

# Perspectives of Molecular Dynamics

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## Synopsis

A brief, tutorial summary of recent developments in molecular dynamics simulations is given, with a view of their application to the interaction of energetic ions with solid substrates. In particular, the following topics are discussed: (i) interatomic potentials, (ii) ensembles and phase space sampling, and (iii) description of inelastic processes.

## 1 Introduction

Molecular Dynamics (MD) simulation is a widely used technique for modelling complicated physical phenomena, with applications ranging from galaxy dynamics to protein folding. In materials science, MD simulations consist of calculating numerically the trajectories of a number of interacting atoms over a given time interval. The technique allows one to model the complex dynamical behavior of materials, provided that the relevant spatial and temporal correlations can be contained within the finite size and time span of the simulation. Physical properties, including thermodynamic quantities (for an excellent treatise, see Allen and Tildesley 1987), can then be calculated as appropriate temporal averages of the simulation data. Statistical analysis of the simulation sequences yields information on the dynamic properties of the system.

Ion-solid and ion-surface collisions, including sputtering processes, constitute a complicated set of problems well amenable to molecular dynamics simulation. In fact, a computer simulation (Gibson et al. 1960) of radiation damage induced by an energetic primary-knock-on atom was one of the earliest applications of the MD technique in materials physics. An MD study of the sputtering process

entails all the important and challenging ingredients of a meaningful simulation: atomic interactions, non-equilibrium (energy transfer) aspects, ensemble averaging, dissipation and boundary conditions. Below, I shall discuss current issues related to these from the viewpoint of sputtering. An extensive treatment of simulation of ion-solid interactions has recently been published (Eckstein 1991). A comprehensive review of computer simulation of sputtering by Robinson is included in this volume (Robinson 1993). Recent MD simulations of sputtering have been summarized and compared in the round-robin study of Sigmund et al. (1989). Several groups are now actively applying the MD techniques to sputtering and related processes (Garrison et al. 1998, Hsieh and Averback 1990, Shapiro and Tombrello 1992, Karetta and Urbassek 1992, Wucher and Garrison 1992).

## 2 Atomic Interactions: The Potential Problem

Depending on the physical circumstances one wants to simulate, the number of atoms included in an MD study ranges from a few tens to hundreds of thousands, and the relevant simulation time span is from femtoseconds up to nanoseconds. One is faced with a compromise as regards the number of atoms, the simulation time, and the description of the interatomic force laws.

At high energies (small interatomic separations), the atom-atom interaction is dominated by the two-body (dimer) term. At lower energies, especially near the equilibrium, the pair potential approximation is usually totally inadequate (except in the case of inert gas systems): the total energy of the condensed state cannot be expressed as a sum over pairwise interactions. It is customary to say that there is a volume or density dependence in the total energy. For a simple metal such as Al, in fact most of the cohesive energy is in the 'electron gas' term due to delocalised conduction electrons, with only a weak dependence on structure and interatomic distances.

There is no well-defined rule to determine when the two-body description becomes invalid. In fact the proper strategy of choosing the potential depends critically on what one wants to simulate. For the most energetic atoms in the collision cascade, with their kinetic energies large compared to the cohesive energy, it is often valid throughout the relevant time span. For example, the scattering trajectories of primary hyperthermal ions (energies above a few tens of eV) can be well calculated from pairwise summed repulsive interactions. The scattered ions mainly bounce off the surface. However, if one in the same situation is interested in such follow-on events as damage production in the substrate, many-atom interactions between the substrate atoms are necessary. Pairwise force laws cannot be used for quantitatively reliable calculations of such quantities as defect formation and

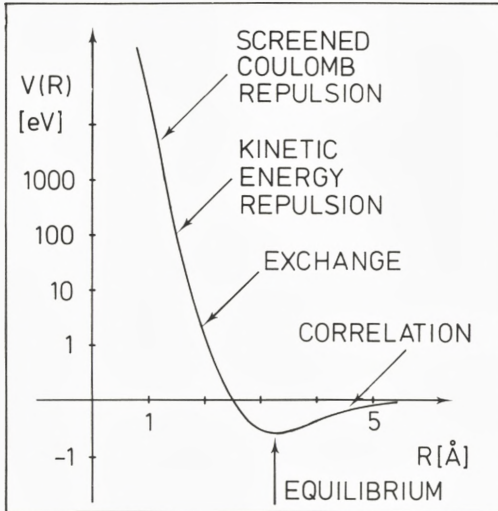


Figure 1. Schematic presentation of the interatomic potential, with the main physical effects indicated for each energy region.

migration energies or, in the case of sputtering, binding energies of surface atoms.

## 2.1 Two-Atom Potentials

The generic form of a two-body interatomic potential is depicted in Fig. 1. First of all, it is important to recognize the difference between the adiabatic and diabatic potential. The former corresponds to the situation where, according to the Born-Oppenheimer principle, the electrons remain at their instantaneous ground state with respect to the nuclear separation. The adiabatic potential allows for charge transfer between the interacting atoms. In the case where the incoming ion is in molecular form, it also allows for its eventual dissociation. The diabatic potential describes the case where the collision takes place at such speed that the electrons have no time to adjust to the ground state, but are constrained. The diabatic potential energy is always higher than the adiabatic one.

Again, there is no quantitative, general rule as to which potential is the physically relevant one. It is intuitive to think that one should use the diabatic description, corresponding to the initially chosen charge states for the atoms, at high kinetic energies which are large compared to the electron ionisation energy or affinity (velocities large compared to Bohr velocity).

Fig. 1 also shows schematically the major physical origin of the adiabatic two-

atom interaction at various separations. The two-atom problem can be essentially regarded as exactly solved (numerically). The two most popular approaches to this problem are known as the Hartree-Fock (HF) method and density-functional theory (DFT) (see, for example, Jones and Gunnarsson 1989). They only differ in the way they treat the electron-electron interactions. HF treats the electronic exchange (Pauli principle) exactly but neglects the remaining correlations. They can be reintroduced using sophisticated perturbation theory (configuration interaction, CI). DFT treats exchange and correlation on the same approximative level, usually within the so-called local density approximation (LDA). Except near the two-body attractive minimum, they give for the present purposes identical results. At the minimum, DFT-LDA usually leads to overbinding while HF gives underbinding. By increasing the sophistication of correlation treatments, both approaches can be pushed near ‘chemical’ accuracy, i.e. binding energies of even larger aggregates than dimers can be calculated to a small fraction of an eV. The proponents of both methods use the description *ab initio* for each of the techniques.

There are by now several computer programs available which provide the HF or DFT numerical solution. Examples of commercially supported programs are the Gaussian92 (trademark of Gaussian, Inc., Pittsburgh, Penn., USA), DMol (trademark of Biosym, Inc., San Diego, Calif., USA) and the UniChem (trademark of Cray Research, Inc., Eagan, Minn., USA) program packages. Thus, for accurate two-atom potentials, there is no need to resort to analytic, statistical or empirical approximations so popular in the past literature. For example, one can evaluate exactly the so-called ‘screening function’ in the high-energy region where the intra-nuclear Coulomb repulsion dominates.

The electronic structure programs can also be used to evaluate the diabatic potentials. This requires that the electronic state be constrained, for example to a fixed electronic configuration (charge state) for the constituents. While the powerful variational property is strictly valid for the ground state only, it can be extended to the total energies of the lowest excited states of a given symmetry.

## 2.2 Many-Atom Interactions

Let us now return to the general case where there are several interacting atoms present in the relevant region. Again, in the adiabatic case the electrons adjust themselves to the ground state corresponding to the given nuclear coordinates. In DFT, the total electron density  $n(\mathbf{r})$  is the key variable, the ‘glue’. The Hohenberg-Kohn theorem (Hohenberg and Kohn 1964) underpinning DFT guarantees that the total energy  $E$  is a unique functional of  $n(\mathbf{r})$  and that  $E\{n(\mathbf{r})\}$  is minimised at the ground state. This guarantees the applicability of the important and useful variational principle. Moreover, the interatomic forces can be exactly calculated

using the Hellmann-Feynman theorem.

### 2.2.1 First-Principles Molecular Dynamics

First-principles MD is a method where one actually solves for the electronic (ground) state at each time step with its nuclear coordinates, and calculates the exact forces as derivatives of the total energy functional with respect to nuclear coordinates. It sounds like a formidable task, but with clever algorithms (Car and Parrinello 1985; for a recent review, see Galli and Parrinello 1991) it is now possible to carry out this task, at least for modest-size systems near their equilibrium.

The key idea is , instead of exact solution of the electronic degrees of freedom ('diagonalisation') at each timestep for nuclear motion, to solve for all the degrees of freedom in unison ('iterative diagonalisation'). This is accomplished by casting the problem into the form of global optimisation of the total energy functional in the space of both the nuclear coordinates  $\mathbf{R}_i$  and the electronic wavefunctions  $\psi_i$ . The search in the phase space is done through classical equations of motion, where the driving forces are the Hellmann-Feynman forces for the nuclear coordinates, and the deviation from exact diagonality for the electronic amplitudes. An arbitrary inertia parameter ('mass') can be assigned the electronic equations of motion, and the associated fictitious kinetic energy ('electron temperature') can be adjusted to obtain optimal convergence and closeness to the Born-Oppenheimer surface. This process is called 'simulated annealing'; alternative techniques can be preconditioned conjugate gradients (Stich et al. 1989). The real temperature is naturally associated to the nuclear kinetic energy, as in classical MD.

The Car-Parrinello technique is usually implemented using plane waves as the basis set for expanding the electronic eigenstates. This set of functions is convenient for dynamic simulations as its resolution is uniform, i.e. no a priori assumptions of the relevant atomic positions need to be made. Moreover, the plane wave expansion (Fourier analysis) can be made efficiently using the Fast Fourier Transform. The drawback is that rapidly varying electronic states cannot be described by feasible numbers of Fourier terms. The technique is thus usually coupled to the pseudopotential method (Heine and Weaire 1970, Bachelet et al. 1982), where the electronic core states are projected ('pseudized') out. This seriously hampers its usefulness for atoms with deep pseudopotentials such as transition and noble metals with d-like electrons. There have recently been suggestions (Vanderbilt 1990, Laasonen et al. 1991) on how to define 'ultrasoft' pseudopotentials for these materials to make them feasible for plane wave -based methods.

Even with the pseudopotential method, the Car-Parrinello technique is computationally heavy, requiring thousands of plane waves for each eigenstate and thus a huge number of degrees of freedom to be optimised. Thus far most of its im-

plementations have been restricted to a few tens of atoms moving gently near the equilibrium. Its most spectacular successes have been with obtaining true ground state geometries and energies in complicated low-symmetry situations, such as the  $(7 \times 7)$  reconstruction on the Si(111) surface (Stich et al. 1992, Brommer et al. 1992). A few studies of true dynamics, such as diffusion processes and phonon densities of states have been reported (Galli et al. 1989, Buda et al. 1989). However, with advances in large-scale computing, such as massively parallel processing, one can expect significant advances in near future. A low-energy sputtering process involves a fairly small number of atoms. If the relevant time span (bond breaking, atomic transport) is not too long (say, 1 psec) one can imagine attacking sputtering with first-principles MD soon.

### 2.2.2 Tight-Binding Molecular Dynamics

Significant savings in computing requirements can be obtained with simplified descriptions of the electronic total energy. The tight-binding (TB) Hamiltonian (see, for example, Harrison 1980) is a well-tested approximation for several condensed matter systems. It retains the quantum-mechanical nature of the electronic kinetic energy, but replaces the electron-ion and electron-electron interactions with a simple operator. The electronic states are represented in terms of a small set of localised basis functions, which leads to a much less heavy diagonalisation problem. The number of atoms in TB-MD can be an order of magnitude larger than in a comparable Car-Parrinello simulation. The TB-MD technique has recently been applied for several problems in semiconductor physics (Laasonen and Nieminen 1990, Virkkunen et al. 1991, Wang et al. 1991).

### 2.2.3 Approximate Many-Atom Energy Functionals

A major simplification of MD results from making the approach totally classical. The overwhelming majority of MD work to date falls into this category. I have already stressed the fact that two-body classical potentials cannot be expected to work in general. Another demonstration of this comes from exact calculations for total energies of ordered atomic structures with different symmetries and coordination numbers (Goodwin et al. 1990). The obtained formation energies show a strong nonlinearity as a function of coordination number, while a pairwise interaction model should give a straight line. In fact, the curvature seems to follow a square-root behavior obtained from a simple tight-binding model.

Another way of looking at the many-atom interactions is to estimate the energy by building, atom by atom, the aggregate of the desired structure. For example, one can estimate the cohesive energy by 'embedding' an atom to an existing vacancy in the medium. The vacancy contains some electron density from the neighboring

atoms. To a first guess, the embedding energy can be approximated by the energy required to immerse the atom into an electron gas (Puska et al. 1981) with that average density. This energy has a nonlinear dependence on the total density, and thus cannot be reduced back to a superposition of pairwise terms from the individual atoms.

The above is the physical motivation to a class of classical many-atom energy functionals. These include the Effective-Medium Theory (EMT (Jacobsen et al. 1987); the Embedded Atom Model (EAM) (Daw and Baskes 1983, 1984); the Finnis-Sinclair-potential and its extensions (Finnis and Sinclair 1984, Ackland et al. 1987); and the Glue Model (Ercolessi et al. 1986, 1988). In all of these, one can write the total energy in the generic form

$$E_{\text{tot}} = \sum_i F(n_i) + \frac{1}{2} \sum_{i,j} \phi(R_i - R_j) + E_{\text{bs}}. \quad (1)$$

Above,  $F$  is a (nonlinear) function of the electron density  $n_i$  at the site of atom  $i$ , arising from the neighboring atoms interacting with it. This term contains the density or volume dependence of the total energy, it depends on the coordination number but is less sensitive to the structure. The second term is a (pairwise) summation of potentials  $\psi$  of electrostatic origin. This term also contains the short range core repulsion necessary to stabilise the structure. The third term is a correction term, in some formulations associated with the single-particle eigenvalues (the band-structure energy).

The many-atom descriptions of the form sketched in Eq. (1) were first developed for close-packed fcc crystals, and contained nearest-neighbor interactions only. They have subsequently been made more general in the sense that other crystal symmetries have been included, and that interactions beyond nearest neighbors have been included (Häkkinen and Manninen 1989). The latter feature is of course necessary in order for the model to distinguish between hcp and fcc structures and to calculate stacking fault energies. For recent summaries, see Jacobsen's review (Jacobsen 1988) for the EMT model and Baskes' article (Baskes 1993) for the EAM model.

Many-atom potentials can also be derived through perturbation theory, based for example on the idea of pseudopotentials and dielectric screening (Moriarty 1982). Summaries of all the recent ideas and results for many-atom interactions have been published in two workshop proceedings (Nieminen et al. 1990, Haydock et al. 1991).

## 2.3 Empirical Many-Atom Potentials

For directionally bonded materials such as tetrahedrally coordinated solids, several classical, empirically motivated many-atom potential models have been proposed. Famous examples include the Stillinger-Weber potential for Si (Stillinger and Weber 1985), the carbon potentials suggested by Tersoff (Tersoff 1989) as well as several models suggested for hydrogen-bonded substances such as water (Schweizer and Stillinger 1984). Their utility in MD simulations for ground state properties varies. In general, one should be aware of the limited general applicability of empirically determined potentials outside the particular set of properties used to fit their parameters: it is sometimes difficult to ‘cheat’ quantum mechanics.

One final remark on the atomic force laws is in order. In sputtering simulations, considerable attention has been paid to modelling of the substrate surface. This is natural, as the ejection energy and angular distribution of the sputtered particles depend on the surface geometry and energetics. A proper MD model should contain the surface structure and binding inherently, without any extra assumptions or explicitly introduced surface potentials.

## 3 Ensembles and Phase-Space Sampling

The traditional and simplest way of performing MD simulations is to use the microcanonical (constant-NVE) ensemble, i.e. to solve the equations of motion for a fixed number of atoms in constant volume and with conserved total energy. Extended systems are simulated by using periodic boundary conditions in one or more dimensions. The standard algorithm for the numerical solution of the equations of motion is the velocity-Verlet method in one of its disguises. The technical issues of MD simulation have been presented in several texts (Heermann 1986).

### 3.1 Constant-Pressure and Constant-Temperature Simulations

In many cases, the microcanonical ensemble is not, however, the physically correct one to perform the simulations in. The MD method can be extended to other ensembles. The constant-NpH simulation corresponds to the case where the pressure  $p$  and enthalpy  $H$  are conserved, and the cell volume can change dynamically. The relevant equations of motion were first presented by Andersen (Andersen 1980), and can be efficiently implemented for MD simulations. Nosé and Klein (Nosé and Klein 1983) developed an extension to the canonical (constant-NVT) ensemble, where the temperature  $T$  is kept constant. The standard implementation of this method nowadays involves the equation of motion for the so-called Nosé-Hoover



(Hoover 1985) thermostat.

The physically most appealing ensemble is one where both pressure  $p$  and temperature  $T$  are the pre-chosen thermodynamical variables. Nosé (Nosé 1984a, 1984b) presented the extension to the constant-NpT case. Unfortunately, the set of equations of motion becomes rather cumbersome in this case, and the method has not yet been extensively applied in practical simulations.

### 3.2 Constrained Molecular Dynamics

An often occurring situation in MD simulations is that one wants to impose constraints on a given subset of degrees of freedom. For example, in a simulation for a molecular system it may make sense to keep the bond lengths fixed, but allow the positions of molecules and their angular orientations to evolve freely under the intermolecular and intramolecular forces. An especially useful technique to treat holonomic constraints has been presented (Ryckaert et al. 1977). This constraint dynamics approach uses a set of Lagrange multipliers to represent the forces required to keep the desired distances (or angles) constant. The constraint forces are updated at each timestep and are correct to the same order of accuracy as the integration algorithm.

### 3.3 Heating and Boundary Effects in Sputtering Simulations

Also in sputtering simulations, the choice of the ensemble is of some importance. For short-time collision dynamics and ejection processes, the microcanonical ensemble seems the obvious choice. However, for longer time scale effects such as structural relaxation, damage production and annealing, and eventual equilibration, other ensembles are more appropriate. For example, swelling and eventual blistering of the sputtered surface requires volume relaxation, i.e. the constant-pressure ensemble.

The incident ion deposits kinetic energy into the substrate. While some of this energy is dissipated to the electronic degrees of freedom (see Ch. 4 below), the temperature (the ion kinetic energy) in the substrate rises. In MD simulations with accumulating dose, this eventually leads to unphysical heating of the sample. Moreover, if periodic boundary conditions are used, the hot and damaged region has periodic images throughout the surface.

A possible way to avoid unphysical heating is to embed the simulation unit cell into an unperturbed and cool substrate. This can be accomplished by defining a ‘skin’ region for the unit cell where the ion velocities are repeatedly scaled so that its mean temperature corresponds to the desired bulk temperature. The ion positions at the cell boundary can be fixed at their unperturbed values. This technique

corresponds to the presence of a heat bath which ‘dissolves’ the deposited kinetic energy, and corresponds to rapid heat diffusion out of the sputtered region in a real physical system. However, care should be taken to choose the simulation conditions such that no spurious effects are introduced, for example by reflection (Laakkonen and Nieminen 1990) of the heat pulse due to the cascade off the skin. It is advisable to carefully test the simulation setup for the size of the unit cell and the cooling strategy so that they do not affect the phenomena from which one is gathering statistical information through the simulation.

Another possibility for introducing heat bath effects is to augment the deterministic MD equations with Langevin-type viscous forces affecting the atoms near the cell boundary (Tully 1980). The friction coefficients can be adjusted so as to mimic the desired heat dissipation into the substrate.

### 3.4 Free-Energy Simulations

MD simulations can also be used to obtain entropic contributions, e.g. free energies. The standard simulation produces a trajectory in the phase space, corresponding to a fixed total or kinetic energy for the Hamiltonian  $H$ . A direct evaluation of the Helmholtz free energy  $F$  would require the computation of a configurational integral, which is very hard due to the rapidly varying integrand. A practical free energy calculation can be based on the idea of coupling constant integration (Squire and Hoover 1969). One chooses as a reference Hamiltonian  $H_0$  one for which the free energy  $F_0$  is known e.g. the ideal gas or the harmonic solid. Then the free energy for the real system is

$$F = F_0 + \int_0^1 d\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle \quad (2)$$

where  $H(\lambda) = H_0 + U(\lambda)$  so that  $\lambda = 0$  corresponds to the reference system while  $\lambda = 1$  corresponds to the real system. The brackets denote the thermodynamic (canonical) average. By performing a series of MD simulations for selected values of the coupling constant  $\lambda$ , one can estimate the free energy.

### 3.5 Hybrid Monte Carlo -Molecular Dynamics

A fundamental limitation of the MD technique is the explicit dependence of the calculated sequences and averages on the chosen time step. On the one hand, this implies the possibility of numerical instabilities for the algorithm. On the other hand, for canonical simulations the MD technique can be extremely inefficient in the sampling of the phase space (long simulations are very costly). Monte Carlo (MC) methods in statistical physics are based on a stochastic process, where atom

positions are updated randomly and the new configurations are accepted using the Metropolis criterion. Even if the updates are usually done locally, the canonical minimum can be found effectively, except near phase transitions where critical slowing down renders the algorithm very slow. The other obvious drawback of the MC method is that there is not a real ‘clock’ in the system, i.e. no quantitative dynamics can be obtained.

The hybrid MC-MD algorithm (Mehlig et al. 1992) is one which combines some of the appealing features of both methods. Like in MD, one generates new configurations through a deterministic algorithm (equations of motion). However, the timestep can be chosen large so that truncation errors introduce a nonconservation of the total energy. After a while, the new configuration (with a new total energy) is checked using the standard Metropolis criterion. If the algorithm for the equations of motion is time reversible and preserves the phase space volume, one can show that the canonical distribution is obtained. The algorithm is effective as most of the updates are global (as in MD), yet large drifts in the internal energy are possible. Even if the interpretation of real time is not clear in this method, it seems to provide an interesting alternative for MD simulations requiring very long time scales.

## 4 Non-Equilibrium MD: Electronic Cooling

Energetic ions transfer energy to the electronic subsystem as well. The phenomenon of electronic stopping is important and much studied in ion implantation. Electronic excitations can lead to direct desorption of surface atoms (‘electronic sputtering’) (Avouris et al. 1987), which can simply be thought as being due to the transfer between the adiabatic and diabatic potential energy curves, induced by the incoming ion. In collisional sputtering, ion-electron energy transfer shows up in two ways. Firstly, the trajectory and the range of the primary ion is affected by the inelastic losses to electrons. Secondly, the kinetic energy of the substrate atoms having undergone collisions decreases. The latter is particularly important in such cases where dense ‘thermal spikes’ are formed near the end of the cascade. The spike can cool much faster if the energy-loss channel to electrons is open. The faster cooling rate has an effect on such phenomena as defect production and mixing, and can also affect sputtering.

Quantitative theories of electronic cooling of collision cascades have recently been presented. The key ingredient in these theories is the energy loss rate for a swift ion, a problem first discussed by Bohr (Bohr 1913), Fermi and Teller (Fermi and Teller 1947), Lindhard (Lindhard 1954) and subsequently dealt with by several investigators. In the case where the ion is traversing an electron-gas-like metal with

a velocity small compared to the electron Fermi velocity, one can rigorously show that the stopping power (energy loss per unit distance) is proportional to the ion velocity:

$$-\frac{dE_{\text{kin}}}{dx} = \alpha(Z, n)\sqrt{E_{\text{kin}}}. \quad (3)$$

The proportionality constant  $\alpha(Z, n)$  can be related to the scattering cross section of Fermi surface electrons off a stationary ion, a quantity which can be calculated exactly using density-functional theory (Puska 1990). It is important to realise that  $\alpha(Z, n)$  depends in a nonlinear fashion on both the ion nuclear charge  $Z$  and the electron density  $n$ . Note that the same or closely related constant appears in such diverse physical quantities as impurity resistivity, vibrational lifetimes, electron-phonon coupling and spin-lattice relaxation time.

Calculated values for the ‘friction parameter’  $\alpha(Z, n)$  have been tabulated by Puska and Nieminen (Puska and Nieminen 1982). The electronic friction can (and should) be implemented in sputtering MD simulations by simply adding a velocity-dependent damping term to the equations of motion.

A problem closely related to the electronic stopping power is the energy transfer rate from a collection of mobile atoms to electronic (single-particle) excitations. Let us consider the ionic motion as being described by the dynamic structure factor  $S(\mathbf{q}, \omega)$  for fluctuations. This can include both single-ion motion and collective (phonon-like) excitations. Using the Fermi Golden Rule, one can write the energy exchange rate  $\dot{U}$  between the ionic and electronic systems as (see, for example, Koponen 1992)

$$\dot{U} = \frac{2\pi}{n} \int_0^\infty d\omega \sum_{\mathbf{k}, \mathbf{k}'} \hbar\omega \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'} - \hbar\omega) |T_{\mathbf{q}}|^2 \cdot [f_{\mathbf{k}}(1 - f_{\mathbf{k}'})S(\mathbf{q}, \omega) - f_{\mathbf{k}'}(1 - f_{\mathbf{k}})S(-\mathbf{q}, -\omega)], \quad (4)$$

where one has assumed a monovalent metal for simplicity. Above,  $\varepsilon_{\mathbf{k}}$  denotes the electron single-particle energy with wavevector  $\vec{k}$ , and  $f_{\mathbf{k}}$  is the Fermi distribution function. By interpreting  $T_{\mathbf{q}}$  as the t-matrix for electron-ion scattering, the nonlinear screening effects are included in Eq. (4) and it can therefore be made consistent with Eq. (3).

Stoneham (1990) has recently reviewed the consequences of electron-ion coupling for collision cascades in solids. Based on the ideas of Flynn and Averbach (1988), Finnis et al. (1991) have recently made a quantitative study of the thermal excitation of electrons in energetic displacement cascades. Using both a continuum (diffusion) model for the cascade and an MD simulation with explicit friction forces derived from a thermal model, they showed that electron-phonon coupling has a pronounced effect on cascade cooling. For example, the 2-keV cascade quenches

much faster in Ni than Cu, basically due to the much higher density of electronic states near the Fermi level. Koponen and Hautala (1993) have carried out related studies of the effect of electronic cooling on ion-beam-induced mixing.

Caro and Victoria (1989) have described a similar scheme of adding a velocity-dependent damping term to the equations of motion. They suggest an empirical interpolation formula, based on the local electron density encountered by the moving ion, for obtaining the energy-dependent electron-ion coupling throughout the whole cascade history. In effect it interpolates between the ‘stopping region’ (Eq. (3)) and ‘thermal region’ (Eq. (4)).

The experimental verification of the electronic effects in collision cascades is still controversial, and the quantitative importance of the ion-electron energy exchange is not settled. The effects manifest themselves indirectly in defect product rates, defect mobility and short-term annealing. It would be highly desirable to devise novel experiments to establish the electronic cooling effect unambiguously.

Recently, the inverse process where energy is transferred from the electronic subsystem to the ions, has been investigated. This is accomplished experimentally by picosecond laser-pulse irradiation of metallic surfaces (Herman & Elsayed-Ali, 1992). Häkkinen & Landman (1993) have carried out MD simulations of the associated superheating, melting, and annealing for Cu surfaces, using the methods outlined above.

## 5 Algorithms and Implementation

MD simulations are typically at the forefront of computational physics. Ambitious projects require supercomputer resources. The computational cost of classical MD with short-range forces scales linearly with the number of particles  $N$ . (Long-range Coulomb forces require special Ewald summation techniques). The time-step  $\delta t$  for numerical solution should be chosen so that the most energetic ions do not move too much (compared to typical atom distances) during  $\delta t$ . In practical sputtering simulations,  $\delta t$  is in the average of the order of  $10^{-15}$  s. Let us assume that one needs 100 floating-point operations per atom and time-step to calculate forces and update the position and velocity. A modern vector supercomputer processor can execute up to the order of  $10^9$  floating-point operations per second. This implies that one can simulate  $10^{-8}/N$  real-time seconds for every computer-second. For a unit cell of  $10^3$  atoms, this means that each computer second corresponds to 10 ps of real time. Assuming that one needs 100 simulation histories to get acceptable statistics, the cost for simulating a 1 nsec real-time physical process is of the order of 3 CPU-hours on a supercomputer.

For first-principles MD, the numbers are much worse. First of all, the time step

is determined by the quantum resolution and is typically around  $10^{-16}$  s, a factor of 10 shorter than in the classical case. The ionic (classical) part scales as discussed above, but the electronic part is much more costly. The computational cost is for large systems proportional to  $N^3$ . This arises from the need to orthogonalise the wavefunctions. Moreover, the proportionality constant can be very large as it depends on the number of basis functions  $M$  required to represent each (occupied) eigenstate. (The iterative Car-Parrinello technique saves one from explicit full matrix construction and diagonalisation. The Fast Fourier Transform takes of the order of  $M \ln M$  operations to go between the real and reciprocal space.) The numbers add up such that even with a  $10^9$ -flop/s supercomputer one is limited to around 100 atoms, and that one computer-second translates to roughly one timestep.

Parallelisation of MD computing, both classical and quantum, is an area of active research and development. It is natural to think that since the physics in Nature takes places in parallel, one should be able to write such algorithms and programs which can effectively utilise the architecture of a (massively) parallel supercomputer. Early experiences show considerable promise that within the next few years one can widen the scale of MD simulations by an order of magnitude. This will bring more dynamic phenomena within the reach of first-principles MD simulation.

## 6 Conclusions

MD simulation techniques have progressed in a spectacular way during the last decade. The sophistication and accuracy of representing atomic interactions has reached a level, where structural, thermodynamic, and energetic properties can be reproduced and predicted reliably. It is also possible to investigate (with classical force laws) dynamic phenomena over time scales in tens of nanoseconds.

MD is basically a deterministic simulation technique, whereby thermodynamic ensemble averages are replaced by temporal averages. Their equivalence assumes the satisfaction of the ergodic principle, and requires that proper care is taken to avoid spurious effects arising from boundary and initial conditions, truncation errors etc. The statistical analysis of the 'computer experiments' should be made properly. The reliability of the assumed force laws should always be critically examined for the physical phenomenon in question. One should be aware of the dangers of over-interpretation of incomplete or unreliable data, just as in the case of real experiments. With those caveats in mind, it is easy to comprehend the enormous possibilities the MD techniques provide in modelling complicated materials phenomena and processes, such as sputtering.

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## References

- Ackland GJ, Tichy G, Vitek V and Finnis MW, 1987: *Phil. Mag.* **A56**, 705
- Allen MP and Tildesley DJ, 1987: *Computer Simulation of Liquids* (Clarendon, Oxford)
- Andersen HC, 1980: *J. Chem. Phys.* **72**, 2384
- Avouris PH, Kawai R, Lang ND and Newns DM, 1987: *Phys. Rev. Lett.* **59**, 2215
- Bachelet GB, Hamann DR and Schlüter M, 1982: *Phys. Rev.* **B26**, 4199
- Baskes MI, 1993: *Phys. Rev. B* (to be published)
- Bohr N, 1913: *Phil. Mag.* **25**, 10
- Brommer KD, Needels M, Larson BE and Joannopoulos JD, 1992: *Phys. Rev. Lett.* **68**, 1355
- Buda F, Chiarotti G, Car R and Parrinello M, 1989: *Phys. Rev. Lett.* **63**, 294
- Car R and Parrinello M, 1985: *Phys. Rev. Lett.* **55**, 2471
- Caro A and Victoria M, 1989: *Phys. Rev.* **A40**, 2287
- Daw MS and Baskes MI, 1983: *Phys. Rev. Lett.* **50**, 1285
- Daw MS and Baskes MI, 1984: *Phys. Rev.* **B29**, 6443
- Eckstein, W, 1991: *Computer Simulation of Ion-Solid Interactions* (Springer, Heidelberg)
- Ercolessi F, Tosatti E and Parrinello M, 1986: *Phys. Rev. Lett.* **57**, 719
- Ercolessi F, Parrinello M and Tosatti E, 1988: *Phil. Mag.* **A58**, 213
- Fermi E and Teller E, 1947: *Phys. Rev.* **72**, 399
- Finnis MW and Sinclair JE, 1984: *Phil. Mag.* **A50**, 45
- Finnis MW, Agnew P and Foreman AJE, 1991: *Phys. Rev.* **B44**, 567
- Flynn CP and Averback RS, 1988: *Phys. Rev.* **B38**, 7118
- Galli G and Parrinello M, 1991: in *Computer Simulation in Materials Science*, eds. M. Meyer and V. Pontikis (Kluwer)
- Galli G, Martin RM, Car R and Parrinello M, 1989: *Phys. Rev. Lett.* **63**, 988
- Garrison BJ, Winograd N, Deaven DM, Reiman CT, Lo DY, Tombrello TA, Harrison DE Jr., and Shapiro MH, 1988: *Phys. Rev.* **B37**, 7197
- Gibson JB, Goland AN, Milgram M and Vineyard GH, 1960: *Phys. Rev.* **120**, 1229
- Goodwin L, Needs RJ and Heine V, 1990: *J. Phys.* **CM 2**, 351
- Harrison WA, 1980: *Electronic Structure and the Properties of Solids* (Freeman, San Francisco)
- Haydock R, Inglesfield JE and Pendry JB (eds.), 1991: *Bonding and Structure of Solids* (The Royal Society, London)
- Heermann DW, 1986: *Computer Simulation Methods in Theoretical Physics* (Springer, Heidelberg)
- Heine V and Weaire D, 1970: *Solid State Phys.* **24**, 250
- Herman JW and Elsayed-Ali HE, 1992: *Phys. Rev. Lett.* **68**, 2952
- Hohenberg P and Kohn W, 1964: *Phys. Rev.* **136**, B864
- Hoover W G, 1985: *Phys. Rev.* **A31**, 1695
- Hsieh H and Averback RS, 1990: *Phys. Rev.* **B42**, 5365
- Häkkinen H and Landman U, 1993: *Phys. Rev. Lett.* **71**, 1023
- Häkkinen H and Manninen M, 1989: *J. Phys.* **CM 1**, 9765
- Jacobsen KW, 1988: *Comment. Cond. Matt. Phys.* **14**, 129
- Jacobsen KW, Nørskov JK and Puska MJ, 1987: *Phys. Rev.* **B35**, 7423

- Jones RO and Gunnarsson O, 1989: *Rev. Mod. Phys.* **61**, 689
- Karetta F and Urbassek HM, 1992: *J. Appl. Phys.* **71**, 5410
- Koponen I, 1992: Thesis, University of Helsinki, Department of Physics
- Koponen I and Hautala M, 1993: *Nucl. Instrum. Methods B*, in press
- Laakkonen J and Nieminen RM, 1990: *Phys. Rev.* **B41**, 3978
- Laasonen K and Nieminen RM, 1990: *J. Phys.* **CM 2**, 1509
- Laasonen K, Car R, Lee C and Vanderbilt D, 1991: *Phys. Rev.* **B43**, 6976
- Lindhard J, 1954: *Kgl. Danske Vidensk. Selsk. Mat. Fys. Medd.* **28/8**, 1
- Mehlig B, Heermann DW and Forrest BM, 1992: *Phys. Rev.* **B45**, 679
- Moriarty J, 1982: *Phys. Rev.* **B26**, 1754
- Nieminen RM, Puska MJ and Manninen M (eds.), 1990: *Many-Atom Interactions in Solids* (Springer, Heidelberg)
- Nosé S, 1984a: *J. Chem. Phys.* **81**, 511
- Nosé S, 1984b: *Mol. Phys.* **52**, 255
- Nosé S and Klein M, 1983: *Mol. Phys.* **50**, 1055
- Puska MJ, 1990: in *Many-Atom Interactions in Solids*, R.M. Nieminen, M.J.Puska and M.Manninen (eds.), (Springer, Heidelberg)
- Puska MJ and Nieminen RM, 1982: *Phys. Rev.* **B25**, 67
- Puska MJ, Manninen M and Nieminen RM, 1981: *Phys. Rev.* **B24**, 3037
- Robinson MT, 1993: *Kgl. Dan. Vidensk. Selsk. Mat. Fys. Medd.* **43**, 27
- Ryckaert JP, Ciccotti G and Berendsen HJC, 1977: *J. Comput. Phys.* **23**, 327
- Schweizer KS and Stillinger FH, 1984: *J. Chem. Phys.* **80**, 1234
- Shapiro MH and Tombrello TA, 1992: *Phys. Rev. Lett.* **68**, 1613
- Sigmund P, Robinson MT, Baskes MI, Hautala M, Cui FZ, Eckstein W, Yamamura Y, Hoska S, Ishitani T, Shulga VI, Harrison DE Jr., Chakarov IR, Karpuzov DS, Kawatoh E, Shimizu R, Valkealahti S, Nieminen RM, Betz G, Husinsky W, Shapiro MH, Vicanek M, and Urbassek HM, 1989: *Nucl. Instrum. Methods* **B36**, 110
- Squire DR and Hoover WG, 1969: *J. Chem. Phys.* **50**, 701
- Stich I, Car R, Parrinello M and Baroni S, 1989: *Phys. Rev.* **B39**, 4997
- Stich I, Payne MC, King-Smith RD, Lin J-S and Clarke LJ, 1992: *Phys. Rev. Lett.* **68**, 1351
- Stillinger F and Weber T, 1985: *Phys. Rev.* **B31**, 5262
- Stoneham AM, 1990: *Nucl. Instrum. Meth.* **B48**, 389
- Tersoff J, 1989: *Phys. Rev.* **B39**, 5566
- Tully JC, 1980: *J. Chem. Phys.* **74**, 1975
- Vanderbilt D, 1990: *Phys. Rev.* **B41**, 7892
- Virkkunen R, Laasonen K and Nieminen RM, 1991: *J. Phys.* **CM 3**, 7455
- Wang CZ, Chan CT and Ho KM, 1991: *Phys. Rev. Lett.* **66**, 189
- Wucher A and Garrison BJ, 1992: *Phys. Rev.* **B46**, 4855