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Laser-matter interactions and modern nanotechnology

Tatiana Itina

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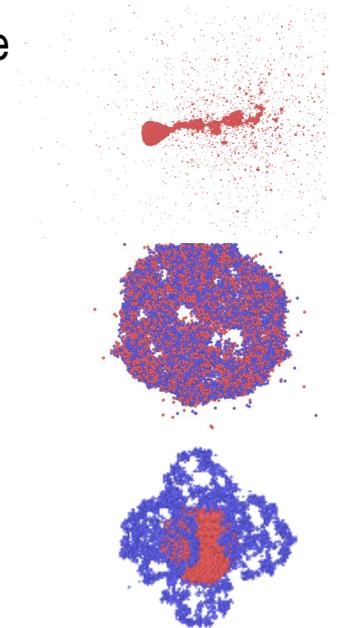
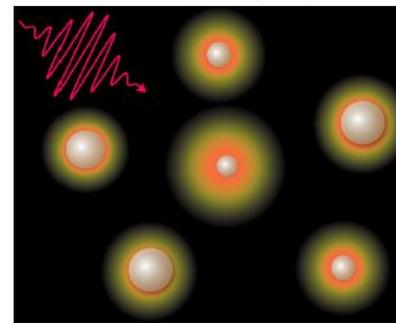
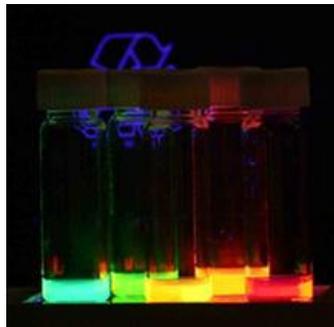
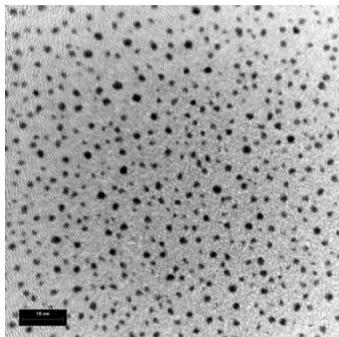
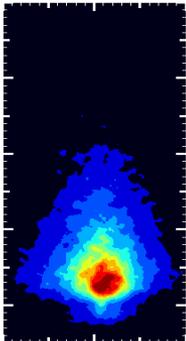
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Laser-Matter Interactions and Modern Nanotechnology

Tatiana E. ITINA

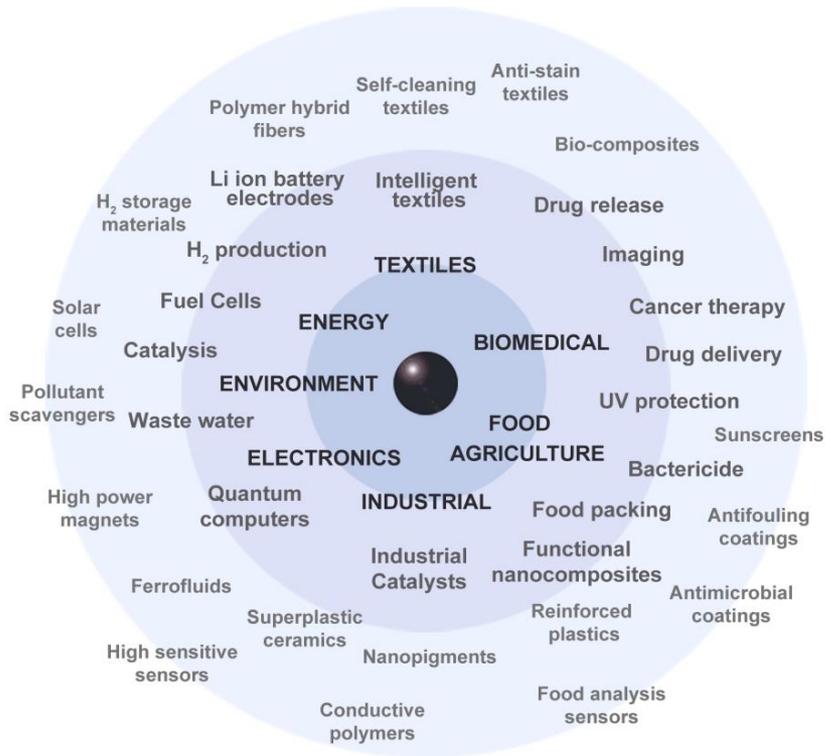
Laboratoire Hubert Curien, UMR CNRS 5516, Saint-Etienne, France

tatiana.itina@univ-st-etienne.fr



**From experiments to simulations,
from fundamental research to applications**

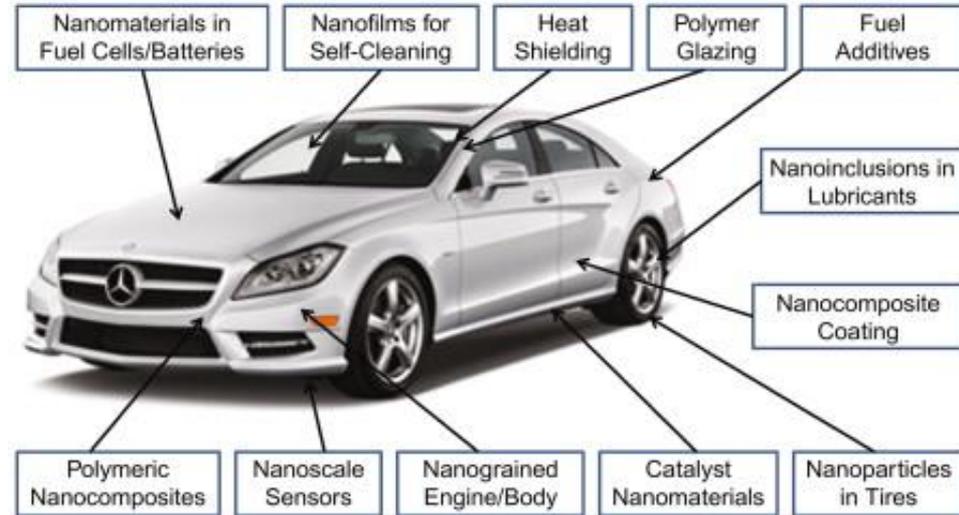
Nanoparticles and Nanocomposites



Aerospace and Defense



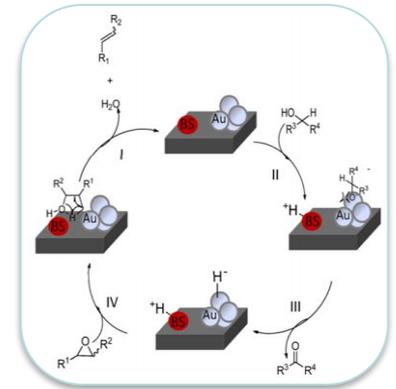
Car industry



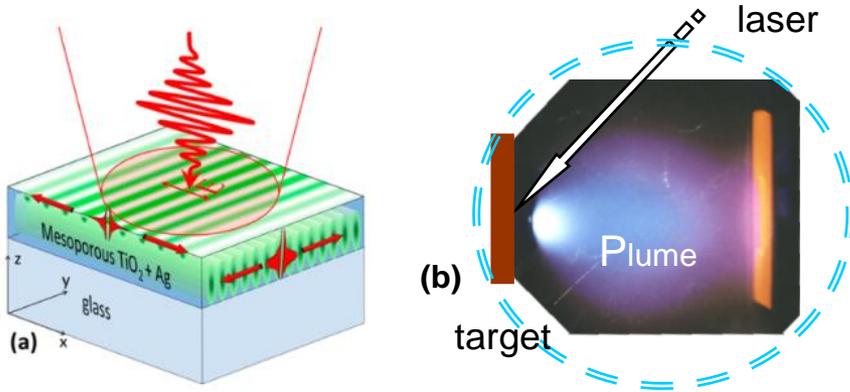
Optics and security



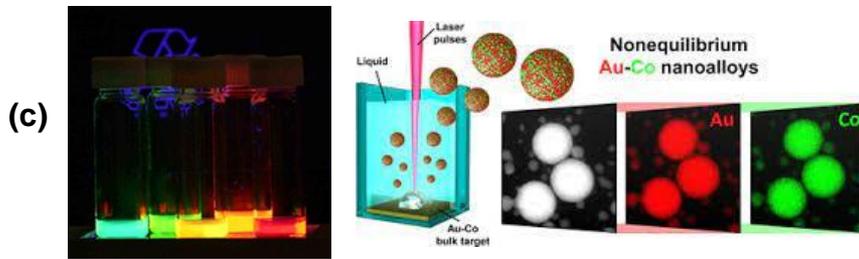
Sensors and Catalysis



Laser Interactions



In gas or in vacuum with different geometry



In liquids or in the presence of colloids

Laser interaction commonly involve:

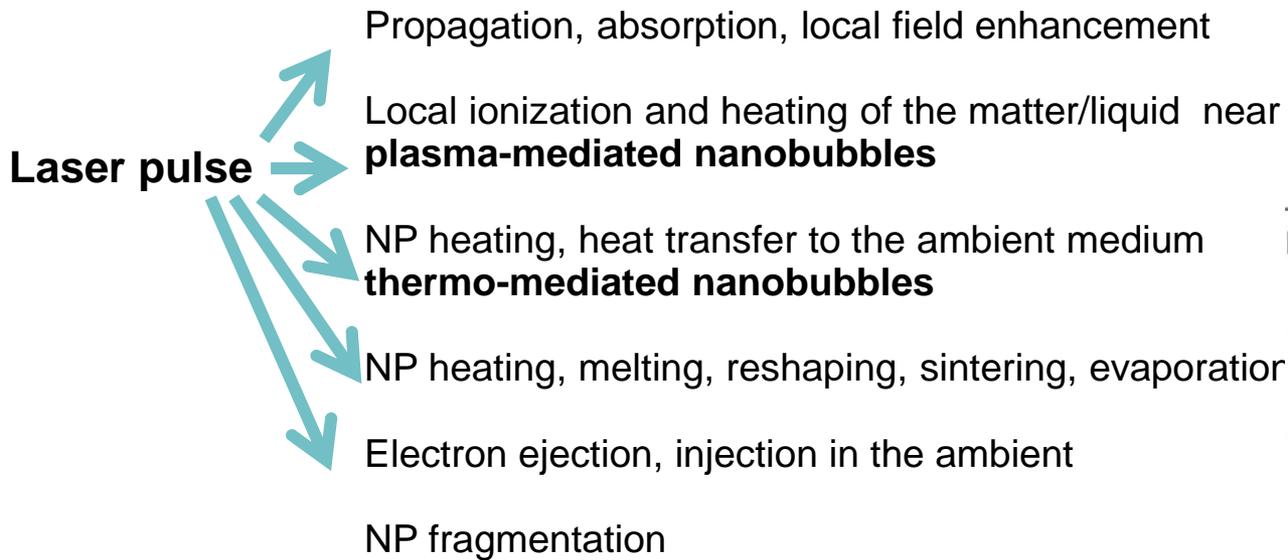
- Energy propagation, electronic excitation, light scattering, reflection and absorption
- Electron-phonon relaxation, heat diffusion, pressure wave propagation, rarefaction and tensile stress, phase transitions, mechanical fragmentation
- Material removal (ablation), plasma plume expansion, reactions,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

Laser-induced nanoparticle formation

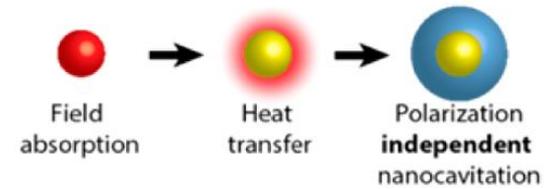
- Green synthesis methods, bio-compatibility
- Control over NP properties
- Scaling-up possibilities
- Possibility to create stable ultra-structures, nanoalloys, hybrids, etc.
- **Additional laser-particle interactions involve many physical and chemical processes**



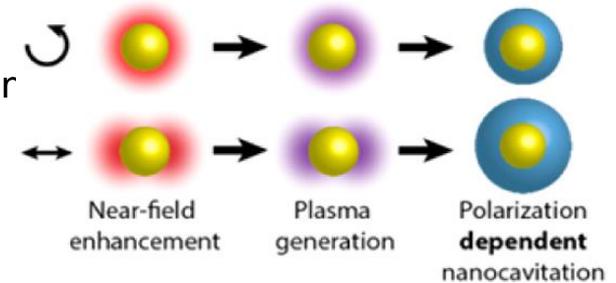
Ultra-short Laser Interactions with NPs



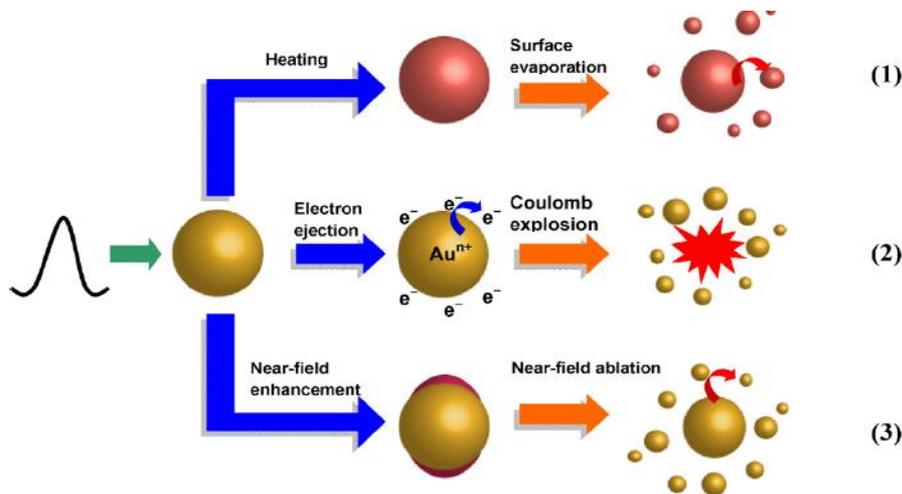
Thermo-mediated nanobubbles



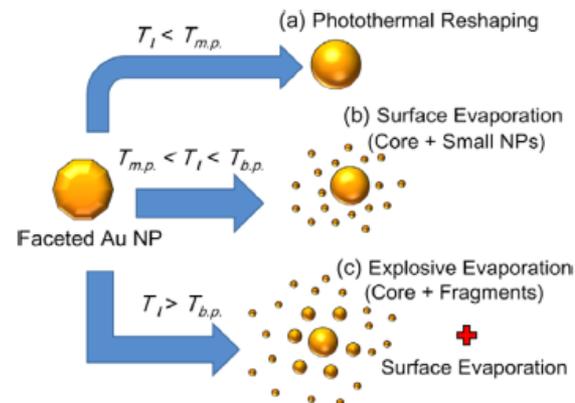
Plasma-mediated nanobubbles



Lachaine et al. Photonics (2013)



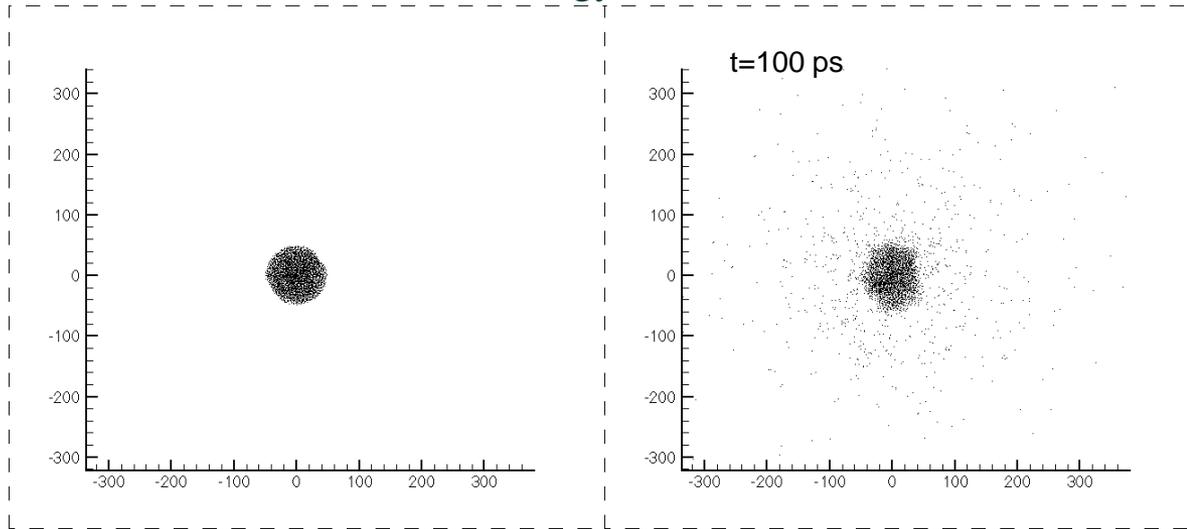
Hashimoto et al. J. PhotChem&PhotBiology (2012)



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

Laser Fragmentation of NPs: MD simulations

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

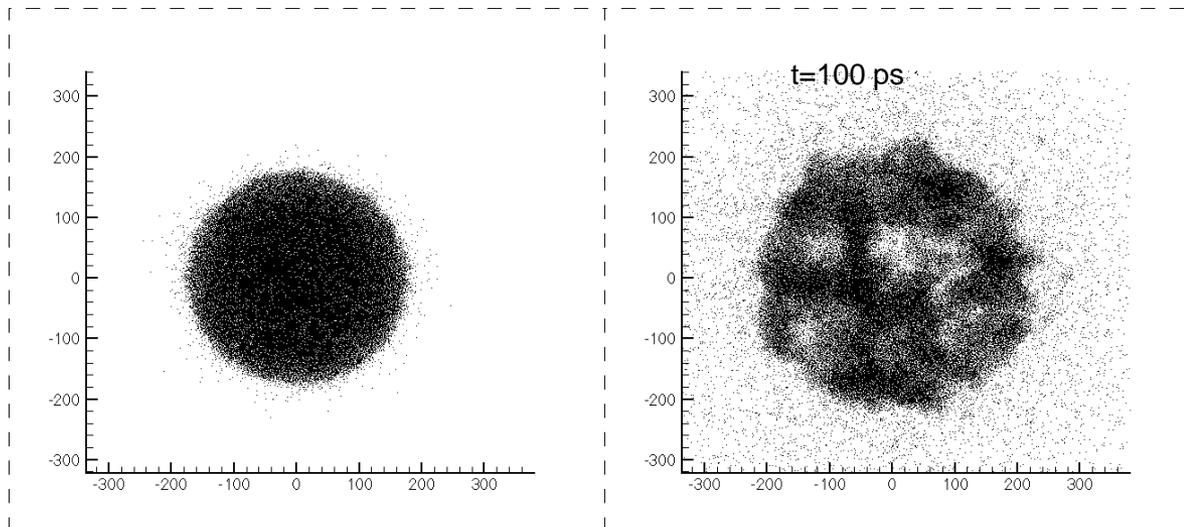


Smaller NPs

Evaporation

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

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

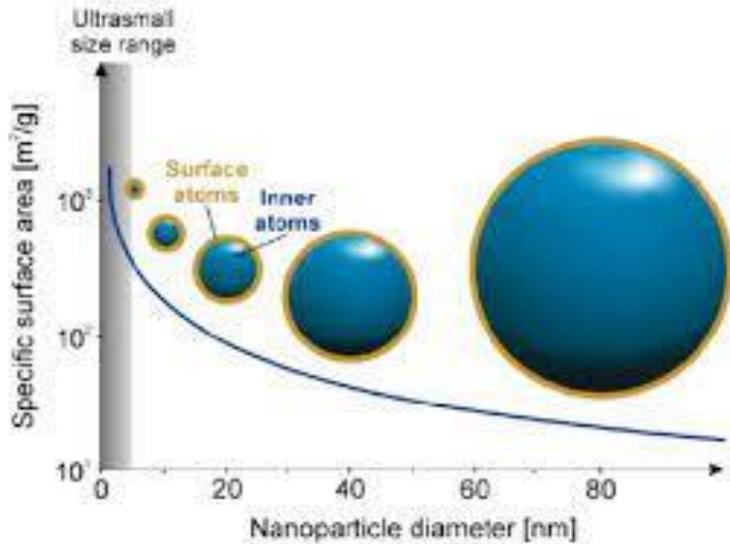


Larger NPs

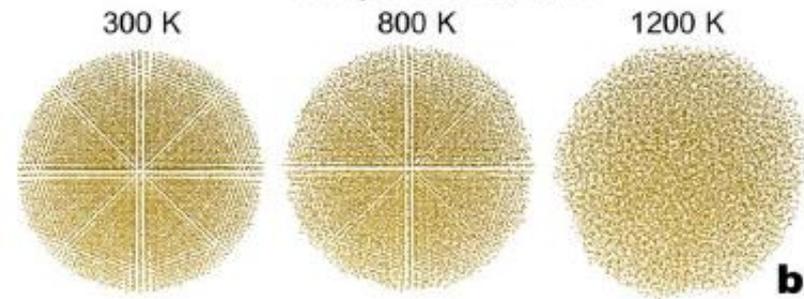
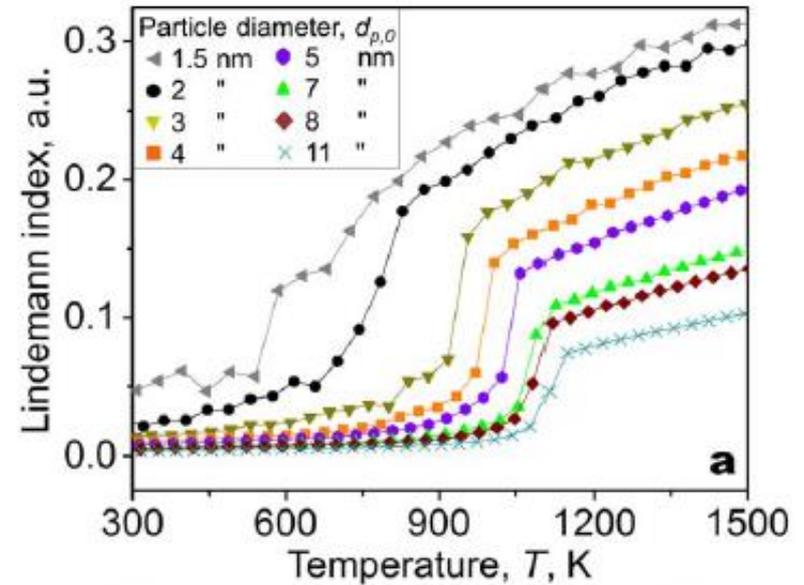
**Fragmentation due to
thermo-mechanical
effects**

NP's Heating and Melting : Size Effects

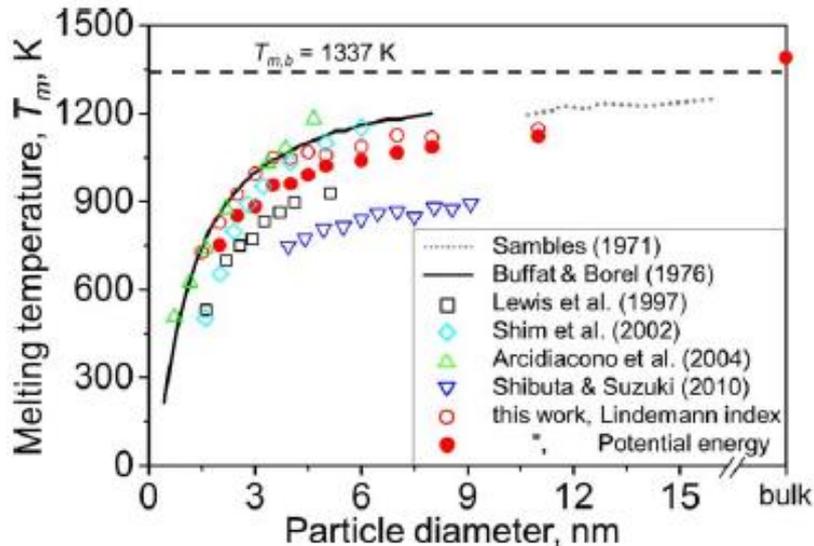
Melting and structural transformations: role of NP's sizes



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

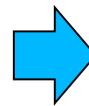
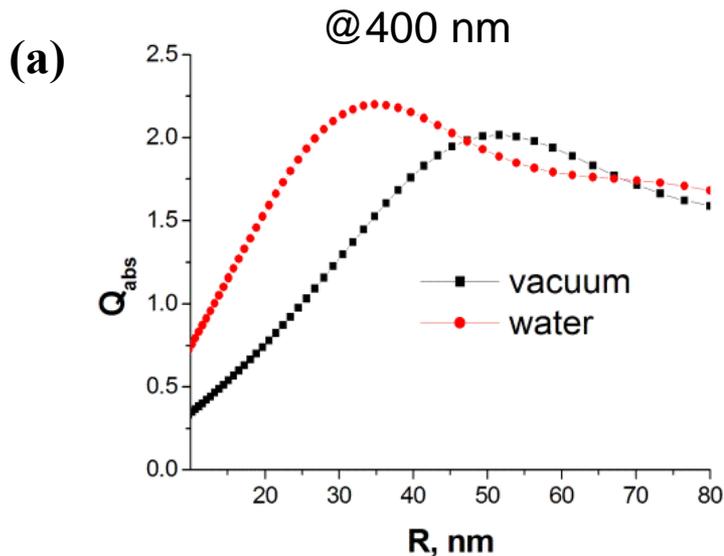


E. Goudeli et al., *AIChE* 2015



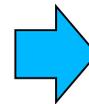
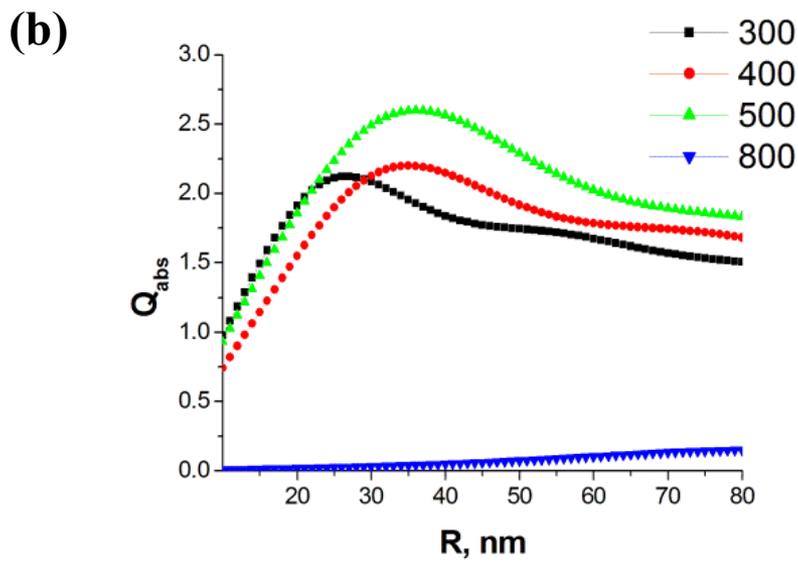
Laser Energy Absorption vs NP's size

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

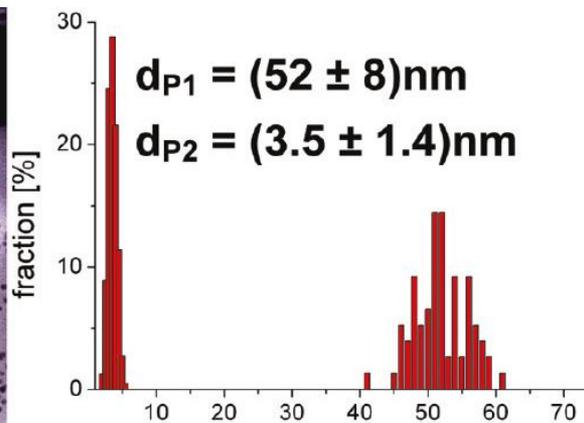
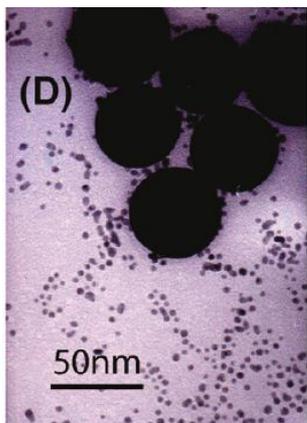
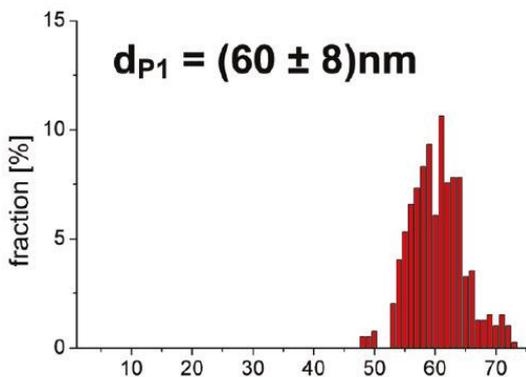
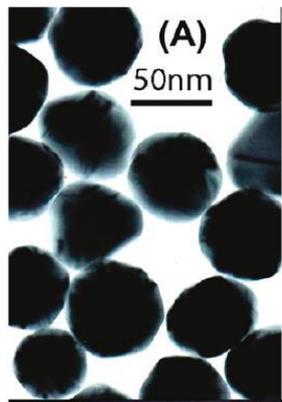


Gold NPs in water for **different**
wavelength @300-800nm

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

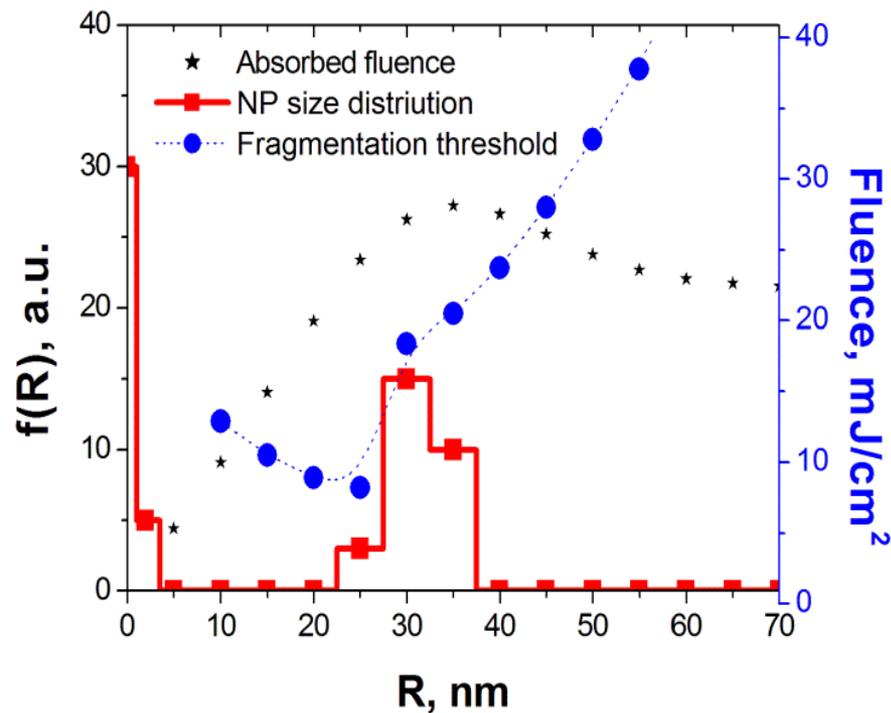
Ultra-short Laser Interaction with Au NPs in Water

Experiments



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

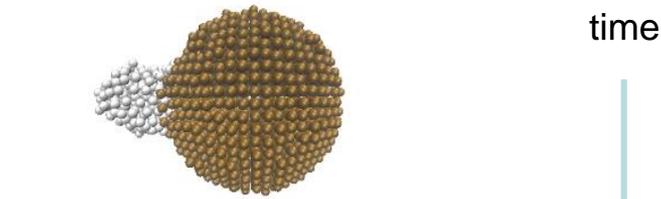
Modeling



Good correlation with
Experimental results

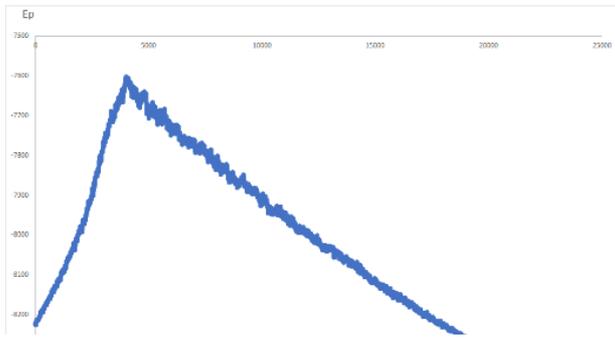
NP Sintering or Alloying

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



Different sizes and species,
but the same temperatures

Time-evolution of energy



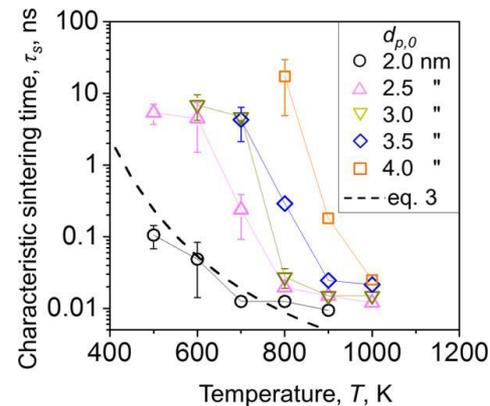
time

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

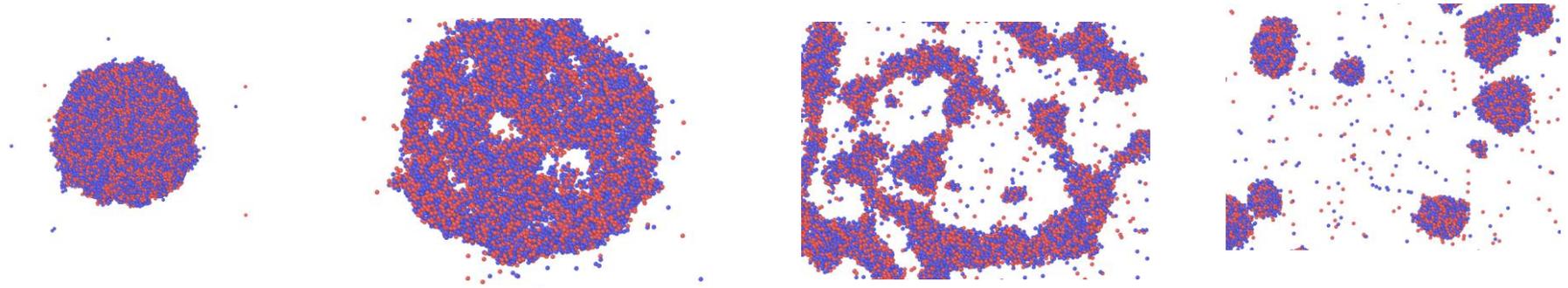
Fragmentation vs Sintering, Additional Fragmentation

Simulations starts from a larger janus AuCo NP, heating to 1700 K

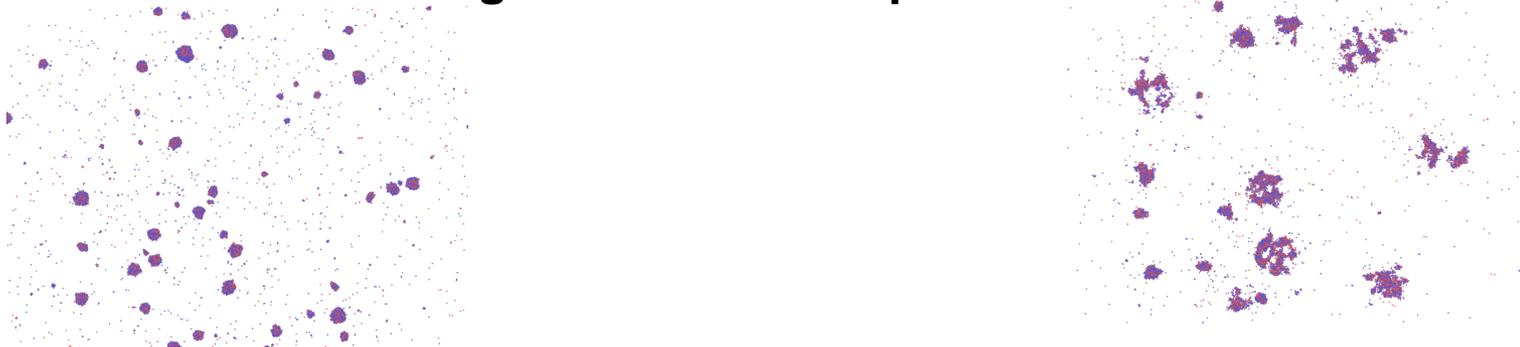
AuCo, Au NP R = 40 un, rapidly heated up to 1700 K



Simulations starts from Alloy AuCo NP, R=40 uc rapid heating above T_c



Simulations starts from the fragmentation results, additional fragmentation takes place



Ion-impregnated Porous Thin Films Treated by Laser

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

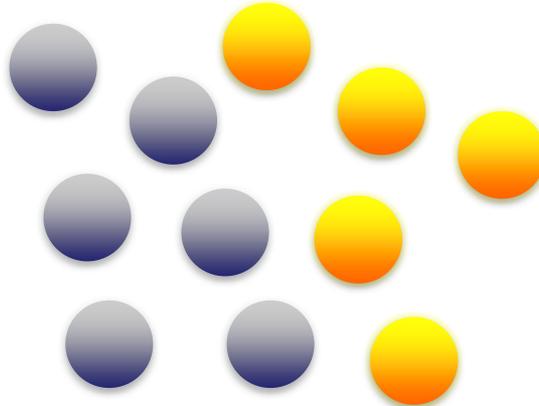
Porous films:
 SiO_2 , TiO_2

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

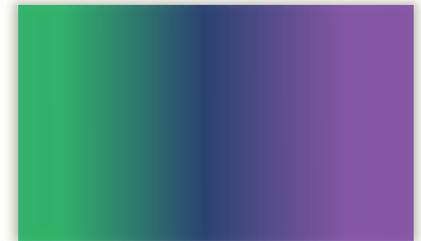


Metallic NPs:
Ag, Au

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

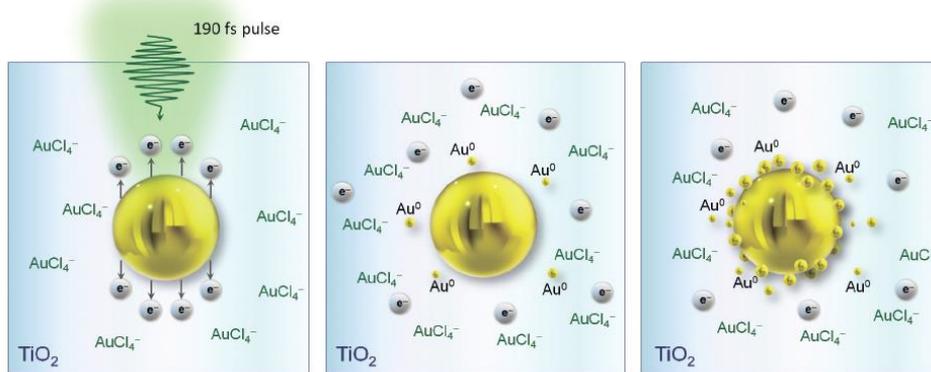


Laser irradiation:
CW
Nanosecond
Picosecond
Femtosecond



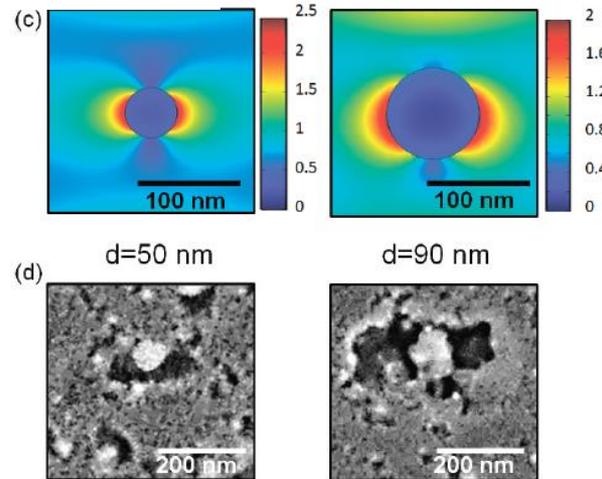
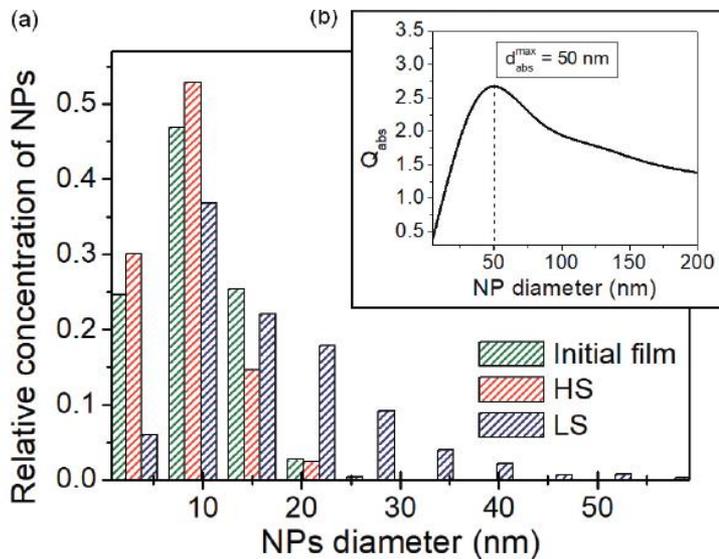
Ion-impregnated porous glasses and semiconductors
can be used as samples for following laser-induced nano-structuring

Au NPs in TiO₂ 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
 $\lambda = 515 \text{ nm}$

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

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

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

(d) SEM images of the NPs produced in LS mode ($F = 57 \text{ mJ/cm}^2$, $V_{sc} = 0.16 \text{ mm/s}$)

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.
 - NPs of smaller sizes easily melt and evaporate, while larger NPs behave more like bulk material, so that thermo-mechanical fragmentation of over-heated material plays a role in their fragmentation. Phase diagrams of NPs smaller than ~30-100 nm should account for NP's size.
 - Fragmentation threshold of alloy nanoparticle strongly depends on their composition (excess energy).
 - When different nanoparticles interact they may **either sinter, mix or even be fragmented** 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.