A model for interatomic forces in metals with excited electrons

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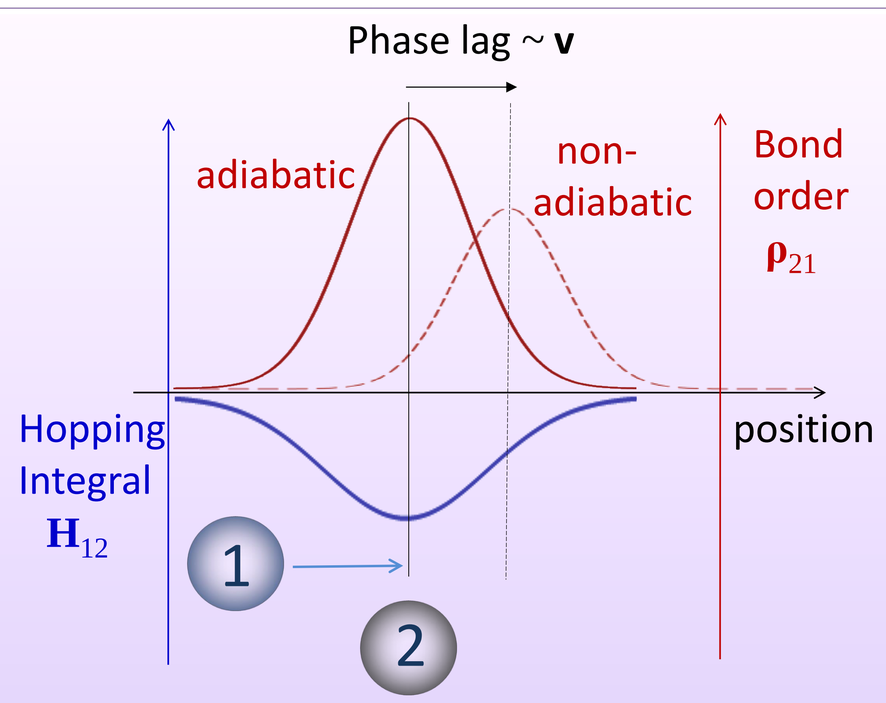
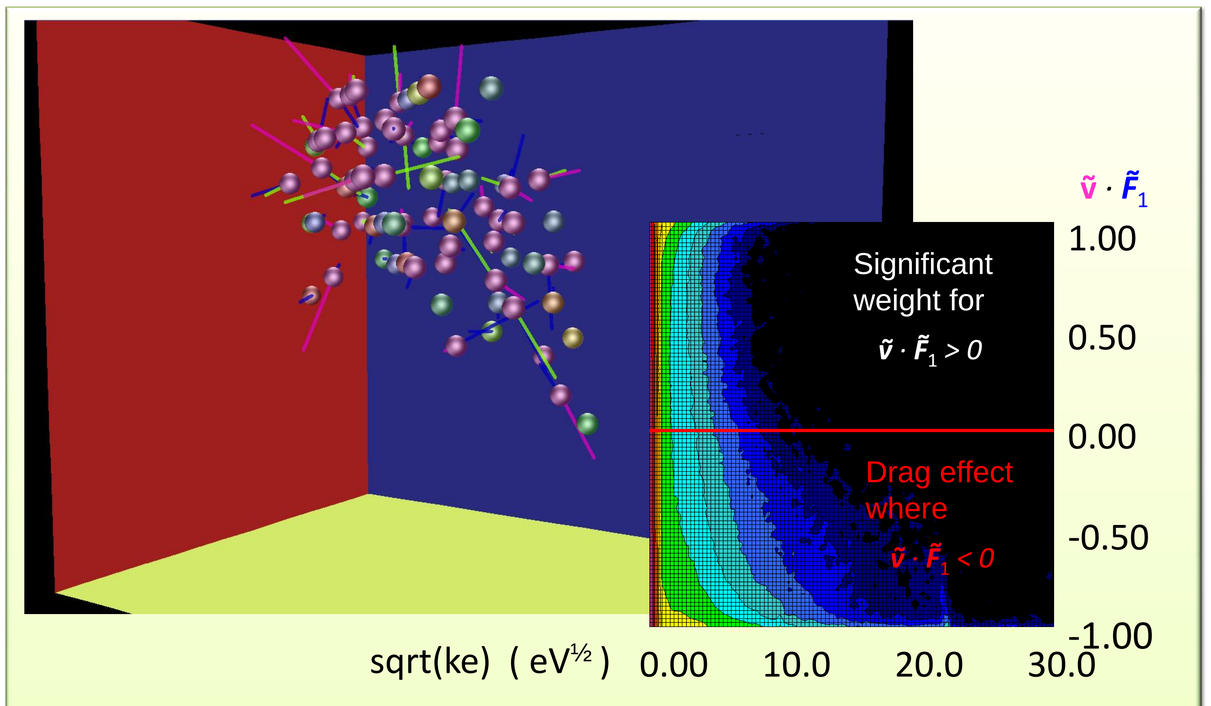
In classical MD simulations of metals, electrons are treated only implicitly within the empirical potentials. Where included non-adiabatic forces are modelled as an electronic friction– an additional viscous drag force– justified by models of electronic stopping in idealised binary collisions or in a homogeneous electron gas. Such treatments successfully predict the statistical behaviour of energy exchange processes [1], but will not capture the microscopic detail of the non-adiabatic forces seen in quantum mechanical cascade simulations.



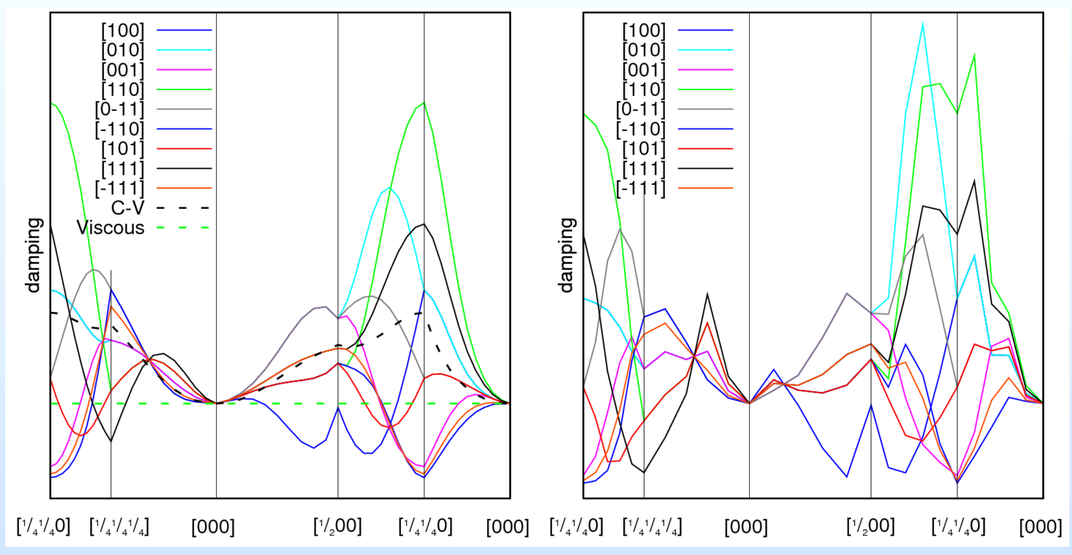
When atom 1 passes atom 2, an attractive electrostatic well forms between them, pulling electrons into bond 1-2. Adiabatic evolution assumes the electron response is infinitely rapid, but in reality it lags behind, changing the Hellman Feynman force $\boldsymbol{F} = -2\mathrm{Tr}(\nabla\hat{\mathbf{H}}\,\hat{\rho})$. We must compute the non-adiabatic force $\boldsymbol{F}_1 = -2\mathrm{Tr}(\nabla\hat{\mathbf{H}}\,\delta)$, where δ is the change in the electron density matrix.



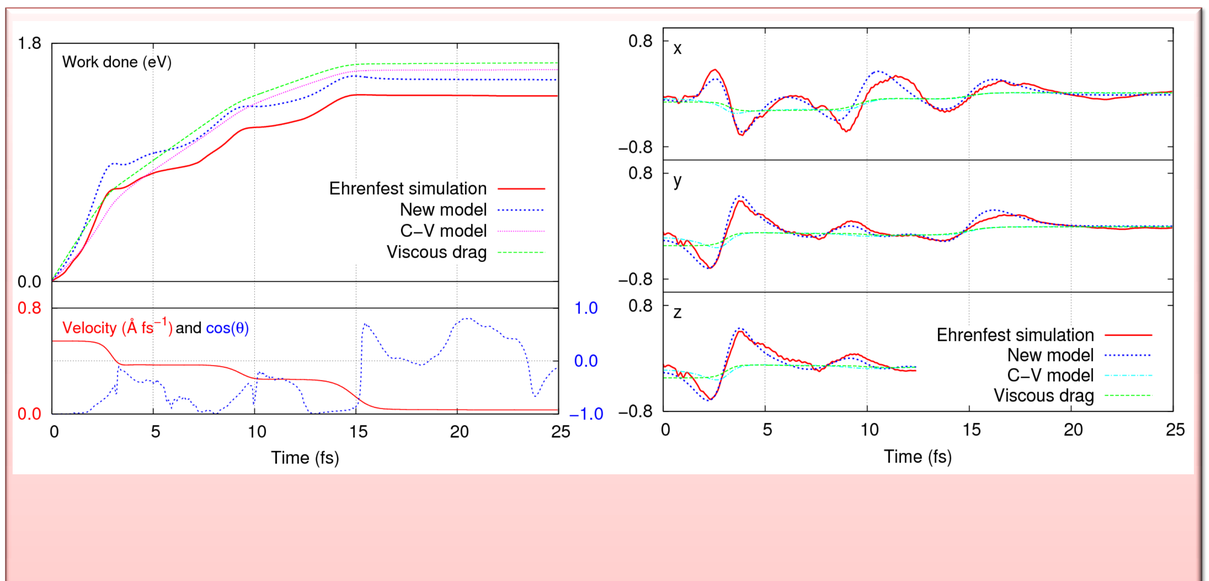
30fs into a 1keV cascade in 2016 atoms computed quantum mechanically within the Ehrenfest approximation. Velocity ***v***, Hellmann-Feynman force ***F***, and non-adiabatic force $\boldsymbol{F}_1$ vectors shown. $\boldsymbol{F}_1$ is scaled for clarity. Note $\boldsymbol{F}_1$ is neither antiparallel to or proportional in magnitude to ***v***. Inset: histogram of the cosine of the angle between unit vectors $\tilde{\boldsymbol{v}}$ and $\tilde{\boldsymbol{F}}_1$.

The non-adiabatic force can be shown to accumulate in the direction $\boldsymbol{F}_1 = \tau\,\mathrm{Tr}[\,(\boldsymbol{v}.\nabla\hat{\rho})\nabla\,\hat{\mathbf{H}}\,]$, where ***v*** is a 3N vector of all velocities. We argue that as electronic excitations produced in collisions rapidly decohere, this expression may be localised both in time and space. In the spirit of a Finnis-Sinclair second-moment approximation we find the non-adiabatic force on atom a in a form suitable for use in MD:

$$\boldsymbol{F}_{1a} \approx -2\hbar x \sum_{b\in N_a} \sqrt{\frac{\mu_0^{(2)}}{\mu_a^{(2)}\mu_a^{(2)}\mu_b^{(2)}}}\left[\nabla_a H_{ab}\cdot\left(\boldsymbol{v}_b-\boldsymbol{v}_a\right)\right]\nabla_a H_{ab}$$



The environment and direction dependence of electronic damping computed with our force model(left) compared with the computed damping experienced by an idealised oscillating interstitial (right) in a tight-binding model metal, (after [2]). One atom in a perfect lattice is displaced to the position indicated on the horizontal axis, then made to oscillate at 0.5 rad/fs in each of 9 different directions. Superimposed on the force model plot predictions from viscous damping and a density dependent damping model (C-V [3]).



Our model reproduces in detail the non-adiabatic forces on individual atoms during a collision and so captures the work done by non-adiabatic forces with unprecedented accuracy. (Left): the upper panel shows the work done by $\boldsymbol{F}_1$ acting on a PKA in a sample Ehrenfest simulation of a collision cascade. The lower panel shows ***v*** and $\tilde{\boldsymbol{v}}.\tilde{\boldsymbol{F}}_1$. (Right): the Cartesian components of the non-adiabatic force (in eV/A).

[1] J. le Page *et al.* How good is damped molecular dynamics as a method to simulate radiation damage in metals? New Journal of Physics,**11**(1):013004, 2009.
[2] D. R. Mason *et al*. Electronic damping of atomic dynamics in irradiation damage of metals. Journal of Physics: Condensed Matter, **19**(43):436209, 2007.
[3] A. Caro and M. Victoria. Ion-electron interaction in molecular-dynamics cascades. Phys. Rev. A, **40**(5):2287–2291, 1989.