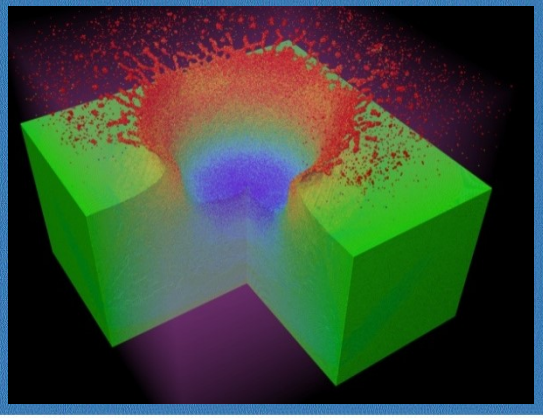
Introduction to Molecular Dynamics (MD) Simulations Part II: Advanced Applications



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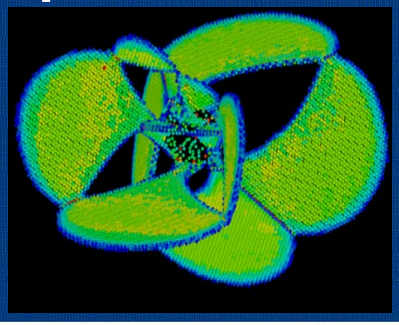
Aplicaciones de simulaciones y programación CUDA: estudios a escala atómica, fenómenos climáticos y ópticos

Centro de Investigaciones Hidráulicas e Hidrotécnicas (CIHH)

UTP, Panamá

September 2019



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SiMAF

Outline

- **Introduction**
- **Main caveats of MD simulations: potentials, time step, boundary conditions.**
- **Nano-thermodynamics and non-LTE conditions: temperature, pressure, melting, thermalization.**
- **Data analysis**
- **Simulation of "realistic" samples (not perfect crystals): dislocations, grains, impurities, porosity.**
- **Mechanical properties at high strain rate.**
- **Summary, conclusions and future perspective**

Two questions …

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Given all the approximations and limitations involved …

➡ Can we hope for quantitative agreement between MD and experiments?

OR …

➡ Is MD just pretty movies and pictures?

Atomistic simulations are extremely helpful but … still have multiple limitations

With MD you can obtain….

"Real" time evolution of your system.

Thermodynamic properties, including T(r,t) temperature profiles that can be used in rate equations.

Mechanical properties, including elastic and plastic behavior.

Surface/bulk/cluster growth and modification.

X-ray and "IR" spectra

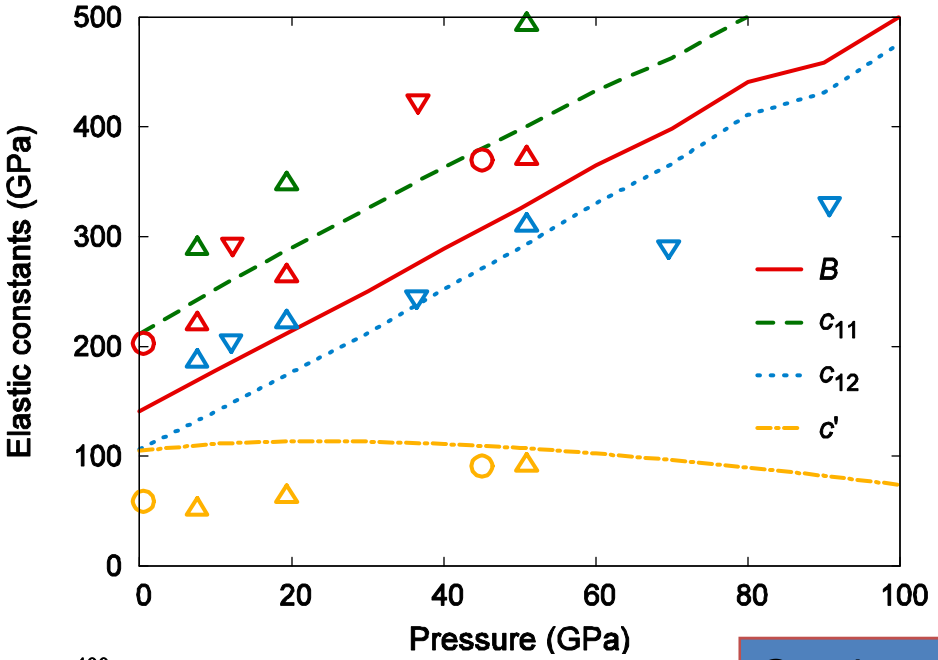
Etcetera …

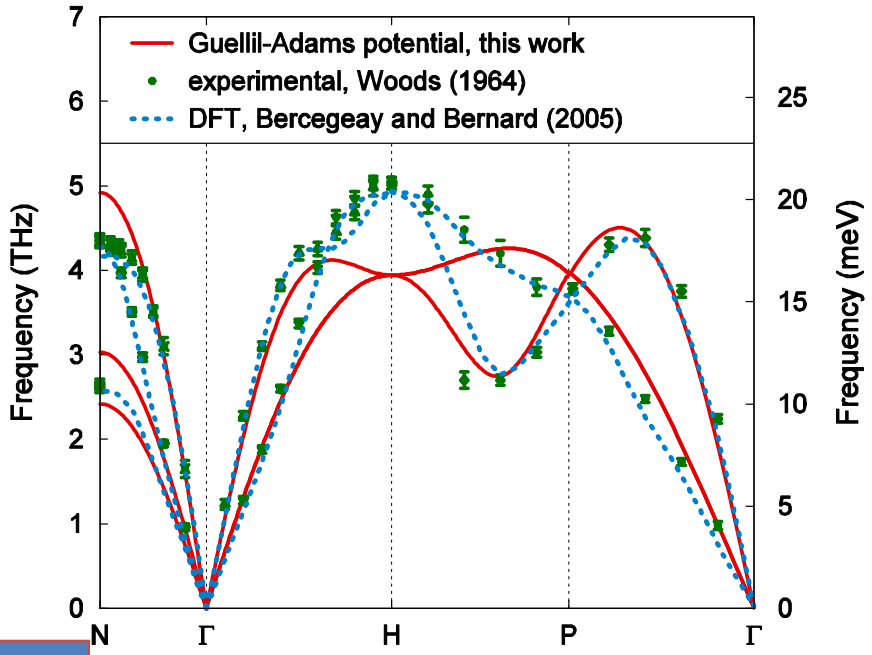
Limitations of MD

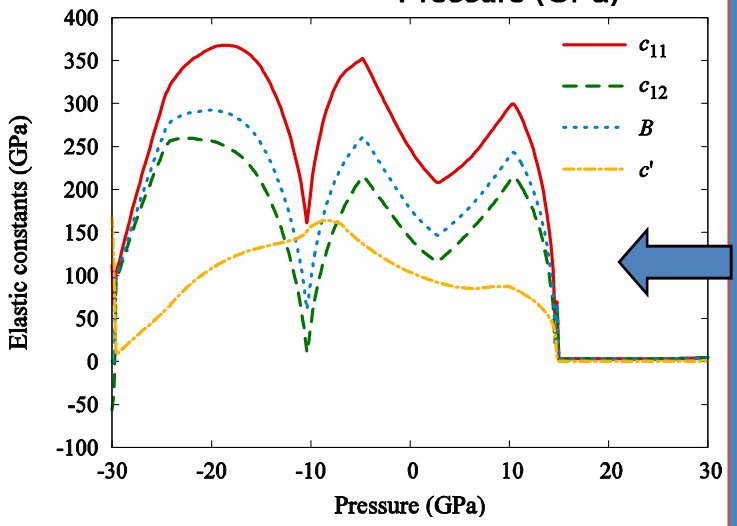
- Can simulate only small samples ($L<1$ μm, up to ~10^9 atoms).
- Can simulate only short times ($t<1$ μs, because $\Delta t \sim 1$ fs).
- Computationally expensive (weeks).
- **Potential's golden rule: trash in → trash out.**
- Interaction potentials for alloys, molecular solids, and excited species not well know.
- Despite its limitations **MD** is a very **powerful tool** to study nanosystems.

"Potential" problems: EAM potentials, phonons and elastic constants

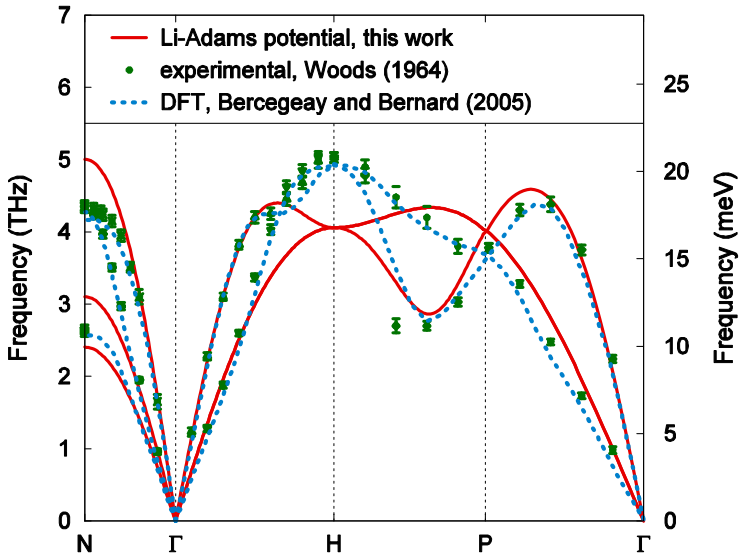
or when, even if the PV EOS is OK, other things can go wrong (Paul Erhart, LLNL)





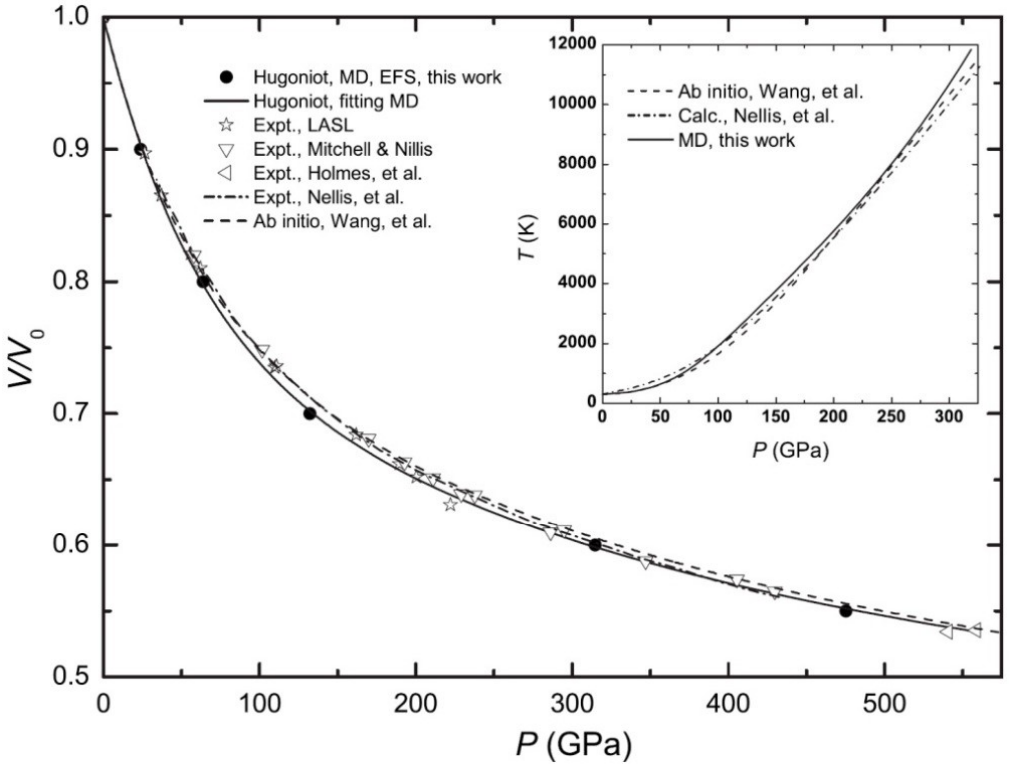


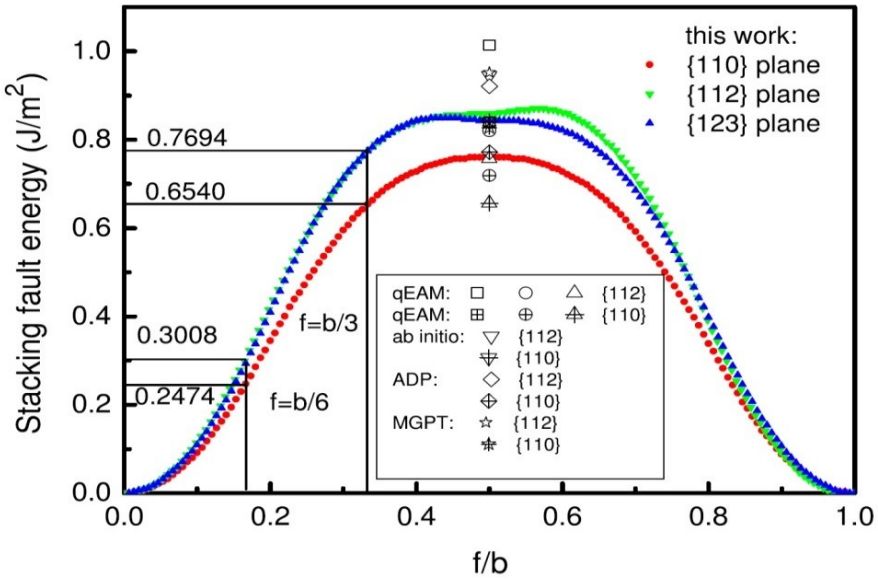
Good agreement with phonons at P=0 GPa, but discontinuities in elastic constants, due to splines in the potential, lead to multiple elastic fronts



Another example: EFS Ta Potential

X.D. Dai, Y. Kong , J. Phys. Cond. Mat. **18** (2006) 4527





Tang, Bringa, Meyers, Acta Mat. **59** (2011) 1354

Z-L Liu, L-C Cai, Phys. Rev. B **77** (2008) 024103

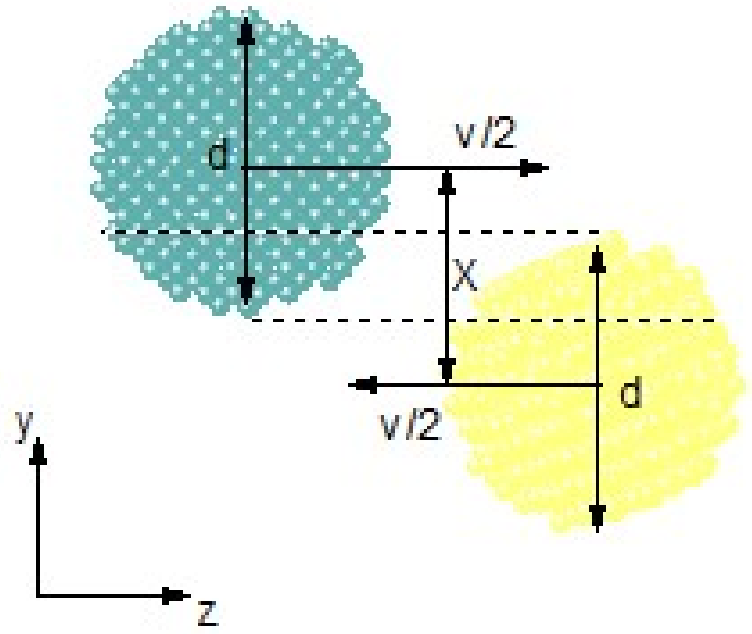
- Excellent agreement with PV, equilibrium Hugoniot, **melt line**, etc.
- Elastic constants OK up to ~1 Mbar.
- **BUT**… BCC→HCP at ~65 GPa (Ravelo *et al*., SCCM-2011).

Potential validity depends strongly on type of fit, which can emphasize a certain property, temperature & pressure range, structure, etc.
Potentials are often non-transferable ☹

Time Evolution: be aware of possible energy drift

COLLISION DYNAMICS OF CARBON CLUSTERS, NVE (D. Bertoldi)

AIREBO potential (2011)



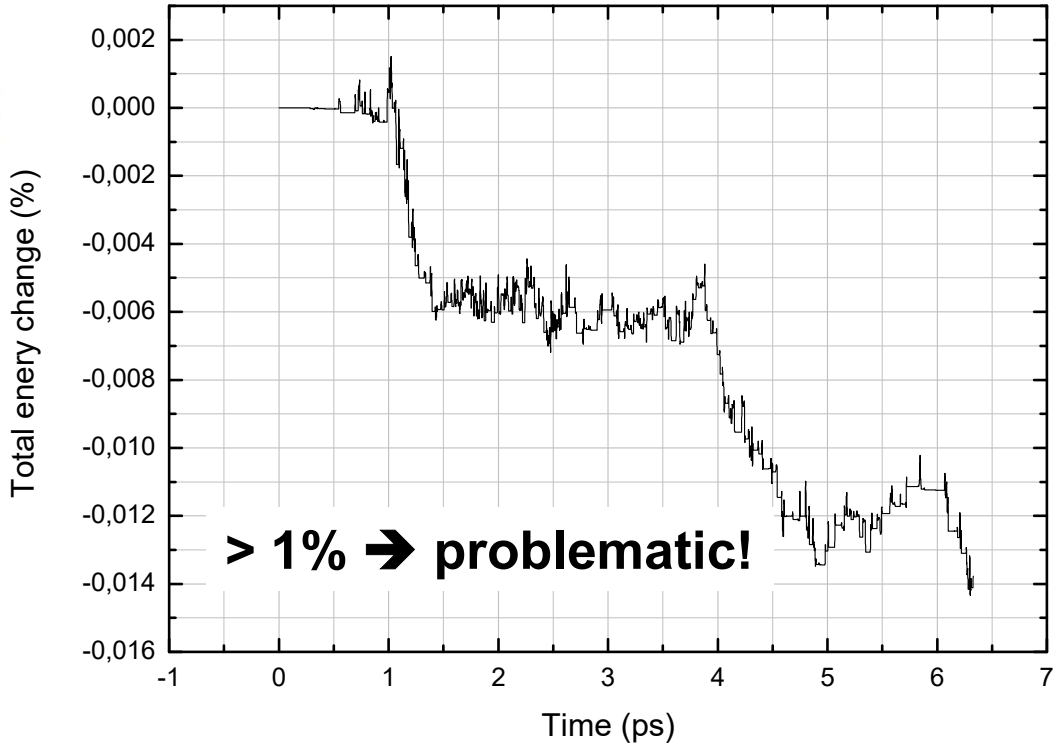
"dt reset"

t_{min} = 1.E(-6) ps

t_{max} = 0,001 ps

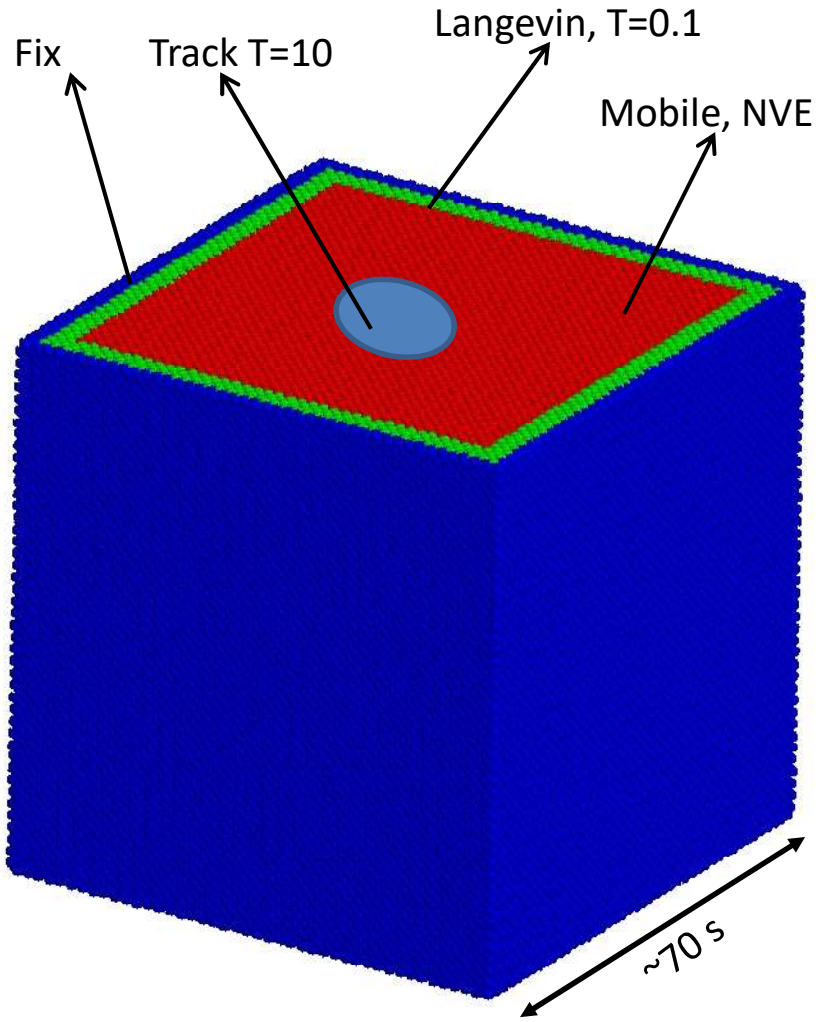
X_{max} = 0,0001 Å

- Energy drift caused by integrator and computational errors.
- Simulations far from equilibrium have to use variable time step schemes,



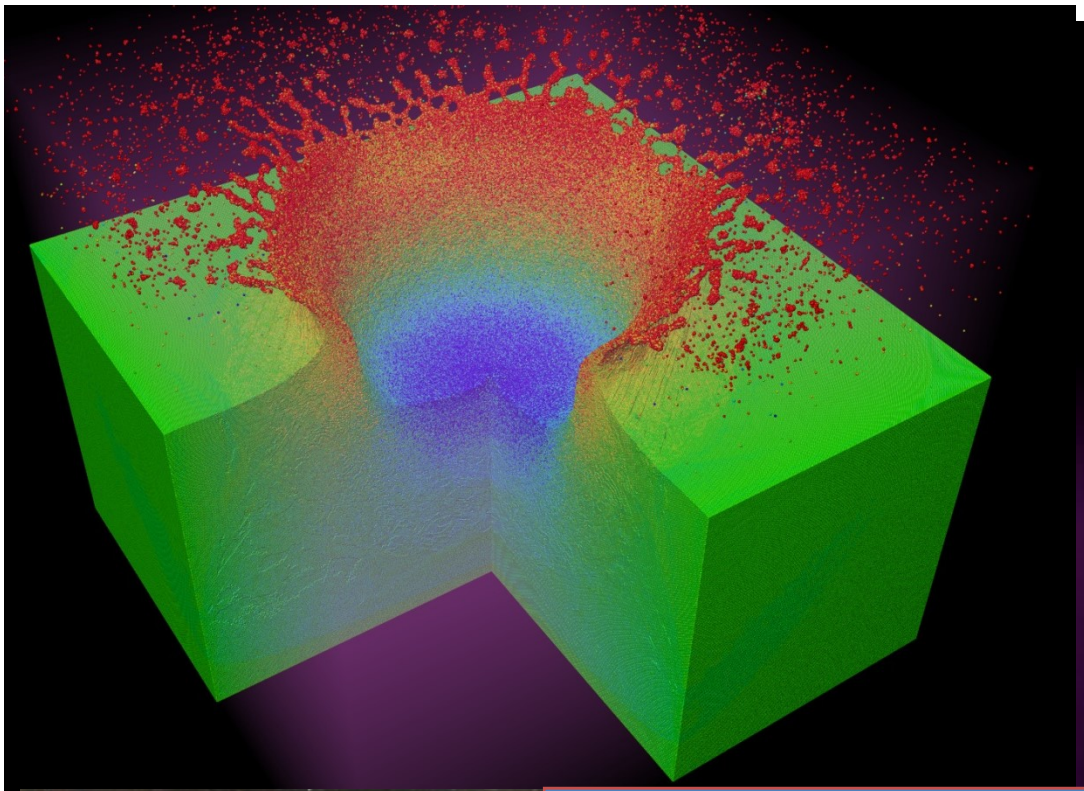
Simulation details need to include info on BC

- PBC in (x,y), free BC with expansion (z). Langevin bath with critical damping at the sides.
- Need to re-calculate damping for each interatomic potential and bath condition.
- There are complex schemes to have impedance matching at boundaries, but none standard.
- Size has to be large enough to capture desired phenomena. Need to verify this by running simulations of different sizes: results should not change beyond certain size L, or they could be extrapolated versus 1/L.



Simulation of hot spot

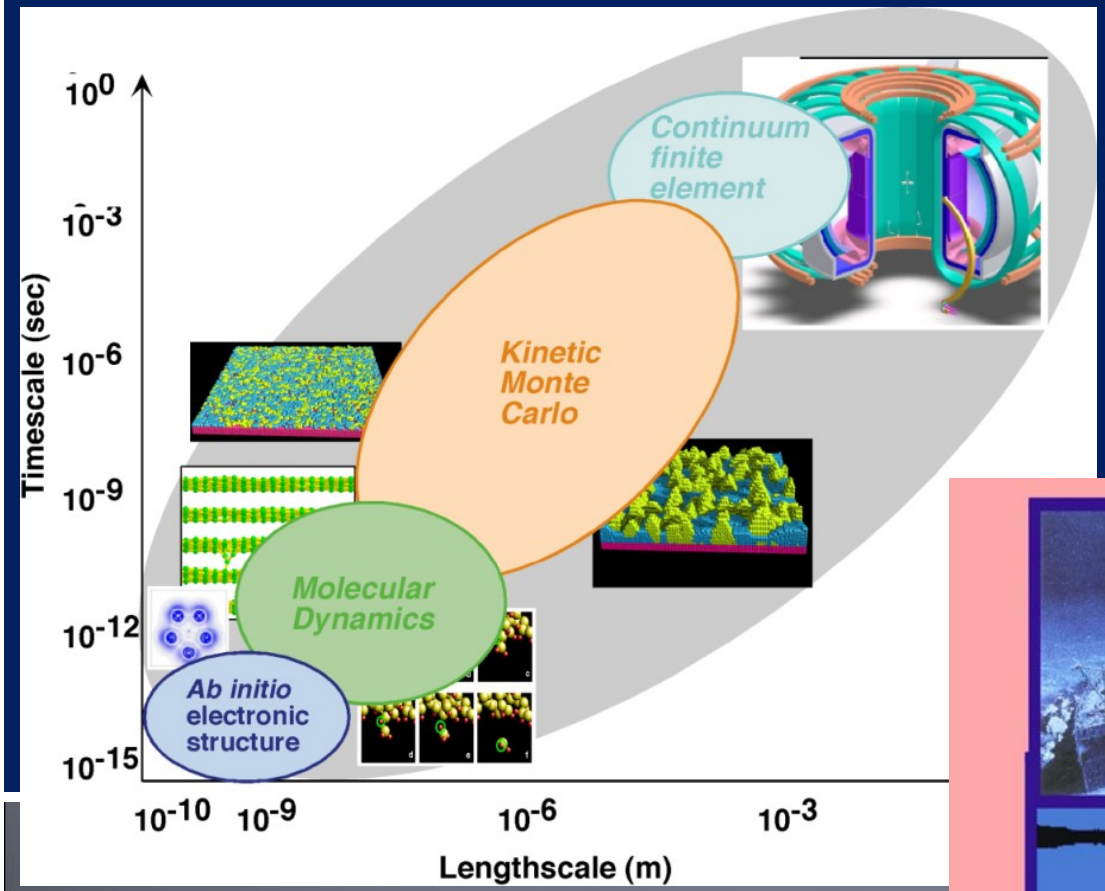
Large-scale MD links nano and microscales in damage induced by nanoprojectiles [C. Anders *et al.*, PRL 108, 027601 (2012)]



Only dislocations + liquid atoms are shown

$R_{cluster}$=20 nm, 20 ps after impact, ~300 10^6 atoms, 15 hours using 3,840 CPU's in Thunder (LLNL)

¿Do we really need multiscale simulations?



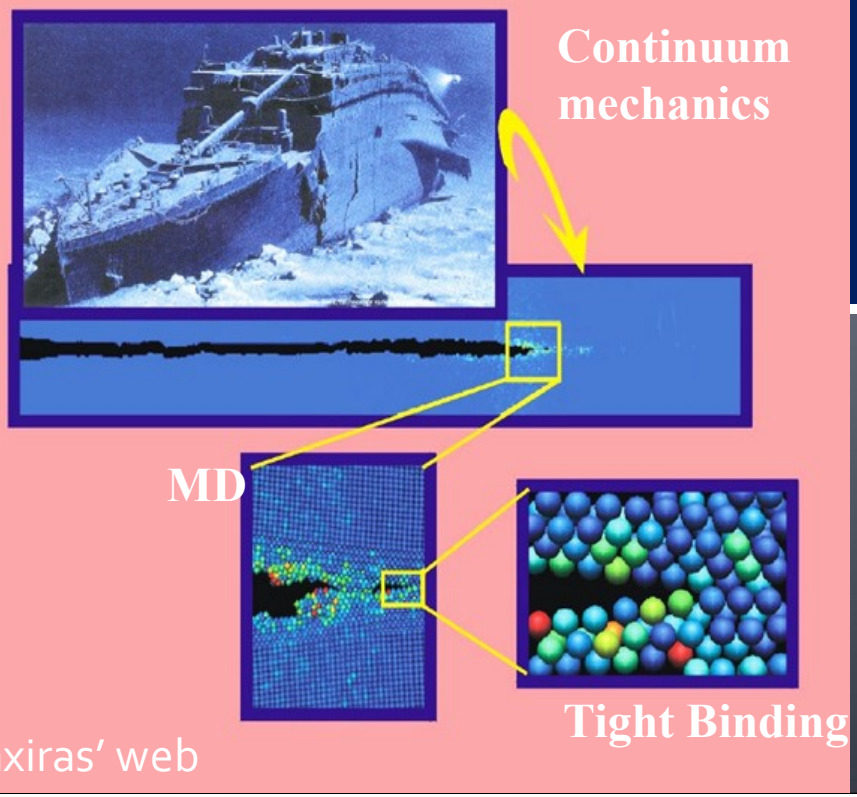
1 meter= 1,000,000 microns

1 meter= 1,000,000,000 nanometers

Human hair's width ~ 200 μm

Estaphilococcus ~ 1 μm

Rhinovirus ~ 200 nm



Nanoscale does affect macro scale and properties of materials.

Coupling TIME and length scales ….

- Concurrent coupling methods have many caveats ….
- Choose set of parameters from MD, save those parameters and "pass" them to a "higher" level code. Example: calculate defect concentrations as the initial configuration for a kinetic Monte Carlo code.
- Use some accelerated technique, which boost the time step, for instance "TAD" by A. Voter (LANL). Very expensive computationally, generally practical only for "2D" simulations or small 3D simulations.

Have to be smart to avoid large/long simulations if possible.
Several people currently working on improved scale-coupling.
Keep tuned!

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(a) Definition of temperature in nano systems

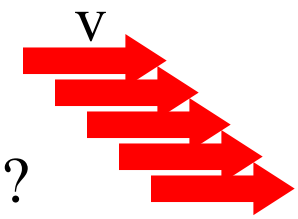
Usual: $(3/2)\, N\, k_B\, T = E_{kin}$

Nano Systems: $$T_\omega = \frac{1}{k}\left[\left(\frac{3N}{2} - 1\right)\langle E_{kin}^{-1}\rangle_\mu\right]^{-1}$$

Jellinek & Goldberg, Chem Phys. (2000)
Pearson et al, PRB (1985)

Correction due to non-zero flow velocity <v>:

$E_{kin} \rightarrow (m/2)\,(v - \langle v\rangle)^2$

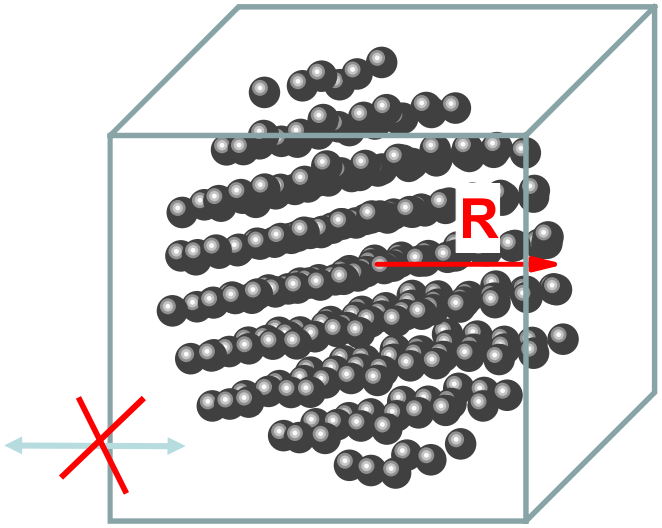


$E_{kin} > 0$, but T=??

"Partial" T's: T_{rot}, T_{vib}, T_{ij}

(b) Al Nanoclusters

D. Bertoldi (ICB)



MD using LAMMPS[1] -

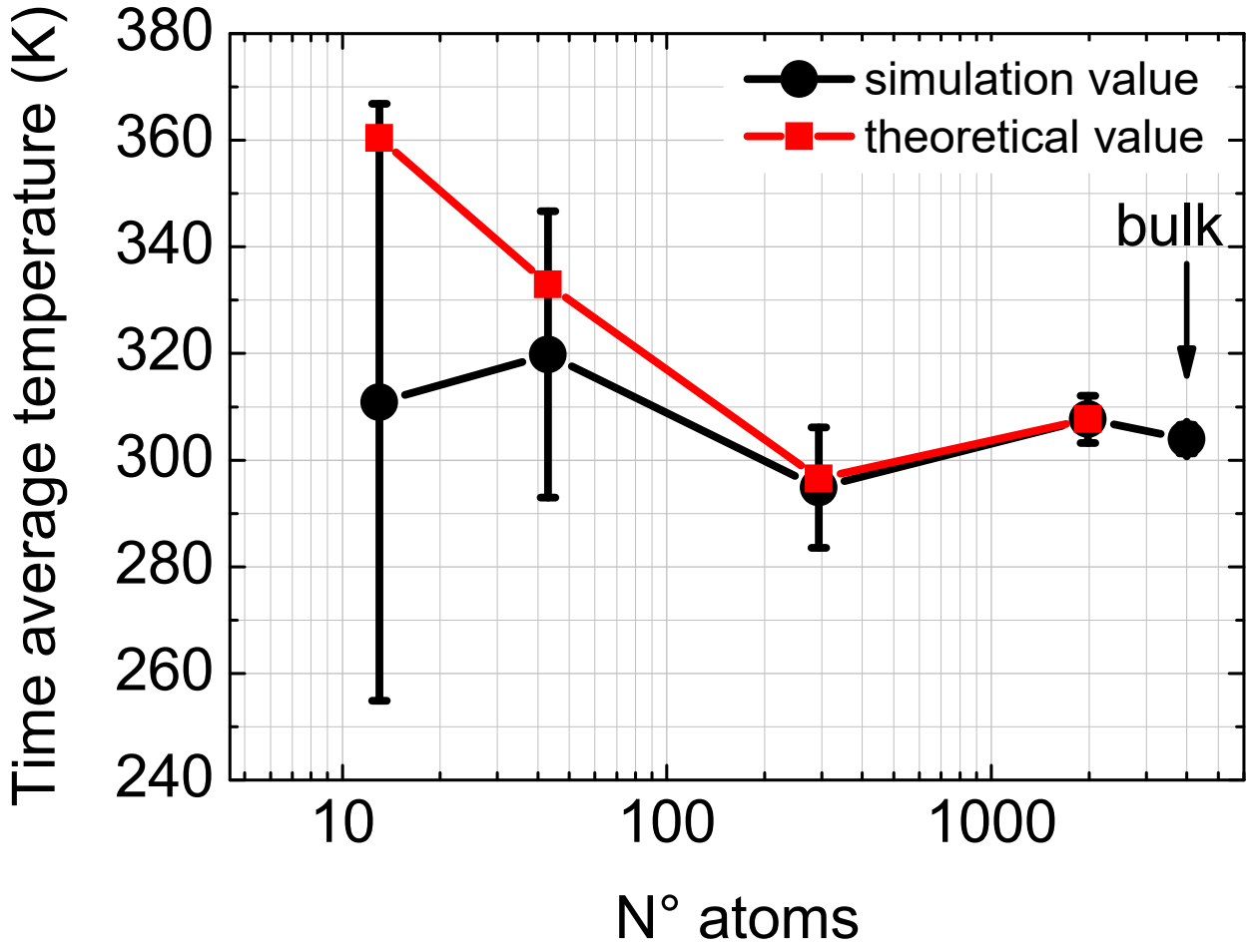
Microcanonical ensemble (N,V,E)
Temperature ~ 300K

EAM potencial by **Mishin**[2]

R =
- 0,3nm → 13 atoms
- 0,5nm → 43 atoms
- 1nm → 249 atoms
- 2nm → 1985 atoms

[1] www.lammps.sandia.gov
[2] Y. Mishin *et al.*, "Embedded-atom potential for B2-NiAl" PRB **65** (2002)

Cluster Temperature



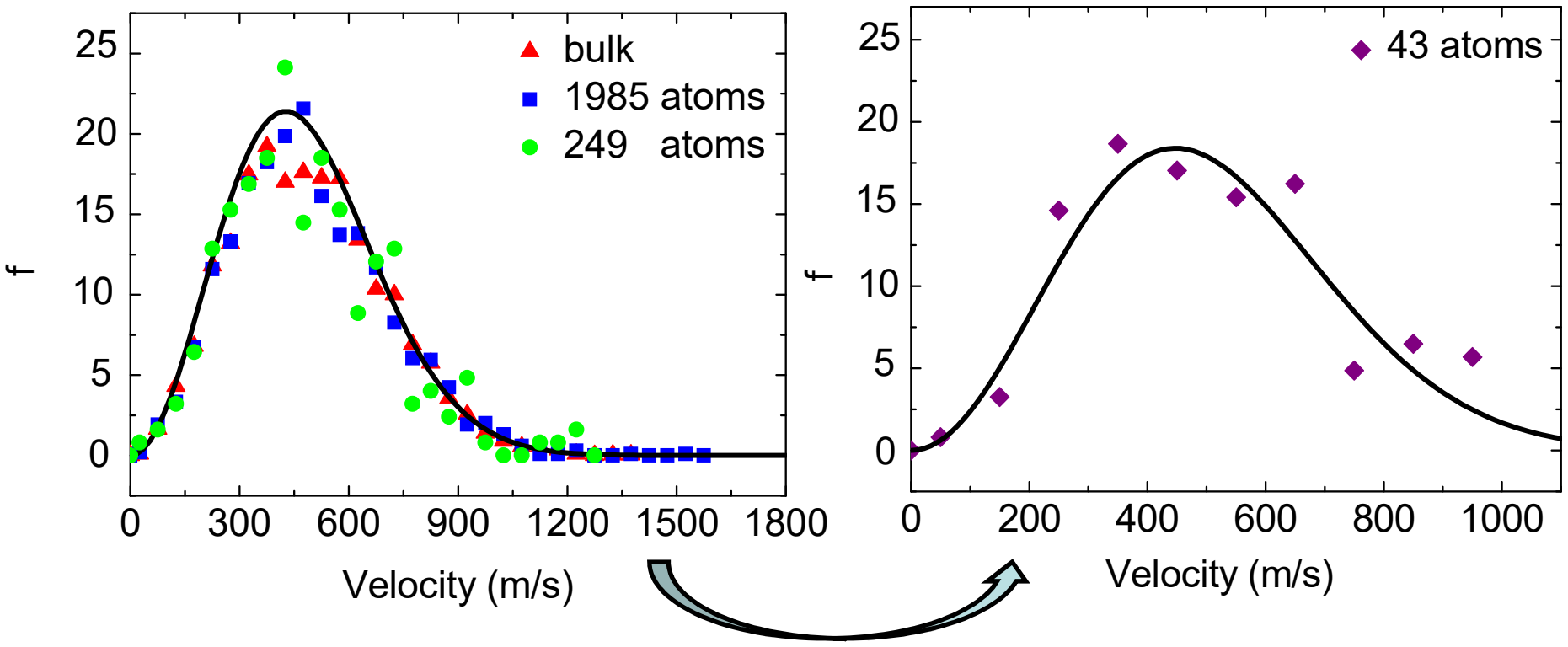
Calculated with T_d (Jellinek et al.)

MD

Averaged during the last 0,1 ps of simulation

Velocity Distribution in clusters

Aproximate with a Maxwell-Boltzmann distribution



When there are not enough atoms, distribution have to be averaged over time, but M-B still works reasonably well.

(c) Can we define an atomic stress tensor? Only with caveats

$$S_{ab} = -\left[mv_a v_b + \frac{1}{2}\sum_{n=1}^{N_p}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b}) + \frac{1}{2}\sum_{n=1}^{N_b}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b}) + \right.$$
$$\frac{1}{3}\sum_{n=1}^{N_a}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b} + r_{3_a}F_{3_b}) + \frac{1}{4}\sum_{n=1}^{N_d}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b} + r_{3_a}F_{3_b} + r_{4_a}F_{4_b}) +$$
$$\left. \frac{1}{4}\sum_{n=1}^{N_i}(r_{1_a}F_{1_b} + r_{2_a}F_{2_b} + r_{3_a}F_{3_b} + r_{4_a}F_{4_b}) + \sum_{n=1}^{N_f} r_{i_a}F_{i_b} \right]$$

Virial stress for atom I (lammps)

a, b= x,y,z . Includes thermal, pair, bond, angle, dihedral, improper, and "fix"

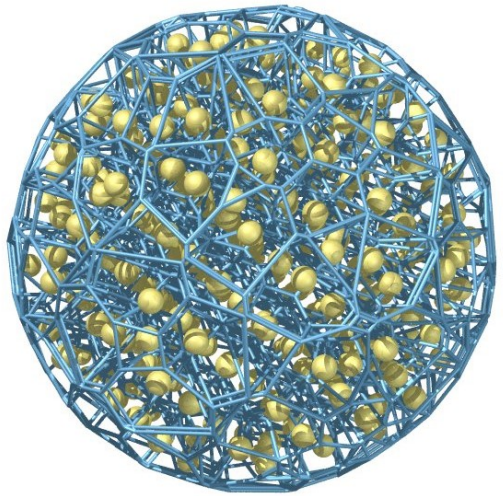
Be careful with Nk_BT term …it should discount flow velocity in calculation of T

S = σ V ➔ how do we define "atomic" volume to calculate momentum flux?

Possible solution: use Voronoi polyhedra

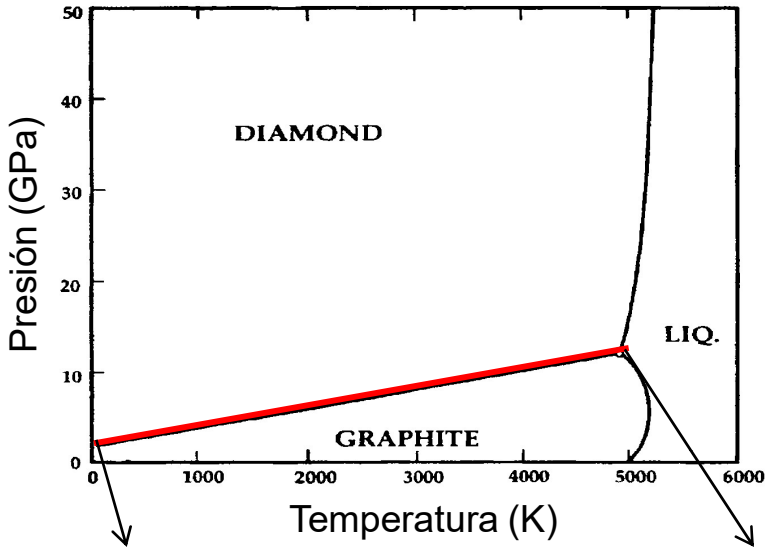
PdH nanoclusters. Using Voronoi or mean volume gives roughly the same results. Work with G. Bertolino, M. Ruda (Centro Atomico Bariloche), S. Ramos, E. Crespo (UN Comahue, Neuquen)

Int. J. Hydrogen Energy (2012)



(d) Phase Diagram for carbon clusters

Diagram for bulk sample



(1700 MPa, 0 K) (12000 MPa, 5000 K)

$P = 1700 + 2.06T$

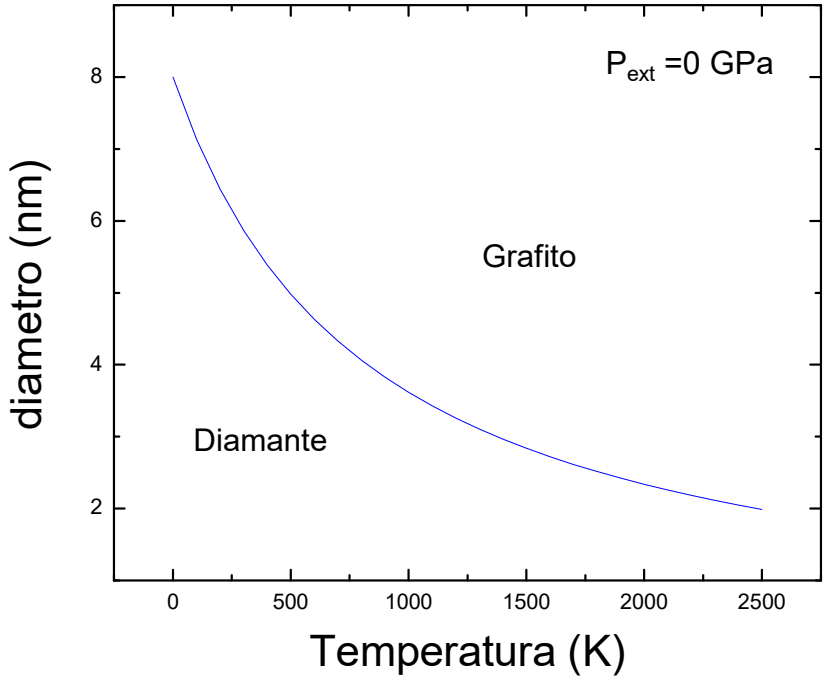
Ec. Laplace-Young : $P = 4\gamma / d$

$d = 4\gamma / (1700 + 2.06T)$

in equilibrium

$\gamma = (\gamma_D + \gamma_G)/2$

Diagram for a spherical cluster

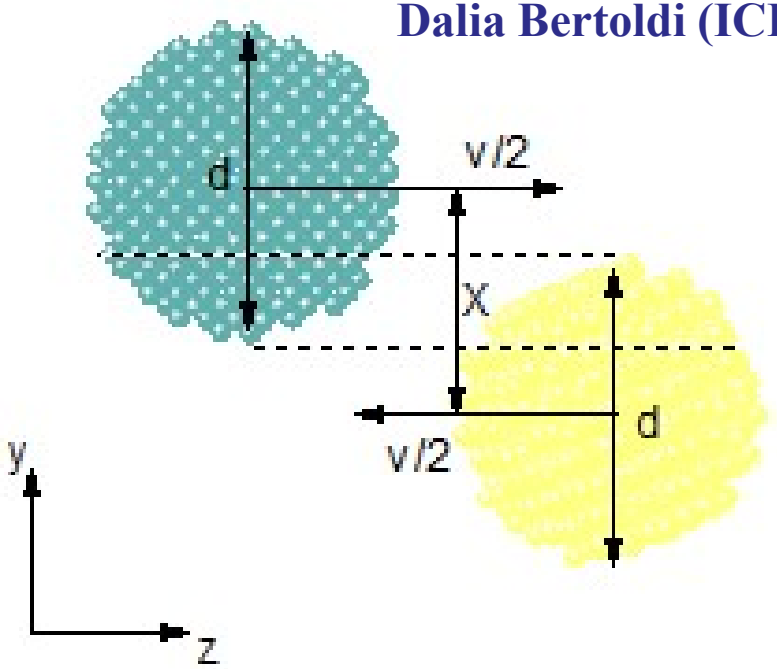


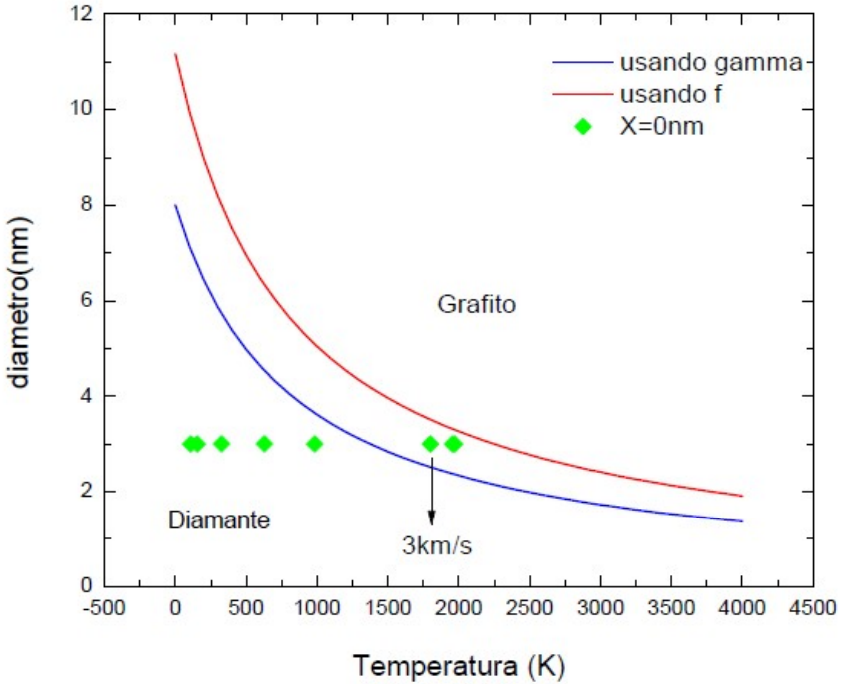
Transitions diamond → graphite and graphite → diamond , have different kinetics

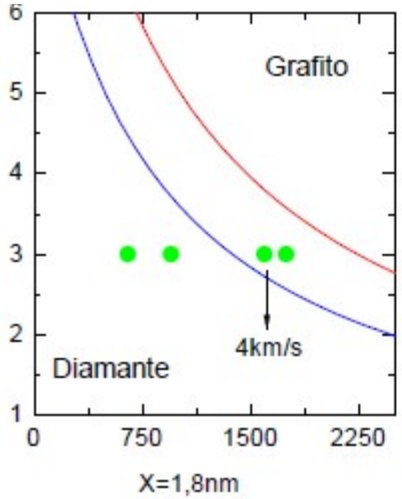
Zhao, D. et al, "Size and temperature dependence of nanodiamond-nanographite transition related with surface stress", Diamond and Related Materials **11** (2002) 234.

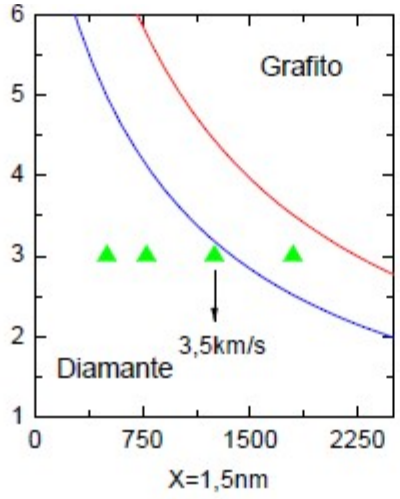
COLLISION OF CARBON NANOGRAINS

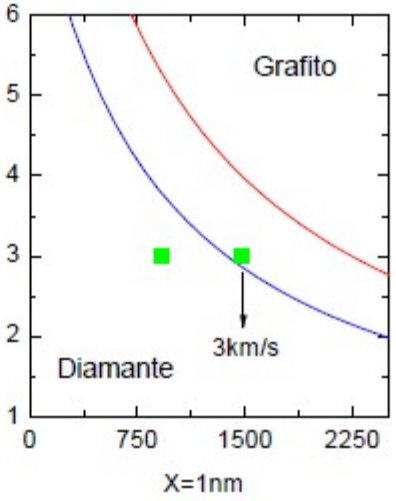
Dalia Bertoldi (ICB)

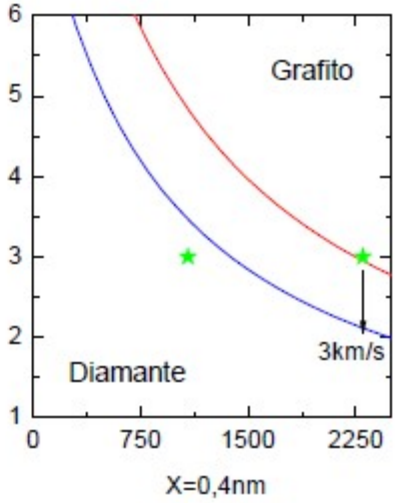




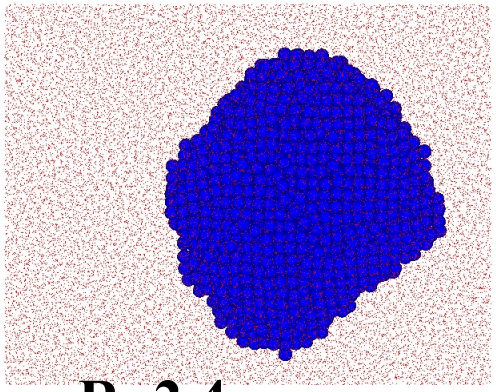




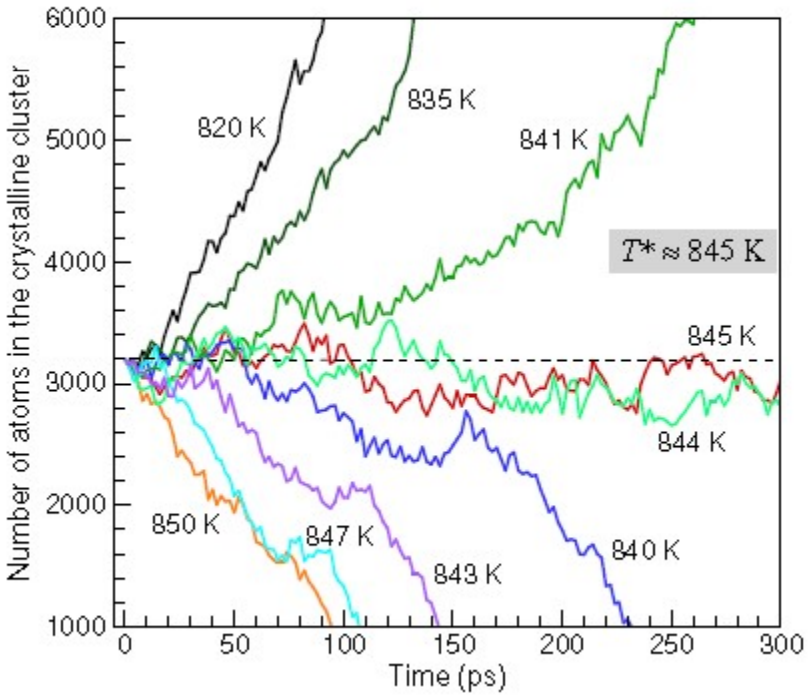


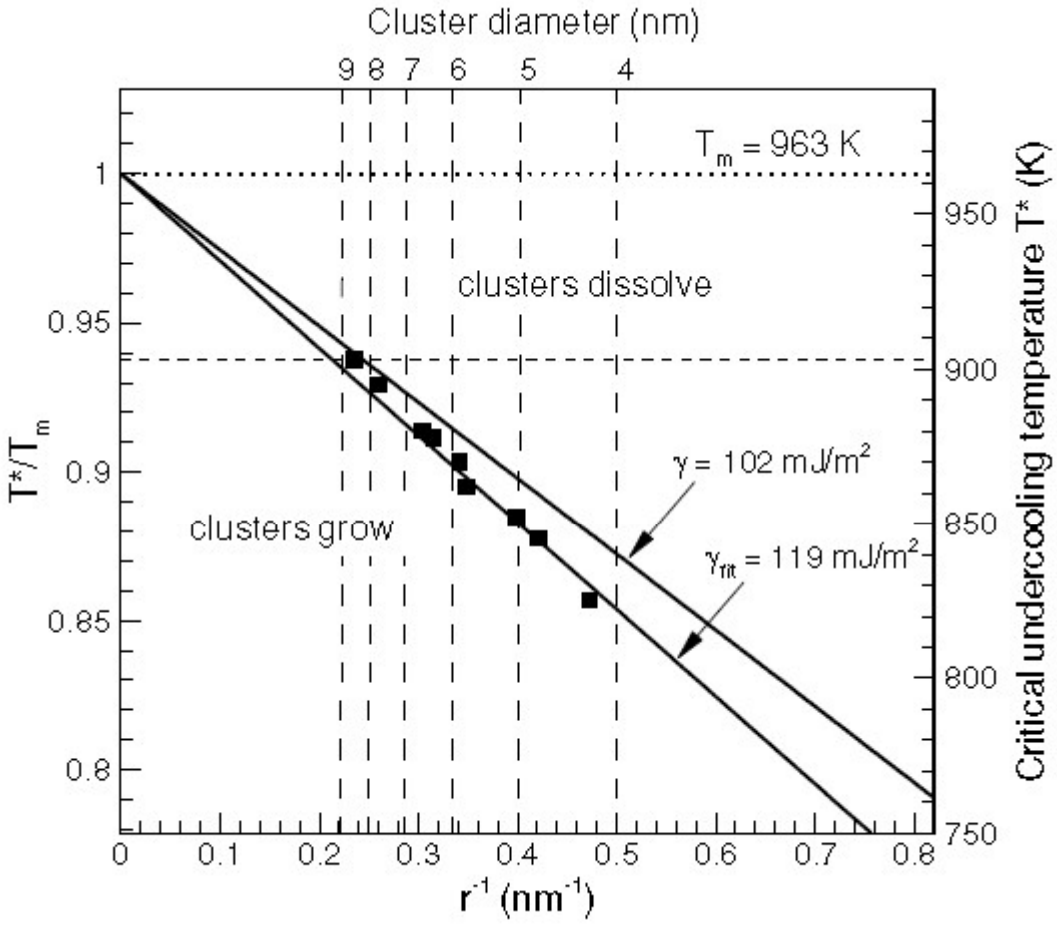


(f) Melting of Au nanoclusters



R=2.4 nm





Lin, Leveugle, Bringa, Zhigilei, J. Phys. Chem. (2010)

Melting temperature changes only ~15%

➔difficult to detect experimentally

(g) Heating a solid without a surface (no transport)

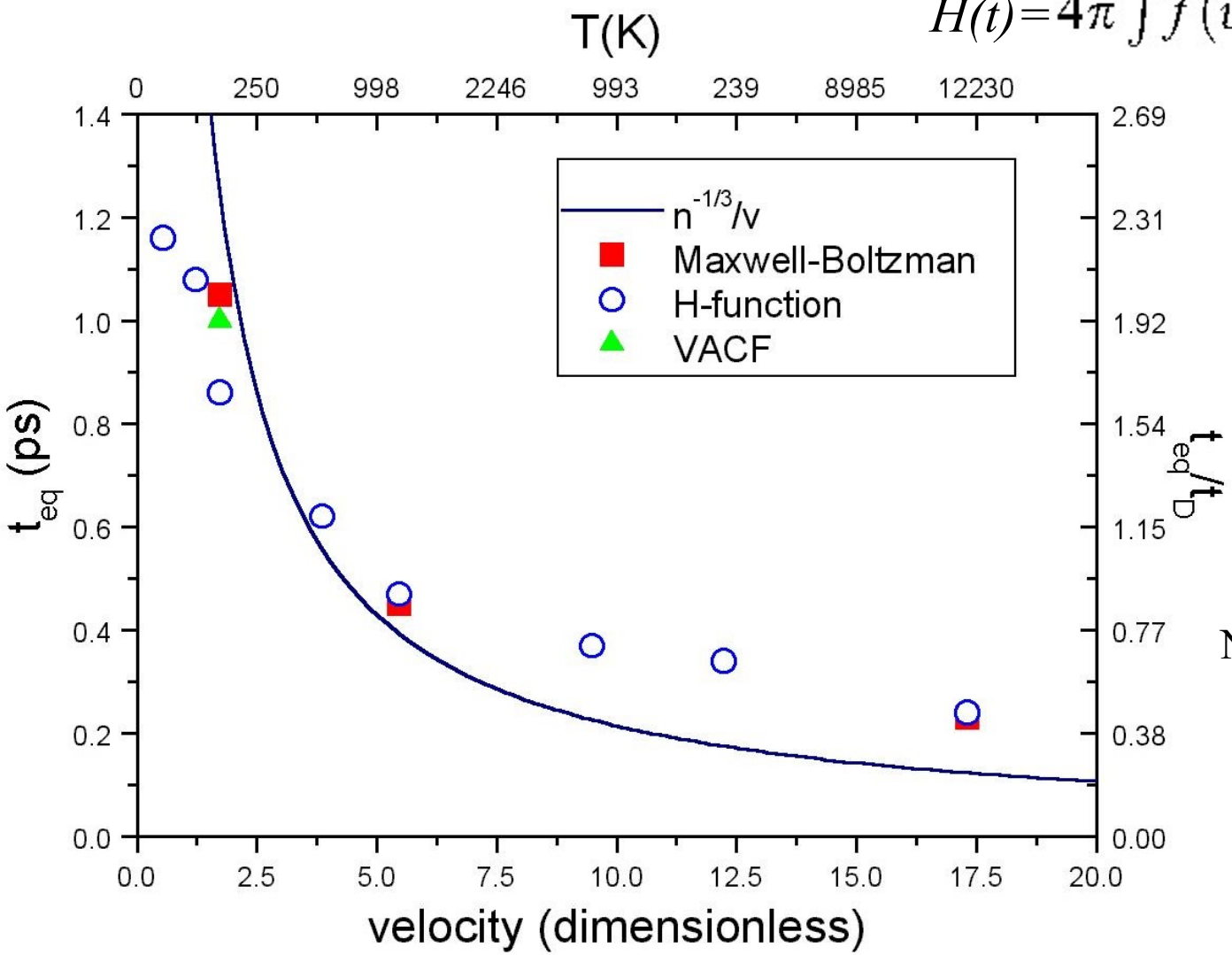
- Is thermodynamics still valid at small times and length scales?
- How long does it take for a "perturbed" system to equilibrate?

LJ solid
Binding energy U
E_{exc}/atom

Thermodynamic Equilibrium?

Equilibration time in homogeneous system

$$H(t) = 4\pi \int f(\vec{v}, t) \log[f(\vec{v}, t)] \mathrm{d}\vec{v}$$

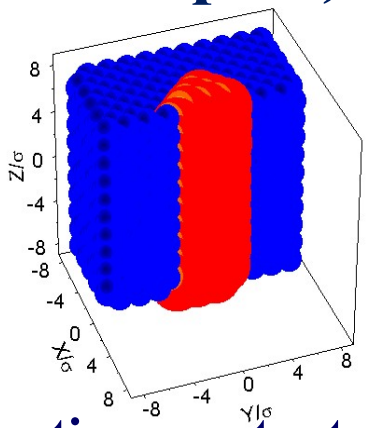


EQUILIBRATION IS FASTER THAN EXPECTED (compared with hard spheres). Each atom interacts with ~80 neighbors

Bringa & Johnson, Nuclear Instruments and Methods in Physics Research B **143** (1998) 513-535

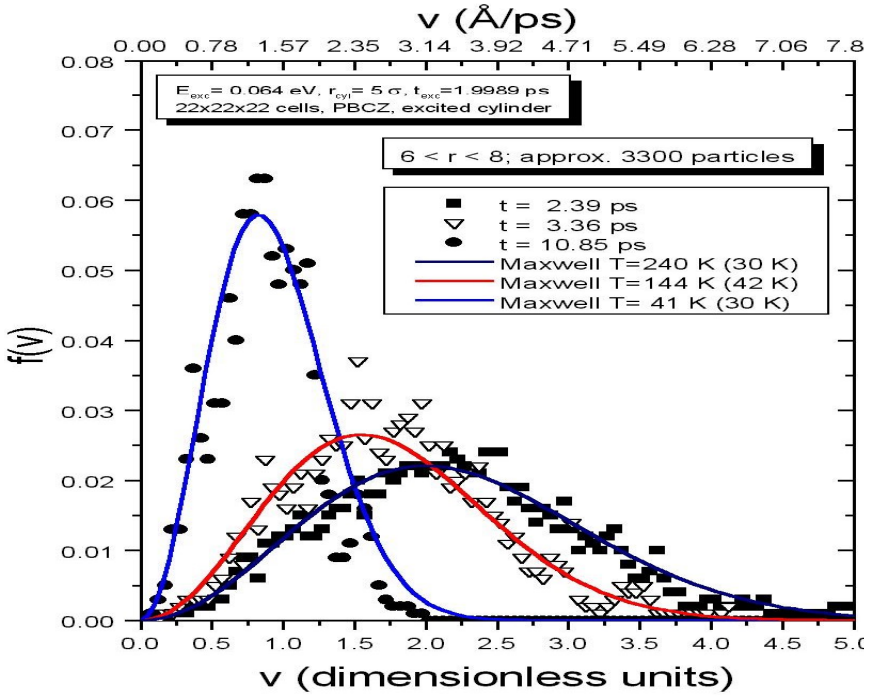
(h) Heating a solid without a surface (only radial transport)

heating of cylinder with radius r_{cyl}



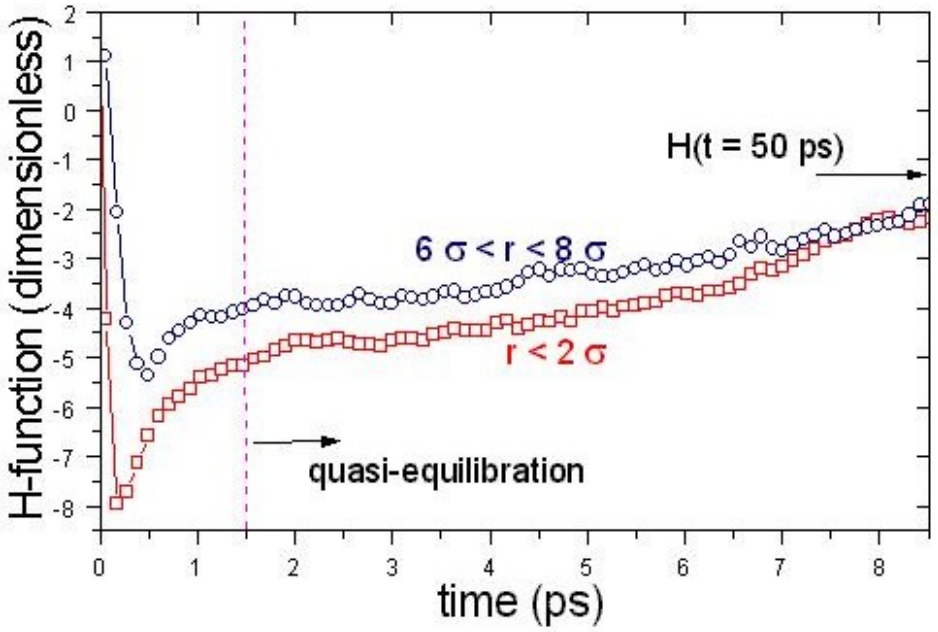
- Large gradients (10^3 K/nm) ….
- How long does it take for LTE?

"Local" M-B distribution



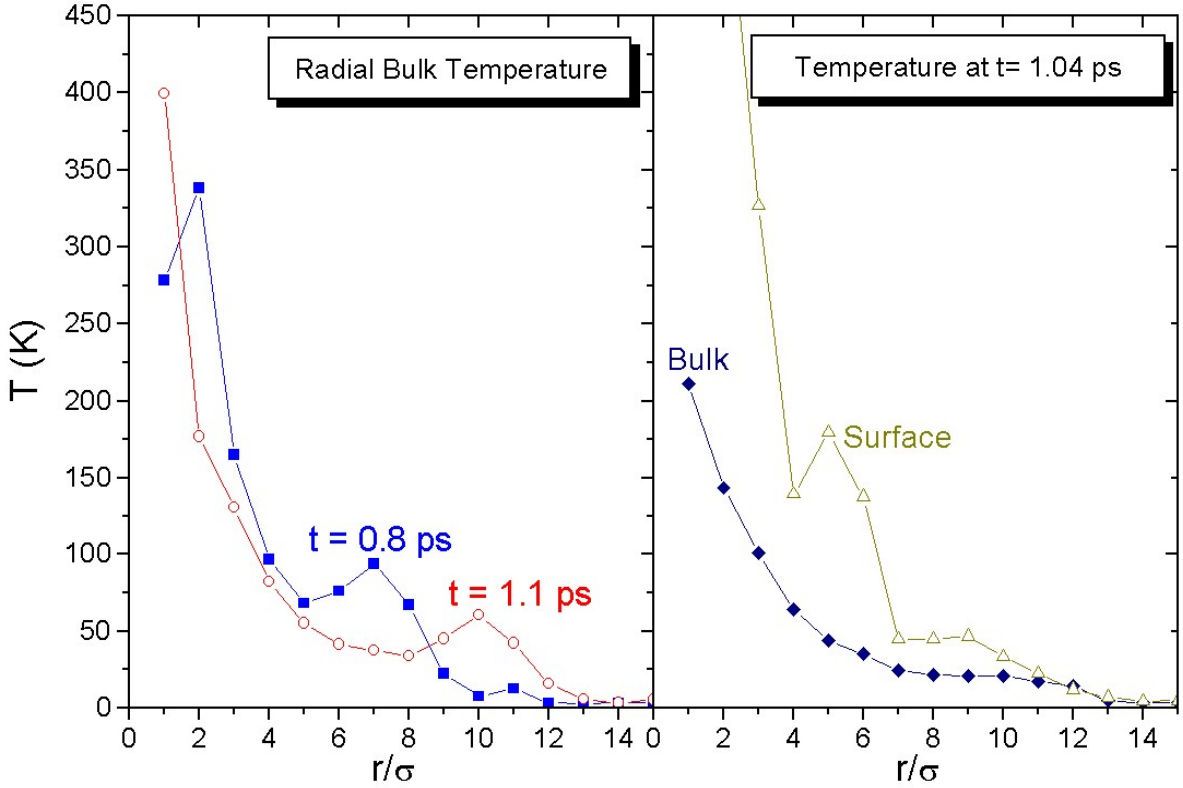
Rough way to obtain equilibration time

"Local" Boltzmann H-Function constant
➔thermal equilibrium



Local equilibration time is <u>longer</u> than equilibration time for homogeneous heating

Temperature profiles (with a surface): lack of LTE and deviations from Fourier equation



T_{radial} for two different times. T_{radial} shows a 'bump' because of the outgoing `shock'. Surface temperature is much higher than Bulk temperature due to energy transport towards the surface. E_{exc} = 4 U, r_{cvl} = 2σ.

Problems:

- **Lack of LTE more serious for molecular solids.** Bringa and Johnson, Surf. Sci. (1997)
- **Parabolic → Hyperbolic**
  D.D. Joshep, L. Preziosi, Rev. Mod. Phys. 61 (1988) 41.
  S. Volz, J. Saulnier, M. Lallemand, B. Perrin, P. Depondt, M. Mareschal, Phys. Rev. B 54 (1996) 340.
- **Stefan problem (moving boundary).**
  Caro, Tarzia, etc.

Temperature profiles show axial energy transport
Large difference between radial and axial temperature

Outline

- **Introduction**
- **Main caveats of MD simulations: potentials, time step, boundary conditions.**
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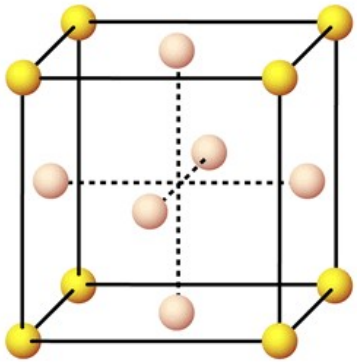
Data analysis

SiMAF

- On the fly and post-processing of data takes considerable time …
- Need to choose appropriate analysis tools to avoid artificial results.
- Whenever possible, carry out the analysis in parallel with domain decomposition and neighbor lists.
- Care must be taken with time averaging.

Centro-Symmetry Parameter (CSP)*

- **Centro-symmetry parameter** *(CSP):* a parameter to measure the local disorder, particularly useful to study cubic structures.

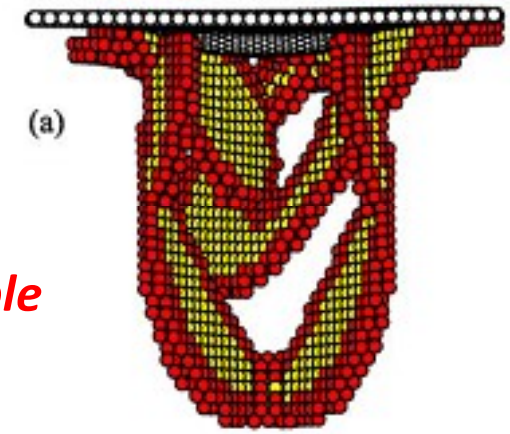


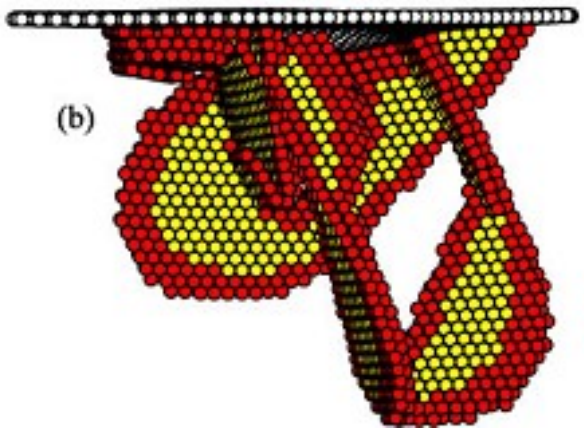
f.c.c structure

$$C = \sum_{i=1}^{6} \left| \vec{R}_i + \vec{R}_{i+6} \right|^2$$

CSP expression for a f.c.c. unit cell

This is done for every atom in the sample
➔ high computational cost





Kelchner et al, FIG. 2, partial view. Defect structure at the first plastic yield point during indentation on Au (111), (a) view along [112], (b) rotated 45° about [111]. The colors indicate defect types as determined by the centrosymmetry parameter: partial dislocation (red), stacking fault (yellow), and surface atoms (white). Only atoms with P>0.5 are shown.

*** Kelchner, Plimpton, Hamilton, Phys Rev B, 58, 11085 (1998)**

Common Neighbor Analysis

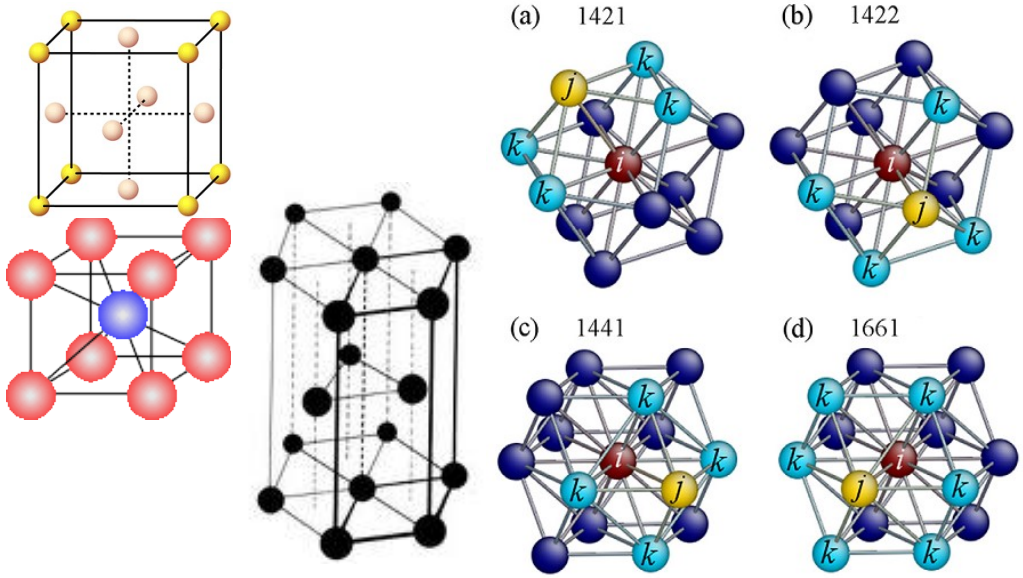
- **CNA***:* a parameter to measure the local disorder
- Sensitive to cutoff radius
- 12 nearest neighbor for perfect FCC and HCP crystals, 14 nearest neighbors for perfect BCC crystals

This is done for every atom in the sample
➔ high computational cost

$$r_c^{fcc} = \frac{1}{2}\left(\frac{\sqrt{2}}{2}+1\right)\mathrm{a} \simeq 0.8536\,\mathrm{a}$$

$$r_c^{bcc} = \frac{1}{2}(\sqrt{2}+1)\mathrm{a} \simeq 1.207\,\mathrm{a}$$

$$r_c^{hcp} = \frac{1}{2}\left(1+\sqrt{\frac{4+2x^2}{3}}\right)\mathrm{a}$$



• Faken, Jonsson, Comput Mater Sci, 2, 279 (1994).
• Tsuzuki, Branicio, Rino, Comput Phys Comm, 177, 518 (2007).

DXA (Dislocation eXtraction Algorithm)

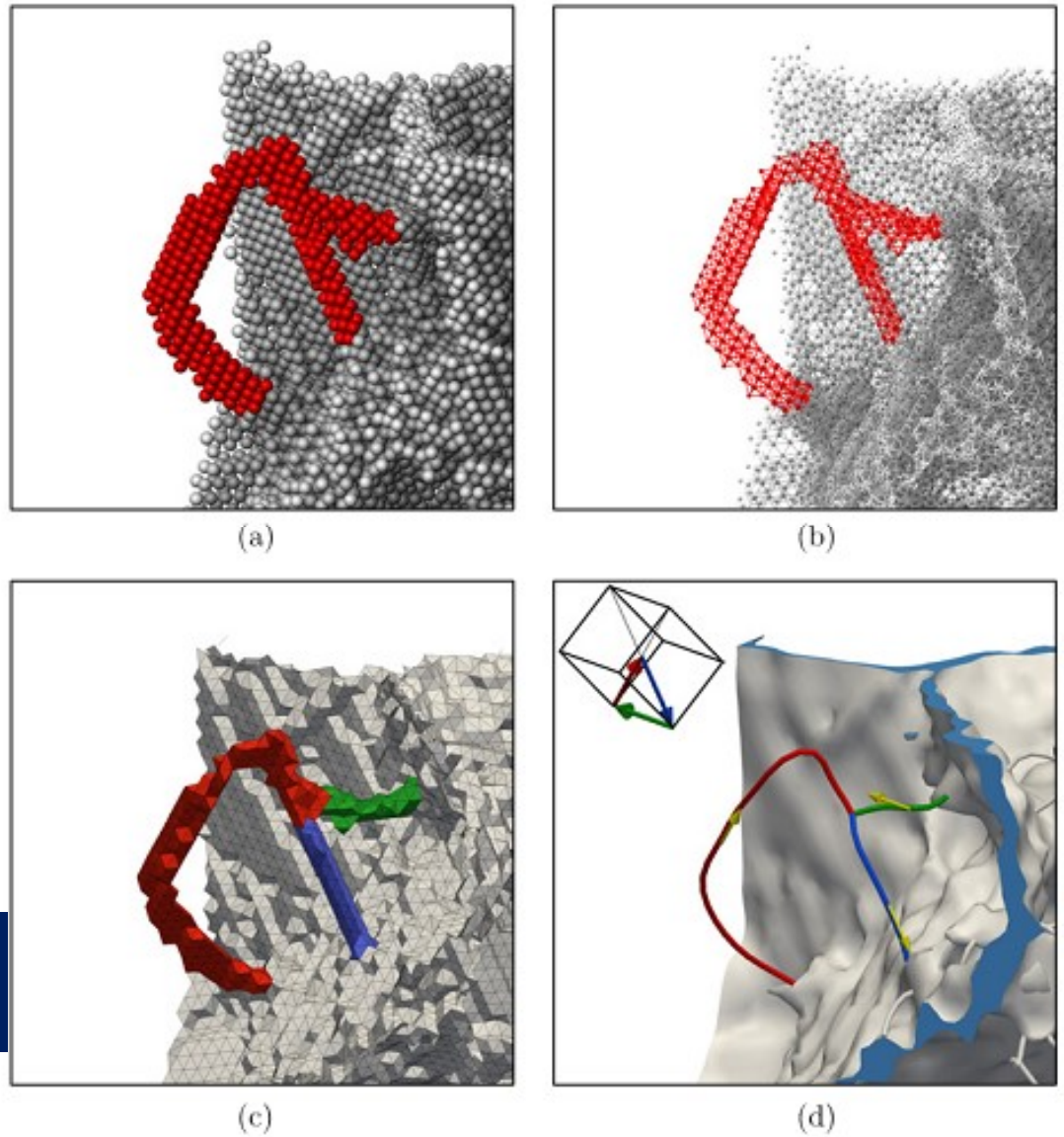
Stepwise conversion of atomistic dislocation cores into a geometric line representation.

(a)Atomistic input data.

(b) Bonds between disordered atoms.

(c) Interface mesh.

(d) Smoothed output.



Changes in DXA parameters can have large effect on results

A. Stukowski and K. Albe, Modelling Simul. Mater. Sci. Eng. 18 (2010) 085001.

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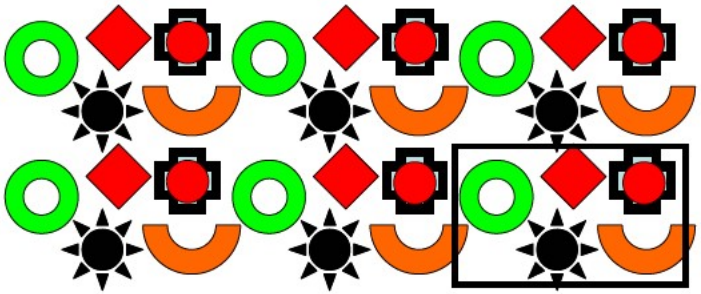
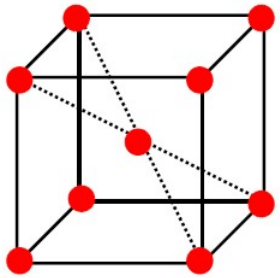
Microstructure of crystalline materials

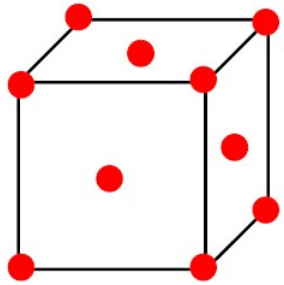


Unit Cell



Body-centred cubic (bcc)

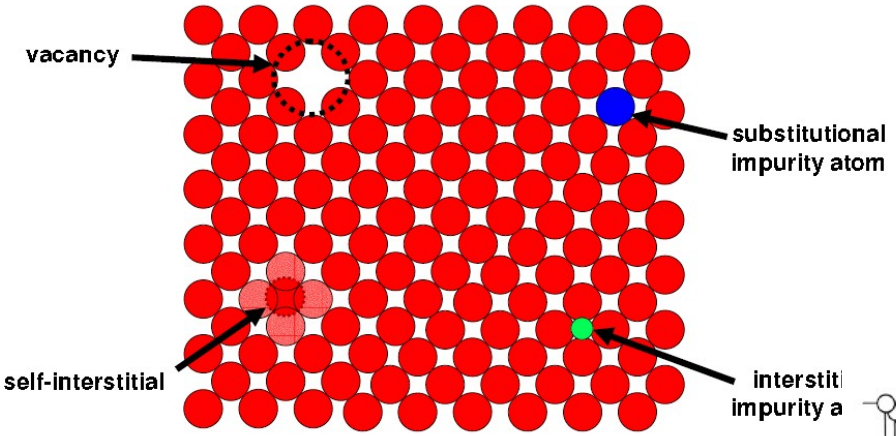
Fe,W,V,Ta,…



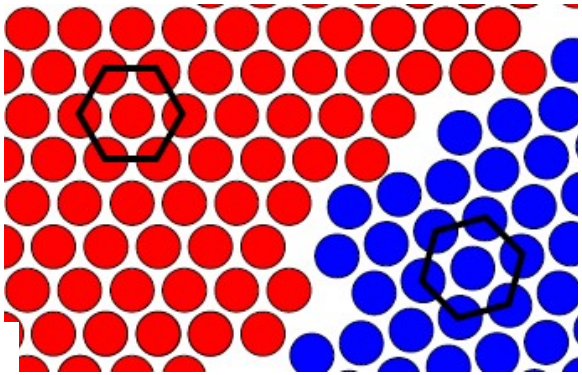
Face-centred cubic (fcc)

Cu,Al,Ni,Au,….

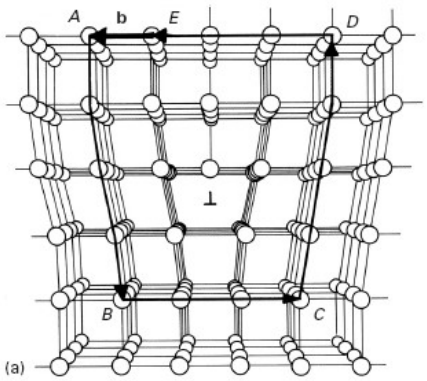
Point defects



Grain boundaries

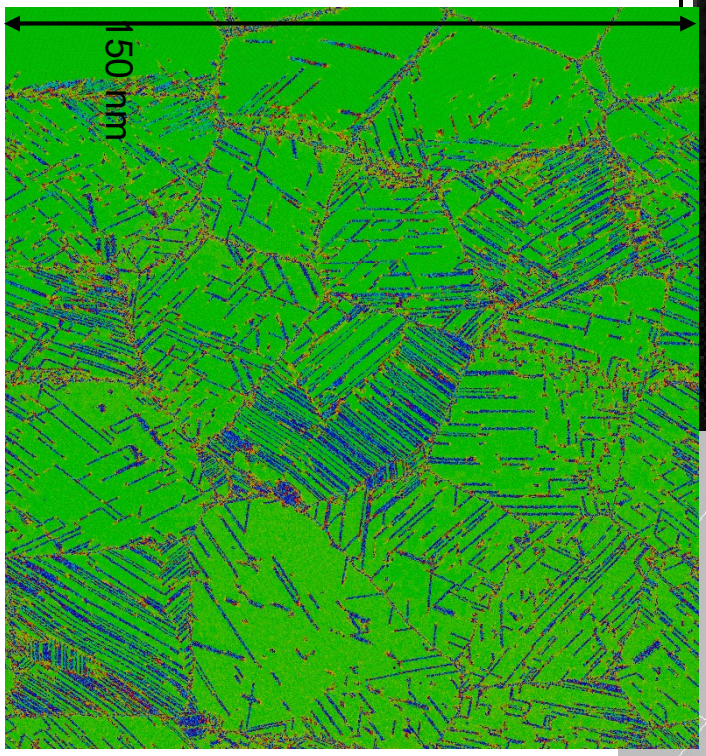


DISLOCATIONS



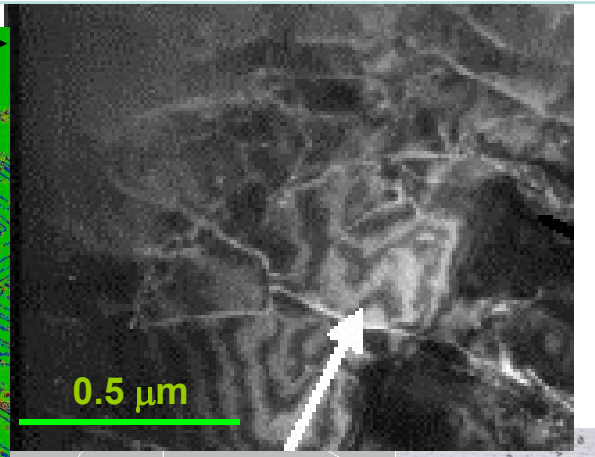
Perfect crystals are the `spherical horse' of atomistic simulations (also for many model Hamiltonians)

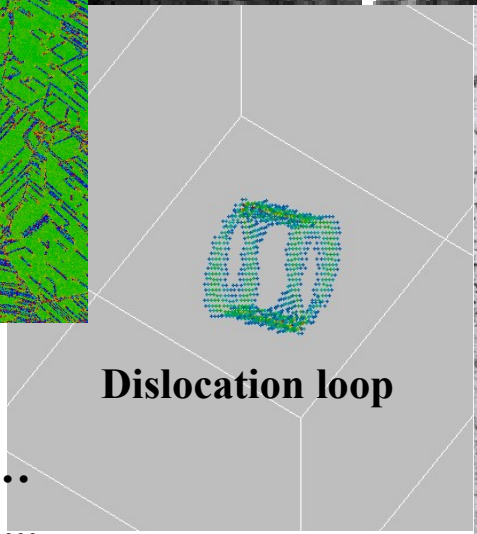
How to make more realistic simulations? Add defects:
vacancies → voids → bubbles, interstitials, dislocation loops/lines,
grain boundaries (bi-cristals → polycrystals), impurities, etc.

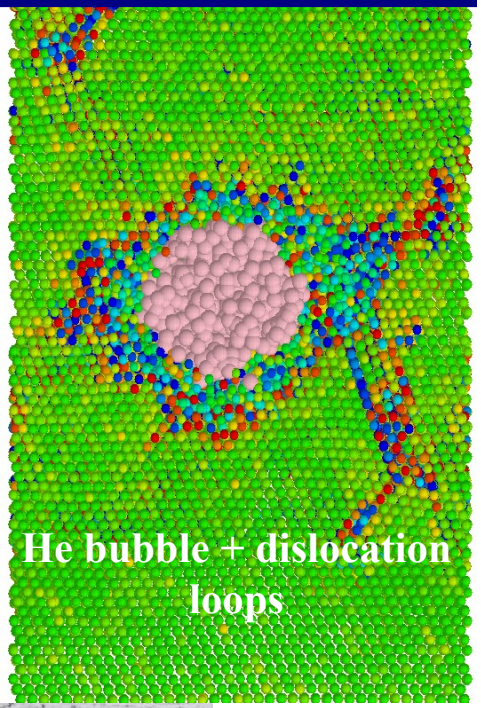


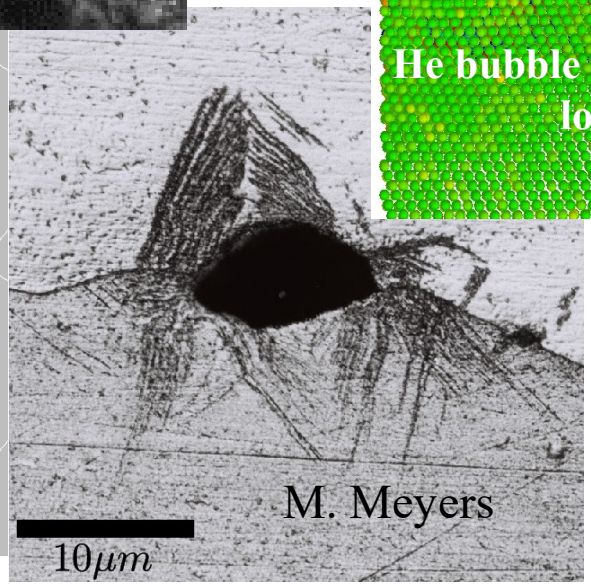
Polycrystal (50 nm grain size)
(400 million atoms)
Few GB are Σ boundaries …
Not 1 dislocation but many …

Cu single crystal, M. Meyers *et al*, TEM

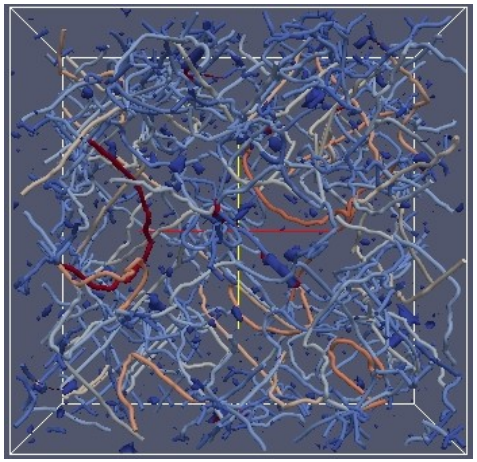




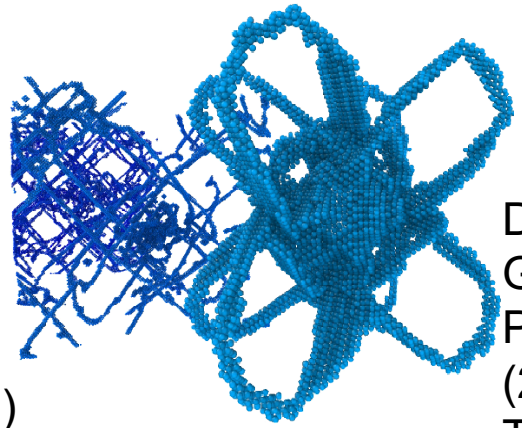




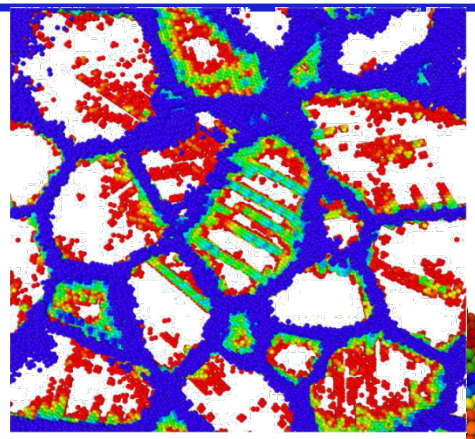
Example: New materials thanks to defective structures
Use dislocations, grain boundaries, porosity, twins, etc.



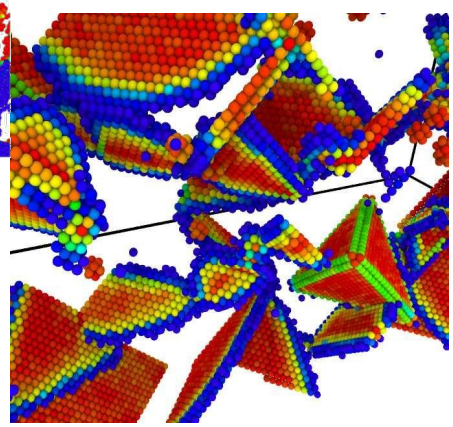
Dislocations in Ta,
Ruestes *et al*.,
Comp. Mat. Sci. (2014)
FCEN/UCSD



Plasticity in Ta,
Tramontina *et al*.,
HEDP (2013)
FCEN/Oxford/LLNL/LA
NL



Dislocations in Fe
Gunkelmann *et al*.,
Phys. Rev. B. Rapid
(2014)
TUK/FCEN/Oxford



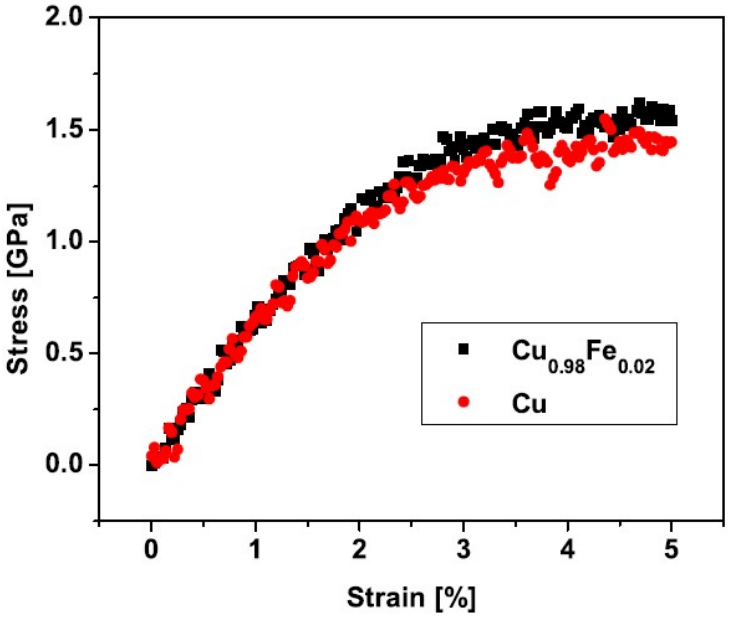
SFT in Au Rodriguez-
Nieva *et al*., Acta Mater.
(2014)
FCEN/MIT/JHU

Could control nano-structure based on strain rate and pre-existing defects → improved properties (hardness, corrosion resistance, etc.)

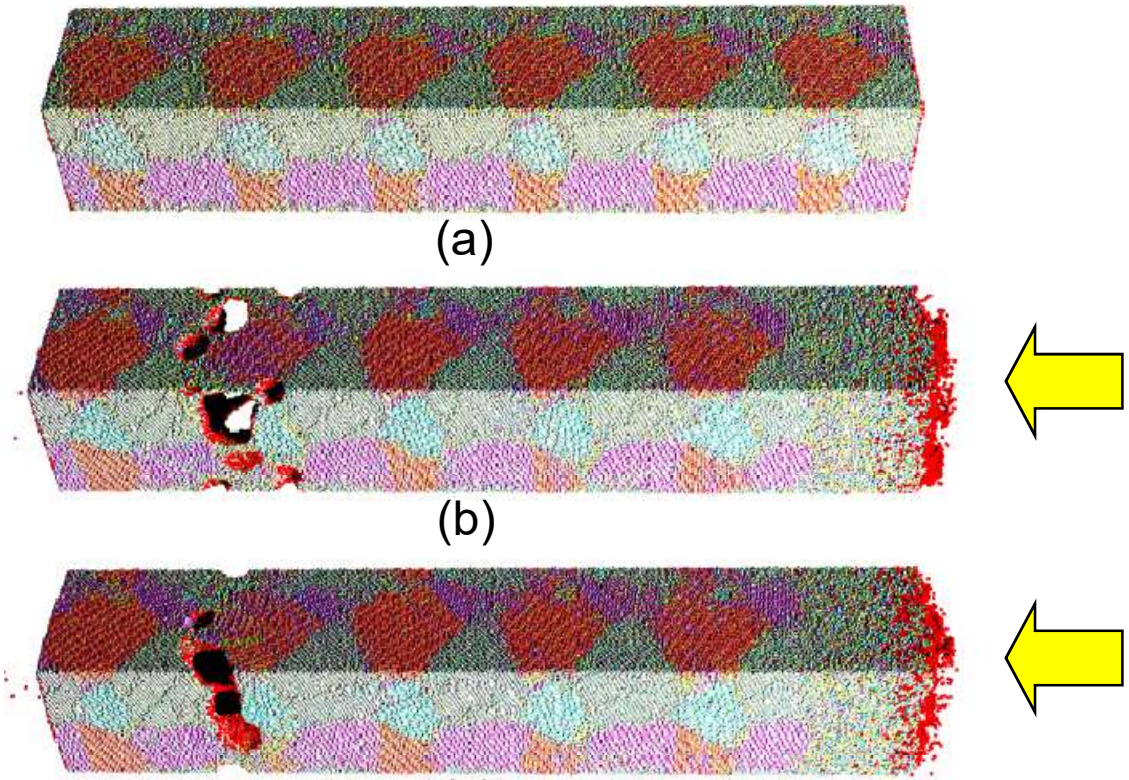
Role of impurities in void nucleation

Combine MD with "parallel grand-canonical Monte Carlo" to place impurities in nano crystalline sample

"Effects of Microalloying on the Mobility and Mechanical Response of Interfaces in Nanocrystalline Cu", Caro et al. , *Materials Science Forum Vols. 633-634 (2010) 21.*



This might lead to suppression of GB sliding ➔ stronger materials



(a)

(b)

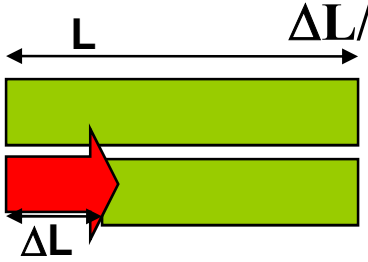
3% Fe (c)

G. Gilmer

Mechanical deformation: can we compare MD with experiments?
Problem: strain rates, dε/dt, are huge!

Simulation time=t

$\Delta L/L \sim 1\% \rightarrow d\varepsilon/dt = 0.01/t$



MD uses $\Delta t \sim 1$ fs

$t = 10$ ns (10^7 steps) $\rightarrow d\varepsilon/dt = 10^6/s$

$t = 1$ s (10^{15} steps) $\rightarrow d\varepsilon/dt = 10^1/s$

In a supercomputer:

10^6 steps $\rightarrow$ 1-5 days

10^{15} steps $\rightarrow$ millions of years …

"Today" MD can do strain rates ~10^6/s only at a supercomputer

Solutions:

a) Suplement MD with models to compare to experiments at low strain rates.

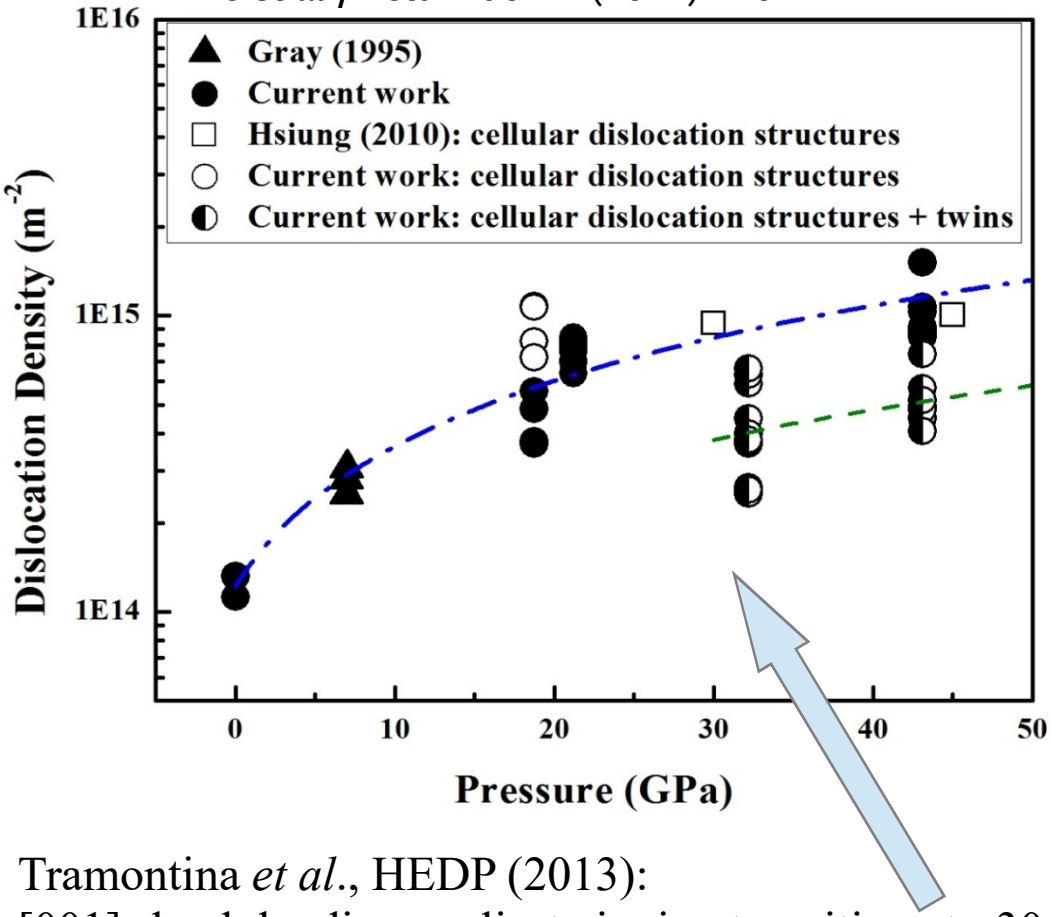
a) Compare with experiments at high strain rates (lasers, shocks, impacts, etc.).

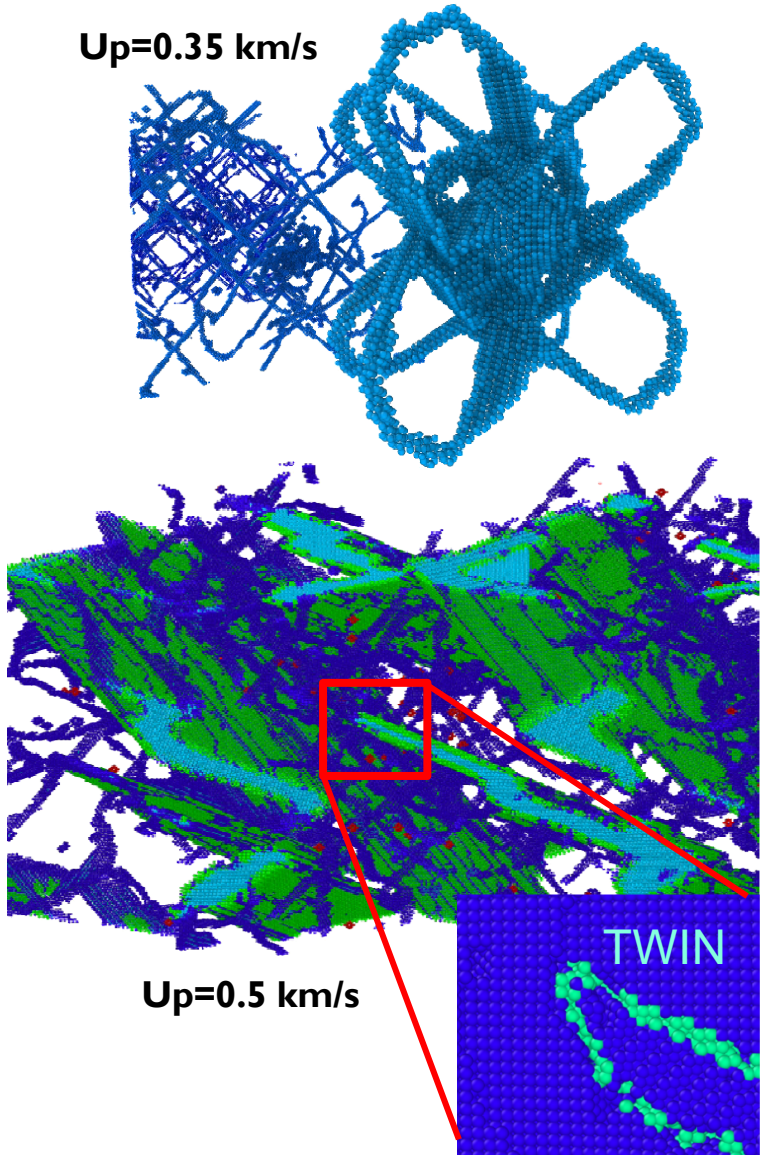
Road-Runner (2010)
A. Voter, LANL $\rightarrow$
nanowire at 10^{-3}/s

Slip-Twinning transition in Ta

Need to include dislocation-twin interaction in constitutive model, as in Florando *et al*., JAP **113** (2013) 83522. Would also need twin nucleation model!

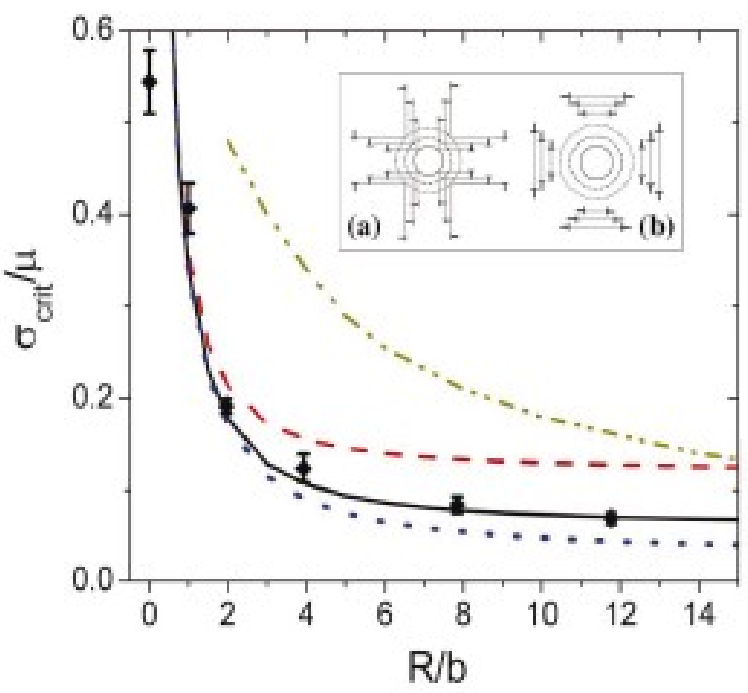
Lu *et al*., Acta Mat. **60** (2012) 6601





Tramontina *et al*., HEDP (2013):
[001] shock loading→ slip-twinning transition at ~30 GPa
Twin nucleation: Suggit *et al*, PRB (2013)

Void failure under compression: comparison between MD & models/experiments is promising for fcc



-------- Reissman *et al* (prismatic loops)

------- Lubarda (shear loops)

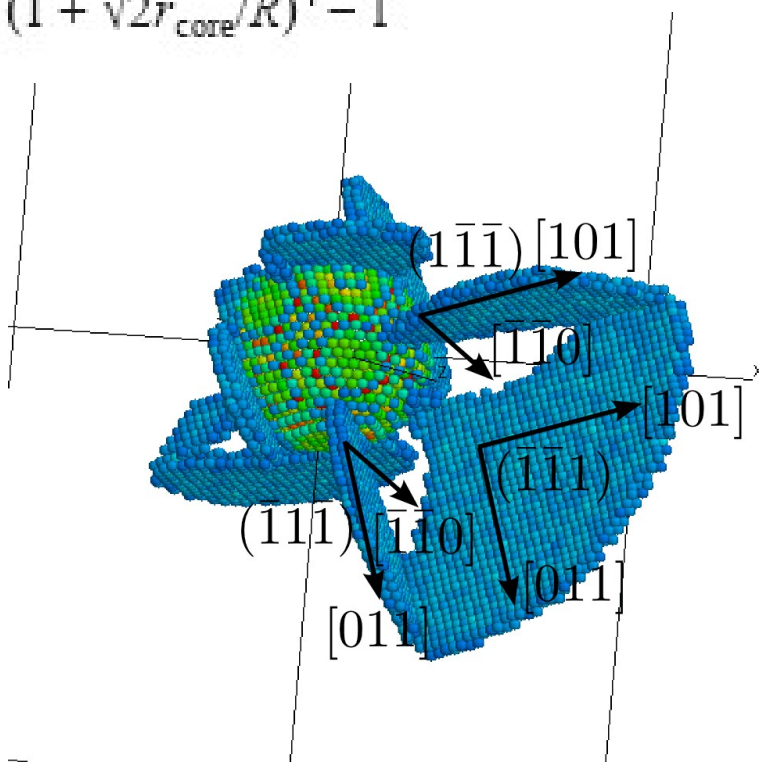
……. Lubarda (shear loops)

_____ MD Davila *et al*

$$\frac{\sigma_{cr}}{\mu} = \frac{b/R}{\sqrt{2}\pi(1-\nu)} \frac{(1+\sqrt{2}r_{core}/R)^4+1}{(1+\sqrt{2}r_{core}/R)^4-1}$$

Davila *et al*., APL (2005) 86,161902.
Traiviratana, Bringa & Meyers, several papers

Void Faceting (Rudd *et al*., Traiviratana *et al*., etc.) recently observed in experiments with sub-micron voids



Cu: Loading on [111] ➔ Triplanar Loops