PREFACE

The school held at Villa Marigola, Lerici, Italy in July, 1997 was very much an educational experiment aimed not just at teaching a new generation of students the latest developments in computer simulation methods and theory, but rather to bring together groups of researchers who share a common problem in the hope that through the process of educational exchange new insights into this common problem might emerge. The research groups represented at the school were from the condensed matter computer simulation community, the biophysical chemistry community, and the quantum dynamics community. The common problem they share is the development of methods to treat the dynamics of quantum condensed phase systems.

The evolution of computer simulation has spanned three main developmental phases: (1) During its infancy, the "founding fathers" demonstrated that statistical mechanics could be implemented through Monte Carlo (MC) and molecular dynamics (MD) methods to extract equilibrium and dynamical properties (by MD) of simple condensed phase systems described by model potentials and classical mechanics. (2) Following the "proof of principle" of phase 1, the powerful classical simulation methodologies were next shown to provide reliable representations of certain phenomena in realistic systems including chemistry in aqueous solutions, biological molecules, and real materials. During this second phase it was recognised that the "black magic" of simulation lay in the construction of the potential. Phase 2 also witnessed the development of the "art of simulations: fundamental new methods which extended the domain of simulation. Phase transitions and critical phenomena were studied by inventing biased sampling schemes, finite size scaling, and other methods which extract the maximum information from a limited exploration of phase space. Rare events such as chemical reactions, activated diffusion, etc. were explored using methods which focus on the important part of the phase space needed to define the activated process. All dynamical systems present many timescales of motion, and methods were developed which could filter out fast timescales, keeping only those important for the physical processes under study. More recently, efficient techniques for handling the effects of fast motions on longer term processes have emerged. Direct methods for treating nonequilibrium phenomena were also explored. Increases in computer power during this phase meant that larger systems could be studied and this lead to the development of efficient methods for handling long range interactions and very large systems. (3) The developments in phase 3 are characterized by the extension of simulation methods to incorporate quantal behavior on various levels: from the explicit treatment of electronic degrees of freedom, to including nuclear quantum effects. As a first step the "black magic" of potential surface construction for condensed phase applications became "science" with the development of *ab initio* molecular dynamics simulations in which the intermolecular forces are computed on-the-fly by approximate, but accurate many body electronic structure calculations. This opened the way to simulation of realistic materials and microscopic chemical processes, allowing for changes in molecular electronic structure as molecules moved from one environment to another, and removed artificial restrictions such as unbreakable bonds which were one of the most frustrating features of the earlier approaches. As another general development Monte Carlo and molecular dynamics methods were applied to solve equations of quantum mechanics: Green's function methods were employed to calculate ground state wavefunctions of quantum many body problems, and path integral methods were used to sample thermal distributions of quantum states. These generalized methods are in principle not restricted to treating just the electrons quantum mechanically, quantal nuclear motion can also be incorporated. These methods are, however, restricted to exploring static equilibrium condensed phase quantum phenomena.

This rich history of achievements in statistical mechanical simulations does not hide the still surviving limitation that quantum dynamics in condensed phase systems is as yet an unsolved problem. Indeed, this remains a major theoretical challenge for the future of simulations in condensed matter.

The road to quantum dynamical condensed matter simulations, however, is not completely untrodden. For example, there have already been attempts to incorporate the effects of dynamical mixing of excited quantum states resulting from the classical motion of nuclear degrees of freedom in realisic model condensed phase systems. However, this mixing of quantum and classical dynamics is just the first step towards meeting the challenge.

Parallel to the developments outlined above, there have been major advances in treating the quantum dynamics of systems consisting of a few degrees of freedom. More pertinent to our condensed phase interest, progress has also been made towards the fully quantum treatment of simplified models of condensed phase systems consisting of a few detailed degrees of freedom coupled to a bath of many variables through highly idealized interactions.

The impetus for the meeting came from two complementary goals of the condensed matter community: (1) To systematically review its own most recent advances in areas where the development of quantum dynamical methods would be extremely important, and (2) to be enlightened as to the significant new developments from the quantum dynamics community. The latter embraced this opportunity since in turn, they were very curious of potential applications of condensed matter methodologies to quantum dynamical problems.

Due to the focus of the school, the contributions divide along natural lines into two broad groups: (1) The most sophisticated forms of the Art of computer simulation including: (a) Biased phase space sampling schemes, (b) methods which address the multiplicity of timescales in condensed phase problems, and (c) static equilibrium methods for treating quantum systems, and (2) The contributions on quantum dynamics including:(a) methods for mixing quantum and classical dynamics in condensed phase simulations, and (b) methods capable of treating all degrees of freedom quantum mechanically.

The chapters have thus been organized into the following three parts to reflect these natural divisions: In Part 1 *Chandler* presents three chapters which serve as motivation for the rest of the book. In these chapters he presents a broad overview of rare events in various contexts and shows how all the methodologies touched on at the school can be brought to bare on an important general class of condensed matter problems. He outlines approaches for treating activated processes in both classical and quantum systems and describes general methods for finding multidimensional pathways through phase space.

In Part 2 *Valleau* and *Frenkel* describe the formal framework underlying biased phase space sampling methods. Next *Berne* and *Ciccotti* detail recent developments in the multiple timescale, and constrained molecular dynamics algorithms. A series of contributions which bring these tools together in different ways to explore rare events in various condensed phase situations are next presented. Thus *Ruiz*, *Janke*, *Theodorou*, *Smit*, and *Succi* present methods to describe processes ranging from molecular diffusion in polymers, zeolites, and model viscous environments, to methods for sampling the phase space of lattice models.

The next series of chapters in Part 2 focus on incorporating static equilibrium quantum effects in simulations. *Sprik* thus shows how density functional methods can be incorporated in MD calculations to study chemical reactions in solution, and *Tuckerman* gives an overview of path integral methods for quantum statistical mechanics. *Marx* shows how these methods can be combined to study equilibrium proton transfer in ice, and *Jónsson* presents a new path integral formulation of quantum transition state theory, as well as an approach for finding pathways to reaction.

Part 2 is concluded with a series of chapters devoted to extensions and applications of these classical and quantum methods to treat biological systems. *Elber* presents a methodology to treat the dynamics of peptide folding, *Roux* describes an approach to activated dynamics in ion channels, and *Klein* reviews the structure and function of these channels.

Part 3 consists of a series of chapters which focus on quantum dynamics in condensed phase systems. In the first few chapters of this part *Tully*, *Rossky*, *Coker*, and *Kapral* explore nonadiabatic MD methods for mixing quantum and classical descriptions of dynamics for condensed phase systems. Next, *Miller* presents a formulation of the nonadiabatic problem which treats electronic and nuclear degrees of freedom on the same semiclassical dynamical footing. The following three chapters describe various approaches to treating all dynamical degrees of freedom quantum mechanically at various levels of approximation. *Makri* reviews her exact, fully quantum dynamical methods which she applies to the study of models of tunneling and dissipation in the condensed phase, *Voth* summarizes his centroid MD approach, and *Filinov* presents a new approach to quantum dynamics based on the Wigner formulation. A series of applications of various approaches to quantum dynamics are presented in the concluding chapters of *Laria* (electron transport), *Borgis* (VB models for proton transfer dynamics), *Doll* (hydrogen transport in metals), *Procacci* (solvent effects on electronic spectra), and *Metiu* (applications to surface diffusion and spectroscopy)

It is certainly unrealistic to expect that this first experiment at uniting condensed matter simulation and quantum dynamics would bear important new algorithmic fruit instantly. Our hope is that some seeds have at least been sown in young fertile minds, and that in the years to come the growth at this frontier will be strong, and have wide reaching implications in many areas of scientific endeavour. These proceedings do not contain all the answers but they certainly do address a lot of the important questions and it is our hope that they will serve to focus future efforts in these directions.

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