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Modeling of laser-induced modifications of nano-objects and nanocomposite materials

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Submitted on 28 Sep 2023

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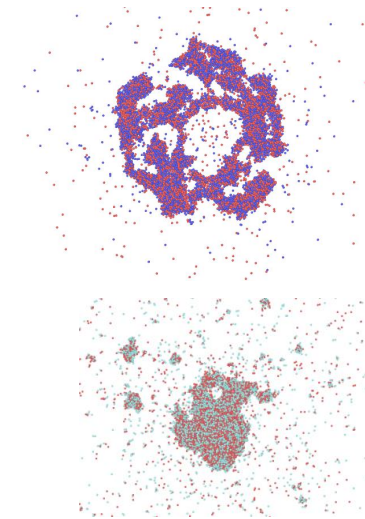
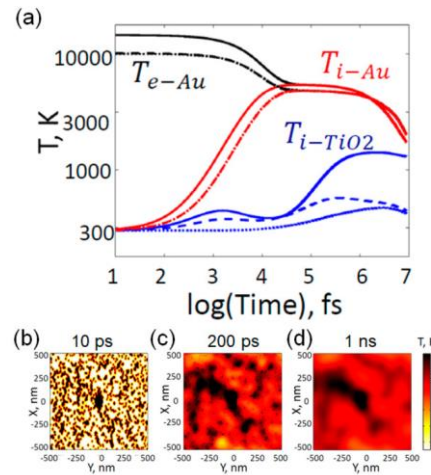
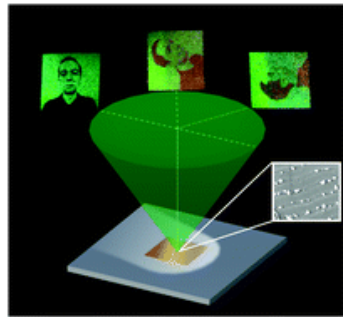
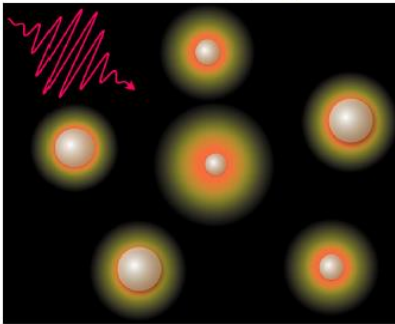
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Modeling of laser-induced modifications of nano-objects and nanocomposite materials

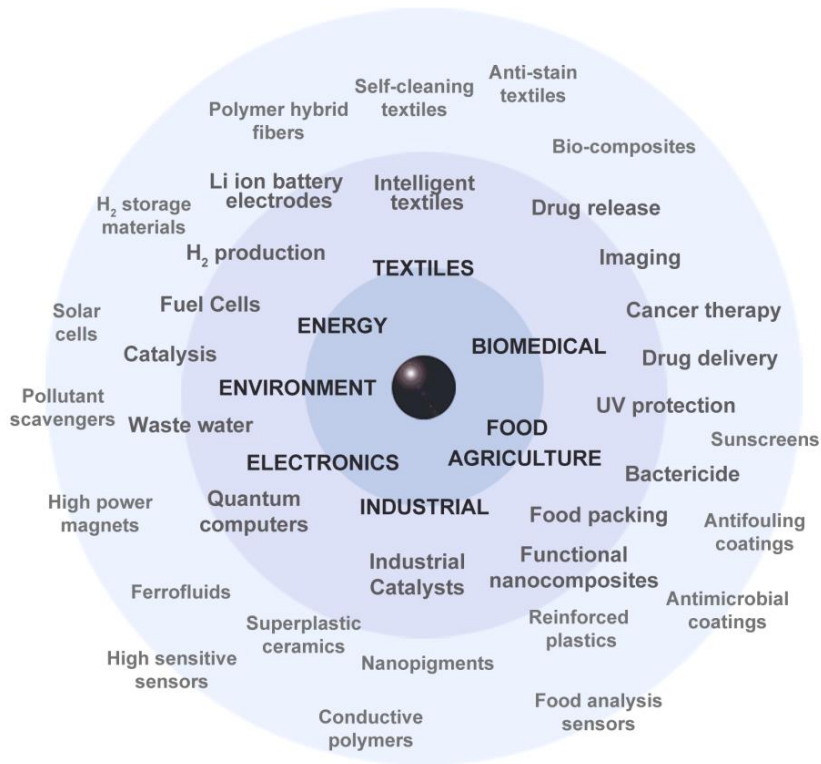
Tatiana E. ITINA¹ and Anton Rudenko²

1-Laboratoire Hubert Curien, UMR CNRS 5516, Saint-Etienne, France

2-College of Optical Sciences/University of Arizona, USA



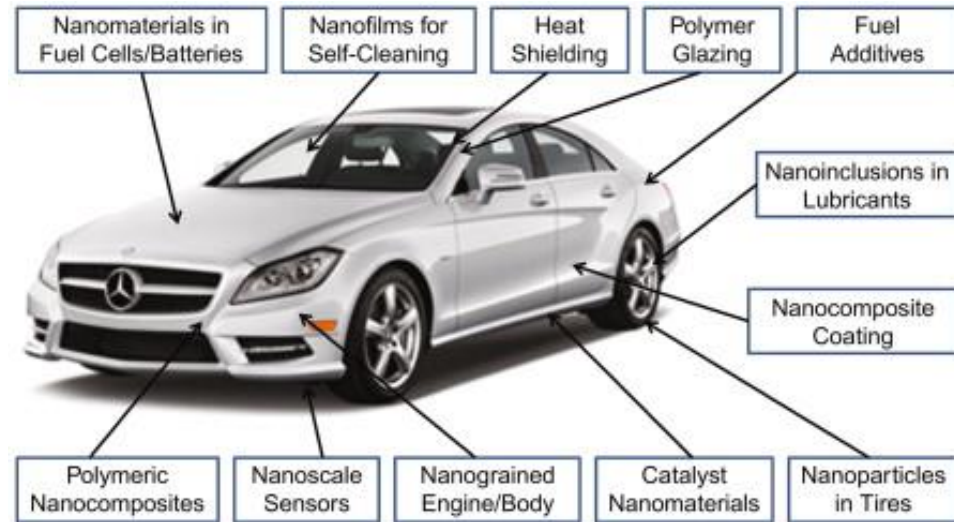
Nanoparticles and Nanocomposites



Aerospace and Defense



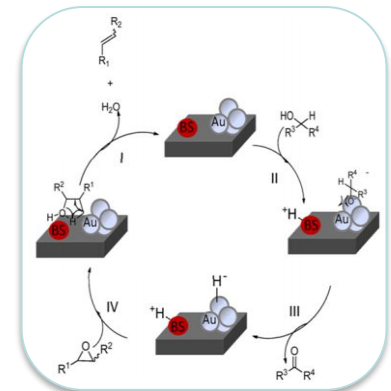
Car industry



Optics and security



Sensors and Catalysis



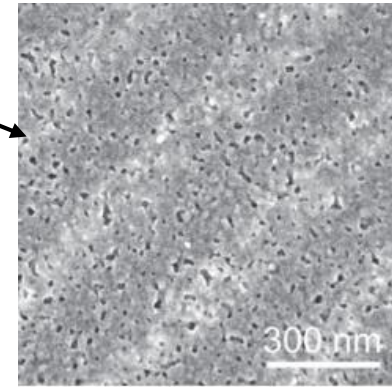
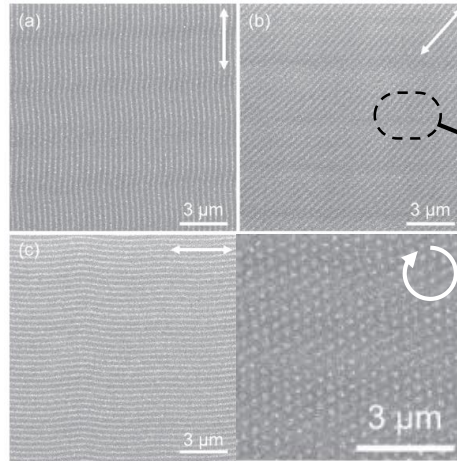
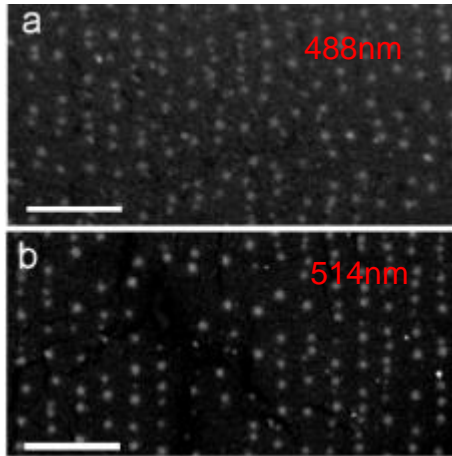
Images and multiplexing (collab. with N. Destouches et. al.)

fs, ns or CW laser
scanning

wavelength

polarizations

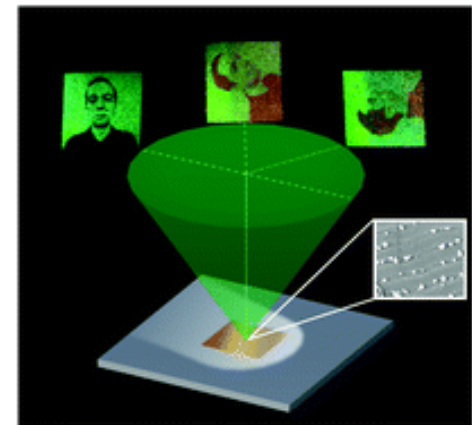
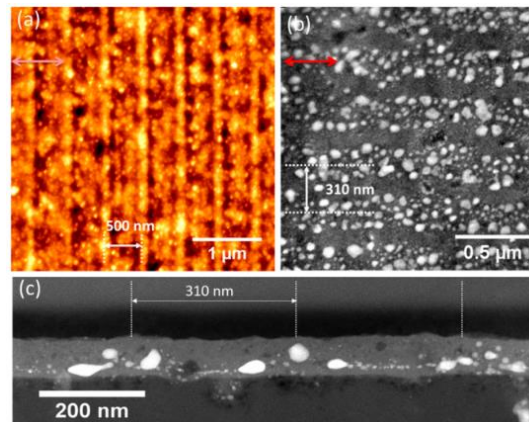
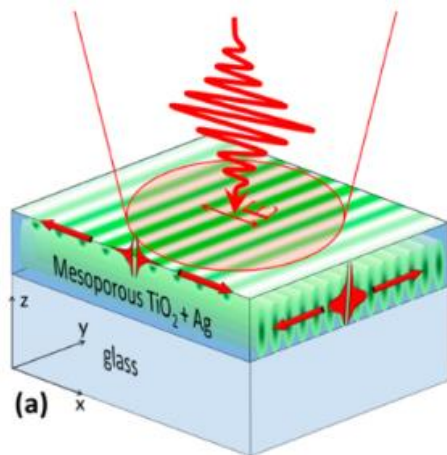
Ag-TiO₂



J. Mater. Chem. C 2.31 (2014);

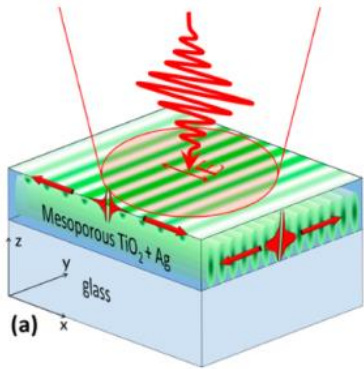
Nanotechnology 28.3 (2016): 035302.

multiplexing

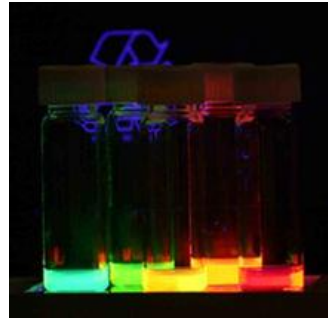


Z. Liu et al., ACS nano 11.5 (2017): 5031-5040.
N. Sharma et al., Materials Horizons 6.5 (2019): 978-983.

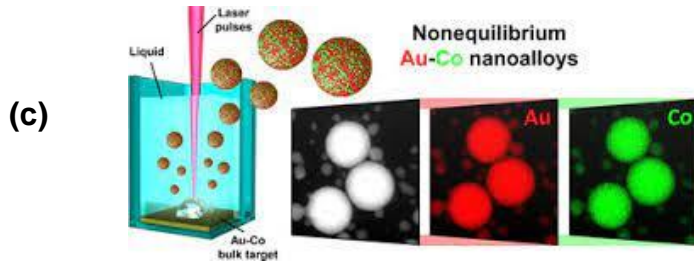
Laser-Assisted Nanotechnology



(b)



In gas or in vacuum with different geometry



In liquids or in the presence of a colloids



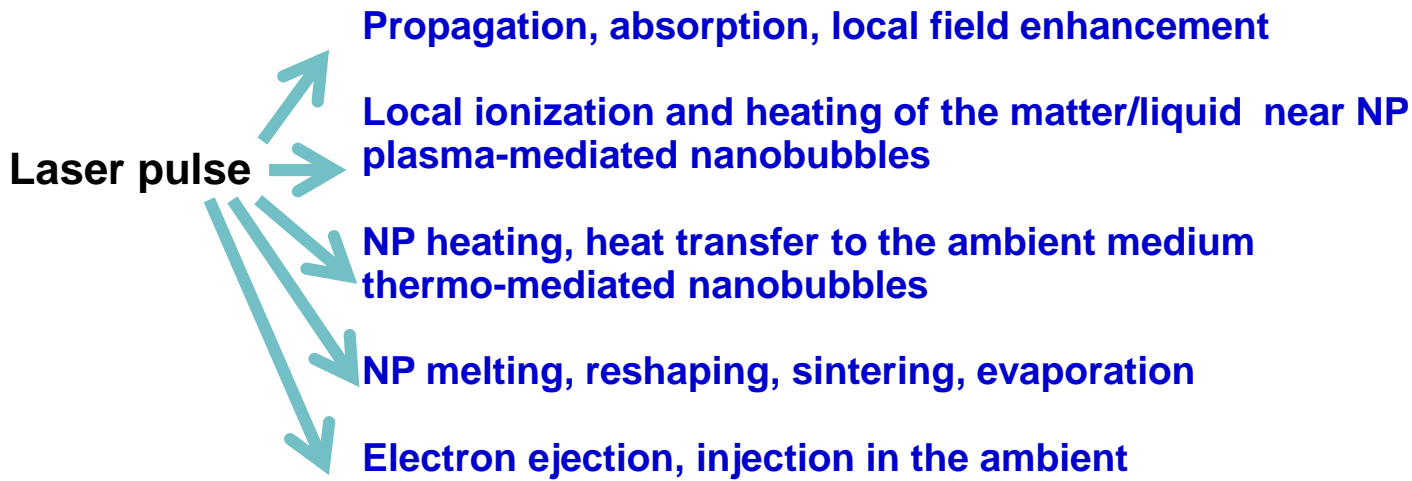
Among main advantages

- **Green synthesis**
- **Non-toxic, bio-compatible**
- **Environment friendly**

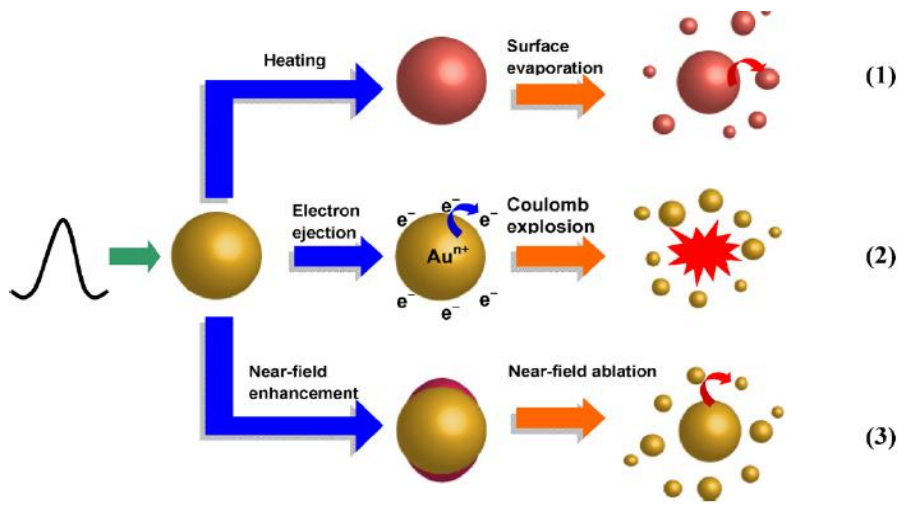
Laser allow

- Control over NP properties
- Scaling-up possibilities
- Possibility to create stable ultra-structures, nanoalloys, hybrids, etc.
- Additional laser-particle and laser-nanocomposite interactions to produce new properties (sizes, colors, opto-magnetic properties, etc.).

Ultra-short Laser Interactions with NPs

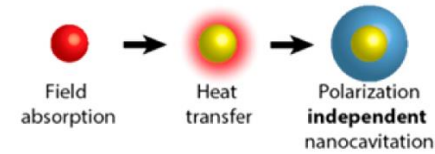


NP fragmentation

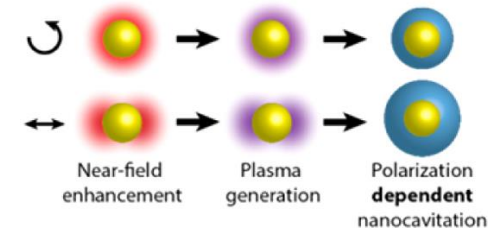


Hashimoto et al. *J. PhotChem&PhotBiology* (2012)

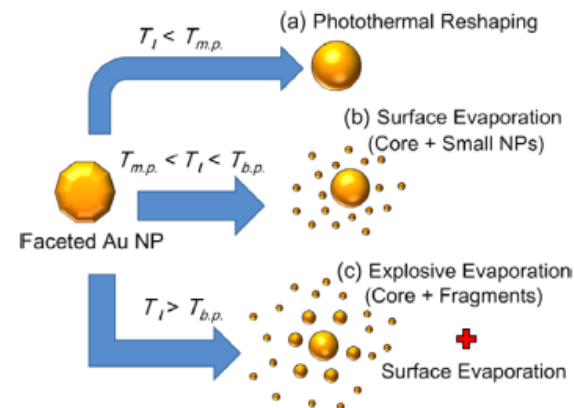
Thermo-mediated nanobubbles



Plasma-mediated nanobubbles



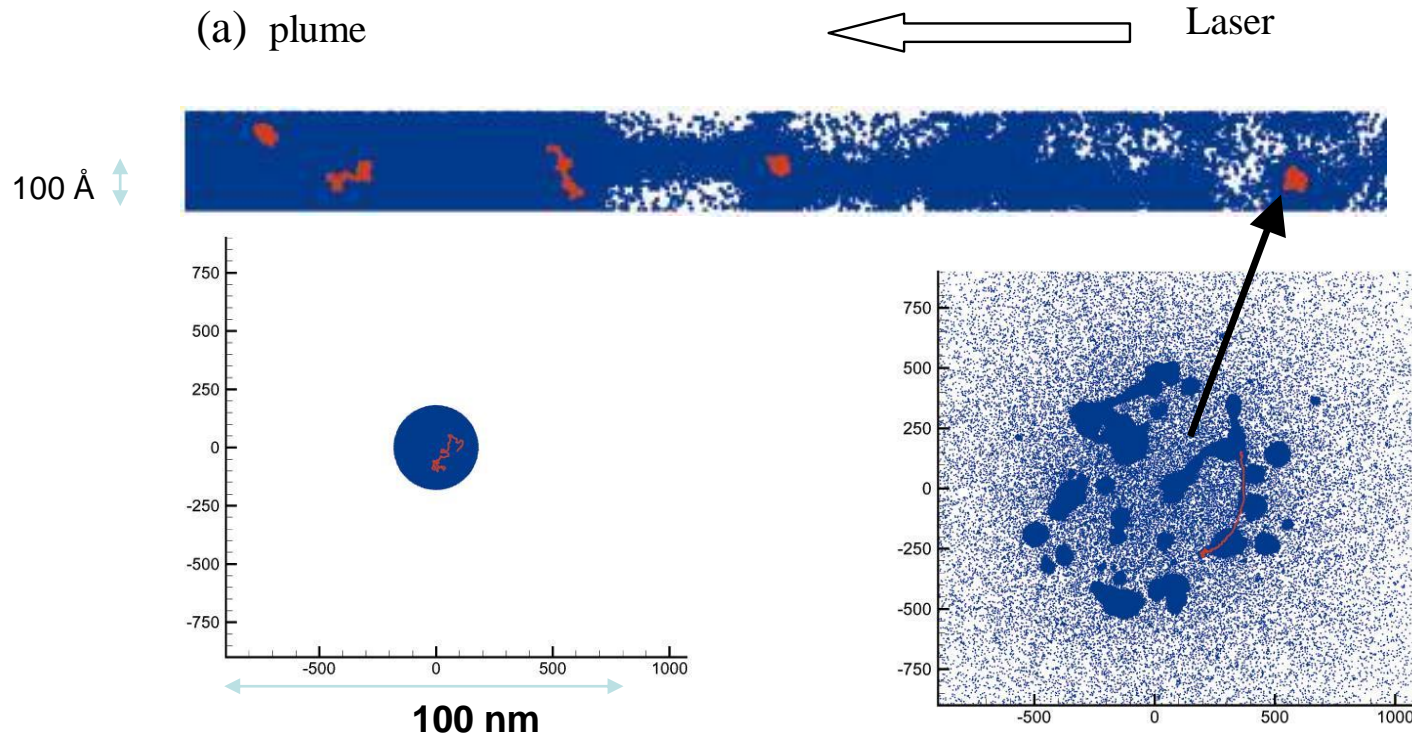
Lachaine et al. *Photonics* (2013)



Strasser et al., *J. Phys.Chem. C* 118, 25748 (2014)

Early MD Simulations (collab. with L. Zhigilei)

Decomposition of the ablated material after pulsed laser irradiation and additional NP's fragmentation



TE Itina, LV Zhigilei, BJ Garrison
The Journal of Physical Chemistry B, 106(2), 303, 2002

T.E. Itina, L. V. Zhigilei, B.J. Garrison,
Nuclear Instruments and Methods in Physics Research Section
B, 180(1-4), 238-244, 2001

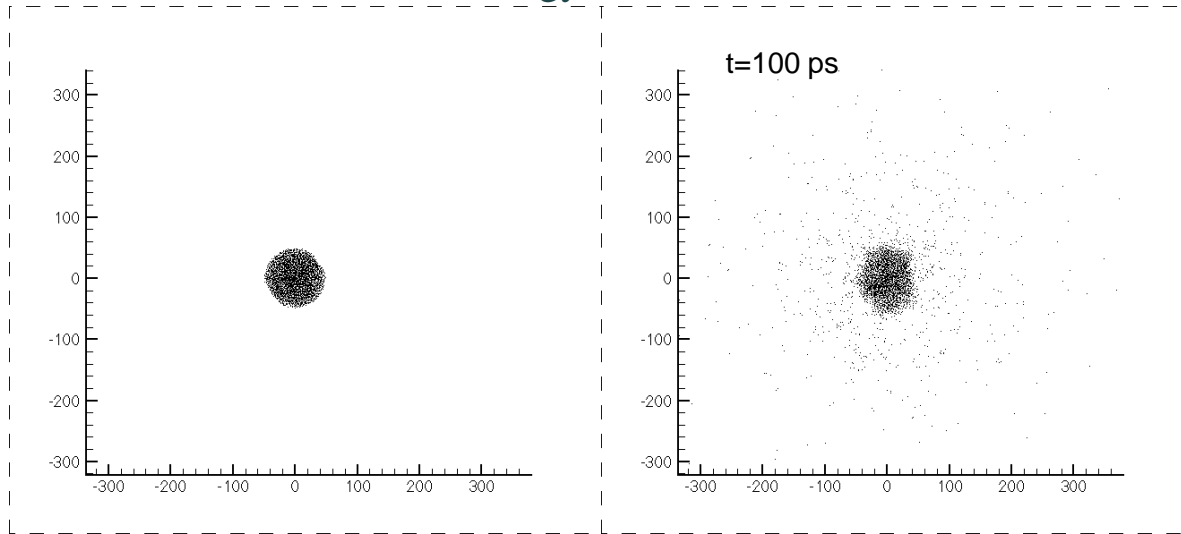
$t = 300 \text{ ps}$

$\tau = 15 \text{ ps}$

$e = 0.6 \text{ eV per molecule}$

MD simulations: Role of NP size

R=50 , absorbed energy $e=0.6$ eV/mol

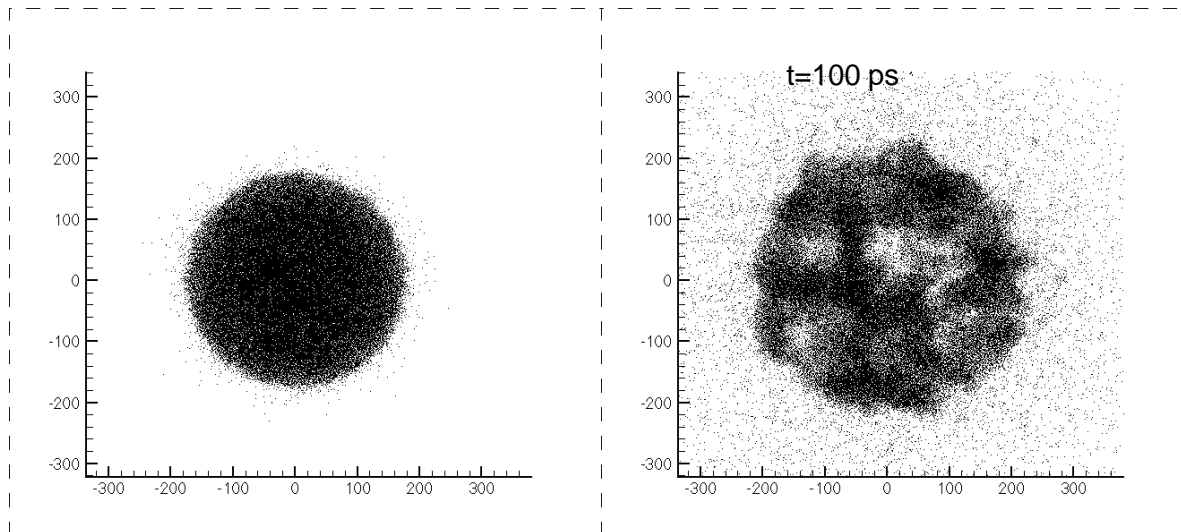


Smaller NPs

Evaporation

but can be also due to
Coulomb Explosion for
small clusters and fs
laser, etc..

R=150 , absorbed energy $e=0.6$ eV/mol.



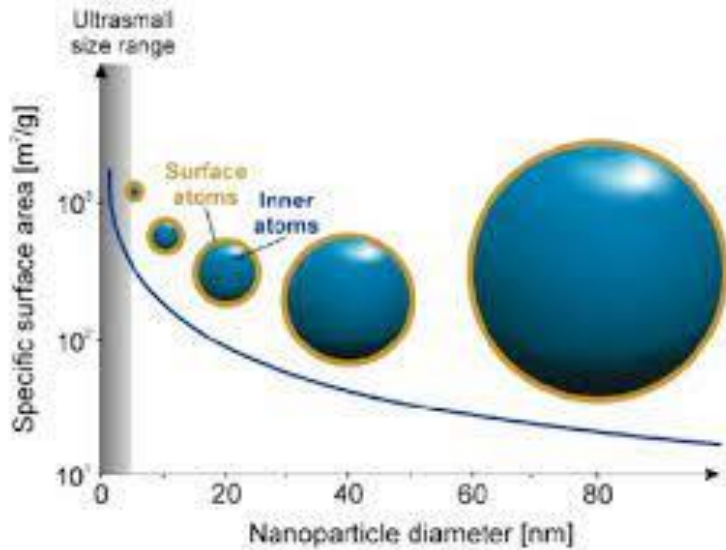
Larger NPs

**Fragmentation due to
thermo-mechanical
effects**

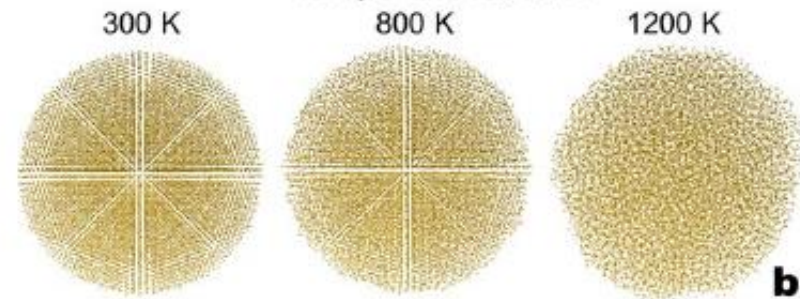
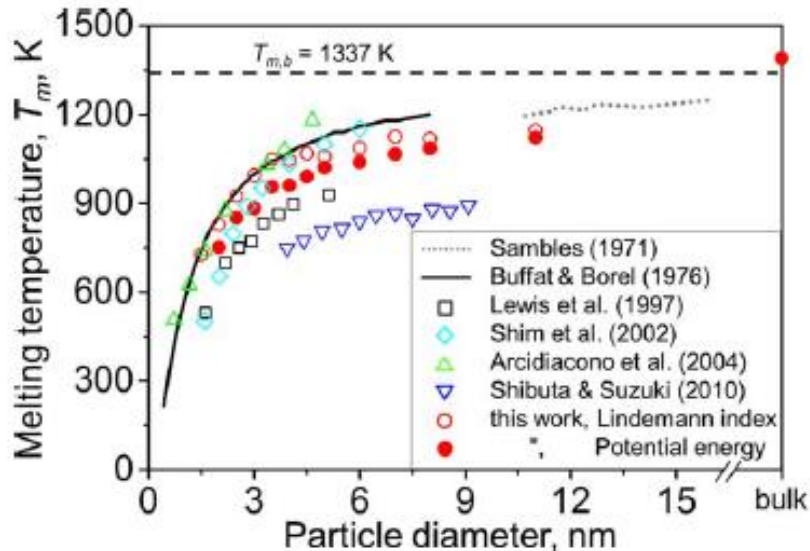
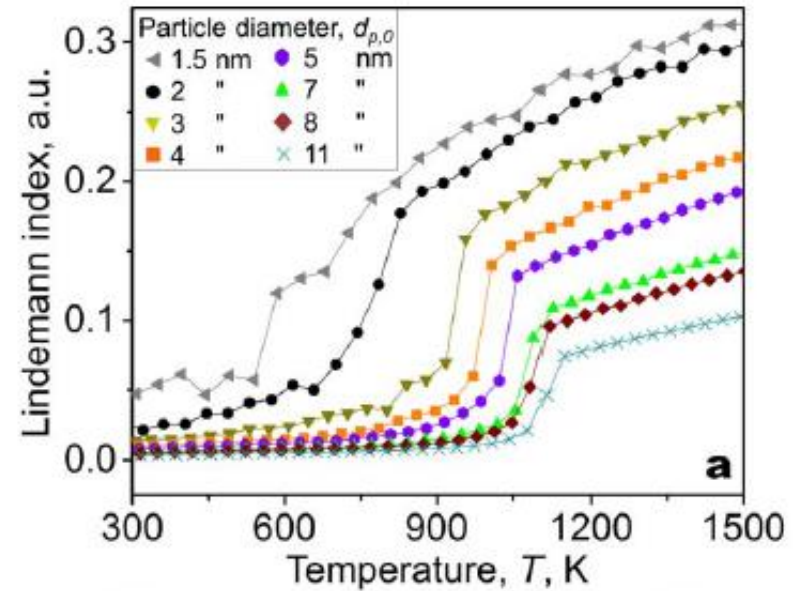
and/or instabilities

NP's Heating and Melting : Size Effects

Melting and structural transformations: role of NP's sizes



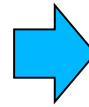
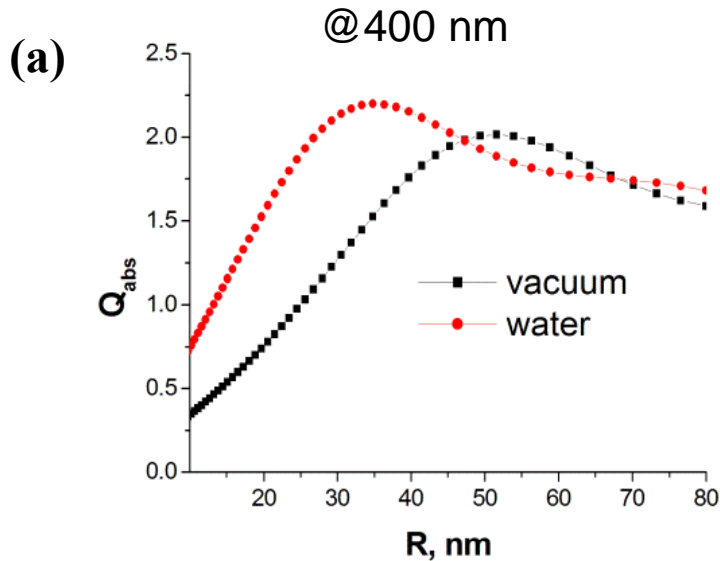
K. Zarschler et al. *Nanomed-Nanotechnol* 12, 1663-1701 (2016).



E. Goudeli et al., *AIChE* 2015

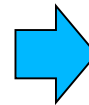
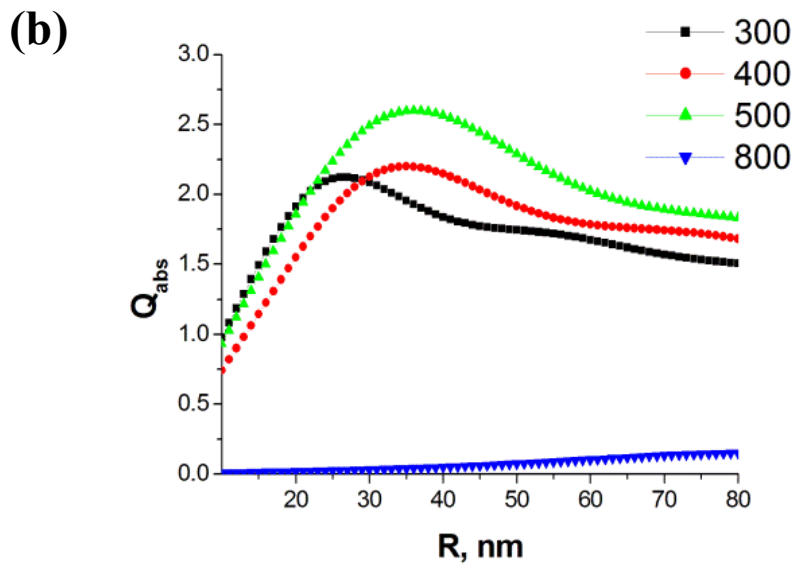
Laser Energy Absorption vs NP's size

Absorption coefficient / efficiency



Generalized Mie theory=>
Red – Gold NPs in for water
Black – Gold NPs in vacuum

peak in absorption at
 $R=R^* \sim 30$ nm for Au NP in
water



Gold NPs in water for **different**
wavelength @300-800nm

peak position is shifted to
larger $R=R^*$ if wavelength rises

Laser Interaction with NP in Water (collab. with A. Rudenko)

Au NP in water

Classical 3T models

Maxwell equations

$$\frac{\partial \vec{E}}{\partial t} = \frac{\nabla \times \vec{H} - \vec{j}}{\epsilon_0}$$

$$\frac{\partial \vec{H}}{\partial t} = -\frac{\nabla \times \vec{E}}{\mu_0}$$

Polarization current

$$\frac{\partial \vec{j}}{\partial t} = -\vec{j}\gamma + \frac{ne^2}{m}\vec{E}$$

Charge conservation, incompressible Fermi flow

$$\frac{\partial n}{\partial t} = -\frac{1}{e}\nabla[\vec{j} + \vec{j}_{em}] + w_{PI}(I) + w_{AI}(I)$$

Photo-ionization Avalanche

Heat energy transfer

Electrons $C_e \frac{\partial T_e}{\partial t} = \nabla \cdot (k_e \nabla T_e) - \gamma_{ei}(T_e - T_i) + \vec{j} \cdot \vec{E}$

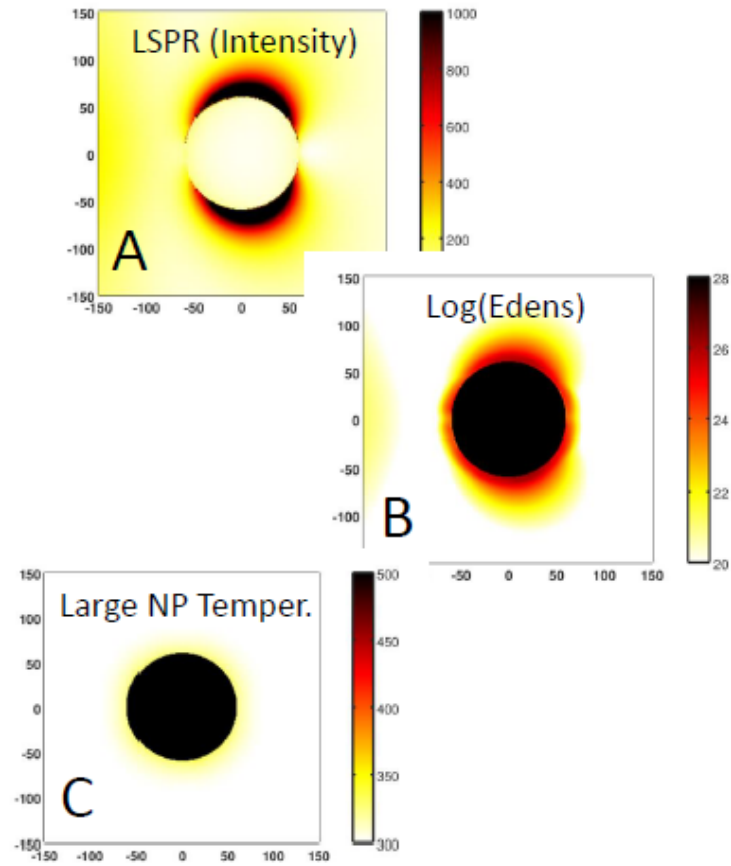
Nanoparticle

$$\rho_{NP} C_{NP} \frac{\partial T_{NP}}{\partial t} = \nabla \cdot (k_{NP} \nabla T_{NP}) + \gamma_{ei}(T_e - T_{NP}) + \frac{3h(T_m - T_{NP})}{R_{NP}}$$

Medium

$$\rho_m C_m \frac{\partial T_m}{\partial t} = \nabla \cdot (k_m \nabla T_m) + \gamma_{ei}(T_e - T_m) + 3h(T_{NP} - T_m)/R_{NP}$$

C_e, C_{NP}, C_m - heat capacities; k_e, k_{NP}, k_m - thermal conductivities;
 T_e, T_{NP}, T_m - temperatures; $\vec{j} \cdot \vec{E}$ - Joule heating source (absorption);
 γ_{ei}, h - energy transfer rates; ρ_{NP}, ρ_m - ion densities.



Advantages: rather easy equations, estimations of temperatures
Limitations: hard to correctly account for electron excitation, ejection/injection

Ultra-Short Laser Interaction with Metallic NPs

Non-Equilibrium Electron Sub-system

Conduction band (free) electrons in metals

Boltzmann equation

$$\frac{\partial f(E)}{\partial t} = \left(\frac{\partial f(E)}{\partial t}\right)_{e-e} + \left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} + \left(\frac{\partial f(E)}{\partial t}\right)_{intra/inter}^{abs} \quad E_{max} = E_F + \varphi$$

Terms for e-e, e-ph scattering & absorption

$$\left(\frac{\partial f(E)}{\partial t}\right)_{e-e} \cong \frac{f(0)C_{ee}}{\sqrt{E}} \frac{\partial}{\partial E} [f(E)(1-f(E)) + k_B T_e \frac{\partial f}{\partial E}]$$

$$\left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} \cong \frac{C_{ep}}{\sqrt{E}} \frac{\partial}{\partial E} [f(E)(1-f(E)) + k_B T_l \frac{\partial f}{\partial E}]$$

$$\left(\frac{\partial f(E)}{\partial t}\right)_{intra/inter}^{abs} \cong \frac{P_{abs(t)}}{K} [f(E-\hbar\omega) - 2f(E) + f(E+\hbar\omega)]$$

Definitions of electron & lattice temperatures

$$k_B T_e = \frac{1}{f(0)} \int_0^{E_{max}} f(E)(1-f(E)) dE$$

$$\rho_{NP} C_{NP} \frac{\partial T_{NP}}{\partial t} = -A \int_0^{E_{max}} \left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} E^{3/2} dE$$

Here, we can transit back to spatial TTM model to add spatial thermal diffusion etc.

Ultra-Short Laser Interaction with Metallic NPs

Can we account for electron emission/injection into ambient medium ?

At metal-water interface

Nonequilibrium approach

Thermionic photo-emission

(electrons with energies exceeding E_{max} leave metal)

$$\left(\frac{\partial N_e}{\partial t}\right)_e = AC_{ee}k_B T_e \left(\frac{\partial f(E)}{\partial E}\right)_{E=E_{max}}$$

$$\left(\frac{\partial N_e}{\partial t}\right)_p = AC_{ep}k_B T_i \left(\frac{\partial f(E)}{\partial E}\right)_{E=E_{max}}$$

Charge transfer

$$\frac{\partial N_e}{\partial t} = -\frac{1}{e} \nabla \vec{J}$$

Photoelectric effect/Photo-emission

$$\left(\frac{\partial N_e}{\partial t}\right)_{ph} = A \int_{E_{max}-h\nu}^{E_{max}} \left(\frac{\partial f(E)}{\partial t}\right)_{intra} \sqrt{E} dE$$

Fowler formulas for current density

Generalized Fowler-DuBridge theory of photoemission

$$J_n(T_e) = a_n \left(\frac{e}{h\nu}\right)^n I^n T_e^2 F\left(\frac{nh\nu - \phi}{k_B T_e}\right)$$

Thermionic emission (Richardson law)

$$J(T_e) = A_0 T_e^2 \exp\left(-\frac{\phi}{k_B T_e}\right)$$

Fowler-Nordheim theory for field emission

(threshold occurs to be above the optical breakdown in water for ultrashort pulse)

$$J(E) = \frac{a}{\phi} E^2 \exp\left(-\frac{v(E)b\phi^{3/2}}{E}\right)$$

Au NPs in Water (collab. with A. Rudenko)

fs laser
 $\lambda = 515 \text{ nm}$

What changes when nanoparticle size increases ?

R = 10 nm

Comparable

to optical penetration depth

Weak field enhancement

Fast energy transfer to water

R = 30 nm

Intermediate

R = 50 nm

Nearly resonant excitation

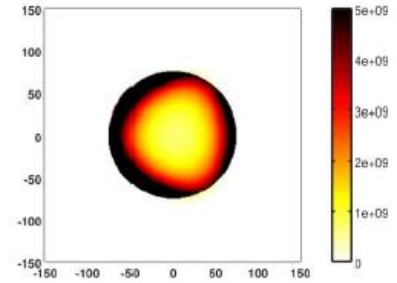
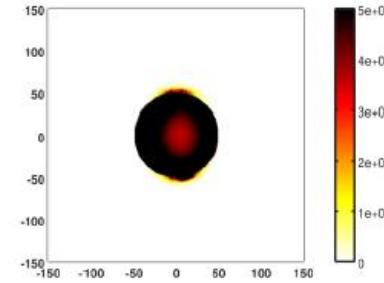
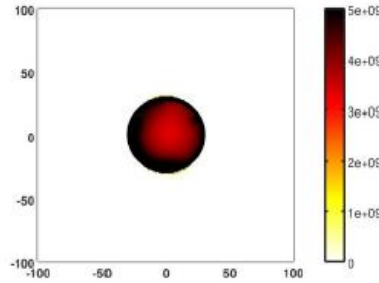
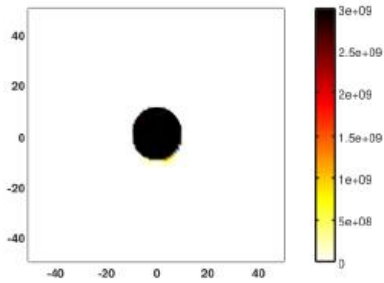
Strong field enhancement

R = 75 nm

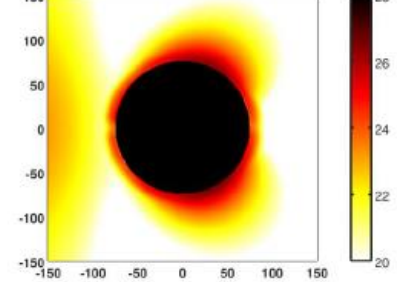
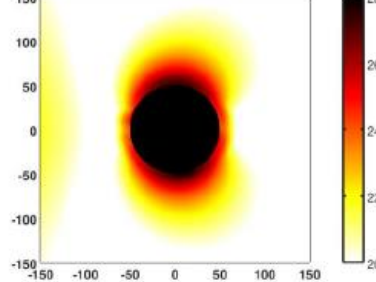
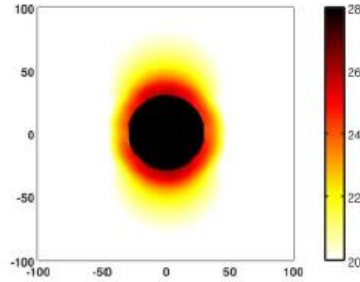
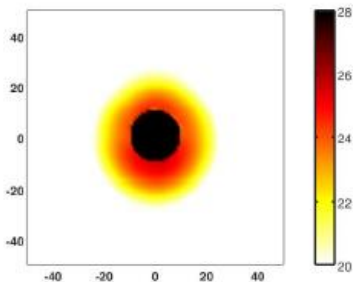
Particle \gg skin depth

Slow energy transfer to water

How the energy is absorbed ? (J/m^3)



How many free carriers are generated ? $\log(\text{m}^{-3})$

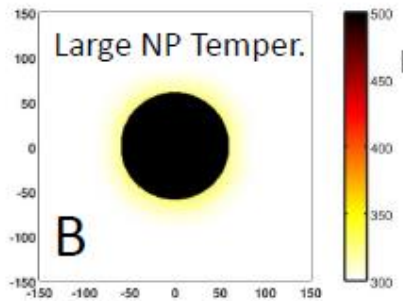
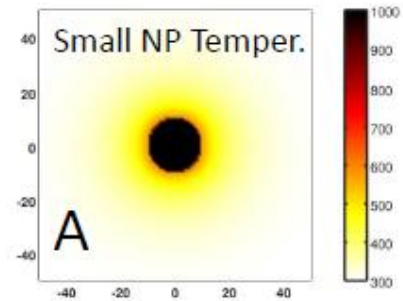


Several Interaction Regimes (collab. with A. Rudenko)

What changes when nanoparticle size increases ?

Regime I

Laser heats Au NP;
Au NP transfers heat to water

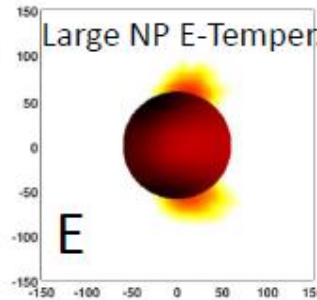
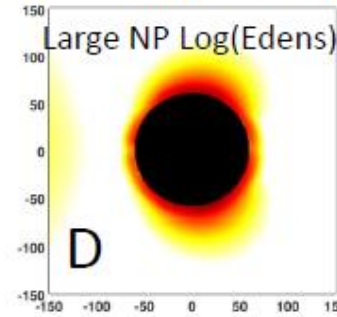
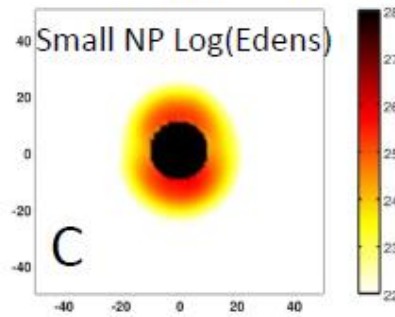


Due to inhomogeneous
distribution
of absorbed energy



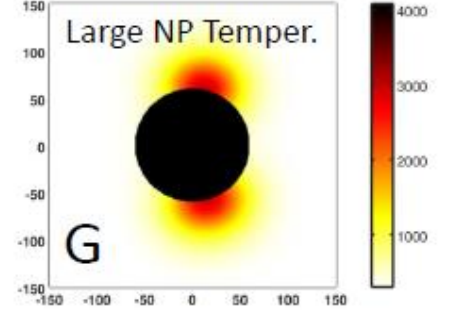
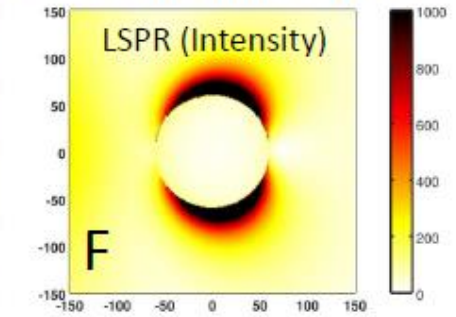
Regime II

E-ph emission from Au NP
to water interface;
Emitted Carriers heat water



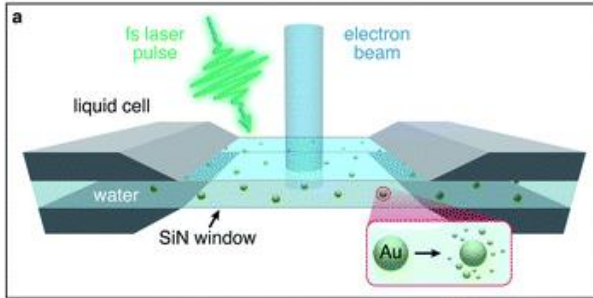
Regime III

LSPR triggers water
photo-ionization;
Induced Carriers heat water

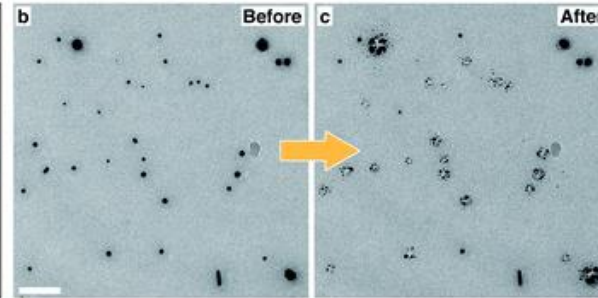


Fragmentation: MD simulations

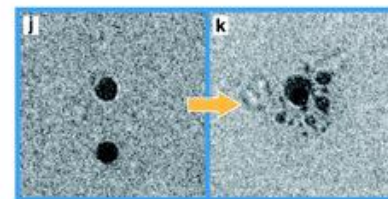
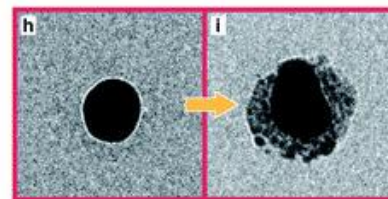
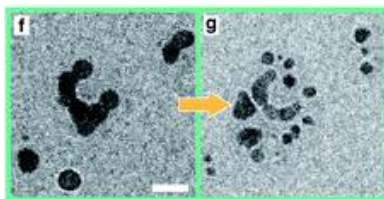
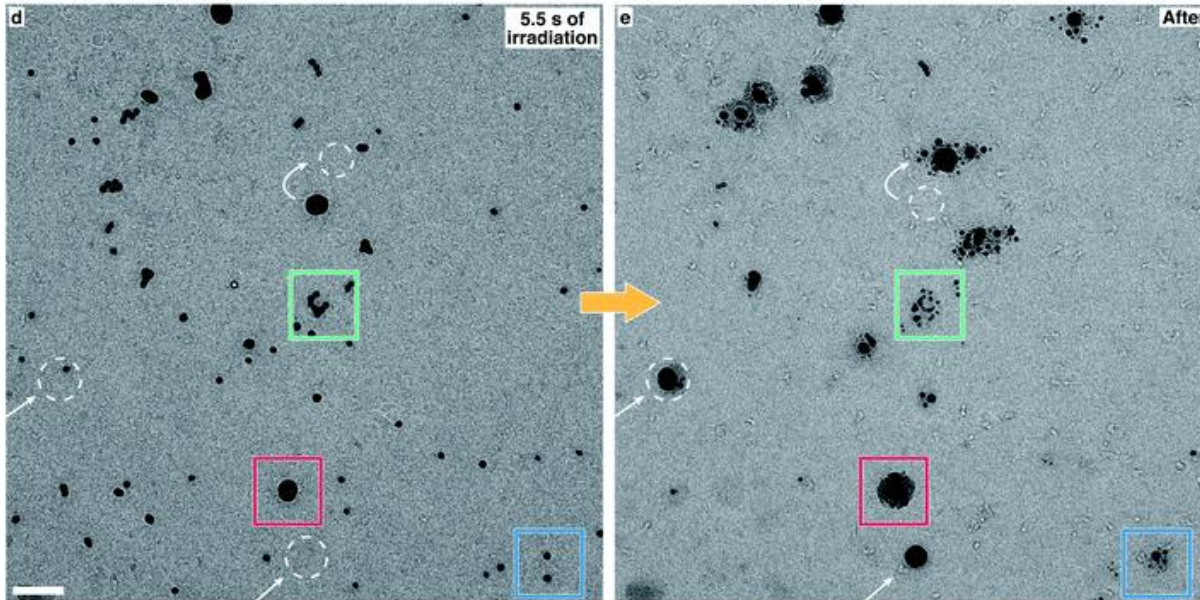
Experimental geometry



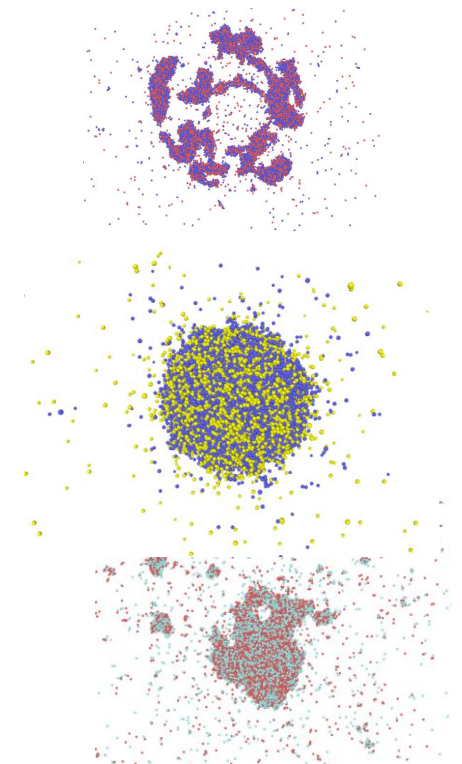
Femtosecond laser irradiation of gold nanoparticles



In situ observation of gold nanoparticle fragmentation under femtosecond laser irradiation



Our MD results for
NPs of
different materials,
absorbed energy,
and sizes

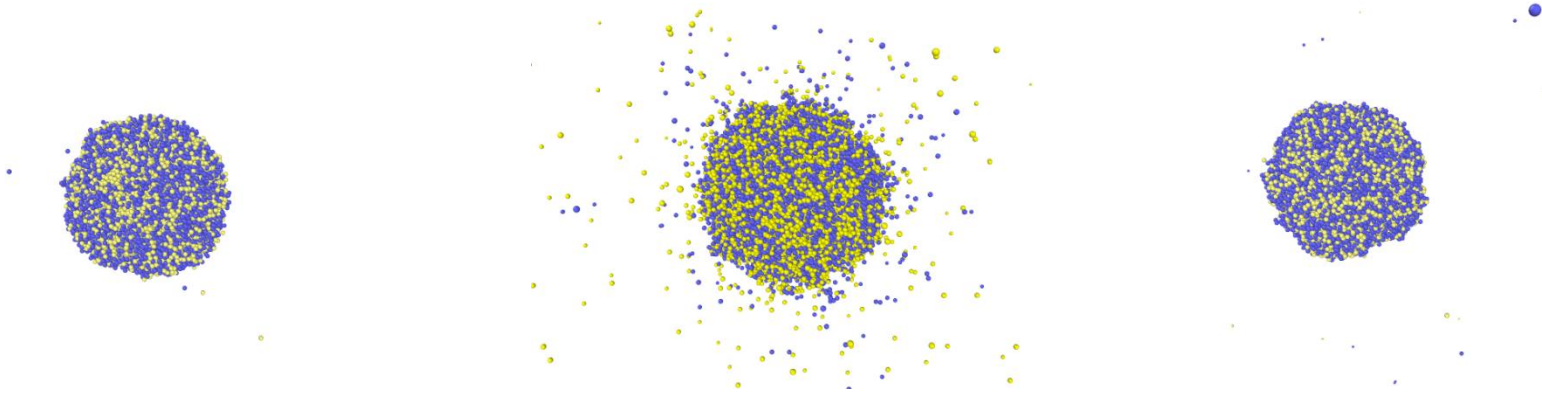


Gold nanoparticles in water

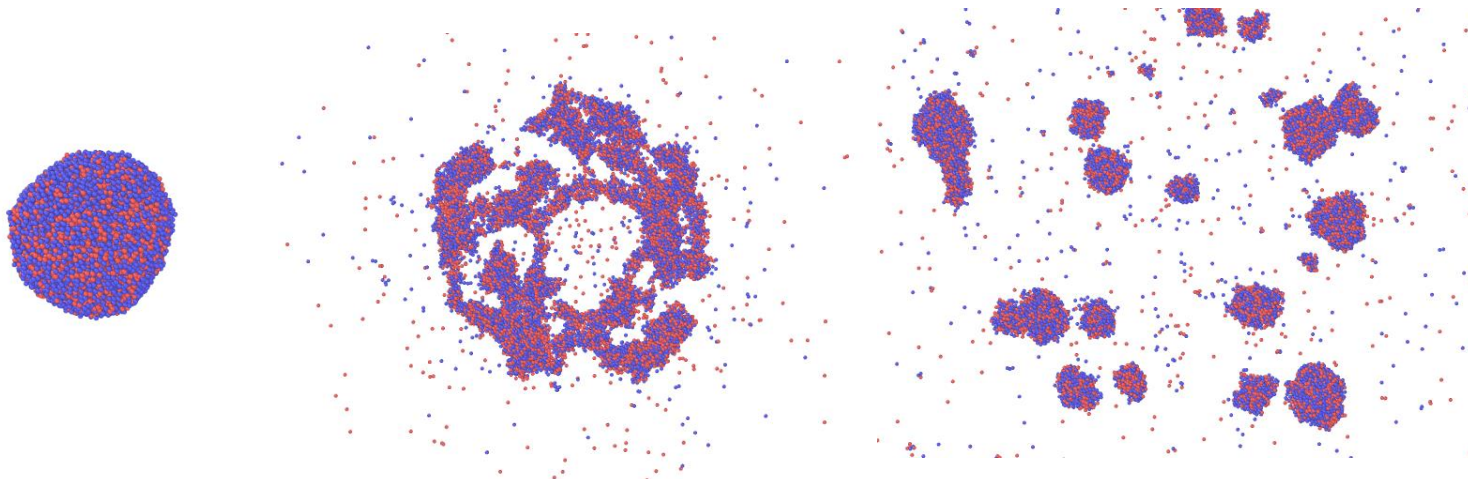
Experiments: *G. Bongiovanni et al.*
Nanoscale Adv., 2021, 3, 5277-5283

Metal alloy NPs: Role of the absorbed energy per atom

Au-Co NP , R= 40 u.cells (d~30 nm) 50%, t= 0, 150, 400 ps
absorbed energy below the threshold



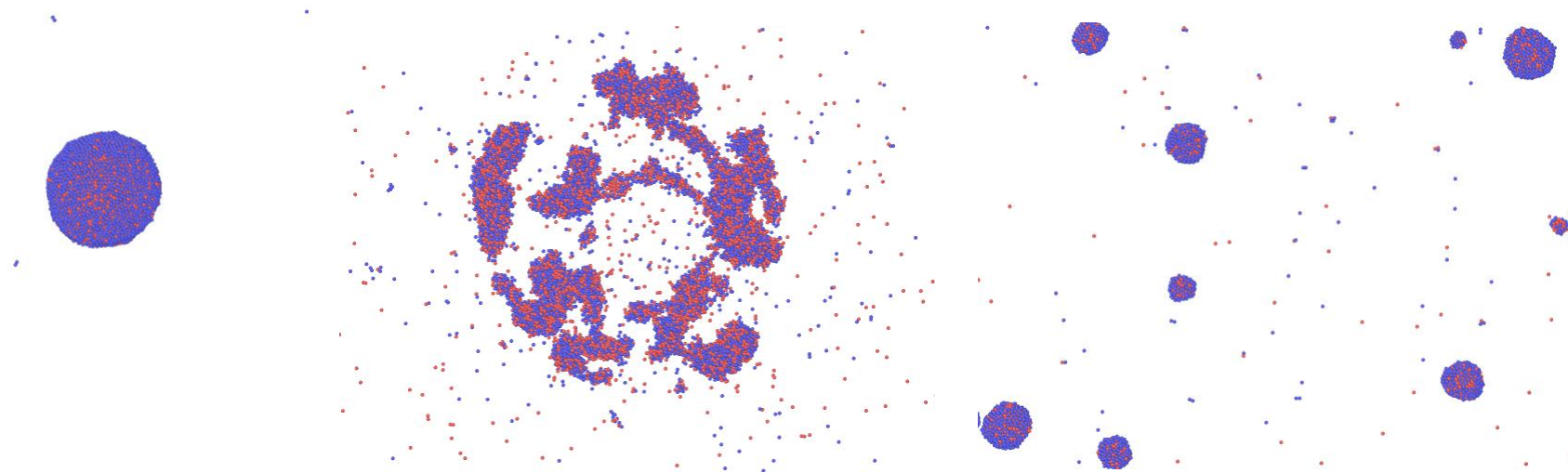
Au-Co NP, 50% R=40 uc t= 0, 150, 400 ps,
absorbed energy above the threshold



Metal Alloy NP : fragmentation, MD results

Au-Co NPs, 50% $R= 40$ u.c. $t= 0, 200, 1600$ ps

The absorbed energy/atom is right above NP fragmentation threshold



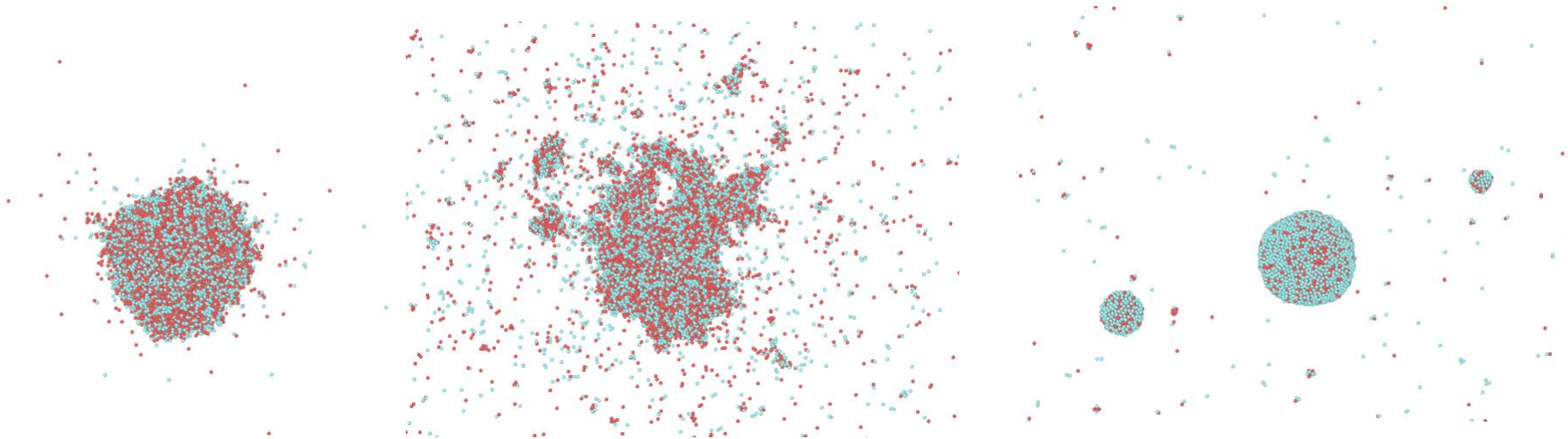
Rather homogenous decomposition and numerous small fragments are observed

Metal Alloy NP : fragmentation, MD results

Au-Ni NP, 50% R=40 t= 0, 200, 1600 ps,

The absorbed energy/atom is right above NP fragmentation threshold

Here, the absorbed energy/atom is 25% smaller for AuNi than for AuCo

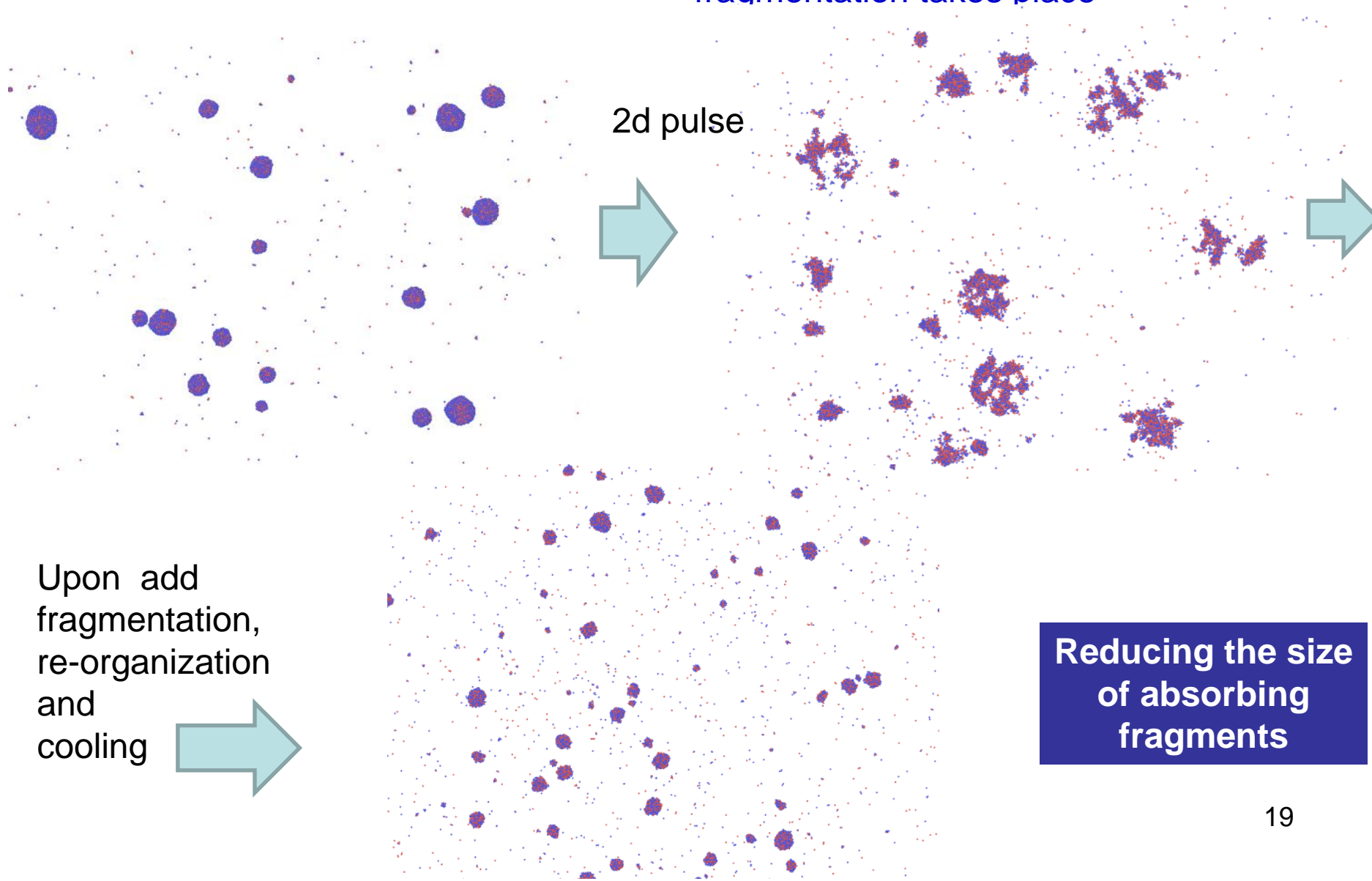


Decomposition to only several fragments

Many Laser Pulses: Additional Fragmentation

AuCo, NP R = 40 u.c.

Simulations starts from the fragmentation results, additional fragmentation takes place



Ion-impregnated Porous Thin Films Treated by Laser

- sol-gel mesoporous films are prepared and impregnated by salts
- these samples are then irradiated by a laser

Porous films:

SiO_2 , TiO_2

Sol-gel synthesized
Porosity ~ 10%
Porous size 5-7 nm

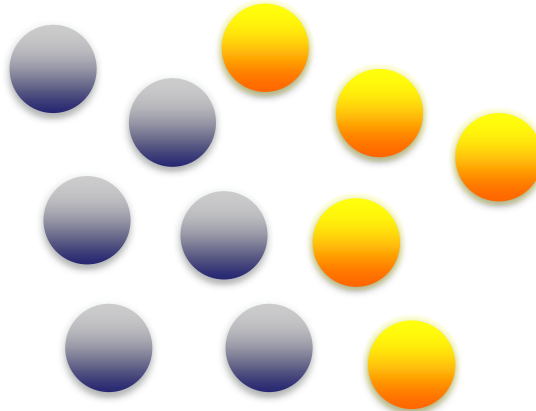


Metallic NPs:

Ag, Au

Produced by soaking in metallic
salts solutions with consequent
reduction

Initial size < 3-5 nm



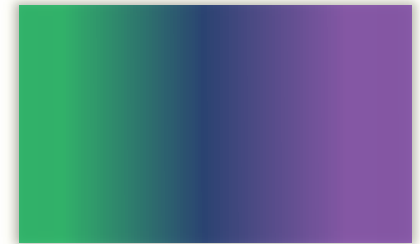
Laser irradiation:

CW

Nanosecond

Picosecond

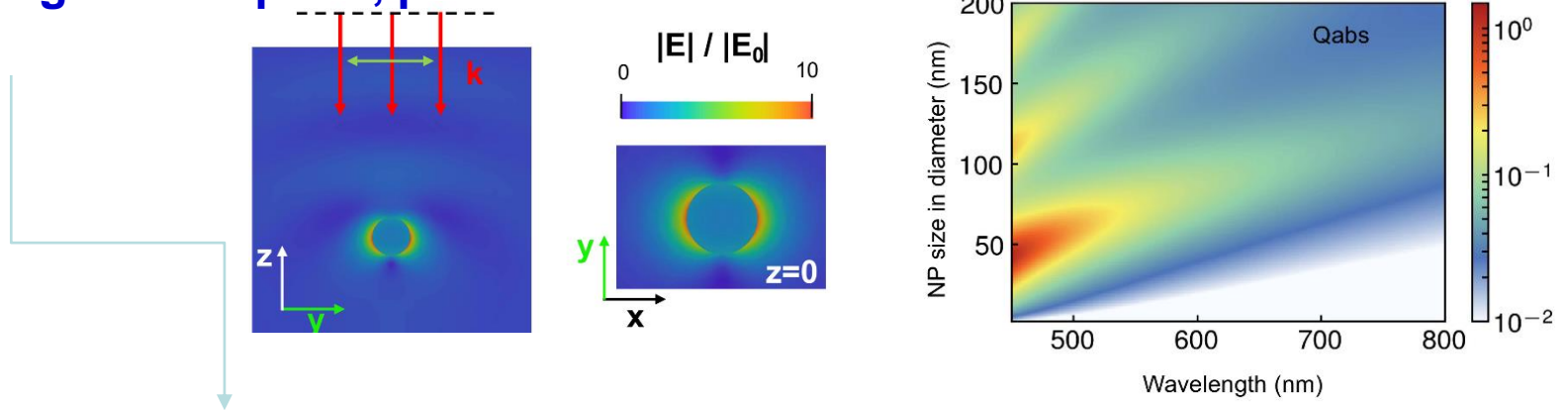
Femtosecond



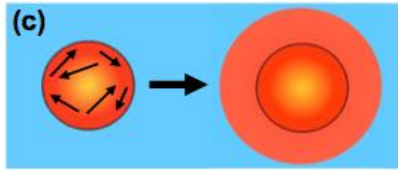
**Ion-impregnated porous glasses and semiconductors
can be used as samples for following laser-induced nano-structuring**

Nanoparticle formation and growth

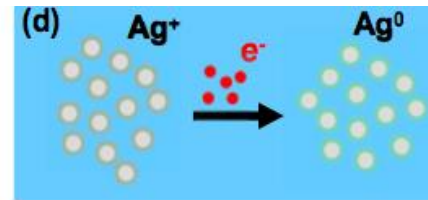
1. Laser light absorption, plasmon resonances



2. Heating and thermal diffusion

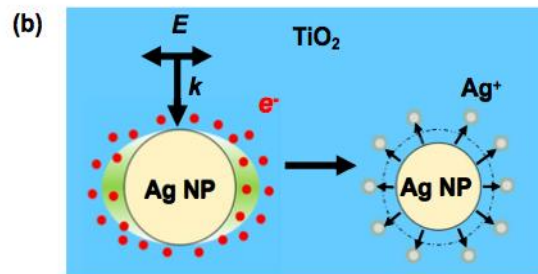
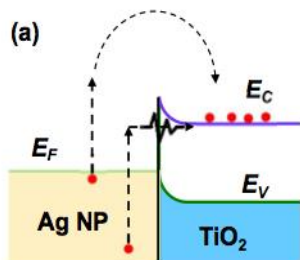


3. Photoemission and reduction

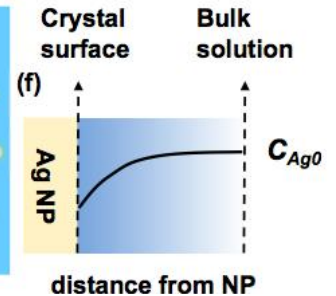
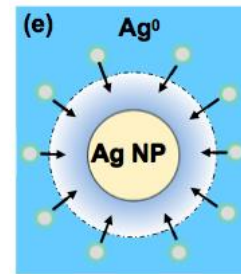


H. Ma et al. *J. Phys. Chem. C* 123.42 (2019): 25898-25907

5. Photo-oxidation

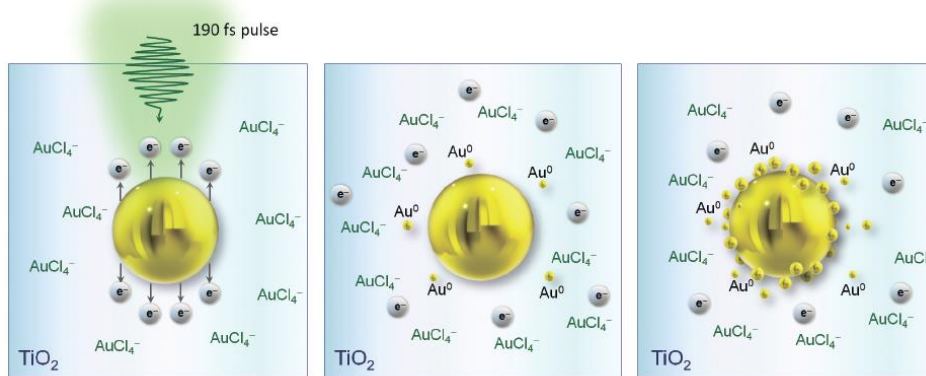


6. NPs growth



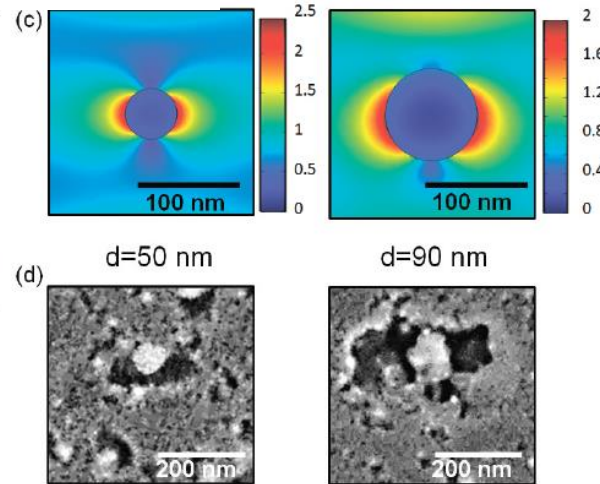
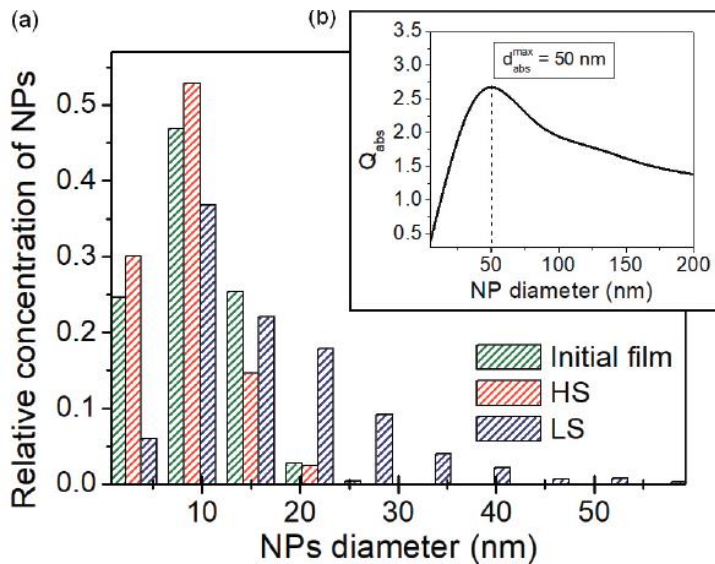
Multi-scale and multi-physical mechanisms are involved.

Au NPs in TiO₂ under Ultra-Short Laser Irradiation



At the beginning, the matrix is solid

The Journal of Physical Chemistry C
124 (18), 10209-10219, 2020



fs laser
 $\lambda = 515 \text{ nm}$

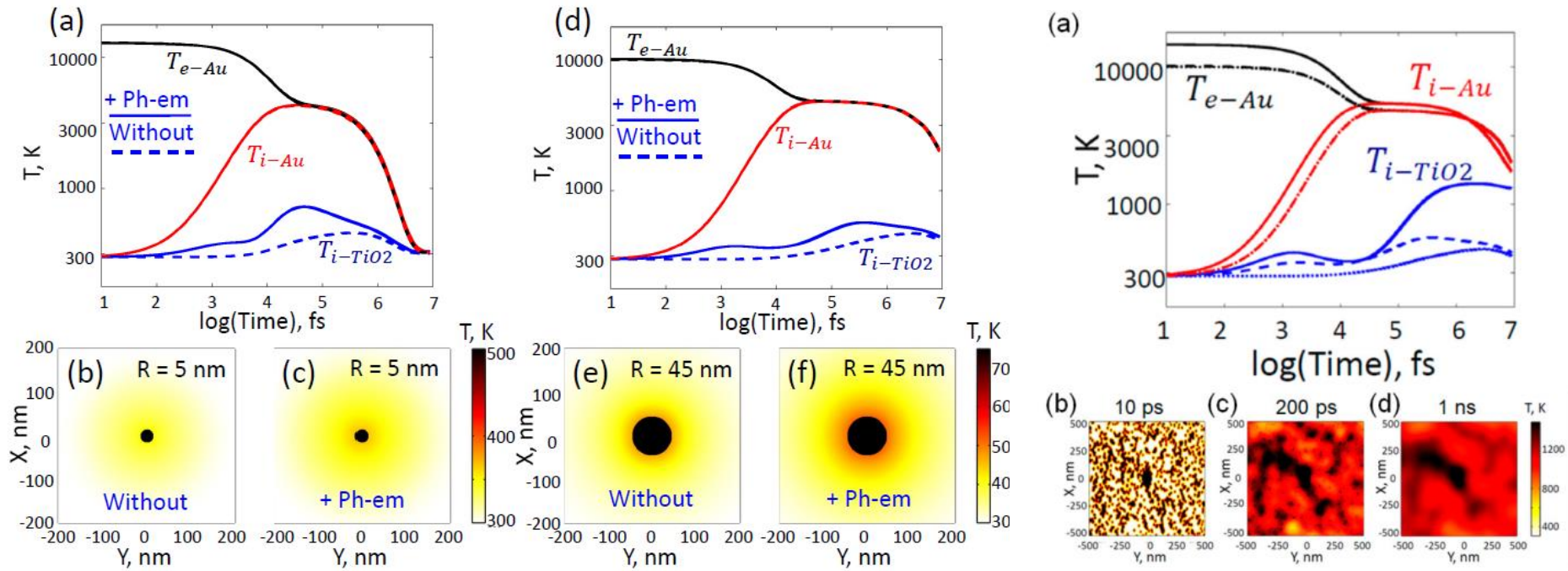
(a) Size distribution of gold NPs in before and after laser treatment.

(b) Calculated absorption efficiency of the nanocomposite based on TiO₂ as a function of the diameter of gold NPs

(c) Calculated field distribution of gold nanoparticles in TiO₂ (n=1.6) for spheres with the diameters of 50 and 90 nm.

(d) SEM images of the NPs produced in LS mode (F = 57 mJ/cm², Vsc = 0:16 mm/s).

Au NPs in TiO₂ under Ultra-Short Laser Irradiation



Electron (black solid) and ion temperature (red solid) of R=45 nm gold NP and titanium dioxide temperature (blue solid)

Here, additionally includes electron photo-emission.

It is important to account for collective heating of NP ensemble with bimodal size distribution, for electron photo-emission from nanoparticles and free carrier generation in titanium dioxide to reach the damage conditions

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$$\frac{P^2}{2\rho_m c_0^2} + \frac{\rho_m \epsilon^2 s^2}{120} \geq \frac{3K^2}{\rho_m c_0^2 s}$$

- **Laser is a very powerful and versatile tool, which is particularly suitable for many applications in the modern nanotechnology.**
- **Particle size, composition, geometry, environment, absorption and scattering, heating/cooling protocols strongly affect the results of laser interactions.**

-NPs of smaller sizes easily melt and evaporate, while larger NPs behave more like bulk material, so that thermo-mechanical fragmentation of over-heated material plays a role in their fragmentation. Phase diagrams of NPs smaller than ~30-100 nm should account for NP's size.

-Fragmentation threshold of alloy nanoparticle strongly depends on the material properties and composition.

- **Optical properties are strongly related to size and distribution of NPs after laser treatment, are controlled by laser processing parameters.**



Special thanks to: *LASERMODE former and actual group members, collaborators (PICS, PHC, ARQUS, ANR, EU, etc.), CNRS, UJM , The Univ. of Arizona*

Thank you very much!

Just published:

"Alternative local melting-solidification of suspended nanoparticles for heterostructure formation enabled by pulsed laser irradiation"
Advanced Functional Materials 2023.

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