Thermally-Activated Processes :

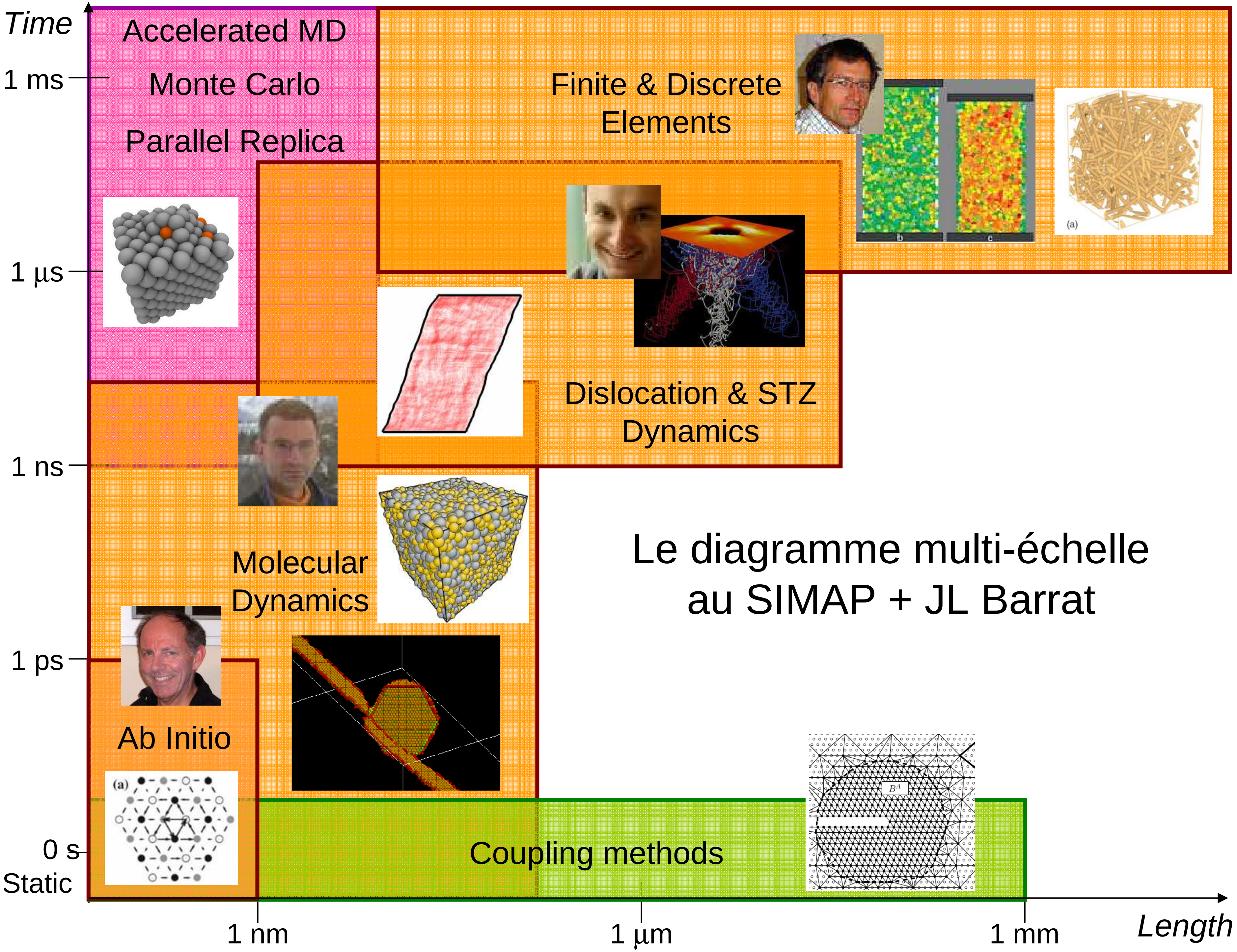
defected crystals and metallic glasses

David RODNEY

SIMAP, INP Grenoble, FRANCE

INP Grenoble

Le diagramme multi-échelle au SIMAP + JL Barrat



Time

1 ms

1 µs

1 ns

1 ps

0 s

Static

1 nm

1 µm

1 mm

Length

Accelerated MD

Monte Carlo

Parallel Replica

Finite & Discrete Elements

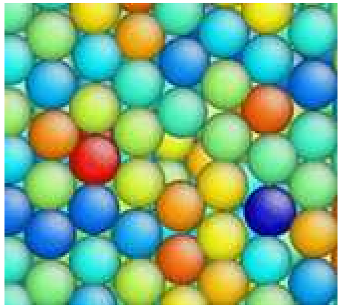
Dislocation & STZ Dynamics

Molecular Dynamics

Ab Initio

Coupling methods

Consequences of MD timescale limitation

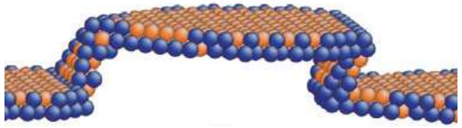


MD can not simulate **diffusion-controlled processes**

➡ no alloy decomposition, segregation, vacancy clustering

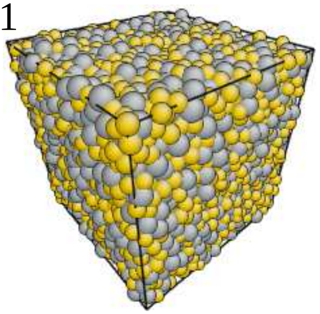
For **plasticity**: $\dot{\varepsilon}_{simul} \approx \frac{0.1 \sim 1}{1\,\mu s} \approx 10^5 s^{-1} \rangle\rangle\, \dot{\varepsilon}_{\exp} \approx 10^{-3} s^{-1}$

➡ MD limited to athermal plasticity, no climb or cross-slip



Mordehai, Phil. Mag. 2008

For **glasses**: $\dot{T}_{simul} \approx \frac{1000\,K}{1\,\mu s} \approx 10^9 K.s^{-1} \rangle\rangle\, \dot{T}_{\exp} \approx 10^3 K.s^{-1}$

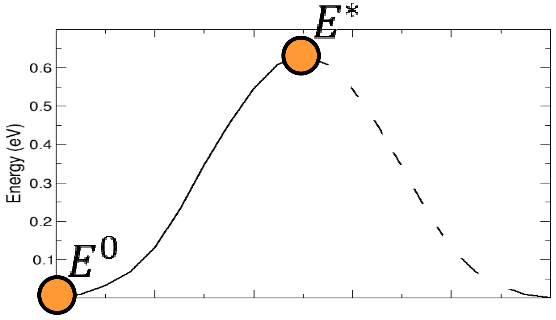


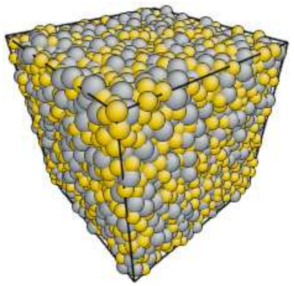
➡ Numerical glasses far less relaxed than real glasses

Static approach

From the classical harmonic Transition State Theory:

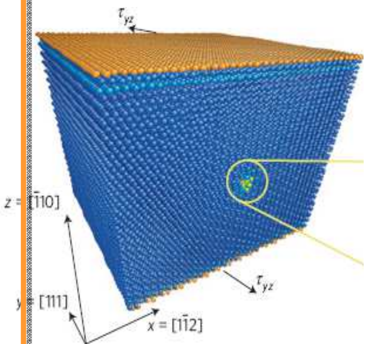
$$\Gamma^{hTST}_{classic} = \underbrace{\frac{\prod_{i=1}^{3N-3}\nu_i^{init}}{\prod_{k=1}^{3N-4}\nu_k^{*}}}_{\textit{Eigenfrequencies from diagonalization of the Hessian matrix}} \exp\underbrace{\left(-\frac{E^{*}-E^{0}}{kT}\right)}_{\textit{Activation energy}}$$

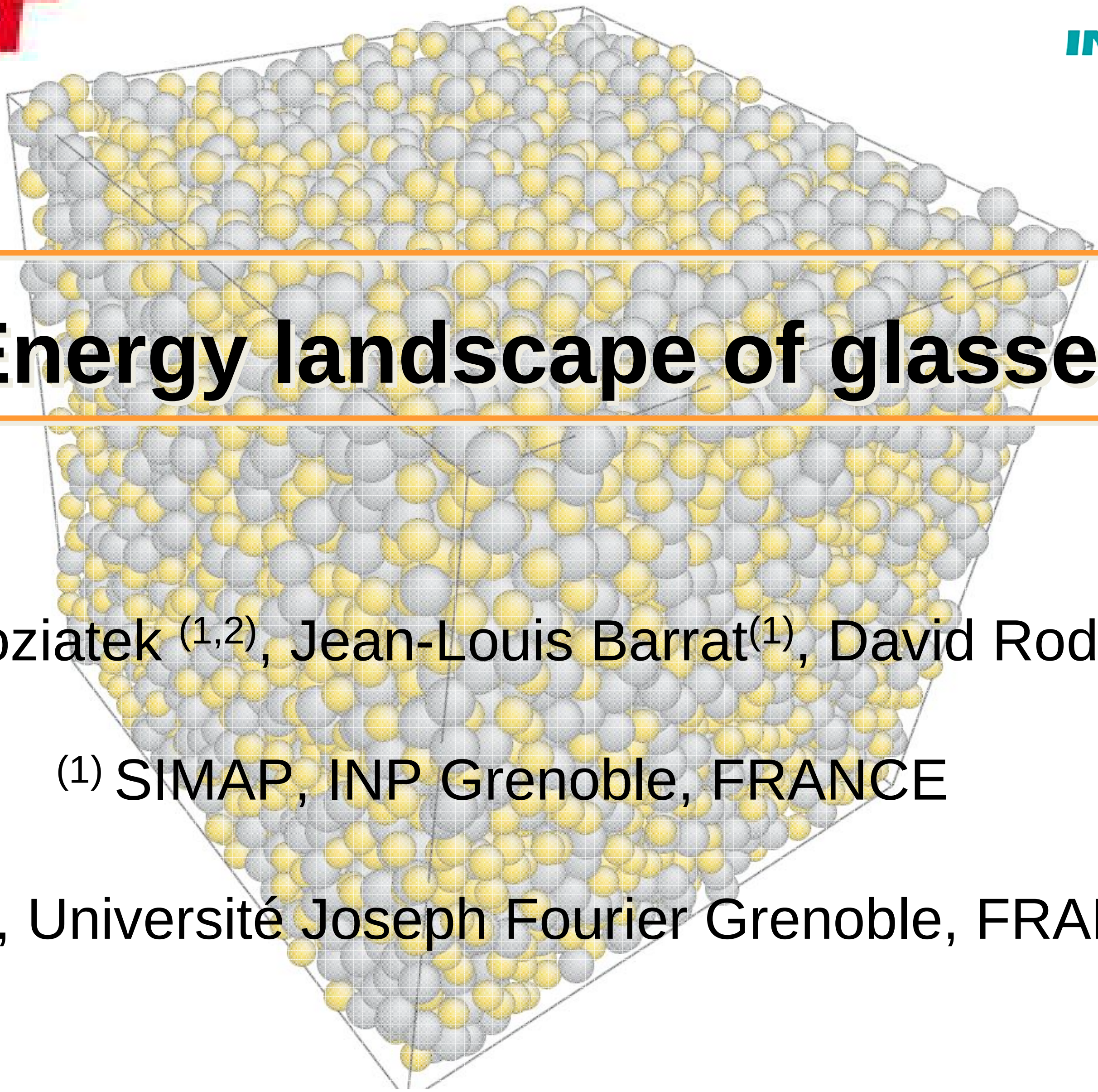




- All information in the initial and activated states
- All we have to do (!) is to find the activated states for the processes of interest:

Static methods:
- Nudged Elastic Band method
- Activation-Relaxation Technique





Energy landscape of glasses

Pawel Koziatek (1,2), Jean-Louis Barrat(1), David Rodney(2)

(1) SIMAP, INP Grenoble, FRANCE

(2) LiPhy, Université Joseph Fourier Grenoble, FRANCE

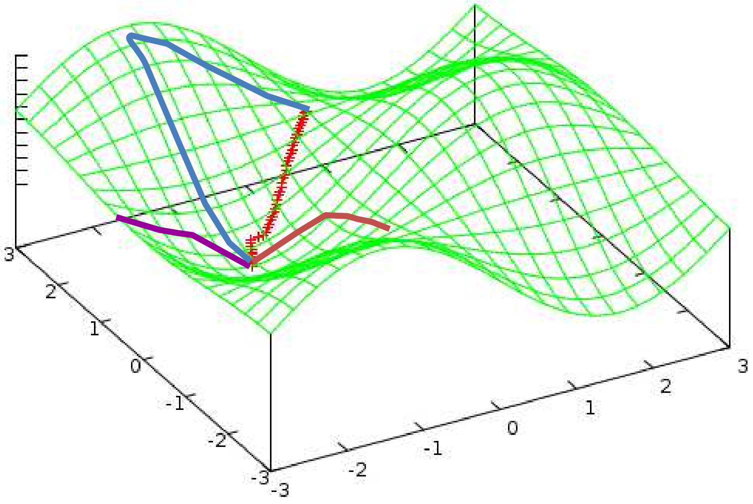
Rodney, Tanguy, Vandembroucq, *Model. Sim. Mat. Sci. Eng.* **19**, 083001 (2011)

Exploration of the Potential Energy Landscape

[Mousseau, PRE 1998
Cancès et al,JCP 2009
Rodney&Schuh, PRB 2009]

Activation-Relaxation Technique

Singled-ended method to determine distributions of transition pathways



1- Choose random direction in phase space

2- Move along that direction + limited energy minimization in orthogonal hyperplane until a configuration with 1 negative curvature

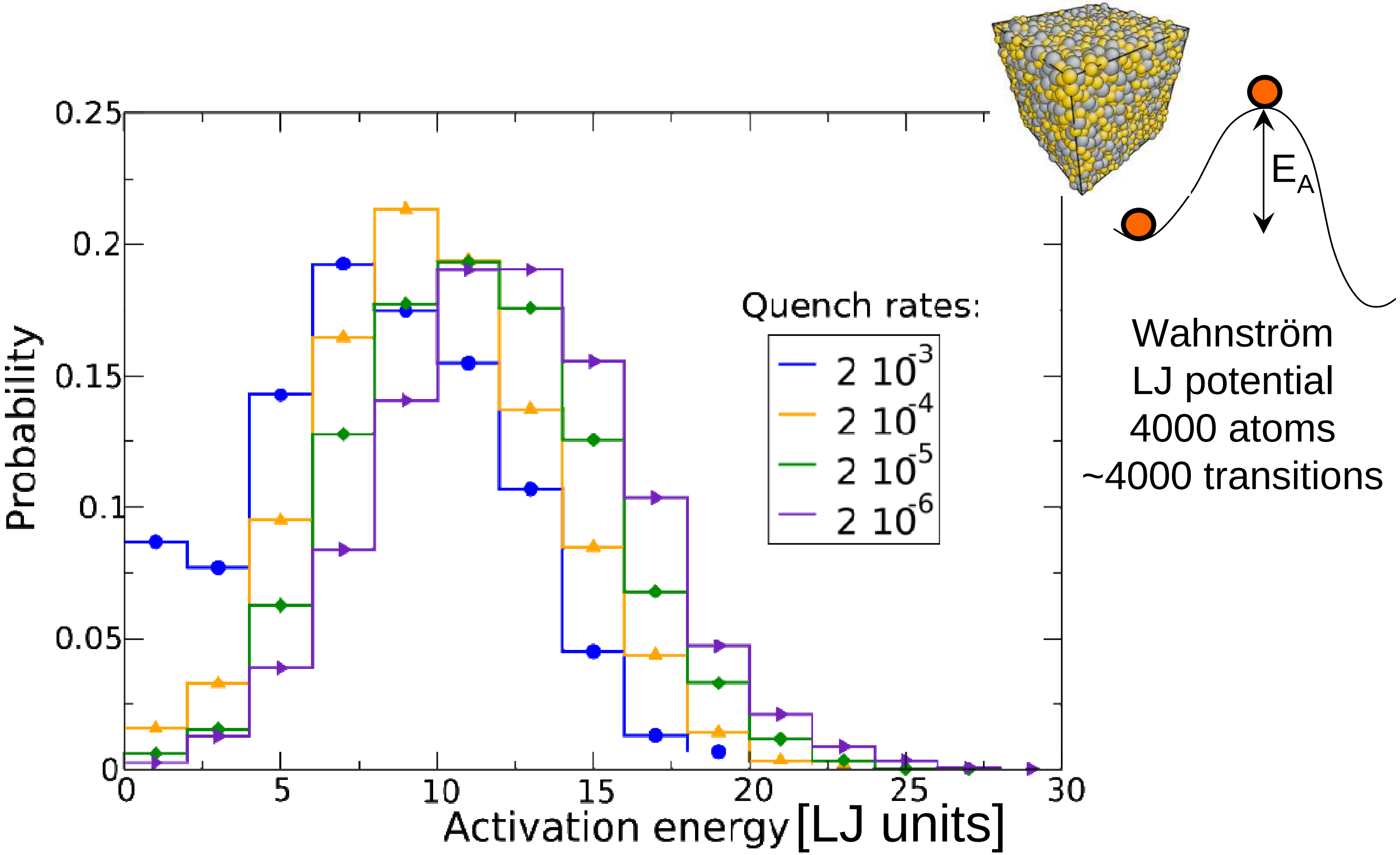
3- Follow negative curvature to saddle point

4- Relax forward and backward to find the transition path

✗ find all transitions

✓ obtain representative samples and compute distributions

Distribution of activation energies



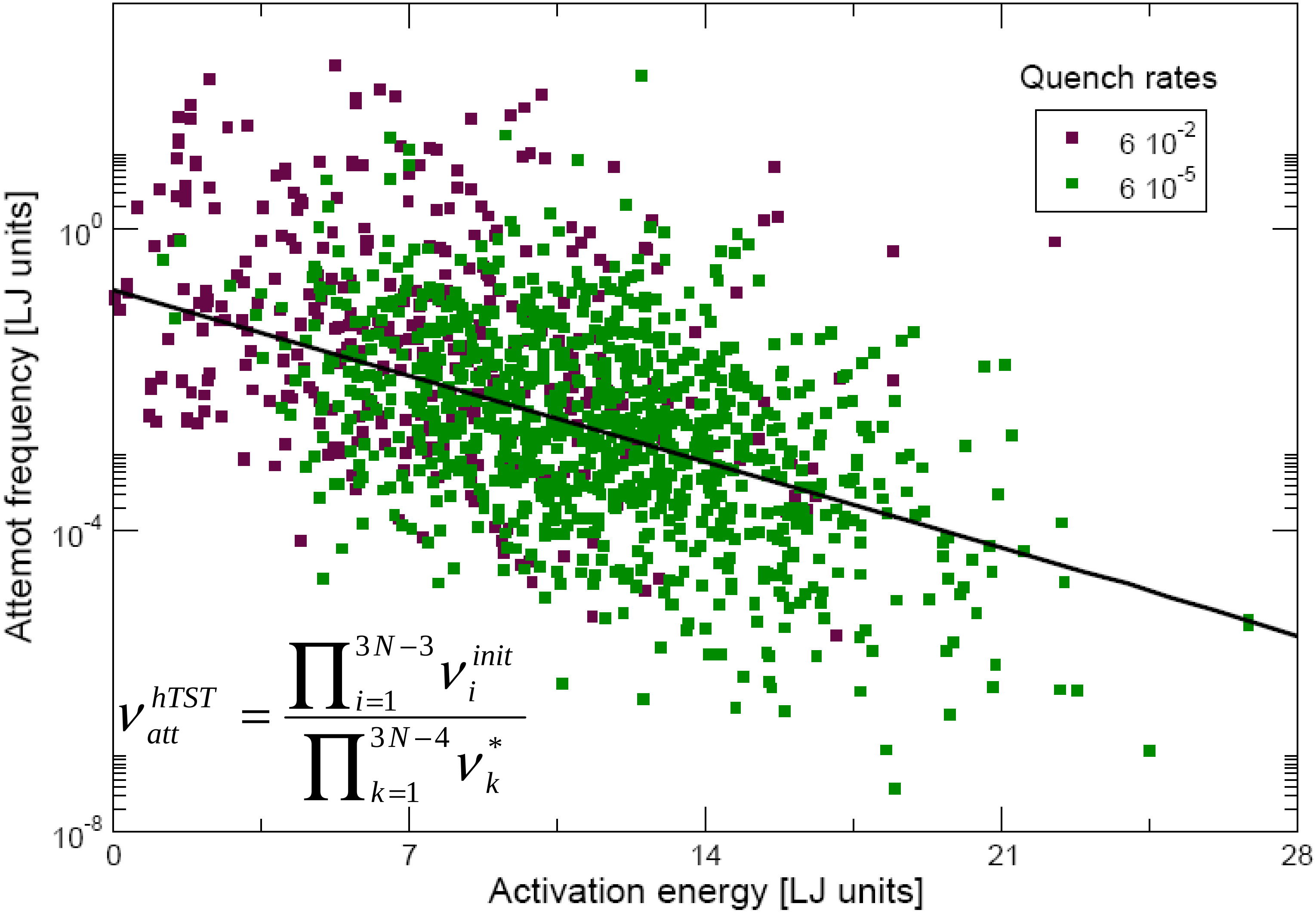
Wahnström
LJ potential
4000 atoms
~4000 transitions

- ✓Complex energy landscape
- ✓Low-energy barriers due to high quench rate

Attempt frequencies

$$\Gamma_{classic}^{hTST} = \underbrace{\frac{\prod_{i=1}^{3N-3} \nu_i^{init}}{\prod_{k=1}^{3N-4} \nu_k^{*}}}_{\text{Eigenfrequencies from diagonalization of the Hessian matrix}} \underbrace{\exp\left(-\frac{E^{*} - E^{0}}{kT} \right)}_{\text{Activation energy}}$$

Attempt frequencies



$$\nu_{att}^{hTST} = \frac{\prod_{i=1}^{3N-3} \nu_{i}^{init}}{\prod_{k=1}^{3N-4} \nu_{k}^{*}}$$

- ✓ Very large frequency range
- ✓ Inverse Meyer Neldel rule: $\nu_{att} \propto \exp\left(-E_A / E_0\right)$

Low-temperature dislocation glide: quantum correction

Laurent Proville(1), David Rodney(2)

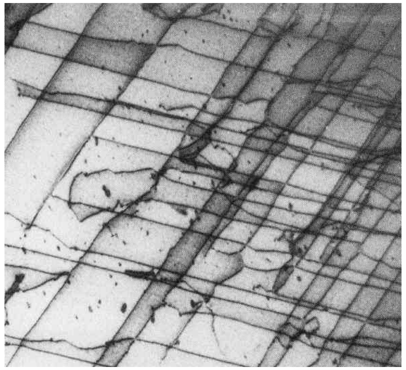
(1) SRMP, CEA Saclay, FRANCE

(2) SIMAP, INP Grenoble, FRANCE

Proville, Rodney, Marinica, *Nature Materials* **11**, 845 (2012)

Thermally-activated plasticity

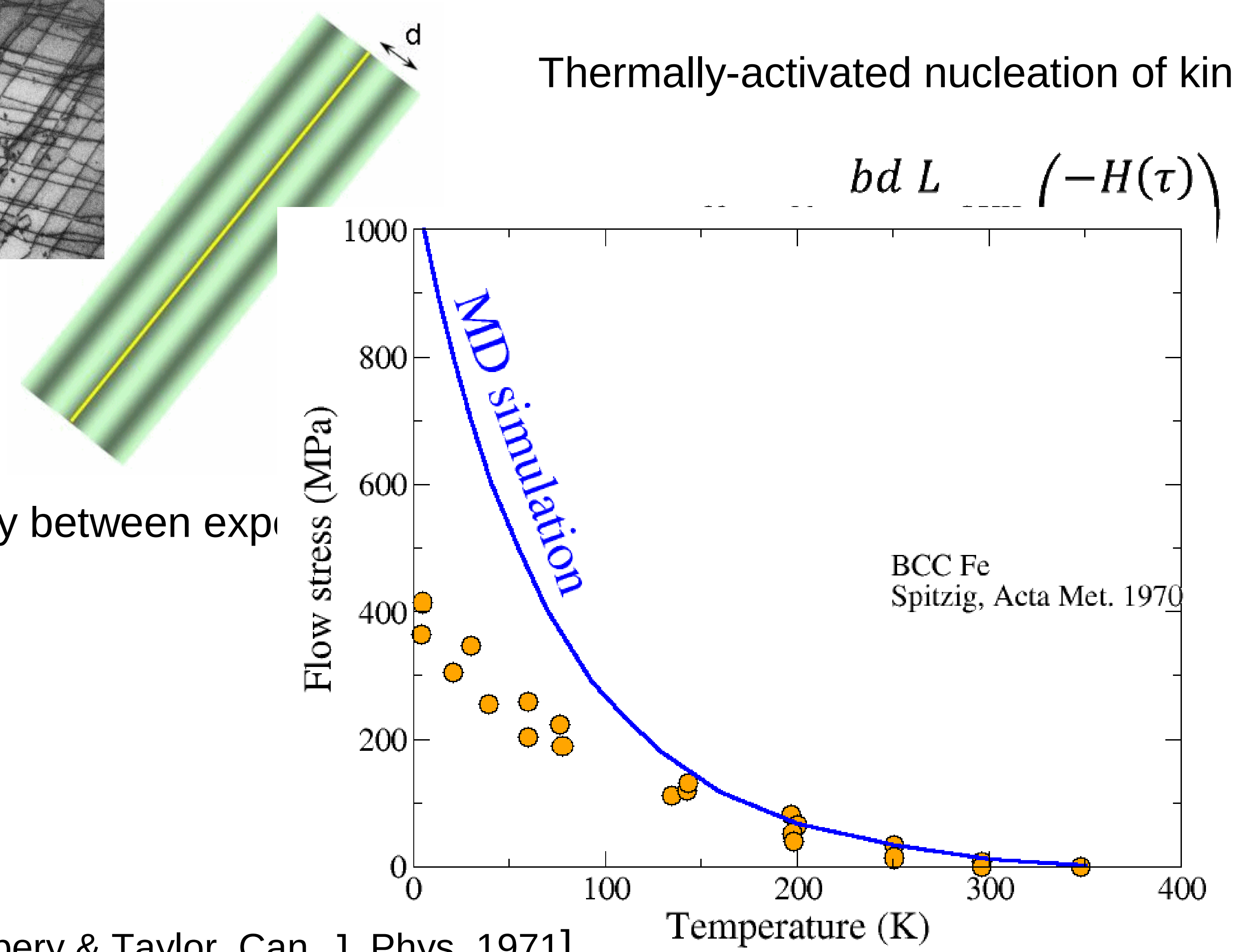
- High Peierls stress dislocations (ex: ½<111> screw dislocation in BCC crystals)



Thermally-activated nucleation of kink pairs

$bd\ L$ $\left(-H(\tau)\right)$

- Discrepancy between exp

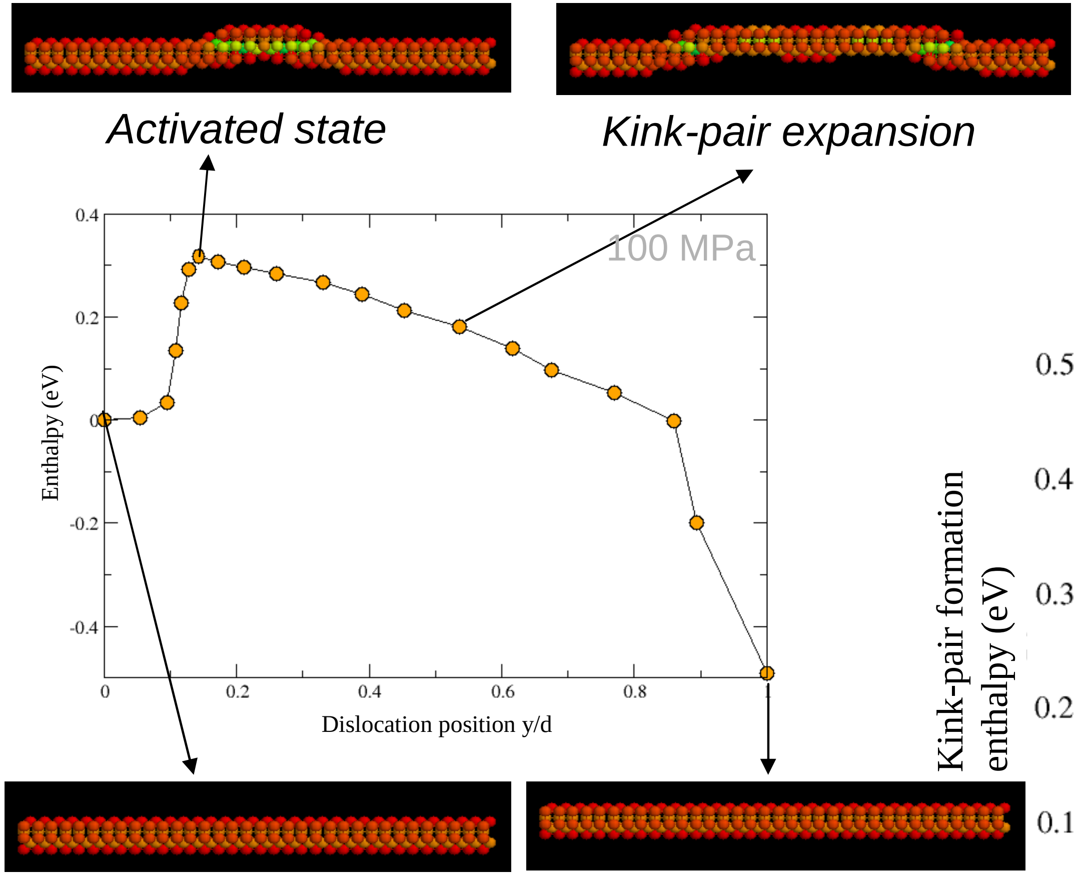


[Basinski, Duesbery & Taylor, Can. J. Phys. 1971]

Kink-pair formation enthalpy

[Rodney, PRB 2007]

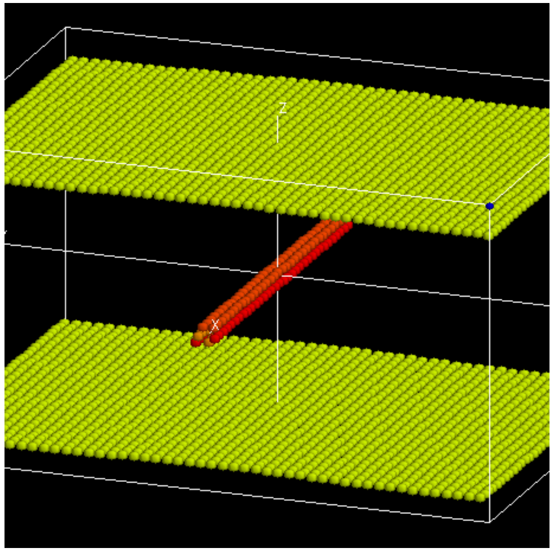
NEB in 3D cell with an initial path
containing an expanding pair of kinks

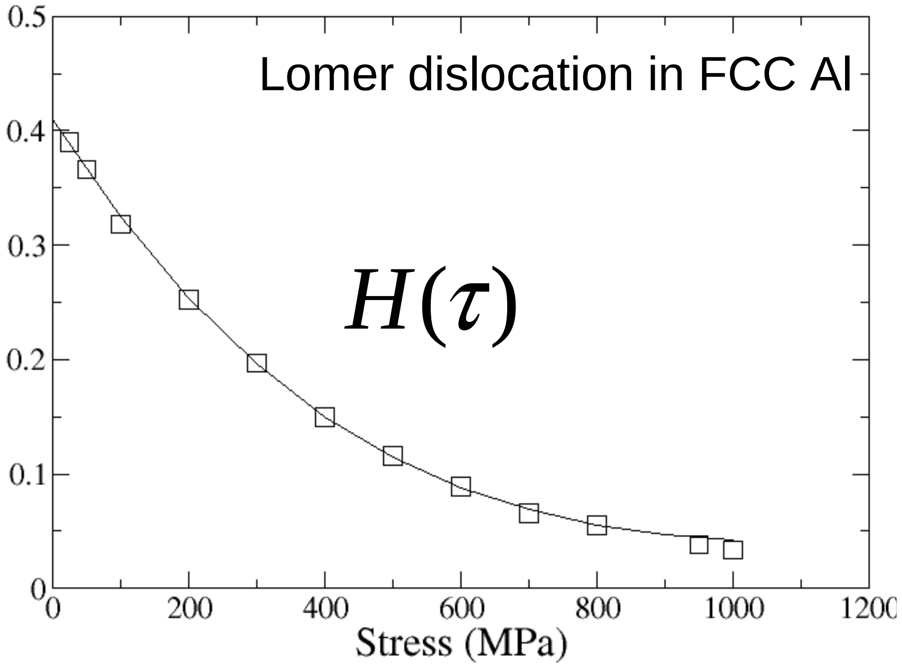

Activated state

Kink-pair expansion

Initial state

Final state





Quantum harmonic Transition State Theory

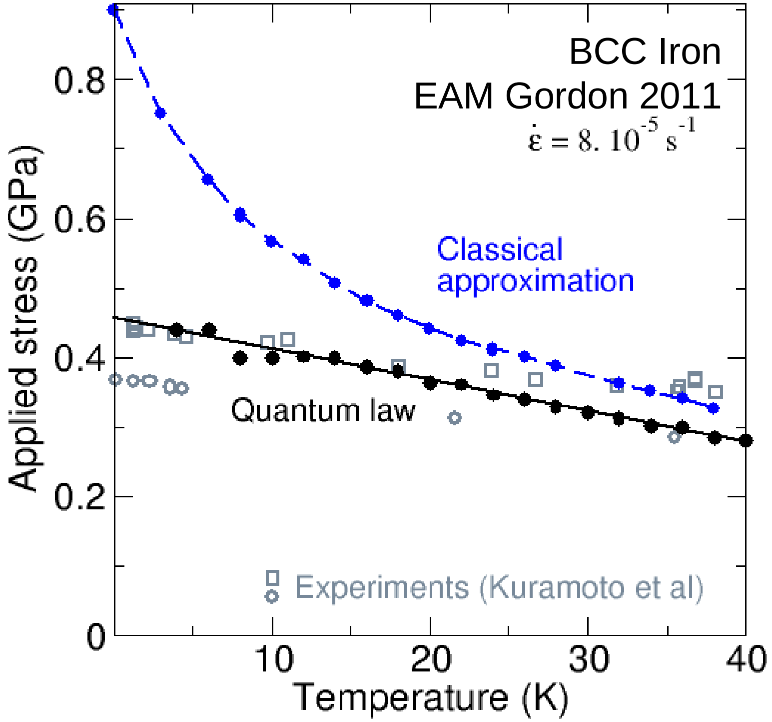
[Wigner, Trans. Faraday Soc. 1938]

- Treat harmonic oscillators quantum mechanically: $Z = 1\Big/\left(\frac{h\nu}{kT}\right) \rightarrow 1\Big/2\sinh\left(\frac{h\nu}{2kT}\right)$

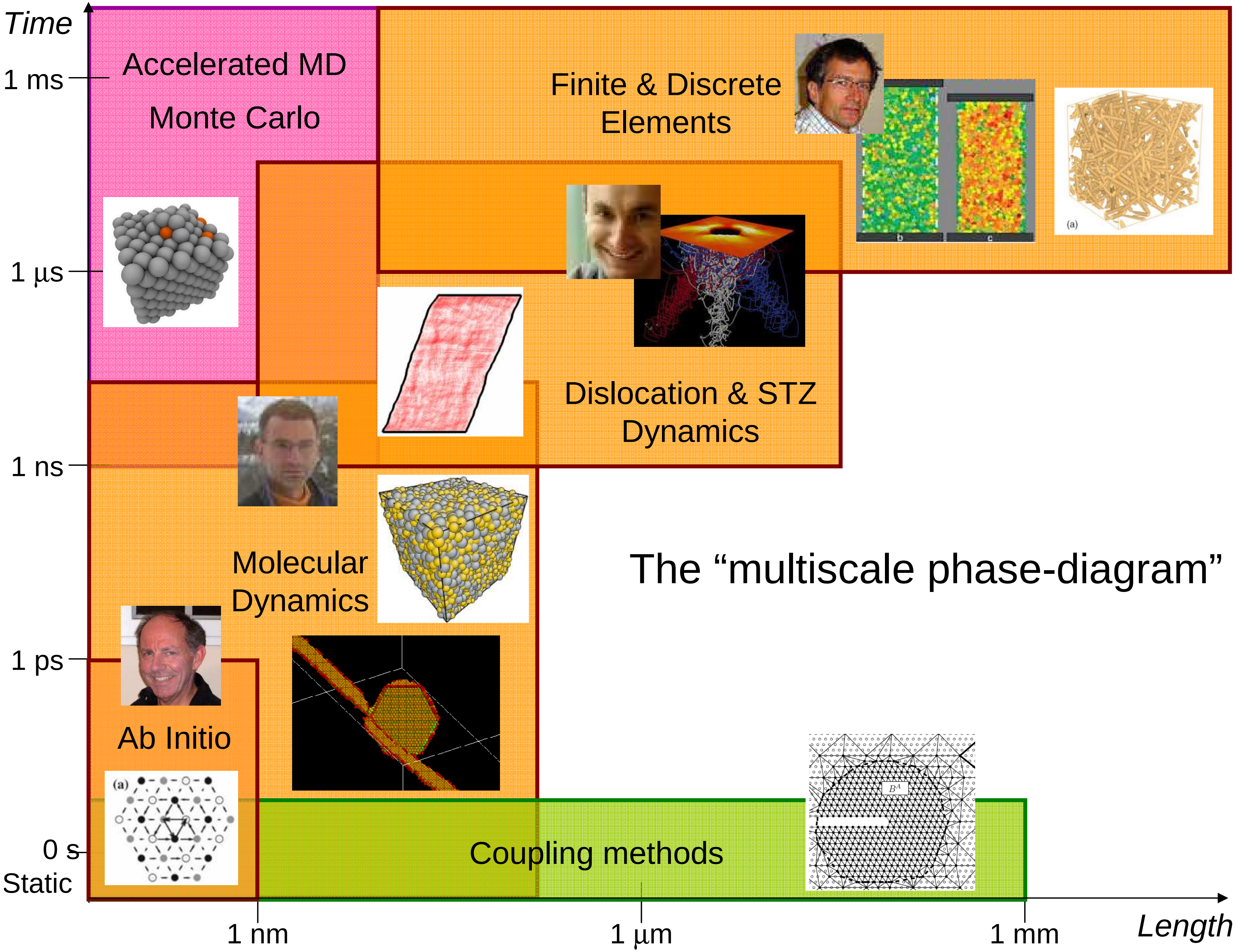
$$\Gamma_{quantum} = L\sqrt{\frac{2\pi m}{kT}}\left(\frac{kT}{h}\right)^2 \frac{\prod_{i=1}^{3N-3} 2\sinh\left(h\nu_i^{init}/2kT\right)}{\prod_{k=2}^{3N-4} 2\sinh\left(h\nu_k^{*}/2kT\right)}\exp\left(-\frac{H(\tau)}{kT}\right)$$

$$\dot{\gamma} = \rho b d \Gamma_{quantum}(\tau, T)$$

$$\tau(T)$$



The “multiscale phase-diagram”



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1 nm

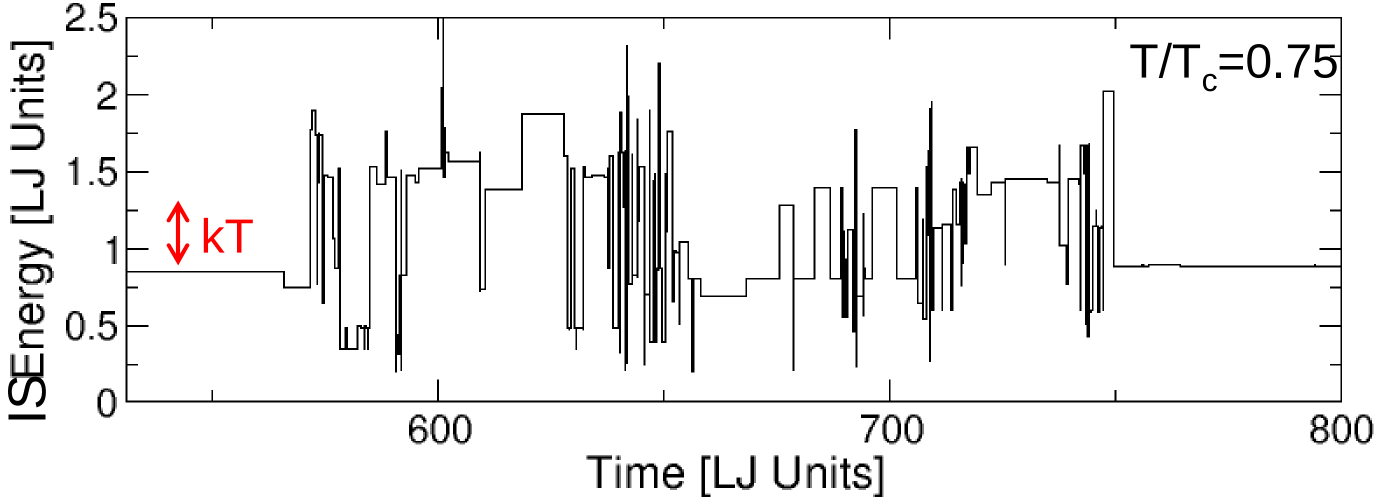
1 μm

1 mm

Length

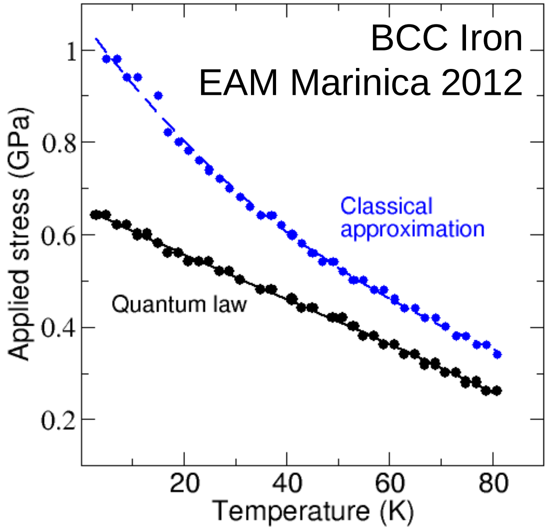
Challenges ahead

- Better relaxed glasses
- Exhaustive sampling is impossible
- Building database is difficult because glasses rarely return to previous configurations
- Transitions are controlled by free energy barriers between metabasins rather than single-step barriers between basins



Challenges ahead

- Realism of interatomic potentials
- Effect of non-glide stresses
- Quantum corrections for other processes: defect migration, low-temperature thermal conductivity, …

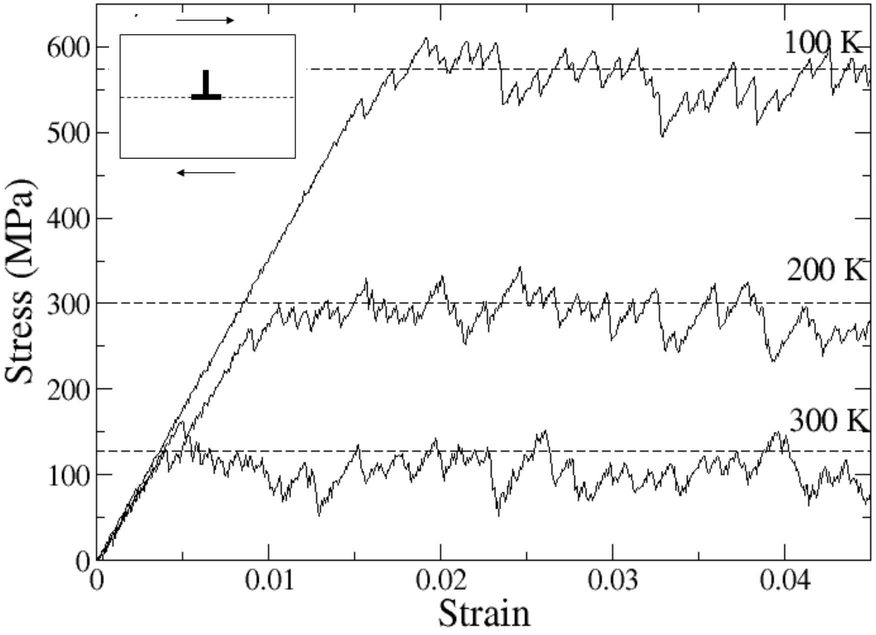


Dislocation kinetics

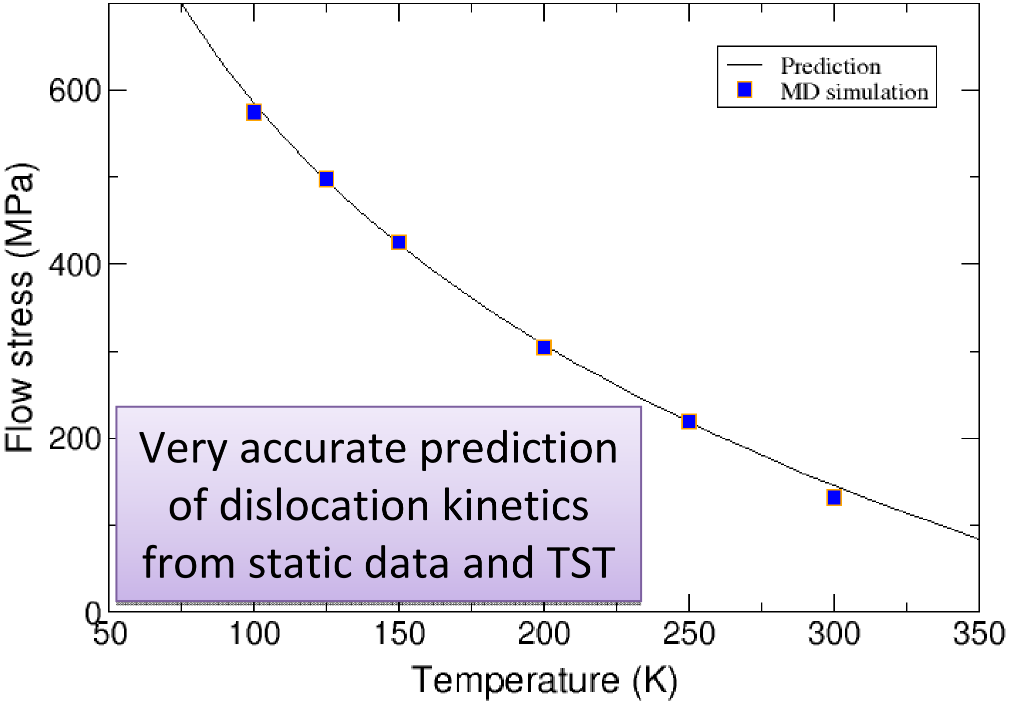
[Rodney, PRB 2007]

From Orowan's law: $$\dot{\gamma} = \rho b d \nu_{att} \exp\left(-\frac{H(\tau)}{kT}\right) \Rightarrow \tau(T)$$

MD simulation at $\dot{\gamma} = 1.5 \times 10^7 s^{-1}$

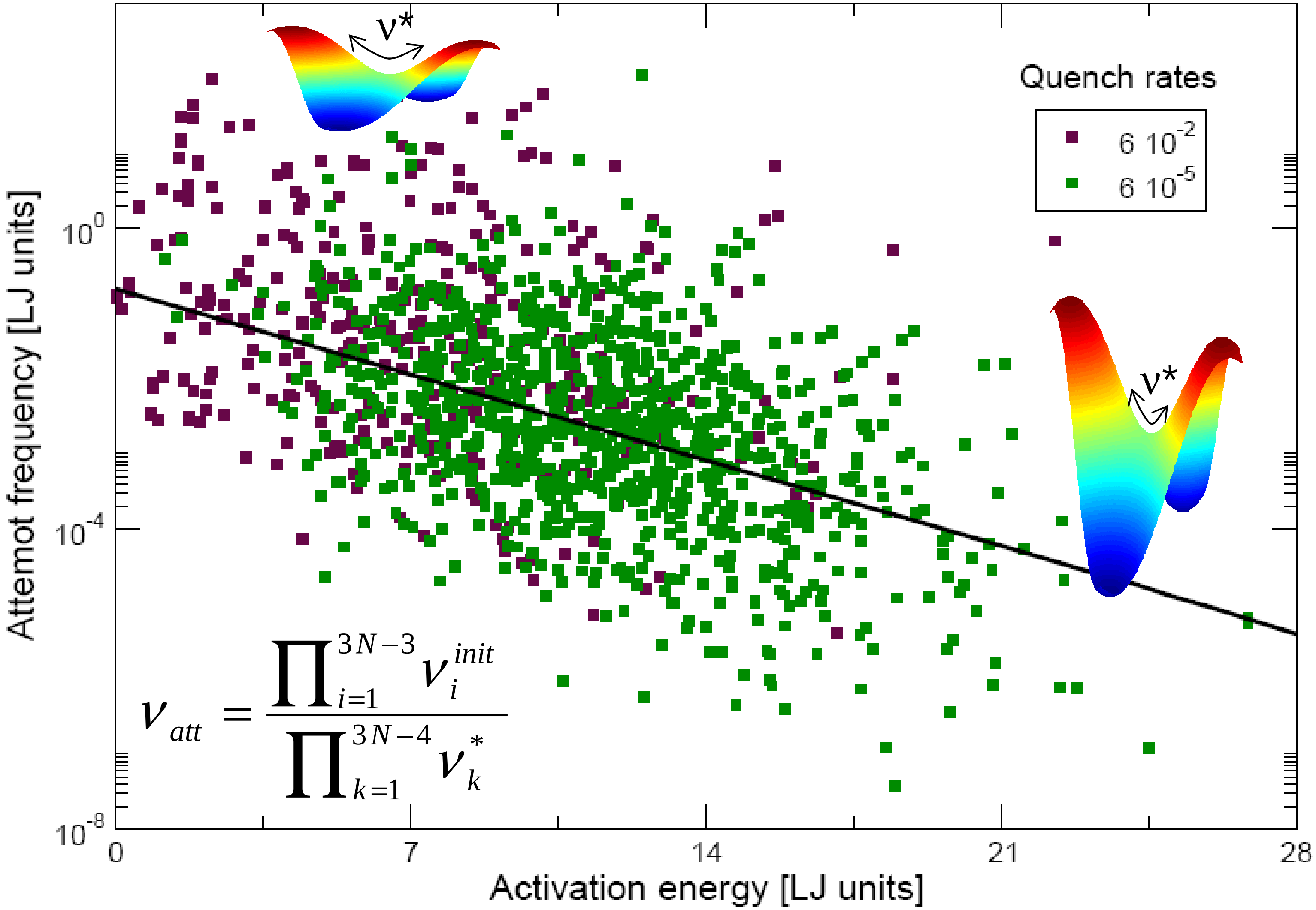


Comparison Statics/Dynamics



Very accurate prediction of dislocation kinetics from static data and TST

Attempt frequencies



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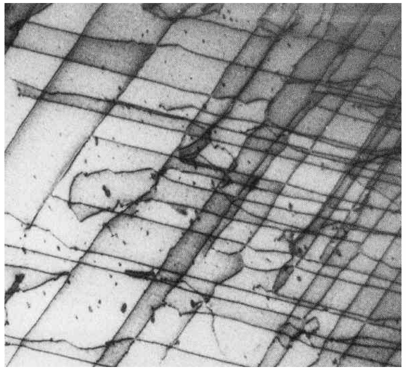
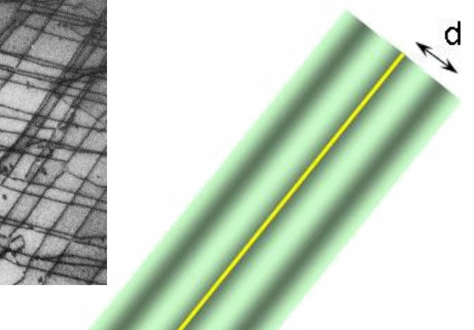
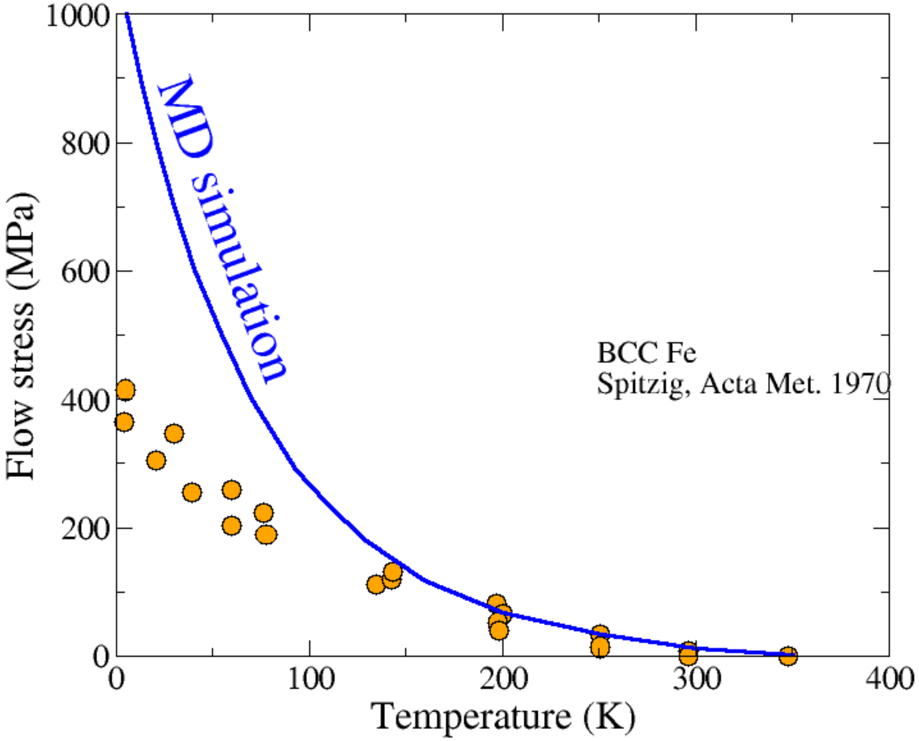




Thermally-activated nucleation of kink pairs

$$v = \nu_D \frac{bd}{l_c}\frac{L}{l_c}\exp\left(\frac{-H(\tau)}{k_B T}\right)$$

- Discrepancy between expe



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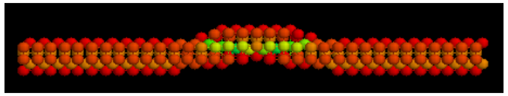
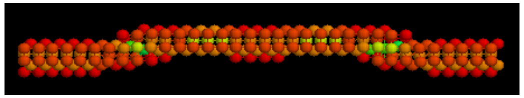
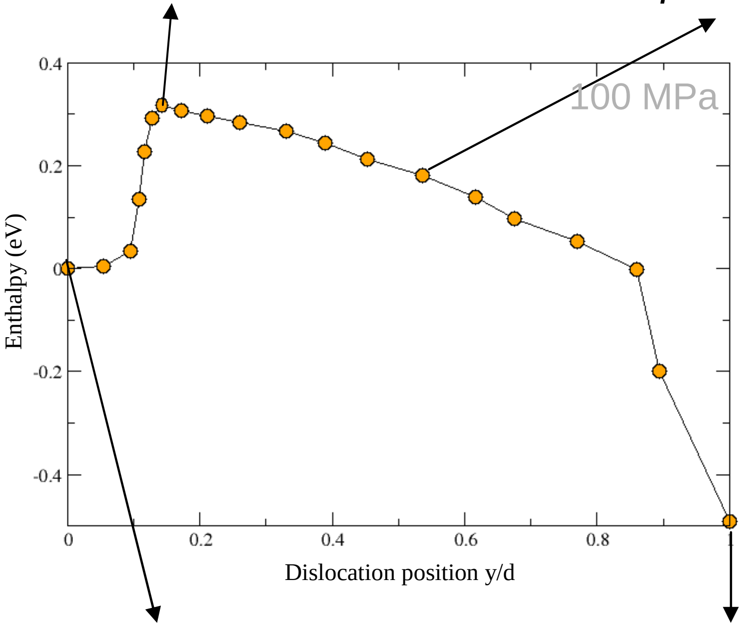
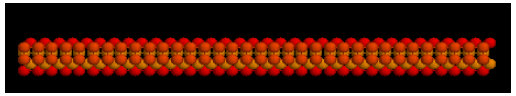


Activated state

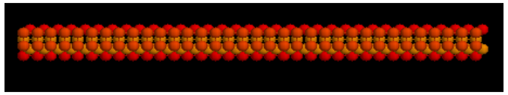


Kink-pair expansion

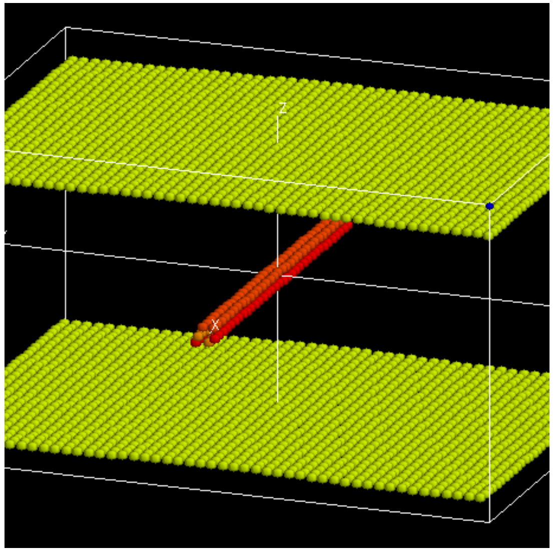


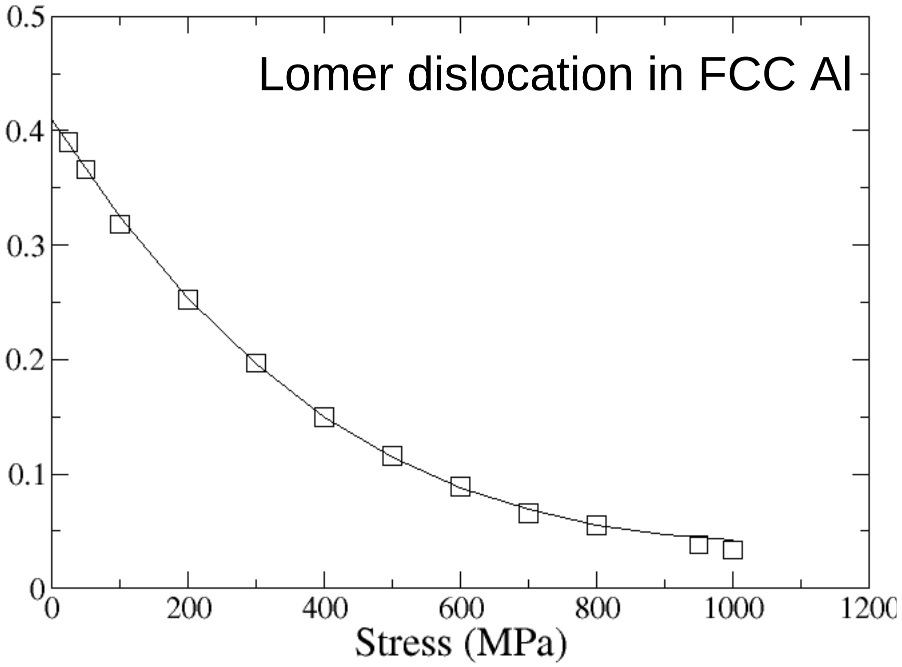


Initial state



Final state





Dislocation kinetics

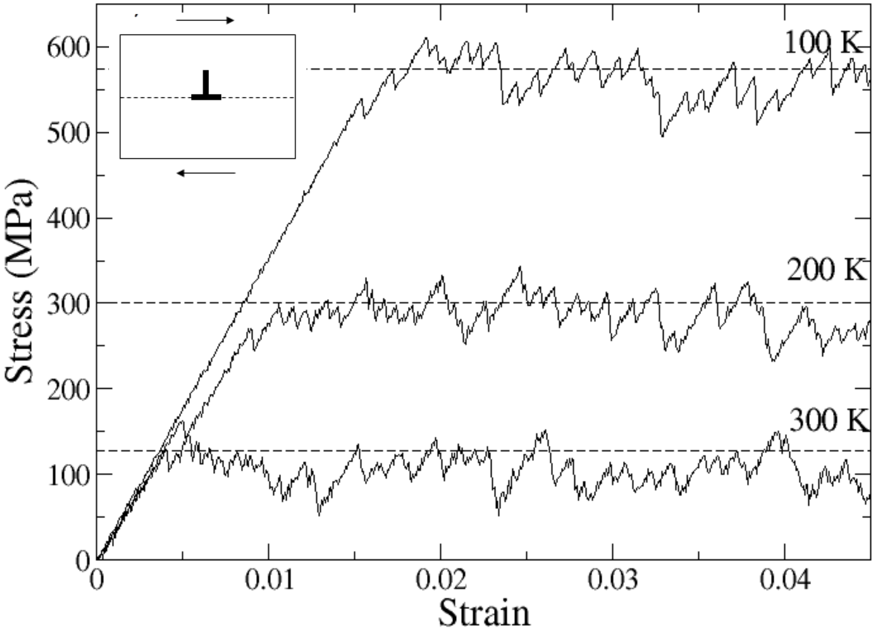
[Rodney, PRB 2007]

If we assume $\mathrm{v} = \nu_D \frac{bd}{\ell_c} \frac{L}{\ell_c} \exp\left(-\frac{H(\tau)}{kT}\right)$ then $\dot{\gamma} = \rho b \mathrm{v} \equiv \dot{\gamma}^* \exp\left(-\frac{H(\tau)}{kT}\right)$

$$H(\tau) = kT \ln\left(\frac{\dot{\gamma}^*}{\dot{\gamma}}\right) \approx kT \ln\left(\frac{\rho \nu_D b L}{\dot{\gamma}}\right) \approx 11kT \quad \Rightarrow \quad \tau(T)$$

$$\rho \sim 10^{16} m^{-2}, \nu_D \sim 0.5\times 10^{13} s^{-1}, b \sim 10^{-10} m, L \sim 10^{-8} m, \dot{\gamma} \sim 1.5\times 10^{7} s^{-1}$$

MD simulation at $\dot{\gamma} = 1.5\times 10^{7} s^{-1}$



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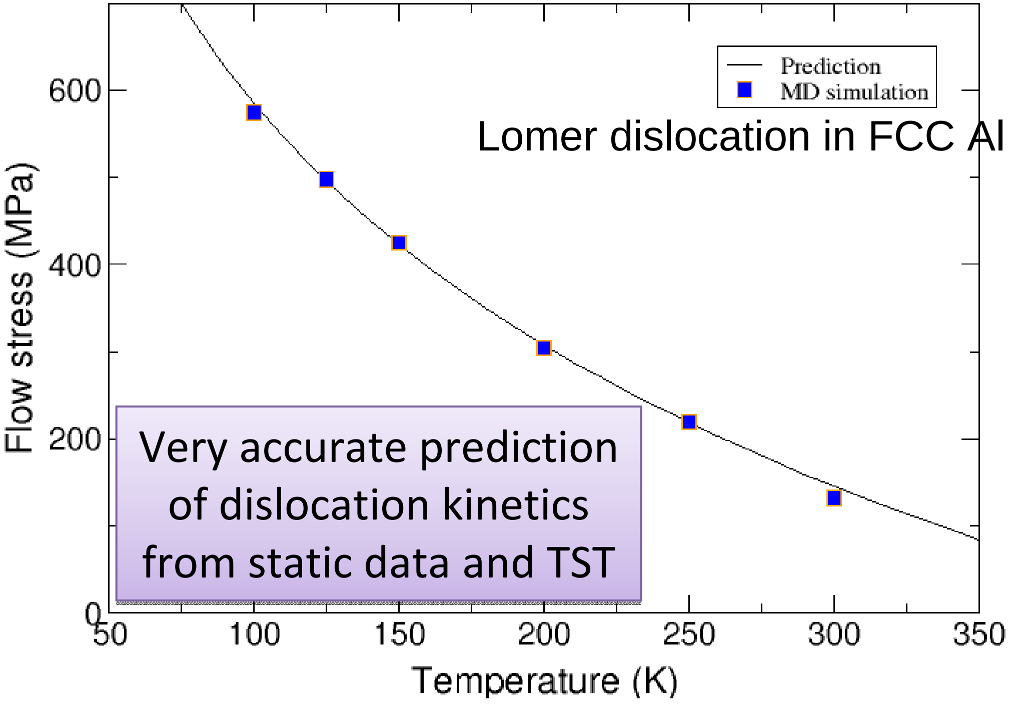

Lomer dislocation in FCC Al

Very accurate prediction of dislocation kinetics from static data and TST

Quantum Transition State Theory

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