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

Tatiana Itina, Rudenko Anton

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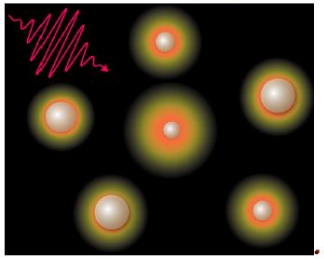
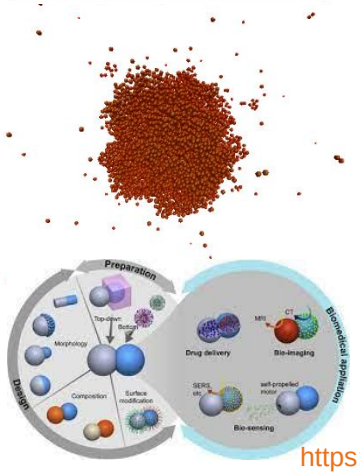
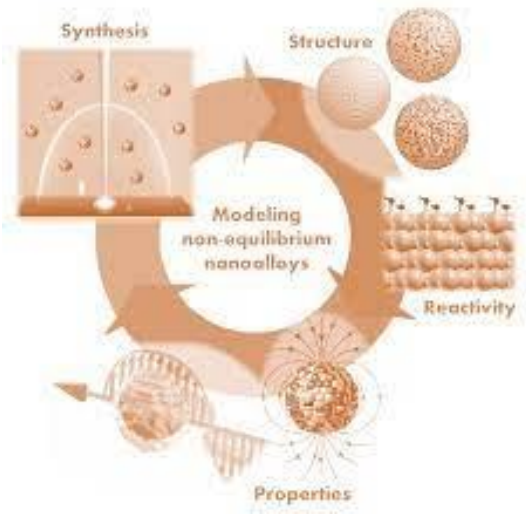
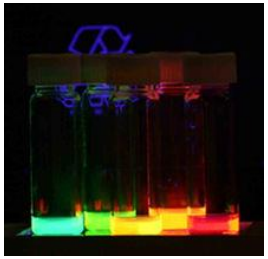
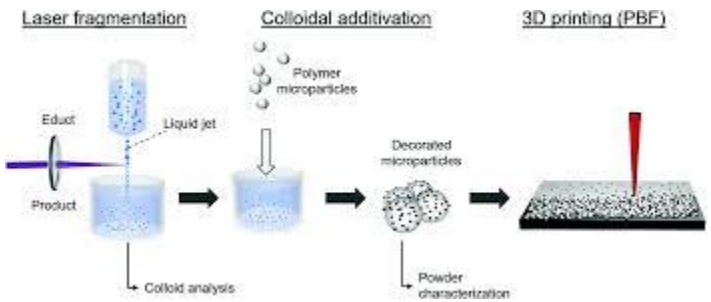








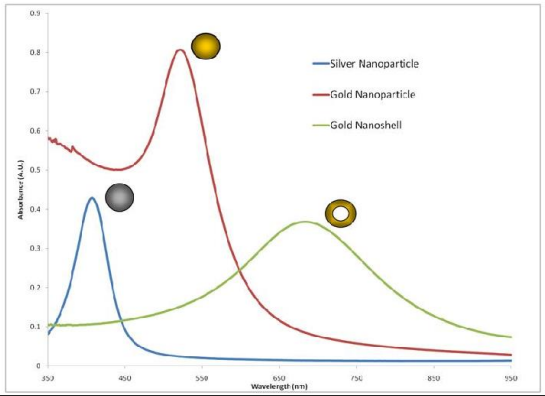


https://doi.org/10.1016/j.mtbio.2019.100033

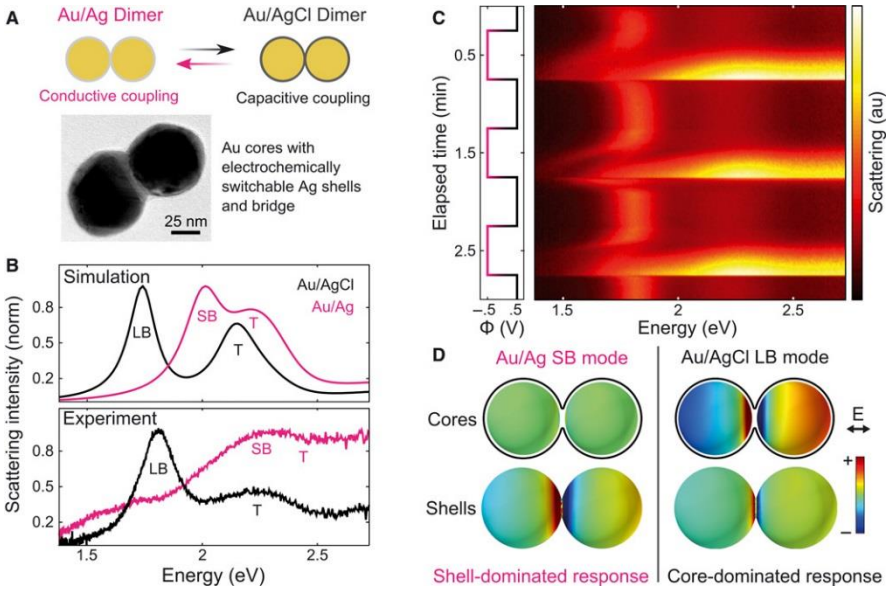
Stephan Barcikowski and Bilal Gökce

Motivation

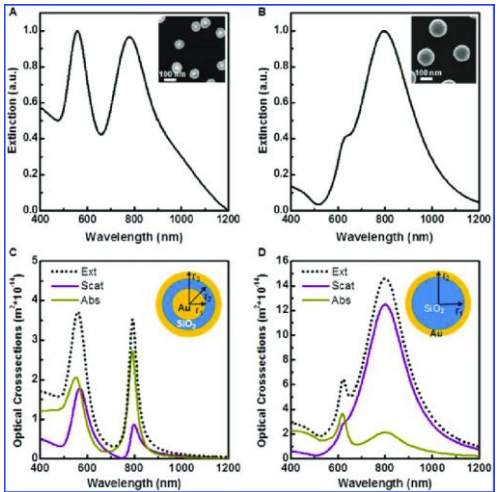
Tailoring optical properties: medical applications, imaging, photo-acoustics, photonics, etc.



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



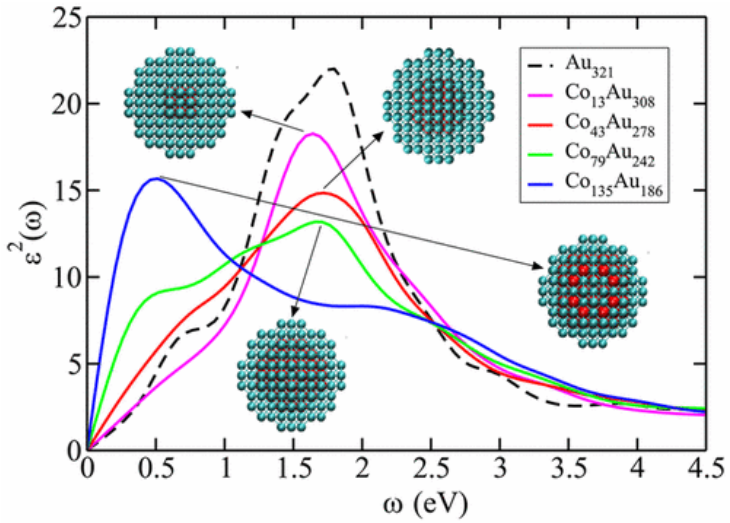
From tunable core-shell nanoparticles to plasmonic drawbridges: Active control of nanoparticle optical properties **Chad P. Byers et al. *Science Advances* 04 Vol. 1, no. 1 (2015)**



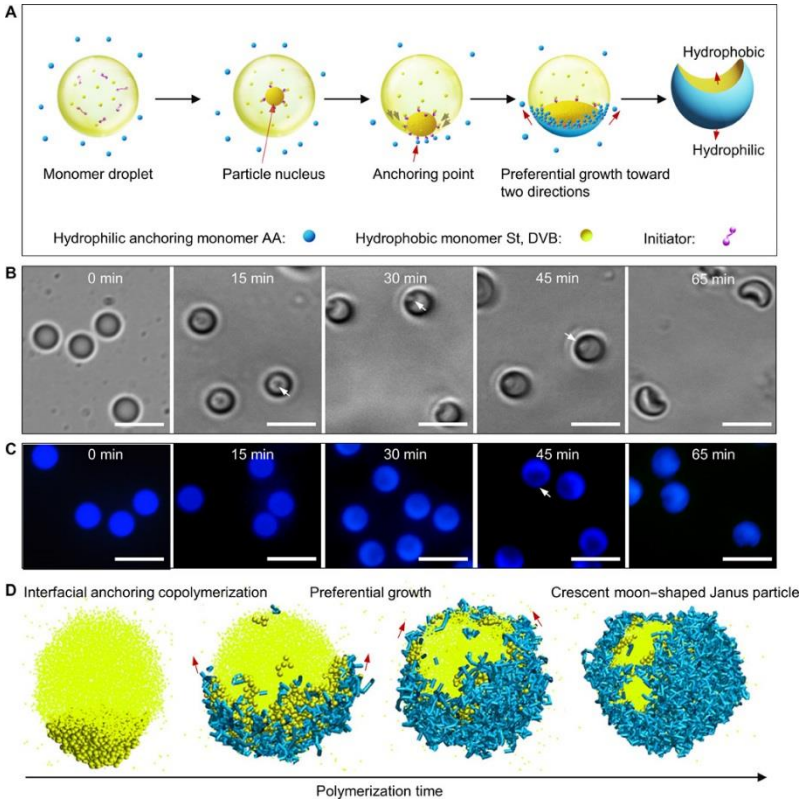
Au Nanomatryoshkas as Efficient Near-Infrared Photothermal Transducers for Cancer Treatment: Benchmarking against Nanoshells, Ciceron Ayala-Orozco et al., ACS Nano 8(6) (2014)

Motivation

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



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



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

Why Lasers ?

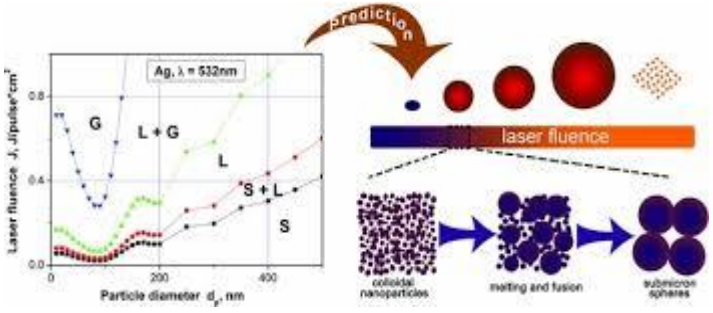
1. Green synthesis methods, bio-compatibility
2. Easy control over NP properties
3. Scaling-up possibilities
4. Possibility to create stable ultra-structures

Laser is a versatile tool that can be used for

- **formation of nanoparticles**
  - in vacuum
  - in gas
  - in liquid
  - in a solid

- **modification of nanoparticles**

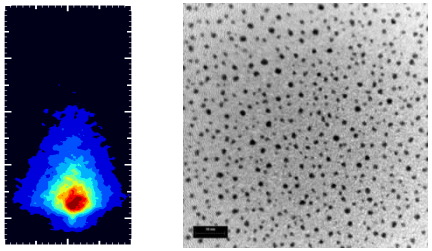
fragmentation –tailoring of sizes
sintering – can create nanohybrides and nanocomposites, thus tailoring their optical, magnetic, and acoustic properties



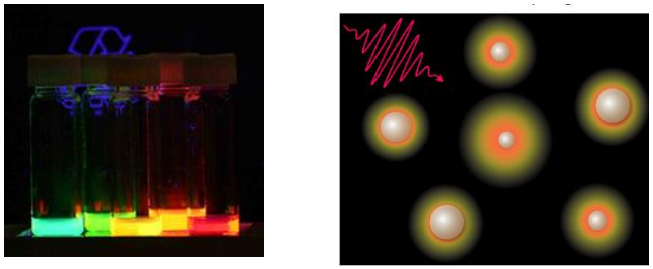
Mechanism of pulse laser interaction with colloidal nanoparticles A. Pyatenko et al., Laser&Phot. Rev. 2013

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

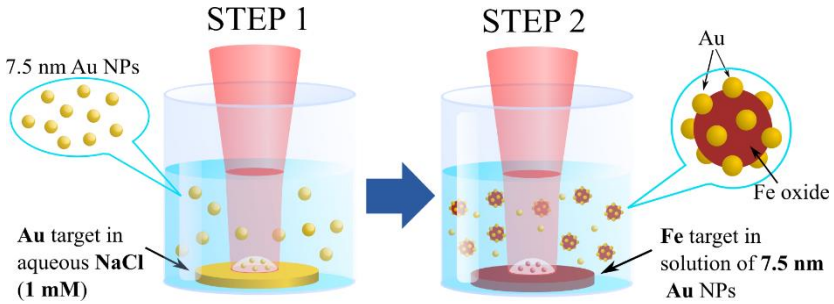
Typical experiments



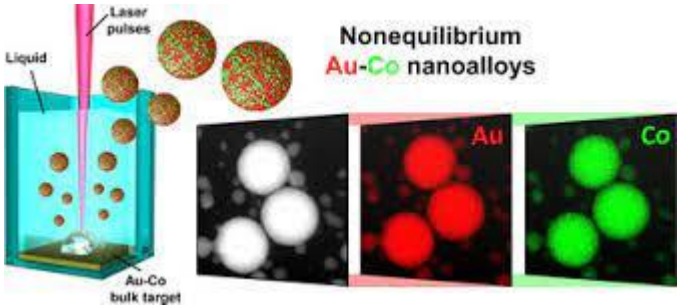
Pulsed laser interactions in vacuum and in a gas phase



Laser-induced ablation/fragmentation in liquids



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



Vincenzo Amendola, Padova, Italy

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

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

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

Laser Interactions with NPs

Laser pulse

Propagation, absorption, local field enhancement

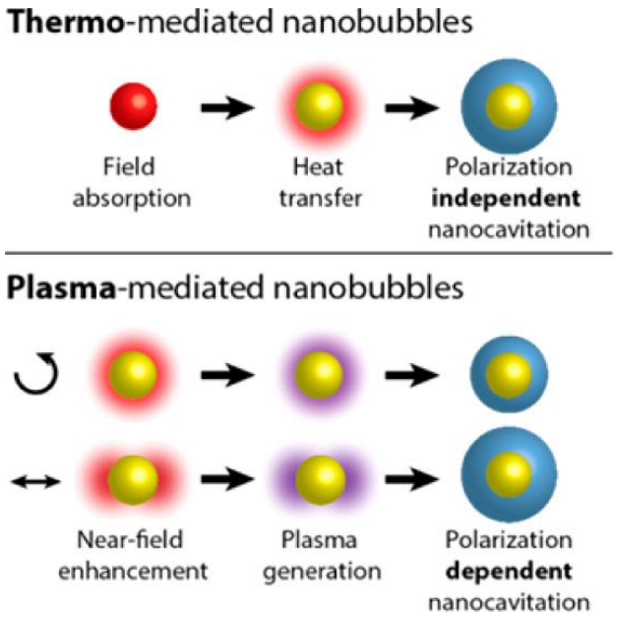
Local ionization and heating of the matter/liquid near NP
plasma-mediated nanobubbles

NP heating, heat transfer to water
thermo-mediated nanobubbles

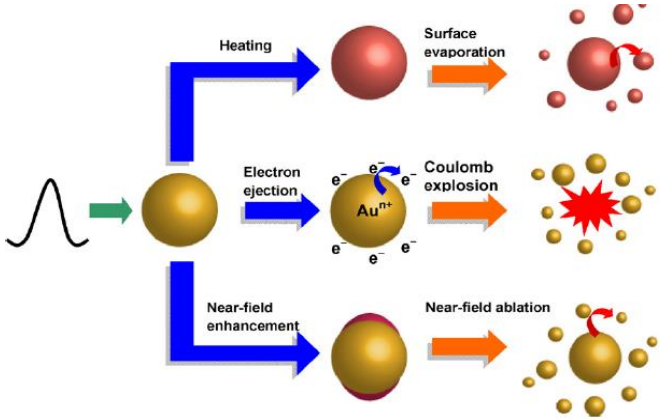
NP heating, melting, reshaping, sintering, evaporation

Electron ejection, injection in the ambient

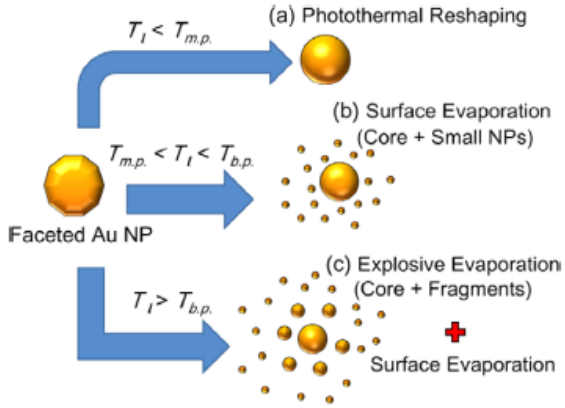
NP fragmentation



Lachaine et al. Photonics (2013)



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



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

Pustovalov et al., LPL (2008)

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

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

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

Laser Interaction with NPs in Liquids

Classical Modeling

Maxwell equations

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

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

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

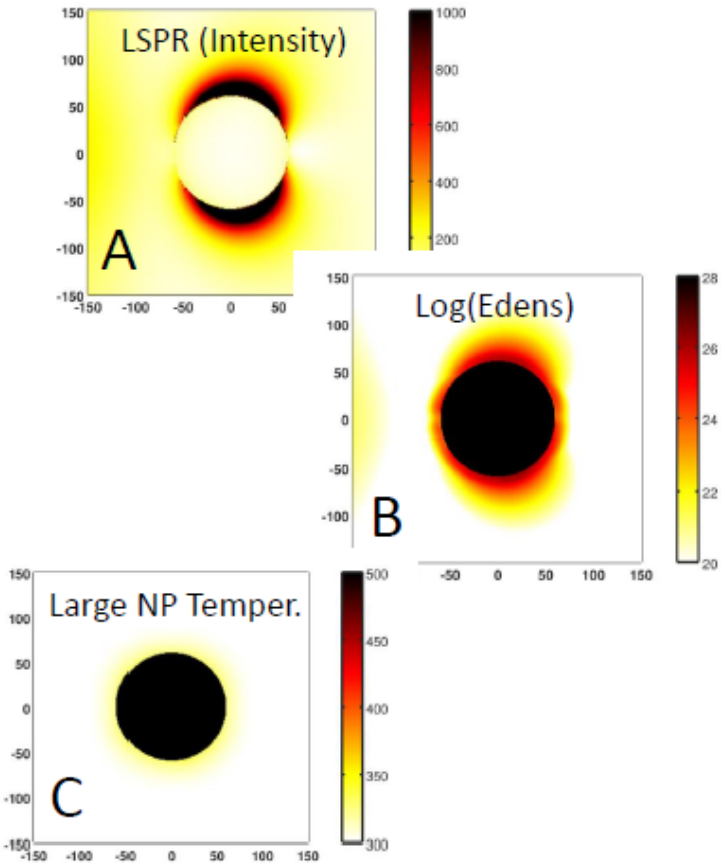
Nanoparticle

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

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 account for electron ejection/injection, etc..

Ultra-Short Laser Interaction with NPs

Non-Equilibrium Electron Sub-system

Conduction band (free) electrons model

Boltzmann equation

$$\frac{\partial f(E)}{\partial t} = \left(\frac{\partial f(E)}{\partial t}\right)_{e-e} + \left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} + \left(\frac{\partial f(E)}{\partial t}\right)^{abs}_{intra/inter}$$

$$E_{max} = E_F + \varphi$$

Terms for e-e, e-ph scattering & absorption

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

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

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

Definitions of electron & lattice temperatures

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

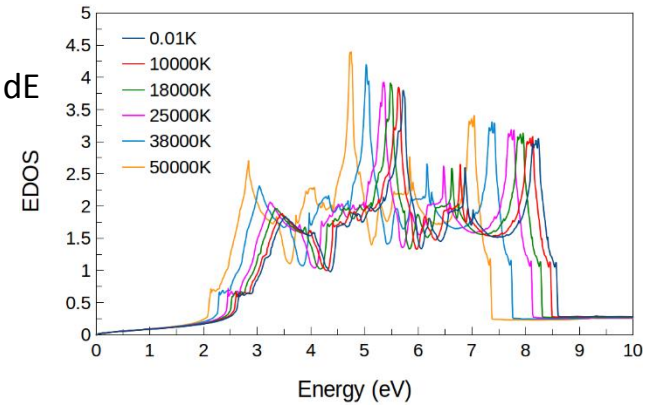
$$\rho_{NP} C_{NP} \frac{\partial T_{NP}}{\partial t} = -A \int_0^{E_{max}} \left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} E^{3/2} dE$$

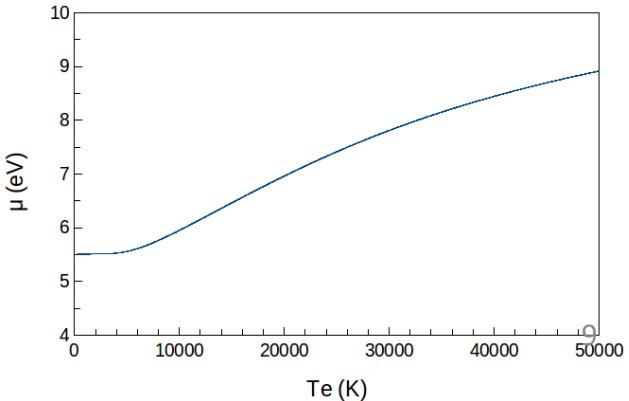
Here, we can transit back to spatial TTM model to add spatial thermal diffusion etc.

Quantum mechanical approach (DFT)

$n_\varepsilon = \int_\varepsilon^\infty EDOS(E) \cdot f(E, \mu(T_e), T_e) \cdot dE$

EDOS(E)





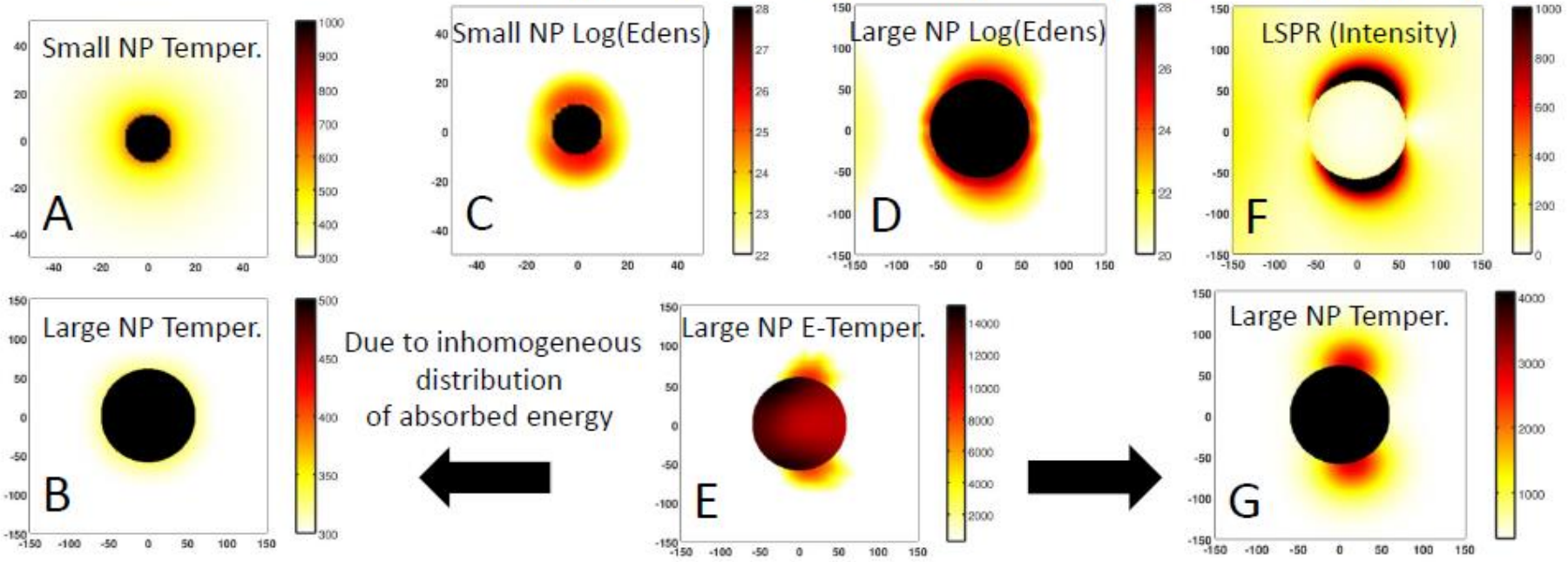
Laser Interaction with NPs in Liquids

Interaction regimes and mechanisms involved

Regime I
Laser heats Au NP;
Au NP transfers heat to water

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

Regime III
LSPR triggers water
photo-ionization;
Induced Carriers heat water



Electron emission

Au : N_{therm} is the total number of emissible electrons emissible : $N_{therm} = \alpha.n_{\varepsilon}$

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

$$n_{\varepsilon} = \int_{\varepsilon}^{\infty} EDOS(E) \, . \, f(E, \mu(T_e), T_e) \, . \, dE$$

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

Criteria of fissility, also called Rayleigh instability factor

if X > 1, where

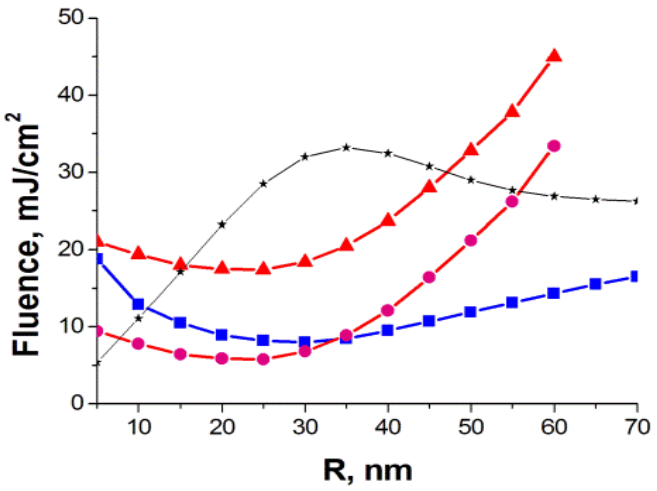
$$\mathbf{X = (N_{therm}^2/N_e) / (16.\pi.r_{ws}^3.\sigma/e^2) \Rightarrow}$$

Particle explosion can occur

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

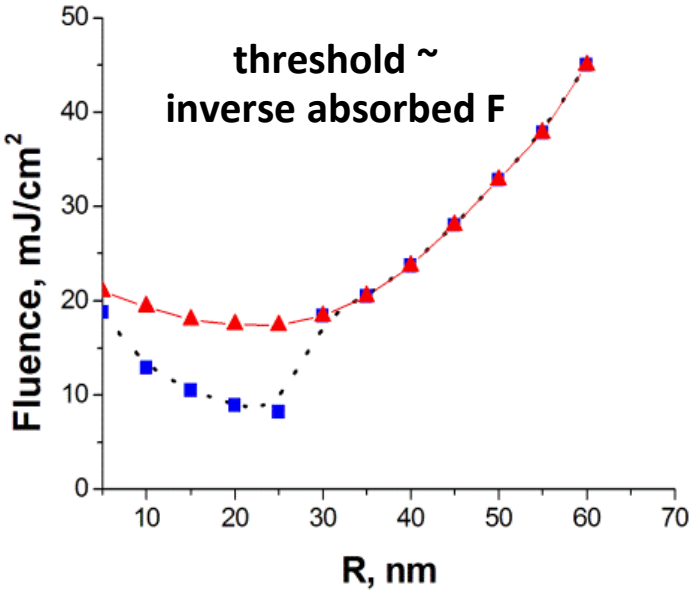
Ultra-short Laser interaction with a single Au NP

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



Calculated threshold fluence

150 fs @400 nm



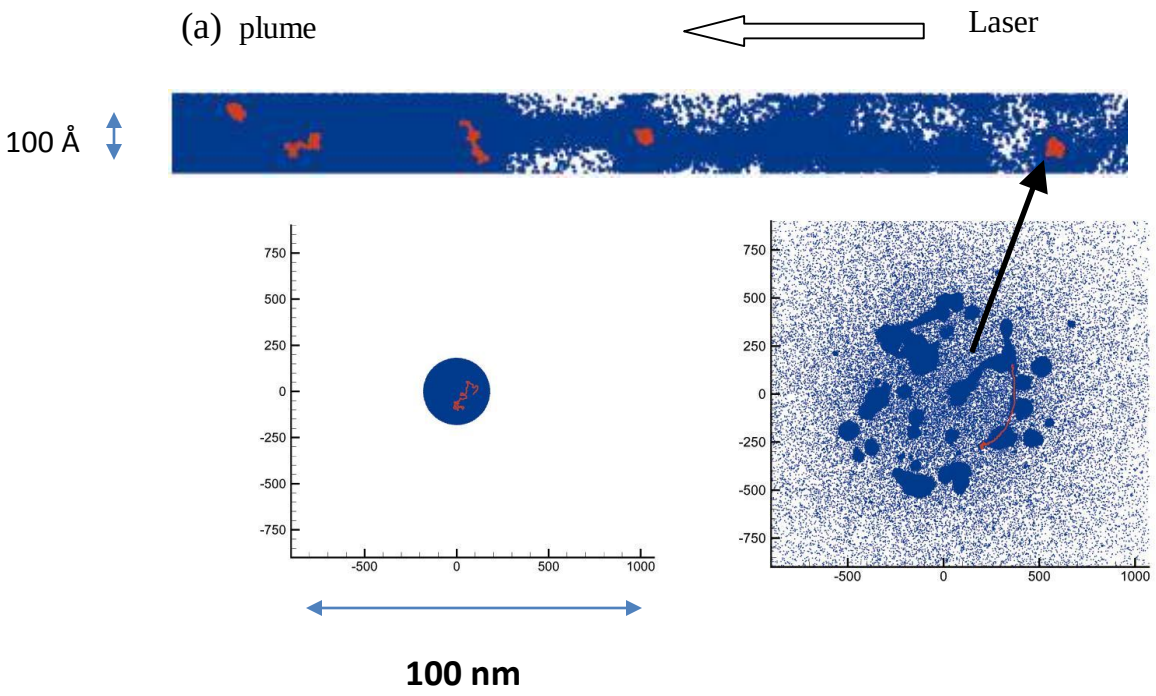
Resonant particles can be decomposed electrostatically…
However,
smaller and larger particles are expected to be fragmented due to classical thermal-mechanical effects.

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

Classical Molecular Dynamics (MD) simulations:

Decomposition of the ablated material after the absorption of laser radiation

and nanoparticle fragmentation



t = 300 ps after the beginning of the laser pulse

τ = 15 ps

e=0.6 eV per molecule

T. E. Itina, L. V. Zhigilei, B. J. Garrison
The Journal of Physical Chemistry B 106 (2), 303-310 (2002)

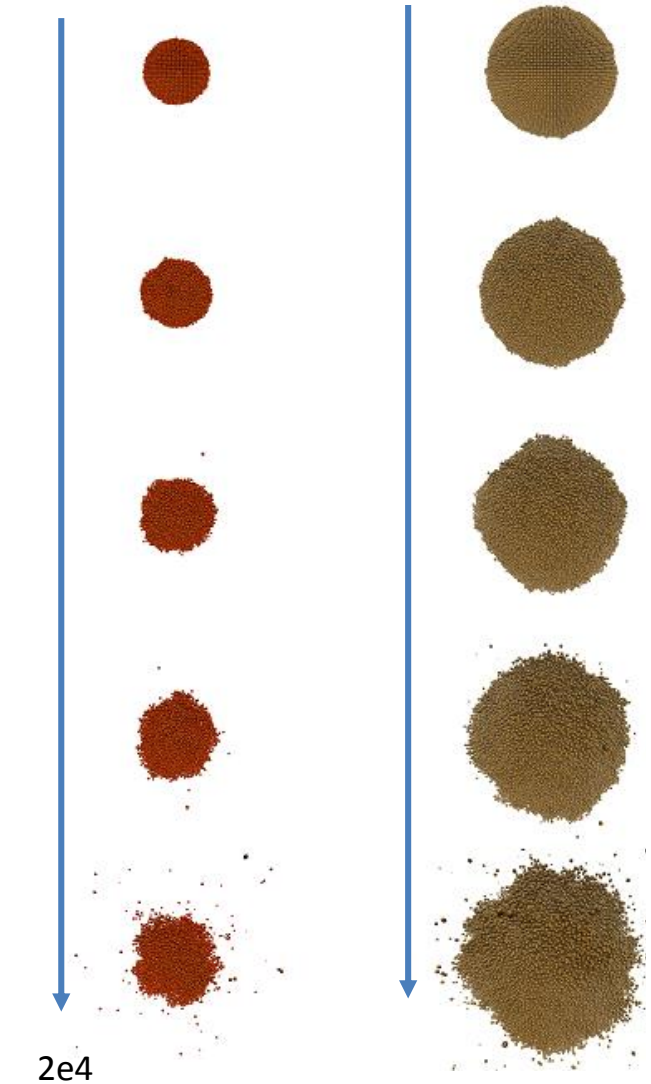
Ultra-short Laser interaction with a single Au NP in vacuum

MD simulations

Au

N_t

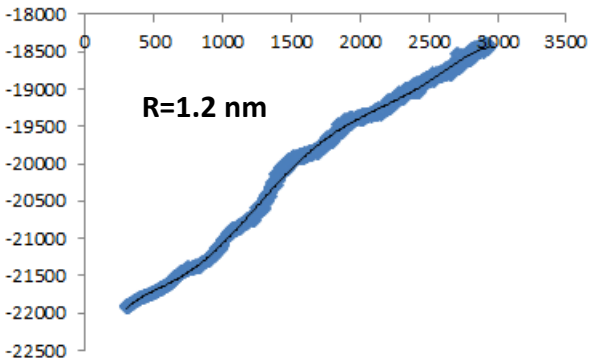
R=1.2 nm and 2.4 nm

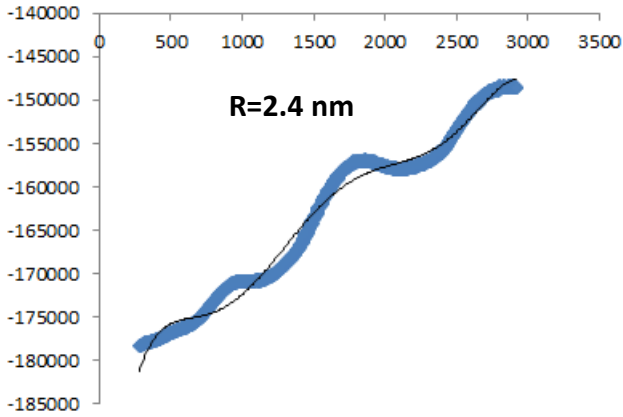


2e4

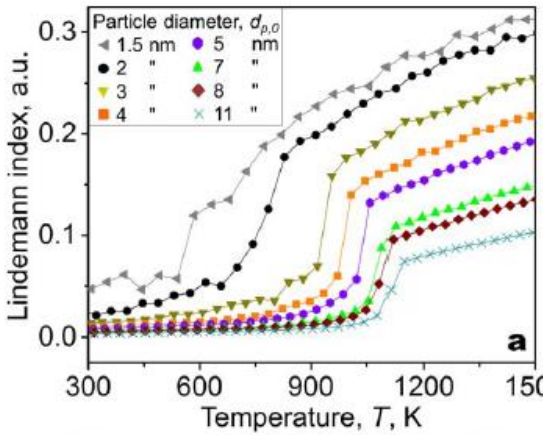
T.E. Itina at al.

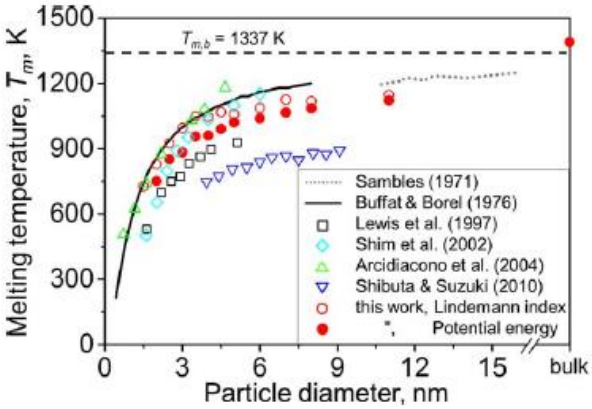
Time-evolution of potential energy, rapid heating

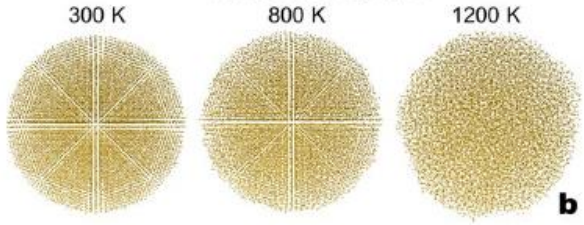




Melting and … structural transformations

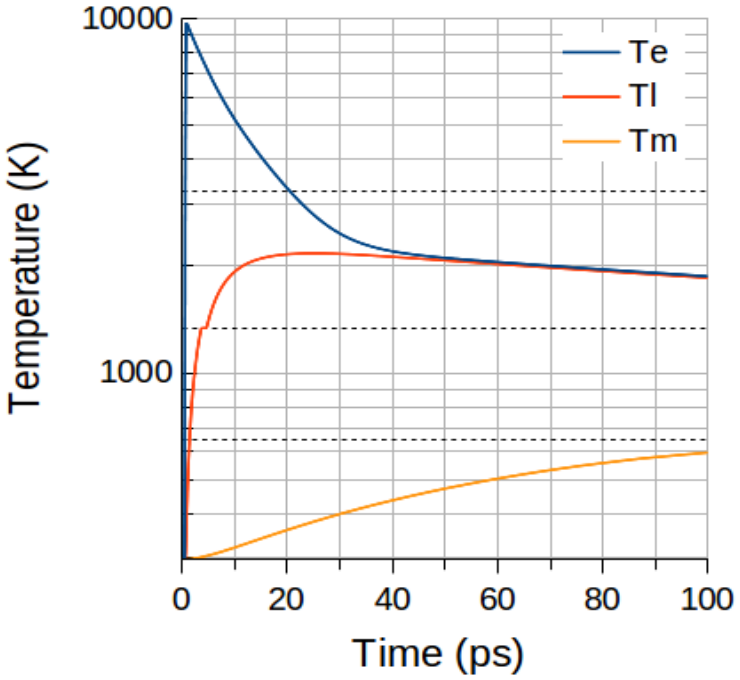






E. Goudeli et al., AIChE 2015

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

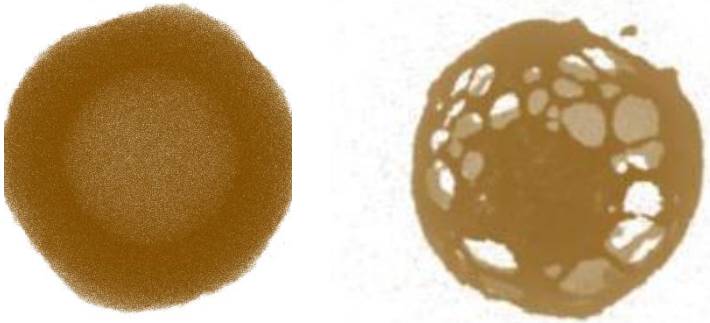


30 nm radius gold particle in water absorbing laser pulse of **150 fs** at **400 nm** with laser fluence of **12.3 mJ/cm²** Gaussian time profile

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

MD simulations

Heating during e-ph coupling

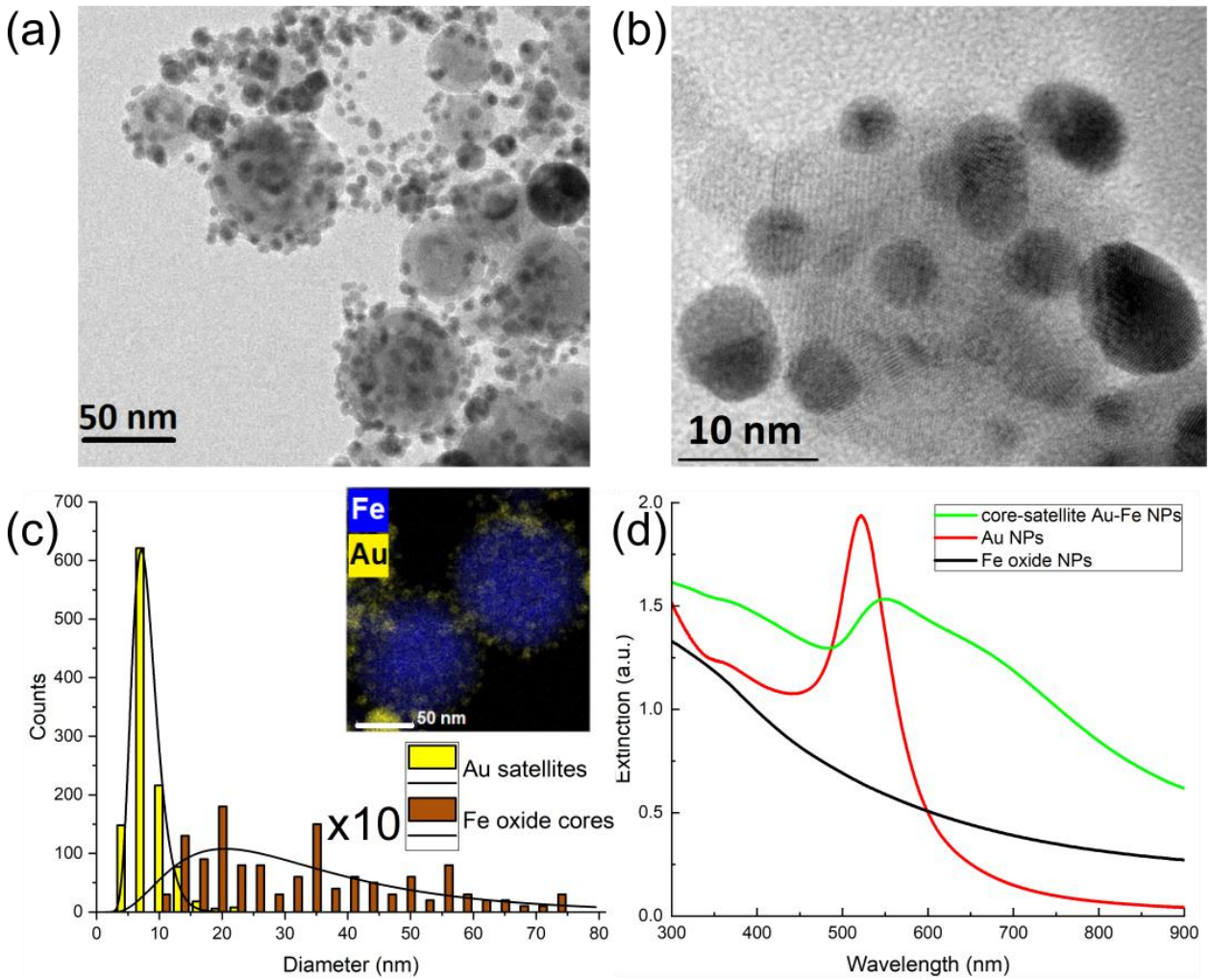


Larger particle – longer heating and cooling, higher thresholds

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

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

Optical properties of nanohybrids

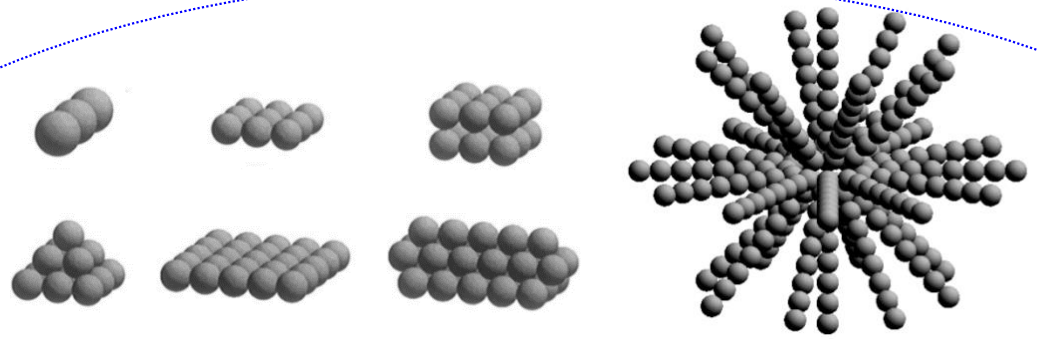


see talk by Anton Popov et al. CECAM 2021

ABSORPTION

Mie theory
light scattering by a sphere

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



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

Good agreement with experimental results
(acrylic spheres)

+

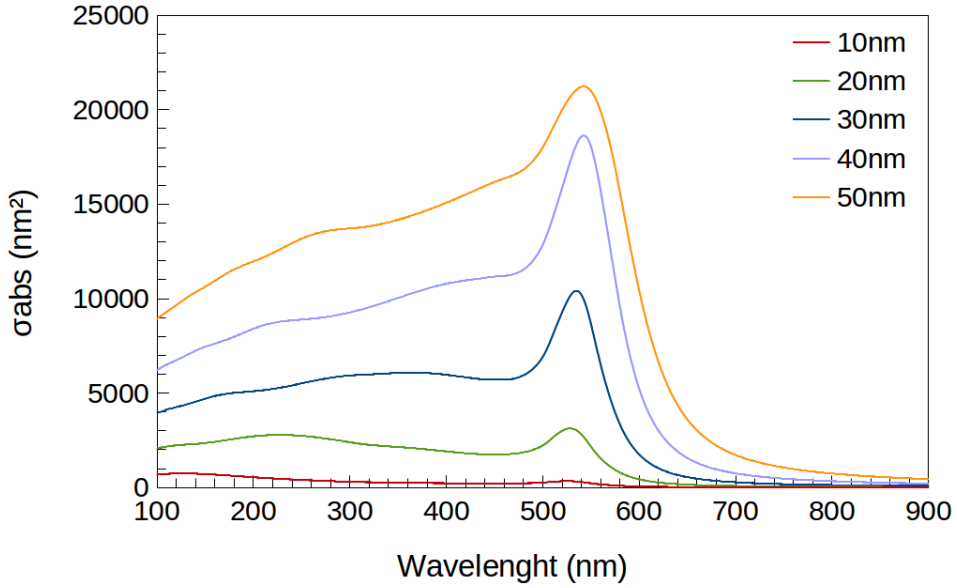
size < 10nm

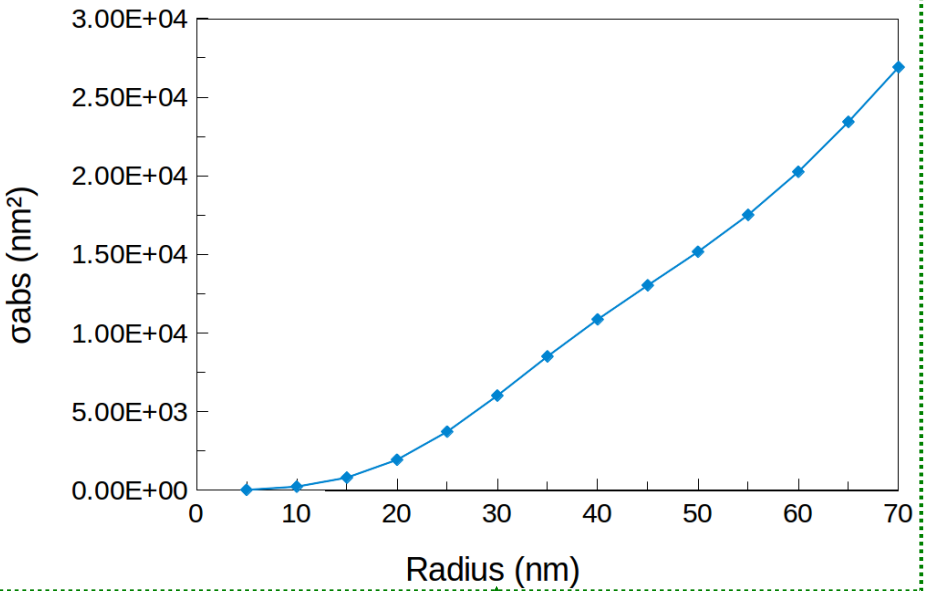
routine that corrects n, k for small particles
(mean free path)
Haiss et al. Analytical Chemistry, Vol. 79, No. 11 (2007)
ok for size NP >5nm

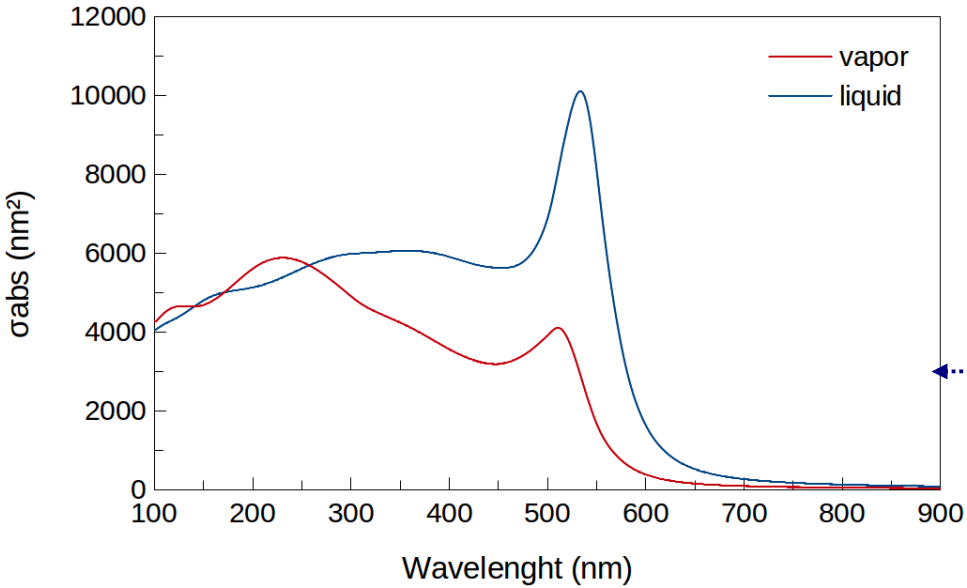
based on { *Bohren-Huffman Mie scattering subroutine (callbhmie.f)*
Generalized Multiparticle Mie-solution (gmm01f.f)

ABSORPTION

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







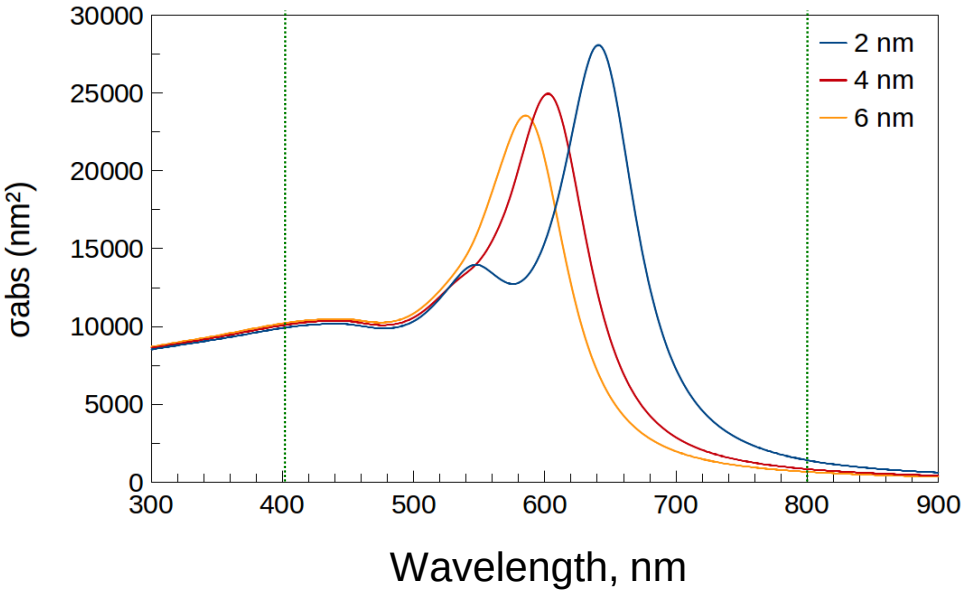
Absorption at 400 nm in liquid water raises with the particle radius (not linear)

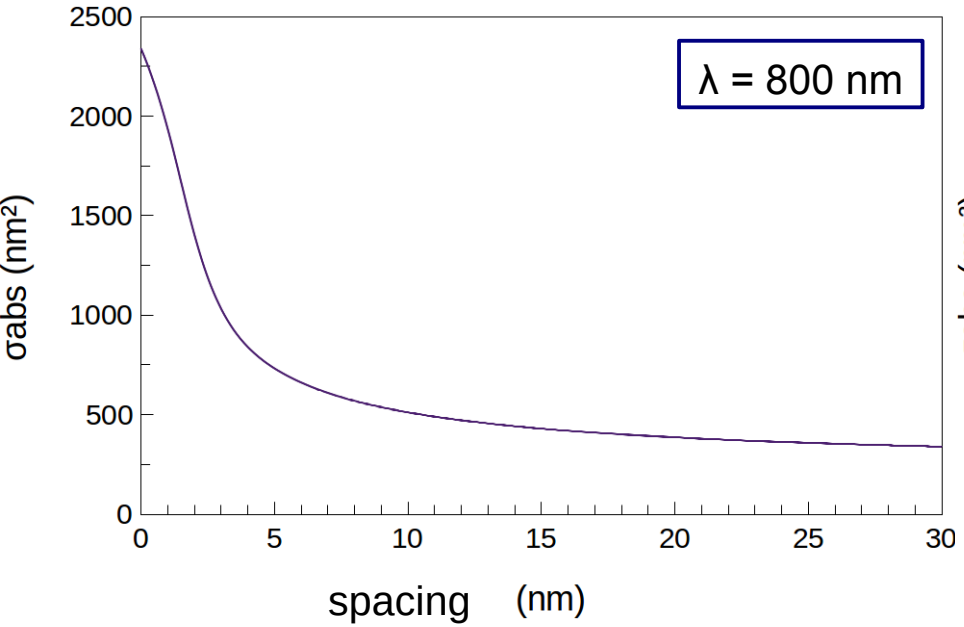
Absorption depends of the medium. At 400 nm, passage from liquid water to water vapor goes with a drop in absorption.

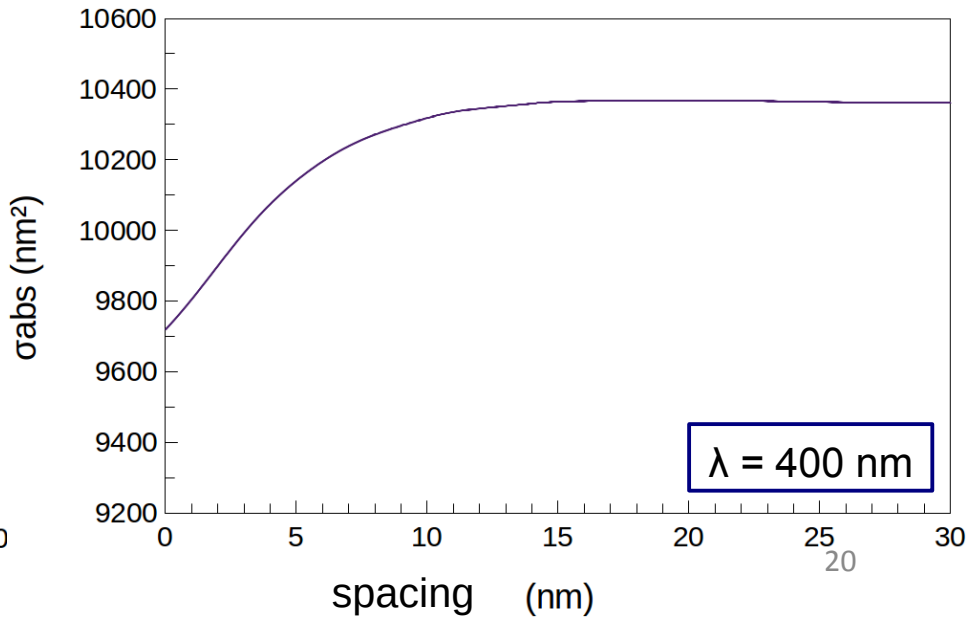
ABSORPTION

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

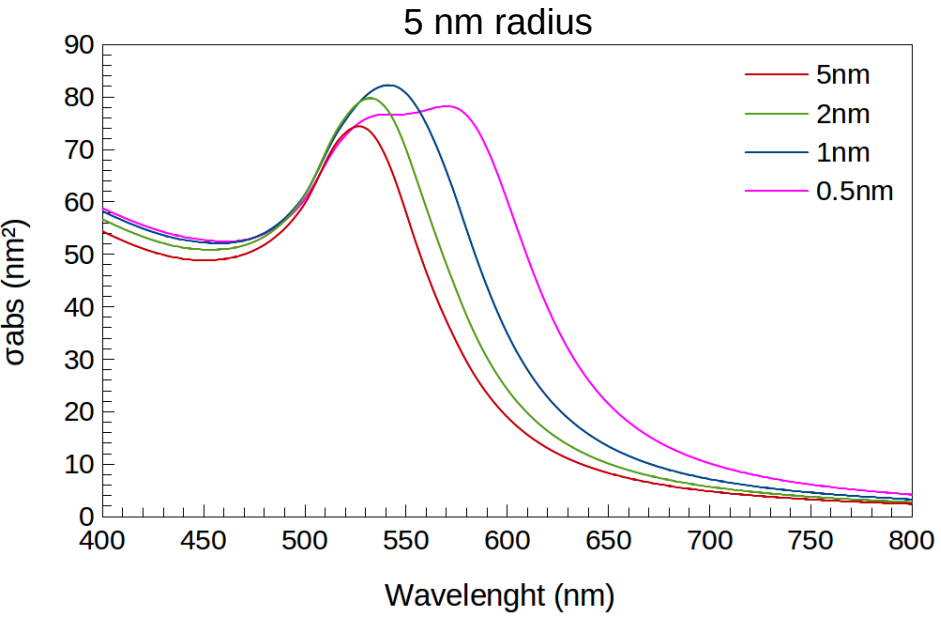
Absorption for **Au dimers** depends on both wavelength and spacing

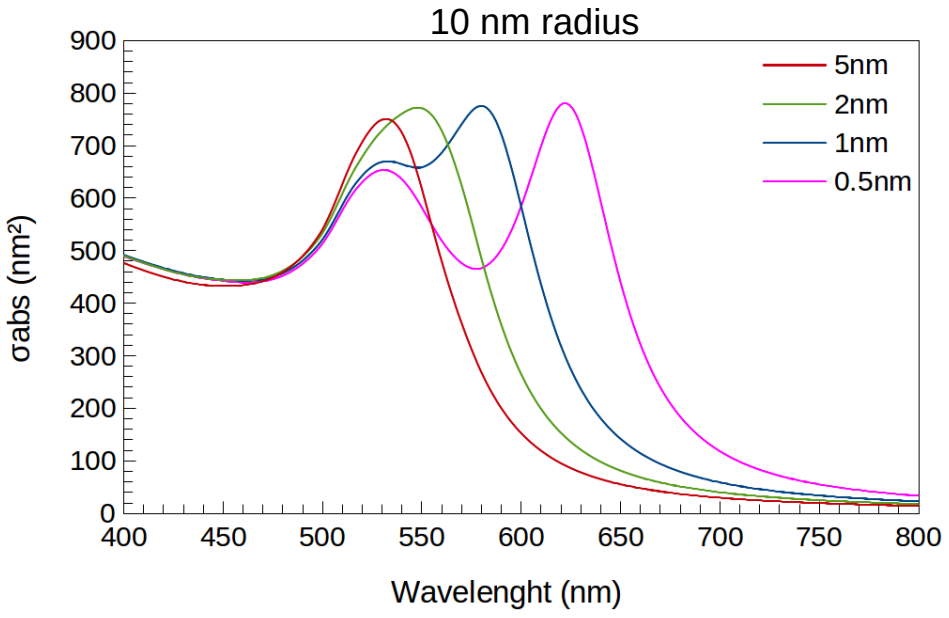






Gold dimers in water





If both particles have the same size

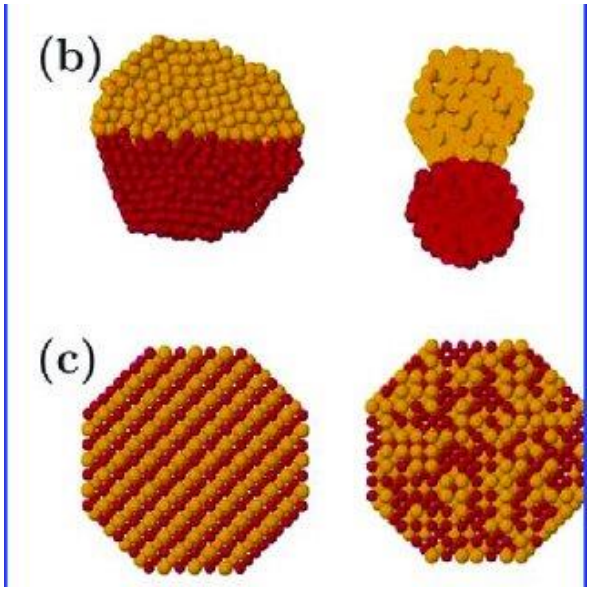
Larger inter particle distance
=> more pics
=> shift towards blue

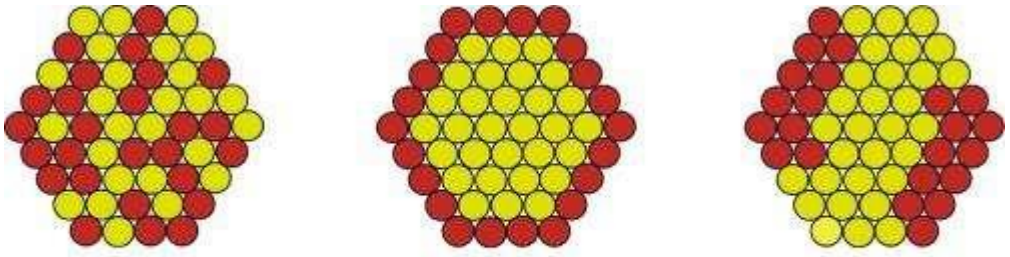
Inter-particle distance remains constant

Larger particles
=> more pics
=> shift towards blue

Absorption depends on size, composition, separation, etc…

Bi-Metallic Nanoparticles and Aggregates: MD simulations





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General Trends in Core–Shell Preferences for Bimetallic Nanoparticles

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

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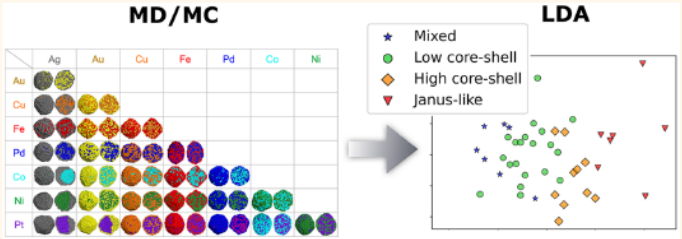
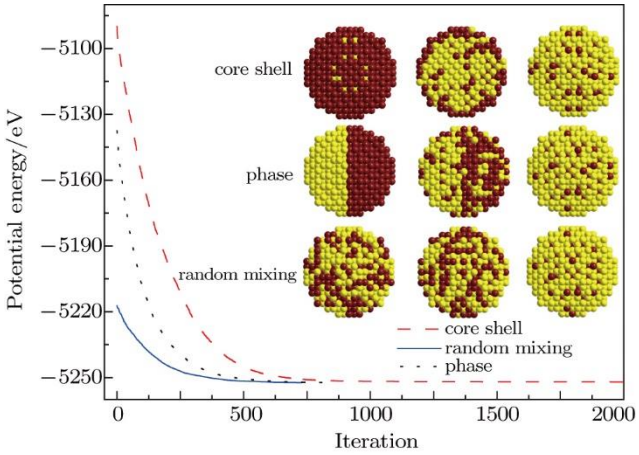
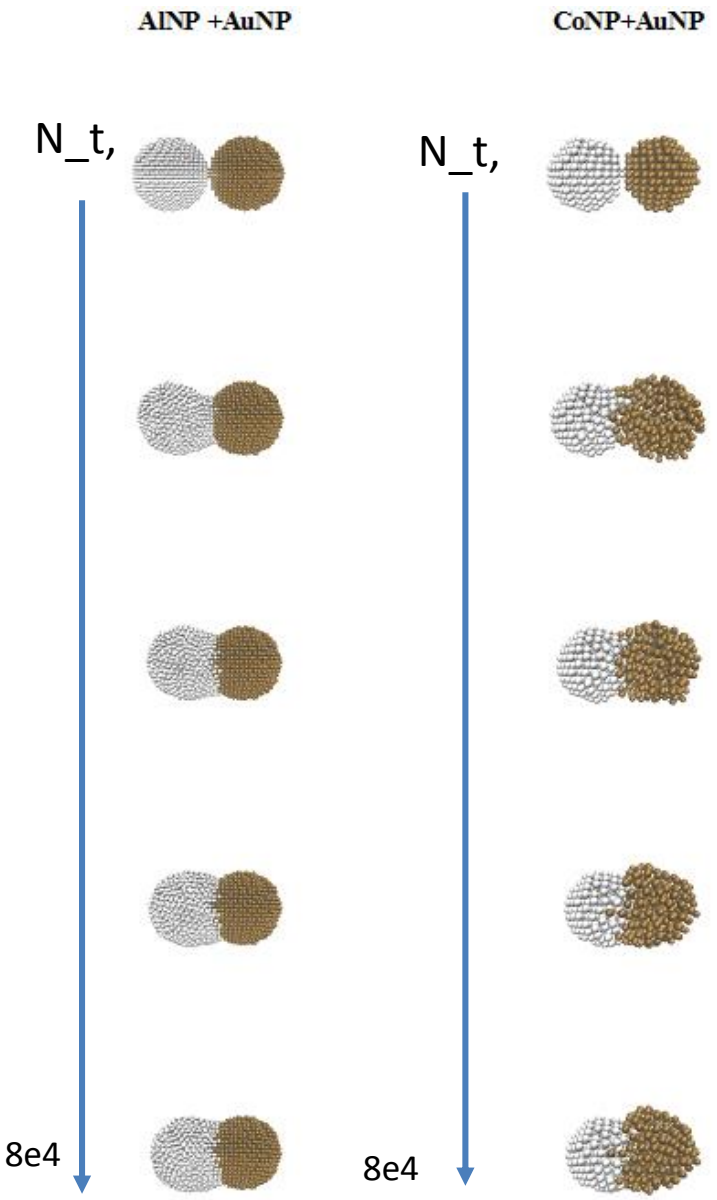




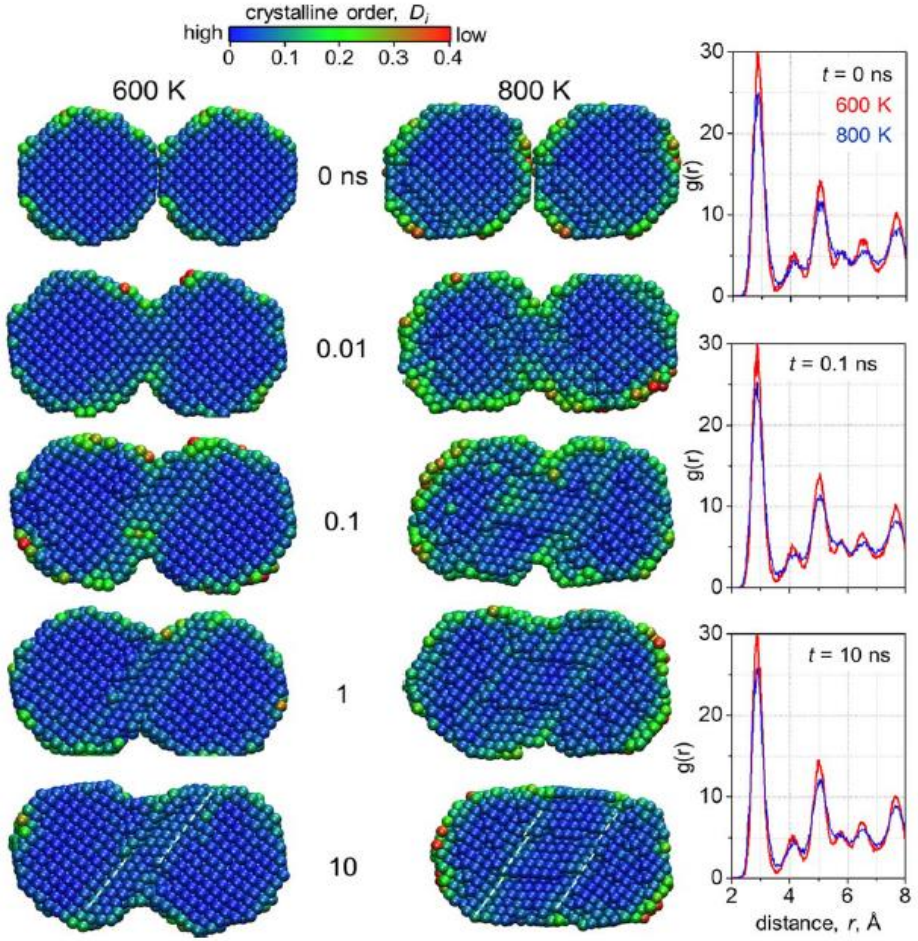
Ultra-short Laser-induced NP sintering, Janus NPs



R1=R2=20 ub (~1 nm)

T.E. Itina at al.

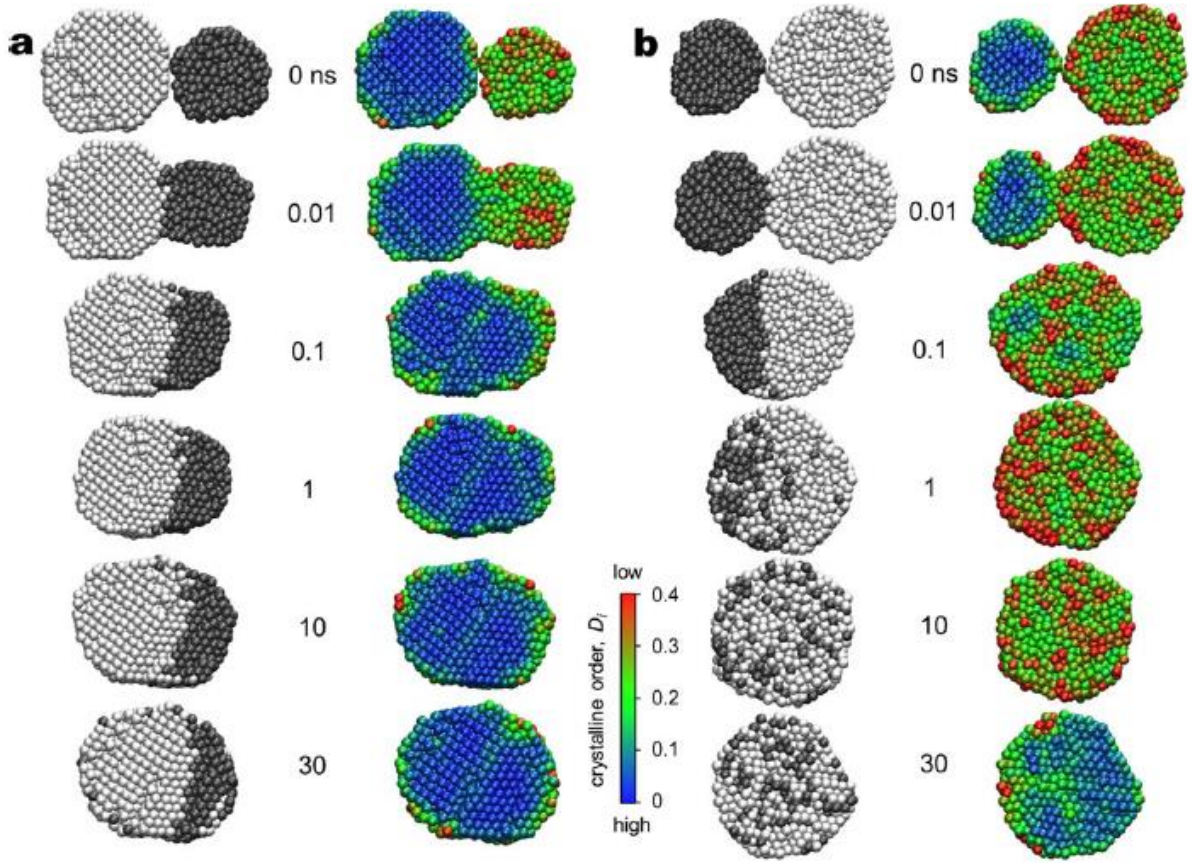
MD simulation: sintering of nanoparticles



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

Ultra-short Laser-induced NP sintering, Janus NPs

AuNP +AuNP, different sizes



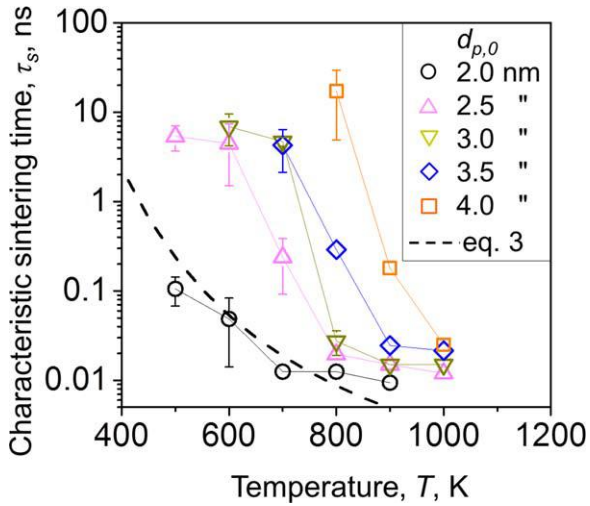


Figure 9. Snapshots of cross-sections of two Au nanoparticles with $d_{p,0} = 3$ (gray) and 4 nm (white) undergoing sintering at $T = 800$ K at $t = 0$, 0.01, 0.1, 1, 10, and 30 ns.

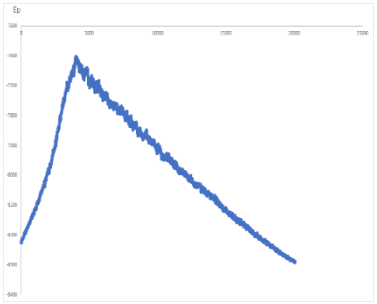
E. Goudeli et al., AIChE 2015

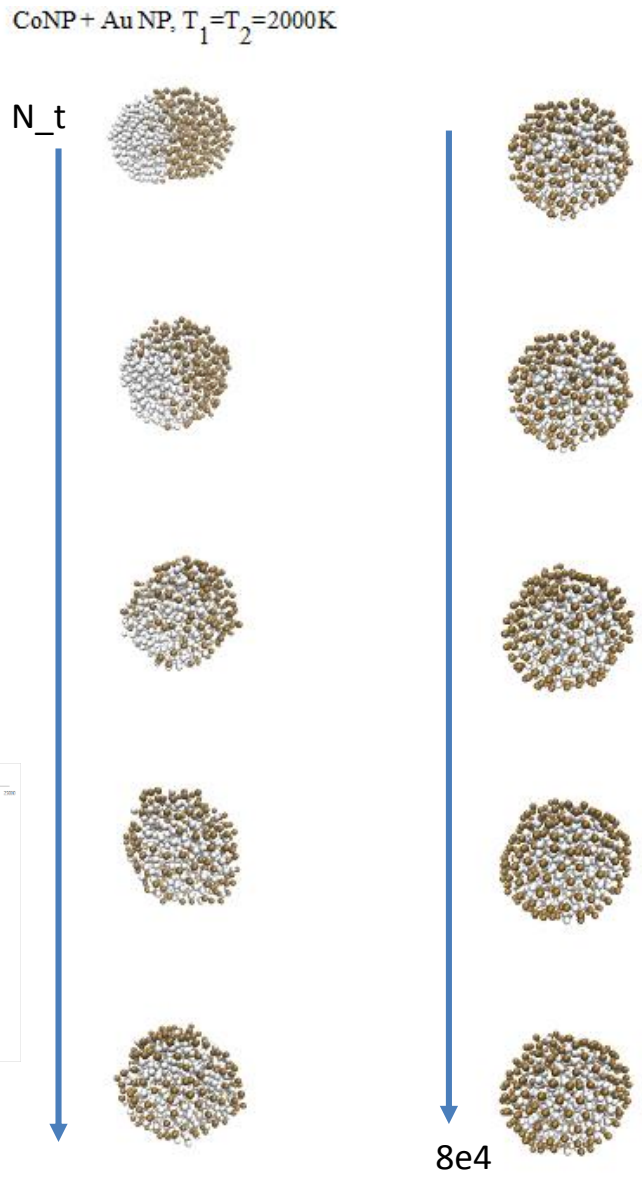
Ultra-short Laser-induced NP mixing (Nanoalloy formation)

MD simulations

R1, R2~10 unit boxes

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



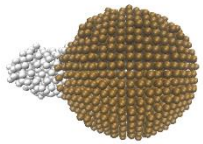


- **Simulation starts from a Janus configuration**
- **Then both particles are heated to the same temperature**
- **Then, the system is cooled down back to room temperature**

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

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

FeNP +AuNP



Au 0.48 nm Fe 0.7 nm

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

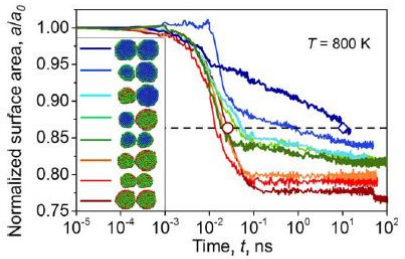
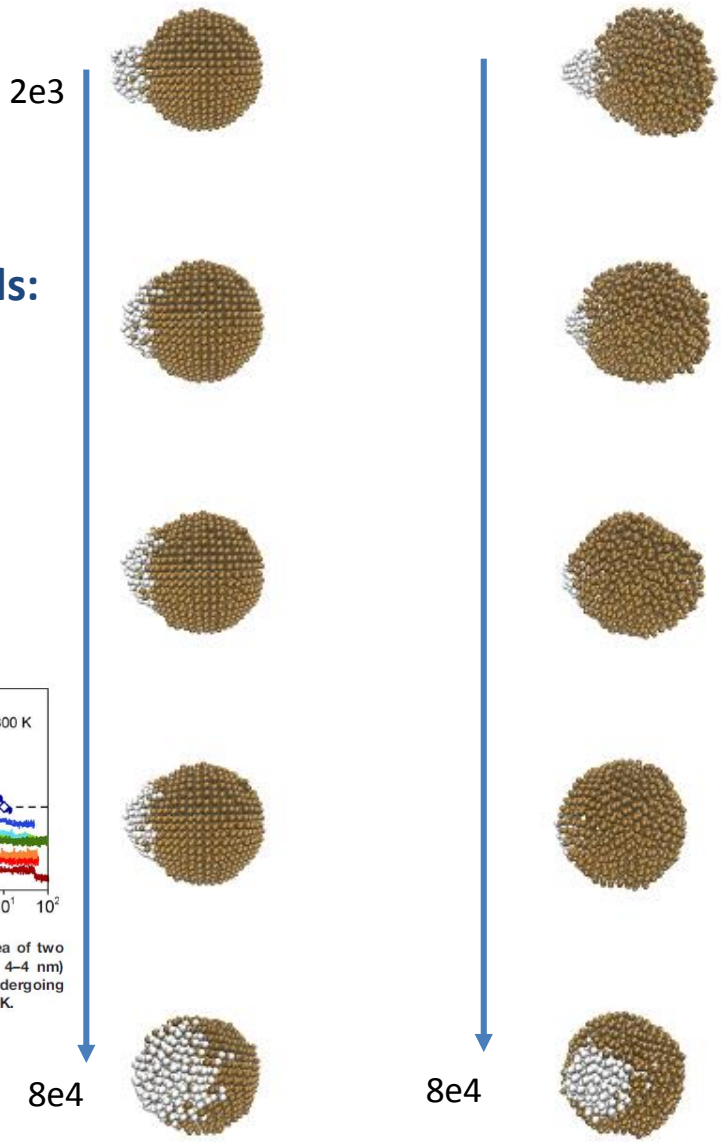


Figure 10. Evolution of normalized surface area of two Au nanoparticles of equal (3–3 or 4–4 nm) and different diameters (3–4 nm) undergoing sintering or coalescence at T = 800 K.

E. Goudeli et al., AIChE 2015

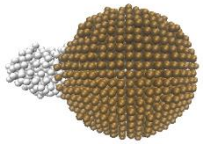


- **Simulation starts from a Janus configuration**
- **Then both particles are heated to different temperatures**
- **Then, the system is cooled down back to room temperature**

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

T.E. Itina at al.

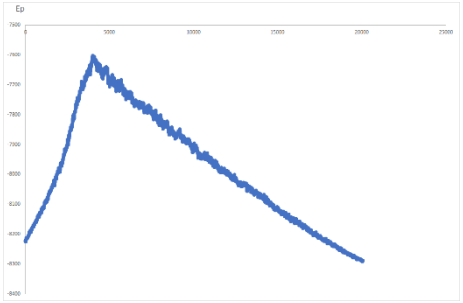
Ultra-short Laser-induced NP hybrid (core-shell) formation



Different materials:
Fe and Au

Different sizes
The same temperatures

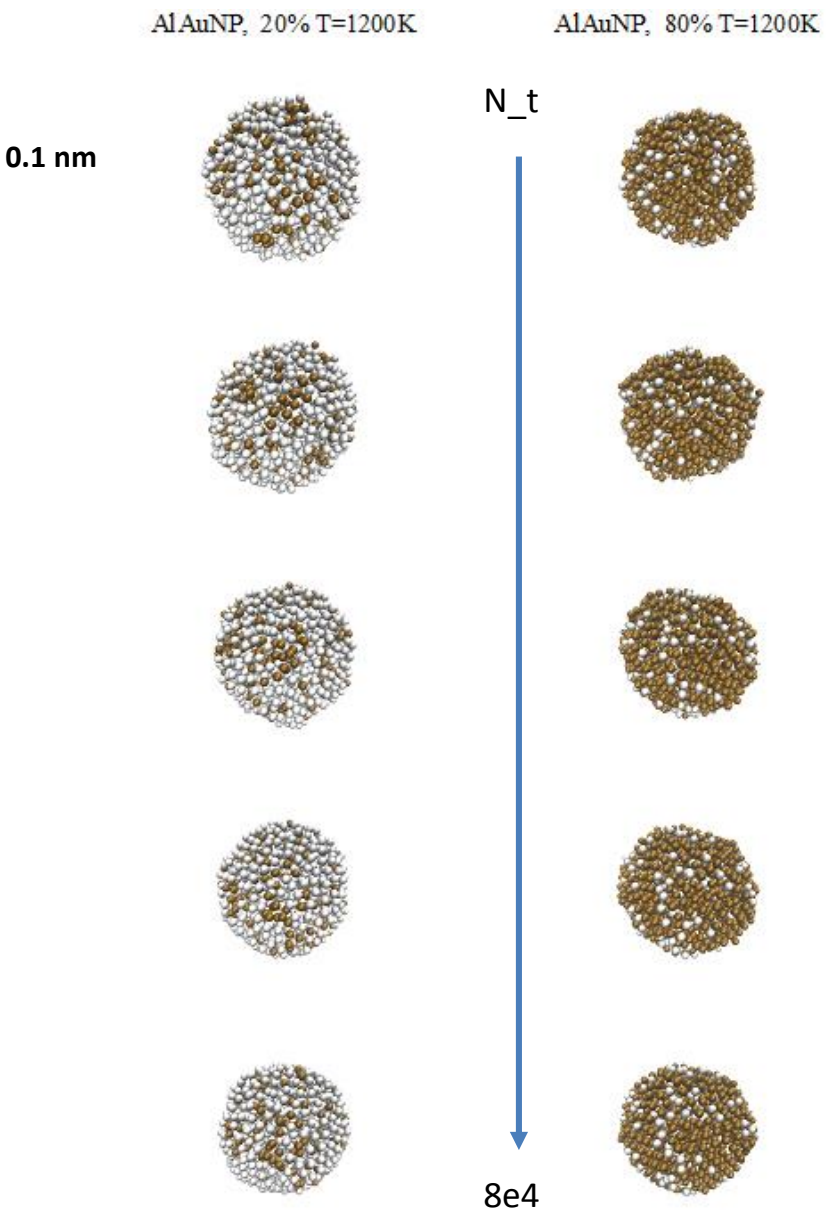
Time-evolution of potential energy



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

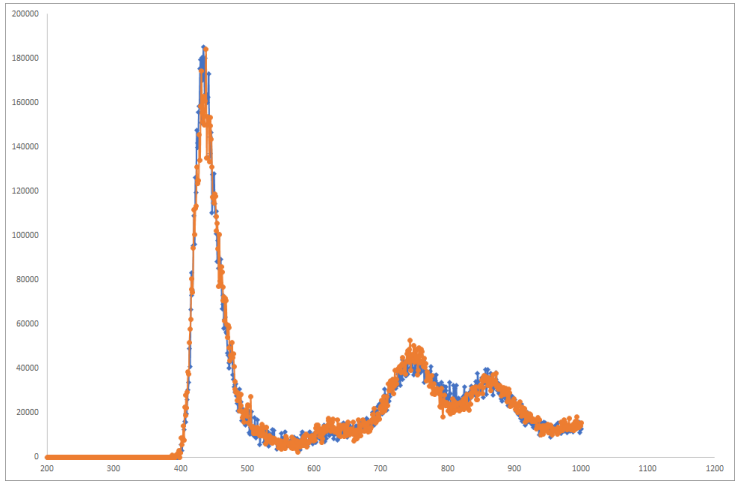
Core-shells can be also formed when one particle is larger, but both particles are heated to the same T

Ultra-fast heating and cooling of alloy NP



Different proportions of Au

Correlation function g(r)



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

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

SUMMARY

1. Laser is a very powerful and versatile tool suitable not only for the control over nanoparticle sizes but also for a wide range of manipulations with nano objects involving processes such as melting, reshaping, sintering, mixing, etc.

2. The involved processes are often non-equilibrium and therefore are still hard to be generalized.

3. Several modeling examples of the processes involved have been demonstrated revealing the role of size, temperature, and composition of nanoparticles, as well as the heating and cooling conditions.

Thank you very much!