Exploring the Potential Energy Landscape of Materials:

from defected crystals to metallic glasses

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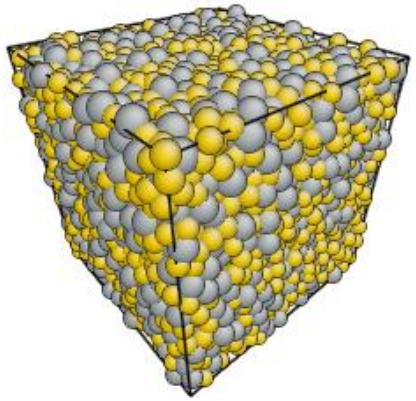
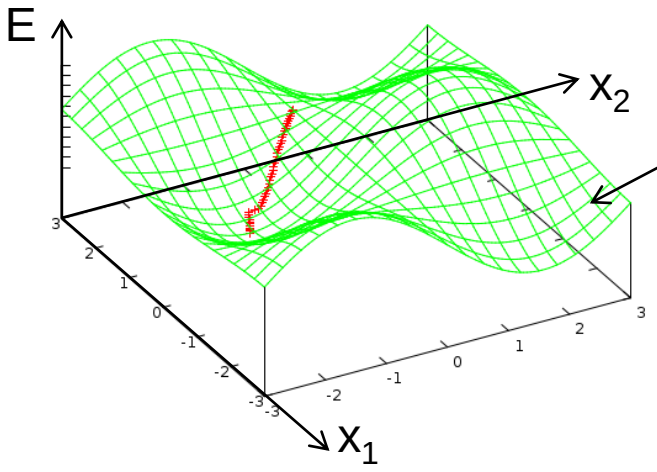
INP Grenoble

What is the Potential Energy Landscape (PEL)?



- Configuration $\vec{\mathrm{R}} = \{x_1, x_2, \ldots x_N\}$, a point in N-dimension configuration space
- Energy $E(x_1, x_2, \ldots x_N)$, N-dimension surface in (N+1)-dimension space $\{\vec{R}, E\}$



Potential Energy Landscape (PEL)
or
Potential Energy Surface (PES)

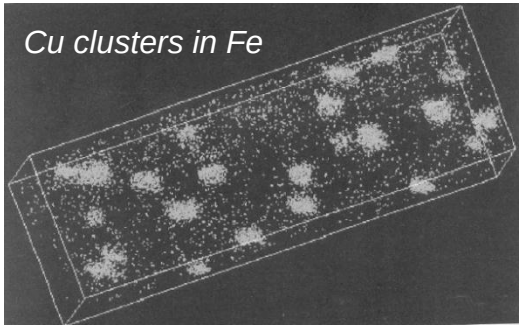
PEL as a unifying concept in Materials Science

- The PEL depends only on the interatomic interactions (and boundary conditions)
- All states (crystal, liquid, glass) share the same PEL, only the region of configuration space visited by the system depends on the state

… but the PEL is quite different near a crystal or a glass

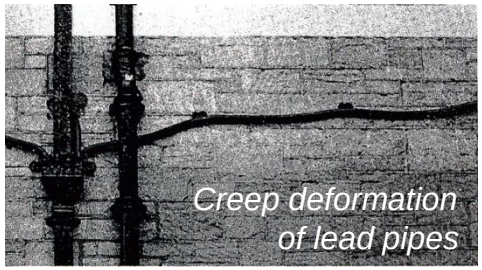
Thermally-activated processes

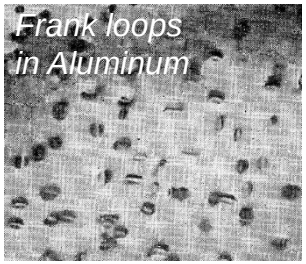
Thermally-activated processes control the slow microstructural evolution of materials in service conditions.



Examples:

- Diffusion-controlled **phase transformations**
- High-temperature **creep** deformation
- **Ageing** in glasses
- Defect **clustering**
- **Cross-slip** in FCC metals
- …

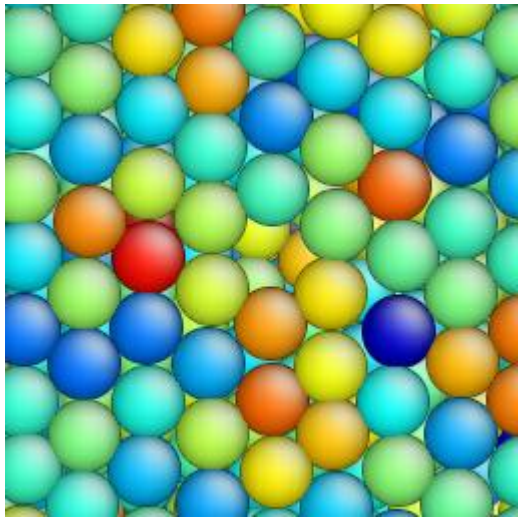




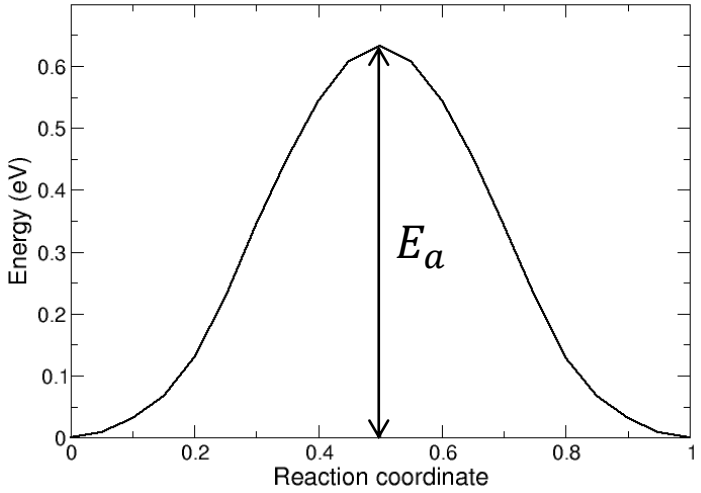
➡ Simulating thermally-activated processes at the atomic scale is a challenge

Molecular Dynamics simulations

Vacancy in Aluminum, 300K



To diffuse, vacancies must overcome an energy barrier



From Transition State Theory: $\langle t_w \rangle \simeq \frac{1}{\nu_D} e^{\frac{E_a}{kT}} \simeq 8.8\ \mathrm{ms}$

with E_a=0.6 eV, ν_D=10^{13}s^{-1}

$$\langle t_w \rangle < 1\ \mathrm{ns} \Rightarrow E_a \lesssim 0.25\ \mathrm{eV}$$

➡ MD can simulate only thermally-activated processes with low activation energies

Time-scale limitation in MD simulations

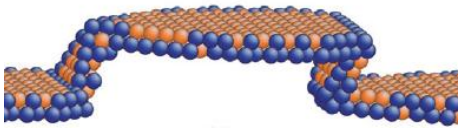
1. MD can not simulate **processes controlled by vacancy diffusion**

   ➡ no segregation, creep, vacancy clustering

2. For **plasticity**, we impose strain rates $\dot{\varepsilon} \approx \frac{0.1 \sim 1}{1\,\mu s} > 10^5\, s^{-1}$

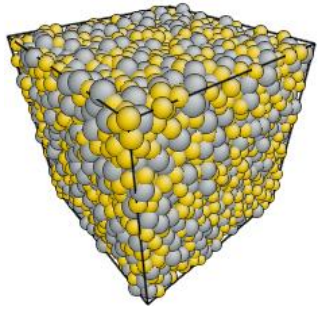
   ➡ MD limited to athermal plasticity, no climb or cross-slip

Mordehai, Phil. Mag. 2008



3. For **glasses**, we impose quench rates $\dot{T} \approx \frac{1000K}{1\,\mu s} > 10^9\, K.s^{-1}$

   ➡ Simulated glasses are far less relaxed than real glasses



Relevance of PEL for thermal activation

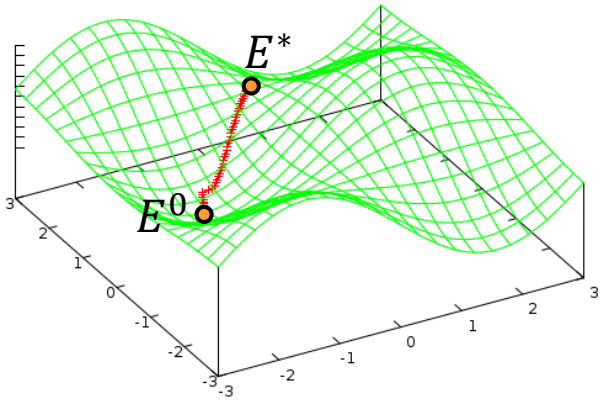
From Harmonic Transition State Theory:

- Activated process: transition between 2 local minima of the PEL along the **Minimum Energy Path** (MEP)
- The MEP passes through a saddle point of order 1 (unstable equilibrium configuration with 1 negative curvature): the **activated state**

$$\langle t_w \rangle = \frac{\prod_{j=1}^{3N-1} \nu^*{}_j}{\prod_{i=1}^{3N} \nu^0{}_i} e^{\frac{E^* - E^0}{kT}}$$

Stable normal mode frequencies from diagonalization of dynamical matrix

$$\bar{\bar{D}}_{ij} = \frac{d^2 E}{dr_i dr_j}$$



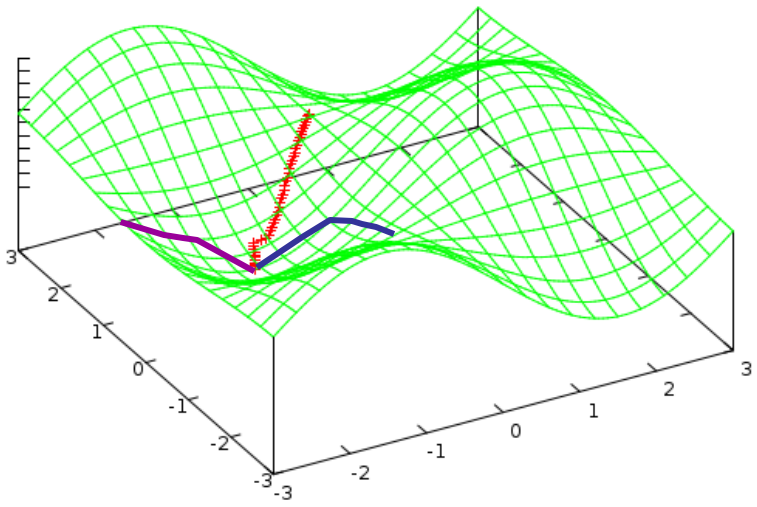
- All information is on the PEL
- All we have to do (!) is to find the activated state of the process of interest

Ways to explore the PEL

[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 a random direction in phase space

2- Move along that direction until you find a configuration with 1 negative curvature

3- Follow negative curvature to a saddle point

4- Relax forward and backward to find the transition path

Vacancy Clustering in FCC Aluminum

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INP Grenoble

*Wang et al, PRB **84**, 220103(R) (2011)*

Vacancy clustering

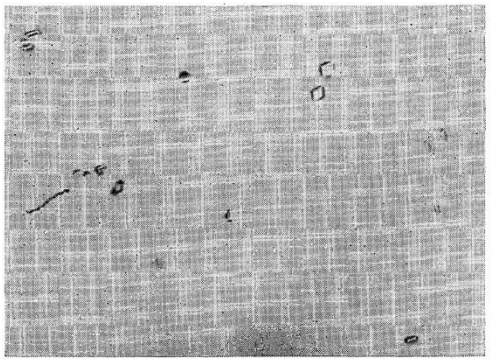
- When produced in supersaturation, for example by *rapid quenching*, *plastic deformation* or *irradiation*, vacancies diffuse to form clusters, dislocation loops and voids

➡ Important for mechanical properties of metals under irradiation

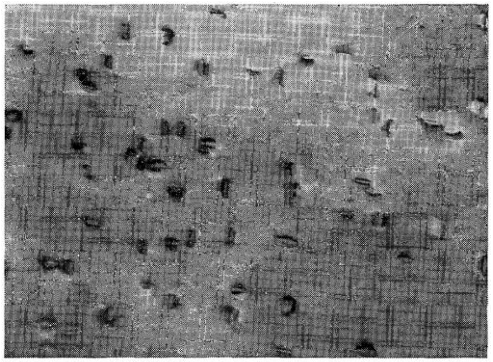
- Early stage of nucleation and nature of critical nucleus unknown.

Question:

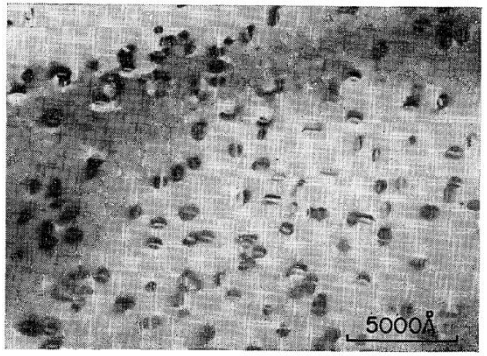
Can we predict the kinetics of vacancy clustering?



(a) t_{AI}=0.5 sec



(d) t_{AI}=6.0 sec

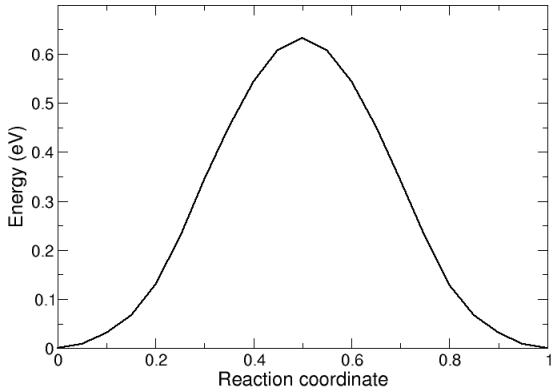


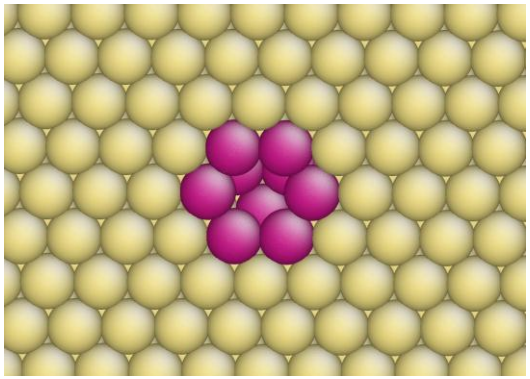
(f) t_{AI}=30.0 sec

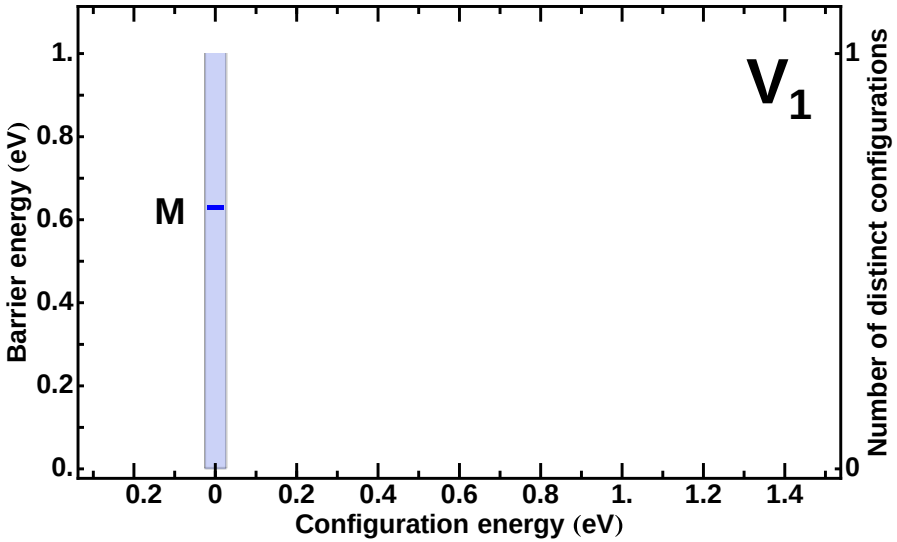
Vacancy clustering in Al (Kiritani 1965)

PEL of defected crystals

- With 1 vacancy: one low barrier for migration

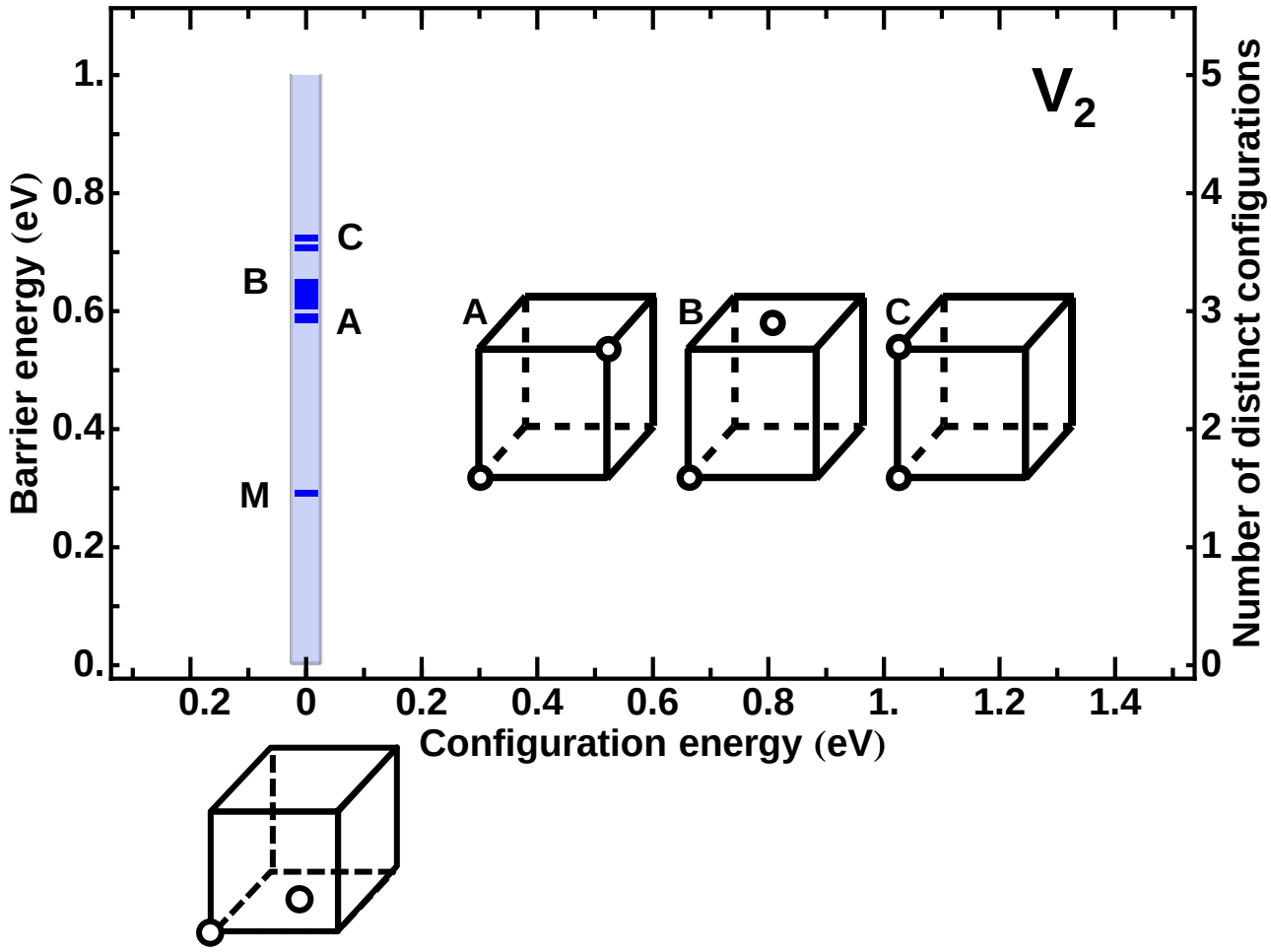






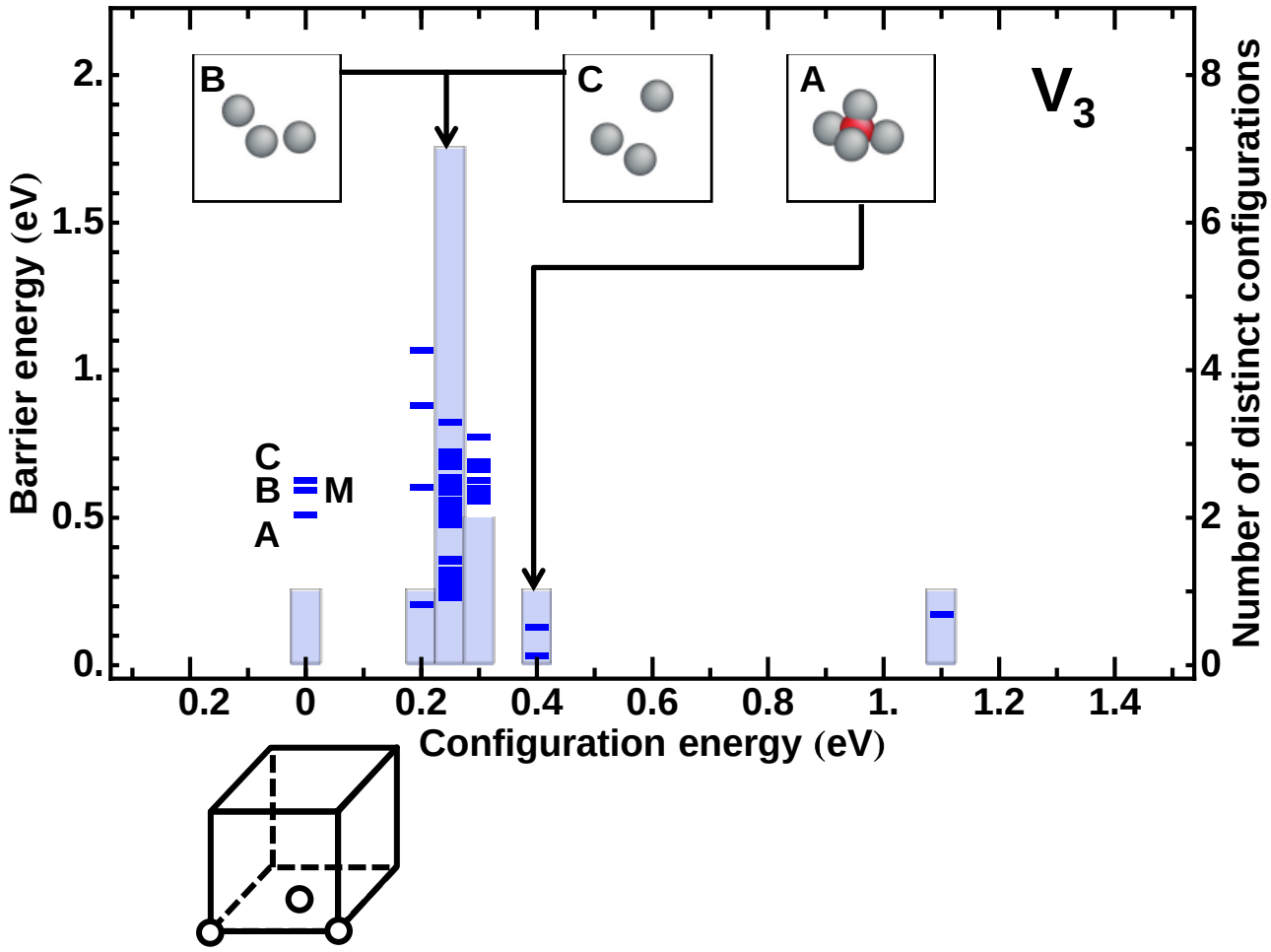
PEL of defected crystals

- With 2 vacancies, more complex: 5 configurations of very close energy
  + transitions + migrations



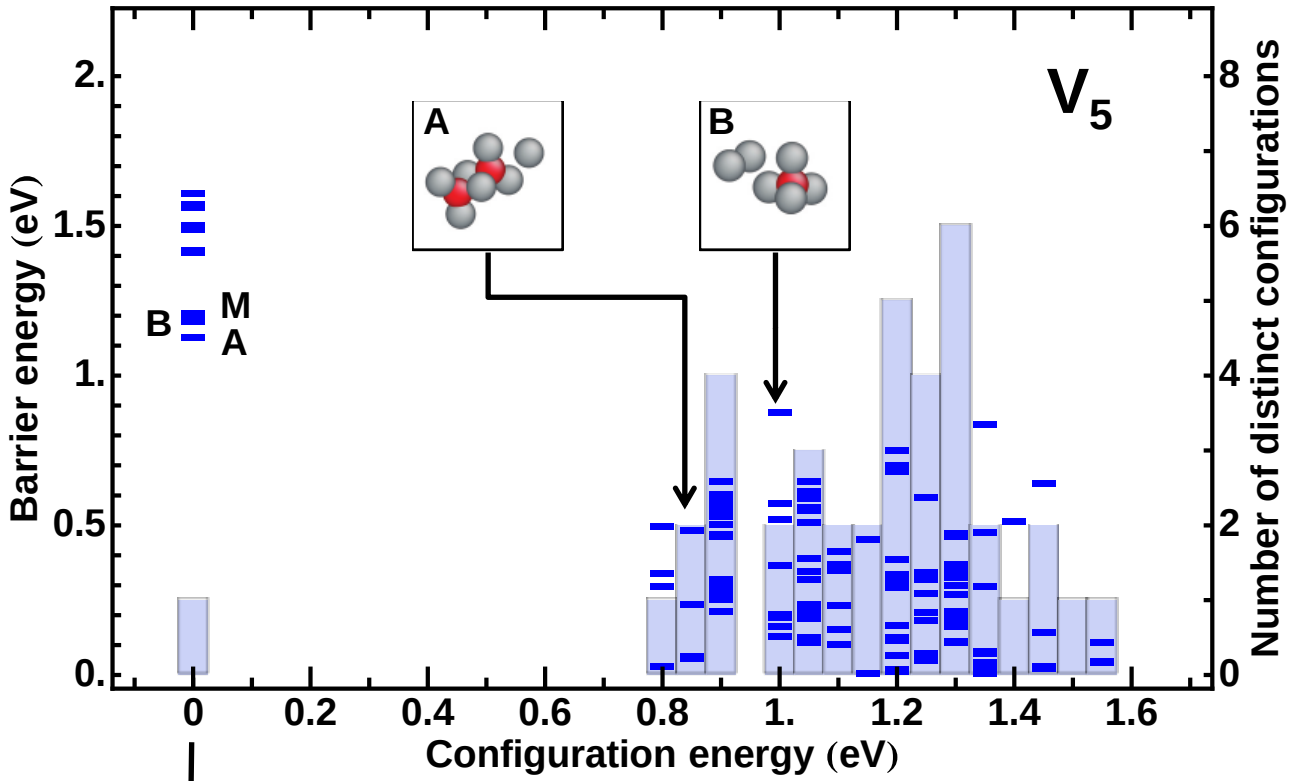
PEL of defected crystals

- With 3 vacancies: one low-energy configuration and several excited states near 0.25~0.3 eV.

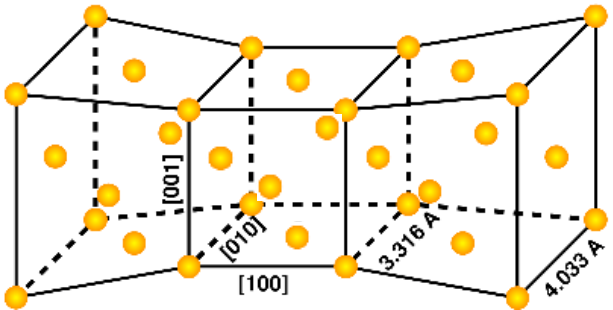


PEL of defected crystals

- With 5 vacancies: one low-energy configuration separated from almost continuum of excited states



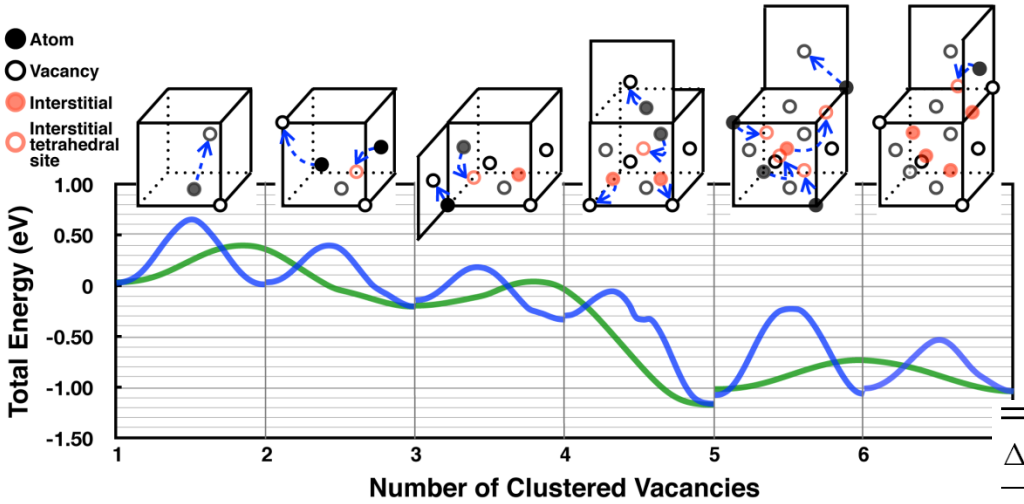
Pentavacancy:
BCC unit cell in
FCC lattice

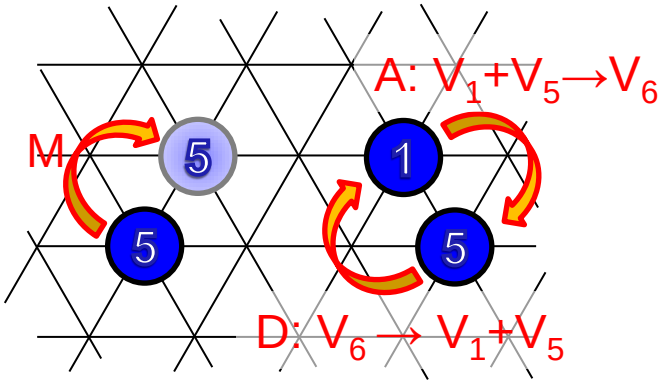


KMC simulations

Object Kinetic Monte Carlo:

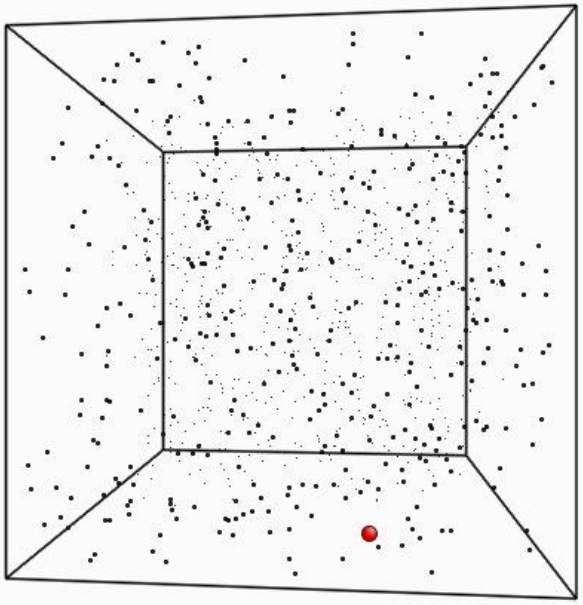
- Clusters of various sizes on an FCC lattice
- Database of activation energies for Migration, Absorption, Dissociation
- Choose events from relative Boltzmann probabilities and increment time



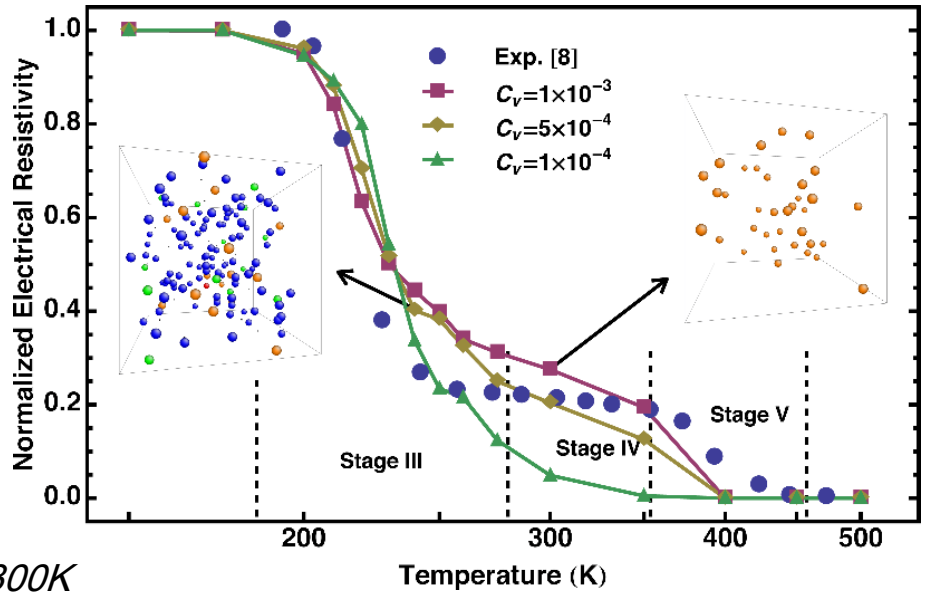


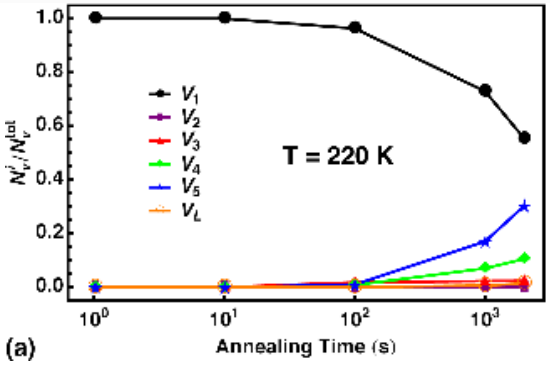
ΔE (eV)	E_{act} (eV)	$\longleftrightarrow$	E_{act} (eV)	ΔE (eV)
0.01	0.63	$V_1 + V_1 \leftrightarrow V_2$	0.62	−0.01
0.24	0.60	$V_2 + V_1 \leftrightarrow V_3$	0.36	−0.24
0.19	0.52	$V_3 + V_1 \leftrightarrow V_4$	0.33	−0.19
0.49	0.88	$V_2 + V_2 \leftrightarrow V_4$	0.39	−0.49
0.87	1.11	$V_4 + V_1 \leftrightarrow V_5$	0.24	−0.87
0.98	1.21	$V_3 + V_2 \leftrightarrow V_5$	0.23	−0.98
−0.01	0.90	$V_5 + V_1 \leftrightarrow V_6$	0.91	0.01
0.71	1.10	$V_4 + V_2 \leftrightarrow V_6$	0.39	−0.71
0.03	0.45	$V_6 + V_1 \leftrightarrow V_7$	0.42	−0.03
0.02	0.28	$V_5 + V_2 \leftrightarrow V_7$	0.26	−0.02

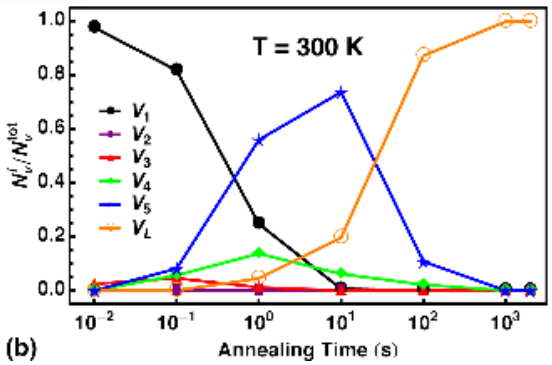
KMC - Results

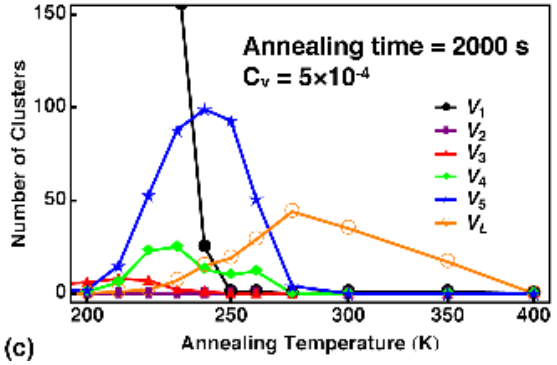


C_v=5.10^{-4}; 300K

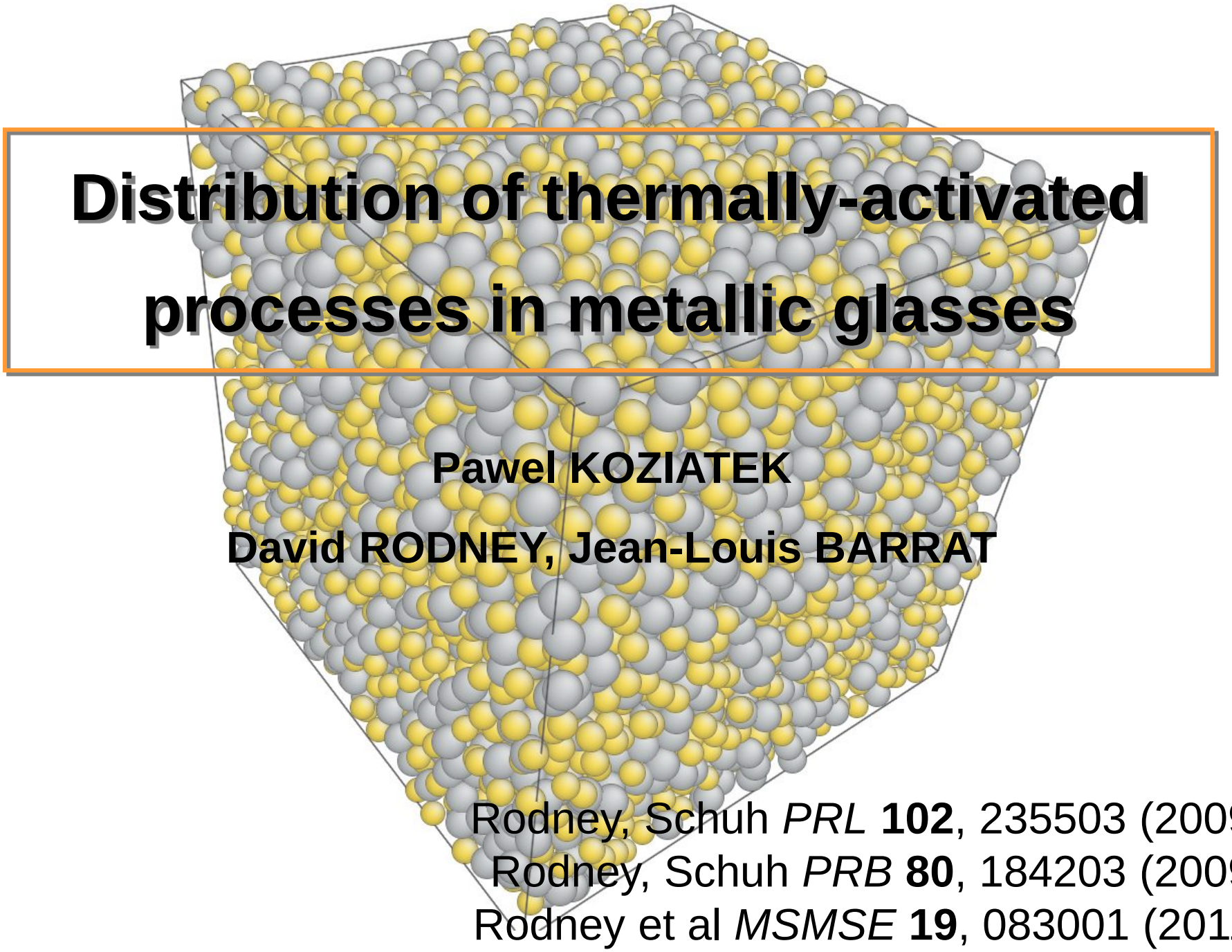








- Pentavacancies dominate the early stage of clustering
- Pentavacancies serve as nuclei for larger clusters
- Specific stability could not be predicted without atomic-scale computations



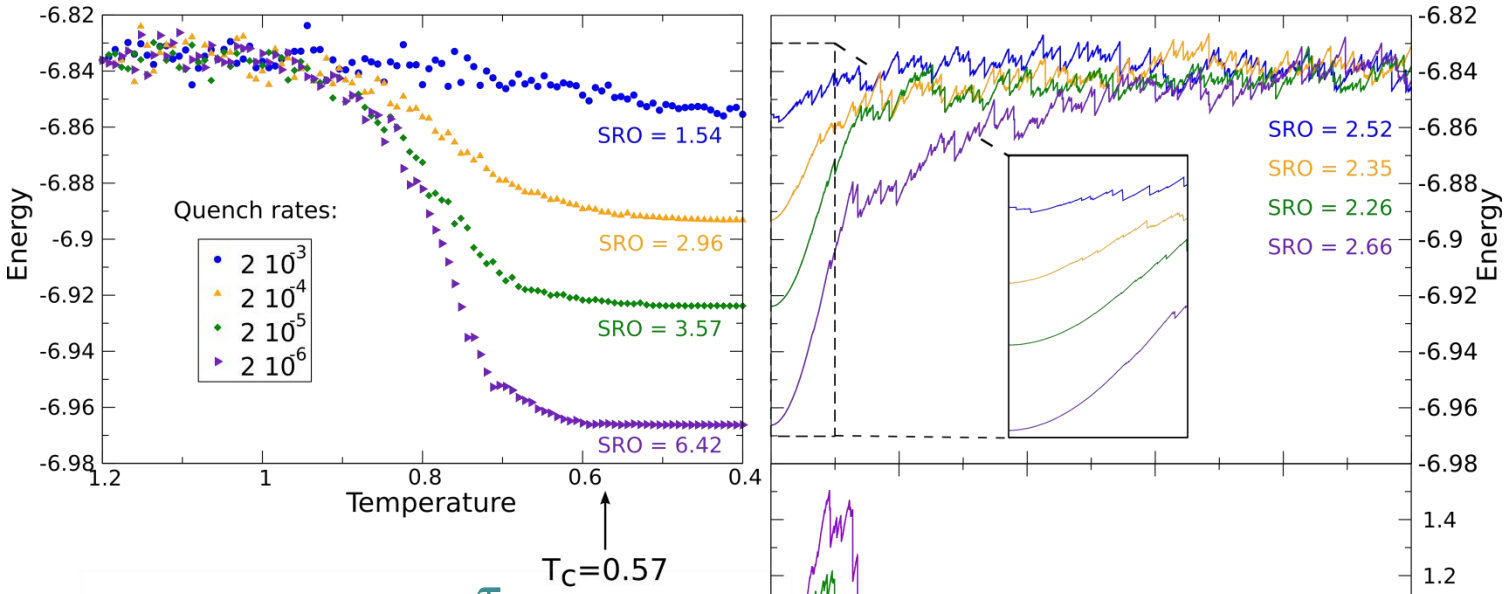
Distribution of thermally-activated processes in metallic glasses

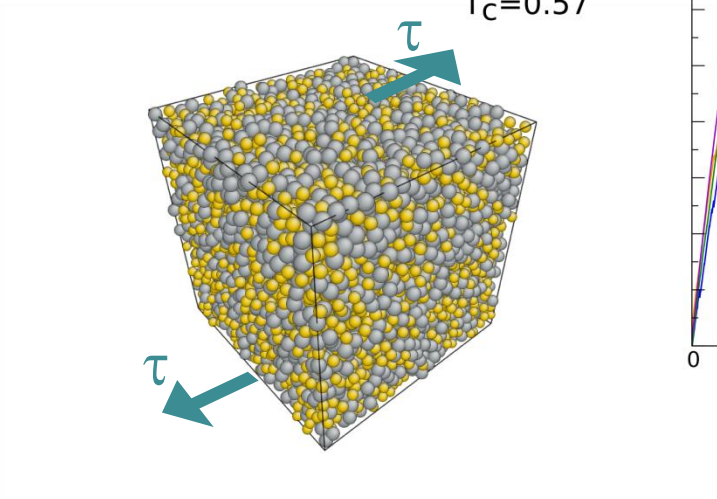
Pawel KOZIATEK

David RODNEY, Jean-Louis BARRAT

Rodney, Schuh *PRL* **102**, 235503 (2009)
Rodney, Schuh *PRB* **80**, 184203 (2009)
Rodney et al *MSMSE* **19**, 083001 (2011)

Influence of the state of relaxation



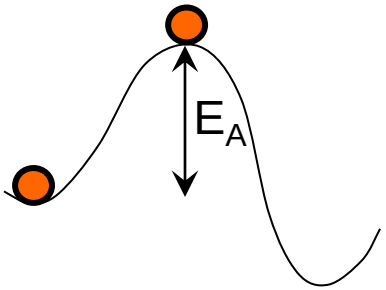


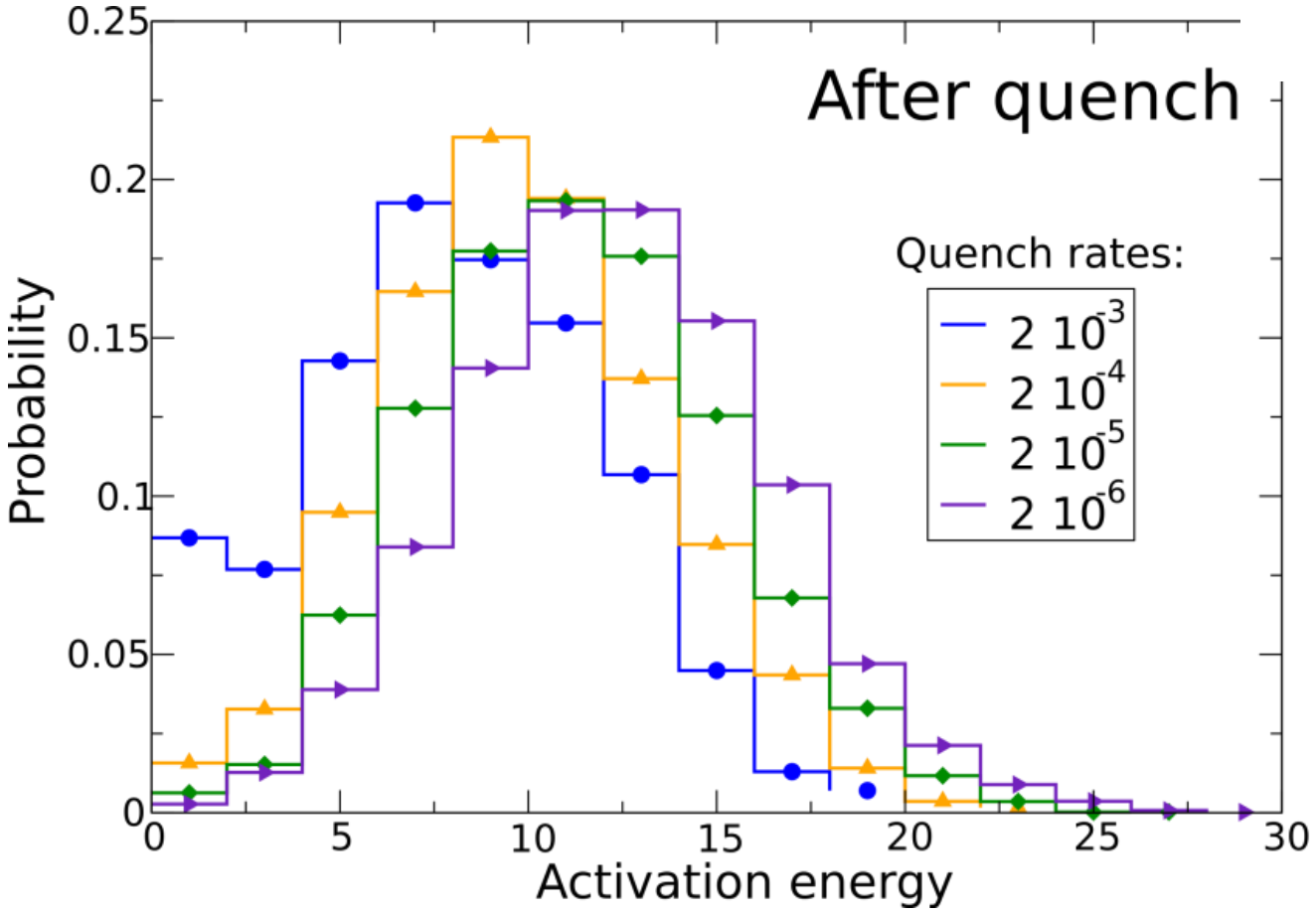
3D Lennard-Jones glass

(Wahnstrom potential)

Influence of the quench rate

Distribution of activation energies in quenched glass

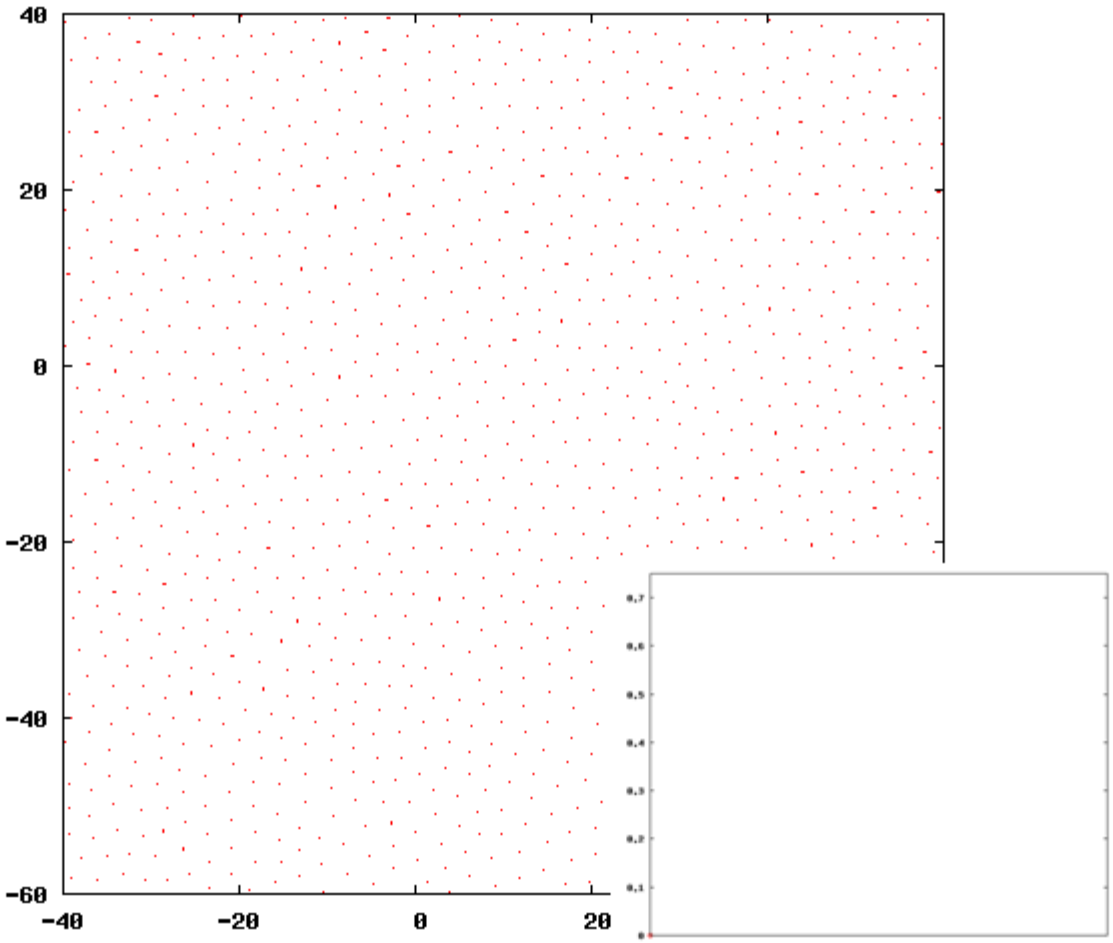




3D Wahnstrom Lennard-Jones

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

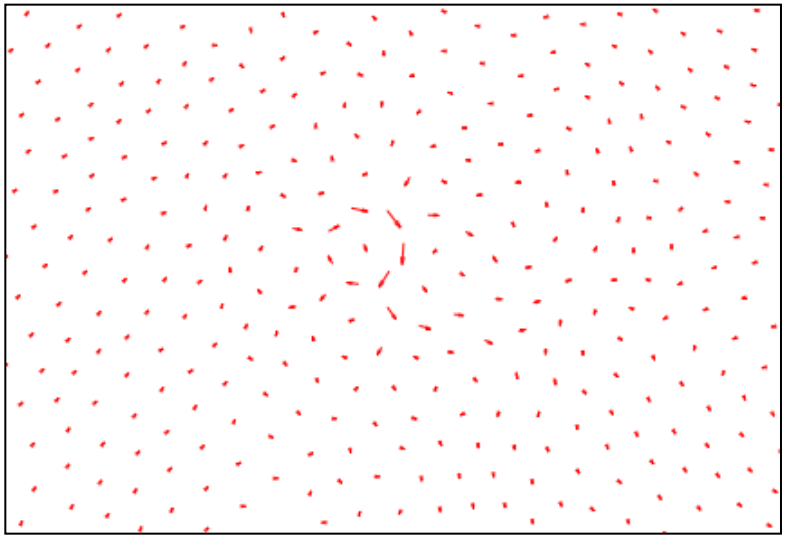
Transition in as-quenched glass

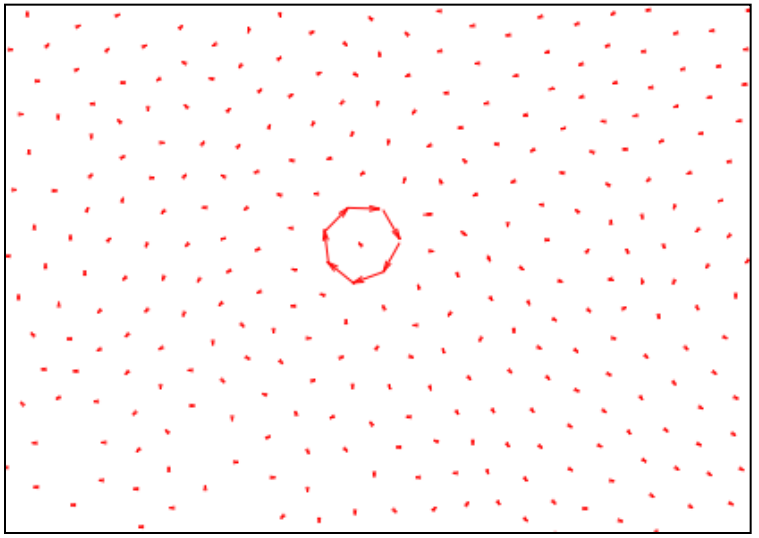


- Local shear in the microstructure … like Shear Transformations
- Volume conservation

Arrow=
Disp x 1

Ring of replacements

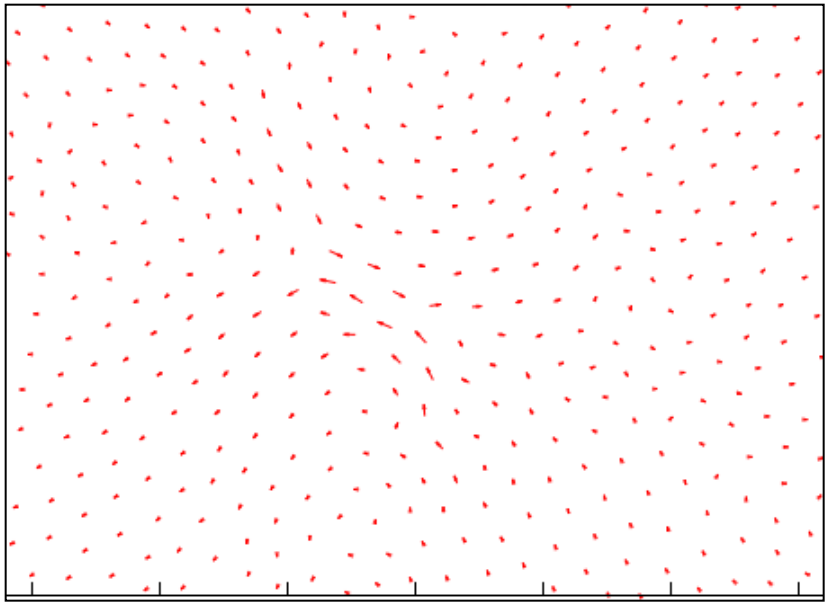


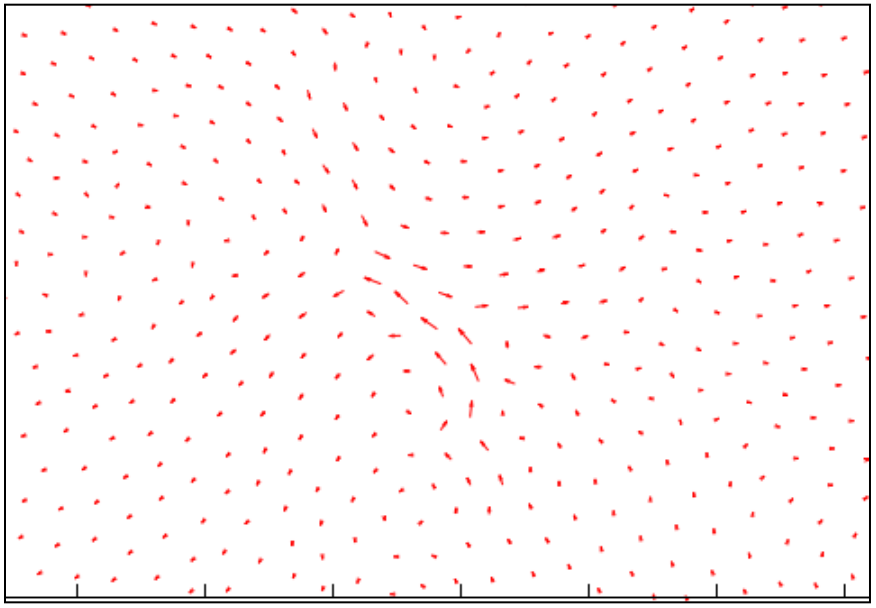


Activated states

Final states

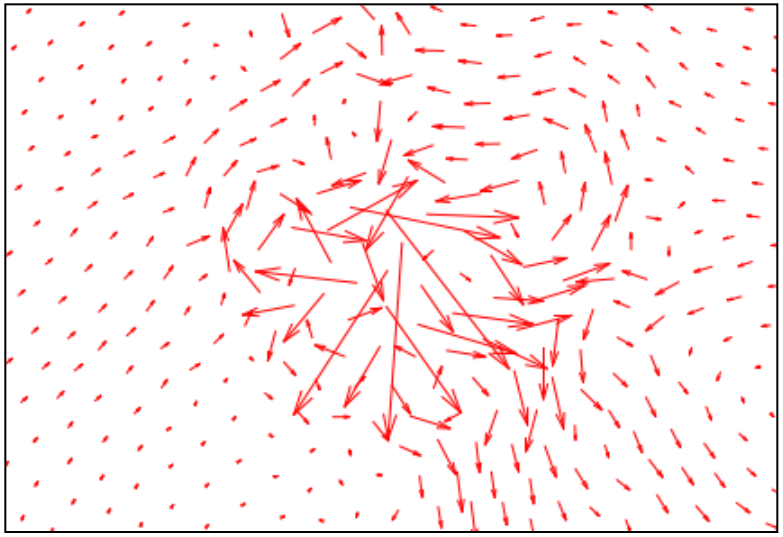
Local shear

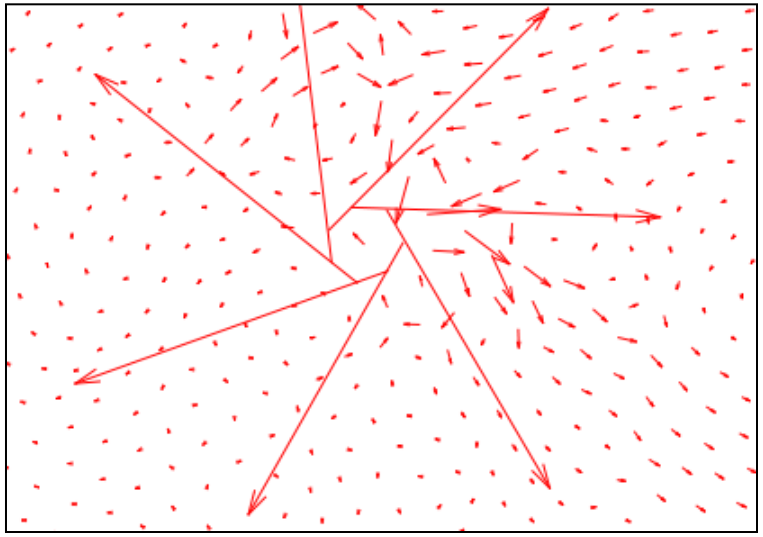




Arrow=
Disp x 10

Ring of replacements

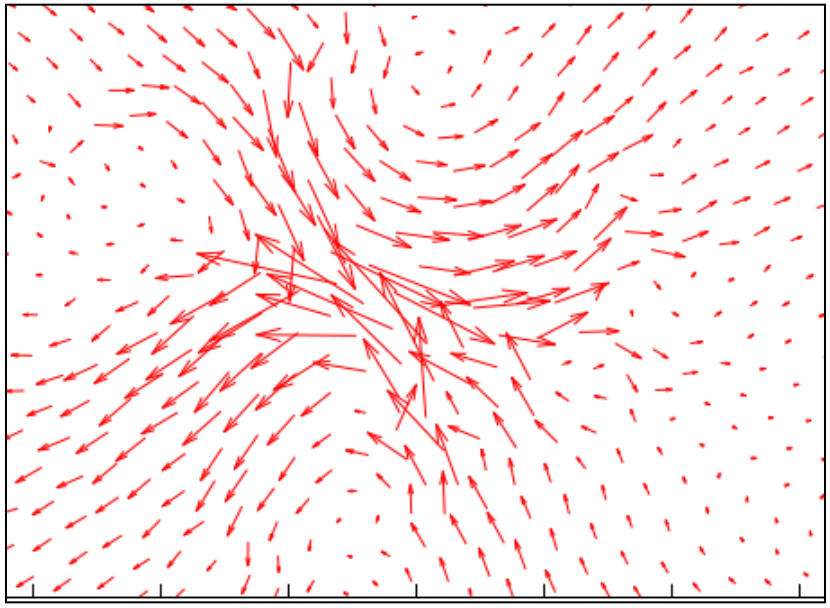


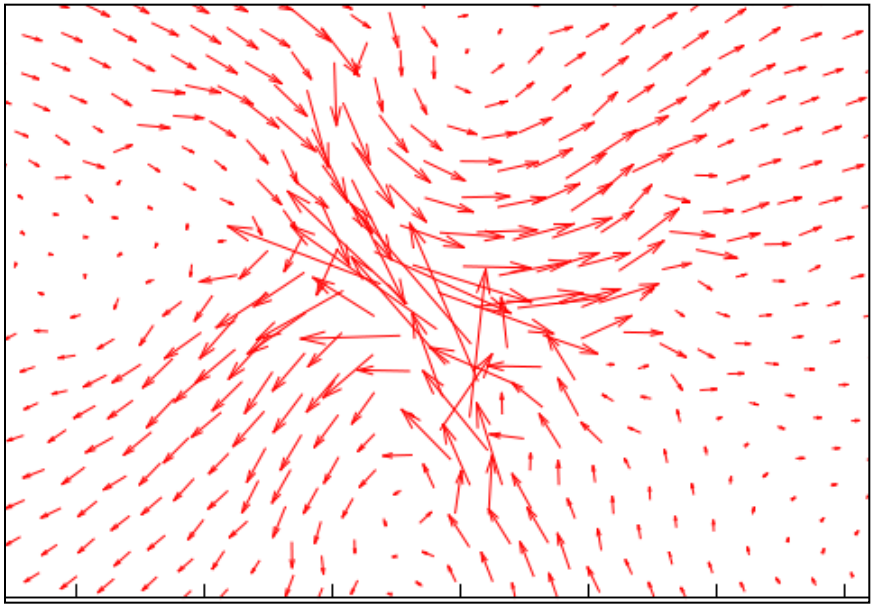


Activated states

Final states

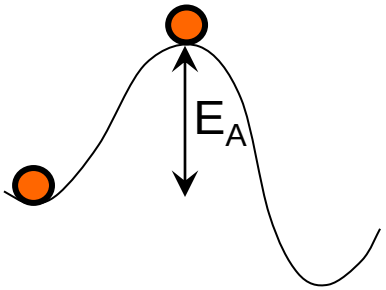
Local shear

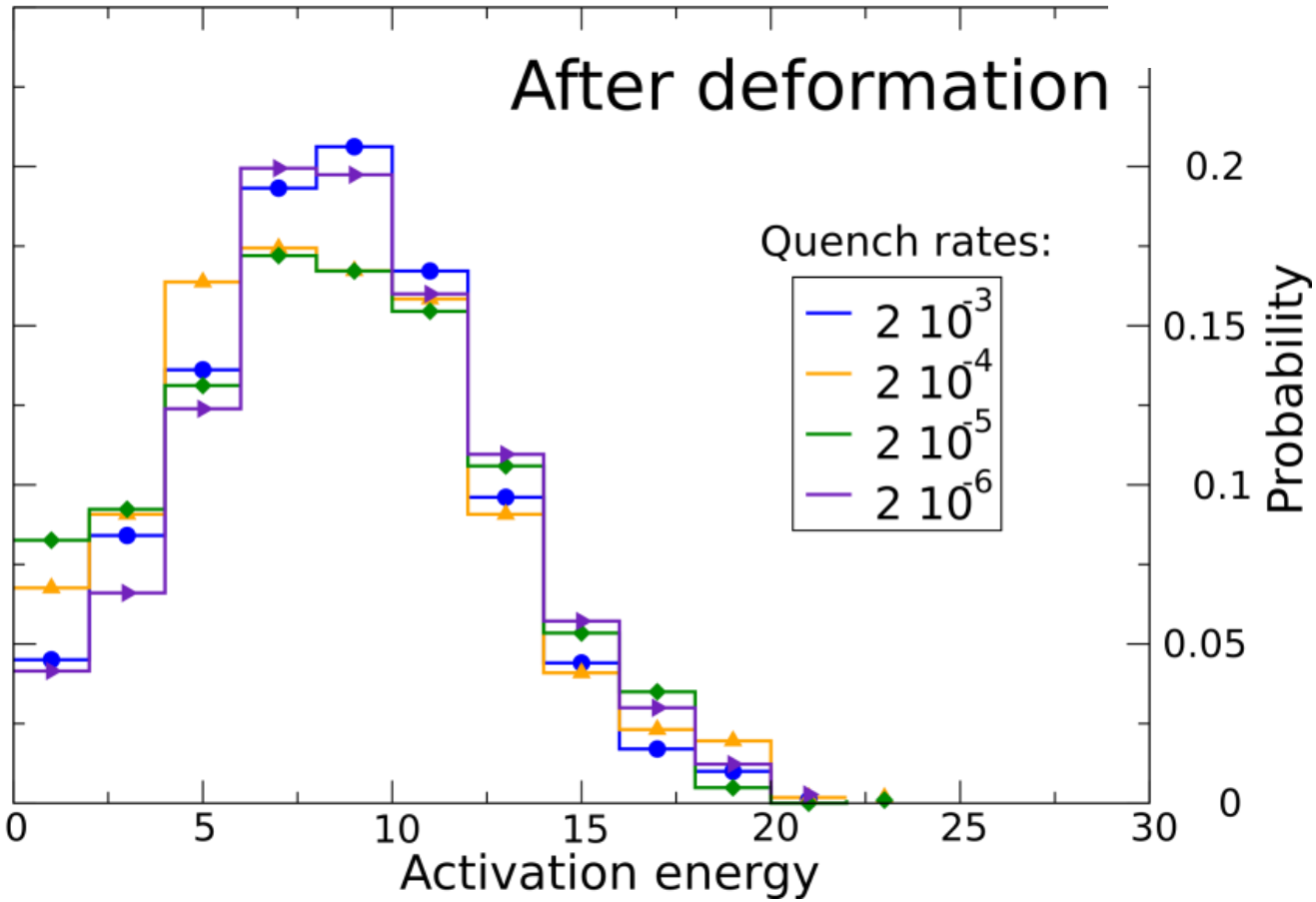




Influence of the deformation

Distribution of activation energies in a deformed glass

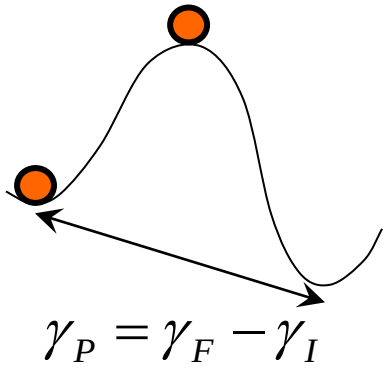


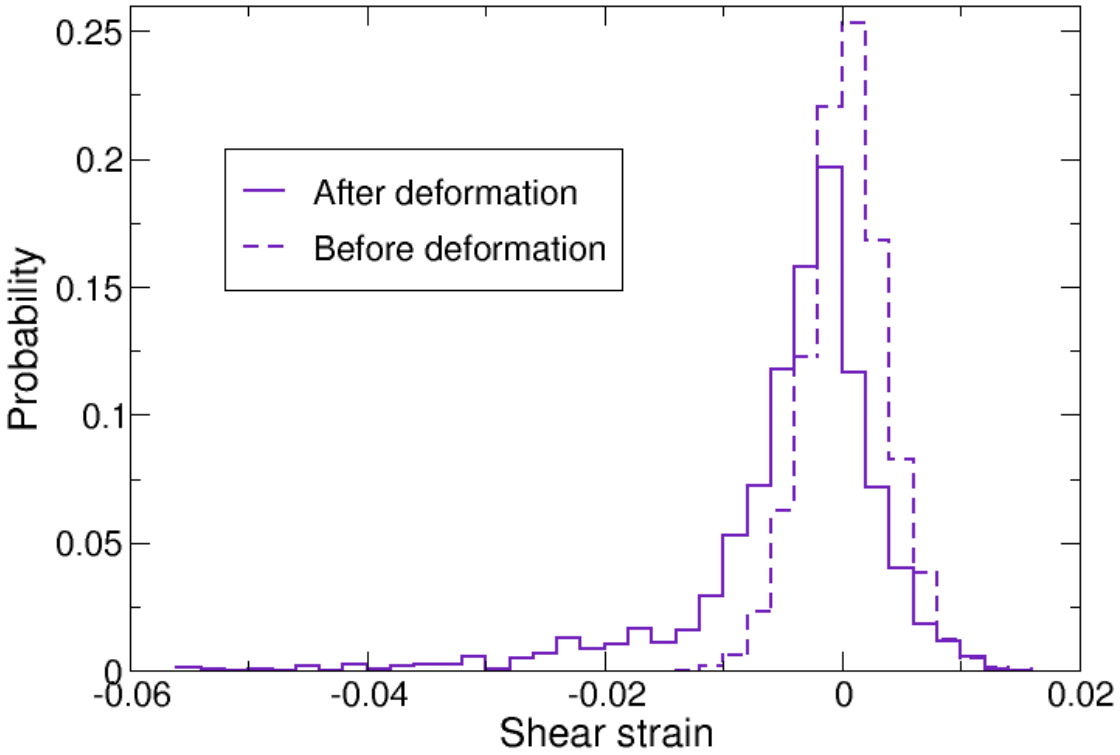


High density of low-energy barriers created during flow

➡ Non-equilibrium flow state

Distribution of inelastic strains





Asymmetrical distributions after flow:

- Anelasticity
- Limit of (isotropic) T_{eff} picture of deformation

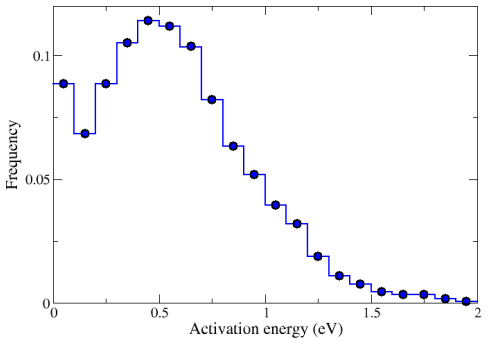
Conclusion

Next step:

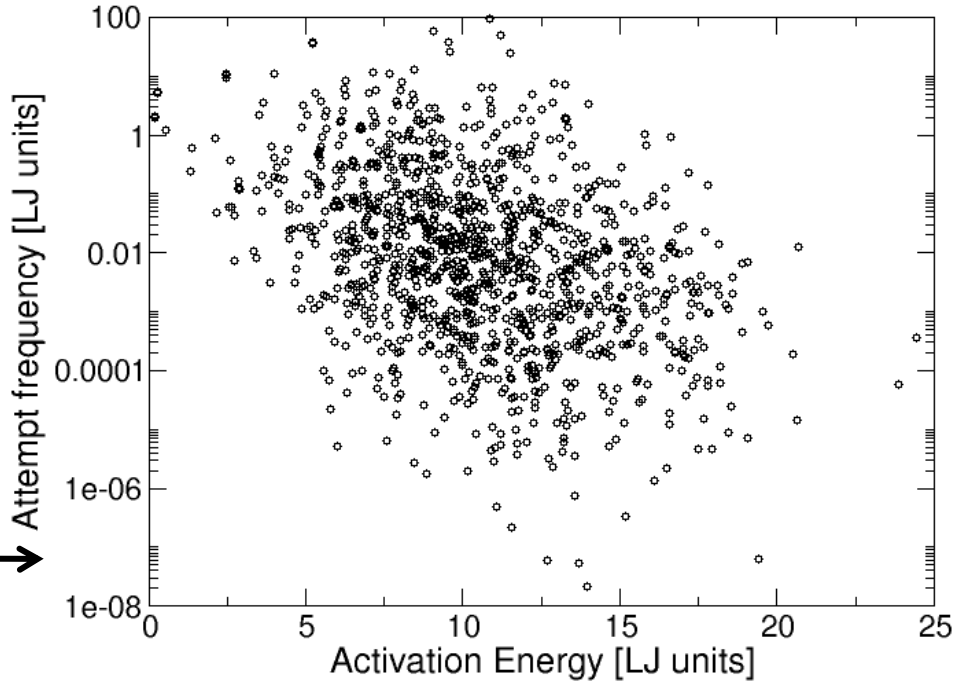
$$\begin{pmatrix}\text{Proba}\\ \text{event}=i\end{pmatrix}=\frac{\nu_i \exp\left(\frac{-E_i}{k_B T}\right)}{\sum_j \nu_j \exp\left(\frac{-E_j}{k_B T}\right)}$$

Kinetic Monte Carlo

Distribution of activated paths



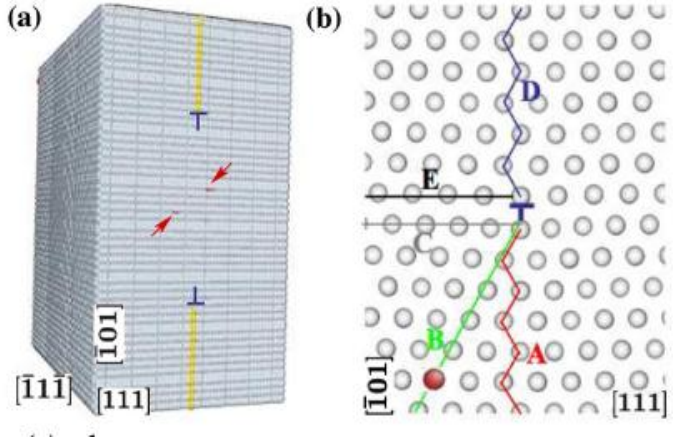
$$\dot{s}=\frac{1}{\langle t_w\rangle}=\frac{\prod_{j=1}^{3N}\nu^0{}_j}{\prod_{i=1}^{3N-1}\nu^*{}_i}e^{\frac{-E_a}{kT}}$$



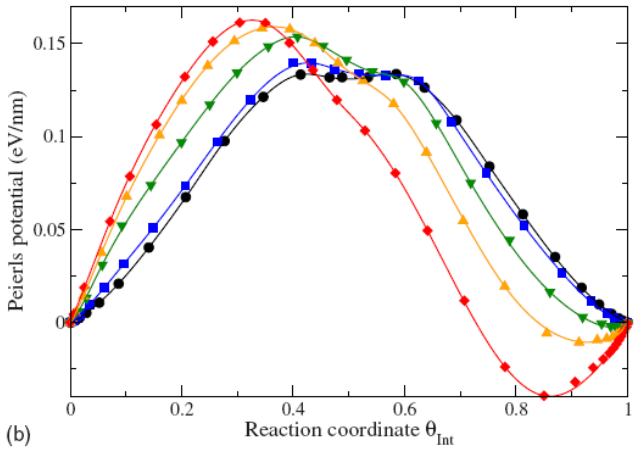
Conclusion

- Efficient exploration of the PEL

- In crystals, few low-energy states separated from a large number of excited states



Dislocation climb
Kabir et al, PRL 2010



Peierls potential
Rodney & Proville, PRB 2009

- In glasses, continuous distribution of states