Summary

Computational hardware has developed to the point where it is possible to conceive of and perform long time simulations of realistic models for complex molecular systems.

This circumstance has led to an intense effort by a multidisciplinary group of scientists whose common goal is to develop algorithms that will take advantage of these computational hardware resources to carry out simulations of molecular systems which, until very recently, could hardly have been imagined. Many of these molecular simulations will have a direct impact on problems that are of crucial interest to society today; for example, the development of novel energy sources, containment of nuclear waste, drug discovery and development, etc. Regardless of the nature, or application, of a particular molecular simulation, an essential feature of most algorithms is the implementation of an appropriate *thermostat*. Broadly speaking, a thermostat (barostat, etc.) is a mathematical and computational device that allows the simulator to mimic the coupling of the external environment to the system being simulated, *without* directly simulating the environment. The development of the theory of thermostats has been motivated by the needs of computational simulations of complex molecular systems and, consequently, fundamental understanding of this essential tool is still at a fairly rudimentary stage.

The workshop *Fundamentals of Deterministic Thermostats* brought together an interdisciplinary group of scientists from mathematics, chemistry, physics, and engineering for the purpose of discussing the necessary properties and requirements for thermostats across a spectrum of diverse applications as well as a detailed examination of related mathematical, theoretical, and computational issues with the goal of outlining and guiding the future development of the field. One outcome of the workshop is that it has became apparent that the subject of thermostats is at a crucial point where theoretical and applied studies have converged. This convergence was evident in the very lively discussions accompanying each talk from attendees across the disciplines. The workshop has not only clarified many of the fundamental aspects of thermostats (both deterministic and stochastic!) and their applications, but it has also stimulated new directions for research in the topic as well as research collaborations that might not have occurred otherwise. We anticipate considerable future progress in the field based on the foundations laid at this meeting.

Workshop activity: talks and discussion

The workshop began with an overview of the use of thermostats in soft matter simulation by Mike Allen (Warwick). Following a review of early applications of stochastic approaches such as Langevin dynamics, the Nosé-Hoover thermostat was introduced and its derivation reviewed. The Nosé-Hoover thermostat is the workhorse of the field, and provides the prototypical example of a deterministic non-Hamiltonian thermostat. The configurational definition of temperature was discussed as an alternative to the usual kinetic expression, and associated Nosé-Hoover configurational thermostats described. In the next section of his talk, Mike Allen reviewed dissipative particle dynamics, which provides a computationally effective but relatively crude description of fluid regions interacting by soft potentials. The relation between control of temperature T and effective viscosity was noted, and several thermalizing schemes based on pairwise temperatures discussed. The final section of the talk covered density of states MD, where the system phase space is sampled according to the inverse of the density of states.

Karl Travis (Sheffield) began his talk by explaining that use of the kinetic definition of T becomes problematic in simulations of nonequilibrium situations such as Couette flow, where artifacts like "string phases" can be generated. It is necessary to define the kinetic energy with respect to a frame moving at the effective shear velosicity. Extension of this idea from atoms to the case of molecules with internal degrees of freedom was discussed, and the difference between center-of-mass based and site-based thermostatting explained. The history of the concept of configurational temperature was then reviewed, and various configurational thermostats described. The Travis-Braga-Jepps version is based on an extended phase space, and is derived within the Bulgac-Kusnezov framework. Outstanding problems, including the justification of the definition of T_{config} far from equilibrium, were identified.

The afternoon session on the first day of the workshop dealt with a number of topics having a geometrical flavor.

The talk by John Maddocks (EPFL) dealt with the treatment of holonomic constraints within the impetus-striction formalism. In this approach, which is dual to the usual Dirac approach to constraints, an unconstrained Hamiltonian formulation is given for a constrained Lagrangian system, where the relevant Hamiltonian is defined implicitly through a minimization procedure. The so-called striction is the time derivative of the Lagrange multiplier in the usual theory of constraints. In the first version of the theory, linear instability of the constraint manifold is replaced by marginal stability; a second version of the theory renders the constraint manifold attractive. The general theory was illustrated using the example of the spherical pendulum. Issues associated with possible numerical implementation of the scheme were discussed.

Bulent Karasozen (METU, Turkey) discussed integration algorithms for Hamiltonian ODEs with Poisson structure. Poisson manifolds and Lie-Poisson systems were defined, and several physically significant generalizations of standard Hamiltonian systems were described: bi-Hamiltonian (Lotka-Volterra); multi-Hamiltonian (Toda lattice); Nambu dynamics. Work on integration algorithms for Lie-Poisson systems and for bi-Hamiltonian pdes was reviewed, and the possibility of treating incompressible flow as a Nambu system was discussed. It was clear from this talk that there is considerable potential for the application of these ideas to the type of mathematical structures arising in deterministic thermostats.

Tony Bloch (Michigan) then discussed dissipative dynamics in non-holonomic systems. First, the venerable but little-known Lamb model of an oscillator coupled to a string was introduced; this model straightforwardly leads to a dissipative equation of motion for the oscillator after elimination of the string degrees of freedom. Next, the concept of non-holonomic constraint was reviewed and examples given. It was shown that a non-holonomic system can be realized as a certain limiting case of a dynamical system coupled to a field. In this way it is possible to accomplish the quantization of non-holonomic systems. The connection between non-holonomic dynamics and thermostats derives from the fact that the isokinetic constraint (constant KE) is an example of a non-linear non-holonomic constraint. A bracket formalism was used to analyze explicitly the dynamics in the case of equal particle masses and different masses. For the examples considered, equipartition of the KE is not obtained.

The second day of the workshop began with a talk by Stephen Bond (UIUC) on the topic of practical methods for correcting algorithmic bias in constant temperature MD simulations. Both statistical and truncation errors in the computation of ensemble averages using trajectories for (presumably) ergodic systems were discussed. The focus of the talk was on the correction for errors in the conputed invariant density induced by discretization. It was shown how computation of the lowest order terms in the expansion of the modified (shadow) Hamiltonian associated with symplectic integration algorithms allows explicit corrections to be made to computed averages in a computationally tractable fashion. Estimates of the configuration temperature were also discussed.

Brian Laird (Kansas) talked about MD simulation for systems with mixed continous/discontinuous potentials. Such systems include many models of great physical interest, such as dipolar hard spheres or the Weeks-Chandler-Andersen model. A hybrid collision-Verlet algorithm for such systems was discussed. Separation of short-range and long-range portions of the continuous part of the potential gives an algorithm which is globally 2nd order. Thermostatting mechanisms can also been incorporated into the collision-Verlet scheme. An application of the method to the elucidation of the role of attractive forces in atomic diffusion was discussed. At low densities, it is found that the diffusion constant decreases as the strength of the attractive component of the interaction increases; on the other hand, at high densities, increased attraction leads to an increase in the diffusion constant. It was argued that attractive interactions inncrease the free volume in the liquid, hence the entropy.

Alessandro Sergi (UKZN Pietermaritzburg) showed how a suitable generalization of the Poisson structure of the classical bracket and of the symplectic structure of the quantum commutator can be exploited to introduce Nosé dynamics in an extended system formulation of quantum theory in phase space. The case of the Wigner formulation of quantum mechanics was explicitly considered. Both the situations when all the quantum degrees of freedom and only part of them are represented in phase

space were illustrated and both stationary Nosé-Wigner functions and partially Wigner-transformed Nosé density matrices were derived as power series in Plank's constant. Simple spin systems coupled to harmonic baths were explicitly addressed in the Wigner-Heisenberg representation (with just the bath represented in phase space). Numerical evidence was provided of the effectiveness of the Nosé dynamics in quantum phase space to represent the dissipative dynamics of the Spin-Boson model and of a two-spin Heisenberg chain coupled to multiple independent harmonic baths. Although in its first stages, the algorithms presented showed potential for being an alternative numerical approach to certain types of open quantum system dynamics.

Greg Ezra (Cornell) discussed the formulation of measure-preserving integrators for thermostatted systems. It was first noted that most of the deterministic thermostats in common use have the almost-Poisson non-Hamiltonian bracket structure identified by Sergi & Ferrario. Exploiting this structure, it is possible to build explicit, reversible and measure-preserving algorithms for thermostatted systems. Applications to the GGMT thermostat and to BK thermostatted spins were outlined. It was noted that measure preserving integration algorithms lead naturally to the notion of trajectory reweighting schemes based upon the instantaneous value of the energy functions, and are an essential component of the Metropolis modified thermostatting approach of Leimkuhler & Reich. The last part of the talk discussed mappings between Hamiltonian and non-Hamiltonian formulations of the isokinetic thermostat, and introduced the idea of using concepts from molecular reaction rate theory to characterize thermostat dynamics.

Frédéric Legoll (LAMI - ENPC) discussed the fundamental issue associated with all thermostats – ergodicity. He presented the first rigorous mathematical results obtained on the lack of ergodicity in a specific deterministic thermostat; the Nosé-Hoover thermostat coupled to a harmonic oscillator. Because of the low dimensionality of this system, KAM-like results could be applied to show the existence of codimension one barriers in the phase space that prevented ergodicity, but the rigorous proof required a large thermostate "mass". He then discussed the prospects for achieving similar results for higher dimensional systems. The necessary theoretical results are not yet developed, but he presented numerical results that strongly hinted at non-ergodicity, or at least the very slow approach to ergodicity. Finally, he presented preliminary results on the issue of ergodicity in the Nosé-Hoover chain. The lack of a Hamiltonian structure proved limiting, but he discussed a statistical estimator of the "nearness to ergodicity" called the *discrepancy*. This diagnostic appears to show promise as a useful tool for molecular dynamics simulations.

Carsten Hartmann (FU Berlin) presented a method for sampling from the canonical density for a system constrained to a surface (for example, a dividing surface separating reactants and products). The main idea is a scheme for systematically perturbing the momentum components of trajectories of Hamilton's equations in such a way that the configuration components of the trajectory properly sample the Gibbs distribution. A stochastic Hamiltonian system is obtained from the underlying deterministic dynamics by imposing an averaging procedure on the momentum components of the deterministic Hamiltonian system. This particular procedure gave rise to a discrete diffusion-like flow on configuration space which could then be rigorously proven to be ergodic. Hartmann applied this approach to the study of ergodicity in constrained Hamiltonian systems. Simulation requires that the system be discretized, and it was shown that the discretization error could be controlled with a hybrid Monte- Carlo algorithm that allowed the Gibbs distribution to be sampled accurately independently of the step size (provided it was within the stability regime of the algorithm). The effectiveness of this approach was shown by applying the algorithm to the computation of the free energy profile of a peptide. The methods and approach described here show great promise for further applications, extensions, and mathematical development.

Carl Dettmann (Bristol) discussed three broad topics – configurational thermostats, a general scheme for stochastic thermostats, and some new aspects of ergodicity issues. His novel approach to configurational thermostats is based on the configurational Smoluchowski equation. He argued that this approach has the potential for much faster simulations. His general scheme for creating thermostats involves deforming the original dynamical equations of the motion by introducing new variables in such

a way that the correct density is sampled, as verified by solving the Liouville equation. He showed that his configurational thermostat fits within this scheme. Dettmann also explored the issue of ergodicity in a reduced dimensionality model Lennard-Jones cluster. Motivated by work of Rom-Kedar, he argued that the most likely locations of ergodicity in the phase space is where the system dynamics has singularities. This was verified in the Lennard-Jones cluster system with numerical simulations. This work serves to provide new insights into the sources of ergodicity in molecular systems.

Julius Jellinek (Argonne National Laboratory) revisited the Nosé extended system approach. The origins of the non-Hamiltonian dynamics commonly referred to as Nosé-Hoover dynamics were reviewed, and the relevant contributions of Nosé and Hoover discussed. The arbitrariness of the many dynamical flows in phase space, which are consistent with the stationary canonical distribution, was addressed (following Jellinek's important 20 year old paper on the subject) within the Hamiltonian extended system approach. The possibilities, inherent in such arbitrariness, to achieve ergodicity without chaining the Nosé thermostats were stressed. Moreover, the arbitrariness of statistically equivalent Nosé phase space flows suggests novel dynamical methods with features yet to be fully understood and exploited. In the last part of his talk, Jellinek tackled the problem of equilibrium relaxation. He showed that a single global Nosé thermostat is not sufficient and he illustrated a microcanonical approach to describe thermalization in a physically realistic way. Throughout his talk, Jellinek strove to put the physical significance of his own chosen extended system dynamics to the forefront. This was done in a stimulating and intellectually provocative way, which elicited many interactions with the audience and a lively discussion at the end of the talk.

Giovanni Bussi (U Modena) presented a novel and suggestive method for thermostatting systems within a stochastic Langevin approach. A global stochastic sampling of the total kinetic energy of the system, a recipe for partitioning such energy among the various degrees of freedom, together with Langevin dynamics, and an ingenious comparison to the Metropolis Monte Carlo rule of acceptance provide a simple and very efficient stochastic method, with a conserved quantity playing the role of an indicator of the goodness of the sampled trajectories (by analogy with conserved energies in the case of deterministic Hamiltonian and non-Hamiltonian dynamics). Bussi illustrated the effectiveness and robustness of his method by means of the calculation of the dynamical spectrum of water molecules in the condensed phase. An extension from white to coloured noise in the Langevin dynamics also permits one to efficiently handle the adiabaticity requirements of *ab initio* Car-Parrinello dynamics. The final part of Bussi's talk illustrated how a suitable generalization of his own brand of Langevin dynamics can address quantum effects in harmonic systems with excellent results: this is achieved by implementing a frequency-dependent temperature. More study is needed for the general case of quantum non-harmonic systems.

Ben Leimhuhler (Edinburgh) gave a pedagogical overview of the mathematical issues associated with thermostats and sampling. He reviewed some of the most commonly used deterministic thermostats, e.g., Nosé, Nosé-Hoover, Nosé-Hoover chains, Bulgac-Kuznesov, and then argued that small amounts of noise could used to overcome possible lack of ergodicity. The resulting stochastic framework gives rise to a Fokker-Planck description of the thermostat dynamics, and it was shown that in this framework powerful mathematical results due to Hormander could be used to provide rigorous proofs of ergodicity for large classes of thermostats. There appears to be much scope for the future development of these method. Finally, he ended with a novel, and very different application of thermostats to a vortex model in fluid mechanics where the number of degrees-of-freedom of the system was reduced by modeling the neglected degrees-of-freedom by a (low dimensional) thermostat. This example points to a new and very promising application for thermostats in areas where one needs to"close" the system by modeling a large number of "unresolved" dynamical degrees-of-freedom.

Assessment of the results and impact of the event on the future direction of the field

This workshop brought together practitioners from three different communities: mathematicians, theoretical chemists, and computational physicists. Despite different backgrounds and perspectives, it was clear that a core knowledge and language was shared. This was (and certainly will be) key to fruitful exchanges between researchers from different disciplines and for the general advancement of the field.

Some key research areas have been clearly identified, together with relevant subareas. Perhaps the broadest topic is that concerning general algorithm development for temperature control in condensed matter systems. Subareas concerned symplectic integration schemes, measure-preserving dynamical algorithms, configuration space based thermostatting methods, the wide field of stochastic dynamics, and first attempts at quantum thermostats. Not surprisingly, the dynamics of constrained systems emerged as an important topic, with the different problems concerning holonomic and non-holonomic constraints to the fore. The last key area regarded analysis and assessment of the dynamical-statistical properties of the algorithms. "Ergodic" issues were widely discussed, as were methods for correcting algorithmic and statistical bias.

General open issues have also been identified. Some of these problems are so fundamental and difficult that solutions cannot be expected in the near future. Others problems present themselves as exciting opportunities for novel research and advancements in the near term. Particular stress was laid onto the necessity of carefully assessing the physical meaning of the various algorithms and generalized dynamics proposed. The statistical mechanical foundations of canonical ensemble sampling must be examined in light of both ergodic *and* mixing dynamics. Similar considerations also hold for the assessment of equilibrium versus nonequilibrium methods. It has also been acknowledged that there remains a need for the continued development of time-reversible (or measure-preserving) integrators for constrained dynamics. Future comparison of deterministic and stochastic methods has emerged as an important theme, given significant recent novel advancements in the latter area. Symplectic geometric properties of phase space have been addressed and a nice pedagogical (and picturesque) manifestation of the non-squeezing theorem, the so-called 'symplectic camel', reviewed. The general implications of such geometrical phase space properties for classical molecular dynamics remain to be elucidated. Their significance for the phase space formulation of quantum mechanics is also an open and interesting line of research. Finally, the existence of tractable and physically relevant quantization methods for non-Hamiltonian and/or dissipative dynamics has been raised.

Future perspectives should concern not only theoretical development *per se* but, of course, tackling scientific challenges in the application of the various techniques (both those already developed and those that will be probably devised in the near future). Some suggestions were brought forth at the workshop. In particular, it was agreed that finding new ways of exploiting the configurational definition of temperature is very promising. Applications of the various methodologies proposed to nonequilibrium steady states was also suggested. Lastly, an interesting field of application has been identified within inhomogeneous systems, i.e., systems which mix equilibrium and nonequilibrium phases, and/or quantum and classical features. In this regard, the general question arises how thermostatting methods would describe temperature fluctuations in such systems.

Given the wealth of scientific potential for both applications and theoretical development, there was a broad consensus among participants to establish a network of interested scientists, and to plan regular meetings in order to enhance collaborations and boost advancement in the field.