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We present a model for non-adiabatic classical molecular dynamics simulations that captures with high accuracy the wave-vector $q-$dependence of the phonon lifetimes, in agreement with quantum mechanics calculations. It is based on a local view of the e-ph interaction where individual atom dynamics couples to electrons via a damping term that is obtained as the low velocity limit of the stopping power of a moving ion in a host. The model is parameter free, as its components are derived from *ab initio*-type calculations, is readily extended to the case of alloys, and is adequate for large scale molecular dynamics computer simulations. We also show how this model removes some oversimplifications of the traditional ionic damped dynamics commonly used to describe situations beyond the Born-Oppenheimer approximation.

I. INTRODUCTION

Computational materials science is one of the fastest growing areas in physics and chemistry. Scientists have long used computers to model materials and their performance; but today, with ever-growing supercomputers, which employ millions of microprocessors to tackle simulations once considered intractable, the accuracy of some simulations are able to reliably predict properties of new materials without testing. However, material properties often depend on phenomena that take place over several scales, from nanometers to meters, from billionth of a second to years. No computer in the near future will be able to solve such challenges within a single theoretical framework, for example, quantum mechanics at the atomic scale.

To bypass this limitation, scientists have for years been developing the concept of multi-scale modeling. This approach combines different models in order to cover the full range of length and time scales of interest for a particular problem. The most common approach to multi-scale modeling is called information passing. In this method simulations of matter at one scale are based on the results of simulations at a lower (more finely detailed) scale. The challenge to perform a coherent simulation of a material lies on building robust connections between such different scales.

One of the most difficult connections is between the electronic and the atomic scales, specifically, between quantum mechanics, QM, for electrons and classical mechanics for the ions, because classical mechanics is not a coarser view of QM. One of the best examples of success in this area is the development of the so called 'classical many body potentials'[1,2] to describe ion-ion interactions, done 30 years ago. It describes the potential energy of an ensemble of atoms as a simple non linear function of the sum of pair interactions. This assumption captures the essence of metallic cohesion, which in a tight binding language says that bonding is a function of band width, which itself is a function of wave-function overlaps, and it does that at an insignificant computational cost compared to any QM model for the electrons. This model gives materials scientists a tremendous power to predict atomic scale behavior in many metals and alloys and represents a seminal contribution to computational materials science, and probably the most successful connection between scales in the multi-scale paradigm.

In this work we present a classical mechanics model that captures the essence of another QM phenomenon namely the electron-phonon, e-ph, interaction, and does so also at an insignificant computational cost. The model presented here captures with high accuracy the wave-vector q dependence of the phonon lifetimes in agreement with sophisticated QM calculations. It is based on a local and instantaneous view of the e-ph interaction where individual atom dynamics couples to electrons via a damping term that is obtained as the low velocity limit of the stopping power of a moving ion in a material. Moreover, the model is parameter free, as its components are derived from *ab initio*-type calculations.

In a recent paper[3] we calculated the e-ph interaction as a particular case of an electronic stopping process, providing a simple solution to the empiricism present today in molecular dynamics simulations of non-adiabatic processes[4,5].

The inclusion of electronic effects into classical MD simulations is usually achieved using Langevin dynamics, where a friction term, $-\beta v$, added to the Newton equations of motion, removes energy from moving atoms, while a random force term simulates the stochastic thermalizing collisions with electrons. The approach proposed years ago by Caro *et al.*[6], treats the β term as a function of the local electronic density of the host, and the electronic system as a large heat bath at a constant temperature. Today, that simple approach has been largely improved by treating the energetics of the elec-
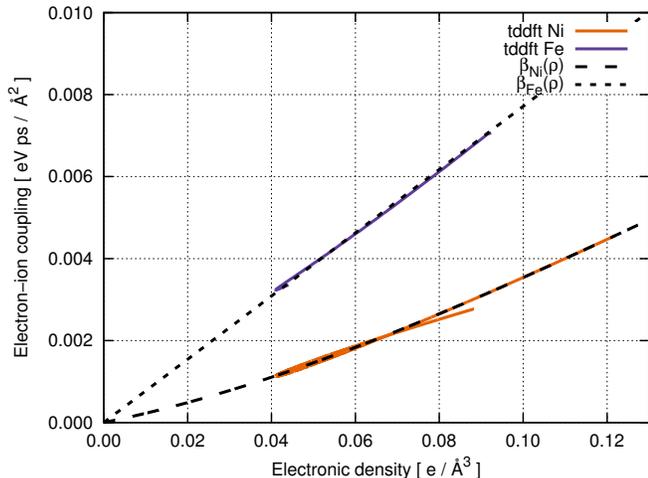
Figure 1: Damping term β in the Langevin equations as a function of local electronic density calculated using TDDFT for Ni and Fe projectiles moving across a vacancy site in an fcc Ni crystal. Also plotted is the fitted quadratic function for $\beta(\rho)$ that was used in MD simulations.
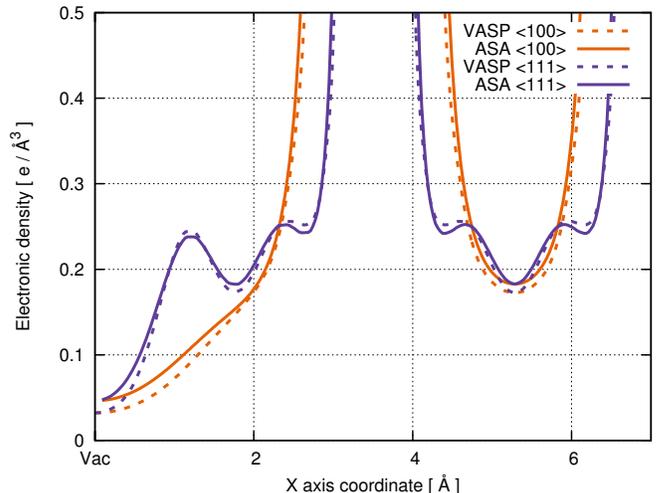

Figure 2: Electronic density in Ni crystal with a single vacancy along $\langle 100 \rangle$ (red) and $\langle 110 \rangle$ (blue) directions. The solid line is obtained with ASA method and dashed calculated using VASP. The symbol Vac shows the location of a vacancy in Ni crystal.

tronic system as a continuum described by a specific heat and a thermal conductivity, whose thermal state is solved via the heat equation on a mesh, simultaneously with the ionic equations of motion. This approach, known as the Two Temperature hybrid MD Model, TTM-MD, represents the state of the art for non-adiabatic MD simulations of radiation damage[5], although it is important to mention that in most cases, the β term is assumed constant. When it is assumed to be a function of the local electronic density, it has been proven to give a much better agreement with quantum mechanical calculations[7].

In Ref.[3] we describe β as a specific function of the local host electronic density, as seen by the moving atom. This simplifying assumption naturally accounts for the differences in β values seen by energetic projectiles visiting regions of high electronic density of the host, and slow, thermal, atoms moving around their equilibrium positions, where the density contributed by the other, host, atoms is at its minimum. We refer the reader to that paper for the introductory discussion to the subject.

II. METHOD

In this paper we first use time dependent density functional theory, TD-DFT, to evaluate $\beta(\rho)$ for both a Ni atom moving around its equilibrium position in a Ni lattice, i.e. $\beta_{\text{Ni}}(\rho)$, and an Fe atom substituting a Ni one in the same Ni lattice, i.e. $\beta_{\text{Fe}}(\rho)$. This last case provides the information needed to describe the e-ph interaction in NiFe alloys. With these functions we then evaluate the phonon lifetime that results from the e-ph interaction; we compare these results with QM calculations based on

perturbation theory.

Our model is a modified version of the Langevin equations of motion describing an ensemble of classical degrees of freedom (Boltzmann statistics) in contact with a heat reservoir, in our case, the electrons, namely,

$$\mathbf{F}_I = -\boldsymbol{\nabla}_I U(\{\mathbf{R}_J\}_J) - \beta_I(\rho^*(\mathbf{R}_I))\mathbf{v}_I^* + \boldsymbol{\eta}_I \quad (1)$$

$$\rho^*(\mathbf{R}_I) = \sum_{J \neq I} \rho_J(R_{IJ}) \quad (2)$$

$$\mathbf{v}_I^* = \frac{1}{\rho^*(\mathbf{R}_I)} \sum_{J \neq I} \rho_J(R_{IJ})(\mathbf{v}_I - \mathbf{v}_J) \quad (3)$$

with each component of the random force $\boldsymbol{\eta}_I$ defined by,

$$\langle \eta_I^{(i)}(t) \rangle = 0 \quad (4)$$

$$\langle \eta_I^{(i)}(t)\eta_I^{(j)}(t') \rangle = \delta_{ij}\delta(t - t')2\beta_I(\rho(\mathbf{R}_I))k_{\text{B}}T_{\text{e}}(\mathbf{R}_I) \quad (5)$$

where $\mathbf{F}_I$ is the force acting on atom I, $U(\{\mathbf{R}\}_J)$ is the potential energy of the system that depends on the coordinate of all the atoms and is given by an empirical potential or by a *ab initio* ground state total energy calculation; $\beta_I(\rho(\mathbf{R}_I))$ is the viscous damping force or ion-electron coupling strength function, which depends on the chemical nature of the atom I, and its argument $\rho(\mathbf{R}_I)$ is the electronic density of the host at the position where atom I is positioned, defined in Eq. 2, $\mathbf{v}_I^*$ is the relative velocity between atom I and the host electronic density, as defined by Eq. II, and η_I is a random force defined by its mean value, Eq. 4, and its variance, Eq. , where k_{B} is the Boltzmann constant, $T_{\text{e}}(\mathbf{R}_I)$ is the electronic temperature at position $\mathbf{R}_I$, and M_I is the mass of ion I.

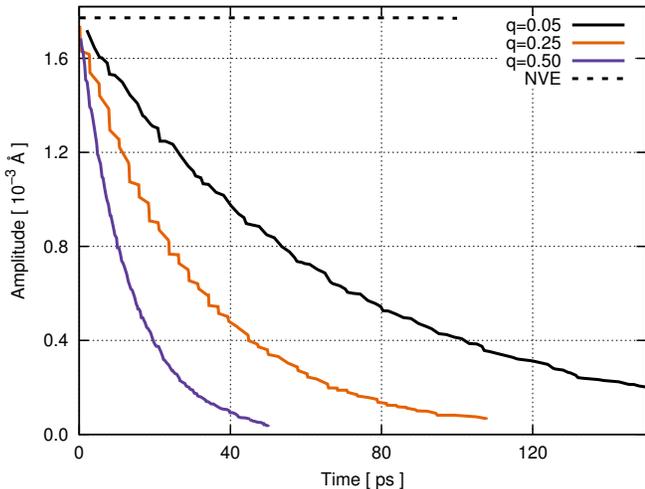Figure 3: The amplitude decay during the e-ph MD simulation of the phonon longitudinal modes in fcc Ni crystal along ⟨100⟩ direction with wave-vectors 0.05, 0.25 and 0.50 (in units of $2\pi/a$). The simulation contains 32000 atoms in a cubic supercell. Horizontal dotted line, shows the result when dissipative term in Eq. 1 is turned off (and energy is conserved as in a normal NVE simulation.)

Figure 4: Inverse phonon lifetimes in a fcc Ni crystal along ⟨100⟩, ⟨110⟩, ⟨111⟩ directions. The polarization vectors investigated are shown in the legend. Results are shown for the model described in the text, for a perturbative QM calculation, and for the standard two temperature model.

Note the way we have written the density $\rho^*(\mathbf{R})$ at position $\mathbf{R}$ in Eq. 2; it is defined as the sum of spherical atomic densities $\rho_J(\mathbf{R}_{IJ})$ of neighboring atoms, which carry the information about the chemical nature of atoms at positions $\mathbf{R}_J$ that contributes to the density at position $\mathbf{R}_I$. $\rho(\mathbf{r})$ itself does not depend explicitly upon the chemical nature of the atoms contributing to it. This atomic sphere approximation, ASA, is similar to that at the basis of the embedded atom model, EAM[1,2], providing a fast algorithm to calculate it on-the-flight. Also note that, according to Eq. the velocity $\mathbf{v}_I^*$ is the velocity of atom I *relative* to the velocity of the electronic density. This point has been so far overlooked in the standard implementation of the TTM-MD in the popular MD code LAMMPS[8] or DL-POLY[9], and has significant consequences on the wave vector dependence of phonon lifetimes, as we show below, and on the presence of an artificial damping for a solid under rigid motion.

The function $\beta_I(\rho)$ is found in a two-step process. First, $\beta_I(\mathbf{R})$ is obtained along a TD-DFT simulations of a low (thermal) velocity atom moving across a vacant site in the crystal. From the total electronic energy in the simulation an instantaneous electronic stopping power, $S_e(\mathbf{R})$ is obtained, whose slope is $\beta_I(\mathbf{R})$. We used the code QBOX with modifications to perform explicit time-dependent electron dynamics (TD-DFT)[10] and the procedure is similar to that described in[3]. Second, the function $\rho^*(\mathbf{R})$ is obtained using the ASA. The atomic spherically-symmetric densities were obtained from the OPIUM package[11] for isolated Ni and Fe atoms. VASP calculations[12,13] for the actual electronic density in bulk
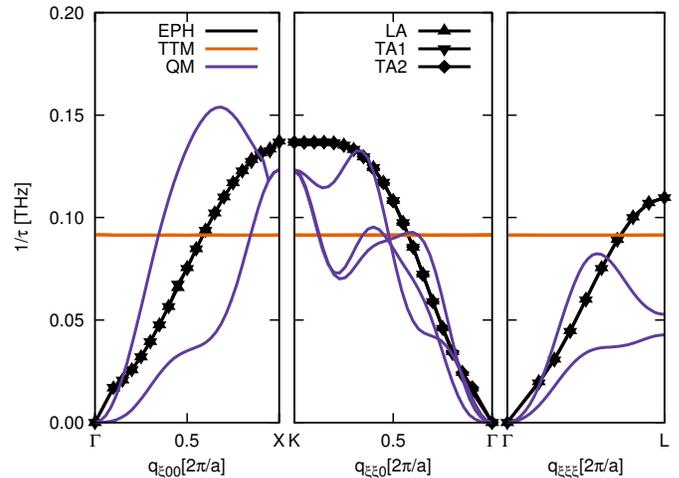
fcc Ni show that ASA is in a reasonably good agreement with DFT results (fig. 2), validating the ASA approach for metals. (GGA was used all along the DFT calculations.) In Fig. 2 we see that the largest discrepancy occurs precisely at the location of the vacancy where the actual density is smaller than the ASA value, reflecting the effects of metallic bonding. Finally, relating $\beta_I(\mathbf{R})$ to $\rho(\mathbf{R})$ and eliminating $\mathbf{R}$, the function $\beta(\rho)$ in Eq. 1 is obtained. Figure 1 shows the results for $\beta_{\mathrm{Ni}}(\rho)$ corresponding to a Ni atom in a fcc Ni lattice, and for $\beta_{\mathrm{Fe}}(\rho)$ corresponding to an Fe atom in the same Ni lattice. The calculations are not magnetic for simplicity, and also because in the envisioned applications the magnetism can be seen as a small perturbation.

Note in this figure, in particular for the case of the Ni atom in fcc Ni where the simulation ran for a longer trajectory, that the actual value of S_e is not exactly a function of the density at the actual position of the moving atom, namely: S_e for the atom approaching the vacancy is not the same as S_e for the atom departing from it, at symmetrical positions, where the host density is the same. This difference reflects the fact that the stopping is in fact a function of the electronic density of the host as well as that of the moving particle, which lags behind its nucleus or, in general, the stopping is a function of the history. This local density approximation is, nevertheless, an excellent approach for low velocity atoms, as Fig 1 suggests, but is less accurate for projectiles in the MeV range. This is analogous in spirit to the EAM, in this case the friction itself is taken as a function of the environment density. We discuss this subject in a forthcoming publication.
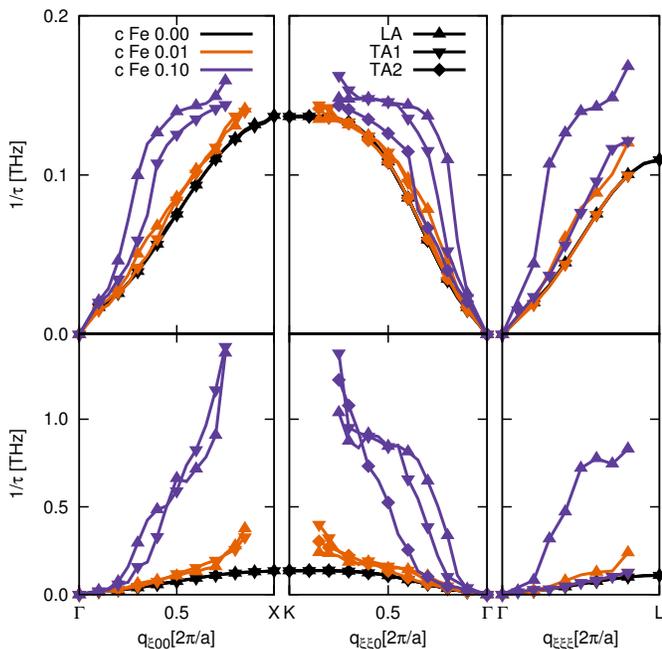
We implemented this model as a new 'fix' in the MD

Figure 5: Inverse phonon lifetimes for a NiFe random solid solution in fcc phase as a function of wavevector q, for three polarizations at various number concentrations (c Fe 0.00, 0.01, 0.10). These are obtained with our MD model from the decay of an initial phonon-like excitation characterized by wavevector q along principal directions in the Brillouin zone, and polarization (longitudinal and two transversal). Values reported on the upper panel correspond to the e-ph contribution alone, measure from the energy transferred to the electronic system; those of the lower panel correspond to the actual decay of the mode that contains the e-ph interaction plus the decay produced by the disorder.

code LAMMPS[8] and treated the electronic system as it is usually done in the TTM-MD, namely by solving the heat diffusion equation on a grid. For our purpose in this work of determining phonon lifetimes, only energy removal from the ionic system to the electrons is studied, with the random force in Eq. 1 turned off. Phonon-phonon scattering is contained in the adiabatic potential U and explicit magnon dynamics is still omitted.

III. RESULTS AND DISCUSSION

To study phonon lifetimes we prepared each initial state with displacements corresponding to particular polarizations and wave-vectors $\mathbf{q}$ along high symmetry directions in the Brillouin zone, and monitor their amplitude of each mode as it decreases with time, as shown in Fig. 3.

The initial amplitude is small enough (0.0018 Å) to make anharmonic effects (*i.e.* phonon-phonon interac-

tions) negligible. From a fitting to the exponential decay of its amplitude we obtain the lifetimes, as reported in Fig. 4.

To check the accuracy of these predictions, we evaluate the phonon lifetimes from density-functional perturbation theory[14–16] (DFPT) in a pseudopotential plane-wave approach, as implemented in Quantum Espresso (QE) package[18], using ultrasoft[19] pseudopotential from the QE database. The results are shown in Fig. (4) as well. The electronic structure and phonon dispersion for nonmagnetic Ni were calculated within the Generalized Gradient Approximation (GGA), with the exchange-correlation functional parameterized according to Perdew, Burke, and Ernzerhof[17]. A plane wave kinetic energy cut off of 40 Ry (and charge density cutoff of 240 Ry) give accurate values of phonon dispersion. The integration over the Brillouin zone (BZ) used a smearing of 0.02 Ry. The calculation of phonon lifetime requires an integration of the double delta over the Fermi surface[20] with a high accuracy. BZ summations were carried out over a $30 \times 30 \times 30$ grid for the k-grid electronic integration, smearing equal to 0.005 Ry and $6 \times 6 \times 6$ for the phononic q-grid integration, according to the Monkhorst-Pack scheme. We performed the phononic BZ integration to calculate the electron-phonon coupling constant, λ[20]. The value obtained, $\lambda = 0.24$, is very close to 0.26, obtained previously[3,21] using a rigid muffin-tin potential approach (RMTA)[22]. This λ value is calculated using value of calculated Hopfield parameter[21] and expression

$$\lambda = \delta/(m\langle\omega^2\rangle), \qquad (6)$$

where δ is Hopfield parameter calculated in RMTA, and $\langle\omega^2\rangle$ is averaged value of calculated phonon frequencies. This value are also in reasonable agreement with the $\lambda = 0.31$ obtained by Allen from resistivity experiment[23].

Finally, Fig 4 also gives the lifetime predictions for the standard TTM-MD approach, which assumes a constant β and uses the absolute ion velocity in the term βv. It can be seen that no $\mathbf{q}$-dependence is obtained, and moreover, damping is present even at $\mathbf{q} = 0$, *i.e.* for rigid translation (evidencing that the total linear momentum is not conserved). Three main conclusions emerge from this figure: (i) the classical mechanics e-ph interaction model that we present here predicts phonon lifetimes in remarkably good agreement with quantum mechanical calculations; (ii) the main limitation of the model seems to be the inability to predict different values for longitudinal and transverse polarization; (iii) the typical model used so far to account for non-adiabatic atomic motion, the TTM-MD with constant β and absolute velocities, is unable to give any q-dependence, however it is captured with our method.

The absence of polarization effect in the life-times stems from the simplicity of the model and the scalar character of the dissipation (friction force is always anti-parallel to the velocity). A more general model (including tensorial β or dependence on acceleration) could in principle also recover polarization effects.

The model presented so far is readily extended for alloys; we study the case of NiFe. According to Eqs. 1 the function β_I depends on the chemical identity of atom I, and its argument is the host density at the location of atom I, which is the sum of atomic densities of atoms at sites J, with their own chemical identity that defines such density, Eq. 2. Therefore describing alloys requires the calculation of the electronic stopping power of all the species in consideration in a host that is representative of the alloy. In the case presented here we assume it to be pure Ni, valid for small concentrations in NiFe.

Fig. 1 shows $\beta_{\text{Fe}}(\rho)$ for an Fe atom moving around a vacancy in fcc Ni. Fig. (5) shows the lifetimes resulting from both the e-ph interaction and the phonon scattering produced by the disorder. Clearly the disorder contribution is at least one order of magnitude larger than the e-ph part. To extract the phonon lifetime from the total attenuation we monitor the energy transferred to the electronic system, instead of the decay of the phonon itself. The results are shown in Fig. 5 which show how alloying increases the coupling mostly at the zone edges. We also observe a splitting between longitudinal and transverse branches, absent in the pure Ni case.

In all the phonon lifetime MD calculations an $20 \times 20 \times 20$ fcc simulation box consisting of 32000 atoms was used. Ni-Fe alloys were constructed by substituting the Ni atoms with Fe randomly to obtain the required concentration. All the structures were initially relaxed to obtain the equilibrium lattice parameter. Afterwards different phonon modes used in the study were created by displacing the atoms. The Ni interatomic potential by Mishin et al.[24] was used in the phonon lifetime studies for pure Ni crystal and the potential by Bonny et al.[25] was used in the case of Ni-Fe alloy.

IV. CONCLUSIONS

We propose a non adiabatic model for classical MD that accurately reproduces e-ph interaction in both strength and **q**-dependence. The model is based on treating the e-ph interaction as a low velocity case of electronic stopping power, and therefore uses a quantum mechanical technique, namely TD-DFT, to evaluate its strength, which becomes then parameter free. Using a local approximation to relate the e-ph coupling to the host electronic density, and complemented with a atomic sphere approximation to obtain the local electronic density at low computational cost, the model is readily extended to alloys. The predictions are validated by comparison to quantum mechanical calculations, showing an excellent agreement. This model represents quantitatively accurate approach to describe non adiabatic aspects of ion-electron dynamics within a classical mechanics framework.

Acknowledgments

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