(Appl. Phys. Lett. 100, 241904 (2012)) Size dependent infrared properties of MgO nanoparticles with evidences of screening effect

Yann Chalopin,[1] Hichem Dammak,[2, 3, *] Marc Hayoun,[3] Mondher Besbes,[4] and Jean-Jacques Greffet[4]

[1]*Laboratoire d'Energétique Moléculaire et Macroscopique, CNRS UPR 288,*
Ecole Centrale Paris, F-92295 Châtenay-Malabry, France
[2]*Laboratoire Structures, Propriétés et Modélisation des Solides,*
CNRS UMR 8580, Ecole Centrale Paris, F-92295 Châtenay-Malabry, France
[3]*Laboratoire des Solides Irradiés, Ecole Polytechnique, CEA-DSM, CNRS, 91128 Palaiseau, France*
[4]*Laboratoire Charles Fabry, Institut d'Optique, Univ Paris Sud,*
CNRS, Campus Polytechnique, RD 128, 91127 Palaiseau, France
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We have investigated the infrared (IR) absorption properties of MgO nanoparticles (NPs) with the means of molecular dynamics simulations. Several size effects have been observed. We show in particular that the absorption of IR radiation does not occur predominantly through the polariton mode but preferentially through size dependent surface modes. This enhanced surface absorption is found to result from a screening effect of the first atomic layers of the NPs. We demonstrate concomitantly that a macroscopic description of electrodynamics is inadequate to capture these unusual IR properties.

Most theoretical approaches dealing with light-matter interaction at nanoscale are based on the use of a bulk dielectric constant and the usual boundary conditions at interfaces. Nanoparticles (NPs) are a natural playground for testing the impact of size effects on optical properties. Mie theory proves to be very efficient for describing absorption and scattering of light by NPs [1]. There is a considerable number of applications including surface enhanced Raman scattering [2, 3], biosensing [4] cancer therapy by local heating [5, 6], heat assisted magnetic recording [7], enhancement of the extraction of light from LEDs or absorption by photovoltaic cells [8, 9]. This list is far from complete. Although in most cases a macroscopic description of the optical properties of the particle is sufficient, this is no longer possible when dealing with NPs with a radius smaller than a few nanometers [10]. Screening effects take place [11] such as the spill-out of electrons. Relaxation is also modified in this regime [12] with a strong increase of the intrinsic electron-phonon interaction for NPs smaller than 10 nm. The calculations based on a model proposed by Lerme *et al.* [13] showed that this effect was due to a surface-induced reduction of the screening efficiency of the Coulomb electron-electron interaction. Screening effects have also been invoked when dealing with the lifetime of excited molecules close to metallic interfaces [14, 15].

In view of the amount of work reported on metallic NPs optical properties, a simple question arises naturally : are there similar nanoscale effects for the infrared (IR) properties of dielectric NPs ? The question is important as many studies have been reported at the nanoscale in the IR. Fuchs and Kliewer [16] have stud-ied the surface phonon resonances in nanospheres in the framework of the Mie theory. They found a resonance when $\varepsilon'(\omega) + (l + 1)/l = 0$. This resonance is similar to the surface plasmon resonances. For $l = 1$, we find the usual dipolar mode that corresponds to a volume oscillation of the polarization charge. The analogy of surface plasmon polaritons and surface phonon polaritons on plane surfaces is well-known. Several effects have been reported such as a superlens [17], total absorption by a grating and coherent thermal emission [18], enhanced radiative heat transfer at nanoscale [19, 20], optical thermal antennas[21]. The question to be addressed for all these phenomena is whether macroscopic electrodynamics is valid at nanoscale. Fuchs and Kliewer [22] analyzed the results in terms of set of modes in a cubic particle within the macroscopic electrodynamics framework. However, experiments reported by Genzel and Martin [23] for 100 nm NPs displayed several absorption peaks not predicted by this theory. In an attempt to use a microscopic theory, lattice dynamics was used by Martin to study the absorption properties of a 64 atoms cluster [24]. Such a cluster has a discrete absorption spectrum similar to a large molecule rather than a particle. However, absorption peaks could be ascribed to edge modes, surface modes and volume modes. For particles with radii smaller than 10 nm, experimental effects that cannot be described by Mie theory were also reported in the paper by Mochizuki *et al.* [25] and a discussion is given by Biju *et al.* [26].

In this letter, we introduce a theoretical investigation of the optical properties of MgO NPs by means of the molecular dynamics (MD) simulation technique. We explore the optical properties of NPs with an edge length varying between 0.84 nm (64 atoms) and 5 nm (13824 atoms). Our approach uses the fluctuation-dissipation theorem to derive the particle polarisability from the sim-

*Corresponding author: hichem.dammak@ecp.fr

ulation of the particle dipole moment fluctuations[27]. We derive the absorption spectra of nanoparticules and compare them with predicted absorption spectra assuming that the bulk dielectric constant is valid. We find significant differences between the spectra. By carefully analyzing the MD data, we can attribute these frequencies to specific modes.

An important result of our analysis is the finding of anomalous absorption peaks attributed to screening effects. In this work, we will assume that potentials developed for bulk and validated for surfaces [28, 29] can be used to capture the key phenomena. The potential model chosen in this study includes explicitly a Coulomb interaction, an effective van der Waals attractive component and an exponential repulsive part. The parameters are taken from [30]. A 1 fs time step ensures that all relevant time scales are properly accounted for in the MD simulations. Equilibrium trajectories as long as 1 ns were obtained in the canonical ensemble using a Langevin thermostat [31]. The bulk optical properties in the IR are reproduced with a fair accuracy. Figure 1 shows the imaginary and real part of the dielectric constant obtained at $T = 300K$. The position of the phonon resonance is recovered with fair accuracy. We then considered MgO NPs and found stable shape for cubic geometry with edges ranging from 0.8 nm (64 atoms) to 4.2 nm (8000 atoms). We report in Fig. 2 the NP absorption spectrum ob-
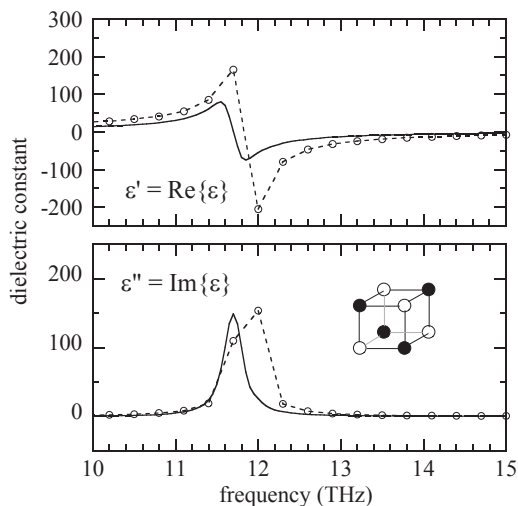

FIG. 1: Dielectric constant of MgO bulk. MD calculations (solid line) and experimental values [32] (dashed line).

tained by MD for a particle with 8000 atoms (radius 4.2 nm), and by a solution of Maxwell equations using a finite element method [33] in the electrostatic approximation. The technique uses node elements, with elements of size 0.1 nm close to the cube summits. The quantity studied is the imaginary part of the particle polarisability[27]. We use an electrostatic solution because retardation effects are negligible given that the wavelengths of interest are between 10 and 20μm which is more than four orders larger than the particle size. The dielectric constant used

in the electromagnetic calculations are the data obtained from the MD simulation for the bulk case presented in Fig. 1. Hence, the differences are genuinely due to size effects. The first remark is that at first glance the absorption range is similar apart from a shift so that there is a general qualitative agreement. Hence, a simple macroscopic model of the optical properties of the NP is able to capture part of the physics of the system. This can be attributed to the fact that both approaches contain a correct information about the optical phonon density of states through the potential for MD, through the dielectric permittivity for the Maxwell approach. So far, we note that using the right geometry and the macroscopic dielectric constant produces a qualitative agreement. We
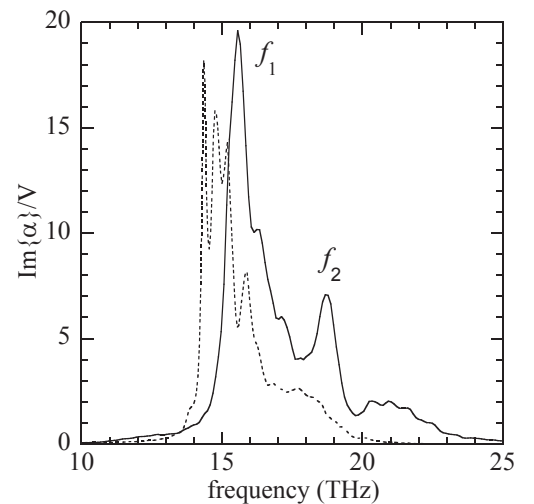

FIG. 2: Imaginary part of the NP polarisability derived from MD simulation (solid line, 4.2 nm size) and compared to finite elements method (FEM) for Maxwell equations in the electrostatic approximation (dashed line, 4.2 nm size). The three FEM peaks around 15 THz are due to the mesh discontinuities at the cube edges. A single peak is observed when smoothing the edges.

now analyze in more detail the absorption spectra of cubic NPs of decreasing size. The results are displayed in Fig. 3.(a). The first obvious observation is that the spectrum evolves from a continuous spectrum towards a discrete molecular absorption spectrum. Clearly, the NP picture is not valid when dealing with only 64 atoms. Our numerical results indicate a discrete spectrum for a size below 1 nm and a continuous absorption spectrum for larger particles. When further analyzing the results, we observe that the peak structure changes as the edge length increases and has not yet converged for an edge length of 4.2 nm. More precisely, the MD simulation shows a peak (f_1) at 16 THz whose frequency decreases towards 15 THz value as the NP size increases. This result is further shown in Fig. 3.(b) where the position of the two main absorption peaks is indicated as a function of the particle size. This behavior cannot be reproduced using the electrostatic approximation since the

wavelength is no longer a natural length scale. The spectrum is thus necessarily size independent. A more de-
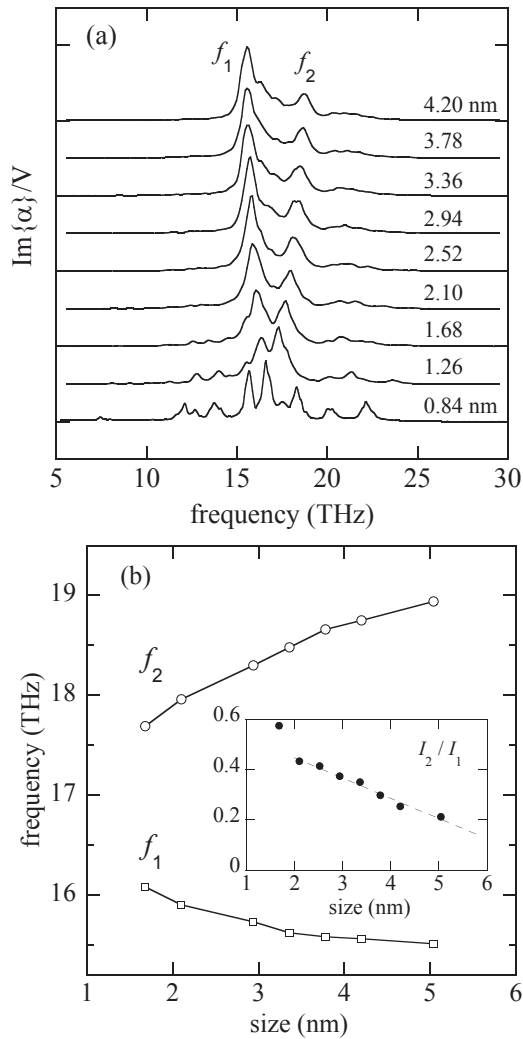

FIG. 3: a) Imaginary part of the NP polarisability per volume unit as a function of frequency derived from MD simulations at 300K. b) Evolution of the characteristic frequencies f_1 and f_2 as a function of the NP size. The inset shows the ratio of their corresponding intensities.

tailed scrutiny of the absorption spectra in Fig. 3 shows further significant differences. The three peaks around 15 THz observed in the electrostatic solution of Maxwell equations correspond to resonances confined in the summits of the cube. These resonances disappear when the summits are rounded with a 0.1 nm radius of curvature so that they are spurious resonances of a continuum model. Furthermore, when refining the mesh, the absorption associated with summits and edges increases because the singularities of the fields are non integrable. This is not a numerical simulation failure but a continuous model failure. Obviously, a mesh refinement is meaningless for distances much smaller than 0.1nm. Numerical convergence was obtained when replacing the cube geometry by a geometry with rounded summits and edges.

The MD simulation predicts a peak (f_2) at 18 THz whereas the electromagnetic simulation shows a broad absorption peak. Note also that this peak tends to vanish as the particle size increases suggesting that it is a surface effect. We also note the presence of absorption peaks above 20 THz is not predicted by the macroscopic calculation using the bulk dielectric constant. In summary, the MD simulation indicates that the 4 nm NP is too small for a macroscopic calculation to be valid. In other words, the IR active vibration modes of the particle results in size dependent resonances and absorption at several frequencies not predicted by an electromagnetic theory using the bulk optical properties.

To understand the origin of the additional resonances observed in the MD simulation, we illuminate the NP with a monochromatic electric field [27] at the corresponding frequencies and observe the dynamical response of each of the 1000 atoms of a 2.10 nm NP. The field amplitude E_0 is chosen so that the system temperature does not exceed a few Kelvin. Figure 4.(a), (b) and (c), show the response obtained by setting the exciting frequency at 16 THz, 18 THz and 21 THz, respectively. By extracting the coherent response of the atoms at the excitation frequency (square modulus of the time Fourier transform of the velocities), we are able to ascribe NP vibration modes to different exciting frequencies. We find that the resonance at 16 THz corresponds to edge modes, the 18 THz resonance is a pure surface mode and the 21 THz mode is a volume mode. Indeed, it is seen in Fig. 4.(a) that the 16 THz frequency corresponds to large movements of atoms belonging to the NP ridges collinear to the electric field direction. In addition, the peak at 18 THz that tends to disappear as the NP size increases (see Fig. 3) corresponds to vibrations of atoms located in topmost planes of the NP surfaces perpendicular to the field (Fig. 4.(a)). On the other hand, Fig. 4.(c) shows that the resonance at 21 THz exhibits a collective response for all the atoms forming the NP. Analyzing the phase of these atomic motions revealed that Mg and O ions undergo opposite displacements suggesting that the 21 THz mode is a polariton resonance.

Finally, we observe a different sequence of absorption peaks in the Maxwell numerical simulation. The four peaks observed in Fig. 2 at 15 THz corresponds to absorption localized in the cube vertices. As frequency increases, the spatial distribution of the field in the cube displays (not shown) edge modes at 17 THz and surface modes at 20 THz although the absorption amplitude is very low. In other words, while the Maxwell simulation does indeed predict edge and surface modes, neither their position nor their amplitude are correct. An important result of the previous discussion is the fact that the surface mode at 18 THz has a spatial extension exactly given by a single atomic monolayer. In the context of macroscopic electrodynamics, the continuity condition of the normal component $\varepsilon \mathbf{E}_n$ indicates that the field is divided by ε at the interface NP-vacuum. This is due to the screening of the external field by the polarization
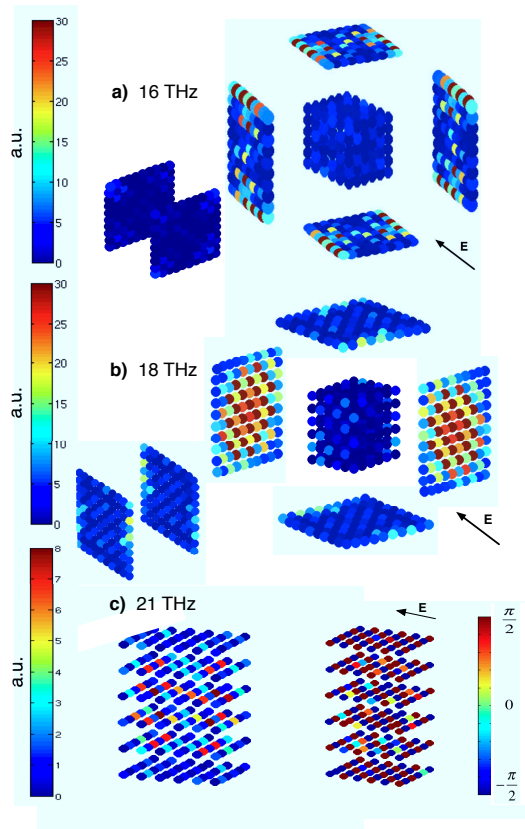
FIG. 4: Square modulus of the time Fourier transform of atomic velocities at three excitation frequencies for the cubic NP of 1000 atoms. a) and b) show the edge and surface response at 16 THz and 18 THz, respectively. For sake of clarity, two of the six faces are shifted from their original location. c) at 21 THz, the volume response (left) and its corresponding phase (right) indicates that the Mg and O ions in the core region of the NP oscillate in an opposite phase.

of the material. Fig. 4.(b) shows that it takes only one monatomic plane to develop a polarization sheet that can screen the external field. The mechanism by which this effect contributes to absorption has been explained by Larkin *et al.* [15] in the context of plasmonics. In brief, the field at the first monatomic layer is not screened so that it is $|\varepsilon|$ times larger than the field in the rest of the crystal [34]. Hence, the absorption at the first atomic layer is enhanced by a factor $|\varepsilon|^2$. In practice, it means that absorption takes place in this monolayer. Clearly, this type of absorption mechanism cannot be accounted for by a continuous approach based on the bulk dielectric properties. This genuine surface effect should not be confused with the phonon polariton, also called surface phonon polariton or Kliewer mode, existing over a penetration length given by the skin depth, typically of the order of tens of nm in the visible and IR. This contribution is associated to the 21 THz peak observed here. Finally, we note that a similar screening effect taking place over a single monatomic layer has also been observed in the context of visible electromagnetic field in oxides[35]. In these materials, visible fields are screened by the polarisability of bounded electrons in the atoms of the first layer.

In summary, using a microscopic approach, we found unusual size dependent absorption peaks in MgO nanoparticles. Several effects have been observed: For sizes below 1 nm, the particle is essentially a large molecule with discrete levels. For sizes between 1 and 5 nm, we observed a size dependence of the absorption spectrum. An important result is that IR absorption does not occur predominantly through the polariton mode due to screening effects. A corresponding screening length-scale has been identified, which is equal to a single monatomic layer. It leads to an enhanced surface absorption mechanism that cannot be accounted for by a macroscopic approach based on bulk dielectric constant.

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