

Melting and superheating of a simple solid: theory and simulation

Gonzalo Gutiérrez <gonzalogutierr@gmail.com>, Sergio Davis

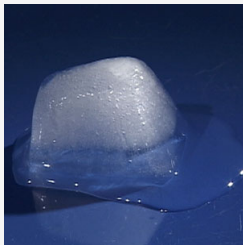
Departamento de Física, Facultad de Ciencias, Universidad de Chile

August 16, 2011



- Melting and Superheating
- Melting in microcanonical ensemble
- Computer simulation: molecular dynamics
- Results
- Conclusion

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.

First order phase transition in microcanonical ensemble

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

$$ds^\alpha = ds^\beta \Rightarrow \quad (2)$$

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

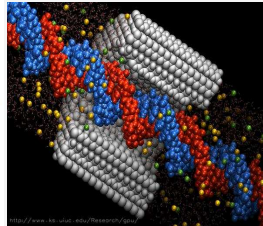
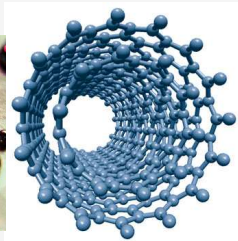
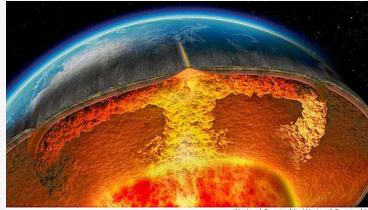
Thus: in contrast to isothermal-isobaric ensemble, here there are different T and p in each phase.

Here we have e and v of melting, instead of T_m and p_m .

The challenge is to relate both frameworks: $(e_m, v_m) \leftrightarrow (T_m, p_m)$

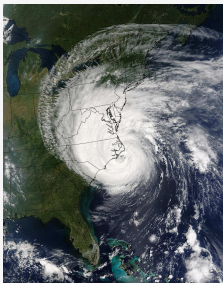
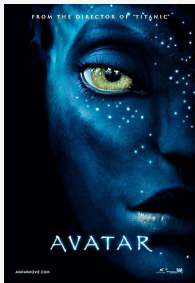
Some limits to purely theoretical and experimental methods

There are some difficult problems to treat experimentally, as well as with pure theoretical methods:



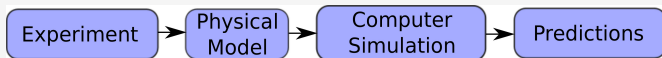
Computers constitute a powerful tool

So, why not use them?



- Computers have been doubling their capabilities every 24 months since 1971 (Moore's law: 18 months)
- Many different applications from climate modelling to “rendering” Hollywood 3D blockbusters
- Extremely parallel supercomputers, parallelism in graphics hardware (GPUs) now available
- Of course we can also use them to model and simulate interesting materials and physical conditions

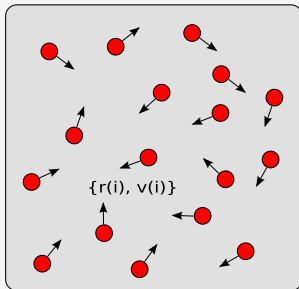
What can computers bring into scientific research?



- Computers are a powerful complement to experimental measurements and theoretical calculations.
- We now can implement and put to the test such complex models as never before
- We can explore conditions (high energies, high temperature and pressure) at the limit or beyond experimental reach.

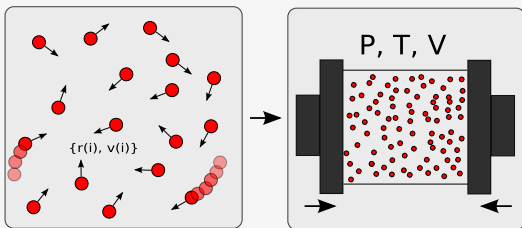
In Condensed Matter Physics, one of the most useful techniques for simulation is Molecular Dynamics (MD)

What is Molecular Dynamics?



- Take a system composed of a finite number of atoms or molecules.
- Interatomic forces are computed via some prescription, atoms are displaced to their future positions according to Newton's 2nd law, $m_i \vec{a}_i = \vec{F}_i$.
- Recorded trajectories of each atom are used to compute averages and obtain macroscopic properties using Statistical Mechanics.

How to obtain properties: Statistical Mechanics



- Statistical Mechanics tells us how to connect the microscopic scale up to the macroscopic description.
- Microscopic description is given by coordinates and momenta (\vec{r}_i, \vec{p}_i) , i.e the phase space of the system.
- Macroscopic description corresponds to thermodynamic quantities such as temperature, pressure, entropy and free energy

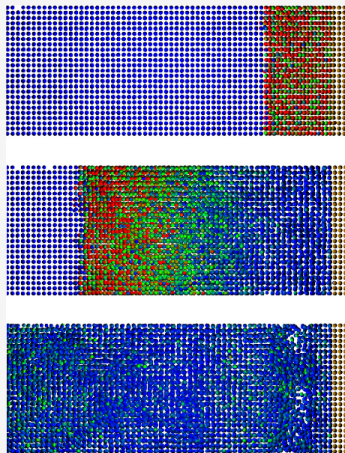
Outreach of Molecular Dynamics

What kind of properties can we calculate with MD? Among others,

- Structural properties (crystal structure, diffraction patterns)
- Mechanical properties (bulk modulus, elastic constants)
- Thermodynamical properties (melting points, free energies, phase diagrams)
- Dynamical properties (phonon spectrum)
- Transport properties (self-diffusion, thermal conductivity)
- Electronic and optical properties (only in the case of first-principles MD)

We can employ visualization tools to watch the onset of phenomena (fracture, melting) and gain qualitative insight.

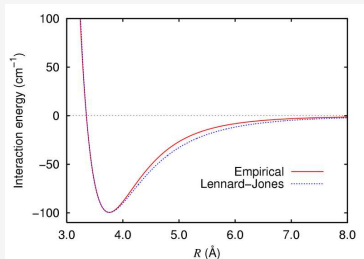
Non-equilibrium MD simulations



C. Loyola, S. Davis, J. Peralta and G. Gutiérrez. *Computational Materials Science* **49**, 582 (2010)

Classical Molecular Dynamics

Forces are obtained as the gradient of a (semi)empirical interatomic potential function. Typical example is the Lennard-Jones potential used for inert gases.

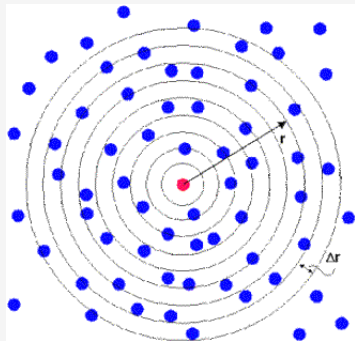


$$U(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right] \quad (4)$$

In the case of argon, $\sigma = 3.41 \text{ \AA}$ and $\epsilon = 119.8 \text{ K} \cdot k_B$

Radial distribution function

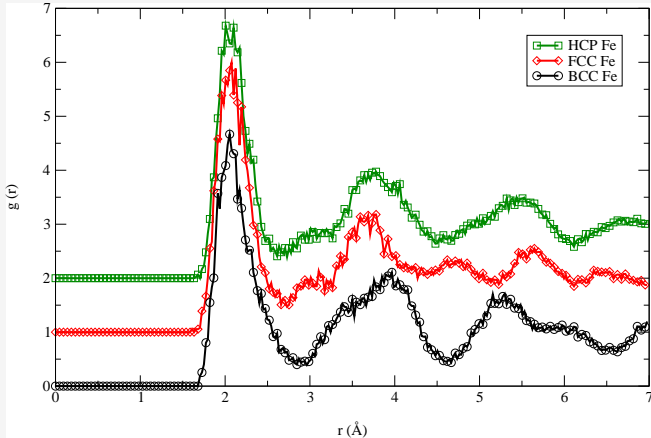
Used to describe the average structure of a solid or liquid. It measures the deviation of the average coordination $n(r)$ from an uniform distribution.



$$g(r) = \frac{V \langle n(r, r + \Delta r) \rangle}{N 4\pi r^2 \Delta r} \quad (5)$$

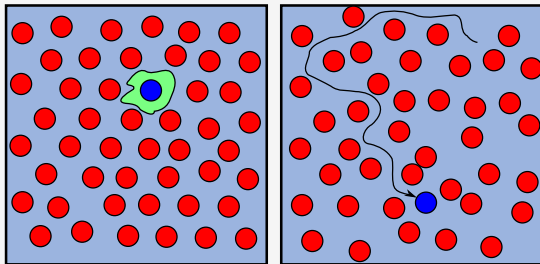
RDF for different phases

Different crystal structures give clear “signatures” through their RDFs:



Mean square displacement

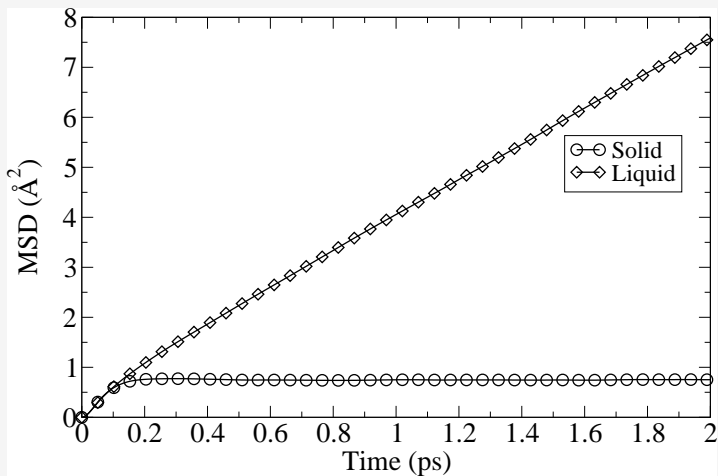
Average “drift” of an atom from its equilibrium position as a function of time. For solid this saturates for very long times, but for liquids it increases linearly.



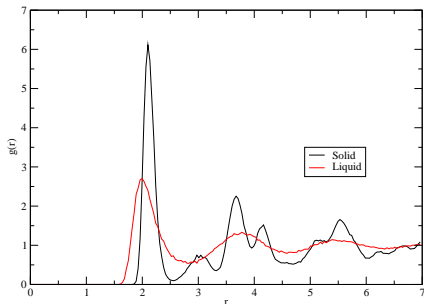
$$MSD(t) = \langle (\vec{r}(t_0 + t) - \vec{r}(t_0))^2 \rangle_{t_0} \propto 6D \cdot t \quad (6)$$

where D is the diffusion coefficient.

Mean square displacement



How do we compute T_m of a solid using MD?



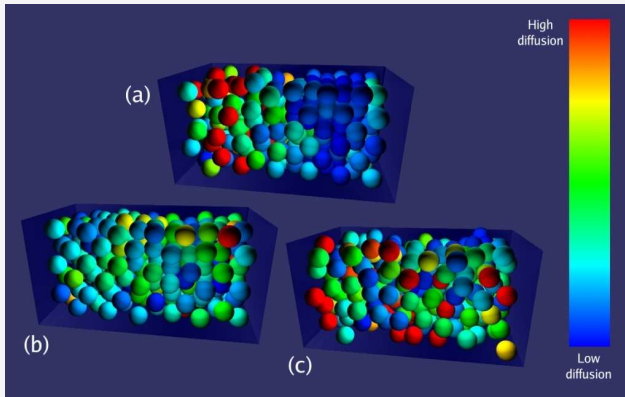
First thing one would try is just heat the solid and see when it changes in terms of structure or transport properties. However, this gives the wrong T_m because of overheating.

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

Two-phase method

J. R. Morris *et al*, Phys. Rev. B **49**, 3109 (1994)

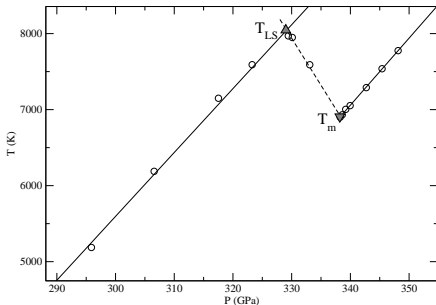
A. B. Belonoshko, Geochim. Cosmochim. Acta **58**, 4039 (1994)



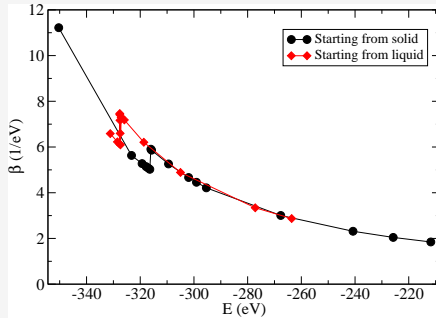
(b) Slightly below T_m both halves are solid, (c) slightly above both halves are liquid.

Z-Method

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

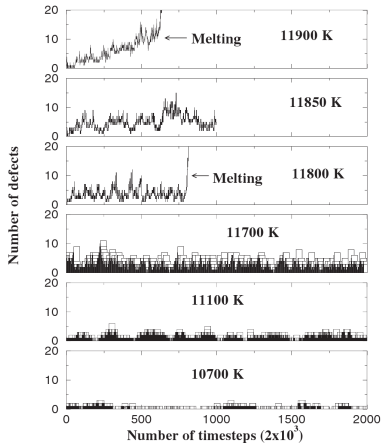


- One-phase simulation, following the isochore $T(P)_V$
- Every (T, P) point from microcanonical (N, V, E) MD at increasing initial kinetic energy K
- At T_{LS} , the smallest increase in K will trigger melting, and the change $\Delta U = U_{liquid} - U_{solid}$ subtracted from K will drop T precisely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



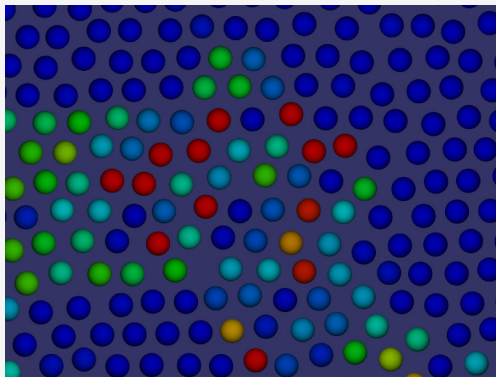
- superheating and supercooling

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

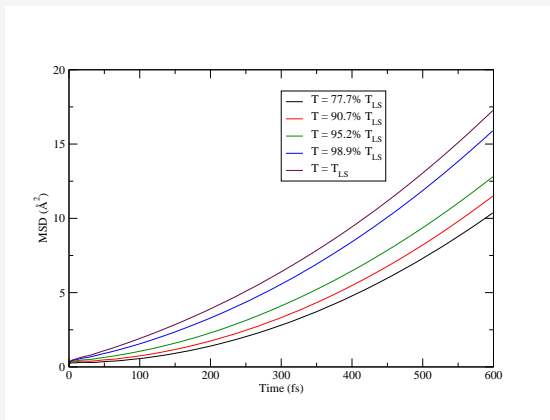


An atom in a crystal will jump to a neighboring site given two conditions:

- 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.

Concluding remarks

- Molecular Dynamics is an effective tool to study phase transitions, and in particular, melting.
- The Z-method has been proven a reliable, one-phase replacement for two-phase simulation.
- The challenge is to give a precise relation between micro and canonical phase transition.

Acknowledgements



- This work was developed the Group of NanoMaterials, University of Chile, together with Prof. Sergio Davis.

Thank you for your attention!