ‘high temperatures’, with essentially no upper limit. Looking again more closely, more of the polymer structure is revealed. This is the universal, entropy dominated coil regime. Again the variation in time can be very large, cf. text. Typical times, as they are present in many experiments, are indicated. Only if the objects are examined much more closely, chemical details of the polymers can be identified. There local chemical details govern the properties and all bond lengths, angles etc. are determined by the energy levels, originating from quantum mechanics. The lower time limit is determined by the highest frequency of oscillations, which depending on the model used are the bond length or bond angle oscillations. To study excited states or reactions, the electronic structure is to be considered and quantum methods are required. Methods for treating individual scales are well developed. The challenge is to connect them systematically.[16]

study on the glass transition of polymers while the latter deals with the problem of vacancy distribution and positronium annihilation in a polymer matrix.

Examples

Dual Scale Simulation

Abrams et al.[26] recently presented a study on the selective adsorption of submonomers of polycarbonate on a transition metal surface (Ni). To do this different steps had to be combined. The general idea behind this approach is given in Figure 2.

The polymer chain is systematically coarse grained, where the repeat unit, cf. Figure 3, is replaced by four spheres representing the two benzenes, the carbonate and the isopropylidene respectively. A similar scheme was successfully used to simulate polycarbonate melts.[27,28] To investigate the interaction with the nickel surface

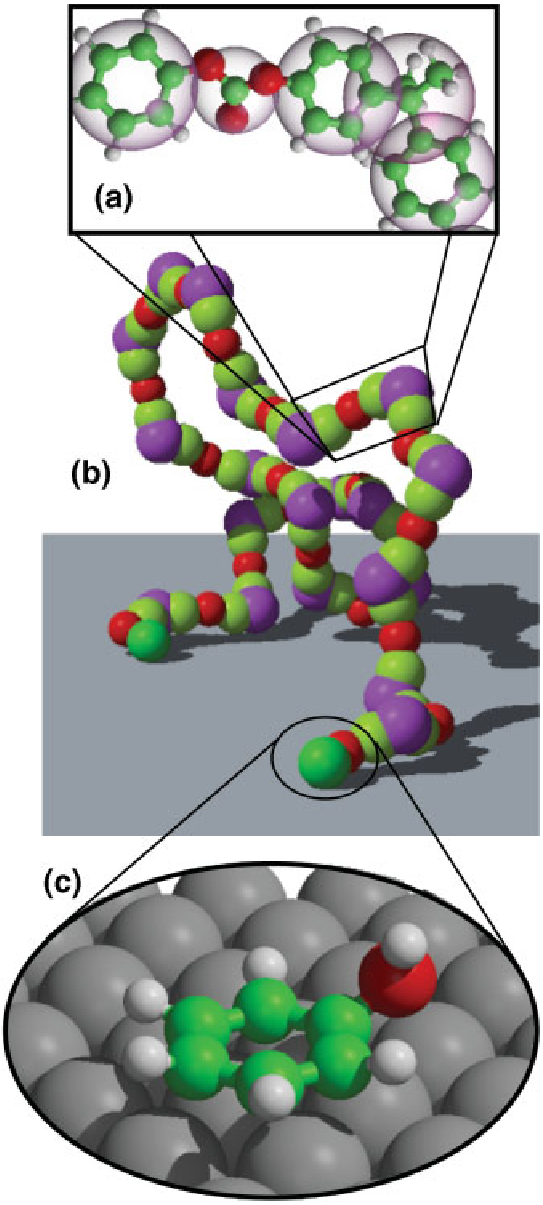

Figure 2. The multiscale model of BPA-PC on nickel. (a) The coarse-grained representation of a BPA-PC segment; the coarse-grained beads are transparent spheres, superimposed on the underlying chemical structure, where the carbon atoms are green, the oxygens red, and the hydrogens white; (b) Coarse-grained model of an $N = 20$ BPA-PC molecule, with ends adsorbed on a flat surface; configuration from a 160-chain liquid simulation. (c) A phenol molecule adsorbed on the bridge site of a (111) nickel surface; configuration computed via CPMD simulation, from.[26]

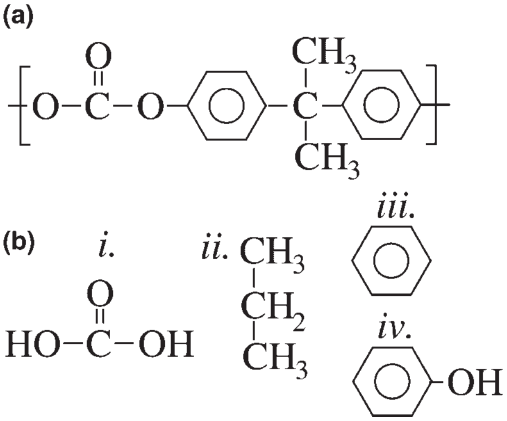

Figure 3. (a) Chemical structure of the repeat unit BPA-PC. (b) Analogous molecules used in the *ab initio* studies: (i) carbonic acid, (ii) propane, (iii) benzene, and (iv) phenol, from ref.[26]

Car-Parrinello DFT calculations for monomer fragments, cf. Figure 3b, have been performed. To study a whole chain repeat unit on that level is still beyond the possibilities. By doing this one finds that only the benzene is strongly adsorbed to the surface with a binding energy of about 1 eV (roughly 20 k_BT at the typical processing temperature of 570 K). However, benzene can only bind to the surface if it is located at the chain ends. In the middle of the chains adsorption is prevented by the strong (longer range) repulsion of the carbonate and the isopropylidene group from the metal surface. However, a phenolic end group is one typical end group which can be found in polycarbonate depending on the chain termination agent used in the production process. For short chains this leads to an interesting consequence, as illustrated in Figure 4.

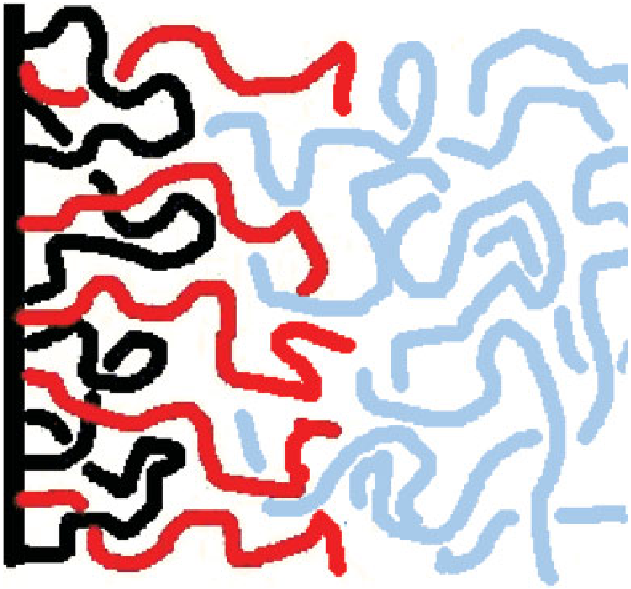

Figure 4. Cartoon of the average chain conformations near the surface. Since the chains are relatively short and only the chain ends adsorb, there is no entanglement network, which would otherwise enhance the bulk adhesion to the surface. Black lines represent chains with both chain ends stuck to the surface, red lines represent chains with only one chain end stuck to the surface and the other in the bulk, and blue lines represent chains in the bulk.[29]

In general, ideas to link different length and time scales are more and more employed as they promise a path towards a very efficient materials simulation scheme. Many groups follow this path as a recent conference in Konstanz demonstrated.[30]

Polymer Glasses: Generic Aspects of Supercooled Polymers

Many technical polymer products are made of polymer glasses. Since in many cases polymers, due to the structure of the monomers combined with the connectivity constraint, cannot or are very difficult to crystallize the solid amorphous state is most important. Because of that also many studies on the glass transition for polymers have been performed.[31] For many years now the group of K. Binder plays a leading role in the computer simulation of glasses in general and particularly for polymer glasses.[32,33] Simulations of the glass transition in general face the problem that the typical cooling rates in computer simulations are many orders of magnitude faster than the fastest experiments. Thus the understanding of the glass transition of undercooled (polymeric) fluids has been a long standing challenge. A general agreement on the cause of the dramatic slowing down of the structural relaxation in the glass forming system is still lacking. In ''fragile'' glass formers, such as typical polymers, the viscosity and thus the longest relaxation time as well increases by about 15 orders of magnitude over a relatively small temperature interval above T_G, the glass transition temperature. The static structure however varies only a very little, at least on the level as it can be determined by scattering techniques. To understand this, is still one of the grand scientific challenges in (soft matter) physics, in spite of the huge progress made over the last decades. The fact that the structural changes are very small makes it especially tempting to study such phenomena by computer simulations, although the simulation quench rates automatically are many orders of magnitude larger than in the experiments with the fastest cooling rates. For low molecular weight systems (''strong'' glass formers) it has been shown that this leads to huge jumps in the observed glass transition temperature. Recently Binder et al.[34] looked at this problem for polymer melts as well, namely for the case of a melt of simple bead spring polymers. These are the already previously mentioned simplest molecular dynamics models and allow, because of their enormous efficiency, to study a rather wide variation of cooling rates. They were able to vary the cooling rate by a little more than three orders of magnitude and observed a shift in T_G by about 10%. What is more important, however, is the distance of the observed T_G to the Vogel-Fulcher Tamman temperature T_o and the mode coupling critical temperature T_c. While experiments typically find T_G relatively close to T_o the simulations are giving T_G closer to T_c. In view of the cooling rate dependent shift of T_G this discrepancy can be, at least partially, attributed to this shift, meaning that discrepancies between simulations and experiment in that case do not hint towards fundamental differences in the physical phenomena observed. While this in most cases was taken ''for granted'' by the authors this actually is the first careful check.

Vacancies in Polymer Matrices

The diffusion of penetrants like gas molecules or small additives through a polymer matrix is intimately related to the atomistic structure of the polymer. Taking the typical polymer densities which are at room temperature slightly above 1 g/cm^3 one can estimate the volume occupied by the macromolecular material. It turns out to be typically a little below 50% of the available space. Thus there is ample space for small objects to diffuse around. However, the diffusivity is related to a number of properties of both, the polymer matrix as well as the diffusant. There is of course the non bonded interaction of the different entities and the dynamics of the polymer matrix. However, first of all the structure of the available volume is of interest. How big are the cavities and how large are they? So far there are no quantitative experiments which unambiguously answer this question. Diffusion constants of small molecules or noble gas atoms give only rather indirect answers, which significantly depend on the underlying models. Here computer simulations in the past already helped significantly to improve our understanding. Another set of experiments is the measurement of positronium life times. The assumption is that positronium moves ballistically through the cavities in the polymer and annihilates with a certain probability when it interacts with the cavity walls. Usually, due to the lack of information, spherical cavities are assumed in the interpretation of the experiments, which try to measure the cavity volume. This is of course a by far too strong simplification and led to conclusions not really consistent with other packing considerations. Müller-Plathe and Schmitz tackled this problem by computer simulations employing a combined approach of classical force field simulations for the polymer matrix and quantum Monte Carlo calculations for the positronium annihilation.[35] First an equilibrated polymer matrix was generated. This was done either by starting from an equilibrated system of coarse grained chains, where then all atomistic details were reintroduced (''inverse mapping''[28]) or by direct equilibrations of a melt of short chains. In a second step then the positronium was introduced and life times calculated. This study not only revealed that the typical vacancies in such a polymer melt obtain rather irregular shapes but also reproduced the life time distribution of positronium in excellent agreement to the experiments by Kirchhoff et al.[36] as is illustrated in Figure 5.

From the two illustrations it is clear that an interpretation of the experiments in terms of spherical vacancies leads to

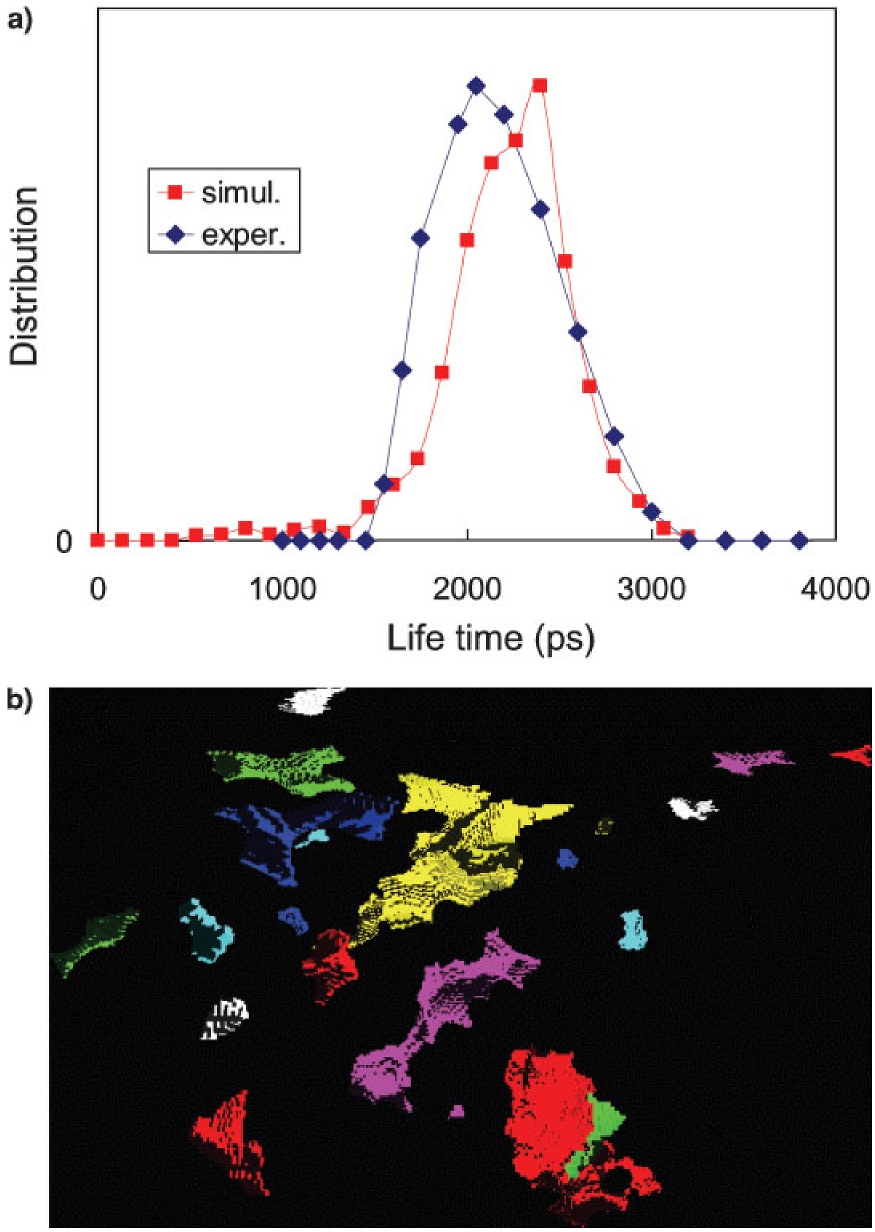

Figure 5. Positronium life time distribution in a polystyrene melt from a combined force field and quantum Monte Carlo calculation in comparison to experiment. Examples of typical shapes of available volume are shown in part b.[35]

strongly misleading results. However, the combination of experiment and simulation is powerful tool!

These were just three examples of recent investigations in the general area of computational polymer materials science. Many other subjects are investigated with great success. Besides the ones mentioned in the introduction and the three specific examples, studies of interfacial properties in mixtures or for block copolymers both by self consistent field calculations as well as by Monte Carlo and molecular dynamics simulations produced a vastly improved insight into the properties of such systems over the last years.[37–39] Also links to finite element calculations, which then lead more into general materials engineering are improving significantly.[1,40] Other approaches try to identify specific copolymer structures which then lead to well defined collapsed/condensed states. This certainly is strongly influenced by ideas coming from protein simulations.[41]

This is of course a very incomplete and short account on recent developments in computational polymer science. It is biased by the personal view of the author and his local surrounding. However, I hope the few examples illustrated the enormous potential hidden behind the various mentioned (and not mentioned) approaches. Computational materials science is steadily growing and becoming a field of its own. Its success however will depend on the link to chemistry and physics, which are needed to ''bench mark'' the modelling results at least in simple limiting cases. Keeping this in mind we will experience an increasingly predictive power of these modern methods.

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