Molecular dynamics simulations of laser-induced damage of nanostructures and solids

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Abstract A theoretical approach to treat laser induced femtosecond structural changes in covalently bonded nanostructures and solids is described. Our approach consists in molecular dynamic simulations performed on the basis of time-dependent, many-body potential energy surfaces derived from tight-binding Hamiltonians. The shape and spectral composition of the laser pulse is explicitly taking into account in a non-perturbative way. We show a few examples of the application of this approach to describe the laser damage and healing of defects in carbon nanotubes with different chiralities and the ultrafast nonequilibrium melting of bulk germanium, initiated by the laser-induced softening and destabilization of transversal acoustic phonon modes.

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1 Introduction

The interaction of femtosecond laser pulses and solids gives rise to a large variety of novel and interesting effects, including nonthermal structural changes. Laser pulses of durations ranging from a few femtoseconds up to half a picosecond and intensities above $10^{12}$ W/cm$^2$ may induce lattice instabilities which lead to thermal and nonthermal structural transformations.

In the last two decades, different types of laser induced reversible and irreversible ultrafast structural changes were observed, like excitation of coherent phonons [1–9] or nonequilibrium phase transitions, the latter including order-disorder [10, 11], solid–solid [12, 13] and solid–liquid [14–26] transformations.

Many different pump-probe techniques were used in the experiments mentioned above. In some works a laser pulse was used as a probe, and the time dependence of the reflectivity or the dielectric function was measured [27]. The development of sources of ultrashort X-ray pulses made it possible to perform time-resolved diffraction experiments [28] recording rocking curves as a function of time. This method has the advantage that it permits a direct visualization of the lattice dynamics upon laser excitation. Finally, in the last years time-resolved electron diffraction experiments were performed.

Most of the results obtained in the mentioned experiments show clear evidences of nonthermal structural changes as a consequence of intense femtosecond laser excitation.

Regarding the systems studied experimentally, a group of materials that merits particular attention includes semiconductors because of their technological significance. Of special interest are materials like silicon (Si), germanium (Ge) and gallium arsenide (GaAs) which are widely used in semiconductor devices; here short time behavior becomes even more important as the frequencies at which these devices are operated increase [18, 29]. The study of electronic relaxation time scales is very important for the development of nanodevices. Carbon nanotubes are potentially good candidates for future technological applications like ultrafast optical storage media or cluster assembled materials [30, 31]. Finally, covalent solids like diamond, graphite and other carbon materials like diamond-like carbon (DLC) are of enormous technological interest because of their physical prop-
erties including extreme hardness and very high thermal conductivity. For these materials there is a large field of research concerning ultrashort laser-induced modification, annealing, ablation and machining [32].

Covalent systems are also interesting from the viewpoint of basic research, since their structural response differs dramatically from that of metals. Femtosecond laser excitation of covalent solids exhibits new and interesting features. First, absorption of photons in covalent solids leads rapidly to bond-breaking processes. As soon as bonds are broken, the picture of electron-phonon coupling is no longer valid. Moreover, the concept of phonons becomes meaningless, since the potential landscape cannot be represented any more by a superposition of harmonic potentials. As a consequence, the widely used two-temperature model breaks down and a different theoretical approach is necessary. Such an approach must take into account explicitly the atomic coordinates and must yield a correct description of the bonding. In this paper we will describe in detail a microscopic theory for laser-induced structural changes in covalent solids.

Despite the intensive experimental activities, only a few theoretical methods were developed in the last years to describe laser induced structural changes.

The pioneer works by Stampfli and Bennemann [33–35] were very successful in describing the laser-induced lattice destabilization in Si, Ge and C and constituted the basis for the theoretical approach presented here. Stampfli and Bennemann analyzed the instabilities caused by the electron-hole plasma in terms of one or two phonon degrees of freedom, and assuming that the entropy of the excited electrons remains constant during and after laser heating. By assuming the instant creation of an electron–hole plasma of a given density $\xi$ at a time $t = 0$, the duration of the laser pulse is set to zero ($\tau = 0$). Other approaches make use of molecular dynamics (MD) simulations based on model potentials, like the Stillinger–Weber potential for the case of Si [36]. However, and as we show below, model interatomic potentials which do not include the electrons as degrees of freedom are not optimally suited for a theoretical treatment of laser-induced structural changes. Recently, this drawback of model potentials was compensated by introducing the electron dynamics in the framework of the two-temperature molecular dynamics model [37]. This improved approach works well for metals, but not for covalent systems.

Parrinello and coworkers employed first principles MD simulations [38–40]. These are based upon a treatment of the electrons and ions in the lattice with density functional theory in the local density approximation and with plane waves as basis functions. The volume of the MD cell was kept constant. The numerical cost of such calculations is very high [40], so that these methods would not permit a study of many different laser intensities and durations on various materials as was the intention of this work. Concerning the results obtained for the laser melting of graphite [41], it seems possible that the choice of a constant volume MD method imposed too severe a restriction on the relaxation channels available to the material. These authors also assume for their melting studies the instant creation of a high electron temperature $T_e$ at a time $t = 0$. Thus, the laser pulses are taken to be delta functions of duration $\tau = 0$ which makes it impossible to analyze the influence of the pulse duration. A similar approach as the one described above, but using a tight-binding basis instead of Kohn–Sham functions has been used by Ho and coworkers [42].

The method which will be presented in the next section was developed by us to study laser excitation of diamond, graphite and silicon in the bulk [43–47] and in ultrathin films [48, 49], C$_{60}$ clusters [50], and carbon nanotubes [51, 52].

Independently of our studies Allen and coworkers developed a similar method to describe the excitation of coherent phonons and laser-induced melting [53, 54]. This method is suitable for the study of the first few femtoseconds after excitation, since the assumption of constant volume is made and it is assumed that the electronic system does not undergo decoherence and thermalization processes after laser excitation.

The aim of our investigations is to understand on which time scale do laser-induced structural transitions occur, which relaxation channels are present and whether these relaxation channels be controlled by laser parameters like intensity, duration, and light frequency.

An important question which we attempt to answer is if there are fundamental differences between laser-induced and thermally induced bond breaking and phase transitions. Important aspects taken into account in our theory are

(a) The admission of all relaxation channels in the response to an electron–hole plasma, including the calculation for all degrees of freedom and the admission of changes in sample volume and geometry

(b) The handling of the electronic nonequilibrium caused by strong laser excitation and its subsequent equilibration and relaxation, and

(c) The treatment of laser pulses with finite durations $\tau > 0$

In this paper we present a sketch of the theory and its application to the dynamics of single-walled carbon nanotubes (CNT) with defects upon femtosecond laser excitation and the ultrafast nonthermal melting of Ge.

2 Theory

Our model for the femtosecond laser excitation of covalent solids is based on the following physical picture: the