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Ion-electron interaction in molecular-dynamics cascades

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We propose a simple model to incorporate inelastic energy losses into molecular-dynamics simulations of high-energy radiation damage, which at the same time describes the metallic thermal conductivity by coupling the ions to a thermal reservoir. Both expressions are based on a local-density description of stopping power. We provide an empirical expression to describe the strength of the ion-electron coupling, which is a function of the local electronic density. The model is then adequate to those simulations where the ion-ion interactions are obtained from many-body potentials based on density-functional formalism.

INTRODUCTION

The important progress recently made in the description of effective many-body interaction potentials in condensed matter, together with the rapidly increasing computer capabilities, allows us today to apply the techniques of molecular dynamics to the study of high-energy displacement cascades. The technological importance of this field of computational physics is out of discussion because the complexity involved in radiation damage is so large that up to now only empirical theories account for quantitative evaluation of damage. The interest of having damage simulations is then evident.

Recent work on large-scale molecular dynamics[1] has brought up the question of the role of the thermal spike in 3- to 5-keV Cu cascades, together with the corresponding implications for atomic mixing, Frenkel pair production, and point-defect clustering. However, the physics involved in the model was too simple and therefore the reliability of the quantitative results may be questioned. In fact the potential was repulsive, pairwise, and restricted to nearest neighbors. The liquid-solid phase transition is certainly poorly described in this framework, since so are the shear constants.

The present status of the simulations can briefly be summarized as follows. On one hand, the effective many-body potentials, like the embedded-atom model[2] (EAM) or the Finis-Sinclair Model[3] (FSM), give the best available and a quite reliable description of crystalline structure, elastic constants, phonon dispersion relations, defect properties, and dynamics correlations in the liquid phase, together with a reasonable computing cost. On the other hand, supercomputers and powerful algorithms can solve a large number of degrees of freedom using molecular dynamics, namely, $N \lesssim 10^6$. Cascades of energies up to some 10^3 eV are now being studied with these means.[4]

However, good potentials and large crystal sizes do not necessarily warrant a good simulation of radiation damage in metals. Two main problems still remain open. The first is a proper account of the electronic inelastic scattering and the second is a good description of the thermal conductivity of the simulated crystal. Both are related to the ion-electron interactions but in quite different domains of ion kinetic energy. In what follows we shall identify the first as the electronic stopping power (ESP) regime and the second as the electron-phonon interaction (EPI) regime. Together they cover an energy range from 10^6 to 10^{-2} eV. The aim of this work is to provide an expression to be included in the molecular dynamics equations to account for the whole energy range. In what follows we first discuss the ESP and the EPI regimes separately and then we merge them using local-density formalism.

ELECTRONIC STOPPING POWER REGIME

Inelastic scattering with target electrons is an important mechanism of energy loss[5] which is, of course, absent in adiabatic molecular dynamics. Compared to elastic collisions (ion-ion collisions) its relative importance depends on the energy of the projectile. It is the main contribution to the total stopping cross section at high energies, $\sim 10^6$ eV; its contribution decreases to 20% or 30% at energies in the range of $\sim 10^4$ eV and at the threshold energy (~ 25 eV) it represents an 8% of the total energy loss. All these figures and those that follows correspond to Cu.[6] These results are obtained using Firsov[7] or Lindhard[8] theories. Although quite old, they are still believed to give a good description of the electron excitation.

The success of those theories arises because there exists a quite general feature of the stopping power in the low-energy regime. Low energy means projectile velocity lower than the relevant electronic velocity in the target, for instance, Fermi velocity in a metal. In fact quasiclassical or quantum theories give a stopping power proportional to the projectile velocity for a large variety of projectiles and targets. The different approaches and projectile-target combinations only give different expressions for the constant of proportionality.[5] This constant depends so much on the model that it is actually used as a fitting parameter. The v dependence of the electronic stopping has been assumed to be correct from energies going from some MeV/amu down to the displacement threshold energies of about 20–50 eV, the lower limit to which these theories have been applied. However, once low velocity is assumed, the results so obtained are valid down to velocities equal to zero since no other velocity comes into play. In this sense it is important to point out that in this regime, calculations of screening are actually made at ion velocity strictly equal to zero.

The concept of stopping power is valid not only in the transport formalism as a continuum slowing down process but also for molecular dynamics where the electron collisions can be included as a dissipative term in the equations of motions. In fact the ion-ion (*i-i*) collisions are very different from ion-electron (*i-e*) collisions because in the latter the energy and the momentum transfer in each event are very small compared to the ion energy. They give in practice a straight trajectory of the projectile. It is therefore justified to incorporate a continuous loss mechanism into the Newton equations of at least the most energetic ions in the cascade.

We recall here the functional form of this interaction. Starting with the electronic stopping cross section $S_e(E)$ from the Lindhard theory,

$$S_e(E)=\lambda E^{1/2} , \tag{1}$$

the stopping power is

$$\frac{dE}{dx}=-nS_e(E) , \tag{2}$$

where n is the density of scatter centers in the target. Since $dE/dx=(1/v)dE/dt$,

$$\frac{dE}{dt}=-n\lambda(M/2)^{-1/2}E=-\tau^{-1}E , \tag{3}$$

where M is the projectile mass and τ is the lifetime of the kinetic energy due to electronic losses. Therefore the equations of motion including stopping power become

$$M\ddot{\mathbf{x}}=\mathbf{F}-n\lambda(M/2)^{1/2}\dot{\mathbf{x}}=\mathbf{F}-\beta\dot{\mathbf{x}} . \tag{4}$$

For Cu a value of λ between 0.3 and 2.5 $\mathrm{eV}^{1/2}\,\text{Å}^2$ has been used,[6] giving $2.3\times10^{-11}<\beta<1.95\times10^{-10}$ g sec and a relaxation time $\tau=(M/2)\beta^{-1}$ between $2.7\times10^{-13}<\tau<2.3\times10^{-12}$ sec.

The application of Eq. (4) to all ions in the simulation, i.e., to those with energies in the thermal region, will be discussed in the next paragraph.

ELECTRON-PHONON INTERACTION REGIME

In a molecular-dynamics simulation the thermal conductivity is given by the anharmonic part of the interatomic potential. It produces phonon-phonon interactions whose magnitude is in general not used as a fitting parameter in the determination of the potential. In the particular case of the EAM the fitting to an equation of state reproduces properties like thermal expansion, Gruneisen parameter, and probably lattice thermal conductivity (which are all three related); instead in the FSM, with less free parameters, the equation of state is not used in the choice of the potential and therefore the anharmonic part is not adjusted. For some materials, incorrect values of properties mentioned above are obtained.[9]

In both models the conductivity obtained is obviously the lattice conductivity. Simulations of cascades should consider that in metals at equilibrium most of the heat is transported by electrons. This certainly will affect the thermal behavior of the cascade since after the collision phase and the athermal recombination an important thermal spike is quenched in the lattice. The quenching rate depends on both thermal conductivities and on the coupling between ions and electrons.

The problem is not simple because in the collision phase part of the energy is deposited in the electronic system and part into the lattice. Electrons and ions are two different systems, each with their temperature-dependent heat capacities and thermal conductivities, coupled by the electron-phonon interaction. It is a formidable task to try to describe the electron-phonon interaction over a range of energies or temperatures going from 10^{-2} eV to those of the thermal spike of the cascades. In addition, both systems are themselves out of equilibrium in the thermal spike because it happens in a time scale of 10^{-13} sec, which is comparable to the period of lattice vibrations.

For our present purposes we need to know the rate of energy transfer to electrons as a function of the mechanical variables of the ions (position, velocity), which are not necessarily related to lattice temperature, and eventually the electronic thermal conductivity as a function of electronic temperature.

Electron-phonon interaction theories are usually based on the hypothesis of local thermodynamic equilibrium between electrons and phonons. At room temperature, thermal equilibration of the electronic system is achieved by electron-phonon interactions (relaxation time $\tau_{e-\mathrm{ph}}\cong10^{-13}$ sec). Similarly, in the phonon system the phonon-electron interaction is as important for the equilibration as the phonon-phonon interaction, since the phonon-phonon relaxation time is $\tau_{\mathrm{ph-ph}}\cong10^{-11}$ sec, while the phonon-electron relaxation time can be estimated from $\tau_{e-\mathrm{ph}}$ and considerations of detailed balance also to be $\tau_{\mathrm{ph}-e}\cong10^{-11}$ sec.[10]

The molecular dynamics (MD) method computes phase-space trajectories of a collection of classical degrees of freedom. The evolution of the system can be forced to obey microcanonical (i.e., number of particles, volume, and energy constants) or canonical (number of particles, pressure, and temperature constants) laws. Usually canonical behavior is obtained by a simple scaling of the kinetic energy (isokinetic MD). However, since average values in MD are obtained under the assumption that ensemble averages are equal to time averages, the algorithm that leads to thermal contact with a reservoir must generate canonical fluctuations. This is not the case with the isokinetic MD. Several other ways, like Gaussian isokinetics,[11] or Nose dynamics,[12] generate fluctuations that obey Boltzman statistics, but have the limitation that the coupling with the thermal bath has no simple physical meaning. For the problem we are interested in, i.e., electrons and phonons initially in thermal equilibrium perturbed by a primary knock-on atom (PKA) of some keV we need a canonical MD where the coupling between phonons and electrons reproduces the electron-phonon coupling when in equilibrium and the electronic stopping power when out of equilibrium. It seems then adequate to propose the well-known classical stochastic Langevin equations[11] which describe the interactions of an ensemble of classical particles with an irreversible thermal reservoir. Although there is no theoretical proof, it is generally accepted that Langevin equations generate the canonical ensemble. In this mechanics the kinetic losses are represented by a constant positive friction coefficient and the particles are accelerated with stochastic forces with random magnitude and orientation. The Langevin equations of motion read

$$M\ddot{\mathbf{x}}=\mathbf{F}+\eta(t)-\beta\dot{\mathbf{x}} \, , \tag{5}$$

where β is a constant measuring the strength of the coupling to the bath (proportional to the inverse of the life time of the energy fluctuations) and η is a random force defined by

$$\begin{gathered}\langle\eta(t)\rangle=0 \, , \\ \langle\eta(t)\cdot\eta(t_0)\rangle=2\beta k_B T\delta(t-t_0) \, , \\ P(\eta)=(2\pi\langle\eta^2\rangle)^{-1/2}\exp(-\eta^2/2\langle\eta^2\rangle) \, .\end{gathered} \tag{6}$$

In this expression T is the temperature of the bath. In order to mimic the equilibrium phonon-electron interaction β must be such that $\tau_{\text{ph}-e}\sim10^{-11}$ sec. A limitation of this average formalism is that it gives the same life time for all normal modes, regardless of their frequency or wave vector. Then, those with frequencies smaller than 10^{11} sec^{-1} (a few in common metals) become overdamped.

Now comparing Eqs. (4) and (5) it becomes evident that the ion-electron coupling may have the same expression in both the ESP and EPI regimes. The coupling parameter, however, differs by one to two orders of magnitude. This is the problem we address in this work.

In order to describe these variations, let us assume that the physics is the same in both regimes and that the differences come from the different target electronic density swept by the projectile. In this picture, the phonon-electron interaction originates in the stopping power that an ion feels when oscillating in a plasma. The density of this plasma is that of the valence electrons of the host at the ion position. On the other hand, in collisions above some 10^2 eV the apical distance is short enough that the ions cross almost all their core electronic charge and the stopping power is correspondingly high. The actual situation is certainly more complex because the density of states at the Fermi level, which contains information on the lattice, becomes relevant.

With this interpretation of the phonon-electron interaction we have a way to describe it in the whole range of energy because the viscous drag of Eqs. (4) and (5) is simply a function of the local host electronic density, in the same way as the embedding energy is obtained in the EAM. There certainly are other ways to introduce variations in the coupling parameter. For example, it can be considered that it depends on the energy of the ion, but it would then introduce cubic frictional forces with, once again, no clear implications on the generated fluctuations. The density-dependent coupling, instead, follows the usual interpretation of the problem, as we see in the next section.

ION-ELECTRON INTERACTION IN THE LOCAL-DENSITY FORMALISM

The local-density approximation in stopping power theory assumes that each volume element in the solid is an independent free plasma of density $\rho(\mathbf{r})$. The stopping power is then position dependent and can be written as[13]

$$S_e(\mathbf{r})=I(v,\rho(\mathbf{r}))[Z_1^*(v)]^2 \tag{7}$$

where I is the interaction of a particle of unit charge and velocity v with a plasma of density ρ and Z_1^* is the velocity-dependent effective charge of the projectile. The binary collision description can be obtained from Eq. (7) by integrating over a given trajectory.

The historical development of the theory provides different expressions for $S_e(\rho)$ according to the complexity of the description of the plasma target. Although all of them give the same $\mathbf{v}$ dependence already mentioned, the density dependence is different depending on whether the plasma is described as an ideal degenerate gas,[14] a Fermi liquid,[15] a Hartree-Fock–type quantum gas,[16] or an electronic system treated with density-functional formalism.[17]

The linear response theory predicts stopping power given by

$$\frac{-dE}{dx}=\frac{4Z_1^2e^4\hbar}{\pi v}\int_0^\infty \omega\, d\omega \int d\mathbf{q}\,\text{Im}K^r(\mathbf{q},\omega) \times\frac{\delta(\hbar\mathbf{q}\cdot\mathbf{v}+\hbar^2q^2/2M+\hbar\omega)}{q^4} \, , \tag{8}$$

where M, v, and Z are the mass, velocity, and atomic number of the incident ion, respectively; $\hbar\mathbf{q}$ is the momentum transfer, and $K^r(\mathbf{q},\omega)$ is the Fourier component of the retarded Green's function.

To obtain $K^r(\mathbf{q},\omega)$, Kitagawa *et al.*[16] make a Hartree-Fock decoupling and obtain that in the low velocity limit Eq. (8) reduces to,

$$\frac{-dE}{dx}=\frac{2Z^{*2}e^4m^{*2}v}{3\pi\hbar^3}\int_0^1 d\xi\frac{\xi}{[\xi+(m/m^*af(\xi)]^2} \, , \tag{9}$$

with m^* an effective electron mass; Z^* an effective projectile charge; $a=e^2/\pi\hbar v_f$; $\xi=\mathbf{q}^2/4\mathbf{q}_f^2$; v_f and $\mathbf{q}_f$ are Fermi velocity and momentum, respectively; and $f(\xi)=(2\xi+1)/(4\xi+1)$. The integral in Eq. (9) can be approximated in the following two limiting cases.

(i) $a \ll 1$ *(high density)*. In this case we have

$$\frac{-dE}{dx}=\frac{2Z_1^2e^2m^2}{3\pi h^3}v\ln(\hbar v_f/e^2) \, , \tag{10}$$

which is nothing other than the Fermi-Teller formula,[18] indicating that for high density plasmas the electron-correlation (in the Hartree-Fock approximation) is not relevant.

(ii) *$a \gg 1$ (low density).* In this case we have

$$\frac{-dE}{dx}=0.32\pi^{7/3}Z_1^3\hbar v\rho^{2/3} . \qquad (11)$$

This $\rho^{2/3}$ dependence is the same found in Ref. 14 without exchange, but the factors are different. A plot of these two limiting functions as well as the numerical integration of Eq. (9) is shown in Ref. 15.

Unfortunately, actual metallic systems exhibit $a \sim 1$. In Fig. 1 we show the stopping power, Eq. (9) as a function of the electronic density.

By considering the electron density in the solid as given by the superposition of atomic densities, as in the EAM, we observe that host density values in the range 10^{-2} to 10^4 $e/\text{Å}^3$ are obtained by moving from the equilibrium lattice position to some tenths of Å close to an ion. These changes in density produce less than a factor of 10 in the stopping power, according to Fig. 1. One could then think that the ion-electron interactions in the EPI and in the ESP regions are due to different mechanisms. However, this small variation is probably due to limitations of the Hartree-Fock approximation. In fact, according to Ref. 17 the stopping power of slow ions can be rewritten in terms of scattering theory as

$$\frac{dE}{dx}=\frac{3v}{k_f r_s^3}\sum_l (l+1)\sin^2[\delta_l(E_f)-\delta_{l+1}(E_f)] , \qquad (12)$$

where $\delta_l(E_f)$ are the phase shifts at the Fermi energy for scattering of an electron of angular momentum l and r_s is the radius associated to a sphere containing one electron. Based on nonlinear calculations of the density fluctuations, which give results quite different to those of linear response theory, Echenique *et al.* evaluate the phase shifts within density-functional formalism. Unfortunately they do not give numerical values of their calculations but a plot which shows that at low density the stopping power is significantly reduced with respect to linear response theory. We plot these results in Fig. 1. The range of densities they calculated covers only the low-density portion in our plot.

From this figure, it can be seen that an important variation of stopping power (two orders of magnitude) results when the density of the host varies from 10^{22} to 10^{27} e/cm^3. In order to have a simple approximate expression that covers the whole range we propose the following fitting equation for β in Eq. (5):

$$\beta = A\log_{10}(\alpha\rho^{1/3}+b) , \qquad (13)$$

where $\alpha=(3\pi^2)^{1/3}\hbar^2/e^2m=3.09a_0$, ($a_0$ is the Bohr radius), A is a fitting parameter close to the value $2Z^2e^4m^2/3\pi\hbar^3=2\times10^{-9}$ g/sec, and b is an adjustable parameter which allows the relation between the ESP and EPI regimes to be varied and contains the information on the EPI coupling (for instance, it accounts for the density of states at the Fermi level for different materials); a value of $b=0.65$ has been used in Fig. 1. The value of A that reproduces the loss in a 1-keV Cu-Cu binary collision as well as the electron-phonon interaction is around $A=2\times10^{-10}$ g/sec. It implies a reasonable relation between effective mass and charge: $(Z^*m^*/Zm)=0.32$.

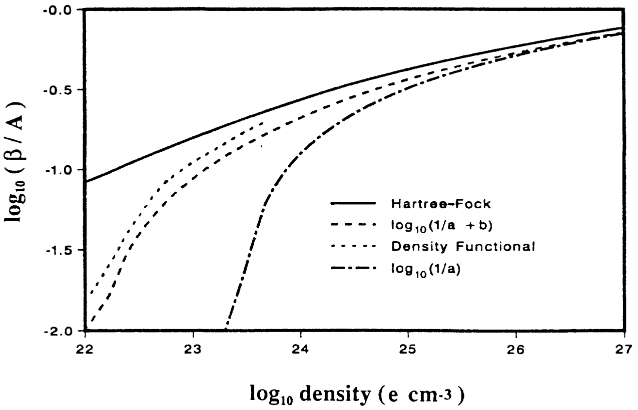

FIG. 1. Ion-electron interaction as a function of electronic density. ——, numerical integration of Eq. (9); —-—-, high-density approximation, Eq. (10), to the exact, Eq. (9); — — —, results of stopping power from Ref. 17 using density functional and nonlinear response; — — —, proposed empirical function to fit the whole density range. For details see text.

It is important to point out that Eq. (13) is only an empirical approximation to the full density dependence but does not have any physical implication. The procedure is empirical and therefore the criterion is that of the best fit to the theoretical predictions over the whole range of electron density. Its advantage is that the energy losses are incorporated in MD for all energy ranges, i.e., for all ions in the simulation, without an excessive increase in computational effort. The density is the overall electron density and not only that of valence electrons as used in EAM.

The last point which remains open is the term $\eta(t)$ in Eq. (5). If energy is transferred to electrons, they heat up. Since $\eta(t)$ depends on electronic temperature, a feedback of this energy into the ions appears. The electronic thermodynamics is not simple because the system is out of equilibrium; however, a simple estimation of the influence of electronic heating can be made in two limiting cases: If the coupling is weak, the electron mean-free path is some hundred of Å, which is larger than the cascade dimension. It means that excited electrons at the early times of the cascade will decay far from the energetic ions. The fact that electronic thermal conductivity is two orders of magnitude larger than the phonon one means that the electronic thermal spike propagates much faster. The radius of the electronic hot sphere is around ten times larger than the cascade radius at any time. Hence the energy feedback into the ions is distributed over a number of ions a thousand times larger than those participating in the cascade. In this approximation we can therefore neglect the electronic heating and keep the electronic temperature appearing in Eq. (6) constant and equal to the desired equilibrium temperature. It is equivalent to consider the electrons as a perfect heat sink or as having infinite thermal conductivity compared to ions. On the contrary, the electronic mean-free path can be comparable to the cascade dimensions in the case of strong coupling,[19] and the electrons would eventually reach thermal equilibrium with the lattice. In this case a description of the evolution of the electronic temperature has to be given in order to correctly define the random force term in Eq. (5).

CONCLUSIONS

Using the local-density formulation of the stopping power we have shown how to incorporate the electronic losses of high-energy particles into the equations of motion of molecular dynamics. The same formalism describes the electron-phonon interaction, responsible for a quenching of the cascades more rapid in metals than in insulators. An empirical expression to match the two regimes is proposed. The formalism is easy to implement in MD codes based on the density-functional formalism like the embedded atom model or the Finnis-Sinclair model, without an excessive increment of computational cost.

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