Electronic excitations and their effect on the interionic forces in simulations of radiation damage in metals

C. P. Race*, D. R. Mason* J. le Page*,
M. W. Finnis* §, W. M. C. Foulkes*, A. P. Horsfield §, A. P. Sutton*.

*Department of Physics, Imperial College London
§ Department of Materials, Imperial College London

Introduction

Using time-dependent tight-binding (TB) simulations of radiation damage cascades in a model metal we directly investigate the nature of the excitations of a system of quantum mechanical (QM) electrons in response to the motion of a set of classical ions. We also investigate the effect of these excitations on the forces between the ions.

A fast neutron impinging on a metal surface transfers kinetic energy to a primary knock-on atom (PKA) of the metal. This PKA collides with other ions, creating a disordered region known as a displacement spike. We go beyond the Born-Oppenheimer approximation of classical molecular dynamics (MD) to explicitly include QM electrons by applying semi-classical Ehrenfest dynamics to an s-band TB model of a metal. We can observe the electronic excitations produced and any effect that these have on the forces between ions. We identify two effects:

- The finite response time of the electron density to ionic motion gives a non-conservative force on the ions.
- Electronic excitations accumulate, reducing the conservative forces between ions.

Here we investigate the second of these effects.

Model and analysis

We use the simplest possible electronic Hamiltonian, for orthogonal *s*-orbitals on ions at $\boldsymbol{R}_I$ and $\boldsymbol{R}_J$,

$$H_{IJ} = \gamma(|\mathbf{R}_I - \mathbf{R}_J|) \quad I \neq J, \quad H_{II} = 0$$

The electrons are represented as a single particle density operator $\hat{\rho}(t)$, initialized according to a Fermi-Dirac (FD) distribution at temperature *T*(0) and evolved under the quantum Liouville equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\hat{\rho}(t) = \left[\hat{H}(\mathbf{R};t), \hat{\rho}(t)\right],$$

In addition to a pairwise repulsive force the ions experience an attractive electronic force given by

$$\mathbf{F} = -\mathrm{Tr}(\hat{\rho}\,\boldsymbol{\nabla}\hat{H}),$$

where $\boldsymbol{\nabla}$ acts on the ionic positions.

We write $\rho(t)$ in the basis of instantaneous eigenstates of the Hamiltonian at time *t* , $\{|\phi_i(\mathbf{R};t)\rangle\}$ with eigenvalues $\{\varepsilon_i(\mathbf{R};t)\}$ as

$$\hat{\rho}(t) = \sum_{i,j} |\phi_i(\mathbf{R};t)\rangle\, \rho_{ij}(t)\, \langle\phi_j(\mathbf{R};t)|$$

which defines the matrix elements $\rho_{ij}(t)$.

An adiabatic evolution in which the ions move infinitely slowly will take an initial eigenstate into the corresponding eigenstate at time *t*. We write an adiabatic density operator by fixing the occupations of the eigenstates at their initial values $\rho_{ii}(t=0)$, :

$$\hat{\rho}^0(\mathbf{R};t) = \sum_i |\phi_i(\mathbf{R};t)\rangle\, f(\varepsilon_i(0);T(0))\, \langle\phi_i(\mathbf{R};t)|.$$

We also define a thermal density operator in which the eigenstates are occupied at a temperature *T*(*t*)

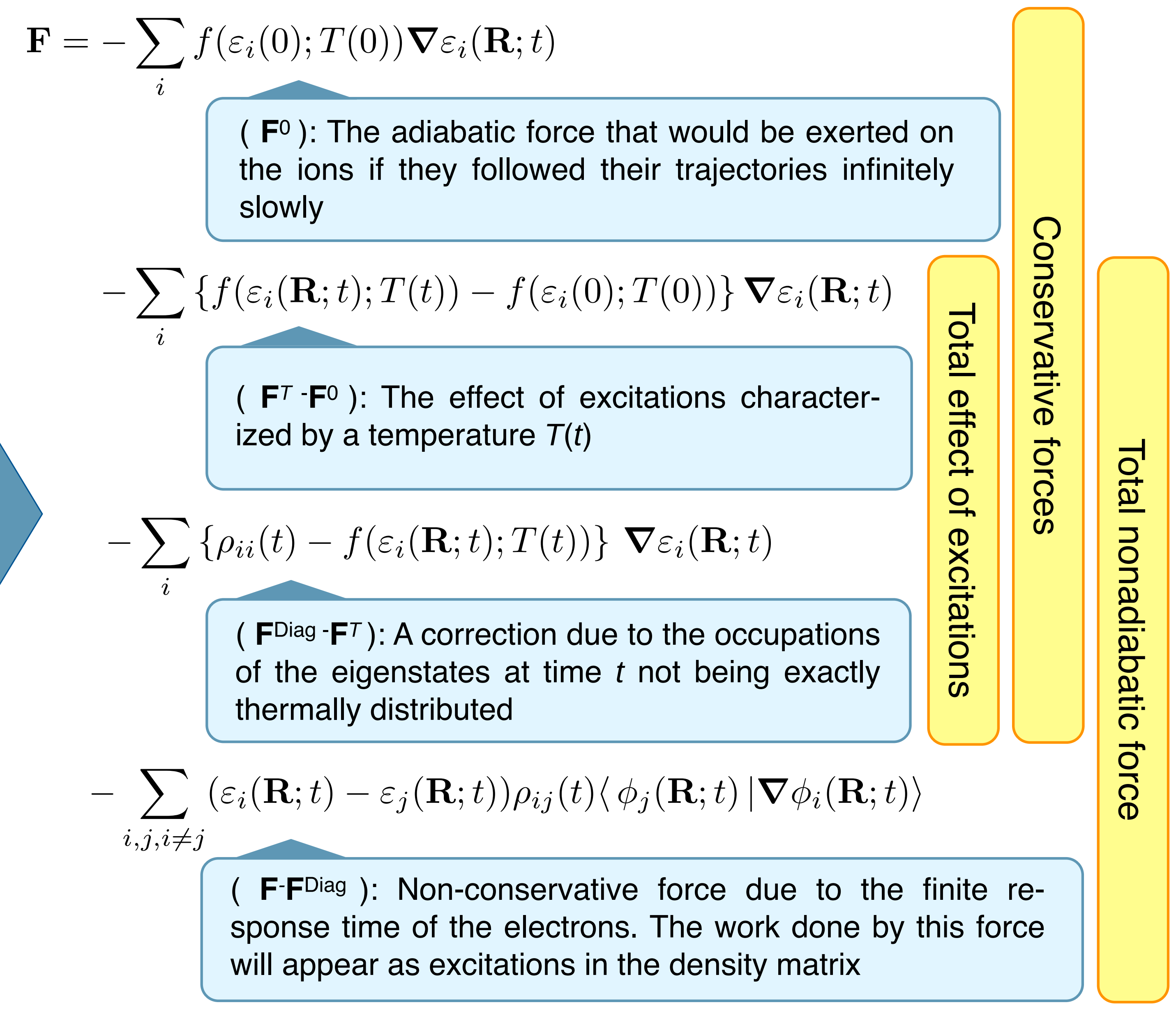
$$\hat{\rho}^T(\mathbf{R};t) = \sum_i |\phi_i(\mathbf{R};t)\rangle\, f(\varepsilon_i(\mathbf{R};t);T(t))\, \langle\phi_i(\mathbf{R};t)|$$

and one in which retain only the diagonal elements of the evolved density operator

$$\hat{\rho}^{\mathrm{Diag}}(t) = \sum_i |\phi_i(\mathbf{R};t)\rangle\, \rho_{ii}(t)\, \langle\phi_i(\mathbf{R};t)|.$$

For these density operators we can calculate corresponding forces, **F**, $\mathbf{F}^0$, $\mathbf{F}^T$ and $\mathbf{F}^{\mathrm{Diag}}$, and break up the total force into meaningful components (see right).

The electronic force



$$\mathbf{F} = -\sum_i f(\varepsilon_i(0);T(0))\boldsymbol{\nabla}\varepsilon_i(\mathbf{R};t)$$

($\mathbf{F}^0$): The adiabatic force that would be exerted on the ions if they followed their trajectories infinitely slowly

$$-\sum_i \{f(\varepsilon_i(\mathbf{R};t);T(t)) - f(\varepsilon_i(0);T(0))\}\,\boldsymbol{\nabla}\varepsilon_i(\mathbf{R};t)$$

($\mathbf{F}^T$ -$\mathbf{F}^0$): The effect of excitations characterized by a temperature *T*(*t*)

$$-\sum_i \{\rho_{ii}(t) - f(\varepsilon_i(\mathbf{R};t);T(t))\}\,\boldsymbol{\nabla}\varepsilon_i(\mathbf{R};t)$$

($\mathbf{F}^{\mathrm{Diag}}$ -$\mathbf{F}^T$): A correction due to the occupations of the eigenstates at time *t* not being exactly thermally distributed

$$-\sum_{i,j,i\neq j} (\varepsilon_i(\mathbf{R};t) - \varepsilon_j(\mathbf{R};t))\rho_{ij}(t)\langle\, \phi_j(\mathbf{R};t)\,|\boldsymbol{\nabla}\phi_i(\mathbf{R};t)\rangle$$

($\mathbf{F}$-$\mathbf{F}^{\mathrm{Diag}}$): Non-conservative force due to the finite response time of the electrons. The work done by this force will appear as excitations in the density matrix

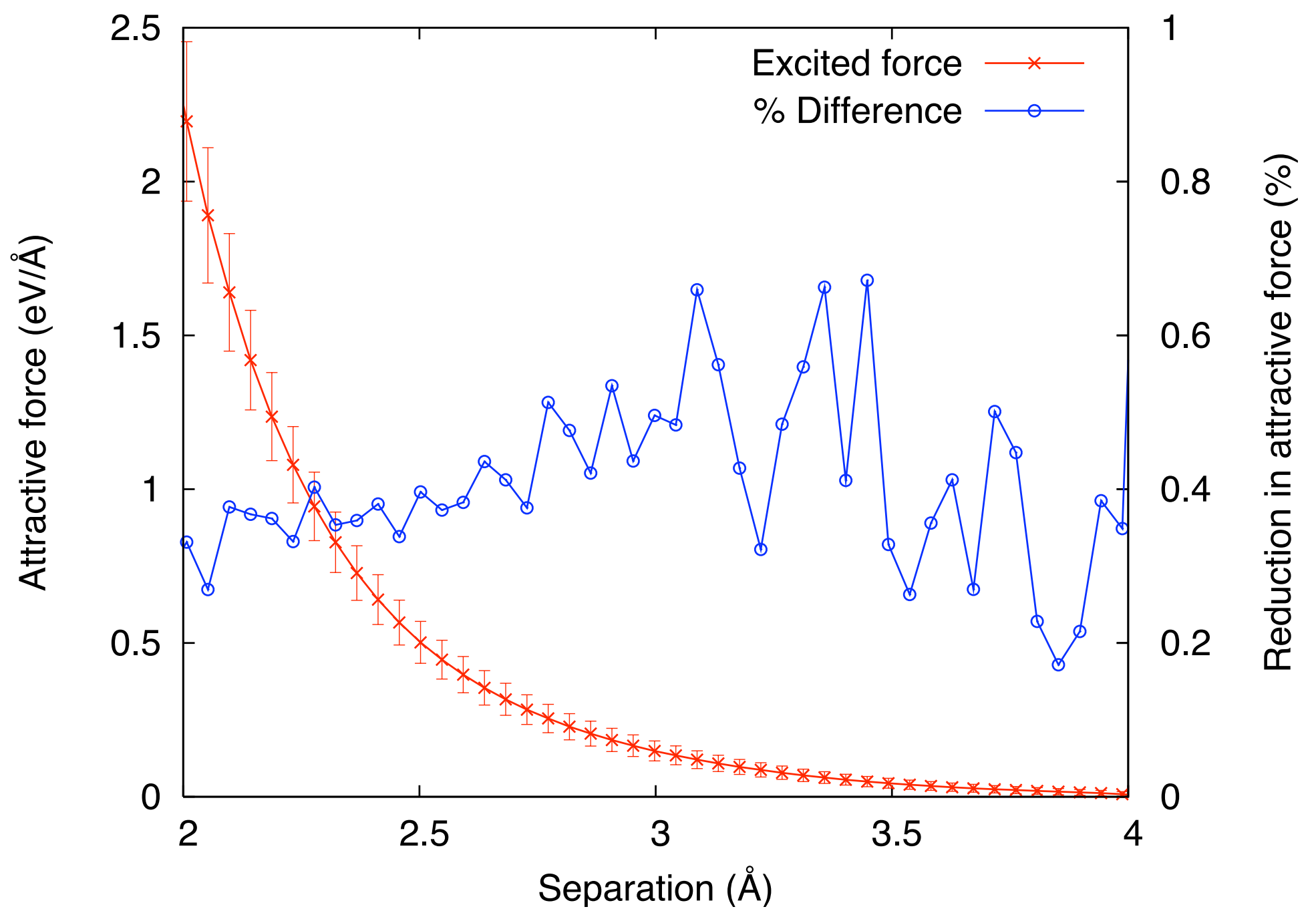
Total effect of excitations

Conservative forces

Total nonadiabatic force

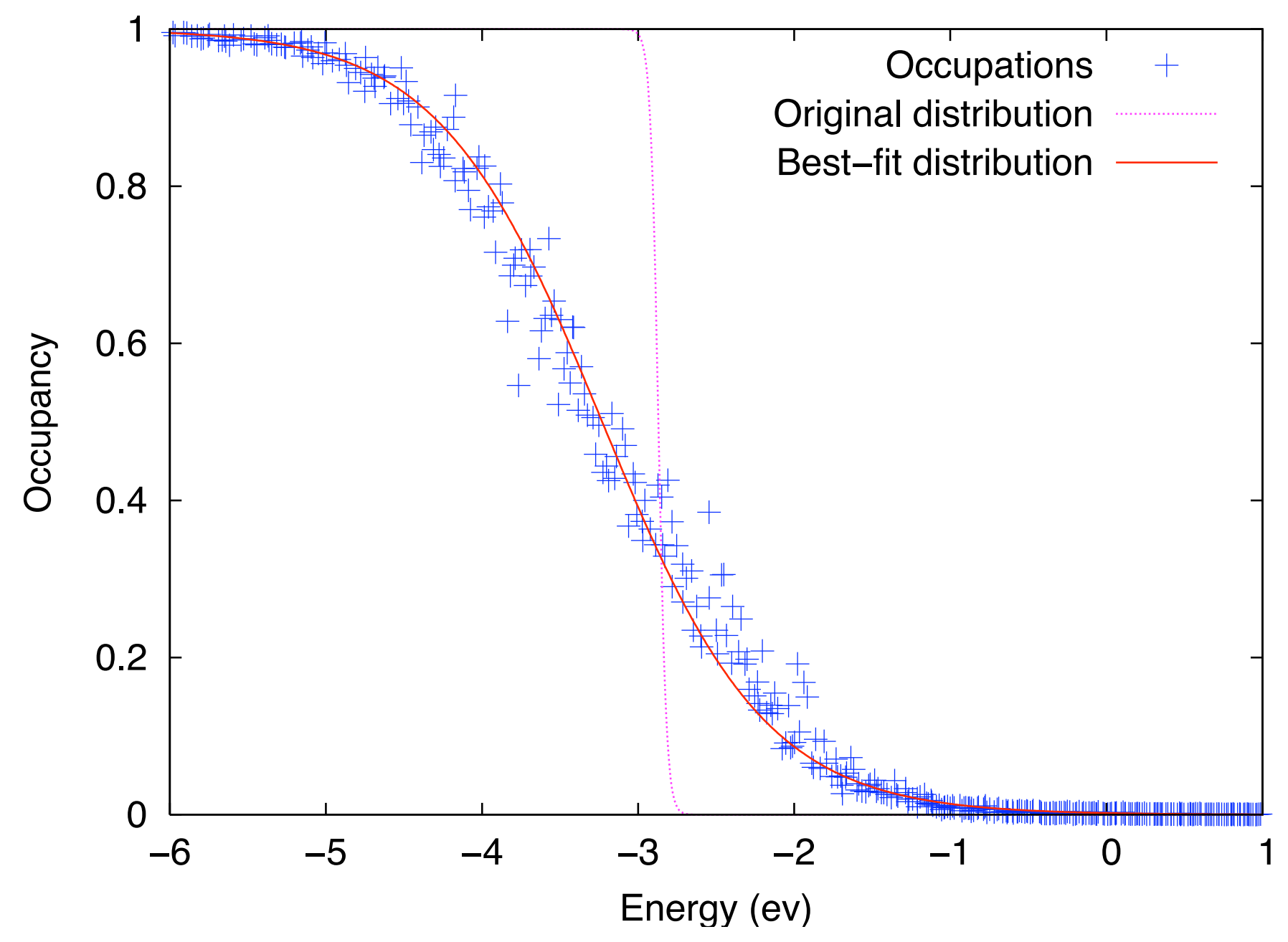
Results

1. Electronic force in 2keV cacade simulations



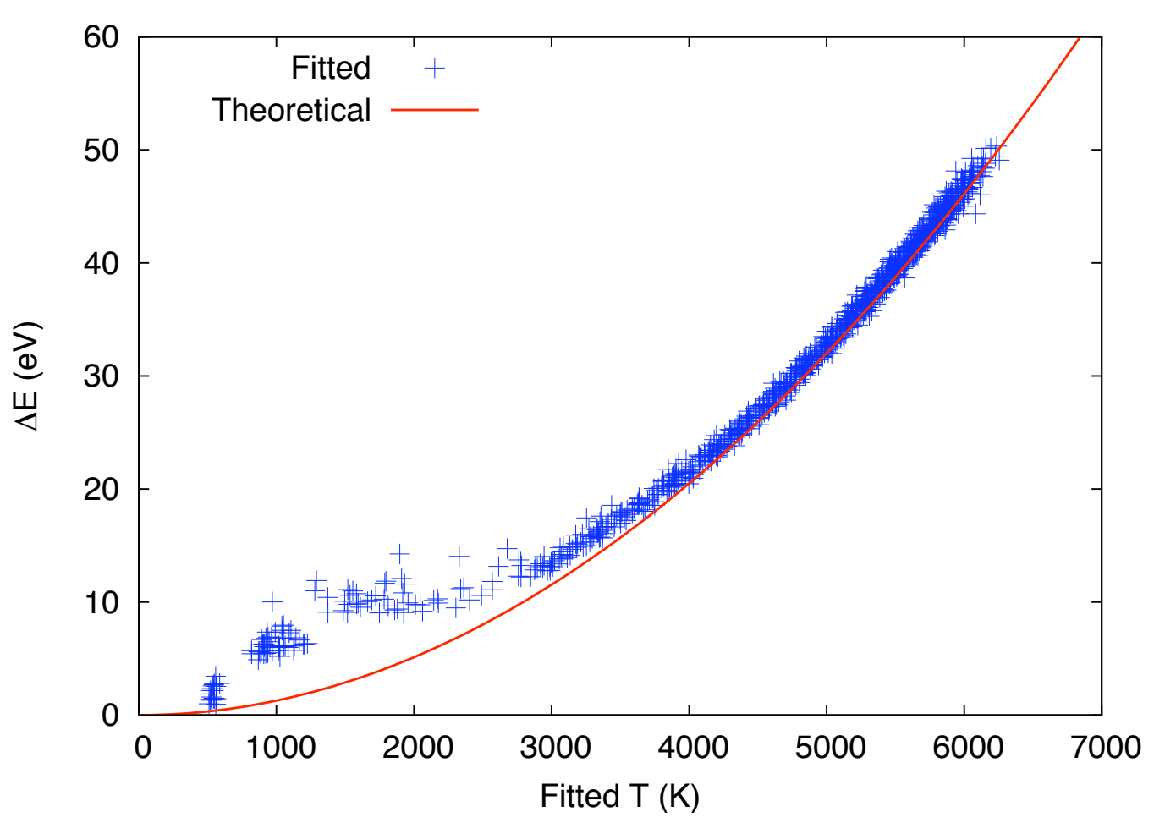
By running 44 simulations of 2keV cascades of 2016 atoms with periodic boundaries and averaging the bond order across all atom pairs with a given interionic separation we can determine the ensemble averaged attractive electronic force as a function of separation. Repeating the exercise for data corresponding to the adiabatic density operator ρ^0 allows us to calculate the percentage reduction in attractiveness, ($\langle F^0\rangle$ - $\langle F\rangle$)/ $\langle F^0\rangle$, due to electronic excitations. The data illustrated correspond to a simulation time of 225fs, at which point around 43eV has been transferred to the electrons.

2. A typical eigenstate occupation spectrum



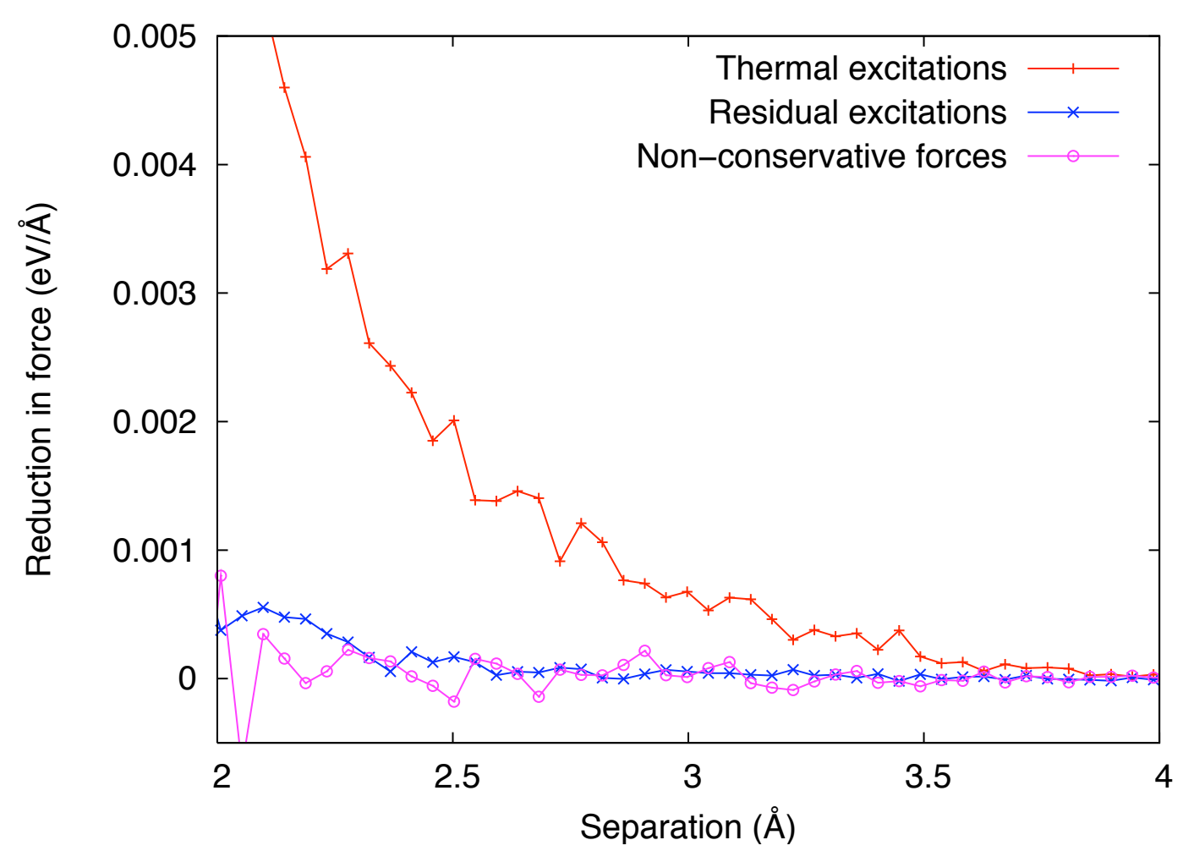
If we examine the occupations ρ_{ii} of the eigenstates of energy ε_{i} we find an approximately thermal distribution at an elevated temperature. This is true even without thermalizing electron-electron interactions because all the individual electronic excitations during the simulation are small on the scale of $k_{\mathrm{B}}T$.

3. Fitting temperatures to the excited spectra



If the excitations are well described by a FD distribution then it should be possible to find a good linear fit to ln(1/ρ_{ii}-1) against ε_{i}-μ that has a relationship to the nonadiabatic energy transfer from ions to electrons $\Delta E=\mathrm{Tr}((\rho-\rho^0)H)$ that is common to all simulations at all times. We find just such a relationship and find also that the behaviour of the fitted temperature T_{fit} corresponds well with a heat capacity calculated using the Sommerfeld expansion.

4. A thermal model for the interionic forces

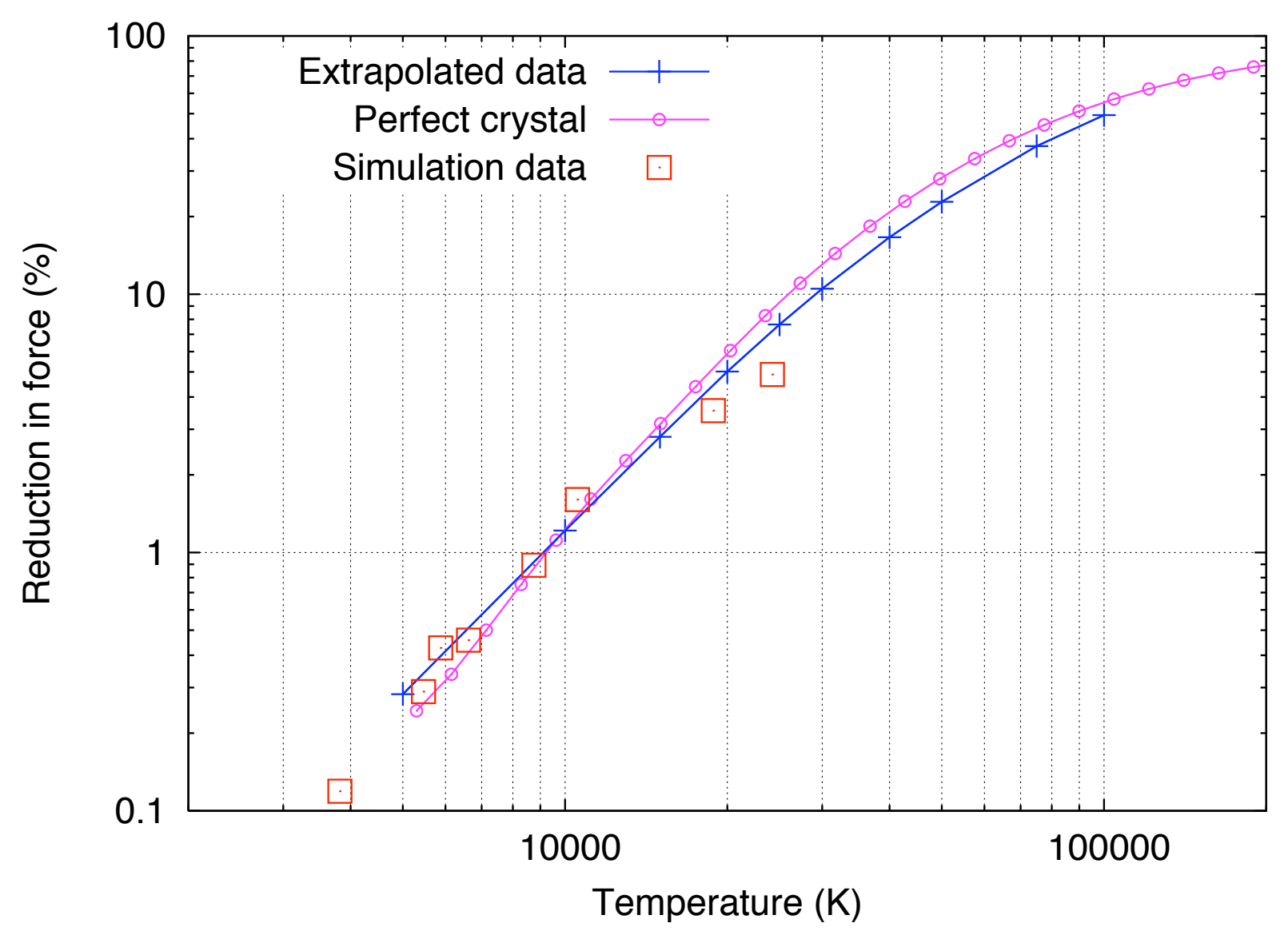


Because a fitted temperature captures well the behaviour of the energy transfer ΔE, we might also hope that it accounts for the majority of the effect of electronic excitations on the electronic force. By comparing the ensemble averages of $\mathbf{F}^T$-$\mathbf{F}^0$, $\mathbf{F}^{\mathrm{Diag}}$-$\mathbf{F}^T$ and $\mathbf{F}$-$\mathbf{F}^{\mathrm{Diag}}$ we find a thermal model for the electronic excitations captures 95% of the effect on the conservative interionic force.

5. Extrapolating to higher excitation energies

Exploiting the good validity of a thermal model for excitations allows us to extrapolate our low energy simulation results to higher energies by:

1) Imposing an elevated electronic temperature on the ionic positions at the end of our initial simulations



2) calculating the effect of elevated electronic temperatures on the bond-orders in a perfect crystal.

We compare the percentage reduction in the attractive force obtained by these two methods along with the output from direct simulation of higher energy cascades (up to 50keV PKA energy). We find good agreement between the three datasets.

Conclusions

We find that the electronic excitations in time-dependent TB simulations of collision cascades using Ehrenfest dynamics are well described by a FD distribution at an elevated temperature and that this temperature is related to the non-adiabatic energy transfer ΔE by the Sommerfeld form for the electronic heat capacity. We also find that a thermal model captures over 95% of the reduction in the attractive electronic force due to the excitations and can thus extrapolate our results to find the effect of higher levels of electronic excitation on the electronic forces between ions.

One way to include the effects of electronic excitation in a classical MD simulation, would be to make the potential dependent on the local electronic temperature. Construction of such a potential will be greatly simplified by the assumption of a FD distribution for the electrons. Our work adds to the justification for that assumption.

More information

Published papers:

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Website:

www.cmth.ph.ic.ac.uk/people/d.mason/RadiationDamage