Lecture Notes in Physics 605

Bridging the Time Scales

Molecular Simulations for the Next Decade

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Preface

"Bridging the Gap!": We had been discussing the challenges to be met by the atomistic simulation community for a few hours when someone came up with this expression. As often happens in animated but exhausting discussions, there was at the same time both enthusiasm and relief. People were relieved by those three simple words which aptly described the main common trend in the approaches analyzed by the participants at the meeting. The meeting itself was held in a small town near Amsterdam, named Bussum, in order to get Daan Frenkel with us, and its aim was to lay the foundations of a large-scale European network in computational condensed matter statistical physics. This was not the end of the story which saw the building of a large collaboration in the form of the European Science Foundation (ESF) program known as SIMU. This program, in fact, required further discussion and effort, but it is probably correct to say that this simple formula helped initiate the network because it succinctly expressed the intellectual attitude shared by the participants in their effort to meet the actual challenges of the field.

First, which attitude? Molecular Dynamics and Monte Carlo simulation techniques are nowadays well accepted theoretical tools to predict, by heavy computing on realistic models, physical properties and dynamical processes in materials. Their scope has steadily increased in the years since the pioneering work of the fifties. Applications are common from the most simple liquid or solid materials to cover also, at least in principle, complex materials like colloids, polymers or poly-electrolytes, not to mention proteins or biological membranes. Most of those materials are studied experimentally, with atomic scale resolution techniques, and are used in many industrial processes. The theoretical understanding of their behavior is crucial in materials science also to analyze the experiments. However, those behaviors extend over length and time scales which are orders of magnitude longer and larger than the ones that can be achieved by brute force simulations in a fully atomistic description. Thus the challenge is to be able to reach scales which can be of the order of micrometers and seconds, starting from a fundamental level of description.

Second, which challenge? There is an agreement on the analysis that most of the progress made in recent years in the atomistic simulation of condensed matter originate in the development of new methods of simulation more than in the increase of available computing power, however impressive the latter has been. No foreseeable increase in computing power will ever be sufficient to give access to the large physical scales needed to describe material properties of realistic complex materials. There is a strong need for further development of methods able to address and, possibly, solve physical problems which are multi-scale in nature. Biased Monte Carlo and *ab initio* MD techniques are two beautiful examples of very successful progress.

There are, however, deeper connections in our community of "simulators" which make possible the transfer of techniques. For example, people working in polymer physics can easily understand the numerical issues which arise in Quantum Monte Carlo techniques and the progress in one field can be quickly transferred to the other. To give another example, the numerical approach behind the Car and Parrinello method can and has been used in classical statistical mechanics, via classical density functional theory, to get "exact" thermodynamic equilibrium averages over solvent configurations. In other words, the technical culture, often based on concepts of statistical physics, is shared, and thus allows an easy exchange of ideas and an efficient form of interdisciplinary collaboration.

This provides another reason (other than the more important one of maintaining the ambition and pride of the community) for the variety of subjects in this book which reproduces articles written after the conference *Bridging the time-scale gap* was held, at the University of Konstanz, in September 2001. The conference was organized within a series of activities supported by the 5-year ESF program SIMU (web site : http://simu.ulb.ac.be/). It focused on the subject of the time scale issue and got a large and enthusiastic participation: besides the 42 invited talks, there were more than one hundred posters and around 250 participants. There have been of course several large conferences dedicated to computational physics, but the peculiarity of this one was its focus on a well-defined theme, one however allowing interdisciplinary participation because of the variety of approaches and levels of description. It had similar spirit to some of the advanced schools organized previously, such as the summer school in Como in 1995 [1] preceded by similar but more restricted initiatives such as the collective book on Monte Carlo methods in statistical physics in 1986 [2] or the proceedings of the Varenna

[1] *Monte Carlo and Molecular Dynamics of Condensed Matter Systems*, edited by K. Binder and G. Ciccotti, SIF, Bologna, (1996).

[2] *Monte Carlo Methods in Statistical Physics*, edited by K. Binder, Topics in Current Physics 7, Springer-Verlag (1986).

school in 1985,[3] which have been important references in the community for many years. At the end of the conference, the scientific committee (the editors plus Daan Frenkel) discussed the possibility of offering selected speakers the opportunity to contribute to a book which would be representative of conference topics and discussions and could remain a good testimony of ideas and techniques on which to build progress in the forthcoming years.

The result goes well beyond our best expectations both for the number and the quality of the contributions that provide a fair picture of the state-of-the-art in the field! We have reproduced the book chapters in the order chosen for the conference, and it is amazing to see that the order follows a kind of logic, starting with the largest scale, where proteins fold and unfold, and ending with Quantum Monte Carlo simulations where, as it was once said, one is bridging the gap in the other direction!

The book starts with contributions dealing with biological and polymer physics. All-atoms and lattice models are used to investigate protein folding dynamics and some of its mechanisms (Eugene I. Shakhnovich et al.) while coarse-grained models are developed in order to describe lipid mono-layers and bi-layers (Steve O. Nielsen and Michael L. Klein) on the relevant time scales. The contribution by Doros N. Theodorou presents a more methodological approach, with various fast (bridging!) algorithms allowing to equilibrate polymers. In his chapter, Alexander Grosberg introduces the new concept of commitor in order to deal with dynamics in conformation space : this concept was elaborated from an analysis of Monte Carlo simulations of protein folding and it is hoped that it could initiate new ideas in the simulation community. Kurt Kremer et al., in turn, describe micro-meso mapping schemes for polymeric materials and present results of a combined approach of mesoscale model simulations and quantum mechanical density functional theory calculations for polycarbonates near surfaces.

The next chapters deal with the statistical mechanics of complex materials. First, the coarse-graining through effective interactions allows Jean-Pierre Hansen and Hartmut Löwen to describe equilibrium properties of polymer and colloid fluid mixtures. The slow dynamic of glasses require not only coarse-graining but also some specific techniques like parallel tempering (Kurt Binder et al.). This problem is examined in a more systematic way by Nigel Wilding and David P. Landau who review several methods allowing faster convergence in lattice and continuous models. The hydrodynamic evolution is then investigated by Christopher P. Lowe and Sauro Succi who apply lattice-Boltzmann and hybrid techniques to various flow problems.

[3] *Molecular-Dynamics Simulation of Statistical-Mechanical Systems*, edited by G. Ciccotti and W.G. Hoover, SIF, Amsterdam, North-Holland (1986).

Multi-scale methods are also described and applied to the problem of solid friction where a direct simulation inspection has permitted progress in the basic mechanisms involved (Martin H. Müser).

Three chapters of a more methodological nature follow: they are the contributions on the transition path sampling (Christoph Dellago and David Chandler), on the stochastic difference equation (Ron Elber et al.) and, finally, on the proper treatment of long range interactions. Transition path sampling was explained as *throwing ropes over a mountain path in the dark* and it deals with the computation of rate constants when the reaction mechanisms are not precisely known. Stochastic dynamics is being introduced in order to generate long-time trajectories. Problems with long-range Coulombic and dipolar systems are then treated by Dominique Levesque.

The last part of the book deals with simulation techniques involving a quantum aspect. It starts with a description of *ab initio* MD recent advances by Glenn J. Martyna and Mark E. Tuckerman. The use of this technique is heavily time-consuming to create a serious time-scale problem. Ways to overcome the time-scale barrier are described in the contribution by Ursula Röthlisberger, Michiel Sprik, and Jürg Hutter: bias potentials and electronic bias potentials are being introduced, together with the explanations on how to apply the method, and to compute rate constants. Often it is necessary to treat part of the system classically and, in the presentation by Raymond Kapral and Giovanni Ciccotti, the embedding of a quantum system interacting with classical degrees of freedom is studied in a systematic way. The book ends with a contribution by David Ceperley, Mark Dewing, and Carlo Pierleoni where a classical Monte Carlo simulation for the ions is coupled to a Quantum Monte Carlo simulation for the electrons in order to describe liquid and metallic behavior of quantum hydrogen. Time scales in this approach are an order of magnitude smaller than in the first chapter, however the numerical problems to overcome are very familiar, as one knows from the similarity with polymer physics.

It is our belief that multi-scale and hierarchical modeling will be used more and more in the future. Our ambition in assembling these contributions is not only to show the great vitality of the field with the many different approaches to the time-scale problem, but also to help readers to understand what are the real issues and difficulties in applying those techniques to the many problems arising in the microscopic description of the thermodynamical properties of matter. Let us hope that the ideas and methods presented in this book will have a lasting impact.

The conference could not have taken place without the support provided by the European Science Foundation. This support came through the program *Challenges in Molecular Simulations* (SIMU) which has been approved for 5 years (1999–2003). It is a pleasure to extend our thanks to Professor J. Rojo, the chairman of the ESF committee, PESC, who accepted our invitation to come and talk at the conference.

The members of the steering committee of the SIMU program have been decisive to the success of the conference, both for their enthusiastic support and financial generosity. Even more important to the success of the meeting has been their participation in chairing the sessions and enlivening the discussions which took place during them. Many thanks to all.

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Fig. 1. Photo taken at the conference *Bridging the time-scale gap* in Konstanz, 10–13.9.2001

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