MOLECULAR DYNAMICS SIMULATIONS OF LASER-MATTER INTERACTIONS

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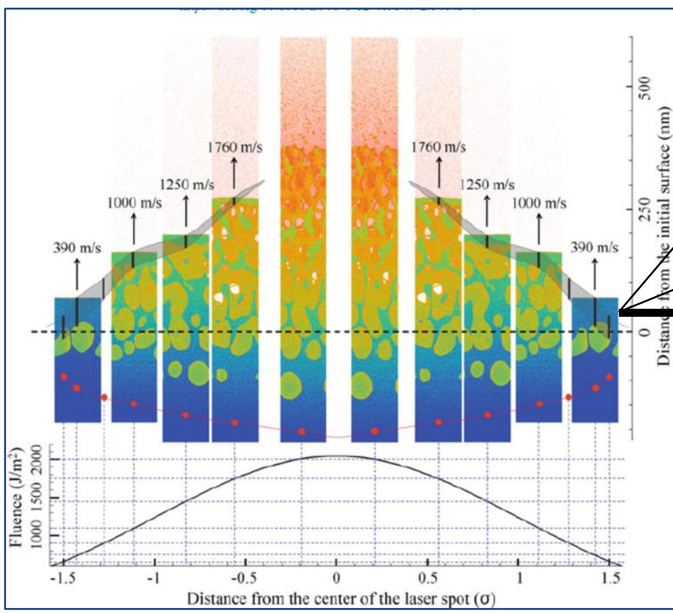
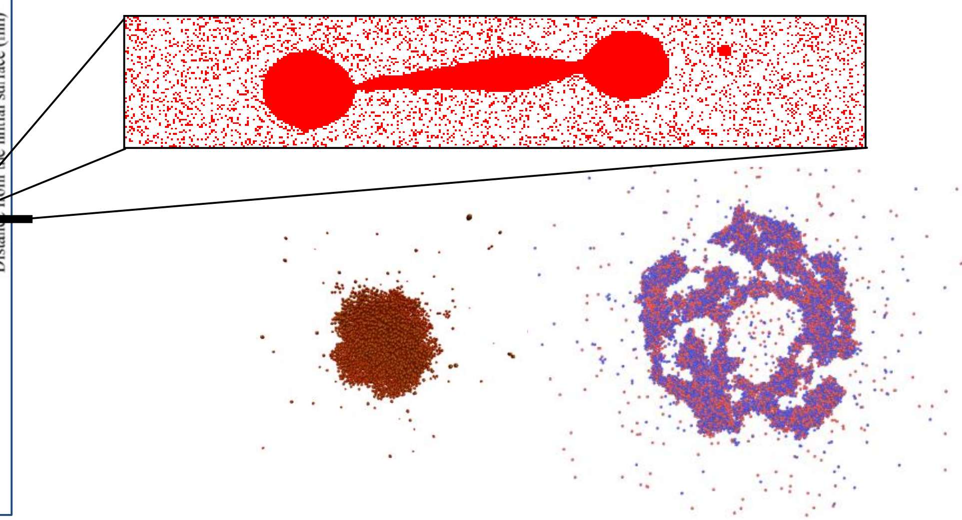
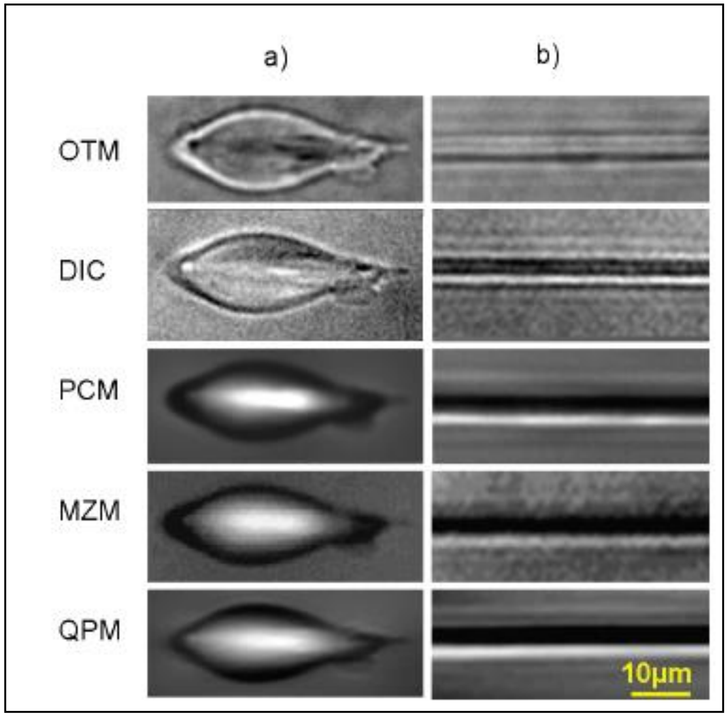




Encyclopedia of Interf. Chem.
(Elsevier, 2018), pp. 594-603.

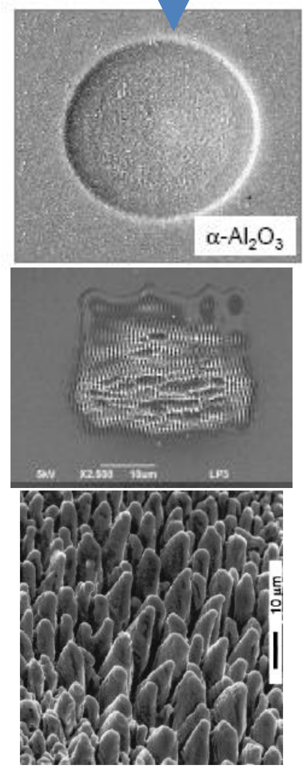
Laser fluence

Structural modifications in volume



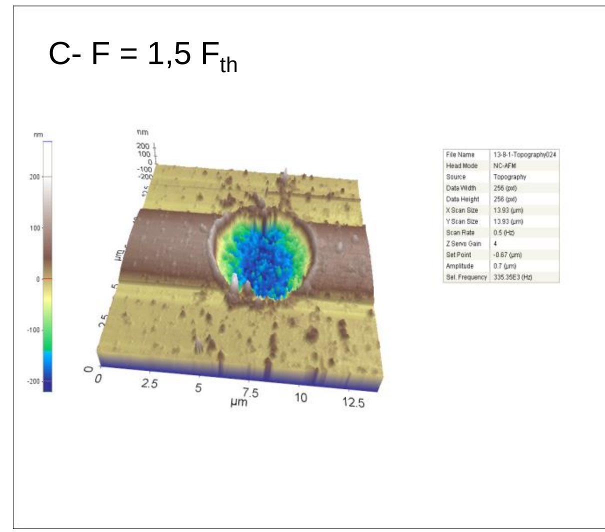
Mauclaire et al. LabHC

Surface texturing



Sarnet et al.

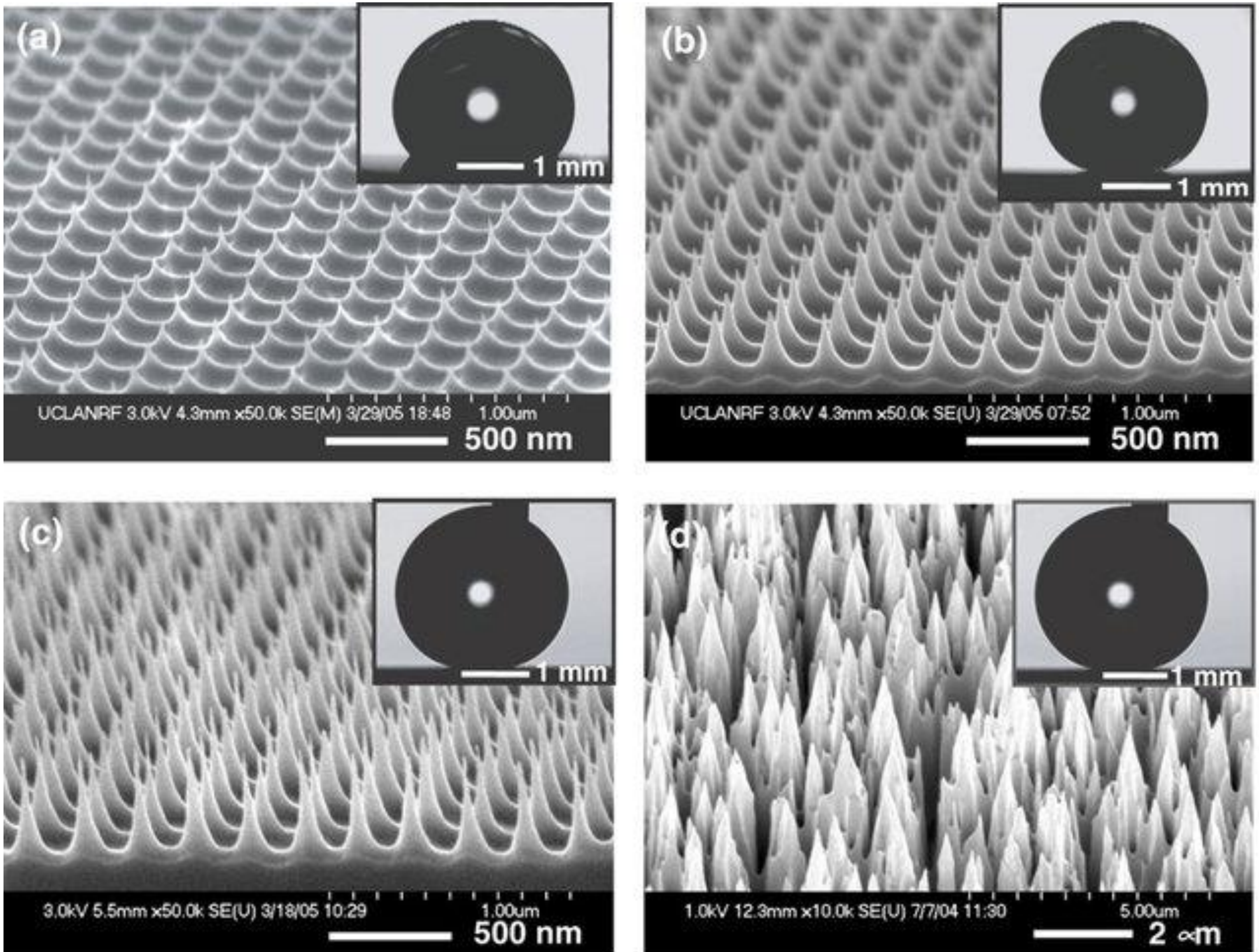
Ablation



Utéza et.

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

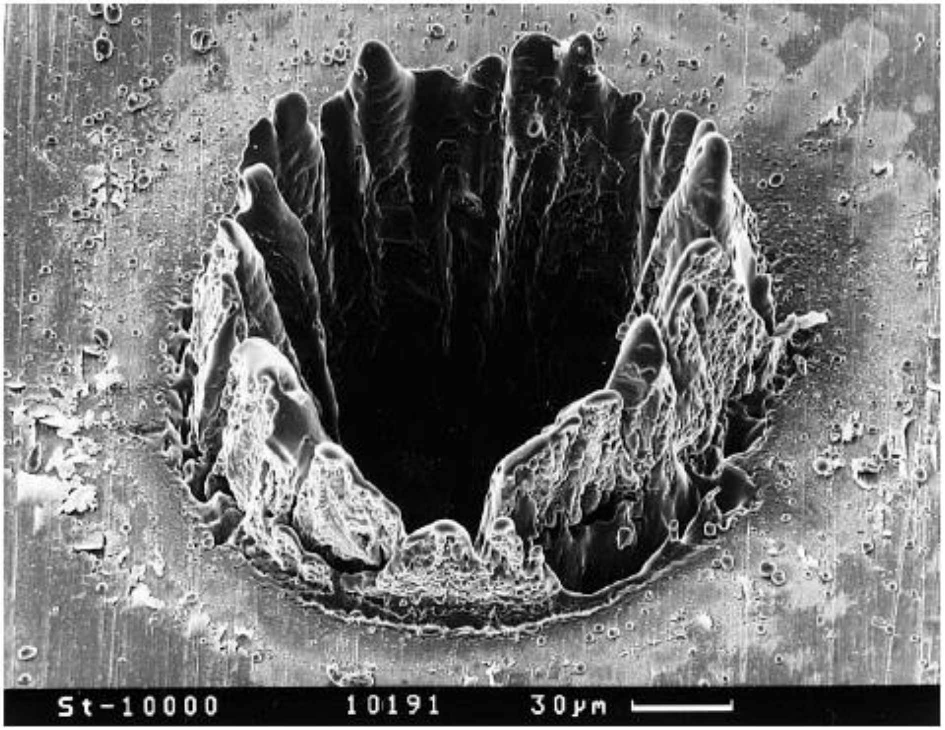
Nanostructuring of Si: Lithography + ion beam



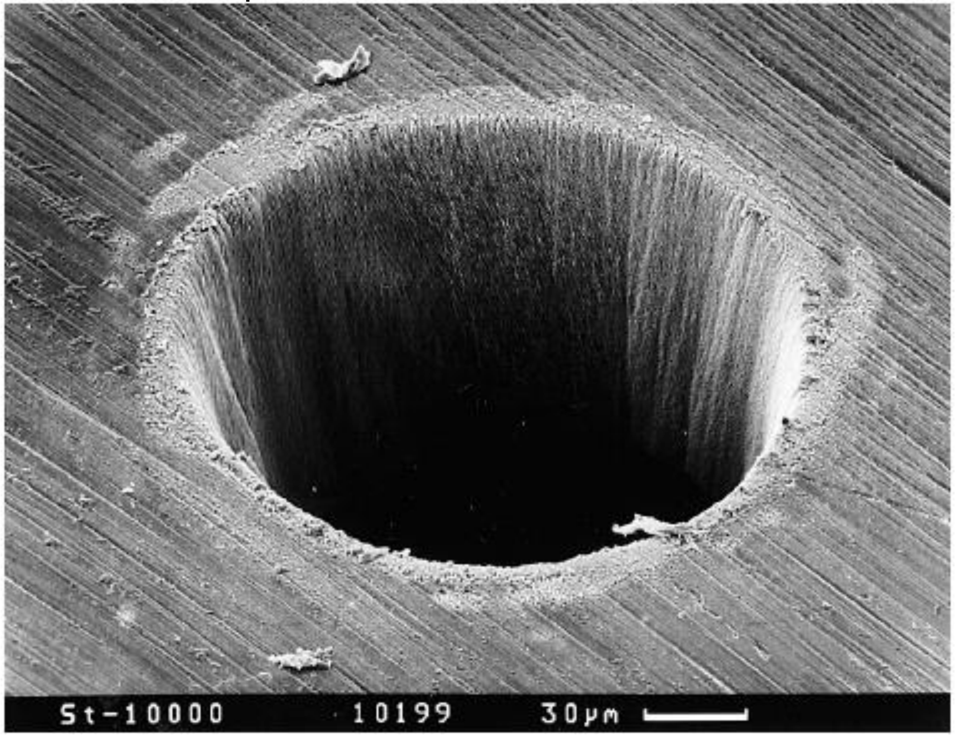
Chang-Hwan Choi and Chang-Jin Kim 2006 *Nanotechnology* **17** 5326

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

laser pulse at F = 4.2 J/cm2, at 780 nm.



laser pulse at F = 0.5 J/cm2, at 780 nm.



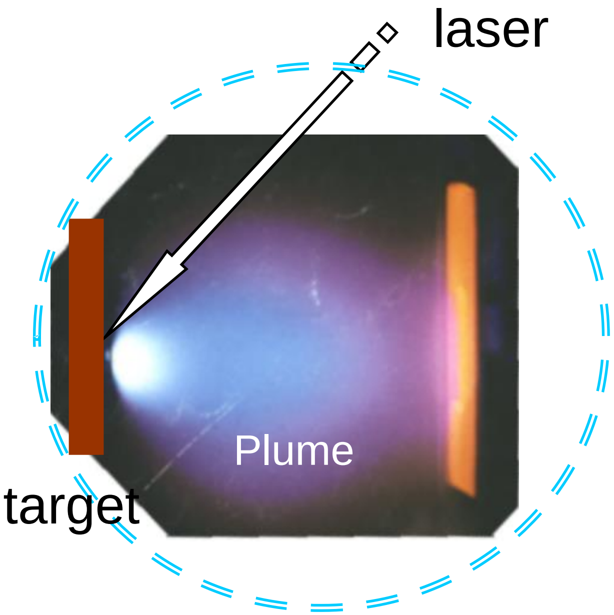
B.N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, A. Tuennermann, *Appl. Phys. A* 63, 109 (1996).

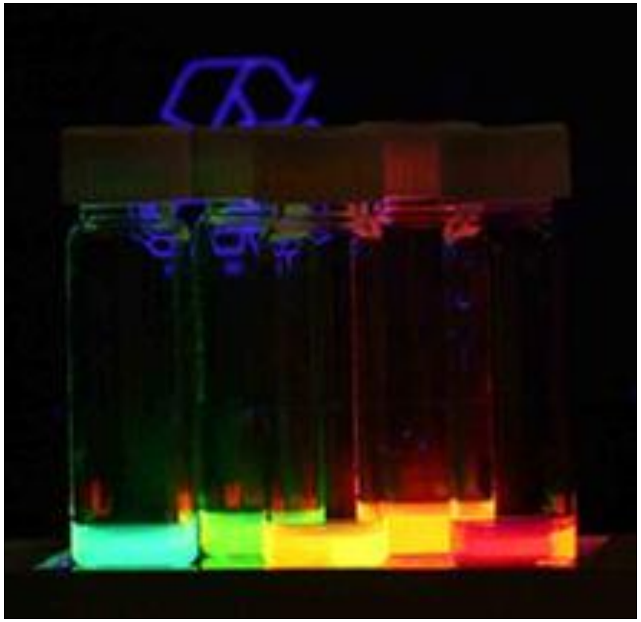
$$\max\{\tau_{pulse}, \tau_{e-ph}\} \approx \tau_{heating} \leq \tau_{mech} \approx \frac{L_{e-diff}}{C_s} \approx \frac{\sqrt{\mathrm{k_e}(T_e, T_{ph}) G_{e-ph}(T_e, T_{ph})}}{C_s}$$

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

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

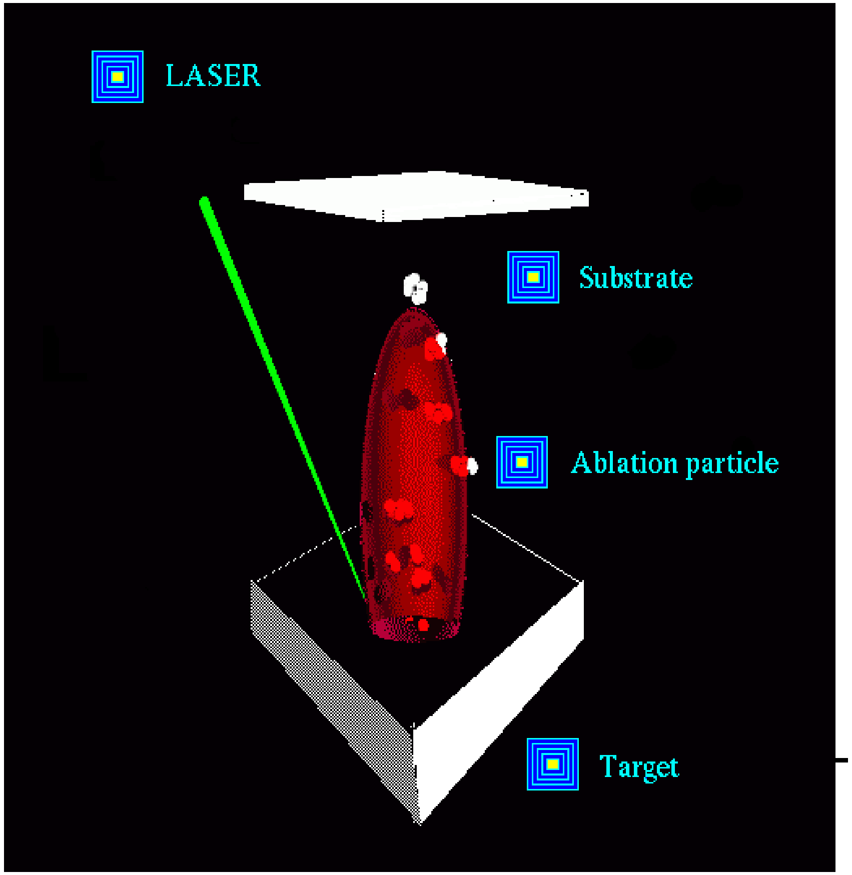
Fundementals of Laser –Matter Interactions





- 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?

- Clssical Thermo and Hydrodynamics
- (CFD, CHD, MHD)

Contunuous medium

Material motion as a hole

Phase transitions

Waves

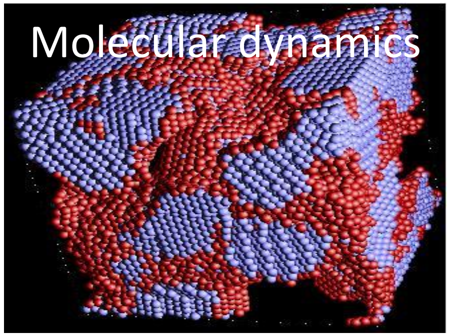
Ionization/plasma formation

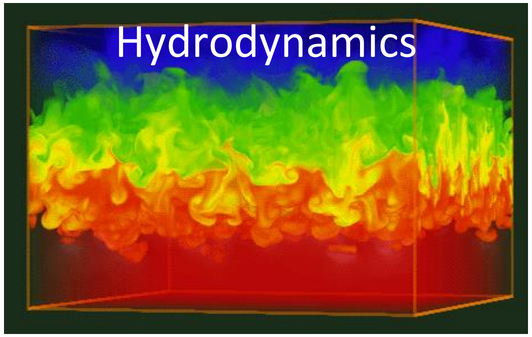
Equation of state?

Non-equilibrium?

Modeling Approaches

Atomistic (MD) vs Hydrodynamics (CFD)





V < 1 μm^3; t ~ 1 ns
Dynamics
Interaction potential
Ionization?

Real temporal and spatial scales
LTE?
Nucleation, surface effects?
Equation of state (EOS)

Ultra-short Laser Interactions

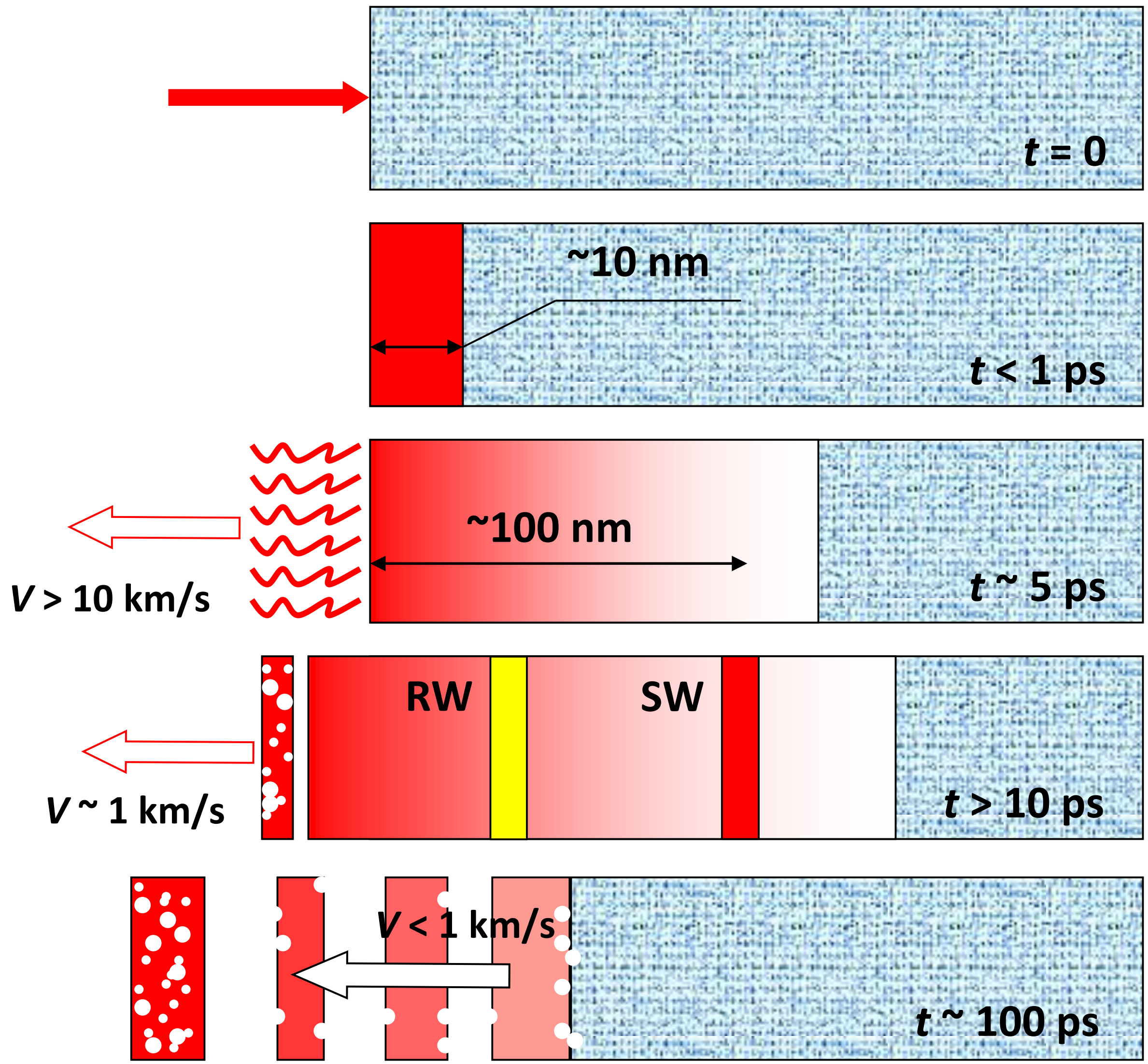
1. Pulse duration τ ~ 100 fs

2. Absorption, e-exitation

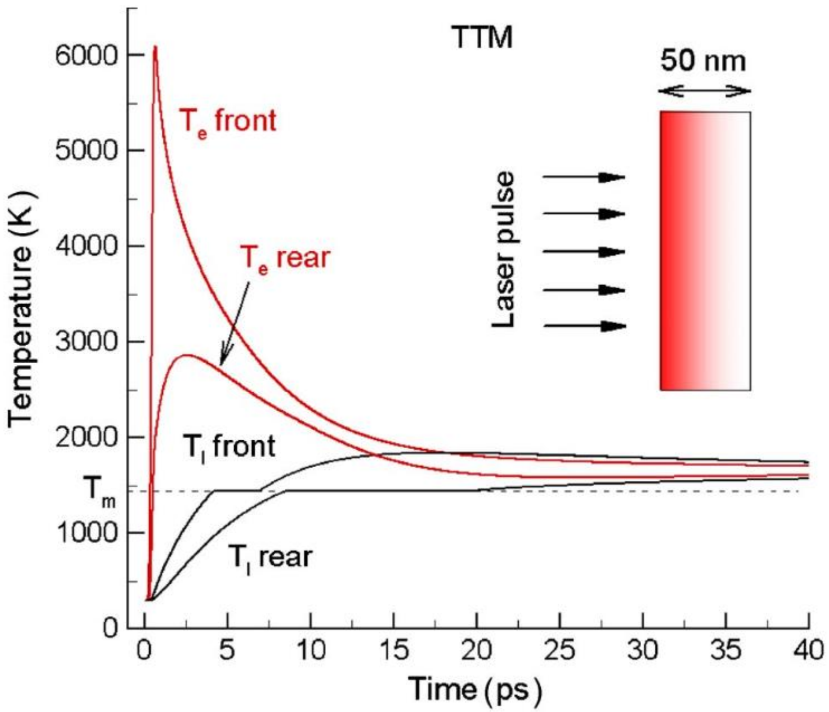
3. Electron-phonon/ion coupling, thermal conductivity

4. Evaporation, shoc waves, rarefaction waves

5. Phase explosion, material decomposition



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

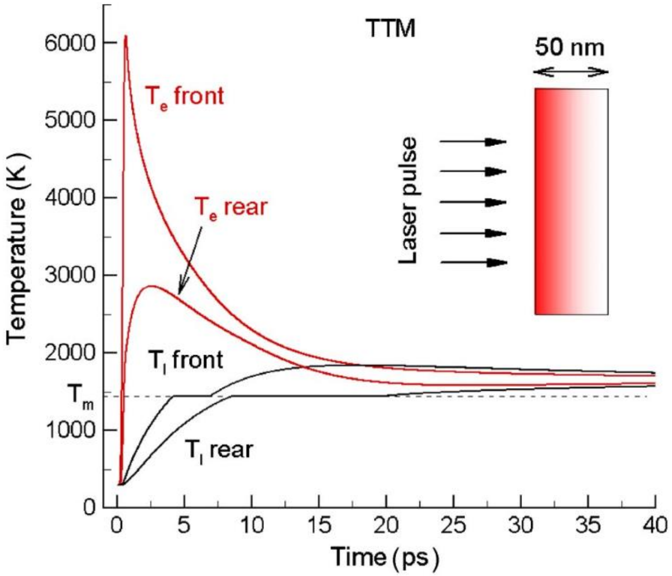


$$C_e(T_e)\frac{\partial T_e}{\partial t} = \nabla[K_e(T_e)\nabla T_e] - G(T_e - T_l) + S(z,t),$$

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

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

Ultra-short Laser Interactions



1. Thermal (TTM) models

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

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

- ⇒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**

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

•**Build a 'system'**

•**Choose parameters**
Cohesion energy, density, other properties,..

•**Integration**

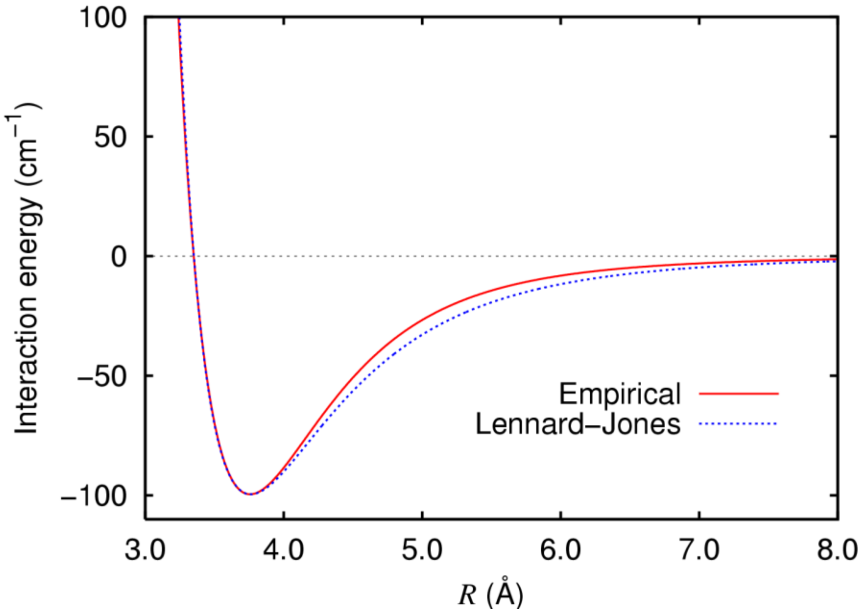
$v(t+\delta t) = v(t) + F(t)*\delta t/m$
$r(t+\delta t) = r(t) + v(t)*\delta t$

•**Gives**
temperature, pressure, composition,
energy & distributions ,
etc...

Classical Molecular Dynamics (MD)

Interaction potentials

$md^2r/dt^2 = F = -\nabla U$



Lennard-Jones *(Ar)*

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

- Morse

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

- Stillinger-Weber (Si, 3 body)

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

- Embedded atom (EAM)
- ReaxFF
- Etc.…

Choice of the potential for MD method

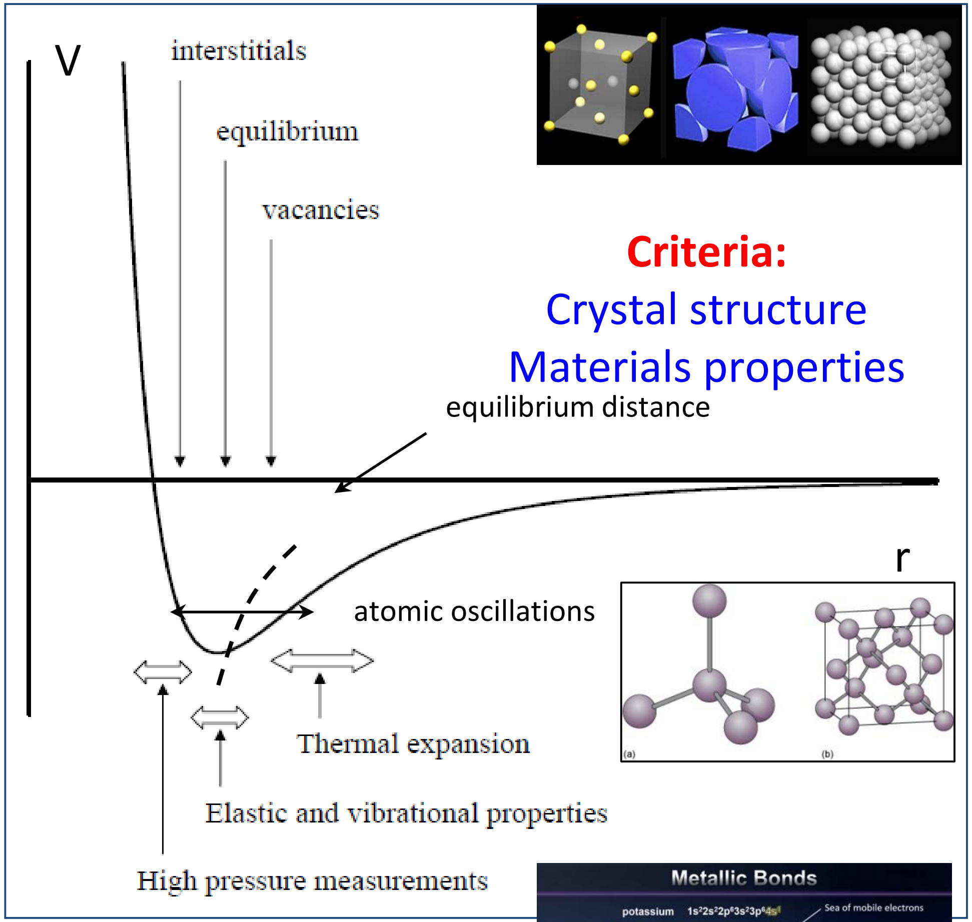
MD: $m_i \vec{a}_i = \vec{F}_i = -gradV(\vec{r}_1, \vec{r}_2, \dots \vec{r}_n)$

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

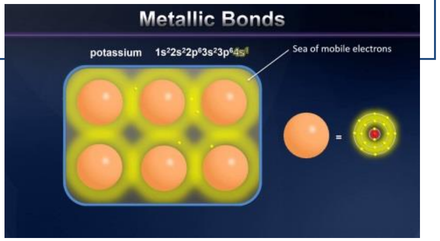
- Lennard-Johns potential for Wan der Vaals interactions in inert gases and molecules: Ar, Kr, and molecular systems

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

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



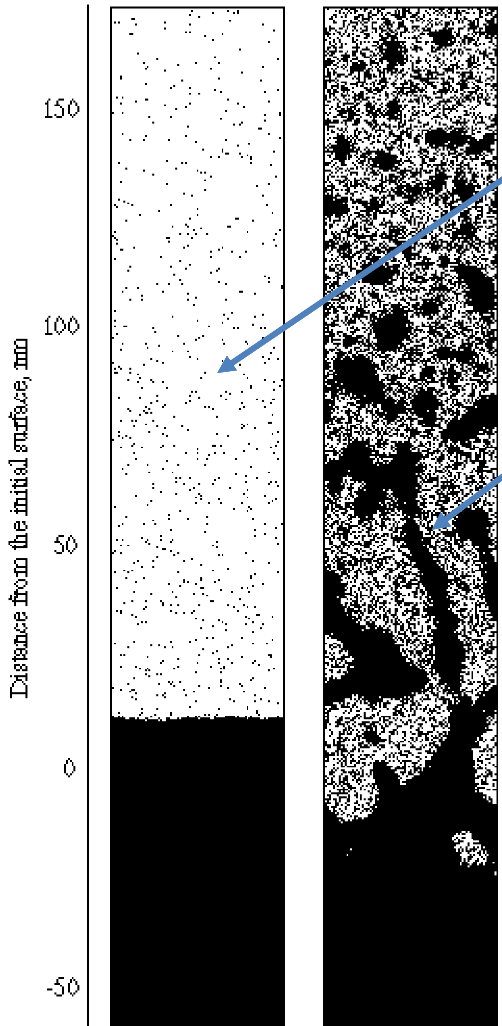
$$V = \sum_i E_i \qquad E_i = F\left(\sum_{i \neq j} \rho(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} U(r_{ij})$$



- 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, Pl, Cu, ..

Classical Molecular Dynamics (MD)

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



F<Fth

Desorption: Atoms, slow surface evaporation

F>Fth

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

Process can be at T-> Tc

Difficult to model by classical methods !

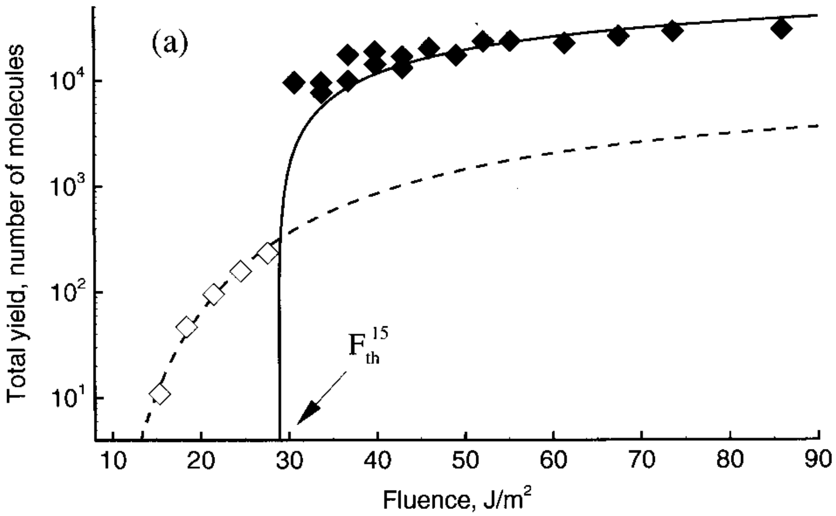
pico

Molecular matrixes

T. E. Itina, L. V. Zhigilei, B. J. Garrison,

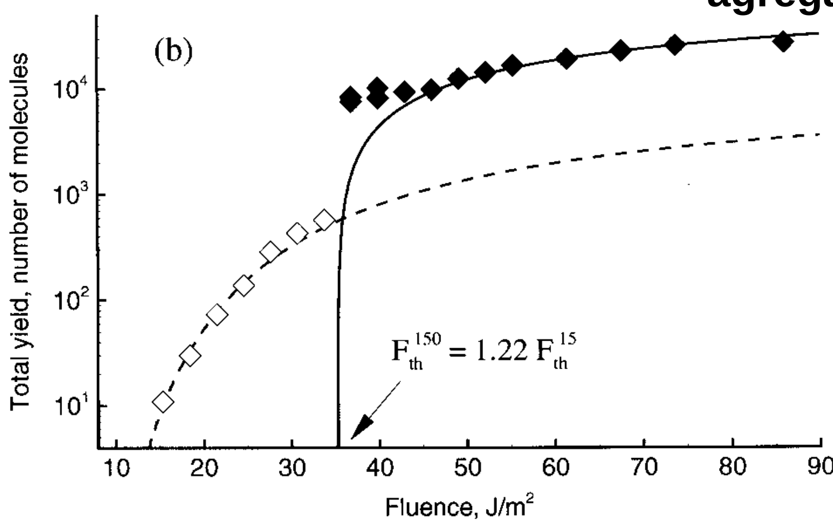
J. Phys. Chem.B , **106**, 303-310 (2002)

Thermal or Mechanical Confinement



Mechanical confinement
pulse ~15 ps

agrégats



monomers

Thermal confinement
pulse 150 ps

For femto laser:

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

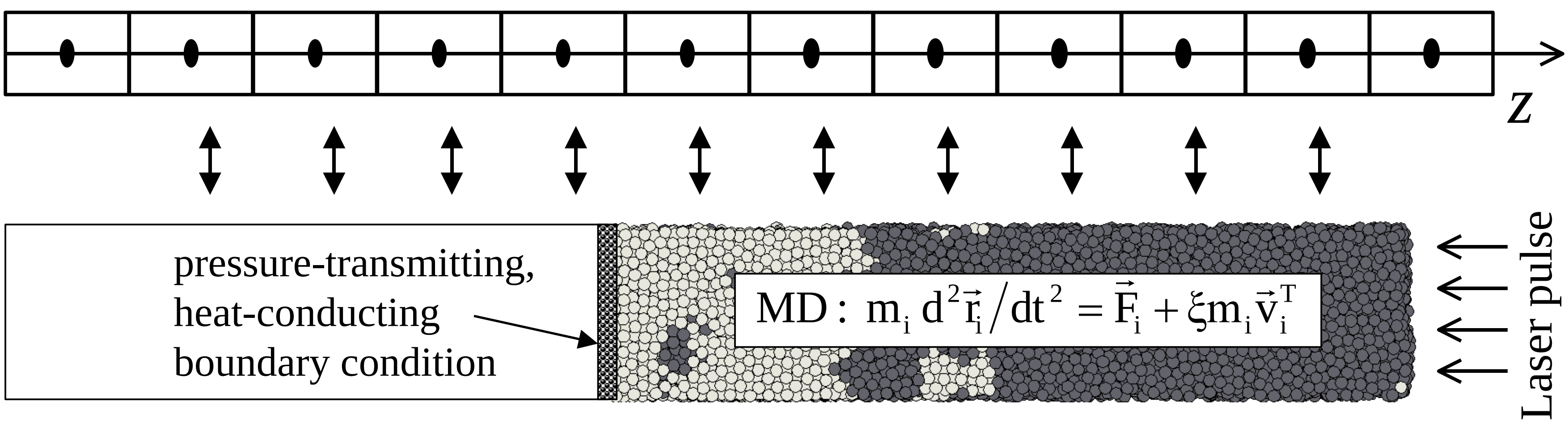
Zhigilei et al. Appl. Phys. A, 69, S75-S80 (1999)

Ultra-short Laser Interactions

Let's combine : TTM –MD

$$C_e(T_e) = \gamma T_e \quad \textbf{?} \qquad\qquad G = const \quad \textbf{?}$$

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

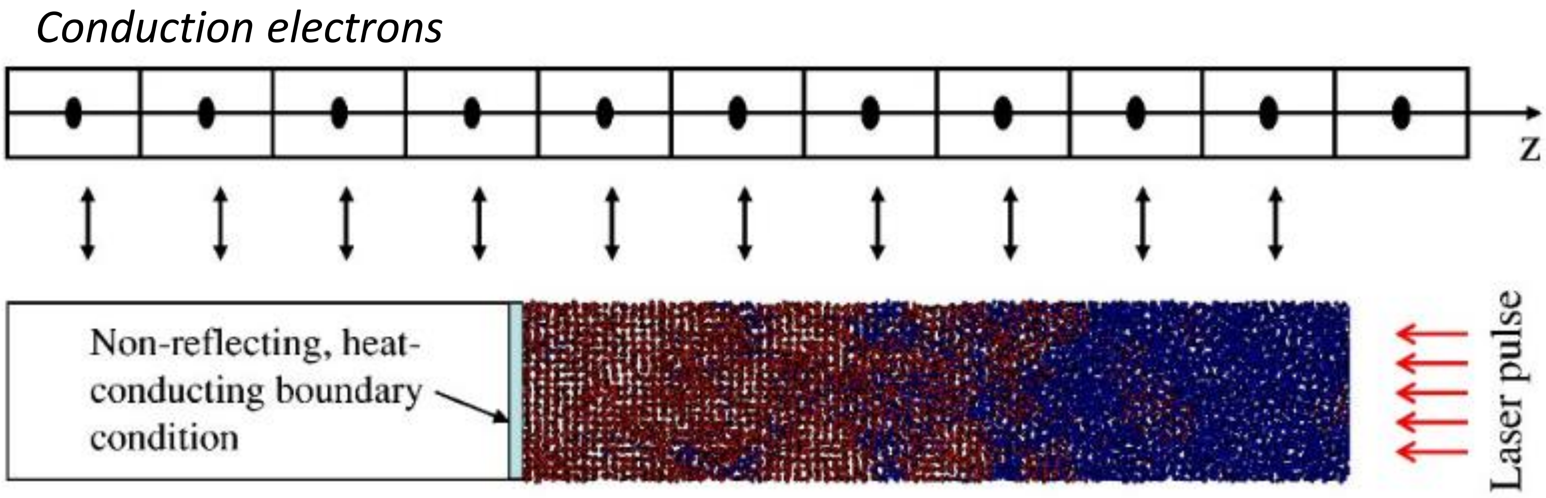


$$C_l(T_l)\frac{\partial T_l}{\partial t} = G(T_e - T_l) \qquad\qquad T_l^{cell} = \sum_{i=1}^{N^{cell}} m_i \left(\vec{v}_i^{\,T}\right)^2 \Big/ \left(3k_B N^{cell}\right)$$

Parameters ?

Ultra-short Laser Interactions

TTM + Molecular Dynamics (TTM-MD)

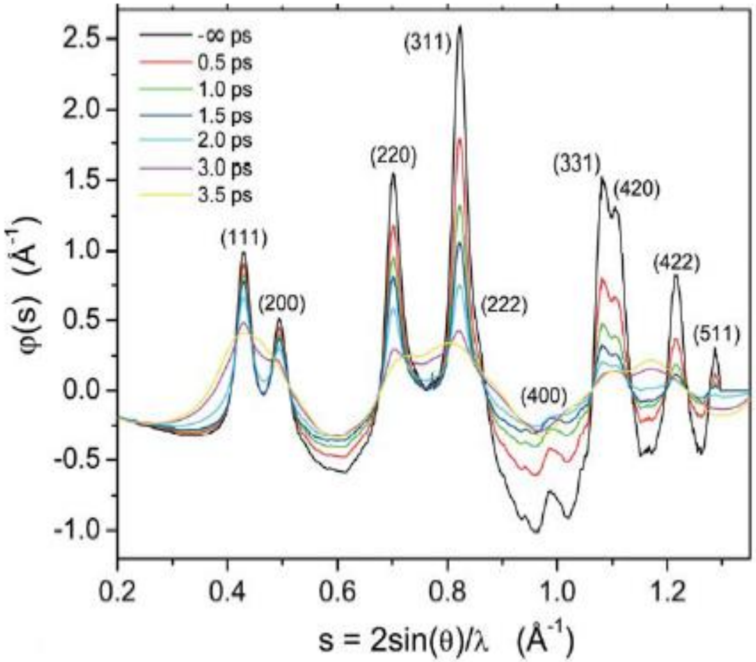


$$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z}\left(K_e(T_e)\frac{\partial}{\partial z}T_e\right) - G(T_e - T_l) + S(z,t), \quad \text{TTM}$$

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

Ivanov & Zhigilei, Phys. Rev. B, 68, 064114 (2003)

TTM- MD used for melting of metal films



<u>Experiments</u>

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

Fluence: 70 mJ/cm^2, Réflectivité 88%

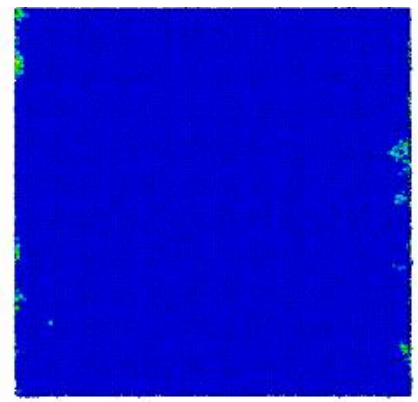
Desordre vers ~3.5 ps

<u>Simulation</u>

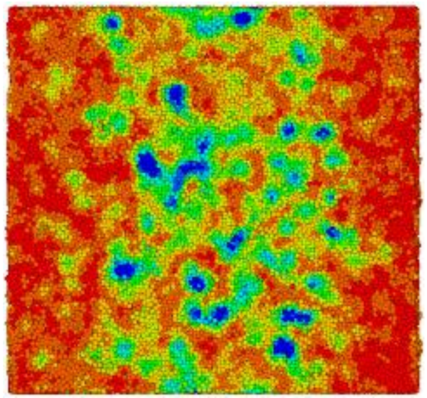
homogeneous melting at 3 ps

(starts at ~1.5 ps ans finishes at 3 ps)

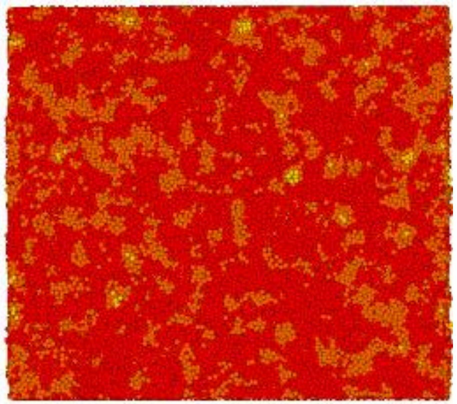
Rather good agreement with experiments



1 ps



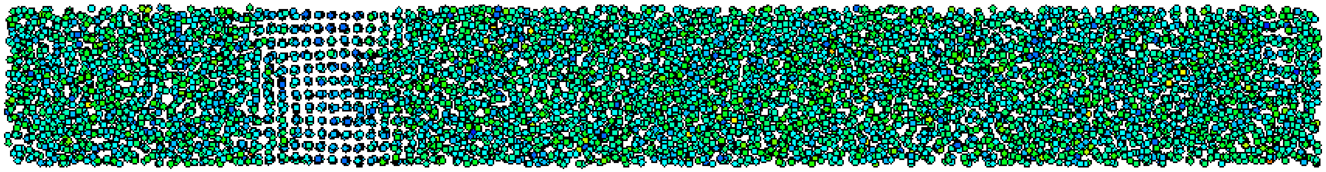
2 ps



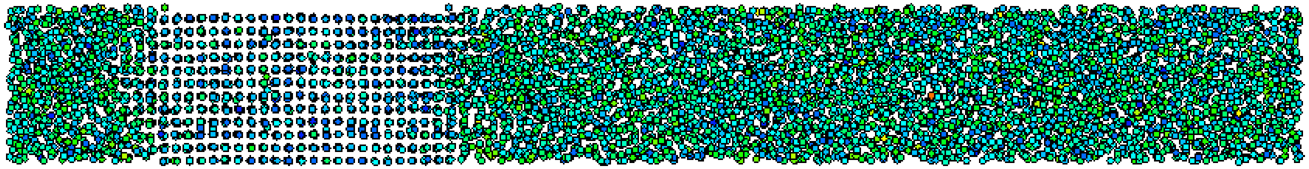
3 ps

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

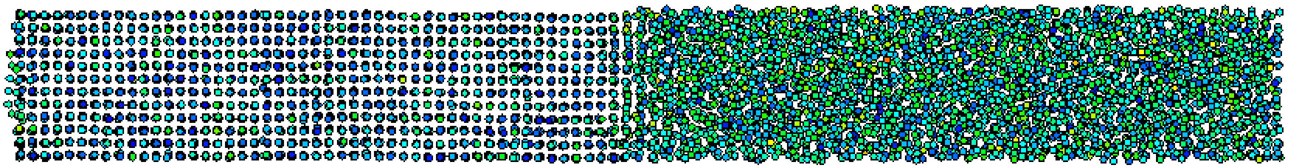
Physical Properties of the EAM Ni Model



T=1238K P=-4.61GPa



T=1378K P=-1.20GPa



T=1579K P=+3.12GPa

Linear fit:

$T = 1439 + 43.1 \times P$

[T in K, P in GPa]

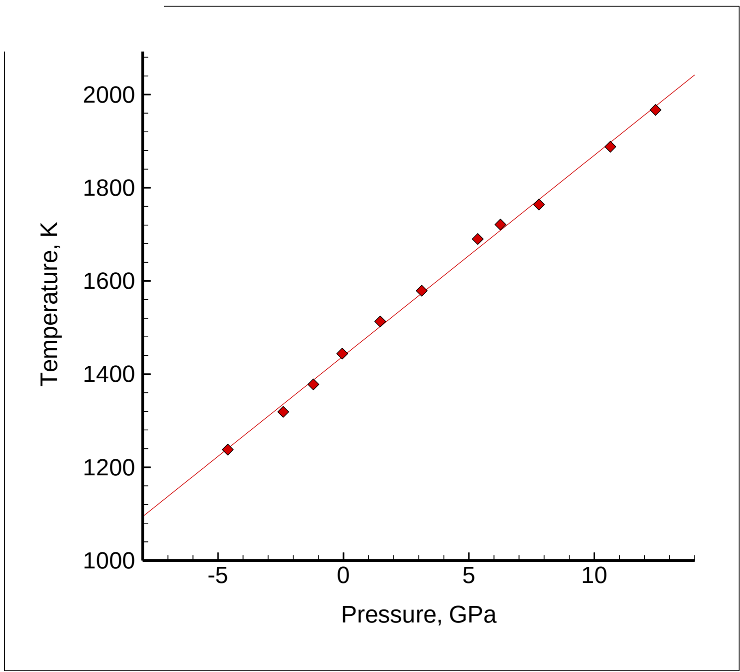
$$\left(\frac{dT}{dP}\right)_m = \frac{\Delta V_m}{\Delta S_m} = \frac{T_m \Delta V_m}{\Delta H_m}$$

At P = 0 Pa

$T_m = 1439$ K

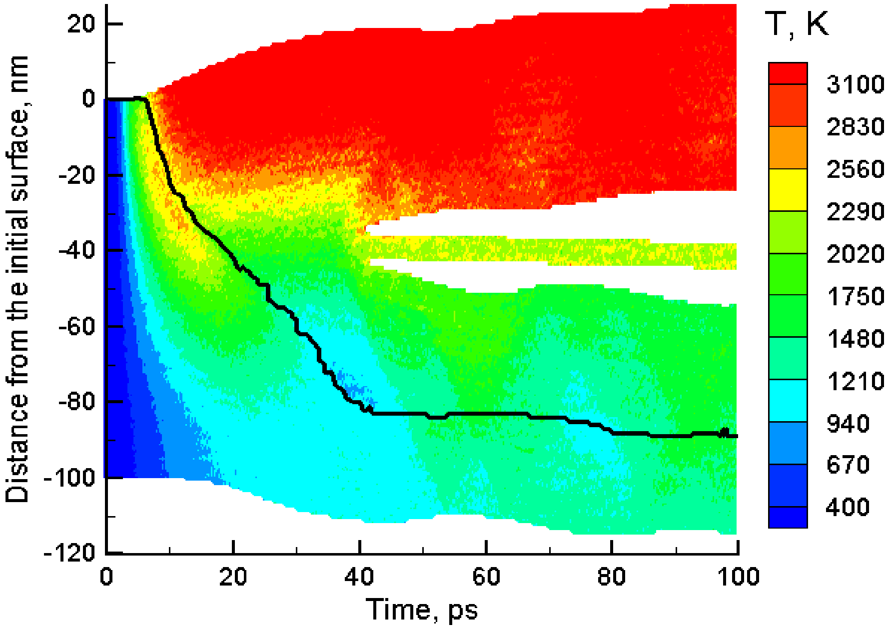
- From liquid-crystal coexistence simulations, the equilibrium melting temperature for the hosen EAM potential for Ni was defined.

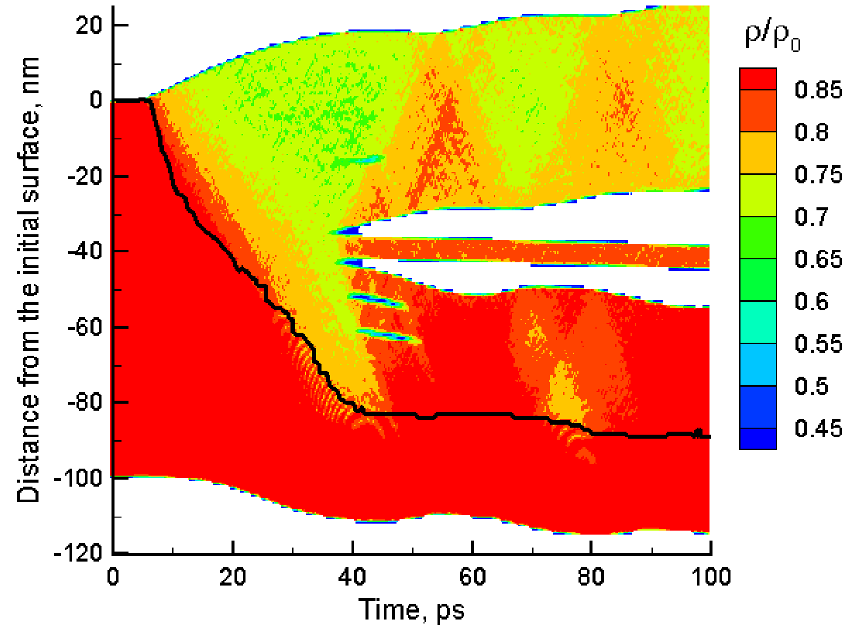
- A linear fit to the sequence of coexistence data gives the value of $(dT/dP)_{Tm}$ that can be related to Clayperon equation.



X. W. Zhou, H. N. G. Wadley, R. A. Johnson, D. J. Larson, N. Tabat, 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



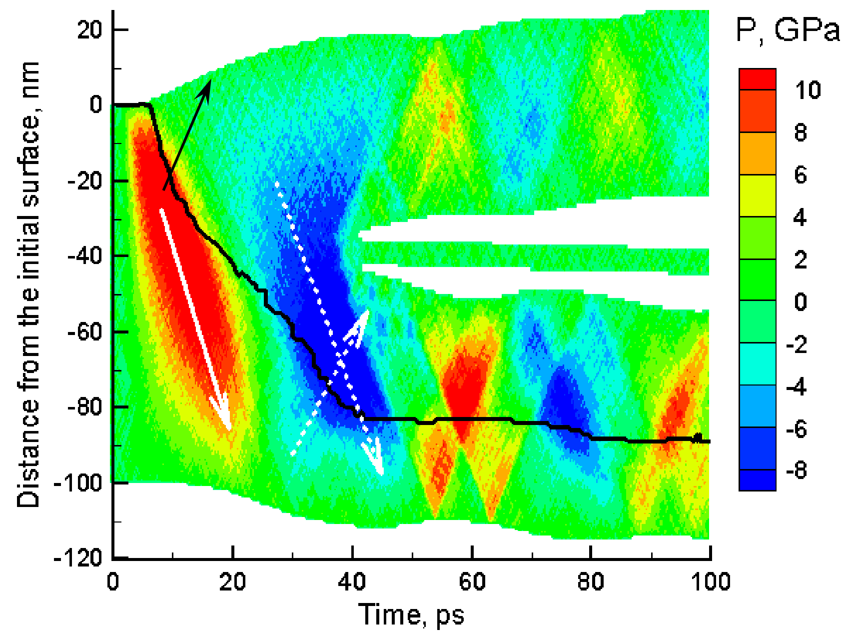


1 ps pulse, fluence 129 mJ/cm^2, 100 nm Ni film

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

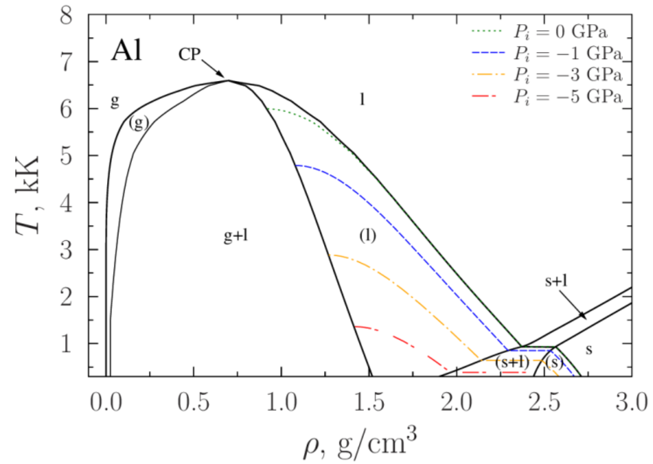
$$\frac{\partial(1/\rho)}{\partial t} - \frac{\partial u}{\partial m} = 0$$

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

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

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

EOS



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

LAMMPS

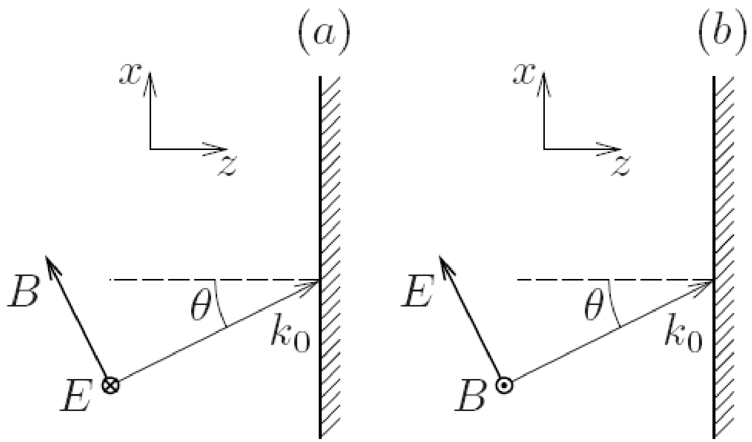
$$\frac{\partial(\rho e_{\text{el}})}{\partial t} + \frac{\partial(\rho e_{\text{el}}u)}{\partial z} + P_{\text{el}}\frac{\partial u}{\partial z} = \frac{\partial}{\partial z}\left(\kappa_{\text{el}}\frac{\partial T_{\text{el}}}{\partial z}\right) - \gamma_{\text{ei}}(T_{\text{el}} - T_{\text{ion}})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

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)

Laser energy absorption (Helmholtz equation)



$$\frac{\partial^2 E}{\partial z^2} + k_0^2[\varepsilon(z) - \sin^2\theta]E = 0.$$

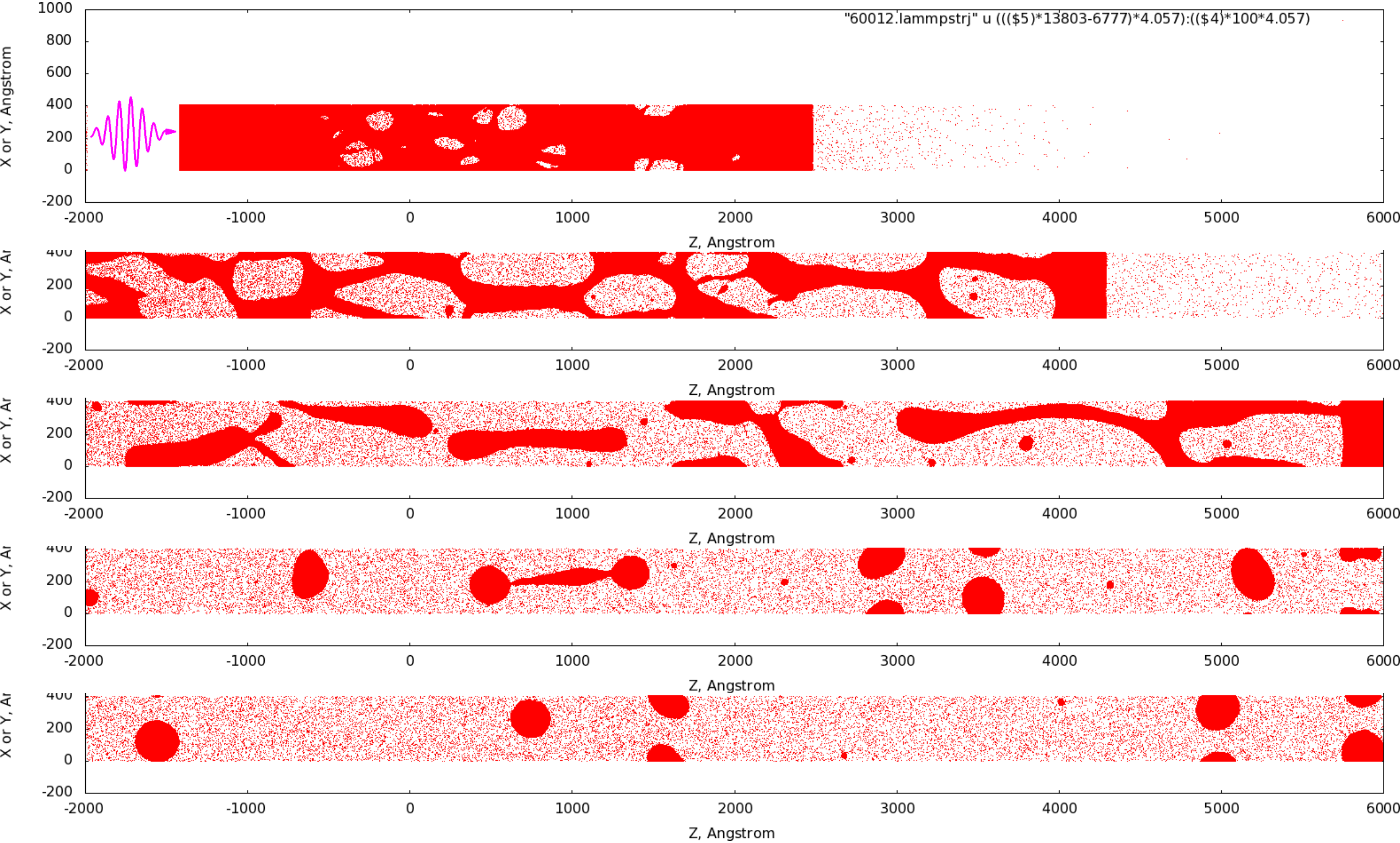
$$\frac{\partial^2 B}{\partial z^2} + k_0^2[\varepsilon(z) - \sin^2\theta]B - \frac{\partial \ln \varepsilon(z)}{\partial z}\frac{\partial B}{\partial z} = 0$$

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

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

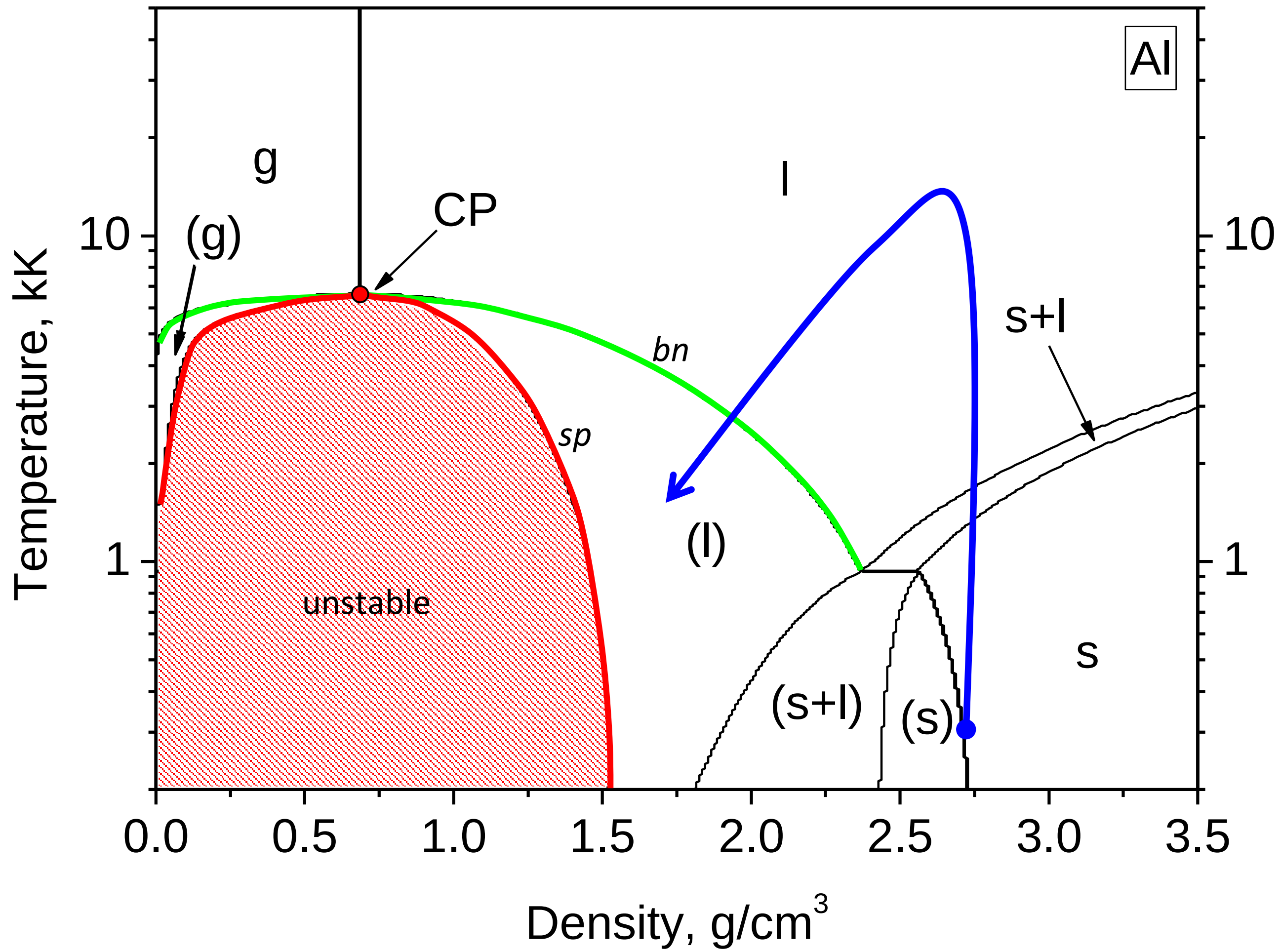
Ultra-short Laser Ablation

Ablation & nanoparticles (10M atoms, F=1 J/cm^2, Al)



Ultra-short Laser Ablation

Equation of state (EOS)



Ultra-short Laser Ablation

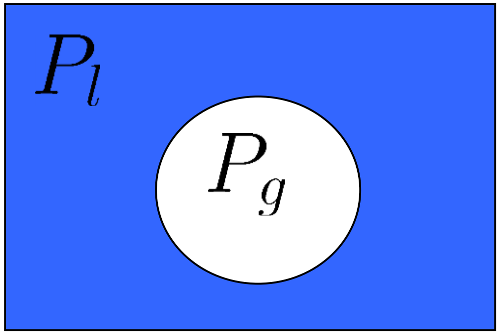
Bubble/Pore Nucleation

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

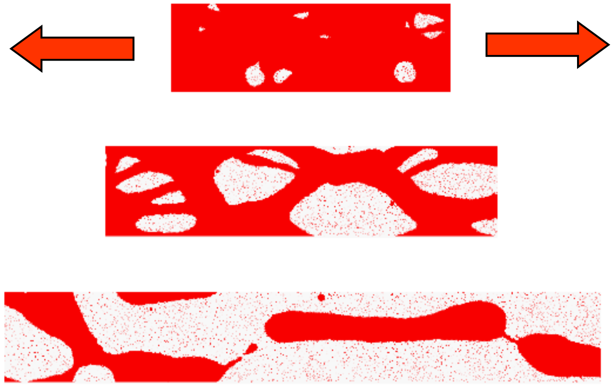
$$C \approx 10^{10}\ s^{-1}$$

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

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



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

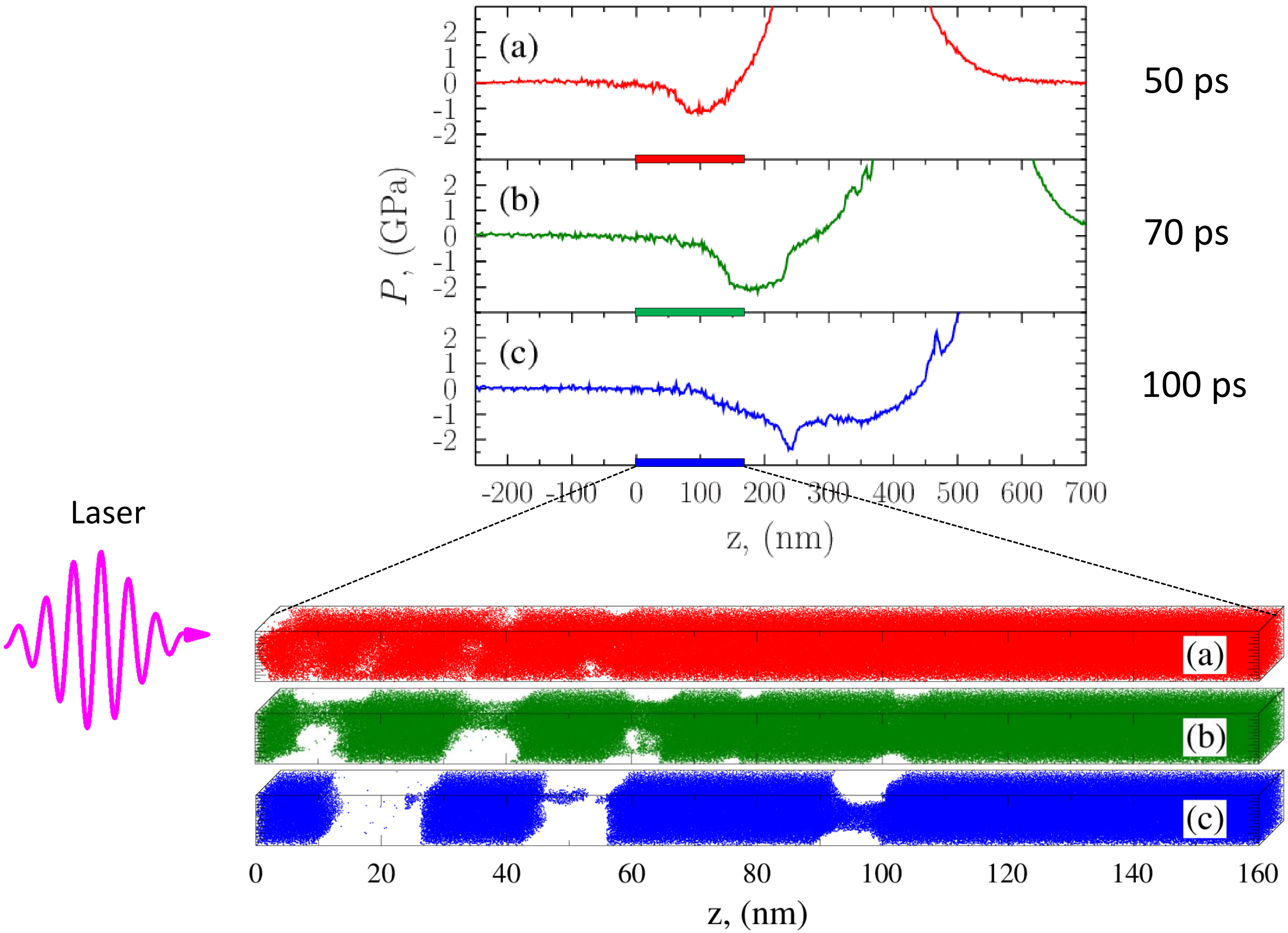


V. P. Skripov, Metastable Liquids. Wiley, New York, 1974.

Ultra-short Laser Ablation

Pressure

Al, F = 2.6 J/cm^2 (DM-TTM)

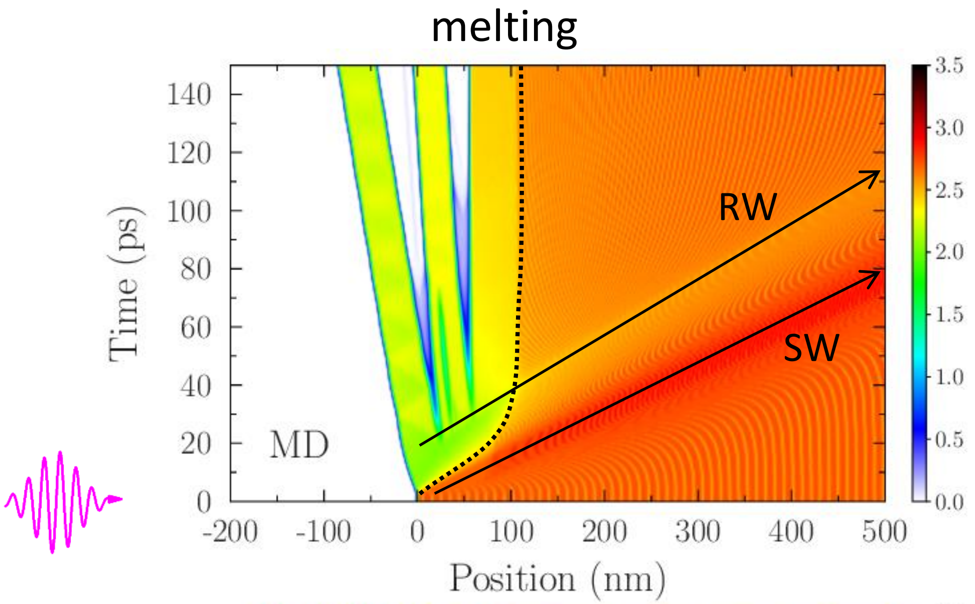


Ultra-short Laser Ablation

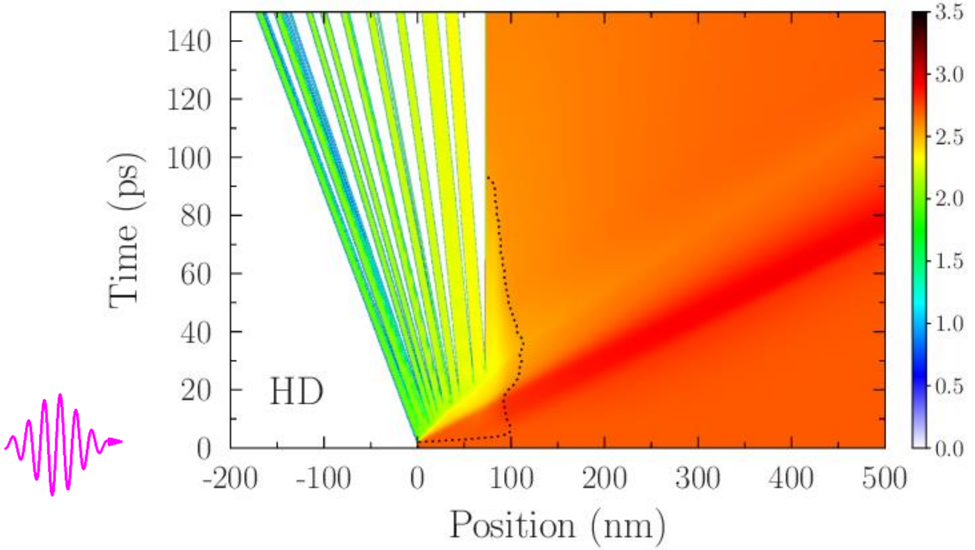
Density

Al, F = 0.5 J/cm^2

TTM-MD



Hydrodynamics



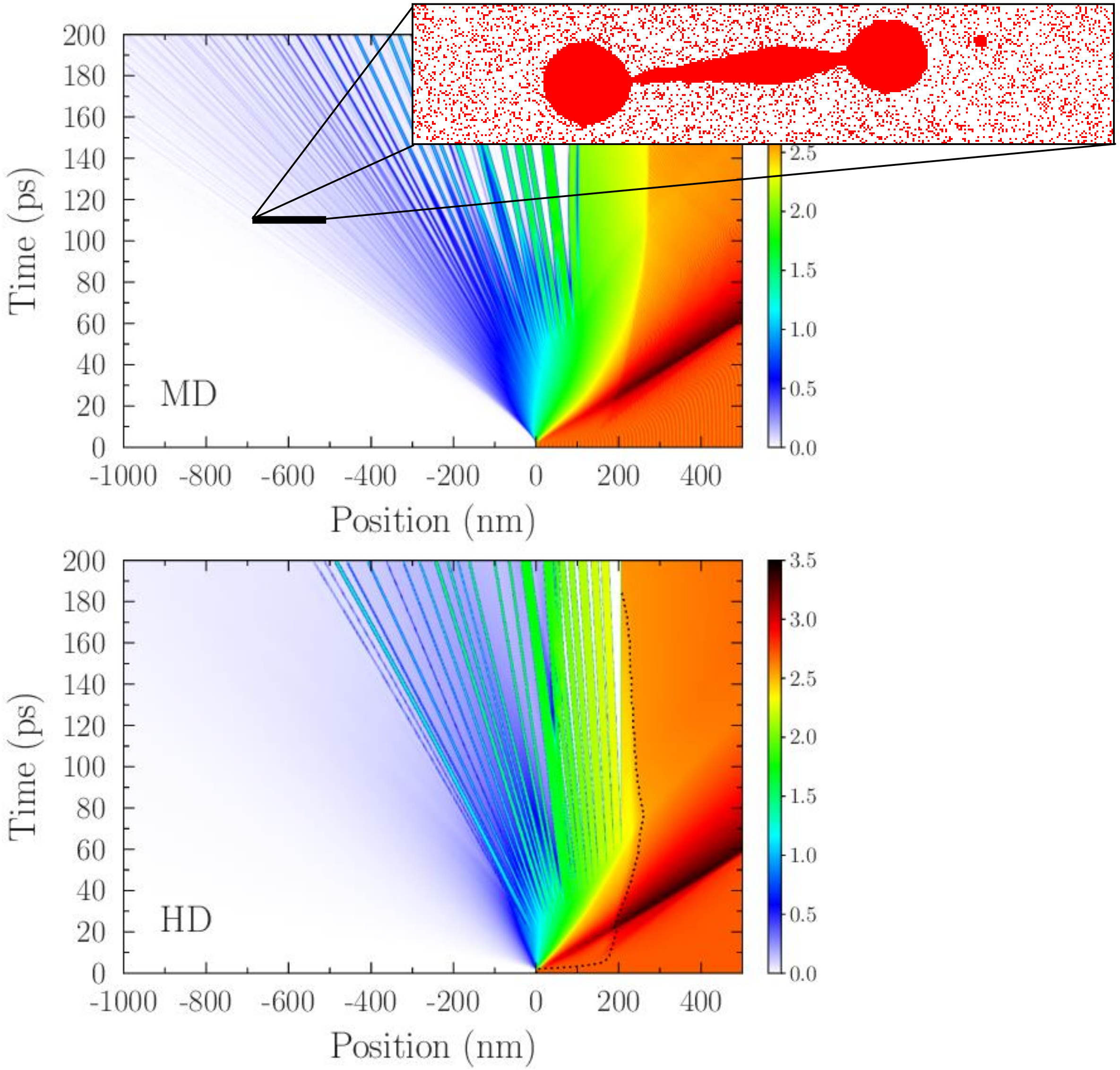
Ultra-short Laser Ablation

Density

Al, F = 2 J/cm^2

TTM-MD

Hydrodynamics

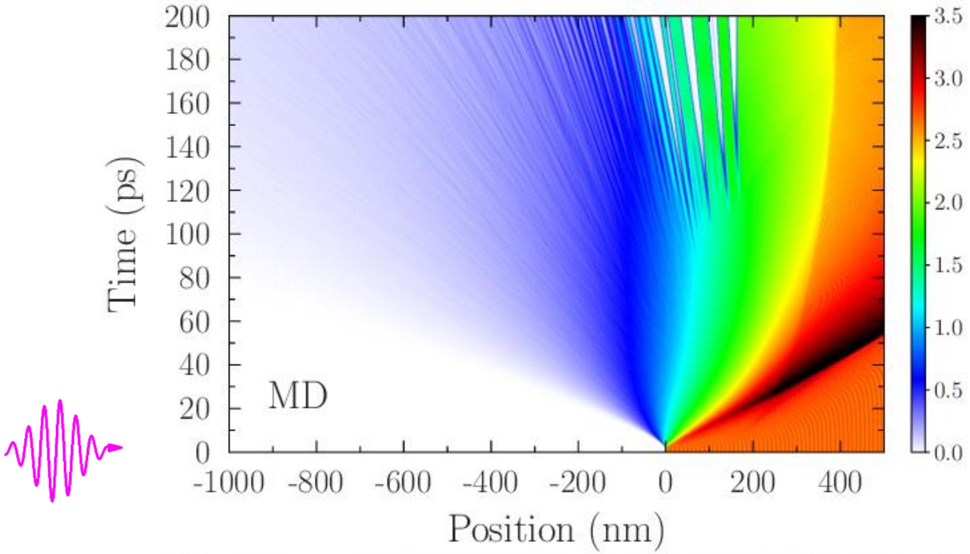


Ultra-short Laser Ablation

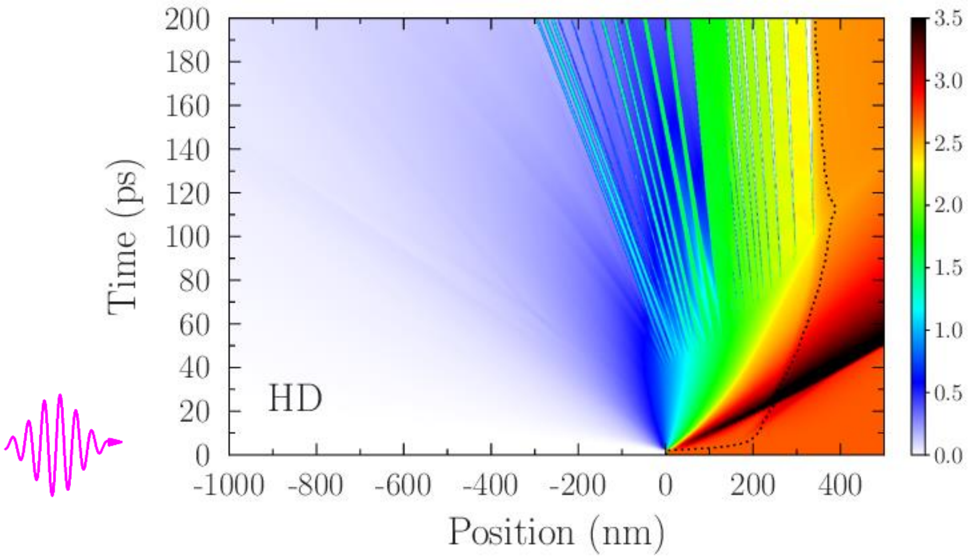
Density

Al, F = 4 J/cm^2

TTM-MD

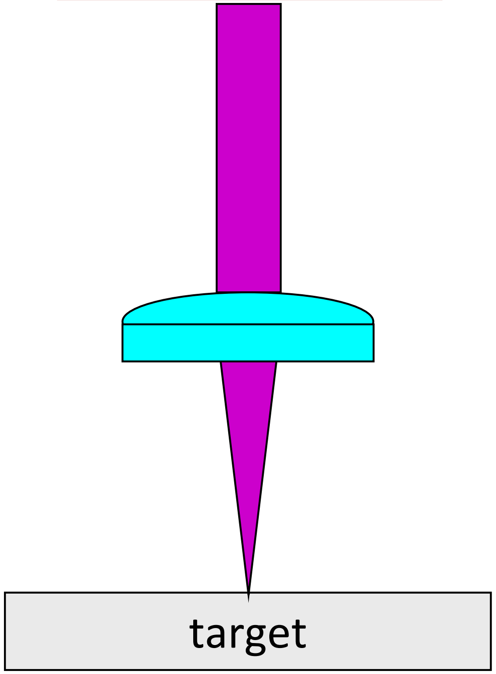


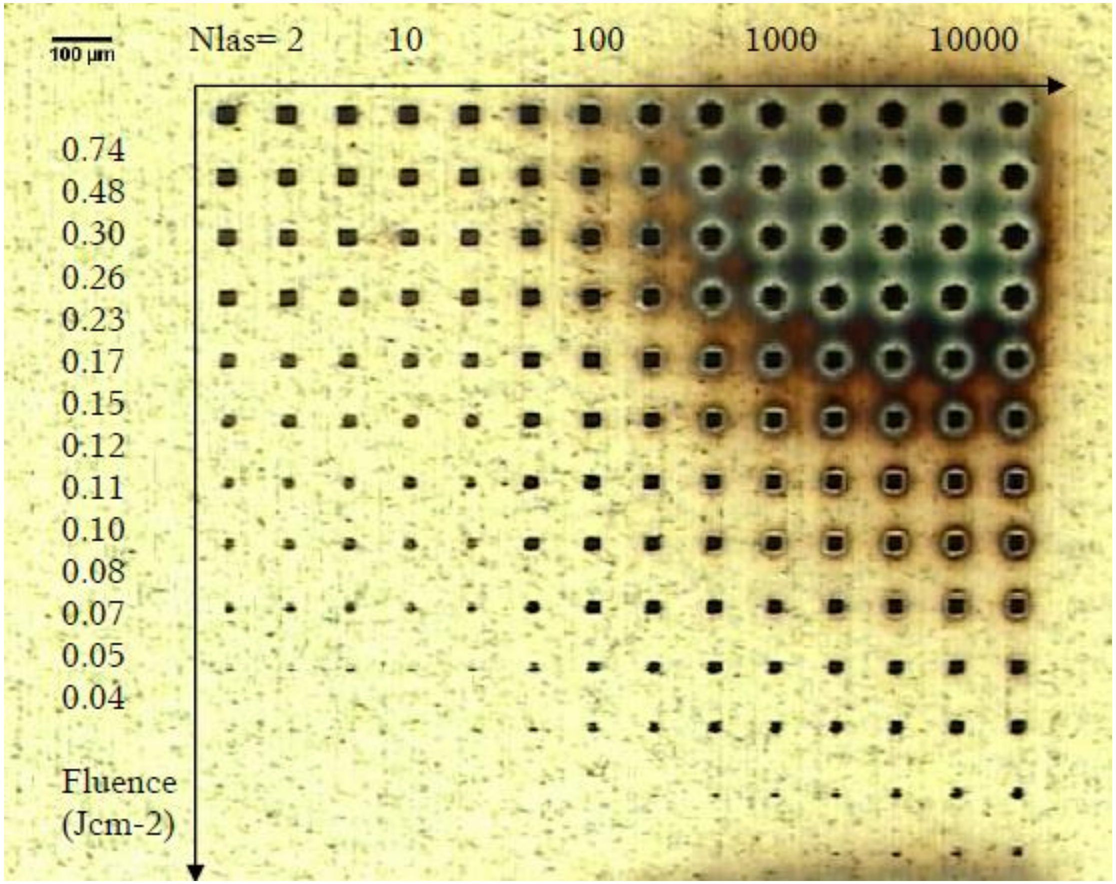
Hydrodynamics



Experimental verification

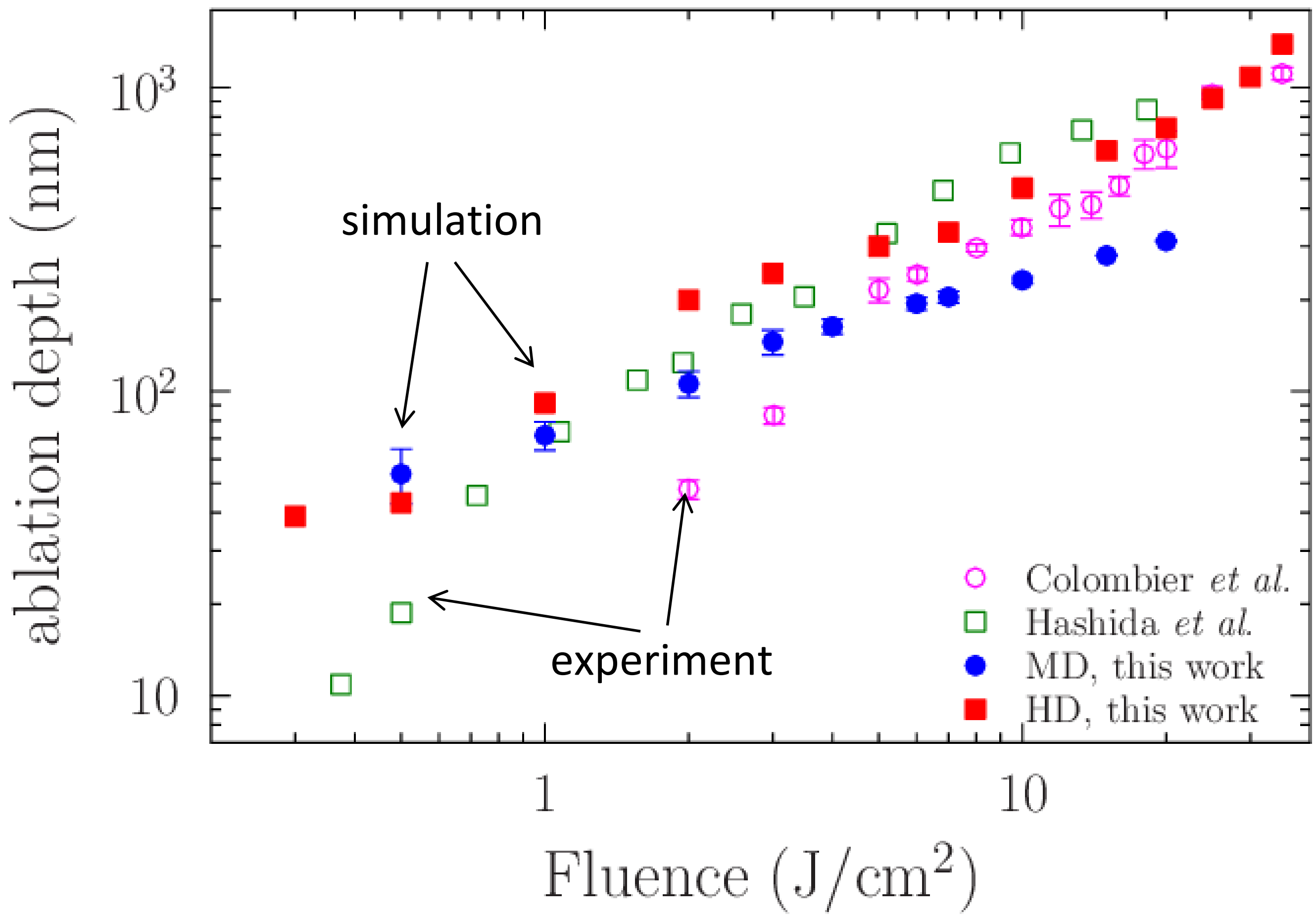
λ = 800 nm
τ = 100 fs
F = 0.1 – 10 J/cm^2





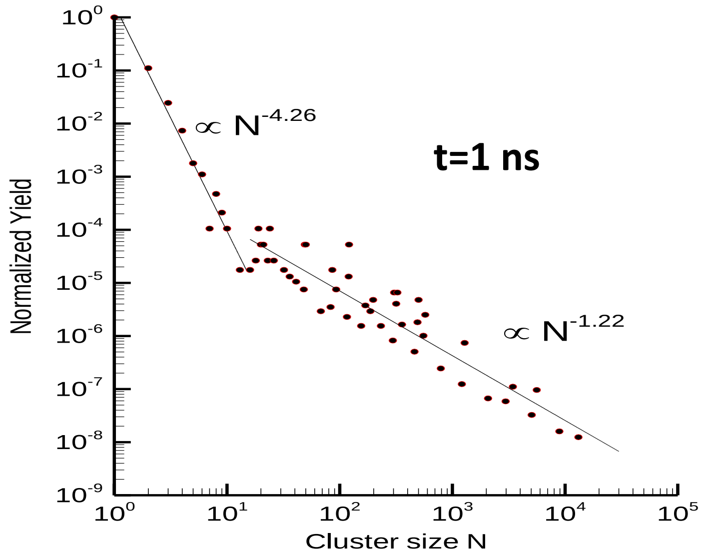
Ablated depth vs laser fluence

100 fs Al

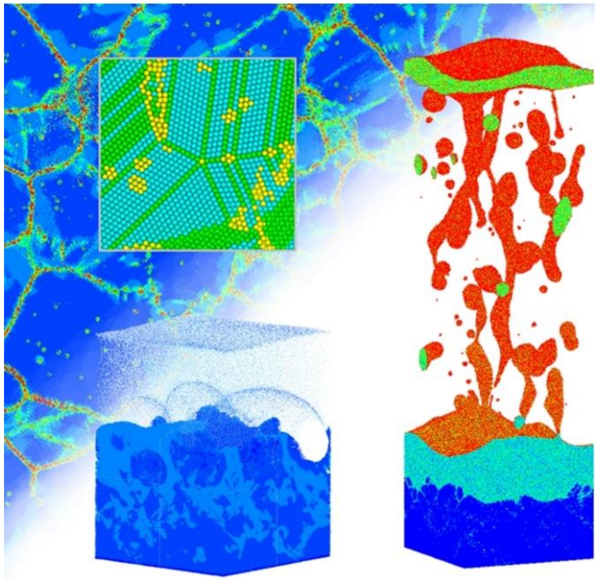


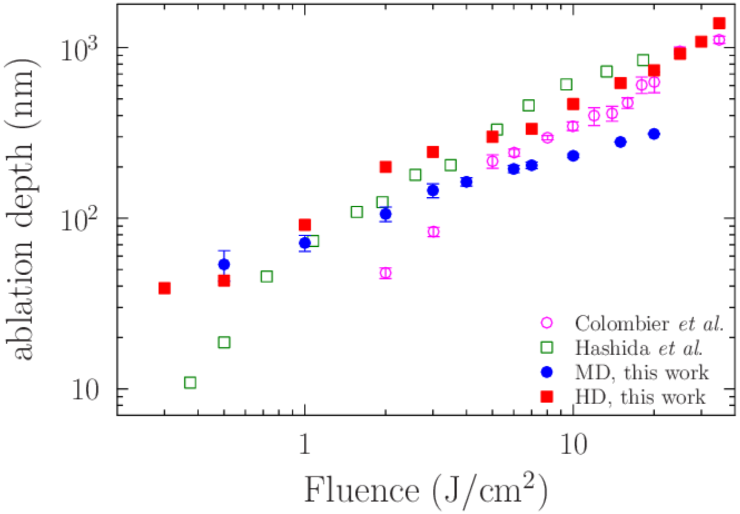
Molecular Dynamics Simulations

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



τ = 15 ps, F ~ 2 Fth, 40×10 nm, t =1 ns





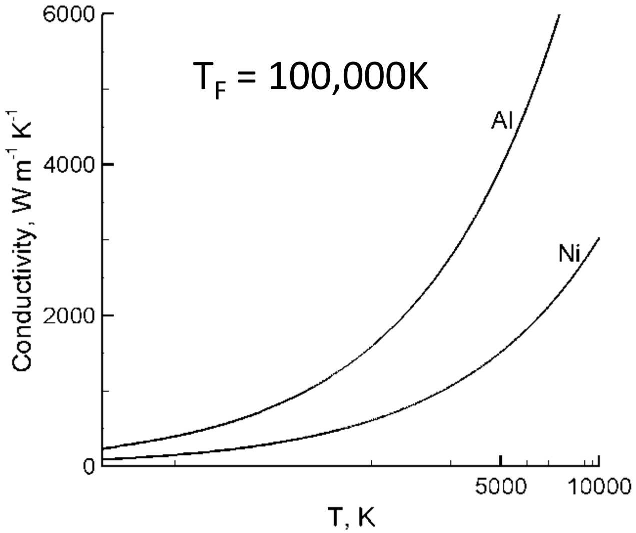
Collaboration with L.V. Zhigilei et al. (Virginia State University, USA)

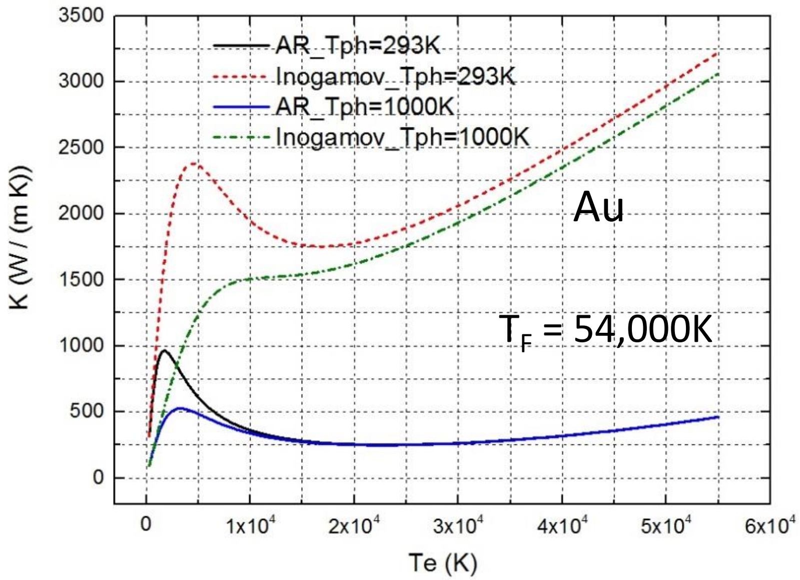
Practically all the molten material is ablated

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

Conductivity models for metals

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





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

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

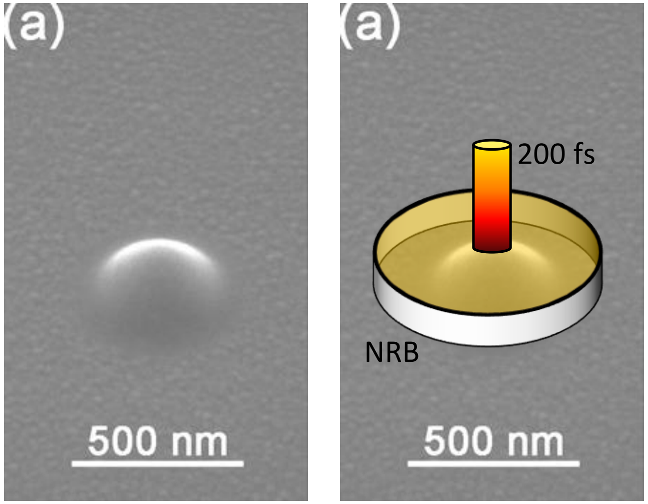
For **noble metals** excitation is high and $k_e(T_e, T_{ph})$ is:

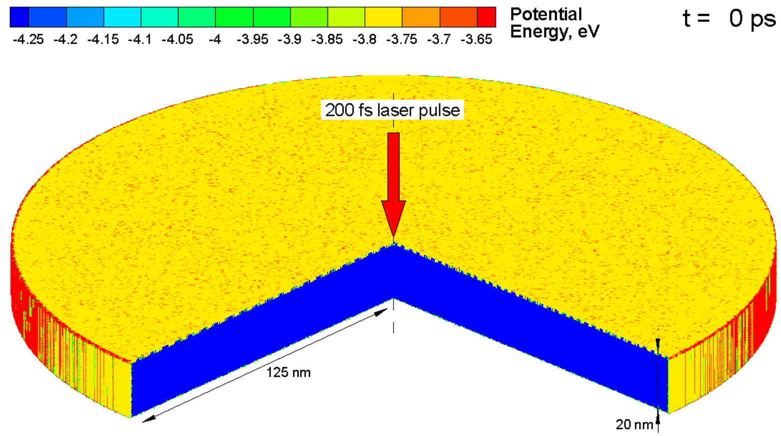
$$k_e = C\frac{\left(\vartheta_e{}^2 + 0.16\right)^{5/4}(\vartheta_e + 0.44)\vartheta_e}{\left(\vartheta_e{}^2 + 0.092\right)^{1/2}\left(\vartheta_e{}^2 + b\vartheta_{ph}\right)}$$

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

Yu.V. Petrov, N.A. Inogamov, S.I. Anisimov, K.P. Migdal, V.A. Khokhlov, and K.V. Khishchenko, *Journal of Physics: Conference Series* 653, 012087 (2015).

Example of TTM-MD : Nanostructuring of Au

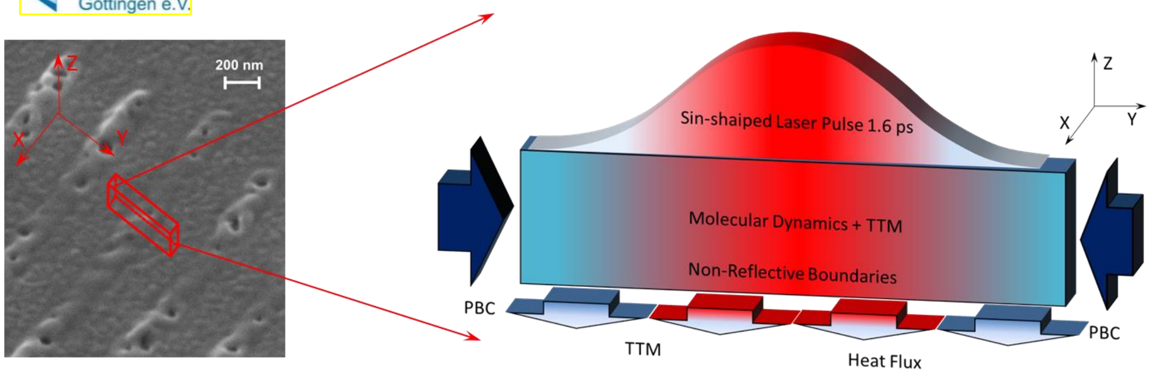


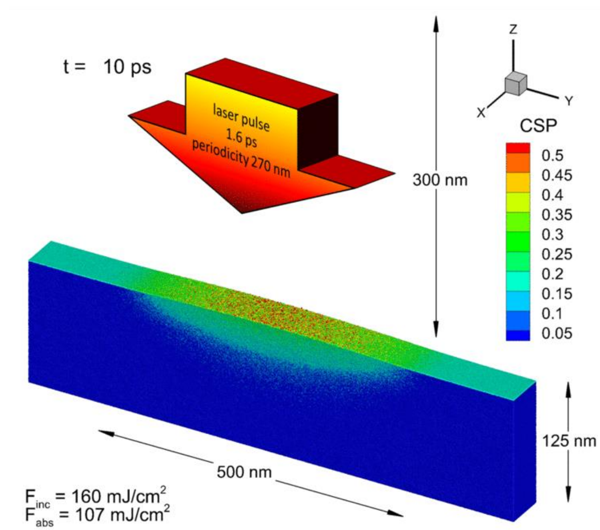


D.S. Ivanov, B.C. Rethfeld, G.M. O'Connor, T.J. Glynn, A.N. Volkov, and L.V. Zhigilei, *Appl. Phys. A*. 92, 791 (2008).

Nanojet: 85,000,000 atoms

Laser-Laboratorium Göttingen e.V.

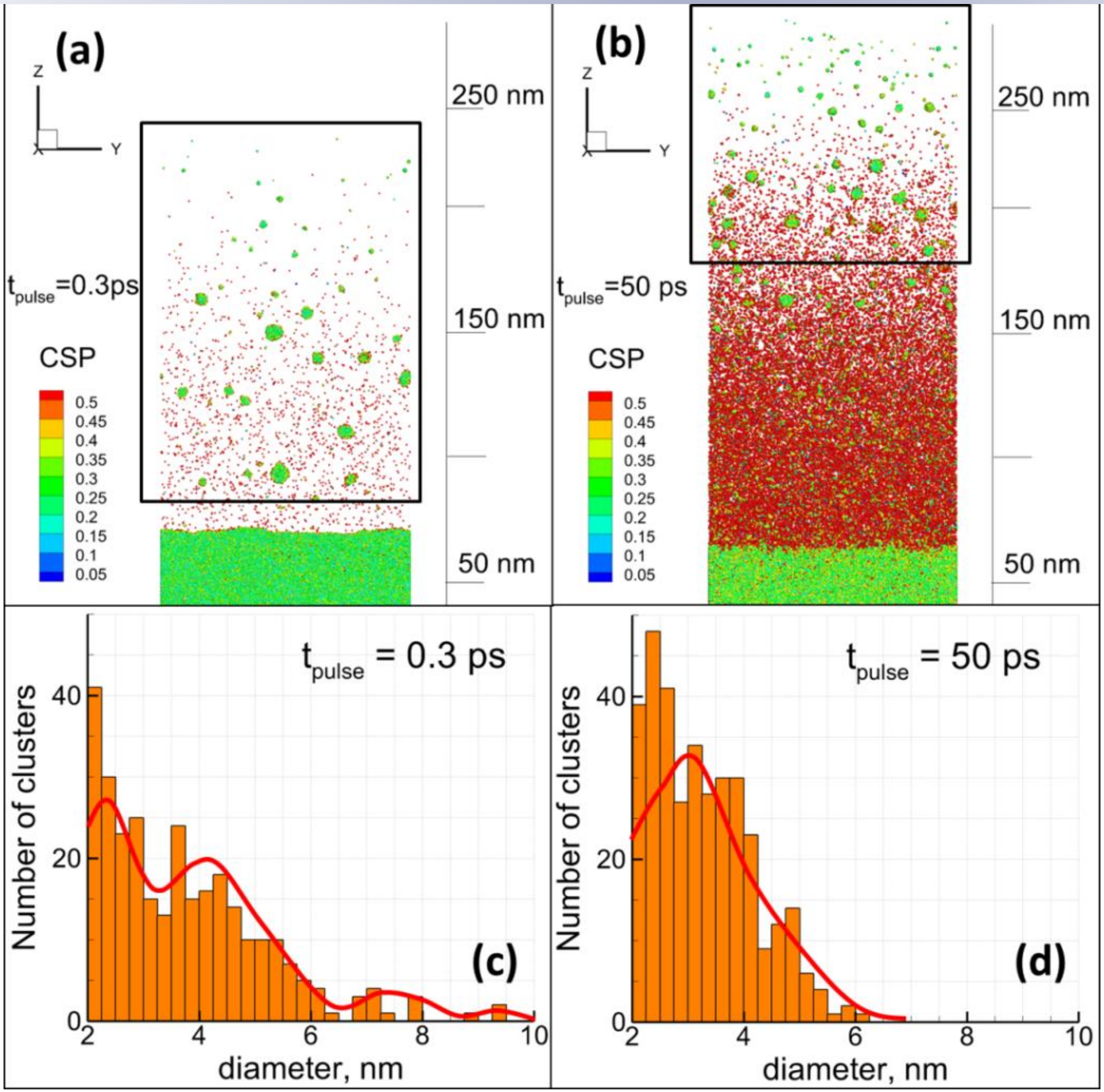




D.S. Ivanov, V.P. Lipp, A. Blumenstein, F. Kleinwort, V.P. Veiko, E. Jakovlev, M.E. Garcia, B. Rethfeld, J. Ihlemann, and P. Simon, *Phys. Rev. Applied* 4, 064006 (2015).

Periodic: 330,000,000 atoms

Varying temporal laser pulse width

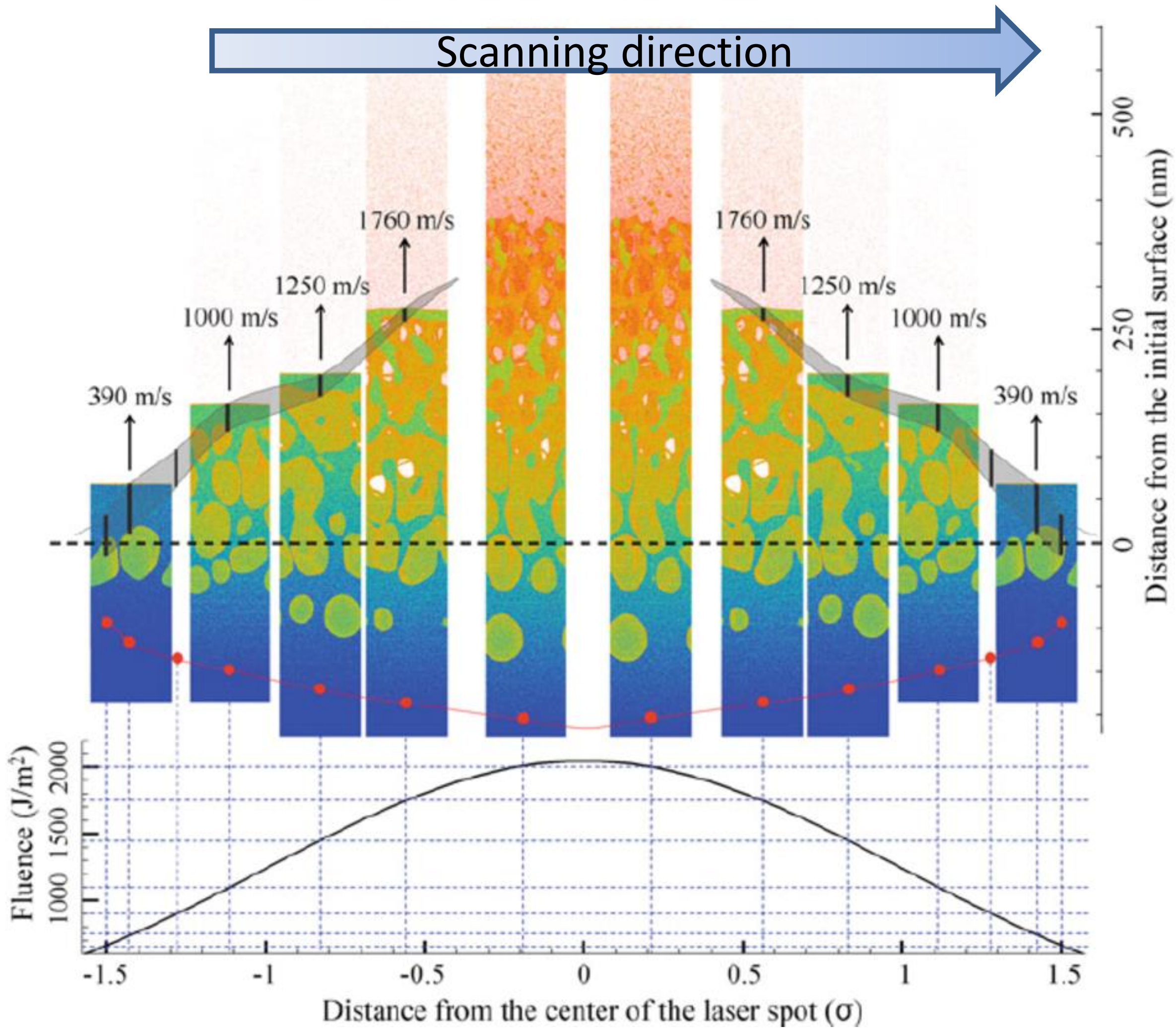


1) Long pulses are more beneficial for generation of NPs of smaller size and narrower size distribution

2) Higher fluence results in smaller NPs and size dsitribution

M. Iqbal, S.A. Khan, D.S. Ivanov, R.A. Ganeev, V.V. Kim, G.S. Boltaev, N.A. Abbasi, S. Shaju, M.E. Garcia, B. Rethfeld and A.S. Alnaser, *Appl Sur Sci* 527, 146702 (2020).

Effects of Fluence, Multi-pulse effects

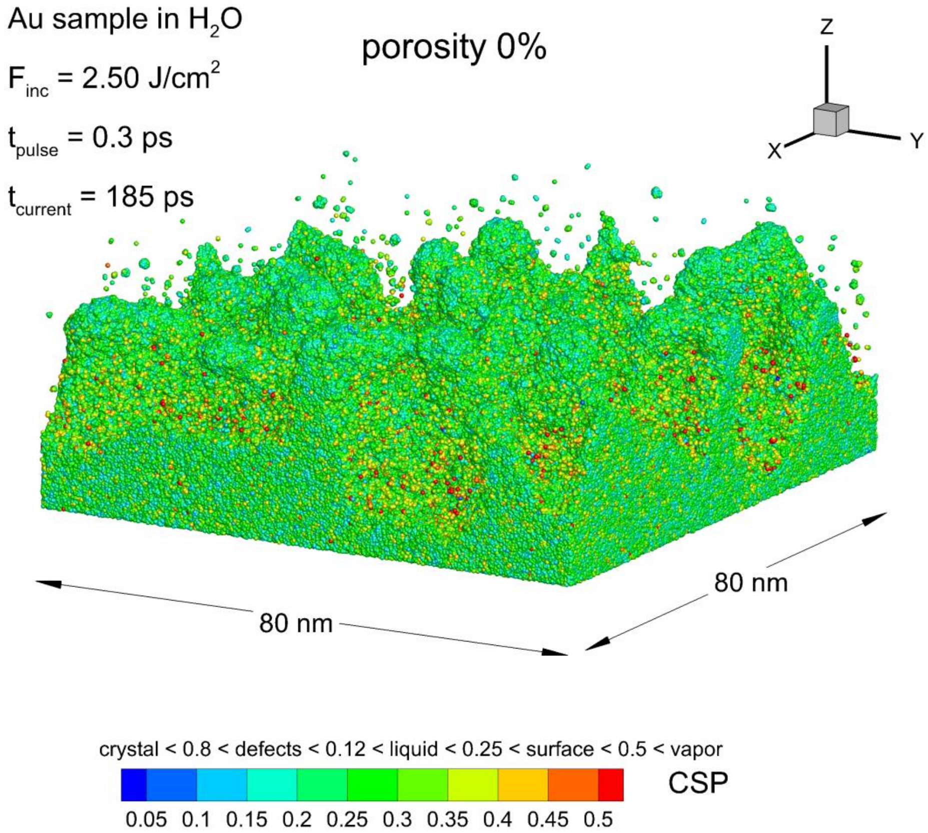


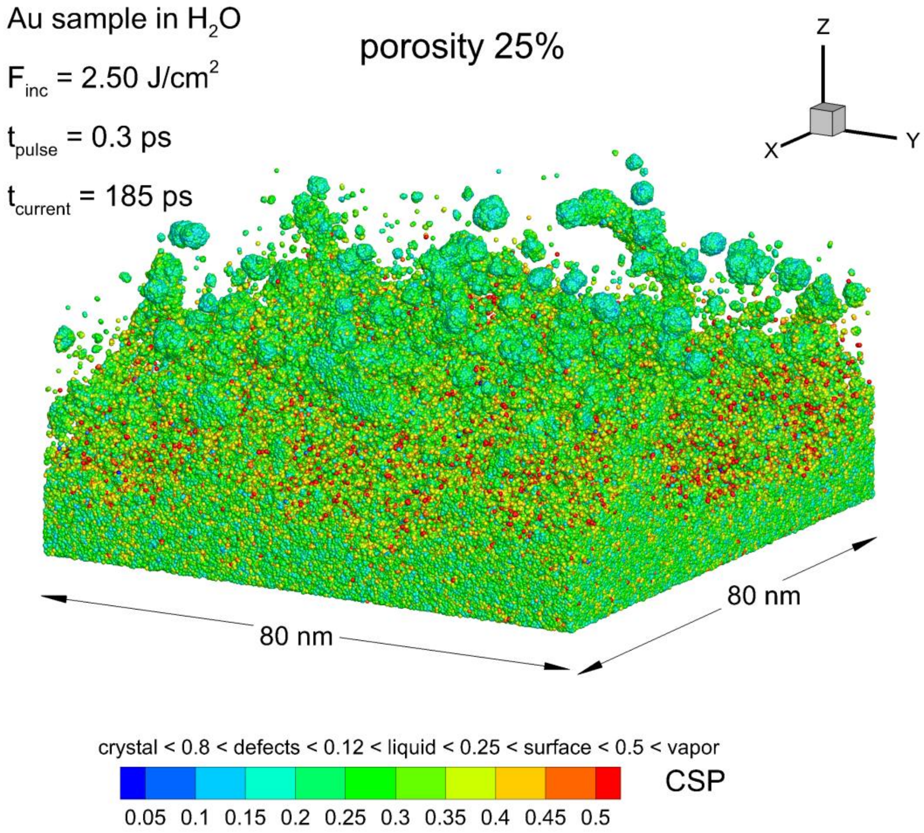
K. W. Kolasinski, M. C. Gupta, and L. V. Zhigilei, Plume and nanoparticle formation during laser ablation, *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry* (Elsevier, 2018), pp. 594-603.

TTM –MD: Effects of Sample Porosity

0 %

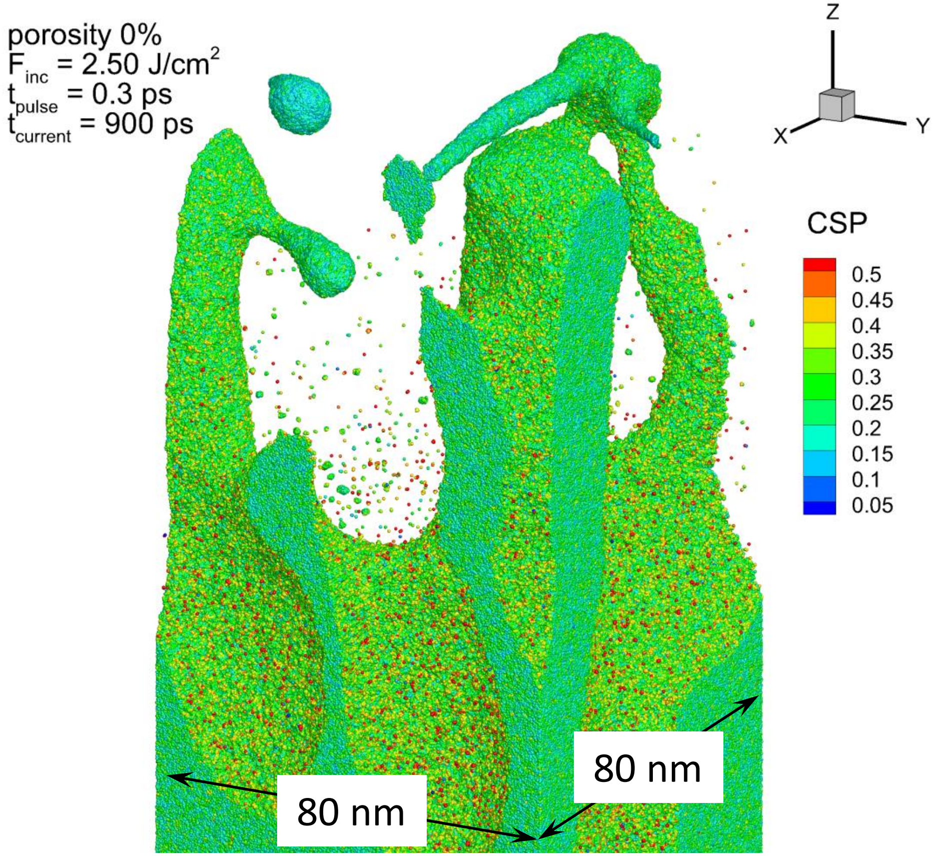
25 %



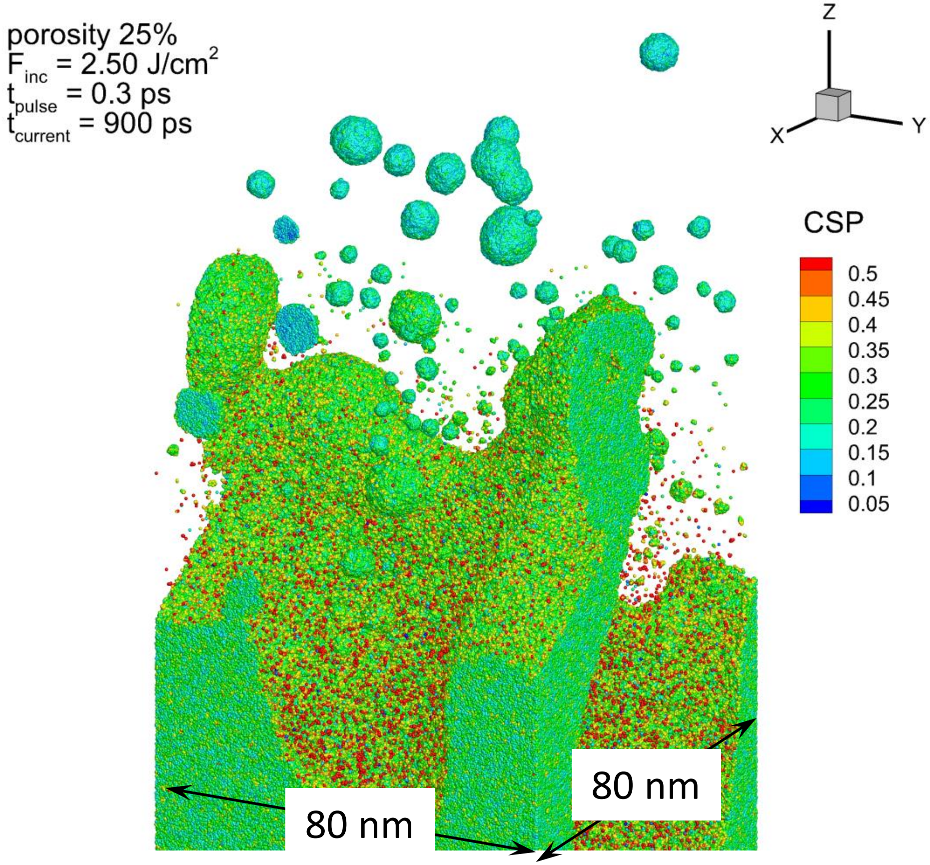


TTM –MD: Effects of Sample Porosity

0 %



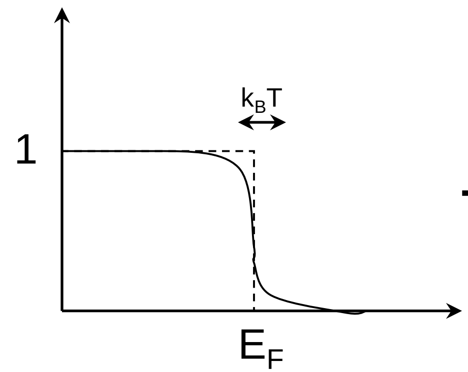
25 %

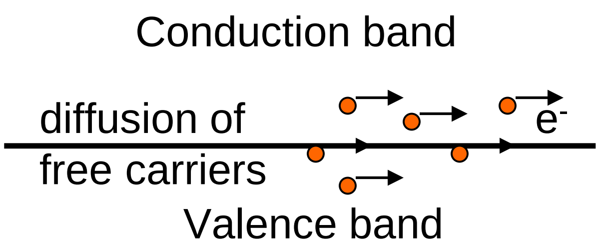


Basics of TTM-MD for Metals

$$f(E) = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$

Fermi-Dirac distribution





Based on the energy balance:

energy | transport | exchange | absorption

TTM:

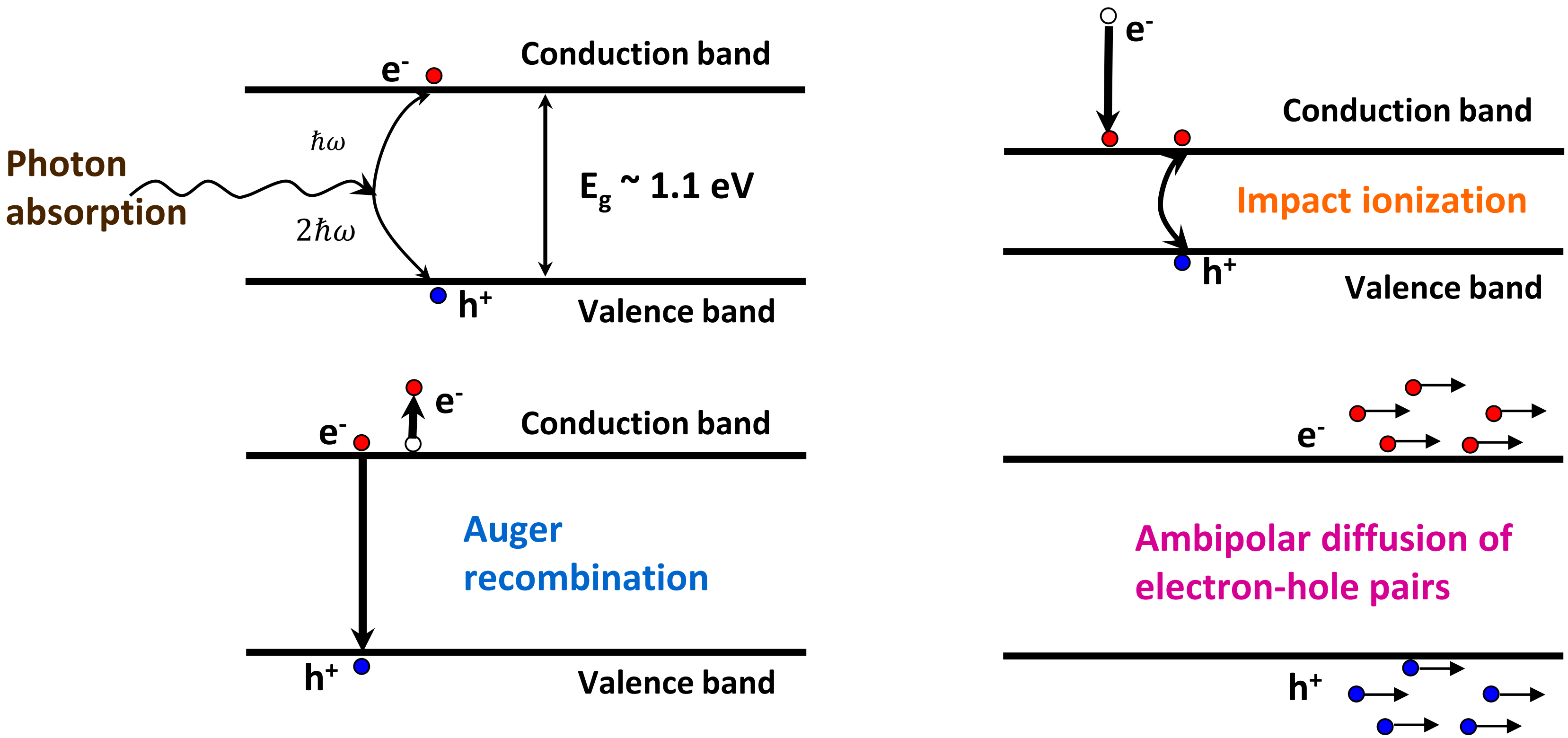
$$\begin{cases} C_e(T_e)\dfrac{\partial T_e}{\partial t} = \vec{\nabla}\cdot\left(K_e(T_e)\vec{\nabla}T_e\right) - G(T_e - T_l) + I(z,t) \\ \cancel{C_l\dfrac{\partial T_l}{\partial t} = \vec{\nabla}\cdot\left(K_l\vec{\nabla}T_l\right) + G(T_e - T_l)} \end{cases}$$

$\Rightarrow$ **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



$$\frac{\partial n}{\partial t} = Source_n(\vec{r},t) + \theta n - \gamma n^3 - div\left(\vec{J}\right)$$

- 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:

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

Energy of electrons in conduction band

Laser source

Energy flux

Energy exchange with atoms

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

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)

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

Carrier density

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

Energy of excited carriers

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

Lattice temperature

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

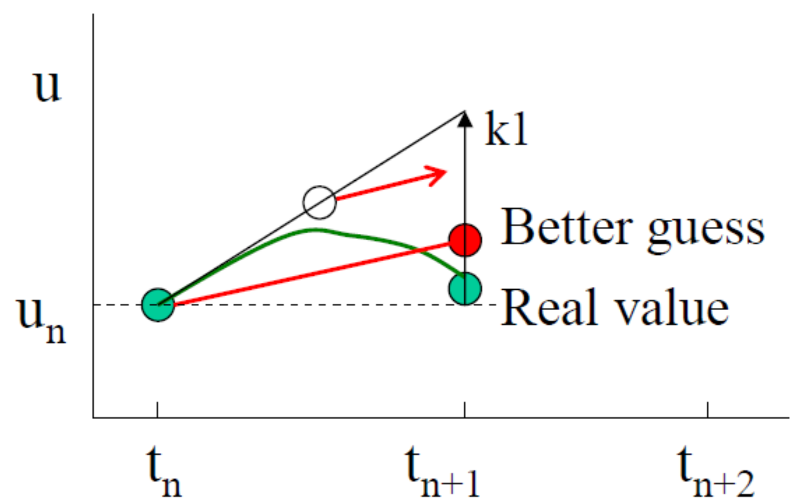
$$\boxed{I(z,t) = -I_0(1-R)\alpha_{\text{abs}} \exp(-\alpha_{\text{abs}} z) \sqrt{\frac{\sigma}{\pi}} \exp\left(-\sigma \frac{(t-t_0)^2}{\tau^2}\right)}$$

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

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

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

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



Continuum modeling for silicon

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

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

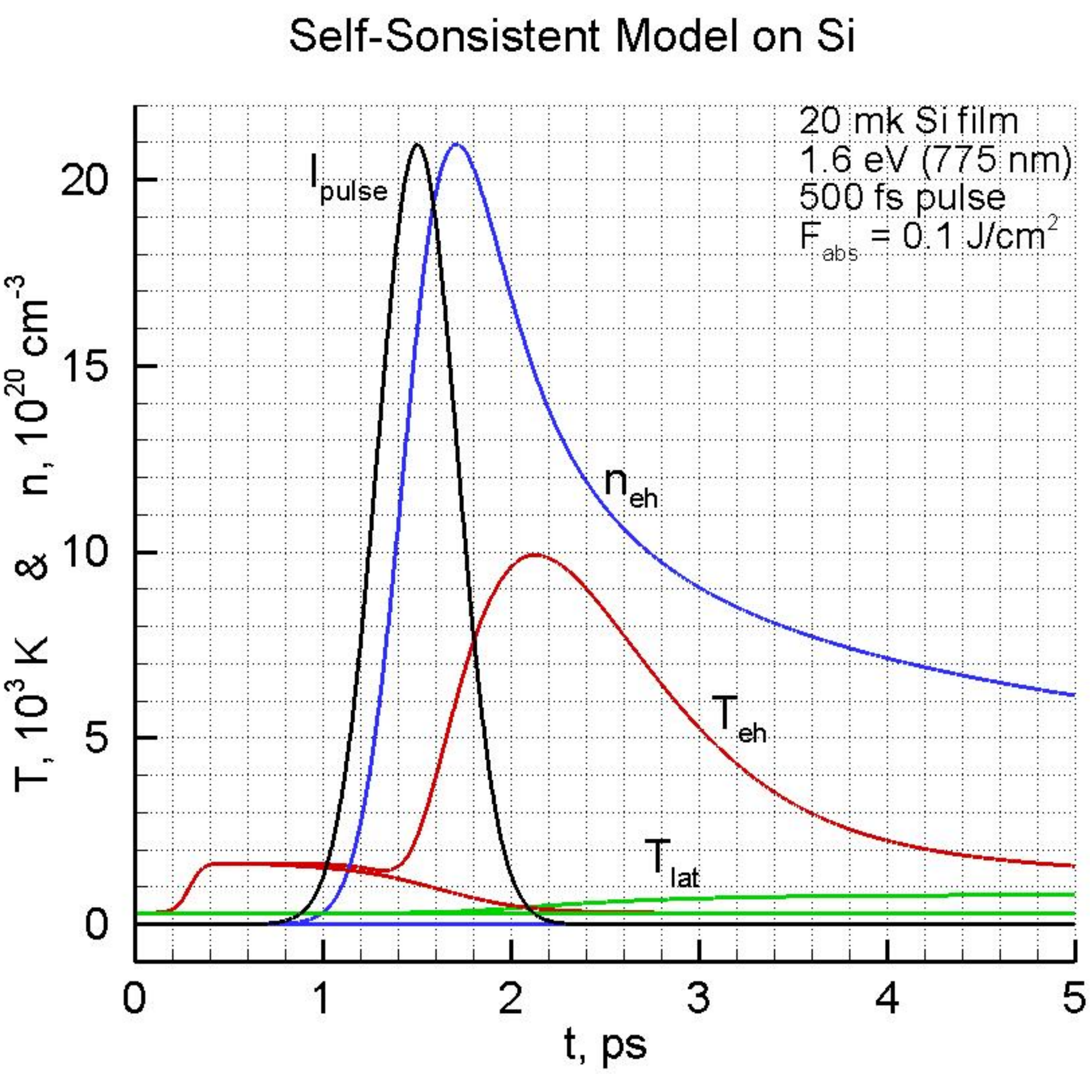
$$-\frac{Dn}{T_e}\left\{2\frac{[H_0^1(\eta_e) + H_0^1(\eta_h)]}{\left[H_{-1/2}^{1/2}(\eta_e) + H_{-1/2}^{1/2}(\eta_h)\right] - \frac{3}{2}}\right\} \vec{\nabla} T_e$$

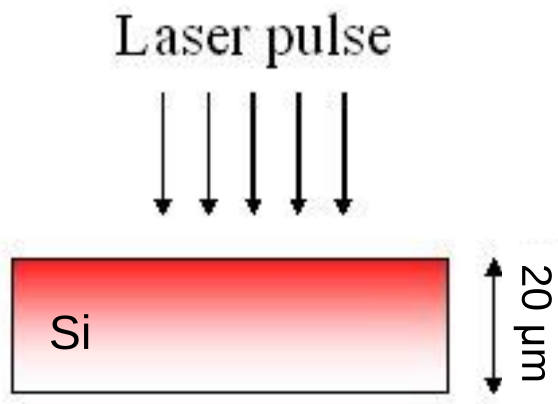
$$\overrightarrow{W} = \left\{E_g + 2k_B T_e[H_0^1(\eta_e) + H_0^1(\eta_h)]\right\}\vec{J} - (\kappa_e - \kappa_h)\vec{\nabla} T_e$$

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

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

nTTM for Si, free carriers, 500 fs laser pulse





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

V.P. Lipp, B. Rethfeld, M.E. Garcia, and D.S. Ivanov, *Phys Rev B* 90, 245306 (2014).

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)

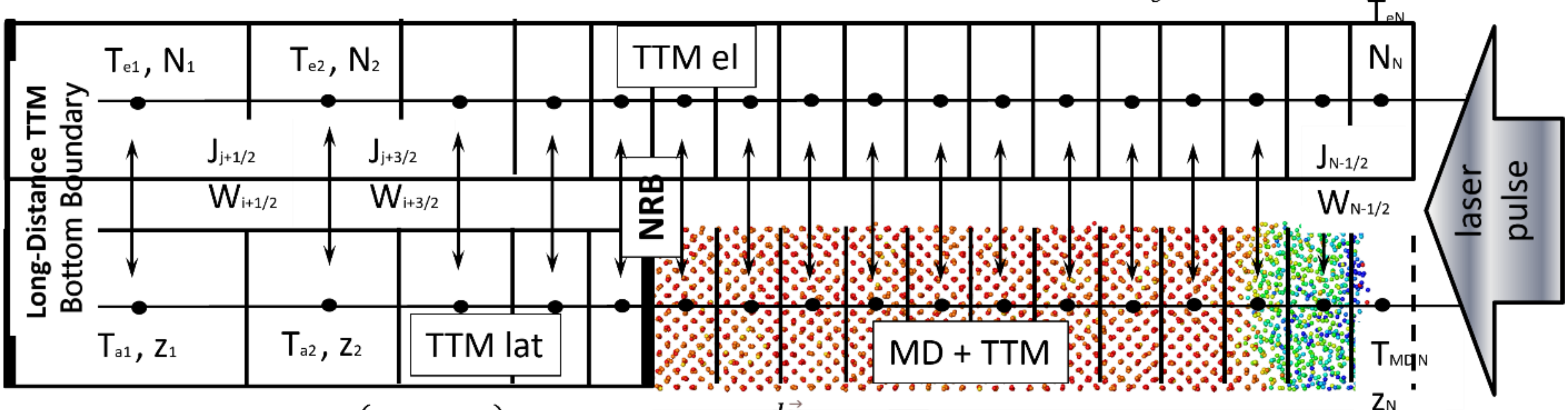
$$\begin{cases} \frac{dI(z,t)}{dz} = -\left(\alpha + \alpha_{FCA}\left(\varepsilon(N_e)\right)\right) I(z,t) - \beta I^2(z,t) \\ \frac{\partial N_e}{\partial t} = \frac{\alpha I(z,t)}{h\nu} + \frac{\beta I^2(z,t)}{2h\nu} + \delta N_e - \gamma N_e^3 - \nabla \cdot \vec{J}(N_e, T_e, E_g) \\ \frac{\partial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

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

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

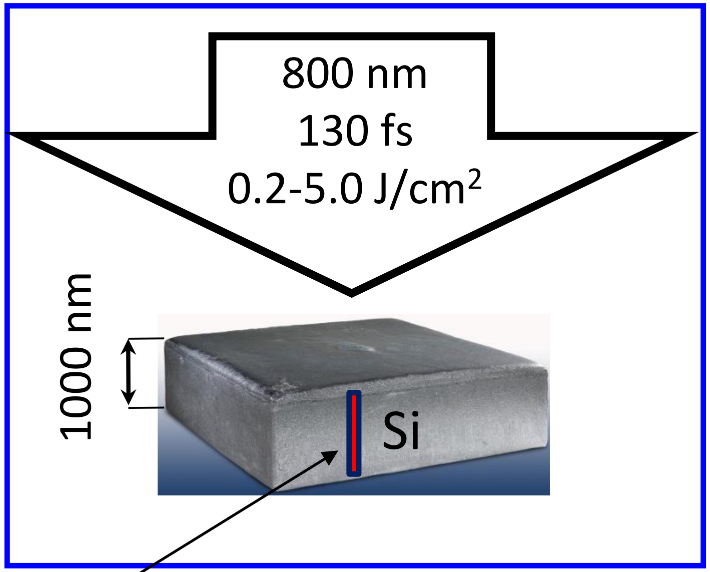
$$\frac{\partial U_e(N_e,T_e,E_g)}{\partial t} = \Big(\alpha + \alpha_{FCA}\big(\varepsilon(N_e)\big)\Big) I(z,t) + \beta I^2(z,t) - \nabla\cdot\vec{W}\big(N_e,T_e,E_g\big) - \frac{C_{e-h}\big(N_e,T_e,E_g\big)}{\tau_e}(T_e - T_l)$$



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

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

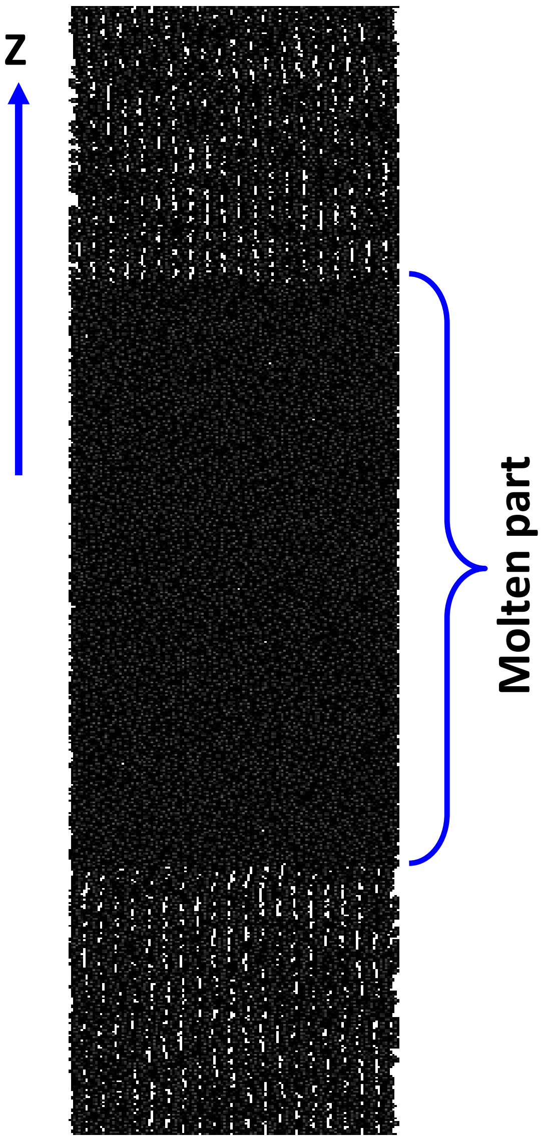
Results of MD-nTTM
Laser melting

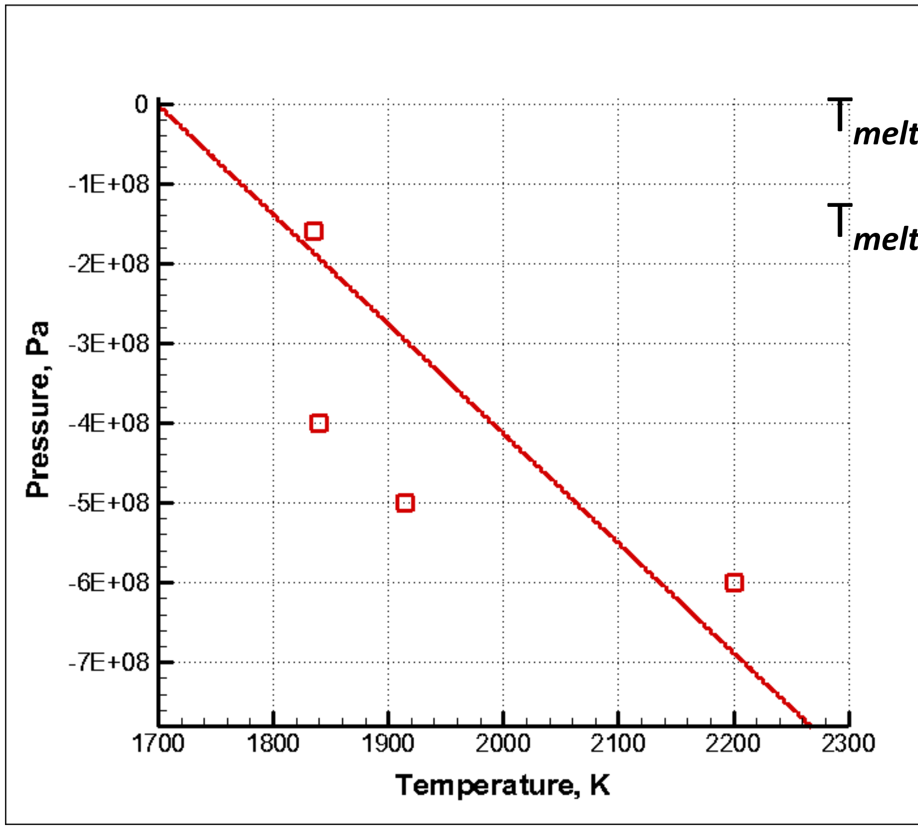


Computational cell

Results of atomistic modeling for silicon

Melting temperature calculation for Si





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

$T_{melting\ exp}$ = 1683 K

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

Linear expansion coefficient: $\alpha = 3\times10^{-6}$ 1/K << α_{metals}

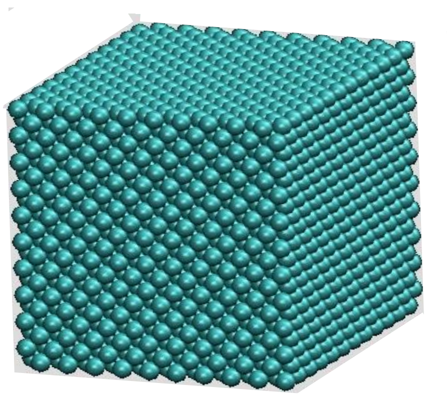
Slope of the melting curve: $[\mathrm{d}P/\mathrm{d}T]_T < 0$

Results of atomistic modeling for silicon

Calculation of bulk modulus

12x12x12 atom layers

T = 300 K

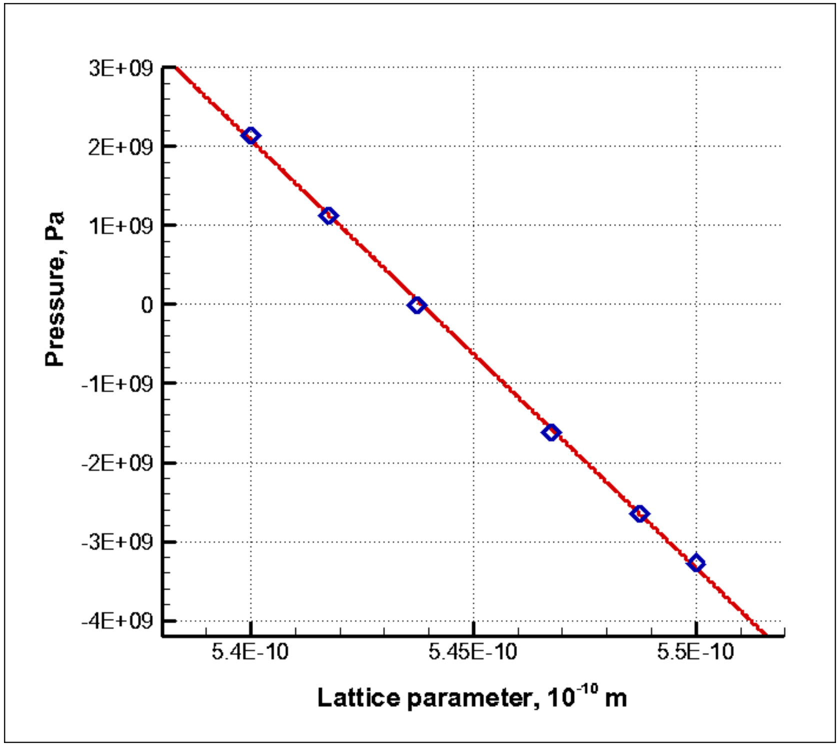


$$B = -\left[V\frac{dP}{dV}\right]_{V=V_0}$$

a_0 = 5.44 Å

$B_{s\text{-}w}$ = 97.7 GPa

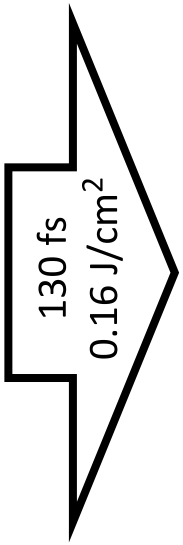
B_{exp} = 99 GPa

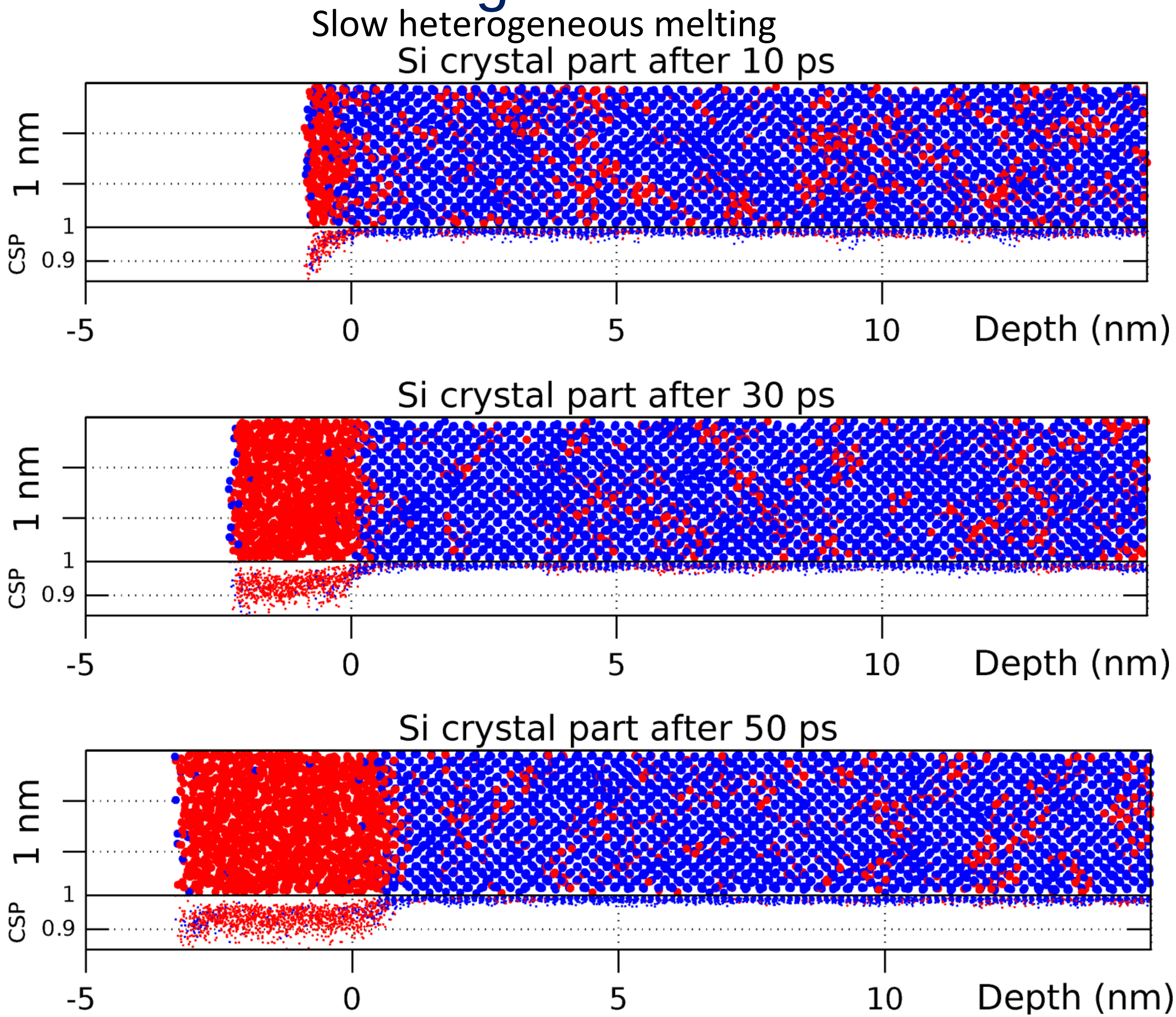


Good agreement with experiment – correct resistance of uniform compression

Phys. Rev. B 46, 2250–2279 (1992)

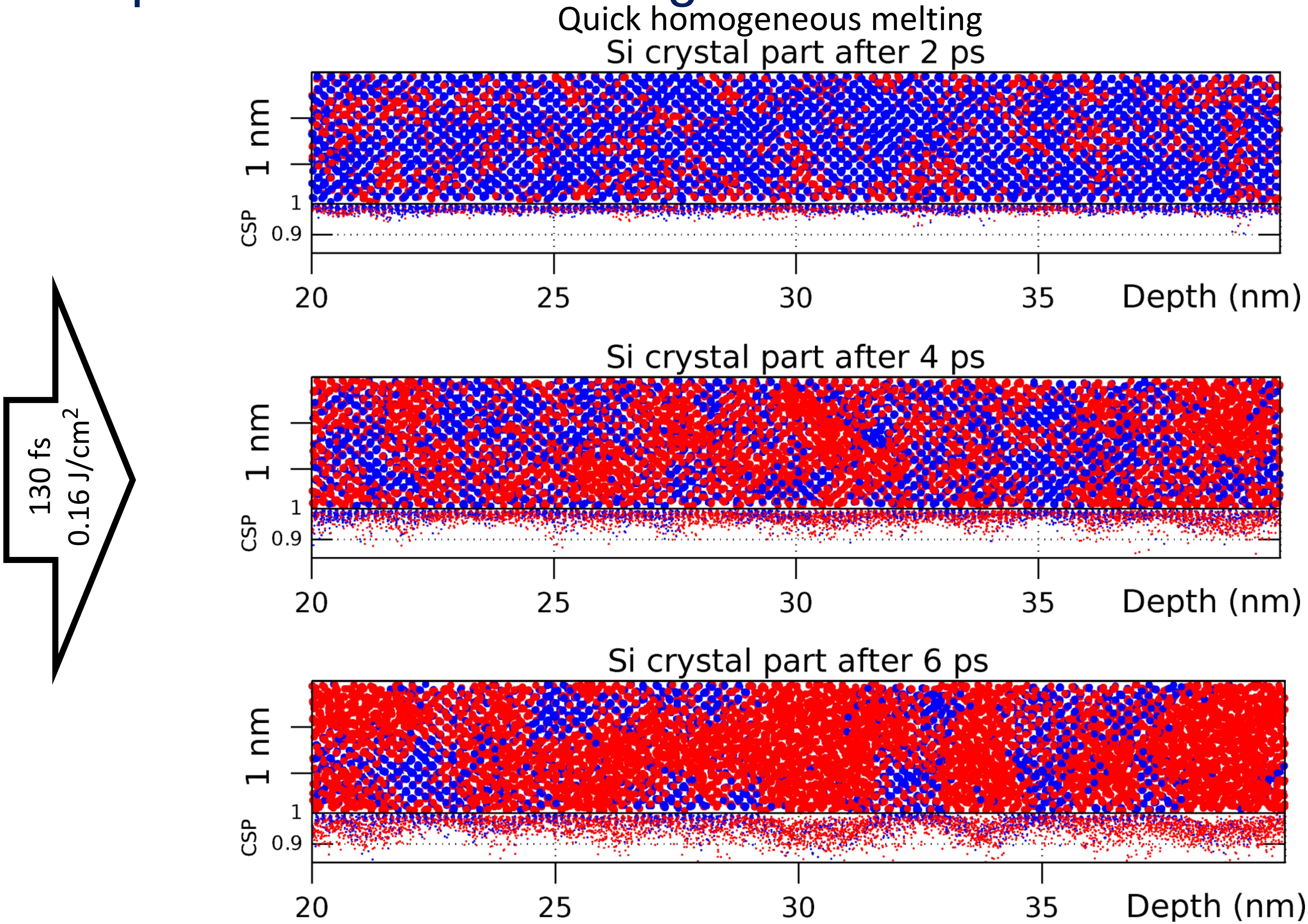
Snapshots of laser melting absorbed fluence 0.16 J/m^2





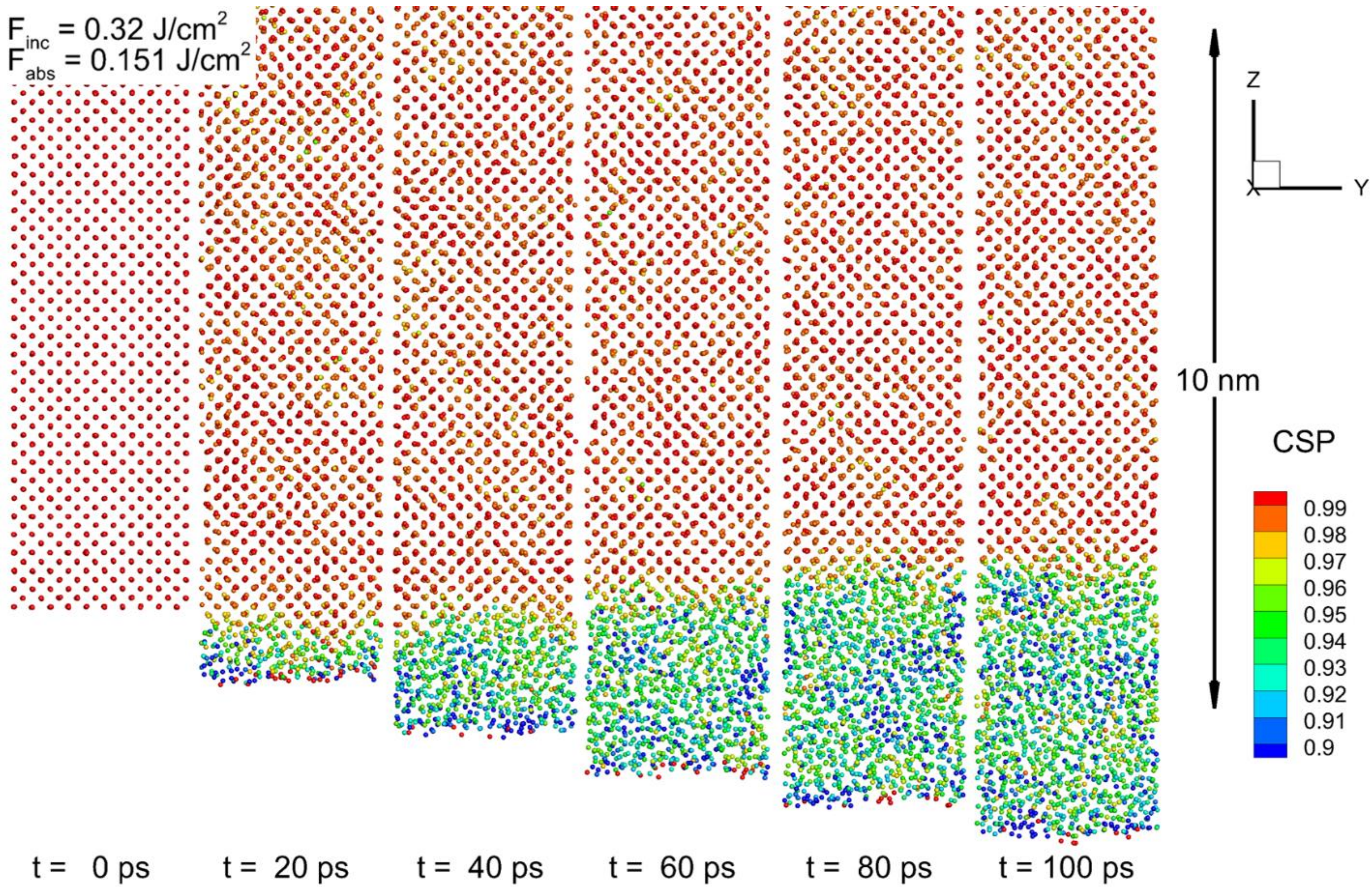
V.P. Lipp, B. Rethfeld, M.E. Garcia, and D.S. Ivanov, "Atomistic-Continuum Modeling of Short Laser Pulse Melting of Si Targets", *Physical Review B* **90**, 245306 (2014).

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

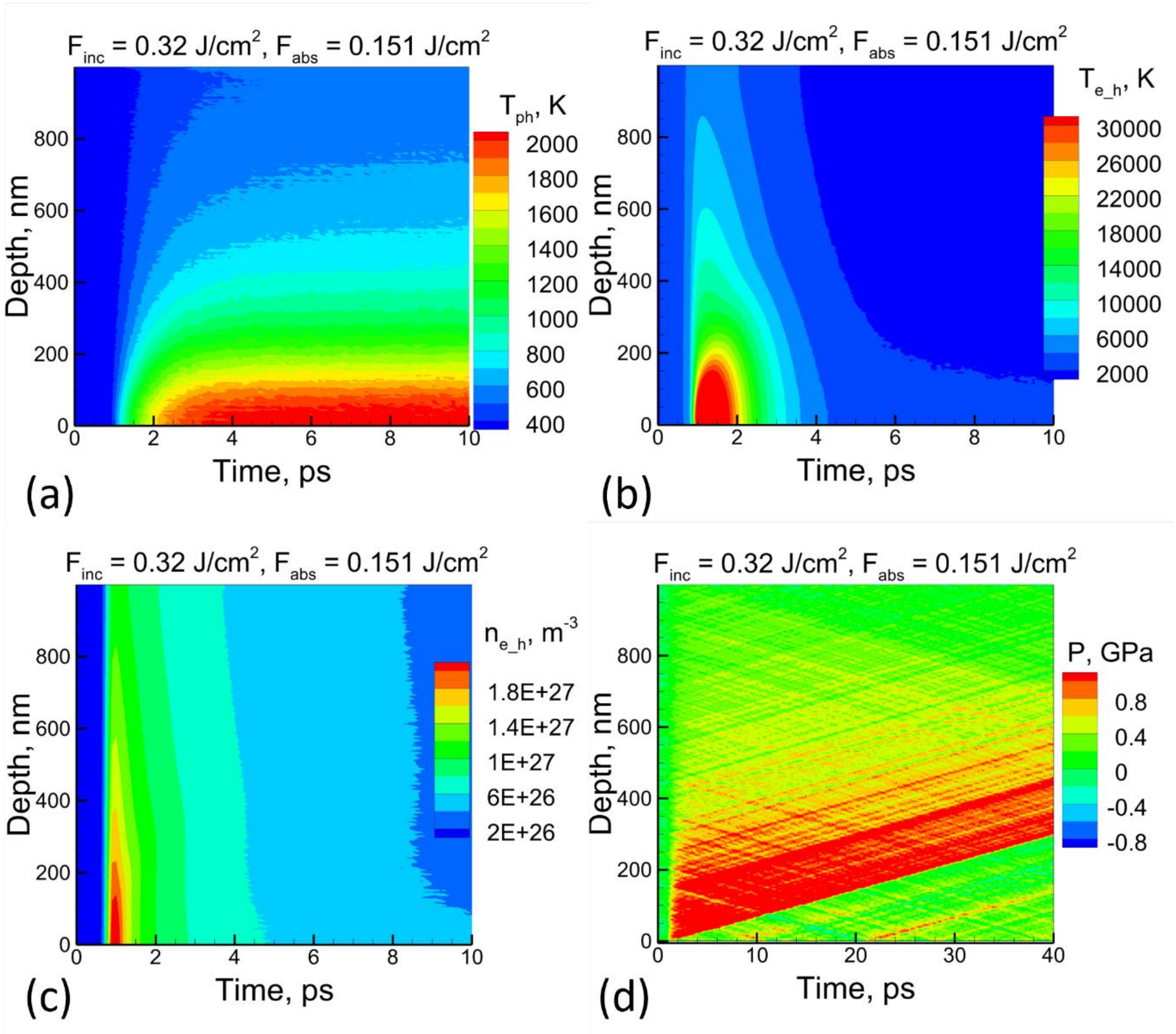


V.P. Lipp, B. Rethfeld, M.E. Garcia, and D.S. Ivanov, "Atomistic-Continuum Modeling of Short Laser Pulse Melting of Si Targets", *Physical Review B* **90**, 245306 (2014).

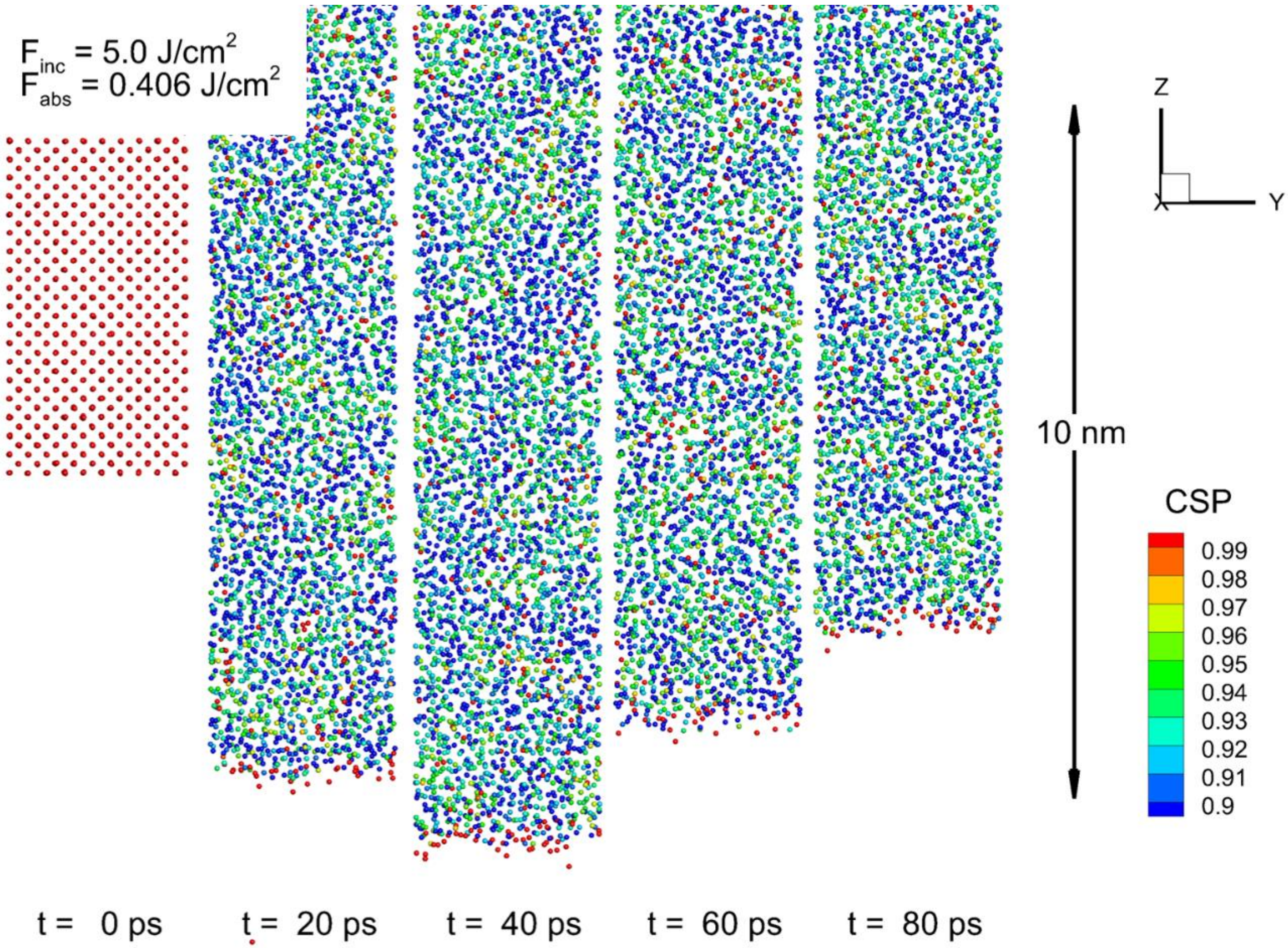
1000 nm Si target after 270fs at 0.32 J/cm2 at 800nm



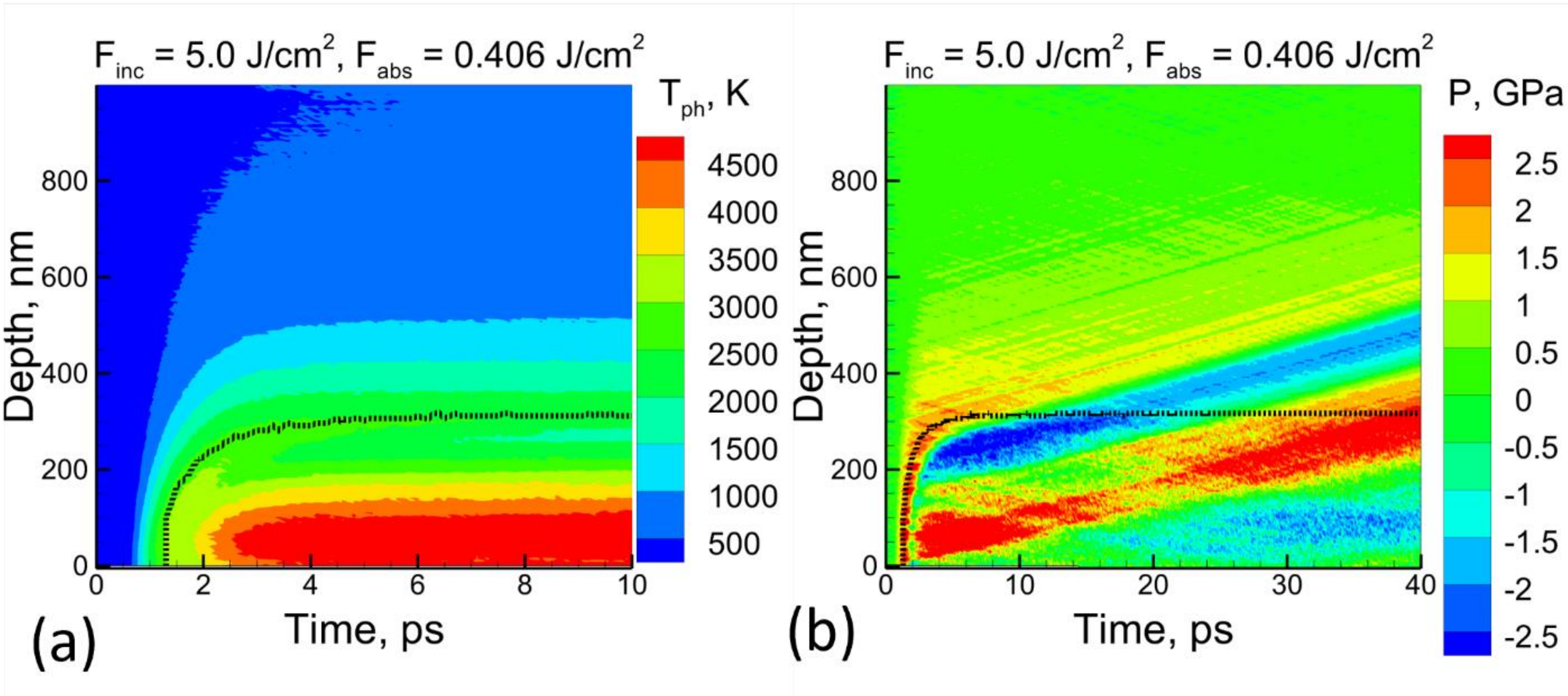
1000 nm Si target after 270fs at 0.32 J/cm2 at 800nm



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

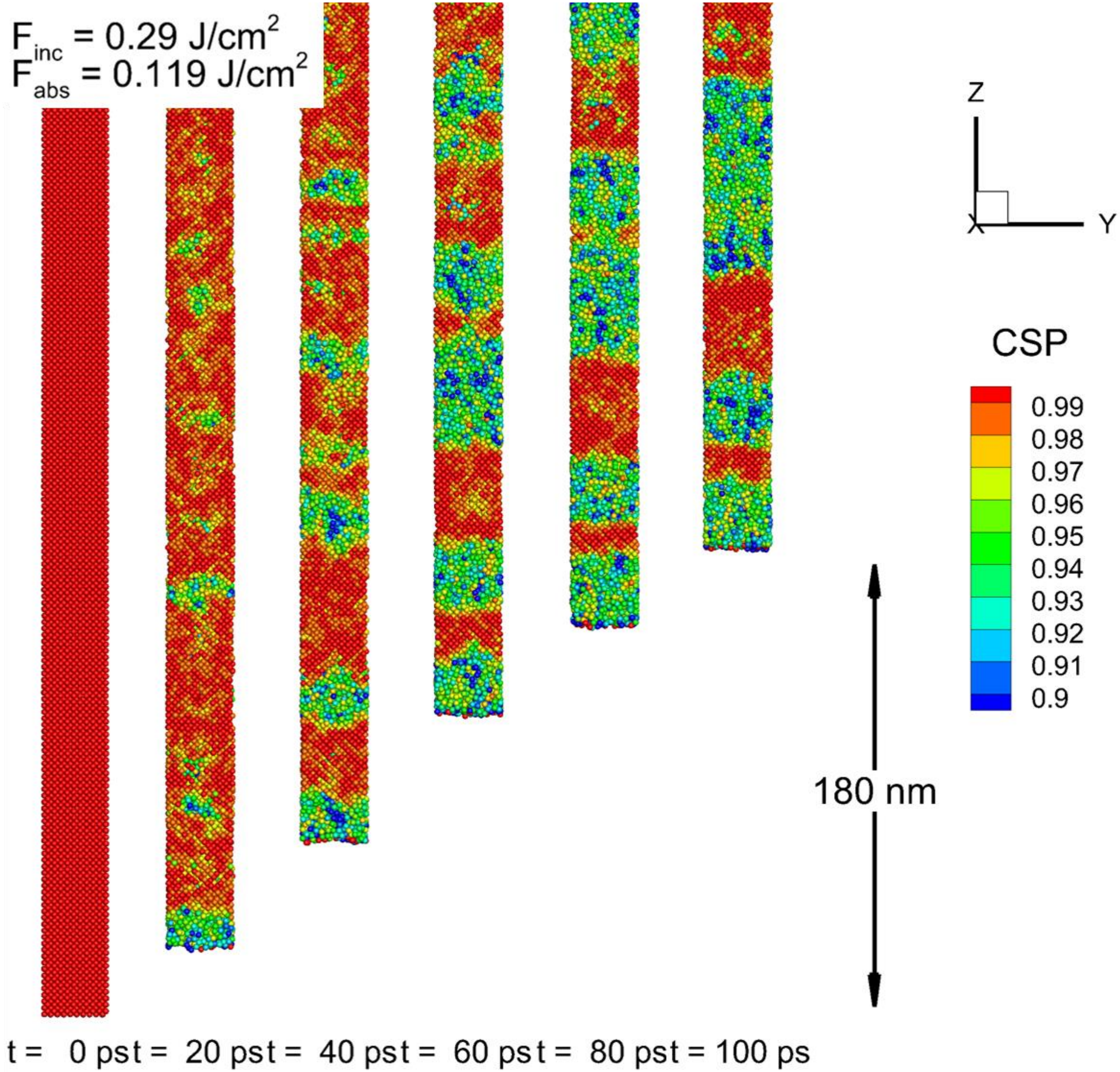
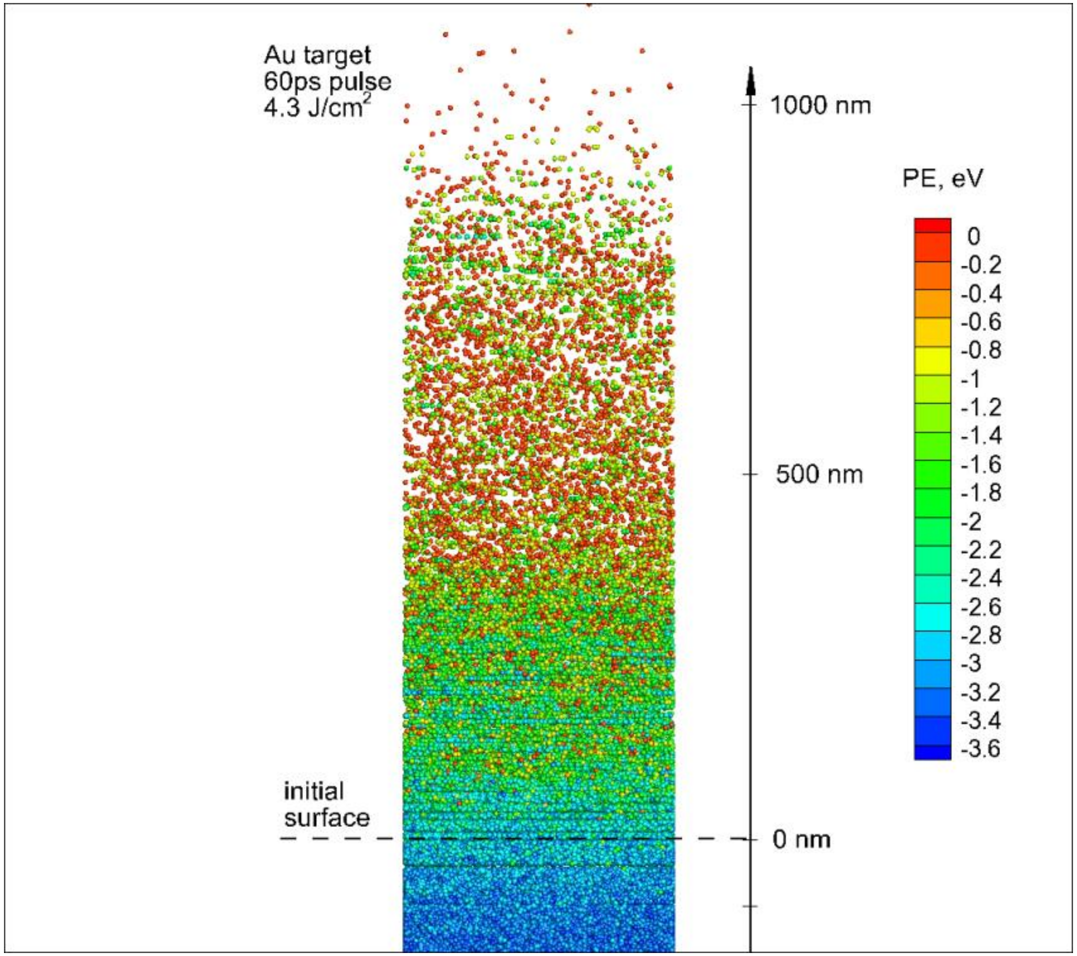


Photo-thermal vs. photo-mechanical damage for Si



Regime of internal stresses confinement Is absent

No Spallation

Explosive Boiling Only

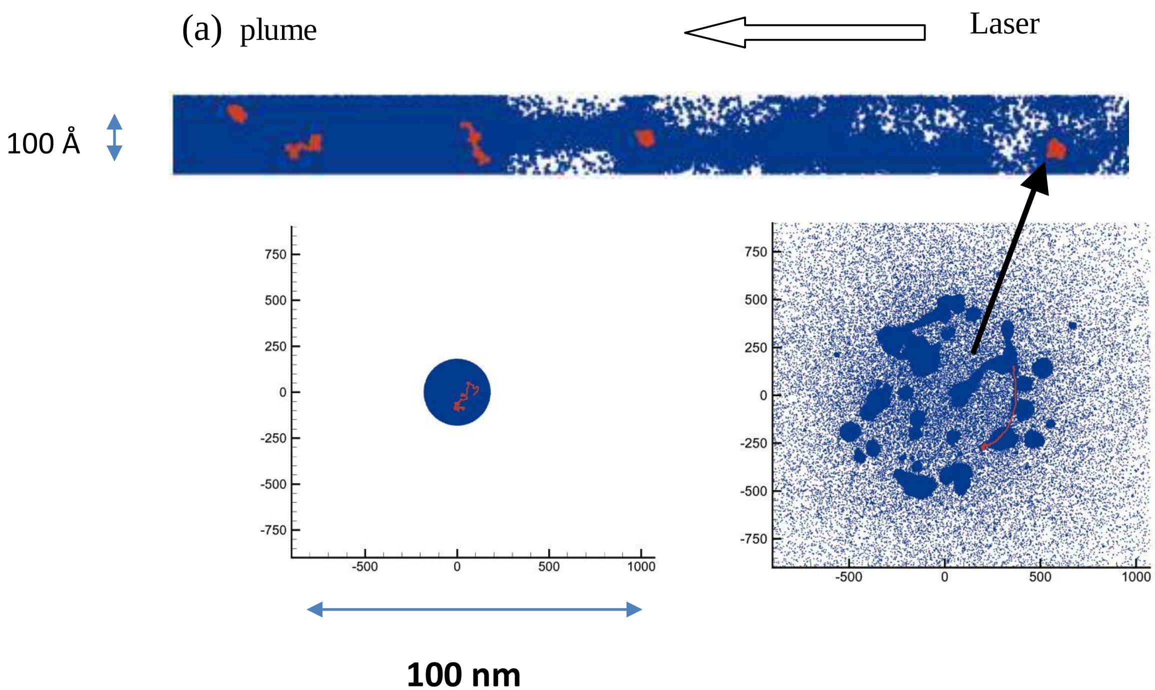
Short Pulse is good for NPs generation

satisfied

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

Laser Interactions with Nanoparticles

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



t = 300 ps after the beginning of the laser pulse

τ = 15 ps

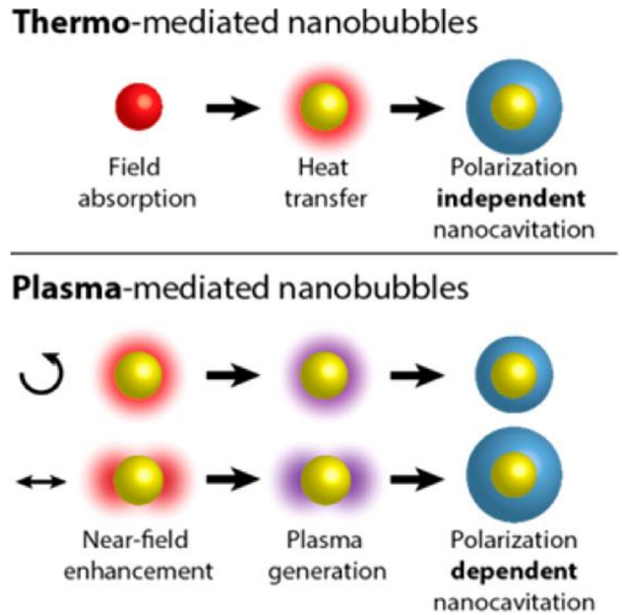
e=0.6 eV per molecule

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

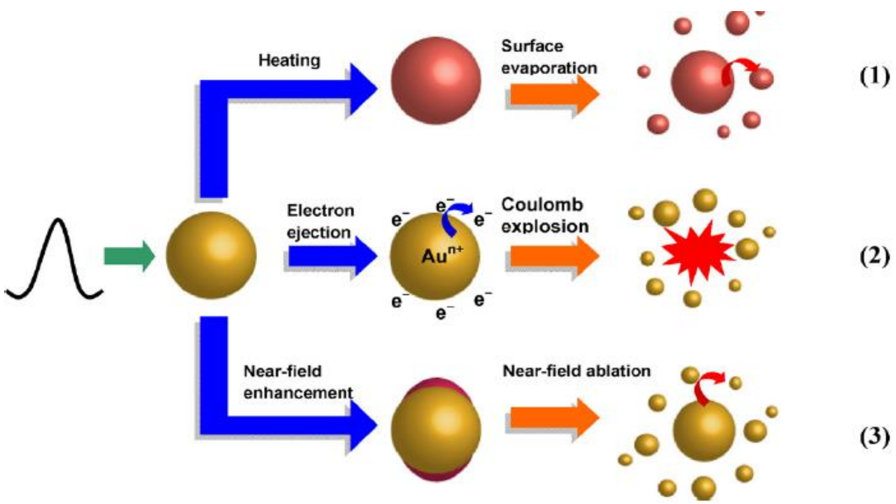
Ultra-short Laser Interactions with Nanoparticles

Laser pulse

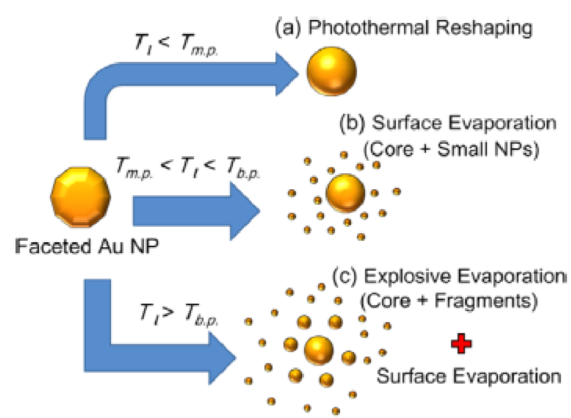
- Propagation, absorption, local field enhancement
- Local ionization and heating of the matter/liquid near NP **plasma-mediated nanobubbles**
- NP heating, heat transfer to the ambient medium **thermo-mediated nanobubbles**
- NP heating, melting, reshaping, sintering, evaporation
- Electron ejection, injection in the ambient
- NP fragmentation



Lachaine et al.Photonics (2013)



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



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

Ultr-short Laser Interactions with Nanoparticles

« Classical » Multi-Physics

Maxwell equations

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

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

Polarization current

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

Charge conservation, incompressible Fermi flow

Photo-ionization Avalanche

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

Heat energy transfer

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

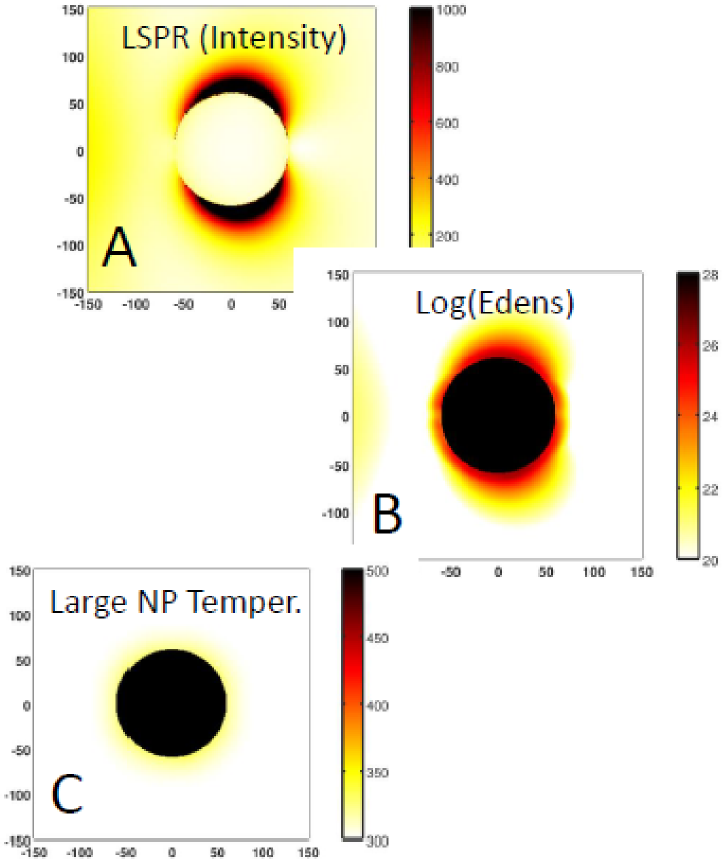
Nanoparticle

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

Medium

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

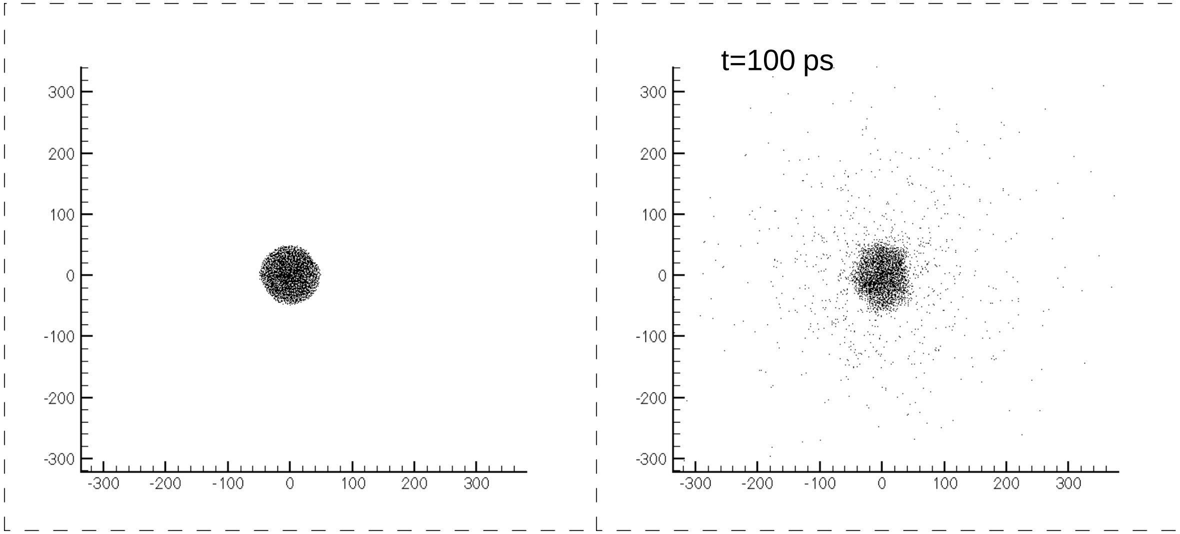
C_e, C_{NP}, C_m - heat capacities; k_e, k_{NP}, k_m - thermal conductivities;
T_e, T_{NP}, T_m - temperatures; $\vec{J} \cdot \vec{E}$ - Joule heating source (absorption);
γ_{ei}, h - energy transfer rates; ρ_{NP}, ρ_m - ion densities.



Advantages: rather easy equations, estimations of temperatures
Limitations: hard to correctly account for electron excitation, ejection/injection

Laser Interaction with NPs: MD simulations

R=50 Å, absorbed energy e=0.6 eV/mol

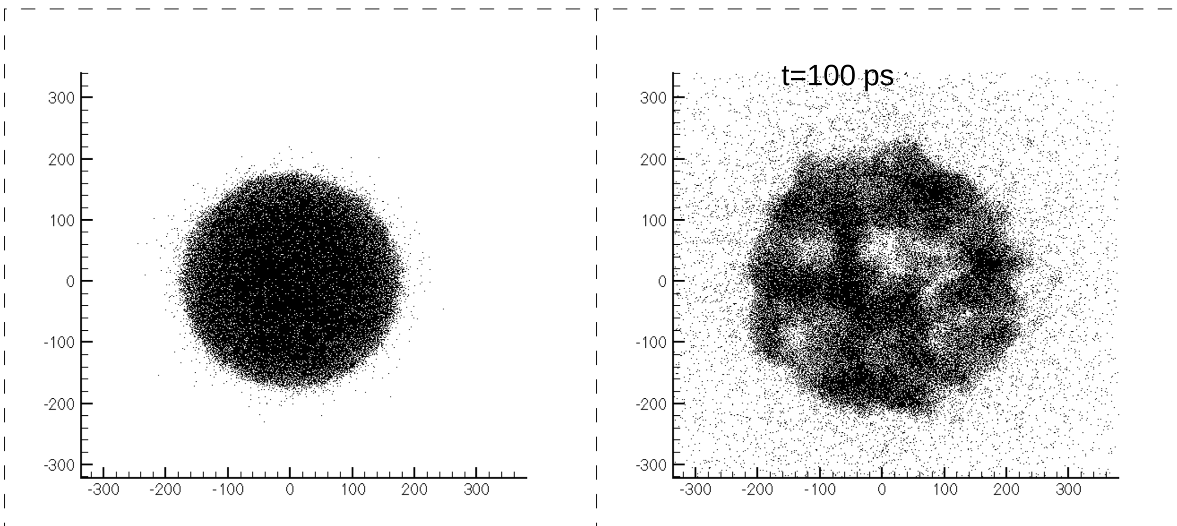


Smaller NPs

Evaporation

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

R=150 Å, absorbed energy e=0.6 eV/mol.

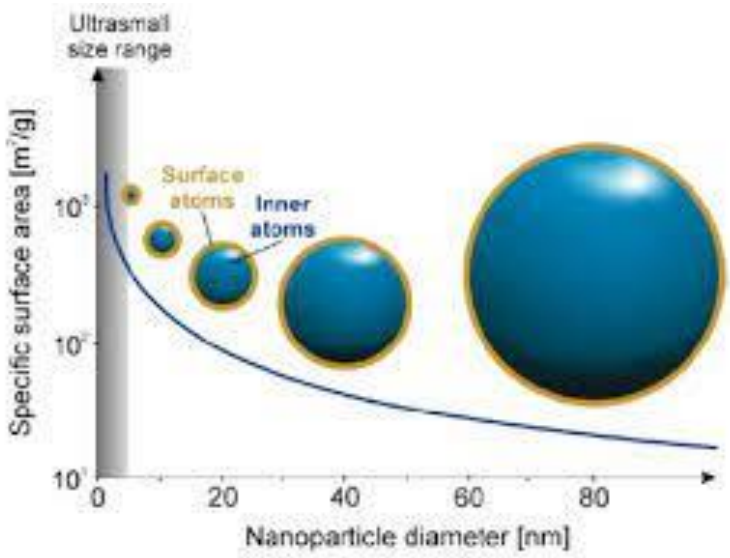


Larger NPs

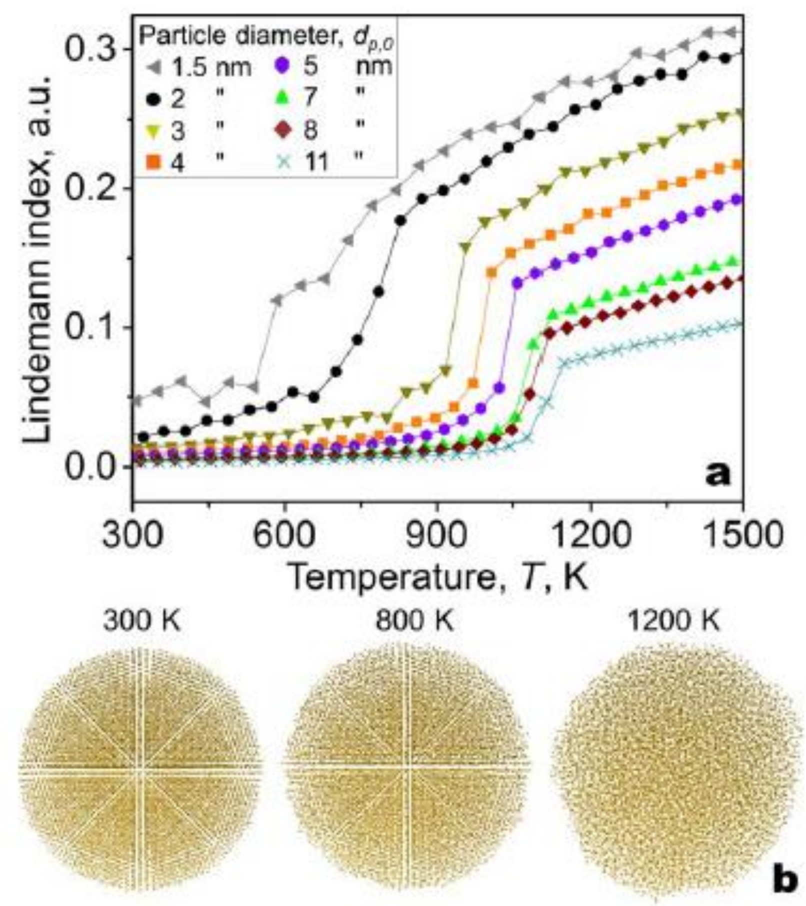
Fragmentation due to thermo-mechanical effects

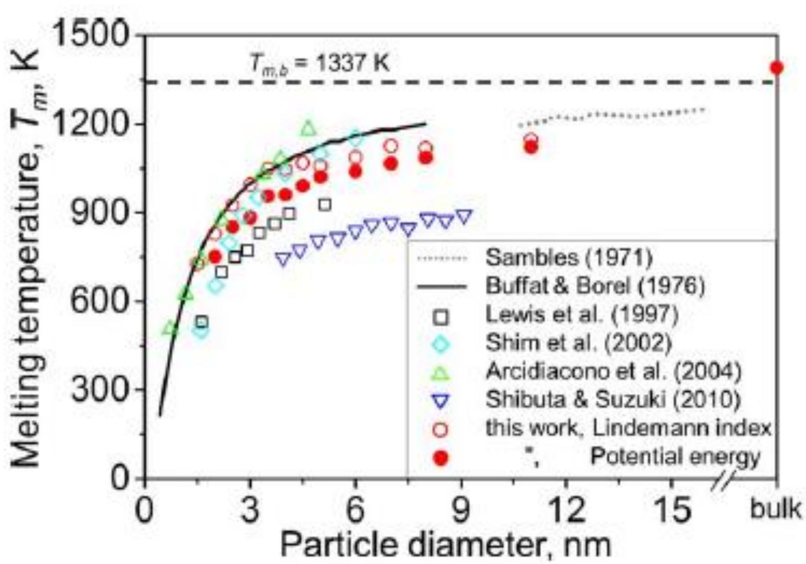
NP's Heating and Melting : Size Effects

Melting and structural transformations: role of NP's sizes



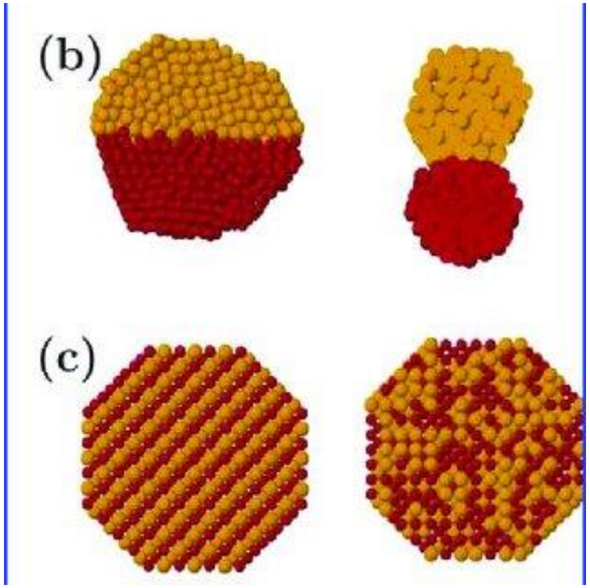
K. Zarschler et al. Nanomed-Nanotechnol 12, 1663-1701 (2016).

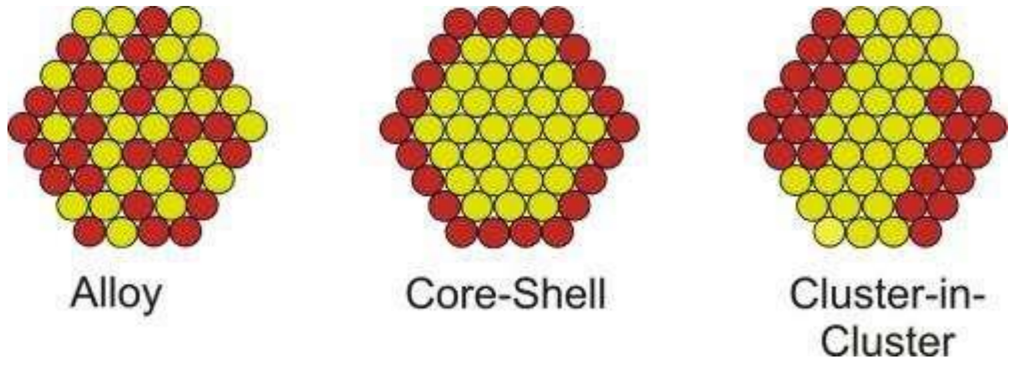




E. Goudeli et al., AIChE 2015

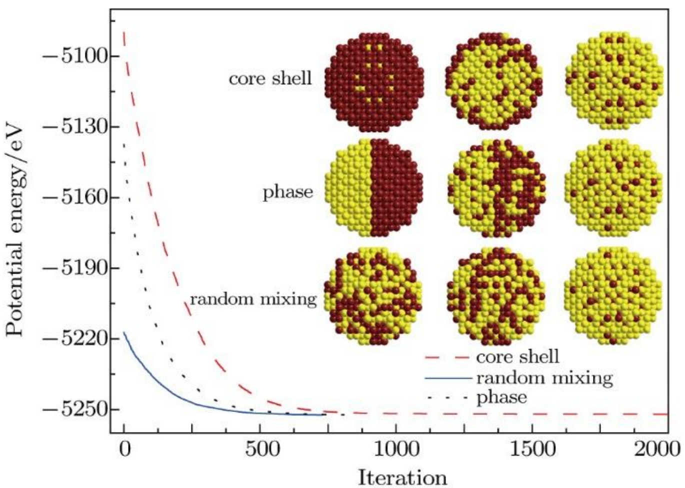
Nanoparticle Alloys and Aggregates



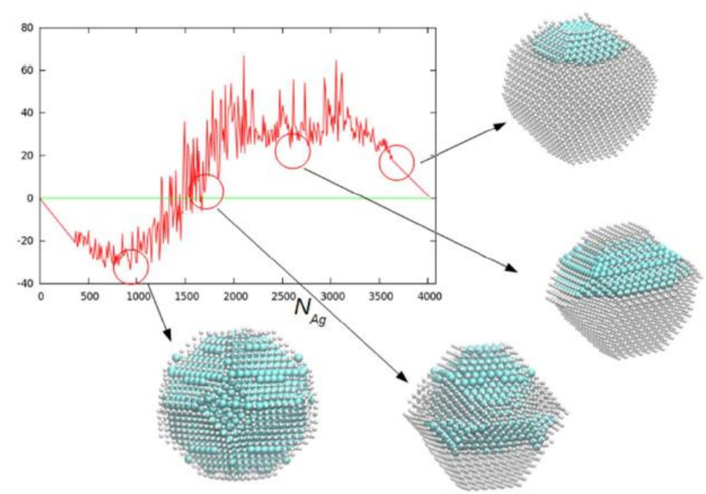


Mixing Energy

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

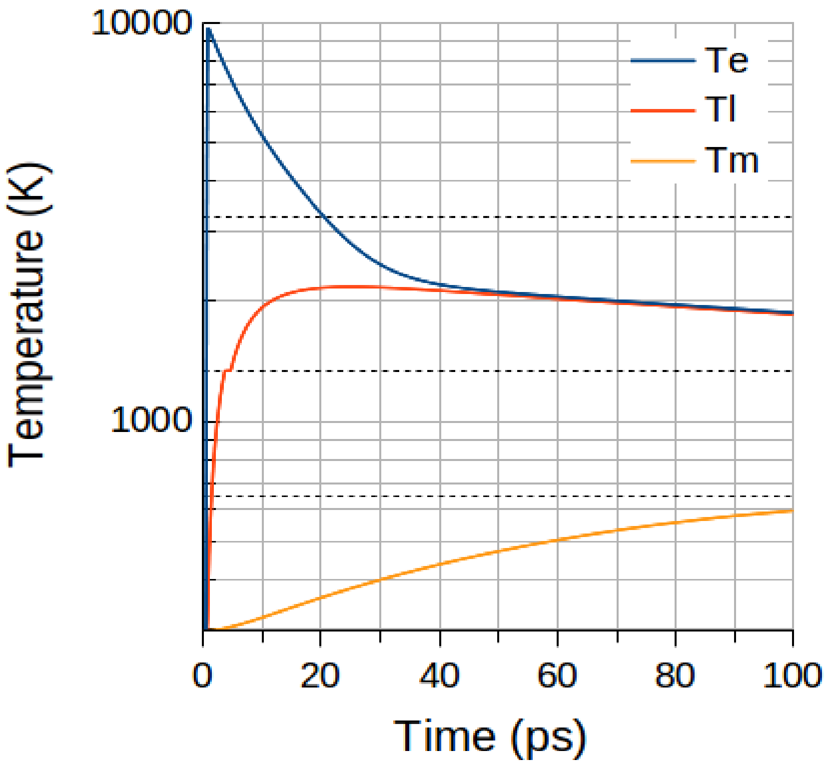


R. Ferrando et al. Chem. Rev. 108(3), 2006



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/cm^2**
Gaussian time profile

T_e rises instantaneously

The energy deposited into the electronic system is transferred to the lattice
=> T_l rises

Particle cools through heat exchange to the surrounding water

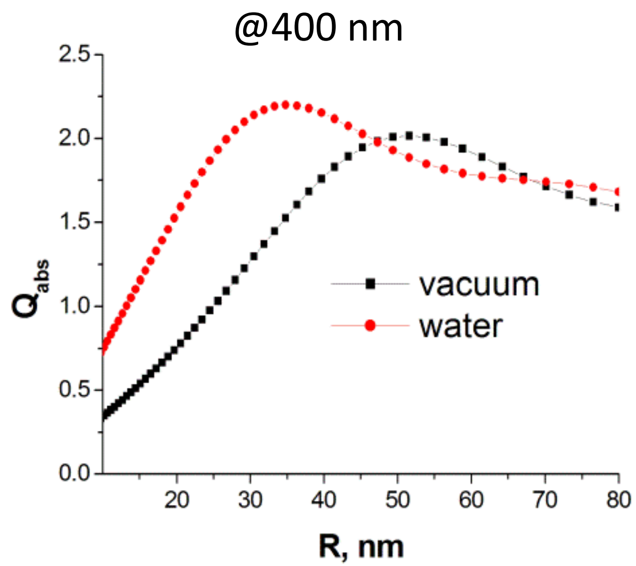
Werner et al. J. Phys. Chem. C, 2011, 115 (17), 8503

Laser Energy Absorption vs NP's size

Absorption coefficient / efficiency

(beyond SPR for gold)

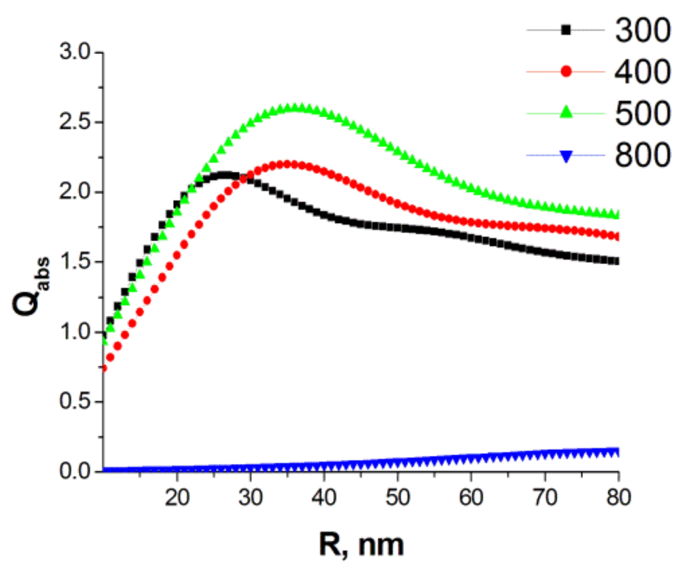
(a)



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

- **peak in absorption at** R=R*~ 30 nm for Au NP in water

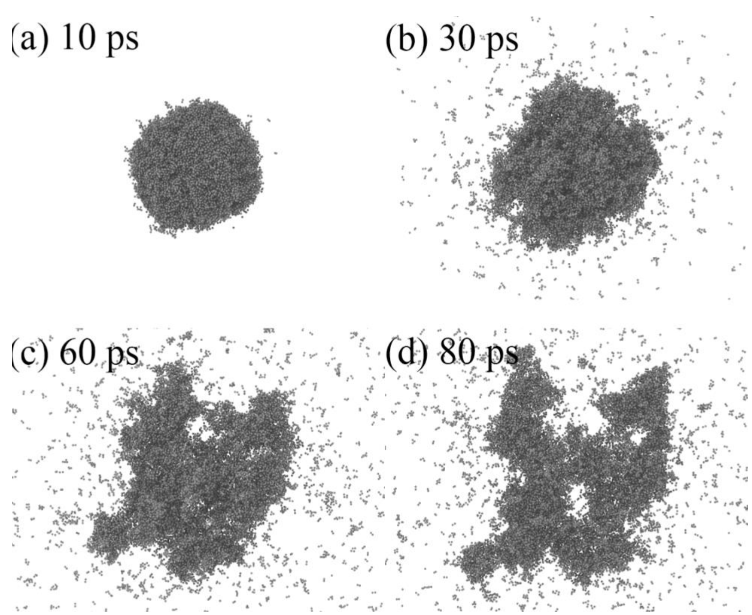
(b)

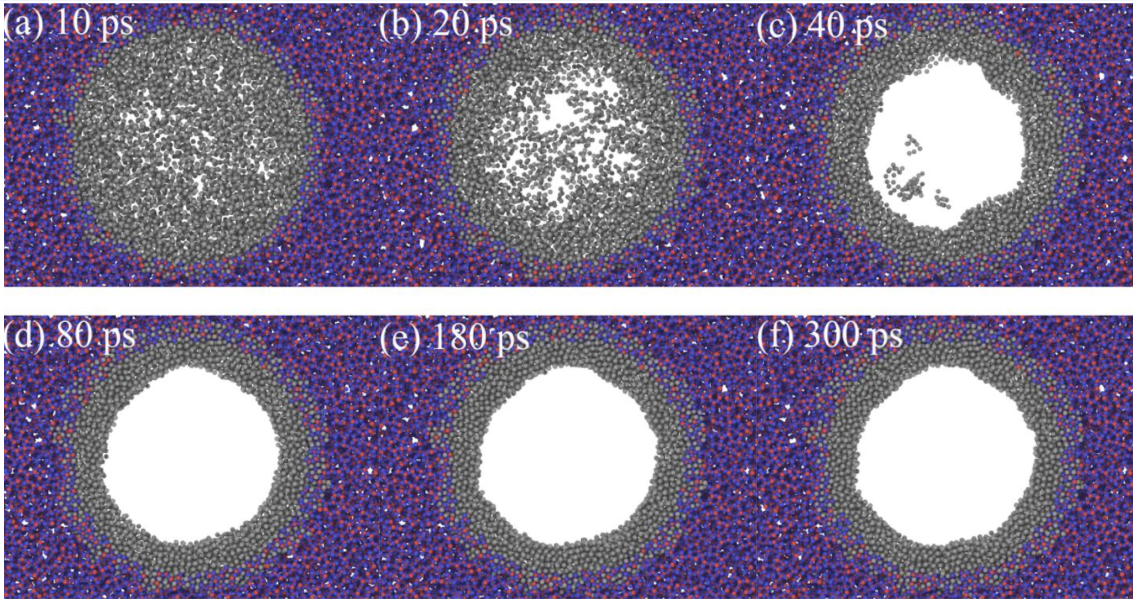


Gold NPs in water for different wavelength @300-800nm

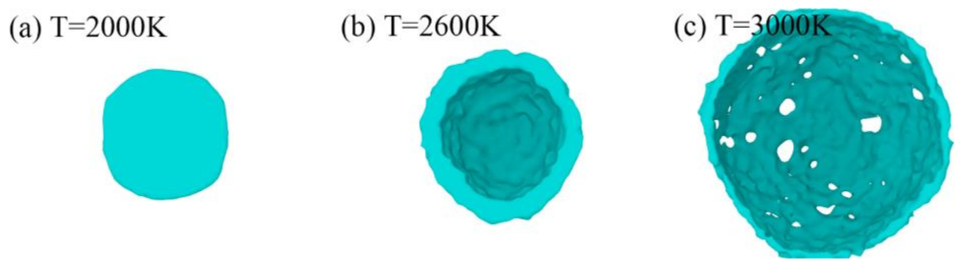
- peak position is shifted to larger R=R* **if wavelength rises**

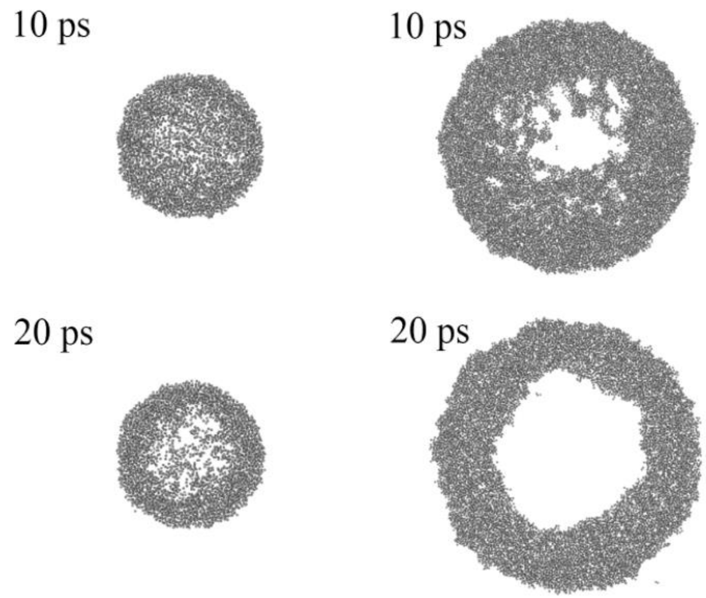
NP’s evolution upon laser pulse absorption





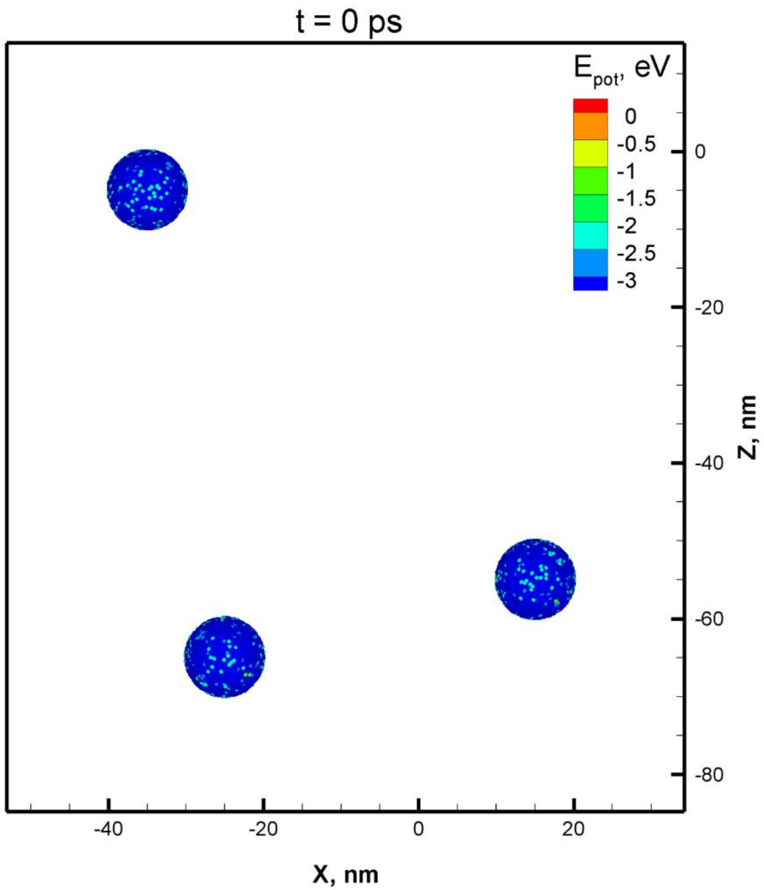
Jiang et al., Computational Materials Science 196 (2021) 110545



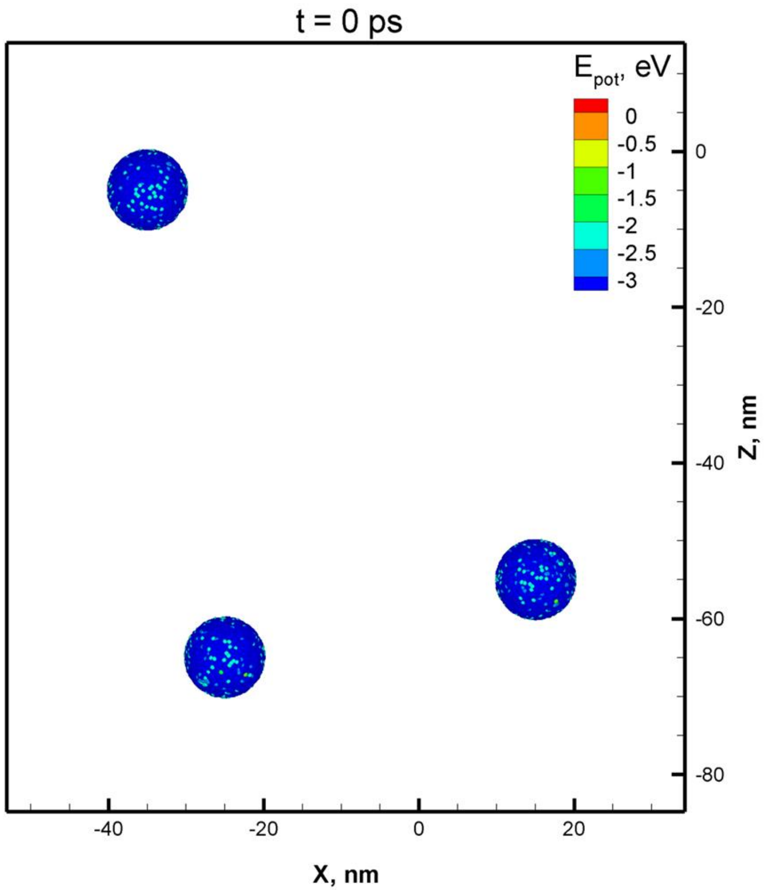


10 nm NP, the incident fluence 200 J/m2

solid

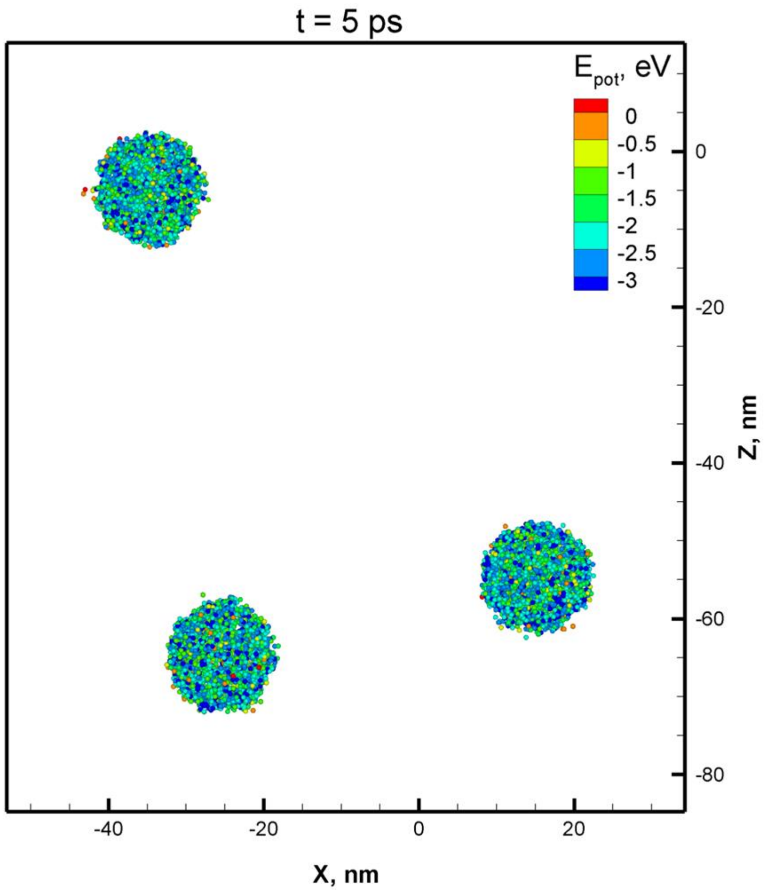


porous

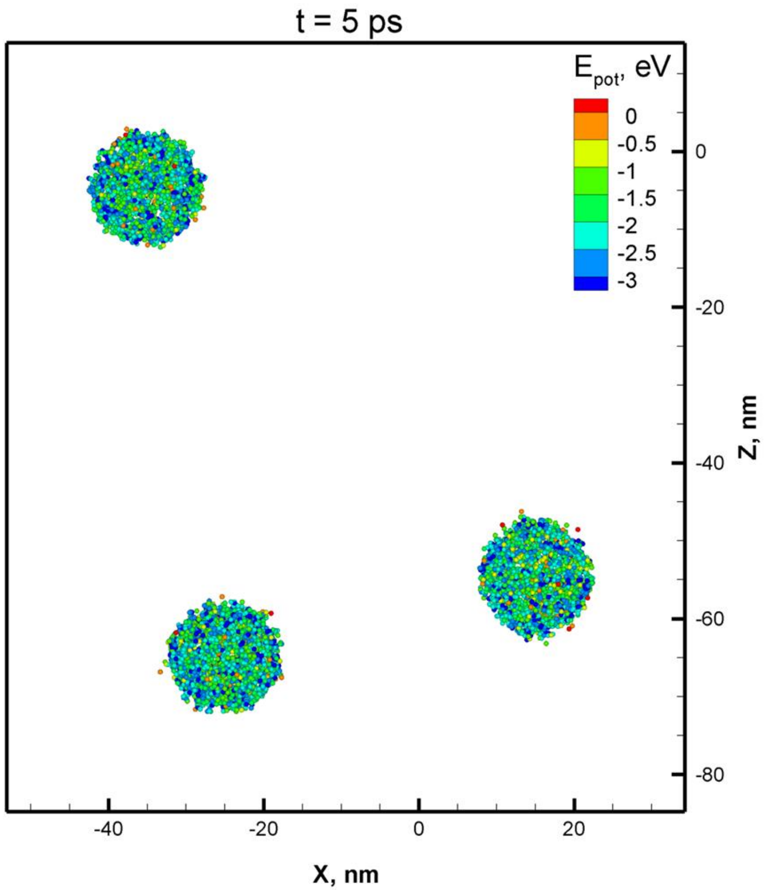


10 nm NP, the incident fluence 200 J/m2

solid

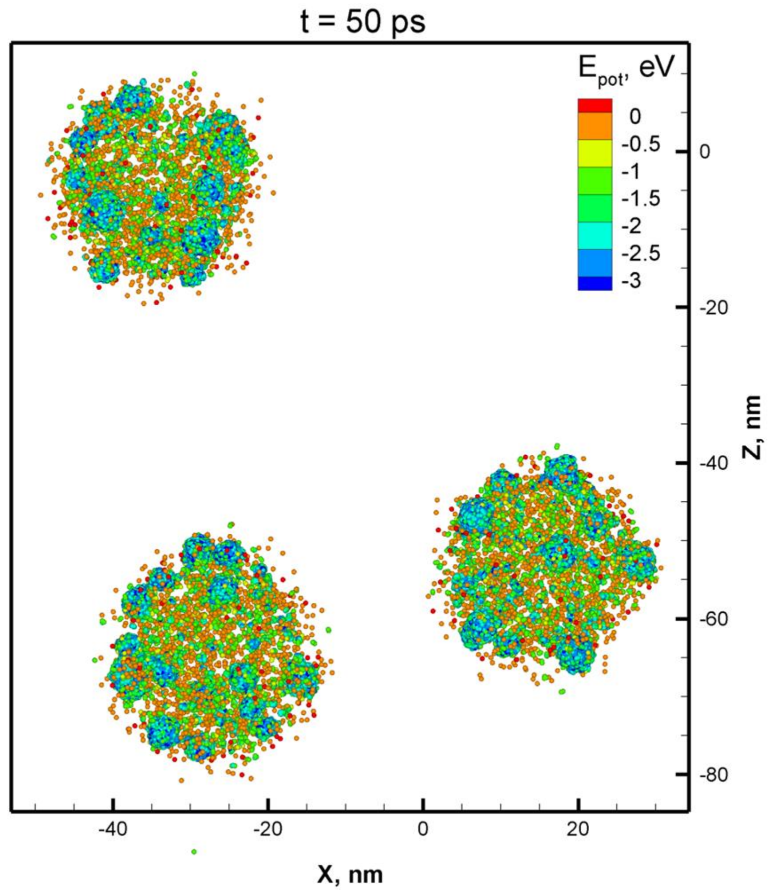


porous

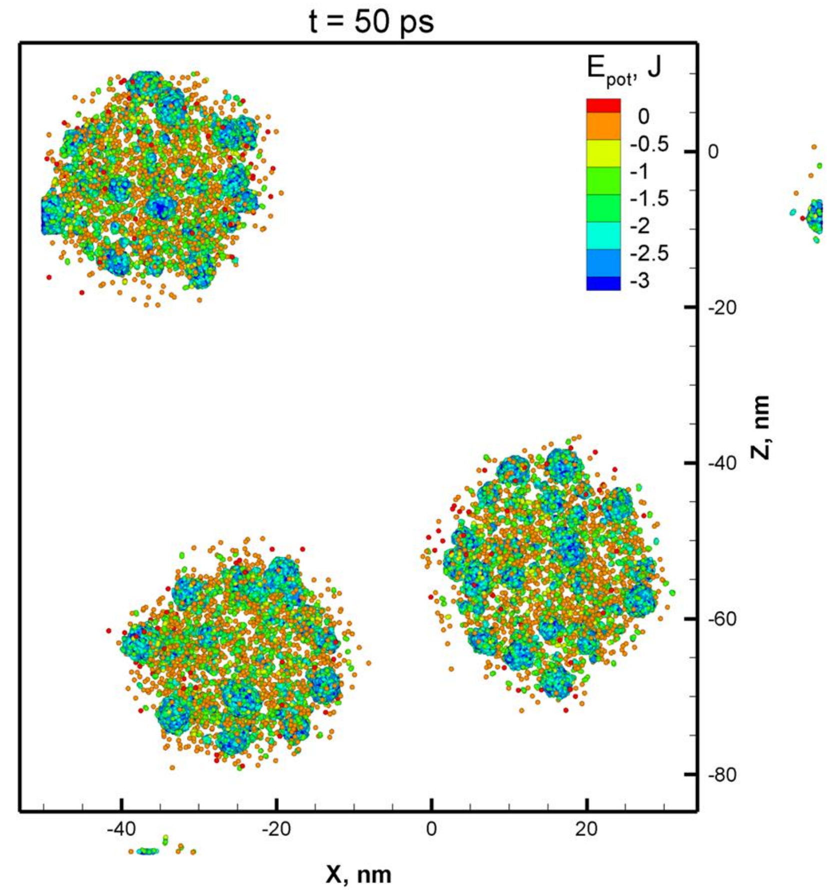


10 nm NP, the incident fluence 200 J/m2

solid

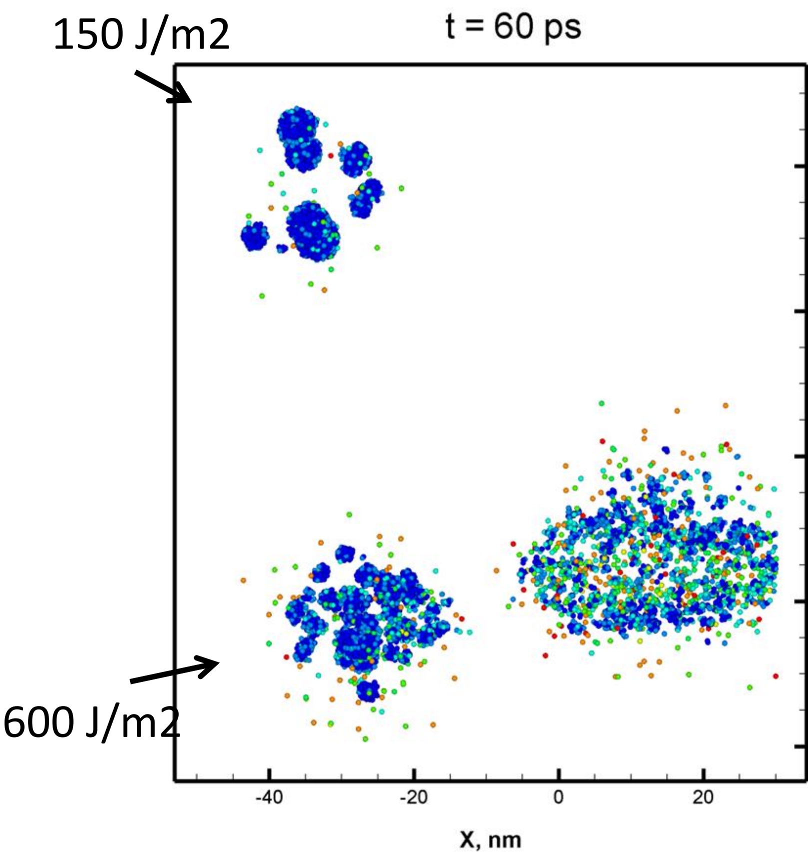


porous

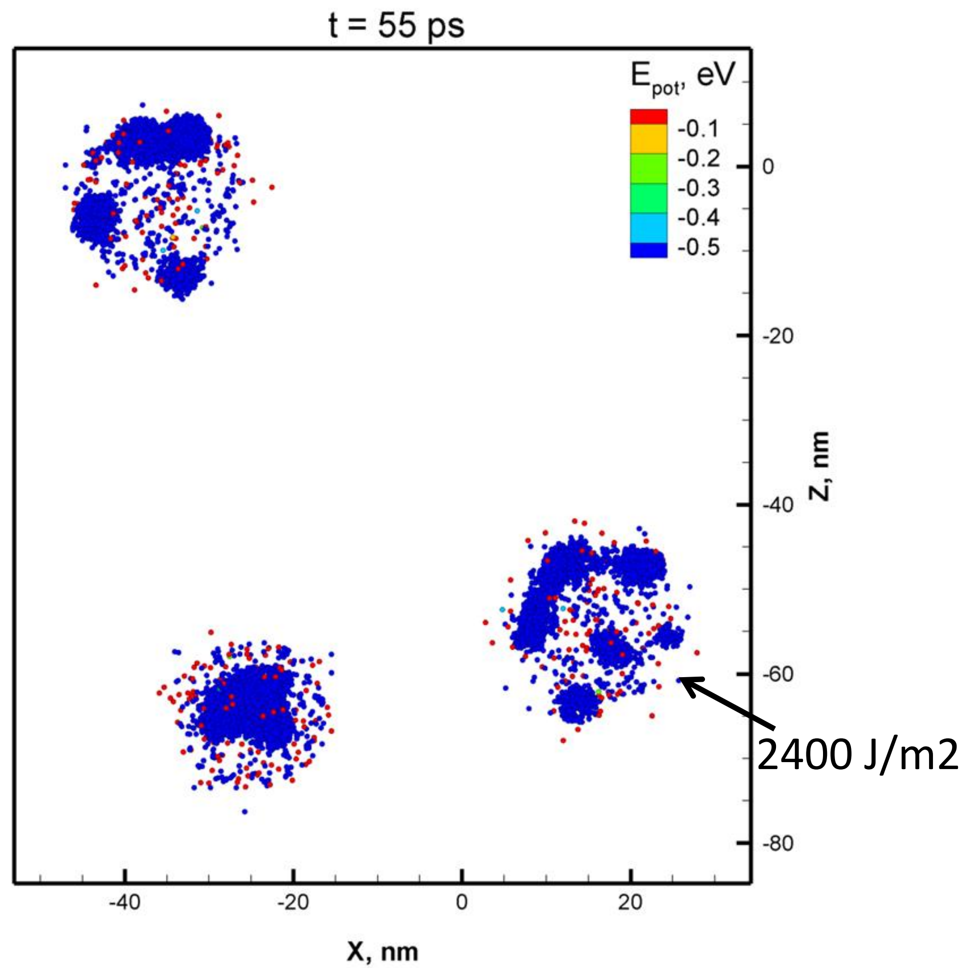


270 fs pulse, 10 nm NPs, different incident fluences

solid

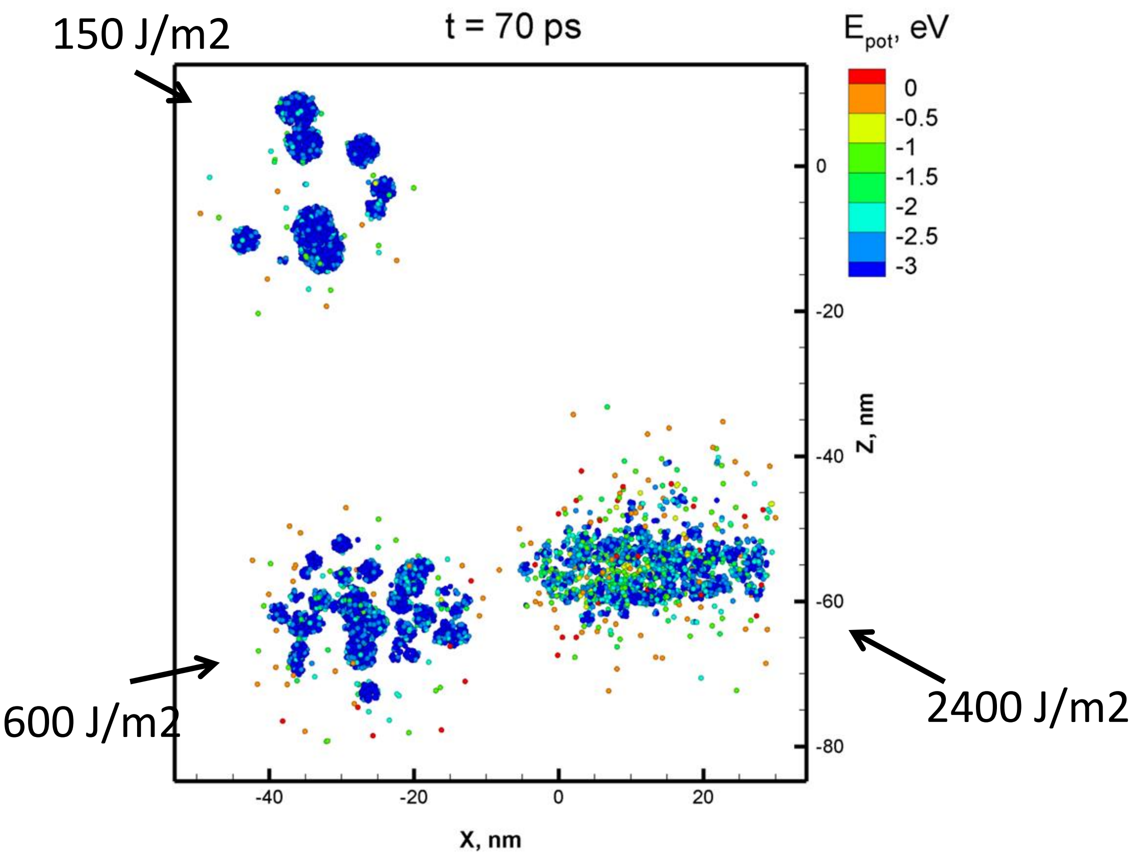


porous



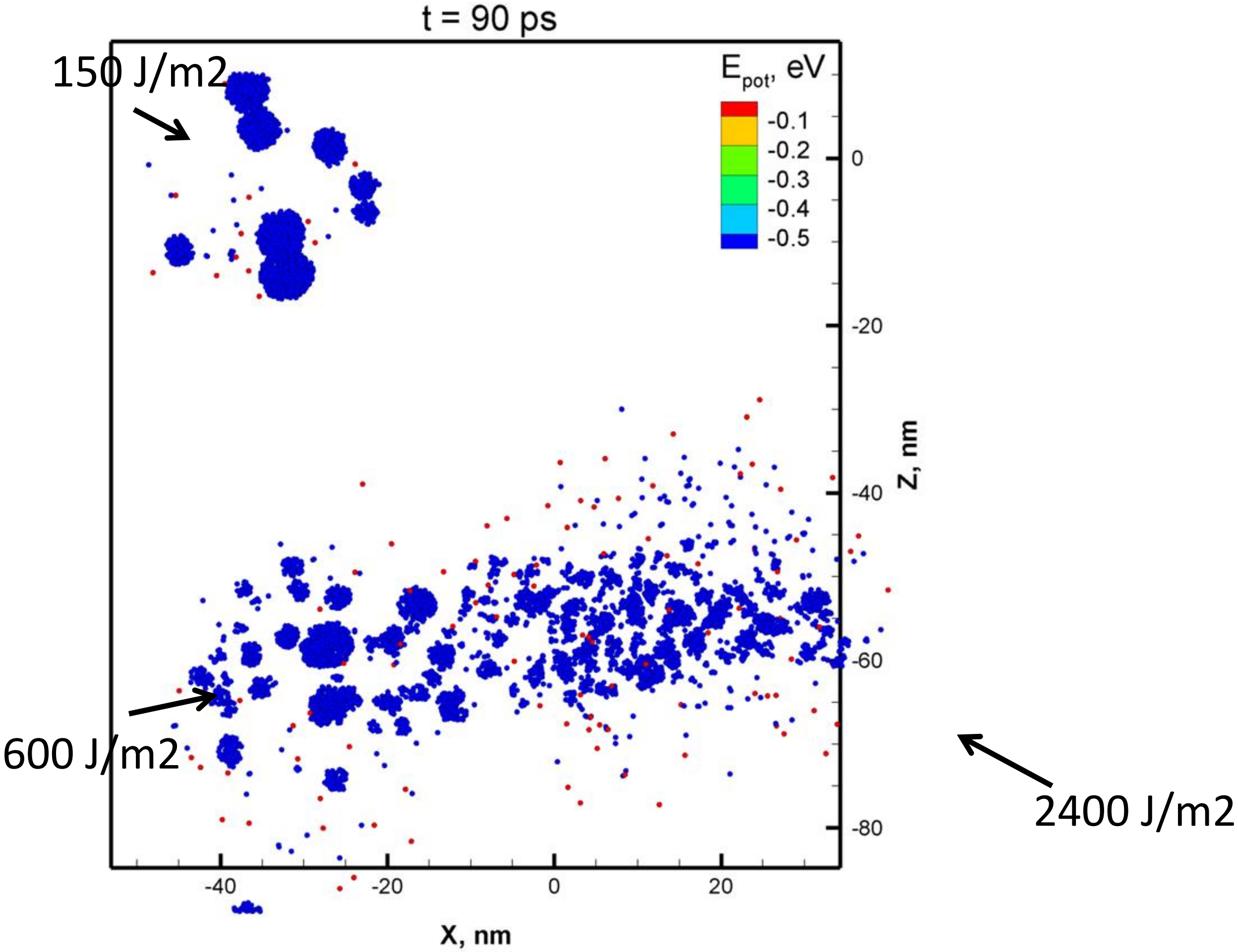
270 fs pulse, 10 nm NPs, different incident fluences

solid



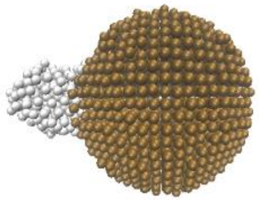
270 fs pulse, 10 nm NPs, different incident fluences

solid



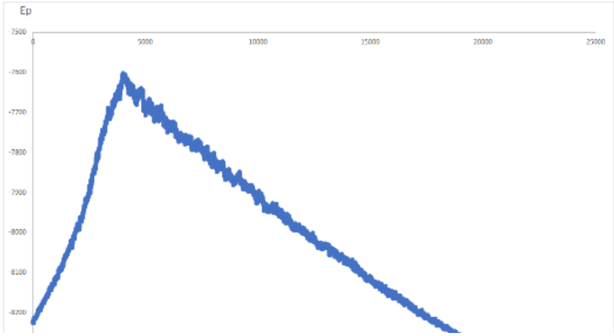
NP Sintering or Alloying

FeNP R=10 uc AuNP R = 20 uc



Different sizes and species, but the same temperatures

Time-evolution of energy



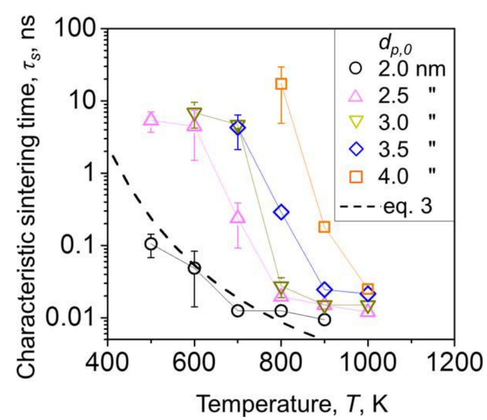
FeNP 1700+AuNP 1700

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

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!