Molecular dynamics investigation on tin

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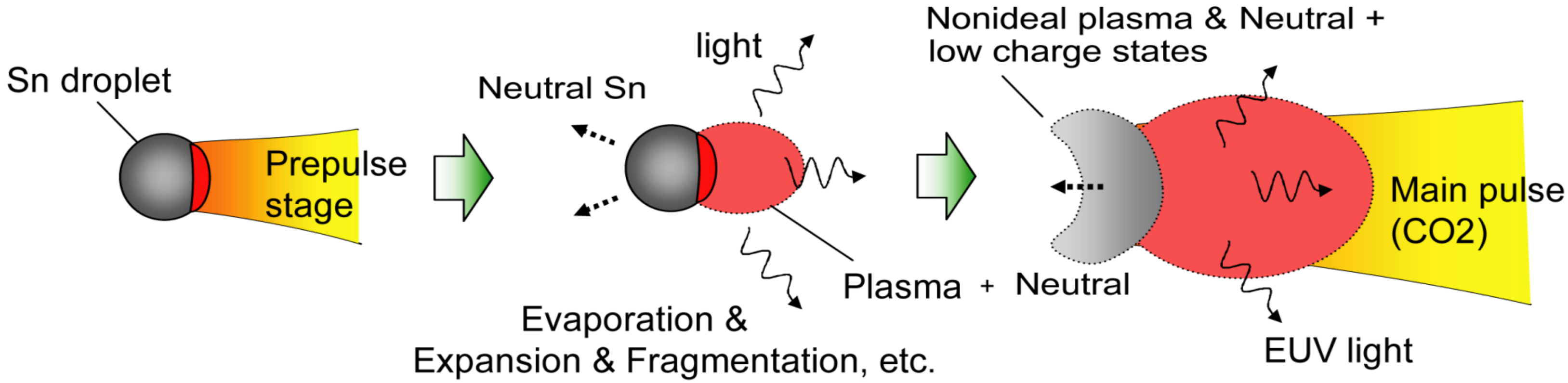
Outline

1. Background & Motivation
2. Introduction:
   - Laser-produced plasma (LPP) modeling
   - Warm dense matter (WDM)
   - Qualitative example
3. Results: Materials Studio code (MS) & Own program
4. Summary
5. Future investigations

Acknowledgments to Gigaphoton Inc.

Background & Motivation



Nakamura, J. Phys. D (2008) & Shimomura, Appl. Phys. Express (2008).

LPP experiments (high heating /cooling rate):

1. **Is really possible to control particle trajectory?**
2. **What is thermodynamic pathway?**
3. **What is equation of state (EOS)?**
4. **Time is not a thermodynamic coordinate.**
   Is kinetic phase transition important?

1. **Debris-mitigation including neutral Sn**
2. **Physics of laser ablation including condensation**
3. **EUV mirror contamination**
4. **Improving plasma radiation**

LPP modeling & Warm dense matter

Exact hydrodynamics modeling needs EOS (+ kinetic effects) on whole ablation pathways.

- Binode & spinode: liquid-gas mixture .

(1) Adiabatic expansion with droplets creation after a weak heating.

(2) Adiabatic expansion with partial re-condensation after strong heating.

(3) Adiabatic expansion with a transition into plasma and gas phases.

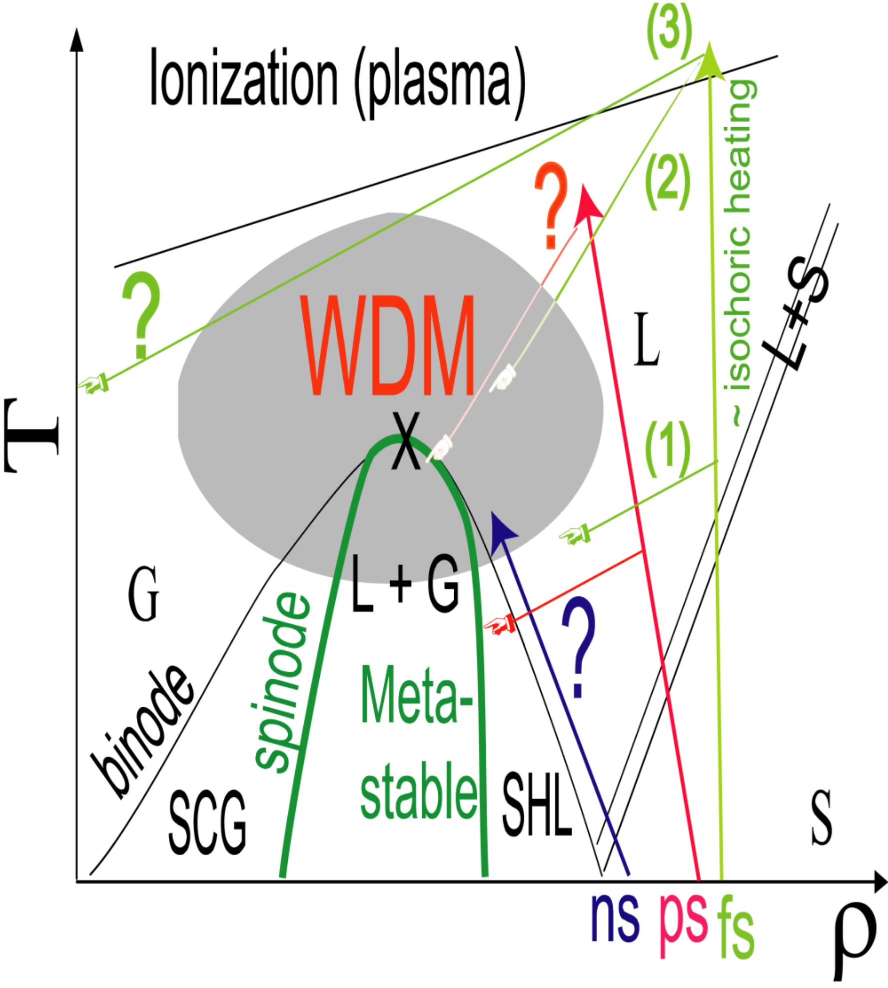
Lescoute, Phys. Plasmas (2008).

Initial stage pass through:

WDM: 0.1 eV ≤ T ≤ 10 eV, 0.01 g/cc ≤ρ ≤ 10 g/cc

Solid & Liquid Sn: ~ (5-7) g/cc

- Warm + dense → rapid hydrodynamic → transient phenomena.
- Evaporation & condensation kinetics are fast.
- Laser absorption: not well-known.
- Critical parameters: not well-known.



Typical density – temperature space. X: critical point.
SHL: superheated liquid. SCG: supercooled gas.
ns & ps & fs : typical laser pulse in EUV source.

LPP modeling & Warm dense matter

Superheating (supercooling) is demonstrated for solid and liquid.

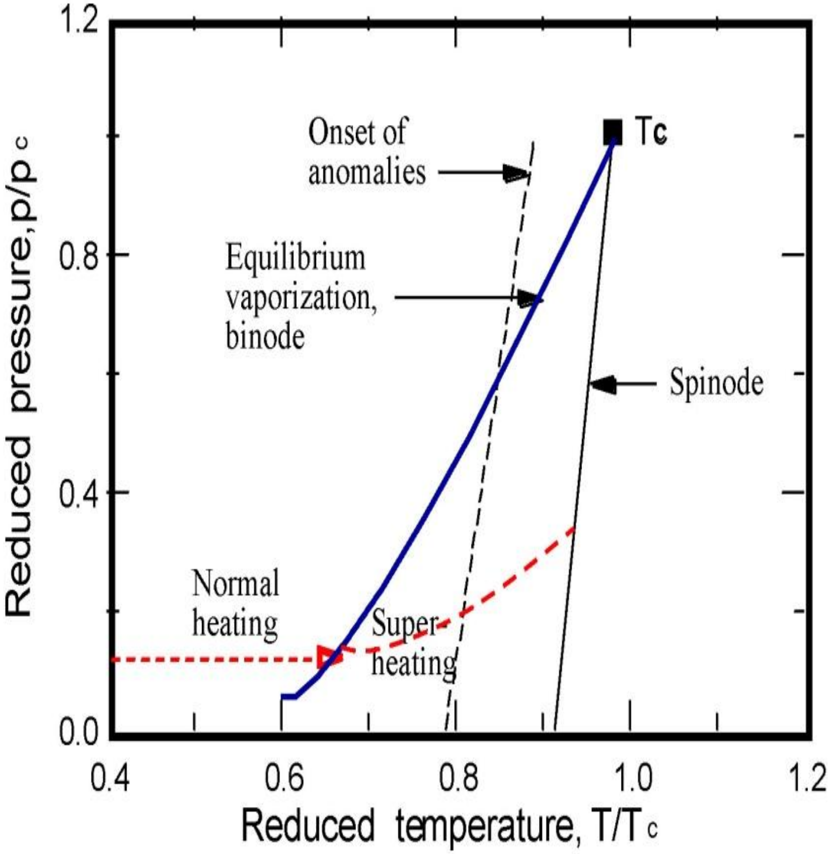
Iglev, Nature (2006) & Luo, Phys. Rev. B (2003) & Xu, J. Heat Trans. (2002) & Lewis , Appl. Surf. Sci. (2009).

Thermodynamic (equilibrium stage)

Slow heating → binode →
Clausius-Clapeyron equation.

Non-equilibrium (metastable liquid)

High energy deposition →
metastable state →
phase explosion,
spallation, fragmentation



Typical P-T diagram of phase explosion. Dome in solid line is binode. Dome in dashed line is spinode. Tc and pc are critical parameters.

- **Pure liquid: homogenous nucleation time ≈ ns.**
- **Liquid metals: spontaneous nucleation is longer or not realized even for very large superheating (is under investigation by molecular dynamics).**

Bulgakova, Appl. Surf. Sci. (2007), etc.

Prelude

High CE: only a thin Sn layer below 40 nm gives efficient EUV emission (opacity effect) → a fully atomistic simulation is needed to study this layer.

Shimomura, Appl. Phys. Express (2008) & Fujioka, J. Phys. Cof. Series (2008).

Current modeling

1) Ns laser: electron temperature (Te) = lattice temperature (T)
2) Ps laser, after a few ps ≈ (1-20 ps): Te = T
3) Fs laser, after a few ps ≈ (1-20 ps): Te = T

Ivanov, Phys. Rev. B. (2003) & Cheng, Phys. Rev. B (2005) & Vatsya, J. Laser Appl. (2003), etc.

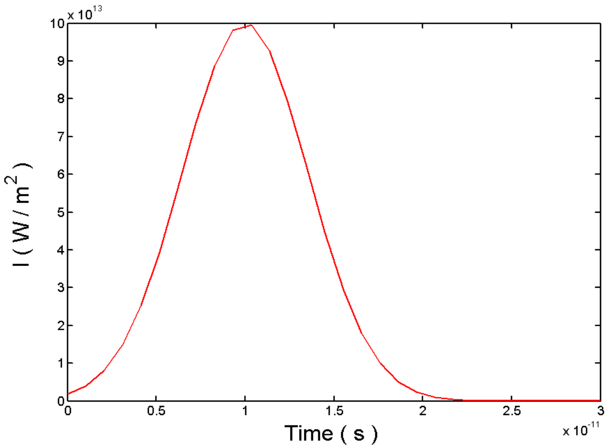
Electron-phonon coupling constant versus Te using density functional theory molecular dynamics code (CASTEP) → couple two-temperatures heat equation model and molecular dynamics.

Lin, Phys. Rev. B (2008) & Hopkins, Nanoscale and Microscale Thermophysical Engineering (2008).

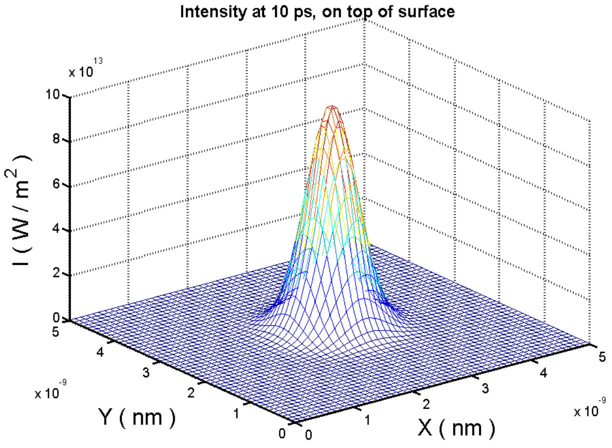
Qualitative example (I), Sn ablation in vacuum

Fast, low power laser heating of a thin layer: not so violent ablation, like stress ablation.

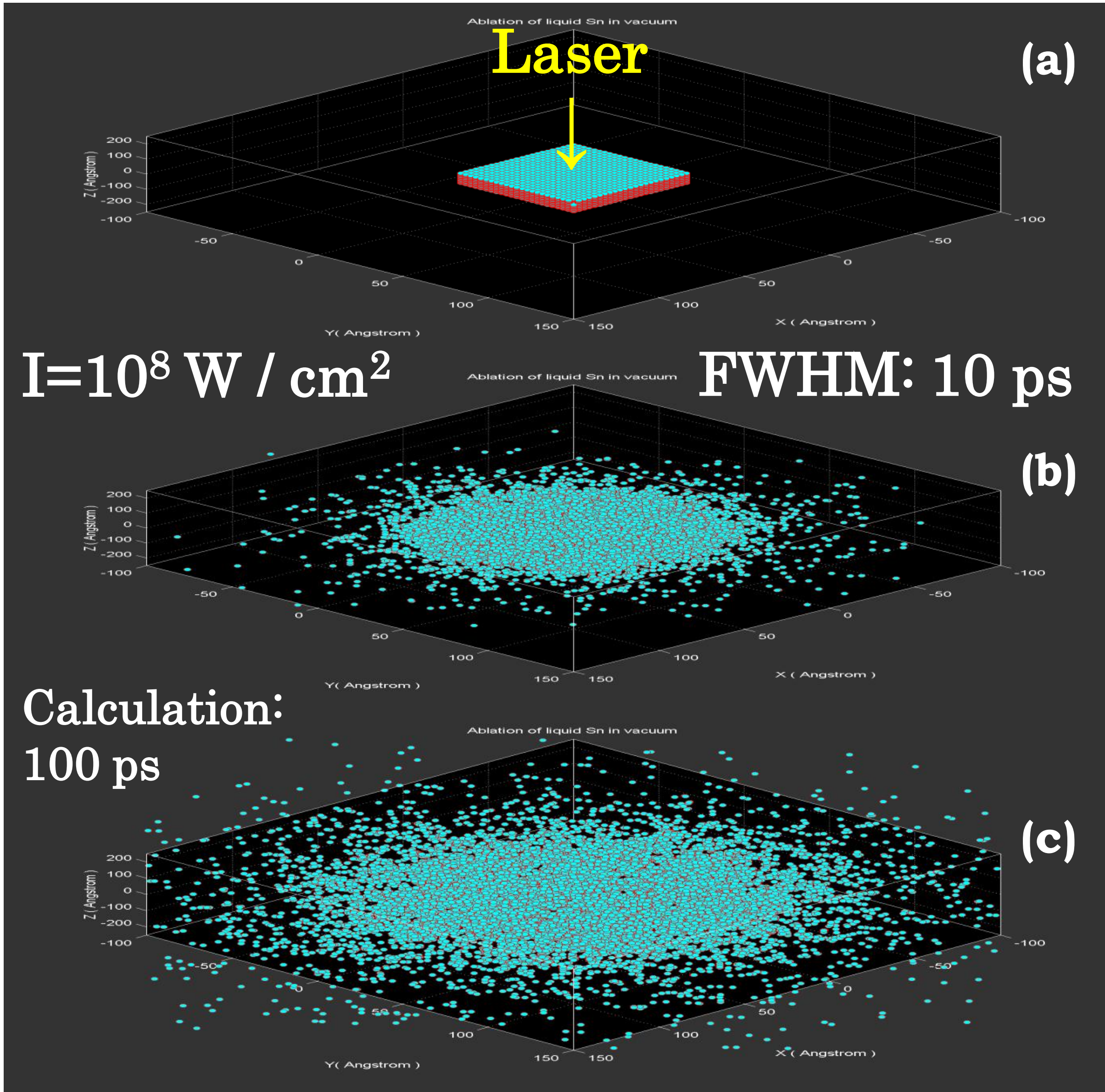
Temporal laser variation



Spatial laser variation on top; Inside: Lambert-Beer's law



Wang, J. Phys. D (2005).



I=10^8 W / cm^2

FWHM: 10 ps

Calculation:
100 ps

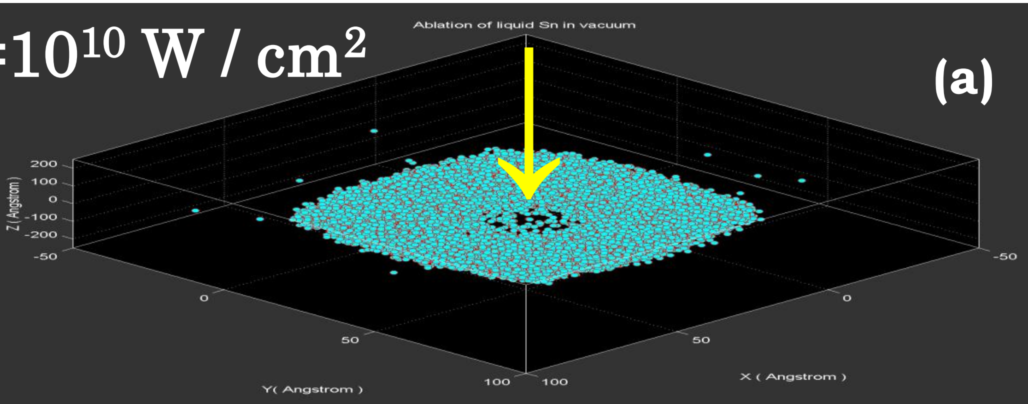
Qualitative example (II)

Fast, high power laser heating of a thin layer → High heating rate (laser drilling) → Rear fragmentation

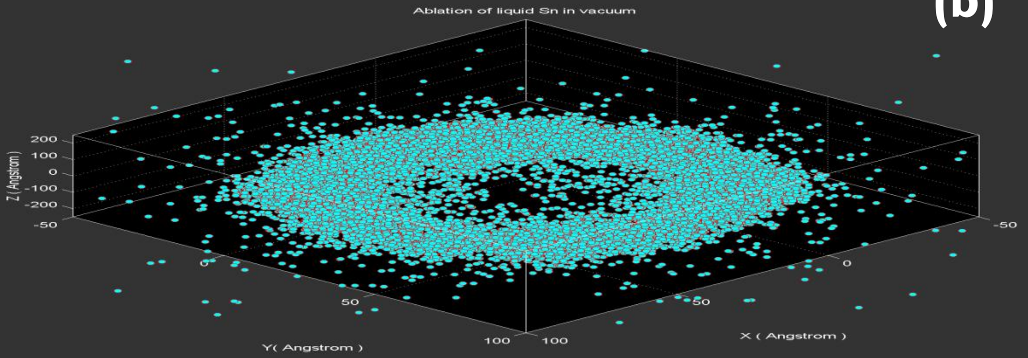
I=10^{10} W / cm^2

High initial heating rate:
$dT/dt \approx 10^{14} - 10^{15}$ K / s

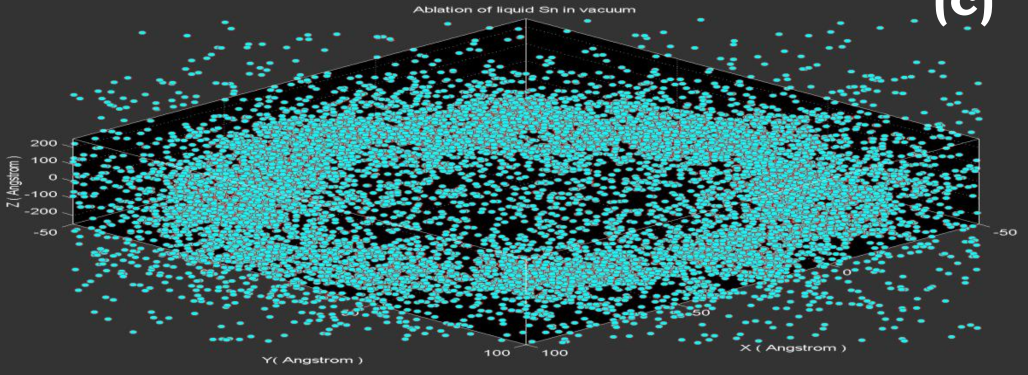
(a)

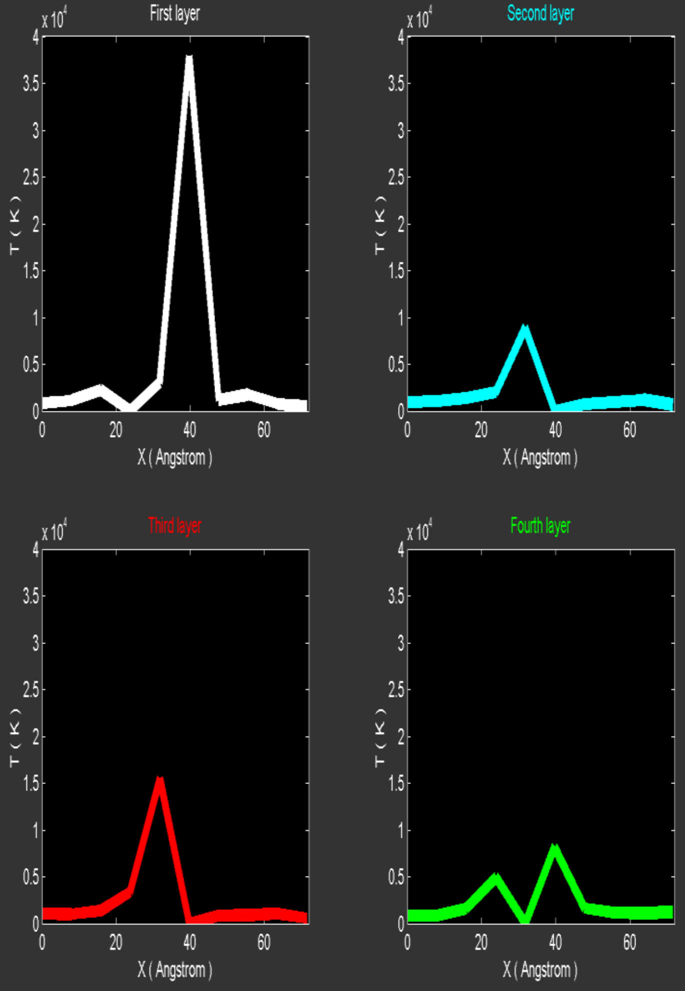


(b)



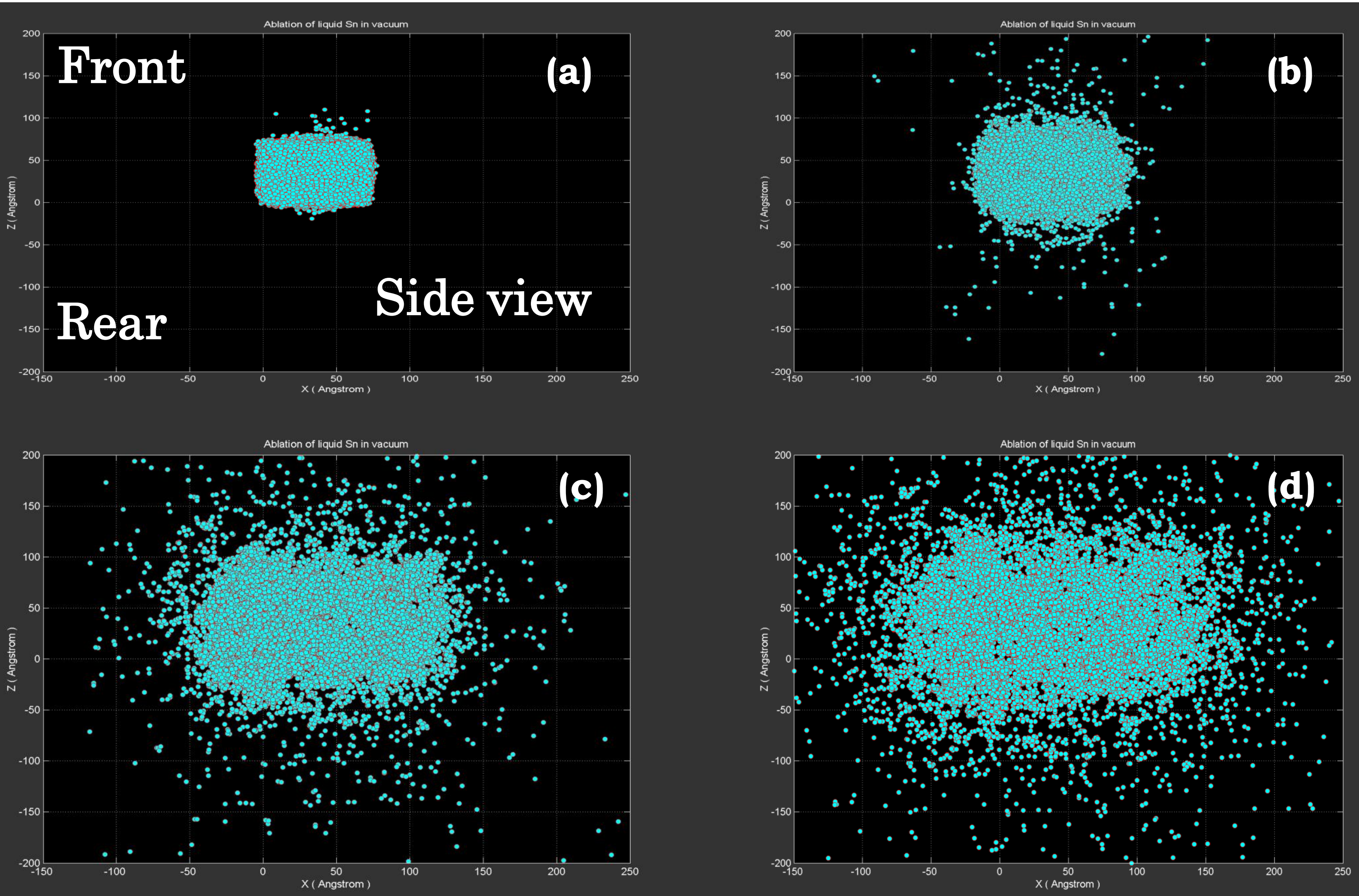
(c)





Qualitative example (II)

Fast, high power laser heating of a thin layer → High heating rate (laser drilling) → Rear fragmentation

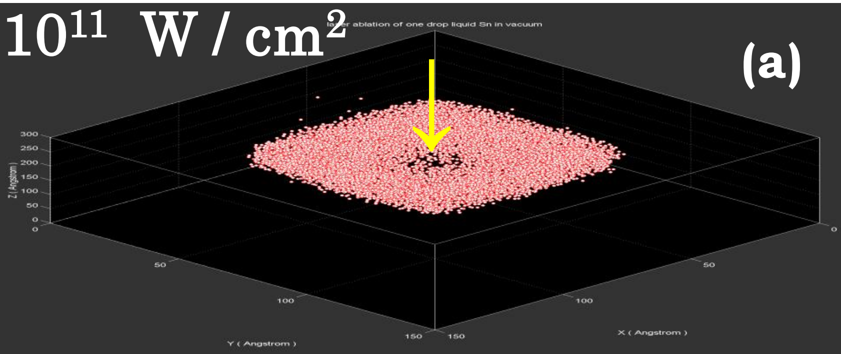


Qualitative example (III)

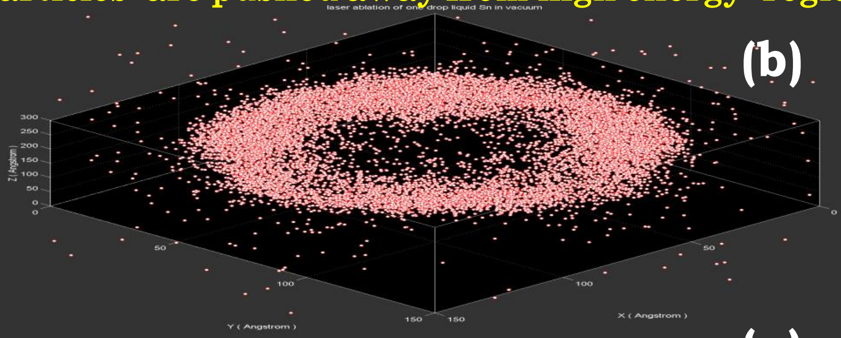
Fast, high power laser heating → Gibbs free energy is not minimum → Non-equilibrium thermodynamics

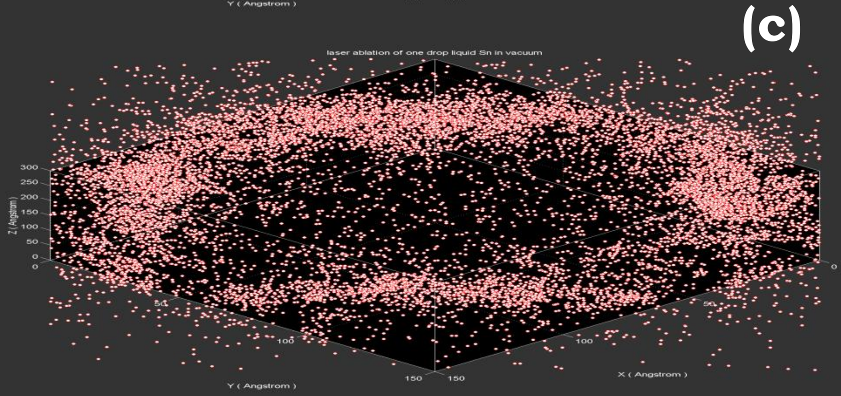
High power laser heating of a thin layer → Laser energy > binding energy of object → Fully disintegration

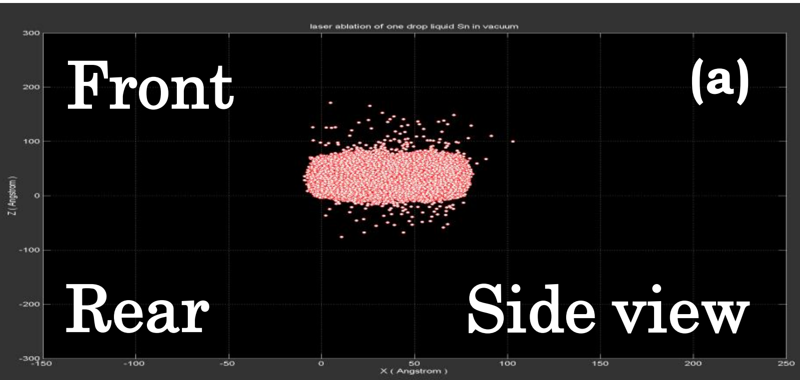
$I=10^{11}\ W / cm^2$

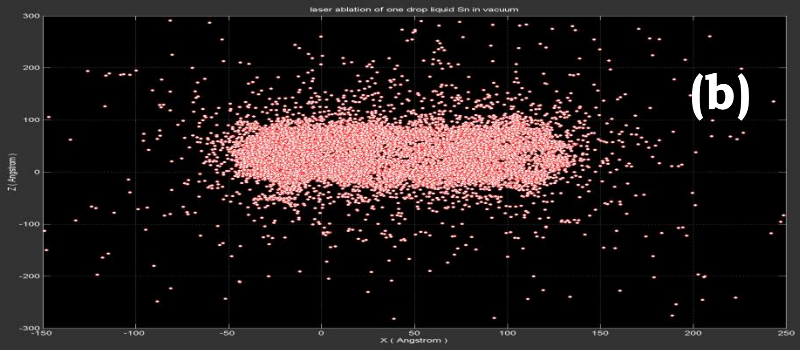


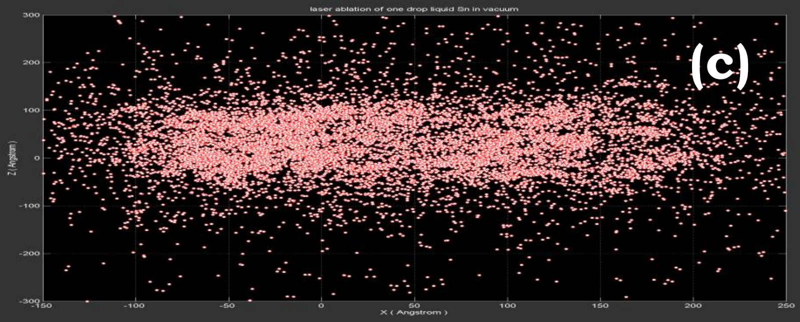
Particles are pushed away from high energy region





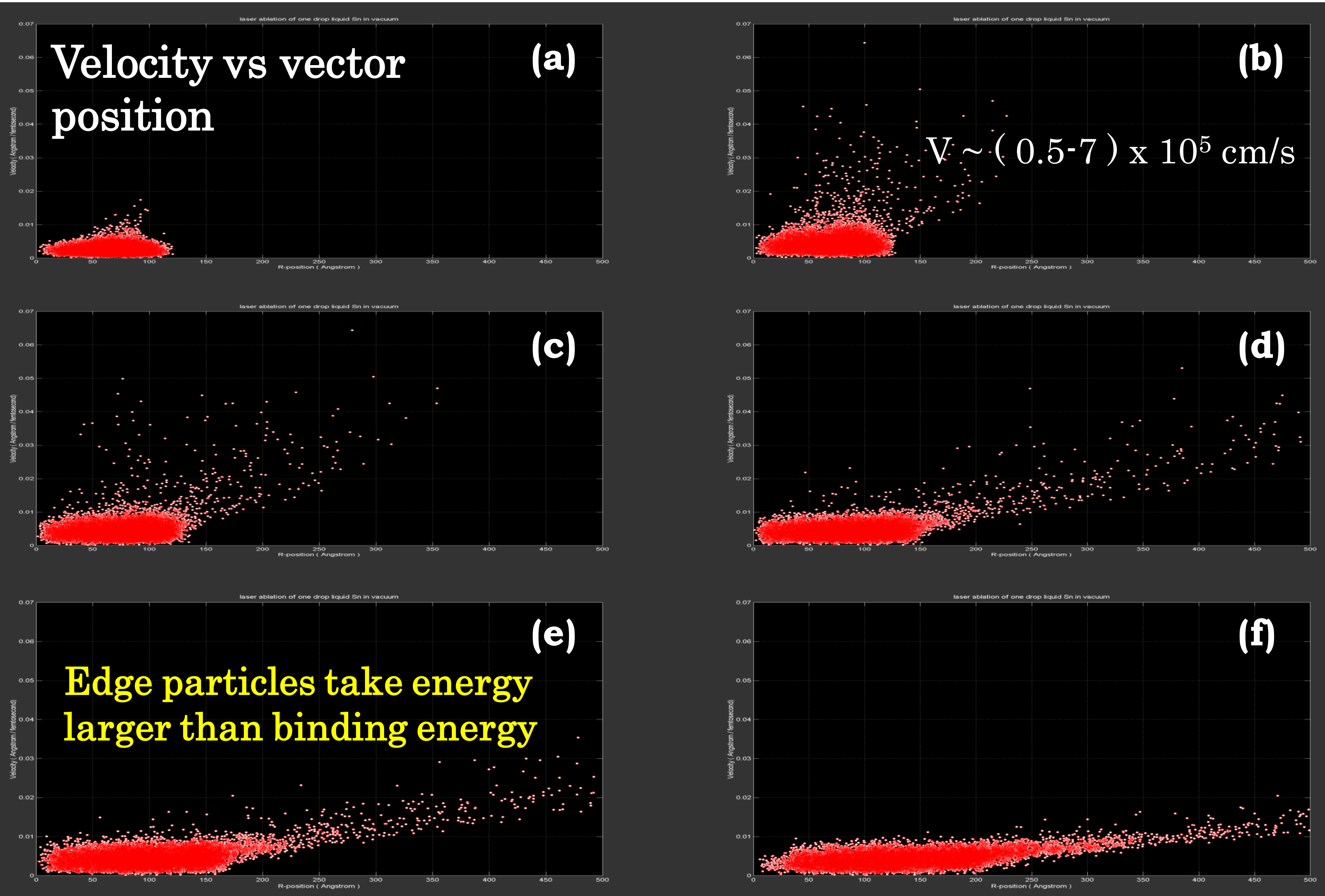






Qualitative example (III)

Thermal and Non-thermal ablation (edge particles)



Velocity vs vector position

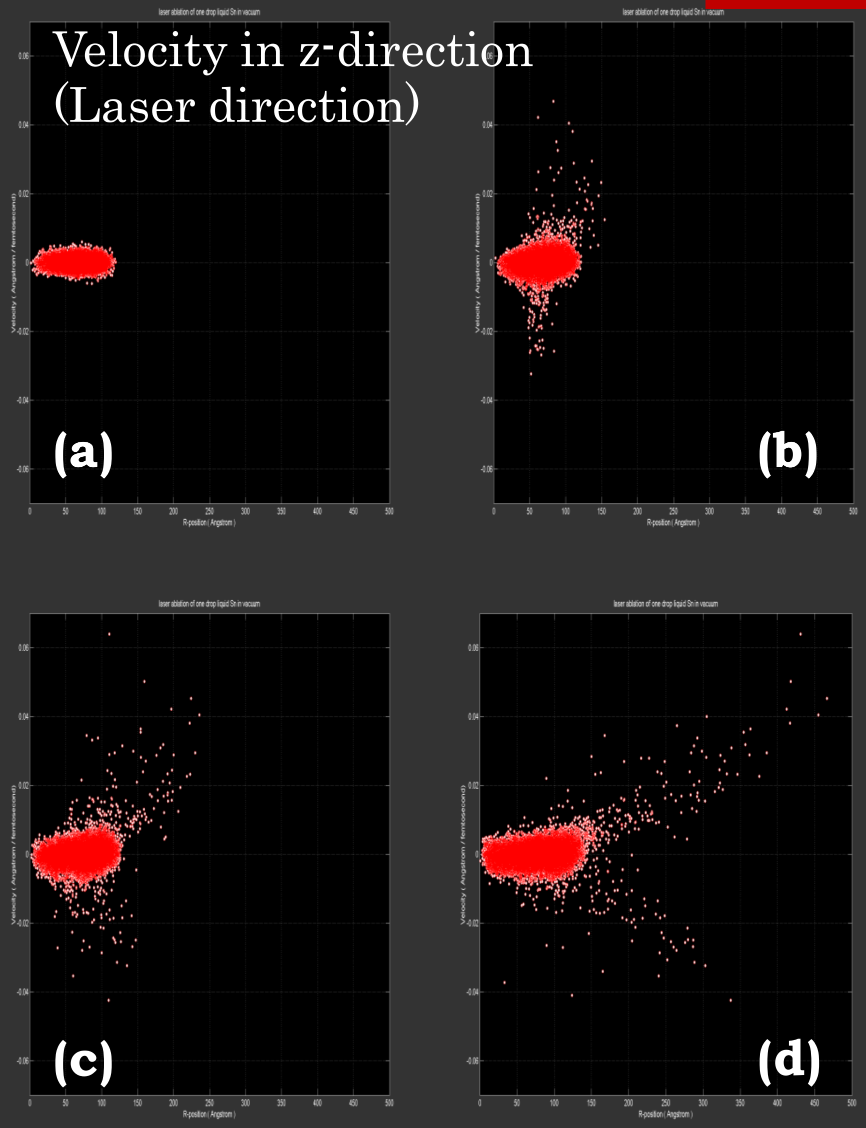
$V \sim (0.5\text{-}7) \times 10^5$ cm/s

Edge particles take energy larger than binding energy

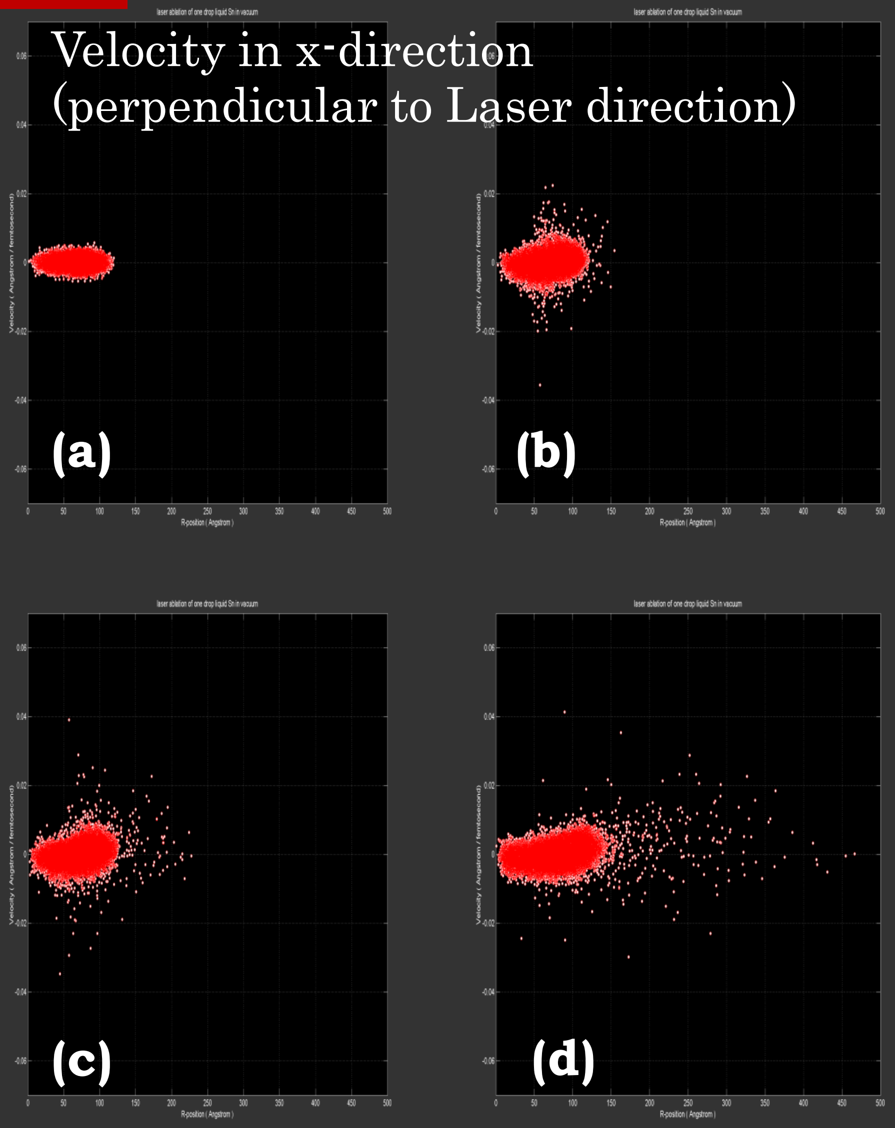
Qualitative example (III)

Thermal and Non-thermal ablation (edge particles)

Vz > Vr (radial direction)



Velocity in z-direction
(Laser direction)

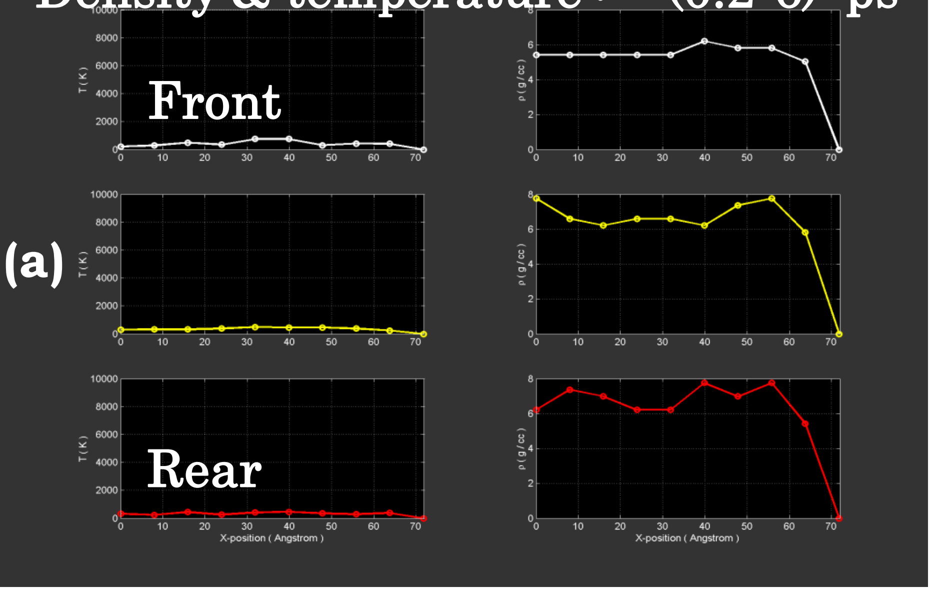


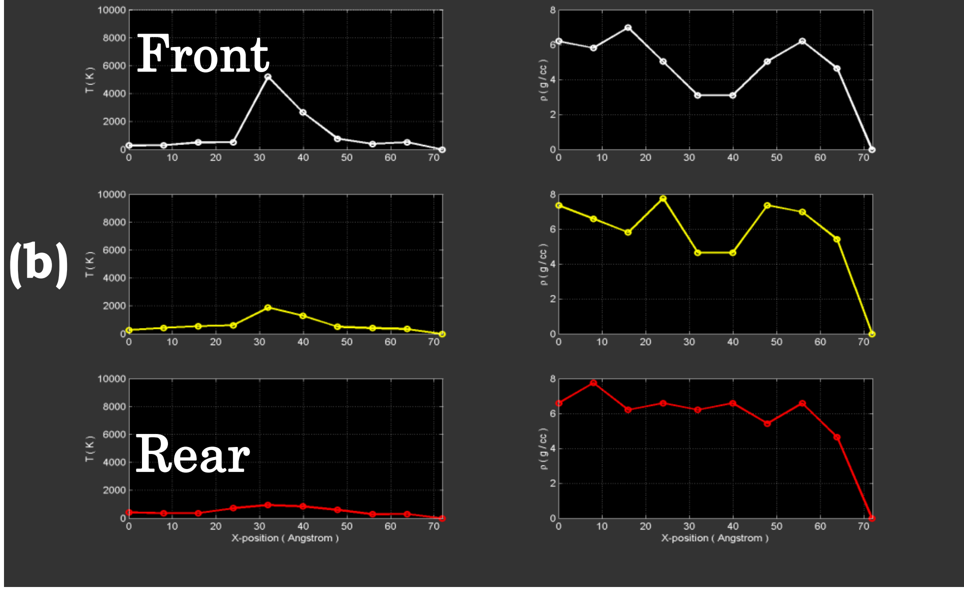
Velocity in x-direction
(perpendicular to Laser direction)

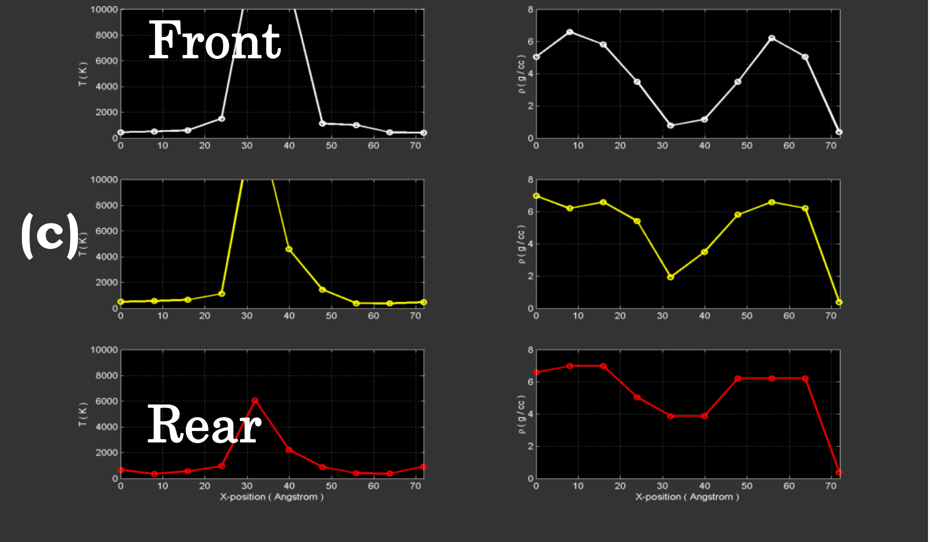
Qualitative example (III)

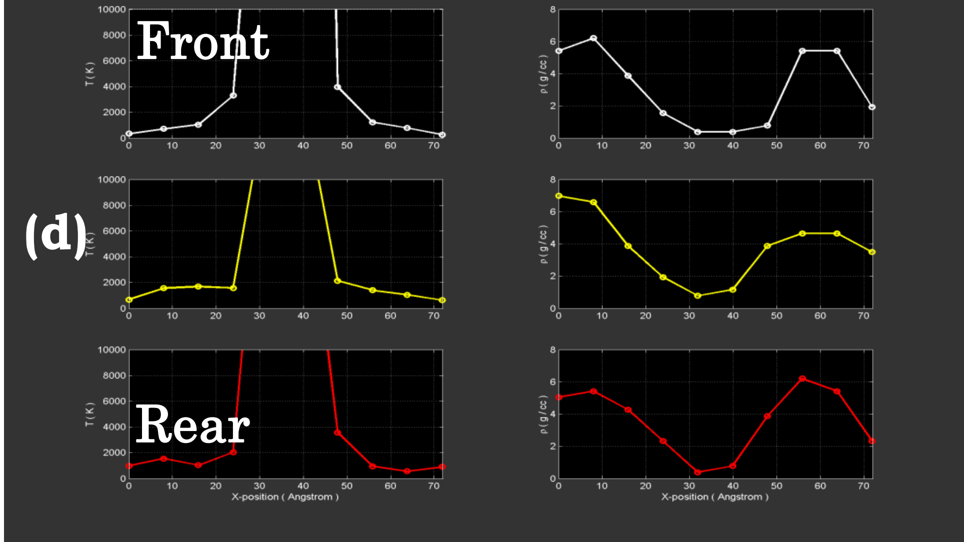
Fast heating, transient situation for layer

Density & temperature : ~ (0.2-6) ps









Prelude

Ablation pathway is under investigation for LPP EUV source.

Thermodynamic parameters such as melting and boiling points of Sn and kinetic effects are investigated using periodic boundary condition for heating (cooling) rate ≤ 10^{13} K / s.

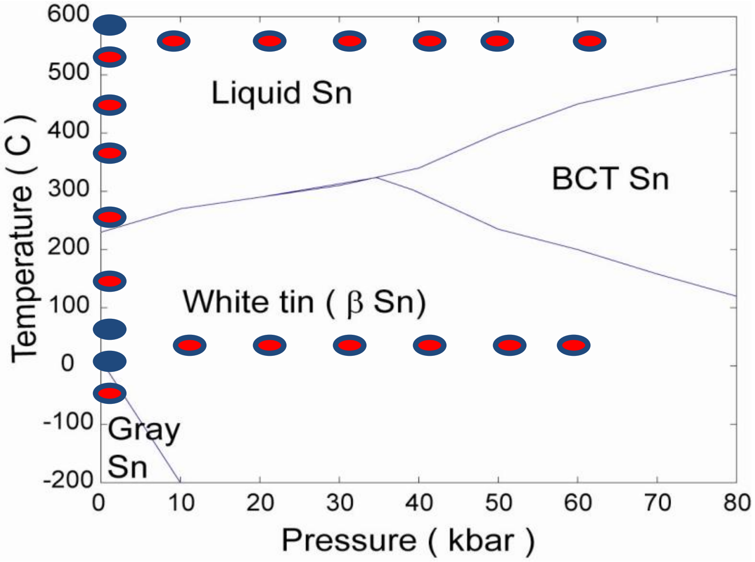
Solid-liquid phase diagram

Classical molecular dynamics (MD) is used to study: gray (diamond), white (β), body centered-tetragonal (BCT) Sn.

🔵 Some of the calculation points using Materials Studio code.

🔴 Some of the calculation points using our program.

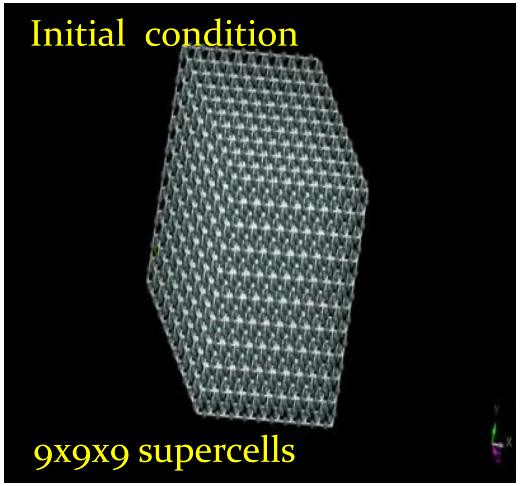
1. Exact thermodynamic condition will be achieved after long relaxation (calculation) time.
2. Thermal history changes any available condition.

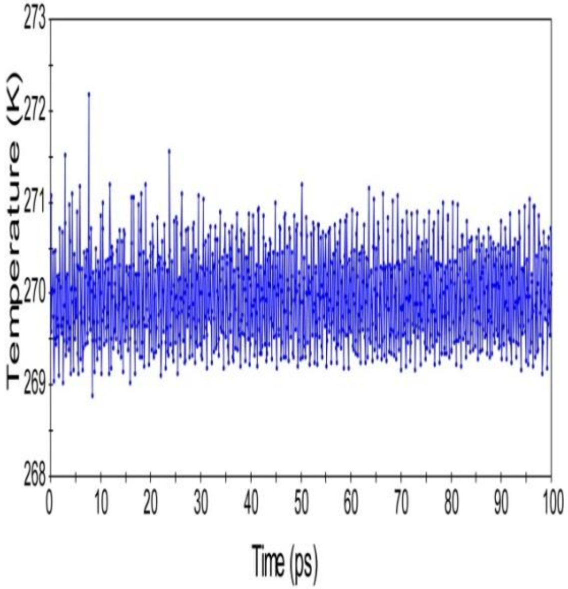


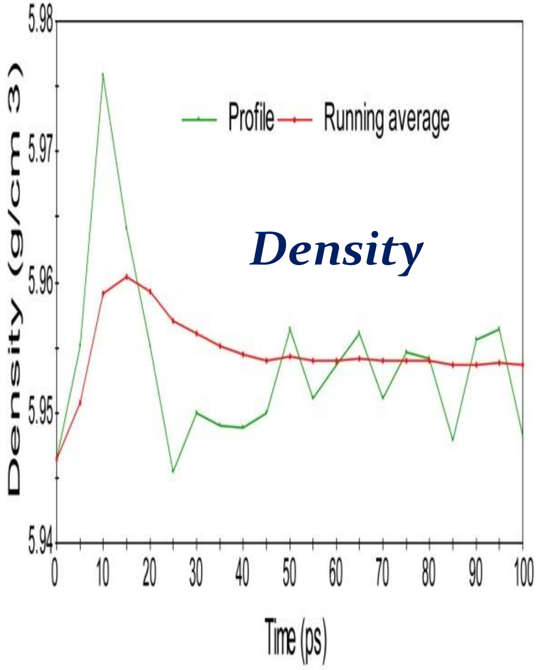
Experimental solid-liquid diagram.

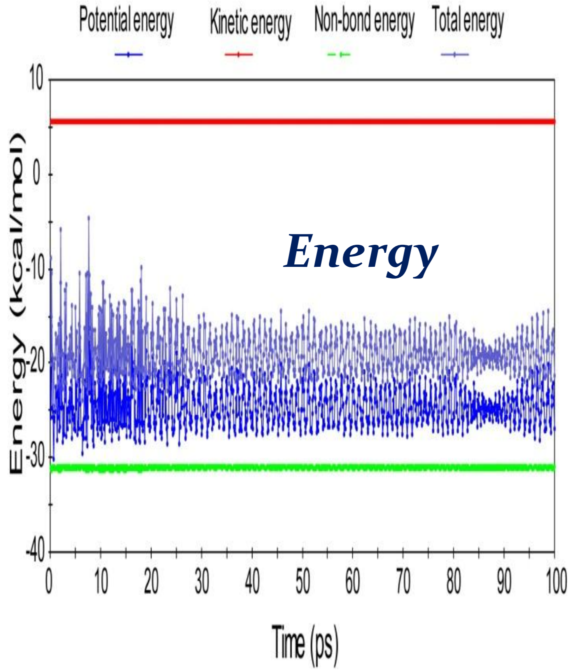
Cannon, J. Phys. Chem. Ref. Data (1974)

MS: Gray Sn at 270 K, ambient pressure





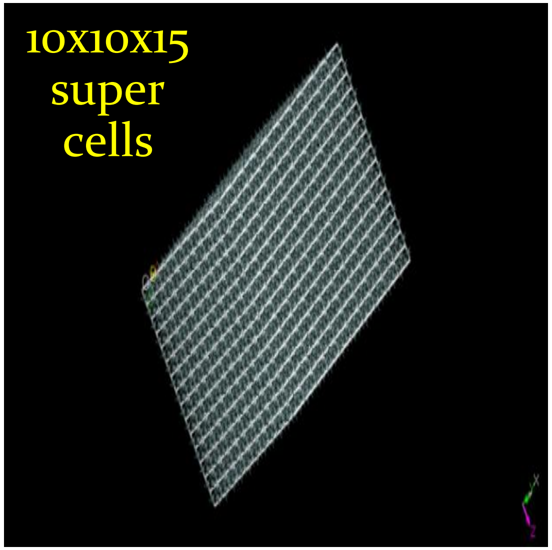




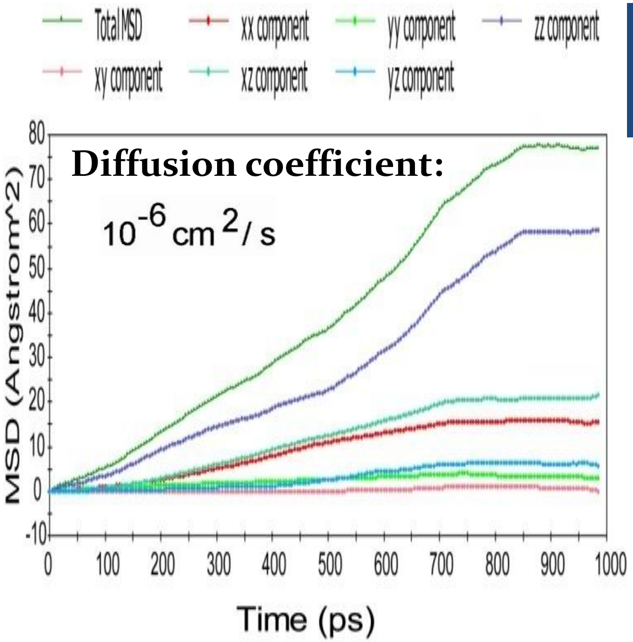
Some of the thermodynamic parameters for this condition are:

- Isobaric heat capacity 26.0221 (J/mol K)
- Isometric heat capacity 15.7 (J/mol K)
- Thermal expansion coefficient -1.299974e-005 (1/K)
- Thermal pressure coefficient -0.15226455 (GPa/K)
- Adiabatic compressibility 5.086978e-005 (1/GPa)
- Isothermal compressibility 8.537603e-005 (1/GPa)
- Gruneisen parameter -193.2275
- Isoenthalpic Joule-Thomson coefficient -758.8 (K/GPa)
- Isothermal Joule-Thomson coefficient 265.7 (1/Ang^3)

MS: White Sn at 300 K, ambient pressure

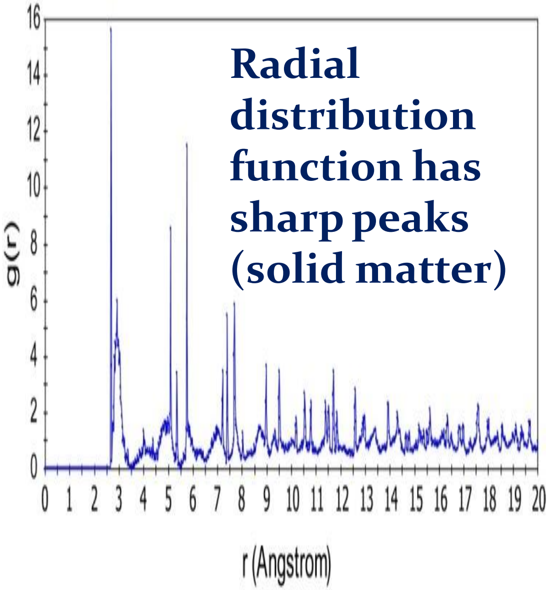


10x10x15 super cells

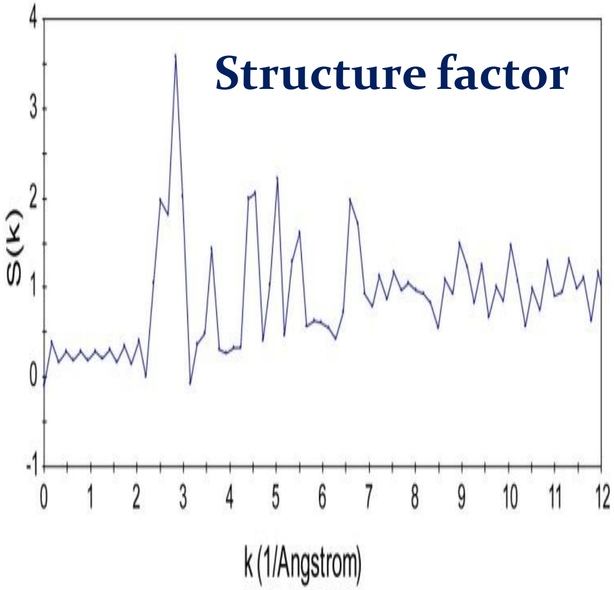


Diffusion coefficient:

10^{-6} cm^2/ s



Radial distribution function has sharp peaks (solid matter)

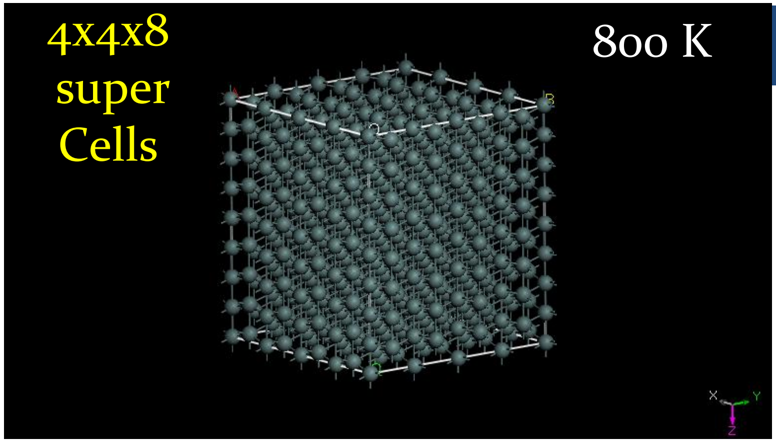


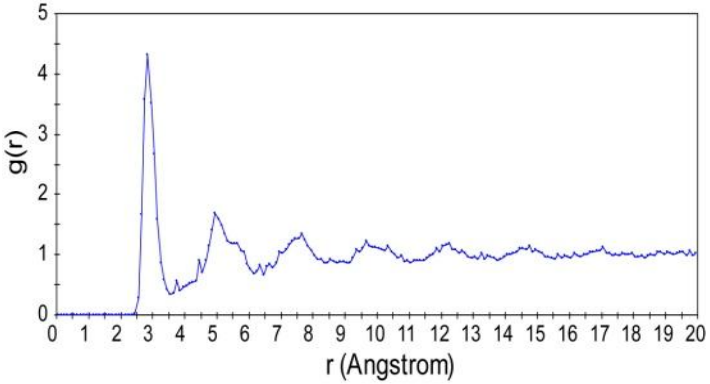
Structure factor

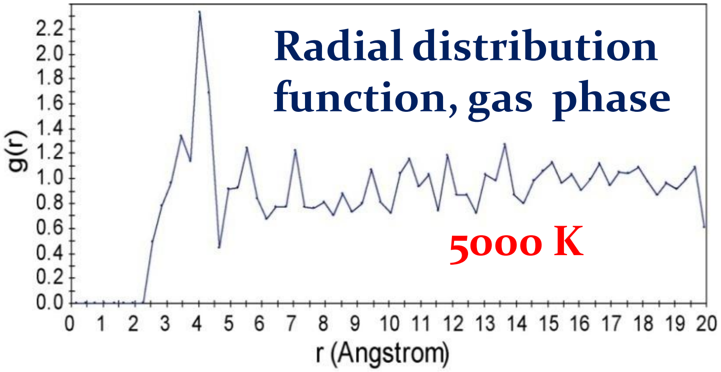
Some of the thermodynamic parameters for this condition are:

- Isometric heat capacity 33 (J/mol K)
- Thermal expansion coefficient 3.5854e-004 (1/K)
- Thermal pressure coefficient 0.074(GPa/K)
- Adiabatic compressibility 5.46e-004 (1/GPa)
- Isothermal compressibility 0.0049 (1/GPa)
- Gruneisen parameter 73.2
- Isoenthalpic Joule-Thomson coefficient -99.55 (K/GPa)
- Isothermal Joule-Thomson coefficient 62.14 (1/Ang^3)

MS: White Sn, high temperature







Radial distribution function, gas phase

Some of the thermodynamic parameters for this condition are:

800 K

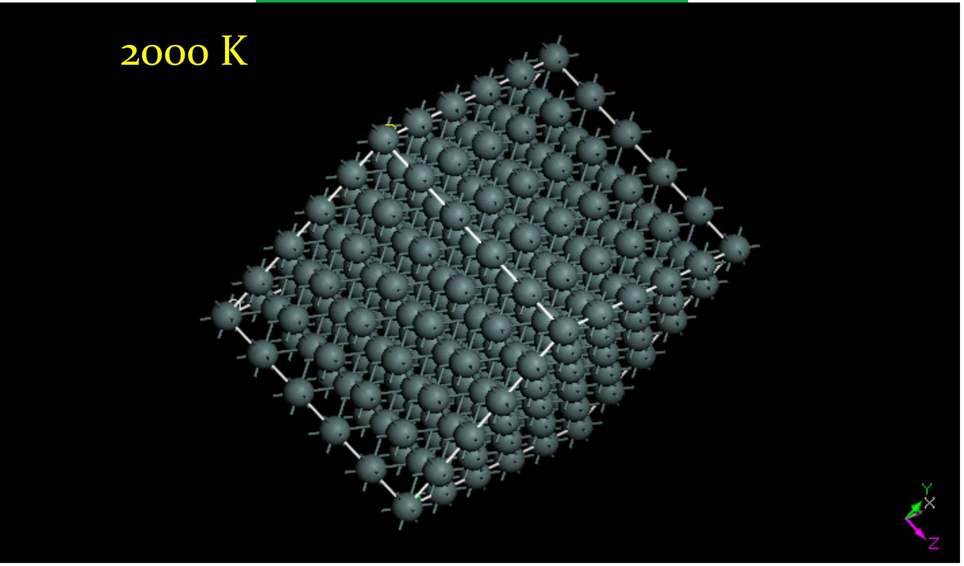
- Thermal pressure coefficient -0.0156(GPa/K)
- Adiabatic compressibility 1.089 (1/GPa)
- Isothermal compressibility 9.8 (1/GPa)
- Gruneisen parameter -0.065
- Isoenthalpic Joule-Thomson coefficient -57.32 (K/GPa)

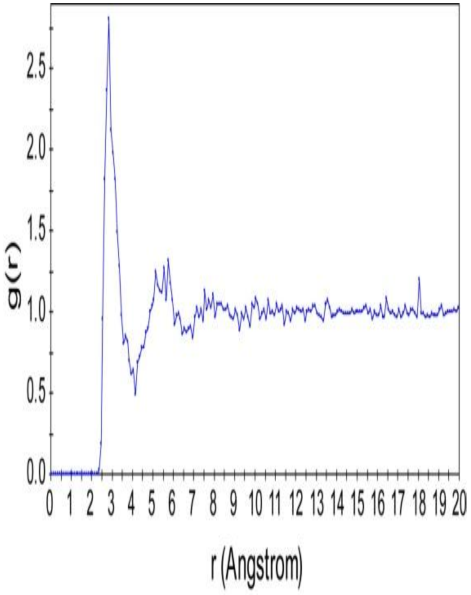
5000 K

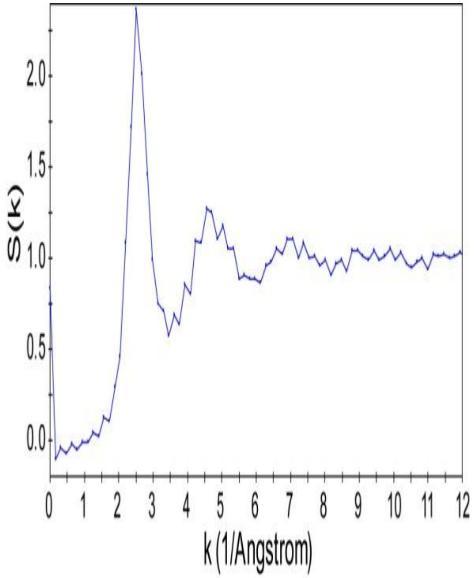
- Thermal expansion coefficient 0.01812 (1/K)
- Thermal pressure coefficient 3.11e-005 (GPa/K)
- Adiabatic compressibility 368.3 (1/GPa)
- Isothermal compressibility 581.99 (1/GPa)
- Gruneisen parameter 0.0064
- Isoenthalpic Joule-Thomson coefficient 1.165e+004 (K/GPa)
- Sonic velocity 1.48e+003 (m/s)

MS: BCT Sn at high temperature

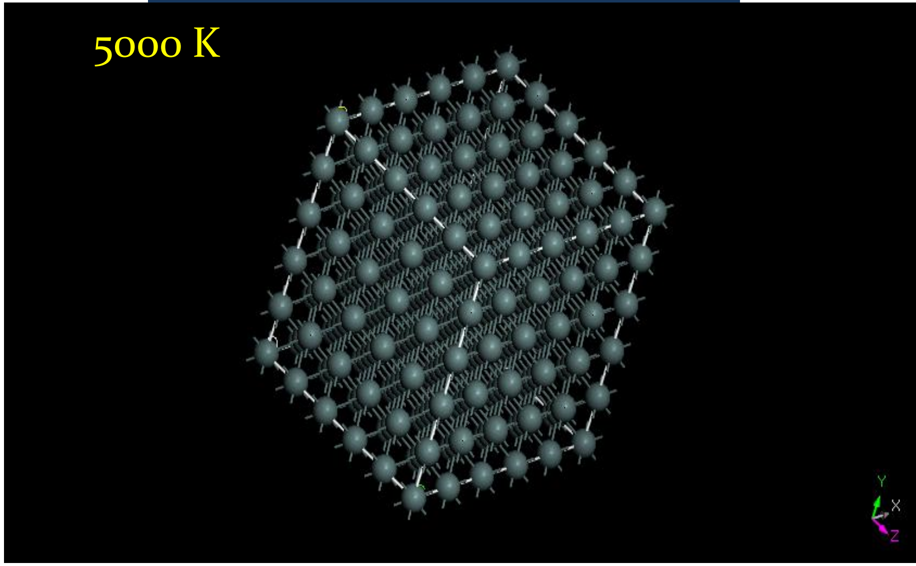
Atmospheric pressure

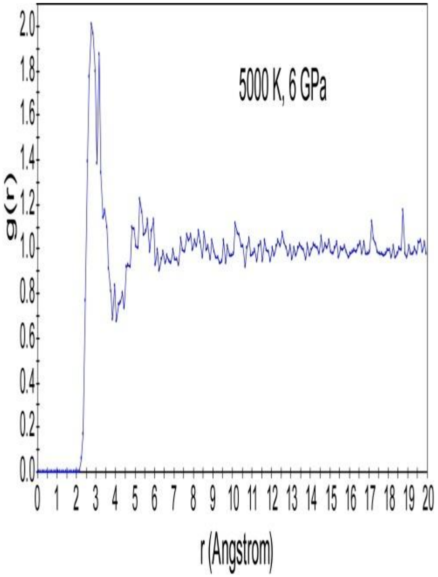


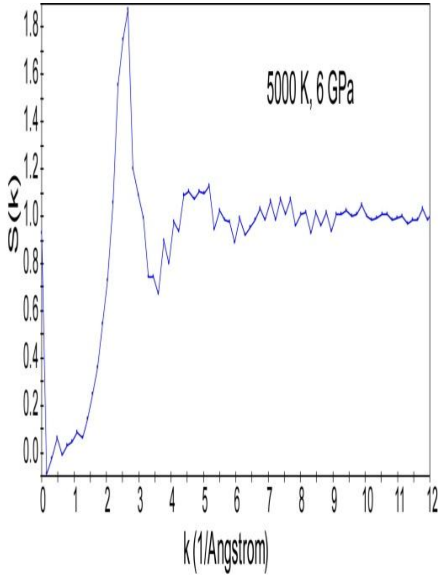




Under 6 GPa external pressure







T-V isobar diagram & Temperature hysteresis

Liquid Sn is cooled to becomes solid and then solid is heated until it melts.

Luo, J. Chem. Phys. (2004) & Phys. Rev. B (2003).

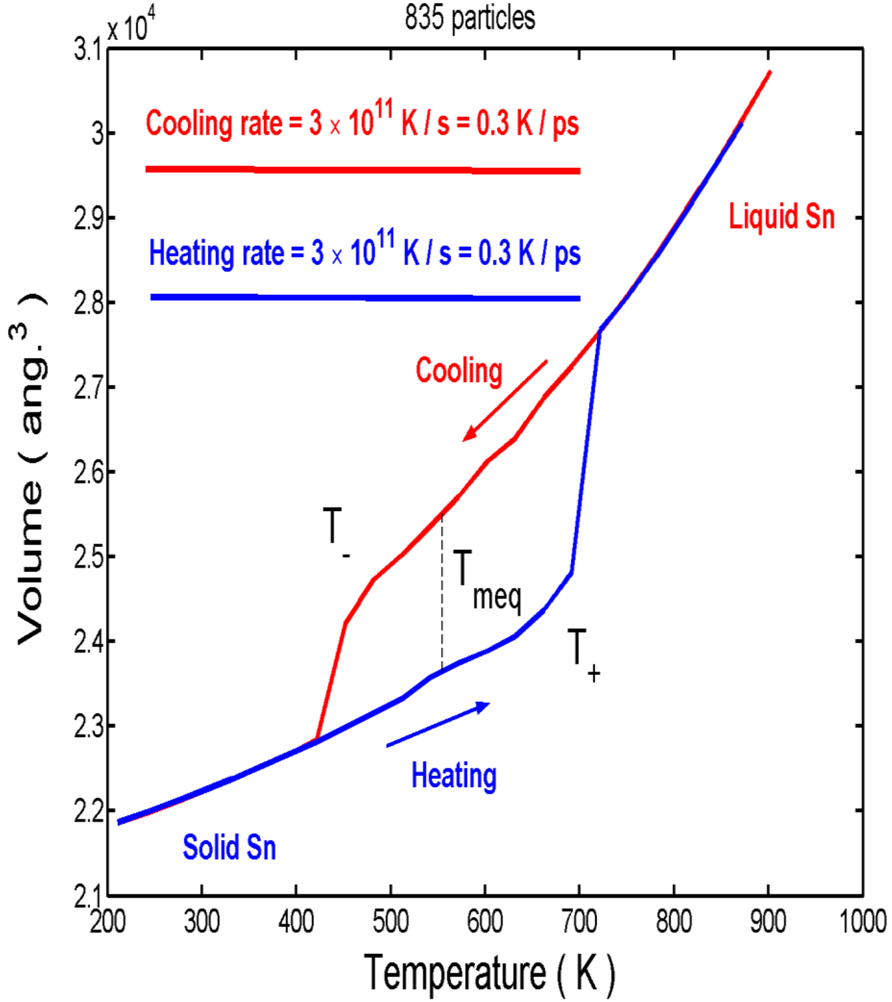
Equilibrium melting temperature, superheating (cooling) degree for this heating rate:

$$T_{meq}=T_+ - (T_+T_-)^{0.5}+T_- \approx 560\ K$$

Superheating $(T_+-T_{meq})/T_{meq} \approx 0.2$

Supercooling $(T_{meq}-T_-)/T_{meq} \approx 0.2$

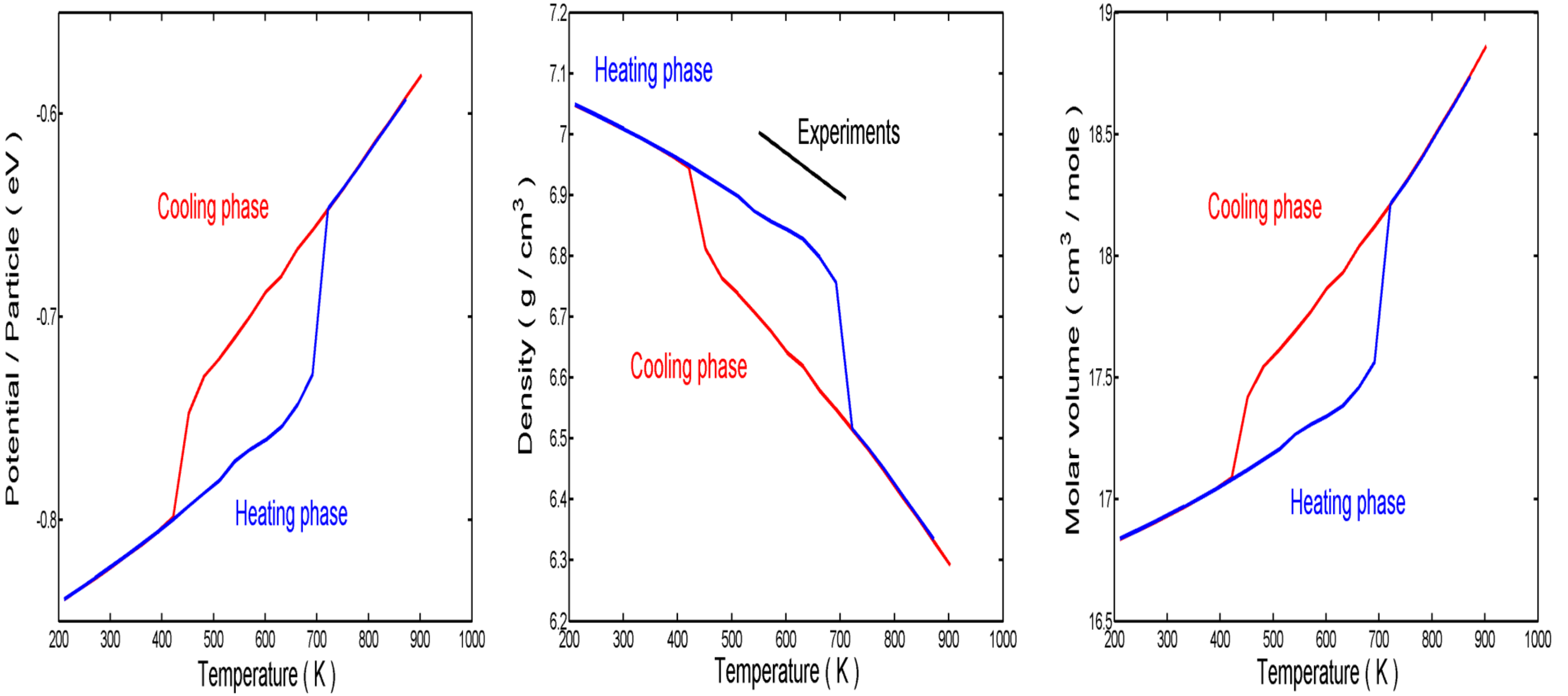
1. In fast experiment [high heating (cooling) rate] kinetic effects become important.
2. Faster heating: solid melts at higher temperature.
3. Faster cooling: liquid may becomes glass or amorphous.



Volume versus temperature.

T-V isobar diagram & Temperature hysteresis

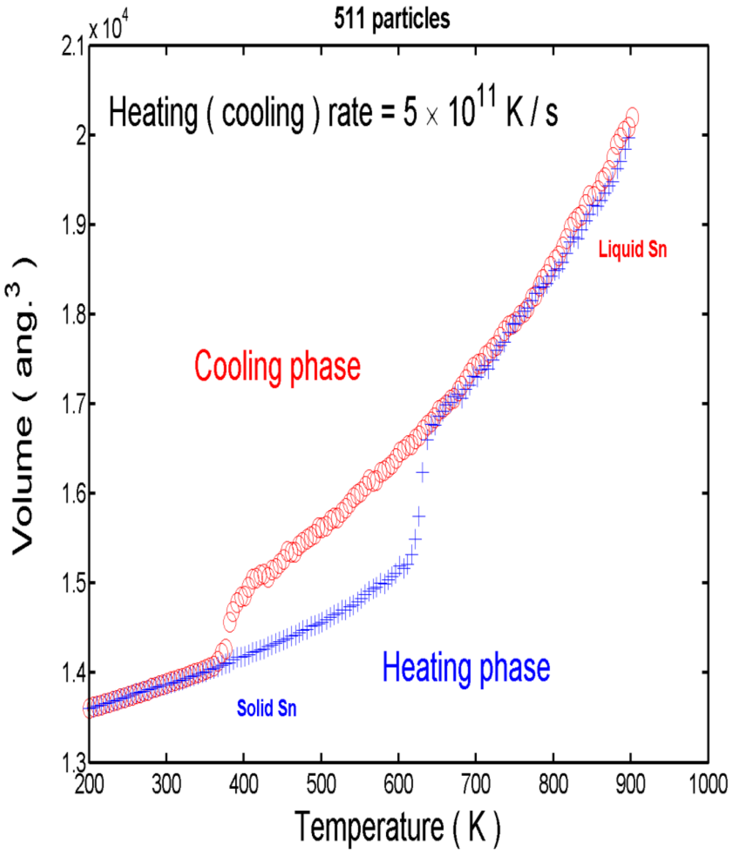
Melting and solidification can also be judged by other parameters like potential, density and molar volume .



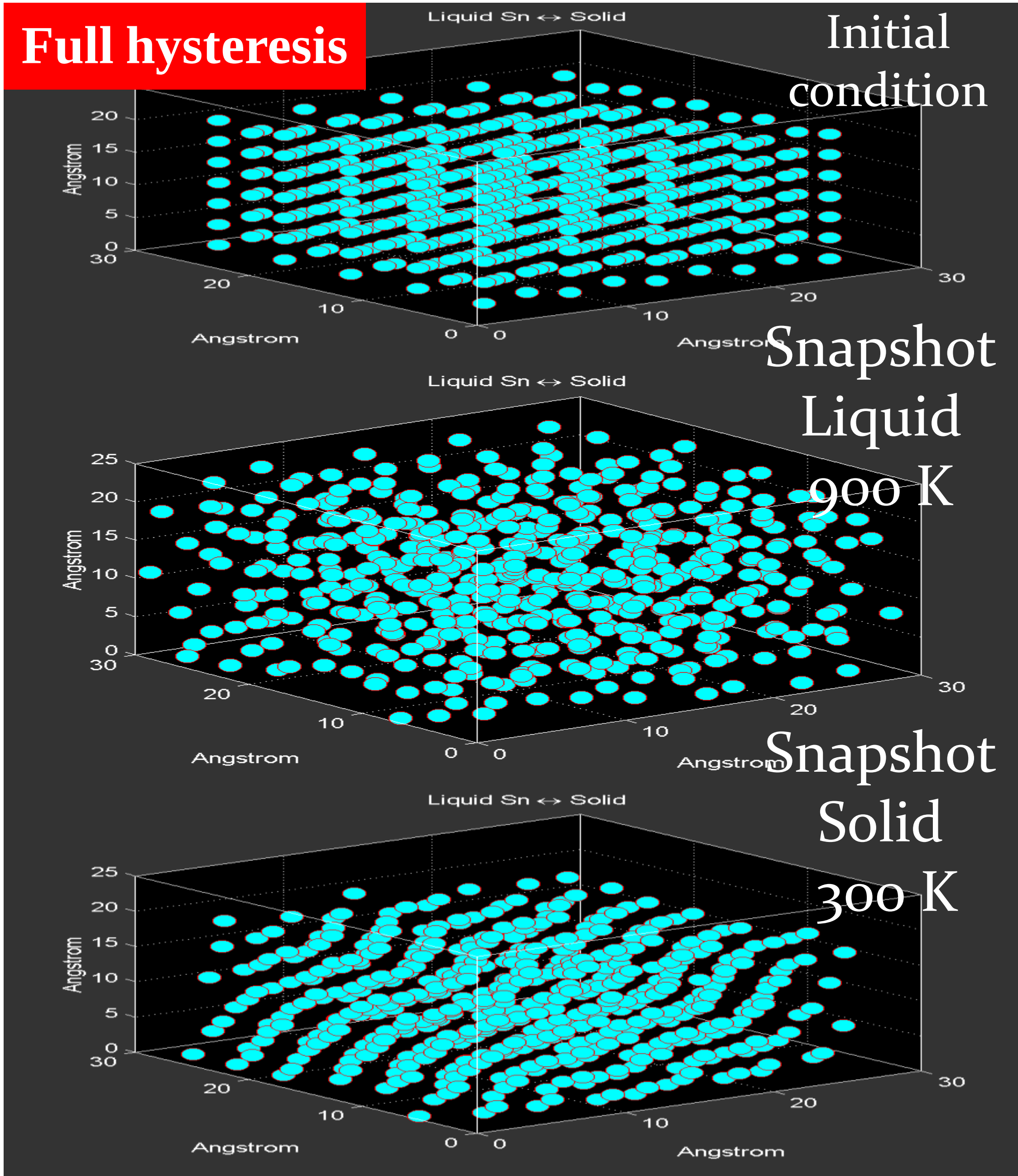
Results are in agreement to previous experimental and theoretical reports, for example, density against temperature of liquid Sn as reported by Alchagirov, High Tem. (2000).

T-V isobar diagram & Temperature hysteresis

Perfect β-Sn is heated at 900 K. After that it cooled down to get crystal (of course not a perfect form) and again it heated to 900 K to find melting temperature .



$$T_{meq} \approx 510 \text{ K}$$



Full hysteresis

Initial condition

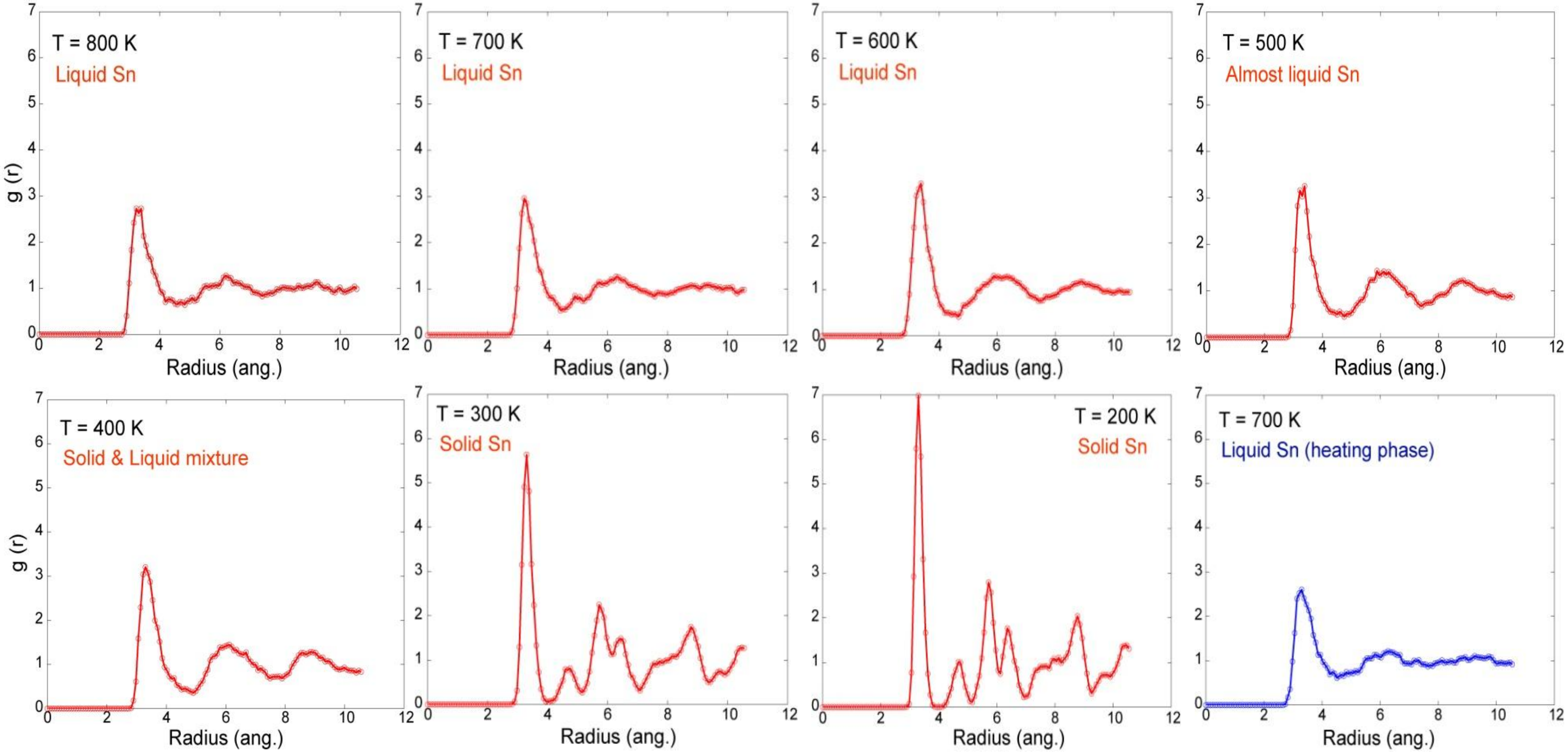
Snapshot Liquid 900 K

Snapshot Solid 300 K

T-V isobar diagram & Temperature hysteresis

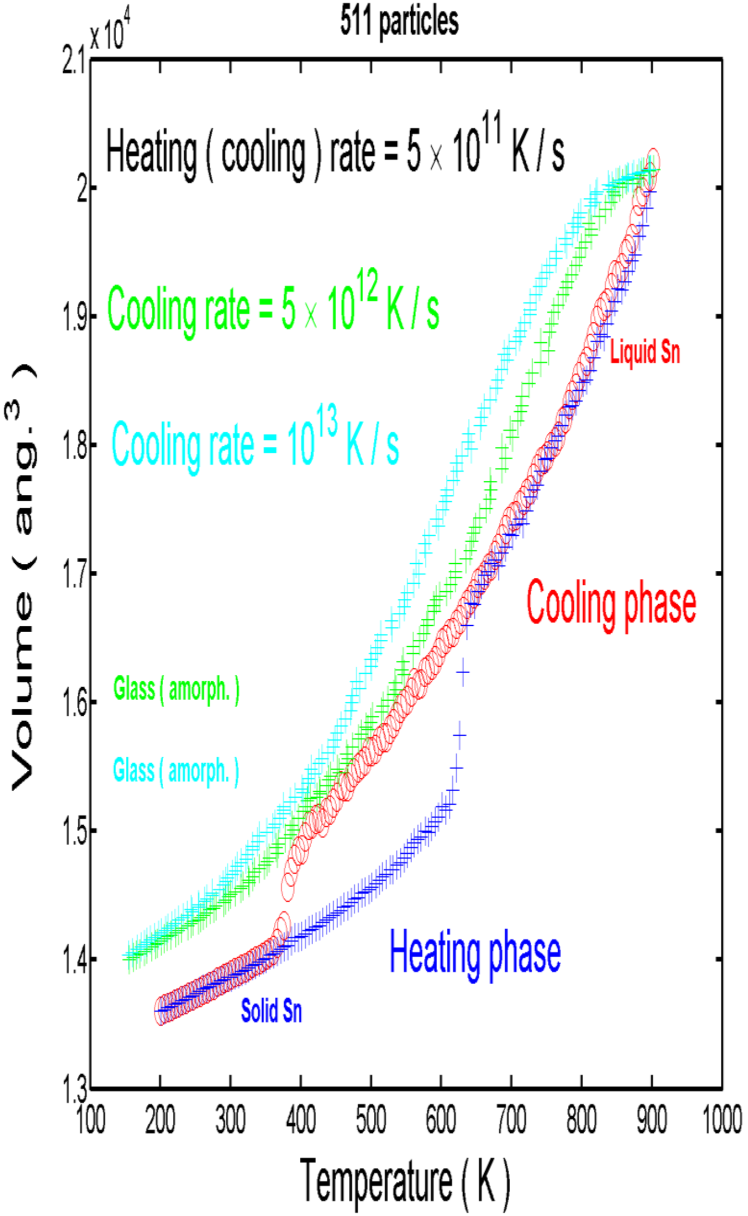
Melting and solidification can also be judged by looking at radial (pair) distribution function, g(r) [X-ray experiment → g(r)].

1. **Solid at low temperature: g(r) has sharp peaks, low thermal broadening (vibration).**
2. **Liquid: g(r) has broader peaks compared to solid, in particular, at long-range.**



Radial distribution function of liquid Sn is almost in agreement with density functional theory molecular dynamics and experiments, see, Calderin , J. Chem. Phys. (2008).

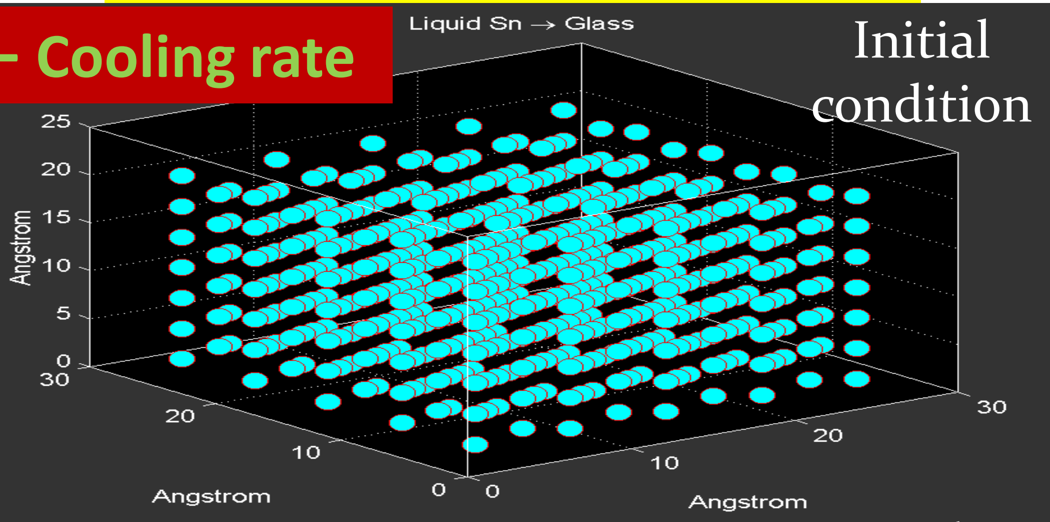
Effect of thermal history, fast cooling



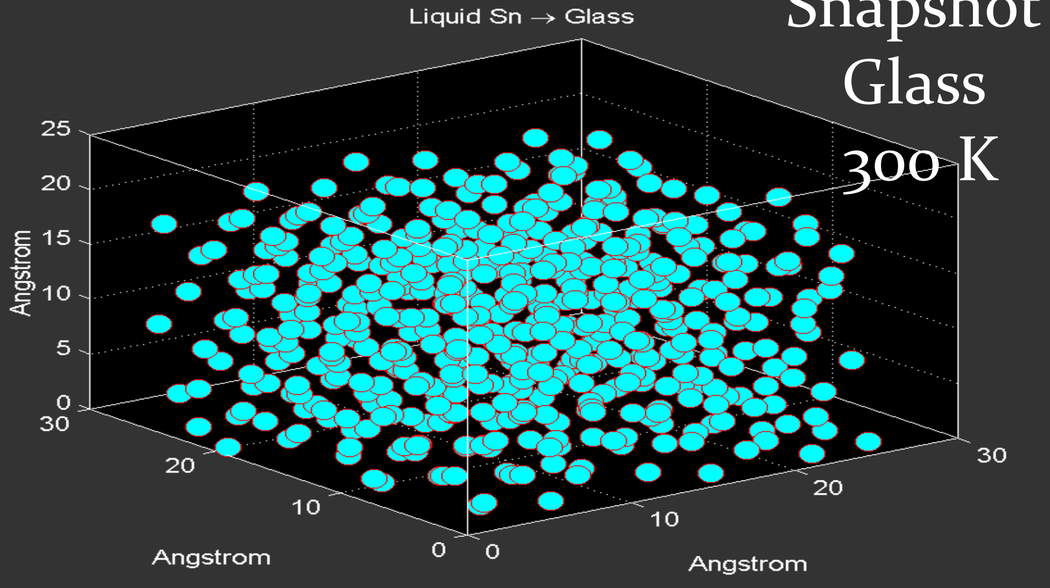
Glass or amorphous formation

→ No regular arrangement

← Cooling rate

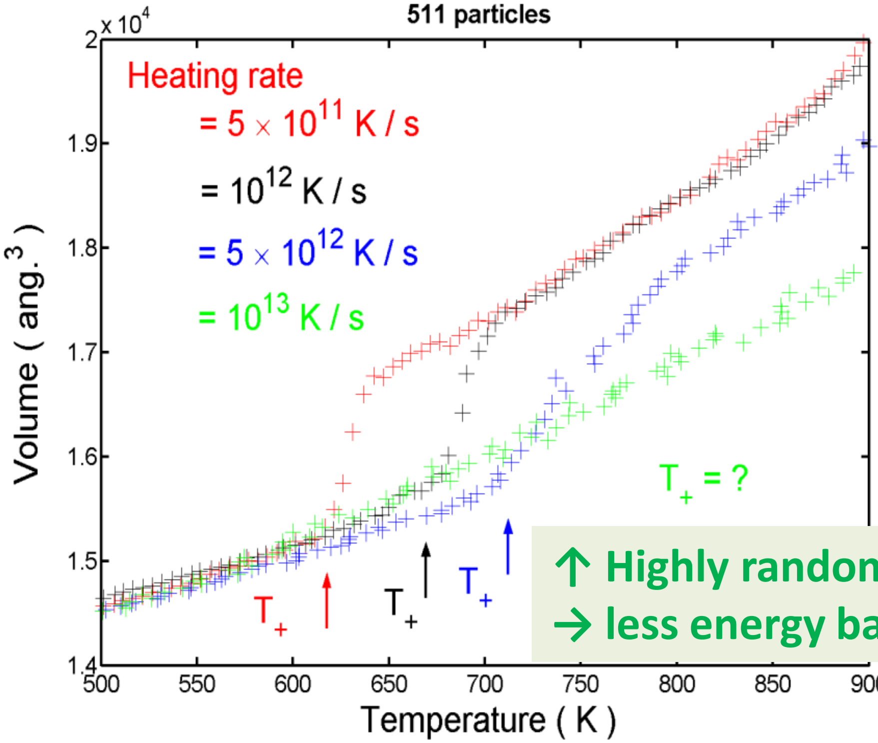


Initial condition

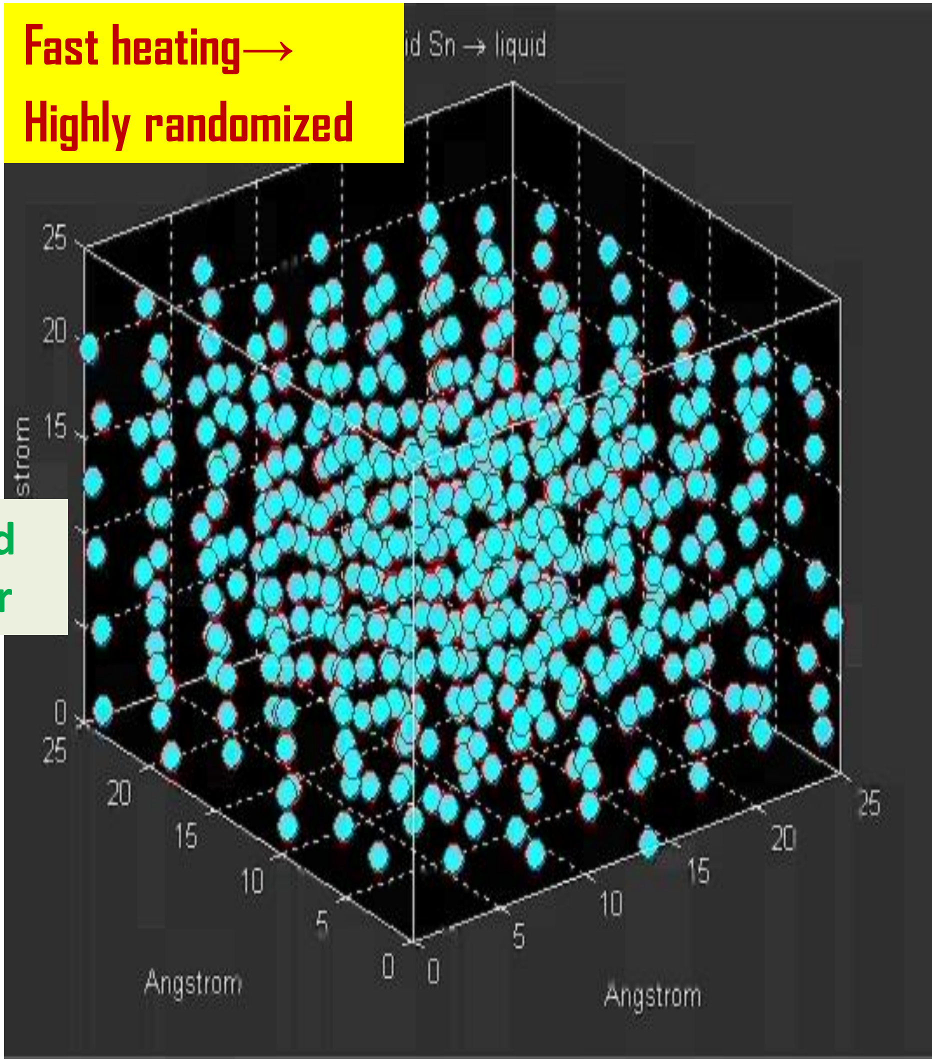


Snapshot Glass 300 K

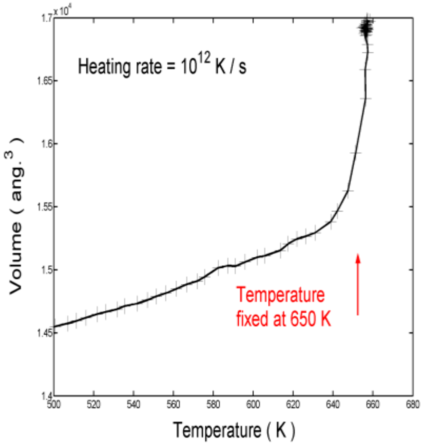
Fast heating & Relaxation time

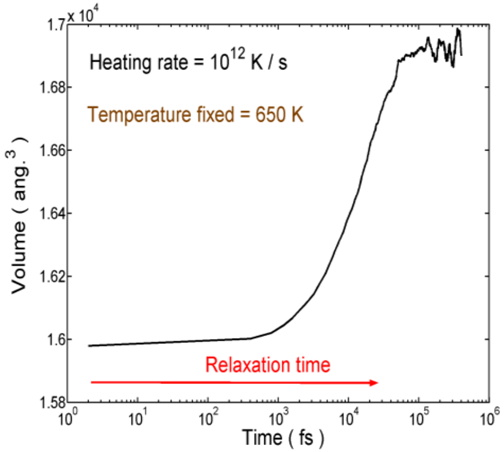


↑ Highly randomized
→ less energy barrier



Fast heating⟶
Highly randomized

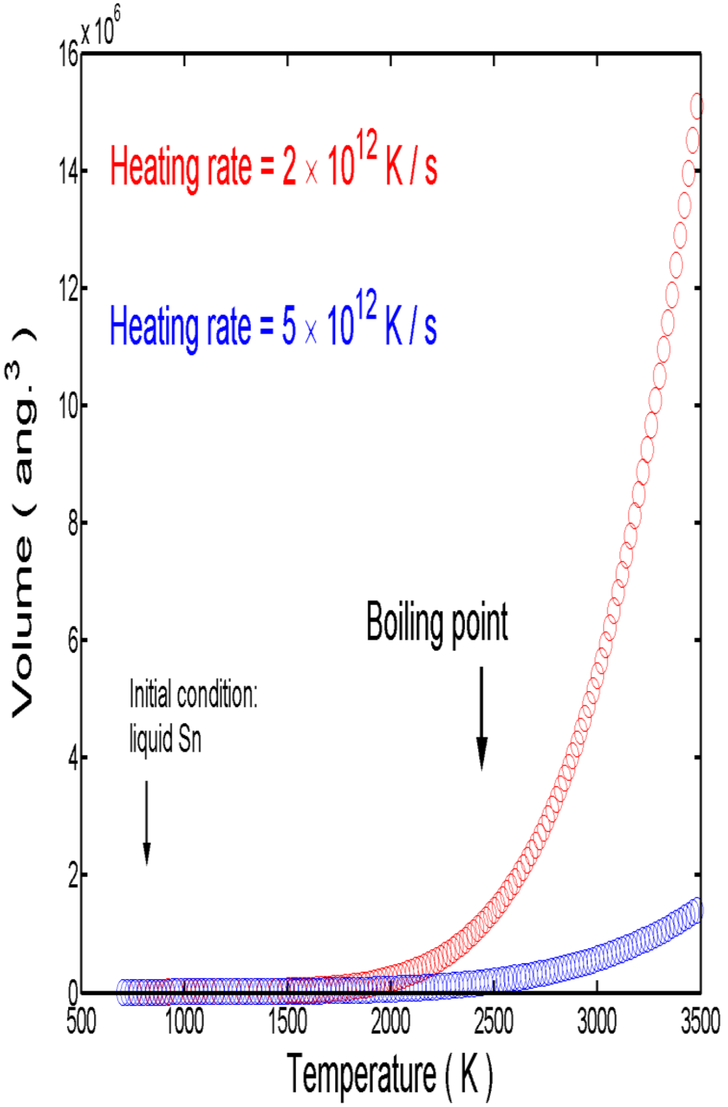




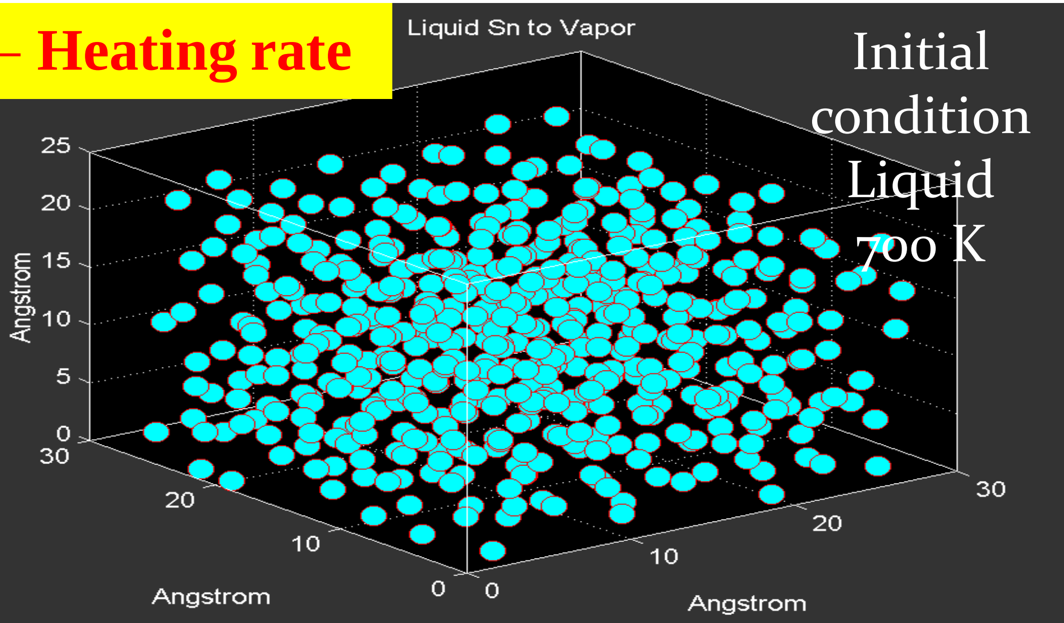
Thermal history changes the thermodynamic pathways.

Boiling & Vaporization

Liquid Sn is heated to get gas phase.

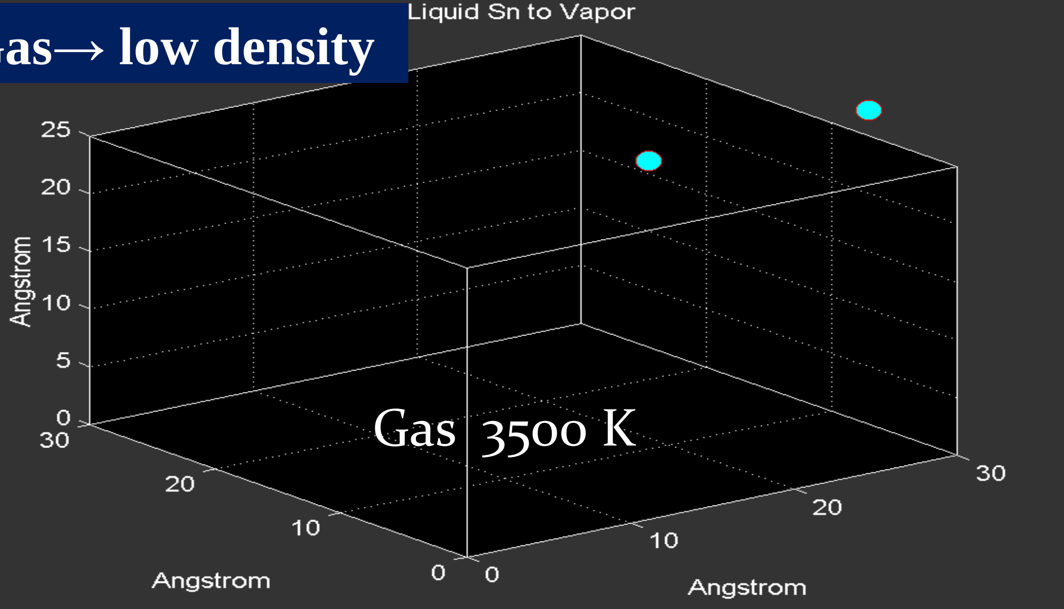


← Heating rate



Initial condition
Liquid
700 K

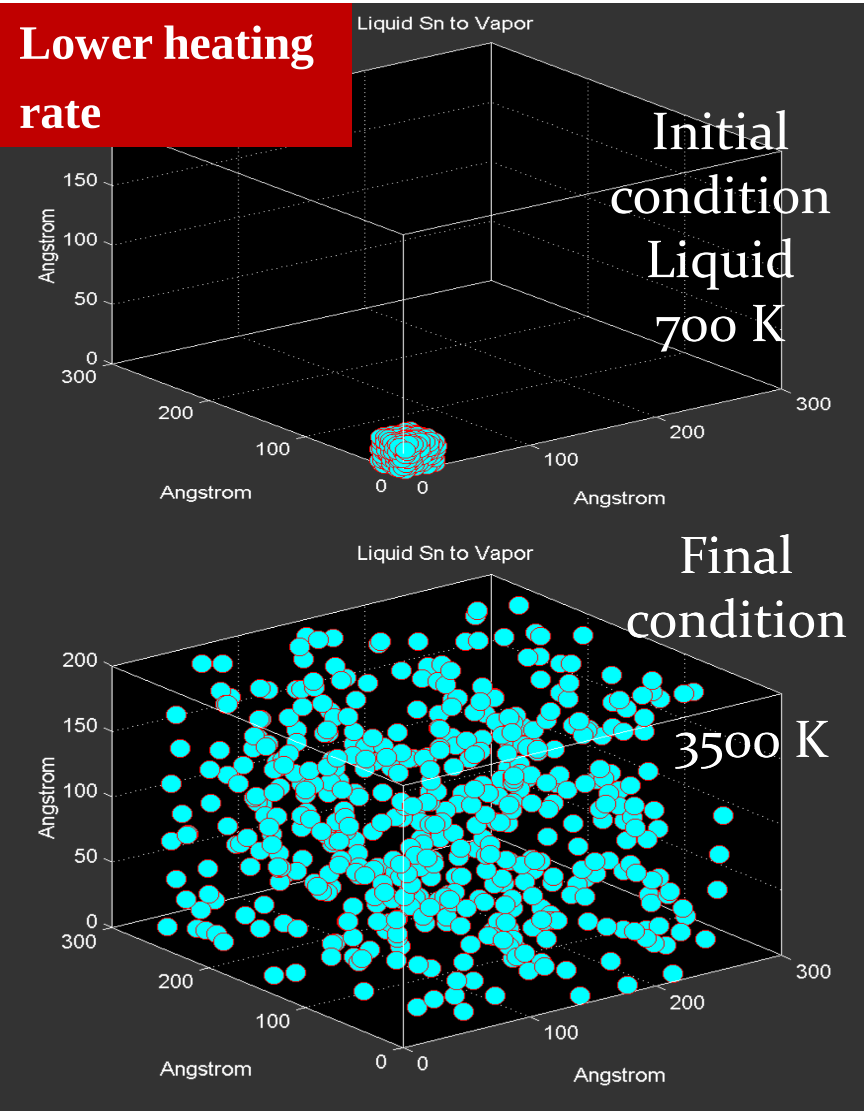
Gas→ low density



Gas 3500 K

Boiling & Vaporization

Inertial confinement effect

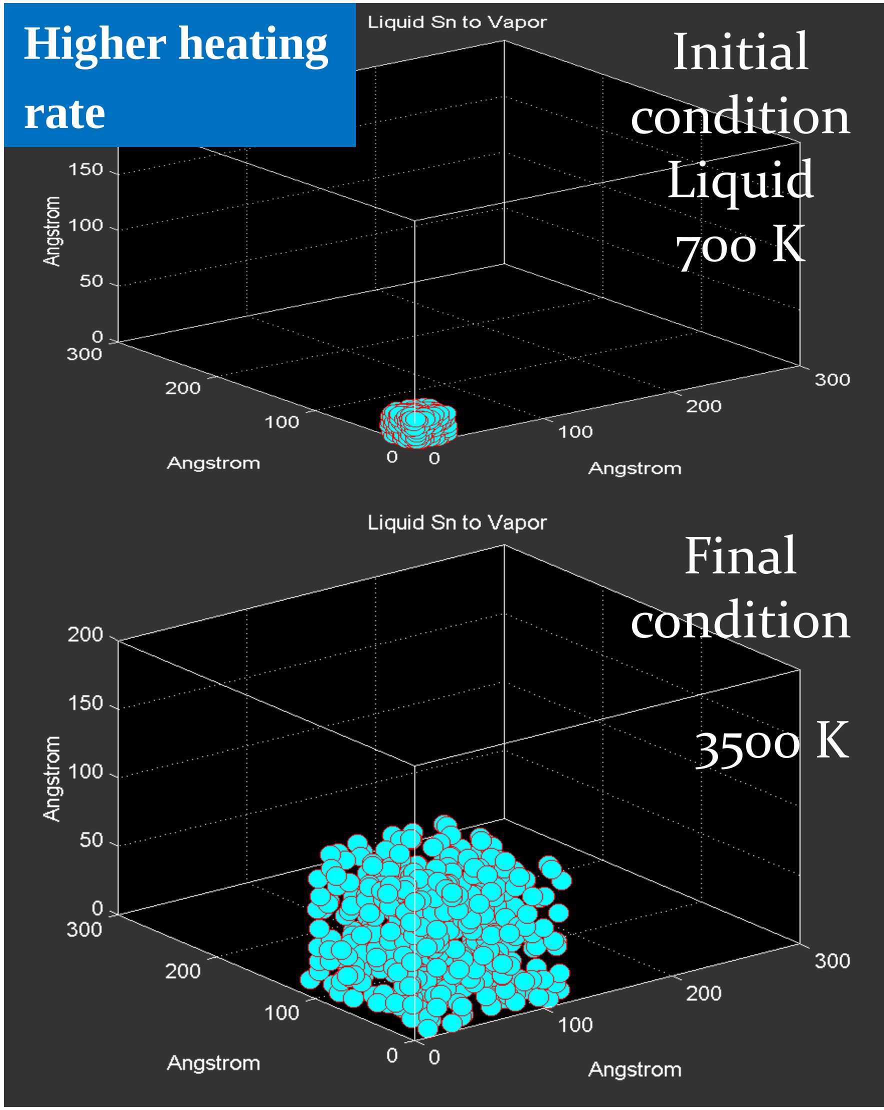


Lower heating rate

Initial condition
Liquid
700 K

Final condition

3500 K



Higher heating rate

Initial condition
Liquid
700 K

Final condition

3500 K

Thermal history changes the thermodynamic pathways.

Summary

1. All of the thermodynamic parameters of Sn can be derived by using classical or based on density functional theory molecular dynamics.
2. In fast experiments (high heating / cooling rate), thermo-physical parameters of Sn not only depend on thermodynamic parameters such as pressure and temperature but also strongly influenced by thermal history of experiment. That means, in LPP EUV experiments, kinetic effects such as super-heating / super-cooling is important on equation of state. Such effects are theoretically demonstrated on melting and boiling points of Sn.
3. In LPP EUV source, the heating rate is about 10^{13} K/s. Thermodynamic pathways to melting, boiling and ablation strongly depends on laser parameters.

Future investigations

1. The equation of state of Sn from solid to plasma phase is preparing to couple molecular dynamics to available 1D hydrodynamic code.
2. Atomistic molecular dynamics simulation will be done for Sn droplet in double pulse experiments. The velocity of particles, pressure and temperature will be calculated by coupling of two-temperatures heat equation to molecular dynamics. The necessary data is under investigation by quantum molecular dynamics code (CASTEP). The thermodynamic pathways will be simulated versus initial laser parameters such as intensity and pulse width.
3. Using quantum molecular dynamics code of Materials Studio, the physics and chemistry behind the kinetics of absorption, desorption and surface degradation owing to residual gas species is under investigation.