



Materials subjected to fast neutron irradiation/Matériaux soumis à irradiation par neutrons rapides

Interatomic potentials for simulating radiation damage effects in metals

Kai Nordlund^{a,*}, Sergei L. Dudarev^{b,c}

^a Association EURATOM/TEKES, Accelerator Laboratory, P.O. Box 43, FI-00014 University of Helsinki, Finland

^b EURATOM/UKAEA Fusion Association, Culham Science Centre, Oxfordshire OX14 3DB, UK

^c Department of Physics, Imperial College, Exhibition Road, London SW7 2AZ, UK

Available online 3 March 2008

Abstract

We critically review the recent developments in the field of semi-empirical interatomic potentials for molecular dynamics simulations, with particular emphasis on the requirements and criteria associated with the simulations of radiation damage effects in metals. We address a range of issues including the suitability of potentials for large-scale simulations, the role of electronic excitations and electron energy losses, and the part played by the dynamics of internal degrees of freedom of atoms, for example magnetic excitations. *To cite this article: K. Nordlund, S.L. Dudarev, C. R. Physique 9 (2008).*

© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Potentiels interatomiques pour la simulation des effets du dommage d'irradiation dans les métaux. Ce papier est une revue critique des développements récents dans le domaine des potentiels interatomiques semi-empiriques utilisés pour les simulations de dynamique moléculaire. Une attention particulière est donnée aux exigences et critères que doivent respecter les simulations des effets du dommage d'irradiation dans les métaux. Nous discutons notamment l'adéquation des potentiels à la simulation d'un grand nombre d'atomes, le rôle des excitations électroniques et des pertes d'énergie des électrons ainsi que la contribution de la dynamique des degrés de liberté internes des atomes, par exemple les excitations magnétiques. *Pour citer cet article : K. Nordlund, S.L. Dudarev, C. R. Physique 9 (2008).*

© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Keywords: Neutron irradiation; Radiation damage

Mots-clés: Irradiation par neutrons ; Dommage d'irradiation

1. Introduction

For several decades analytical interatomic potentials remained one of the key elements of the multiscale hierarchy of modelling methods for simulating radiation damage effects in metals. In a multiscale modelling framework, the dynamics of motion of atoms is investigated using molecular dynamics (MD) computer simulations. In these simulations

* Corresponding author.

E-mail addresses: knordlun@acclab.helsinki.fi (K. Nordlund), sergei.dudarev@ukaea.org.uk (S.L. Dudarev).

the evolution of a system of interacting atoms is followed by integrating the many-body classical equations of motion numerically. The numerical MD algorithms are now well established, and the solutions of the corresponding differential equations can be found as accurately as desired, although of course these solutions always remain approximate. Hence the main, and often the only, source of uncertainty in MD simulations appears to be the model describing interaction between atoms. A suitable model gives the potential energy of the system, and the forces acting on each atom. In general, the interaction models can be classified into two main categories: quantum-mechanical and the classical ones. In a quantum mechanical model, for example based on density-functional theory (DFT) or tight-binding (TB) [1,2], the energies and forces are found by explicitly solving the Schrödinger equation for the system of atoms and electrons. Even though major methodological and computer capacity advances have occurred over the last 30 years, the quantum mechanical methods are still too slow for modelling the kind of dynamical processes that are of interest to studying irradiation effects in metals. So far the only case known to us where a direct quantum-mechanical method involving matrix diagonalisation was applied to the evaluation of interatomic forces in a MD simulation of a collision cascade, was the case of the second-order matrix potential [3]. In this article we limit ourselves to discussing only the case of classical interatomic potentials.

The notion of a classical interatomic potential is understood as a concise, easy to program, and sufficiently accurate analytical functional representation of the law of interaction between atoms in a material. Most classical potentials, i.e. the expression for the potential energy of a system of atoms as a function of their coordinates, have the form [4]

$$V_{\text{TOT}} = \sum_{i,j} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,j,k} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \sum_{i,j,k,l} V_4(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l) + \dots \quad (1)$$

where the sum is performed over all the atoms in the simulation cell. Here V_2 is a two-body potential, V_3 is a three-body potential, and so on. A V_1 term is not included in this expansion since it would have represented an external potential rather than the law of interaction between atoms themselves. The force acting on an atom (say, atom i) is found by taking the three-dimensional derivative (gradient ∇) of the total energy of the system with respect to the coordinate of this atom:

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} V_{\text{TOT}} \quad (2)$$

or in other words,

$$\mathbf{F}_{i,x} = -\frac{\partial V_{\text{TOT}}}{\partial x_i}; \quad \mathbf{F}_{i,y} = -\frac{\partial V_{\text{TOT}}}{\partial y_i}; \quad \mathbf{F}_{i,z} = -\frac{\partial V_{\text{TOT}}}{\partial z_i} \quad (3)$$

Functions V_2 , V_3 , etc. are usually represented by analytical expressions that give the value of the total potential energy of a system of atoms for a given set of atomic coordinates $\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \dots$

The development of an interatomic potential usually involves first the derivation of a suitable general functional form for $V_{\text{TOT}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ containing some adjustable parameters, followed by fitting the adjustable parameters to energies or forces found for a set of atomic configurations using more accurate approximations, for example density functional theory. The functional form for V_{TOT} may be chosen as an analytical function, or as a set of discrete points accompanied by a rule defining how this function is interpolated between the data points. Cubic splines [5] are often used to interpolate between the data points since this ensures the continuity of both V_{TOT} as well as its first derivatives over the entire range of variation of atomic positions.

Applications of molecular dynamics to radiation damage places special requirements on the potentials. In this paper we first discuss these requirements and then proceed to discussing the general principles governing the derivation of the effective interatomic potentials. We then consider several applications of the potentials to modelling radiation damage effects, making particular emphasis on the cases where direct comparison with experimental observations is possible.

2. Potentials

2.1. Requirements associated with modelling radiation damage

A typical collision cascade event induced by an energetic electron, neutron or an ion involves several fairly well identifiable stages [6]. The cross-section of interaction of a neutron with the nuclei is small, but once a collision between a neutron and a nucleus does occur, the kinetic energy transferred in this event is typically in the keV range.

Electrons, on the other hand, give rise to atomic recoils with energies typically in the eV range. Radiation damage results from these recoil events. A similar general picture applies also in the case of ion irradiation. Thus to simulate electron, neutron or ion radiation damage, it is sufficient to be able to simulate the resulting atomic motion. Initially, atomic motion at keV energies can be approximated as a sequence of ballistic binary collisions, which can be considered essentially as a nuclear physics process. However, the secondary and tertiary recoils have considerably lower energies than the primary ones, and roughly 1 ps after the initial recoil event the collision cascade thermalizes, i.e. the distribution of velocities of atoms in the densest part of the cascade approaches the Maxwell distribution corresponding to fairly high temperature $\sim 10\,000$ K [7]. This means that locally the crystal melts, and a region of hot high-pressure liquid with an under-pressurized core is formed. On the time scales of 10–100 ps the liquid cools down, undergoing a phase transition to a crystalline or an amorphous state. Finally, once the system has fully cooled down, the defects formed in the cascade undergo thermal migration that only stops once they fully recombine or form clusters stable on the timescale of the simulations (~ 10 ns or longer). The amorphous zones formed in the molten cascade regions may also thermally recrystallize.

It is clear that the treatment of the radiation damage processes described above places stringent requirements on the choice of interatomic potentials, since ideally they should be able to describe all the effects associated with the evolution of cascades and beyond. In particular, this implies the following points that are not essential for more conventional equilibrium simulations. To handle the ballistic phase of collisions, it is necessary to have a potential which describes interactions at very short interatomic distances. To ensure that the phase transition back to a crystalline or an amorphous phase is treated correctly, it is crucial that the potentials predict the correct experimental ground state, and that they exhibit no false artificial minima. Moreover, since the heat spike phase involves very high pressures, the non-equilibrium high-pressure phases should also be taken into account. Since the outcome of a recoil event usually involves the production of interstitial defects, vacancies, and even dislocations, it is natural to expect that a suitable potential has to describe all these structures reasonably well, too.

2.2. Repulsive potentials

Since in a head-on collision of like particles half of the kinetic energy of the incident particle is converted into the potential energy of interatomic interaction, the repulsive part of the potential should remain valid up to small interatomic separations where the potential energy is comparable with the kinetic energy of interacting atoms. Somewhat paradoxically, the law of interatomic interactions is often known much more accurately in the limit of high energy of interacting particles. At very small separations between a pair of interacting atoms, the repulsive interaction can be approximated by pure Coulomb repulsion between the nuclei,

$$V_2^{\text{highest energies}}(r) = \frac{e^2}{4\pi\epsilon_0} \frac{Z_1 Z_2}{r} \quad (4)$$

At greater distances, inner-shell electrons screen the nuclei from each other. The repulsive potential can be approximated by multiplying the Coulomb repulsion between nuclei by a screening function:

$$V_2^{\text{repulsive}}(r) = \frac{e^2}{4\pi\epsilon_0} \frac{Z_1 Z_2}{r} \varphi(r) \quad (5)$$

An approximation now frequently used in simulations of high-energy impacts was developed by Ziegler, Biersack and Littmark, and is known as the ZBL universal repulsive potential [8]. It is constructed by fitting a universal screening function to the radial dependence of the energy of interaction between a pair of ions found using the quantum mechanical Thomas–Fermi approximation:

$$\varphi(x) = 0.1818e^{-3.2x} + 0.5099e^{-0.9423x} + 0.2802e^{-0.4029x} + 0.02817e^{-0.2016x} \quad (6)$$

where

$$a = a_u = \frac{0.8854a_0}{Z_1^{0.23} + Z_2^{0.23}} \quad (7)$$

and where a_0 is the Bohr radius. This universal form was found to remain accurate within $\sim 10\%$ uncertainty interval [8–10]. If even more accurate potentials are needed, one can derive a pair-specific ZBL potential using the formalism

described in Ref. [8], or directly evaluate the law of interaction using one of the all-electron density functional theory (DFT) or Hartree–Fock methods [10,11]. Such potentials have been found (by comparing different electronic structure calculation methods) to be accurate within $\sim 1\%$ uncertainty range. Such accuracy may be needed in molecular dynamics or binary collision approximation (BCA) studies of ion range distributions [12,13], while for the description of damage production in collision cascades the outcome was found to remain independent of small (a few percent) variations in the form of the high-energy potential.

The high-energy potentials can be used entirely on their own in the ion scattering and the range calculations, while in full simulations of collision cascades they have to be smoothly matched to the low-energy potential. The matching can, for example, be calibrated to reproduce experimental threshold displacement energies [14], high-pressure equations of states and the melting point [15], or DFT calculations of high-energy states [16].

2.3. The ‘equilibrium’ low-energy interaction potentials

Finding an accurate function form for the law of interaction between atoms at low energies of the order of several electron volts remains one of the most challenging issues in the field of radiation damage modelling. Results of MD simulations of cascades, and the predicted rates of generation of defects depend sensitively on the choice of the low-energy part of the interaction potential.

The MD methods for simulating collision cascades are now fairly well established, and good understanding exists of, for instance, how sensitive the results are to the choice of boundary conditions used in simulations [17]. At the same time it is not at all a simple and straightforward matter to define a criterion for testing the reliability and validity of the potentials. For example, defects observed in experiments are almost invariably studied for temperatures above the temperature of stage I, where self-interstitial atoms migrate, and hence interact and recombine with other defects. As a result the observed defect production yield cannot serve as a quantitative test for validating results of MD simulations. Another subtle point is related to the fact that only defects exceeding a certain critical size (typically of the order of 1 nm across) can be visualized using electron microscopy, giving rise to uncertainty associated with attempts to match the predicted and the experimentally observed defect yields. On the other hand, the ion beam mixing and sputtering yields are more directly related to the initial stages of the development of cascades. The experimental ion beam mixing [15] in Ni, Pd and Pt has been found to be well reproduced by potentials that predict the correct melting temperature, and a one of the potentials for gold was found to reproduce fairly well the experimentally observed sputtering yields over a large range of variation of energy of incident particles spanning 3 orders of magnitude [17].

Unfortunately not enough experimental data are available to enable such comparisons for the majority of materials. Moreover, a good match to a particular experimentally observed quantity, for example describing collision cascades, does not guarantee the equally good description of other parameters; for instance in the study of ion beam mixing in Pd and Pt the interstitial energies changed and became clearly higher once the melting point of the material was tuned to match experimental values [15], making it likely that while ion beam mixing was well described, the production of interstitial atom defects was not. Hence further development of interatomic potentials based on more accurate electronic structure calculations will likely remain a field of active research even in the distant future.

2.4. Many-body potentials for metals

By far the most often used potentials in the field of radiation damage are those that can be cast in the general functional form of a combination of *spherically symmetrical* functions

$$V_{\text{TOT}} = \sum_{i,j} V_{\text{pair}}(r_{ij}) + \sum_i F_i \left(\sum_j \rho_{ij}(r_{ij}) \right) \quad (8)$$

These, generally non-pairwise many-body potentials, which are often called ‘EAM-like’ after the popular embedded-atom method [18], share the advantage that any of them can be parametrized in the form of a set of three data tables tabulating $V_{\text{pair}}(r)$ and $\rho_{ij}(r)$ as functions of r , and $F_i(x)$ as a function of the sum over ρ ’s. Any of these potentials can then be evaluated using a generic EAM subroutine that reads in the data tables; thus no code modification is required in order to switch between different potentials. Another advantage is that when well implemented, evaluating the EAM potentials requires no 3-body loops, and thus these potentials are only about a factor of 2 slower than pure pairwise potentials with a comparable cut-off interatomic distance. The exact implementation of the functional form

may differ; for instance some potentials use atom-centered electron densities ρ_i , others use the pair-specific ρ_{ij} , and some require the pairwise part to be purely repulsive while others use pairwise potentials of a general kind having taking both positive and negative values as a function of r .

Interestingly, several independent physical motivations have been proposed in order to justify the same functional form (8). Most of them are originally related to the effective medium theory (EMT) approximations [19,20], which is derived from density-functional theory and consider metal atoms as positive ions embedded in an electron fluid called ‘jellium’. The attractive interaction energy between the positive ions and the negative jellium gives rise to the cohesion of the material. In the original EMT method the ion-jellium interaction was derived by DFT [19], whereas in the embedded-atom method (EAM) potentials based on the same general idea [21,18] a more empirical fitting approach was used. Among the effective-medium theory potentials developed more recently we note the MD/MC CEM potentials [22].

An alternative way of motivating an EAM-like functional form is to derive it starting from the so called second-moment approximation of the tight-binding theory of solids [23]. In this approximation the quantum mechanical treatment gives rise to a potential of the form (8) with the embedding function being simply a square root: $F(x) = -\sqrt{x}$. For instance the Finnis–Sinclair [24,25] and the Rosato group [26,27] potentials were motivated in this way.

Notably, the second-moment tight-binding approximation also underpins the derivation of the Tersoff-like potentials that are used for simulating covalent materials [28,29], and in fact it can be shown that the ‘square root’ EAM-like metal potentials and the Tersoff-like potentials are equivalent [29,30]. Thus, although originally the Tersoff-like potentials were developed to describe covalent solids, they can also be used to develop potentials for metals of quality comparable to the EAM-like potentials [30–32]. While the Tersoff-like potentials tend to be slower than the EAM-like ones due to an explicit 3-body loop, they offer the advantage of being well suited for modelling compounds involving metals and non-metals [30,31,33].

Several other schemes for developing potentials with the EAM-like functional form exist [34–37]. Also more complicated functional forms have been proposed; for instance Pettifor [38], and Moriarty et al. [39,40] have shown that the treatment of phase stability of BCC metals requires going beyond the second-moment tight-binding approximation, and hence interatomic interactions involve 4-body terms [41].

2.5. Recent developments

The previously described potentials, while being successful in describing a wide range of materials properties at least qualitatively correctly, have some known shortcomings. For instance, until recently none of the available potentials describing magnetic materials actually accounted for magnetic effects. For example, potentials developed for iron compensated for the lack of explicit treatment of magnetic effects by fitting the parameters to the experimental cohesion energy and elastic constants. Such a compensation works well for properties which do not depend explicitly of magnetism; for instance, any potential which reproduces the experimental first-order elastic constants of a material, will describe materials properties which depend only on linear elasticity correctly. However, such ‘compensation fitting’ is not fundamentally satisfying and it restricts the transferability of the potential. In the case of iron or magnetic alloys it is known that finite temperature magnetic fluctuations are responsible for various phase transitions. It is not possible to model these transitions by relying solely on formalism where only phonon excitations (i.e. displacements of atoms from their equilibrium lattice sites) are included and where no account is taken of other types of excitations, for example spin fluctuations that play an equally significant part in determining properties of materials. A direct and striking fact illustrating the failure of the conventional fitting-based approach to modelling elevated-temperature properties of iron is the strong dependence of elastic constants on temperature [42,43], with one of the elastic constants actually nearly *vanishing* at 912 °C well below the melting temperature of the material. None of the non-magnetic BCC metals exhibits anomalies of similar nature.

Furthermore, while many of the common EAM-like potentials describe interstitials in FCC metals reasonably well [44,45], many of the potentials developed for BCC Fe incorrectly predicted that the lowest energy interstitial configuration was the 111 dumbbell [46].

For alloys the situation remained even less clear. Relatively few potentials were available, and those were developed based on some simple averaging schemes [47] or on fitting to only a small number of data points [48].

The last few years have witnessed progress in the physical understanding of magnetic effects [49–51] as well as the development of new potentials for magnetic alloys [53,54]. In effect, in the treatment of magnetic materials we

encounter a case that had never been explicitly addressed before in atomistic simulations. A conventional treatment of interatomic interactions assumes that the positions of atoms are uniquely related to forces acting between them. This is not the case in a magnetic alloy. Indeed, now the forces acting between atoms depend not only on the positions of atoms, but also on the magnitudes and orientations of magnetic moments associated with the atoms. The fundamental Hamiltonian providing the starting point for the derivation of an interatomic potential now includes terms describing interaction between electrons that form the interatomic bonds [51]. The derivation of an interatomic potential can no longer rely on the conventional tight-binding, or similar, treatments where electrons are treated as independent and non-interacting particles [55]. One of the new concepts that has been introduced to describe the formation of magnetic moments on atoms is the notion of symmetry-breaking and the resulting energy multi-branching of an interatomic potential [49].

To overcome the problem of the incorrect structure of self-interstitials, several recent potentials have been developed which take this into account during the potential construction. These include several variations of the Mendelev potential [37,56], the Dudarev–Derlet magnetic potential [49] and the Tersoff-like Fe potential developed by the Albe group [32]. Application of these potentials to cascade simulations has shown that the previously observed very large fluctuations in the predicted defect production yield can be significantly reduced [14]. Similarly, a new family of potentials has been developed for the non-magnetic BCC metals (vanadium, niobium, tantalum, molybdenum, and tungsten) with the objective of reproducing the correct structure and energies of formation of interstitial and vacancy defects in these materials [52].

The lack of availability of potentials for alloys has been a particular problem hindering understanding of radiation damage in high-Cr steels, where it is well known that radiation damage effects strongly depend on the Cr concentration. Developing potentials for the FeCr system is challenging since the heat of mixing changes sign with increasing Cr content, which cannot be easily accounted for in EAM-like potentials. However, the two recent potentials have solved this problem by extending the basic EAM functional form. In the model developed by Caro et al. [54] the potential is made dependent on the Cr content, while in the potential of Olsson et al. [53] the electron density is separated into the s and d electron contributions, and corresponding distinct embedding functions. The latter one is handled as an atom-centered density ρ_i , and the former one as a pair-specific density ρ_{ij} for the FeCr interaction. Both approaches correctly predict that Cr is miscible with Fe up to a concentration of roughly 10% and immiscible above it, in the temperature range $\lesssim 600$ K most relevant for fission and fusion reactors.

Although major advances thus have recently been made with respect to modelling irradiation effects in metals, there are several obvious points for future development. For example, the FeCr potentials and the magnetic Fe potential are incompatible with each other, so up to now there is no FeCr potential with magnetic terms included. On a fundamental level, the existing magnetic potential cannot yet deal with the temperature dependence of the magnetism; for example it does not provide the framework for the treatment of magnon excitations and magnetic phase transitions. While it might seem obvious that the correct treatment should combine a three-dimensional Heisenberg-like model for the treatment of dynamics of magnetic moments, with molecular dynamics for the treatment of motion of atoms, new fundamental concepts and developments in numerical methods are required to implement this hypothesis practically. The most recent developments in magnetic molecular dynamics (MMD) look promising [57] although further work is required to combine the treatment of finite-temperature magnetism with the treatment of dynamics of atoms.

Modelling radiation damage in reactor-relevant conditions also has the particular feature that H and He interactions with the metals have a strong effect on the development of damage. Hence in addition to good models for the metal elements, it is important to have reliable interaction models for H and He interactions with the metal matrix. At the very least, the solubility and migration energies as well as the ground-state lattice position of H and He should be well described. For He this requirement can be fulfilled with carefully constructed pair potentials (due to the closed 1s shell of He, using many-body potentials is not necessary) [58,59]. For H, environment-dependent potentials can achieve describing both these bulk features as well as the properties of small H-metal molecules adequately well [31].

2.6. Electronic effects

In the interatomic potentials described hitherto in this article, all the electronic effects (i.e. the formation of interatomic bonds) were effectively embedded into the functional form of the interatomic potential. This approximation is suitable for treating the dynamics of motion of atoms at relatively low temperatures not far from equilibrium, since by the Born–Oppenheimer approximation the electronic subsystem has time to reach its ground state before any signifi-

cant atomic motion occurs. However, for irradiation effects this is not always the case, and the electronic effects may need to be accounted for in MD simulations.

While effects such as photon and electron emission require an explicit treatment of electrons, we restrict ourselves here to discussing two effects which may affect the motion of a large body of atoms in a cascade: electronic stopping and electron–phonon coupling.

The electronic stopping power describes energy loss to electrons by ions moving ballistically through the solid. It has several distinct physical origins [8], and can be characterized by the experimental observation that it is significant both in metals and insulators down to quite low energies (at least a few hundred eV) [60,61]. The magnitude of electronic stopping has been experimentally measured for a wide range of materials and energies [8] and was parametrized for all the materials and compounds for energies up to 1 GeV in the TRIM/SRIM codes [62,63]. Electron stopping can be included in an MD simulation as an effective friction force determined from the electronic stopping power curve, obtained e.g. from SRIM [64]. This approach can be tested directly against experiments by comparing the simulated and experimentally observed range profiles. Such comparisons [65,66,12,13] show that this implementation of the electronic stopping in MD is very reliable, apart from the possible uncertainties associated with the stopping power itself.

The issue of how to include the so-called electron–phonon coupling (the transfer of energy from the hot ionic subsystem to the initially cooler electronic subsystem at the later stages of development of cascades) remains unclear. The electron–phonon coupling is conventionally associated with the transfer of energy from hot electrons to lattice atoms, and this process is fairly well understood [67,68]. However, during ion irradiation the atomic subsystem is first heated by the ballistic collisions, and since these also destroy the lattice structure, the process is not symmetric with the electrons-to-atoms energy transfer.

Several theoretical attempts have been made to describe the electron–phonon coupling in cascades [69–72] but due to the uncertainty of how to treat phonons in the high-density-gradient, high-temperature liquid in a cascade, the parameters in these have considerable uncertainty, and in fact one of the most recent theoretical studies concludes that nothing certain can be said about the strength of electron–phonon coupling in a cascade [73].

Comparisons with experimental data have also been used to attempt to understand electron–phonon coupling. The major differences in the ion beam mixing between Cu- and Ni-group metals were early on interpreted as evidence of strong coupling in the latter reducing the heat spike lifetime [72], but later on the same differences were shown to be more accurately explained by the melting point differences [74,15]. Differences in defect production data have been interpreted as evidence of electron–phonon coupling [75], but considering the many other factors affecting defect cluster production before they are imaged in an electron microscope, this evidence is clearly indirect. Also in Fe the electron–phonon coupling has been suggested to be strong, but the experimental measurement of the heat spike lifetime to be about 6 ps [76] is at least roughly consistent with MD simulations without electron–phonon coupling. The most recent developments in the treatment of electron–phonon interaction in cascades rely on the use of the fluctuation–dissipation theorem and the treatment of energy transfer from electrons to atoms via the action of effective random force [77]. Still, considerable uncertainty remains about how the electron–phonon coupling should be treated, the most recent evidence indicates it is at least not the most dominant factor influencing the evolution of collision cascades.

3. Benchmarking and verification of potentials

There have naturally been at least several attempts to explicitly verify whether the potentials used to simulate irradiation effects are qualitatively or quantitatively correct. Unfortunately, direct comparison with experiments is not always straightforward, but still here we can give a few examples of such comparisons.

That the repulsive part of the potential is treated correctly can be relatively well verified by simulating ion range profiles in the energy regime where nuclear stopping dominates, and comparing these to experimental profiles. Such comparisons have shown that especially when the repulsive interaction is treated with pair-specific density functional theory potentials, which are more accurate than the ZBL universal potential, excellent agreement with experiments can be achieved [65,13,78].

The intermediate-energy part can to some extent be tested by comparing sputtering yields with experiments. Such comparisons have shown that usually most potentials give reasonable agreement within a factor of ~ 2 (comparable to the experimental uncertainties) [79,80]. Quite recently a comparison of sputtering yields in Au with high-quality

experimental data over 3 orders of magnitude in energy showed that certain EAM-like potentials can reproduce the experimental yields correctly, while others overestimate the yields strongly in some parts of the energy range [17].

The ion beam mixing is another quantity that depends directly on the outcome of cascade simulations and that can be compared with experiments. Simulations and experiments on ion beam mixing in Ni, Pd and Pt have shown excellent agreement of the calculated mixing coefficients with experimental observations [15].

Unfortunately the comparison of a quantity most important for the treatment of the long-term radiation damage evolution, namely the rate of production of primary defects, is an example of the case where direct comparison of the outcome of an MD simulation with experimental information is very difficult. Since the irradiation-induced interstitials in metals are mobile already at a few tens of Kelvins [81], the only way to perform a direct comparison would be to carry out both the irradiation and the subsequent analysis fully below the onset temperature of interstitial migration. Very few such experiments have been performed so far. Comparison of near-surface damage in W with field ion microscopy experiments has shown good (within $\sim 30\%$) agreement of vacancy production yields with experiment [82]. A demonstration that stacking fault tetrahedra can form directly in collision cascades, in agreement with experiments carried out below the vacancy migration temperature, indicates that at least on a qualitative level the description of heat spikes in metals is appropriate [83]. However, it would be highly desirable to have additional experiments against which the predicted rates of defect production could be validated.

4. Summary and outlook

The developments in the methodology of large-scale molecular dynamics simulations has brought into focus one of the most fundamental problems of theoretical materials science, namely how to use quantum-mechanical principles that are known to determine the nature of interatomic interactions in order to derive simplified yet reasonably accurate and internally consistent effective *classical* models suitable for predictive modelling the behaviour of complex materials. Concerted effort in this direction has recently resulted in the development of a family of new, more accurate yet still fast and effective interatomic potentials.

It has become clear that in some cases it is unavoidable that the electronic degrees of freedom have to be included explicitly in the treatment of interatomic interactions. Magnetic materials, for example ferritic steels, are examples of a class of materials where electronic effects responsible for the formation of interatomic bonds *and* magnetic moments on atoms, are also responsible for the unusual and technologically significant properties of these materials. The development of new conceptual methods of molecular dynamics, and magnetic molecular dynamics, for simulating these materials is one of the challenging tasks that we expect to face in this field in the near future.

On a more practical level, considerable effort will be required to develop potentials with superior accuracy, comparable to the accuracy of electronic structure based methods. New algorithms for fitting parameters of models based on computational steering, as well as the development of new more satisfactory and mathematically consistent approximate forms of potentials, is a requirement that atomistic models will have to address to justify their role in the hierarchy of methods for the development of future nuclear fission and fusion materials and technologies.

Acknowledgements

We would like to thank D.G. Pettifor, D. Nguyen-Manh, R. Drautz, P.M. Derlet, F. Willaime, C. Marinica, G.J. Ackland, A. Caro, A.V. Barashev, L. Malerba and J. Wallenius for stimulating discussions.

SLD acknowledges support by the UK Engineering and Physical Sciences Research Council, by EURATOM, and by EXTREMAT integrated project under contract number NMP3-CT-2004-500253. KN acknowledges support from the Finnish Centre of Excellence in Computational Molecular Science (CMS), financed by The Academy of Finland and the University of Helsinki, and Association EURATOM/TEKES under the FUSION programme.

References

- [1] For a review, see R.O. Jones, O. Gunnarsson, Rev. Mod. Phys. 61 (1989) 689.
- [2] C.M. Goringe, D.R. Bowler, E. Hernandez, Rep. Prog. Phys. 60 (1997) 1447.
- [3] S.L. Dudarev, J. Phys.: Condens. Matter 18 (2006) S447.
- [4] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, England, 1989.

- [5] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, *Numerical Recipes in C; The Art of Scientific Computing*, second ed., Cambridge University Press, New York, 1995.
- [6] R.S. Averback, T. Diaz de la Rubia, in: H. Ehrenfest, F. Spaepen (Eds.), *Solid State Physics*, vol. 51, Academic Press, New York, 1998, pp. 281–402.
- [7] T. Diaz de la Rubia, R.S. Averback, R. Benedek, W.E. King, *Phys. Rev. Lett.* 59 (1987) 1930;
T. Diaz de la Rubia, R.S. Averback, R. Benedek, W.E. King, *Phys. Rev. Lett.* 60 (1988) 76 (Erratum).
- [8] J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Range of Ions in Matter*, Pergamon, New York, 1985.
- [9] P. Haussalo, K. Nordlund, J. Keinonen, *Nucl. Instrum. Meth. Phys. Res. B* 111 (1996) 1.
- [10] K. Nordlund, N. Runeberg, D. Sundholm, *Nucl. Instrum. Meth. Phys. Res. B* 132 (1997) 45.
- [11] M.A. Karolewski, *Nucl. Instrum. Meth. Phys. Res. B* 243 (2005) 43.
- [12] J. Peltola, K. Nordlund, J. Keinonen, *Nucl. Instrum. Meth. Phys. Res. B* 212 (2003) 118.
- [13] K.M. Beardmore, N. Grønbech-Jensen, *Phys. Rev. E* 57 (1998) 7278.
- [14] C. Björkas, K. Nordlund, *Nucl. Instrum. Meth. Phys. Res. B* 259 (2007) 853.
- [15] K. Nordlund, L. Wei, Y. Zhong, R.S. Averback, *Phys. Rev. B (Rapid Comm.)* 57 (1998) 13965.
- [16] V. Belko, M. Posselt, E. Chagarov, *Nucl. Instrum. Meth. Phys. Res. B* 202 (2002) 18.
- [17] J. Samela, J. Kotakoski, K. Nordlund, J. Keinonen, *Nucl. Instrum. Meth. Phys. Res. B* 239 (2005) 331.
- [18] M.S. Daw, S.M. Foiles, M.I. Baskes, *Mat. Sci. Engr. Rep.* 9 (1993) 251.
- [19] M.J. Puska, R.M. Nieminen, M. Manninen, *Phys. Rev. B* 24 (1981) 3037.
- [20] M. Manninen, *Phys. Rev. B* 34 (1986) 8486.
- [21] S.M. Foiles, *Phys. Rev. B* 32 (1985) 3409.
- [22] C.L. Kelchner, D.M. Halstead, L.S. Perkins, N.M. Wallace, A.E. DePristo, *Surf. Sci.* 310 (1994) 425 and references therein.
- [23] N.W. Ashcroft, N.D. Mermin, *Solid State Physics*, Saunders College, Philadelphia, 1976.
- [24] M.W. Finnis, J.E. Sinclair, *Phil. Mag.* A 50 (1984) 45;
M.W. Finnis, J.E. Sinclair, *Phil. Mag.* A 53 (1986) 161 (Erratum).
- [25] G.J. Ackland, R. Thetford, *Phil. Mag.* A 56 (1987) 15.
- [26] F. Cleri, V. Rosato, *Phys. Rev. B* 48 (1993) 22.
- [27] G. Mazzone, V. Rosato, M. Pintore, F. Delogu, P. Demontis, G.B. Suffriti, *Phys. Rev. B* 55 (1997) 837.
- [28] J. Tersoff, *Phys. Rev. B* 37 (1988) 6991.
- [29] D.W. Brenner, *Phys. Rev. B* 42 (1990) 9458;
D.W. Brenner, *Phys. Rev. B* 46 (1992) 1948.
- [30] K. Albe, K. Nordlund, R.S. Averback, *Phys. Rev. B* 65 (2002) 195124.
- [31] N. Juslin, P. Erhart, P. Träskelin, J. Nord, K.O.E. Henriksson, K. Nordlund, E. Salonen, K. Albe, *J. Appl. Phys.* 98 (2005) 123520.
- [32] M. Müller, P. Erhart, K. Albe, *Phys. Rev. B* (2006), in press.
- [33] P. Erhart, N. Juslin, O. Goy, K. Nordlund, R. Müller, K. Albe, *J. Phys.: Condens. Matter* 18 (2006) 6585.
- [34] F. Ercolessi, J.B. Adams, *Europhys. Lett.* 26 (1994) 583.
- [35] D.J. Oh, R.A. Johnson, *J. Mater. Res.* 3 (1988) 471.
- [36] R.A. Johnson, D.J. Oh, *J. Mater. Res.* 4 (1989) 1195.
- [37] M.I. Mendeleev, S. Han, D.J. Srolovitz, G.J. Ackland, D.Y. Sun, M. Asta, *Phil. Mag.* 83 (2003) 3977.
- [38] D.G. Pettifor, *Phys. Rev. Lett.* 63 (1989) 2480.
- [39] W. Xu, J. Moriarty, *Phys. Rev. B* 54 (1996) 6941.
- [40] J.A. Moriarty, J.F. Belak, R.E. Rudd, P. Söderlind, F.H. Streitz, L.H. Yang, *J. Phys.: Condens. Matter* 14 (2002) 2825.
- [41] D.G. Pettifor, *Acta Mater.* 51 (2003) 5649.
- [42] D.J. Dever, *J. Appl. Phys.* 43 (1972) 3293.
- [43] H. Hasegawa, M.W. Finnis, D.G. Pettifor, *J. Phys. F: Metal Phys.* 15 (1985) 19.
- [44] N.Q. Lam, L. Dagens, N.V. Doan, *J. Phys. F: Metal Phys.* 13 (1983) 2503.
- [45] K. Nordlund, J. Keinonen, T. Mattila, *Phys. Rev. Lett.* 77 (1996) 699.
- [46] L. Malerba, *J. Nucl. Mater.* 351 (2006) 28.
- [47] S.M. Foiles, M.I. Baskes, M.S. Daw, *Phys. Rev. B* 33 (1986) 7983;
S.M. Foiles, M.I. Baskes, M.S. Daw, *Phys. Rev. B* 37 (1988) 10378 (Erratum).
- [48] K. Nordlund, R.S. Averback, *Phys. Rev. B* 59 (1999) 20.
- [49] S.L. Dudarev, P.M. Derlet, *J. Phys.: Condens. Matter* 17 (2005) 1.
- [50] P.M. Derlet, S.L. Dudarev, *Prog. Mater. Sci.* 52 (2007) 299.
- [51] S.L. Dudarev, P.M. Derlet, in: P. Gumbsch (Ed.), *Proceedings of the 3rd International Conference on Multiscale Materials Modelling*, Freiburg, Germany, September 18–22, 2006, Fraunhofer IRB Verlag, 2006, pp. 713–720.
- [52] P.M. Derlet, D. Nguyen-Manh, S.L. Dudarev, *Phys. Rev. B* 76 (2007) 054107.
- [53] P. Olsson, J. Wallenius, C. Domain, K. Nordlund, L. Malerba, *Phys. Rev. B* 72 (2005) 214119.
- [54] A. Caro, D.A. Crowson, M. Caro, *Phys. Rev. Lett.* 95 (2005) 075702.
- [55] M.W. Finnis, *Interatomic Forces in Condensed Matter*, Oxford University Press, Oxford, 2003.
- [56] G.J. Ackland, M.I. Mendeleev, D.J. Srolovitz, S. Han, A.V. Barashev, *J. Phys.: Condens. Matter* 16 (2004) S2629.
- [57] P.W. Ma, C.-H. Woo, S.L. Dudarev, *Magnetic Molecular Dynamics Simulation of Spin-Lattice Relaxation in Ferromagnetic Iron*, Programme and Abstracts of EUROMAT-2007, Nuremberg, Germany, September 2007.
- [58] K.O.E. Henriksson, K. Nordlund, J. Keinonen, D. Sundholm, M. Patzschke, *Simulations of the initial stages of blistering in helium implanted tungsten*, *Physica Scripta T* 108 (2004) 95.

- [59] N. Juslin, K. Nordlund, Pair potential for Fe–He, *J. Nucl. Mater.* (2007), submitted for publication.
- [60] R. Smith (Ed.), *Atomic & Ion Collisions in Solids and at Surfaces: Theory, Simulation and Applications*, Cambridge University Press, Cambridge, UK, 1997.
- [61] N. Arista, *Mat. Fys. Medd. Kong. Dan. Vid. Selsk.* 52 (2006) 595.
- [62] J.F. Ziegler, TRIM-92 computer code, private communication, 1992.
- [63] J.F. Ziegler, SRIM-2003 software package, available online at <http://www.srim.org>.
- [64] K. Nordlund, *Comput. Mater. Sci.* 3 (1995) 448.
- [65] K. Nordlund, J. Keinonen, E. Rauhala, T. Ahlgren, *Phys. Rev. B* 52 (1995) 15170.
- [66] H. Hausmann, A. Pillukat, P. Ehrhart, *Phys. Rev. B* 54 (1996) 8527.
- [67] F.C. Wellstood, C. Urbina, J. Clarke, *Phys. Rev. B* 49 (1994) 5942.
- [68] C. Dufour, E. Paumier, M. Toulemonde, *Nucl. Instrum. Meth. Phys. Res. B* 122 (1997) 445.
- [69] C.P. Flynn, R.S. Averback, *Phys. Rev. B* 38 (1988) 7118.
- [70] A. Caro, M. Victoria, *Phys. Rev. A* 40 (1989) 2287.
- [71] M.W. Finnis, P. Agnew, A.J.E. Foreman, *Phys. Rev. B* 44 (1991) 44.
- [72] I. Koponen, *J. Appl. Phys.* 72 (1992) 1194.
- [73] I. Koponen, *Phys. Rev. B* 47 (1993) 14011.
- [74] K. Nordlund, M. Ghaly, R.S. Averback, *J. Appl. Phys.* 83 (1998) 1238.
- [75] I.M. Robertson, D.K. Tappin, M.A. Kirk, *Philos. Mag. A* 68 (1993) 843.
- [76] A.E. Stuchbery, E. Bezakova, *Phys. Rev. Lett.* 82 (1999) 3637.
- [77] D.M. Duffy, A.M. Rutherford, *J. Phys.: Condens. Matter* 19 (2007) 016207.
- [78] H.Y. Chan, et al., *Thin Solid Films* 504 (2005) 121.
- [79] M. Ghaly, K. Nordlund, R.S. Averback, *Philos. Mag. A* 79 (1999) 795.
- [80] A. Wucher, B.J. Garrison, *J. Chem. Phys.* 105 (1996) 5999.
- [81] P. Ehrhart, in: H. Ullmaier (Ed.), *Properties and Interactions of Atomic Defects in Metals and Alloys*, in: Landolt–Börnstein, New Series III, vol. 25, Springer, Berlin, 1991, p. 88 (Chapter 2).
- [82] Y. Zhong, K. Nordlund, M. Ghaly, R.S. Averback, *Phys. Rev. B (Brief Reports)* 58 (1998) 2361.
- [83] K. Nordlund, F. Gao, *Appl. Phys. Lett.* 74 (1999) 2720.