

A new directional model for the electronic frictional forces in molecular dynamics simulations of radiation damage in metals

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Abstract

The damage caused by collision cascades in irradiated materials forms the initial conditions for longer term microstructural evolution. The exchange of energy between electrons and ions during cascades can significantly affect this damage. Models for incorporating this exchange within classical molecular dynamics (MD) simulations exist, but most approximate the ion-electron energy transfer via a damping force, opposed to ionic motion. Although such forces predict the total energy transfer over the duration of cascades, they do not capture the complex dependence of the non-conservative electronic friction force on the speed, direction and atomic environment of individual ions. Here we present a new model for the electronic friction force, derived from quantum-classical Ehrenfest dynamics, which captures this complexity and is suitable for inclusion in existing MD codes at near-zero computational cost.

We show that our model reproduces the atomic level detail of the non-conservative electronic force in time-dependent tight-binding simulations of cascades.

Keywords: radiation damage, electronic friction, electronic excitation, stopping power, classical potential, atomistic simulation

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1. Introduction

1.1. *The effect of electronic excitations on collision cascade damage*

Collision cascades initiated within the functional metallic materials of nuclear reactors by high energy particulate radiation create damage at the atomic scale. This damage forms the initial conditions for long term microstructural evolution. Because such damage is formed on picosecond time-scales, beyond the reach of direct experimental observation, computational simulations of collision cascades play a crucial part in furthering our understanding of the performance of materials under irradiation. In recent decades, the method of choice for simulating radiation damage has been classical molecular dynamics (MD), in which the ions of a target material are represented as classical point particles moving under conservative bonding forces dependent only on their instantaneous positions; the role of electrons in determining the particle dynamics is limited to their implicit presence in the model employed for these conservative forces. The electrons are thus assumed to remain in the ground state and the simulations take place within the Born-Oppenheimer approximation [1].

In reality, the ions move sufficiently quickly during many radiation damage processes that the response of the electronic system is not quasi-instantaneous and the Born-Oppenheimer approximation is strongly violated. During a collision cascade, the electron cloud screening the moving ions cannot keep pace. It exerts non-conservative forces on the ions and gives rise to so-called *electronic stopping* phenomena. The electronic stopping forces extract energy from the developing cascade and act to reduce the extent of the initial damage distribution [2, 3]. The work done by the non-conservative electronic forces appears as a gradual excitation of the electrons in the vicinity of the cascade [4, 5]. Following the initial damage phase of the cascade, further exchange of energy between ions and electrons can significantly affect the residual defect population: further loss of ionic kinetic energy to the electrons can quench in a larger than expected number of defects or return of energy from the excited electrons to the ions can anneal the damaged region, reducing the number of defects. The balance between these processes will depend on the strength of the electron-phonon interaction and on the electronic thermal conductivity, as well as on the initial excess kinetic energy of the cascade [3, 6].

1.2. Incorporating electronic effects in classical MD

Determining the effects of electron-ion energy exchange on the long-term performance of materials under irradiation will require a simulation methodology capable of adequately capturing the physics of the energy exchange processes. Given the length- and time-scales of many radiation damage phenomena, computational constraints imply that classical MD will remain the method of choice for some time to come. A form of ‘fixed-up’ MD, accounting for energy exchange, would be a very useful tool and much progress towards such models has already been made [7, 8]. Various groups have carried out simulations in which a viscous drag force on the ions is used to represent either an electronic-stopping force [9] or the effects of electron-phonon coupling [2, 10].

These simple drag force models are often informed by theoretical treatments of the electronic stopping process as either the result of interaction of the ions with a homogeneous electron gas [11, 12] or of the excitation of electrons during isolated binary collisions [13, 14]. The former have also inspired an extension of the simple drag model to incorporate a dependence on the local electron density [15]. A common feature of all the drag force models is that they take no account of the excited state of the electrons. Recent work by Duffy et al. [16, 16, 6, 3, 17] takes steps to rectify this situation by representing the electrons within a classical MD simulation as an inhomogeneous electronic temperature distribution.

The model of Duffy et al. is generalised in figure 1 to present a prototype ‘fixed-up’ MD model for use in the simulation of radiation damage. The primary effect of the electrons is captured in the conservative forces $\mathbf{F}^0$ acting on the ions as in normal classical MD. The electrons themselves are represented explicitly via additional classical degrees of freedom, which keep track of the extent of the excitation of the electronic system. This classical model of the electrons may also include some form of internal evolution to account for the spatial redistribution of energy. Coupling between the ions and the electronic degrees of freedom is effected by additional non-conservative forces $\mathbf{F}_e^{\text{nc}}$ acting on the ions. The work done on the ions by these forces must be accounted for by a corresponding change in the energy of the electrons (given by some function of the electronic degrees of freedom). Figure 1 also represents an embedding environment in which the simulation system sits. A primary role of this environment is to allow for energy transport out of the

simulation region².

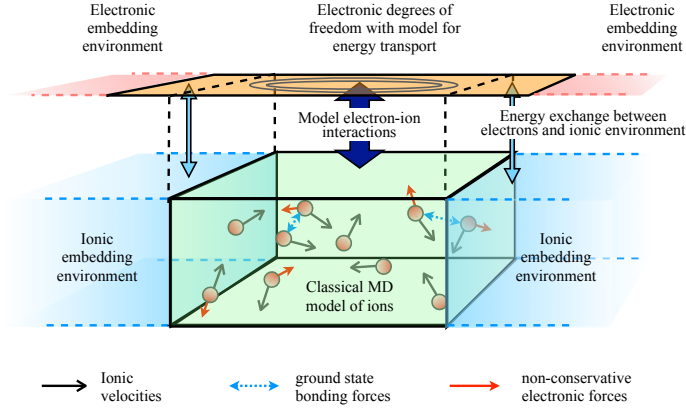


Figure 1: A schematic illustration of a prototype ‘fixed-up’ MD model. The details of such a model are discussed in the text of section 1.2.

In the model of Duffy et al. [6, 3], the electrons are modelled as an inhomogeneous temperature distribution, whose energy will then be determined by the electronic heat capacity. Drag and stochastic forces act on the ions to transfer energy respectively in and out of the electronic system, which itself evolves according to a heat diffusion equation. This model has an appealing simplicity and extendibility (e.g. via more complex models for electronic energy and heat flow), but it rests on several key assumptions. First, the action of the electrons in removing energy from the ions is assumed to be captured by a simple drag force, proportional to each ion’s velocity and acting in the opposite direction. As discussed above, such drag forces are informed by electronic stopping power theory, but these theories are based on highly simplified situations, in which many-atom effects and local atomic environment dependence are completely neglected. In general, we should expect the non-conservative forces to take a much more complex form. Second, the excited state of the electronic system is assumed to be well represented by a thermal (Fermi-Dirac) distribution at an elevated temperature. The validity of

²Because the dynamic model used to represent the electrons is likely to be much more computationally lightweight than the explicit MD representation of the ions, the core electronic model may extend beyond the bounds of the ionic MD region and so an additional type of energy exchange process between the electronic degrees of freedom and the ionic embedding environment must be accounted for in a full treatment.

this assumption is not completely obvious given that in many metals, the time-scale for the electron-ion interaction is similar to that for the electron-electron interaction so that excitations could well occur faster than thermal equilibrium within the electronic system can be established³.

The above assumptions are difficult to test experimentally, but we can gain the necessary insight into the energy exchange processes by making use of theoretical models in which such processes are explicitly represented. We consider a set of classical ions, labelled by a , mass M , with positions $\mathbf{R} = \{\mathbf{R}_a\}$ and momenta $\mathbf{P} = \{\mathbf{P}_a\}$, and a set of quantum mechanical independent electrons whose state is characterised by a set of evolving single-particle wavefunctions $\{|\psi_i\rangle\}$ with fixed occupations $\{f_i\}$. We can conveniently represent the electronic system with a single-particle density matrix $\hat{\rho} = \sum_i f_i |\psi_i\rangle\langle\psi_i|$. The energy of the combined system of ions and electrons can be written

$$E = |\mathbf{P}|^2/2M + U(\mathbf{R}) + 2\text{Tr}(\hat{\rho}\hat{H}(\mathbf{R})), \quad (1)$$

where $\hat{H}$ is a non-self-consistent single-electron Hamiltonian (the factor of two before the trace accounts for spin-degeneracy) and U is a repulsive ion-ion potential (representing the electrostatic energy of the ion core interactions and the exchange-correlation energy [20])⁴. This energy is conserved in a coupled evolution of the electron-ion system known as Ehrenfest dynamics, whose equations of motion are [21],

$$\frac{d\mathbf{R}}{dt} = \frac{\mathbf{P}}{M}, \quad (2)$$

$$\frac{d\mathbf{P}}{dt} = \mathbf{F} = -\nabla_{\mathbf{R}}U(\mathbf{R}) - 2\text{Tr}(\hat{\rho}\nabla_{\mathbf{R}}\hat{H}), \quad (3)$$

$$\frac{d\hat{\rho}}{dt} = \frac{1}{i\hbar}[\hat{H}, \hat{\rho}]. \quad (4)$$

³Femtosecond laser experiments by Del Fatti et al. [18] suggest that electron-electron interaction time-scales are of the order of a few hundred femtoseconds (they find time-scales of 350 fs in silver and 500 fs in gold). This is certainly not short on the time-scale of a typical collision cascade, in which the displacement phase is over within several picoseconds and is of a similar order of magnitude to the time-scale of the electron-phonon interaction (Qiu and Tien [19] use experimental data to find values of 650 fs in copper and only 64 fs in vanadium)

⁴We have omitted from Eq. 1 a term to account for Coulomb interactions between charged ions. This term is insignificant in the case of metals where efficient screening ensures that the ions remain close to neutral during collision cascades.

The transfer of energy between classical ions and quantum mechanical electrons in Ehrenfest dynamics arises because of the dependence of the evolution of the density matrix on the Hamiltonian $\hat{H}$ (which is itself a function of the ionic positions), and because of the electronic forces (of Hellmann-Feynman form) acting on the ions. It can be shown [22] that Ehrenfest dynamics is able to capture correctly the physics of stimulated emission and absorption of phonons. Spontaneous phonon emission is not accounted for, but will be insignificant in processes where the flow of energy is predominantly from the ions to the electrons, such as in the early stages of a collision cascade.

The electronic force $\mathbf{F}_e = -2\text{Tr}(\hat{\rho}\nabla_{\mathbf{R}}\hat{H})$ is dominated by the ground state electronic bonding forces, which the force models in classical MD simulations attempt to capture. However, as discussed above, the rapid ionic motion in radiation damage events means that electronic excitations in $\hat{\rho}$ can also contribute significantly to the force. The effects of excitations are of two types. First, excitations accumulate in $\hat{\rho}$ over time, gradually weakening the electronic bonding forces. We have previously shown that these accumulated excitations are manifest in radiation damage as a gradually rising electronic temperature [5] and so their effect on the conservative forces between ions could be captured in an MD simulation with an electronic temperature dependent potential. Note that the existence of this electronic temperature is *not* dependent on having a rapid thermalization of the electronic system: because the excitation is the result of the generation of many low-energy electron-hole pairs, the excited electronic occupations are close to thermal *in the first place* [5, 23]. The second effect of excitations on the electronic force is more complex and is the one that we will consider in this paper. The finite response time of the density matrix to changes in the electronic Hamiltonian gives rise to non-conservative electronic forces $\mathbf{F}_e^{\text{nc}}$. It is the work done by these forces that is manifest in the accumulating electronic excitations and as an energy loss from energetic ions. In the following section we will present a new classical model for these non-conservative quantum mechanical forces. A detailed derivation of this model has been presented elsewhere [24, 25] and so in the present paper we will focus on a discussion of the physics embodied in the model and its performance in simulations of radiation damage cascades in a model metal.

In section 2 we sketch the derivation of our model and consider the physics of electronic stopping in terms of lagged bonding responses in a real-space tight-binding picture. In section 3 we consider how our model could be used in practice. We derive a form of the model that can be directly compared with

the results of time-dependent tight-binding simulations of collision cascades evolving under quantum-classical Ehrenfest dynamics. This provides a direct test of the simplifying assumptions underlying our model.

2. A new model for the electronic frictional forces in MD

Our aim is to find an expression for the non-conservative contribution of electronic excitations to the total electronic force $\mathbf{F}_e = -2\text{Tr}(\hat{\rho}\nabla_{\mathbf{R}}\hat{H})$ that is simple enough to be incorporated within classical MD simulations of radiation damage, but that captures the complexity of the effects of the many-atom environment missing in simple drag models. The major difficulties in this task arise because the density matrix is not spatially local and its state at any time is dependent on the entire history of the combined system of classical ions and quantum mechanical electrons. We will begin by writing the total density matrix as the sum of a reference ground state and an excited part:

$$\hat{\rho}(t) = \hat{\rho}_0(\mathbf{R}) + \hat{\delta}(\mathbf{R}, t). \quad (5)$$

The reference state $\hat{\rho}_0$ is a function of the positions of the ions, and so has only an implicit dependence on time. We can choose this reference state to be either a fixed-temperature canonical state, in which the instantaneous eigenstates of the Hamiltonian $\hat{H}$ are occupied according to a Fermi-Dirac function, or an adiabatic state in which the occupations of the eigenstates are fixed⁵. If we consider a velocity Verlet time-stepping algorithm for our combined electron-ion system, then the momentum of the ions at some time $t + \delta t$ will be, to second order in the small interval δt ,

$$\mathbf{P}(t + \delta t) = \mathbf{P}(t) + \mathbf{F}(t)\delta t + \left. \frac{d\mathbf{F}}{dt} \right|_t \frac{\delta t^2}{2} + \mathcal{O}(\delta t^3). \quad (6)$$

We write the force as $\mathbf{F} = \mathbf{F}^0 - 2\text{Tr}(\hat{\delta}\nabla_{\mathbf{R}}\hat{H})$ where $\mathbf{F}^0 = -\nabla_{\mathbf{R}}U - 2\text{Tr}(\hat{\rho}_0\nabla_{\mathbf{R}}\hat{H})$ is the ground state force accounted for by the usual MD potential. If we now assume that at time t the excitations in the density matrix are negligible, i.e. $\hat{\delta}(t) \approx 0$, then $d\mathbf{F}/dt = \dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}}\mathbf{F}$ (where $\dot{\mathbf{R}} = d\mathbf{R}/dt$) because $\hat{\rho}_0$ has no explicit dependence on time and $i\hbar\partial\hat{\delta}/\partial t = [\hat{H}, \hat{\delta}] = 0$. Now,

⁵The distinction between these two choices is discussed in ref [24], but since it is a detail that does not affect our final model and is usually ignored in the classical potentials it is designed to augment we will ignore it here.

$\nabla_{\mathbf{R}}\mathbf{F} = \nabla_{\mathbf{R}}\mathbf{F}^0 - 2\text{Tr}(\nabla_{\mathbf{R}}\hat{\delta}\nabla_{\mathbf{R}}\hat{H})$, but since⁶ $\nabla_{\mathbf{R}}\hat{\rho} = 0$ we have, from Eq. 5, $\nabla_{\mathbf{R}}\hat{\delta} = -\nabla_{\mathbf{R}}\hat{\rho}_0$ and Eq. 6 becomes

$$\mathbf{P}(t + \delta t) \approx \mathbf{P}(t) + \left(\mathbf{F}^0(t)\delta t + \dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}}\mathbf{F}^0 \frac{\delta t^2}{2} \right) + 2\text{Tr}\left((\dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}}\hat{\rho}_0) \nabla_{\mathbf{R}}\hat{H} \right) \frac{\delta t^2}{2}. \quad (7)$$

The second term represents, to second order in δt , the effect of the force in the reference state. The final term represents the effect of the excitations arising over the period δt . To arrive at Eq. 7, we assumed that at time t , $\hat{\delta} = 0$. Clearly at a general time the density matrix $\hat{\rho}$ will have accumulated significant excitations. However, the electronic excitations occurring at widely separated times will tend to add incoherently and so will shorten the dependence of the non-conservative forces on the history of the evolution of the system. Our hope (one borne out by the results presented in section 3) is that there will be a correlation time τ , over which excitations in $\hat{\rho}$ contribute coherently to the non-conservative force $\mathbf{F}_e^{\text{nc}}$ that is short enough on the time-scale of ionic motion for us to be able to write,

$$\mathbf{F}_e^{\text{nc}} \approx 2\tau\text{Tr}\left((\dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}}\hat{\rho}_0) \nabla_{\mathbf{R}}\hat{H} \right). \quad (8)$$

Equation 8 has a physically appealing form: the non-conservative forces are analogous to Hellmann-Feynman-like forces but with the density matrix replaced by $\tau\dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}}\hat{\rho}_0$, which represents the extent to which the full time-evolved density matrix lags behind the reference state $\hat{\rho}_0(\mathbf{R})$. The faster $\hat{\rho}_0$ changes as a result of the movement of the ions, the greater this lag becomes and the larger are the non-conservative forces.

2.1. Lagged bonds - the non-conservative force in real-space

To make further progress towards a suitable form for the non-conservative forces we must now tackle the problem of the long spatial range of the density matrix. Our approach considers the effect of excitation of the density matrix

⁶This is clear if we recall that the full-density matrix is a time-evolved state, coupled to the motion of the ions, but without explicit dependence on their positions - in the same way that the position of a given ion has no *explicit* dependence on the position of any other, despite their inter-dependent co-evolution.

on the individual bonding interactions between moving ions. This provides a view of the origin of the stopping power that is both physically intuitive and consistent with the model of the interactions in classical MD.

We adopt a tight-binding approach and consider an orthonormal basis $\{|a_l\rangle\}$, where $|a_l\rangle$ is the l^{th} orbital on the ion at position $\mathbf{R}_a$. We define $|a\rangle = \sum_l |a_l\rangle$ (and similarly $|b\rangle$ and $|c\rangle$ for the ions at $\mathbf{R}_b$ and $\mathbf{R}_c$) and write the total electronic force,

$$\mathbf{F}_e = -2 \sum_{bc} \langle b | \hat{\rho} | c \rangle \langle c | \nabla_{\mathbf{R}} \hat{H} | b \rangle. \quad (9)$$

Since $\hat{H}$ is real-symmetric and $\hat{\rho}$ Hermitian we can write the electronic force on ion a as a sum over bonds with its neighbours ($\mathcal{N}_a$). The force acting along the bond between ions a and b is thus the product of the bond-order and the gradient of a hopping integral ($\hat{H}$) $_{ab}$.

Figure 2 illustrates the case in which two ions undergo a collision. In figure 2(a) we see the history of the inter-ionic separation. As the ions approach one another, the hopping integral between them (figure 2(b)) becomes increasingly negative, reaching its maximum magnitude at the point of closest approach and giving rise to a low energy bonding state. Figure 2(c) shows the gradient of this hopping integral. As the ions come closer together, electrons pile into the low energy localised bonding state as it forms and the bond-order increases (figure 2(d)). However, the electrons take a finite time to respond to the changing atomic environment and so the bond does not form and break symmetrically about the point of closest approach: the response of $\hat{\rho}$ lags behind the Born-Oppenheimer density matrix $\hat{\rho}_0$. The lagged response of the bond-order implies a corresponding asymmetry in the electronic force acting between the two ions (figure 2(e)) and so the moving ions do net work on the electronic system during the course of the collision (figure 2(f)).

In effect, the colliding ions are under-bonded on the way in to the collision and over-bonded on the way out. The non-conservative force on the projectile ion is thus at first decelerating and then accelerating, with the reverse being true of the target ion.

If we consider our expression in Eq. 8 in the same tight-binding picture, then we can write the *non-conservative* force acting on the ion at $\mathbf{R}_a$ as

$$(\mathbf{F}_e^{\text{nc}})_a \approx 2\tau \sum_{bc} \langle b | \dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}} \hat{\rho}_0 | c \rangle \langle c | \nabla_{\mathbf{R}_a} \hat{H} | b \rangle. \quad (10)$$

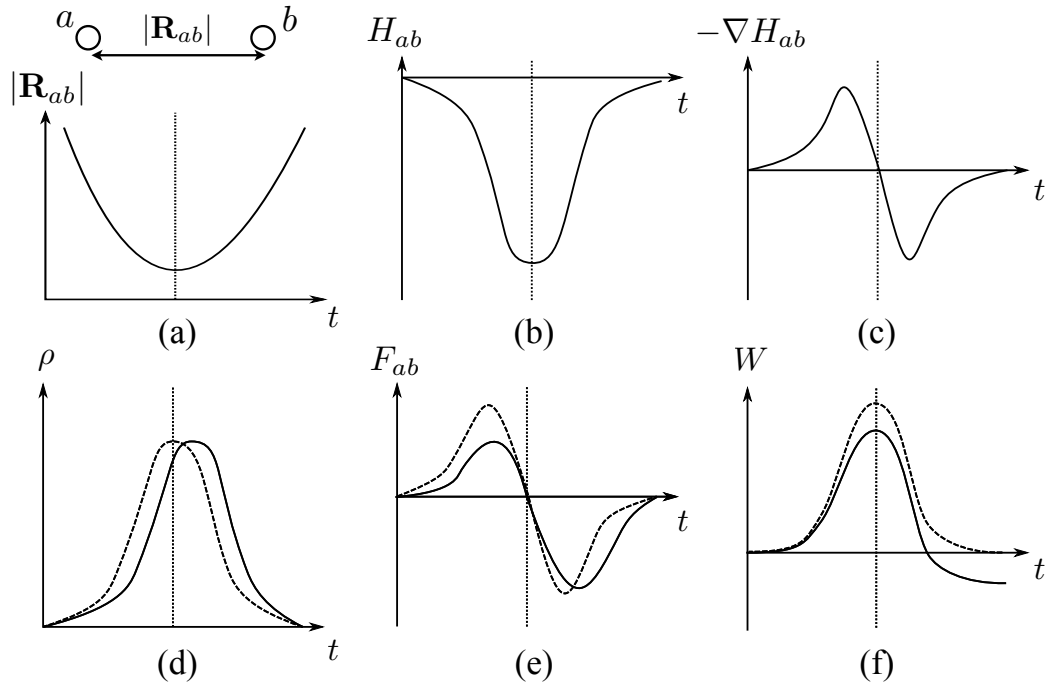


Figure 2: Schematic illustrations of the variation of various bond parameters during the collision of a pair of ions. (a) The separation of the ions; (b) the hopping integral between the ions; (c) the gradient of the hopping integral; (d) the bond-order; (e) the force on ion a from ion b in the direction $\mathbf{R}_{ab}$; (f) the cumulative work done against this force by ion a . In (d), (e) and (f) the dashed lines show the ground state response of the system ($\hat{\rho}_0$ and its corresponding forces).

The non-conservative force is proportional to rate of change of the bond length, but also of the bond-order. This makes sense: even if bond length is changing quickly, if the strength of the bond is not changing then there is no way for a lag in the response to give rise to a significant force. The neglect of three-body terms in $\hat{H}$ means that either $b = a$ or $c = a$ and because the electronic Hamiltonian is local the ion c or b respectively must be a neighbour of a . In contrast the excited portion of the density matrix, $2\tau\text{Tr}(\dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}}\hat{\rho}_0)$, contains contributions from all ions (since the gradient is with respect to the full position vector $\mathbf{R}$ and $\hat{\rho}$ is fundamentally long-ranged). To arrive at a useful expression we make the following assumptions:

1. That the electronic excitations that contribute to the non-conservative force from a given bond are those which result from the recent history of changes in the length of *that same bond*. The physical justification for this assumption is clearest in the case of energetic collisions during a cascade: such collisions are inherently local events and the changes taking place in the system will be strongly concentrated in just a few bonds. In the case of lower energy excitations, this assumption is pragmatically motivated and its validity must be demonstrated in practice.
2. That the excitation in a given bond-order between a given pair of ions a and b will be proportional to the local densities of states at those two ions, D_a and D_b . The individual electronic excitations generated in collision cascades are small on the scale of the band-width and so the non-conservative effects will be strongest where many low energy electronic excitations are available.
3. That the correlation time-scale τ will be proportional to the local density of states (which is a measure of the local electron-electron scattering time).

The basis and implications of these assumptions are considered in detail in reference [24], where we arrive at an expression for the non-conservative force on ion a of

$$(\mathbf{F}_e^{\text{nc}})_a \approx 4\hbar \sum_b \frac{D_a^2 D_b}{D} \left((\nabla_{\mathbf{R}_a} \hat{H})_{ab} \cdot (\dot{\mathbf{R}}_b - \dot{\mathbf{R}}_a) \right) (\nabla_{\mathbf{R}_a} \hat{H})_{ab}, \quad (11)$$

where D is the global density of states. Here we simply quote the result and note that due to the complexity of the system under study all our arguments,

irrespective of algebraic rigour, can only address the *plausibility* of our simplifying assumptions. Proof of the efficacy of the model rests on its success in application, which we will consider in the following section.

3. Results - assessing the performance of the model

3.1. Implementation of the model - an example

To illustrate how our model in Eq. 11 could be applied in classical MD simulations we will consider the case of potentials derived within the Finnis-Sinclair second-moment approximation [26]. In such potentials the binding energy of a set of ions is written

$$E_{\text{bind}} = \sum_a \sum_{b \in \mathcal{N}_a} \tilde{U}(R_{ab}) - \sum_a \alpha \sqrt{\sum_{b \in \mathcal{N}_a} H(R_{ab})^2 + P^2/2M}, \quad (12)$$

where $\tilde{U}$ is a pairwise ionic repulsion, $R_{ab} \equiv |\mathbf{R}_b - \mathbf{R}_a|$, $H(r)$ are model hopping integrals, $\mathcal{N}_a$ is the set of neighbours of ion a and α is an empirical constant. With this binding energy, the conservative force on ion a , the usual force in classical MD, will be

$$(\mathbf{F}^0)_a = \nabla_{\mathbf{R}_a} E_{\text{bind}} = \sum_{b \in \mathcal{N}_a} \nabla_{\mathbf{R}_a} \tilde{U}(R_{ab}) - \alpha \sum_{b \in \mathcal{N}_a} \left(\frac{1}{\sqrt{\Phi_a}} + \frac{1}{\sqrt{\Phi_b}} \right) H_{ab} \nabla_{\mathbf{R}_a} H_{ab}, \quad (13)$$

where we have defined $H_{ab} \equiv H(R_{ab})$ and $\Phi_a \equiv \sum_{b \in \mathcal{N}_a} H(R_{ab})^2$ to simplify the notation. The factor $\sqrt{\Phi_a}$ is the second moment of the local density of states on ion a which we identify as a measure of $1/D_a$. The non-conservative force corresponding to our Finnis-Sinclair potential can now be written using our model as

$$(\mathbf{F}_e^{\text{nc}})_a \approx -4\hbar x \sum_{b \in \mathcal{N}_a} \sqrt{\frac{\Phi_0}{\Phi_a^2 \Phi_b}} \left(\nabla_{\mathbf{R}_a} H_{ab} \cdot (\dot{\mathbf{R}}_b - \dot{\mathbf{R}}_a) \right) \nabla_{\mathbf{R}_a} H_{ab}, \quad (14)$$

x is a fitting constant, which we introduce to mitigate the approximations made in deriving Eq. 11 and in identifying $\sqrt{\Phi_a}$ with $1/D_a$. Because the hopping integrals are simple functions of the inter-ionic separations, this

non-conservative force is a function only of ionic positions and velocities, with summations only over near-neighbours and so could be implemented in an MD code at very low computational cost.

The presence of the fitting constant x in Eq. 14 should not be considered a weakness in comparison, for instance, to the simple drag model. Superficially it seems that experimental measures of electronic stopping powers could be directly incorporated as drag coefficients in the simple drag models. However, experiments typically measure electronic stopping powers in particular (usually channelling) geometries and at kinetic energies orders of magnitude higher than those found in collision cascades. Hence the adoption of an experimental stopping power in a simple drag model would be an implicit (and often poorly justified) fitting decision.

We can similarly use experimental stopping power data to fit x in our model, by calculating the model non-conservative force for a geometry comparable to that probed by the experiment under consideration and comparing it to the stopping power. Another approach would employ the results of time-dependent density functional theory (TDDFT) calculations of low velocity stopping powers to fit x . Progress towards such calculations has already been made [27] and, if problems with basis set convergence can be solved, this will be a more reliable approach than making use of experimental data from very different energy ranges.

Though here we have considered the case of Finnis-Sinclair potentials, a form of our model could be written down for any classical potential that incorporates some model form for the electronic hopping integrals. It is less clear how an analogue of Eq. 14 might be derived for more general ‘glue-model’ potentials, where the physical interpretation of the potential functions is different. However, there would be no logical inconsistency in using a form for the non-adiabatic force derived from, say, a Finnis-Sinclair potential for a given material to augment *any* model for the conservative forces: the non-conservative force will be captured within the validity of the second-moment approximation and the assumptions used to arrive at Eq. 11.

3.2. *Time-dependent tight-binding simulations of collision cascades*

Because the Finnis-Sinclair potentials underlying Eq. 14 derive from second-moment tight-binding, it will be instructive to compare the predictions of our model with the results of quantum-classical Ehrenfest dynamics simulations in a time-dependent tight-binding framework [21]. By using the same form for the hopping integrals in our simulations and in Eq. 14 we can largely

eliminate the effects of the details of the ground-state bonding model and so test the validity of the assumptions of spatial and temporal locality embodied in Eq. 11.

We have previously presented a methodology for simulating radiation damage cascades in a time-dependent tight-binding framework with Ehrenfest dynamics [28, 29]. By employing a simple single s -orbital tight-binding model for a generic metal [30] we can afford to follow the evolution of a fully quantum mechanical system of electrons coupled to moving classical ions. We have access to detailed information about the electronic excitations and non-conservative electronic forces in such simulations, which we can compare to the predictions of our new model.

In our tight-binding model, the hopping integrals are simple functions of the inter-ionic separations and so we can write $(\hat{H})_{ab} = H(R_{ab})$, where $R_{ab} = |\mathbf{R}_b - \mathbf{R}_a|$, and these functions are directly transferable to Eq. 14.

We have previously presented results from twenty-four simulations of small collision cascades with a 1 keV primary knock-on atom (pka) [24]. Here we extend the testing of our model to higher energies with the results of an equivalent set of simulations with 5 keV primary knock-on atoms. In each simulation, one ion amongst 2016 in a perfect static face-centred cubic (fcc) lattice is given 5 keV of kinetic energy in one of twenty-four non-equivalent directions. The electronic density matrix is initialized at a temperature of 300 K. The combined system of ions and electrons is allowed to evolve for⁷ 20 fs and every 0.05 fs the difference between the time-evolved density matrix $\hat{\rho}(t)$ and the ground state $\hat{\rho}_0(\mathbf{R}(t))$ (here chosen to be a canonical ground state at a fixed electronic temperature of 300 K) is used to calculate the non-conservative electronic forces and the net energy transferred from the ions to the electrons by the action of those forces. For each snapshot of each simulation we can then calculate the forces and energy transfer predicted by our model in Eq. 14.

We also calculate these quantities for two alternative models commonly employed in the literature: a simple drag model (labelled ‘viscous drag’ from now on), in which the non-conservative force is directly opposed to the ionic motion with a magnitude proportional to the ion speed, $(\mathbf{F}_e^{\text{nc}})_a = -\beta \dot{\mathbf{R}}_a$, and the environment-dependent model of Caro and Victoria (‘C-V model’) [15] in which the strength of the drag coefficient depends on a measure of the

⁷This typically takes 72 hours on a single 2.66GHz processor.

local electron density, $(\mathbf{F}_e^{\text{nc}})_a = -\beta(\rho(\mathbf{R}_a))\dot{\mathbf{R}}_a$.

Figure 3 presents data showing the net energy transferred to the electrons calculated for each model compared with the results from our direct quantum-classical simulations. To ensure fair comparison between the models, we have fitted a coefficient of proportionality for each one based on our simulation data. To test for transferability to the higher energy 5 keV cascades these coefficients are fitted only to the data for our previous 1 keV cascades and so take the values reported previously [24]. In figure 3(a) we show data for the directly fitted 1 keV cascades. Figure 3(b) shows the new 5 keV data. Both plots tell a similar story: the drag models are unable to account for the significant 2-3 $\times$ variation in the energy transfer with the initial pka direction. Our proposed model does a much better job of capturing this behaviour, both for the fitted 1 keV data and the new 5 keV cascade.

This failure of the simple drag models to predict the energy transfer on short time-scales in the early stages of a cascade should be contrasted with some of our previous results. In Ref. [29] we found that the simple models did a good job of capturing the *average* energy transfer over longer time-scales of 200 fs, encompassing the entire displacement phase of low energy (up to 1 keV pka energy) collision cascades. This contrast between poor performance of the drag models on the short term and greater success on longer time-scales is explained if we note that the energy loss due to a simple drag force is proportional to the time integral of the total ionic kinetic energy. Early in a cascade the total excess kinetic energy of the pka is shared between a relatively small number of ions and so the drag models predict almost the same energy loss for all the cascades simulated. On longer time-scales, the excess kinetic energy is more widely shared and much will have been converted to potential energy of the inter-ionic interactions. The rate at which a given cascade decays into a disordered state (and the pka energy is repartitioned) will then determine the energy loss predicted by the drag models on the longer term. If this rate of repartitioning correlates with the energy loss in the Ehrenfest simulations then the drag models will capture the variation between cascades.

In figure 4 we compare the detailed behaviour of the non-conservative force for a sample of ions in our simulations at 5 keV with the predictions of our model and the drag force models from the literature. For each of these ions we compare the magnitude of the Cartesian components of the non-conservative force and the work done by that force during the simulation. In each case, we can see that our new model reproduces much of the detail in the

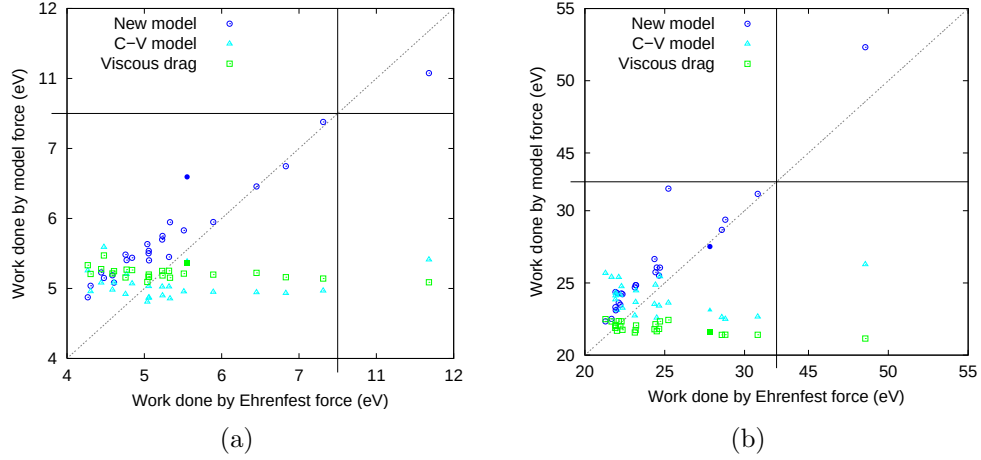


Figure 3: Comparisons of the work done by model non-conservative forces with the work done by the non-conservative forces in quantum-classical time-dependent tight-binding simulations under Ehrenfest dynamics. Each data-point represents a single simulation. The simulations are of cascades with (a) 1 keV pka energy and (b) 5 keV pka energy.

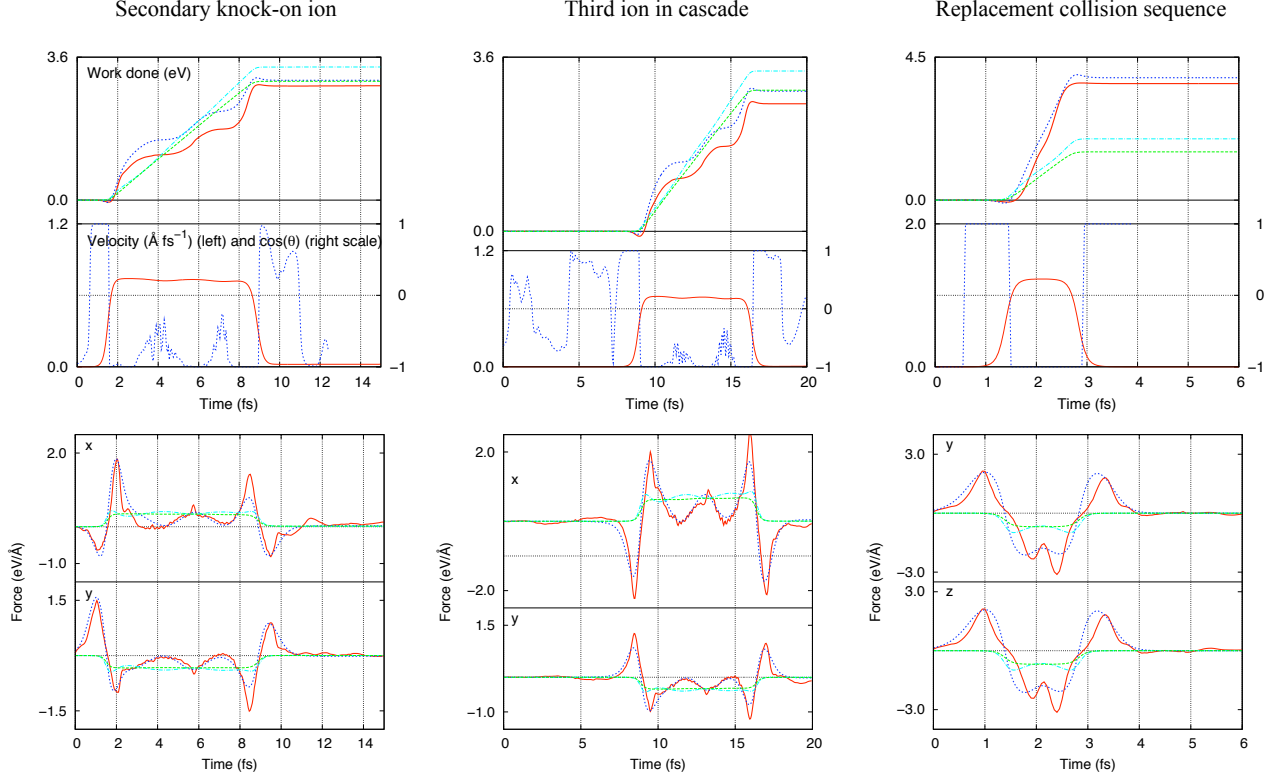
force in the quantum-classical Ehrenfest simulations. The drag force models miss this detail and so do a less good job of reproducing the energy loss of each ion. In particular, we see that the non-conservative force is certainly not, in general, anti-parallel to the ionic velocity.

In figure 5 we show a sequence of snapshots of a sample collision from our cascade simulations. We can clearly see the effects of directionality in our force model. Data on the bond-orders between ions are also shown and the lag in the bonding response is clearly evident.

4. Discussion and conclusions

In section 2 we presented a general expression for the non-conservative electronic forces on ions in Ehrenfest dynamics in a tight-binding framework (Eq. 11). To arrive at a form suitable for inclusion in classical MD simulations we made assumptions about the spatial and temporal locality of the effects of excitations in the electronic density matrix. These assumptions were pragmatically motivated, but we discussed their physical justification and presented evidence from simulations for their validity.

In section 3.1 we showed an example (Eq. 14) of a form of our model corresponding to a particular choice of classical potential (the Finnis-Sinclair



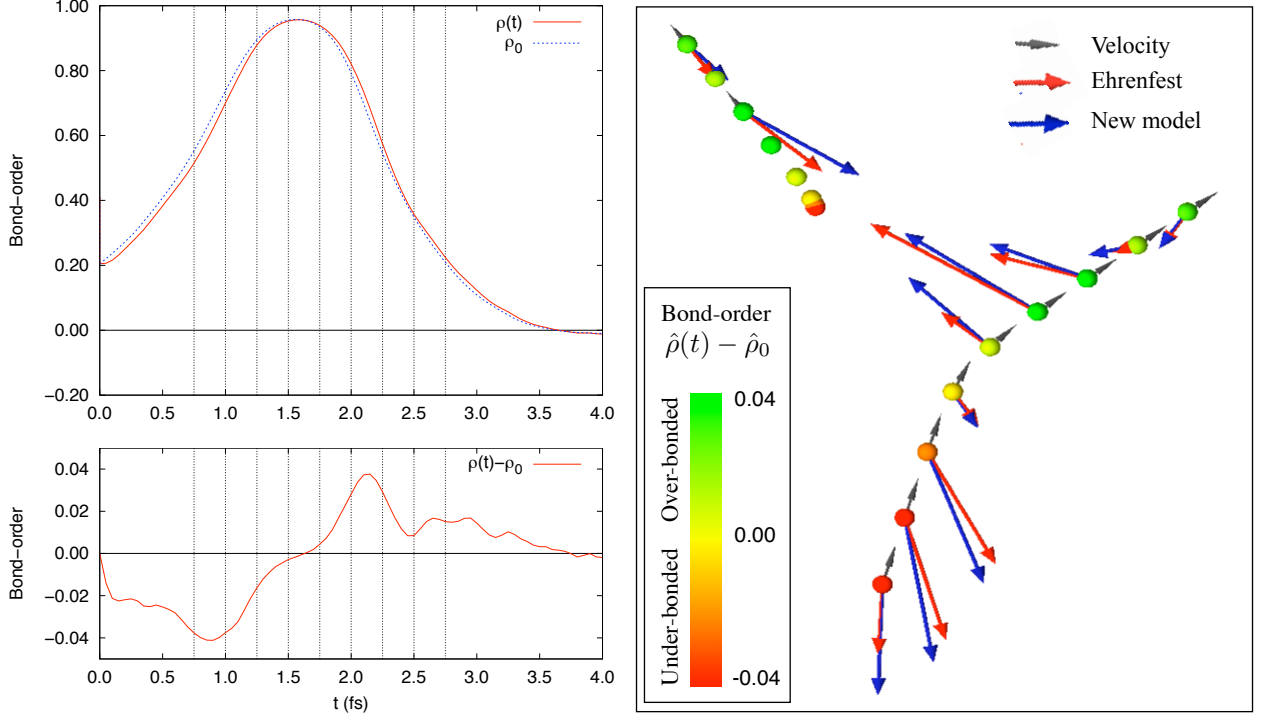


Figure 5: The bond-orders and non-conservative forces during an oblique collision. On the left-hand side are shown the bond-orders between the colliding ions in the electronic ground-state $\hat{\rho}_0$ and the evolved excited state $\hat{\rho}(t)$. The difference between these two bond-orders is also shown and a period of under-bonding, followed by one of over-bonding is clearly evident. On the right-hand side are shown snapshots of the ionic positions every 0.5 fs at the times marked by vertical lines in the plots. The ions are coloured according to the difference between the ground state and excited state bond-orders. Dark grey arrows indicate the velocities, red arrows show the non-conservative forces from the quantum-classical Ehrenfest simulation and blue arrows the predictions of our new model (for the target ion, these forces are only shown for two snapshots).

potential). In section 3.2 we compared the predictions of our model with the results of time-dependent tight-binding simulations of collision cascades. By using a simple tight-binding model metal we could directly test the validity of the simplifying assumptions behind Eq. 11, independent of the details of the underlying model for inter-ionic interactions. We found that our model performed well, capturing much of the fine detail in the direction, strength and work done by the non-conservative electronic forces. In contrast, simple drag models do not capture this detail and so are unable to account for a significant variation in the ion-electron energy transfer with pka direction in the early stages of the collision cascades.

In the simulations presented here, we have tested a form of our model (Eq. 14) at the level of the second-moment approximation to the density of states. This is consistent with the level of approximation in the conservative forces used in classical MD simulations of radiation damage and also makes a direct validation of our model using full quantum-classical simulations computationally tractable. In theory an equivalent to Eq. 14 could be derived from a more realistic electronic structure model, either by considering a more complex tight-binding model in Eq. 11 or working directly from the more fundamental expression in Eq. 8. However, at the present time it would be difficult to test such a model by direct quantum-classical simulation. In any case, it does not make sense to model the non-conservative forces in a more physically complete manner than the conservative forces that they correct.

The effect of the detailed directional and local-environment dependence of the non-conservative electronic forces on initial defect populations has not been established here. Implementation of our model in a large-scale MD code would allow for simulations on sufficient time- and length-scales to probe the difference in defect yields (or other measures of damage such as atomic mixing) between our model and simple drag models.

Another key issue for future work to address is the value of the fitting constant x in Eq. 14. As discussed, this constant could be chosen to agree with experimental results or with the output of the SRIM⁸ code [31]. This would parallel the approach used to determine the damping coefficients β in the simple drag models, but it is unsatisfactory, since SRIM and experiment address the problem of electronic stopping at very high energies. A more

⁸SRIM stands for ‘the stopping and range of ions in matter’.

satisfying approach would use TDDFT simulations to predict low velocity stopping powers and so determine x (or β) at energy ranges suitable for cascade simulations.

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