LECTURE NOTES IN PHYSICS

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(Eds.)

Computer Simulations in Condensed Matter: From Materials to Chemical Biology – Vol.1

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Computer Simulations in Condensed Matter Systems: From Materials to Chemical Biology Volume 1

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Preface

The school that was held at the Ettore Majorana Foundation and Center for Scientific Culture (EMFCSC), Erice (Sicily), in July 2005, aimed to provide an up-to-date overview of almost all technical advances of computer simulation in statistical mechanics, giving a fair glimpse of the domains of interesting applications. Full details on the school programme and participants, plus some additional material, are available at its Web site, `http://cscm2005.unimore.it`

Computer simulation is now a very well established and active field, and its applications are far too numerous and widespread to be covered in a single school lasting less than 2 weeks. Thus, a selection of topics was required, and it was decided to focus on perspectives in the celebration of the 65th birthday of Mike Klein, whose research has significantly pushed forward the frontiers of computer simulation applications in a broad range, from materials science to chemical biology. Prof. M. L. Klein (Dept. Chem., Univ. Pennsylvania, Philadelphia, USA) is internationally recognized as a pioneer in this field; he is the winner of both the prestigious Aneesur Rahman Prize for Computational Physics awarded by the American Physical Society, and its European counterpart, the Berni J. Alder CECAM Prize, given jointly with the European Physical Society. The festive session held on July 23rd, 2005, highlighting these achievements, has been a particular focus in this school. In the framework of the EMFCSC International School of Solid State Physics Series, the present school was the 34th course of its kind.

However, this school can be considered as being the third (and perhaps last?) event in a series of comprehensive schools on computer simulation, 10 years after the COMO Euroconference on "Monte Carlo and Molecular Dynamics of Condensed Matter systems," and 20 years after the VARENNA Enrico Fermi Summer School on "Molecular Dynamics of Statistical Mechanical Systems." Comparing the topics emphasized upon in these schools, both the progress in achieving pioneering applications to problems of increasing complexity, and the impressive number of new methodological developments are evident. While the focus of the Varenna School was mostly on Molecular Dynamics (MD) and its applications from simple to complex fluids, the Como school included both Monte Carlo (MC) simulations of lattice systems (from

quantum problems to the advanced analysis of critical phenomena in classical systems like the simple Ising model), and the density functional theory of electronic structure up to the Car-Parrinello ab initio Molecular Dynamics techniques (CPMD). At the Erice school, a new focus was put on the paradigma of "Multiscale Simulation", i.e. the idea to combine different methods of simulation on different scales of length and time in a coherent fashion. This method allow us to clarify the properties of complex materials or biosystems where a single technique (like CPMD or MD or MC etc.) due to excessive needs of computer resources is bound to fail. Good examples presented at this school for such multiscale simulation approaches included MD studies of polymers coupled with a solvent, which is described only in a coarse-grained fashion by the lattice Boltzmann technique and hybrid quantum mechanical/molecular mechanics (QM/MM) methods for CPMD simulations of biomolecules, etc.

As a second "leitmotif," emphasis has been put on rapidly emerging novel simulation techniques. Techniques that have been dealt with at this school include the methods of "transition path sampling" (i.e. a Monte Carlo sampling not intending to clarify the properties of a state in the space of thermodynamic variables, but the properties of the dominating paths that lead "in the course of a transition" from one stable state to another), density of state methods (like Wang-Landau sampling and multicanonical Monte Carlo, allowing an elegant assessment of free energy differences and free energy barriers, etc.) and so on. These techniques promise substantial progress with famous "grand challenge problems" like the kinetics of protein folding, as well as with classical ubiquitous problems like the theory of nucleation phenomena. Other subjects where significant progress in methodological aspects was made included cluster algorithms for off-lattice systems, evolutionary design in biomedical physics, construction of coarse-grained models describing the self-assembly and properties of lipid layers or of liquid crystals under confinement and/or shear, glass simulations, novel approaches to quantum chemistry, formulation of models to correctly describe the essence of dry friction and lubrication, rare event sampling, quantum Monte Carlo methods, etc. The diversity of this list vividly illustrates the breadth and impact that simulation methods have today.

While the most simple MC and MD methods have been invented about 50 years ago (the celebration of the 50th anniversary of the Metropolis algorithm was held in 2003, the 50th anniversary of the Alder-Wainwright spectacular first discovery by MD of the (then unexpected) phase transition in the hard sphere fluid is due in 2007), even the "second generation" of scientists, who started out 30-40 years ago as "simulators" are now already the "old horses" of the field, either close to the end of their scientific career, or, in the best case, near it. Thus, we can clearly observe that the task of developing the computer simulation methodology is further taken over with vigor by the "third generation" of well-established younger scientists who have emerged in the field. Because two of the organizers of the school (KB, GC) do belong to the "old horse" category, it was clearly necessary to get an energetic younger

co-organizer involved (MF), and we also felt it was the appropriate time that the most senior experts need not give the main lectures of the school, but rather the younger generation who are now most actively driving forward the frontier of research. Of course, it was crucial to involve the very valuable experience and knowledge of our senior colleagues into the school as well, and we are very glad that so many of them have accepted our invitation to give one-hour seminars providing tutorial introductions to various advanced research topics, which is at the heart of the research interests of the speakers. In this way, it was possible to produce an exciting event on the forefront of research on computer simulation in condensed matter, in a very stimulating and interactive atmosphere, with plenty of fruitful discussions.

It is with great pleasure that we end this preface with several acknowledgments. This school, of which the lecture notes are collected here, could not have taken place without the generous support of the European Community under the Marie Curie Conference and Training Courses, Contract No. MSCF-CT-2003-503840. We are grateful to the coordinators of this program, Michel Mareschal and Berend Smit, for their help in securing this support. We also wish to thank the CECAM secretaries, Emmanuelle Crespeau and Emilie Bernard.

We thank the Ettore Majorana Foundation and Centre for Scientific Culture in Erice, Sicily, for providing their excellent facilities to hold this school, and also Giorgio Benedek, Director of the International School of Solid State Physics, for the opportunity to hold our school as its 34th course: for his enthusiastic support during the school, and for his personal scientific participation. We are particularly grateful to him for providing the beautiful facilities of Erice.

MF thanks Davide Calanca, INFM-S3, Modena, for his valuable help in setting up the Web site of the school.

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We are very grateful to Daan Frenkel, Mike Klein, and Peter Nielaba for their very valuable input when setting up the scientific program of the school, to all the lecturers, for their willingness to engage in the endeavor, and to all the participants, for their engagement and enthusiasm.

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Introduction: Condensed Matter Theory by Computer Simulation

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The basic laws of physics that govern the phenomena on the scales of length and energy relevant for condensed matter systems, ranging from simple fluids and solids to complex multicomponent materials and even problems of chemical biology, are well known and understood: one just deals with the Schrödinger equation for the quantum many-body problem of the nuclei and electrons interacting with Coulomb potentials (for simplicity, we disregard, here throughout, the need for relativistic corrections in electronic structure calculations of matter containing heavy atoms). Statistical mechanics then supplies the framework to extend this quantum many-body theory to provide a statistical description in terms of averages taken at nonzero temperature.

However, it is also well-known that one cannot carry out this program with any mathematical rigor. Even the problem of one nucleus (or a few nuclei) with the associated electrons is still a challenge for the methods of quantum chemistry. Dealing with the quantum-many-body problem in terms of approximations such as the Hartree-Fock method, which tries effectively to reduce the many-body problem to a single electron problem, introduces errors that at least for excited states, cannot be controlled. Similarly, statistical mechanics, as founded by Boltzmann, Maxwell, Gibbs and others more than one-hundred years ago, can only make analytically precise predictions for problems of a type where the many-body problem can be reduced to a system of independent particles or quasiparticles. Such problems are, for instance, the ideal gas, the ideal paramagnet, or the multidimensional harmonic oscillator describing phonons in perfectly harmonic crystals. Of course, these problems are useful and nicely illustrate the spirit of the general theoretical framework and hence, we all teach them to our students. But we should not fail to admit that the predictive power that emerges from these few problems is very scarce. One has to be very careful about concluding anything about the problems of real matter as it occurs in nature or in the experimentalist's laboratory. For instance, in gases and paramagnets the degrees of freedom considered almost never do not interact at all; real solids show thermal expansion and finite lifetime of the phonon excitations, unlike strictly harmonic crystals; etc.

It is true that one can try to account for those neglected interactions either by systematic expansions, e.g. dealing with anharmonic terms in crystals via perturbative methods, or by closed-form approximations, e.g. exchange interactions among the magnetic moments in a crystal may be treated within molecular field theory. But the parameter range over which the systematic expansions are accurate is often doubtful; carrying them to high enough order often requires extremely heavy use of very sophisticated computer programs, which typically give relatively little reward in the form of physical insight. A characteristic example is the study of critical phenomena in systems of interacting spins with the high temperature series expansion method. This method indeed can give very good estimates for critical exponents at second order transitions, but still may suffer from the problem that the answers gotten are misleading: if the model system studied exhibits a phase transition that is weakly of first order, rather than second order, it has no critical exponents at

all. In addition, it is hard to improve such methods systematically by going to still higher order, since the effort then typically increases exponentially fast.

The situation with closed-form approximations is even worse, since these are typically uncontrolled in a mathematical sense and often lead to very bad and misleading results. Although the simplest of these approximations are standard material of university courses in statistical thermodynamics, one must not sweep under the rug that approximations such as the molecular field theory of magnetism erroneously predict long range order in a one-dimensional chain although there is none; the van der Waals theory of the liquid-gas transition produces isotherms with spurious loops, and none of these approximations can describe the critical behavior near second order phase transitions correctly. The reason of these shortcomings is that nontrivial correlations between the degrees of freedom of the many-body system arise. These correlations cannot be dealt with appropriately by these approximations, which always involve unjustifiable factorization of such correlations in one way or another. For more complicated problems, even such a mean-field like factorization requires very heavy and technically demanding computer use. For instance when one deals with quantum-many-body problems by Hartree-Fock techniques and their extensions, or when one deals with the glass transition of supercooled fluids by the mode-coupling theory beyond schematic models, cumbersome numerics is required. In such cases it is particularly difficult to justify which steps of the approximate theoretical treatment are accurate. Often direct comparison to experiment may be misleading, too, since the simplified model on which the theory is based does not correspond to a real system in sufficient detail. Hence discrepancies between "analytical theory" and experiment can be attributed to the choice of an inappropriate model, an inappropriate approximation, or both. Conversely, sometimes agreement between experiment and theory is claimed which is completely spurious because inadequacies of a model somehow are effectively more or less compensated by wrong approximations. An example of such spurious agreement are fits of the Flory-Huggins equation of state to phase diagrams of polymer mixtures.

A long list of theories to which these criticisms apply could be compiled, notwithstanding the fact that there are some special models, for instance, lattice models like the one- and two-dimensional Ising and Potts models with nearest neighbor interactions, which can be solved exactly by analytical methods. While one has certainly learned a lot of physics from the results of these exceptional nontrivial models that were exactly soluble, usually the method of solution is fairly special – if not tricky – and not illuminating the physics of the problem. And, in addition, the overwhelming majority of problems that one encounters in the physics of condensed matter does not fall in this category of solvable problems. While very respectable research on mathematical statistical mechanics is still going on, it is not likely that it will change this situation.

Hence, until about 50 years ago, condensed matter theory was in a very unsatisfactory status: although a formal framework for the theoretical