Multi-scale Modeling for Laser-based Nanotechnology

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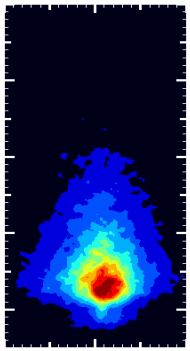
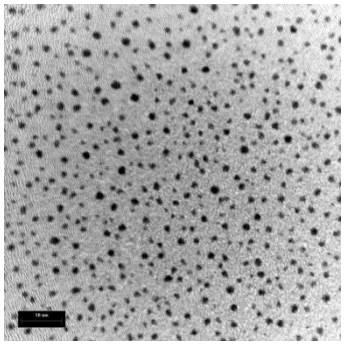
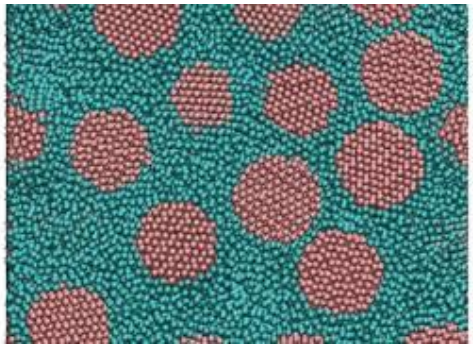





Ablation experiments,
LP3, France

https://www.photonics.com/Articles/Nanoparticles_Probing_the_Plasma_Threshold/a57306

From laser plume to complex multi-material nanoparticles

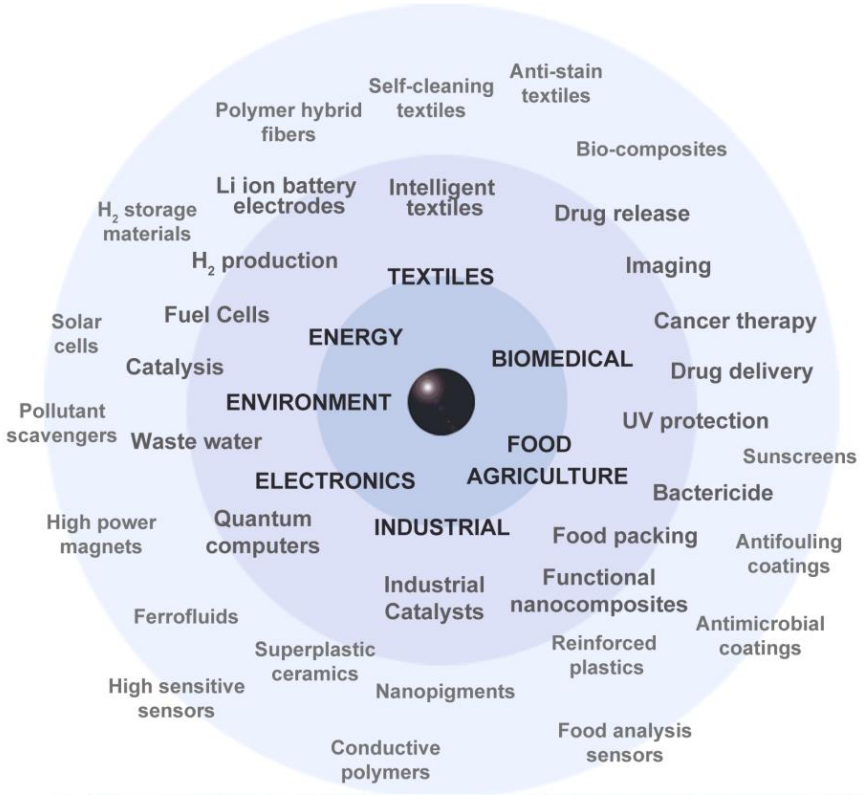
Outline

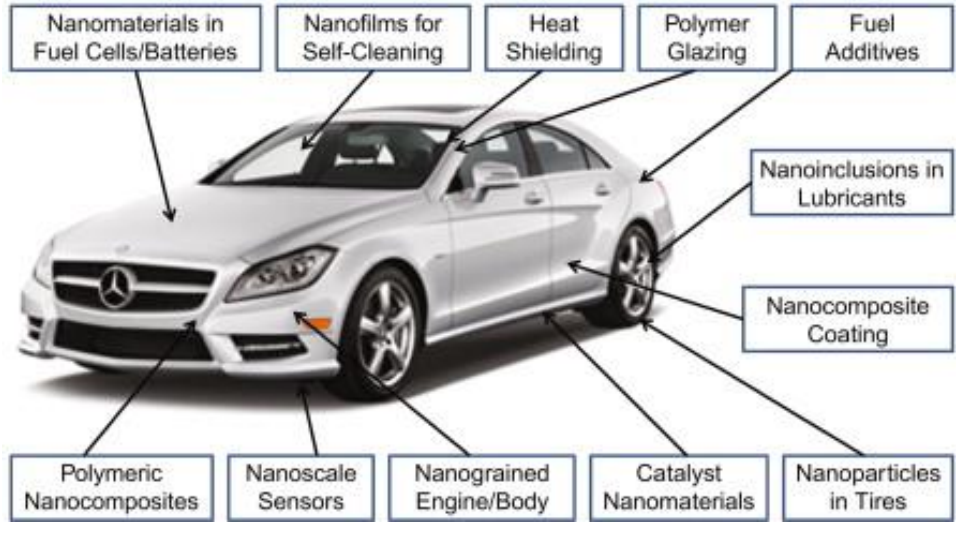
1. Motivations and applications
2. Modeling ultra-short laser interactions and nanoparticle formation in vacuum, in gases and in liquids
3. Laser interaction with nanoparticles
   - Molecular dynamics simulation of nanoparticle collisions
   - Molecular dynamics simulation of alloy nanoparticles
   -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

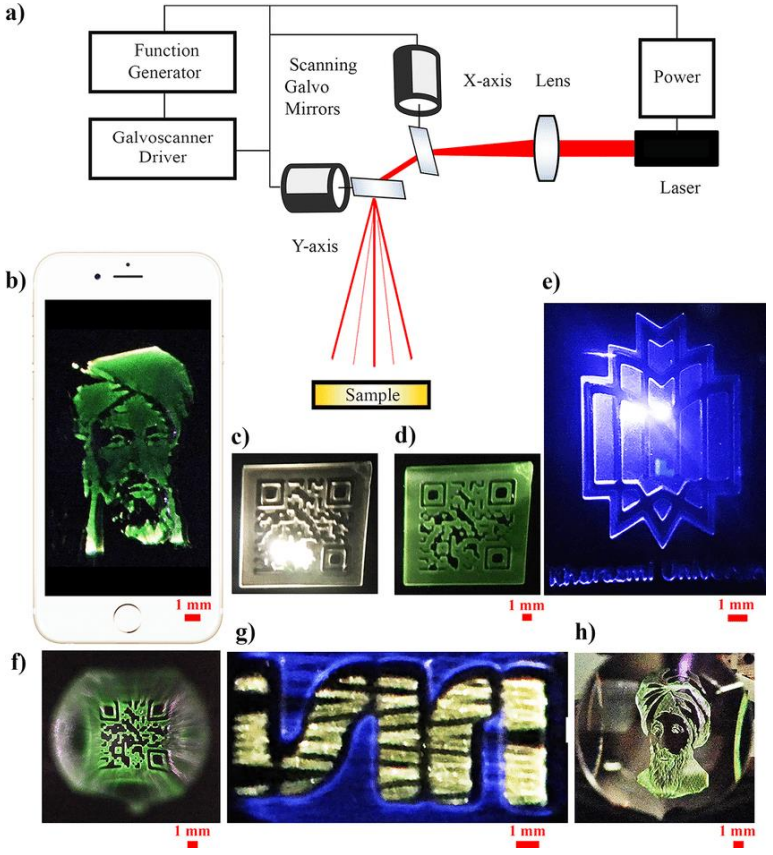
Outline

1. Motivations and applications

Nanoparticles and Nocomposites







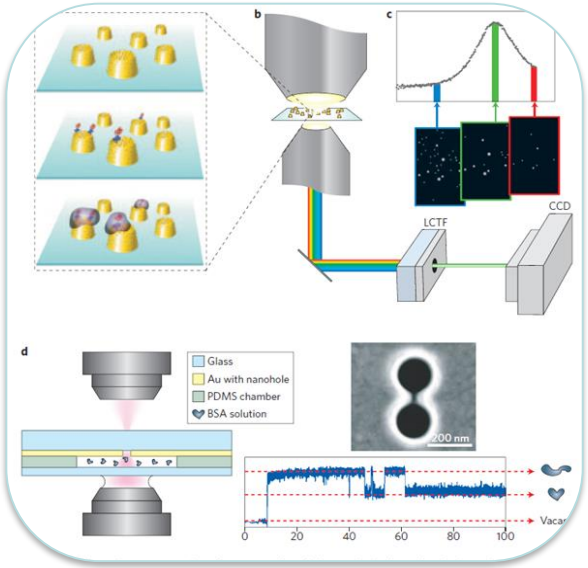
Kaboli et al. ACS Appl.NanoMater

Optics and Security

Z. Liu, et al. JPC C 119.17 (2015): 9496-9505.

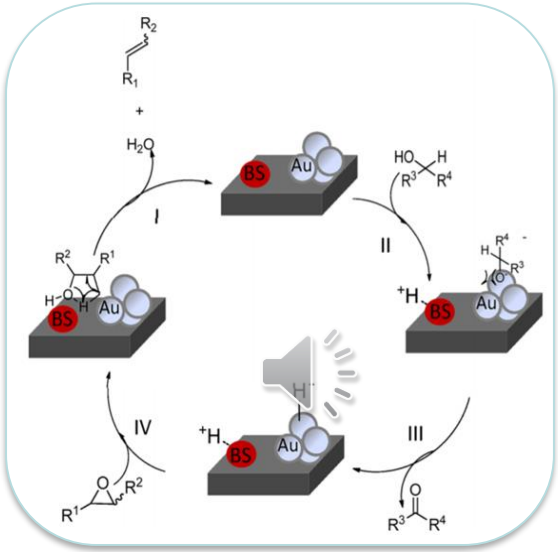
Random and periodic nanocomposite structures

Sensing



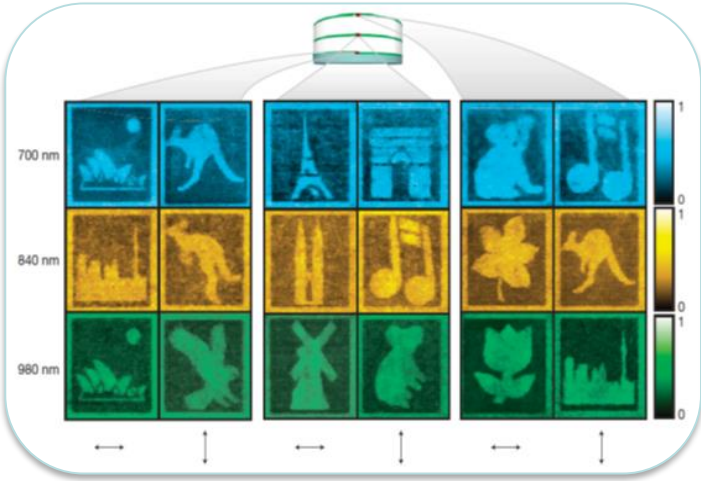
Nature Photonics 6, 709–713 (2012)

Catalysis



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

Optical recording, security, etc.



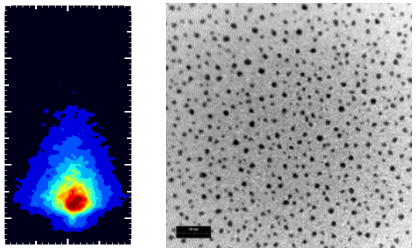
Nature, 459, 410 (2009)

multiplexing

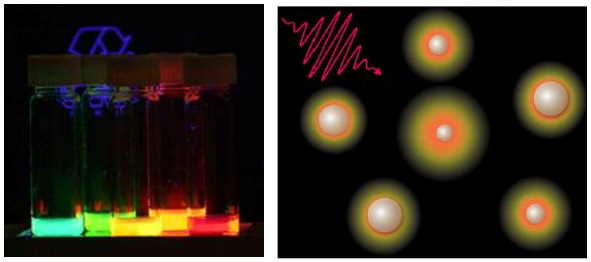
Periodic nanocomposite structures are particularly interesting for optical applications, however the understanding of their formation is still challenging.

Main research directions

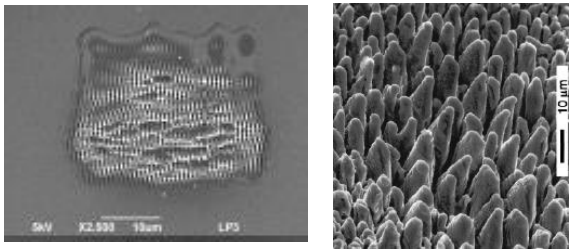
- **Laser-induced formation and modification of nanoparticles, monohybrids and nanostructures: modeling vs experiments**



Pulsed laser interactions

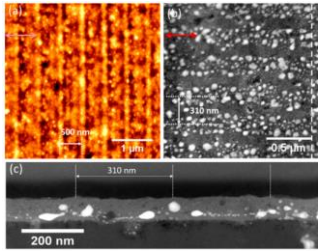


Laser ablation/fragmentation

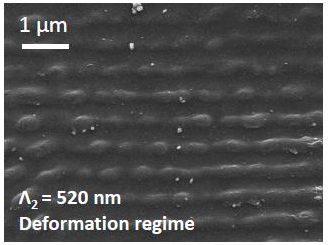


Laser-induced surface/volume structures

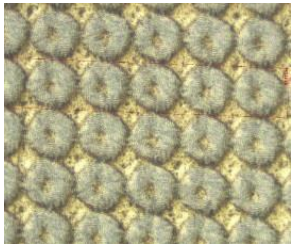
- **Laser-assisted formation of nanocomposite materials and metasurfaces**



Nanoparticles inside

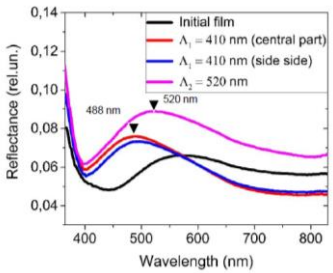


Nanoparticles on the surface



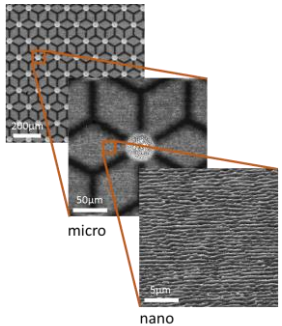
Hierarchical surface structures

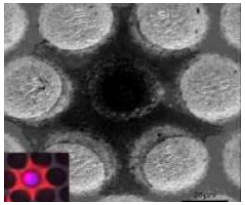
- **Properties and applications of the obtained materials: optical properties, wettability, cells and bacterial adhesion/repulsion**

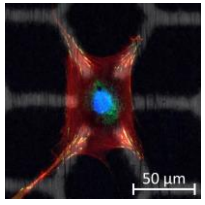


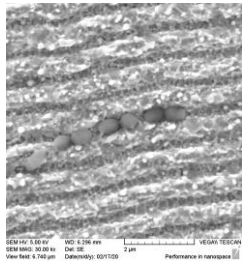
Optical spectra

Wettability







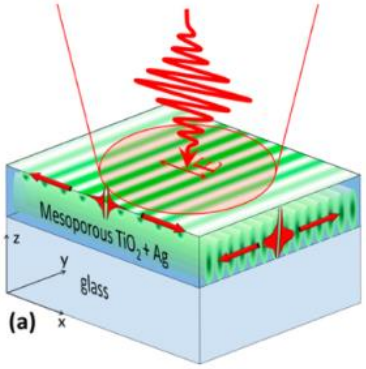


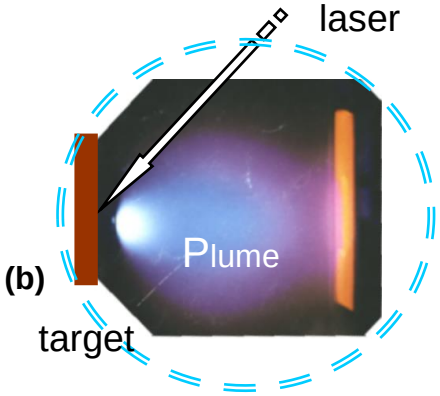
cell and bacteria adhesion

Outline

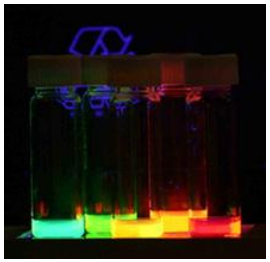
2. Modeling of laser interactions and nanoparticle formation in vacuum, in gases and in liquids

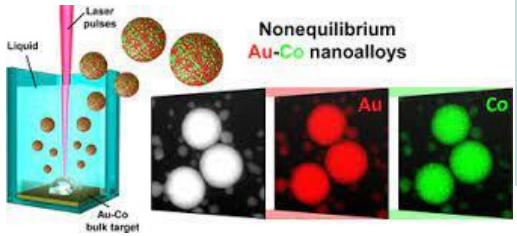
Laser Interactions





In gas or in vacuum with different geometry





In liquids or in the precence of a colloids

Laser interaction commonly involve:

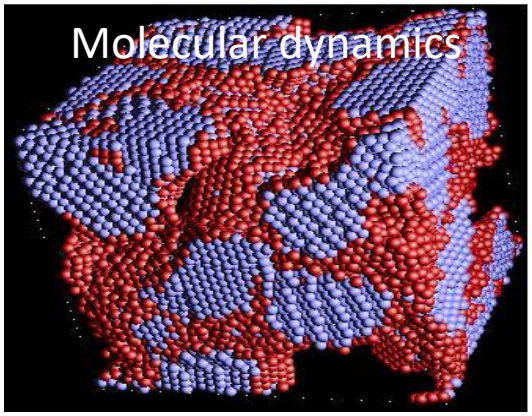
- Energy propagation, electronic excitation, light scattering, reflection and absorption
- Electron-phonon relaxation, heat diffusion, pressure wave propagation, rarefaction and tensile stress, phase transitions, mechanical fragmentation
- Materal removal (ablation), plasma plume expansion, reactions,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

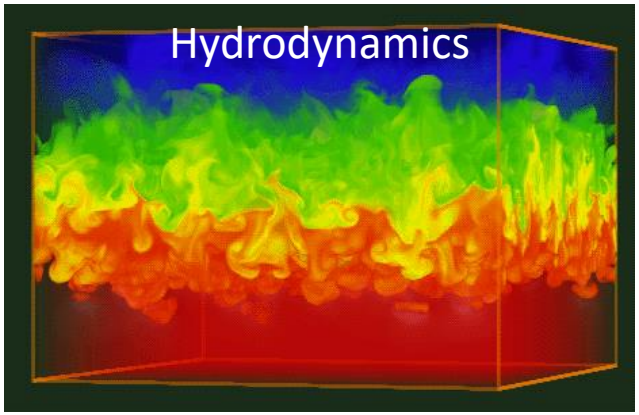
Laser-induced nanoparticle formation

- **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)





$V < 1\ \mu m^3$; $t \sim 1$ 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

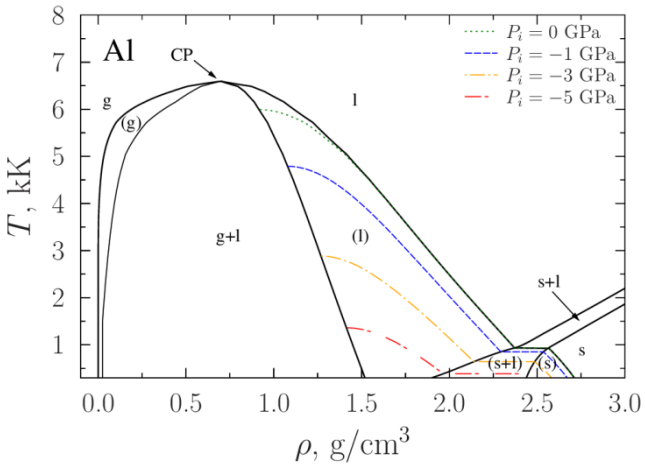
$$\frac{\partial(1/\rho)}{\partial t} - \frac{\partial u}{\partial m} = 0$$

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

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

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

EOS



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

LAMMPS

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

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.

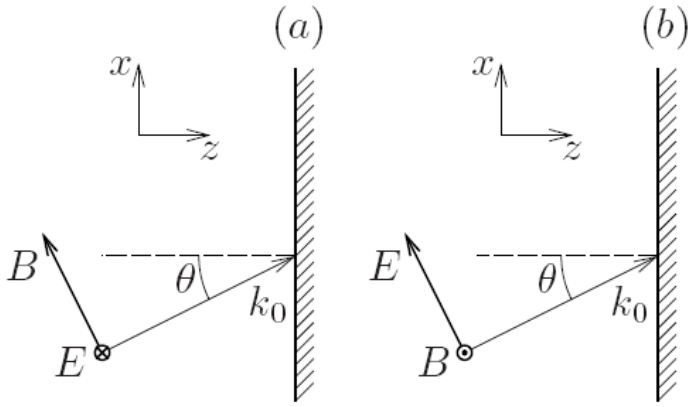


Figure 3. Polarization of laser light: (a)—s; (b)—p.

1D metal ablation: Helmholtz equation

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

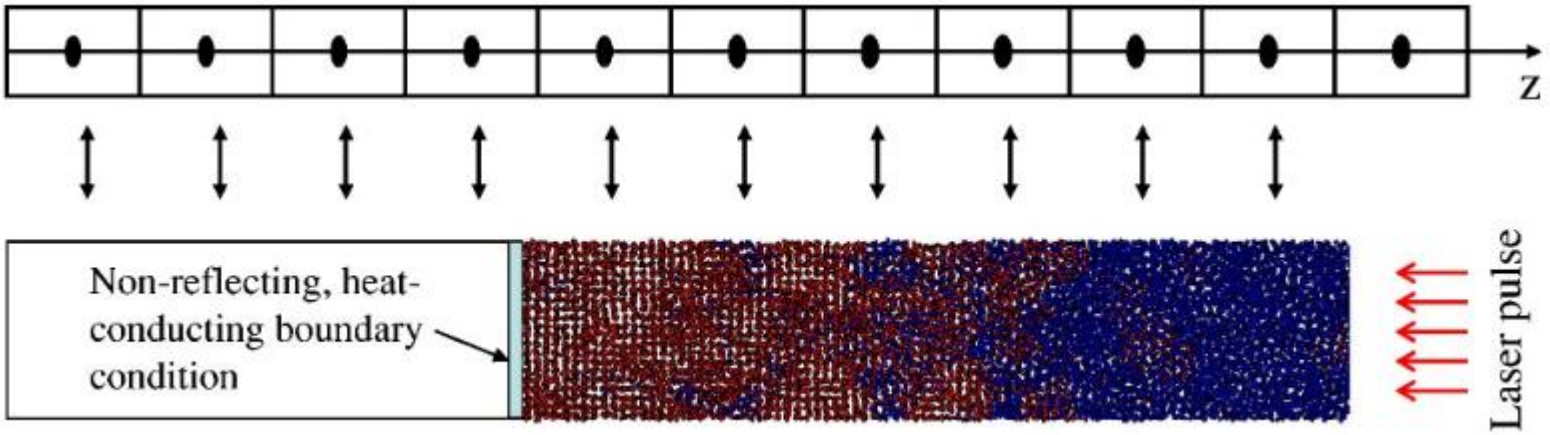
$$\frac{\partial^2 B}{\partial z^2} + k_0^2[\varepsilon(z) - \sin^2\theta]B - \frac{\partial \ln \varepsilon(z)}{\partial z}\frac{\partial B}{\partial z} = 0$$

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

Ultra-short Laser Interactions

Molecular Dynamics + TTM (TTM-MD)

Conduction electrons

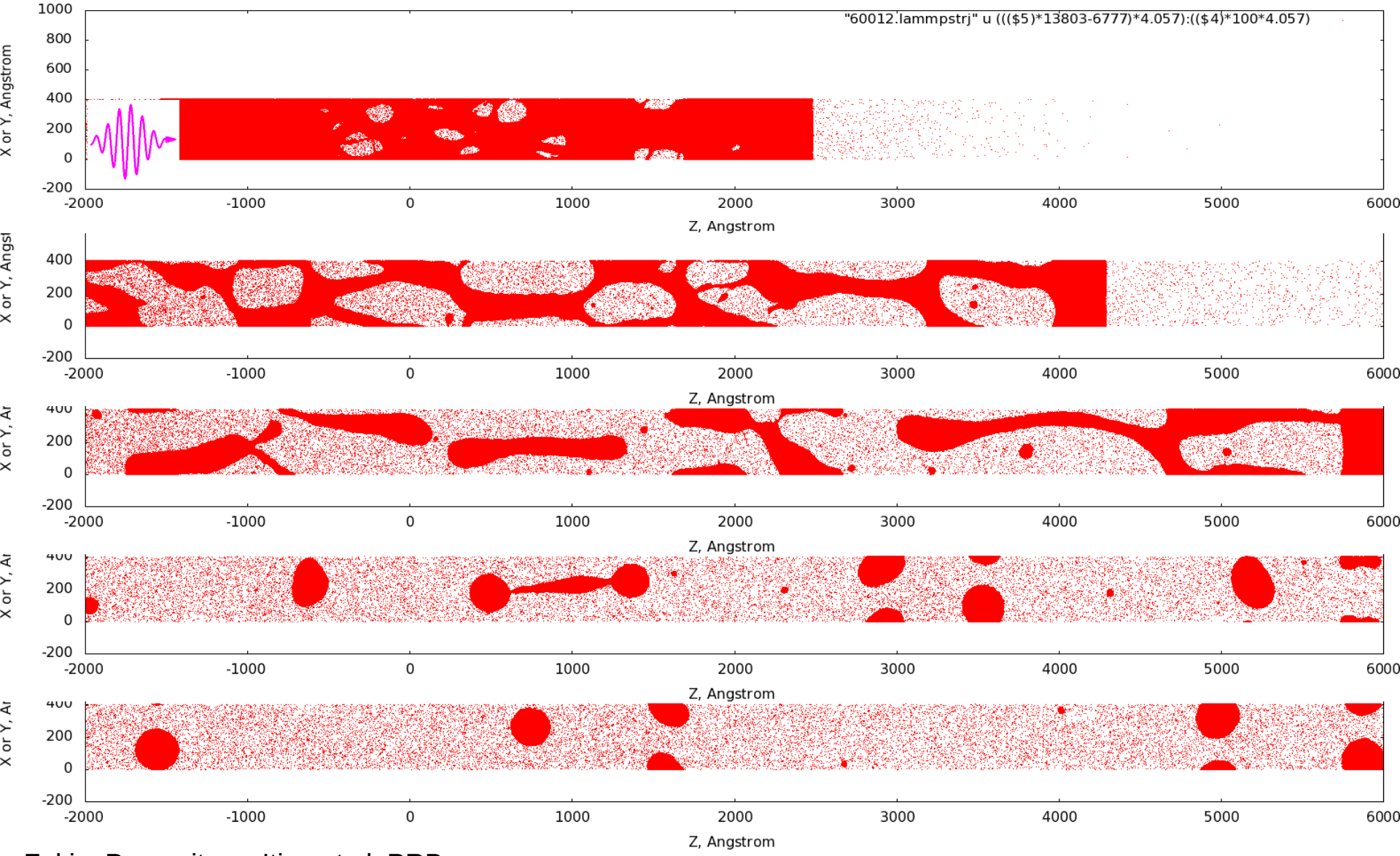


$$C_e(T_e)\frac{\partial T_e}{\partial t}=\frac{\partial}{\partial z}\left(K_e(T_e)\frac{\partial}{\partial z}T_e\right)-G(T_e-T_l)+S(z,t), \quad \text{TTM}$$

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

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

Ablation & Nanoparticles (10M atoms, F=1 J/cm^2, Al)



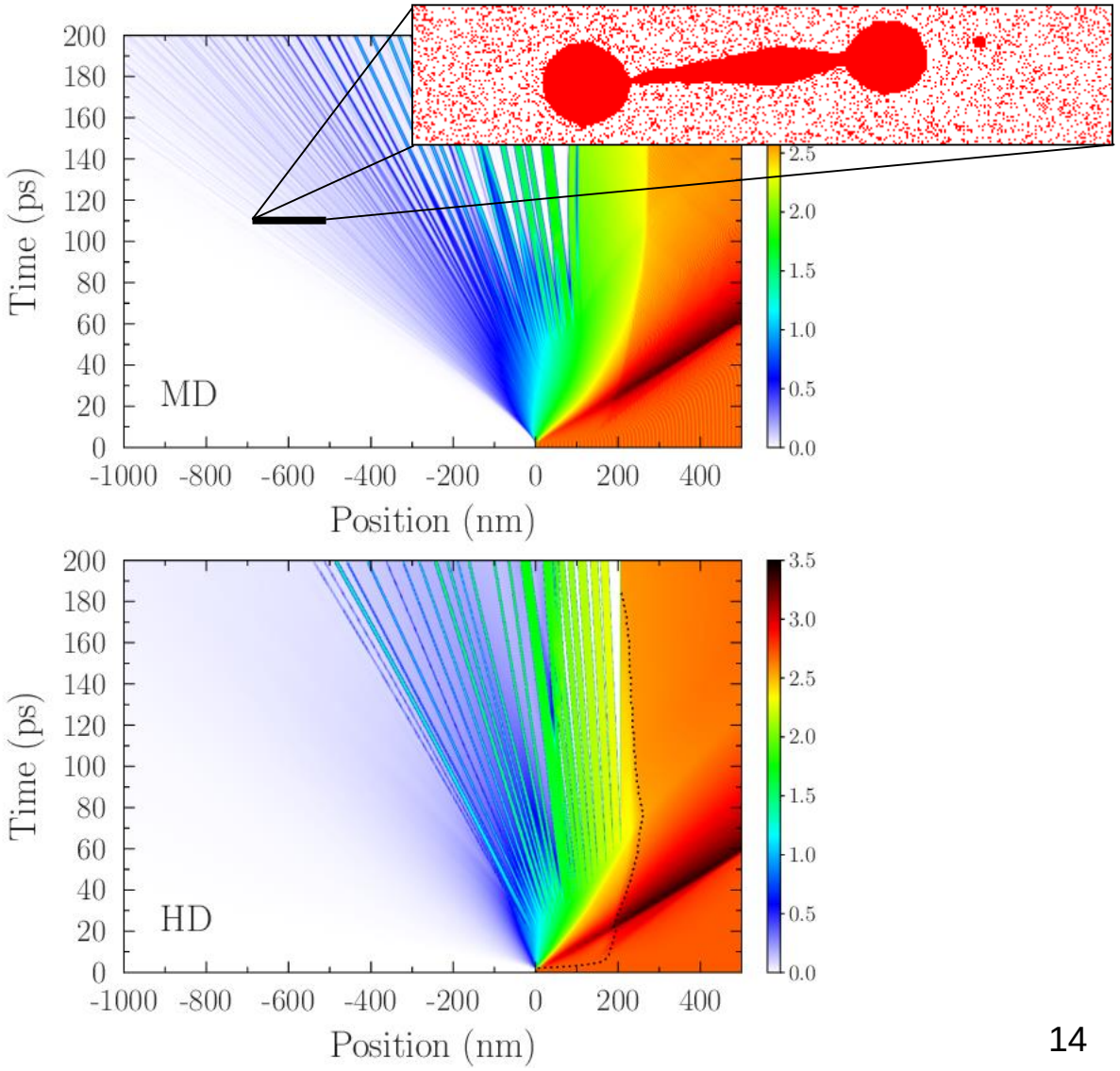
Fokin, Povarnitsyn, Itina et al. PRB

Density

Al, F = 2 J/cm^2

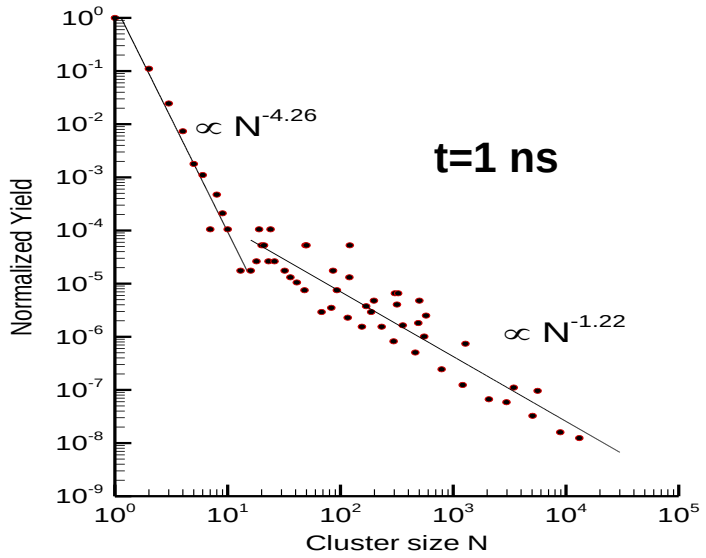
TTM-MD

Hydrodynamics

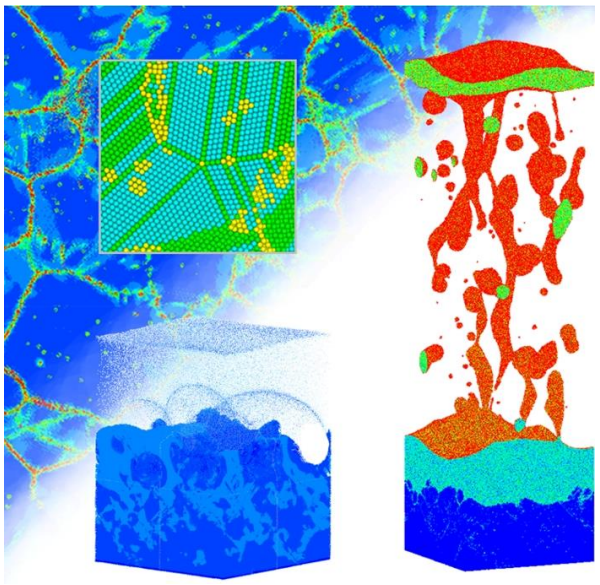


Molecular Dynamics Simulations

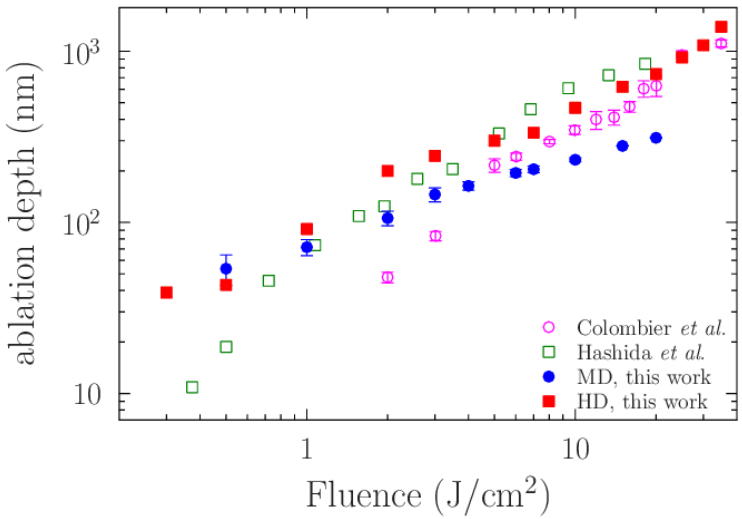
Allow to get nanoparticle size distributions and describe non-equilibrium processes



τ = 15 ps, F ~ 2 Fth, 40×10 nm, t =1 ns



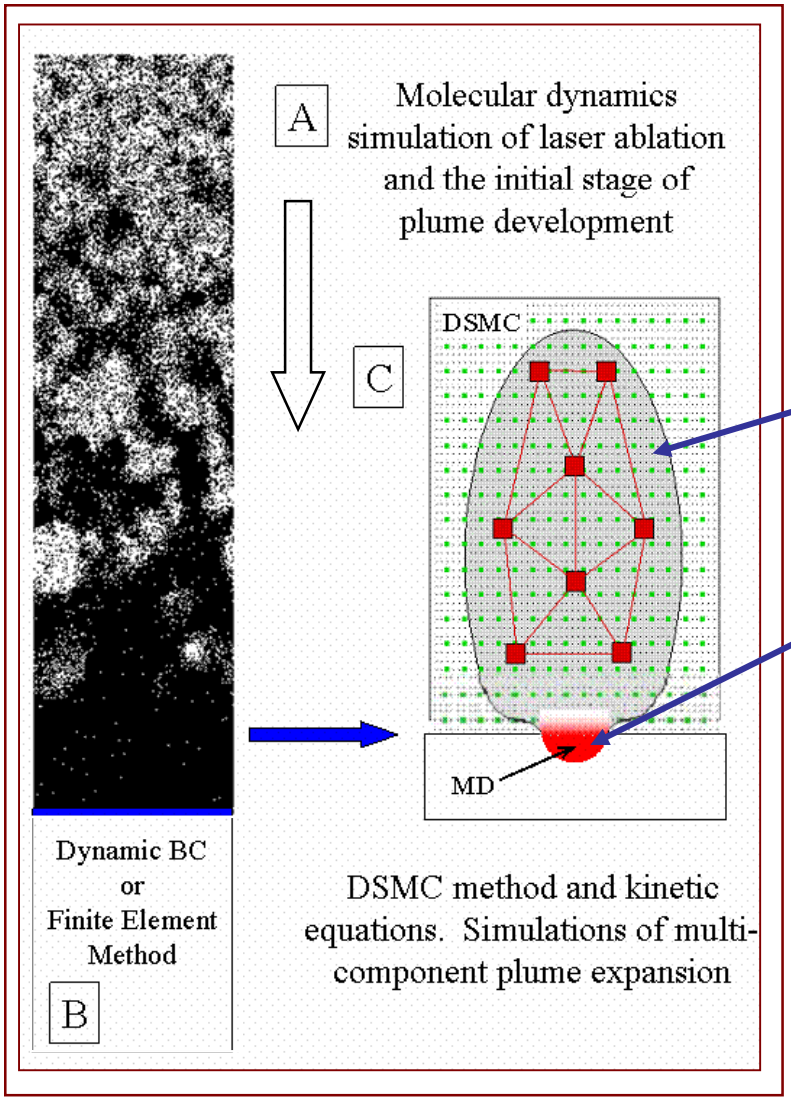
Collaboration with L.V. Zhigilei et al. (Virginia State University, USA)



Practically all the molten material is ablated

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

Longer Plume expansion: Combined Models



Combinaton

- Direct Simulation Monte Carlo

- Molecular Dynamics

Detailed information

Continuous plume

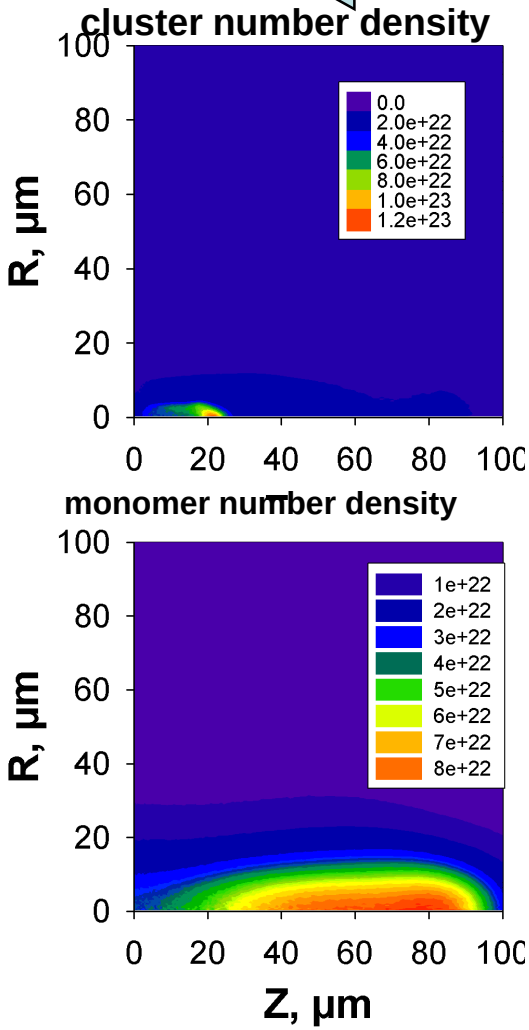
Size distribution of aggregates

K. Gouriet, thèse (2008)

Combined Models vs Experoments

MD-DSMC

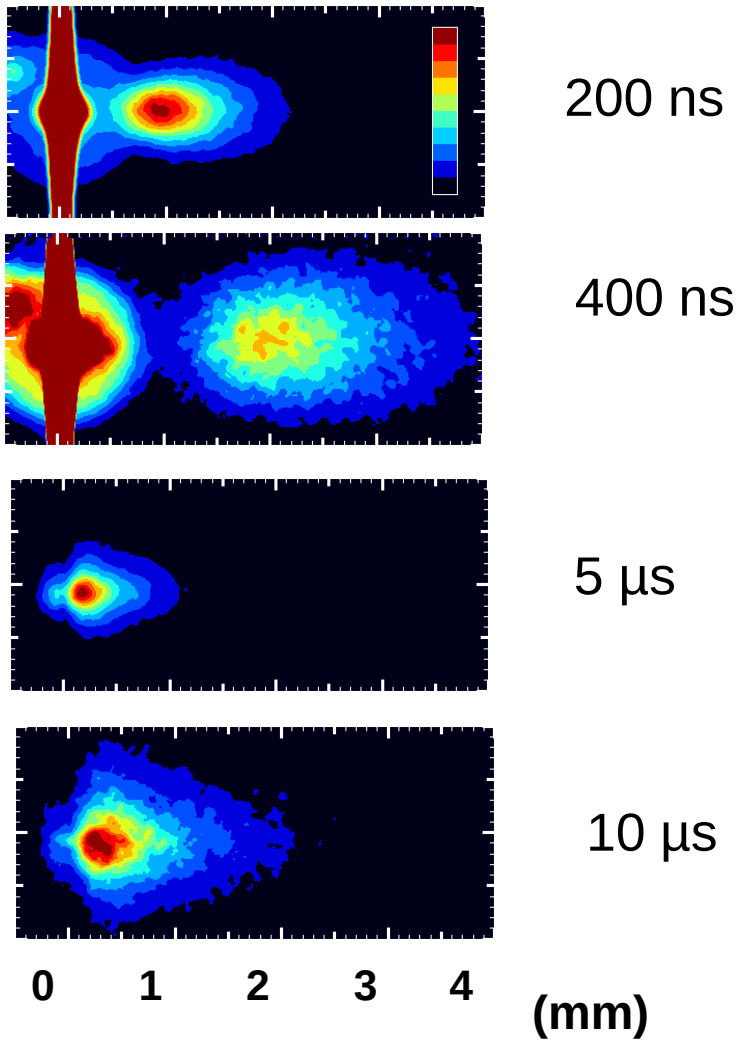
Laser



Numerical results

t= 50 ns, 15 ps, F=61 J/m2, R=10 μm

F_{las} = 4 Jcm^{-2}



Experimental results (J. Hermann, S. Noël)

100 fs F=4 J/cm2

Itina et al. Appl. Surf. Sci. , 253, 7656-7661 (2007)

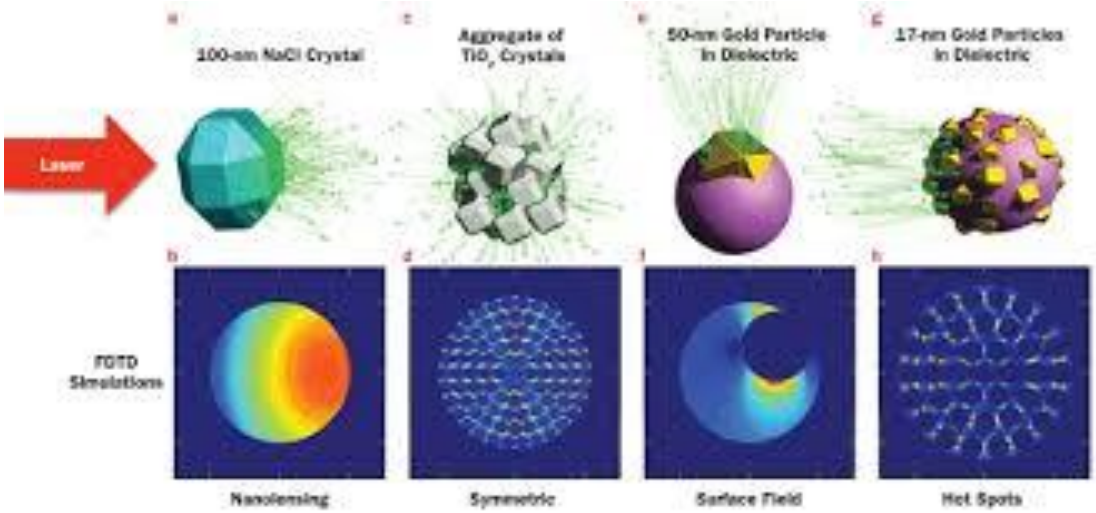
Outline

3. Laser interactions with nanoparticles.

   Molecular dynamics simulation of nanoparticle collisions

   Molecular dynamics simulation of alloy nanoparticles

   Complex nano-objects



https://www.photonics.com/Articles/Nanoparticles_Probing_the_Plasma_Threshold/a57306

Laser Interaction with NPs in Ambien Medium

« Classical » Multi-Physics

Maxwell equations

$$\frac{\partial \vec{E}}{\partial t} = \frac{\nabla \times \vec{H} - \vec{J}}{\varepsilon_0}$$

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

Polarization current

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

Charge conservation, incompressible Fermi flow

Photo-ionization Avalanche

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

Heat energy transfer

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

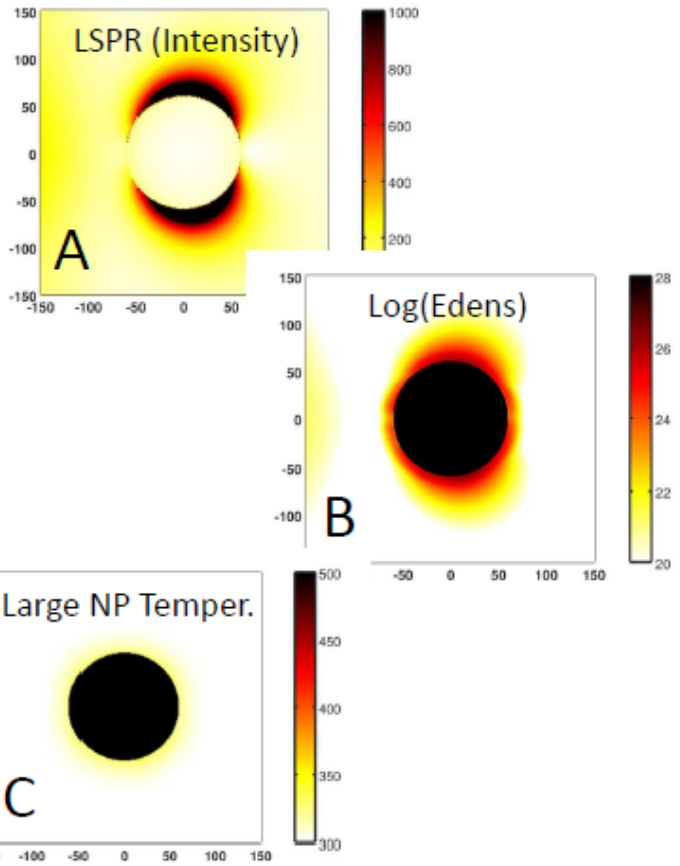
Nanoparticle

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

Medium

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

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



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

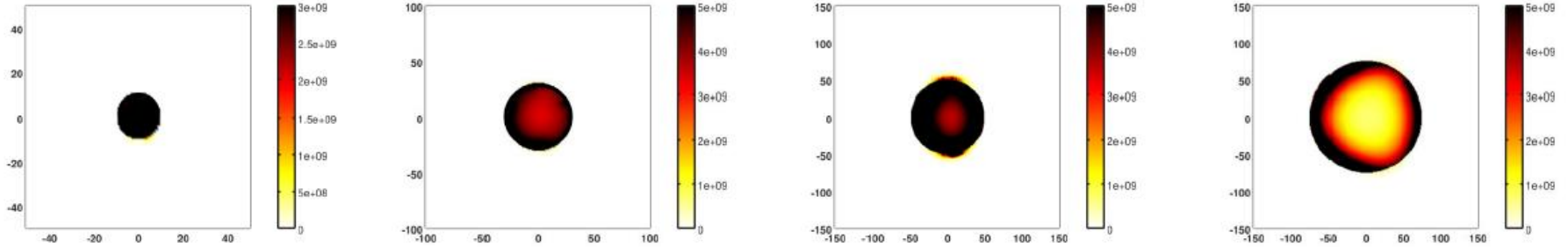
Ultra-Short Laser Interaction with Au NPs in Water

fs laser
λ =515 nm

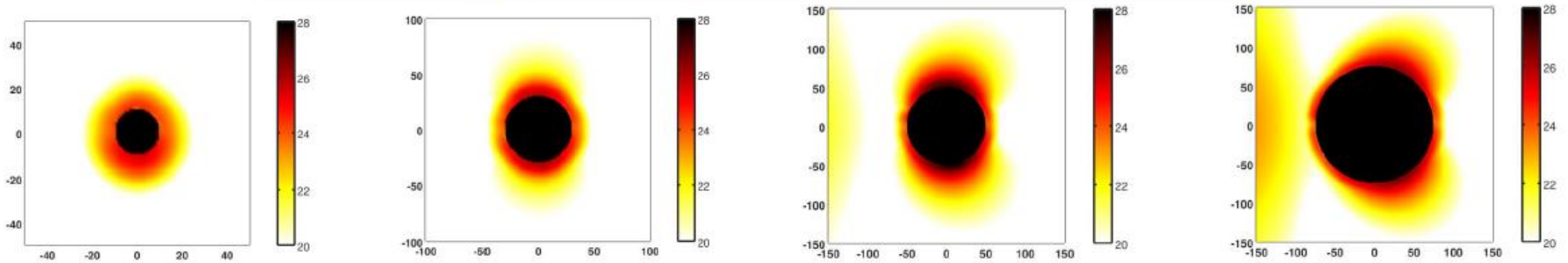
What changes when nanoparticle size inceases ?

R = 10 nm	R = 30 nm	R = 50 nm	R = 75 nm
Comparable to optical penetration depth Weak field enhancement Fast energy transfer to water	Intermediate	Nearly resonant excitation Strong field enhancement	Particle >> skin depth Slow energy transfer to water

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



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



Laser Interaction with Au NPs in Water

Thee interaction regimes and the mechanisms involved

Regime I

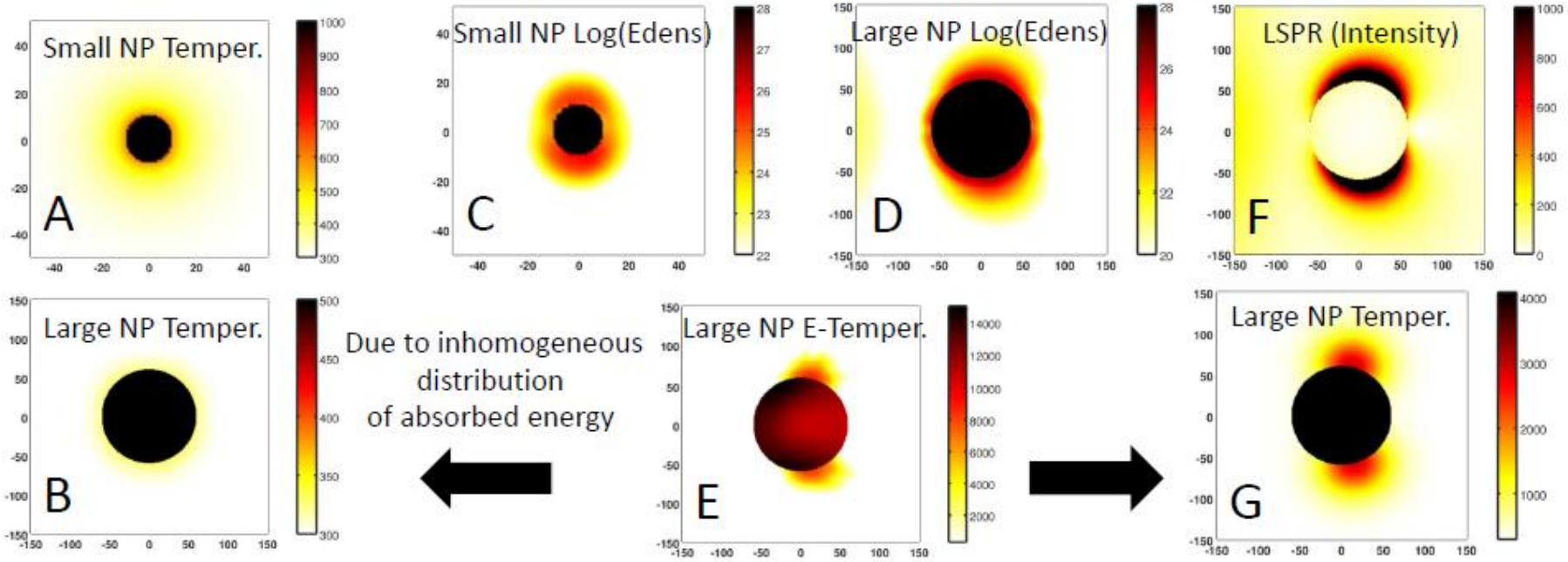
Laser heats Au NP;
Au NP transfers heat to water

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



Ultra-Short Laser Interaction with Au NPs in Water

Thee regimes are distiguished 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

$$\frac{\partial \vec{E}}{\partial t} = \frac{\nabla \times \vec{H} - \vec{J}}{\varepsilon_0}$$

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

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

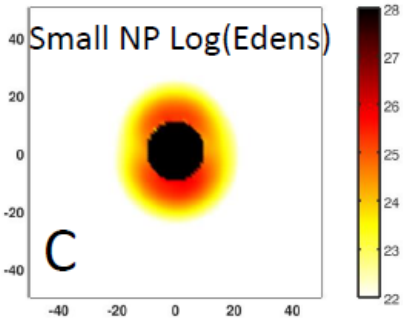
$$\frac{\delta G}{\delta n} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} + \cdots$$

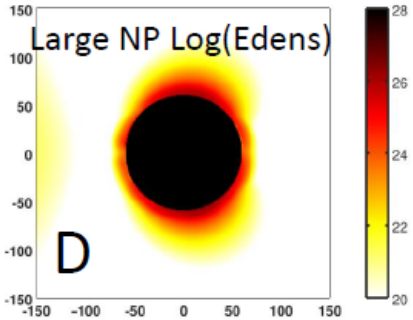
Thomas-Fermi
Quantum kinetic energy
for uniform gas

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

Photo-ionization

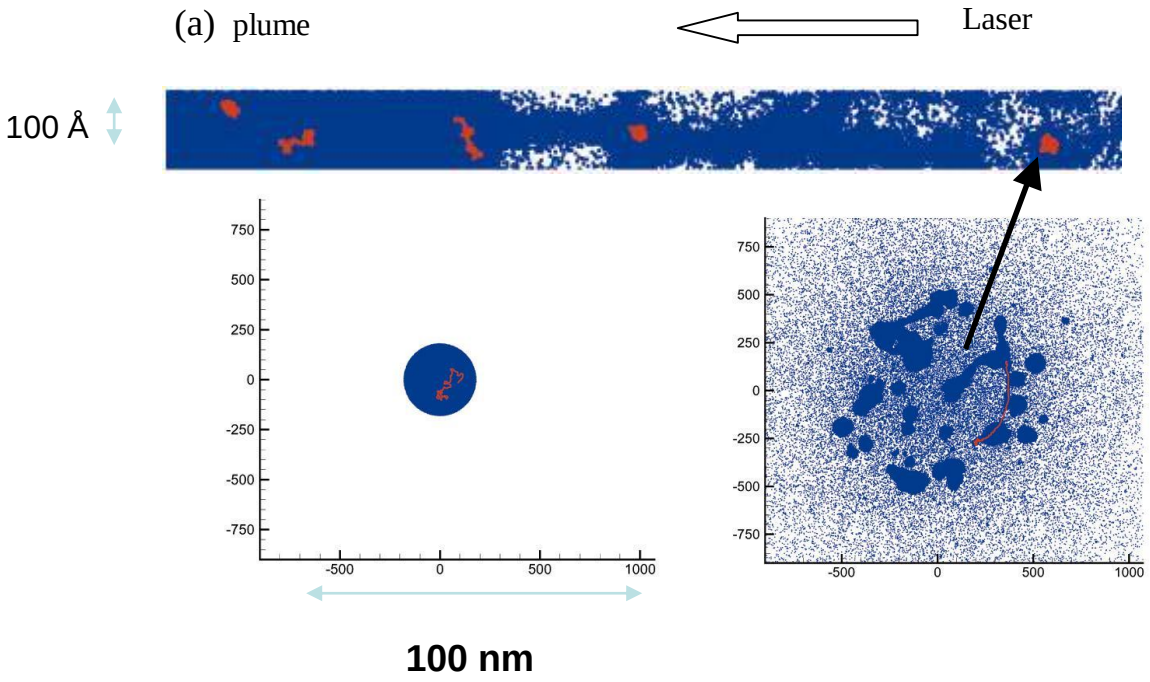
Avalanche ionization





Molecular Dynamics Simulations

Decomposition of the ablated material after the absorption of laser radiation



t = 300 ps after the beginning of the laser pulse

τ = 15 ps

e=0.6 eV per molecule

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

Ultra-short Laser Interactions with NPs

Laser pulse

Propagation, absorption, local field enhancement

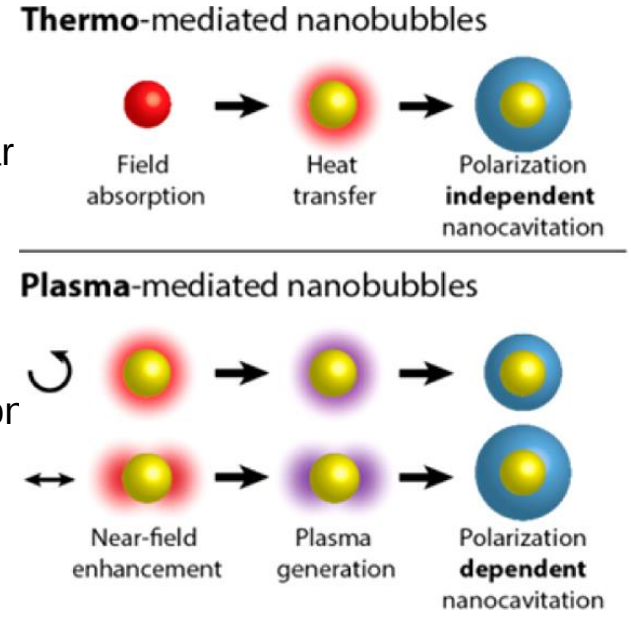
Local ionization and heating of the matter/liquid near **plasma-mediated nanobubbles**

NP heating, heat transfer to the ambient medium **thermo-mediated nanobubbles**

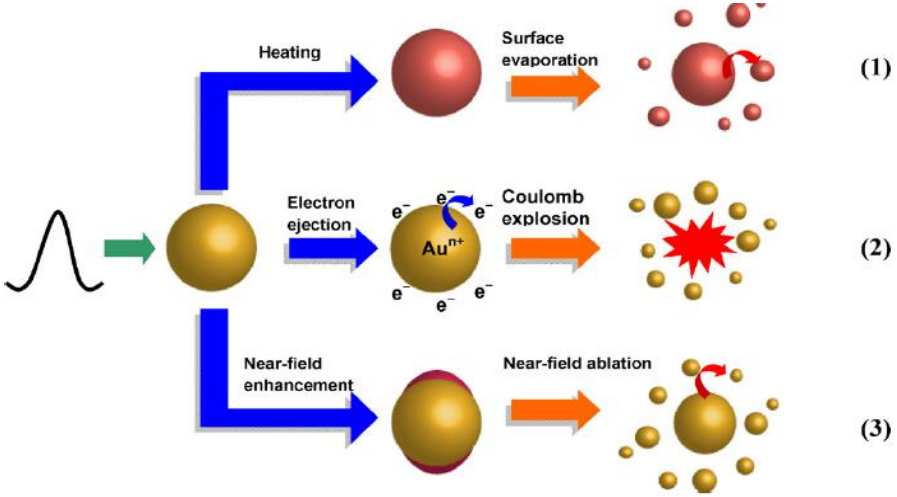
NP heating, melting, reshaping, sintering, evaporation

Electron ejection, injection in the ambient

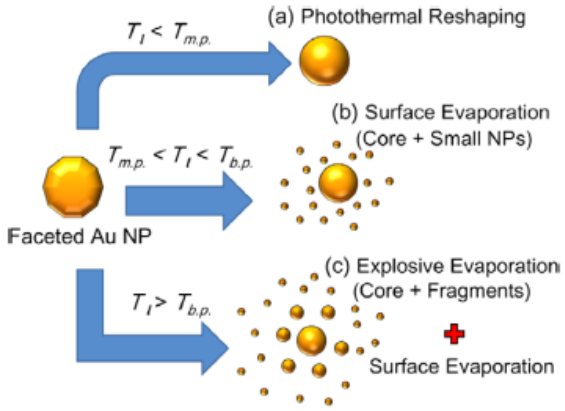
NP fragmentation



Lachaine et al.Photonics (2013)



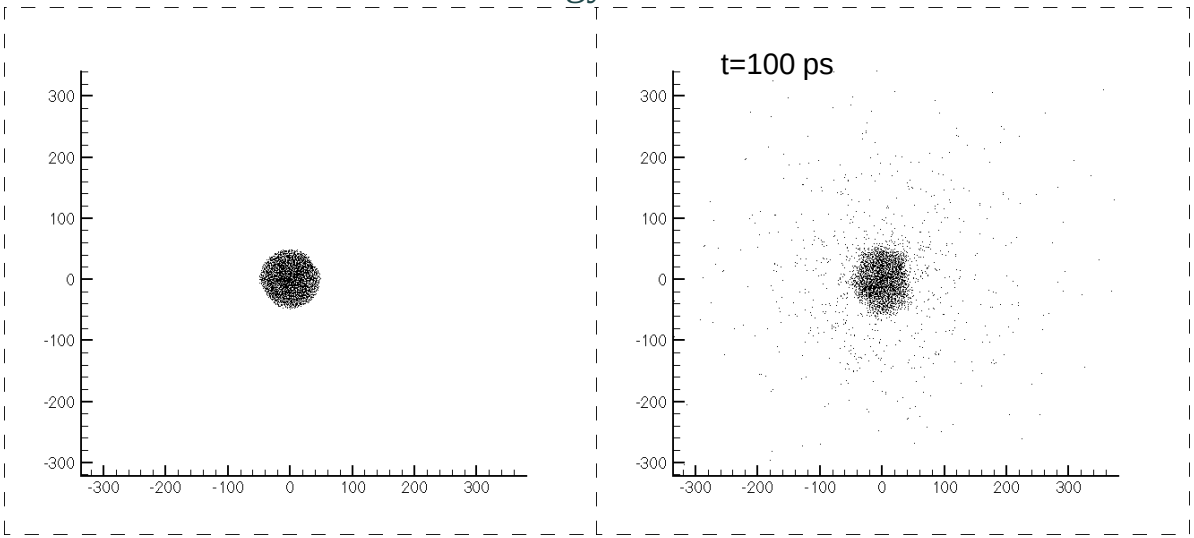
Hashimoto et al. J. PhotChem&PhotBiology (2012)



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

Laser Fragmentation of NPs: MD simulations

R=50 Å, absorbed energy e=0.6 eV/mol

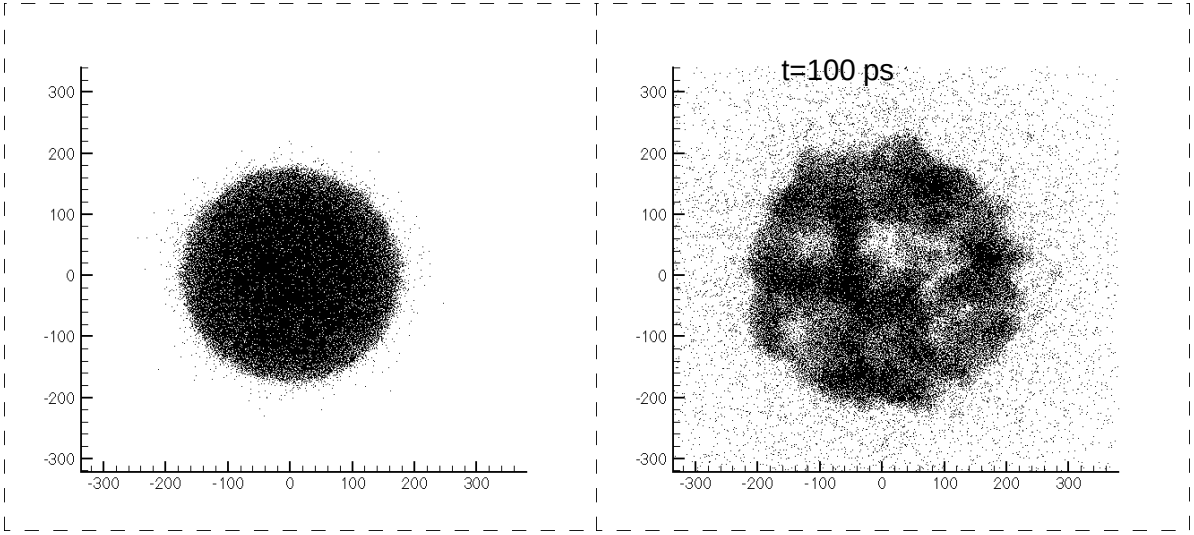


Smaller NPs

Evaporation

(can be also due to Coulomb Explosion for small clusters and fs laser)

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

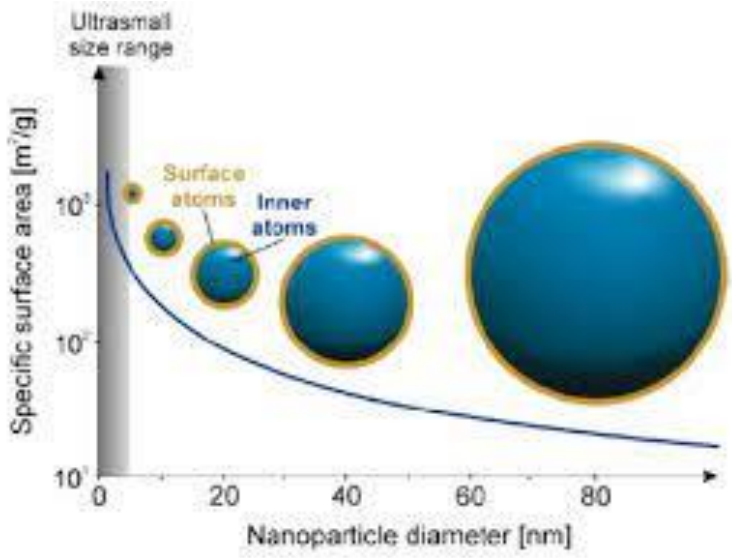


Larger NPs

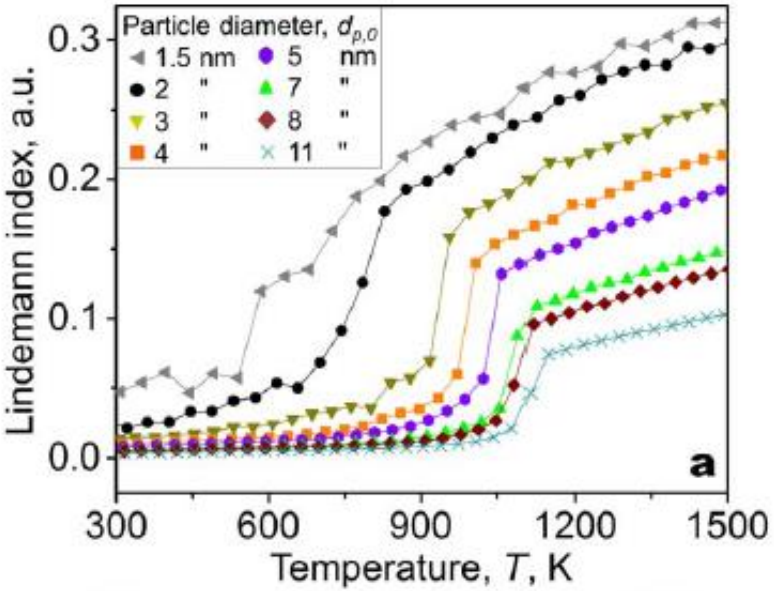
Fragmentation due to thermo-mechanical effects

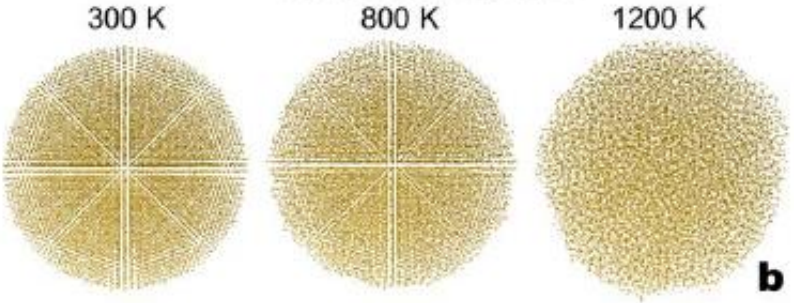
NP's Heating and Melting : Size Effects

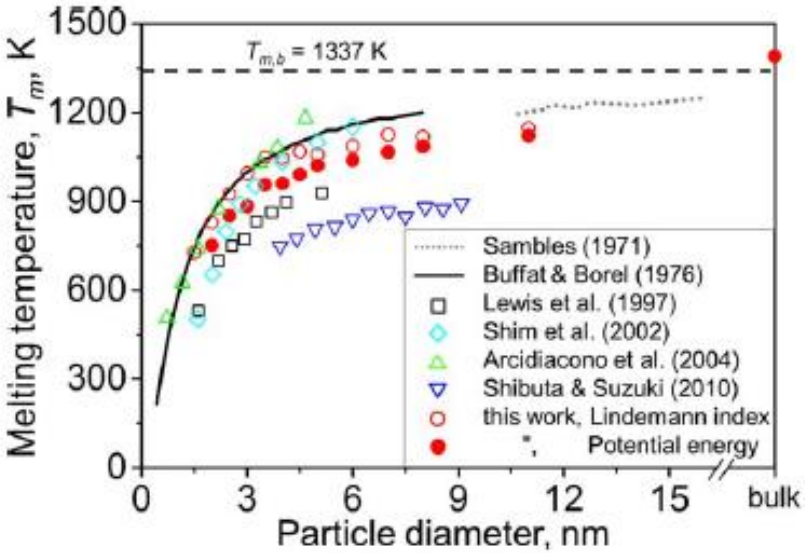
Melting and structural transformations: role of NP's sizes



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







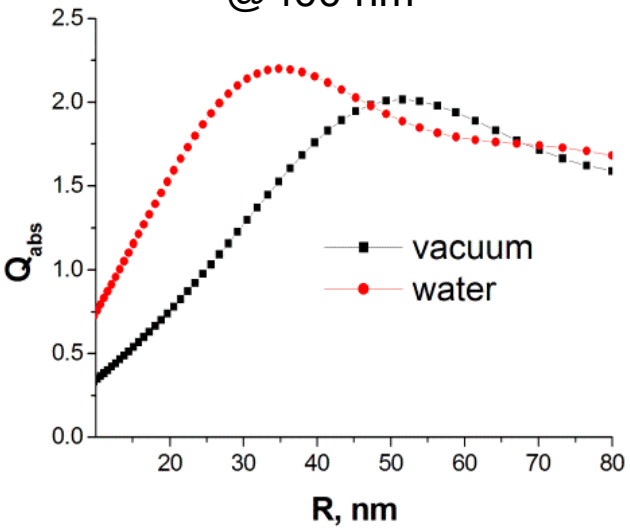
E. Goudeli et al., AlCheE 2015

Laser Energy Absorption vs NP's size

Absorption coefficient / efficiency
(beyond SPR for gold)

(a)

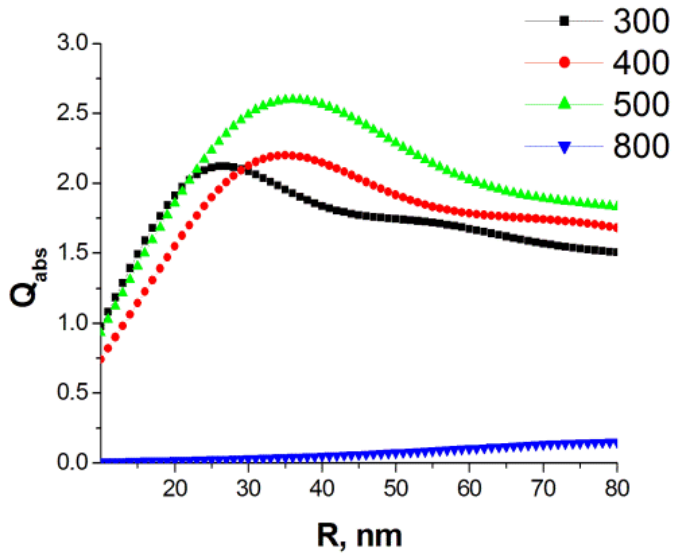
@400 nm



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

- **peak in absorption at** R=R*~ 30 nm for Au NP in water

(b)

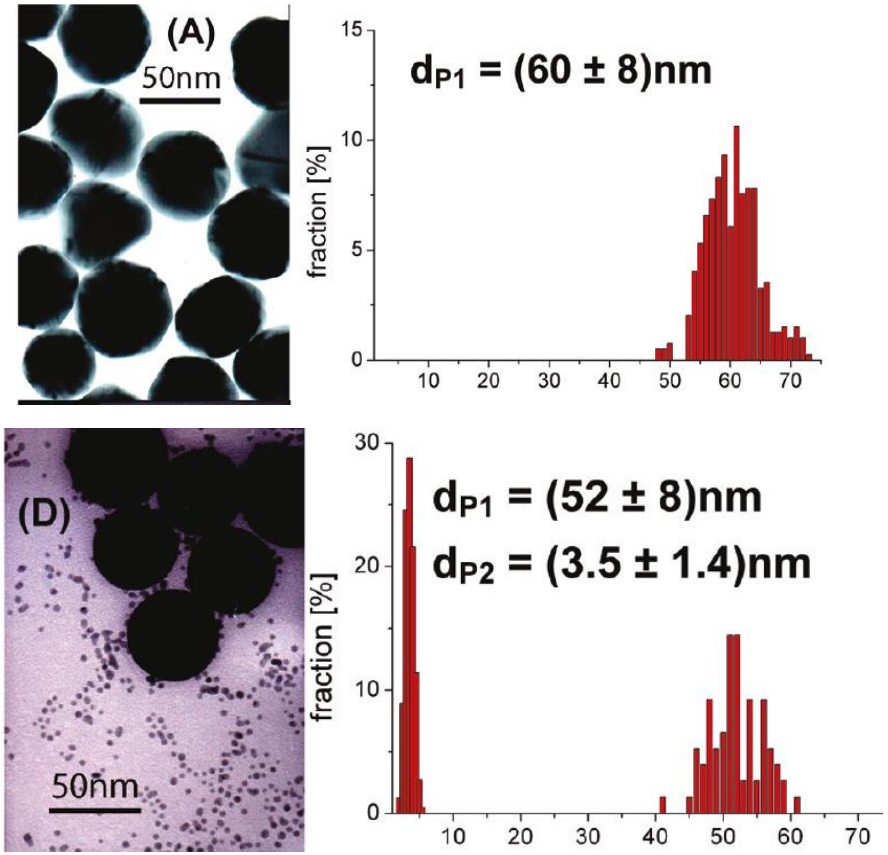


Gold NPs in water for different wavelength @300-800nm

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

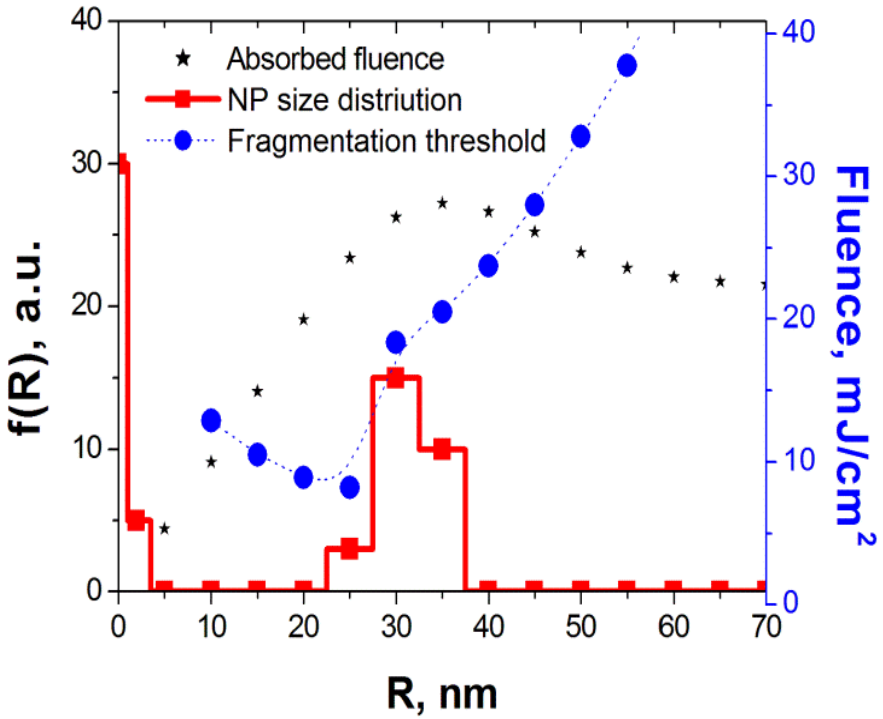
Ultra-short Laser Interaction with Au NPs in Water

Experiments



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

Modeling

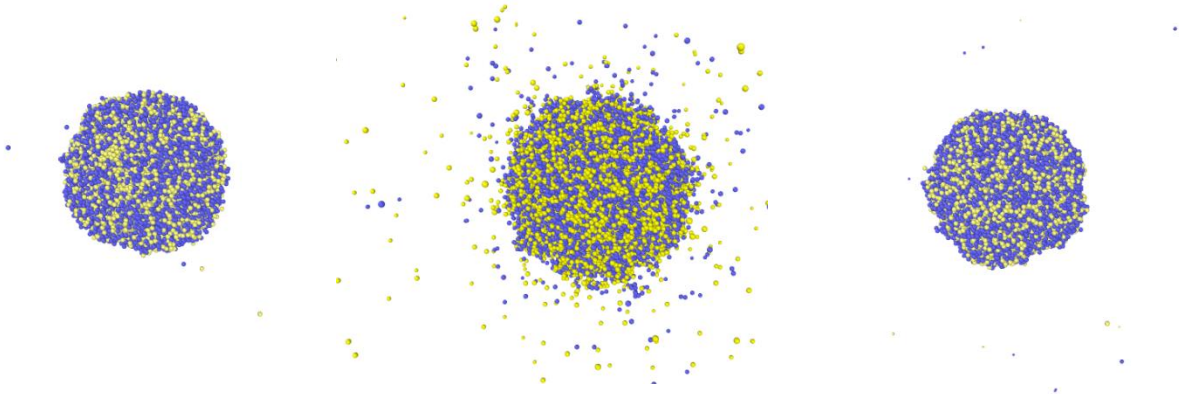


Good correlation with evaporation threshold vs R

L. Delfour and T.E. Itina J. Phys. Chem. C 119 (24), 13893 (2015)

Metal NPs: Evaporation vs Fragmentation

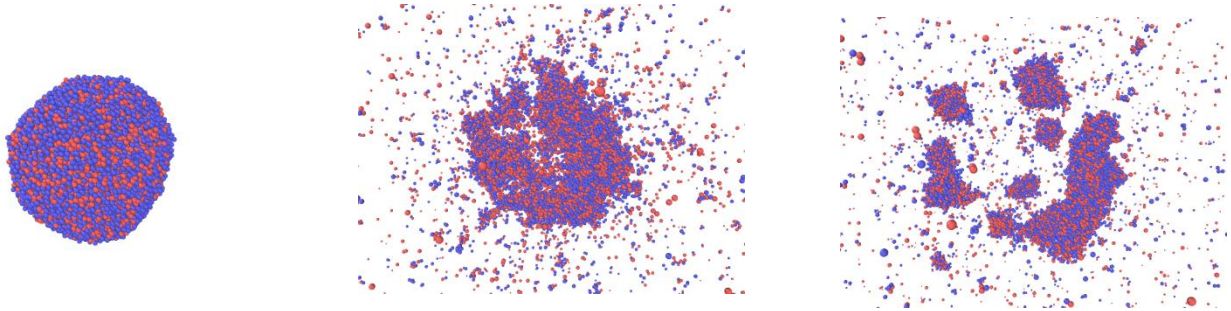
Au-Co , R= 40 50%,
absorbed energy below threshold



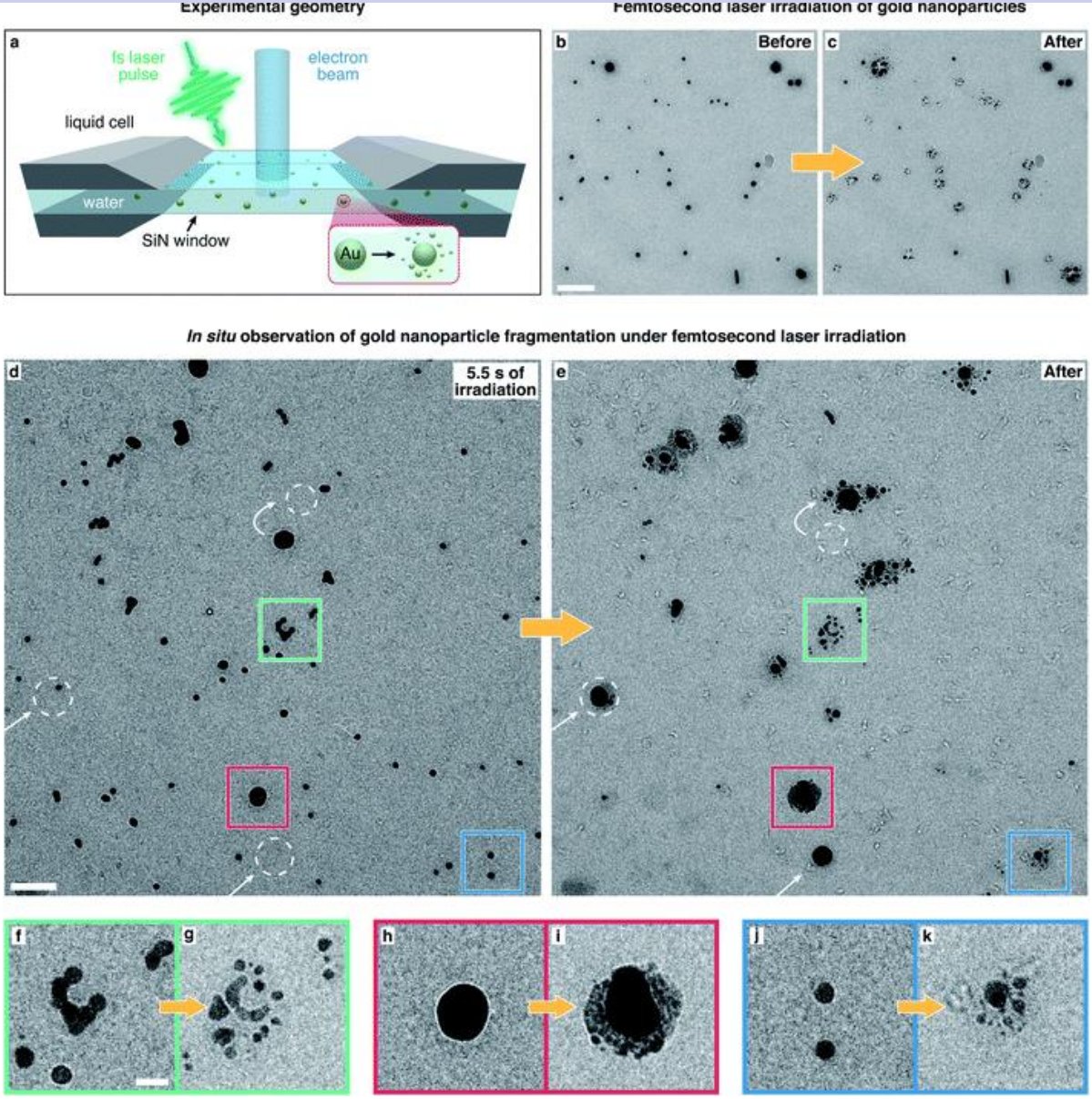
We number
(drag force/coherence force)

Wed=(Ed/Ek) We
(deformation energy)/ kinetic energies

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

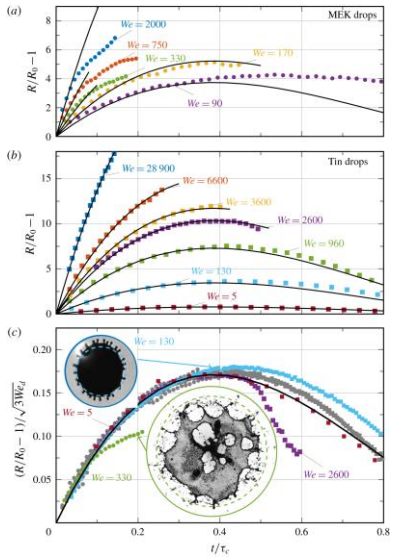


Metal NPs Fragmentation: Experiments

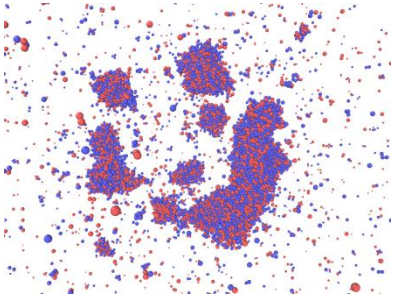


Gold nanoparticles in water

AL Klein · 2020 drop model



Look similar to MD results for NP

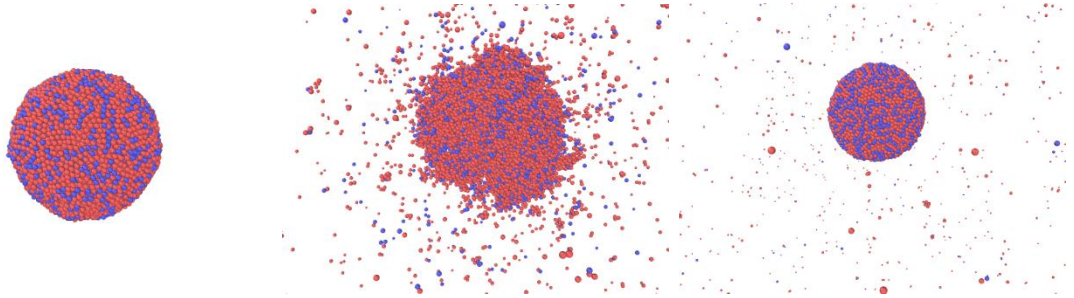


G. Bongiovanni et al.
Nanoscale Adv., 2021, **3**, 5277-5283

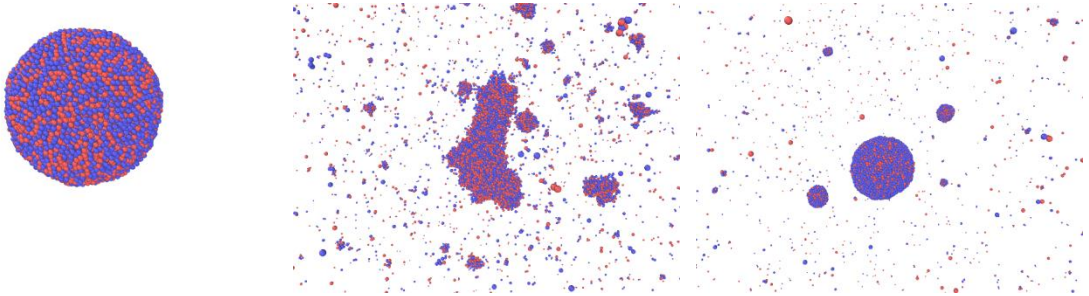
Alloy NPs: Composition affects fragmentation

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

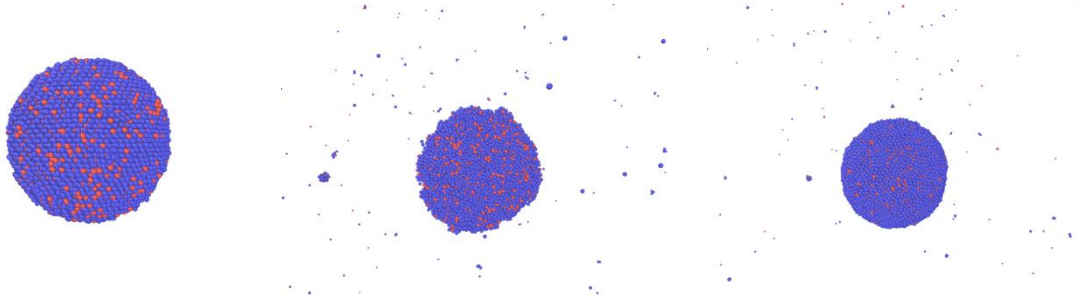
20%



50%

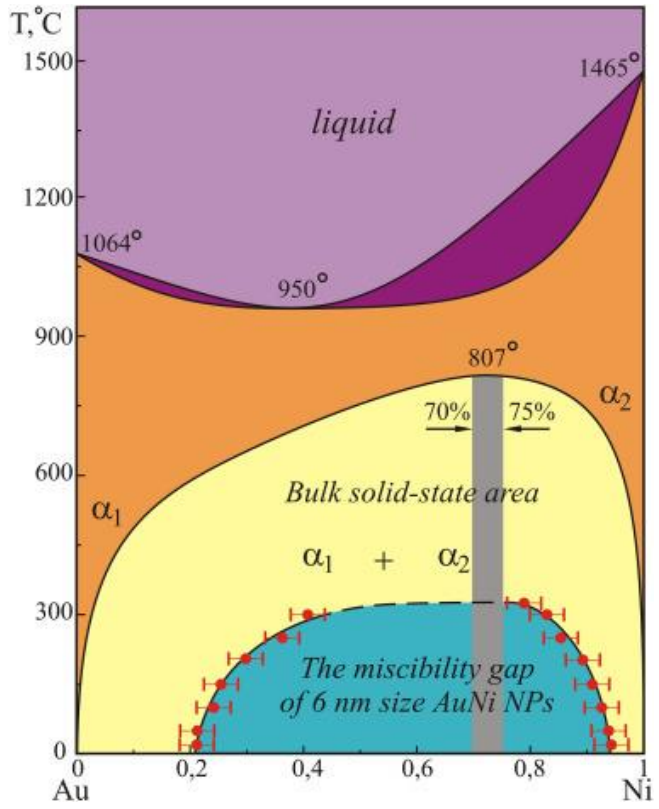


80%



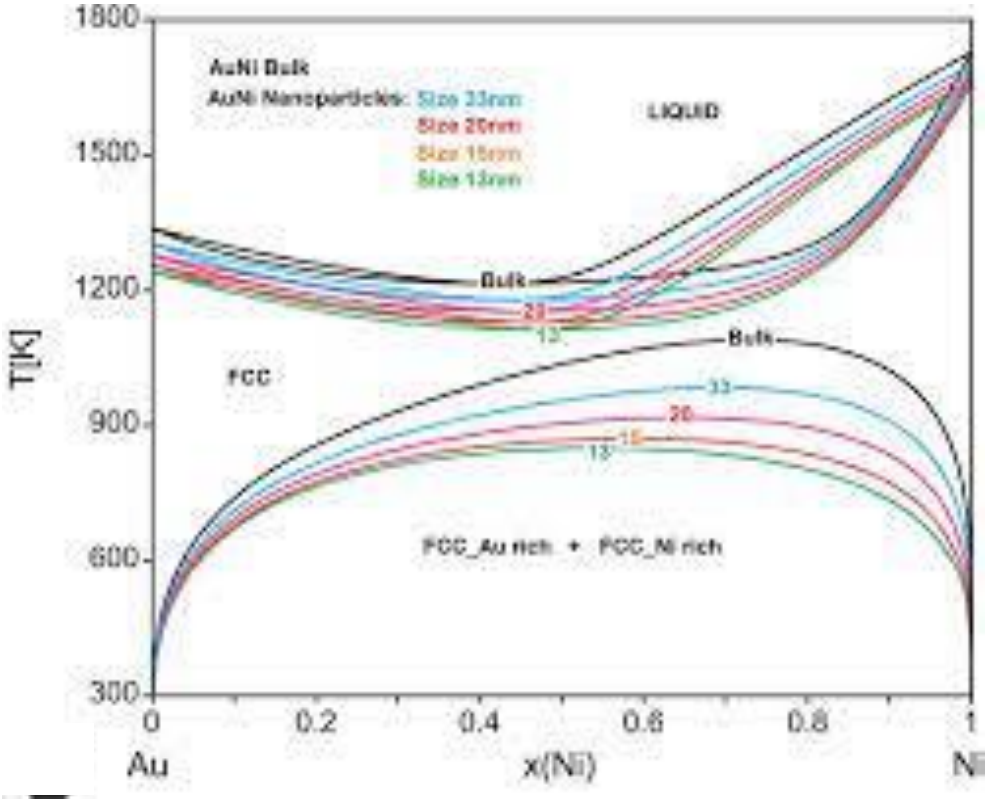
Phase diagrams: NP vs Bulk Material

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



Au-Ni NP

NB: Under equilibrium conditions



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

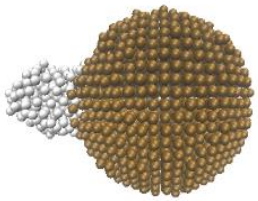
*H.Okamoto. ASM International. (2000), 828.

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

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

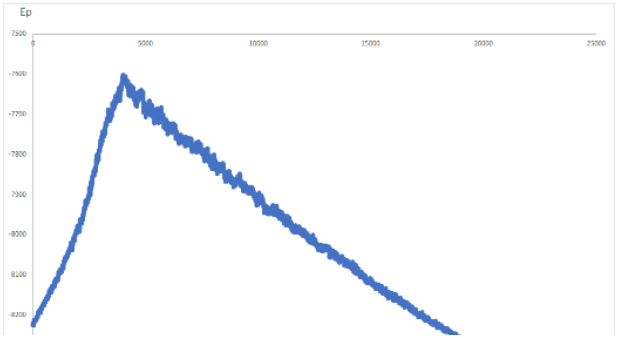
NP Sintering or Alloying

FeNP R=10 uc AuNP R = 20 uc



Different sizes and species, but the same temperatures

Time-evolution of energy



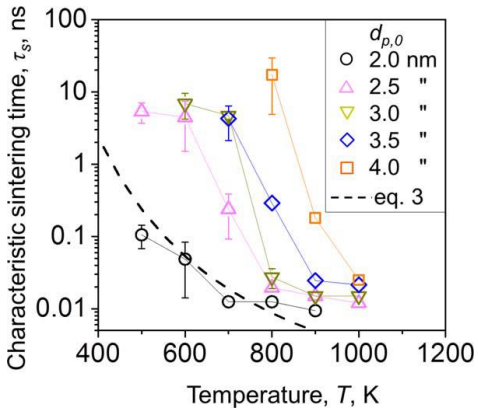
FeNP 1700+AuNP 1700

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**

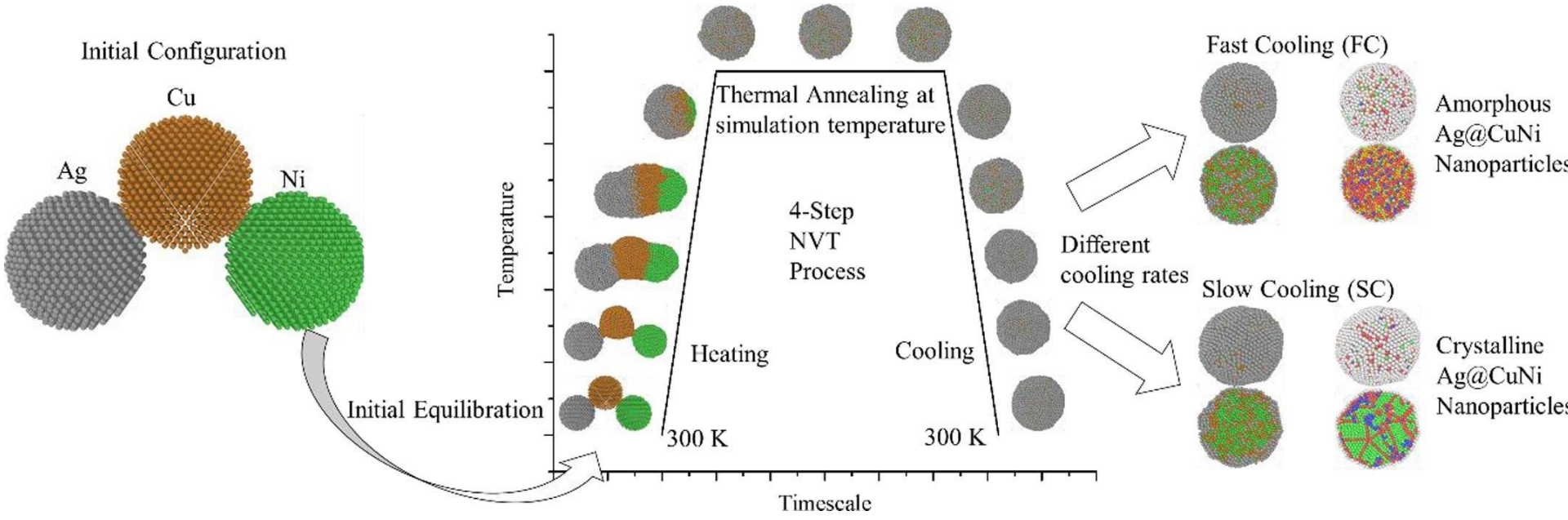
Core-shells can be formed when one particle is much larger and is composed of a material with different cohesive energy



E. Goudeli et al., AIChE 2015

Sintering vs Alloying, High-Entropy Alloys

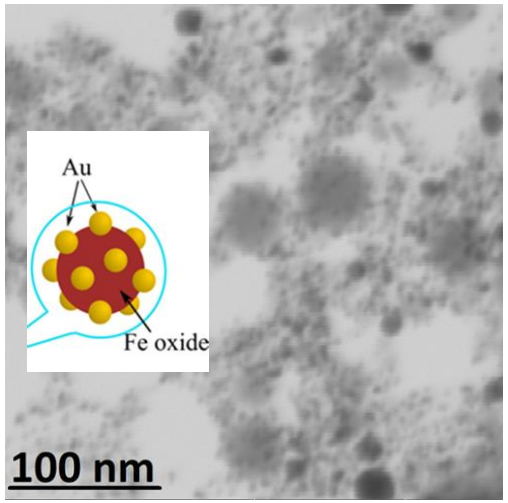
AgCuNi, 10,843 atoms

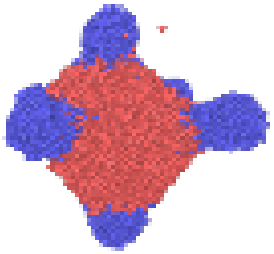


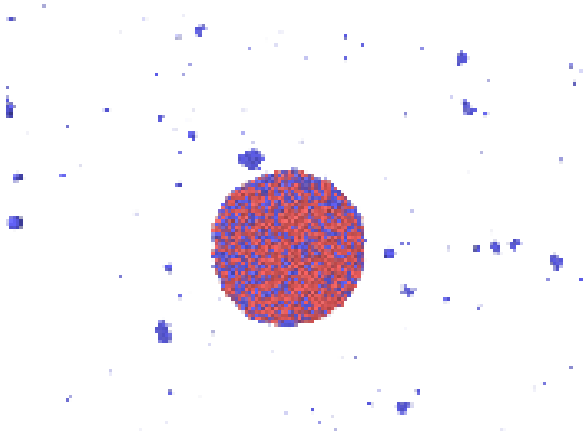
For heating simulations, we studied only the heating part. For cooling simulations, we studied full timescale. Right, cooling part investigated with 2 cooling rates, fast cooling (FC), 1×10^{13} K s^{-1} and slow cooling (SC), 1×10^{11} K s^{-1}

S. Safaltin et al. Computational Materials Science
Volume 183, October 2020, 109842

Complex Nano-Objects Formation by Laser Co-Ablation

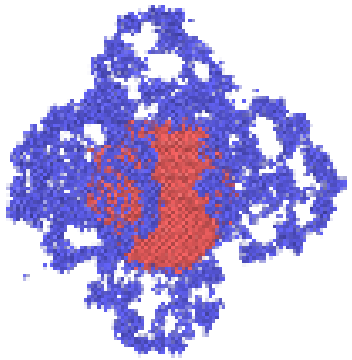


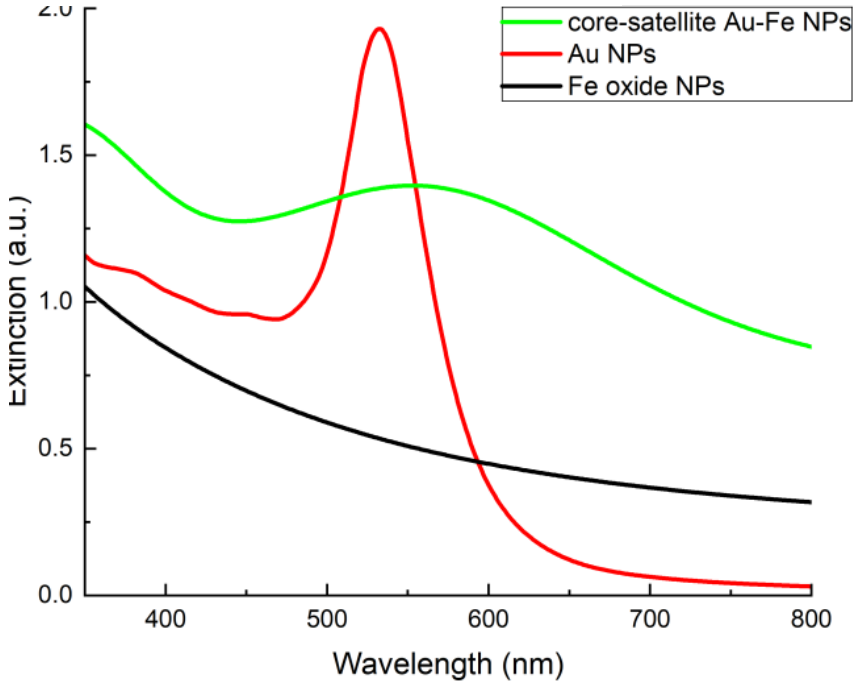




Raspberry –like, core-shells or alloys

: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).





Experiments: Popov et al.10.3390/nano12040649, modeling: T. E. Itina, LabHC

Outline

4. Modeling nanoparticle formation in porous matrices

Ion-impregnated porous thin films

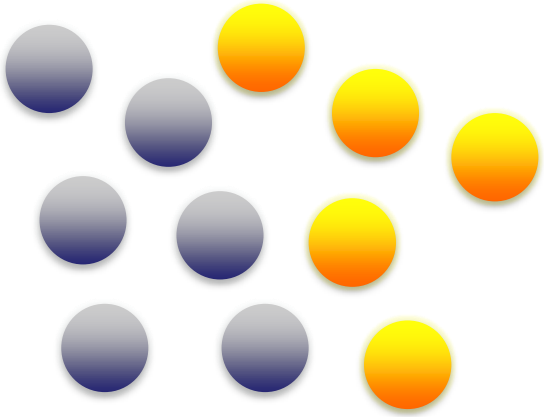
- sol-gel mesoporous films are prepared and impregnated by saults
- these samples are then irradiated by laser

Porous films:
SiO_2 , TiO_2

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

Metallic NPs:
Ag, Au

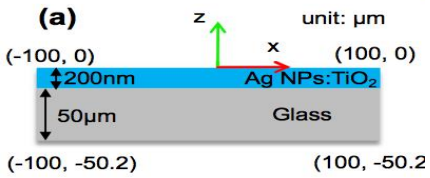
Produced by soaking in metallic salts solutions with consequent reduction
Initial size < 3-5 nm

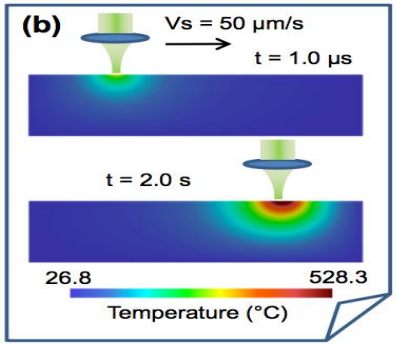


Laser irradiation:
CW
Nanosecond
Picosecond
Femtosecond

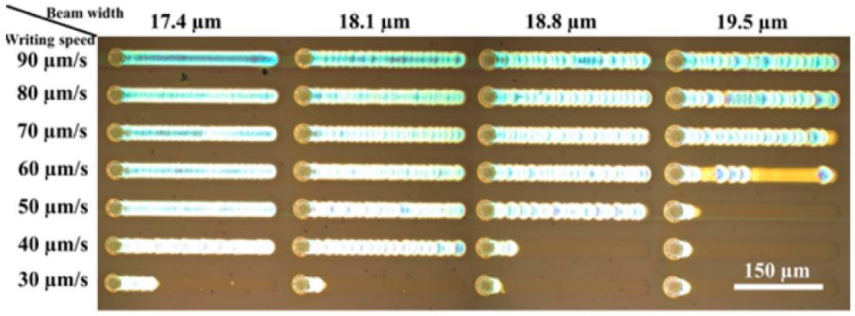
Ion-impregnated porous glasses and semiconductors
can be used as samples for following laser-induced nano-structuring

Scanning laser irradiation of Ag-TiO_2





2 different regimes



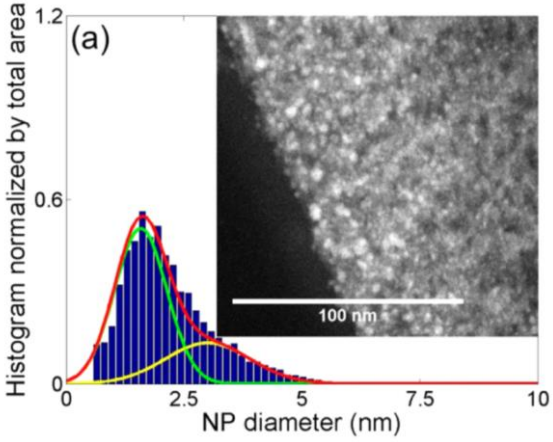
Random NPs

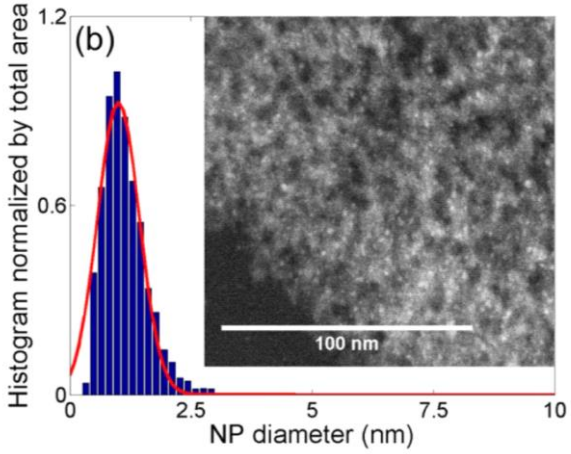
Periodic NPs self-organization

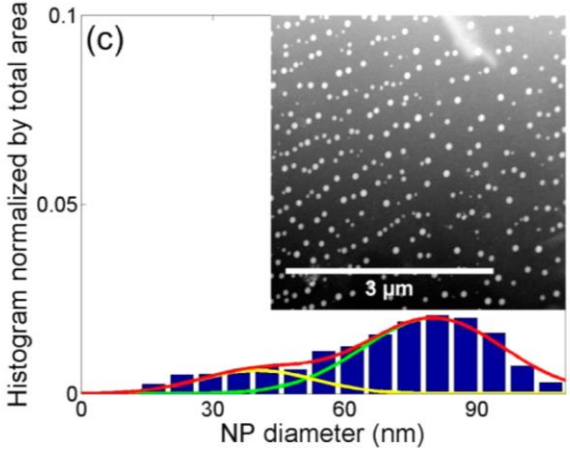
Initial state

Scan speed below threshold

Scan speed above threshold





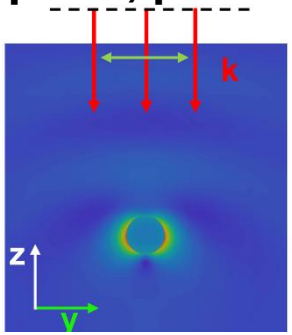


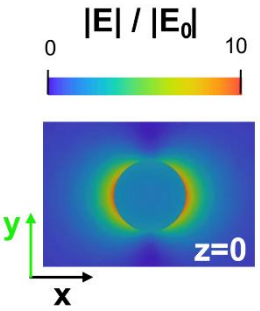
P_{av} = 150 mW , d_0=22.9 μm.

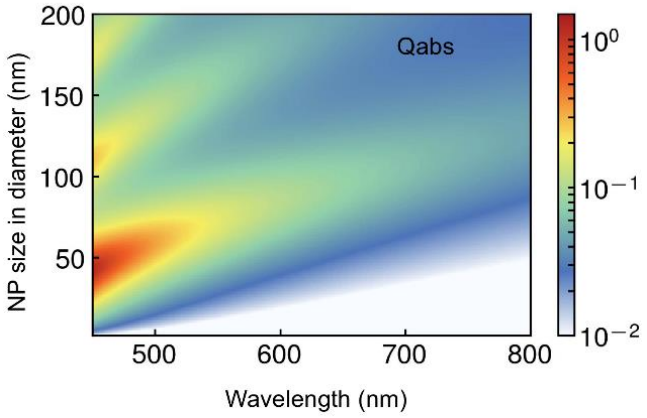
Z. Liu, et al. The Journal of Physical Chemistry C 119.17 (2015): 9496-9505.

Nanoparticle formation and growth

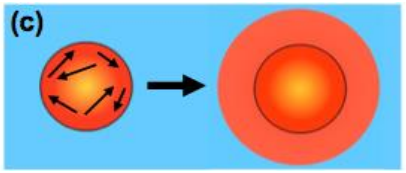
1. Laser light absorption, plasmon resonances



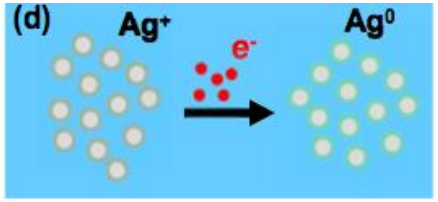




2. Heating and thermal diffusion



3. Photoemission and reduction



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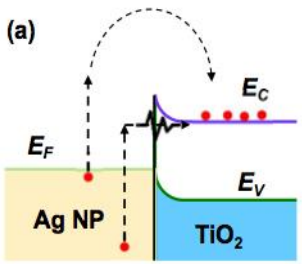
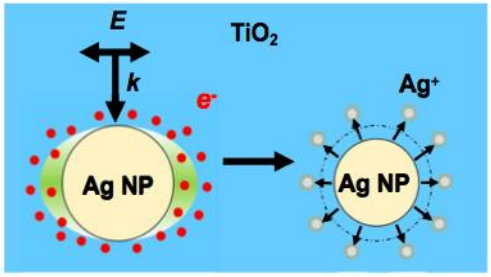
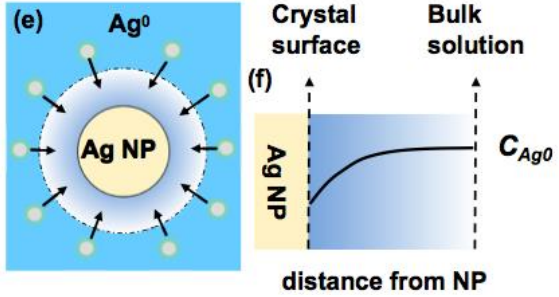
5. Photo-oxydation





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^+ variations

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

Ag^0 variations

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

NPs radius

heat diffusion

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

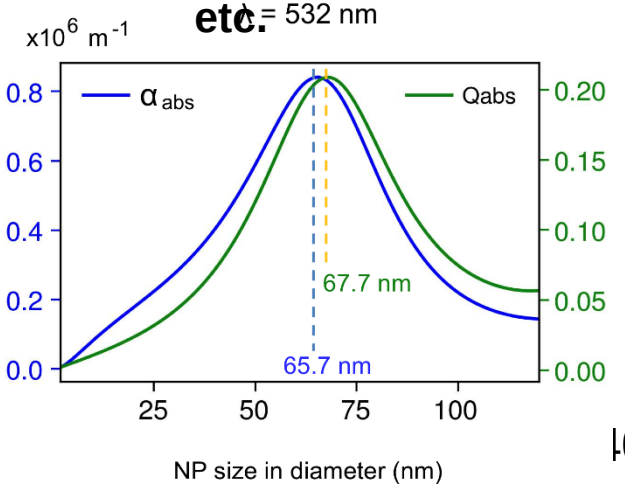
reflection

Absorption

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

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

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



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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

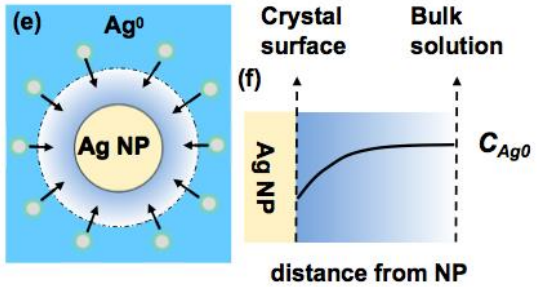
$$\frac{dC_{Ag^+}}{dt}|_{red} = \exp\left(-\frac{E_p}{N_A k_B T}\right) \cdot D_0^{red} \exp\left(-\frac{E_D}{N_A k_B T}\right) \cdot C_{red} C_{Ag^+}^{2/3}$$

reduction

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

NP growth

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



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

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

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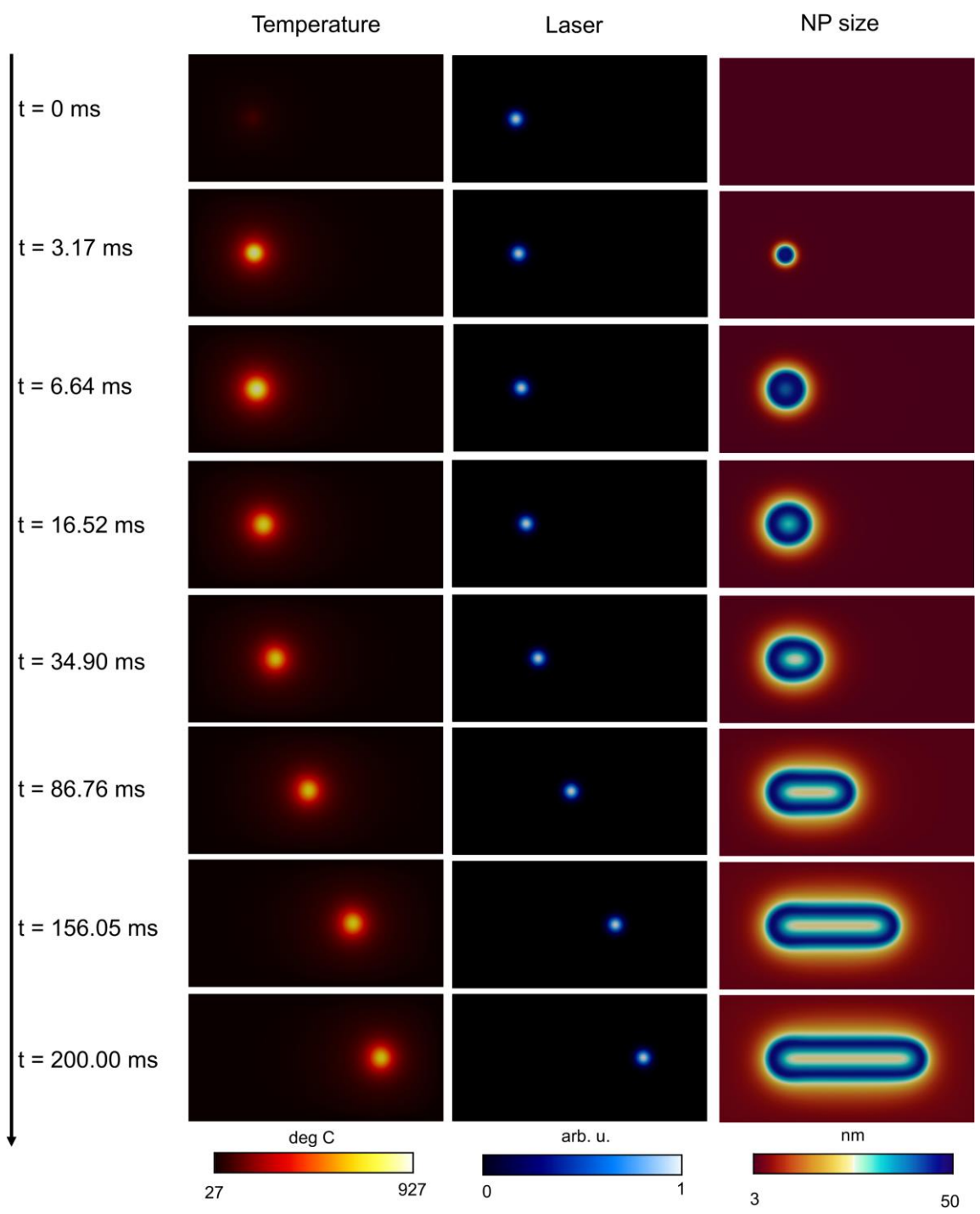

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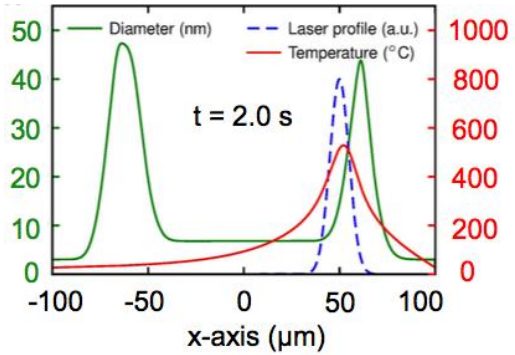
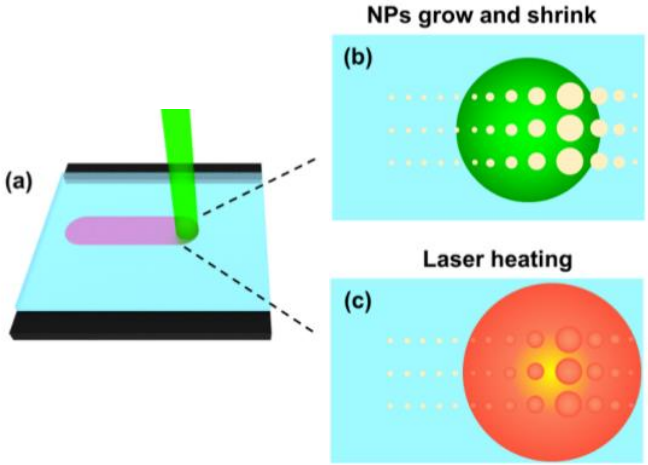
2D Simulation

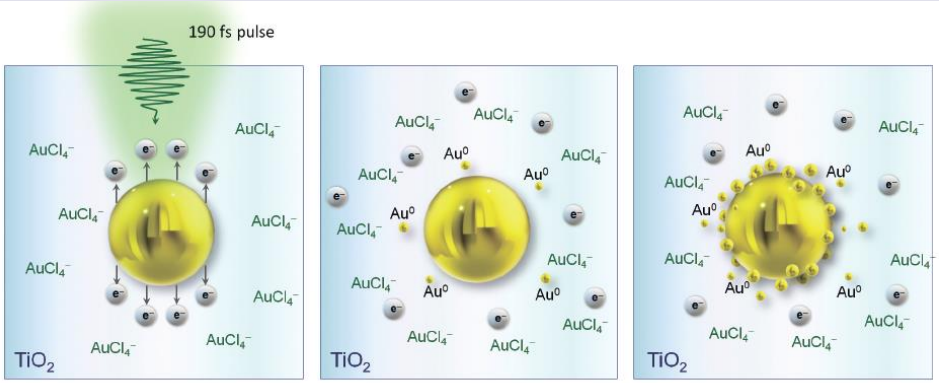




Absorption and scattering by a set of NPs within the laser spot:

-effective medium

Au NPs in TiO_2 under Ultra-Short Laser Irradiation



At the beginning, the matrix is solid

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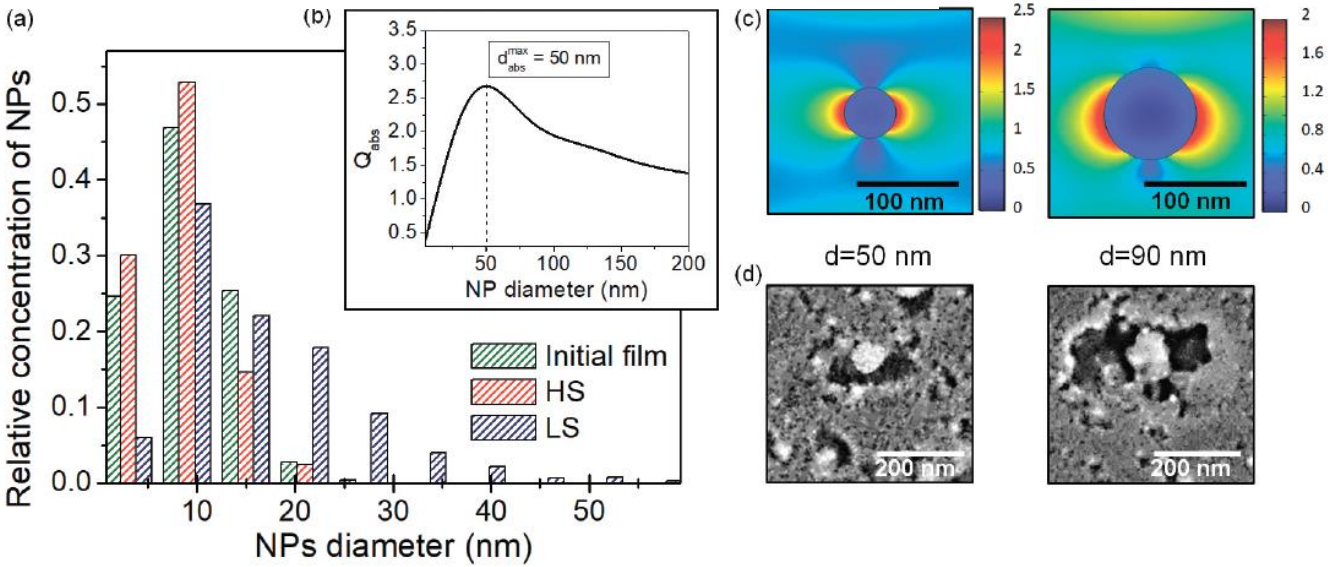
124 (18), 10209-10219, 2020



fs laser
λ =515 nm

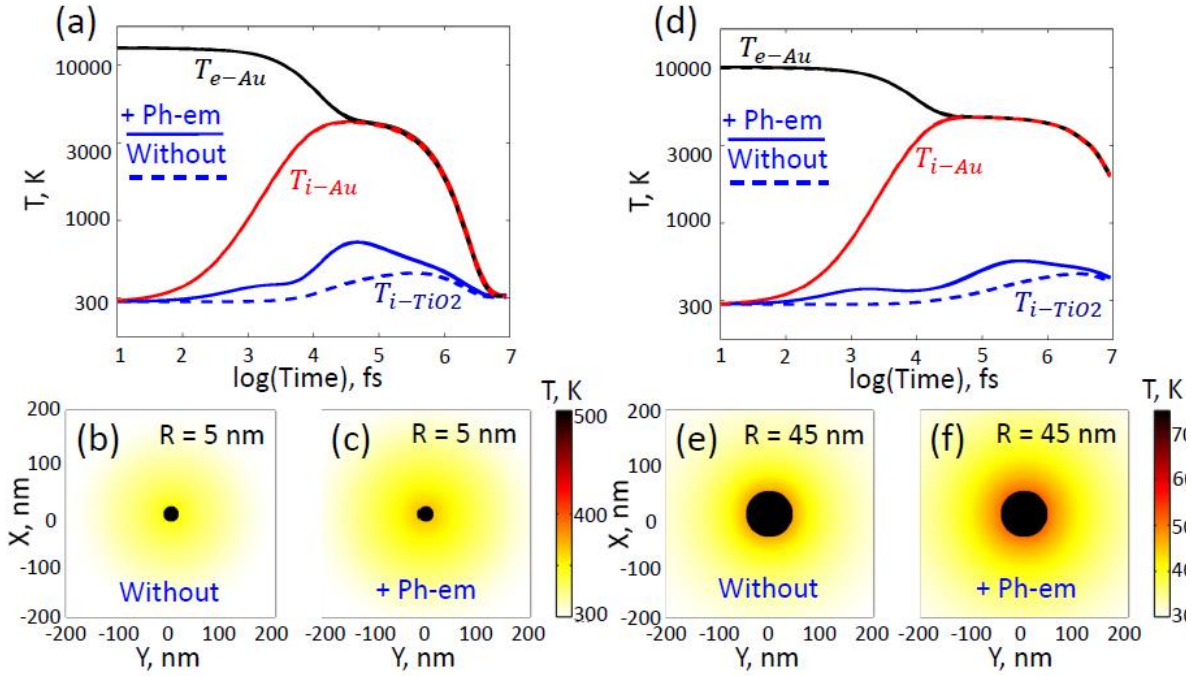
(a) Size distribution of gold NPs in before and after laser treatment. Laser F = 57 mJ/cm2, scan speed for LS structures is 0:16 mm/s, for HS structures is 1:6 mm/s.

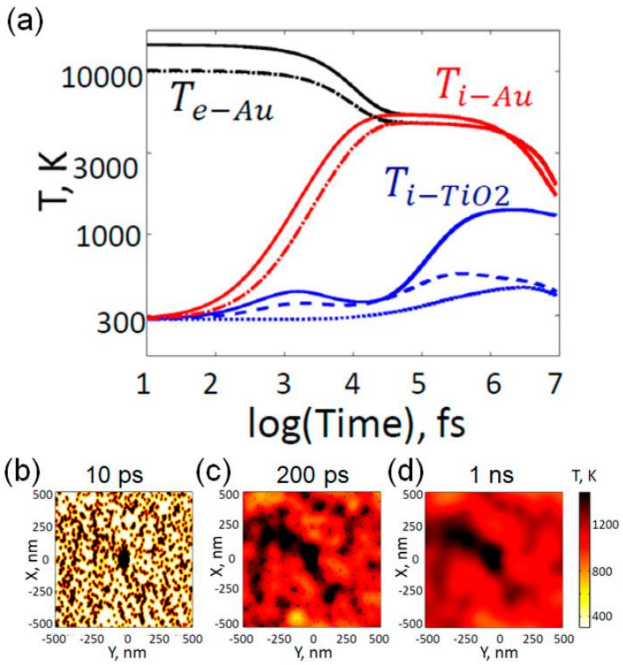
(b) Calculated absorption efficiency of the nanocomposite based on TiO2 as a function of the diameter of gold NPs (refractive index of surrounding media n = 1:6).

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

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

Au NPs in TiO_2 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 J/cm2 irradiation. Blue dotted line indicates temperatures attained if only heating from single nanoparticle is considered and blue dashed line additionally includes electron photo-emission.

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Only when the collective heating by smaller R = 5 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.

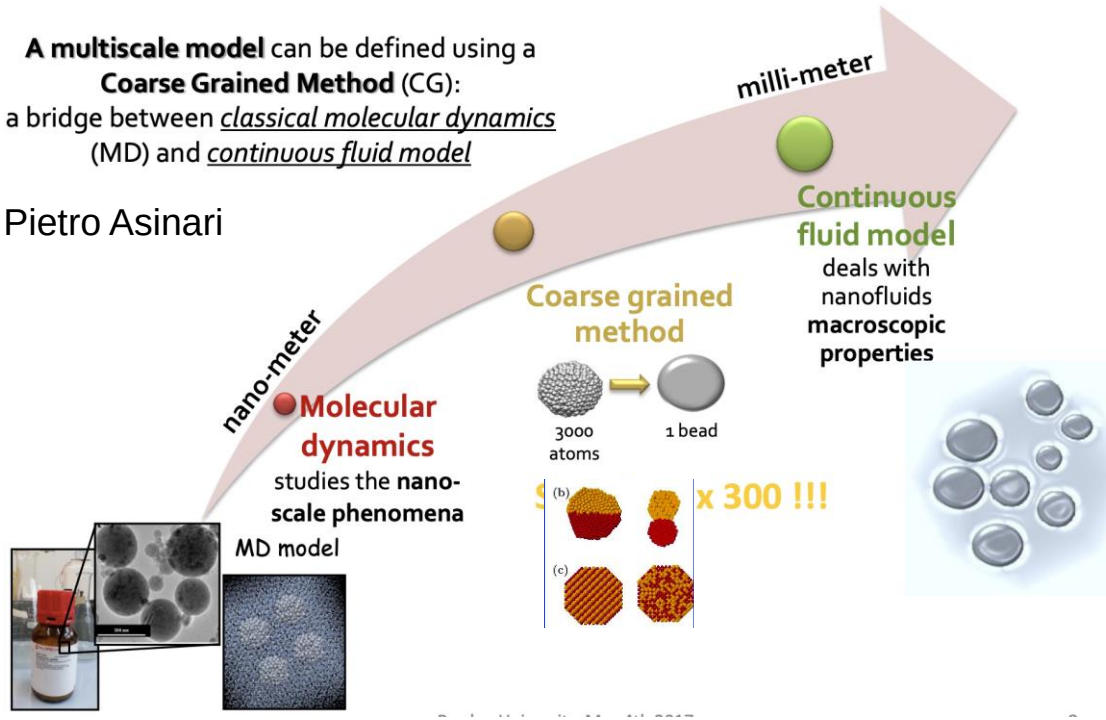
  -NP's of smaller sizes easily melt and evaporate, while larger NPs behave more like bulk material, so that thermo-mechanical fragmentation of over-heated material plays a role in their fragmentation. Phase diagrams of NPs smaller than ~30-100 nm should account for NP's size.

  -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



- MD (fully atomistic and coarse-grained)
  - Distribution of Sizes
  - Morphology(alloy, etc)
  - Transition to coarse-grained case
- DLVO theory (force field from MD)
  - Aggregation
  - Disaggergation
- CFD or DNS (two phase hydrodynamics)
  - Rules of theory:
    - Conservation of Mass
    - Conservation of Energy
    - DNS: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:

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CNRS and UJM

Thank you for your attention!

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