Melting and superheating by atomistic simulation

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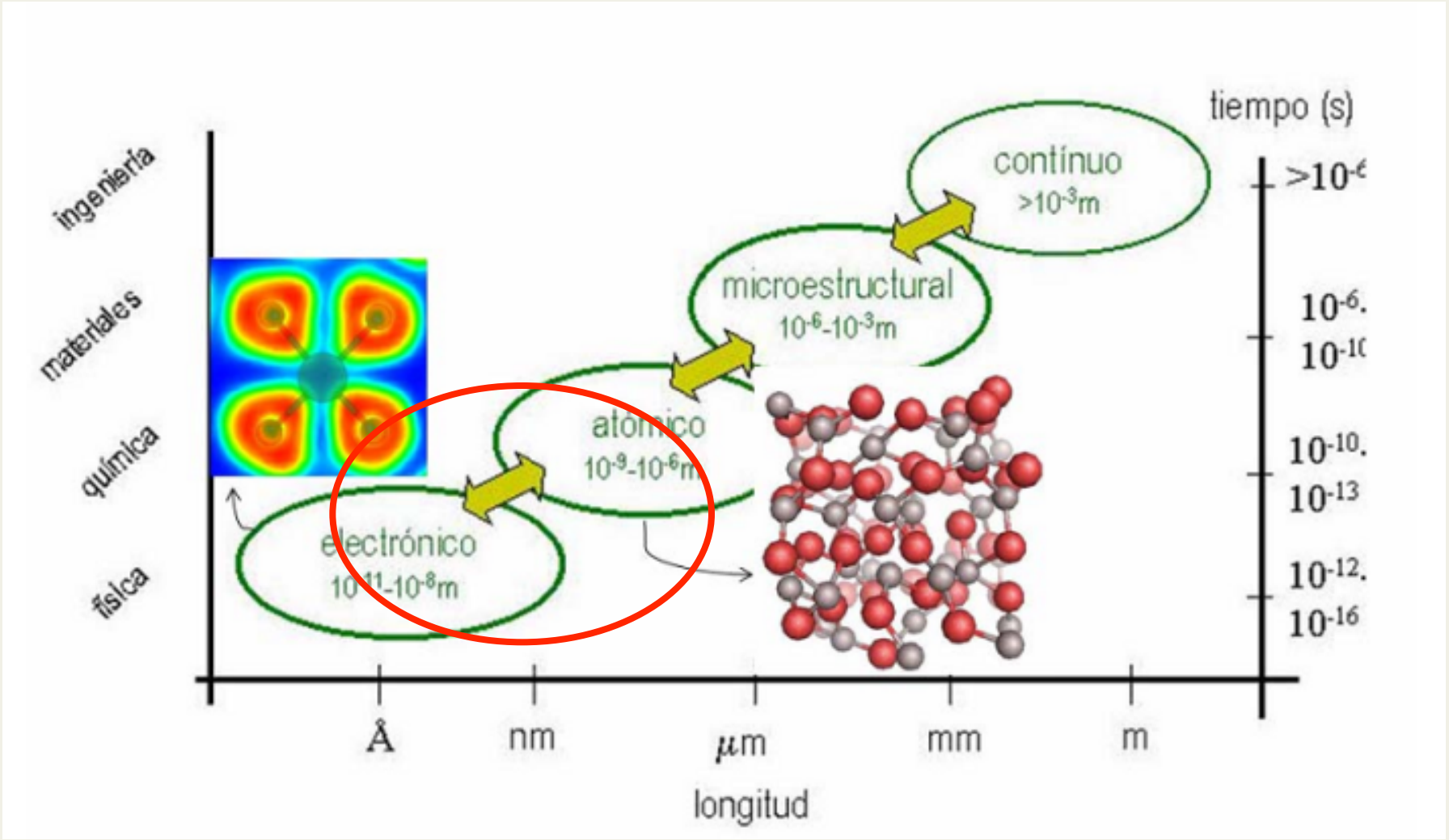
- Postgrad students: F. González, Y. Navarrete, N . Amigo, J. Wachter, M. Sepúlveda, D. González.
- Several undergrad per year
- Collaborators in Chile and abroad: E. Bringa (Arg), K. Rajan(IU), CACS (USC), Uppsala U.

Computer simulation at atomic level

Classical and ab-initio MD; MC;



GNM: Research areas (www.gnm.cl)

1. Foundations of statistical mechanics:
a) melting theory
b) information theory and bayesian probability
c) non-extensive statistics

2. Material science
a) solar cell materials: electronic and optical properties (ab-initio)
b) nano-structured materials: carbon nanotubes
c) glasses: structures, dynamical and mechanical properties
d) materials under extreme conditions: melting curve, structure & dynamics
e) mechanical properties of metals
f) nuclear materials: radiation damage
e) biological systems: protein molecular simulation

3. Computer simulation techniques
a) Computer programming: Las Palmeras Molecular Dynamics, www.lpmd.cl (Computer Physics Communications, 181(12):2126 – 2139, 2010)
b) Free energy and entropy; melting curve
c) Algorithms for MD and MC: mpi, CUDA

Past projects

Al_2O_3 : Crystalline, amorphous and liquid

GeO_2 : amorphous and liquid

MAX phases: TiSiC, TiGaN

Current projects

- *Mechanical properties of metals: influence of impurities in Cu*
- *Mechanical properties of BMG: shear bands in* Cu-Zr-Ag
- *Radiation damage:* stacking fault tetrahedron in Au nanowires under irradiation; softening and hardenning; W

Statistical mechanics

- *Estimation of Tsallis' q-index in non-extensive systems*,
  Sergio Davis and Gonzalo Gutiérrez.
  AIP Conference Proceedings **1578**, 1779 (2013).

- *Newtonian dynamics from the principle of maximun caliber*

D. González, S. Davis, G. Gutiérrez, ArXiv:1310.1382 (2013).

- *Conjugate variables in continuous maximum-entropy inference*,
  S. Davis and G. Gutiérrez..
  Physical Review E 86, 051136 (2012).

Materials

- *Bayesian inference as a tool for analysis of first-principles calculations of complex materials: an application to the melting point of Ti_2GaN*,
  Sergio Davis and Gonzalo Gutiérrez.
  Modelling and Sim. in Mat. Sc. and Eng. **21**, 683-690 (2013)

- *Hypervelocity impact of copper nano-projectiles on copper*,
  N. Amigo, C. Loyola, S. Davis and G. Gutiérrez.
  Computational Materials Science 68, 245 (2013)

- *Ultrathin Carbon Nanotube With Single, Double, and Triple Bonds*,
  E. Menéndez-Proupin, A.L. Montero-Alejo, and J.M. García de la Vega.
  Physical Review Letters 109, 2 (2012).

Computer simulation techniques

- *Maximum entropy reconstruction of the configurational density of states from microcanonical simulations*,
  Sergio Davis.
  Journal of Physics: Conference Series 410, 012161 (2013)

- *Calculation of microcanonical entropy differences from configurational averages*,
  S. Davis.
  Physical Review E 84, 050101(R) (2011)

- *SearchFill: A stochastic optimization code for detecting atomic vacancies in crystalline and non-crystalline systems*,
  S. Davis, Anatoly B. Belonoshko and Börje Johansson.
  Physical Review B 84, 064102 (2011).

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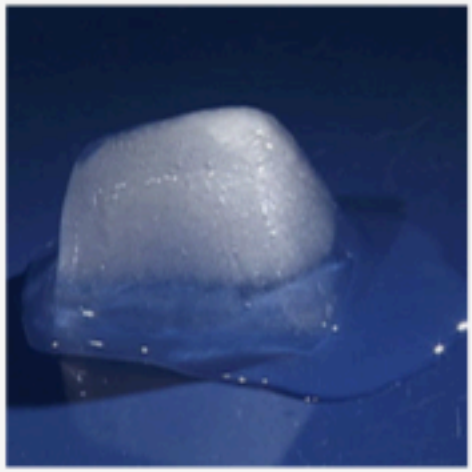
Sergio Davis, Gonzalo Gutiérrez

The solid-liquid phase transition (melting)



Although melting is common in everyday life, its mechanism is not fully understood.

- Thermodynamics define the **melting point** T_m as $G_{solid}(T_m, P) = G_{liquid}(T_m, P)$
- It is possible to heat a solid, homogeneously, over T_m without melting, until reaching the limit of superheating T_{LS}
- We don't know much about the atomistic meaning of T_m and T_{LS}, or when exactly a material has high T_m.

Some "classical" criteria for melting

F. Lindemann (1910)

Melting happens when the mean displacement of the atoms around their equilibrium positions reaches a certain fraction δ_L of the nearest-neighbor distance, $k_B T_m \propto m\omega^2(\delta_L a)^2$.

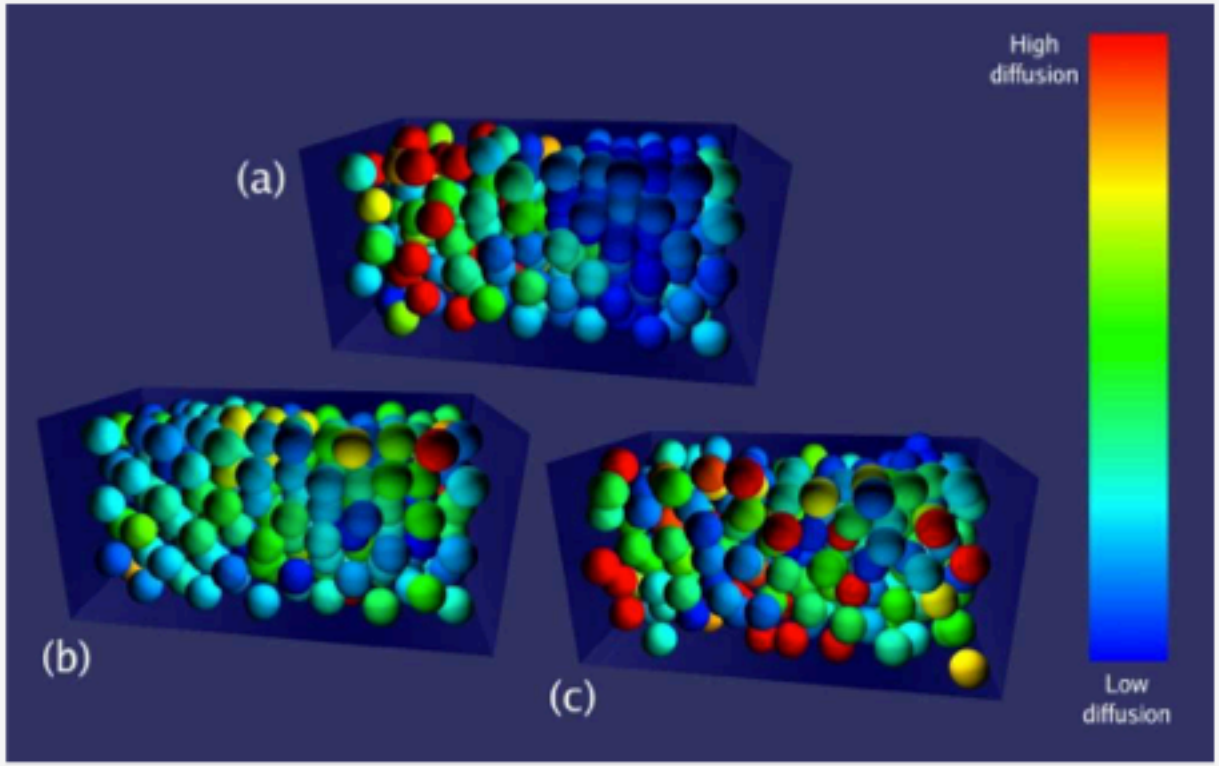
M. Born (1937)

Melting happens when the crystal loses its resistance to shear, i.e., at a temperature T_m such that the elastic constant $C_{44}(T_m)=0$.

- However, it has been shown that, before the Lindemann and Born conditions are fulfilled, liquid starts to nucleate inside the crystal.
- Vacancies, point defects and dislocations have been shown to play a role in the process.

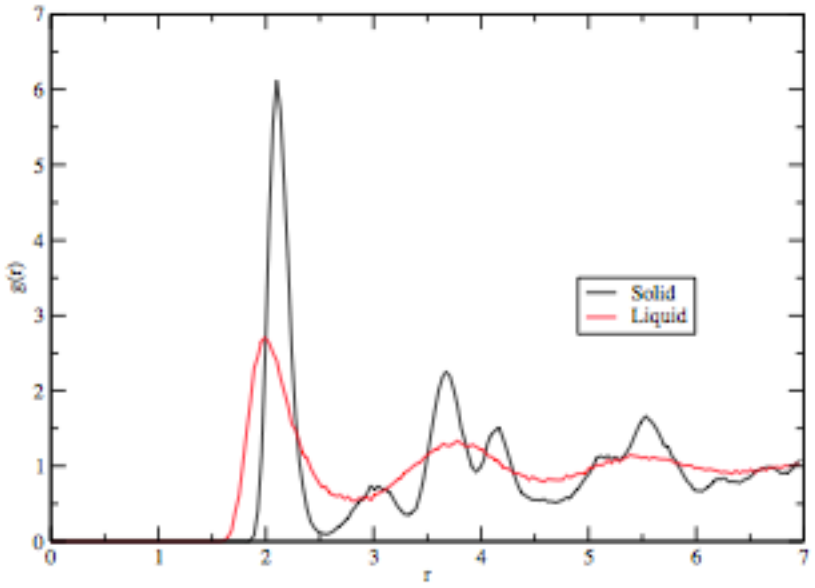
Two–phase method

J. R. Morris *et al*, Phys. Rev. B **49**, 3109 (1994)
A. B. Belonoshko, Geochim. Cosmochim. Acta **58**, 4039 (1994)



(b) Slightly below T_m both halves are solid, (c) slightly above both halves are liquid.

How do we compute T_m of a solid using MD?

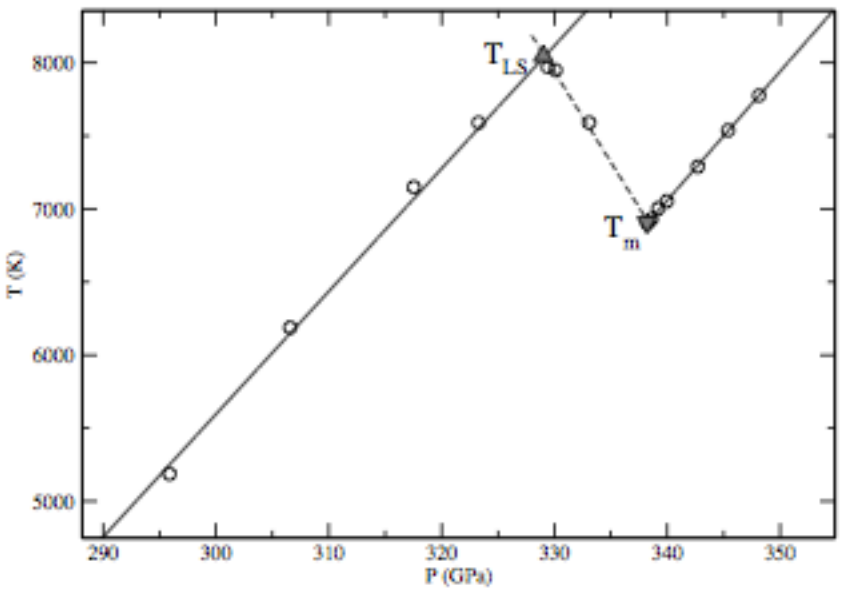


First thing one would try is just heat the solid and see when it changes in terms of structure or transport properties. However, this gives the wrong T_m because of overheating.

The usual approach to solve this is to use the coexistence of solid and liquid to detect the melting point...

Z–Method

Belonoshko *et al*, Phys. Rev. B **73**, 012201 (2006)



- One-phase simulation, following the isochore $T(P)_V$
- Every (T, P) point from microcanonical (N,V,E) MD at increasing initial kinetic energy K
- At T_{LS}, the smallest increase in K will trigger melting, and the change $\Delta U = U_{liquid} - U_{solid}$ substracted from K will drop T precisely to T_m

First order phase transition in microcanonical ensemble

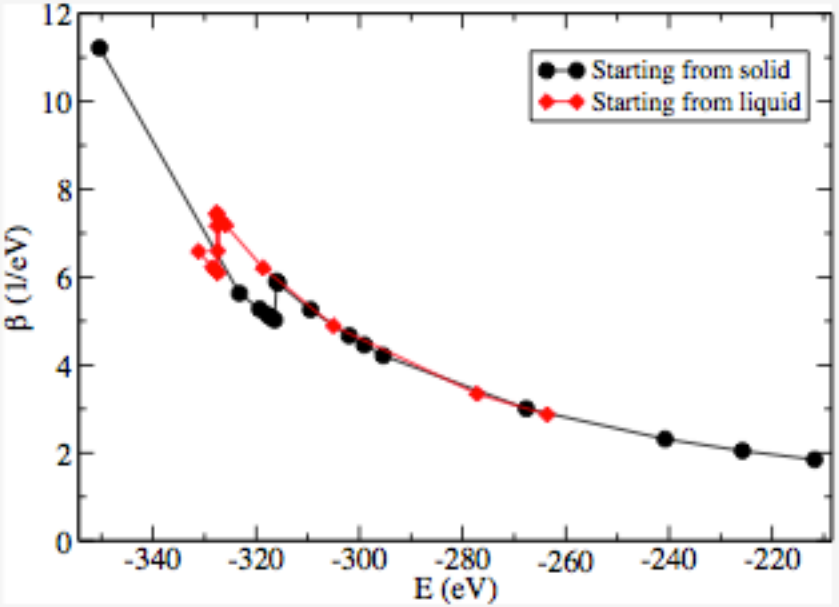
$$S = S(E, V, N) \Rightarrow ds = \frac{de}{T} + \frac{p}{T} dv \tag{1}$$

$$ds^{\alpha} = ds^{\beta} \Rightarrow \tag{2}$$

$$\left(\frac{de}{dv}\right)_{eq} = \frac{p^{\beta} T^{\alpha} - p^{\alpha} T^{\beta}}{T^{\beta} - T^{\alpha}} \tag{3}$$

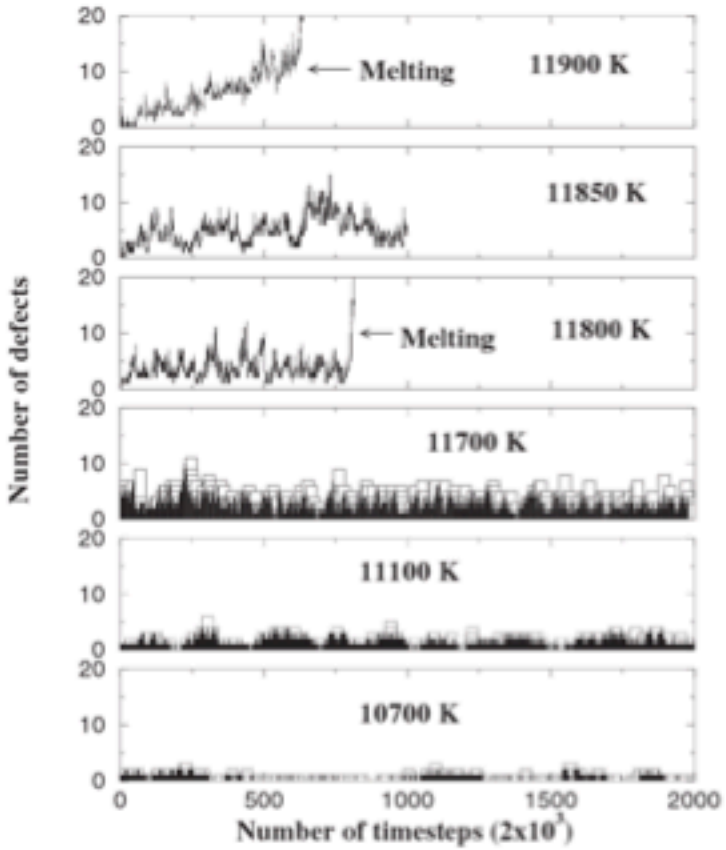
Thus: in contrast to isothermal-isobaric ensemble, here there are differents T and p in each phase.
Here we have e and v of melting, instead of T_m and p_m.
The challenge is to relate both framework: $(e_m, v_m) \leftrightarrow (T_m, p_m)$

Z–Method



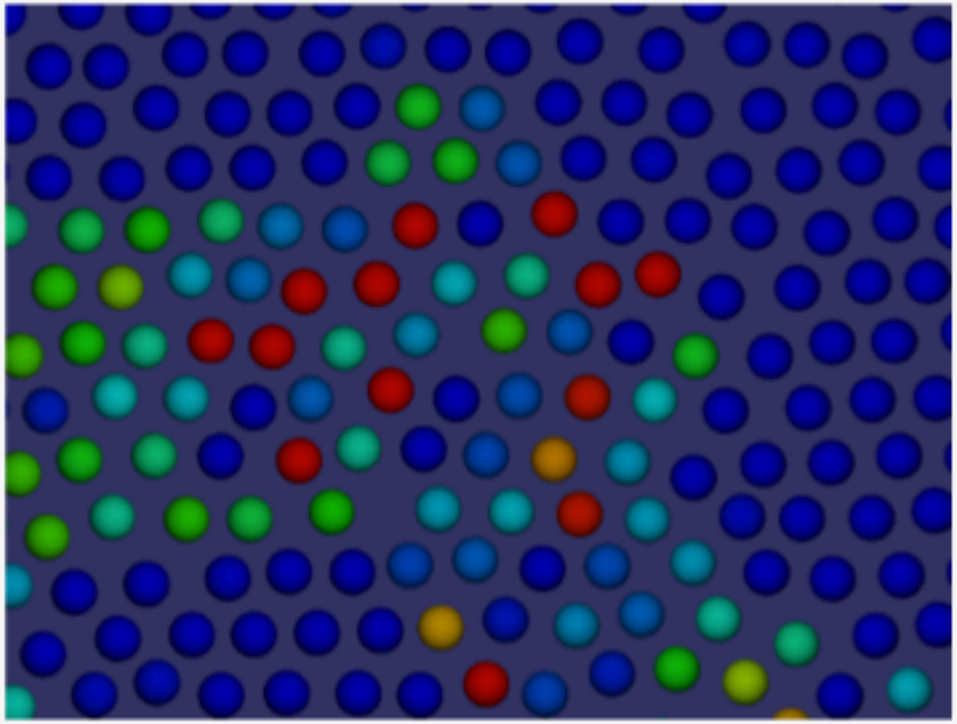
- superheating and supercooling

Role of thermal defects in the superheating limit



The number of defects sharply increases on melting (instead of accumulating gradually). This suggests a mechanism of melting not due to the nucleation of liquid, but due to the generation of percolating defects on the system.

Diffusion through percolating defects

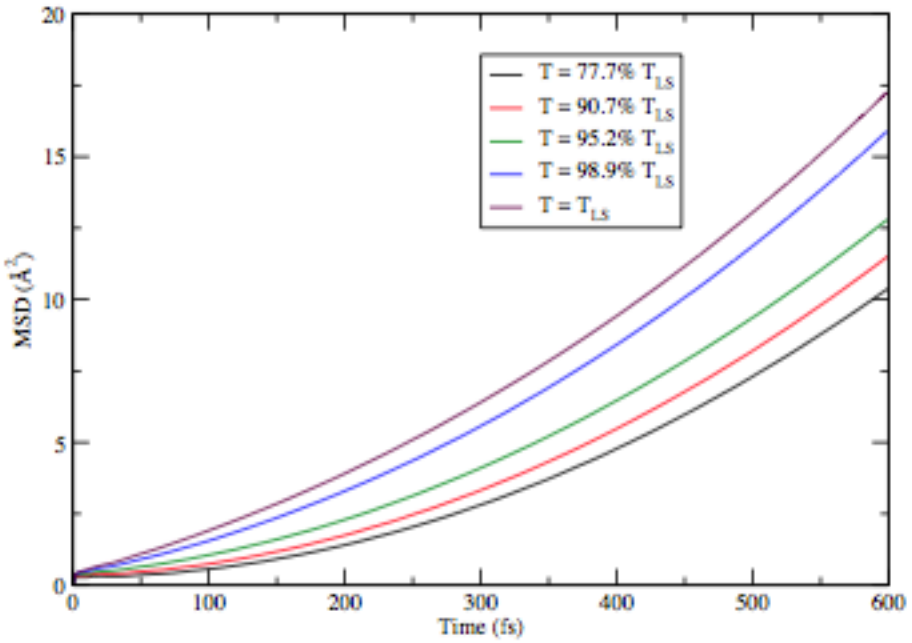


An atom in a crystal will jump to a neighboring site given two conditions:

1. The atom needs a vacant neighboring place next to it, this costs energy (E_v)
2. It also needs enough energy (E_c) to cross the energy barrier imposed by its neighbors

Anomalous diffusion close to T_{LS}

The MSD behaves neither like an ideal solid nor liquid near T_{LS}, it follows a power law: $\langle r^2(t) \rangle \propto t^{\gamma}$, with $1 < \gamma < 2$



However, being just an average over all atoms, the MSD cannot tell us much about the distribution of diffusing atoms.

Thank you!