Reconciling Anomalously Fast Heating Rate in Ion Tracks with Low Electron-Phonon Coupling

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Abstract

Formation of swift heavy ion tracks requires extremely fast energy transfer between excited electrons and a lattice. However, electron-phonon energy exchange is too slow, as known from laser-irradiation experiments and calculations. We resolve this contradiction noticing that electron-phonon coupling is not the sole mechanism of energy exchange between electrons and ions: heating of electrons also alters potential energy surface of atoms, accelerating them and increasing their kinetic energy.

Introduction

Upon ultrafast high-energy-density deposition into matter, e.g. with femtosecond lasers or swift heavy ions (SHI), an electronic system of a solid is heated to temperatures significantly above the atomic one. This transient state then relaxes leading to equilibration of the electronic and atomic temperatures. This process of equilibration takes place *via* so-called electron-phonon (or, more generally, electron-ion) coupling. It has been predicted with various theoretical approaches that electron-ion coupling is a relatively slow process, leading to typically picosecond timescales of equilibration between the electronic and the atomic temperatures at typical irradiation conditions: dynamic structure factor calculations ^{1,2}, a coupled modes approach ³, tight-binding molecular dynamics ⁴, all show similar results. They are supported by state-of-the-art experimental observations of electron-ion coupling in solids, suggesting that it may be even slower than most theories predict ^{5,6}.

In a stark contrast to those results, it has been known for over decades that SHI irradiation of solids leads to creation of ion tracks at extremely short timescales. SHIs primarily deposit energy into the electronic system, similarly to laser pulse irradiation ⁷. The difference from the laser spot is that excited electrons appear within a sub-nanometer vicinity around the ion trajectory ⁷. Such extremely localized energy deposition leads to fast energy transport and cooling of the electronic system in an ion track within hundred-femtosecond timescales – much shorter than those required for electron-phonon coupling to heat the atomic system ¹. Yet, SHI tracks are detected experimentally ⁸, implying that much faster atomic heating takes place there.

A necessity of significant heating of materials in SHI impacts to form observable tracks during times of cooling of the electronic system suggests extremely fast coupling of the electron system to the atomic one, see Fig. 1 extracted from the data from Ref. ⁹. Those estimates imply that the atomic heating must be orders of magnitude faster than that measured in laser-irradiation experiments and consistently calculated with various models. A contradiction ensued, puzzling the respective communities for over two decades.

In this work, we point out that the electron-phonon coupling is not the only mechanism of atomic heating. Ultrafast energy deposition into the electronic system also affects an atomic potential energy surface because electrons form an interatomic potential. Excitation of electrons changes the electronic distribution, which in turn modifies the interatomic potential ^{10,11}. This converts into increase of the

kinetic energy of atoms because altered interatomic forces push atoms towards their new equilibrium positions^{10,12}.

At high deposited doses, or correspondingly high electronic temperatures, it may lead to phase transitions even without significant atomic heating. The most famous example of this effect is the so-called nonthermal melting^{13,14}. It is known since 1990s to take place in covalently bonded semiconductors^{10,12,15}. Recently, it has been theoretically shown that the same effect also takes place in ionic crystals¹⁶, oxides¹⁷ and polymers¹⁸. Thus, nonthermal phase transitions may be regarded as a universal effect taking place in non-metallic targets upon energy deposition faster than the electron-ion (electron-phonon) coupling (while an even more complex picture of various nonthermal effects may take place in metals¹⁹). Such nonthermal phase transitions are accompanied by increase of the atomic temperature as a consequence of atomic acceleration as a reaction to interatomic potential changes^{18,20}.

At doses below a nonthermal phase transition threshold, excited electrons also trigger some “nonthermal” atomic heating *via* modification of the potential energy surface. This effect is known as displacive excitation of coherent phonons²¹, or squeezed phonons as a precursor to nonthermal melting²².

Atomic heating due to modification of the interatomic potential after excitation of the electronic system forms a distinct mechanism from the electron-phonon coupling. The latter one relies on the electron transitions between electronic energy levels triggered by atomic displacements, i.e. it is a nonadiabatic effect^{4,23,24}. In contrast, nonthermal atomic heating via modification of the interatomic potential is an adiabatic effect, occurring within Born-Oppenheimer approximation^{20,22}, without nonadiabatic electron-ion coupling involved.

Below we will consider the nonthermal atomic heating in various materials, its rate and timescales at various doses. We will also analyze a synergy between nonthermal heating and electron-ion coupling, considering the dependence of the coupling parameter on the atomic temperature.

Model

To model materials response to an ultrafast electronic excitation, we used XTANT-3 code²⁵. It is based on Tight-Binding Molecular Dynamics simulation. Within XTANT-3, electrons populating the valence and the bottom of the conduction band are assumed to adhere to the Fermi-Dirac distribution. This defines the fractional populations of electrons on the energy levels (molecular orbitals) of the material.

Transferable tight binding (TB) method describes transient molecular orbitals, interatomic forces depending on the configuration of all the atoms in the simulation box and electronic distribution function, as well as matrix elements for nonadiabatic electron-ion coupling. We apply DFTB method with matsci-0-3 parameterization to describe studied materials²⁶. This parameterization uses sp^3d^5 LCAO basis set²⁷. The TB Hamiltonian and all related properties evolve on each time step of the simulation, thereby tracing evolution of the material parameters as a response to an elevated electronic temperature.

Atomic motion is modeled with Molecular Dynamics (MD) using Martyna *et al.* 4th order algorithm with 0.1 fs time-step²⁸. The forces acting on atoms are derived from the potential energy surface provided from the TB method. They also depend on the transient electronic distribution function, thus tracing effects of nonthermal melting due to electronic excitation.

The simulation may be performed either within the Born-Oppenheimer (BO) approximation, or beyond it with nonadiabatic effects included²⁹. The Born-Oppenheimer approximation excludes electron-phonon coupling and resulting energy exchange. Non-BO electron-ion coupling is described with the Boltzmann collision integral⁴. The tight binding molecular dynamics calculates matrix elements entering the collision integrals at each time step. Energy exchange from the nonadiabatic coupling of electrons is fed to atoms via velocity scaling²⁵. A microcanonical (NVE) ensemble is used with periodic boundary conditions in the simulation box.

The supercell contains 240 atoms for simulation of Al₂O₃, and 216 atoms for MgO, TiO₂ and SiO₂ (quartz). The simulation starts with random velocities assigned to atoms according to the Maxwellian distribution with the room temperature. Atoms are allowed to thermalize for some hundred femtoseconds. Then, the electronic temperature is smoothly increased during 10 fs according to Gaussian function centered at 0 fs.

Results And Discussion

Born-Oppenheimer simulations of electronic and atomic dynamics in Al₂O₃, MgO, SiO₂ and TiO₂ are performed with help of XTANT-3 at various deposited doses. The resulting increase of the atomic temperature is shown in Fig. 2. After the rise of the electronic temperature, we see that the atomic temperature starts to increase in all considered materials. The rate of its increase rises with increase of the dose. At doses close to or above the nonthermal damage dose (reported in Ref.¹⁷), the atomic temperature increase occurs within ~ 100 fs.

We emphasize that this increase of the kinetic energy of atoms is *not* due to electron-ion (electron-phonon) coupling, as this channel of energy exchange is absent within the Born-Oppenheimer simulations. This can be clearly seen in Fig. 3a which shows that the electronic and atomic temperatures do not equilibrate within the BO approximation (as was discussed in more detail e.g. in Ref.³⁰). Atoms are heated purely due to nonthermal (Born-Oppenheimer) effects – changes in the atomic potential energy surface due to electronic excitation. The same effect was reported to take place during nonthermal phase transitions in diamond²⁰, silicon³⁰ and polyethylene¹⁸, and experimentally observed in bismuth³¹, suggesting it may be universal in non-metallic targets.

It is also known that the electron-ion (electron-phonon) coupling parameter depends on both, the electronic and the atomic temperatures⁴. Its dependence on the atomic temperature is nearly linear⁴. A strong kick to atoms due to nonthermal heating thus additionally increases the electron-ion coupling. This synergy, in turn, increases the atomic temperature even faster, see Fig. 3b. Further equilibration of the

electronic and the atomic temperatures takes place at the picosecond timescale – this will not be relevant to the fast ion tracks problem because of the very fast quenching of electrons due to the fast transport of the electronic energy away from the track core, but is important for laser irradiation of materials ^{18,30}.

The results demonstrated that the atomic heating at the doses above a few eV per atom can take place within a hundred femtoseconds. Energy densities delivered by fast ions may transiently reach even higher doses ^{8,32}. The timescales of this atomic heating are also comparable with the lifetime of the excited electrons and valence holes in SHI tracks. Monte Carlo simulations showed that electrons cool down and travel outwards from the track core within ~ 100 fs, but the valence holes, which are typically heavier than conduction band electrons, last longer in the track core ³³. Those times may be sufficient if not for a completion of a nonthermal phase transition, at least for significant nonthermal energy transfer from the electronic to the atomic system. Adding to it the energy transferred to atoms due to scattering of fast ballistic (nonthermalized) electrons, having energies up to tens of keV, is sufficient to induce structure transformations and form tracks in many materials even without slow electron-phonon coupling ^{32,34}.

It thus resolves the discrepancy between the anomalously fast heating of atoms in SHI tracks and much too slow electron-phonon coupling: heating of atoms in a track takes place mainly *via* combined channels of nonthermal atomic heating and scattering of ballistic electrons, not *via* electron-phonon coupling.

Thus, estimates of the “electron-phonon coupling” extracted from the fast ion tracks parameters, such as in Fig. 1, must be interpreted as reflecting the speed of nonthermal atomic heating and not as a real electron-ion (electron-phonon) coupling parameter.

A similar notion of heating of atoms via mechanisms other than electron-phonon coupling has been previously discussed in terms of the Coulomb explosion model ³⁵. The major shortcoming of that suggestion was that the Coulomb explosion is known to take place in small molecules and nanoclusters, or possibly thin layers or surface of materials, but is dubious in solids ⁷. Valence holes in solids may transport out of the track, and a massive amount of electrons in the surrounding solid neutralizes the uncompensated charge around an ion trajectory within a few femtoseconds ³⁶. In contrast, nonthermal effects do not require an unbalanced charge. Born-Oppenheimer heating of atoms is thus a universal effect in nonmetallic materials, which must be accounted for in models of any type of ultrafast electronic excitation.

Conclusions

In conclusion, the estimates of the electron-phonon coupling parameter extracted from the data on swift heavy ion track sizes do not reflect the electron-phonon coupling *per se*, but must be interpreted as a quantity reflecting the nonthermal heating of atoms *via* modifications of the potential energy surface due to electronic excitation. This notion reconciles the much debated problem of extremely fast atomic

heating in swift ion impacts (on hundred femtosecond timescales) with slow electron-phonon coupling (acting on picosecond timescales).

Our results suggest that the nonthermal heating of atoms is a universal effect, present in nonmetallic materials under ultrafast energy deposition, and thus must be taken into account in appropriate models. The effect is especially pronounced at doses above the nonthermal damage threshold. It leads to extremely fast increase of the atomic temperatures, on the order of a hundred femtoseconds. This effect is not limited to ion impacts but is important for all kinds of ultrafast energy deposition into the electronic system and is expected to play a role, e.g., in femtosecond laser ablation.

Declarations

Conflict of Interest

The authors declare no conflict of interests, financial or otherwise.

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Figures

Figure 1

Fitted electron-phonon coupling parameter in various materials, extracted from the data from Ref. 9.

Figure 2

Atomic temperature increase after ultrafast energy deposition into the electron system in Al₂O₃ (top left panel), MgO (top right panel), SiO₂ (bottom left panel), and TiO₂ (bottom right panel). Melting temperatures are shown as grey dashed lines for comparison.

Figure 3

Electronic and atomic temperature changes after ultrafast deposition of 4 eV/atom into the electron system in Al₂O₃, MgO, SiO₂, and TiO₂, modelled (a) within BO (excluding nonadiabatic electron-ion coupling); (b) with electron-ion coupling included.