



Compaction, sintering and defects in metals

Peter M Derlet
Condensed Matter Theory
Paul Scherrer Institut

peter.derlet@psi.ch

Semestre d'hiver 2017

Week- DATE	File. no.	Powder Technology – Wednesday 10.15-12.00 – MXG 110
1- sept 20	1	Introduction - PB
2 – sept 27	2	Powder packing and compaction - 1- PB -
3 – oct 4	3	Powder packing and compaction - 2-PB- and guest lecturer - MS
4 – oct 11	4	Powder packing and compaction -3- PD
5 – oct 18	4	Powder packing and compaction - 4 – PD
6 – oct 25	5	Particle – Particle Interactions 1 - PB
7 – nov1	6	Particle – Particle Interactions 2- PB
8 – nov 8	7	Particle – Particle Interactions - 3-PB
9 – nov -15	8	Introduction to atomistic scale simulations PD
10 – nov 22	9	Compaction, Sintering & Defects in metals at atomistic scale - PD
11 -nov-29	10	Sintering Mechanisms& New Technologies - 1 – PB
12 - dec 6	11	Sintering Mechanisms & New Technologies - 2 - PD
13 – dec 13	11	Sintering Mechanisms &New Technologies -3 PD
14 – dec 20	11	Sintering Mechanisms & New Technologies- and exam 4 – PB
		PB – Prof. Paul Bowen (EPFL), PD – Dr. Peter Derlet (PSI)
		MS- Dr. Mark Sawley (EPFL)

References

- See last week's lecture
- See given research papers and references throughout the talk

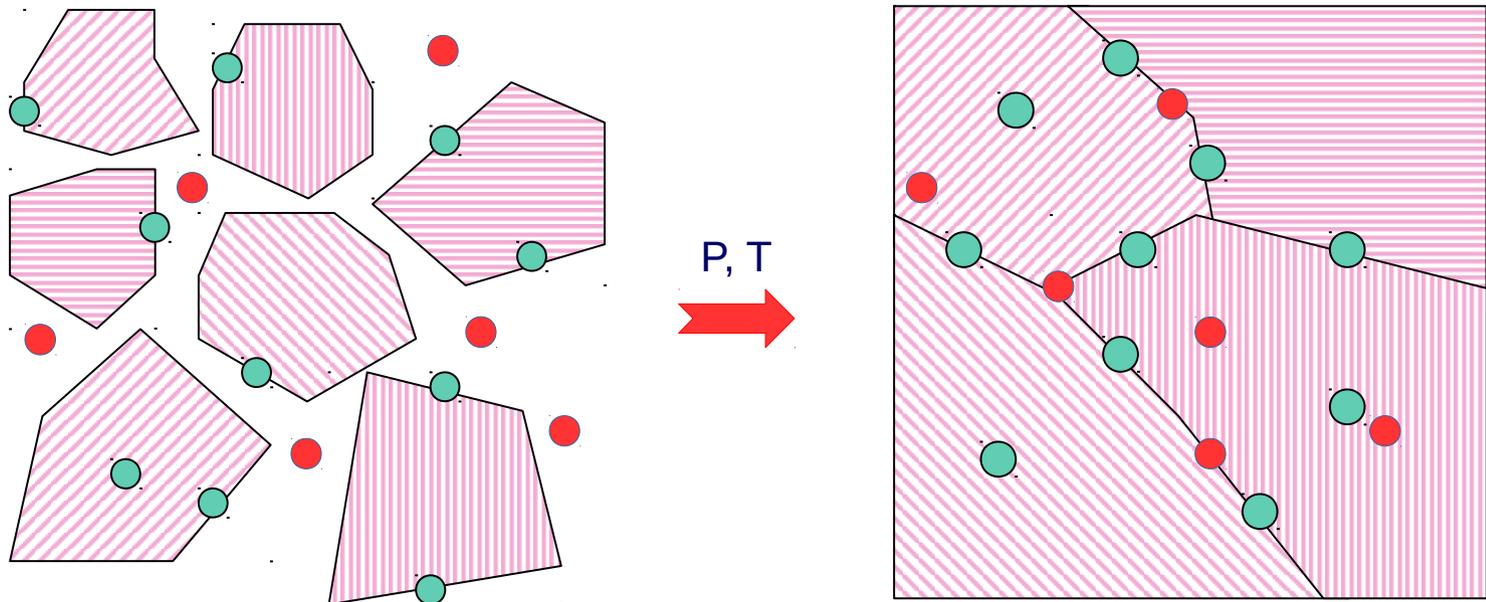
Lecture outline

- Compaction, sintering and defects – what needs to be modelled
- The Potential Energy Landscape (PEL) of a solid
- The timescale problem in MD
- MD examples
 - Example 1: nanocrystalline metals – structure & athermal plasticity
 - Example 2: Sintering processes of two nano-particles
 - Example 3: The sintering and densification behaviour of many copper nanoparticles

Compaction, sintering and defects – what needs to be modelled

Compaction, Sintering and Defects

The generic problem

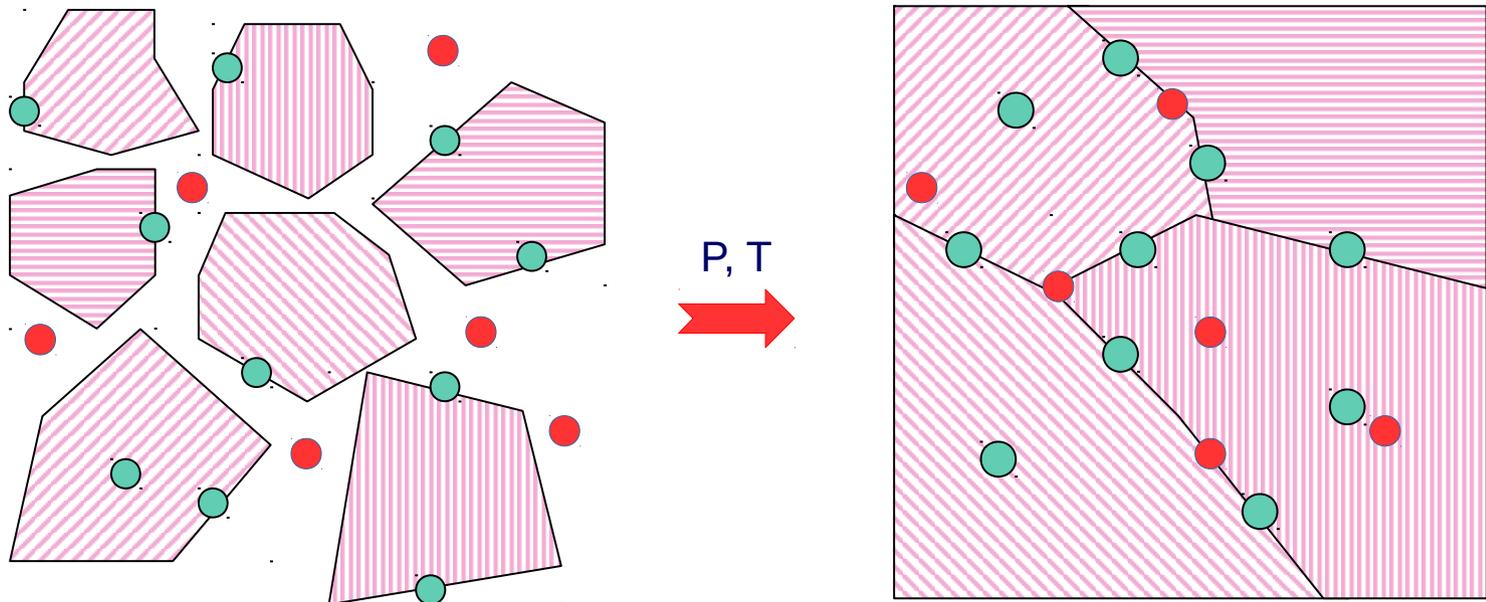


Questions

- What are the shape and volume of initial clusters? Initial cluster structure?
- Porosity during compaction and its evolution?
- What is the nature of the resulting interface?
- What is the internal stress state of the resulting grain boundary network?
- Where do (introduced?) defects end up → what are the transport mechanisms?
- What are the final mechanical properties?

Compaction, Sintering and Defects

The generic problem



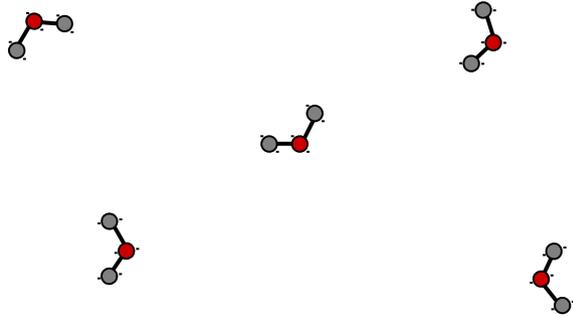
Phenomenon

- Surface ab/adsorption
- Diffusion
- Segregation
- Interface
- Structural evolution
- Mechanical properties

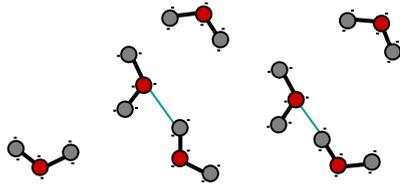
As a function of temperature and stress

The Potential Energy Landscape (PEL) of a solid

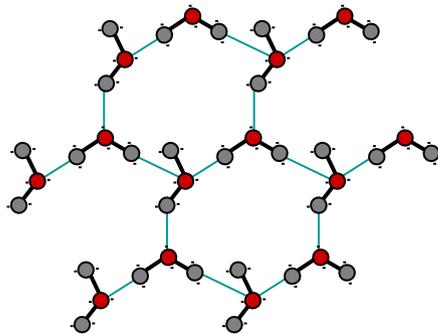
The regimes of atoms



Gas:
Atoms relatively far apart
Few collisions
Disordered



Liquid:
Atoms closer
Many collisions
No long range correlations



Solid:
Atoms closest
Long range order
Most atoms are approximately stationary

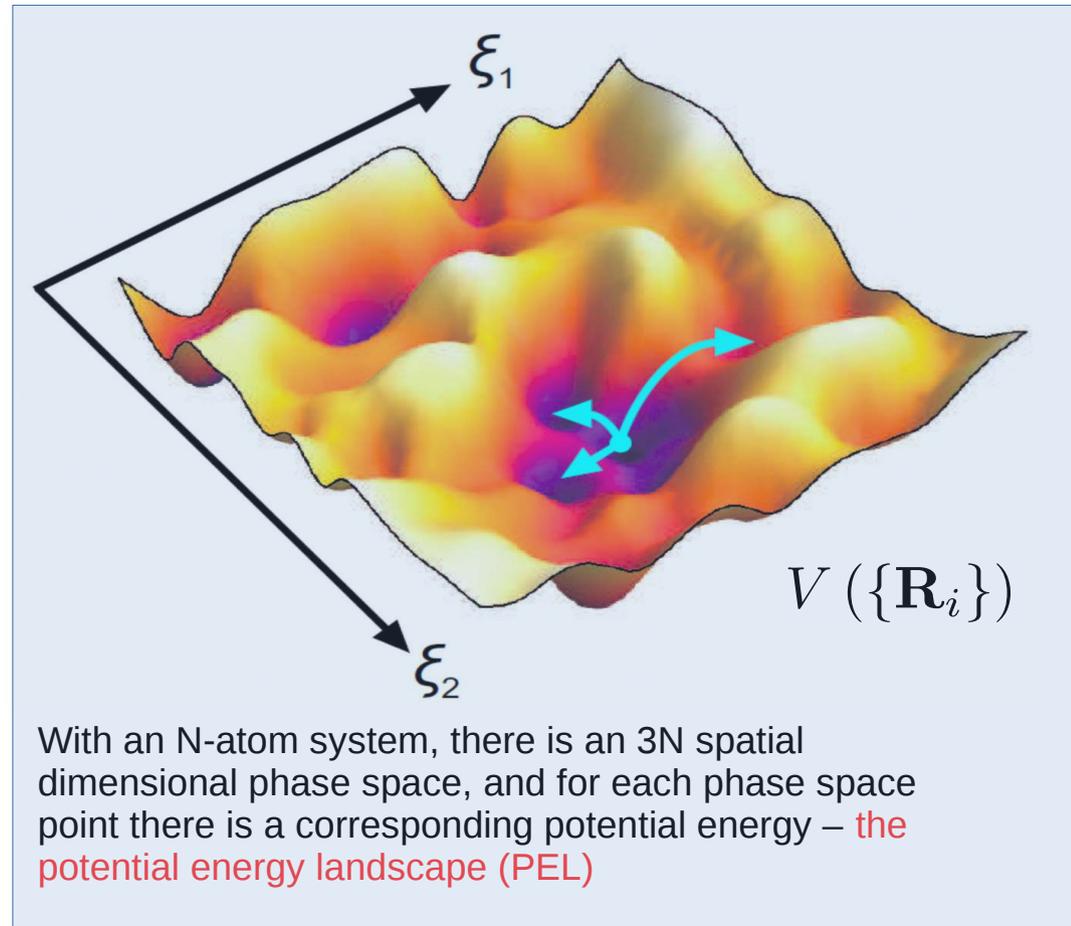
The potential energy landscape picture of a solid

For a gas or liquid, excitations away from equilibrium are short lived.

However for a solid, excitations are mainly long lived.

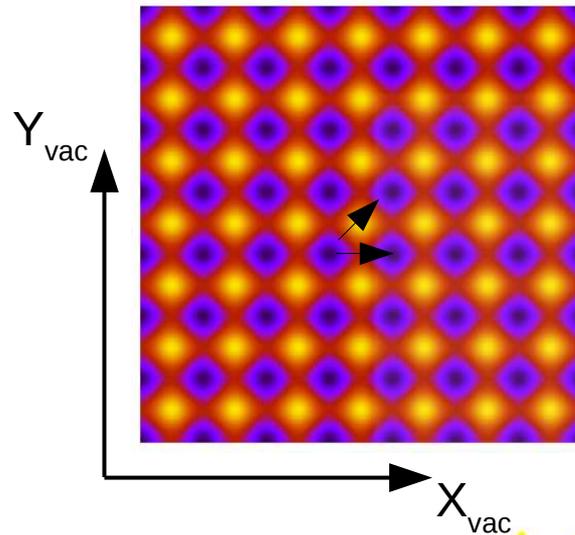
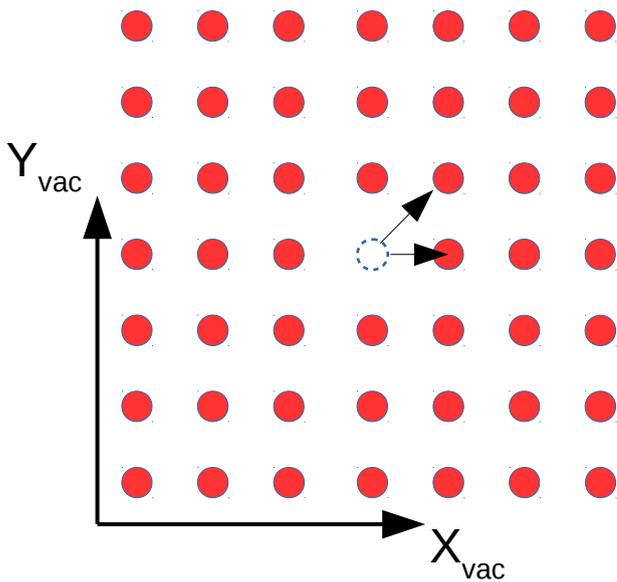
Why?

In this regime (of the solid) the PEL is characterized by a topography of well defined valleys and ridges.



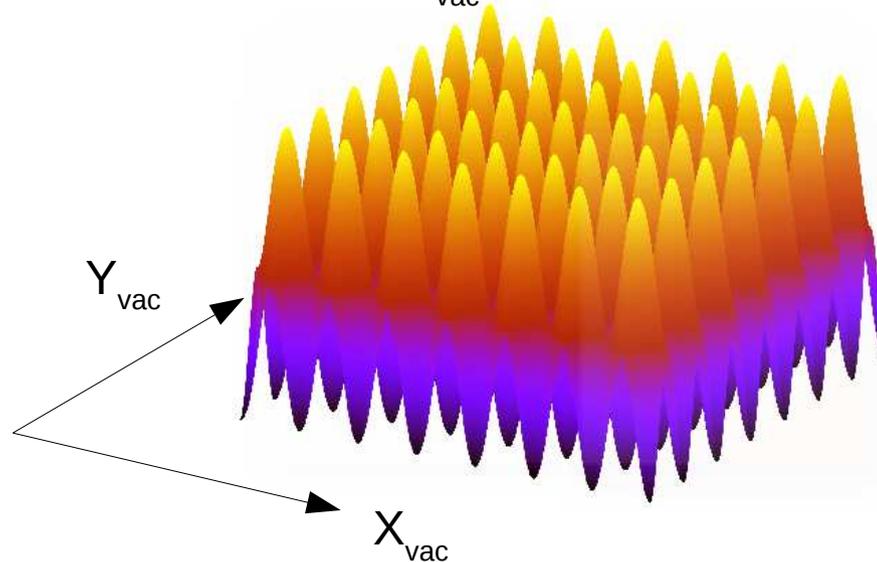
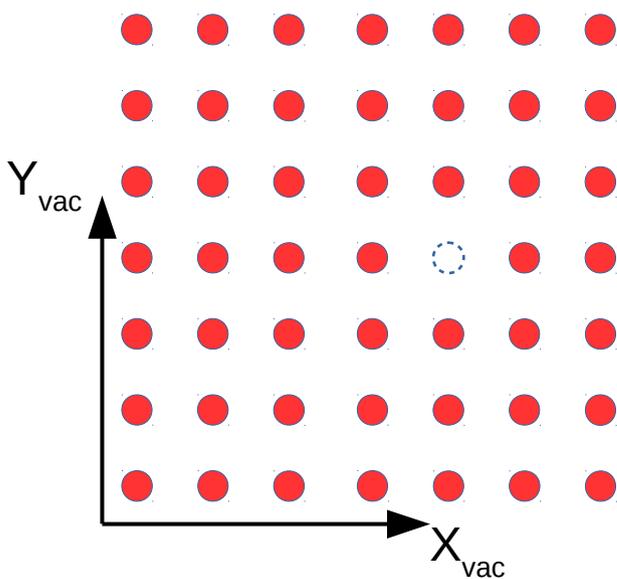
A solid spends most of its time in the valleys of the PEL – a local region of phase space – occasionally transiting (via thermal fluctuations) to a new valley via a ridge.

The PEL of a vacancy in a 2D solid



The vacancy can move vertically/horizontally by one of its neighbouring atoms moving vertically/horizontally.

It can also move diagonally by atoms moving diagonally → usually the potential ridge is higher since it must come closer to other atoms.

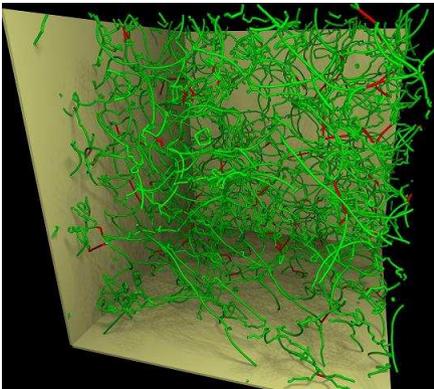


Thus (sometimes) the location in phase space can be easily correlated with the position of a defect

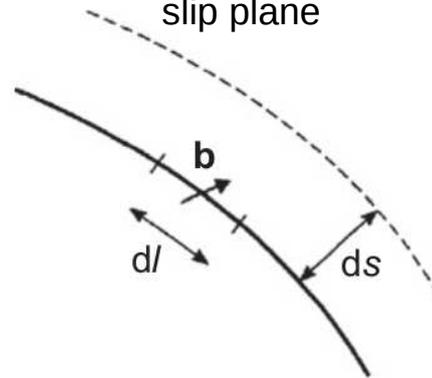
The PEL picture of a dislocation

Dislocations are topological line defects that interact elastically with each other and can undergo a variety of reactions which preserve the total Burgers vector

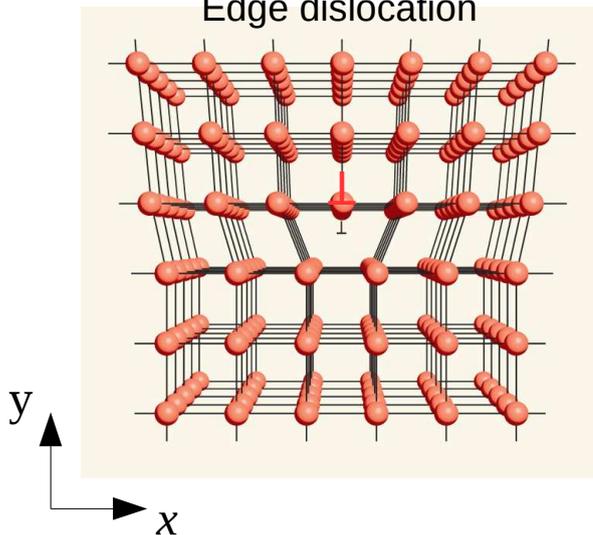
Network of dislocations



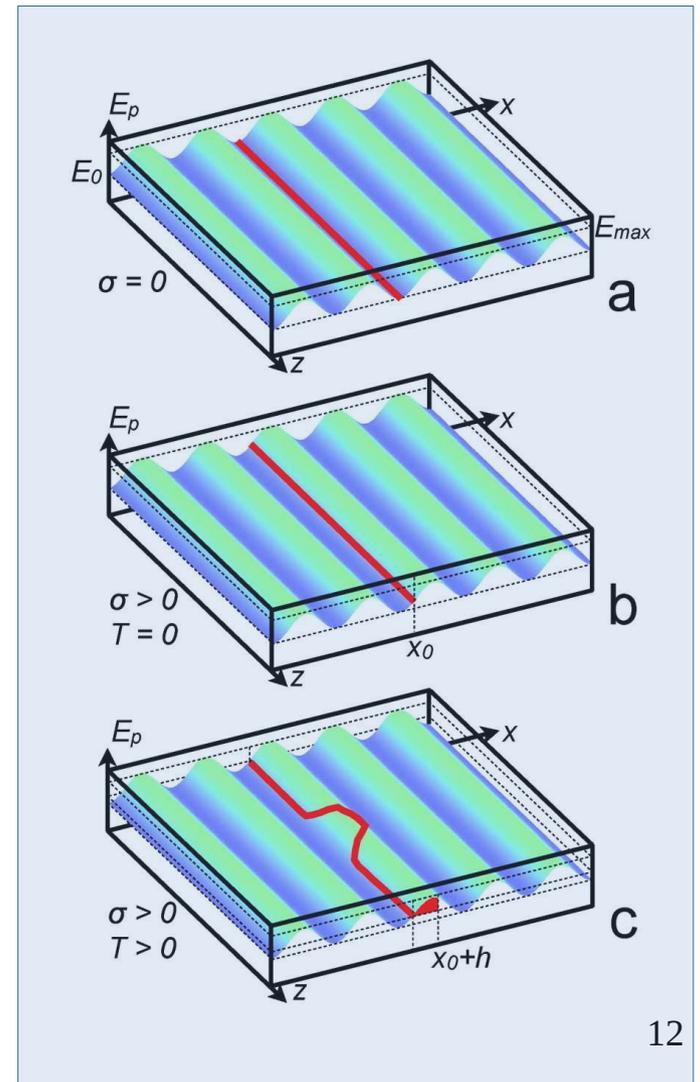
A dislocation is a line defect defined by a Burgers vector and slip plane



Edge dislocation



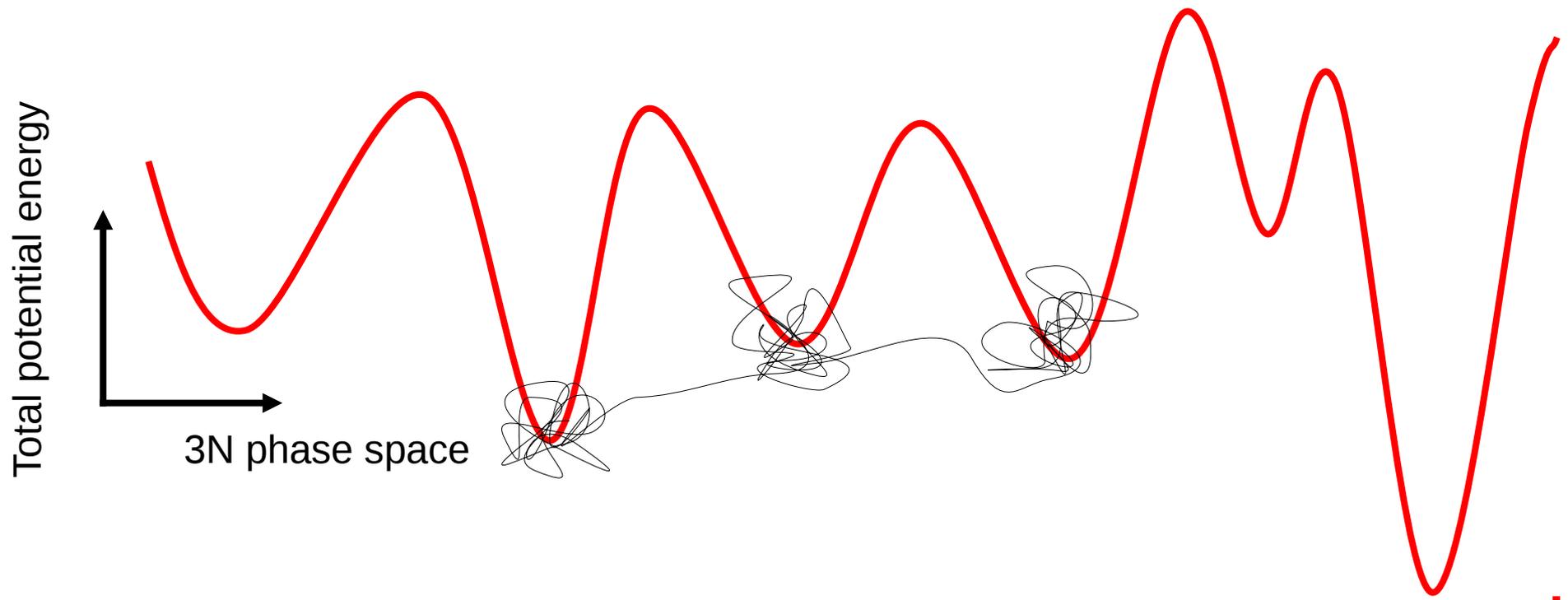
Dislocation core structure and dynamics are determined by atomic structure – the dislocation sees a PEL determined by the crystal lattice



The timescale problem in MD

The PEL is traversed via thermal fluctuations

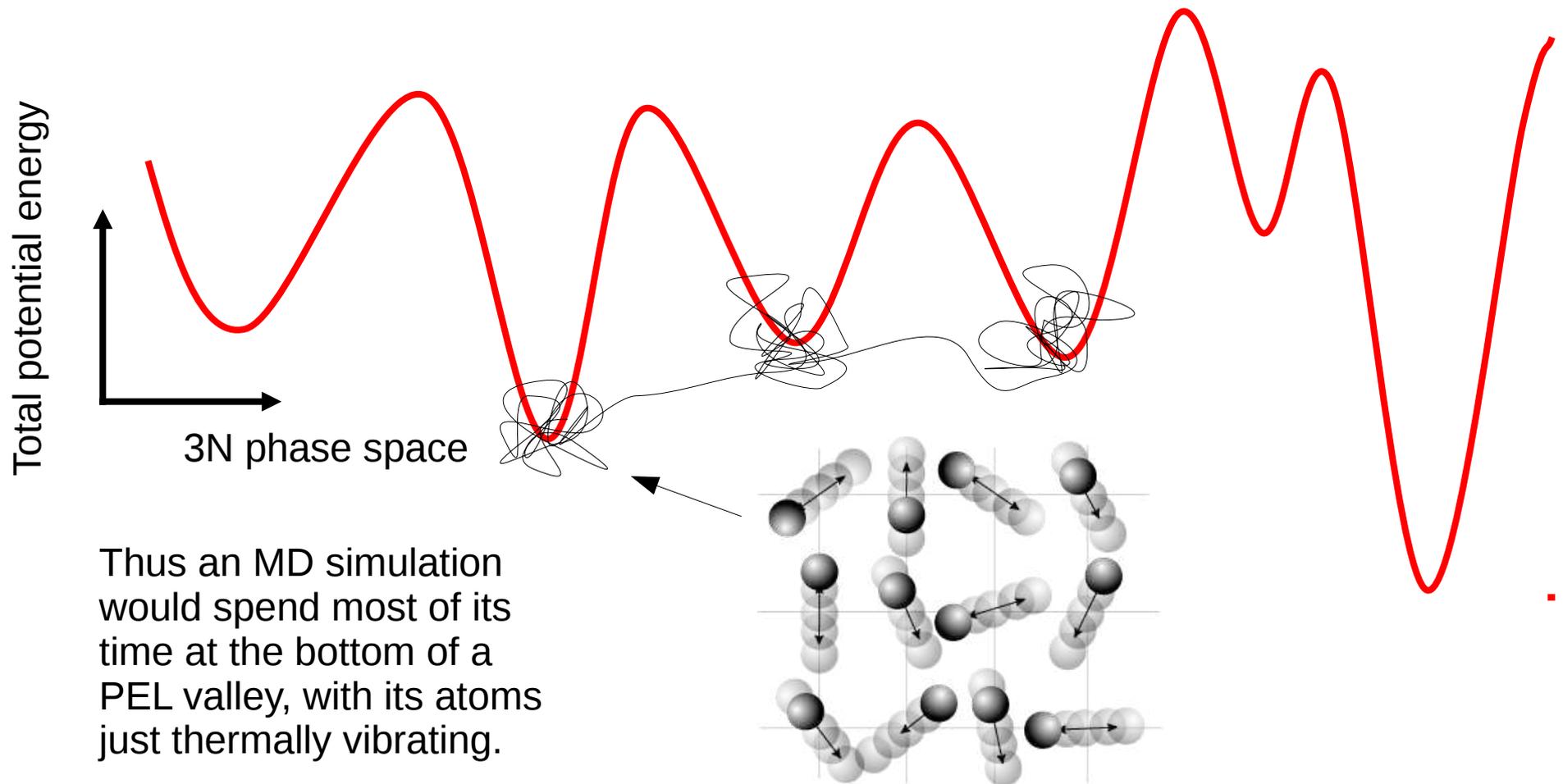
An atomic configuration will spend most of its time in a local potential energy minimum occasionally undergoing a transition, through thermal activation, to another local minimum.



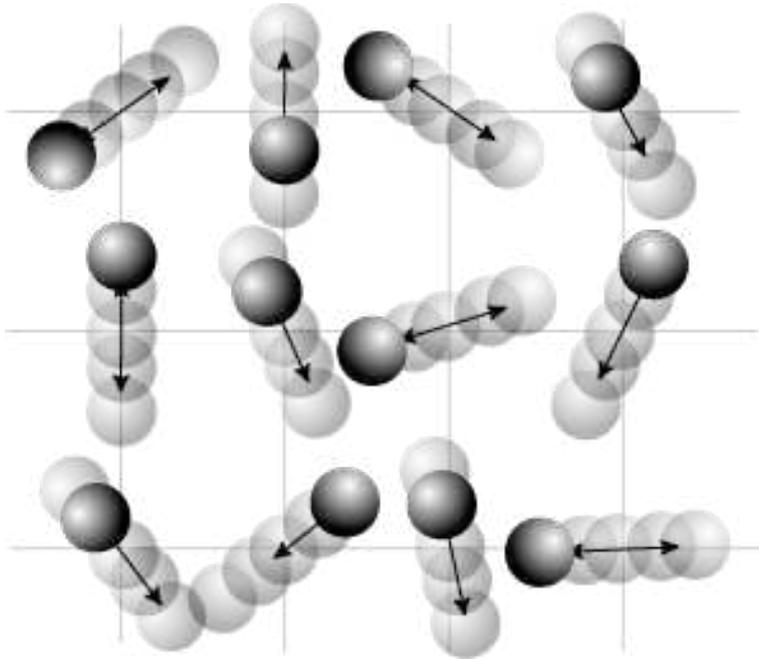
The defect will have a thermal energy that fluctuates around a mean value, and occasionally the fluctuation will be large enough for it to overcome a PEL ridge → if the energy barrier (ridge minus valley energy) is large, then this will happen only very rarely.

The PEL is traversed via thermal fluctuations

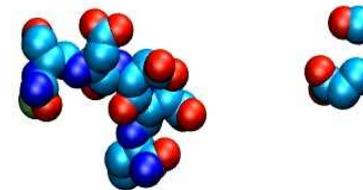
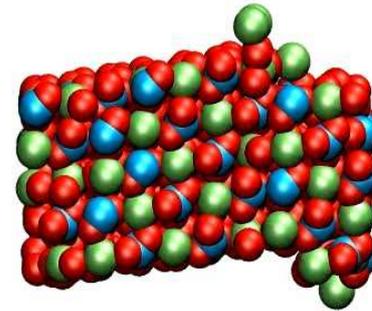
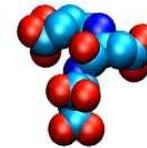
An atomic configuration will spend most of its time in a local potential energy minimum occasionally undergoing a transition, through thermal activation, to another local minimum.



In the solid state, atoms spend most of their time vibrating



The characteristic frequency of atomic vibration is ~ 1 THz



Polymer absorption on calcite (CaCO_3)

The timescale problem in MD

The MD algorithm evolves the atomic coordinates using numerical integration

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t + \frac{1}{2m_i} \mathbf{F}_i(t) \Delta t^2$$
$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2m_i} (\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)) \Delta t$$

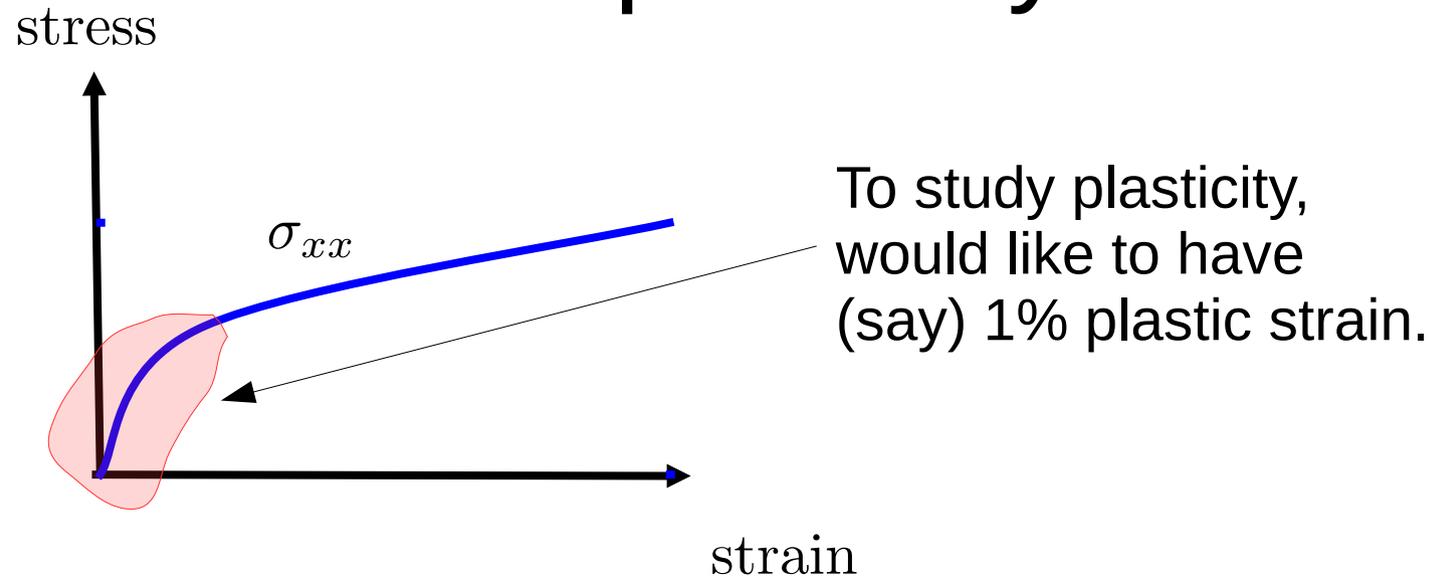
Velocity Verlet integrator (see slides 27-28 of previous lecture)

MD integrators typically use a time step of 1 fsec=1e-15 sec → why?

- The characteristic frequency of atomic vibration is ~1 THz, which means an atom entirely changes its direction of motion every ~1/THZ~1000 fsec.
- Thus atomic forces fluctuate at a timescale of ~1000 fsec.
- The numerical integrators assume that over the time step, Δt , the forces are constant → $\Delta t \ll 1000$ fsec → $\Delta t \sim 1$ fsec.

One million MD iterations correspond to one nano-second of simulation,
this is the timescale problem of MD.

The timescale problem in MD plasticity



Consider plasticity at a constant strain rate: $\epsilon_{\text{plastic}} = \dot{\epsilon}_{\text{plastic}} \times \text{simulation time}$

$$\dot{\epsilon}_{\text{plastic}} = \frac{\epsilon_{\text{plastic}}}{\text{simulation time}} = \frac{0.01}{1 \times 10^{-9} \text{ sec}} = 10^7 \text{ sec}^{-1}$$

Simulation time is typically no more than several nano-seconds, resulting in strain rates 10^7 - 10^9 /sec

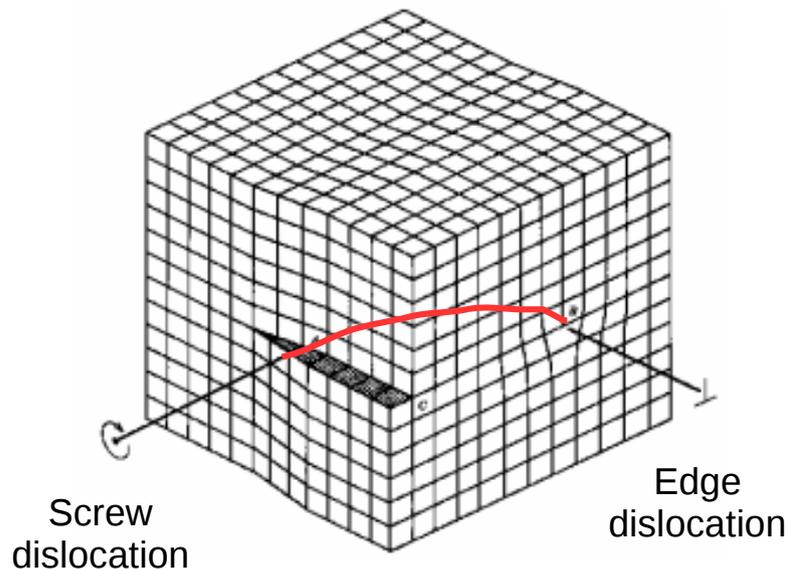
$$\dot{\epsilon}_{\text{plastic}} \sim 10^{-4} - 10^{-1} \text{ sec}^{-1} \leftarrow \text{Experiment}$$

Simulation differs from experimental strain rates by up to 10 orders of magnitude!

The timescale problem in MD plasticity

Processes such as diffusion, surface growth, grain growth, grain boundary migration, creep, plastic deformation, and dislocation motion typically occur at the micro-second and higher time scales.

Consider (BCC) dislocations – the mediators of crystalline plasticity



*BCC Ferritic Steels
at elevated
temperature*

Professor Hideharu Nakashima of [Kyushu University](#), Japan

BCC Ferritic Steel at elevated temperature



A very “slow” dislocation

From the previous movie the dislocation velocity can be estimated to be:

$$v_{\text{dislocation}} = \frac{4 \times 10^{-6} \text{ m}}{60 \text{ sec}} \simeq 10^{-8} \text{ m/sec}$$

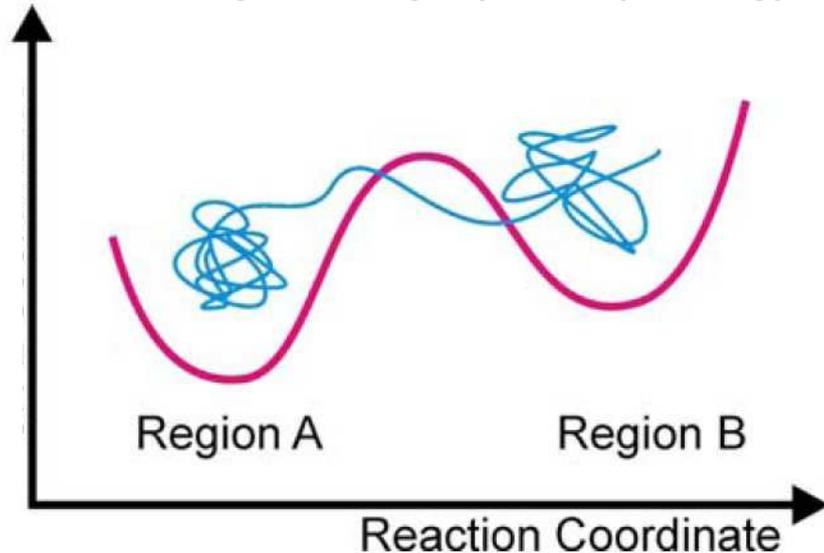
In one nanosecond (one million MD steps), the dislocation therefore travels:

$$d \simeq 1 \times 10^{-7} \text{ \AA}$$

In the time frame of MD simulation, these dislocations do not move!

Thermally activated processes

An energy barrier is overcome via thermal fluctuations – locally there can exist a large enough (kinetic) energy fluctuation such that a migration can occur.



When such migrations are rare, transition state theory gives:

$$\text{rate of occurrence} \rightarrow \Gamma = \nu \exp\left(-\frac{Q_b}{k_b T}\right)$$

activation energy

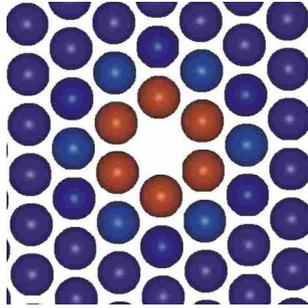
attempt rate

probability of success

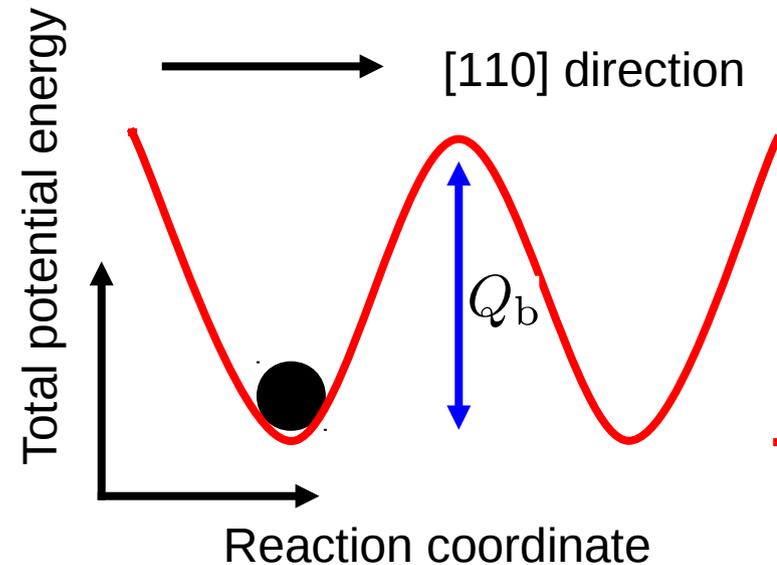
When the activation energy (Q_b) is comparable to the thermal energy ($k_b T$), the probability of success is close to one and each attempt is likely to be successful – this is the athermal regime of activity.

Thermal activation is the regime when the thermal energy is much less than the activation energy, and traversing the PEL is a rare event.

Vacancy diffusion in fcc Al



Vacancy diffusion involves the movement of a neighbouring atom along a [110] direction. For this atom to move it must overcome an energy Q_b barrier equal to



rate of occurrence \rightarrow $\Gamma = \nu \exp\left(-\frac{Q_b}{k_b T}\right)$

\uparrow attempt rate \downarrow activation energy

For Al

$\nu \simeq 10^{12}$ Hz $Q_b \simeq 0.5$ eV

At room temperature

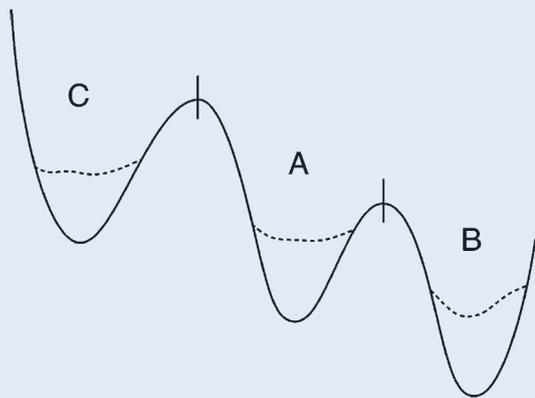
\rightarrow $1/\Gamma \simeq 1$ μ sec

1 million MD iterations for 1 nanosecond means 1 billion MD iterations for a microsecond

Direct Acceleration Methods

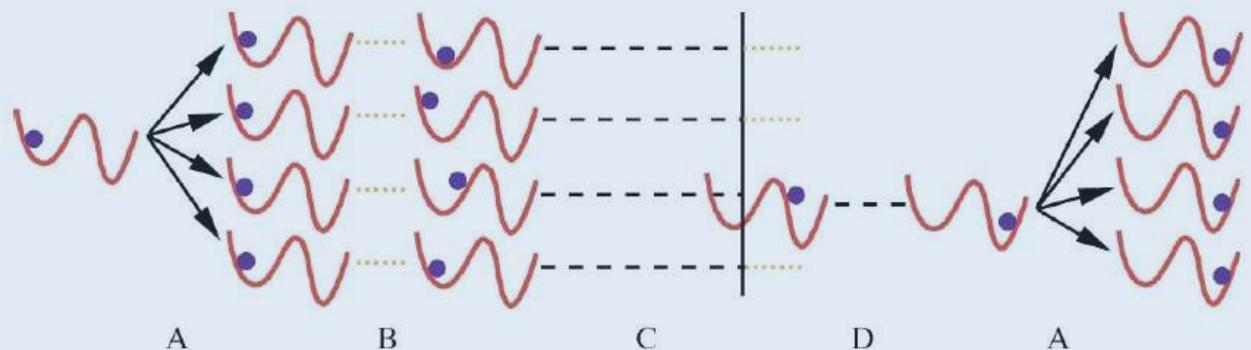
- **Hyper-dynamics** – follows the lowest eigenvalue of the instantaneous Hessian and uses this to switch on & off a bias potential.
- **Temperature acceleration** – raises the temperature until a transition occurs, filtering for entropically favoured high-barrier transitions.
- **Parallel replica method** – runs multiple copies of a system until a transition occurs, and then copies the configuration which experienced the transition to all processors, and then the process is repeated.

Hyper-dynamics



Hyper-dynamics works by preserving the ratio of (say) the CA and AC transition rates \rightarrow maintains detailed balance

Parallel replica method



By having n copies of a system, the rate of something occurring will increase by a factor of n

Direct Acceleration Methods

- **Meta-dynamics** – adds an adaptable bias potential to excite the system out of its local minimum

At a fixed time interval a Gaussian is added to the bias potential

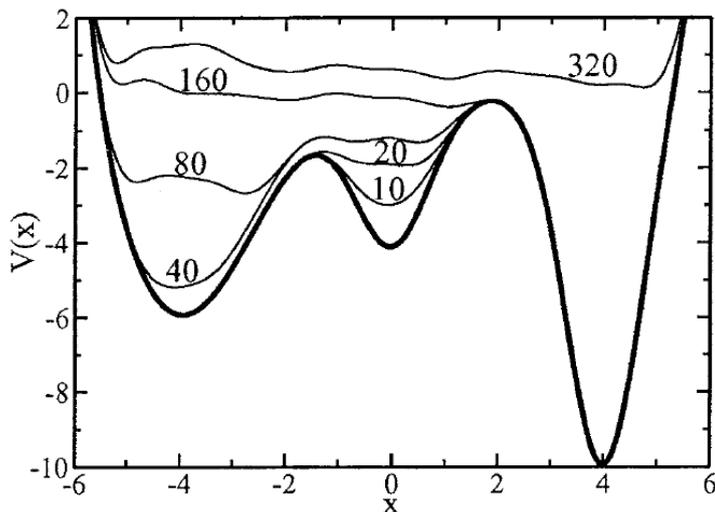
$$V_{\text{bias}}(\{\mathbf{r}(t)\}) = \sum_{n=0}^{t/\tau_G} V_G \exp\left(-\frac{|\bar{\mathbf{r}}(t) - \bar{\mathbf{r}}(t_n)|^2}{2\sigma_G^2}\right)$$

$$t_n = n\tau_G$$

→ time step

$$\bar{\mathbf{r}}(t) = f(\{\mathbf{r}(t)\})$$

→ Coarse grained coordinates



Escaping free-energy minima

Alessandro Laio and Michele Parrinello*

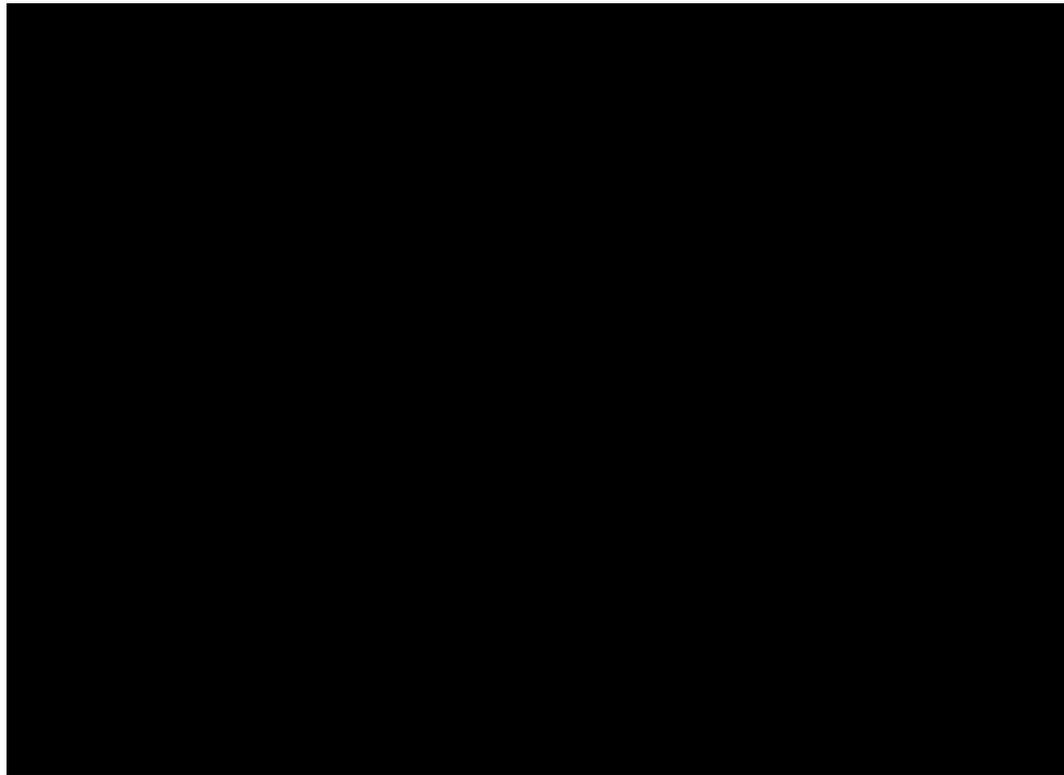
Centro Svizzero di Calcolo Scientifico, Via Cantonale, CH-6928 Manno, Switzerland; and Department of Chemistry, Eidgenössische Technische Hochschule, Hönggerberg HCI, CH-8093 Zurich, Switzerland

Communicated by David Chandler, University of California, Berkeley, CA, July 18, 2002 (received for review May 8, 2002)

PNAS 99, 12562 (2002)

Direct Acceleration Methods

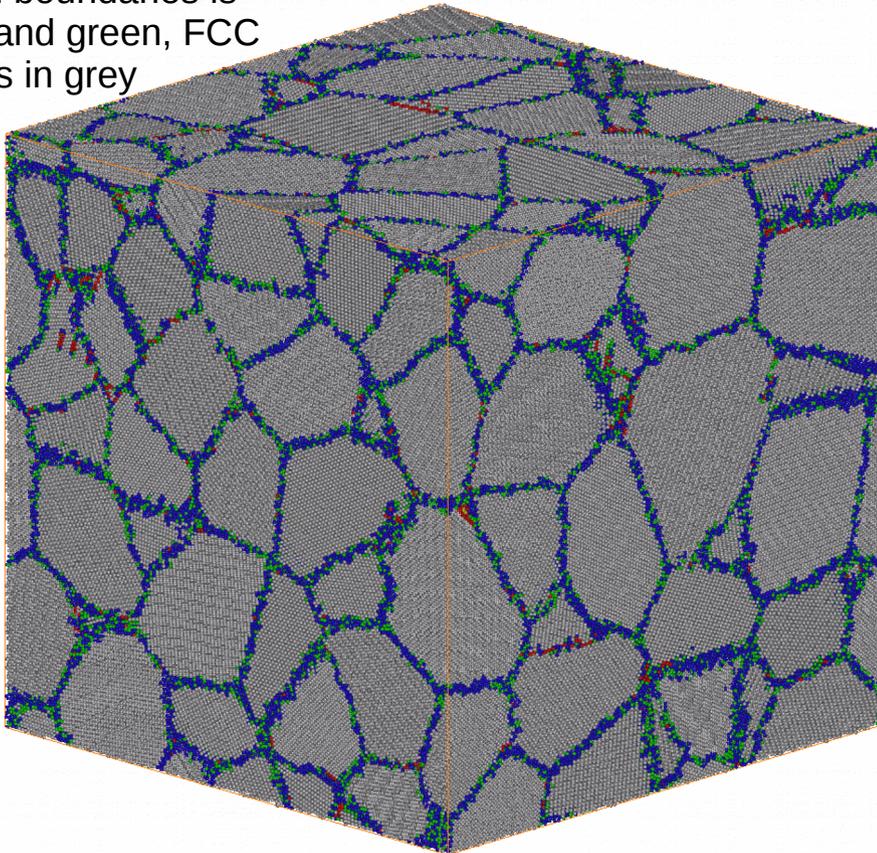
- **Meta-dynamics** – adds an adaptable bias potential to excite the system out of its local minimum.



Example 1: nanocrystalline metals – structure & athermal plasticity

Nanocrystalline metals: structure & athermal plasticity

Grain boundaries is blue and green, FCC grains in grey



- Nanocrystalline samples are constructed geometrically and then thermally equilibrated to 300K

- The sample to the left contains ~5 million atoms – 100 grains with a mean diameter of ~10nm

Medium Range Order (MRO) Classification Scheme

Grey atoms – FCC

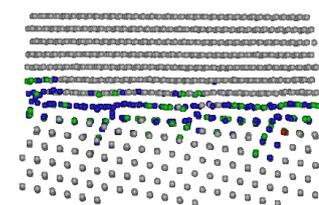
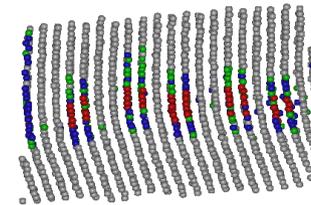
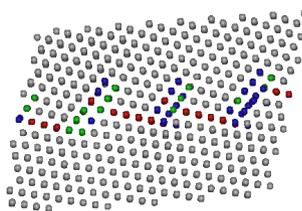
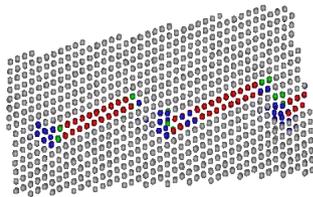
Red atoms – HCP

Green atoms – Other 12 coordinated symmetries

Blue atoms – Non-12 coordinated symmetries

H. Van Swygenhoven & P. M. Derlet, Dislocations in Solids, Ch 81, 1-42 (2008) Eds. J. Hirth, 2007.

A wide variety of grain boundary structure



H. Van Swygenhoven, D. Farkas, A. Caro, Phys. Rev. B 62 831, (2000).

Nanocrystalline metals: structure & athermal plasticity

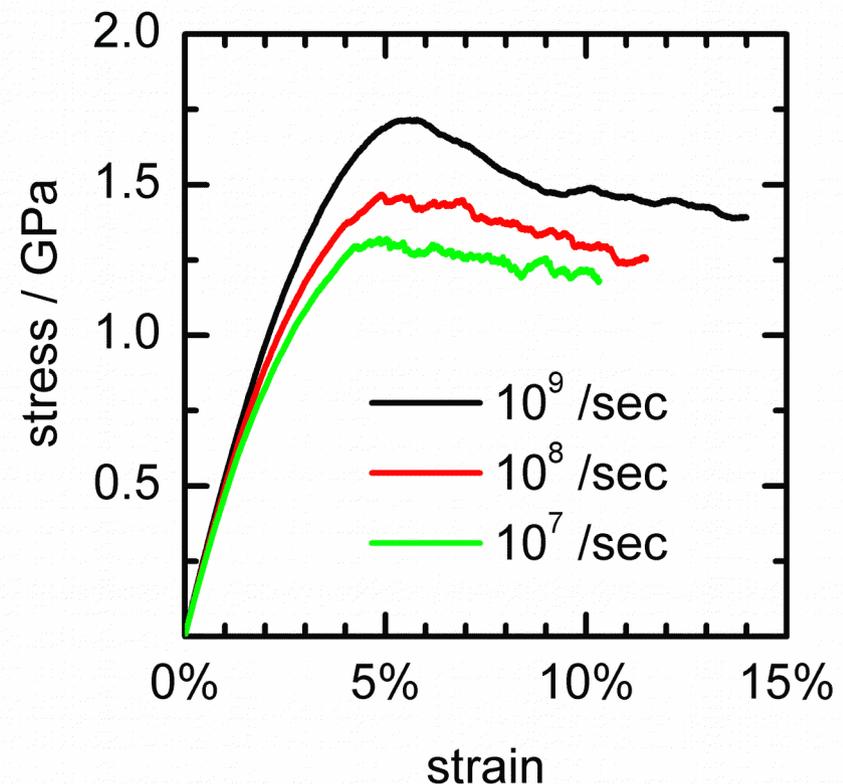
Loading via Parrinello-Rahman Lagrangian framework (last week's lecture)

Constant uni-axial tensile load → strain versus time

Constant uni-axial tensile strain rate → stress versus strain

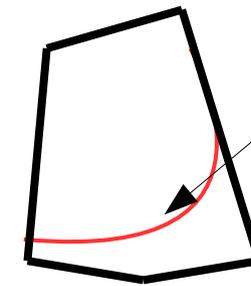
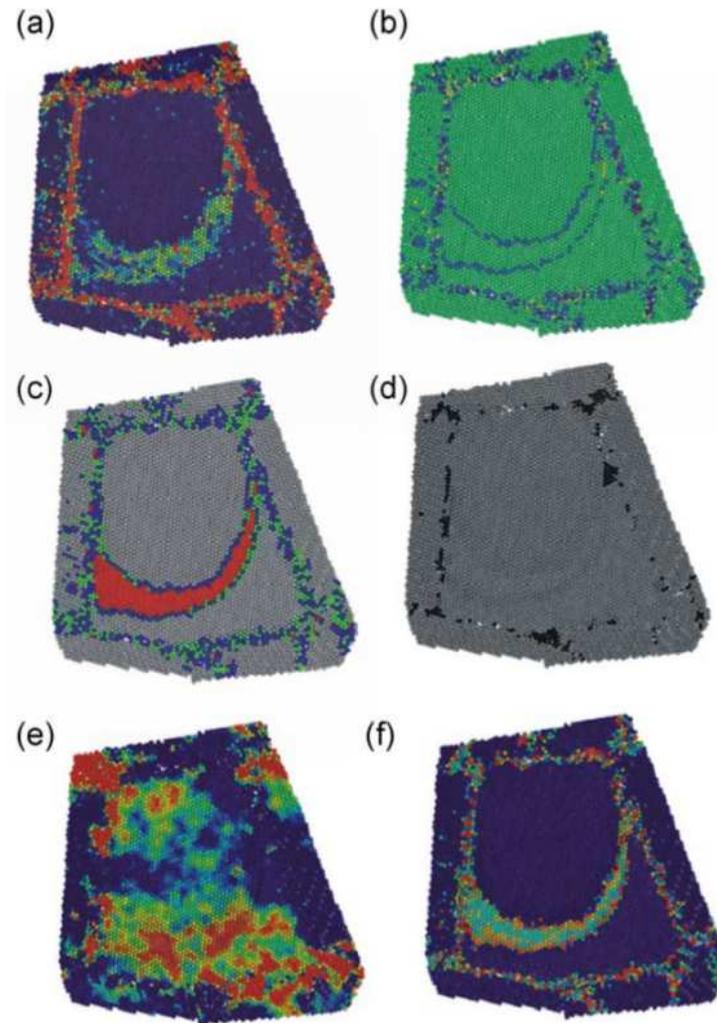
Stress-strain curves can be obtained, but at strain rates that are **ten orders of magnitude** higher than that normally seen in experiment.

This is the time scale restriction of MD, allowing only predominantly athermal plastic processes to be studied.



Nanocrystalline metals: structure & athermal plasticity

One atomic scale process seen in the atomistic simulation of nanocrystalline metals, is the nucleation, propagation, and absorption of dislocations.



Dislocation propagating through grain

There are many ways to identify the presence of a dislocation

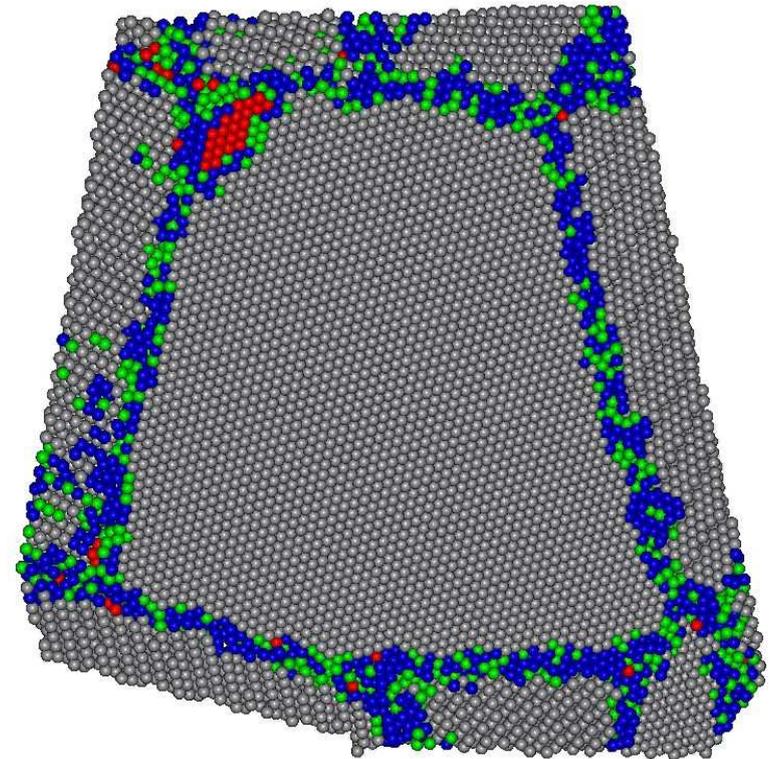
- a) local potential energy
- b) coordination
- c) medium range order
- d) positional disorder
- e) local pressure
- f) centro-symmetric parameter

Nanocrystalline metals: structure & athermal plasticity

In FCC metals, a perfect dislocation disassociates into two partial dislocations. Between the leading and trailing partial, a stacking fault exists (red atoms).

Dislocation nucleation at a grain boundary, first involves the nucleation of the leading partial and then (often elsewhere) the nucleation of the trailing partial.

Then the leading and trailing partial dislocations (the full dislocation) propagates through the grain depositing itself in the surrounding grain boundary network.

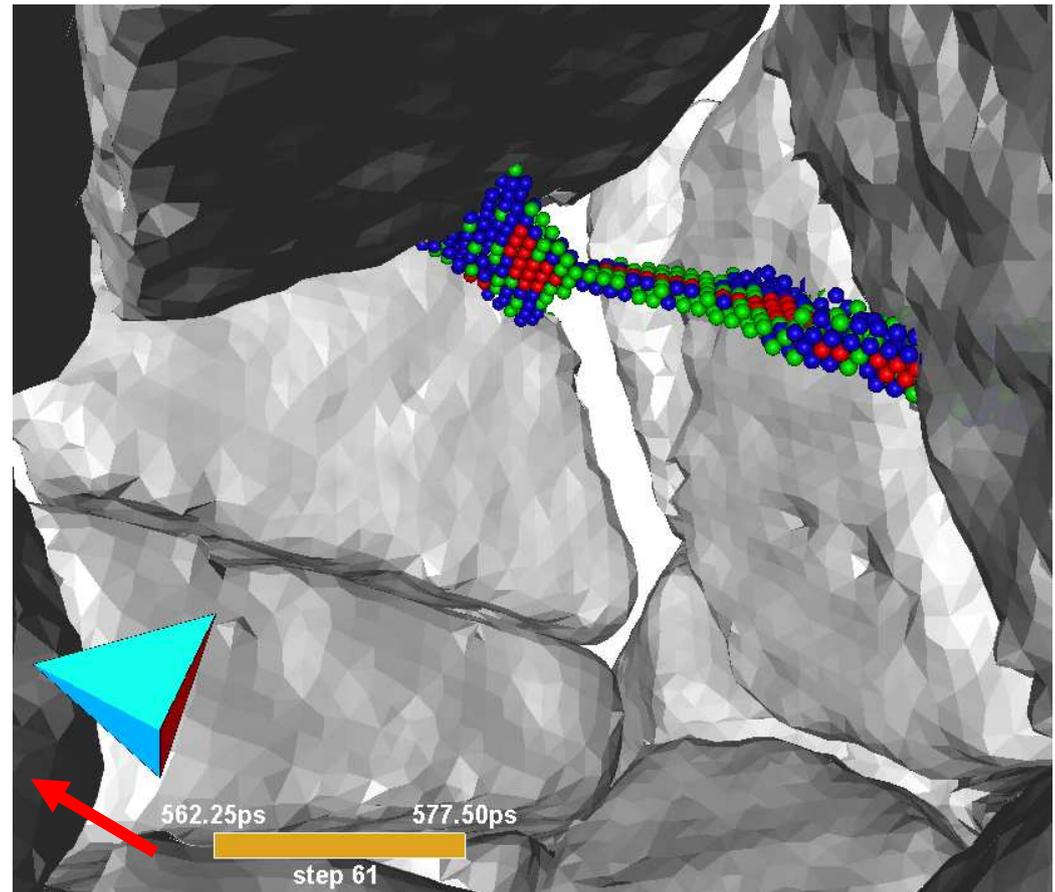


300K: T = 16

Nanocrystalline metals: structure & athermal plasticity

Dislocation motion can become quite complex in which the propagating full dislocation changes its habit plane – cross-slip.

It does this to avoid high stress regions within the surrounding grain boundary network.



Example 2: Sintering processes of two nano-particles

Sintering processes of two nanoparticles: a study by molecular-dynamics simulations

By HUILONG ZHU† and R.S. AVERBACK‡

†Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

‡Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

[Received 3 August 1995 and accepted 3 October 1995]

ABSTRACT

Molecular-dynamics computer simulations were employed to investigate the mechanisms of sintering of two single-crystal nanoparticles of Cu at a temperature of 700 K. Owing to their ultra-fine size (4–8 nm in diameter), the local shear stresses in the necks were sufficiently large to induce plastic deformation and densification. For both aligned and randomly oriented spheres, dislocations formed in the neck glided on the normal slip system of fcc Cu to the surface. The misaligned particles rotated about 17° relative to each other during deformation and formed a low-energy boundary. For the aligned nanoparticles, deformation occurred by glide of screw dislocations, but without rotation.

Sintering processes of two nanoparticles

Two Cu single-crystal spheres, each sphere containing 4688 atoms and having a diameter of 4.8 nm, were placed in contact at 700 K.

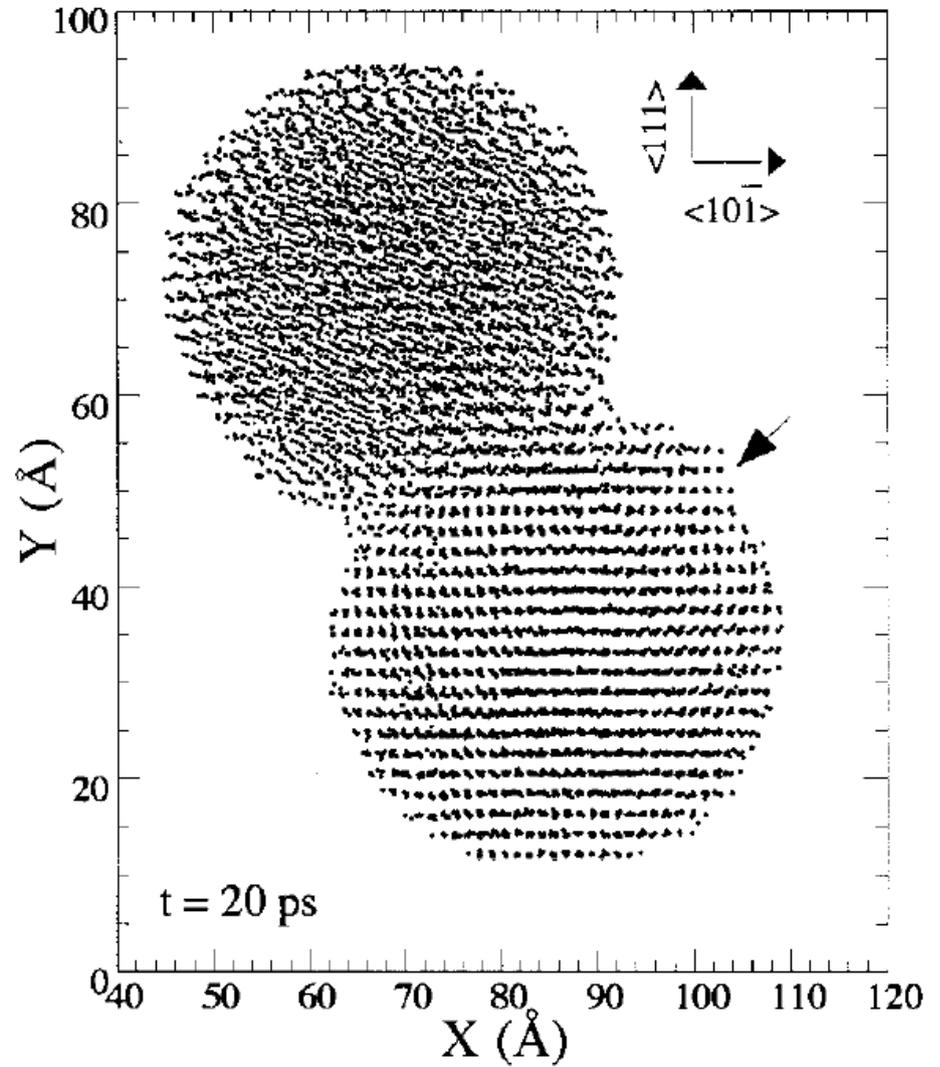
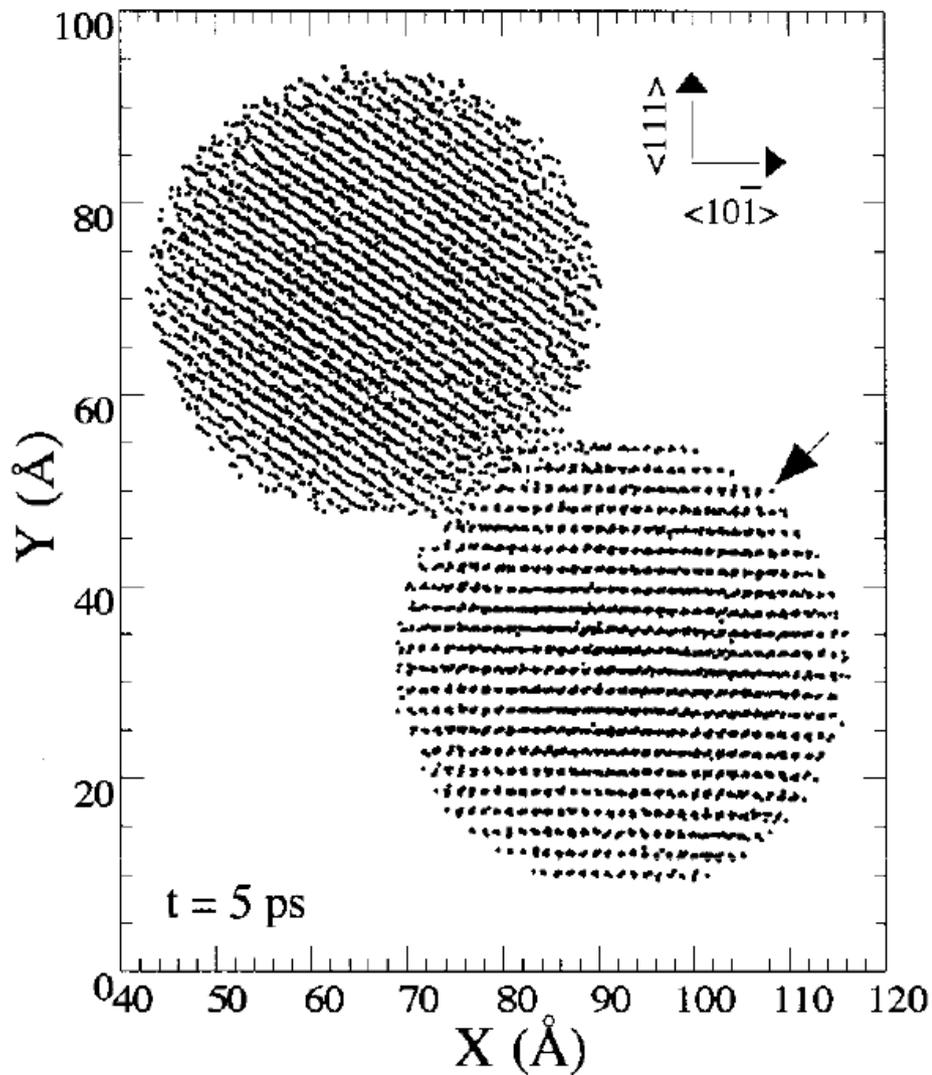
An embedded-atom potential was employed to represent the forces in Cu.

The relative crystallographic axes of the two nano-particles were randomly oriented when the particles were brought into contact at a centre-to-centre distance equal to:

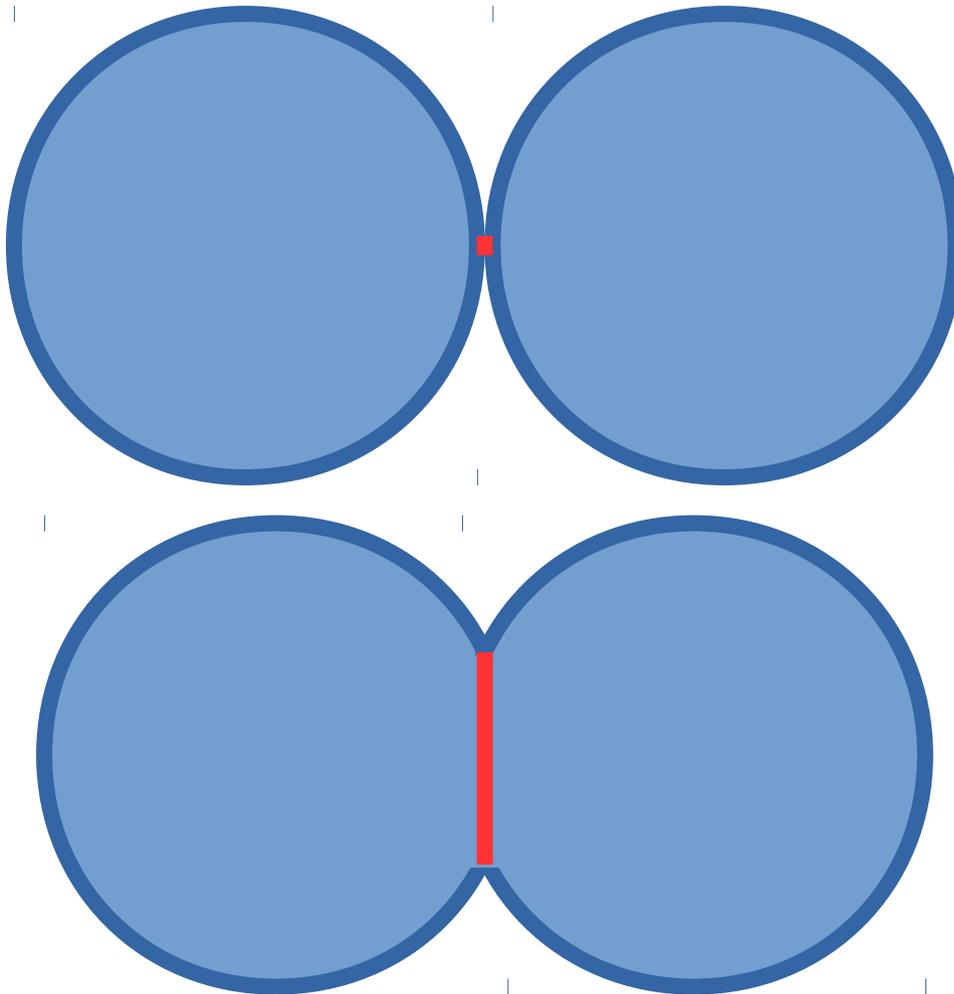
$$l_c = 2R + 0.2\text{nm}$$

$$\text{Relative shrinkage} \rightarrow y = \frac{\Delta l_c}{2R}$$

Sintering processes of two nanoparticles



Shrinkage due to elastic deformation



Three contributing energies:

- Elastic energy
- Surface energy
- Interface (GB) energy

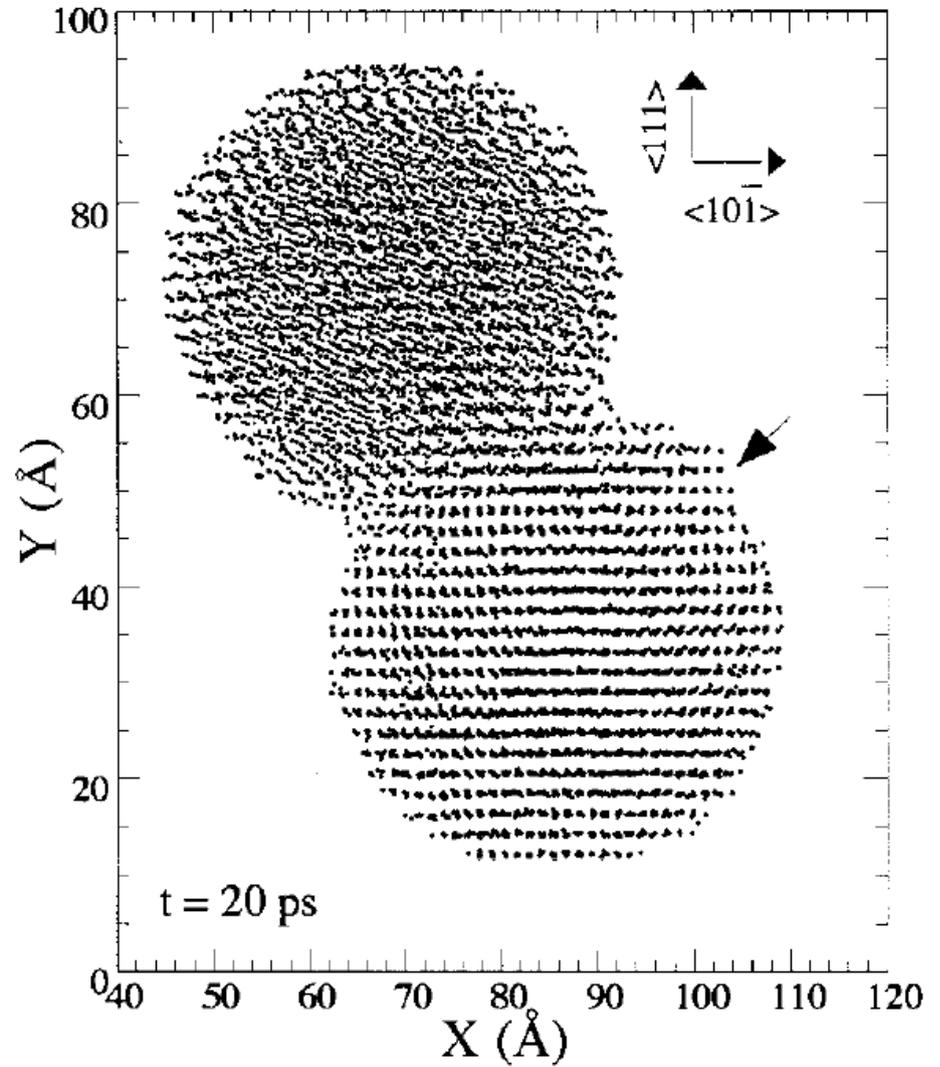
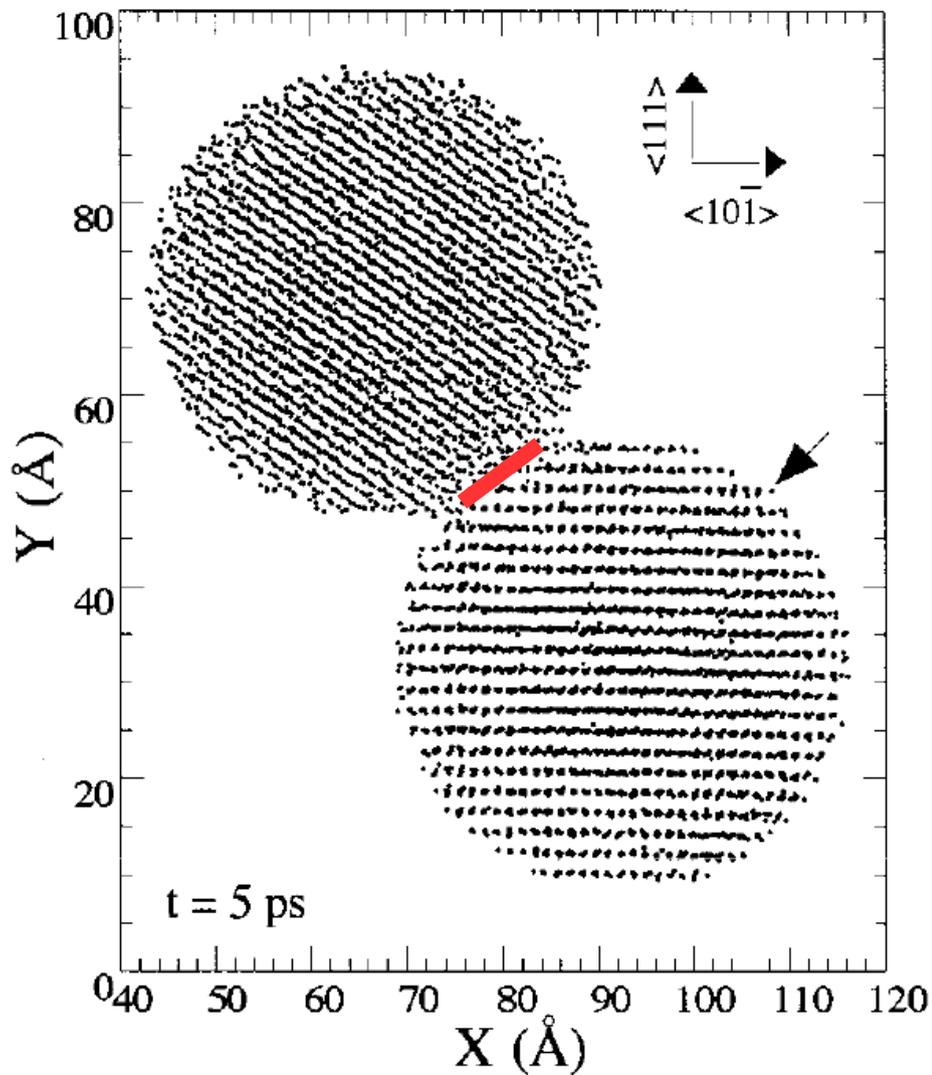
Total energy minimized when

$$a \simeq \left(\frac{\gamma_{\text{effective}}}{GR} \right)^{\frac{1}{3}} R$$

$$\gamma_{\text{effective}} = 2\gamma_{\text{surface}} - \gamma_{\text{GB}}$$

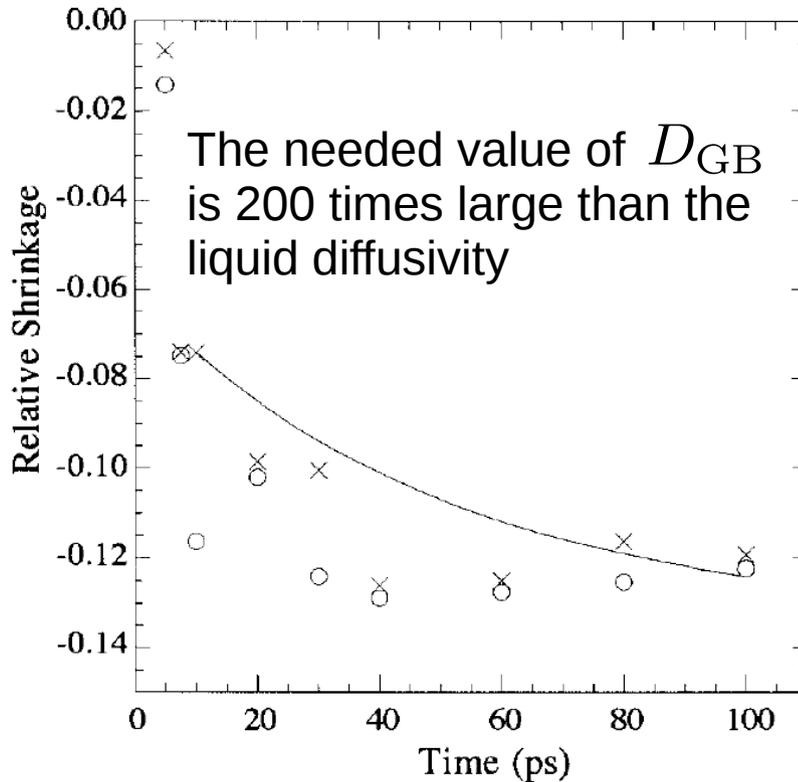
$$\rightarrow a \simeq 0.84\text{nm}$$

Sintering processes of two nanoparticles



Additional shrinkage is seen

$$y = \frac{\Delta l_c}{2R}$$



$$\dot{y} = \frac{2CA_{GB}D_{GB}(x-r)}{\pi x^4 r}$$

$$\dot{x} = \frac{4CA_{GB}D_{GB}(x-r)}{A_r x^2 r}$$

$$C = \frac{\gamma_s \Omega}{k_B T R^3}$$

$$A_{GB} = \frac{2\pi x \delta}{R}$$

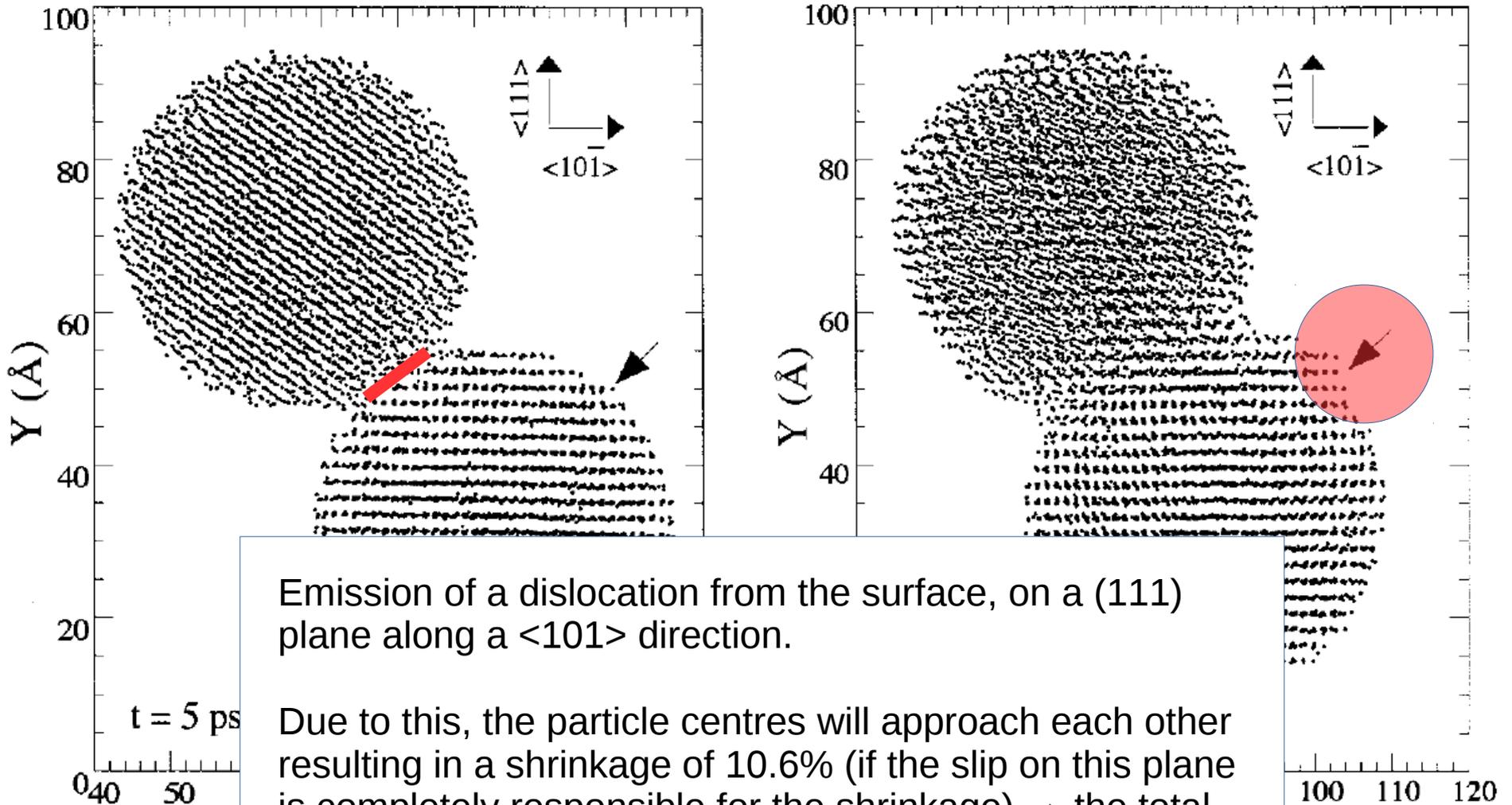
Area of neck surface intersected by the grain boundary (units of R^2)

$$A_r = 4[\theta(x+r) - r \sin \theta]$$

Total surface area of the neck (units of R^2)

- x - radius of neck (units of R)
- y - shrinkage of neck (units of R)
- r - curvature of neck surface
- δ - GB thickness

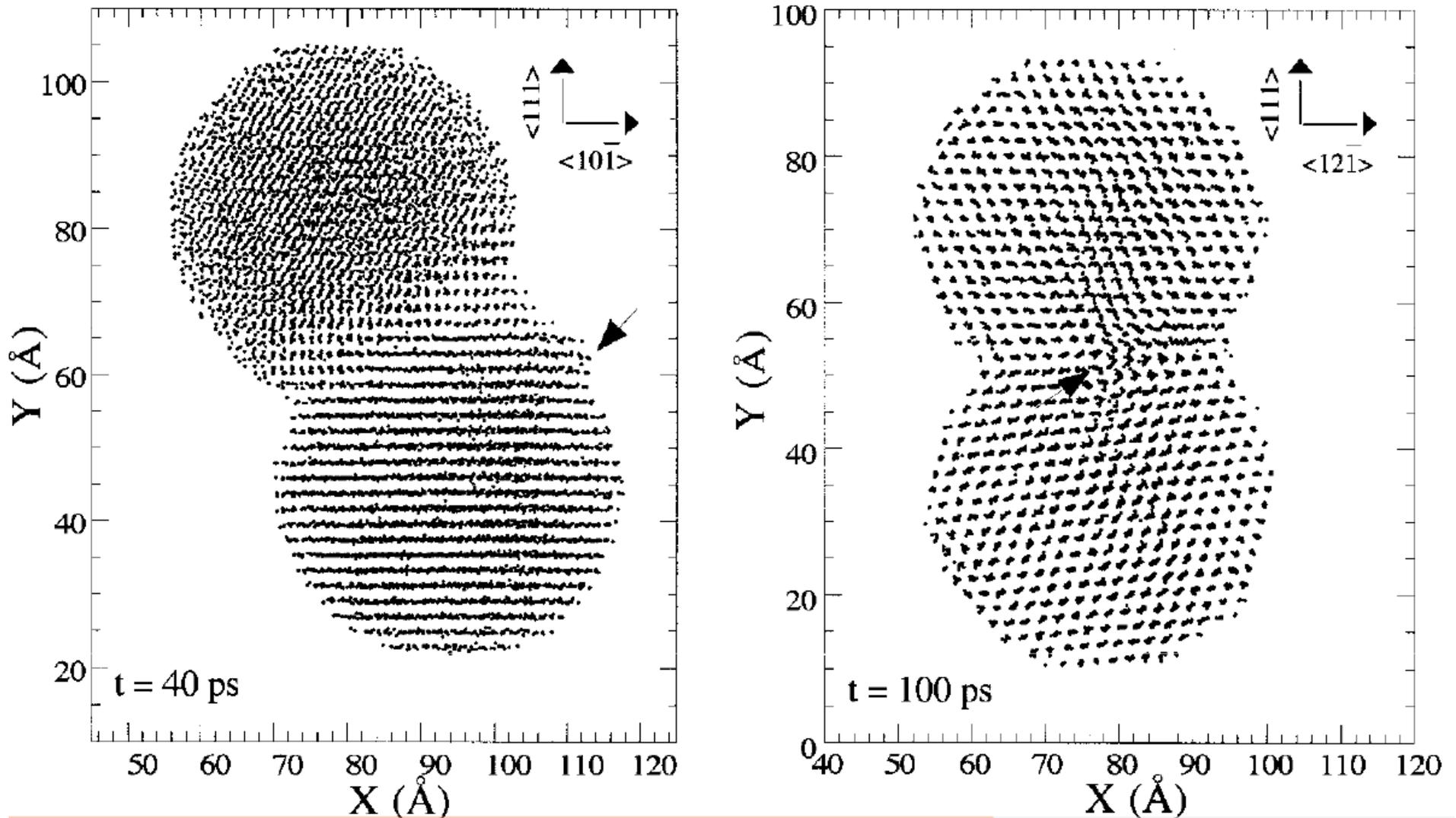
Sintering processes of two nanoparticles



Emission of a dislocation from the surface, on a (111) plane along a $\langle 101 \rangle$ direction.

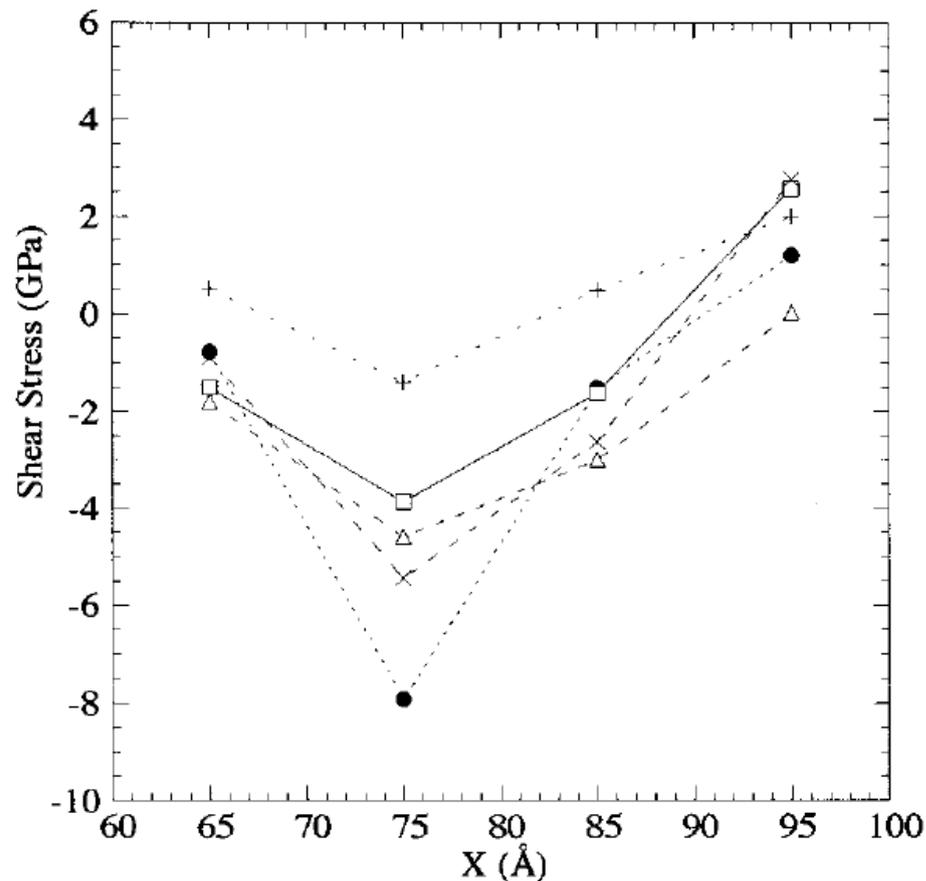
Due to this, the particle centres will approach each other resulting in a shrinkage of 10.6% (if the slip on this plane is completely responsible for the shrinkage) \rightarrow the total shrinkage was 12.6%.

Sintering processes of two nanoparticles



Dislocation slip is completed by about 40 ps

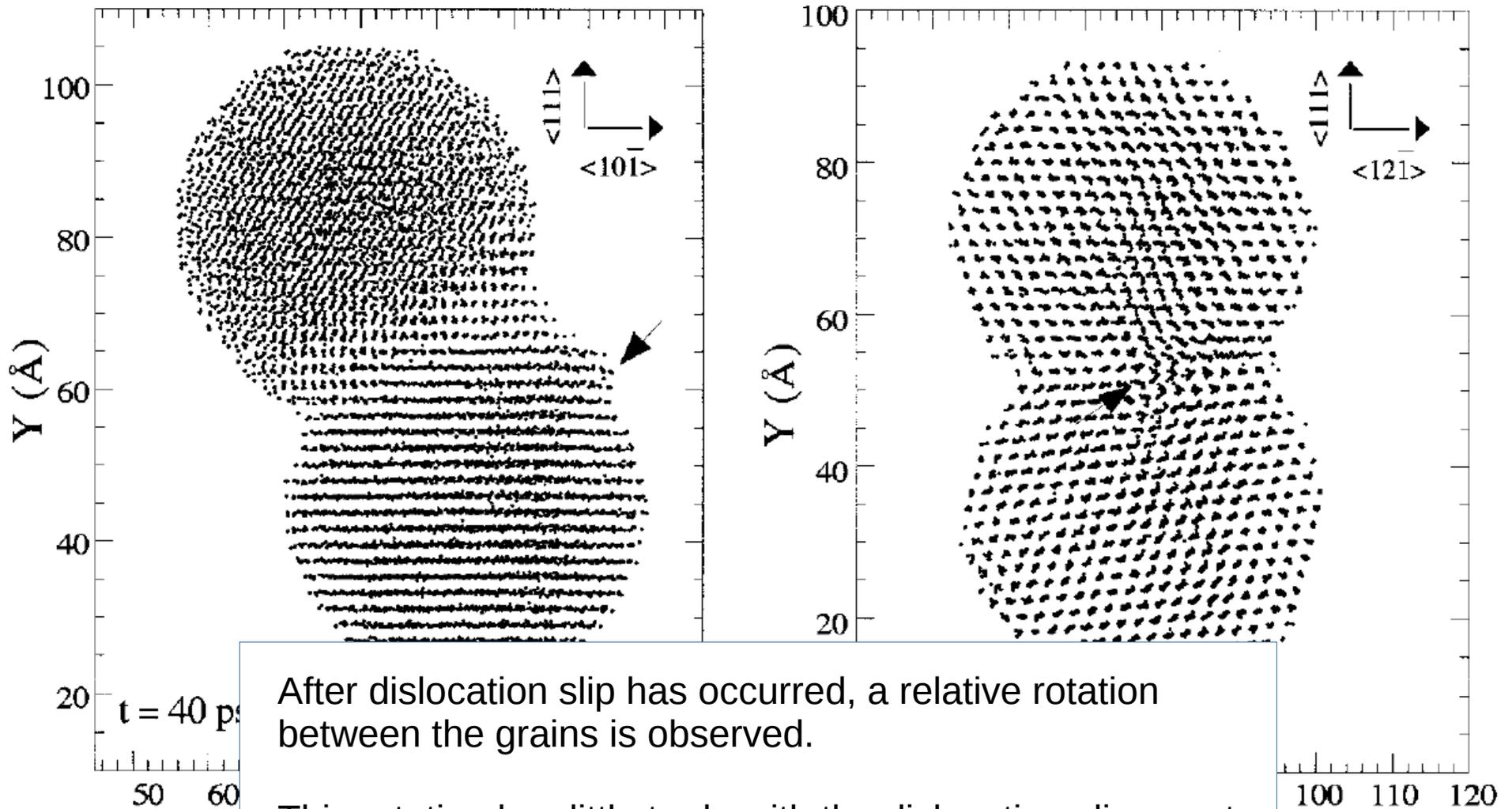
Sintering processes of two nanoparticles



Evolution of the shear stress within the shear plane (undergoing slip)

(●), 5 ps; (□), 10 ps; (○), 20 ps; (×), 30 ps; (+), 40 ps.

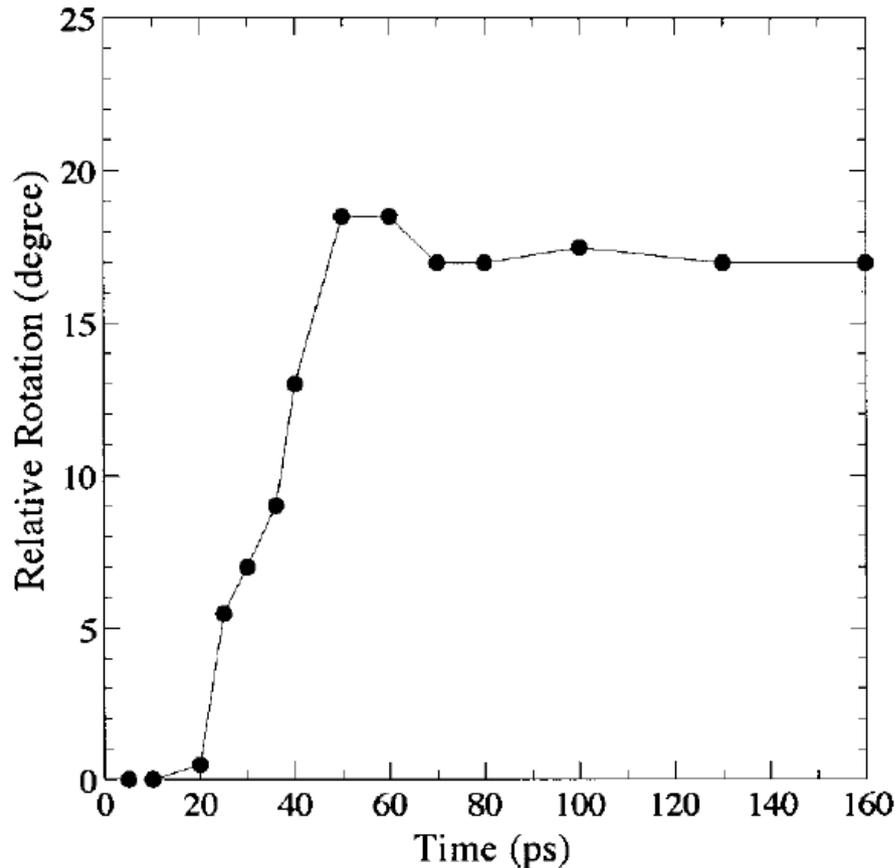
Sintering processes of two nanoparticles



After dislocation slip has occurred, a relative rotation between the grains is observed.

This rotation has little to do with the dislocation slip event (rather about the axis joining the centres of the spheres).

Sintering processes of two nanoparticles

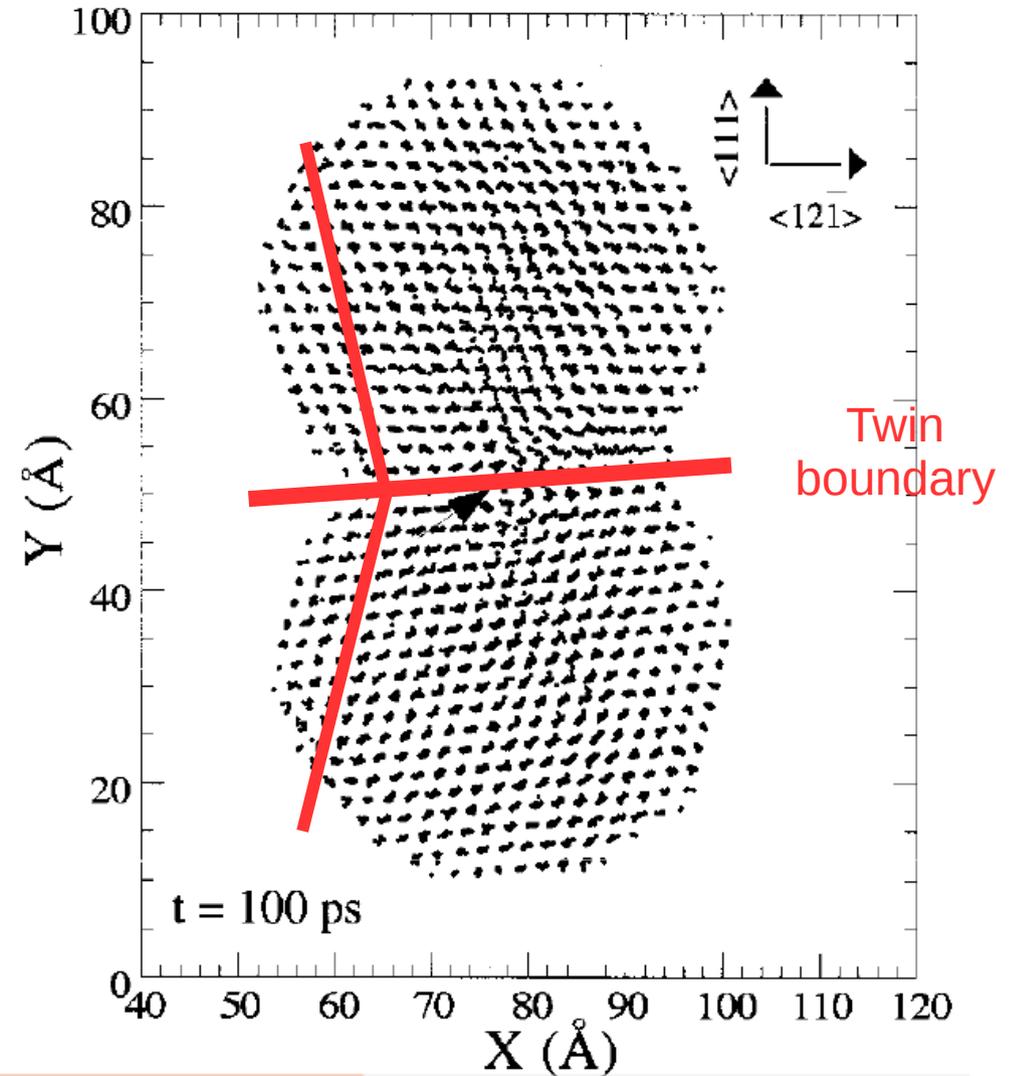
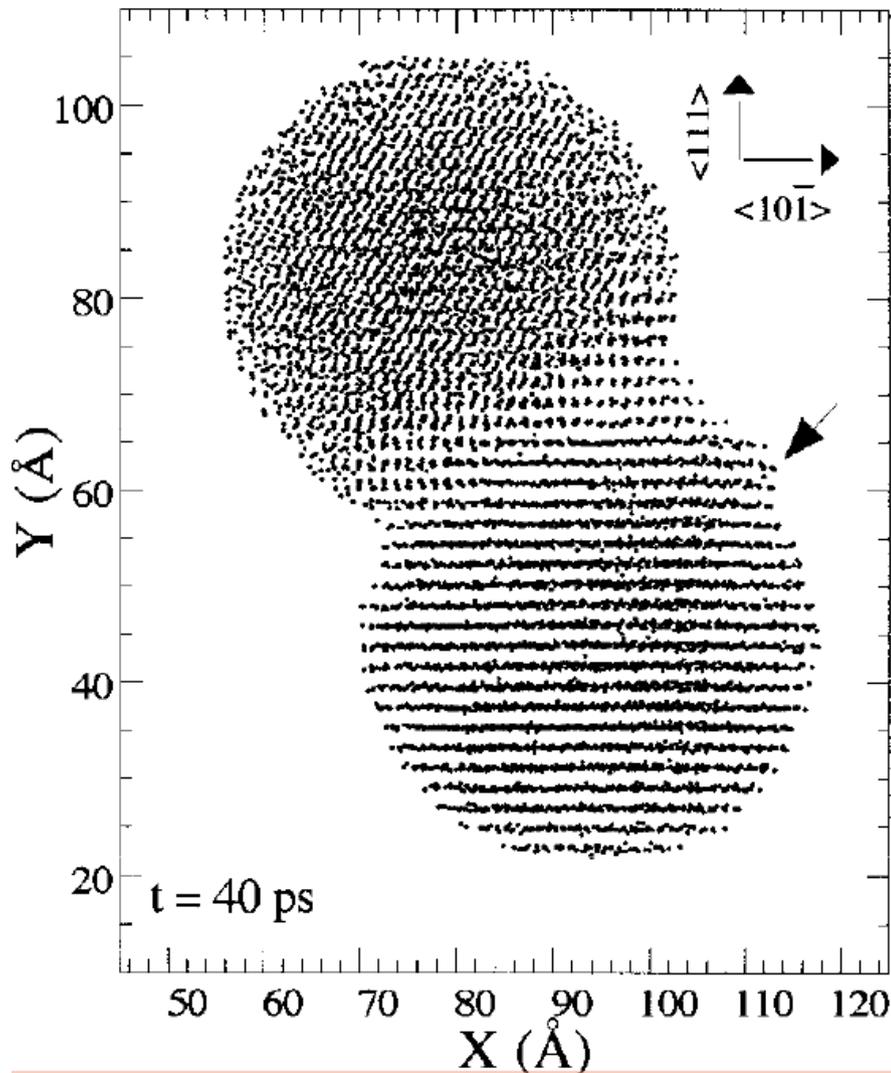


The rotation axis is the $\langle 111 \rangle$ crystallographic axis of the sphere on the bottom.

The rotation continues until the orientation of the spheres finds a low-energy grain boundary between them, in this case a twin involving a rotation of 180 degrees

(●), 5 ps; (□), 10 ps; (○), 20 ps; (×), 30 ps; (+), 40 ps.

Sintering processes of two nanoparticles



Example 3: The sintering and densification behaviour of many copper nanoparticles



Contents lists available at [SciVerse ScienceDirect](#)

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci



The sintering and densification behaviour of many copper nanoparticles: A molecular dynamics study



Bingqing Cheng*, Alfonso H.W. Ngan

Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China

ARTICLE INFO

Article history:

Received 28 November 2012

Received in revised form 7 February 2013

Accepted 1 March 2013

Available online 1 April 2013

Keywords:

Nanoparticle

Sintering

Densification

Grain growth

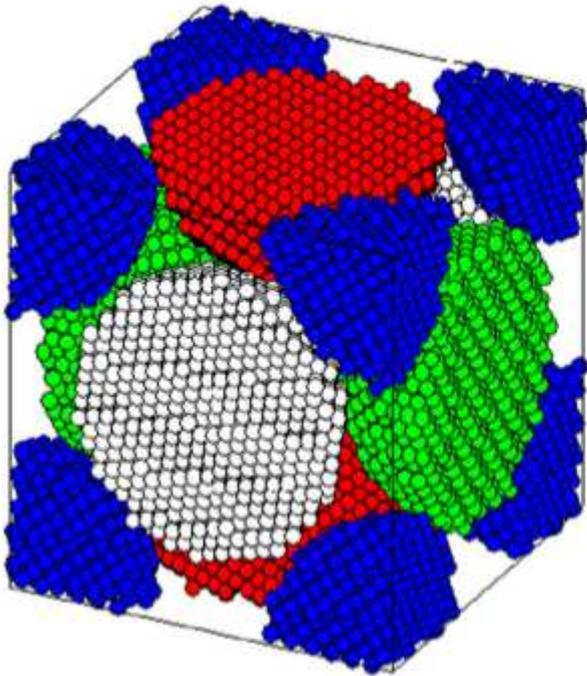
Two-sphere model

ABSTRACT

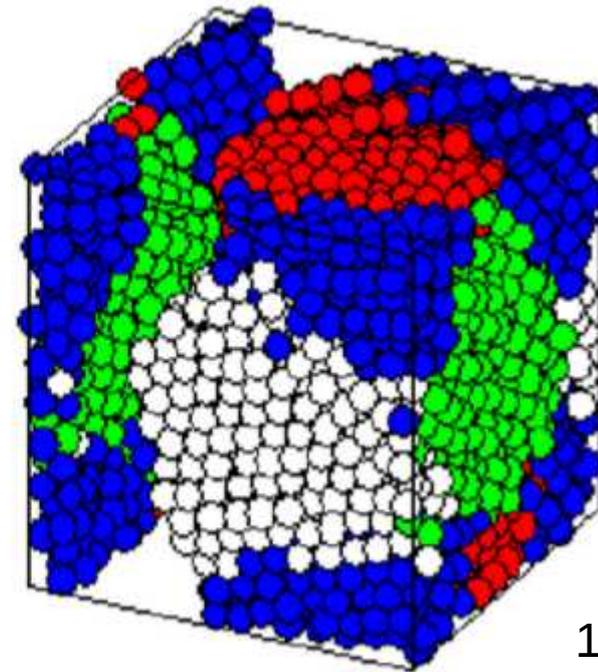
Despite its relevance to a range of technological applications including nanocrystalline material fabrication, the sintering mechanisms of nanoparticles have not been well understood. It has been recognized that extrapolation from understanding of macro-particle sintering is unreliable for the nano-particle size regime. In this work, the sintering behaviour of copper nanoparticles under periodic boundary conditions at different temperatures and pressures was investigated by Molecular Dynamics simulations. It was found that smaller particle sizes, higher temperature and higher external pressure facilitate densification. Through a comparison with a two-sphere model, the governing mechanisms for many nanoparticles sintered at low temperature ($T \leq 900$ K) were identified to be a variety of plasticity processes including dislocation, twinning and even amorphization at the contact neck regions, due to the presence of high stresses.

© 2013 Elsevier B.V. All rights reserved.

Initial & final sample configurations



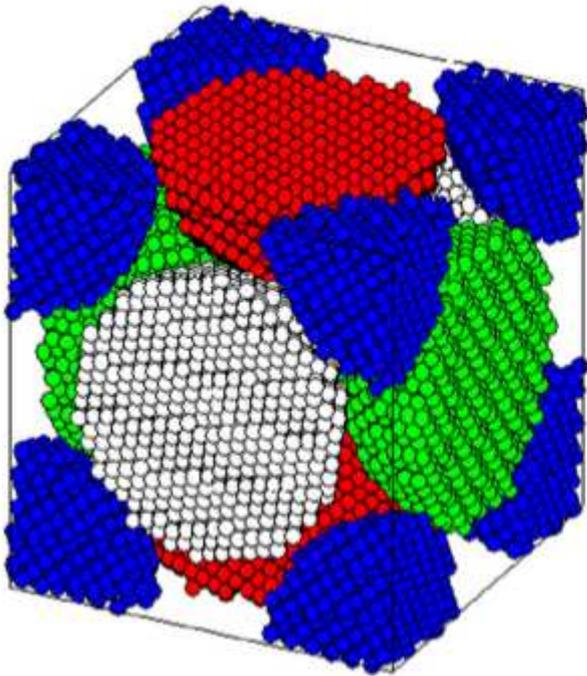
Starting (Green) compact consists of four randomly oriented equal sized spheres arranged in a closed packed configuration – NPT and periodic boundary conditions are used, and the initial particle separation is 4-6 Angstroms.



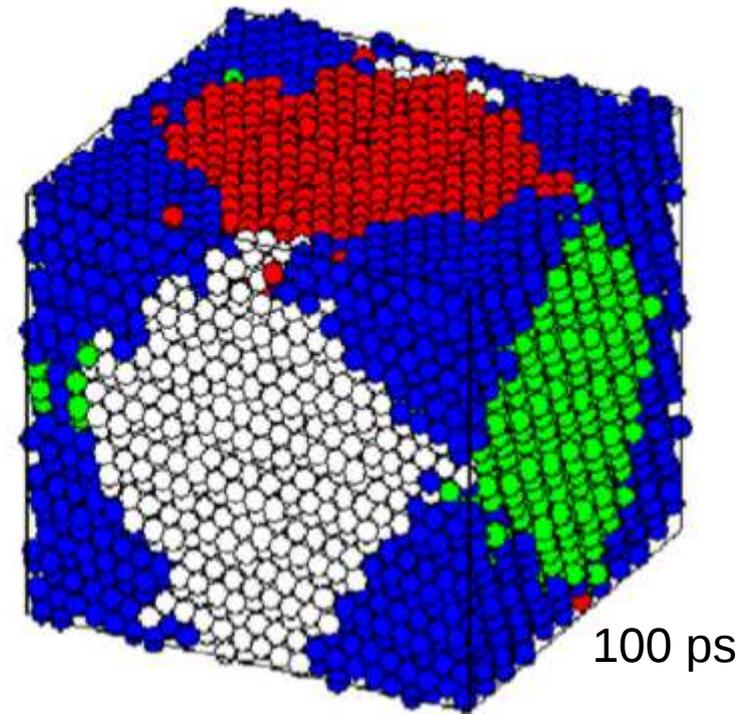
100 ps

For very small nanoparticles (diameter < 3 nm), sometimes large pores with diameters > 0.65 nm remain in the sintered product. In some cases, two crystalline parts are completely detached from each other

Initial & final sample configurations

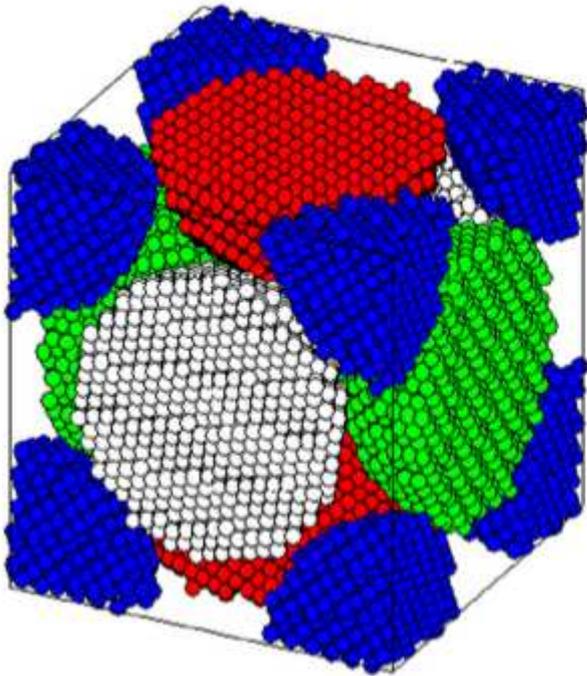


Starting (Green) compact consists of four randomly oriented equal sized spheres arranged in a closed packed configuration – NPT and periodic boundary conditions are used, and the initial particle separation is 4-6 Angstroms.

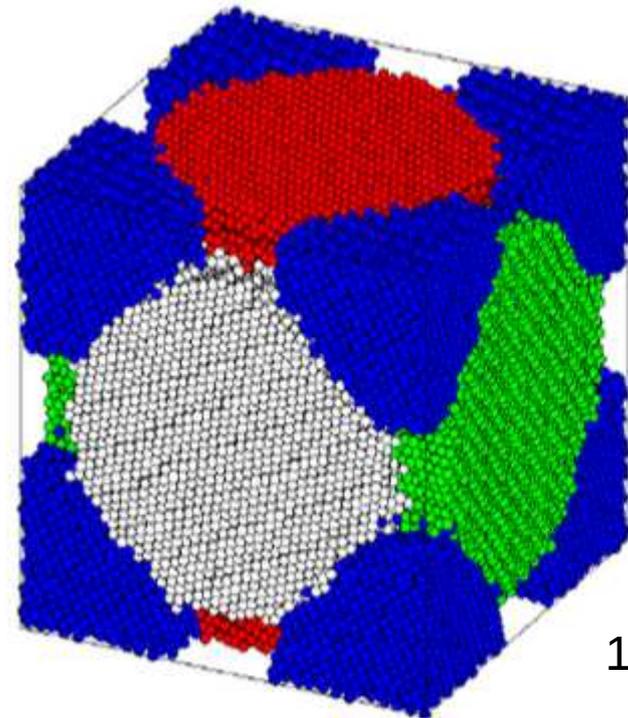


At intermediate sizes (5-6 nm) all pores disappear and full densification is reached. The sintered product is seldom perfect fcc crystal but generally carries defects such as vacancies, twinning, stacking faults and dislocation loops.

Initial & final sample configurations

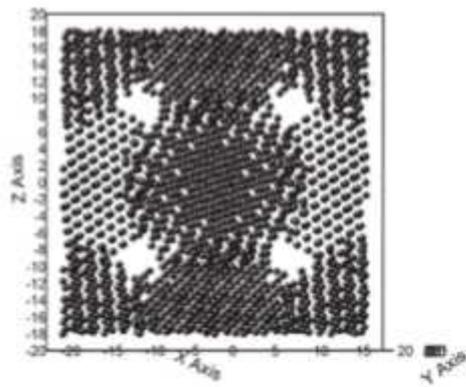


Starting (Green) compact consists of four randomly oriented equal sized spheres arranged in a closed packed configuration – NPT and periodic boundary conditions are used, and the initial particle separation is 4-6 Angstroms.

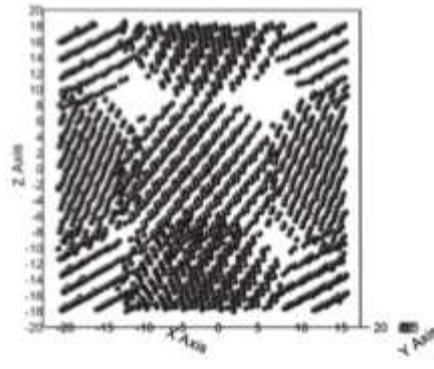


100 ps

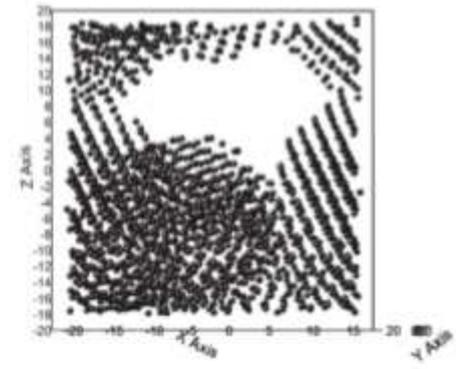
At the largest sizes considered (12nm), the pores between particles become disconnected and quasi-spherical. The pore shrinkage is significant, but full densification is not reached



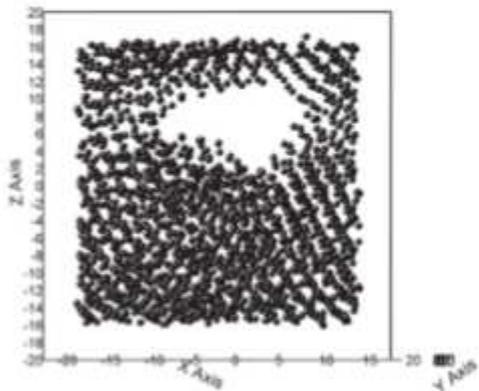
$t = 0\text{ps}$ porosity: 0.46



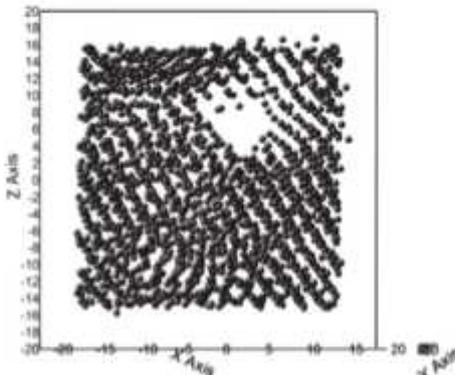
$t = 5\text{ps}$ porosity: 0.46



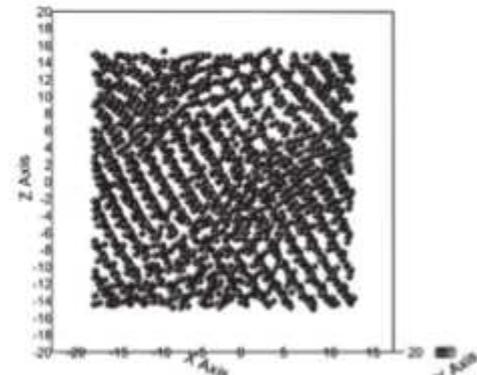
$t = 10\text{ps}$ porosity: 0.45



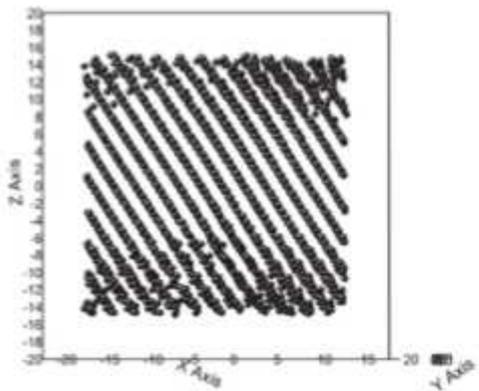
$t = 25\text{ps}$ porosity: 0.22



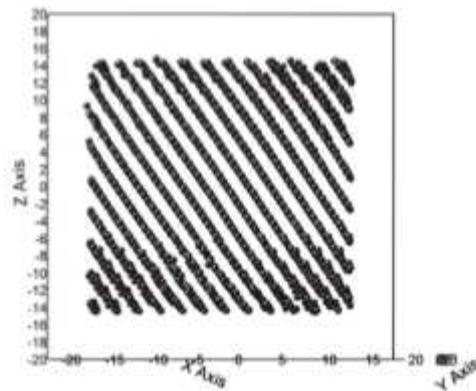
$t = 32.5\text{ps}$ porosity: 0.11



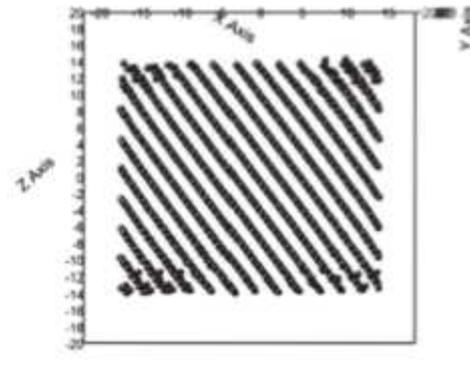
$t = 37.5\text{ps}$ porosity: 0.05



$t = 42.5\text{ ps}$ porosity: 0.01

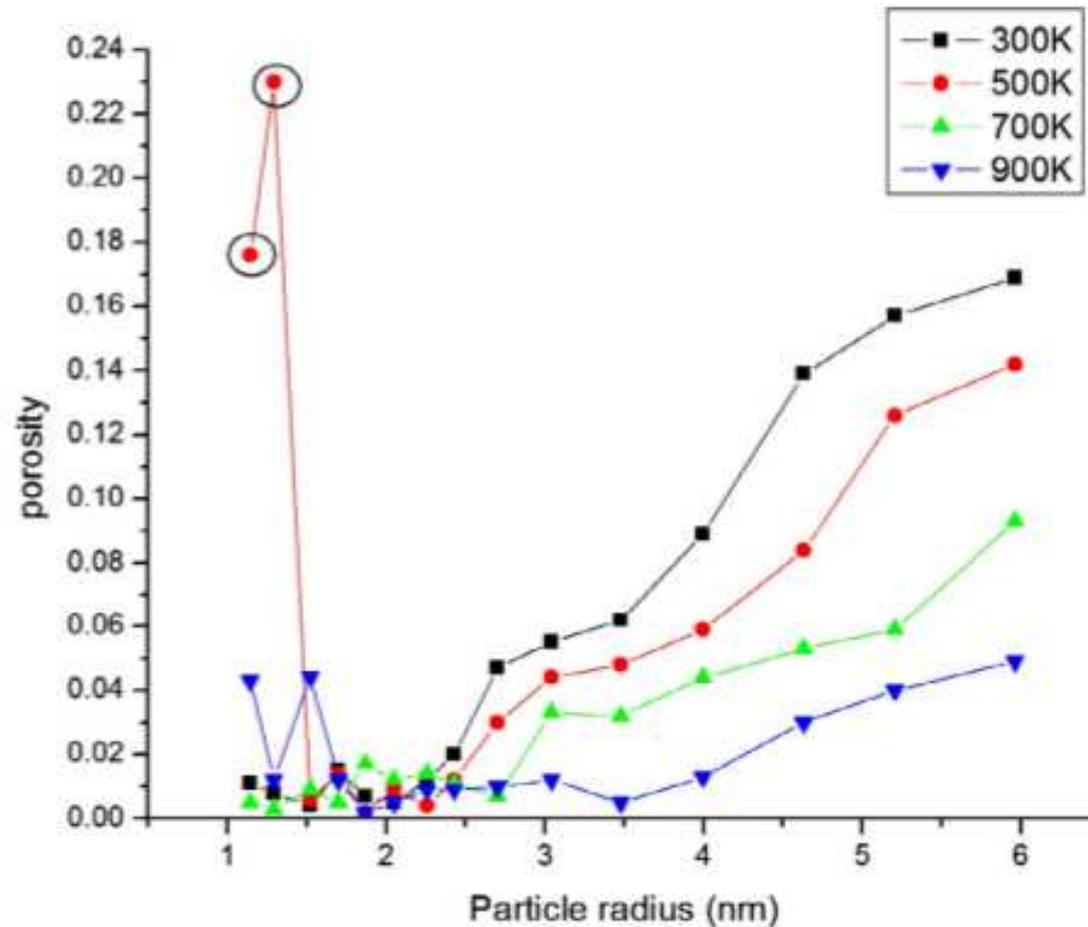


$t = 50\text{ps}$ porosity: 0.01

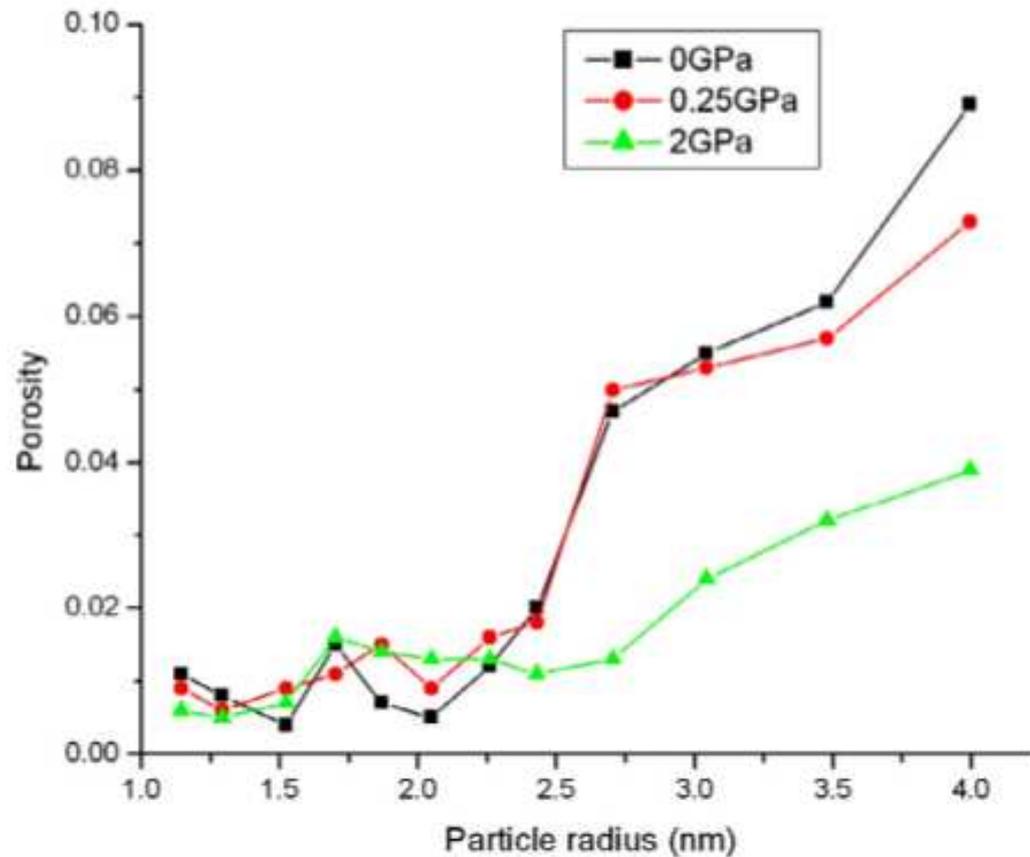


$t = 250\text{ps}$ porosity: 0.01

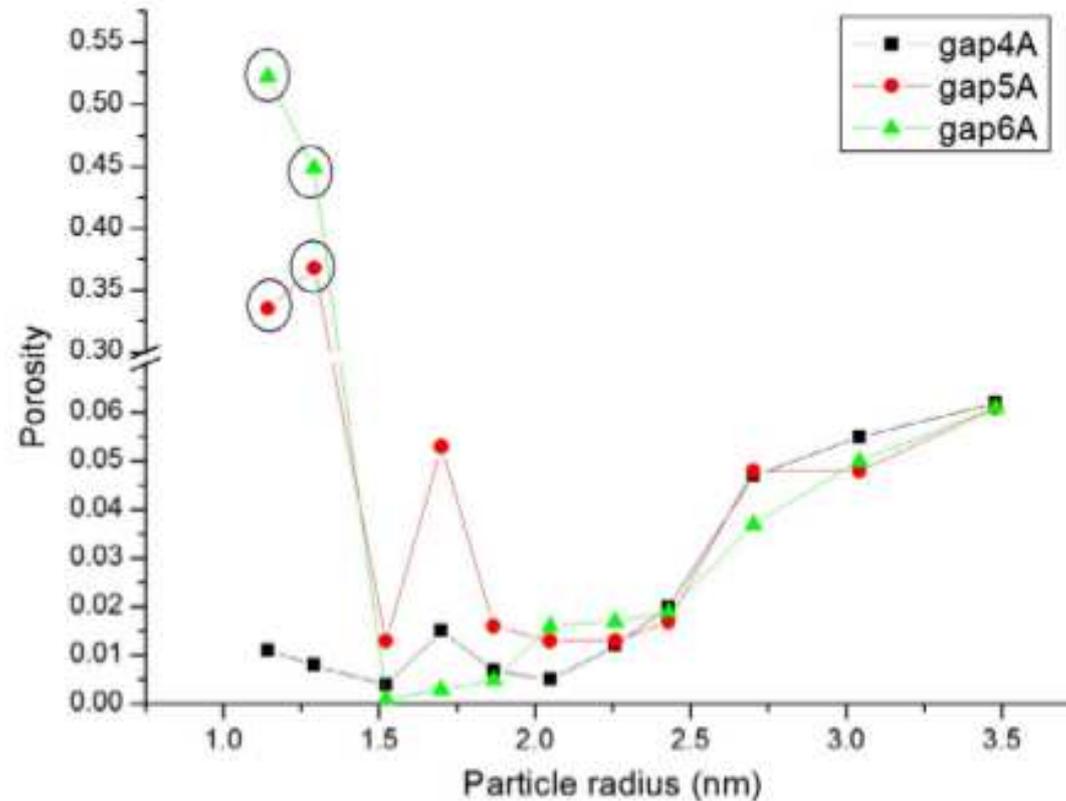
Final porosity as a function of particle radius – temperature effects



Final porosity as a function of particle radius – pressure effects



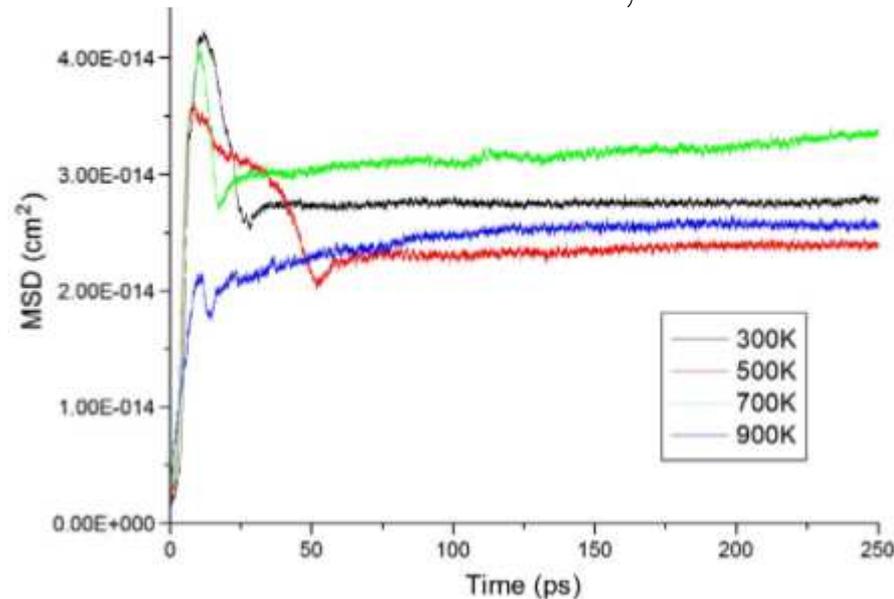
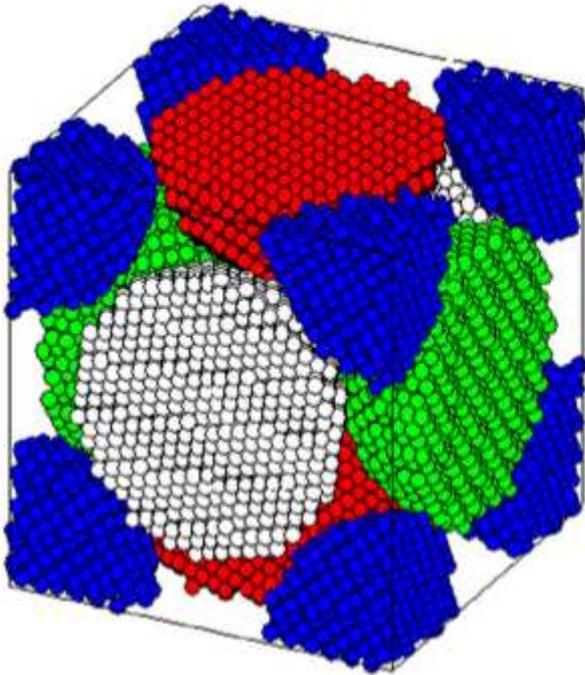
Final porosity as a function of particle radius – initial gap effects



Underlying mechanisms

The mean-square-displacement of particles is defined as

$$\langle (\Delta r(t))^2 \rangle = \frac{1}{N} \sum_{i=1, N} |\mathbf{r}(0) - \mathbf{r}(t)|^2 \sim 4Dt$$



Measured gradients are far too high to be diffusion

Initial densification ($t < 100$ ps) is due to the high stress in the neck region causing the material to deform plastically by either dislocation or twinning mechanisms, or even by viscous flow following amorphization.

Such plasticity mechanisms can explain the large MSD and the amorphous region at the neck at the early stage of sintering.

Concluding remarks

The MD method provides a way in which to simulate atomic scale processes which may not be directly experimentally accessible, but which play a central role in determining macroscopic material properties.

The two main caveats of the technique are:

- 1) The accuracy and transferability of the empirical potential description (can be overcome by using density function theory methods to calculate the interatomic forces).
- 2) Direct MD can only simulate processes happening at the nanosecond timescale.

This makes it non-trivial to connect simple atomistic simulation to the experimental regime → acceleration methods are available, but you need to understand your particular problem → it is not a “black box”.

Questions

- What types of atomistic simulations were presented in the course? Give one example of its use.
- What are the three general types of bond descriptions of interatomic forces in simulations?
- What are the general limitations of atomistic scale simulations?
- What is the difference between molecular dynamics and molecular statics?
- What limits the time step in molecular dynamics? How? What is a typical real time period for a MD simulation?
- What are the essential features of a potential energy landscape?
- State the “timescale” problem of MD in terms of a potential energy landscape picture?
- State the two ways the time scale problem can be overcome using standard MD (in terms of temperature and athermal processes)? What are their disadvantages?
- In terms of the potential energy landscape picture, describe one method to accelerate MD simulation to overcome the timescale limitation of MD.
- Give an example of an experimentally relevant atomic scale process for which MD would have difficulty simulating at the relevant timescales. How could this be overcome using the acceleration or transition pathway methods?
- Which modelling approach – from any part of the course – do you think in your opinion gives the biggest impact on powder technology and why?