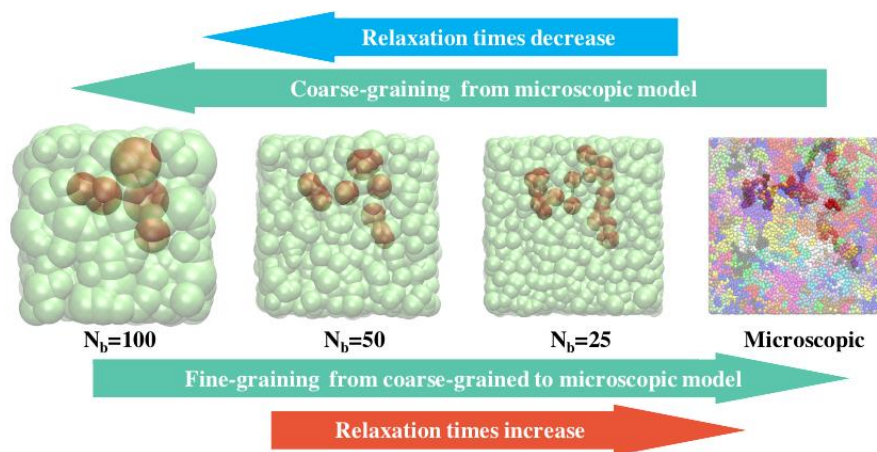




E-CAM case study

The implementation of a hierarchical equilibration strategy for polymer melts, to help studying the rheological properties of new composite materials



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Interviewer: Dr. Donal Mackernan, University College Dublin



Abstract

The ability to accurately determine and predict properties of newly developed polymer materials is highly important to researchers and industry, but at the same time represents a significant theoretical and computational challenge. In a pilot project in collaboration with Michelin¹ we have developed a novel multiscale simulation method based on the hierarchical equilibration strategy, which significantly decreases the equilibrium properties calculation time while satisfying the thermodynamic consistency. A number of E-CAM modules was developed and implemented in the ESPResSo++ software package.

What are the goals of your pilot project?

Our project aims to study the properties of A-B-A block copolymer melts, i.e. mechanical properties, rheological properties etc., by numerical simulations. Thus, equilibrated configurations must be prepared. However, high molecular weight polymer melts require a long relaxation time which increases with the third power of the molecular weight. In fact, for technically interesting molecular weights, equilibrated configurations cannot be obtained at all with acceptable computational effort if one uses brute-force Molecular Dynamics. For example, the CPU time for 1000 polymer chains consisting of 2000 monomers each is roughly estimated to be about four million hours on a single processor (2.2 GHz), just in order to get a single relaxed configuration - of which one however needs many to obtain meaningful values for material properties. Hence, we need an effective method for decreasing the equilibration time. The multiscale simulation method is a suitable way to achieve this.

Why is this project important in general scientifically, and from an industry perspective in particular?

The development of a multiscale method for polymer blends and block copolymers is fundamentally new and needs to be based on first-principles theory. The existing approach² is extremely successful in reducing the equilibration time, but it can only be applied to homopolymer melts, which do not exhibit a phase transition (i.e. no phase separation, no microstructure formation). For a homopolymer melt, one “only” has to solve the packing problem of putting chains into a box in such a way that they are neither stretched nor squeezed. This problem is essentially always the same, regardless of the level of the hierarchical tree, and regardless of whether the levels are thermodynamically consistent with each other or not. Therefore, such consistency was not strictly enforced in references² because it was not required. For blends and block copolymers the situation is quite different: There one additionally needs to worry about the structure of interfaces between species, and of block copolymer microstructures like e.g. lamellae. These additional structures need to be the same on each level of the hierarchical tree, and this is only possible if the interaction parameters of each level are thermodynamically consistent with each other. Otherwise, one will run into a situation where the system is ordered (or phase-separated) on one level of the

¹ <http://www.michelin.com/eng>

² Murat, Kremer *J. Chem. Phys.* **108** (1998) 4340; Eurich, Karatchentsev, Baschnagel, Dieterich, Maass *J. Chem. Phys.* **127** (2007) 134905; Zhang, Moreira, Stuehn, Daoulas, Kremer *ACS Macro Lett.* **3** (2014) 198; Zhang, Stuehn, Daoulas, Kremer, *J. Chem. Phys.* **142** (2015) 221102

tree, but disordered (or homogeneous) on the neighbouring level. This would then very severely hamper the efficiency of the approach, and in fact make it unusable. To find such consistent parameters is only possible by applying advanced statistical-mechanical theory. In short, our development is thus an intellectual challenge in its own right. This is intended to then pave the way to analyse the physical properties (in particular, the mechanical and elastic properties) of novel composite materials that attract the attention of industrial companies. Such materials may be promising ingredients of new products like e.g. efficient and environment-friendly car tires.

How is E-CAM helping Michelin to solve this problem?

For simple polymer melts comprising only a single species of monomers, the group in Mainz had already developed the hierarchical equilibration strategy³. I have implemented this in the publicly available package ESPResSo++ and thus made it available to be used by industrial researchers. Furthermore, we are working on the generalization of the method to make it applicable to systems that are more relevant to industry, i.e. blends and block copolymers.

Can you elaborate a little bit more on your approach and explain to what extent it is built on, what was there before and to what extent there are new things?

The strategy consists of recursive coarse-graining (CG) combined with sequential back-mapping (or inverse coarse-graining) and can drastically decrease the relaxation time of polymer melts (see Figure 1). The procedure combines a group of several monomers along the chain into one new super-monomer and thus maps a system of high molecular weight onto one with a decreased molecular weight, whose relaxation time is much shorter. For the inverse process, relaxation is only necessary on a local scale and therefore fast as well.

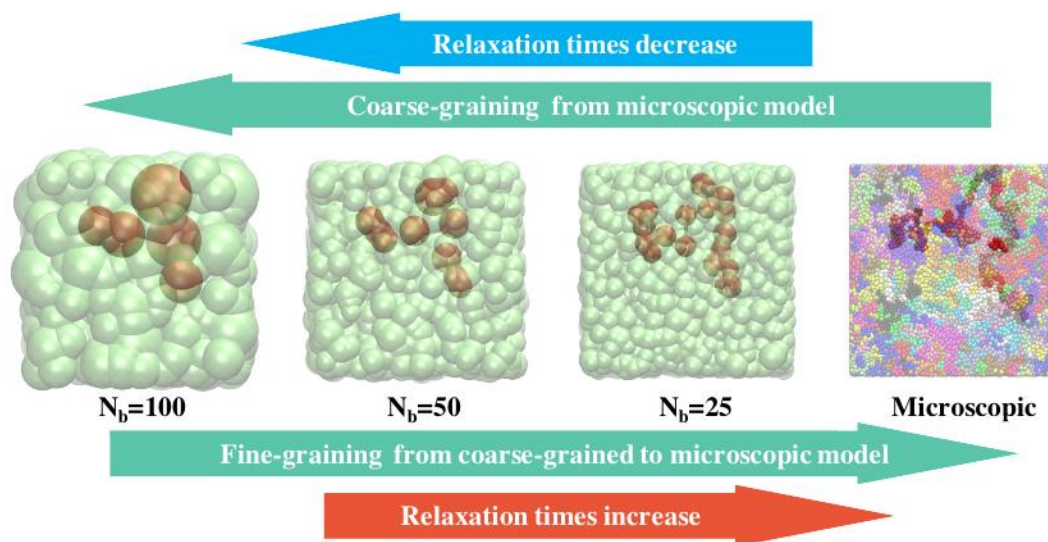


Figure 1: Schematic illustration of the hierarchical equilibration strategy.

³ Zhang, Moreira, Stuehn, Daoulas, Kremer *ACS Macro Lett.* **3** (2014) 198; Zhang, Stuehn, Daoulas, Kremer, *J. Chem. Phys.* **142** (2015) 221102



The super-monomers or softblobs are represented by the model developed by Vettorel⁴. The softblobs are linked by a harmonic bond potential and an angular bond-bending potential that provides some stiffness. The interactions between non-bonded blobs are taken into account by an IECG potential, i.e. the effective interaction calculated within the framework of the formalism developed by M. Guenza and collaborators⁵. Therefore, the relaxation time is not only decreased because of the lower molecular weight, but also because of the softened interactions, which allow the chains to easily pass through each other.

After equilibrating a configuration at very coarse resolution, each CG polymer chain is replaced with a more fine-grained (FG) chain. In this back-mapping procedure, a CG blob is divided into several FG blobs. The centre of mass of the FG blobs coincides with the position of the CG blob's centre and is being kept fixed during the relaxation of the local conformation of the FG monomers within the CG blob. Consequently, a microscopic equilibrated configuration can be reproduced by sequential back-mapping.

A good test that checks if the hierarchical method does indeed provide correctly equilibrated configurations consists of a comparison of results with those obtained from brute-force MD (which is feasible for molecular weights that are not too high). Here in turn one needs to pick a quantity which is very sensitive to distortions of the chain conformations, relative to their ideal structure, and which also relaxes particularly slowly in brute-force MD. In our experience, a useful set of quantities that satisfies these criteria are the mean square internal distances (MSID) of individual polymer chains. For high molecular weights, where such a direct comparison is no longer possible, we have to rely on the fact that polymer physics tells us unambiguously how to scale up from a low to a high molecular weight, both for structure and for dynamics.

All of these developed functions were implemented into the ESPResSo++ program package.

Does your approach scale well or has potential to scale well on a massively parallel machine?

In principle, our approach scales well. ESPResSo++ is a fully parallelized Molecular Dynamics package utilising domain decomposition. However, for the coarse-grained systems, we cannot use a lot of cores due to the long cut-off distance of the interactions, while using too many cores would imply too much communication overhead. The interaction range is of order of the polymer size (i.e. the gyration radius) and therefore always significantly smaller than the overall simulation box size. In other words, we do not have a situation of a truly long-ranged interaction like electrostatics, meaning that advanced techniques like Ewald summation or similar need not (and should not) be applied. To alleviate the problem, one may think of a hybrid programming paradigm which combines distributed memory (e.g. MPI) with shared memory (e.g. openMP). This would require a major restructuring of the basic MD engine, and we think it is very questionable that this is worth the effort: One should keep in mind that the CG systems take only a small fraction of the overall computational effort anyway. For the microscopic system, our calculations scale well, at least up to 2048 cores (beyond which we did not yet run tests).

⁴ Vettorel, Besold, Kremer *Soft Matter* **6** (2010) 2282

⁵ Dinpajoo, Guenza *J. Phys. Chem. B* **122** (2018) 3426



Are your codes already being applied to the systems of interest?

No, not yet. According to our roadmap, we first wish to apply the hierarchical strategy to polymer melts with attractive interactions, then to polymer blends and finally to A-B-A block copolymer melts. Polymer melts with attractive interactions are running already. We have also started to tackle the polymer blend systems.

What do you think are the future prospects and likely impact of this project?

The original goal of computational materials design for non-trivial dense polymer systems was ambitious and is perhaps more ambitious than originally anticipated. Nevertheless, I think that it is achievable, however only with significant additional effort with respect to both fundamental theory (here we are on a good track) and with respect to coding.

Are there any publications which describe the method in more detail?

We intend to submit two papers: One paper shall describe the implementation of the hierarchical strategy into ESPResSo++, while the other shall focus on the improved hierarchical strategy satisfying thermodynamic consistency.

