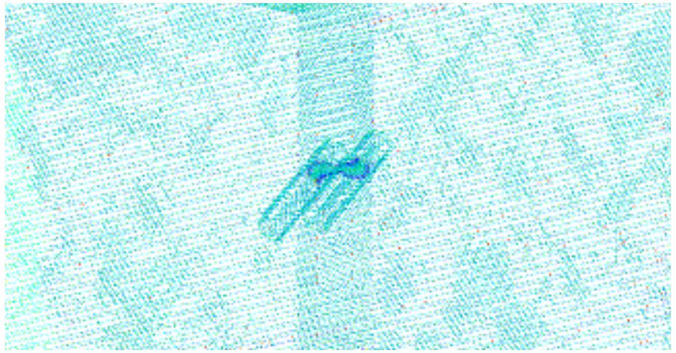
Strong Entropic Contributions to Thermally-activated Kinetics: A Case-study in Dislocation Nucleation

Soumendu Bagchi, Danny Perez

Theoretical Division

IPAM Long Program: *New Mathematics for the Exascale: Applications to Materials Science*
Workshop I: Increasing the Length, Time, and Accuracy of Materials Modeling Using Exascale Computing

Dislocations Multiplication from Pre-Existing Sources



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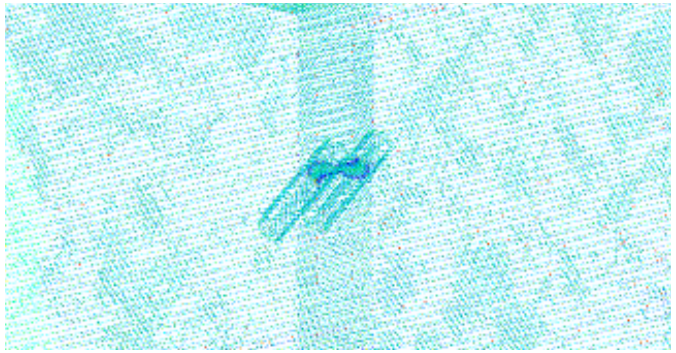
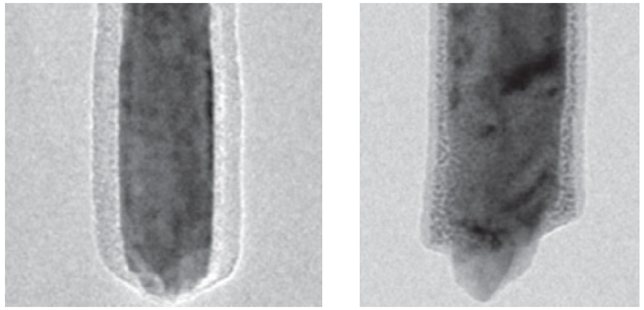
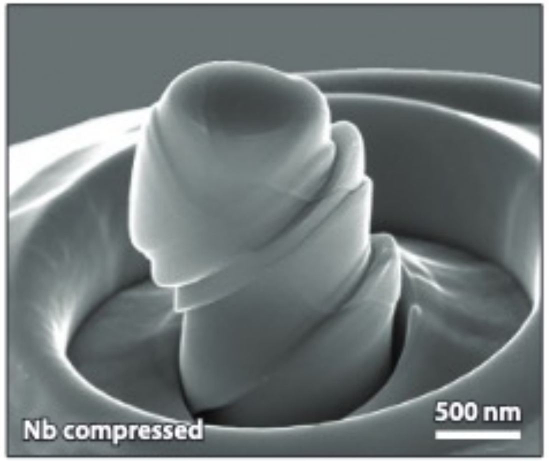
- Strain is accommodated through slip, beyond elastic level

Nucleations of *new* dislocations are rare (?)





Chen et al. 2015



Greer J. et al., 2005

- Strength and ductility of crystals is dictated by plastic response
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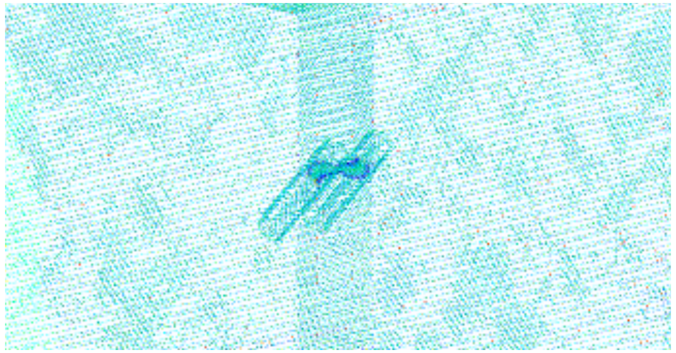

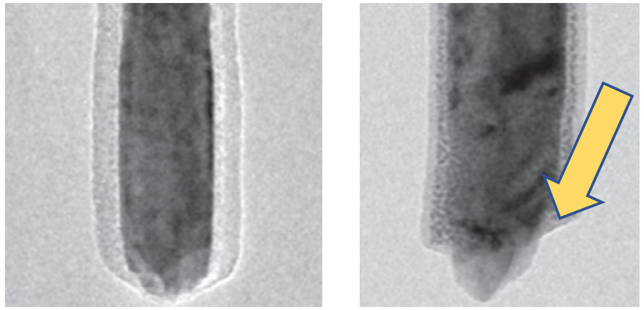

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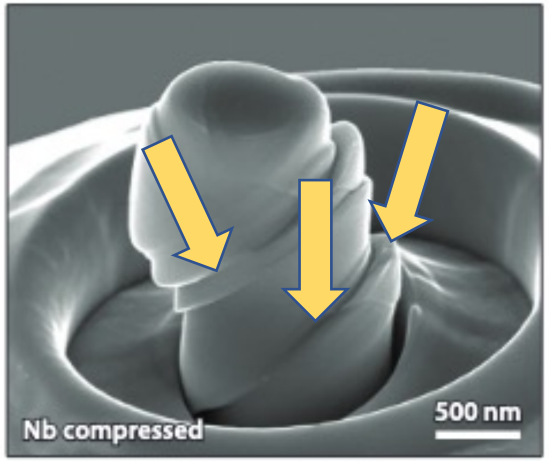

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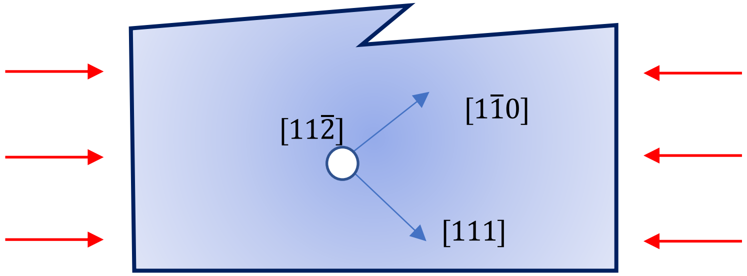
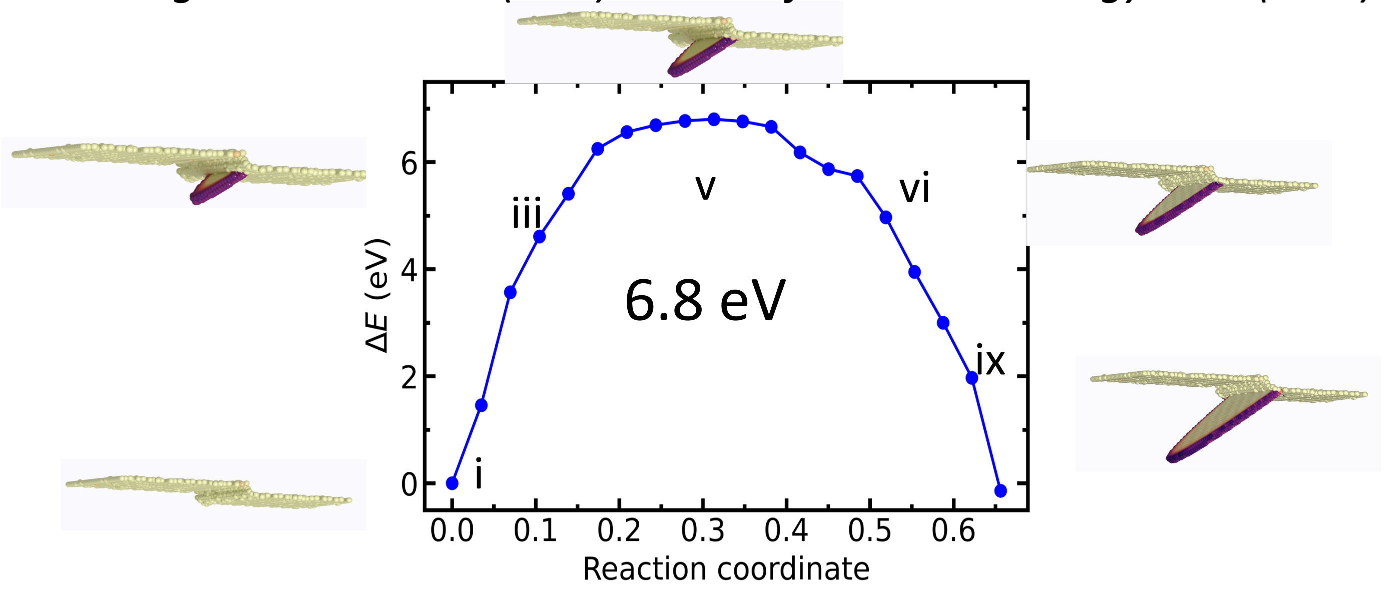
- *Nano-/micro-pillars could be "almost" defect free*
- *Nucleation of new dislocations from stress concentrators govern onset of plasticity*

Surface Nucleation Pathways: How Feasible are they?

under low (2%) compressive strain

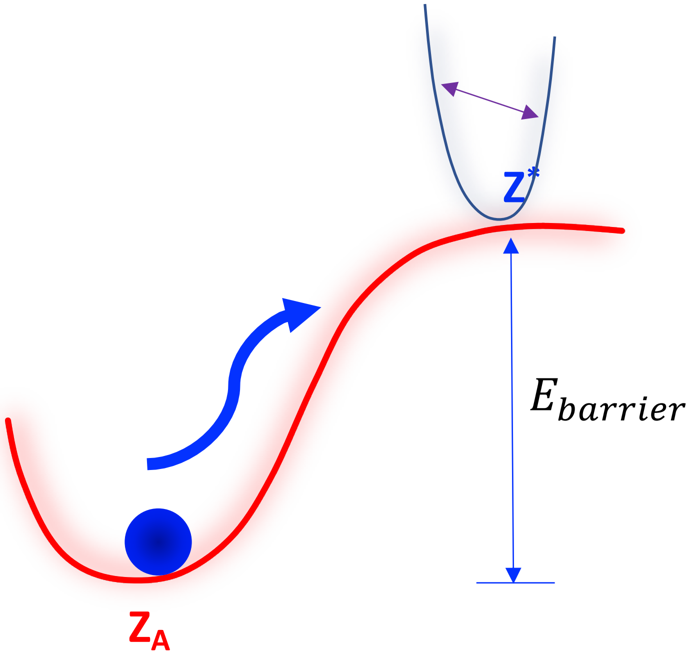


Nudged Elastic Band (NEB) Search of Minimum Energy Path (MEP)



Classical Transition State Theory Approach

From TST based approximations,



An upper bound for rate (i.e. no recrossing)

$$k = \frac{K_B T}{h} \frac{Z^*}{Z_A}$$

$$= \frac{\prod_{i=1}^{3N} v_i^A}{\prod_{i=1}^{3N-1} v_i^*} e^{\frac{-E_b}{K_B T}} \quad \textit{Harmonic Approx.}$$

$$= v_0 e^{\frac{-E_b}{K_B T}}$$

(Arrhenius rate)

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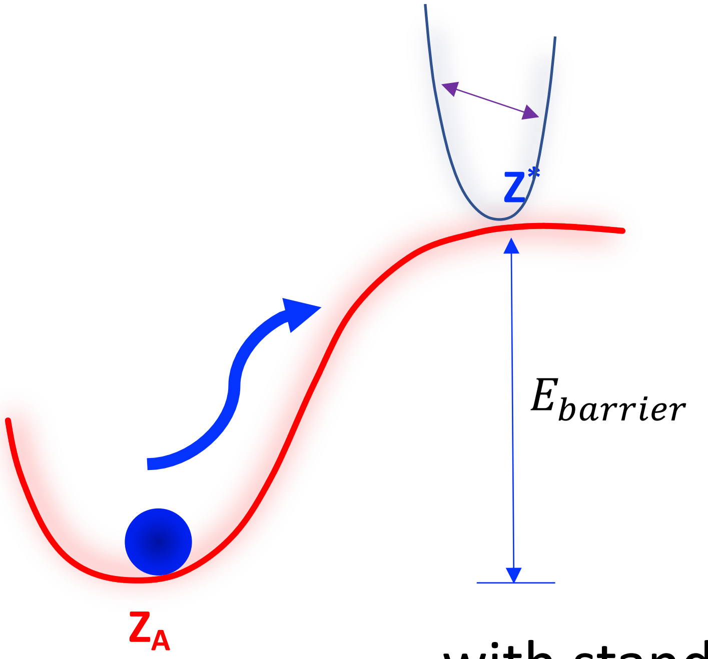

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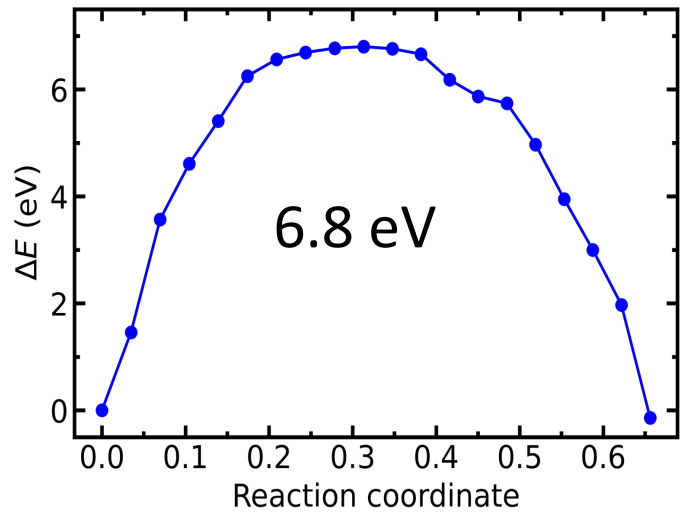
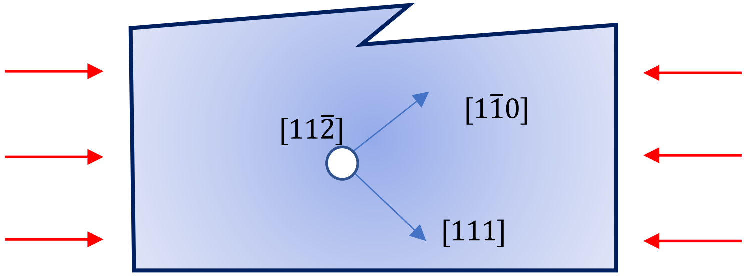


with standard prefactors ($v_0 = 10^{12}\ /s$) would predict $t_{nuc} \gg$ ***Age of the universe***!

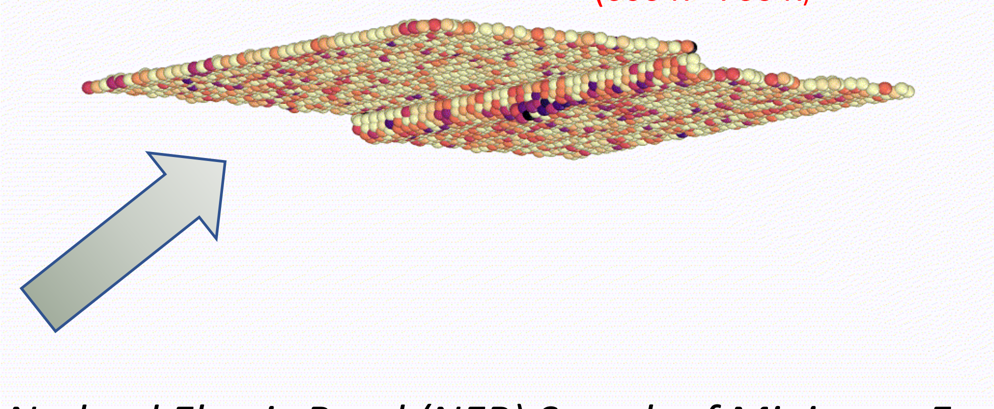
Surface Nucleation Events from MD Simulations

under low (2%) compressive strain



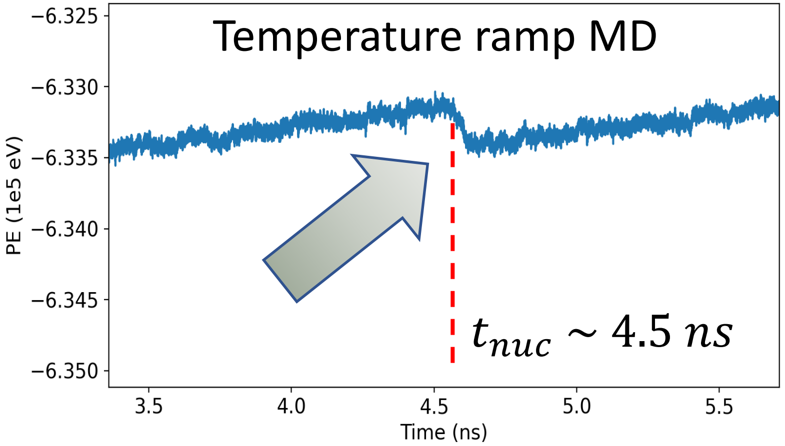
With ~40 Million EAM Cu atoms

(600 K - 700 K)



(only defect-atoms are shown)

(10K/ns)



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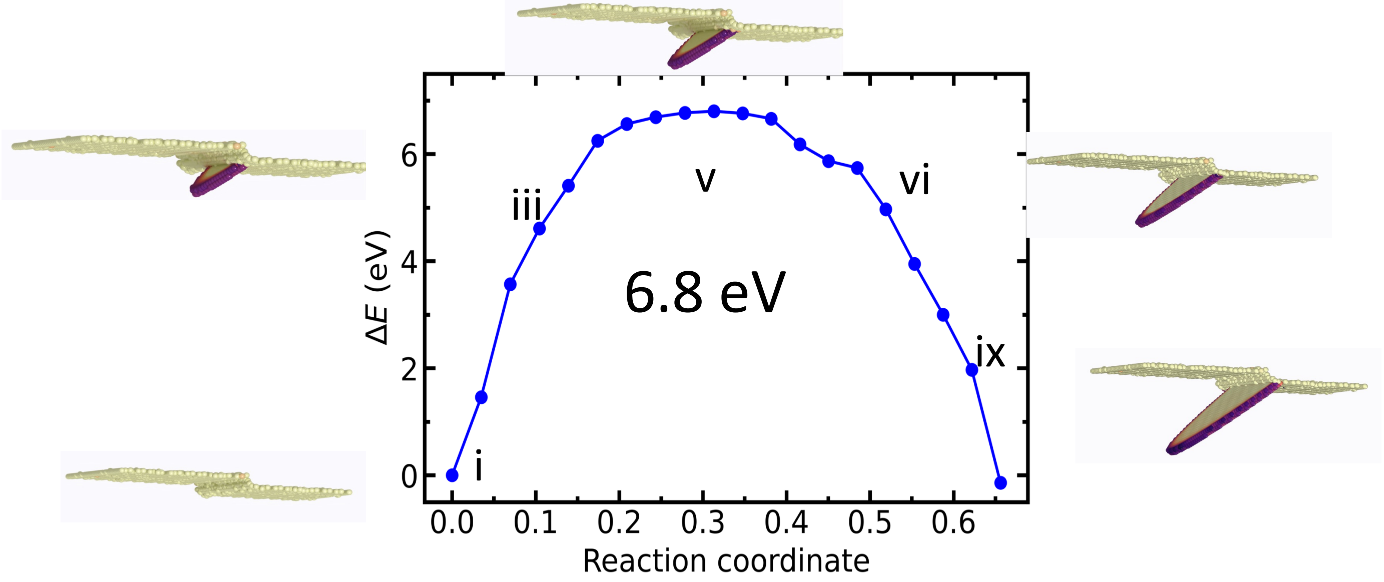
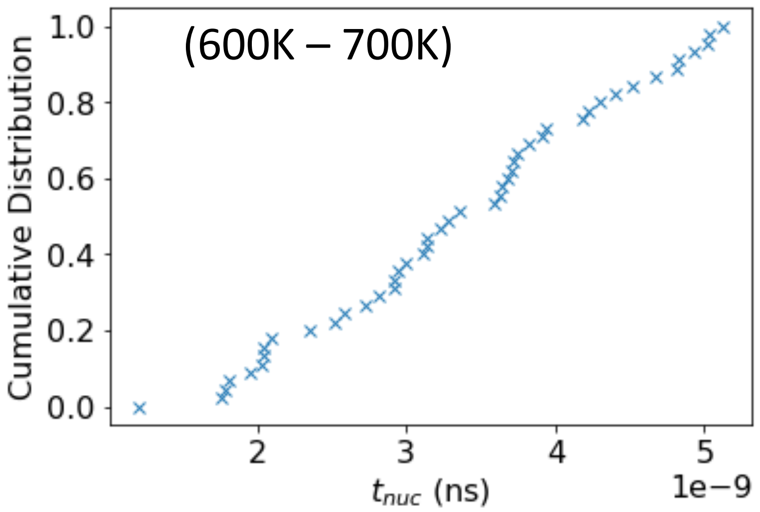


Maximum Likelihood of Rate Parameters

From a series of (~100) 40 million atom MD runs



According to rate theories,

$p_i(t) \sim k(t)e^{-\int k(t)dt}$, where $k(t) = v_0 e^{\frac{-E_b}{K_B T(t)}}$

$\sim p(t, v, E_b)$

considering MD runs as i.i.d

$$L(v, E_b | t_{nuc}) = \prod_i p_i$$

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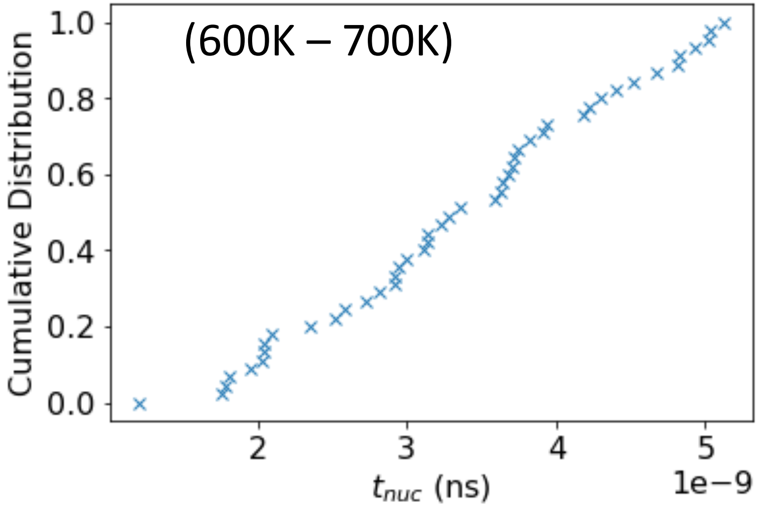

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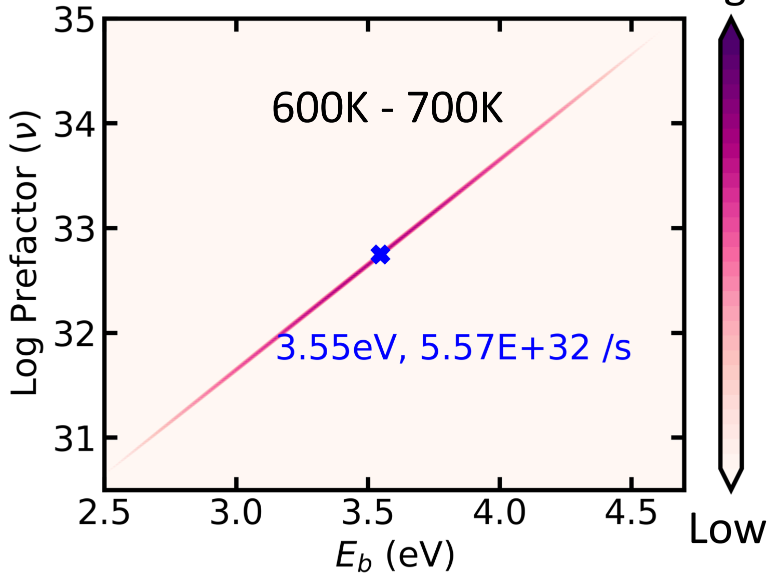

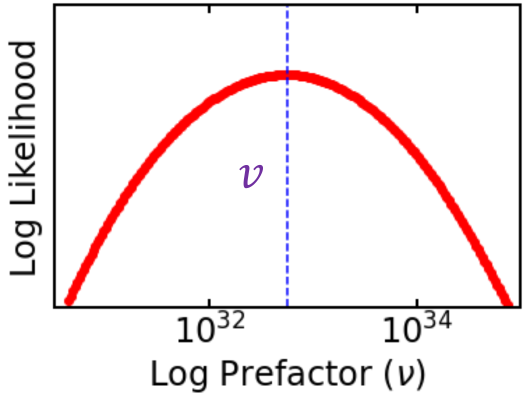

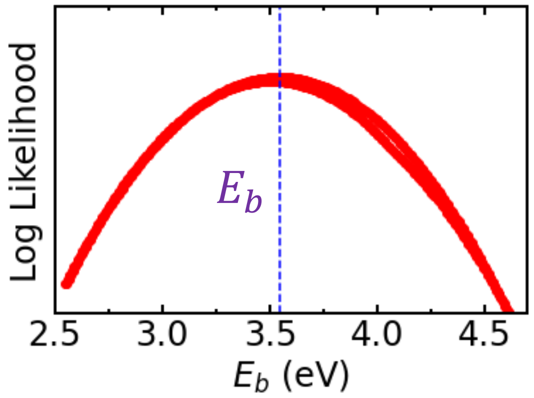

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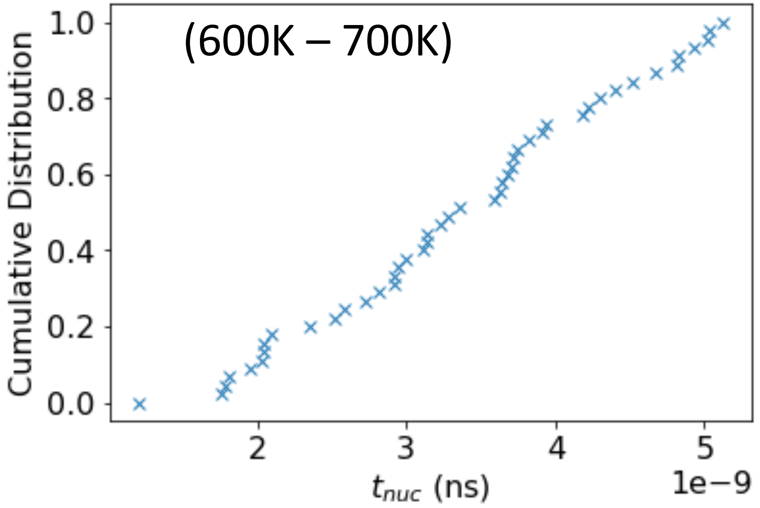

But $10^{32} - 10^{33}$ /s is huge w.r.t typical prefactors of 10^{12} /s

$p_i(t)dt \sim$ probability of nucleating between time t and $t + dt$

$p_i(t) \sim k(t)e^{-\int k(t)dt}$, where $k(t) = \nu_0 e^{\frac{-E_b}{K_B T(t)}}$

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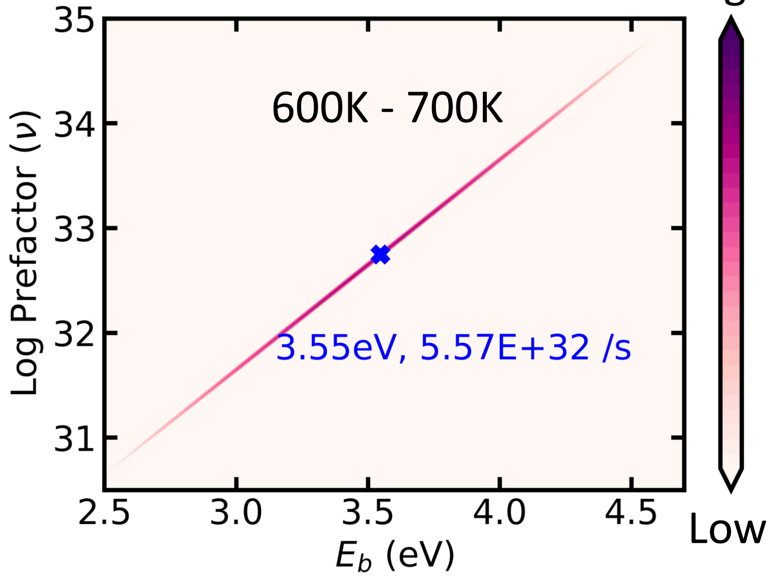

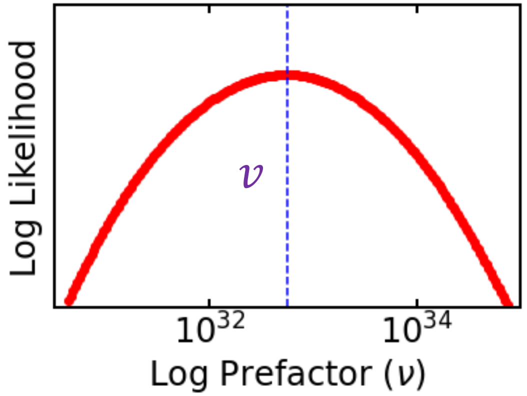

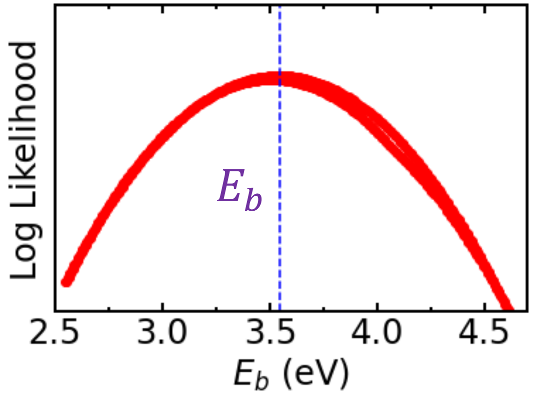

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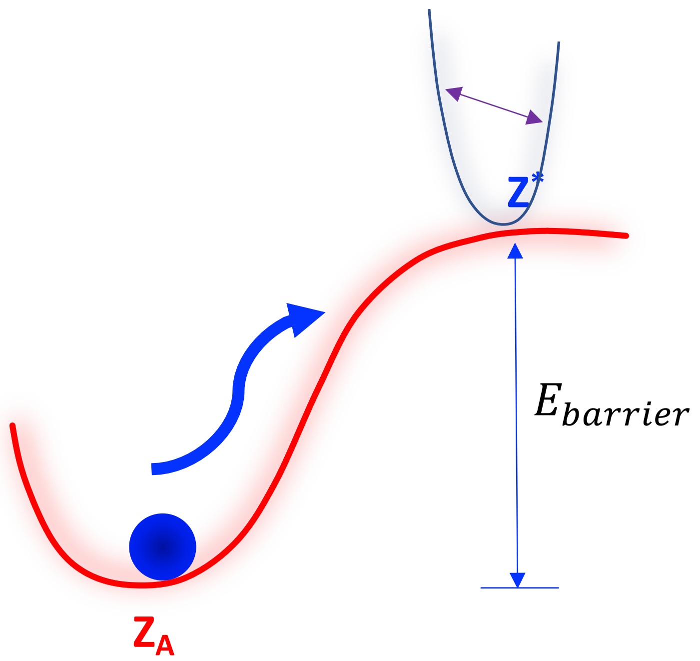

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N is usually a large number → which means a small change in frequency multiplicatively high!

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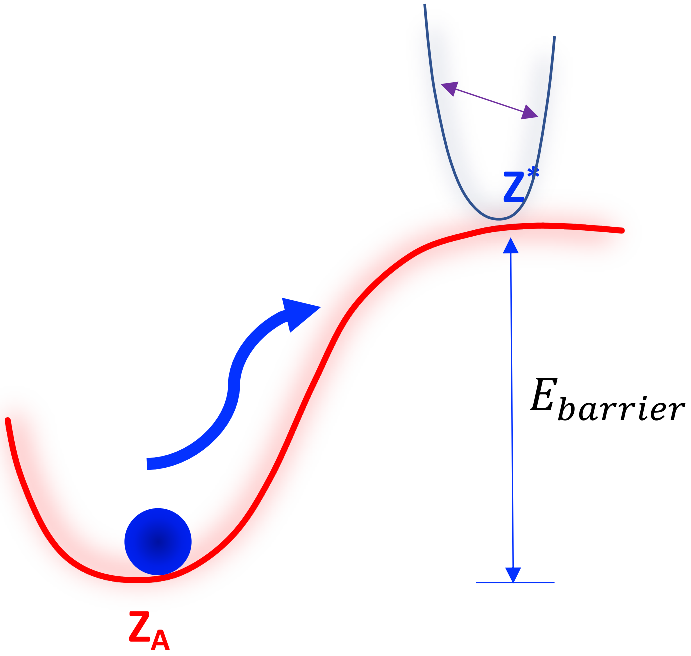

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Need:

- Hessian at minimum and saddle

But:

- Computationally expensive

(Typically million atoms systems)

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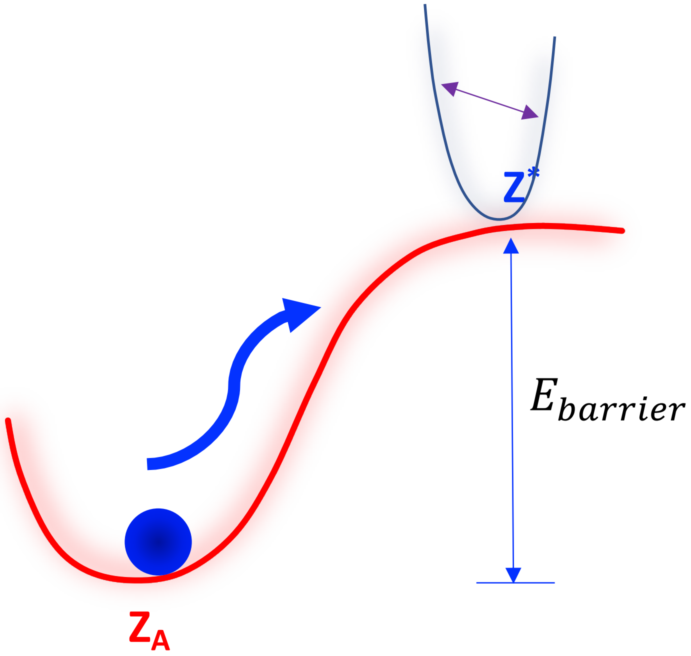

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Finite T-string/PAFI methods to compute free energy—but still involved!

Need:

- Hessian at minimum and saddle

But:

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Entropy computation from higher order free-energy approximation

Following Schroek 1980,

Higher order approx. of free-energy density as function of temp. (T) and Green-Lagrange strain $E_{ij} = \frac{1}{2}[F_{ik}F_{kj} - \delta_{ij}]$

$$f(T, E_{ij}) = f_0 + f_{T,ik} T E_{ik} + \frac{1}{2} f_{ik,lm} E_{ik} E_{lm} + \ldots$$

Higher order entropy density

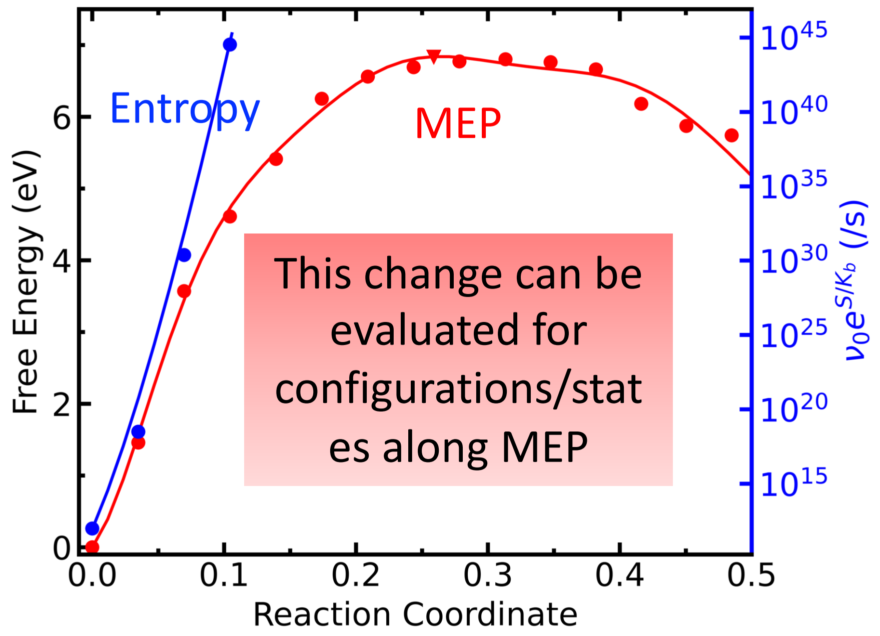
$$\Delta s = -\frac{\partial \Delta f}{\partial T} = -f_{T,ik} E_{ik} - \frac{1}{2} f_{T,ik,lm} E_{ik} E_{lm} = \alpha_{lm} f_{ik,lm} E_{ik} - \frac{1}{2} f_{T,ik,lm} E_{ik} E_{lm}$$

Total Entropy change

$$S = \int \Delta s dV = \alpha_V K \int E_{ii} dV - \frac{1}{2} \frac{\partial C_{iklm}}{\partial T} \int E_{ik} E_{lm} dV$$

Thermal expansion coefficient

T-dependences of elastic modulii



Free Energy along MEP : *under compression*

- Steep increase of entropy along the MEP!
- Caused by **release of compressive strain** in the faulted region, leading to phonon **softening**

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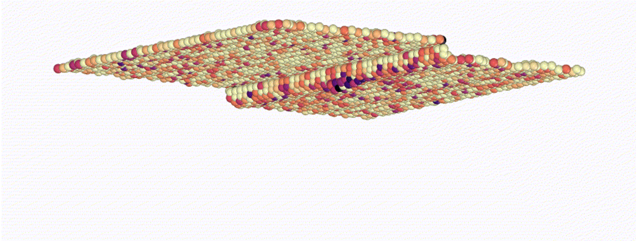

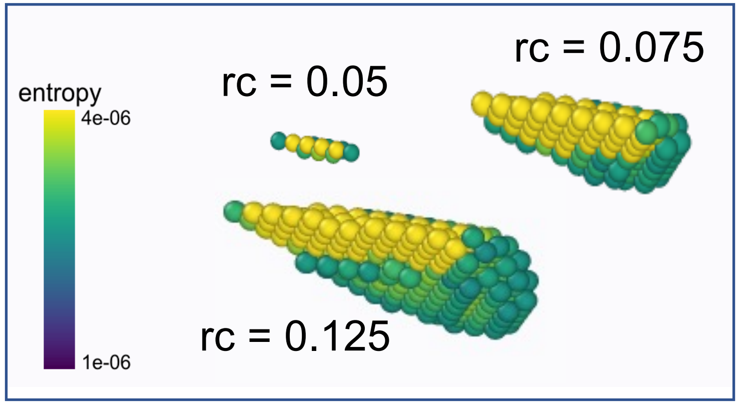

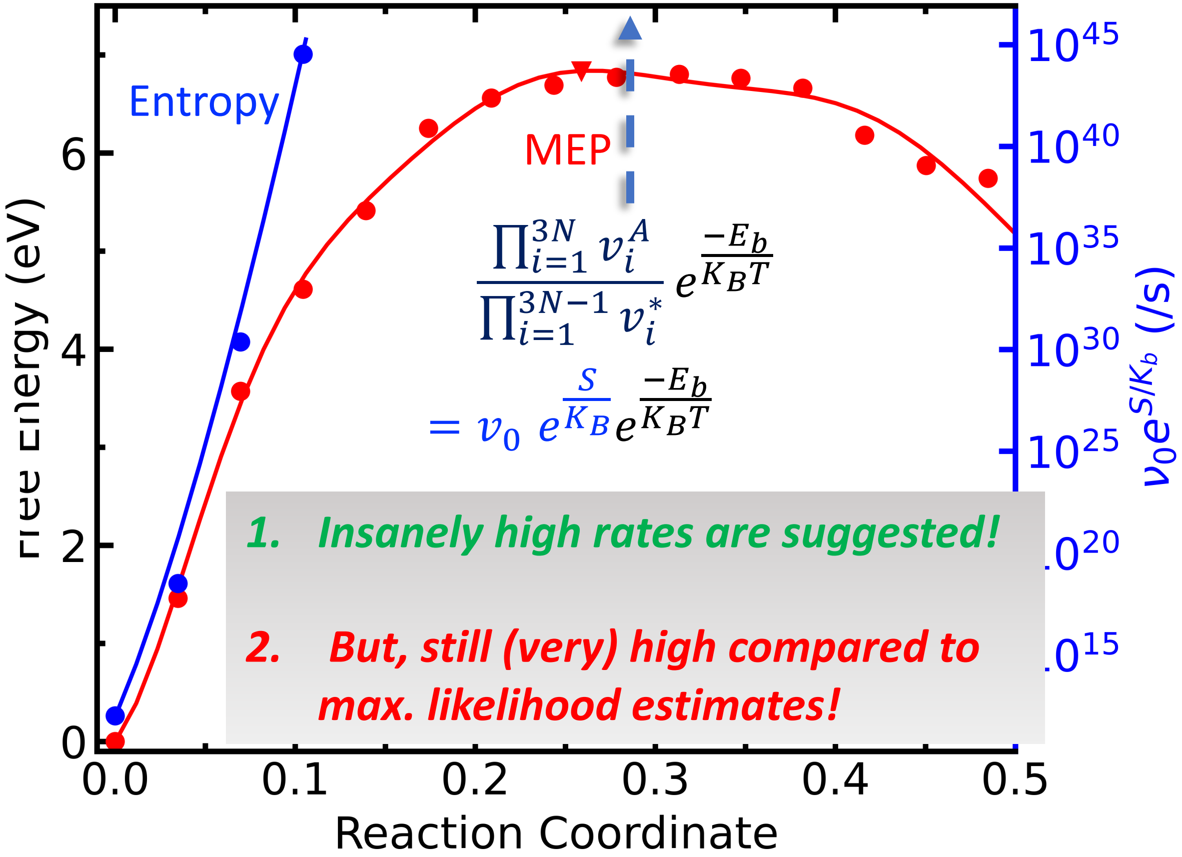

1. ***Insanely high rates are suggested!***
2. ***But, still (very) high compared to max. likelihood estimates!***

Free Energy along MEP : *under compression*

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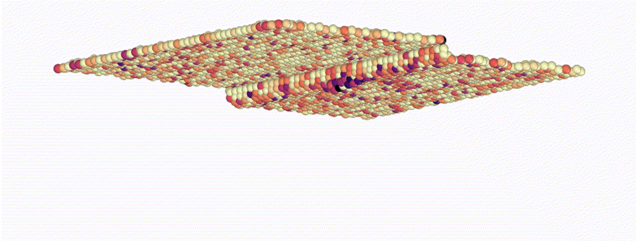
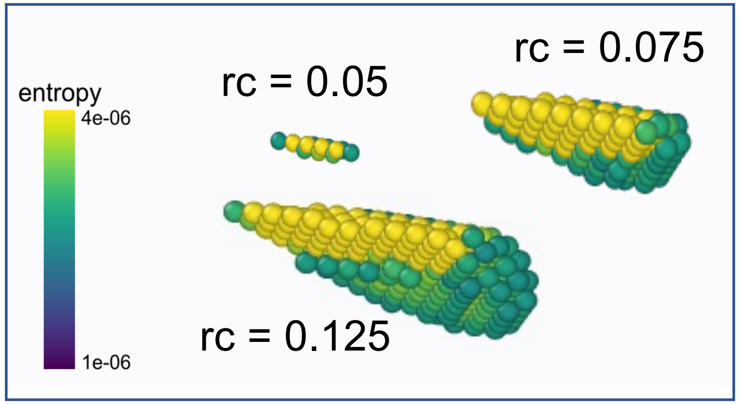
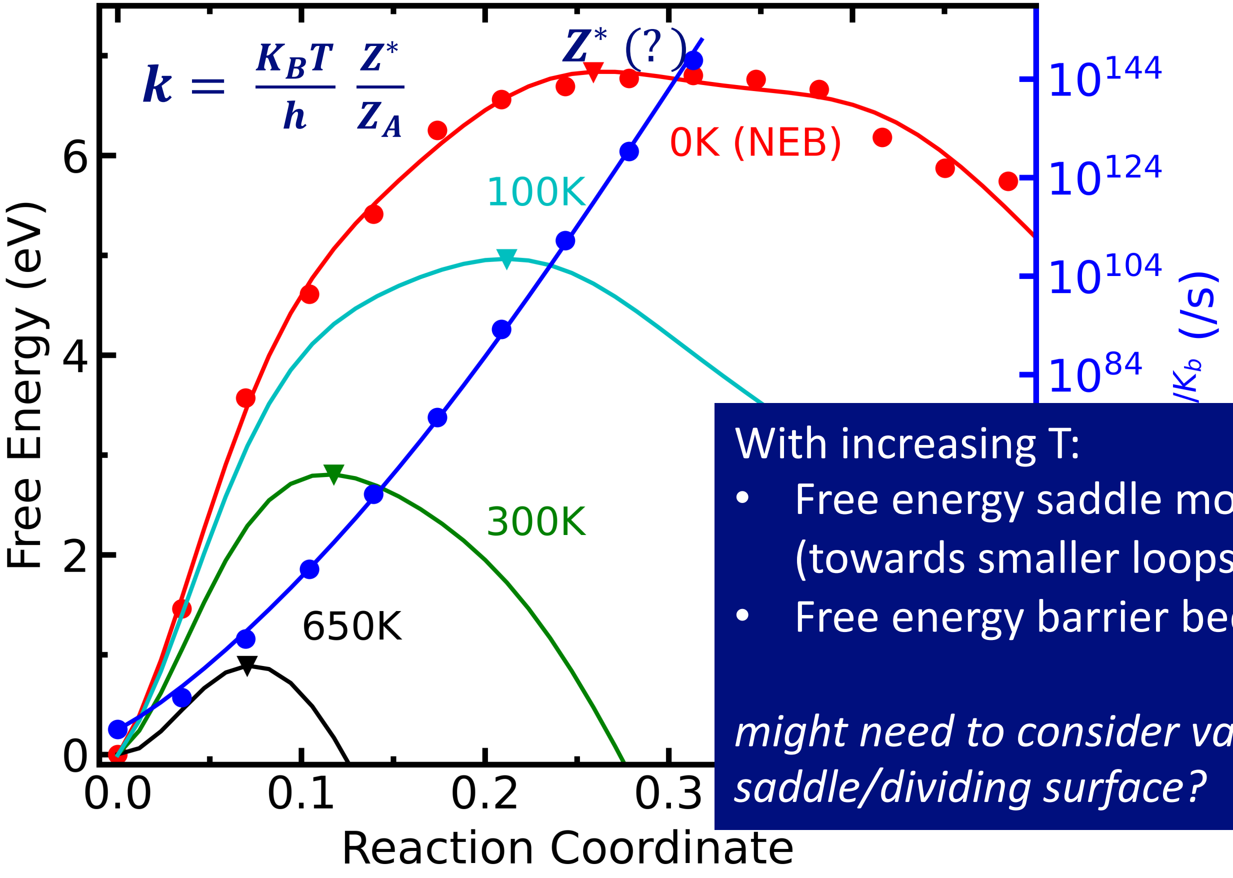
$$\boxed{\mathcal{F} = E - TS}$$







With increasing T:

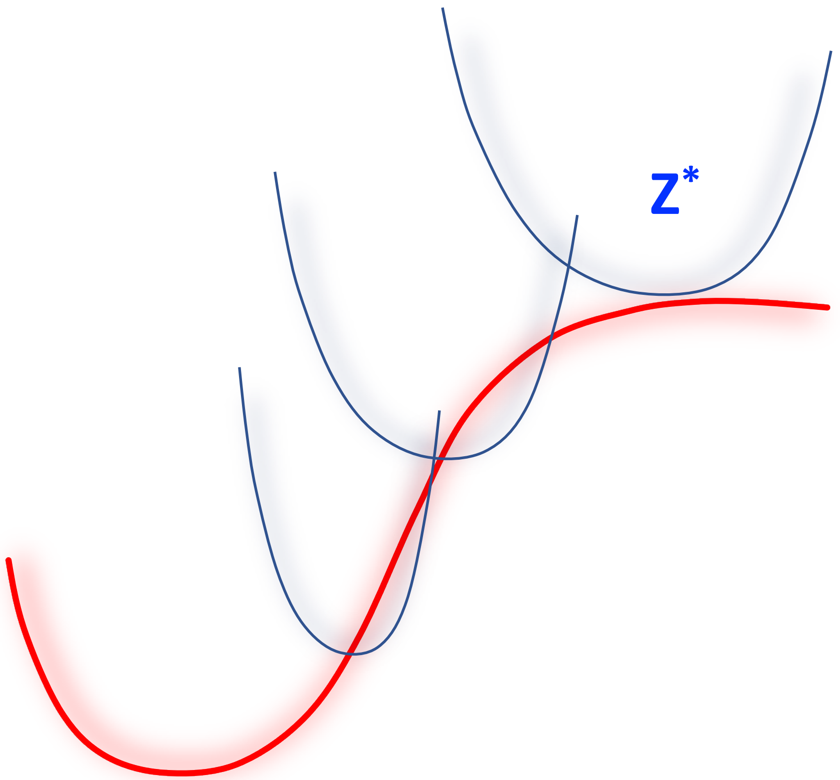
- Free energy saddle moves inwards (towards smaller loops)
- Free energy barrier becomes smaller

might need to consider variations of saddle/dividing surface?

Variational Transition State Theory

The "best" dividing surface
is the one the predicts the smallest
TST rate
(since TST is an upper bound
to the true rate)

I.e., the (T-dependent) dividing surface
should be at the **free-energy saddle**,
not the energy saddle



Free Energy Pathway for Dislocation Nucleation

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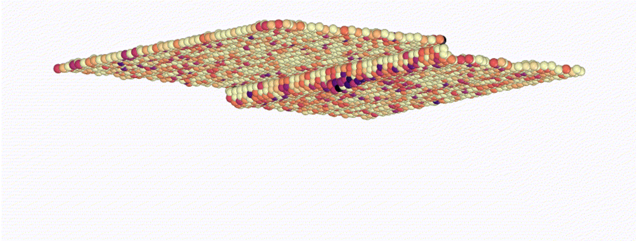

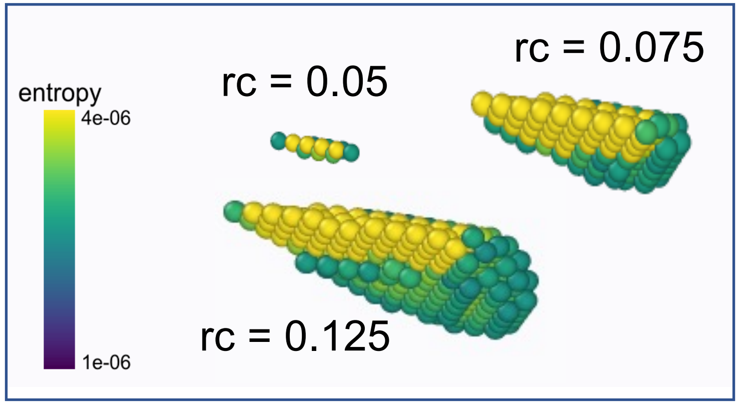

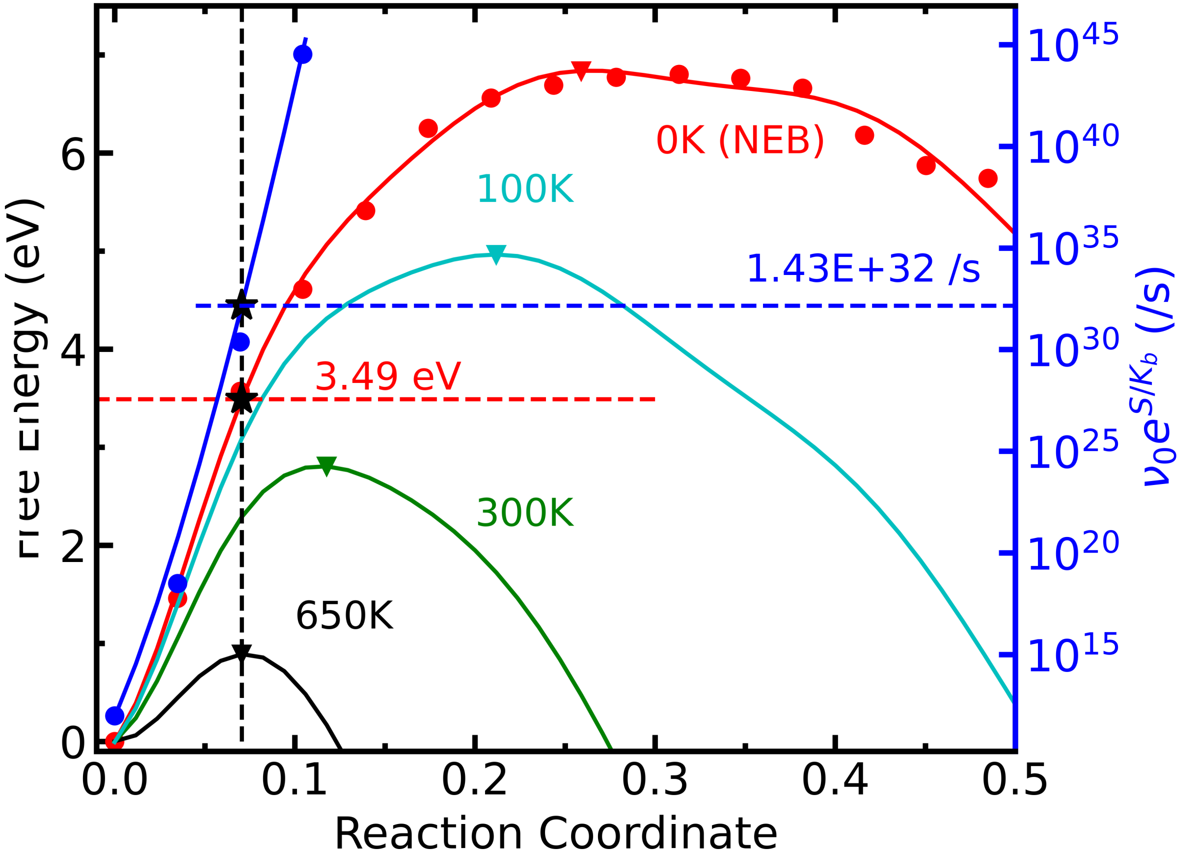

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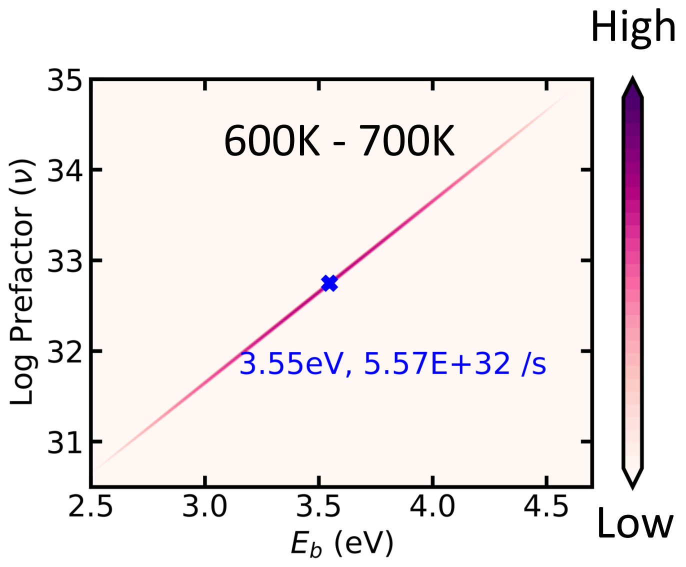
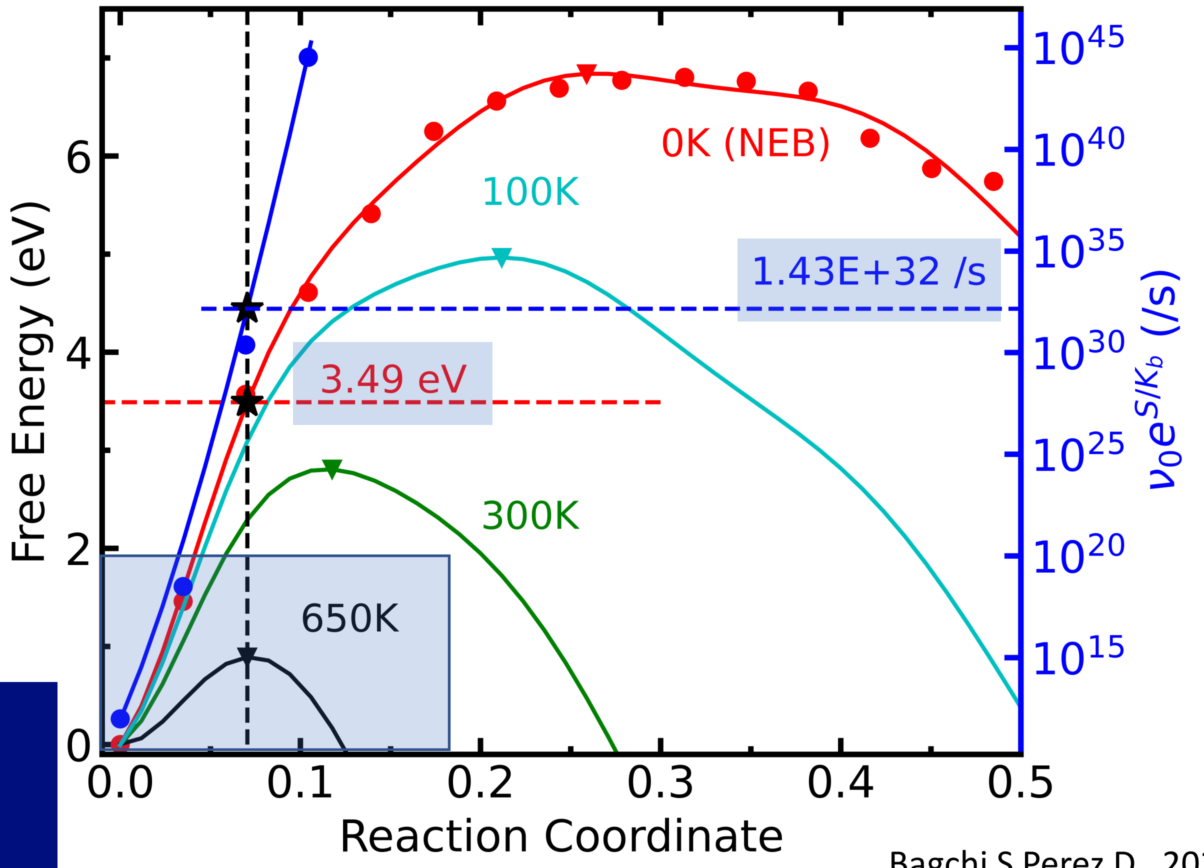


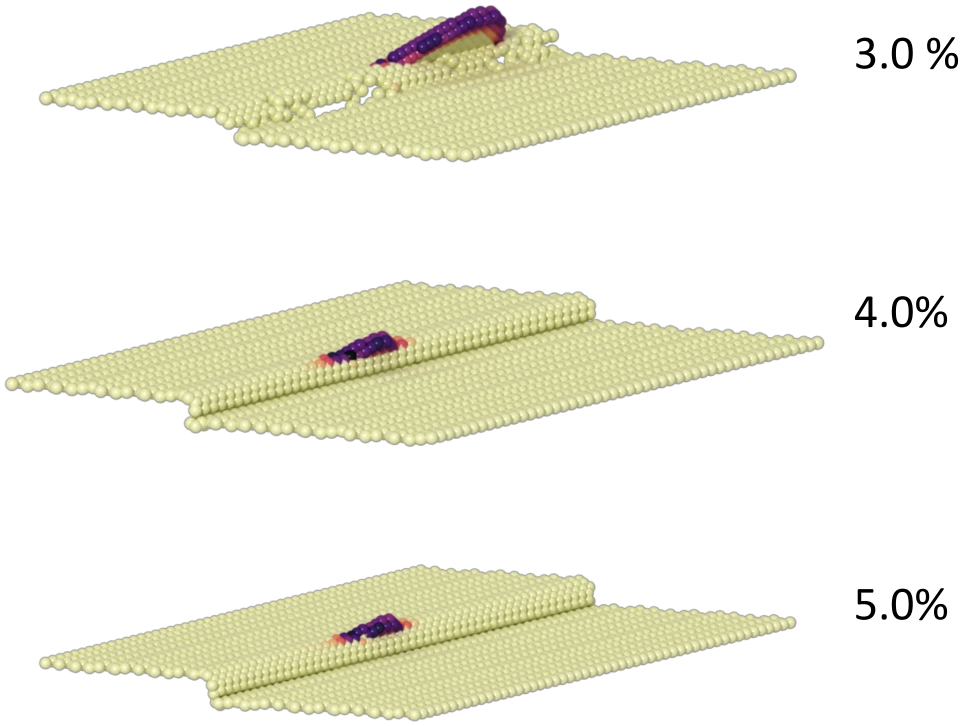


predictions are quantitative

as long as <u>MFEP</u> does not deviate much from <u>MEP</u>

Bagchi S Perez D., 2022 (*in preperation*)

Variational TST can capture anharmonic kinetic rates



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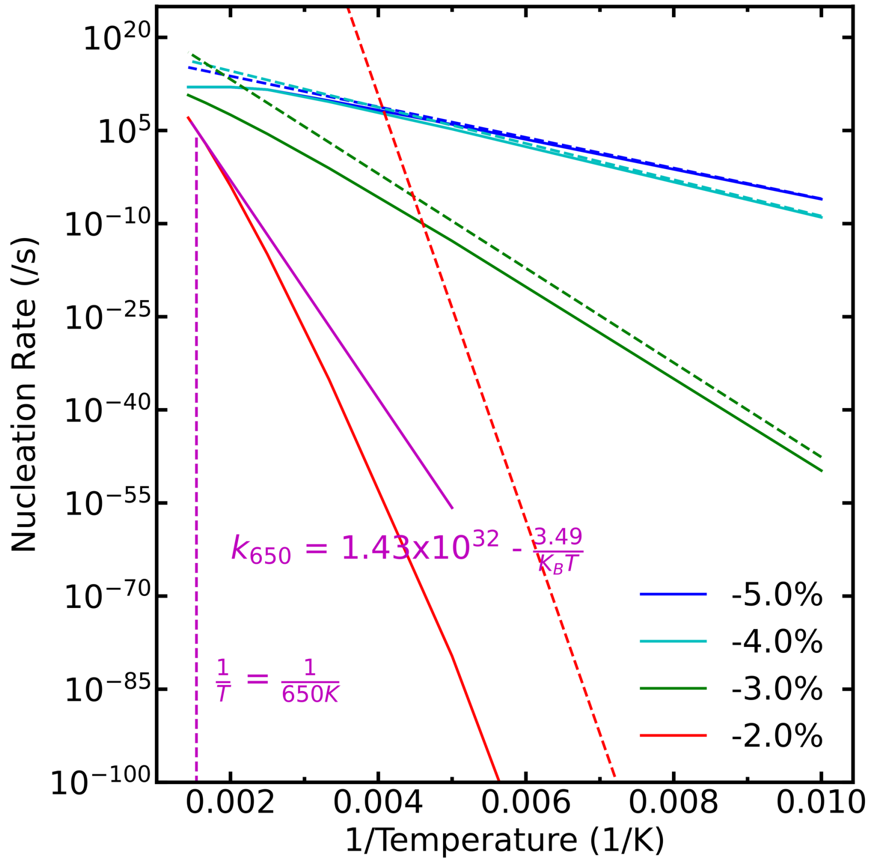


HTST is asymptotically recovered at low-T and high compressive strains

Vibrational Entropy could be crucial for plasticity

Summary:

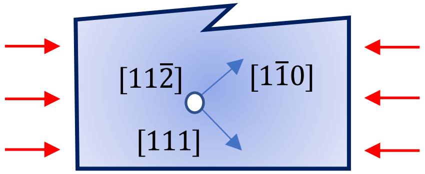
Finite temperature dynamics show **surprisingly high** nucleation rates

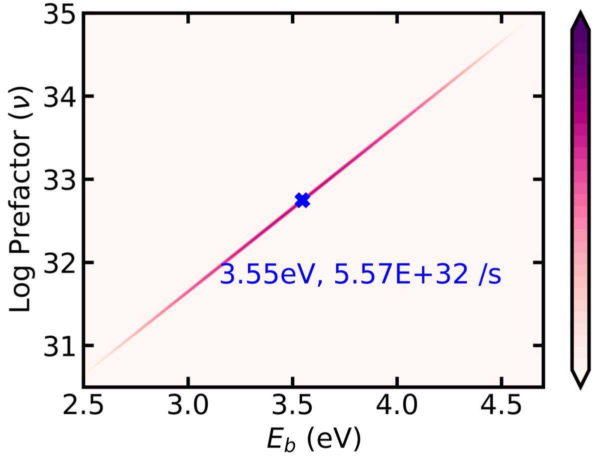
We have implemented a continuum approximation to the entropy change that predicts:

- Free energy barriers << Energy barriers
- HUGE prefactors (10^{32} vs 10^{12} 1/s !)
- Nucleation rates in good agreement with direct MD

Data-driven ways to quantify path deviations at finite–T (also benchmanrk with other methods e.g. PAFI)

Strong anharmonicity can also facilitate other activated plasticity (large strain release) events





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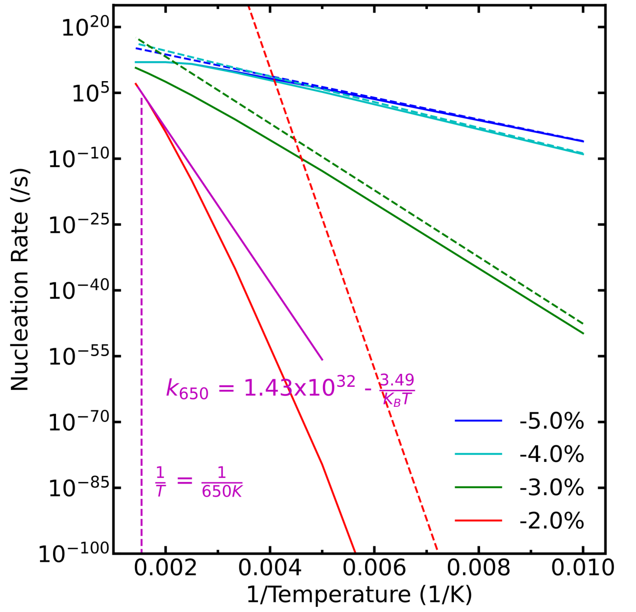
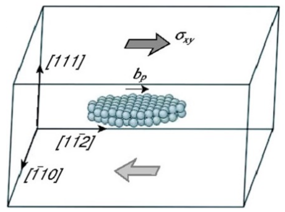
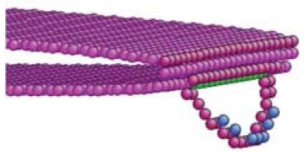
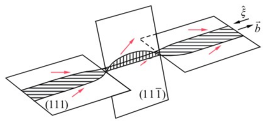




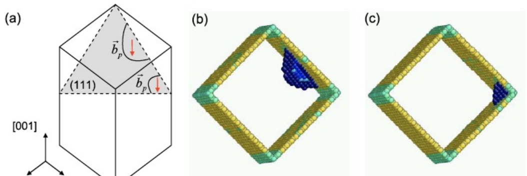
Ryu, PNAS 2012



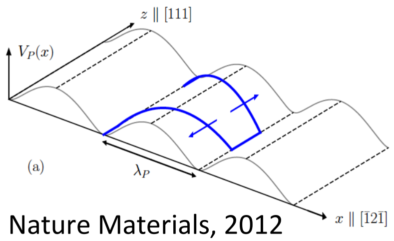
Zhu, PRL, 2010



Cai, JMPS, 2020



Zhu, PRL, 2012



Proville, Nature Materials, 2012

Acknowledgements

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