

# THE TRANSITION STATE THEORY

Normand Mousseau

Professor, Département de physique and Institut Courtois  
Université de Montréal

[normand.mousseau@umontreal.ca](mailto:normand.mousseau@umontreal.ca)



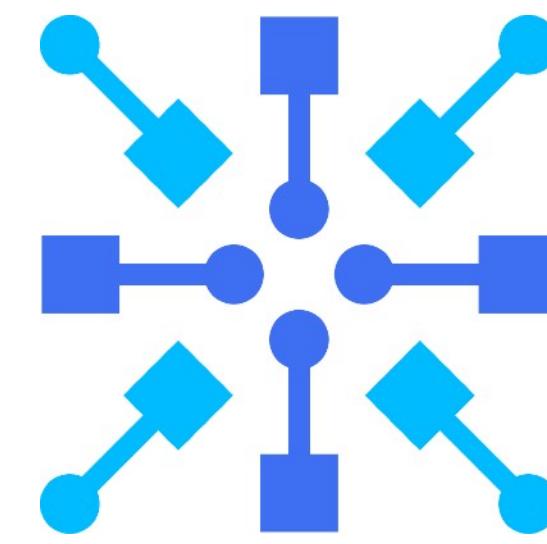
INSTITUT  
DE L'ÉNERGIE  
**TROTTIER**

## Mission

The **academic training** of a new generation of engineers, scientists and innovators with a systemic and trans-disciplinary understanding of energy issues;

The **research** for sustainable solutions for our energy future, while supporting knowledge generation and innovation in the energy sector to help face the coming decades challenges;

The **dissemination** of knowledge on energy related topics, contributing to the societal dialogue on energy issues.



# CARREFOUR DE MODÉLISATION ÉNERGÉTIQUE

---

## ENERGY MODELLING HUB

The Energy Modelling Hub (EMH) is a pan-Canadian boundary organization that ensures the development of, maintains and makes accessible energy models and brings together public policymakers and energy modelling communities.

With the aim of leveraging existing knowledge, expertise and capabilities, the EMH will pursue the following objectives:

- Promote the role of modelling as a support for the development of public policies and the energy transition;
- Fill data and modelling gaps in collaboration with decision makers, stakeholders and modellers;
- Coordinate the development of models useful for policy development aimed at the major transformation of Canada's energy system in achieving its climate objectives;
- Provide support to the community in the development and use of models and in the interpretation of modelling results and their policy implications.
- Maintain open and transparent datasets and models as well as an inventory of models, modelling projects and modellers; and
- Serve as a liaison to increase exchanges between decision makers and Canada's modelling community.

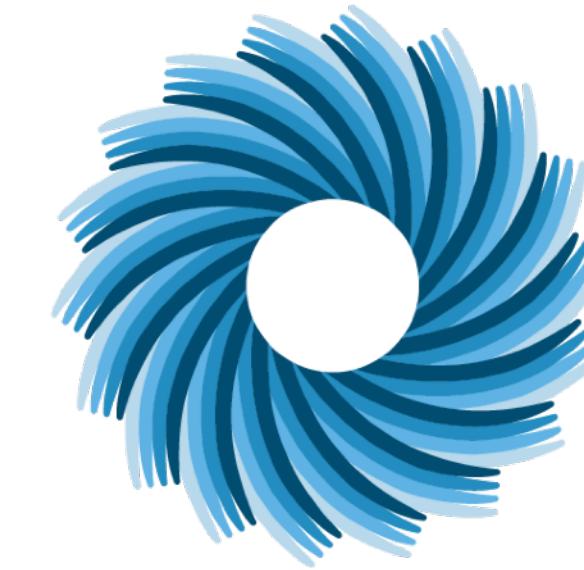
CANADIAN  
**CLIMATE**  
INSTITUTE



L'INSTITUT  
**CLIMATIQUE**  
DU CANADA

Provides analysis for public policies to help Canada face of climate change and advance a net-zero future.

## The Transition Accelerator



## L'Accélérateur de transition

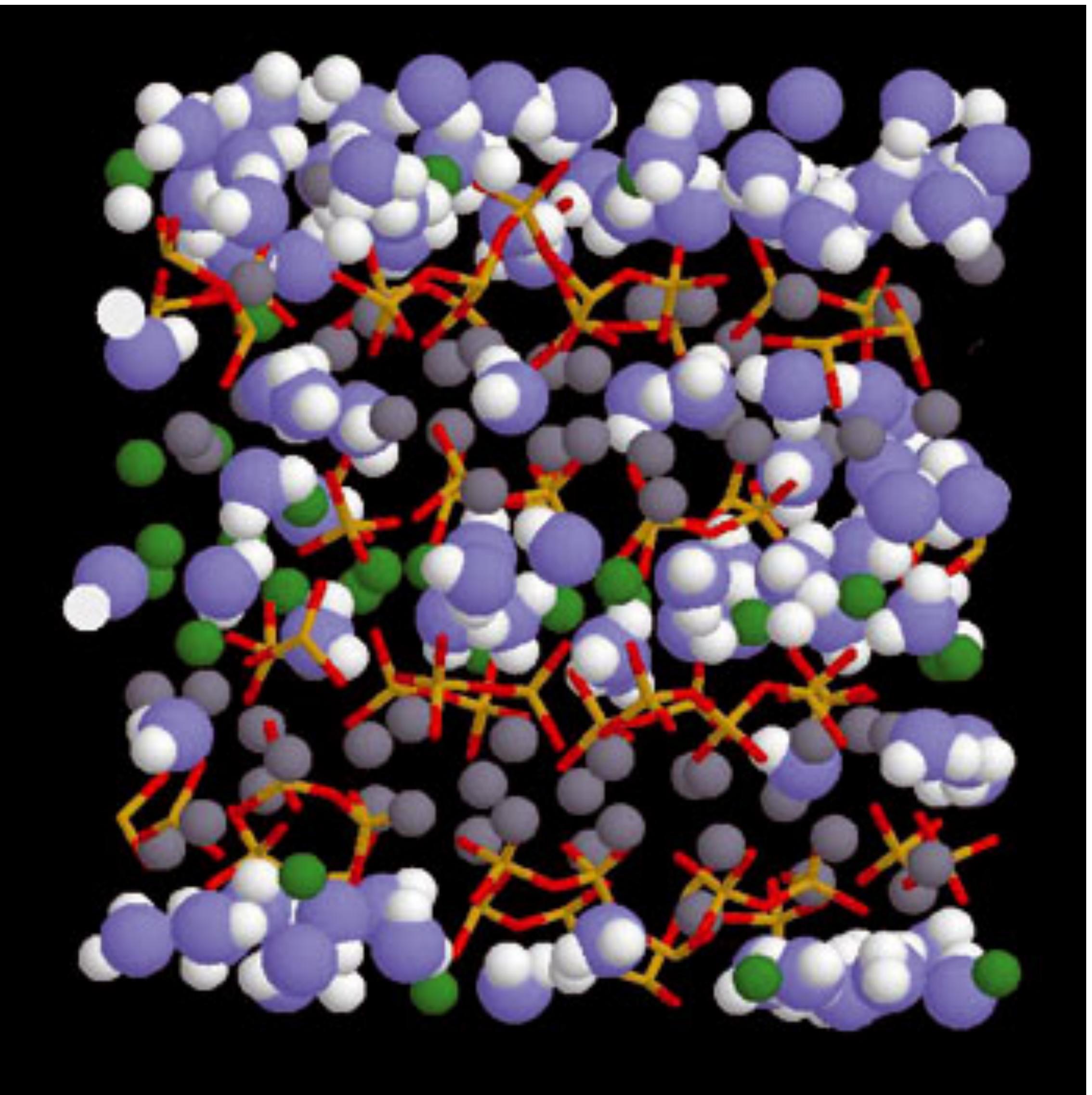
The Transition Accelerator is a pan-Canadian charity that works with groups across the country to direct these disruptions to solve business and social challenges while building viable transition pathways to a net zero future.

Our current priorities are Canada's hydrogen economy, electric vehicle market penetration, building decarbonization and electrification, and grid integration.

# MATERIALS CONSTANTLY EVOLVE AROUND US

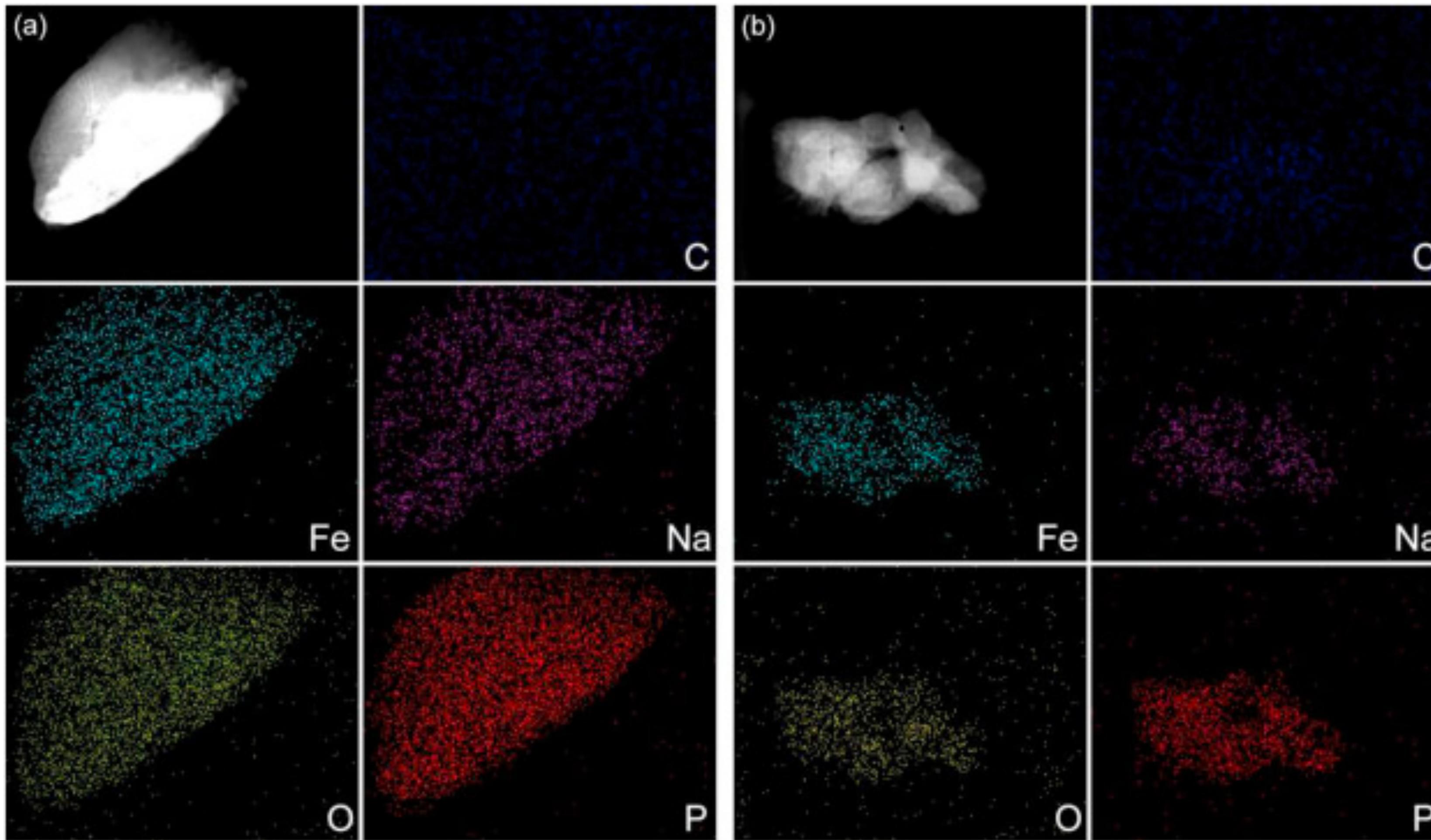


# HOW DOES CIMENT EVOLVE?



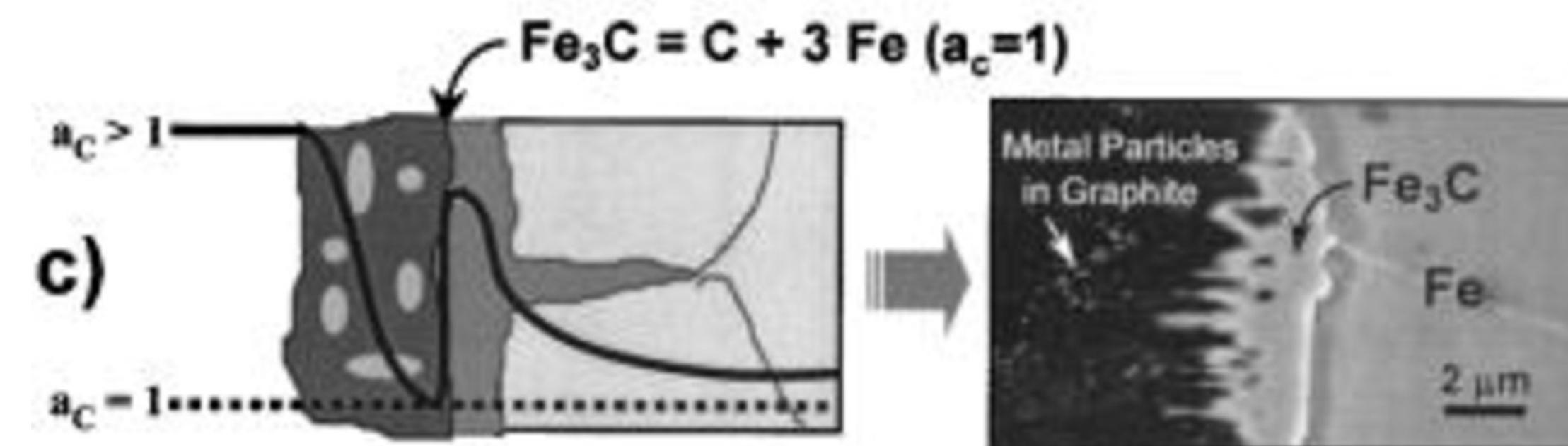
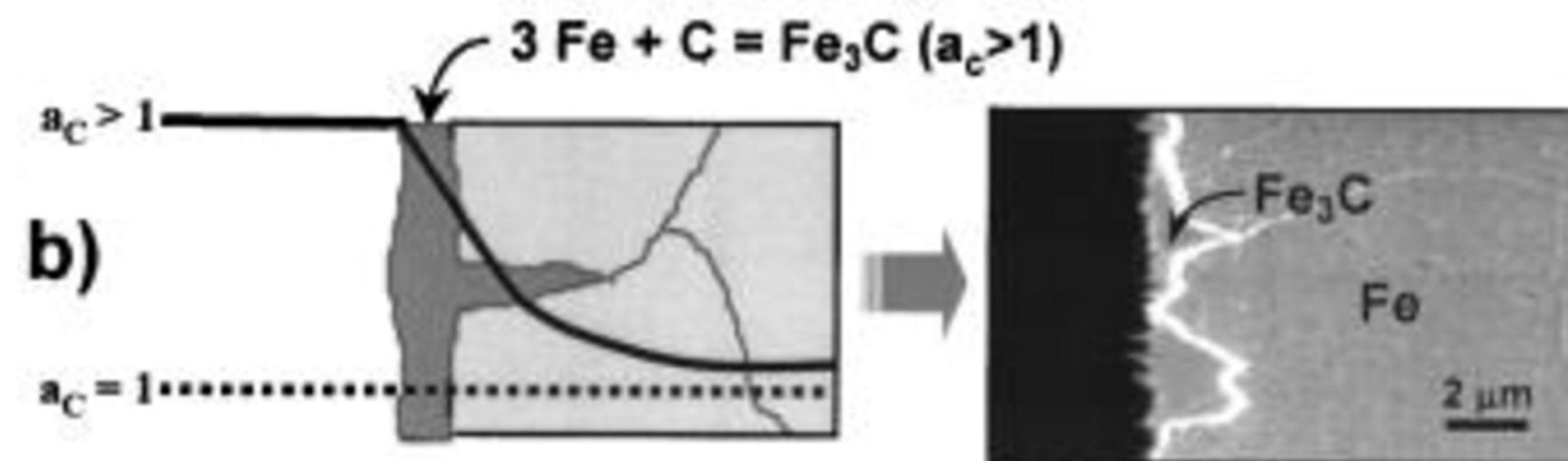
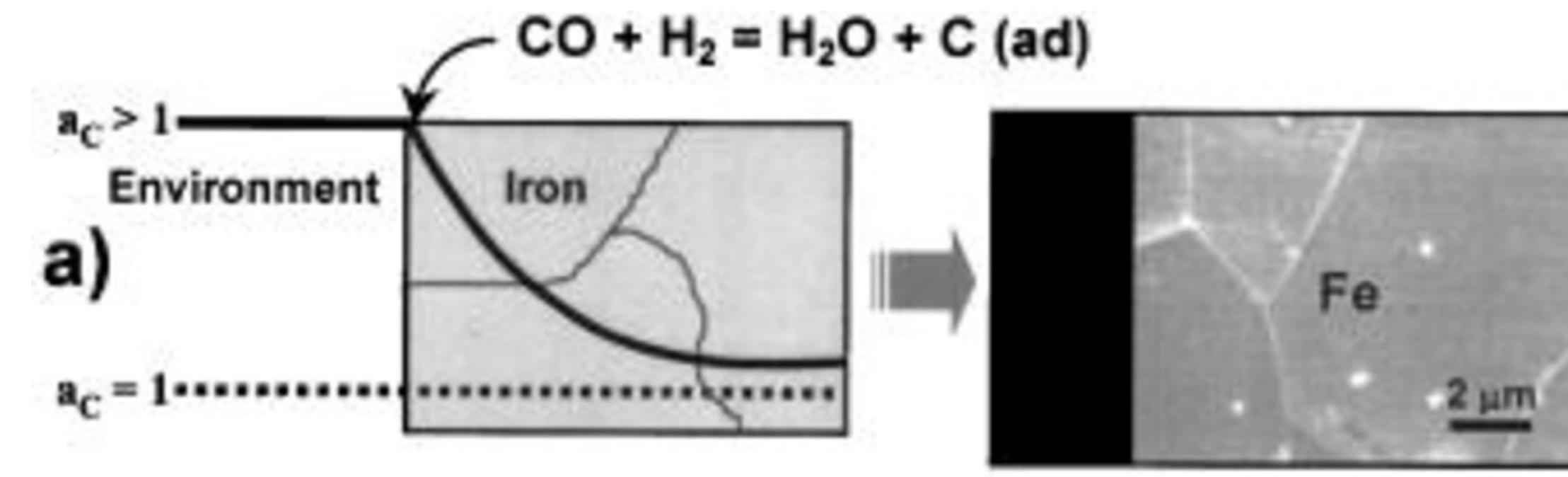
# HOW DOES SODIUM DIFFUSE IN NA-BATTERIES?

Diffusion in  $\text{Na}_2\text{FeP}_2\text{O}_7$ -carbon nanotubes composite



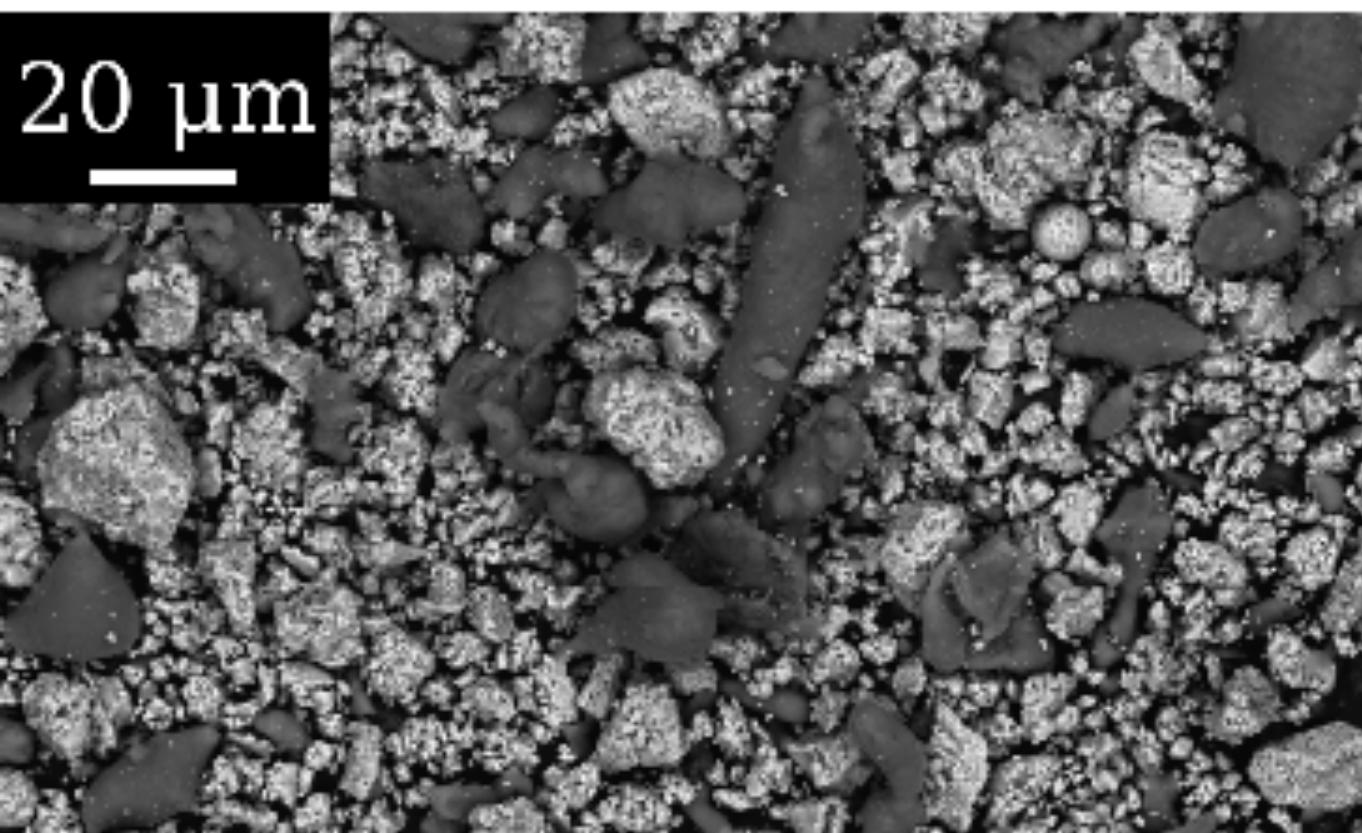
G Longoni, JE Wang, YH Jung, DK Kim, CM Maria, R Ruffo,  
Journal of Power Sources 302 (2016).

# WHAT IS THE MICROSCOPIC ORIGIN OF METAL DUSTING?



Chun *et al.*, J.  
Electrochem. Soc. (2002)

# HOW TO OPTIMIZE THERMITE-INTERMETALLIC HYBRID MIXTURES?



Unmilled mixture Al-CuO

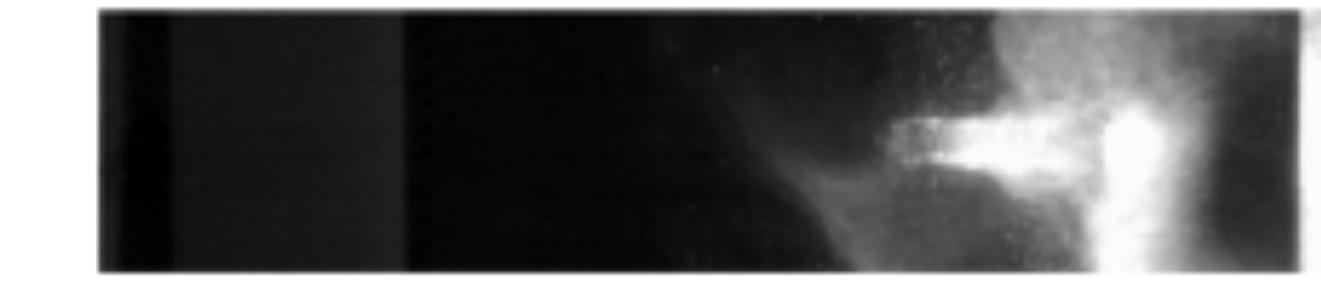
Thermite mixture can represent an interesting way to store energy

J.M. Bergthorson, S. Goroshin, M.J. Soo, P. Julien, J. Palecka, D.L. Frost, D.J. Jarvis,  
Applied Energy **160** (2015).

Images: C. Poupart, M.Sc. Thesis, University of Ottawa (2015)



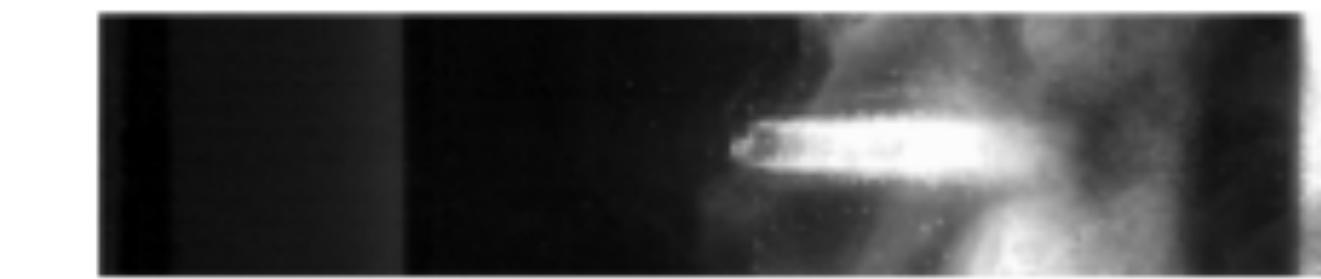
(a)  $t = 0\mu s$



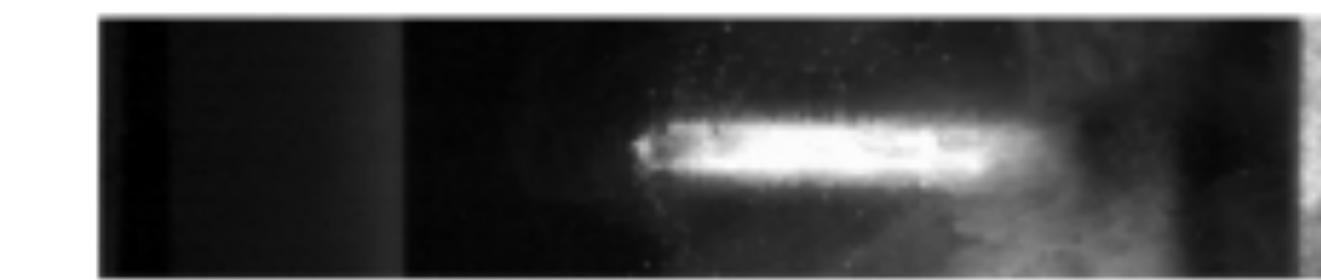
(b)  $t = 3,333\mu s$



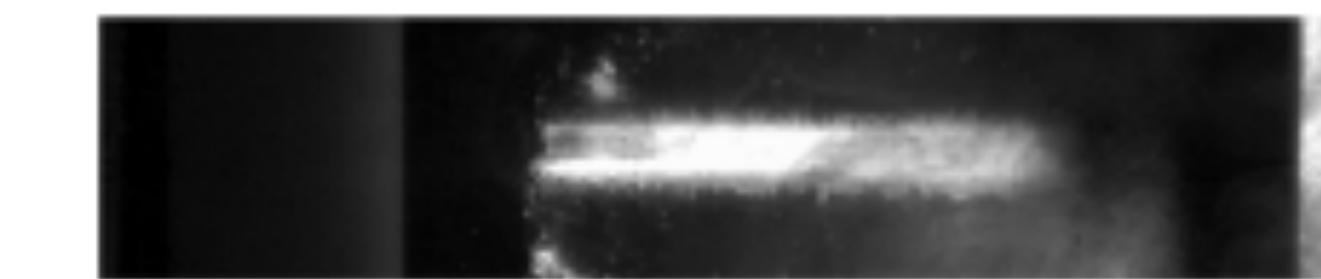
(c)  $t = 6,667\mu s$



(d)  $t = 10,000\mu s$



(e)  $t = 13,333\mu s$



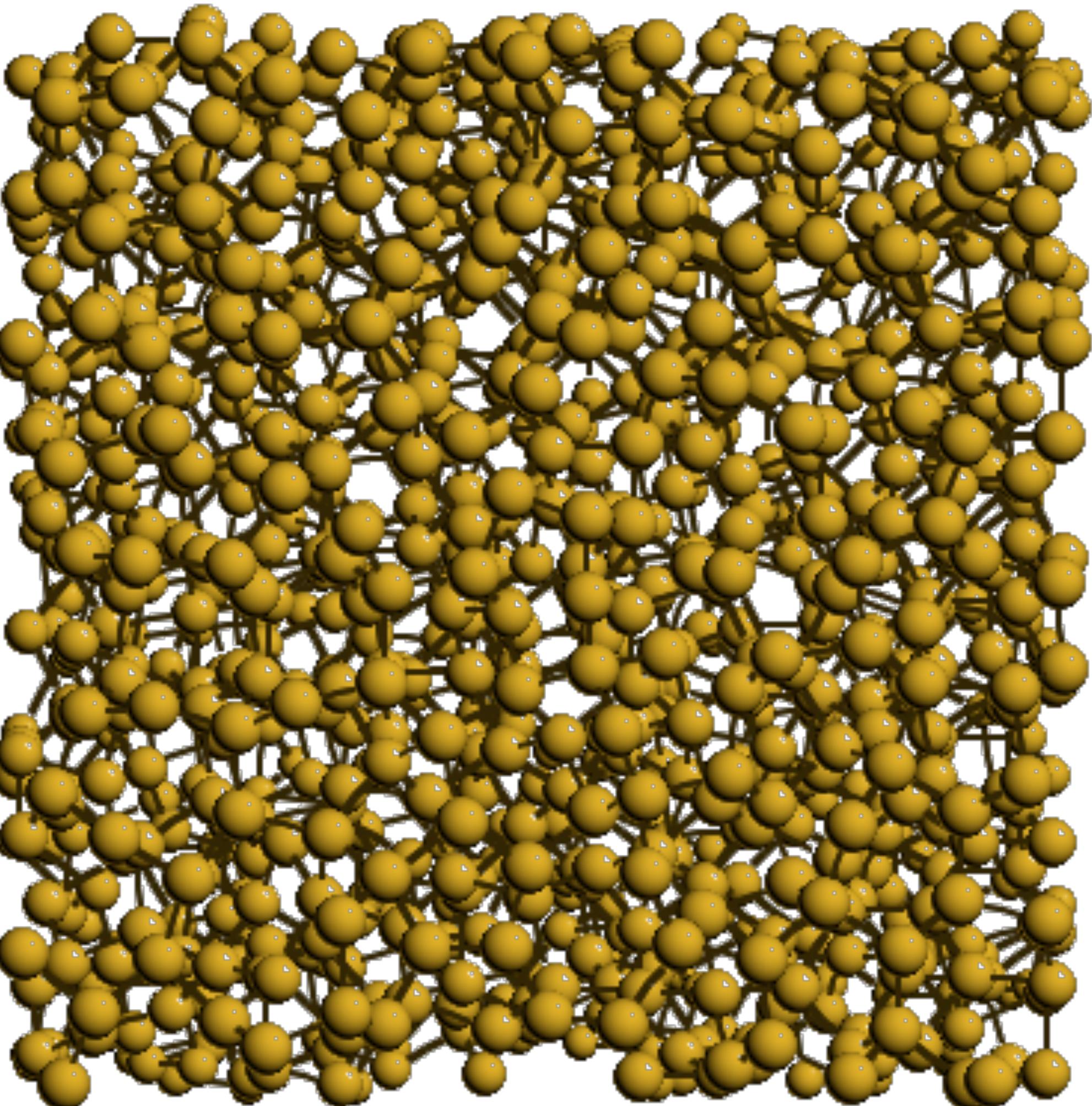
(f)  $t = 16,667\mu s$

# WHAT IS THE KINETICS OF DISORDERED MATERIALS

How do glasses relax at low T?

What are the defects?

What is the impact of impurities (e.g.: H in Si)



# HOW DO LIQUIDS FREEZE?

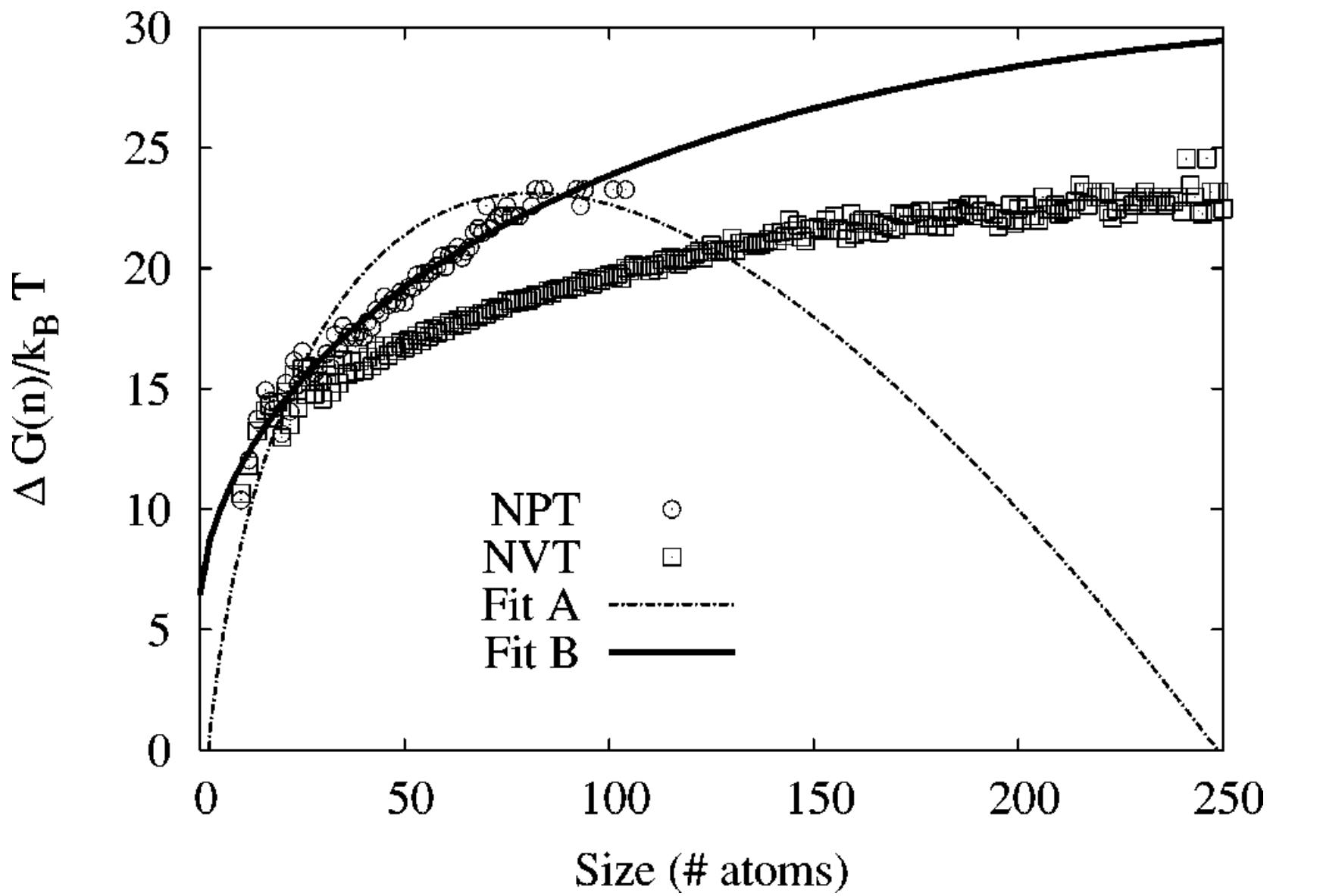
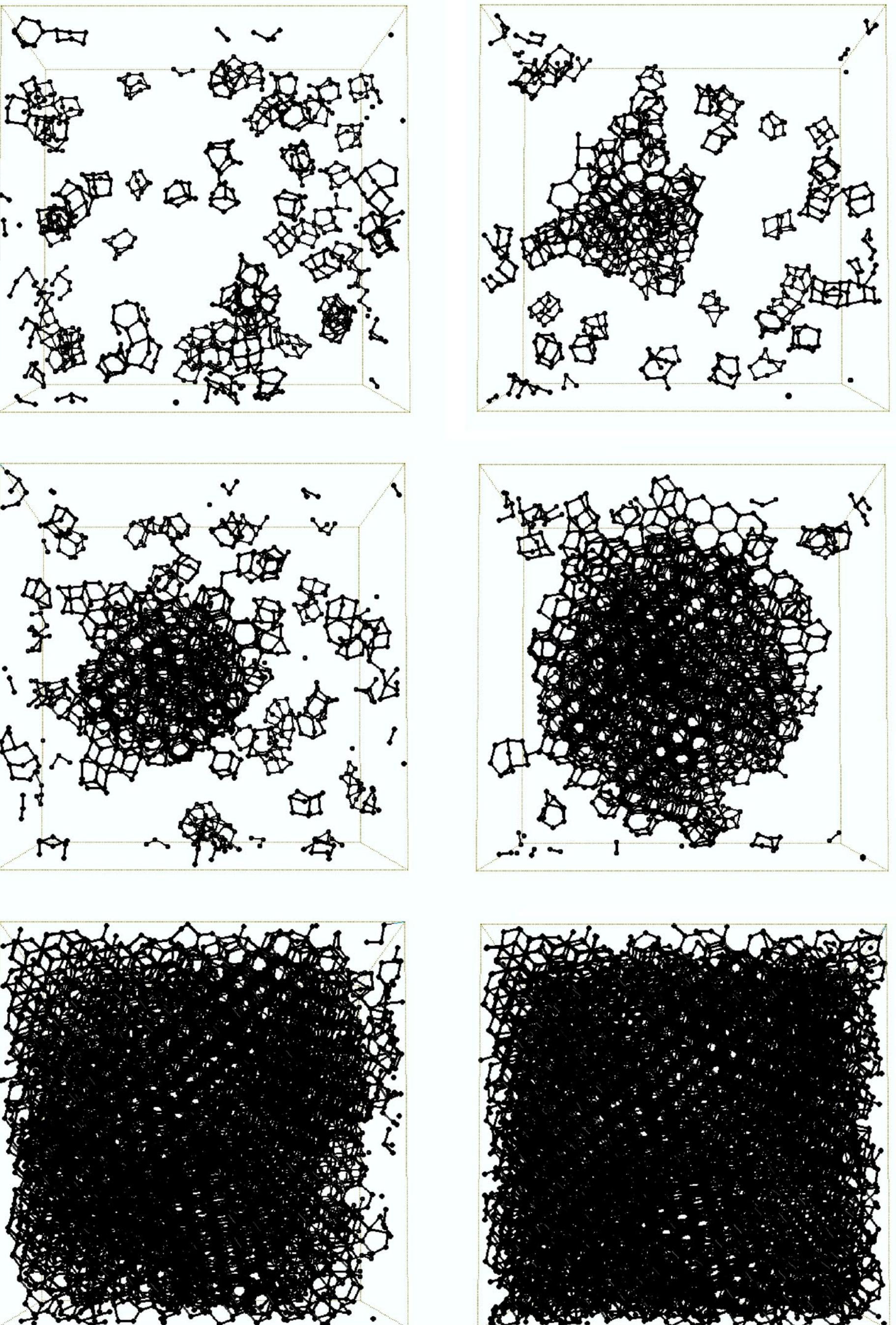


FIG. 8. Free energy (divided by  $k_B T$ ) of crystallites as a function of their size in NPT conditions (NPT) compared to NVT conditions (NVT). The simulation data are computed from the equilibrium probability of presence for clusters with the basic blocks analysis. The CNT curve computed with the  $\Delta G_{sl}$  of Broughton et Li (fit A) is closer to the free-energy data originating from  $P_{eq}(n)$ . However, a better fit (fit B) requires a value five times lower.



Nucleation and crystallization process of silicon using the Stillinger-Weber potential

Philippe Beaucage and Normand Mousseau

PHYSICAL REVIEW B 71, 094102 (2005)

# SUMMARY

- ✳ The problem
- ✳ The challenge of simulating over multiple time scales.
- ✳ Energy landscapes.
- ✳ The transition state theory.
- ✳ Overview of various methods for breaching these time scales.

# **THE CHALLENGE**

**Thermodynamics**

**Kinetics**

# THE CHALLENGE

## Thermodynamics

We need to sample correctly the phase space

- access all relevant points in phase space
- establish their relative probability or, better, their absolute probability

## Kinetics

# THE CHALLENGE

## Thermodynamics

We need to sample correctly the phase space

- access all relevant points in phase space
- establish their relative probability or, better, their absolute probability

## Kinetics

We need to establish the dynamical evolution of the system

- focus on out-of-equilibrium property
- describe accurately the dynamical relation between points in phase space

# THE CHALLENGE

## Equilibrium/Quasi-equilibrium systems

- Defects
- Polymers Multiphase materials

Difficult to identify the states, to establish their relative weight

## Out-of-equilibrium processes

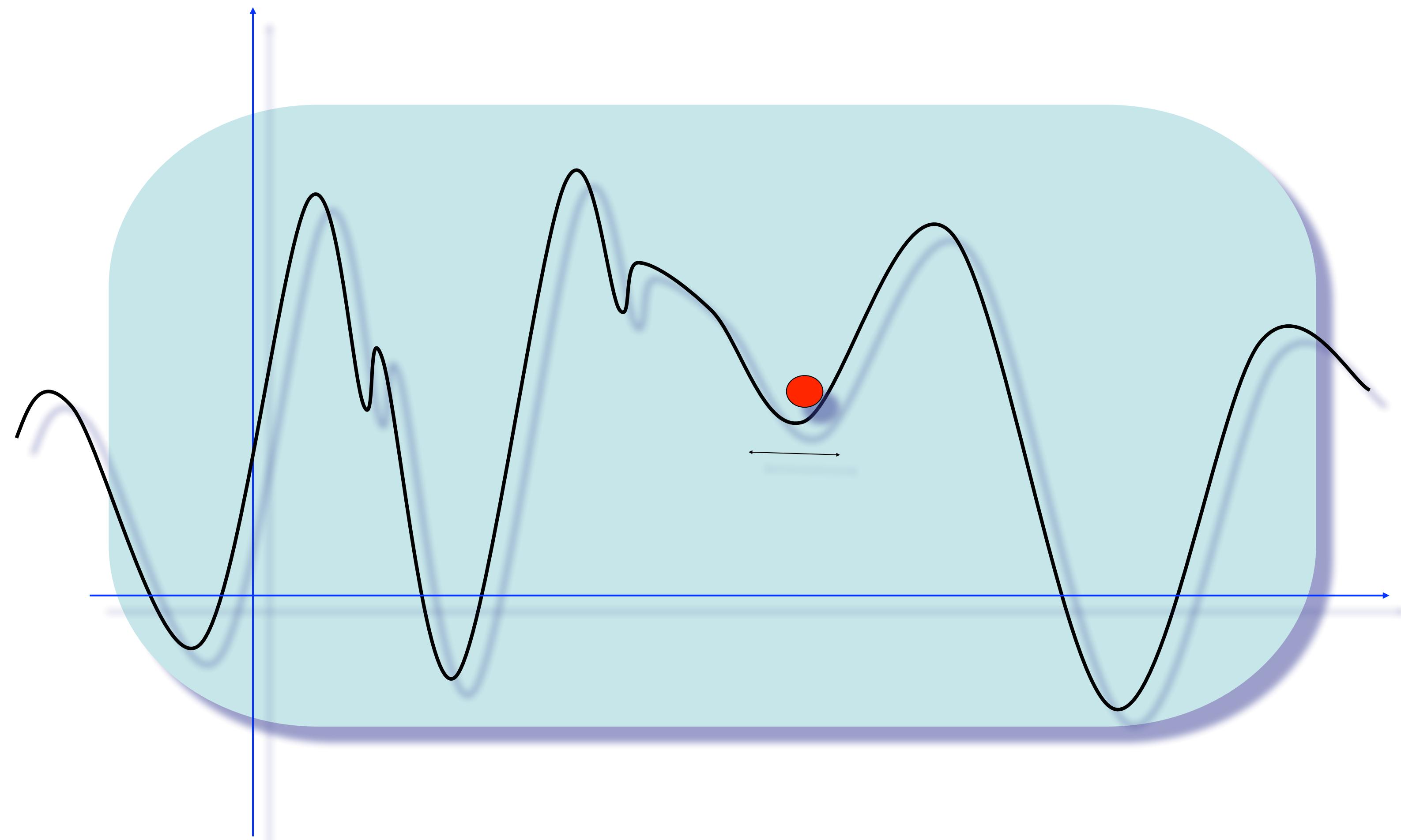
- Growth processes
- Self-Assembly
- Chemical reactions
- Glasses

How to find the pathways?  
How to access the right time scale?

# ENERGY LANDSCAPES

Atoms vibrate at  $10^{12}$  Hz

Rare events (activated events)  
occur at  $10^6$  Hz or less

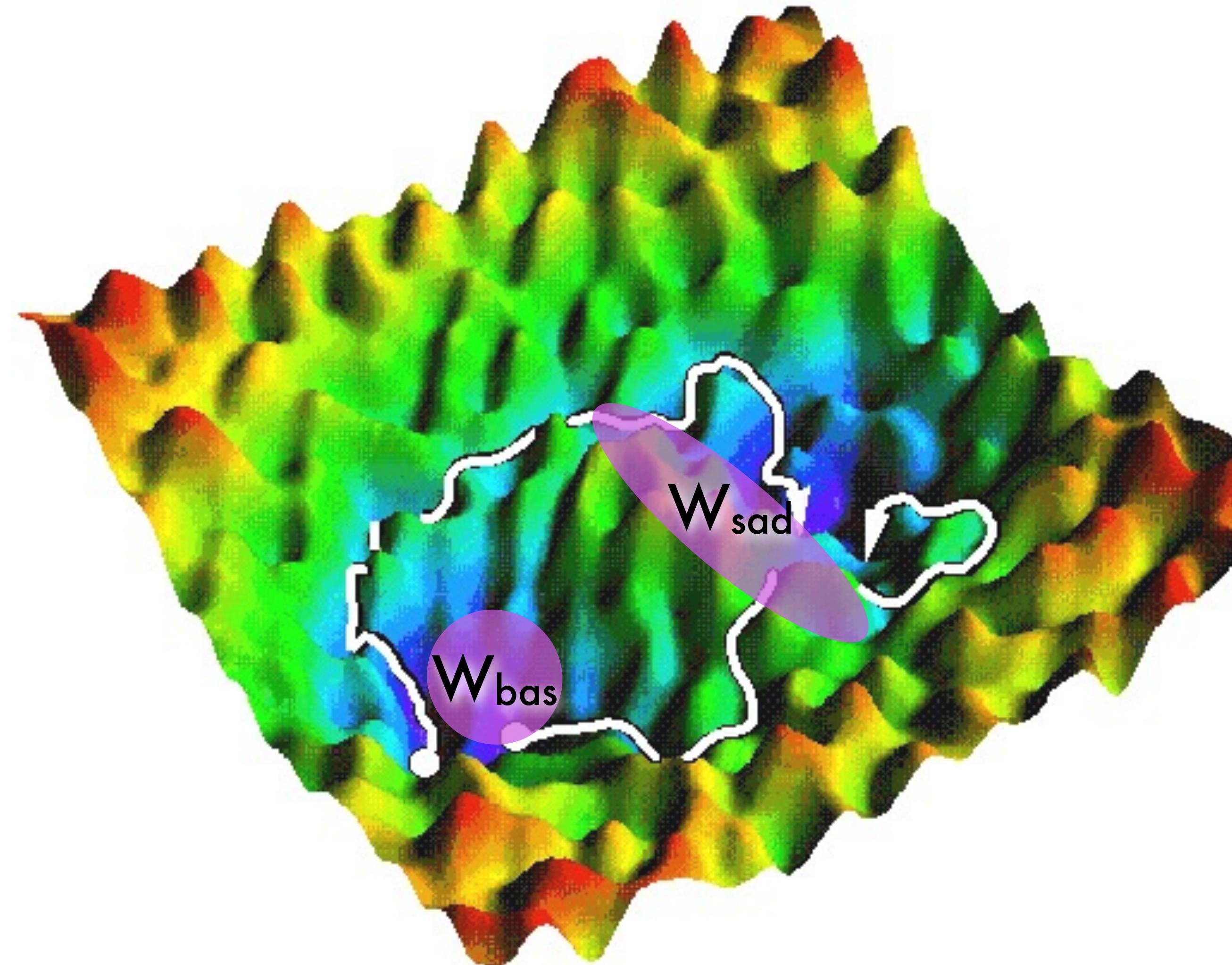


Generic problem:

How to explore the space of variables of a high dimensional cost function?

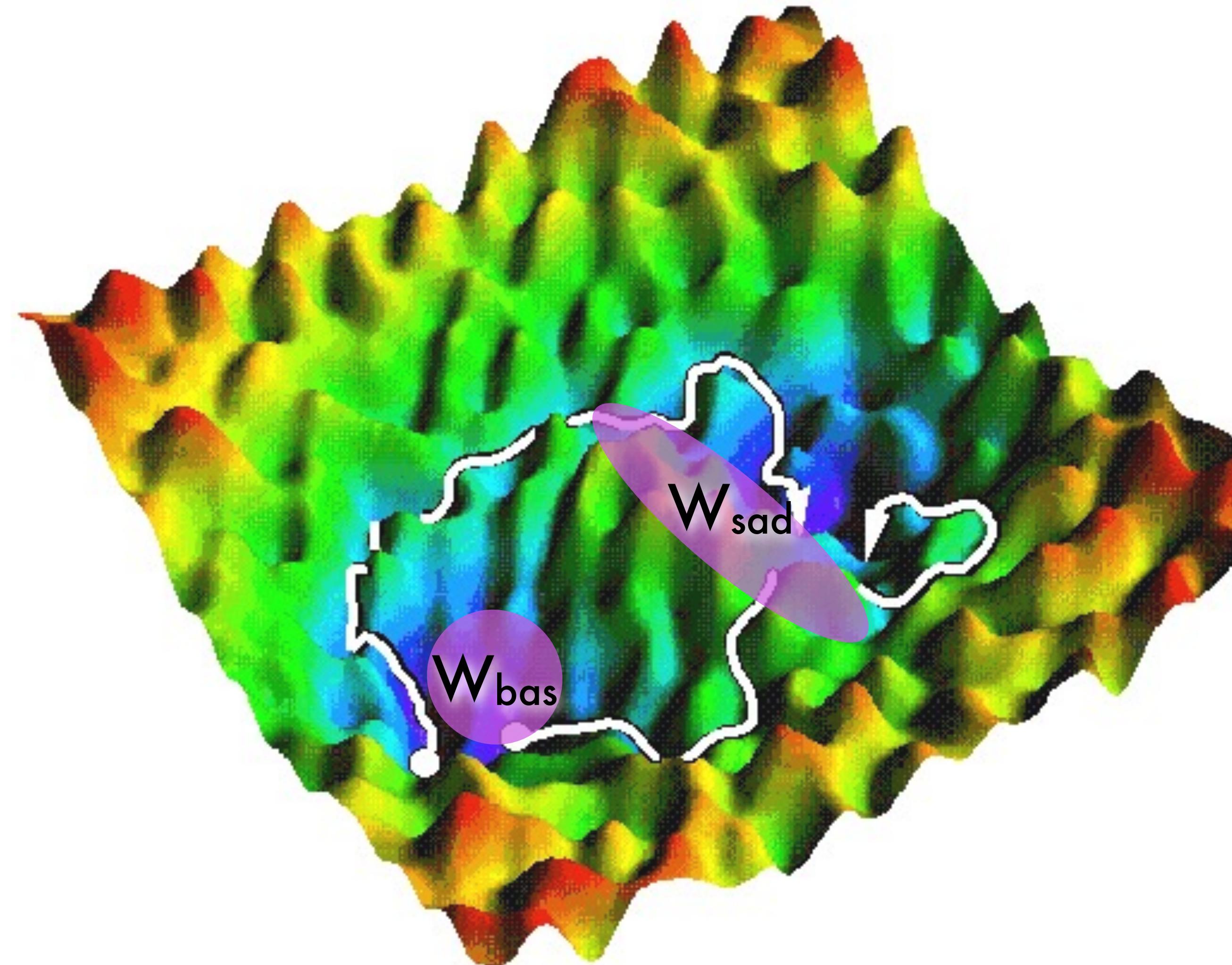
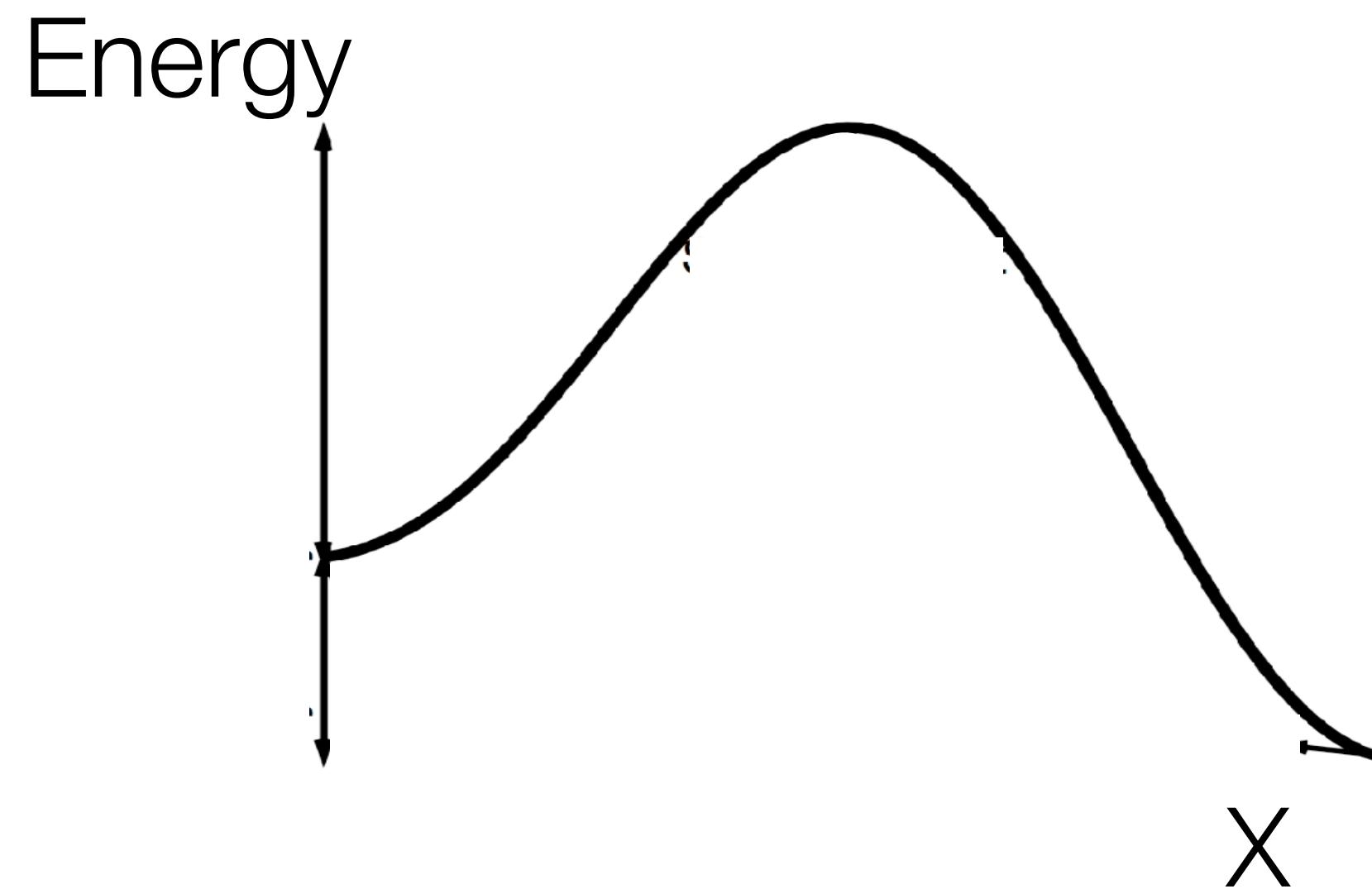
# HOW DO WE APPROACH THE PROBLEM?

Entropy  
State  
Thermal vibration



# PUTTING IT TOGETHER

Free energy : entropy + energy  
and  
Temperature or external driving



# CAN BE SUMMARIZE INTO THE «ENERGY LANDSCAPE»

$$\Delta W = W_{\text{bas}} - W_{\text{sad}}$$

The rate is

$$k = \kappa \cdot k_{\text{TST}}$$

with

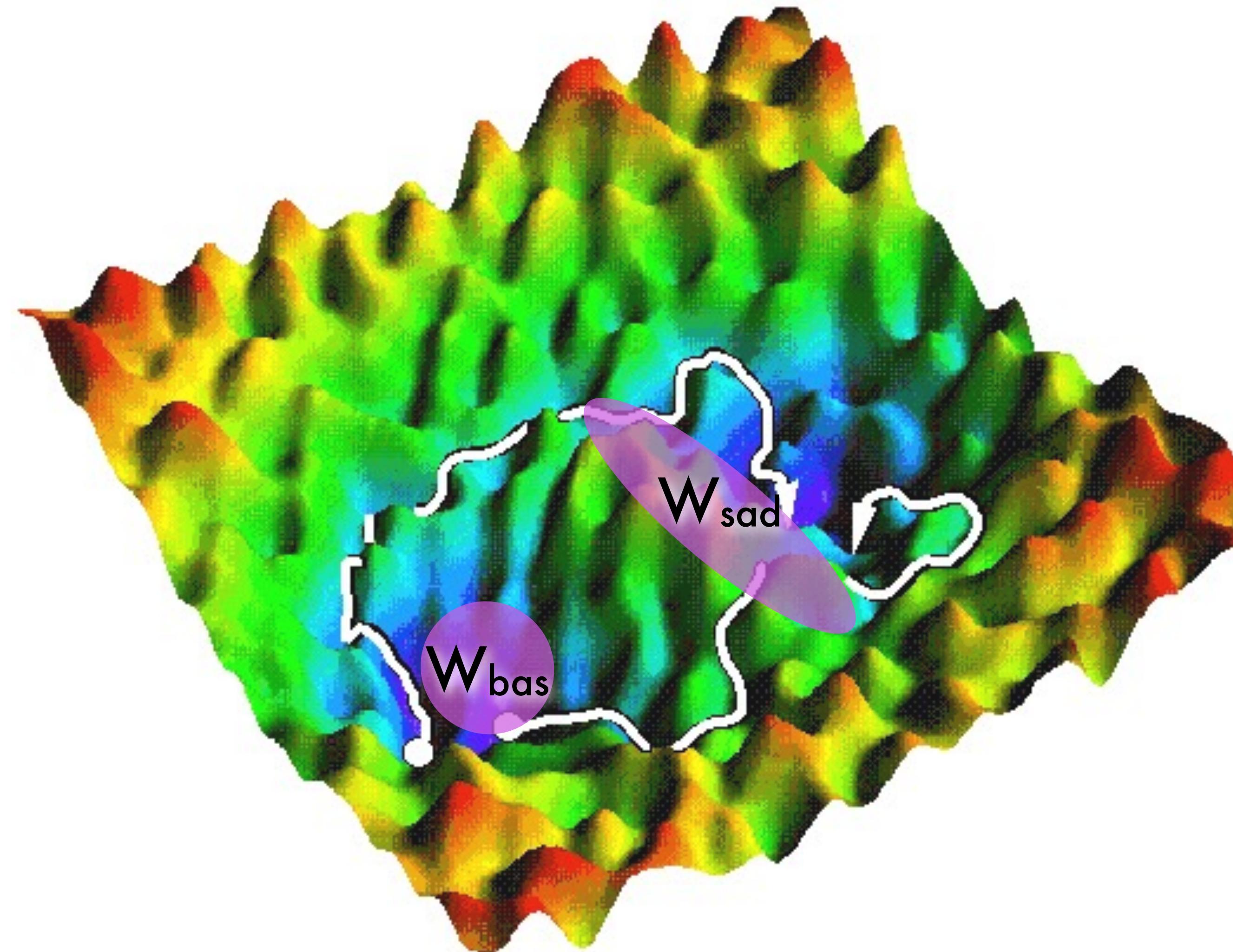
$$k_{\text{TST}} = \nu e^{-\Delta W/k_B T}$$

$\kappa$  : Crossing rate

$\kappa$  : Transmission coefficient

$\nu$  : Attempt frequency

$\Delta W$  : Activation energy



Marcelin (1915), Eyring and Wigner (1930s)

# THE TRANSITION STATE THEORY

The attempt frequency is defined as

$$\nu = \left[ \frac{k_B T}{2 \pi m} \right]^{1/2} \left[ \int_{\text{well}} \exp\{-[W(x) - W(x_m)]/k_B T\} dx \right]^{-1}$$

where  $W(x)$  is the potential of mean-force

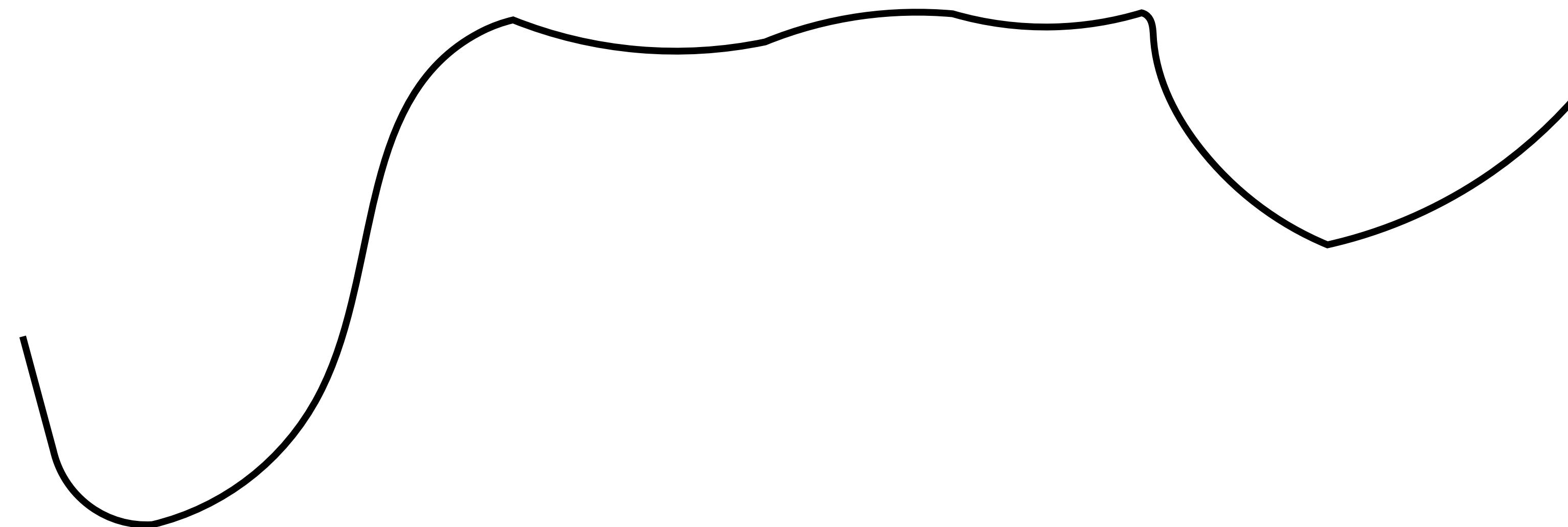
$$W(x) = \int_{x_m}^x \langle f(\lambda) \rangle_{\lambda=x'} dx'$$

And the averaged over the force is taken along the reaction pathway defined by the reaction coordinate  $\lambda$

# THE TRANSITION STATE THEORY

While the transmission coefficient is given by

$$\kappa = \langle \Theta[x(+t) - x_b] - \Theta[x(-t) - x_b] \rangle_{t \gg \tau_{\text{vib}}}$$



# COMPUTING THE PRE-FACTOR: THE HARMONIC APPROXIMATION

If the barrier is simple and chosen correctly,  $\kappa \approx 0.5$ , so that we can ignore it and write the rate as

$$\Gamma \simeq \nu e^{-\Delta W/k_B T} = \nu_0 e^{\Delta S/k_B} e^{-\Delta E/k_B T} = \Gamma_0 e^{-\Delta E/k_B T}$$

with

$$\Gamma_0 = \nu e^{\Delta S/k_B}$$

In the harmonic approximation, we can obtain this entropy difference with

$$\Gamma_0 = \frac{\sum_{i=1}^{3N} \nu_i^{min}}{\sum_{i=1}^{3N-1} \nu_i^{sad}}$$

In the the **quasi**-harmonic approximation, we adjust the volume to the temperature to take into account thermal expansion

# TST: ACTIVATED DYNAMICS

To compute the dynamics in a system dominated by activation barriers, i.e.:

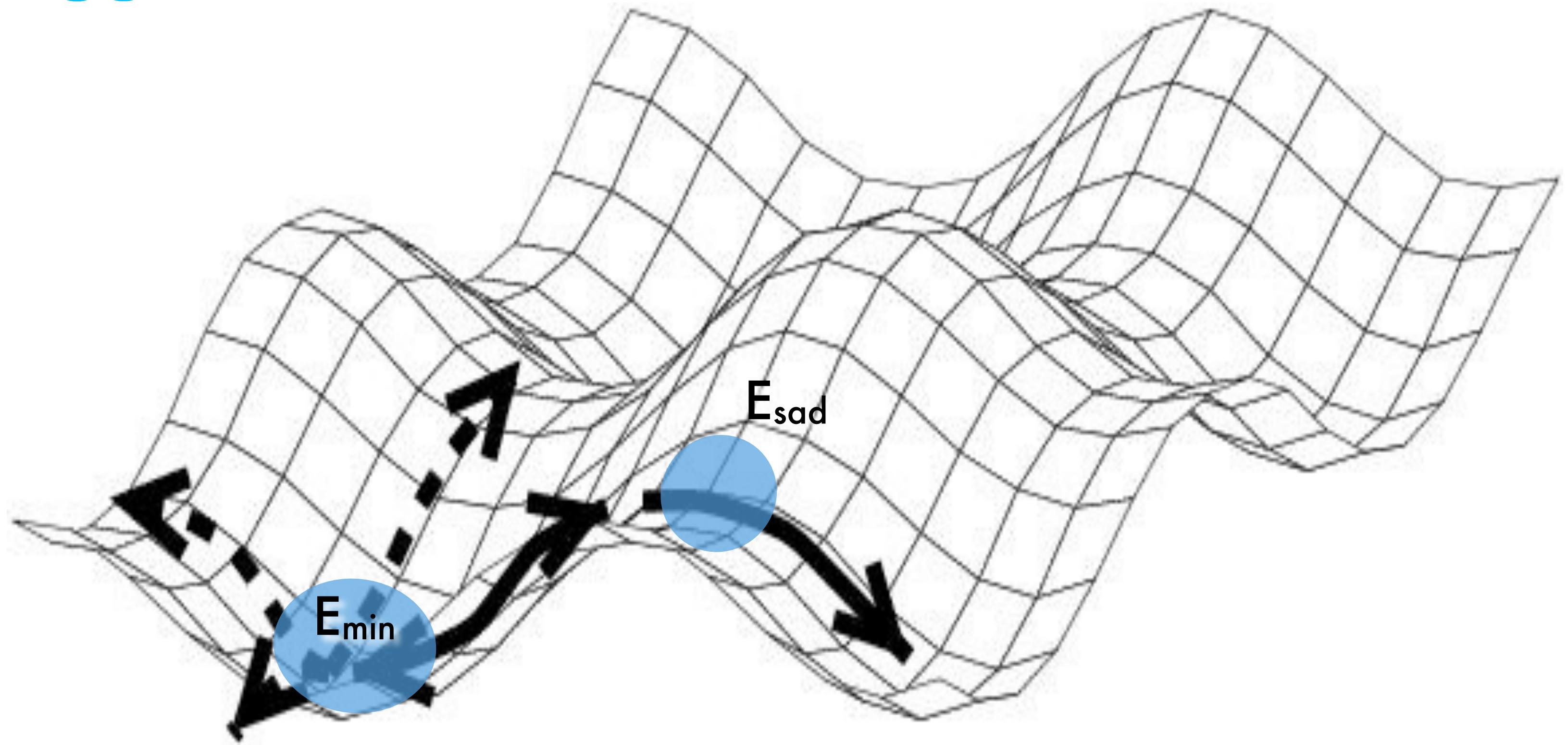
1. Uncorrelated jumps
2. High barriers wrt  $k_B T$
3. No diffusive mechanism

we need to know:

1. Knowledge of saddle points
2. Prefactor

Prefactor approximation:

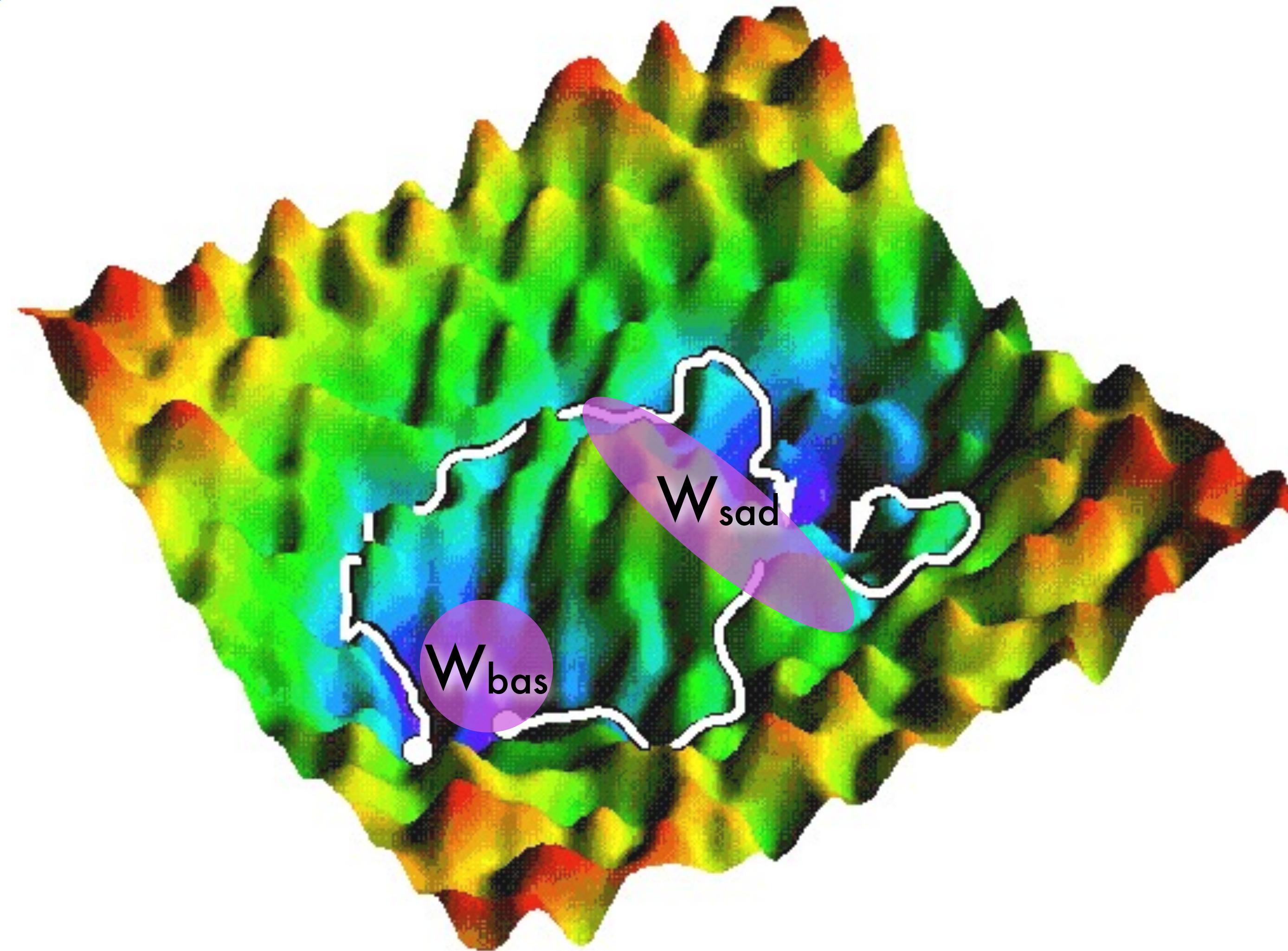
1. Homogeneous
2. Well-separated pathways



$$\Gamma = \Gamma_0 e^{-\Delta E / k_B T}$$

# HARMONIC TST: WHEN IT FAILS

1. Correlated jumps (diffusive mechanisms)
2. Multiple pathways



Adapted from PG. Bolhuis, D Chandler, C Dellago,  
PL Geissler, Annu. Rev. Phys. Chem. **53**, 291 (2002)

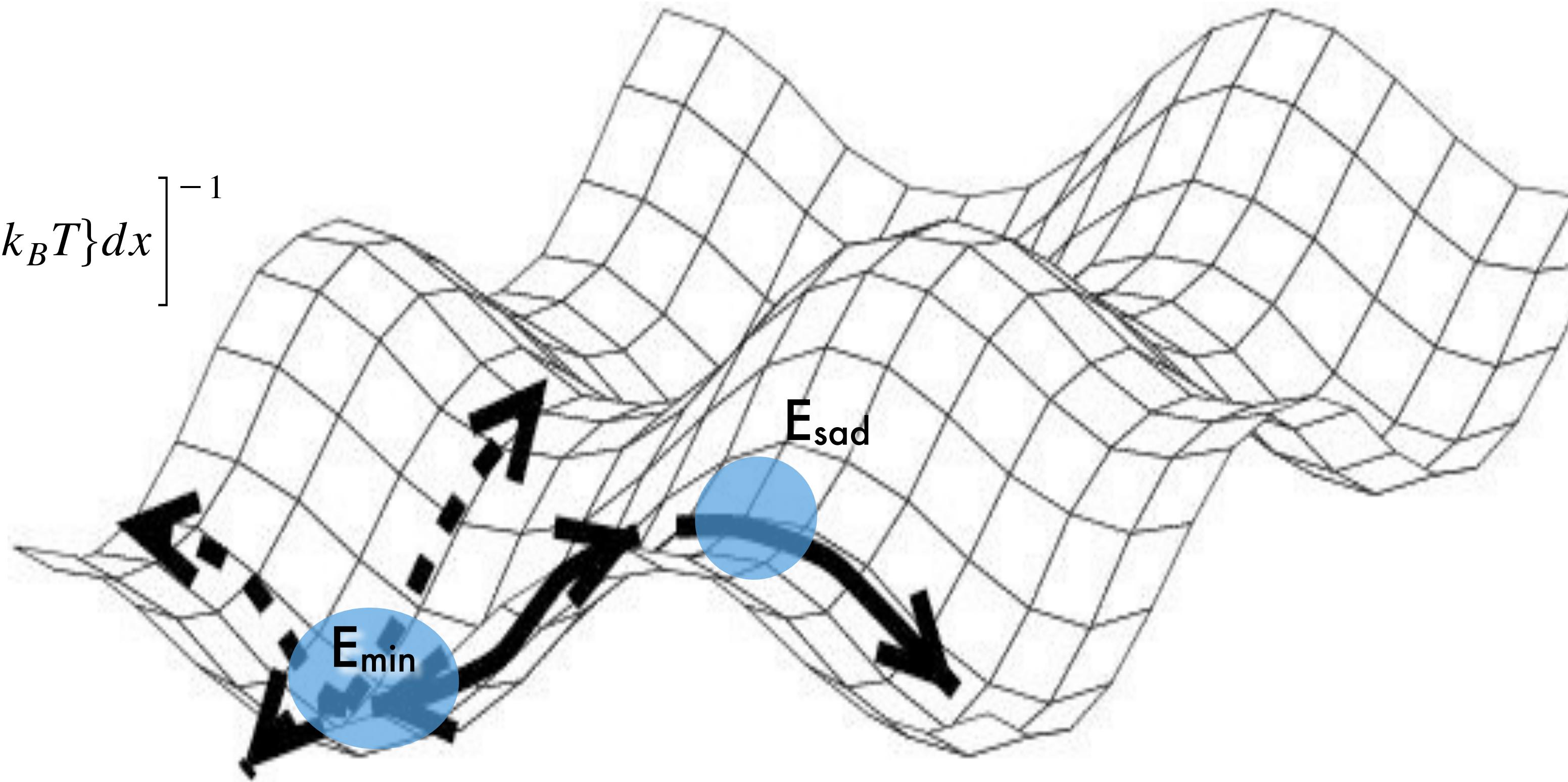
# FOCUSING ON SIMPLE EVENTS

1. Finding barriers (next talks)
2. Computing prefactors

# THERMODYNAMICAL INTEGRATION

$$\nu = \left[ \frac{k_B T}{2\pi m} \right]^{1/2} \left[ \int_{\text{well}} \exp\{-[W(x) - W(x_m)]/k_B T\} dx \right]^{-1}$$

$$W(x) = \int_{x_m}^x \langle f(\lambda) \rangle_{\lambda=x'} dx'$$



where  $\lambda$  is a point on the reaction pathway

# THERMODYNAMICAL INTEGRATION

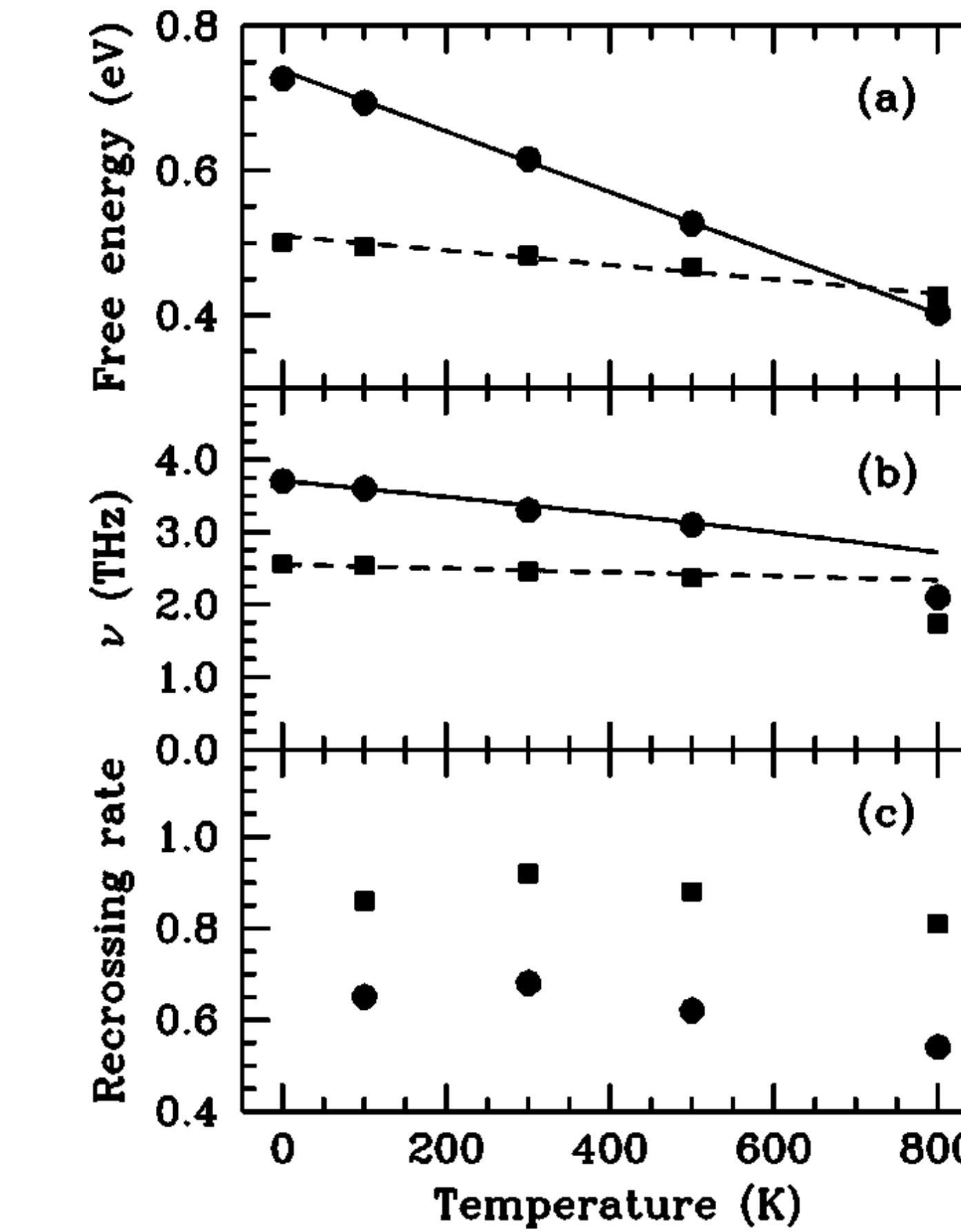
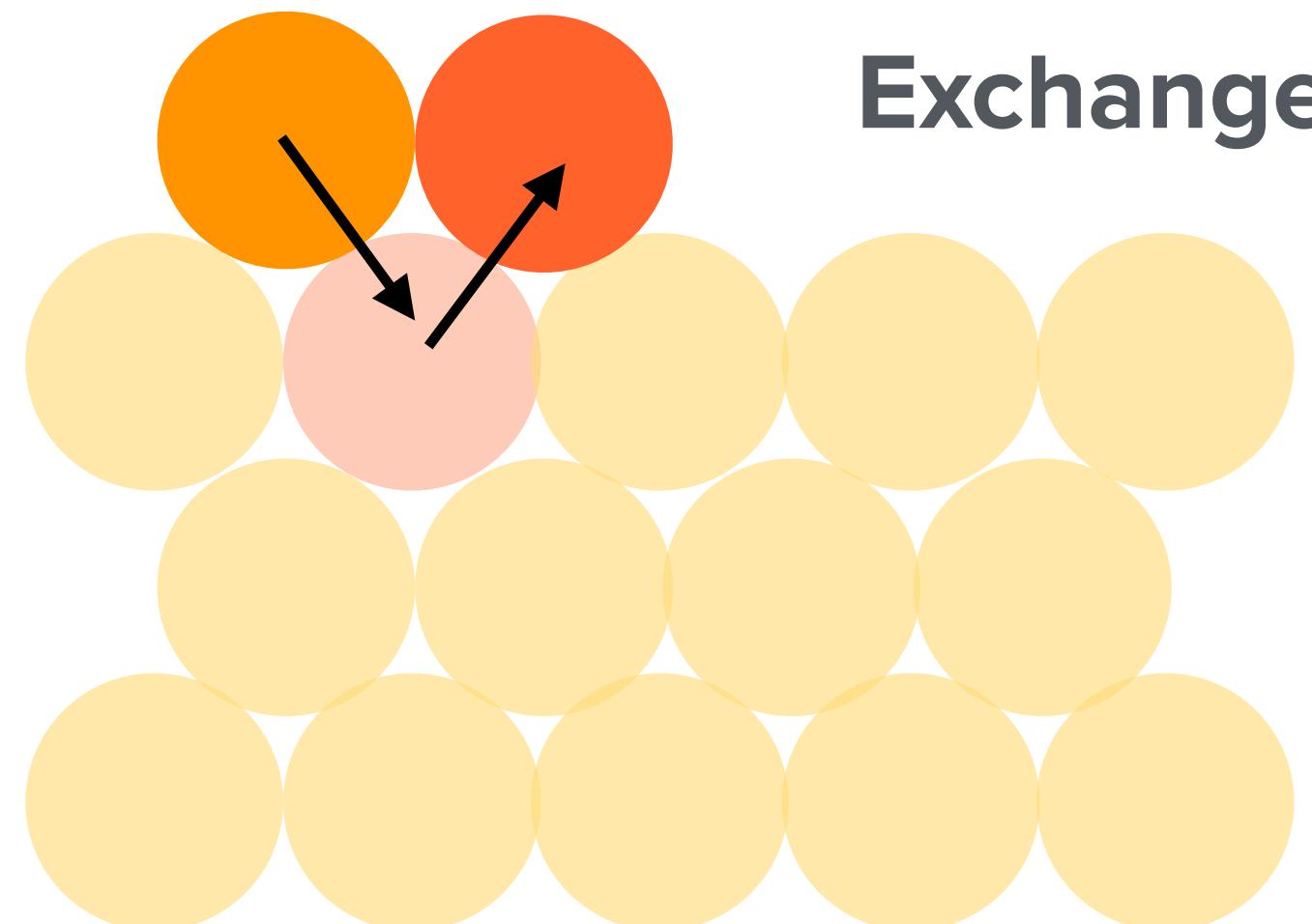
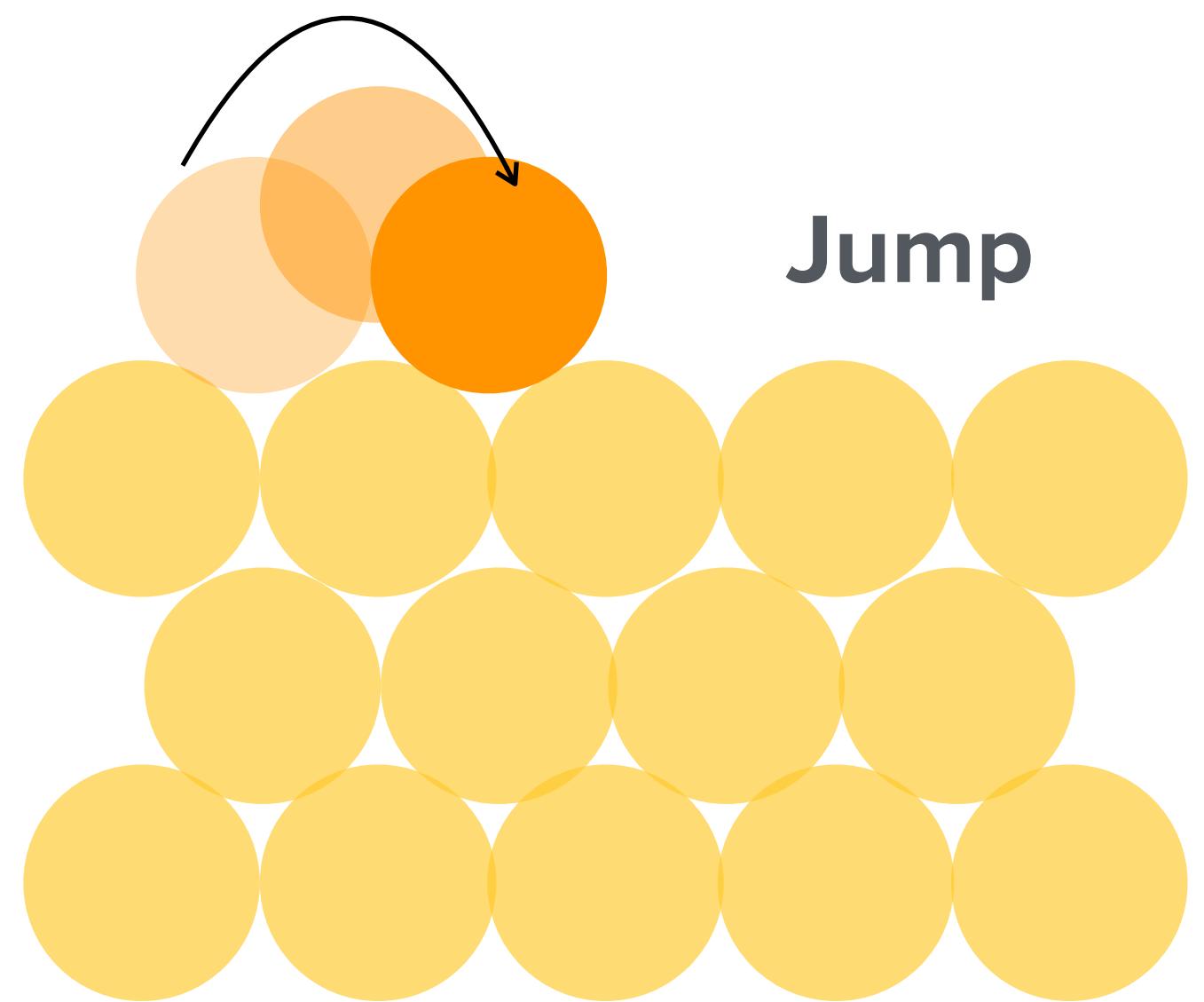


FIG. 1. (a) Activation free energy vs temperature for jumps (squares, dashed line) and exchanges (circles, full line); the lines are linear fits to the finite-temperature points. (b) Attempt-to-diffuse frequencies vs temperature; the lines are the predictions of the simple model discussed in the text. (c) Transmission coefficients vs temperature.

# THERMODYNAMICAL INTEGRATION VS HARMONIC APPROXIMATION

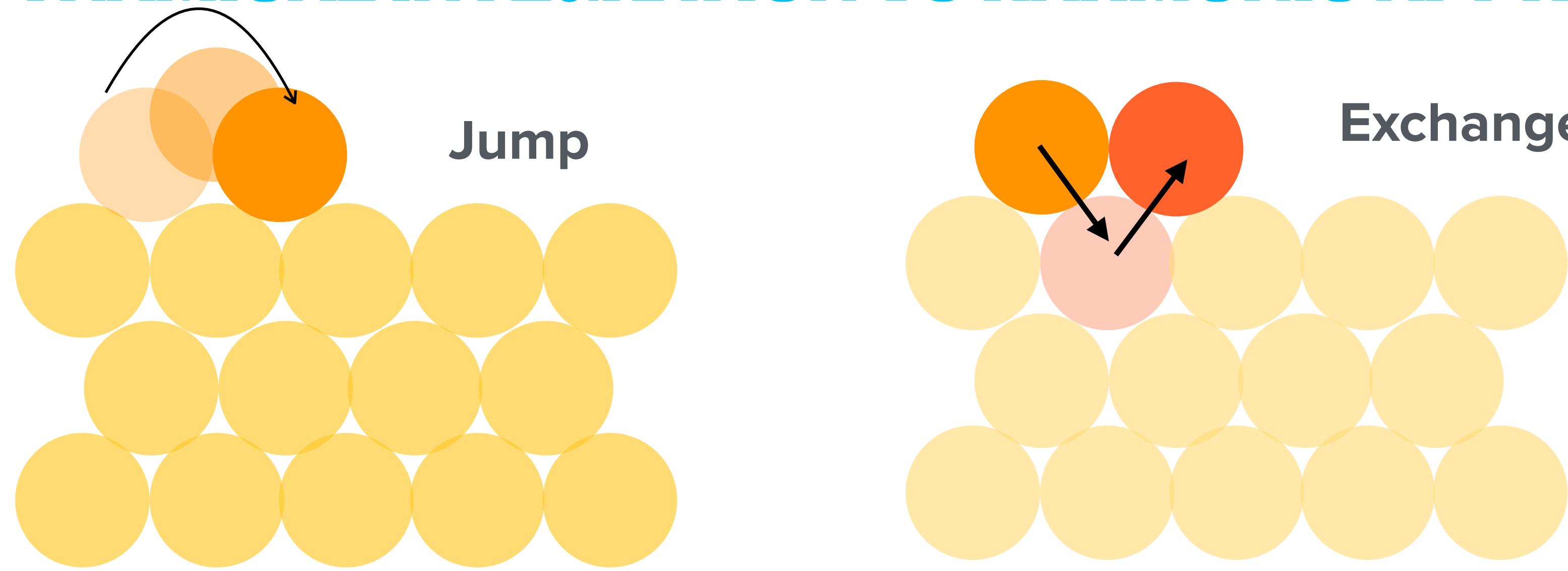


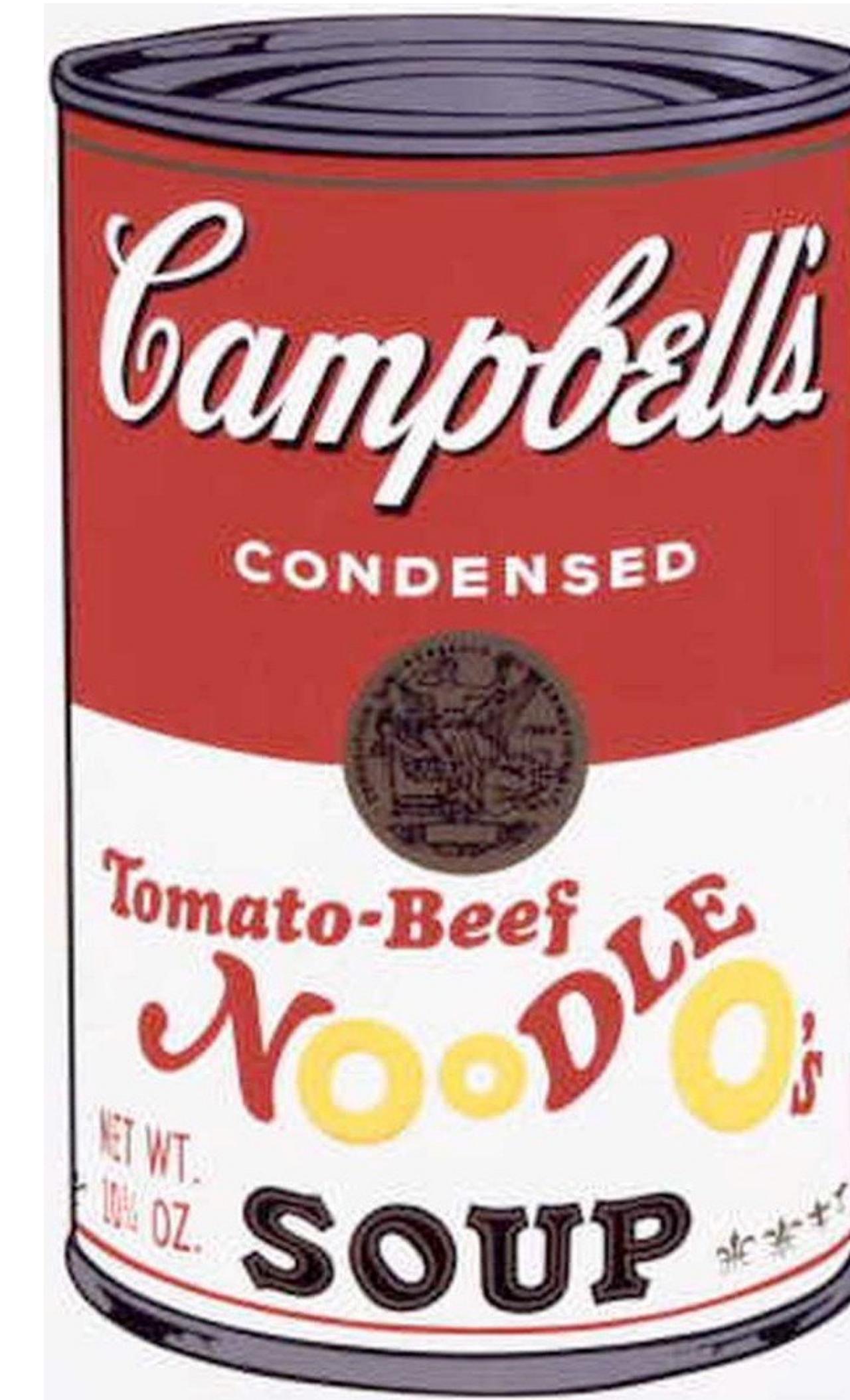
TABLE I. Comparison between TI and MD results for the jump ( $J$ ) and exchange ( $X$ ) diffusion activation barriers  $\Delta E$  (in eV) and rate prefactors  $\Gamma_0$  (in THz); also given are the entropy  $\Delta S$  (in  $k_B$ ) and the static energy barrier,  $\Delta E(0)$ . Estimated errors are given in parenthesis.

	$\Delta S$	$\Delta E$	$\Delta E$	$\Delta E(0)$	$\ln \Gamma_0$	$\ln \Gamma_0$
	(TI)	(TI)	(MD)		(TI)	(MD)
$J$	1.1(0.2)	0.51(0.02)	0.49(0.01)	0.50	2.9(0.2)	3.0(0.2)
$X$	4.9(0.6)	0.74(0.02)	0.70(0.04)	0.73	6.5(0.6)	6.1(0.7)

# Properly-obeying-probability activation-relaxation technique

A different view of thermodynamical  
integration

POP-ART   POP-ART  
POP-ART   POP-ART



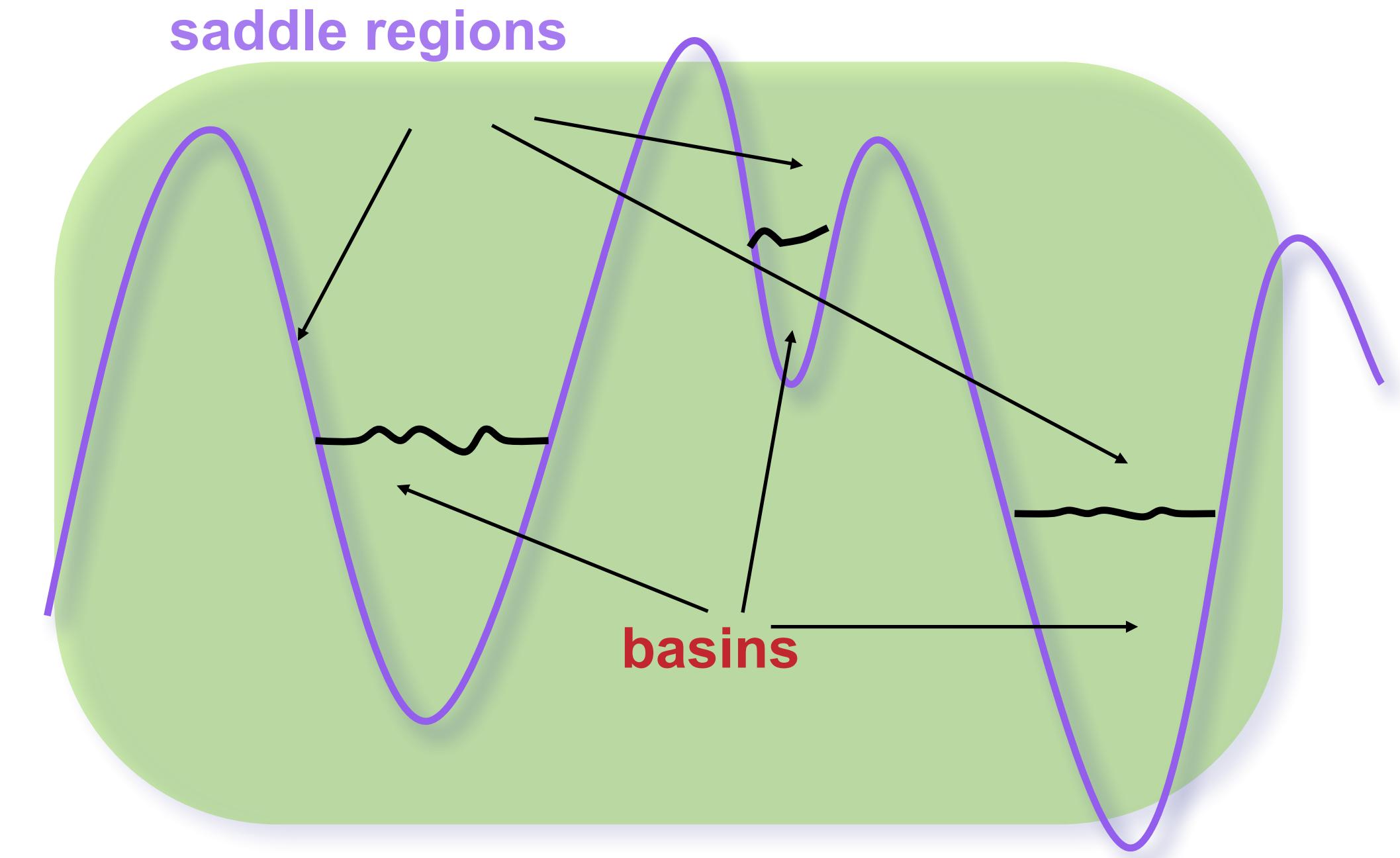
## Basic idea

We divide the landscape into two regions :

**basins:** regions where all the eigenvalues associated with the curvature of the energy landscape are **above** a give threshold

**saddle regions:** regions where at least one eigenvalue is **below** the threshold.

At low temperature, the system samples only the region of phase space associated with the **basin** regions



The saddle regions are not visited often and do not contribute significantly to the thermodynamics

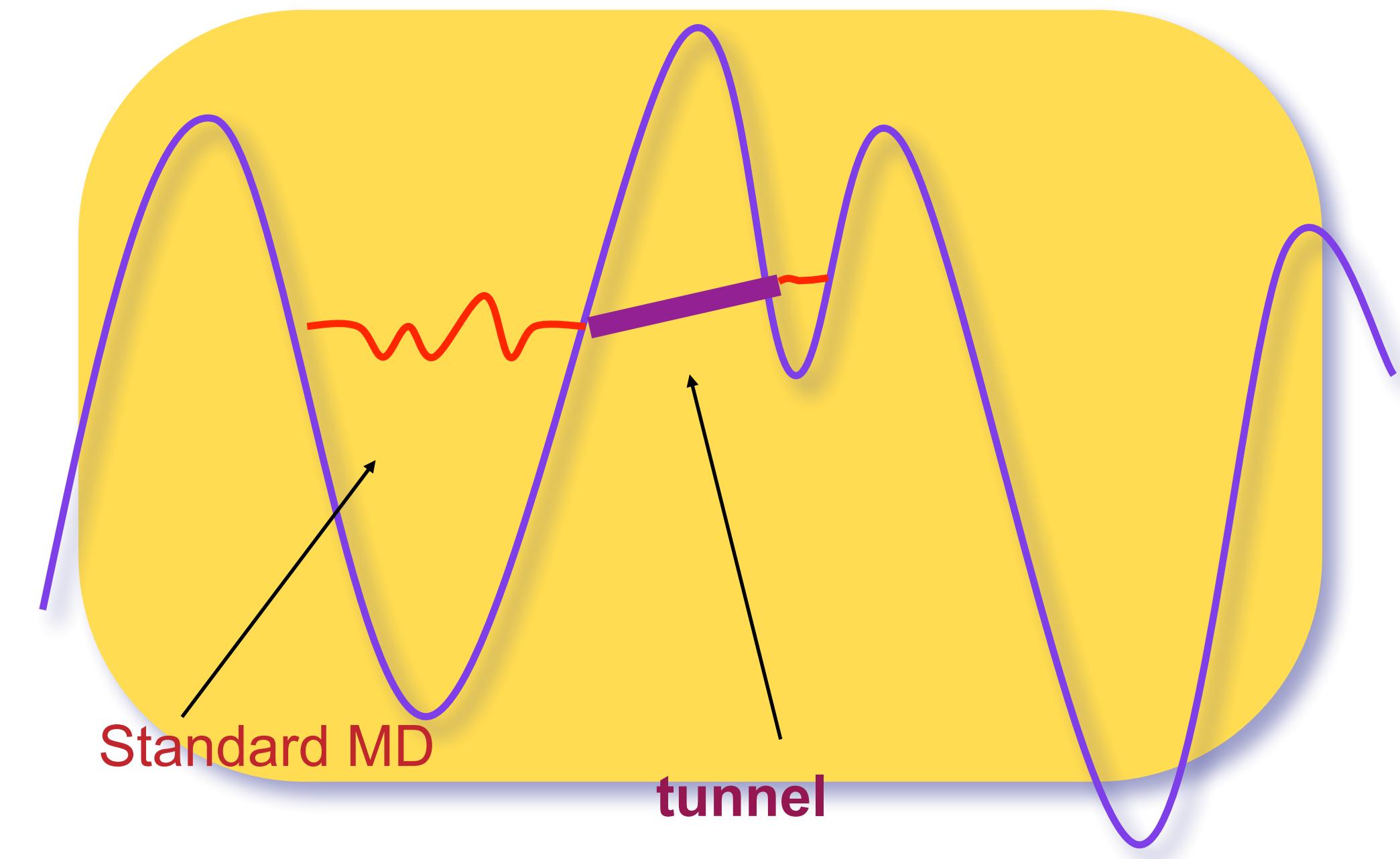
# Algorithm

Three steps:

1. Standard finite temperature molecular dynamics in a minimum well.
2. As we find a negative eigenvalue, we move on a constant configurational- energy surface following the direction associated with the lowest eigenvalue.

$$\vec{x}_{i+1} = \vec{x}_i + \frac{\Delta\tau}{2} \left( \vec{h}_i + \vec{h}_{i+1} \right) + c\Delta\tau \left( \vec{F}_i + \vec{F}_{i+1} \right)$$

3. We compute the Jacobian of transformation and accept or reject based on this value.



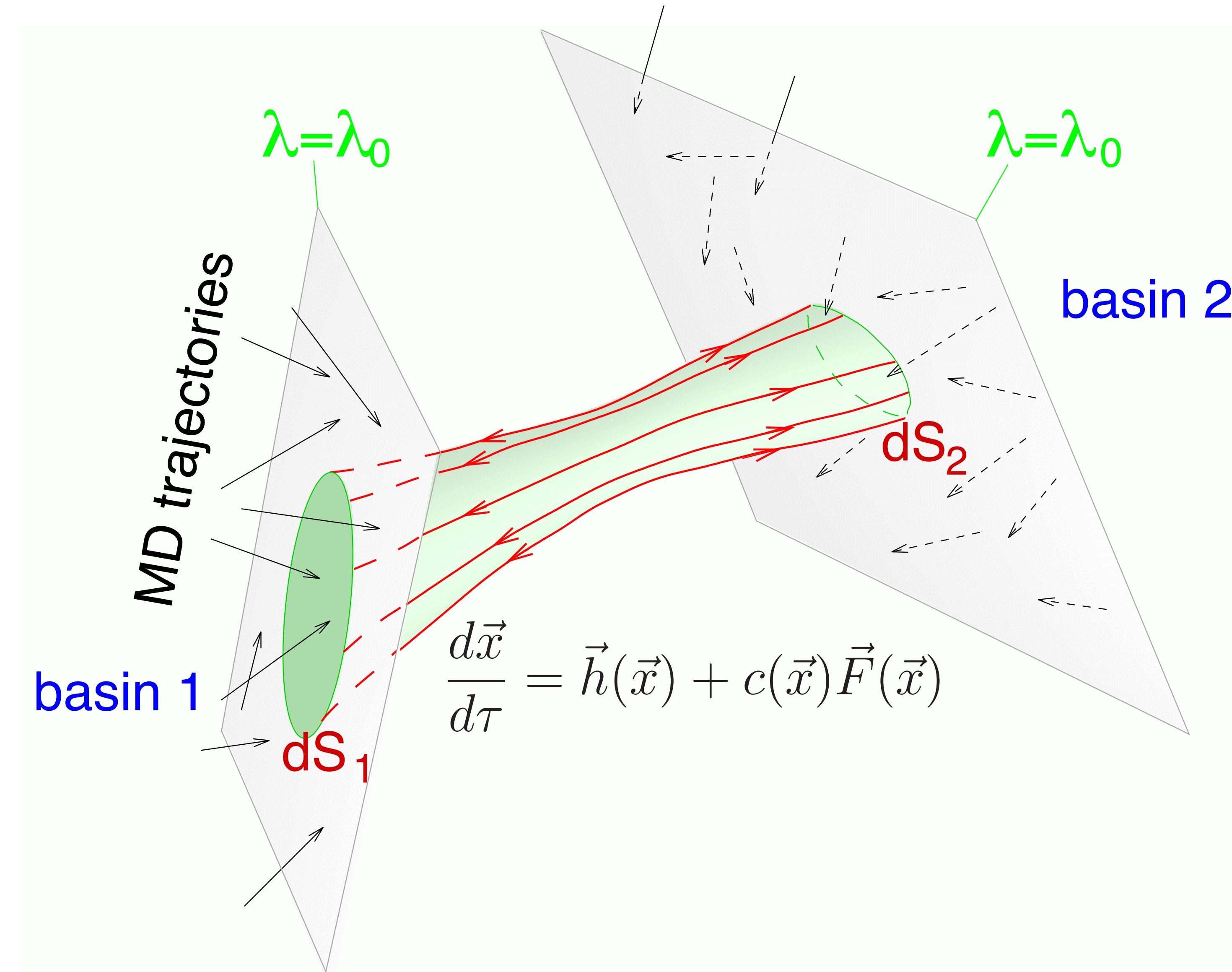
This algorithm respects detailed balance.

# Contributions to the Jacobian of transformation

$h(x)$  is the normalized eigenvector at  $x$  corresponding to the lowest eigenvalue in  $H$ .

$F$  is the force at  $x$

$c$  is a multiplicative constant chosen to project the trajectory onto a hyper surface of constant energy



# The cross-section Jacobian

The displacement along curve is given by

$$\frac{d\vec{x}}{d\tau} = \vec{f}(\vec{x})$$

With

$$\vec{f}(\vec{x}) = \vec{h}(\vec{x}) + c(\vec{x})\vec{F}(\vec{x})$$

As  $\tau \rightarrow \tau + d\tau$  then  $\vec{x} \rightarrow \vec{x} + \vec{f}(\vec{x})d\tau$

$$\ln J_{xs} = \int_0^\tau j(\vec{x}(\tau'))d\tau'$$

$$j = \operatorname{div} \vec{h} + c \operatorname{div} \vec{F}$$

$$J = \exp(\int j(x_0)dx_0) = \exp [-(\Delta U_0 - T\Delta S)/k_B T]$$

$$= \exp[-\Delta \mathcal{F}/k_B T],$$

# The boundary Jacobian

The correction on the area (entrance and exit) is simply the ratio of the cosine with respect to the normal

$$J_b = \frac{\cos \alpha_1}{\cos \alpha_2}$$

where

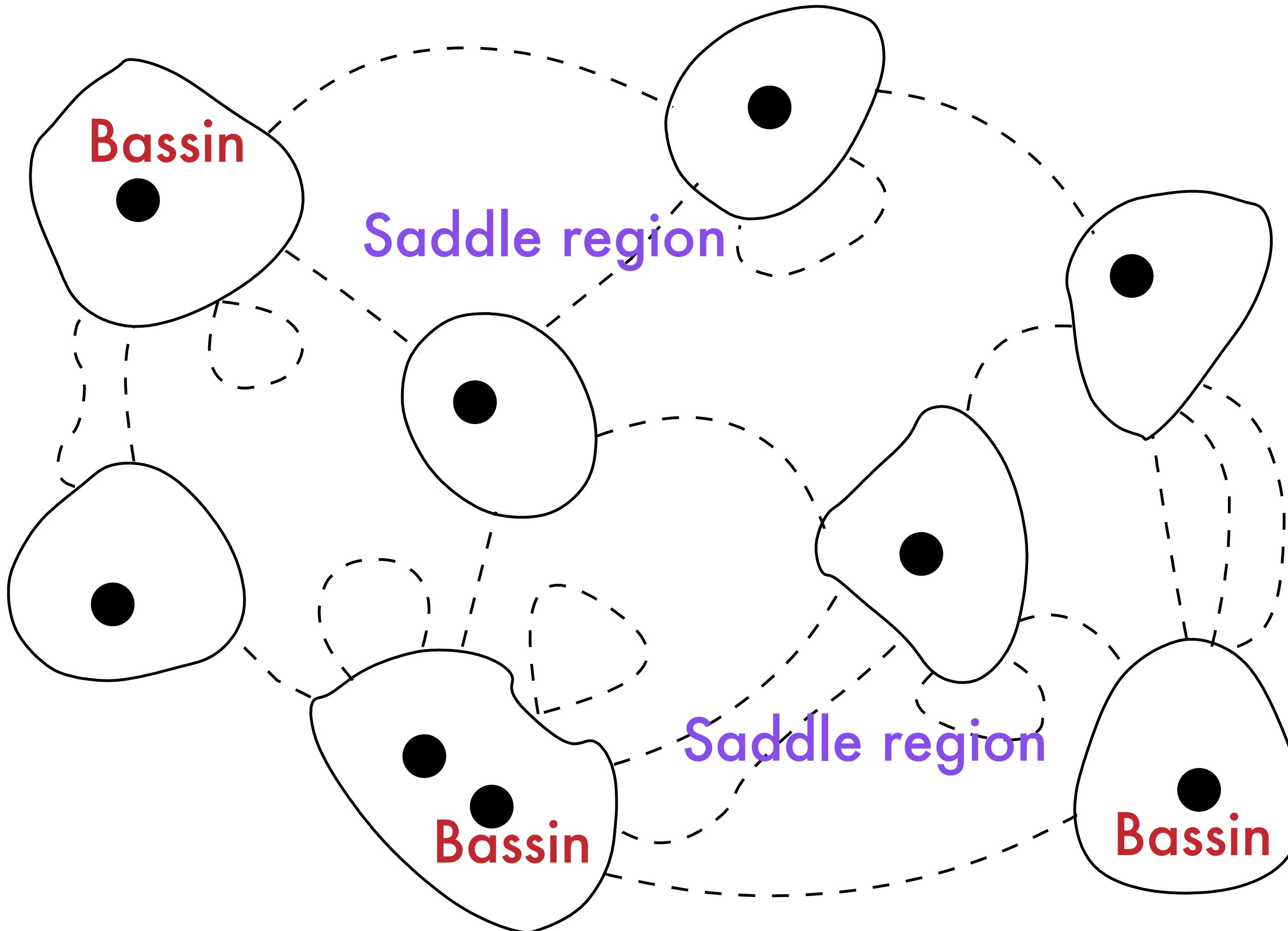
$$\cos \alpha_{1,2} = \frac{\vec{h} \cdot \nabla \lambda}{|\nabla \lambda|}$$

and

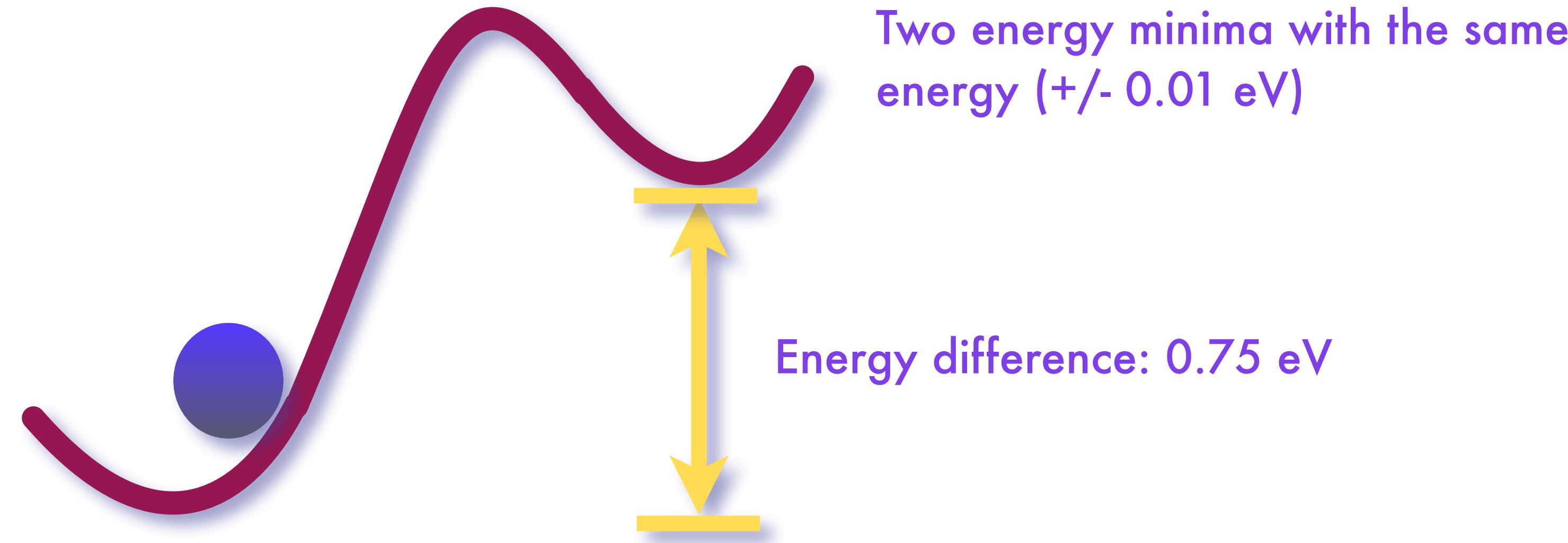
$$\nabla \lambda(\vec{x}) = \lim_{\delta \rightarrow 0} \frac{2\vec{F}(\vec{x}) - \vec{F}(\vec{x} + \delta \cdot \vec{h}) - \vec{F}(\vec{x} - \delta \cdot \vec{h})}{\delta^2}$$

This last quantity is the gradient of the lowest eigenvalue - the direction perpendicular to the surface of constant value

# POP-ART Trajectories



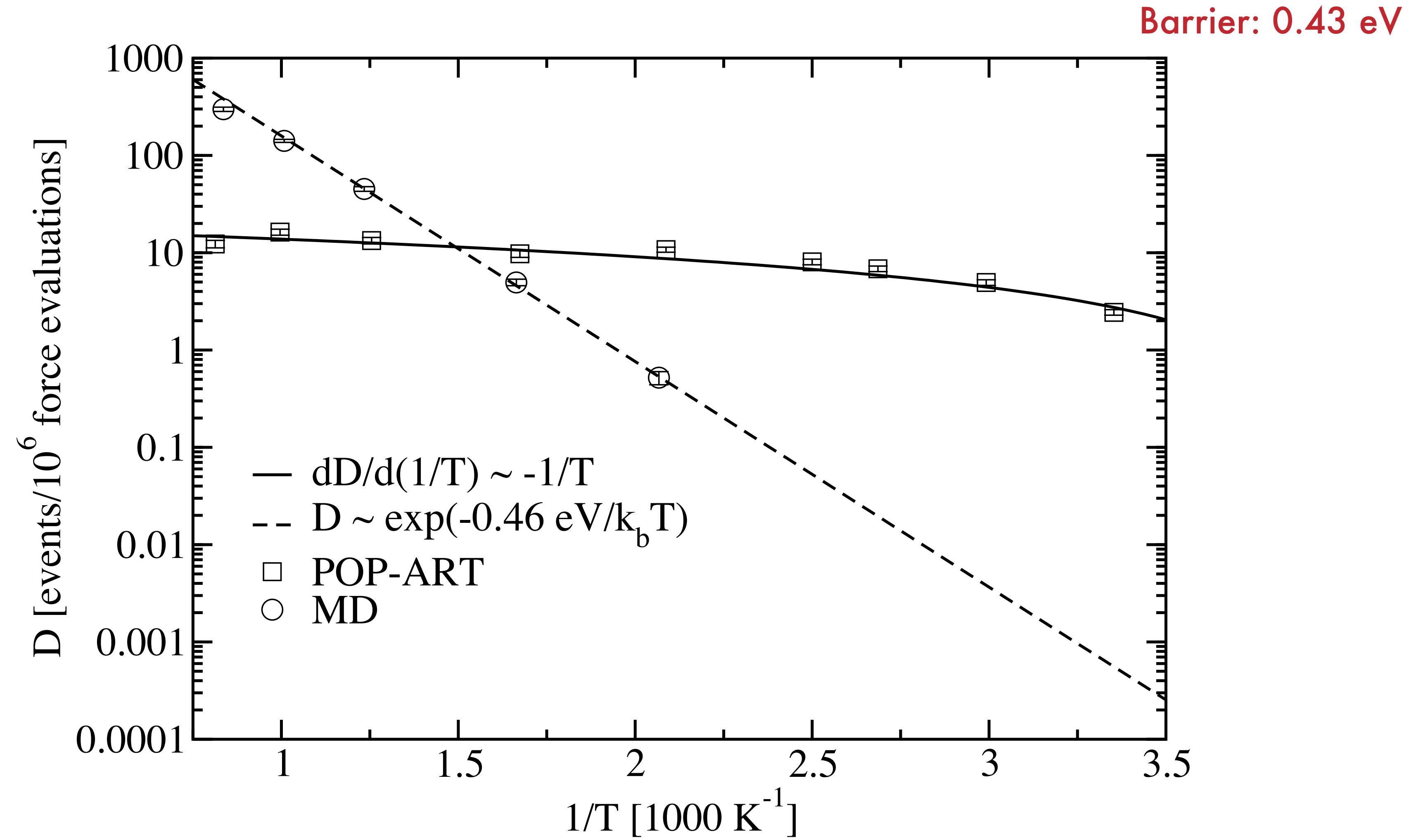
# POP-ART Trajectories



To establish the validity of the implementation of POP-ART we compute the probability of begin in the top states vs. the bottom state at 1000 and 1200 K

	MD	POP-ART
Ratio top to bottom at 1000 K	1.6 +/- 0.1 %	1.3 +/- 0.3%
Ratio top to bottom at 1200 K	3.6 +/- 0.1 %	3.5 +/- 0.3%

# Sampling the phase space : vacancy in Si



At room temperature: POP-ART samples 10000 faster than MD

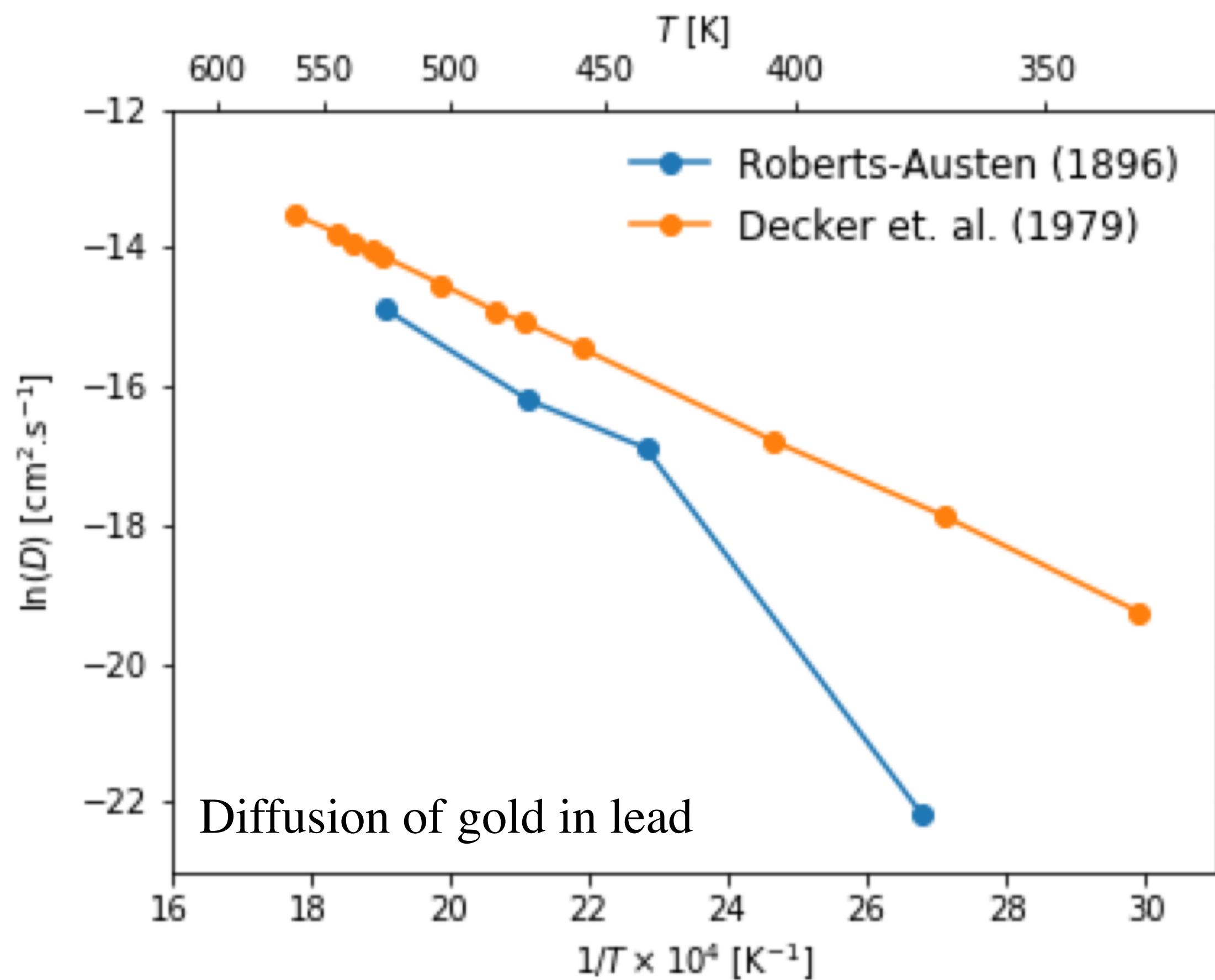
# Conclusions

- POP-ART is a promising method to sample thermodynamically the phase space of complex systems
  - it respects detailed balance
  - it requires only local information
  - it computes exactly the free energy difference (no harmonic approximation)
- POP-ART can be up to 10000 faster than MD even at room temperature
- Suffers from low-barrier - a problem that we did not manage to solve

# WHY WORRY ABOUT PREFACTORS?

# The law of compensation

Enthalpy-entropy compensation of atomic diffusion originates from softening of low frequency phonons



Simon Gelin  <sup>1,2,3</sup>✉, Alexandre Champagne-Ruel  <sup>1</sup> & Normand Mousseau  <sup>1</sup>✉

Nature Communications 11, 3977 (2020).

Arrhenius law :

$$D(T) = D_0 \times \exp(-E_a/k_B T)$$

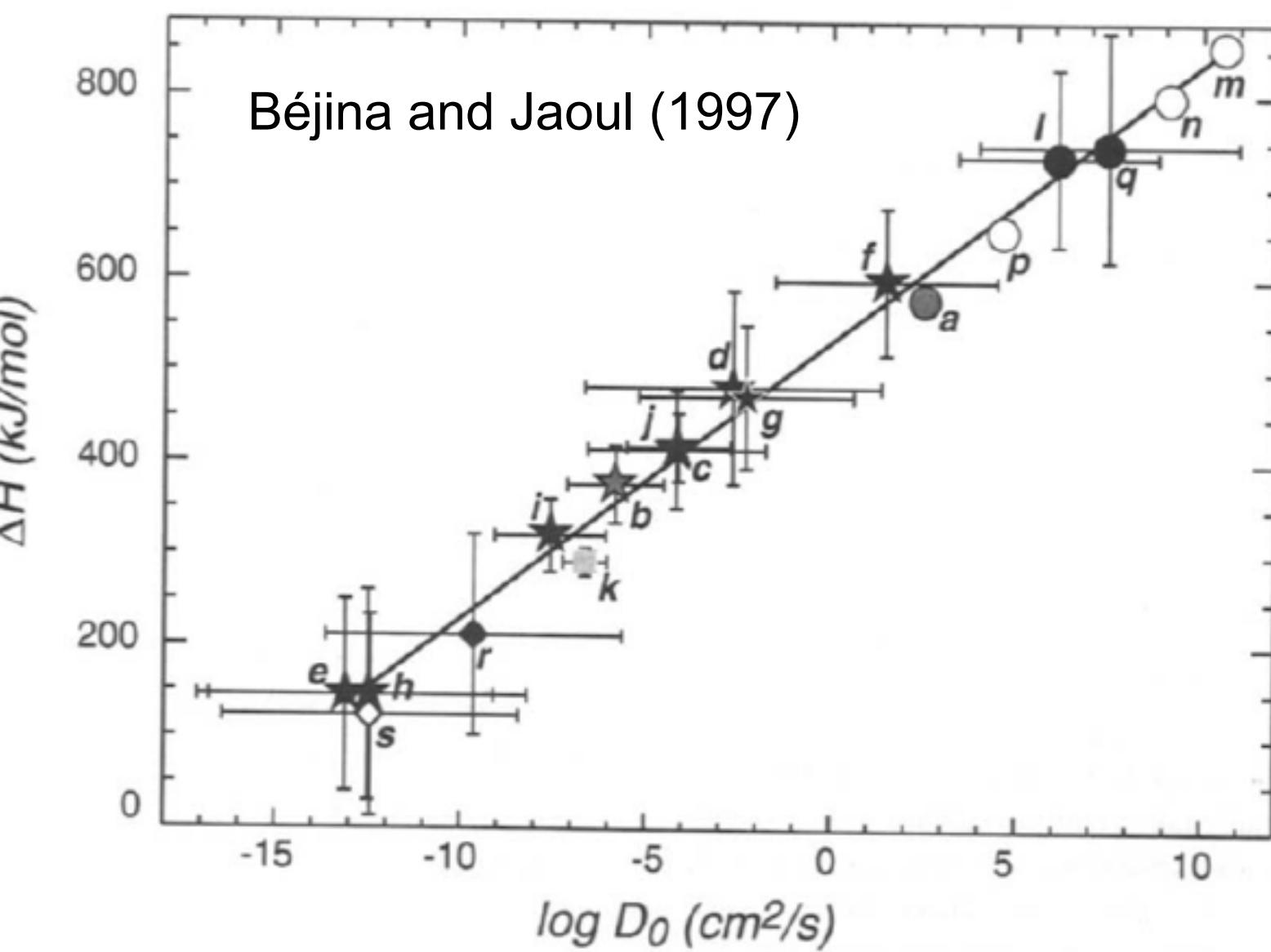
Are there relations between

$D_0$  and  $E_a$  ?

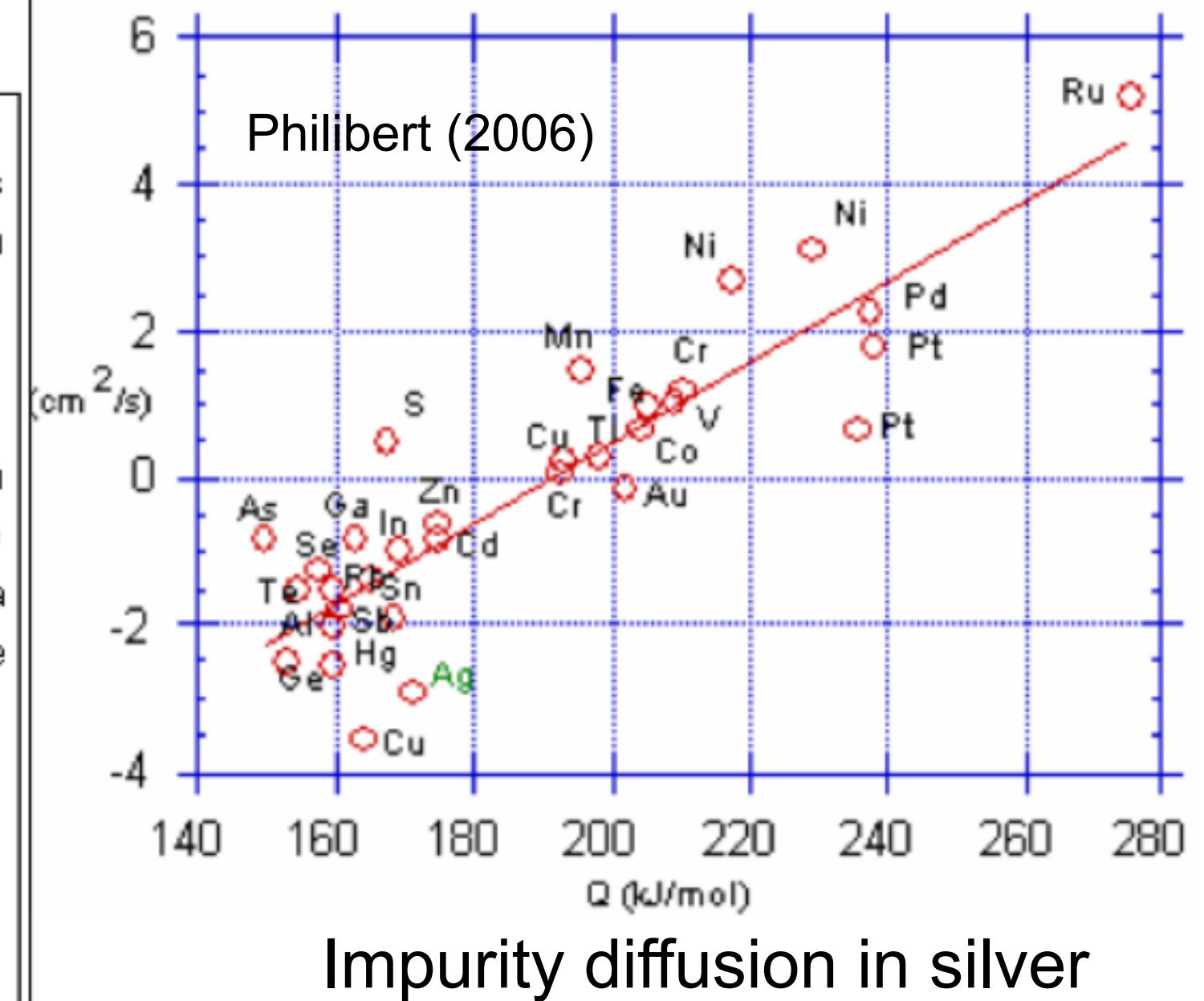
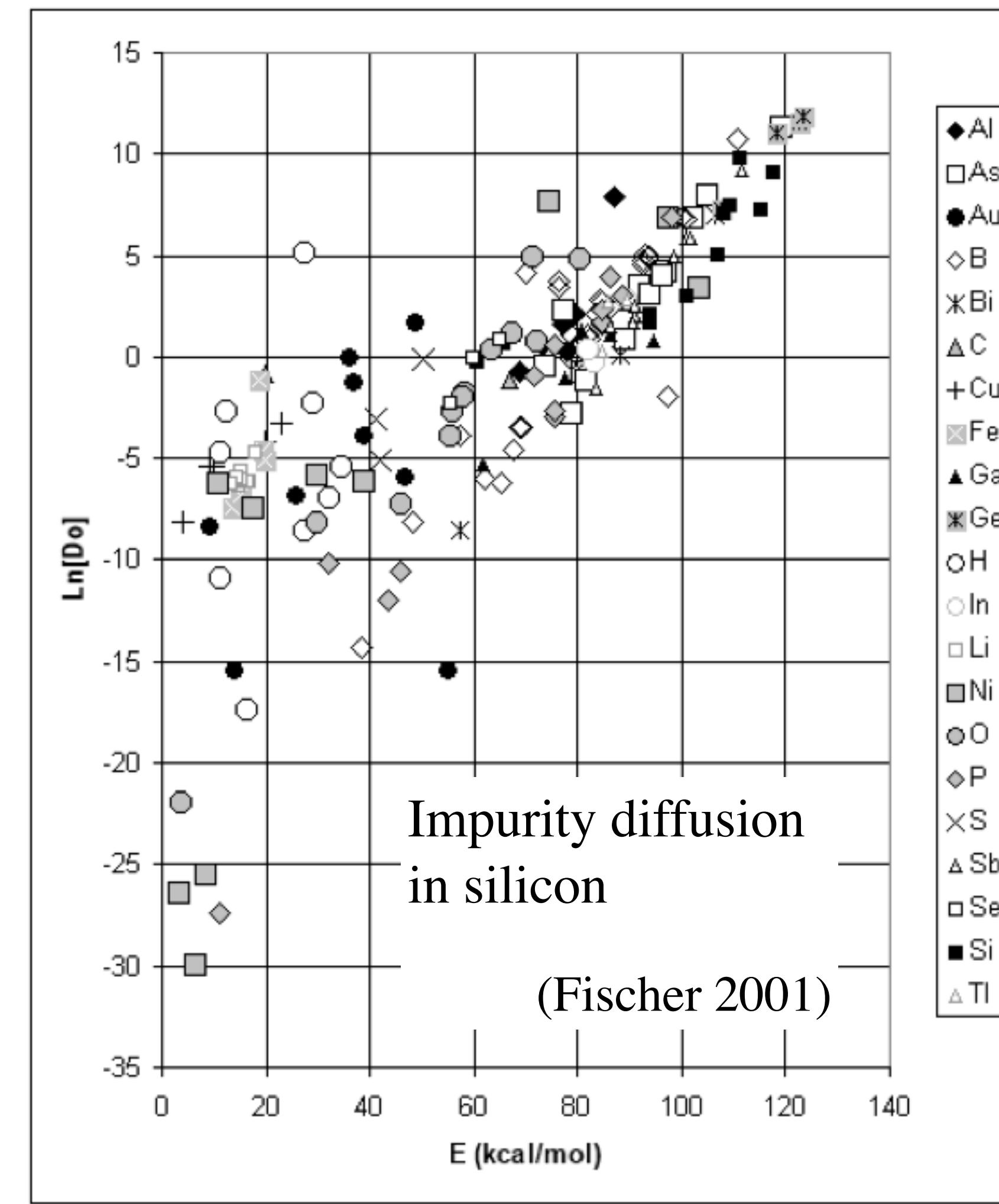
# The law of compensation : experimental results

$$D(T) = D_0 \times \exp(-E_a/k_B T)$$

$$D_0 = D_{00} \times \exp(\gamma_c E_a)$$

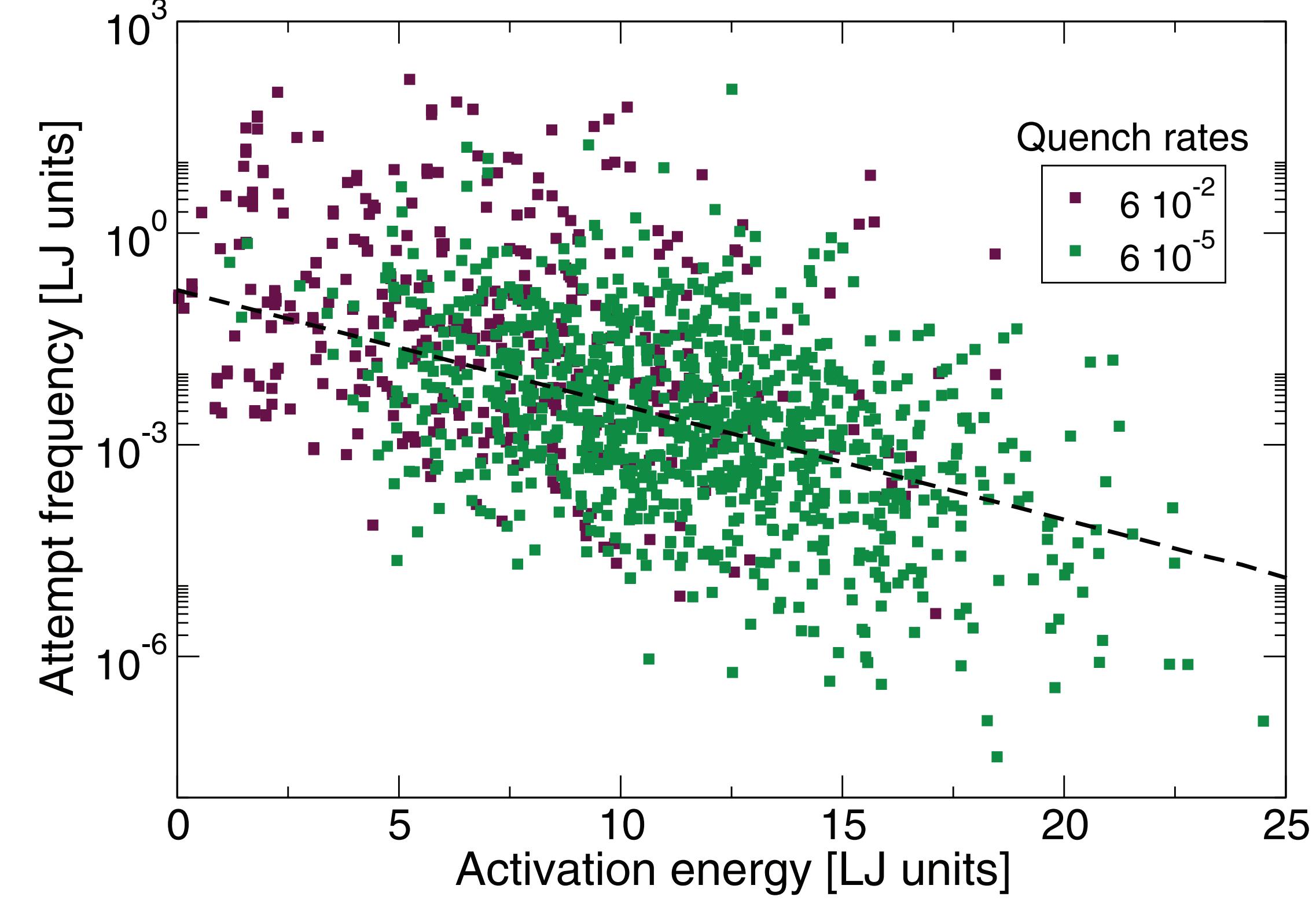
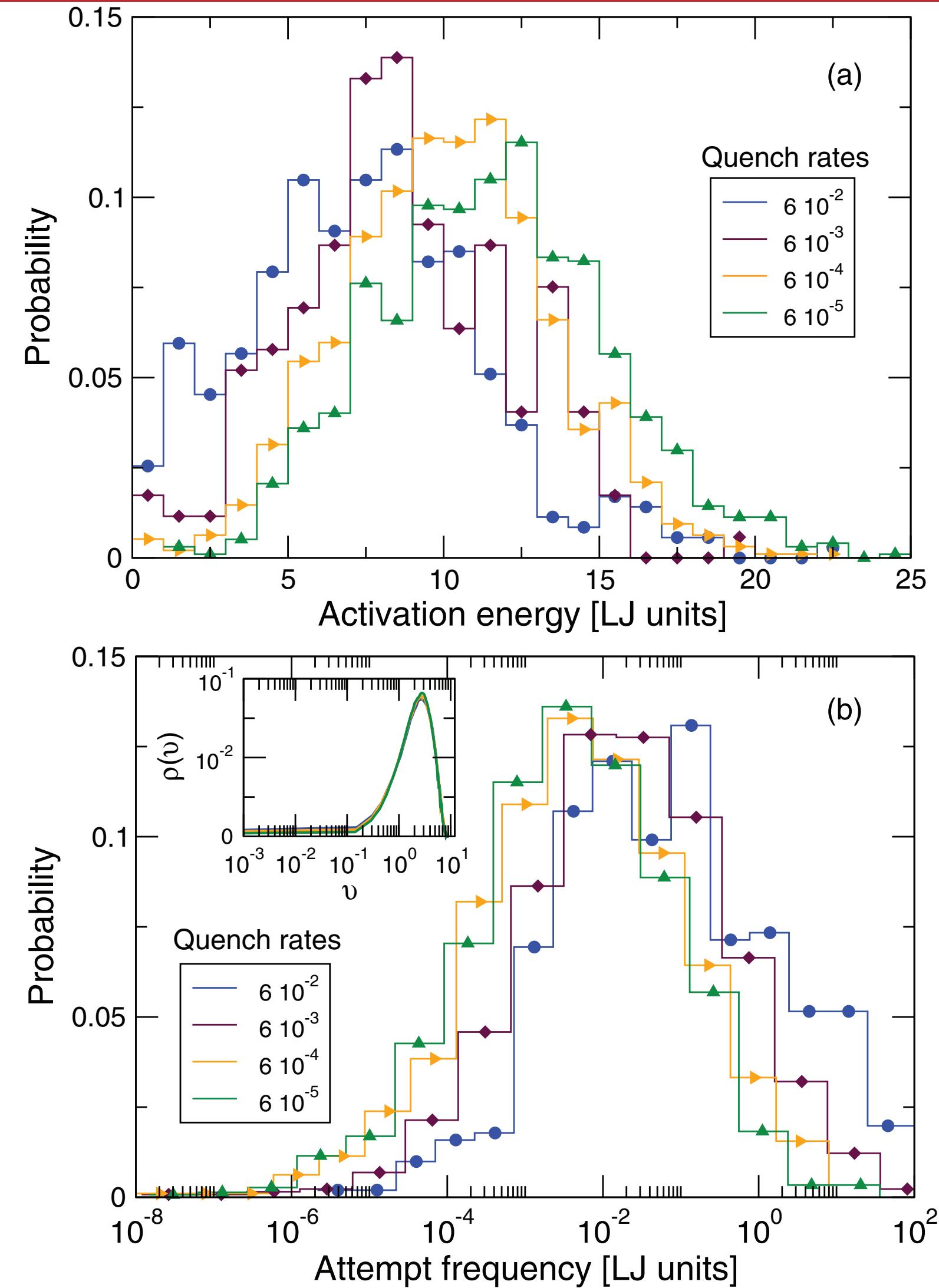


Silicon in silicate minerals



# Recent numerical results

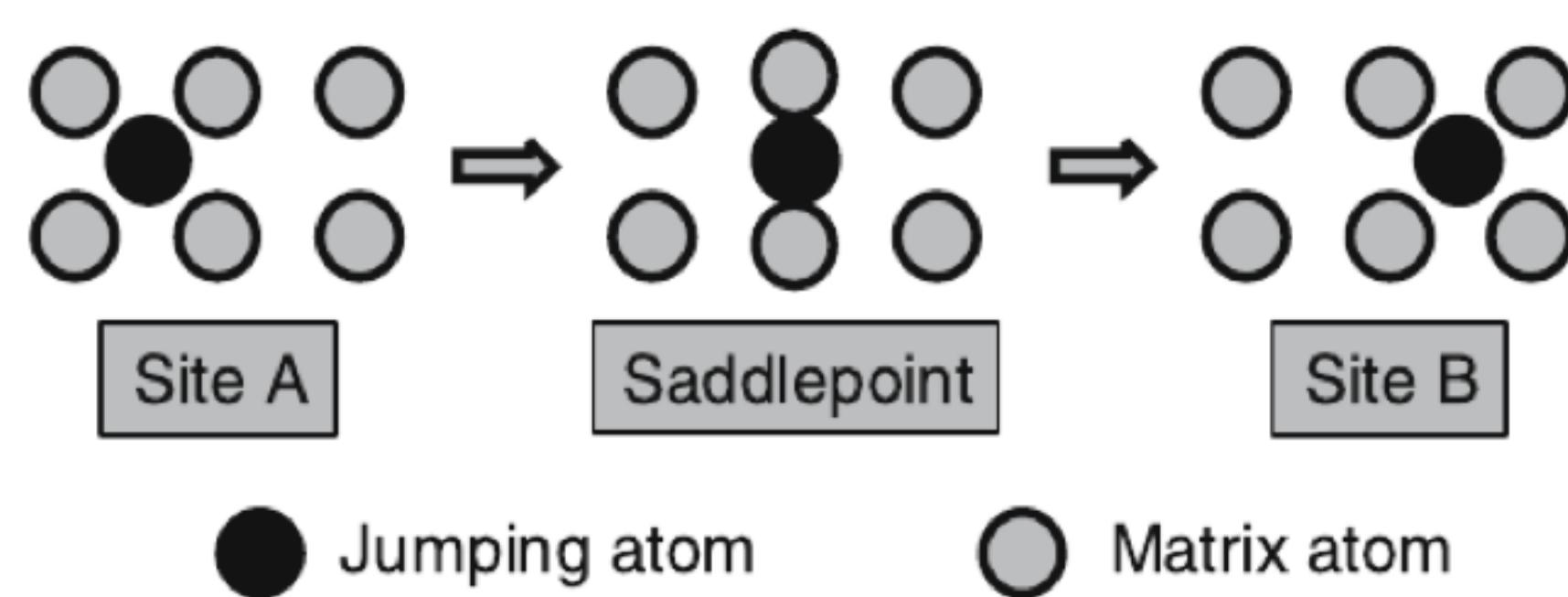
Inverse Meyer-Neldel behavior for activated processes in model glasses



Pawel Koziatek, Jean-Louis Barrat, Peter Derlet, and  
David Rodney, Phys. Rev. B 87, 224105 (2013)

# The law of compensation : models

Basic theory



$$D(T) = \frac{fa^2}{2d} \times n_{path} \times \nu(T)$$

Going further

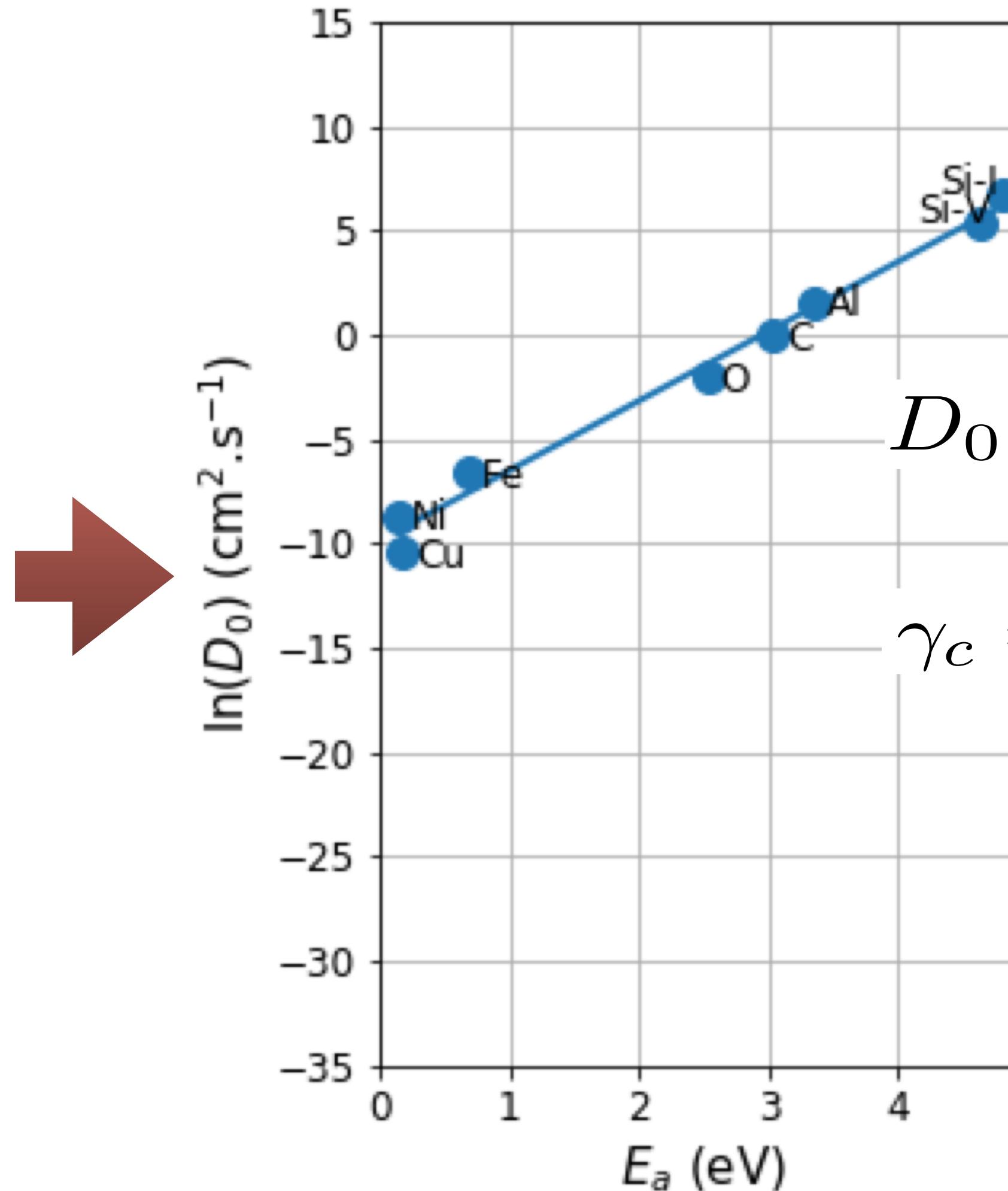
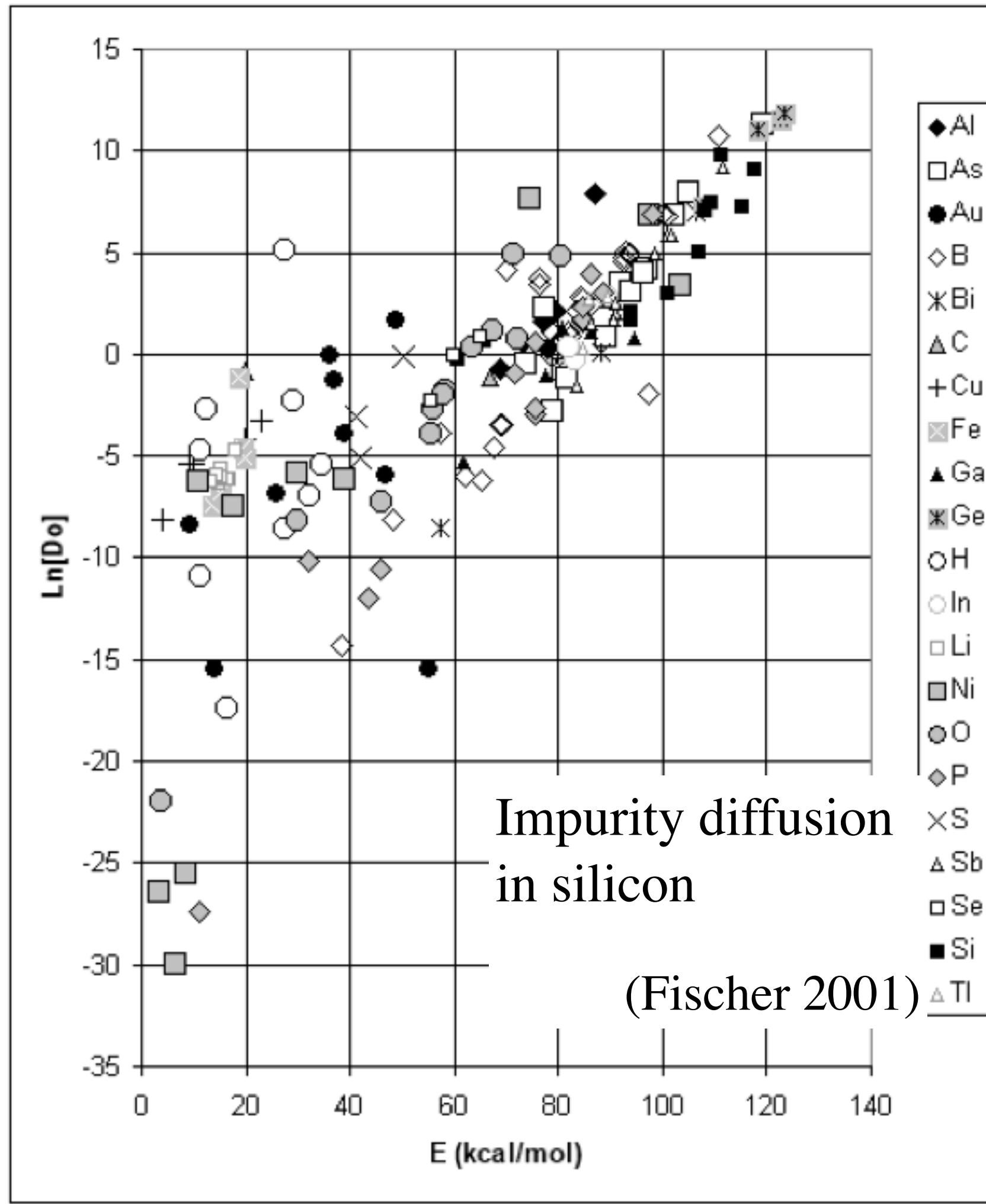
$$\nu(T) = \nu_0 \exp(\Delta S/k_B) \times \exp(-\Delta H/k_B T)$$

**Strain Energy Model (Zener 1950)**

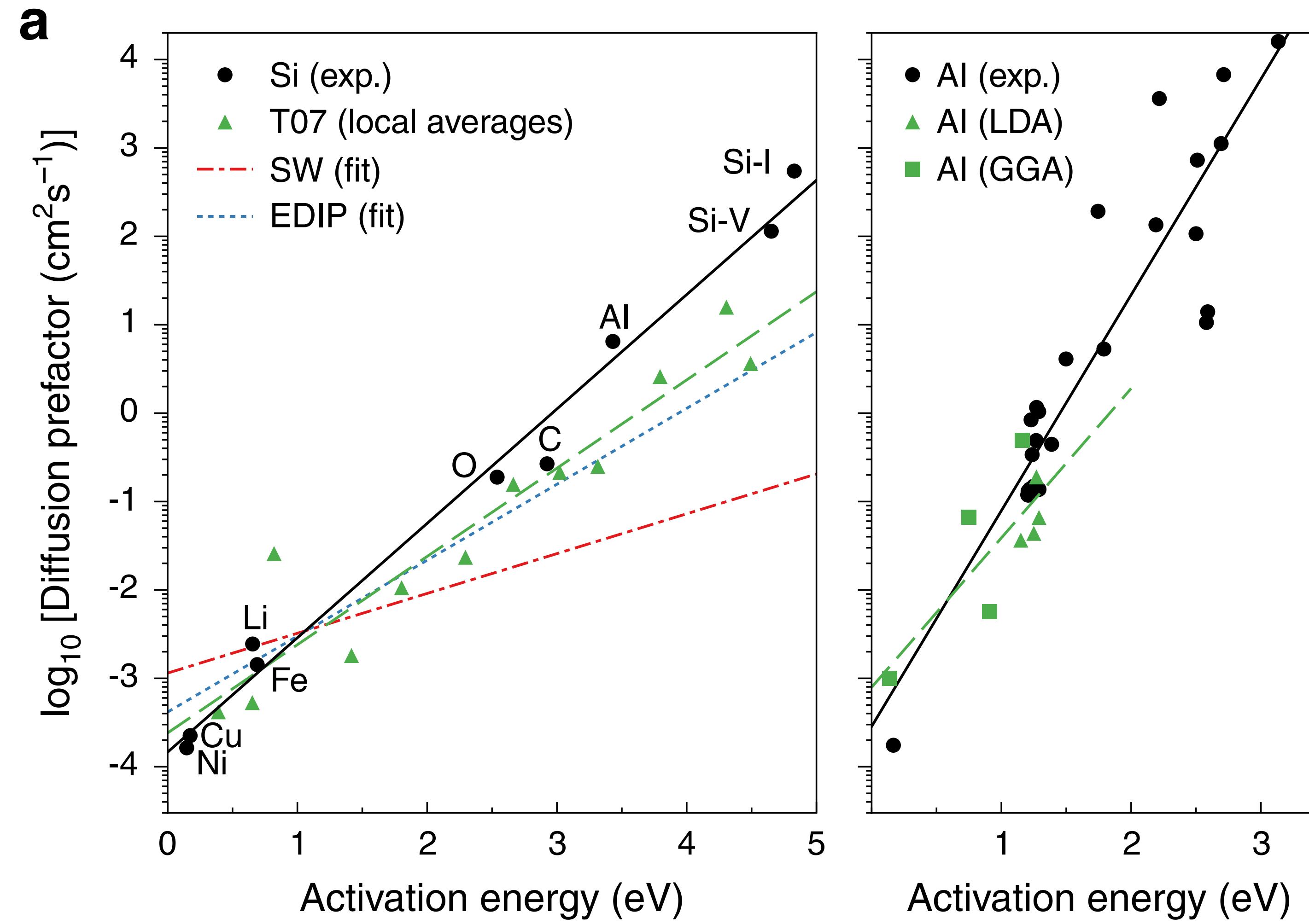
$$\Delta S = \lambda \Delta H \times \frac{d\mu/\mu_0}{dT}$$

**Multi-excitation entropy model  
(Yelon and Movaghari 1990)**

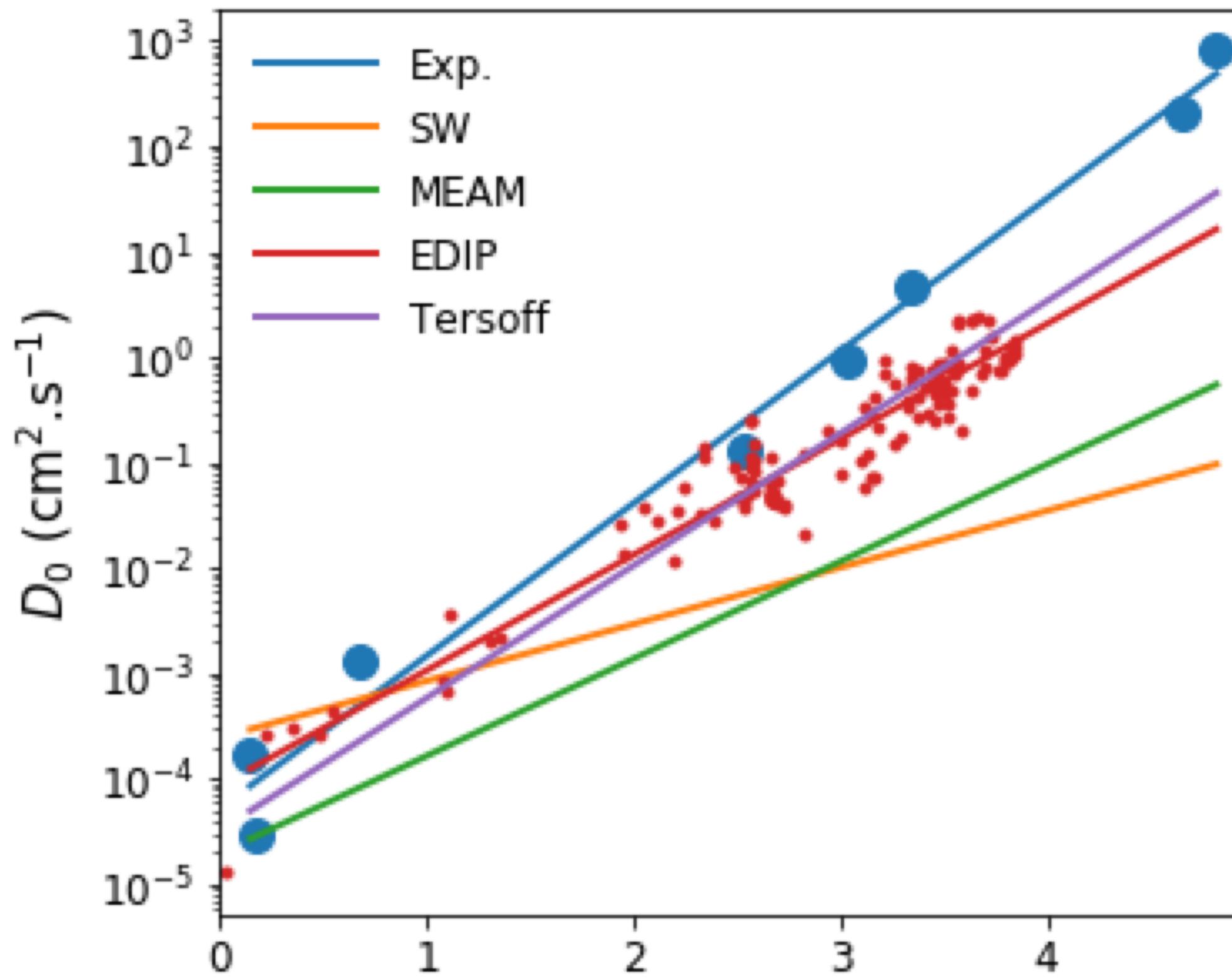
# Revisiting experimental results



# Does the harmonic approximation work?



# The law of compensation - vacancy in c-Si



1. Sample events using ARTn

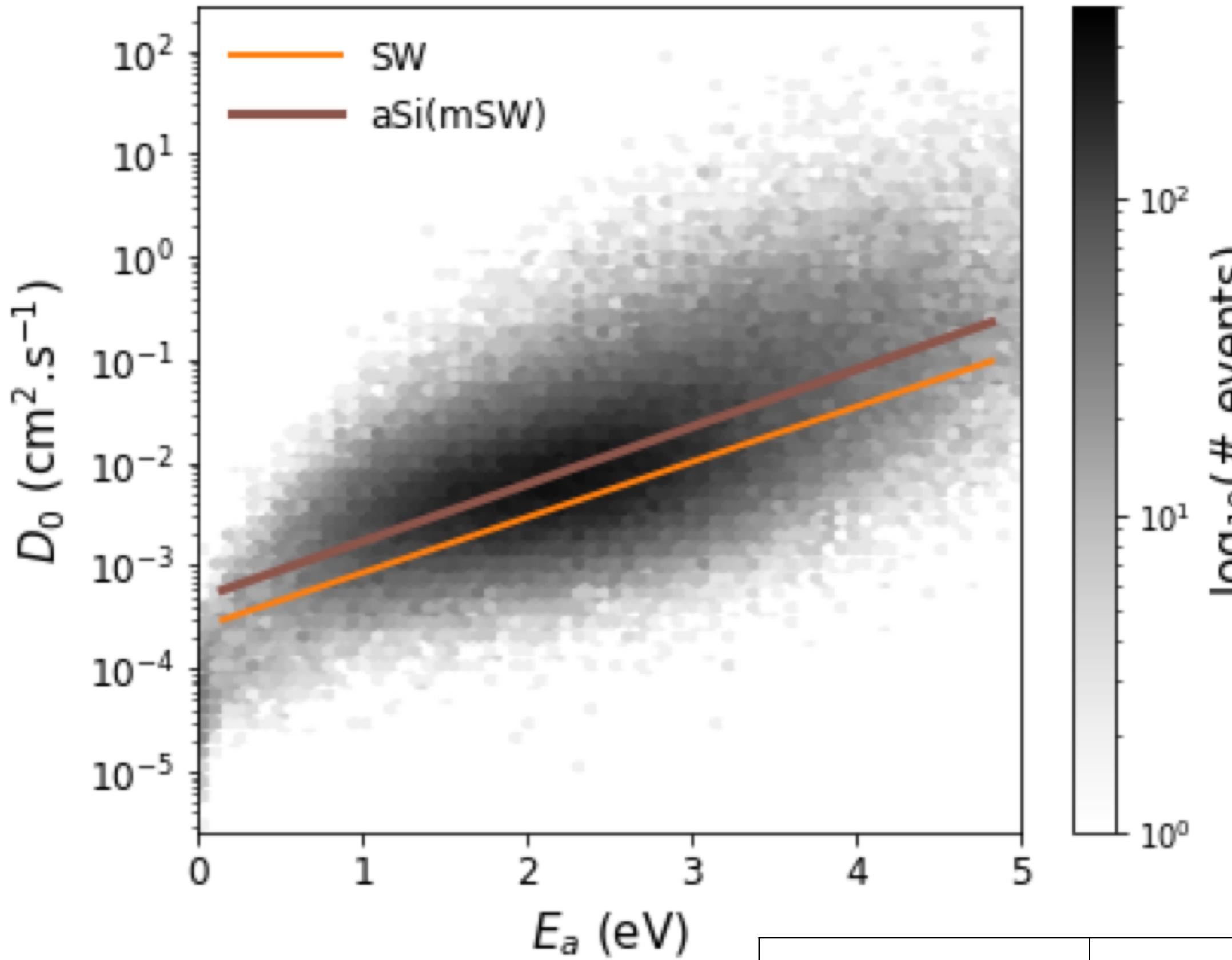
2. For each event  $e$ , compute :

$$D_0(e) = a^2(e) \times \nu_0^{hTST}(e)$$

3. Fit with the compensation law

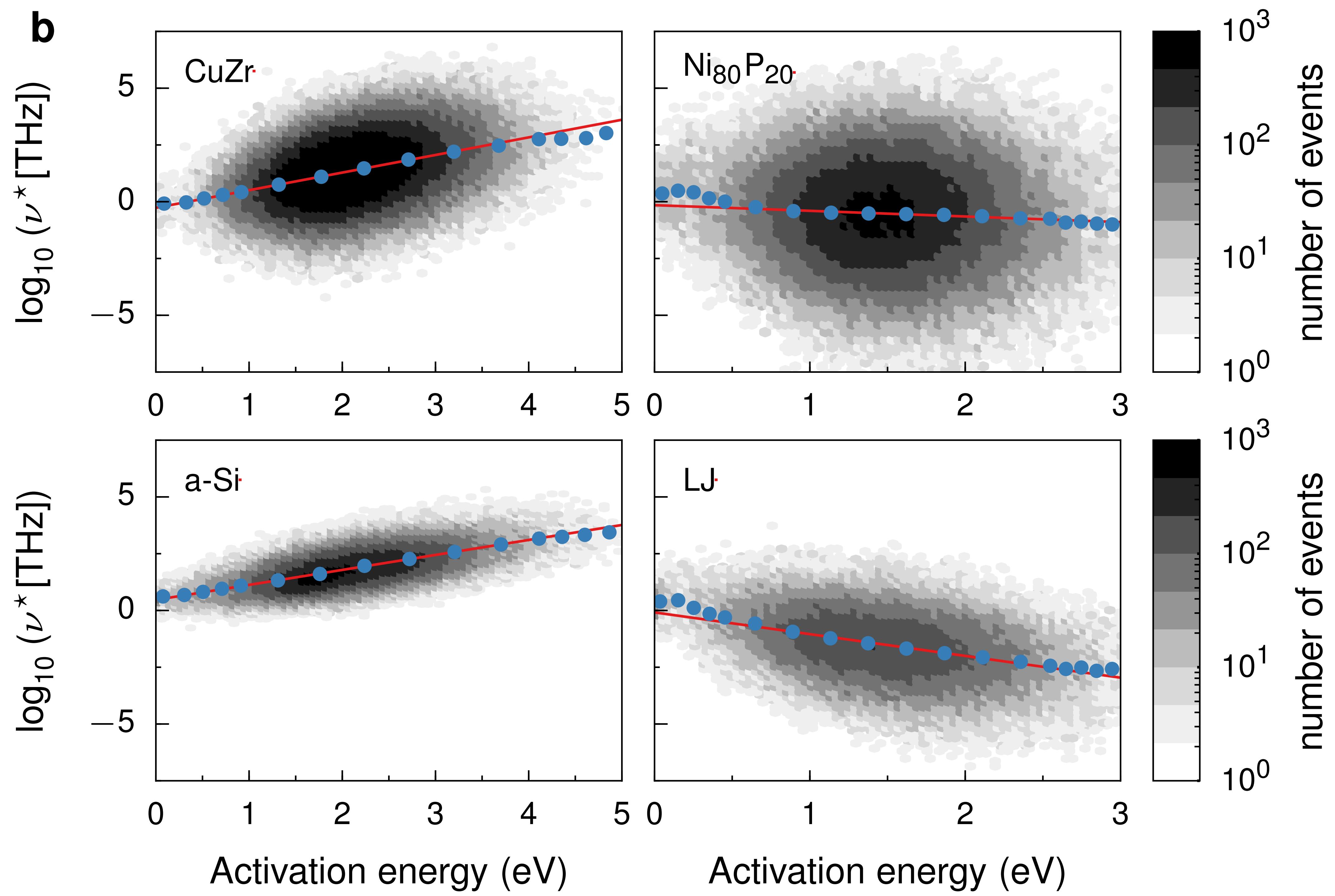
$E_a$ (eV)	Exp.	SW	MEAM	EDIP	Tersoff
$\gamma_c$ [eV $^{-1}$ ]	$3.3 \pm 0.15$	$1.2 \pm 0.24$	$2.1 \pm 0.23$	$2.5 \pm 0.07$	$2.9 \pm 0.21$
$\gamma_c / \gamma_c(\text{exp})$	100 %	37 %	64 %	76 %	87 %

# The law of compensation



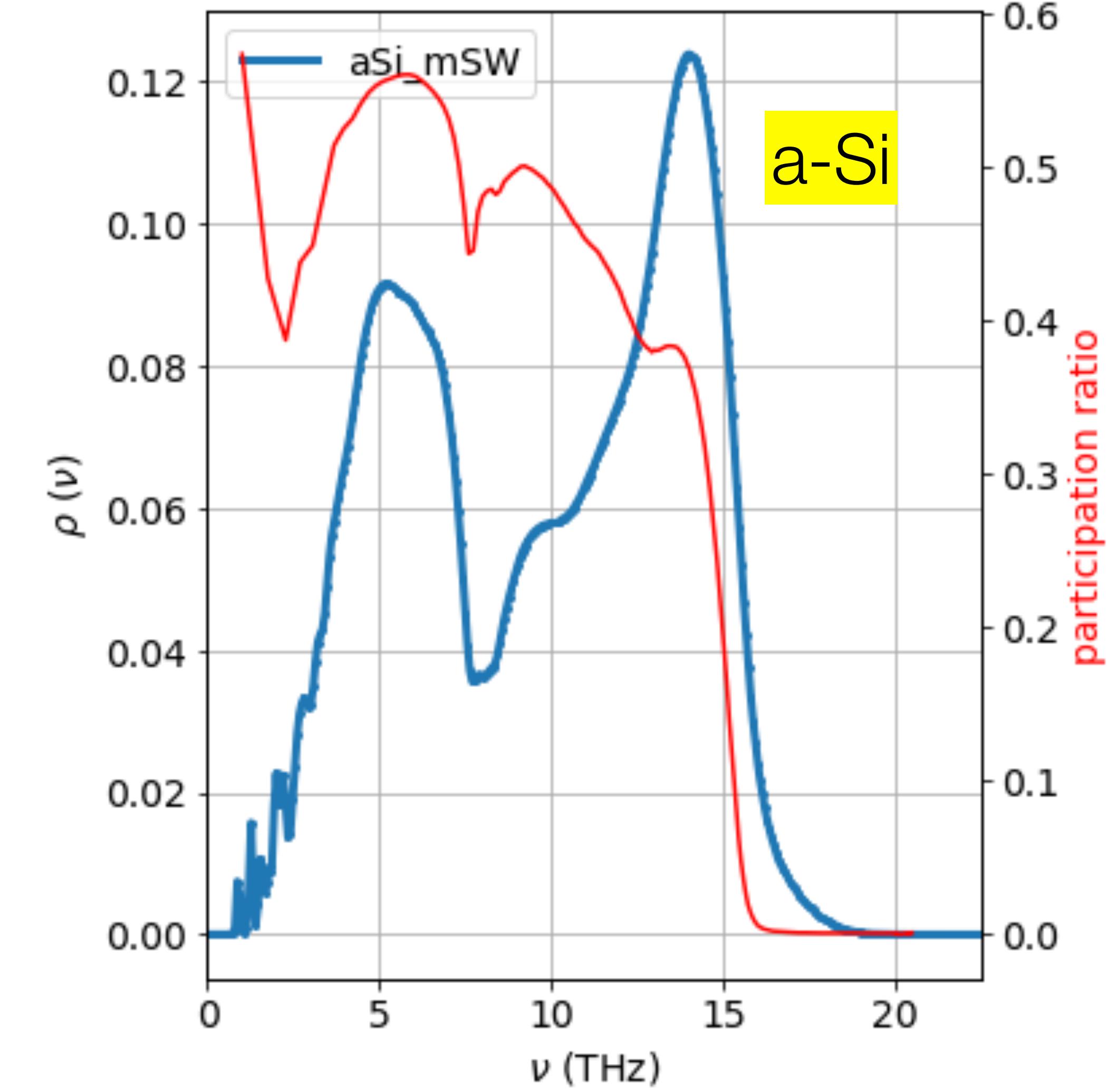
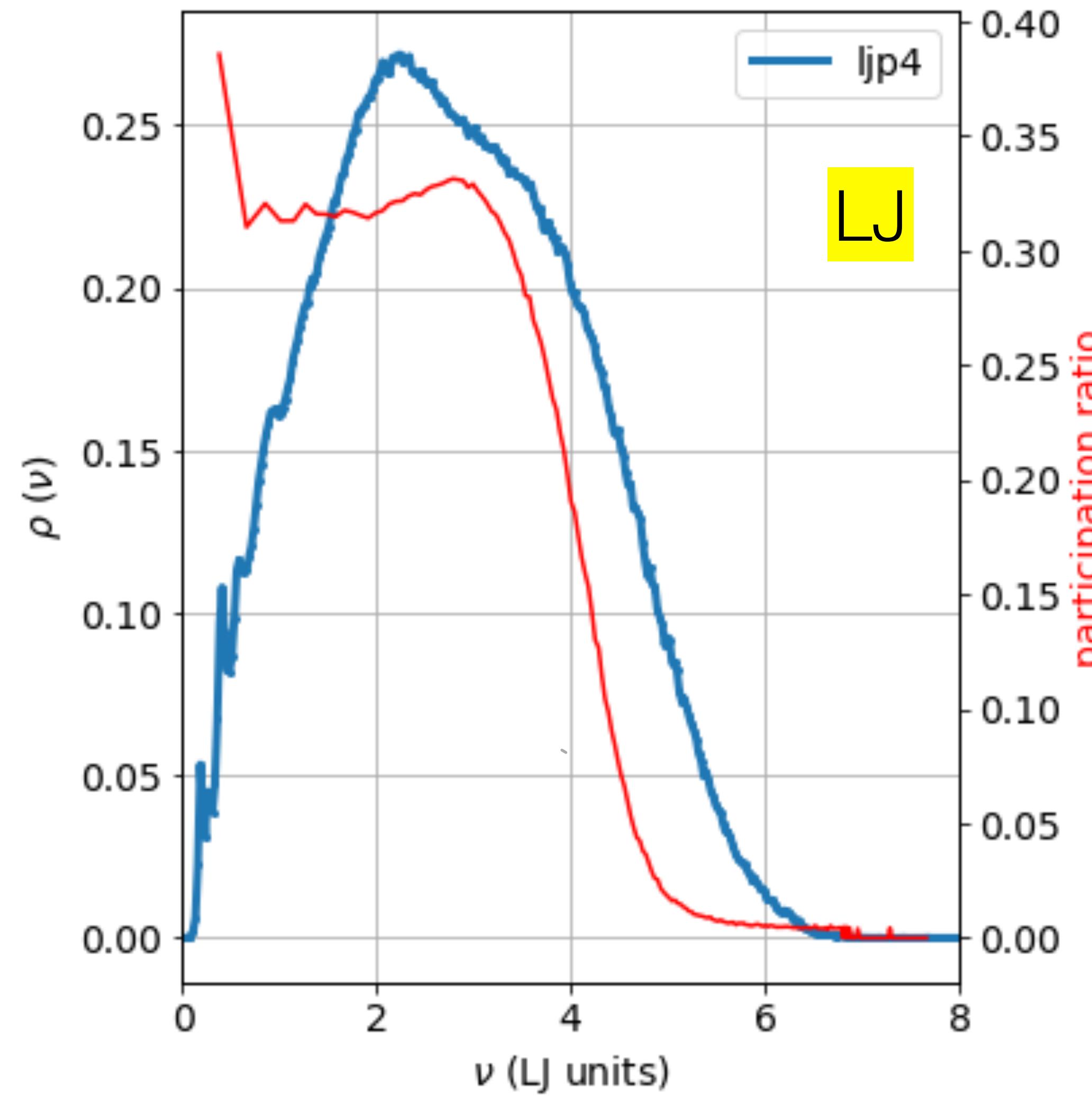
100 configurations of 4096 atoms  
~ 10,000 events per configuration

	Exp.	SW	MEAM	EDIP	Tersoff	aSi(mSW)
$\gamma_c$ [eV <sup>-1</sup> ]	$3.3 \pm 0.15$	$1.2 \pm 0.24$	$2.1 \pm 0.23$	$2.5 \pm 0.07$	$2.9 \pm 0.21$	$1.28 \pm 0.004$
$\gamma_c / \gamma_c(\text{exp})$	100 %	37 %	64 %	76 %	87 %	39 %

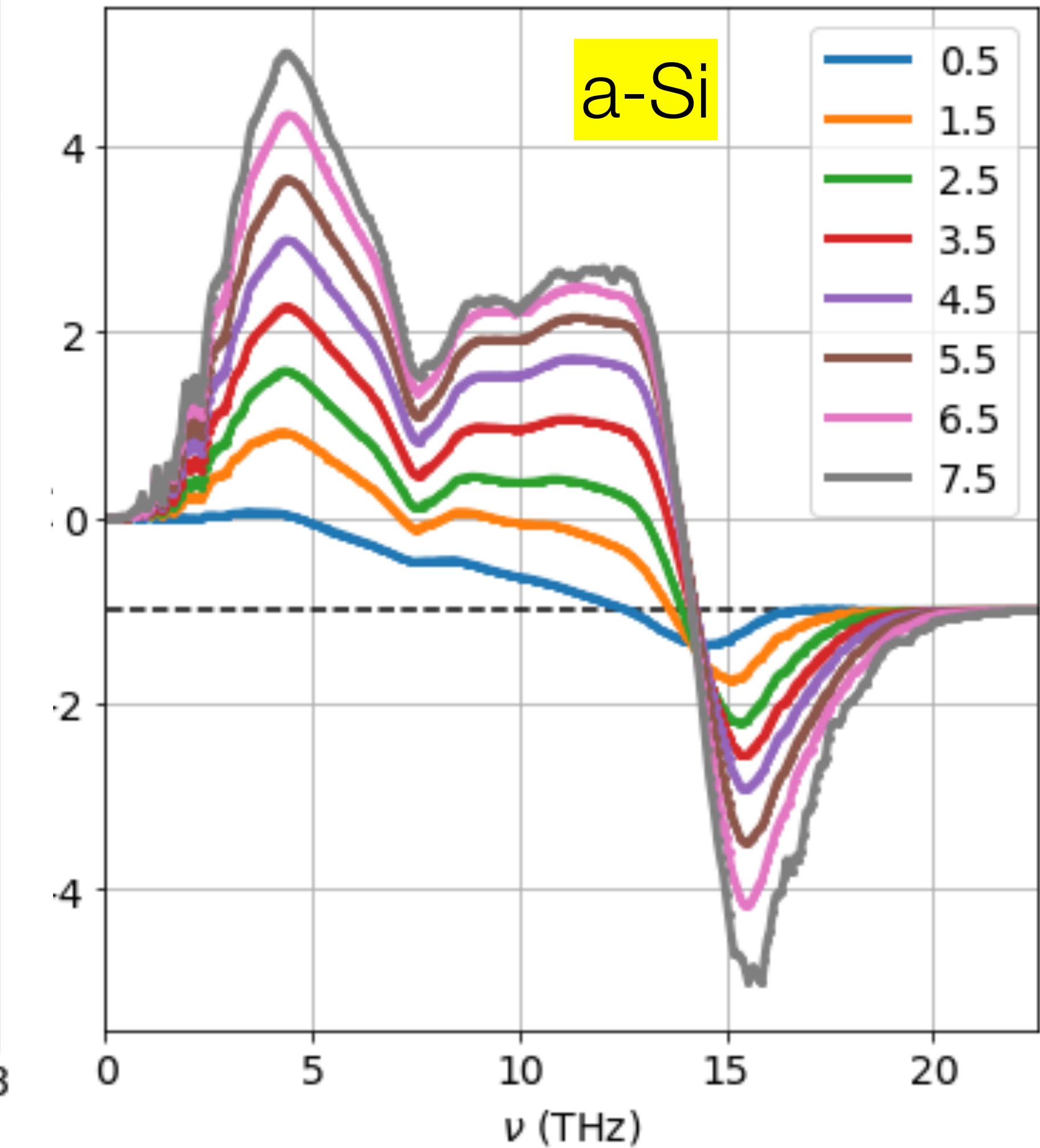
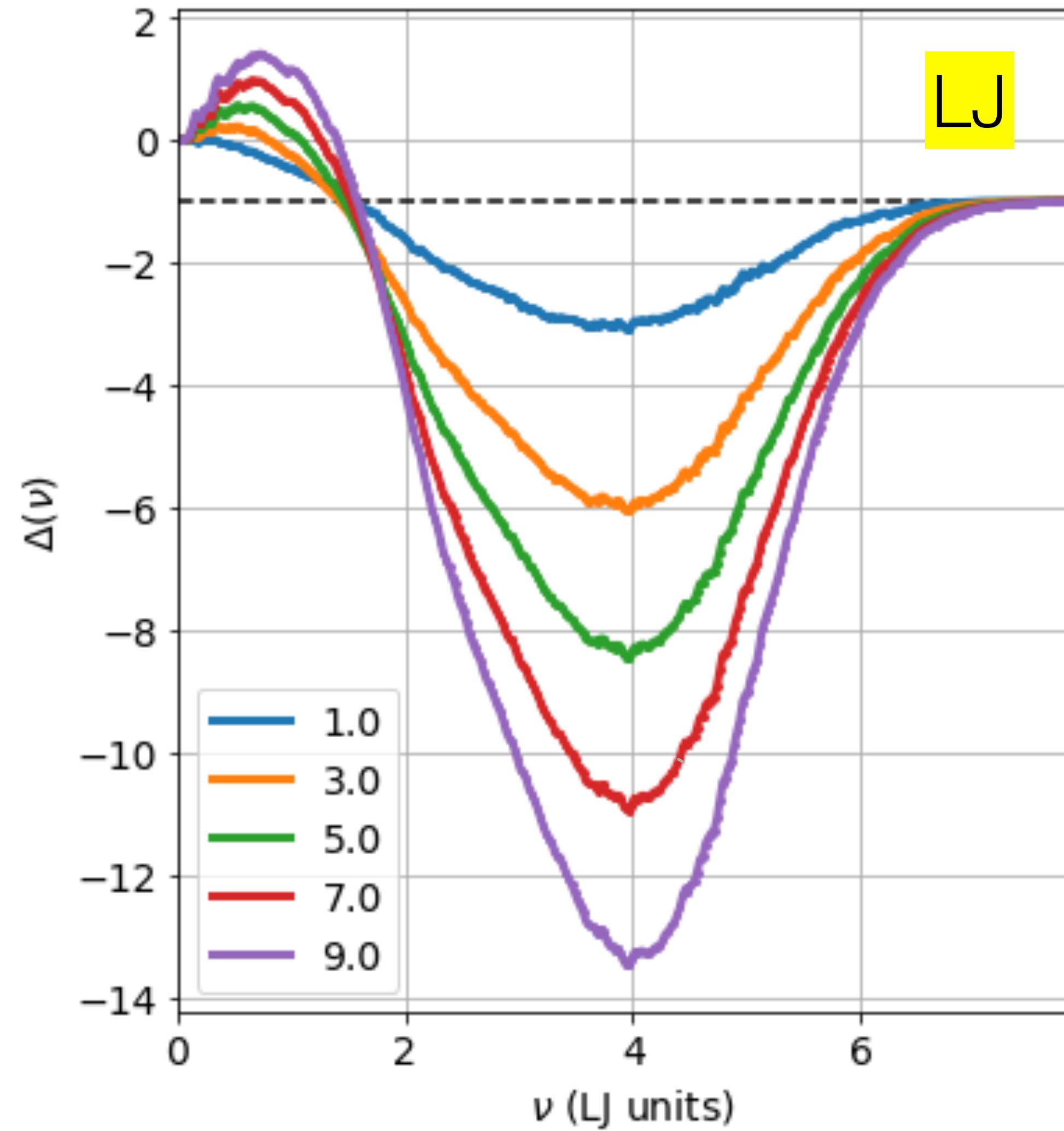


# **Understanding the origin of the compensation law**

# 1- VDOS at minimum and Participation ratio

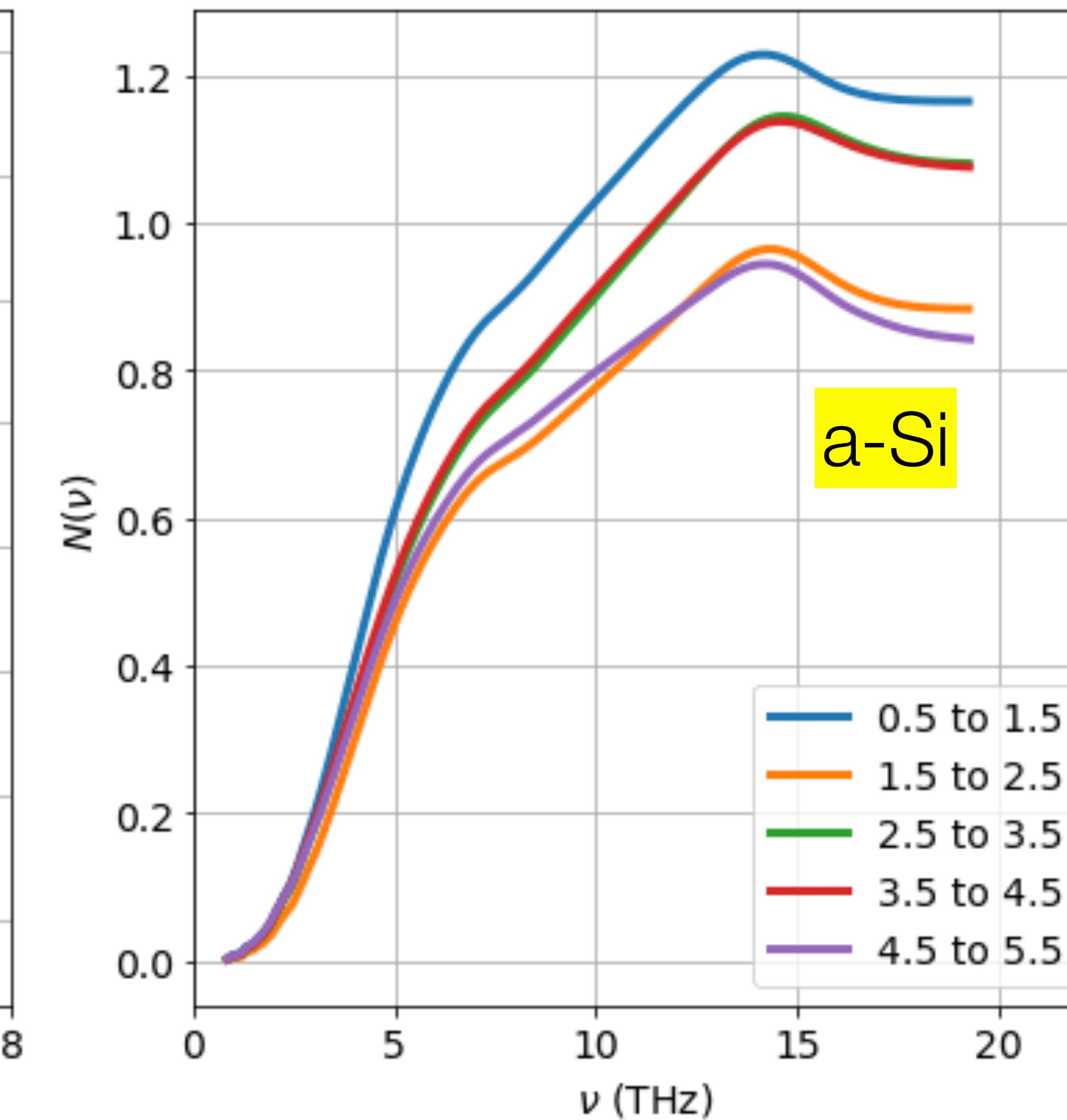
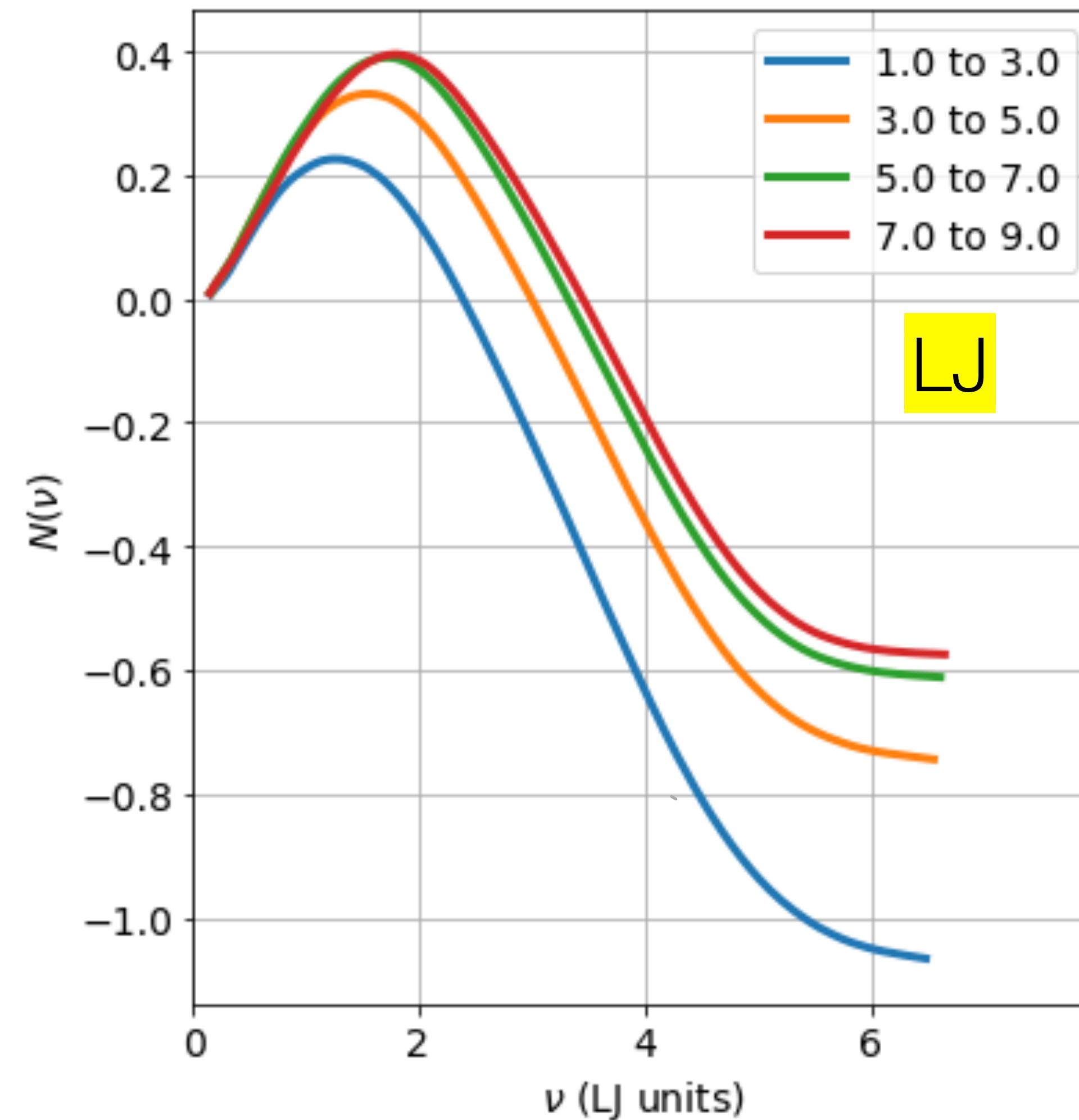


## 2- Difference between VDOS at saddle and minimum

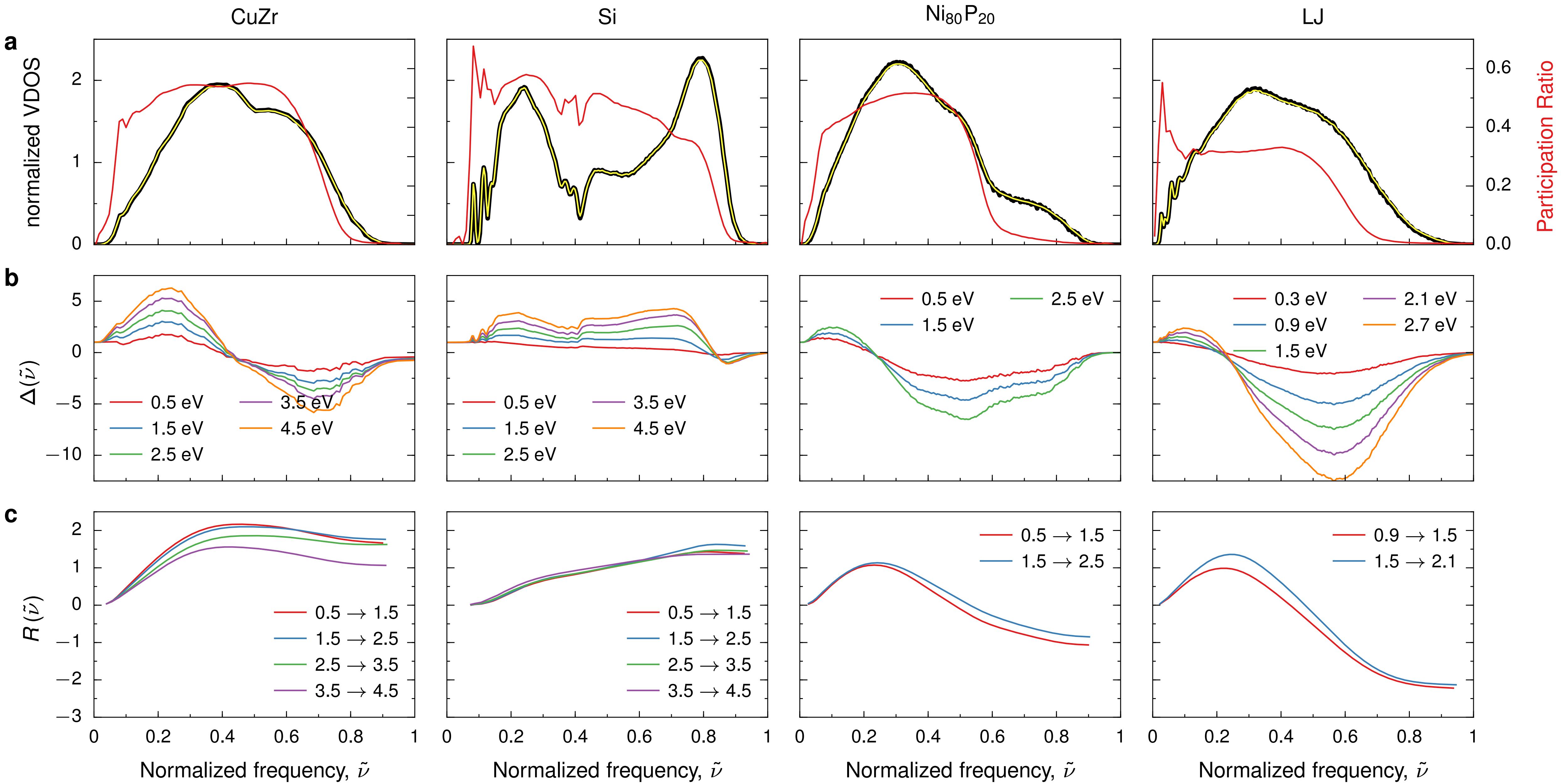


Barrier height  
←

### 3- Difference between prefactors for barriers of various heights



Barrier height  
←



# The law of compensation

1. The hTST description is compatible with both:
  - The Arrhenius law
  - The law of compensation
2. The law of compensation is purely determined by the saddle point
3. It depends on the network much more than on the impurity
4. The jump rate can be written as  $\nu(T) = \underbrace{\nu_{00}}_{\text{low frequencies}} \times \underbrace{\exp(\gamma_c E_a)}_{\text{high frequencies}} \times \exp\left(-\frac{E_a}{k_B T}\right)$

# **High-entropy alloys and concentrated solid solutions**

# High-entropy alloys and concentrated solid solutions

High entropy alloys : solid-solutions composed of five or more elements in near equimolar proportions (introduced by Yeh et al. in 1996)

Interesting properties include:

- decrease in the shear modulus with an increase of point defect concentration<sup>4</sup>
- a high-temperature strength
- indications of a potentially high resistance to neutron radiation damage
- sluggish in Co-Cr-Fe-Mn-Ni high entropy alloys

# High-entropy alloys and concentrated solid solutions

Sluggish diffusion in Co–Cr–Fe–Mn–Ni high-entropy alloys

Acta Materialia 61 (2013) 4887–4897

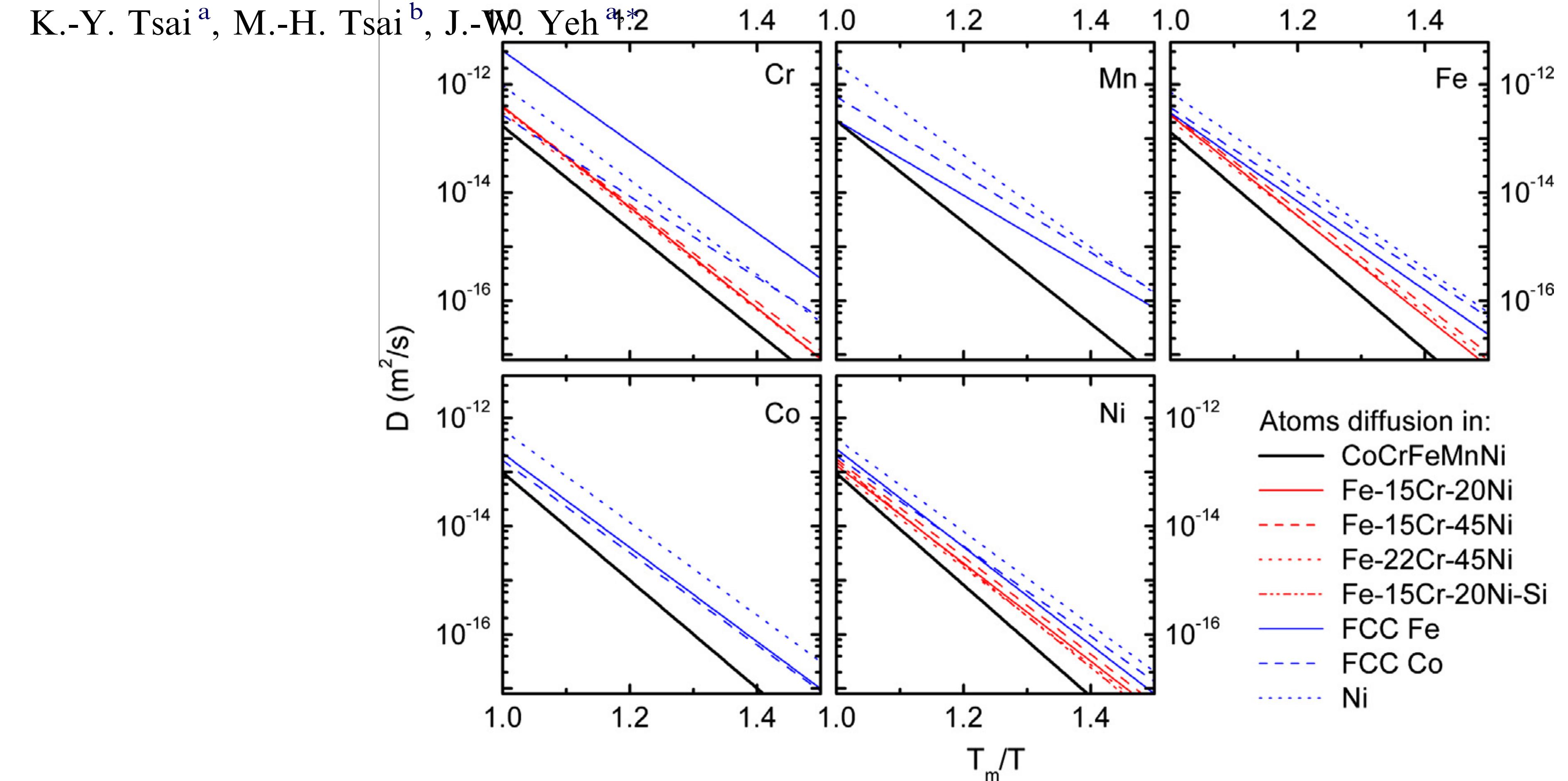


Fig. 6. Temperature dependence of the diffusion coefficients for Cr, Mn, Fe, Co and Ni in different matrices.

# Concentrated solid solutions

## Diffusion in Fe–Ni–Cr Alloys with an F.C.C. Lattice

B. MILLION, J. RŮŽIČKOVÁ and J. VŘEŠTÁL

*Materials Science and Engineering*, 72 (1985) 85–100

TABLE 5

Average values of self-diffusion characteristics of iron  
in Fe–Ni–Cr alloys

Composition of alloys		$\log \bar{D}_{0\text{Fe}}^*$ ( $\text{cm}^2 \text{s}^{-1}$ )	$\bar{Q}_{\text{Fe}}^*$ ( $\text{kJ mol}^{-1}$ )	$n$
Cr (wt.%)	Ni (wt.%)			
0	0	-0.054	279.7	5
0	15.5	0.293	286.5	3
0	30.7	0.728	298.9	2
0	46.6	0.675	295.4	3
0	61.7	1.22	306.0	2
0	71.1	1.15	304.1	2
0	76.2	0.935	299.9	3
0	80.6	1.06	302.9	2
0	90.5	1.11	303.4	2
0	100	0.766	293.3	5
4.2	95.8	0.395	285.9	2
12.9	87.1	0.666	296.5	3
21.5	78.5	0.727	299.9	4
27.0	73.0	0.169	287.0	2
31.7	68.3	0.065	285.1	3
35.6	64.4	0.177	287.3	2
44.7	55.3	0.264	286.6	2
10.1	78.7	0.239	281.3	2
10.1	64.6	0.042	276.5	2
9.9	55.1	0.691	295.2	2
10.1	35.0	0.574	295.1	2
20.0	63.5	0.346	286.7	2
19.9	55.1	0.882	307.8	2
19.6	43.0	0.075	284.1	2
20.0	34.9	0.677	298.7	2
19.1	19.1	-0.263	278.4	2
30.4	65.3	0.089	280.1	2
30.4	54.8	-0.088	273.0	2
30.4	34.8	0.384	291.0	2

# Question

What is the relative role of prefactors and barriers for vacancy diffusion in concentrated solid-solution alloys?

## First approach

Characterize the energy landscape

# Question

What is the relative role of prefactors and barriers for vacancy diffusion in concentrated solid-solution alloys?

Unexpected role of prefactors in defects diffusion: The case of vacancies in the 55Fe-28Ni-17Cr concentrated solid-solution alloys

Alecsandre Sauvé-Lacoursière<sup>a</sup>, Simon Gelin<sup>a,b,c</sup>, Gilles Adjanor<sup>d</sup>, Christophe Domain<sup>d</sup>, Normand Mousseau<sup>a,\*</sup>

Acta Materialia 237 (2022) 118153

2048-atom box (-1 for vacancy)

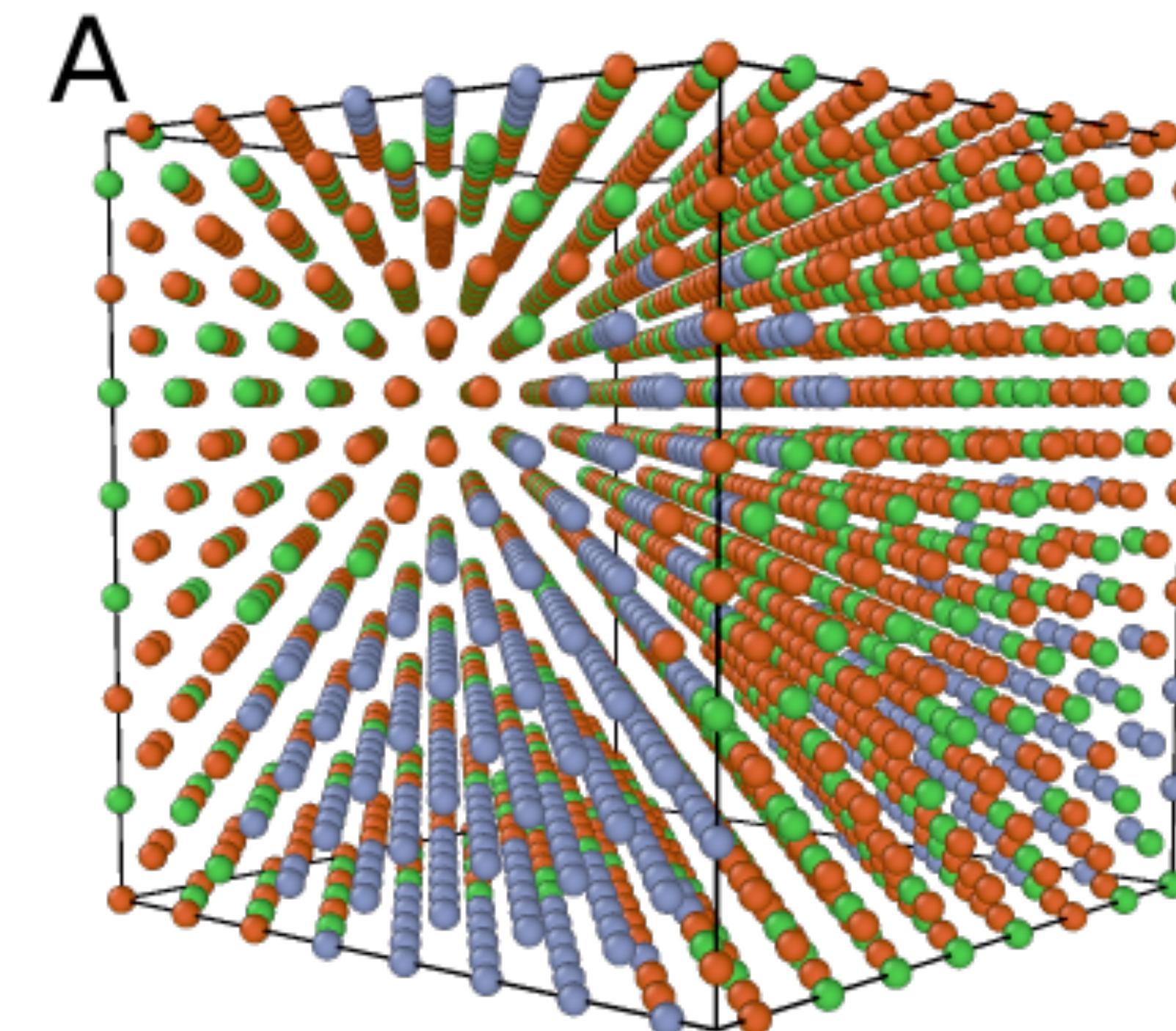
55Fe-28Ni-15Cr CSA

EAM Potential from

G. Bonny, N. Castin, D. Terentyev, Model.

Simul. Mater. Sci. Eng. 21 (8) (2013) 085004

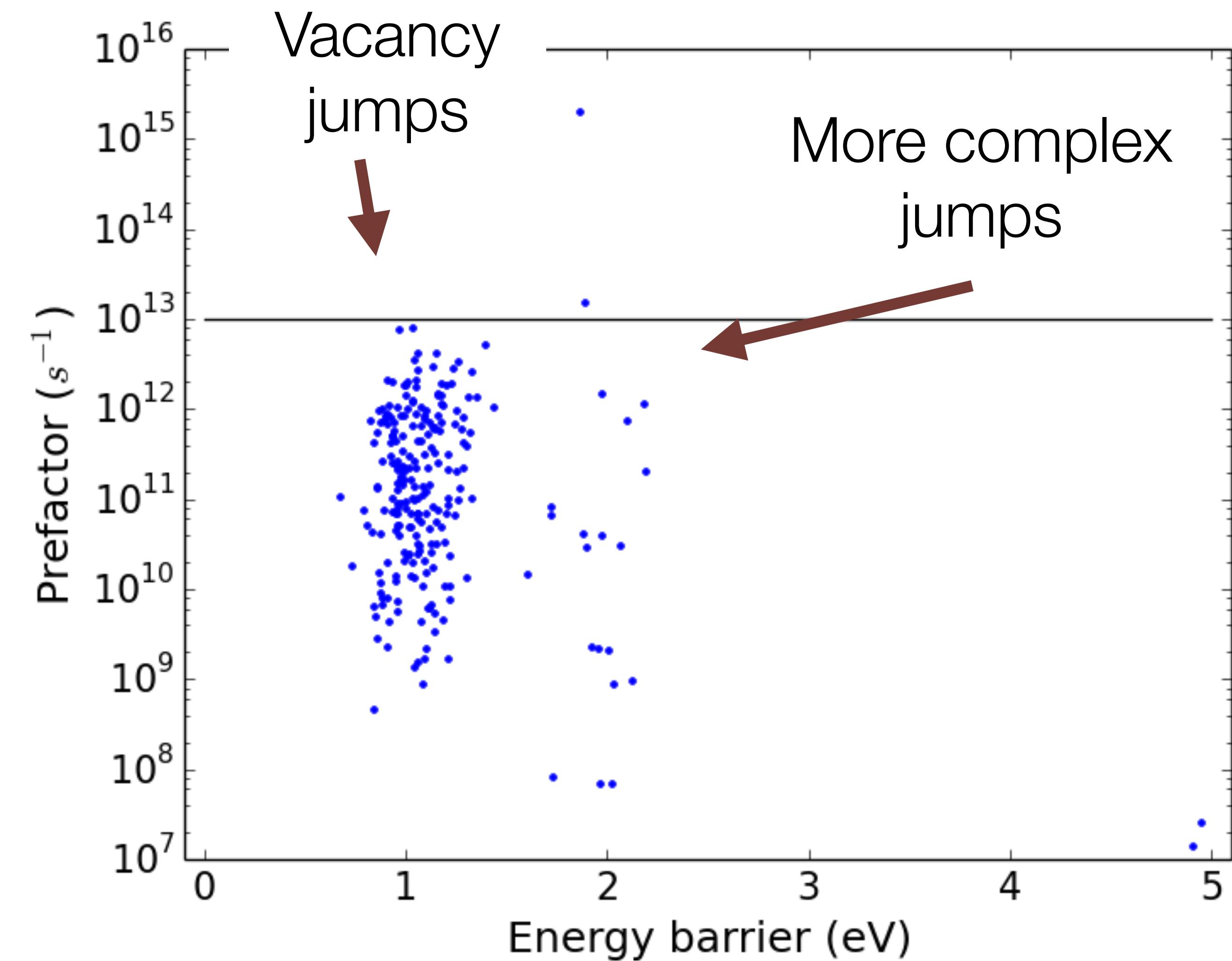
ARTn exploration of energy landscape  
(243 events from 22 configurations)



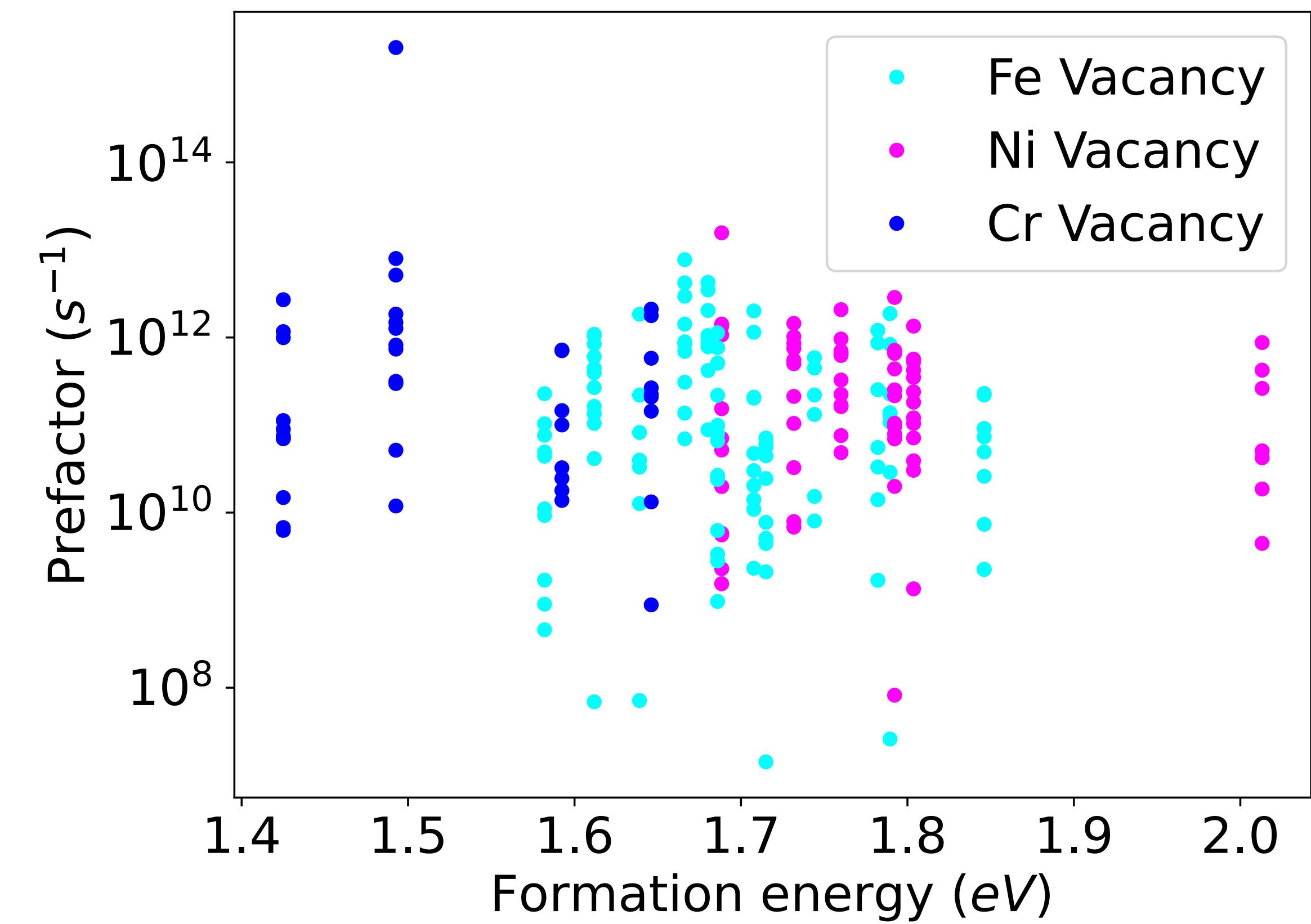
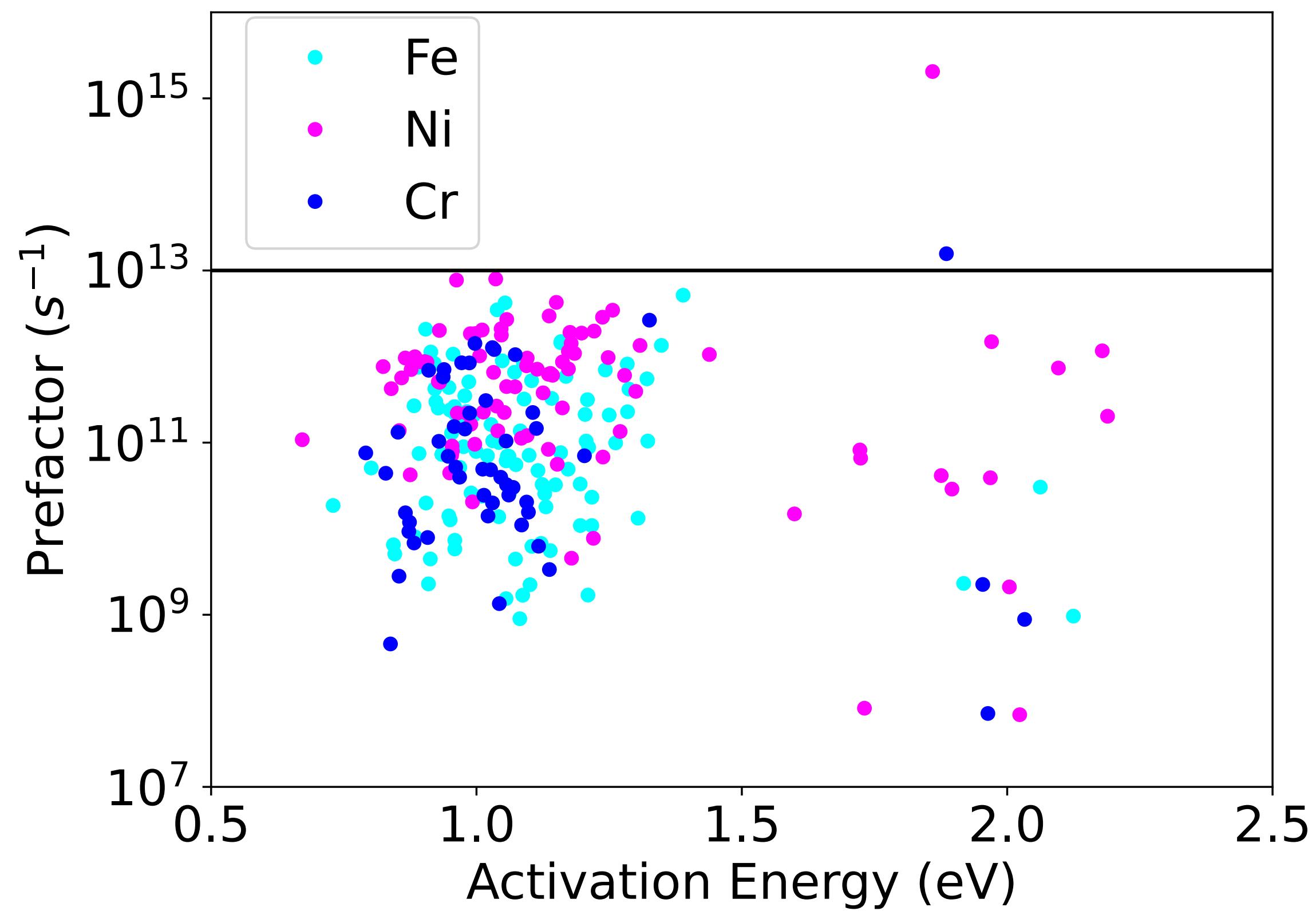
# Prefactors vs barrier

$$D(T) = D_0 \times \exp(-E_a/k_B T)$$

More than  
4 orders of  
magnitude  
for the  
same  
barrier!



# Effect of diffusing species



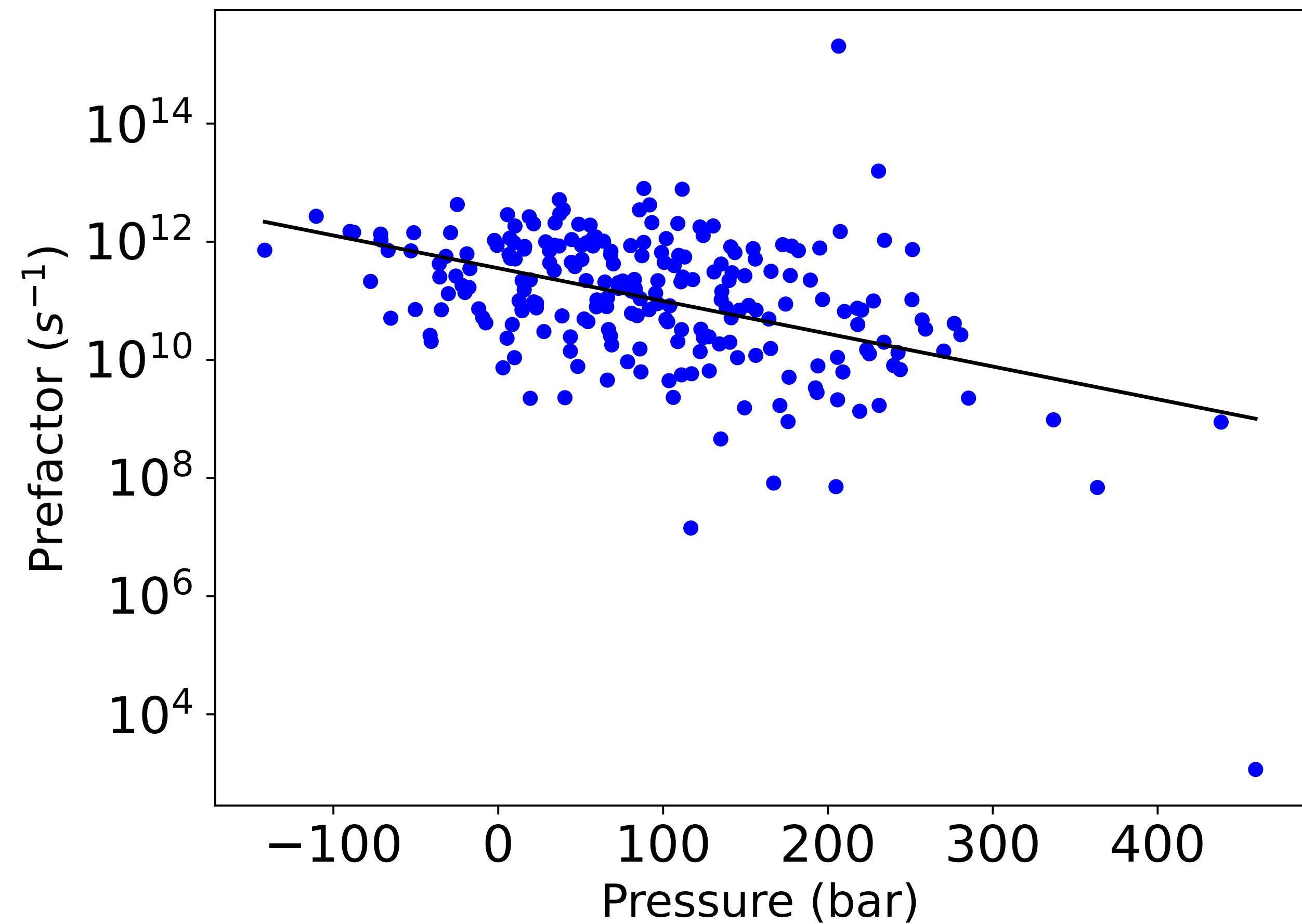
# Conclusions

## Conclusion

- Unexpected effect of prefactor in these systems
- Correlation with local pressure

## Questions

- Impact on kinetics?
- Role of various species?



# Details

Joseph Lefèvre López, Gilles Adjanor,  
Christophe Domain and NM (in preparation)

2048-atom box (-1 for vacancy)

55Fe-28Ni-15Cr CSA

EAM Potential from

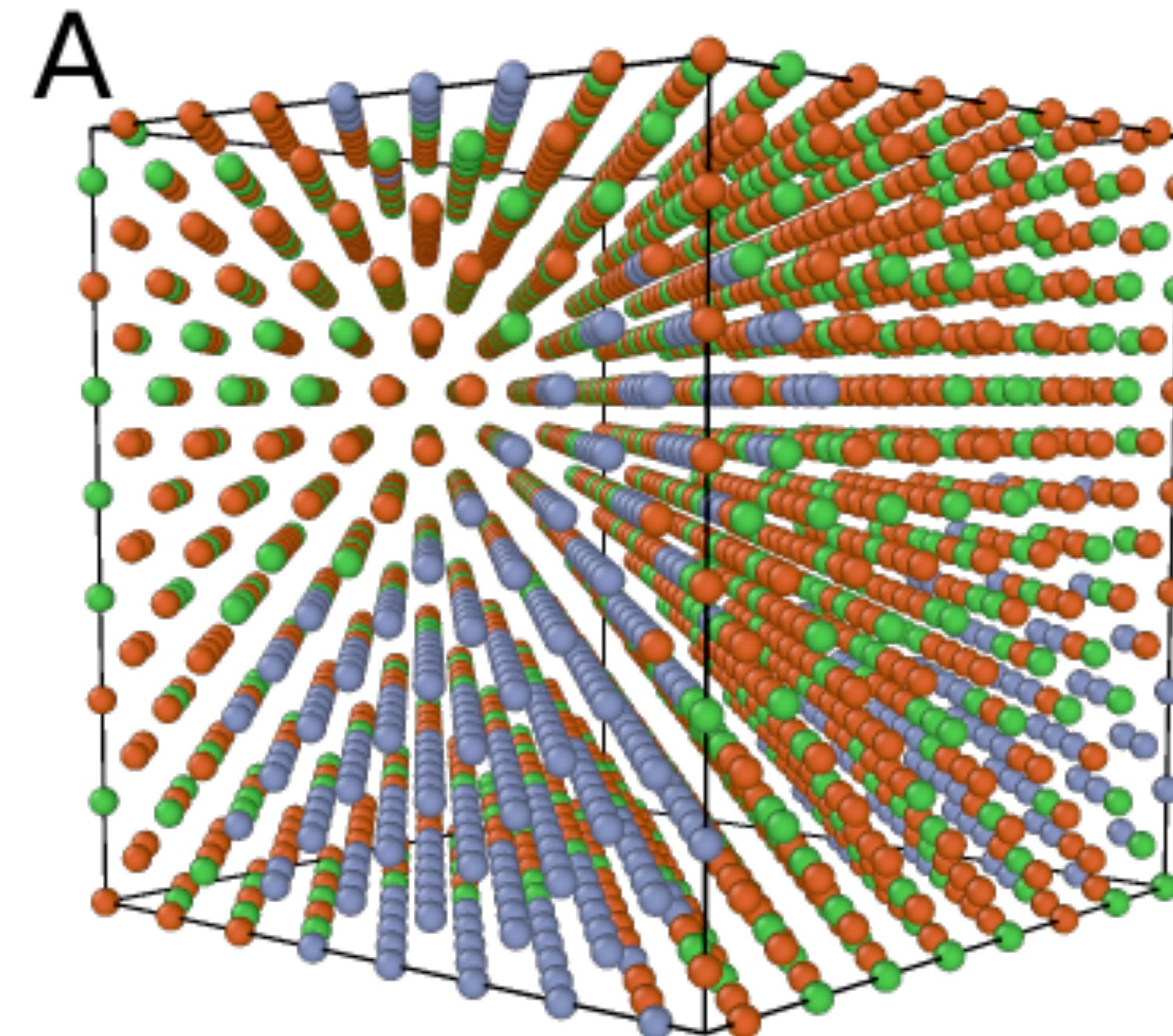
G. Bonny, N. Castin, D. Terentyev,, Model. Simul.  
Mater. Sci. Eng. 21 (8) (2013) 085004

Use of kinetic ART:

500 K

192 simulations of 2000 steps each

**(380 000 steps - 3,6 million events)**



# EVALUATING THE PREFACTOR WITH ML APPROACHES

## Machine learning surrogate models for strain-dependent vibrational properties and migration rates of point defects

Clovis Lapointe,<sup>1,\*</sup> Thomas D. Swinburne,<sup>2,†</sup> Laurent Proville,<sup>1</sup> Charlotte S. Becquart<sup>3</sup>, Normand Mousseau,<sup>4</sup> and Mihai-Cosmin Marinica<sup>1,‡</sup>

PHYSICAL REVIEW MATERIALS **6**, 113803 (2022)

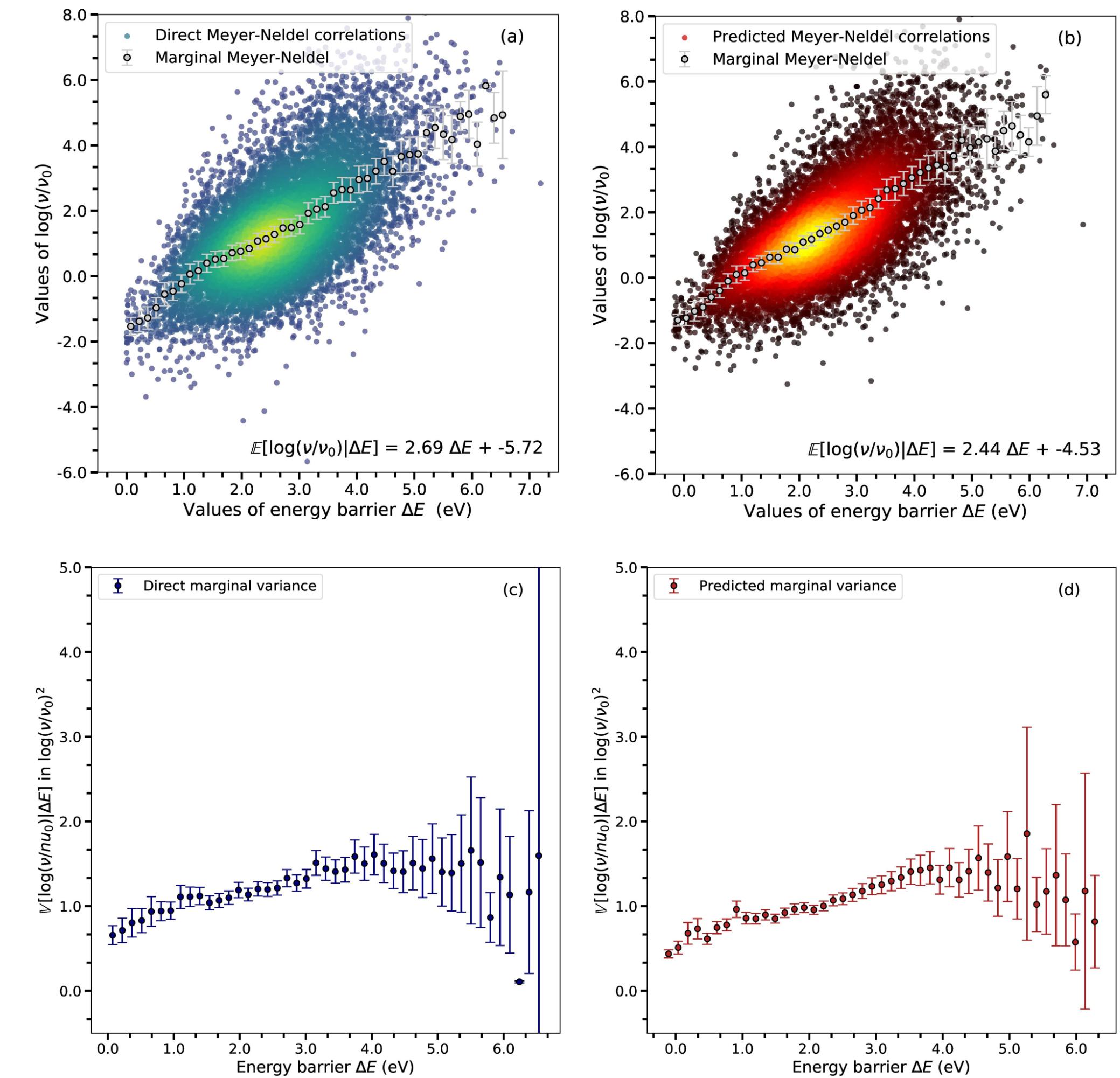


FIG. 5. Drawing the enthalpy-entropy compensation relation for the Si amorphous database. (a) shows values of  $\Delta E$  and  $\ln(v/v_0)$  computed with ARTN method. (b) shows predicted values of  $\Delta E$  and  $\ln(v/v_0)$  with linear model. The color gradient represents data distribution; yellow corresponds to dense data zones for both types of points. Adjusted EEC relations, following Eq. (29), for both direct and surrogate models are emphasized in (a) and (b) by white points with black contour. Both models, the direct and the surrogate, have distributions with very close correlation indicators. Marginal variance distribution for both dataset is presented in (c) and (d) for direct and surrogate data respectively. The marginal variance is quantitatively almost the same for both dataset.

**MERCI!**