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► **To cite this version:**

Tatiana E Itina. Smart Nanohybrids and Multi-Material Nanoparticles: Synthesis, Properties, Modeling and Applications. The 8th Ed. of the Smart Materials and Surfaces - SMS 2023, SETCOR, Oct 2023, Albufeira-Algarve, Portugal. ujm-04265215v2

HAL Id: ujm-04265215

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Submitted on 27 Nov 2023

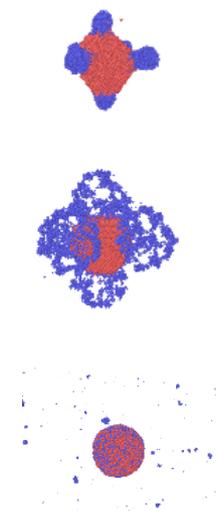
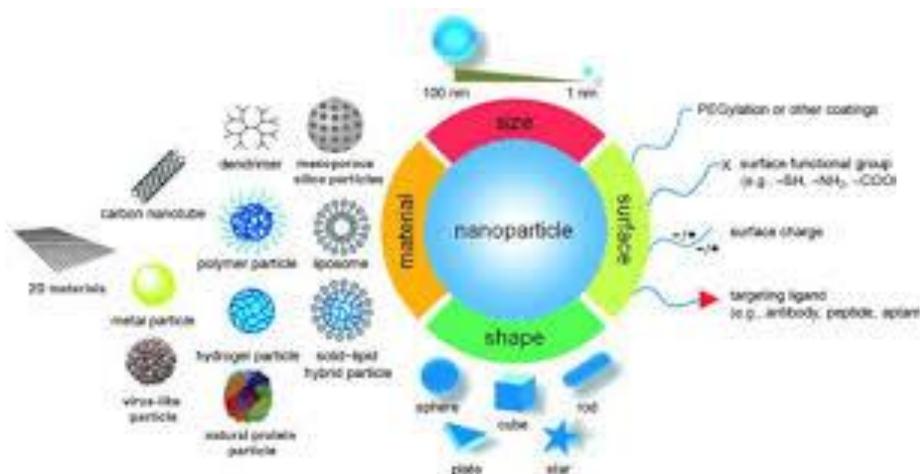
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Smart Nanohybrids and Multi-material Nanoparticles: Synthesis, Properties, Modeling and Applications

Tatiana E. ITINA

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



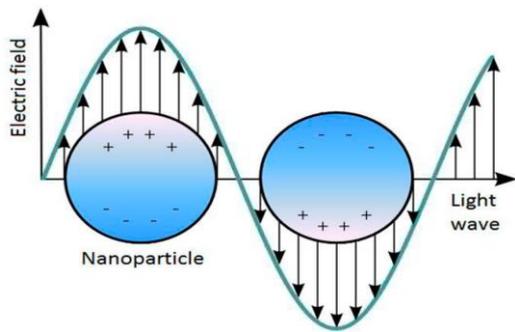
Plan

- 1. Motivation and smart nanomaterials**
- 2. Laser-based nanoparticle synthesis**
- 3. Laser-nanoparticle interactions**
- 4. Bi-material and bi-particle systems**
- 5. Many particle systems**

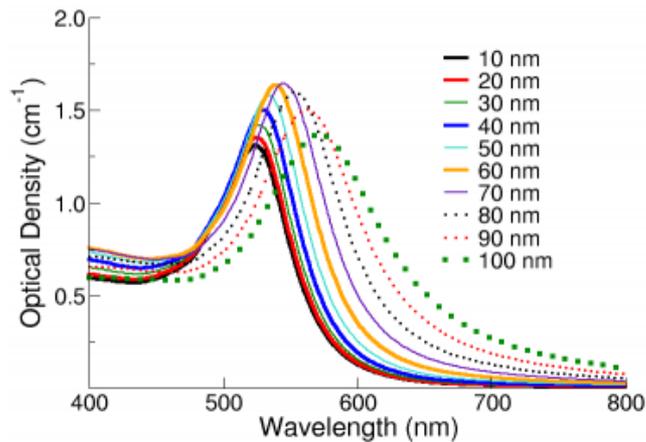
Motivation and Smart Nanomaterials

Properties of Nanoparticles

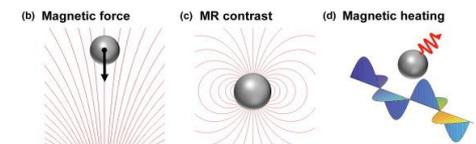
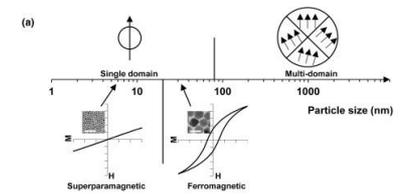
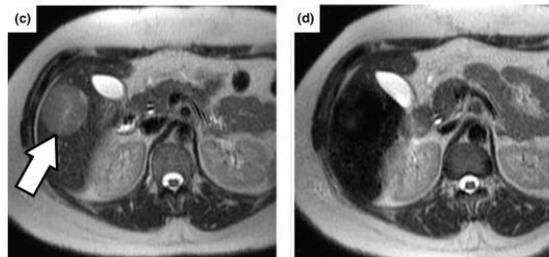
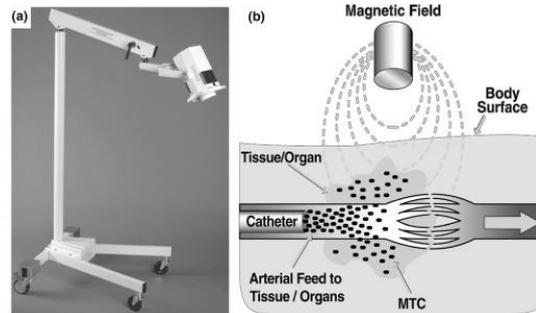
Localized Surface Plasmon Resonance



Sensors **2015**, *15*(7), 15684-15716.



Magnetic nanoparticles

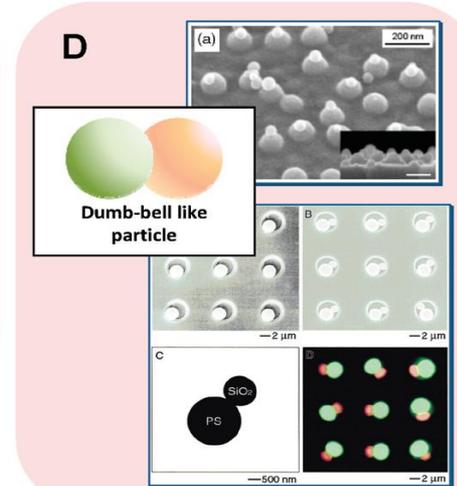
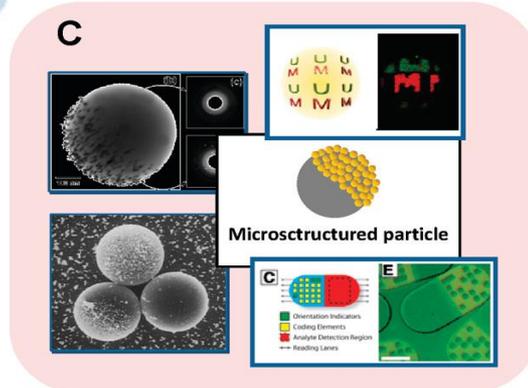
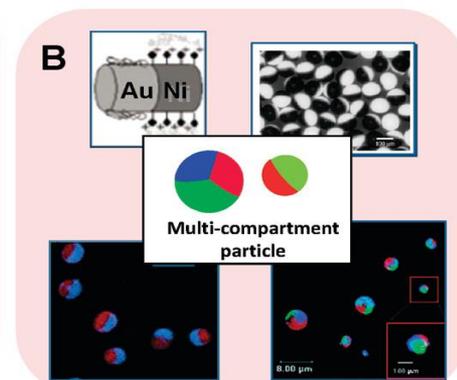
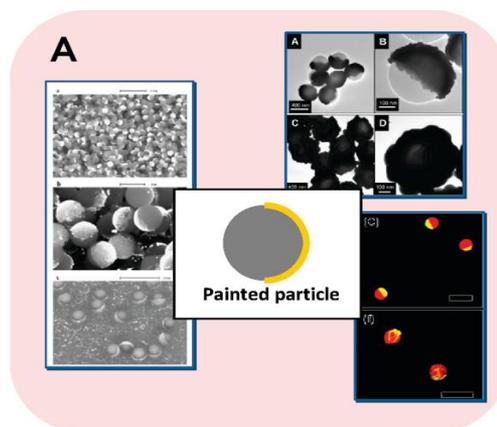
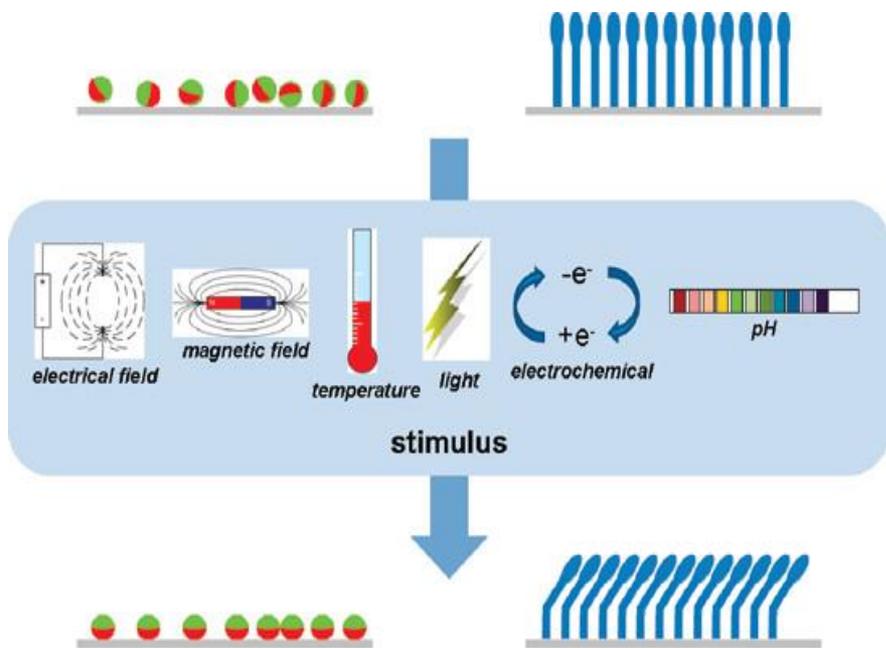


<https://nanocomposix.com/pages/gold-nanoparticles-optical-properties>

<https://doi.org/10.1016/j.mattod.2019.06.003>

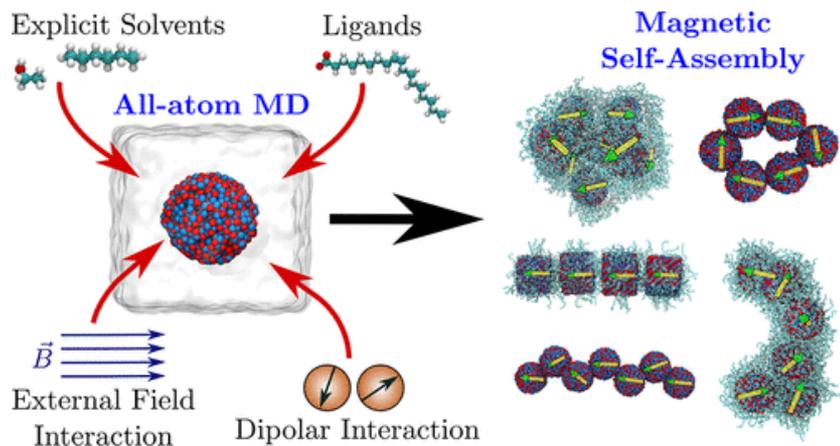
Smart Nanomaterials

“Smart” materials—materials that respond to a stimulus or their environment to produce a dynamic and reversible change in critical properties—have enabled progress in many areas, including display technologies, drug delivery, and self-healing materials for coating applications, among others.

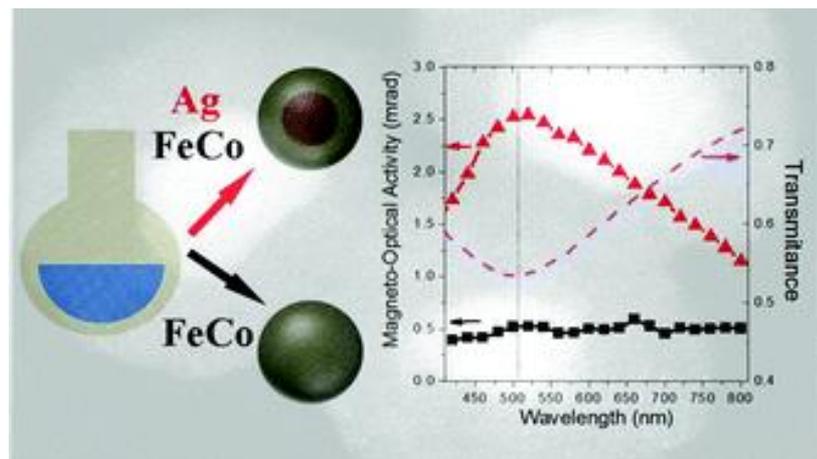


Magnetic and Magneto-Optical Nanoparticles

Zeeman Alignment and Dipolar Assembly of Magnetic Nanoparticles



Plasmon induced magneto-optical enhancement in metallic Ag/FeCo core/shell nanoparticles synthesized by colloidal chemistry



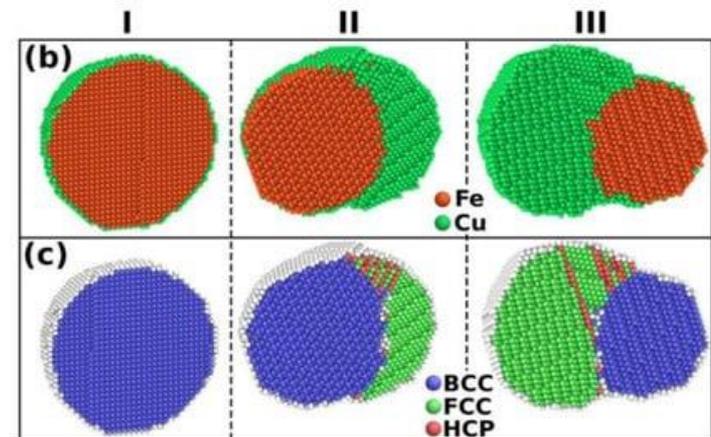
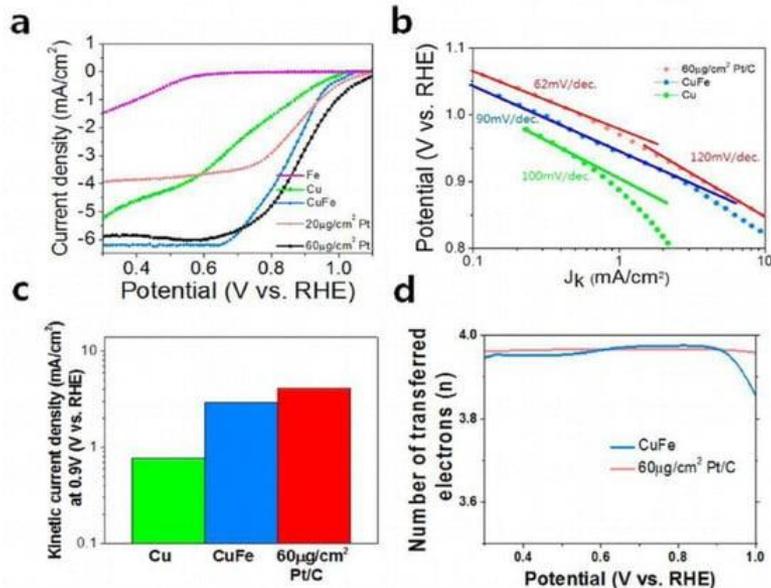
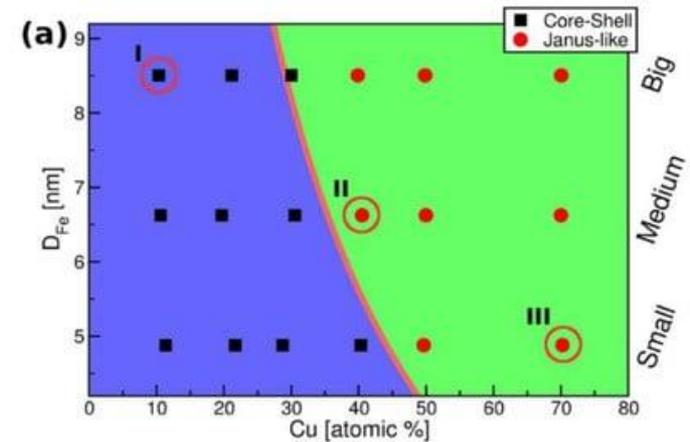
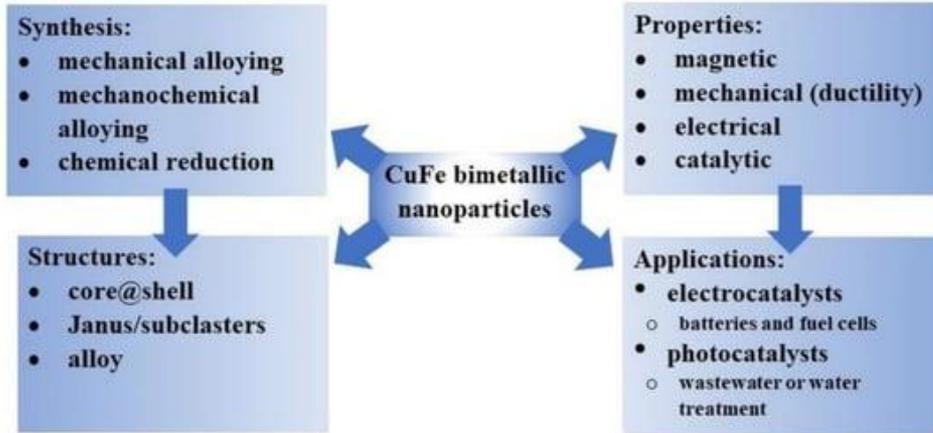
J. Chem. Theory Comput. 2022, 18, 5, 3122–3135

Nanoscale, 2018,10, 18672-18679

The combination of magnetic and plasmonic materials and their nanostructuring have revealed a prominent pathway to develop novel photonic materials for the active control of the light polarization using a magnetic field.

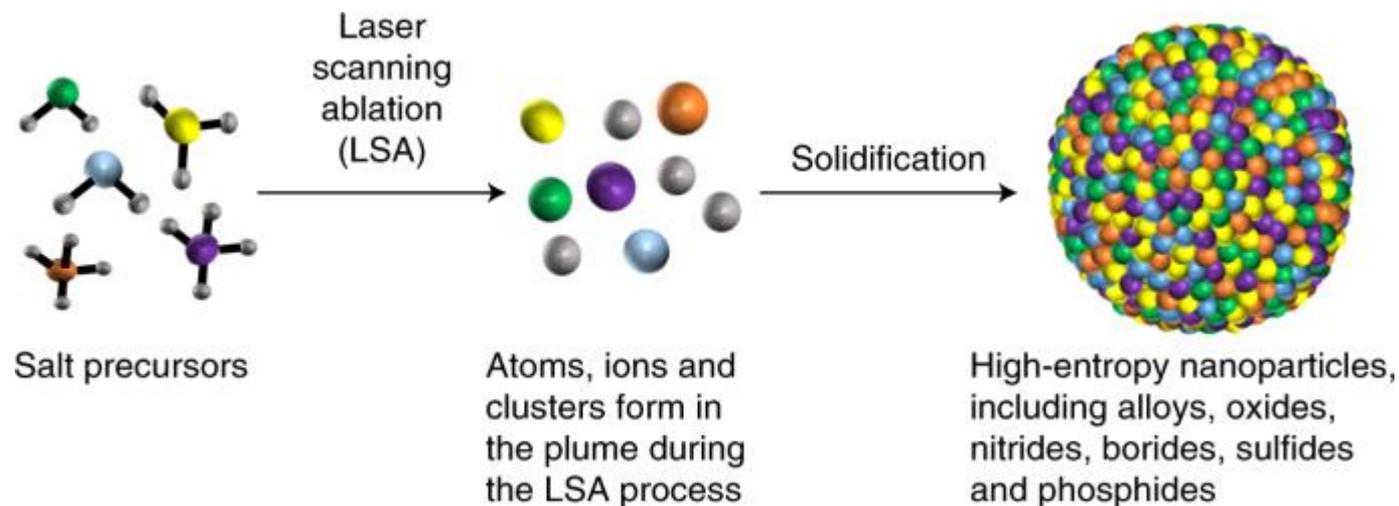
Electro-Catalytic Activity of CuFe Nanoparticles

Bimetal CuFe Nanoparticles: Synthesis and Electro-catalytic Activity

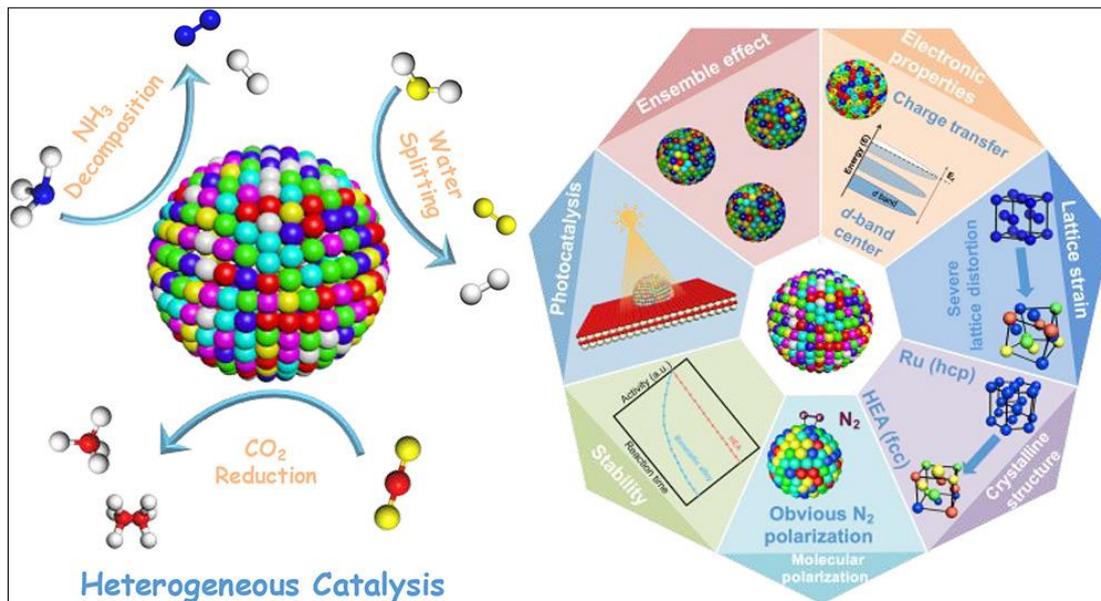


Rojas-Nunez, et al. Toward Controlled Morphology of FeCu Nanoparticles: Cu Concentration and Size Effects. *J. Phys. Chem. C* **2018**, *122*, 8528–8534.

High-Entropy Alloy (HEA) Nanoparticles

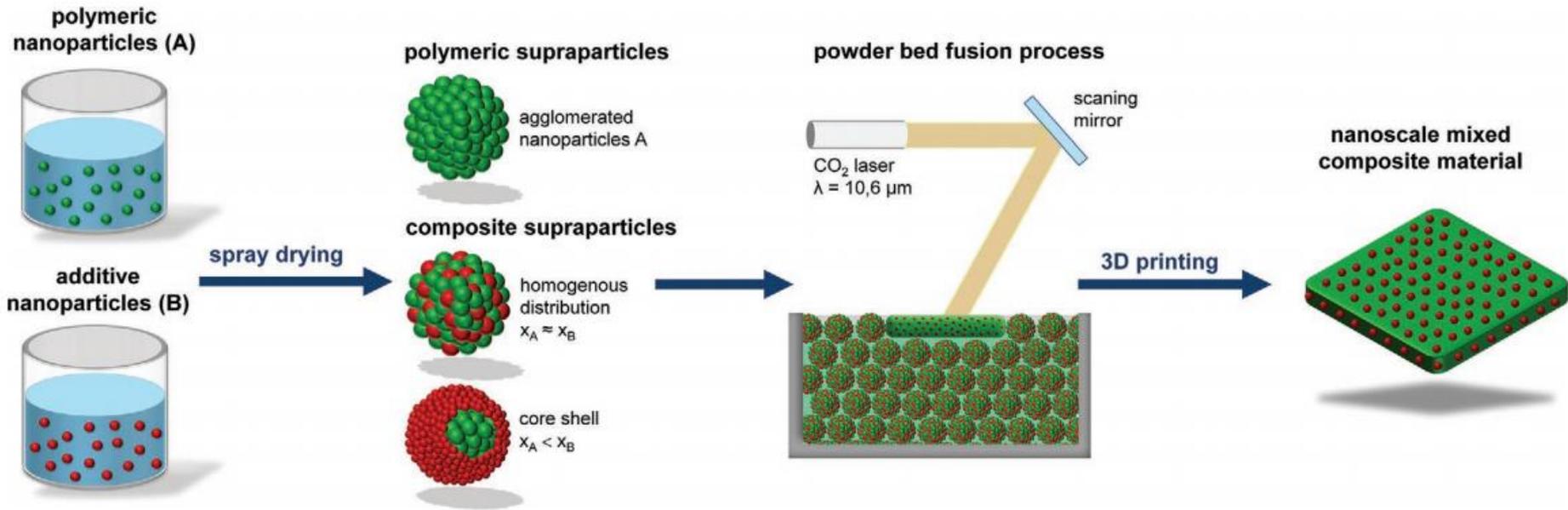


Nature Synthesis volume 1, pages138–146 (2022)

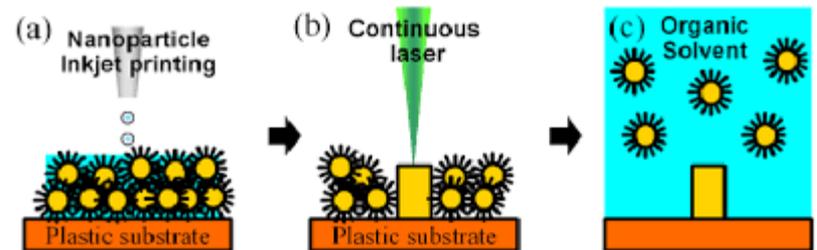
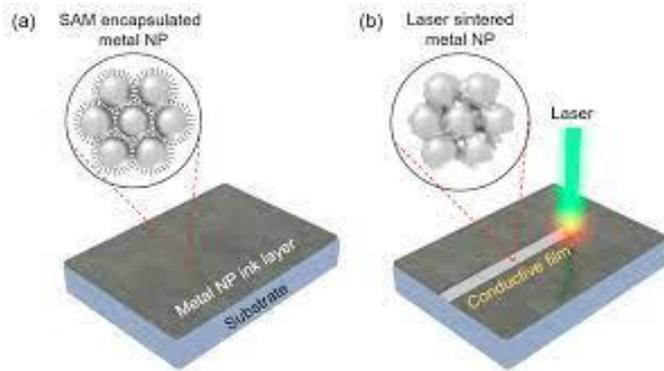


HEAs NPs: complex compositions and crystal size effects may together bring distinct functionality.

Laser 3D Printing



<https://3dprint.com/270462/bottom-up-design-composite-supraparticles-sls-3d-printing/>

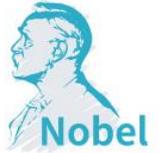


Micromachines 2017, 8(5), 153

Nanotechnology 18(34):345202, 2007



Nobel prize for chemistry 2023



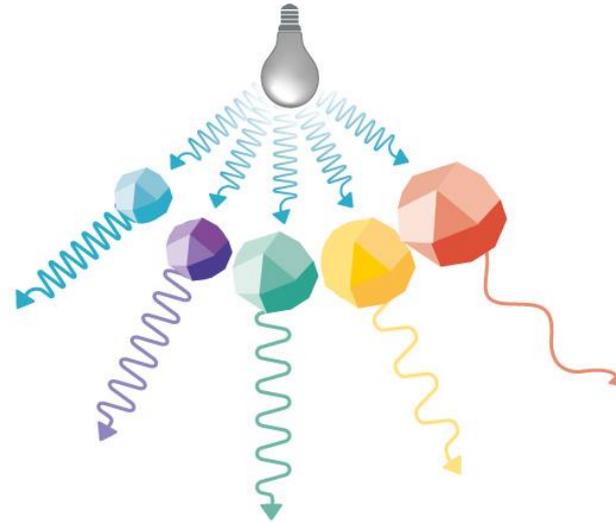
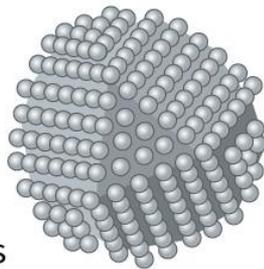
Alexei Ekimov, Louis Brus and Moungi Bawendi were awarded the Nobel prize for chemistry for the discovery and synthesis of quantum dots

Quantum dots are tiny crystals, often consisting of just a few thousand atoms, made from semiconductor materials



The size ratio of a quantum dot to a football is about the same as a football to the Earth

Because their size is reduced to the **nanometre scale**, they exhibit **quantum effects** that determine their characteristics



By manipulating their size, scientists can precisely control their properties and make them emit light of specific colours when they are excited by light

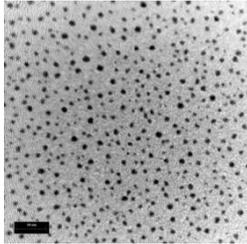
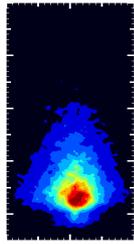
SOME APPLICATIONS

- TV screens / illumination sources
- Biomedical imaging
- Producing photons for quantum communication
- Making better and cheaper solar cells

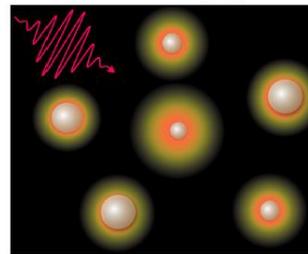
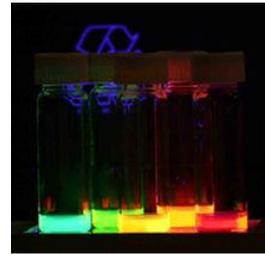
Laser-Based Nanoparticle Synthesis

Ultra-short Laser Pulses for Nanotechnology

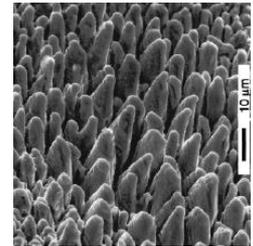
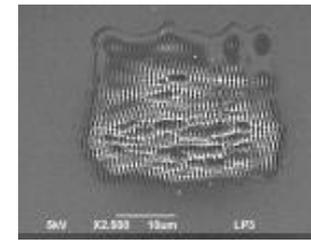
- Laser-induced formation and modification of nanoparticles, monohybrids and nanostructures: modeling vs experiments



Pulsed laser interactions

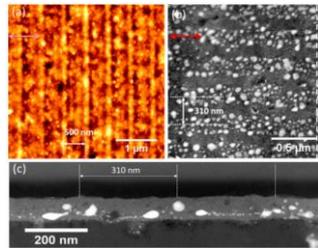


Laser ablation/fragmentation

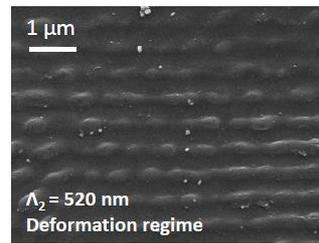


Laser-induced surface/volume structures

- Laser-assisted formation of nanocomposite materials and metasurfaces



Nanoparticles inside

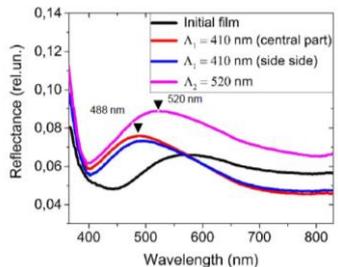


Nanoparticles on the surface



Hierarchical surface structures

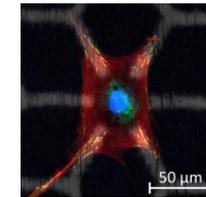
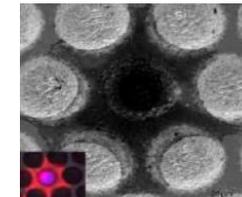
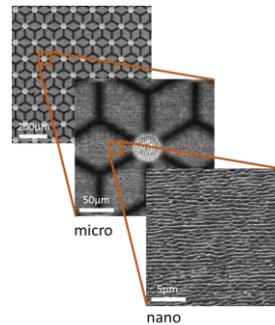
- Properties and applications of the obtained materials: optical properties, wettability, cells and bacterial adhesion/repulsion



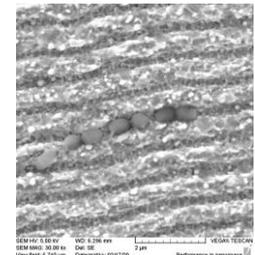
Optical spectra



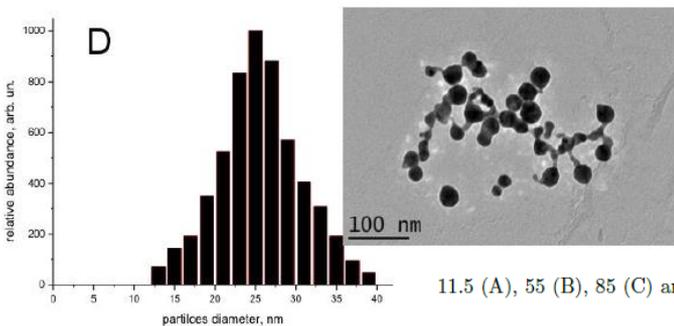
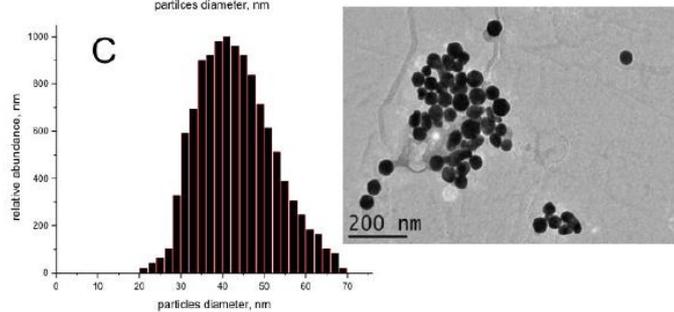
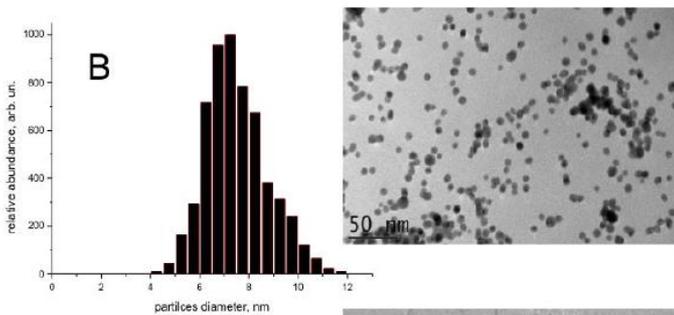
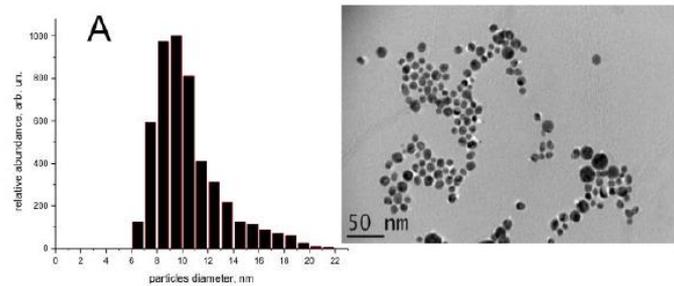
Wettability



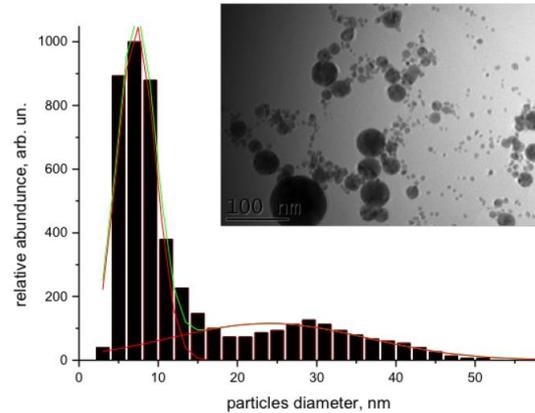
cell and bacteria adhesion on



Ultra-short Laser Interactions with NPs



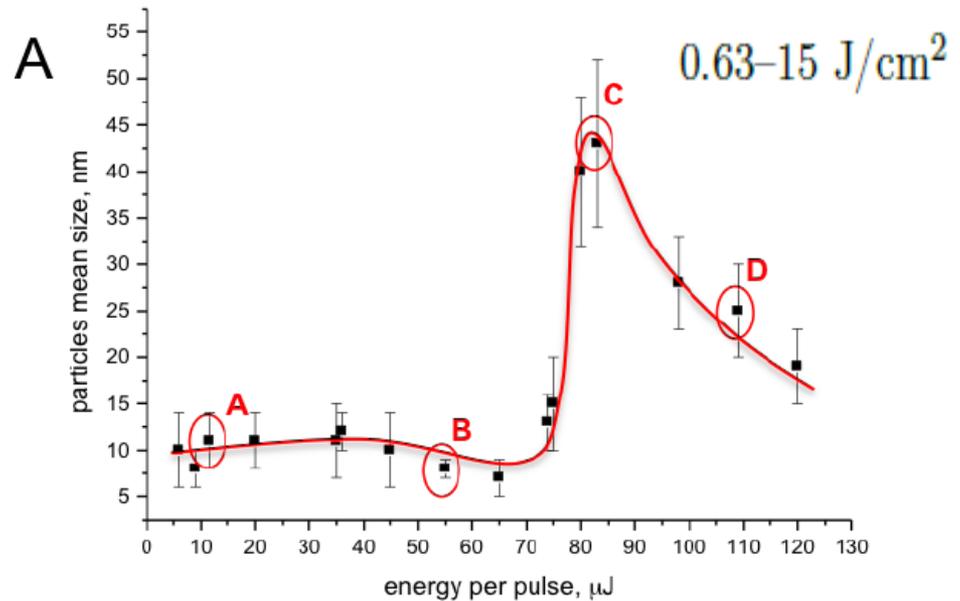
11.5 (A), 55 (B), 85 (C) and 109 (D) μJ



*Upon ablation
1064 nm*

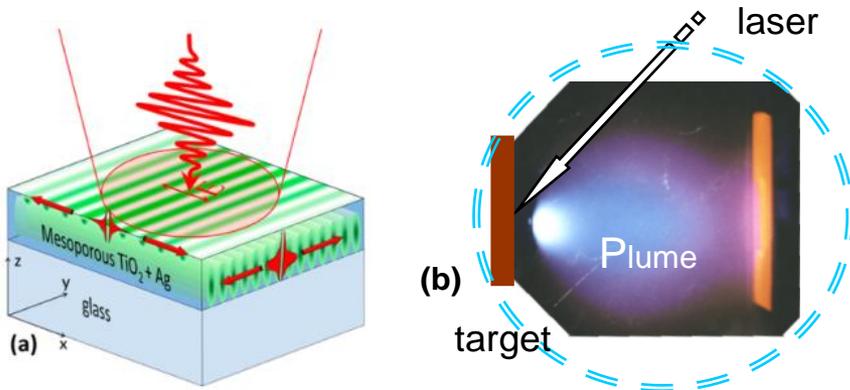
*Additional
fragmentation*

Role of laser energy: non-linear dependency

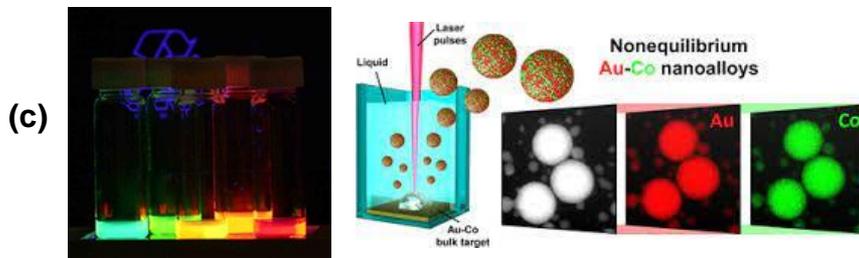


K. Maksimova, PhD thesis Aix-Marseille University, France, 2014

Physics of Laser Interactions



In gas or in vacuum with different geometry



In liquids or in the presence of colloids

Laser interactions 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

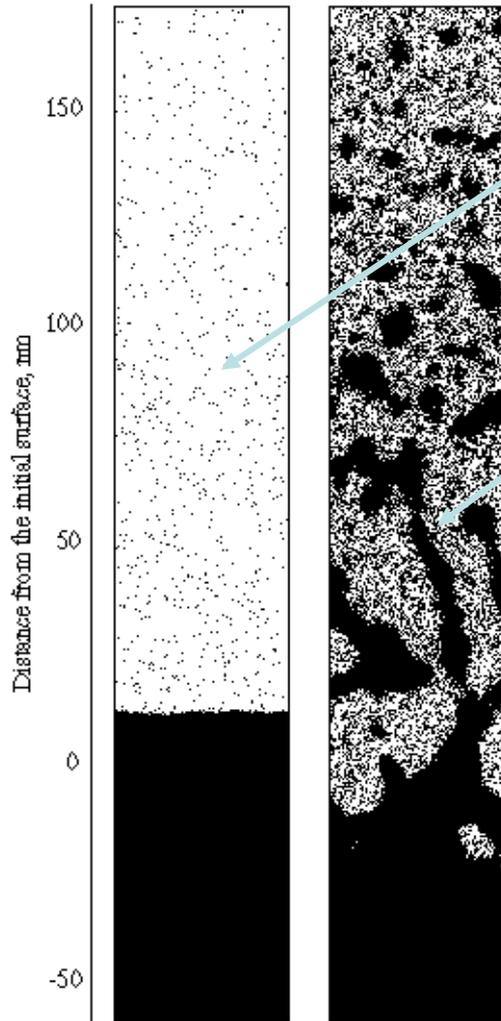
Laser-induced nanoparticle formation

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



Classical Molecular Dynamics (MD)

Short (ps) and ultra-short (fs) laser pulses



$F < F_{th}$

Desorption: Atoms, slow surface evaporation

$F > F_{th}$

Ablation: rapid process, mixture of atoms, clusters and drops

Process can be at $T \rightarrow T_c$

Difficult to model by classical methods

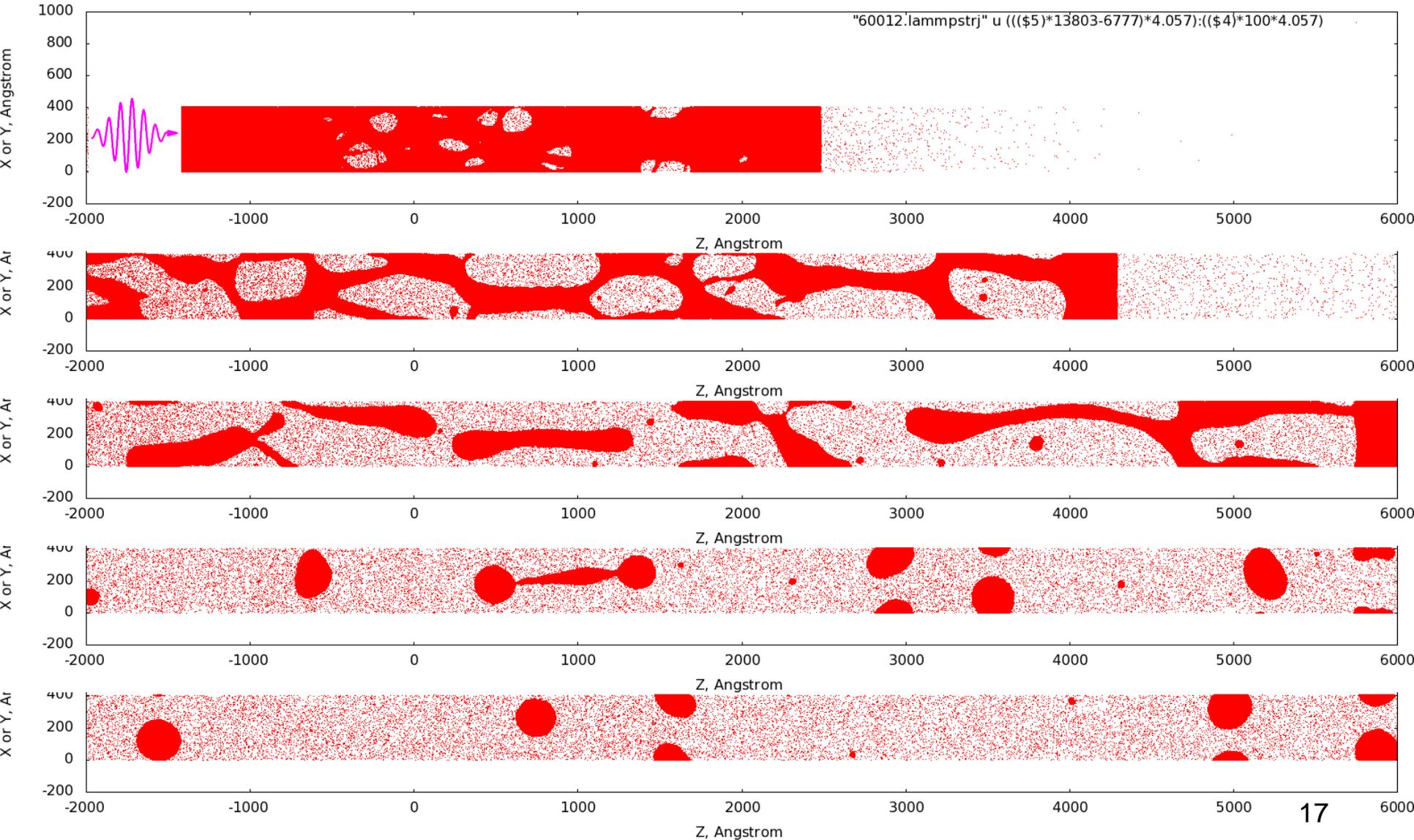
pico

Molecular matrixes

T. E. Itina, L. V. Zhigilei, B. J. Garrison,
J. Phys. Chem.B , **106**, 303-310 (2002)

Ultra-short Laser Ablation

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

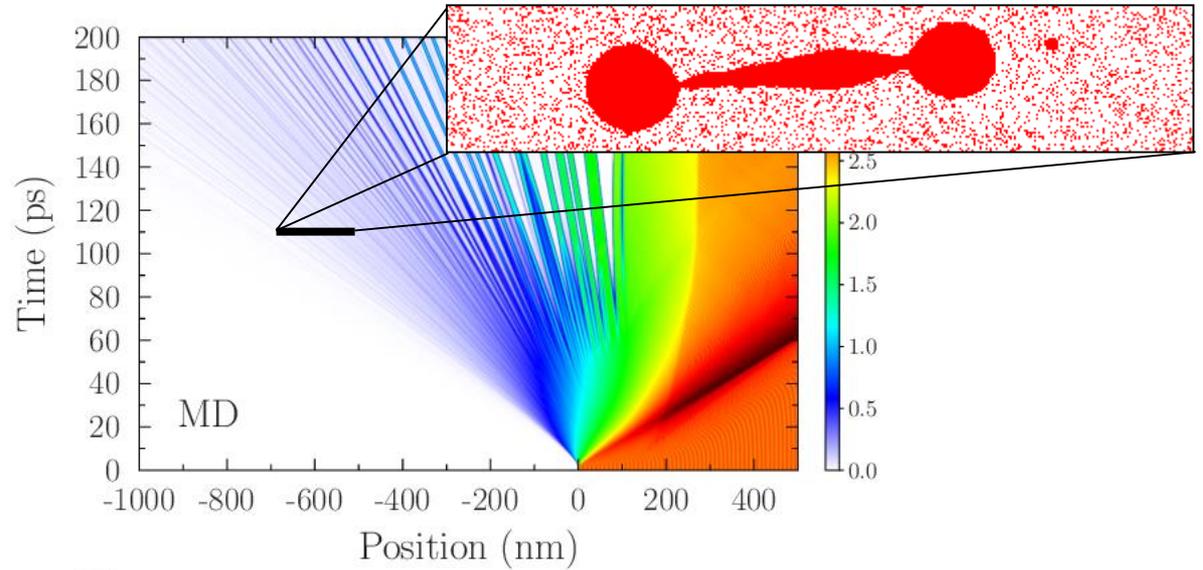


Ultra-short Laser Ablation

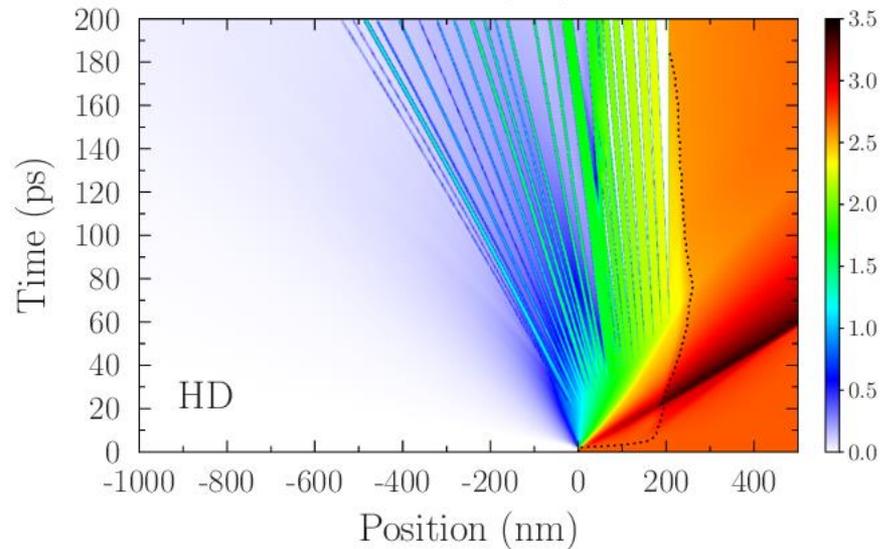
Density

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

TTM-MD

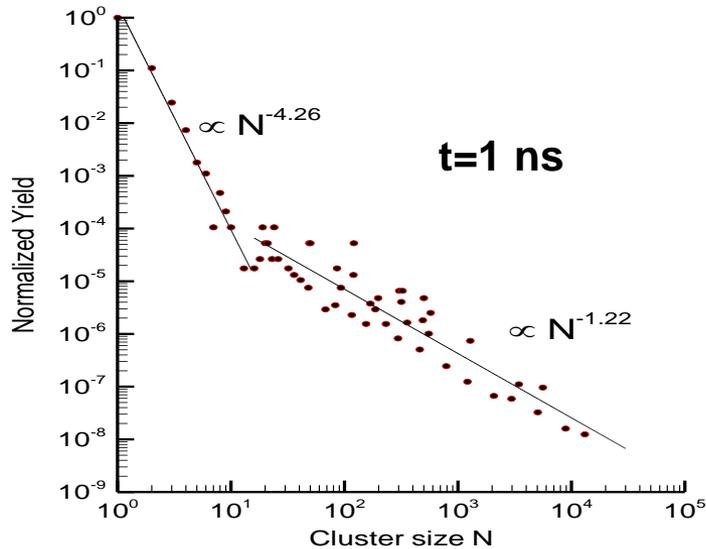


Hydrodynamics

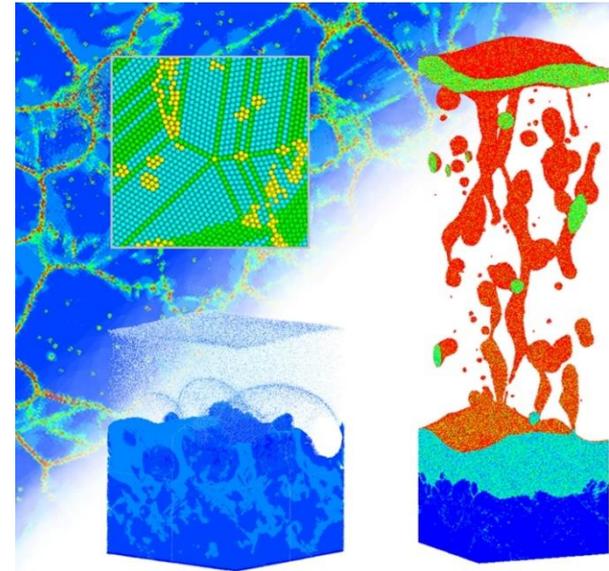
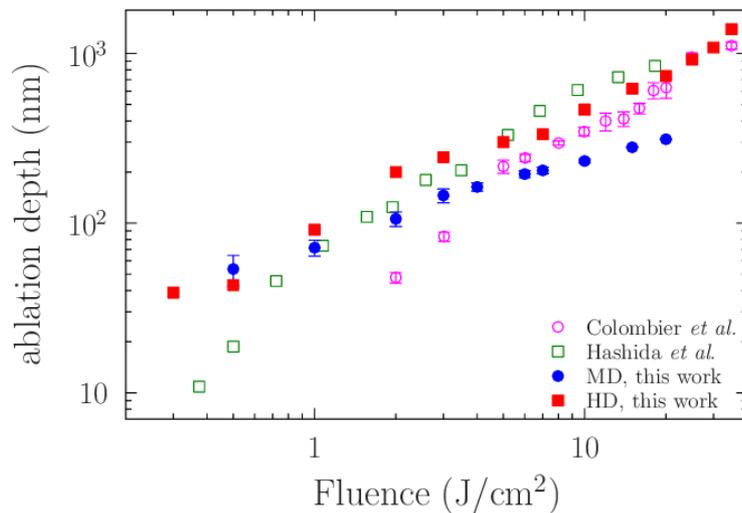


Molecular Dynamics Simulations

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



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

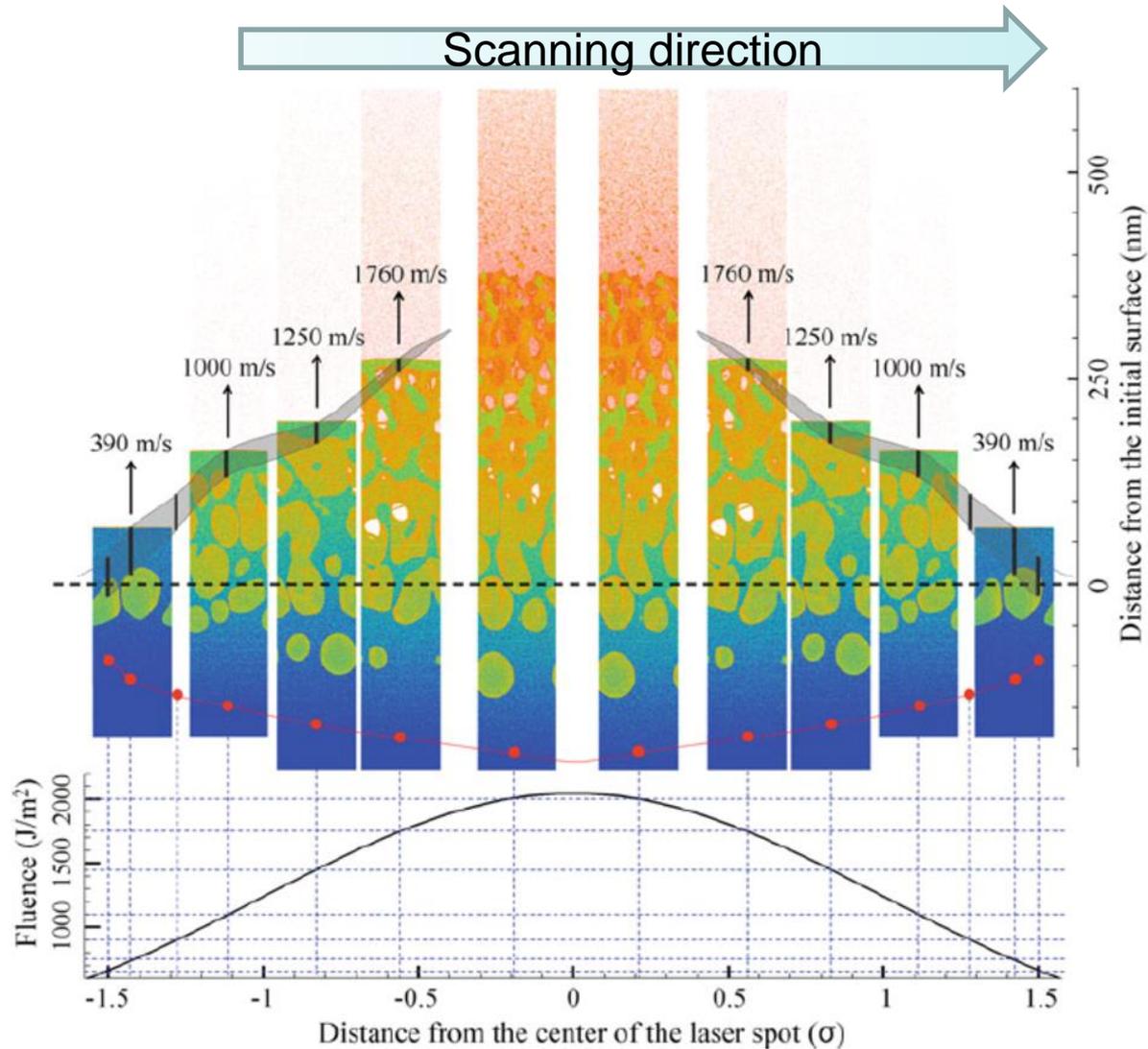


Collaboration with L.V. Zhigilei et al. (Virginia State University, USA)

Practically all the molten material is ablated

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

Effects of Fluence, Multi-pulse Effects

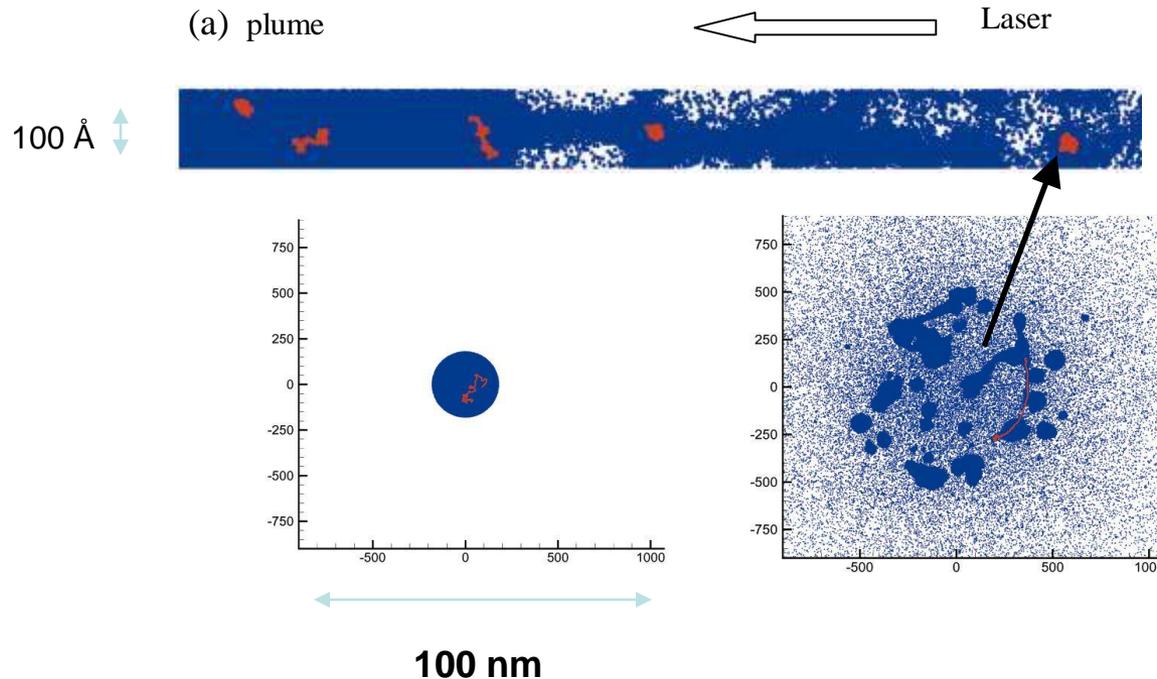


K. W. Kolasinski et al. *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry* (Elsevier, 2018), pp. 594-603.

Laser–Nanoparticle interactions

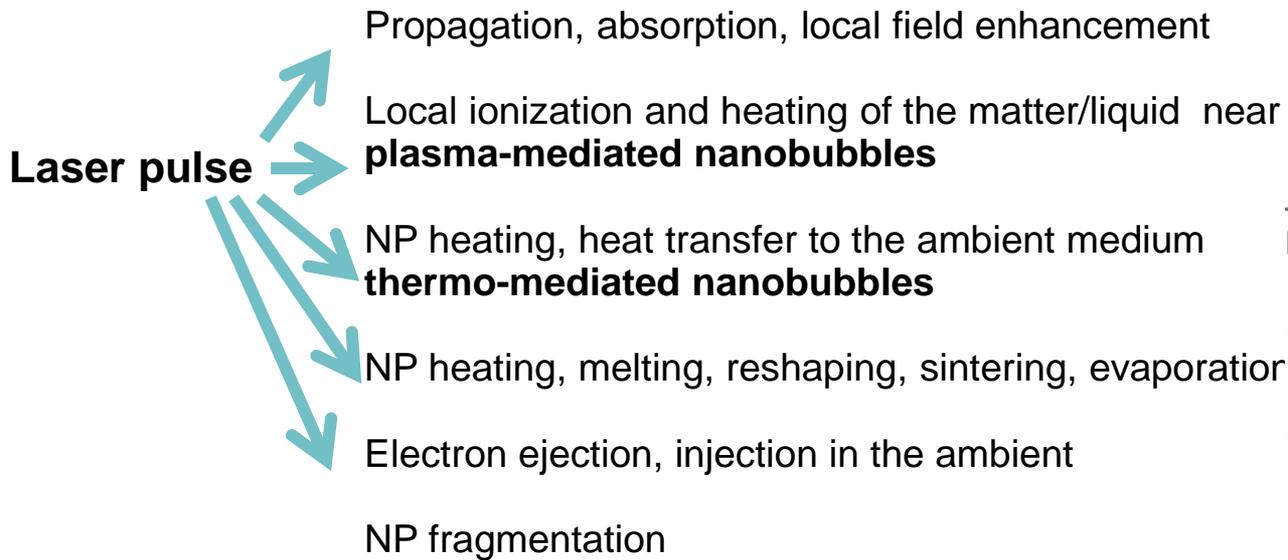
Laser Interactions with Nanoparticles

Molecular Dynamics (MD) simulations are particularly interesting for phase transitions and decomposition of the ablated material upon the absorption of laser radiation, but also can be used for **heating, melting, fragmentation or sintering of NPs**

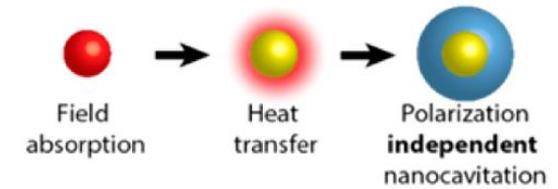


$t = 300$ ps after the
beginning of the laser pulse
 $\tau = 15$ ps
 $e = 0.6$ eV per molecule

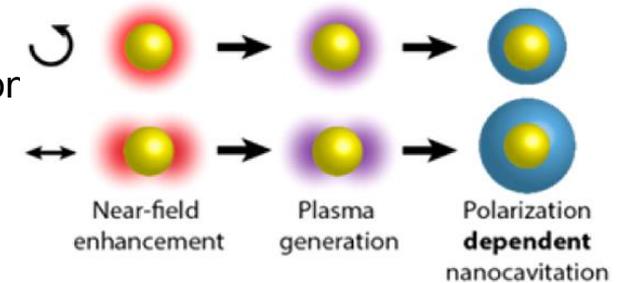
Ultra-short Laser Interactions with Nanoparticles



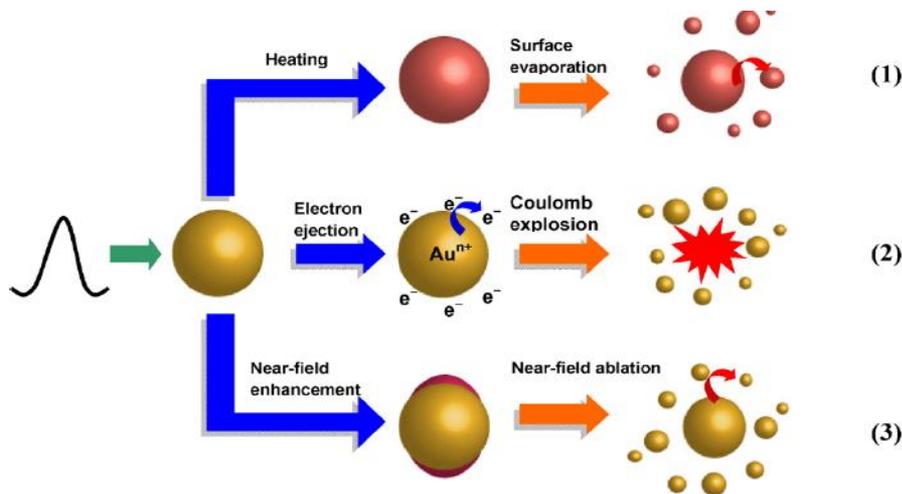
Thermo-mediated nanobubbles



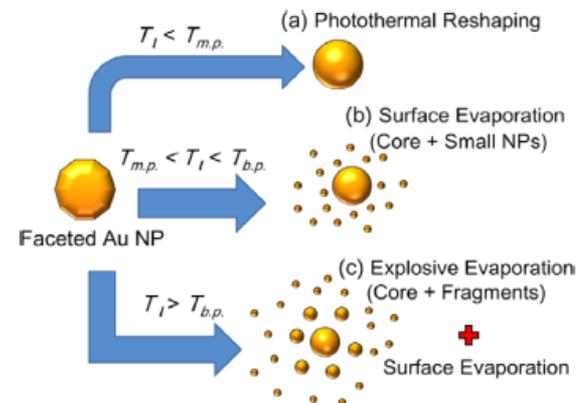
Plasma-mediated nanobubbles



Lachaine et al. Photonics (2013)



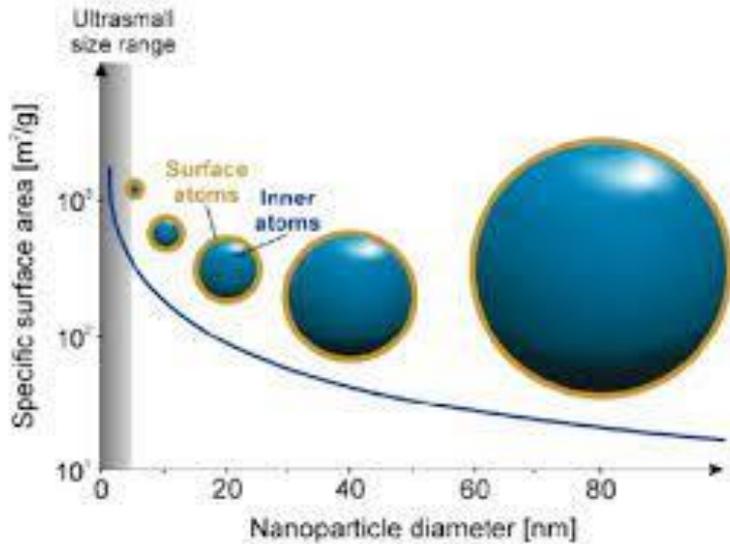
Hashimoto et al. J. PhotChem&PhotBiology (2012)



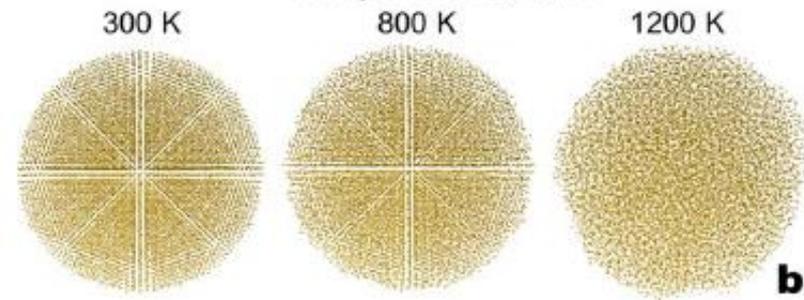
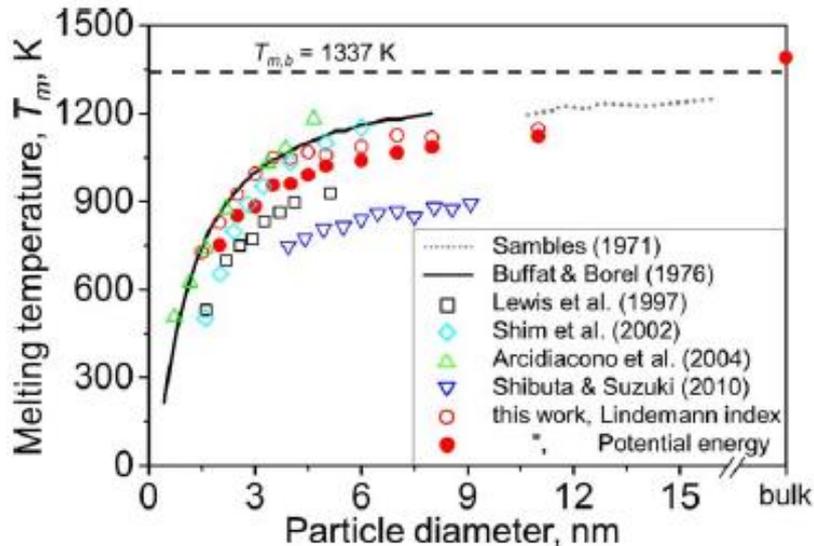
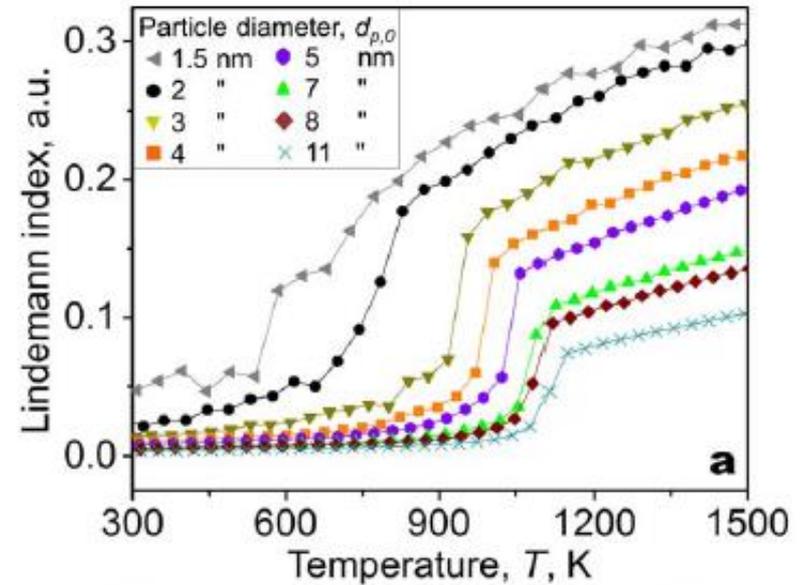
Strasser et al., J. Phys.Chem. C 118, 25748 (2014)

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

Ultr-short Laser Interactions with Nanoparticles

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

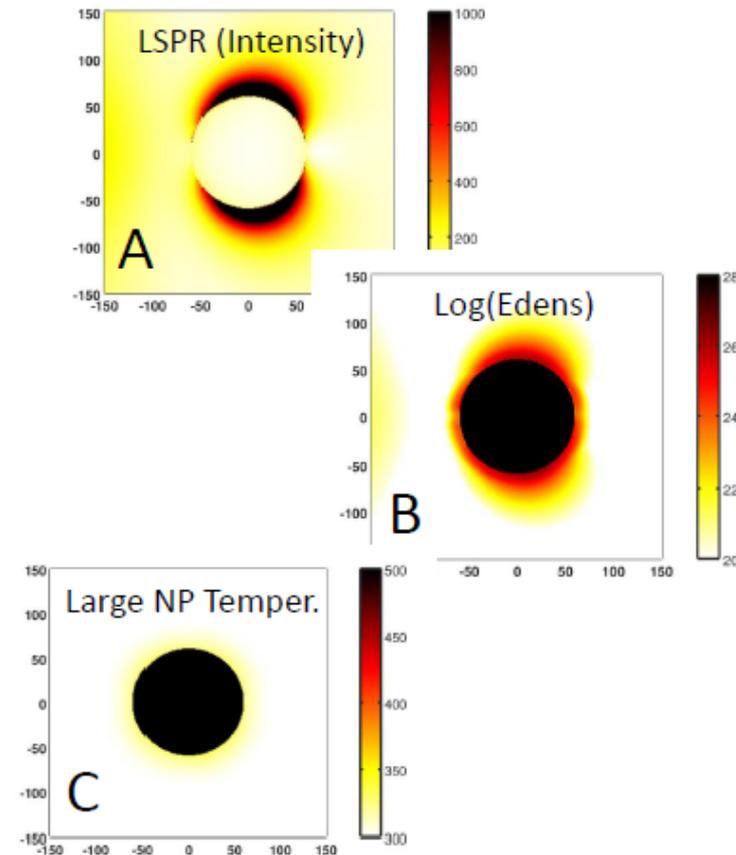
Nanoparticle

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

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);
 γ_{ei}, h - energy transfer rates; ρ_{NP}, ρ_m - ion densities.

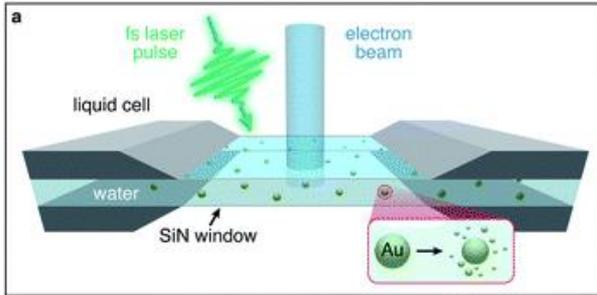


A. Rudenko, Univ. of Arizona, USA

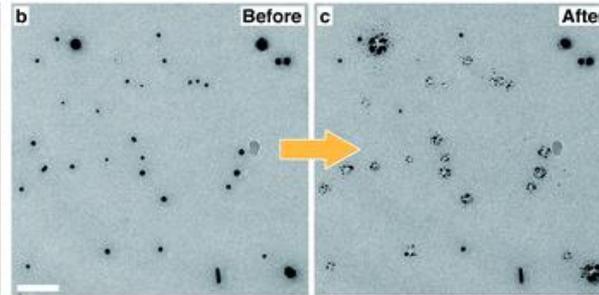
This coupled electromagnetic- thermal 3T model should be introduced
in MD simulations

Fragmentation: MD simulations

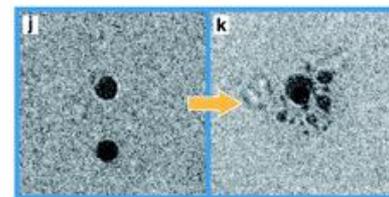
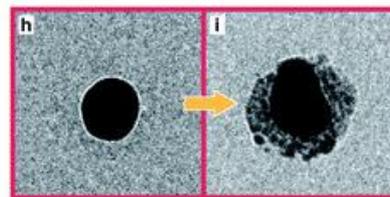
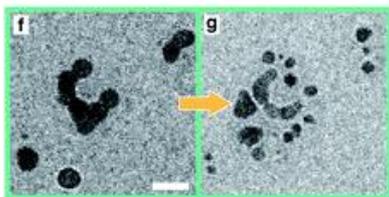
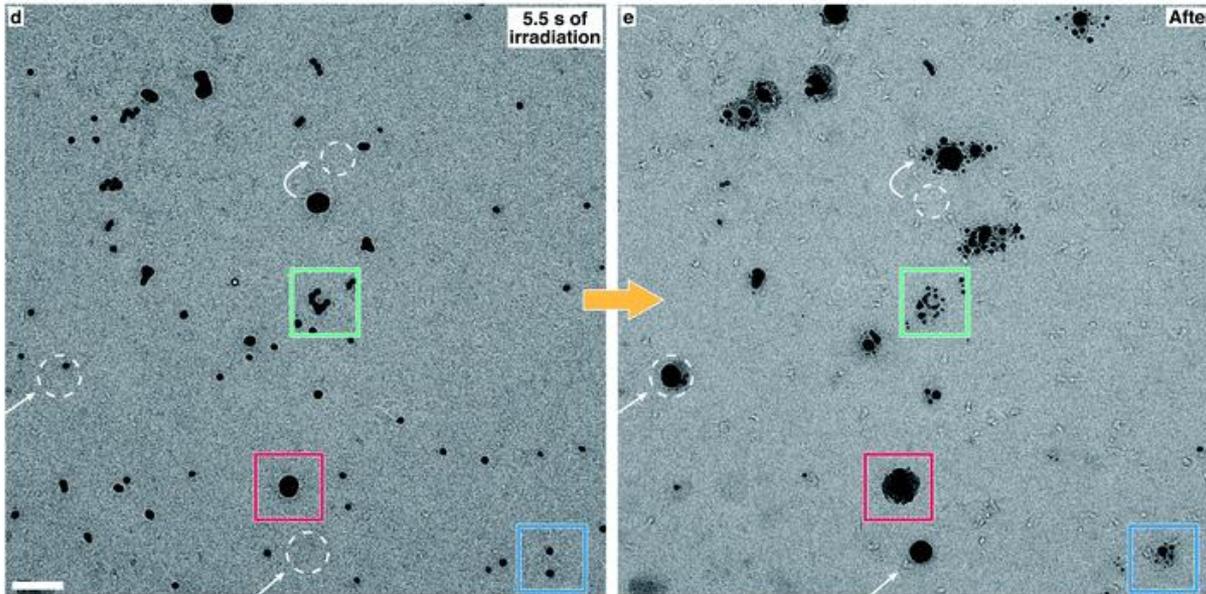
Experimental geometry



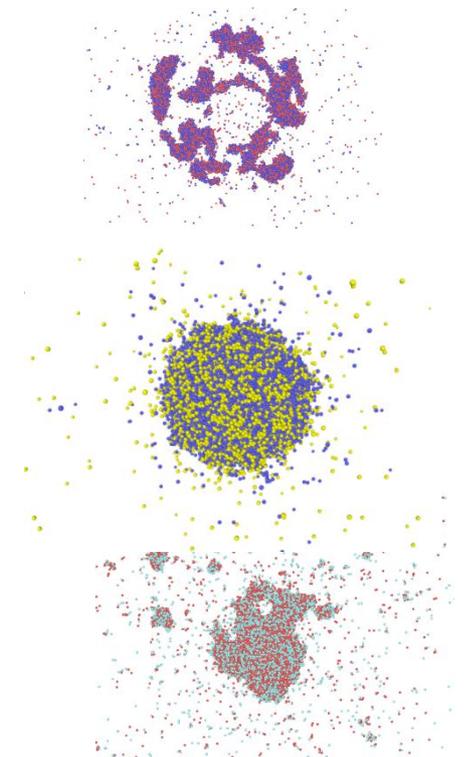
Femtosecond laser irradiation of gold nanoparticles



In situ observation of gold nanoparticle fragmentation under femtosecond laser irradiation



Our MD results for
NPs of
different materials,
absorbed energy,
and sizes

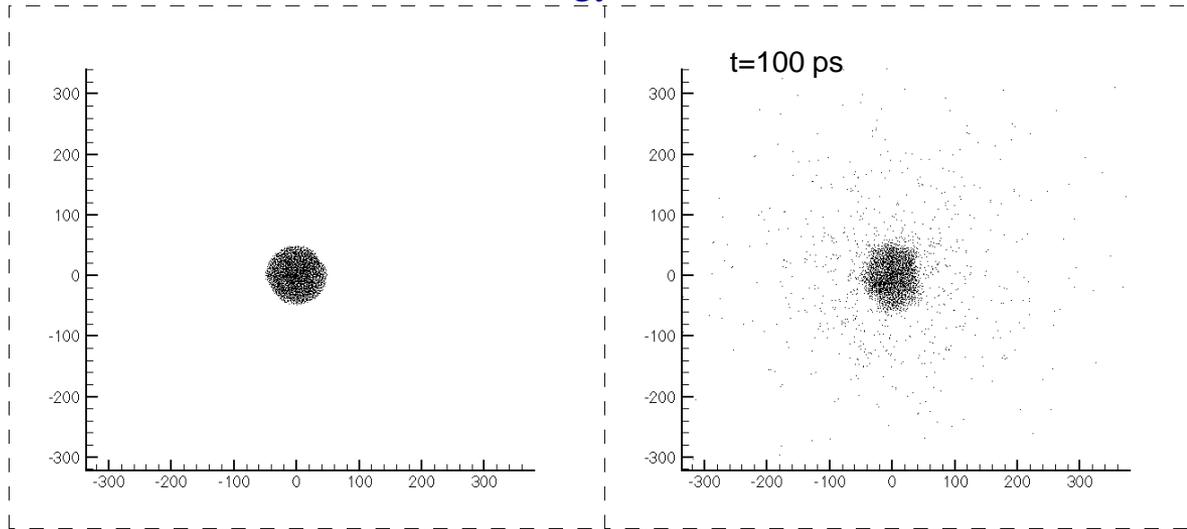


Gold nanoparticles in water

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

Size Effects in Laser Interaction with NPs

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

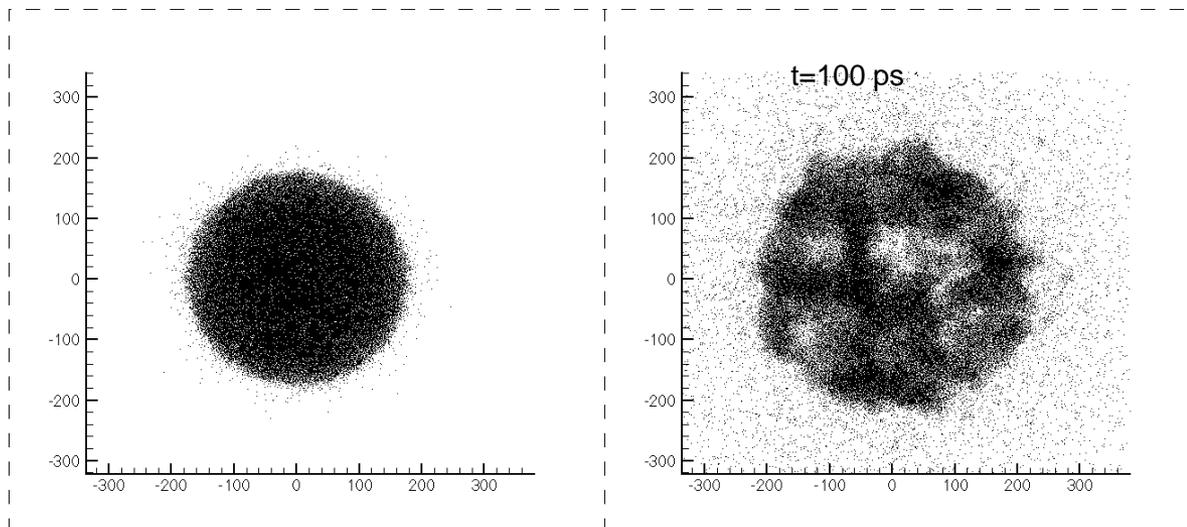


Smaller NPs

Evaporation

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

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

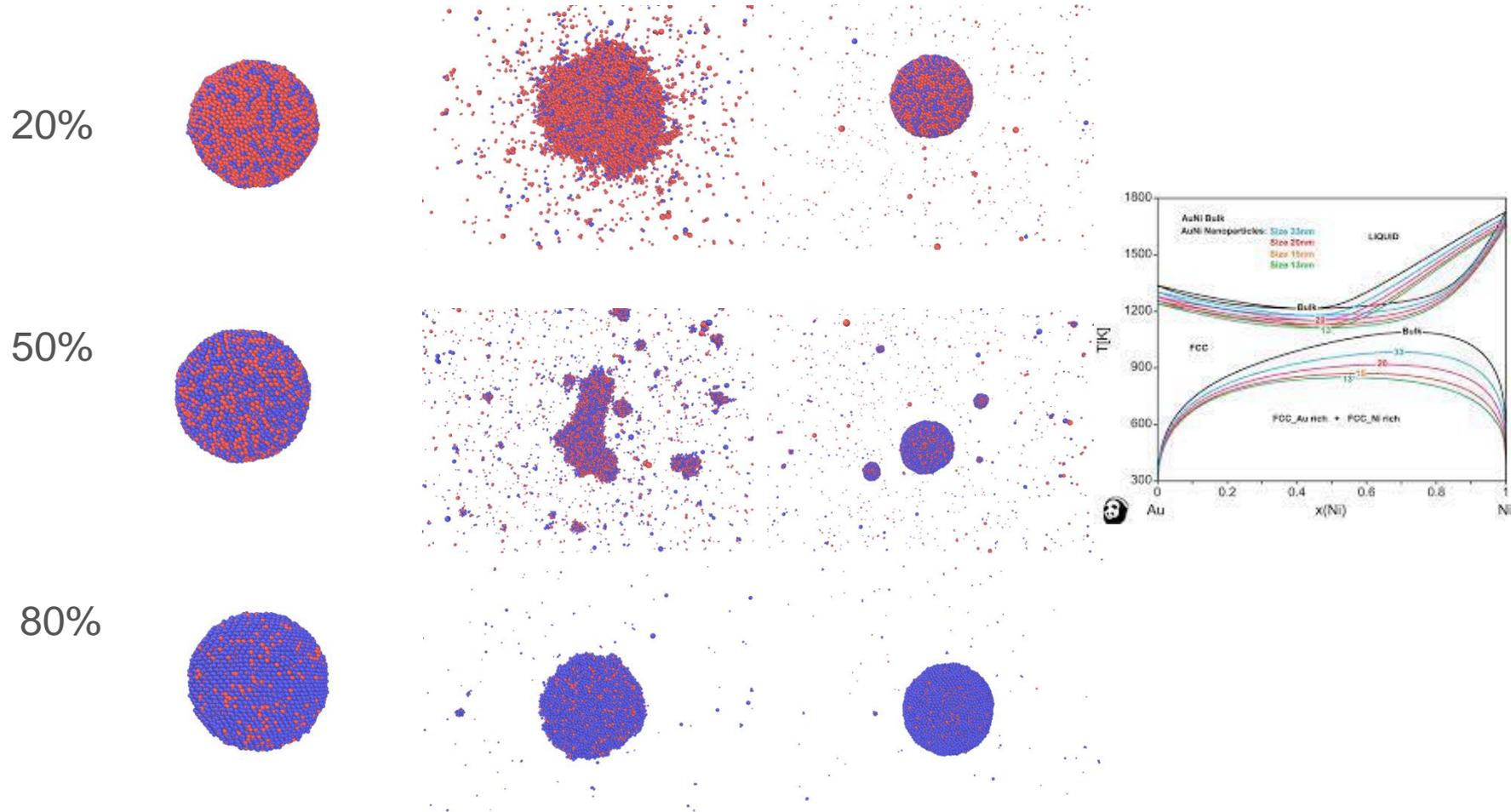


Larger NPs

**Fragmentation due to
thermo-mechanical
effects**

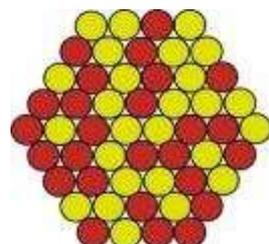
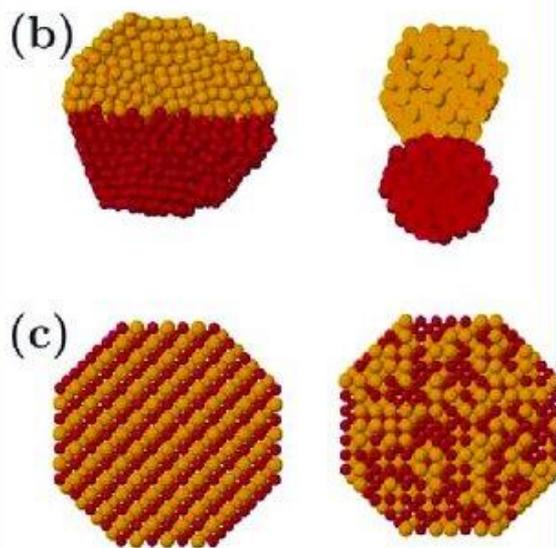
Composition Effects in NP's fragmentation

Au-Ni 0, 500, 1600, NP's ragmentation threshold depends on Ni atomic fraction

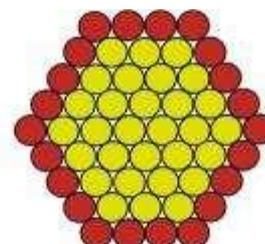


Bi-Material and Bi-Particle Systems

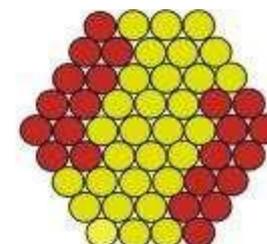
Nanoparticle Alloys and Aggregates



Alloy



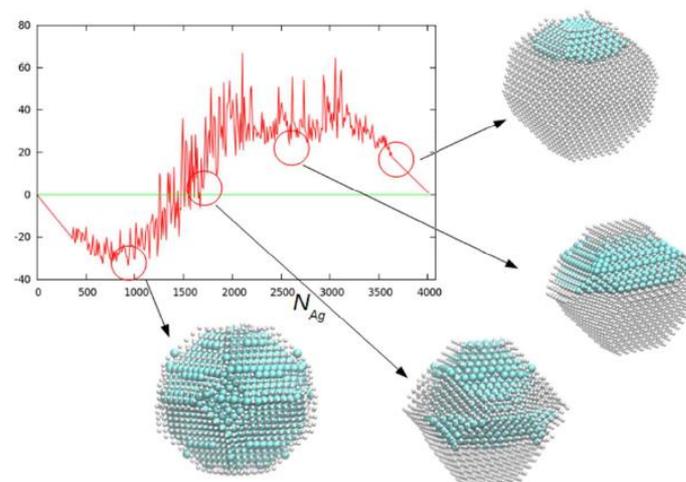
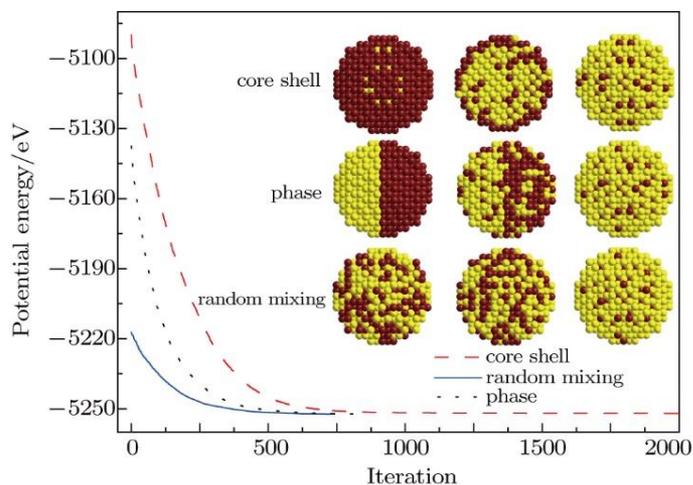
Core-Shell



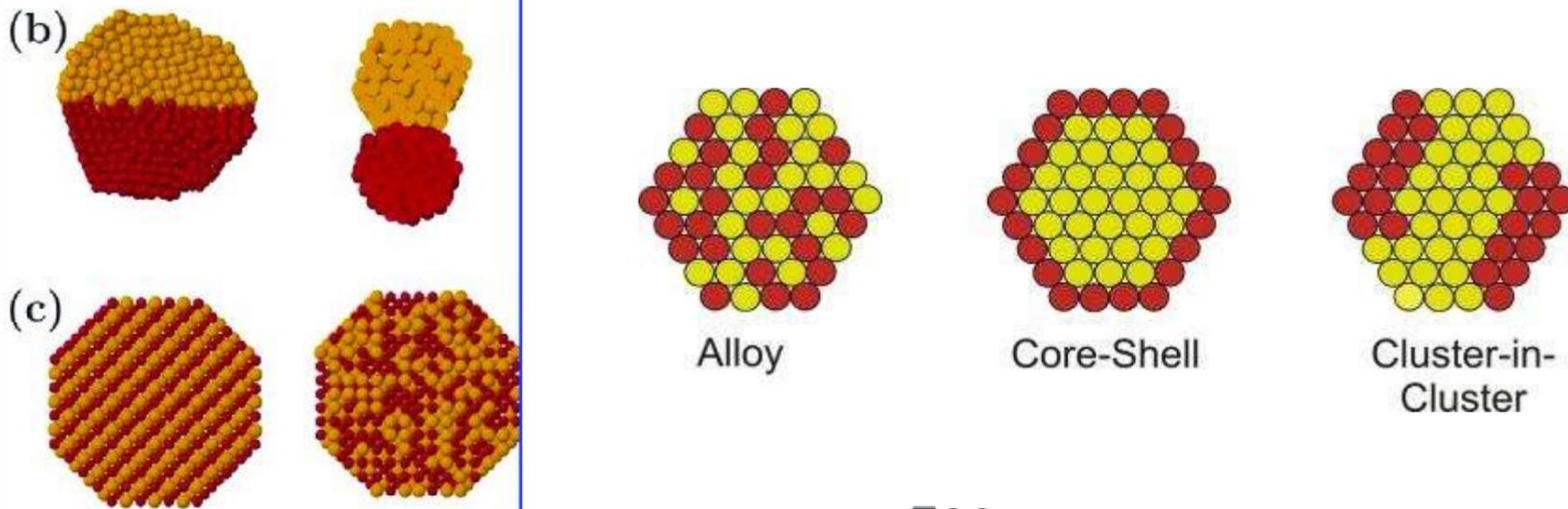
Cluster-in-Cluster

Mixing Energy

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



Bi-Metallic Nanoparticles and Aggregates: MD simulations



www.acsnano.org

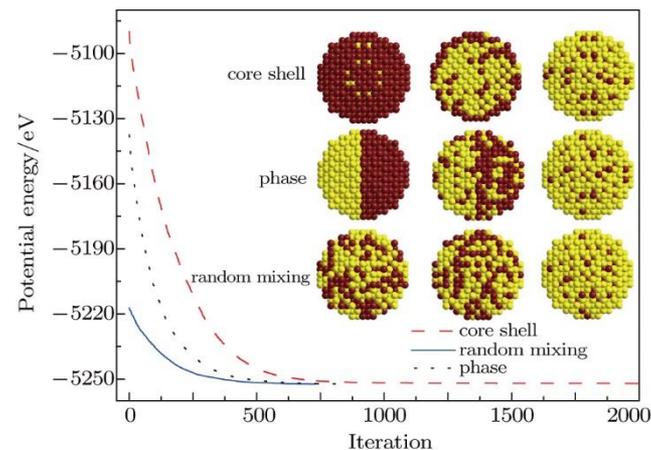
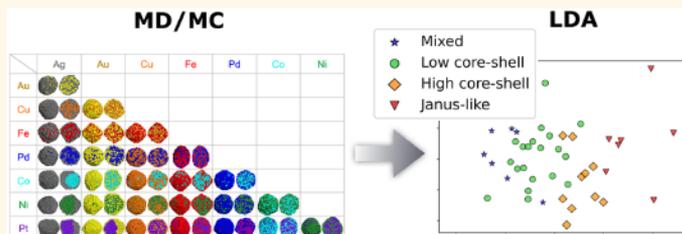
General Trends in Core–Shell Preferences for Bimetallic Nanoparticles

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

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

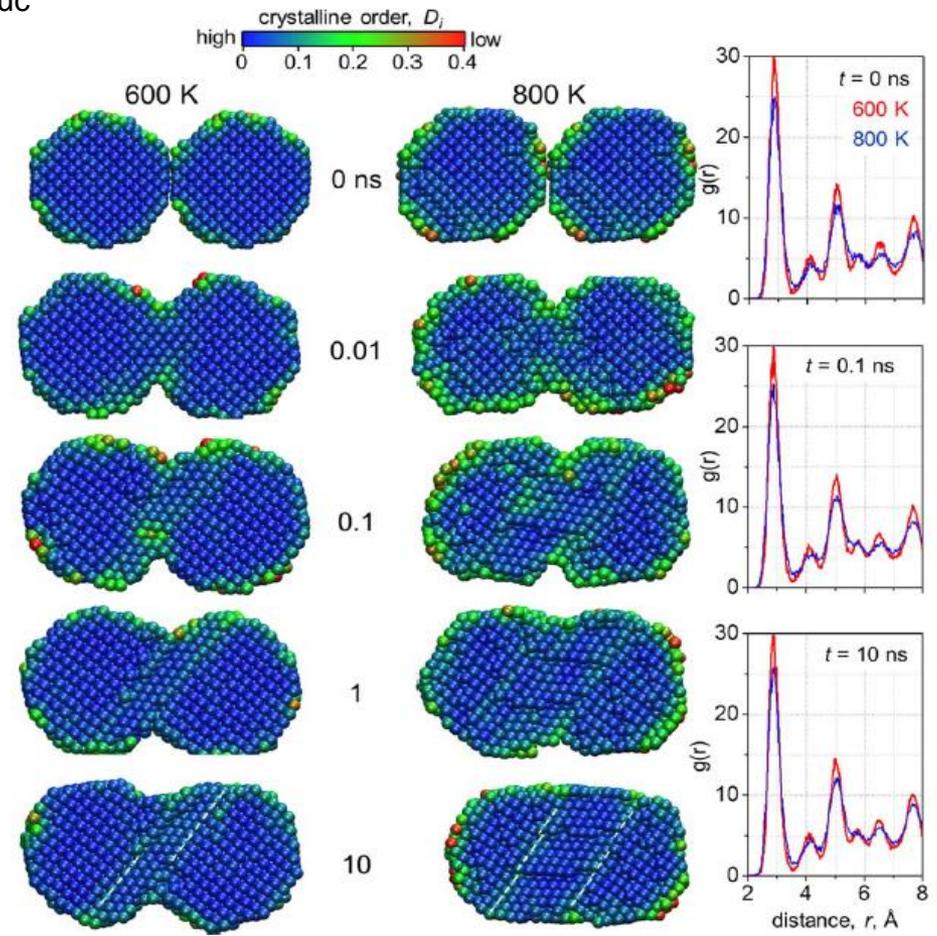
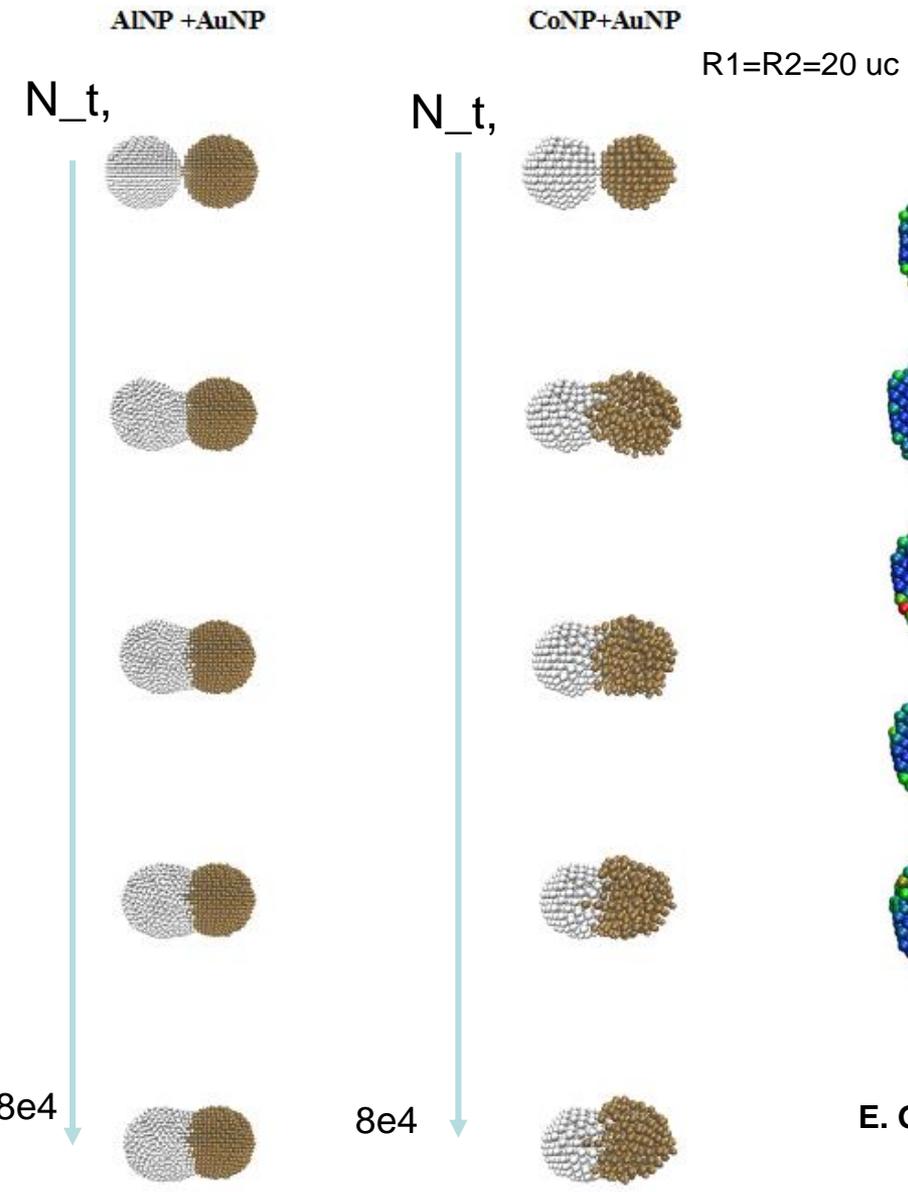
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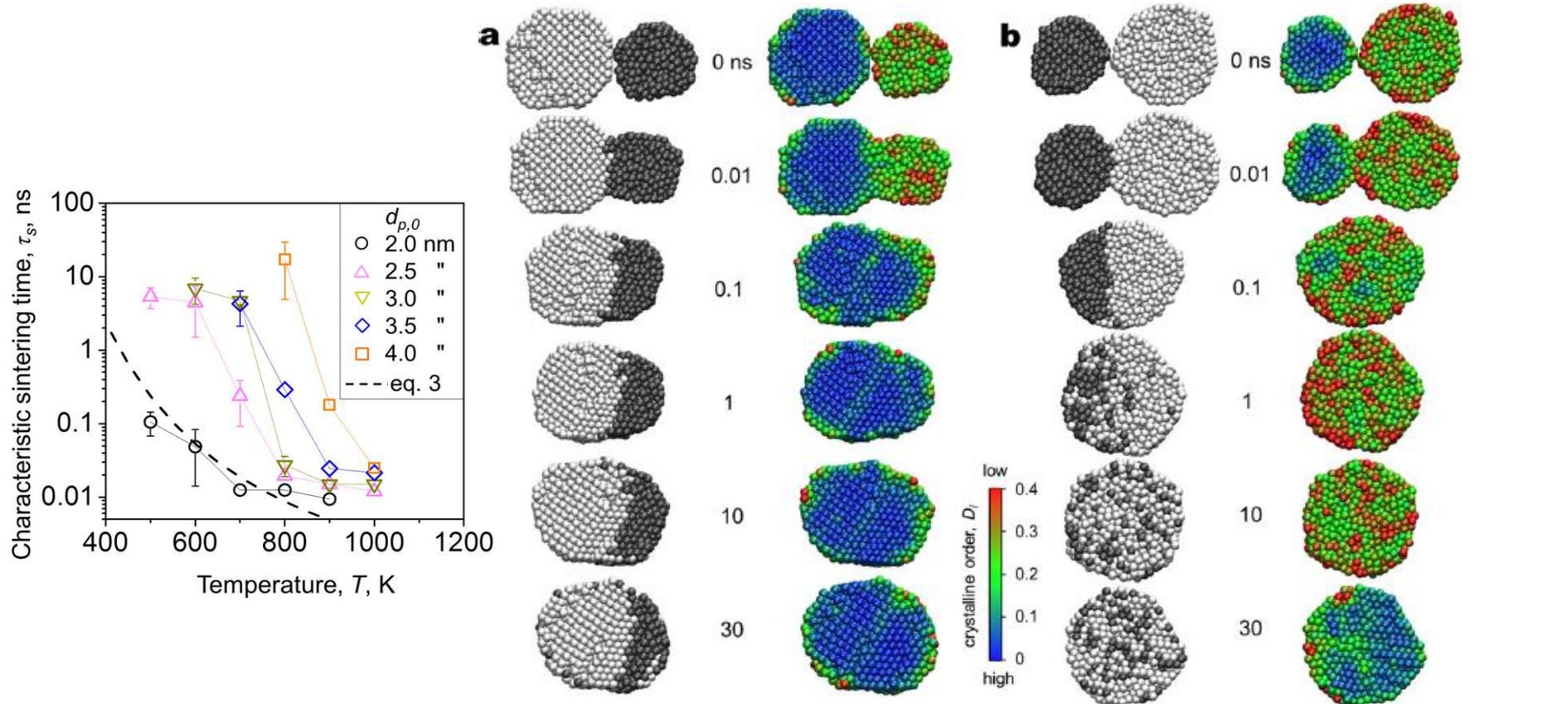
Ultra-short Laser-induced NP sintering, Janus NPs

MD simulation results



Ultra-short Laser-induced NP sintering, Janus NPs

AuNP + AuNP, different sizes



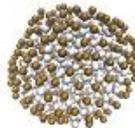
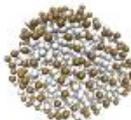
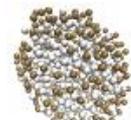
Snapshots of cross-sections of two Au nanoparticles with $d_{p,0}=3$ (gray) and 4 nm (white) undergoing sintering at $T = 800$ K at $t = 0, 0.01, 0.1, 1, 10,$ and 30 ns.

Ultra-short Laser-induced NP sintering, Janus NPs

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

$R1 = R2 = 10\text{ uc}$

N_t



$8e4$

mixed

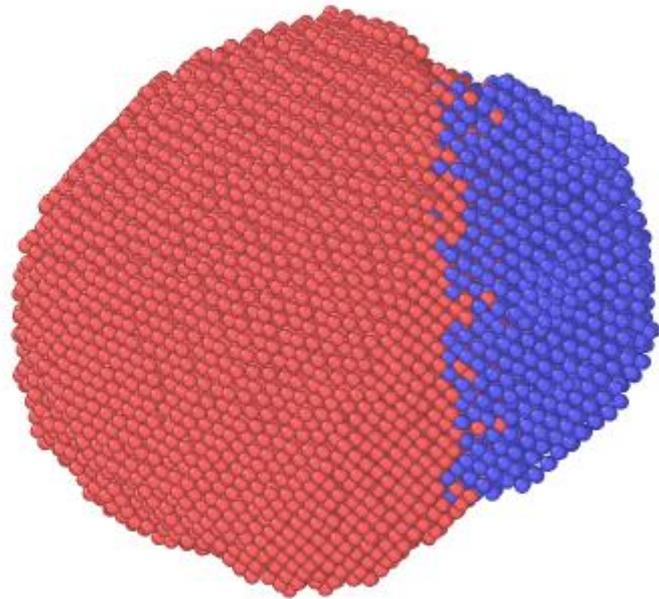
The same sizes
The same T

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

Mixing is easier when both particles have comparable sizes and temperatures

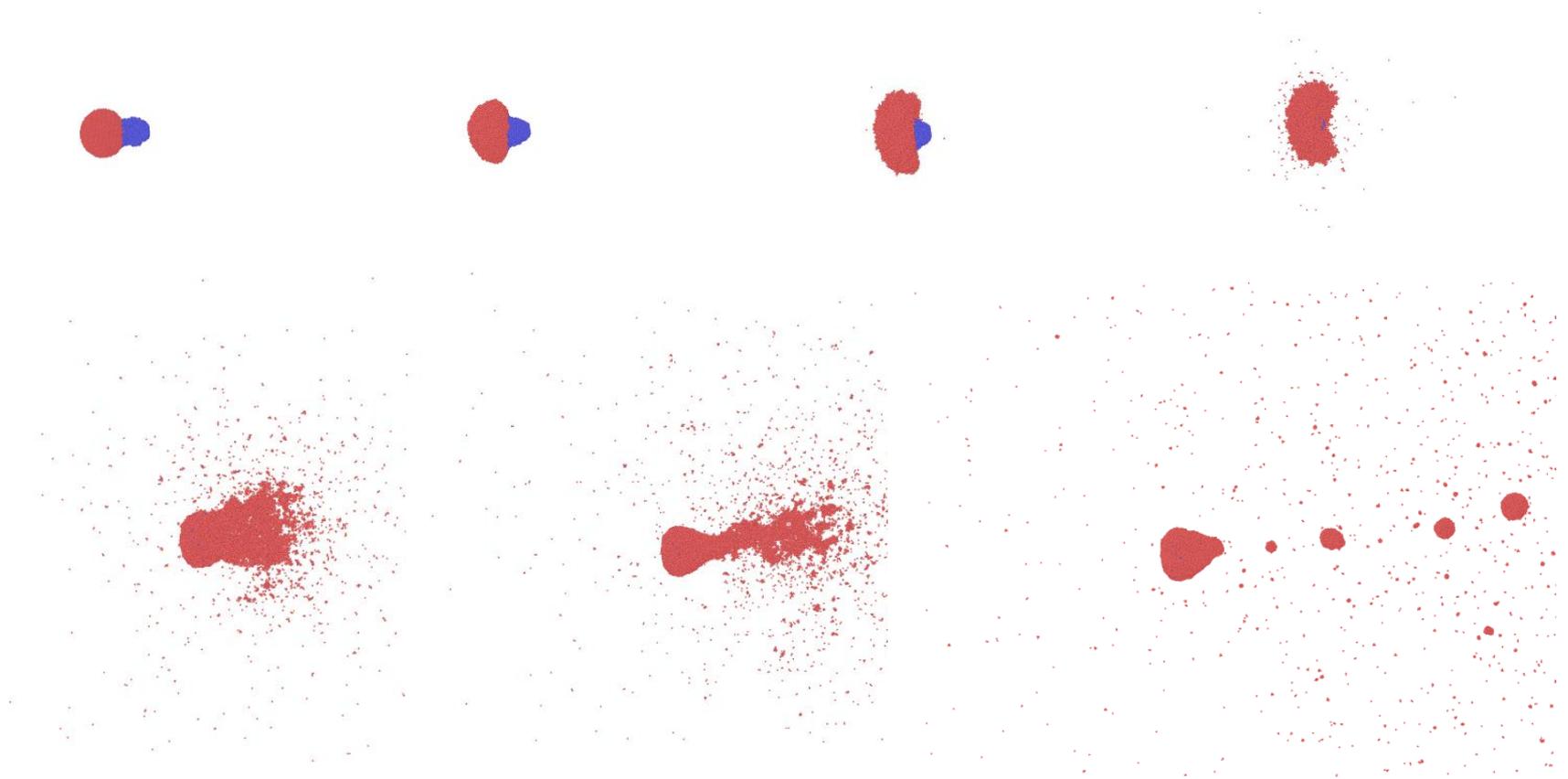
Ultra-short Laser-induced NP sintering, Janus NPs

Sintering of a larger metallic Janus NPs with different sizes upon rather weak laser heating



Ultra-short Laser-induced NP sintering, Janus NPs

Same size Janus NP: strong laser heating



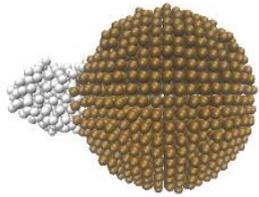
- 0, 100, 150, 200
- 300, 400, 800

Complex dynamics leading to core-shell formation and partial fragmentation

NP Sintering or Alloying: FeAu Small Janus NP

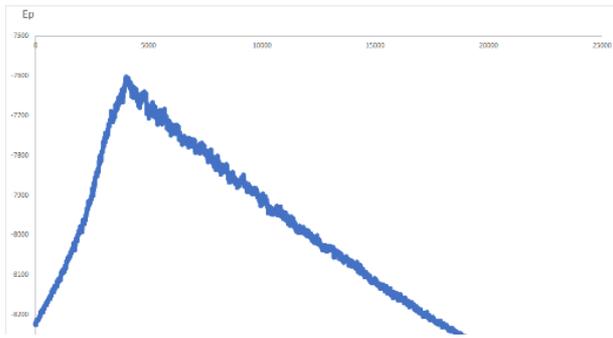
FeNP R=10 uc AuNP R = 20 uc FeNP 1700+AuNP 1700

time



Different sizes and species, but the same temperatures

Time-evolution of energy

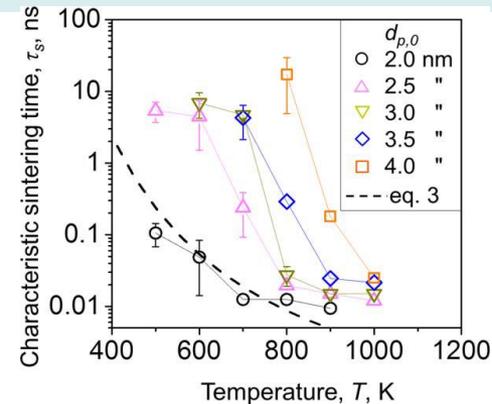


100ps



- 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

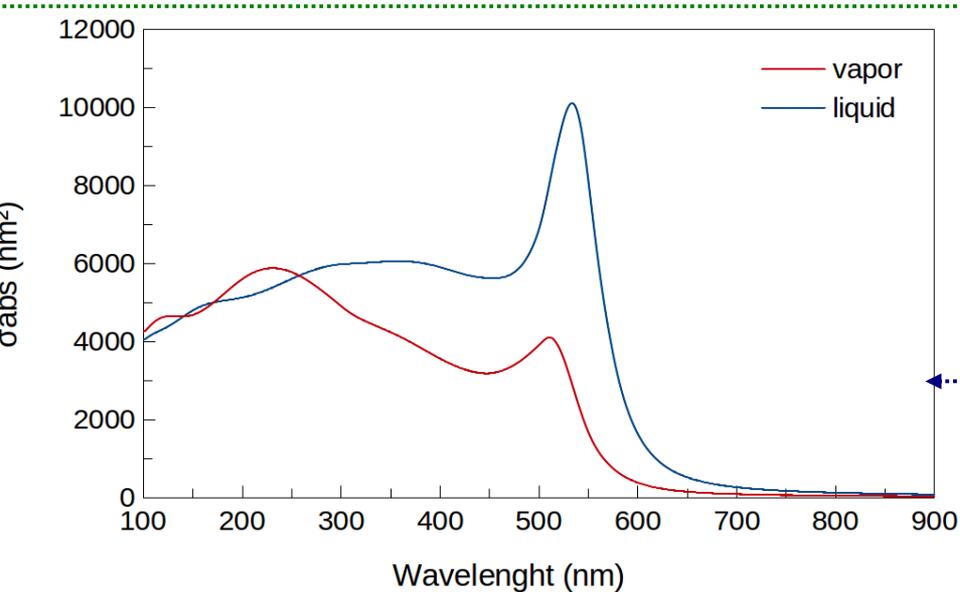
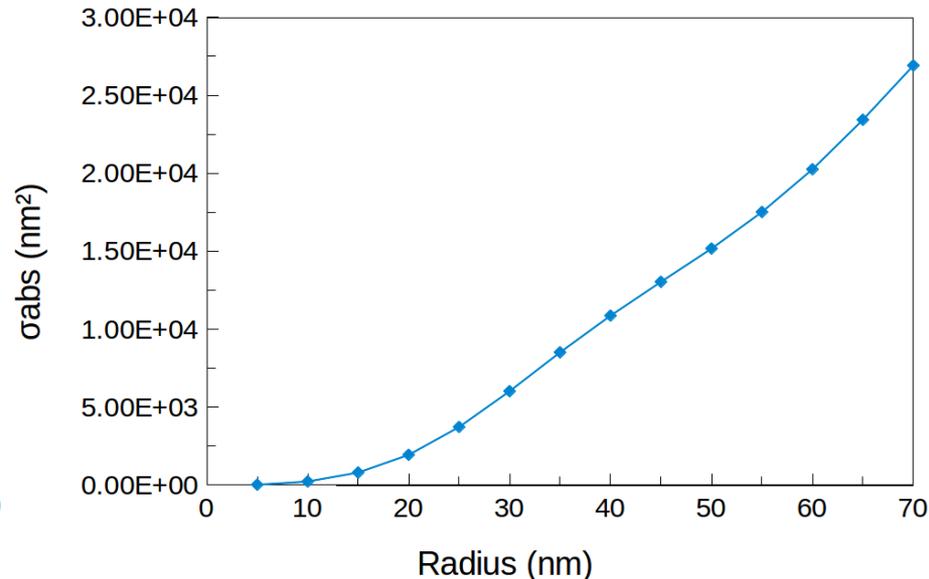
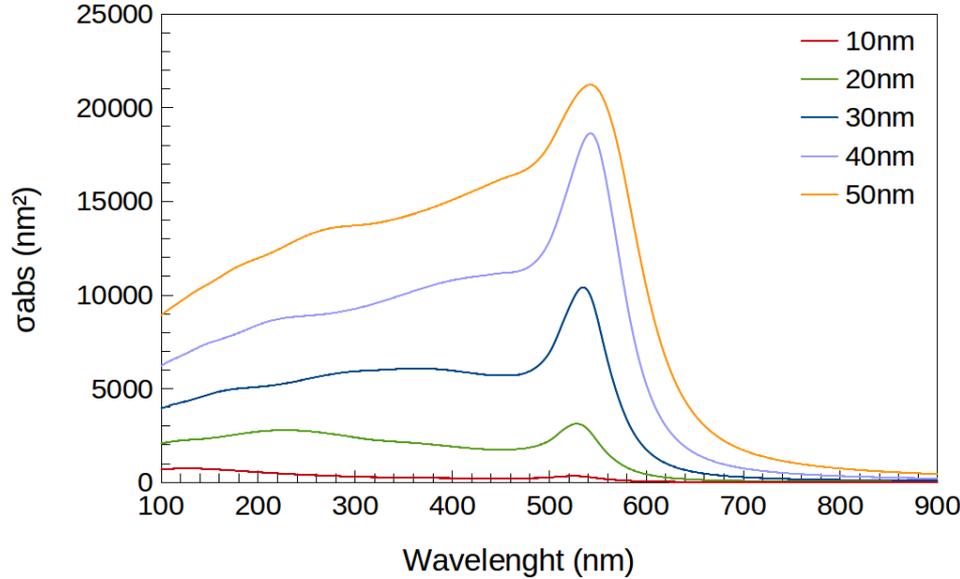
Core-shells can be formed when one particle is much larger and is composed of a material with different cohesive energy



E. Goudeli et al.,
AIChE 2015

ABSORPTION

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

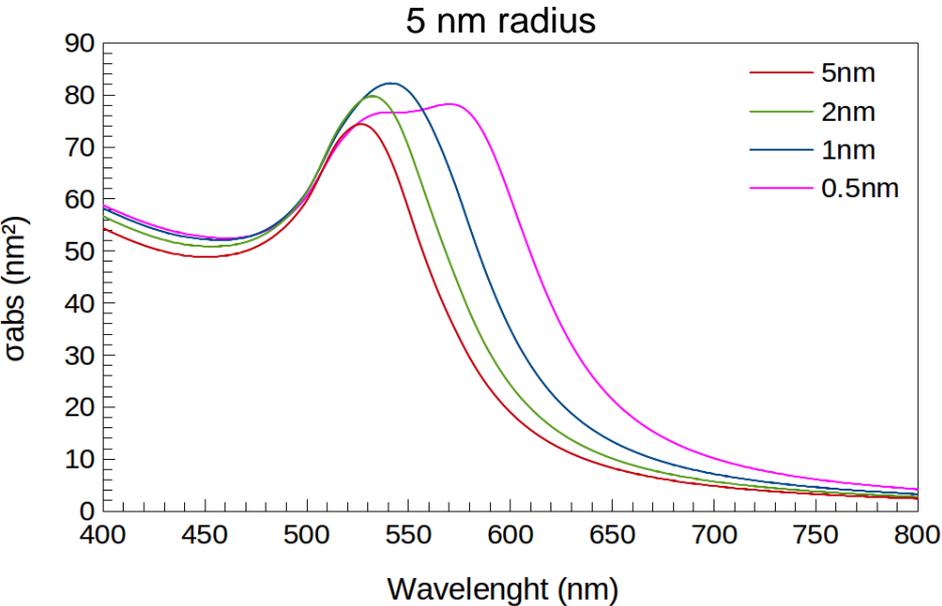


Absorption at 400 nm in liquid water raises with the particle radius (not linear)

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

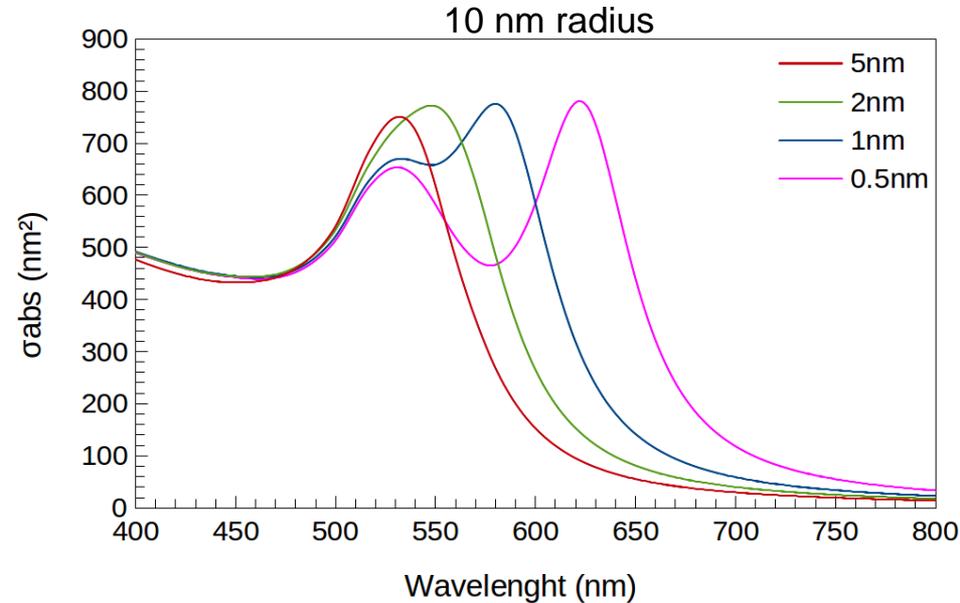
ABSORPTION

Gold dimers in water



If both particles have the same size

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



Inter-particle distance remains constant

Larger particles
=> more pics
=> shift towards blue

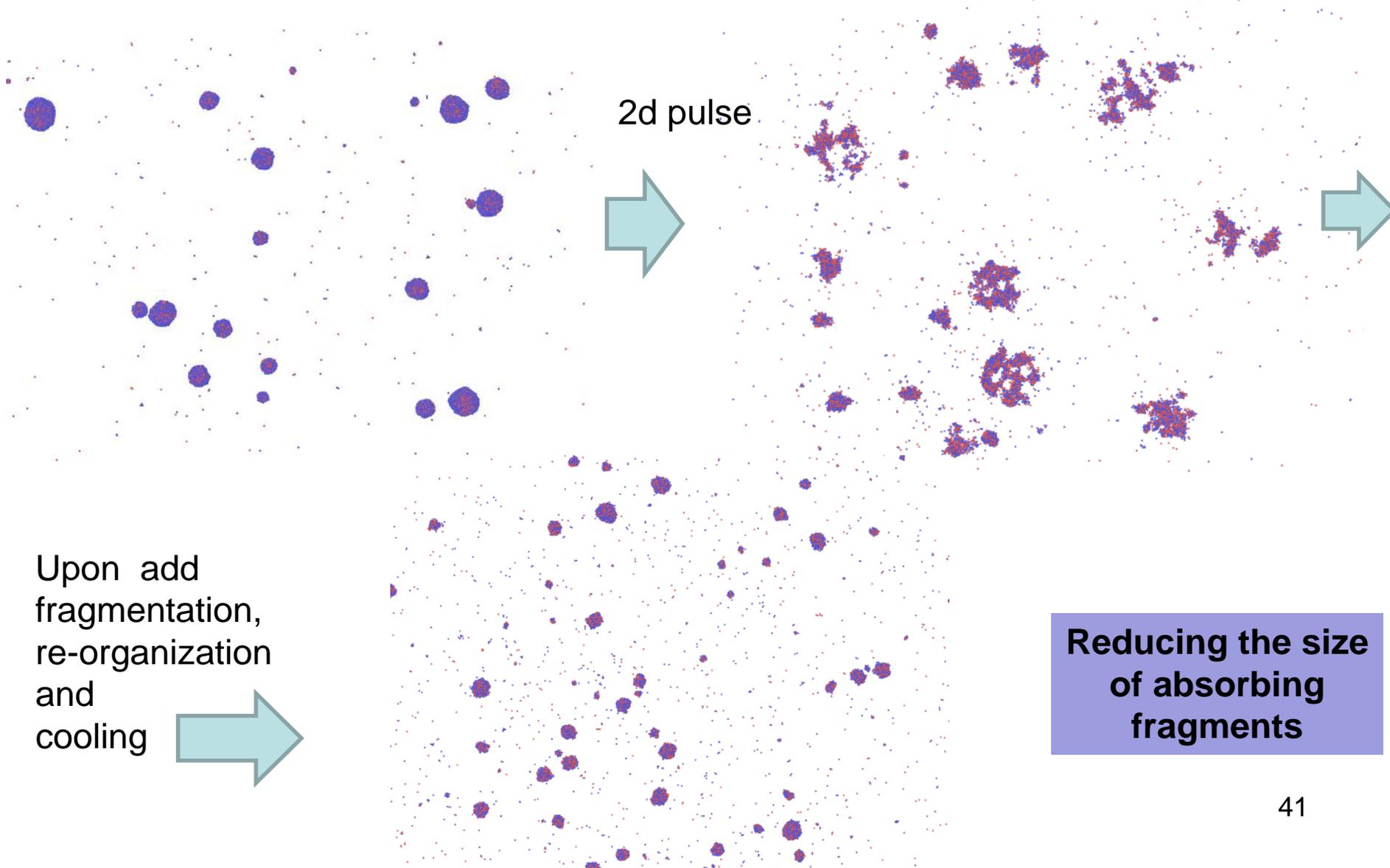
Absorption depends on size, composition, separation, etc...

Many Particle Systems

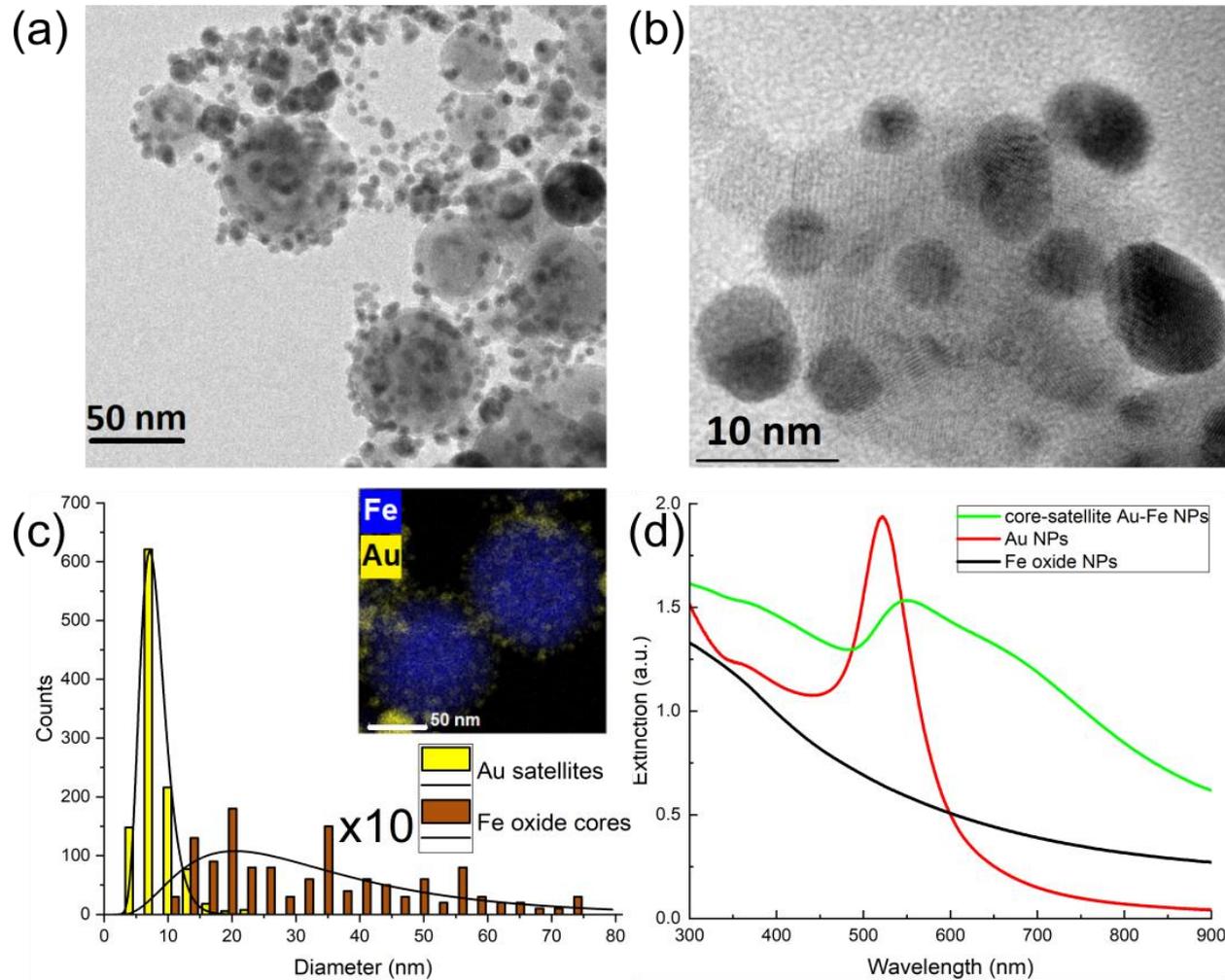
NP's Fragmentation

AuCo, NP R = 40 u.c.

Simulations starts from the fragmentation results, additional fragmentation takes place



Optical properties of core-shells and nanohybrids



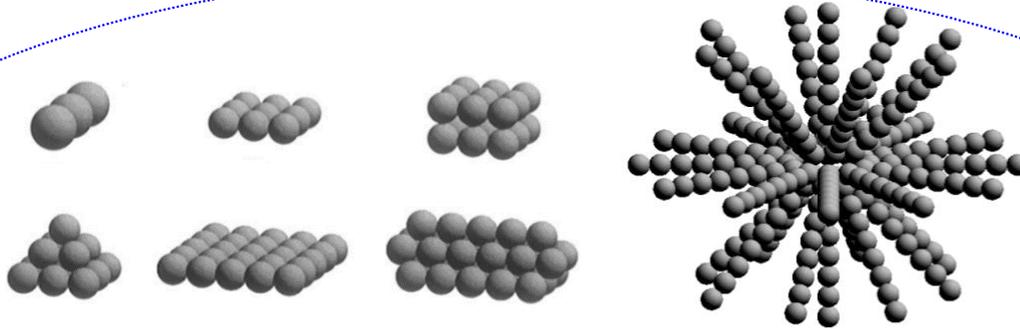
see talk by [Anton Popov et al. CECAM 2021](#)

OPTICAL PROPERTIES

Mie theory
light scattering by a sphere



extinction, scattering, absorption cross section
 σ_{ext} , σ_{scat} , σ_{abs}



A generalized multiparticle Mie-solution: further experimental verification

Yu-lin Xu et al.

FDTD, EM FEM, DDSCAT, etc..

+

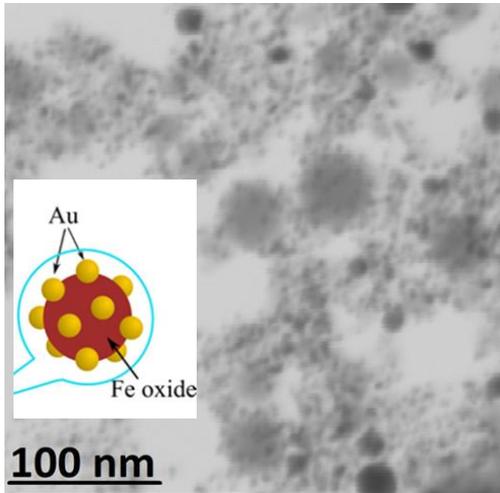
routine that corrects n , k for small particles
(mean free path)

Haiss et al. Analytical Chemistry, Vol. 79, No. 11 (2007)

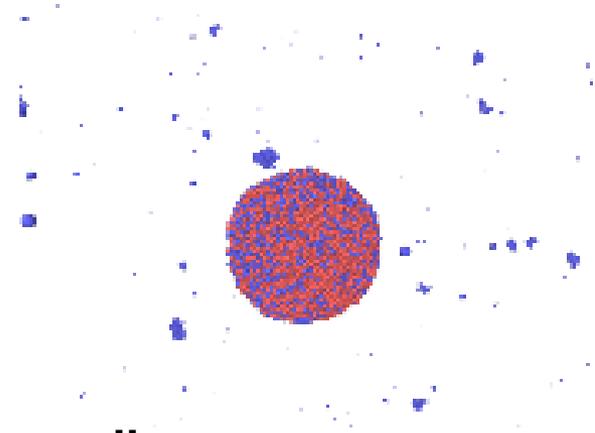
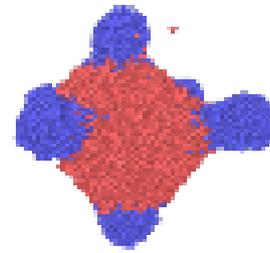
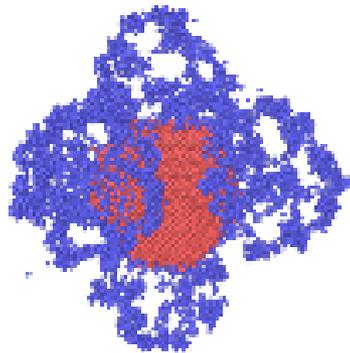
ok for size NP >5nm

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

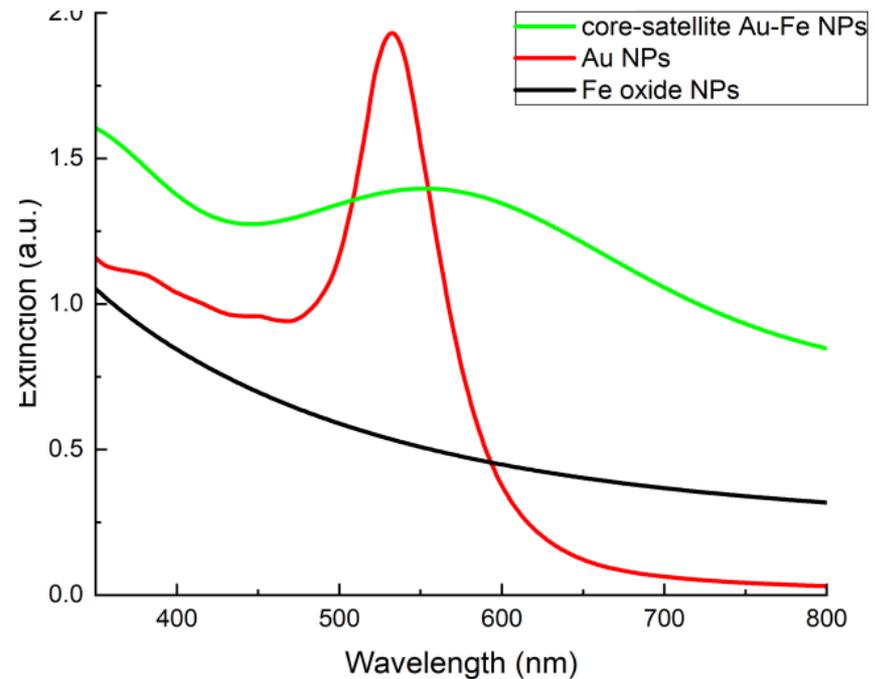
Complex Nano-Objects Formation by Laser Co-Ablation



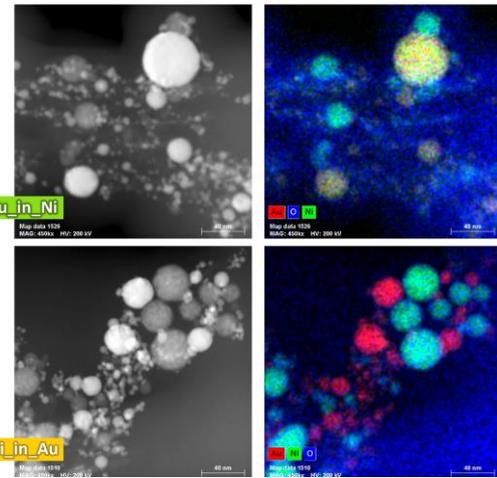
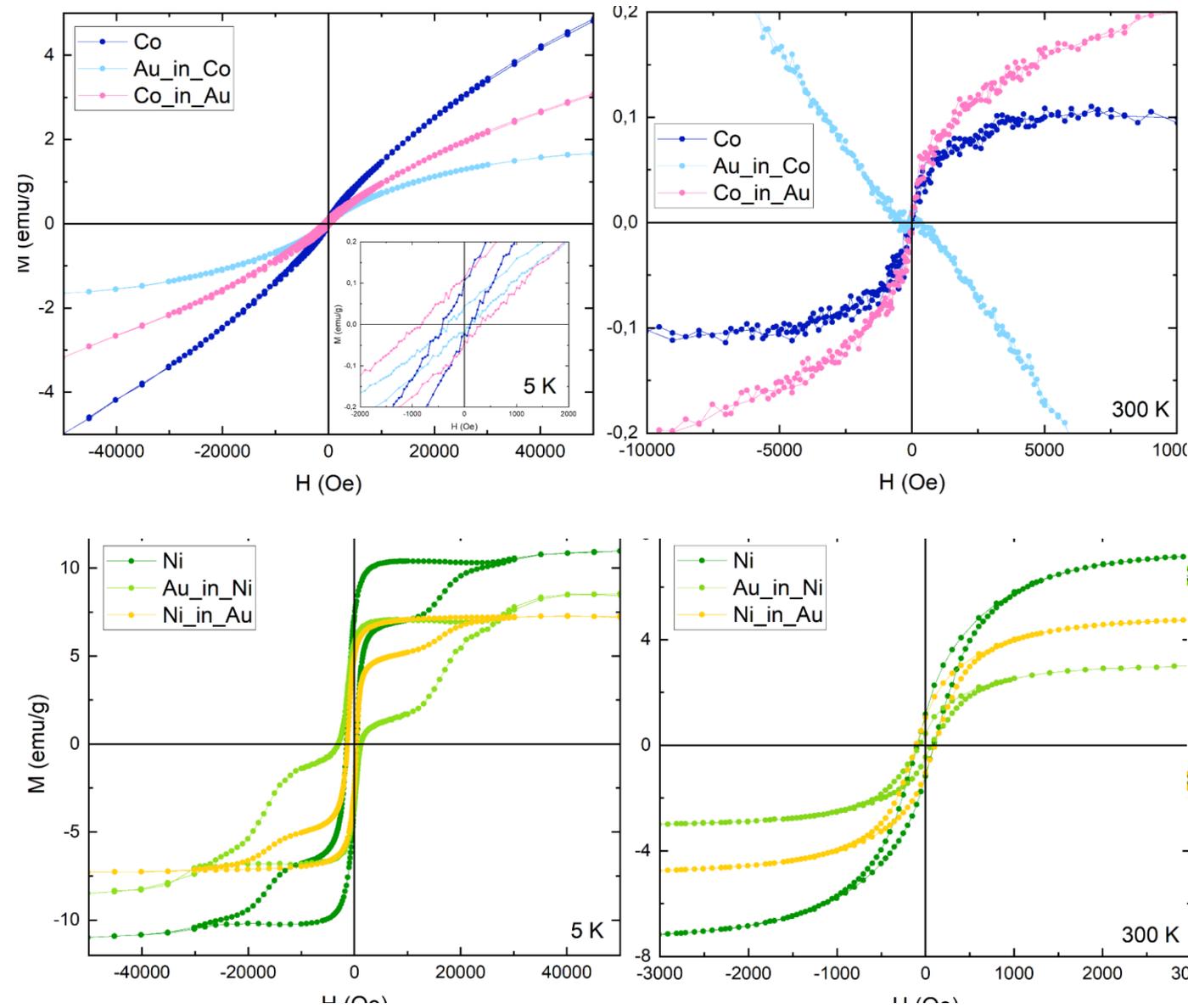
:STEM image of nanostructures, obtained by mixing of negatively charged laser-ablated Au NPs and positively charged laser-ablated Fe oxide NPs. Right: Calculated extinction spectra of bare Au NPs (red line), Fe oxide NPs (black line) and core-



Raspberry-like, core-shells or alloys



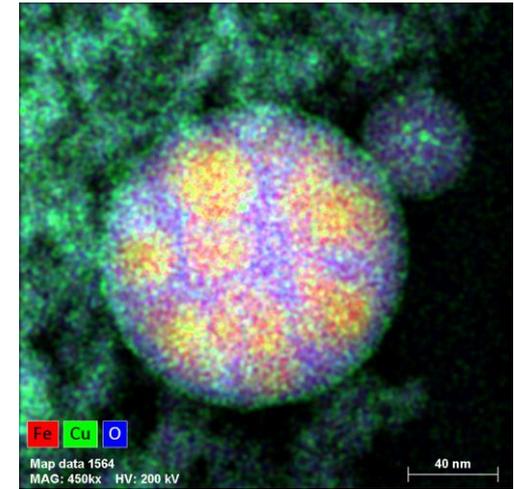
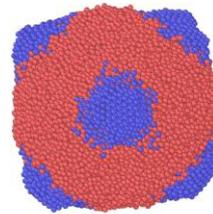
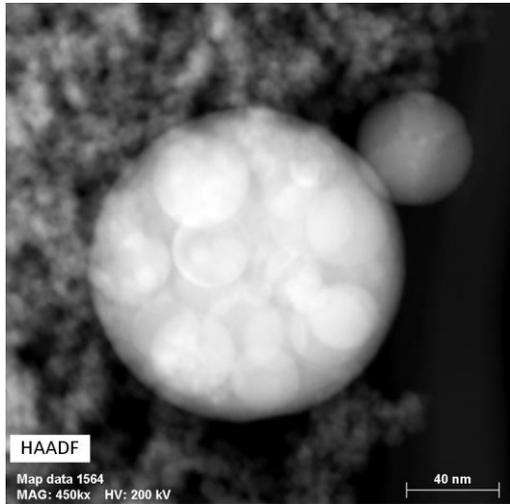
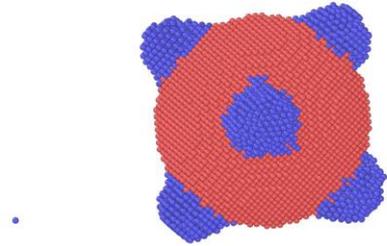
MAGNETIC PROPERTIES OF COMPLEX NANOPARTICLES



: O. Polit et al. In press

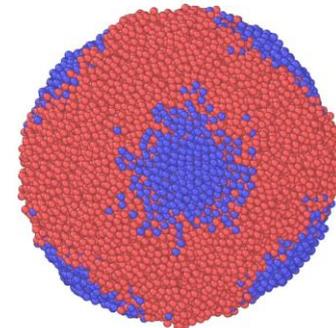
Complex Nano-Objects Formation by Laser

0, 125, 250
MD simulations



M. Shareri et al, in press

One bigger particle with many smaller ones inside



Summary

1. Laser is a very powerful and versatile tool suitable not only for the control over nanoparticle sizes but also for a wide range of manipulations with nano objects involving processes such as melting, reshaping, sintering, mixing, etc.
2. Examples of laser-induced modifications of smart nano-hybrids, nano-alloys, and multi-material nanoparticles have been presented revealing the role of size, temperature, and composition of nanoparticles, as well as the heating and cooling conditions.
3. The obtained results are of interest for **the analysis of pulsed laser-induced nanoparticle formation in liquids (PLAL), nanoparticle aggregation-fragmentation experiments, sintering, 3D manufacturing, etc.**



Special thanks to:

LASERMODE group members and many collaborators (PICS, PHC, ARQUS, ANR, EU, etc.), CNRS, UJM , The Univ. of Arizona, INP PAN, IHT, etc.

Thank you very much!

Just published:

"Alternative local melting-solidification of suspended nanoparticles for heterostructure formation enabled by pulsed laser irradiation"
Advanced Functional Materials 2023.

tatiana.itina@univ-st-etienne.fr