



# Introduction to atomic scale simulations

Peter M Derlet  
Condensed Matter Theory  
Paul Scherrer Institut

[peter.derlet@psi.ch](mailto:peter.derlet@psi.ch)

## Semestre d'hiver 2018

Week- DATE	File. no.		<b>Powder Technology – Wednesday 10.15-13.00 – MXG 110</b>
1- sept 19	1&2	PB	Introduction – example rheology – Yodel - Powder packing and compaction – 1 (i) – (3hrs)
2 – sept 26	2&3	PB MS	Powder packing and compaction – 1(ii), 2- Examples and DEM guest lecturer – (3hrs)
3 – oct 3	4	PD	Powder packing and compaction -3 & 4(i) – (3hrs)
4 – oct 10	4&5	PD	Powder packing and compaction - 4 (ii) – (1hr)
		PB	Particle – Particle Interactions 1 - 2hrs
5 – oct 17	6&7	PB	Particle – Particle Interactions 2 & 3(i) – (3hrs) – Download Hamaker
6 – oct 24	7	PB	Particle – Particle Interactions – 3(ii) YODEL-PB (1hr) <b><u>Exercices</u></b> – Intro to Hamaker & YODEL software & groups project (2hrs)
7 – Oct 30		AK M	<b><u>Exercices</u></b> - Hamaker and Yodel Modelling – group projects
8 – nov 7	8	PB	<b><u>Exercices</u></b> –presentation of interparticle project results (1 hr)
		PD	Introduction to atomistic scale simulations – (2hrs)
9 – nov -14	9&	PD	Compaction, Sintering & Defects in metals at atomistic scale (2hrs)
	11		Sintering Mechanisms – 1(i) (1 hr)
10 – nov 21	11	PD	Sintering Mechanisms - 1 (ii) & 2 (3hrs)
11 -nov-28		PD	<b><u>Exercices</u></b> -Introduction to Molecular Dynamics Modelling using LAMMPS (3hrs) .
12 - dec 5		PD	<b><u>Exercices</u></b> - MD- DEM modelling exercise using LAMMPS –particle packing - Effect of parameters (3 hrs)
13 – dec 12	10	PB	New Technologies -1 Processing – Forming – Shaping (2hrs) <b><u>Exercices or invited lecture or visit of AM lab (1hr)</u></b>
14 – dec 19	10	PB	New Technologies-2 – Sintering Methods <b><u>Exercices or invited lecture or visit of AM lab (1 hr) &amp; Exam method</u></b>

# Outline of lecture

- The big picture of materials modelling
- Classical Molecular Dynamics – basic definitions
- Atomic interaction
- The Molecular Dynamics algorithm
- Boundary Conditions
- An MD example – equipartition theorem
- Controlling temperature and load
- An MD example – thermal expansion
- Concluding remarks

*Understanding Molecular Simulation (Second Edition): From Algorithms to Applications*  
Daan Frenkel and Berend Smit (<http://www.sciencedirect.com/science/book/9780122673511>)

*Interatomic Forces in Condensed Matter*  
Mike Finnis, Oxford series on materials modelling

# The big picture of materials modelling

# Many problems, parameters & possibilities

**HAYNES® 230® ALLOY**

A Ni-Cr-W alloy that offers  
 dimensional and high-temperature  
 strength and excellent corrosion  
 resistance with excellent formability  
 and good weldability.

**Contents**

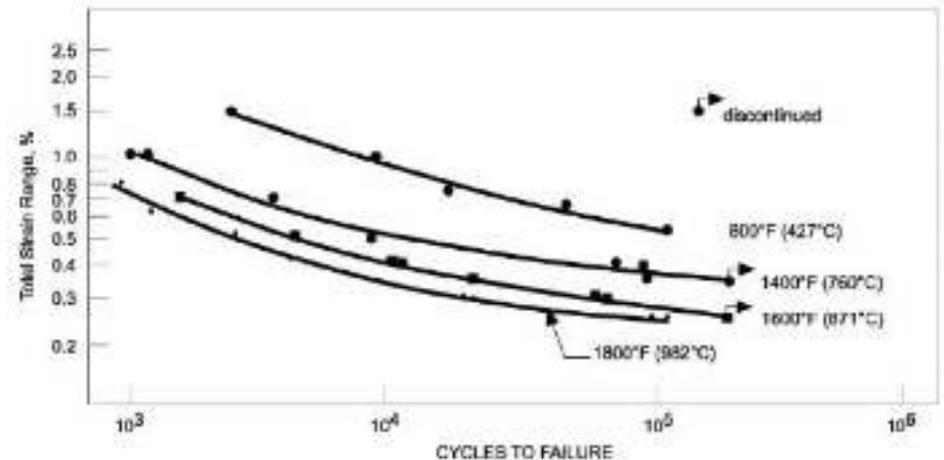
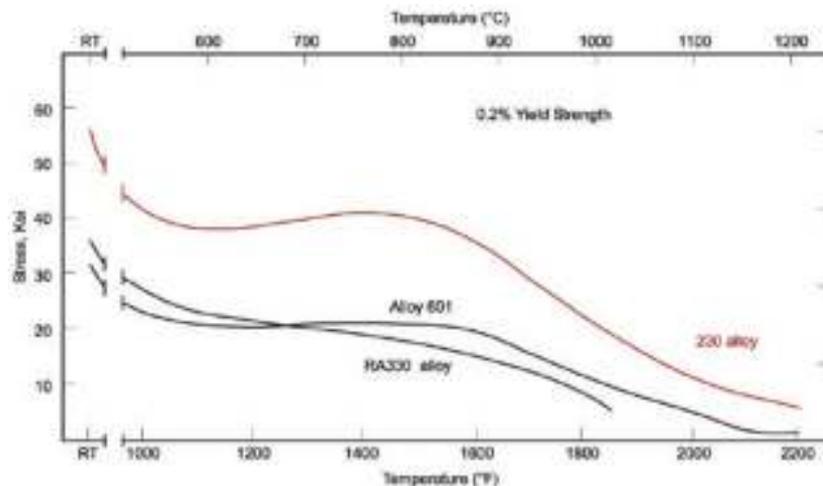
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- Creep and stress-rupture strength
- Low cycle fatigue
- Tensile properties
- Thermal stability
- Resistance to grain growth
- Oxidation
- Nitriding
- Carbonization
- Hydrogen embrittlement
- Aqueous corrosion
- Fabrication
- Microstructure
- Welding
- Machining

Nominal Chemical Composition, Weight Percent

Ni	Cr	W	Mo	Fe	Co	Mn	Si	Al	C	La	B
57*	22	14	2	3*	5*	0.5	0.4	0.3	0.10	0.02	0.015*

\*Maximum    \*\*As balance

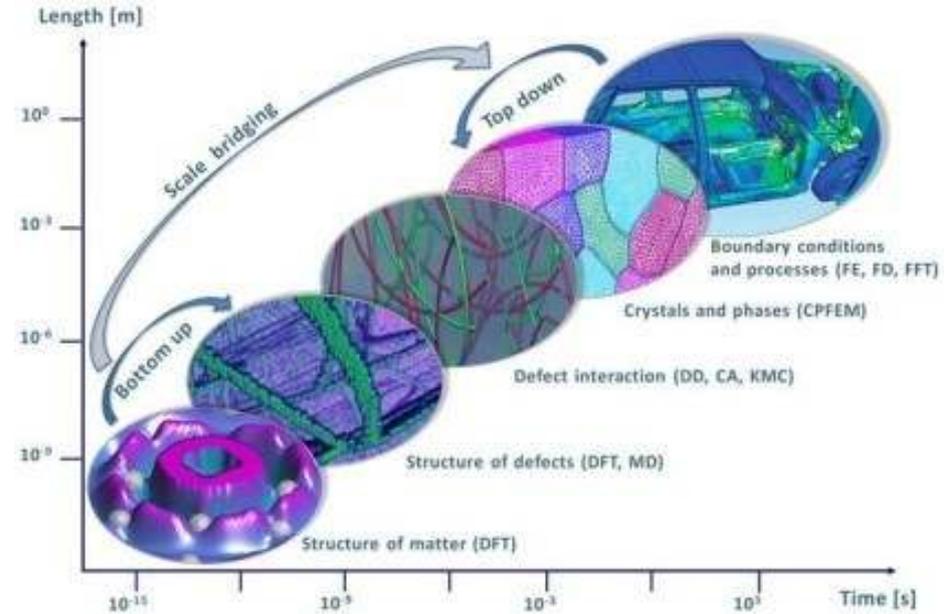


# The need for strong materials



# Material properties is a multi-scale problem

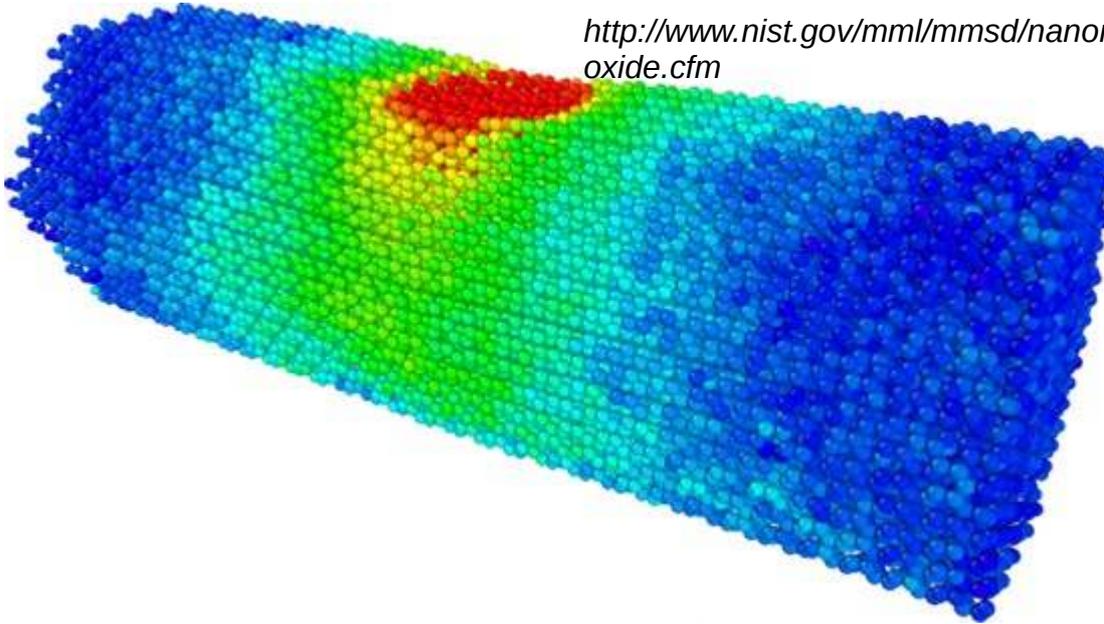
- From atoms to the quantitative prediction of macroscopic properties.
  - Atoms → micro-structure → effective material mediums



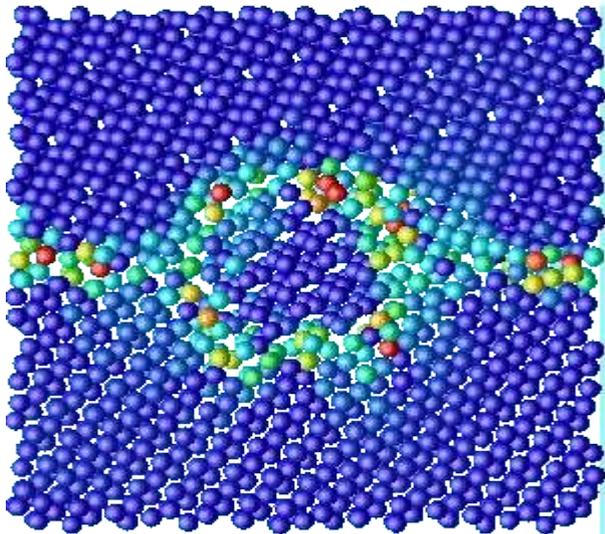
<http://www.dierk-raabe.com>

# It all about atoms!

[http://www.nist.gov/mml/mmsd/nanomechanical\\_properties/molecular-dynamics-zinc-oxide.cfm](http://www.nist.gov/mml/mmsd/nanomechanical_properties/molecular-dynamics-zinc-oxide.cfm)



Investigating the Diameter-Dependence of Elastic Moduli of Zinc Oxide Nanowires using Molecular Dynamics Simulations



Grain boundary energies and cohesive strength as a function of geometry

<http://www.lassp.cornell.edu/sethna/DM/mdwebservices/>

# The Theory of Everything

R. B. Laughlin\* and David Pines†‡§

\*Department of Physics, Stanford University, Stanford, CA 94305; †Institute for Complex Adaptive Matter, University of California Office of the President, Oakland, CA 94607; ‡Science and Technology Center for Superconductivity, University of Illinois, Urbana, IL 61801; and §Los Alamos Neutron Science Center Division, Los Alamos National Laboratory, Los Alamos, NM 87545

For experts we write

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \mathcal{H}|\Psi\rangle$$

where **Born-Oppenheimer limit**

$$\mathcal{H} = - \sum_j^{N_e} \frac{\hbar^2}{2m} \nabla_j^2 - \sum_{\alpha}^{N_i} \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 - \sum_j^{N_e} \sum_{\alpha}^{N_i} \frac{Z_{\alpha} e^2}{|\vec{r}_j - \vec{R}_{\alpha}|} + \sum_{j \ll k}^{N_e} \frac{e^2}{|\vec{r}_j - \vec{r}_k|} + \sum_{\alpha \ll \beta}^{N_j} \frac{Z_{\alpha} Z_{\beta} e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|}$$

But the schemes for approximating are not first-principles deductions but are rather art keyed to experiment, and thus tend to be the least reliable precisely when reliability is most needed, i.e., when experimental information is scarce, the physical behavior has no precedent, and the key questions have not yet been identified. There are many notorious failures of alleged *ab initio*

By replacing this term with the classical expression for a particle's kinetic energy, MD treats each atom as a classical deterministic particle

$$\frac{|\mathbf{P}_i|^2}{2M_i}$$

R. Laughlin & D. Pines, "The theory of everything" PNAS 97, 28 (2000)

Atomistic simulations use an empirical based Hamiltonian

$$H(\{\mathbf{R}_i, \mathbf{P}_i\}) = \sum_i \frac{|\mathbf{P}_i|^2}{2M_i} + V(\{\mathbf{R}_i\})$$

$$V(\{\mathbf{R}_i\}) = \frac{1}{2} \sum_{i \neq j} V_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|) + \frac{1}{6} \sum_{i \neq j \neq k} V_{t_i, t_j, t_k}(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \dots$$

This potential energy can sometimes be accurately calculated using Density Functional Methods, but usually suitably parameterized analytical functions are used

# Classical Molecular Dynamics – basic definitions

# What is classical MD?

MD involves simulating the classical dynamics of N interacting atoms.

Each atom:

- is defined by its atom type (mass, atomic number)

- has a coordinate (position, velocity)  $\left\{ \begin{array}{l} \{\mathbf{r}_1, \dots, \mathbf{r}_N\} \\ \{\mathbf{v}_1, \dots, \mathbf{v}_N\} \end{array} \right. \longrightarrow$  6N-dimensional phase space

- feels a force that depends on the type and coordinates of other (nearby) atoms

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_N) = -\nabla_i V(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

N-body coupled non-linear differential equation – can only be solved numerically

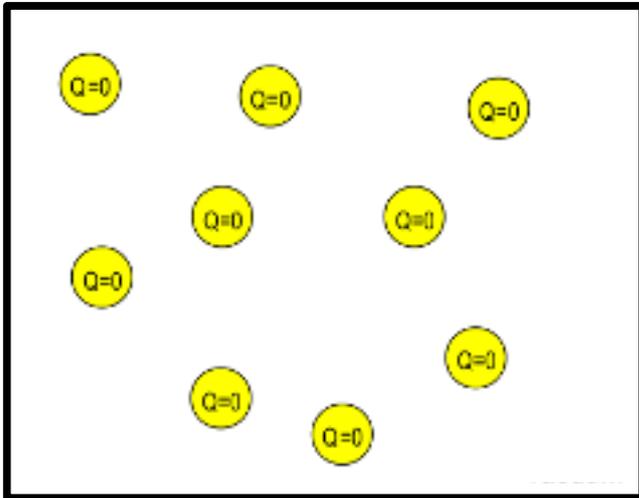
# What is classical MD?

What is needed to perform an MD simulation?

- An efficient & accurate method to calculate the forces/energy between atoms
- An efficient numerical integrator to perform an MD iteration
- An MD code to implement the above that is able to:
  - Extract & control “equilibrium” material properties (thermodynamics)
  - Allow for observation of non-equilibrium atomic scale processes (visualization)

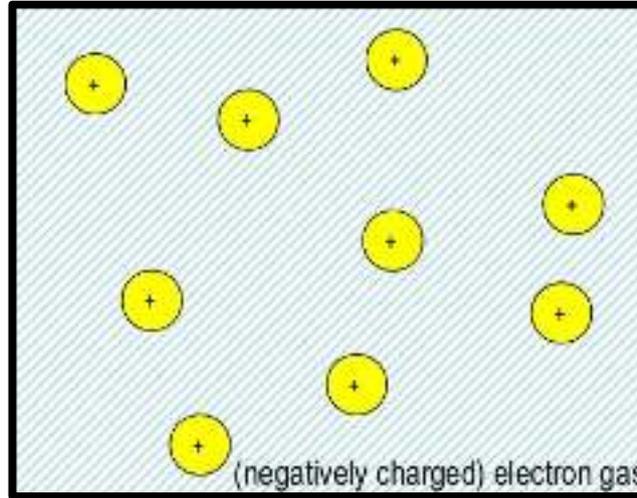
# Atomic interaction

# Three (very broad) regimes of bonding



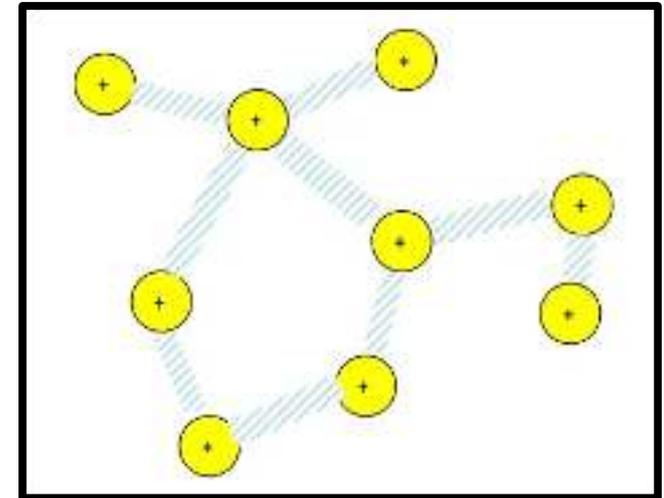
When the electrons remain localized to an atom, the interatomic interaction is well described by a pair potential.

Inert gases,  
some ionic solids



When the valence electrons are de-localized, forming an electron gas, then an additional term must be added to model the binding energy of the electron gas

FCC sp-valent metals and  
some BCC transition metals



When the electrons remain localized to the bonds between atoms, then more complex angular dependent interactions are needed

Covalent materials  
such as Si and C.



Some FCC and BCC metals

# Classes of potentials

There are three classes of potentials that occur frequently in the literature

– Pair potentials (LJ, Ionic, Morse ...)

$$V(r) = Ae^{-Br} - \frac{C}{r^6} \quad \text{Common examples}$$

$$V(\{\mathbf{R}_i\}) = \frac{1}{2} \sum_{i \neq j} V_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|) \quad V(r) = D(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)})$$

(Morse potential – originally used for diatomic molecules)

– Many-body potentials (2<sup>nd</sup> moment, Embedded Atom Method)

$$V(\{\mathbf{R}_i\}) = \frac{1}{2} \sum_{i \neq j} V_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|) + \sum_i F_{t_i} \left[ \sum_j f_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|) \right]$$

– Explicit angular interactions (Stillinger-Weber, MEAM ...)

$$V(\{\mathbf{R}_i\}) = \frac{1}{2} \sum_{i \neq j} V_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|) + \frac{1}{6} \sum_{i \neq j \neq k} V_{t_i, t_j, t_k}(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k)$$

# The Lennard-Jones Potential

*On the Determination of Molecular Fields.—II. From the Equation of State of a Gas.*

By J. E. JONES, D.Sc., 1851 Exhibition Senior Research Student,  
Trinity College, Cambridge.

(Communicated by Prof. S. Chapman, F.R.S.—Received April 22, 1924.)

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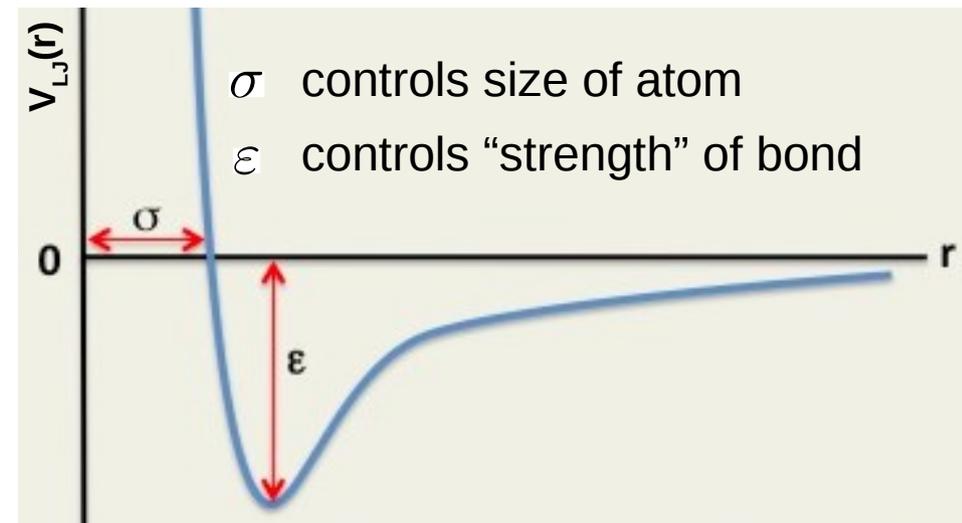
Sir John Edward Lennard-Jones  
(1894 – 1954)

then 
$$f(r) = \frac{\lambda_n}{r^n} - \frac{\lambda_m}{r^m}$$

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

An empirical representation  
of Pauli repulsion

Van der Waals (attraction) – dipole-dipole  
interactions due to electron dispersion

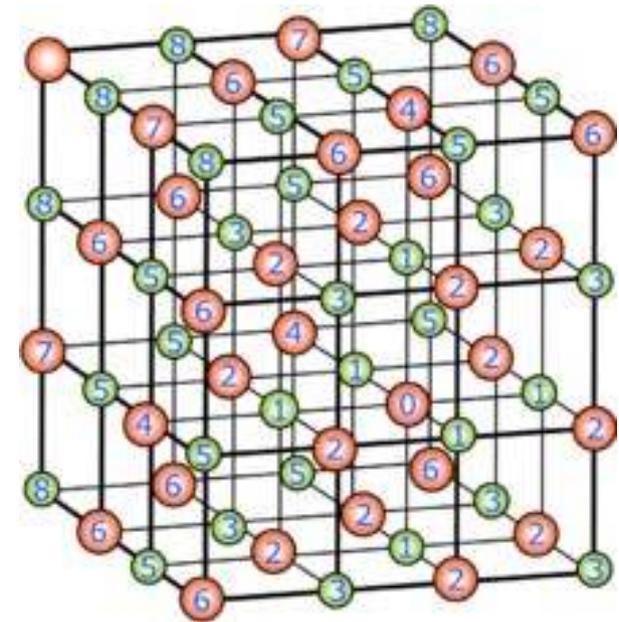


# Ionic interactions

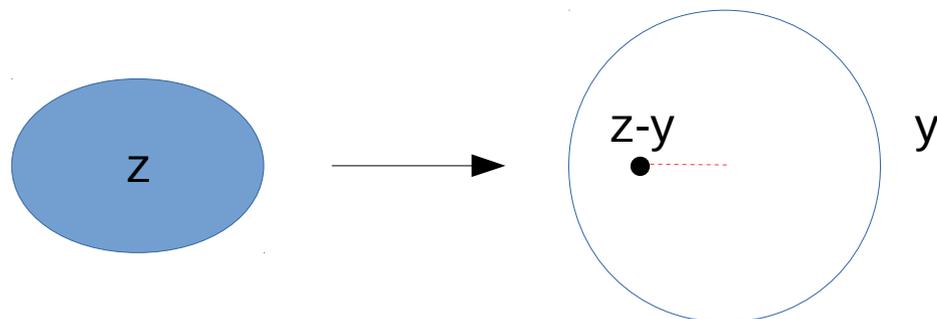
In strongly ionic systems things are “simple” - the calculation of the Madelung lattice energy

$$V_{\text{Madelung}} = \frac{e^2}{4\pi\epsilon_0} \sum_{i < j} \frac{z_i z_j}{r_{ij}}$$

Good for well localized ions in which the ionic charge can be approximated as a structureless point



In this approximation, ions do not polarize → lattice distortions polarize ions



Shell model (for ceramics) in which the heavy central (z-y) ion interacts with a massless charge (y), and:

- there is a long range (effective) ion-ion interaction
- a short range shell-shell interaction

# Many-body potentials of metals

$$V(\{\mathbf{R}_i\}) = \frac{1}{2} \sum_{i \neq j} V_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|) + \sum_i F_{t_i} \left[ \sum_j f_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|) \right]$$

Written as 
$$V(\{\mathbf{R}_i\}) = \frac{1}{2} \sum_{i \neq j} V_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|) + \sum_i F_{t_i} [\rho_i]$$

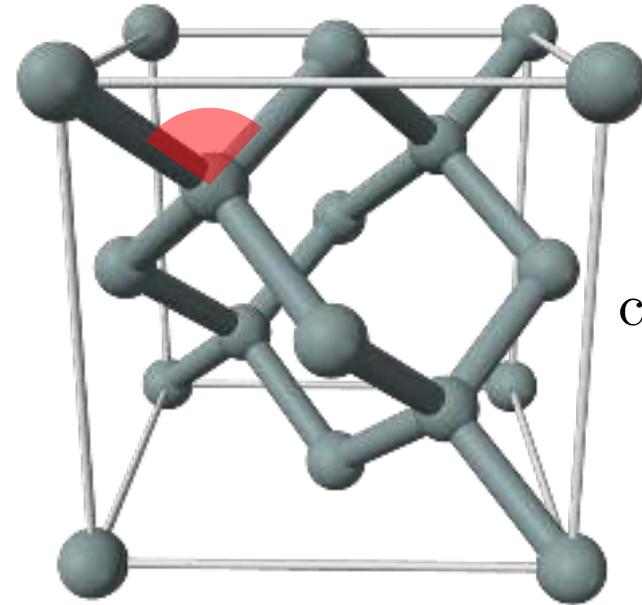
with 
$$\rho_i = \sum_j f_{t_i, t_j}(|\mathbf{R}_i - \mathbf{R}_j|)$$

- The first term represents the electro-static interaction and overlap repulsion between neighbouring ions.
- The second term is an embedding potential representing the energy of embedding an atom in the local charge density coming from the tails of the atomic charge clouds of neighbouring atoms

# The Stillinger-Weber potential for Si

## I. INTRODUCTION

In contrast to most other elements, the tetrahedral semiconductors Si and Ge shrink when they melt.<sup>1</sup> The crystalline forms of these substances have the open diamond structure with each atom bonded to four others in a tetrahedral pattern. Diffraction experiments<sup>2-4</sup> show that melting causes a partial collapse of this structure whereby coordination number 4 in the crystal increases substantially to an average value exceeding 6. Electrical properties are strongly affected by this profound structural change: Conductivity jumps by a factor of 20 in Si, and of 11 in Ge.<sup>1</sup>



$$\cos \theta_t = -\frac{1}{3}$$

$$V(\{\mathbf{R}_i\}) = \frac{1}{2} \sum_{i \neq j} V(|\mathbf{R}_i - \mathbf{R}_j|) + \frac{1}{6} \sum_{i \neq j \neq k} V(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k)$$

$$V(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) = V(r_{ij}, r_{ik}, \theta_{jik}) + V(r_{ji}, r_{jk}, \theta_{ijk}) + V(r_{ki}, r_{kj}, \theta_{ikj})$$

$$V(r_{ij}, r_{ik}, \theta_{jik}) = f(r_{ij})f(r_{jk}) \left[ \cos \theta_{jik} + \frac{1}{3} \right]^2$$

# Accuracy & reliability

- The analytical form of the pair interactions and the embedding energies are fitted to a variety of known material parameters.
- It is hoped that the model will work well in environments not considered within the materials property data-base (transferability).

Empirical models for inter-atomic forces constitute a drastic approximation to the quantum mechanics of material bonding – systematic and transferable accuracy cannot really be expected.

It is important to understand the limitations of any potential used.



# Use a data-base of material properties (experimental and DFT)

An example of a data base used for a well known Aluminium potential

TABLE I. Properties of Al predicted by EAM potentials in comparison with experimental and *ab initio* data. \*Fitted with high weight. † Fitted with low weight.

	Experiment or <i>ab initio</i>	Present Voter and Chen work	(Ref. 9)
Lattice properties:			
$a_0$ (Å)*	4.05 <sup>d</sup>	4.05	4.05
$E_0$ (eV/atom)*	-3.36 <sup>b</sup>	-3.36	-3.36
$B$ (10 <sup>11</sup> Pa)*	0.79 <sup>c</sup>	0.79	0.79
$c_{11}$ (10 <sup>11</sup> Pa)*	1.14 <sup>c</sup>	1.14	1.07
$c_{12}$ (10 <sup>11</sup> Pa)*	0.619 <sup>c</sup>	0.616	0.652
$c_{44}$ (10 <sup>11</sup> Pa)*	0.316 <sup>c</sup>	0.316	0.322
Phonon frequencies:			
$\nu_L(X)$ (THz) <sup>†</sup>	9.69 <sup>d</sup>	9.31	8.55
$\nu_T(X)$ (THz) <sup>†</sup>	5.80 <sup>d</sup>	5.98	5.20
$\nu_L(L)$ (THz)	9.69 <sup>d</sup>	9.64	8.86
$\nu_T(L)$ (THz)	4.19 <sup>d</sup>	4.30	3.70
$\nu_L(K)$ (THz)	7.59 <sup>d</sup>	7.30	6.87
$\nu_{T_1}(K)$ (THz)	5.64 <sup>d</sup>	5.42	4.80
$\nu_{T_2}(K)$ (THz)	8.65 <sup>d</sup>	8.28	7.76
Other structures:			
$E$ (hcp) (eV/atom)*	-3.33 <sup>e</sup>	-3.33	-3.34
$E$ (bcc) (eV/atom)*	-3.25 <sup>e</sup>	-3.24	-3.28
$E$ (diamond) (eV/atom) <sup>†</sup>	-2.36 <sup>e</sup>	-2.33	-2.06

Y. Mishin, D. Farkas, M. J. Mehl and D. A. Papaconstantopoulos, PRB 59 3393 (1999)

Vacancy:			
$E_v^f$ (eV)*	0.68 <sup>f</sup>	0.68	0.63
$E_v^m$ (eV)*	0.65 <sup>g</sup>	0.64	0.30
Interstitial:			
$E_i^f(O_n)$ (eV)		2.79	2.10
$E_i^f$ ([111]-dumbbell) (eV)		3.00	2.51
$E_i^f$ ([110]-dumbbell) (eV)		2.91	2.24
$E_i^f$ ([100]-dumbbell) (eV)		2.59	2.06
Planar defects:			
$\gamma_{SF}$ (mJ/m <sup>2</sup> )*	166 <sup>h</sup> , 120–144 <sup>i</sup>	146	76
$\gamma_{us}$ (mJ/m <sup>2</sup> )		168	93
$\gamma_T$ (mJ/m <sup>2</sup> )	75 <sup>h</sup>	76	42
$\gamma_{gb}(210)$ (mJ/m <sup>2</sup> )		495	366
$\gamma_{gb}(310)$ (mJ/m <sup>2</sup> )		467	320
Surfaces:			
$\gamma_s(110)$ (mJ/m <sup>2</sup> ) <sup>†</sup>	980 <sup>j</sup>	1006	959
$\gamma_s(100)$ (mJ/m <sup>2</sup> ) <sup>†</sup>	980 <sup>j</sup>	943	855
$\gamma_s(111)$ (mJ/m <sup>2</sup> ) <sup>†</sup>	980 <sup>j</sup>	870	823

# Potential generation: science or art?

- Some properties cannot be included in direct fit. Indirect fitting is tricky.
- The choice of weights is more important than the optimization algorithm. The choice of weights is subjective.
- It is impossible to fit to all desired properties. Finding a reasonable compromise (through weights) requires “human intervention” (creativity, experience, luck)
- It is not always good to find the global minimum.
- Rule of thumb (based on personal experience): one publishable potential a year

Potential generation is largely based on experience, intuition, tricks of the trade, and luck. It is currently art rather than science.

**Yuri Mishin**  
Professor of Physics  
George Mason University

# Three types of published potentials

- “Quick-fix” and ad hoc potentials
  - Fitted to a few numbers, tested for a limited number of properties
  - Specific to a particular application, not tested for others
- “Proof-of-principle” potentials
  - Demonstrate a particular fitting method or trends across a series of materials
  - Parametric potentials (e.g. composition-dependent)
  - Not tested carefully for a variety of properties
- “Universal” potentials
  - Usually fit to a large database (experimental and first-principles)
  - Successfully tested against a large number of properties
  - Successfully applied in many different types of simulations
  - Identified with a particular element or binary system (“canonized”)

# <http://www.ctcms.nist.gov/potentials/>

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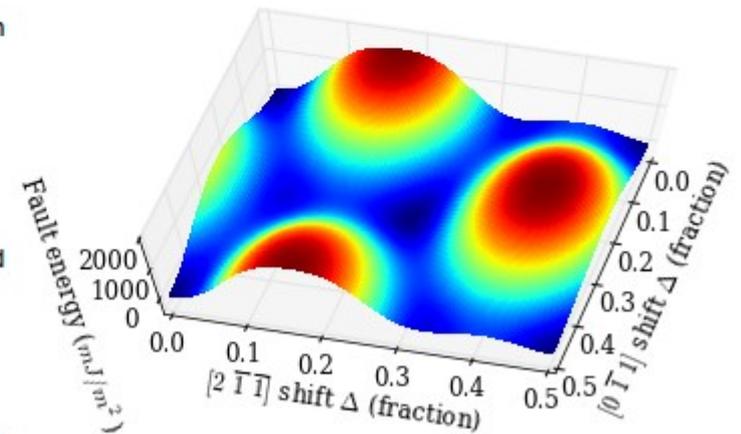
## Interatomic Potentials Repository Project

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### Overview

This repository provides a source for interatomic potentials (force fields), related files, and evaluation tools to help researchers obtain interatomic models and judge their quality and applicability. Users are encouraged to download and use interatomic potentials, with proper acknowledgement, and developers are welcome to contribute potentials for inclusion. The files provided have been submitted or vetted by their developers and appropriate references are provided. All classes of potentials (e.g., MEAM, ADP, COMB, Reax, EAM, etc.) and materials are welcome. Interatomic potentials and/or related files are currently available for various metals, semiconductors, oxides, and carbon-containing systems.

If you do not find the element or alloy potential you are seeking, send an email to [Chandler.Becker@nist.gov](mailto:Chandler.Becker@nist.gov), and we may be able to help. This site reflects what has been submitted, so it is not a complete survey of interatomic potentials for any or all systems. [Here is a list of recent requests for potentials.](#)



# openkim.org

## About KIM

The Knowledgebase of Interatomic Models (KIM) project is based on a four-year NSF cyber-enabled discovery and innovation (CDI) grant and has the following main objectives:

- Development of an online open resource for standardized testing and long-term warehousing of interatomic models ...
- Development of an application programming interface (API) standard for atomistic simulations...
- Fostering the development of a quantitative theory of transferability of interatomic models to provide guidance for selecting application-appropriate models based on rigorous criteria, and error bounds on results.



# The MD algorithm

# Equations of motion – numerical integrators

To obtain Newton's equations of motion, can use the method of Lagrangian mechanics

$L = \text{Kinetic Energy} - \text{Potential Energy}$

$$= \frac{1}{2} \sum_i m_i |\mathbf{v}_i(t)|^2 - V(\{\mathbf{r}_i(t)\})$$

Lagrangian's equations of motion

$$\frac{\partial L}{\partial \mathbf{r}_k} - \frac{d}{dt} \frac{\partial L}{\partial \dot{\mathbf{r}}_k} = 0$$

Newton's equations of motion

$$\longrightarrow \mathbf{F}_i(t) = m_i \ddot{\mathbf{r}}_i(t)$$

$$\mathbf{F}_i(t) = m_i \ddot{\mathbf{r}}_i(t) \left\{ \begin{array}{l} \mathbf{F}_i(t) = m_i \frac{d\mathbf{v}_i(t)}{dt} \approx m_i \frac{\mathbf{v}_i(t + \Delta t) - \mathbf{v}_i(t)}{\Delta t} \\ \mathbf{v}_i(t) = \frac{d\mathbf{r}_i(t)}{dt} \approx \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t)}{\Delta t} \end{array} \right.$$

$$\longrightarrow \mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\mathbf{F}_i(t)}{m_i} \Delta t$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t$$

Such an approach works well when the forces do not vary greatly over the time step,  $\Delta t$ .

# Equations of motion – numerical integrators

The integrators developed in the previous slide should never be used, since they are not numerically stable to the conservation of total energy.

Much better integrators exist (Verlet & more general predictor/corrector algorithms)

Velocity Verlet integrator

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

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

Note that to determine the new velocities both the old and new atomic positions are needed

See for example:

- [http://en.wikipedia.org/wiki/Verlet\\_integration](http://en.wikipedia.org/wiki/Verlet_integration)
- “Understanding Molecular Simulation”, Frenkel & Smit, Chapter 4

# Calculation of instantaneous energy & temperature

$$V_{\text{pe}}(t) = V(\{\mathbf{r}_i(t)\}) = \frac{1}{2} \sum_{i \neq j} V_{t_i, t_j} (|\mathbf{r}_i(t) - \mathbf{r}_j(t)|) + \dots$$

$$V_{\text{ke}}(t) = \frac{1}{2} \sum_i m_i |\mathbf{v}_i(t)|^2$$

In equilibrium, each atom has thermal energy

$$3k_b T$$

which is distributed equally between the kinetic and thermal potential energy

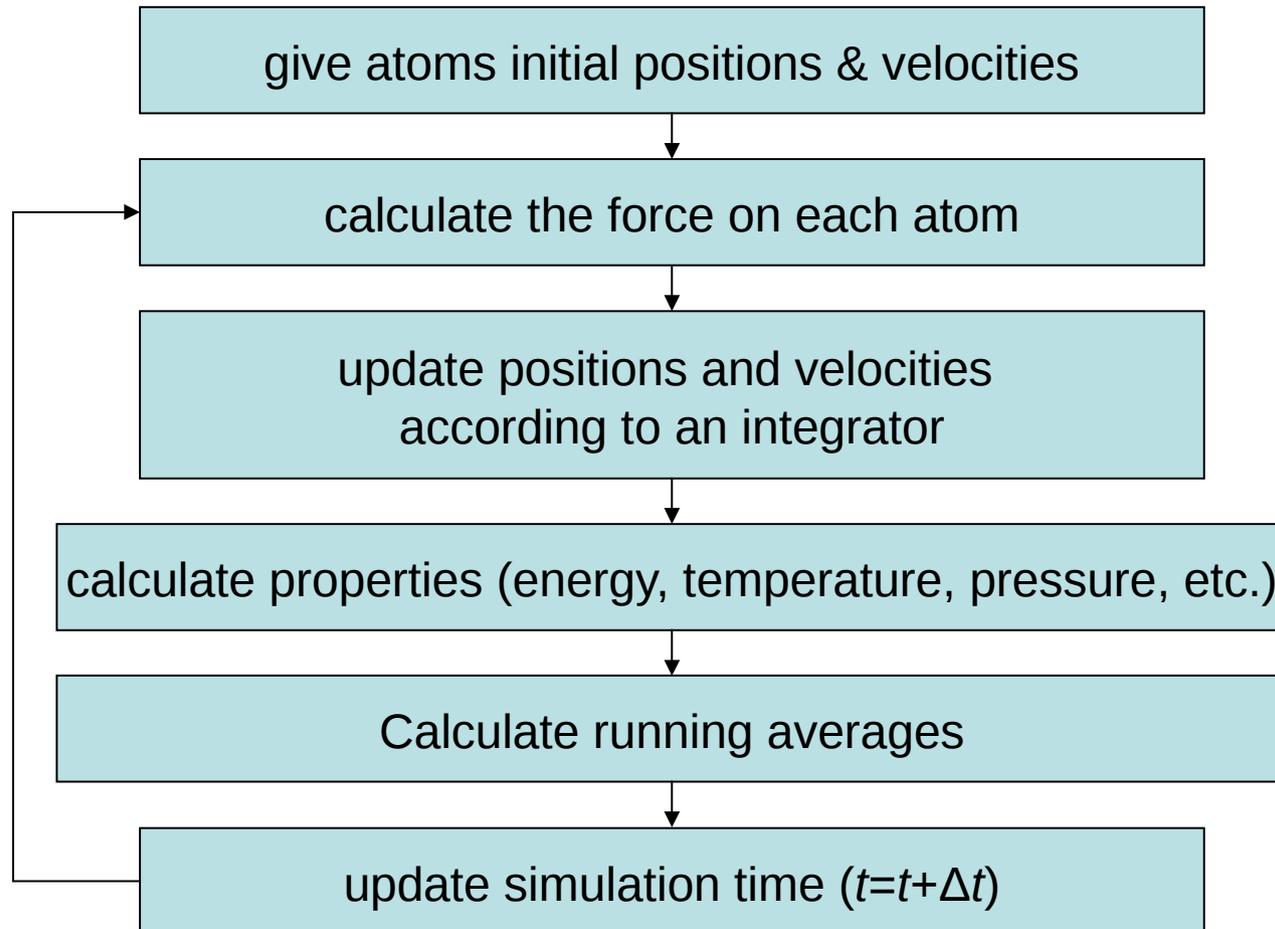


The temperature is calculated through the use of the equipartition theorem

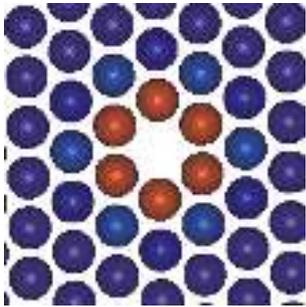
$$\frac{3}{2} N k_b T = \langle V_{\text{ke}} \rangle = \frac{1}{2} \sum_i m_i \langle |\mathbf{v}_i|^2 \rangle \longrightarrow \text{Average over time}$$

Instantaneous temperature  $\longrightarrow \frac{3}{2} N k_b T(t) = \frac{1}{2} \sum_i m_i |\mathbf{v}_i(t)|^2$

# The basic MD algorithm

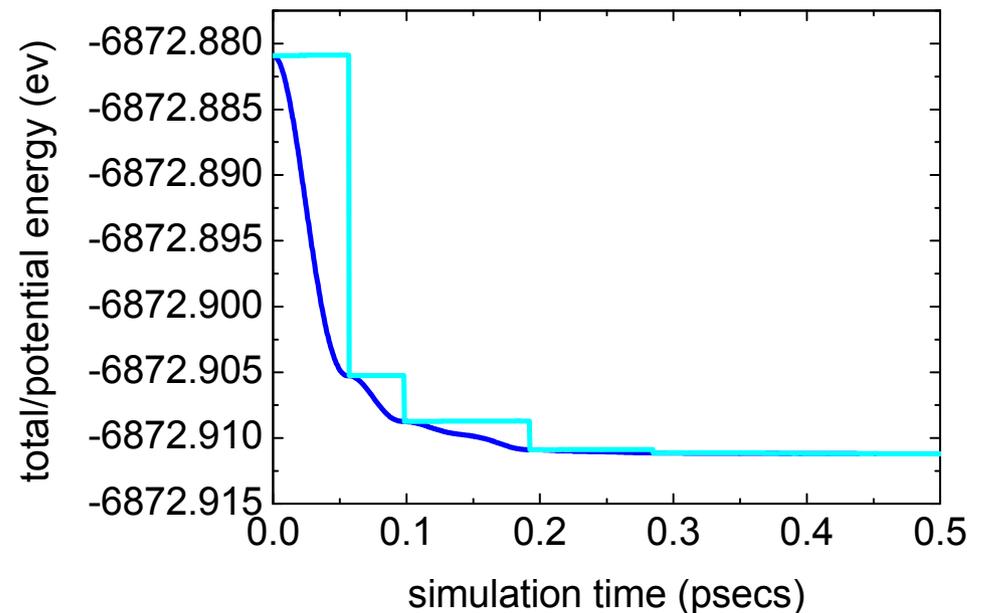
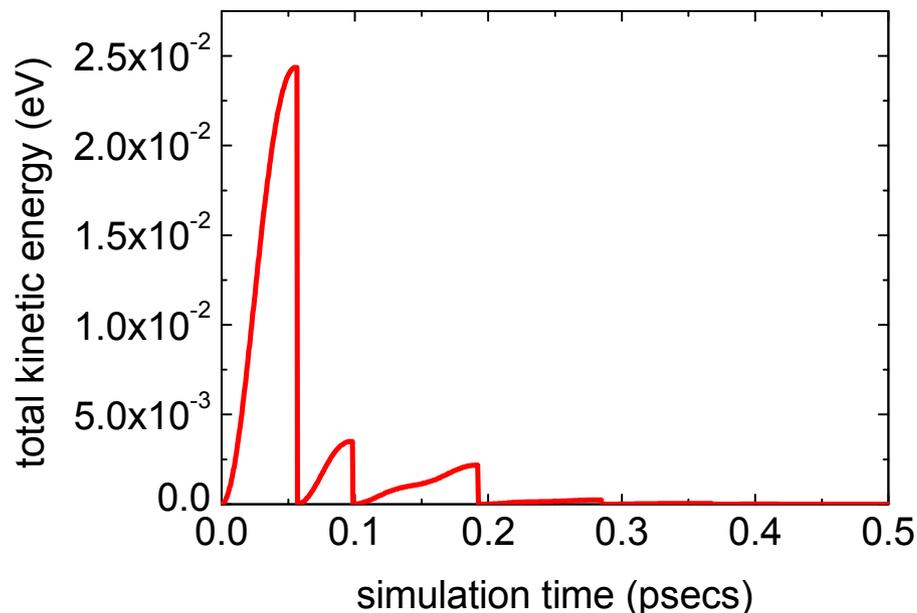


# Molecular statics – structural relaxation (at 0K)



By removing an atom to create a vacancy, the surrounding atoms gain a force which initially either accelerates the atoms away or towards the vacancy defect. Via molecular statics, new positions in which the forces are all zero can be found, giving the minimum energy configuration of a vacancy.

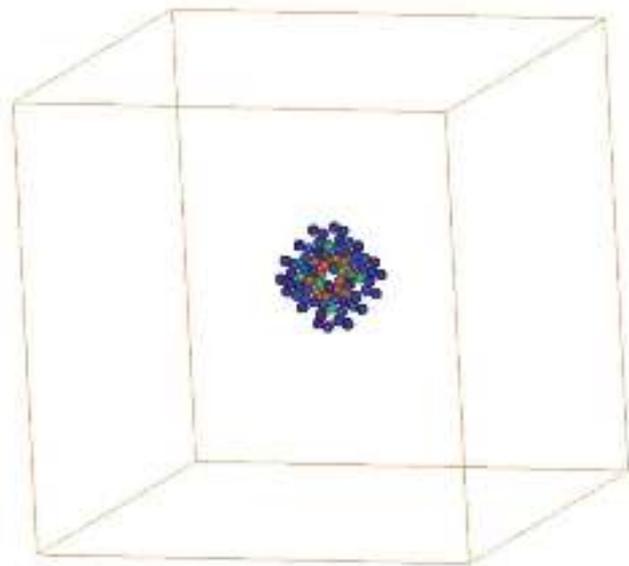
Atoms coloured by local energy



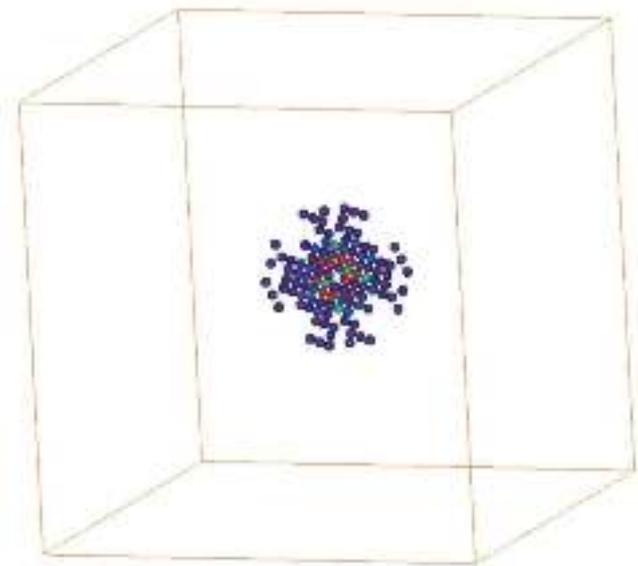
The MD done here, removes the kinetic energy from the system as soon as it begins to decrease, and continues to do this until the forces on the atoms are all zero <sup>31</sup>

# Molecular statics – structural relaxation (at 0K)

→ The new positions, can be defined as a strain field around the vacancy defect



Unrelaxed atomic positions



Relaxed atomic positions

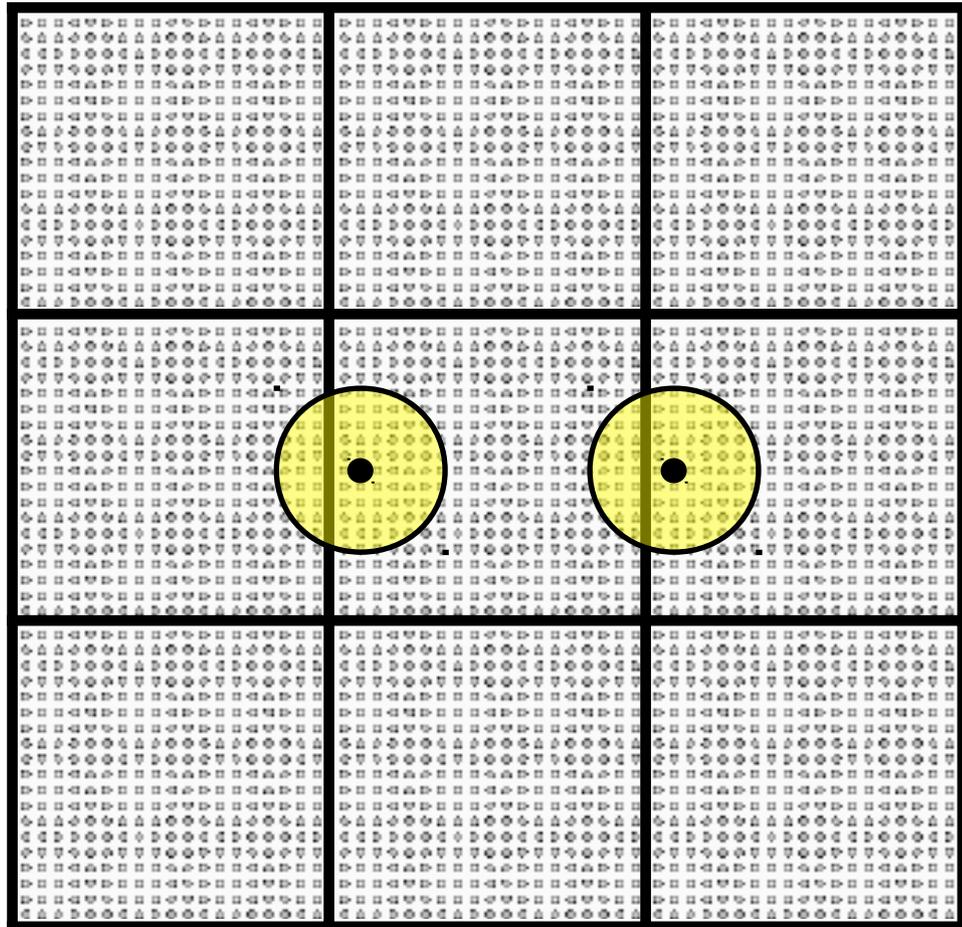
The above picture only shows those atoms with an energy higher than that of the perfect lattice. By removing an atom, all remaining atoms that directly interacted with the removed atom have a higher energy (and a non-zero force). By relaxing this force, new positions are found for the surrounding atoms which can be identified as the strain field of the vacancy defect

# Boundary conditions

# Simulating the bulk: periodic boundary conditions

By introducing an array of periodic images of the atomic configuration, a bulk crystalline sample can be simulated.

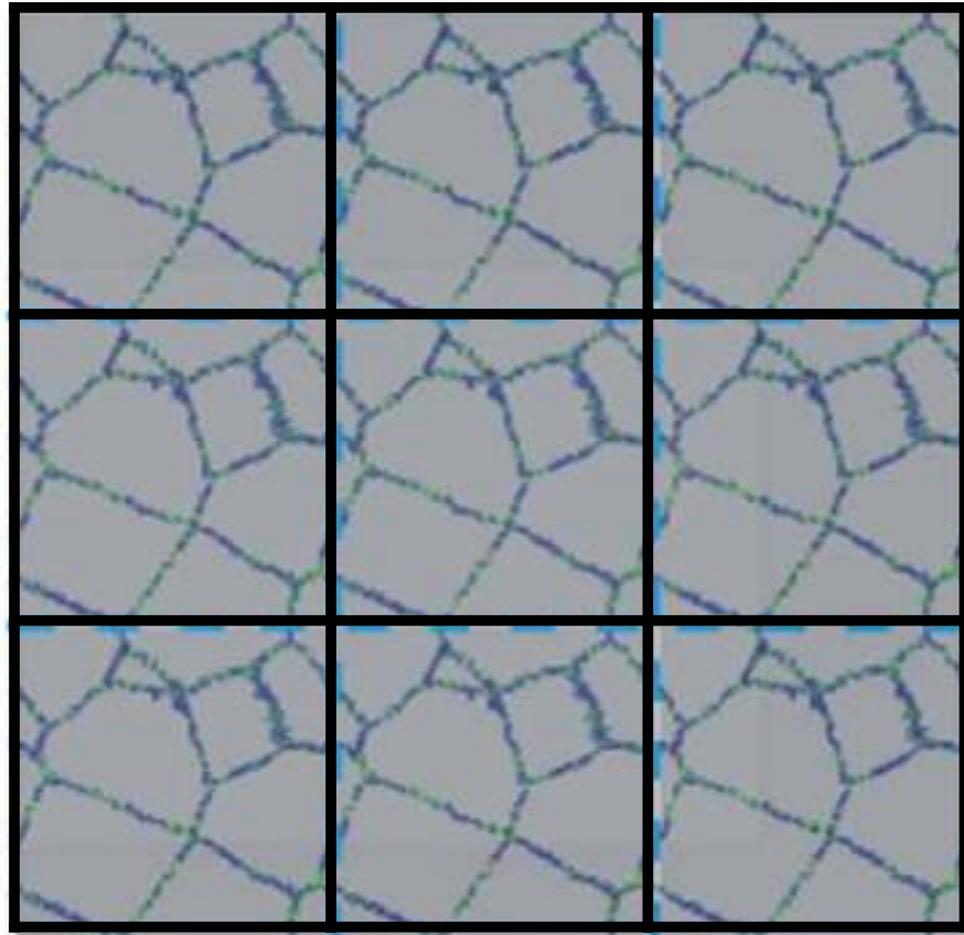
Thus despite the finite size of the configuration, surface effects need not be considered.



# Simulating the bulk: periodic boundary conditions

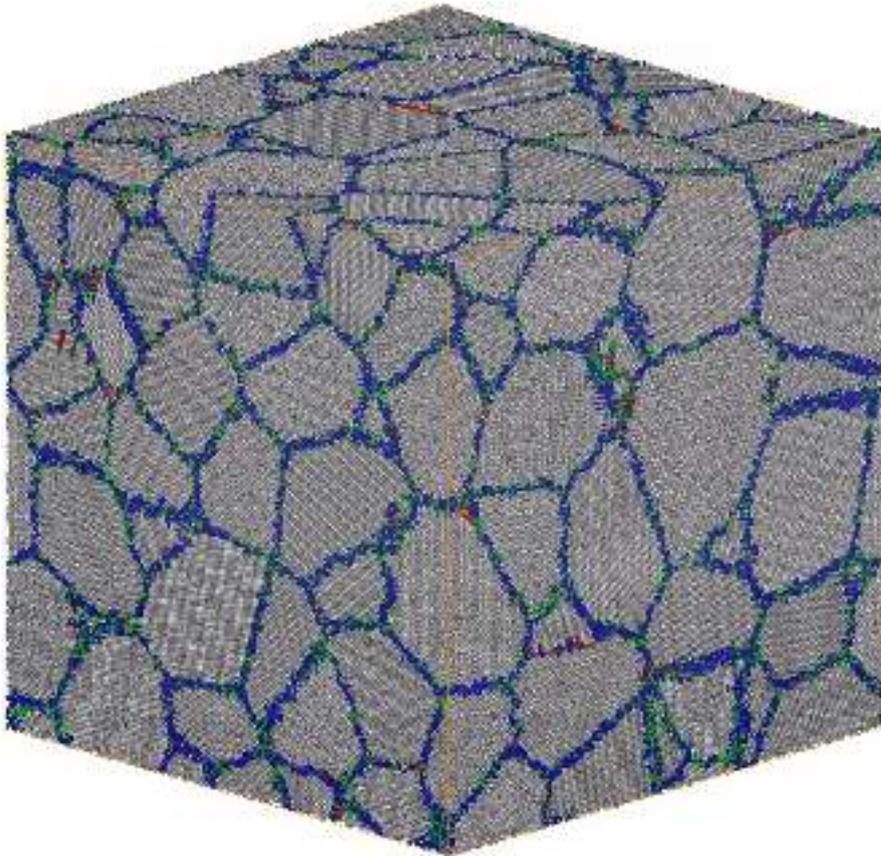
By introducing an array of periodic images of the atomic configuration, a bulk crystalline sample can be simulated.

Thus despite the finite size of the configuration, surface effects need not be considered.

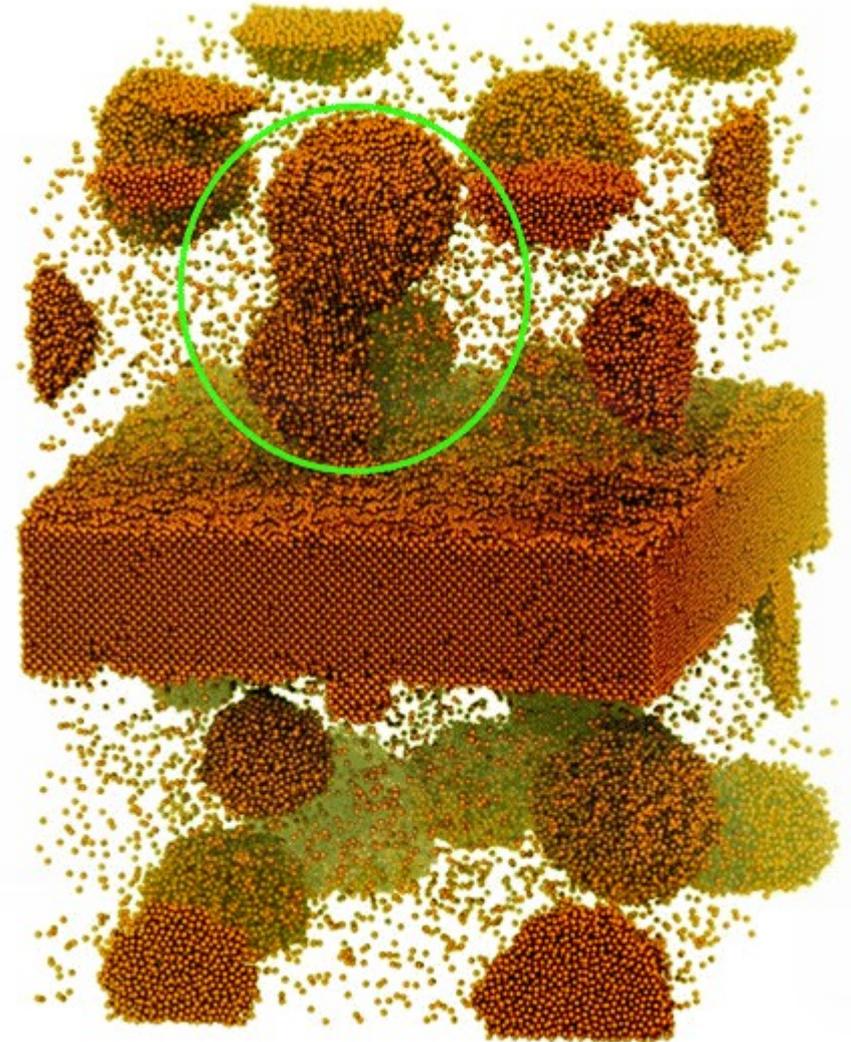


(but micro-structure becomes repetitive)

# Examples of 3D periodic boundary conditions

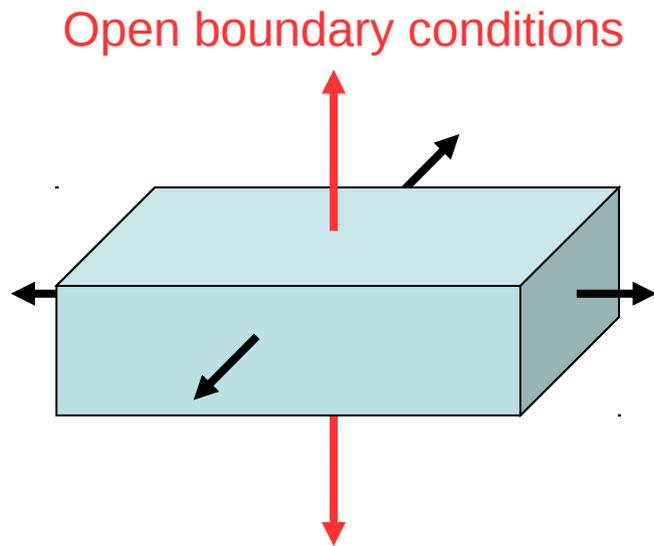


Nanocrystalline Ni containing 100 grains with a mean grain size of 10 nm (4.8 million atoms)

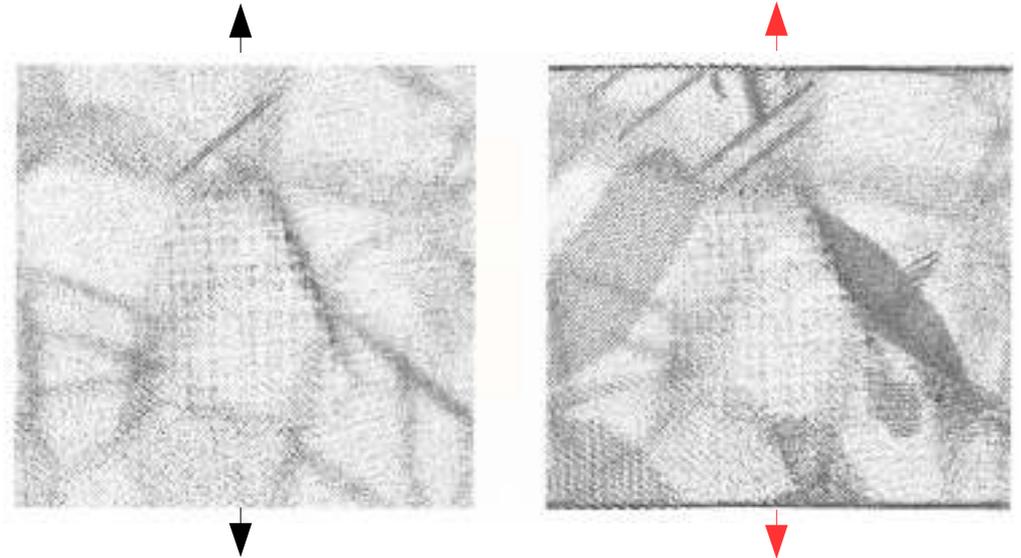


Molecular self-assembly and clustering in nucleation processes: general discussion, S. Price et al, Faraday Discuss., 2015, 179, 155-197

# Periodicity need not be in all directions



2D periodicity: surface or slab geometry (here only the black arrows indicate periodic boundary conditions)

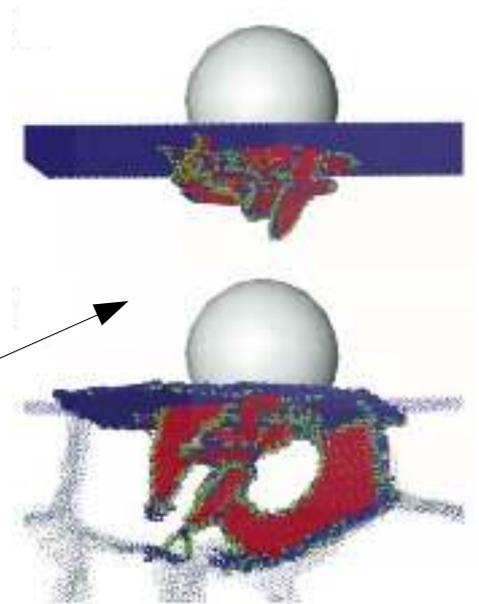


The effect of a surface on the deformation properties of nc Ni

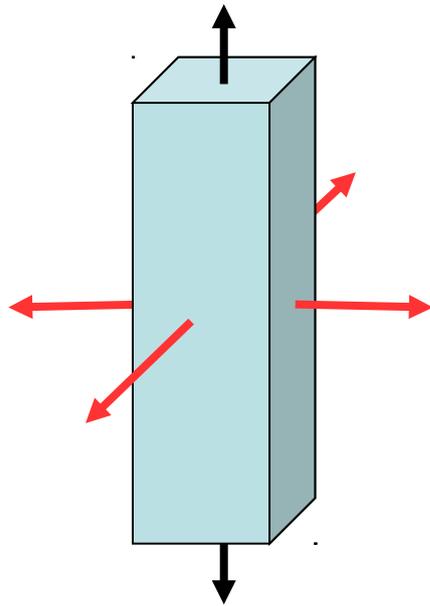
*Phil. Mag. A 82, 1 (2002).*

Nano-indentation simulation on single crystal and nc Au

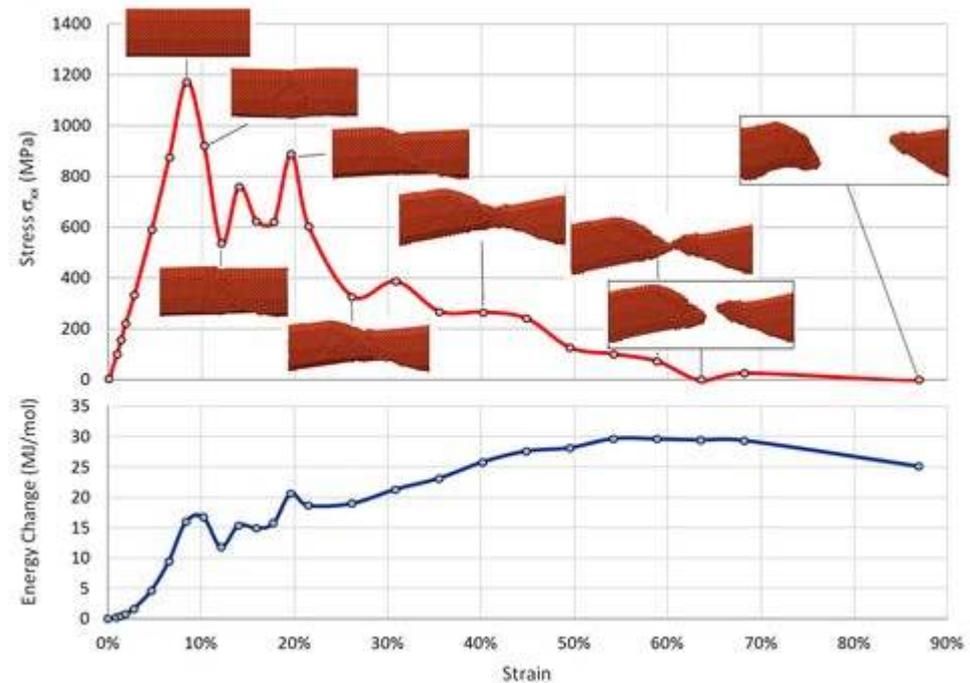
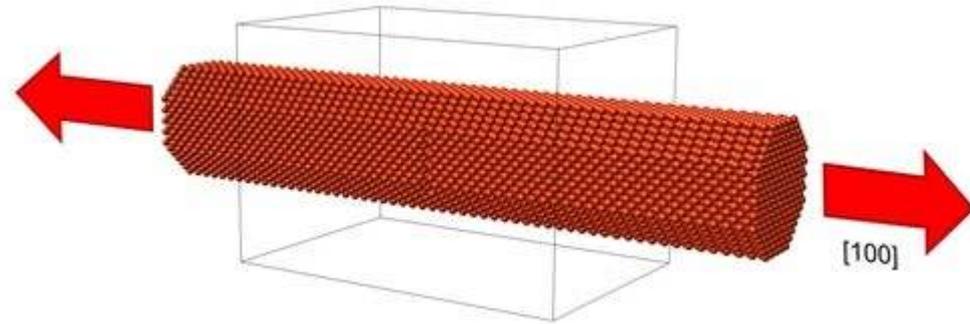
*PRB 67, 024113 (2003).*



# Periodicity need not be in all directions



1D periodicity: wire geometry (here only the black arrows indicate periodic boundary conditions)



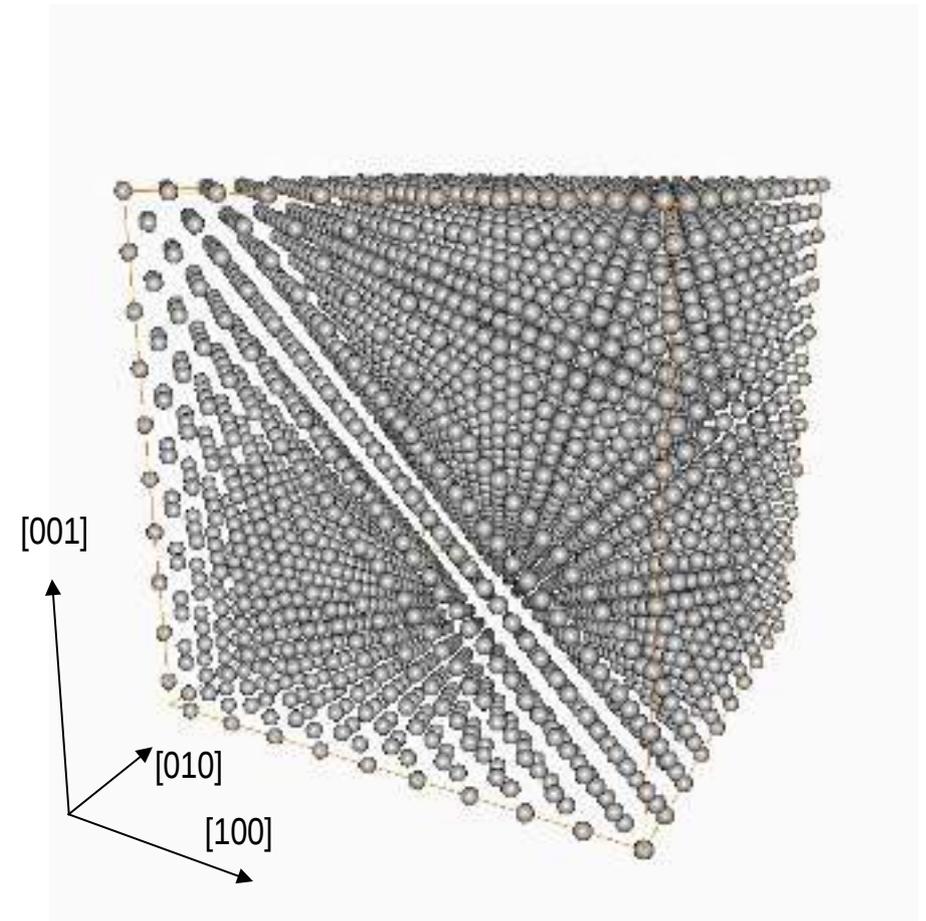
# An MD example – equipartition theorem

# A perfect FCC lattice at 300K

Consider a face-centred-cubic (FCC) lattice of 4000 (Al) atoms.

The initial positions of the atoms are at the ideal lattice sites (0K configuration).

A lattice of infinite extent (the bulk limit) may be simulated by using periodic boundary conditions.

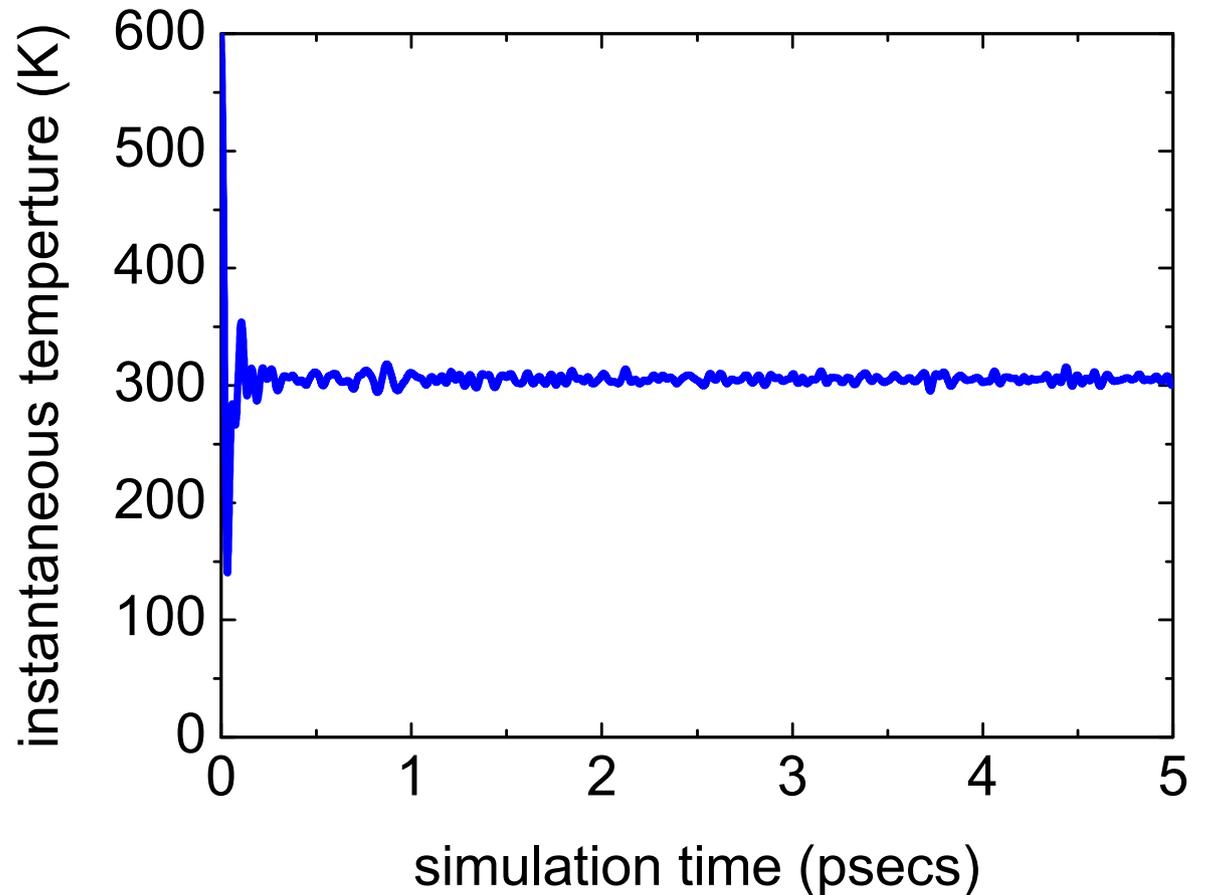


# A perfect FCC lattice at 300K

Give each atom a random velocity such that the temperature is 600K

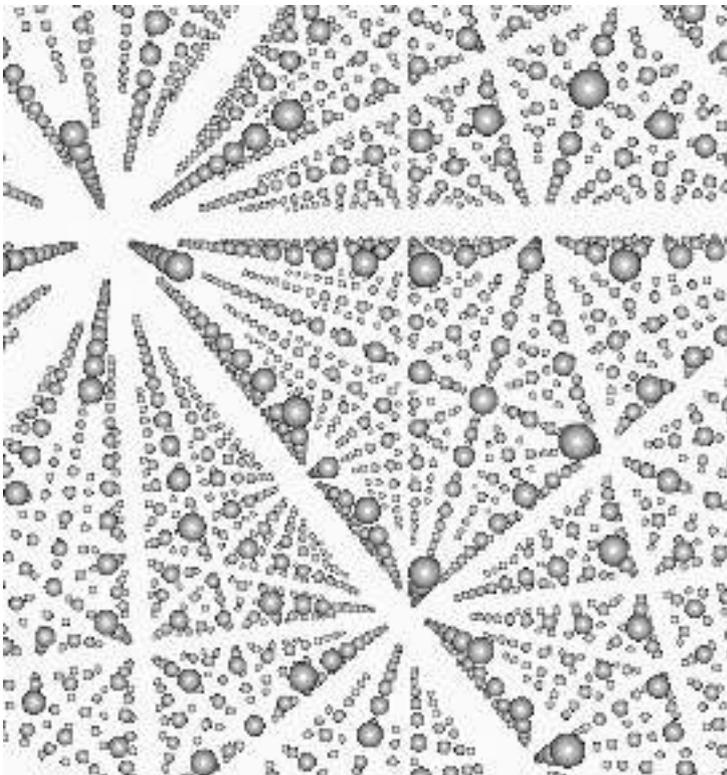
$$\frac{3}{2}Nk_bT = \frac{1}{2} \sum_i m_i \langle |\mathbf{v}_i|^2 \rangle$$

.... and start the MD

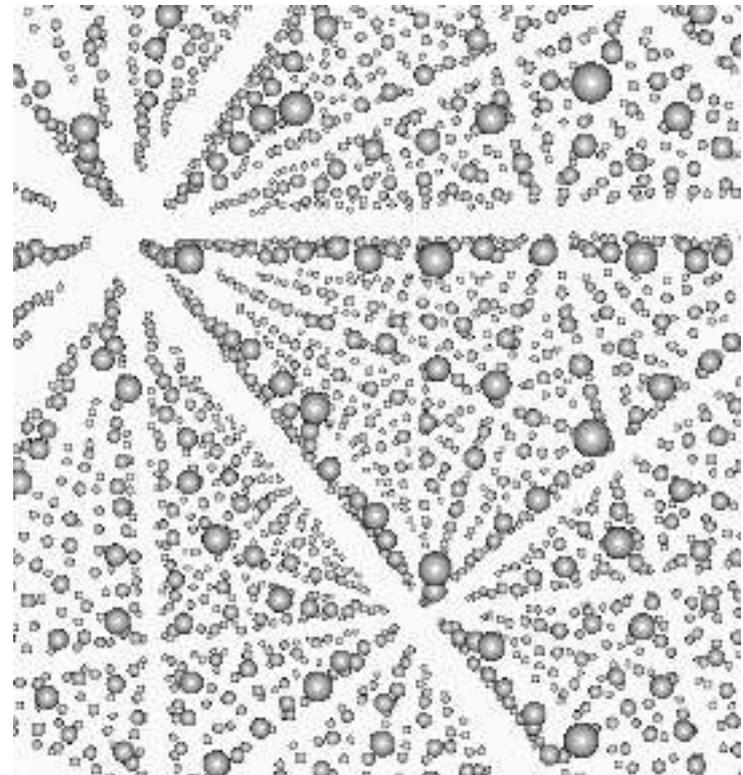


# A perfect FCC lattice at 300K

At 300K, atoms undergo vibrational motion about their lattice sites.



Initial configuration



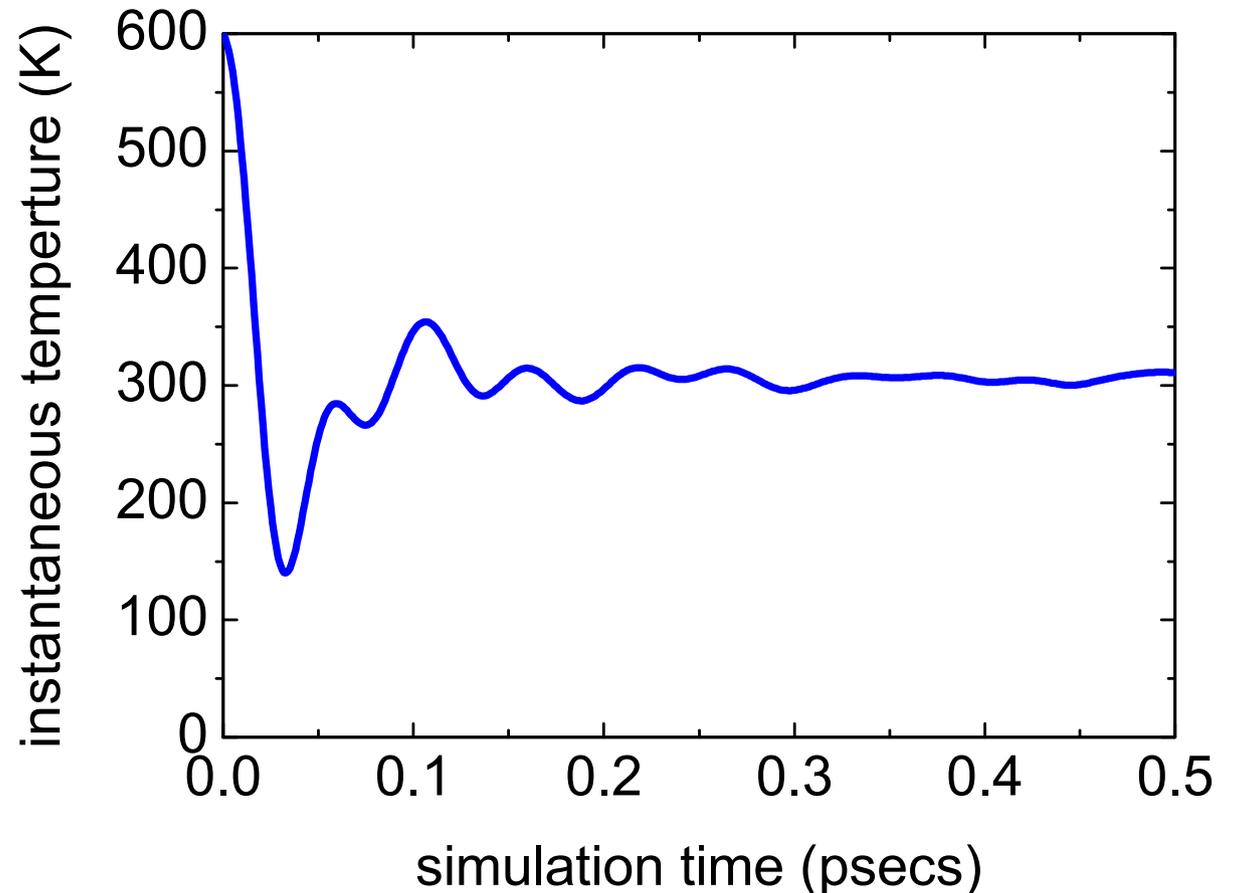
Snapshot at 5psec, 300K

# A perfect FCC lattice at 300K

Give each atom a random velocity such that the temperature is 600K

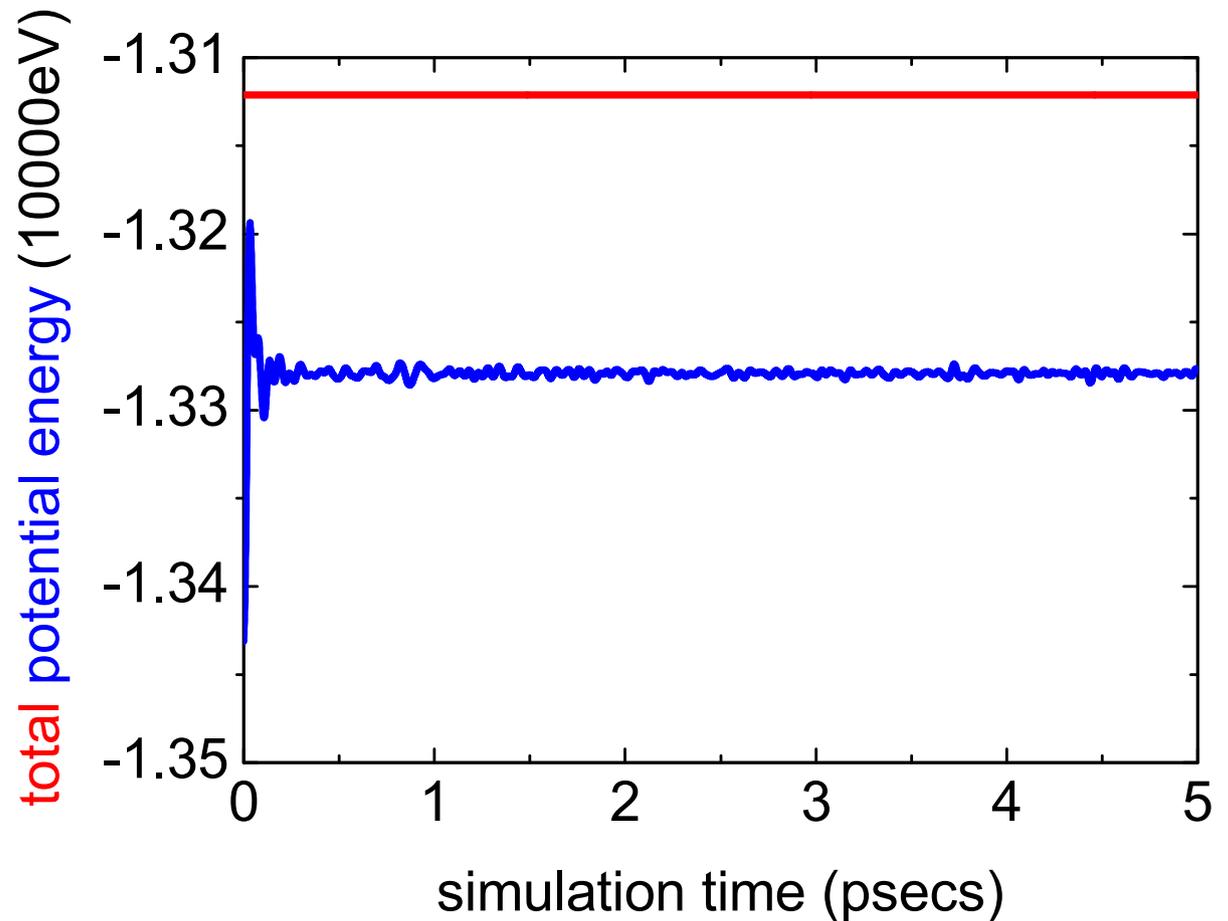
$$\frac{3}{2}Nk_bT = \frac{1}{2} \sum_i m_i \langle |\mathbf{v}_i|^2 \rangle$$

.... and start the MD



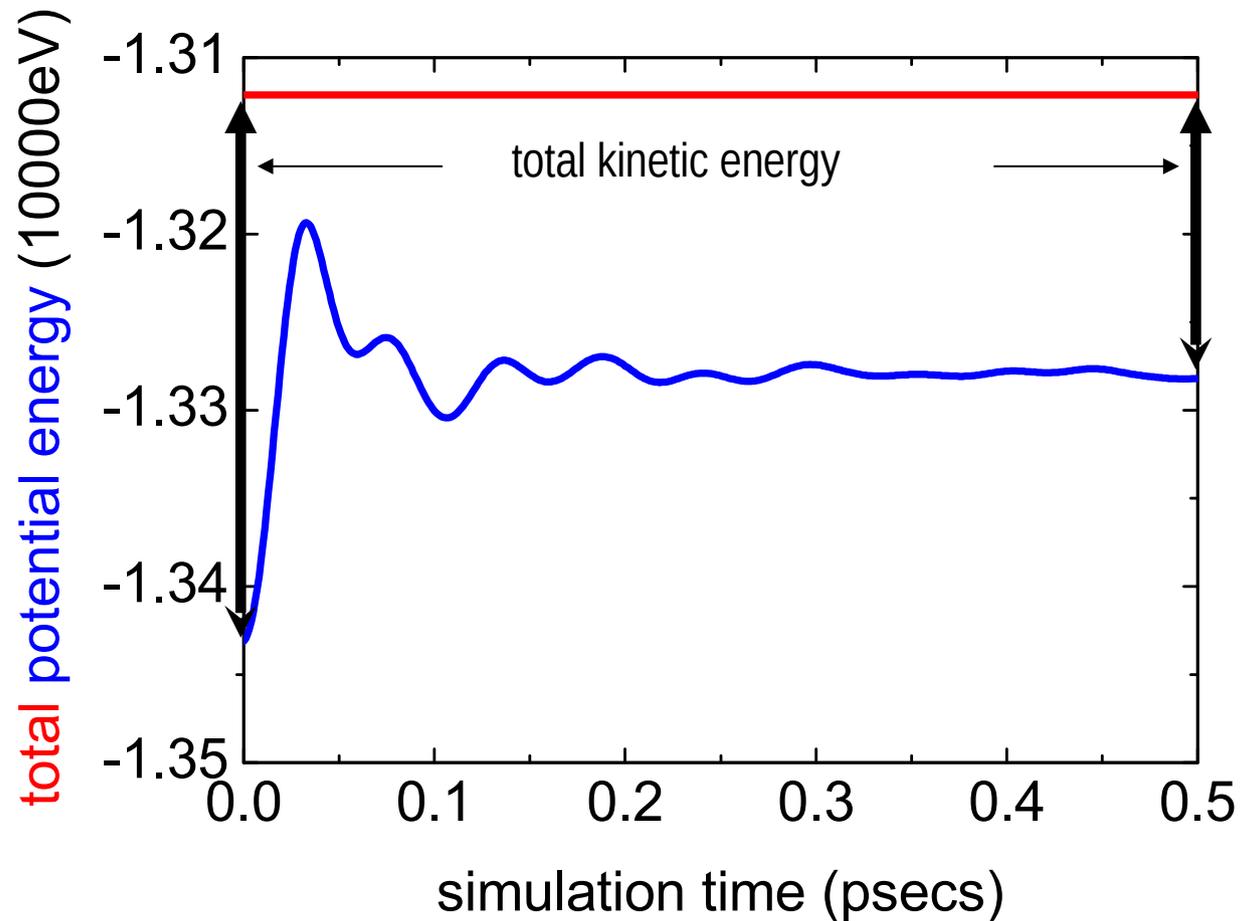
# A perfect FCC lattice at 300K

The potential energy responds accordingly, since the total energy is conserved.



# A perfect FCC lattice at 300K

The potential energy responds accordingly, since the total energy is conserved.



# A perfect FCC lattice at 300K

- By giving each atom a random velocity such that the temperature of the system is initially 600K, kinetic energy has been introduced into the system.
- From the MD simulation, the kinetic energy reduces by half and thus the temperature decreases to 300K.
- By conservation of total energy (kinetic + potential), this other half has been converted to potential energy – thermal potential energy.

$$\begin{aligned}V_{\text{total}} &= V_{\text{pe}} + V_{\text{ke}} = V_{\text{pe},0\text{K}} + V_{\text{tpe}} + V_{\text{ke}} \\ &= V_{\text{pe},0\text{K}} + 3Nk_{\text{b}}T\end{aligned}$$

An example of the classical equipartition theorem at NVT thermal equilibrium.

# Controlling temperature and load

# MD Ensembles

- So far we have considered constant energy simulations at fixed volume, and fixed particle number → the so-called NVE (microcanonical) ensemble.
- MD can also simulate the NVT (canonical) ensemble in which a temperature, rather than the total energy, is fixed
- MD can also simulate the NPT ensemble in which a stress, rather than a fixed volume, is defined.

# How to control temperature?

Temperature can be controlled via:

- Velocity rescaling

$$\mathbf{v}_i(t) \rightarrow \mathbf{v}_i(t) \sqrt{\frac{T_{\text{required}}}{T(t)}}$$

The new kinetic energy will be equal to  $\frac{3}{2} N k_b T_{\text{required}}$

- Nosé-Hoover thermostat

$$\mathbf{F}_i(t) \rightarrow \mathbf{F}_i(t) - \zeta \left( \frac{T(t)}{T_{\text{required}}} \right) \mathbf{v}_i(t)$$

Can be seen as a temperature dependent drag force

- Langevin dynamics

$$\mathbf{F}_i(t) \rightarrow \mathbf{F}_i(t) - \zeta \mathbf{v}_i(t) + \boldsymbol{\eta}(t) \quad \langle \boldsymbol{\eta}(t) \boldsymbol{\eta}(t') \rangle = 2\zeta k_b T \delta(t - t')$$

Here there is a fixed drag (dissipative) parameter (value is optimally chosen) whose effect is balanced by the addition of a random force which is not correlated in time. The ratio of damping coefficient to the magnitude of the stochastic force defines the temperature of the equilibrium system

# The stress tensor and hydrostatic pressure

The instantaneous stress tensor of the simulation box can easily be calculated

$$\sigma^{\mu\nu} = \frac{1}{\Omega} \left( \sum_{i=1}^N \frac{1}{2} m_i v_i^\mu v_i^\nu + \sum_{i \neq j}^N F_{ij}^\mu r_{ij}^\nu \right)$$

Thermal component

Potential component

Hydrostatic pressure

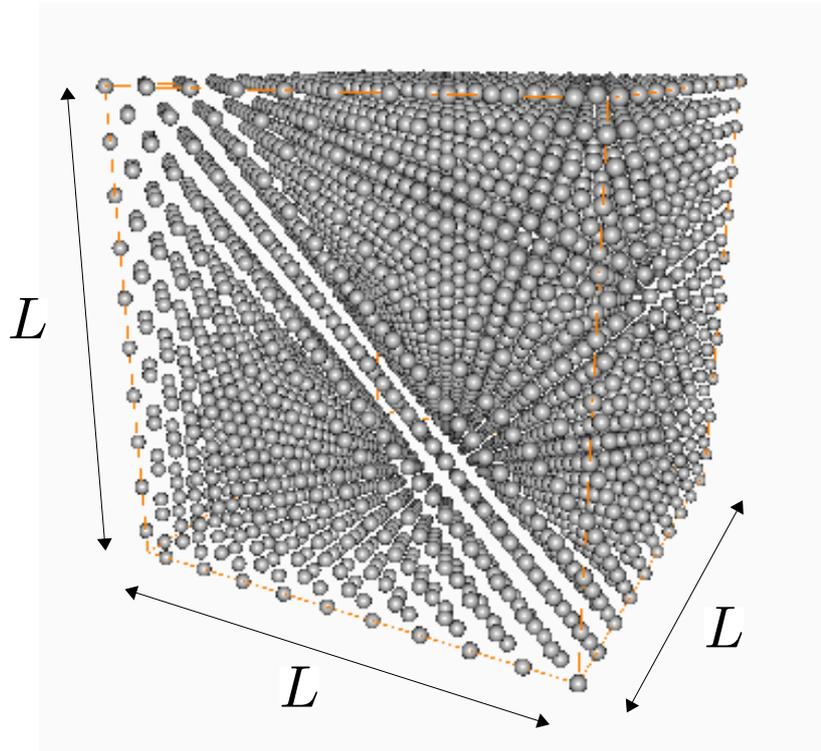
$$P = \frac{1}{3} \text{Tr}[\tilde{\sigma}]$$



$$P = - \frac{dV_{\text{pe}}}{d\Omega}$$

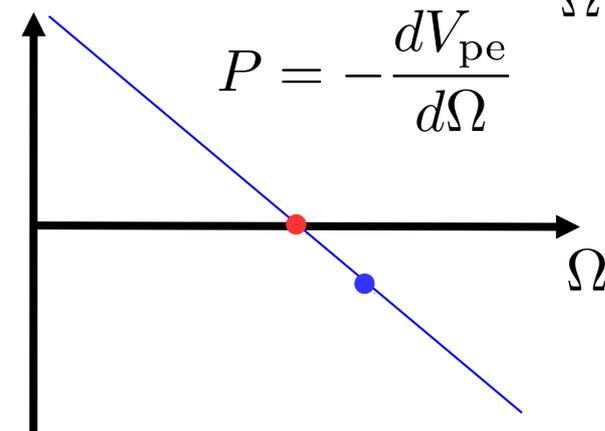
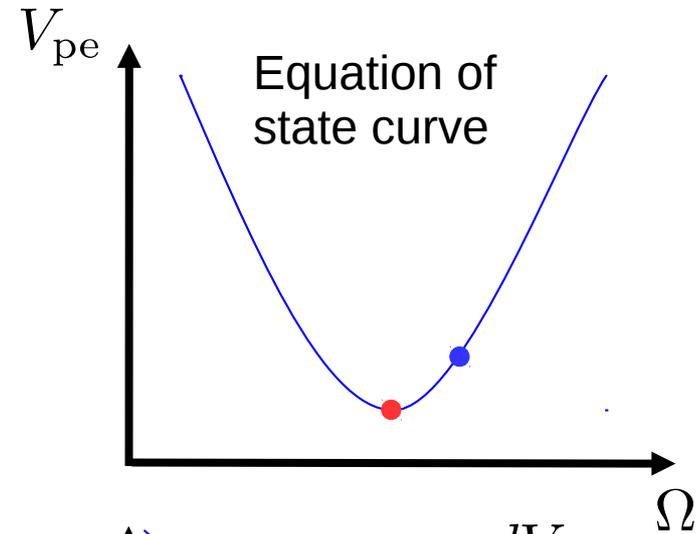
@ zero Kelvin

# Hydrostatic pressure at 0K – isotropic strain



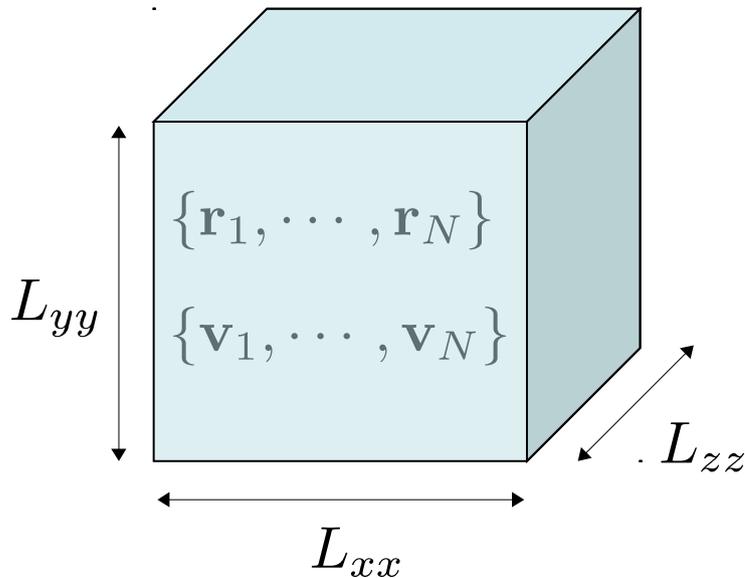
Change volume isotropically  
(done by changing periodicity  
length and rescaling the lattice  
positions)

$$\Omega = L \times L \times L \rightarrow \Omega' = L' \times L' \times L'$$



$$\tilde{\sigma} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \text{or} \quad \begin{bmatrix} P & 0 & 0 \\ 0 & P & 0 \\ 0 & 0 & P \end{bmatrix}$$

# The stress tensor and distortion of simulation cell



How to generally distort the simulation volume under periodic boundary conditions?

Introduce a new variable, the box matrix:

$$\mathbf{r}_i = \tilde{\mathbf{L}}\mathbf{s}_i \longrightarrow \tilde{\mathbf{L}} = \begin{bmatrix} L_{xx} & L_{xy} & L_{xz} \\ L_{yx} & L_{yy} & L_{yz} \\ L_{zx} & L_{zy} & L_{zz} \end{bmatrix}$$

$\{\mathbf{s}_1, \dots, \mathbf{s}_N\}$   
 $\{\dot{\mathbf{s}}_1, \dots, \dot{\mathbf{s}}_N\}$  } are the dimensionless atomic coordinates.

A strain can be applied by changing the box matrix and the response of the system can be measured by calculating the stress tensor

$$\tilde{\mathbf{L}} \longleftrightarrow \langle \sigma^{\mu\nu} \rangle$$

# Parrinello-Rahman method: applying an external load

## Polymorphic transitions in single crystals: A new molecular dynamics method

M. Parrinello

*University of Trieste, Trieste, Italy*

A. Rahman

*Argonne National Laboratory, Argonne, Illinois 60439*

(Received 1 July 1981; accepted for publication 14 August 1981)

A new Lagrangian formulation is introduced; it can be used to make molecular dynamics (MD) calculations on systems under the most general, externally applied, conditions of stress. In this formulation the MD cell shape and size can change according to dynamical equations given by this Lagrangian. This new MD technique is well suited to the study of structural transformations in solids under external stress and at finite temperature. As an example of the use of this technique we show how a single crystal of Ni behaves under uniform uniaxial compressive and tensile loads.

The equations of motion for the atoms become:

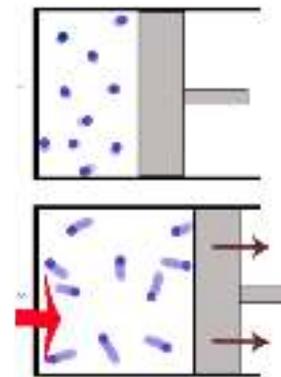
$$m_i \ddot{\mathbf{s}} = \tilde{\mathbf{L}} \mathbf{F}_i - \tilde{\mathbf{G}}^{-1} \dot{\tilde{\mathbf{G}}} \dot{\mathbf{s}} \quad \left( \tilde{\mathbf{G}} = \tilde{\mathbf{L}}^T \tilde{\mathbf{L}} \right)$$

Whilst for the simulation cell

$$W \ddot{\tilde{\mathbf{L}}} = f \left( \tilde{\boldsymbol{\sigma}}_{\text{app}}, \tilde{\mathbf{L}} \right)$$

↑  
Effective simulation cell mass

≈



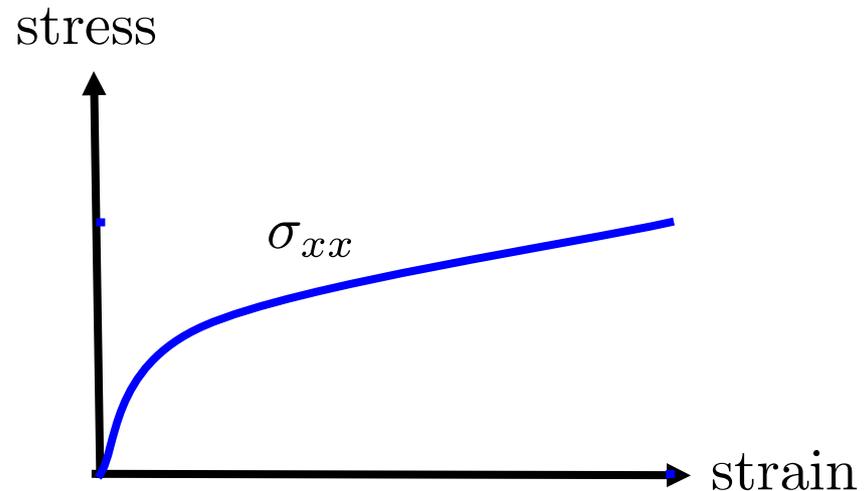
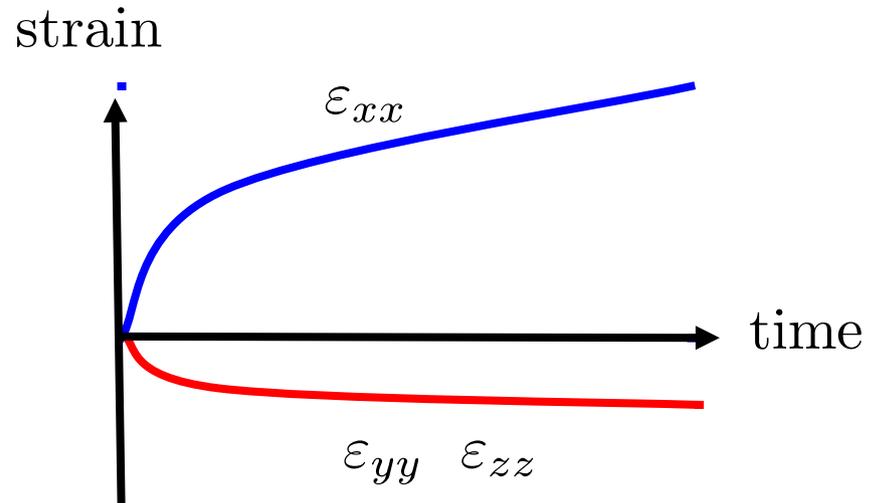
# Parrinello-Rahman method: uni-axial deformation

For a constant stress uni-axial deformation use Parrinello-Rahman with

$$\tilde{\sigma} = \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

For a constant strain rate uni-axial deformation, increment  $L_{xx}$  and measure  $\sigma_{xx}$ , and use a 2D version (in the gauge plane) of Parrinello-Rahman with:

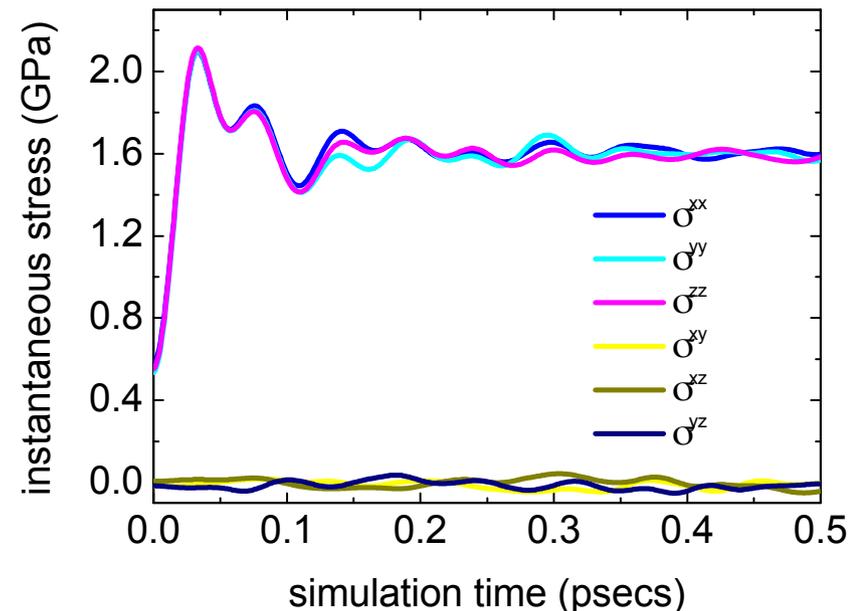
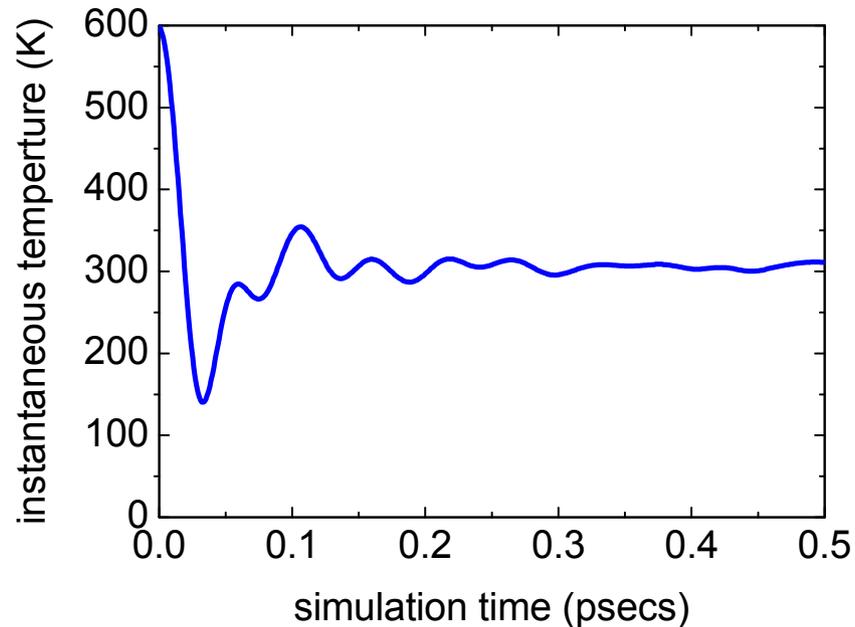
$$\tilde{\sigma}_{2D} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$$



Here, Parrinello-Rahman is used to simulate Poisson contraction

# An MD example – thermal expansion

# A perfect FCC lattice revisited



At constant volume, large internal hydrostatic stresses develop due to thermal vibration

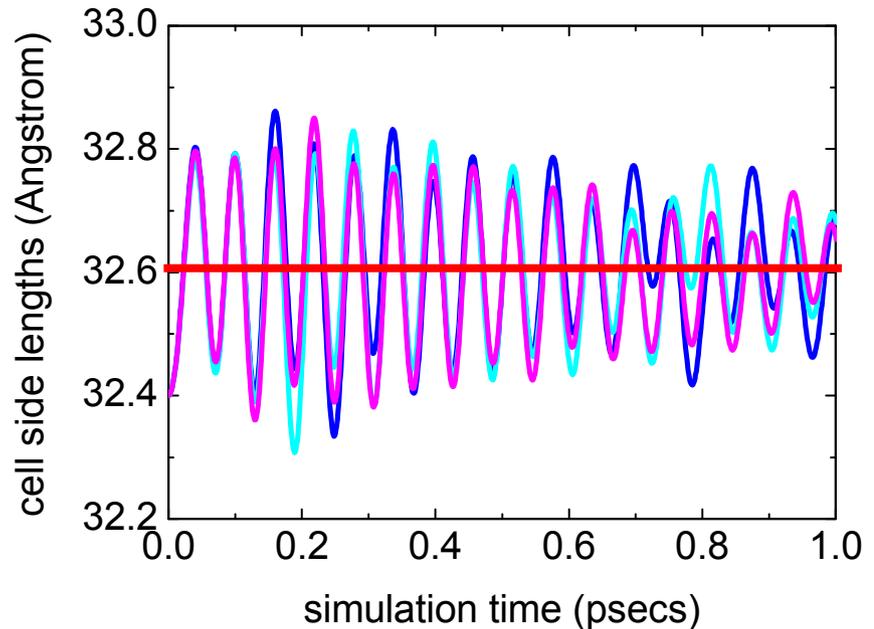
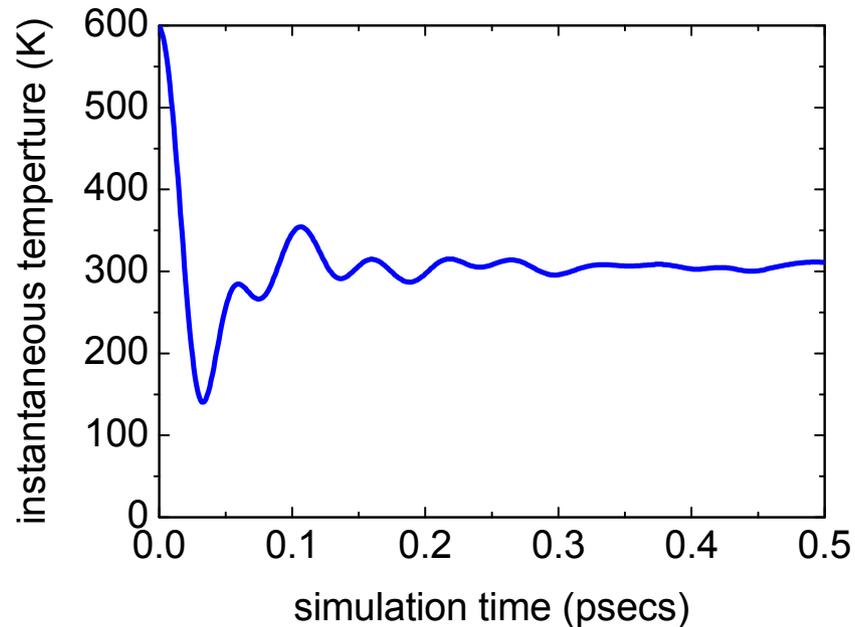
$$\tilde{\sigma} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$

Thermal expansion parameter

$$\alpha_V = \frac{1}{B} \frac{dP}{dT}$$

→ NVT Ensemble

# A perfect FCC lattice revisited



By setting the applied stress to zero, thermal expansion can be simulated using the Parrinello-Rahman method:

$$\tilde{\sigma} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

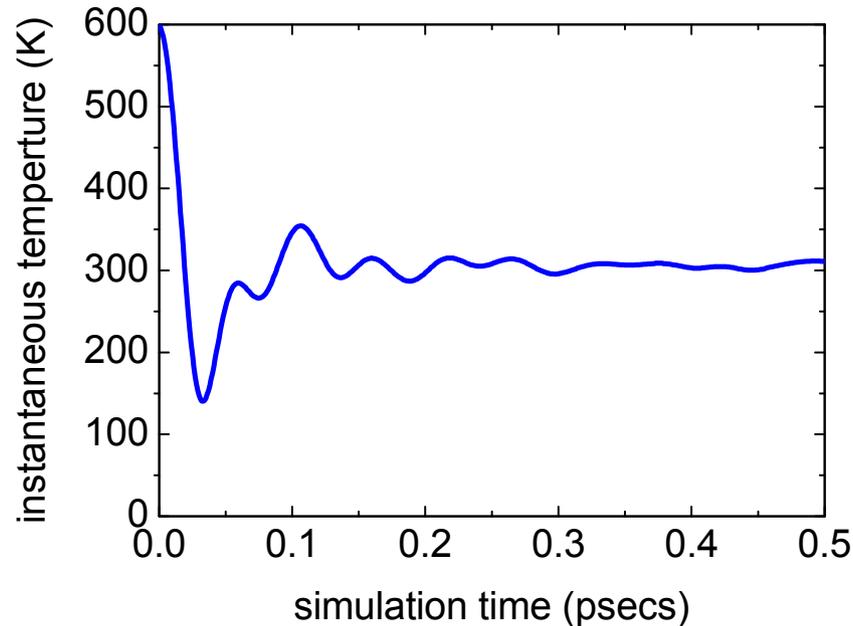
Thermal expansion parameter

$$\alpha_P = \frac{1}{V} \frac{dV}{dT}$$

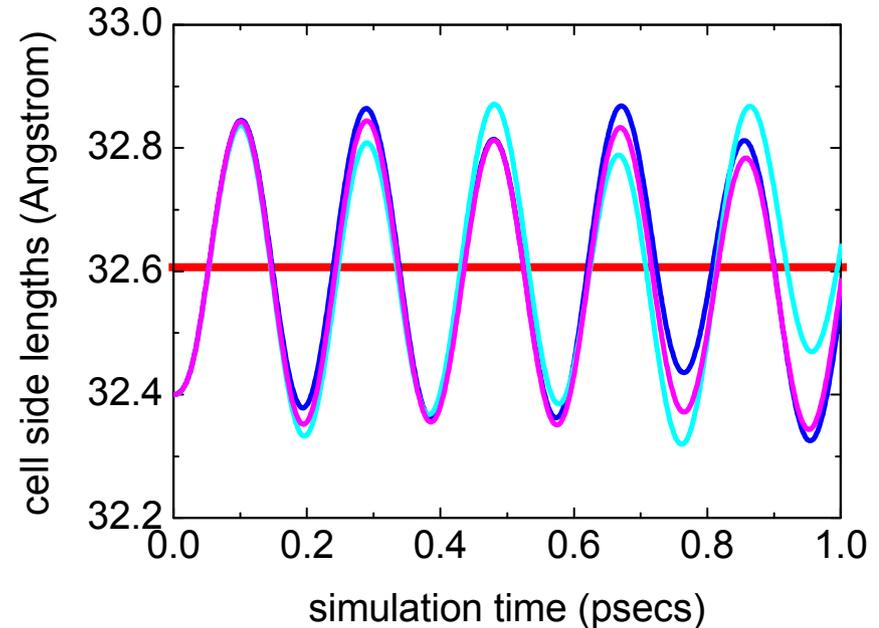


NPT Ensemble

# A perfect FCC lattice revisited



Simulation cell mass increased 10-fold



By setting the applied stress to zero, thermal expansion can be simulated using the Parrinello-Rahman method:

$$\tilde{\sigma} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

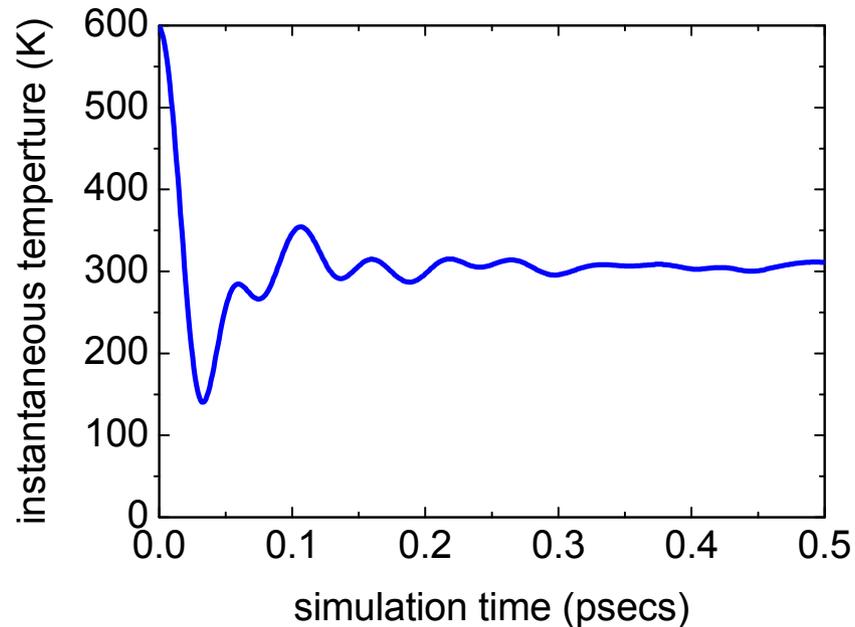
Thermal expansion parameter

$$\alpha_P = \frac{1}{V} \frac{dV}{dT}$$

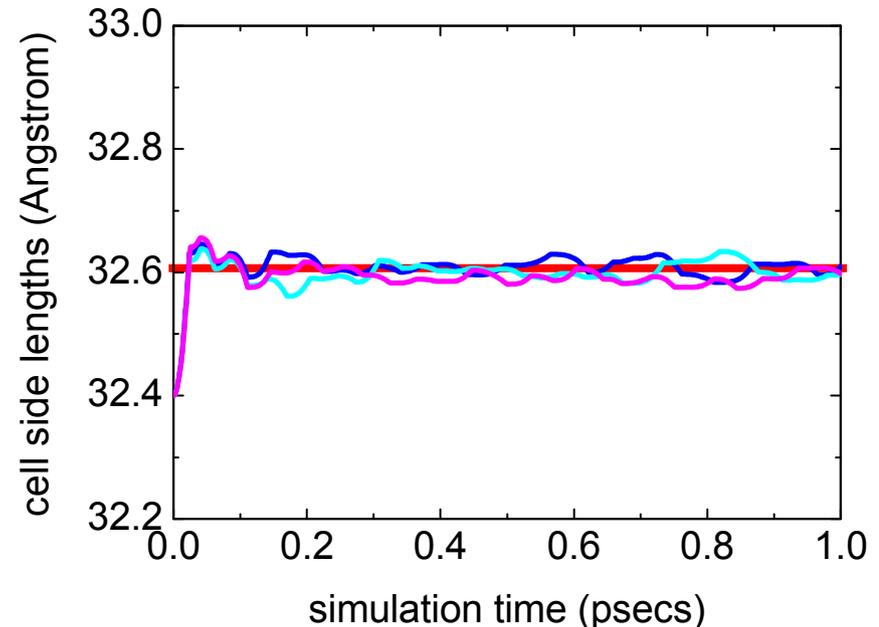


NPT Ensemble

# A perfect FCC lattice revisited



Simulation cell mass with active damping



By setting the applied stress to zero, thermal expansion can be simulated using the Parrinello-Rahman method:

$$\tilde{\sigma} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Thermal expansion parameter

$$\alpha_P = \frac{1}{V} \frac{dV}{dT}$$



NPT Ensemble

# Concluding remarks

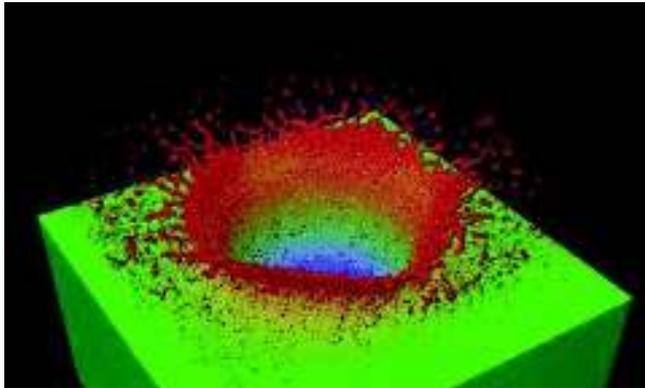
Inter-atomic force model

- Have in mind that you are using a severely uncontrolled approximation to model your material.
- Read **all** the literature associated with your potential.
- If you see something interesting, repeat the simulation using another potential.

Molecular dynamics is a wonderful tool to study and classify atomic scale processes → but it can be difficult to compare results with experiments because of a very large disparity between experimental and simulated timescales.

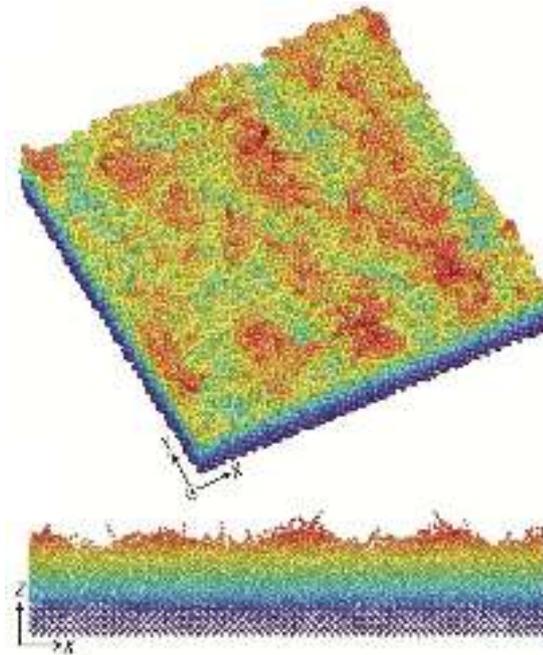
# LAMMPS ([lammps.sandia.gov/](http://lammps.sandia.gov/))

*lamp: a device that generates light, heat, or therapeutic radiation; something that illumines the mind or soul*



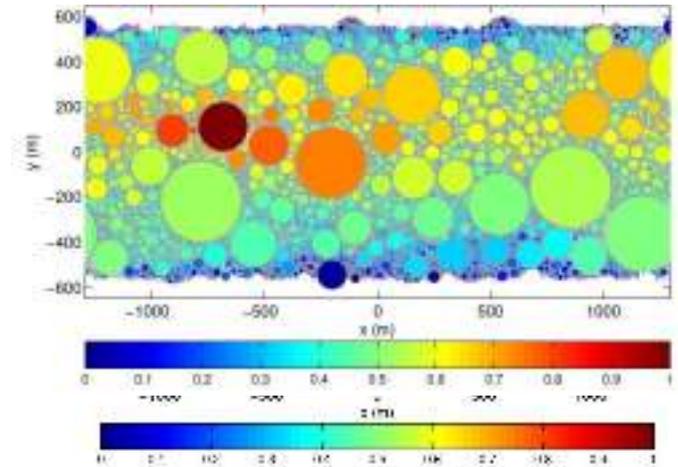
Nanoprojectile impacts - model the impact of nanoparticles up to 55 nm in diameter hitting substrate targets with up to 10 billion particles.

*Phys Rev Lett 108, 027601 (2012).*



Amorphous carbon film growth view of the surface after 36,000 C impacts

*Carbon, 50, 404 (2012).*



Jamming and deformation of extremely polydisperse granular materials

*Entropy, 15, 4802 (2013)*

There also exists the ITAP Molecular Dynamics Program ([imd.itap.physik.uni-stuttgart.de/](http://imd.itap.physik.uni-stuttgart.de/))

# References

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

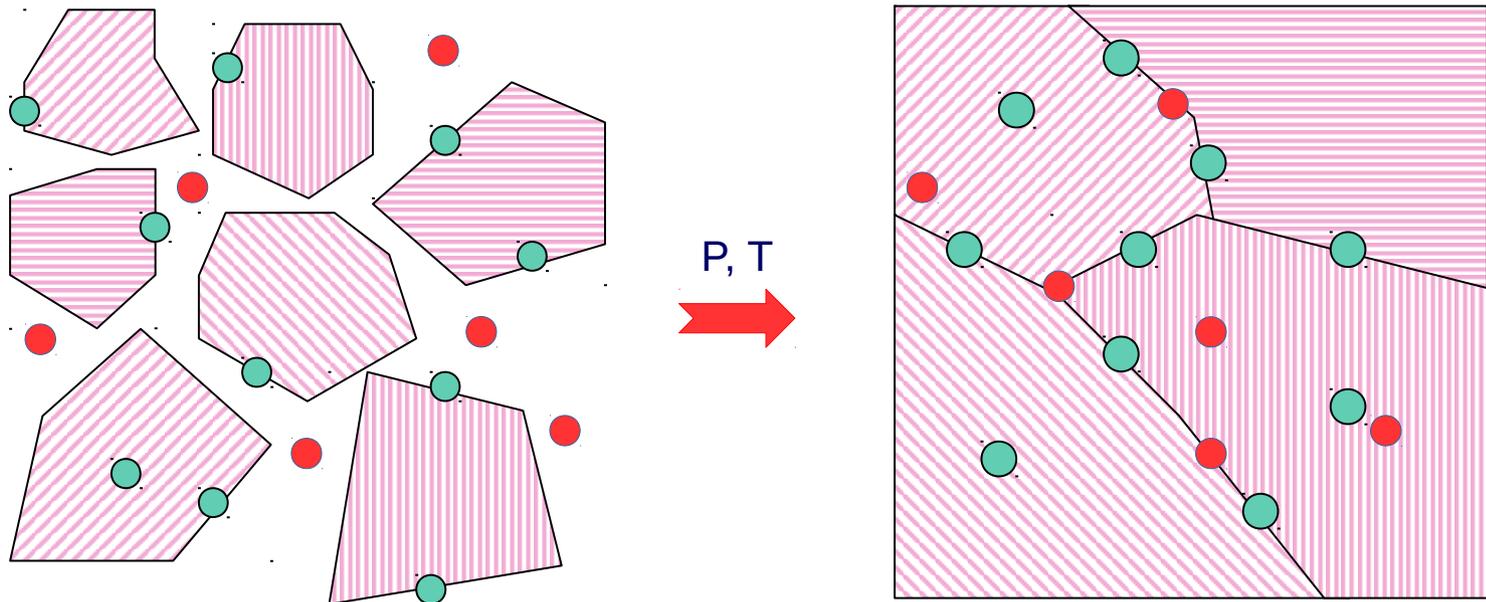
# Lecture outline

- 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 ....

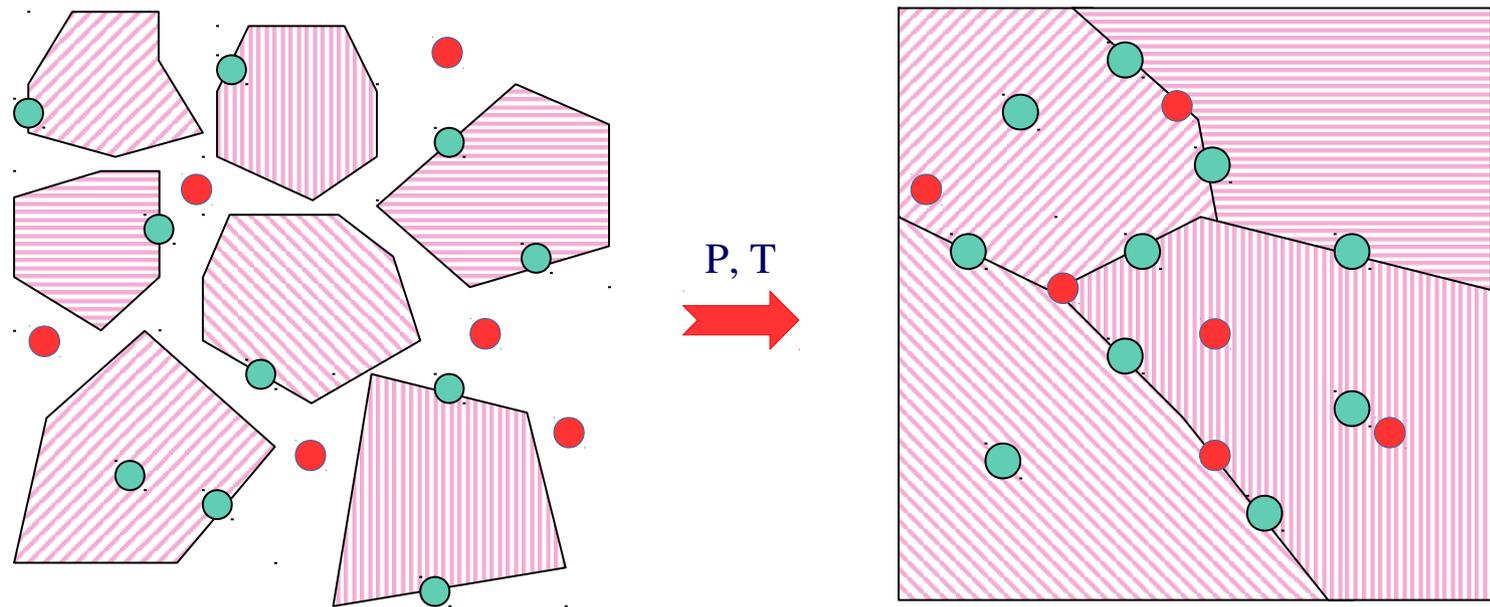


## Questions

- 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 .....

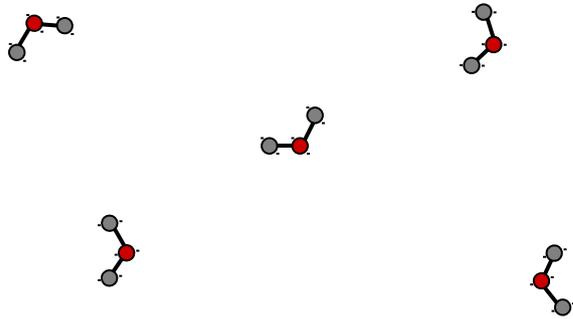


- Phenomenon - Surface ab/adsorption
- 
- Diffusion -
- 
- Segregation -
- 

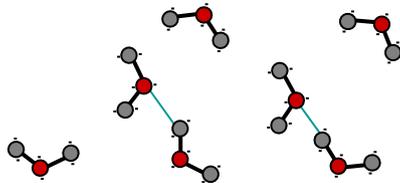
As a function of temperature and stress

# The Potential Energy Landscape (PEL) of a solid

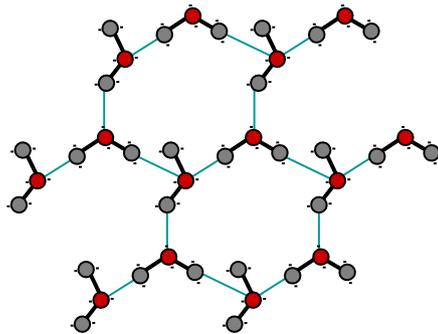
# The regimes of atoms



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

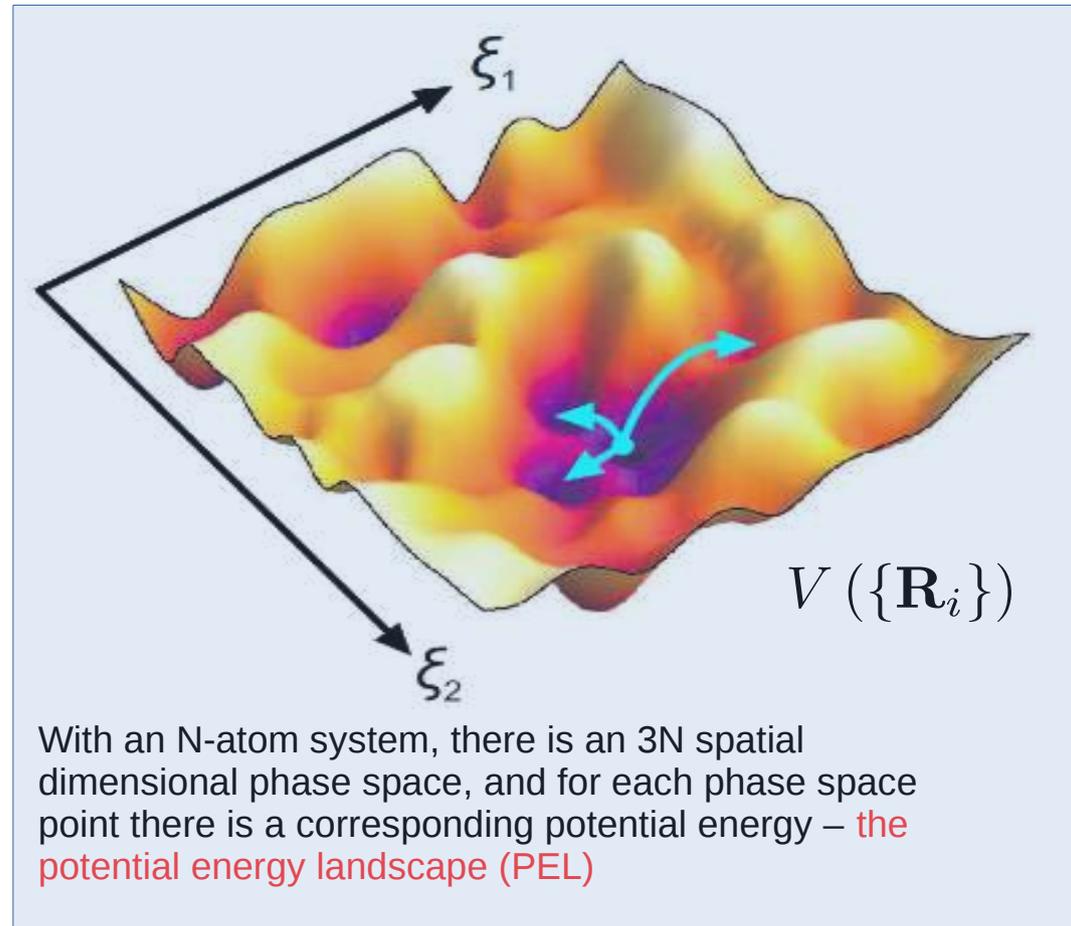
# The potential energy landscape picture of a solid

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

However for a solid, excitations are mainly long lived.

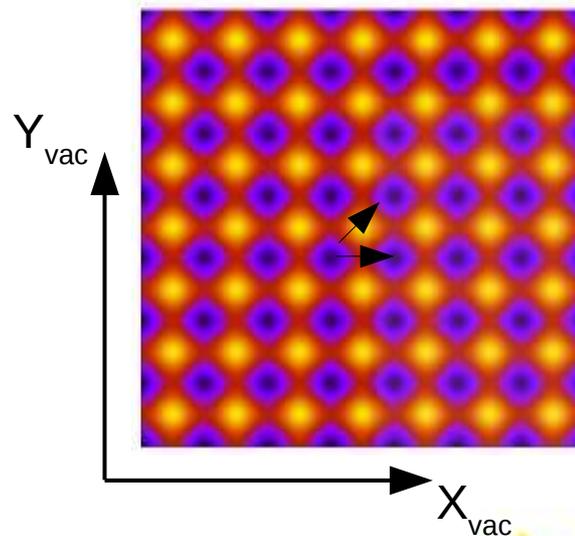
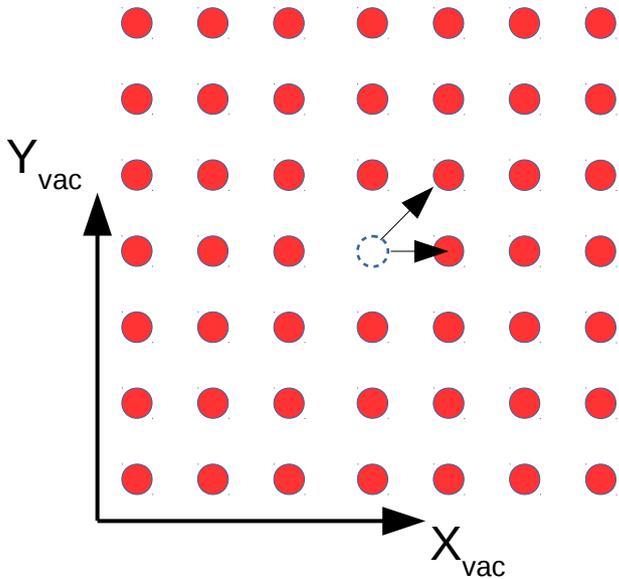
Why?

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



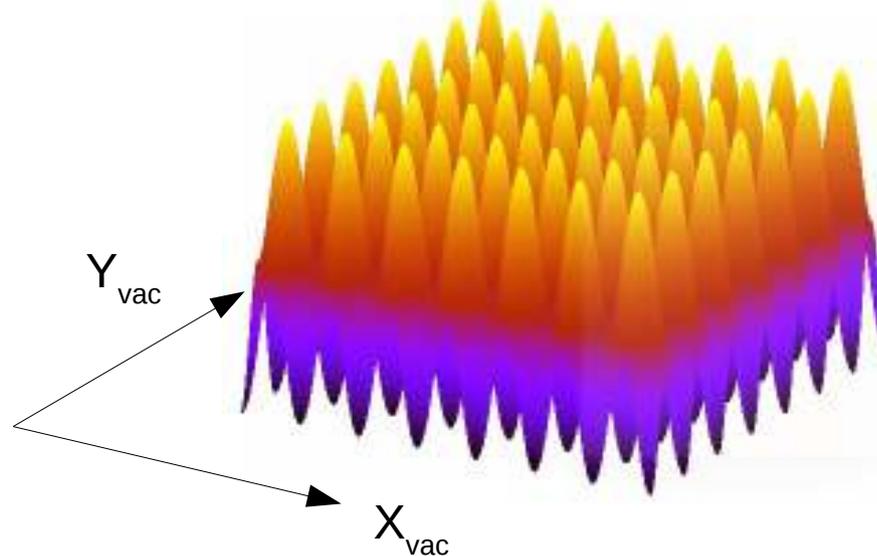
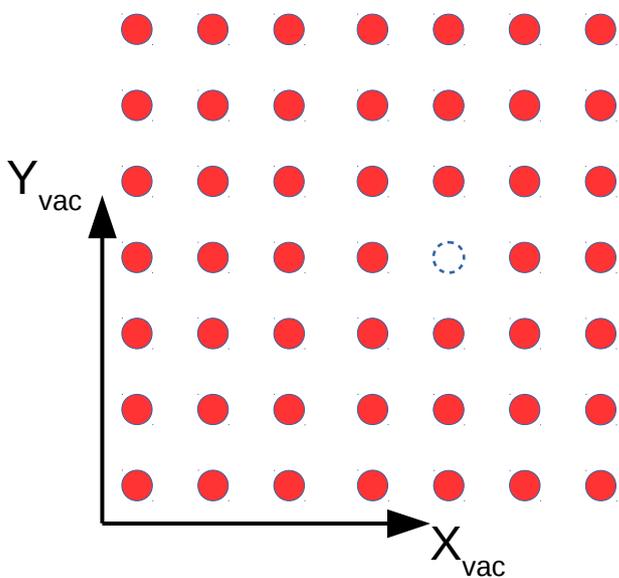
A solid spends most of its time in the valleys of the PEL – a local region of phase space – occasionally transiting (via thermal fluctuations) to a new valley via a ridge.

# 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.

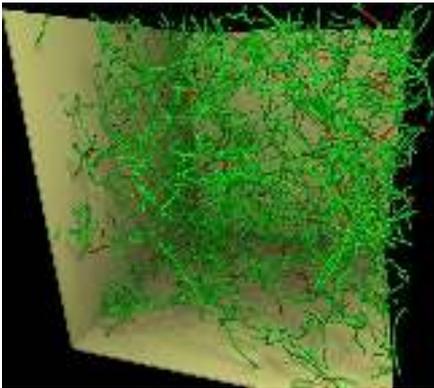


Thus (sometimes) the location in phase space can be easily correlated with the position of a defect

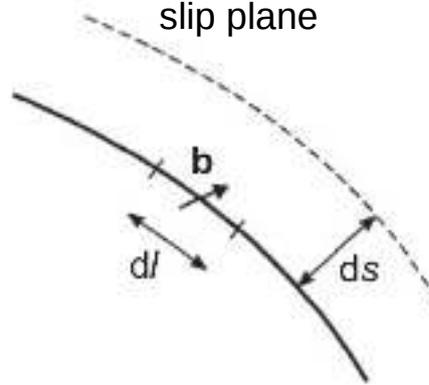
# The PEL picture of a dislocation

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

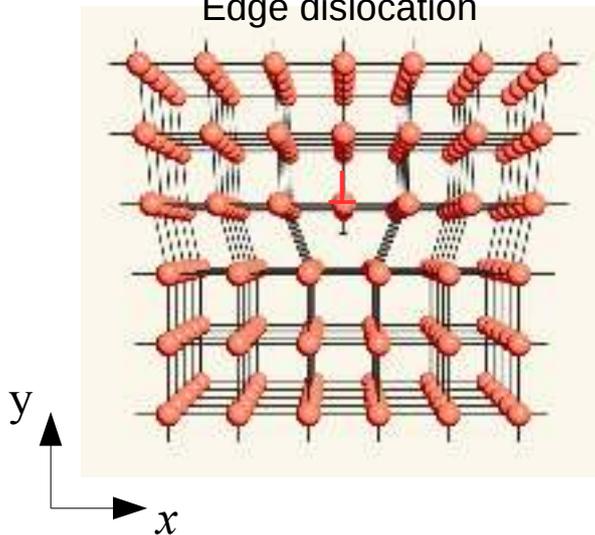
Network of dislocations



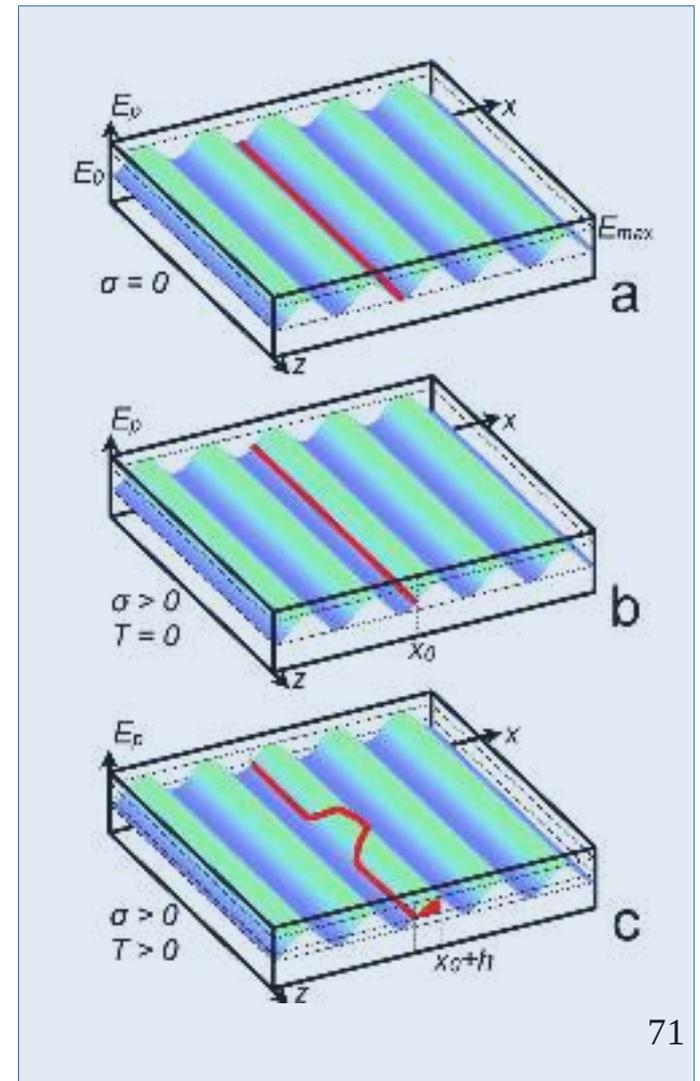
A dislocation is a line defect defined by a Burgers vector and slip plane



Edge dislocation



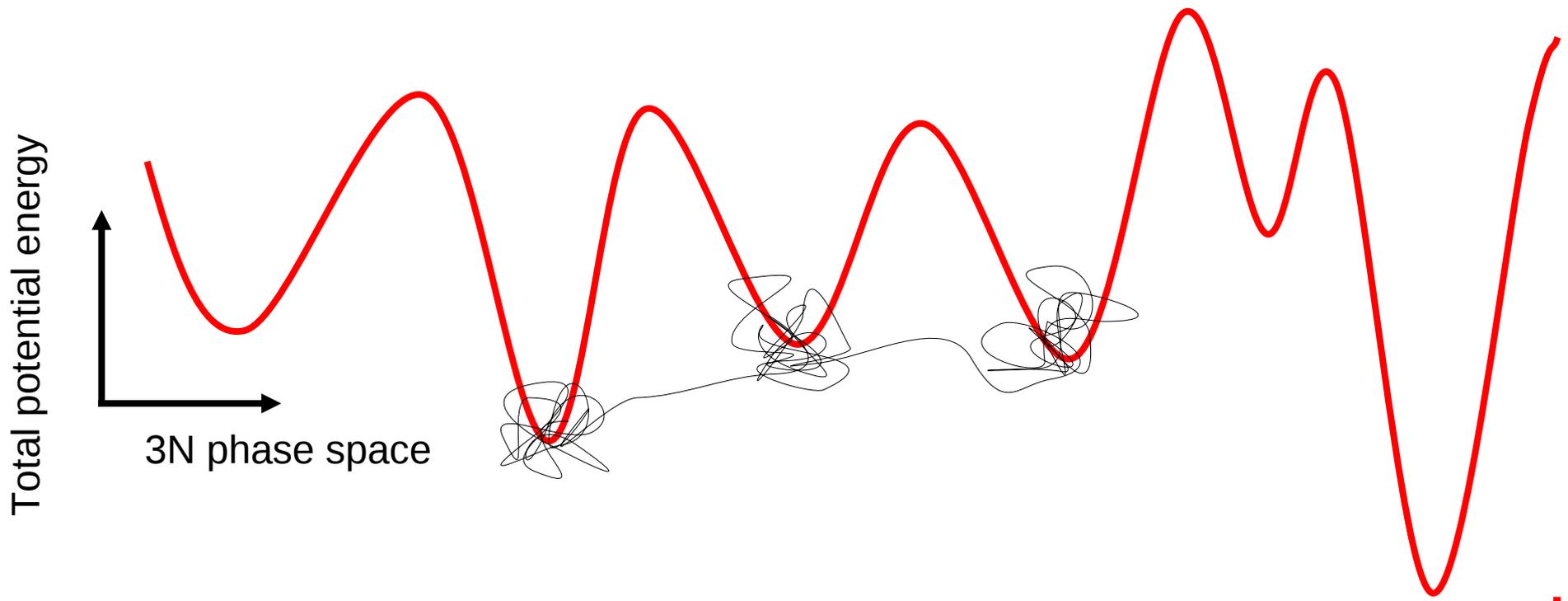
Dislocation core structure and dynamics are determined by atomic structure – the dislocation sees a PEL determined by the crystal lattice



# The timescale problem in MD

# The PEL is traversed via thermal fluctuations

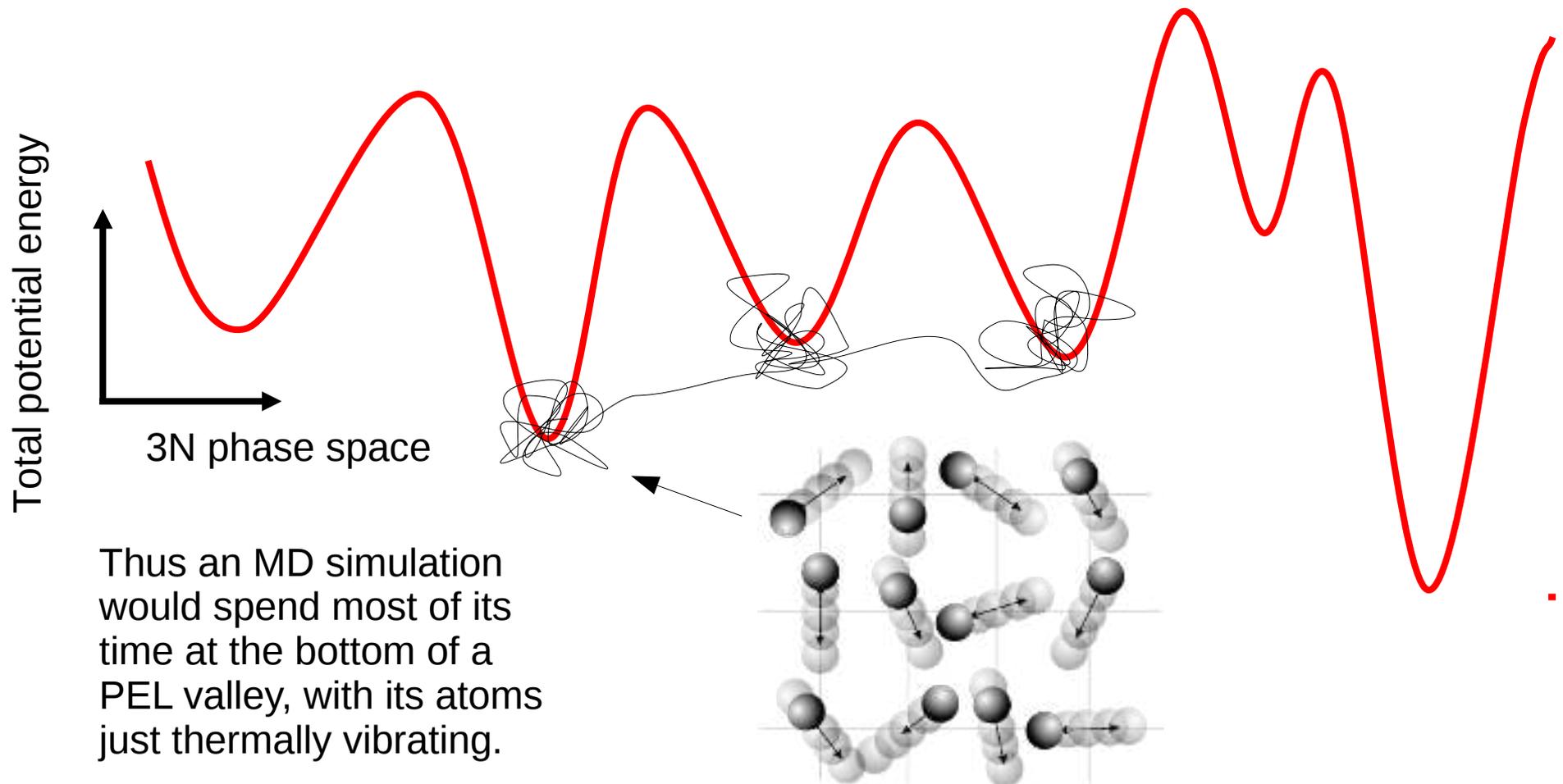
An atomic configuration will spend most of its time in a local potential energy minimum occasionally undergoing a transition, through thermal activation, to another local minimum.



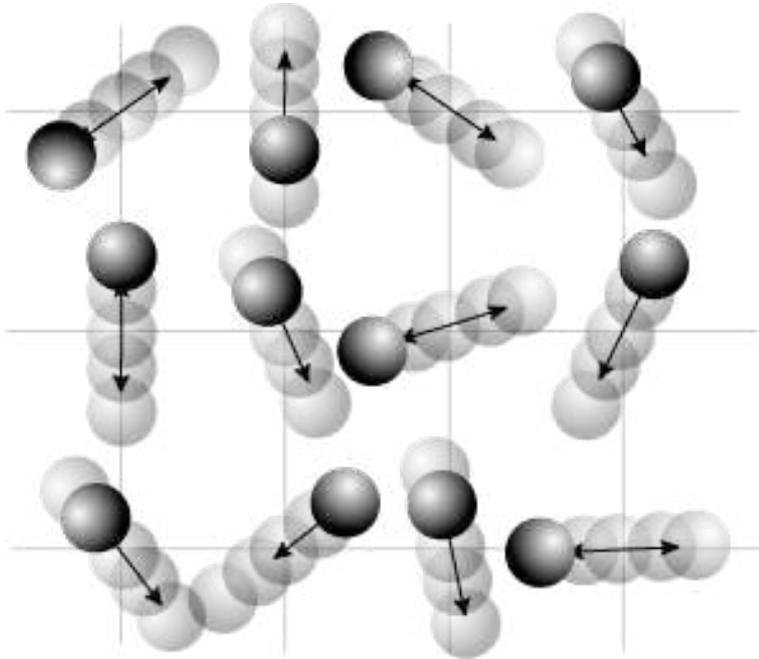
The defect will have a thermal energy that fluctuates around a mean value, and occasionally the fluctuation will be large enough for it to overcome a PEL ridge → if the energy barrier (ridge minus valley energy) is large, then this will happen only very rarely.

# The PEL is traversed via thermal fluctuations

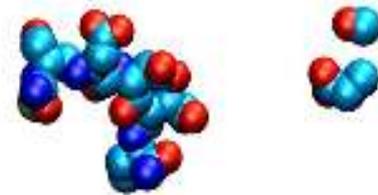
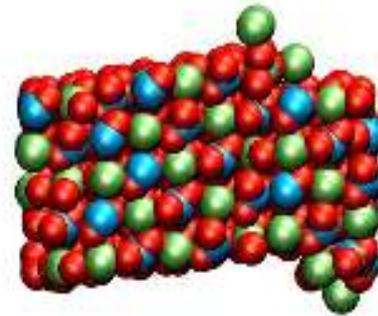
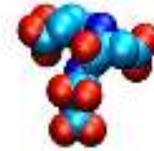
An atomic configuration will spend most of its time in a local potential energy minimum occasionally undergoing a transition, through thermal activation, to another local minimum.



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



The characteristic frequency of atomic vibration is  $\sim 1$  THz



Polymer absorption  
on calcite ( $\text{CaCO}_3$ )

# The timescale problem in MD

The MD algorithm evolves the atomic coordinates using numerical integration

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

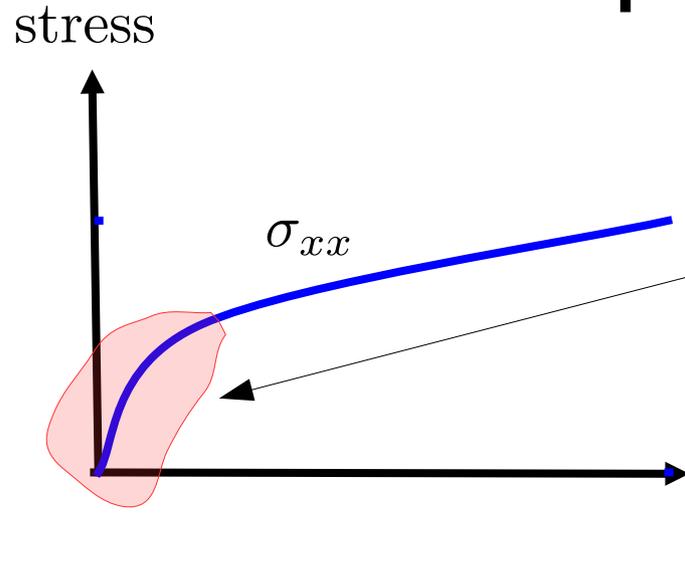
Velocity Verlet integrator (see slides 27-28 of previous lecture)

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,  $\Delta t$ , 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



To study plasticity,  
would like to have (say)  
1% plastic strain.

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

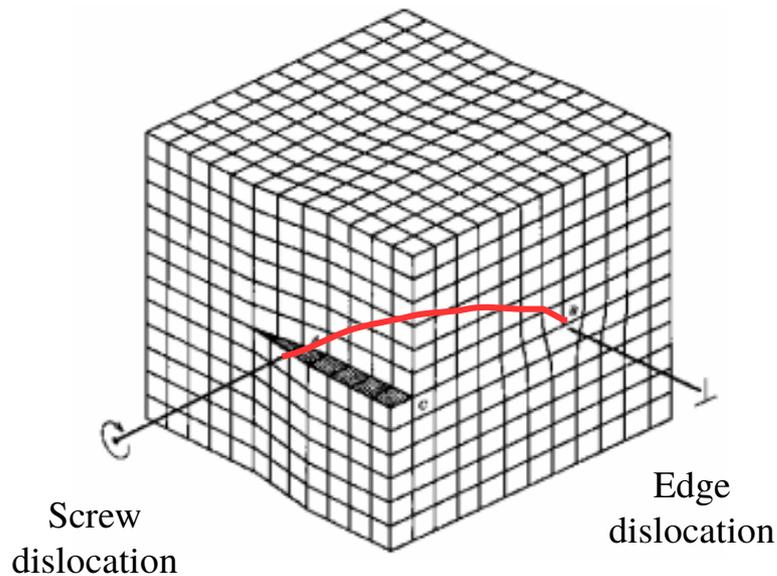
$$\dot{\epsilon}_{\text{plastic}} \sim 10^{-4} - 10^{-1} \text{ sec}^{-1} \leftarrow \text{Experiment}$$

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.

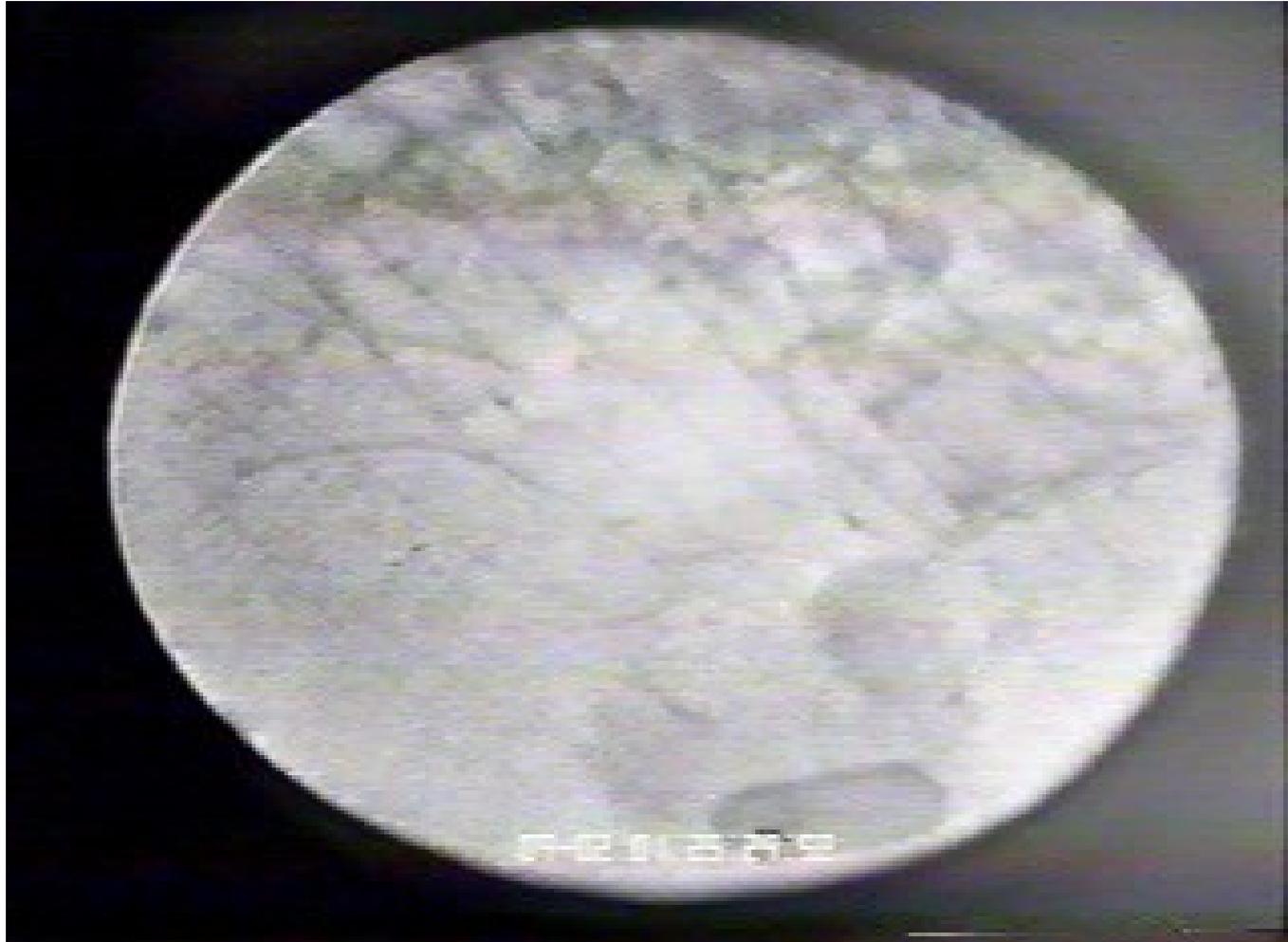
Consider (BCC) dislocations – the mediators of crystalline plasticity



*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:

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

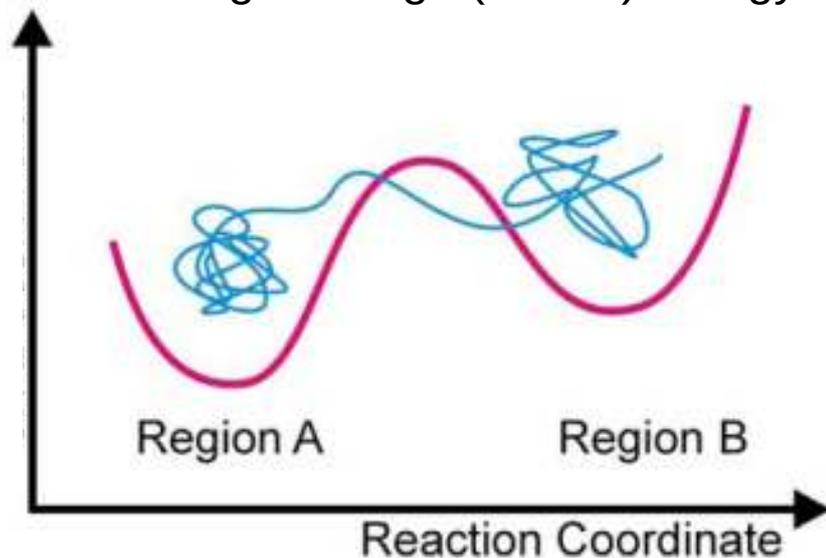
In one nanosecond (one million MD steps), the dislocation therefore travels:

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

**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:

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

activation energy  $\downarrow$

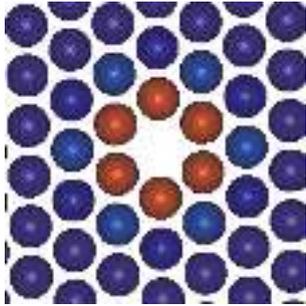
attempt rate  $\uparrow$

probability of success  $\swarrow$

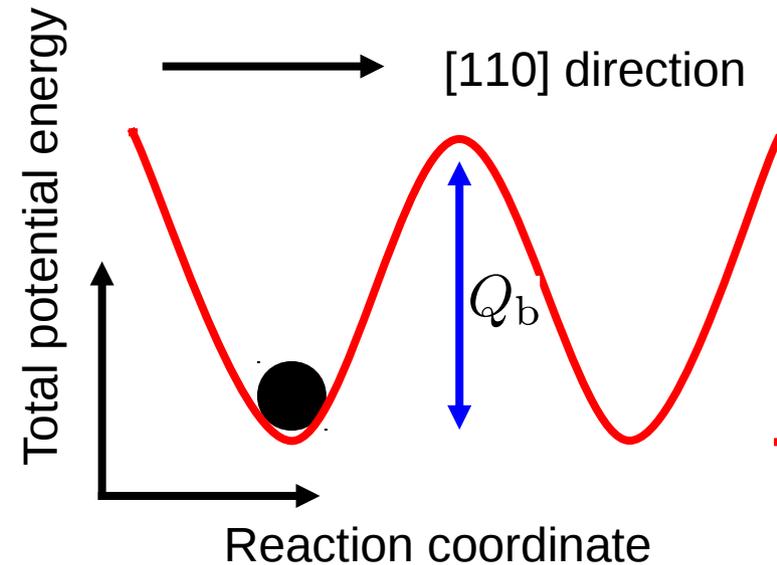
When the activation energy ( $Q_b$ ) is comparable to the thermal energy ( $k_b T$ ), the probability of success is close to one and each attempt is likely to be successful – this is the athermal regime of activity.

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

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

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

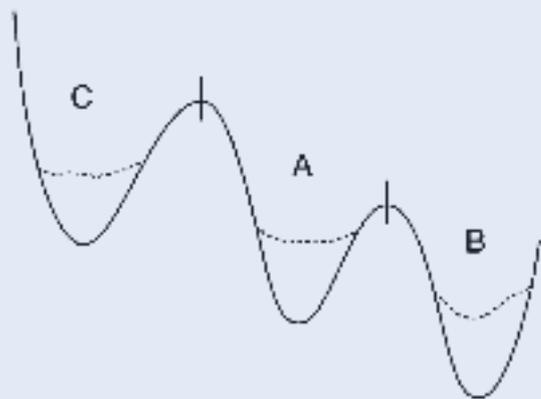
# Direct Acceleration Methods

**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.

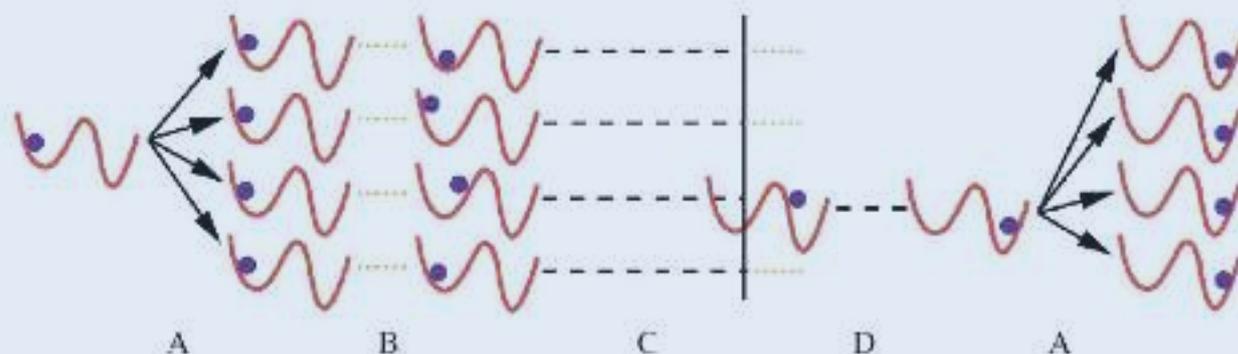
**Parallel replica method** – runs multiple copies of a system until a transition occurs, and then copies the configuration which experienced the transition to all processors, and then the process is repeated.

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

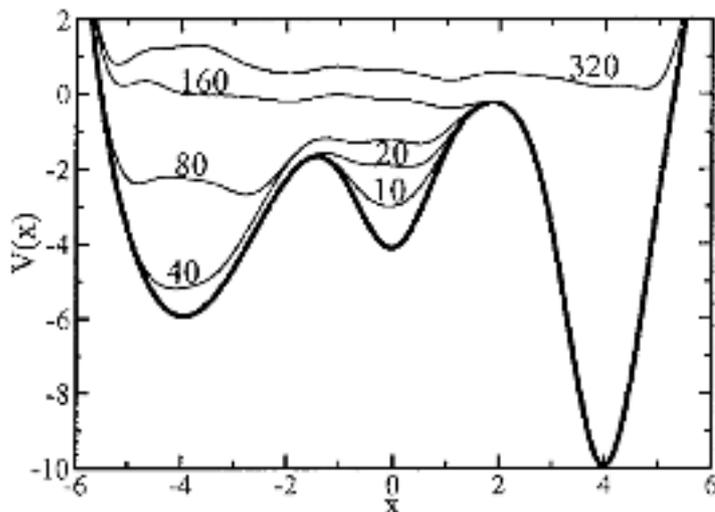
$$V_{\text{bias}}(\{\mathbf{r}(t)\}) = \sum_{n=0}^{t/\tau_G} V_G \exp\left(-\frac{|\bar{\mathbf{r}}(t) - \bar{\mathbf{r}}(t_n)|^2}{2\sigma_G^2}\right)$$

$$t_n = n\tau_G$$

→ time step

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

→ Coarse grained coordinates



## Escaping free-energy minima

Alessandro Laio and Michele Parrinello\*

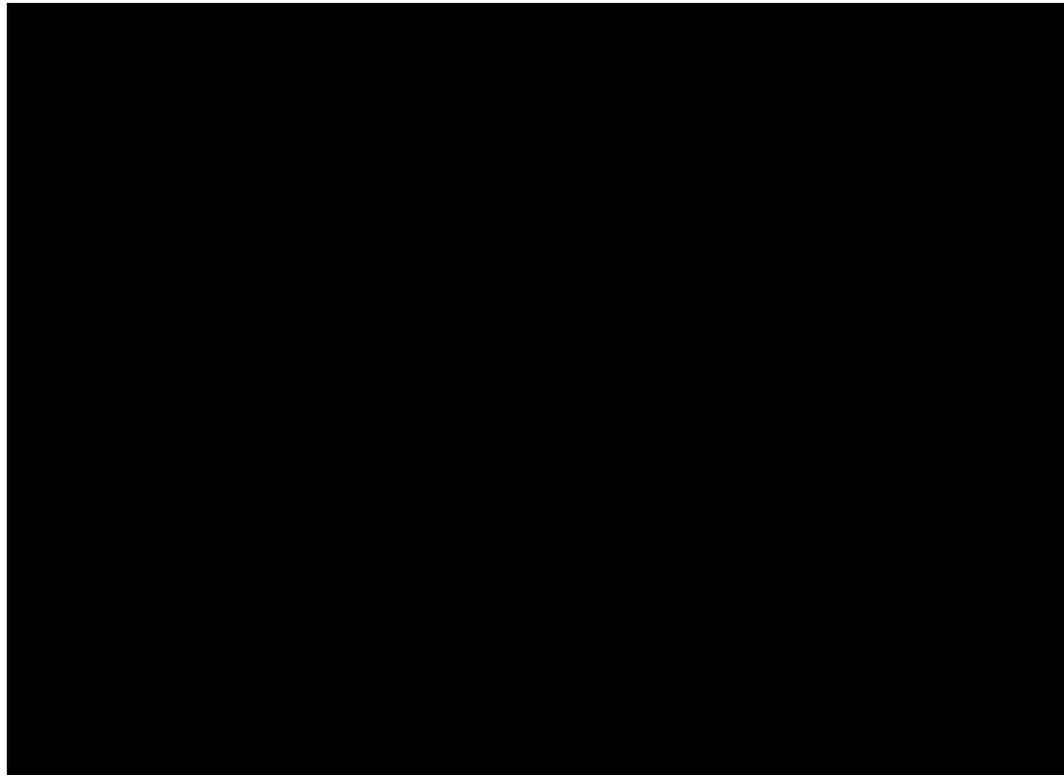
Centro Svizzero di Calcolo Scientifico, Via Cantonale, CH-6928 Manno, Switzerland; and Department of Chemistry, Eidgenössische Technische Hochschule, Hönggerberg HCI, CH-8093 Zürich, Switzerland

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

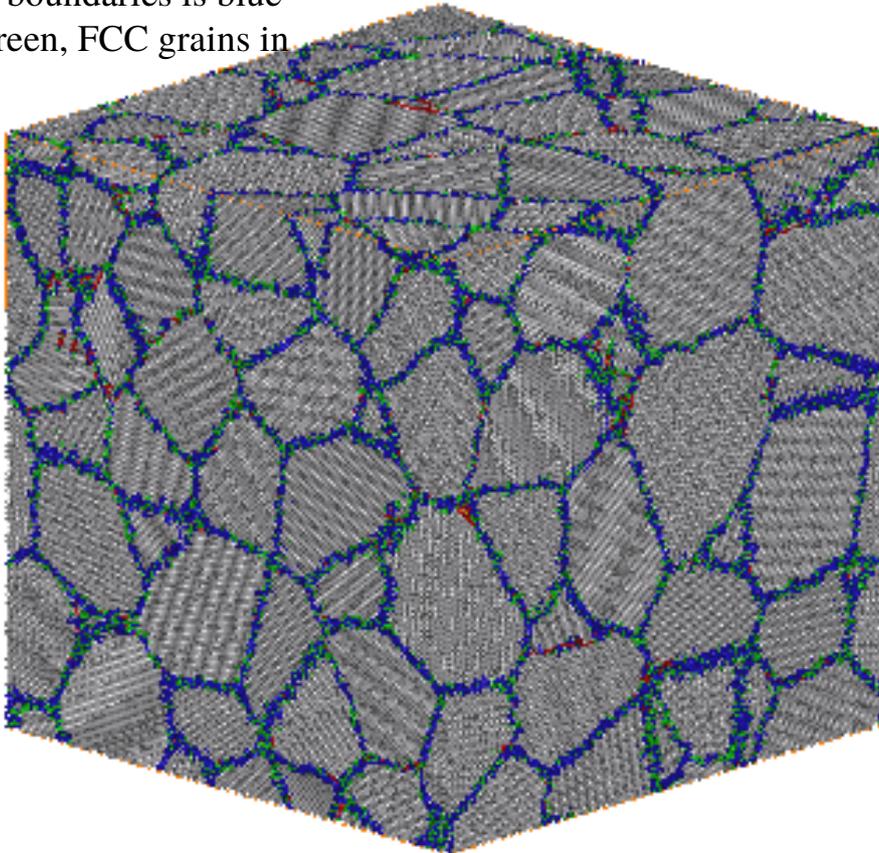
**Meta-dynamics** – adds an adaptable bias potential to excite the system out of its local minimum.



# Example 1: nanocrystalline metals – structure & athermal plasticity

# Nanocrystalline metals: structure & athermal plasticity

Grain boundaries is blue and green, FCC grains in grey

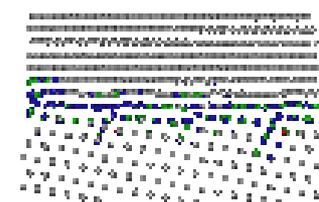
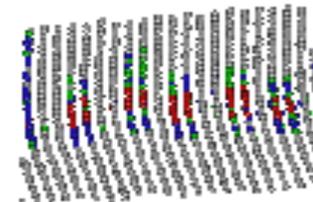
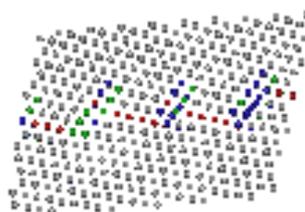
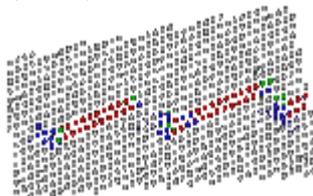


- Nanocrystalline samples are constructed geometrically and then thermally equilibrated to 300K
- The sample to the left contains ~5 million atoms – 100 grains with a mean diameter of ~10nm

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



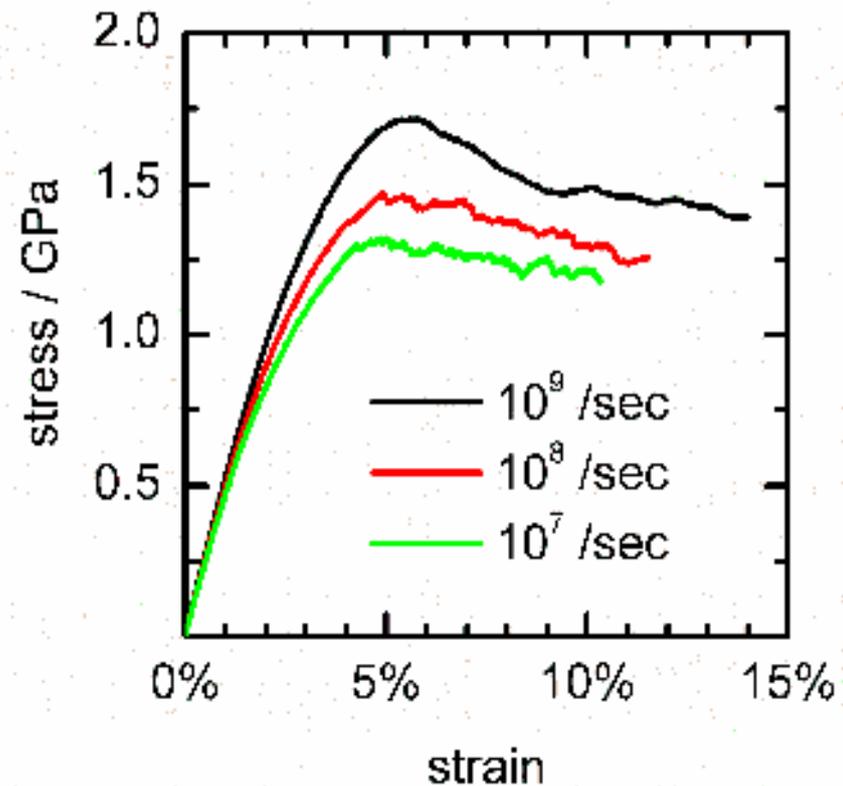
*H. Van Swygenhoven, D. Farkas, A. Caro, Phys. Rev. B 62 831, (2000).*

# 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

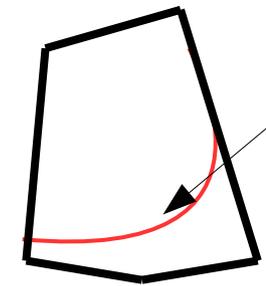
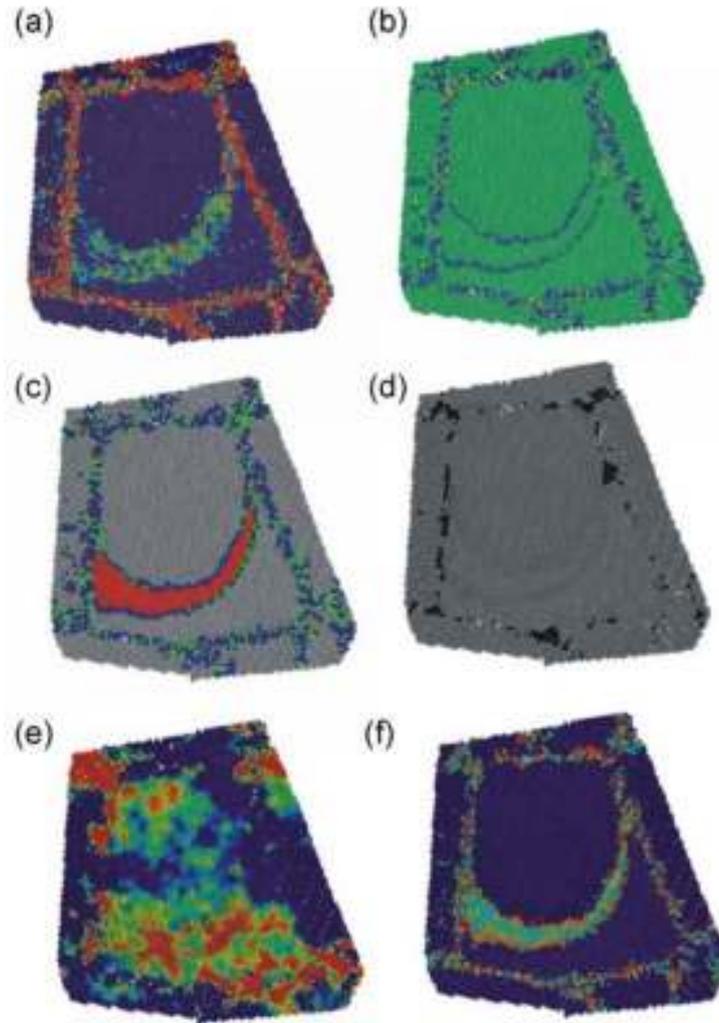
Stress-strain curves can be obtained, but at strain rates that are **ten orders of magnitude** higher than that normally seen in experiment.

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

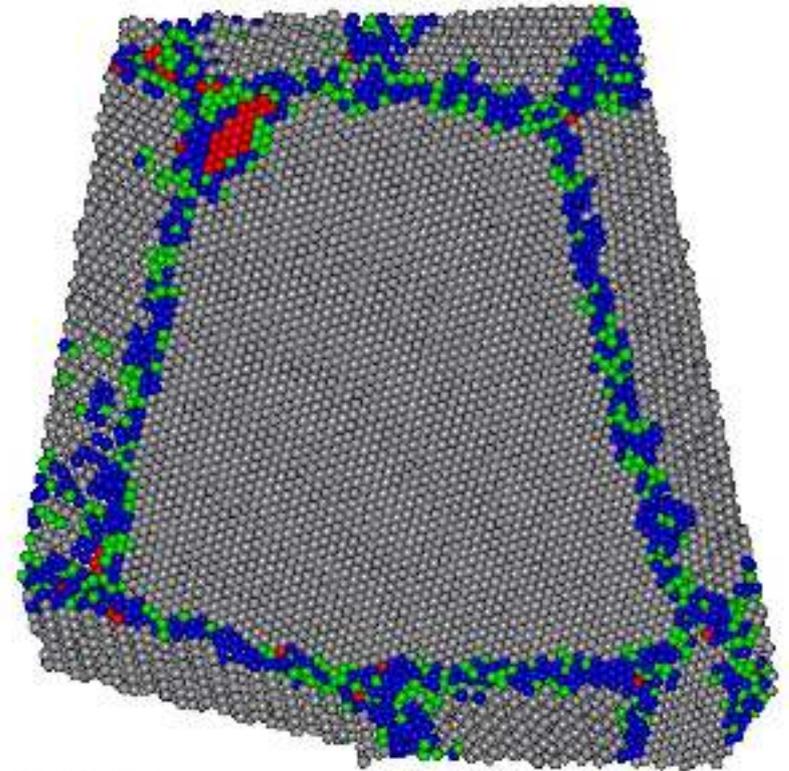
- a) local potential energy
- b) coordination
- c) medium range order
- d) positional disorder
- e) local pressure
- f) centro-symmetric parameter

# 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.

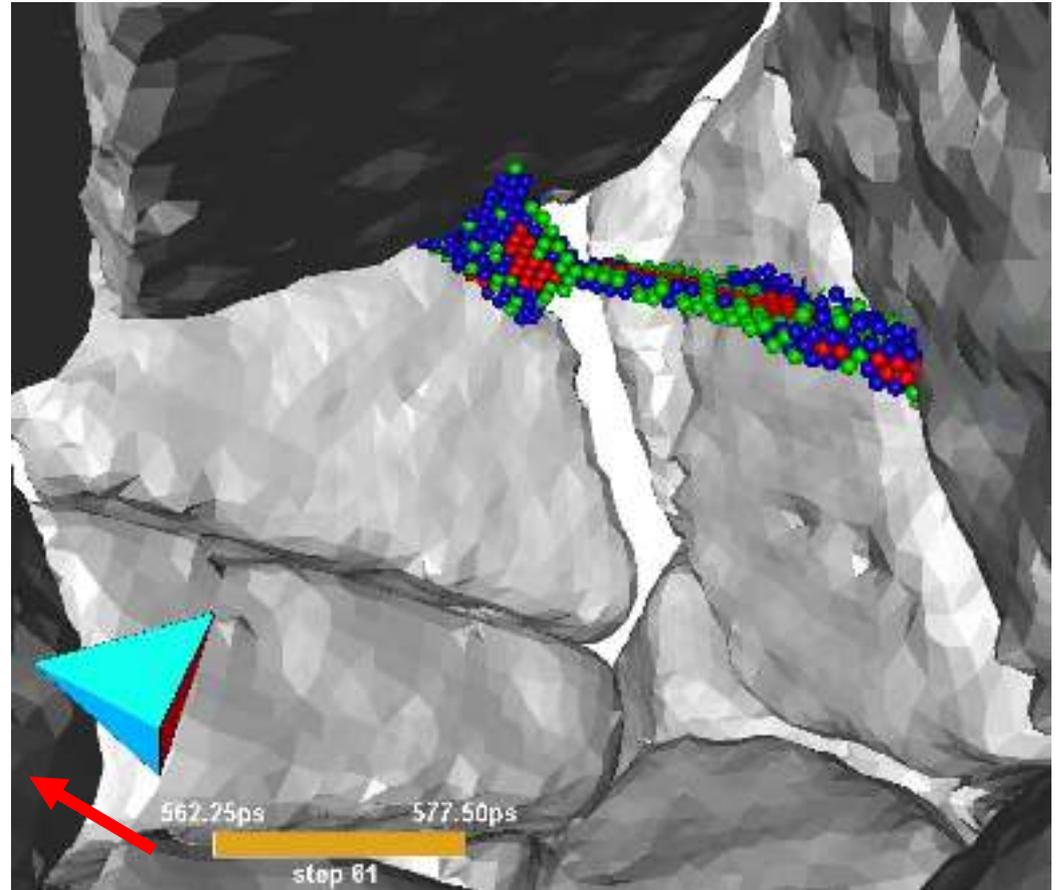


300K: T = 16

# 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  $17^\circ$  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.

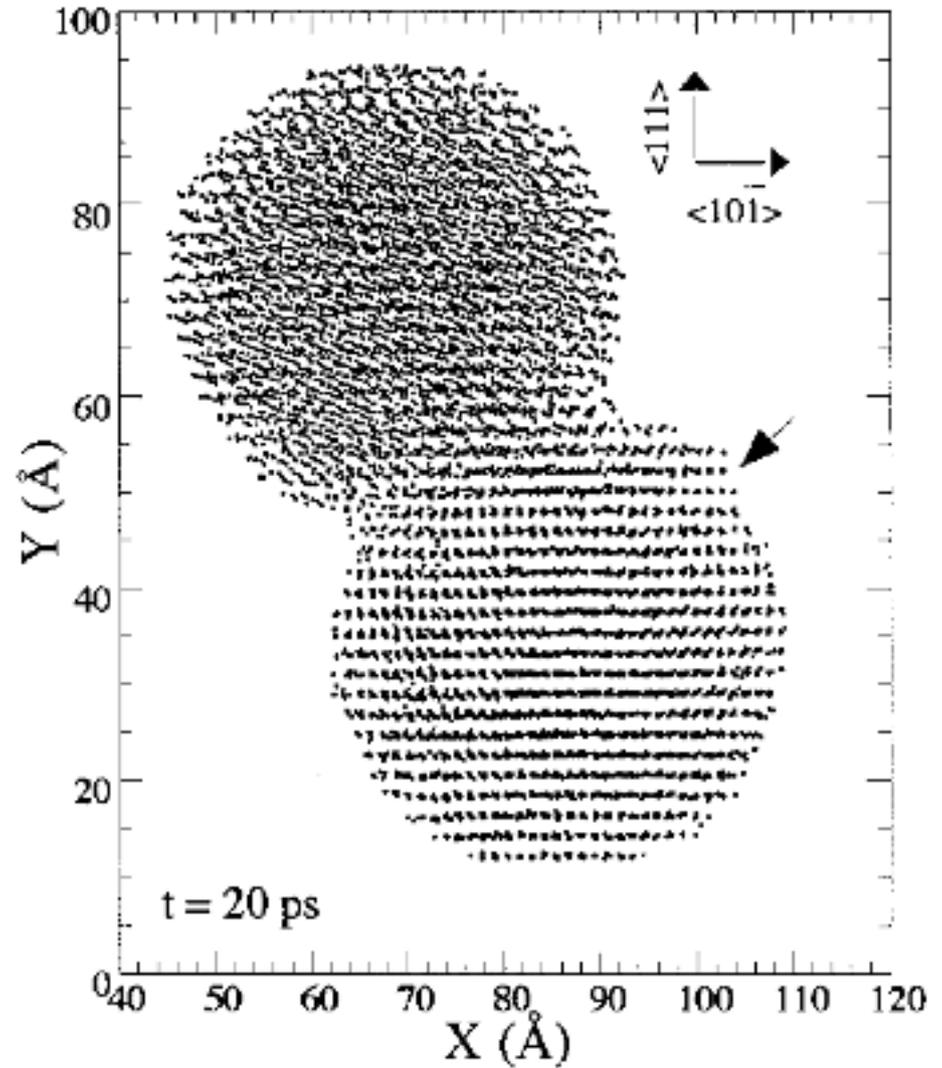
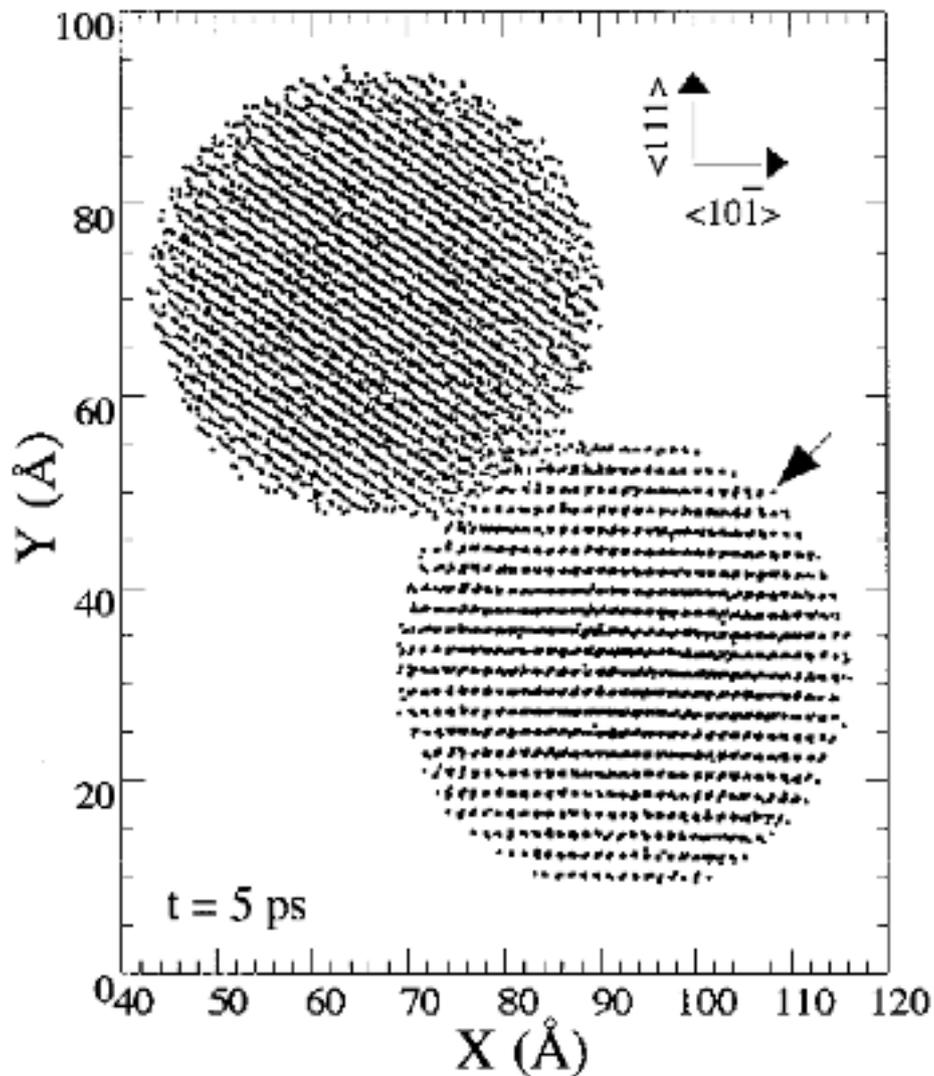
An embedded-atom potential was employed to represent the forces in Cu.

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

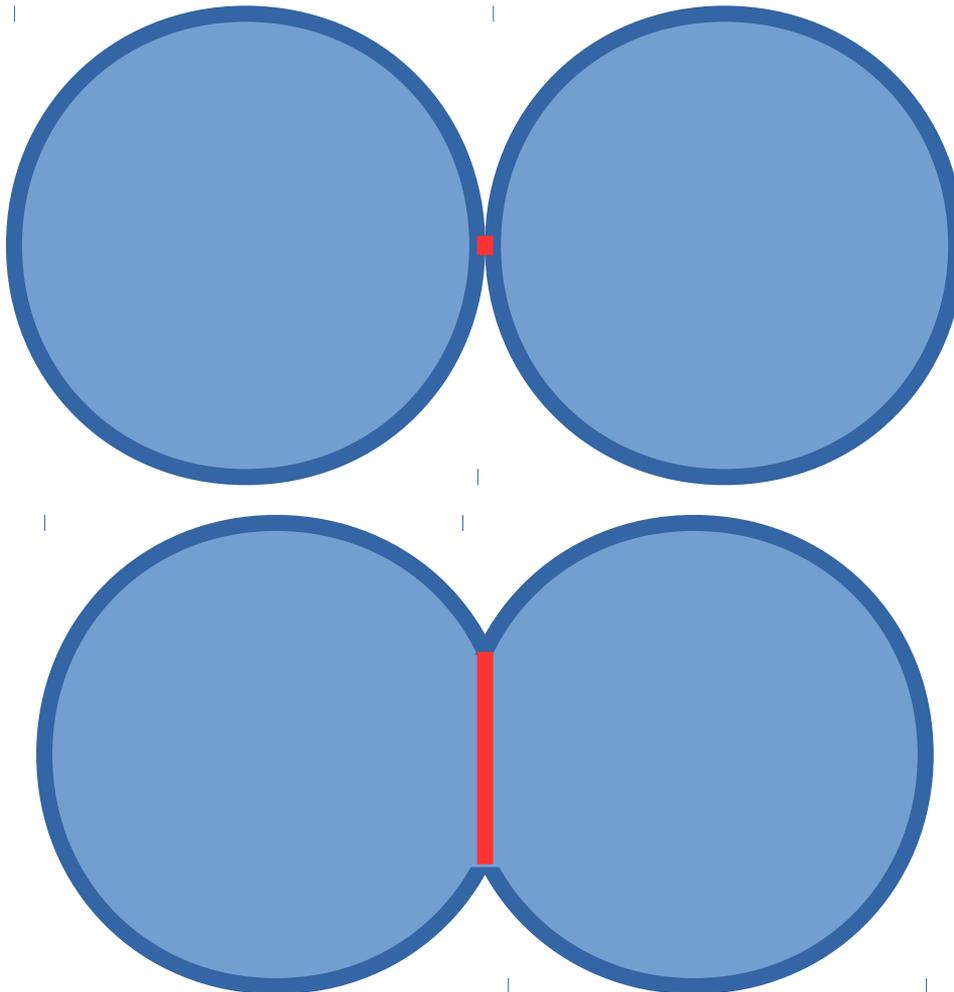
$$l_c = 2R + 0.2\text{nm}$$

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

# Sintering processes of two nanoparticles



# Shrinkage due to elastic deformation



Three contributing energies:

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

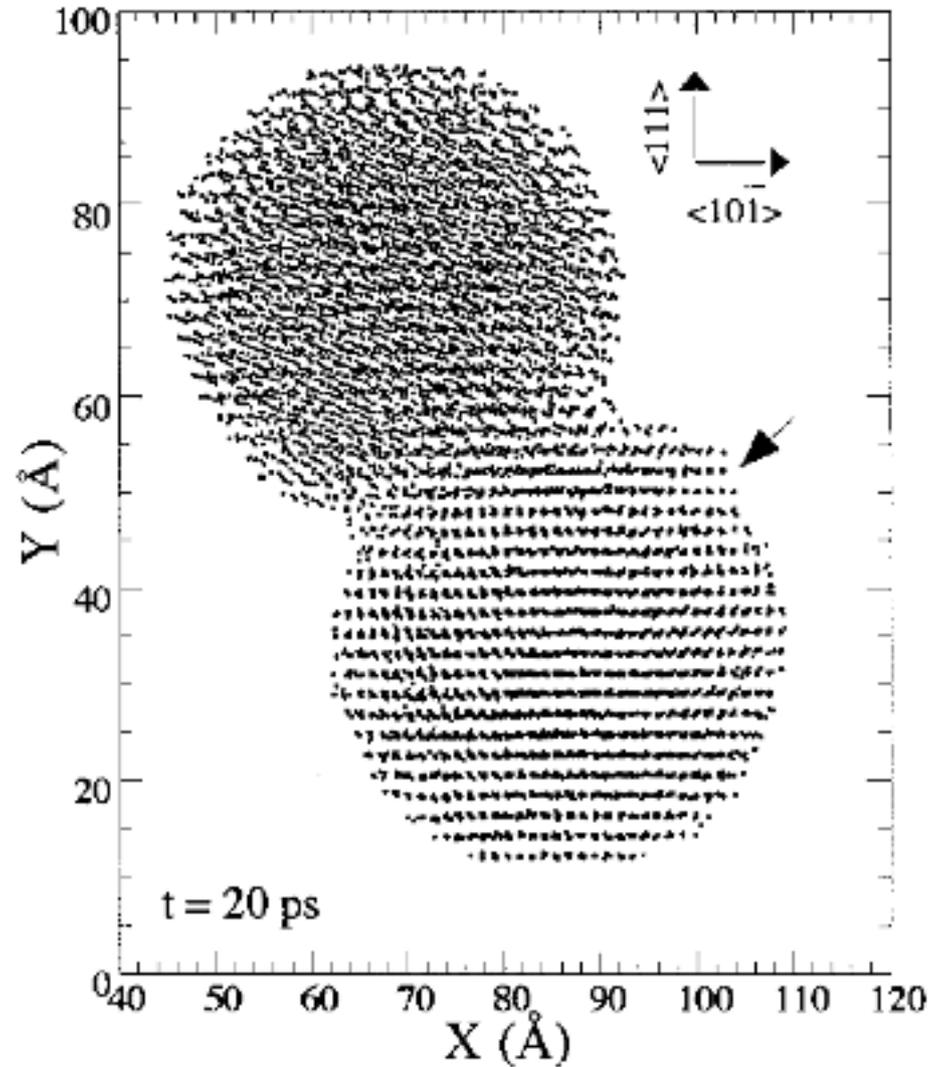
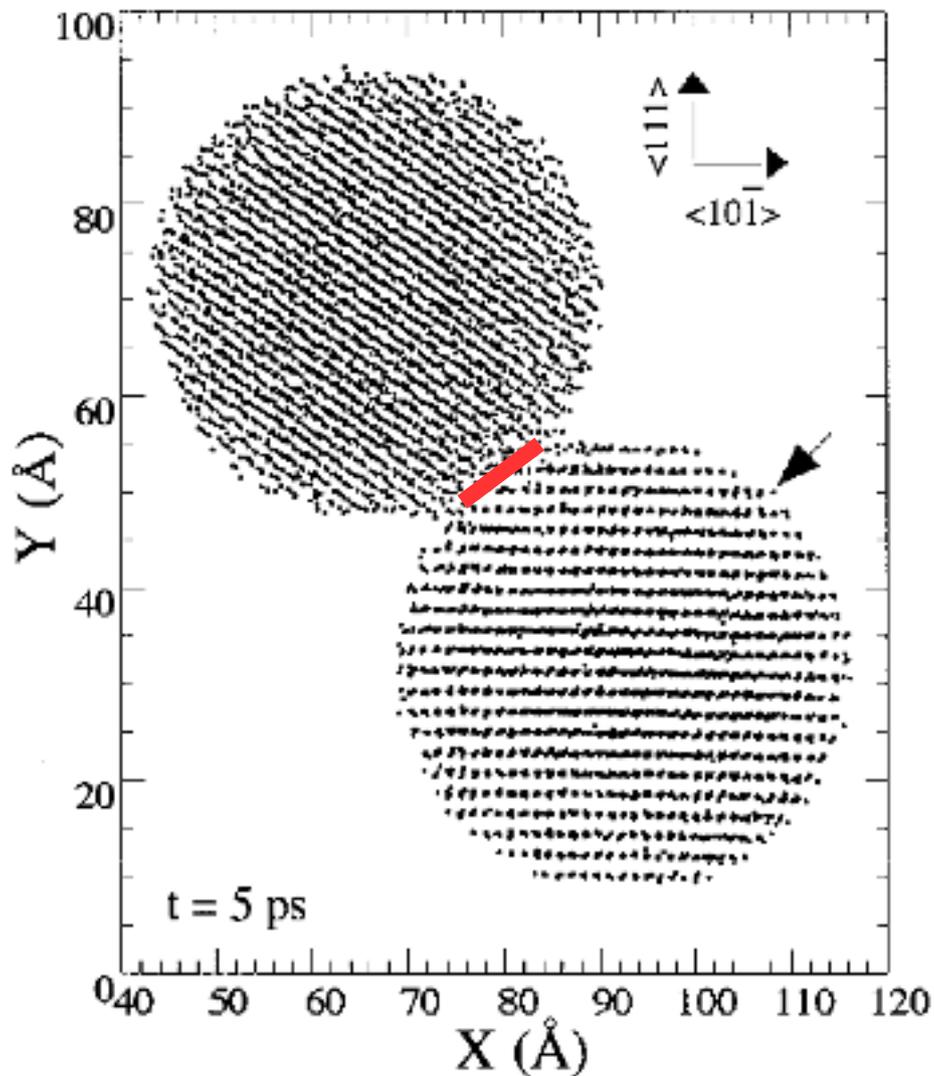
Total energy minimized when

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

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

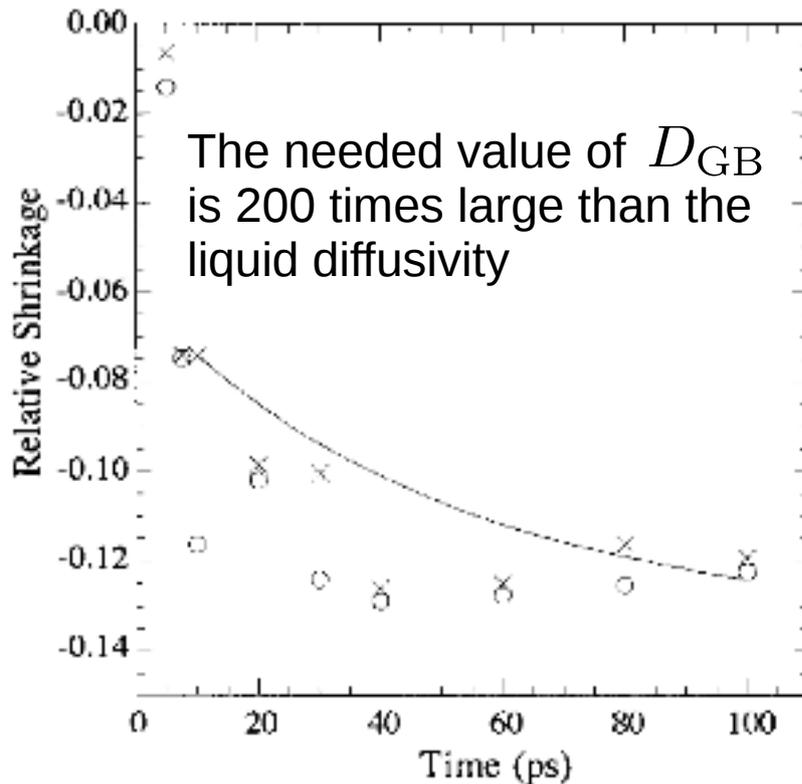
$$\rightarrow a \simeq 0.84\text{nm}$$

# 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  $R^2$ )

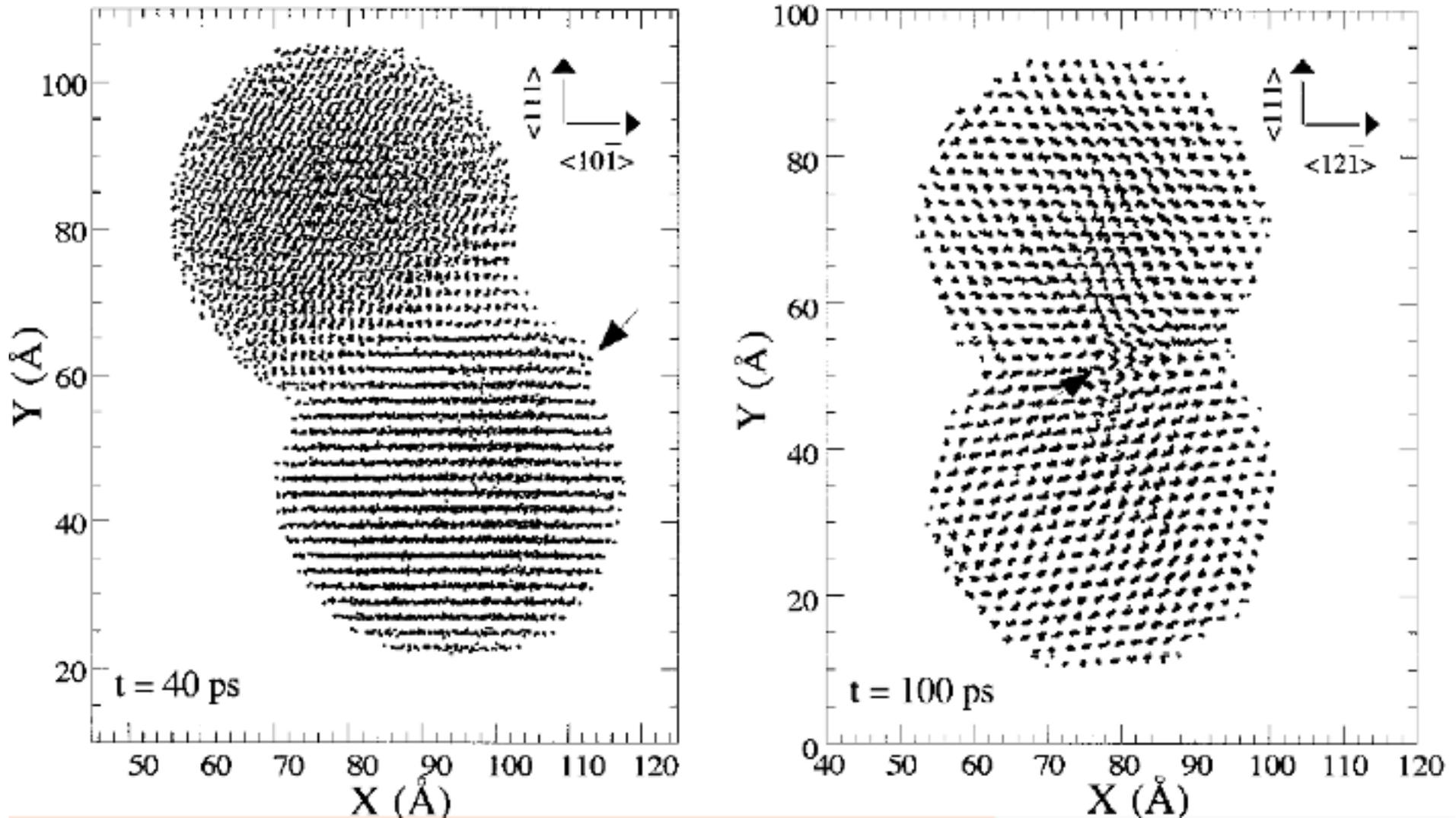
$$A_r = 4[\theta(x+r) - r \sin \theta]$$

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
- $\delta$  - GB thickness

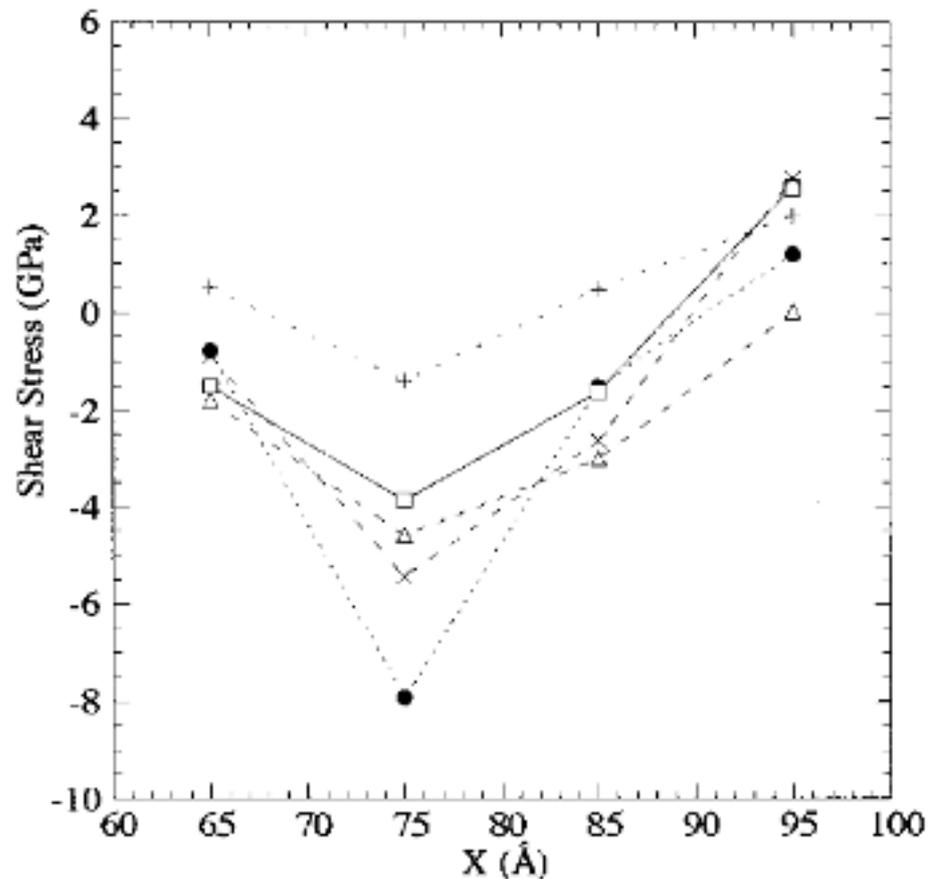


# Sintering processes of two nanoparticles



Dislocation slip is completed by about 40 ps

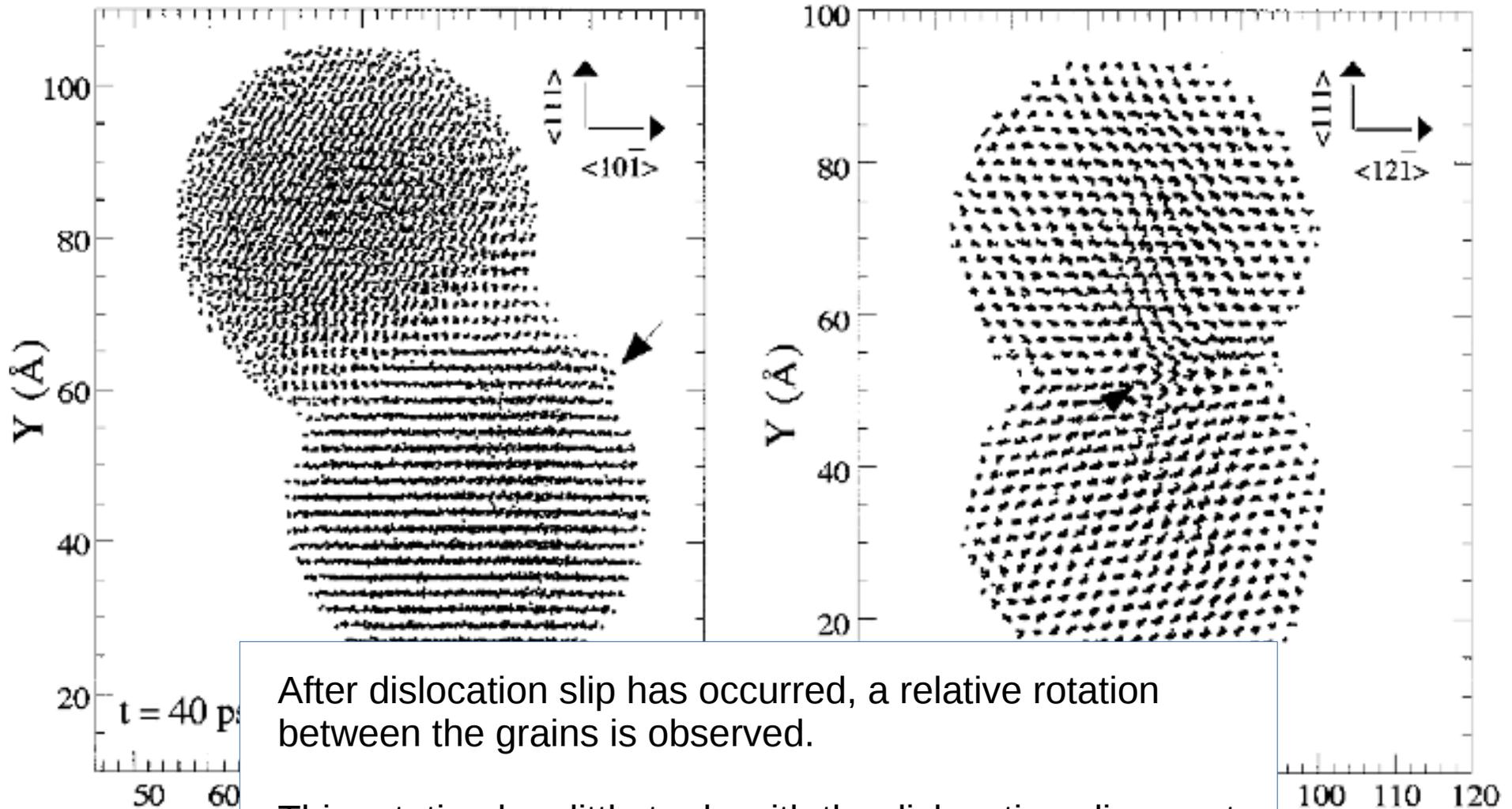
# Sintering processes of two nanoparticles



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

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

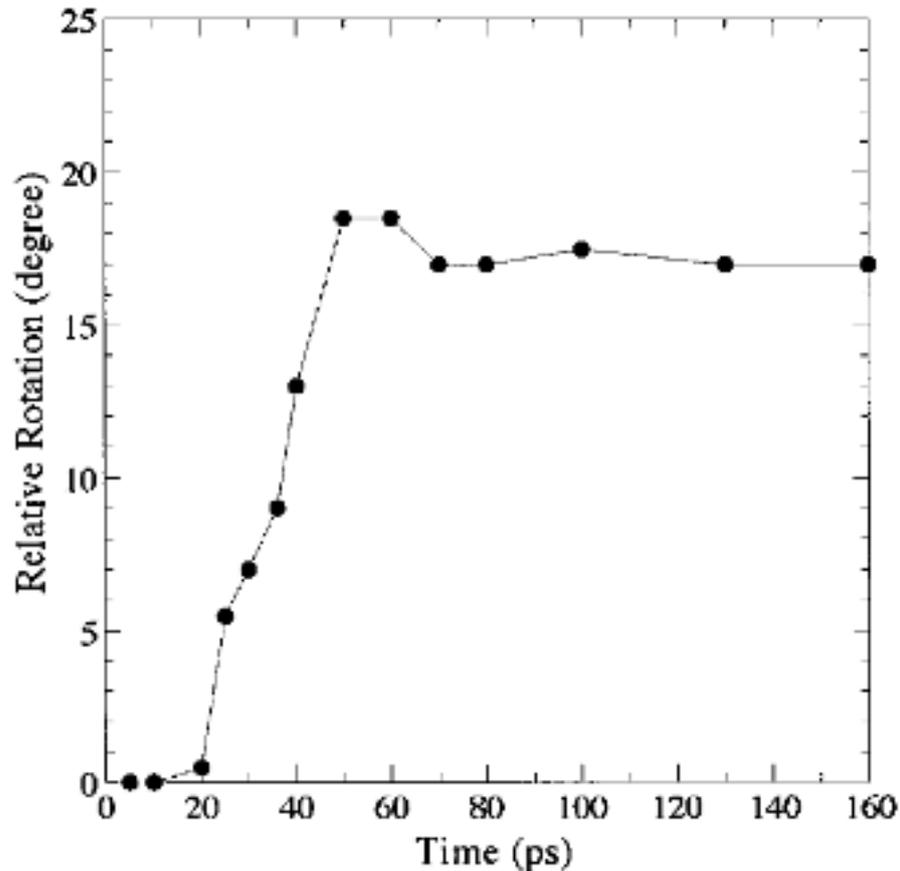
# Sintering processes of two nanoparticles



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

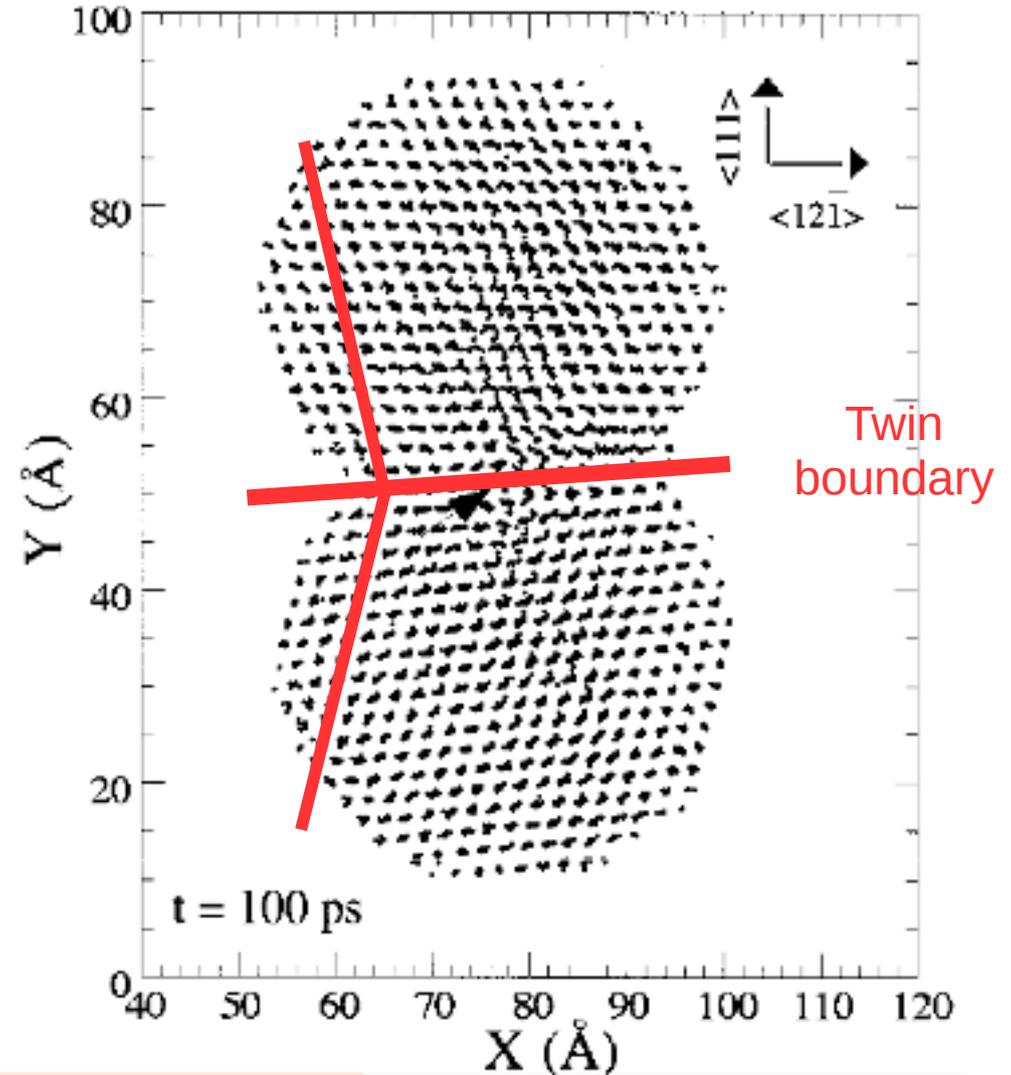
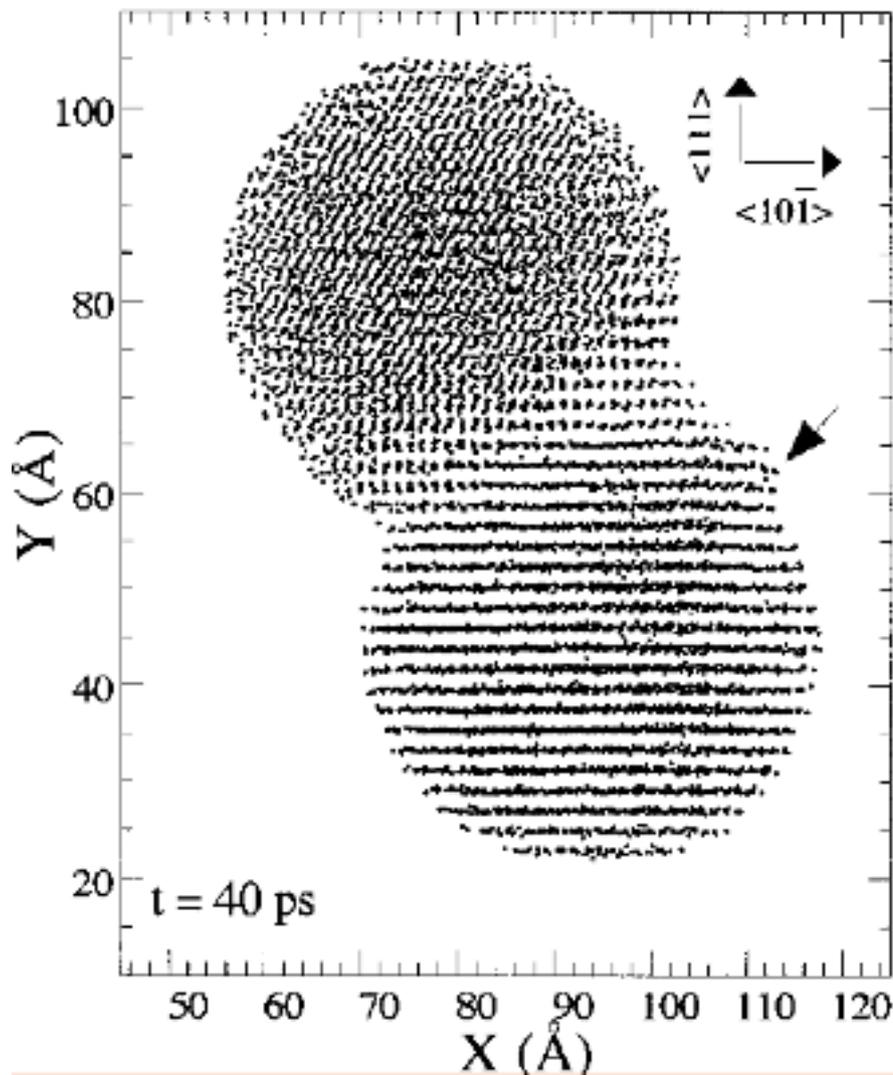


The rotation axis is the  $\langle 111 \rangle$  crystallographic axis of the sphere on the bottom.

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



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## 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*

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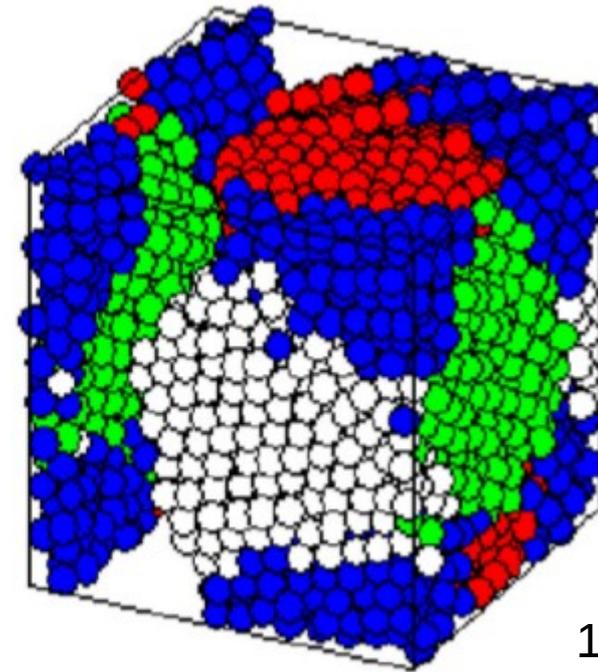
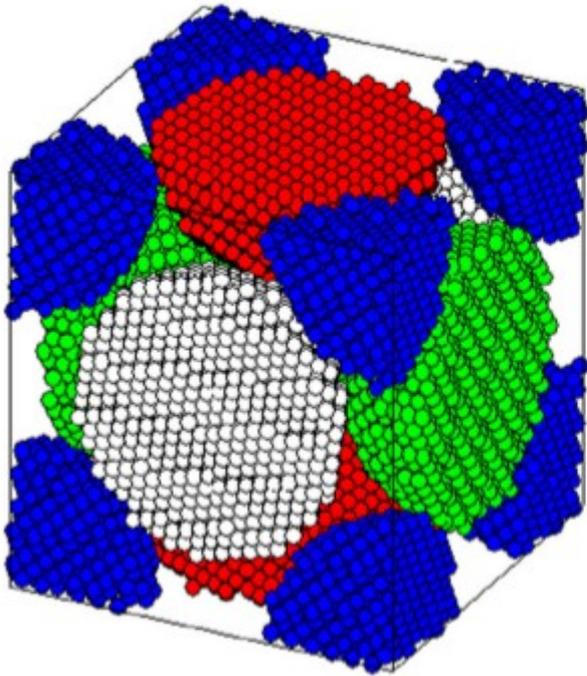
Two-sphere model

### 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.

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# Initial & final sample configurations

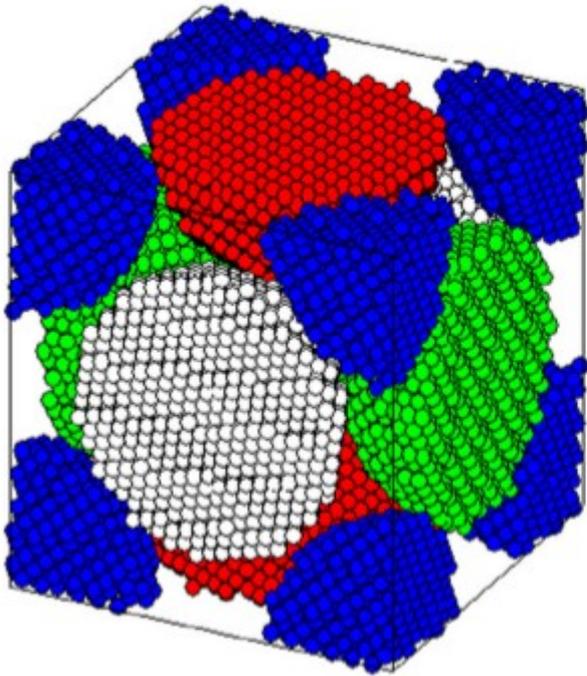


100 ps

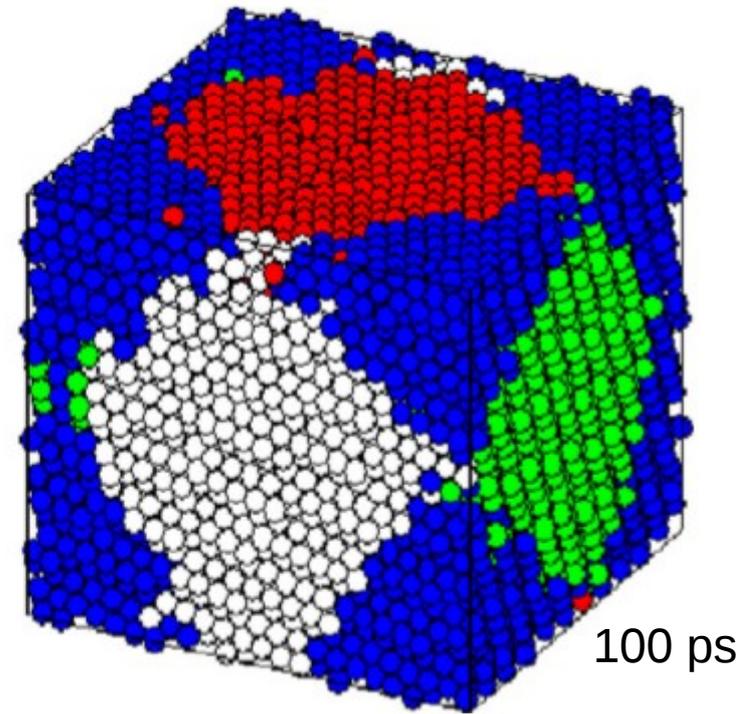
Starting (Green) compact consists of four randomly oriented equal sized spheres arranged in a closed packed configuration – NPT and periodic boundary conditions are used, and the initial particle separation is 4-6 Angstroms.

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

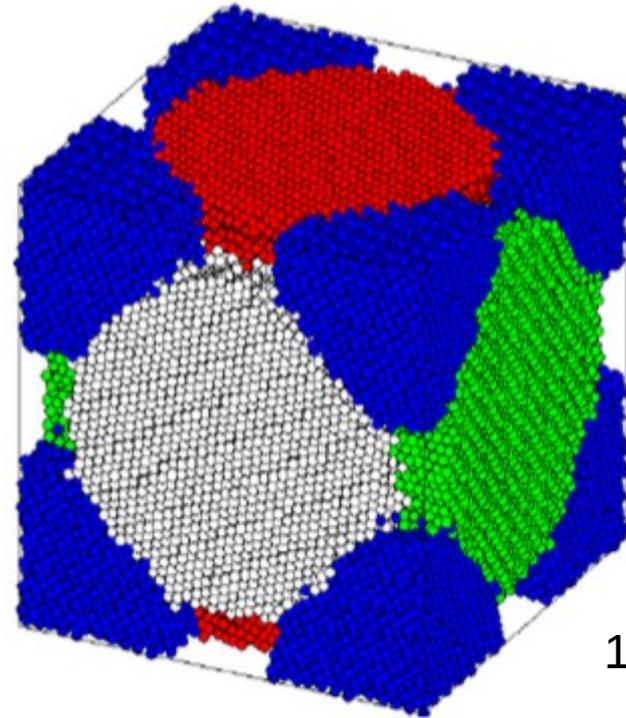
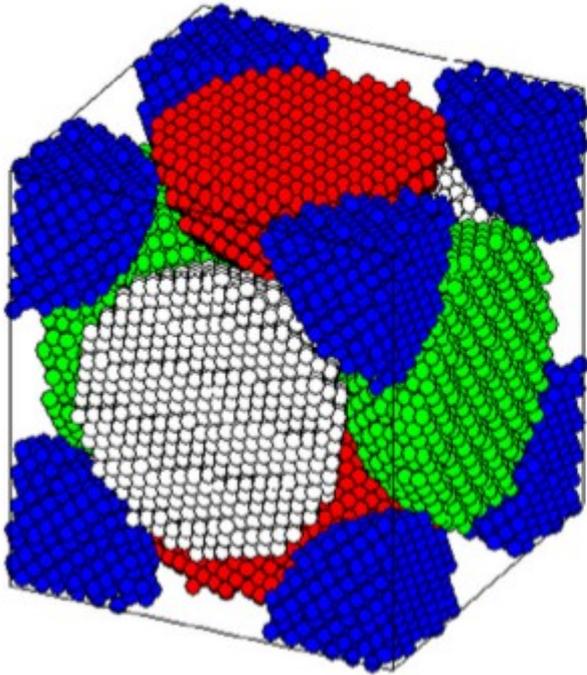


Starting (Green) compact consists of four randomly oriented equal sized spheres arranged in a closed packed configuration – NPT and periodic boundary conditions are used, and the initial particle separation is 4-6 Angstroms.



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 <sup>108</sup> and dislocation loops.

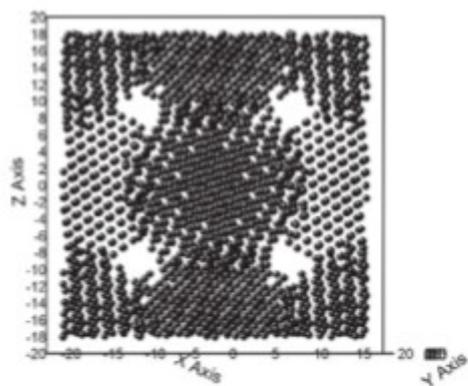
# Initial & final sample configurations



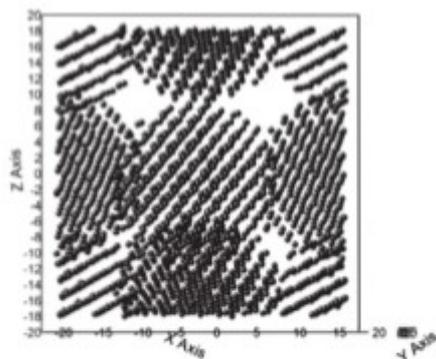
100 ps

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.

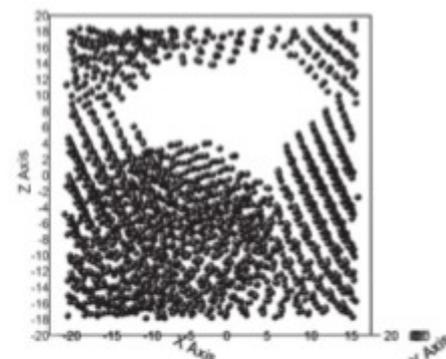
At the largest sizes considered (12nm), the pores between particles become disconnected and quasi-spherical. The pore shrinkage is significant, but full densification is not reached



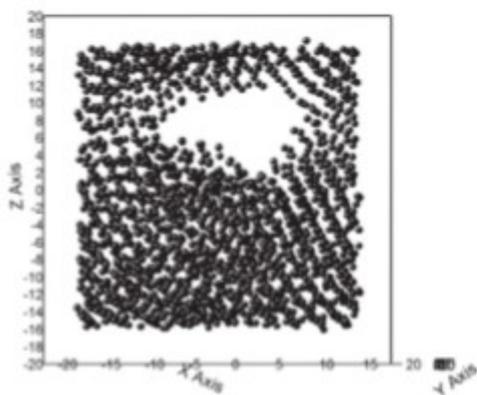
$t = 0\text{ps}$  porosity: 0.46



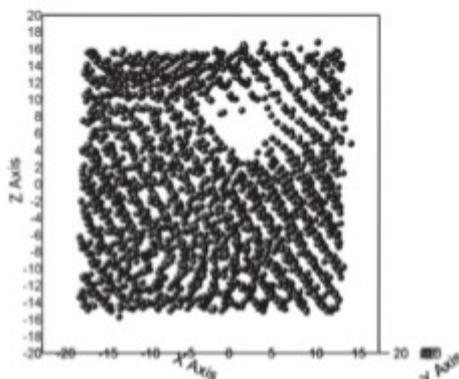
$t = 5\text{ps}$  porosity: 0.46



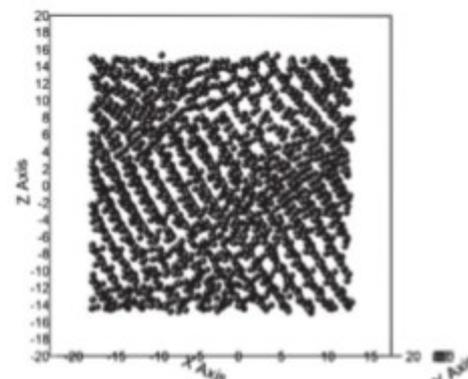
$t = 10\text{ps}$  porosity: 0.45



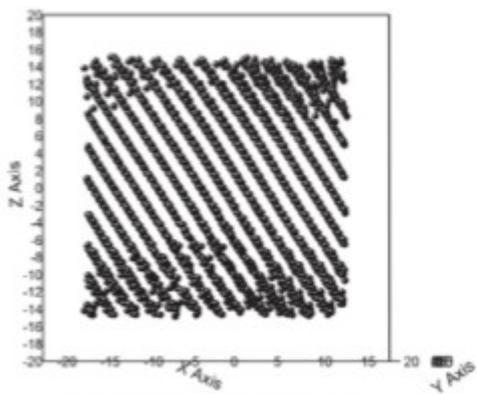
$t = 25\text{ps}$  porosity: 0.22



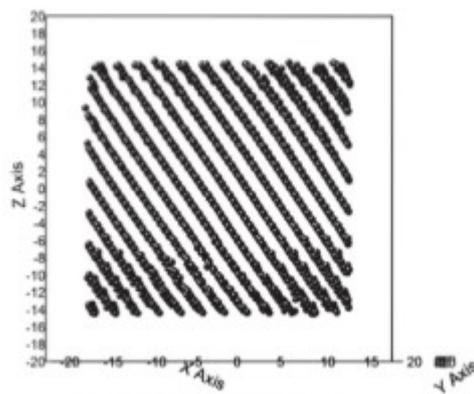
$t = 32.5\text{ps}$  porosity: 0.11



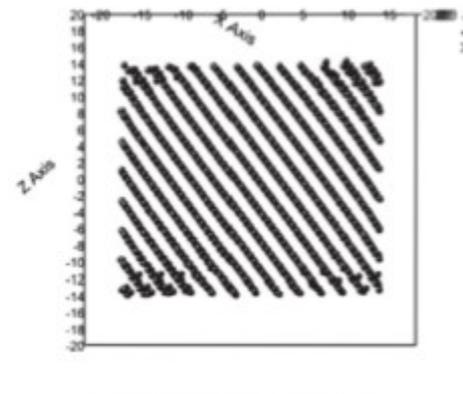
$t = 37.5\text{ps}$  porosity: 0.05



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

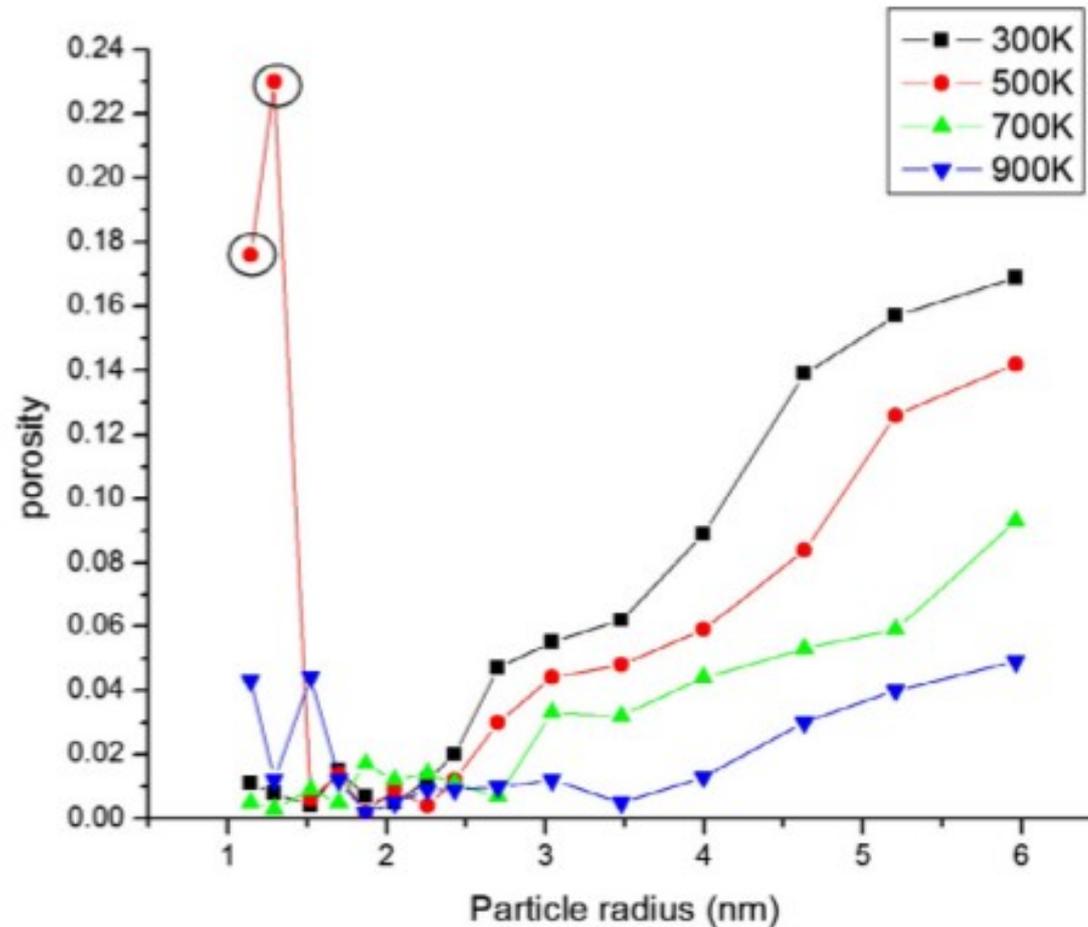


$t = 50\text{ps}$  porosity: 0.01

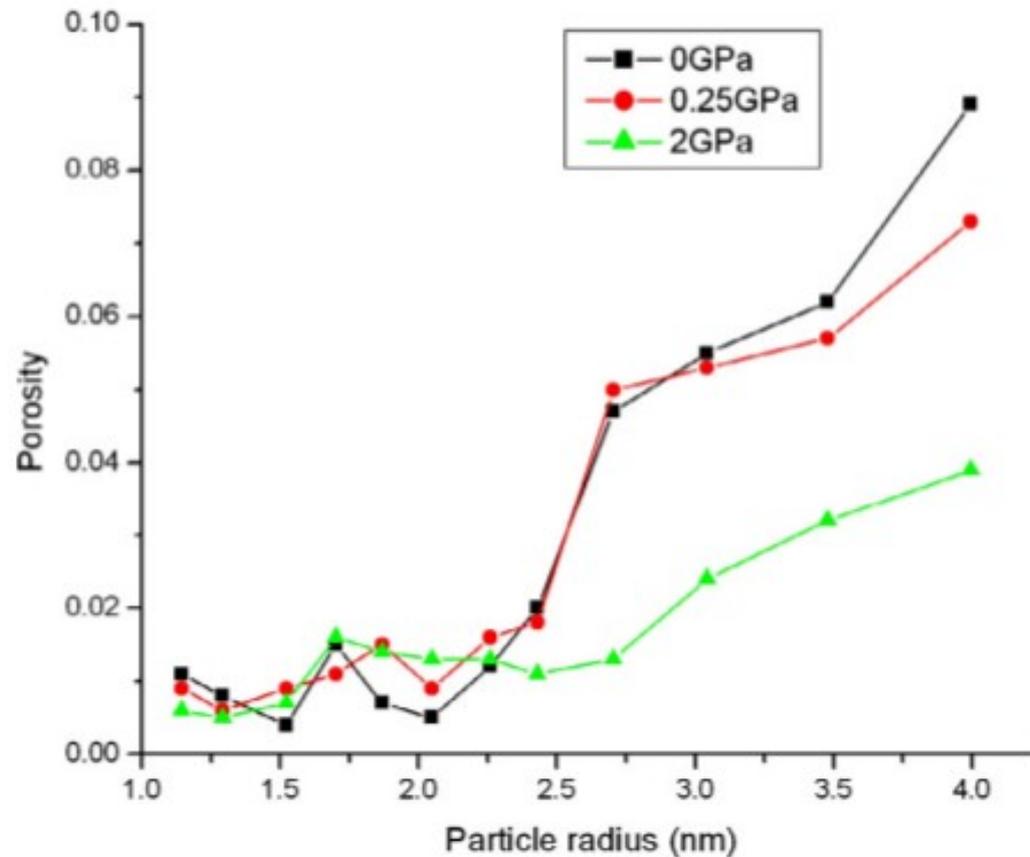


$t = 250\text{ps}$  porosity: 0.01

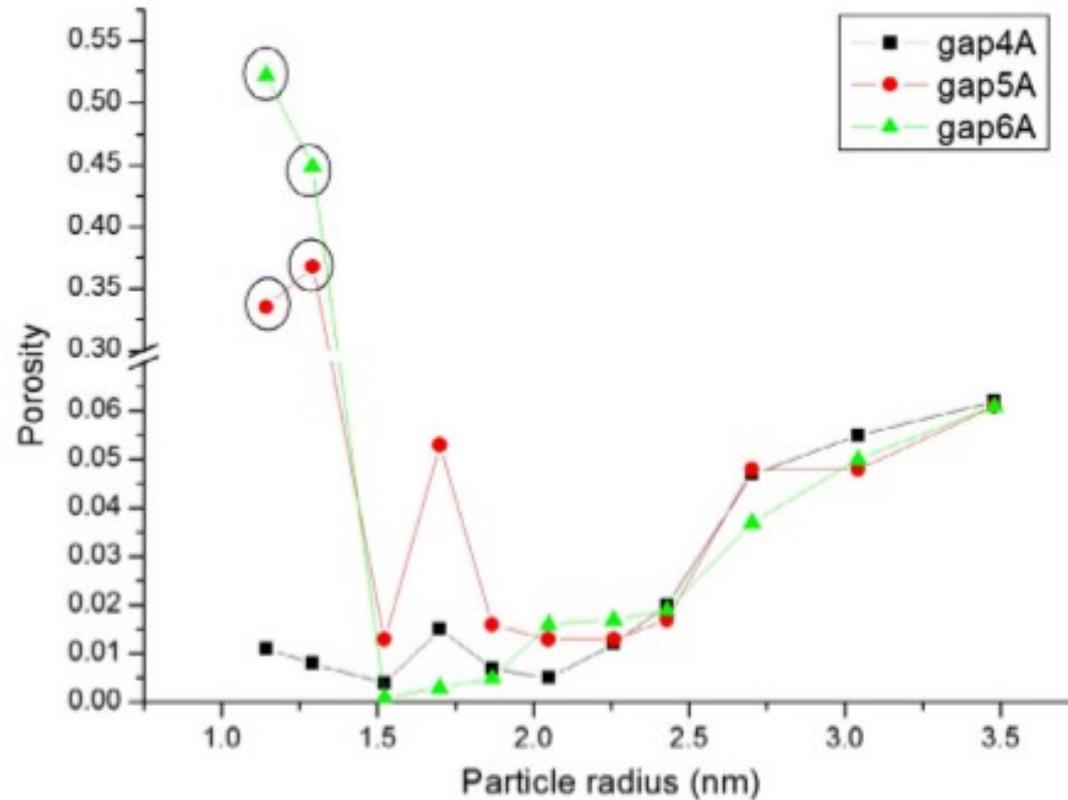
# Final porosity as a function of particle radius – temperature effects



# Final porosity as a function of particle radius – pressure effects



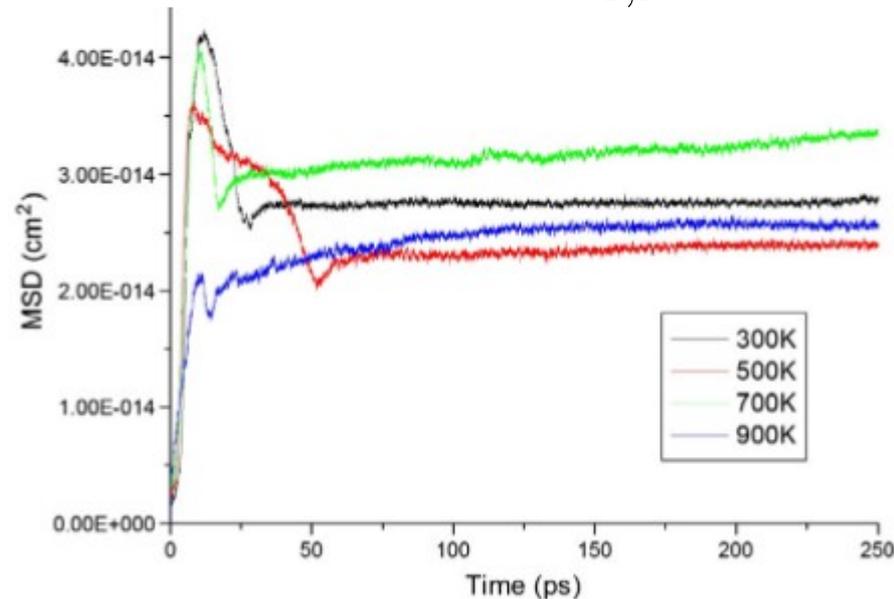
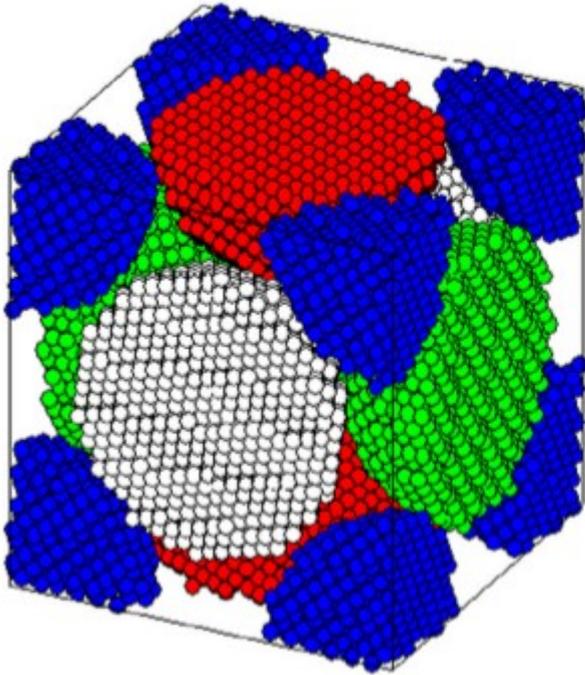
# Final porosity as a function of particle radius – initial gap effects



# 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?