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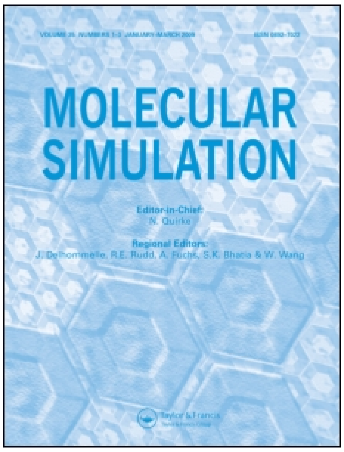

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Multiscale simulation in polymer science

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MULTISCALE SIMULATION IN POLYMER SCIENCE

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The paper gives a short overview on recent approaches to link several time and length scales in soft matter simulations. Special attention is given to the fact that in contrast to low molecular weight compounds, intramolecular entropy is as important as the energetic contribution. First applications to industrially relevant problems are mentioned.

Keywords: Computer simulation (Monte Carlo, Molecular dynamics); Atomistic models; Coarse-grained models; Multiscale modelling

INTRODUCTION

Polymers can be crystalline, amorphous (glasses, melts, rubber, gel) or in solution. Polymer melts in the glassy state are standard materials for many applications (yoghurt cups, compact discs, housings of technical equipment, etc.). They combine relatively low specific weight and ductitility with processing at moderate temperatures. In the melt state, polymers are viscoelastic liquids where the crossover from elastic to viscous behaviour can be adjusted by the chain length. Added to a solvent, polymers can be used as viscosity modifiers and, depending on parameters, be either shear thickening or shear thinning, used e.g. for drag reduction. Crosslinking chains into a disordered network results in

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gels or rubbers. Applications range from gels in (low fat) food, hydrogels in modern body care (nappies) via biological systems (cytoskeleton) all the way to classical elastomers (e.g. car tyres), to name very few. Here, the interplay of connectivity, chain length and chain stiffness determines the properties.

The wide range of applications is made possible by the variability of physical properties, which is based on many different chemical molecular building blocks as well as on many molecular architectures and molecular weights of polymers. It is the combination and the rather delicate interplay of local chemical with more global architectural and size properties, which makes macromolecules so versatile and interesting. This means that many different length and time scales are relevant, and that understanding the properties on one scale is not at all sufficient.

Chemical Repeat Units: Material Specific Aspects

The simplest polymers are chain molecules with identical chain segments, repeat units or monomers. To give a very few examples, there are PE $(CH_2)_N$, polyethylene; PS $(CH_2(CH(C_6H_5))_N$, polystyrene; PEO $((CH_2)_2O)_N$, polyethylene oxide; BPA-PC $((C_6H_4)C(CH_3)_2(C_6H_4)CO_3)_N$, bisphenyl A polycarbonate: from the widely used PE (e.g. plastic bags) to the more complicated, but technically very relevant polycarbonate BPA-PC (compact discs). There are many other cases, which can become very complex as especially biological examples demonstrate (DNA, proteins), where several different building blocks are present in one huge molecule. While most polymers are not water soluble, PEO has the exceptional property, that it is both water and oil soluble. Other important water soluble polymers are polyelectrolytes, which in water dissociate into ions and due to this are soluble even though their backbone is hydrophobic. Those are currently in the centre of research along the border line between physics and biology, which is beyond the scope of the present contribution. The typical simulation approaches for polyelectrolytes however are conceptually very similar to the ones discussed here [1–4].

Architecture/morphology: Universal Structural Aspects

The most simple polymers are long linear objects of identical repeat units. Due to their intrinsic flexibility, they can assume of the order of $O(q^N)(q > 1;$ $N =$ number of repeat units), distinct spatial conformations in a melt or solution. q is a number close to the number of distinct torsional states of the subsequent bonds. PE e.g. has a fixed bond angle between subsequent carbon–carbon bonds.

In order to follow the tetrahedral bond sequence of carbon, each added bond is in principle allowed to take one of the three tetrahedral angles (*trans*, *gauche* $^+$, *gauche* $^-$). Due to excluded volume effects, the actual q is typically slightly smaller than three and depends also on temperature. Thus, not only an assembly of polymer molecules, but already the individual polymer molecule itself with the $O(3N)$ degrees of freedom necessitates a statistical mechanical description. Depending on solvent properties, the chain in solution can be expanded ($\langle R^2 \rangle \propto N^{\nu}$, $\nu \approx 3/5$, $\langle R^2 \rangle$ being the mean squared extension of the chain), if in good solvent. In so-called marginal or θ-solvent, where the monomer–monomer attraction just compensates the mutual chain–chain excluded volume in the virial expression, one finds $\nu = 1/2$ while chains in poor solvent collapse into a dense globule and precipitate out of solution. In a melt, the other chains essentially act as a marginal solvent resulting in $\nu = 1/2$. Mixtures of different chains pose special problems as only very tiny differences in the interaction energy of order $O(k_B T/N)$, T being the temperature and k_B the Boltzmann constant, are sufficient to initiate phase separation since the interaction is to be compared to the translational and not the conformational entropy of the chain.

Current research has progressed to much more complicated cases, such as star like polymers, dendritic structures, crosslinked systems (having both chemical bonds and/or physical links such as hydrogen bonds) etc. Another special class with both nontrivial but interesting dynamics and morphology are block copolymers. These range from long chains consisting of two blocks of A- and B-repeat units to random copolymers or objects containing flexible and rigid pieces. Though of utmost scientific and technical interest, they will not be discussed here any further [5,6].

Length and Time Scales for Polymer Simulations

To illustrate the importance of different time and length scales, we start with a technically important quantity, the shear viscosity η of a polymer melt. It contains the whole complexity of the problem. If one changes the process temperature of a BPA-PC melt from 500 to 470 K, the viscosity rises by a factor of ten. This is a direct result of the local interactions on the atomistic level, as it could—in principle—also have been achieved by an equivalent change of the chemical structure of the monomer. (The glass transition temperature T_G of BPA-PC is around 420 K and different polymers display huge differences in T_G.) On the other hand, increasing the chain length by a factor of 2 also shifts the viscosity by a factor of ten, since for long chain melts, one has $\eta \propto N^{3.4}$. This power law is a universal linear-polymer property, and holds for all known polymers independently of the chemical structure of the backbone. Thus, both material-specific as well as universal properties produce a comparable variation of the macroscopic dynamic properties. This variation can easily extend over several orders of magnitude.

At first sight, it might be tempting to perform an all-atom computer simulation of a melt of polymers in order to determine properties like viscosity, morphology etc. However, there are two major complications. The first stems from the choice of interaction potentials, while the second is related to the many scales involved. An all atom simulation necessarily has to use an empirical force field. All quantum simulations (Car Parinello density functional simulations, path integral quantum Monte Carlo or combinations thereof) are still confined to very small systems and orders of magnitude slower than force field approaches [1]. The precondition for such an approach is an empirical potential energy function for the interaction of all atoms in the system. This determines the force field to solve Newton's equations of motion for the system. Though conceptually straightforward, such an attempt contains a number of unsolved problems and complications. First, though usually not considered, are quantum effects. One might think that typical temperatures for macromolecular systems (room temperature and higher) are well above the Debye temperature of the relevant atoms. This is true for the carbon atoms, however, not necessarily for the many hydrogens present. Their thermal de-Broglie wave length at room temperature is about 1 Å. A recent paper by Martonak *et al.* [7] employing path integral quantum Monte Carlo simulations of a PE crystal revealed, that even at room temperature quantum effects are crucial to understand their anisotropic thermal expansion. This is obviously a rather special example. However, it should be kept in mind. Secondly, for the force field the intramolecular interactions can be derived from a proper parameterisation of quantum calculations on chain fragments. To parameterise the intermolecular or nonbonded interactions, usually experimental quantities like the heat of vaporization of low-molecular weight liquids are used. There, additional difficulties can arise from the quality and availability of experimental data. Moreover, it is often impossible to optimise all properties to the same degree of accuracy and confidence. Thus, one has to be very careful and there is no force field for a system, which without further verification, can be used at significantly different temperatures or compositions. Hence, there is NO universal force field. In principle, a new parameterisation has to be performed for every new set of simulation parameters. Keeping this in mind, force field simulations can be very useful and have provided important insight into microscopic properties. Typical examples can be found in the overviews [2,4].

Whether such a fully atomistic simulation, if possible, would be useful at all, is actually very questionable, since it would provide an enormous amount of data.

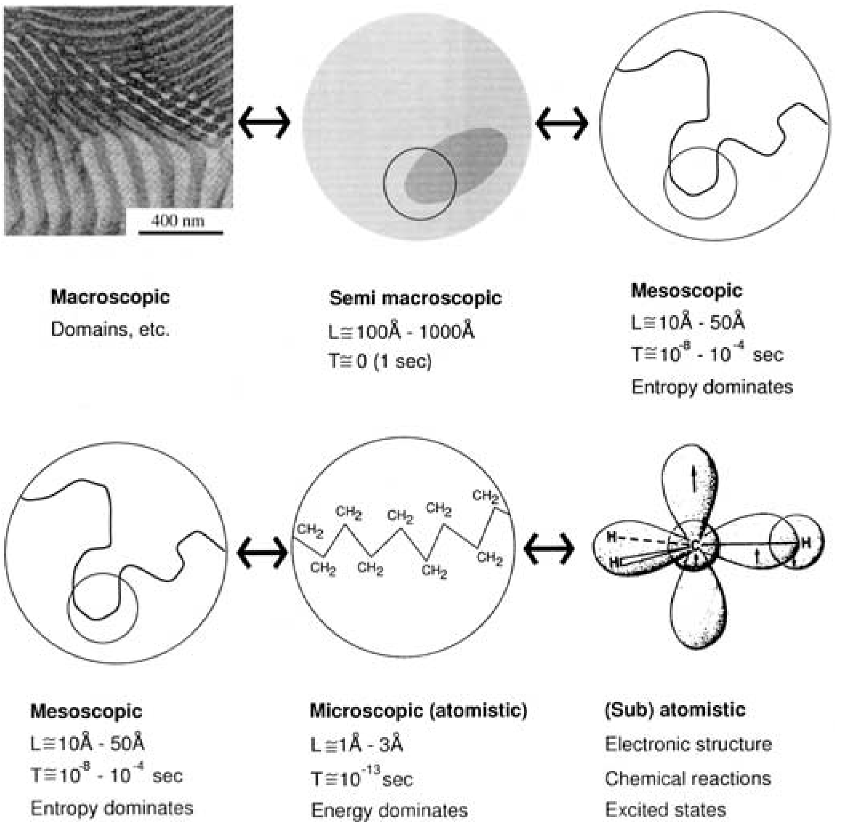


FIGURE 1 Polymers exhibit phenomena on many length scales (from entire devices down to electrons) and associated time scales (from years to femtoseconds). Starting from the top left side, one can observe the overall morphology of a polymer material. Looking a little bit more closely, e.g. by marking 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.

Almost all the generated information would be irrelevant for the questions under consideration, e.g. the above mentioned viscosity η. In order to make suggestions for material improvements, or to qualitatively and quantitatively understand certain properties, it is crucial to structure and understand the results rather than just collect data. This also is often easier with simplified models.

This leads us to the second problem field, the topic of this article. Polymers can be characterised by a hierarchy of different length and especially time scales, which span a wide range. Figure 1 illustrates this and shows the typical range needed. On the microscopic level the properties are dominated by the local vibrations of bond angles and lengths. The typical time is of 10^{-13} s as given in the figure resulting in a simulation time step to integrate Newton's equations of motion of about 10^{-15} s. This *Ångström*-regime is well characterized by the bond angles and bond lengths resulting from the quantum mechanical energy levels. Up to torsional degrees of freedom, chains are in their vibrational ground states, at typical experimental temperatures. The properties on this level are solely determined by the detailed chemical structure molecules involved.

On a more coarse-grained level, one cannot resolve all the atomistic details of the chains any more. A chain looks like a more or less flexible thread. This is the universal, entropy-dominated coil regime. The many possible conformations of the chains and the many ways to pack chains in a melt determine the morphology. In many questions, the intrachain entropy plays the most important role. However, once two states of similar intrachain entropy are available (e.g. chains in a mixture of two different polymer species A and B and in the two phase regime of an A-rich and a B-rich phase) tiny interaction energy differences, originating from the microscopic structure, of order $O(k_{\mathrm{B}}T/N)$ are sufficient to change the morphology completely and to drive the phase separation. A striking illustration of this fact is, that even protonated and deuterated polystyrene phase separate, if the chains are long enough [8]. On the mesoscopic level many properties can be understood on the basis of simple coarse-grained (bead spring) models. Characteristic time and length scales, as they are present in typical experiments are indicated in Fig. 1. On the even coarser level, the semi-macroscopic level the behaviour is dominated by the overall relaxation of conformations of the objects. The typical overall relaxation time, depending on chain length varies between N^2 for short and $N^{3.4}$ for longer chains. As explained in the beginning of this chapter, prefactors originating from the microscopic interaction of the monomers, cause an equally large variation of scales. The resulting times can easily reach seconds. If one approaches the glass transition temperature even much longer characteristic times can be observed. Thus a satisfactory numerical description of material properties needs a combination of both aspects.

This illustrates the long-standing challenge within the modelling of complex materials, to develop methods which allow to cover the range from microscopic to mesoscopic and then on to the semi-macroscopic regime.

MULTI-SCALE MODELLING

Mapping from Atomistic to Mesoscopic Models—and Back

The successful mapping of an atomistic to a mesoscale model has the advantage that, on the mesoscopic level, time and length scales are accessible that are far beyond the reach of atomistic simulations. Thus, qualitatively different physical problems can be treated. A good mesoscale model preserves enough of the original chemical identity of the atomistic model that it does not behave like a generic Gaussian chain. Instead, it contains just enough information to reproduce certain aspects of, say, polystyrene or polypropylene chains under the corresponding conditions. It is no surprise that in recent years, a number of atomistic-to-mesoscopic mappings have been published (see, e.g. Refs. [9–16]; a review encompassing scale bridging from electronic to macroscopic degrees of freedom, cf. Fig. 1 is presented in Ref. [2]).

Moreover, it has turned out that coarse-grained models are useful not only in their own right to study large scale phenomena. They are also a reliable tool for the generation of well-equilibrated atomistic structures, provided one can perform an inverse mapping from the mesoscopic model back to a fully atomistic model which can then be analysed. In many cases, the fully atomistic model is needed for comparison with experiment because the experimental information often necessarily involves atoms, like in nuclear-magnetic-resonance (NMR) spectroscopy [18], neutron scattering [11] or positron annihilation spectroscopy [19].

Approaches to coarse-graining vary substantially, and to date no “standard” procedure has emerged. The mesoscopic models include both continuous models [7,11–13] and lattice models [14–17]. Among the continuous models are versions with purely repulsive interactions and those that have attractive monomer–monomer interactions, too. The lattice models include the bond-fluctuation model [14,15] (8 lattice sites per monomer) and fcc lattices [16,17] (1 lattice site per monomer). For a given complexity of the model, like given by the range of the nonbonded interactions, continuous models and lattice models seem to be roughly comparable in computational cost and performance, as far as static polymer properties are concerned. The continuous models have some advantage when it comes to dynamic problems like shear behaviour or to questions requiring changes in the simulation volume, as for swelling. To study dynamical quantities, continuous models allow equations of motion (often molecular or Brownian dynamics), which are well-controlled approximations. Monte Carlo moves for continuous space models as well as for lattice models only show physical dynamics, if well known standard criteria for the moves of the beads are obeyed [1,3,20]. The most important condition is, that the moves are local, involving only a small number of beads in a small spatial region not exceeding the size of a few beads at a time. Then the dynamics can be mapped on essentially a Brownian dynamics.

The study of different polycarbonate melts [9,10] is a successful example of mapping atomistic to coarse-grained models. In the case of bisphenol-A-polycarbonate (BPA-PC), for example, the atomistic monomer is mapped onto two coarse-grained beads (Fig. 2), one centred at the isopropylidene group (S_1), the other at the carbonate moiety (S_2). Thereby, a reduction of the number of interaction sites per monomer from 33 to 2 is achieved. What remains of the chemical identity of the polymer is contained in 4 intrachain interactions: 1 bond stretch (S_1–S_2), 2 bond angles (S_1–S_2–S_1 and S_2–S_1–S_2) and 1 torsion (S_1–S_2–S_1–S_2). These interactions are parameterised in 3 steps: Firstly, the atomistic potential energy surface of a fragment is calculated by *ab initio* quantum chemistry. Secondly, with this potential surface a Monte Carlo calculation of a single random walk chain in free space is performed, from which distributions of

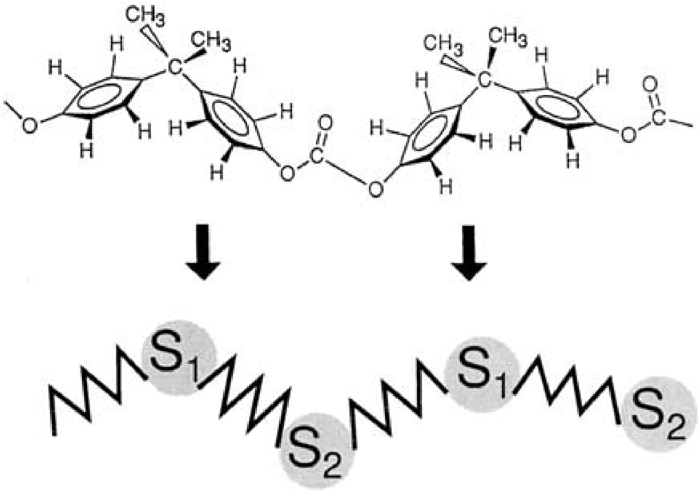


FIGURE 2 Atomistic bisphenol-A polycarbonate is mapped onto a coarse-grained model consisting of 2 beads per monomer, which are centred at the isopropylidene and the carbonate groups (from Refs. [9,10]).

the above 4 intrachain degrees of freedom are extracted. Since this is done at each temperature separately, the distributions contain the complete intrachain information of the coarse-grained model chain. This is used in the third step, as they are transformed into an effective coarse-grained potential energy function (potential of mean force: since they contain energetic and entropic contributions of the atomistic chains directly derived from the distribution functions) by simply taking the logarithm of the distribution functions [9,10]. This determines the interaction potentials without further parameter fitting. Taking the overall density of the melts from experiments with this approach, one was able to reproduce the shift of the Vogel-Fulcher temperature T_o for 3 different polycarbonates almost quantitatively and the shift in the generalized activation energy qualitatively, with energies in the right order of magnitude. Taking this, one can extrapolate the viscosities from the high temperature solutions runs into the experimentally relevant regime and vice versa. Figure 3 shows this for BPA-PC. The only fit parameter is the absolute time scale at $T = 500\,\mathrm{K}$, where both experiments and simulations are available. The interchain interactions are, so far, modelled as purely repulsive. In this way, the interactions are short ranged and the simulations are fast. The polymer sample, however, has no intrinsic cohesion but is kept

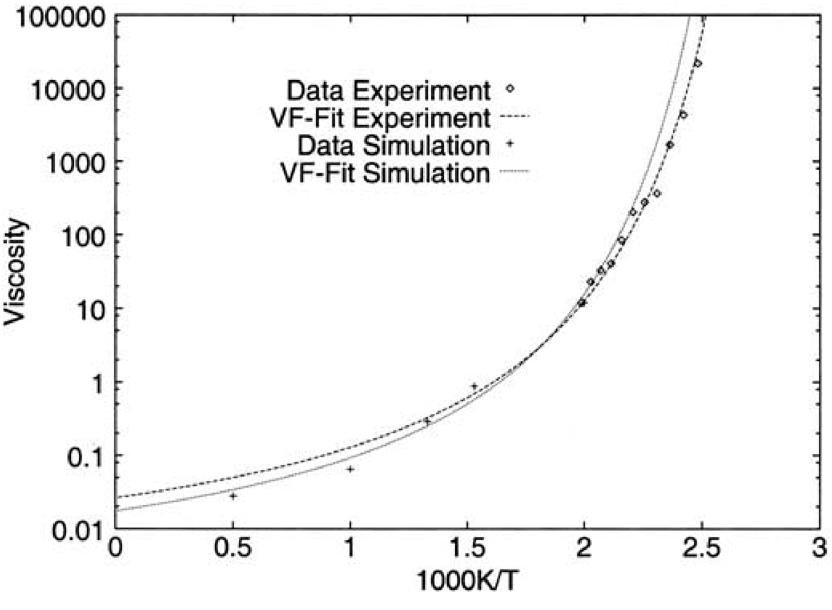


FIGURE 3 Plot of the viscosity for BPA-PC determined from simulation of the CG model and data taken from experiment. The simulation and experimental data are then used to extrapolate into the other regime within the Vogel-Fulcher scheme. The highest temperature for experiment and the lowest for simulation is $T = 500\,\mathrm{K}$, allowing an absolute time scaling (from Refs. [9,10]).

together by the constant-volume condition or an applied (high) pressure. This is acceptable as long as one is interested in bulk polymers of known homogeneous density. When the simulated system is expected to develop density heterogeneities (e.g. in the presence of several phases) or if one is concerned about properties of free surfaces, one has to make amends to the model. Work is presently under way in our laboratory to develop suitable attractive coarse-grained potentials [21].

Automatic Coarse-graining

Developing a reliable mesoscopic polymer model is a cumbersome process. A number of different steps, which may vary between approaches, have to be taken: (i) the degree of coarse-graining, how many real atoms per coarse-grained bead, has to be chosen and the positions of the coarse-grained (CG) beads in relation to the atoms have to be determined, (ii) the form of the intrachain and interchain potentials need to be chosen, if they are not directly derived from the distributions, (iii) their free parameters, especially for the nonbonded interactions, have to be optimised in a way that the CG model reproduces the structure of the model. While (i) and (ii) are intellectual challenges, (iii) often is a menial task which should be automated to the extent possible. Yet, surprisingly little effort has been made in this direction. This section describes a recent approach to systematically and automatically parameterise interaction parameters of mesoscale models. Its purpose is to be able to carry out the parameterisation (iii) for a given degree of coarse-graining (i) and form of the potential (ii) quickly and reproducibly, so that every physical model can be evaluated with a set of optimum parameters. As a side effect, the coworkers involved can concentrate on the more intriguing parts of the project.

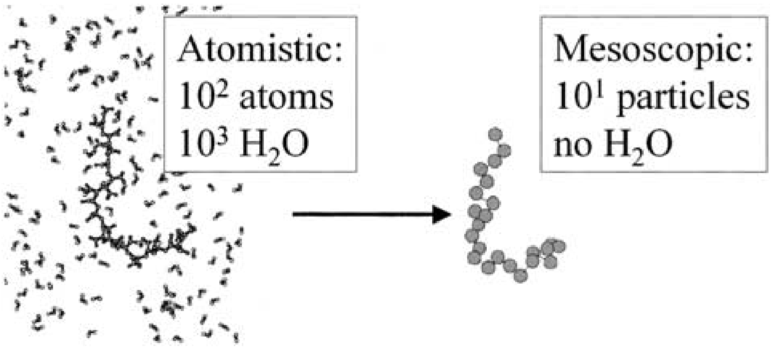


FIGURE 4 An example for mapping between atomistic and mesoscopic models: The sodium salt of poly(acrylic acid) (2 wt%) in aqueous solution (from Ref. [20]).

First, reference data have to be obtained, such as structural properties of the polymer of interest. In the present study we concentrate on the sodium salt of poly(acrylic acid) (PAA) as an aqueous solution of about 2 wt%. They were obtained by performing an atomistic simulation of an oligomer (23 monomers) solvated by about 3200 water molecules. The coarse-grained model contained one bead per monomer cantered at the centre of mass of the atomistic monomer, reducing the number of polymer atoms by 8. More importantly, the coarse-grained model disposed of the explicit solvent, so that the total number of sites was reduced from approximately 10000 to 23 (Fig. 4). The coarse-grained intrachain interactions consisted of a harmonic bond potential, a Gaussian expansion of the multiple-minima bond-angle potential and a short cosine expansion of the dihedral angle potential. The piecewise continuous nonbonded potential between monomers is of the form

$$V(r) = \begin{cases} \epsilon_1[(\sigma_1/r)^8 - (\sigma_1/r)^6] & r \le \sigma_1 \\ \epsilon_2\left[\sin\left(\frac{(\sigma_1 - r)\pi}{(\sigma_2-\sigma_1)2}\right)\right] & \sigma_1 < r \le \sigma_2 \\ \epsilon_3\left[\cos\left(\frac{(r-\sigma_2)\pi}{(\sigma_3-\sigma_2)} - 1\right)\right] - \epsilon_2 & \sigma_2 < r \le \sigma_3 \\ \epsilon_4\left[-\cos\left(\frac{(r-\sigma_3)\pi}{(\sigma_4-\sigma_3)} + 1\right)\right] - \epsilon_2 - 2\epsilon_3] & \sigma_3 < r \le \sigma_4 = r_{\mathrm{cutoff}} \end{cases}$$

This choice at first sight appears complicated and arbitrary, however it has proven useful [13], and it contains enough flexibility to encompass an effective description of the solvent. For a more detailed discussion see Ref. [13]. The reference data include distributions of bond lengths and bond angles as well as radial distribution functions $RDF_{\mathrm{target}}(r)$ obtained from the atomistic simulation but calculated for the coarse-grained beads.

Now it would be tempting to Boltzmann-invert these distributions as well, in order to obtain the parameters for corresponding potentials. However, here the bonded and nonbonded parts of the effective interaction potentials cannot be separated any more, and the previously employed procedure cannot be used. A direct Boltzmann inversion to get the potential of mean force would not properly account for the different interactions in solution.

To avoid this problem, the 23-mer of PAA was simulated with the CG model, in other words the same oligomer as with the atomistic model. The CG parameters were adjusted, until the target RDFs and other distributions were reproduced satisfactorily. We defined a least-squares merit function $f(p_1, p_2, \ldots)$ which was to be minimised

$$f(\{p_1, p_2, \ldots\}) = \int_0^{\text{cutoff}} w(r)[\text{RDF}(r, \{p_1, p_2, \ldots\}) - \text{RDF}_{\text{target}}(r)]^2 \, \mathrm{d}r \qquad (1)$$

where $p_1, p_2, \ldots$ are the parameters in the optimisation set and $w(r)$ is an optional weighting function. For the minimisation, we use a standard amoeba simplex scheme [23]. Note, that every evaluation of f involves an entire molecular dynamics (or Brownian dynamics) simulation of the CG system, including equilibration, check for convergence etc. At this point, the apparently straightforward scheme can become technically tricky and computationally expensive, which we had noted already in the first application of the automatic parameterisation method, namely the development of atomistic force fields from experimental data [24]. The typical agreement of the target RDF of PAA and two CG RDFs, which can be obtained after parameter optimisation is shown in Fig. 5.

With the CG model parameterised, the simulation was extended to much longer chains of PAA in aqueous solution. The results for the calculated hydrodynamic radius of such chains match well the results from dynamic light scattering (Fig. 6). This shows that the CG model retains enough of the true

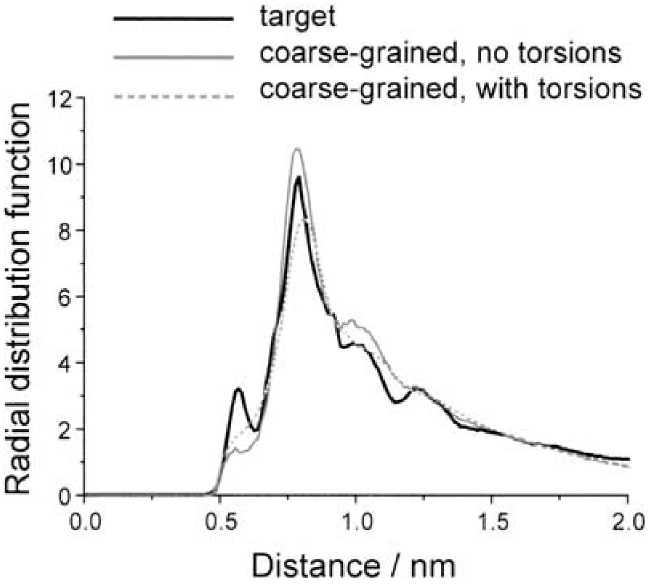


FIGURE 5 Monomer-monomer radial distribution function for poly(acrylic acid), first and second neighbours excluded. The target function from the reference atomistic simulation is shown as well as two different coarse-grained models after convergence (from Ref. [22]).

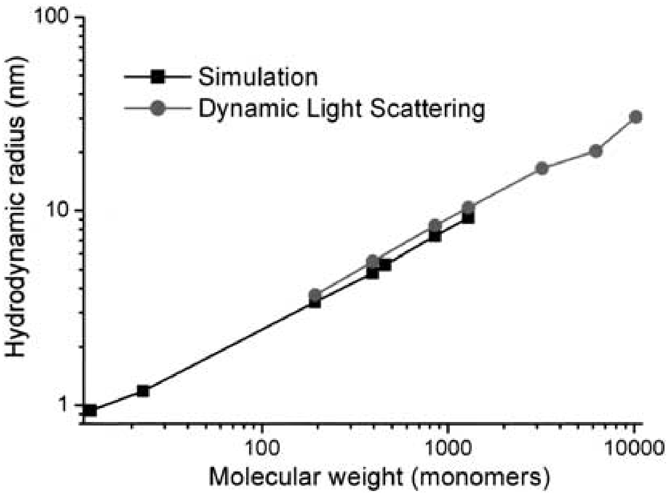


FIGURE 6 The hydrodynamic radius of poly(acrylic acid) in aqueous solution as a function of molecular weight. Experimental data courtesy of Beate Müller and Simone Wiegand, Max-Planck-Institut fur Polymerforschung (unpublished).

identity of PAA to reproduce its structure on a scale much larger than that of the atomistic model from which it was developed. In the meantime this approach has been extended not only to other polymers in solution but also to bulk polymer melts, For the latter case, it turned out to be convenient to optimise the parameters simultaneously against structural and thermodynamical quantities [24].

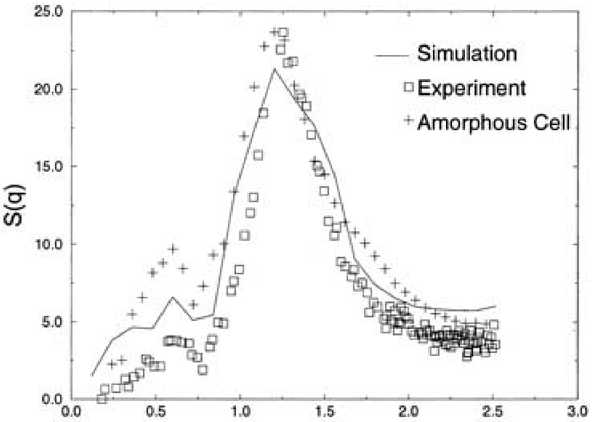


FIGURE 7 Structure factor of fully protonated bisphenol-A polycarbonate from simulation (solid line) and neutron scattering (open circles) (from Ref. [9]).

Atomistic Results after Reverse Mapping

Equilibrated coarse-grained models can be mapped back to an atomistic model. If the position of a coarse-grained site is defined in terms of the atom positions of the atomistic model, the reverse mapping is relatively straightforward. The atomistic monomers are placed at or near the corresponding positions in space and oriented such that as many as possible of their intrachain degrees of freedom are in low-energy conformations. Local stresses, close contacts between different chains etc. are left to relax out by atomistic molecular dynamics (MD) simulations. Where necessary, these can be preceded by a geometry optimisation or MD with soft-core potential or force-capping. Our atomistic MD software YASP [25] contains some of these features.

Large equilibrated samples of bisphenol-A polycarbonate (BPA-PC) have been used to compare structure factors to neutron scattering data [11]. Simulation and experiment compared very well (Fig. 7), also for partially deuterated samples, which indicates that the atomistic structures generated by the detour via a coarse-grained equilibration are faithful representations of the microscopic structure of BPA-PC. This was further supported by an analysis of the polycarbonate structures with a new method for the calculation of positron life times [19]. Again, the agreement between experiment (2.1 ns) and simulation (2.4 ns) was very satisfactory, from which we deduce that also the free-volume distribution in BPA-PC is correctly reproduced [26], even though for the intermolecular interaction of the coarse-grained beads only a repulsive potential was considered. Such large equilibrated computer samples are now being used for other "applications", where the atomistic details are essential. One example, which is also of immediate industrial relevance, is the study the diffusion of the polycondensation by-product phenol in BPA-PC melts [27]. These studies have not only led to a hitherto unknown mechanism of penetrant diffusion in polymers (Fig. 8), but also to more accurate values of diffusion coefficients which have already found their way into a polycarbonate production. We should like to emphasize that none of these studies would have been possible without the help of systematic coarse-graining and reverse fine graining of polymer models.

BEYOND PARTICLE BASED CHAIN MODELS

In the examples above the mapping of length scales was on a level, that a given coarse-grained bead represented roughly one repeat unit of the polymer. Thus, the objects simulated still contained many particles. On this level a number of alternative approaches have been followed, where mean field theories and

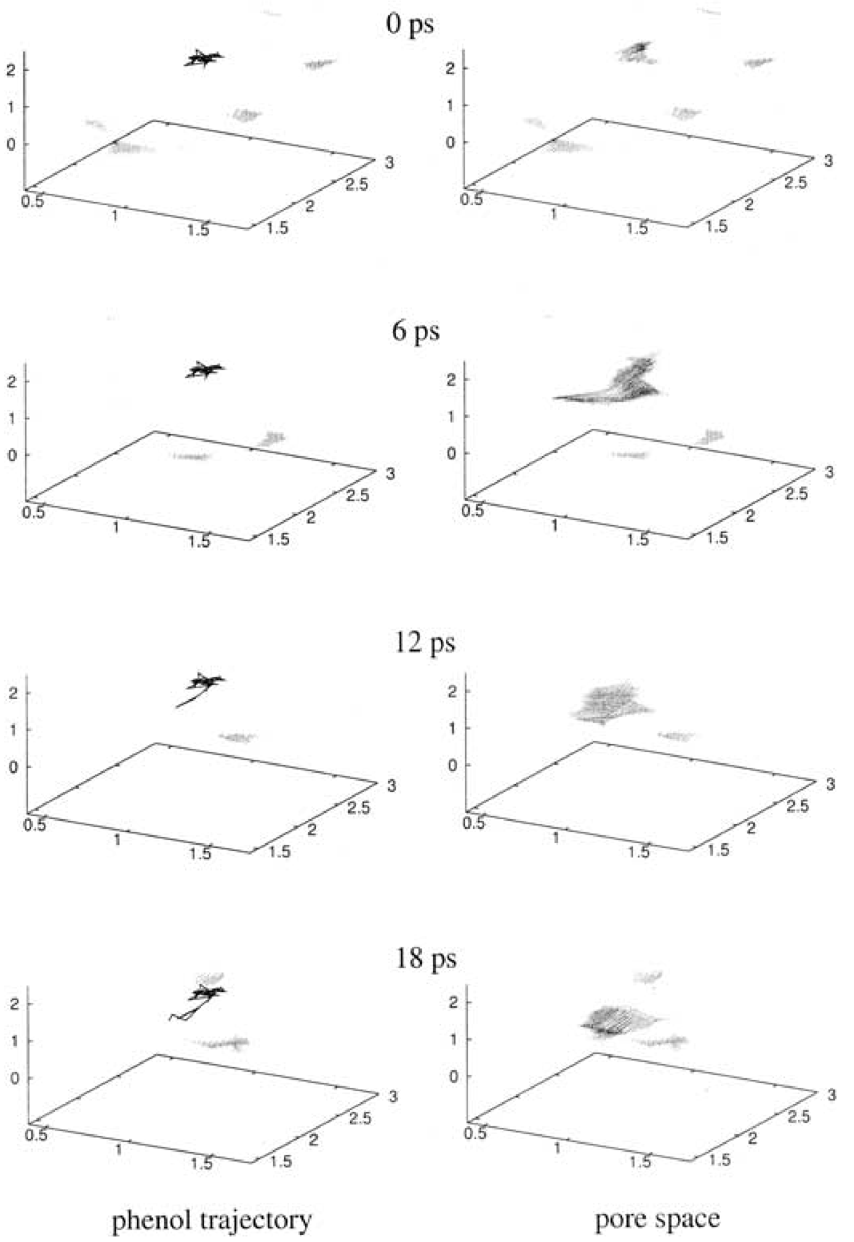


FIGURE 8 The bubble diffusion mechanism for the transport of phenol through a bisphenol-A polycarbonate melt. The structures on the left show the evolution of the trajectory of a selected phenol molecule during one jump event, the structures on the right the corresponding cavity of free volume ("bubble") that contains the molecule. The cavity develops a small side pocket (6 Ps), into which the phenol migrates (12 Ps), followed by contraction of the cavity behind the phenol molecule (18 Ps) (from Ref. [27]).

random walk statistics are combined. On the self-consistent field theory side, we refer to a review by Schmid [28]. The wide applications of such an approach, especially for the understanding of morphologies of block copolymer systems, can be found in a series of papers by Fredrickson and Bates [5,6]. A commercially

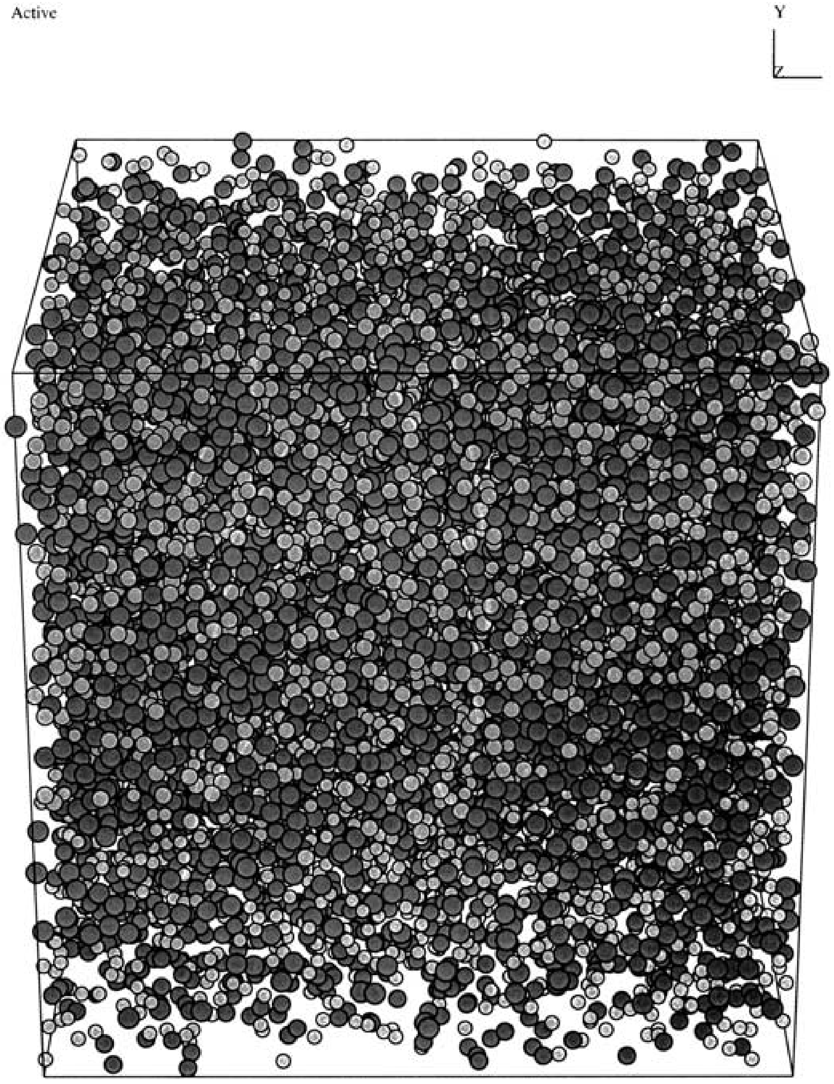
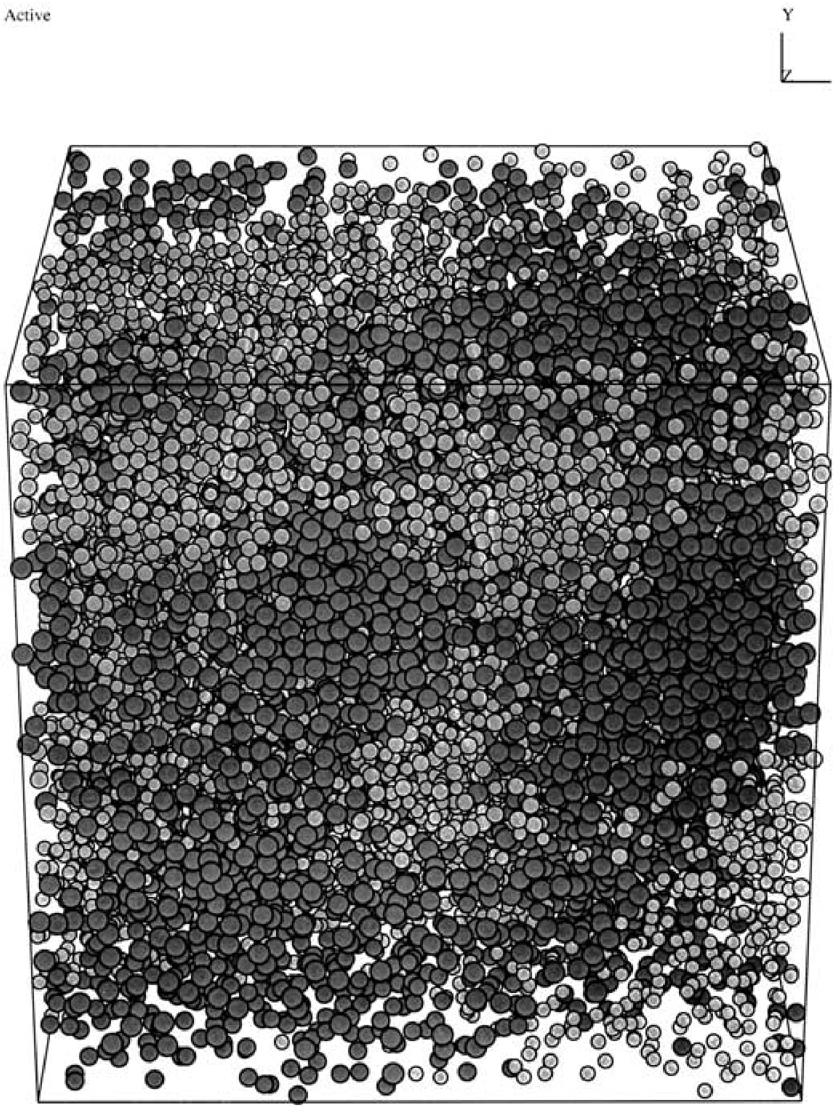


FIGURE 9 Two examples of particle distributions for a mixture of 5,000 A-chains and 5,000 B-chains at the beginning (part a) and at the end (part b) of the run. Each sphere shows the centre of a whole chain! The total box size can be mapped onto a cubic box of about 100 nm (length depending on the chain length).

available simulations program employing those and related methods can be obtained through the MesoDyn project headed by Fraaije [29].

Coarse-graining on the next level up can be performed by combining many monomers into one big soft and fluffy particle [30–32]. All systems considered in



Chapter 2 still allow the one-to-one correspondence of a bead of the coarse-grained polymer model to the repeat unit of a given chemical species. This means that the number of degrees of freedom to be considered is proportional to the number of monomers of a given chain. This is problematic if one wants to simulate big systems, namely tens of thousands chains instead of tens of thousands monomers. In order to arrive at a situation where one can simulate many chains we go back to Fig. 1. A whole chain, or at least a large part of it, is replaced by one ellipsoidal particle with three internal degrees of freedom given by the axes of the mass tensor **R** of the chains. To do this one can follow a philosophy which is very similar to the coarse-graining procedures discussed before. The idea is to separate the free energy of a system into an intrachain and an interchain part. For the total free energy F, we make the ansatz [30]:

$$F = F_{\text{inter}} + \sum_{i=1}^{M} F^{i}_{\text{intra}} \tag{2}$$

The sum runs over all M chains of the system. First consider the intra part of the free energy from chain i

$$F^{i}_{\text{intra}} = -k_{\text{B}} T \ln P(\mathbf{R}^{i}) \tag{3}$$

$P(\mathbf{R})^{i})$ is the probability of a mass tensor $\mathbf{R}^{i}$ of the chain. This defines, as before, an intrachain potential of mean force with the assumption, that the inter and the intra parts are additive. The interchain interaction is proportional to the pairwise density overlap ρ_i and ρ_j of the ellipsoids representing the different chains i and j:

$$F^{(ij)}_{\text{inter}} = \epsilon(N) \int \rho_i(r, \mathbf{R}^{i}) \rho_j(r, \mathbf{R}^{j})\, \mathrm{d}^3 r \tag{4}$$

$\epsilon(N)$ is a fit parameter for the excluded volume, but can also be determined self-consistently. In a melt of chains of length N of the order of $\sqrt{N}$ chains overlap. The computational cost per step can, at best, be reduced by a factor $\sqrt{N}$. The most significant speedup however is related to the fact, that to first order, the relaxation time of the internal degrees of freedom of an ellipsoid becomes independent of N. Meanwhile this approach was improved by Maass *et al.* [31] by taking the intrachain excluded volume into account via a Flory ansatz. This allowed them to study not only dense or dilute systems, but also the semidilute regime, which is of importance for polymer solutions. In a different approach the link to classical liquid theories was investigated [32]. The systems used so far to test this ansatz, are simple coarse-grained polymer bead spring models. An extension to a more refined coarse-grained model for e.g. polycarbonate is conceptually straightforward and an objective of current work. Within this scheme it was possible simulate on one DEC-Alpha processor polymeric melts of the order of several thousands of particles each representing an entire polymer chain. Typical runs consist for instance of 10,000 chains of $N = 50$ monomers. The simulation procedure is a standard Metropolis Monte Carlo simulation procedure for translation, rotation and shape change of the ellipsoids, however other methods can be used as well. Figure 9 illustrates a typical application for the study of the phase separation of a mixture of $M_{\mathrm{A}} = 5,000$ A-chains and $M_{\mathrm{B}} = 5,000$ B-chains. First the polymers are randomly placed in the melt and equilibrated. In a very similar way as in earlier studies on phase separation of polymers, we can now also introduce an $\epsilon(N)$, which is able to distinguish between the two different species A and B. By doing this, one is able to investigate phase separation and morphology development of μm-sized polymer samples.

Hydrodynamic properties on a coarse-grained level beyond the bead spring chain picture with all the topological constraints are studied by dissipative particle dynamics (DPD) [33,34]. Its potential is similar in spirit to the ellipsoidal model. The chains also can move freely through each other. So far this was not used for chain models, where the properties of the "bead" are derived from micro or mesoscopic information.

Beyond such particle based methods, continuum approaches are used to study the properties of macroscopic samples. The most prominent one is the finite element method [35]. Recently, this approach was combined by Gusev *et al.* [36,37] with Monte Carlo techniques in order to study composite materials. While globally homogeneous, composites locally are heterogeneous. One of the central problems is to decide, whether a given finite element is a faithful representative of the material to describe its overall constitutive behaviour. They used Monte simulations to generate "samples" of small composites and studied the size and number of systems needed to reproduce e.g. elastic constants of fibre-reinforced materials. They were able to determine the minimal size for a number of composite structures and improve previous approaches considerably.

CONCLUSIONS, OUTLOOK

Despite of all progress made over the last years a number of challenges remain. On each level of description, new and improved methods have been developed. Still better models are needed. Most important, however, is the controlled and systematic improvement of links between the different simulation schemes, i.e.:

- Systematic coarse-graining procedures, including the inverse mapping step are to be improved and developed. Steps must cover the Micro (many atoms)

⟨ ↔ ⟩ Meso (many monomers) ⟨ ↔ ⟩ Macro (many chains) regimes and link to quantum simulations at the low end and to self-consistent field calculations and finite element like approaches at the upper end.

In order to achieve the longstanding goal of predicting macroscopic material properties from first principles, much effort is needed over the coming years. In particular, a few key ingredients have to be developed, such as

- quantum simulations of reasonably sized systems (Car Parinello techniques, path integral quantum Monte Carlo, combinations of both): coupling electronic and conformational degrees of freedom,
- improved methods to parameterise and validate force fields for atomistic classical molecular simulations, especially suitably parameterised intermolecular interactions (for polar molecules),
- new methods for static and dynamic studies on the semimacroscopic to macroscopic level, such as dissipative particle dynamics for composite materials based on the microstructure of the polymers.

This needs a significant interdisciplinary coordinated effort of researchers coming from different fields of expertise. Sizeable projects are underway at a number of places in the world and range from more software development oriented activities, such as the NEDO project in Japan and European activities within the Training and Mobility program to more basic method development oriented activities like the materials simulation competence centre funded by the German ministry of science and technology which is coordinated by our group.

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