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# Atomistic Modeling as a Key to Unraveling Ultra-Short Laser Nano-Synthesis and Nano-Treatment

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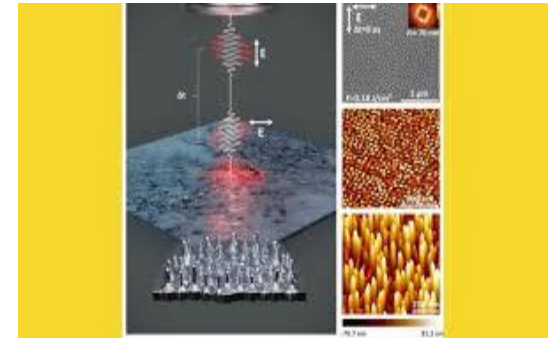


HAL Authorization

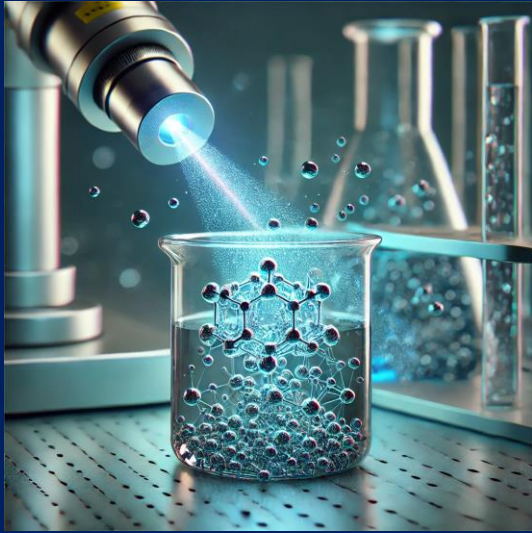
# Atomistic Modeling as a Key to Unraveling Ultra-Short Laser Nano-Synthesis and Nano-Treatment

Tatiana E. ITINA, Dmitry S. IVANOV, Ilemona S. OMEJE

Lab. Hubert Curien, UMR CNRS 5516, UJM, Campus Manufacture, 42000 St-Etienne, France

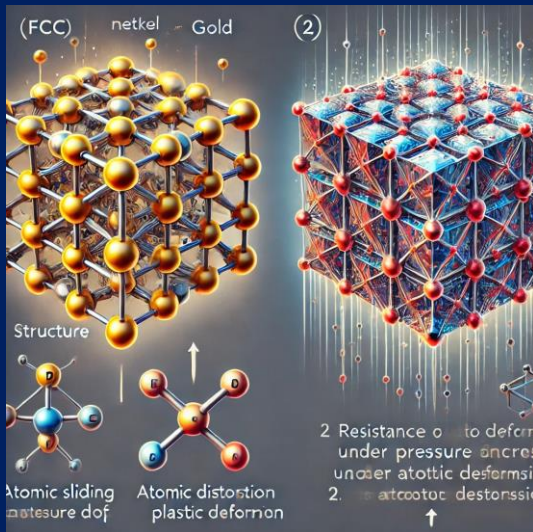


# INTRODUCTION



- The interaction of **ultrashort laser pulses** with materials has opened new frontiers in nanotechnology, offering unprecedented control at the atomic scale. These femtosecond (fs) and picosecond (ps) pulses facilitate localized heating and structural modifications, making them invaluable in nanomaterials engineering.

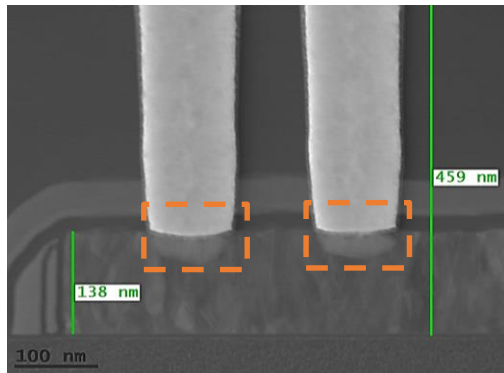
- A critical aspect of laser-material interactions is the **interplay between thermal and electronic excitations**, driving phenomena such as surface melting, amorphization, phase transitions, and nanoparticle generation.



- Atomistic modeling, using molecular dynamics (MD) simulations coupled with the two-temperature model (TTM), provides a detailed understanding of these mechanisms, bridging theoretical predictions with experimental results. This study employs **atomistic simulations** to elucidate ultrashort laser-induced processes, exploring their potential for advancing nanomaterials science and technology.

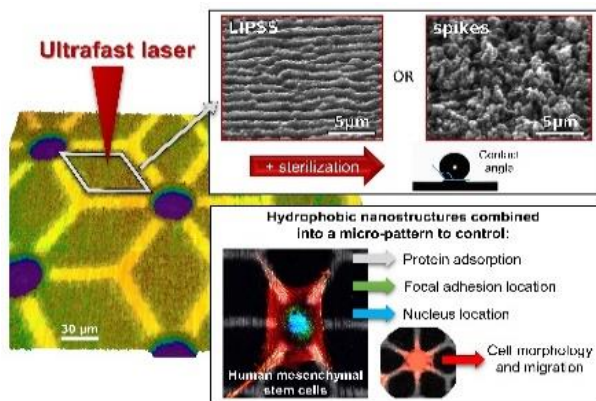
# MOTIVATIONS

- The study emphasizes that atomistic modeling not only enhances our understanding of these complex **phenomena** but also **guides the development of innovative applications in advanced technologies**.



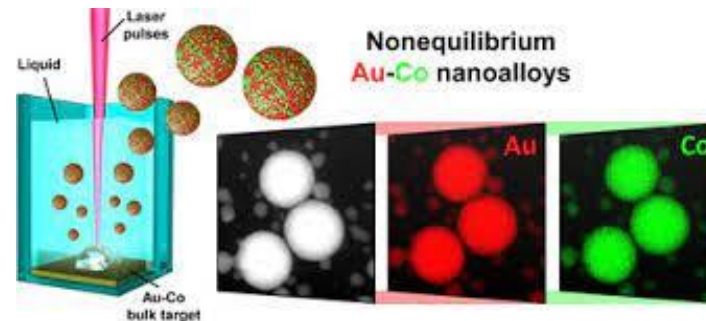
TEM C54-TiSi<sub>2</sub> contacts

ST-Microelectronics



Klos et al. LAbHC CNRS

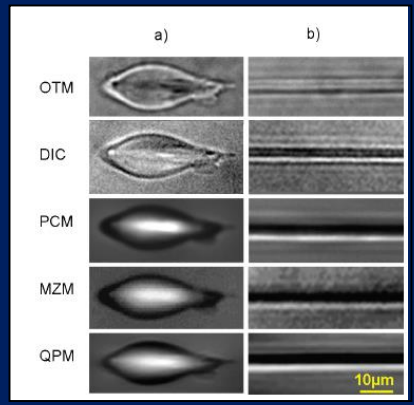
- Si amorphization for microelectronics
- Ti surface nano- et microtexturing for implants and prothesis
- Nanoparticle formation for catalyses, bio-medical applications, water cleaning, etc



Amendola et al., Univ. Padova

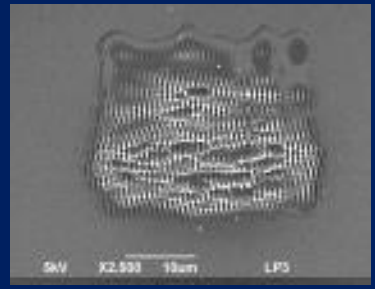
# Laser fluence

## Structural modifications in volume or near the surface

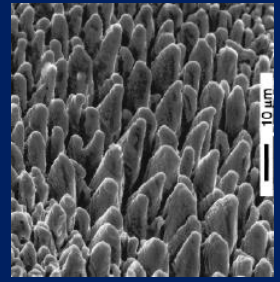


Mauclair et al. LabHC CNRS

## Surface texturing

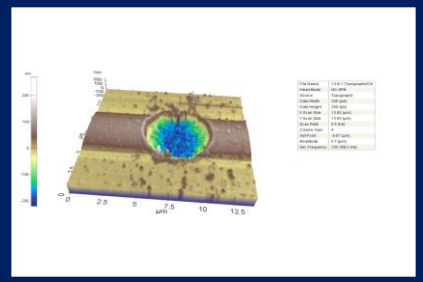


Uteza et al. LP3 CNRS

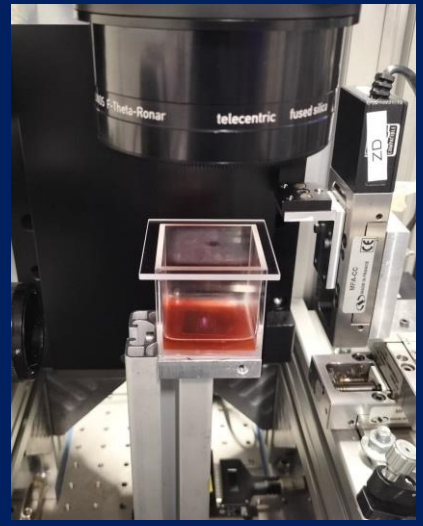


Sarnet et al.

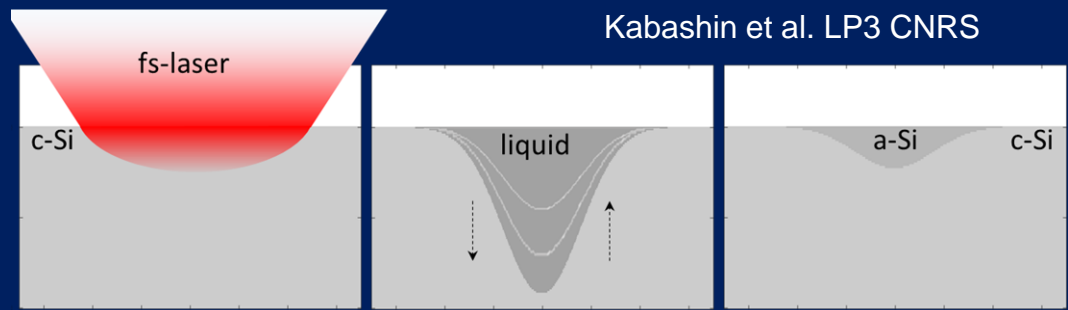
## Ablation



Kabashin et al. LP3 CNRS



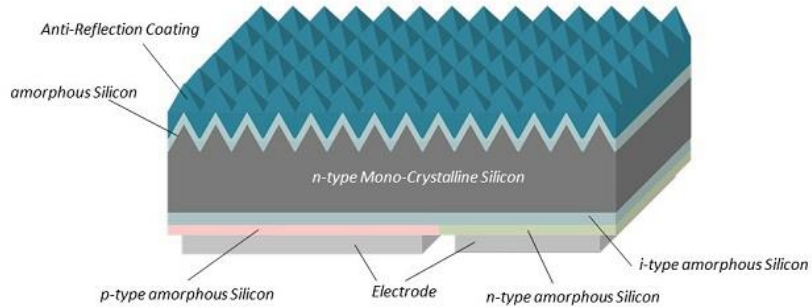
Polit et al. Pastukhov et al, LP3 CNRS



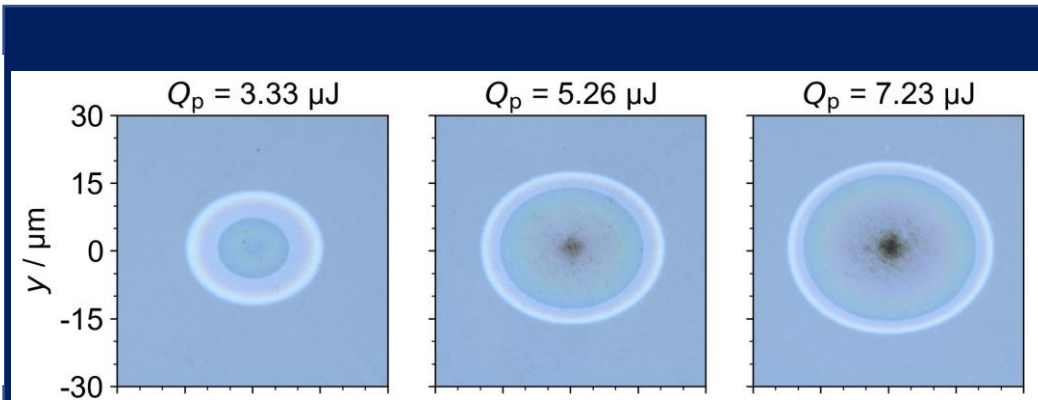
Groho et al. LP3

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

# Amorphization of Si (ANR LAMRSIM)



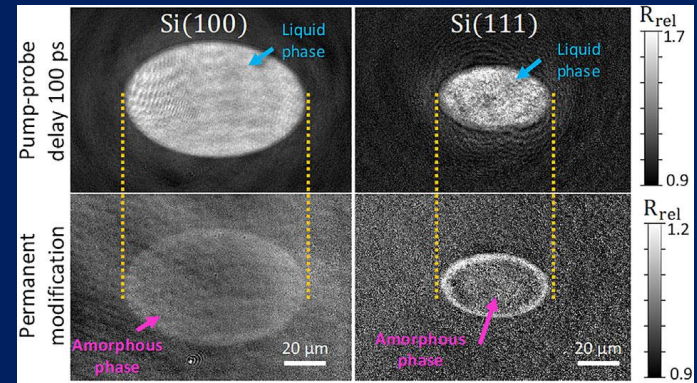
<https://global.sharp/corporate/news/180327.html>



A. Engel, Th. Pflug, M. Olbrich, and A. Horn

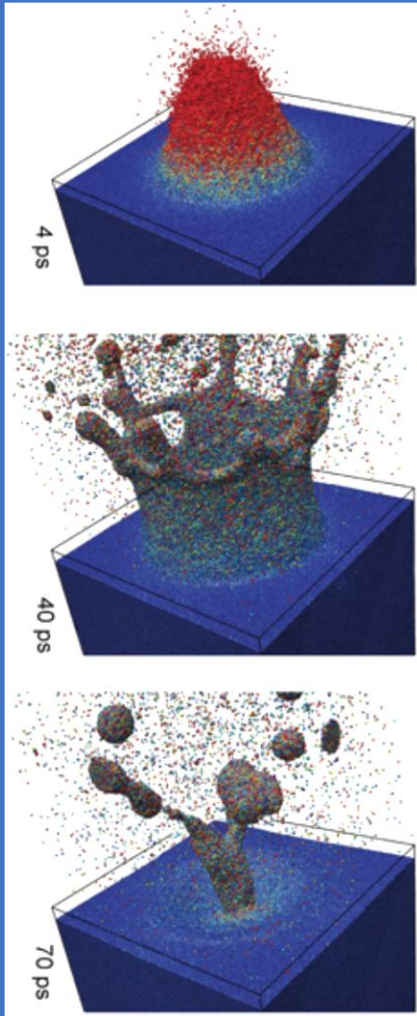


Feiyu Xu et al, Chemical Engineering Journal, 430, 2022,133140



David Grojo et al, Laser Photonics Rev. 2024, 2301327

# Material ejection in femtosecond laser ablation



InSiDE • Vol. 10 No. 1 • 2012

Ivanov et al. (2003)

## Two-temperature model (TTM)

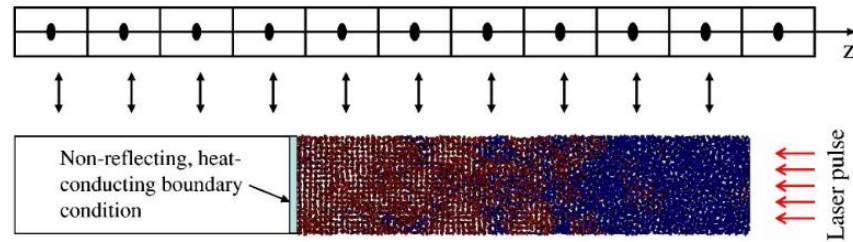
$$C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla [K_e(T_e) \nabla T_e] - G(T_e - T_l) + S(z, t),$$

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

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

## TTM-MD model

Ivanov & Zhigilei, (2003)



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

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

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



# MD-nTTM model

$$\frac{dI(z,t)}{dz} = - \left( \alpha + \alpha_{FCA}(\varepsilon(N_e)) \right) I(z,t) - \beta I^2(z,t)$$

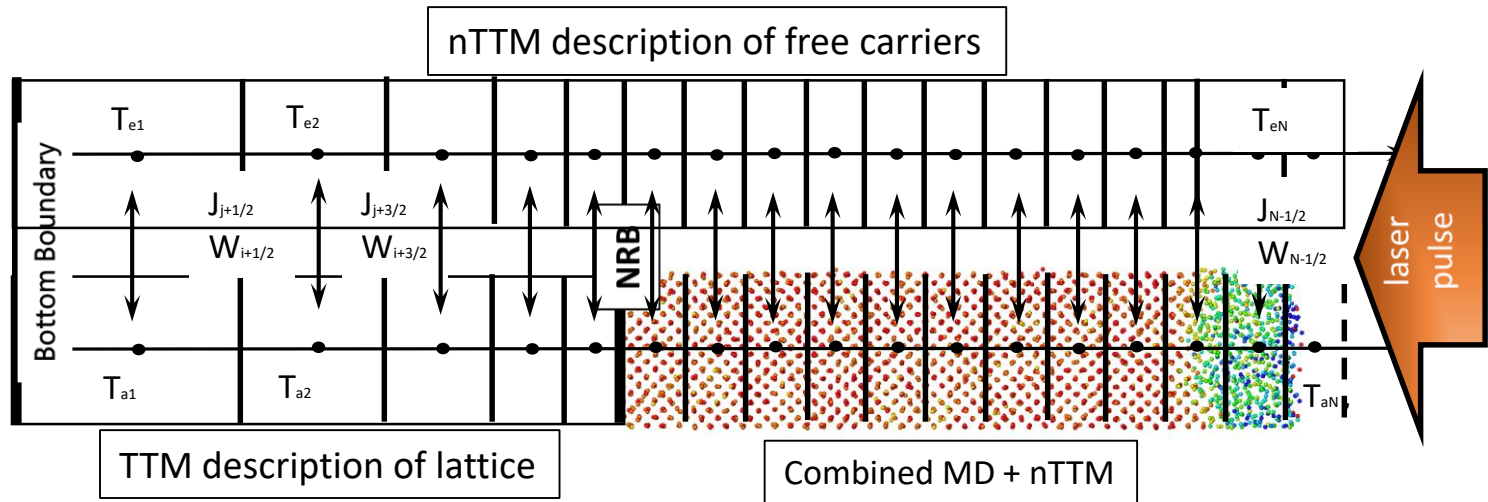
$$\frac{\partial n_e}{\partial t} = \frac{\alpha I(z,t)}{h\nu} + \frac{\beta I^2(z,t)}{2h\nu} + \delta n_e - \gamma N_e^3 - \nabla \cdot \vec{J}(n_e, T_e, E_g)$$

$$\frac{\partial U_e(N_e, T_e, E_g)}{\partial t} = \left( \alpha + \alpha_{FCA}(\varepsilon(N_e)) \right) I(z,t) + \beta I^2(z,t)$$

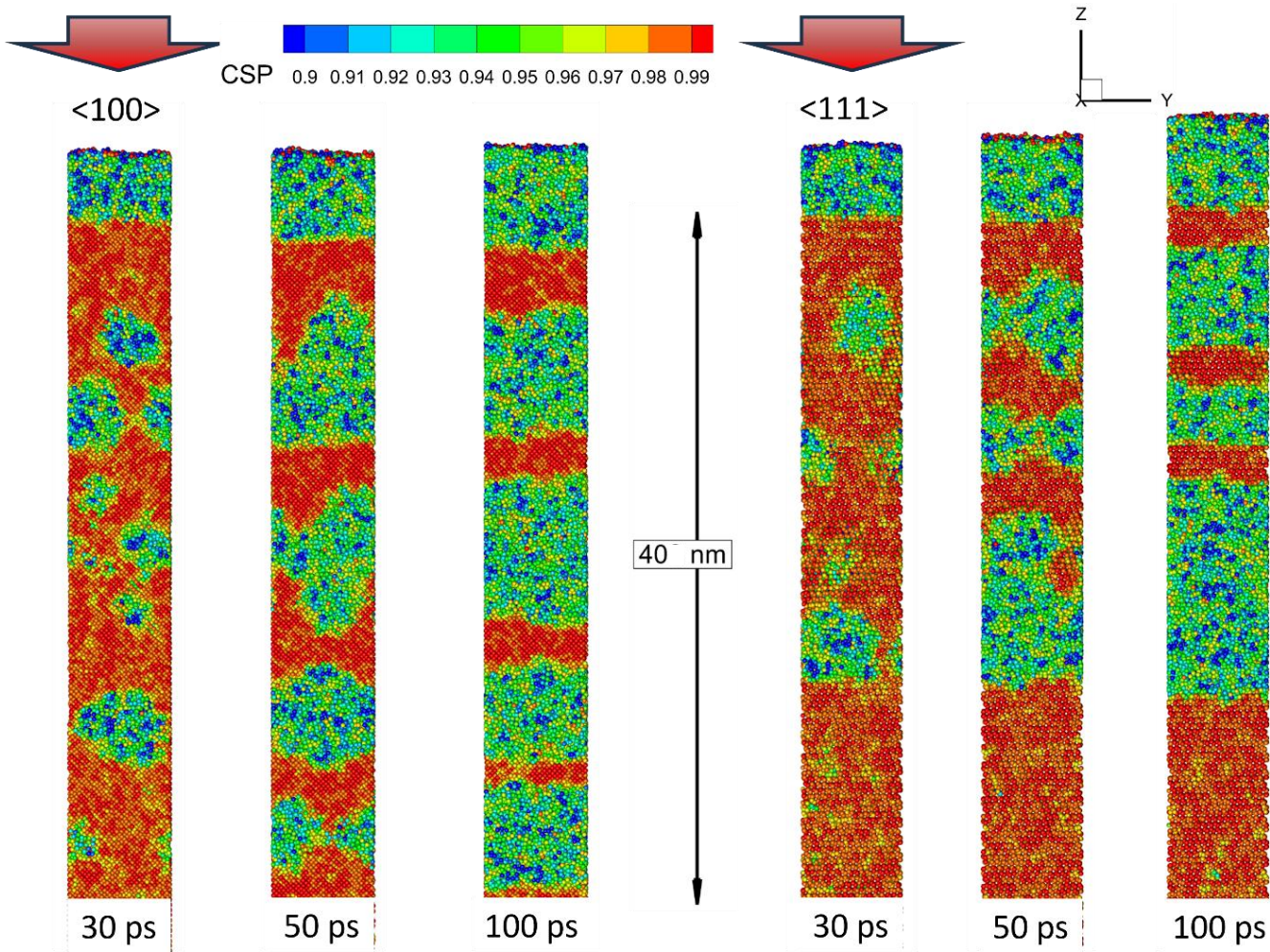
$$-\nabla \cdot \vec{W}(N_e, T_e, E_g) - \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l)$$

$$C_l \frac{\partial T_l}{\partial t} = \nabla \cdot (\kappa \nabla T_l) + \frac{C_{e-h}(N_e, T_e, E_g)}{\tau_e} (T_e - T_l) \rightarrow m_i \frac{d\vec{r}_i}{dt^2} = - \sum_{j=1,N} \nabla U(\vec{r}_{ij}, T_e) + \xi m_i \vec{V}_i^T$$

1. TTM + additional eq for the density of carriers
2. Implicit Crank-Nicolson algorithm needs parallel.
3. Drude-Lorenz model for reflectivity and free car abs

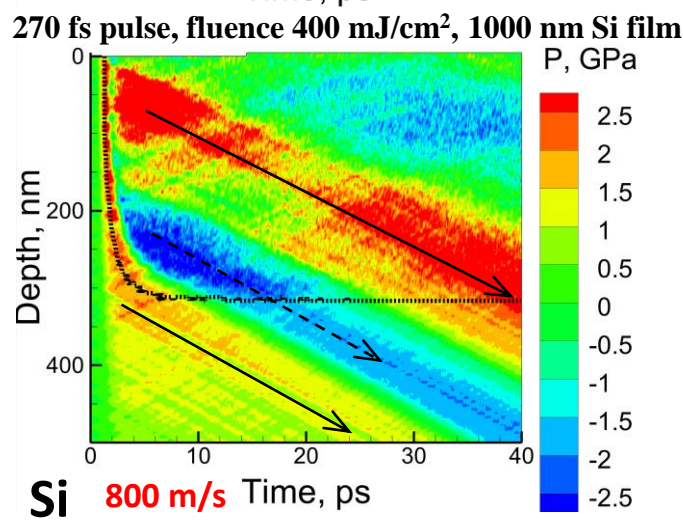
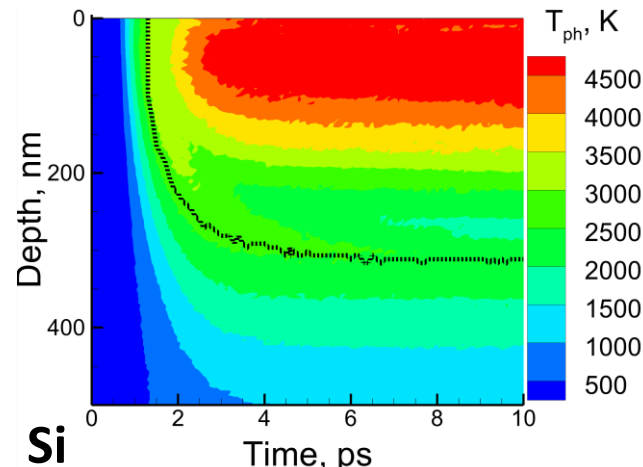
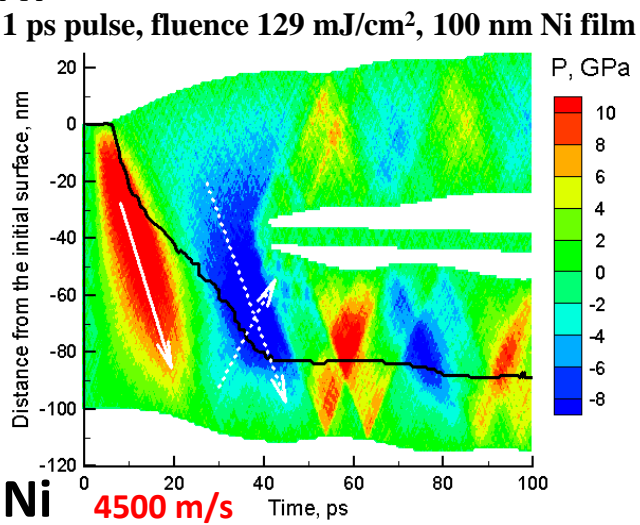
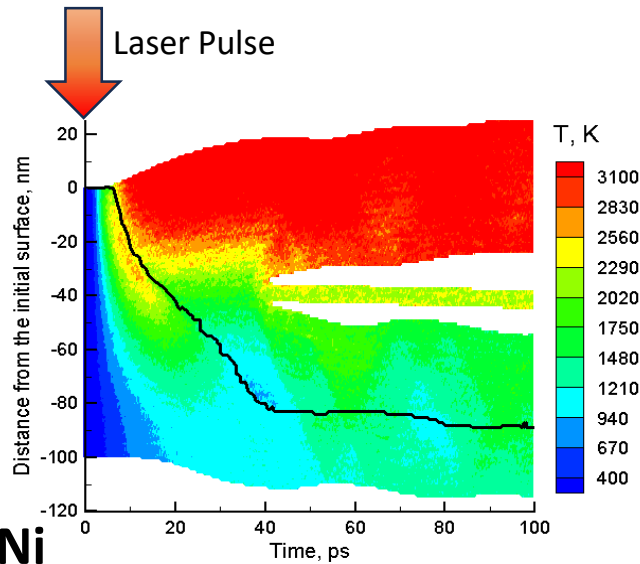


# Melting kinetics in Si with $\langle 001 \rangle$ and $\langle 111 \rangle$ crystal orientation

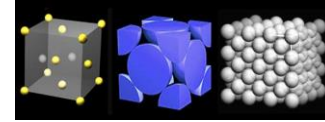


1. Two identical samples but  $\langle 001 \rangle$  and  $\langle 111 \rangle$
2. 100fs, 0.3 J/cm<sup>2</sup>
3. Heterogeneous vs homogeneous melting mechanism
4.  $\langle 001 \rangle$  results 26% more melt
5. Speed of sound in  $\langle 111 \rangle$  8% more
6. Optical properties can be refined

# Melting Kinetics of Si vs Metals

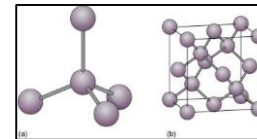


**Ni: face center cubic**



1. Well distinguished solid-liquid interface propagation
2. T/P interplay results in both heterogeneous and homogeneous melting mechanism
3. The melting start upon the **drop** in pressure

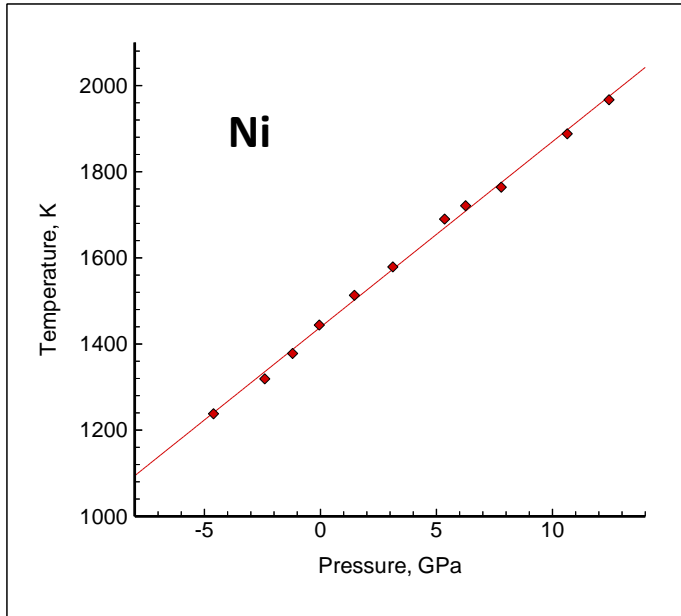
**Si: Diamon cubic**



1. Rapid/instant advancement of the melting front
2. T/P interplay results in mainly homogeneous melting mechanism
3. The melting starts upon the **rise** of pressure

# Solid-liquid transition in metals and in Si

## Crystal structure effect



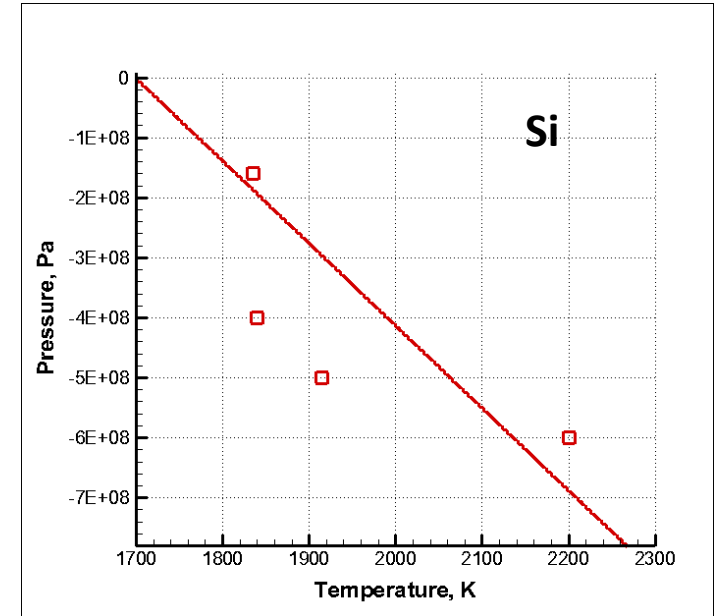
At  $P = 0$  Pa  
 $T_m = 1439$  K

Face center cubic structure:  $V_{\text{melt}} = 5\%$

Volume expands results in internal stresses increase

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

1. For metals  $dT/dP > 0$ , so an increase of  $P$  reinforces the crystal stability against of melting.
2. For Si  $dT/dP < 0$ , so the an increase of pressure destabilizes the crystal structure and facilitates the onset of melting.

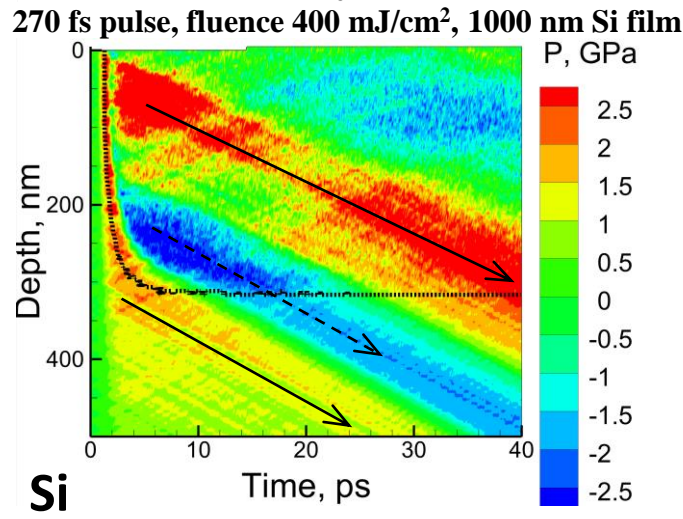
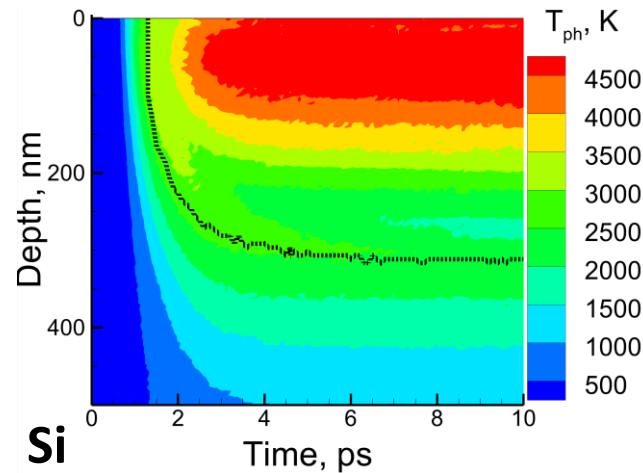
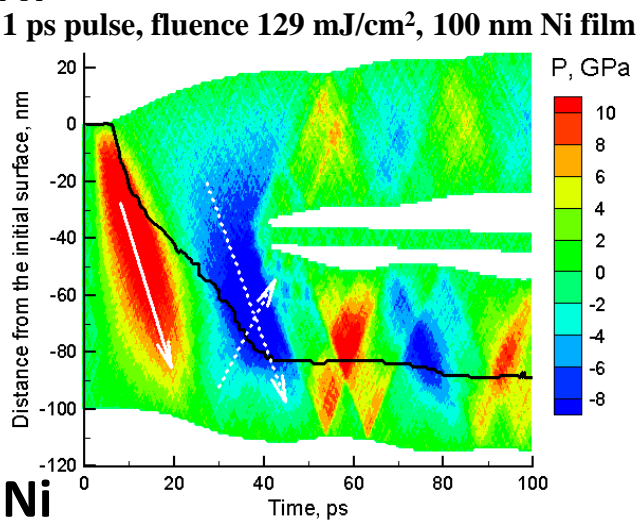
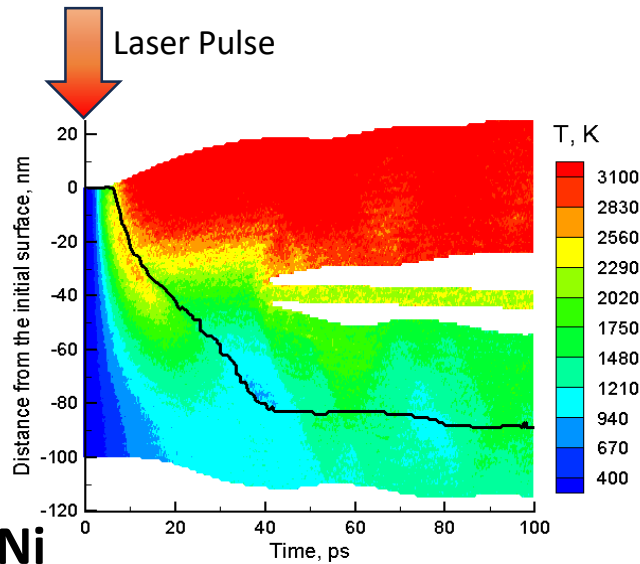


At  $P = 0$  Pa  
 $T_m = 1699$  K

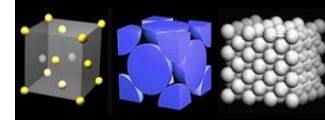
Open diamond crystal structure:  $V_{\text{melt}} = -7.5\%$

Volume contracts results in internal stresses drop

# Melting Kinetics of Si vs Metals

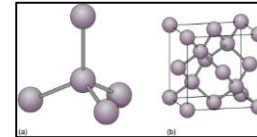


**Ni: face center cubic**



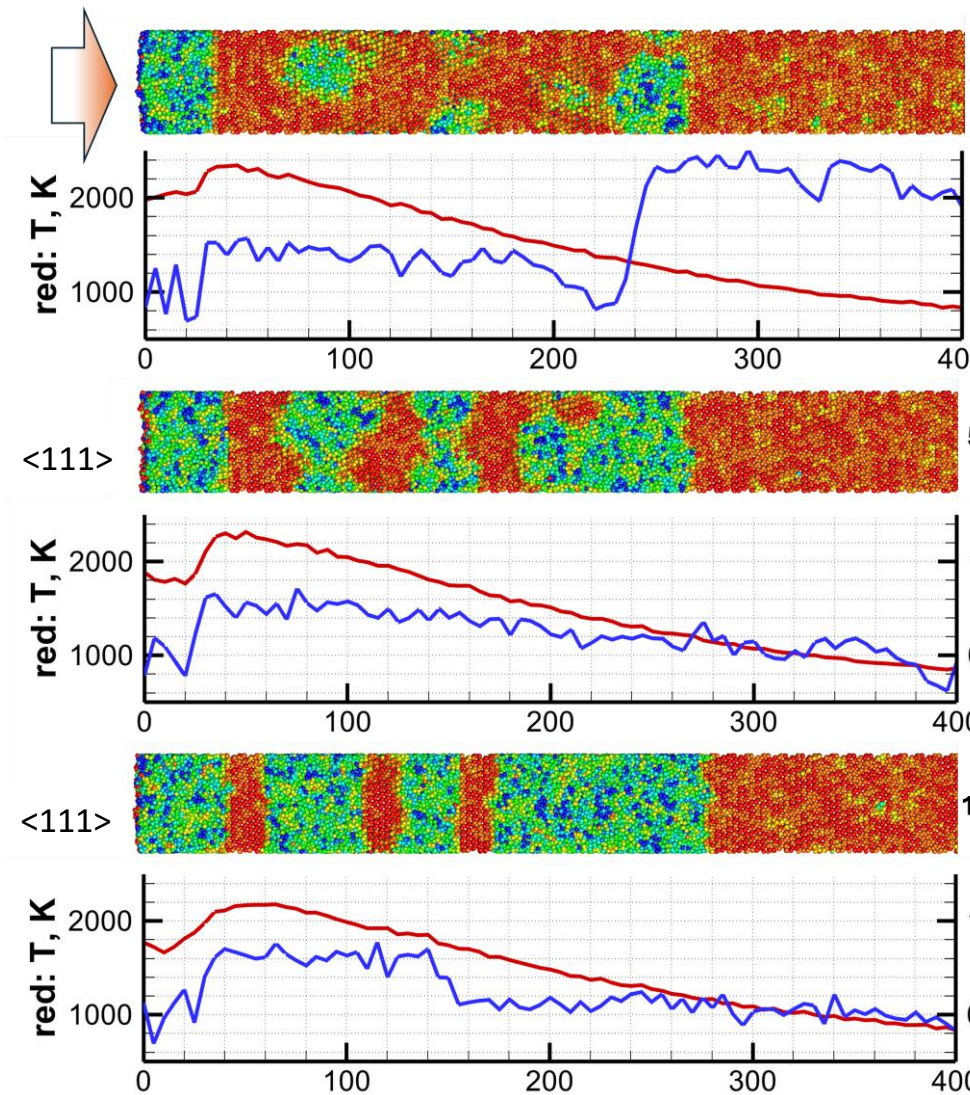
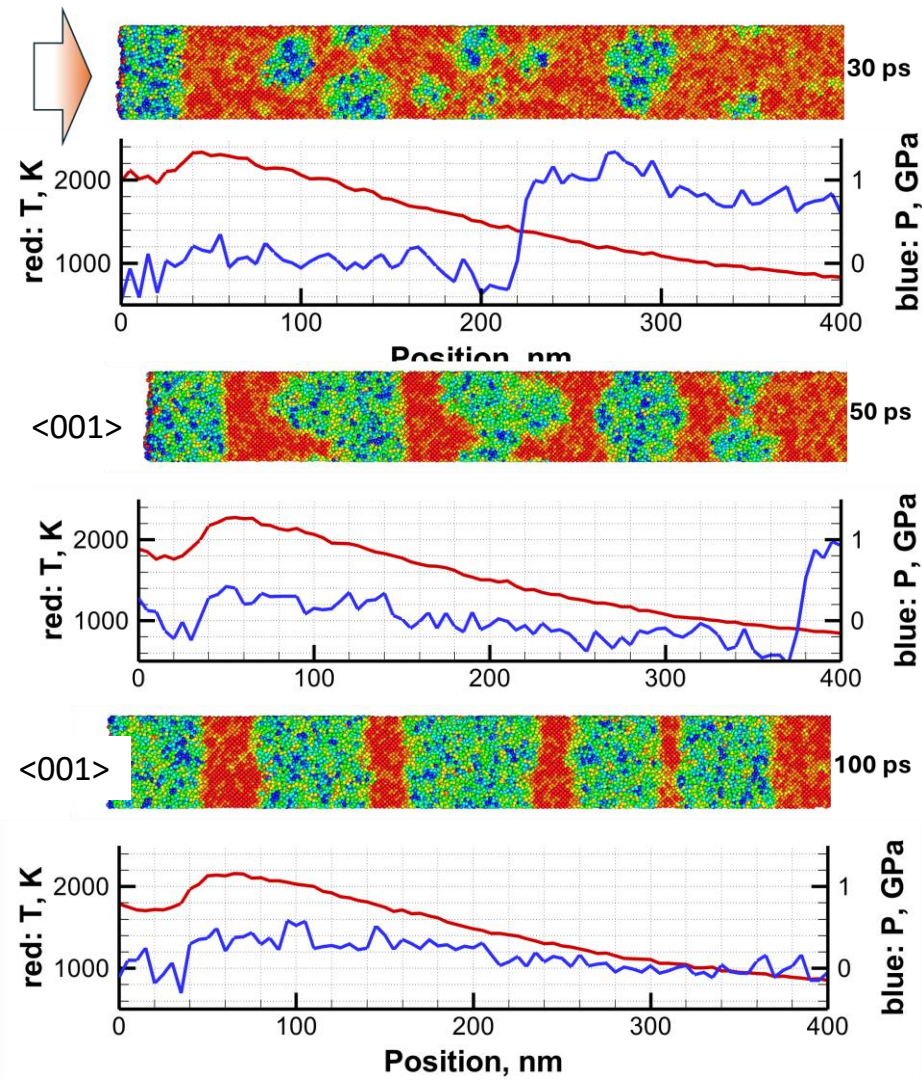
- At the fluences around melting threshold the solid-liquid transition via **heterogeneous mechanism** is more energetically favorable.

**Si: Diamond cubic**

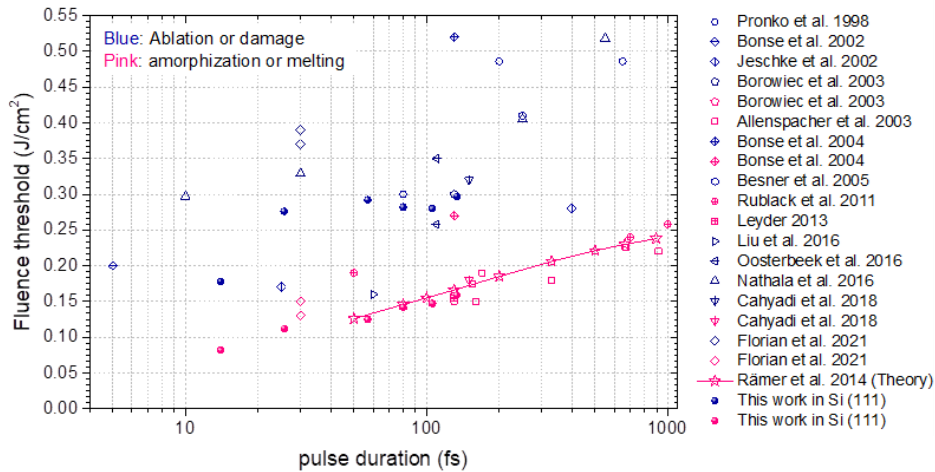


- At the fluences around melting threshold, the **homogeneous melting** mechanism plays a determinant role and makes formation of the solid-liquid interface at a significant depth instantly.

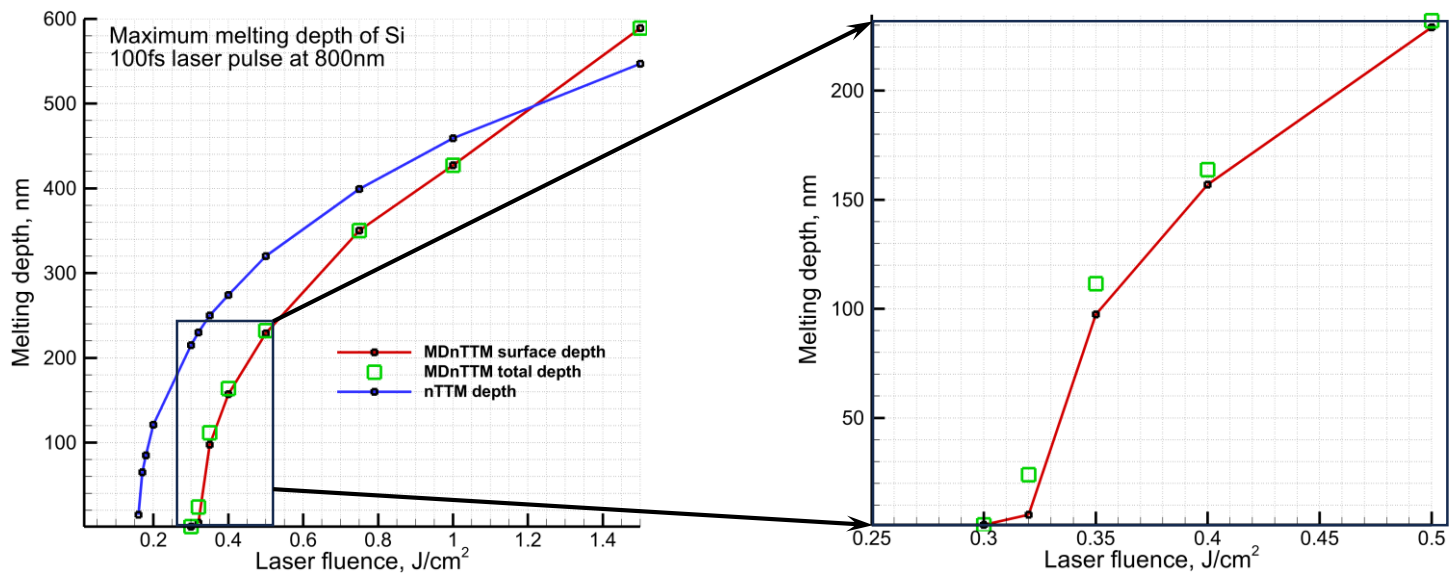
# Melting Kinetics of Si (001) vs (111)



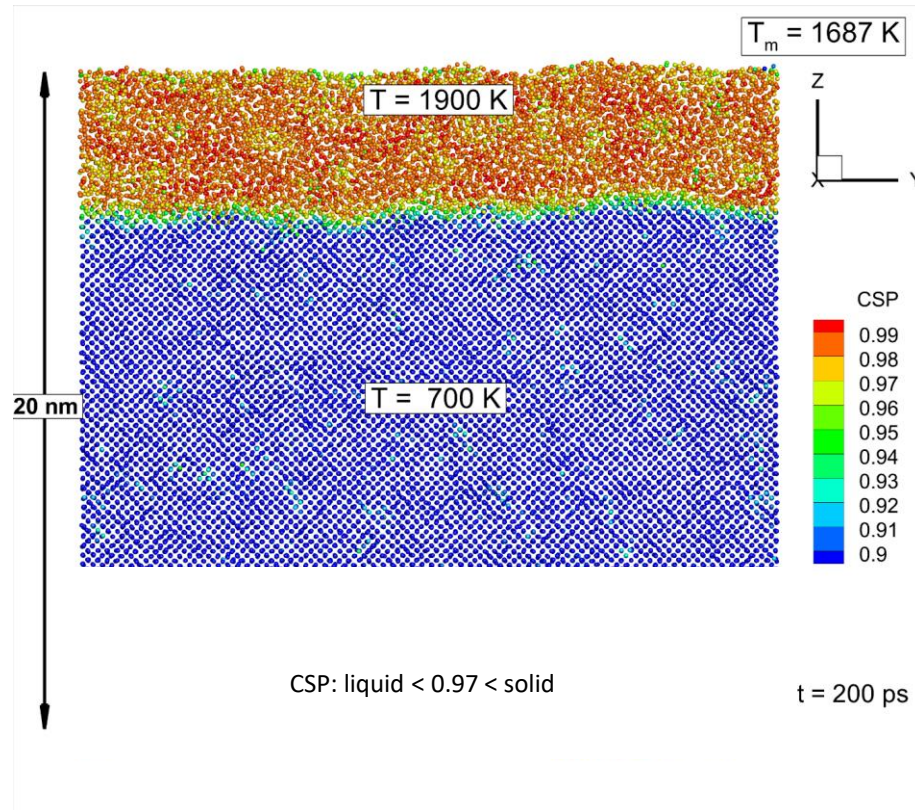
# Depth of melting vs laser fluence



1. Melting threshold  $0.3 \text{ J}/\text{cm}^2$
2. The results are for  $\langle 001 \rangle$
3. There some experimental results matching our measurements
4. Two melting mechanisms at low fluence
5. Heterogeneous mechanism is suppressed at high fluences
6. Discrepancy ????



# Amorphization mechanism in Si



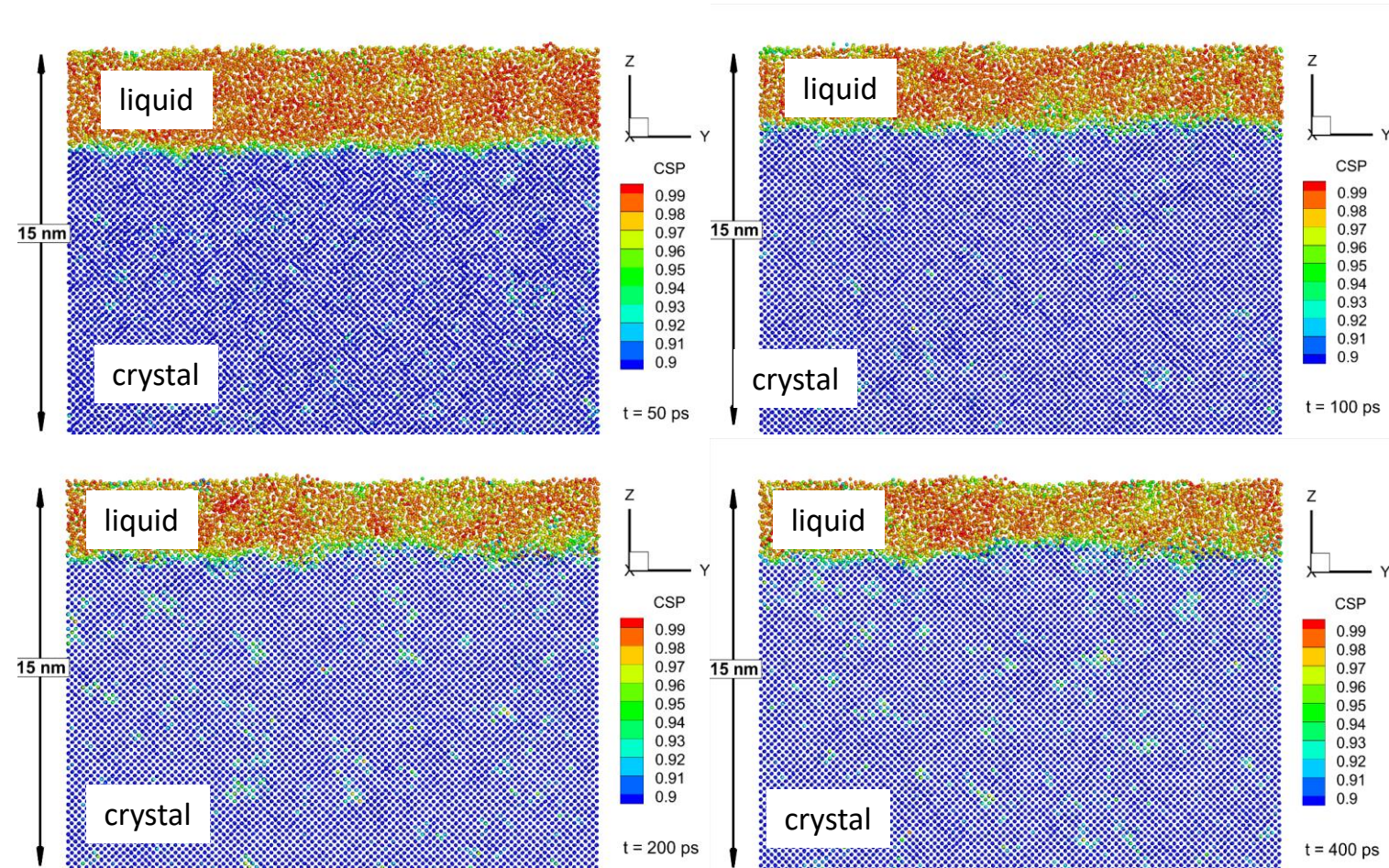
Prepare the initial (1,0,0) Si 300 K

Introduce rapid heating to 2000 K of the surface layers

Follow the equilibration procedure

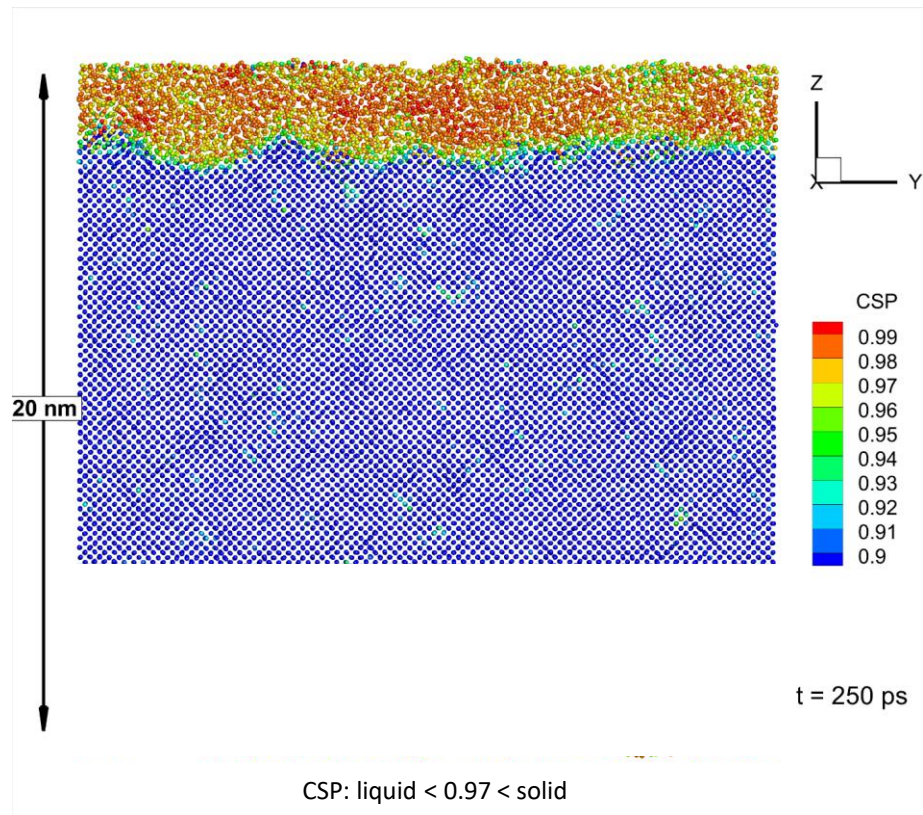
This is a preliminary consideration of the cooling mechanism due to free carrier's flux and their thermal diffusion process

# Amorphization of Si

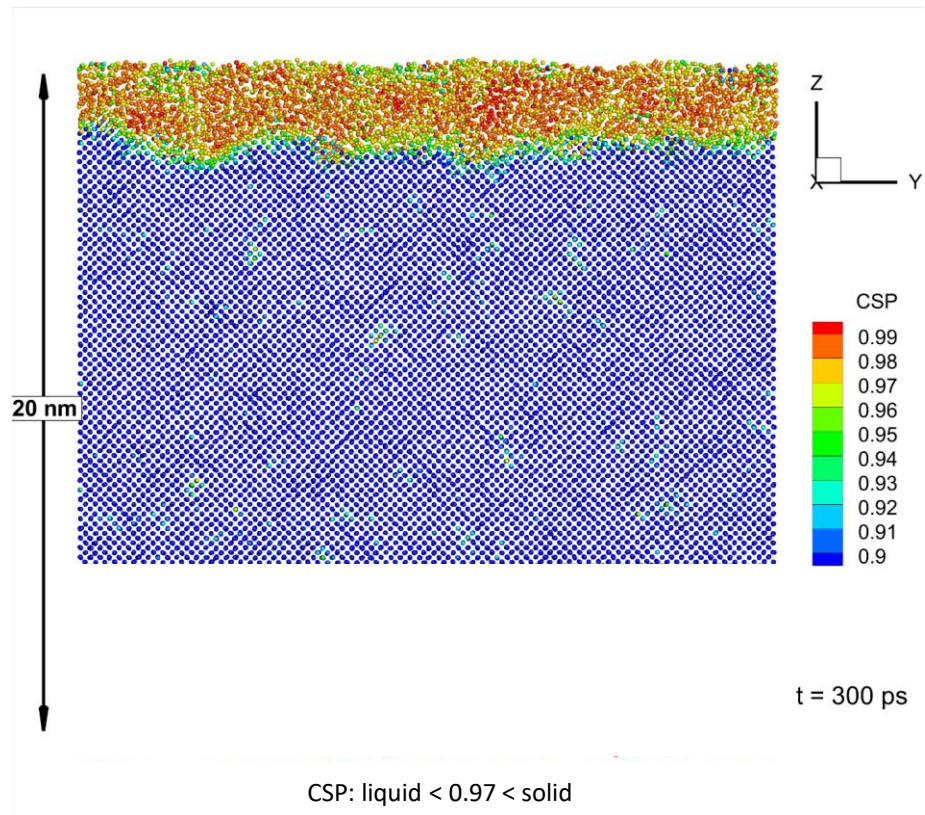


1. Re-crystallization procedure
2. We want to provide the cooling rate strong enough
3. Solid-liquid interface is incapable of moving fast enough
4. CSP does not distinguish melt from amorphous

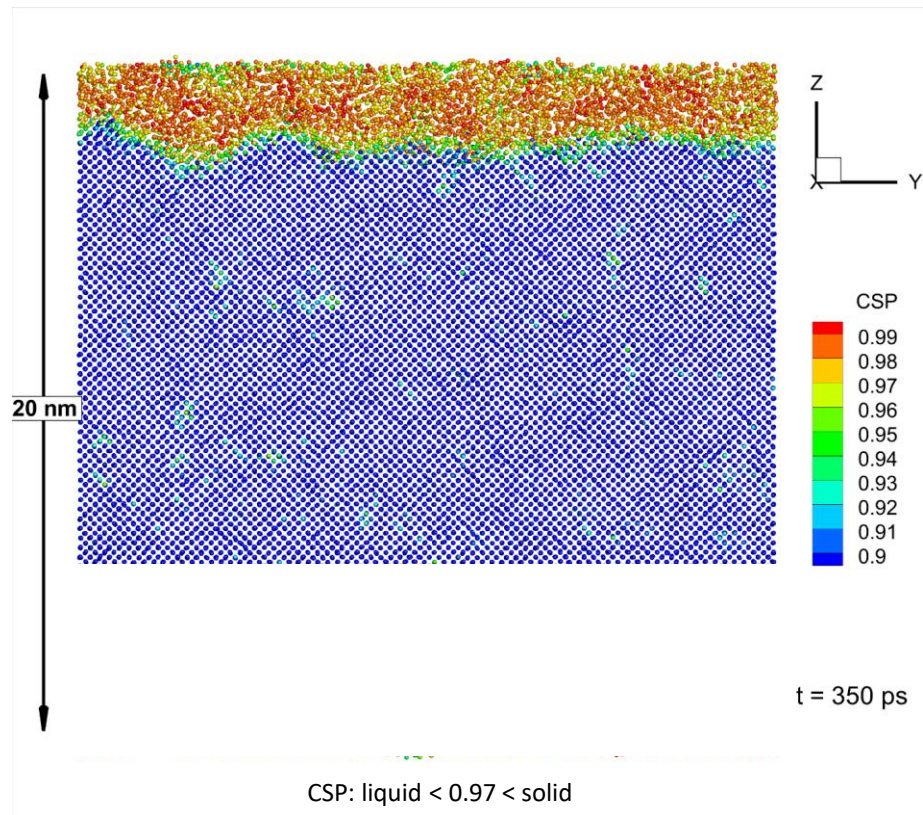
# Amorphization of Si



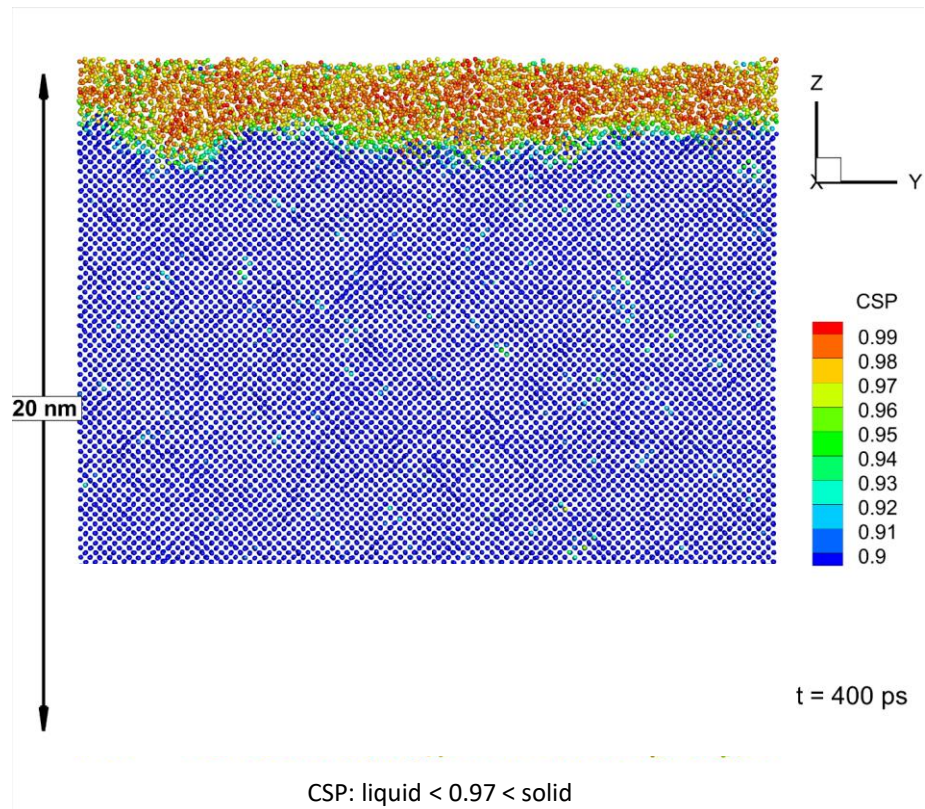
# Amorphization of Si



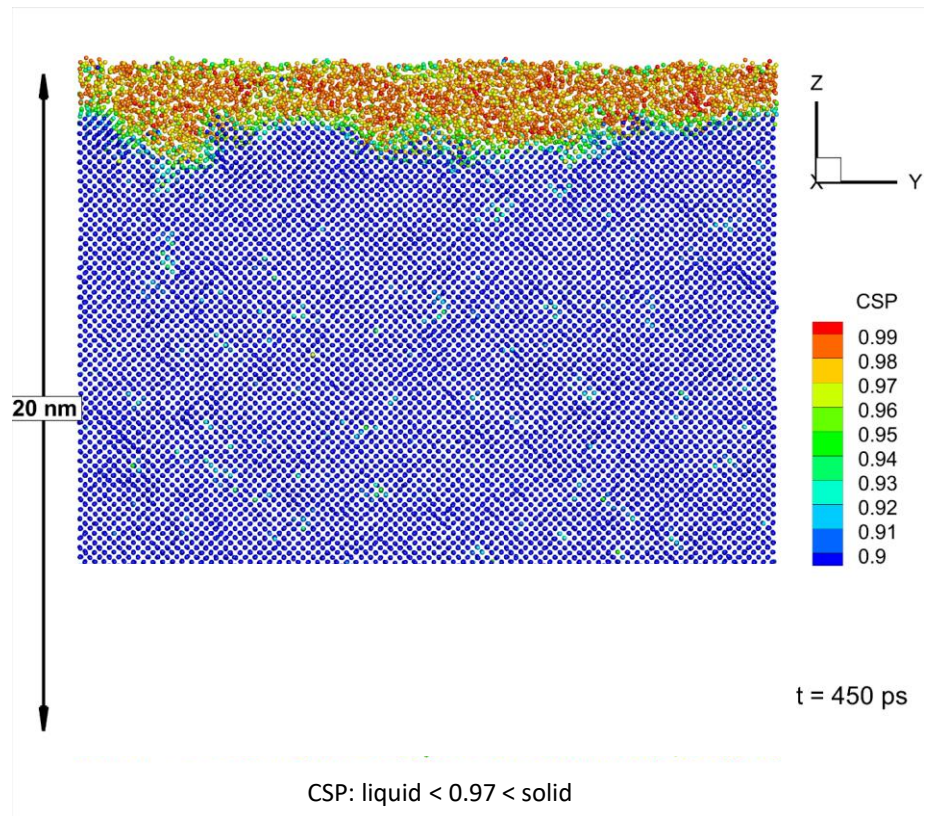
# Amorphization of Si



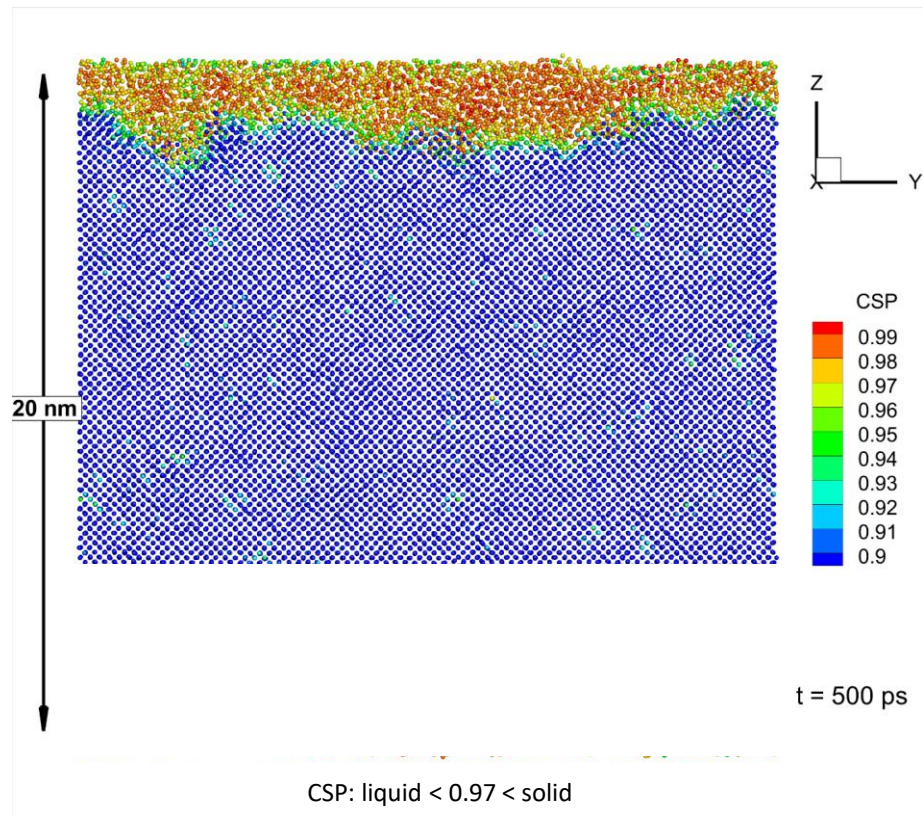
# Amorphization of Si



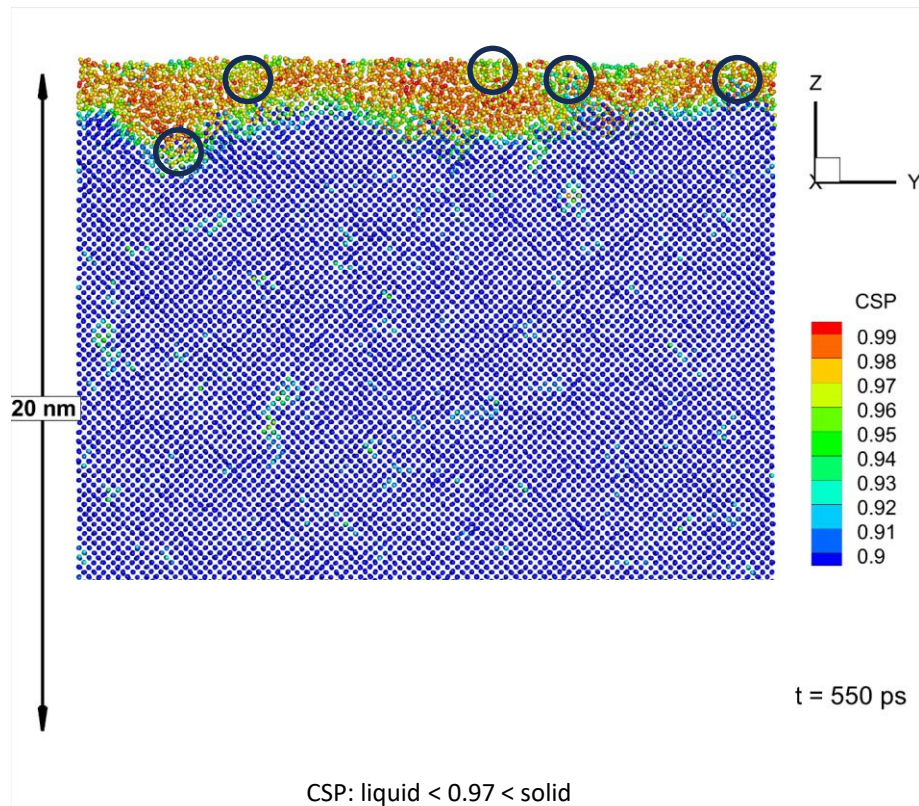
# Amorphization of Si



# Amorphization of Si



# Amorphization of Si



The nucleation sites of the amorphous phase are indicated by circles

MD requires T drop rate 30K/ps

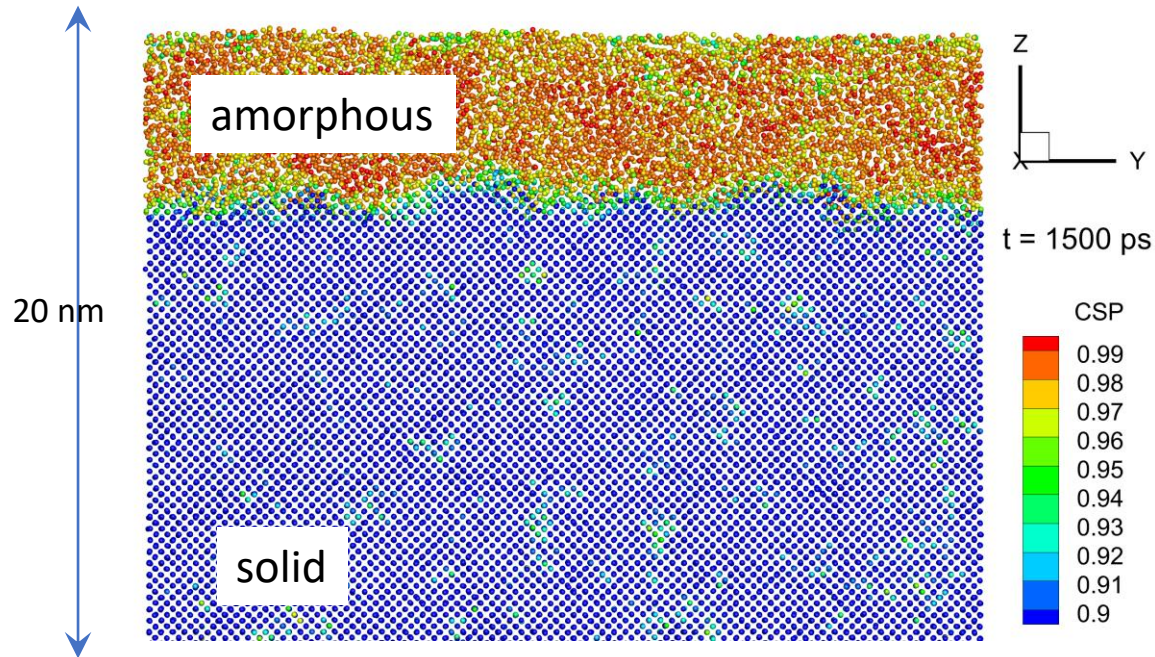
nTTM modeling exhibit 2.5 K/ps

Standard Stillinger-Webber  
F. Stillinger and T.A. Weber,  
*Phys. Rev. B* **31**, 5262 (1985).

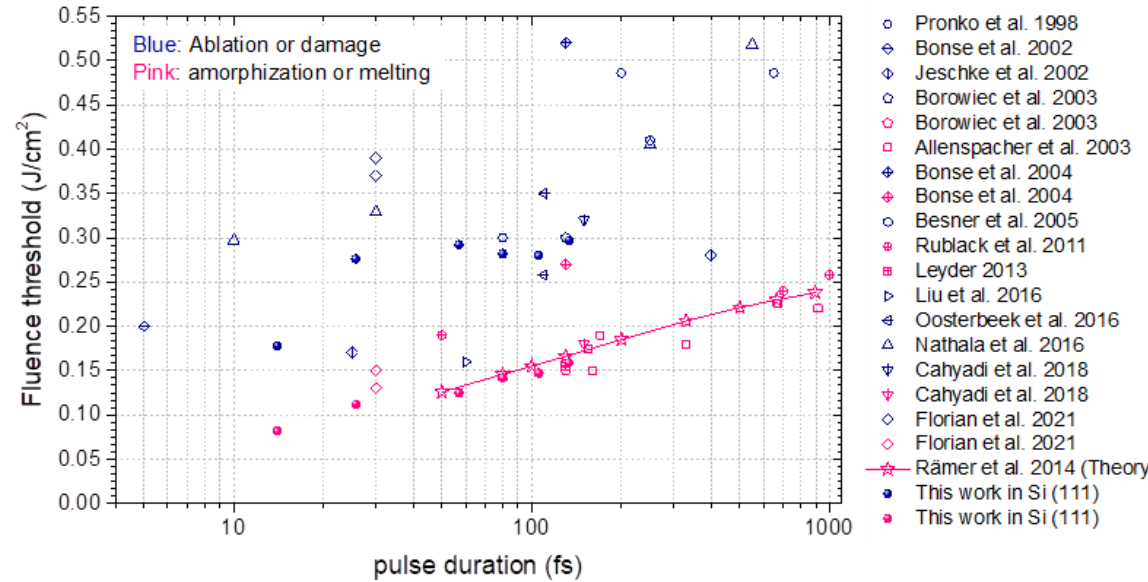
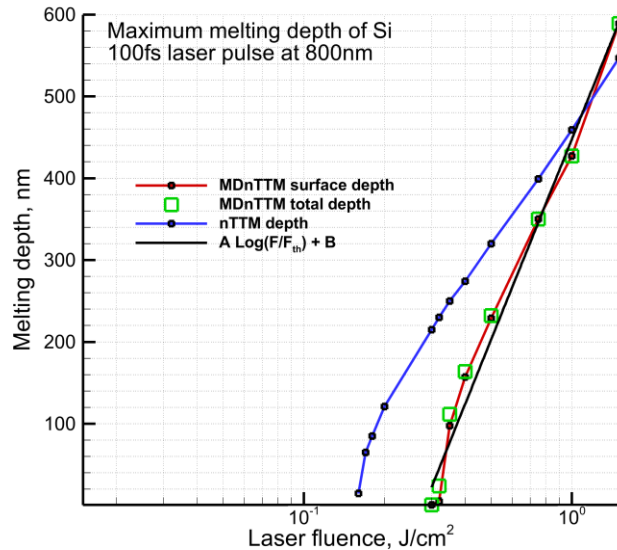
Modified Stillinger-Webber  
R.L.C. Vink, G.T. Barkema, W.F.  
van Weg, and N. Mousseau,  
*Journal of Non-Crystalline Solids*  
**282**, 248-255 (2000).

**K. Schelling, *Comput. Mater. Sci.* 44, 274–279 (2008).**

# Amorphization of Si due to cooling



# Theory vs Experiments



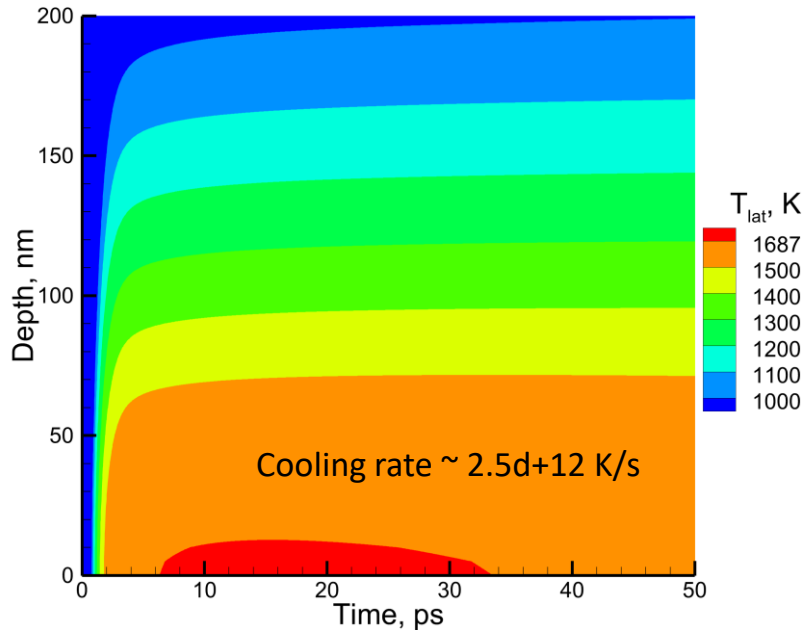
$$d_{\text{melt}} = A \ln(F/F_{\text{th}}) + B$$

$$A = 600\text{nm} \text{ and } B = -220\text{nm}$$

Ivanov, D. S., & Itina, T. E. (2024). Numerical Investigation of the Kinetics of Non-Equilibrium Phase Transitions in Silicon Induced by an Ultra-Short Laser Pulse. *arXiv preprint arXiv:2411.10073*.

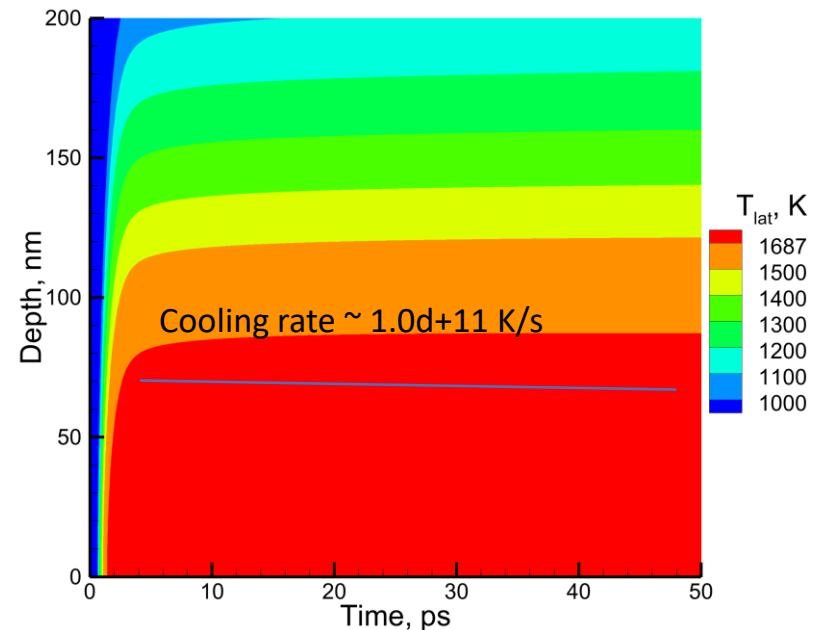
# Cooling rate of Si surface vs fluence

100 fs pulse, fluence 0.16 J/cm<sup>2</sup> at 800nm



Fast cooling rate makes it possible for the formation of the amorphous phase

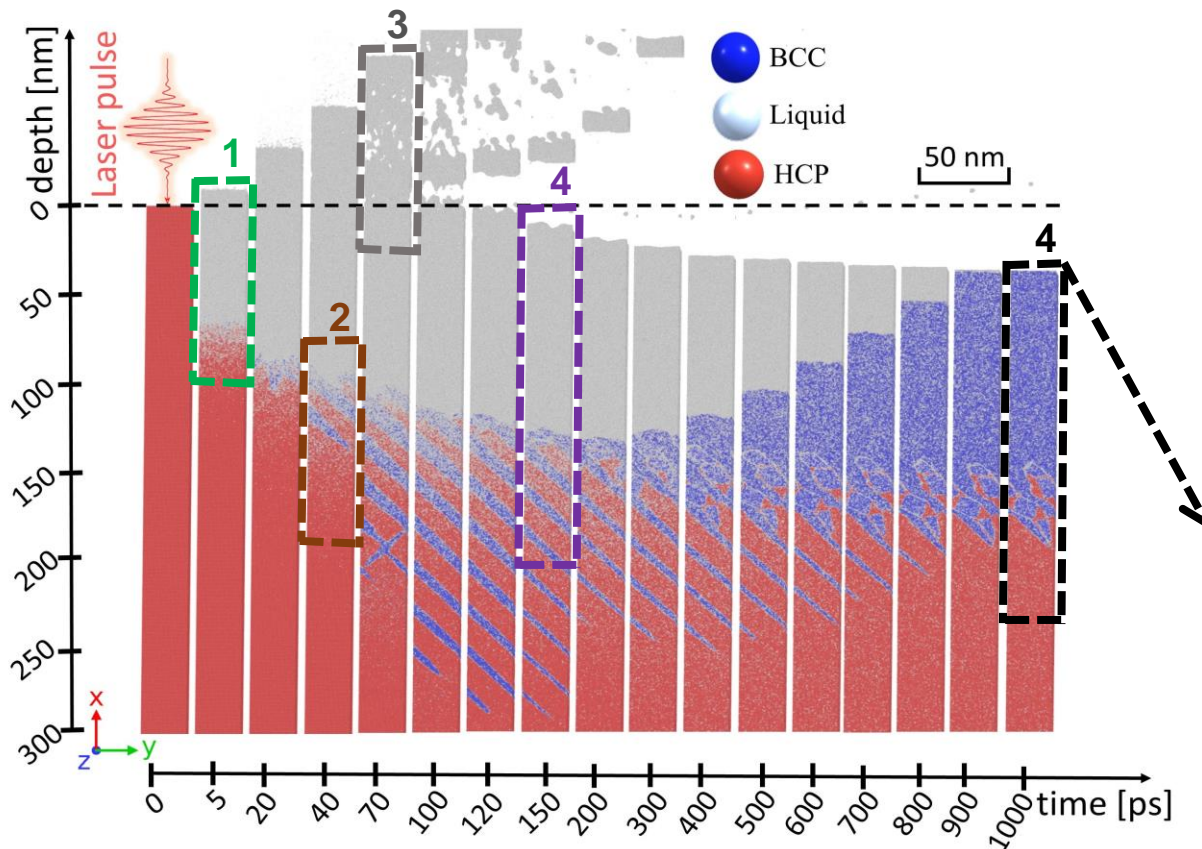
100 fs pulse, fluence 0.18 J/cm<sup>2</sup> at 800nm



Relatively slow cooling rate facilitates the recrystallization process during the liquid-solid transition

**Working just above the melting threshold warrant the surface melting  $\sim$  (10-20)nm with fastest cooling rate, which makes the amorphization possible**

# TTM-MD for ultrafast laser irradiation of Ti



Omeje I. S. et. al. (2024): in preparation.

**1 - Melting**

**2 - BCC nucleates  
(nanotwinned structures)**

**3 - Rapid expansion  
(nanovoids)**

**4 - Resolidification**

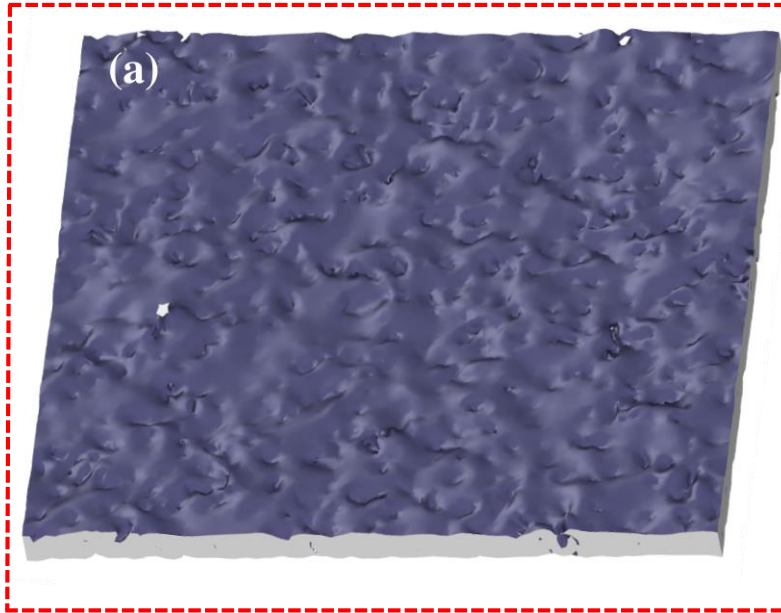
**5 - Preserved crystalline  
(BCC like phase)**

**Subsurface post-  
ablation is extracted  
for: wetting, oxidation,  
etc.**

Atomic evolution during ultrafast laser irradiation with  $\tau = 500$  fs and  $F_{\text{abs}} = 300$  mJ/cm<sup>2</sup>.

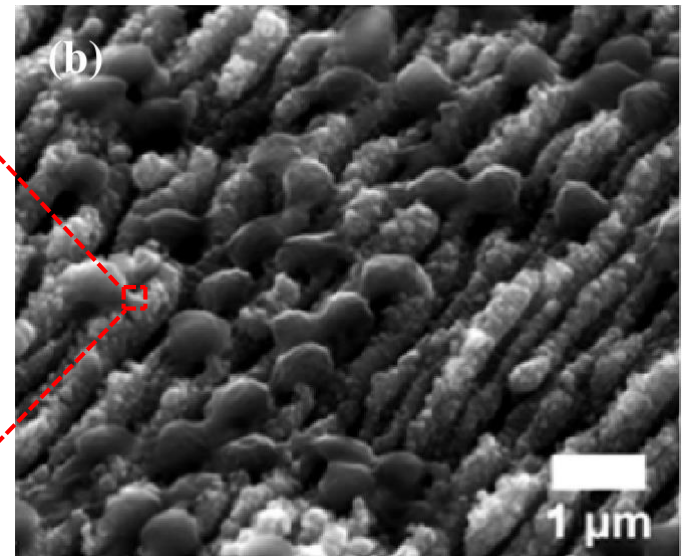
# Ti surface post-ablation in comparison with experiment

## Fs laser irradiation of Ti



**TTM-MD**

Omeje I. S. et. al. (2024): in preparation.



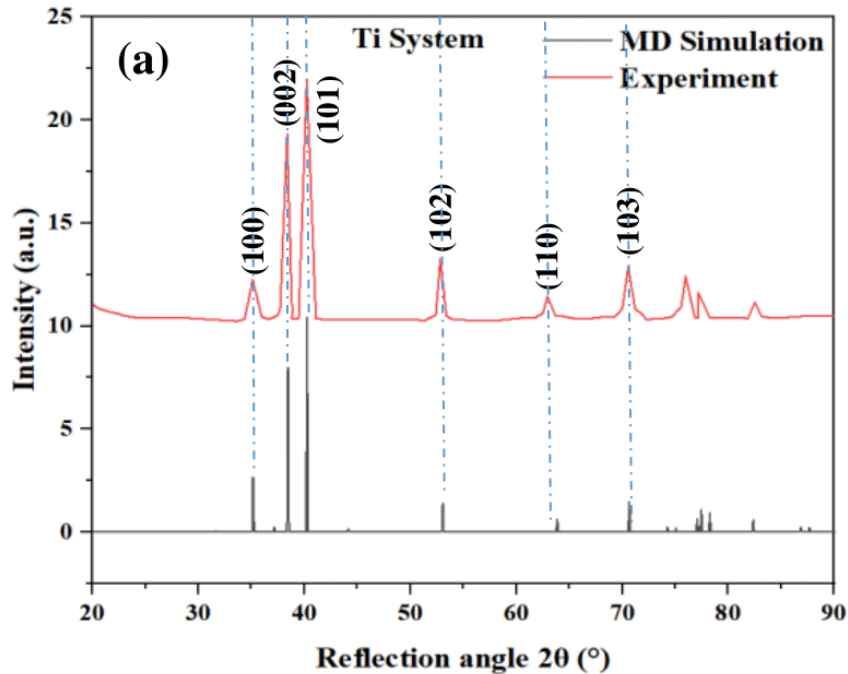
**Experiment**

Alexandre Cunha et al. (2016), pp. 485–493.

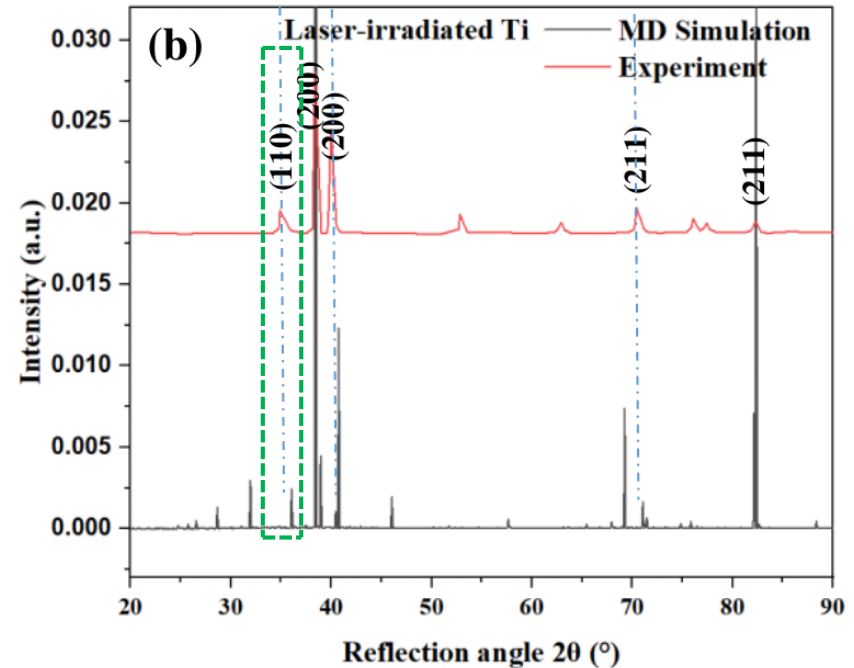
□ **Extracted subsurface compared to that of the experiments**

# Modeling vs Experiments

## XRD patterns



Omeje I. S. et. al. (2024): in preparation.

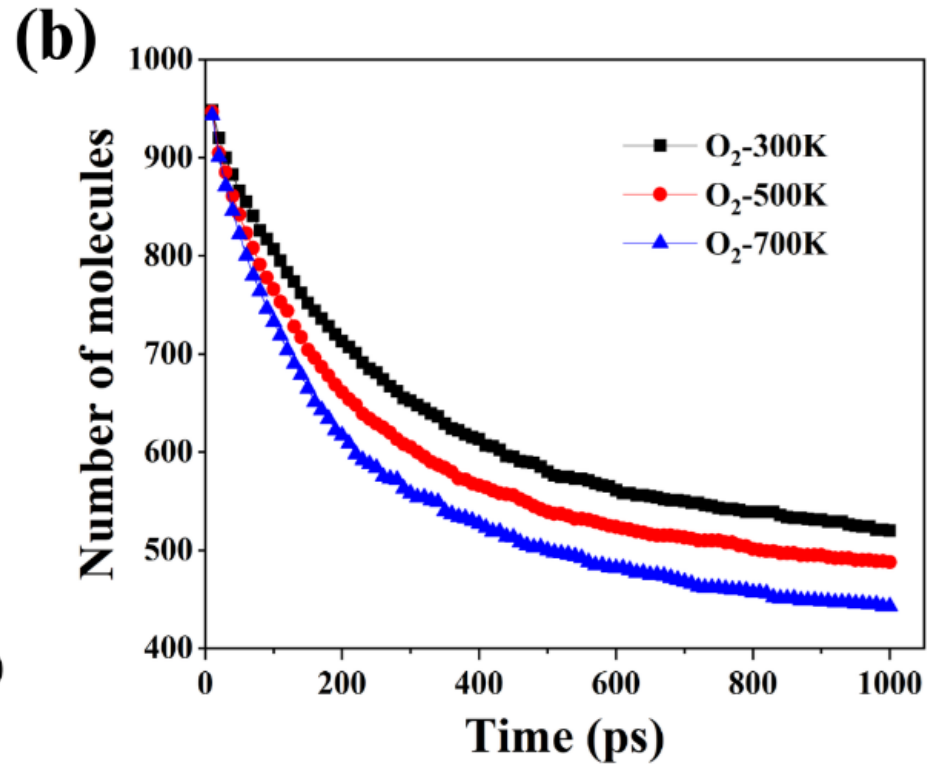
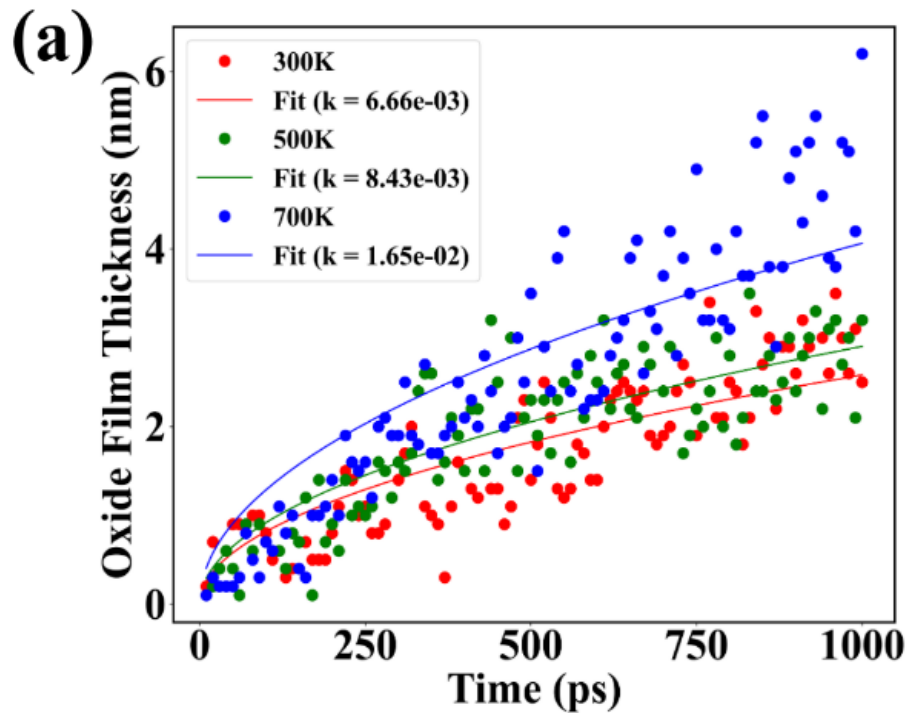


Alexandre Cunha et al. (2016), pp. 485–493.

Crystallography orientation of virtual XRD pattern of non-irradiated Ti of simulation and experiment are in agreement .

For laser-irradiated Ti, BCC like crystallography orientation of 110 of simulation and experiment are in agreement.

# ReaxFF MD Simulations of Early Oxidation



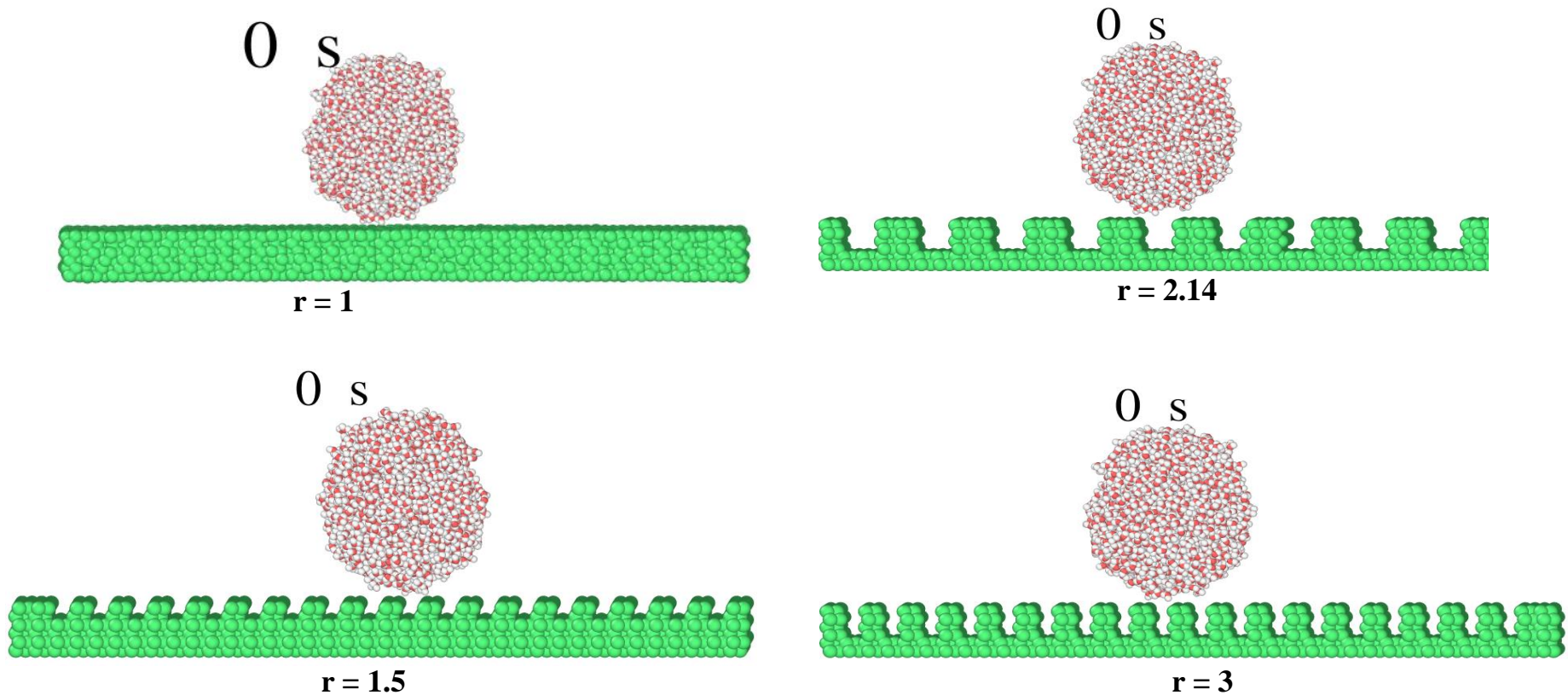
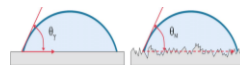
Calculated oxide film thickness formed on Ti surface and change in the number of molecules

Shakeri et al. (2023). Alternative Local Melting-Solidification of Suspended Nanoparticles for Heterostructure Formation Enabled by Pulsed Laser Irradiation. *Advanced Functional Materials*, 33(43), 2304359.

I. S. Omeje et al. 2025, in press, PhD in LabHC in 2024 (Ti oxydation)

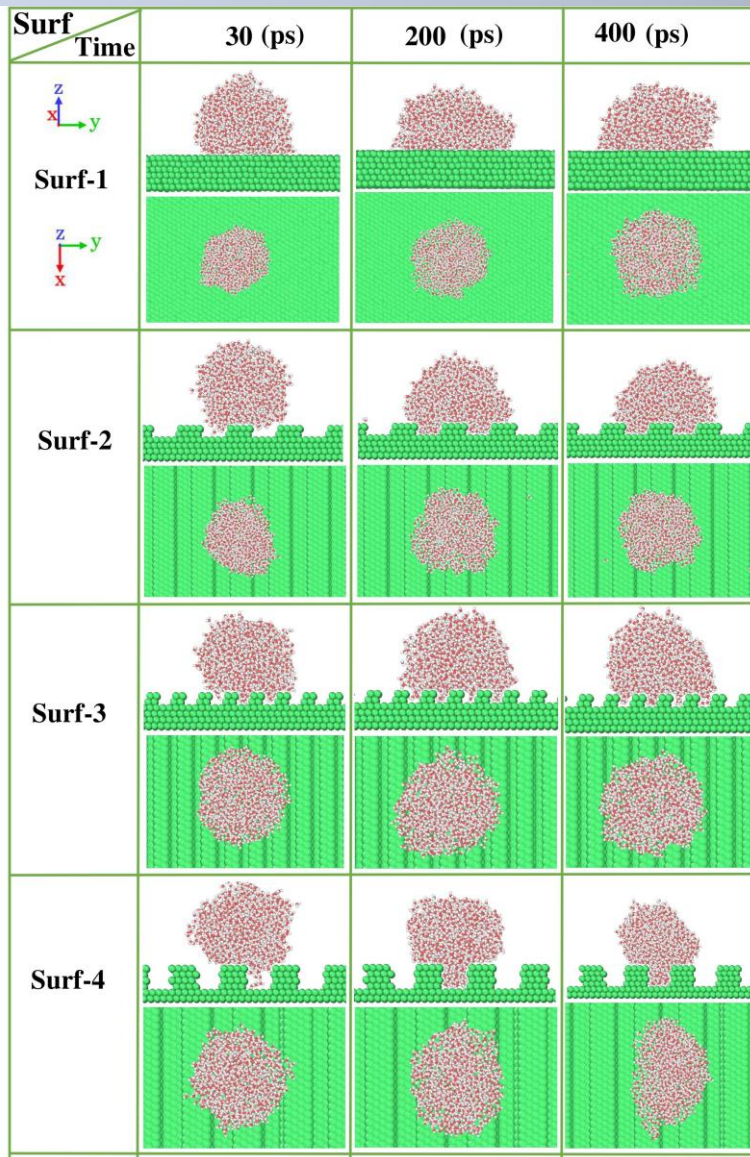
# Effect of nano-roughness on wettability of Ti

I. S. Omeje et al (2024). *ACS Applied Nano Materials*, 7(21), 24426-24436.



A control over nanostructure dimensions presents a viable approach to tailor the wettability of surfaces.

# Effect of nano-roughness on wettability of Ti

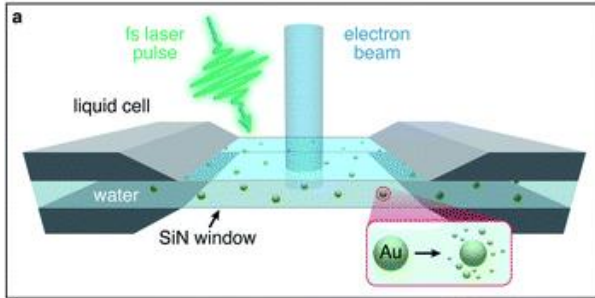


Omeje, I. S., Iabbaden, D., Ganster, P., & Itina, T. E. (2024). Atomistic Simulations of Wetting Dynamics of Water Nanodroplets on Nanotextured Titanium: Implications for Medical Implants. *ACS Applied Nano Materials*, 7(21), 24426-24436.

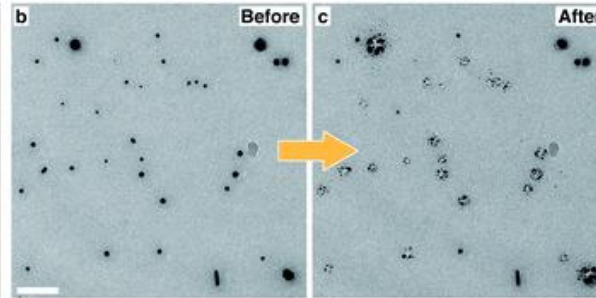
Snapshots of the side and front views of the spreading process of a water nanodroplet on Ti surfaces with different surface structure scales as a function of time.

# Fragmentation: MD simulations

Experimental geometry

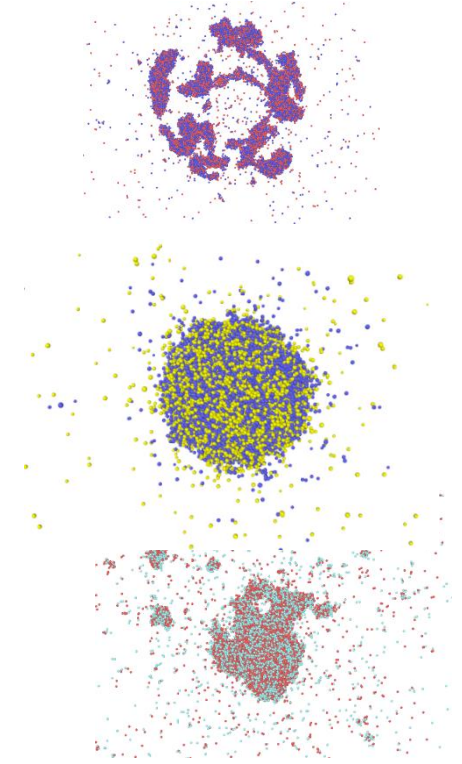
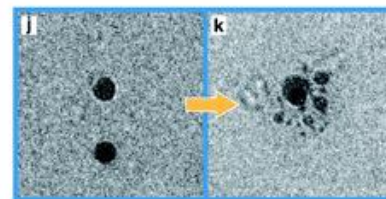
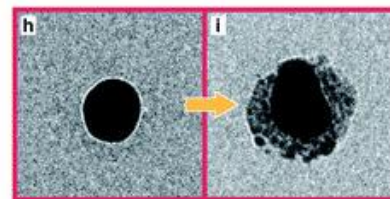
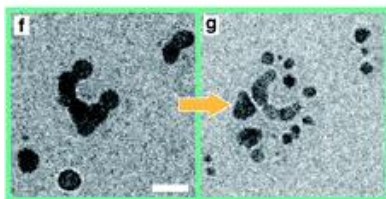
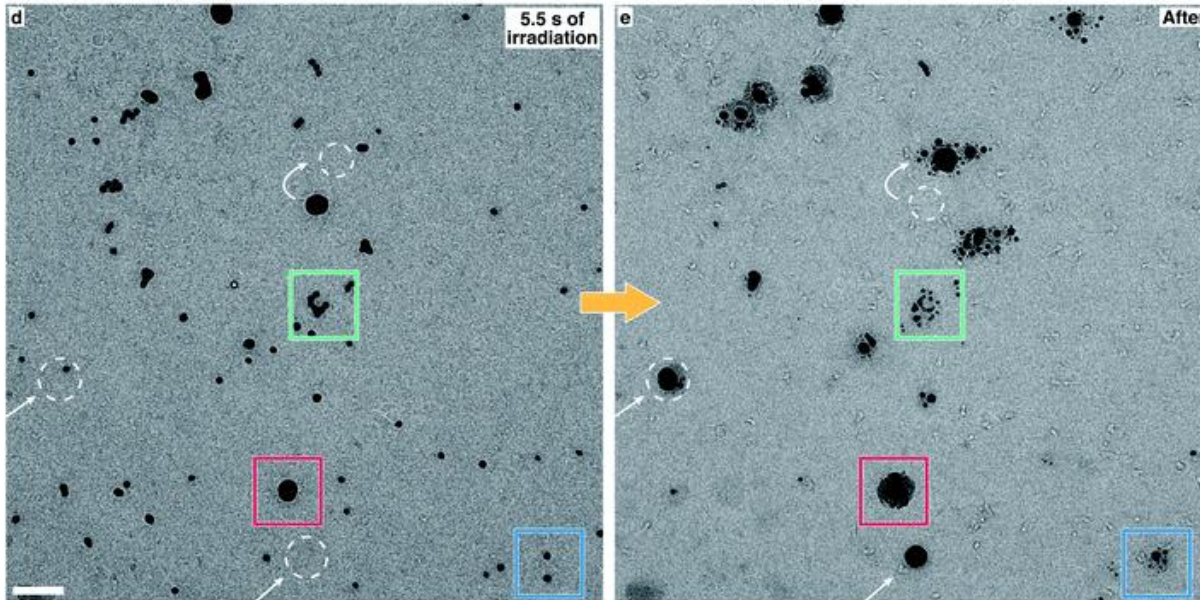


Femtosecond laser irradiation of gold nanoparticles



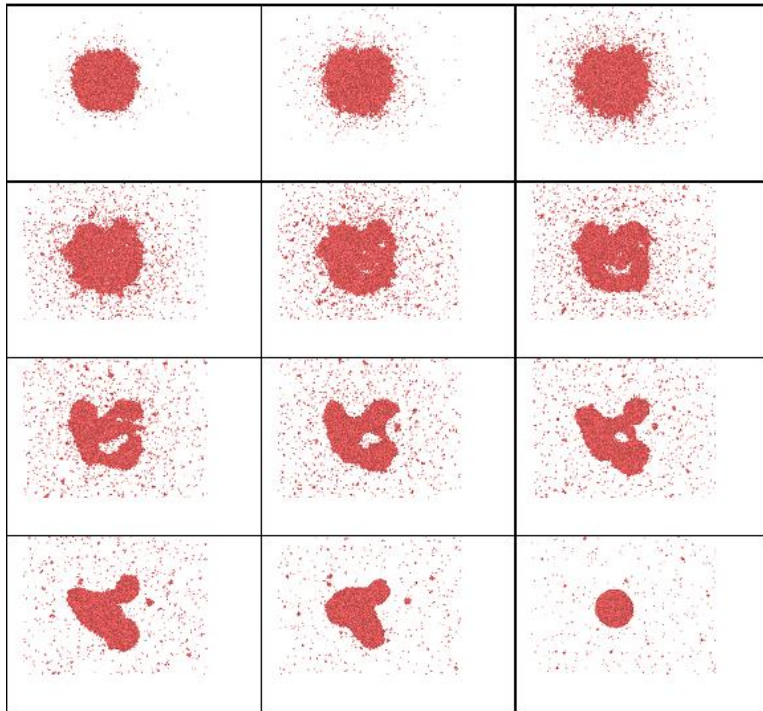
MD results for NPs of different materials, absorbed energy, and sizes

In situ observation of gold nanoparticle fragmentation under femtosecond laser irradiation

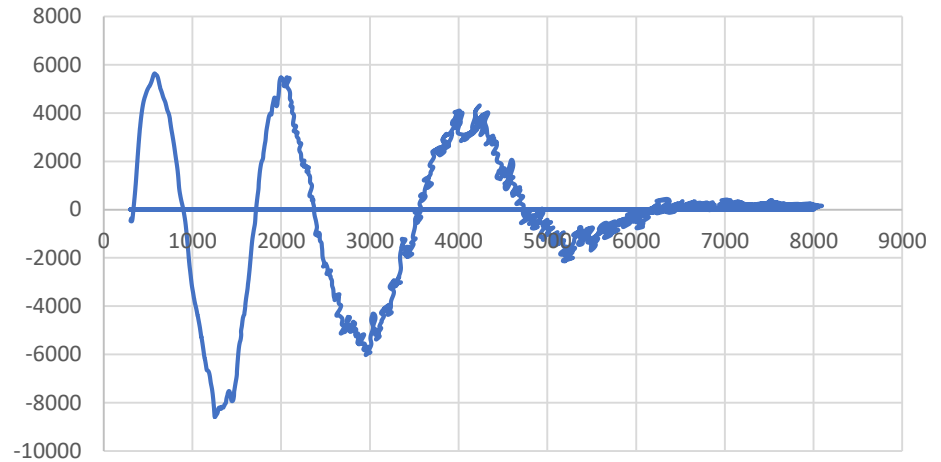


# Laser Interaction with NPs

Vibrations and fluid instabilities



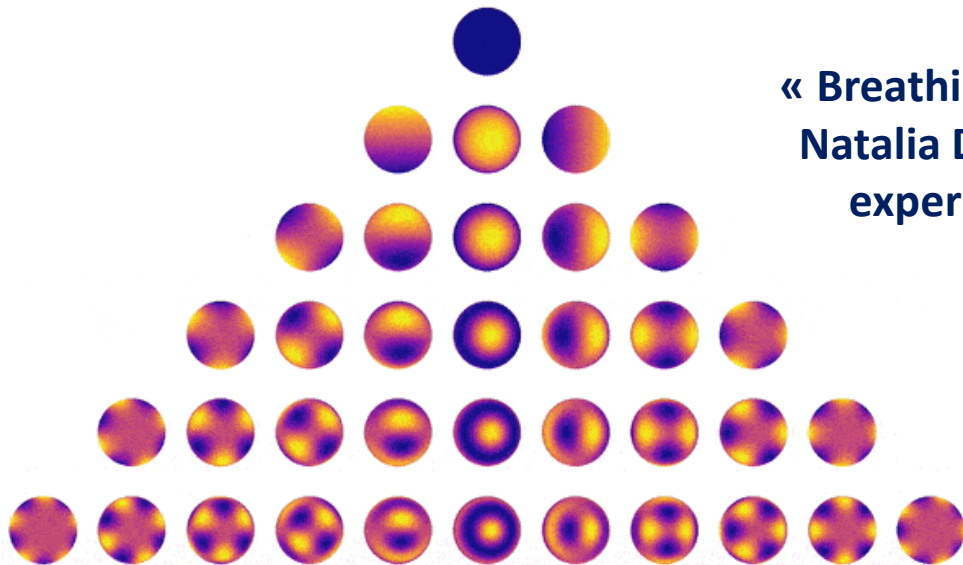
Pressure vs Temperature



Au nanocluster with radius  $R=50$  uc  
(uc is unit cells length, 0.407 nm for Au),  
 $N=30845$  atoms and maximum  
temperature  $T_{\max}=8000\text{K}$  obtained at  
time delays  $t=0.1, 5, 10, 20, 50, 100$  ps  
after the beginning of strong and short  
(20ps) heating

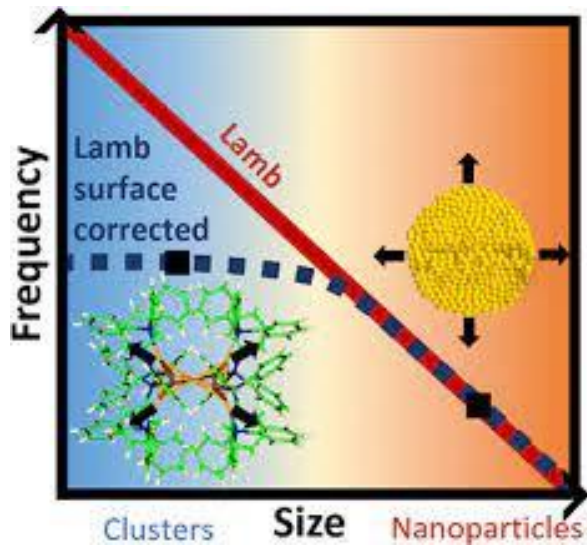
T. E. Itina, RCS Nanoscale Advances  
6, 5451 (2024)

# Spherical vibrational modes (Lamb's modes)

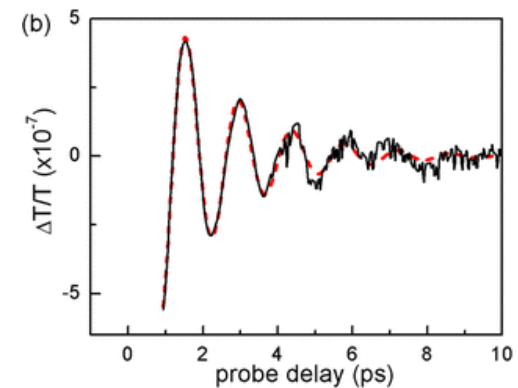
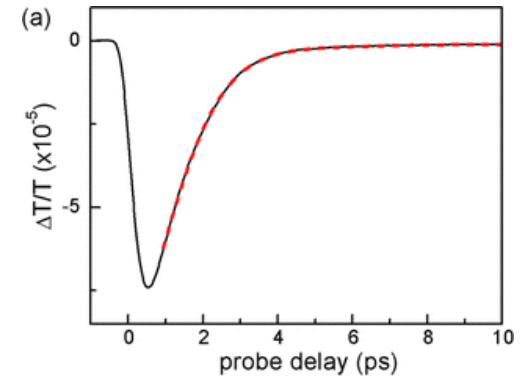


« Breathing of NP »  
Natalia Del Fatti's  
experiments

[https://mlmlovevs.live/product\\_details/30121909.html](https://mlmlovevs.live/product_details/30121909.html)



[doi: 10.1021/acs.jpcc.0c04722](https://doi.org/10.1021/acs.jpcc.0c04722)



<https://doi.org/10.1021/jp309499t>

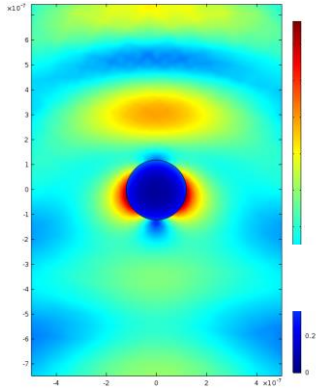
**Acoustic vibrations of nanoparticles:**

**Complex spherical modes**

(dipole, quadrupole etc. modes : similar to electromagnetic ones)

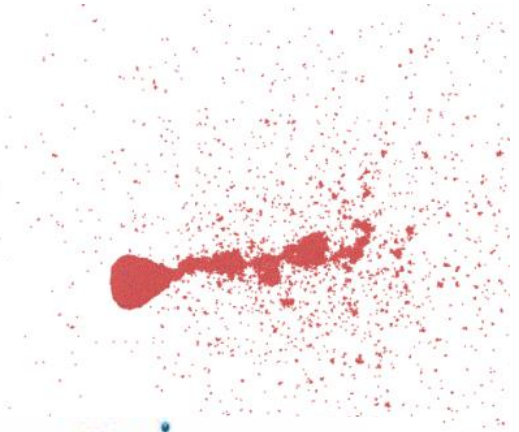
# Symmetry breaking ?

Au NP in water



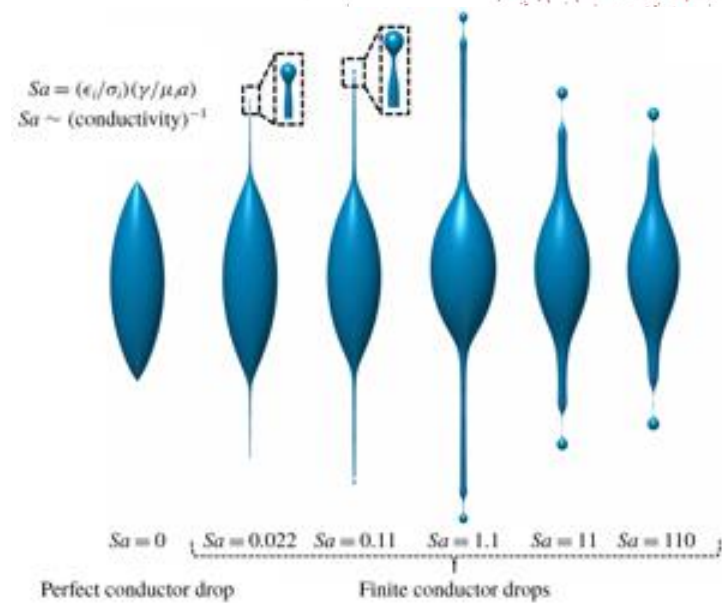
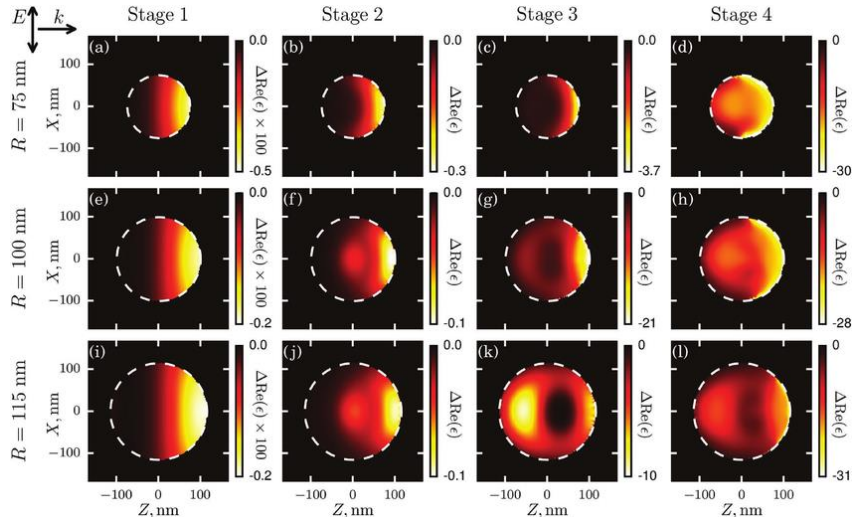
Itina T.E, *Nanoscale Adv* 2024, 6, 5451

Fluid instabilities



Bhuyan, M. K., Soleilhac, A., Somayaji, M., Itina, T. E., Antoine, R., & Stoian, R. (2018). *Scientific Reports*, 8(1), 9665.

Si NP



Ion Jets and Rayleigh break-up

*Journal of Fluid Mechanics*, Volume 884, 10 February 2020, A31  
DOI: <https://doi.org/10.1017/jfm.2019.970>

Rudenko, A., Ladutenko, K., Makarov, S., & Itina, T. E. (2018).

Nanoparticle. *Advanced Optical Materials*, 6(7), 1701153.

# SUMMARY

**In this study, we have employed atomistic simulations to investigate ultrafast laser interactions with metallic and silicon materials. The results highlight the diverse strongly non-equilibrium phenomena induced by ultrashort pulses, from subtle modifications to nanoparticle formation and surface oxidation. Key insights include:**

- The critical role of material structure and electron-lattice coupling in determining material responses.
- Non-equilibrium processes, such as melting, ablation, oxidation can be simulated both at low and high lattice temperatures.
- The sensitivity of surface modifications to laser fluence and to ambient environment.
- The potential for tailoring material properties through controlled laser parameters.
- Thus, atomistic modeling are particularly valuable in advancing femtosecond laser-based technologies and provide a framework for future research into nanofabrication and material treatment.

## ACKNOWLEDGEMENTS

We acknowledge the financial support of the French National Research Agency (ANR) under LAMORSIM project [Project-ANR-23-CE08-0029], and CINES of France for the computational resources needed for large-scale simulations.

**Thank you very much  
for your attention!**

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