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# Mechanisms of laser-based synthesis and modifications of nanomaterials

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## ABSTRACT

Lasers are known to be extremely versatile tools suitable both for the synthesis and modifications of numerous nanomaterials with unique and extremely interesting optical properties suitable for a wide range of applications in various fields ranging from optics and photonics to medical applications. Efficient control over these processes is still challenging and often requires numerical simulations because of the complex interplay of many physical and chemical processes involved that depend on the combination of both material properties and laser parameters. To simulate these processes, multi-physical modeling should be used including electromagnetic, thermal, mechanical, and chemical effects taking place at several time and space scales. Depending on the experimental conditions, nanoparticles can be formed, grow, aggregate, or on the contrary decay, so that a set of transient variations often take place, particularly when multi-pulse laser irradiation is applied. In the case of short and ultra-short laser pulses, strongly non-linear and time-dependent processes play a role involving not only ionization but also phase transitions, acoustic vibrations, shock waves, as well as void formation, and cavitation. If a considerable energy is released in a very short time, firstly aggregates decay, then nanoparticles are fragmented. Here, based on numerical calculations, the roles of several above-mentioned effects are analyzed. The performed simulations can be used for a better understanding of laser interactions with nanoobjects.

**Keywords:** Laser, nanoparticles, synthesis, nanocomposite, vibrations, sintering, fragmentation, modeling, simulation

## 1. INTRODUCTION

A wide variety of recently developed laser systems from continuous wave (CW) to nanosecond, short (picosecond), and ultra-short (femtosecond) pulsed ones, have enabled the development of numerous laser applications in various fields ranging from optics and photonics to biology and medicine.<sup>1</sup> Among the main advantages of a typical laser treatment is the possibility to carefully choose laser parameters (energy, wavelength, pulse duration polarization, temporal and spatial pulse shape) for the required results. All these parameters affect the resulting material response. This is particularly true in the case of nanocomposite materials and nano- and meta-objects because effects such as electromagnetic field enhancement and plasmonic absorption enter into play. Lasers are also used to generate nanoparticles by laser ablation in liquids, gases, or in a vacuum. Additional laser irradiation can be used to sinter fragment nanoparticles, induce aggregation, melting, or coalescence, create Janus, core-shells, or alloy nanoparticles with unique conjugated properties, such as magneto-optical or chemical-plasmonic, etc. This opens ways for the fabrication of smart nanomaterials with combined properties reacting in a very particular way that can be subjected to several external forces or fields.

To better understand the mechanisms involved in laser-based synthesis and modifications of nanomaterials, computer simulations were used in addition to numerous experiments. Several numerical approaches were developed describing the involved multi-scale effects and ranging from ab initio methods, such as DFT and TD-DFT, molecular dynamics (quantum and classical), mesoscopic models, thermal models, thermo-mechanical and hydrodynamical models, etc.<sup>2</sup>. By using such approaches, many mechanisms involved were described in detail ranging from optical parameter modifications, structural defects formation, other photo-thermal, photo-chemical, photo-mechanical effects that occur at relatively low laser energies, to much more violent ablative behavior involving material spallation, overheating, explosive boiling, cavitation, and/or dynamic fragmentation<sup>3</sup>. Because of the collective nature of such effects and the rather large number of atoms or molecules involved, classical molecular dynamics and hydrodynamic approaches were found to describe these mechanisms quite correctly. However, only a very limited number of materials, mostly homogeneous, were considered. In reality, however, even in the initially homogeneous material, nano-defects are often generated as a result of multiple pulse irradiation. Additionally, nanoparticles are formed or either are suspended in the

ambient gas or form colloids that can be transformed into nanocomposites with unique and adjustable properties. Furthermore, particles can be also ejected into a vacuum deposited on a distance substrate, or re-deposited back on the surface. Lasers can also induce their vibrations and lead to their complete or partial decomposition inducing nanobubbles' complexity. Many questions remain in the case of bi-metallic or complex nanoparticles, concerning not only their thermal stability but also the effects of laser on their shape, morphology, composition, optical and other properties.

## 2. SIMULATION DETAILS

Classical all-atom molecular dynamics<sup>4</sup> is used that allows one to follow the detailed dynamics of nano-systems at different time scales based just on the interaction potentials, or force fields. All nanoparticles were firstly slightly heated above their melting and properly quenched for a sufficiently long time to form surface energy. Then such samples were subjected to much stronger heating during 20 ps well above melting and boiling points that was followed by a long cooling (up to several nanoseconds). The output of the calculations not only provides intriguing insights into the mechanisms involved but also allows one to describe non-equilibrium phase transitions and instabilities rather easily

## 3. RESULTS AND DISCUSSION

### 3.1 Nanoparticle oscillations upon laser heating

As soon as a nanoparticle has absorbed sufficient laser energy, it starts vibrating with frequency depending on its material and decreasing with increasing its size (Figure 1). This is actually the first observation that molecular dynamics simulation provides in agreement with several experiments performed.<sup>5</sup>

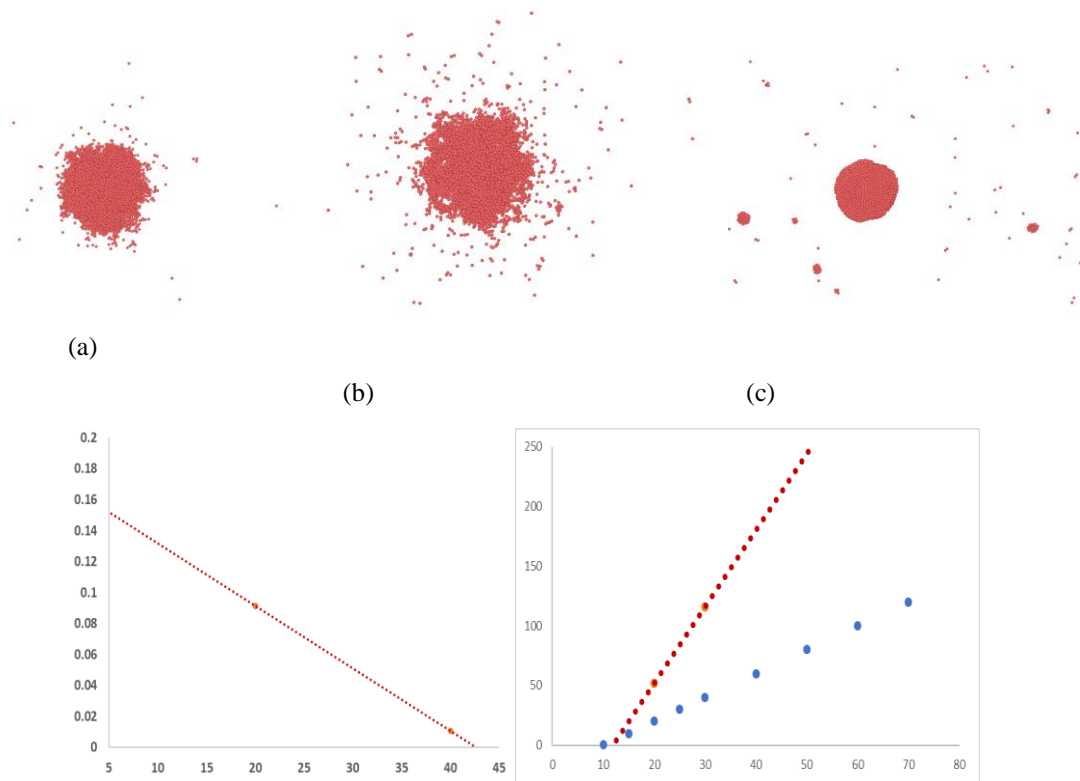


Figure 1. (a)-Upper plots show typical time-evolution of Au nanoparticle with radius  $30 a_{Au}$ ,  $t=20ps, 50ps, 1.6ns$ ,  $T_{max}= 8 kK$ ; (b) Lambs vibration frequency (in THz) vs size for gold nanoparticle, where radius is normalized by unit cell length ( $a_{Au} = 4.05 \text{ \AA}$ ); (c) - Calculated time to decay (ps) for Au NP (red) and Al NP (blue) vs radius normalized by unit cell lengths.

In addition to the so called “breathing mode”, several acoustic vibrational modes are developed, as described by the classical Lamb model which remains valid down to the sizes of around 1 nm. At smaller sizes, corrections are required since system behaves differently, but because here studies the behavior of particles larger than several nanometers, this model remains applicable. Nanoparticles are known to be small objects and the role of surface increases when their size drops below a certain size in nanometric range, when the contribution of the surface potential energy in the total Gibbs energy overcomes the one of the volume or bulk potential energy

### 3.2 Nanoparticle fragmentation upon single pulsed laser heating

Upon of a nanoparticle, its surface experience instabilities. For clusters, Coulomb explosion model was often discussed<sup>6</sup>. For larger particles, however, effects can be similar to the ones observed in small liquid droplets and are characterized by well-known classical models like the ones based on instabilities (namely, Plateau-Rayleigh and/or Rayleigh -Taylor), multi-modal fragmentation, dynamic fragmentation, etc.<sup>7</sup>

To better understand nanoparticle response, elucidate mechanisms major and verify theoretical concepts, molecular simulations are carried out as a function of particle size and maximum temperature. The obtained results show that in fact such effects lead to the surface breakage facilitating nanoparticle deformation (Figure 2).

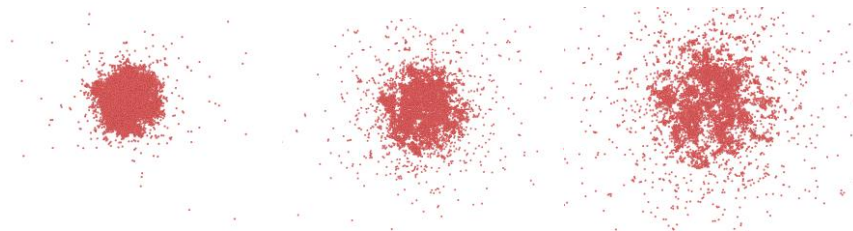


Figure 2. (a) Snapshot from a simulation for Au NP with initial radius of  $30 a_{Au}$  and when heating is above threshold ( $T_{max}=9500$  K) at  $t=20, 50$  and  $100$  ps, ( $a_{Au} = 4.05$  Å).

In fact, the role of the surface is to confine the heat and to compensate expansion forces and mechanical stresses. As a result of the fast heating, surface tension drops down, and surface is destroyed. Typically, particle melting and evaporation start from the surface. At stronger heating, ejections of clusters and small junks can be observed. Further heating leads particle fragmentation due to a set of thermo-mechanical effects.<sup>8,9</sup> This happens if particle temperature approaches the thermodynamic critical one ( $T_c$ , rather than boiling point) known to define the limit of thermal stability. This criterion does not depend on particle size. However, a set of the accompanying effects, such as void formation, subnano-cavitation, dynamic fragmentation<sup>10</sup>, depend on nanoparticle size, as well as nanoparticle's time to fracture (Figure 2), which rises with particle size and is proportional to  $\sim N r_p/C_s$ , where  $r_p$  is particle radius and  $C_s$  is speed of sound in the particle material.

### 3.3 Multiple pulse irradiation

A series of simulations were performed where the ensemble of fragments formed upon single pulsed heating experienced fast heating again. The resulting effects look similar, even if the daughter particles are much smaller (Figure 3). If the concentrating of fragments is locally high, they can collide and sinter reforming novel nanoobjects. Thus, in the experiments, typically dynamic effects are observed as a function of the number of applied laser pulses involving aggregation and either desegregation or alternative melting. We note that here we neglect chemical effects, but they were considered recently in the presence of water.<sup>1</sup> Other commonly used solvents reduce oxidation and are therefore more interesting for future studies that are underway.

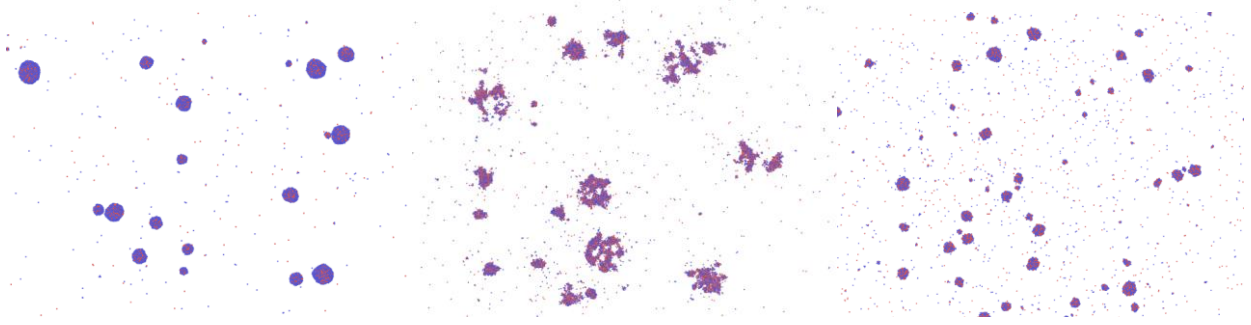


Figure 3. Snapshot from multi-pulse irradiation of a nanoparticle showing fragment formation, interaction and new particle formation. The presented results are obtained for an alloy CoAu nanoparticle. ( $t=0$ ,  $t=50$  ps,  $t=1.6$  ns),

## 4. CONCLUSIONS

In this study, several questions have been addressed concerning nanoparticle behavior upon laser heating, and, namely, upon pulsed laser heating. The performed numerical atomistic modeling allows us to formulate the following conclusions:

-(i) The obtained results show how nanoparticles firstly start vibrating upon laser heating. The corresponding vibration frequencies depend on nanoparticle material and they decrease with size if it is larger than  $\sim 1$  nm. Down to particle sizes of several nanometers the typical vibration modes are still well described by the classical Lamb model. These vibrations can be considerably enhanced in case of resonances.

-(ii) Small size of nanoparticles leads to the confinement of heat and stresses. Both surface energy and surface tension that help particle to keep its shape, drop dramatically with temperature upon heating, so that particle's surface starts experiencing common instabilities (mostly, Plateau-Rayleigh and/or Rayleigh-Taylor) as well as structural change facilitating particle deformation.

-(iii) As a result of a sufficient pulsed heating not only atom by atom evaporation takes place, but also surface fragmentation if maximum particle temperature reaches the critical thermodynamic one, or the limit of its stability. Furthermore, thermo-mechanical effects, play a role for particles larger than 1-10 nm, when considerable stresses and strains are created in the particle. Then, sub-nano voids are formed and oscillate. Depending on particle size and affecting the time when particle starts to break up. This time rises almost linearly as  $\sim N r_p / C_s$  with time indicating several periods of stress or pressure waves passing toward the surface and back to center.

-(iv) In the case of multiple laser irradiation, modifications of nanoparticle can become dynamic at rather moderate energy since nanoparticles can be disintegrated or broken, but then aggregate and sinter again. As a result, preferential growth instead of fragmentation takes place. Above a certain rather high threshold, however, mostly breakage takes place.

## 5. ACKNOWLEDGEMENTS

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