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## Modeling of laser-assisted nanoparticle fragmentation, sintering, and alloying

Tatiana Itina, Rudenko Anton

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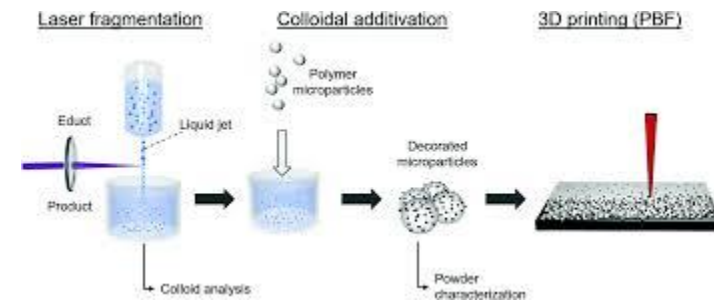
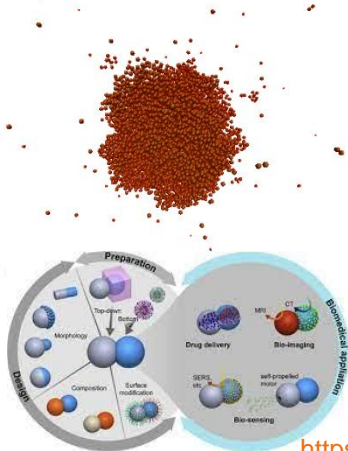
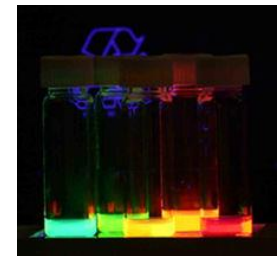
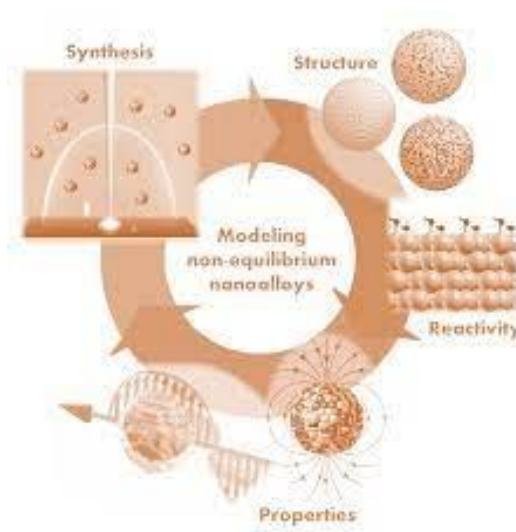
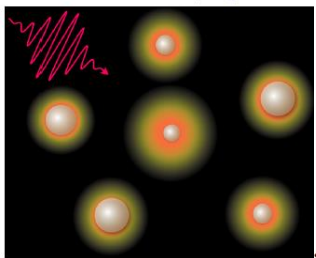
# Modeling of laser-assisted nanoparticle fragmentation, sintering, and alloying

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

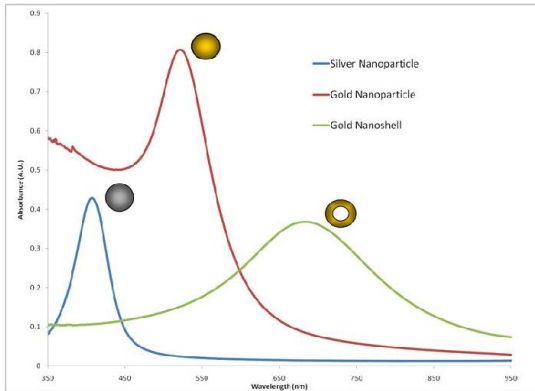
Arizona State University, USA

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

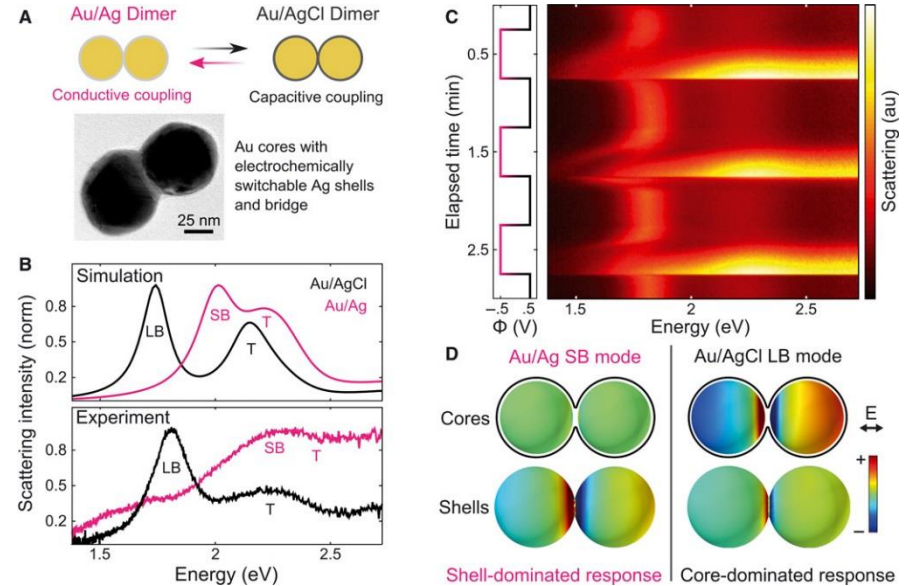


# Motivation

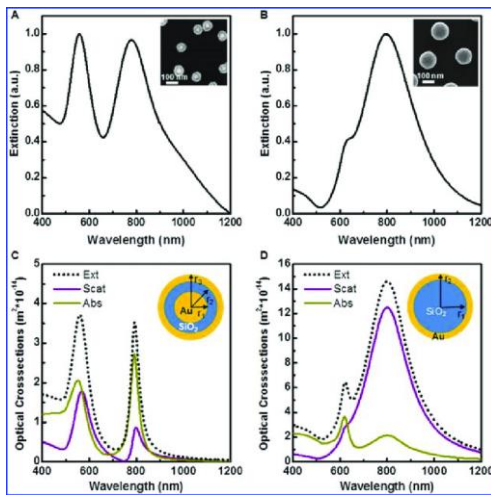
Tailoring optical properties: medical applications, imaging, photo-acoustics, photonics, etc.



Optical properties of multilayer-polyelectrolyte films with incorporated gold nanomaterials (solid nanoparticles and hollow nanoshells)  
R. W. Day, Materials Science (2009)



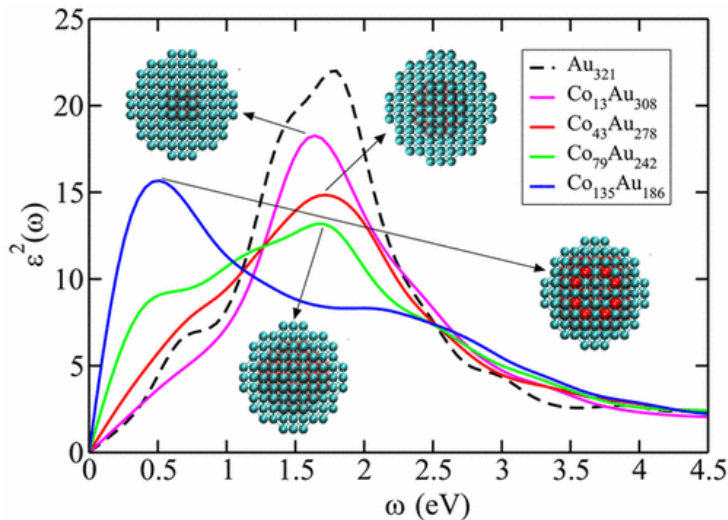
From tunable core-shell nanoparticles to plasmonic drawbridges: Active control of nanoparticle optical properties Chad P. Byers et al. *Science Advances* 04 Vol. 1, no. 1 (2015)



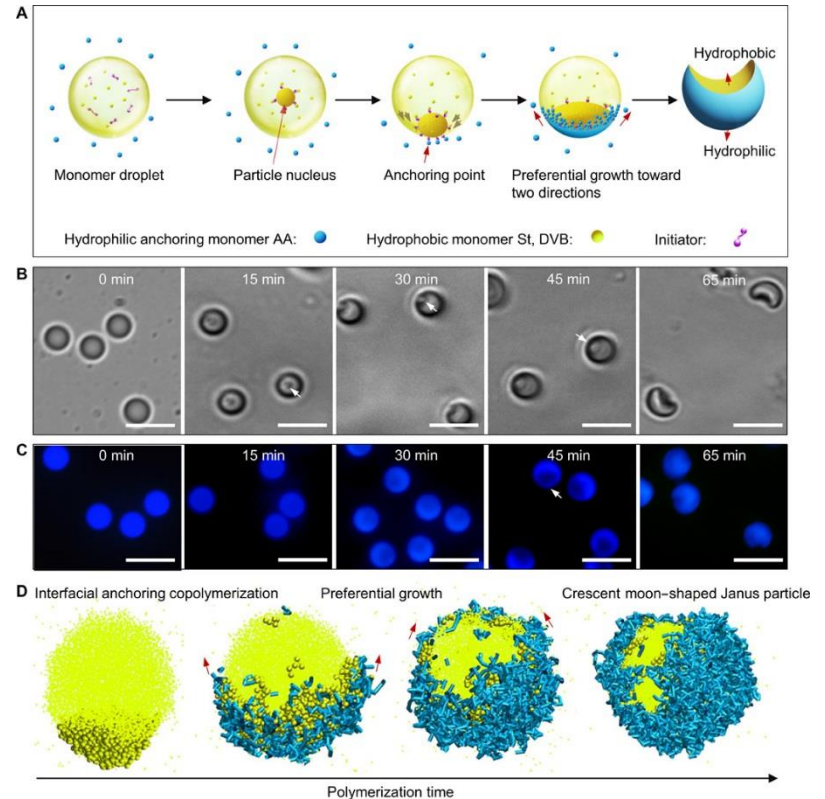
Au Nanomatryoshkas as Efficient Near-Infrared Photothermal Transducers for Cancer Treatment: Benchmarking against Nanoshells, Ciceron Ayala-Orozco et al., ACS Nano 8(6) (2014)

# Motivation

Tailoring magneto-optical properties for medical applications, imaging, water-splitting, etc.



**Evolution of the Magnetic and Optical Properties in CocoreAushell and (CoRh)coreAushell Core-Shell Nanoparticles**, Junais Habeeb Mokkath *The Journal of Physical Chemistry C*, (2017)



**A general strategy to synthesize chemically and topologically anisotropic Janus particles**  
Jun-Bing Fan, *Science Advances* 21, Vol. 3, no. 6 (2017)

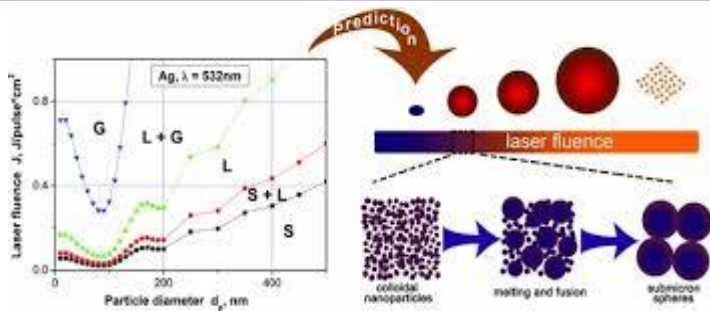
# Why Lasers ?



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**

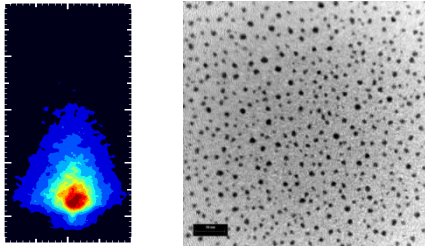


**Laser –induced modifications of nanoparticles are promising for many applications in photonics, medicine, optics, etc.**

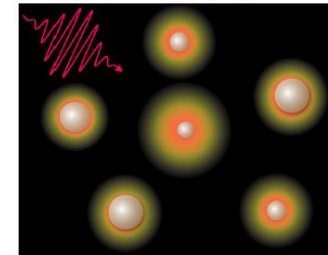
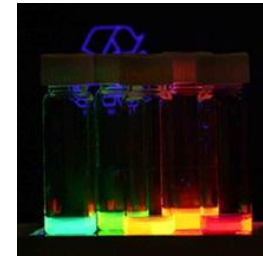
Mechanism of pulse laser interaction with colloidal nanoparticles A. Pyatenko et al., Laser&Phot. Rev. 2013



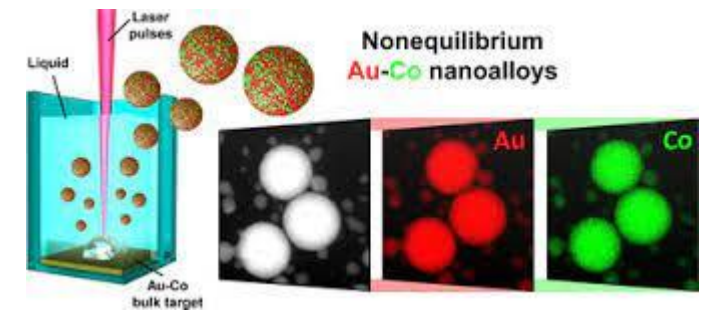
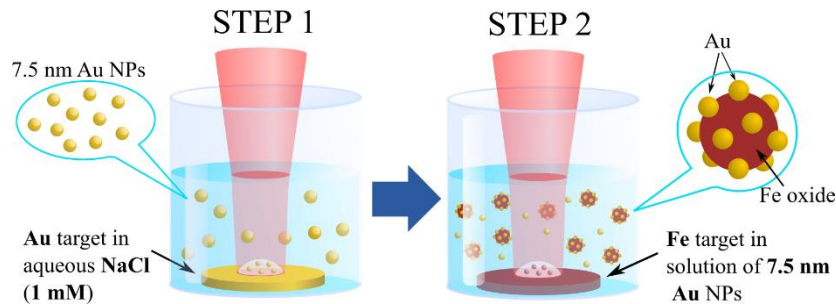
# Typical experiments



Pulsed laser interactions in vacuum and in a gas phase



Laser-induced ablation/fragmentation in liquids



Laser-assisted multi-functional nanohybrids fabrication in liquids: see talks by **Zhaneta Swiatkowska** and by **Anton Popov et al.** at SECAM 2021

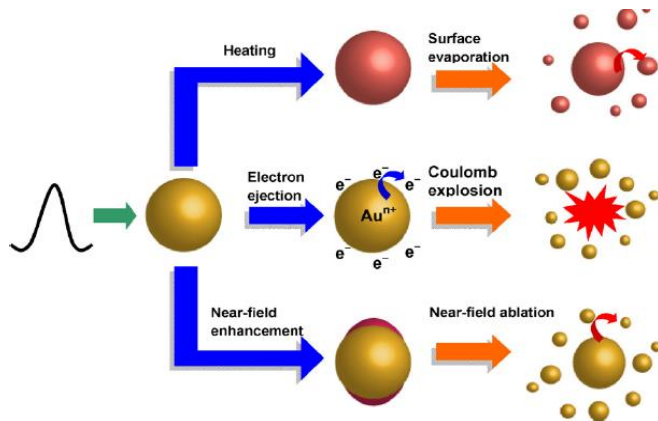
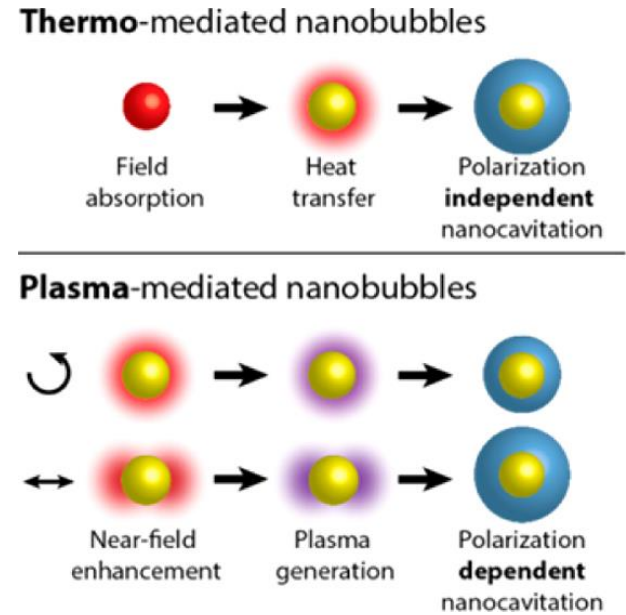
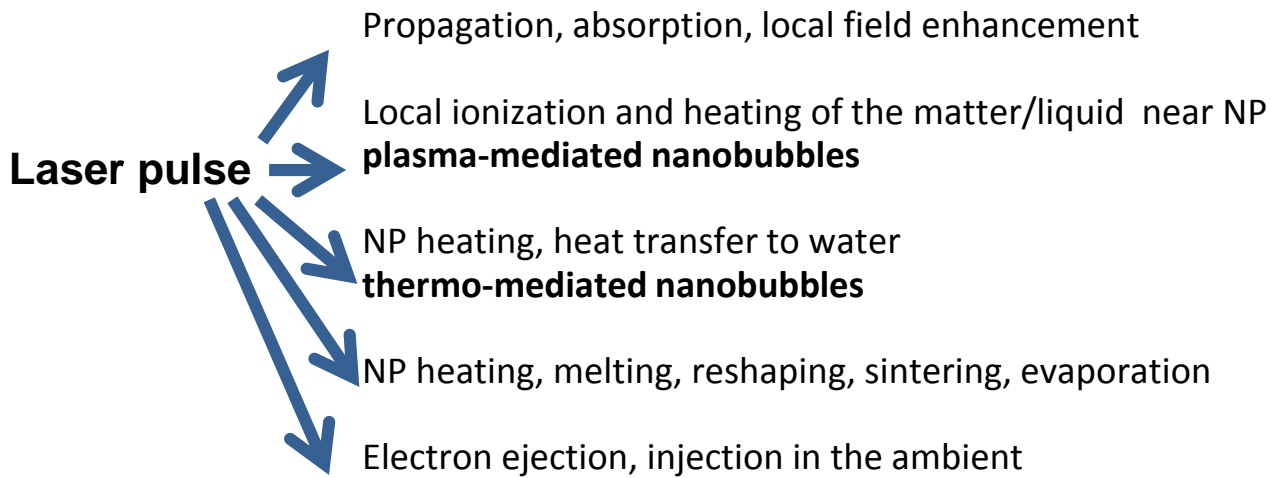
**Vincenzo Amendola**, Padova, Italy

<https://doi.org/10.1002/cphc.202100021>

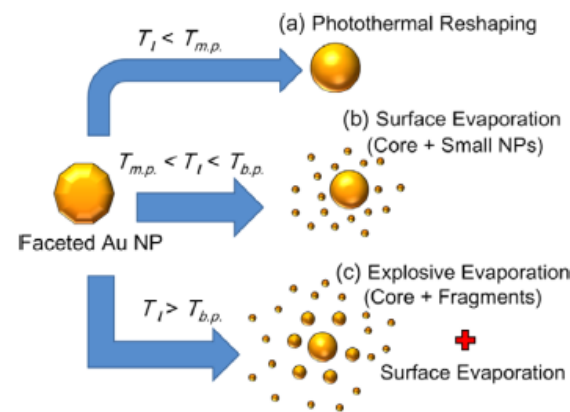
Kinetically Stable Nonequilibrium Gold-Cobalt Alloy Nanoparticles with Magnetic and Plasmonic Properties

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

# Laser Interactions with NPs



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



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

Lachaine et al. *Photonics* (2013)

Pustovalov et al., *LPL* (2008)

$$I_{th} \approx \frac{4c_0\rho_0(T_{th} - T_\infty)r_0}{3K_{abt_p}}$$

$$r_{1\max} \approx \left( \frac{3}{4\pi} \frac{E}{p_\infty} \right)^{\frac{1}{3}}$$

***SINGLE NANOPARTICLES***  
***heating, melting, structural transformations,***  
***evaporation, fragmentation***



# Laser Interaction with NPs in Liquids

## Classical Modeling

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

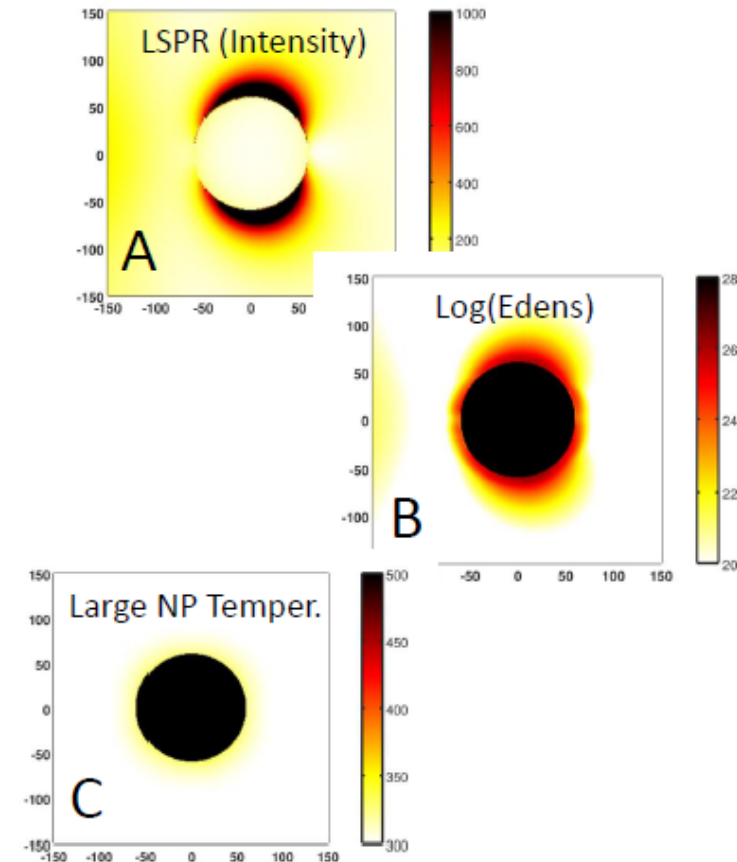
### Nanoparticle

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

### 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 account for electron ejection/injection, etc..

# Ultra-Short Laser Interaction with NPs

## Non-Equilibrium Electron Sub-system

### Conduction band (free) electrons model

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

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

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

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

Definitions of electron & lattice temperatures

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

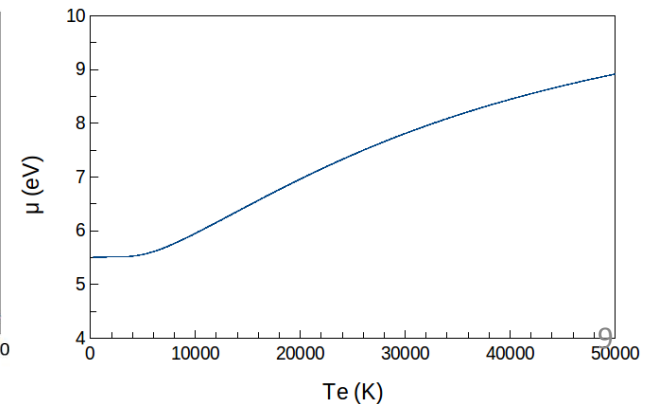
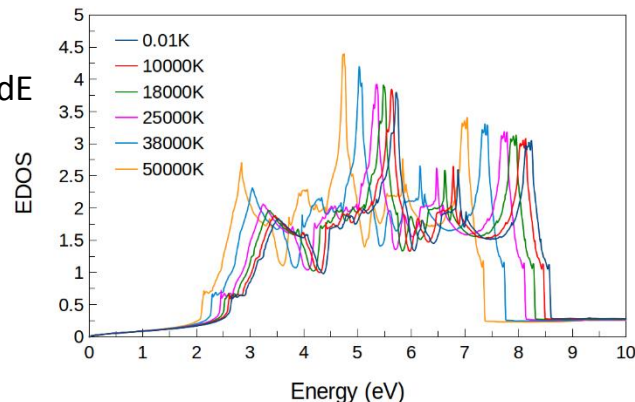
$$\rho_{NP} C_{NP} \frac{\partial T_{NP}}{\partial t} = -A \int_0^{E_{max}} \left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} E^{3/2} dE$$

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

### Quantum mechanical approach (DFT)

$$n_\epsilon = \int_\epsilon^\infty \text{EDOS}(E) \cdot f(E, \mu(T_e), T_e) \cdot dE$$

EDOS(E)



# Laser Interaction with NPs in Liquids

## Interaction regimes and mechanisms involved

### Regime I

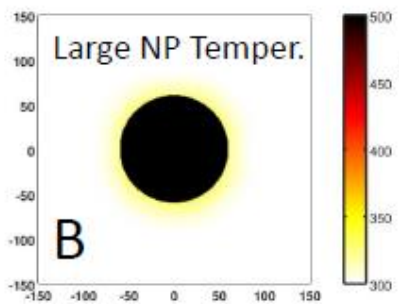
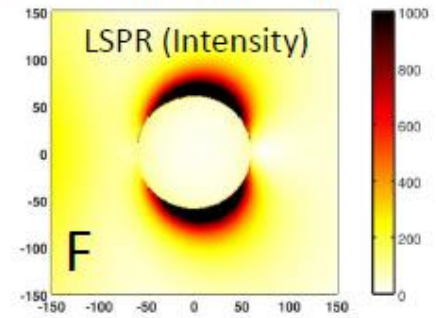
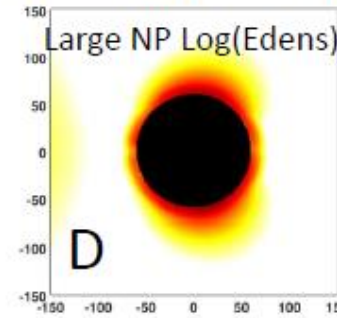
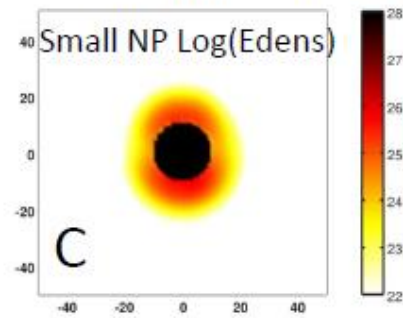
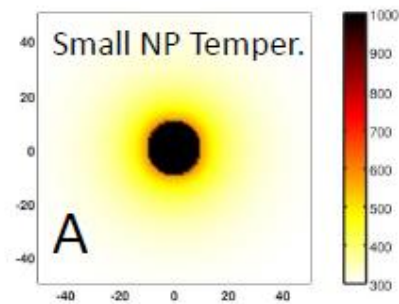
Laser heats Au NP;  
Au NP transfers heat to water

### Regime II

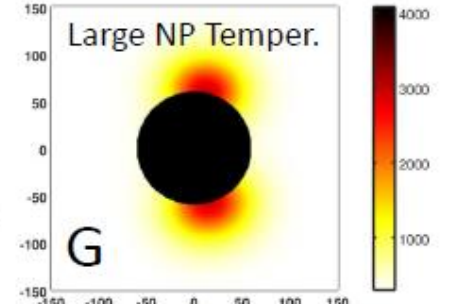
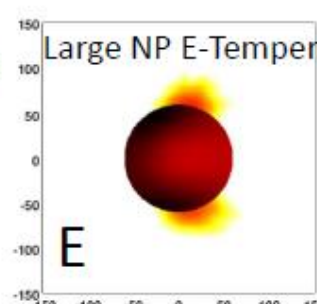
E-ph emission from Au NP  
to water interface;  
Emitted Carriers heat water

### Regime III

LSPR triggers water  
photo-ionization;  
Induced Carriers heat water



Due to inhomogeneous  
distribution  
of absorbed energy



# Electron emission

Au :  $N_{\text{therm}}$  is the total number of emissible electrons :  $N_{\text{therm}} = \alpha \cdot n_{\epsilon}$

where  $n_{\epsilon}$  is a number of electrons with kinetic energy that exceeds the work function per atom at an electron temperature of  $T_e$

$$n_{\epsilon} = \int_{\epsilon}^{\infty} \text{EDOS}(E) \cdot f(E, \mu(T_e), T_e) \cdot dE$$

electronic density of states for a broad range of  $T_e$  chemical potential value depends on  $T_e$

***Criteria of fissility, also called Rayleigh instability factor***

if  $X > 1$ , where

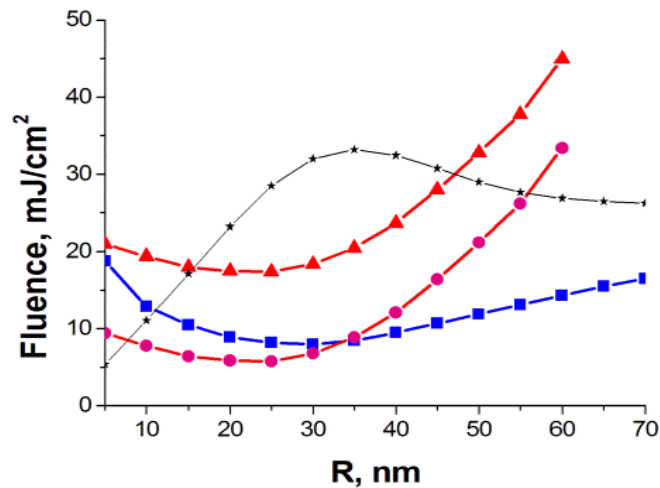
$$X = (N_{\text{therm}}^2 / N_e) / (16 \cdot \pi \cdot r_{\text{ws}}^3 \cdot \sigma / e^2) \Rightarrow$$

***Particle explosion can occur***

$$\alpha = 4V / a_{\text{fcc}}^3 \text{ total number of atoms in the particle}$$

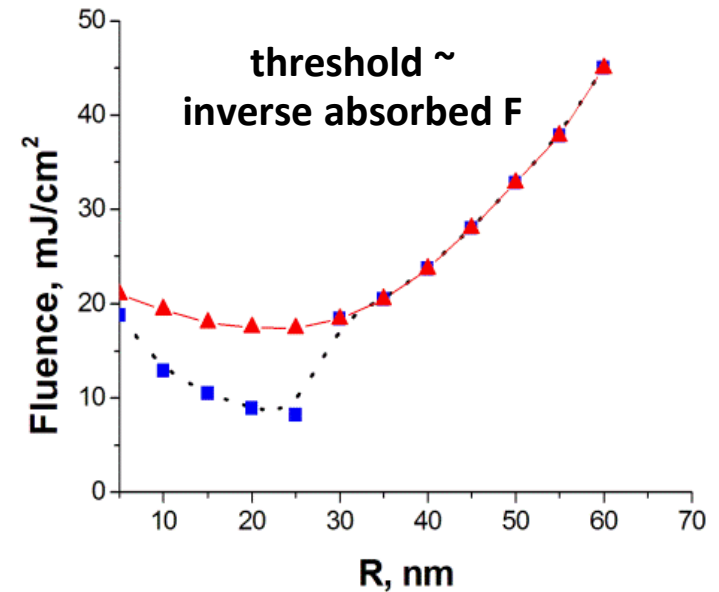
# Ultra-short Laser interaction with a single Au NP

Calculated absorbed fluence, fluence needed for boiling/evaporation (red), for melting (magenta) and for electrostatic decomposition (blue)



## Calculated threshold fluence

150 fs @ 400 nm



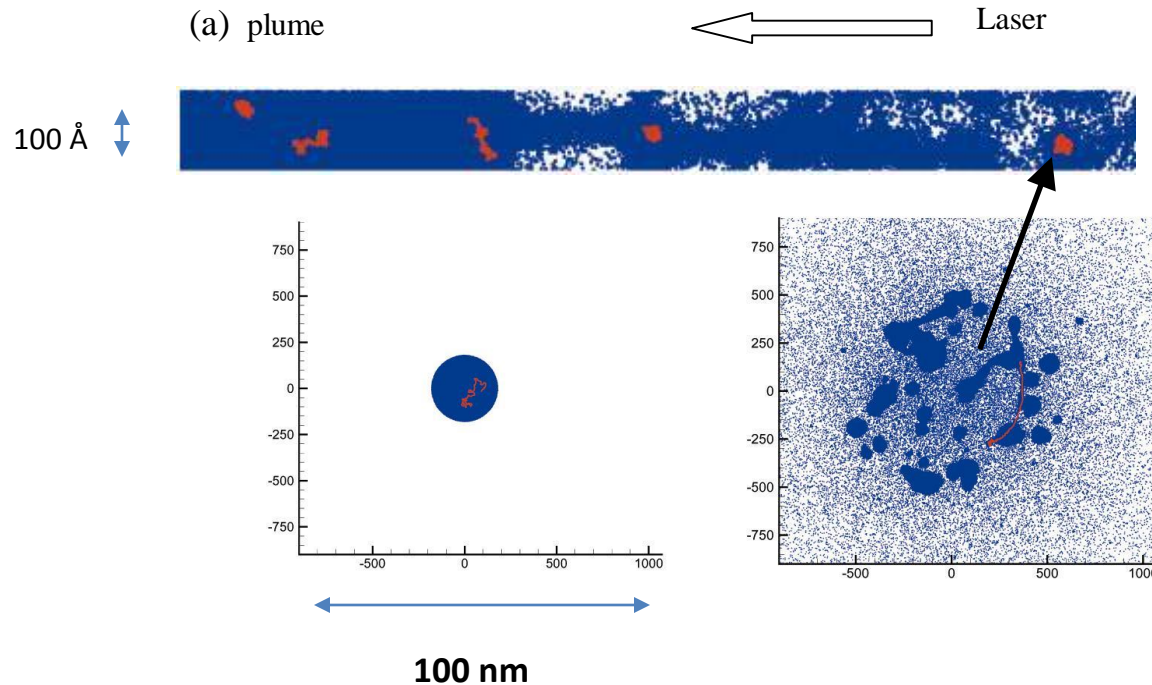
Resonant particles can be decomposed electrostatically...  
However,  
smaller and larger particles are expected to be  
fragmented due to classical thermal-mechanical effects.



# Ultra-short Laser interaction with a single Au NP in vacuum

## Classical Molecular Dynamics (MD) simulations:

Decomposition of the ablated material after the absorption of laser radiation and nanoparticle fragmentation



$t = 300$  ps after the beginning of the laser pulse  
 $\tau = 15$  ps  
 $e = 0.6$  eV per molecule

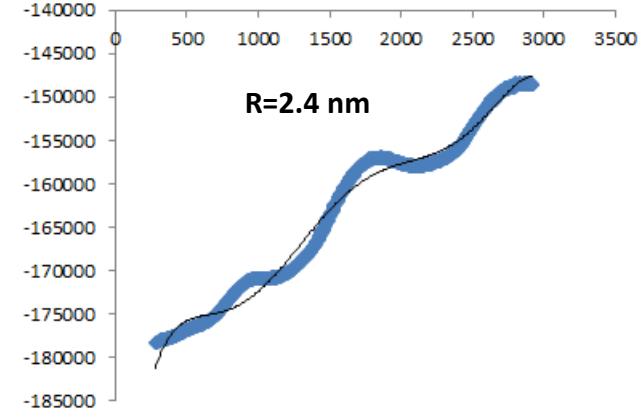
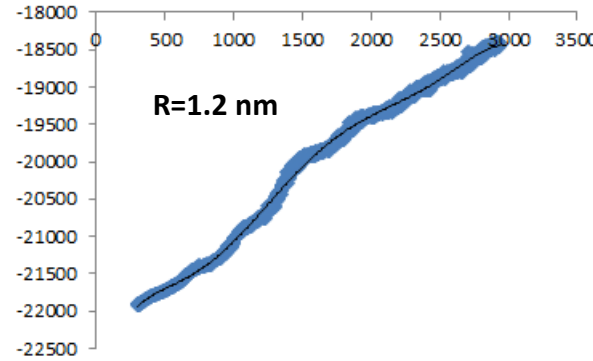
# Ultra-short Laser interaction with a single Au NP in vacuum

## MD simulations

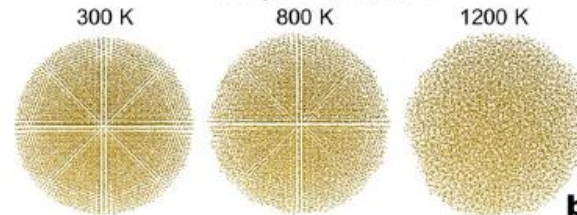
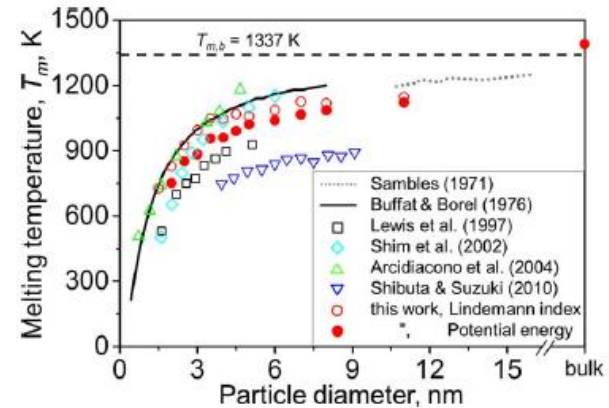
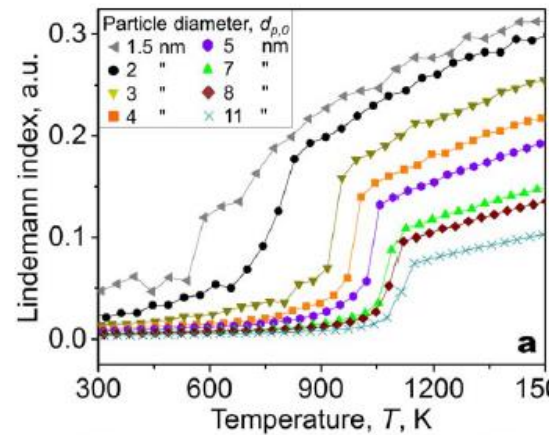
### Time-evolution of potential energy, rapid heating

Au

R=1.2 nm and 2.4 nm

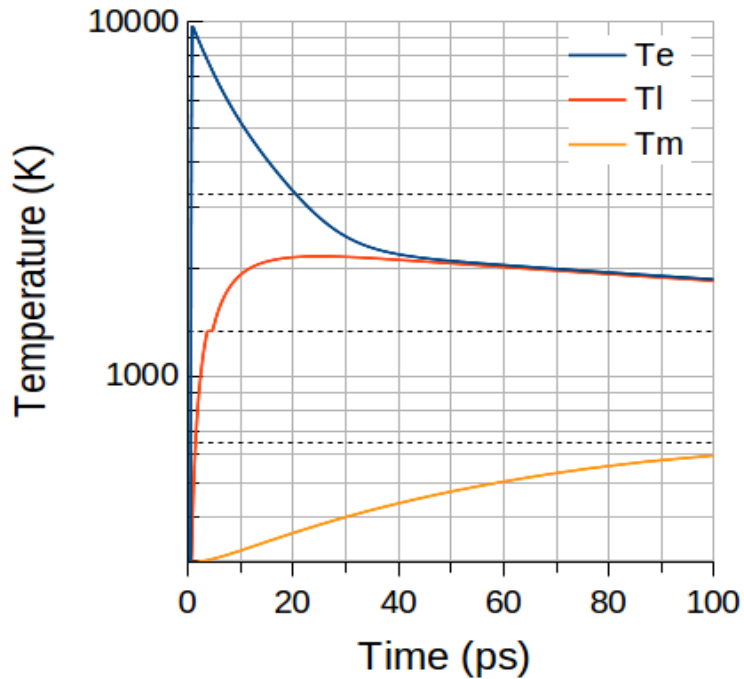


## Melting and ... structural transformations



E. Goudeli et al.,  
AIChE 2015

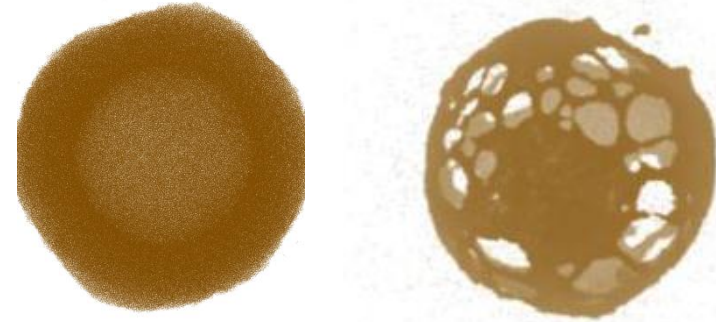
# Ultra-short Laser interaction with a single Au NP in liquid



**30 nm** radius gold particle in water  
absorbing laser pulse of **150 fs** at **400 nm**  
with laser fluence of **12.3 mJ/cm<sup>2</sup>**  
Gaussian time profile

## MD simulations

Heating during e-ph coupling

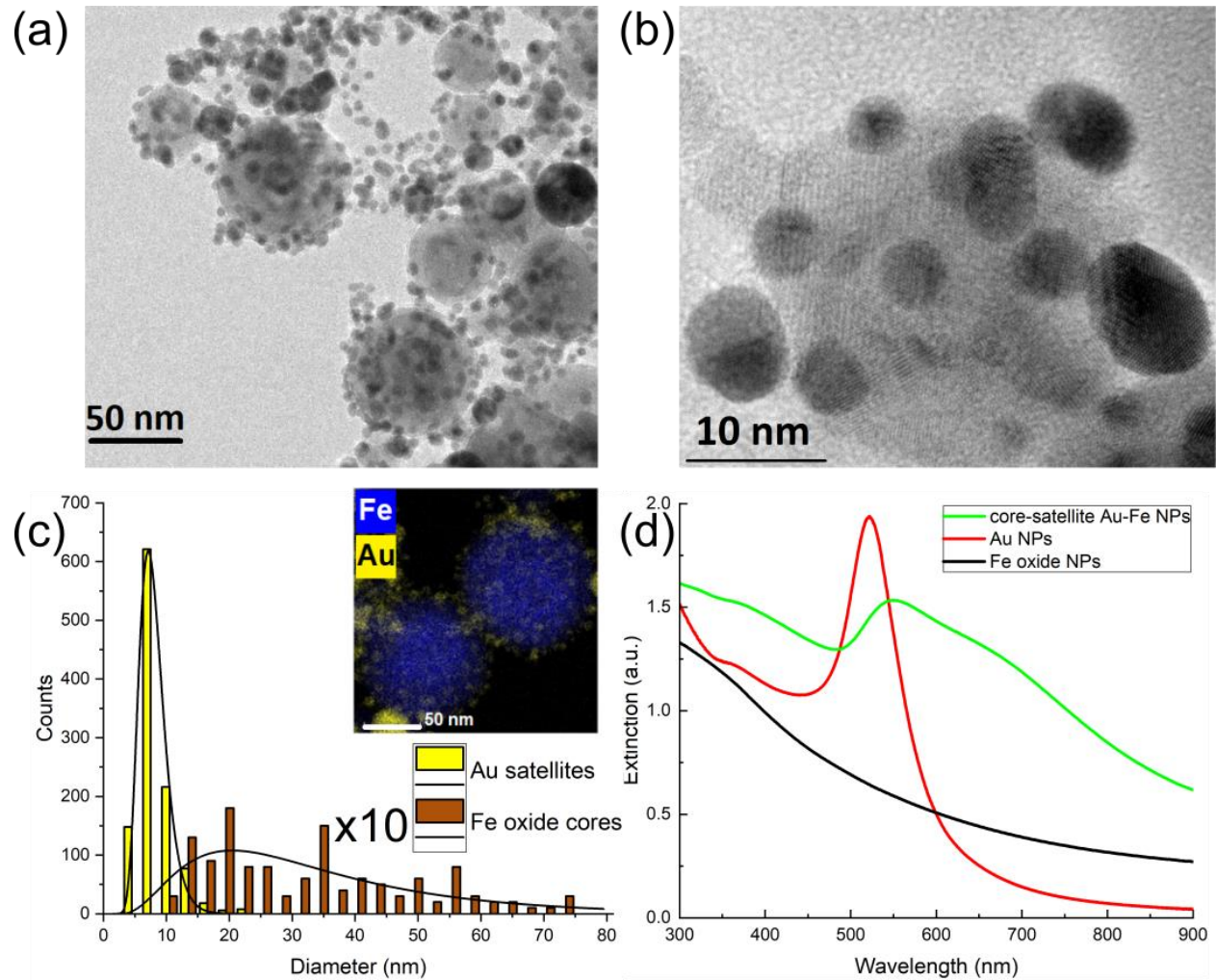


**Larger particle – longer heating and cooling, higher thresholds**

NB: Liquid or matrix participate in NP cooling down affects the final configuration

***DOUBLE NANOPARTICLES AND NANOHYBRIDS***  
***melting, sintering, mixing,***  
***core-shells and Janus nanoparticles***

# Optical properties of nanohybrids

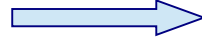


see talk by [Anton Popov et al. CECAM 2021](#)



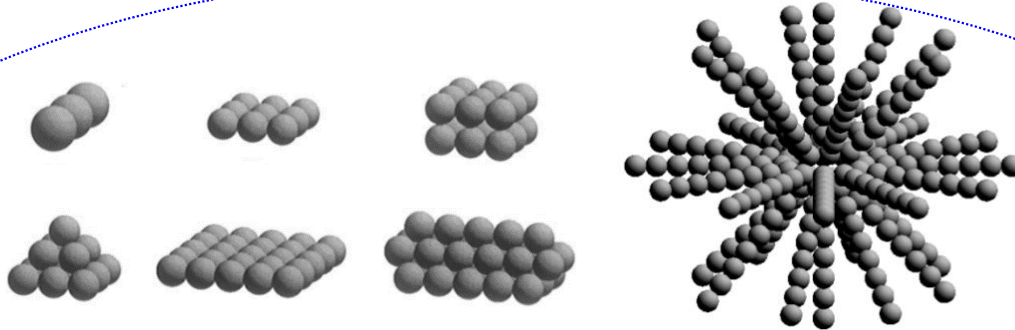
# ABSORPTION

**Mie theory**  
light scattering by a sphere



extinction, scattering, absorption cross section

$$\sigma_{\text{ext}}, \sigma_{\text{scat}}, \sigma_{\text{abs}}$$



A generalized multiparticle Mie-solution: further experimental verification  
*Yu-lin Xu et al.*

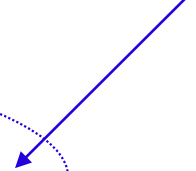
Good agreement with experimental results  
(acrylic spheres)

+

routine that corrects  $n$ ,  $k$  for small particles  
(mean free path)

*Haiss et al. Analytical Chemistry, Vol. 79, No. 11 (2007)*  
ok for size NP >5nm

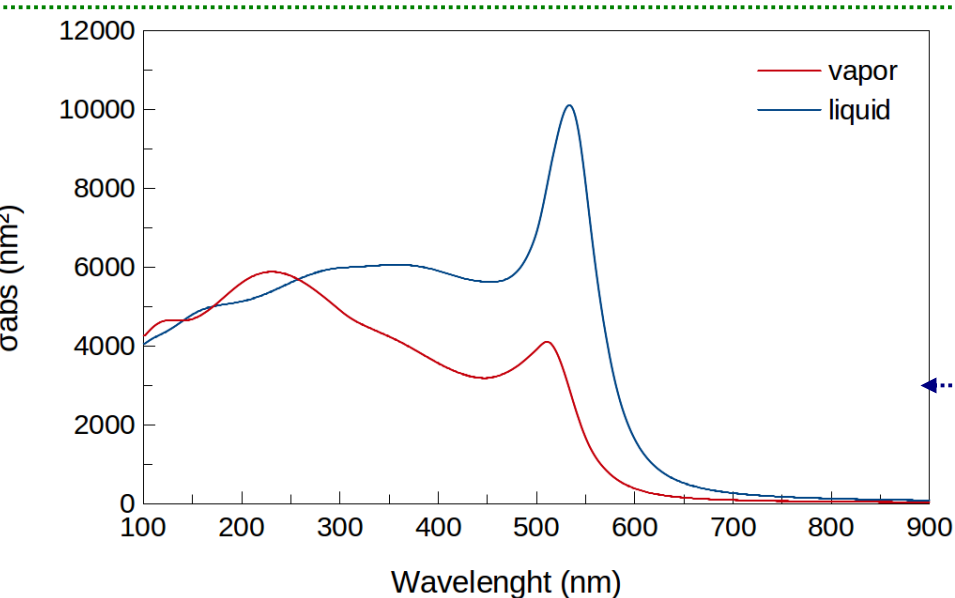
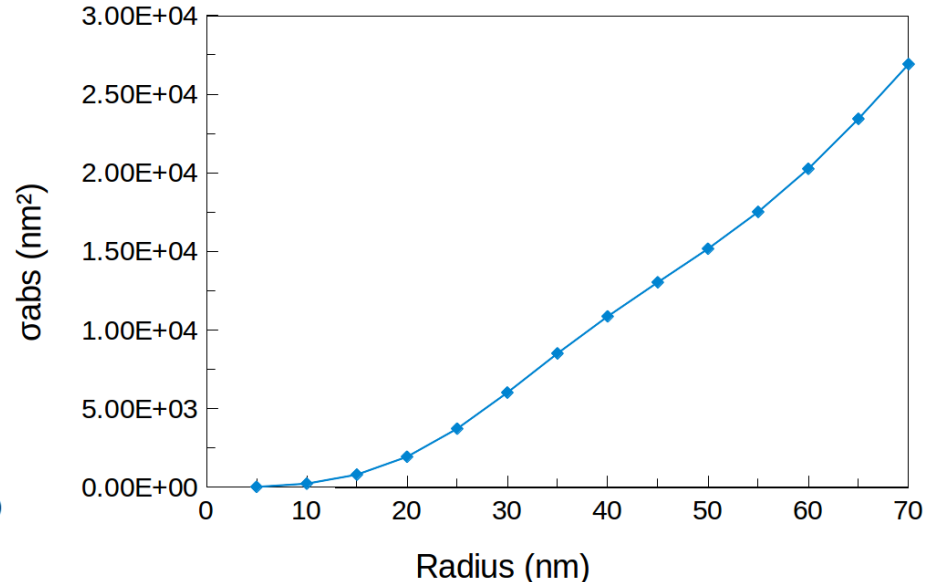
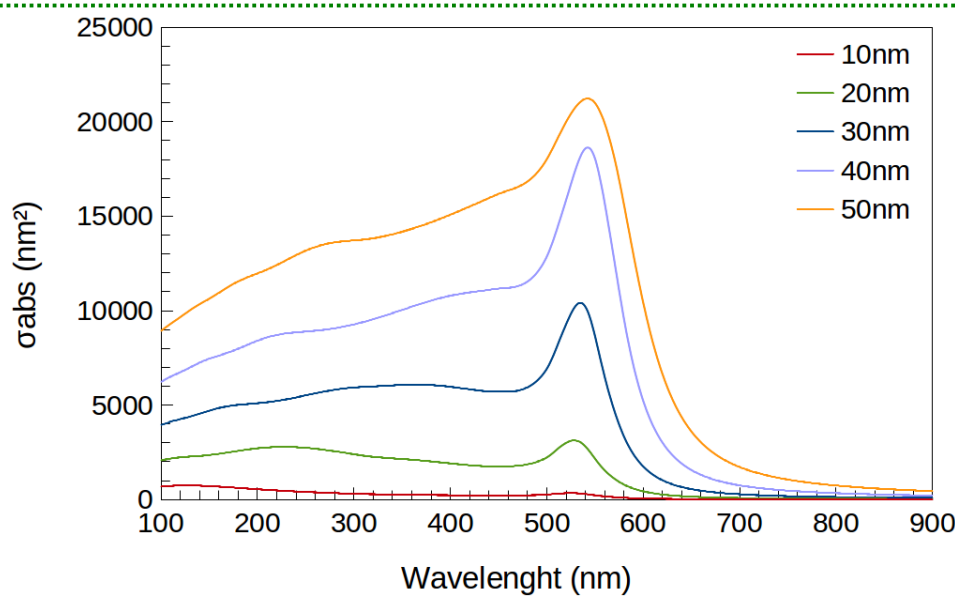
size < 10nm



based on { *Bohren-Huffman Mie scattering subroutine (callbhmie.f)*  
*Generalized Multiparticle Mie-solution (gmm01f.f)*

# ABSORPTION

## Au NPs with radius in the range [10-100] nm



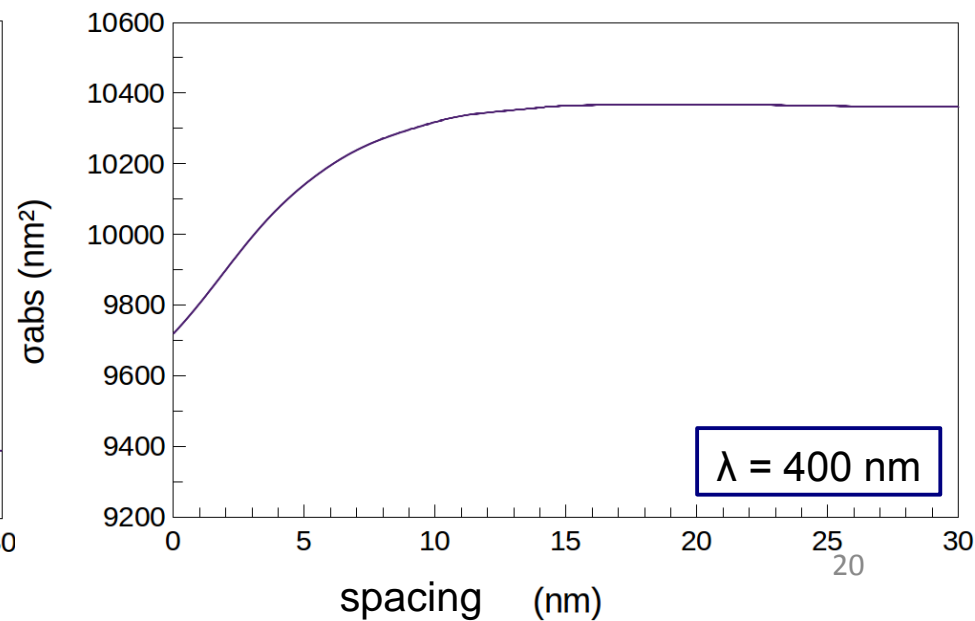
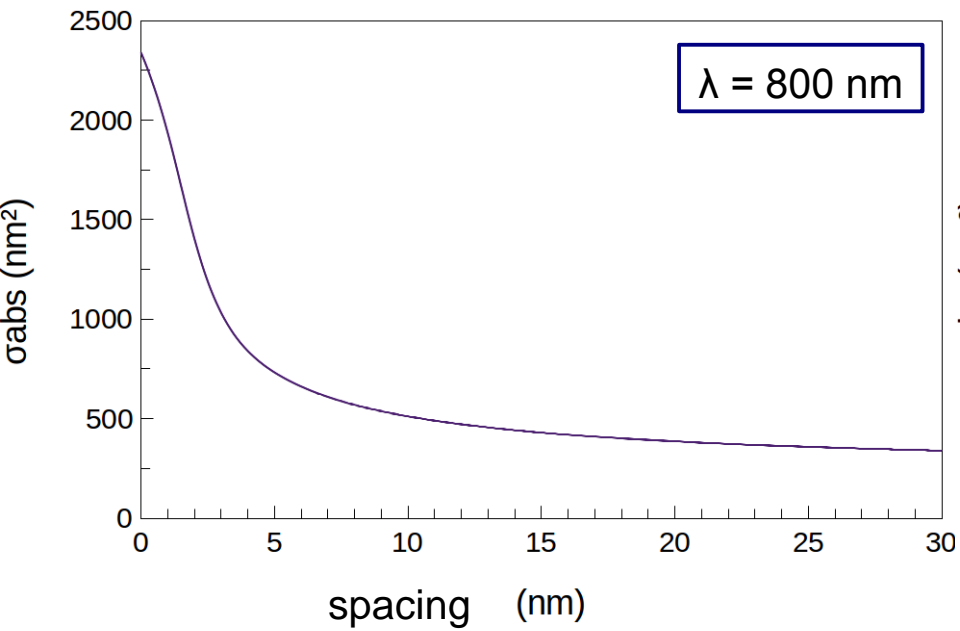
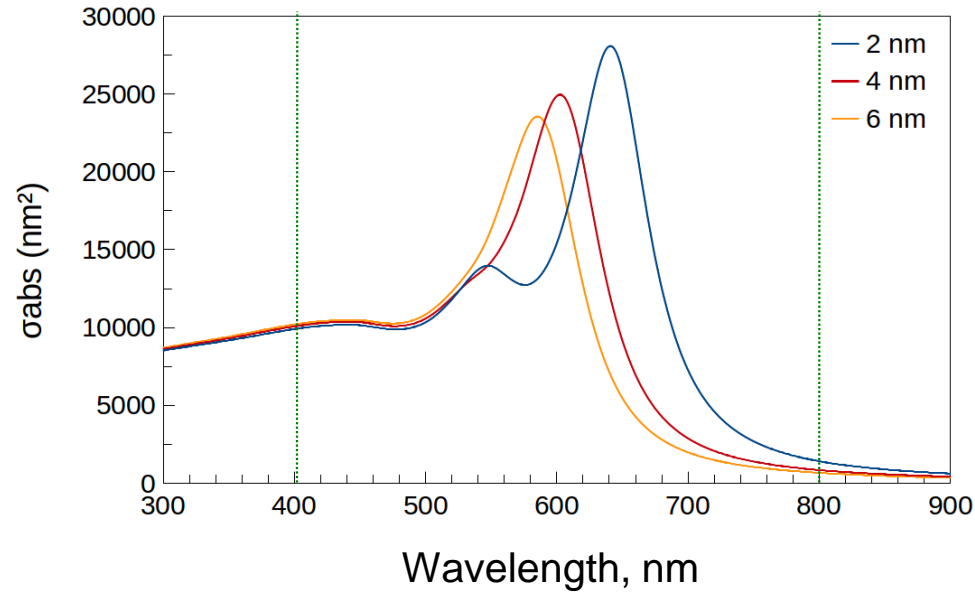
Absorption at 400 nm in liquid water raises with the particle radius (not linear)

Absorption depends of the medium. At 400 nm, passage from liquid water to water vapor goes with a drop in absorption.

# ABSORPTION

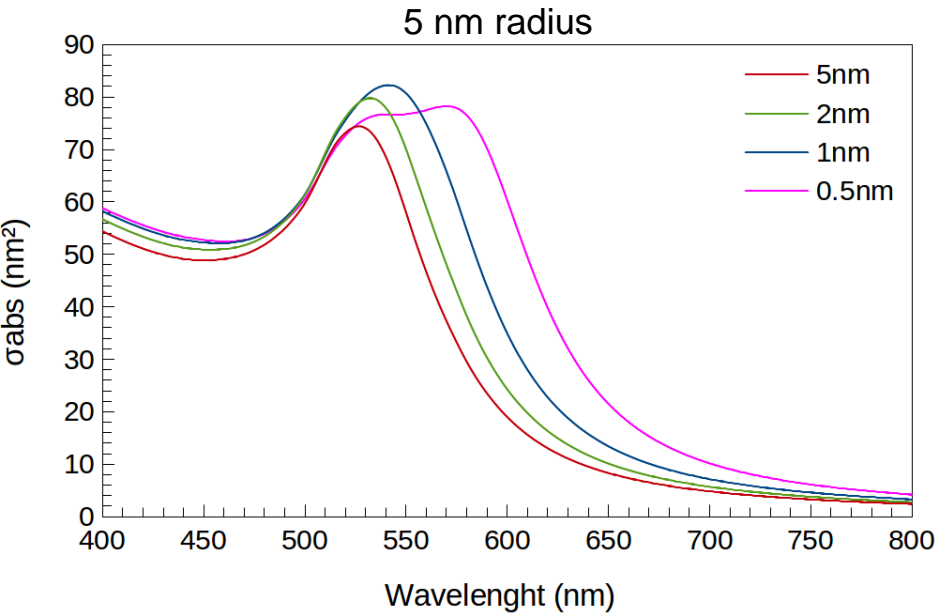
Absorption as a function of inter-particle distance (spacing)  
for 30nm radius Au Nps

Absorption for **Au dimers** depends on both wavelength and spacing



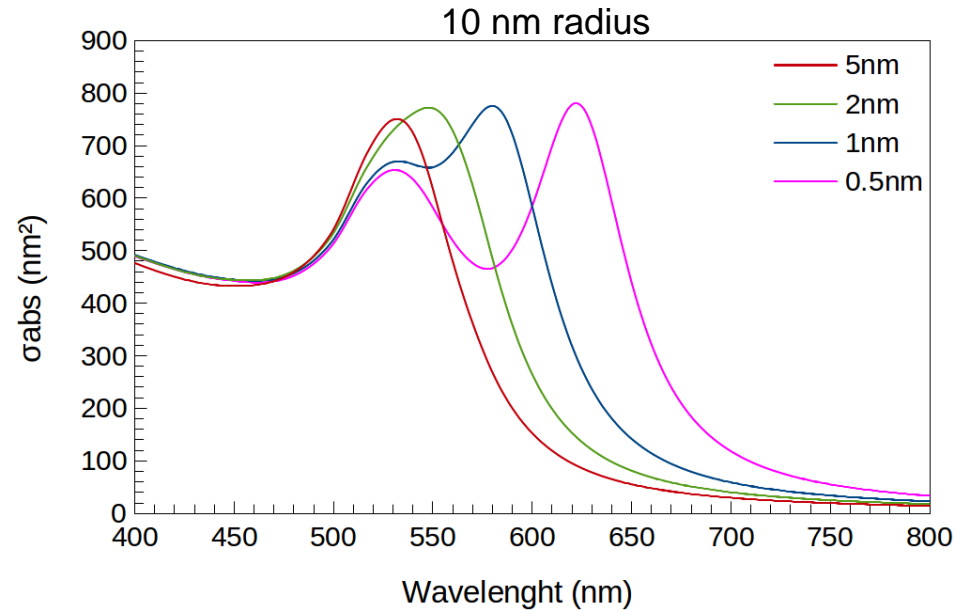
# ABSORPTION

## Gold dimers in water



**If both particles have the same size**

Larger inter particle distance  
=> more pics  
=> shift towards blue

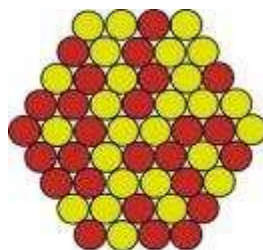
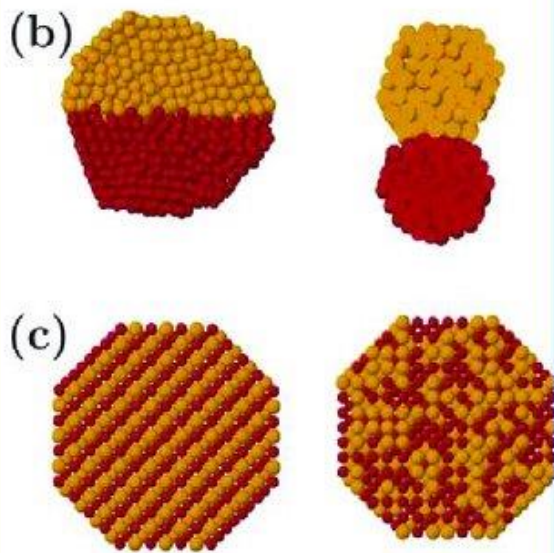


**Inter-particle distance remains constant**

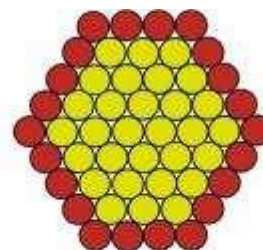
Larger particles  
=> more pics  
=> shift towards blue

Absorption depends on size, composition, separation, etc...

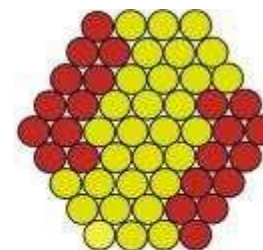
# Bi-Metallic Nanoparticles and Aggregates: MD simulations



Alloy



Core-Shell



Cluster-in-Cluster



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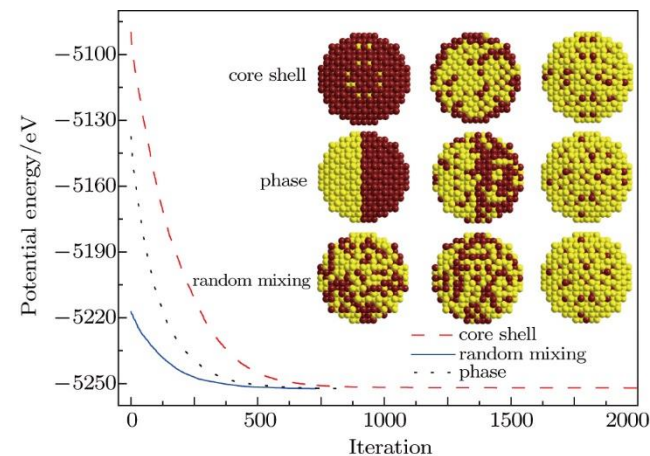
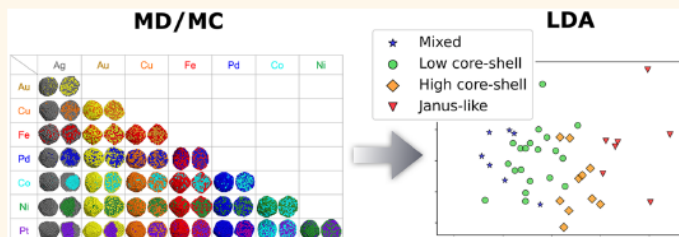
## General Trends in Core–Shell Preferences for Bimetallic Nanoparticles

Namsoon Eom, Maria E Messing, Jonas Johansson, and Knut Deppert\*

Cite This: *ACS Nano* 2021, 15, 8883–8895

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# Ultra-short Laser-induced NP sintering, Janus NPs

AlNP + AuNP

CoNP + AuNP

## MD simulation: sintering of nanoparticles

$N_t$ ,

$N_t$ ,

crystalline order,  $D_i$   
high 0 0.1 0.2 0.3 0.4 low

600 K

800 K

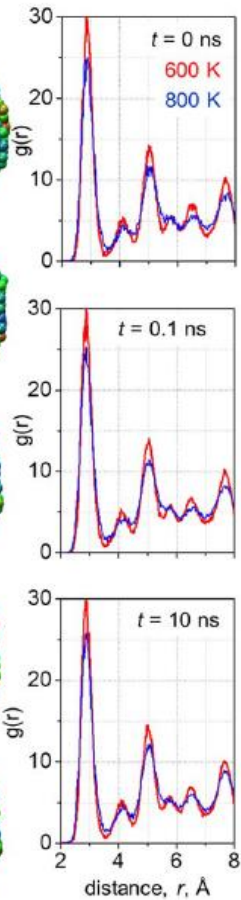
0 ns

0.01

0.1

1

10



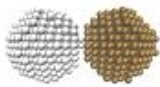
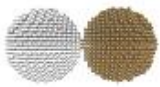
E. Goudeli and S. E. Pratsinis at al.  
Crystallinity dynamics of Au NPs,  
AIChE 2015

$R_1=R_2=20$  ub ( $\sim 1$  nm)

T.E. Itina at al.

$8e4$

$8e4$



# Ultra-short Laser-induced NP sintering, Janus NPs

AuNP + AuNP, different sizes

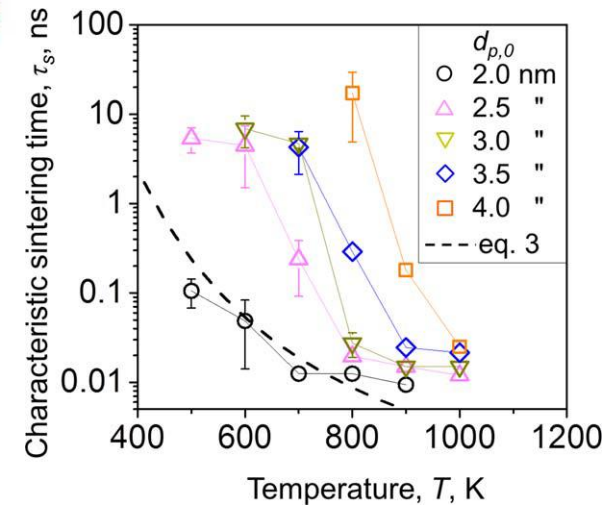
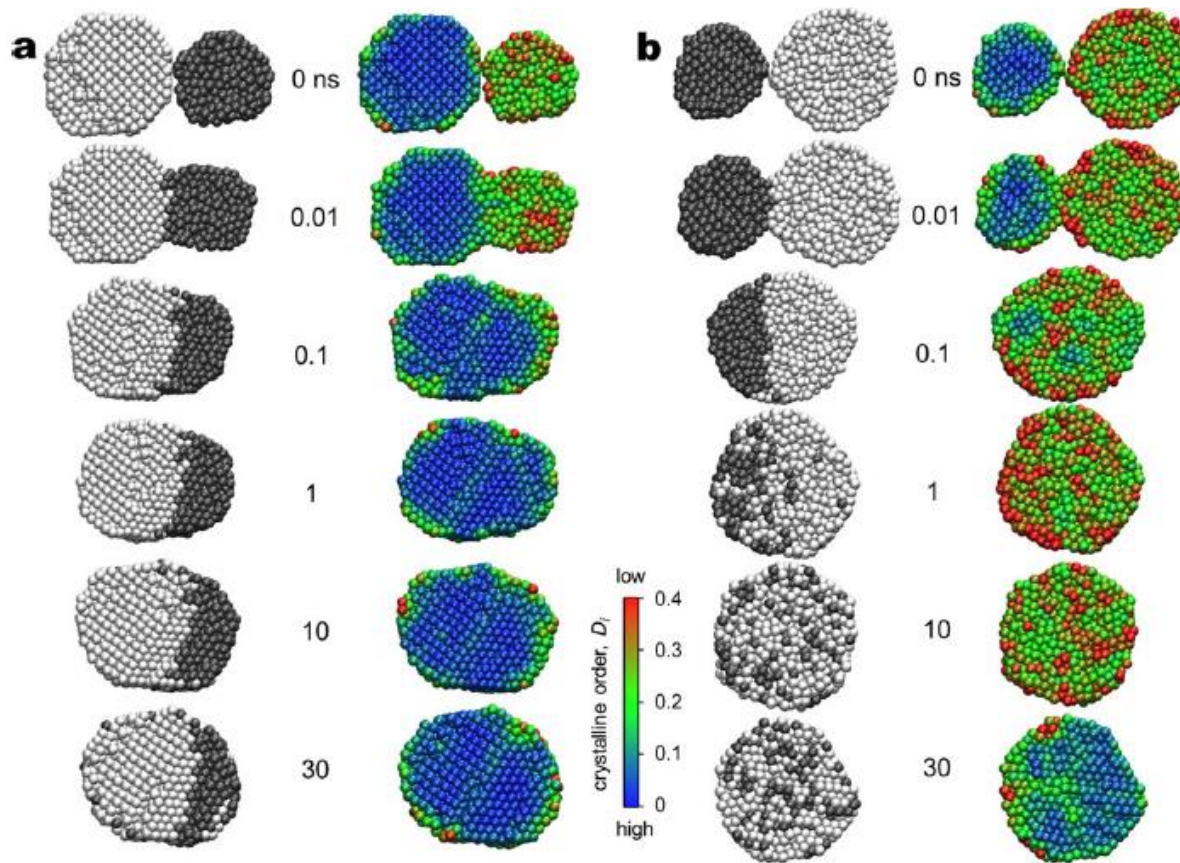


Figure 9. Snapshots of cross-sections of two Au nanoparticles with  $d_{p,0} = 3$  (gray) and  $4$  nm (white) undergoing sintering at  $T = 800$  K at  $t = 0, 0.01, 0.1, 1, 10, 30$  ns.

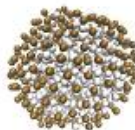
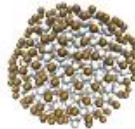
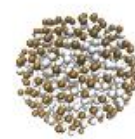
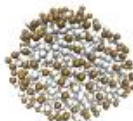
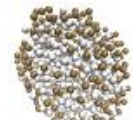
# Ultra-short Laser-induced NP mixing (Nanoalloy formation)

## MD simulations

R1, R2~10 unit boxes

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

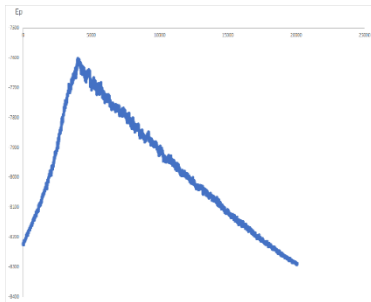
N\_t



8e4

mixed

Similar sizes  
the same T,  
but  
different materials  
Co and Au



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

Mixing seems to be easier when both particles have comparable sizes and temperatures

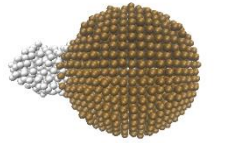


# Ultra-short Laser-induced NP hybrid (core-shell) formation

FeNP + AuNP

FeNP 1700+AuNP 300

FeNP 300+AuNP 1700



Au 0.48 nm Fe 0.7 nm

2e3



Different materials:  
Fe and Au  
Different sizes  
(AuNP is larger)  
Different T

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

When one particle is larger and this particle is more absorbing, partial Janus configuration or an almost core-shell one is observed

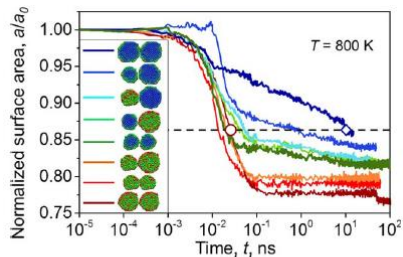


Figure 10. Evolution of normalized surface area of two Au nanoparticles of equal (3–3 or 4–4 nm) and different diameters (3–4 nm) undergoing sintering or coalescence at  $T = 800$  K.

E. Goudeli et al.,  
AIChE 2015

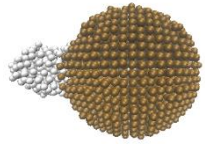
8e4

8e4

T.E. Itina et al.

# Ultra-short Laser-induced NP hybrid (core-shell) formation

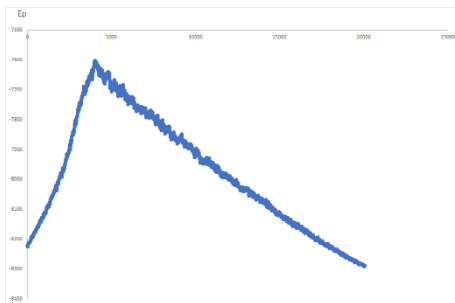
FeNP 1700+AuNP 1700



Different materials:  
Fe and Au

Different sizes  
The same temperatures

Time-evolution of  
potential energy



N\_t

8e4



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

Core-shells can be also formed when one particle is larger, but both particles are heated to the same T



# Ultra-fast heating and cooling of alloy NP

AlAuNP, 20% T=1200K

AlAuNP, 80% T=1200K

0.1 nm



$N_t$

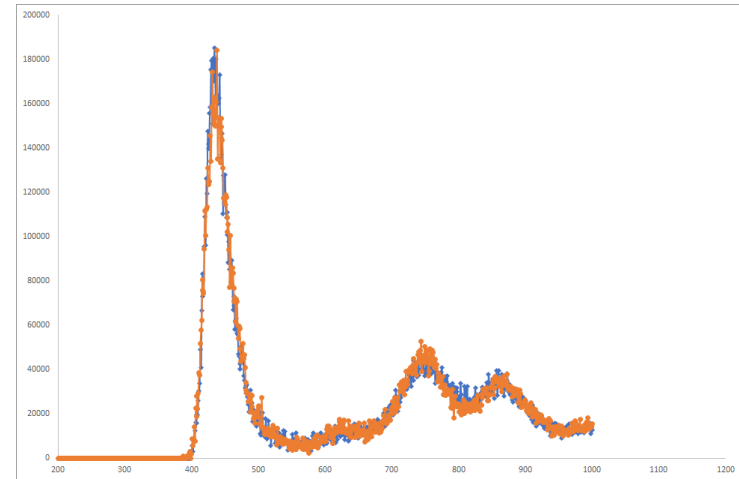


8e4



Different proportions of Au

Correlation function  $g(r)$



When Au fraction is smaller, Au atoms tend to aggregate at the surface during NP cooling

When Au fraction is larger, the nanoparticle suffers less thermal expansion and is more stable

## 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, mixing, etc.
2. The involved processes are often non-equilibrium and therefore are still hard to be generalized.
3. Several modeling examples of the processes involved have been demonstrated revealing the role of size, temperature, and composition of nanoparticles, as well as the heating and cooling conditions.

**Thank you very much!**