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Microscopic model of IR properties of MgO nanoparticles: size effects

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We assess the validity of macroscopic electrodynamics at the nanoscale by studying the IR properties of MgO nanoparticles. The absorption spectrum is computed using a numerical solution of Maxwell equations with a local macroscopic dielectric constant. The result is compared with an absorption spectrum obtained using molecular dynamics simulation. Significant differences are reported and we find evidence of the presence of non-local effects. This indicates that a local macroscopic model is not valid at the nanoscale.

One of the key issues in nanophotonics is the validity of macroscopic electrodynamics at nanoscale. Most theoretical approaches dealing with light-matter interaction at nanoscale

are based on the use of a local 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 successful for describing absorption and scattering of light by NPs [1]. There is a considerable number of applications including surface enhanced Raman scattering [2], cancer therapy by local heating [3], heat assisted magnetic recording [4], enhancement of the extraction of light from LEDs or absorption by photovoltaic cells [5, 6]. This list is far from complete. Although in most cases a local 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 [7]. Non-local effects take place such as the spill-out of electrons. Relaxation is also modified in this regime [8] with a strong increase of the intrinsic electron-phonon interaction for NPs smaller than 10 nm. The calculations based on a model proposed by [9] showed that this effect was due to a surface-induced reduction of the screening efficiency of the Coulomb electron-electron interaction. Methods for solving Maxwell's equations for light scattering from particles of arbitrary shape in a complex environment accounting for nonlocality have been recently introduced [10]. Non local effects have also been invoked when dealing with the lifetime of excited molecules close to metallic interfaces [11, 12].

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 infra-red (IR) properties of dielectric NPs? The literature is limited on this topic. Fuchs and Kliewer [13] have studied the surface phonon resonances in small particles in the framework of 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 bulk 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 [14], total absorption by a grating and coherent thermal emission [15], enhanced radiative heat transfer at nanoscale [16, 17]. The question to be addressed for all these phenomena is whether macroscopic electrodynamics is valid at nanoscale. Fuchs and Kliewer [18] analysed the results in terms of set of modes in a cubic particle within the macroscopic electrodynamics framework. However, experiments reported by Genzel and Martin [19] for 100 nm NPs displayed several absorption peaks not predicted by this theory. Lattice dynamics was used by Martin to provide a microscopic analysis of the absorption

properties of a 64 atoms cluster [20]. For such a large molecule, absorption peaks were clearly different from macroscopic models and could be ascribed to wedge modes, surface modes and bulk 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.* [21] and a discussion is given by Biju *et al.* [22].

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 a diameter varying between 0.84 nm (64 atoms) and 5 nm (13824 atoms). Our approach uses the fluctuation-dissipation theorem to derive the linear optical properties from the simulation of the polarization fluctuations. We derive the absorption spectra of nanoparticles and compare them with predicted absorption spectra assuming that the bulk dielectric constant is valid. We find significant differences between the spectra. By carefully analysing the MD data, we can attribute these frequencies to specific modes. An important result of our analysis is the finding of nonlocal effects in the resonant absorption.

In this work, we will assume that potentials developed for bulk and successfully used for surfaces [23, 24] can be used to capture the key phenomena. The potentials chosen in this study include explicitly a Coulomb interaction, an effective van der Waals attractive component and an exponential repulsive part. The parameters are taken from [25]. 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 [26]. The bulk optical properties in the IR are successfully reproduced. Figure 1 shows the imaginary and real part of the dielectric constant obtained at $T = 300\text{K}$. 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 5.0 nm (13824 atoms).

We now analyse the absorption spectra of cubic NPs of increasing size. The quantity studied is the imaginary part of the particle polarisability. The results are displayed in Fig. 2.(a). The first observation is that the spectrum evolves from a discrete molecular absorption spectrum towards a continuous spectrum. Clearly, the NP picture is not valid when dealing with 64 atoms. Our numerical results indicate a discrete spectrum for size below 1 nm and a continuous absorption spectrum for larger particles. When analysing the results, we observe that the peak structure changes as the diameter increases and has not

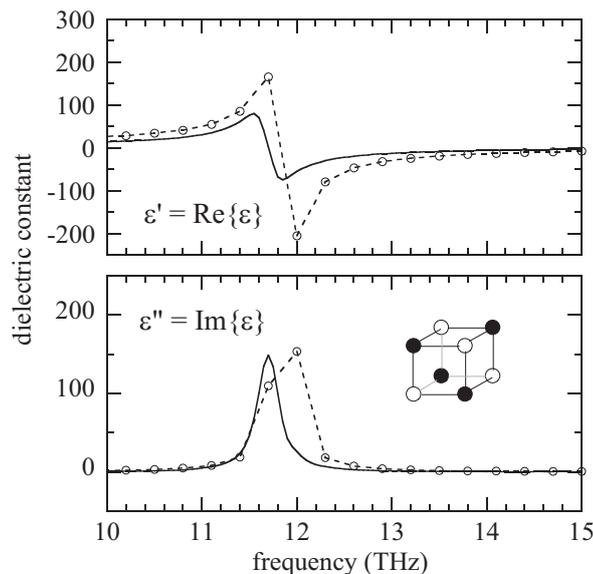


FIG. 1: Dielectric constant of MgO bulk. MD calculations (solid line) and experimental values [27] (dashed line).

yet converged for a diameter of 4.2 nm. This result is further shown in Fig. 2.(b) where the position of the two main absorption peaks is indicated as a function of the particle size. It is therefore clear that a macroscopic calculation using electrostatic approximation cannot reproduce the optical properties of the particles. Indeed, within the electrostatic approximation, the absorption spectrum does not depend on the size of the particle. Let us examine this issue in more detail.

For the sake of comparison, we report in Fig. 3 the NP absorption spectrum obtained by MD for one of the largest sizes (8000 atoms, 4.2 nm) and by a solution of Maxwell equations using a finite element method [28]. 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 so that there is a general qualitative agreement. Hence, a simple local continuous model of the optical properties of the NP is able to capture part of the physics of the system. Note that both the electromagnetic calculation and the MD simulation predict a resonant absorption close to 15 THz. 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.

A more detailed scrutiny of the absorption spectra shows significant differences. As

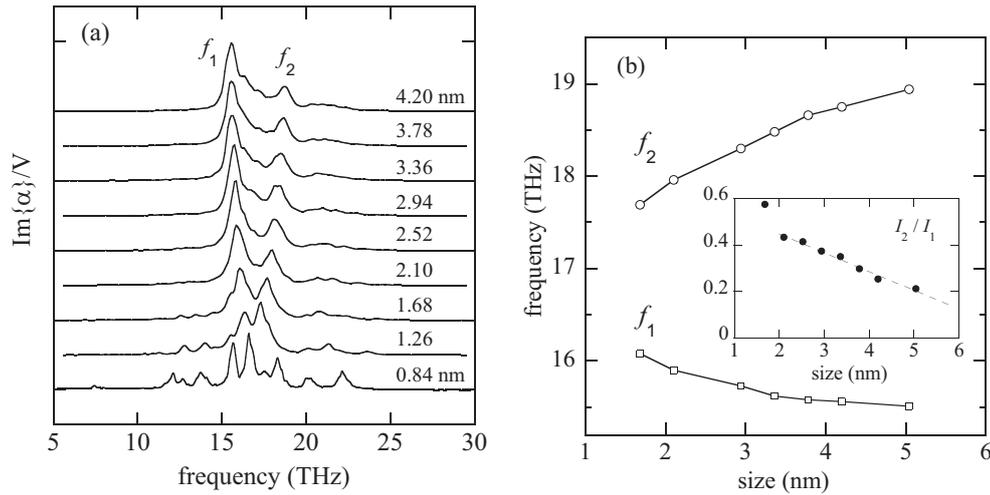


FIG. 2: a) Imaginary part of the NP polarisability per volume unit as a function of frequency derived from MD simulations at 300K. b) Evolution of the characteristic frequencies f_1 and f_2 as a function of the NP size. The inset shows the ratio of their corresponding intensities.

already noted, the NP spectrum is size dependent whereas the macroscopic model is size independent as long as the size is much smaller than the wavelength, so that retardation effects are negligible. The MD simulation predicts a peak (f_2) at 18 THz which is completely absent in the electromagnetic model. We also note the presence of absorption peaks above 20 THz attributed to bulk absorption which are not predicted by the macroscopic calculation with local dielectric constant. In summary, the MD simulation indicates that the 4 nm radius NP is too small for a macroscopic calculation to be valid. We have shown that this is indeed a failure due to the use of the local dielectric constant. However, two questions arise: which resonance corresponds to the phonon polariton mode? What is the origin of the other absorption peaks?

To understand the origin of the additional resonances, we illuminate the NP with a monochromatic electric field at the corresponding frequency and observe the dynamical response of each of the 1000 atoms of a 2.10 nm radius 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

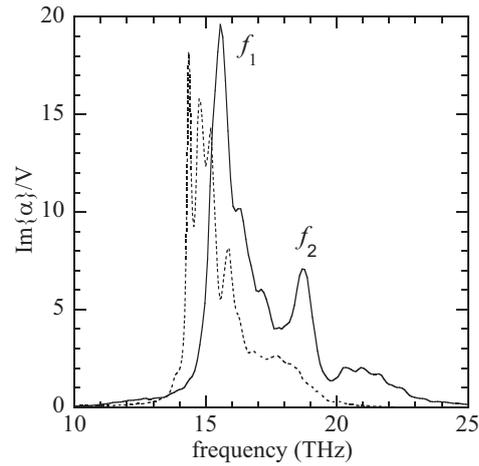


FIG. 3: Imaginary part of the NP polarisability derived from MD simulation (solid line, 4.2 nm size) and compared to finite elements method for Maxwell equations (dashed line, 4 nm size).

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 colinear to the electric field direction. In addition, the peak at 18 THz that tends to disappear as the NP size increases (see Fig. 2) 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. Analysing 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. Although the 64 atoms cluster has a molecule-type absorption spectrum displaying separated lines, a lattice dynamics analysis of molecular clusters [20] has also shown that absorption peaks could be attributed to similar modes. Finally, we also note that this sequence of absorption peaks is also present in the Maxwell numerical simulation. The peak observed in Fig. 3 at 15 THz corresponds to absorption localized in the cube summits. 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 our analysis is the fact that the surface mode at 18 THz has a spatial extension given by a single atomic monolayer. This is the manifestation of a nonlocal electromagnetic behaviour. In the context of local macroscopic

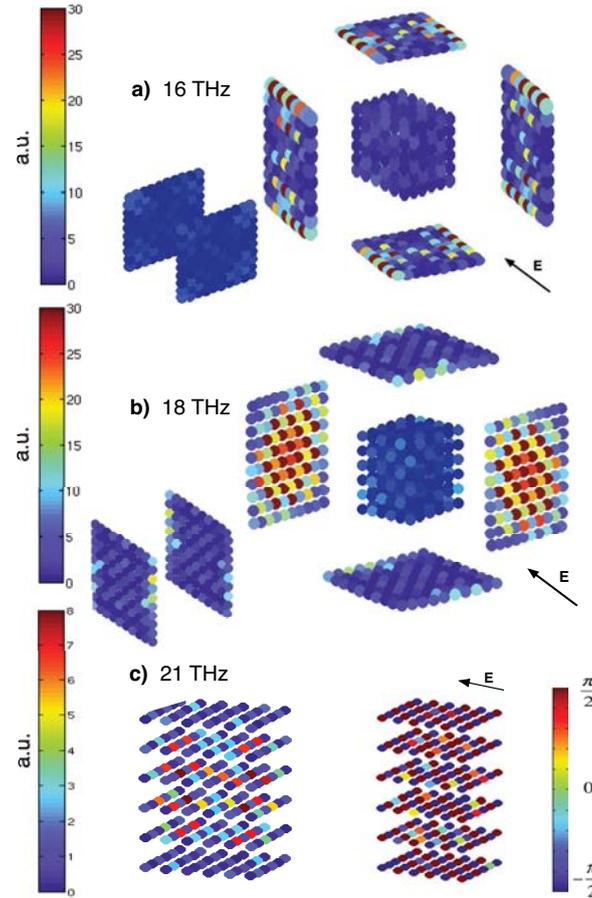


FIG. 4: Square modulus of the time Fourier transform of atomic velocities at three excitation frequencies for the cubic NP of 1000 atoms. a) and b) show the edge and surface response at 16 THz and 18 THz, respectively. For sake of clarity, two of the six faces are shifted from their original location. c) at 21 THz, the bulk 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.

electrodynamics, the continuity condition of $\varepsilon \mathbf{E}_\perp$ indicates that the field is divided by ε at the interface NP-vacuum. In practice, the screening of the field is due to the polarization of the material. Figure 4.(b) shows that it takes only one monatomic plane to develop a polarization sheet that can screen the external field. This is a pure non-local effect with a length scale given by half the lattice period. The mechanism by which this type of surface modes contribute to absorption has been explained by Larkin *et al.* [12] 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. Hence, the absorption by the atoms

of the first 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 finite element method using a local dielectric constant. This genuine surface effect should not be confused with the phonon polariton, also called surface phonon, 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.

In summary, we found that a description of absorption spectrum of NPs in the THz regime based on local macroscopic dielectric constants is inadequate. With a microscopic approach, several effects have been observed. For sizes below 1 nm, the particle is essentially a molecule with discrete levels so that a continuous approach is not relevant. For sizes between 1 and 5 nm, non local effects play a key role due to the preponderance of surface atoms. We observed a size dependence of the absorption spectrum not accounted for by Maxwell equations. In addition, we have seen that IR-absorption does not occur predominantly through the phonon-polariton mode. Non-local absorption mechanisms have been identified indicating that a microscopic description is crucial to fully capture optical properties of NPs. It would be interesting to study if a macroscopic approach using a non-local model can recover the main features of the absorption spectrum.

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