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Laser-induced coherent phonons in graphite and carbon nanotubes: model and simulations

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ABSTRACT We present a microscopic description of the excitation of coherent phonons as a response to femtosecond laser excitation. Using molecular dynamics simulations based on a tight-binding electronic Hamiltonian we discuss two examples of laser-induced coherent phonons: (1) excitation of the E_{2g1} phonon mode in graphite under high external pressure and (2) the displacive excitation of two perpendicular phonon modes in carbon nanotubes. We discuss the influence of these coherent phonons on the ablation mechanisms.

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Recent theoretical and experimental works have shown that it is possible to use femtosecond laser pulses to induce reversible and irreversible ultra-fast material modifications in solids. Such laser-induced structural changes occur in the form of solid–liquid [1, 2, 4, 21] or solid–solid transitions [5–7, 9–11]. These findings can become of fundamental importance since they open the possibility of manipulating lattice arrangements and shapes of nanostructures, including the recently discovered carbon nanotubes (CNTs) [12]. A particularly interesting class of ultra-fast structural modifications consists of those caused by large-amplitude coherent phonons induced by laser excitation, such as in Peierls-distorted Bi [6] or ferroelectric GeTe [7] materials. Recent experiments show that the excitation of coherent phonons plays an important role in the stages of pre-melting and pre-ablation.

Laser-induced coherent phonons have been intensively studied in recent years in different materials [13–17]. Two excitation mechanisms were proposed, namely the impulsive stimulated Raman scattering (ISRS) [16] and the displacive excitation of coherent phonons (DECP) [18]. However, it is still controversial which of these mechanisms applies for the laser-induced coherent phonons observed in different materials.

We present in this paper two examples of DECP in (1) graphite under high external pressure (10 GPa) and (2) carbon nanotubes. In particular, the latter example shows the possibility to induce coherent phonons and ultra-fast lattice transformations at the nanoscale level.

There are two distinct time regimes for the excitation of phonons in nanostructures or solids by an intense laser pulse: on a shorter time scale (~ 100 fs), the promotion of electrons to antibonding states immediately leads to weakening of the bonds and the possibility of coherent atomic motion. In contrast, on a relatively longer time scale (> 1 ps), as the energy of the photoexcited electrons is transferred into atomic thermal motion, phonons are excited incoherently.

In order to simulate the dynamical process of laser-induced coherent phonons, we employ a nonadiabatic molecular dynamics (MD) method combined with a density matrix formulation to describe the coupled dynamics of valence electrons and ionic cores, previously employed in studies of ultra-fast ablation and melting [9, 19–21].

Briefly, our treatment is based on a microscopic electronic Hamiltonian $H_{\mathrm{TB}} + H_{\mathrm{laser}}(t)$, where H_{TB} is a tight-binding Hamiltonian with hopping matrix elements which depend on the interatomic distances $\{r_{ij}\}$, and $H_{\mathrm{laser}}(t)$ accounts for the coupling of the CNT's valence electrons to a time-dependent laser field of shape $E(t)$ and frequency ω. Our formulation assumes that the nondiagonal elements of the density matrix vanish rapidly in time due to dephasing effects.

From the Hamiltonian H_{TB} we calculate forces $\boldsymbol{f}_k(\{r_{ij}(t)\}, t)$ acting on the atoms [8]. The forces depend on the time-dependent occupations $n(\epsilon_m, t)$ of the electronic energy levels (eigenvalues of H_{TB}). This special feature of the theory makes it applicable to optically excited materials. While in thermal equilibrium the occupation numbers are calculated from a Fermi–Dirac distribution function $n^0(\varepsilon_m) = 2/(1 + \exp\{(\varepsilon_m - \mu)/k_{\mathrm{B}}T_{\mathrm{e}}\})$ at a given electronic temperature T_{e}, electronic nonequilibrium is accounted for by solving equations of motion for the occupation of electronic states:

$$\frac{\mathrm{d}n(\varepsilon_m, t)}{\mathrm{d}t} = \int_{-\infty}^{\infty} \mathrm{d}\omega\, g(\omega, t - \Delta t) \times \Big\{ [n(\epsilon_m - \hbar\omega, t - \Delta t) + n(\varepsilon_m + \hbar\omega, t - \Delta t) - 2n(\varepsilon_m, t - \Delta t)] \Big\} - \frac{n(\varepsilon_m, t) - n^0(\varepsilon_m)}{\tau_1}\,. \quad (1)$$

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This equation is derived from the equation of motion for the density matrix under the assumption described before. Thus, the electronic distribution is at each time step folded with the pulse-intensity function $g(\omega, t)$. This means that, at each time step, the occupation of an energy level ε_m changes in proportion to the occupation difference with respect to levels at $\varepsilon_m - \hbar\omega$ and at $\varepsilon_m + \hbar\omega$. In (1), constant optical matrix elements are assumed. The second term of (1) describes the electron–electron collisions that lead to an equilibration of the electronic system with a rate equation of the Boltzmann type for the distribution $n(\varepsilon_m, t)$. Hence, with a time constant τ_1, the distribution $n(\varepsilon_m, t)$ approaches a Fermi–Dirac distribution $n^0(\varepsilon_m)$.

With this theoretical model, in conjunction with previously determined tight-binding parameters for carbon [22], we have performed simulations of the response of bulk graphite and capped (10, 0)-CNTs consisting of 200 atoms. The time step of $\Delta t = 0.1$ fs used in treating both the electron and ion dynamics is small enough to capture the amplitude changes of the external e.m. field and to guarantee energy conservation for the time when the external e.m. field is absent. The relaxation time $\tau_{\text{e-e}}$ was taken to be 10 fs for both systems [21].

In the case of bulk graphite we have performed the simulations assuming a high external pressure. The effect of the pressure is to reduce the interlayer distance in graphite and therefore to increase the interlayer coupling. This increased coupling allows the laser pulse to easily produce a displacive excitation of graphite phonon modes. Thus, we have investigated the behavior of hexagonal graphite under a pressure of $p = 10$ GPa in response to femtosecond laser pulses. An absorbed energy of $E_0 = 1.3$ eV/atom from a laser pulse of $\tau = 20$-fs duration does not damage the graphite planes, as we know from previous investigations [21]. But, we observe that the graphite planes which remain in the ABAB layer sequence indefinitely at room temperature start to rearrange very slowly due to the electron–hole plasma of $\xi = 6\%$ created by the laser pulse. This is shown in Fig. 1. The electron–hole plasma leads to an increase of the lattice vibrations that are already present at $T = 300$ K, and the slight coherent movements of the graphite atoms lead to a loss of the precise ABAB layer sequence. The large-amplitude shear phonon excited by the laser pulse continues its evolution in time, and reaches a layer sequence close to the AAAA ordering at a time $t = 500$ fs. Thus, our results seem to indicate that in hexagonal graphite under pressure a coherent shear mode with a period of about 1 ps can be induced by a laser pulse of moderate intensity. This result agrees well with experiments performed by Kitajima and coworkers, who observed the creation of an E_{2g1} mode of graphite with a frequency of 1.3 THz [14].

Now we discuss the excitation of coherent phonons in CNTs. The most salient feature of the CNT response to a femtosecond light pulse is an impulsive excitation of the radial breathing mode (RBM), as one can observe from the computer visualization of the motion in real space, or from studies of vibrational motion power spectra. The driving mechanism is a displacive excitation [18], which can be described as follows. Since the electronic configuration $n(\mu, T_e)$ is not the ground-state one after the action of the femtosecond pulse, the atomic positions are no longer in equilibrium. In fact, the equilibrium structure of the CNT at the high T_e produced by the laser exhibits a bond-length increase of 1%–2% with respect to the structure at $T_e = 0$. As a consequence, the atoms will start to move towards the new minimum and oscillate around it.

For the capped (10, 0)-CNTs, the displacive excitation will produce two coherent phonons, localized in the spherical caps and cylindrical body. We show these oscillations in Fig. 2, which displays the temporal evolution of $R_C(t)$ and $R_T(t)$, the average spherical cap and tubular radii. The relatively low laser absorbed energy of 1 eV/atom insures that the original connectivity is preserved. We observe that the two oscillation frequencies are different, and in fact correspond to the individual RBMs of C_{60} ($\omega_s = 500\,\text{cm}^{-1}$) and (10, 0)-CNTs ($\omega_c = 300\,\text{cm}^{-1}$). The two coherent phonons therefore seem to be decoupled due to the perpendicular directions of oscillation. This result agrees with the experimental CNT vi-

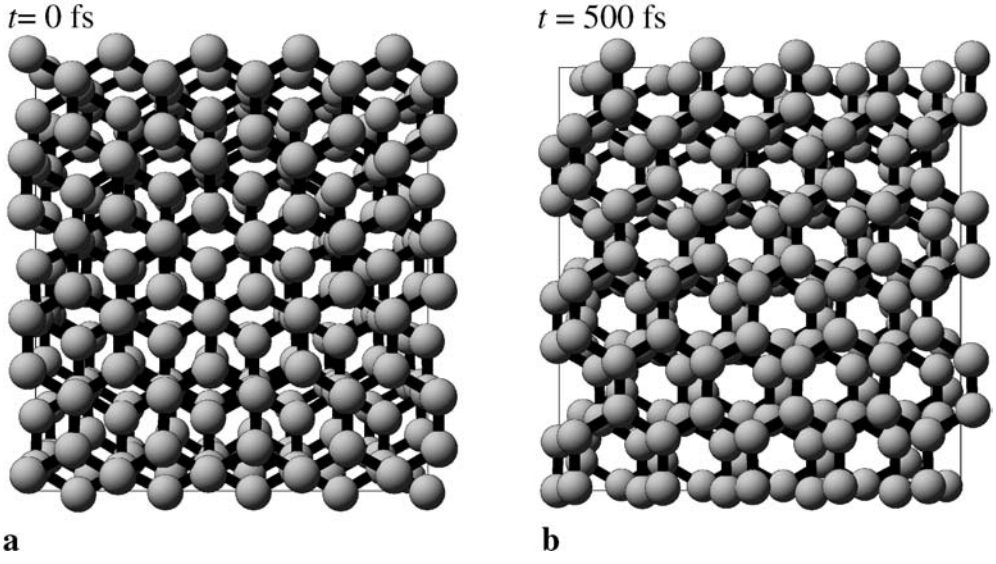

FIGURE 1 Two snapshots of the structure of graphite during the coherent shear motion produced by femtosecond laser excitation ($\tau = 20$ fs pulse duration, $E_0 = 1.3$ eV/atom absorbed energy). Before the action of the pulse, the graphite sample was equilibrated under a pressure of $p = 10$ GPa at $T = 300$ K. The hexagonal graphite with an ABAB layer sequence at $t = 0$ fs is shifted to a layer sequence close to AAAA at $t = 500$ fs by the action of the large-amplitude E_{2g1} coherent phonon

brational spectra, where a distinct RBM peak was attributed to the caps [23].

Figure 2 shows that both the caps and the CNT's body start expanding in phase, reaching their maximum amplitude after 50 fs, measured from the laser peak time. The initial correlation is not preserved due to different characteristic RBM oscillation frequencies, and after 100 fs the two oscillations become out of phase. To understand this behavior in a broader context, it is worth noting that, although RBM frequencies are curvature dependent, the fraction ω_s/ω_t remains constant, according to

$$\omega_s/\omega_t = 2\sqrt{(\lambda+\mu)/(\lambda+2\mu)}\,, \qquad (2)$$

where λ and μ are the Lamé material coefficients [24].

We can conclude that, in the nonthermal regime, laser excitation of long-lived coherent phonons is possible as an impulsive excitation of RBMs.

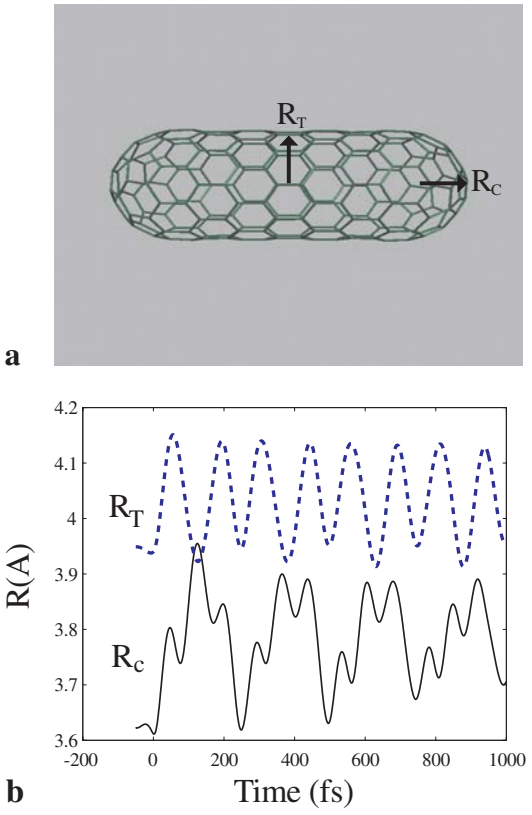

FIGURE 2 **b** Time evolution of $R_C(t)$ and $R_T(t)$, the CNT's cap (*dashed line*) and cylindrical part (*full line*) averaged radii (shown in (**a**)), upon femtosecond laser excitation at a sub-threshold absorbed energy of 1.0 eV/atom. Time is measured from the peak time of the 10 fs pulse

In conclusion, in a series of extensive MD simulations, we provided a microscopic picture of the response under pressure of graphite CNTs to ultra-fast laser pulses of moderate intensities, below the damage threshold. A more detailed analysis of the mechanisms for the excitation of coherent phonons will be the subject of a future study [25].

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