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# Multi-scale Modeling for Laser-based Nanotechnology

Tatiana Itina

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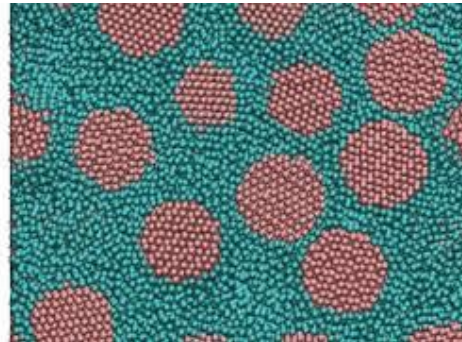
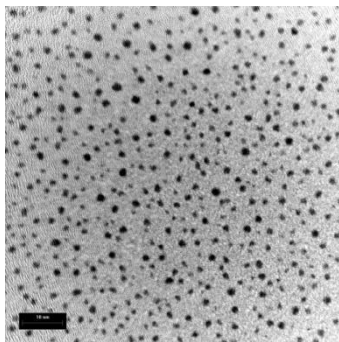
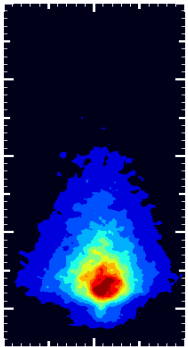
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# Multi-scale Modeling for Laser-based Nanotechnology

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Ablation experiments,  
LP3, France

[https://www.photonics.com/Articles/Nanoparticles\\_Probing\\_the\\_Plasma\\_Threshold/a57306](https://www.photonics.com/Articles/Nanoparticles_Probing_the_Plasma_Threshold/a57306)

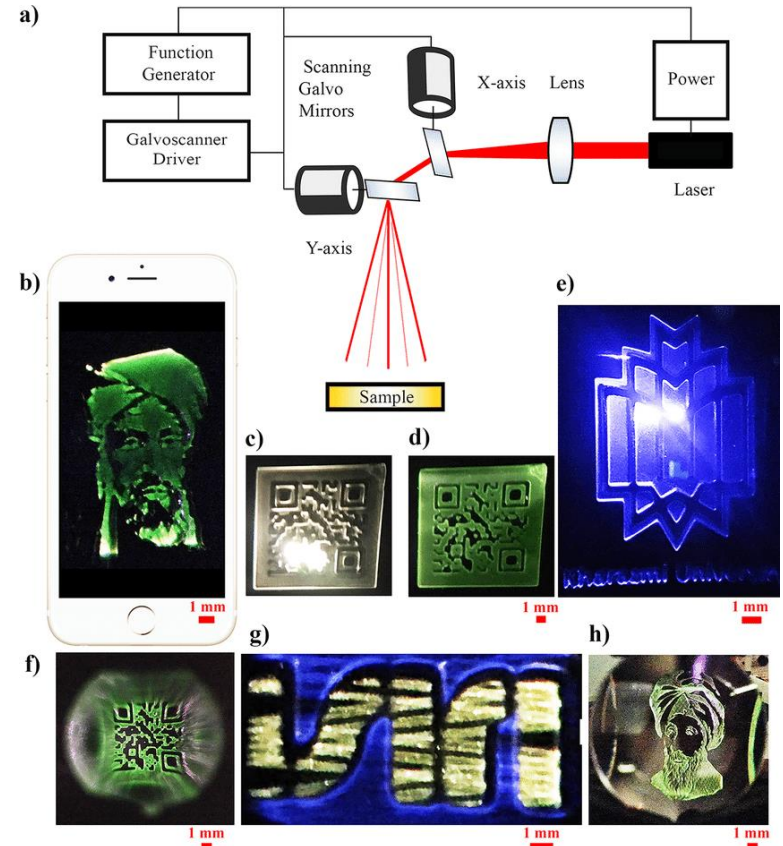
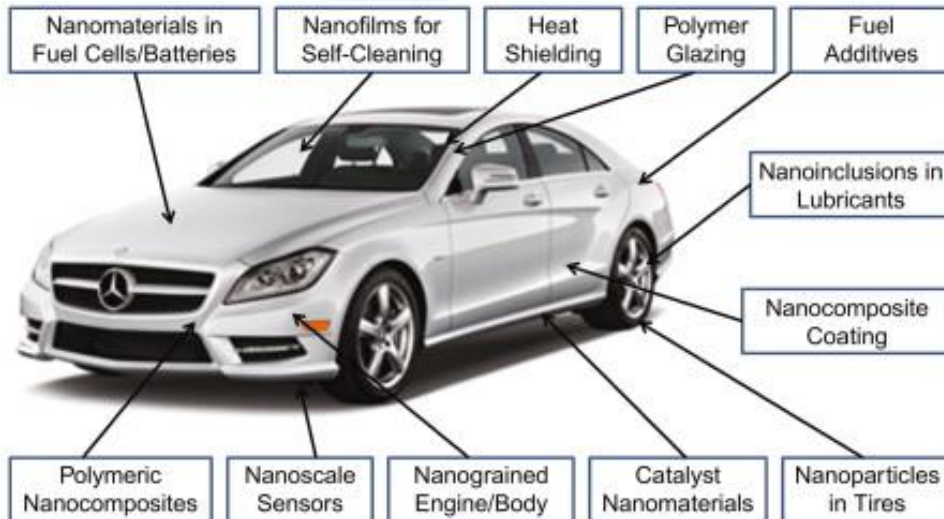
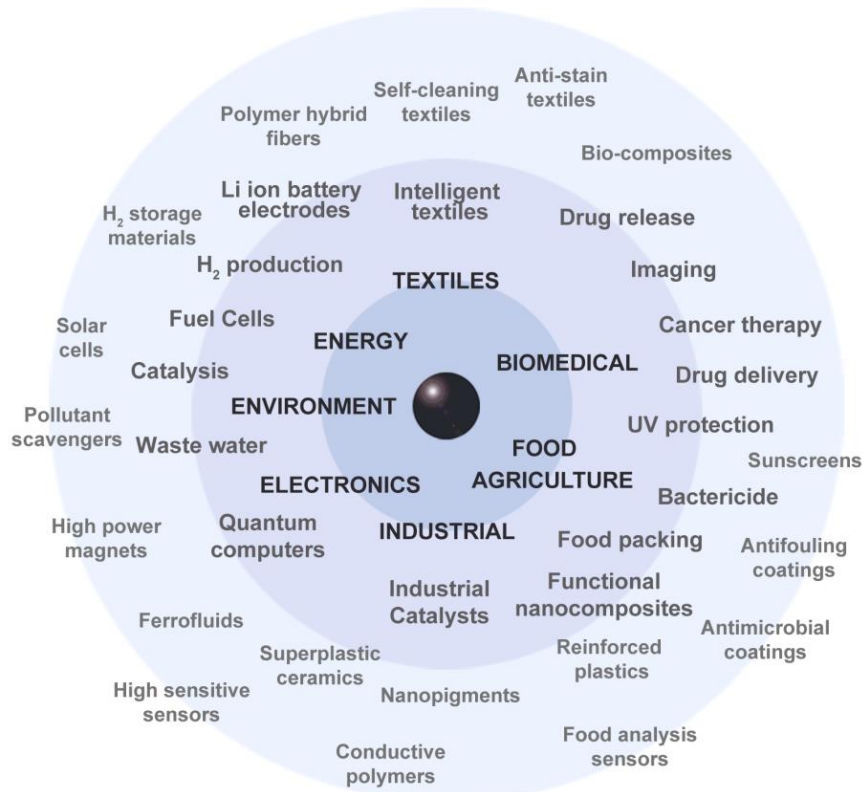
*From laser plume to complex multi-material nanoparticles*

# Outline

1. Motivations and applications
2. Modeling ultra-short laser interactions and nanoparticle formation in vacuum, in gases and in liquids
3. Laser interaction with nanoparticles
  - Molecular dynamics simulation of nanoparticle collisions
  - Molecular dynamics simulation of alloy nanoparticles
  - Complex nano-objects
4. Modeling nanoparticle formation in porous matrices
5. Summary and conclusions

## 1. Motivations and applications

# Nanoparticles and Nanocomposites



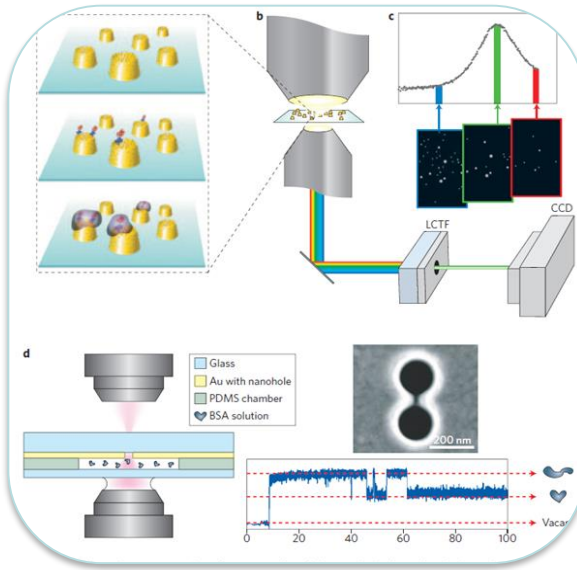
Kaboli et al. ACS Appl. Nano Mater



Optics and Security

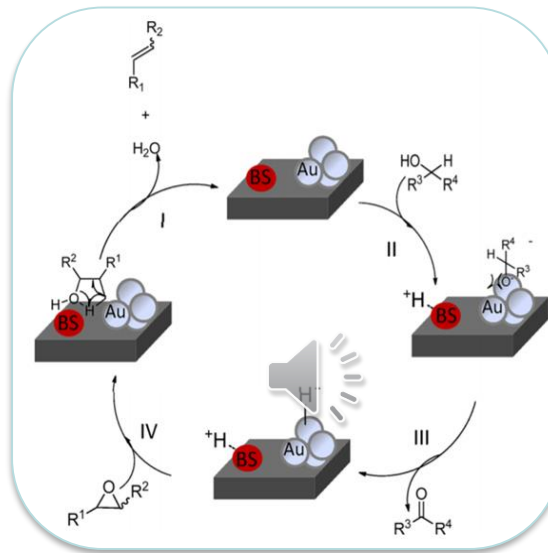
# Random and periodic nanocomposite structures

## Sensing



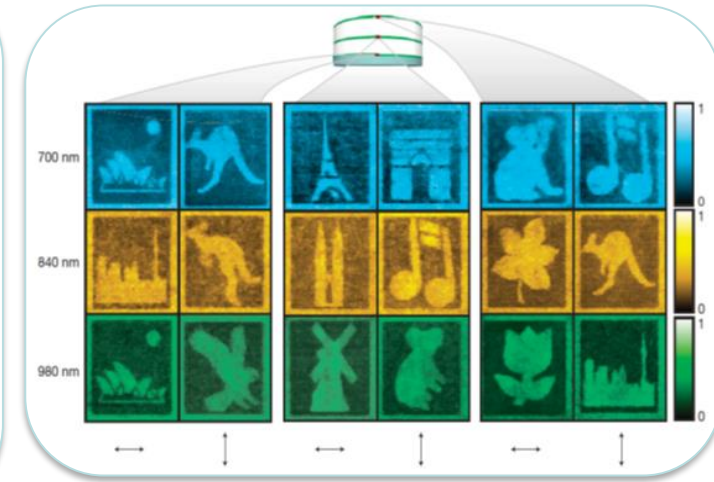
Nature Photonics 6, 709–713 (2012)

## Catalysis



Chem., Int. Ed., 49, 5545 (2010)

## Optical recording, security, etc.



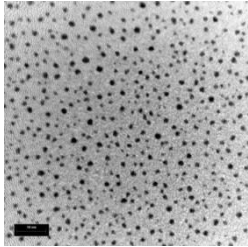
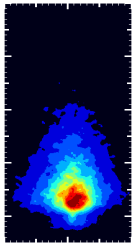
Nature, 459, 410 (2009)

**multiplexing**

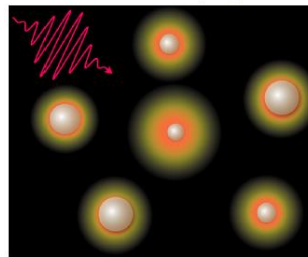
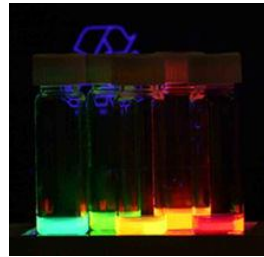
**Periodic nanocomposite structures are particularly interesting for optical applications, however the understanding of their formation is still challenging.**

# Main research directions

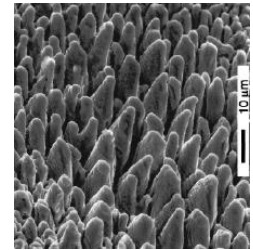
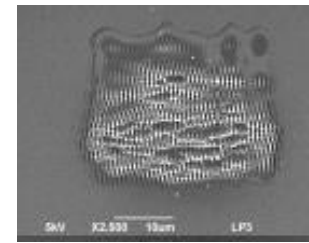
- **Laser-induced formation and modification of nanoparticles, monohybrids and nanostructures: modeling vs experiments**



Pulsed laser interactions

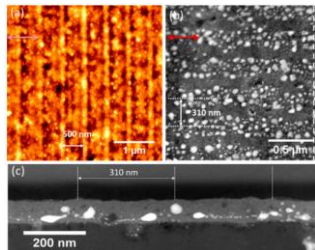


Laser ablation/fragmentation

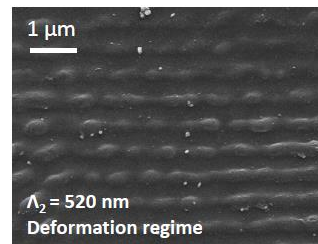


Laser-induced surface/volume structures

- **Laser-assisted formation of nanocomposite materials and metasurfaces**



Nanoparticles inside

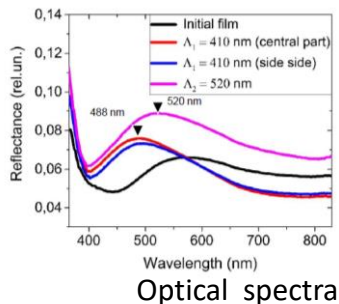


Nanoparticles on the surface



Hierarchical surface structures

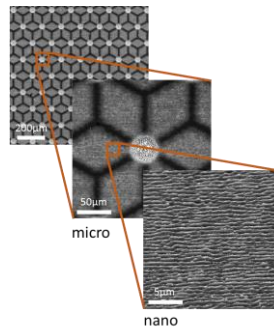
- **Properties and applications of the obtained materials: optical properties, wettability, cells and bacterial adhesion/repulsion**



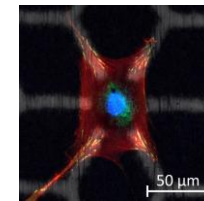
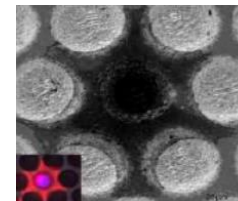
Optical spectra



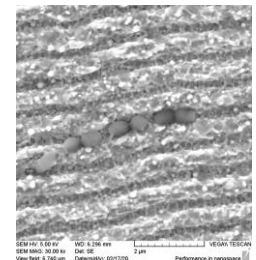
Wettability



nano



cell and bacteria adhesion on

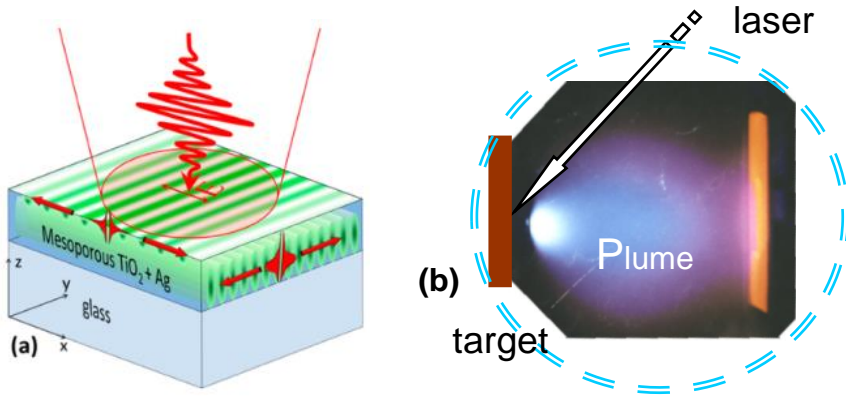


# Outline

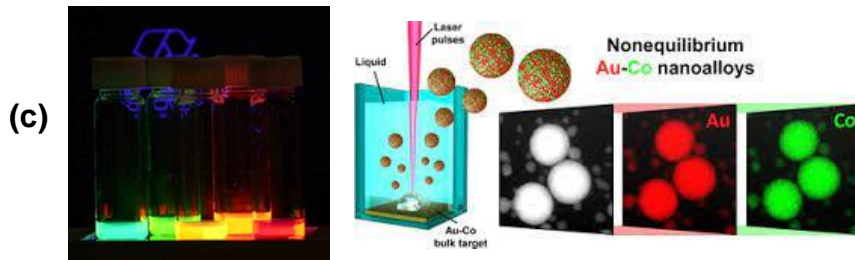
2. Modeling of laser interactions and nanoparticle formation in vacuum, in gases and in liquids



# Laser Interactions



In gas or in vacuum with different geometry



In liquids or in the presence of a colloids

## Laser interaction commonly involve:

- Energy propagation, electronic excitation, light scattering, reflection and absorption
- Electron-phonon relaxation, heat diffusion, pressure wave propagation, rarefaction and tensile stress, phase transitions, mechanical fragmentation
- Material removal (ablation), plasma plume expansion, reactions, clustering, etc...
- Often multi-pulse irradiation is used with various scanning and focusing conditions

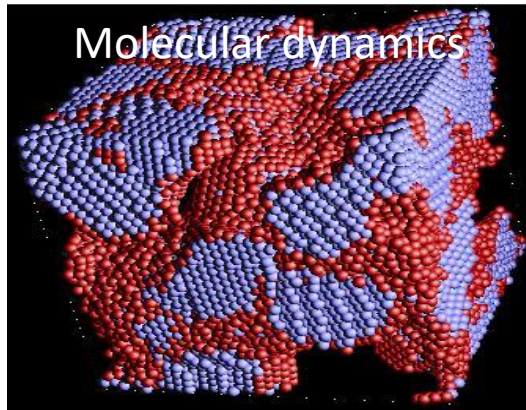
## Laser-induced nanoparticle formation

- Green synthesis methods, bio-compatibility
- Control over NP properties
- Scaling-up possibilities
- Possibility to create stable ultra-structures, nanoalloys, hybrids, etc.
- **Additional laser-particle interactions involve many physical and chemical processes**



# Modeling Approaches

## Atomistic (MD) vs Hydrodynamics (CFD)

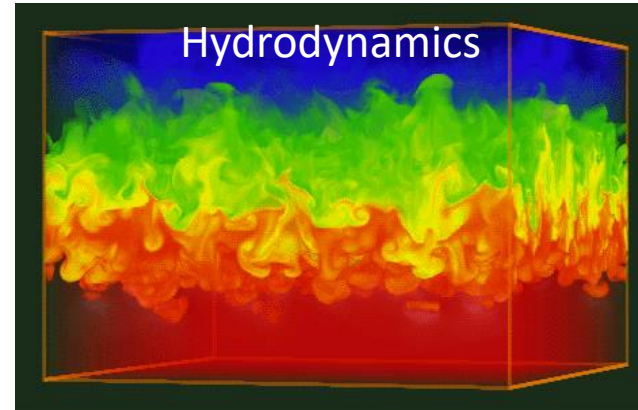


$V < 1 \mu\text{m}^3$ ;  $t \sim 1 \text{ ns}$

Dynamics

Interaction potential

Ionization?



Real temporal and spatial scales

LTE?

Nucleation, surface effects?

Equation of state (EOS)

# Ultra-short Laser Interactions

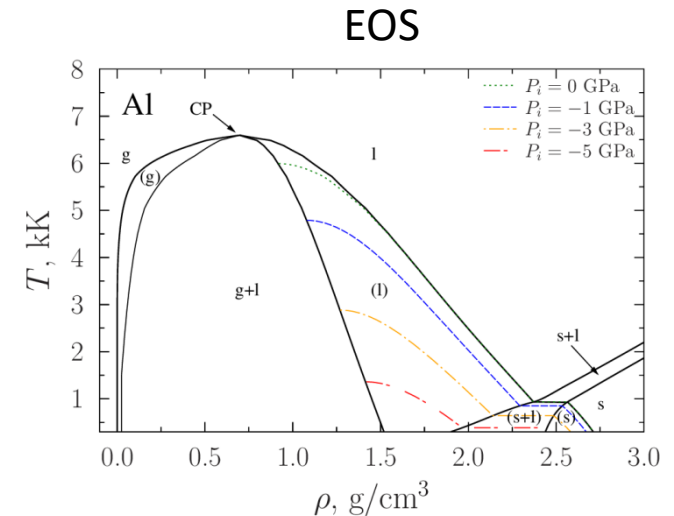
## CFD vs MD, Equation of State vs Interaction Potential

$$\frac{\partial(1/\rho)}{\partial t} - \frac{\partial u}{\partial m} = 0$$

$$\frac{\partial u}{\partial t} + \frac{\partial(P_{\text{ion}} + P_{\text{el}})}{\partial m} = 0$$

$$\frac{\partial e_{\text{ion}}}{\partial t} + P_{\text{ion}} \frac{\partial u}{\partial m} = \gamma_{ei}(T_{\text{el}} - T_{\text{io}})/\rho$$

$$\frac{\partial e_{\text{el}}}{\partial t} + P_{\text{el}} \frac{\partial u}{\partial m} = \frac{\partial}{\partial m} \left( \rho \kappa_{\text{el}} \frac{\partial T_{\text{el}}}{\partial m} \right) - \gamma_{ei}(T_{\text{el}} - T_{\text{ion}})/\rho + Q_L/\rho$$



$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i + \xi_i m_i \mathbf{v}_i^T + \mathbf{F}_i^{\text{el}} \quad \text{LAMMPS}$$

$$\frac{\partial(\rho e_{\text{el}})}{\partial t} + \frac{\partial(\rho e_{\text{el}} u)}{\partial z} + P_{\text{el}} \frac{\partial u}{\partial z} = \frac{\partial}{\partial z} \left( \kappa_{\text{el}} \frac{\partial T_{\text{el}}}{\partial z} \right) - \gamma_{ei}(T_{\text{el}} - T_{\text{ion}}) + Q_L(t, z)$$

Embedded atom "EAM"

$$E_i = F_{\alpha} \left( \sum_{j \neq i} \rho_{\beta}(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij})$$

Zhakhovskii *et al.* Appl. Surf. Sci. 255 (2009)

# Ultra-short Laser Interactions

## Laser energy propagation and absorption

In general: Maxwell equations combined with material ionisation

Numerically: Depending on the material and on the geometry

3D FDTD , NSE, Maxwell-Bloch, etc combined with electronic excitation-relaxation, currents, diffusion, etc.

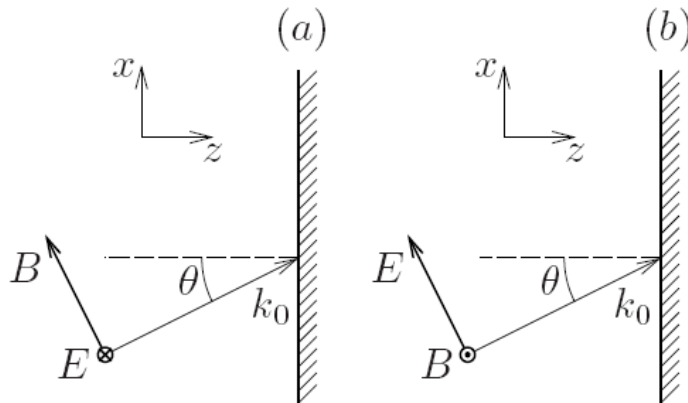


Figure 3. Polarization of laser light: (a)—s; (b)—p.

1D metal ablation: Helmholtz equation

$$\frac{\partial^2 E}{\partial z^2} + k_0^2 [\varepsilon(z) - \sin^2 \theta] E = 0.$$

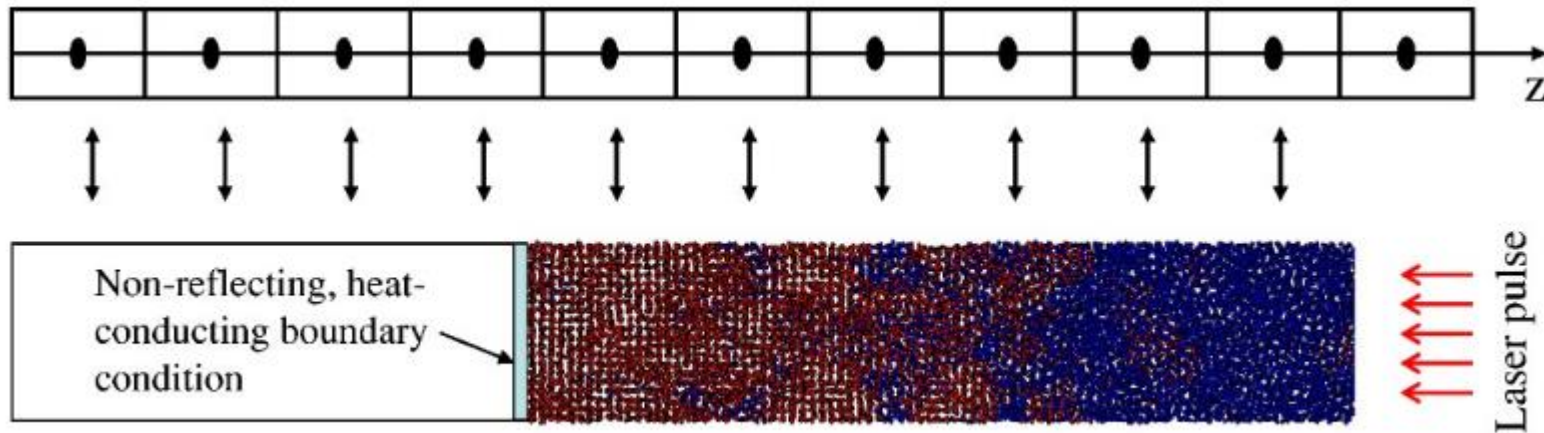
$$\frac{\partial^2 B}{\partial z^2} + k_0^2 [\varepsilon(z) - \sin^2 \theta] B - \frac{\partial \ln \varepsilon(z)}{\partial z} \frac{\partial B}{\partial z} = 0$$

$$Q_L(t, z) = I(t) \frac{\omega_L}{c} \text{Im}\{\varepsilon(t, z)\} |E(t, z)/E_L(t)|^2$$

# Ultra-short Laser Interactions

## Molecular Dynamics + TTM (TTM-MD)

Conduction electrons

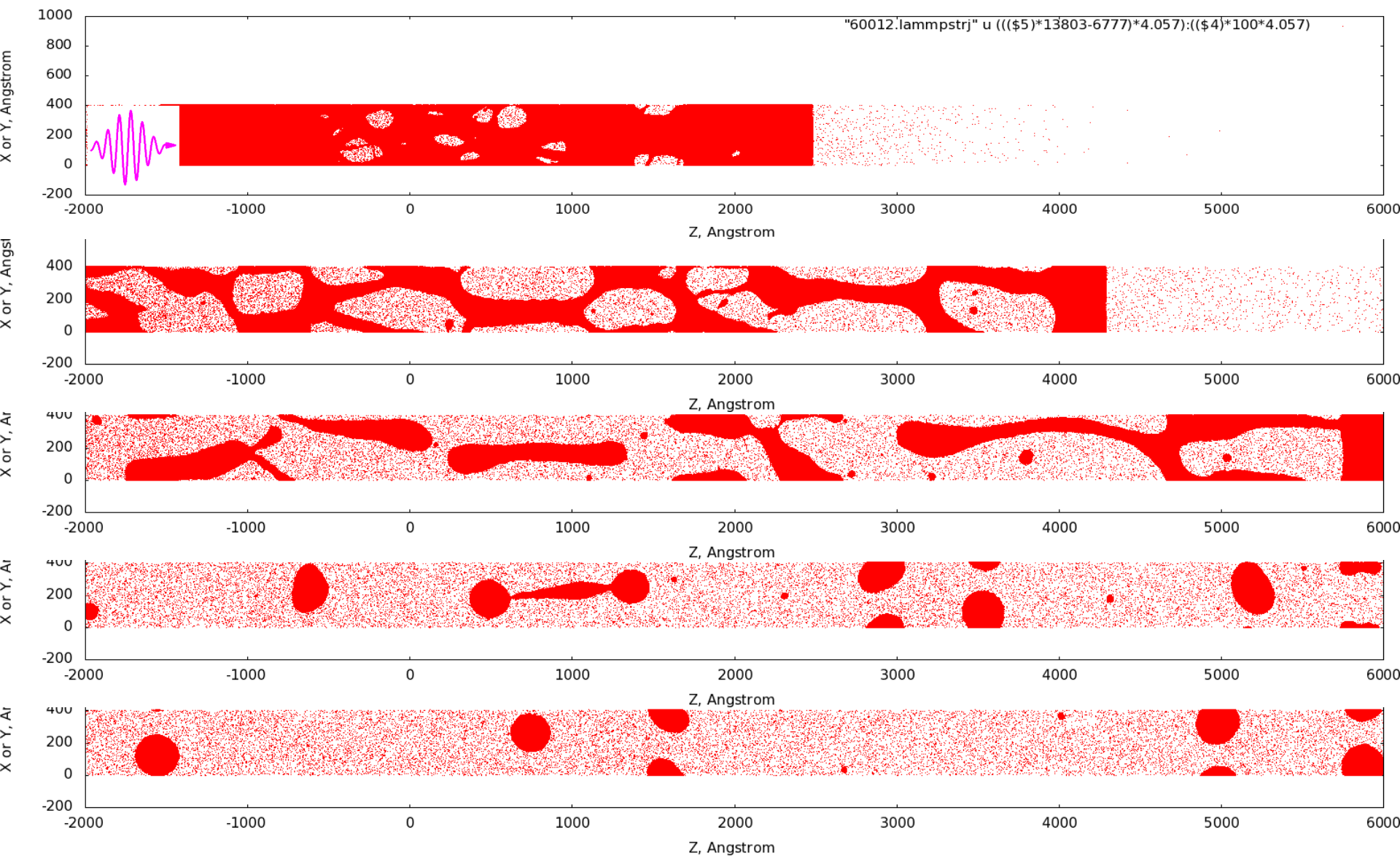


$$C_e(T_e) \frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z} \left( K_e(T_e) \frac{\partial T_e}{\partial z} \right) - G(T_e - T_l) + S(z, t), \quad \text{TTM}$$

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i + \xi m_i \mathbf{v}_i^T, \quad \text{MD} \quad \xi = \frac{1}{n} \sum_{k=1}^n G V_N (T_e^k - T_l) \bigg/ \sum_i m_i (\mathbf{v}_i^T)^2$$

Ivanov & Zhigilei, Phys. Rev. B, 68, 064114 (2003)

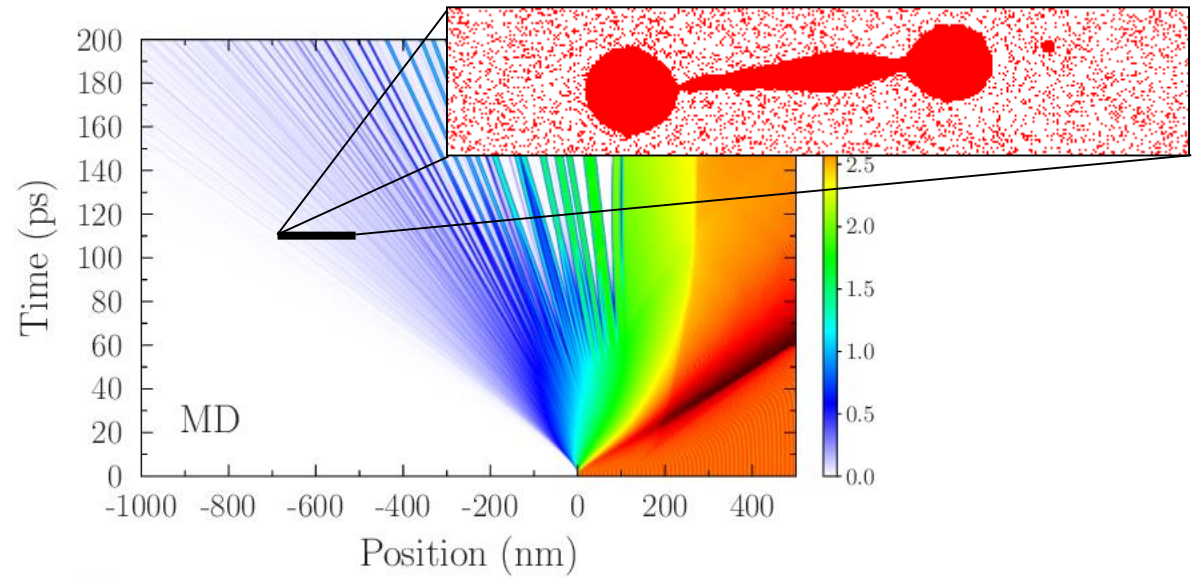
# Ablation & Nanoparticles (10M atoms, $F=1 \text{ J/cm}^2$ , Al)



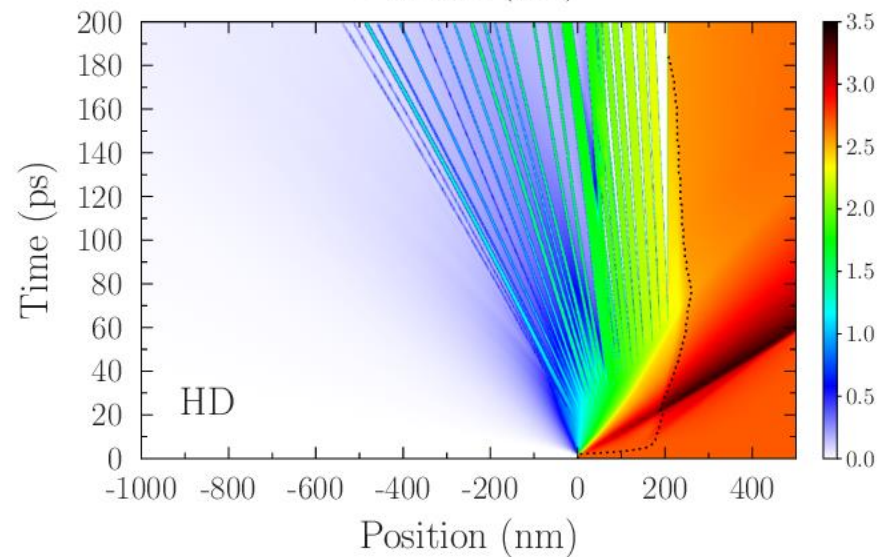
## Density

$$\text{Al}, F = 2 \text{ J/cm}^2$$

TTM-MD

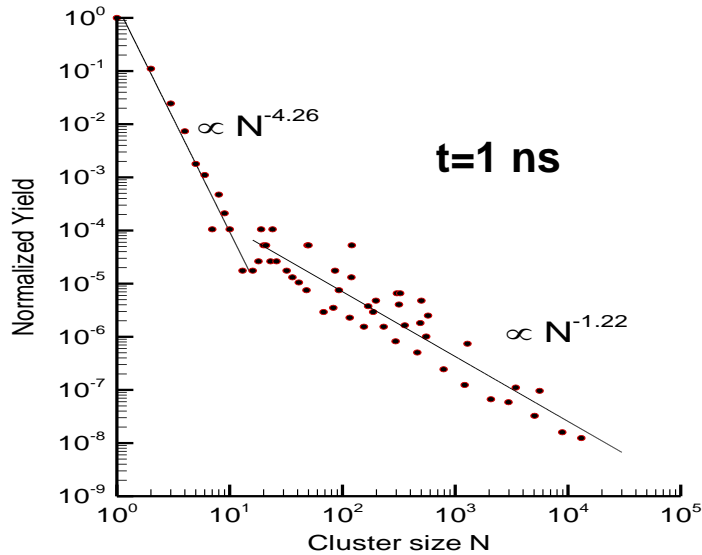


Hydrodynamics

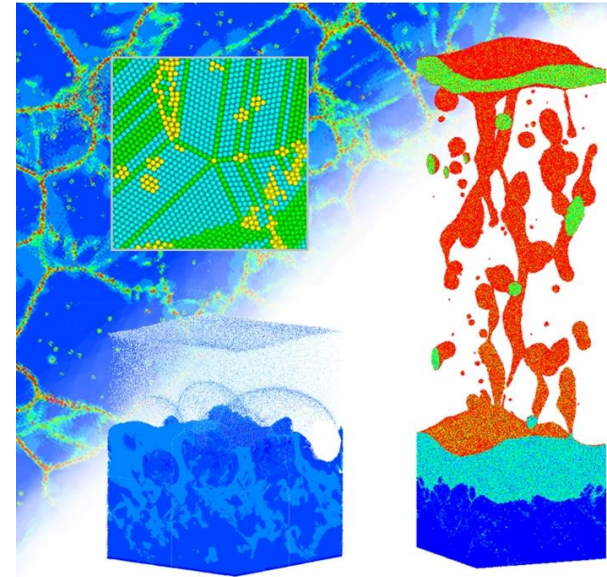
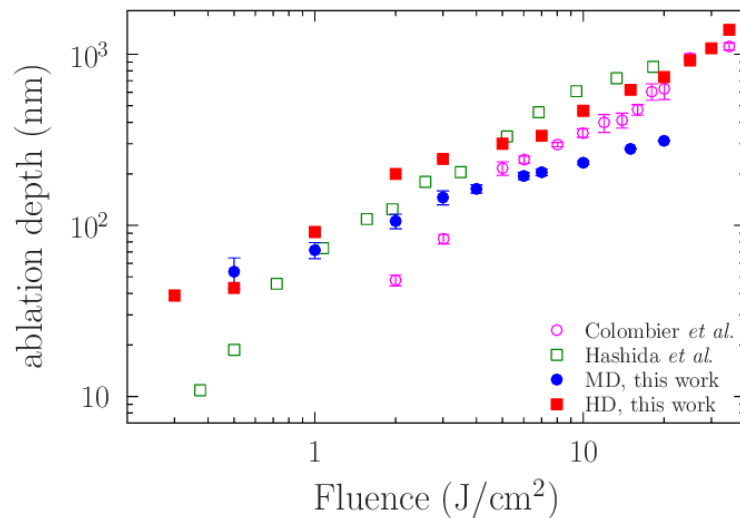


# Molecular Dynamics Simulations

Allow to get nanoparticle size distributions and describe non-equilibrium processes



$\tau = 15 \text{ ps}$ ,  $F \sim 2 \text{ Fth}$ ,  $40 \times 10 \text{ nm}$ ,  $t = 1 \text{ ns}$



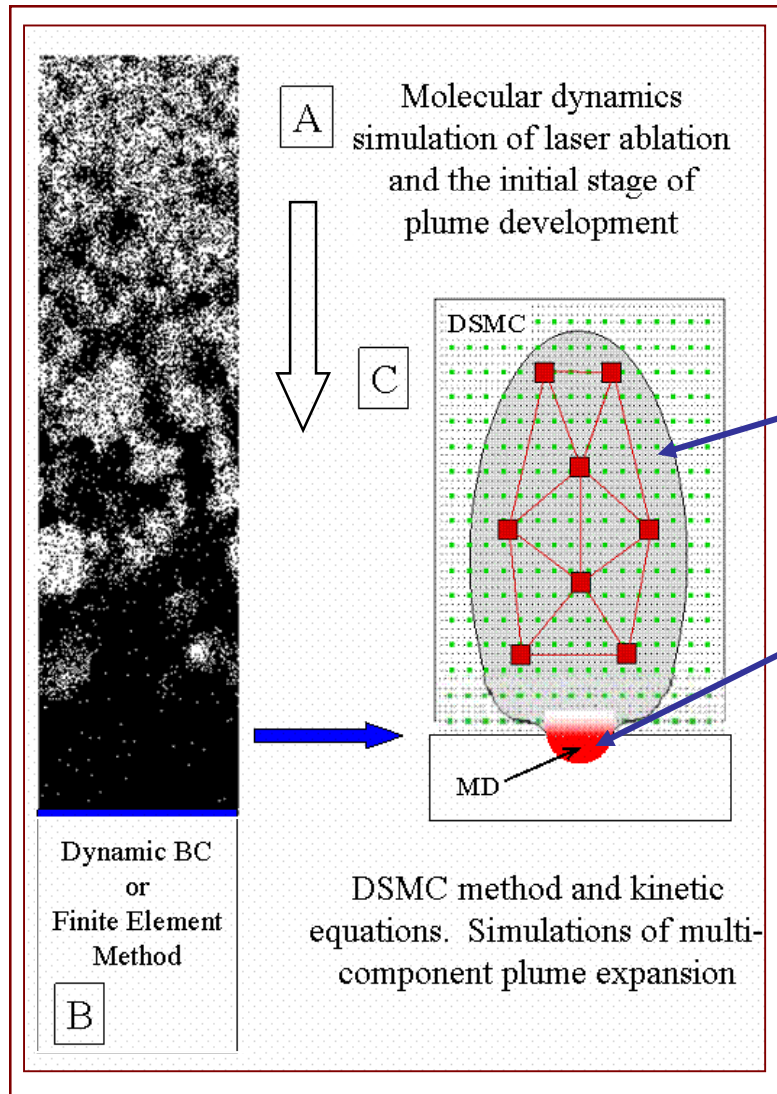
Collaboration with L.V. Zhigilei et al. (Virginia State University, USA)

Practically all the molten material is ablated

$$Labl \sim L_0 \ln(F_{abs}/F_0), \quad E > E_b$$



# Longer Plume expansion: Combined Models



## Combinaton

- Direct Simulation Monte Carlo

- Molecular Dynamics

Detailed information

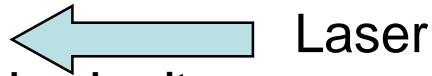
Continuous plume

Size distribution of aggregates

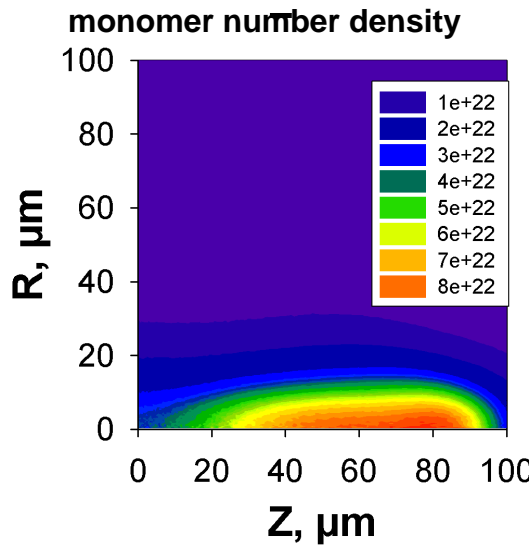
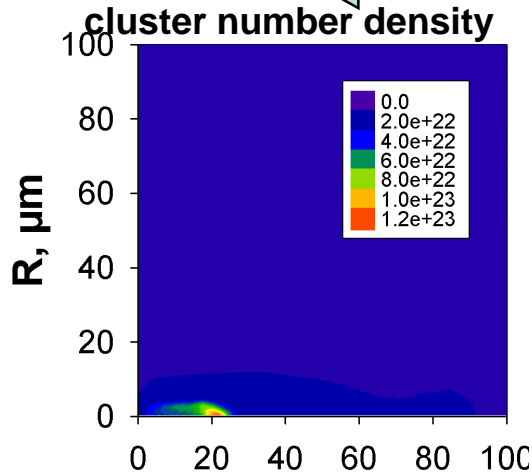
K. Gouriet, thèse (2008)

# Combined Models vs Experiments

## MD-DSMC

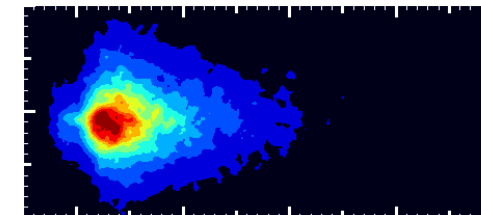
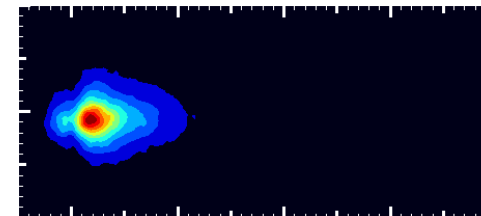
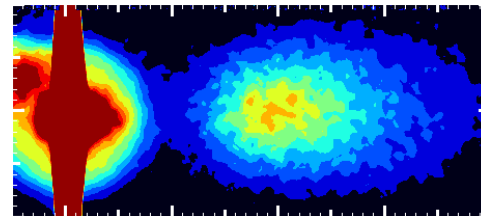
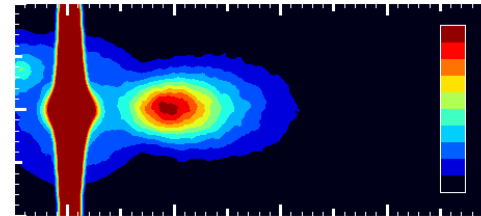


$$F_{las} = 4 \text{ Jcm}^{-2}$$



Numerical results

$t = 50 \text{ ns}, 15 \text{ ps}, F = 61 \text{ J/m}^2, R = 10 \mu\text{m}$



0 1 2 3 4 (mm)

Experimental results (J. Hermann, S. Noël)

100 fs  $F = 4 \text{ J/cm}^2$

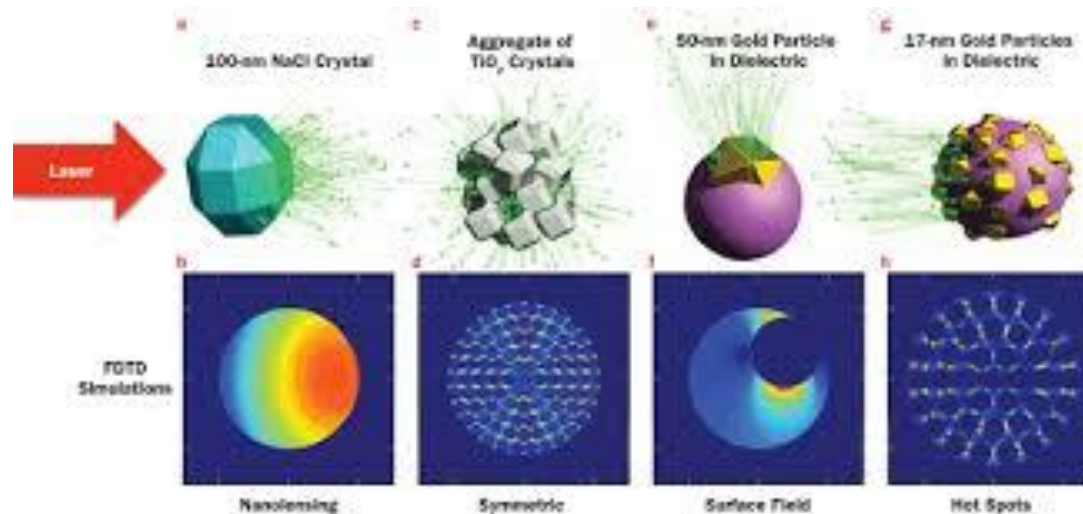
# Outline

## 3. Laser interactions with nanoparticles.

Molecular dynamics simulation of nanoparticle collisions

Molecular dynamics simulation of alloy nanoparticles

Complex nano-objects



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

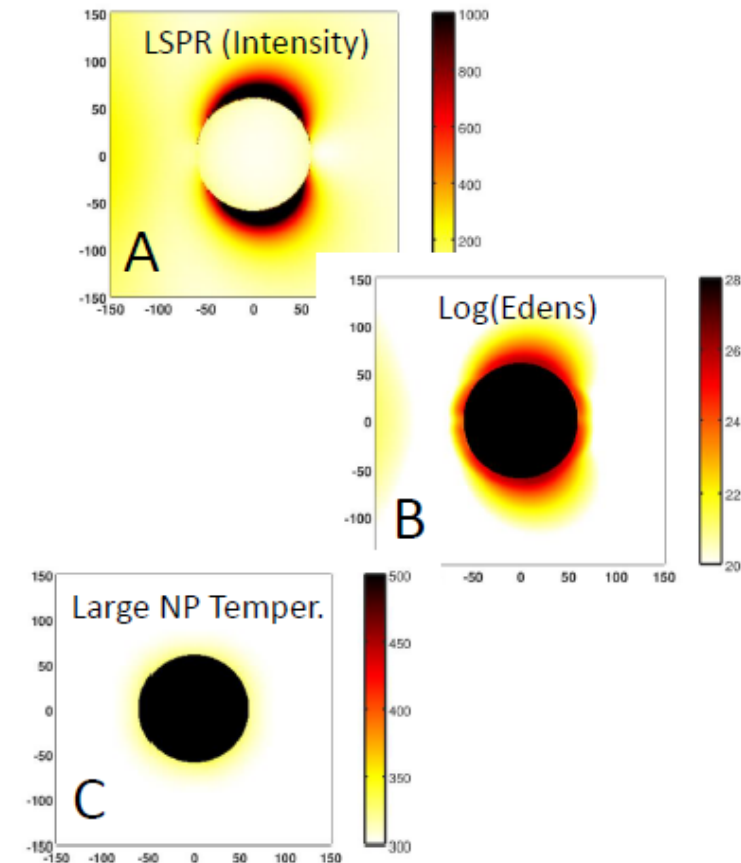
### Nanoparticle

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

### 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 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

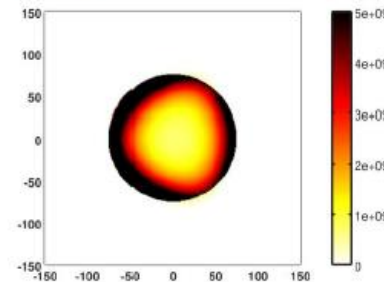
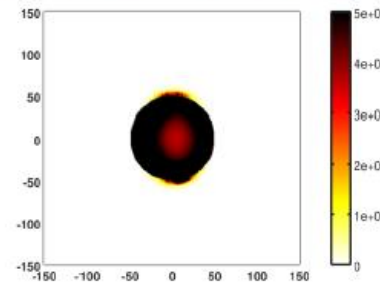
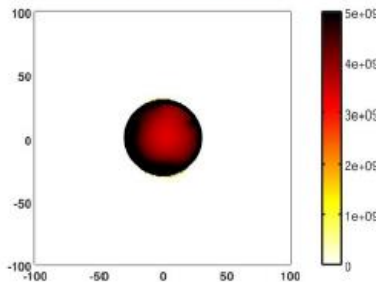
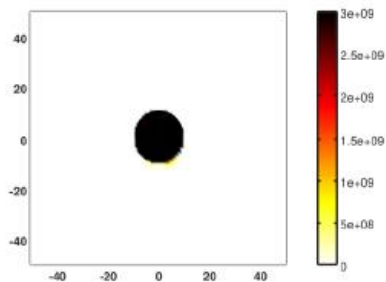
Strong field enhancement

R = 75 nm

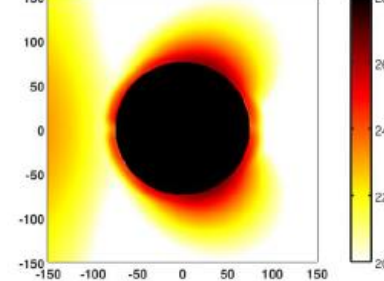
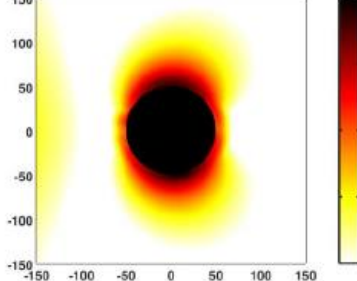
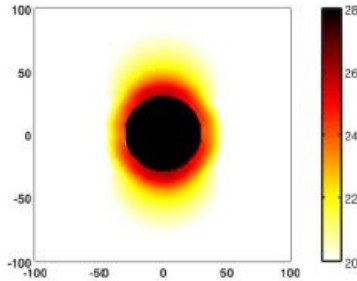
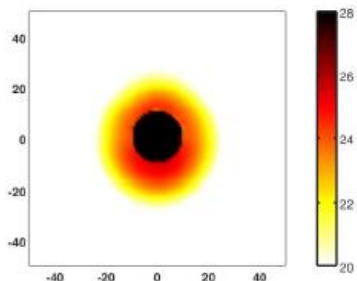
Particle  $\gg$  skin depth

Slow energy transfer to water

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



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



# Laser Interaction with Au NPs in Water

## Three interaction regimes and the mechanisms involved

### Regime I

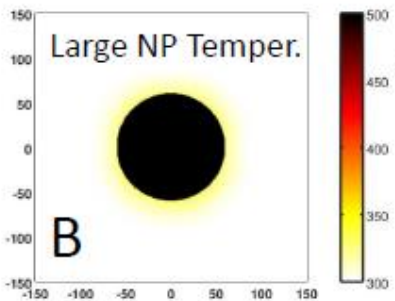
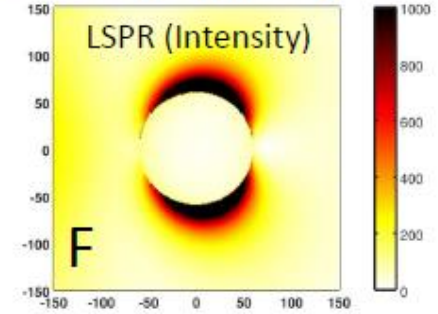
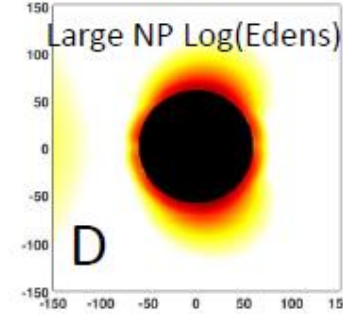
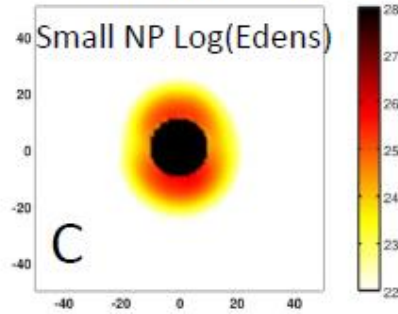
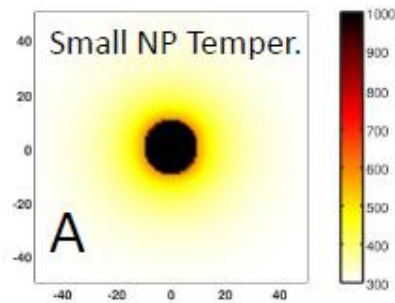
Laser heats Au NP;  
Au NP transfers heat to water

### Regime II

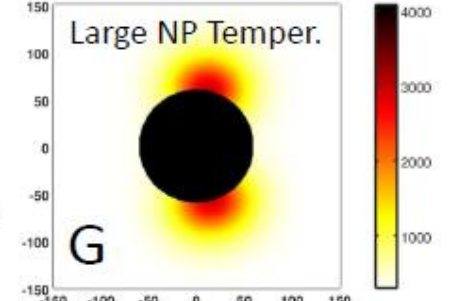
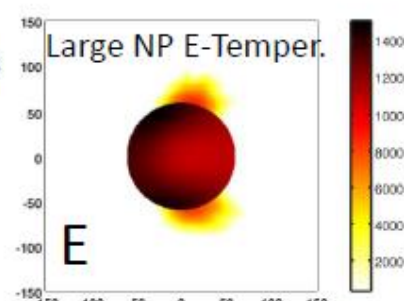
E-ph emission from Au NP  
to water interface;  
Emitted Carriers heat water

### Regime III

LSPR triggers water  
photo-ionization;  
Induced Carriers heat water



Due to inhomogeneous  
distribution  
of absorbed energy



# 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

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

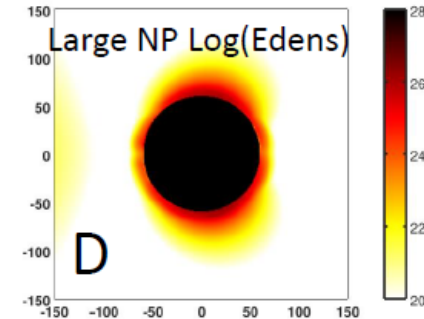
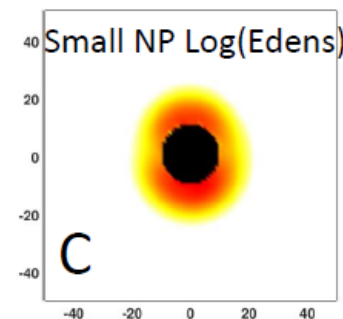
Thomas-Fermi

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

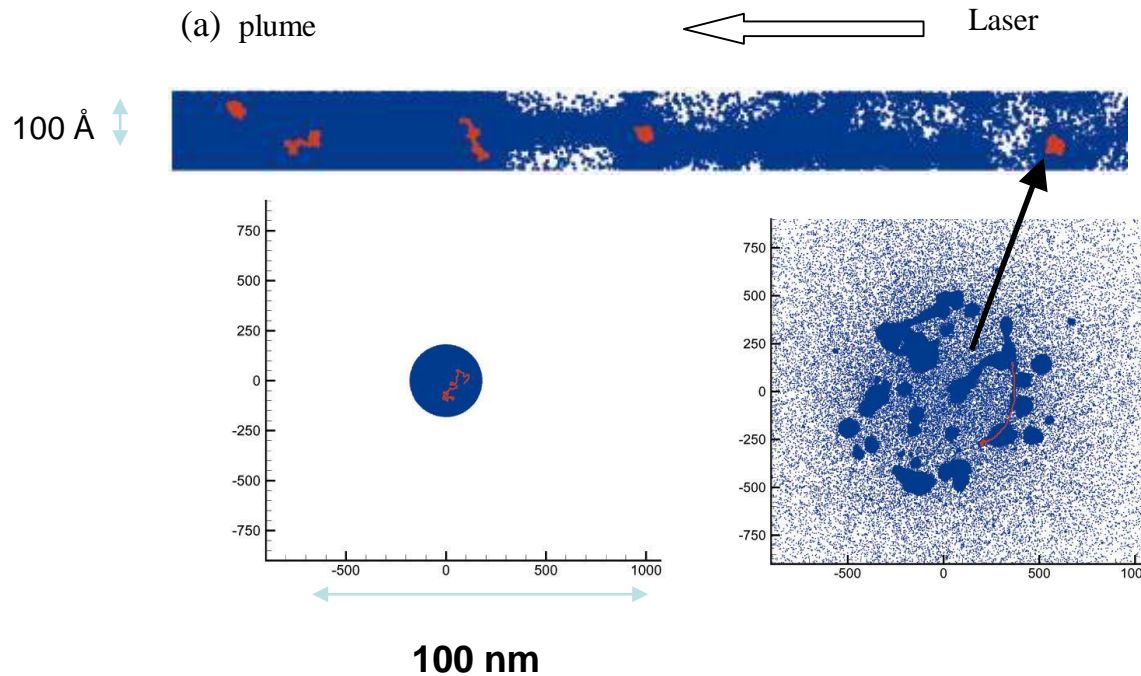
Avalanche  
ionization



# Molecular Dynamics Simulations

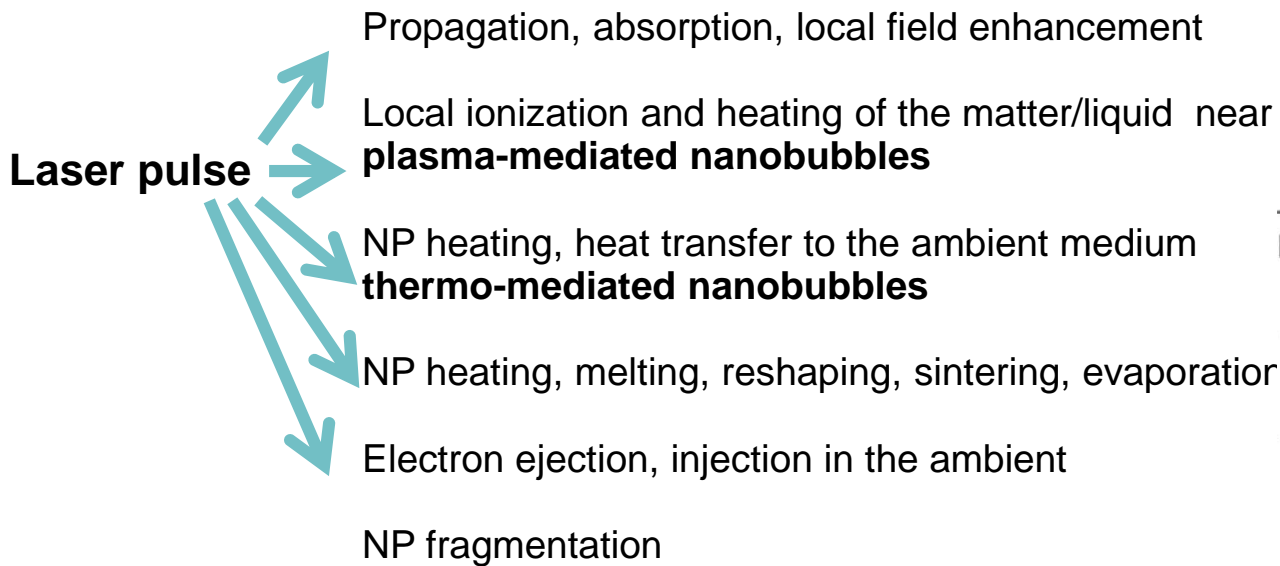
Decomposition of the ablated material after the absorption of laser radiation

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

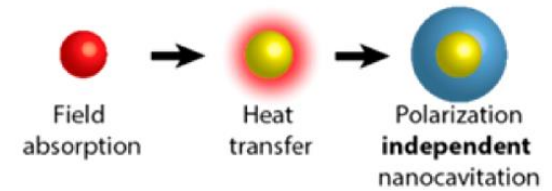




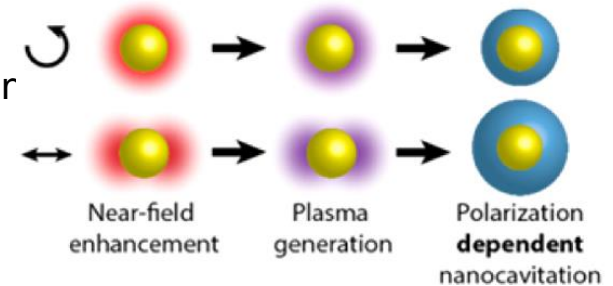
# Ultra-short Laser Interactions with NPs



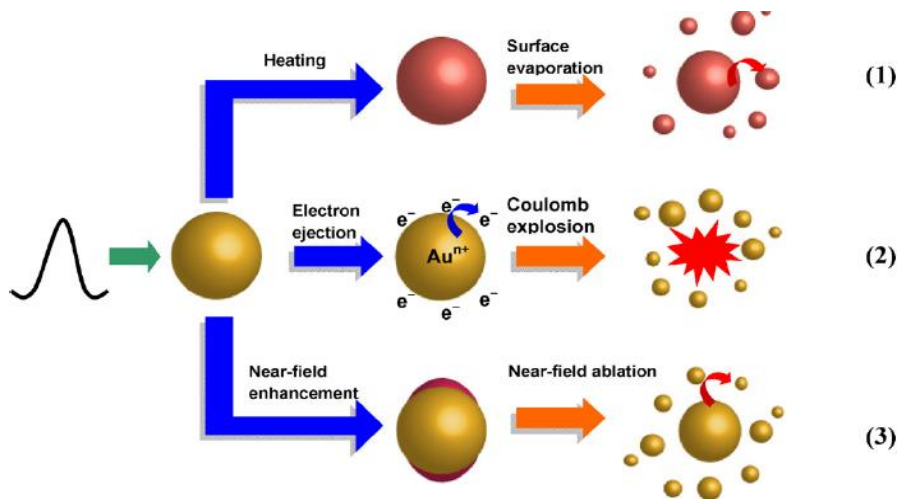
## Thermo-mediated nanobubbles



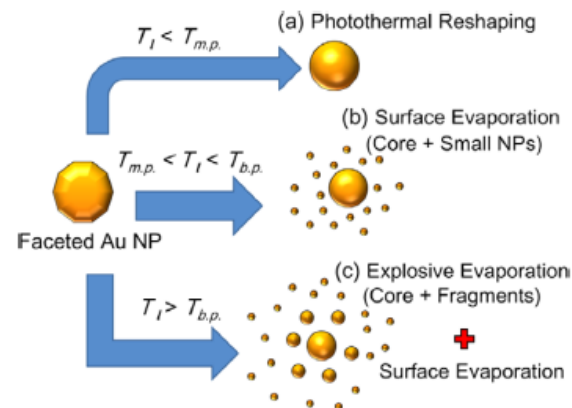
## Plasma-mediated nanobubbles



*Lachaine et al. Photonics (2013)*



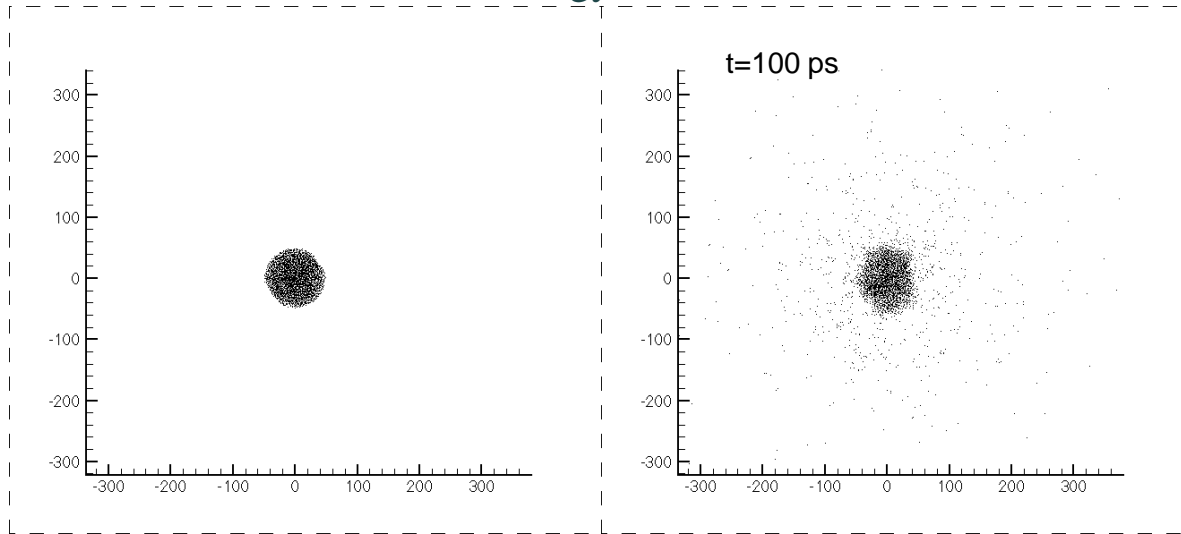
*Hashimoto et al. J. PhotChem&PhotBiology (2012)*



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

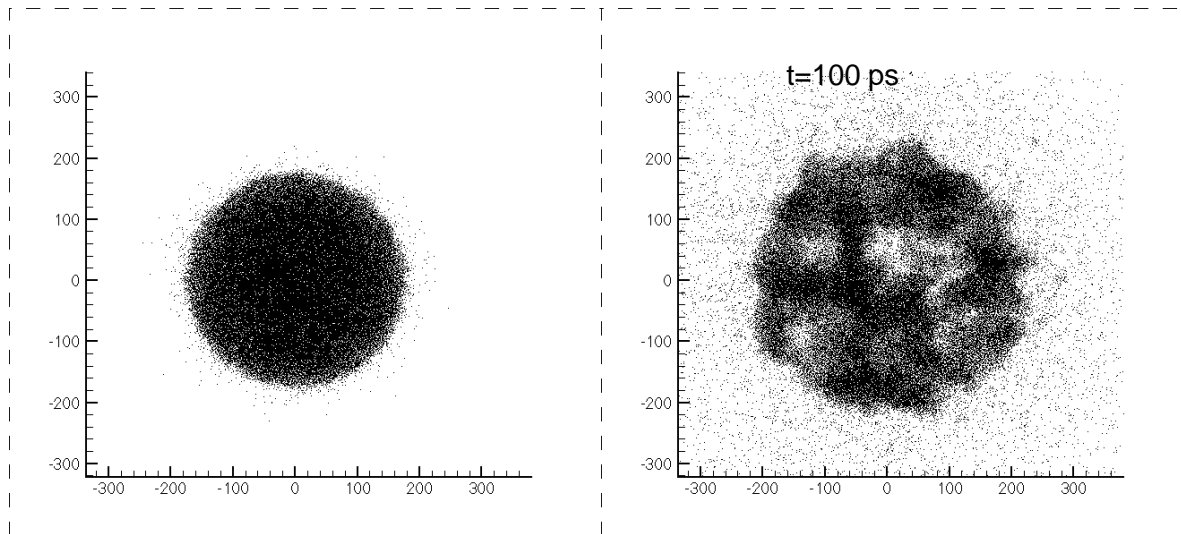
# Laser Fragmentation of NPs: MD simulations

$R=50 \text{ \AA}$ , absorbed energy  $e=0.6 \text{ eV/mol}$



Smaller NPs  
**Evaporation**  
(can be also due to Coulomb Explosion for small clusters and fs laser)

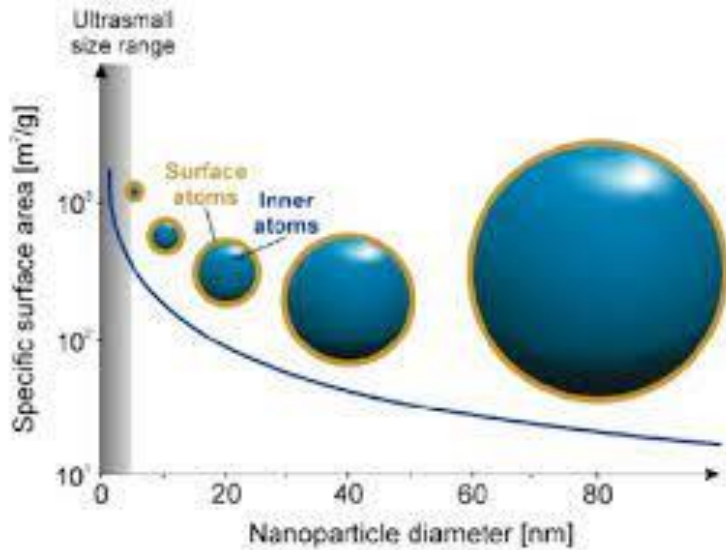
$R=150 \text{ \AA}$ , absorbed energy  $e=0.6 \text{ eV/mol}$ .



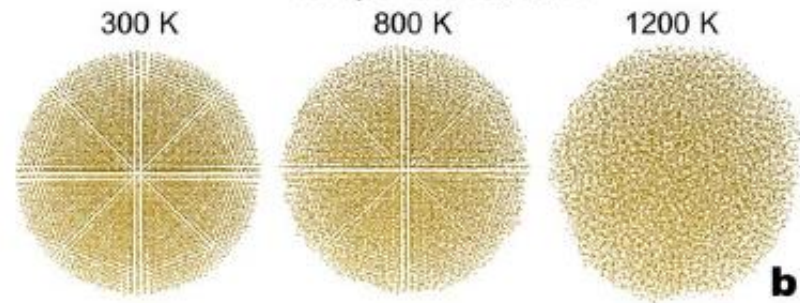
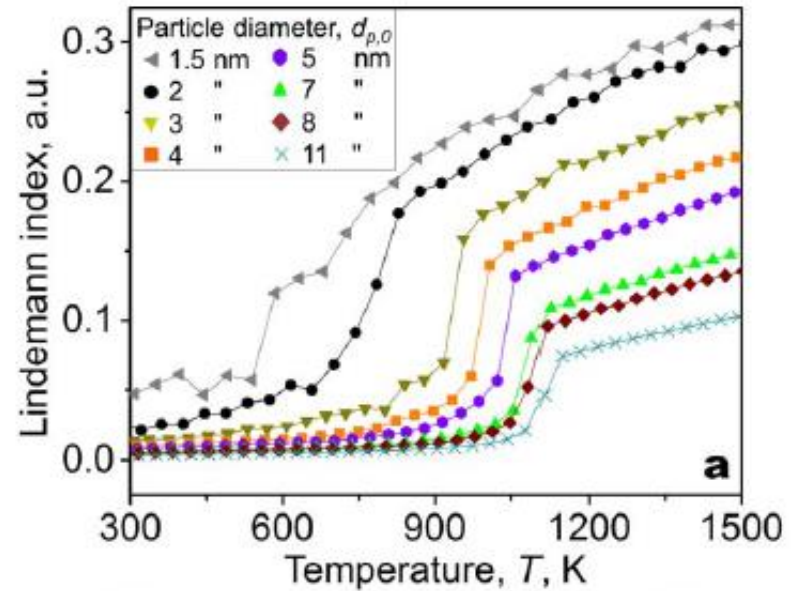
Larger NPs  
**Fragmentation due to thermo-mechanical effects**

# NP's Heating and Melting : Size Effects

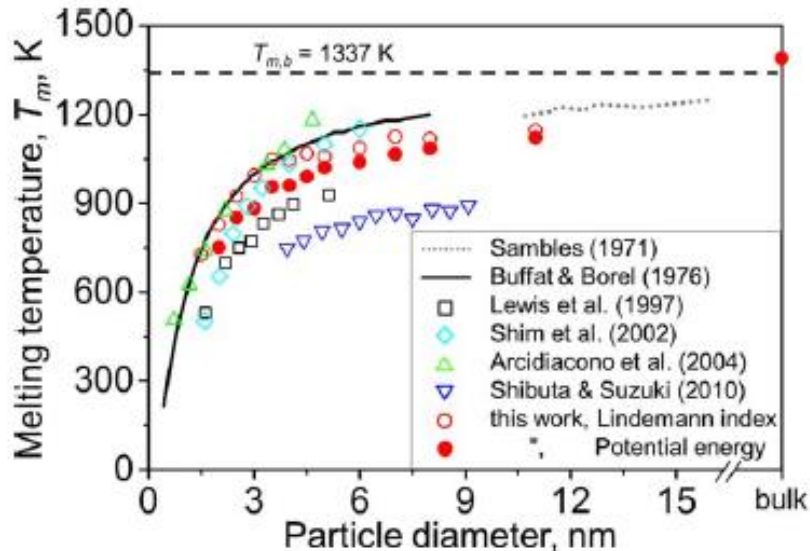
## Melting and structural transformations: role of NP's sizes



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

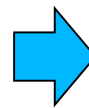
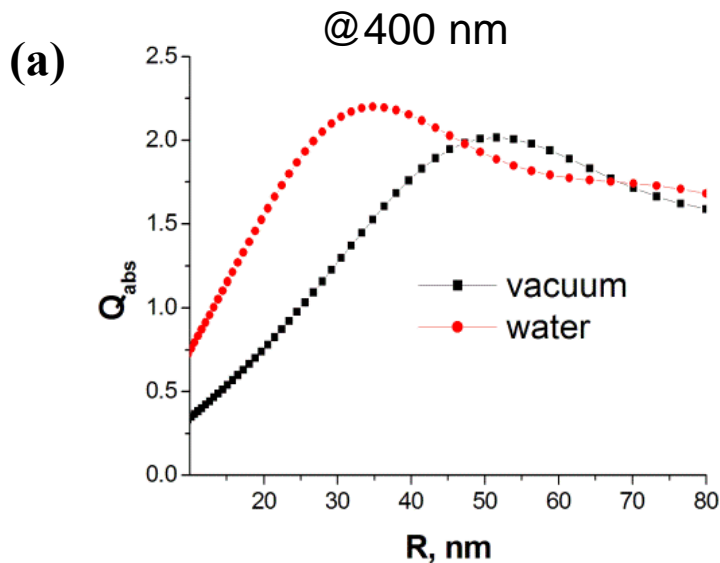


E. Goudeli et al., *AIChE* 2015



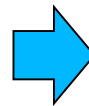
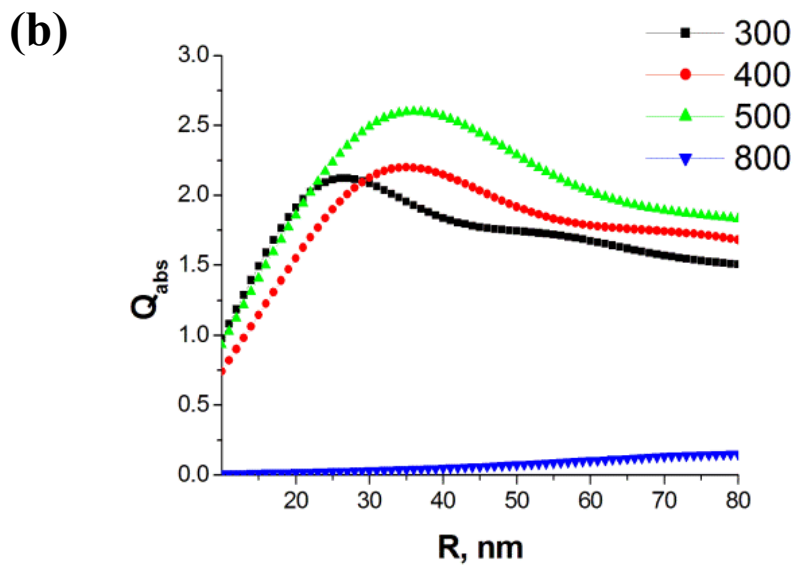
# Laser Energy Absorption vs NP's size

Absorption coefficient / efficiency  
(beyond SPR for gold)



**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

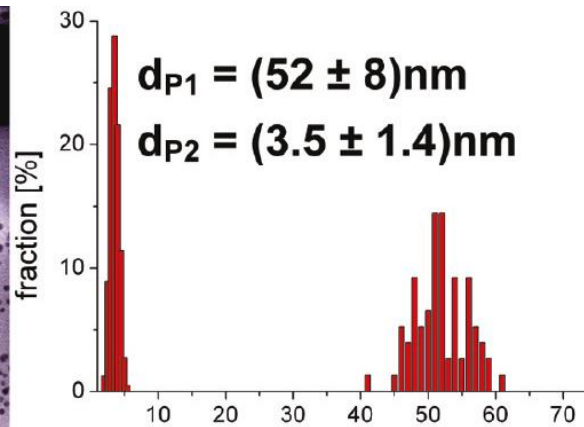
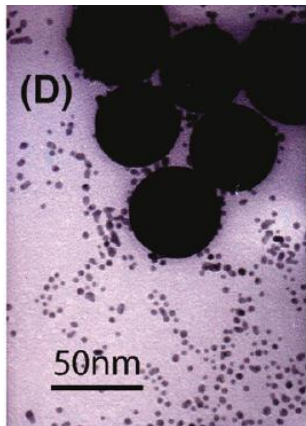
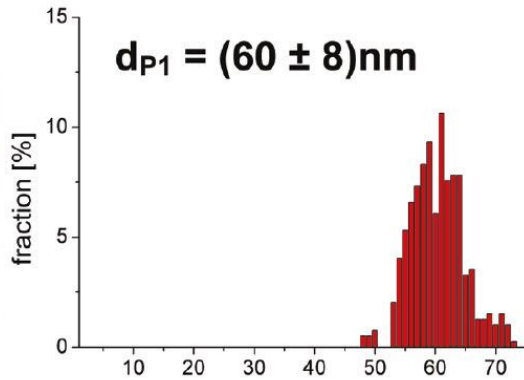
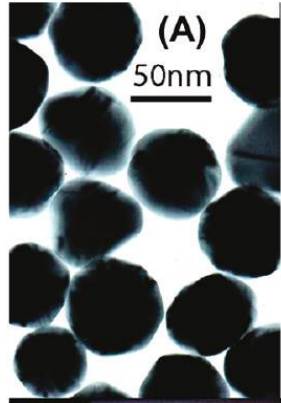


Gold NPs in water for different wavelength @300-800nm

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

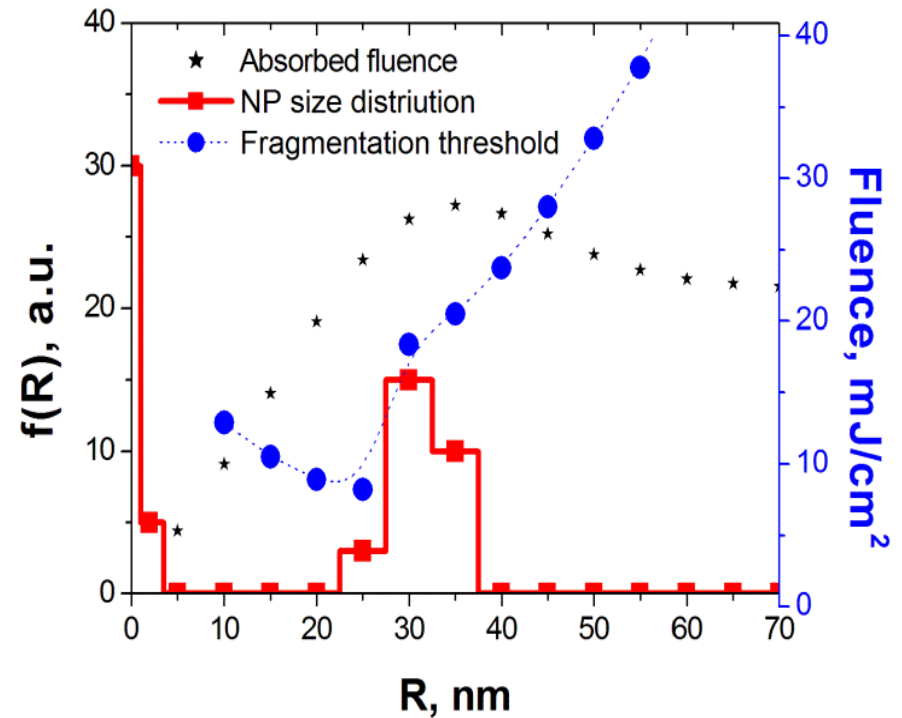
# Ultra-short Laser Interaction with Au NPs in Water

## Experiments



Werner et al. *J. Phys. Chem. C*, 2011,  
115, 8503

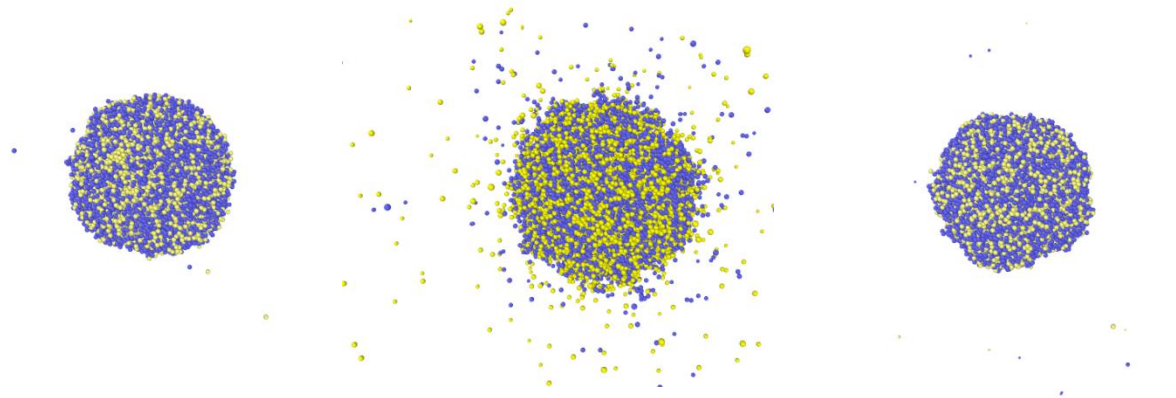
## Modeling



Good correlation with  
evaporation threshold vs R

# Metal NPs: Evaporation vs Fragmentation

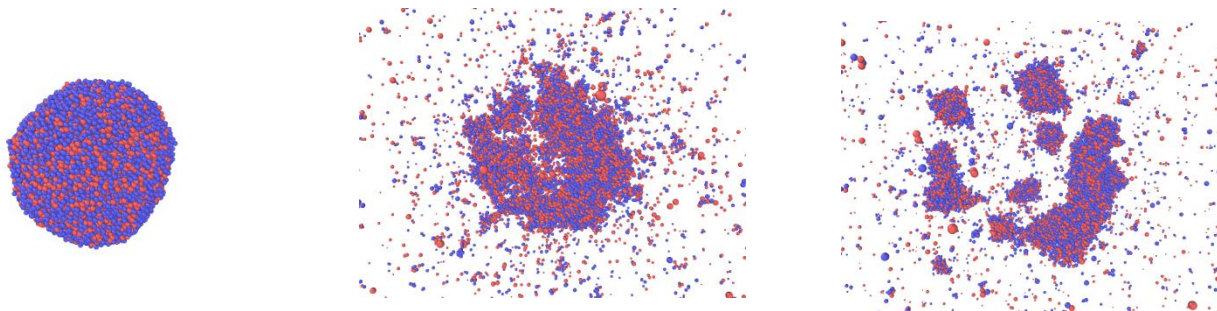
Au-Co , R= 40 50%,  
absorbed energy below threshold



We number  
(drag force/coherence  
force)

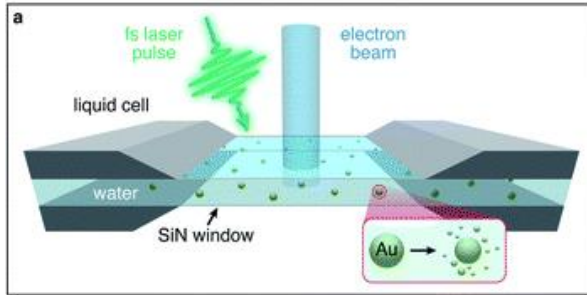
$W_{ed} = (E_d/E_k) W_e$   
(deformation energy)/  
kinetic energies

Au-Co , 50% R40 time: 0, 150, 400,  
absorbed energy above threshold

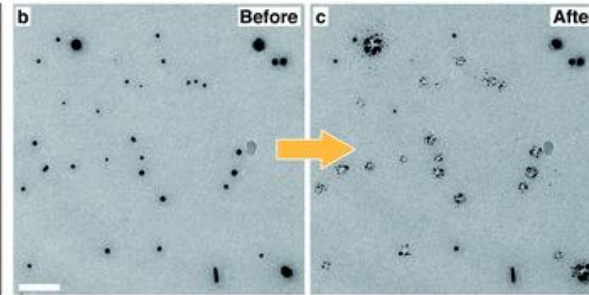


# Metal NPs Fragmentation: Experiments

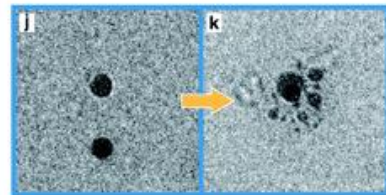
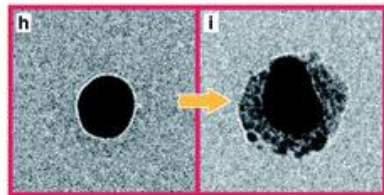
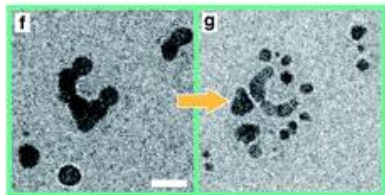
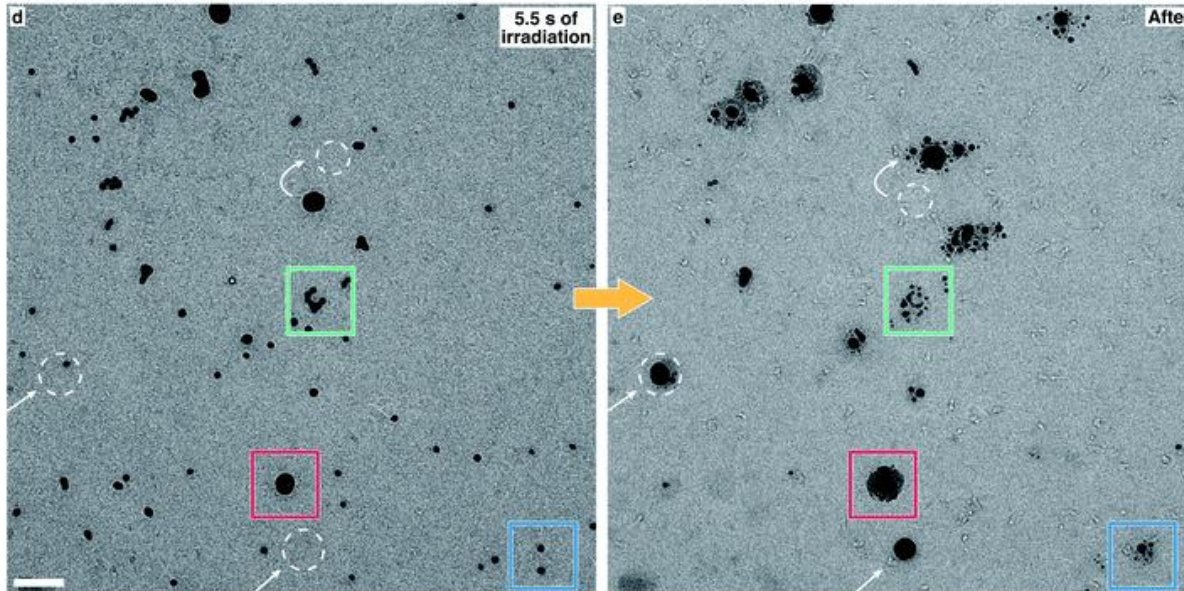
Experimental geometry



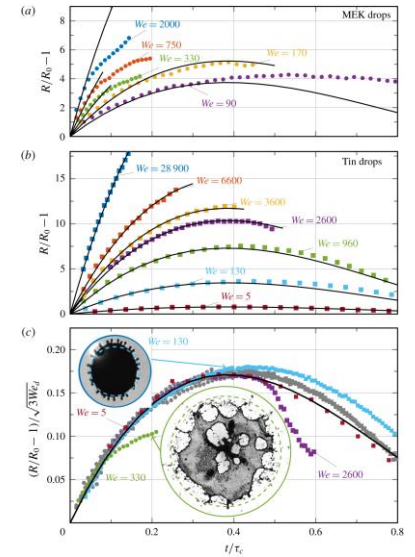
Femtosecond laser irradiation of gold nanoparticles



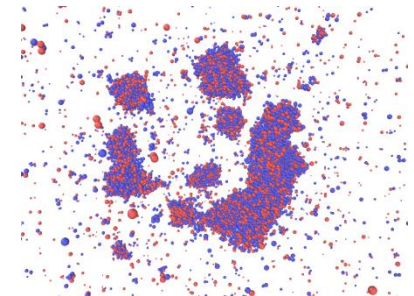
In situ observation of gold nanoparticle fragmentation under femtosecond laser irradiation



AL Klein · 2020 drop model

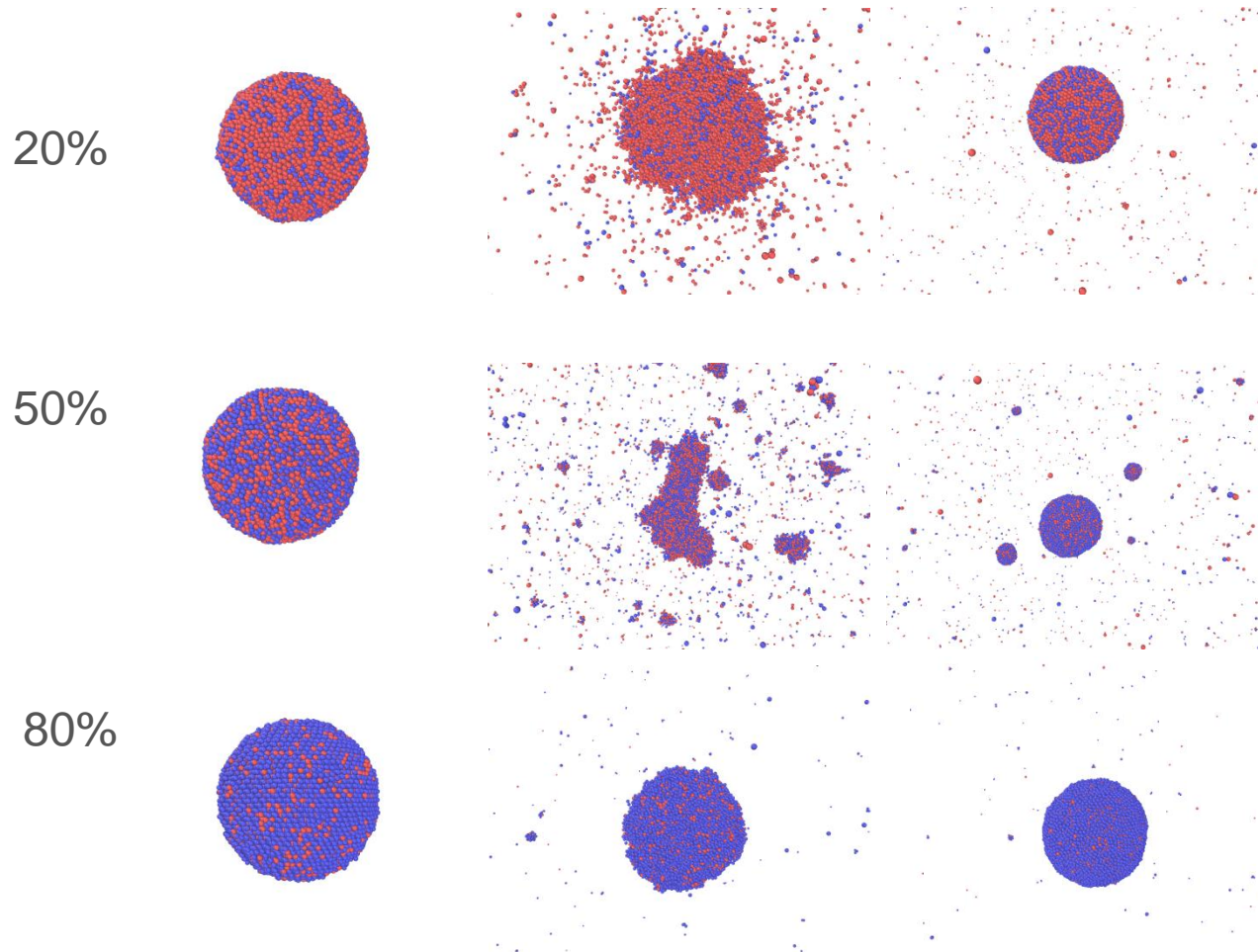


Look similar to MD results for NP



# Alloy NPs: Composition affects fragmentation

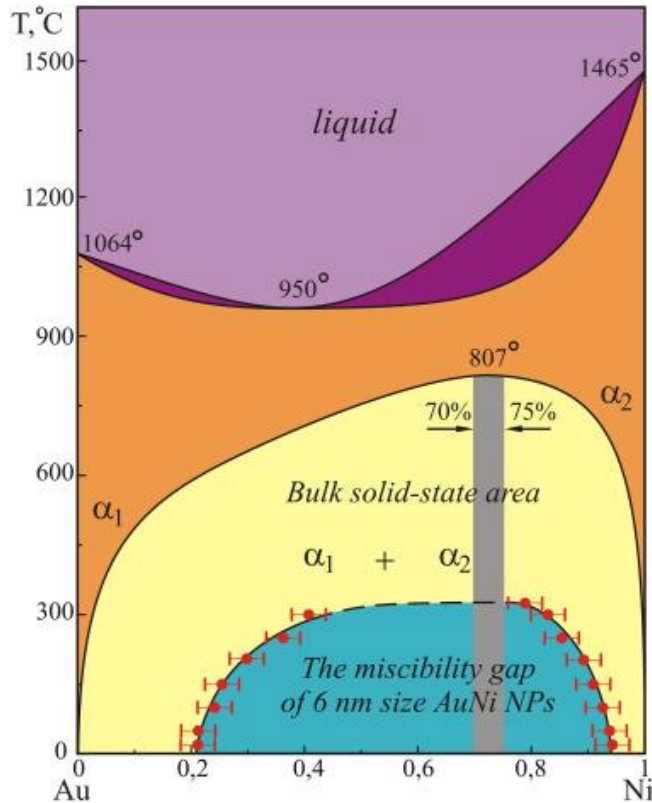
Au-Ni 0, 500, 1600, NP's fragmentation depends non-linearly on Ni fraction



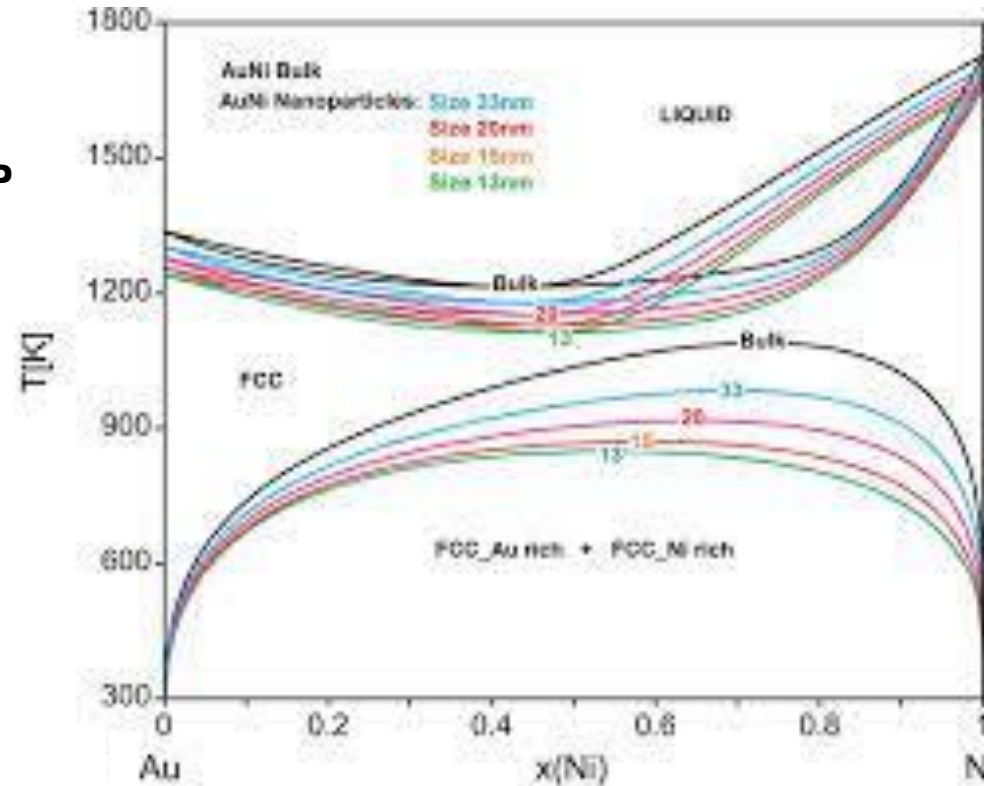


# Phase diagrams: NP vs Bulk Material

The Au Ni system [phase diagram](#) [\*] and the experimentally constructed miscibility gap.



NB: Under equilibrium conditions



J. Sopoušek et al CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 58 (2017) 25–33

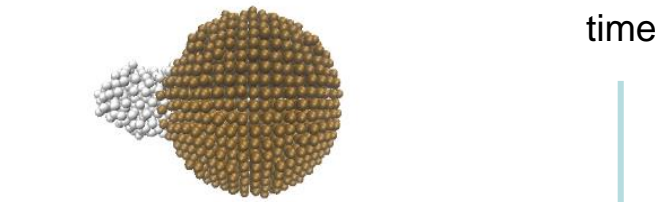
\*H.Okamoto. ASM International. (2000), 828.

S. Bogatyrenko et al, Scripta Materialia, 170 September  
Pages 57-61

$$G^{XS} = X_{Ni} X_{Au} (24,140 X_{Au} + 38,280 X_{Ni} - 14,230 X_{Au} X_{Ni}) \left( 1 - \frac{T}{2660} \right) J$$

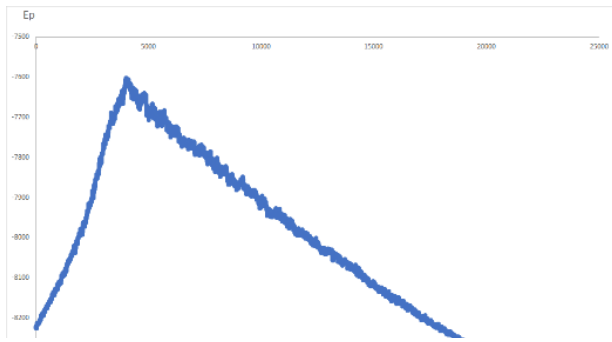
# NP Sintering or Alloying

FeNP R=10 uc   AuNP R = 20 uc   FeNP 1700+AuNP 1700



Different sizes and species, but the same temperatures

Time-evolution of energy



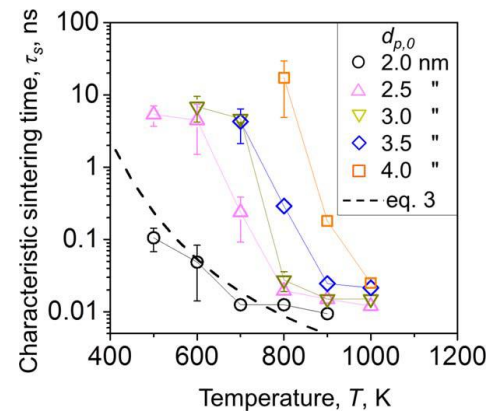
time

100ps



- 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

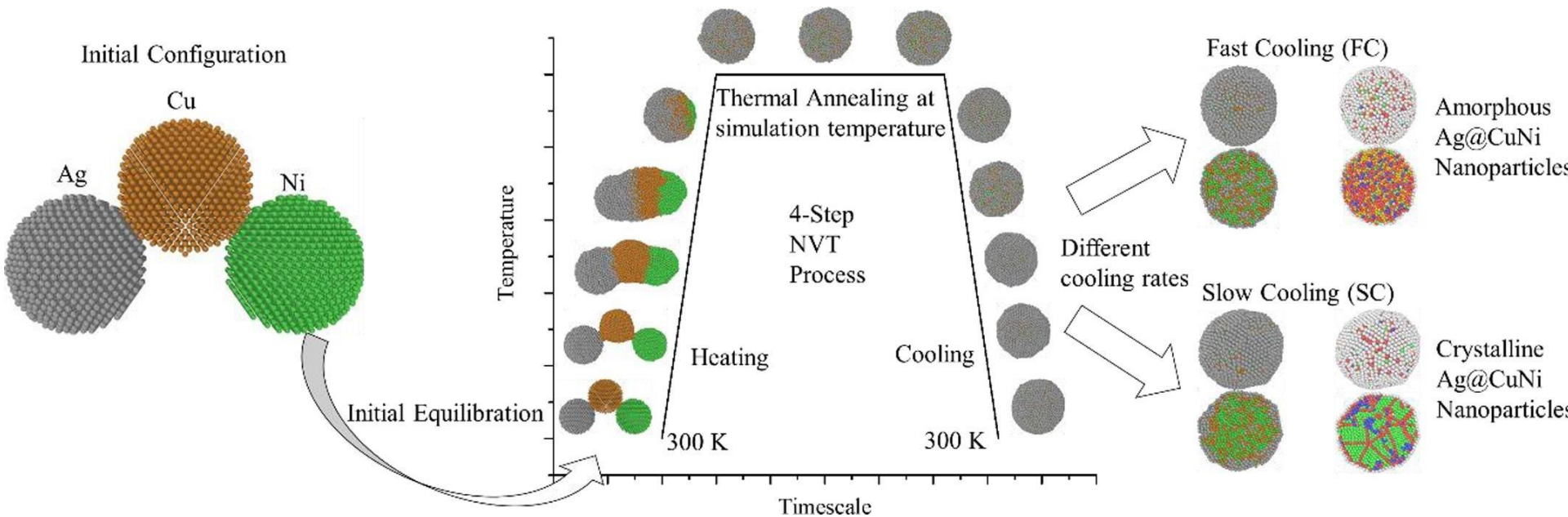
Core-shells can be formed when one particle is much larger and is composed of a material with different cohesive energy



E. Goudeli et al.,  
AIChE 2015

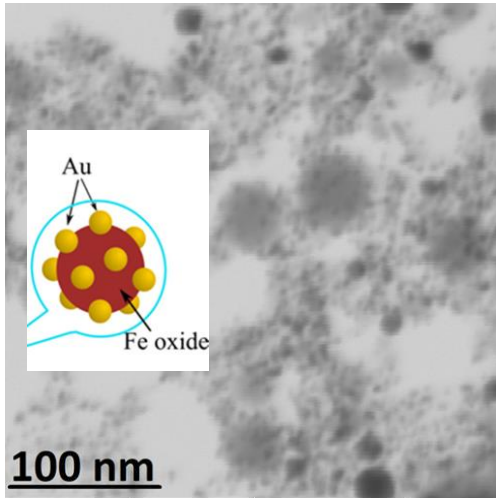
# Sintering vs Alloying, High-Entropy Alloys

AgCuNi, 10,843 atoms

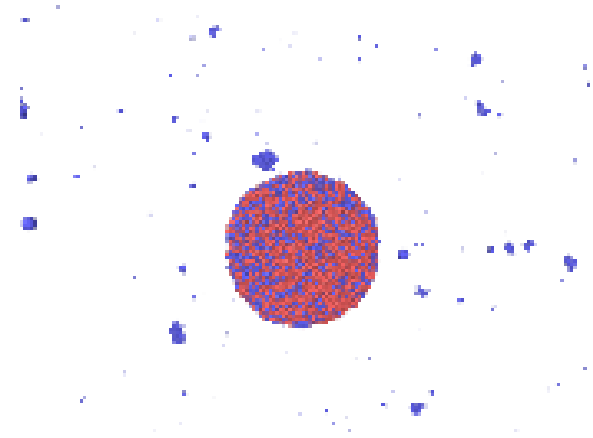
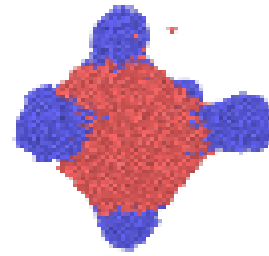
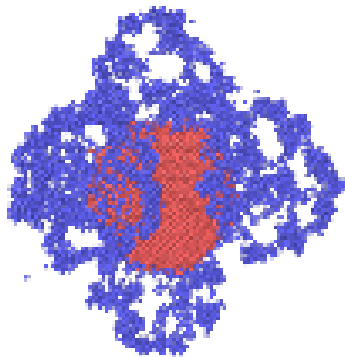


For heating simulations, we studied only the heating part. For cooling simulations, we studied full timescale. Right, cooling part investigated with 2 cooling rates, fast cooling (FC),  $1 \times 10^{13} \text{ K s}^{-1}$  and slow cooling (SC),  $1 \times 10^{11} \text{ K s}^{-1}$

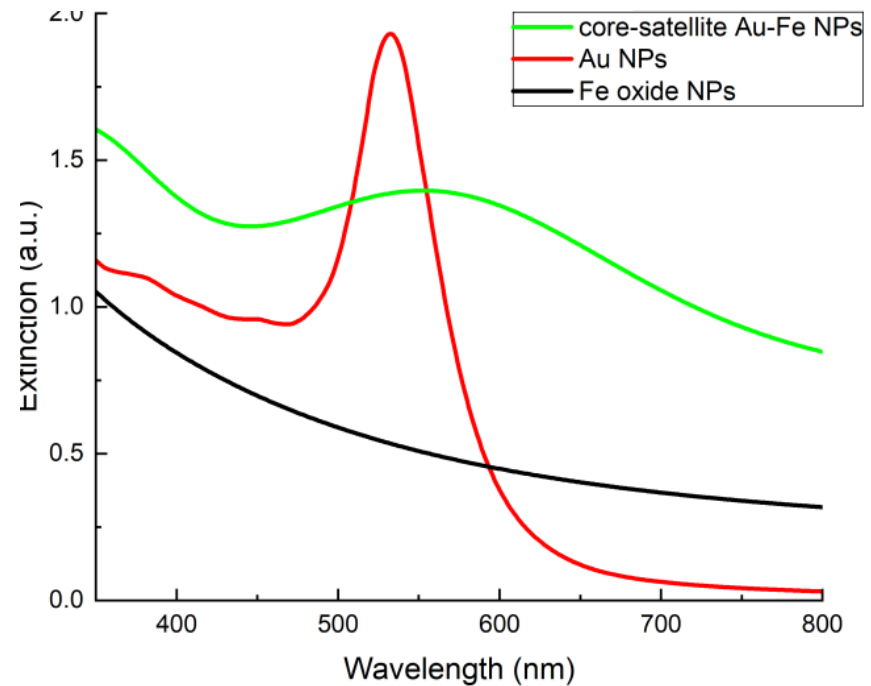
# Complex Nano-Objects Formation by Laser Co-Ablation



:STEM image of nanostructures, obtained by mixing of negatively charged laser-ablated Au NPs and positively charged laser-ablated Fe oxide NPs. Right: Calculated extinction spectra of bare Au NPs (red line), Fe oxide NPs (black line) and core-satellite Au-Fe NPs (green line).



Raspberry –like, core-shells or alloys



## 4. Modeling nanoparticle formation in porous matrices

# Ion-impregnated porous thin films

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

Porous films:

$\text{SiO}_2$  ,  $\text{TiO}_2$

Sol-gel synthesized

Porosity ~ 10%

Porous size 5-7 nm

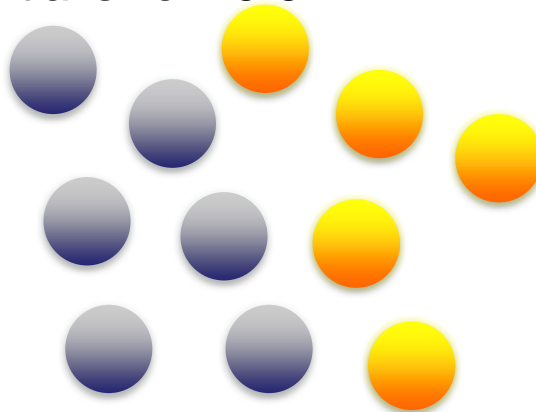


Metallic NPs:

Ag, Au

Produced by soaking in metallic salts solutions with consequent reduction

Initial size < 3-5 nm



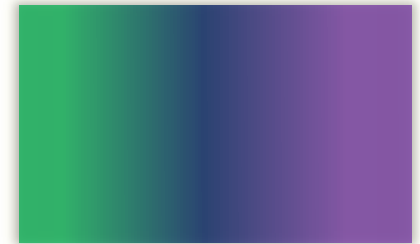
Laser irradiation:

CW

Nanosecond

Picosecond

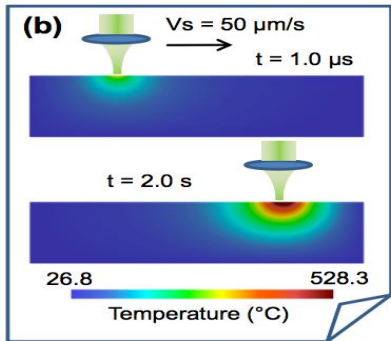
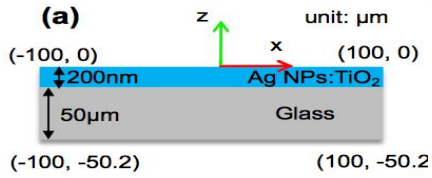
Femtosecond



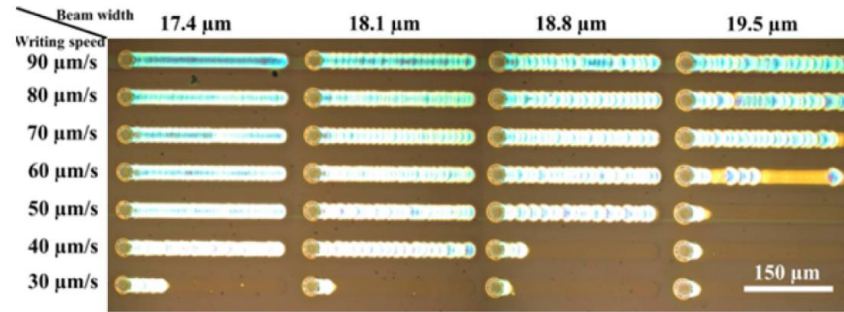
**Ion-impregnated porous glasses and semiconductors**  
can be used as samples for following laser-induced nano-structuring

# Scanning laser irradiation of Ag-TiO<sub>2</sub>

2 different regimes



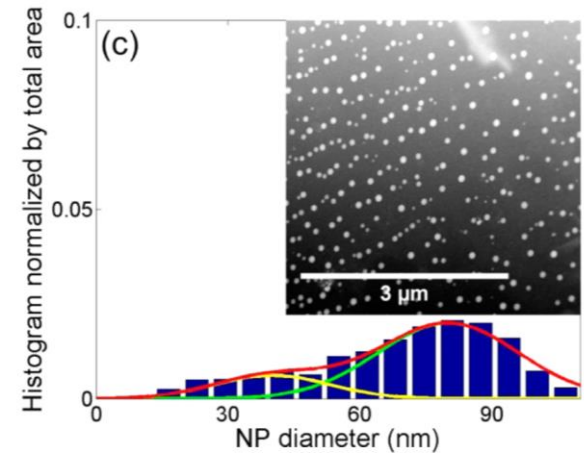
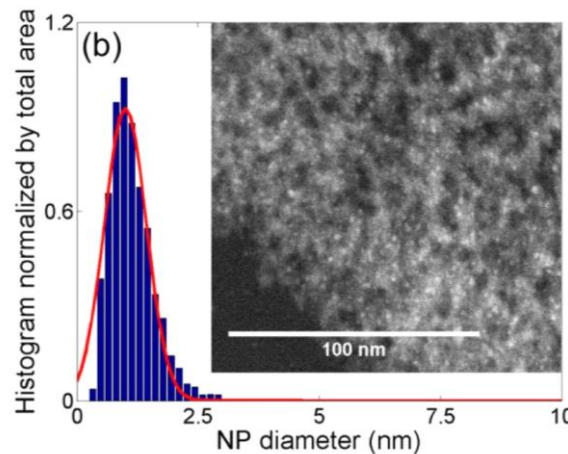
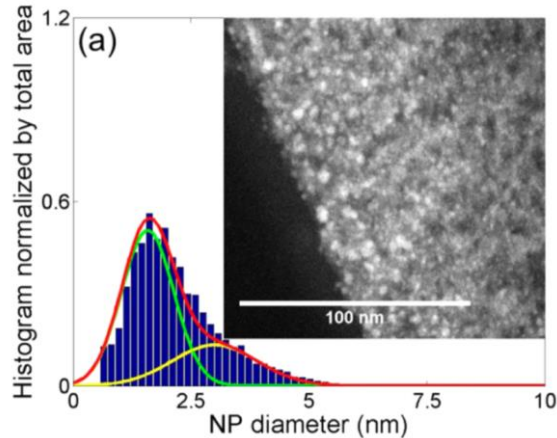
Initial state



Random NPs

Periodic NPs self-organization

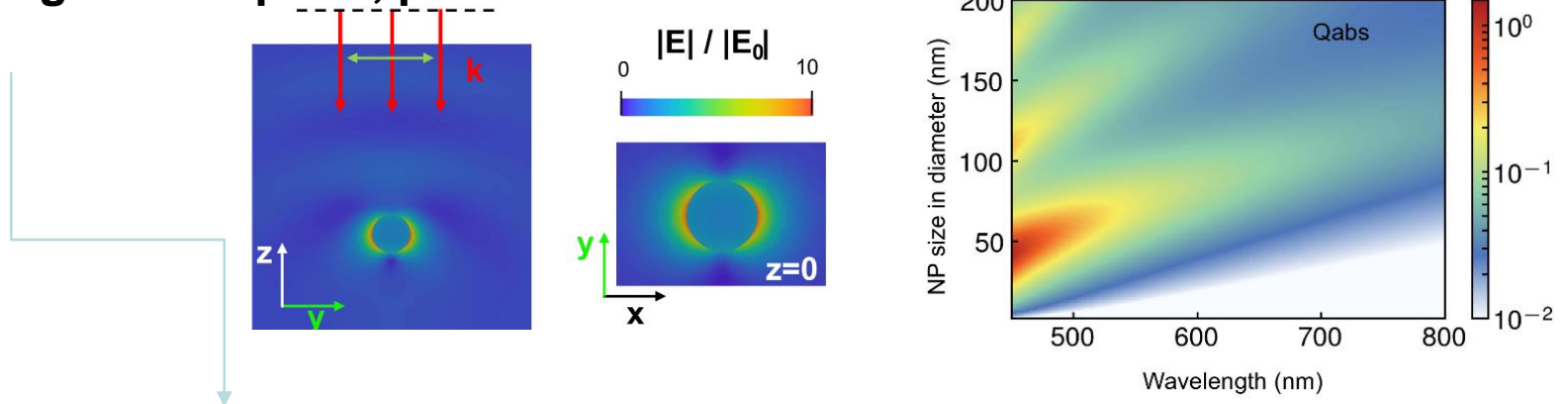
Scan speed below threshold    Scan speed above threshold



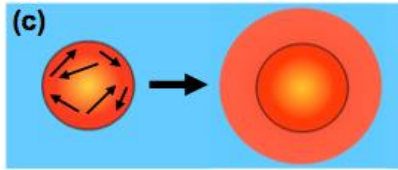
$$P_{av} = 150 \text{ mW} , d_0 = 22.9 \mu\text{m}.$$

# Nanoparticle formation and growth

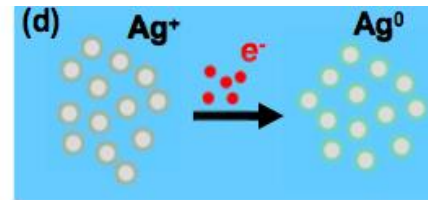
## 1. Laser light absorption, plasmon resonances



## 2. Heating and thermal diffusion

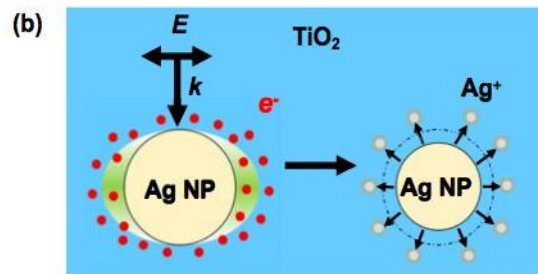
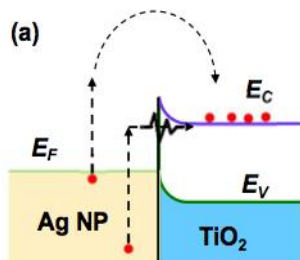


## 3. Photoemission and reduction

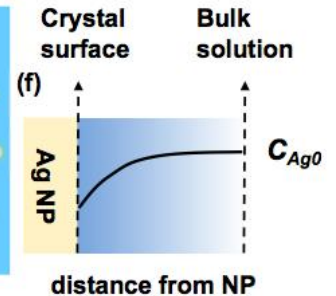
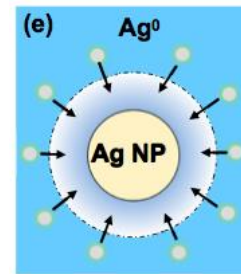


H. Ma et al. *J. Phys. Chem. C* 123.42 (2019): 25898-25907

## 5. Photo-oxydation



## 6. NPs growth



Multi-scale and multi-physical mechanisms are involved.



# Self-consistent absorption, kinetics and heat transfer

$$\frac{dC_{Ag^+}}{dt} = n_{oxi}(t)[C_{NP}(t) + \frac{R(t)}{3} \frac{dC_{NP}}{dR}] - \frac{dC_{Ag^+}}{dt}|_{red}$$

Ag<sup>+</sup> variations

$$\frac{dC_{Ag^0}^{BS}}{dt} = -n_{abs}(t)[C_{NP}(t) + \frac{R(t)}{3} \frac{dC_{NP}}{dR}] + \frac{dC_{Ag^+}}{dt}|_{red}$$

Ag<sup>0</sup> variations

$$\frac{dR}{dt} = [n_{abs}(t) - n_{oxi}(t)] \cdot \frac{\omega}{4\pi R^2}$$

**NPs radius**

$$C_m \frac{\partial T}{\partial t} = \nabla \cdot (k_m \nabla T) + \alpha_{abs} \cdot I(x, y, z, t)$$

**heat diffusion**

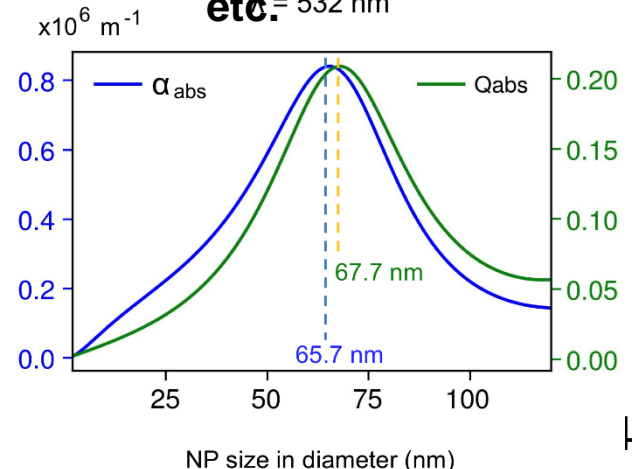
reflection

$$I(x, y, z, t) = [1 - \Lambda(x, y)] I_0(x, y, t) \exp(-z\alpha_{abs})$$

Absorption

**Mie theory and/or effective medium models: Maxwell-Garnett, C-M, Bergman, etc.** = 532 nm

$$I_0(x, y, t) = \frac{P_0}{\pi w_0^2/2} \cdot \exp\left\{-\frac{2[(x-V_s t)^2 + y^2]}{w_0^2}\right\}$$



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

H. Ma, PhD thesis, UJM 2020

# Modeling details

$$n_{oxi}(t) = \eta_0 \frac{\sigma_{abs}(R, \lambda) I(x, y, z, t)}{h\nu}$$

NP photo-oxidation

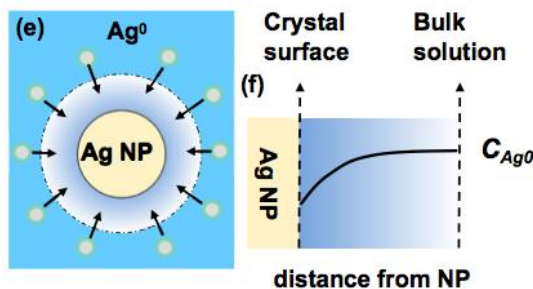
$$\frac{dC_{Ag^+}}{dt} \Big|_{red} = \exp\left(-\frac{E_p}{N_A k_B T}\right) \cdot D_0^{red} \exp\left(-\frac{E_D}{N_A k_B T}\right) \cdot C_{red} C_{Ag^+}^{2/3}$$

reduction

$$n_{abs}(t) = 4\pi R^2 D_{Ag^0}(T) \frac{dC_{Ag^0}}{dr} \Big|_{r=R}$$

NP growth

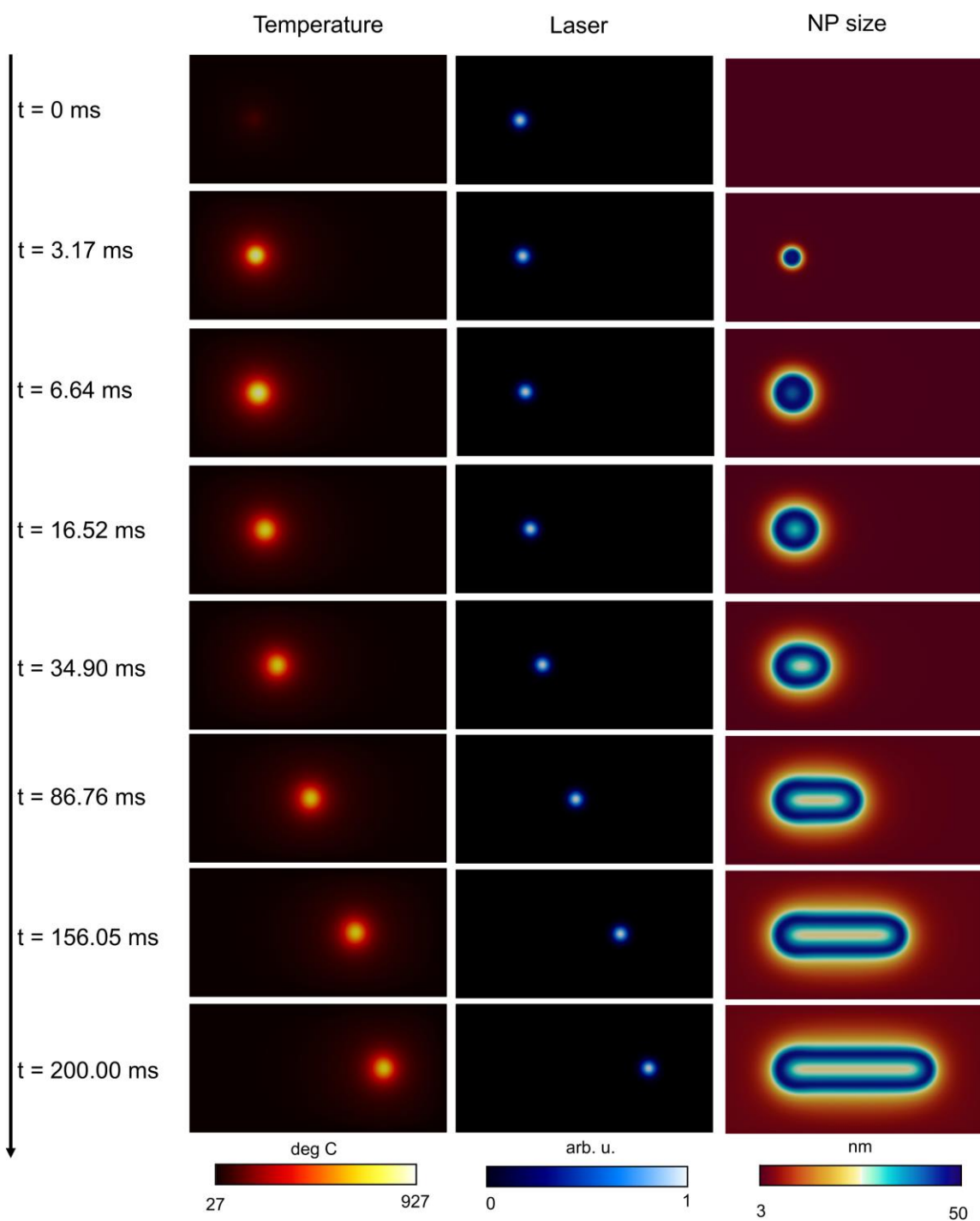
$$\frac{1}{r} \frac{\partial^2}{\partial r^2} r C_{Ag^0}(r) = 0$$



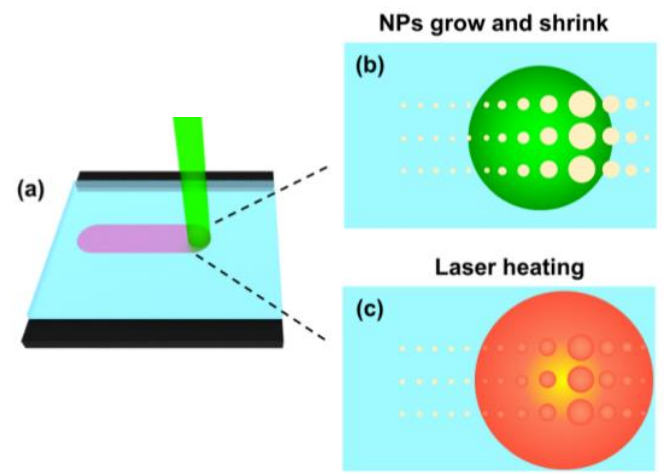
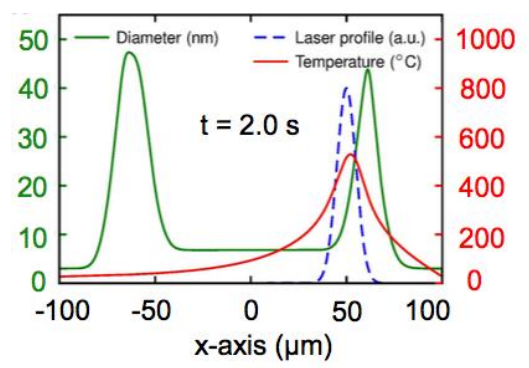
$$C_{Ag^0}(r) = C_{Ag^0}(\infty) - [C_{Ag^0}(\infty) - C_{Ag^0}(R)] \frac{R}{r}$$

$$n_{abs}(t) = 4\pi R D_{Ag^0}(T) \left[ C_{Ag^0}^{BS} - S_{Ag^0} \left( 1 + \frac{2\gamma\omega}{Rk_B T} \right) \right]$$

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



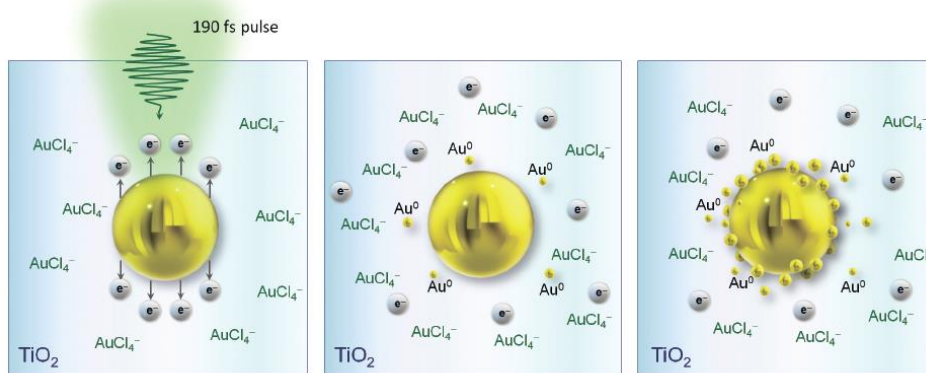
### 2D Simulation



**Absorption and scattering by a set of NPs within the laser spot:**

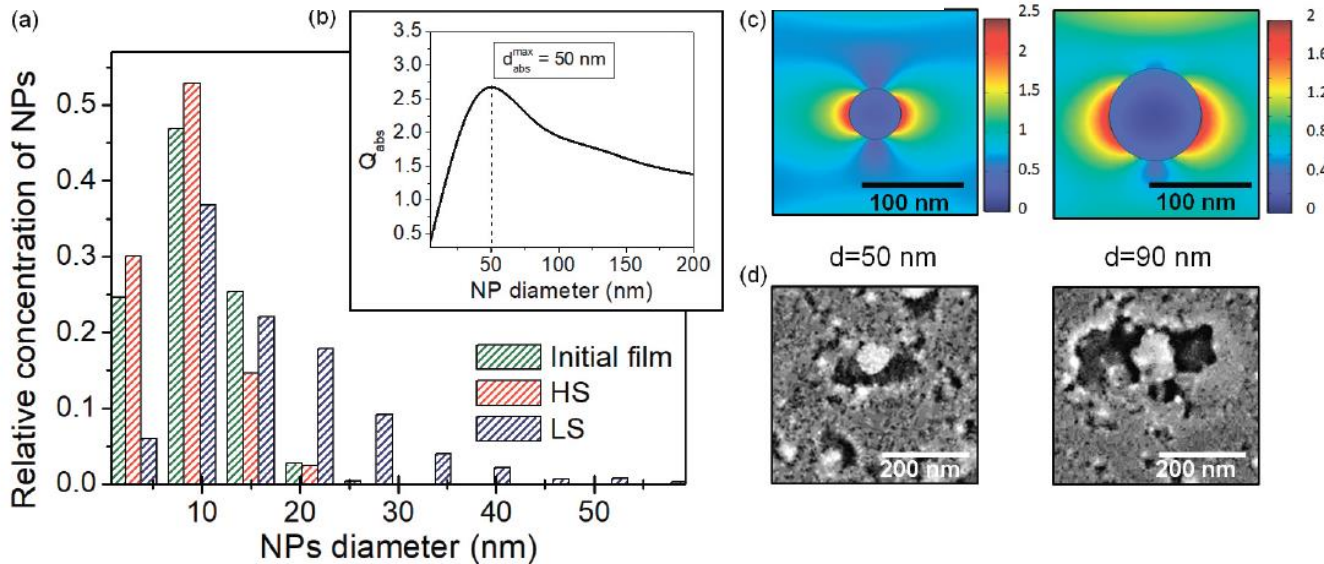
**-effective medium**

# 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

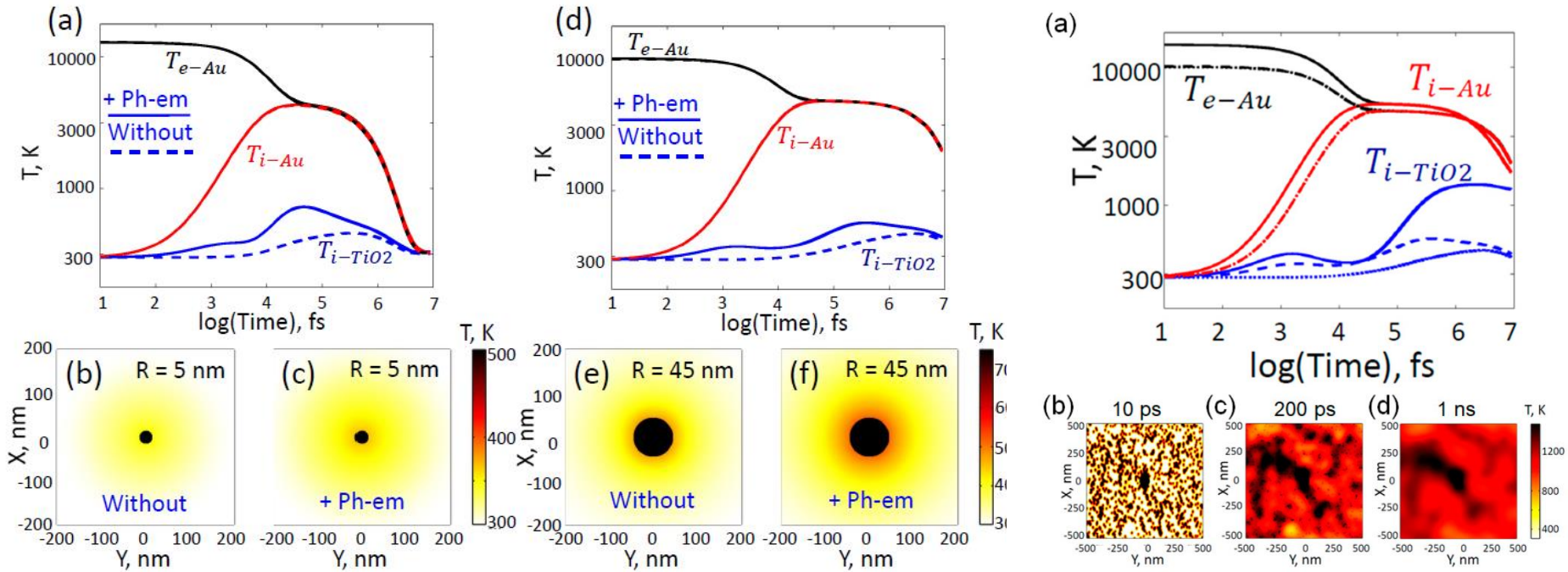
(a) Size distribution of gold NPs in before and after laser treatment. Laser  $F = 57$  mJ/cm<sup>2</sup>, scan speed for LS structures is 0:16 mm/s, for HS structures is 1:6 mm/s.

(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) dynamics in the vicinity of 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 the collective heating by smaller  $R = 5 \text{ nm}$  nanoparticles, electron photo-emission from nanoparticles and free carrier generation by ionization processes in titanium dioxide are included, the ambient damage conditions are reached:

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

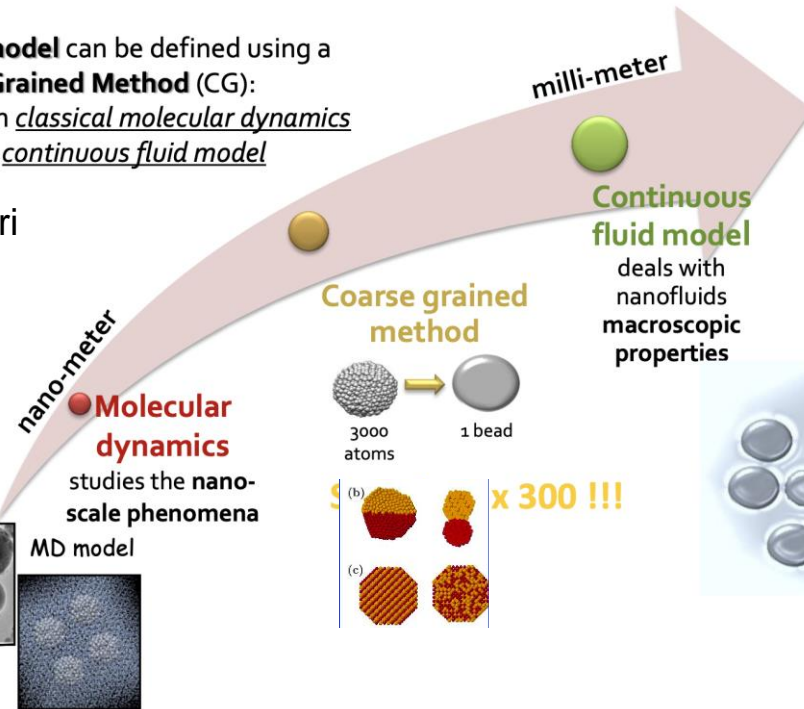
## Summary and Conclusions

- Laser is a very powerful and versatile tool suitable not only for laser ablation but also for nanoparticle synthesis.
- Particle size, composition, geometry, atomic masses, binding energies, excess energy, environment, heating/cooling protocol affect the results of laser interactions.
  - NP's 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 their composition (excess energy).
  - When different nanoparticles interact they may either sinter or mix depending on their sizes and heating/cooling rate. To reach alloying without fragmentation NP should not be over-heated.
- Optical properties are strongly related to size and distribution of NPs after laser treatment, are controlled by laser processing parameters.

# Laser-Scale Mesoscopic Modeling Based on MD

A multiscale model can be defined using a **Coarse Grained Method (CG)**: a bridge between *classical molecular dynamics* (MD) and *continuous fluid model*

Pietro Asinari



- MD (fully atomistic and coarse-grained)
  - Distribution of Sizes
  - Morphology(alloy, etc)
  - Transition to coarse-grained case
- DLVO theory (force field from MD)
  - Aggregation
  - Disaggregation
- CFD or DNS (two phase hydrodynamics)
  - Rules of theory:
    - Conservation of Mass
    - Conservation of Energy
    - DNS: [10.1016/j.ijmultiphaseflow.2021.103762](https://doi.org/10.1016/j.ijmultiphaseflow.2021.103762)
  - Fluid Dynamics:
    - Friction, Thermal Conduction & Mass diffusion
  - Navier–Stokes relationships
    - velocity, pressure, temperature, and density of a moving fluid

Thanks to:

*My collaborators (PICS, PHC and ARQUS projects)  
CNRS and UJM*

**Thank you for your attention!**

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