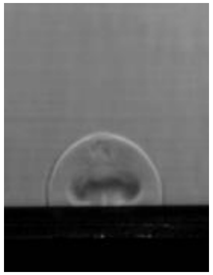
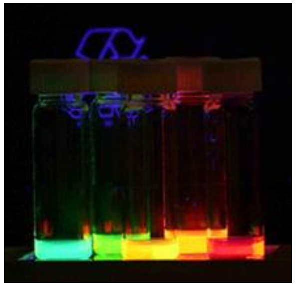
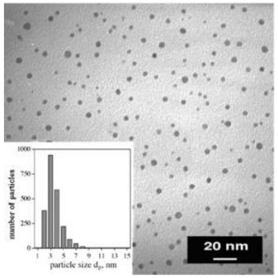
LASER-INDUCED NANOPARTICLE FORMATION IN LIQUIDS: INVOLVED MECHANISMS AND ROLE OF THE EXPERIMENTAL PARAMETERS

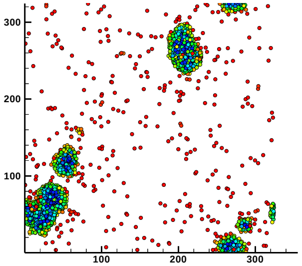
T. E. Itina,[1] L. Delfour,[1] A. Rudenko,[1]
K. Maksimova[2], A. V. Kabashin[2], M. E. Povarnitsyn[3],
A. A. Antipov,[4] S. Arakelyan,[4] S. Kutrovskaya,[4] and
A. Kucherik[4]

[1]Hubert Curien Laboratory, CNRS/Lyon University, Saint-Etienne, France
[2]LP3 Laboratory, CNRS/Aix-Marseille University, Marseille, France
[3]Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia
[4]Stoletov's Vladimir State University, Vladimir, Russia









tatiana.itina@univ-st-etienne.fr

OUTLINE

1. **Importance and motivation**
2. **Laser ablation in vacuum and in a background gas**

   -Shock waves (SW) and NP formation

3. **Laser ablation in liquids**

   -“Primary” particles: direct ejection, nucleation in bubble or in solution ?

   -Secondary” particles: evaporation/growth, coalescence, agglomeration

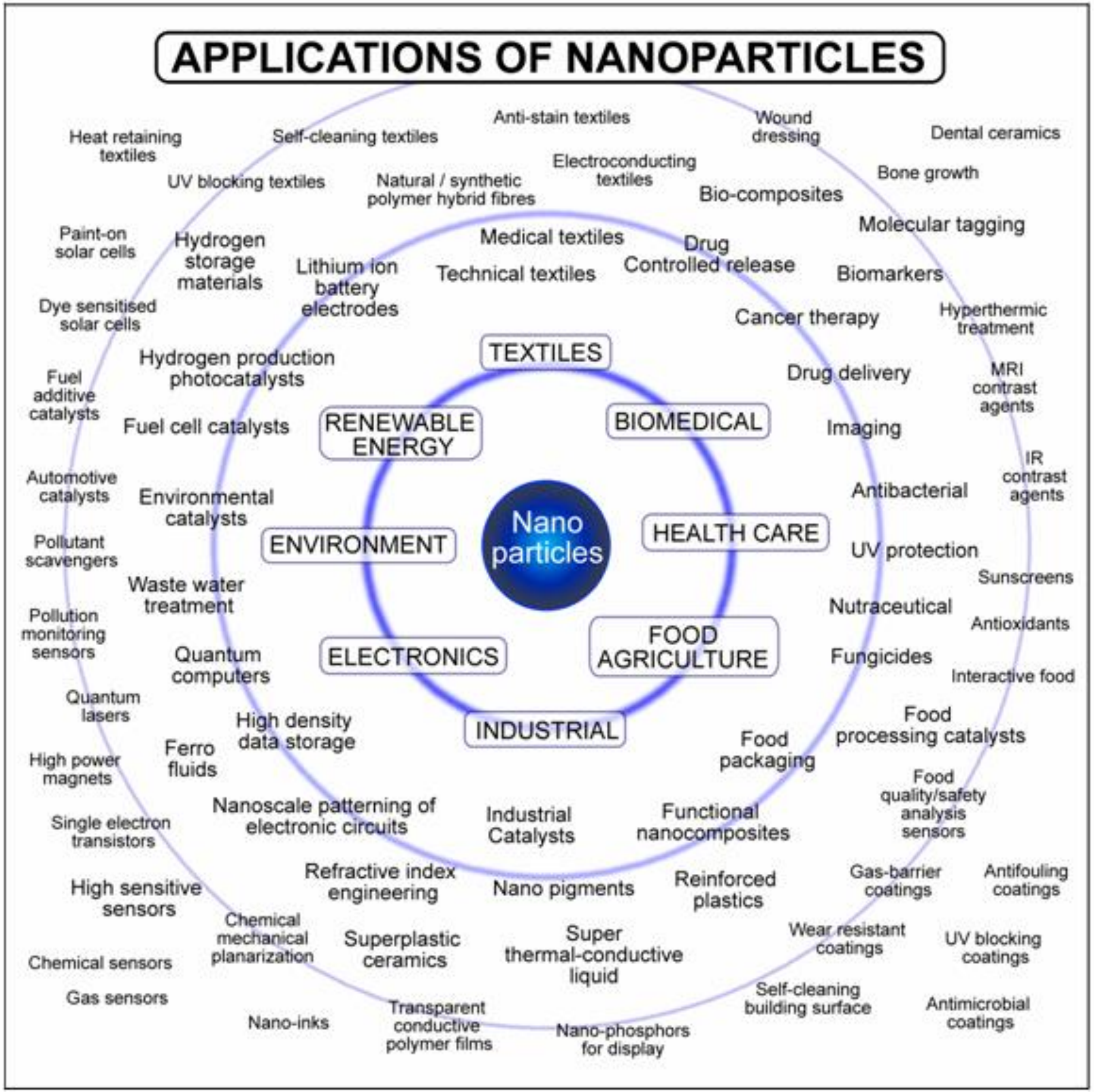
4. **Laser-induced particle size reduction and fragmentation**

   -Role of laser absorption by particles, fragmentation, stabilization

5. **Summary**

1. Importance and motivation

Motivation



APPLICATIONS OF NANOPARTICLES
Nano particles
TEXTILES
BIOMEDICAL
HEALTH CARE
FOOD AGRICULTURE
INDUSTRIAL
ELECTRONICS
ENVIRONMENT
RENEWABLE ENERGY
Heat retaining textiles
Self-cleaning textiles
Anti-stain textiles
Wound dressing
Dental ceramics
UV blocking textiles
Natural / synthetic polymer hybrid fibres
Electroconducting textiles
Bio-composites
Bone growth
Molecular tagging
Paint-on solar cells
Hydrogen storage materials
Lithium ion battery electrodes
Medical textiles
Technical textiles
Drug Controlled release
Biomarkers
Dye sensitised solar cells
Cancer therapy
Hyperthermic treatment
Hydrogen production photocatalysts
Drug delivery
MRI contrast agents
Fuel additive catalysts
Fuel cell catalysts
Imaging
IR contrast agents
Automotive catalysts
Environmental catalysts
Antibacterial
Pollutant scavengers
UV protection
Sunscreens
Waste water treatment
Nutraceutical
Antioxidants
Pollution monitoring sensors
Quantum computers
Fungicides
Interactive food
Quantum lasers
High density data storage
Food processing catalysts
Ferro fluids
Food packaging
High power magnets
Food quality/safety analysis sensors
Single electron transistors
Nanoscale patterning of electronic circuits
Industrial Catalysts
Functional nanocomposites
Refractive index engineering
Nano pigments
Reinforced plastics
Gas-barrier coatings
Antifouling coatings
High sensitive sensors
Chemical mechanical planarization
Superplastic ceramics
Super thermal-conductive liquid
Wear resistant coatings
UV blocking coatings
Chemical sensors
Gas sensors
Nano-inks
Transparent conductive polymer films
Nano-phosphors for display
Self-cleaning building surface
Antimicrobial coatings

Applications of Metallic Nanoparticles (NPs)

Plasmonic properties

-**Sensors**

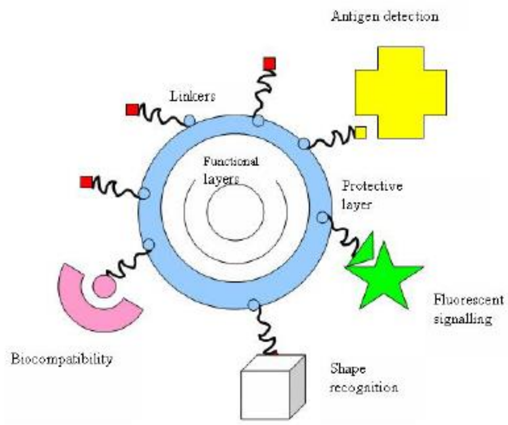
-**New generation of solar cells**

-**Cancer treatment** (photodynamic therapy, photo-thermal therapy, radiation therapy, drug delivery, etc…)

-**Diagnostic imaging** MRI (contrast agents), fluorescence Imaging, optical coherence tomography, opto-acoustic tomography, radionuclide Imaging, ultrasound imaging

-**Antiseptics and tissue engineering**

Green Chemistry ? ***Laser-produced colloidal NPs are chemically clean and biocompatible***

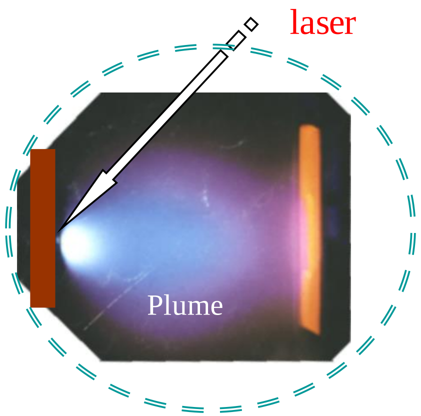


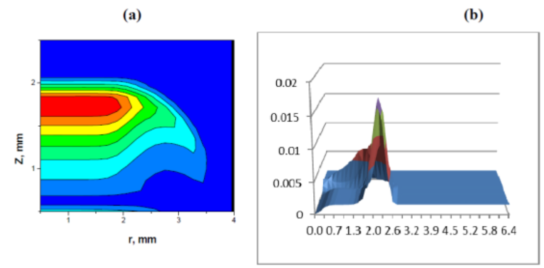
•*Photon-based nanoscience and nanobiotechnology, Nato Science Series Vol. 239*

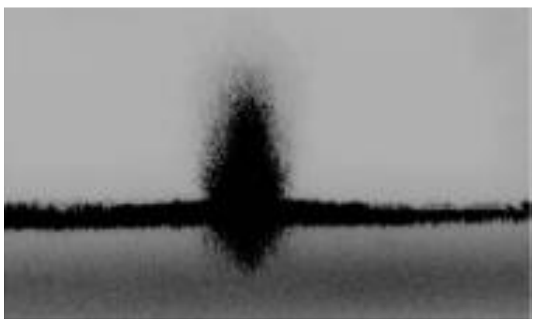
•*Journal of NanoBiotechnology*

Salata, 2004

Laser-assisted NP formation

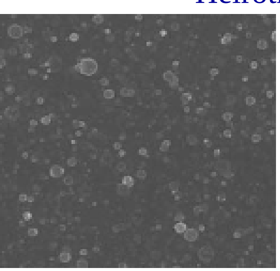




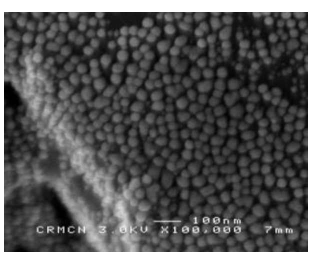


- Laser beam is focused on a target
- Target material is heated and ejected
- Nanoparticles are formed

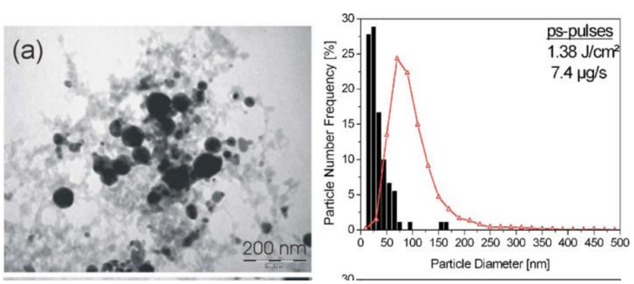
Heiroth et al. JAP 2009



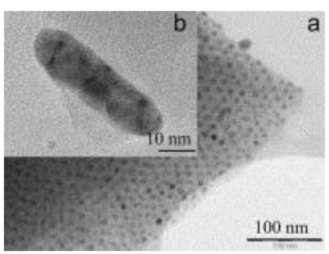
Deposited nanoparticles, Courtesy of Garrelie et al.



Nanoparticles produced on the target Kabashin et al.



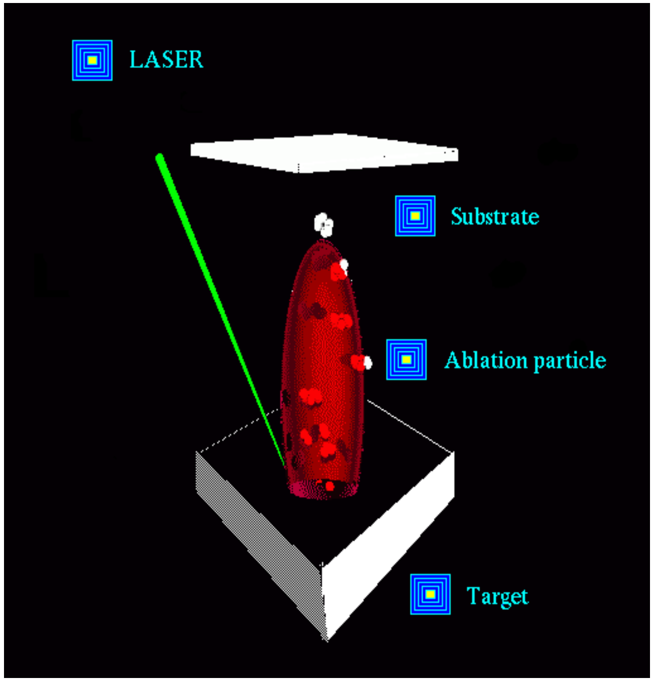
Colloidal nanoparticles Barcikowski et al. APL 2007



Sol-gel nanoparticle arrays Bois et al. J. Sol. State Chem. 2009

2. *Laser ablation in vacuum and in a background gas*

Processes involved



- Radiation absorption by target and by plasma
- Creation of regions with high T et P
- Propagation of pressure and thermal waves
- Phase transitions and material decomposition
- Ionization
- Ejection of electrons , ions and particles
- Plasma plume formation
- Collisions and chemical reactions
- Formation of clusters and nanoparticles (NPs)
- Emission
- More ...

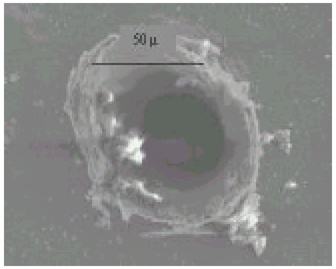
$\Rightarrow$ *Many physico-chemical processes*

$\Rightarrow$ *Depend on target material and laser source*

$\Rightarrow$ *Different time scales*

Role of Pulse Duration

NANOSECOND



•heat diffusion

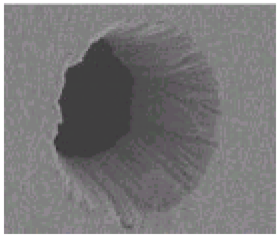
•melting

•boiling

•evaporation

$$J \sim \frac{p_b}{(2\pi k T m)^{1/2}} \exp\left\{ \frac{\Delta H_\upsilon(T_b) m}{k} \left(\frac{1}{T_b} - \frac{1}{T} \right) \right\}$$

FEMTOSECOND



• τ is shorter than τ_{ei}

•thermal conductivity during the pulse is negligible

•strong pressure gradients

•less energy is transformed into heat and more into motion

★ **Ablation mechanisms ?**

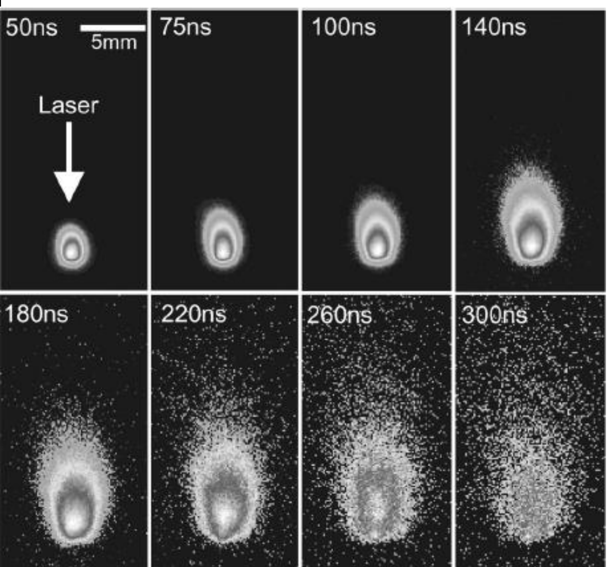
Nanosecond Laser Pulses

In vacuum

In a gas

Low pressure

Atmospheric pressure



Harilal et al, JAP 2003

Nd/YAG laser (8 ns, 700 mJ, Al target)

J. Appl. Phys., Vol. 93, No. 5, 1 March 2003

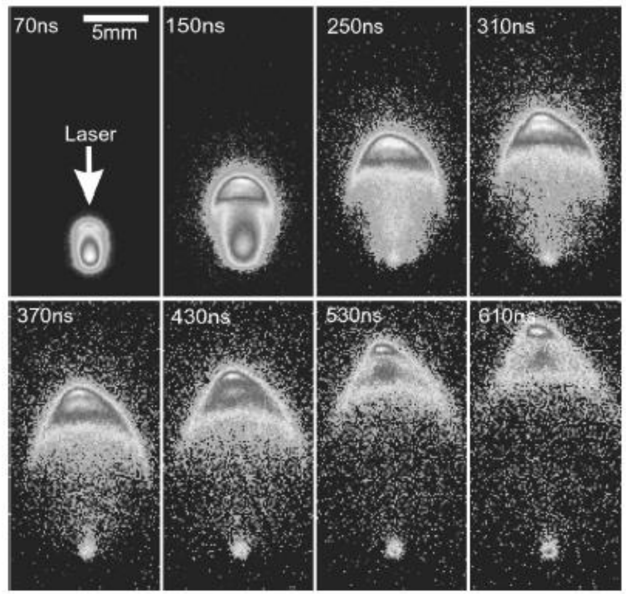
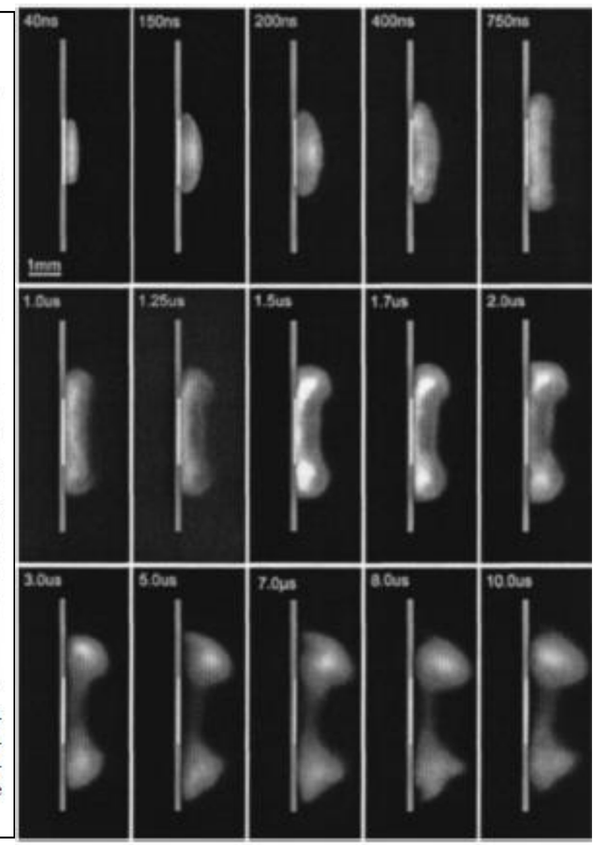


FIG. 4. ICCD photographs of visible emission from laser-produced aluminum plasma at 150 mTorr background air pressure. The experimental parameters are the same as described in Fig. 2. All of the images are normalized to their maximum intensity. Plume splitting and sharpening are observed in this pressure regime.



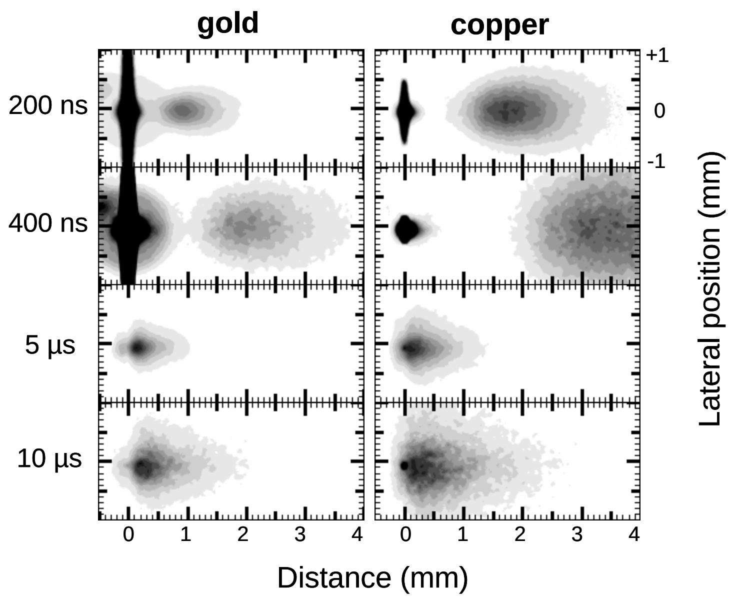
Pereira *et al.* XeCl, 30 ns, 10 J/cm2, steel

J. Appl. Phys. **98**, 064902 (2005)

Stoichiometry is better preserved than in SD!

Femtosecond Laser Pulses

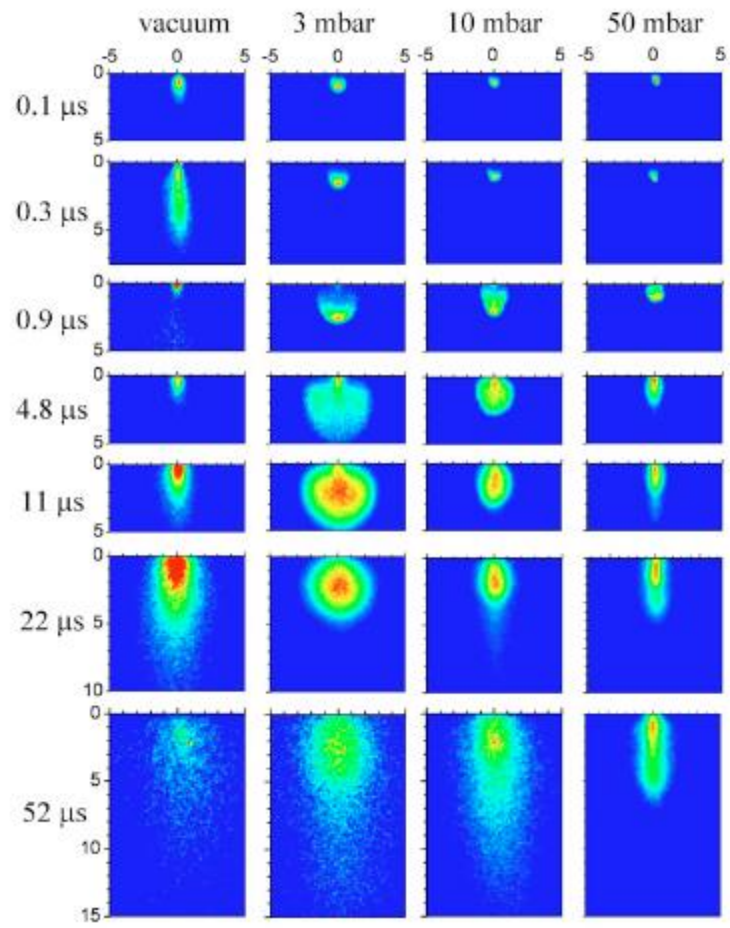
In vacuum



Plume images recorded during ablation of gold and copper for several times and a laser fluence of 4 J cm^{-2}

Hermann et al., Laser Phys. 2008

In a gas



Plume images recorded during ablation of Fe in a background gas

Amoruso et al, APL 2008

Two components were also observed

- by Garrelie et al. for fs ablation of carbon in vacuum (2001)
- By Grojo et al for fs ablation of Ti, Zr, Hf in vacuum (2002-2003)

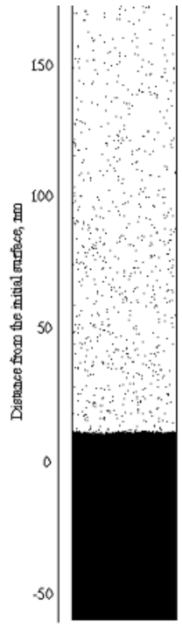
NP’s formation in vacuum

Molecular dynamics simulations

Longer laser pulses (>ns)
Small laser intensity

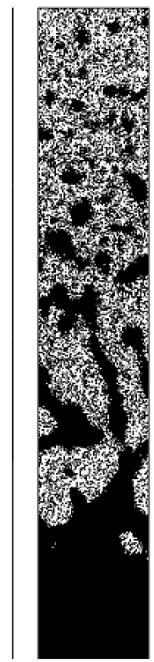
Laser

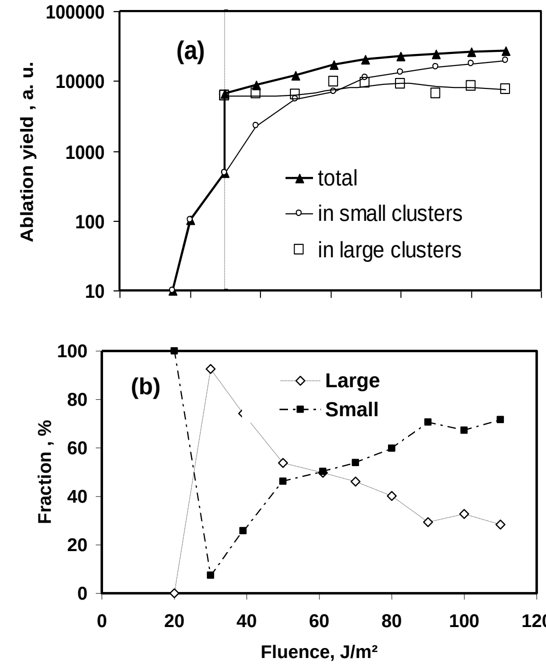
Target



+ nucleation/growth in the plume via condensation, coalescence and/or aggregation

Short laser pulses (ps, fs)
High laser intensity





⇒**direct ejection** of nanoclusters

⇒the higher is F the smaller are the particles

J. Phys. Chem. B , **106**, 303-310 (2002)

Two temperature hydrodynamics

$$\frac{\partial V}{\partial t} - \frac{\partial u}{\partial m} = 0, \qquad (1)$$

$$\frac{\partial u}{\partial t} + \frac{\partial (P_i + P_e)}{\partial m} = 0, \qquad (2)$$

$$\frac{\partial e_e}{\partial t} + P_e \frac{\partial u}{\partial m} = -\gamma_{ei}(T_e - T_i)V + Q_L V + \frac{\partial}{\partial m}\left(\kappa \frac{\partial T_e}{\partial z}\right), \qquad (3)$$

$$\frac{\partial e_i}{\partial t} + P_i \frac{\partial u}{\partial m} = \gamma_{ei}(T_e - T_i)V. \qquad (4)$$

- *2T Lagrangian hydrodynamics*
- *2T semi-empirical equations of state (for metal, gold here)*
- *Electron-ion coupling*
- *Thermal conductivity*
- *Wide range permittivity*

$$\nu_{\text{eff}} = \min(\nu_{\text{met}}, \nu_{\max}, \nu_{\text{pl}}) \qquad \gamma_{ei} = \frac{3 k_B m_e}{m_i} n_e \nu_{\text{eff}}$$

$$\kappa_{\text{met}} = \frac{\pi^2 k_B^2 n_e}{3 m_e \nu_{\text{eff},t}} T_e \qquad T_e << T_F$$

$$\kappa_{\text{pl}} = \frac{16\sqrt{2} k_B (k_B T_e)^{5/2}}{\pi^{3/2} Z e^4 \sqrt{m_e} \Lambda} \qquad T_e >> T_F$$

$$\kappa = \kappa_{\text{pl}} + (\kappa_{\text{met}} - \kappa_{\text{pl}}) e^{-A_4^t T_e / T_F}$$

$$\varepsilon = \varepsilon_{\text{pl}} + (\varepsilon_{\text{met}} - \varepsilon_{\text{pl}}) e^{-A_4^p T_e / T_F}$$

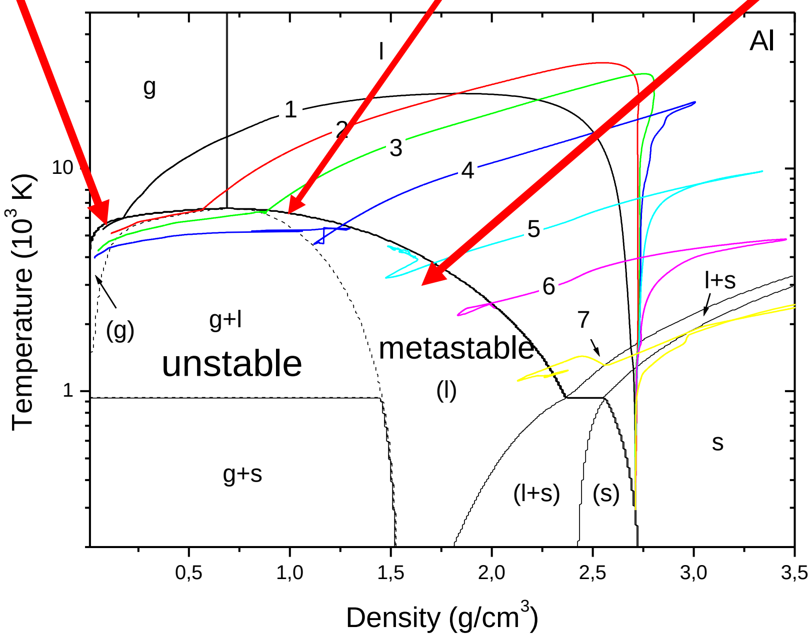
Thermodynamic analysis of laser ablation in vacuum

1-Phase explosion

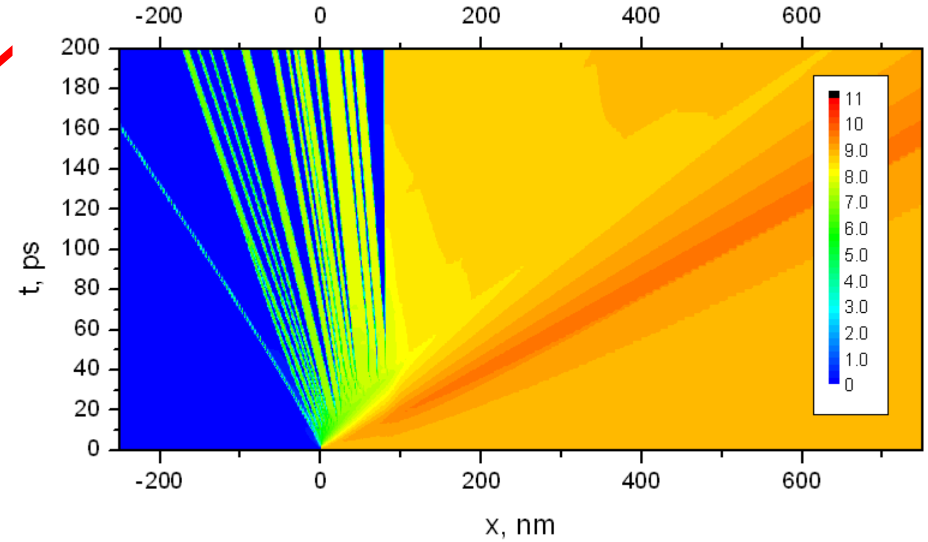
0.9Tc<T<Tc

3-Nucleation and condensation

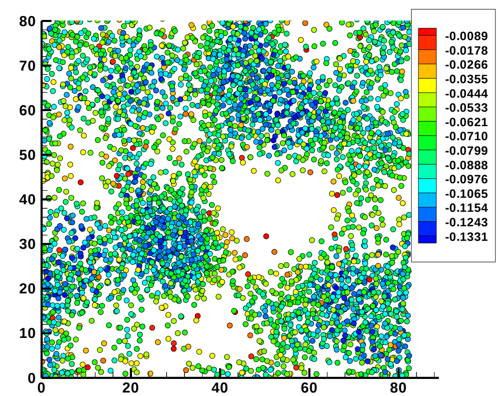
2- Fragmentation



τ_L = 100 fs, λ = *800 nm*, *F* = 5.0 J/cm^2



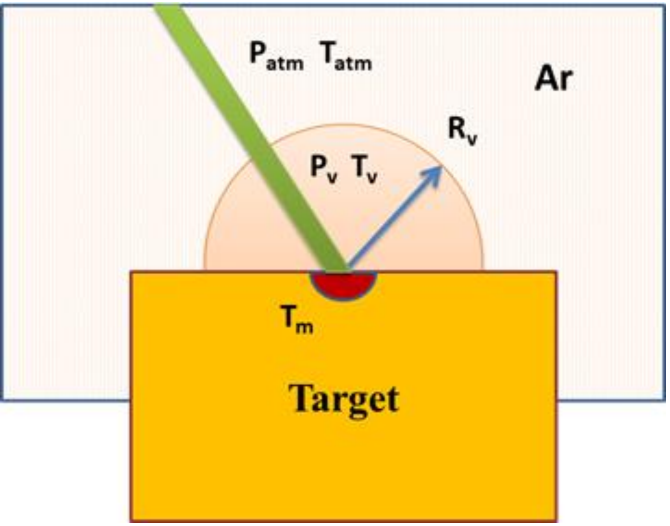
Phys. Rev. B , 75, 235414 (2007)



Chem. Phys. Lett. (2008)

- In vacuum, fragmentation of metastable liquid leads to the ejection of clusters an chunks
- What is the mechanism in liquid ?

In a gas: Shock wave



Shock wave (SW)
Estimation : 3D blast wave

$$R = \xi \left(\frac{2E_0}{\rho}\right)^{1/5} t^{2/5}$$

$$\frac{T}{T_0} = \left(\frac{V_0}{V}\right)^{\gamma-1} \Rightarrow T = T_0 \left(\frac{R_0}{R}\right)^{3(\gamma-1)}$$

$$T_{eq} = \left\{\frac{1}{T_b} - \frac{k}{Q}\ln\left(\frac{P}{P_0}\right)\right\}^{-1}$$

$$\theta = \frac{T_{eq} - T}{T_{eq}},$$ *see Zel'dovich & Raizer*

Supersaturation degree vs time:

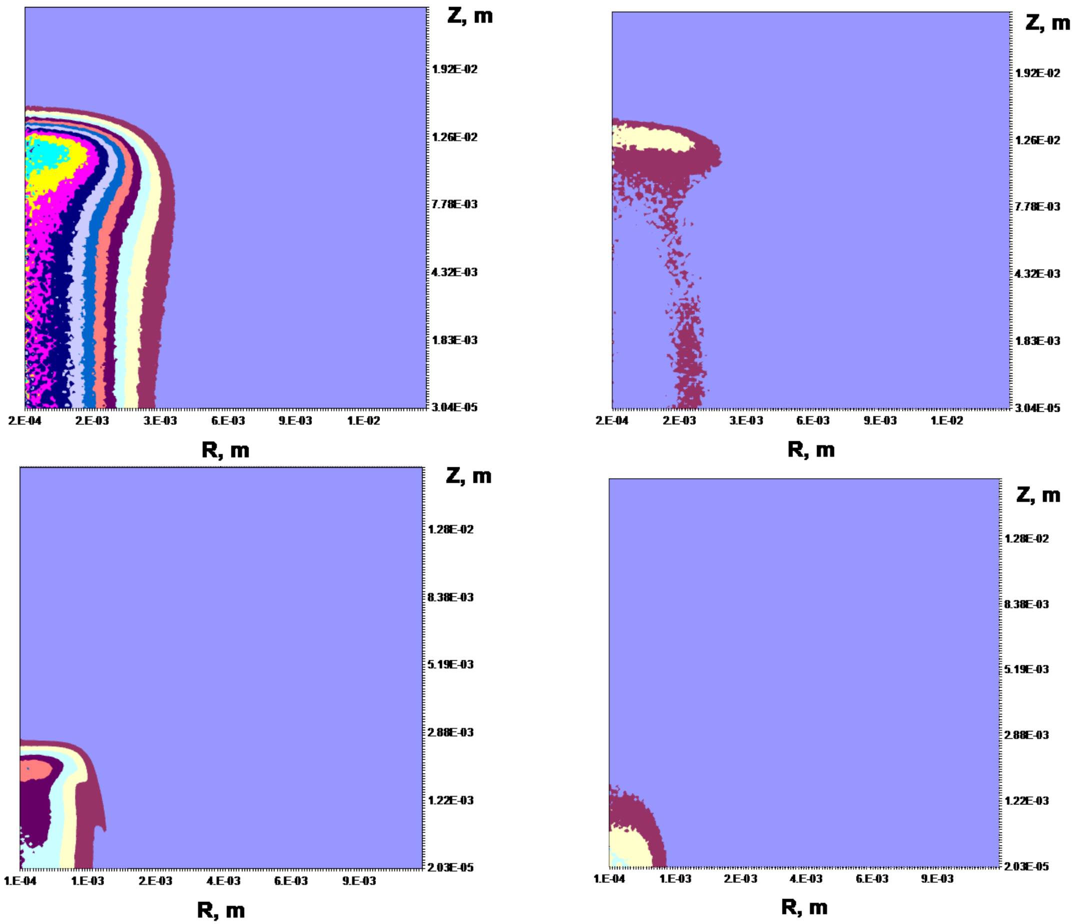
$$r^* = \frac{2\sigma v}{\theta k Q}$$

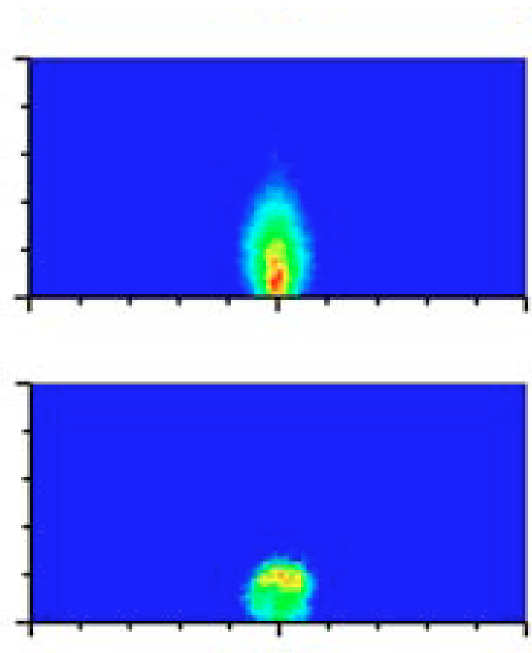
$$\theta = 1 - \frac{T}{T_{eq}} = 1 - T\left\{\frac{1}{T_b} - \frac{k}{Q}\ln\left(\frac{P}{P_{atm}}\right)\right\} =$$
$$1 - \frac{T_0}{T_b}\left(\frac{R_0}{R}\right)^{3(\gamma-1)}\left\{1 - \frac{kT_b}{Q}\ln\left[\frac{3*N_{tot}*k*T_0}{2*\pi*R^3*P_{atm}}\left(\frac{R_0}{R}\right)^{3(\gamma-1)}\right]\right\}$$

Itina, Voloshko, Appl. Phys. B 2013

Fs ablation in a gas : Plume contains NPs

atoms **nanoparticles**





Calculated plume dynamics for the Ni expansion **in Ar gas at 300 Pa**

up –density of clusters at **t=10 μs**

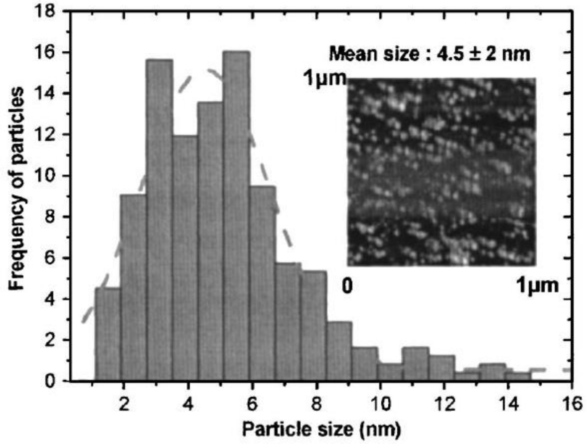
down–density of clusters at **t=0.55 μs**

Experiments:

Amoruso et al. Phys. Lett. 93, 191504 (2008)

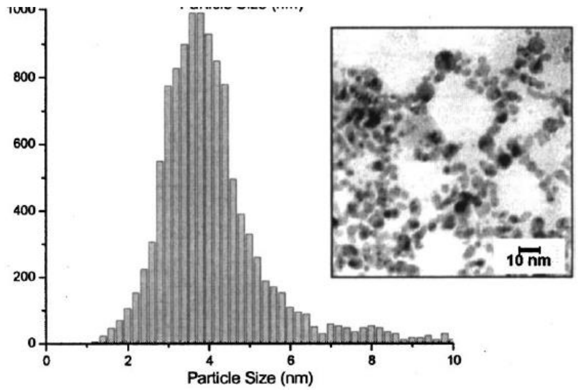
NP Size Distributions (in a gas or a liquid)

Laser ablation in air (ns)

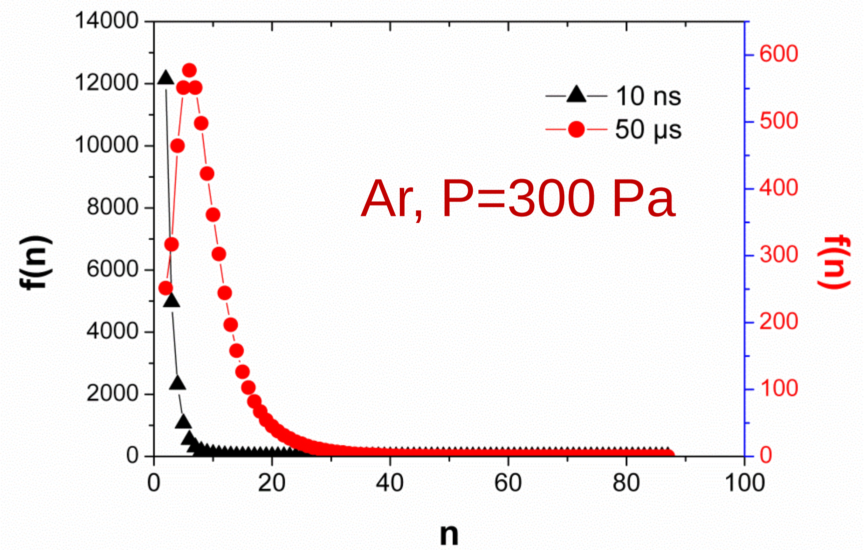


Pereira et al. AFM steel in air, 25ns F=10 Jcm^{-2}

Fs laser ablation in liquid



Kabashin et al. Au, TEM F=60 Jcm^{-2}



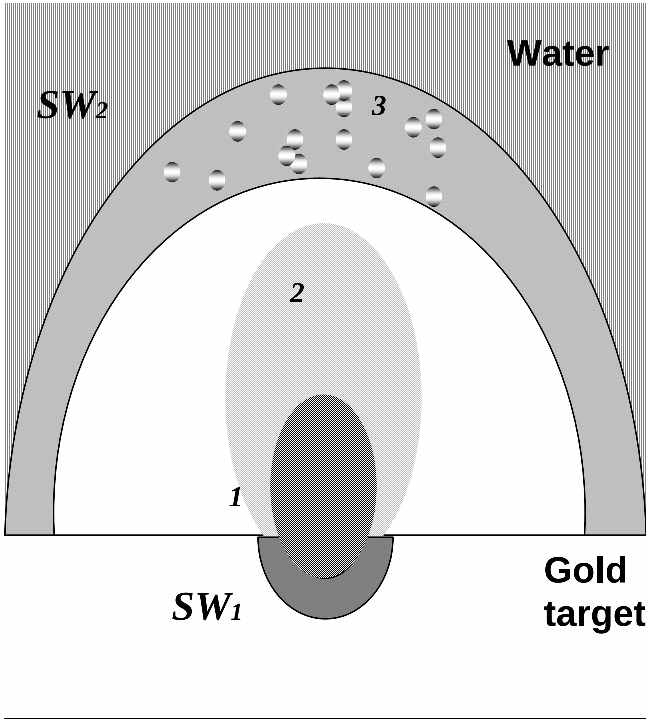
Background gas or liquid=> LogNormal functions

3. *Laser ablation in liquids*

-“Primary” particles: direct ejection, nucleation in bubble or in solution ?

-Secondary” particles: evaporation/growth, coalescence, agglomeration

NPs formation in liquids



1. **Early stage** – laser energy absorption, material ejection, plume formation

2. **Intermediate stage** – plume expansion in the presence of a confining liquid environment, formation of a cavitation bubble (CB)

3. **Late stage** – CB's collapse, plume mixing with the liquid, NP coalescence/aggregation processes.

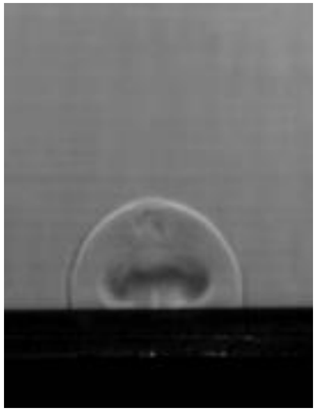
Main questions

⇒ **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 the presence of a liquid



-In a liquid=> different ablation threshold and yield

-shock wave formation, **but also**

-bubble formation

$\Rightarrow$ **Origin of "primary" particles?**

$\Rightarrow$ **"Secondary" particles will be formed later by coagulation, coalescence/aggregation**

$\Rightarrow$ **fragmentation**

$\Rightarrow$ **…**

Confinement by liquid

$$R_n(t)=\left\{R_{na}^3+\frac{R_{nb}^3-R_{na}^3}{2\tau}\left[t-\frac{\tau}{\pi}\sin\left(\frac{\pi}{\tau}t\right)\right]\right\}^{1/3}.$$

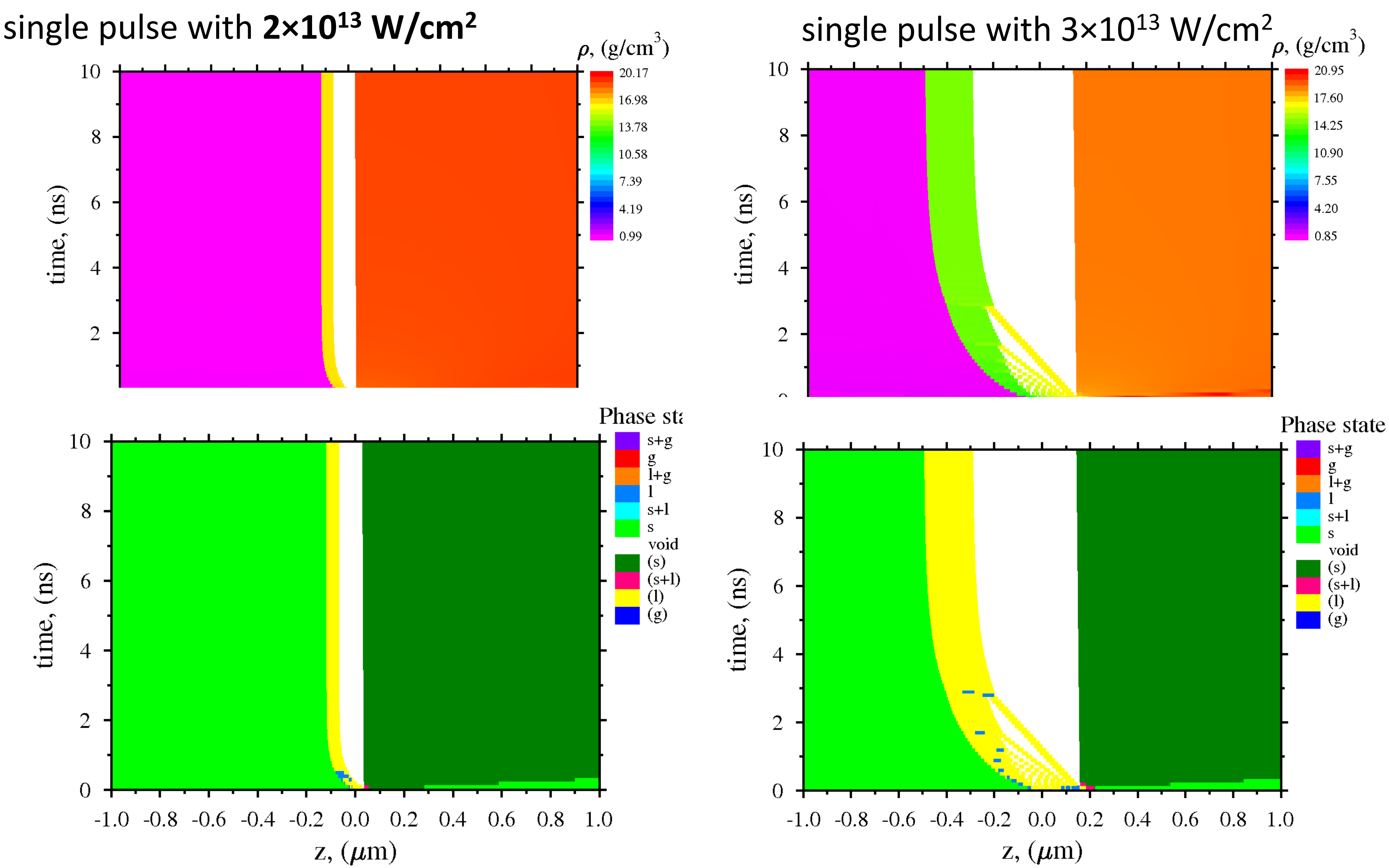
Vogel et al., J. Acoust. Soc. Am. 100(1), 1996

=>Hydrodynamic modeling

- ***Gold target in water***
- *2T semi-empirical equations of state (for metal, gold here)*
- *EOS for water*

$I(t)=I_0\exp(-4\ln 2\ t^2/\tau^2)$, **$\tau$=200 fs, 800 nm, I_0 = 2, 3, 4, 5 × 10^{13} W/cm^2**

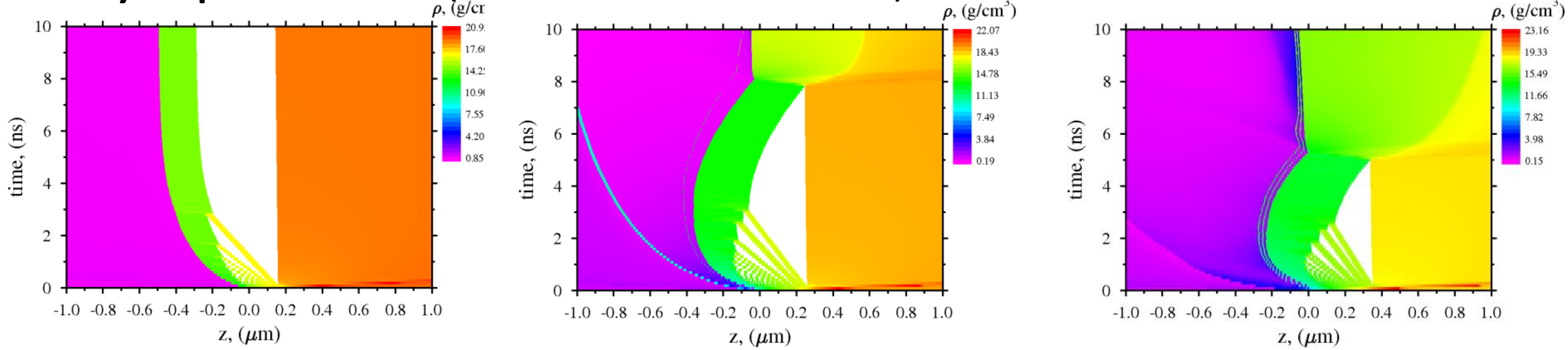
Single fs pulse, Au in water: simulation close to threshold



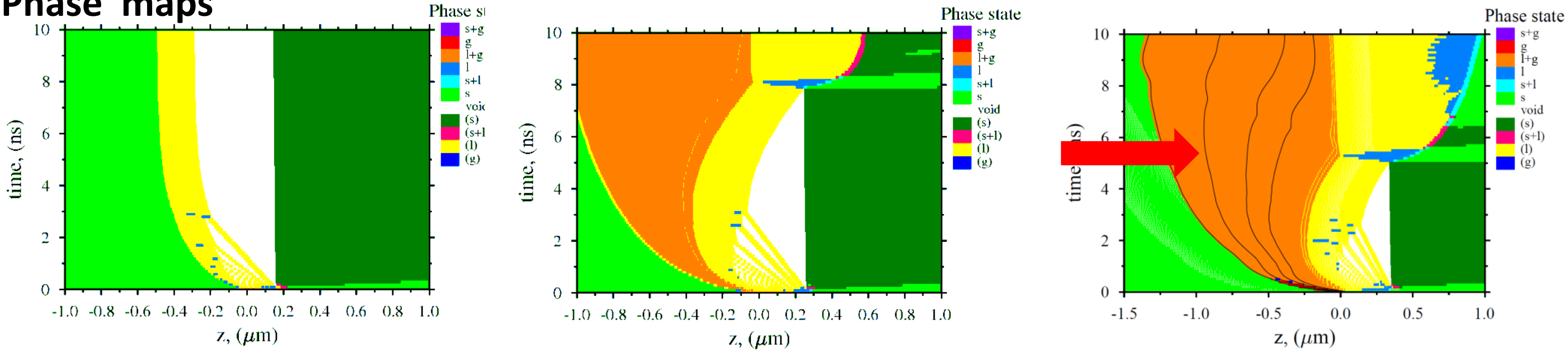
=> **Void formation, higher threshold, fragments cannot escape**

Increase in laser intensity

Density maps 3×10^{13} W/cm^2 4×10^{13} W/cm^2 5×10^{13} W/cm^2



Phase maps



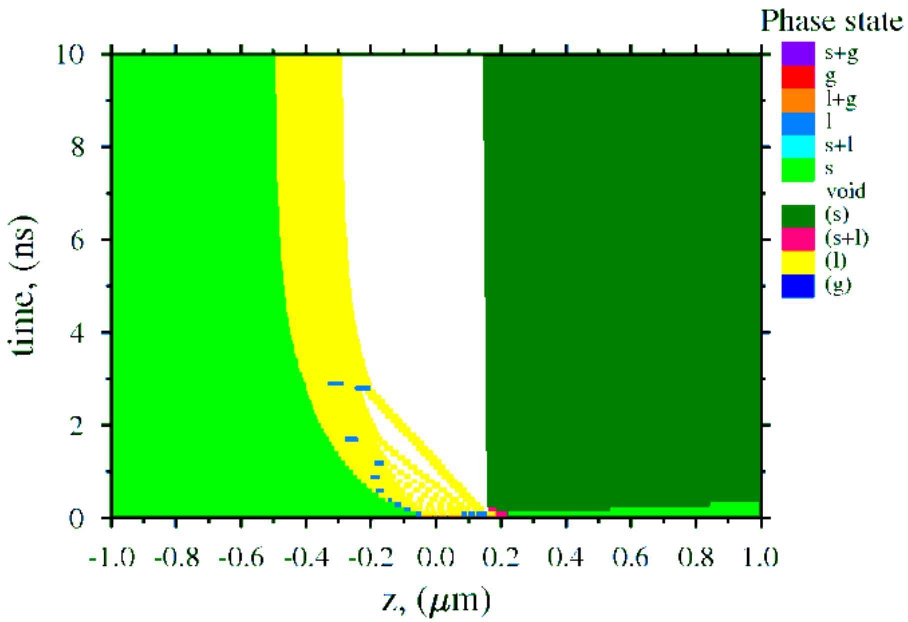
Near ablation threshold, ejected droplets stick together under the pressure

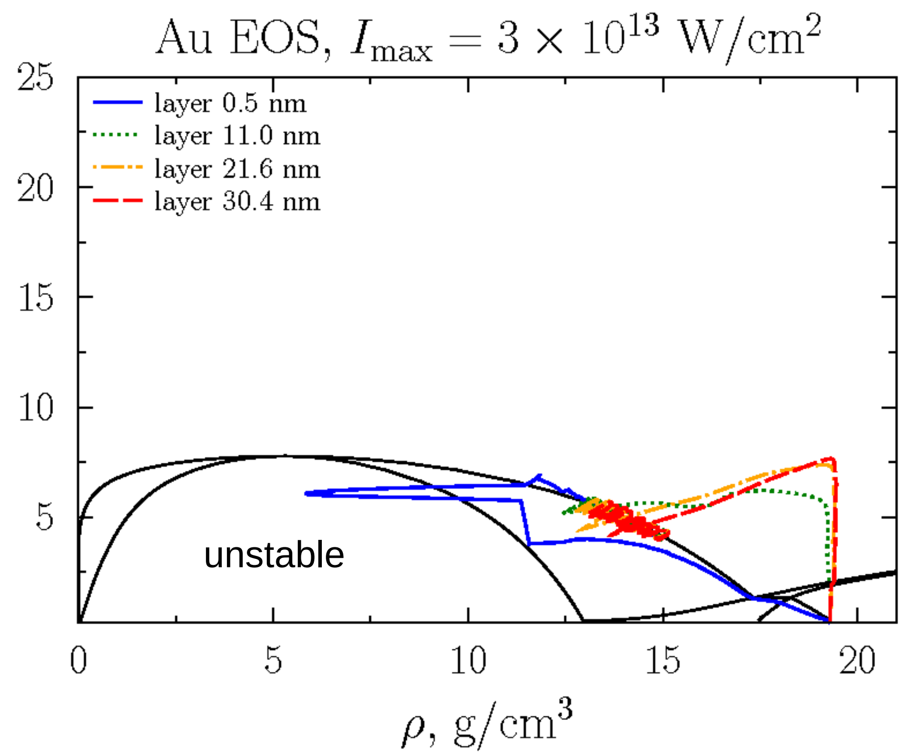
F>> **unstable liquid-gas phase (orange) extends** and presses liquid back (t=5ns)

=>NPs are formed in the unstable liquid+gas region (under spinodal)

rather then by condensation or fragmentation

Near ablation threshold

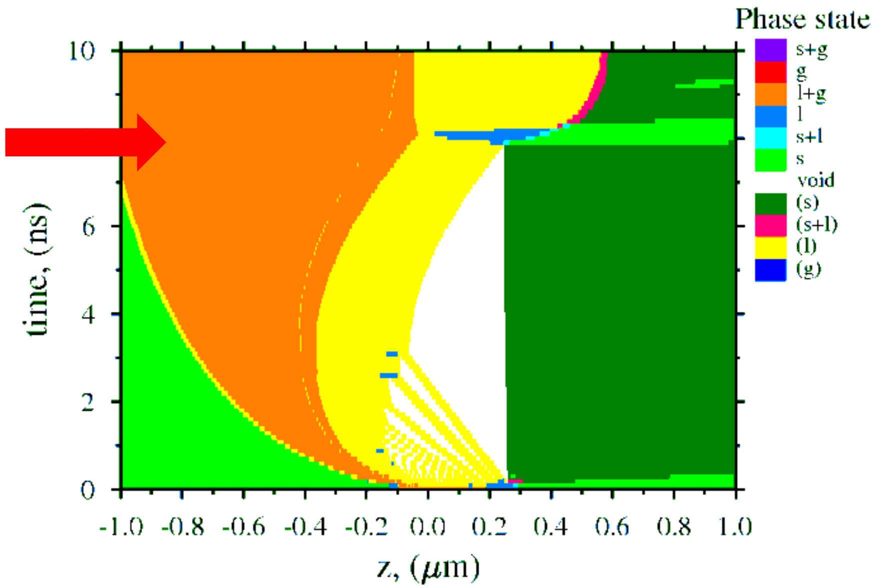


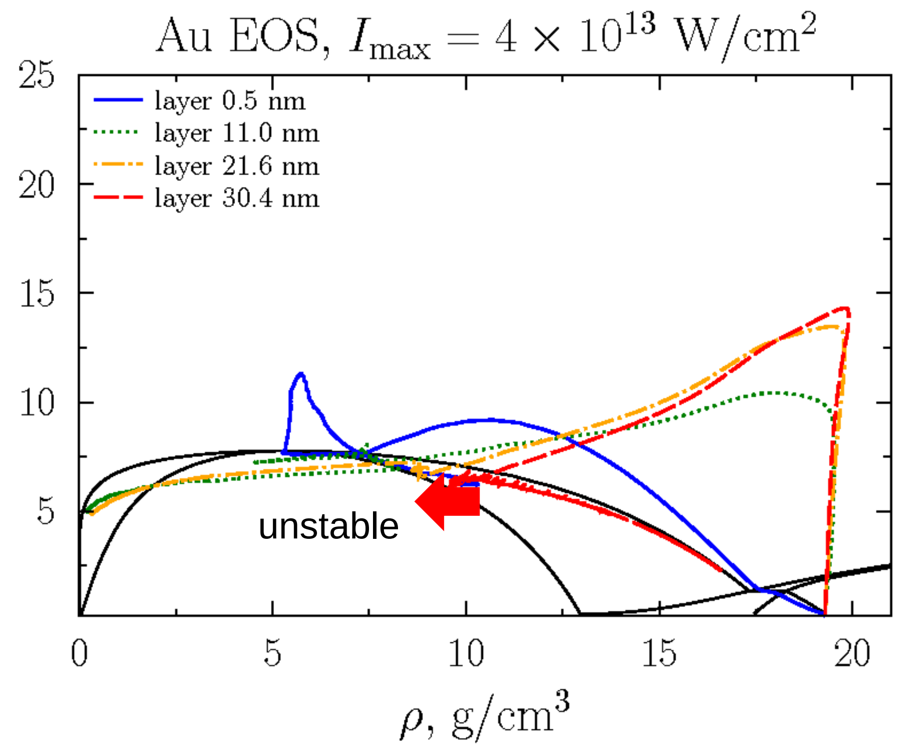


- Fragmentation does occur, but ambient liquid prevents the expansion
- The fragments stick together under the pressure of the ambient liquid

=> no NPs are expected

With the increase in laser fluence

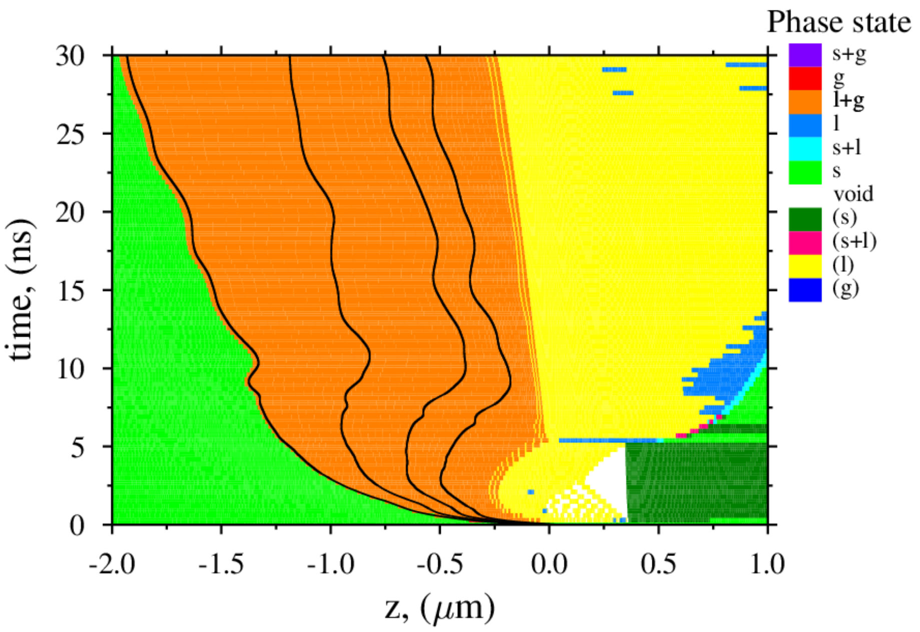


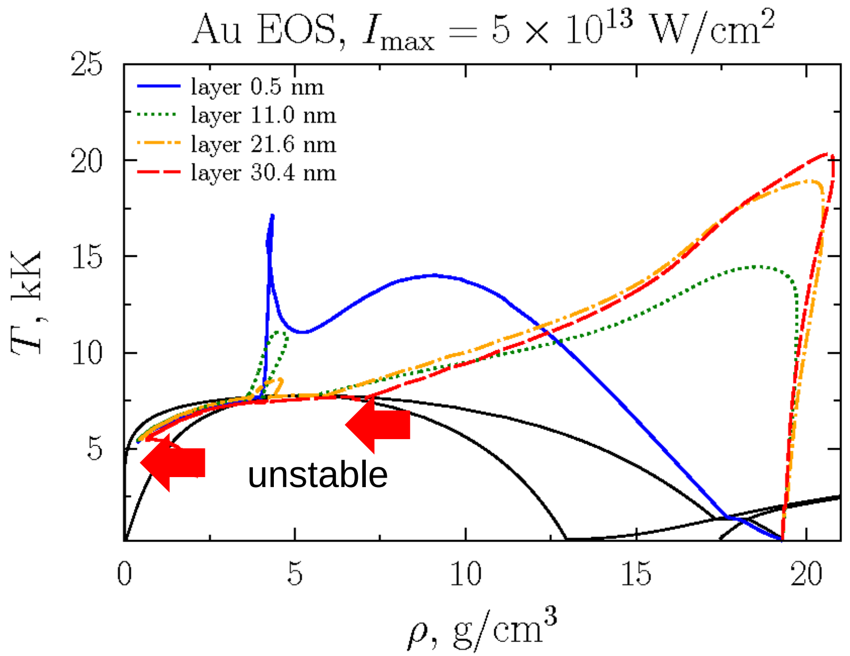


- Upper layers cross the spinodal and enter into unstable liquid-gas region (orange zone)=> **NPs can be formed here**

- Part of trajectories reach supersaturated gas region, where condensation takes place

Single pulse in liquid: large laser fluence



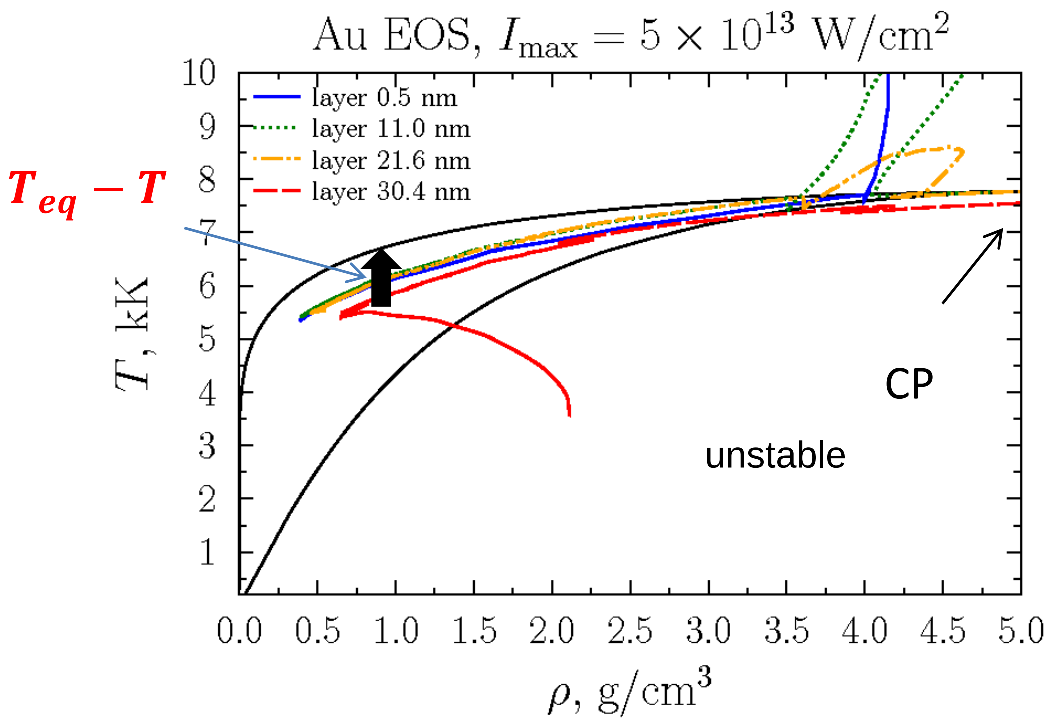


- more trajectories enter to the gas-liquid zone (orange region) **=> more important yield of « primary »NPs**
- In addition **condensation** takes place in the region of supersaturated vapor

=> Two generations of primary NPs: larger particles from unstable liquid-gas and smaller ones due to nucleation

Zoom into the region of supersaturation

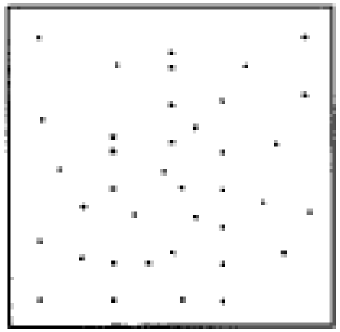
Phase trajectories for 4 layers, single pulse with 5×10^{13} W/cm^2



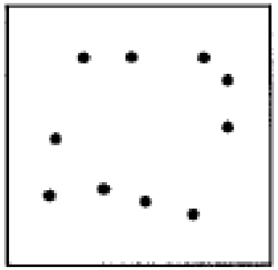
- **In the supercooled gas (SCG) region, saturation degree** $\Theta = \frac{T_{eq}-T}{T_{eq}} \in \{0.1, 1\}$
- **Nucleation, critical radius** $r_c = \frac{2\sigma\omega}{q\ \Theta_{max}}$~ 10^{-8}/$\Theta_{max}$ ~ 10 - 100 nm

Later stage: two processes

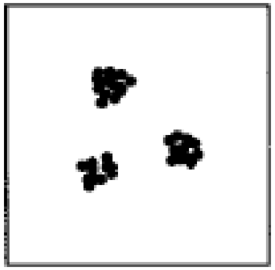
Supersaturated solution



1-nucleation
In liquid solution



2-coalescence/aggregation



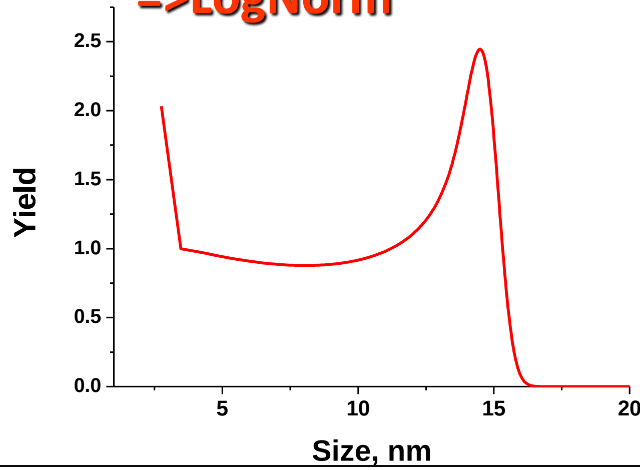
$$\rho(t) = K_c c^2 \exp\left[\frac{-\Delta G(n_c, c)}{kT}\right]$$

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

$$\frac{dN}{dt} = K_{S-1} N_1 N_{S-1} - K_S N_1 N_S \quad (s \geq 3)$$

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

=>LogNorm

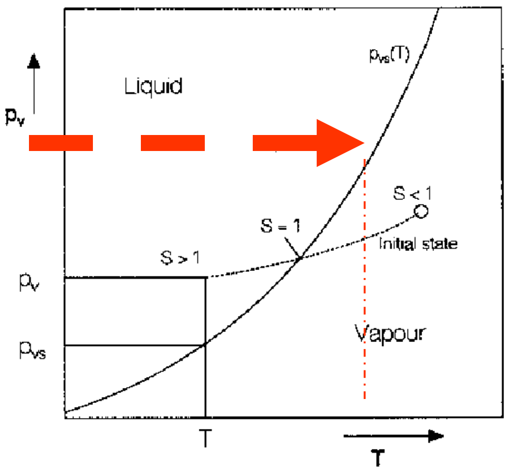


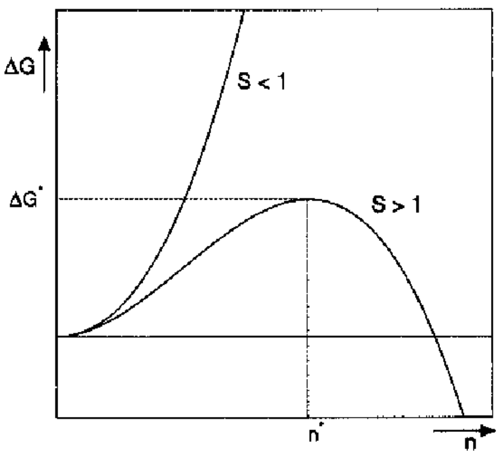
Park et al. J. Chem. Phys. B 105, 11603-11635 (2001)

Diffusion-driven nucleation

$$\Delta G(n,c) = -nkT\ln(c/c_0) + 4\pi a^2 n^{2/3}\sigma$$

Saturation curve





Supersaturation ratio

$$S = c/c_0$$

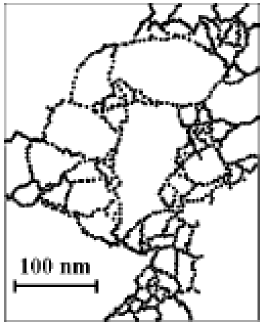
The peak of the nucleation barrier corresponds to the critical cluster size

$$n_c = \left[\frac{8\pi a^2\sigma}{3kT\ln S}\right]^3$$

$$Jnuc \sim \exp\left[\frac{-\Delta G(n_c,c)}{kT}\right]$$

At given T pressure should be high => need of high loading

Secondary particles => Aggregation/Coalescence



Smoluchowski master equation

$$\frac{\partial n}{\partial t} = \frac{1}{2}\int_0^{\upsilon} \beta(\tilde{\upsilon}, \upsilon - \tilde{\upsilon}) n(\tilde{\upsilon}) n(\upsilon - \tilde{\upsilon}) d\tilde{\upsilon} - \int_0^{\infty} \beta(\upsilon, \tilde{\upsilon}) n(\tilde{\upsilon}) n(\upsilon) d\tilde{\upsilon}$$

$$N_p = \frac{v}{v_p} = A\left(\frac{r}{r_p}\right)^{D_f}$$

Petrus J. Dekkers*,[1] and Sheldon K. Friedlander

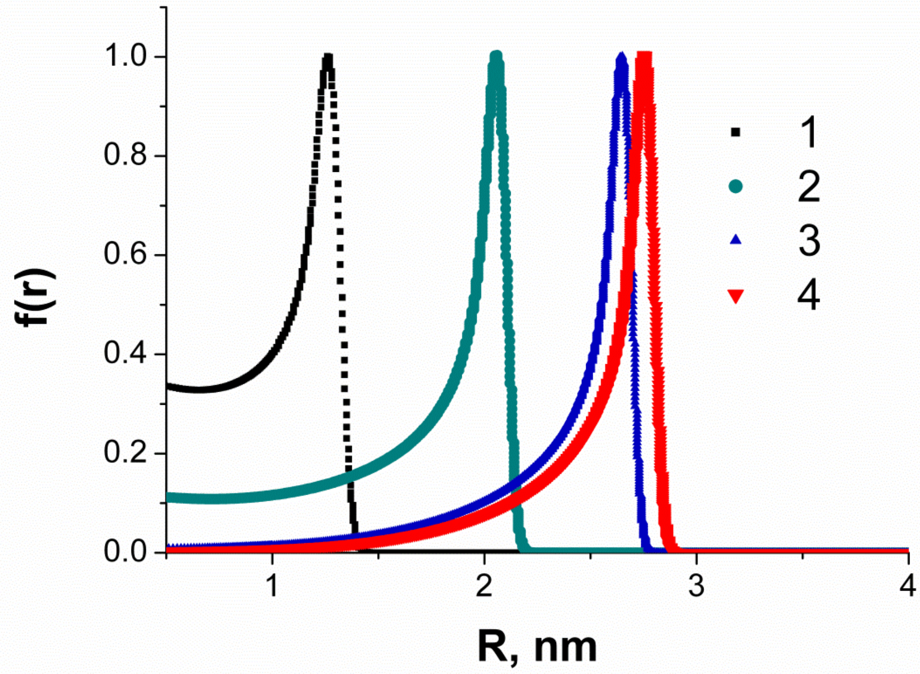
Kernel depends on the regime

1. Free molecular regime (Kn >>1)
2. Continuum regime (Kn <<1)
3. Near-Continuum transition regime (0.01<Kn<1)

- **The distribution is the narrowest in the near-continuum transition regime (0.01<Kn<1) when there are collisions between the primary particles, but not too much**

Collisional growth of secondary particles

$$\frac{dN_1}{dt} = \rho(t) - \sum_{j=2}^{\infty} j \frac{dN_j}{dt} \qquad \frac{dN_2}{dt} = fK_1 N_1^2 - K_2 N_1 N_2 \qquad \frac{dN}{dt} = K_{S-1} N_1 N_{S-1} - K_S N_1 N_S \;\; (s \geq 3)$$



Calculated size distribution obtained for 1-10, 2-100, 3-1000 and 4-2000 pulses. Here, laser frequency is 1 kHz, gold solution in water is considered with a=1.9 10^{-10} m.

How to reduce mean size and/or size dispersion ?

-**Reduce the number of collisions to avoid aggregation**

Ablation yield/loading reduction=>near free-molecular regime

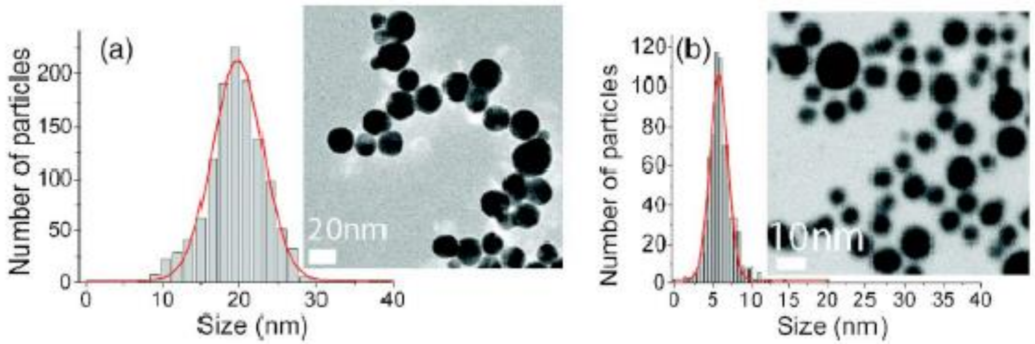
-**Reduce the probability of aggregation**

Chemical composition of the solution, surfactant molecules

-**Reduce background temperature**

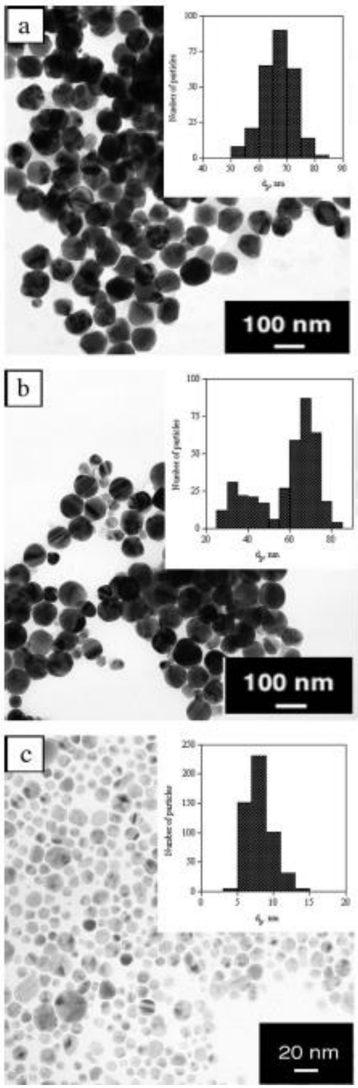
-Irradiate solution by light

(continuum generation followed by particle fragmentation in a solution)



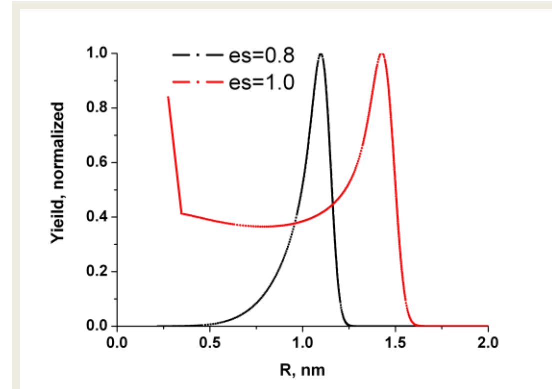
Besner et al. APL 2006 (with dextran)

How to reduce NP's size ?



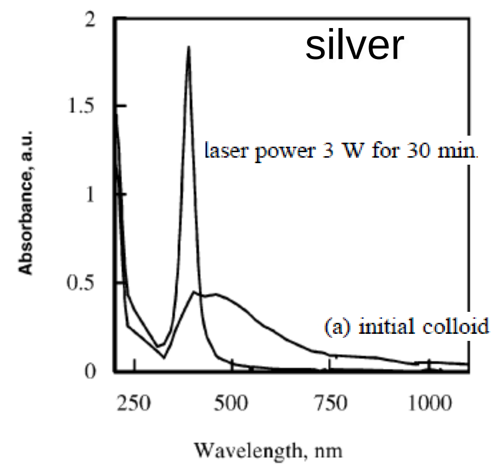
⇒ **Surfactant molecules**

Change in stiking parameter



=> **Additional laser irradiation**

depends on laser wavelength, fluence and size of particles



=>mechanisms ?

Träger et al.
Sylvestre et al. 2004
Pustovalov et al. 2005
Pyatenko et al. 2005

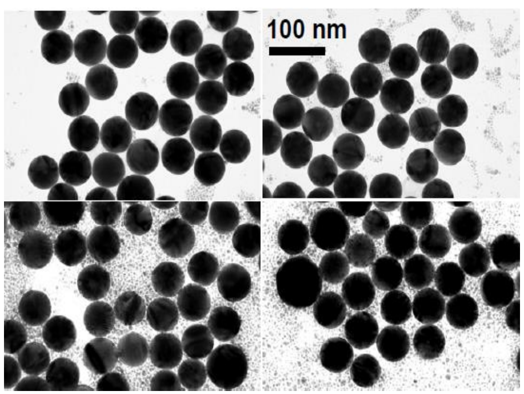
4. *Laser-induced particle size reduction and fragmentation*

Main goal: ***understanding ultra-short laser interactions with metallic nanoparticle (NP) for better control over laser-assisted NP formation in liquids***

For different applications, such as

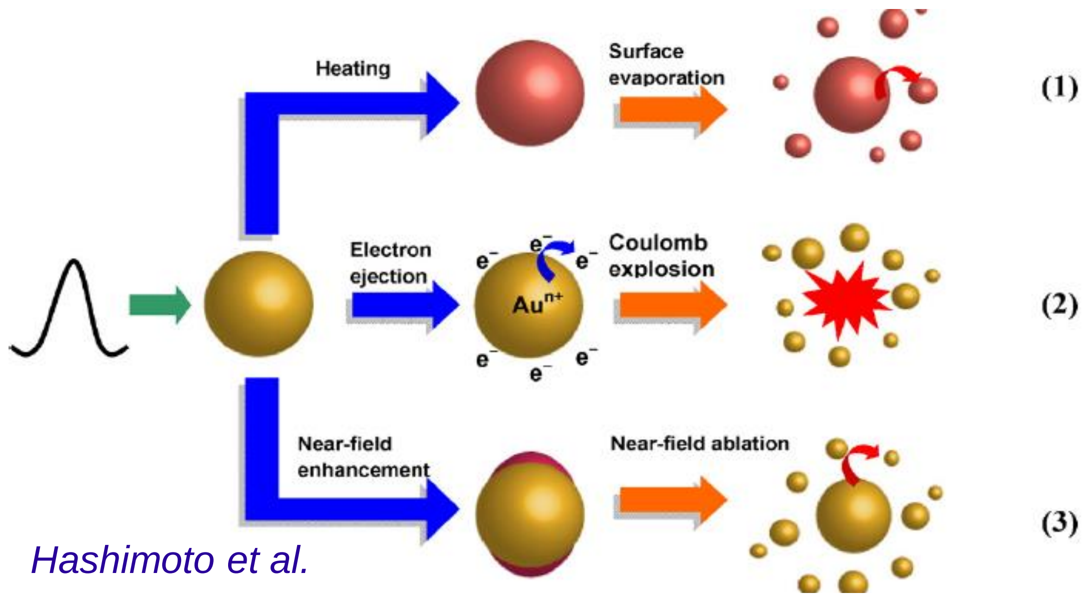
-photodynamic therapy, cancer treatment
-photonic and plasmonic devices
-sollar cells, novel energy sources
-sensors

Werner et al.
J. Phys. Chem. C, 2011, 115 (12), 5063



J. Phys. Chem. C, 2011, 115 (12), 8503

Mechanisms?

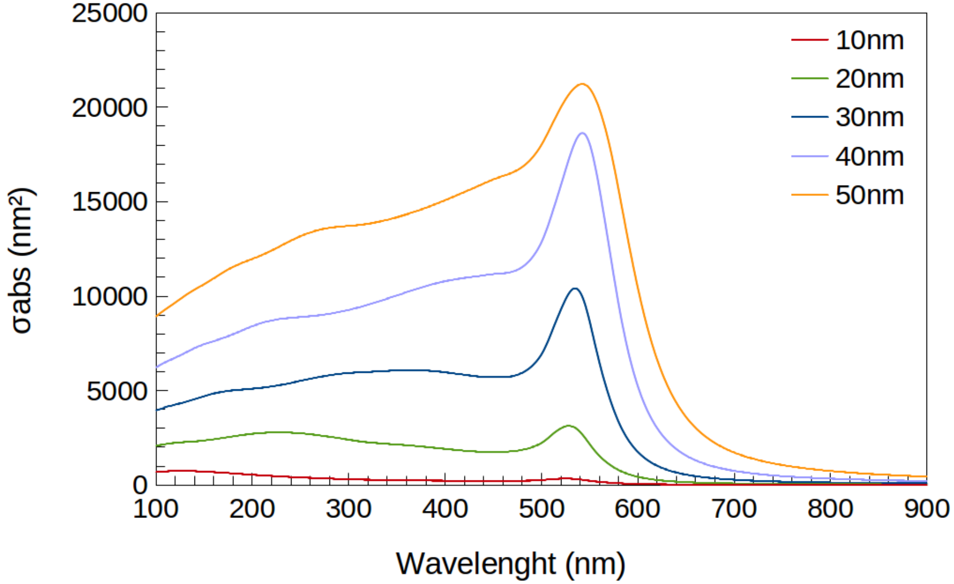


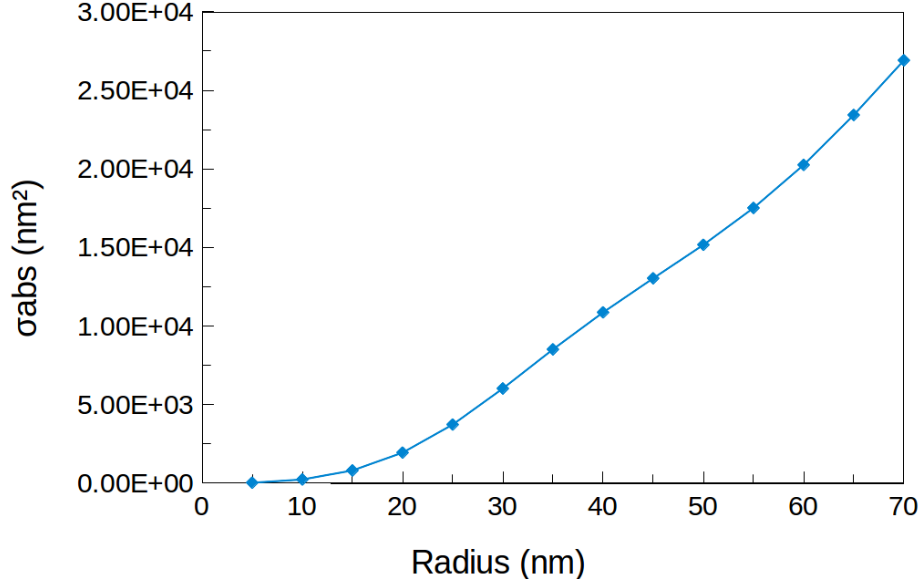
Hashimoto et al.

Journal of Photochemistry and Photobiology C: Photochemistry Reviews 13 (2012) 28–54

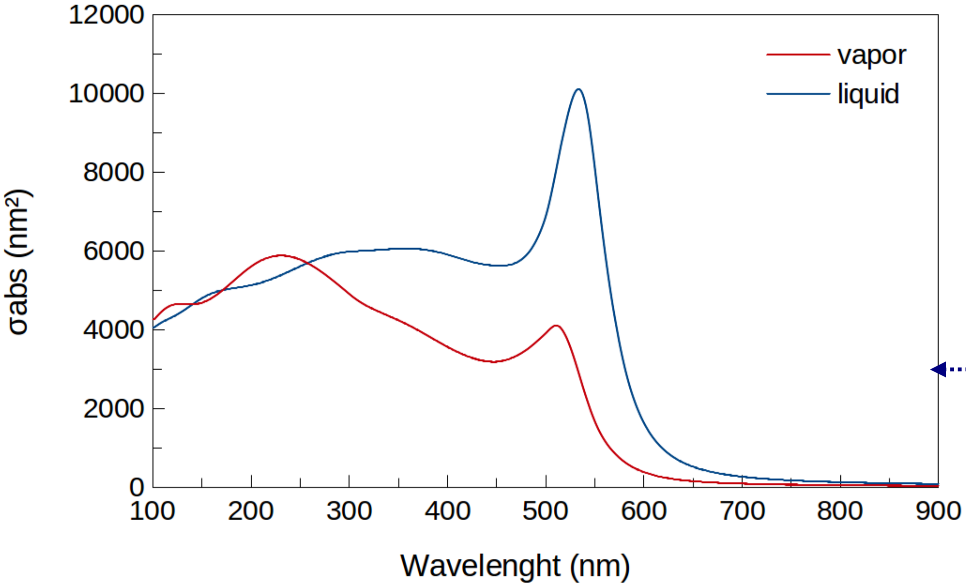
ABSORPTION

Au NPs with radius in the range 10-100 nm





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

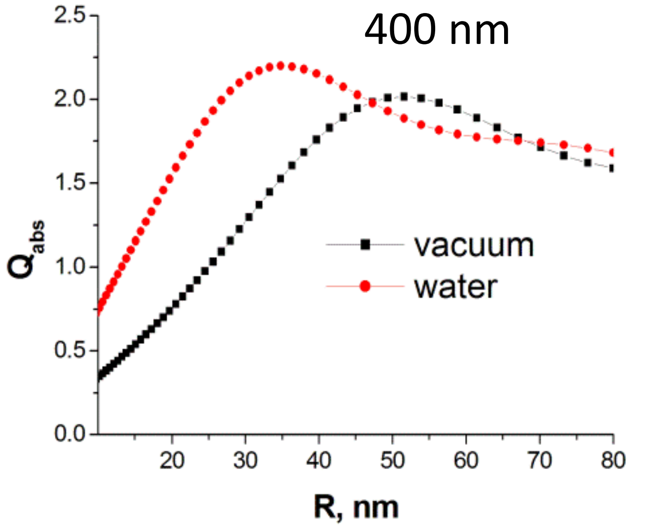


Absorption depends of the medium.
At 400 nm, a change from liquid water to vapor results in a considerable decay in absorption.

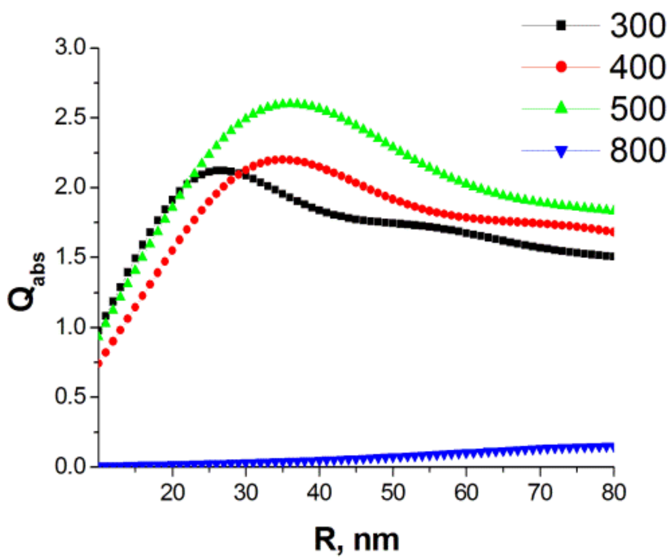
ABSORPTION COEFFICIENT vs RADIUS

Gold NPs water

(a)



(b)



Generalized Mie theory=>

1- calculated absorption coefficients vs AuNP's radius, R For water (red) and vacuum (black) at 400 nm

=> peak in absorption at R~ 30nm for AuNP in water

2- calculated absorption, coefficients vs NP's radius, R for AnNPs in water and different wavelength (300-800nm)

=> peak position is shifted to larger R if wavelength rises

HEATING by FS LASER: TWO TEMPERATURE MODEL (TTM)

Laser => heating of a metallic particle
energy absorbed by the conduction electrons

Energy is transfered :
- first to the lattice (electron-phonon collision)
- then to the surrounding medium (thermal diffusion)

solve

$$\begin{cases} C_e(T_e).dT_e/dt = -g(T_e).(T_e-T_l) + S(t) \\ C_l(T_l).dT_l/dt = g(T_e).(T_e-T_l) - F \\ C_m(T_m).dT_m/dt = F \end{cases}$$

evolution of T_e coupling to the lattice

dynamics of T_l including heat transfer

neglect heat conduction during calculation time ~ several ps

with

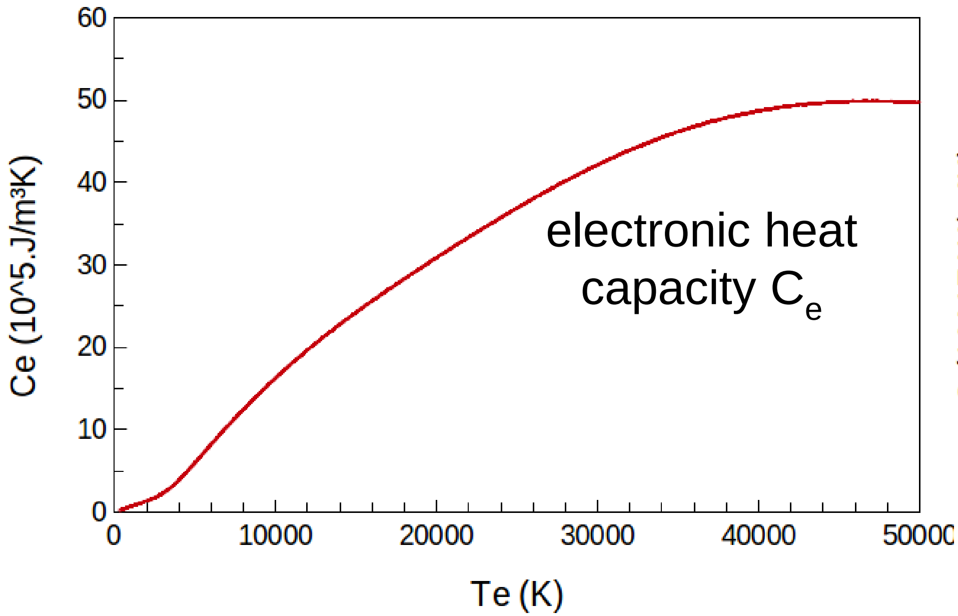
$$\begin{cases} S(t) = \sigma_{mie}(n_m,R_{NP}).P(t) / V(T_l) \\ P(t) = (2\sqrt{(\ln 2)}*flu / \tau\sqrt{\pi}) * \exp(-4(\ln 2)t^2 / \tau^2) \\ F = 3h.(T_l-T_m) / R_{NP} \end{cases}$$

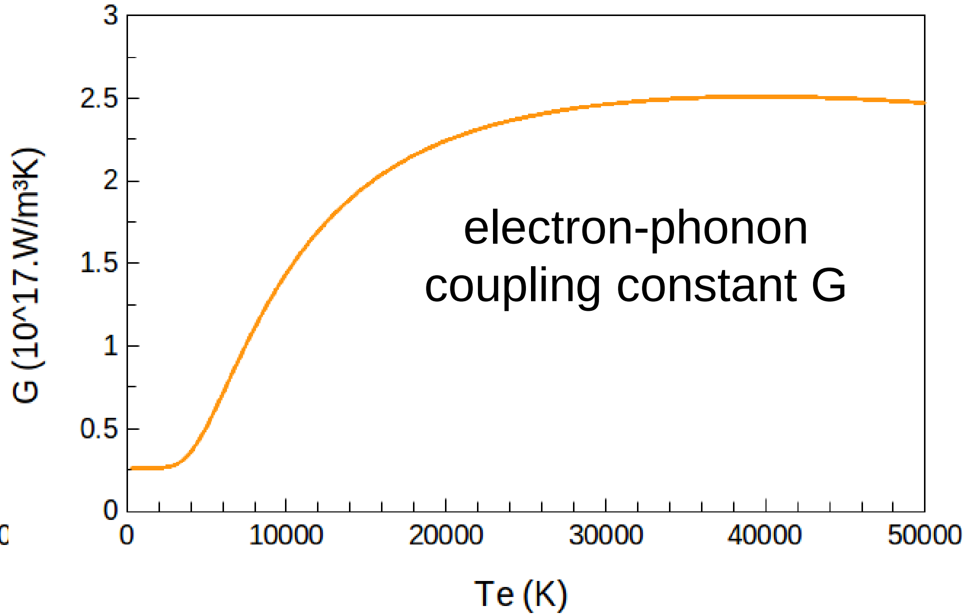
S(t) energy-exchange with the laser pulse
P(t) gaussian pulse
F empirically found energy loss term

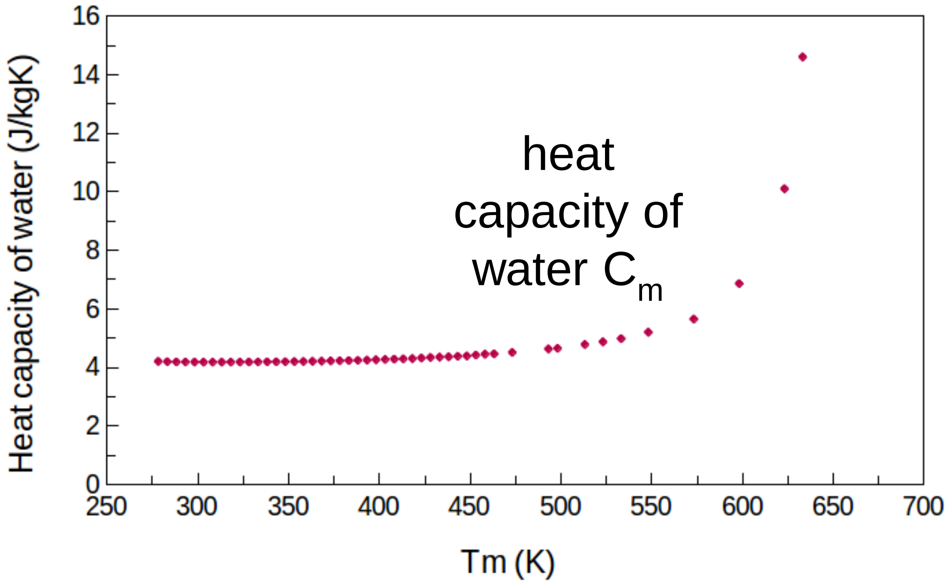
Giammanco et al. J. Phys. Chem. C, 2010, 114 (8), pp 3354–3363

Werner et al. J. Phys. Chem. C, 2011, 115 (12), pp 5063–5072

PARAMETERS FOR TTM



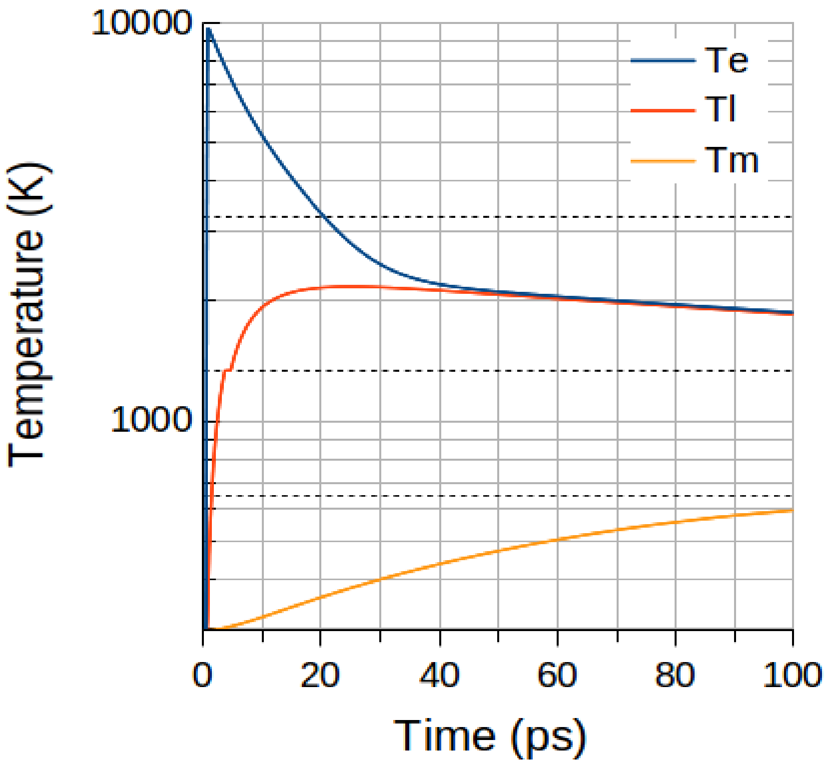




=> based on electron density of states, t*aking into account the effect of thermal excitation of the electrons (including d electrons) located below* E_F

Lin et al.
Phys.Rev. B 77, 075133 (2008)

ELECTRONIC & LATTICE TEMPERATURES



30 nm radius gold particle in water absorbing laser pulse of **150 fs** at **400 nm** with laser fluence of **12.3 mJ/cm^2** Gaussian time profile

Agreement with

Werner et al. J. Phys. Chem. C, 2011, 115 (17), 8503

=>T_e rises instantaneously, then energy deposited into the electronic system is transferred to the lattice => T_l rises

=>Particle cools through heat exchange with the surrounding water

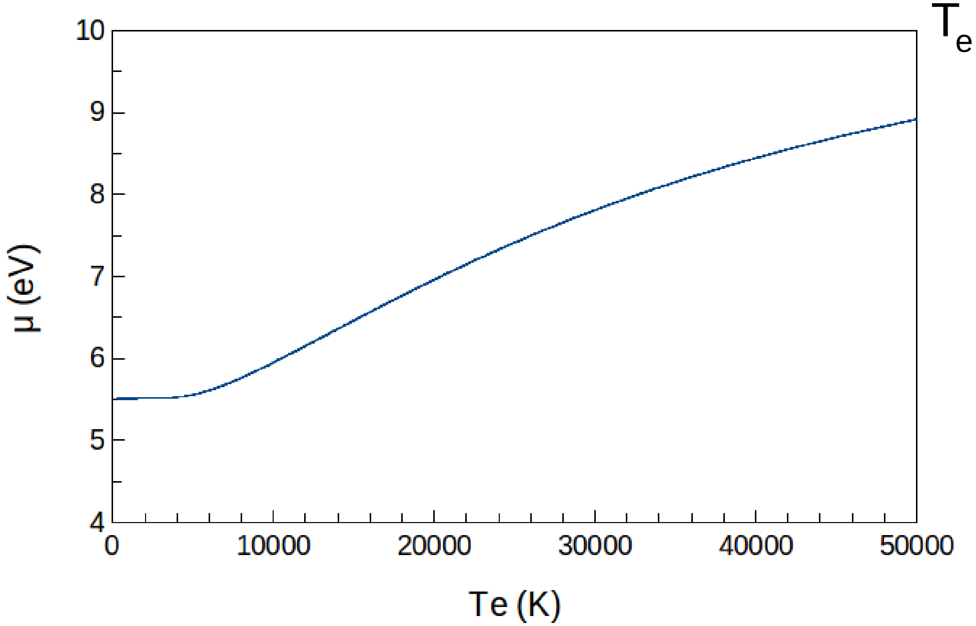
ELECTRON EMISSION

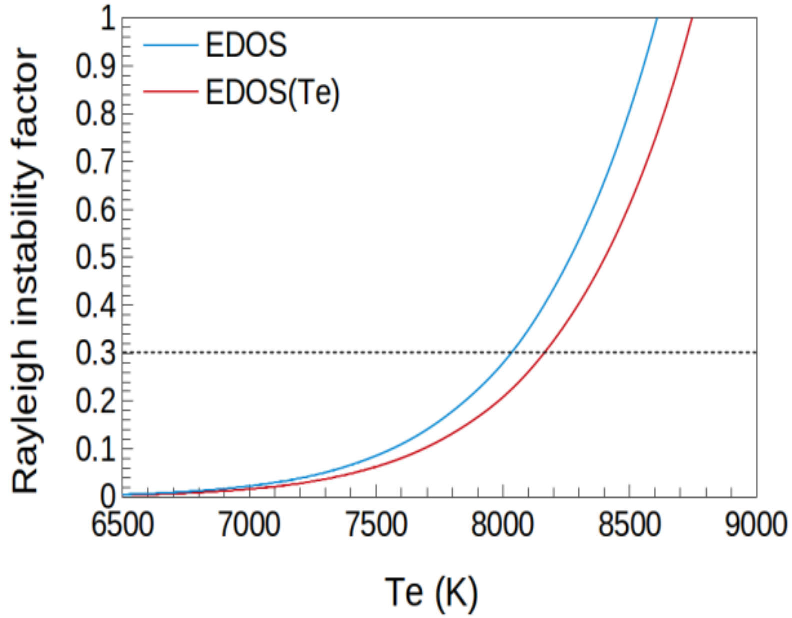
N_{therm} is the total **number of emissible electrons** : $N_{therm} = \alpha . n_\varepsilon$

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





Bévillon et al. Phys. Rev. B 89, 115117 (2014)

The criterion is based on Rayleigh instability factor ("Liquid drop"):

Electrostatic explosion can occur **if X > 0.3**, where $X = (N_{therm}{}^2/N_e) / (16.\pi.r_{ws}{}^3.\sigma/e^2)$

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

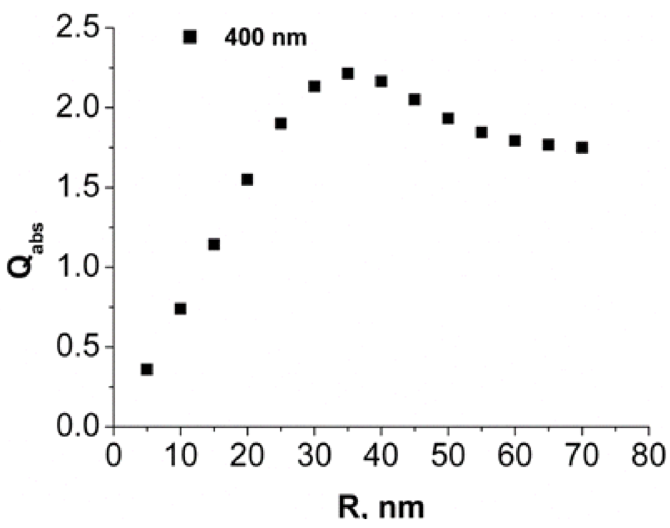
RESULTS for fs laser interaction with AuNPs

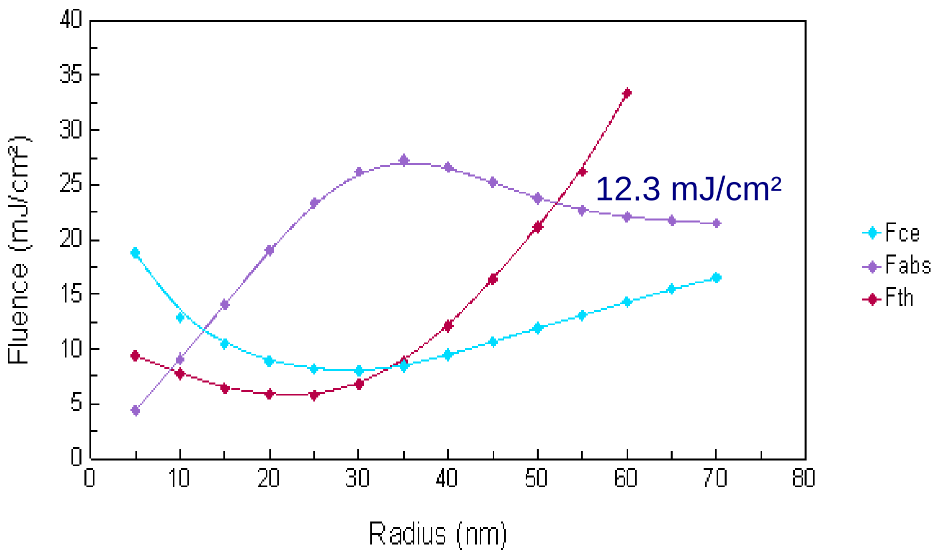
Absorption coefficient vs radius

Absorbed laser fluence,
fluence required for melting,
fluence required for Coulomb explosion

for

150 fs at 400





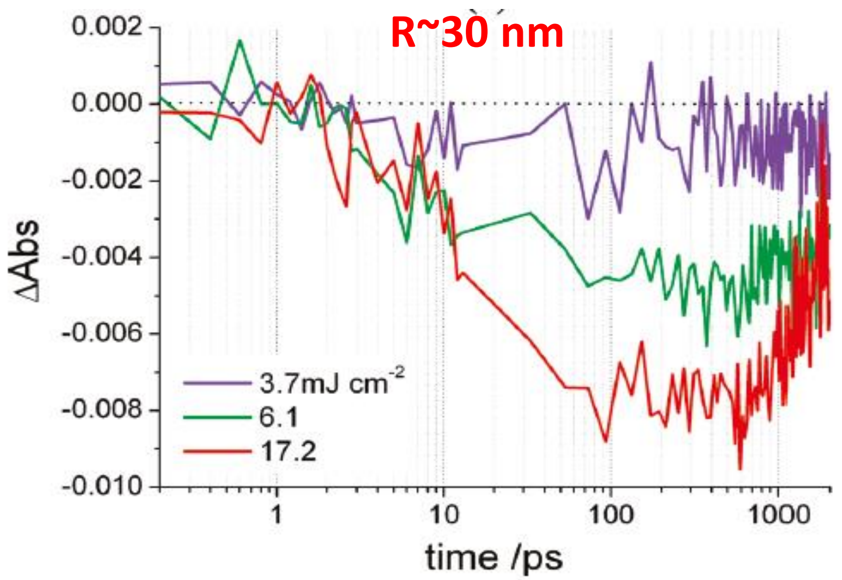
Fluences required for melting are smaller than the ones for CE if radius <~30 nm

RESULTS FOR fs LASER and AuNPs

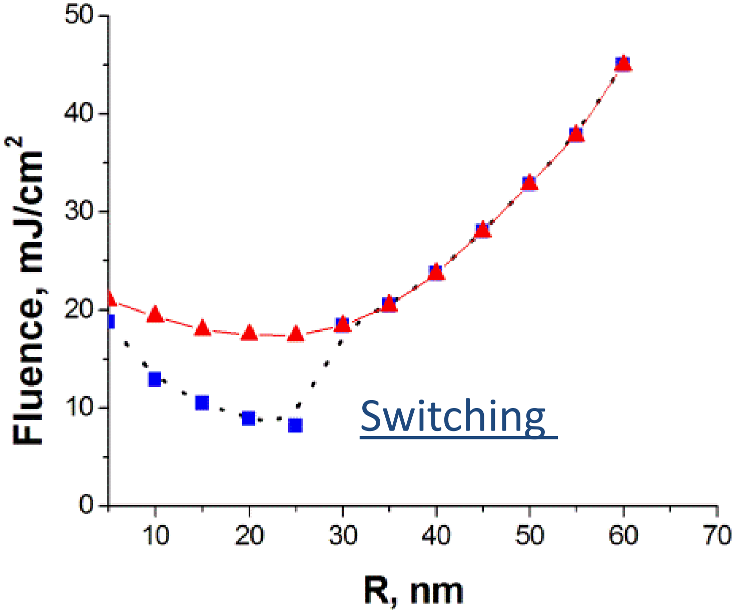
Experiments

Threshold fluence

Modelling



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



If *F>~17.2mJ/cm²*, thermal evaporation of R~30 nm AuNP occurs

For smaller F => no size reduction of 30 nm particles

=> To decompose such particles, one needs an increased fluence

=>confirms the switching to the red curve

5.1 Summary

- *Primary NPs* are formed in or even before the cavitation bubble **mostly by spinodal decomposition and by condensation**

- **Later stage =>** formation of "*secondary" particles* due to **nucleation and aggregation**

- **Size distribution is log-normal** *due to collisional growth*

- **Mean size of nanoparticles can be also reduced by**
  -Surfactant molecules
  -Additional laser irradiation

Discussions with:

S. Mottin,
A. Tishchenko

Support from:

PALSE ERTIGO project
PICS CNRS/RAS project
FP7 EU project BUONAPART-E
CINES of France

THANK YOU FOR YOUR ATTENTION!

tatiana.itina@univ-st-etienne.fr