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## Advances in Understanding Nanoparticle Synthesis and Growth by Laser Ablation and Spark Discharge.

Tatiana Itina

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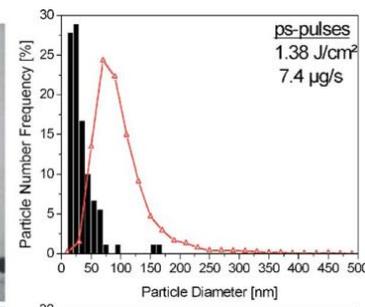
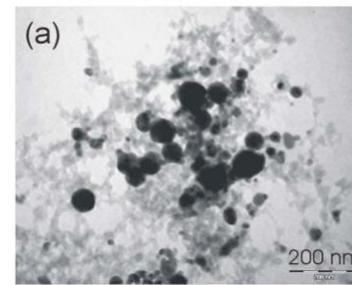
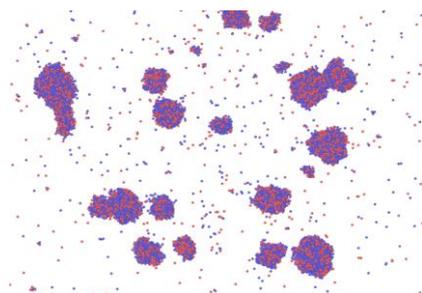
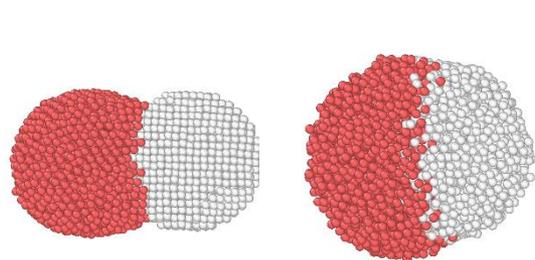
**HAL Id: ujm-04620662**

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Submitted on 21 Jun 2024

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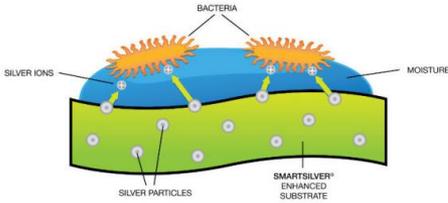
# Advances in Understanding Nanoparticle Synthesis and Growth by Laser Ablation and Spark Discharge

**Tatiana E. ITINA**

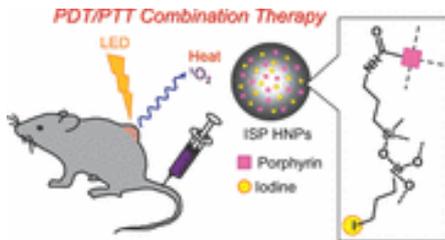
Laboratoire Hubert Curien, UMR CNRS 5516, Saint-Etienne, France

[tatiana.itina@univ-st-etienne.fr](mailto:tatiana.itina@univ-st-etienne.fr)

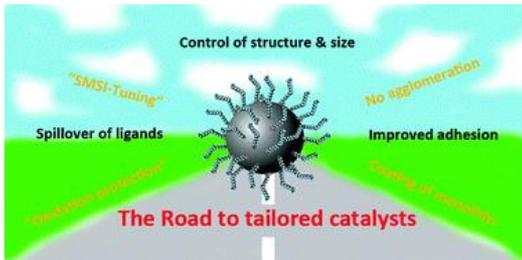
# Main Applications of NPs



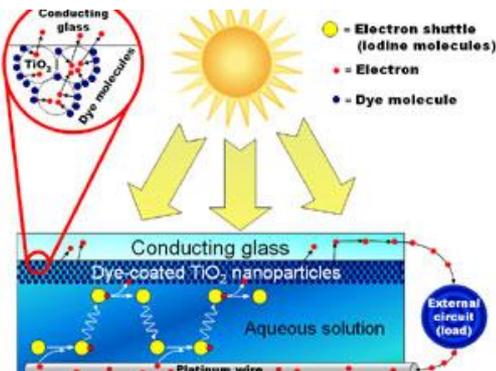
<http://www.nanowerk.com/spotlight/spotid=19451.php>



Hayashi et al.



DOI: 10.1039/C1CP22048A



**Textiles:** anti-bacterial properties, odor elimination, self-cleaning, UV protection, fireproof, release of active agents, luminescence, durability, heat, antistatic, ... (Ag, ZnO, TiO<sub>2</sub>, SiO<sub>2</sub>, CNT, etc.)

**Health:** tumor treatments, imaging, sensors, SPR, etc.. (colloidal/gas Au, Ag, Si, etc)

**Chemistry, catalysis, cosmetics:**

(colloidal metal NPs, TiO<sub>2</sub>, nanoalloys, ex: AgPd, etc...), etc.

**Food:** flavor modifications, water treatment (Ag, nanocomposites: Cu, Ni, No) can be dangerous

**Energy** (solar cells), **transport** (cooling, nanofluidics, anti-wetting, nanocomposites, etc.)

**Airspace industry, buildings, furniture, etc.**

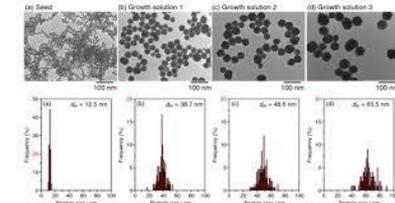
# NP synthesis

Main needs ?

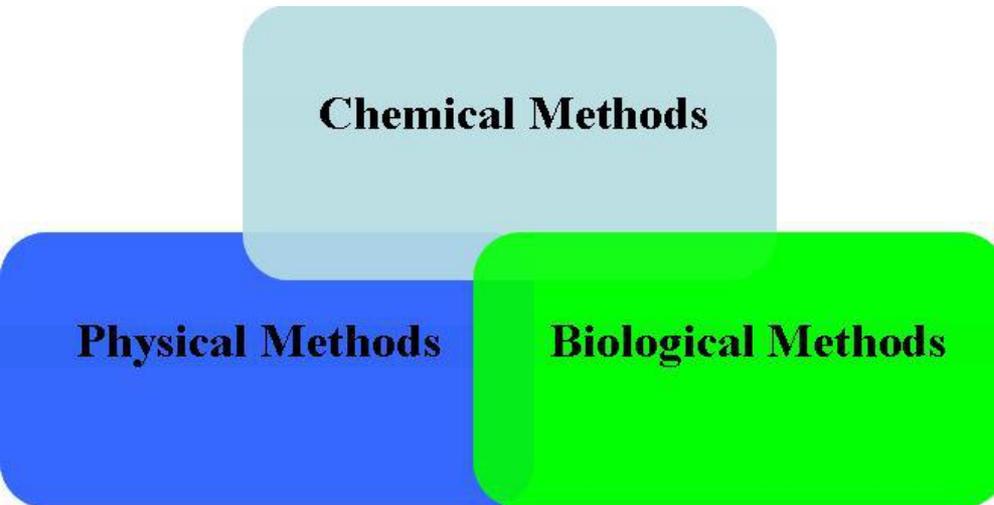
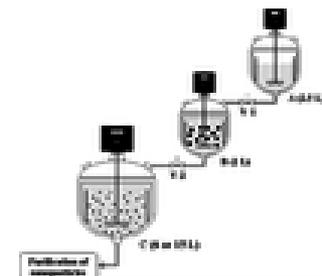
## 1. Green methods



## 2. Control over properties



## 3. Scaling-up possibility



AgNPs synthesis

Physical method

Ultrasonication, irradiation, laserablation, microwave, electrochemical

Chemical method

Chemical reduction, sol gel method, inert condensation method

Biological method

Microorganisms

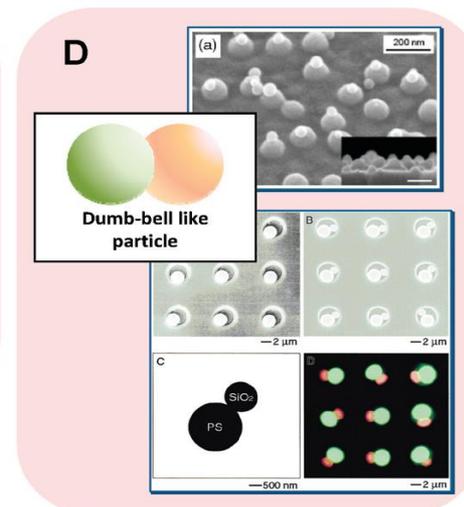
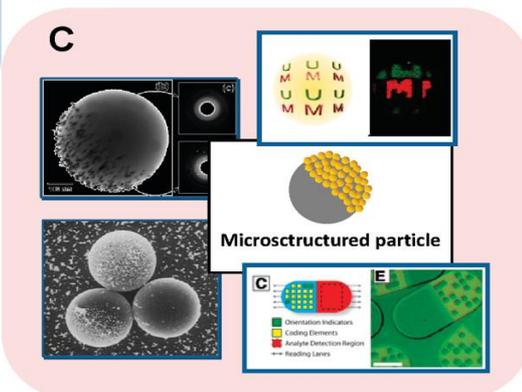
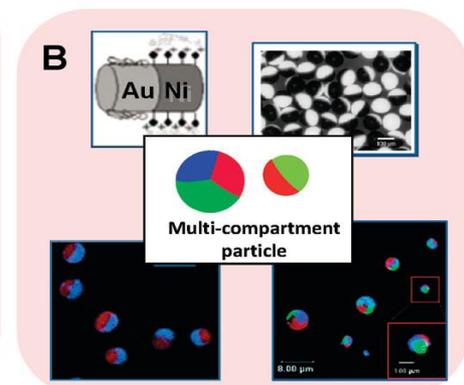
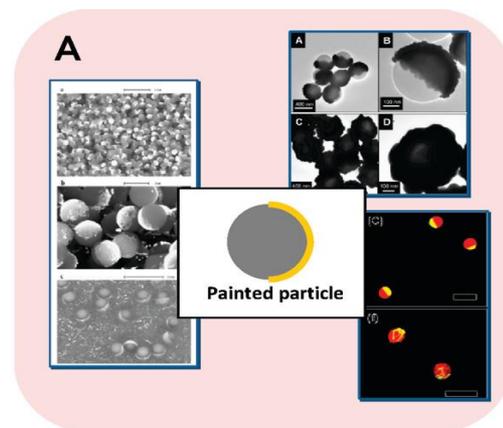
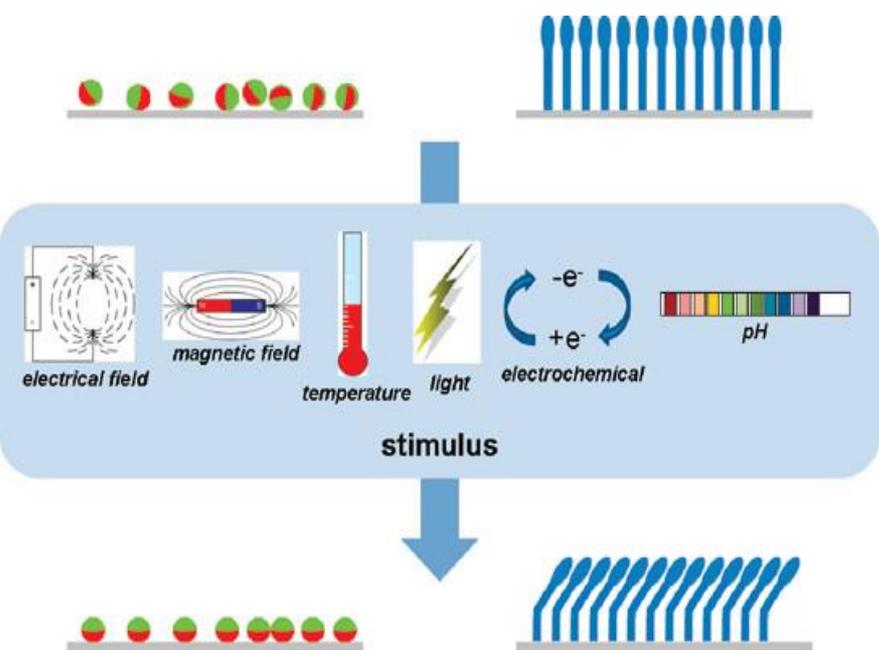
Bacteria, fungi, algae, Yeast, Actinomycetes

Plants

Gymnosperms  
To  
Angiosperms

# Smart Nanomaterials

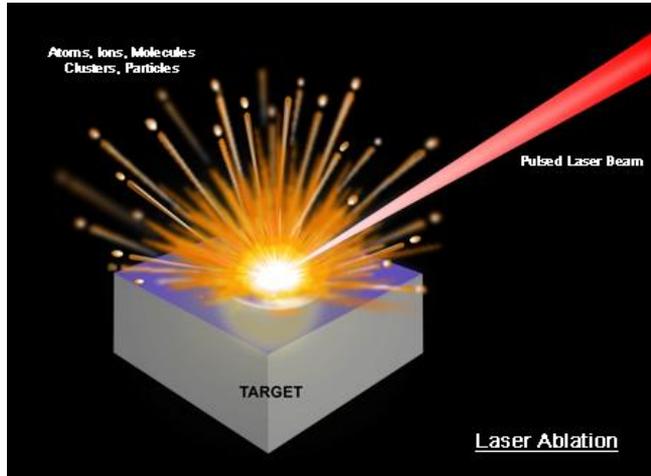
Materials that respond to a stimulus or their environment to produce a dynamic and reversible change



ACS Nano 2008, 2, 6, 1101-1107

# Laser and Plasma - based Synthesis of NPs

## Laser ablation

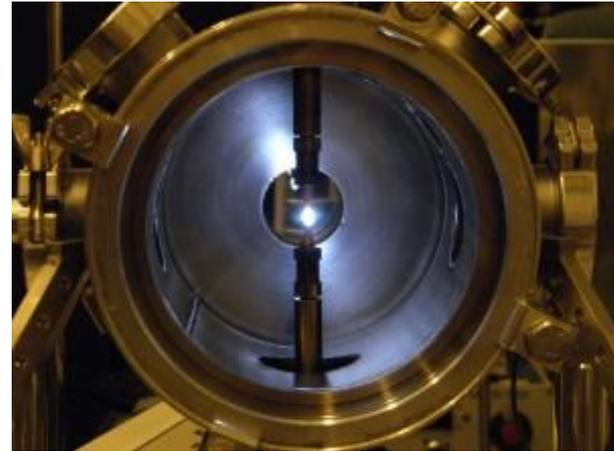


<http://appliedspectra.com/>

- Different laser systems (CW, ns, ps, fs)
- Green methods
- Complex stoichiometry
- Possibility to scale up

-Not easy to control

## Plasma discharges



<http://www.buonapart-e.eu/>

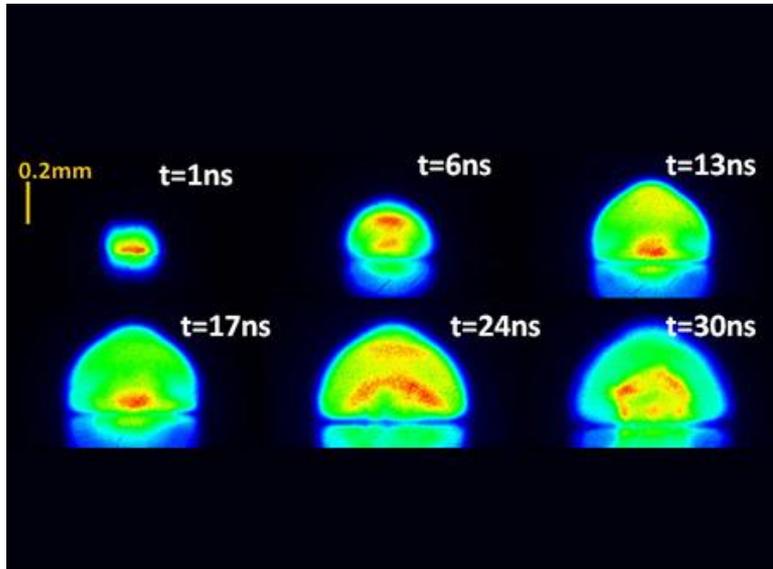
- Spark, arc, glow discharges
- Green methods
- Good scaling-up

-High voltage

-Hard to control

**How to better control? What are main mechanisms?  
Are they different or similar?**

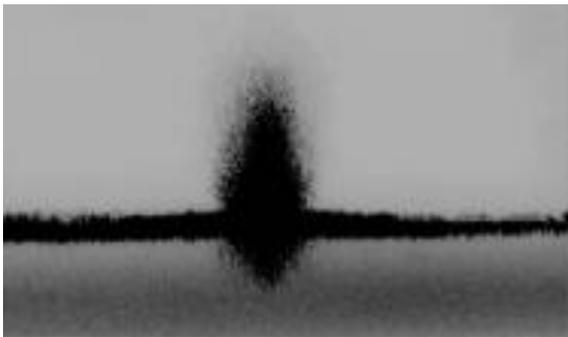
# Laser Ablation (LA) for NP Formation



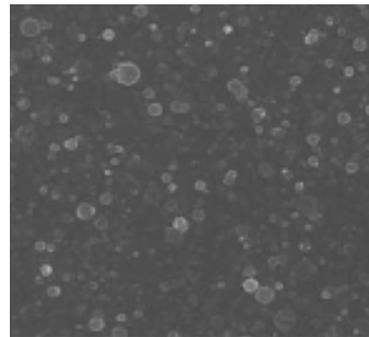
<http://appliedspectra.com/>

- Ablation threshold fluence
- Target material is heated and ejected
- Nanoparticles (NPs): in vacuum, in a background gas or a liquid
- **Colloidal nanoparticles**
- **Scaling up is possible**

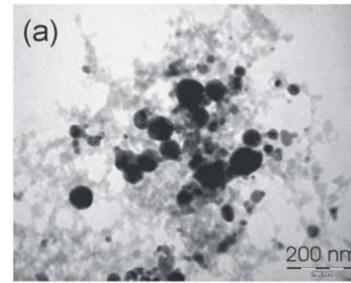
## Experimental evidences of nanoparticle formation by LA



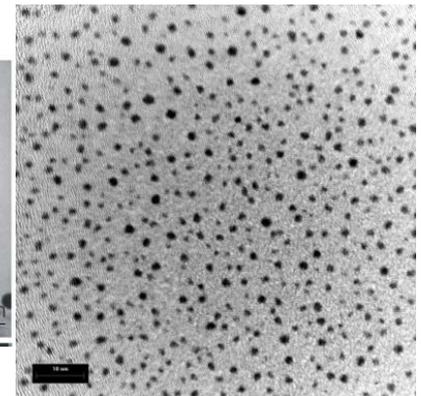
Heiroth et al. JAP  
2009



Deposited nanoparticles,  
courtesy of Garrelie et al.



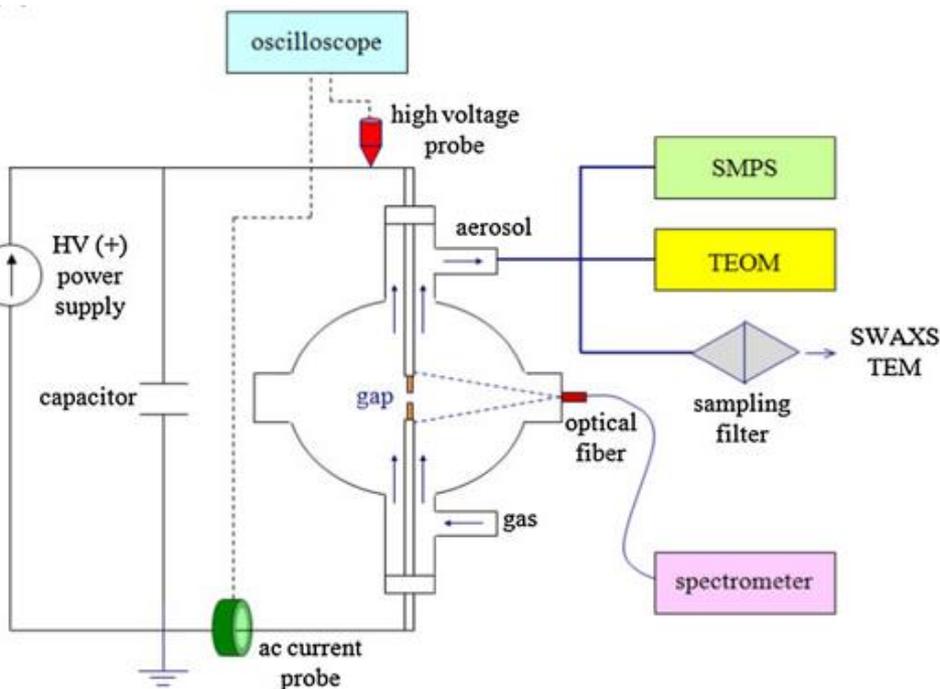
Colloidal nanoparticles  
Barcikowski et al. APL  
2007



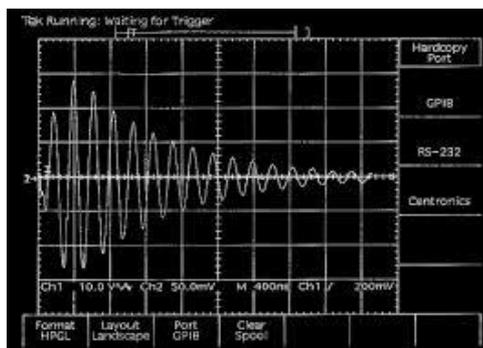
TEM images, courtesy of  
Kabashin et al.

# Spark Discharge (SD) for NP Formation

## Typical set-up



Tabrizi et al, 2009



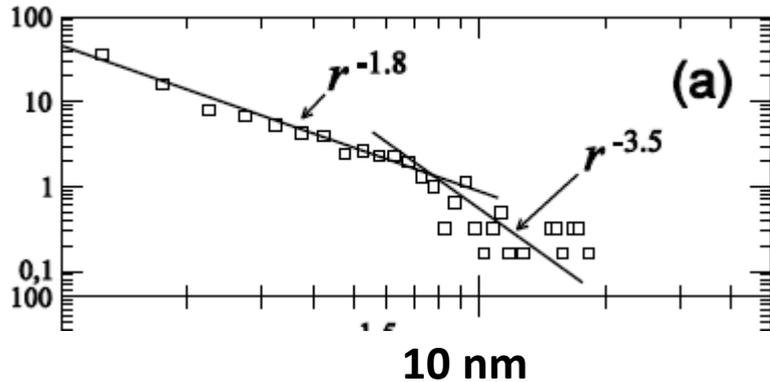
- Background gas with seed electrons
- Breakdown voltage
- Electrodes are heated and evaporated
- Nanoparticles are formed
- **Scaling-up is possible**



Stein et al., CENID, Germany

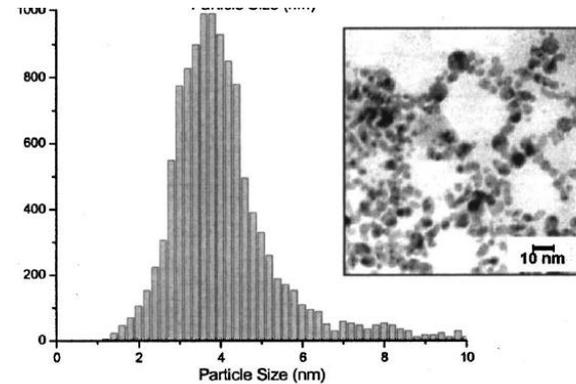
# Experimental NP Size Distributions

## Fs laser ablation in vacuum



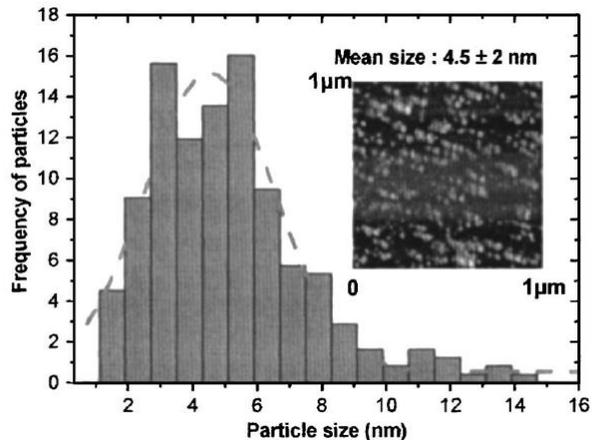
Noël et al. AFM: Cu, 100 fs,  $F=0.8 \text{ Jcm}^{-2}$

## Fs laser ablation in liquids



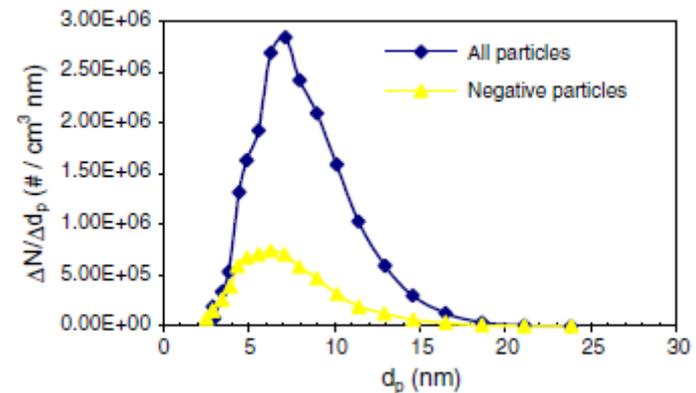
Kabashin et al. AuNPs

## Ns laser ablation in air



Pereira et al. AFM steel in air, 25ns  $F=10 \text{ Jcm}^{-2}$

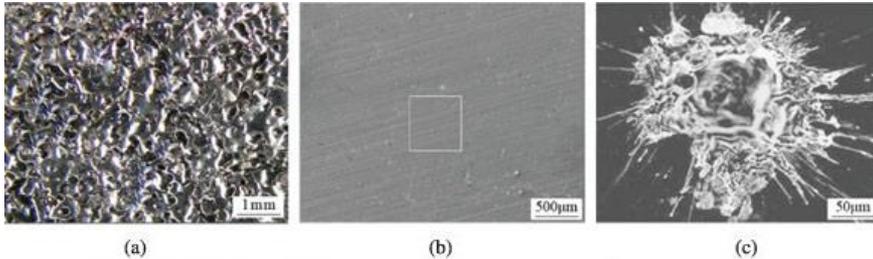
## Spark discharge at atmospheric P



Tabrizi et al. Au, TEM, Au in Ar,  $C=5 \text{ nF}$ ,  $d=1 \text{ mm}$

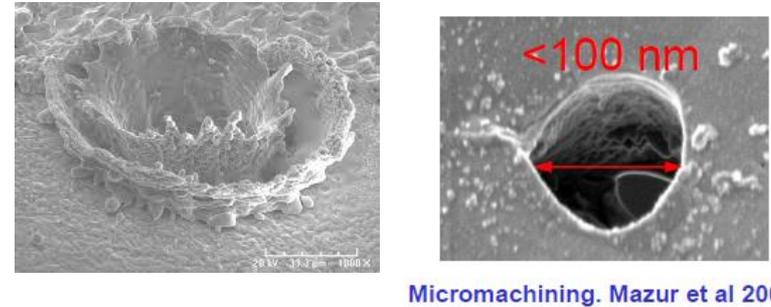
# Main Physical Processes Involved

## Spark discharge (SD)



- (i) streamer formation, ionization wave propagation
- (ii) streamer-to-spark transition
- (iii) electrode evaporation
- (iv) cylindrical expansion of plasma column
- (v) nanoparticles formation

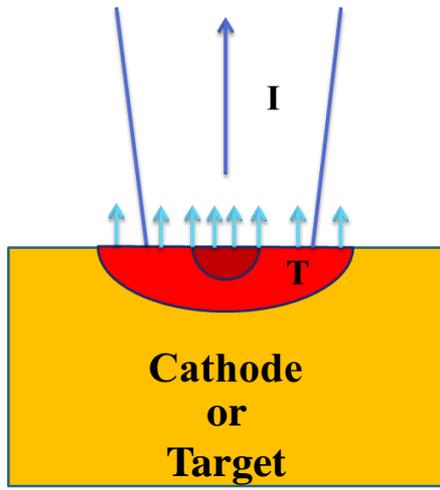
## Laser ablation (LA)



Micromachining. Mazur et al 2001

- (i) laser heating of the surface
- (ii) evaporation of the target
- (iii) absorption by the evaporated material, ionization
- (iv) hemispherical expansion of plasma plume
- (v) nanoparticles formation

# Material Ejection in LA and in SD



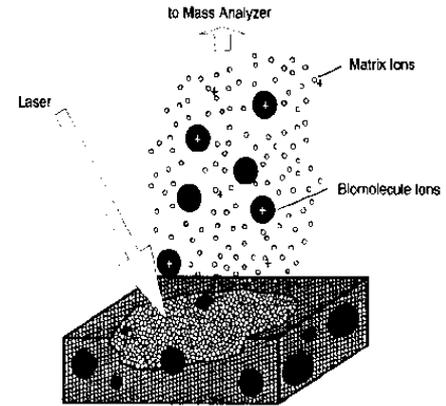
Evaporation

## Thermal effects

- **Heating of the sample**

SD : Joule heating of the electrodes

LA: Laser energy absorption in the target, e-ph relaxation



- **Heat diffusion and melting**

## Spark (SD)

$$c \frac{\partial T_s}{\partial t} = \vec{\nabla} \cdot \left( \chi_T \vec{\nabla} (kT_s) \right) + \frac{\vec{j}_e^2}{\rho \sigma_m}$$

## Laser (LA)

$$c \frac{\partial T_s}{\partial t} = \vec{\nabla} \cdot \left( \chi_T \vec{\nabla} (kT_s) \right) + Q$$

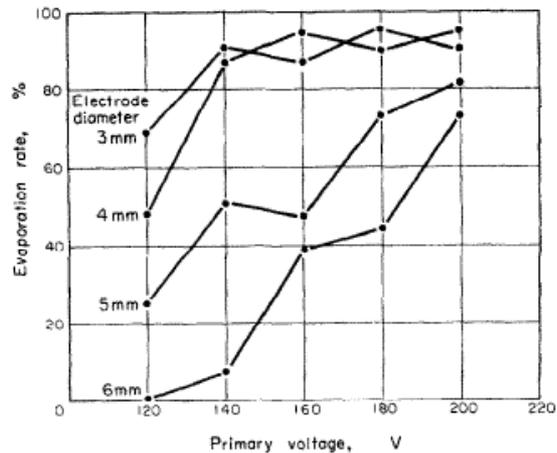
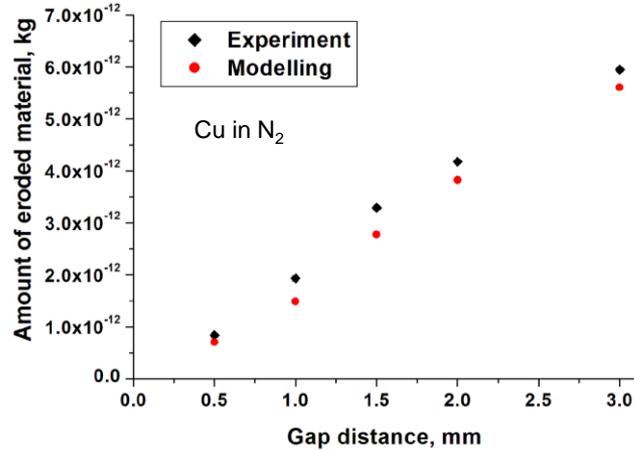
- Evaporation

$$j_{surf} = \frac{\alpha(P_{eq} - P_s)}{\sqrt{2\pi m k T_m}} \text{ Hertz -Knudsen}$$

A. Voloshko, J-Ph.Colombier, T. E. Itina,.,  
Appl. Surf. Sci.336, 143-149 (2014).

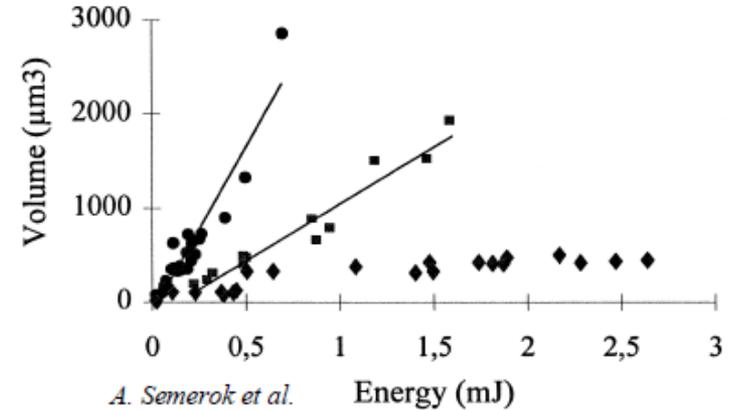
# Typical Crater Depth

## Spark discharge (SD)

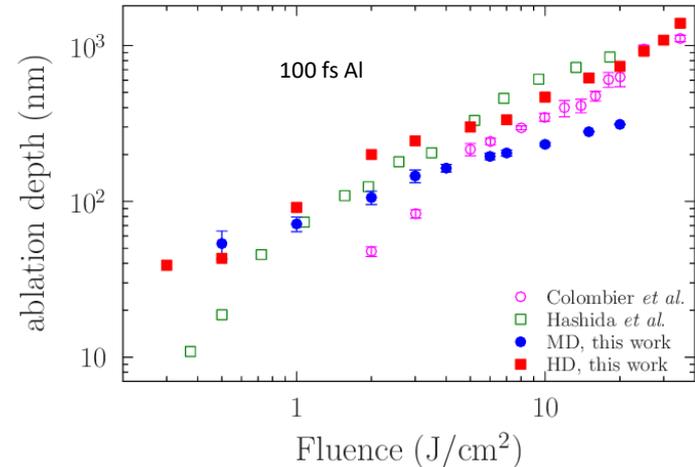


T. NAKAJIMA and H. KAWAGUCHI

## Laser ablation (LA)



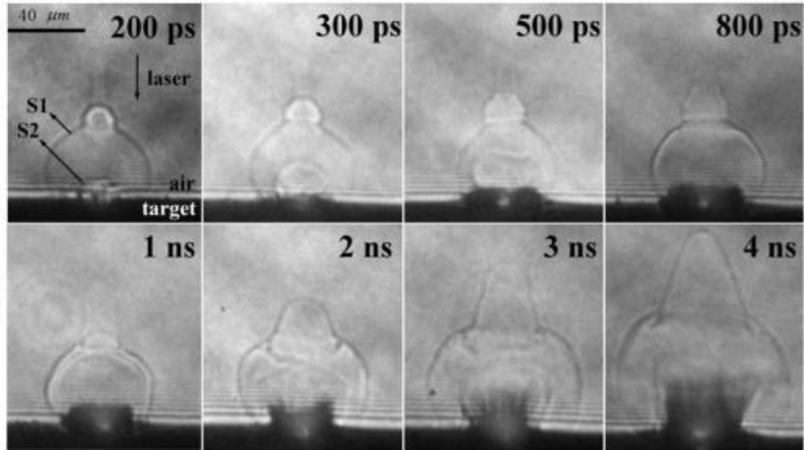
after single laser pulse with different wavelengths ( $\lambda$ ) and beam diameters ( $d$ ). ◆,  $\lambda = 1064$  nm,  $d(\text{FWHM}) = 20$   $\mu\text{m}$ ; ■,  $\lambda = 532$  nm,  $d(\text{FWHM}) = 9.5$   $\mu\text{m}$ ; ●,  $\lambda = 266$  nm,  $d(\text{FWHM}) = 6.5$   $\mu\text{m}$ .



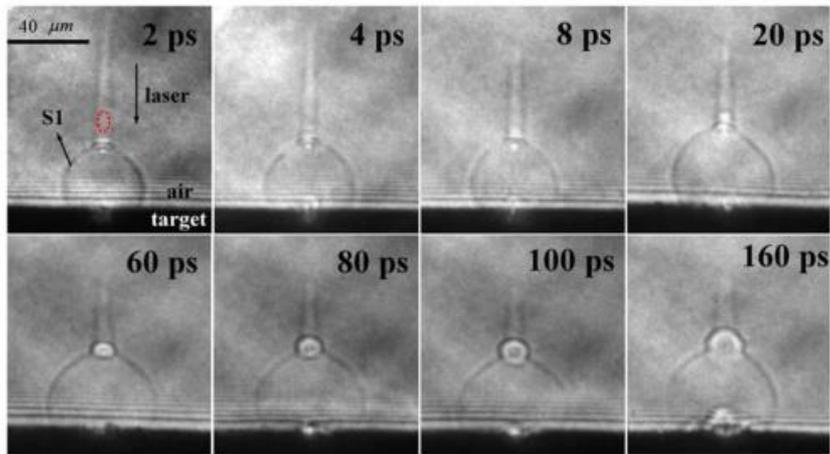
Crater depth defines the amount of the ejected material and strongly depends on the experimental conditions (laser or spark parameters)

# Plasma Expansion: LA vs SD

Laser ablation (LA)  
~Hemispherical plume

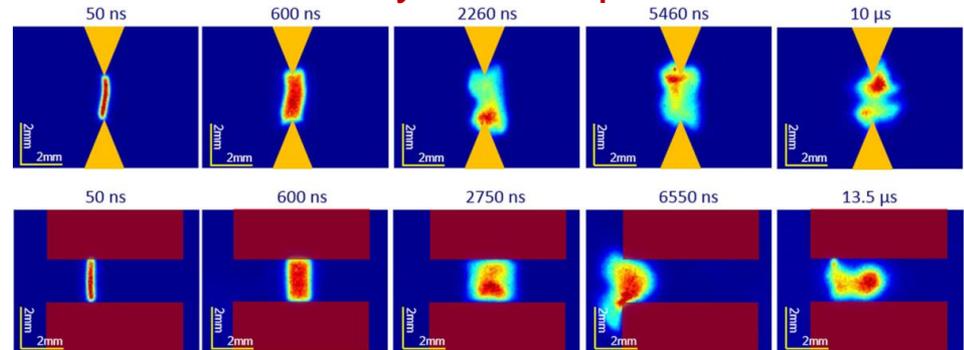


SW due to phase explosion

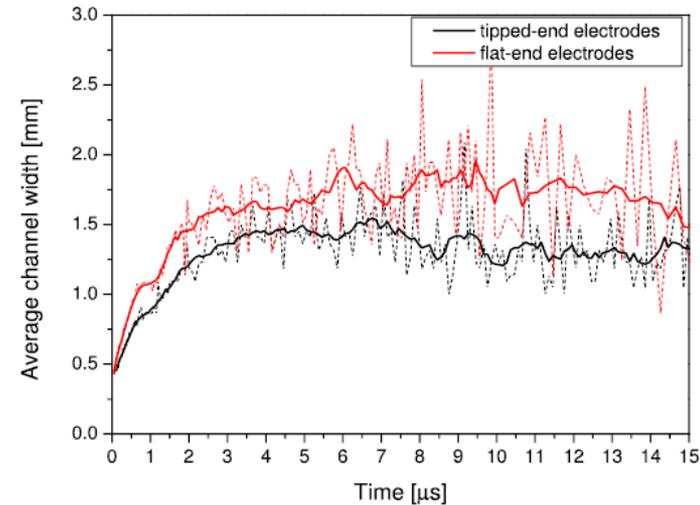


SW due to laser-induced air breakdown

Spark discharge (SD)  
~Cylindrical plasma column



Palomares et al. JAP 2015



After ~2-5 μs ->  
Diffusion & thermalization

# Plasma Expansion

$$\begin{cases} \frac{\partial n}{\partial t} + \vec{\nabla} \cdot (n \cdot \vec{u}) = 0 \\ \frac{\partial n \vec{u}}{\partial t} + \vec{\nabla} \cdot (\vec{u} \otimes (n \cdot \vec{u})) + \vec{\nabla} P = \mu \Delta \vec{u} \\ \frac{\partial E}{\partial t} + \vec{\nabla} \cdot (\vec{u} E) = F(E) \end{cases}$$

$$F(E) = Q - S_{ion} - S_{dis} - R + \delta E(\mu) + \chi \Delta T$$

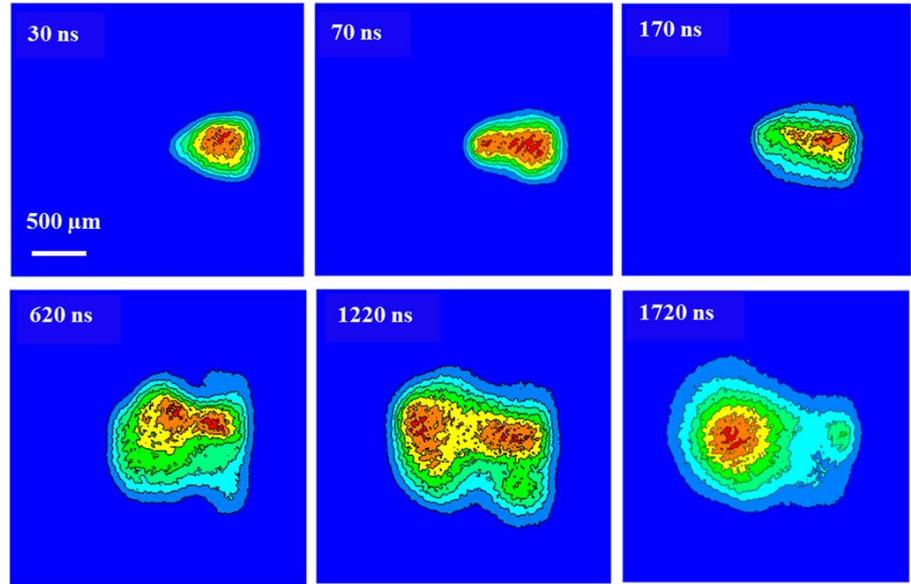
Chapman and Cowling :

$$D_{12} = \frac{3}{8n_0\sigma_{12}^2\Omega_{12}} \sqrt{\frac{kT}{2\pi} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)}$$

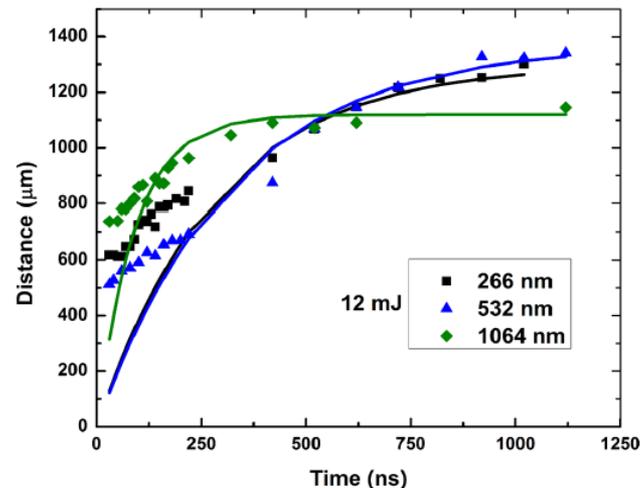
Collision integral of the Lennard-Jones potential:

$$\Omega_{12} = AT_*^{-B} + Ce^{-DT_*} + Ee^{-FT_*} + Ge^{-HT_*}$$

$$\text{With } T_* = \frac{kT}{\epsilon_{12}} ; \quad \epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$$



Time evolution of Al plasma plume at atmospheric pressure for 1064 nm LA at 25 mJ  
Hussein et al. JAP 2013



After ~0.5-2 μs

Diffusion & thermalization

# NP Growth

## Nucleation

$$\theta = \ln\left(\frac{P}{P_{eq}}\right) \approx \frac{T_{eq} - T}{T_{eq}}$$

$$p = p_b \exp\left\{\frac{\Delta H_v(T_b)m}{k}\left(\frac{1}{T_b} - \frac{1}{T_{eq}}\right)\right\}$$

$$r_c = \frac{2\sigma\omega}{kT\theta}$$

$$J = 2n_1^2 u \omega \sqrt{\frac{\sigma}{kT}} \cdot \exp\left(-\frac{b}{\theta^2}\right)$$

Depends on crater shape & ejection rate, P and T

## Growth

$$\frac{\partial n_1}{\partial t} = -\rho_g n_1 \sum_{j=1}^{\infty} \beta_{1,j} n_j$$

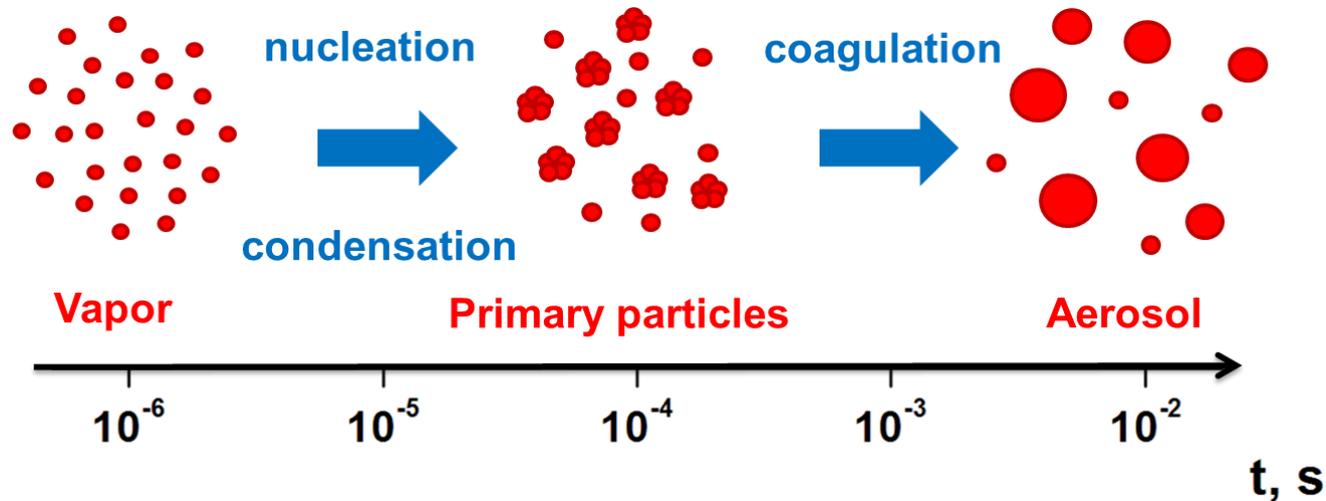
$$\frac{\partial n_i}{\partial t} = \frac{\rho_g}{2} \sum_{j=1}^{i-1} \beta_{i,j} n_i n_j - \rho_g n_i \sum_{j=1}^{\infty} \beta_{i,j} n_j$$

$$\beta_{i,j} = 2.2 \sqrt{\frac{6kT}{Mn_1}} \left(\frac{3}{4\pi n_1}\right)^{\frac{1}{6}} \sqrt{\frac{1}{m_i} + \frac{1}{m_j}} \left(m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}}\right)^2$$

Very large number of populations...

Need to simplify

# Typical Time Scales of NP Formation in SD



~99% of vapor is condensed during the nucleation phase

In most of the considered cases, nucleation and coagulation could be calculated **separately**

Itina *et al.*, Nanoparticle Technology, Intech (2015)  
A. Voloshko, PhD thesis, UJM, Saint-Etienne

# Self-Preserved Distribution ?

## Time-evolution

Only the following parameters of the log-normal distribution change due to collisions (adaptation for polydisperse case)

$$N(t) = \frac{N_0}{1 + KN_0t(1 + e^{\ln^2(\sigma_0)})} \quad \text{concentration}$$

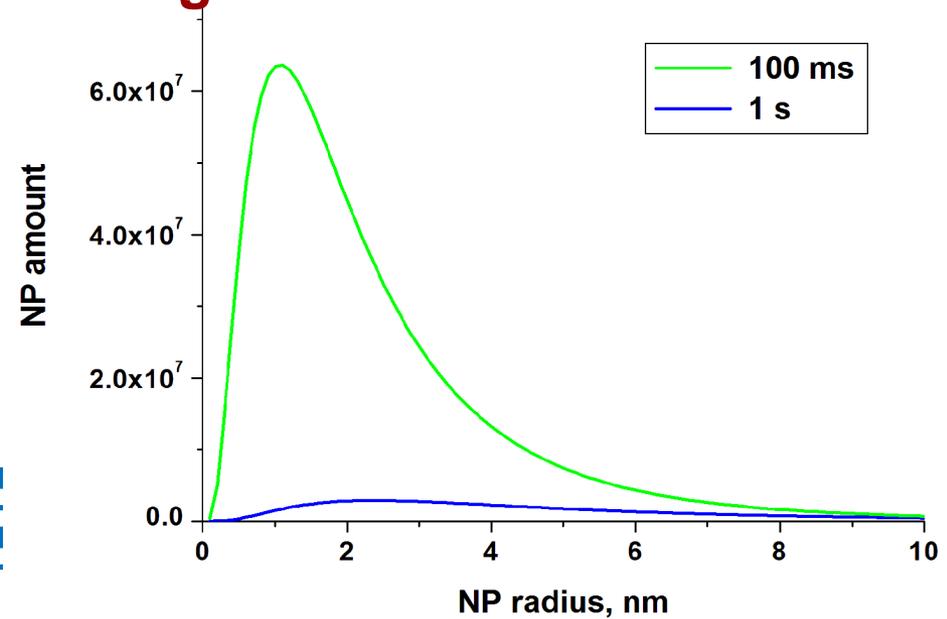
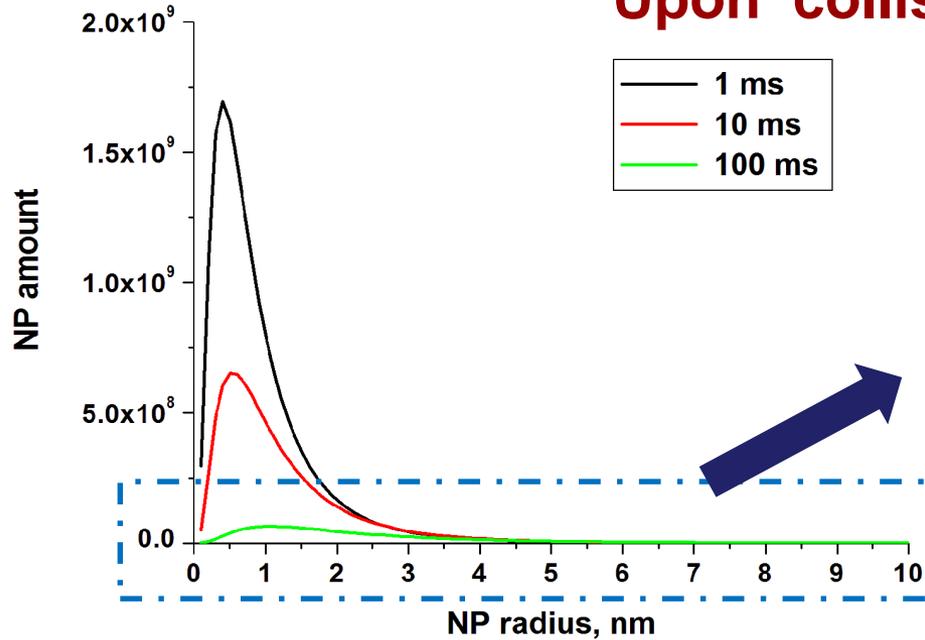
$$V(t) = \frac{V_0 e^{\frac{9}{2}\ln^2(\sigma_0)} \left(1 + KN_0t(1 + e^{\ln^2(\sigma_0)})\right)}{\sqrt{2 + \frac{e^{9\ln^2(\sigma_0)} - 2}{1 + KN_0t(1 + e^{\ln^2(\sigma_0)})}}} \quad \text{mean volume}$$

dispersion

$$\ln^2(\sigma(t)) = \frac{1}{9} \ln \left( 2 + \frac{e^{9\ln^2(\sigma_0)} - 2}{1 + KN_0t(1 + e^{\ln^2(\sigma_0)})} \right) \quad \begin{array}{l} \text{(standard geometrical} \\ \text{deviation)} \end{array}$$

# NP Size Distribution

Upon collisional growth



$$N(t) = \frac{N_0}{1 + KN_0t(1 + e^{\ln^2(\sigma)})}$$

$$r(t) = r_0 \left( \frac{e^{\frac{9}{2}\ln^2(\sigma)} \left( 1 + KN_0t(1 + e^{\ln^2(\sigma)}) \right)}{2 + \frac{e^{9\ln^2(\sigma)} - 2}{1 + KN_0t(1 + e^{\ln^2(\sigma)})}} \right)^{\frac{1}{3}}$$

Cu in  $N_2$

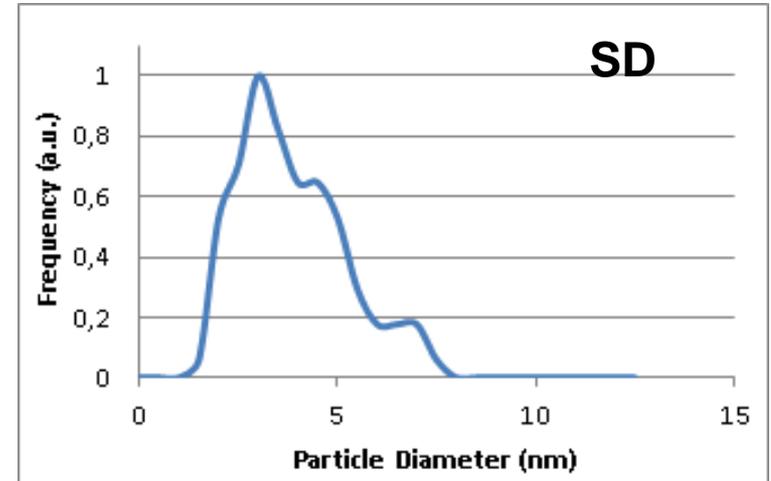
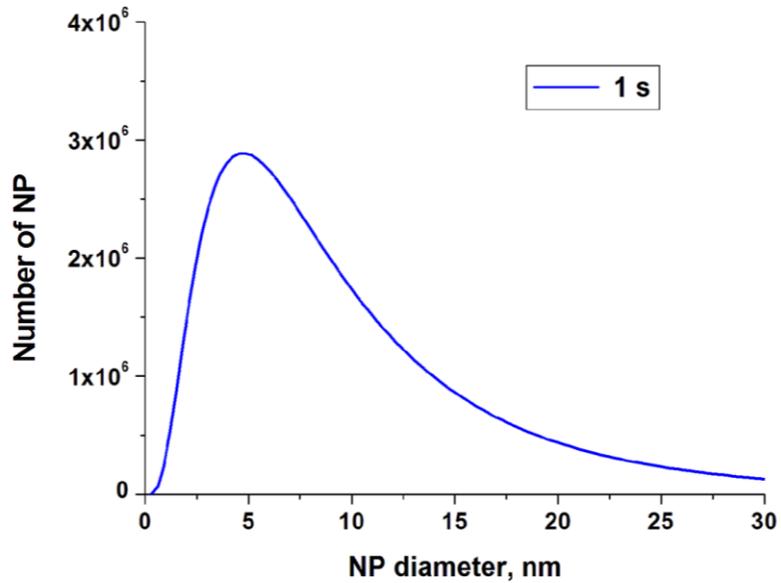
d=1mm

at high pressures ( $P=P_{\text{atm}}$ )

Here, change with time depends only on the initial concentration, mean radius and dispersion

# NP Size Distribution

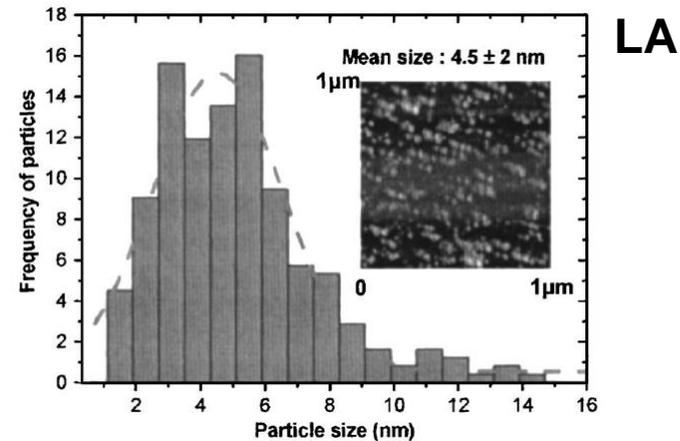
## Modeling vs Experiments



Proximity sampling result, obtained by ULUND  
(N<sub>2</sub>, after 0.5 s)

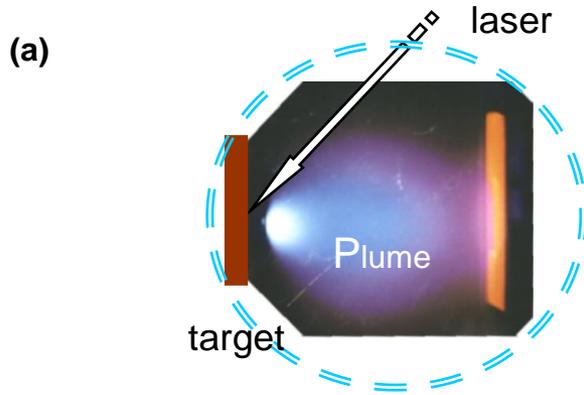
For both SD and LA

in the presence of a high-pressured ambient gas

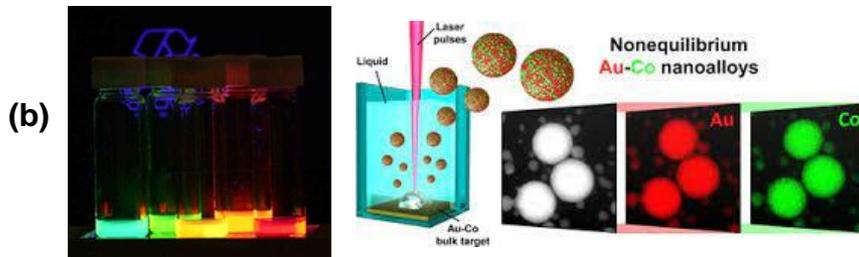


Pereira et al. 25ns  $F=10 \text{ Jcm}^{-2}$

# 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

**Often multi-pulse irradiation is used with various scanning and focusing conditions**

**Laser-induced nanoparticle formation, sintering and fragmentation**

- 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**

# 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

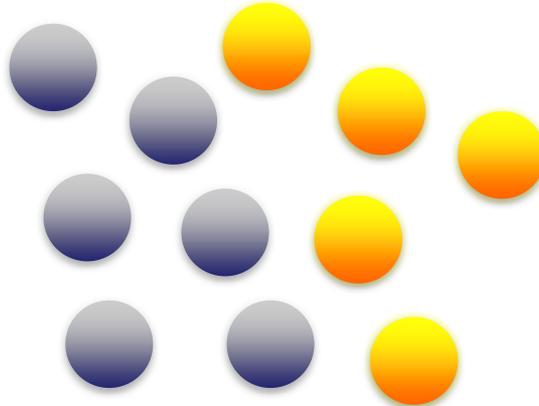
Porous films:  
 $\text{SiO}_2$  ,  $\text{TiO}_2$

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



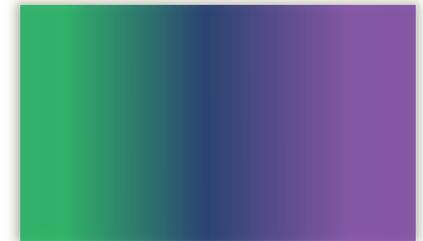
Metallic NPs:  
Ag, Au

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



Laser irradiation:  
CW

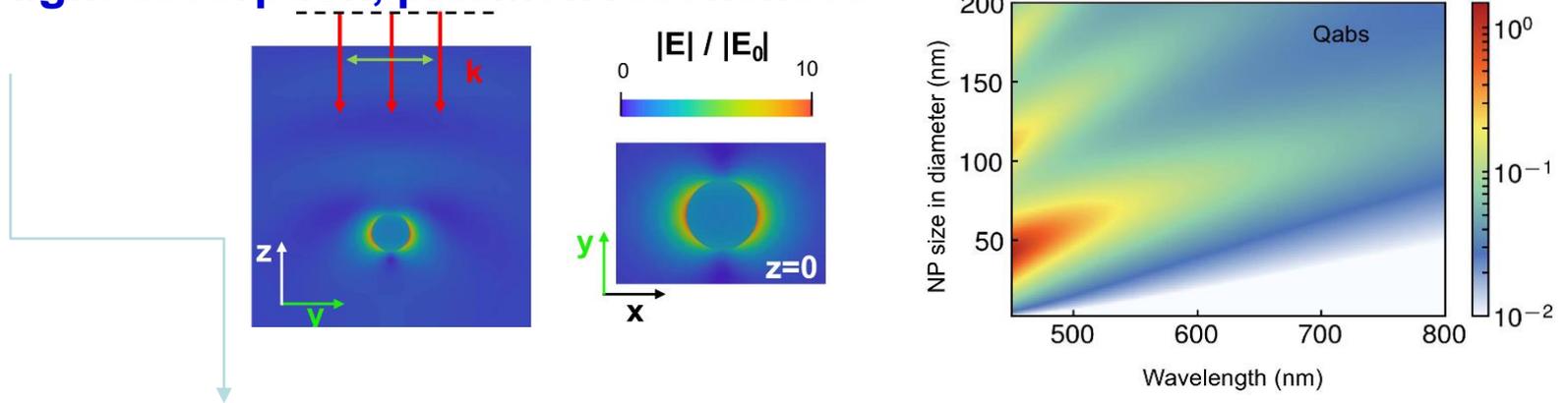
Nanosecond  
Picosecond  
Femtosecond



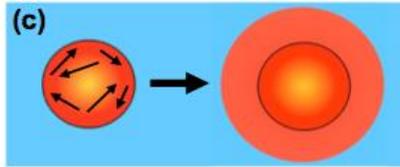
**Ion-impregnated porous glasses and semiconductors  
can be used as samples for following laser-induced nano-structuring**

# Nanoparticle formation and growth

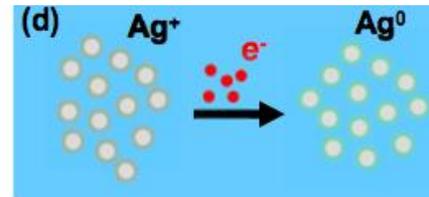
## 1. Laser light absorption, plasmon resonances



## 2. Heating and thermal diffusion

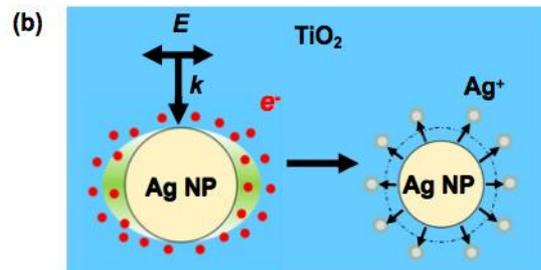
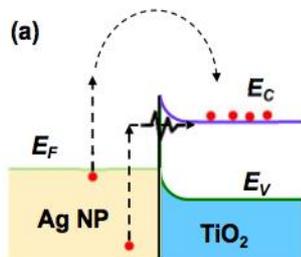


## 3. Photoemission and reduction

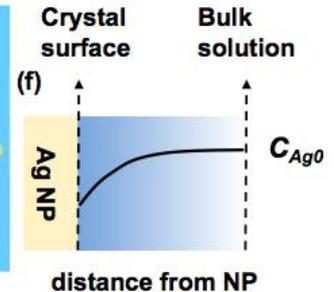
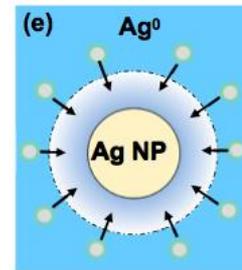


H. Ma et al. *J. Phys. Chem. C* 123.42 (2019): 25898-25907

## 5. Photo-oxidation



## 6. NPs growth



**Multi-scale and multi-physical mechanisms are involved**

# Multi-Scale and Multi-Physical Modeling

$$Grw(t) = D_0 \cdot e^{-\frac{E_{D0}}{k_B T(t)}} \cdot \frac{C_{Ag^0 Sol} - C_{RNP}}{R_{NRP}} \cdot 4\pi R_{NRP}^2$$

**Growth**

$$Oxy(t) = \frac{\eta I(t) \cdot e^{-\alpha z} \cdot \sigma_{abs}(R_{NRP})}{h_{planck} f_{inc}}$$

**Photo-oxidation**

$$Red(t) = D_{red} \cdot e^{-\frac{E_p}{k_B T(t)}} \cdot C_{red} \cdot e^{-\frac{E_D}{k_B T(t)}} \cdot C_{Ag^+ Sol}^{\frac{2}{3}}(t)$$

**Reduction**

$$\frac{d}{dt} C_{Ag^+ Sol}(t) = -Red(t) + Oxy(t) \cdot (C_{NRP}(t) + \frac{R_{NRP}}{3} \frac{dC_{NRP}(t)}{dR_{NRP}(t)})$$

**Ag<sup>+</sup> ions**

$$\frac{d}{dt} C_{Ag^0 Sol}(t) = Red(t) - Grw(t) \cdot (C_{NRP}(t) + \frac{R_{NRP}}{3} \frac{dC_{NRP}(t)}{dR_{NRP}(t)})$$

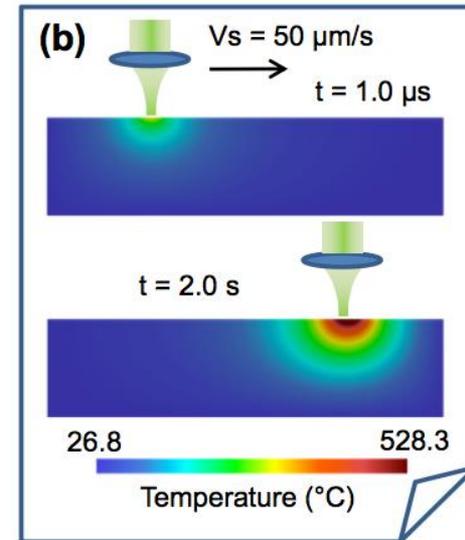
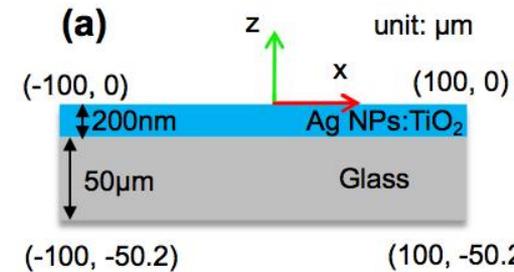
**Ag<sup>0</sup> atoms**

$$\frac{d}{dt} R_{NRP} = \frac{\omega}{4\pi R_{NRP}^2(t)} (Grw(t) - Oxy(t))$$

**NPs size**

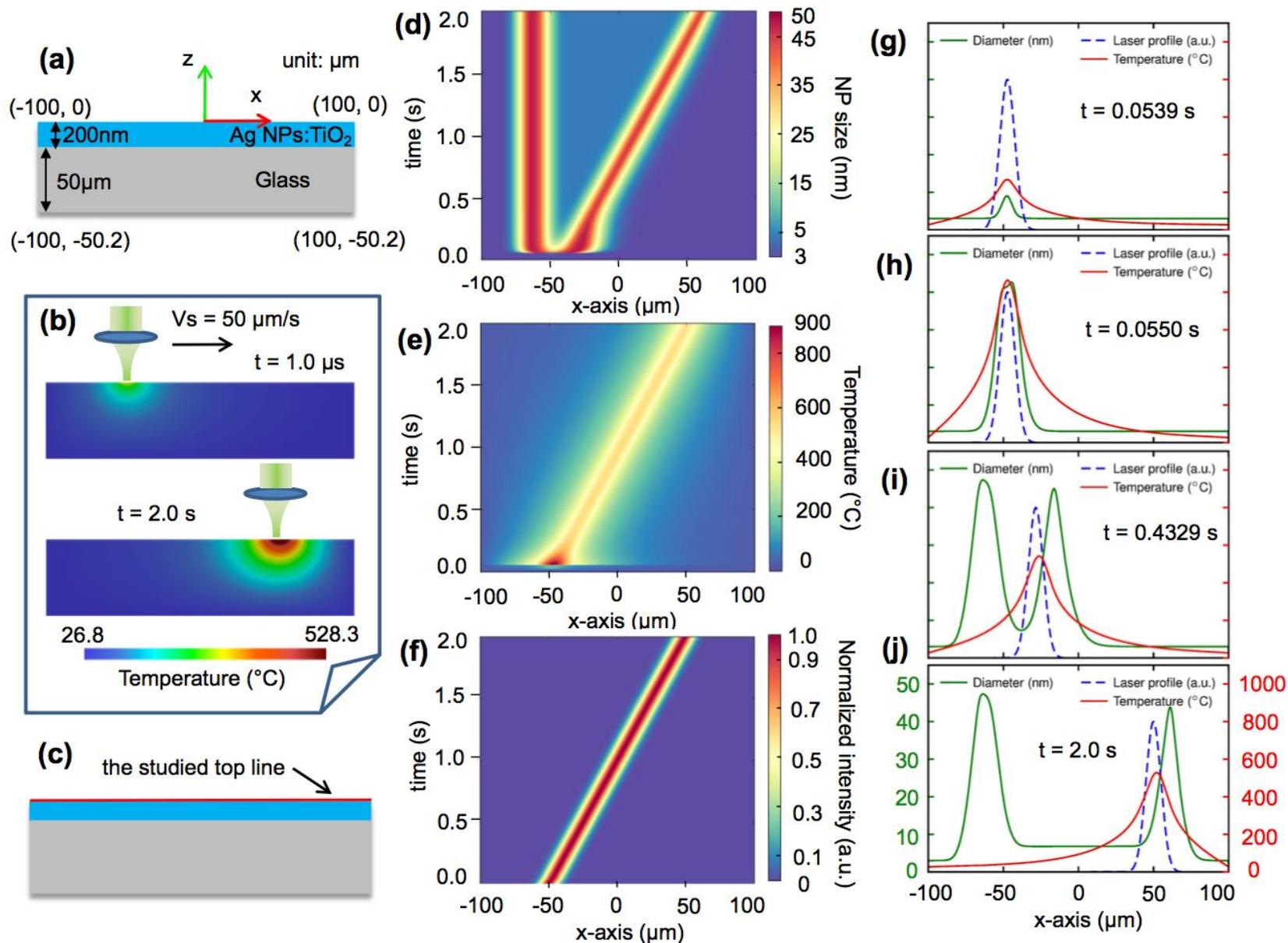
$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + \alpha \cdot I(x, y, t) \cdot e^{-\alpha z}$$

**Temperature**

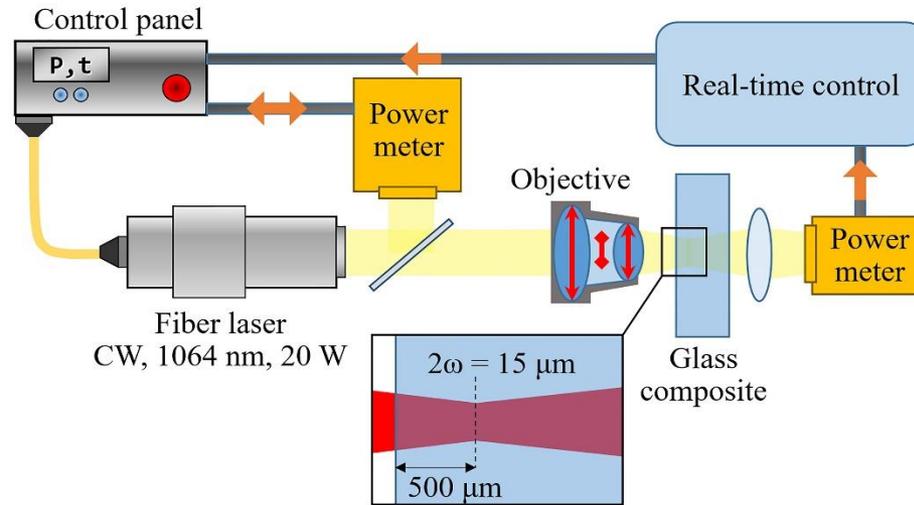


H. Ma et al.  
*J. Phys. Chem. C*, 123(42), 25898-25907 (2019)

# Calculation Results

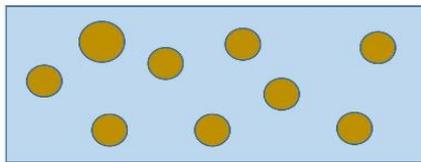


# Is a real-time control possible?

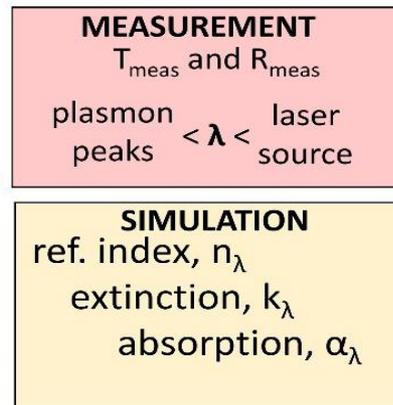


## I. Input data

1. Initial GC
2. Reference sample - Sintered GC



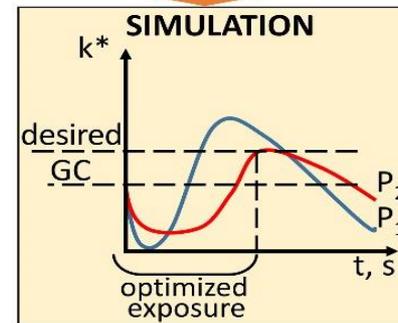
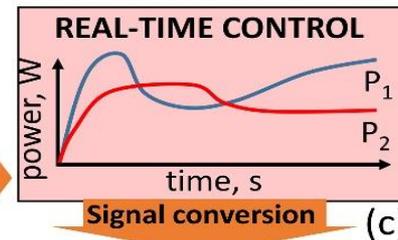
## II. Base Block



(a)

(b)

## III. Laser irradiation



**Bergman-Garnett  
effective medium  
approximation**

M.M. Sergeev et al. *Nanomaterials* 10.6 (2020): 1131

# Modeling details

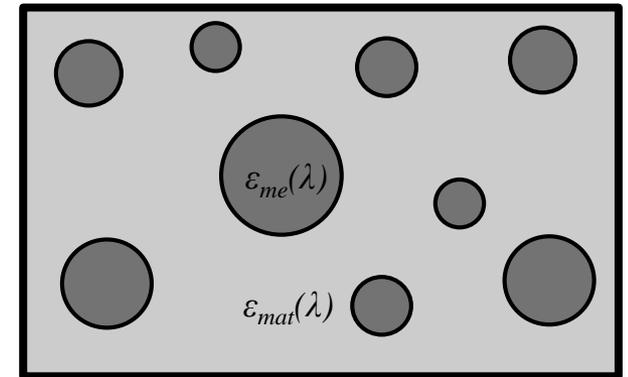
## Effective-medium approximation

NP's dielectric function [1]

$$\varepsilon_{me}(\lambda) = \varepsilon_b(\lambda) + \frac{\omega_p^2}{\omega} \left[ \frac{1}{\omega + i\gamma_b} - \frac{1}{\omega + i\gamma} \right]$$

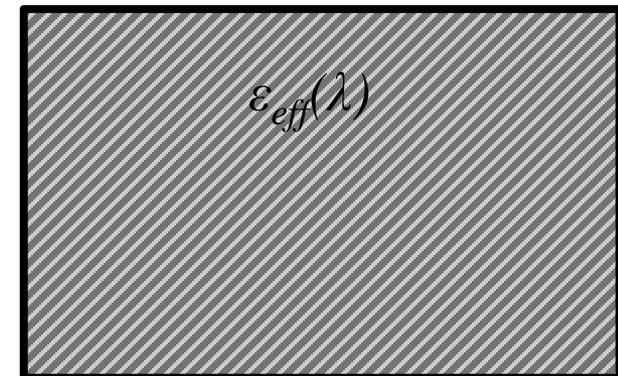
Ambient medium's dielectric function [2]

$$\varepsilon_{mat}(\lambda) = n_{mat}^2(\lambda) - k_{mat}^2(\lambda) + i \left[ 2n_{mat}(\lambda)k_{mat}(\lambda) \right]$$



Composite material's dielectric function [3] Bergman-Garnett

$$\varepsilon_{eff}(\lambda) = \varepsilon_{mat}(\lambda) \cdot \left[ 1 - v_{np} \int_0^1 \frac{g(u, v_{np})}{\varepsilon_{mat}(\lambda) / [\varepsilon_{mat}(\lambda) - \varepsilon_{me}(\lambda)] - u} du \right]$$

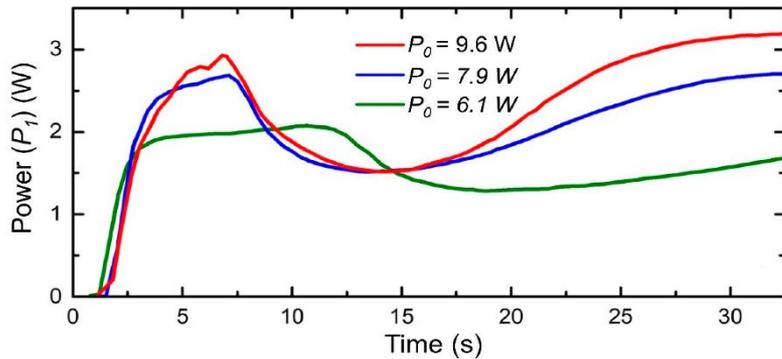
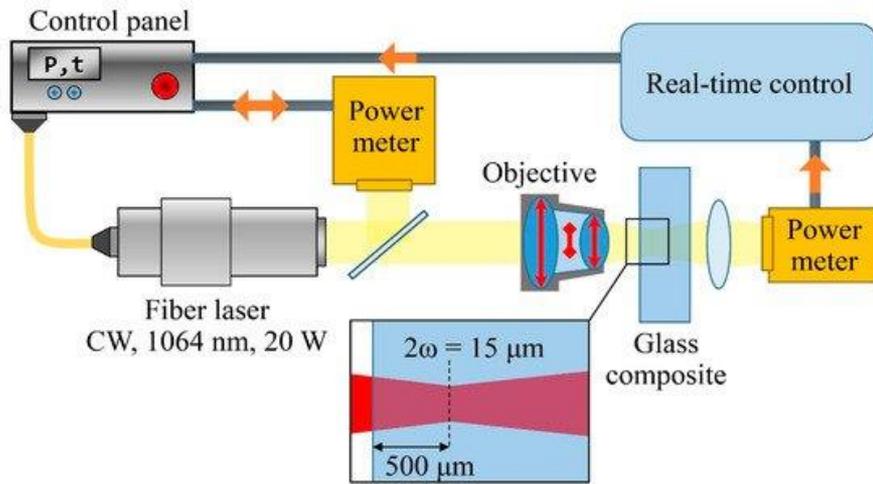


[1] Cavaliere E. et al. *Nanomaterials* (2017) 7 (12), p; 442.

[2] Sancho-Parramon J. et al. *Advances in Optical Thin Films II. International Society for Optics and Photonics* (2005) 5963, p. 596320.

[3] Kreibig U., Vollmer M. *Optical properties of metal clusters. – Springer Science & Business Media* (2013) 25.

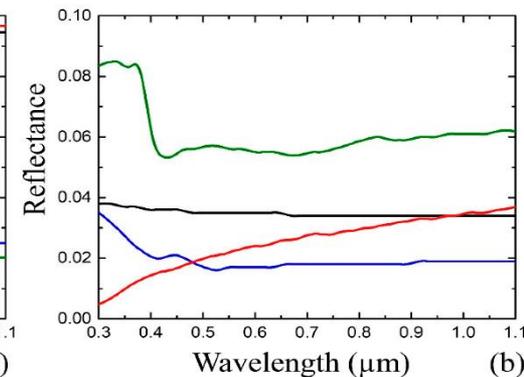
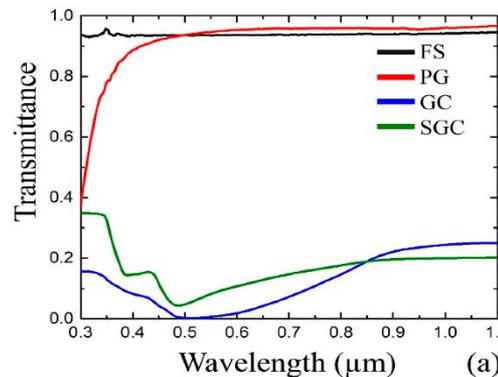
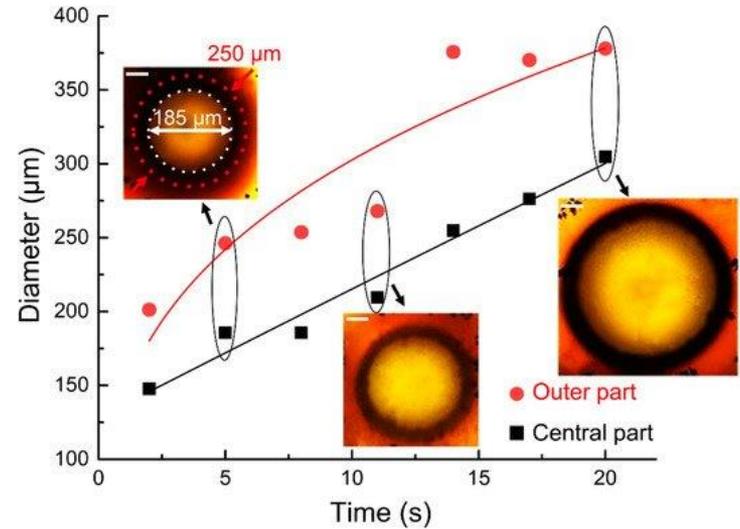
# Laser-induced changes (without scanning)



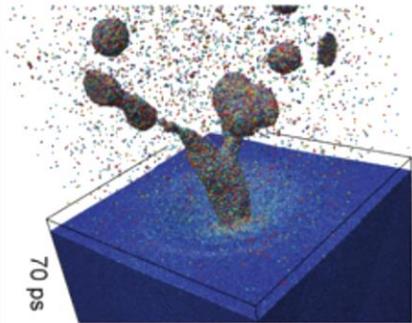
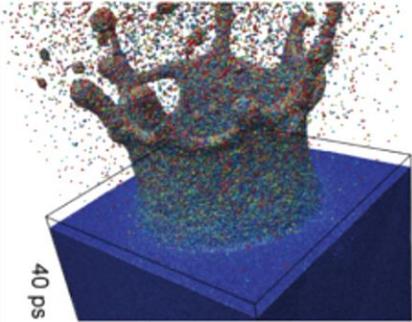
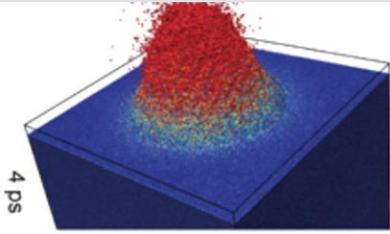
Time-evolution of the transmitted laser power ( $P_1$ ) during the structure fabrication. Here,  $P_0 = 6.1$  W (green),  $7.9$  W (blue), and  $9.6$  W (red).

**Reversible bleaching**

Time evolution of the structure central and outer diameter for 20 s laser exposure at  $P_0 = 9.6$  W.



# Material ejection in femtosecond laser ablation



## Two-temperature model (TTM)

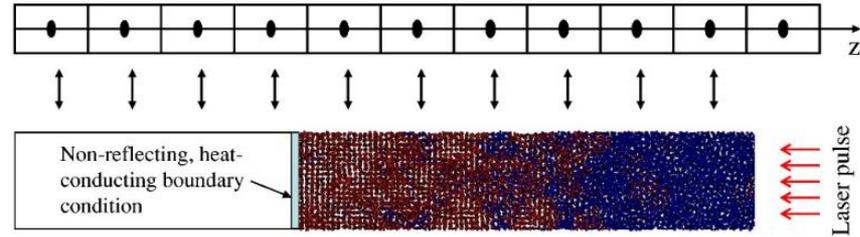
$$C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla [K_e(T_e) \nabla T_e] - G(T_e - T_l) + S(z, t),$$

$$C_l(T_l) \frac{\partial T_l}{\partial t} = \nabla [K_l(T_l) \nabla T_l] + G(T_e - T_l),$$

Kaganov et al. Sov. Phys. JETP 4, 173 (1957)

## TTM-MD model

Ivanov & Zhigilei, (2003)



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

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i + \xi m_i \mathbf{v}_i^T, \quad \text{MD}$$

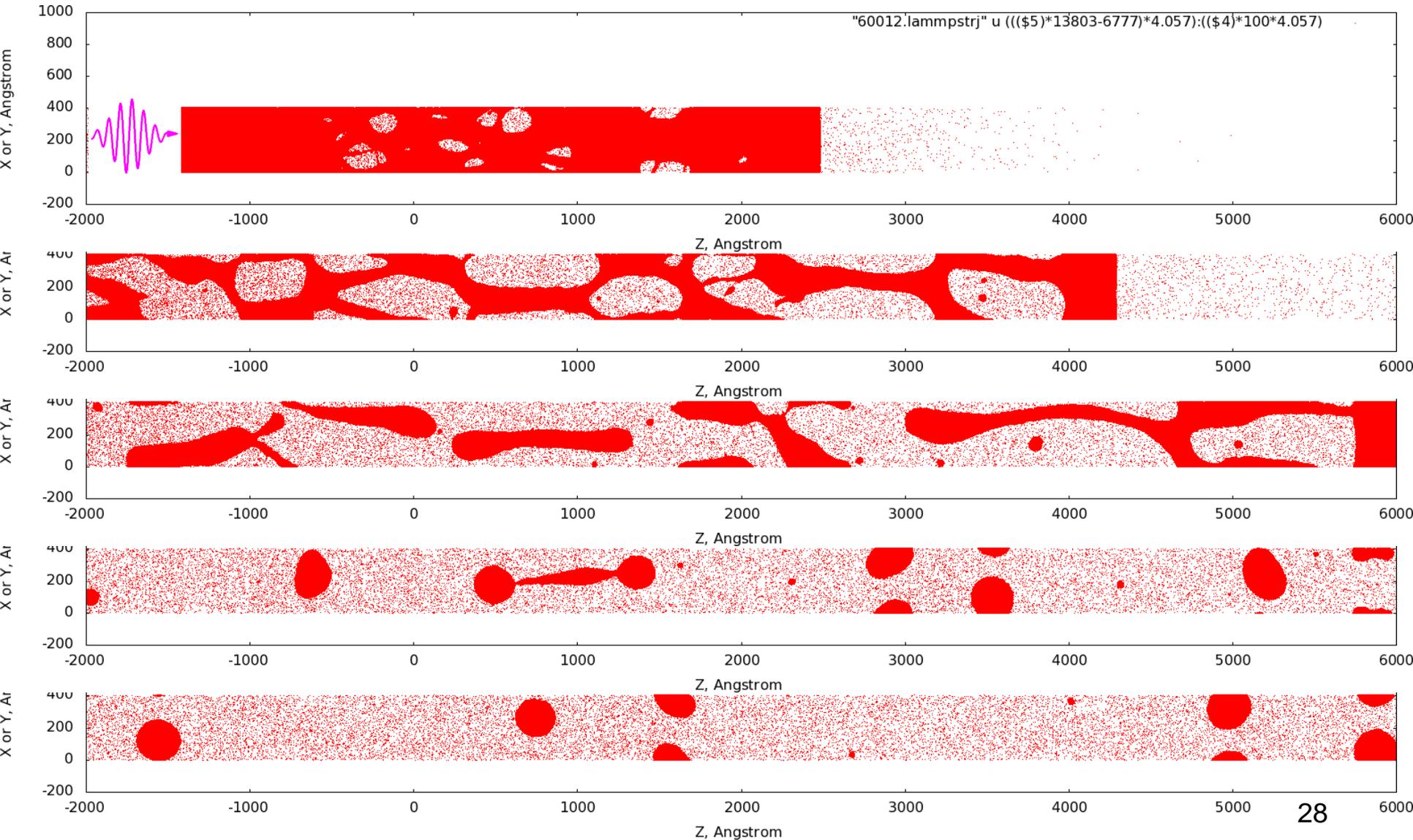
$$\xi = \frac{1}{n} \sum_{k=1}^n G V_N (T_e^k - T_l) \Bigg/ \sum_i m_i (\mathbf{v}_i^T)^2$$

InSiDE • Vol. 10 No. 1 • 2012

Povarnitsyn M & Itina, T. E.  
Physical Review B, 92(17), 174104.

# Ultra-short Laser Ablation

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

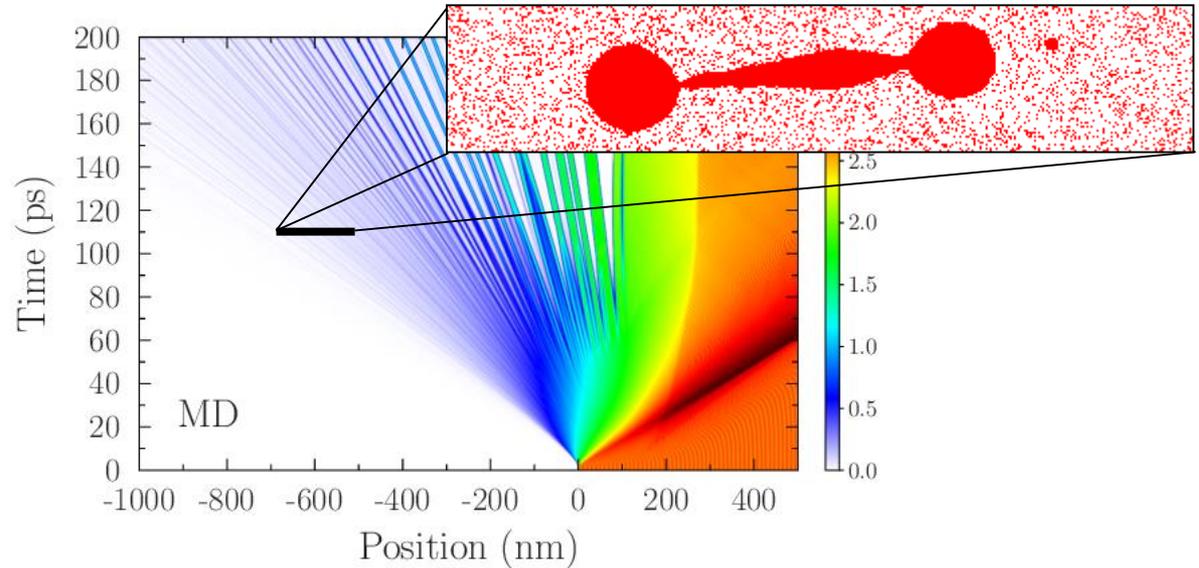


# TTM-MD simulations vs TTM-Hydro

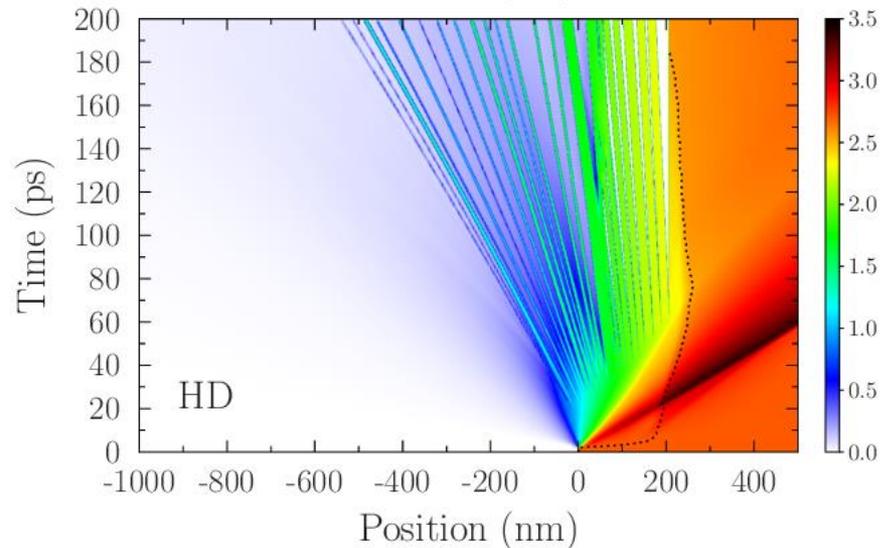
## Density

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

TTM-MD

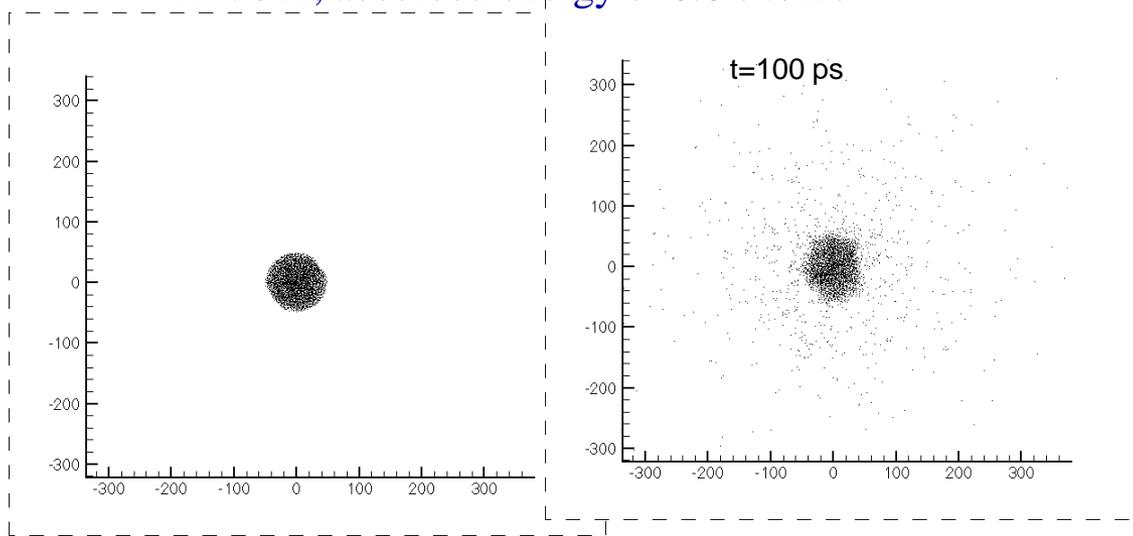


Hydrodynamics



# Laser Interaction with NPs: MD simulations

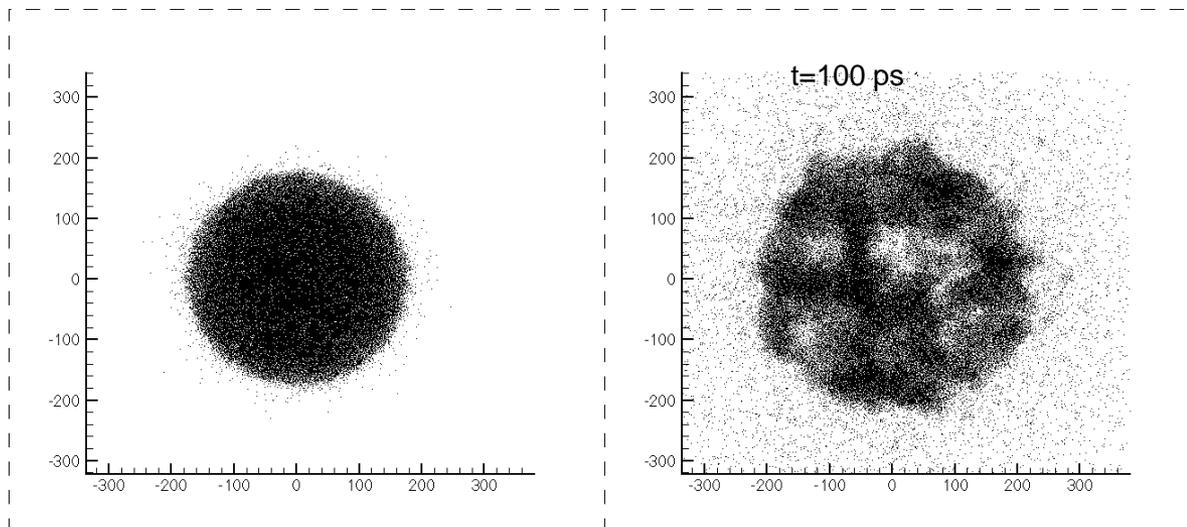
$R=50 \text{ \AA}$ , absorbed energy  $e=0.6 \text{ eV/mol}$



## Evaporation

+Coulomb Explosion  
for very small clusters  
if fs laser

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



Fragmentation due to  
thermo-mechanical  
effects

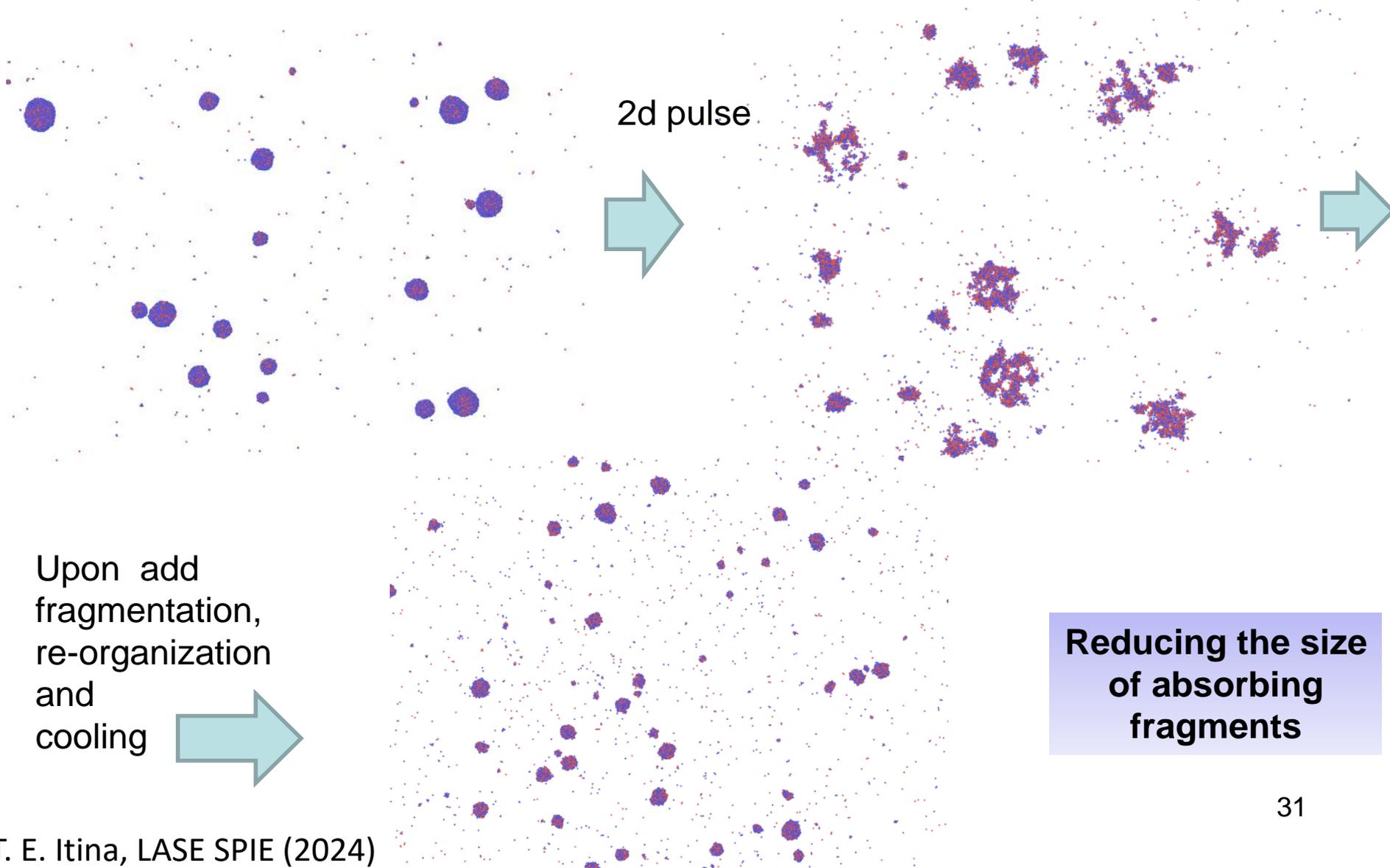
**vibration modes**  
**-breathing**  
**-surface instabilities**  
**-sub-nano cavitation**

T. E. Itina, HdR 2008

# NP's Fragmentation: Multiple Pulses

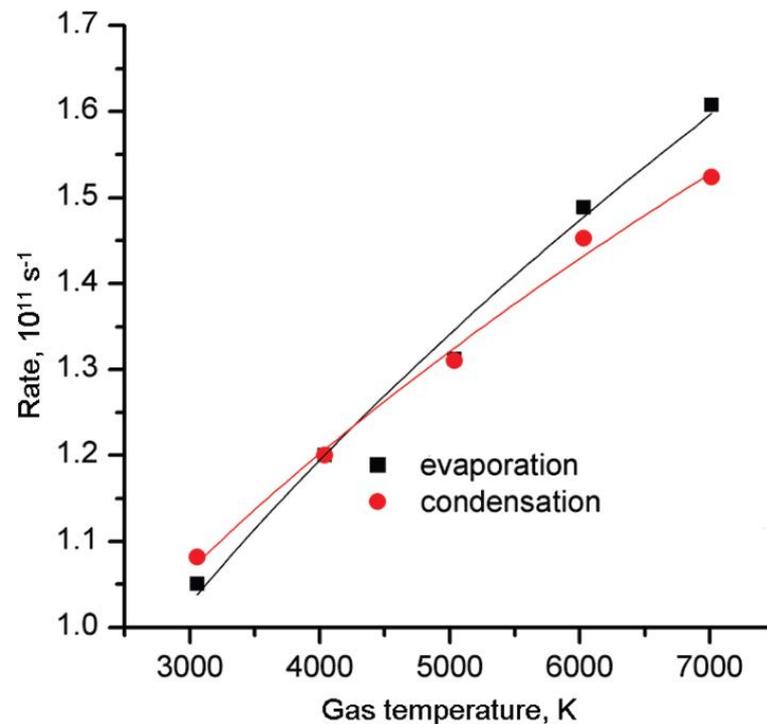
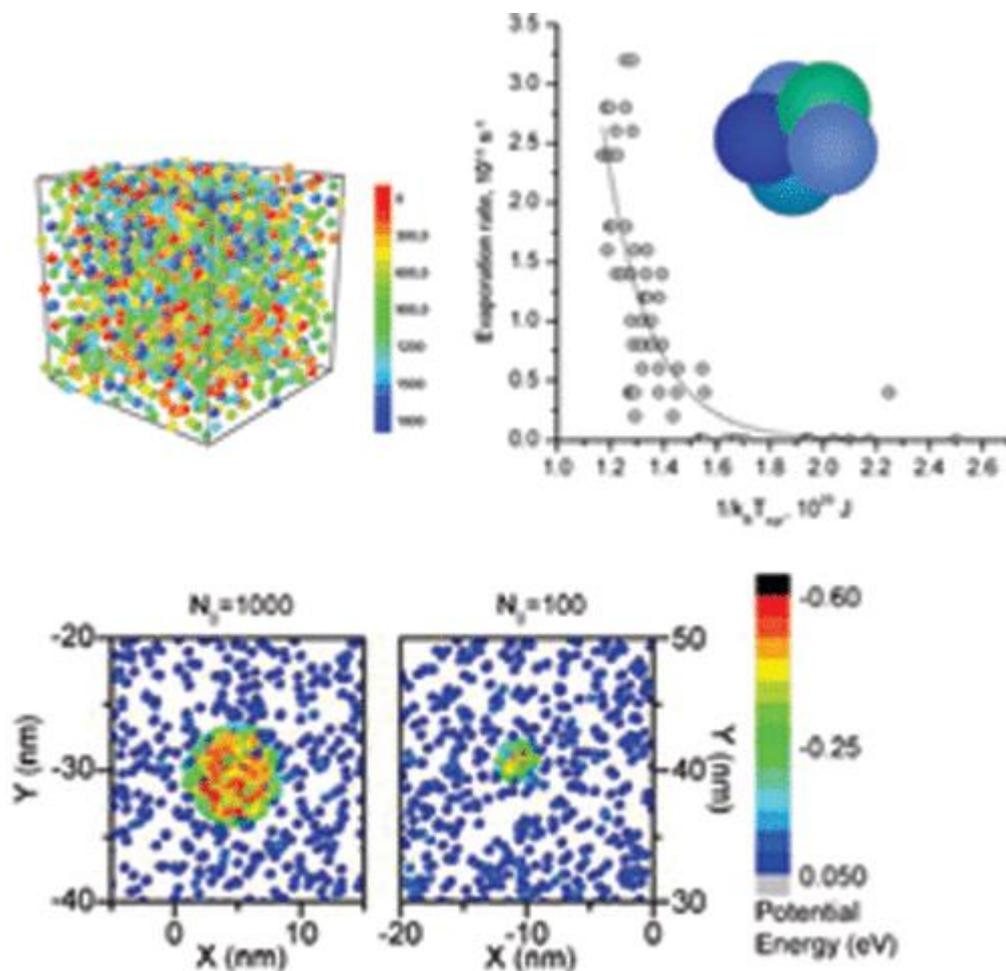
AuCo, NP R = 40 u.c.

Simulations starts from the fragmentation results, additional fragmentation takes place



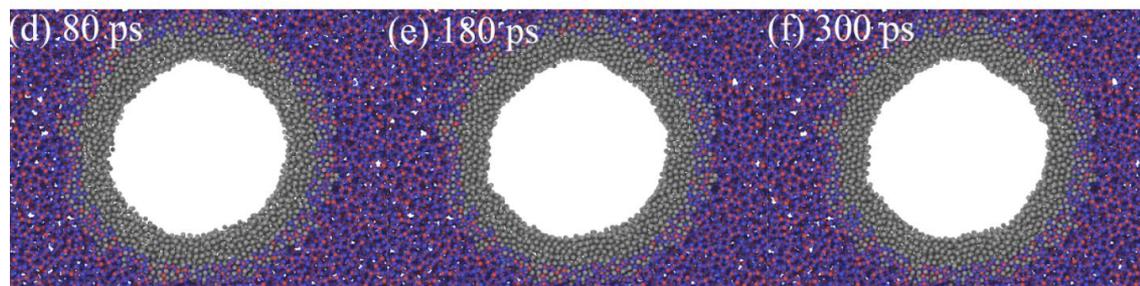
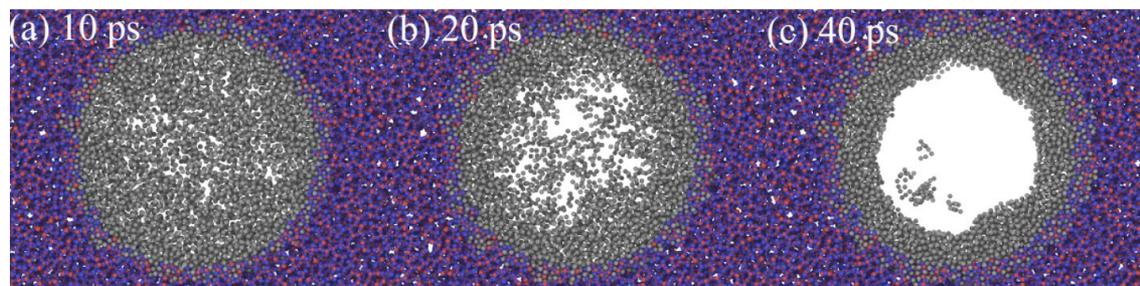
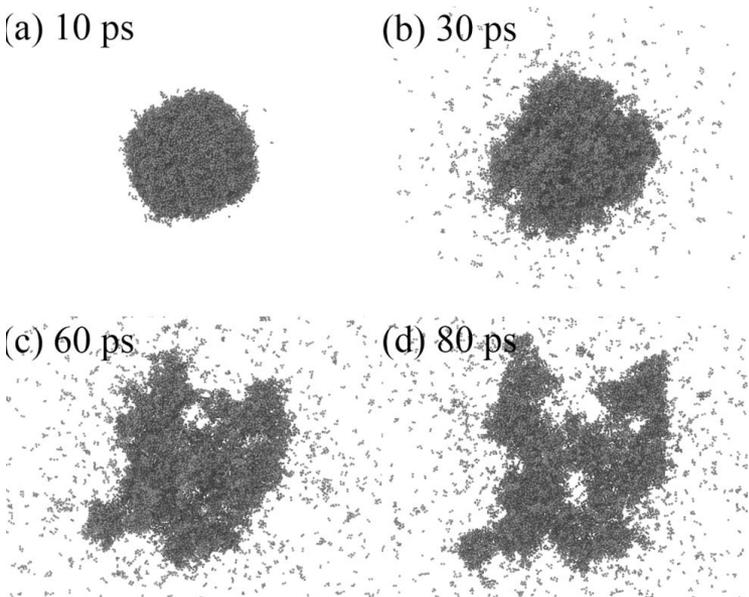
# Laser Interaction with NP in a Hot Gas

## Evaporation and condensation: RRK theory

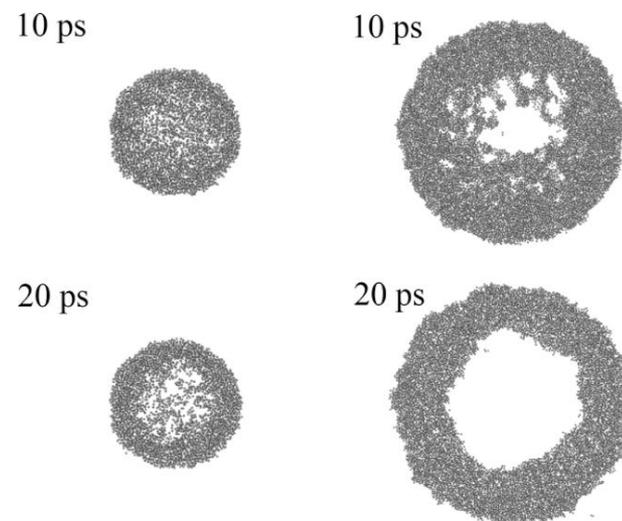
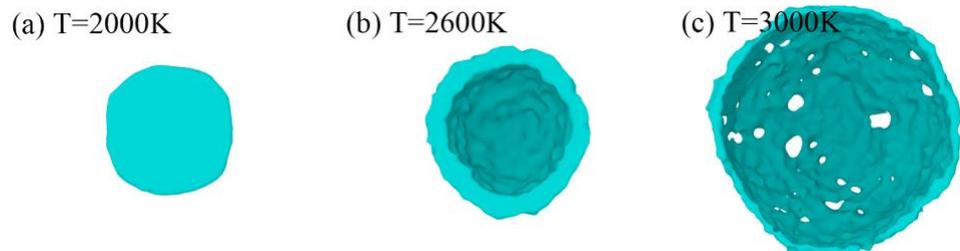


Evaporation rates and condensation rates for a nickel cluster initially at 2490K as a function of gas temperature.

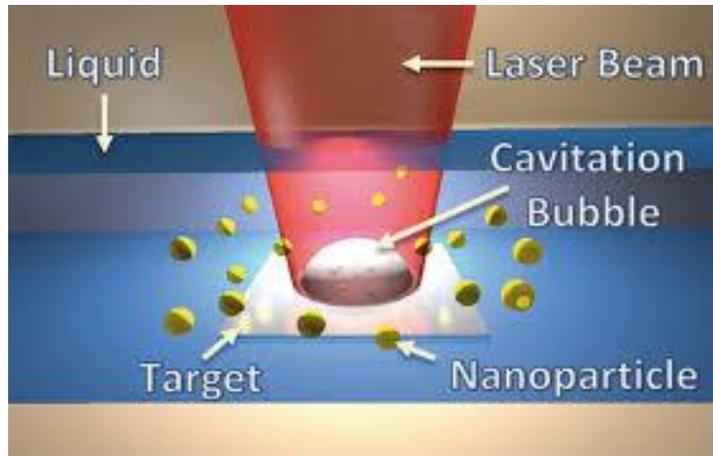
# NP in a Solid Matrix upon Pulsed Laser Irradiation



Jiang et al., *Comp. Materials Science* 196 (2021) 110545



# Pulsed Laser Ablation in Liquids: PLAL



Doi: 10.1007/978-3-030-63647-0\_30

1. **Early stage** – laser energy absorption, material ejection, plume formation
2. **Intermediate stage** – plume expansion in the presence of a confining liquid environment
3. **Late stage** – plume mixing with the liquid, NP coalescence/aggregation processes.

## Main questions:

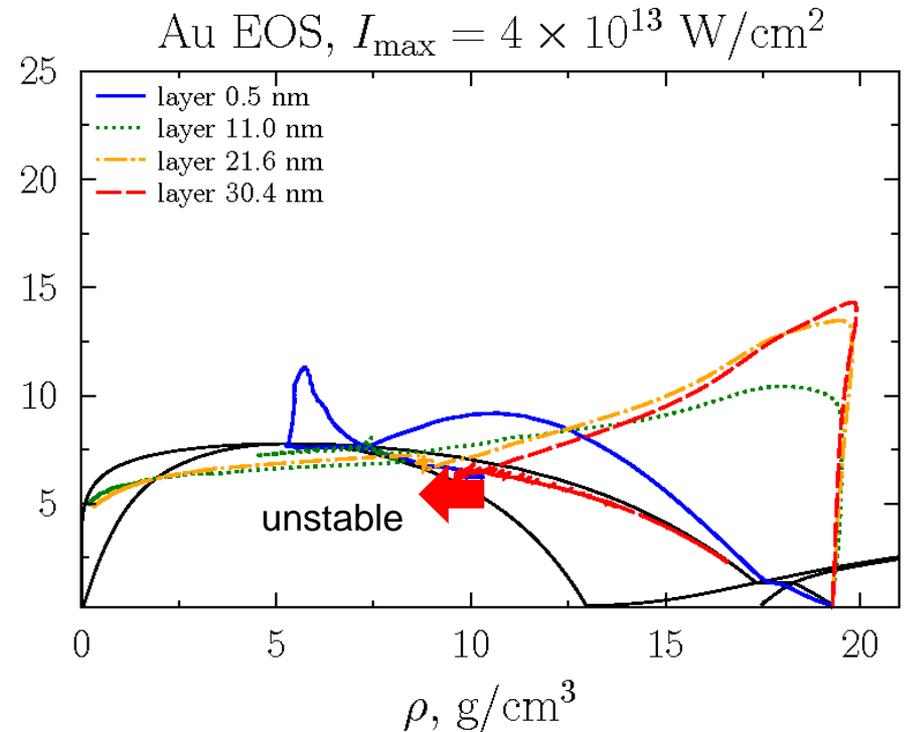
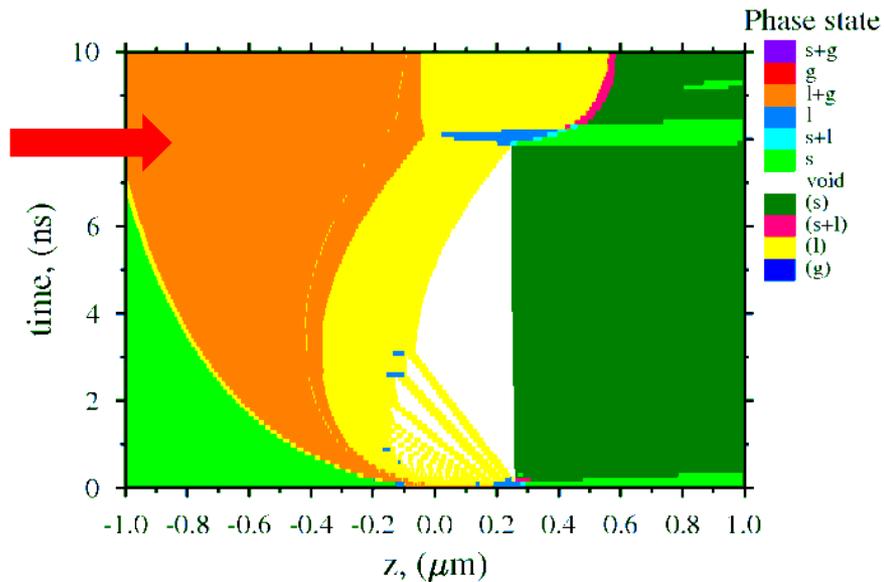
- Can NPs be directly ejected from the target?
- Are NPs formed by condensation in the plume/cavitation bubble or later in liquid solution ?
- What stage plays the major role ?

# Ablation in liquid (PLAL) Simulations: TTM-HD

Itina T. E., ANGEL 2012, Invited talk

Povarnitsyn, M. E., Itina, T. E., Levashov, P. R., & Khishchenko, K. V.

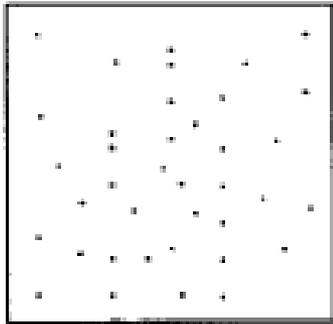
(2013). *Physical Chemistry Chemical Physics*, 15(9), 3108-3114.



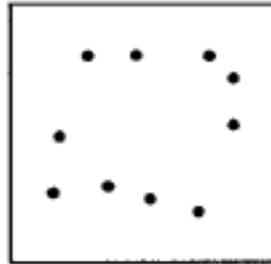
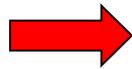
- Upper layers cross the spinodal and enter into unstable liquid-gas region (orange zone). **NPs can be formed here.**
- Some trajectories reach supersaturated gas region, where **condensation takes place**, but this process will not yield many particles

# Later stage: two processes

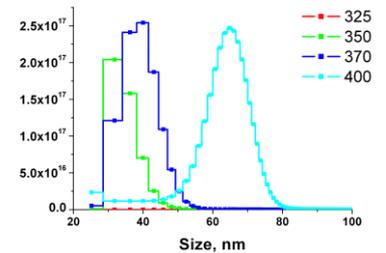
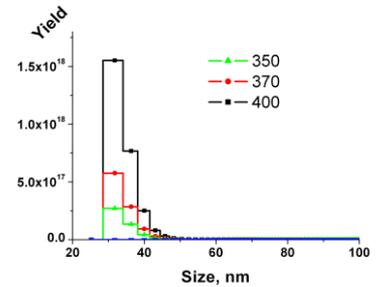
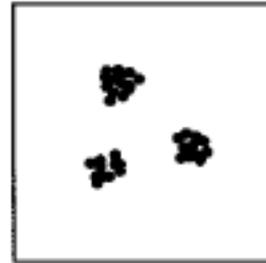
Supersaturated solution



**1-nucleation  
In liquid solution**



**2-coalescence  
aggregation**



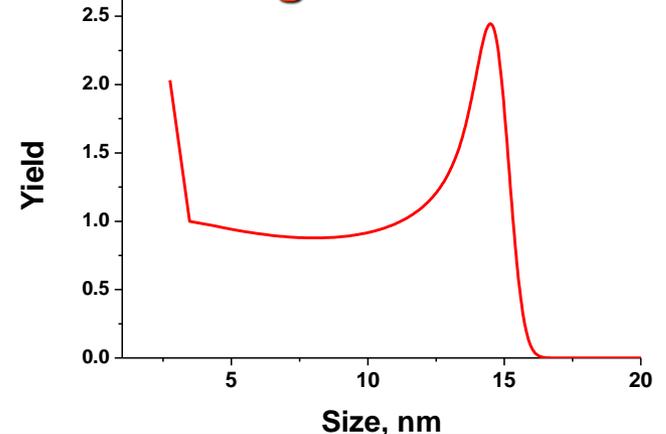
$$\rho(t) = K_c c^2 \exp\left[\frac{-\Delta G(n_c, c)}{kT}\right]$$

$$\frac{dN_1}{dt} = \rho(t) - \sum_{j=2}^{\infty} j \frac{dN_j}{dt} \quad \frac{dN_2}{dt} = fK_1 N_1^2 - K_2 N_1 N_2$$

$$\frac{dN_s}{dt} = K_{s-1} N_1 N_{s-1} - K_s N_1 N_s \quad (s \geq 3)$$

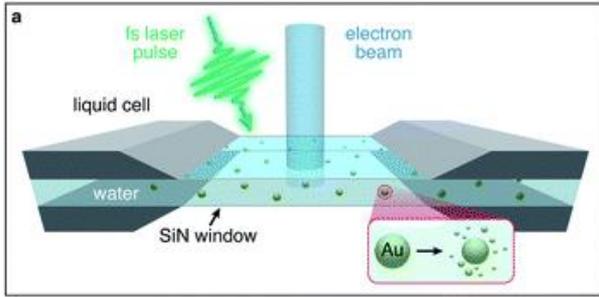
$$K_n = 4\pi(a + an^{1/3})(D_a + D_a n^{-1/3}) \approx 4\pi a n^{1/3} D_a$$

**=> LogNorm**

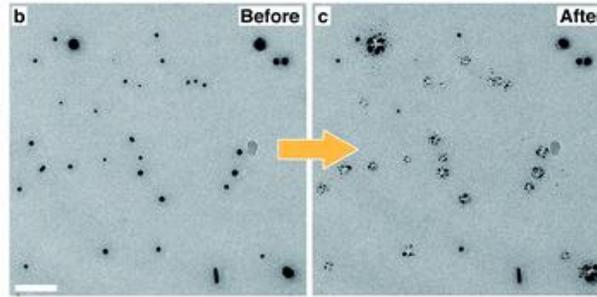


# Laser Fragmentation: Experiments and Simulation

Experimental geometry

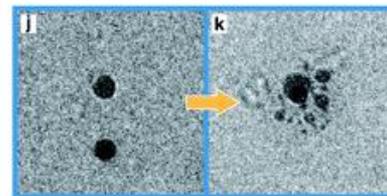
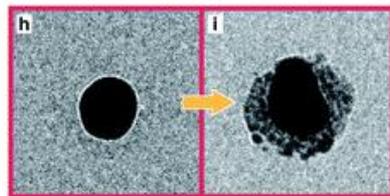
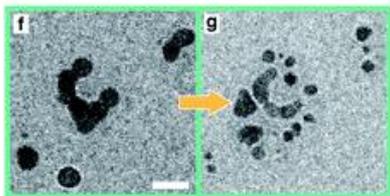
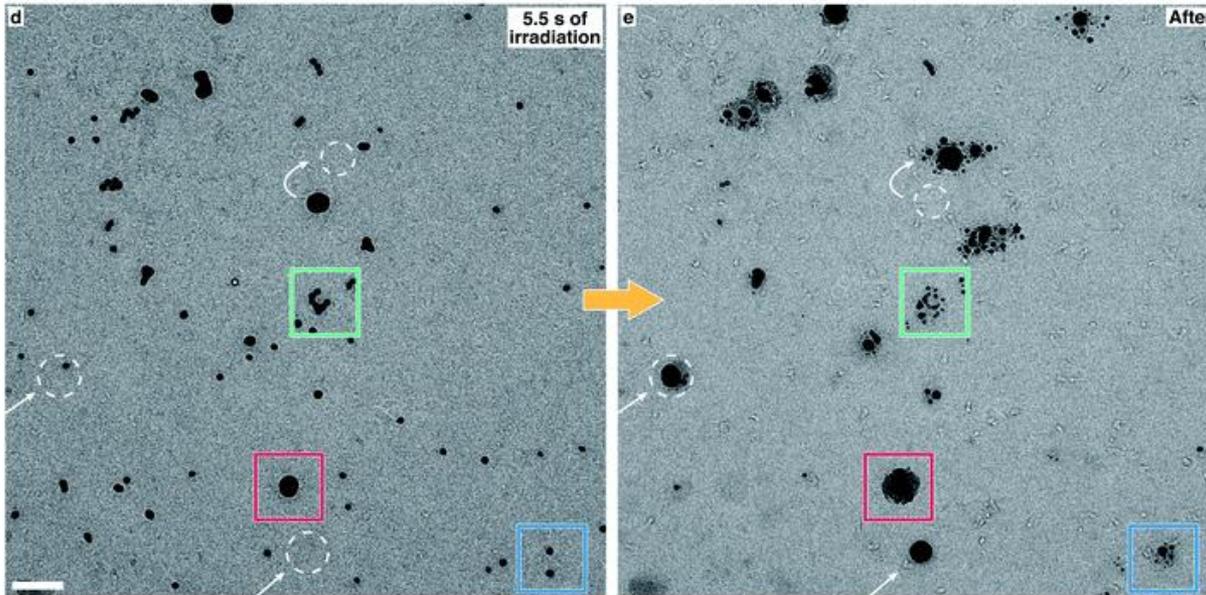


Femtosecond laser irradiation of gold nanoparticles

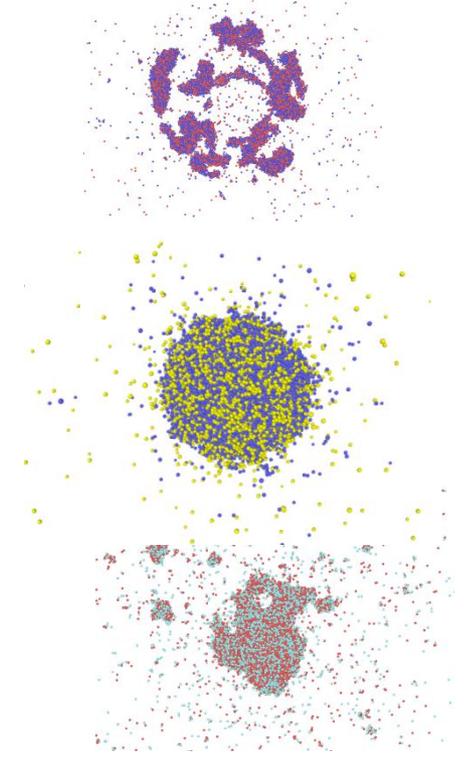


Good agreement  
with MD results for  
NPs

In situ observation of gold nanoparticle fragmentation under femtosecond laser irradiation



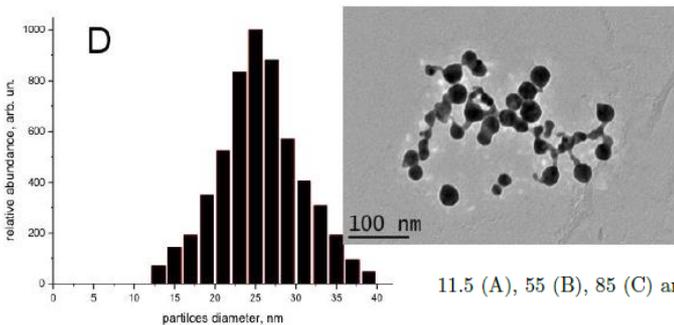
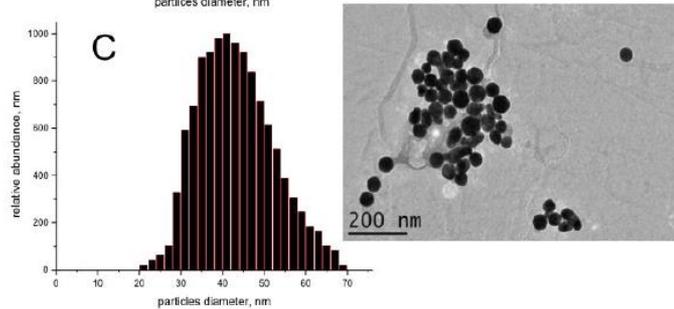
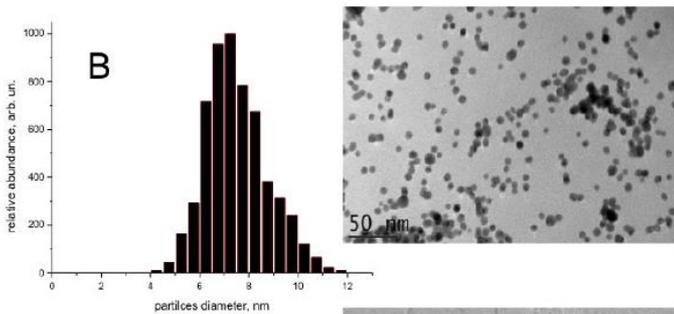
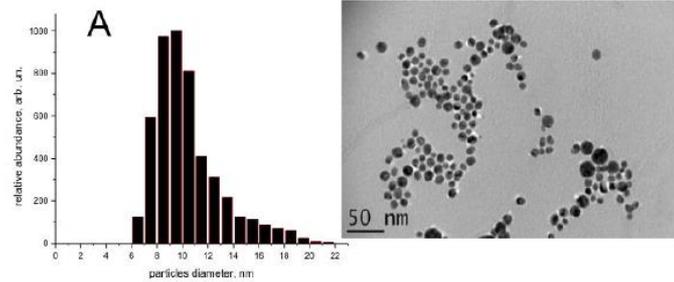
T. E. Itina, SMS 2023



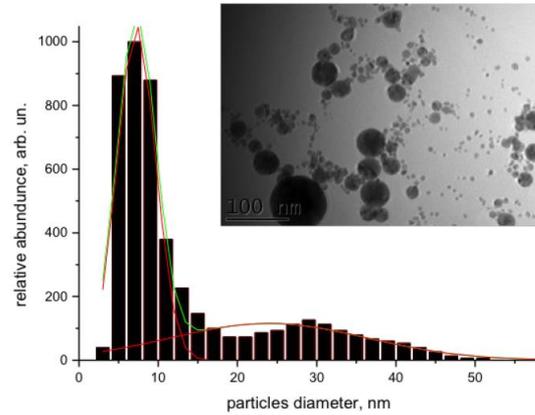
Gold nanoparticles in water

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

# Laser Interaction with NP in a Liquid



11.5 (A), 55 (B), 85 (C) and 109 (D)  $\mu\text{J}$

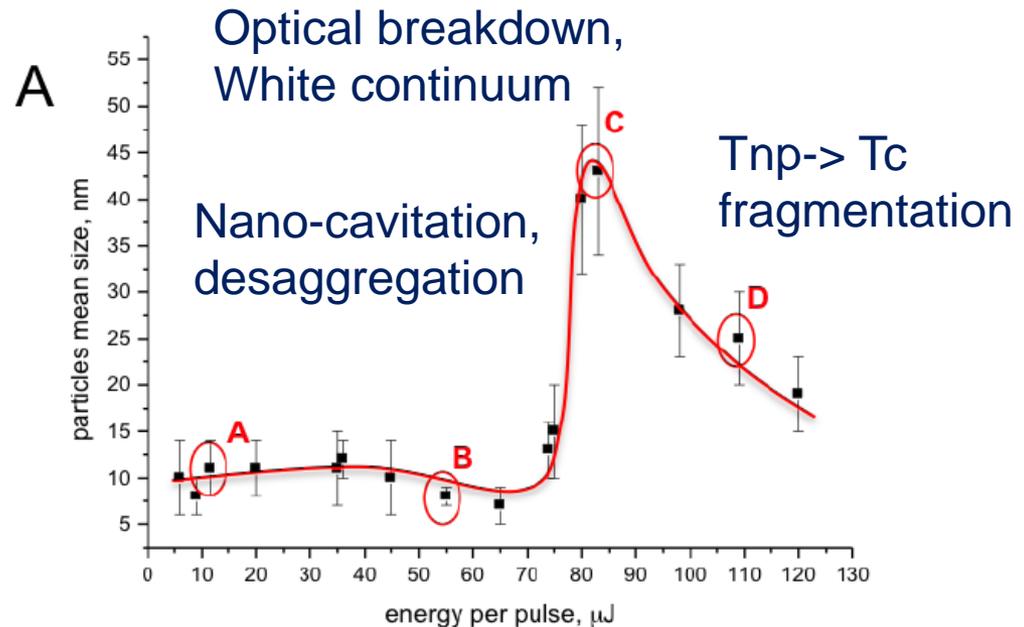


Upon ablation  
1064 nm

Additional  
fragmentation

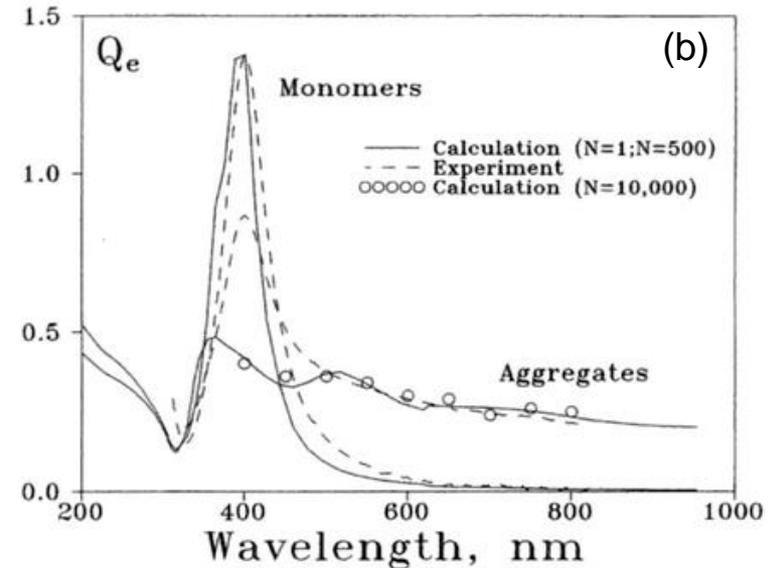
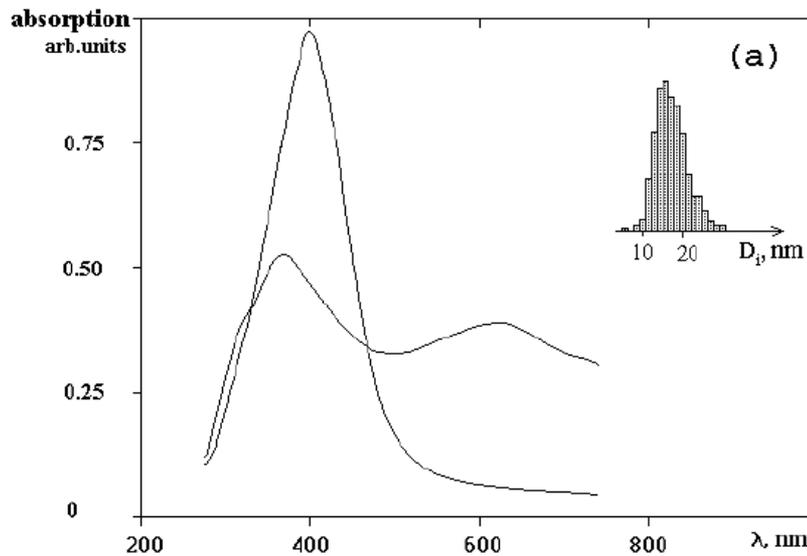
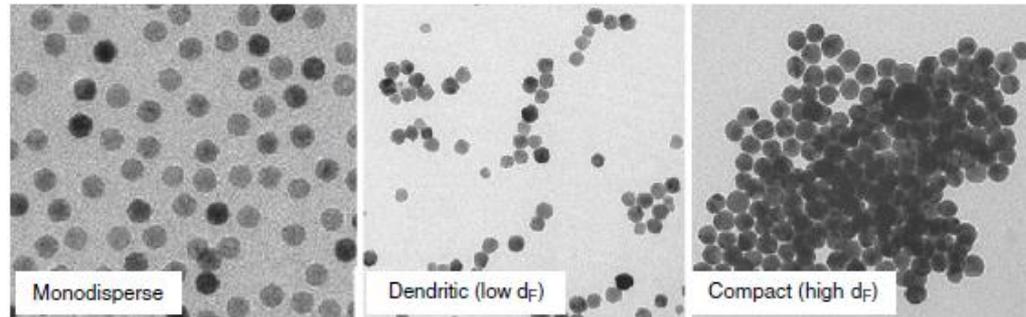
$0.63\text{--}15 \text{ J/cm}^2$

Role of laser energy: non-linear dependency



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

# Monomers (Primary NPs) vs Aggregates



Mean-field theory calculations

**Experimental and calculated absorption (a) and extinction (b) spectra of silver colloids**

Shalaev, « *Nonlinear optics of Random media* »  
Itina T. E., ANGEL 2016, Invited talk

# Aggregation-disaggregation

(DLVO: Deryaguin, Landau, Verwey and Overbeek)

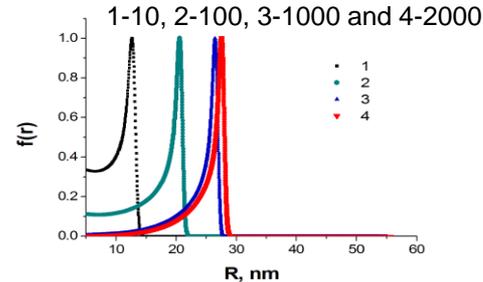
$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} \alpha(r_i, r_j) \beta(r_i, r_j) n_i n_j - n_k \sum_{i=1} \alpha(r_i, r_k) \beta(r_i, r_k) n_i$$

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} J_{ij} - \sum_{i=1} J_{ki}$$

For spherical particles the agglomeration rate

$$J_{ij} = \frac{2K_B T}{3\mu W_{ij}} (r_i + r_j) \left( \frac{1}{r_i} + \frac{1}{r_j} \right) n_i n_j$$

(Smoluchowski)



Diffusion

$$D = \frac{k_B T}{6\pi\mu r_H}$$

(Stokes-Einstein)

The stability ratio,  $W_{ij}$ , measures the effectiveness of the potential barrier in preventing the particles from aggregating.

For collisions between particles, this ratio is given by the following expression (Sonntag and Strenge, 1986):

$$V_T = V_A + V_R$$

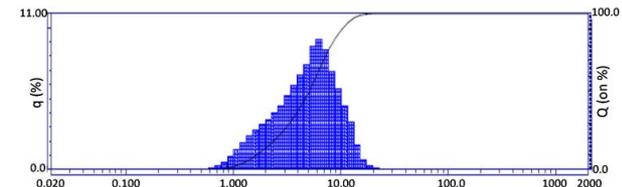
$$W = \frac{\int_0^\infty \frac{\beta(y)}{(y+2)^2} \exp\left[\frac{V_T(y)}{k_B T}\right] dy}{\int_0^\infty \frac{\beta(y)}{(y+2)^2} \exp\left[\frac{V_A(y)}{k_B T}\right] dy}$$

$$\beta(y) = \frac{6y^2 + 13y + 2}{6y^2 + 4y}$$

With disaggregation terms:

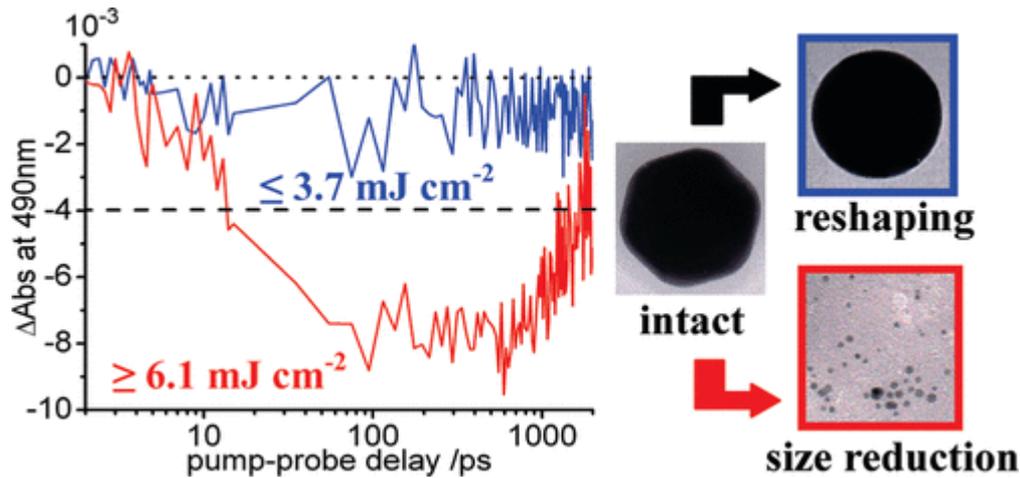
$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} J_{ij} - \sum_{i=1} J_{ki} + \sum_{j=1}^\infty b_{jk} n_{j+k} - \sum_{j=1}^{k-1} (1 + \delta_{j,k-j}) b_{j,k-j} n_k$$

Changed shape, wider dispersion



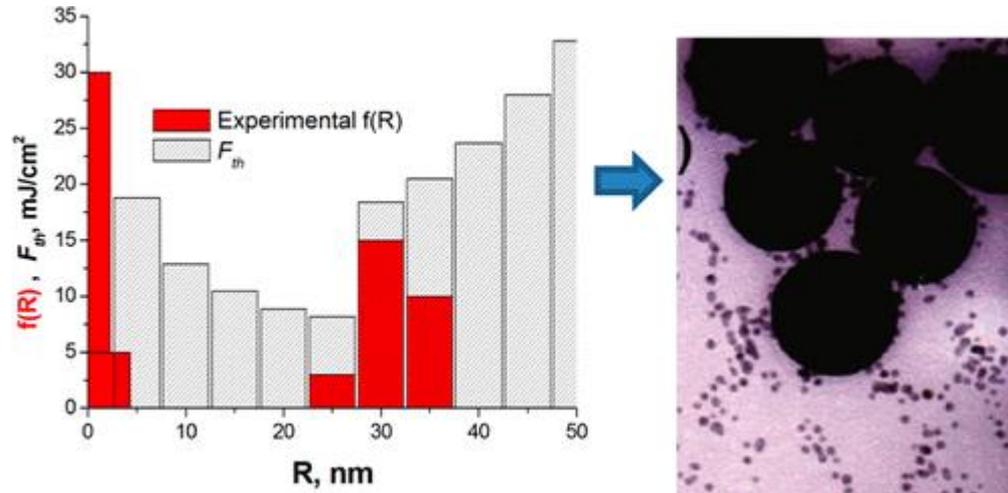
where  $b_{ij}$  is the rate at which size  $i+j$  aggregates break into size  $i$  and size  $j$  aggregates

# Laser Interaction with NP in a Liquid



**Bleaching indicates strong changes, such as NP's fragmentation**

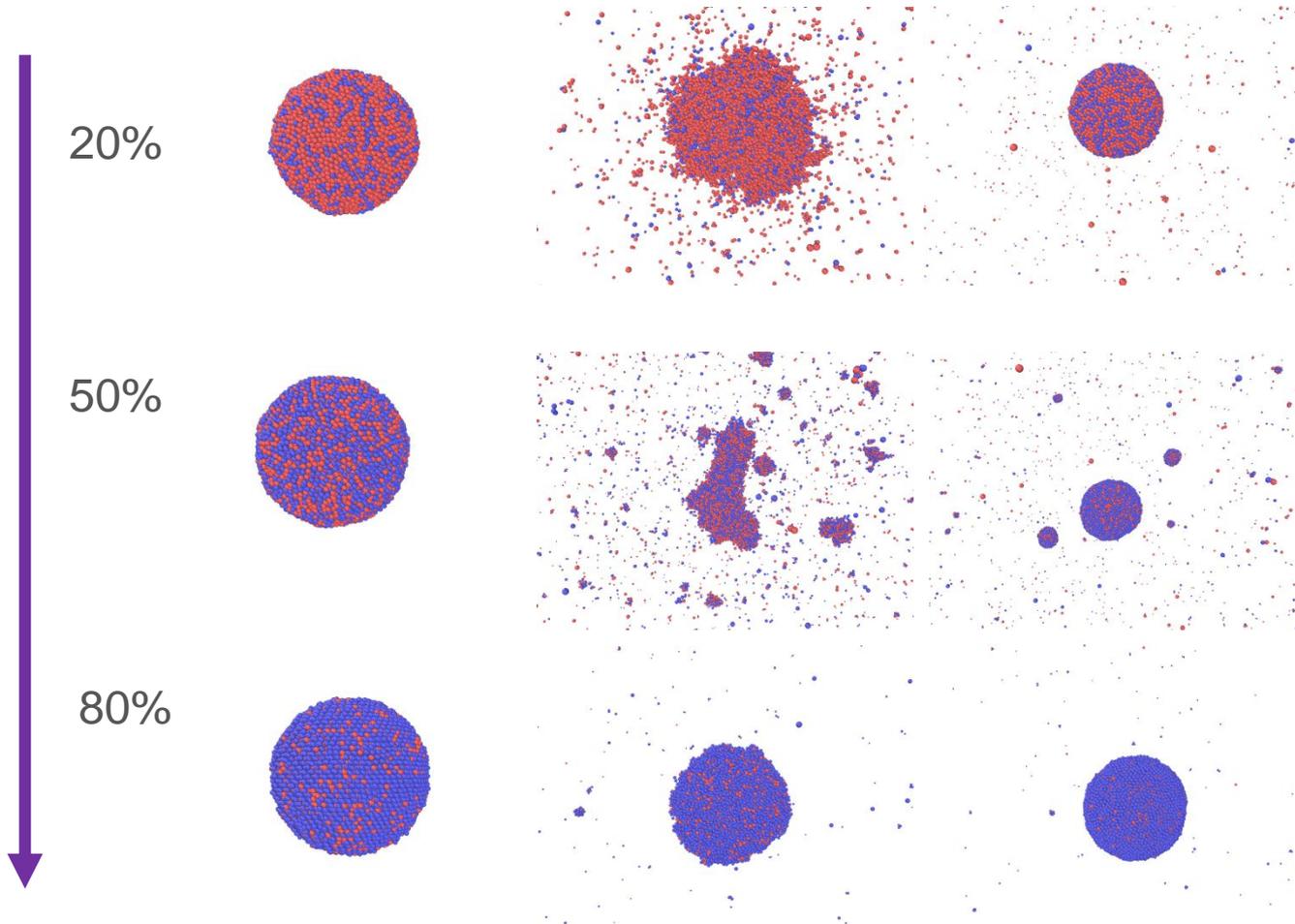
D. Wener et al. J. Phys. Chem. C 2011, 115, 12, 5063–5072



L. Delfour et T.E. Itina, J. Phys. Chem. C 2015, 119, 24, 13893–13900

# Alloy NPs: Composition affects fragmentation

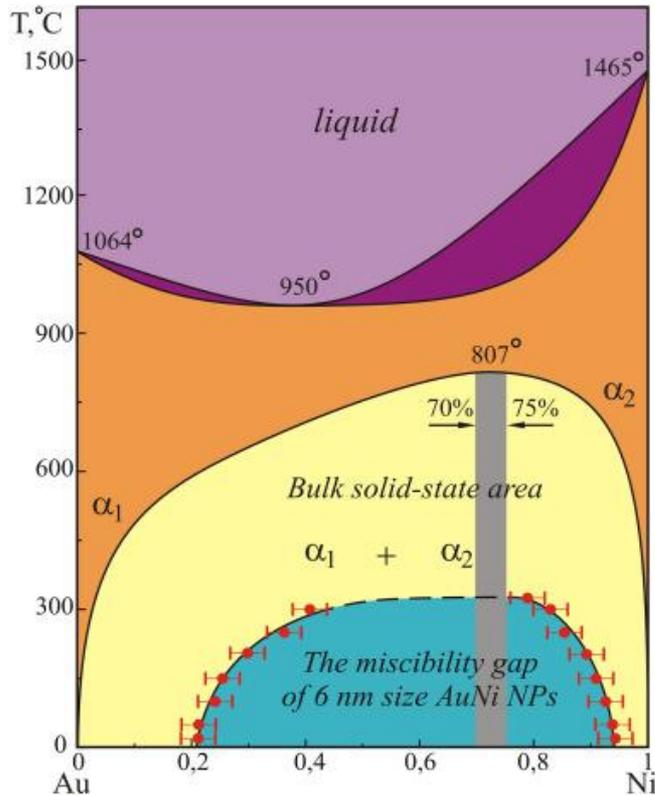
Au-Ni 0, 500, 1600, NP's fragmentation depends on Ni fraction



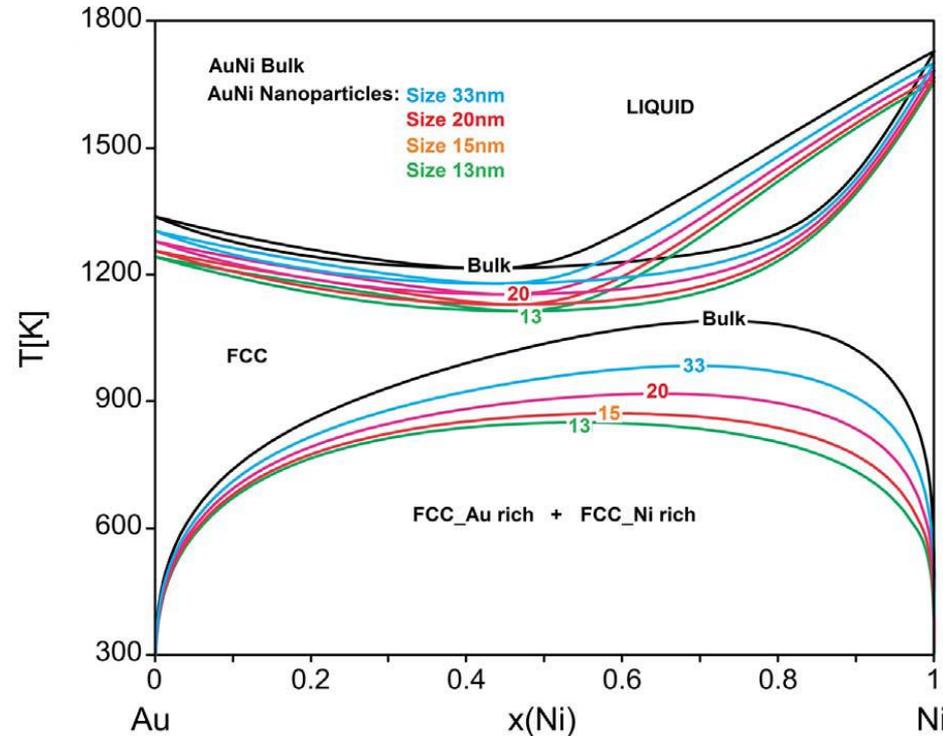
T. E. Itina, invited talk, Orsay (2023).

# Phase diagrams: NP vs Bulk Material

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



NB: Under equilibrium conditions



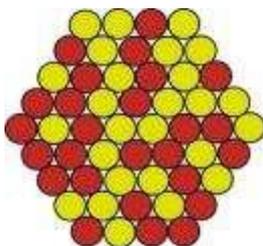
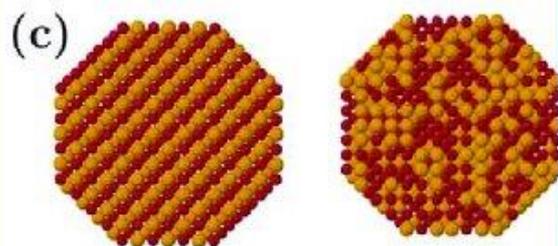
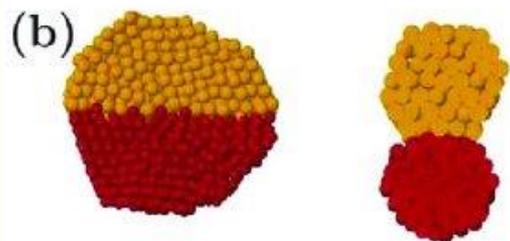
J. Sopoušek et al CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 58 (2017) 25–33

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

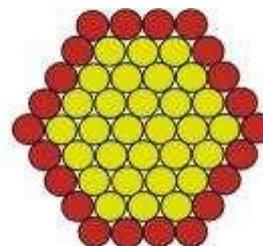
S. Bogatyrenko et al, Scripta Materialia, 170 September  
Pages 57-61

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

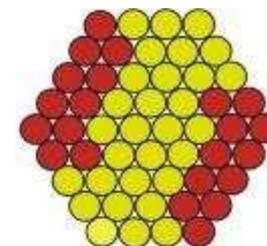
# Nanoparticle Sintering, Janus, Core-Shells and Alloy NPs



Alloy



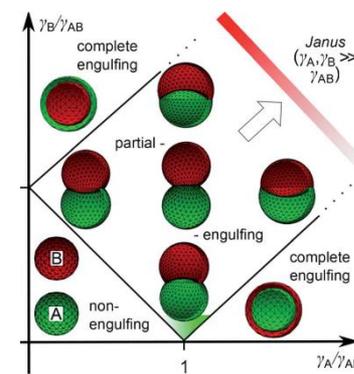
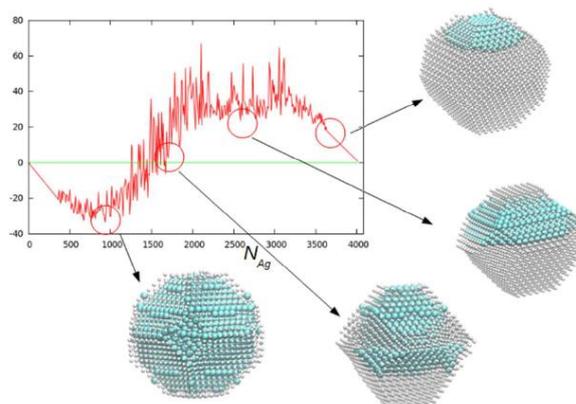
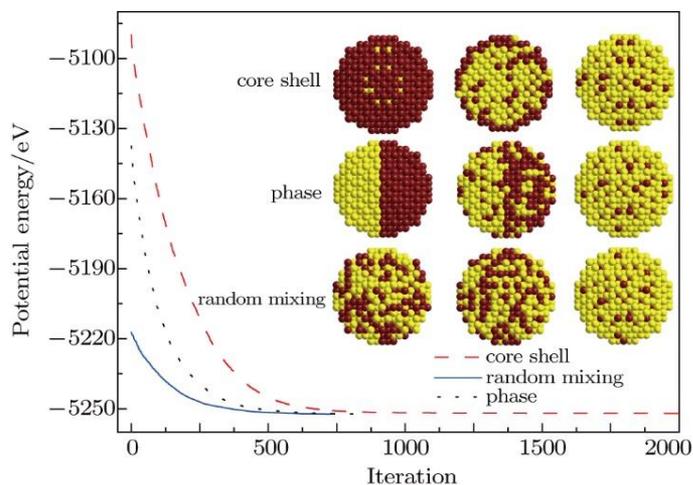
Core-Shell



Cluster-in-Cluster

## Mixing Energy

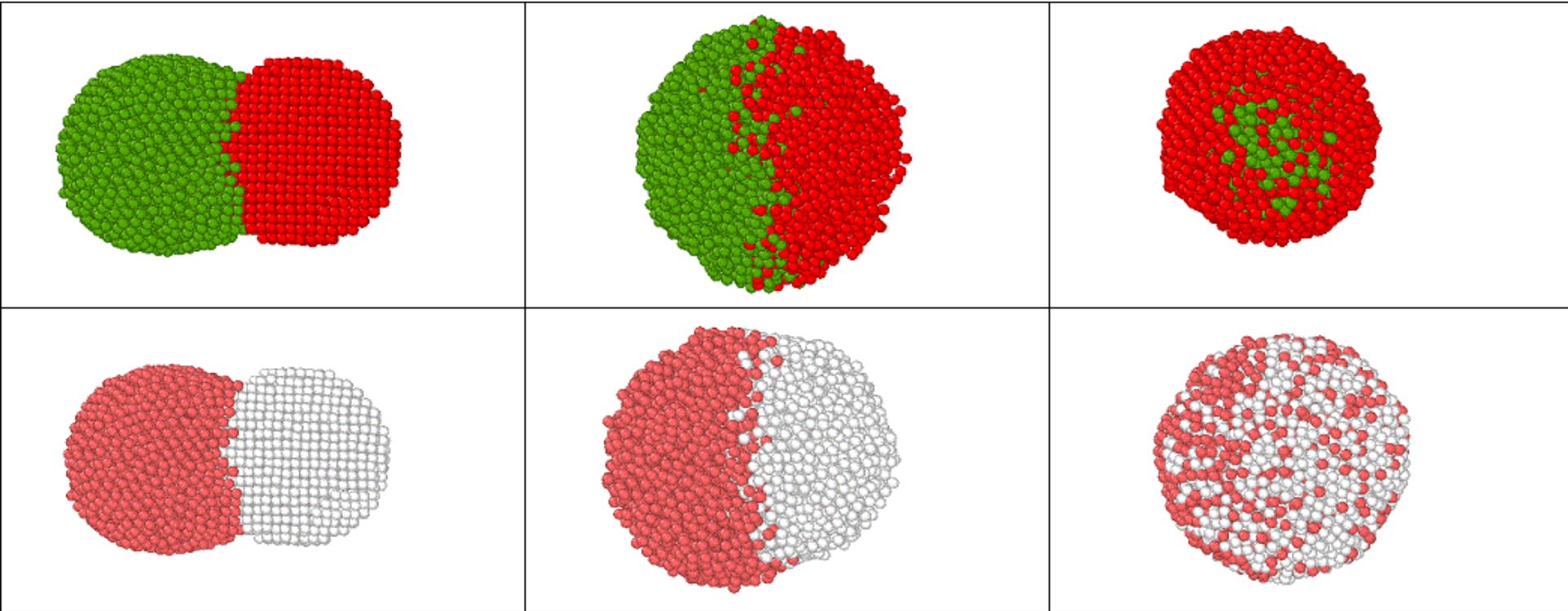
$$\Delta[N_A, N_B] = E_{\text{alloy}}[N_A+1, N_B-1] - E_{\text{alloy}}[N_A, N_B] - E_A[\text{ref}] + E_B[\text{ref}]$$



J. Guzowski et al.

# Sintering vs Alloying

AuNi vs AuCo rapidly heated to a high temperature, well above the melting point [0, 100, 500]



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

Excess energy:

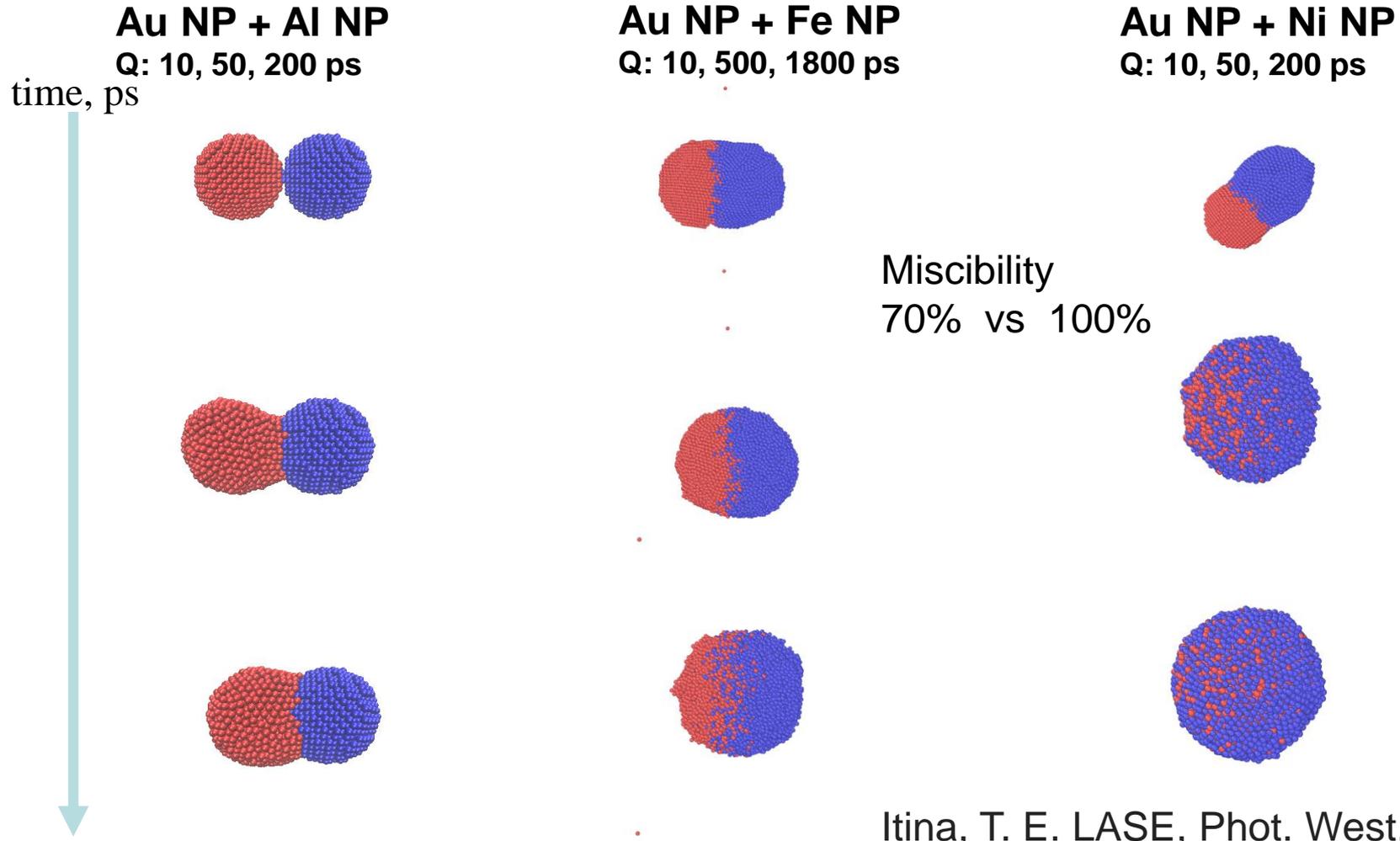
$$E_{\text{ex}} = E_{\text{vdW}} + E_{\text{el}} + E_{\text{steric}} + E_{\text{o}}$$

Sintering:  $E_{\text{ex}} < 0$

Mixing:  $E_{\text{ex}} > 0$

T. E. Itina et al., in press, 2024

# MD simulations for NPs: Sintering or Alloy NP formation

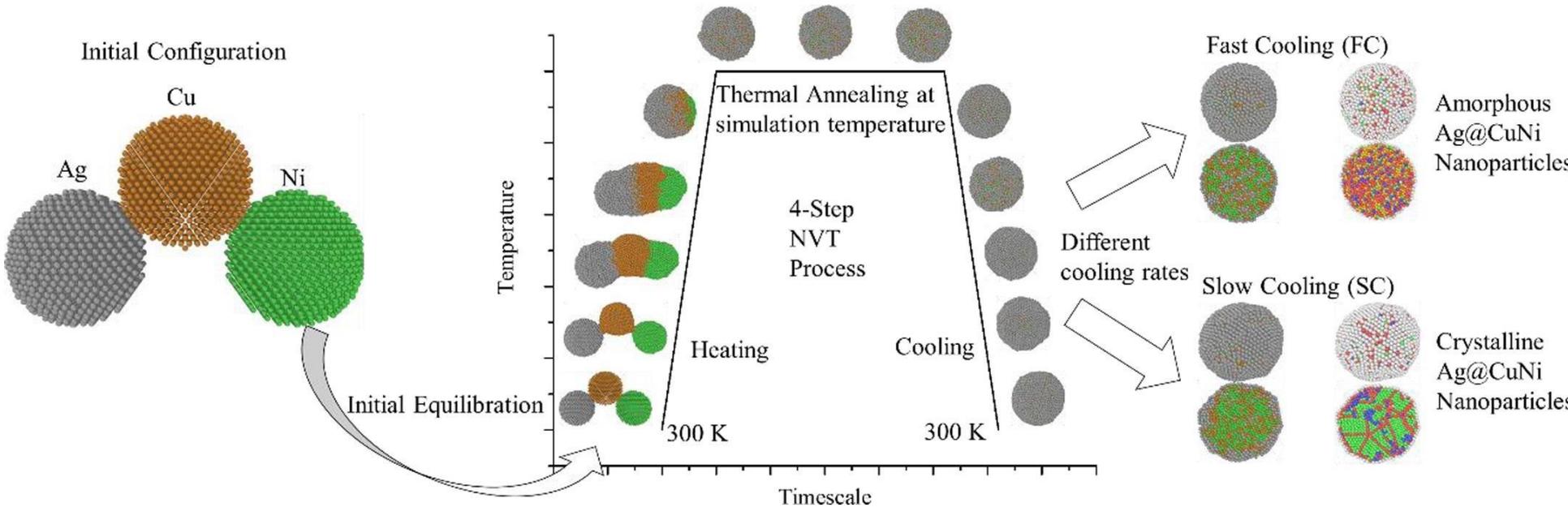


Itina, T. E. LASE, Phot. West. (2024).

**Alloy miscibility plays a role even for fast heating.  
Very fast cooling allows one to create/quench non-equilibrium  
structures.**

# Sintering vs Alloying, High-Entropy Alloys

AgCuNi, 10,843 atoms

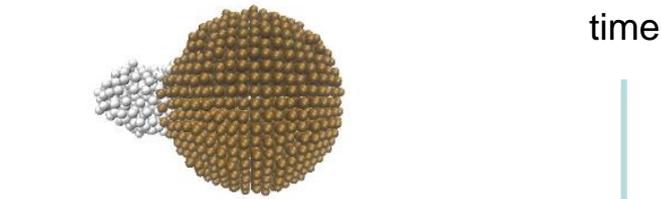


For cooling simulations, full timescale was studied. Right, cooling part investigated with 2 cooling rates, fast cooling (FC),  $1 \times 10^{13} \text{ K s}^{-1}$  and slow cooling (SC),  $1 \times 10^{11} \text{ K s}^{-1}$

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

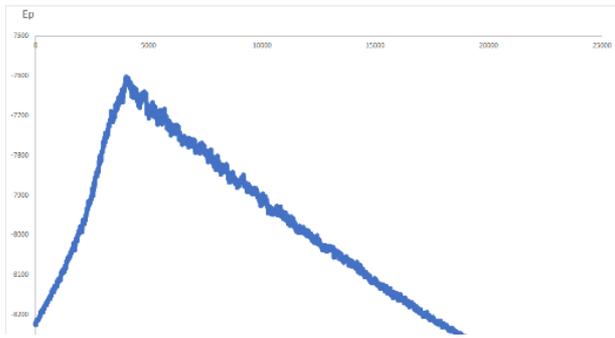
# NP Sintering or Alloying

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



Different sizes and species, but the same temperatures

Time-evolution of energy



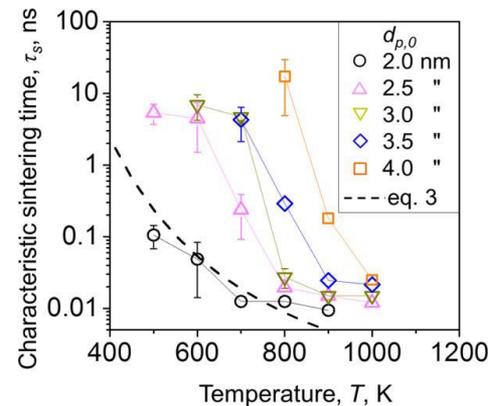
time

100ps



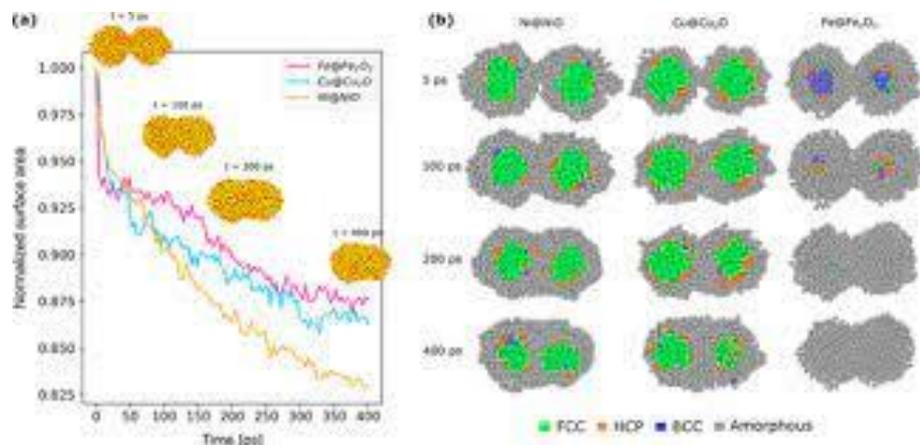
- Simulation starts from a Janus configuration
- Then both particles are heated to the same temperature
- Then, the system is cooled down back to room temperature

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

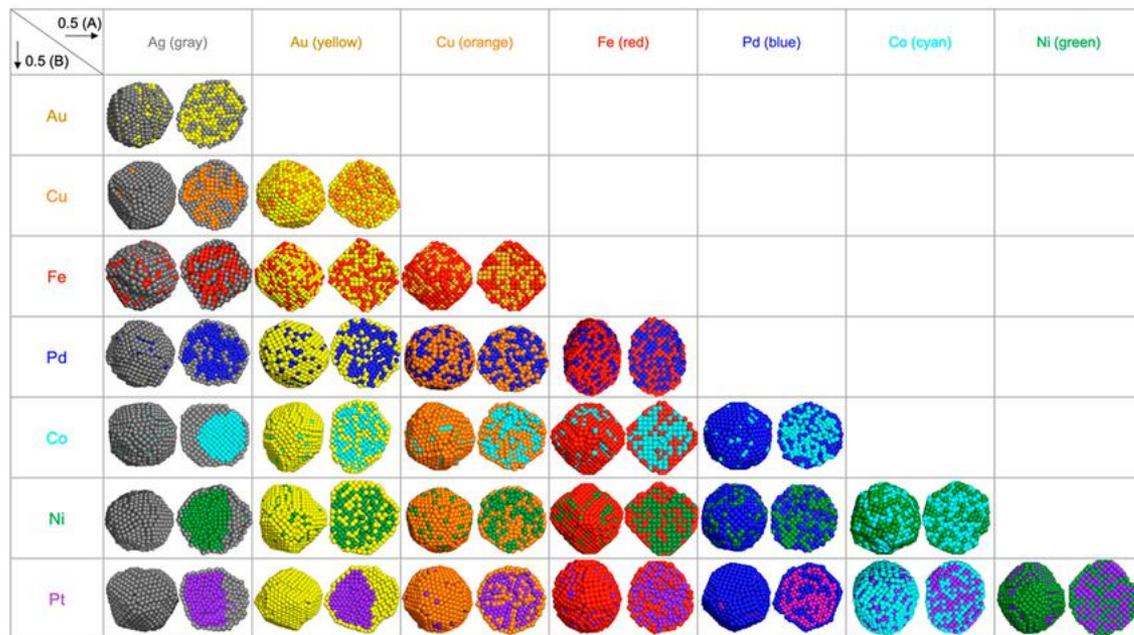
# General Trends For Bimetallic Nanoparticles



*J. Phys. Chem. C* 2021, 125, 29, 16220–16227

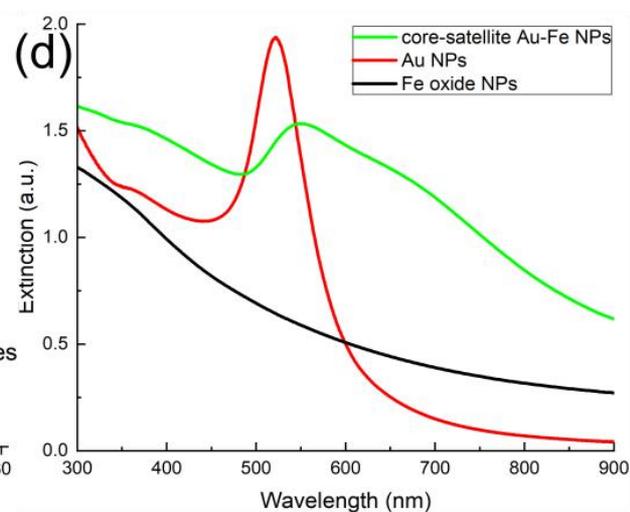
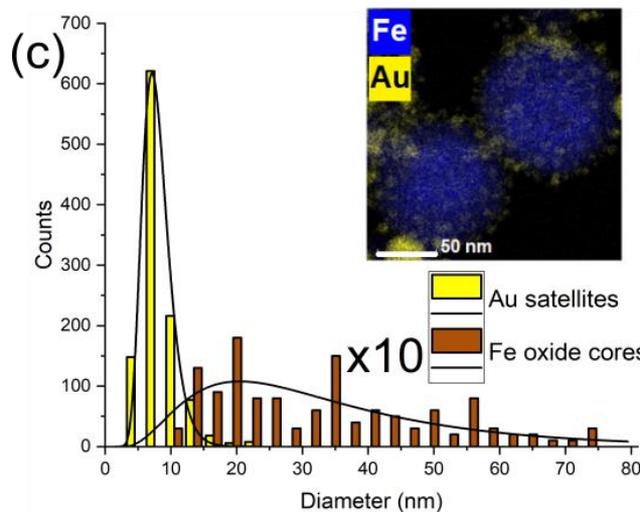
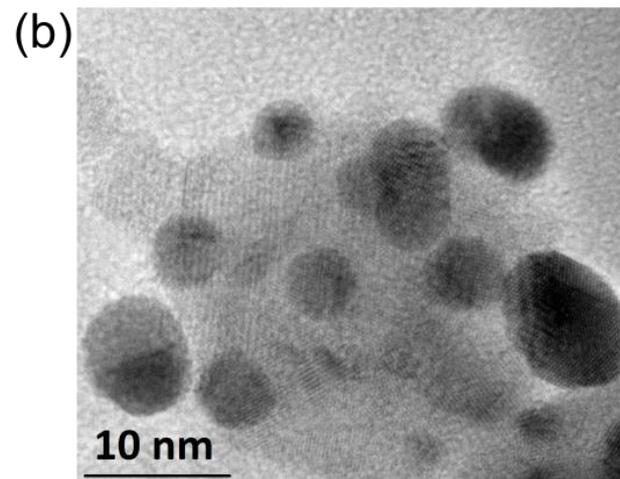
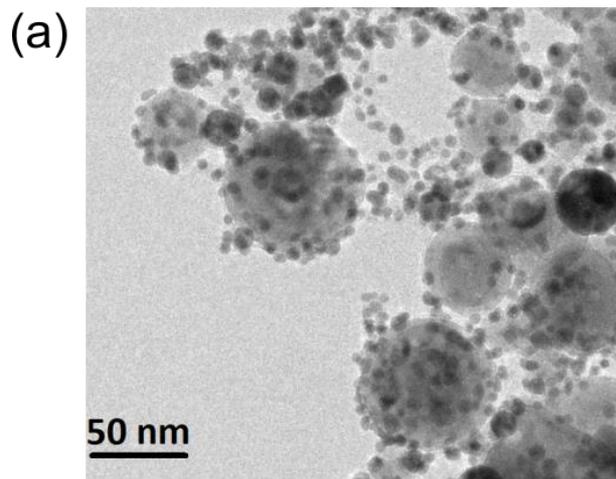
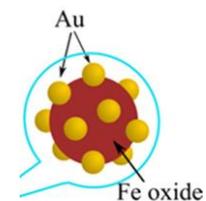
Namsoon Eom et al., Lund University

When the element with the higher **cohesive energy** also has the larger Wigner-Seitz **radius**, its core preference decreases, and thus this combination forms less segregated structures than what one would expect from the cohesive energy difference alone.



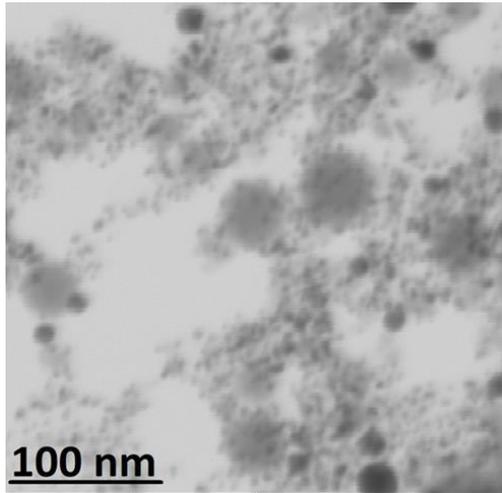
**Highly segregated structures (highly segregated core-shell or Janus-like) are expected to form when both the relative cohesive energy difference is greater than ~20%, and the relative Wigner-Seitz radius difference is greater than ~4%.**

# Core-shells and Nanohybrids

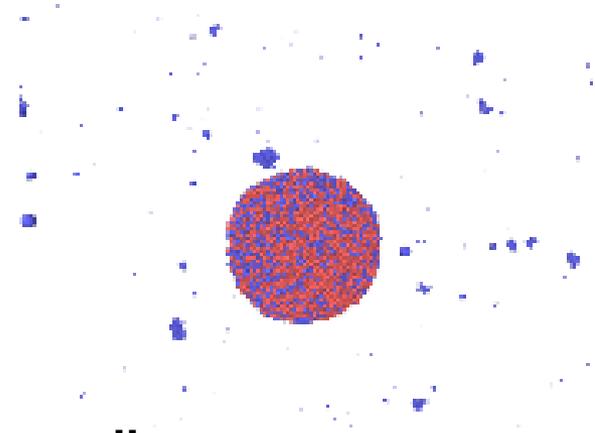
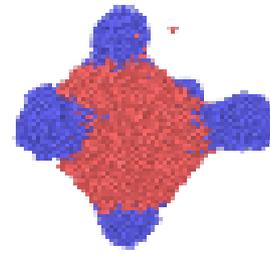


see talk by [Anton Popov et al. CECAM 2021](#)

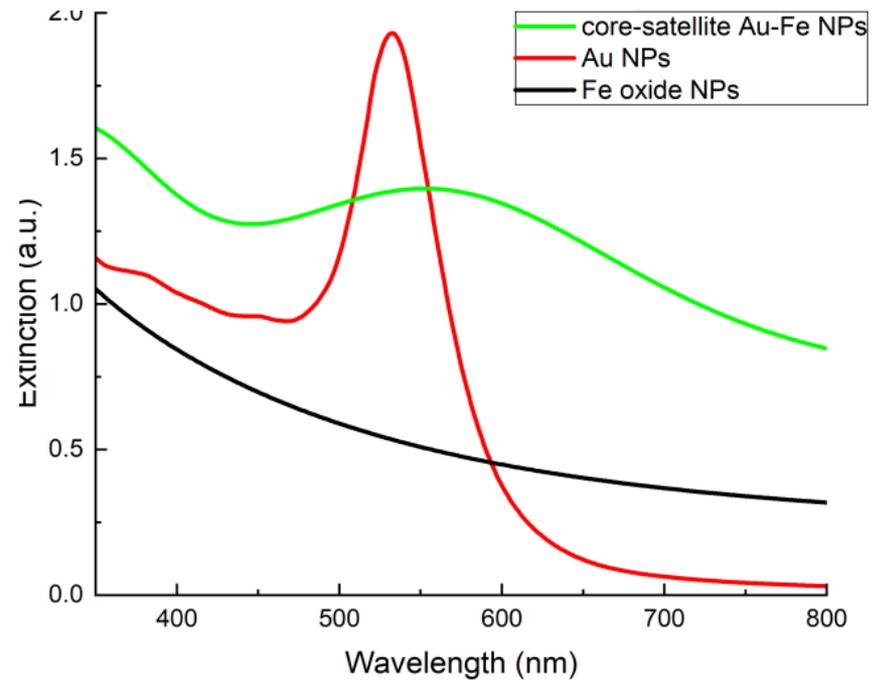
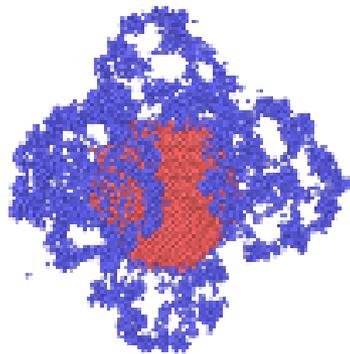
# Complex Nano-Objects Formation by Laser Co-Ablation



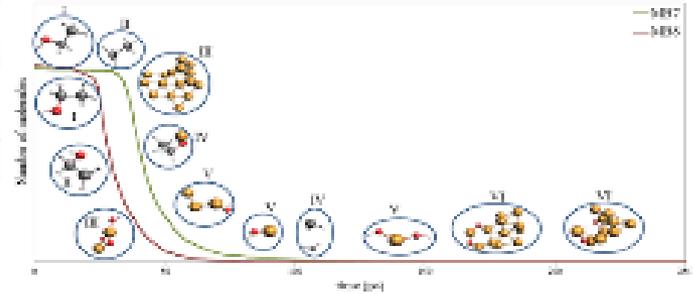
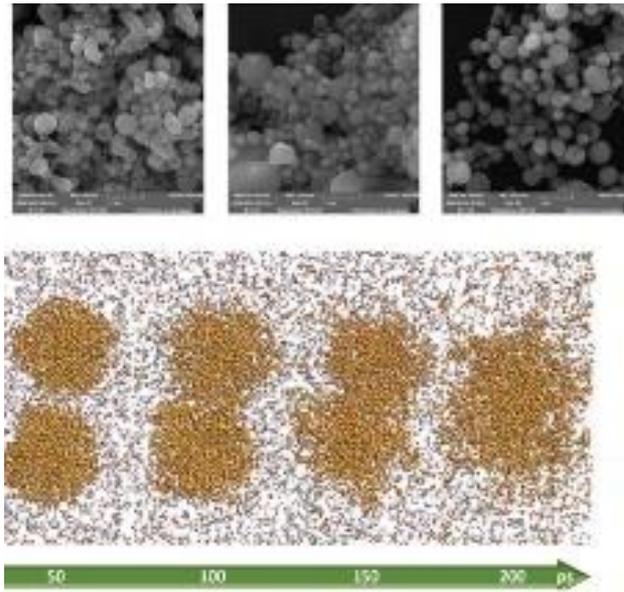
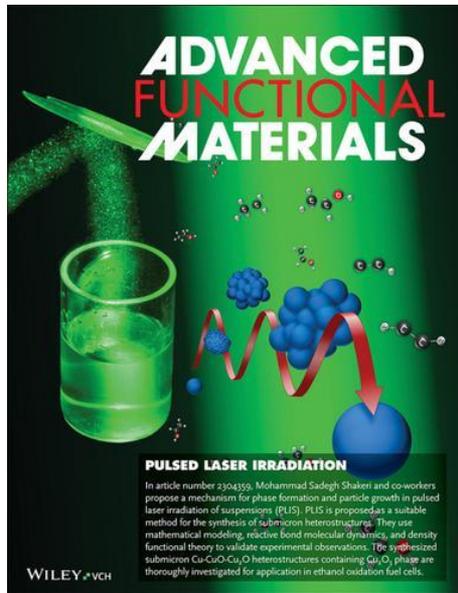
STEM image of nanostructures, Au-Fe



Raspberry-like, core-shells or alloys



# Laser Interactions with NP in Ethanol: Surface Chemistry



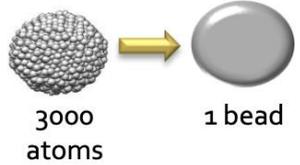
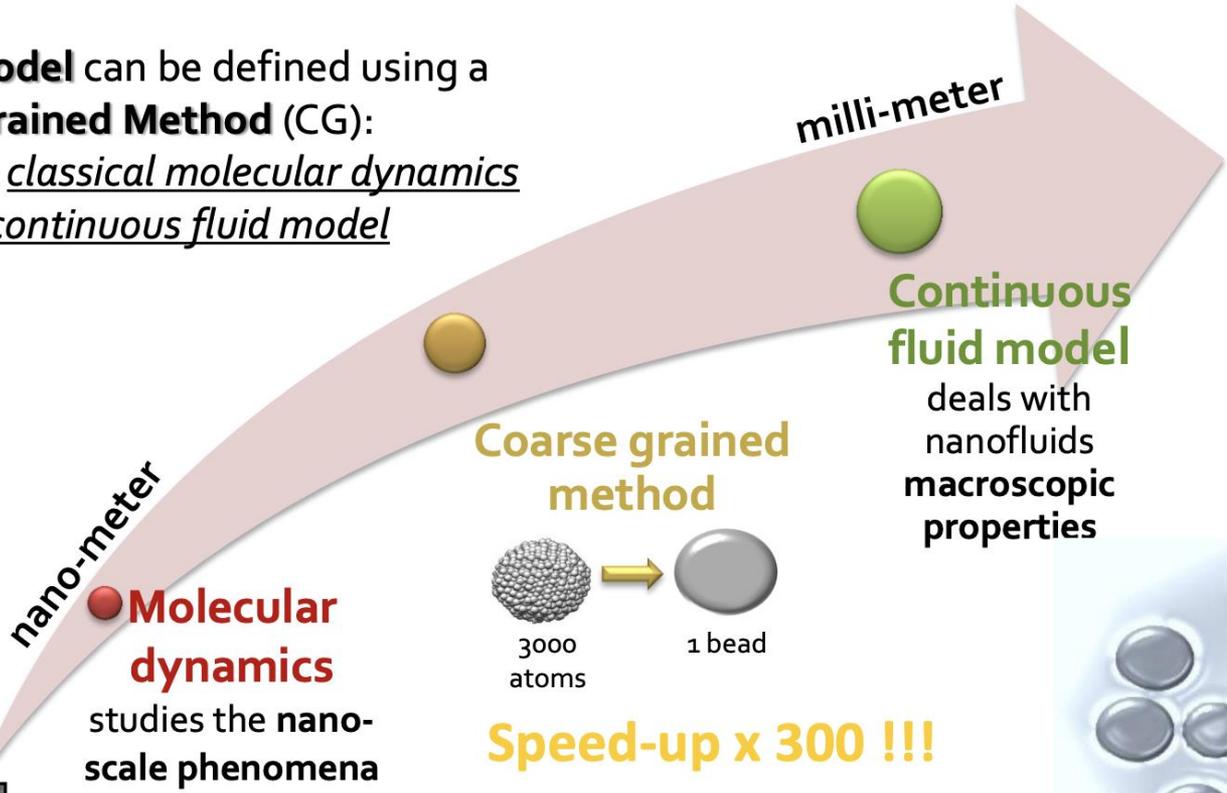
**Reactive bond molecular dynamics and DFT**

Beyond the physical transitions, the local interface between dissociated ethanol and the molten sphere is responsible for **the oxidative/reductive interactions** resulting in the formation of catalytic-augmented Cu<sup>3+</sup> by-product.

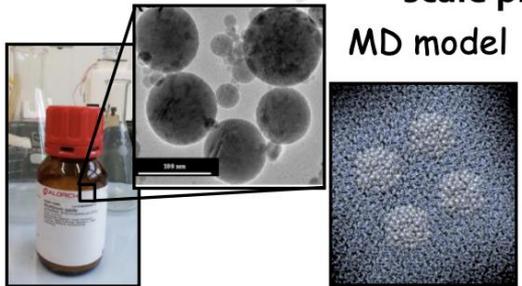
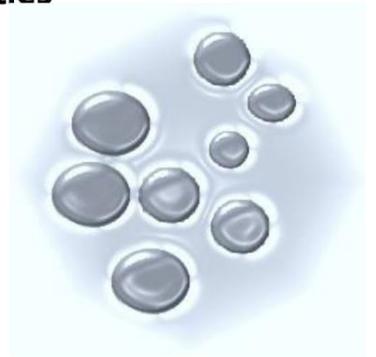
Shakeri, M. S. et al. (2023). *Advanced Functional Materials*, 33(43), 2304359

# Future: MULTISCALE MODELLING APPROACH and/or IA ?

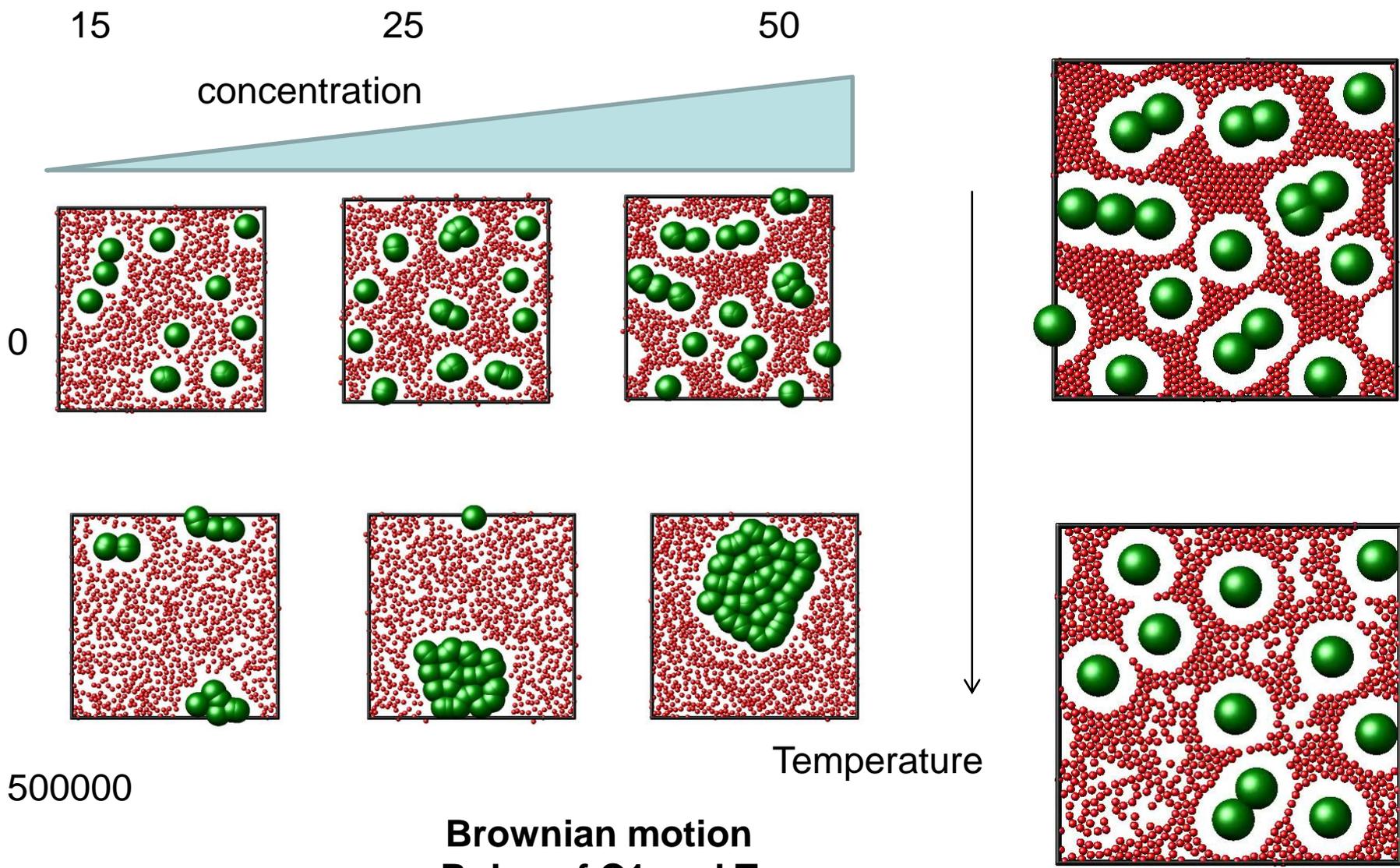
A multiscale model can be defined using a **Coarse Grained Method (CG)**:  
a bridge between *classical molecular dynamics* (MD) and *continuous fluid model*



**Speed-up x 300 !!!**



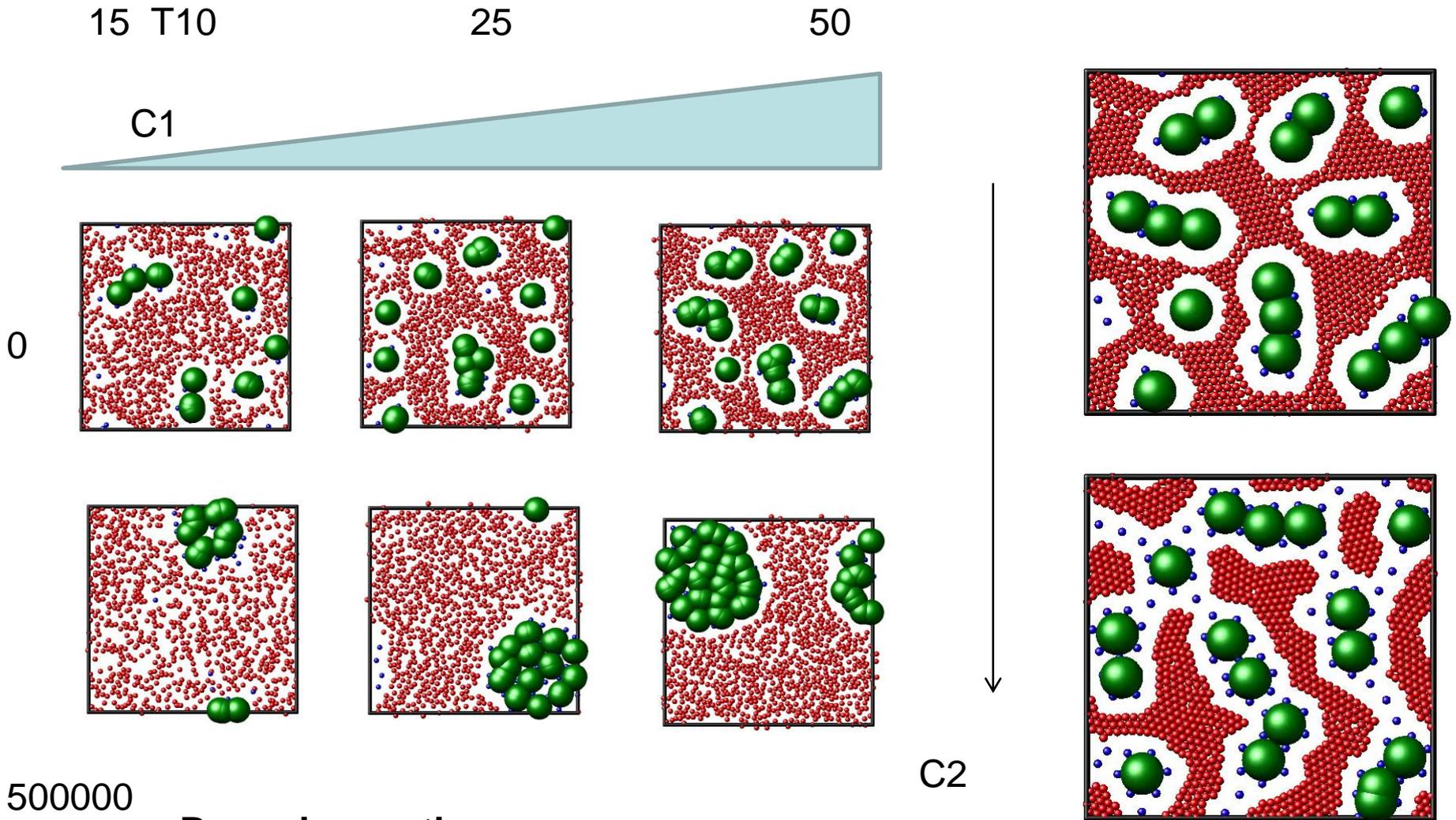
# MD simulation of NP's ensembles: aggregation



**Brownian motion**  
**Roles of C1 and T**

L-J potentials here, but there also results with Yukawa

# MD simulation: adding one more component



**Brownian motion**

**Roles of C1, C2 and T**

L-J potentials here, but there also results with Yukawa

# Summary

- Can one predict/calculate NP size, distribution, amount?  
-To some extent if there is enough data.
- Are NP sizes different or similar for spark and for laser ablation ? –Can be rather similar, but there are differences.
- What parameters affect NP formation? -Absorbed energy, pressure, temperature, concentration, ...
- Can modeling explain experimental results? -Several examples have been shown.
- AI will also provide new perspectives.

## Special thanks to

**LASERMODE** former and actual group members and invited researchers in LabHC

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**NANOPARTICLES** group: **F. Vocançon, N. Destouches**

**LP3: K. Maximova, A. Kabashin, K. Gouriet**

**ITMO: Y. Andreeva, R. Zakoldaev, M. Sergeev:**

**IPN: Mohammad Sadegh Shakeri, Zaneta Swiatkowska-Warkocka, Oliwia Polit**

**Projects: EU, PICS, PHC**

**Organizations: CNRS, UJM, INP PAN, IHT  
CINES of France**

# Thank you very much!

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