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MOLECULAR DYNAMICS SIMULATIONS OF LASER-MATTER INTERACTIONS

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Zhigiley

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MOLECULAR DYNAMICS SIMULATIONS OF LASER-MATTER INTERACTIONS

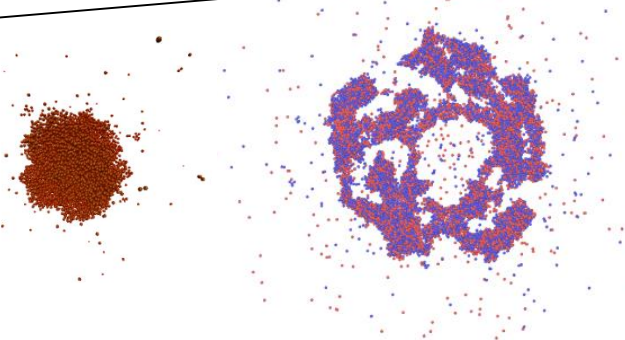
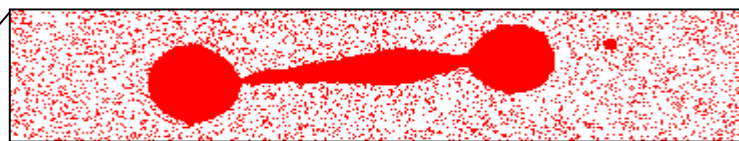
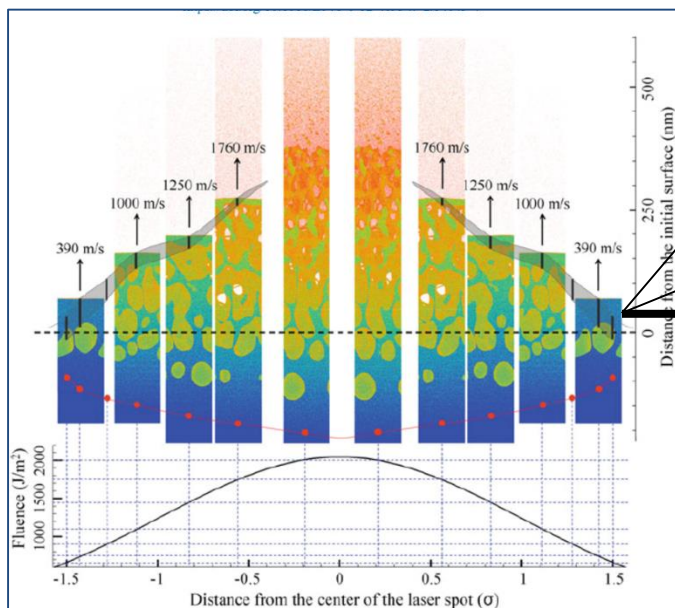
Tatiana ITINA, Lab. Hubert Curien, UMR CNRS 5516, UJM, 42000 St-Etienne, France

Mikhail POVARNITSYN, MIPT, Ecole Polytechnique, France

Dmitry IVANOV, University of Kassel, Germany

Anton RUDENKO, University of Arizona, USA

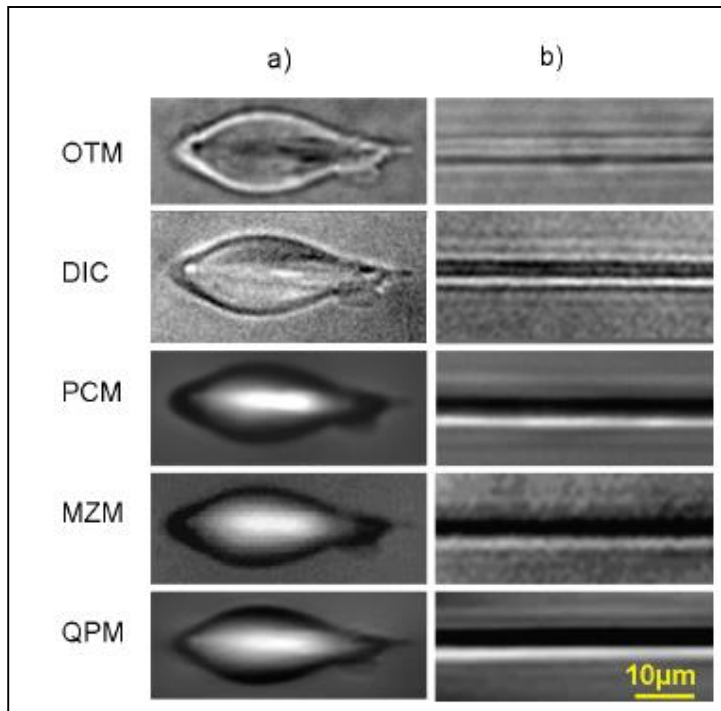
Leonid ZHIGILEY, Virginia State University, USA



Encyclopedia of Interf. Chem.
(Elsevier, 2018), pp. 594-603.

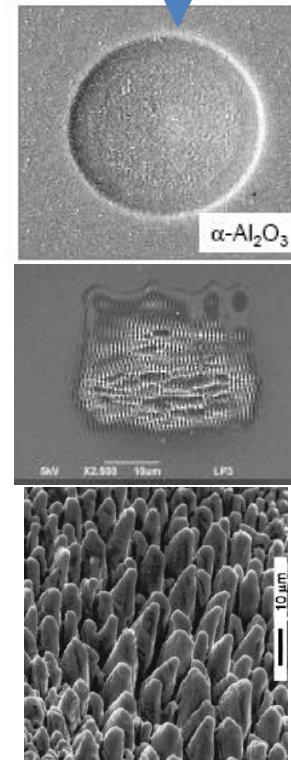
Laser fluence

Structural modifications in volume



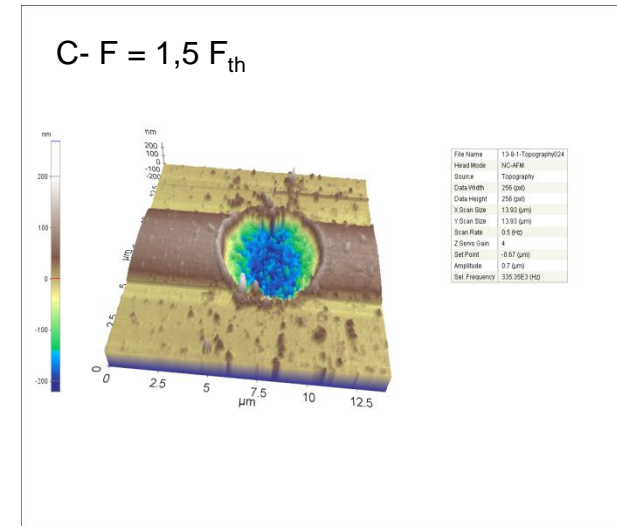
Mauclair et al. LabHC

Surface texturing



Sarnet et al.

Ablation



Utéza et.

- In laser-matter interactions, the effects produced strongly depend on both laser parameters and materials properties.

Nanostructuring of Si: Lithography + ion beam

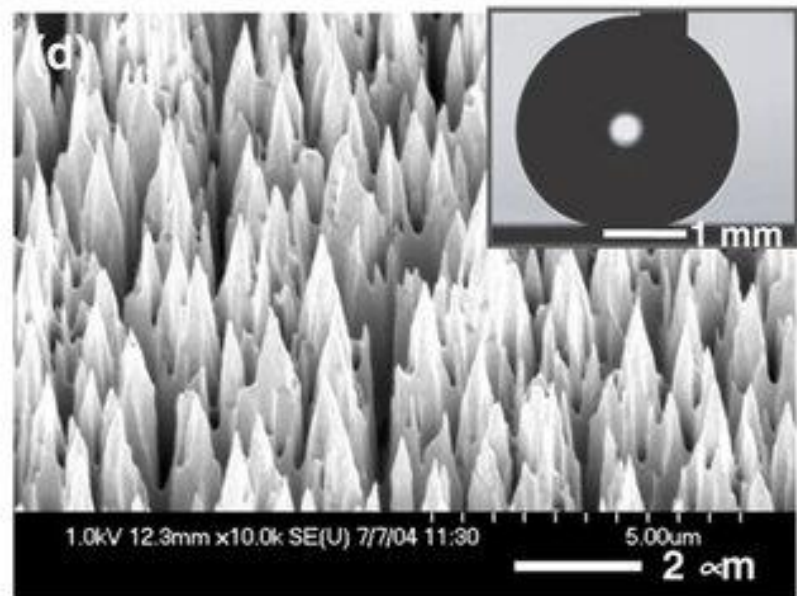
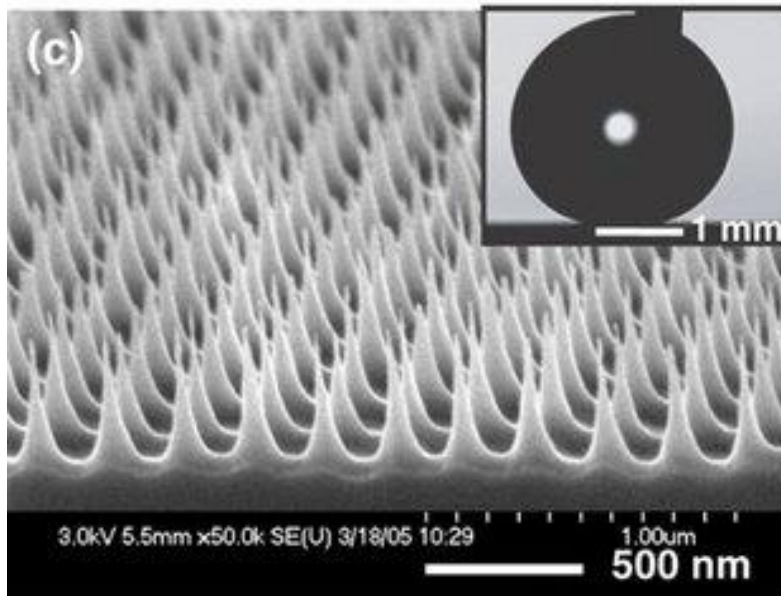
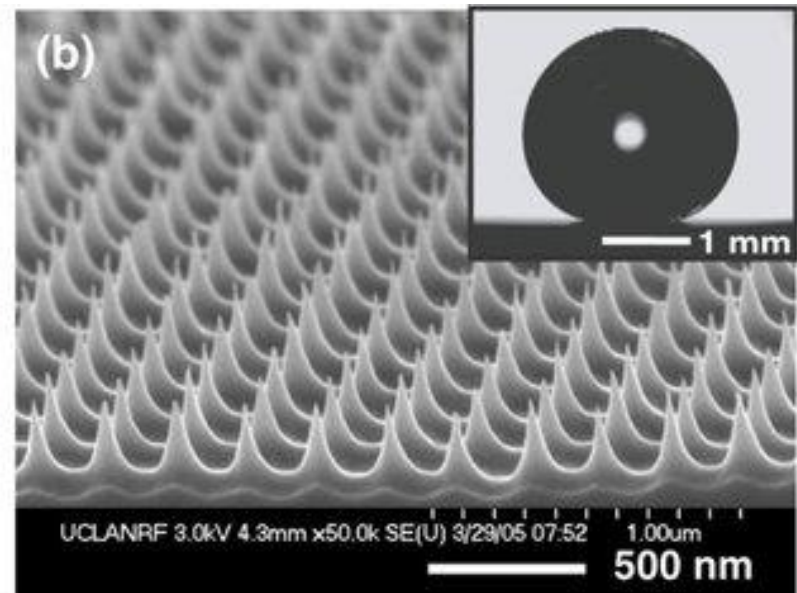
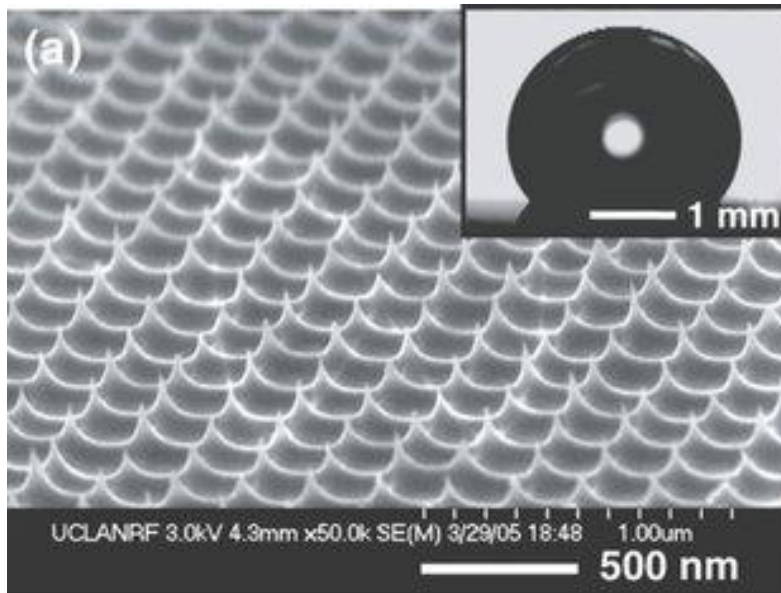
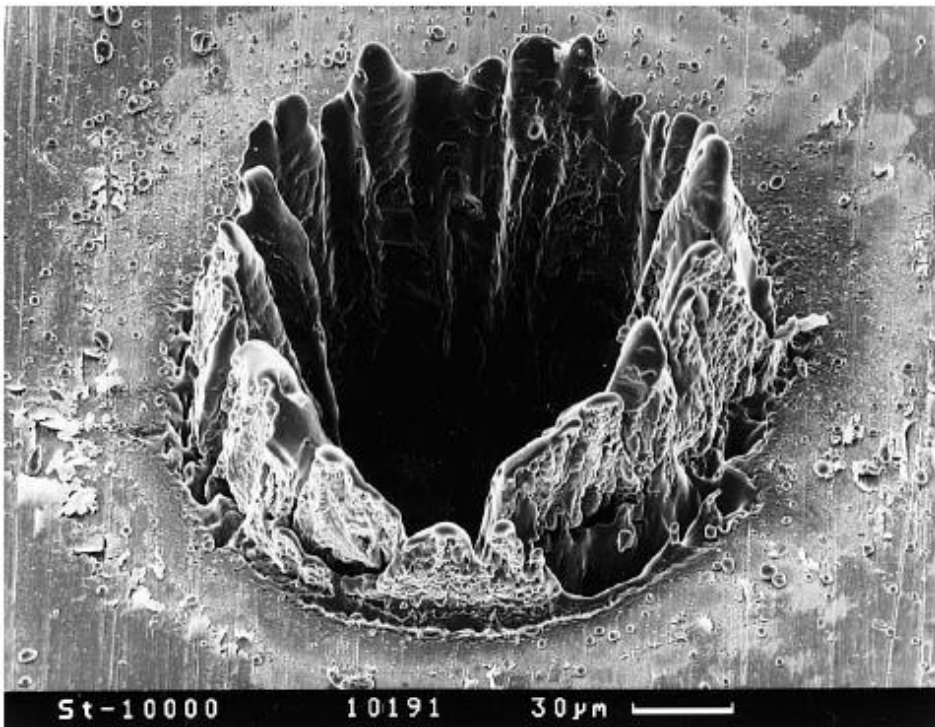
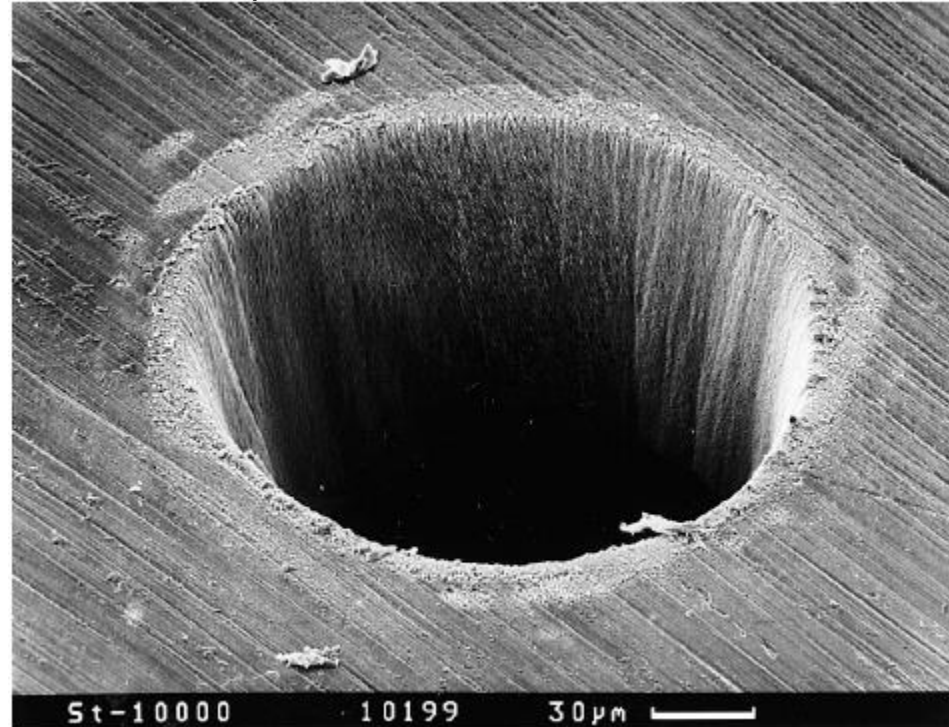


Photo-thermal, photo-mechanical, photo-chemical..

laser pulse at $F = 4.2 \text{ J/cm}^2$, at 780 nm.



laser pulse at $F = 0.5 \text{ J/cm}^2$, at 780 nm.



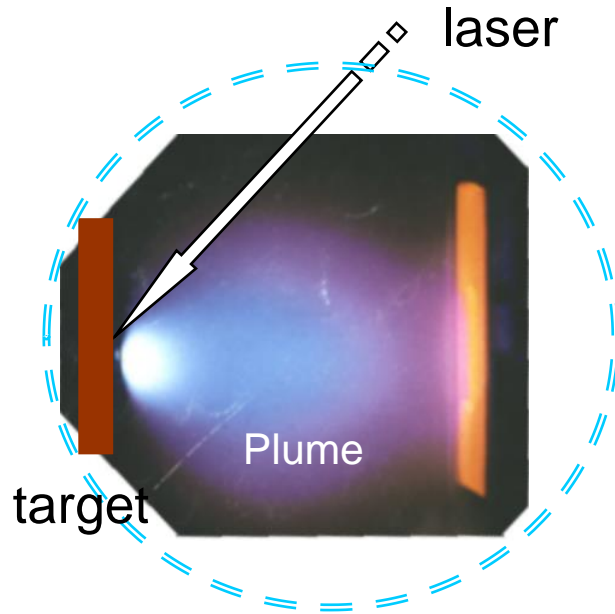
B.N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, A. Tuennermann, *Appl. Phys. A* 63, 109 (1996).

$$\max\{\tau_{pulse}, \tau_{e-ph}\} \approx \tau_{heating} \leq \tau_{mech} \approx \frac{L_{e-diff}}{C_s} \approx \frac{\sqrt{k_e(T_e, T_{ph})G_{e-ph}(T_e, T_{ph})}}{C_s}$$

$$T_e \sim F_{las}, \tau_{pulse}$$

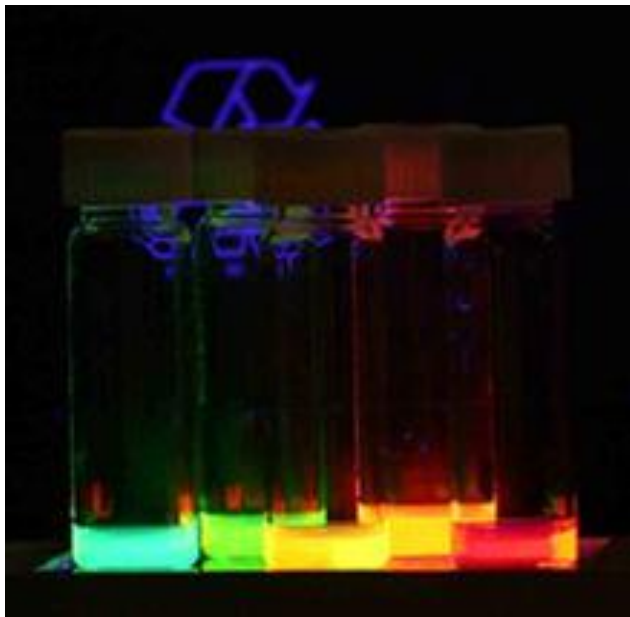
L.V. Zhigilei, Z. Lin, and D.S. Ivanov,
J. Chem. Phys. 113, 11892 (2009).

Fundamentals of Laser –Matter Interactions



- Laser interaction with a solid or a liquid target

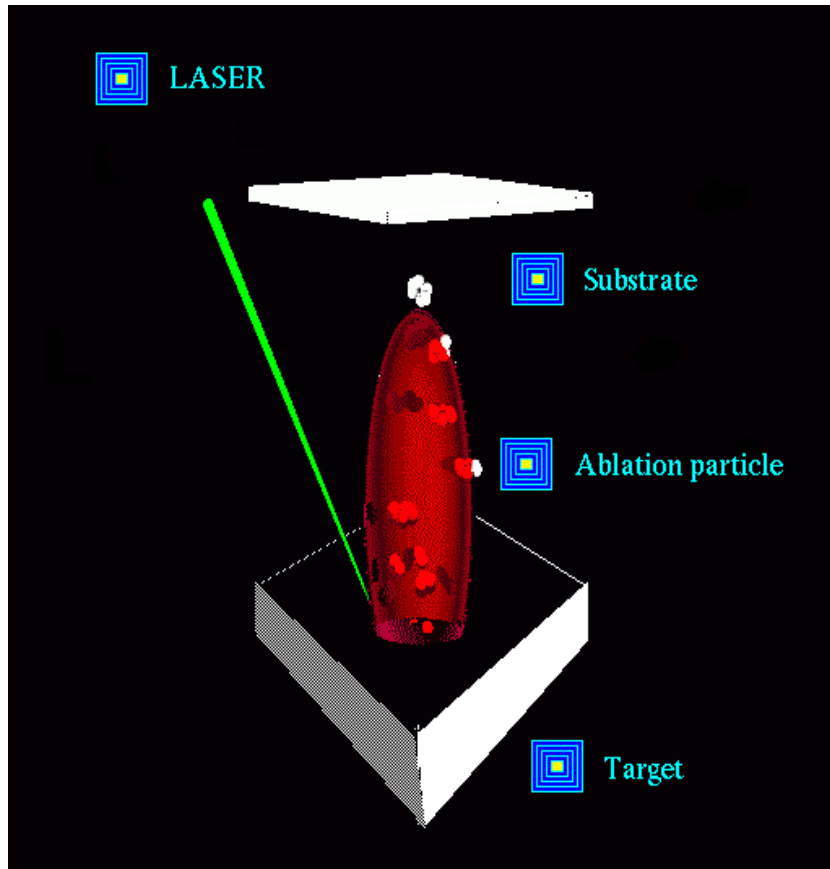
- Different laser pulse shape and width, energy, focusing, scanning, polarization, etc.



- Different ambient environment (vacuum, atmosphere, gases, liquids)

- Often multi-pulse irradiation is used.

Main Processes Involved in Laser Interactions



- *Propagation*
- *Ionization (MPI/tunnel, avalanche)*
- *Electronic processes*
- *Absorption*
- *Relaxation (collisions, excitons, etc.)*
- *Phases transitions: melting, evaporation or phase explosion*
- *Thermo-mechanical and chemical processes*
- *Cluster and nanoparticle formation*
- *Ablation*
- ...

**A large number of physical and chemical effects
taking place at very different scales**

Modeling Approaches

**-Quantum
Molecular
dynamics
(MD), ab-initio**

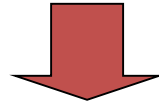
**Very detailed
and based on
quantum
mechanics**

Small systems

« in a point »

**Ion motion is
often neglected**

**Longer and
larger scales?**



-Classical MD

Melting

Evaporation

Phase explosion

Pressure waves, SW

Decomposition

Interaction potential ?

Electronic su-system?

Longer scales?

**- Classical Thermo
and
Hydrodynamics
- (CFD, CHD, MHD)**

**Contunuous
medium**

**Material motion as
a hole**

Phase transitions

Waves

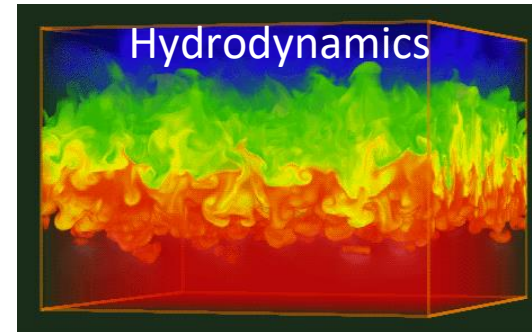
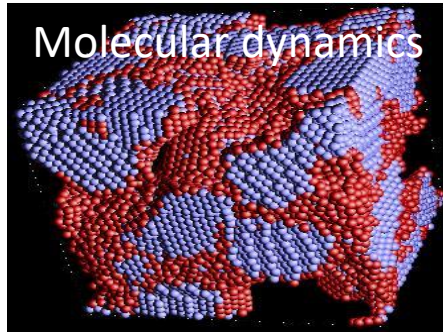
**Ionization/plasma
formation**

Equation of state?

Non-equilibrium?

Modeling Approaches

Atomistic (MD) vs Hydrodynamics (CFD)



$V < 1 \mu\text{m}^3$; $t \sim 1 \text{ ns}$

Dynamics

Interaction potential

Ionization?

Real temporal and spatial scales

LTE?

Nucleation, surface effects?

Equation of state (EOS)

Ultra-short Laser Interactions

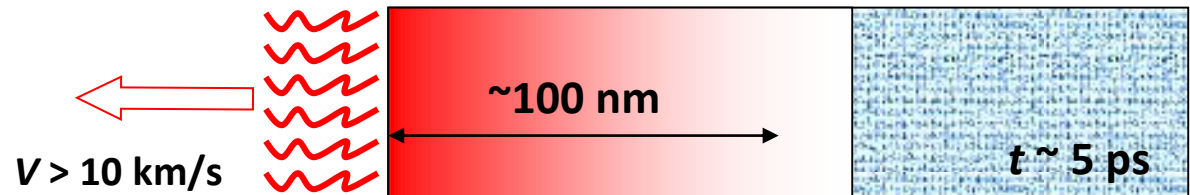
1. Pulse duration $\tau \sim 100$ fs



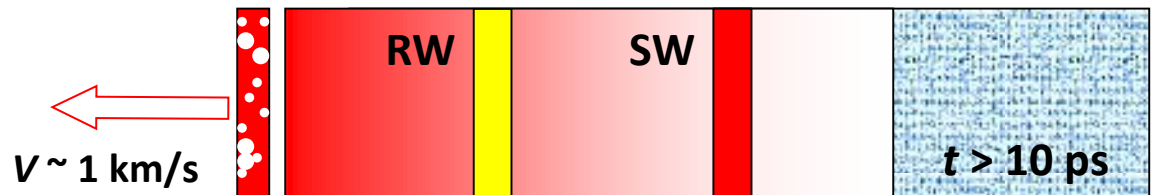
2. Absorption, e-excitation



3. Electron-phonon/ion coupling, thermal conductivity



4. Evaporation, shock waves, rarefaction waves

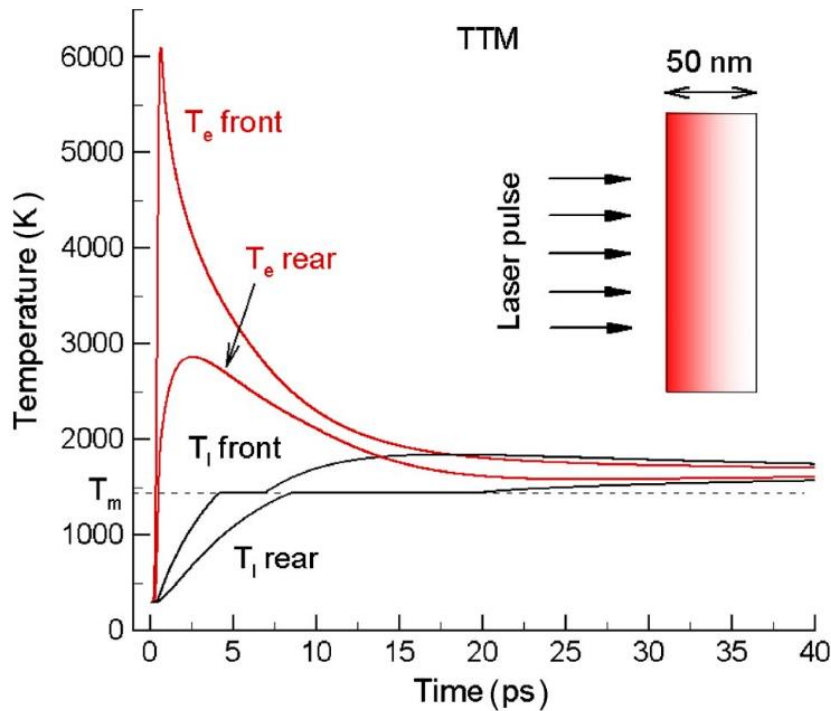


5. Phase explosion, material decomposition



Ultra-short Laser Interactions

Classical Two-Temperature Model (TTM) (was firstly developped only for metals)

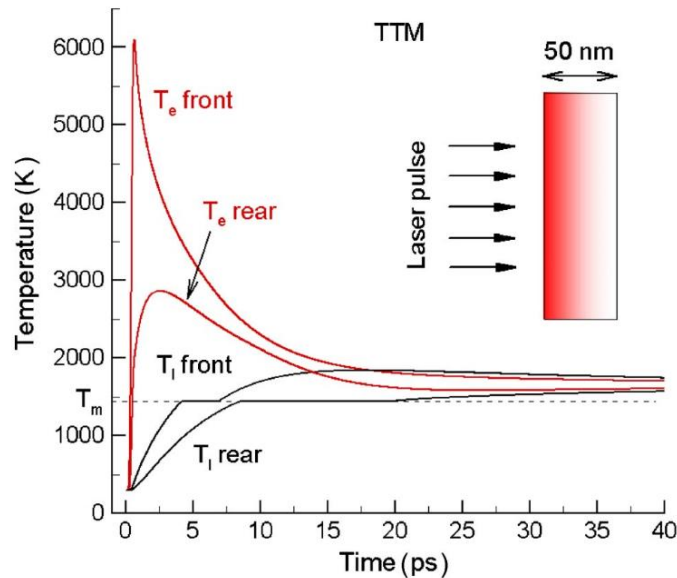


$$C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla [K_e(T_e) \nabla T_e] - G(T_e - T_l) + S(z, t),$$

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

M.I. Kaganov, I.M. Lifshitz, and L.V. Tanatarov, Sov. Phys. JETP 4, 173 (1957)

Ultra-short Laser Interactions



1. Thermal (TTM) models

$$C_e \frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z} \left(k_e \frac{\partial T_e}{\partial z} \right) - \gamma (T_e - T_i) + Q_{abs}$$

$$C_i \frac{\partial T_i}{\partial t} = \frac{\partial}{\partial z} \left(k_i \frac{\partial T_i}{\partial z} \right) + \gamma (T_e - T_i)$$

⇒ **Melting without ablation**

⇒ **Many assumptions**

⇒ **No motion**

⇒ **Hard to describe phase changes**

⇒ **Have to know many coefficients**

2. Molecular dynamics approach (MD or TTM-MD)

⇒ **melting, ablation**

⇒ **interaction potential is often assumed to be constant**

3. Hydrodynamics (1T, 2T, one fluid, two fluids, etc.)

⇒ **Need all transport coefficients**

⇒ **Need equation of state (EOS)**

⇒ **Need additional sub-models for ionisation**

Classical Molecular Dynamics (MD)

- **Newton or Hamilton equation**

$$m d^2 r / dt^2 = F = -\nabla U,$$

- **Build a 'system'**

- **Choose parameters**

Cohesion energy, density, other properties,..

- **Integration**

$$v(t+\delta t) = v(t) + F(t) * \delta t / m$$

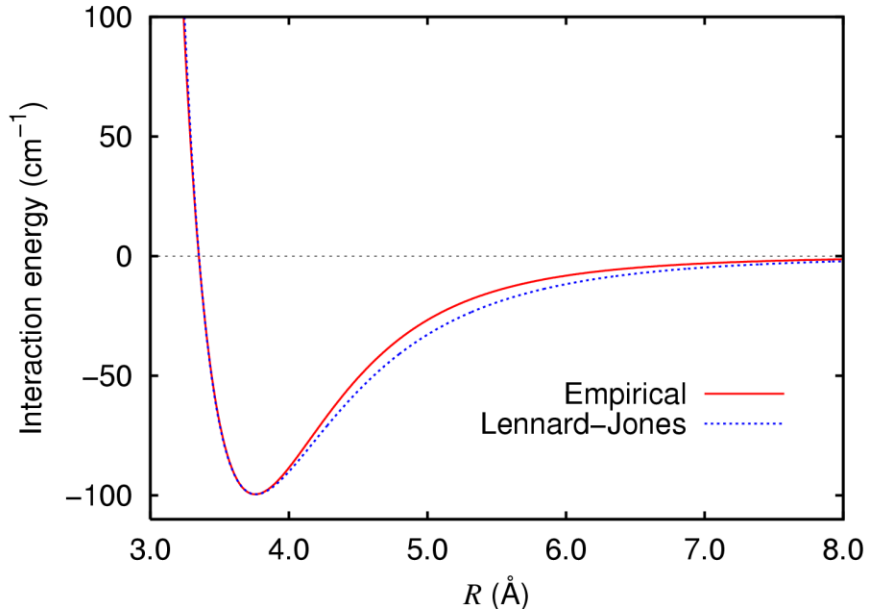
$$r(t+\delta t) = r(t) + v(t) * \delta t$$

- **Gives**

temperature, pressure, composition,
energy & distributions ,
etc...

Classical Molecular Dynamics (MD)

Interaction potentials



$$m\frac{d^2r}{dt^2} = F = -\nabla U$$

Lennard-Jones (Ar)

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right],$$

- Morse
- Stillinger-Weber (Si, 3 body)
- Embedded atom (EAM)
- ReaxFF
- Etc....

$$V(r) - D_e = D_e(e^{2a(r_e-r)} - 2e^{a(r_e-r)})$$

$$V = \frac{1}{2} \sum_{ij} \phi(r_{ij}) + \sum_{ijk} g(r_{ij})g(r_{ik}) \left(\cos \theta_{jik} + \frac{1}{3} \right)^2$$

Choice of the potential for MD method

MD: $m_i \ddot{\vec{r}}_i = \vec{F}_i = -\text{grad}V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$

$$V = \sum_{i \neq j} U(r_{ij}) = \sum_{i \neq j} 4\epsilon \left(\left(\frac{r_{ij}}{\sigma} \right)^{12} - \left(\frac{r_{ij}}{\sigma} \right)^6 \right)$$

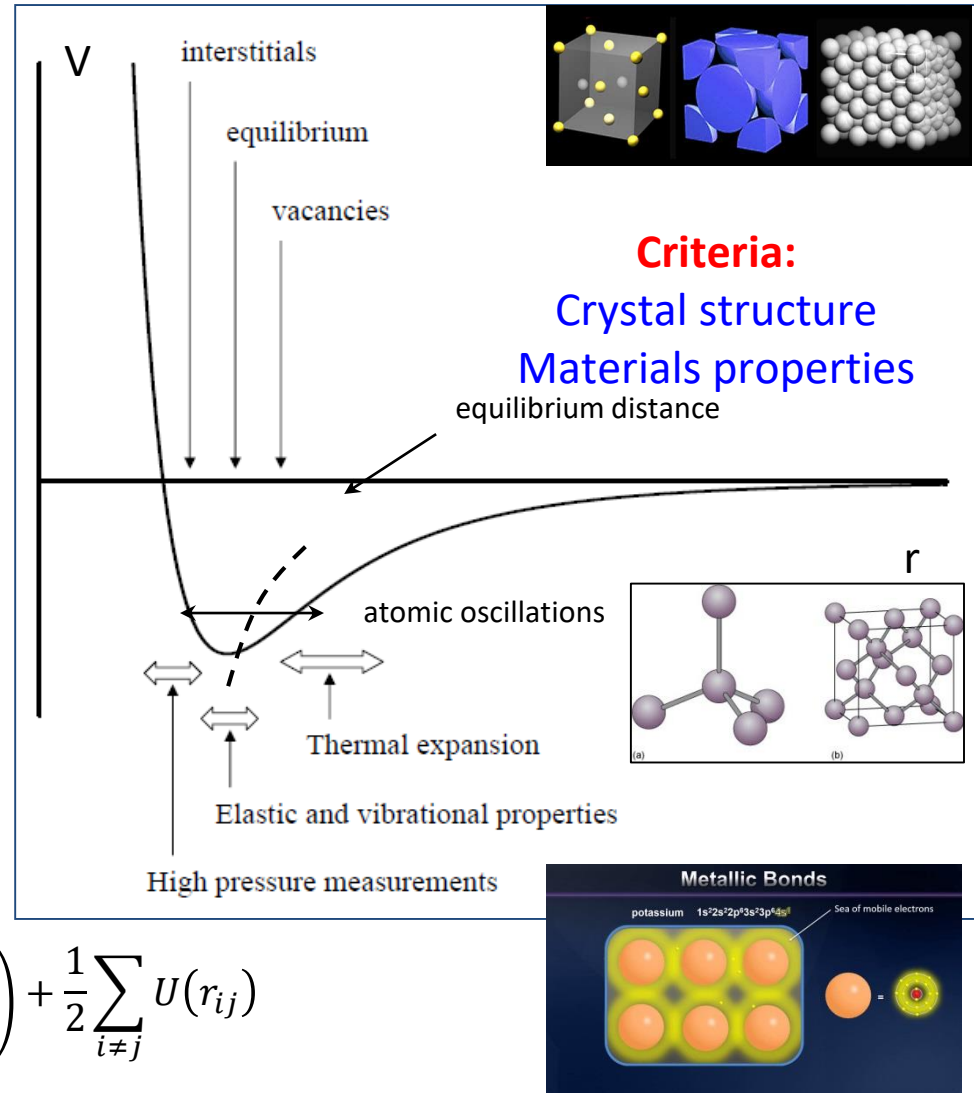
- Lennard-Johns potential for Van der Waals interactions in inert gases and molecules: Ar, Kr, and molecular systems

$$V = \frac{1}{2} \sum_{ij} U(r_{ij}) + \sum_{ijk} g(r_{ij})g(r_{jk}) \left[\cos \theta_{ijk} + \frac{1}{3} \right]^2$$

- Stillinger-Webber potential with many body angular part for opened structures as in Si

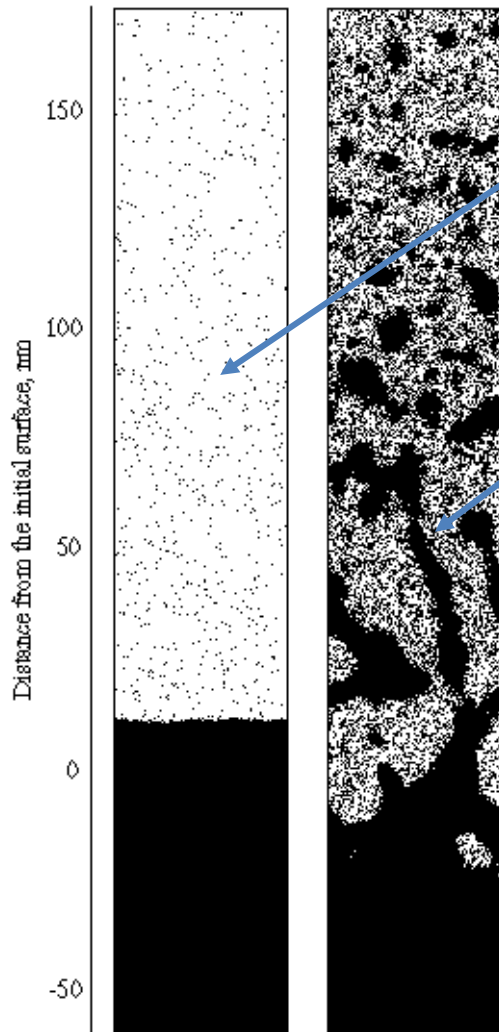
$$V = \sum_i E_i \quad E_i = F \left(\sum_{i \neq j} \rho(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} U(r_{ij})$$

- Many body potential by Embedded Atom Method for description of metallic bonding in the presence of free electron bath as it is in Au, Ni, Pt, Cu, ..



Classical Molecular Dynamics (MD)

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



$F < F_{th}$

Desorption: Atoms, slow surface evaporation

$F > F_{th}$

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

Process can be at $T \rightarrow T_c$

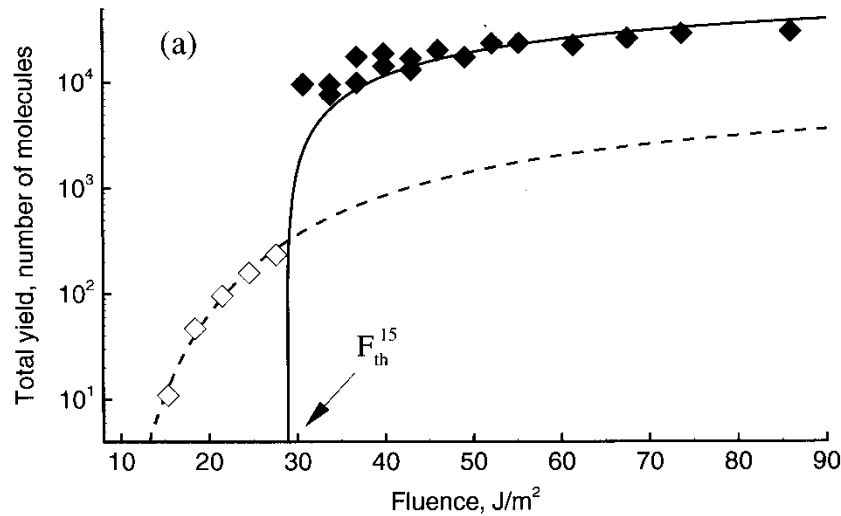
Difficult to model by classical methods !

pico

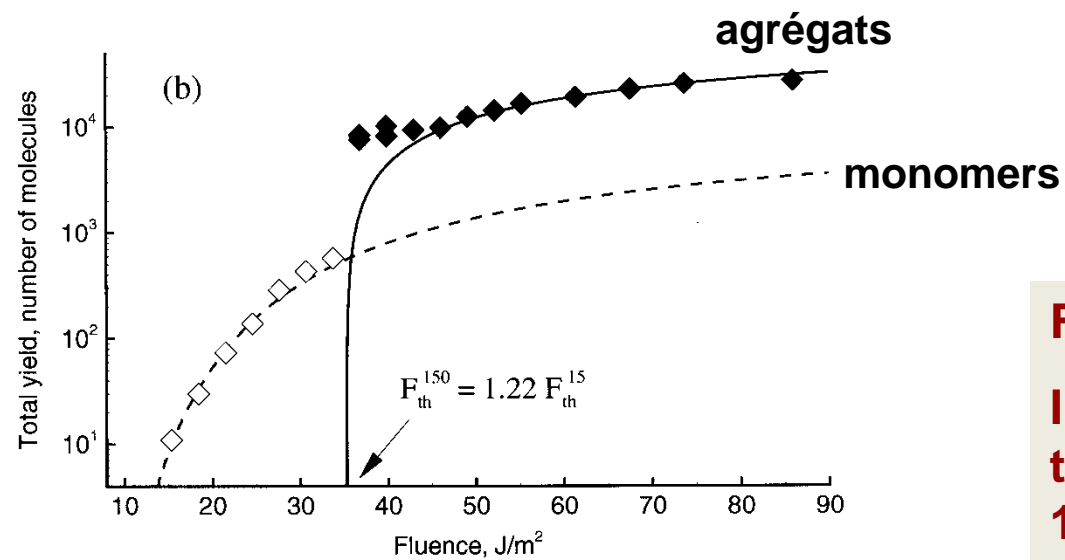
Molecular matrixes

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

Thermal or Mechanical Confinement



Mechanical confinement
pulse ~ 15 ps



Thermal confinement
pulse 150 ps

For femto laser:

Instead of pulse duration,
take e-i relaxation time (1-
100 ps)

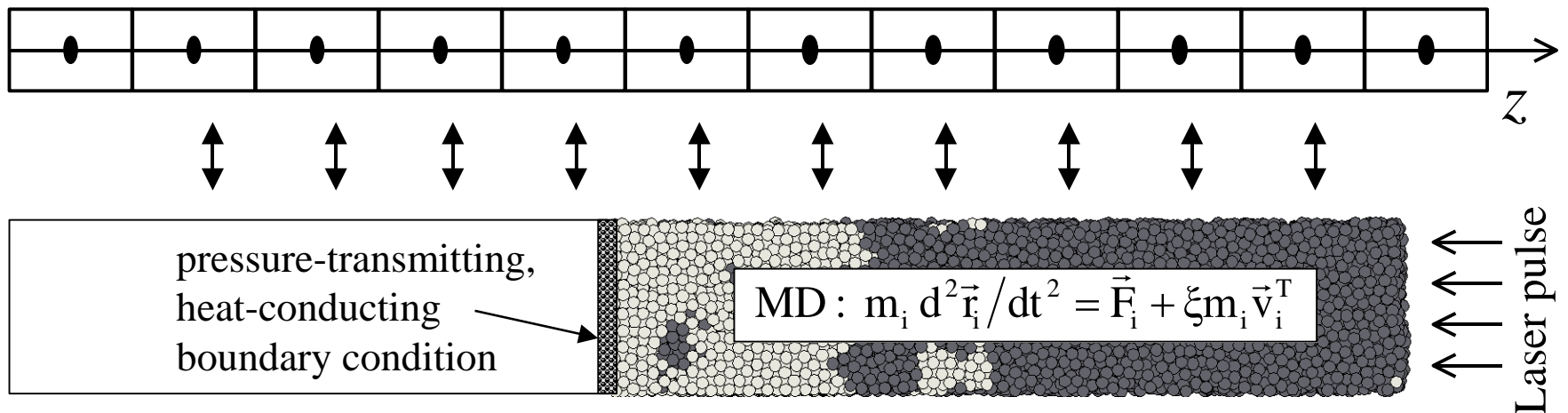
Ultra-short Laser Interactions

Let's combine : TTM –MD

$$C_e(T_e) = \gamma T_e \quad ?$$

$$G = \text{const} \quad ?$$

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



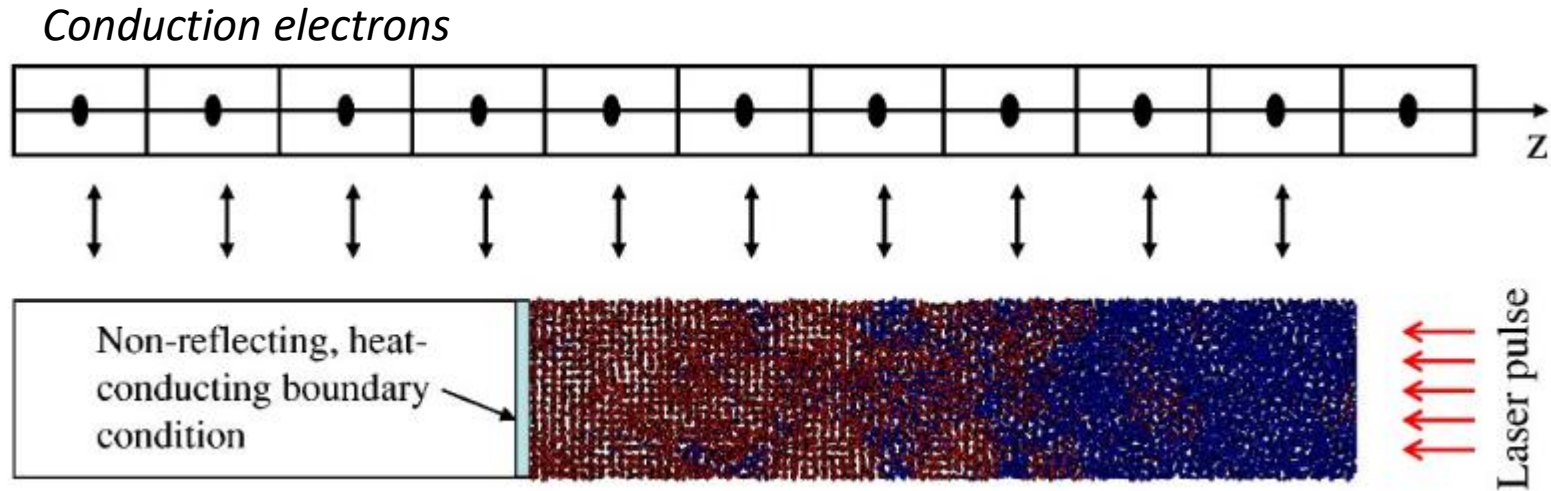
$$C_l(T_l) \frac{\partial T_l}{\partial t} = G(T_e - T_l)$$

$$T_l^{\text{cell}} = \sum_{i=1}^{N^{\text{cell}}} m_i (\vec{v}_i^T)^2 / (3k_B N^{\text{cell}})$$

Parameters ?

Ultra-short Laser Interactions

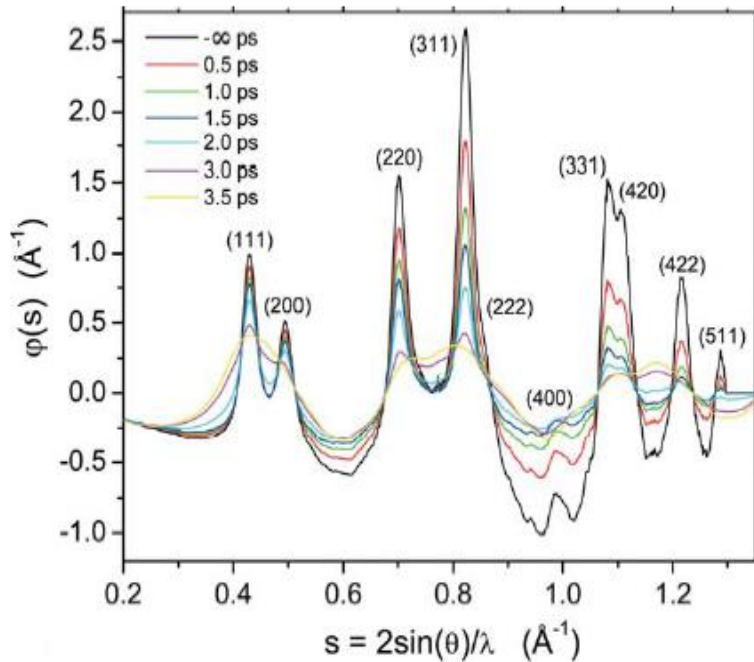
TTM + Molecular Dynamics (TTM-MD)



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

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i + \xi m_i \mathbf{v}_i^T, \quad \text{MD} \quad \xi = \frac{1}{n} \sum_{k=1}^n G V_N (T_e^k - T_l) \bigg/ \sum_i m_i (\mathbf{v}_i^T)^2$$

TTM- MD used for melting of metal films

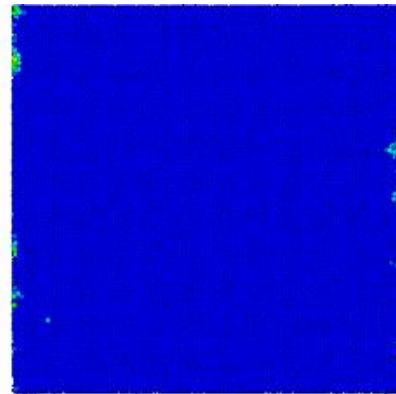


← Experiments

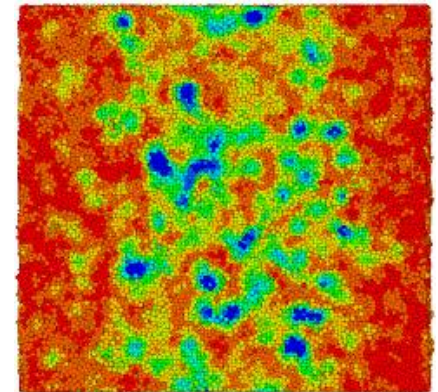
Siwick et al. *Science* **302**, 1382, 2003

Fluence: 70 mJ/cm^2 , Réflectivité 88%

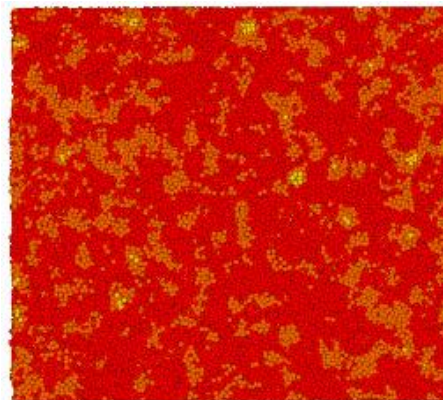
Desordre vers $\sim 3.5 \text{ ps}$



1 ps



2 ps



3 ps

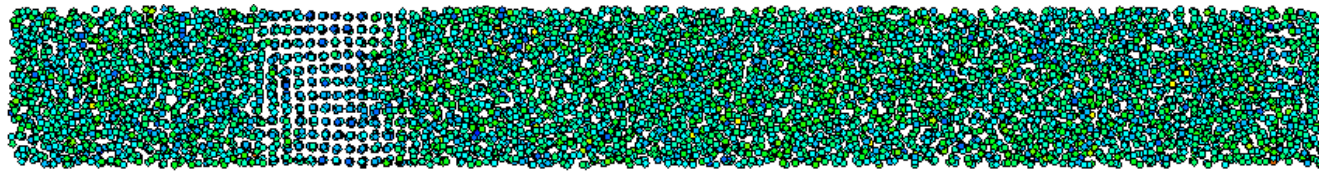
Simulation →

homogeneous melting at 3 ps
(starts at $\sim 1.5 \text{ ps}$ and finishes at 3 ps)

Rather good agreement with experiments

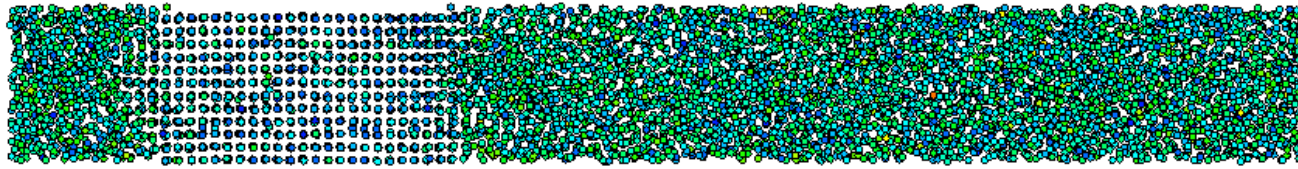
Z. Lin, L. V. Zhigilei, *Phys. Rev. B* **73**, 184113, 2006.
Al thin films

Physical Properties of the EAM Ni Model



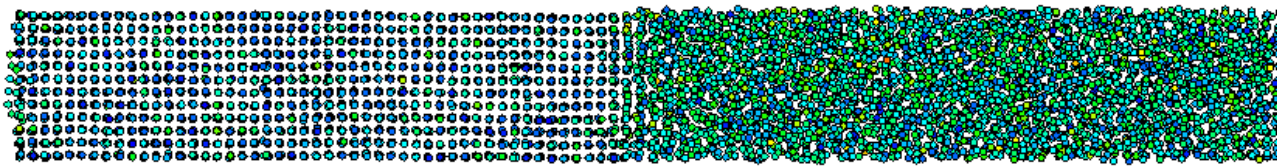
T=1238K

P=-4.61GPa



T=1378K

P=-1.20GPa



T=1579K

P=+3.12GPa

- From liquid-crystal coexistence simulations, the equilibrium melting temperature for the hosen EAM potential for Ni was defined.
- A linear fit to the sequence of coexistence data gives the value of $(dT/dP)_{T_m}$ that can be related to Clayperon equation.

Linear fit:

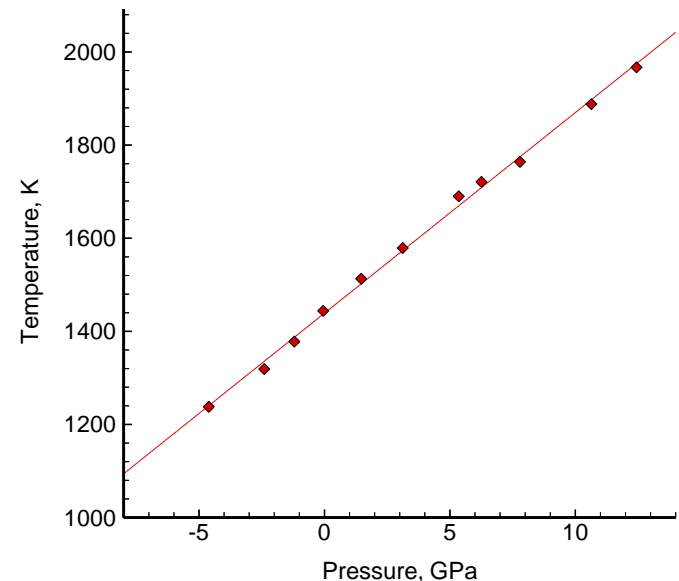
$$T = 1439 + 43.1 \times P$$

[T in K, P in GPa]

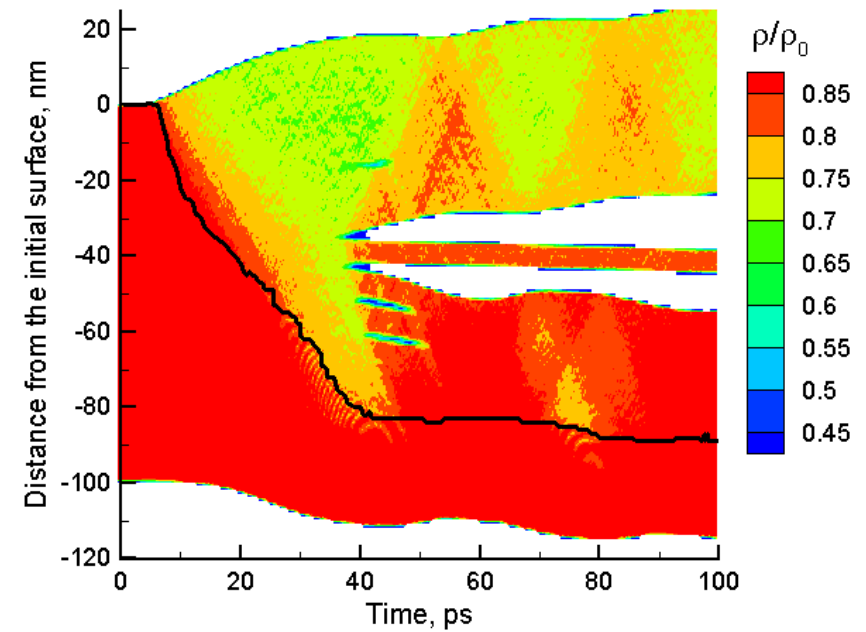
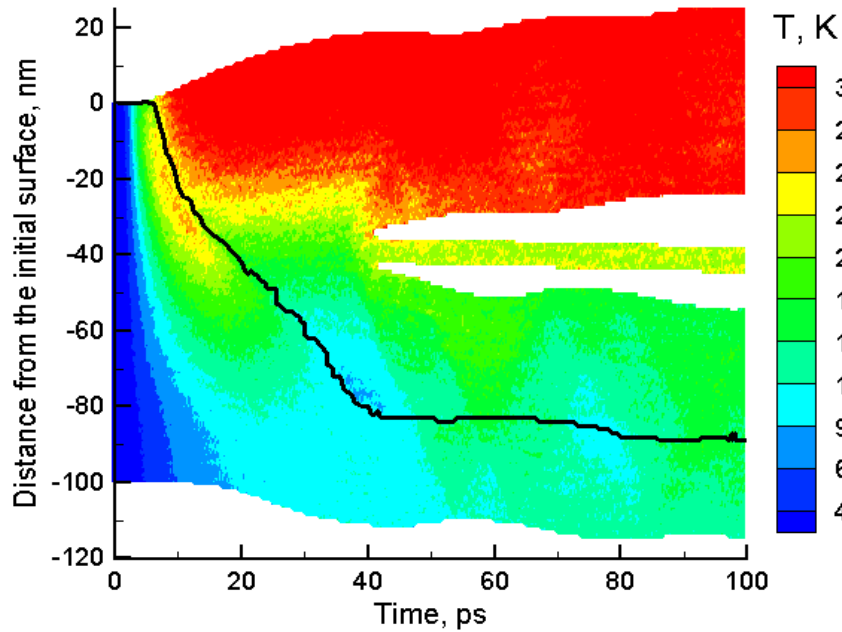
$$\left(\frac{dT}{dP}\right)_m = \frac{\Delta V_m}{\Delta S_m} = \frac{T_m \Delta V_m}{\Delta H_m}$$

At P = 0 Pa
 $T_m = 1439$ K

X. W. Zhou, H. N. G. Wadley, R. A. Johnson, D. J. Larson, N. Tabaat, A. Cerezo, A. K. Petford-Long, G. D. W. Smith, P. H. Clifton, R. L. Martens and T. F. Kelly, *Acta Mater.* **49**, 4005 (2001).



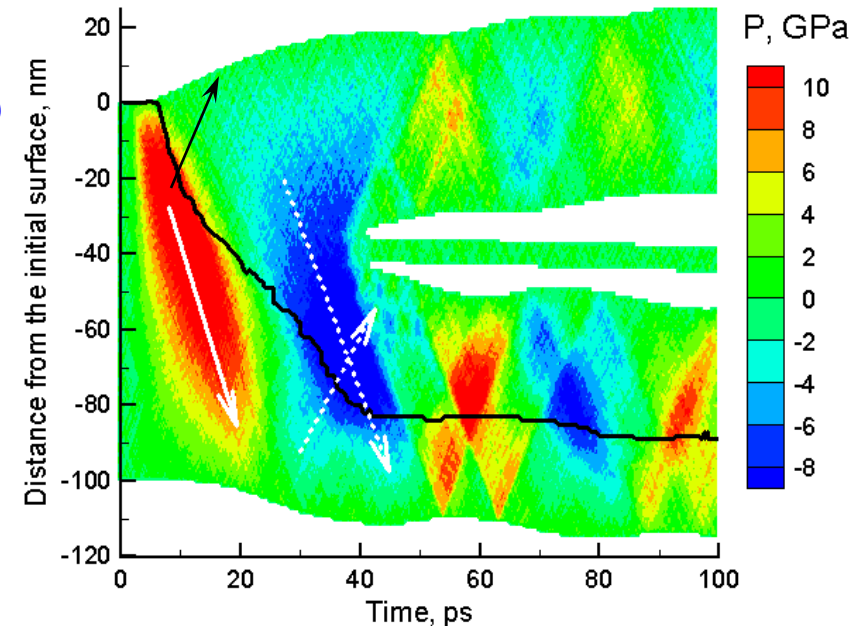
Spallation of Ni thin films



1 ps pulse, fluence 129 mJ/cm², 100 nm Ni film

D.S. Ivanov and L.V. Zhigilei, *Phys. Rev. Lett.* 91, 105701 (2003)

- Relaxation of the laser-induced stresses determines the mechanism of melting with the onset of spallation
- There are conditions for the inertial stress confinement establishment



Ultra-short Laser Ablation

MD vs CFD

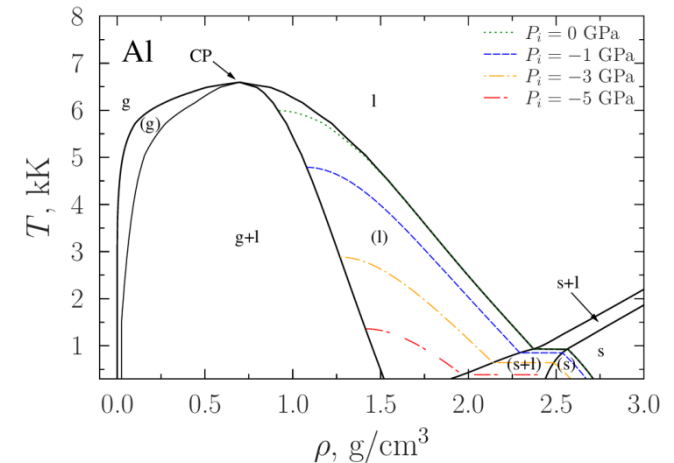
$$\frac{\partial(1/\rho)}{\partial t} - \frac{\partial u}{\partial m} = 0$$

$$\frac{\partial u}{\partial t} + \frac{\partial(P_{\text{ion}} + P_{\text{el}})}{\partial m} = 0$$

$$\frac{\partial e_{\text{ion}}}{\partial t} + P_{\text{ion}} \frac{\partial u}{\partial m} = \gamma_{ei}(T_{\text{el}} - T_{\text{io}})/\rho$$

$$\frac{\partial e_{\text{el}}}{\partial t} + P_{\text{el}} \frac{\partial u}{\partial m} = \frac{\partial}{\partial m} \left(\rho \kappa_{\text{el}} \frac{\partial T_{\text{el}}}{\partial m} \right) - \gamma_{ei}(T_{\text{el}} - T_{\text{ion}})/\rho + Q_L/\rho$$

EOS



$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i + \xi_i m_i \mathbf{v}_i^T + \mathbf{F}_i^{\text{el}} \quad \text{LAMMPS}$$

$$\frac{\partial(\rho e_{\text{el}})}{\partial t} + \frac{\partial(\rho e_{\text{el}} u)}{\partial z} + P_{\text{el}} \frac{\partial u}{\partial z} = \frac{\partial}{\partial z} \left(\kappa_{\text{el}} \frac{\partial T_{\text{el}}}{\partial z} \right) - \gamma_{ei}(T_{\text{el}} - T_{\text{ion}}) + Q_L(t, z)$$

Embedded atom "EAM"

$$E_i = F_{\alpha} \left(\sum_{j \neq i} \rho_{\beta}(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij})$$

Zhakhovskii *et al.* Appl. Surf. Sci. 255 (2009)

Ultra-short Laser Ablation

Laser energy absorption (Helmholtz equation)

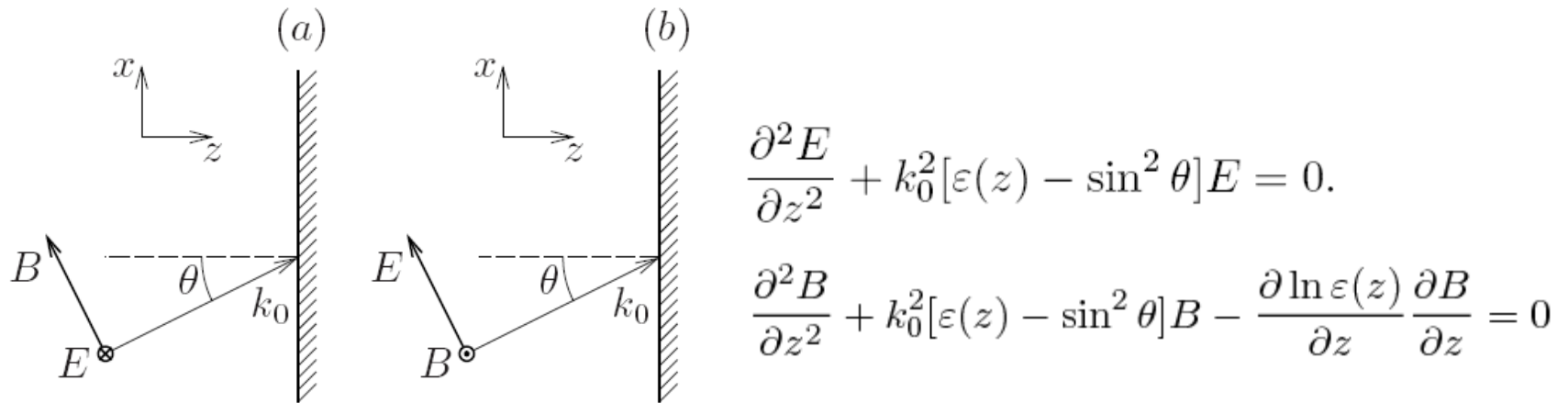
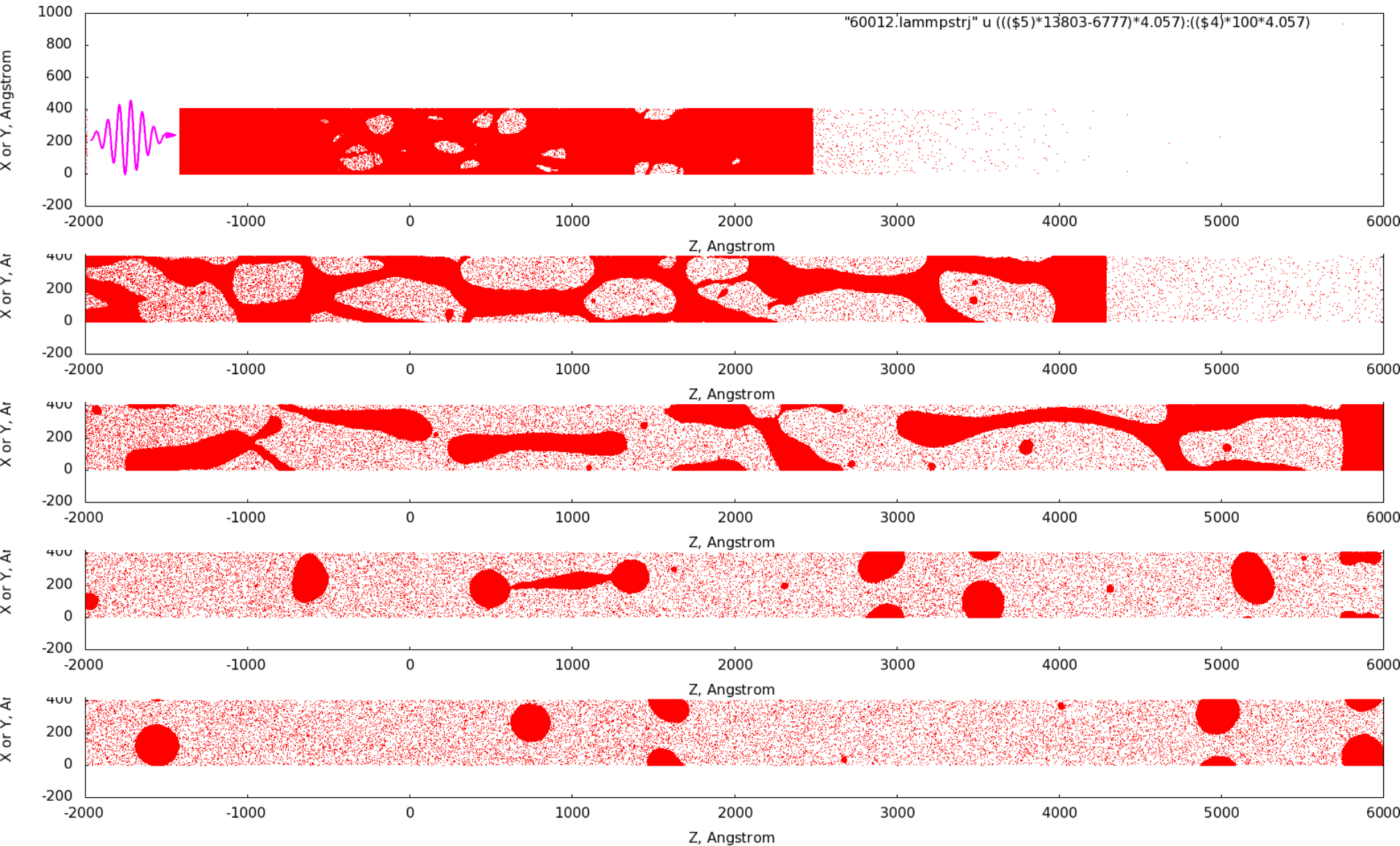


Figure 3. Polarization of laser light: (a)—s; (b)—p.

$$Q_L(t, z) = I(t) \frac{\omega_L}{c} \text{Im}\{\varepsilon(t, z)\} |E(t, z)/E_L(t)|^2$$

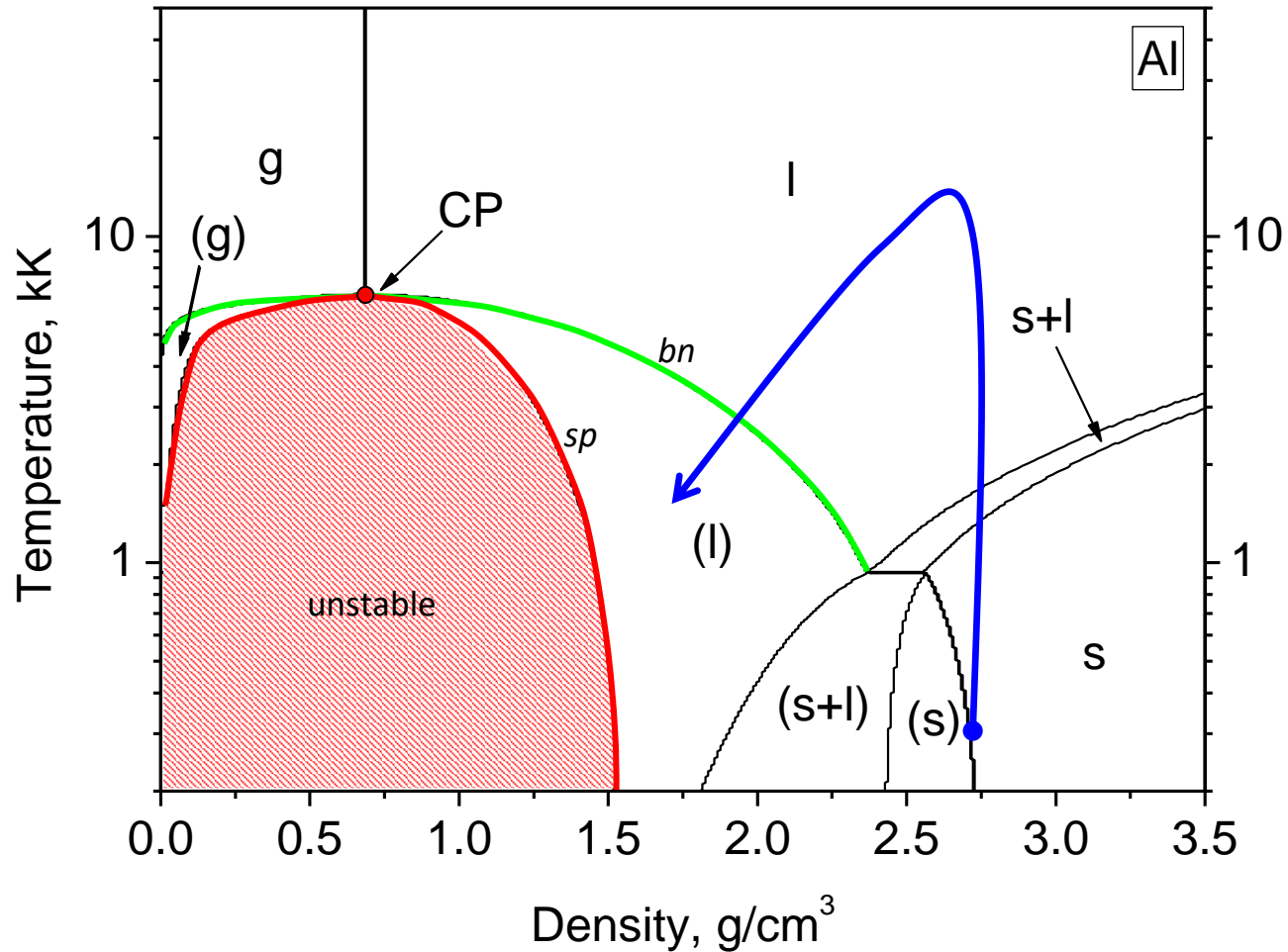
Ultra-short Laser Ablation

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



Ultra-short Laser Ablation

Equation of state (EOS)



Ultra-short Laser Ablation

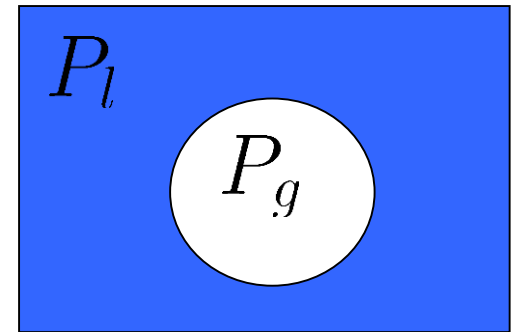
Bubble/Pore Nucleation

$$\tau_{\text{wait}} = (CN)^{-1} \exp(W/k_B T)$$

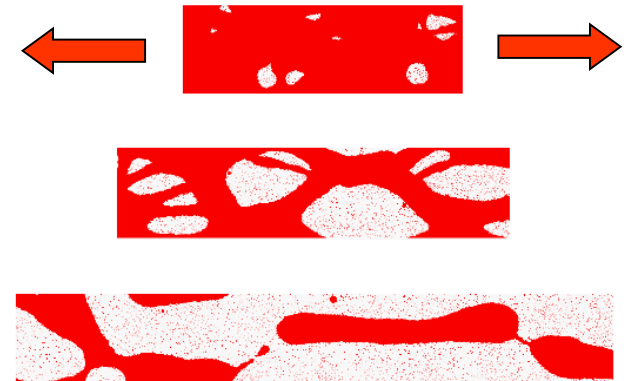
$$C \approx 10^{10} \text{ s}^{-1}$$

$$W = \frac{16\pi\sigma^3}{3(P_g - P_l)^2}$$

$$\tau_{\text{nucl}} = \tau_{\text{wait}} + \tau_{\text{grow}}$$



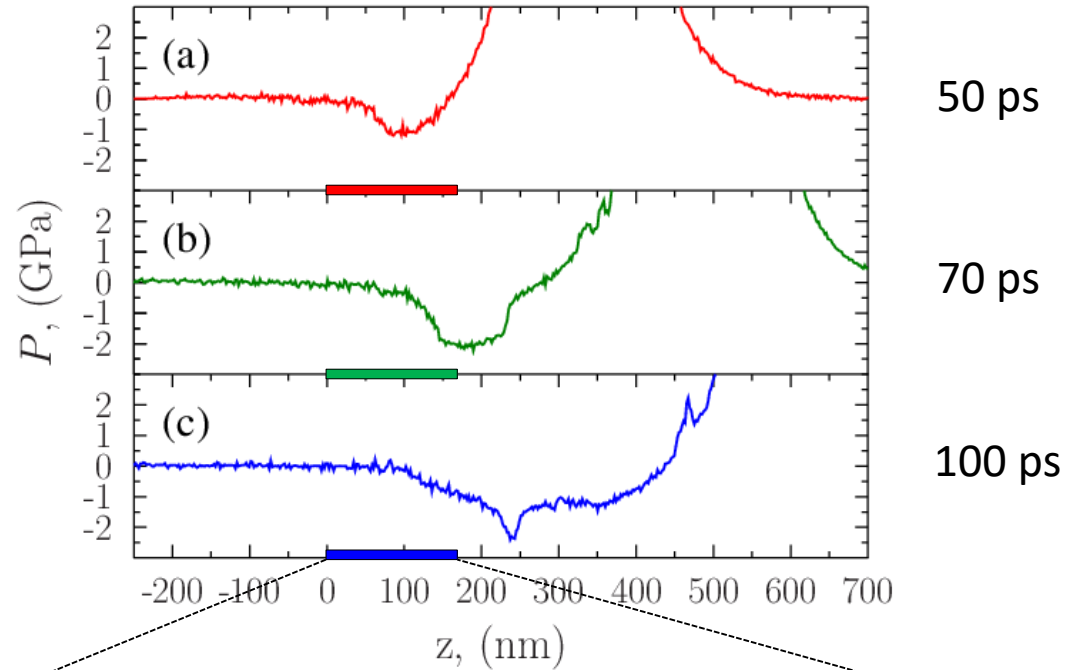
$$P_g > P_l + \frac{2\sigma}{R}$$



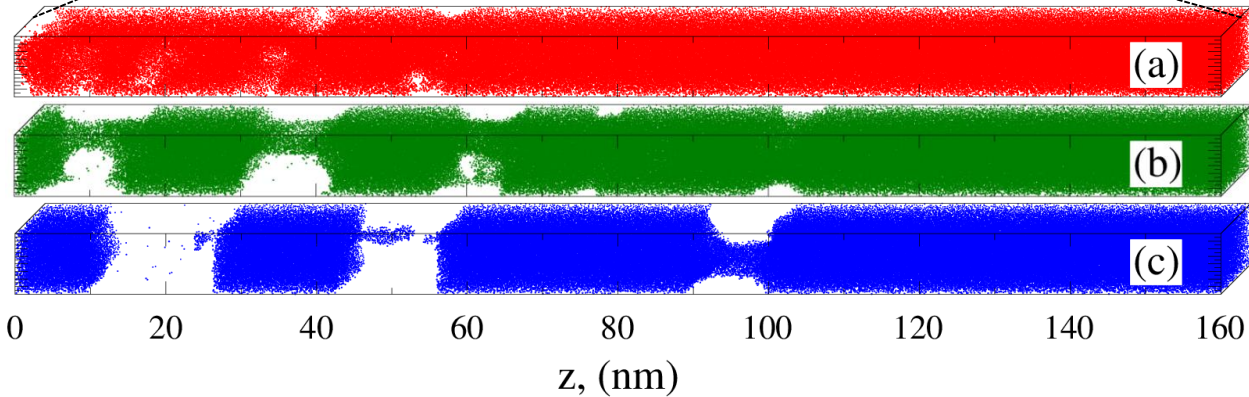
Ultra-short Laser Ablation

Pressure

Al, $F = 2.6 \text{ J/cm}^2$ (DM-TTM)



Laser



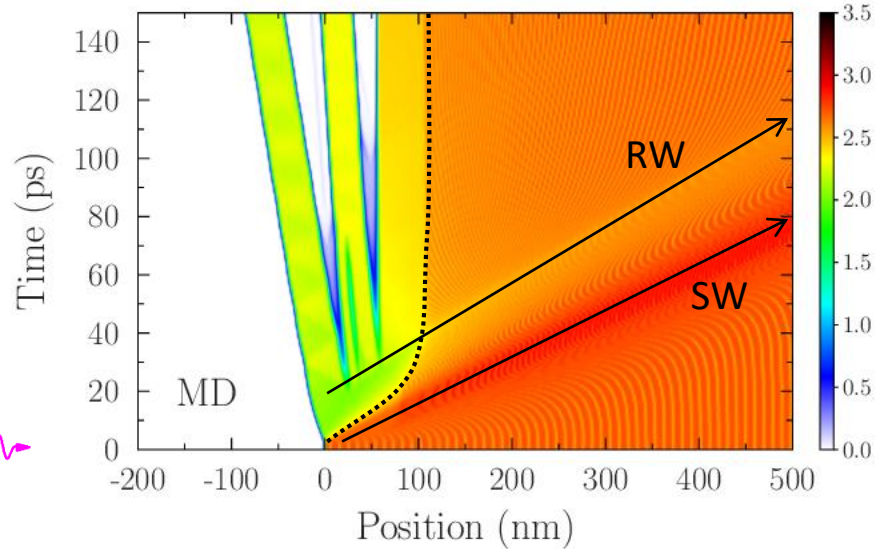
Ultra-short Laser Ablation

Density

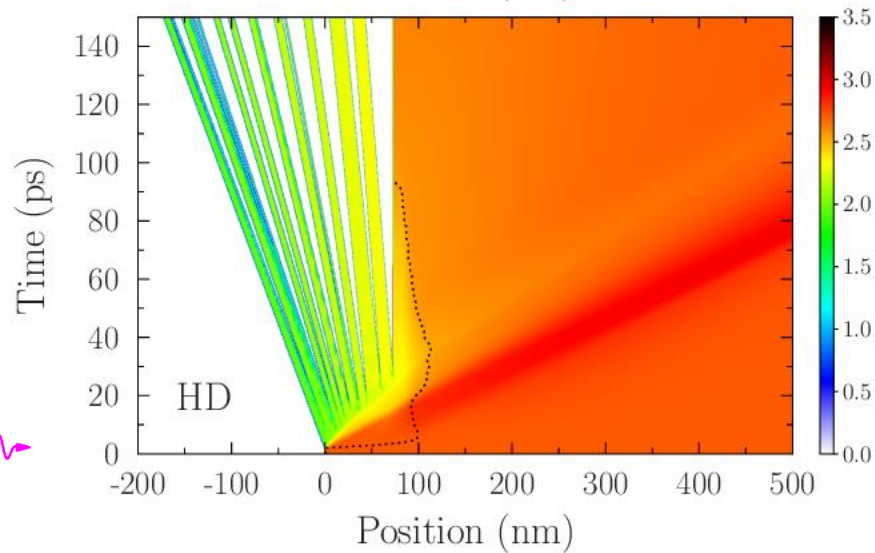
$$Al, F = 0.5 \text{ J/cm}^2$$

melting

TTM-MD



Hydrodynamics

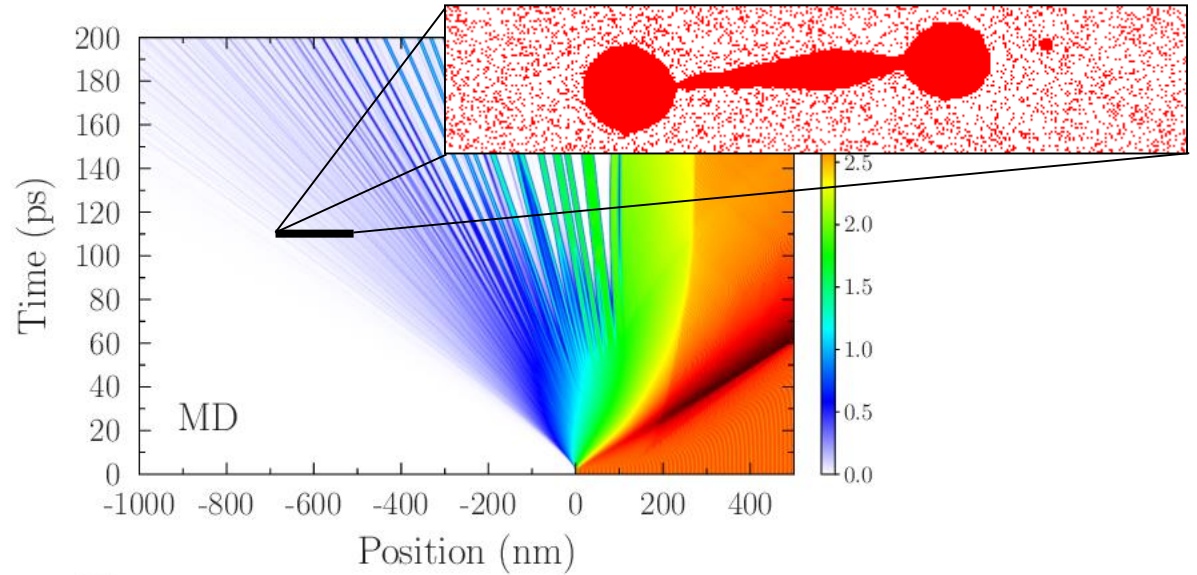


Ultra-short Laser Ablation

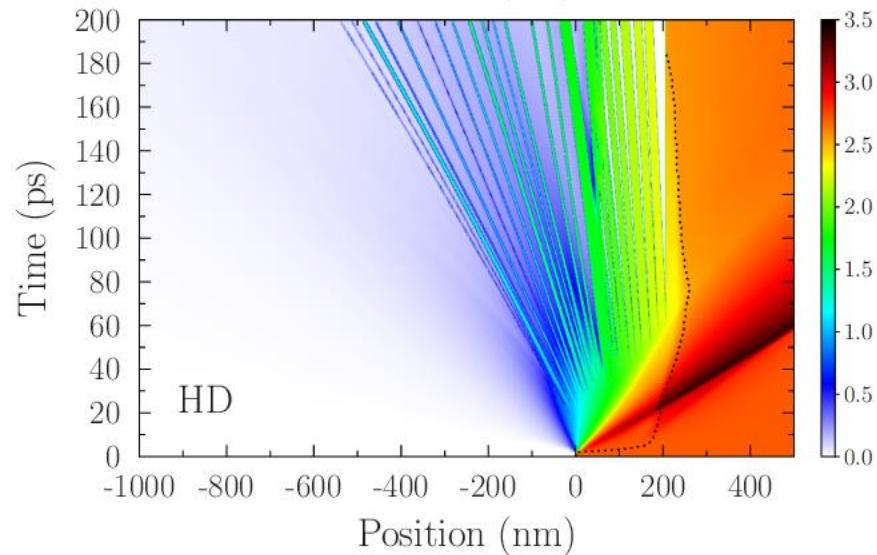
Density

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

TTM-MD



Hydrodynamics

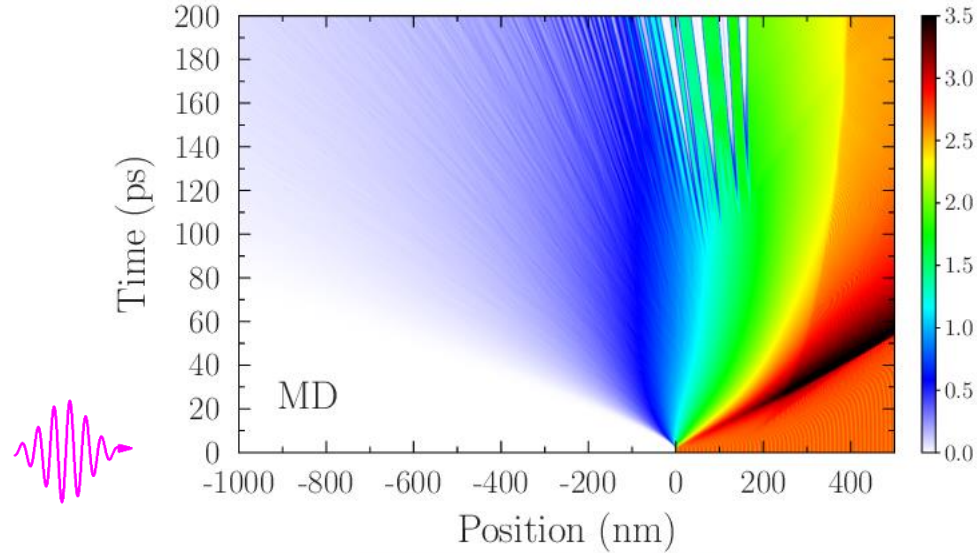


Ultra-short Laser Ablation

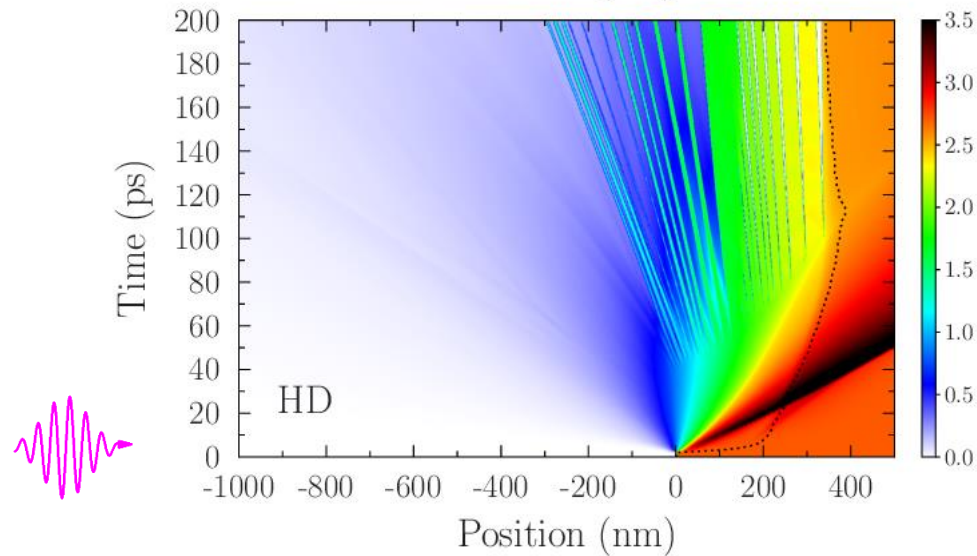
Density

Al, $F = 4 \text{ J/cm}^2$

TTM-MD



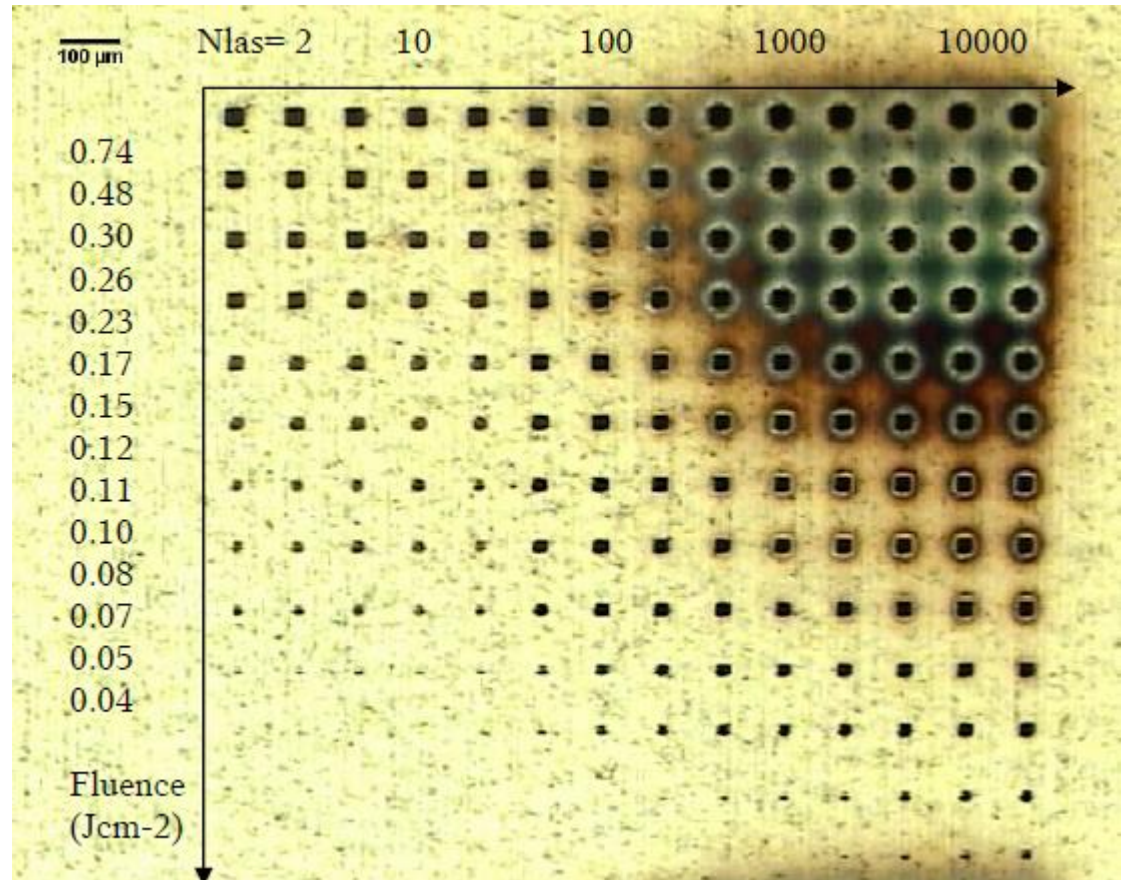
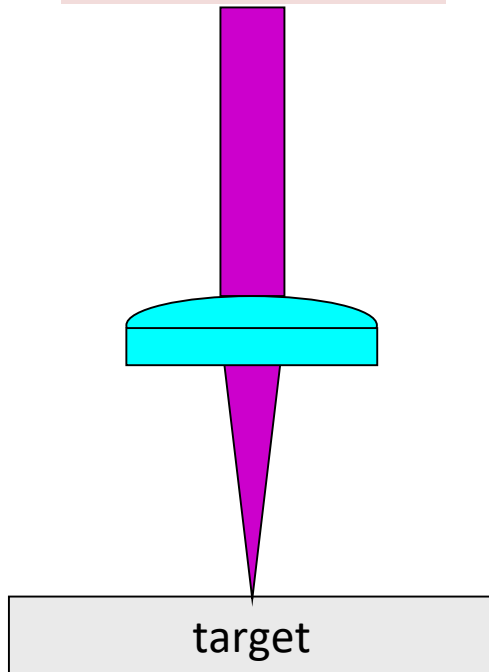
Hydrodynamics



Typical Experiments

Experimental verification

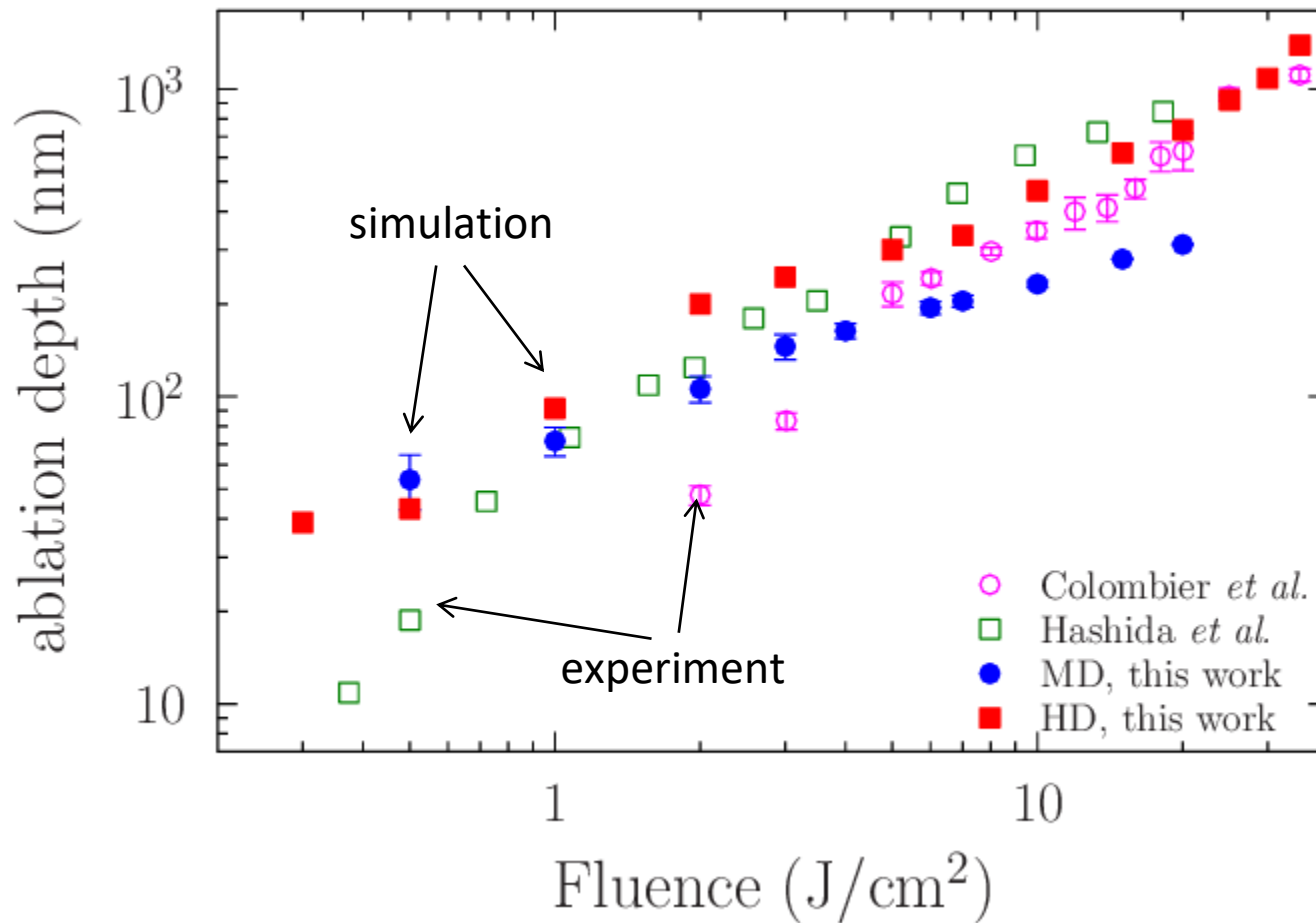
$\lambda = 800 \text{ nm}$
 $\tau = 100 \text{ fs}$
 $F = 0.1 - 10 \text{ J/cm}^2$



Ultra-short Laser Ablation

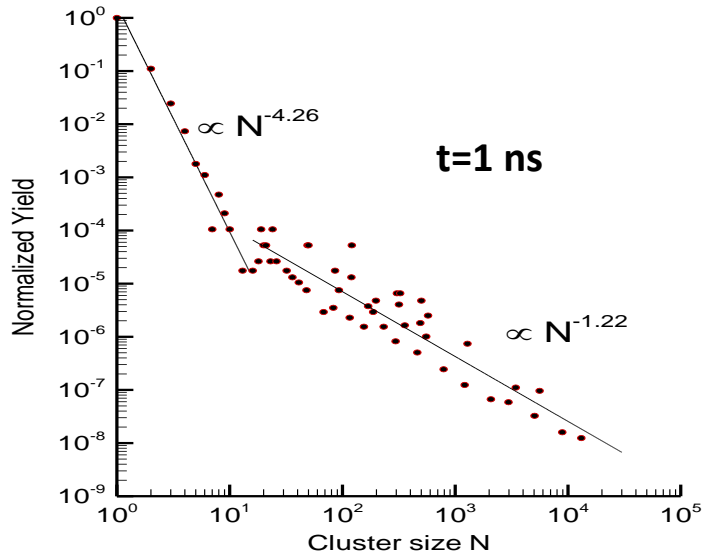
Ablated depth vs laser fluence

100 fs Al

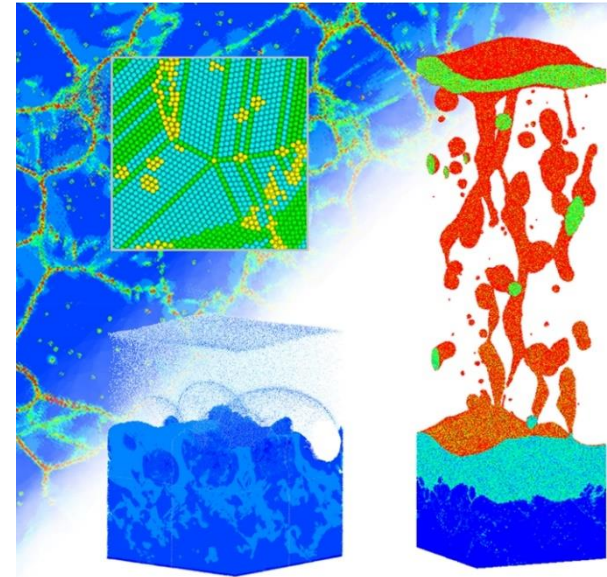
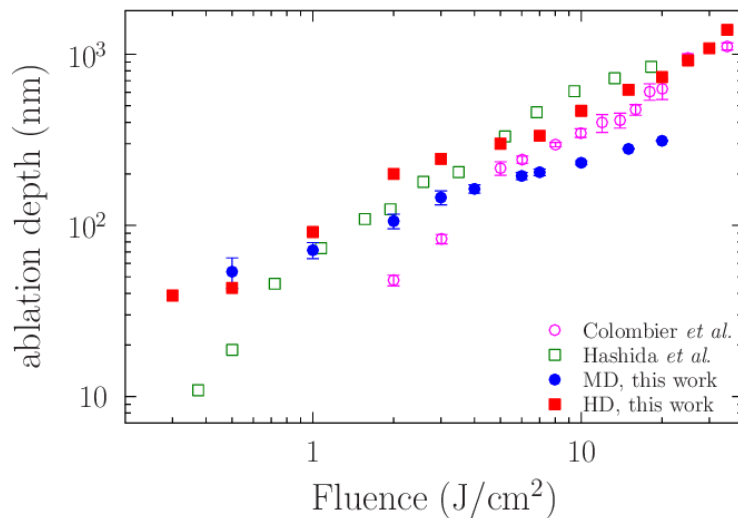


Molecular Dynamics Simulations

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



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



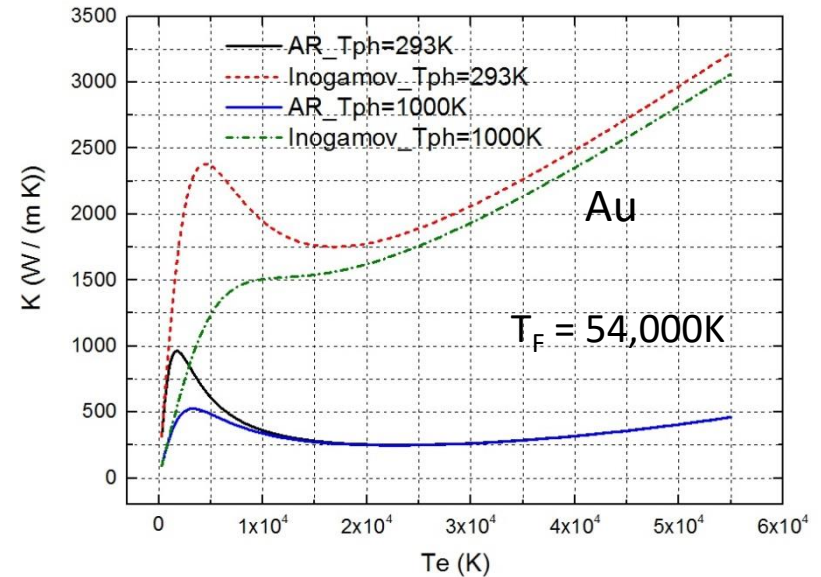
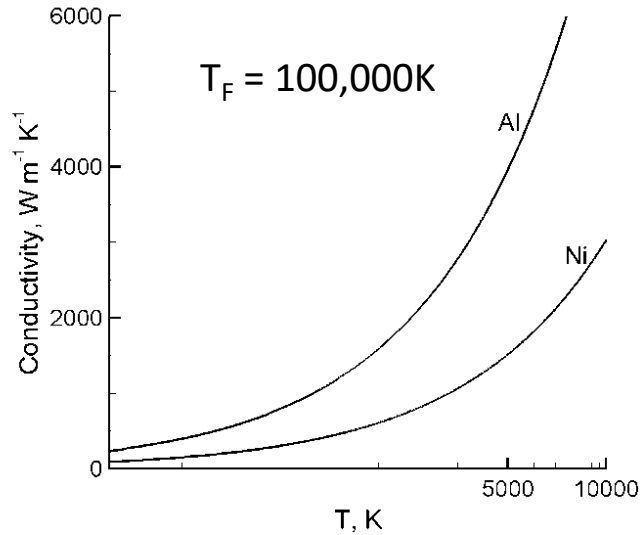
Collaboration with L.V. Zhigilei et al. (Virginia State University, USA)

Practically all the molten material is ablated

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

Conductivity models for metals

$$\text{TTM: } \begin{cases} C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla(K_e(T_e)\nabla T_e) - G(T)(T_e - T_l) + S(\vec{r},t) \\ C_l(T_l) \frac{\partial T_l}{\partial t} = \nabla(K_l\nabla T_l) + G(T_e - T_l) \end{cases}$$



For **transitional metals** excitation is low and $k_e(T_e, T_{ph})$ is:

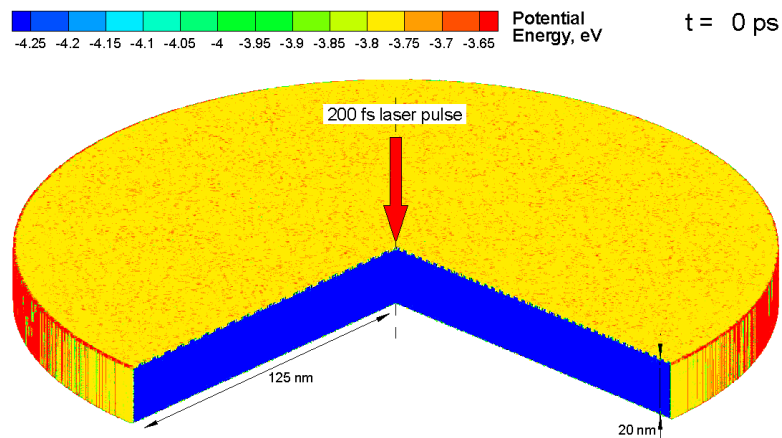
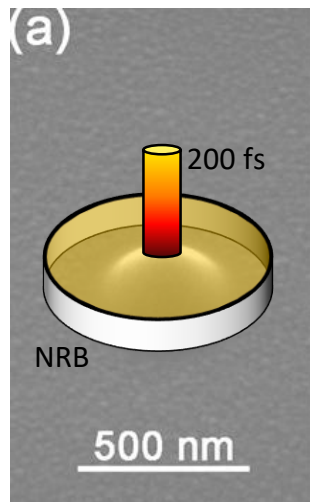
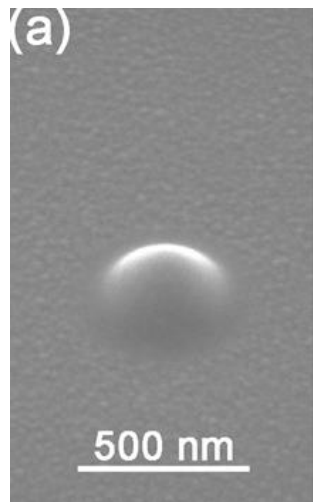
$$k = k_0 \frac{T_e}{T_{ph}}$$

For **noble metals** excitation is high and $k_e(T_e, T_{ph})$ is:

$$k_e = C \frac{(\vartheta_e^2 + 0.16)^{5/4} (\vartheta_e + 0.44) \vartheta_e}{(\vartheta_e^2 + 0.092)^{1/2} (\vartheta_e^2 + b\vartheta_{ph})}$$

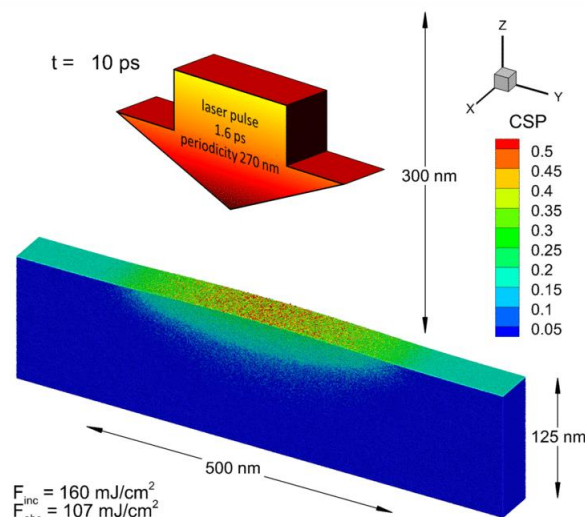
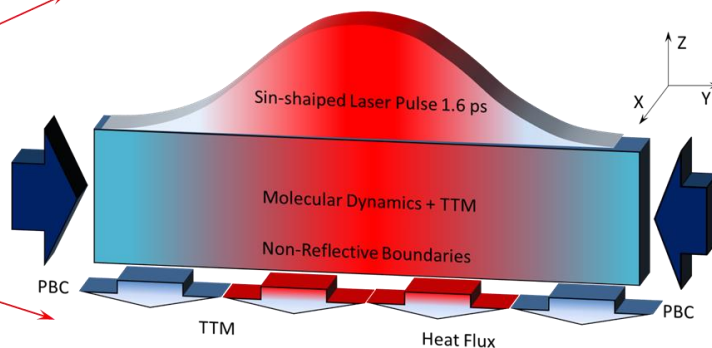
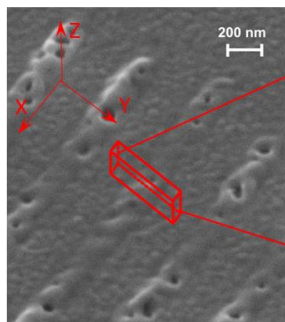
$$\vartheta_e = k_B T_e / E_F \quad \vartheta_l = k_B T_l / E_F$$

Example of TTM-MD : Nanostructuring of Au



D.S. Ivanov, B.C. Rethfeld, G.M. O'Connor, T.J. Glynn, A.N. Volkov, and L.V. Zhigilei, *Appl. Phys. A* 92, 791 (2008).

Nanojet: 85,000,000 atoms



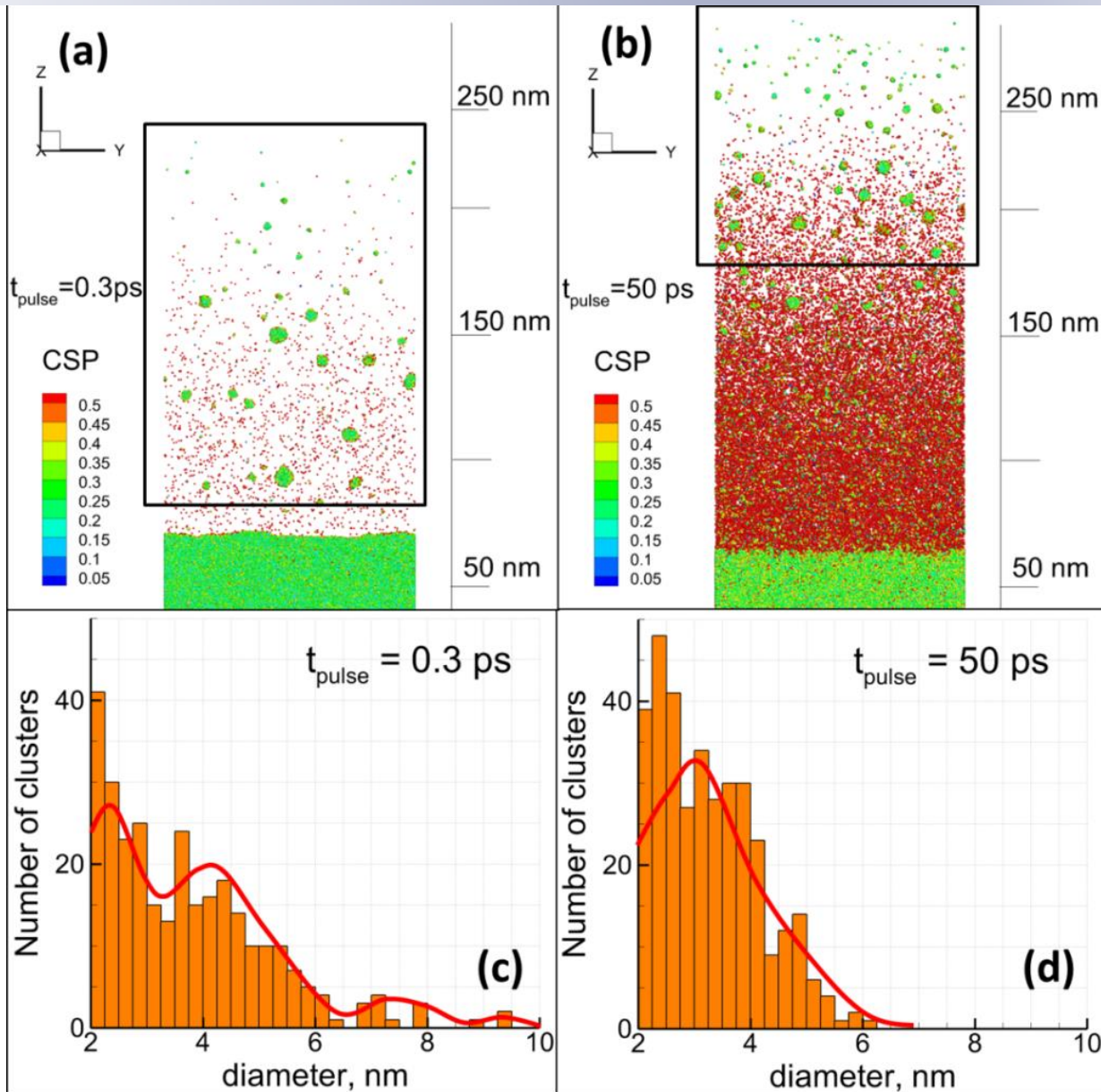
$$F_{inc} = 160 \text{ mJ/cm}^2$$

$$F_{abs} = 107 \text{ mJ/cm}^2$$

Periodic: 330,000,000 atoms

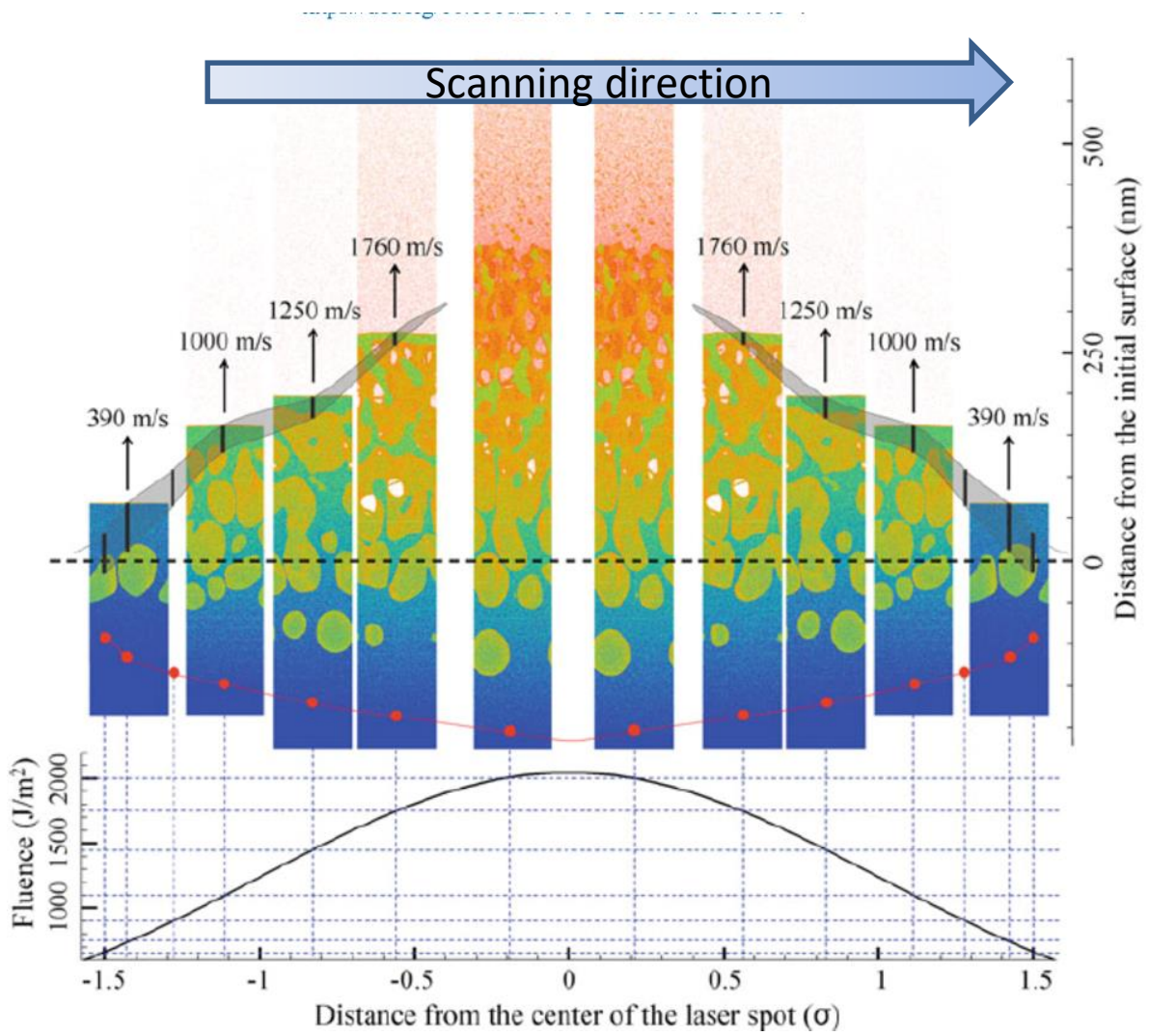
D.S. Ivanov, V.P. Lipp, A. Blumenstein, F. Kleinwort, V.P. Veiko, E. Jakovlev, M.E. Garcia, B. Rethfeld, J. Ihlemann, and P. Simon, *Phys. Rev. Applied* 4, 064006 (2015).

Varying temporal laser pulse width



- 1) Long pulses are more beneficial for generation of NPs of smaller size and narrower size distribution
- 2) Higher fluence results in smaller NPs and size distribution

Effects of Fluence, Multi-pulse effects



K. W. Kolasinski, M. C. Gupta, and L. V. Zhigilei, Plume and nanoparticle formation during laser ablation, *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry* (Elsevier, 2018), pp. 594-603.

TTM –MD: Effects of Sample Porosity

0 %

25 %

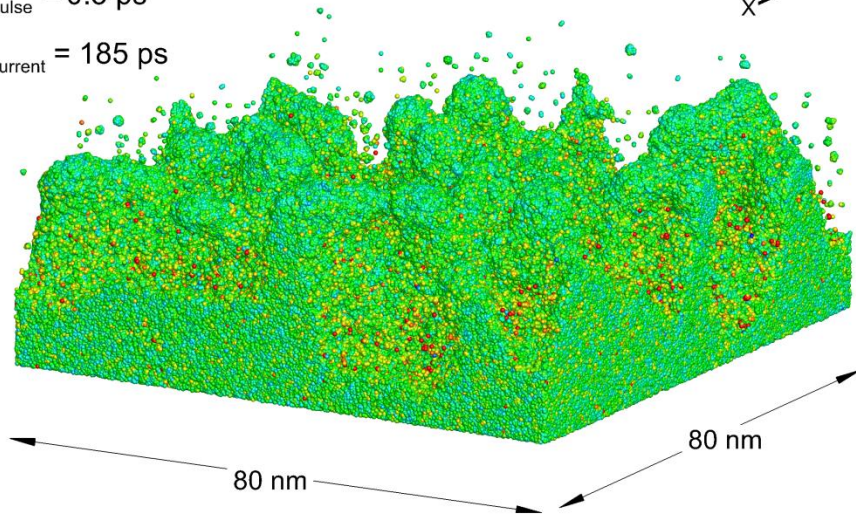
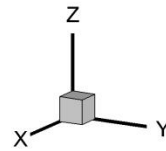
Au sample in H₂O

$F_{inc} = 2.50 \text{ J/cm}^2$

$t_{pulse} = 0.3 \text{ ps}$

$t_{current} = 185 \text{ ps}$

porosity 0%



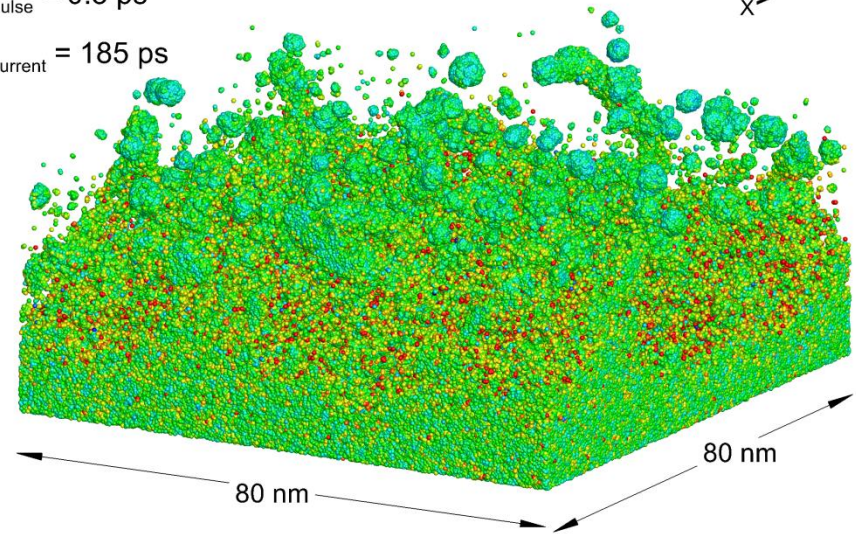
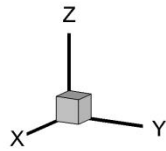
Au sample in H₂O

$F_{inc} = 2.50 \text{ J/cm}^2$

$t_{pulse} = 0.3 \text{ ps}$

$t_{current} = 185 \text{ ps}$

porosity 25%



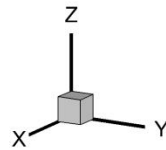
crystal < 0.8 < defects < 0.12 < liquid < 0.25 < surface < 0.5 < vapor
0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 0.45 0.5 CSP

crystal < 0.8 < defects < 0.12 < liquid < 0.25 < surface < 0.5 < vapor
0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 0.45 0.5 CSP

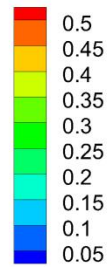
TTM –MD: Effects of Sample Porosity

0 %

porosity 0%
 $F_{inc} = 2.50 \text{ J/cm}^2$
 $t_{pulse} = 0.3 \text{ ps}$
 $t_{current} = 900 \text{ ps}$

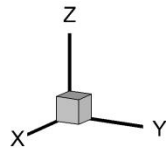
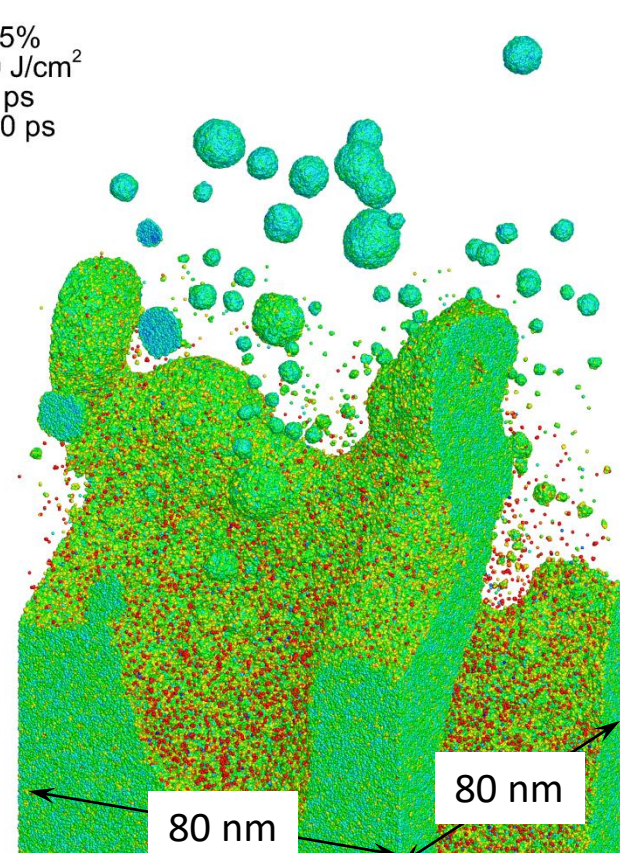


CSP

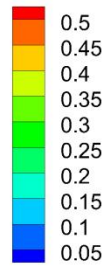


25 %

porosity 25%
 $F_{inc} = 2.50 \text{ J/cm}^2$
 $t_{pulse} = 0.3 \text{ ps}$
 $t_{current} = 900 \text{ ps}$



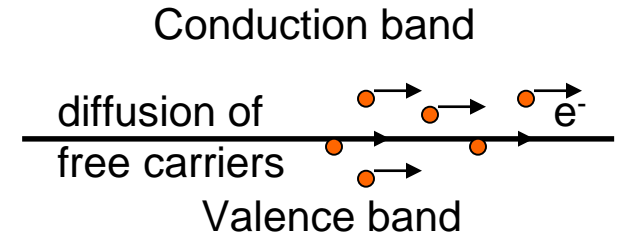
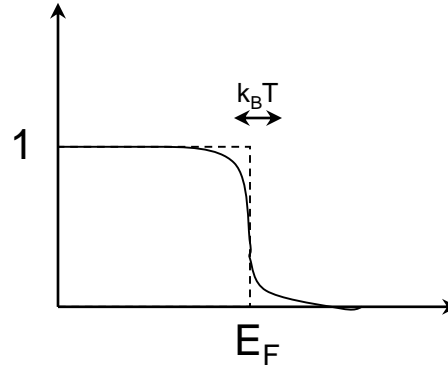
CSP



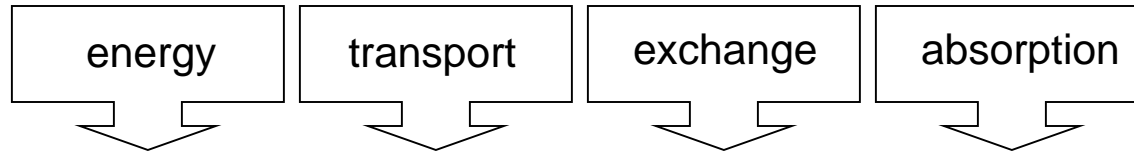
Basics of TTM-MD for Metals

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$$

Fermi-Dirac distribution



Based on the energy balance:



TTM:

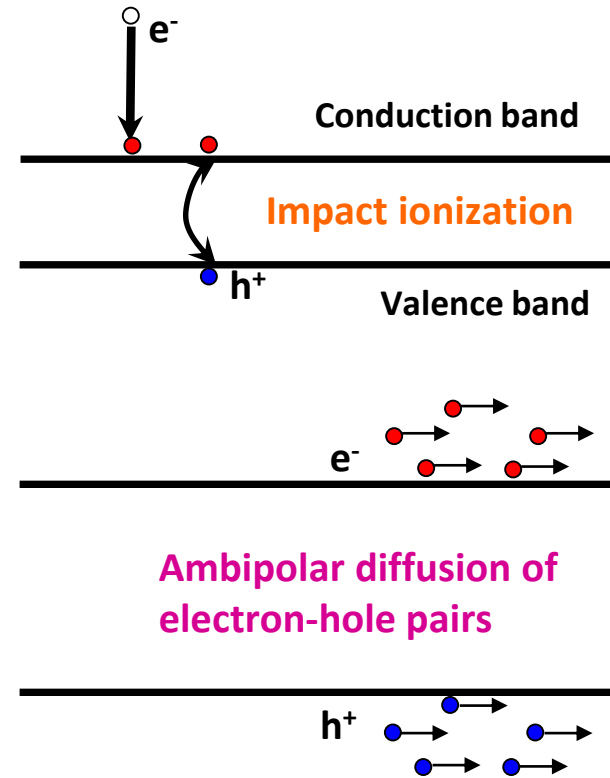
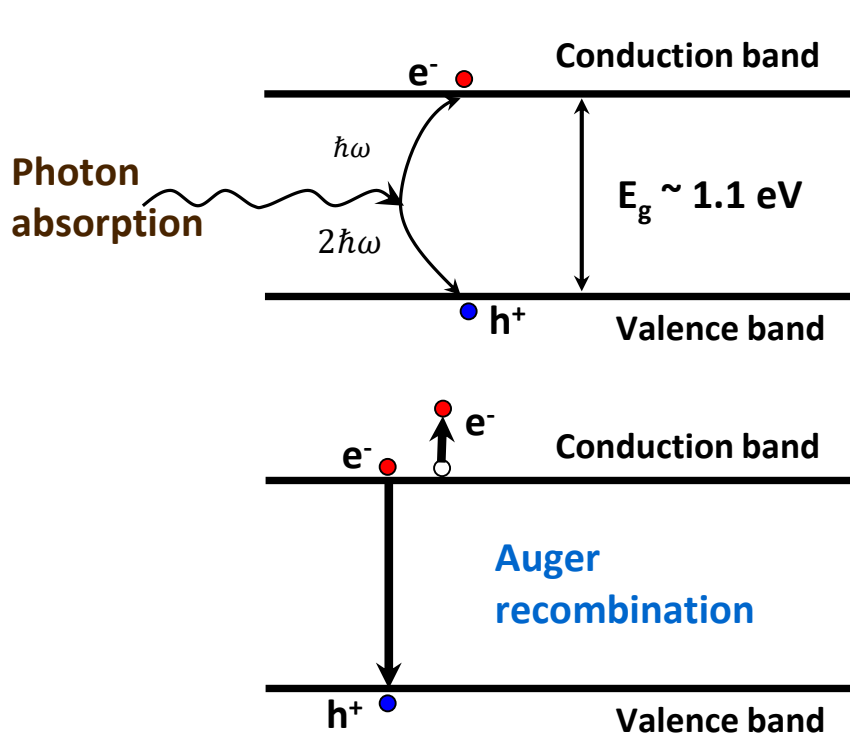
$$\begin{cases} C_e(T_e) \frac{\partial T_e}{\partial t} = \vec{\nabla} \cdot (K_e(T_e) \vec{\nabla} T_e) - G(T_e - T_l) + I(z,t) \\ C_l \frac{\partial T_l}{\partial t} = \vec{\nabla} \cdot (K_l \vec{\nabla} T_l) + G(T_e - T_l) \end{cases}$$

⇒ MD

TTM-MD for Semiconductors (Si)

- Modification of the classical TTM-MD model
- Carriers (electrons and holes)
- Conduction band modifications
- Including carrier excitation/relaxation
- Ambipolar diffusion
- Different potentials
- Etc.

Continuum modeling for silicon



$$\frac{\partial n}{\partial t} = \text{Source}_n(\vec{r}, t) + \theta n - \gamma n^3 - \text{div}(\vec{J})$$

Density of carriers
in conduction band

Excitation of
new carriers

Impact
ionization

Auger
recombination

Ambipolar
diffusion

Continuum modeling for silicon

Energy conservations for carrier subsystem:

$$\frac{\partial U_e}{\partial t} = \text{Source}(\vec{r}, t) - \text{div}\vec{W}(\vec{r}, t) - G(T_e - T_L)$$



Energy of electrons
in conduction band



Laser
source



Energy
flux



Energy exchange
with atoms

$$\text{Source}(\vec{r}, t) = \alpha I(\vec{r}, t) + \beta I^2(\vec{r}, t) + \Theta n I(\vec{r}, t)$$



1-photon
absorption



2-photon
absorption



Free carriers
absorption

Continuum modeling for silicon

Self-consistent model on Si (analogue to TTM)

J.K. Chen, D.Y. Tzou, and J.E. Beraun, Int. J. of Heat and Mass Transfer 48, 501-509 (2005)

$$\frac{\partial n}{\partial t} = \frac{\alpha I}{\hbar\omega} + \frac{\beta I^2}{2\hbar\omega} + \theta n - \gamma n^3 - \text{div}(\vec{J})$$

Carrier density

$$\frac{\partial U}{\partial t} = (\alpha + \Theta n)I + \beta I^2 - \text{div}(\vec{W}) - G(T_e - T_a)$$

Energy of excited carriers

~~$$C_a \frac{\partial T_a}{\partial t} = \text{div}(k_L \nabla T_L) + G(T_e - T_a)$$~~

Lattice temperature

$$\text{MD: } m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i + \xi m_i \frac{d\vec{r}_i^T}{dt}$$

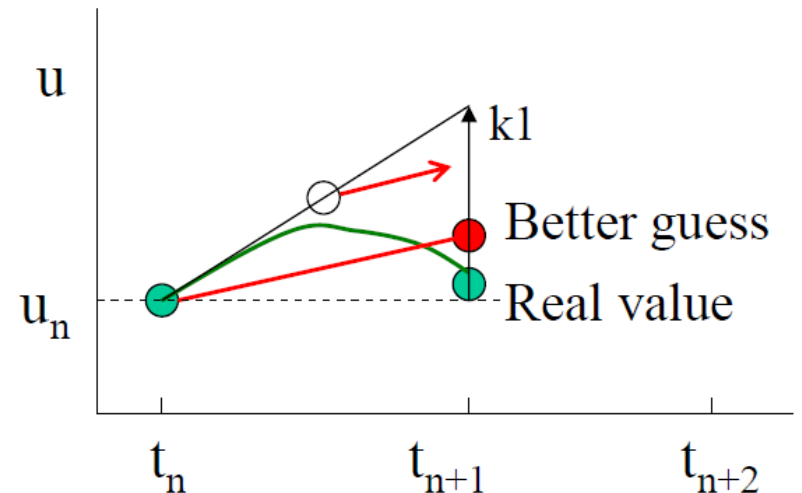
$$I(z, t) = -I_0(1 - R)\alpha_{\text{abs}} \exp(-\alpha_{\text{abs}}z) \sqrt{\frac{\sigma}{\pi}} \exp\left(-\sigma \frac{(t-t_0)^2}{\tau^2}\right)$$

$$\left\{ \begin{aligned} \frac{dI(z, t)}{dz} &= -\left(\alpha + \alpha_{FCA}(\varepsilon(N_e))\right) I(z, t) - \beta I^2(z, t) \\ \frac{\partial N_e}{\partial t} &= \frac{\alpha I(z, t)}{h\nu} + \frac{\beta I^2(z, t)}{2h\nu} + \delta N_e - \gamma N_e^3 - \nabla \cdot \vec{J}(N_e, T_e, E_g) \\ \frac{\partial U_e(N_e T_e, E_g)}{\partial t} &= \left(\alpha + \alpha_{FCA}(\varepsilon(N_e))\right) I(z, t) + \beta I^2(z, t) \\ -\nabla \cdot \vec{W}(N_e, T_e, E_g) &- \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l) \\ C_l \frac{\partial T_l}{\partial t} &= \vec{\nabla} \cdot (\kappa \vec{\nabla} T_l) + \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l) \rightarrow m_i \frac{d\vec{r}_i}{dt^2} = - \sum_{j=1, N} \vec{\nabla} U(\vec{r}_{ij}, T_e) + \xi m_i \vec{V}_i^T \end{aligned} \right.$$

$$k1 = h^* f(u_n, t_n)$$

$$k2 = h^* f(u_n + k1/2, t_n + h/2)$$

$$u_{n+1} = u_n + k2 + O(h^3)$$



Continuum modeling for silicon

$$\left\{ \begin{array}{l} \frac{dI(z,t)}{dz} = -\left(\alpha + \alpha_{FCA}(\varepsilon(N_e))\right) I(z,t) - \beta I^2(z,t) \\ \frac{\partial N_e}{\partial t} = \frac{\alpha I(z,t)}{h\nu} + \frac{\beta I^2(z,t)}{2h\nu} + \delta N_e - \gamma N_e^3 - \nabla \cdot \vec{J}(N_e, T_e, E_g) \\ \frac{\partial U_e(N_e, T_e, E_g)}{\partial t} = \left(\alpha + \alpha_{FCA}(\varepsilon(N_e))\right) I(z,t) + \beta I^2(z,t) \\ - \nabla \cdot \vec{W}(N_e, T_e, E_g) - \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l) \\ C_l \frac{\partial T_l}{\partial t} = \vec{\nabla} \cdot (\kappa \vec{\nabla} T_l) + \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l) \rightarrow m_i \frac{d\vec{r}_i}{dt^2} = - \sum_{j=1, N} \vec{\nabla} U(\vec{r}_{ij}, T_e) + \xi m_i \vec{V}_i^T \end{array} \right.$$

$$\vec{J} = -D \left\{ \vec{\nabla} n + \frac{n}{k_B T_e} \left[H_{-1/2}^{1/2}(\eta_e) + H_{-1/2}^{1/2}(\eta_h) \right]^{-1} \vec{\nabla} E_g \right\} -$$

$$- \frac{Dn}{T_e} \left\{ 2 \frac{[H_0^1(\eta_e) + H_0^1(\eta_h)]}{\left[H_{-1/2}^{1/2}(\eta_e) + H_{-1/2}^{1/2}(\eta_h) \right] - \frac{3}{2}} \right\} \vec{\nabla} T_e$$

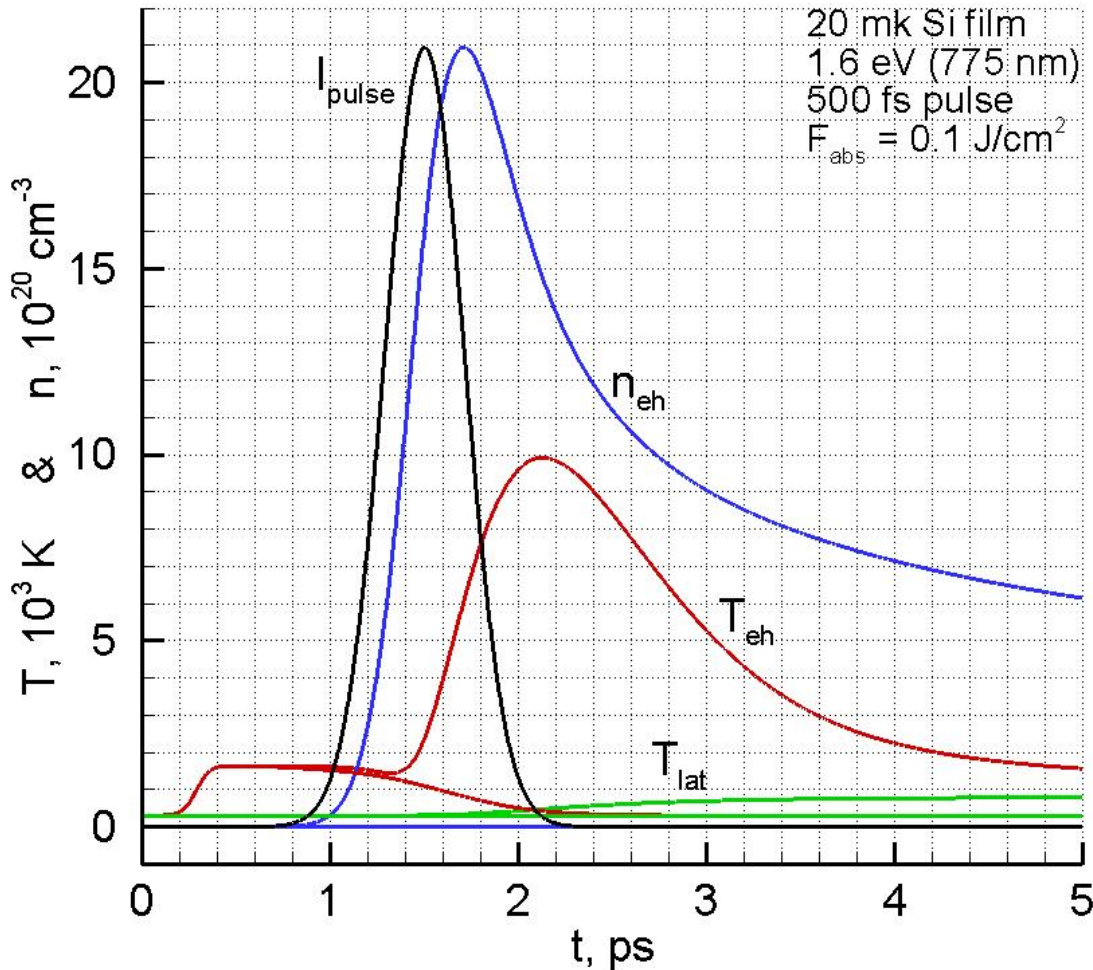
$$\vec{W} = \{ E_g + 2k_B T_e [H_0^1(\eta_e) + H_0^1(\eta_h)] \} \vec{J} - (\kappa_e - \kappa_h) \vec{\nabla} T_e$$

$$C_{e-h} \frac{\partial T_e}{\partial t} = (\alpha + \Theta n) I(\vec{x}, t) + \beta I^2(\vec{x}, t) - \nabla \cdot \vec{W} - \frac{C_{e-h}}{\tau_e} (T_e - T_l) -$$

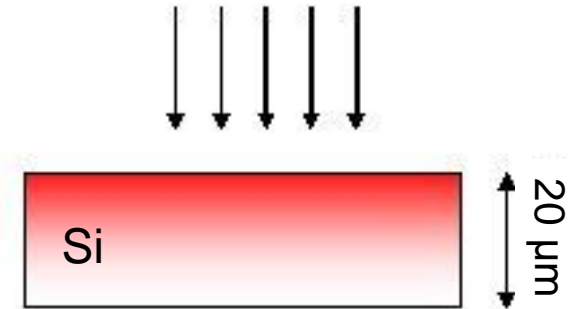
$$- \frac{\partial n}{\partial t} \left\{ E_g + \frac{3}{2} k_B T_e \left[H_{1/2}^{3/2}(\eta_e) + H_{1/2}^{3/2}(\eta_h) \right] \right\} - n \left(\frac{\partial E_g}{\partial n} \frac{\partial n}{\partial t} + \frac{\partial E_g}{\partial T_l} \frac{\partial T_l}{\partial t} \right)$$

nTTM for Si, free carriers, 500 fs laser pulse

Self-Sonsistent Model on Si



Laser pulse



- First peak of T_{e-h} is due to small heat capacity of the $e-h$ pairs
- Second peak of T_{e-h} is due to direct absorption by free $e-h$ carrier
- $\Delta t \sim 10\text{d}-22$ at $\Delta z \sim 200\text{nm}$

Atomistic-Continuum Model for silicon

Self-consistent model on Si (analogue to TTM)

J.K. Chen, D.Y. Tzou, and J.E. Beraun, *Int. J. of Heat and Mass Transfer* 48, 501-509 (2005)

$$\left\{ \begin{aligned} \frac{dI(z,t)}{dz} &= - \left(\alpha + \alpha_{FCA}(\varepsilon(N_e)) \right) I(z,t) - \beta I^2(z,t) \\ \frac{\partial N_e}{\partial t} &= \frac{\alpha I(z,t)}{h\nu} + \frac{\beta I^2(z,t)}{2h\nu} + \delta N_e - \gamma N_e^3 - \nabla \cdot \vec{J}(N_e, T_e, E_g) \\ \frac{\partial U_e(N_e, T_e, E_g)}{\partial t} &= \left(\alpha + \alpha_{FCA}(\varepsilon(N_e)) \right) I(z,t) + \beta I^2(z,t) \\ -\nabla \cdot \vec{W}(N_e, T_e, E_g) &- \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l) \\ C_l \frac{\partial T_l}{\partial t} &= \vec{\nabla} \cdot (\kappa \vec{\nabla} T_l) + \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l) \rightarrow \rightarrow m_i \frac{d\vec{r}_i}{dt^2} = - \sum_{j=1, N} \vec{\nabla} U(\vec{r}_{ij}, T_e) + \xi m_i \vec{V}_i^T \end{aligned} \right. \quad (1)$$

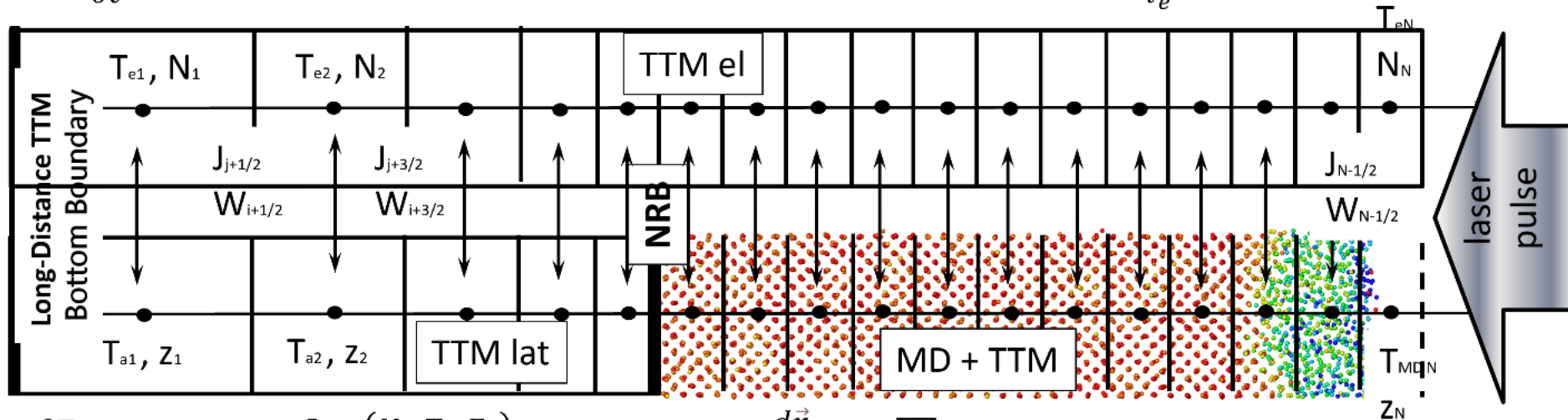
$$\left\{ \begin{aligned} \vec{W} &= \{E_g + 2k_B T_e [H_0^1(\eta_e) + H_0^1(\eta_h)]\} \vec{J} - (k_e + k_h) \nabla T_e \\ \vec{J} &= -D \left\{ \nabla n + \frac{N_e}{k_B T_e} \left[H_{-\frac{1}{2}}^{\frac{1}{2}}(\eta_e) + H_{-\frac{1}{2}}^{\frac{1}{2}}(\eta_h) \right]^{-1} \nabla E_g + \frac{N_e}{T_e} \left[2 \frac{H_0^1(\eta_e) + H_0^1(\eta_h)}{H_{-\frac{1}{2}}^{\frac{1}{2}}(\eta_e) + H_{-\frac{1}{2}}^{\frac{1}{2}}(\eta_h)} - \frac{3}{2} \right] \nabla T_e \right\} \\ D &= \frac{k_b T_e}{q_e} \frac{\mu_e \mu_h H_{\frac{1}{2}}^0(\eta_e) H_{\frac{1}{2}}^0(\eta_h)}{\mu_e H_{\frac{1}{2}}^0(\eta_e) + \mu_h H_{\frac{1}{2}}^0(\eta_h)} \left[H_{-\frac{1}{2}}^{\frac{1}{2}}(\eta_e) + H_{-\frac{1}{2}}^{\frac{1}{2}}(\eta_h) \right] \end{aligned} \right. \quad (2)$$

M.S. Grigoryeva, I.A. Kutlubulatova, S.Yu. Lukashenko, D.S. Ivanov, A.P. Kanavin, V.Yu. Timoshenko, and I.N. Zavestovskaya, "Investigation of the Mechanism of Short Pulse Laser Ablation of Porous Si targets with Atomistic-Continuum Numerical Approach", submitted to *Appl Sur Sci*

Atomistic-Continuum Model for silicon

MD-nTTM

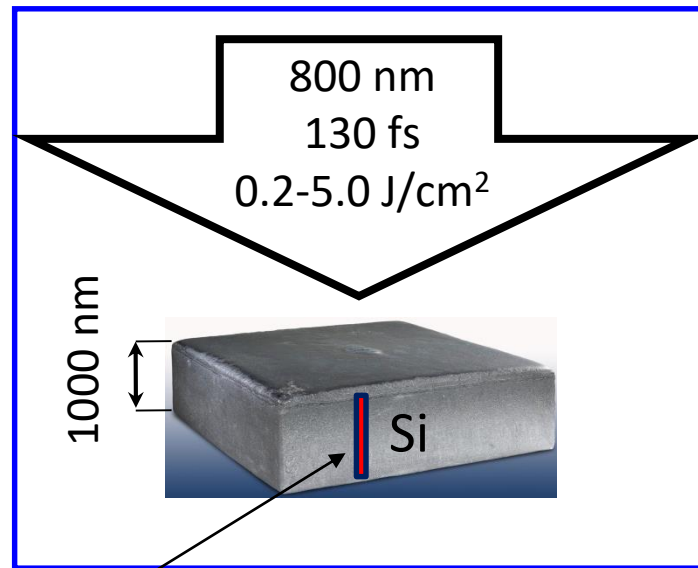
$$\frac{\partial U_e(N_e, T_e, E_g)}{\partial t} = \left(\alpha + \alpha_{FCA}(\varepsilon(N_e)) \right) I(z, t) + \beta I^2(z, t) - \nabla \cdot \vec{W}(N_e, T_e, E_g) - \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l)$$



$$C_l \frac{\partial T_l}{\partial t} = \vec{\nabla} \cdot (k \vec{\nabla} T_l) + \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l)$$

$$m_i \frac{d\vec{r}_i}{dt^2} = - \sum_{j=1, N} \vec{\nabla} U(\vec{r}_{ij}, T_e) + \xi m_i \vec{V}_i^T$$

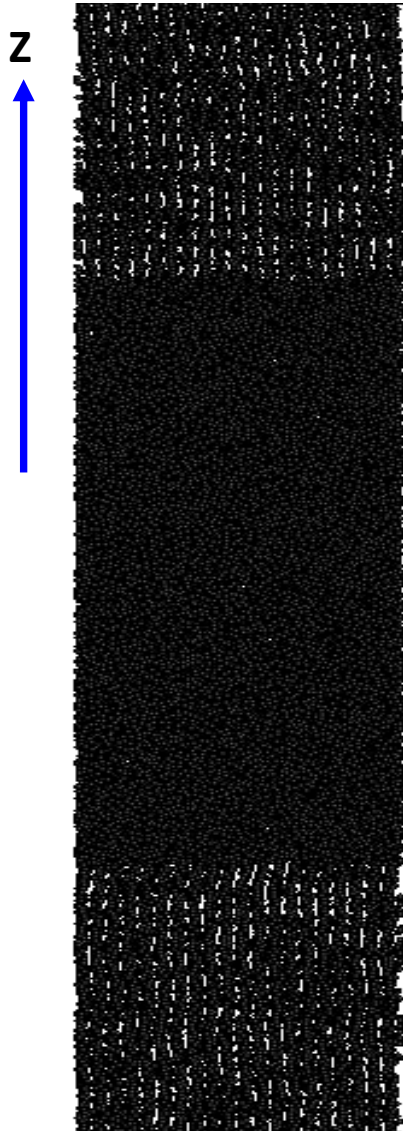
Results of MD-nTTM Laser melting



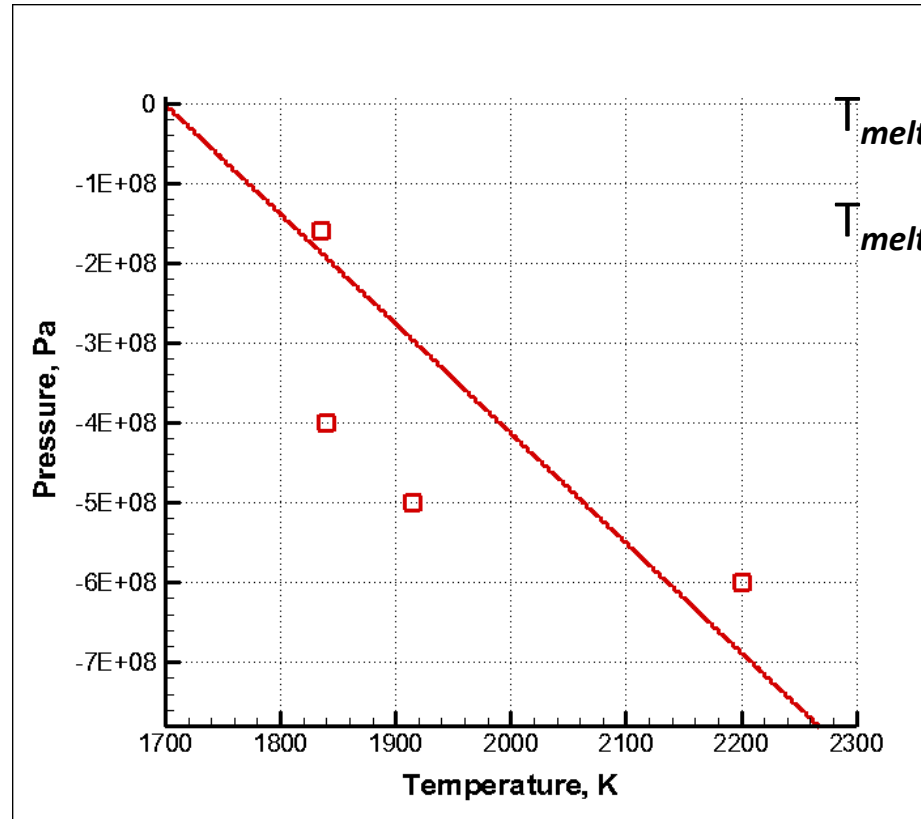
Computational cell

Results of atomistic modeling for silicon

Melting temperature calculation for Si



Molten part



$T_{melting\ S-W} = 1699\ K$

$T_{melting\ exp} = 1683\ K$

Open diamond crystal structure: $V_{melt} = -7.5\%$

Linear expansion coefficient: $\alpha = 3 \times 10^{-6}\ 1/K \ll \alpha_{metals}$

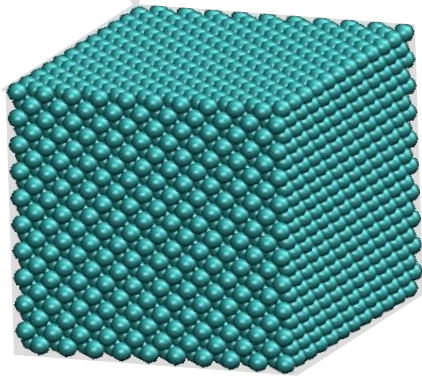
Slope of the melting curve: $[dP/dT]_T < 0$

Results of atomistic modeling for silicon

Calculation of bulk modulus

12x12x12 atom layers

T = 300 K

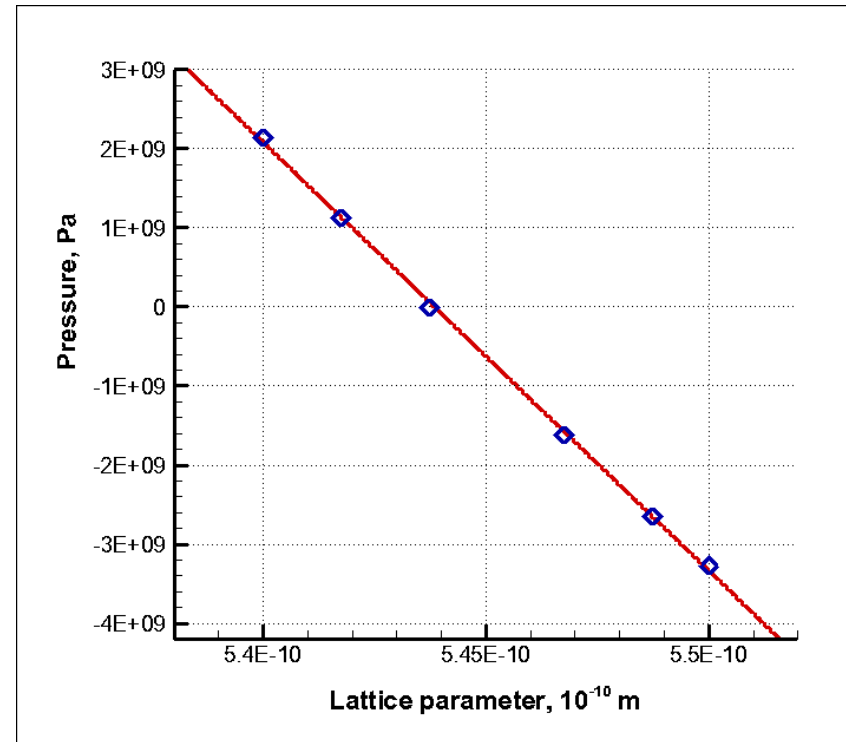


$$\mathbf{B} = - \left[V \frac{dP}{dV} \right]_{V=V_0}$$

$$a_0 = 5.44 \text{ \AA}$$

$$B_{S-W} = 97.7 \text{ GPa}$$

$$B_{exp} = 99 \text{ GPa}$$



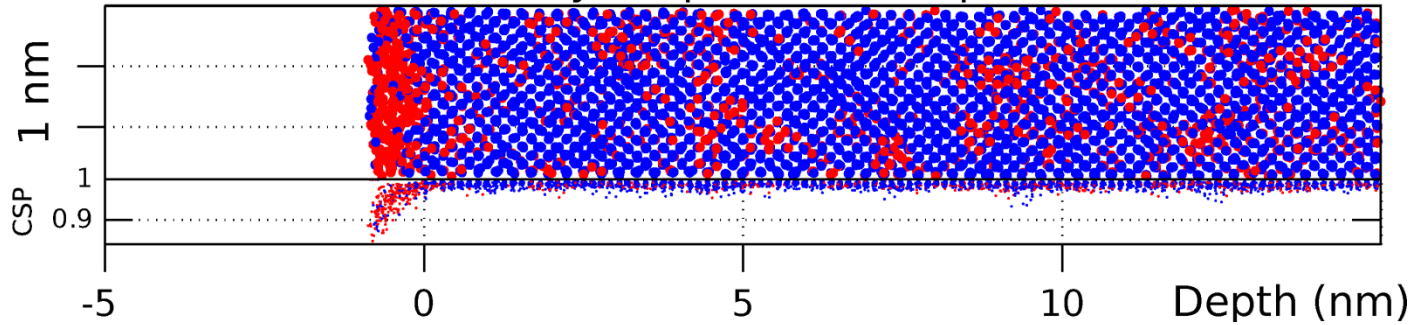
Good agreement with experiment – correct resistance of uniform compression

Phys. Rev. B 46, 2250–2279 (1992)

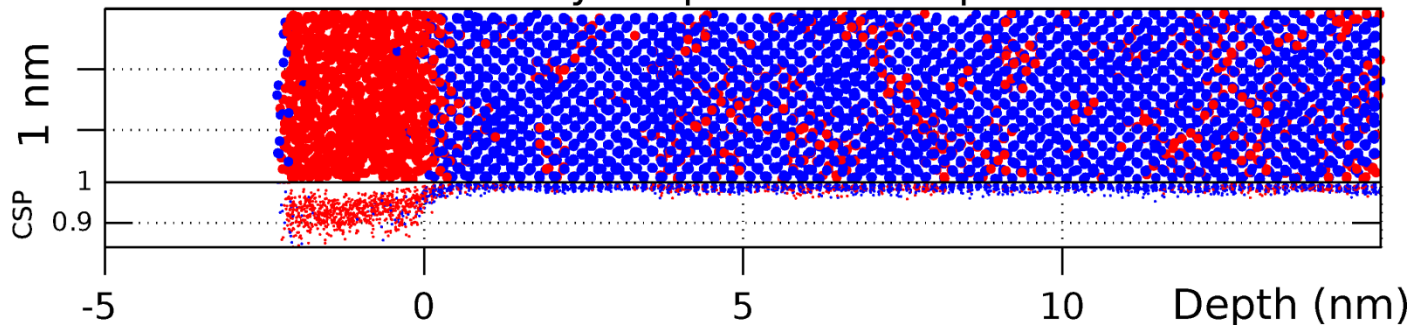
Snapshots of laser melting absorbed fluence 0.16 J/m^2

Slow heterogeneous melting

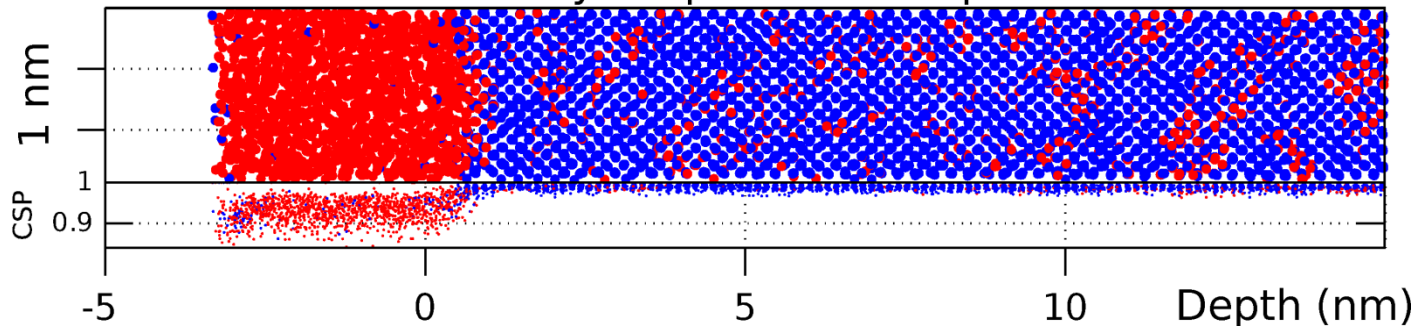
Si crystal part after 10 ps



Si crystal part after 30 ps



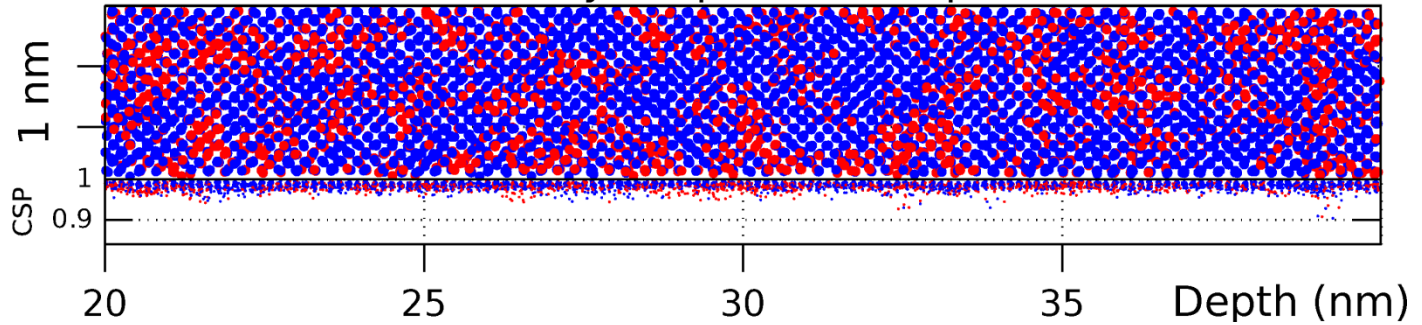
Si crystal part after 50 ps



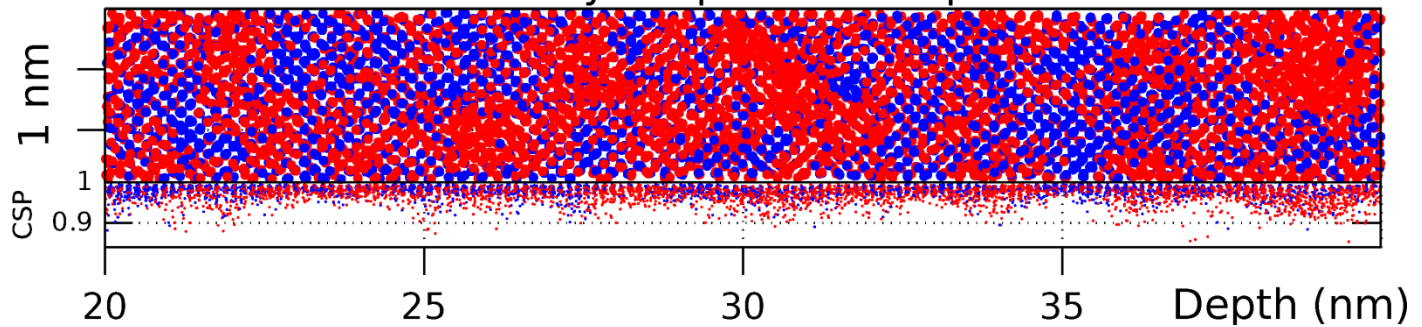
130 fs
 0.16 J/cm^2

Snapshots of laser melting absorbed fluence 0.21 J/m^2

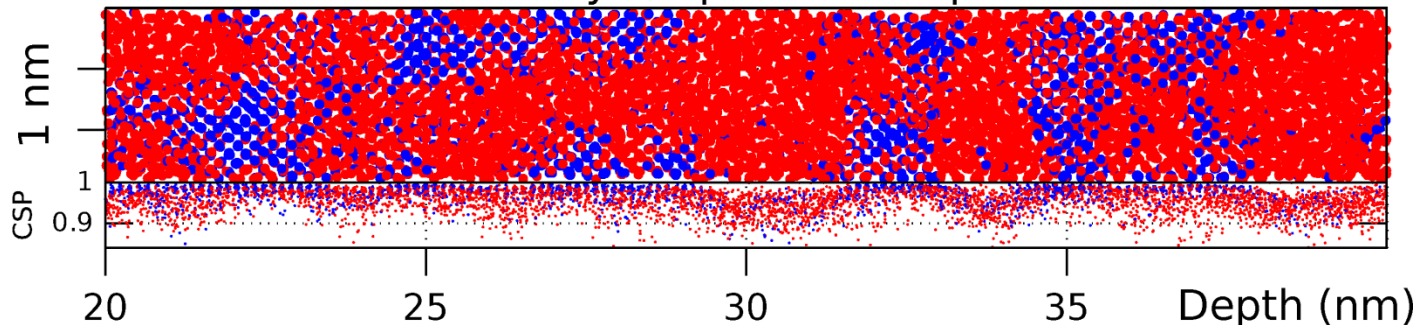
Quick homogeneous melting
Si crystal part after 2 ps



Si crystal part after 4 ps

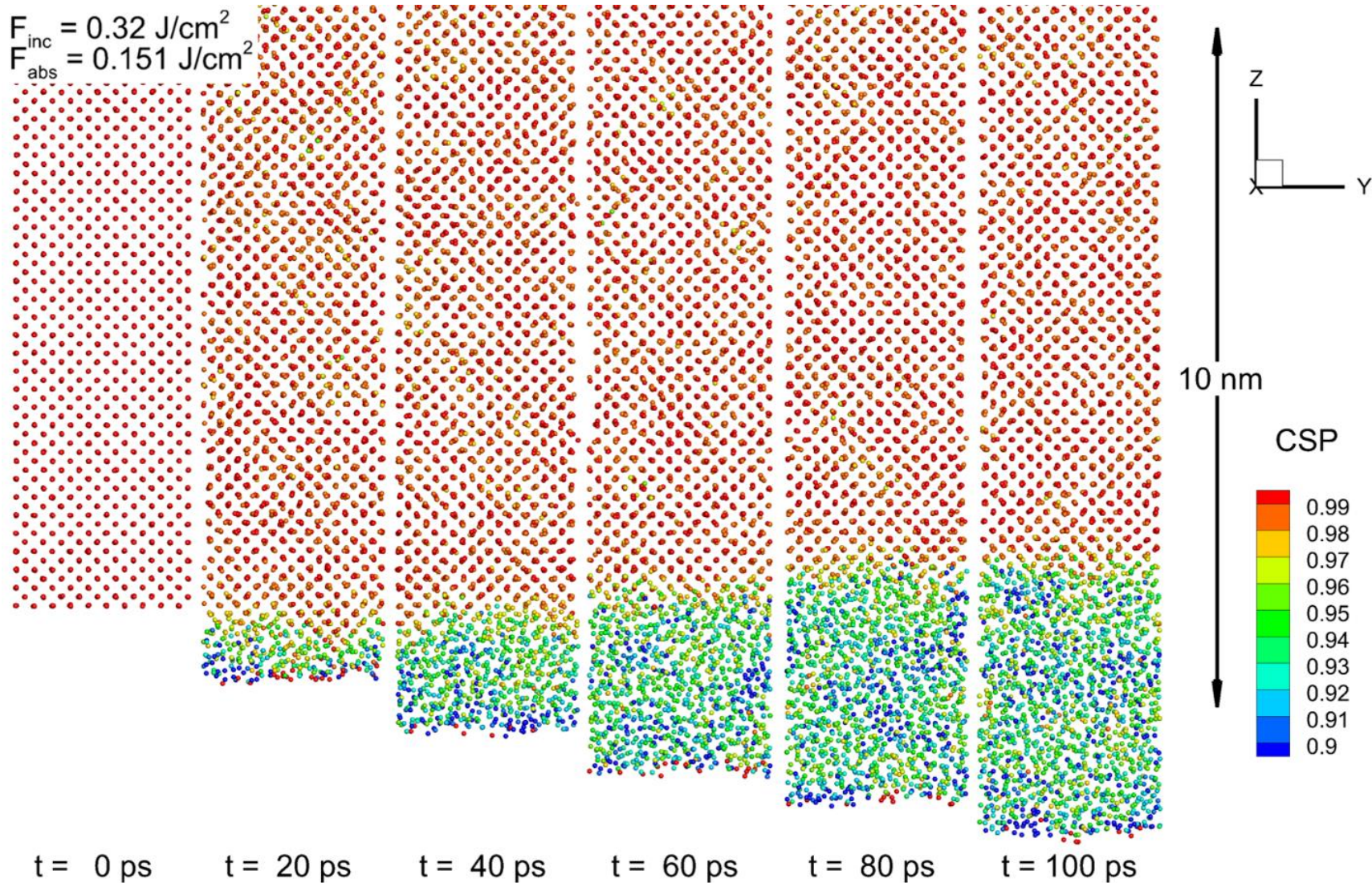


Si crystal part after 6 ps

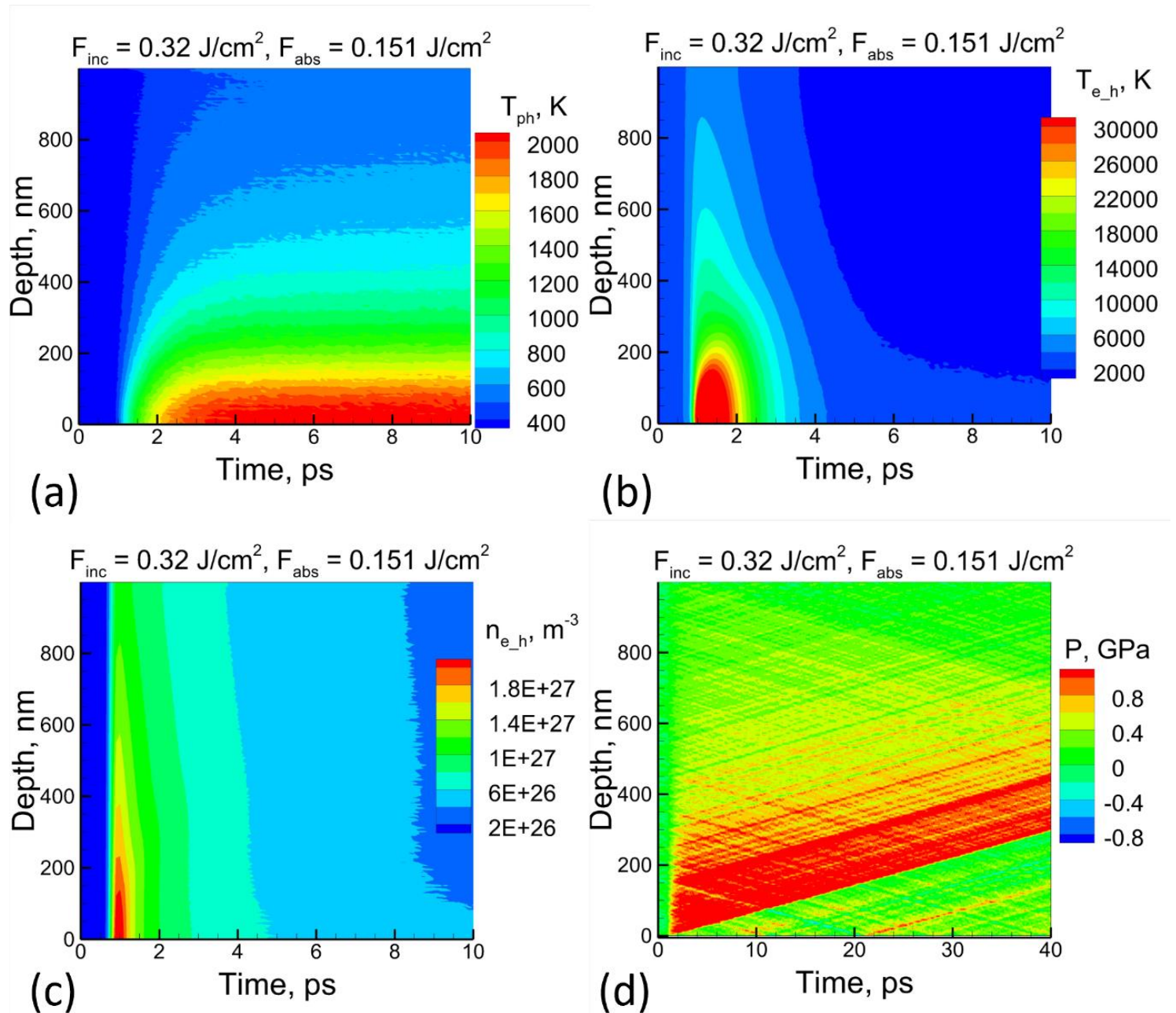


130 fs
0.16 J/cm²

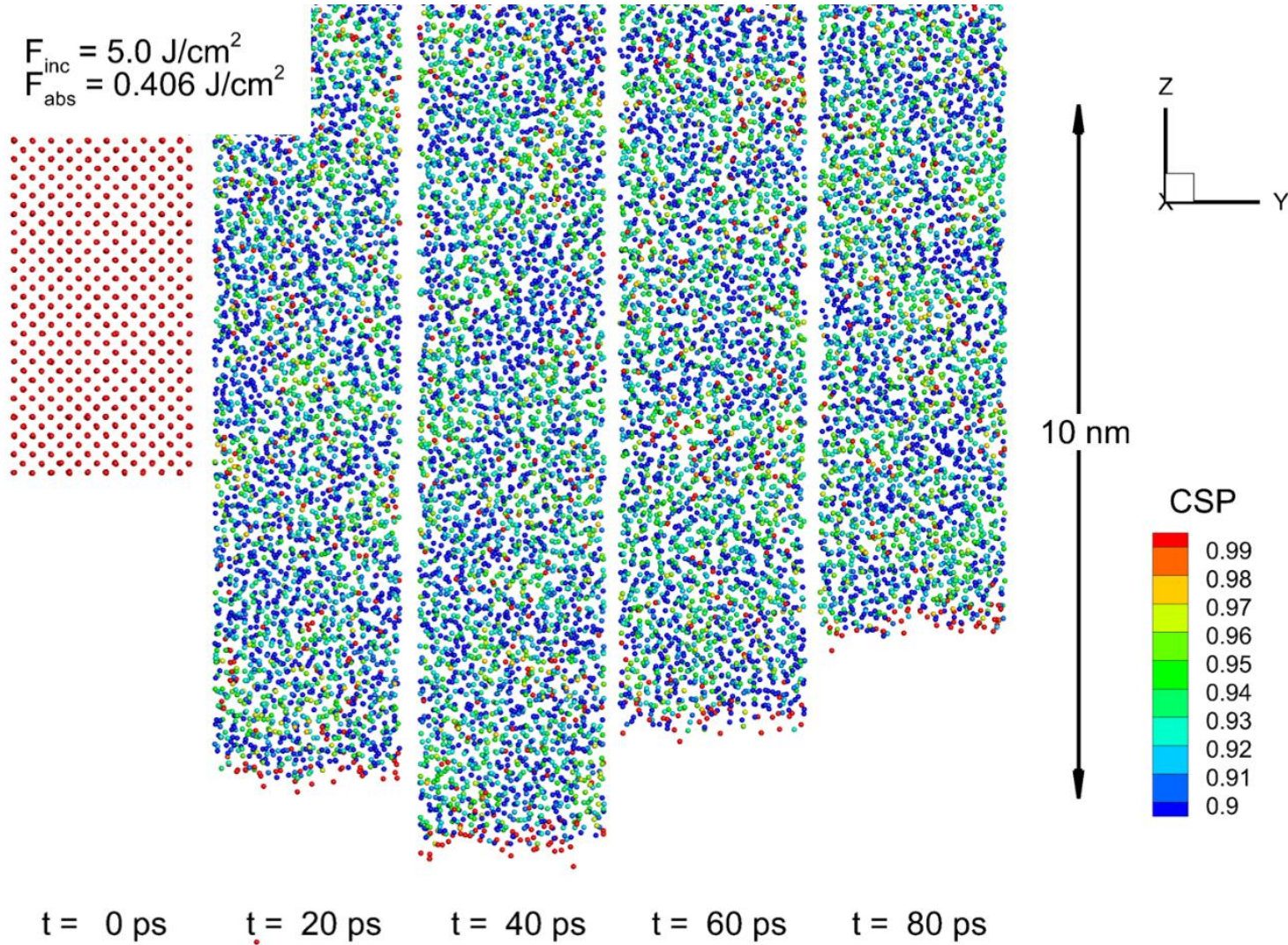
1000 nm Si target after 270fs at 0.32 J/cm² at 800nm



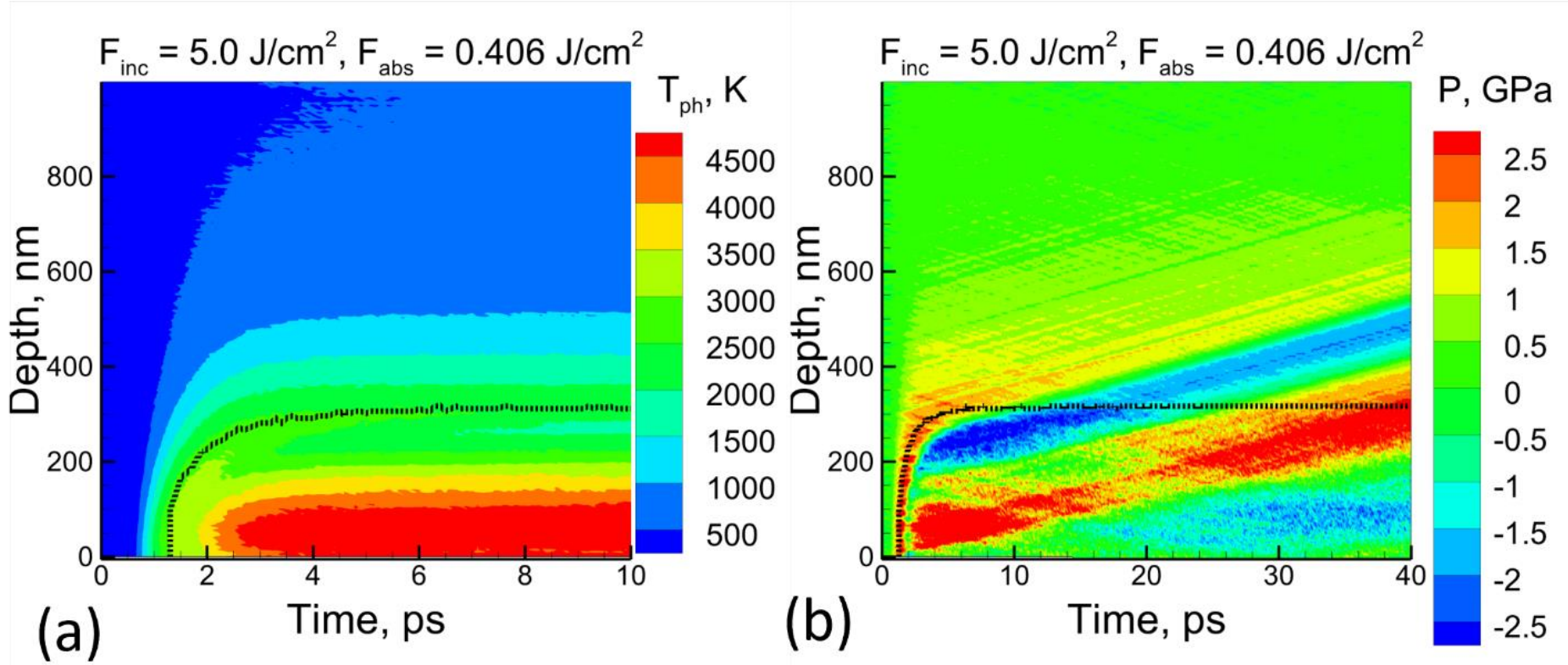
1000 nm Si target after 270fs at 0.32 J/cm² at 800nm



1000 nm Si target after 270fs at 5.00 J/cm² at 800nm

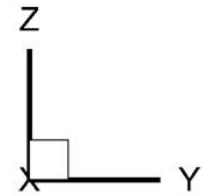
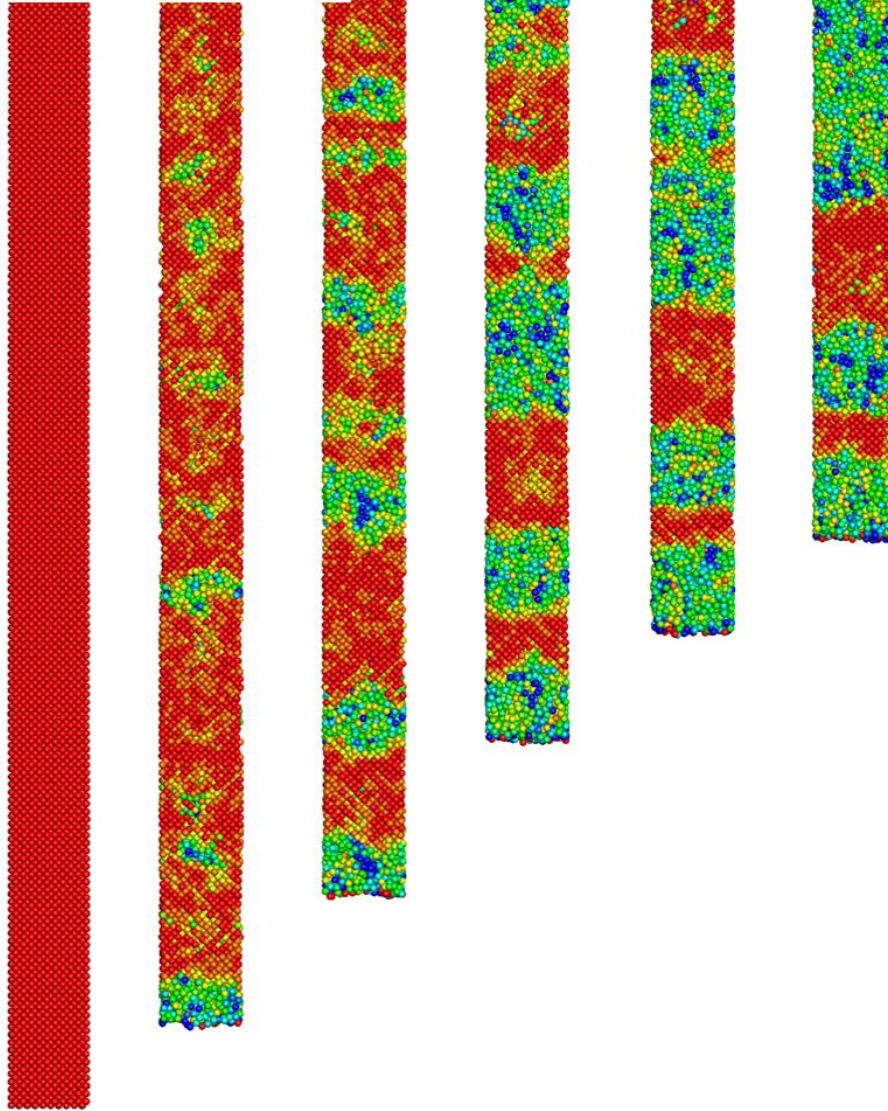


1000 nm Si target after 270fs at 5.00 J/cm² at 800nm

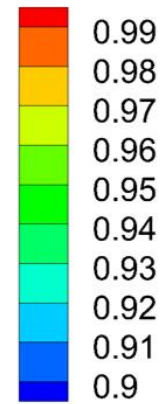


1000 nm porous Si target after 270fs at 0.29 J/cm² at 800nm

$$F_{\text{inc}} = 0.29 \text{ J/cm}^2$$
$$F_{\text{abs}} = 0.119 \text{ J/cm}^2$$



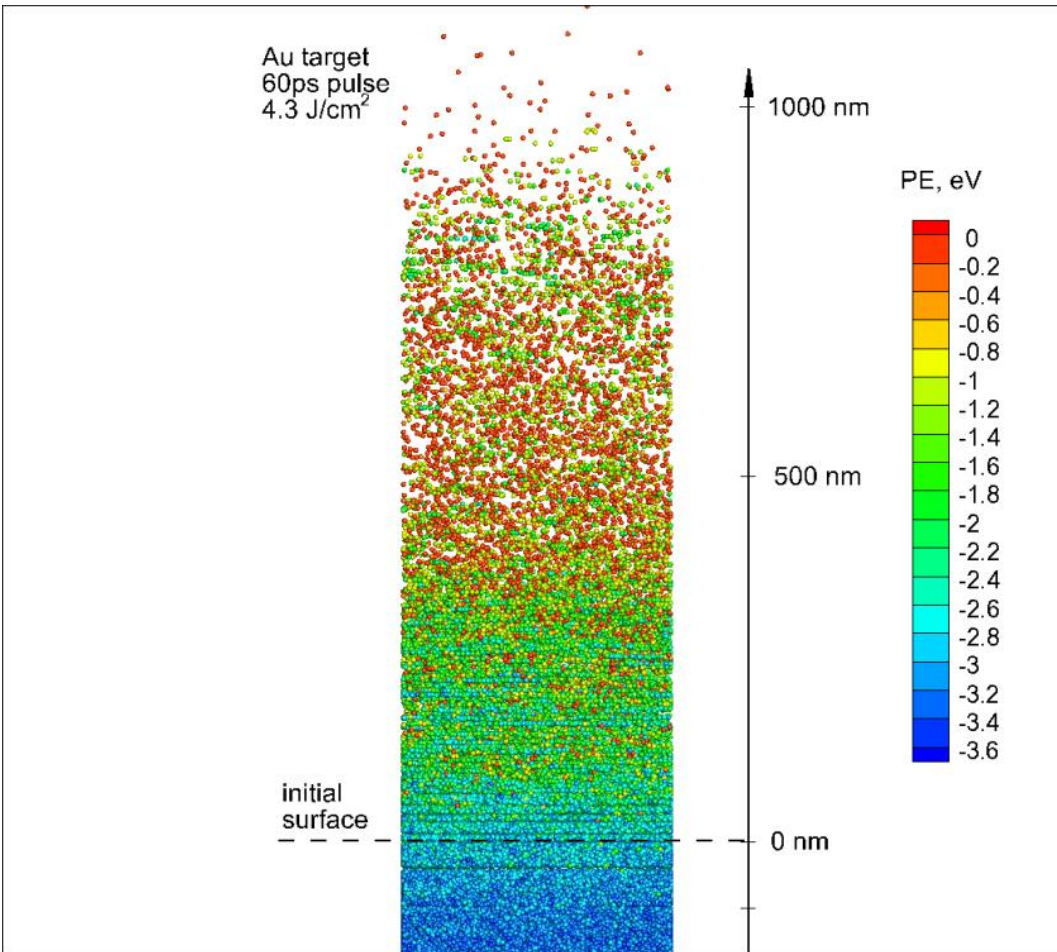
CSP



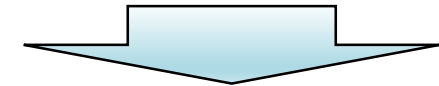
180 nm

t = 0 pst = 20 pst = 40 pst = 60 pst = 80 pst = 100 ps

Photo-thermal vs. photo-mechanical damage for Si



**Regime of internal stresses confinement
Is absent**



No Spallation



Explosive Boiling Only

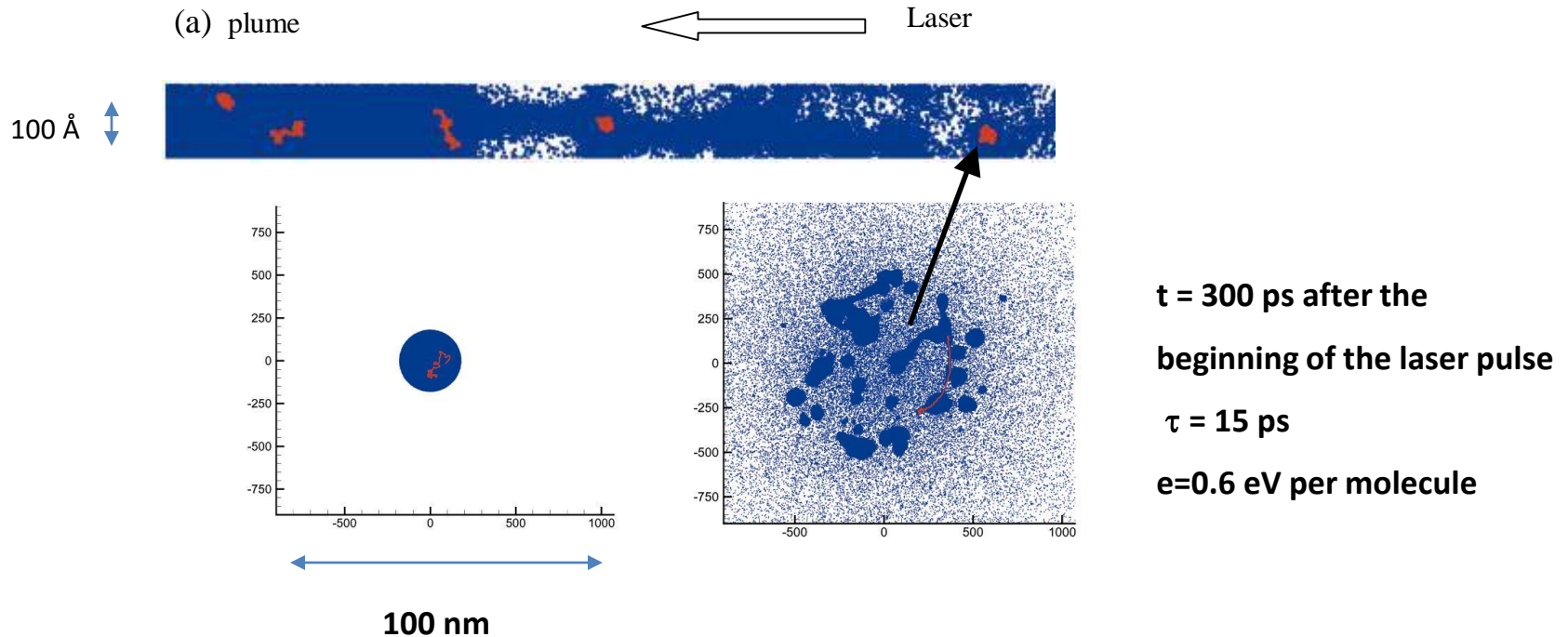
Short Pulse is good for NPs generation

satisfied

$$\max\{\tau_{pulse}, \tau_{e-ph}\} = \tau_{heating} \leq \tau_{mech} = \frac{L_{e-diff}}{C_s}$$

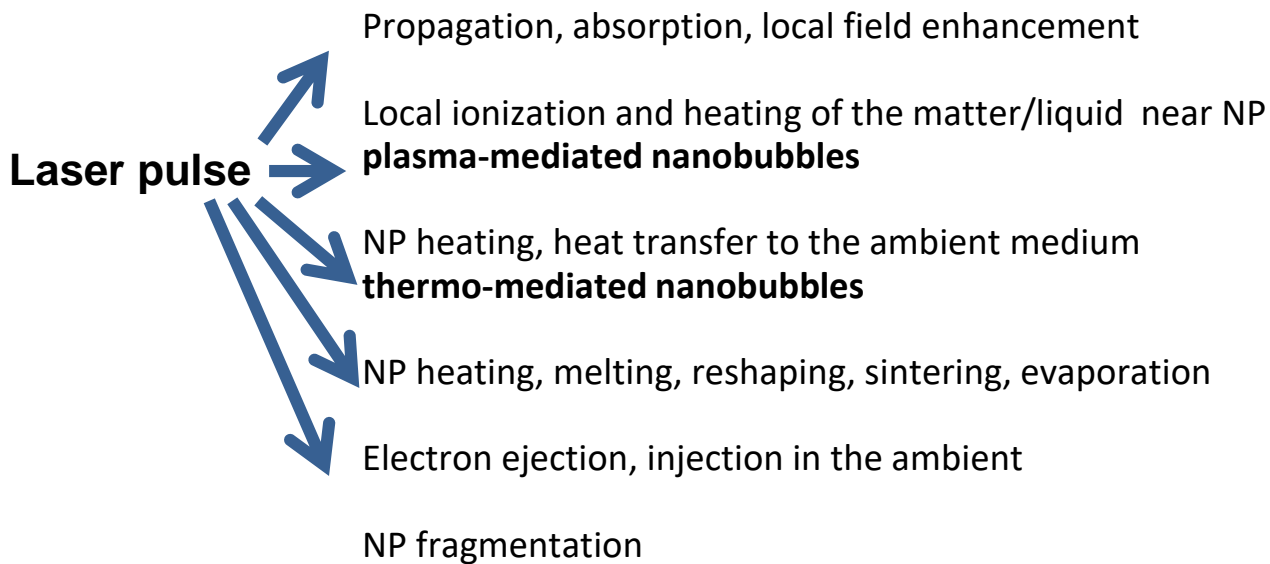
Laser Interactions with Nanoparticles

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

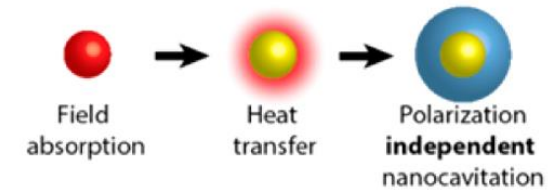


T. E. Itina, L. V. Zhigilei, B. J. Garrison
The Journal of Physical Chemistry B 106 (2), 303-310 (2002)

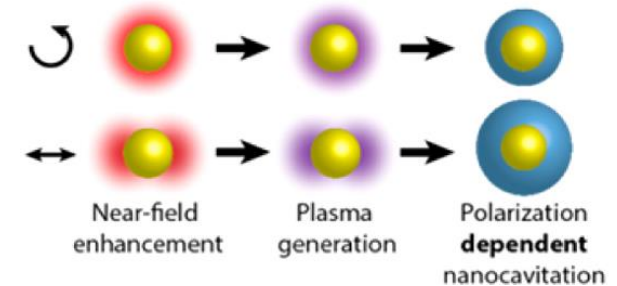
Ultra-short Laser Interactions with Nanoparticles



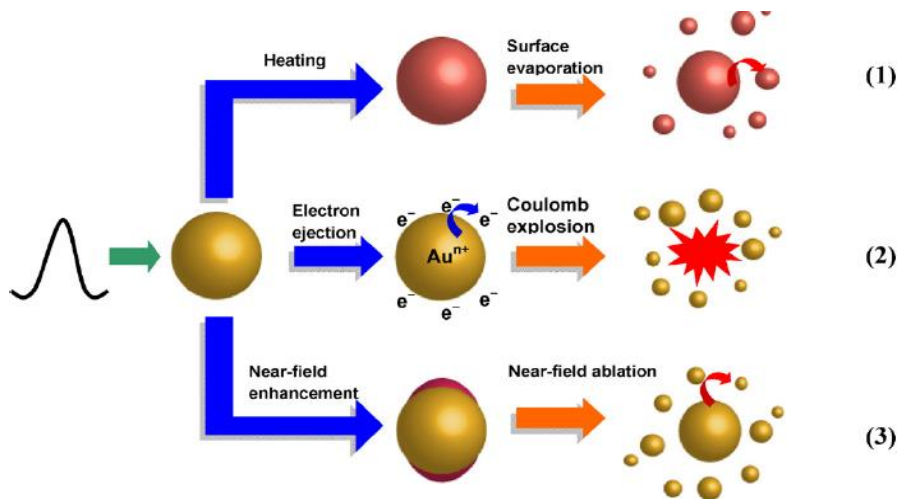
Thermo-mediated nanobubbles



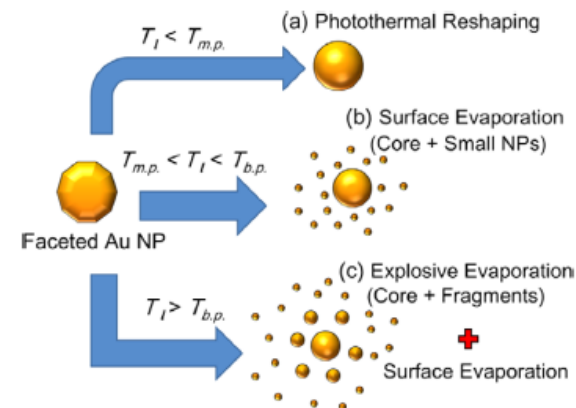
Plasma-mediated nanobubbles



Lachaine et al. Photonics (2013)



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



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

Ultr-short Laser Interactions with Nanoparticles

« Classical » Multi-Physics

Maxwell equations

$$\frac{\partial \vec{E}}{\partial t} = \frac{\nabla \times \vec{H} - \vec{J}}{\epsilon_0}$$

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

Polarization current

$$\frac{\partial \vec{J}}{\partial t} = -\vec{J}\gamma + \frac{ne^2}{m}\vec{E}$$

Charge conservation, incompressible Fermi flow

$$\frac{\partial n}{\partial t} = -\frac{1}{e}\nabla \cdot [\vec{J} + \vec{J}_{em}] + w_{PI}(I) + w_{AI}(I)$$

Photo-ionization Avalanche

Heat energy transfer

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

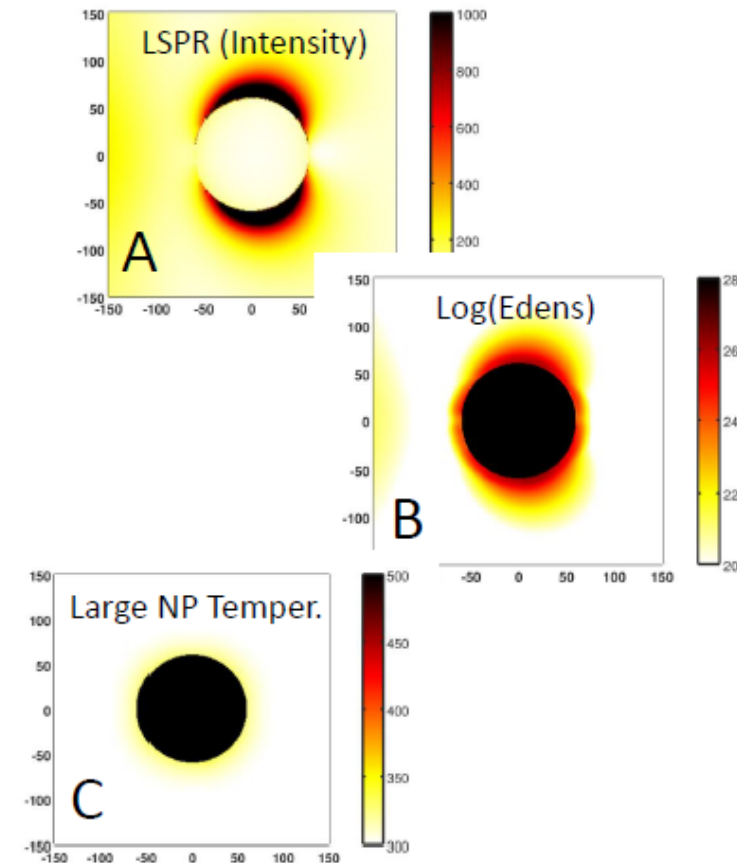
Nanoparticle

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

Medium

$$\rho_m C_m \frac{\partial T_m}{\partial t} = \nabla \cdot (k_m \nabla T_m) + \gamma_{ei}(T_e - T_m) + 3h(T_{NP} - T_m)/R_{NP}$$

C_e, C_{NP}, C_m - heat capacities; k_e, k_{NP}, k_m - thermal conductivities;
 T_e, T_{NP}, T_m - temperatures; $\vec{J} \cdot \vec{E}$ - Joule heating source (absorption);
 γ_{ei}, h - energy transfer rates; ρ_{NP}, ρ_m - ion densities.

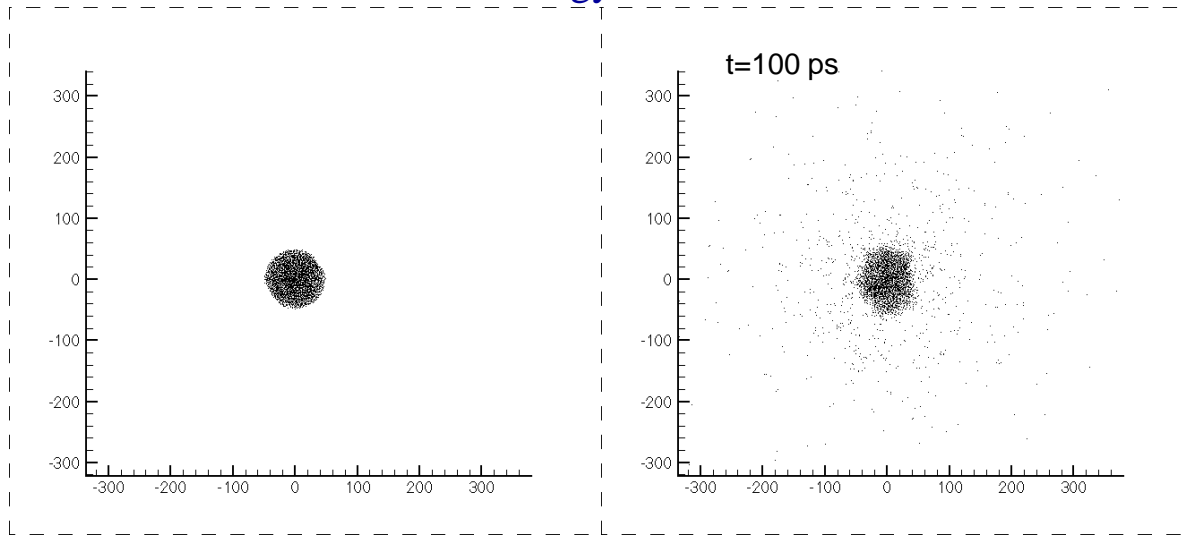


Advantages: rather easy equations, estimations of temperatures

Limitations: hard to correctly account for electron excitation, ejection/injection

Laser Interaction with NPs: MD simulations

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

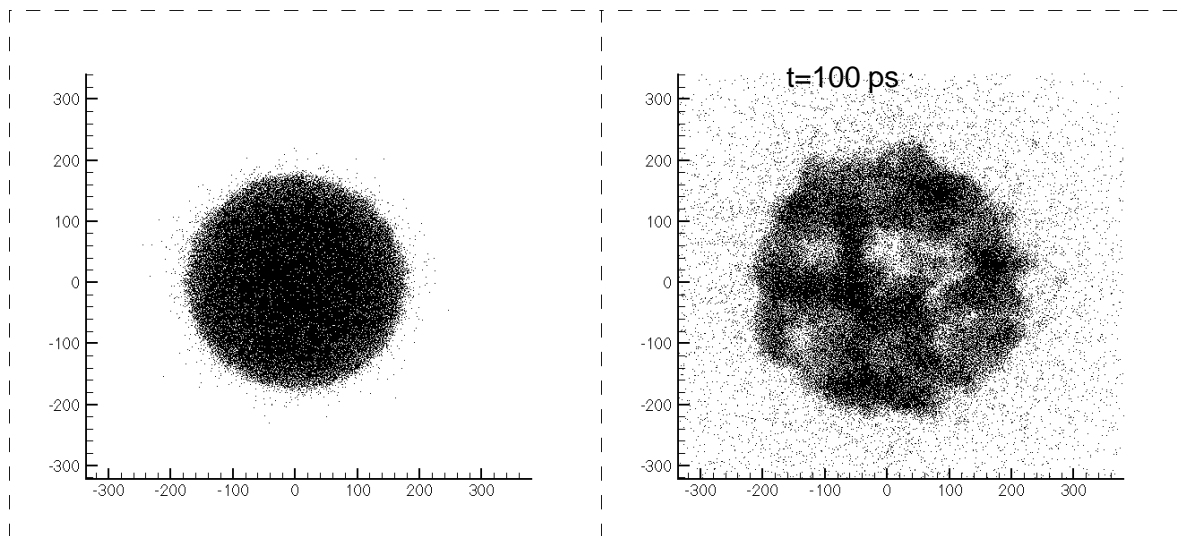


Smaller NPs

Evaporation

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

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

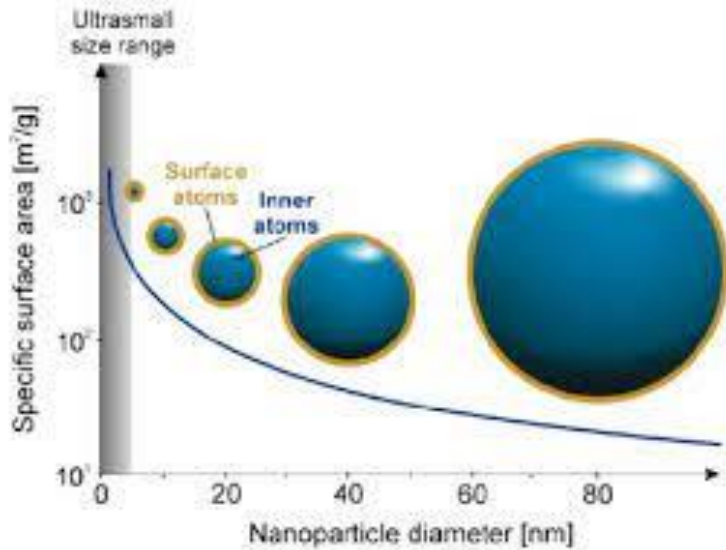


Larger NPs

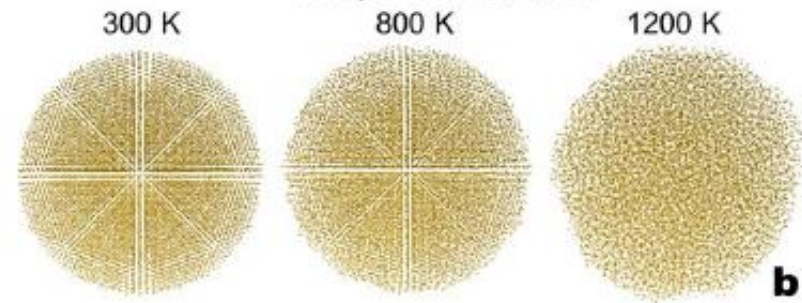
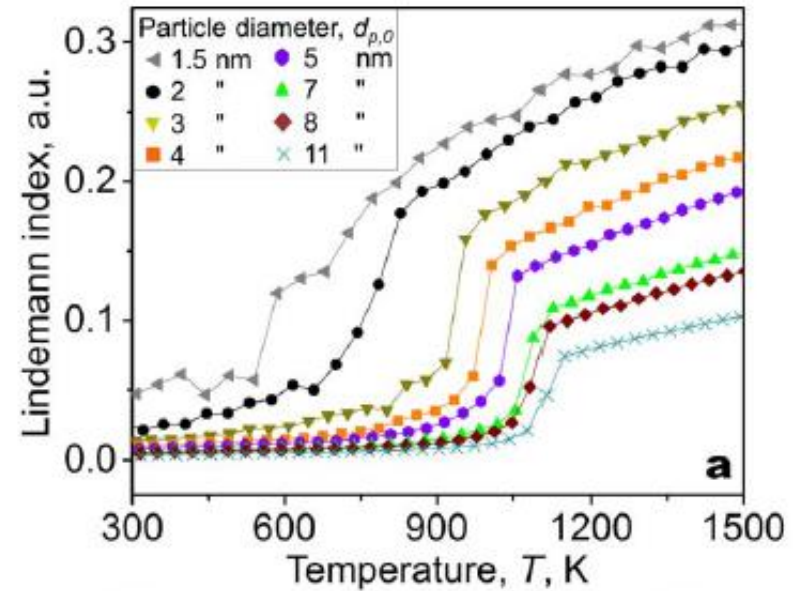
Fragmentation due to thermo-mechanical effects

NP's Heating and Melting : Size Effects

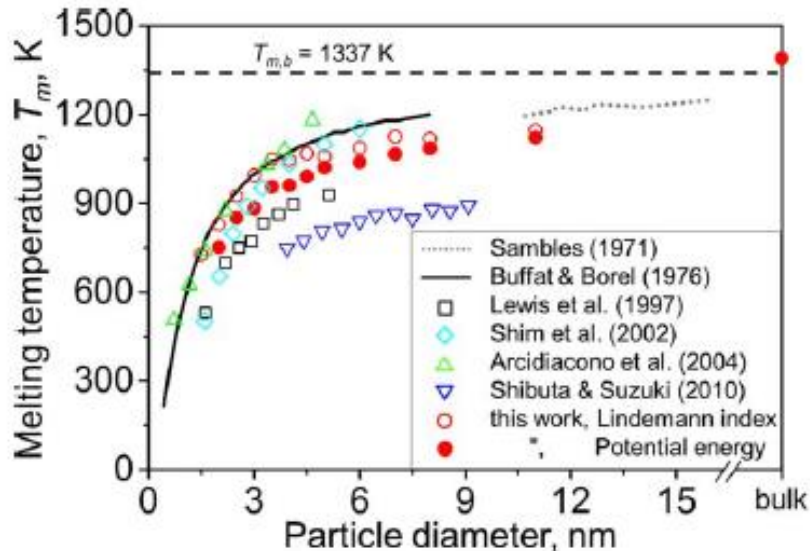
Melting and structural transformations: role of NP's sizes



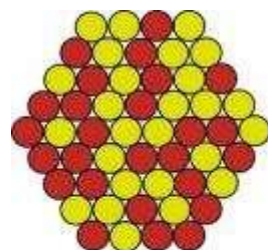
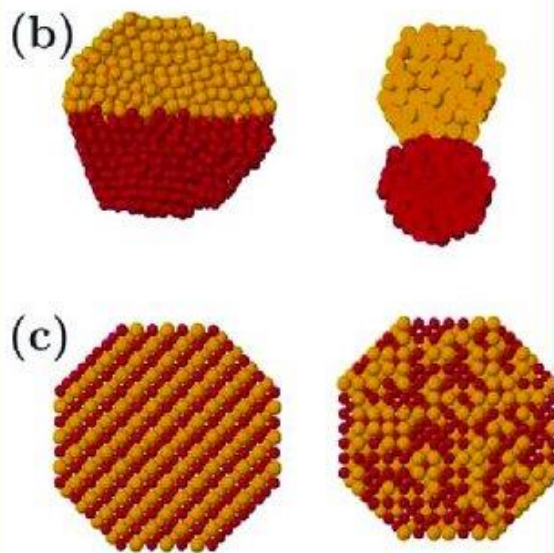
K. Zarschler et al. *Nanomed-Nanotechnol* 12, 1663-1701 (2016).



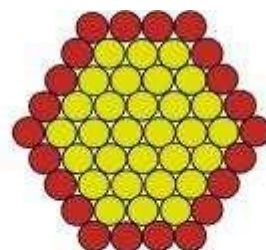
E. Goudeli et al., *AIChE* 2015



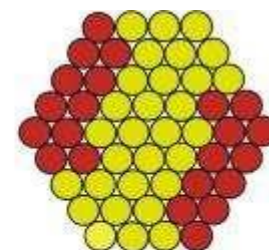
Nanoparticle Alloys and Aggregates



Alloy



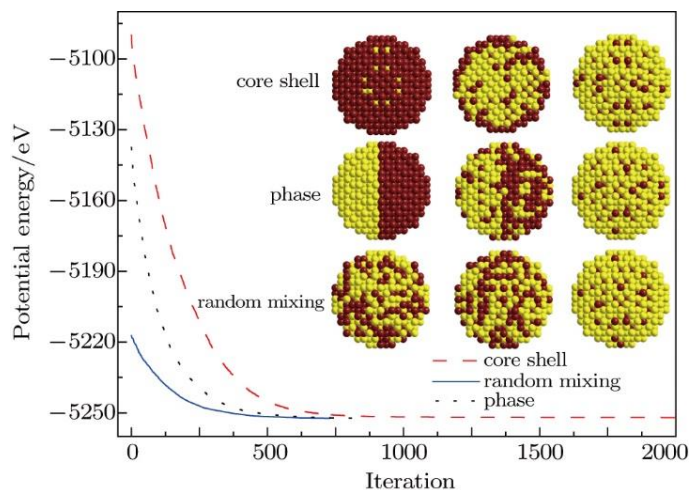
Core-Shell



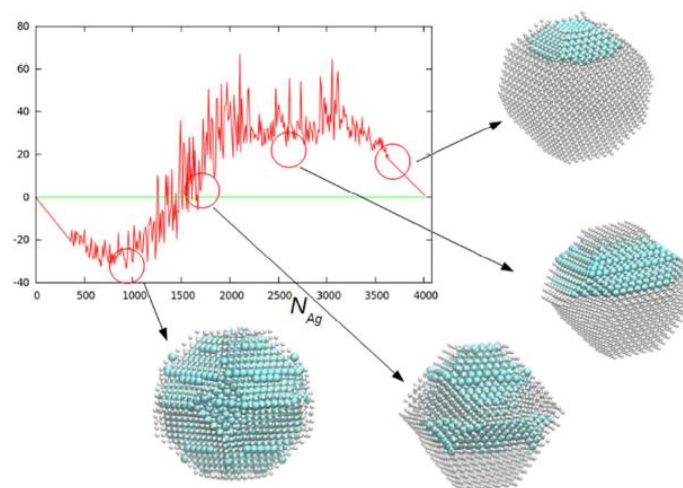
Cluster-in-Cluster

Mixing Energy

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



R. Ferrando et al. *Chem. Rev.* 108(3), 2006



G. Barcaro et al. *Phys. Chem. Chem. Phys.*

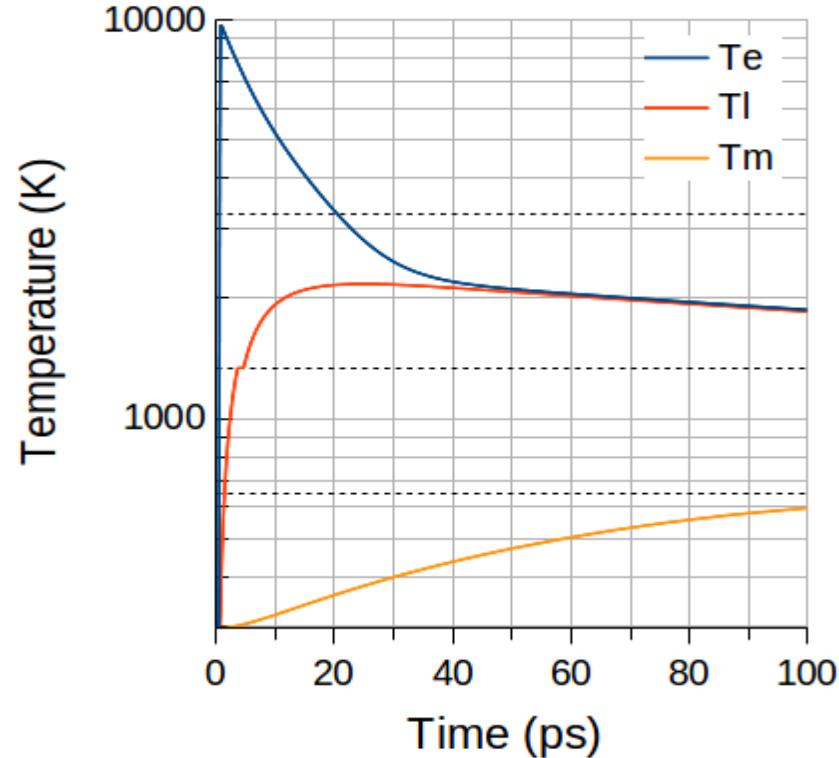
Electronic, Lattice and Medium Temperatures (3TM)

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

T_e rises instantaneously

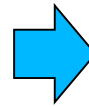
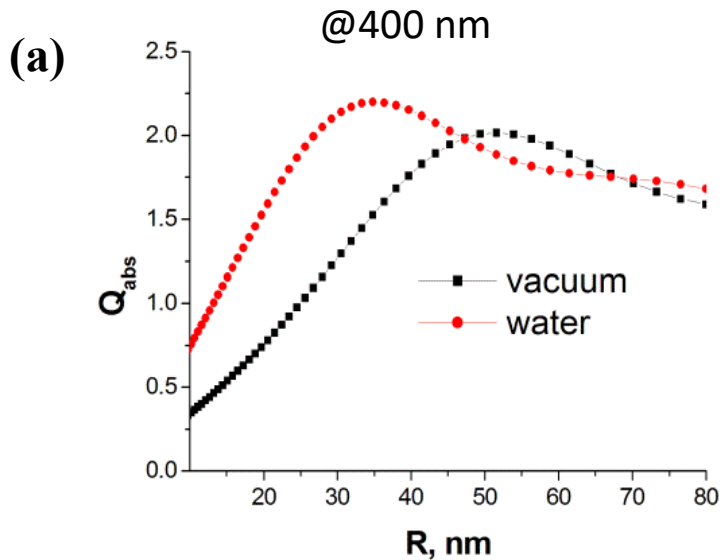
The energy deposited into the
electronic system is transferred to the
lattice
 $\Rightarrow T_l$ rises

Particle cools through heat exchange
to the surrounding water



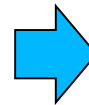
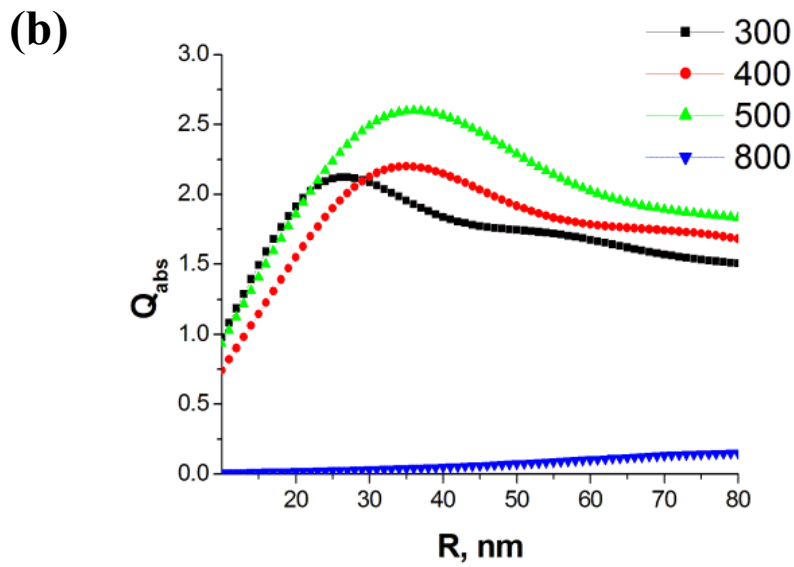
Laser Energy Absorption vs NP's size

Absorption coefficient / efficiency (beyond SPR for gold)



Generalized Mie theory =>
Red – Gold NPs in for water
Black – Gold NPs in vacuum

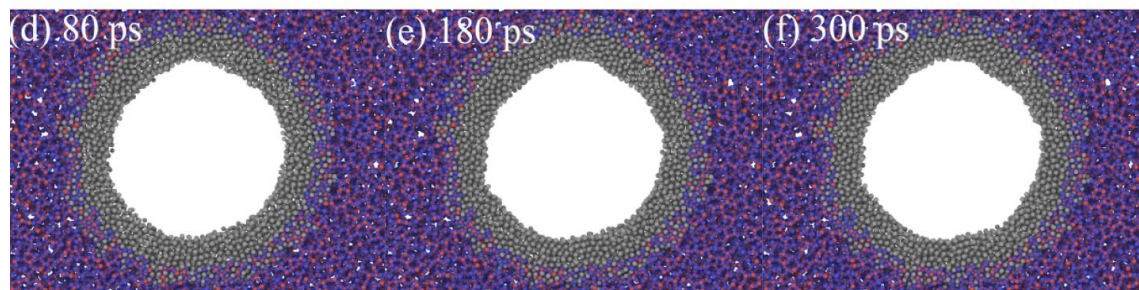
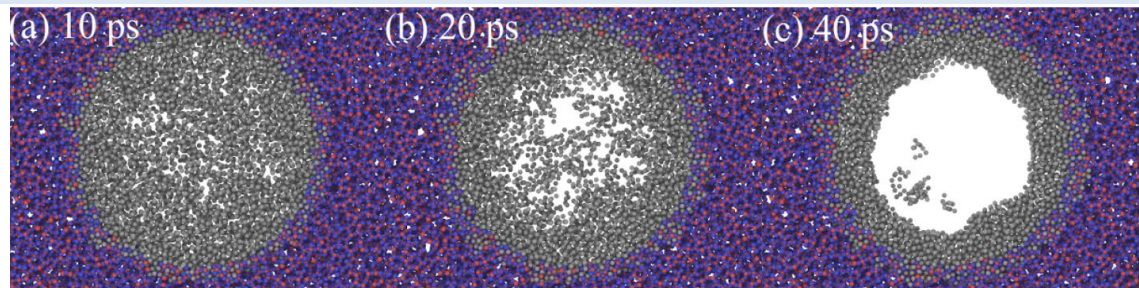
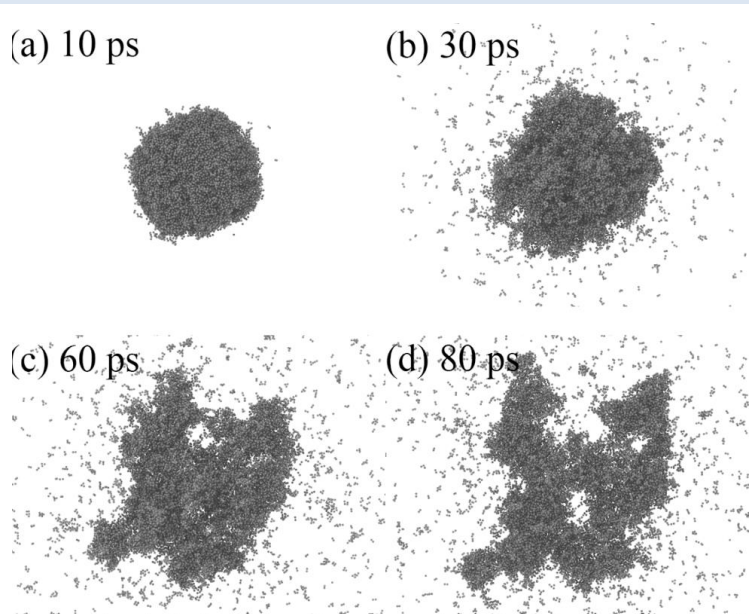
- **peak in absorption at**
 $R=R^* \sim 30$ nm for Au NP in water



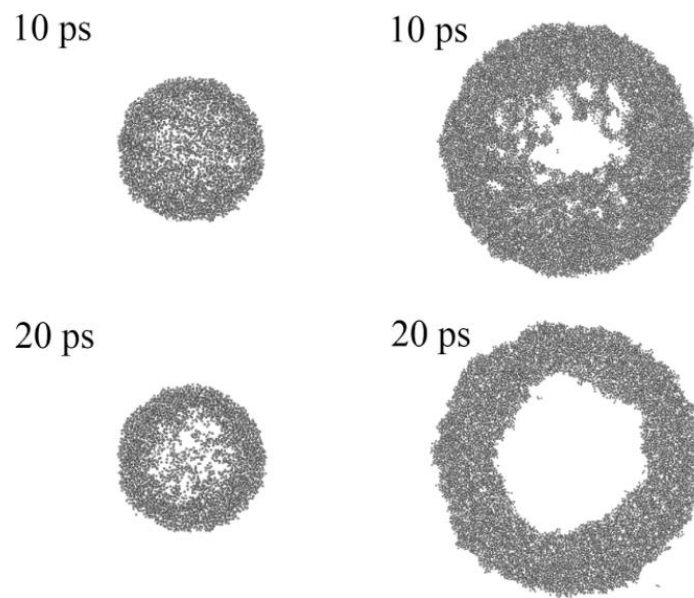
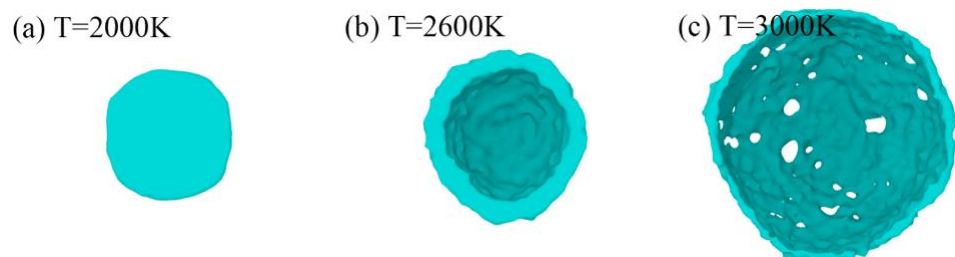
Gold NPs in water for different wavelength @300-800nm

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

NP's evolution upon laser pulse absorption



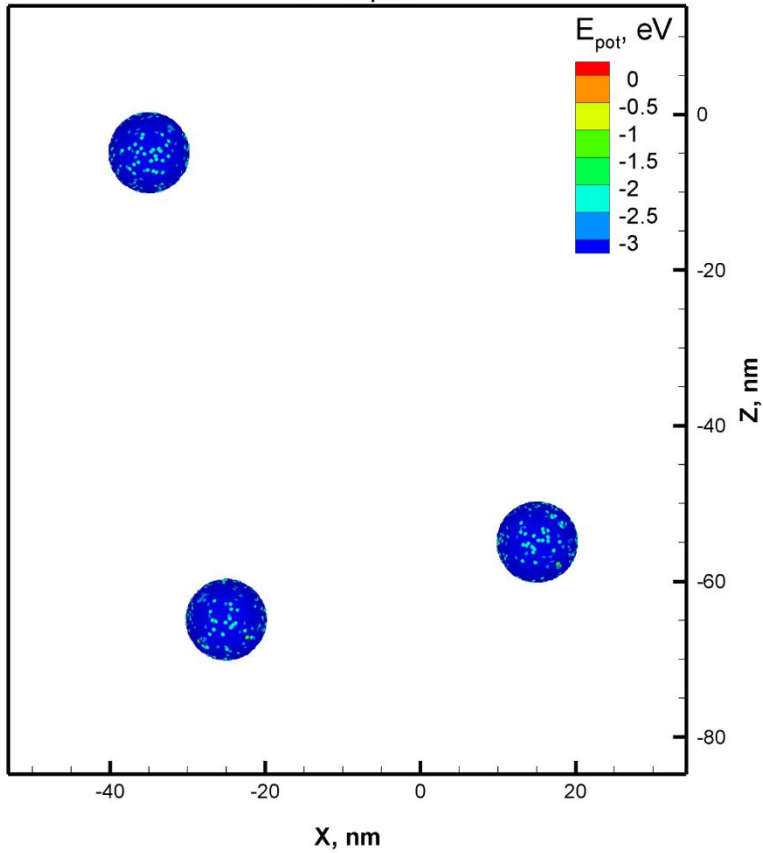
Jiang et al., Computational Materials Science 196 (2021) 110545



10 nm NP, the incident fluence 200 J/m²

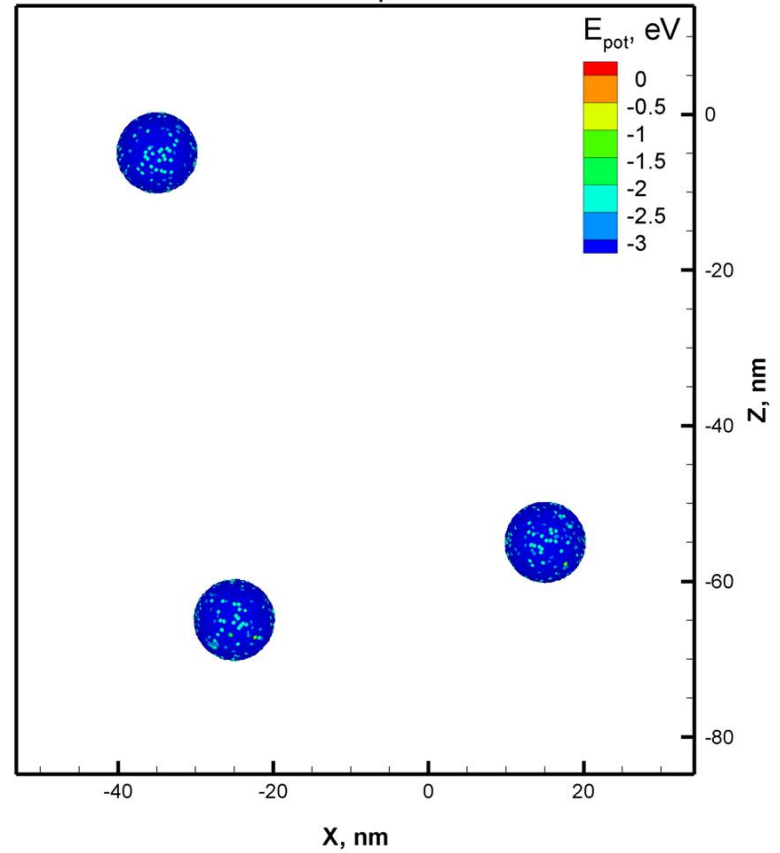
solid

t = 0 ps



porous

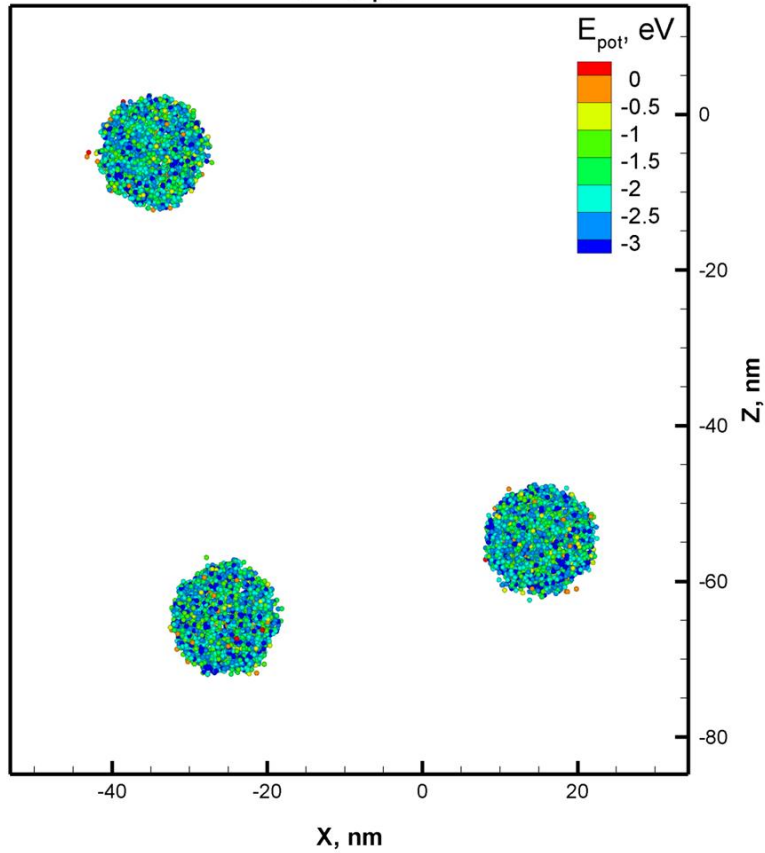
t = 0 ps



10 nm NP, the incident fluence 200 J/m²

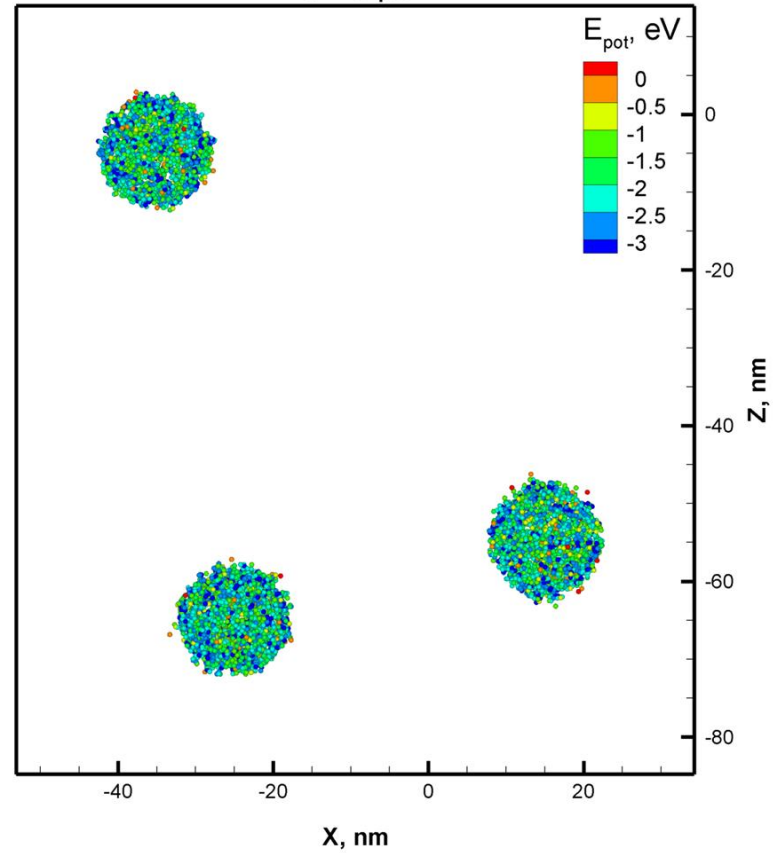
solid

t = 5 ps



porous

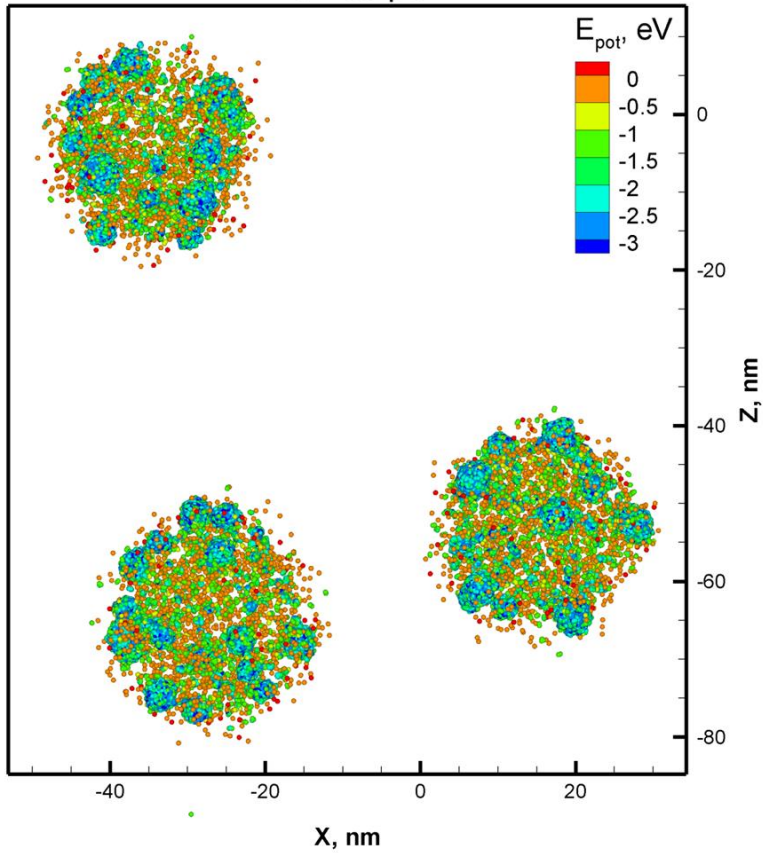
t = 5 ps



10 nm NP, the incident fluence 200 J/m²

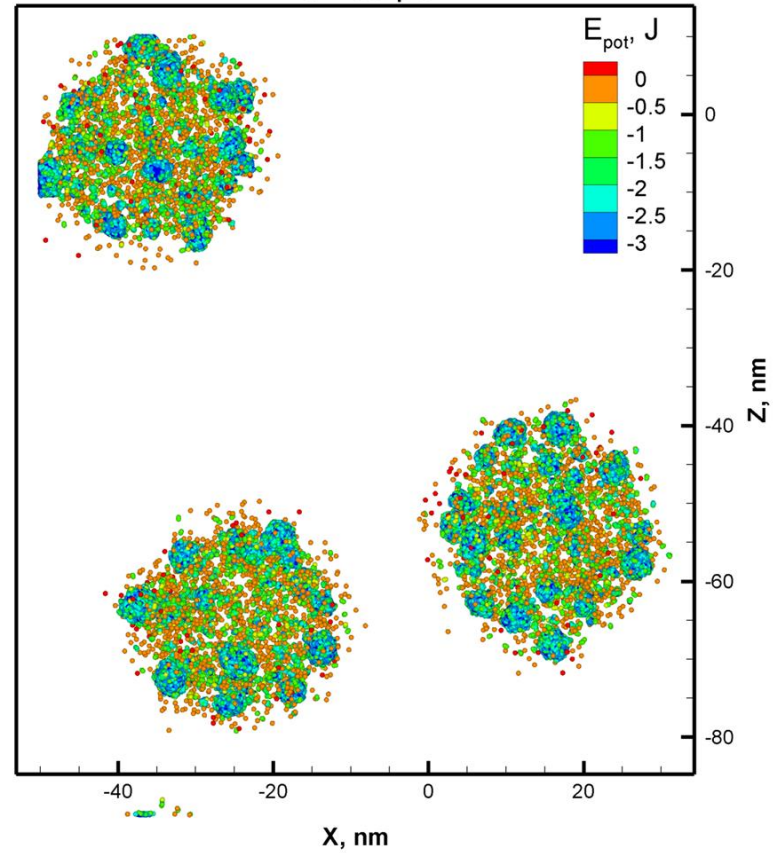
solid

t = 50 ps



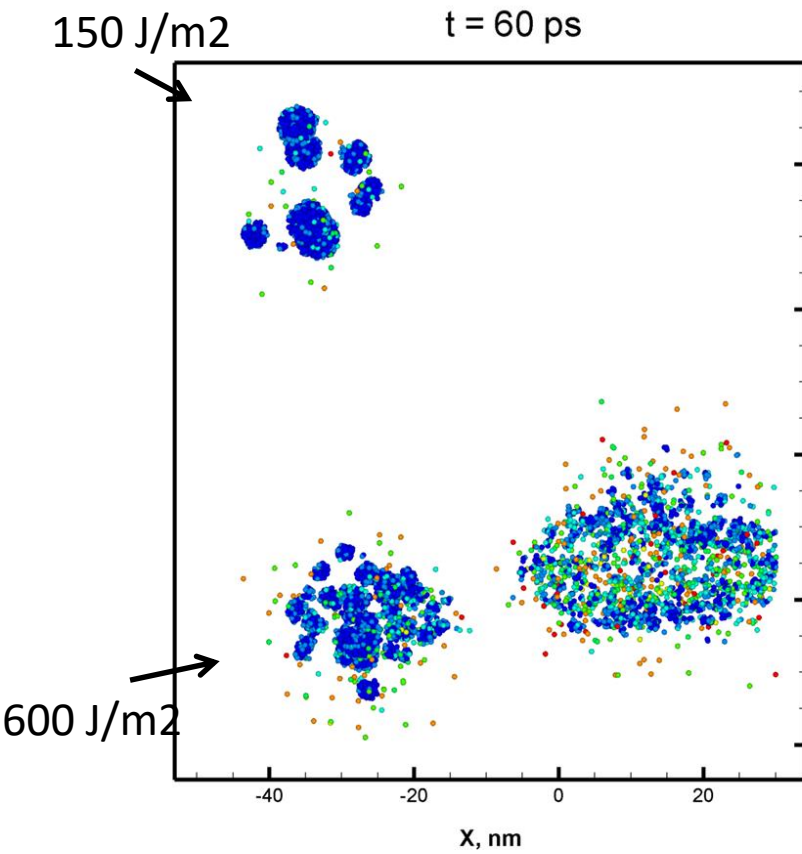
porous

t = 50 ps

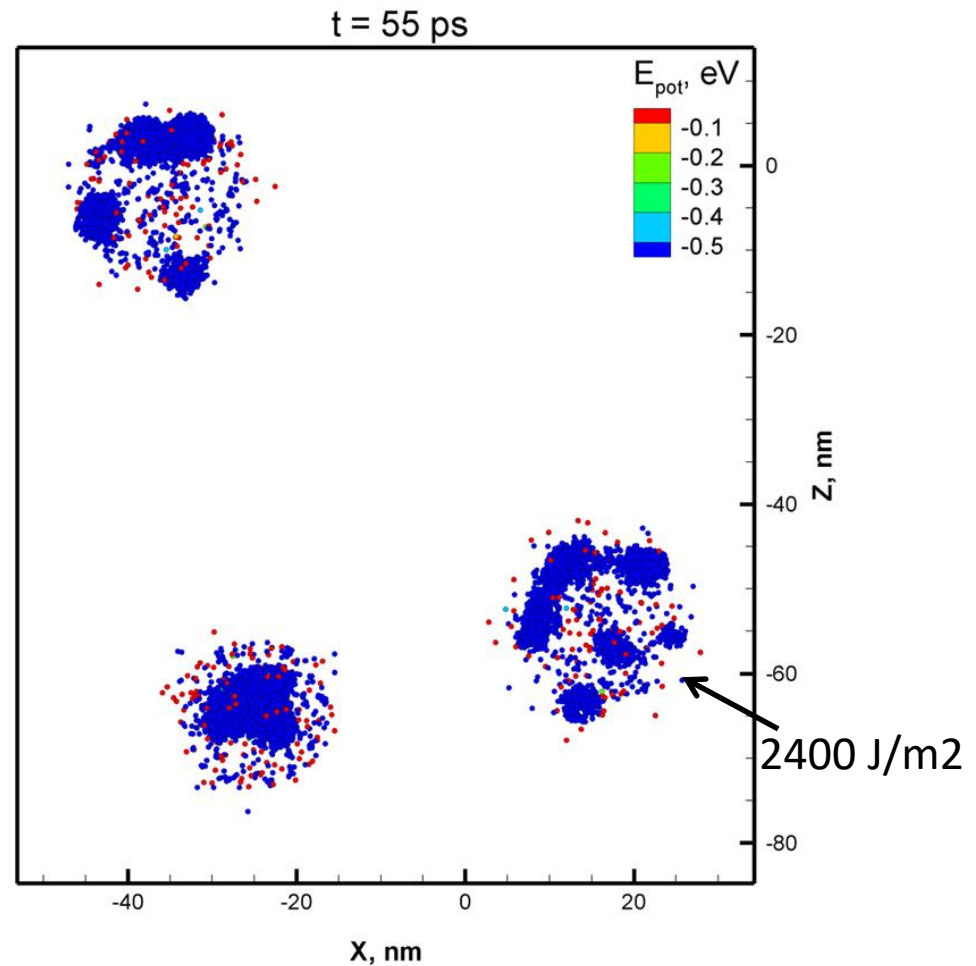


270 fs pulse, 10 nm NPs, different incident fluences

solid

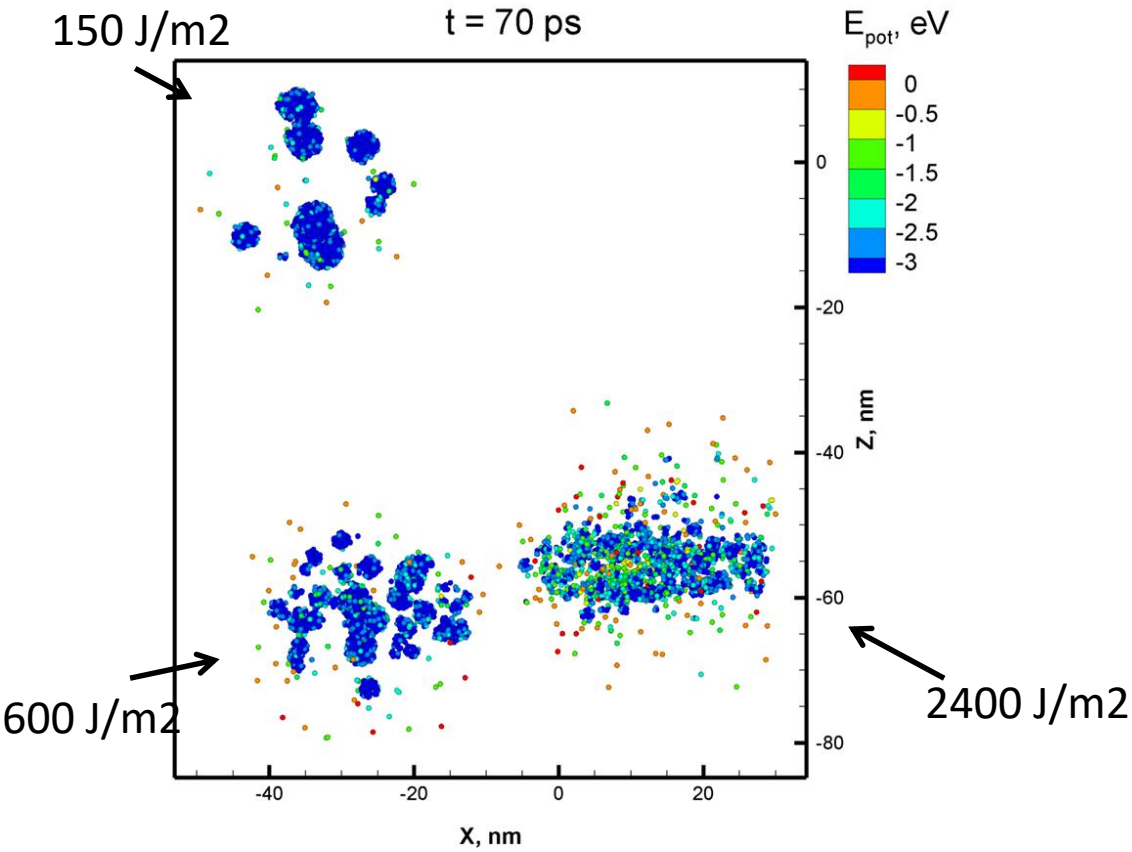


porous



270 fs pulse, 10 nm NPs, different incident fluences

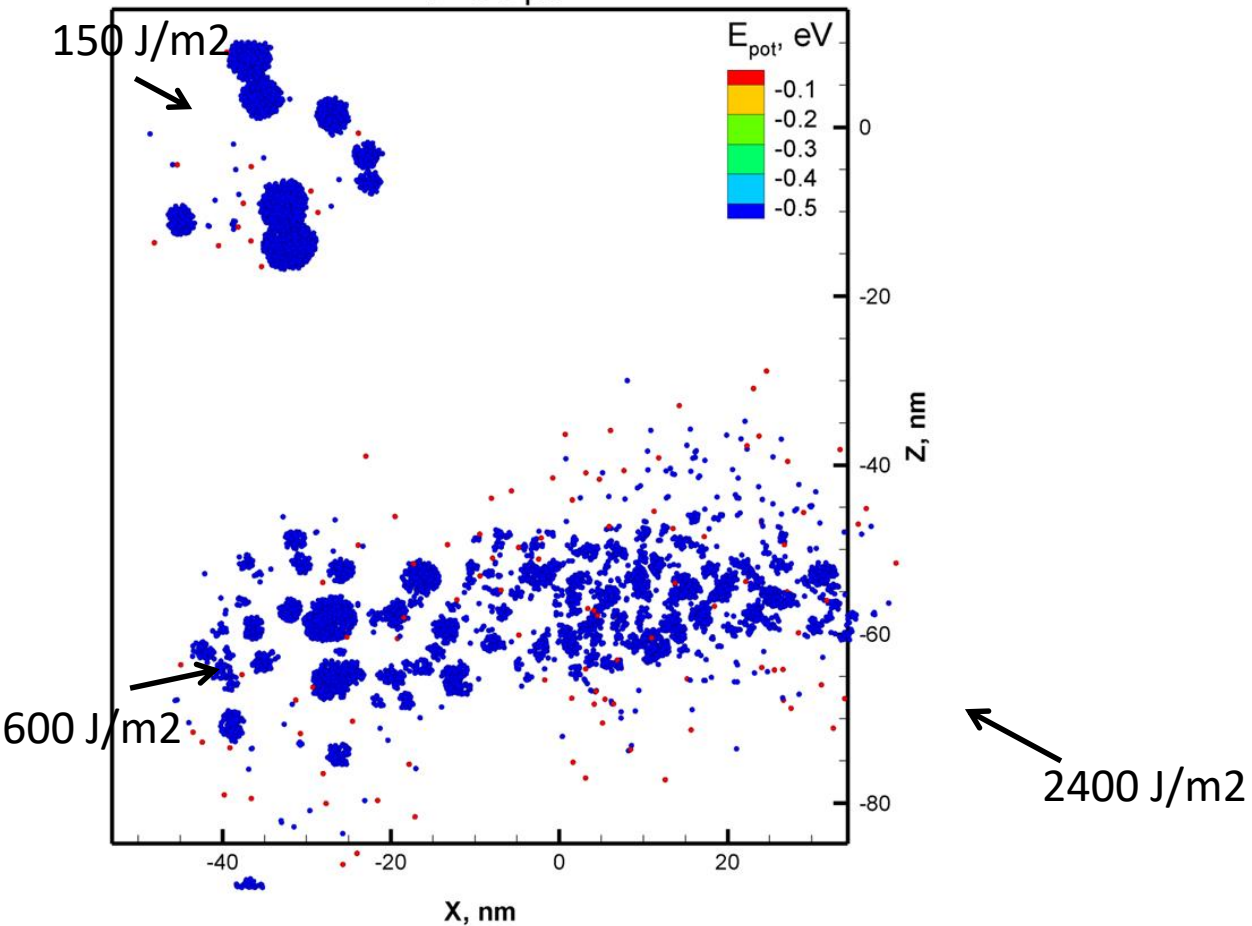
solid



270 fs pulse, 10 nm NPs, different incident fluences

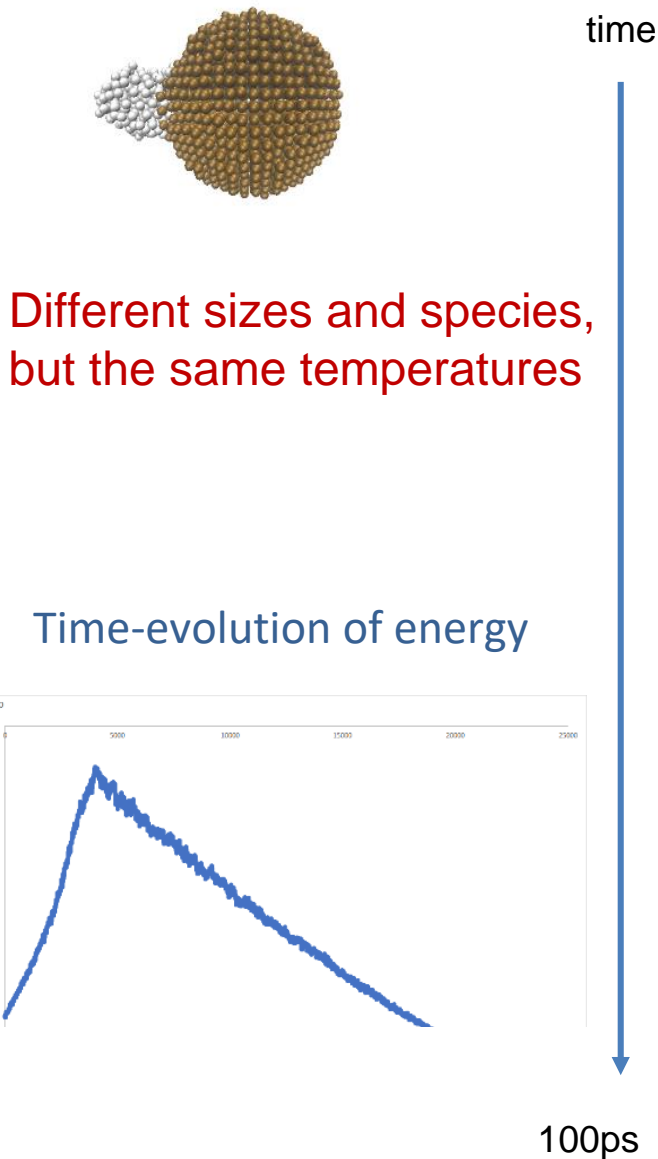
solid

$t = 90 \text{ ps}$



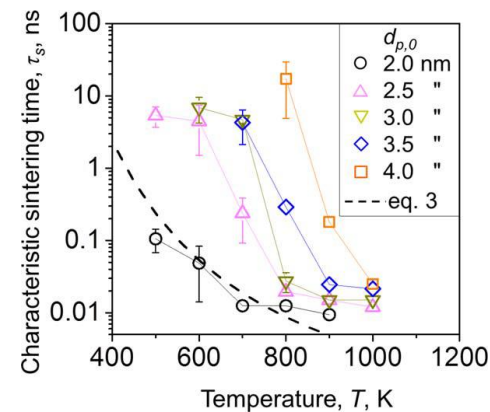
NP Sintering or Alloying

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



- 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

SUMMARY

- Many processes are involved in laser interactions and numerous parameters play important roles.
- MD-TTM for metals and modified MD-nTTM for Si were presented.
- MD modeling is promising in the elucidation of the main mechanisms for the particular experimental conditions.

Thank you very much for your attention!