Modelling non-adiabatic processes in materials with correlated electron-ion dynamics

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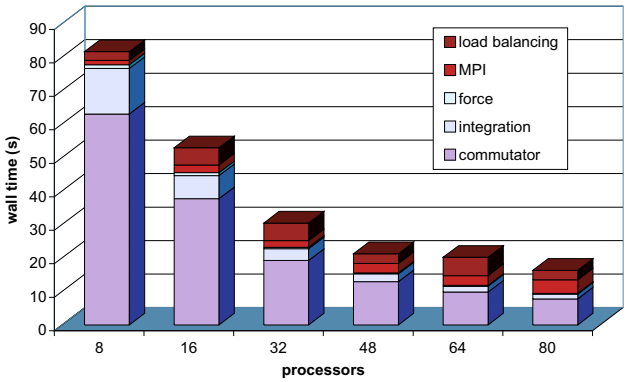

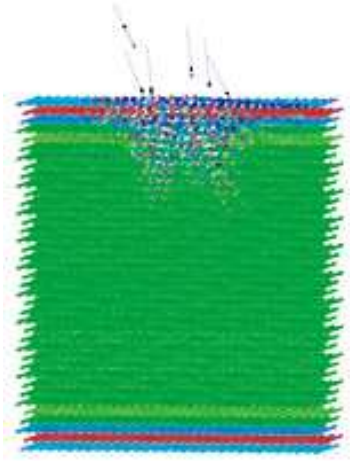

Figure 1 (far left): Performance of splCED on HPCx – wallclock time per update step for a 17,473 atom simulation.

Figure 2 (left): Sputtering simulation using splCED. The system comprises 17473 copper atoms making a film 8nm thick in the y-direction and periodic in the x- and z-directions. A copper ion having a kinetic energy of 500eV is fired at normal incidence into the film. The figure corresponds to a snapshot taken 150fs after the start of the simulation.

An understanding of charge and energy transfer processes is crucial in modelling nanoscale systems in contact with an environment because of their large surface to volume ratio. In modelling these processes, different levels of approximation can be invoked depending upon the problem under investigation. These approximations range from considering the atomic configuration to be essentially fixed in space – the Born-Oppenheimer approximation (BOA) – through mixed quantum-classical descriptions in which a quantum evolution of the electronic subsystem is coupled to a classical description of the ionic subsystem – such as the Ehrenfest approximation – to fully quantum descriptions. The principle drawback of making the BOA is that processes involving the irreversible flow of energy cannot be treated. Examples of such irreversible processes include the heating of metallic atomic wires due to current flow; polaron formation in polymer chains; and friction, plastic deformation and radiation damage in metals. While Ehrenfest dynamics does allow energy transfer, it has recently been shown [1] that although a correct description of the heating of cold electrons by energetic ions is provided, the reverse process – namely the heating of ionic vibrations by hot electrons – is wholly incorrect. The reason for this failure of the Ehrenfest approximation (the treatment of the electrons as a structureless fluid together with a neglect of the correlations between quantum fluctuations of the positions and momenta of the ions with those of the electrons) has recently been addressed in a new method called Correlated Electron-Ion Dynamics (CEID) [2].

As part of EPSRC's Materials Modelling Initiative, a number of groups (based at QUB, UCL and Imperial College) have joined together in a consortium to tackle three exemplar areas of fundamental and strategic significance in materials science where irreversible exchanges of energy between electrons and ions play a central role. They are a) inelastic transport in nanostructures; b) radiation damage in metals; and c) excited states in polymers. This collaboration has resulted in the development of theory, algorithms and associated computer codes that exploit the power of high-performance computer architectures, allowing the treatment of progressively more complex systems at increasing levels of sophistication. Two computational packages have been developed within the consortium to address these scientific problems.

splCED: an Ehrenfest dynamics code for radiation damage

At Imperial College, the focus of research within the CEID consortium has been the investigation of energy transfer from the ionic to the electronic subsystems using dynamical simulations within the Ehrenfest approximation. The aim is to understand the role and characteristics of electronic damping in radiation damage and sputtering. The magnitude of this damping has an important influence on the number of Frenkel defects produced in low energy cascades, and can be directly compared to the frictional damping terms used in classical molecular dynamics simulations [3].

Ehrenfest dynamics simultaneously solves Newton's equations for the motion of classical ions with the quantum Liouville equation for the electrons, with an electronic Hamiltonian that depends parametrically on the ionic positions. As each ion has only n interacting neighbours, the Hamiltonian is sparse. The electronic density matrix describes the electronic state, which in a metal is a dense NxN Hermitian matrix, N being the number of tight-binding (TB) orbitals used. This density matrix is not truncated and its memory cost is thus $N^2/2$ complex numbers, which must be distributed across P processors. The main algorithmic cost is the time evolution of the density matrix, evaluated as the commutator

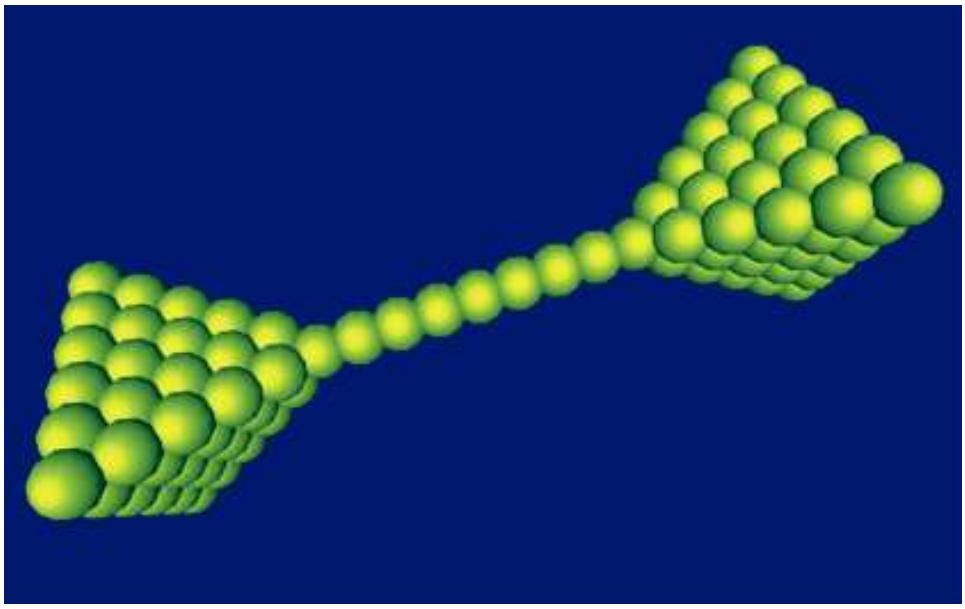

Figure 3: Schematic representation of a nanoscale wire (nine atoms long) connected through two pyramidal contacts to semi-infinite electrodes (the electrodes are not shown). In a typical simulation the electrodes are connected to a charge reservoir (for instance a battery), which results in current flow in the system.

of the Hamiltonian and density matrices, which takes nN^2 floating point operations. A parallel time-dependent TB code (spICED) has been developed to perform Ehrenfest dynamic simulations for systems comprising more than 10,000 atoms and for picosecond timescales. For the first time, we can perform non-adiabatic dynamics in metals at scales hitherto accessible only to classical molecular dynamics. Currently, spICED can handle over 30,000 atoms and scales well up to 128 processors. We still have some load balancing issues, but as the density matrix is updated using only local message passing, we achieve a calculation wall time speed of $3.5nN^2$ nanoseconds per timestep (the timestep is set to 0.05fs simulation time) on 64 processors of HPCx. Figure 1 presents scaling results for a typical simulation for a system comprising 17,473 copper atoms making a film 8nm thick in the y-direction and periodic in the x- and z-directions.

In Figure 2 we present a snapshot taken 150fs after the start of a simulation for the system considered in Figure 1. A copper ion having a kinetic energy of 500eV is fired at normal incidence into the film. In this case we see that six ions are ejected from the surface, with directions indicated in the figure. Atoms are coloured according to their electronic charge, with red denoting 5% electronic charge (ie positive) and blue −5% electronic charge (ie negative). Friedel charge oscillations are seen at the surface, and long focussed collision sequences drive the disturbance deep into the layer.

pDINAMO: an implementation of the CEID equations of motion

The CEID equations extend the Ehrenfest approximation through an expansion of the equations of motion (EOMs) in terms of a hierarchy of electron-ion correlation functions. pDINAMO has evolved from a serial code (DINAMO) originally developed inhouse at QUB to solve the CEID equations. The equations to be solved constitute a tightly coupled set of equations that are currently truncated at second order in electron-ion correlations. This results in a closed set of equations that are propagated in time. As compared to the Ehrenfest approximation, algorithmic and memory costs of the second-order CEID equations scale as $(6M + 1)N^2$ where M is the number of moving CEID ions, and N is the number of basis functions used in our description of the electronic subsystem (currently tight-binding models are used).

One re-engineering phase of pDINAMO has already taken place and a second is commencing. Each of these phases has been initiated by a need to both improve performance and scalability of the code (thus increasing the range of problems that can be tackled) and also in order to implement additions to the continuously developing theory. In order to produce a fully scalable code, two levels of parallelization are required: firstly, the distribution of correlation matrices (the N^2 scaling); secondly, the distribution of correlation matrices corresponding to different moving ions (the $6M + 1$ scaling). The code currently implements the first level of parallelization and scales in a similar fashion to spICED. Implementation of the second level of parallelization is currently underway and will allow us to treat large numbers of moving CEID ions: currently we are limited to the treatment a maximum of 40 CEID ions, depending on the size of the system under investigation. As an example, the treatment of a large number of CEID ions (>100) is crucial in order to correctly describe electron-phonon couplings in photoexcited conjugated polymers and in the subsequent investigation of the influence of these couplings on the dynamics.

Very recently, a revised formalism for CEID has been developed to address some theoretical and numerical features of the original

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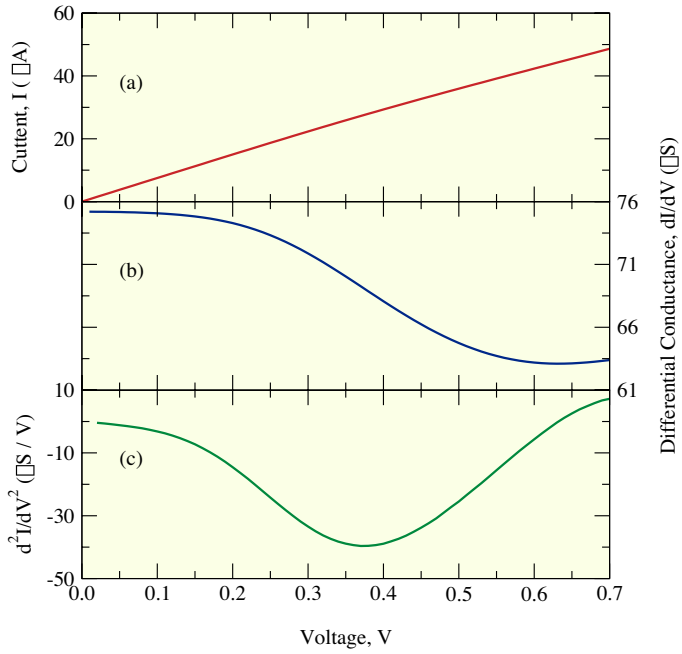

Figure 4: current-voltage (I-V) spectrum of a perfect chain. The chain consists of 601 gold atoms (with the atomic masses set to one atomic mass unit), the three central atoms being allowed to move. The equilibrium bond length of all atoms in the chain is 2.45Å. In the Figure, (a) represents the current as a function of applied voltage, (b) is the differential conductance and (c) the derivative of the differential conductance.

Modelling non-adiabatic processes continued

truncation scheme [4]. Numerical simulations of a model two-level system based on this new approach have provided further evidence of the soundness and generality of the CEID idea. As a consequence, this formalism – originally introduced for purely theoretical reasons – has made necessary substantial code development at UCL. Simulations of test models involving many degrees of freedom (e.g. the spin-boson model) are now under consideration at UCL to validate the scheme for more complex and physically relevant cases. Once again, the long-term goal of this revised CEID formalism is a general-purpose code to simulate the non-adiabatic dynamics of a many-atom system, and in particular non-radiative processes in polymers. A final merging of this code into pDINAMO is also an interesting future possibility.

To date, pDINAMO has been extensively applied to the study of electrical conduction in atomic wires at QUB. Experimentally, it has become possible to make chains of single atoms between two electrodes, pass a current along this chain and study the effects of the current flow on the atoms in the wire. A typical setup is shown in Figure 3. Theoretically, it has become possible to calculate the current that flows through an atomic wire and to make predictions about the local heating of the wire, about forces that the current exerts on individual atoms, and about the critical voltages at which the current blows the wire to pieces [5]. These predictions have been verified experimentally [6]. Most recently, a fresh wave of theory has started to focus on the dynamical quantum description, in real time, of current and of the interaction between current-carrying electrons and vibrating ions in nanodevices. In addition to current-induced local heating, we are interested in modelling inelastic current-voltage (I-V) spectroscopy [7]. Correlated inelastic interactions between electrons and ions under current flow result in inelastic features in the I-V spectrum, which appear as peaks or dips in the second derivative of current with respect to voltage. Figure 4 illustrates the I-V spectrum of a perfect chain, with equilibrium bond length of 2.45Å. In the simulation, the chain consists of 601 gold atoms (with the atomic masses set to one atomic mass unit), the three central atoms being allowed to move. The I-V features were obtained by calculating the steady-state current for 100 applied voltages (100 separate calculations). In the absence of inelastic interactions, the current as a function of voltage would be a straight line with slope 77.46 μA/V (the Landauer conductance G_0). With the inclusion of electron-phonon interactions in this system, the current (Figure 4, a) is reduced due to inelastic backscattering and the conductance is no longer constant (as is seen from Figure 4, b and c). Further analysis of the time-dependent results has allowed us to ascertain that the dominant contribution to the inelastic spectrum comes from a vibrational mode corresponding predominantly to motion of the central atom with much smaller amplitudes on the other two. Future work in this area will include the simulation of more realistic geometries (going beyond simple atomic chains and considering much larger system sizes) and investigating the effect of electron-electron screening.

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