Nucleation barrier for complex materials determined by guided molecular dynamics

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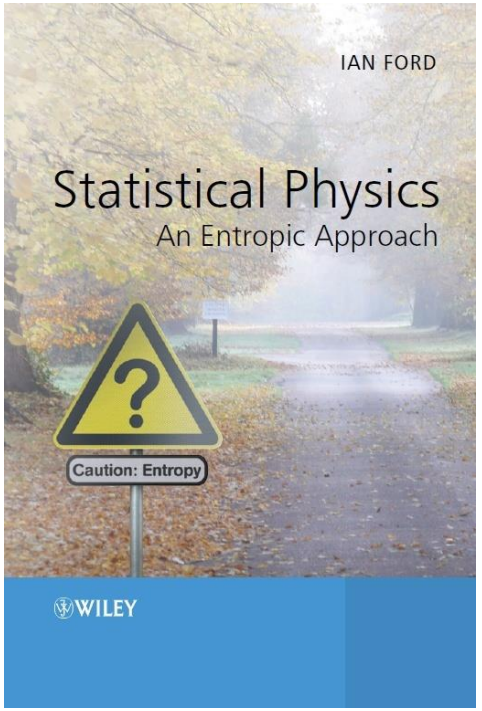
THE MESSAGE

- Challenge of free energy determination for small liquid-like clusters
- Guided molecular dynamics as an alternative to methods based on zero temperature properties
- Nonequilibrium MD version of thermodynamic integration
- Nucleation barriers computable for simple and complex systems

A no-nonsense approach

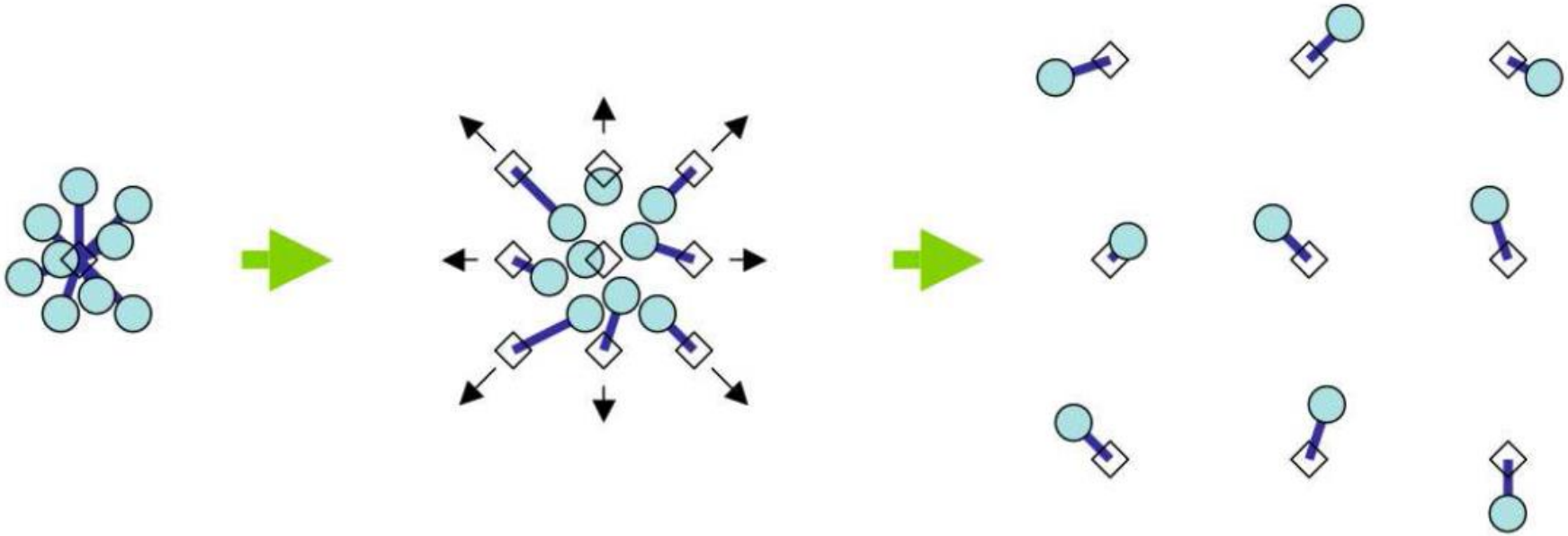
- free energy change = **isothermal quasistatic external work**
- So tear the clusters apart using mechanical forces!



advertising alert!

Quasistatic in molecular dynamics?

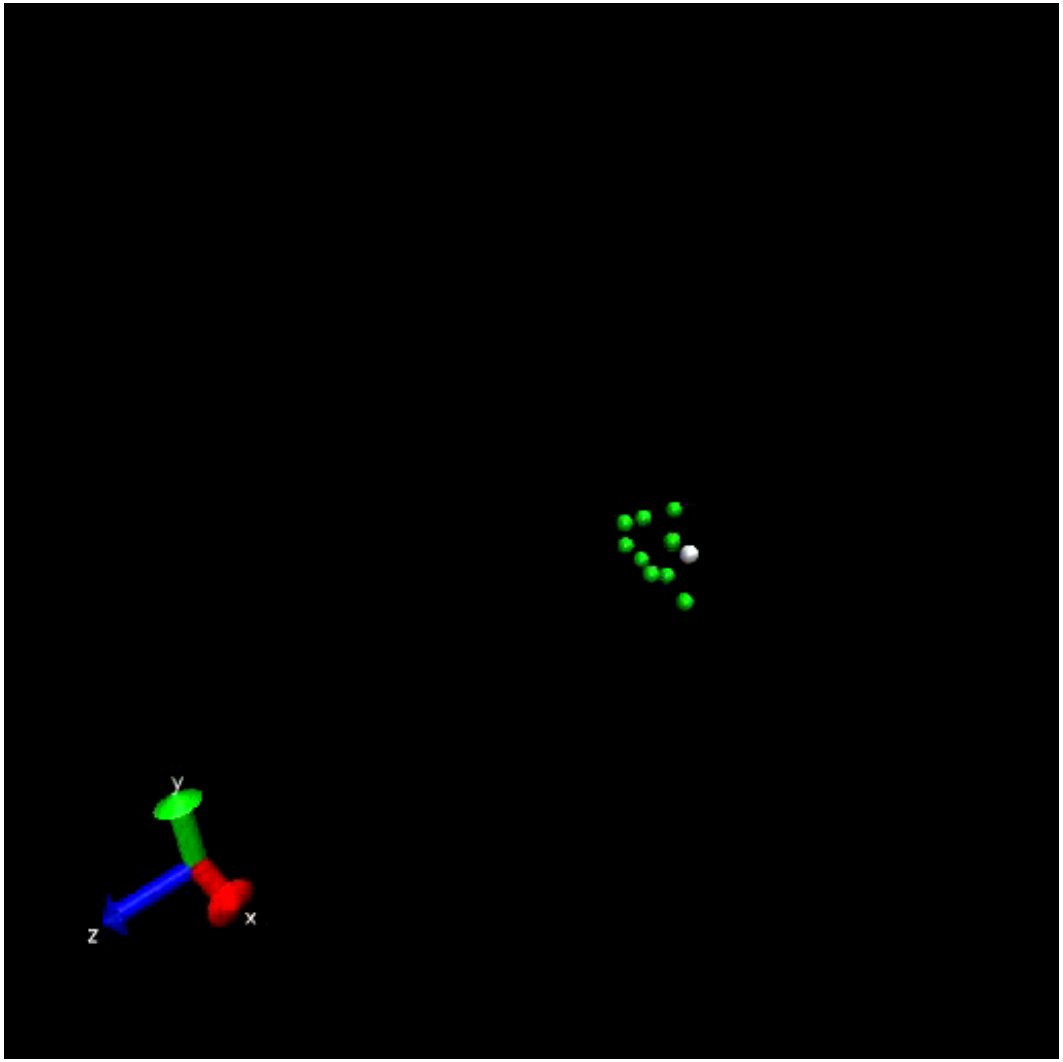
‘Guide particles’ pull cluster apart nonquasistatically



Jarzynski equality emulates quasistatic conditions

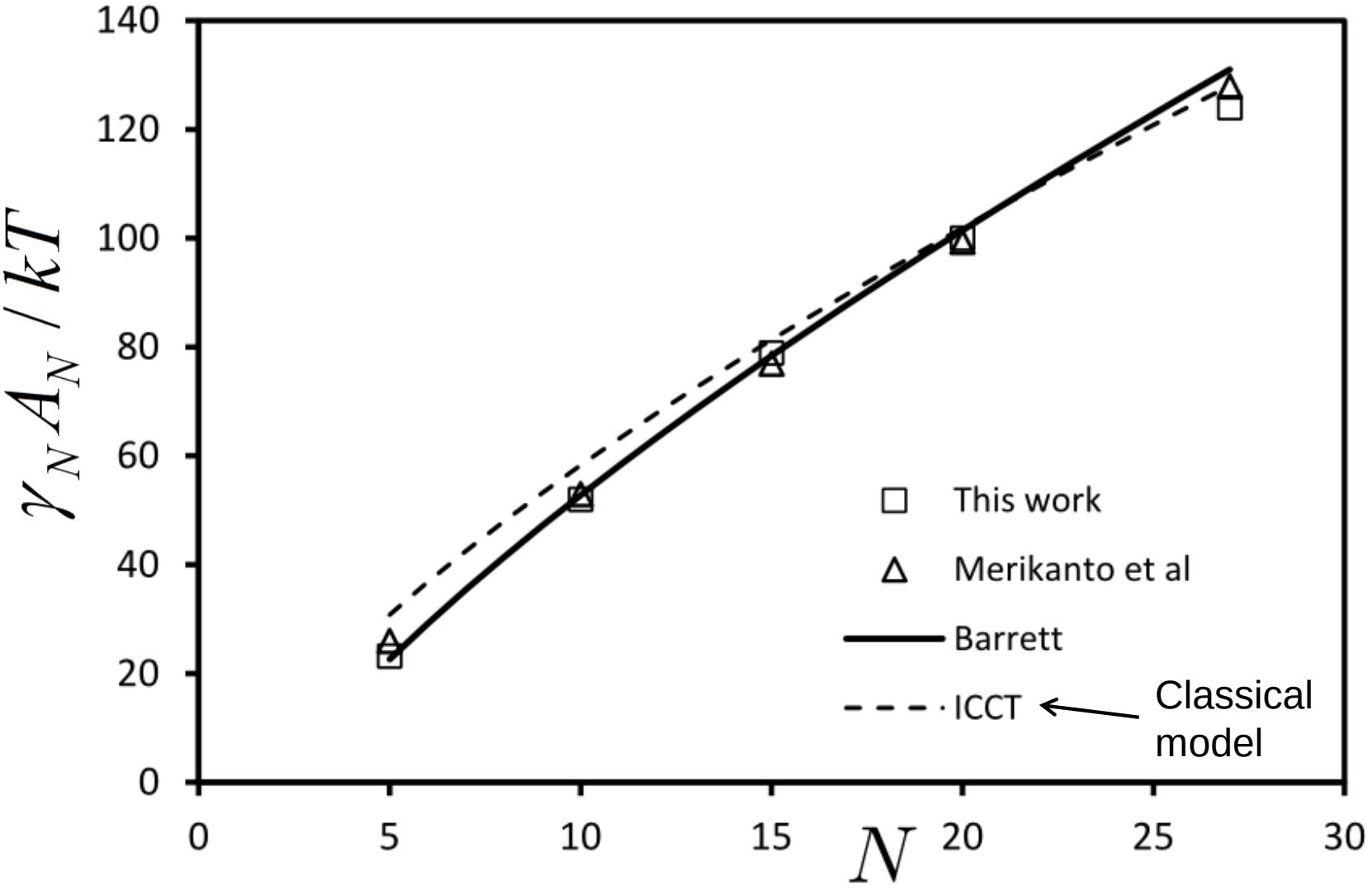
$$\exp(-\Delta F / kT) = \left\langle \exp(-\Delta W / kT) \right\rangle$$

10-atom argon cluster disassembly Tang+Ford 2015

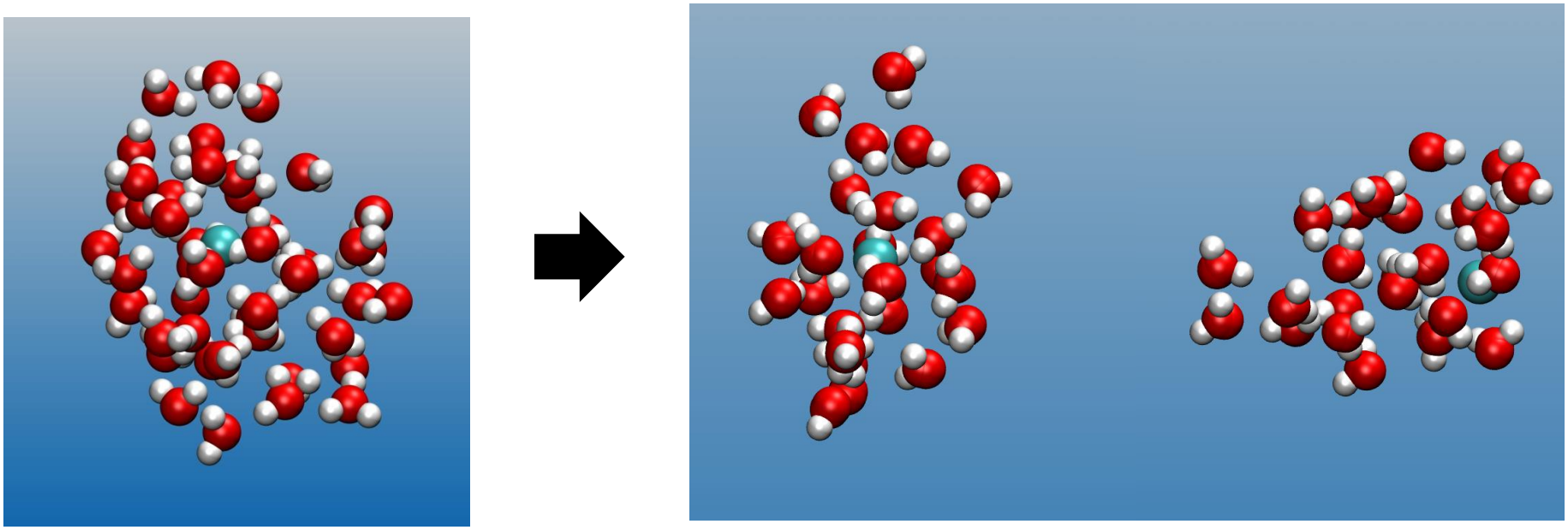


60 K

Excess free energy $F_s \equiv \gamma_N A_N$ of argon clusters

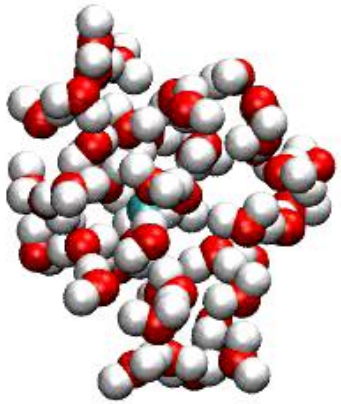


Guided mitosis is even better



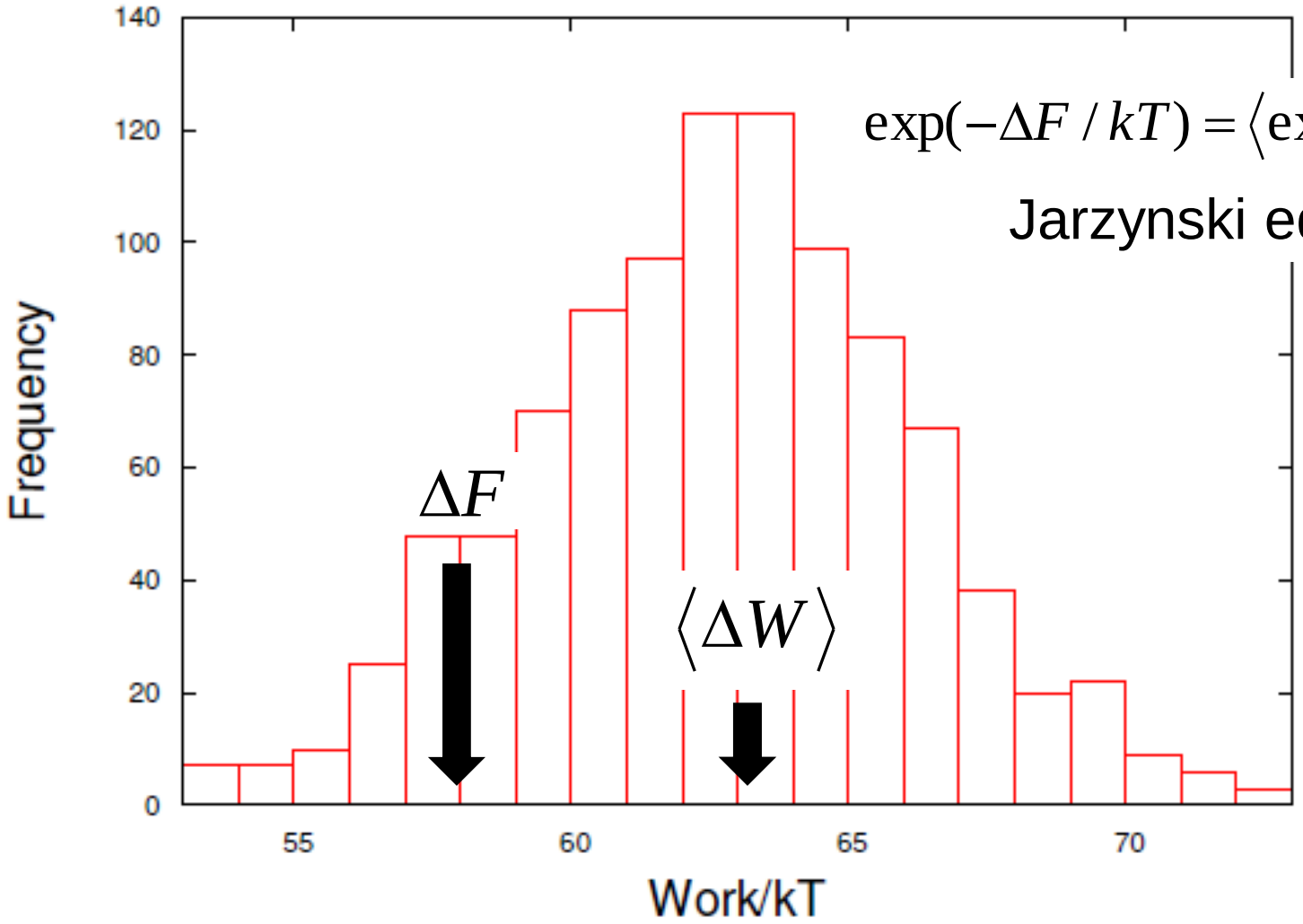
Water described by TIP4P/2005 classical force field

Mitosis of TIP4P/2005 water cluster



$$\Delta F = 2\gamma_{N/2}A_{N/2} - \gamma_N A_N + \text{tethering corrections}$$

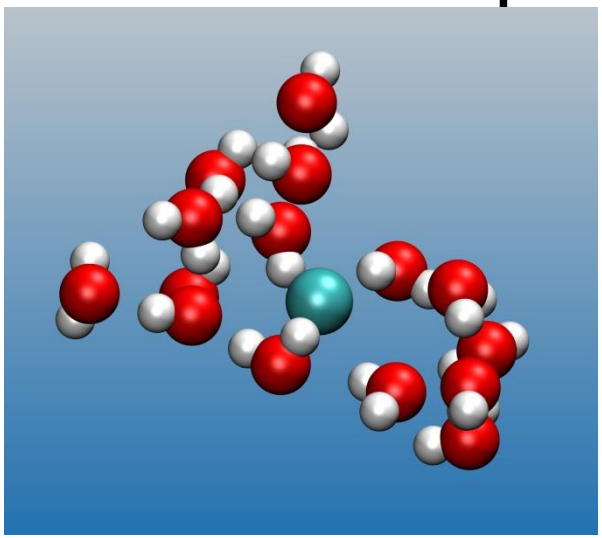
Mitosis work distribution: TIP4P/2005 force field, one 48-cluster split into two 24-clusters

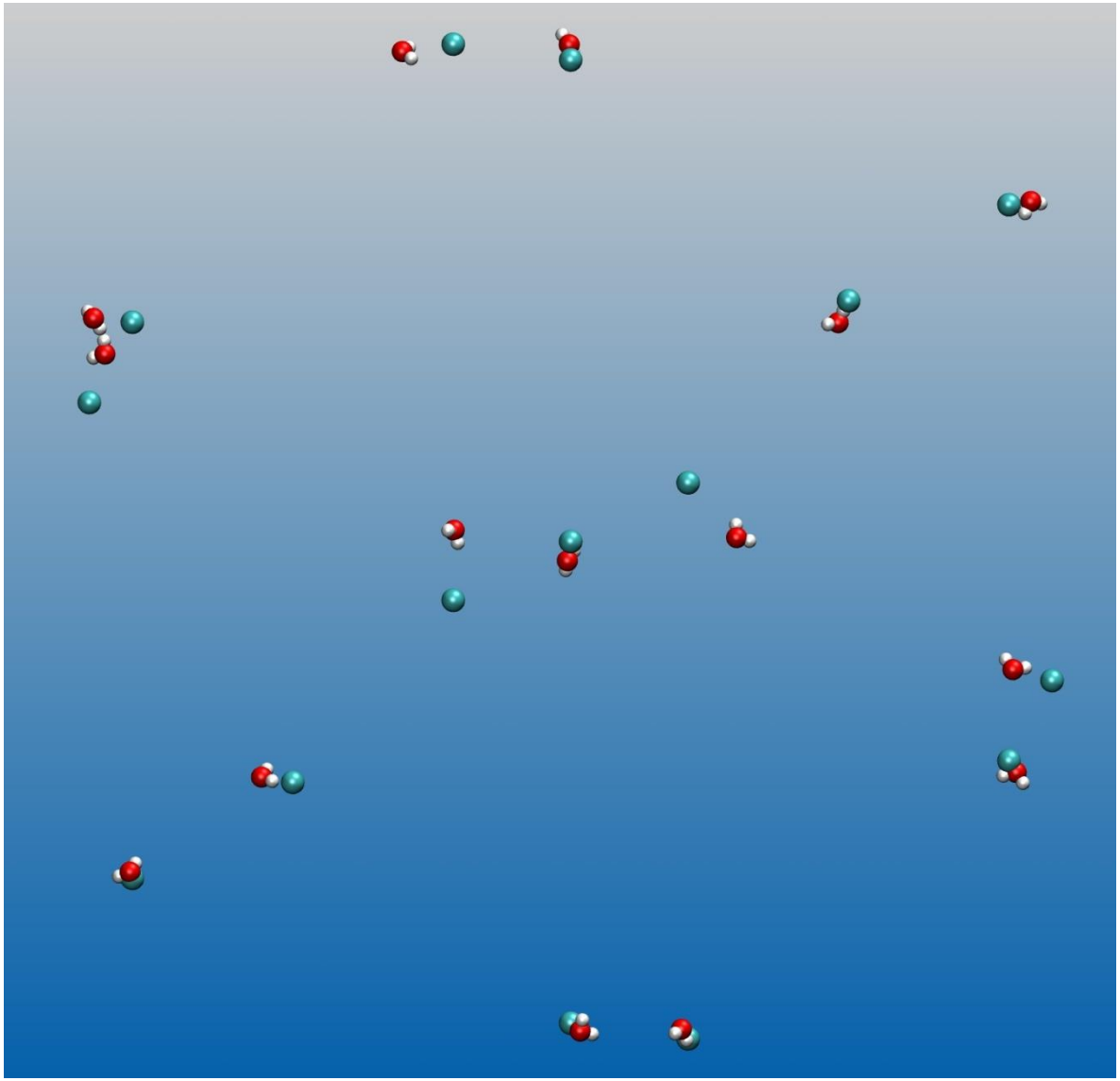


$$\exp(-\Delta F / kT) = \langle \exp(-\Delta W / kT) \rangle$$

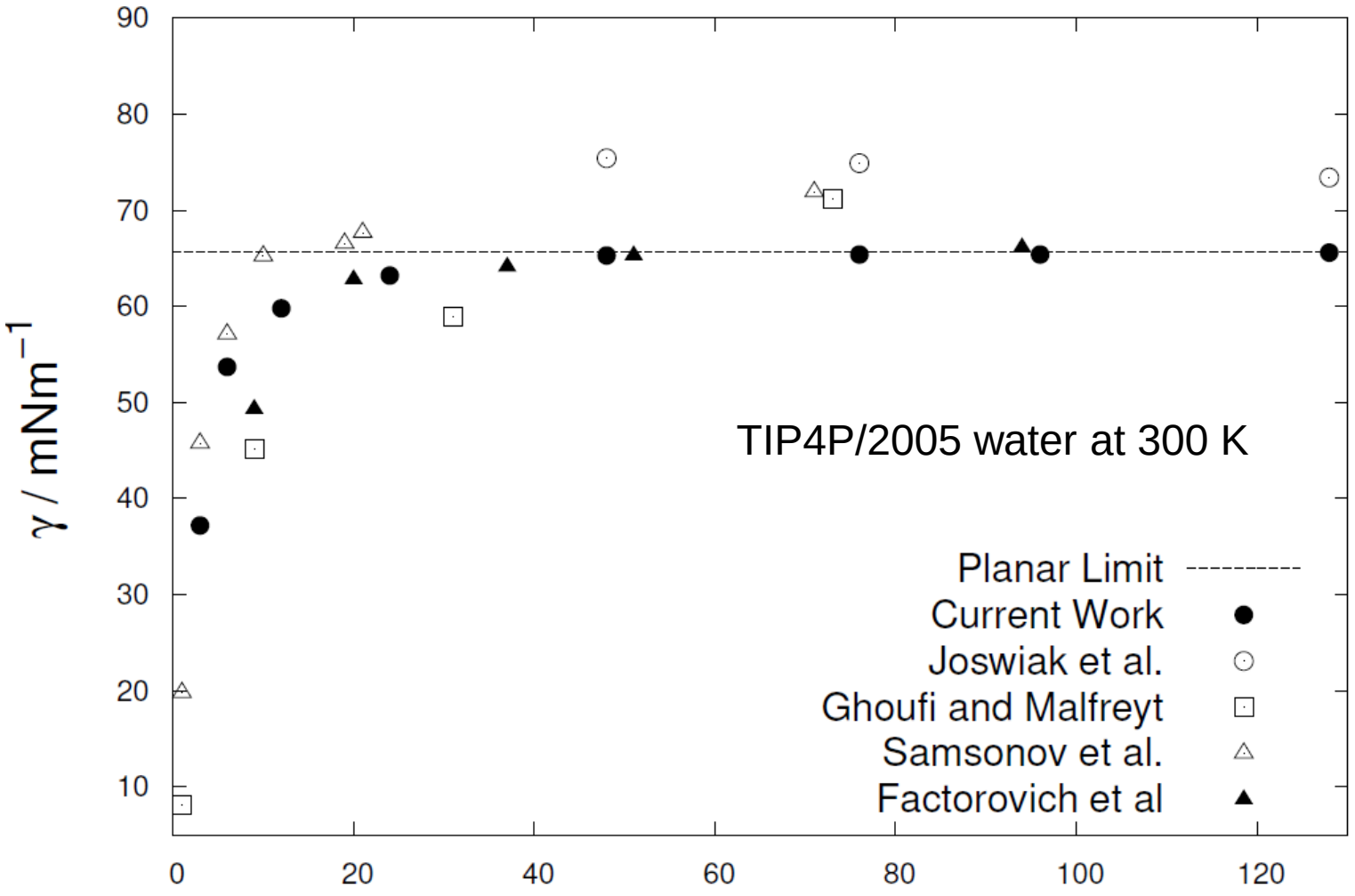
Jarzynski equality

Complete disassembly of a water cluster





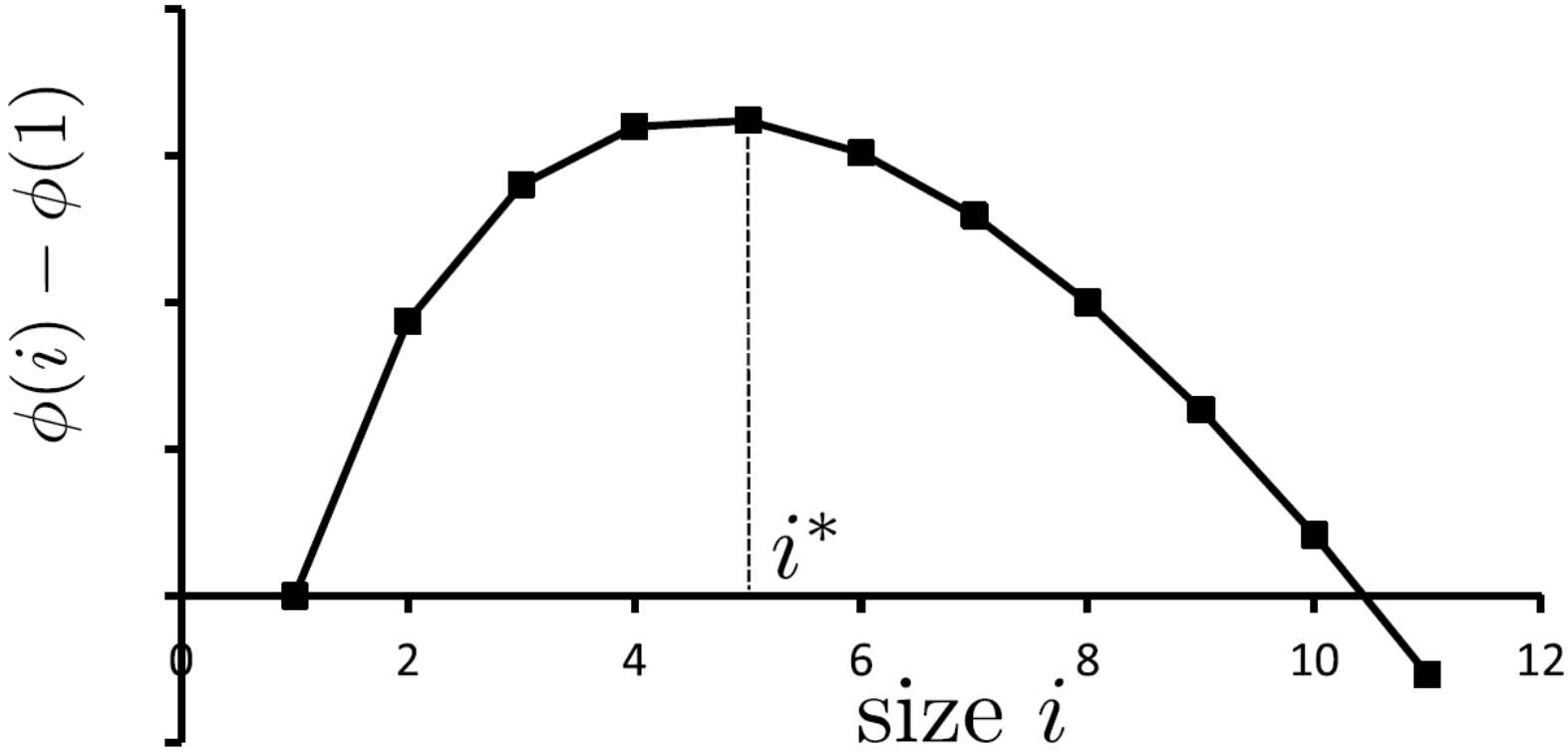
Size-dependent surface tension for water



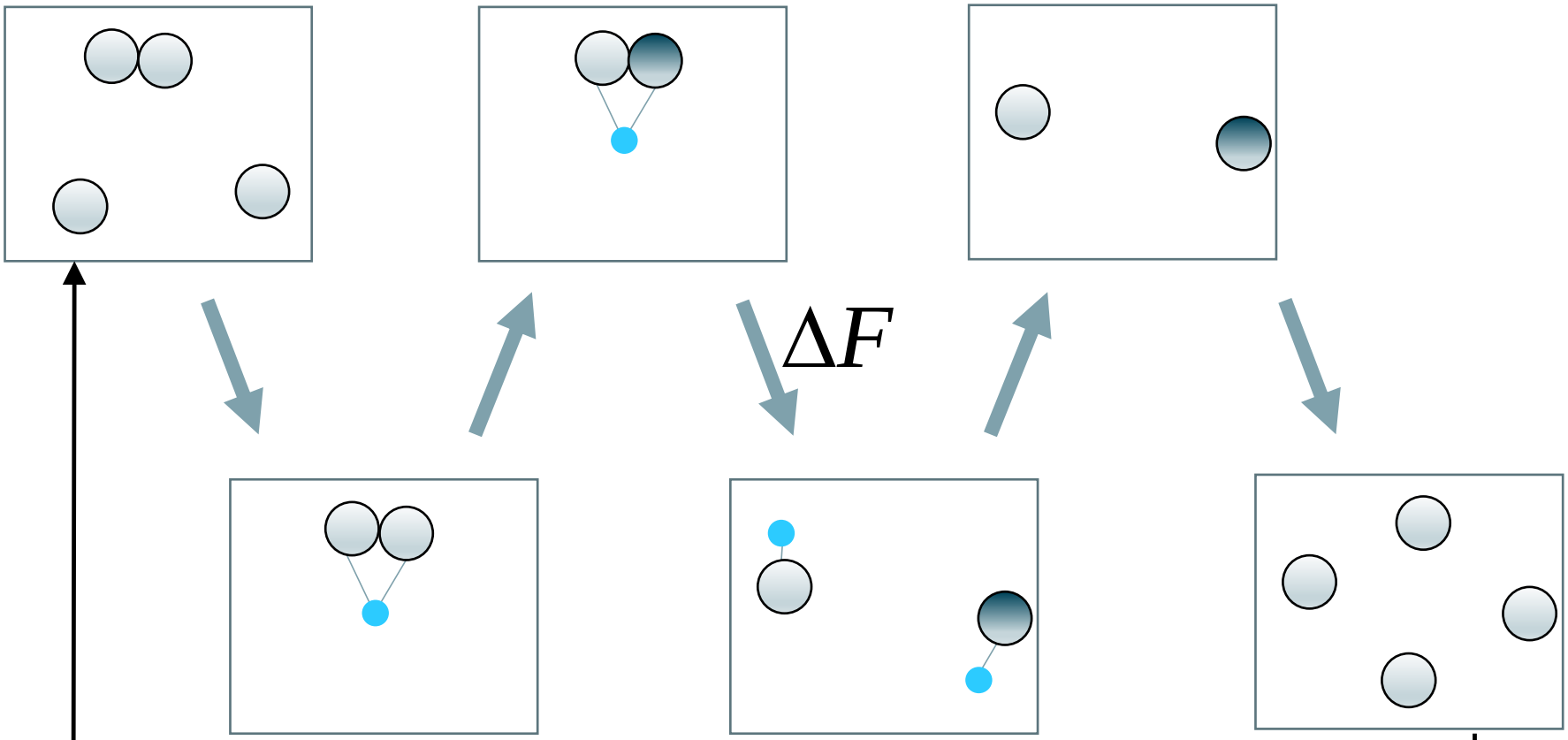
Lau et al, in preparation

Nucleation free energy barrier from free energy of disassembly

$$\phi(i) - \phi(1) = F_s(i) - (i-1)kT \ln S$$

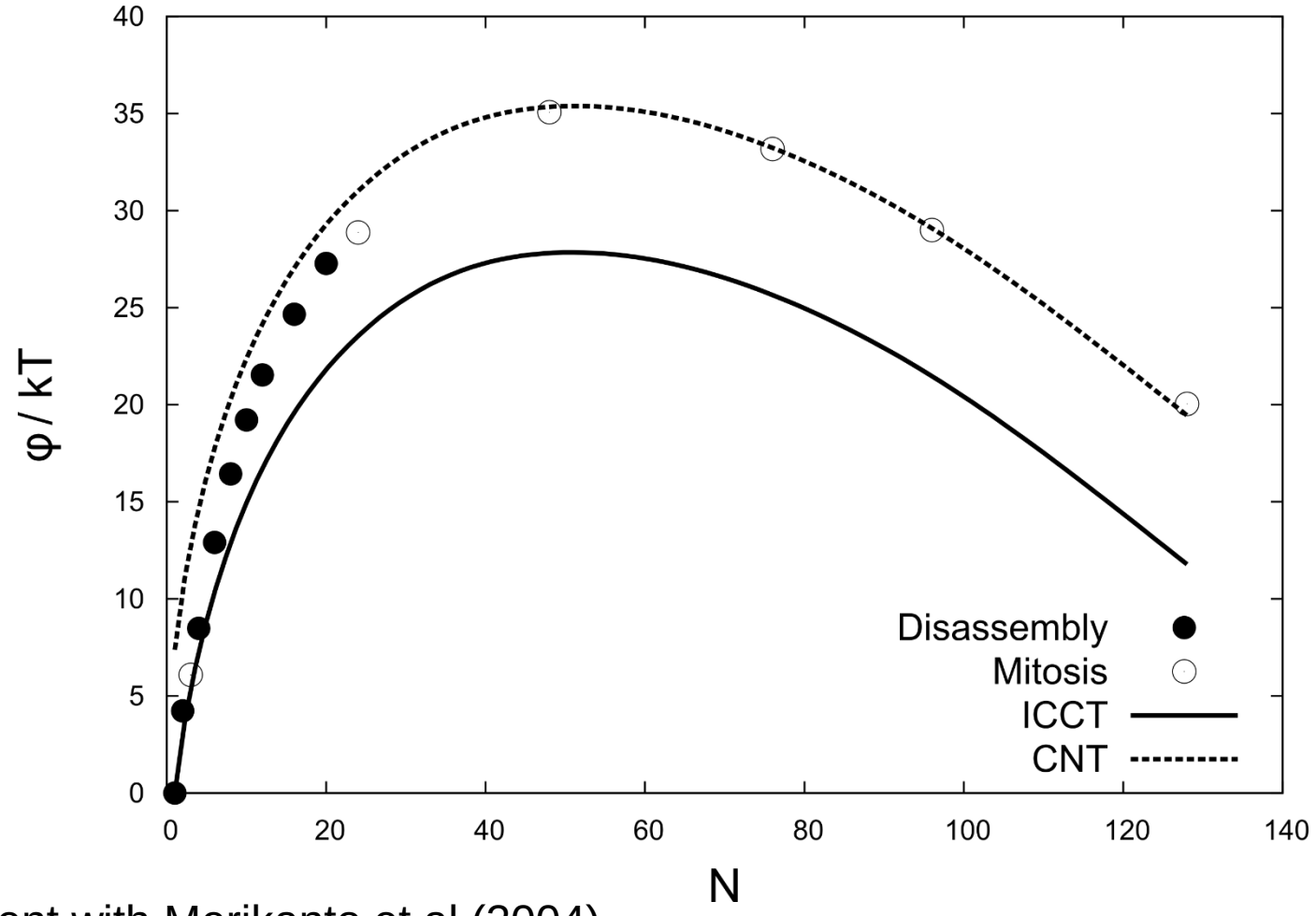


Tethering corrections



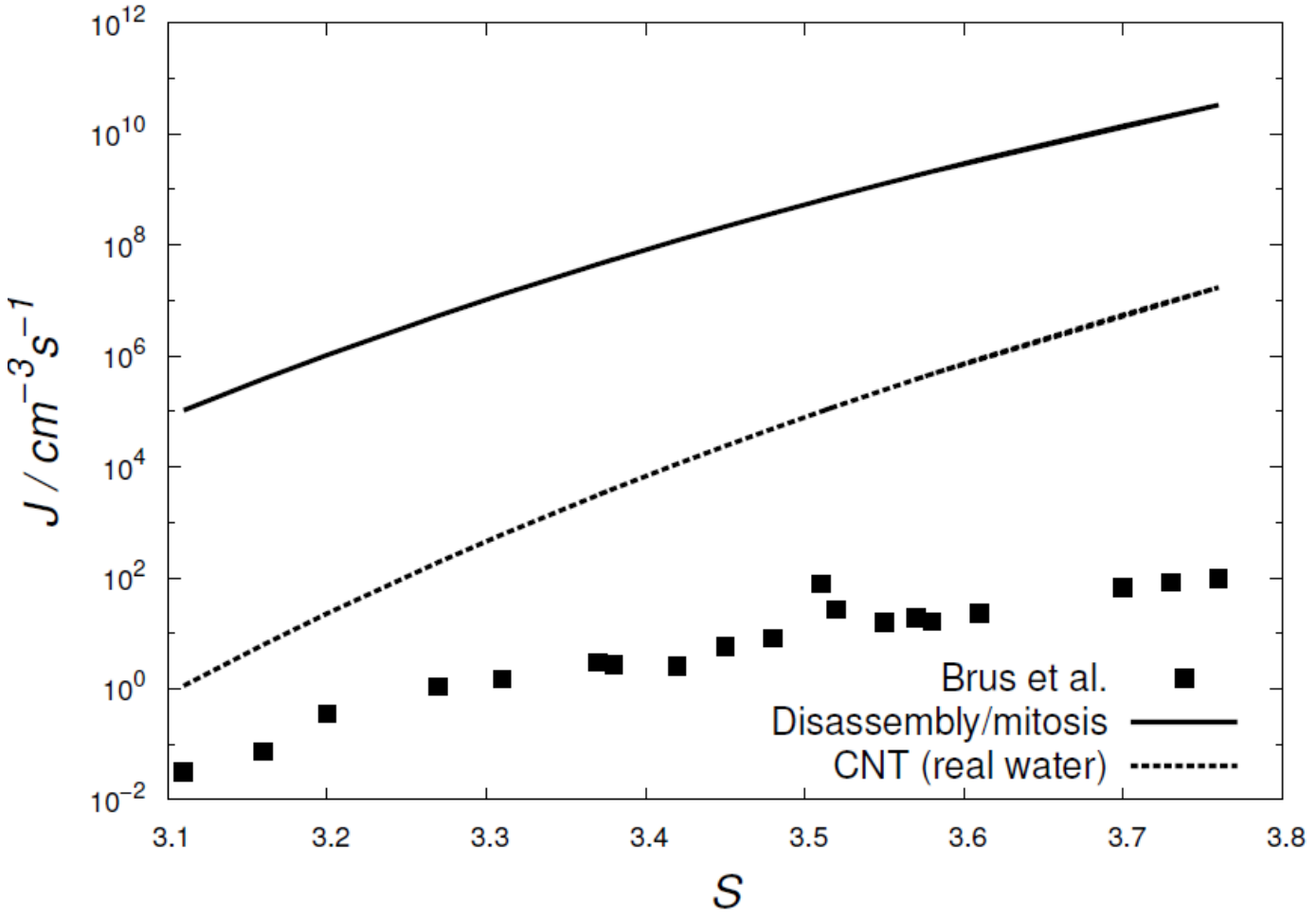
Change in free energy is a work of cluster formation plus corrections

Work of cluster formation, TIP4P/2005 water at 300K, with vapour supersaturation *S*=3.76



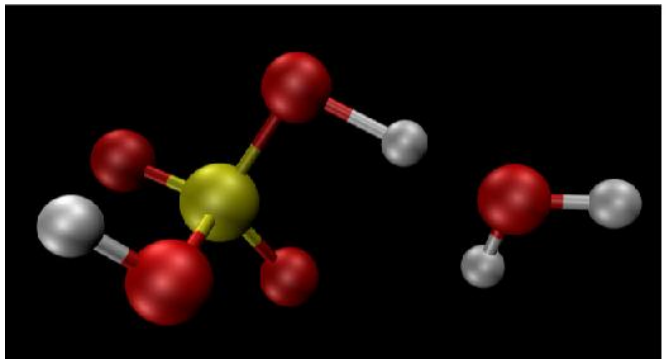
Consistent with Merikanto et al (2004)

Comparison with Classical Nucleation Theory for real water and with experiments at 300 K

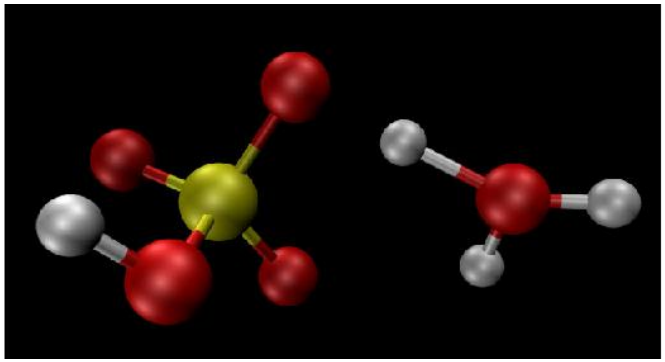


Now for sulphuric acid+water clusters. EVB model: ‘empirical valence bonds’

A force field that interpolates between patterns of chemical bonding as atomic separations change



or

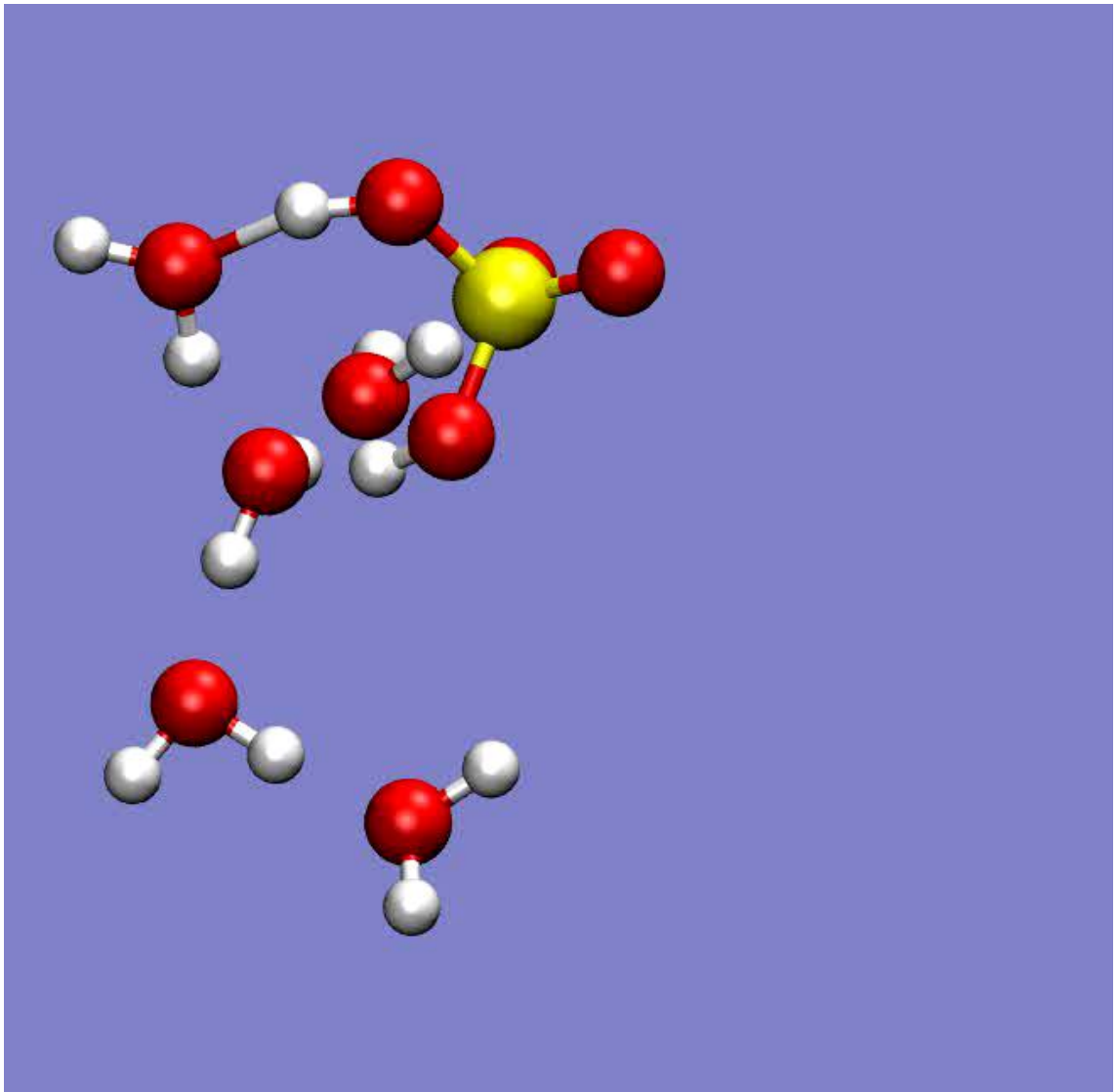


?

Based on a classical force field (Loukonen et al 2010) for each pattern.

Stinson, Kathmann and Ford, submitted

Binary system: sulphuric acid and water

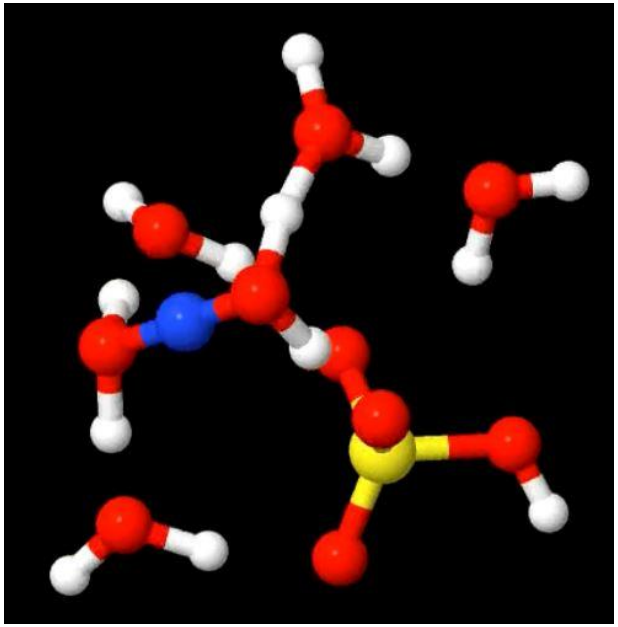


Disassembly of acid-water cluster at 300 K

Computed free energies of disassembly ΔF

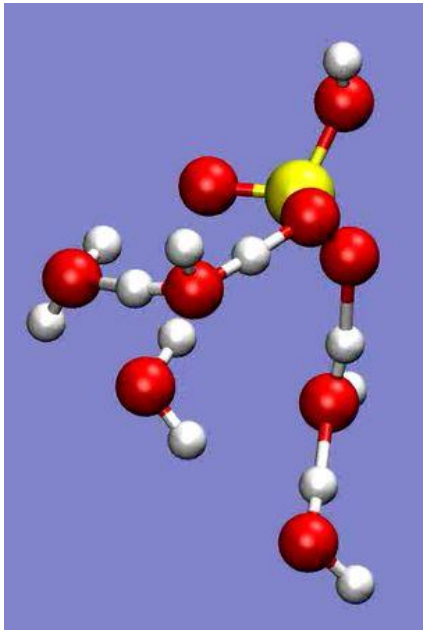
- Need tethering corrections for two species

- One acid, four waters: 43.3 kT
- Two acids, five waters: 69.3 kT
  - Compare with free energy change of mitosis of 48-water: 57.8 kT



- Need to compare results with other approaches
- Work in progress!

Summary



- A tool for free energy determination
- Most suitable for weakly bound systems
- Based on nonequilibrium MD
- Not reliant on properties at zero temperature
- Argon, water and sulphuric acid
  - next: caesium iodide and hydroxide for particle formation from fission product vapours; also amines with acid/water
- H. Y. Tang and I. J. Ford, Phys. Rev. E 91, 023308 (2015)
- G. V. Lau et al, in preparation
- **Thanks for listening!**