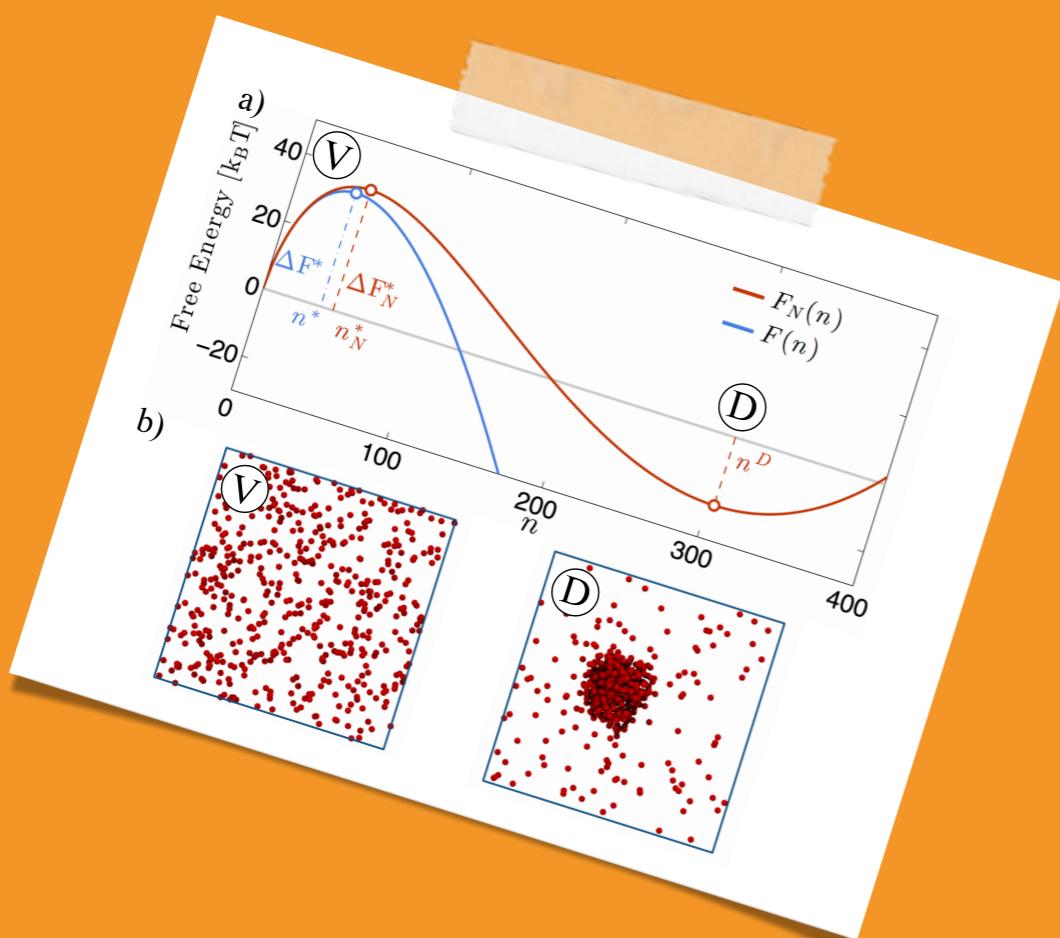


# Studying concentration-driven processes with finite-sized molecular simulations

plumed meeting 2017 - Trieste - 26.5.2017

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## concentration driven processes:

processes in which the **driving force** is **determined by** the (local or global) **density** of a chemical specie

- nucleation in multicomponent systems
- nucleation of a liquid from a vapour phase (@NVT)
- crystal growth
- adsorption processes
- diffusive mass transfer

...

### where is the issue?

in small volumes (i.e. in a NVT/NPT simulation box) the driving force is coupled with the progress of the transformation

# this talk:

1

How important are finite size effects in concentration driven processes?

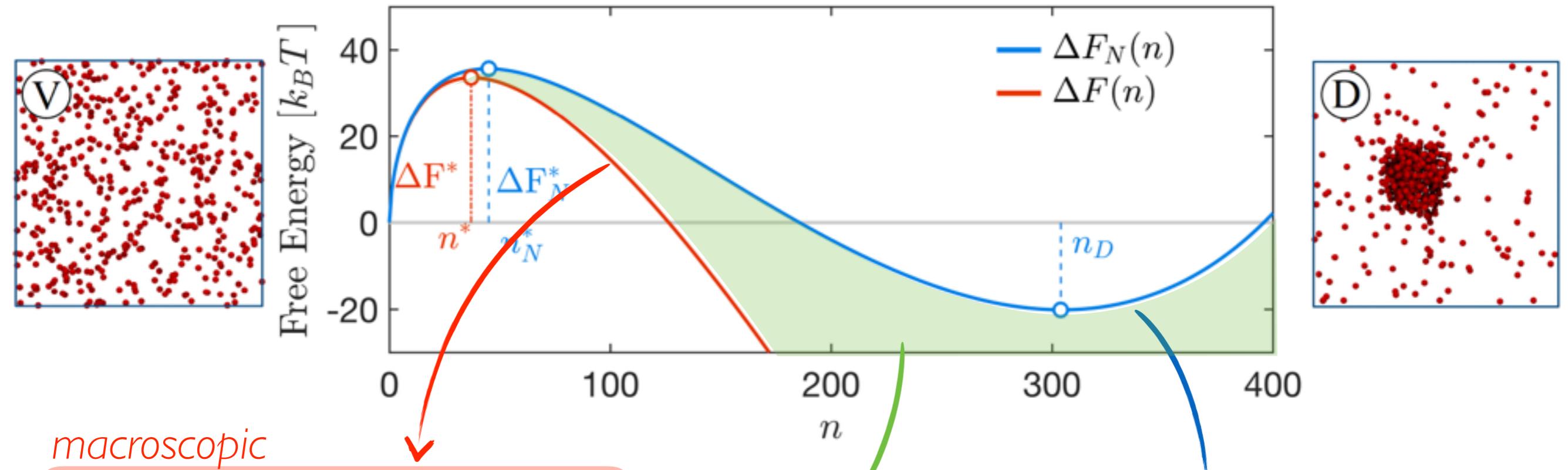
2

C $\mu$ MD: a PLUMED-based workaround

3

Steady state, out of equilibrium diffusive mass transfer

# nucleation driving force



*macroscopic*

$$\Delta F(n) = -nk_B T \ln S_0 + \gamma(an)^{2/3}$$



the **growth of supercritical nuclei** ( $n > n^*$ ) is **dominated** by **finite size effects**

$$\Delta F^* < \Delta F_N^*$$

$$p(N, n, V, T) = \frac{(N - n) k_B T}{V - nv_\ell}$$

when  $O(N) \sim 10-100 O(n)$   
(i.e. in a typical simulation box)

*finite-sized*

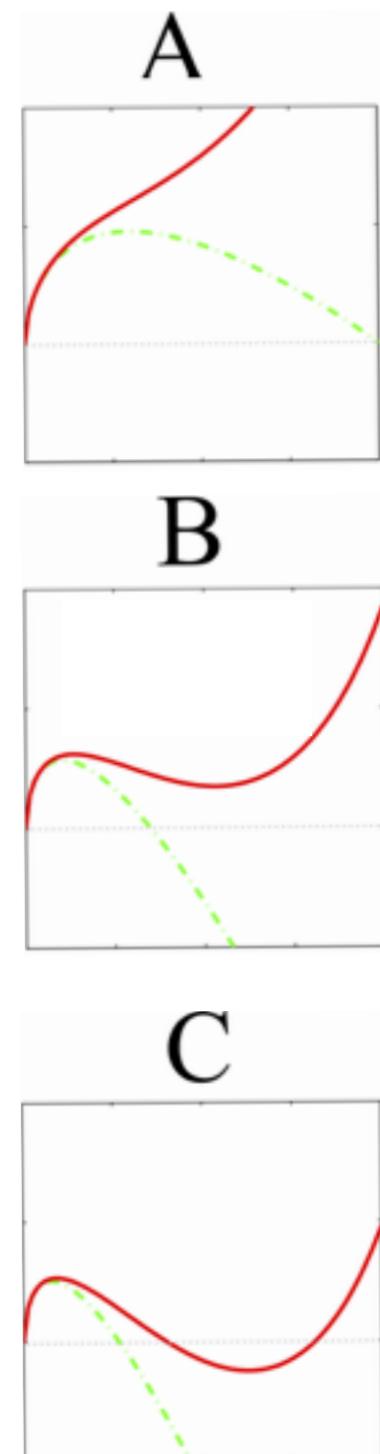
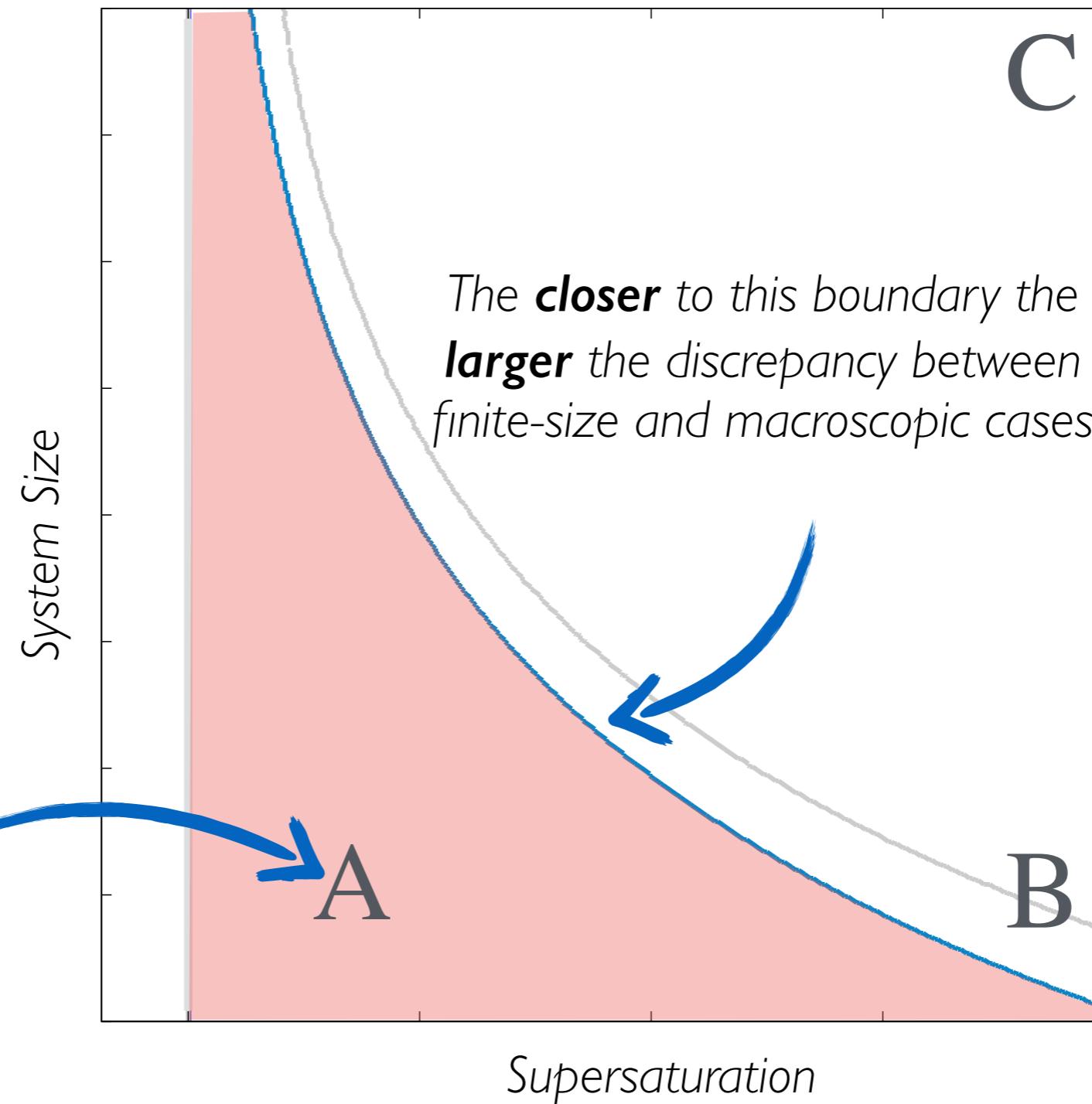
$$\begin{aligned} \Delta F_N(N, n, V, T) = & -n\beta^{-1} \ln \left( \frac{p}{p_e} \right) + \gamma(an)^{2/3} \\ & + N\beta^{-1} \ln \left( \frac{p_0}{p_e} \right) + n(\beta^{-1} - v_\ell p_e) \end{aligned}$$

# How important are finite-size effects?

The **free energy profile** associated to nucleation **depends** on **finite size**: **this may have a very significant effect on the qualitative behaviour of your simulation**

here nucleation  
rates **cannot be directly  
computed!!**

In region A the “**product  
basin**” does not exist!





# Nucleation timescale depends on finite-size

Characteristic time

$$\tau = \frac{1}{J(S, T)V} \quad \text{System Volume}$$

Nucleation rate

a

@ $T, S = \text{const}$

$$\tau \propto \frac{1}{V}$$

@ $V = \text{const}$

b

$$\tau \propto \frac{1}{J(S, T)} \propto S^{-1} \exp(\beta \Delta F^*) = S^{-1} \exp\left(\frac{4(\beta \sigma a)^3}{27 (\ln S^2)}\right)$$

for  $S$  approaching 1, the characteristic time diverges

To compute  $J$  for  $S$  approaching 1  
**very large systems** (1E6 atoms)  
and/or  
**extremely long timescales** (hours)  
are required

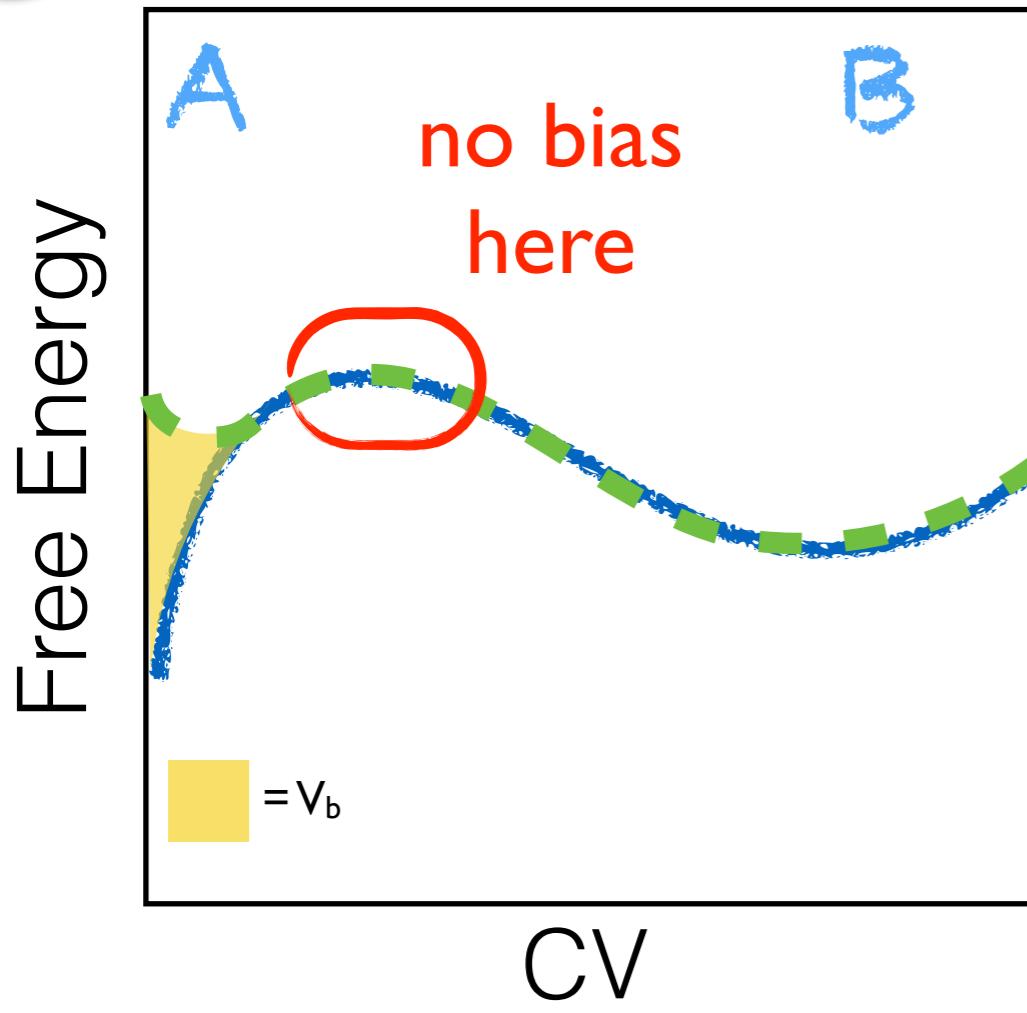
finite size  
macroscopic

$$\tau_N \propto S^{-1} \exp(\beta \Delta F_N^*)$$

$$\tau \propto S^{-1} \exp(\beta \Delta F^*)$$



# Nucleation rates from metadynamics



$$k_{A \rightarrow B} = k_{A \rightarrow B}^* \langle e^{-\beta V_b} \rangle$$

UNBIASED BIASED BIAS  
FREQUENCY FREQUENCY

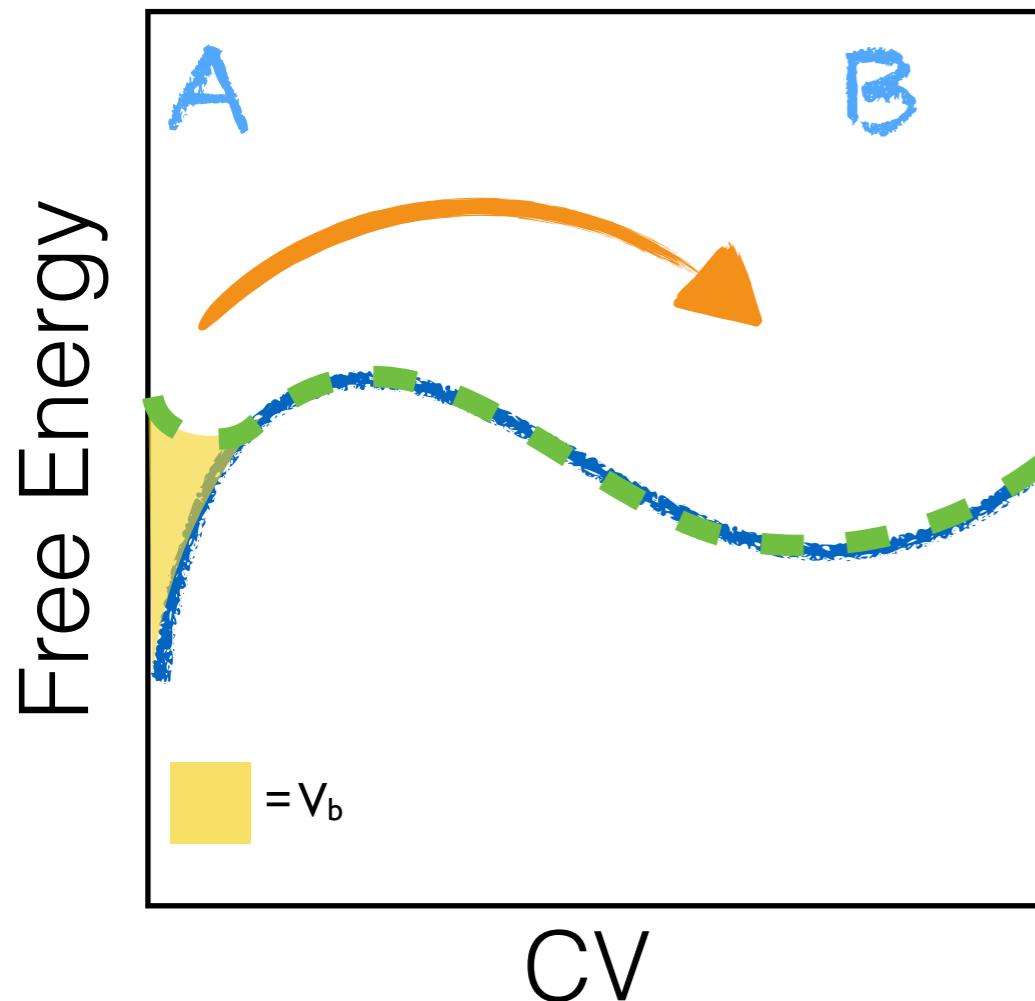
○  $k_{A \rightarrow B} = \kappa \frac{Z_{TS}}{Z_A}$

○  $k_{A \rightarrow B}^* = \kappa^* \frac{Z_{TS}^*}{Z_A^*}$

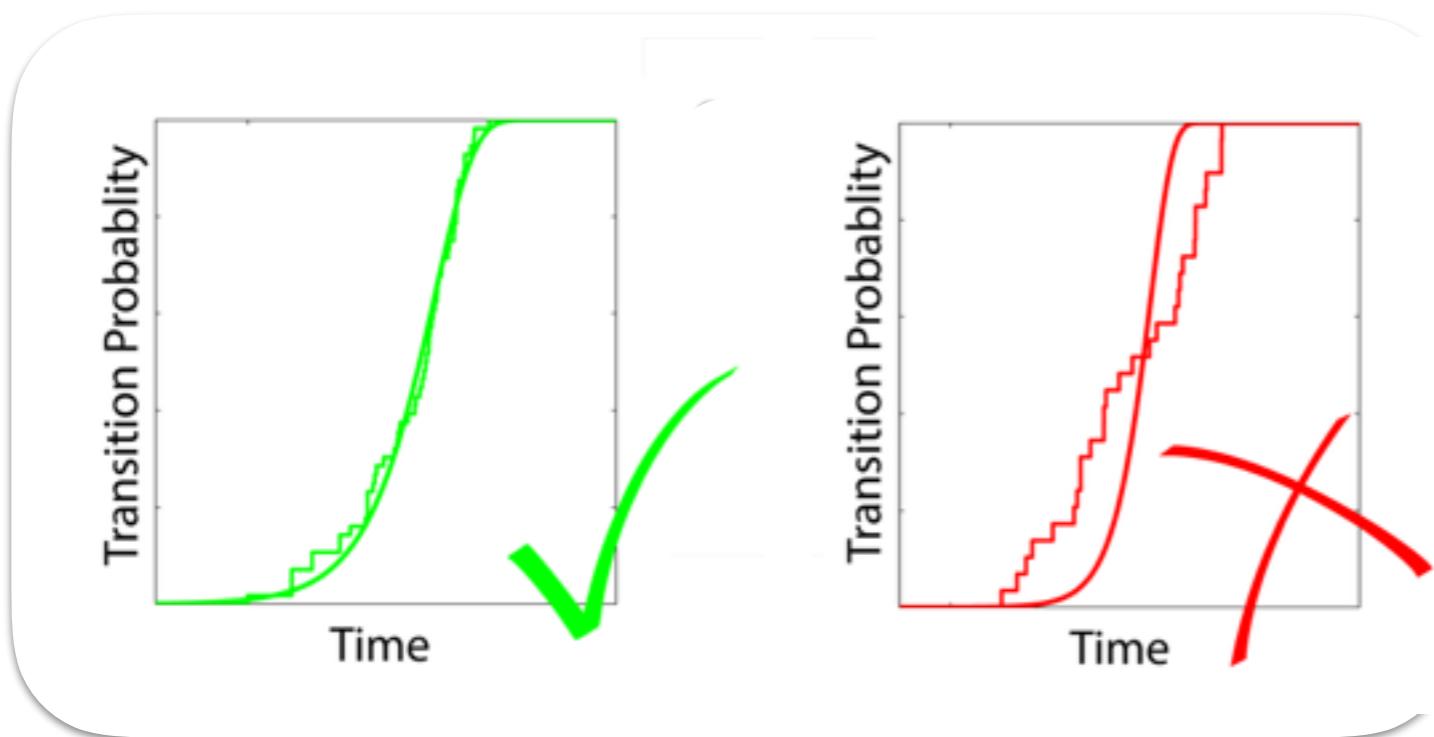
$$\frac{k_{A \rightarrow B}^*}{k_{A \rightarrow B}} = \frac{Z_A}{Z_A^*} \frac{\kappa^* Z_{TS}^*}{\kappa Z_{TS}}$$

$$\boxed{\frac{k_{A \rightarrow B}^*}{k_{A \rightarrow B}} = \frac{Z_A}{Z_A^*} = \langle e^{\beta V_b} \rangle}$$

# How to check that the TS is not affected by bias deposition?



- The **transition** between basins A and B is a **rare event**.
- The **escape** from a metastable state can be interpreted as a **Poisson process**.
- The **survival probability** is **exponentially distributed**.
- This **feature** has to be **preserved** in the calculation of the transition times distribution from **biased simulations**



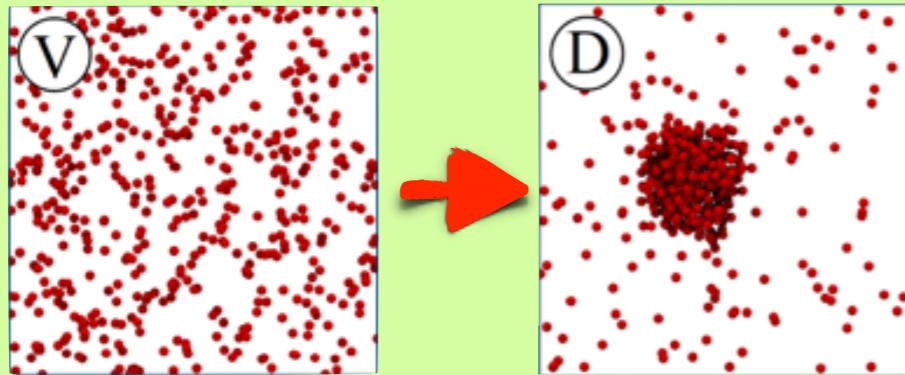
measuring the **compatibility** of the transition probability **with** that of a **Poisson process reveals** the **corruption** of the transition state

# Estimating nucleation timescales

I Setup initial conditions:  $T, S, V$

liquid argon from supersaturated vapour

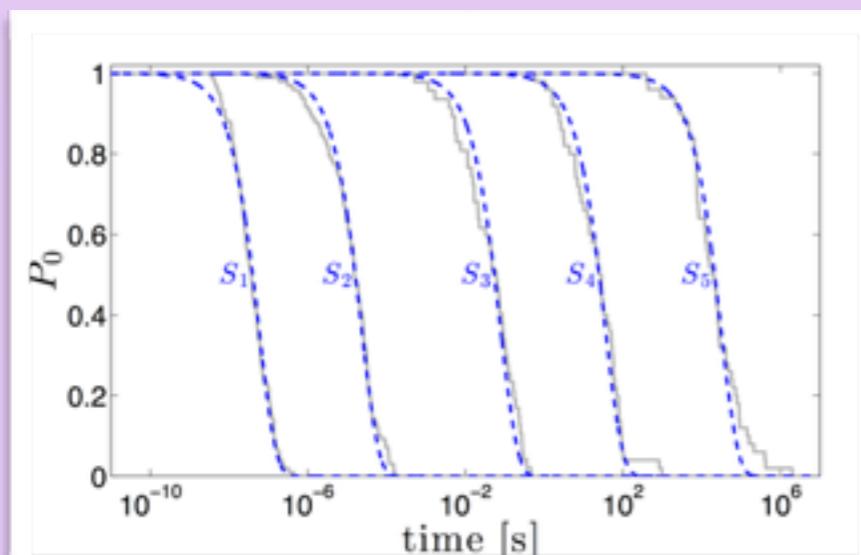
Run a series of WTmetaD simulations



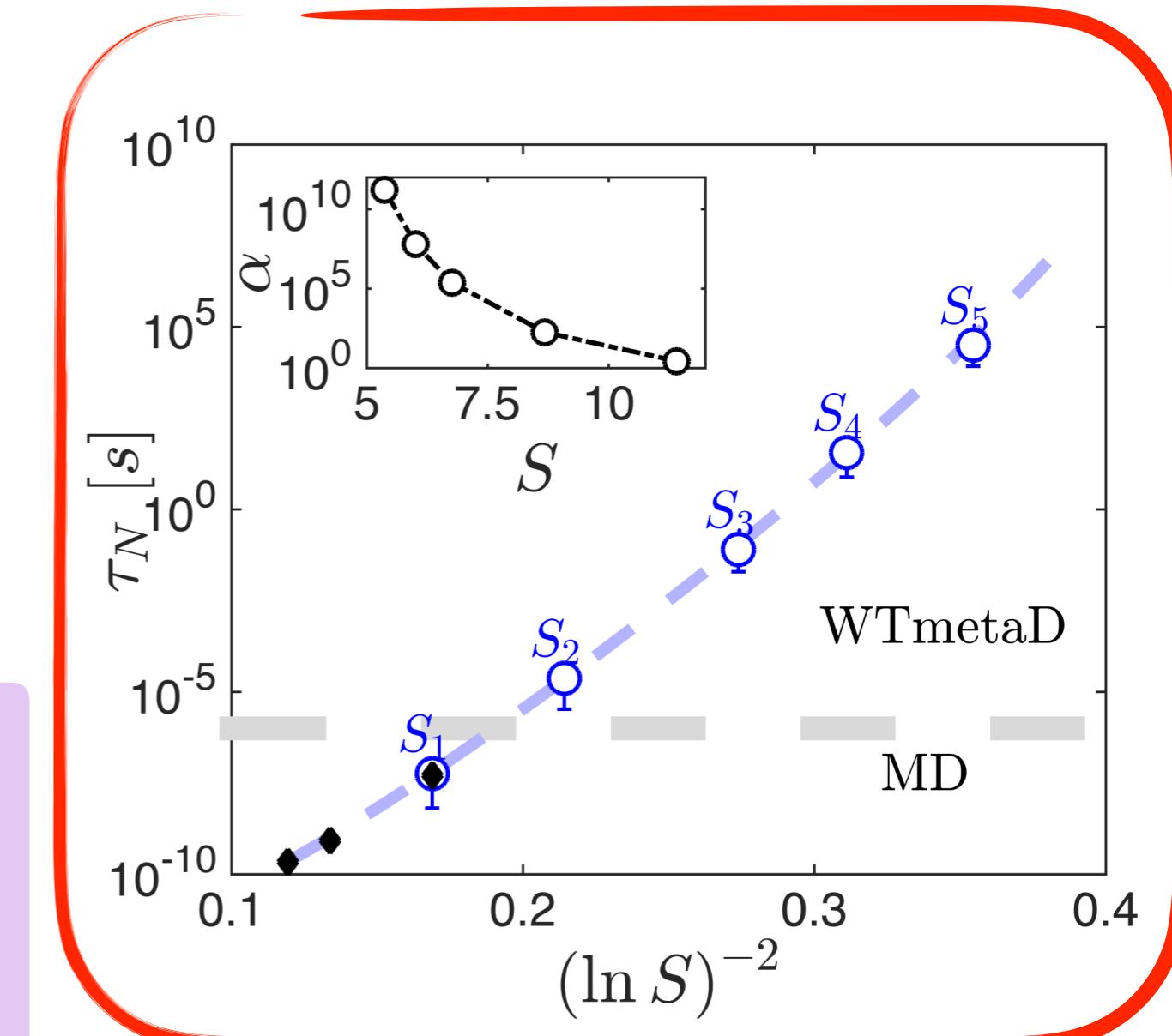
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each simulation provides one realisation of the transition time

Build survival probability distributions and compute the average nucleation time in the finite-size system



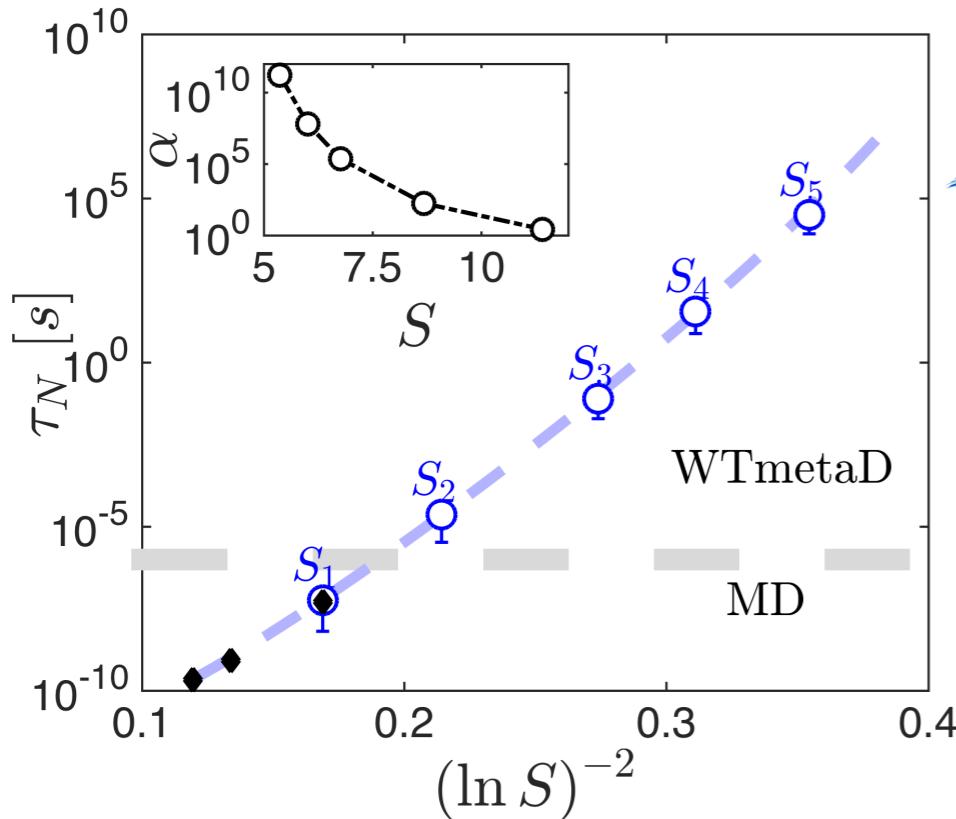
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Timescale



# Correcting for finite size effects

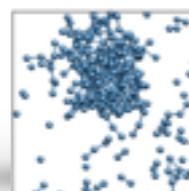


$$J_N = 1/\tau_N V$$

$$\tau_N \propto S^{-1} \exp(\beta \Delta F_N^*)$$

- Free energy barrier in the finite-sized system
- function of  $T, S, V$  and the **surface tension**

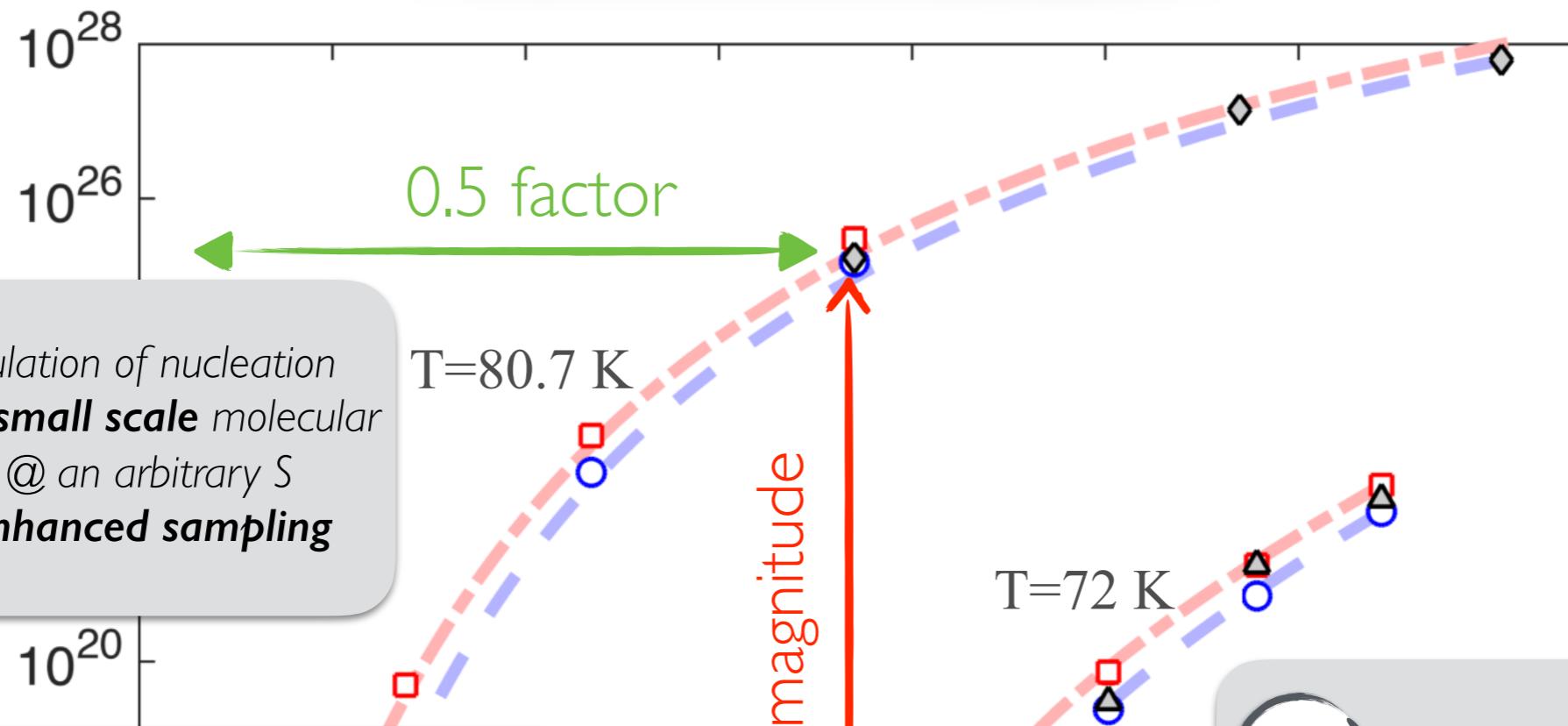
$$J = \phi J_N \simeq J_N \exp(\beta (\Delta F_N^* - \Delta F^*))$$



Finite Size



# take home messages



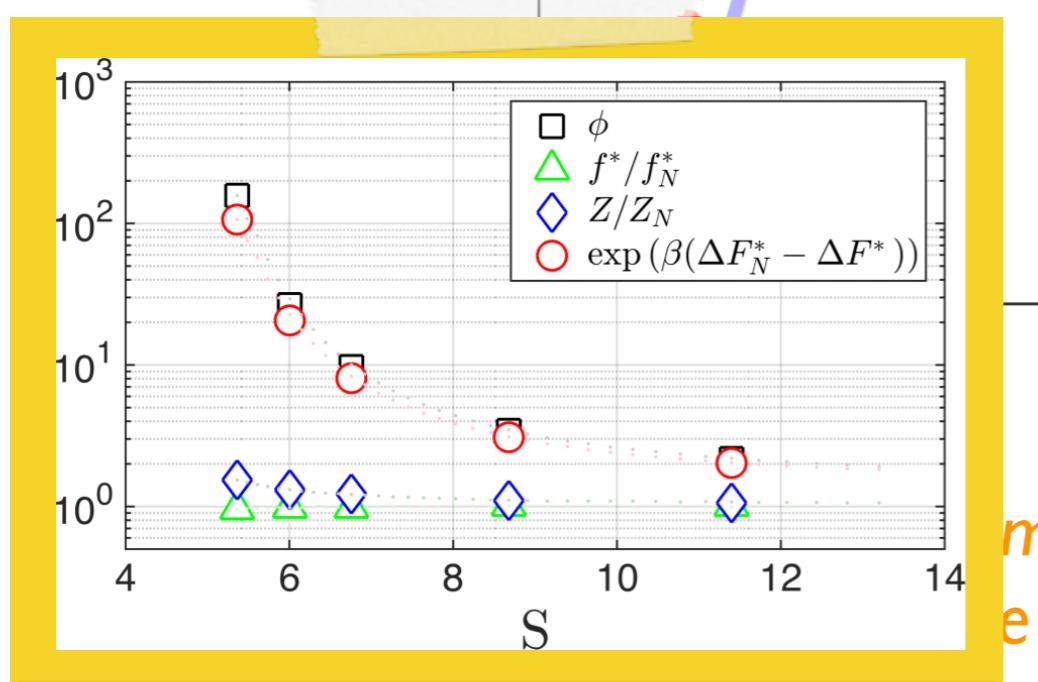
10 orders of magnitude

T=72 K

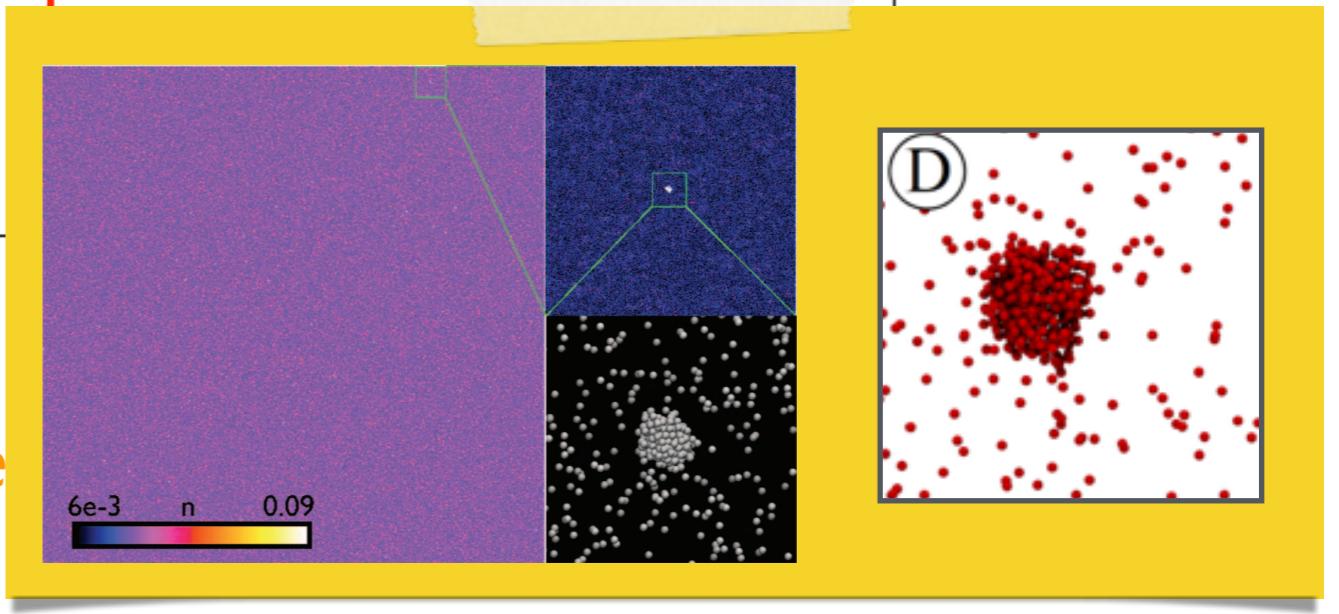
$J_N$  WTmetaD

**3**

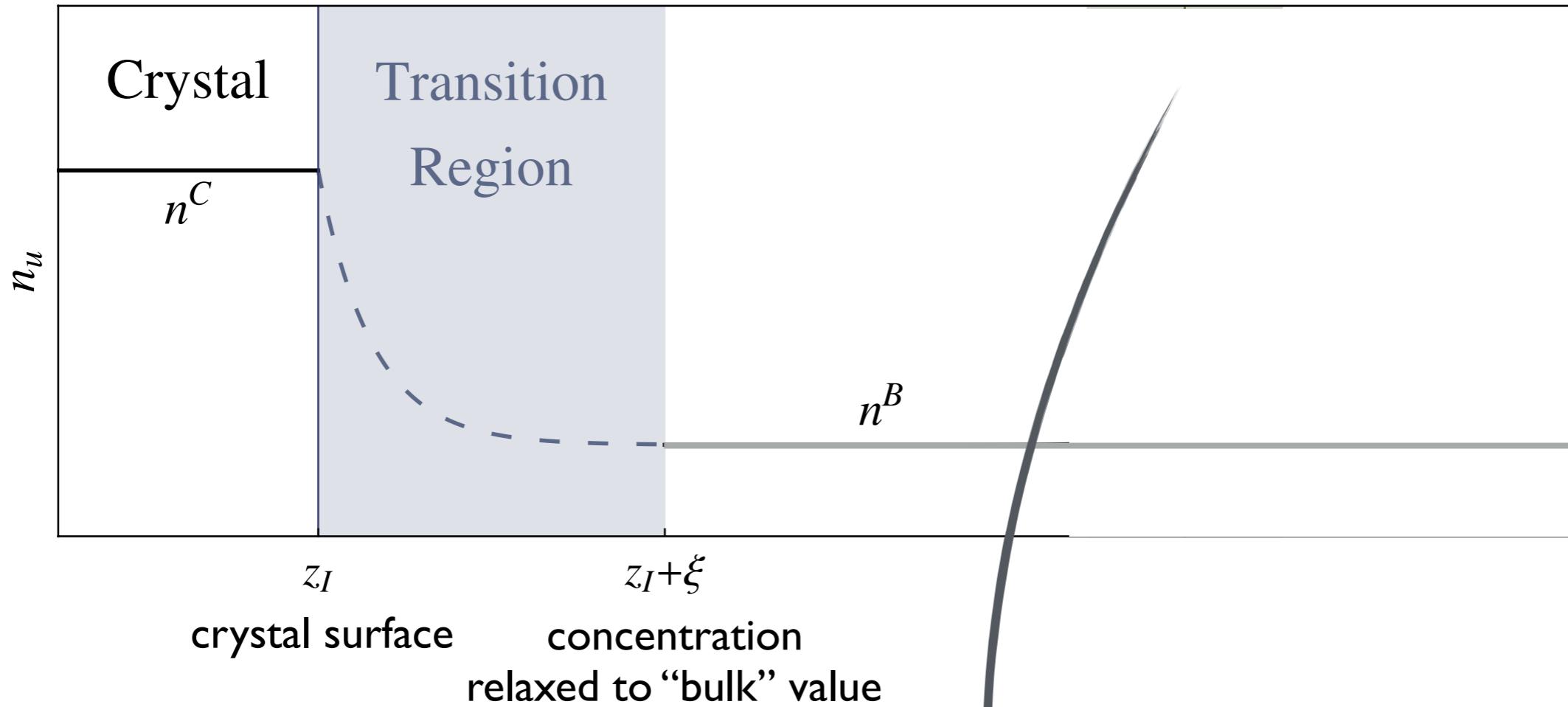
Nucleation rates can be computed with ordinary computational **resources\***



magnitude  
size effects



# C $\mu$ MD: a plumed-based workaround



$$F_i^\mu(z) = k_i(n_i^{\text{CR}} - n_{0i})G(z, Z_F)$$

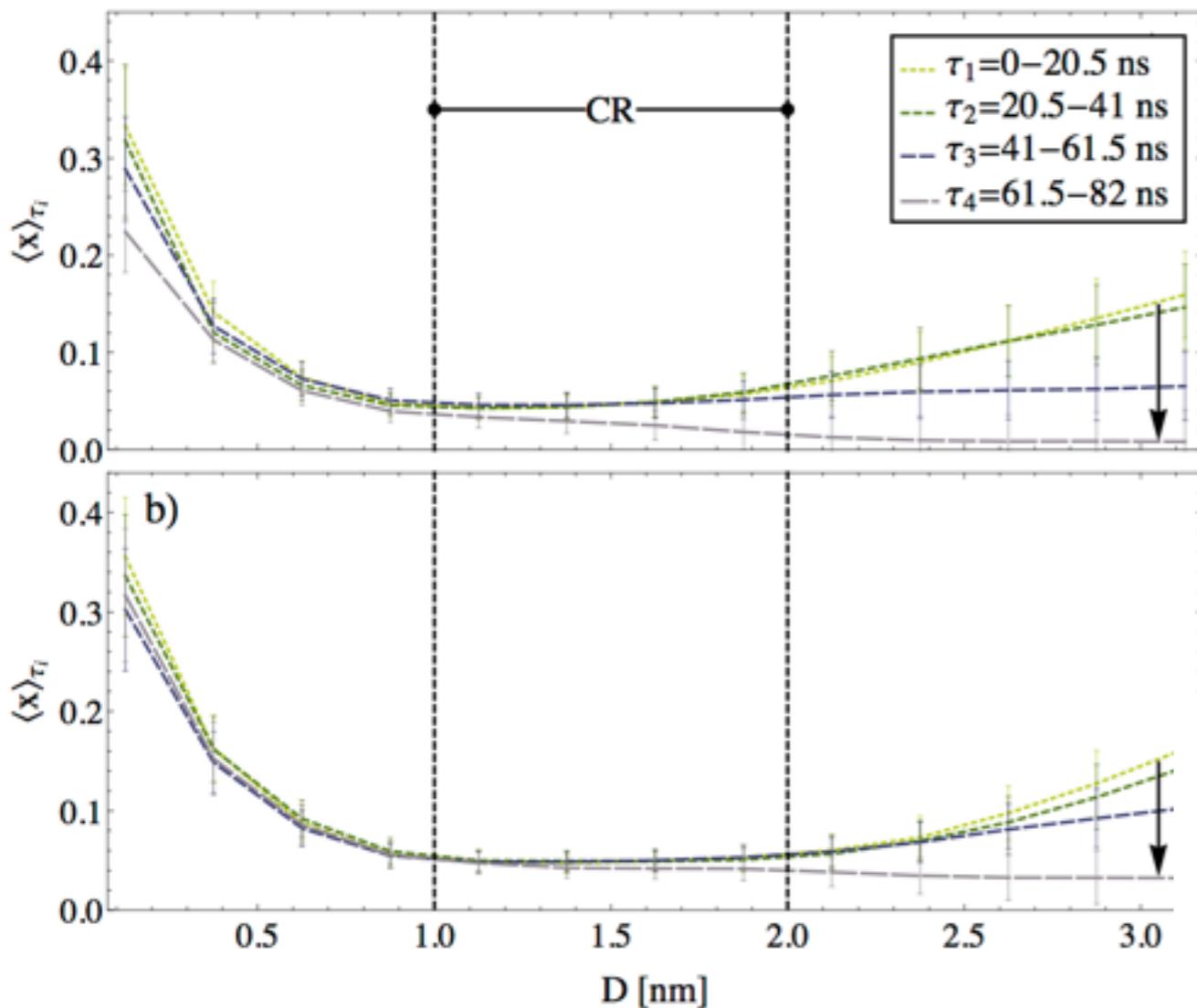
$$n_i^{\text{CR}} = \frac{1}{\mathcal{V}^{\text{CR}}} \sum_{j=1}^{N_i} \theta(z_j),$$

$$\theta(z_j) = \begin{cases} 1 & \text{if } z_j \in \text{CR} \\ 0 & \text{otherwise} \end{cases}$$

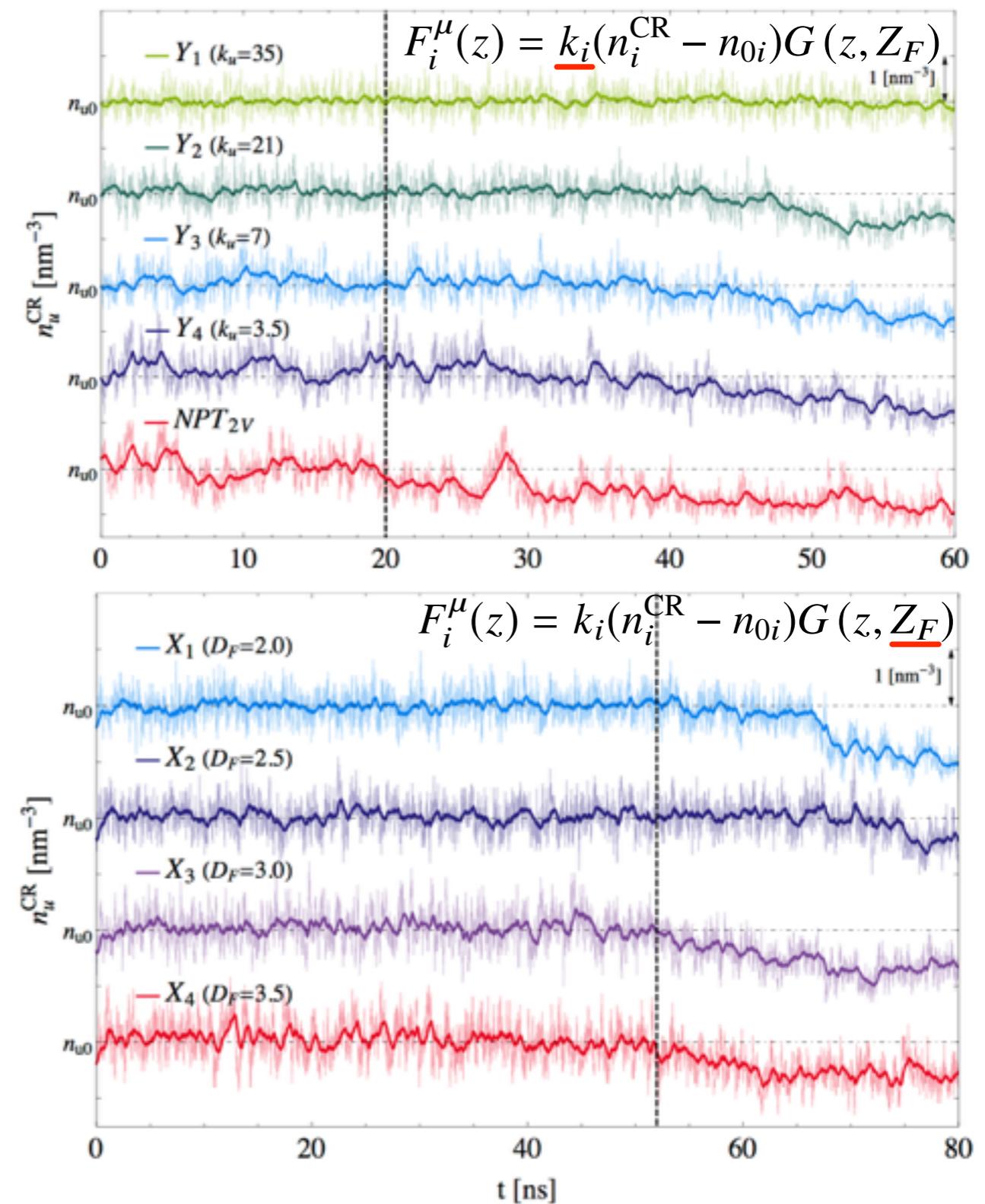
$$G_w(z - Z_F) = \frac{1}{4w} \left[ 1 + \cosh \left( \frac{z - Z_F}{w} \right) \right]^{-1}$$

# C $\mu$ MD: does it work?

is the concentration within the control region stationary?

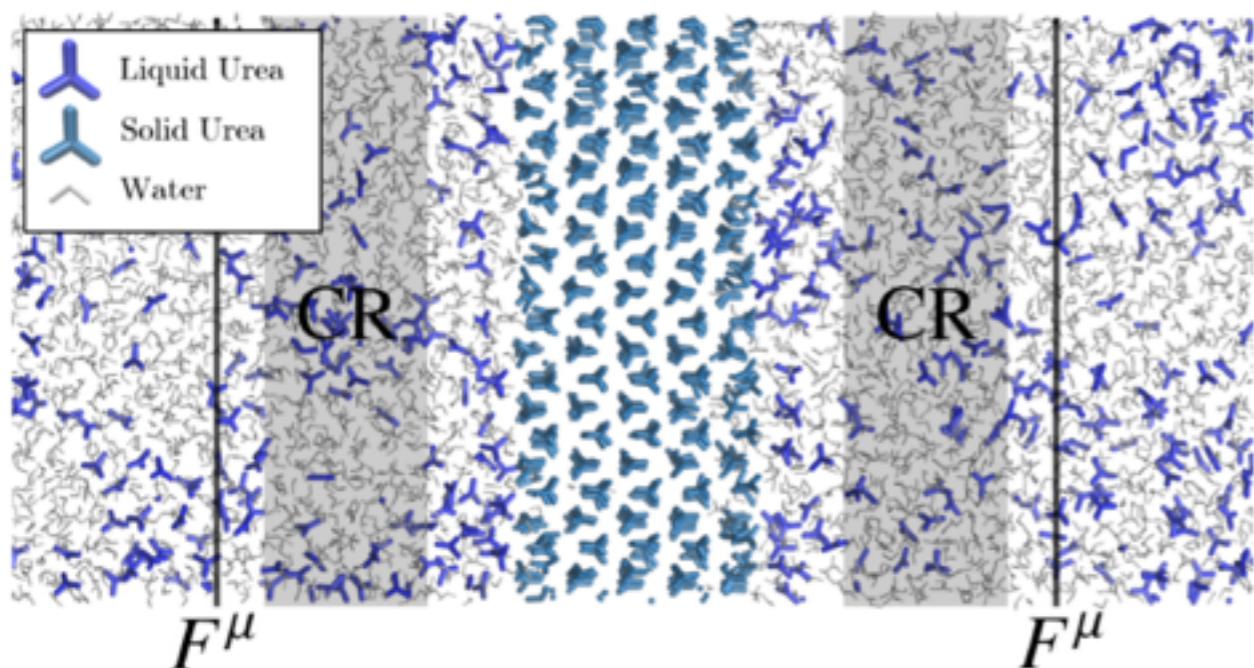


how does the concentration in the CR depends on  $F^\mu$  parameters?

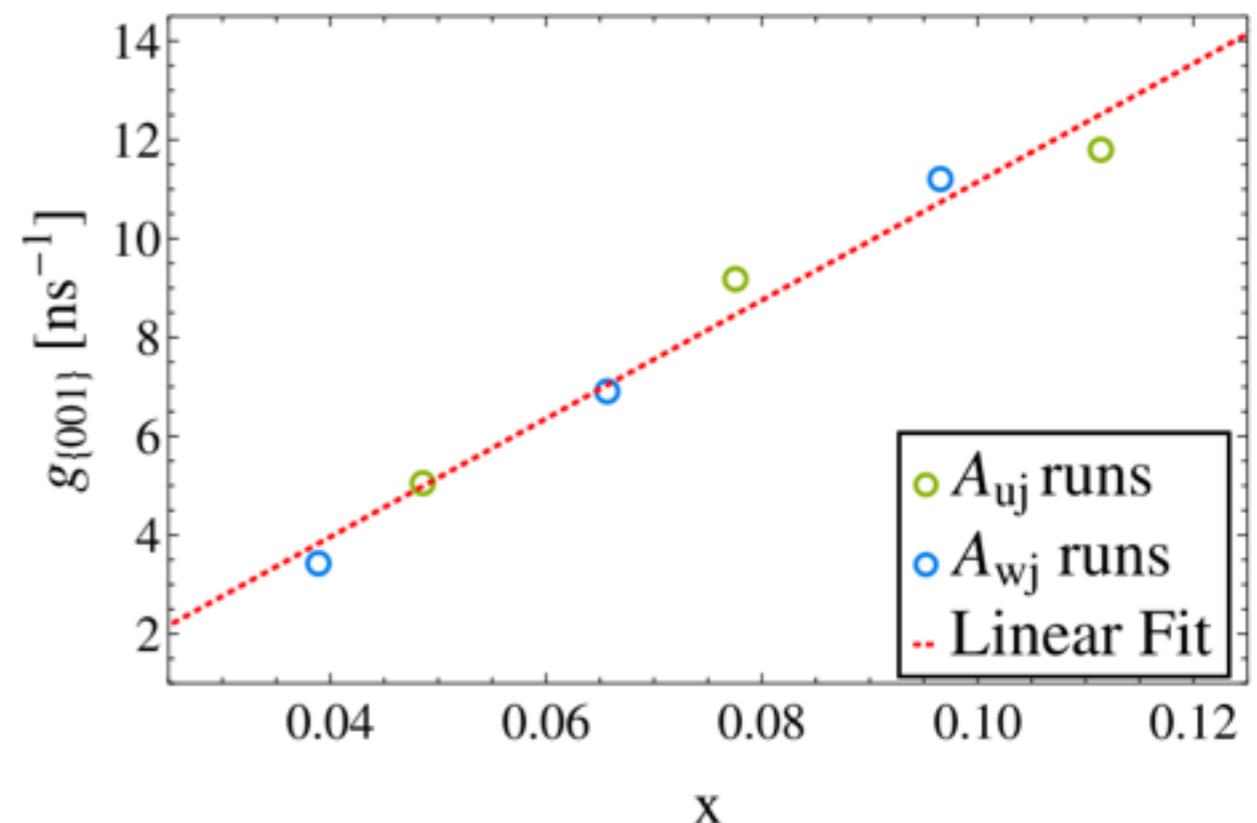
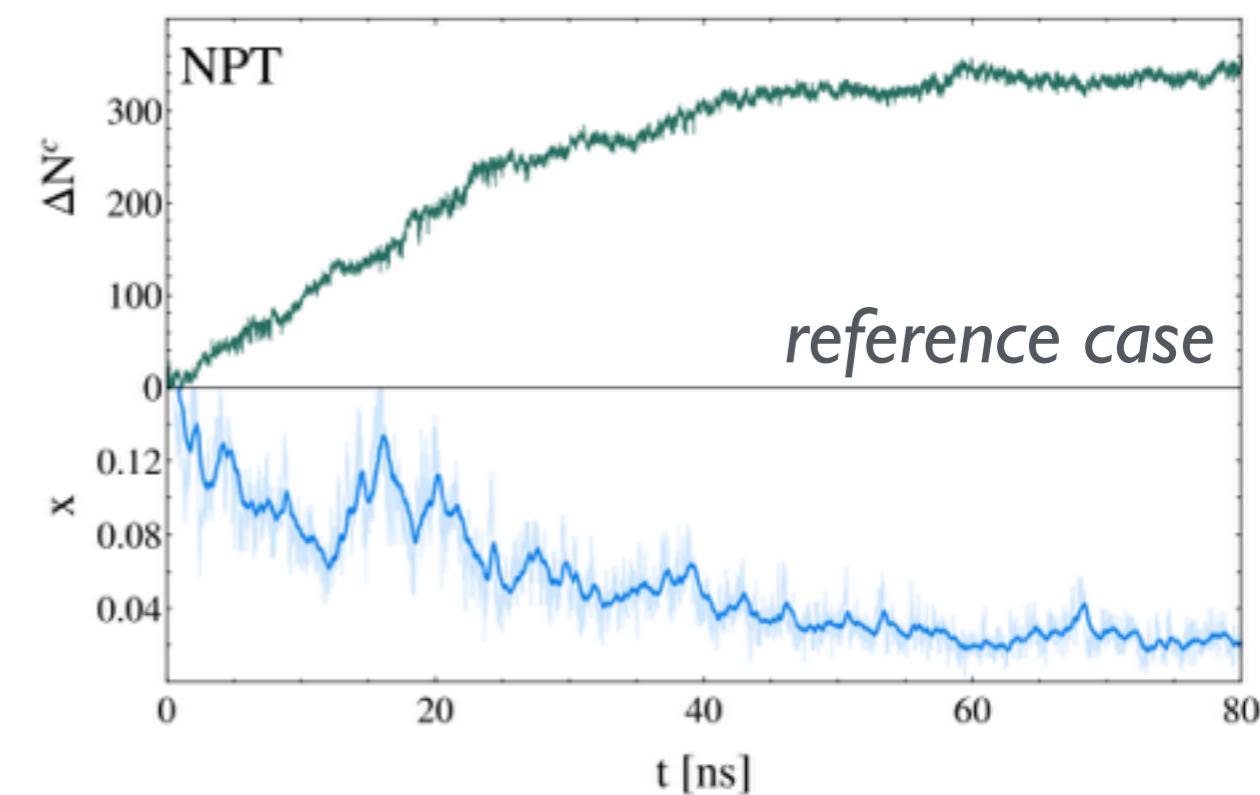
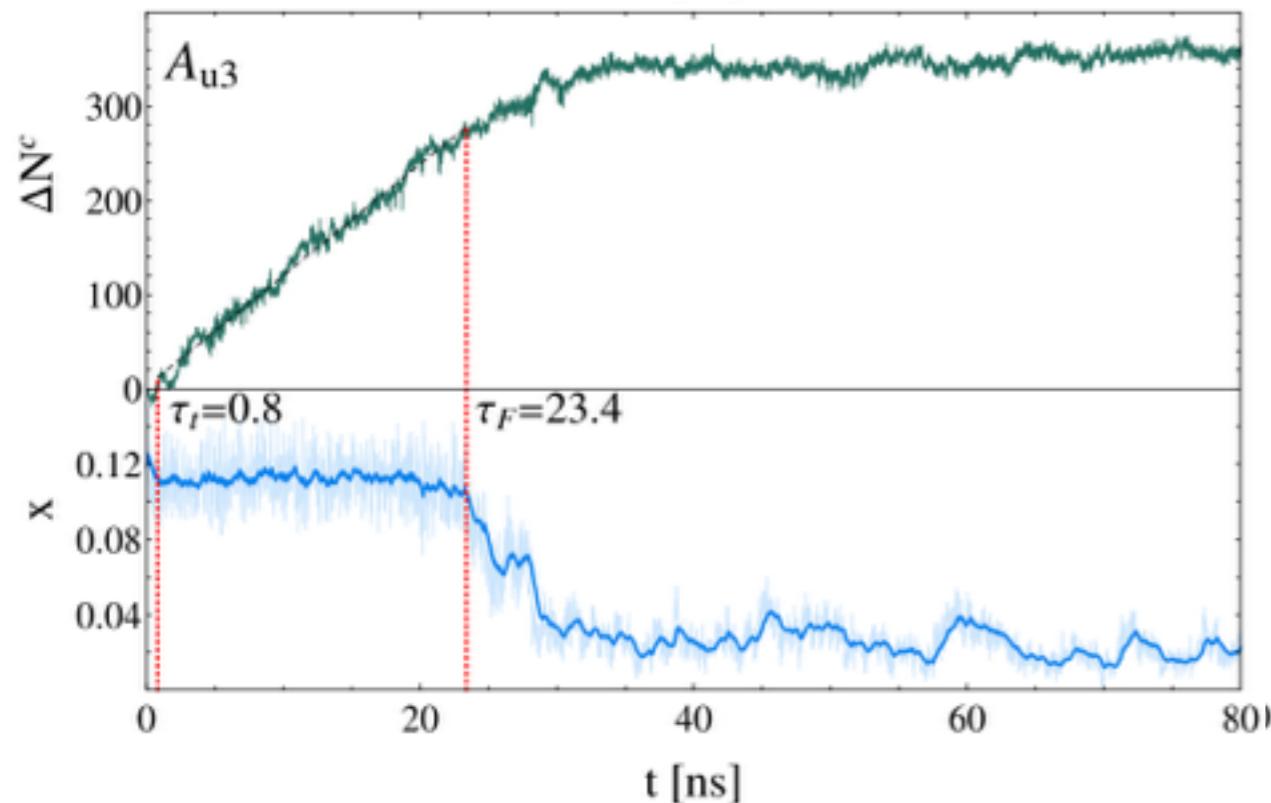


# C $\mu$ MD: does it work?

{001} urea crystal face

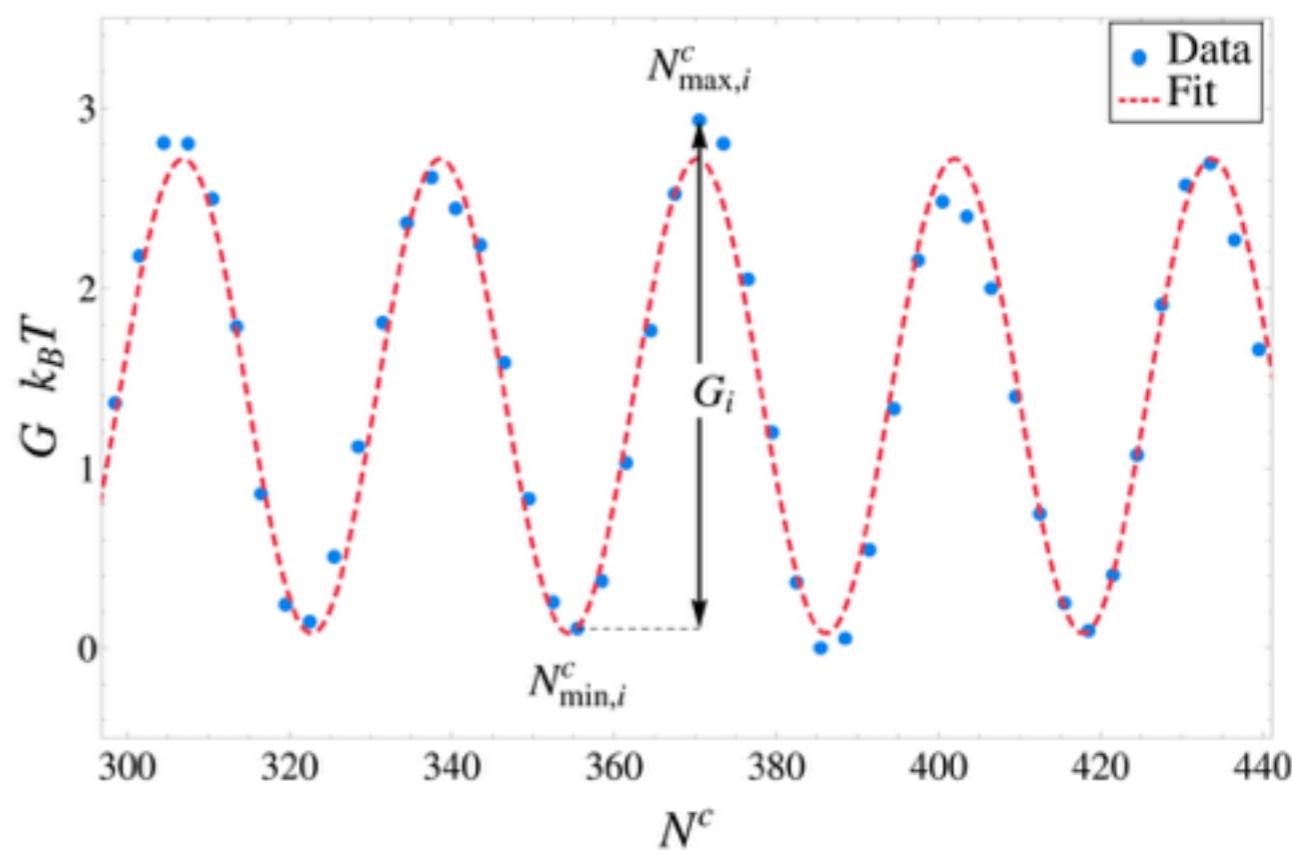
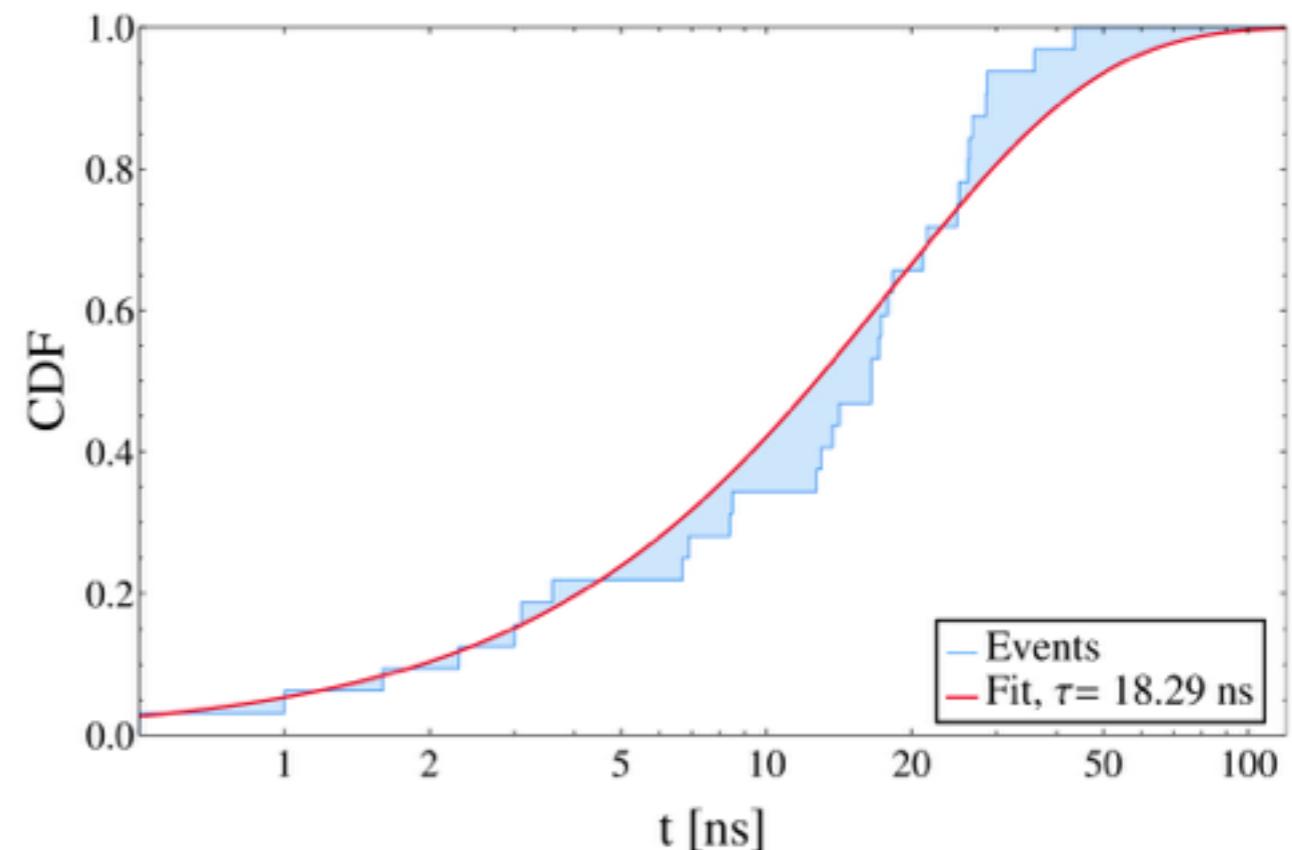
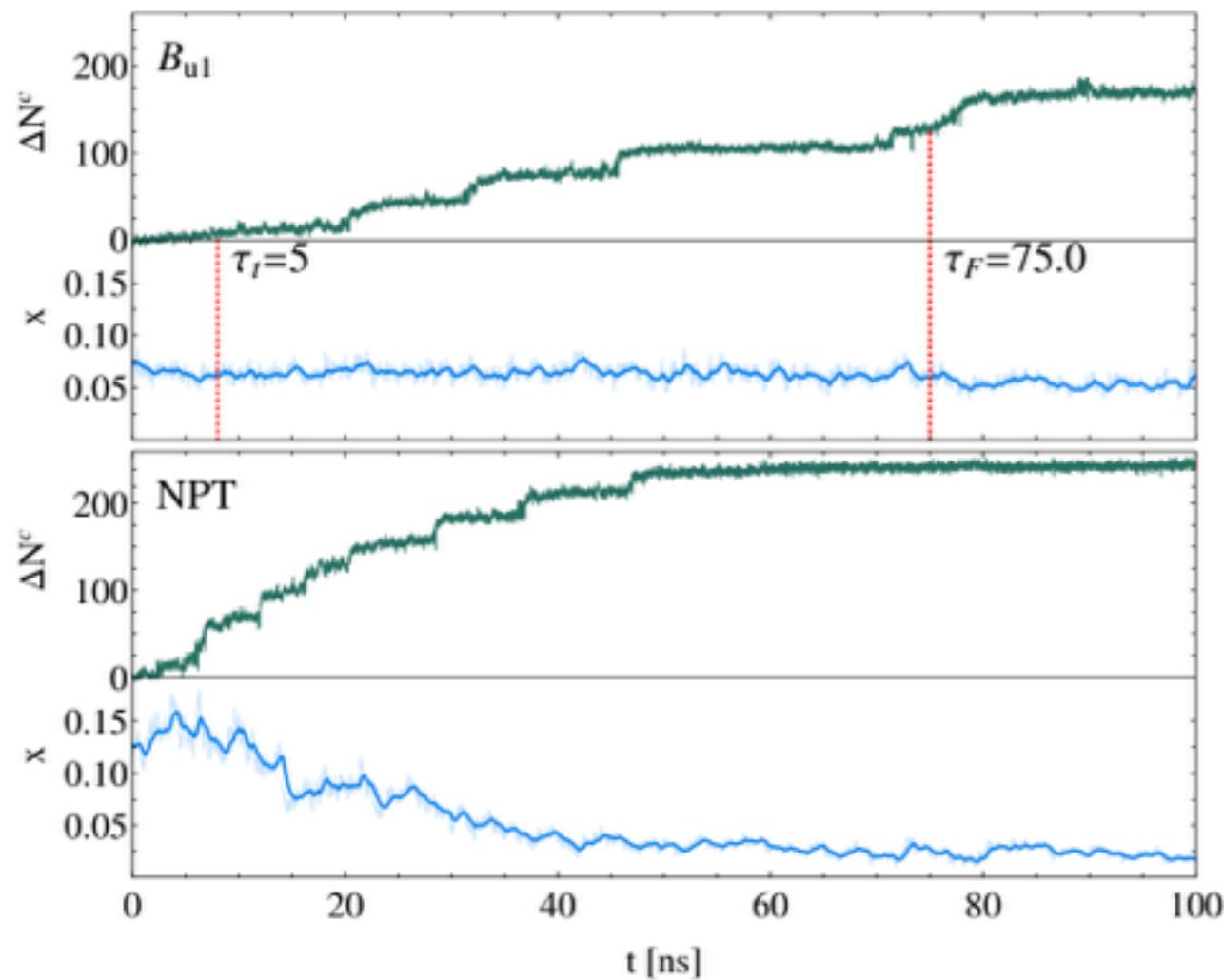


C $\mu$ MD



# C $\mu$ MD: does it work?

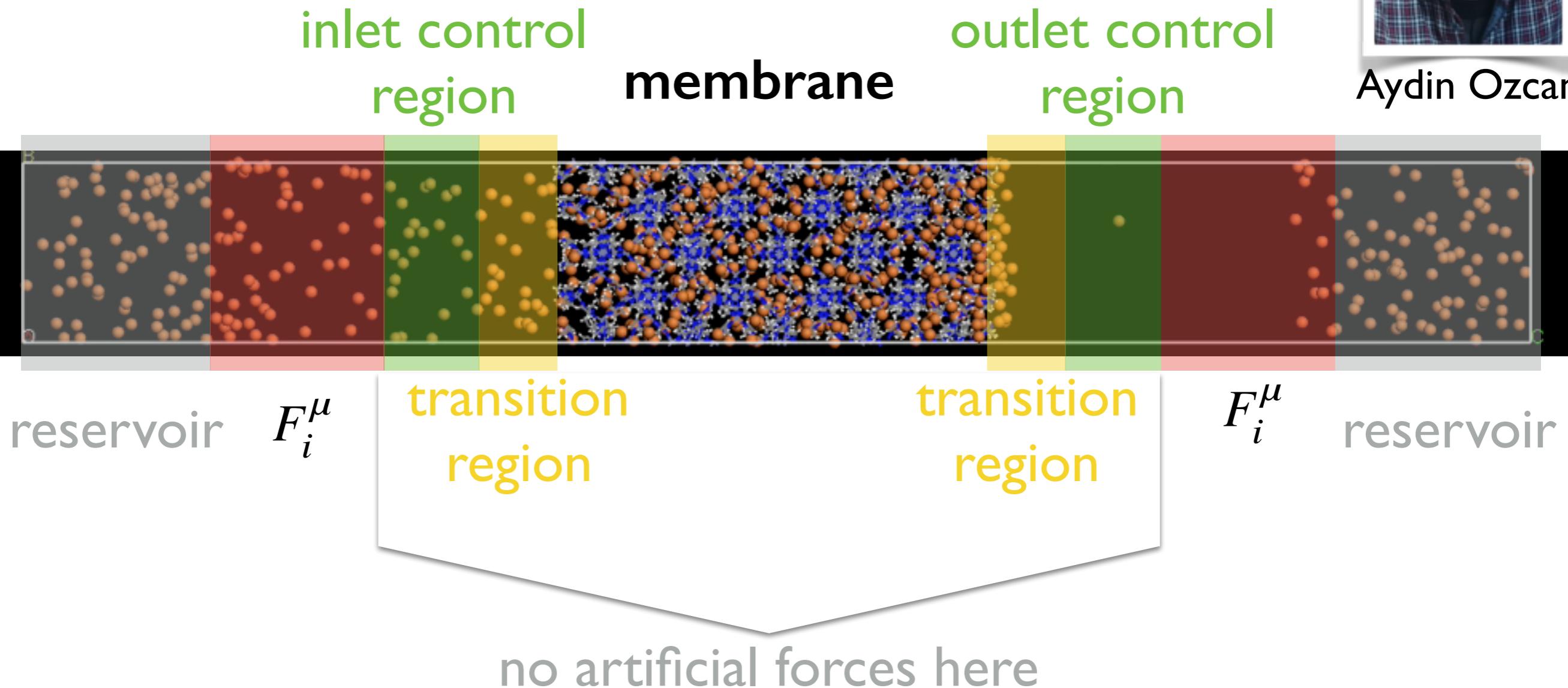
{110} urea crystal face



# Simulating a steady state diffusive flux



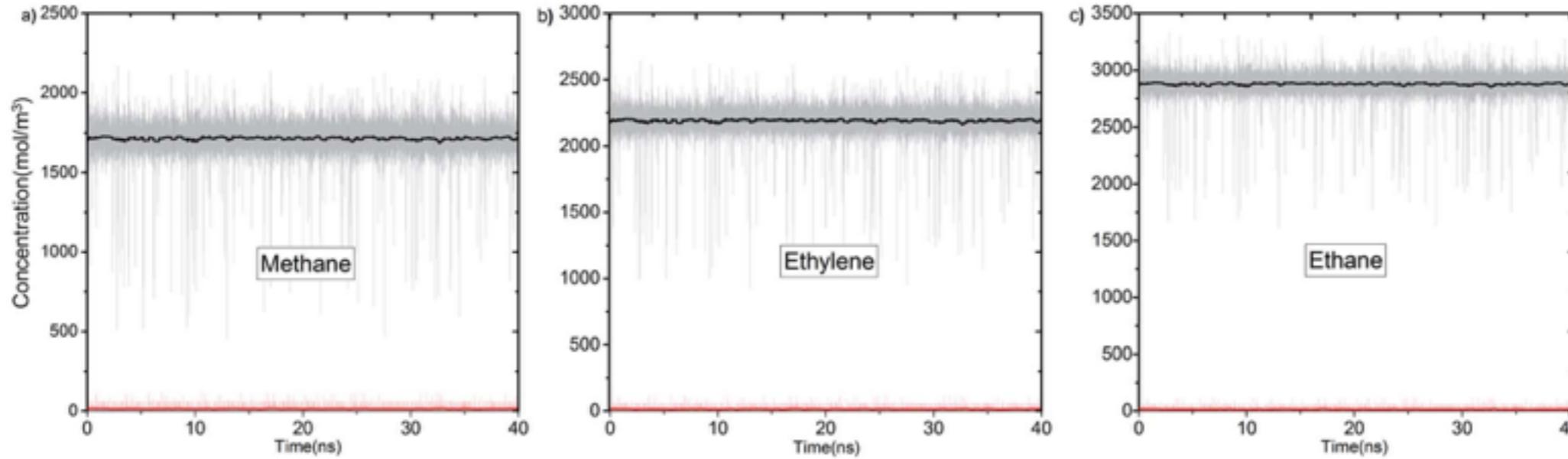
Aydin Ozcan



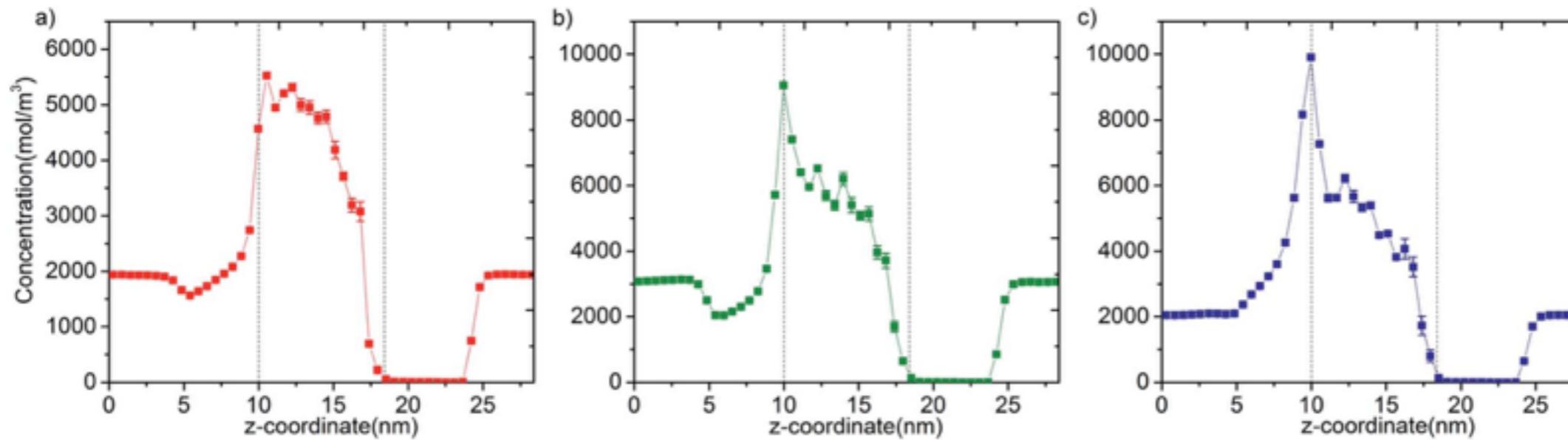
Simulations performed for Methane, Ethane, Ethylene, and Ethylene/Ethane mixtures

# Diffusion in a MOF (ZIF-8) membrane: key outcomes I

## I. inlet/outlet concentration is reliably controlled



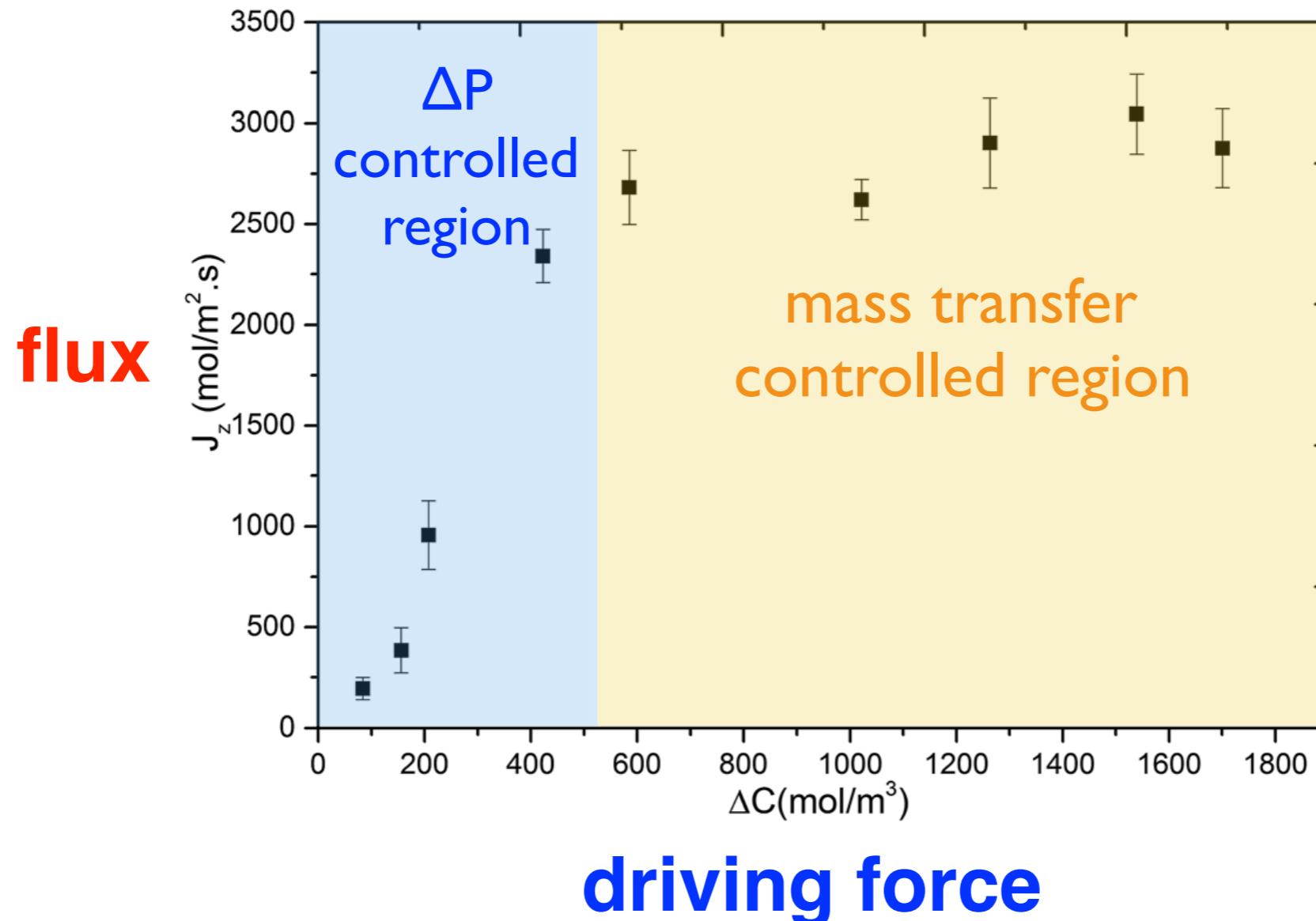
## 2. a steady-state concentration profile is achieved within the unbiased region



## 3. multicomponent permeation under constant driving force can be simulated

# Diffusion in a MOF (ZIF-8) membrane: key outcomes II

4. Behaviour coherent with experiments is recovered:



5. Ethylene/Ethane selectivity from multicomponent simulation:  
2 (comp.) vs. 2.6 (exp.)

# this talk:

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# Acknowledgements



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## papers

- M Salvalaglio, P Tiwary, GM Maggioni, M Mazzotti, M Parrinello, JC P 145 (21), 211925, 2016
- C Perego, M Salvalaglio, M Parrinello, JCP 142 (14), 144113, 2015
- A Ozcan, C Perego, M Salvalaglio, M Parrinello, O Yazaydin, Chemical Science 8 (5), 3858-3865, 2017

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