Plasmon-driven sub-picosecond breathing of metal nanoparticles†

Franco P. Bonafé, a Bálint Aradi, b Mengxue Guan, c Sheng Meng, c,d Oscar A. Douglas-Gallardo, a Chao Lian, c Sheng Meng, c,d Thomas Frauenheim b and Cristián G. Sánchez d a

We present the first real-time atomistic simulation on the quantum dynamics of icosahedral silver nanoparticles under strong laser pulses, using time dependent density functional theory (TDDFT) molecular dynamics. We identify the emergence of sub-picosecond breathing-like radial oscillations starting immediately after laser pulse excitation, with increasing amplitude as the field intensity increases. The ultrafast dynamic response of nanoparticles to laser excitation points to a new mechanism other than equilibrium electron–phonon scattering previously assumed, which takes a much longer timescale. A sharp weakening of all bonds during laser excitation is observed, thanks to plasmon damping into excited electrons in anti-bonding states. This sudden weakening of bonds leads to a uniform expansion of the nanoparticles and launches coherent breathing oscillations.

1. Introduction

For decades, since the invention of femtosecond spectroscopy techniques, scientists have been studying thermalization of electrons excited by laser pulses in metal nanoparticles and thin films. 1 By the end of the 1990s, mechanical oscillations at the picosecond time scale after laser illumination were observed for the first time in semiconductors 2 followed by silver 3 and gold 4 nanoparticles, evidenced by a transmission signal change in pump–probe measurements. These oscillations were quickly found to match the lowest frequency radial mode (or breathing mode) of the particles, modeled as an elastic sphere by classical calculations. Their frequency is inversely proportional to the nanoparticle radius. 5,6 Similar behavior was observed in tin and gallium nanoparticles. 2 This discovery paved the way to more research in electron–phonon dynamics in metal nanoparticles in the following years. 1,7–14

In particular, experimental studies for monolayer-protected nanoparticles also confirmed relaxation of electronic excitation to vibrational modes, although differences in features such as excited state lifetime and vibrational periods with respect to uncapped nanoparticles were found. 12,15,16

The proposed explanation, supported by experimental evidence, considers that electrons thermalize in the hundred femtosecond timescale, and then transfer heat to phonons faster than the period of the breathing mode (typically in the order of 1–2 ps); the consequent increase in lattice temperature increases suddenly the equilibrium radius of the particle, inducing atoms to oscillate around the new potential energy minimum. 5,6,9 Experimental evidence in uncapped nanoparticles is consistent with this mechanism, since oscillations could not be observed for small particles (for which the characteristic oscillation time is shorter). 5

However, even though thermalization dynamics are clearly understood, the reason why the oscillations are launched is yet not very clear. In particular, investigations within the small size and short time regime are needed to prove that electron–phonon coupling driving an indirect displacive mechanism is the main cause for the oscillations in all size and time regimes. In particular, hot-electron pressure has been reported as responsible for the mechanical vibrations in small particles and for the initial phase of the oscillations. 10,17–20

Computational studies have helped to explore the aforementioned conditions 21–23 but have not yet been able to account for real-time laser induced phenomena. Here, we report the first real-time computational study that shows evidence of breathing oscillations in the sub-picosecond regime, via surface plasmon excitation. Since our method does not explicitly account for dissipation from electrons to
phonons, the breathing oscillations we see occur as a quasi-adiabatic process, in the sense that no direct dissipative electron–phonon interaction is included in the model. An explanation for the observed results is proposed based on a displacive excitation mechanism. The use of a density functional tight binding method for larger particles is proved to be valid by comparing with the results obtained by time-dependent density functional theory.

2. Computational methods

2.1. Time-dependent density functional theory

Time-dependent density functional theory (TDDFT) calculations were performed using the time-dependent ab initio package, as implemented in SIESTA. This method has been used recently to study dynamics after excitation in several systems. Numerical atomic orbitals with double zeta polarization (DZP) were used as the basis set, while the electron-nuclear interactions were described by Troullier–Martins pseudopotentials in the local density approximation (LDA) and a real-space grid equivalent to a plane-wave cut-off of 250 Ry was adopted.

Structures were converged using a standard conjugate-gradient technique until an energy tolerance of $10^{-6}$ eV was reached. Forces on each atom were found to be less than $0.01$ eV Å$^{-1}$.

Absorption spectra were computed from real-time propagation of the density matrix (DM) $\rho$ of the system after an initial step perturbation (eqn (1)) to the ground state DM. The frequency-dependent polarizability tensor $\alpha$ is obtained within the linear response regime by deconvoluting the dipole moment signal in the time domain, leading to the absorption cross-section which is directly proportional to the imaginary part of the polarizability:

$$E(t) = E_0 (1 - \Theta(t)).$$

Non-adiabatic molecular dynamics simulations were performed integrating the time-dependent Kohn–Sham equations as described by Meng and Kaxiras. We used a time step of 0.05 fs and reached a total simulation time of 800 fs. The laser pulse was described as shown in eqn (2), where the frequency $\omega_p$ matches the plasmon energy (3.8 eV). The pulse peak time was set at $t_0 = 20$ fs while the width was chosen to be $\sigma = 6$ fs. $E_0$ was set to 0.5 V Å$^{-1}$:

$$E(t) = E_0 \cos(\omega_p t) \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right).$$

This highly accurate method could be used to describe the time-dependent behavior of particles of up to 55 atoms, due to its high computational cost. For larger systems we used the more approximate time-dependent density functional tight-binding method.

2.2. Time-dependent density functional tight-binding

The electronic description of the ground state is achieved using the self-consistent charge density functional tight-binding (DFTB) approach, as implemented in the DFTB+ package. This method is based on a second order expansion of the Kohn–Sham functional around a reference density and has proven useful for accurate descriptions of the properties of metallic nanostructures, semiconductors and large molecules. The Slater–Koster parameters were obtained using the Hyb-0-2 parameter set. The conjugate-gradient method was used to optimize the structures.

The methodology used to calculate the absorption spectra is similar to the one described in section 2.1, using in this case a Dirac-delta-like perturbation. The Liouville–von Neumann equation for non-orthogonal basis (eqn (3)) is then numerically integrated using the Leapfrog algorithm. In eqn (3) $S_{ij} = \langle \phi_i | \phi_j \rangle$ is the overlap matrix, $H$ is the Hamiltonian matrix and $i$ the imaginary unit:

$$\dot{\rho} = -i(S^{-1}H[\rho] - \rho H[\rho]S^{-1}).$$

In this case, the polarizability tensor can be calculated by Fourier-transforming the dipole moment signal in the time domain and dividing by the Dirac-delta-like pulse field intensity (eqn (4)). A damping factor of 0.1 fs$^{-1}$ was used to obtain uniform broadening of the peaks. This choice of damping is related to the length of the trajectory used as the input in eqn (4) and is only used to obtain a well-resolved plasmon peak and to identify its energy precisely. This methodology has been applied to study the optical properties of a range of molecular and nanostructured systems.

$$\alpha(\omega) = \frac{\mu(\omega)}{E_0}.$$
The formalism described as follows was derived from formulations reported in the literature\(^{26,33}\) and implemented in the DFTB+ package. The equation of motion of the DM is similar to the Liouville–von Neumann equation but including non-adiabatic coupling terms (eqn (5)):

\[
\dot{\rho} = -i(S^{-1}H[\rho] - \rho H)[S^{-1}] - (S^{-1}D\rho + \rho D\rho^\dagger S^{-1})
\]

where \( D_{kl} = \langle \phi_k | V_{AB} | \phi_l \rangle \) is the non-adiabatic coupling matrix, \( \phi_k \) being the wavefunction of atom A and \( V_{AB} \phi_l \) the gradient of the orbital \( \phi_l \) (which is localized on atom A) with respect to the coordinates of A. In our implementation, we approximated \( \langle \phi_k | V_{AB} | \phi_l \rangle \) as the gradient of the overlap matrix with respect to the AB interatomic vector, \( R_{AB} \), for \( A \neq B \), and 0 otherwise (see eqn (6), where \( \delta_{AB} \) is Kronecker’s delta function):

\[
\langle \phi_k | V_{AB} | \phi_l \rangle = \nabla_{AB} \delta_{kl} (1 - \delta_{AB}).
\]

An external laser field can be applied by adding a time-dependent term to the Hamiltonian of the form \( V = -\mu(t)E(t) \). For a \( \sin^2 \) shaped pulse, the electric field is determined by using eqn (7), where \( \omega_p \) matches the plasmon energy for each case, and the total duration of the pulse was set to \( \tau = 25 \) fs for all simulations. We varied \( E_0 \), exploring the range between 0.001 V Å\(^{-1}\) and 0.75 V Å\(^{-1}\). Here \( \Theta(t) \) is the Heaviside step function. The pulse envelope function is different from what is shown in section 2.1, but its effect in the dynamics is minor, affecting only its amplitude (see the ESI†).

\[
E(t) = E_0 \sin(\omega_p t) \sin^2(\pi t/\tau)(1 - \Theta(\tau)).
\]

Time-dependent forces are calculated at each electronic step and are used to propagate the nuclei simultaneously using the velocity Verlet algorithm. The expression for the forces can be found in the ESI†. Phonon frequencies and displacement vectors were calculated using the modes program of the same package (see below for explanation of the method).

2.3. Normal mode analysis

The mass-weighted Hessian matrix \( F \), defined in eqn (8), is computed by numerical differentiation using either self-consistent DFT or DFTB for the energy calculation. Within the harmonic approximation, the normal modes frequencies and the normalized displacement vectors are the eigenvalues and eigenvectors of \( F \), respectively:

\[
F_{ij} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 E}{\partial q_i \partial q_j}.
\]

The eigenvectors are then projected along the radial direction, and the modes with the highest projection are analyzed to find the fundamental radial mode, hereafter called the quasi-breathing mode (QBM), since the pure breathing mode exists only up to \( n = 13 \).\(^{40}\)

2.4. Model systems

Icosahedral silver nanoparticles (NPs) of three different sizes (number of atoms \( n = 55, 147, 309 \)) were studied in this work.

### Table 1

<table>
<thead>
<tr>
<th>( n )</th>
<th>55</th>
<th>147</th>
<th>309</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d/\text{nm} )</td>
<td>1.09</td>
<td>1.64</td>
<td>2.19</td>
</tr>
<tr>
<td>( h\omega_p/\text{eV} )</td>
<td>3.21</td>
<td>2.95</td>
<td>2.85</td>
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</tbody>
</table>

Their diameter and plasmon energy as calculated by TDDFTB are summarized in Table 1.

3. Results and discussion

The 55-atom NP, after geometry optimization and having zero initial velocities, was illuminated with laser pulses of intensity \( E_0 = 0.5 \) V Å\(^{-1}\) as described in sections 2.1 and 2.2. The system evolves freely after this initial perturbation for 800 fs. The NP average radius, calculated by averaging the distance of all surface atoms to the central atom, is shown as a function of time in Fig. 1 for both methods. An oscillatory behavior is observed for both simulations, although similarities are only qualitative. There is an evident mismatch of the period between the two methods, being ca. 300 fs for TDDFT and ca. 390 fs for TDDFTB. By normal mode analysis with DFT and DFTB we found that the QBM periods for each method (304 fs and 393 fs, respectively) are strikingly similar to the ones found by the TD calculations. The dashed lines in Fig. 1 are
sin functions with a period equal to the QBM. This confirmed that the QBM is selectively excited in the system under analysis. Different periods can be attributed to the different hard-nesses of the potential energy surface that is obtained using the two approaches. The same fact can account for the difference in amplitude.

TDDFT’s higher accuracy is due to a larger basis set and a better description of the electronic interaction through exchange and correlation effects, and it is an excellent tool to study these processes. However, for practical limitations only the $n = 55$ NP could be studied using this method. In the previous discussion, we have validated TDDFTB as a valid approach to study this process, with quantitative differences in the results when compared to TDDFT. As we were mostly interested in trends and elucidating the general mechanism rather than reproducing exact results, we used TDDFTB for the remaining part of this work.

Molecular dynamics on the three NPs described in section 2.4 were run after illumination with 25 fs-long laser pulses as described in section 2.2, in resonance with plasmon excitation (identified as the lowest-energy peak in the absorption spectra, see the ESI†). The fact that the laser pulse is shorter than in most experimental studies (where 100–180 fs pulse widths are commonly used) does not alter the validity of the results, since as long as the pulse is shorter than the period of the QBM (as it is explained below), the main effect of a longer pulse (using a weaker field) would be to start the oscillations later in time, precluding us from studying an adequate time span due to its high computational cost.

The electronic energy (mostly the band component) increases quadratically with the laser field.41 In Fig. 2(a) the changes of the average radii of the NPs are shown as time evolves. For laser intensities higher than the threshold value of 0.1 V Å$^{-1}$ an oscillatory behavior is observed. The shaded area indicates the length of the laser pulse. Even when the period is clearly dependent on the size (see below for detailed discussion), the amplitude of the change in the radius seems to be independent of the NP size and radius (note that the scale in the vertical axis is the same for each row). An interesting feature is that vibrations start during the laser pulse, implying that they are directly launched as a consequence of the electron excitation.

The change in the lattice temperature with these field intensities ranged from 0.15 K to 70 K, while higher temperatures and oscillation amplitudes were found using higher field intensities.†

The observed oscillations show a large radial component by visual inspection of the animations. To find out whether the QBM is excited, normal modes are computed within the DFTB framework as described in section 2.3 and the QMB period is plotted as a function of the NP diameter as shown in Fig. 2(b). A linear relationship is found, in agreement with the expected trend from atomistic and elastic sphere calculations according to Lamb’s theory,42−44 plotted in the same figure. The oscillation period observed in the molecular dynamics simulations is also shown in the same figure, evidencing good agreement with the result obtained from the normal mode analysis, emphasizing the fact that the QBM is excited by the laser pulse. These differences can be attributed to the anharmonicity in the potential (discussed below) and excitation of other modes. In Fig. 2(b) the QBM period calculated by Sauceda et al.21 by normal mode analysis using the Gupta potential is also plotted for comparison. Even though there is an offset between the trends of about 70 fs, the slopes are very similar. As it has been reported, the slope of the period vs. diameter relationship is a characteristic of the QBM mode. The offset can then arise from systematic differences related to the employed methodology (i.e. the DFTB method).

Given that our method does not account explicitly for electron-phonon inelastic scattering, which would allow heat transfer to occur, this result is puzzling in light of the mechanism reported in the literature.

To understand the origin of such oscillations we investigated the band component of the pairwise bond energy for all pairs of atoms $A \neq B$, hereafter denoted as $E_{\text{PB}}^{\text{A}}$ (eqn (9)), as a
function of time. This quantity is practically zero unless A and B are the nearest neighbors. The self-consistent charge (sc) and repulsive contributions to the energy\(^2\) are not considered since their variation is much smaller than the band contribution:

\[
E_{PB}^{AB} = \sum_{\mu A} \sum_{\nu B} \rho_{\mu \nu} H_{\mu \nu}^{0}.
\]

In Fig. 3 the change in \(E_{PB}\) for all nearest-neighbor pairs of atoms and its mean value are plotted for the \(n = 309\) NP with \(E_0 = 0.25\) V Å\(^{-1}\). The inset shows the first 50 fs, where all bond energies increase due to the excitation of electrons caused by the laser pulse (25 fs). We conclude that such homogeneous weakening of all bonds launches the atomic oscillations. During the first 700 fs the mean bond energy oscillates accompanying the nuclei but does not decrease to its original value, consistently with the fact that no electron–phonon dissipation mechanism is considered in the simulations. Fig. 3 also shows which bonds weaken and strengthen the most (top and bottom NP diagrams embedded in the figure, respectively).

The proposed mechanistic picture is then given as follows: as electrons absorb energy they populate the excited states, which are of antibonding character (see Fig. 4 which evidences electrons being promoted from the occupied states of the sp and d bands to the antibonding states). These excitations are highly delocalized all over the particle due to the delocalized nature of the plasmon excitation, uniformly weakening all bonds. As a consequence of this, the potential energy surface changes (bonds become looser) and the equilibrium radius \(R_0\) of the particle increases. The initial expansion is isotropic, and when the particle reaches \(R_0\) it overshoots by inertia of the atoms, contracting afterwards due to the attractive component of the force, which results in an impulsive excitation of the quasi-breathing mode.

The described mechanism is very similar to the displacive excitation of coherent phonons previously reported,\(^4\) which considers excited electrons as the driving force for the initial expansion instead of fast heat transfer from the electrons to the lattice. This result is also in agreement with the calculations by Lethiec et al.,\(^2\) where it was found that, for tetrahedral silver clusters, breathing mode excitation arises from internal conversion after excitation rather than from vertical excitation itself.

This kind of impulsive nuclear motion induced by electronic excitation is caused by the sudden change in the expectation value of the force at the expectation value of the position, a process that is correctly described by the first order term in the expansion mentioned in section 2.2.\(^3\)\(^,\)\(^3\)\(^6\)\(^,\)\(^3\)\(^7\) This is the case for other impulsive processes such as the induced dissociation of molecules described in ref. 25 and 26. This is the reason why displacive excitation is observed in the simulations despite that no direct electron–phonon coupling (i.e. quantum scattering) can occur within the used simulation scheme.

Several studies have reported features in the vibrations that are compatible with the displacive excitation mechanism. Direct coupling processes such as hot-electron pressure show a sine response with amplitude increasing with the frequency of the mode,\(^9\) which is larger for smaller particles. Experiments on non-spherical particles with anisotropic acoustic vibrations have shown that hot-electron pressure is an important contribution to thermal expansion\(^1\)\(^7\) and can even excite a particular mode.\(^1\)\(^8\)

Further support of this mechanism comes from measurements in monolayer-protected clusters. High-frequency vibrations observed in gold clusters of the 1.1–4 nm size range capped with hexane thiolate were explained using this approach.\(^1\)\(^2\) However, unlike our results, the vibrational fre-
quency was found to be size-independent and compatible with a local mode of the core gold atoms, not the breathing mode of the whole cluster. This effect may be explained considering that ligands induce strong surface disorder\textsuperscript{44,45} leaving a crystalline core (at least for NPs larger than 2 nm) leading to the aforementioned feature which has also been seen in other relevant studies.\textsuperscript{15,16}

The validity of the displacive excitation mechanism was analyzed by Hodak et al.\textsuperscript{5} and did not succeed in explaining their experimental results since (i) the lifetime of excited electrons in metals is too short and (ii) it would lead to higher amplitudes as the field intensity increases, while the opposite behavior is observed. The reason given for (ii) is that for high fields/small particles the heat transfer to the lattice is slower than the QBM period, leading to non-coherent excitation which precludes its experimental observation in ensemble experiments. However, for our modeled scenario these arguments are less important since (i) we consider shorter times than the electron–phonon coupling times, so most electrons remain excited (only redistribution of energy in the electronic subsystem occurs) and (ii) we look at a single particle and hence coherent excitation in a polydisperse sample is not considered.

With this picture in mind, simple scaling laws relating to the parameters of the oscillation with the external perturbation can be obtained. Both the new equilibrium radius $R_0$ and amplitude $A$ increase proportionally with the external field $E_0$, but they remain almost independent of the particle size.\textsuperscript{1} Better insight can be drawn if the absorbed electronic energy $\Delta E_{\text{el}}$, is considered instead of $E_0$. Since $\Delta E_{\text{el}}$ is proportional to the absorbed power, it is directly proportional to the number of atoms $n$ and quadratically proportional to $E_0$ (since the cross section increases with volume\textsuperscript{12} ($\propto n$) and the instantaneous power absorbed from the external field is proportional to its square\textsuperscript{41}). Also $\Delta E_{\text{el}} \approx \sum \Delta E_{\text{el}}^\text{AB}$, therefore, $\Delta E_{\text{el}}/n$ is a good approximation to the increase of bond energy per unit volume. In Fig. 5(a) the amplitude is plotted vs. $\Delta E_{\text{el}}/n$ for all particle sizes. A linear trend is found where slopes are all similar regardless of the particle size. Hence, this relationship can help predict the oscillation amplitude as a function of field intensity.

The change in the equilibrium radius $\Delta R_0$ also follows a similar trend, as plotted in Fig. 5(b), but considering $\Delta E_{\text{el}}/n^{2/3}$ as the abscissa. This is explained considering that the average increase of the particle radius due to the excited electrons has to be proportional to the radius itself. Hence, to the volume-normalized weakening of bonds $\Delta E_{\text{el}}/n$ should be multiplied by $n^{1/3}$ (since $R \propto n^{1/3}$) to account for the previous conditions. This leads to $\Delta E_{\text{el}}/n^{1/3} = \Delta E_{\text{el}}/n^{2/3}$.

These simple scaling laws nicely illustrate the proposed picture of how the plasmon excitation drives the displacive QBM excitation in our simulations.

4. Conclusions

We have proved for the first time that mechanical oscillations compatible with the quasi-breathing mode can be launched in small silver nanoparticles even “turning off” electron–phonon interactions. Hence, the mechanism in this case is based on a quasi-adiabatic process in which excited electrons populate the excited states of antibonding character, weakening the bonds uniformly and causing an expansion of the nanoparticle, which then vibrates around a new equilibrium radius. New scaling laws can be derived from this explanation, in which the amplitude is proportional to the absorbed electronic energy normalized by the number of atoms $n$ and the change in the equilibrium radius follows the same trend using $n^{2/3}$ as the normalization factor. These conclusions have been validated by highly accurate TDDFT calculations, despite differences observed due to the hardness of the oscillator that emerges from the different approaches.

Our results imply that a different, quasi-adiabatic mechanism, might be playing a role in the short-time small-size regime where electron–phonon scattering is not relevant due to its longer time scale.

Conflicts of interest

There are no conflicts of interest to declare.

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