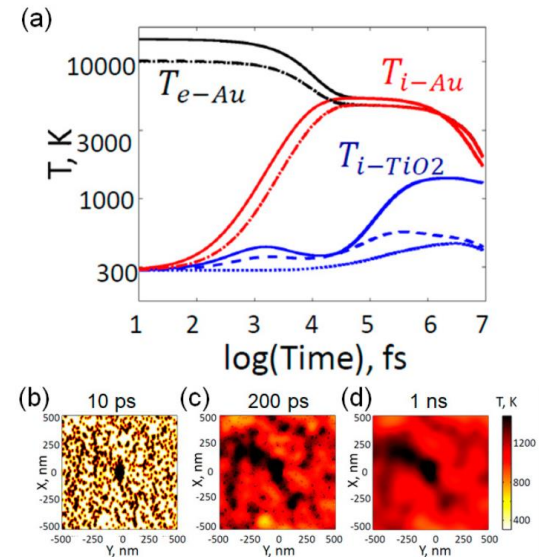
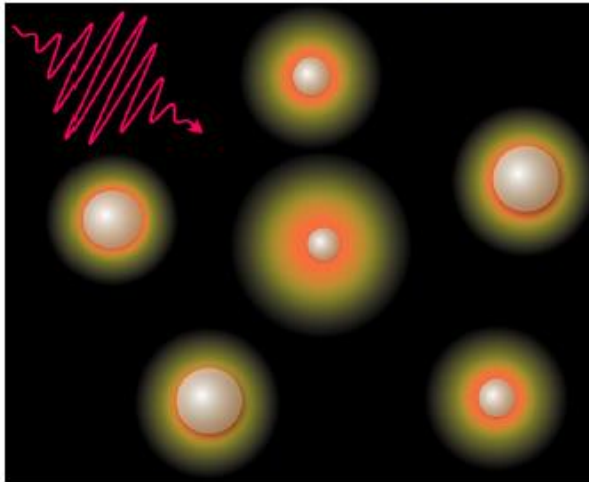


# Numerical studies of thermoplasmonic effects and nanoalloy formation in ultra-short laser interactions with nanoparticles

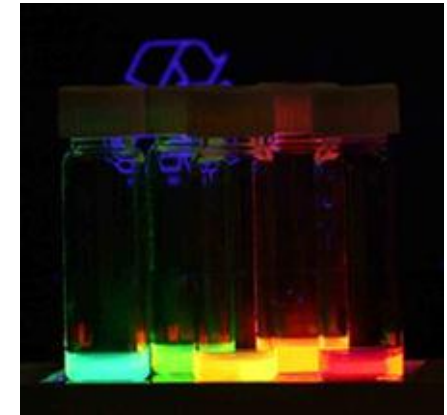
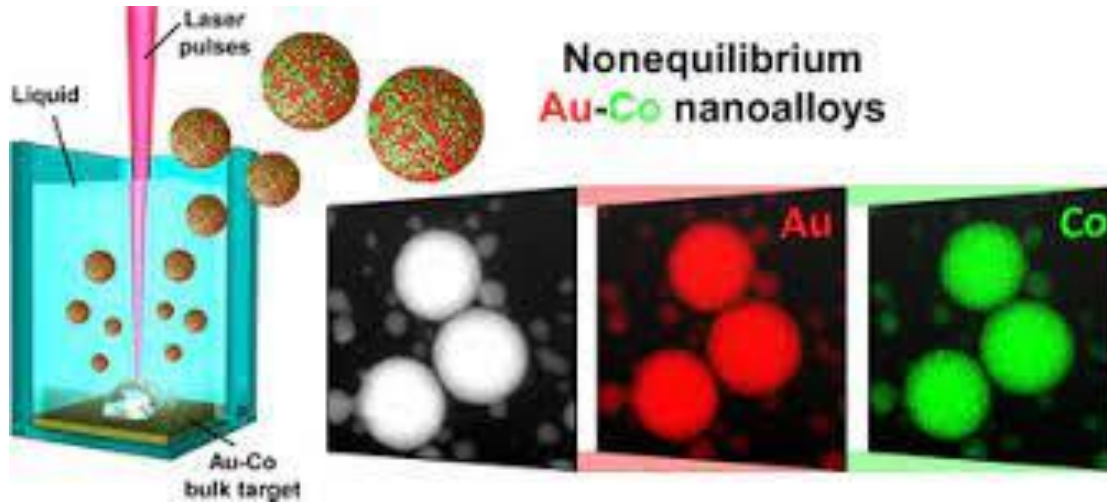
Tatiana E. Itina<sup>1</sup> and Anton Rudenko<sup>1,2</sup>

<sup>1</sup> Laboratoire Hubert Curien, UJM/Université de Lyon, 42000 Saint-Etienne, France  
 University of Arizona in Tucson, USA

\* [tatiana.itina@univ-st-etienne.fr](mailto:tatiana.itina@univ-st-etienne.fr)



# Typical experiments



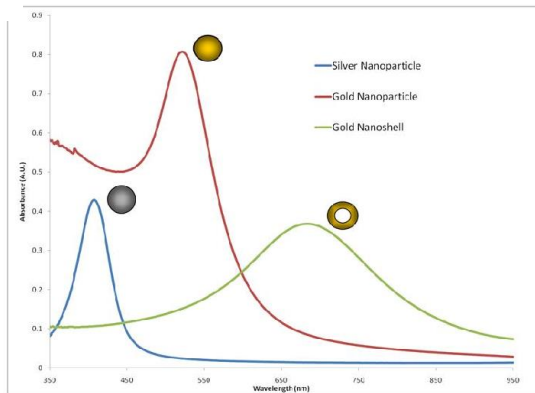
*Vincenzo Amendola et al.*  
*Kinetically Stable Nonequilibrium Gold-Cobalt Alloy*  
*Nanoparticles with Magnetic and Plasmonic*  
*Properties*

*Laser-induced*  
*ablation/fragmentation in liquids*

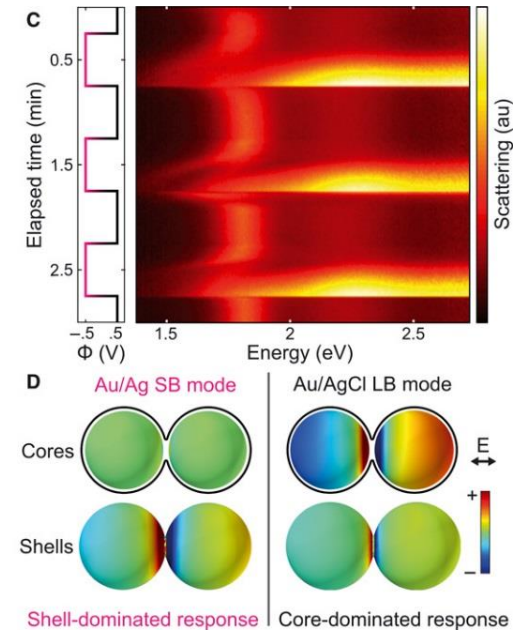
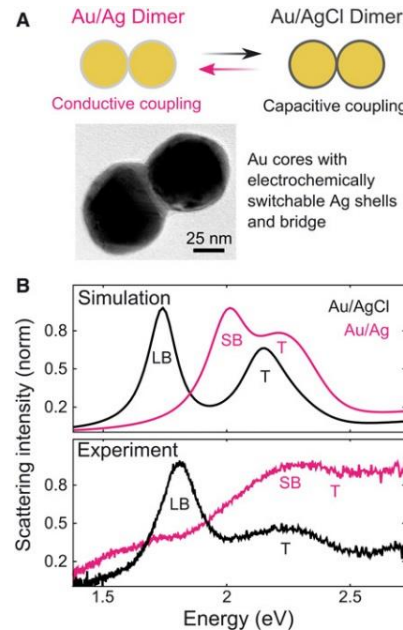
**The mechanisms involved are still not enough understood...  
How modeling can help?**

# Motivation

Tailoring optical and or magneto-optical properties: medical applications, imaging, photo-acoustics, photonics, etc.



Optical properties (solid nanoparticles and hollow nanoshells) R. W. Day, Materials Science (2009)



From tunable core-shell nanoparticles to plasmonic drawbridges C. P. Byers et al. Science Advances 04 Vol. 1, no. 1 (2015)

# Why Lasers ?



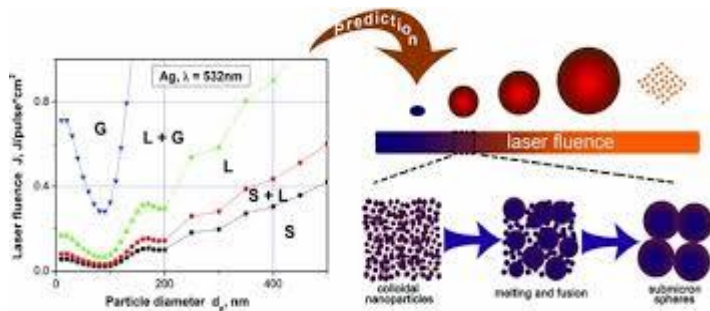
1. Green synthesis methods, bio-compatibility
2. Easy control over NP properties
3. Scaling-up possibilities
4. Possibility to create stable ultra-structures

Laser is a versatile tool that can be used for

- **formation of nanoparticles**
  - in vacuum
  - in gas
  - in liquid
  - in a solid
- **modification of nanoparticles**
  - fragmentation–tailoring of sizes
  - sintering – can create nanohybrides and nanocomposites, thus tailoring their **optical, magnetic, and acoustic properties**

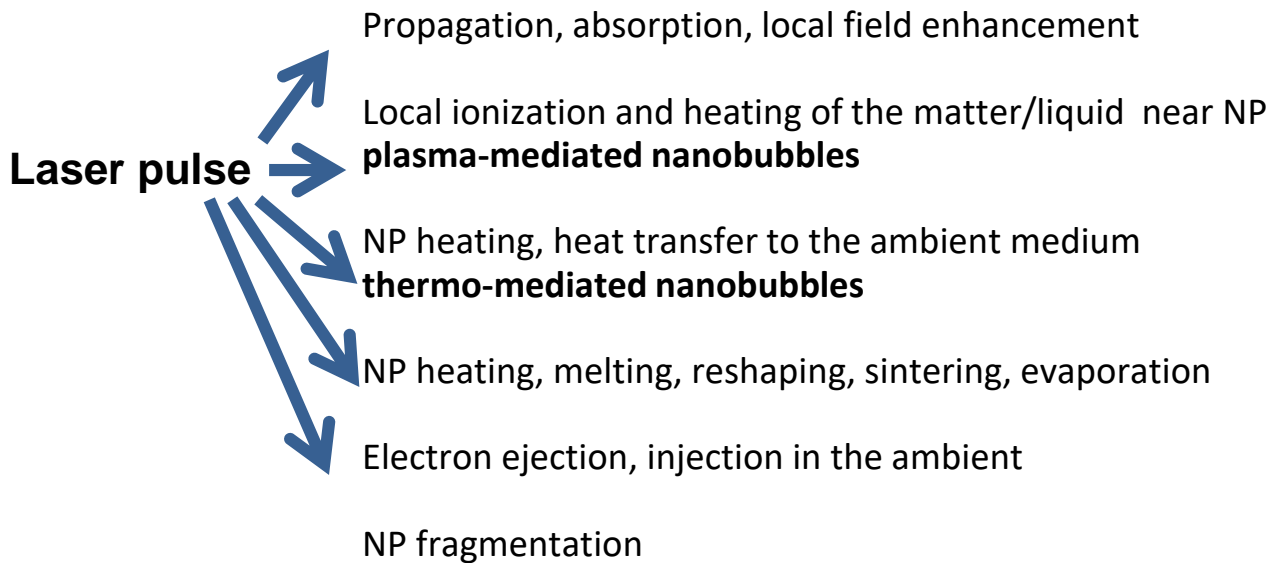
We can also form alloy NPs composed of normally immiscible species, high-entropy alloys

**Both laser-induced nanoparticle formation and laser-based modifications of nanoparticles involve many physical and chemical process.**

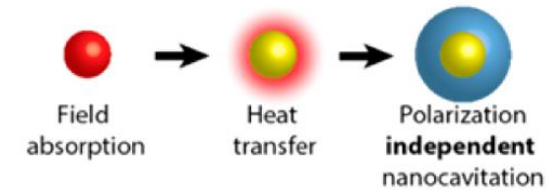


*Mechanism of pulse laser interaction with colloidal nanoparticles A. Pyatenko et al., Laser&Phot. Rev. 2013*

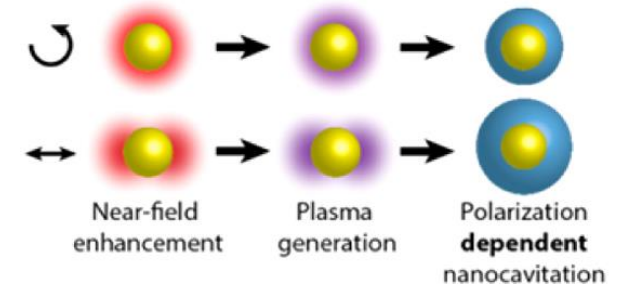
# Ultra-short Laser Interactions with NPs



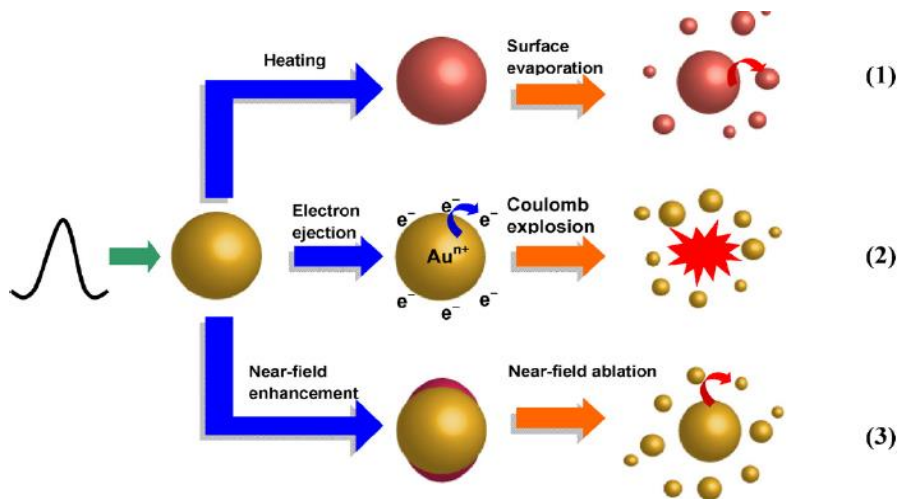
## Thermo-mediated nanobubbles



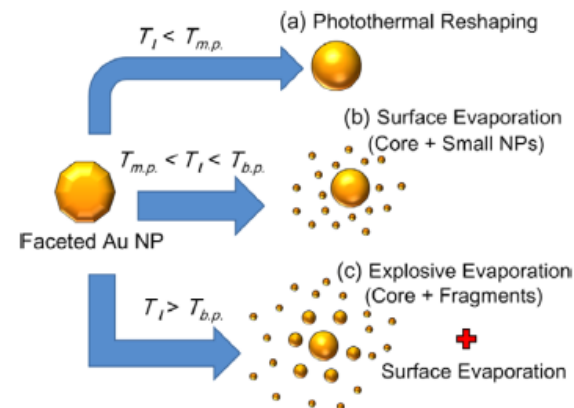
## Plasma-mediated nanobubbles



*Lachaine et al. Photonics (2013)*



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



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

# Laser Interaction with NPs in Ambient Medium

## « Classical » Multi-Physics

### 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

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

Photo-ionization      Avalanche

### Heat energy transfer

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

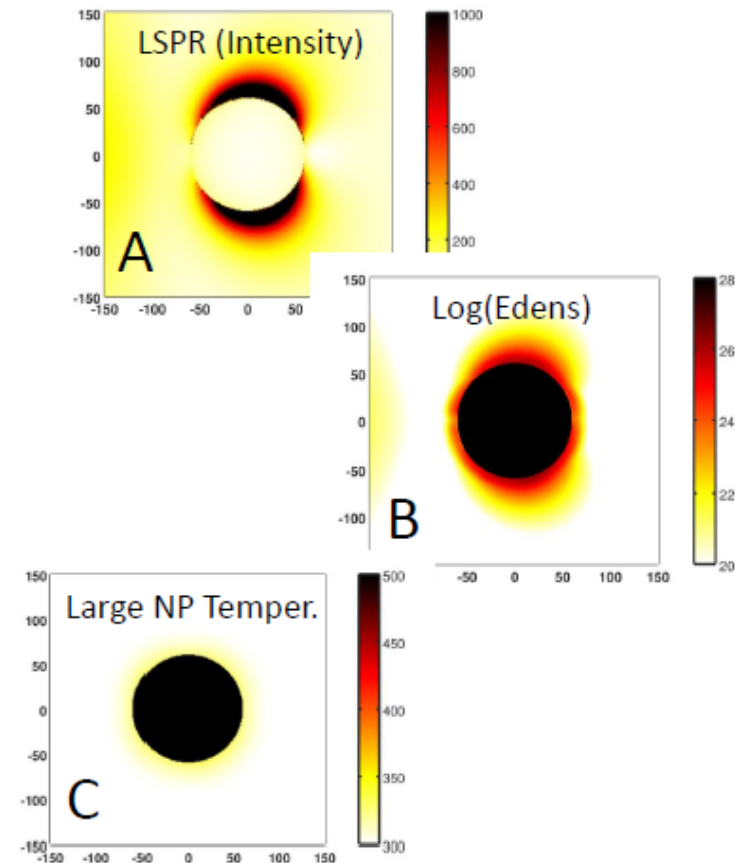
### Nanoparticle

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

### 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);  
 $\gamma_{ei}, h$  - energy transfer rates;  $\rho_{NP}, \rho_m$  - 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

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

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

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

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

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

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)

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



# Ultra-Short Laser Interaction with Au NPs in Water

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

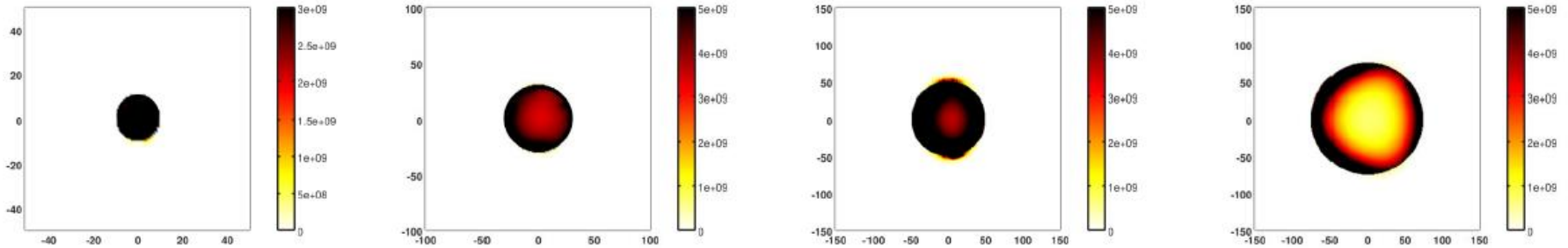
R = 50 nm

Nearly resonant excitation  
Strong field enhancement

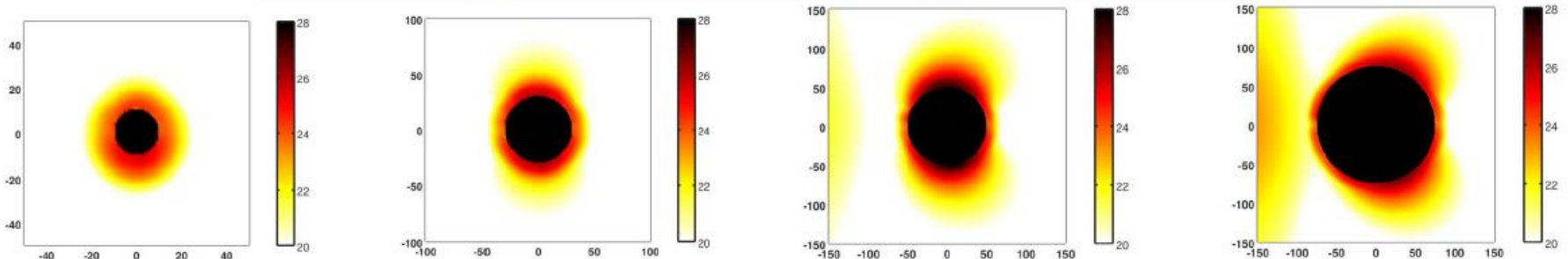
R = 75 nm

Particle  $\gg$  skin depth  
Slow energy transfer to water

*How the energy is absorbed ? ( $\text{J}/\text{m}^3$ )*



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



# Ultra-Short Laser Interaction with Au NPs in Water

These regimes are distinguished a function of nanoparticle sizes

## Regime I

Laser heats Au NP;  
Au NP transfers heat to water

## 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

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 with quantum corrections

$$\frac{\partial \vec{j}}{\partial t} = -\vec{j}\gamma + \frac{ne}{m} [e\vec{E} + \nabla \frac{\delta G}{\delta n}]$$

Quantum pressure

$$\frac{\delta G}{\delta n} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} + \dots$$

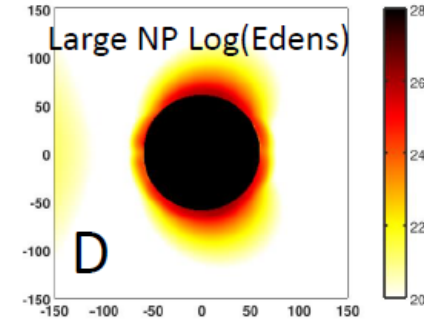
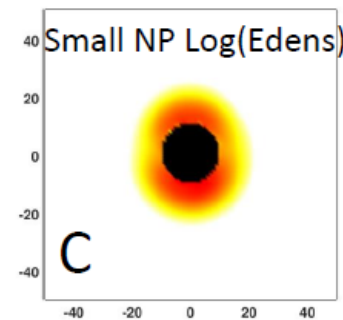
Thomas-Fermi

Quantum kinetic energy  
for uniform gas

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

Photo-ionization

Avalanche  
ionization

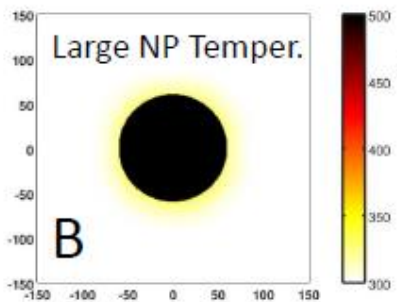
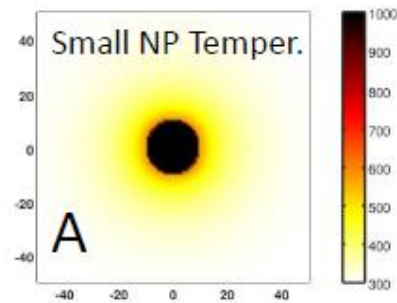


# Laser Interaction with Au NPs in Water

## Three interaction regimes and the mechanisms involved

### Regime I

Laser heats Au NP;  
Au NP transfers heat to water

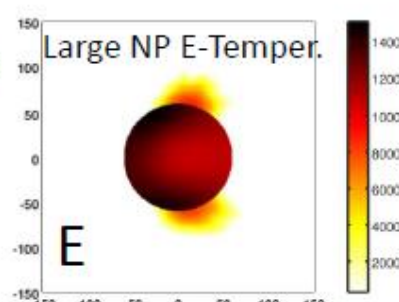
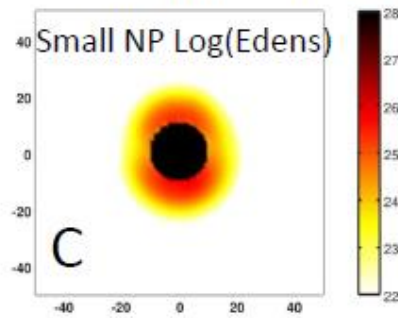


Due to inhomogeneous  
distribution  
of absorbed energy



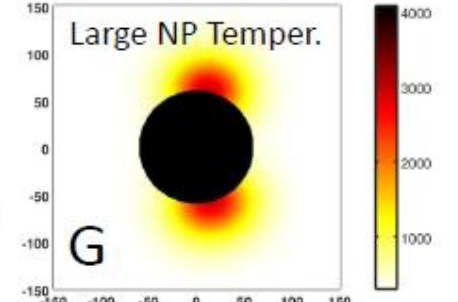
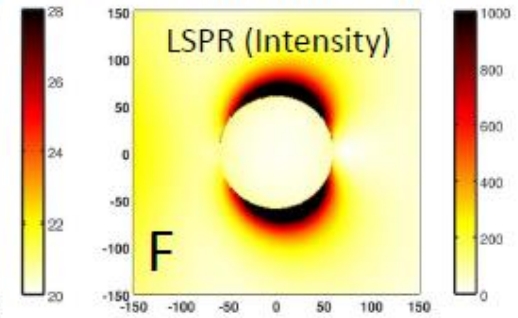
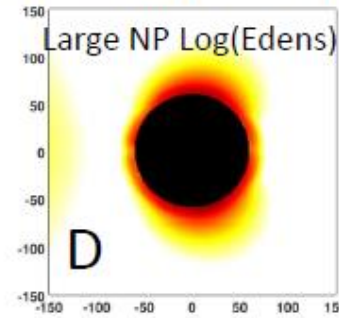
### Regime II

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

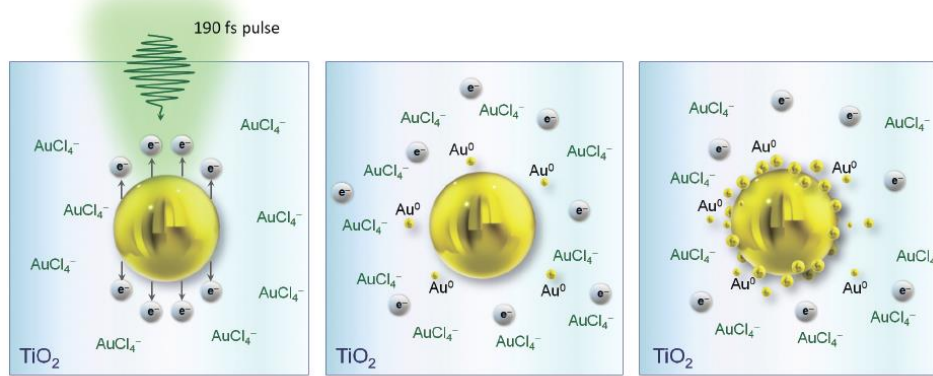


### Regime III

LSPR triggers water  
photo-ionization;  
Induced Carriers heat water

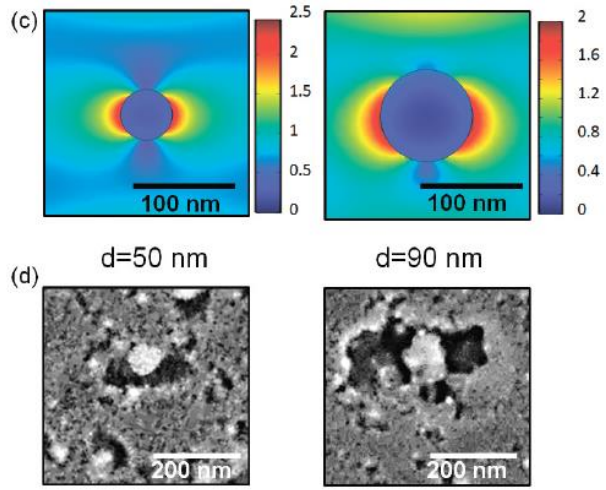
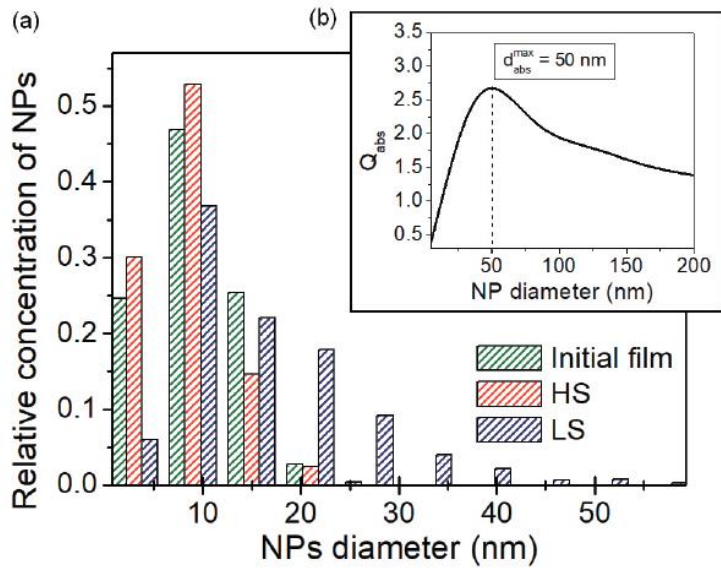


# Au NPs in TiO<sub>2</sub> under Ultra-Short Laser Irradiation



**At the beginning, the matrix is solid**

*Y Andreeva et al. The Journal of Physical Chemistry C 124 (18), 10209-10219, 2020*

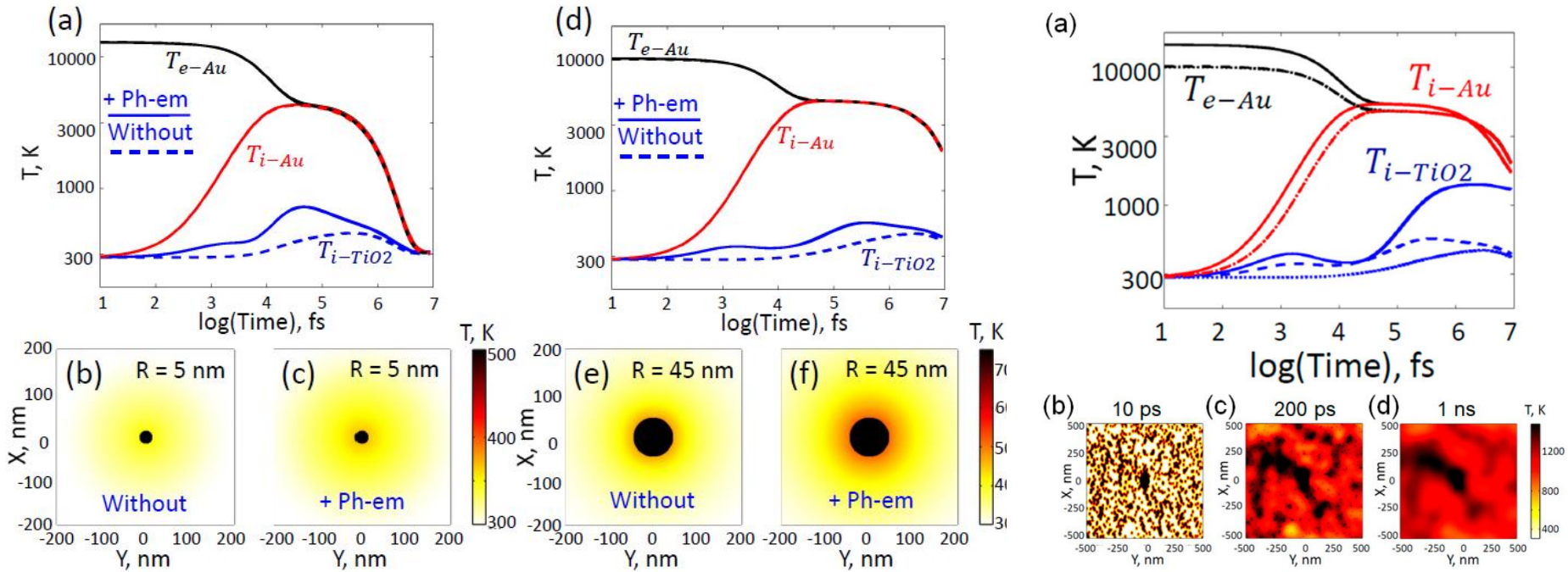


fs laser  
 $\lambda = 515$  nm

(a) Size distribution of gold NPs before and after laser treatment. Laser  $F = 57$  mJ/cm<sup>2</sup>, scan speed for LS structures is 0.16 mm/s, for HS structures is 1.6 mm/s.  
 (b) Calculated absorption efficiency of the nanocomposite based on TiO<sub>2</sub> as a function of the diameter of gold NPs (refractive index of surrounding media  $n = 1.6$ ).

(c) Calculated field distribution of gold nanoparticles in TiO<sub>2</sub> ( $n=1.6$ ) for spheres with the diameters of 50 and 90 nm.  
 (d) SEM images of the NPs produced in LS mode ( $F=57$  mJ/cm<sup>2</sup>,  $V_{sc} = 0.16$  mm/s).

# Au NPs in TiO<sub>2</sub> under Ultra-Short Laser Irradiation



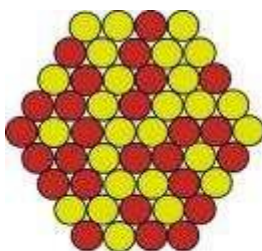
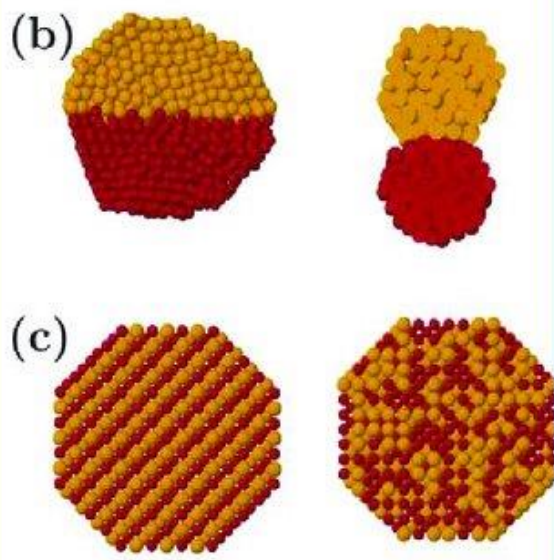
Electron (black solid) and ion temperature (red solid) of R=45 nm gold NP and titanium dioxide temperature (blue solid) in the vicinity of the contact upon  $F = 50 \text{ J/cm}^2$  irradiation. Blue dotted line indicates temperatures attained if only heating from single nanoparticle is considered and blue dashed line additionally includes electron photo-emission.

Only when **collective heating by smaller R=5nm nanoparticles**, electron photo-emission from nanoparticles and free carrier generation by ionization processes in titanium dioxide are included, **the ambient damage conditions are reached**.

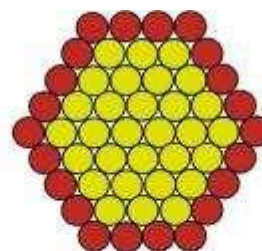
Y Andreeva et al. *The Journal of Physical Chemistry C* 124 (18), 10209-10219, 2020

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

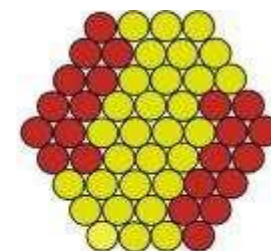
# Nanoparticle Alloys and Aggregates: MD simulations



Alloy



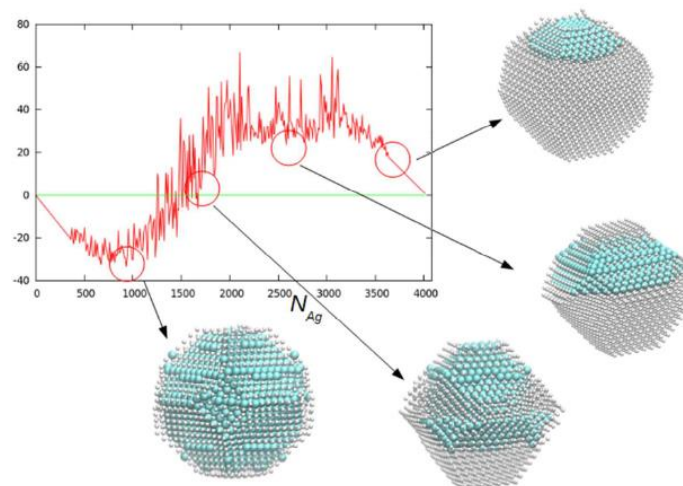
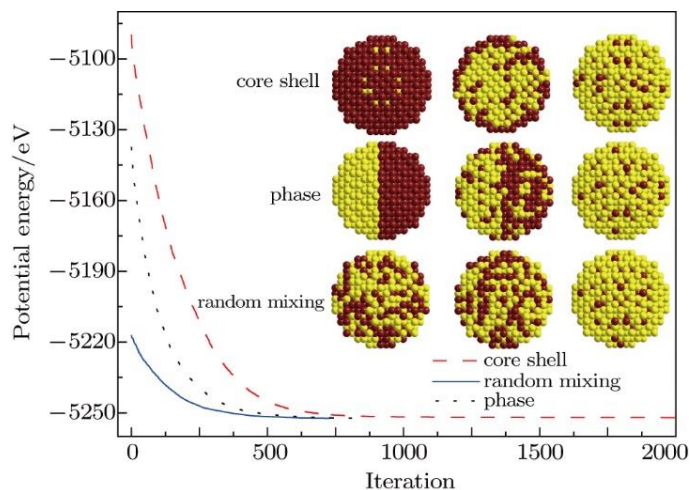
Core-Shell



Cluster-in-Cluster

Mixing Energy

$$\Delta[N_A, N_B] = E_{\text{alloy}}[N_A+1, N_B-1] - E_{\text{alloy}}[N_A, N_B] - E_A[\text{ref}] + E_B[\text{ref}]$$



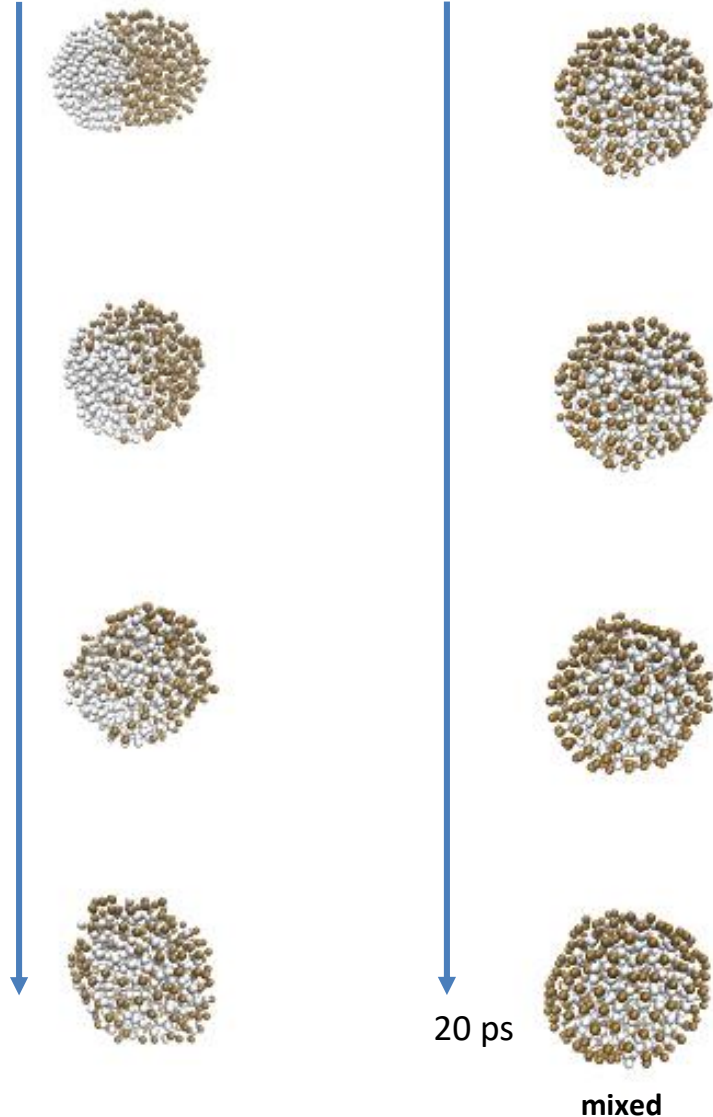
# Ultra-short Laser-induced NP Mixing (nanoalloys)

Co NP Au NP  
R=4 nm

CoNP + Au NP,  $T_1 = T_2 = 2000\text{K}$   
time

Molecular  
dynamics  
(MD)

The same sizes  
The same T

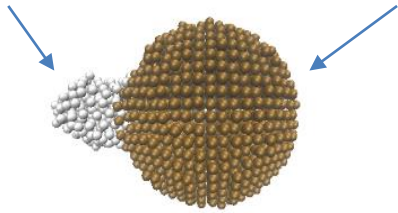


- Simulation starts from a Janus configuration
- Then both particles are heated to the same temperature during time around e-ph coupling time
- Then, the system is cooled down back to room temperature

**Mixing is easier when both particles have comparable sizes, temperatures and are composed of species with similar cohesive energies**

# Ultra-short Laser-induced NP Hybrid (core-shell) Formation

Fe NP R=3.5 nm Au NP R =8 nm

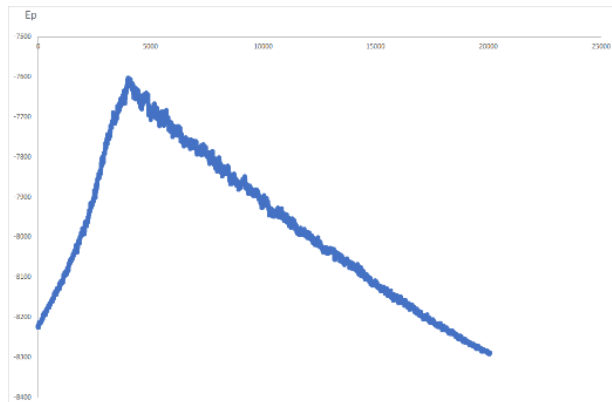


FeNP 1700+AuNP 1700

time

Different sizes and species,  
but the same temperatures

Time-evolution of  
potential energy



200 ps



- Simulation starts from a Janus configuration
- Then both particles are rapidly heated to the same temperature
- Then, the system is cooled down back to room temperature

**Core-shells can be formed when one particle is much larger and is composed of a material with different cohesive energy**



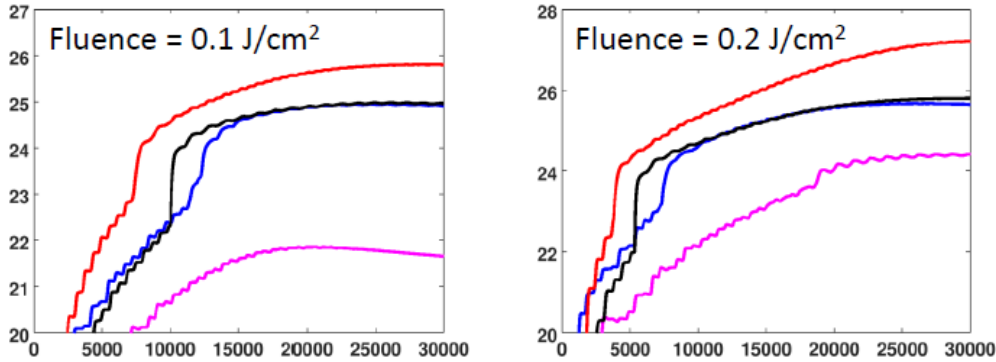
## SUMMARY

1. Laser is a very powerful and versatile tool suitable not only for the control over nanoparticle sizes but also for a wide range of manipulations with nano objects involving processes such as melting, reshaping, sintering, and mixing.
2. The involved processes have been considered:  
the roles of electron ejection/injection, ionization and heating of the ambient medium, the presence of several particle populations have been examined for different NP sizes and ambient environments.
1. Modeling is promising to predict the roles of size, temperature, and composition of nanoparticles, as well as the heating and cooling conditions.

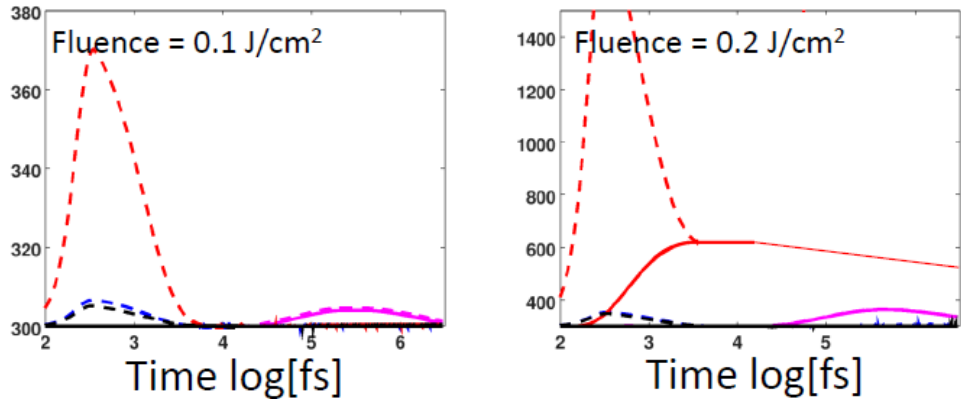
**Thank you very much for your attention!**

# Ultra-Short Laser Interaction with Au NPs in Water

## Electron density $\log(m^{-3})$



## Electron/ion temperature in water (K)



## Electron/ion temperature

### in nanoparticle (K)

