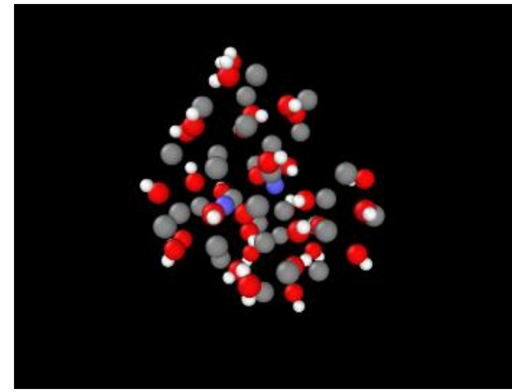
Nucleation theory:
are we nearly there yet?



Ian Ford
Department of Physics and Astronomy
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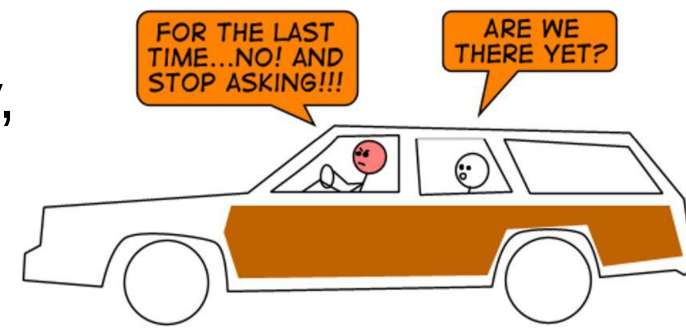
University College London



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A digression:

Are we nearly there yet?

Betteridge's law of headlines

From Wikipedia, the free encyclopedia

Any headline that ends in a question mark can be answered by the word ‘no’.

https://en.wikipedia.org/wiki/Betteridge%27s_law_of_headlines

http://betteridgeslaw.com/

UCL

EXPRESS Home of the Daily and Sunday Express

Are these ancient rock drawings PROOF that aliens visited Earth?

ANCIENT rock art in could prove aliens once visited Earth, according to conspiracy theorists.

By SEAN MARTIN
PUBLISHED: 03:01, Sun, Jul 9, 2017 | UPDATED: 09:24, Sun, Jul 9, 2017

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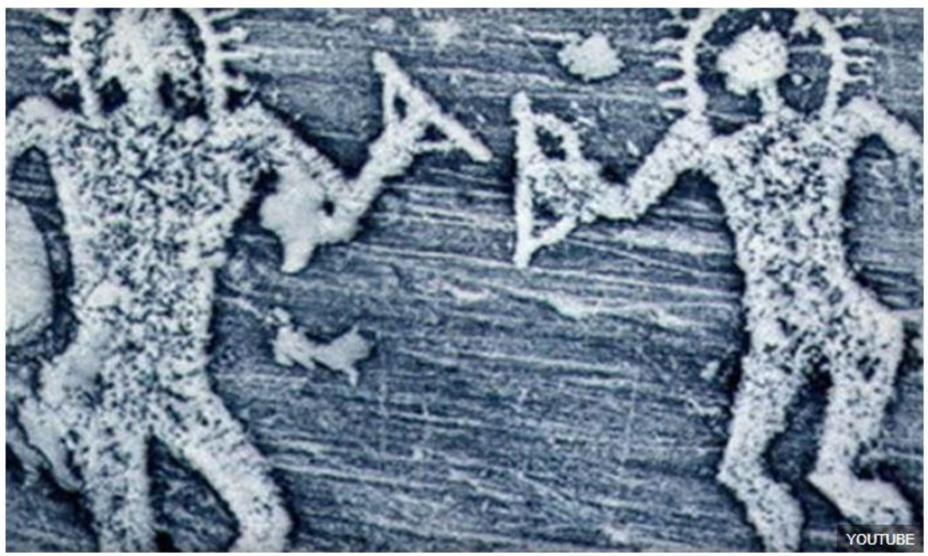
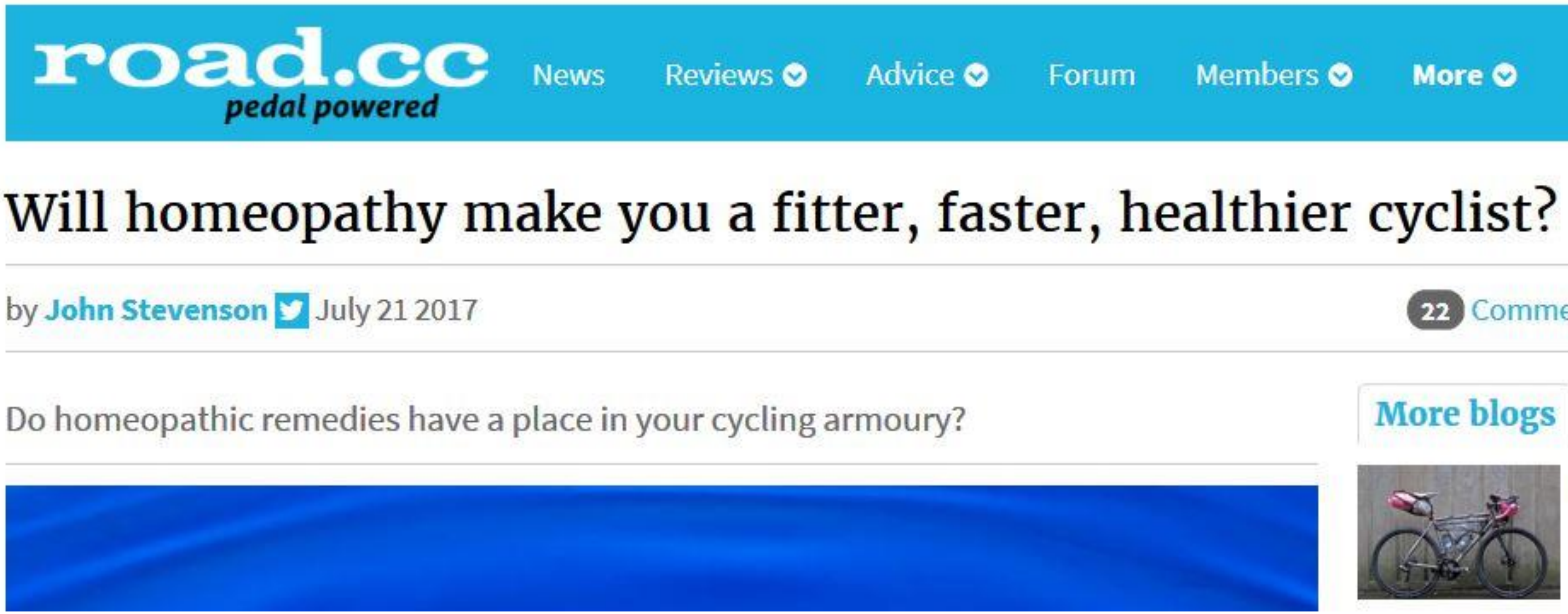


Is this proof aliens visited Earth?

http://www.express.co.uk/news/science/826076/aliens-visited-Earth-proof-petroglyph



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by John Stevenson July 21 2017 22 Commen

Do homeopathic remedies have a place in your cycling armoury?

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Is Boris Johnson running the country?

By Chris Mason
Political correspondent, BBC News

15 August 2016

http://www.bbc.co.uk/news/37086680

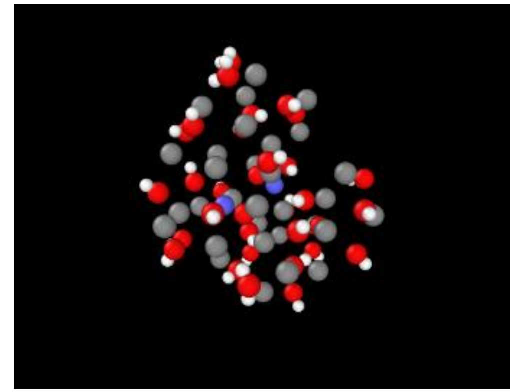
And here?

Scientometrics (2016) 108:1119–1128
DOI 10.1007/s11192-016-2030-2

Do scholars follow Betteridge's Law? The use of questions in journal article titles

James M. Cook[1] · Dawn Plourde[1]

Nucleation theory:
are we nearly there yet?



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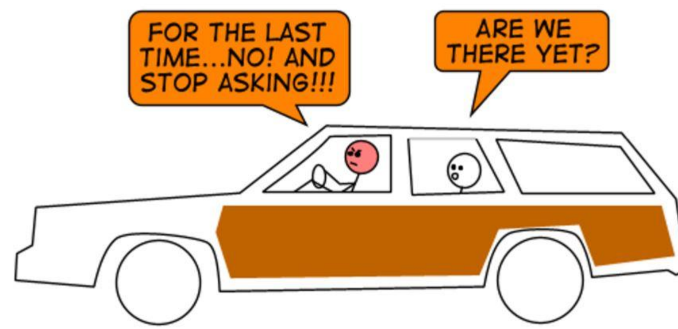

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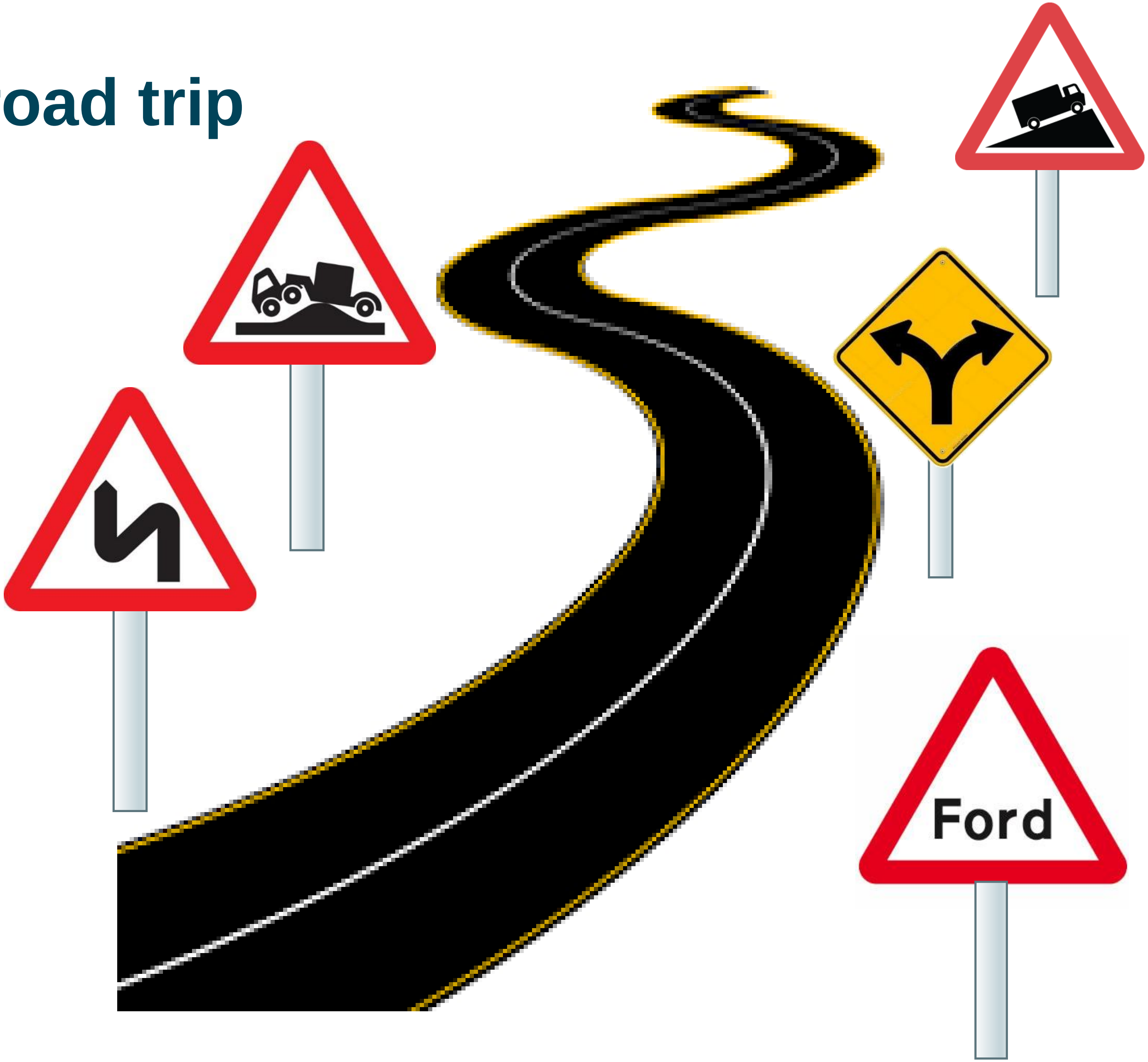
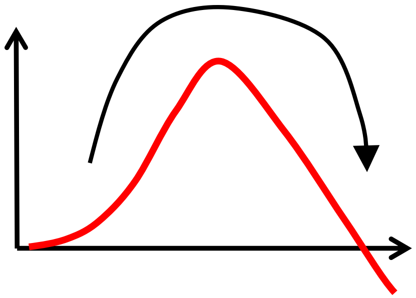
A road trip



THE PLAN



1. The long history of nucleation theory
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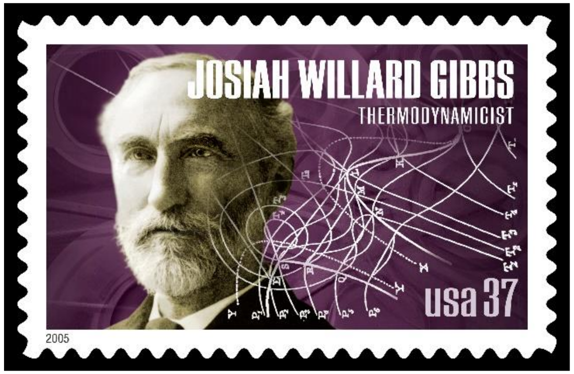
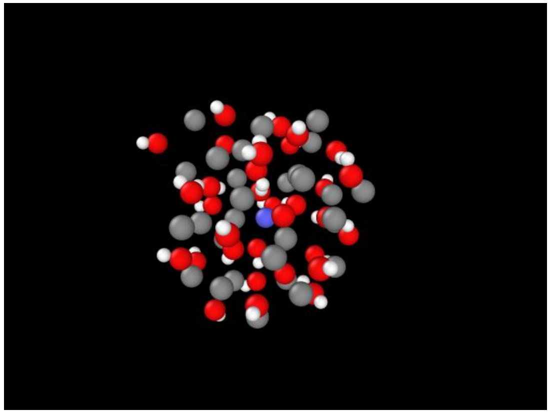
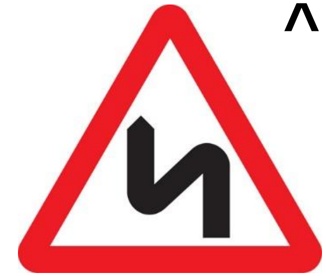




homogeneous for aerosols

Part 1. The long history of nucleation theory



- Gibbs droplet model (1870s)
- Becker-Döring kinetics of nucleation (1930s)
- Classical nucleation theory (1930s-1950s)
- The rotation-translation free energy controversy (1960s)
- Phenomenological free energy functions (1980s $\rightarrow$ present)
- Nonisothermal and carrier gas pressure effects (1990s-2000s)
- Nucleation theorems (1980s-2000s)
- Computation of cluster free energies (1960s $\rightarrow$ present)
- ‘Brute force’ simulation (2000s $\rightarrow$ present)

- Ford review, Proc. Instn Mech. Eng. Part C: J. Mech. Eng. Sci. (2004)
- Kalikmanov book: *Nucleation Theory* (Springer 2012)

homogeneous for aerosols

Part 1. The long history of nucleation theory

^ ^

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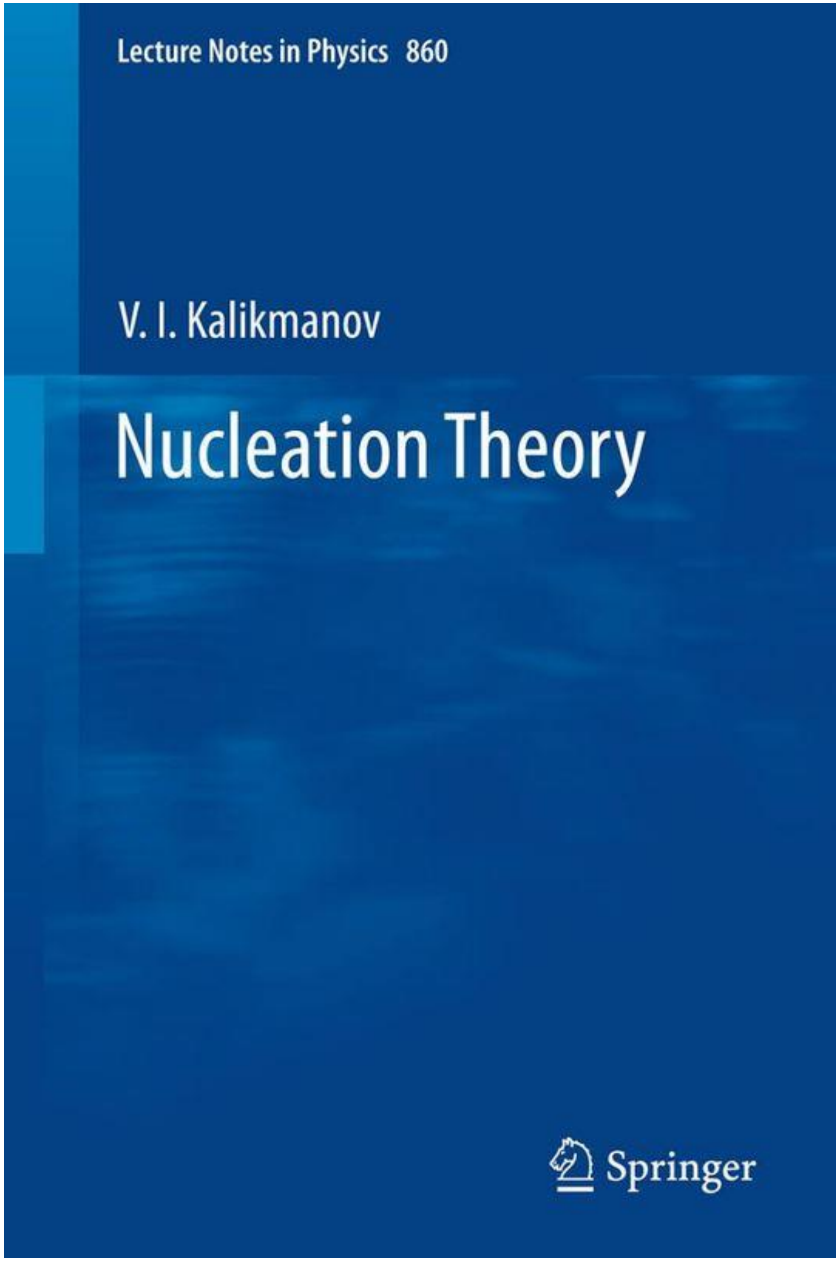
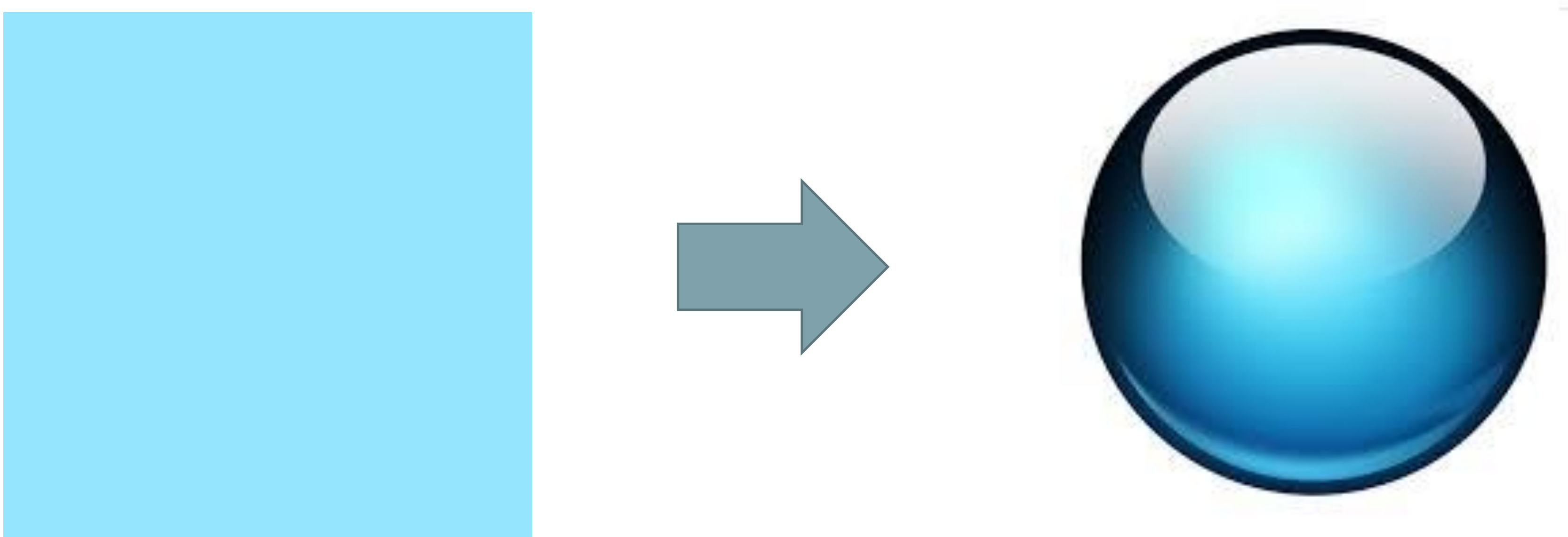


Springer
2012

Gibbs droplet model: the continuum viewpoint



Probability of formation from a vapour $\propto \exp(-\Delta\phi / kT)$

Change in appropriate thermodynamic potential ('free energy')

For droplets with N>>1 molecules

$$\text{prob} \propto \exp(-\Delta\phi / kT)$$

$$\Delta\phi(N) \approx F_{\text{CNT}}(N) - (\mu_{\text{vapour}} - \mu_{\text{coexist}})N$$

free energy cost of creating surface

thermodynamic payback for the transition ($kT \ln S$)

supersaturation $S = \dfrac{\text{vapour pressure}}{\text{saturated vapour pressure}}$

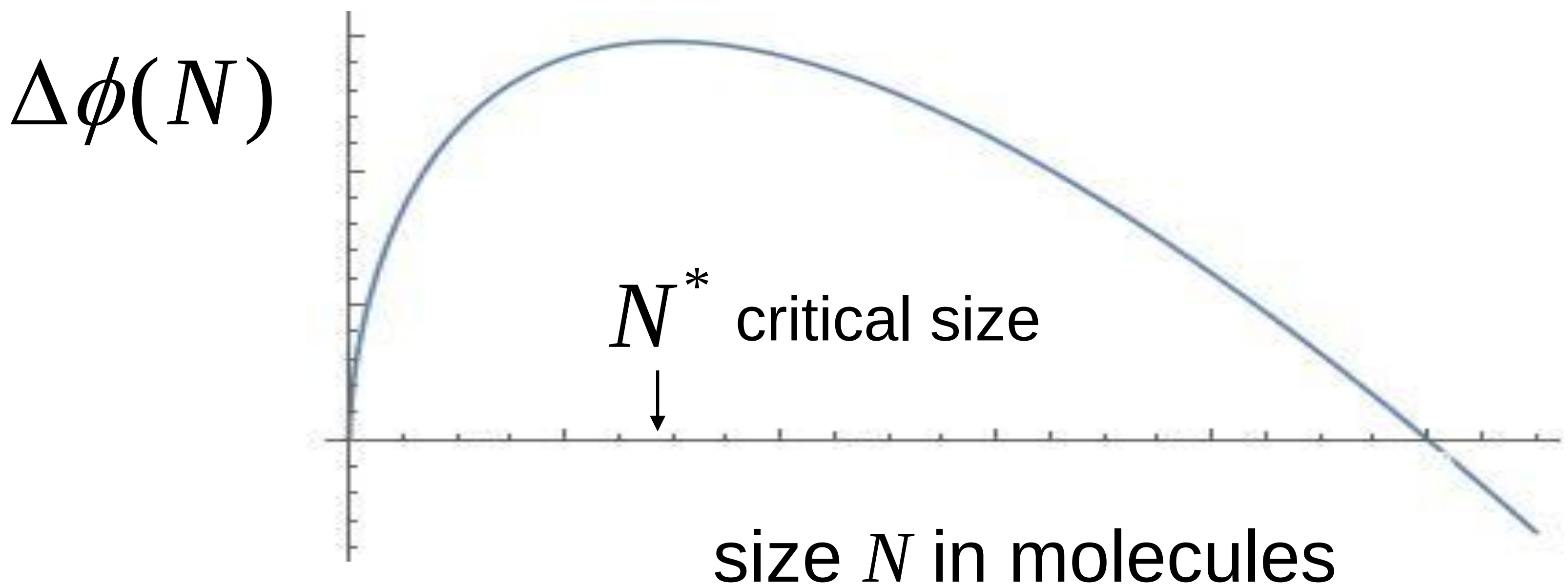
$$F_{\text{CNT}}(N) = \text{surface area} \times \text{surface tension}$$

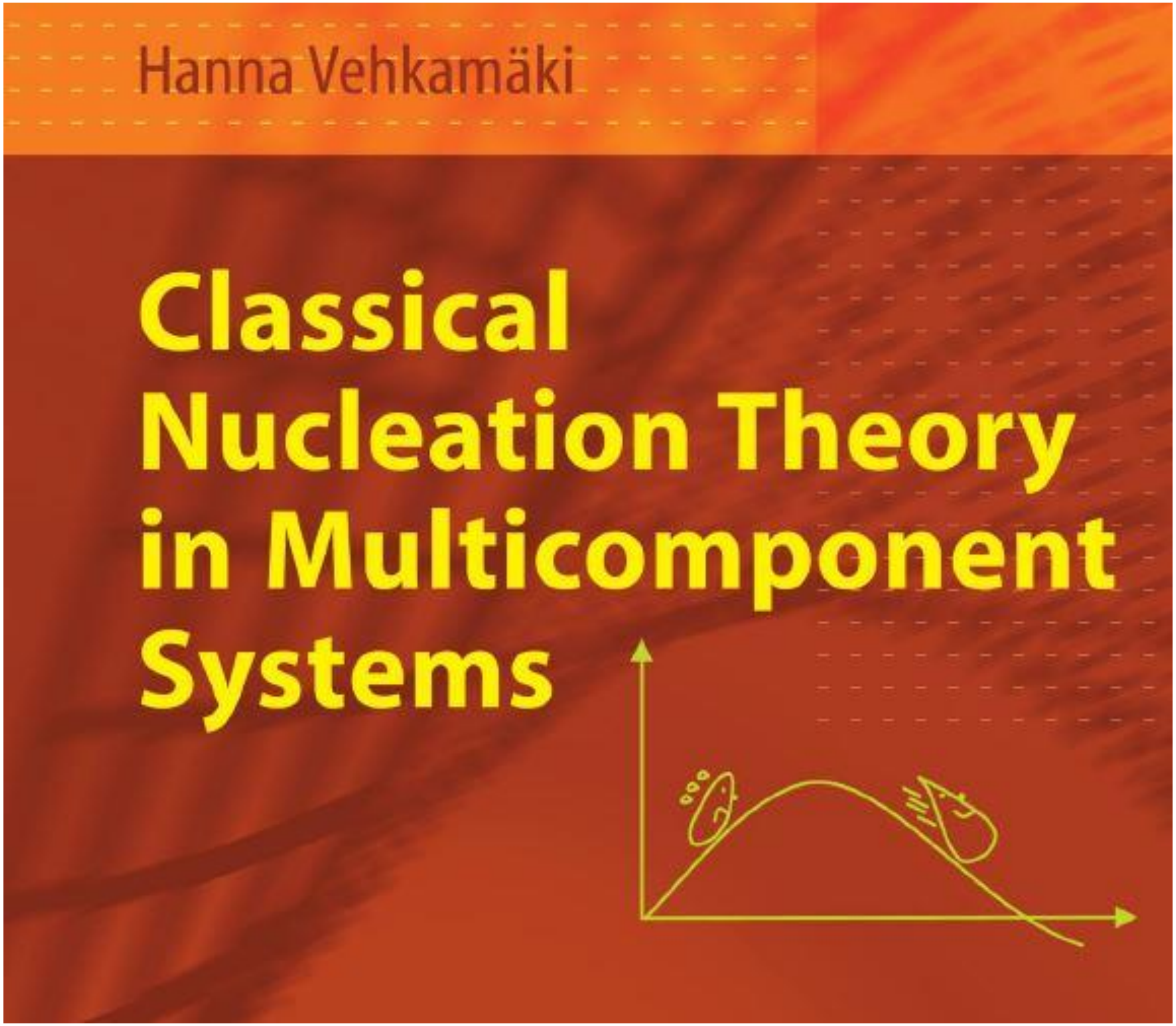
Barrier in classical nucleation theory

$$\Delta\phi(N) = aN^{2/3} - bN$$

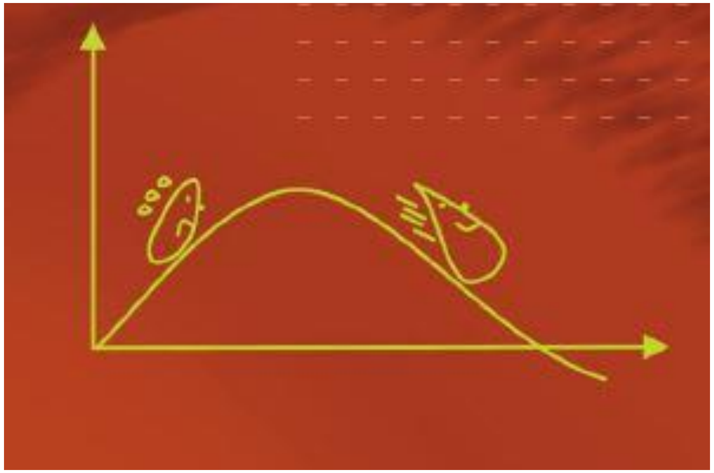
surface volume

$$\text{nucleation rate} \propto \exp(-\Delta\phi(N^*)/kT)$$





Springer 2006



Springer 2006

Nucleation theorems

$$J(S,T)$$

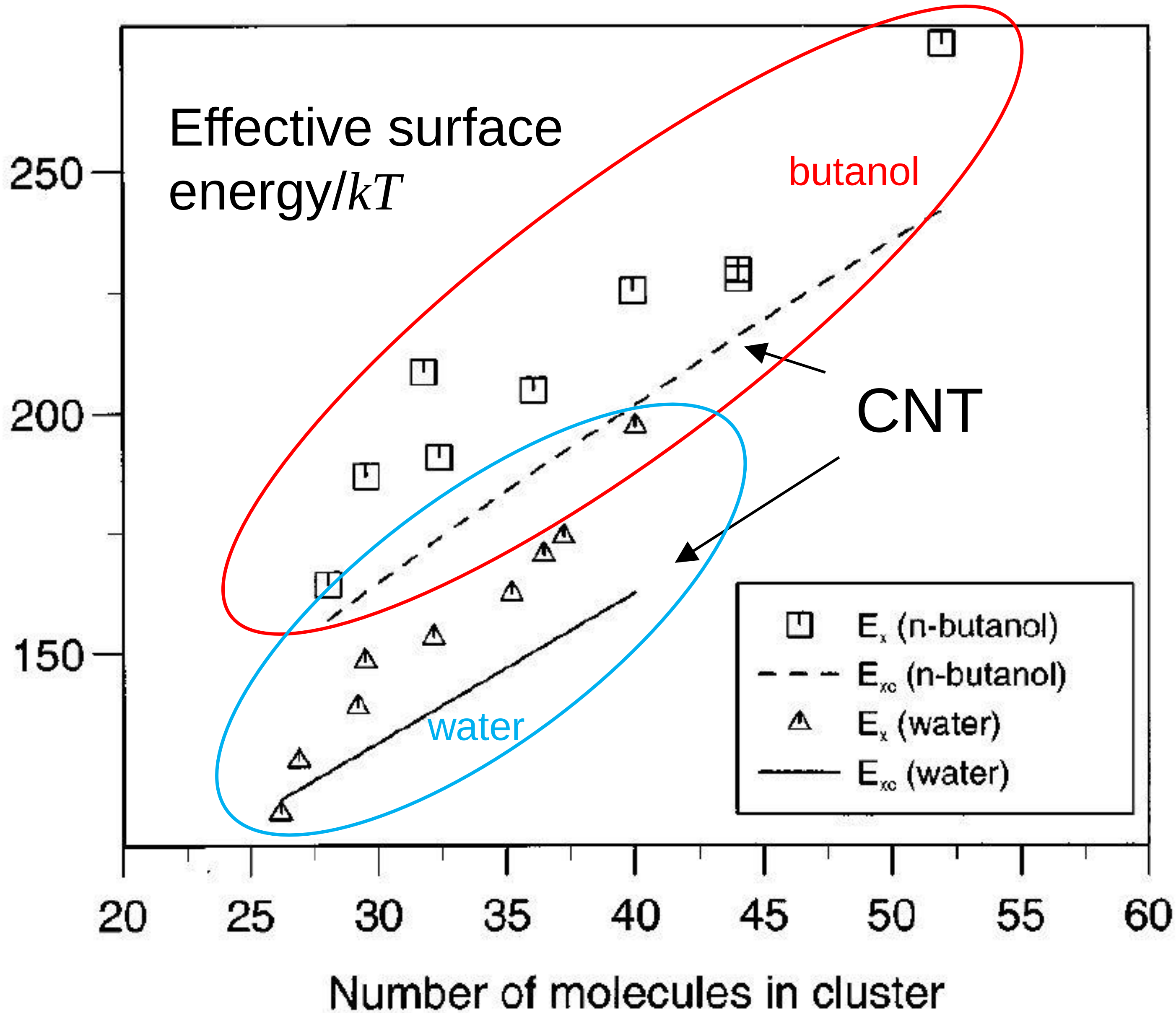
- ***Supersaturation*** dependence of the nucleation rate:
  - extract the critical size
  - Kashchiev (1982)

data ➡ N^*

- ***Temperature*** dependence of nucleation rate:
  - extract the *energy* of the critical size
  - Ford (1996,1997)

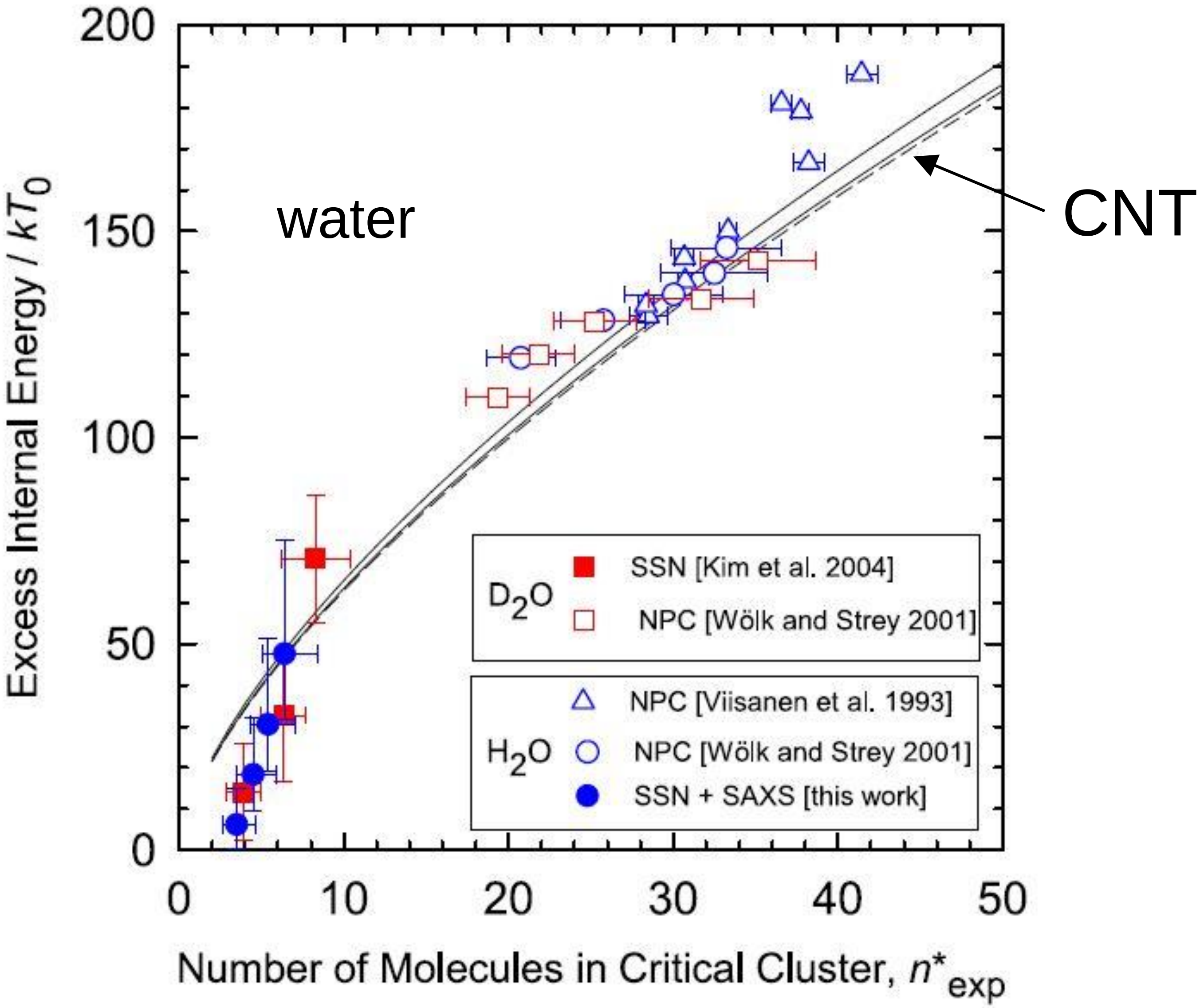
data ➡ $E(N^*)$

- Surprise: classical theory sometimes works!



IJF, Phys Rev E (1997)

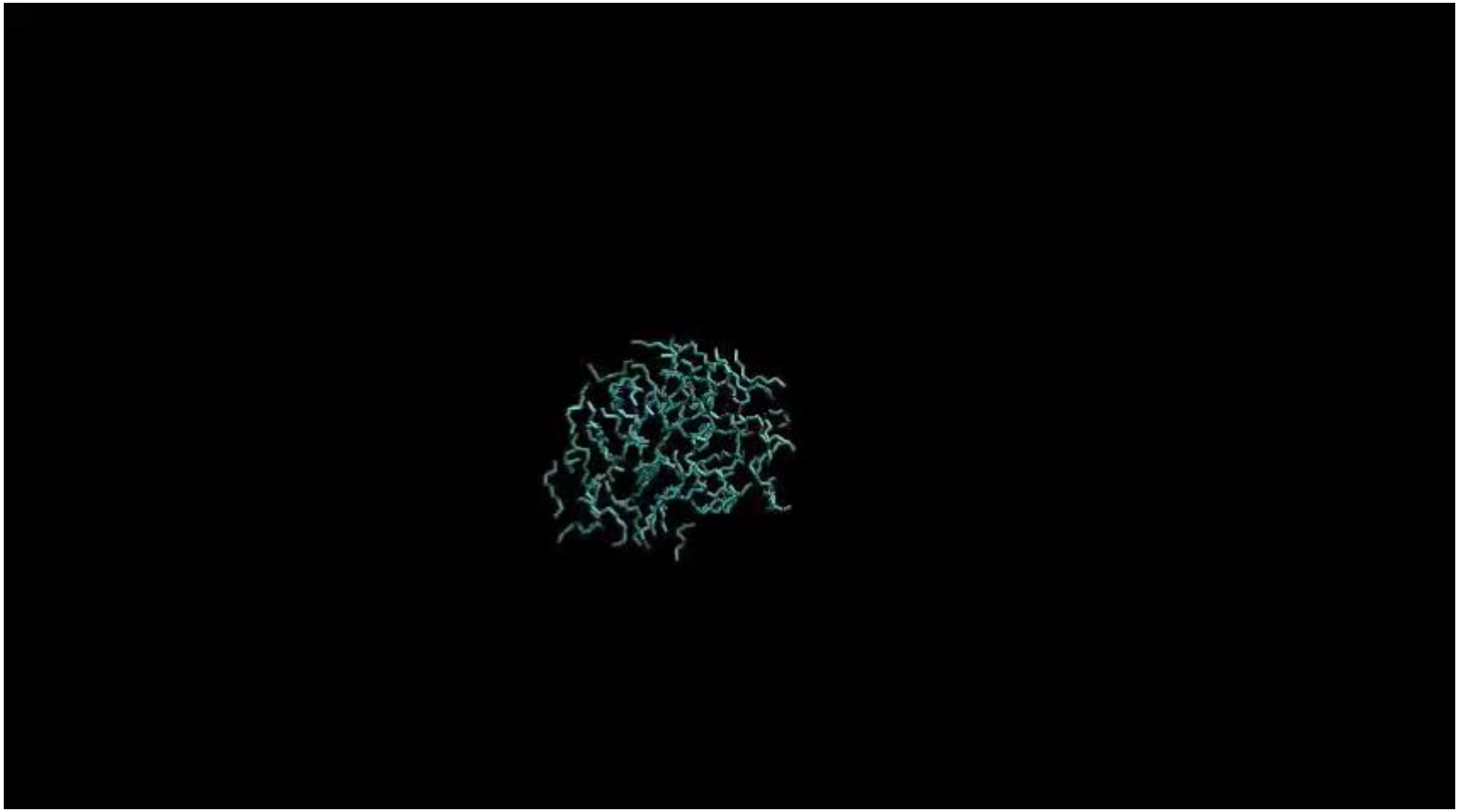
Wyslouzil and Wölk, J. Chem. Phys. 145, 211702 (2016)




ARE WE THERE YET !?!
MATT GROENING

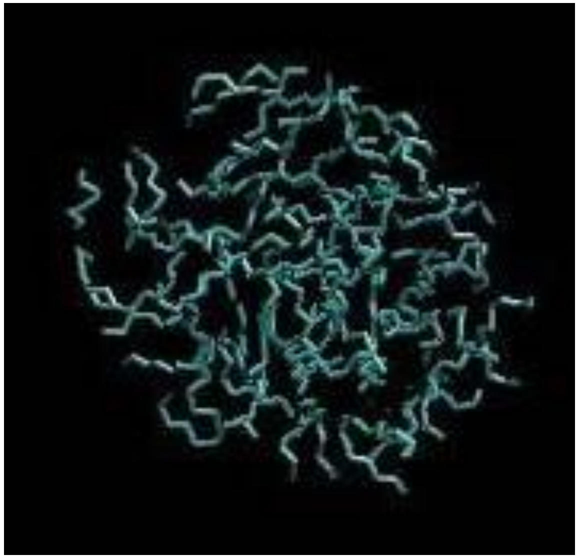
Structure and dynamics of molecular clusters

Cluster of 67 nonane molecules:

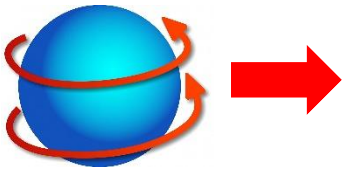


Problems with classical nucleation theory

$\neq$

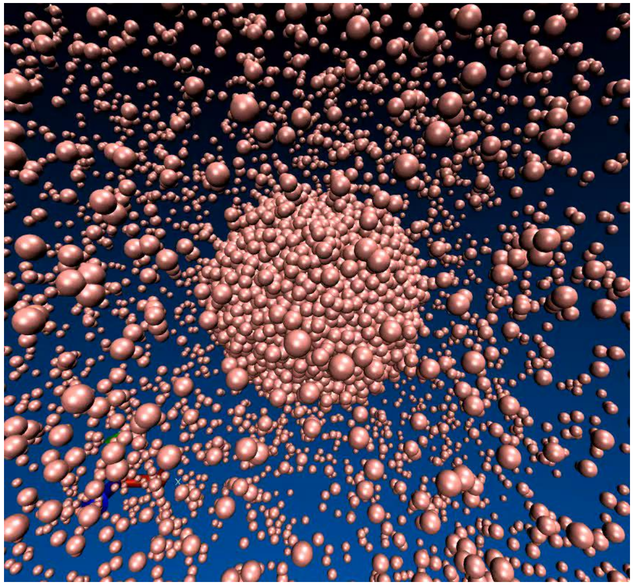


surface area? radius? density?

- Translation-rotation free energy? ((
  - Controversy in 1960s: extra factor of 10^{17} in rate?

‘Brute force’ simulation of an entire vapour

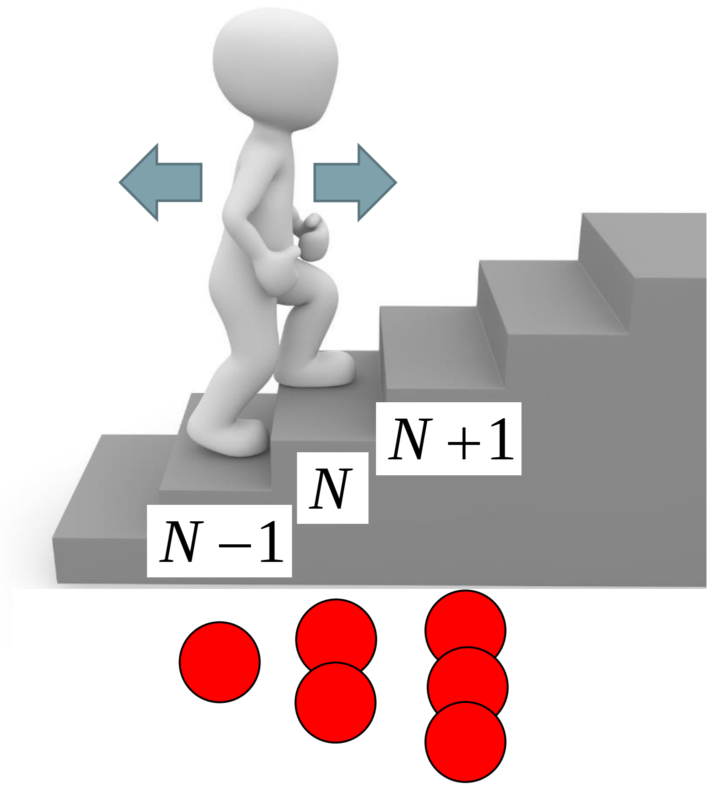
- Large scale molecular dynamics simulation
- e.g. Diemand, Angélil, Tanaka and Tanaka
  - Argon:
    - J. Chem. Phys. **140**, 074303 (2014)
  - Water:
    - J. Chem. Phys. **143**, 064507 (2015)
- Also Matsumoto,Yasuoka, Wedekind, Reguera, Suh,…
- Powerful, but expensive



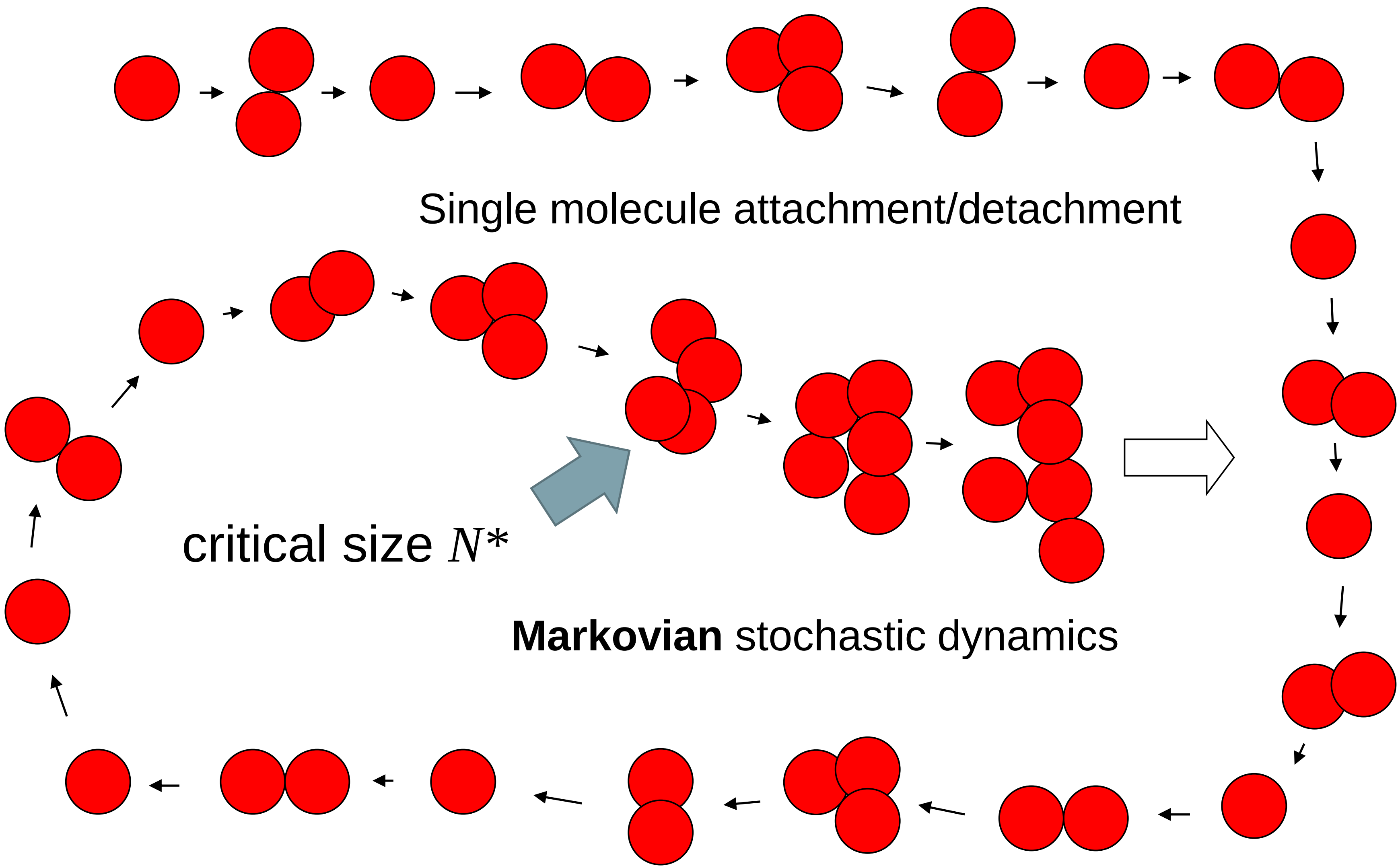
Movie downloaded from JCP

Nucleation: a stochastic process undertaken by a single cluster

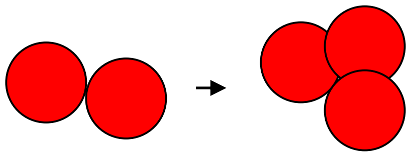
Random walk in size space



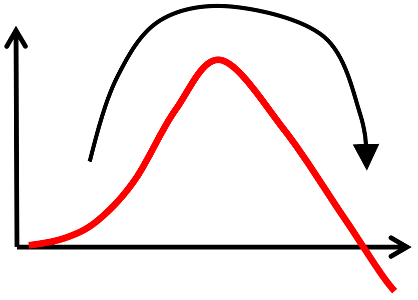
Becker-Döring kinetics of nucleation



Transition rates required



- Many studies of molecular attachment/detachment dynamics
  - Natarajan, Harris and Ford (2006)
  - Napari, Julin and Vehkamäki (2009)
  - Halonen and Zapadinsky (2017)
  - ….
- Rates are combined to build the barrier




ARE WE THERE YET !?!
MATT GROENING

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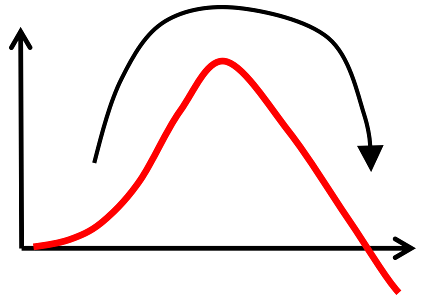

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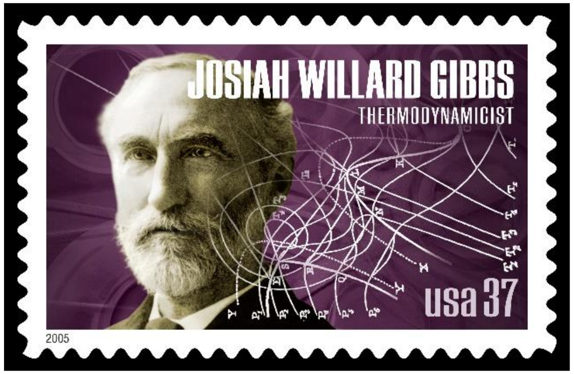
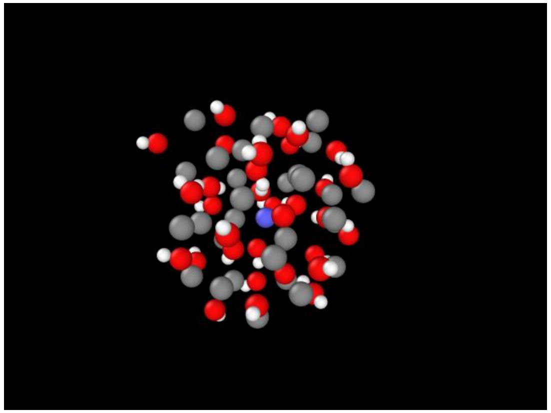




Part 2: What is the nucleation barrier made of?

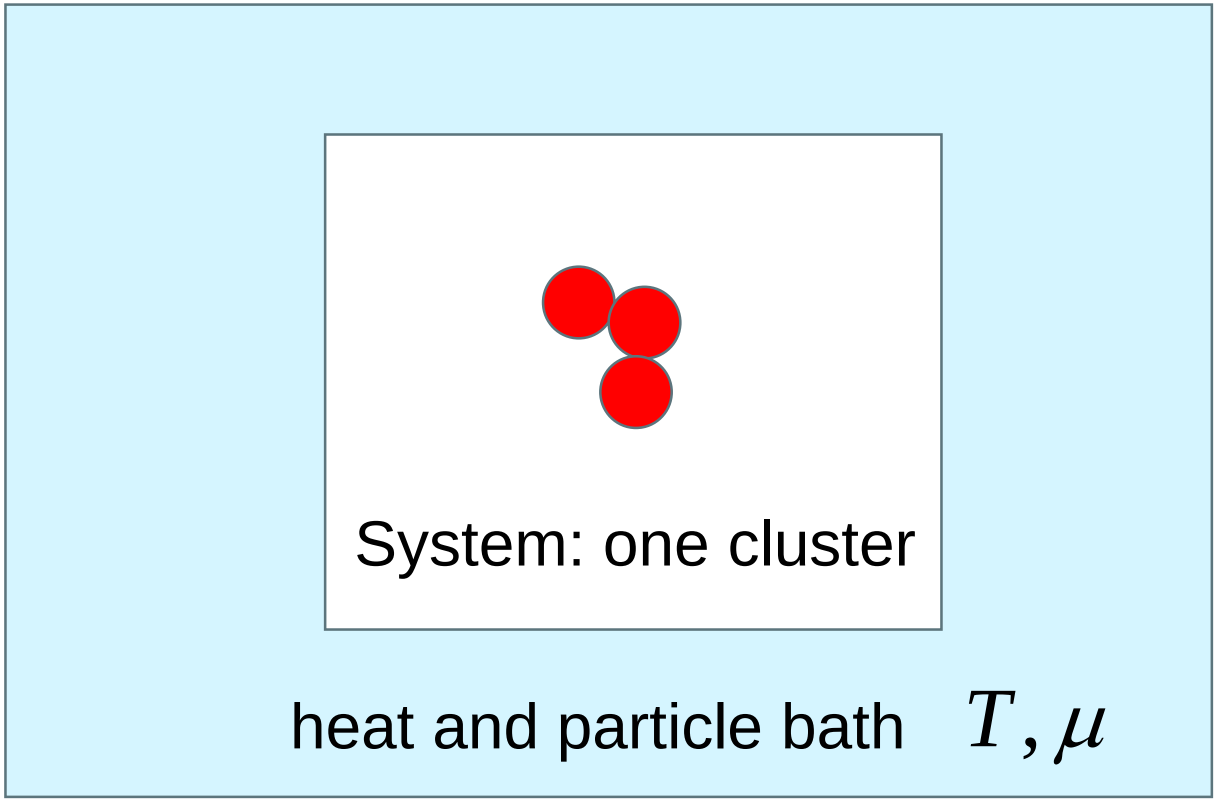
- Long history of confusing terminology

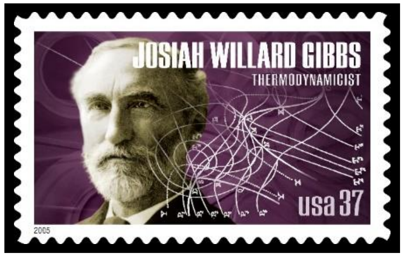
  ☹

- Something to do with the rates of molecular attachment and detachment

- Related to a **thermodynamic potential**
  - under certain conditions

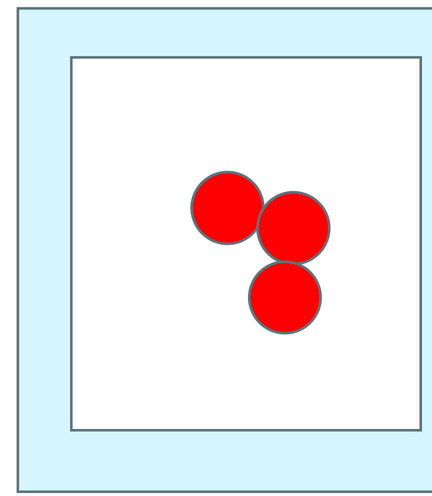
Grand canonical cluster statistical mechanics





Grand canonical cluster statistical mechanics

$$N\text{-cluster probability} = \exp\left(\Phi / kT\right)\exp\left(-A(N)/kT\right)$$



Φ is the grand potential

$$\Phi = \langle F(N) \rangle - \mu \langle N \rangle$$

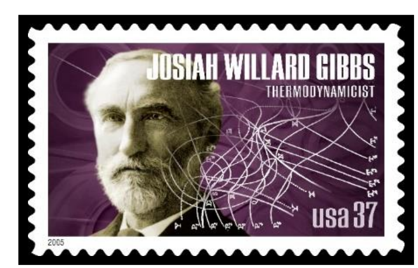
(*brackets denote ensemble averaging*)

$A(N)$ is the ***availability*** potential:

$$A(N) = F(N) - \mu N$$

Helmholtz free energy:

$$F(N) = \langle E \rangle - TS$$



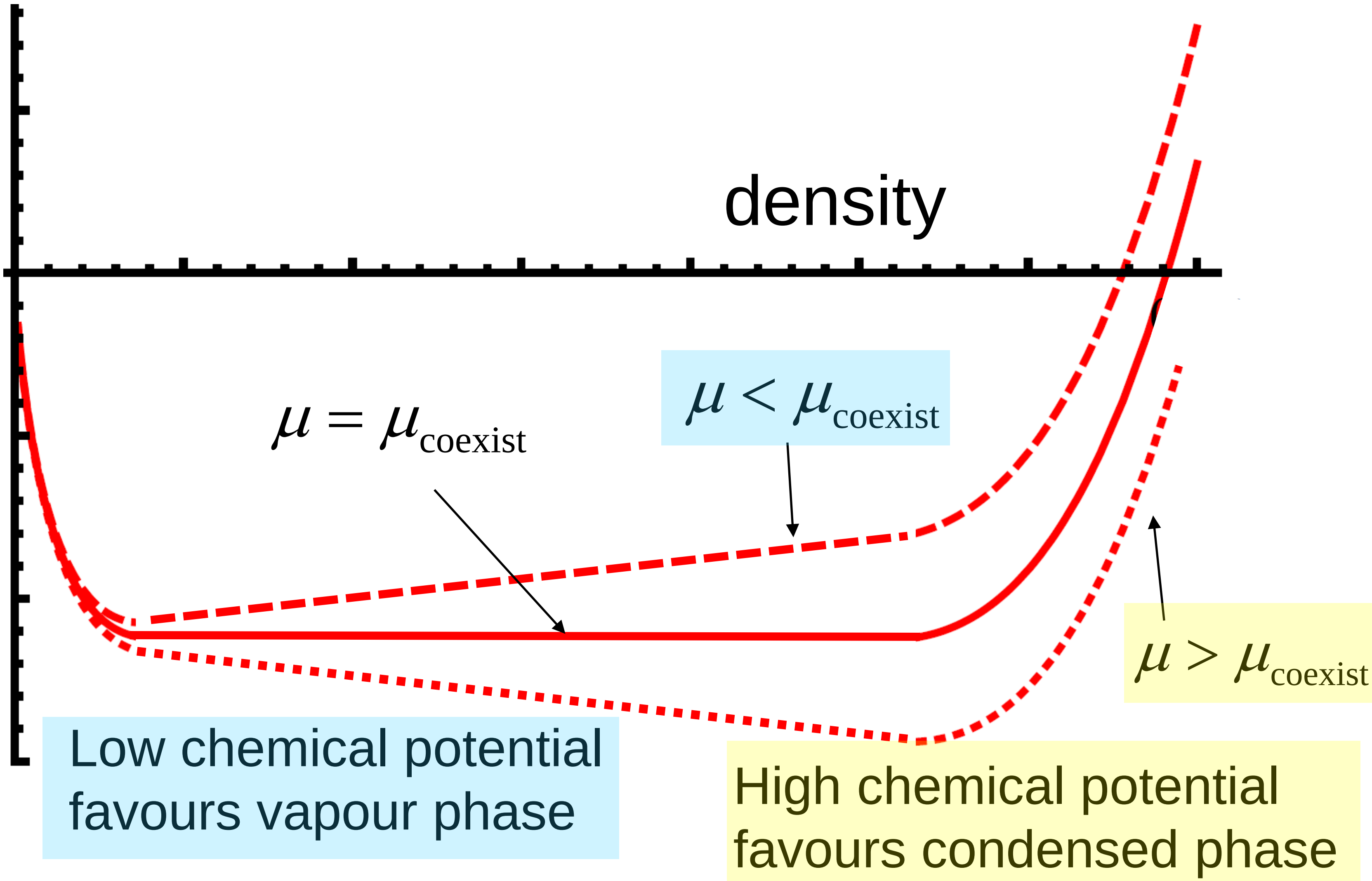
Second law of thermodynamics

Die Entropie der Welt strebt einem Maximum zu (Clausius 1865)

$$\Delta S_{\text{world}} \geq 0$$

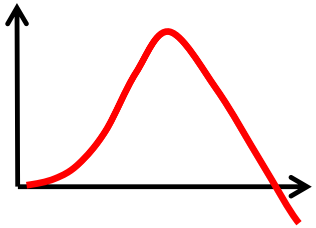
$$\Delta A_{\text{system}} = -T\Delta S_{\text{world}} \leq 0$$

System availability (at fixed chemical potential)



The nucleation barrier is made of *availability*

$$\Delta\phi(N) = A(N) - A(1)$$



- Cluster availability for an environmental chemical potential μ :

$$A(N) = F(N) - \mu N$$

- Cluster partition function $\rightarrow$ Helmholtz free energy

$$F(N) = -kT \ln Z_N$$

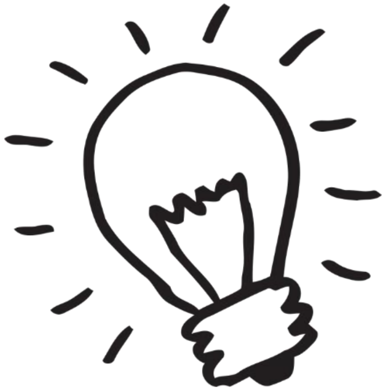
Effective surface free energy $F_s(N)$ (excess free energy)

$$\Delta\phi(N) = F_s(N) - (\mu_{\mathrm{vapour}} - \mu_{\mathrm{coexist}})N$$

generalisation of F_{CNT}

- Includes cluster rotation-translation free energy
- Typically requires lengthy computation

Models for effective surface free energy



- Physics-based
- Parametrised by data
  - equation of state, phase diagram, spinodals
- Too many to mention:
  - Tolman
  - Dillmann-Meier
  - Virial-Fisher
  - Extended modified droplet
  - Mean field kinetic nucleation theory
  - Density functional theory

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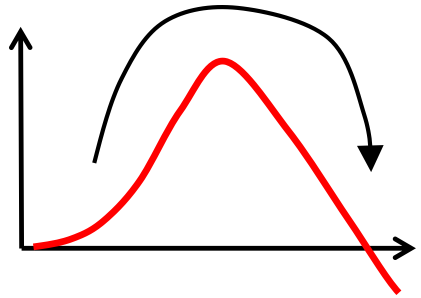

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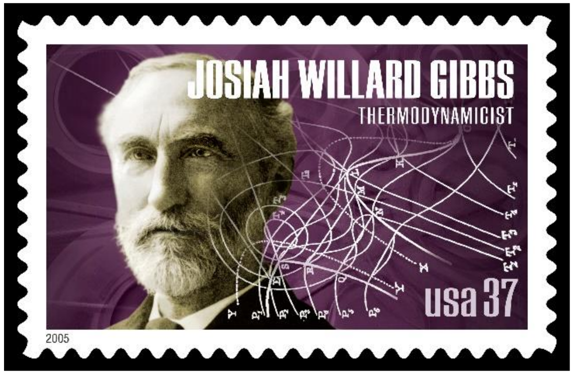
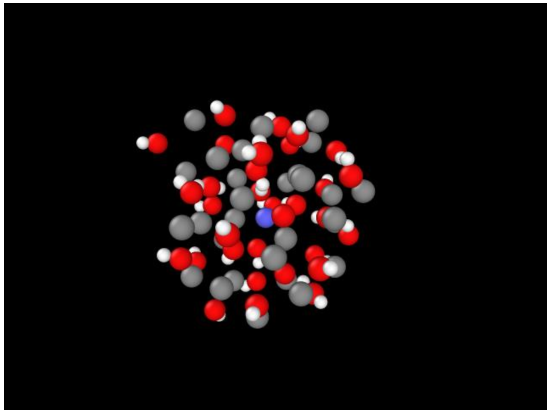




Part 3: Free energy by guided cluster disassembly

We need $\boxed{F(N) - F(1)}$

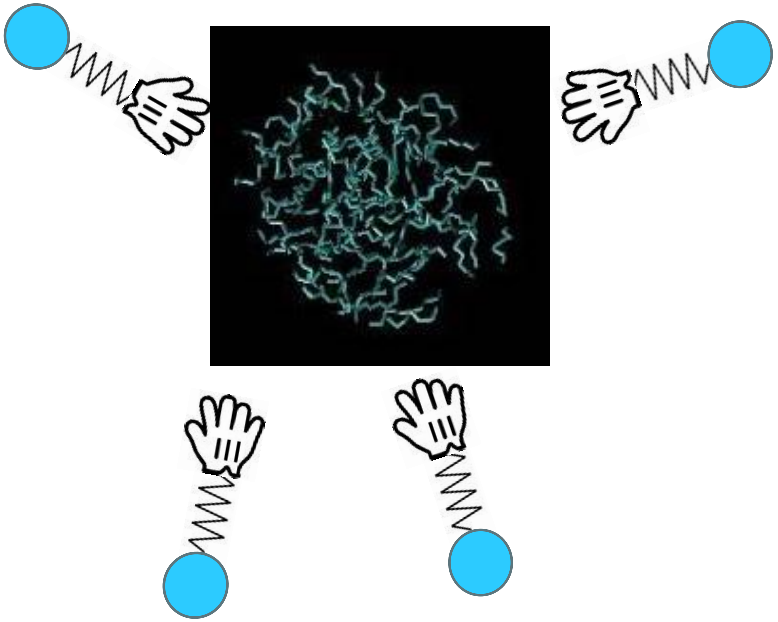
with $$F(N) = -kT \ln Z_N$$

$$Z_N = \frac{1}{h^{3N} N!} \int dX dP \exp(-H_N / kT)$$

Part 3: Free energy by guided cluster disassembly

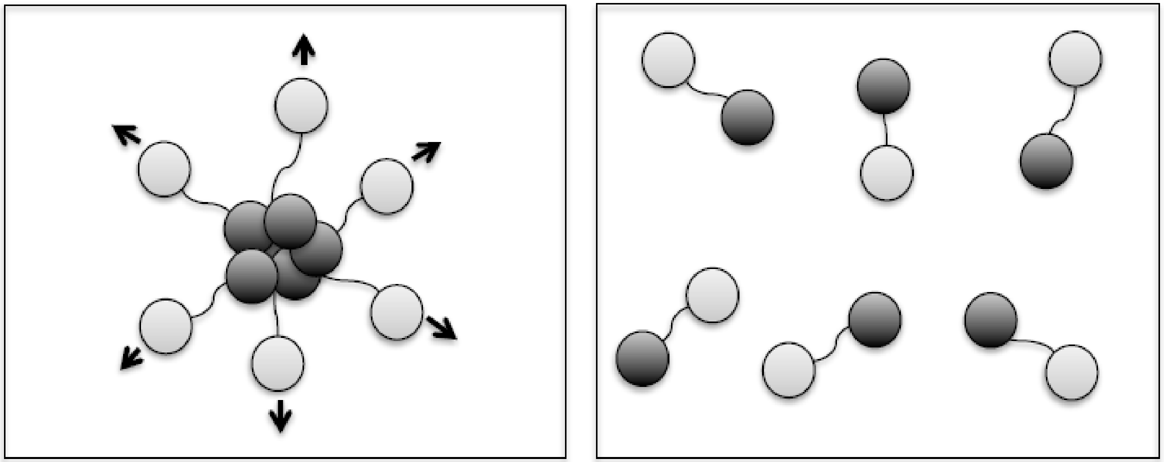
- Free energy change = **isothermal quasistatic work**

- Let's pull a cluster apart in NVT molecular dynamics
  - using *guide particles*



Jarzynski equality emulates quasistatic conditions

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



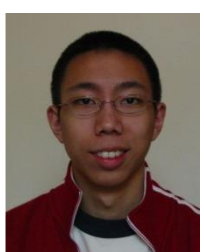
Guides move while tethered to each cluster molecule

Acknowledgements to:

- Sukina Natarajan
- Hoi Yu Tang
- Gabriel Lau
- Jake Stinson
- Jamie Parkinson
- Julian Thompson

Papers available from
www.ucl.ac.uk/~ucapijf

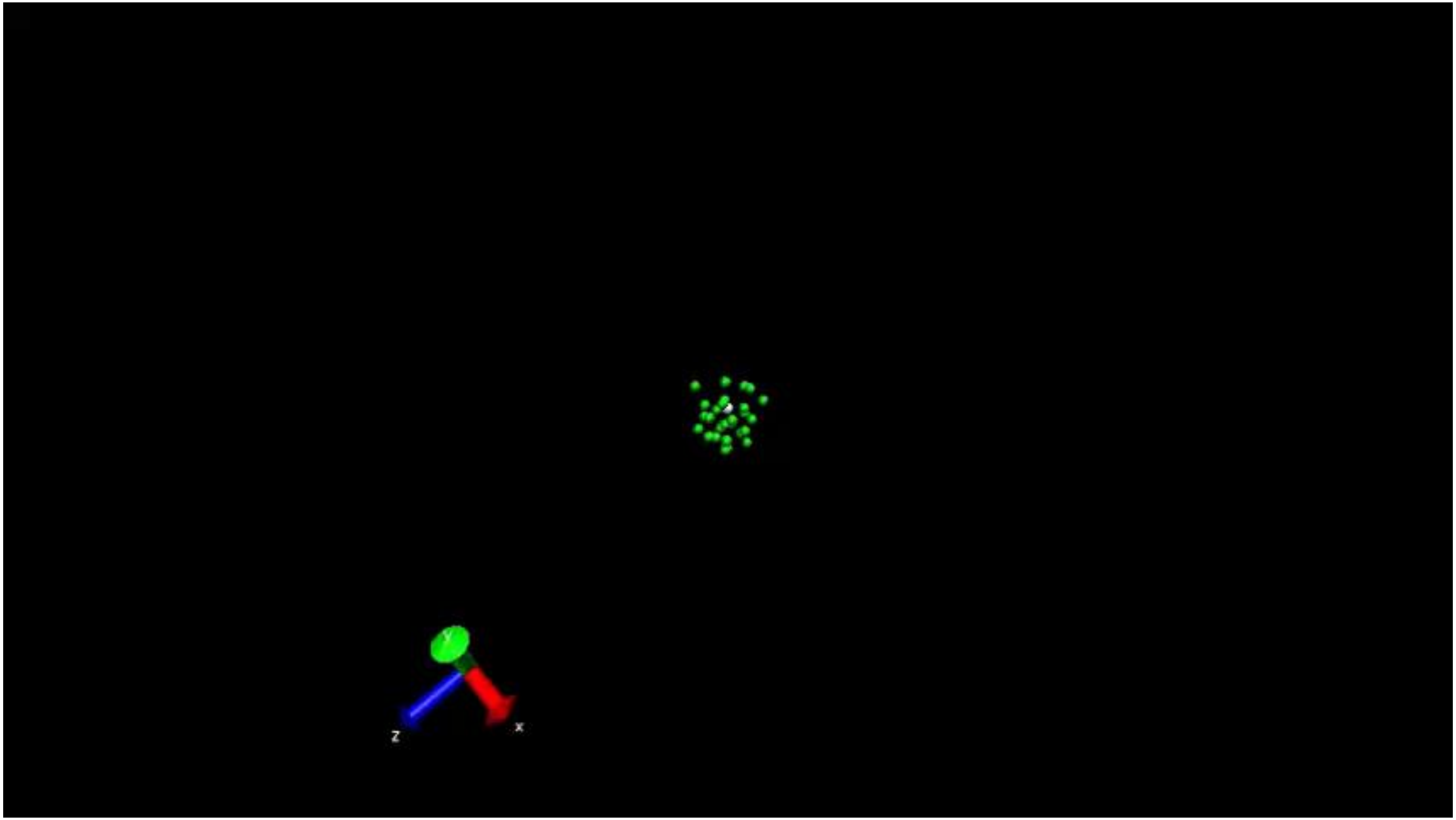
H.Y. Tang and I.J. Ford, Phys. Rev. E 91 (2015) 023308
G.V. Lau et al, J. Chem. Phys. 143 (2015) 244709
J.Y. Parkinson, G.V. Lau and I.J. Ford, Molecular Simulation 42 (2016) 1125-1134



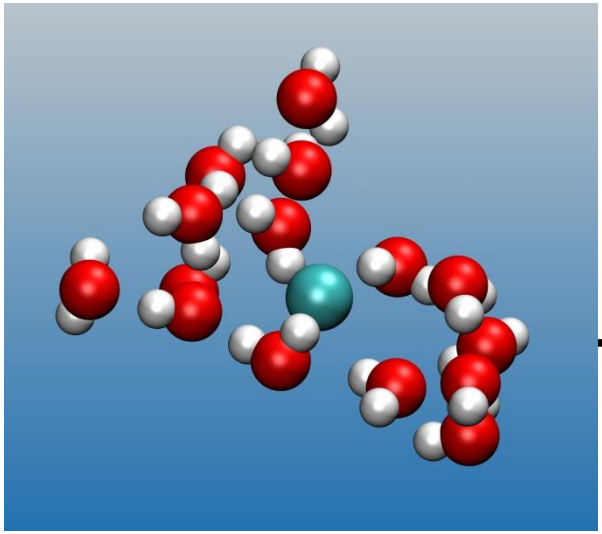
Complete cluster disassembly

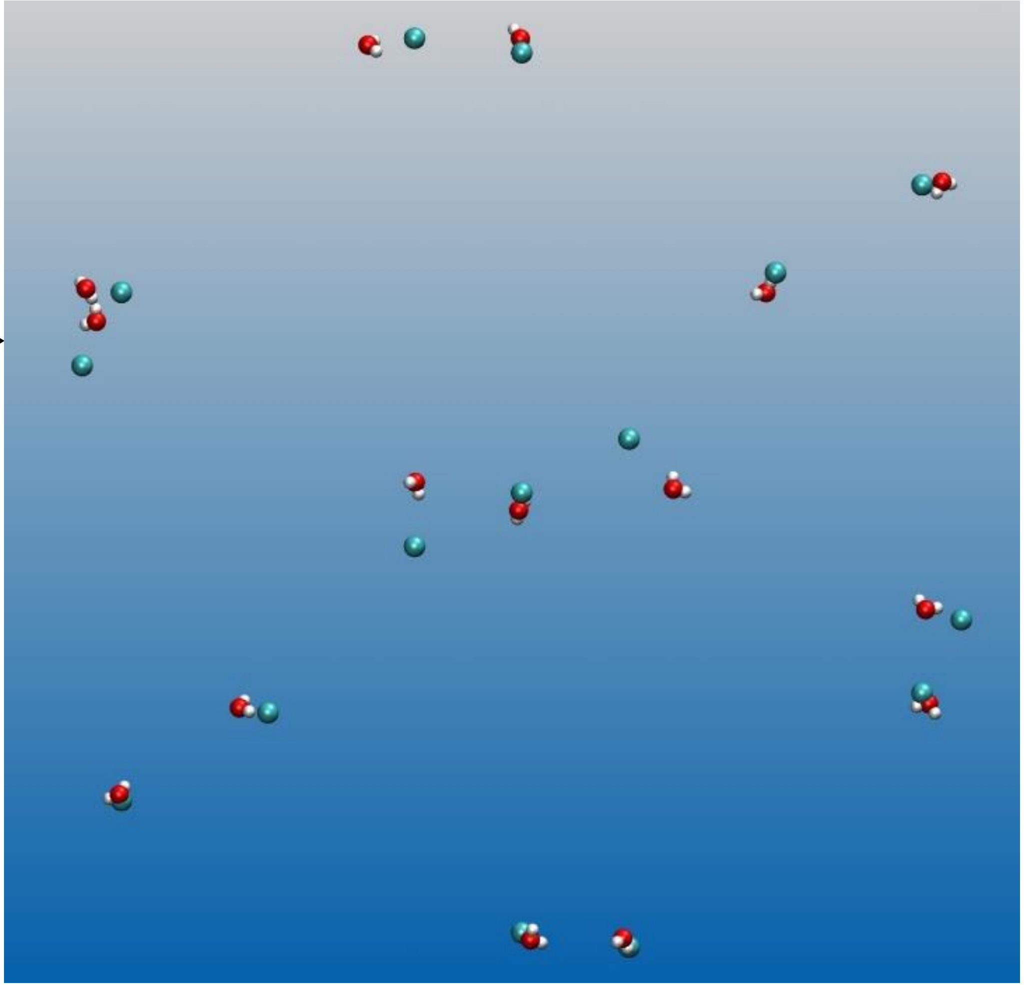
green: argon
white: guides



Disassembly of a water cluster

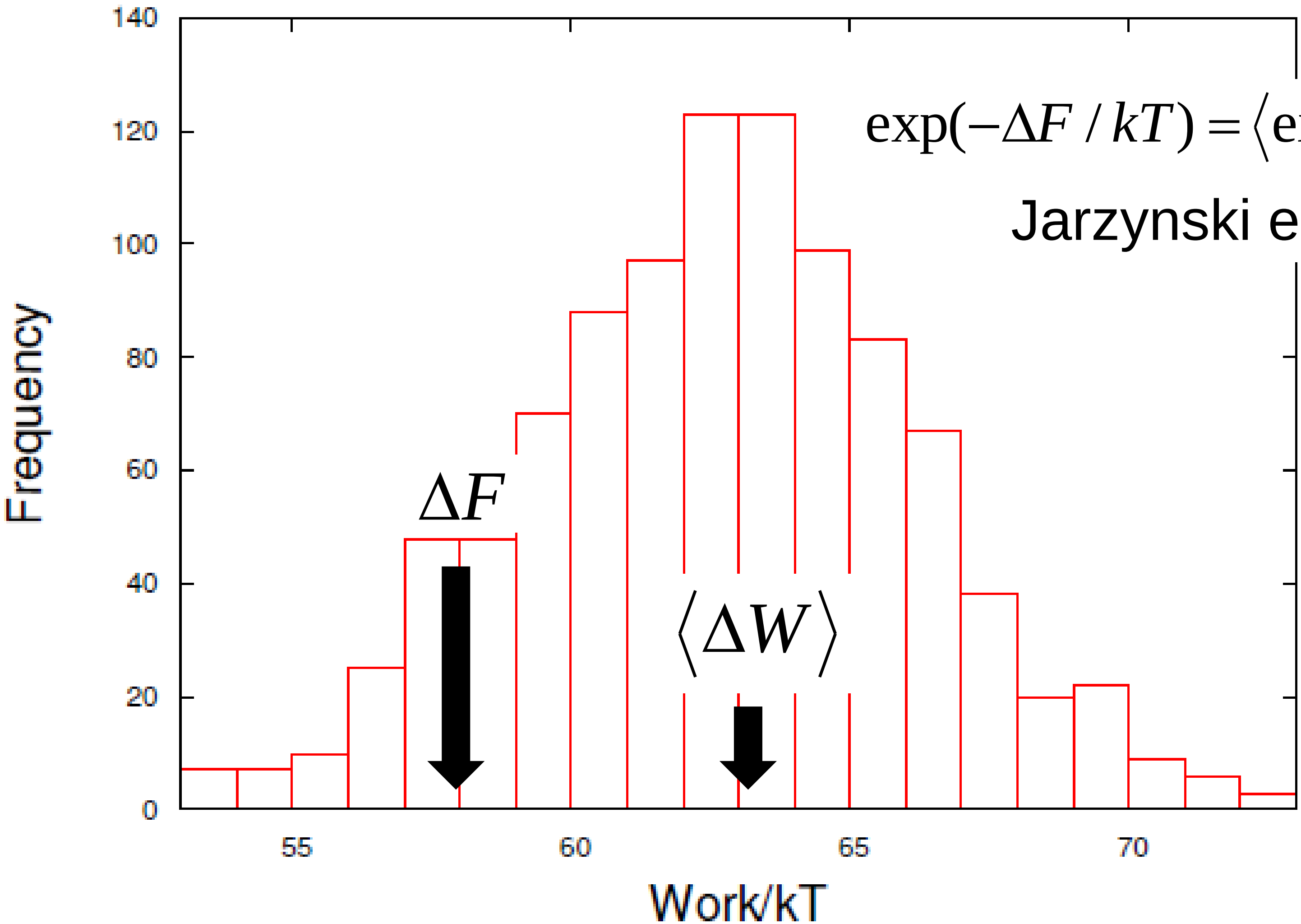
TIP4P/2005 force field





red: oxygen
white: hydrogen
blue: guide particles

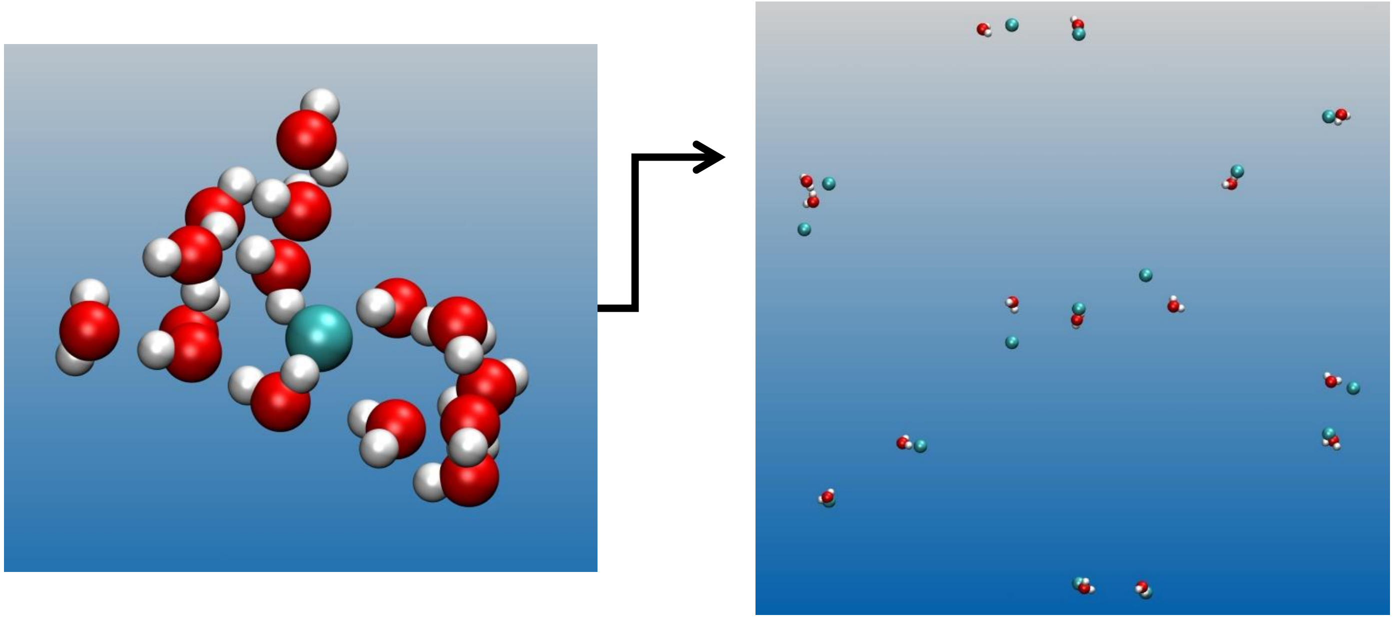
Distribution of mechanical work ΔW



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

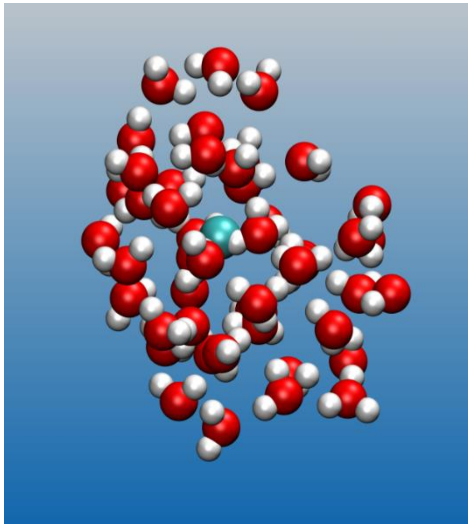
Jarzynski equality

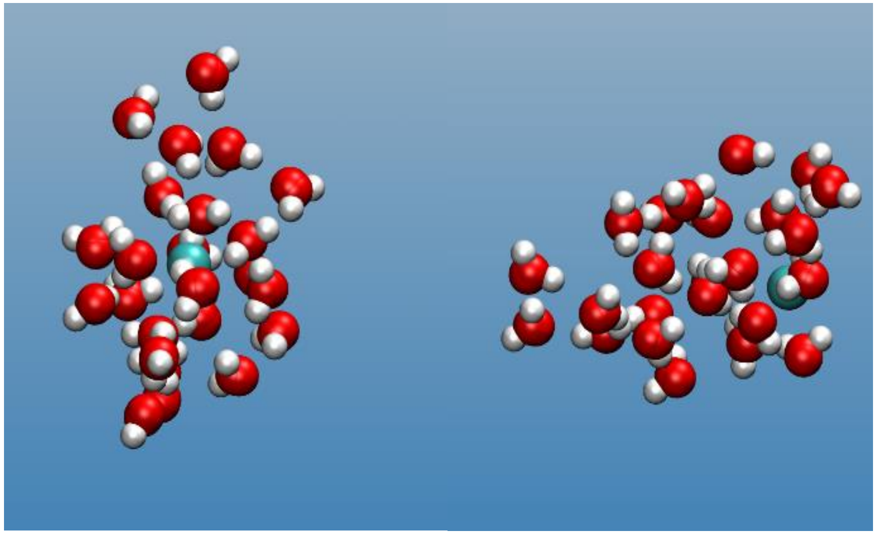
Extraction of excess free energy



$$\Delta F_{\text{dis}} = -F_s(N) + \text{other terms}$$

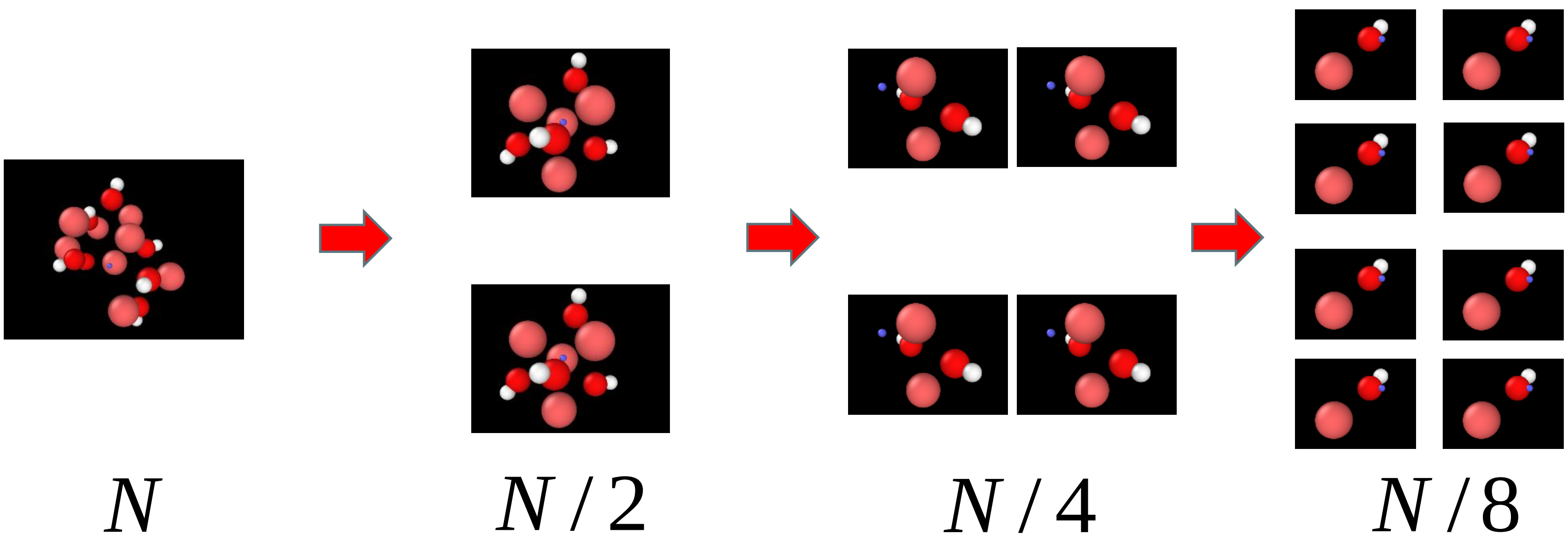
Guided *mitosis*: two guide particles



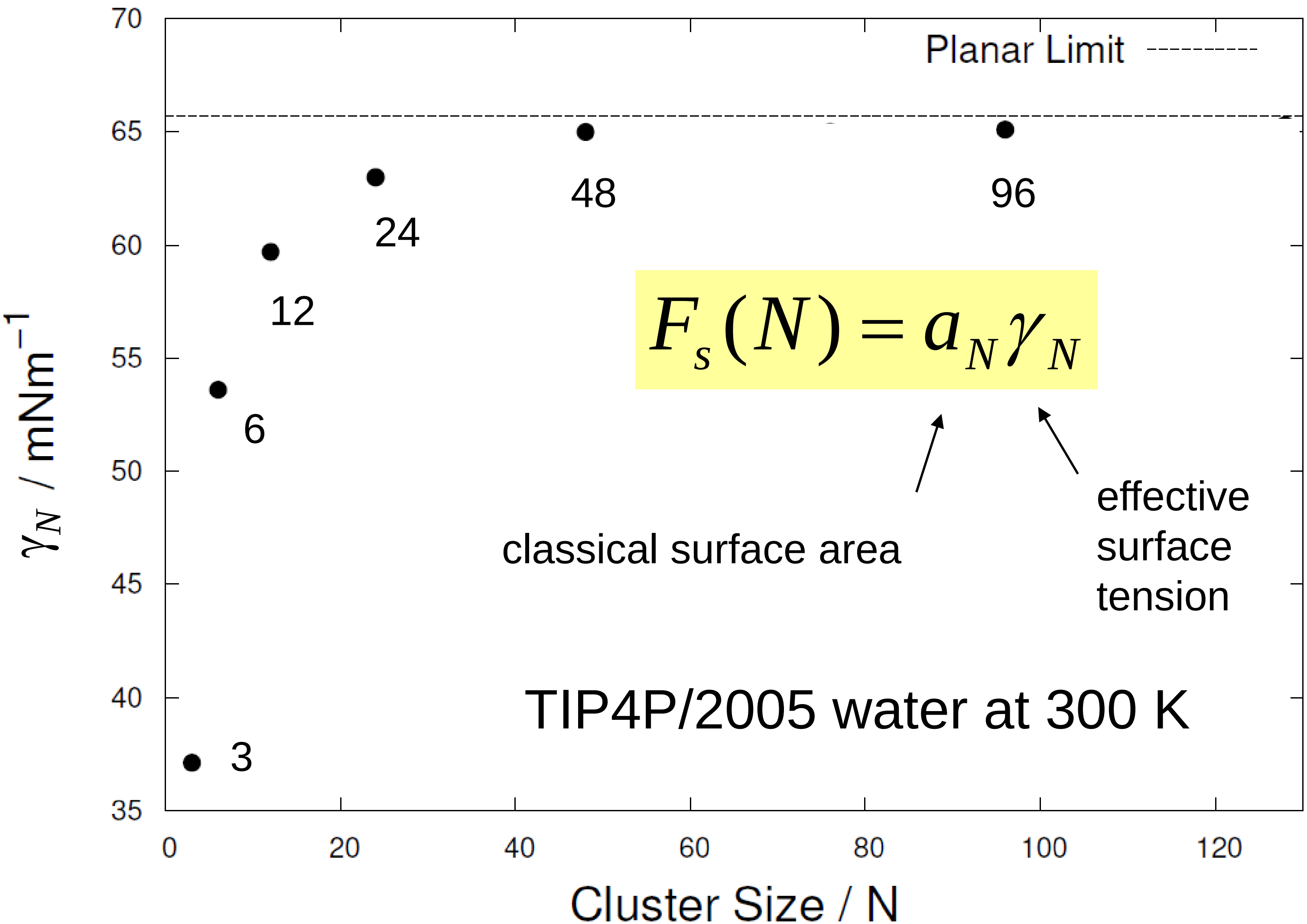


$$\Delta F_{\text{mit}} = 2F_s(N/2) - F_s(N) + \text{other terms}$$

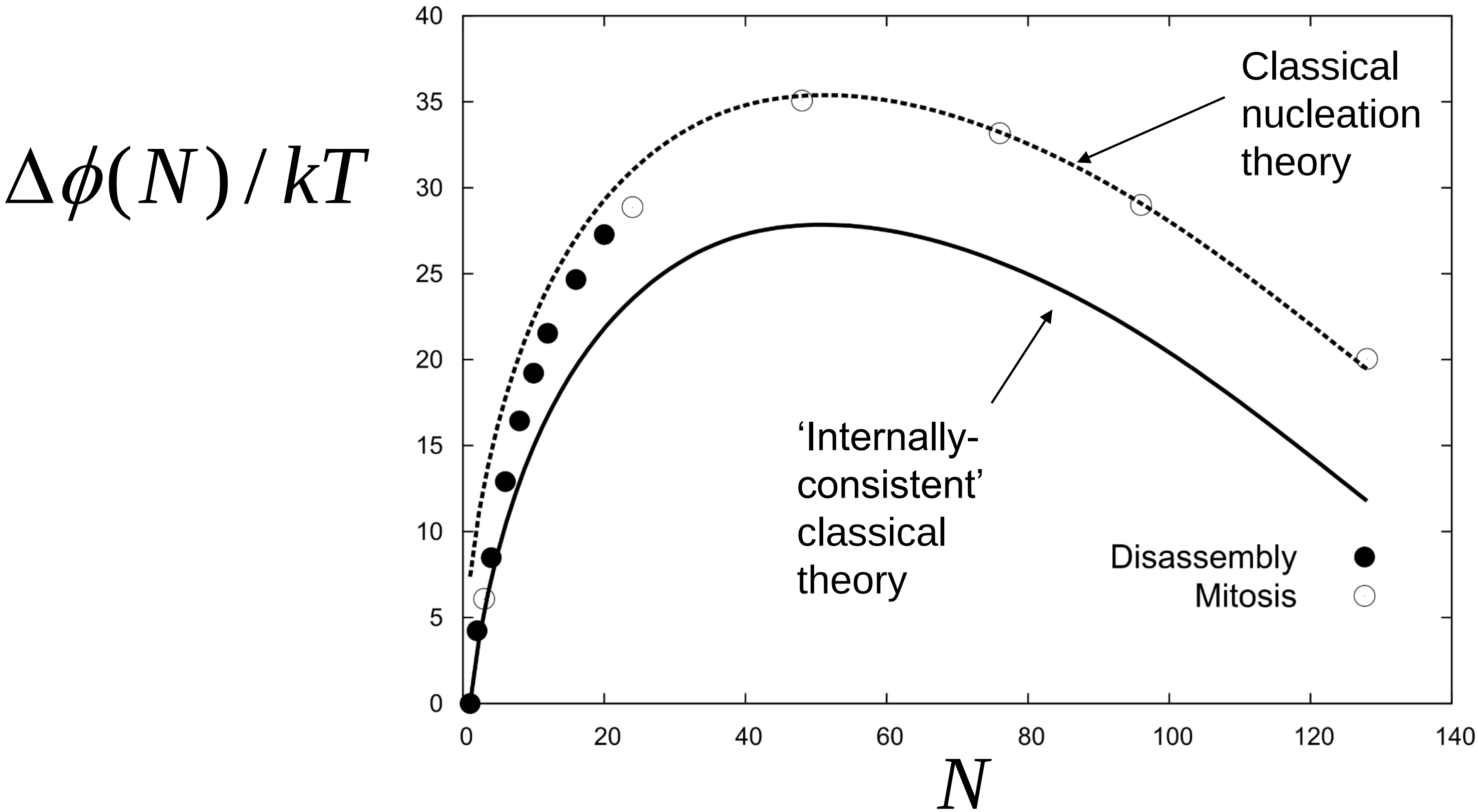
Repeated mitosis for full disassembly



Effective surface tension for water

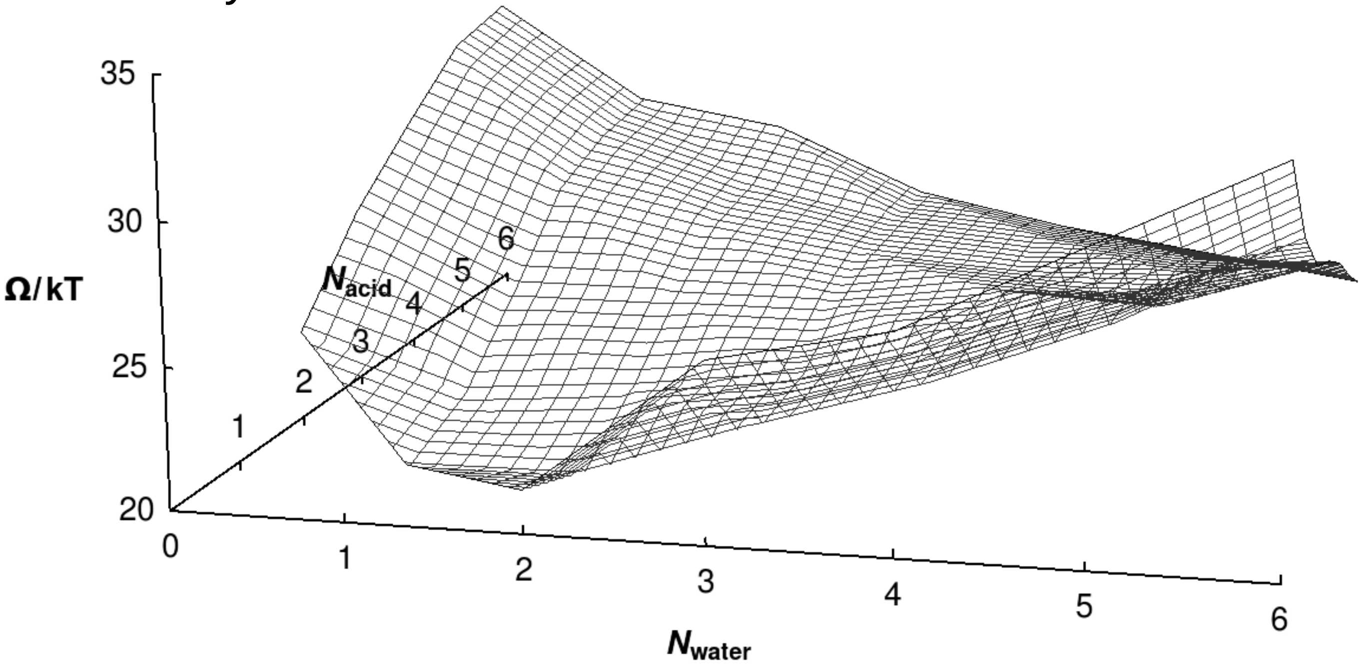


Nucleation barrier, TIP4P/2005 water at 300K, with vapour supersaturation S=3.76

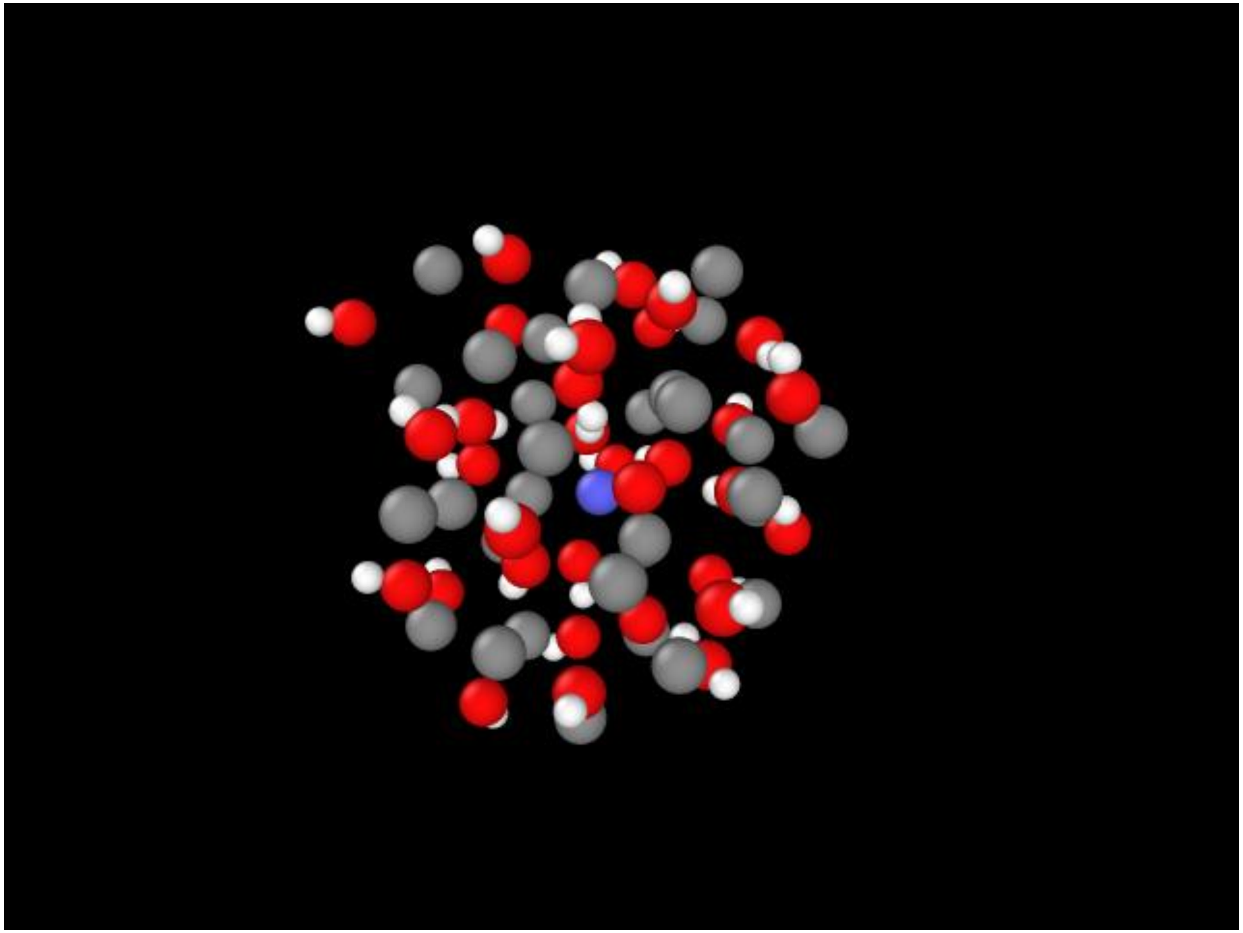


Sulphuric acid/water

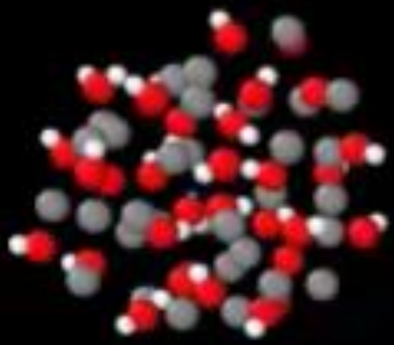
Availability/kT



More complex case: CsOH cluster mitosis

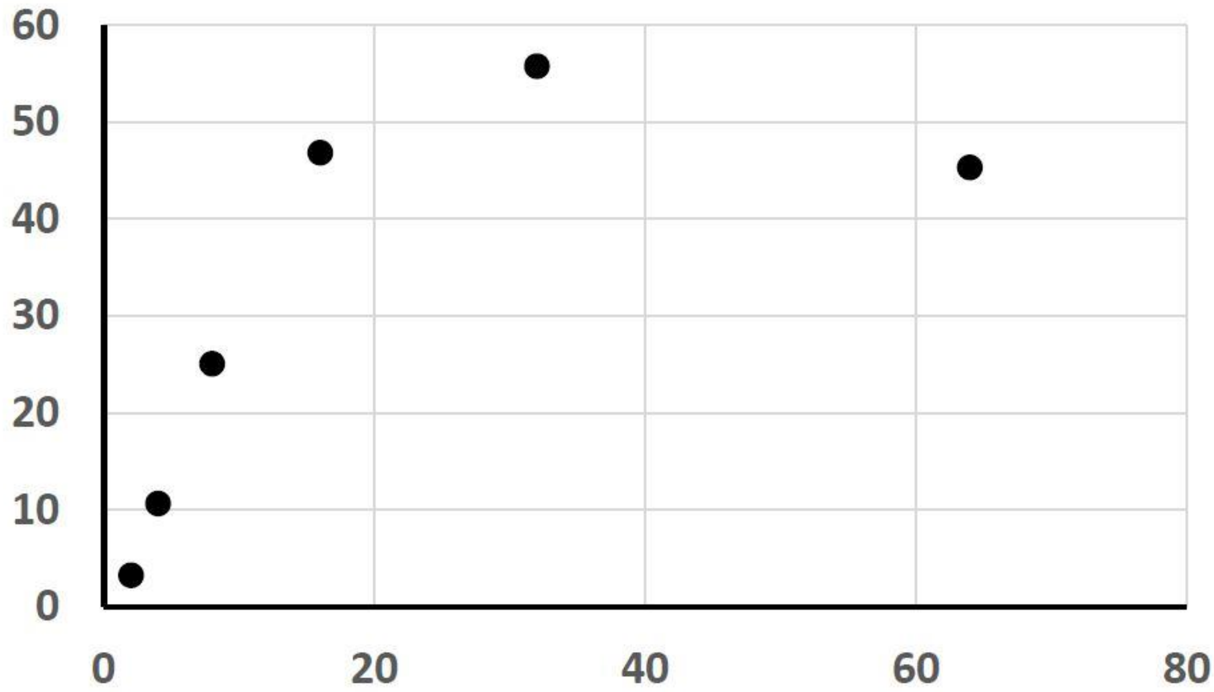


caesium: grey
oxygen: red
hydrogen: white



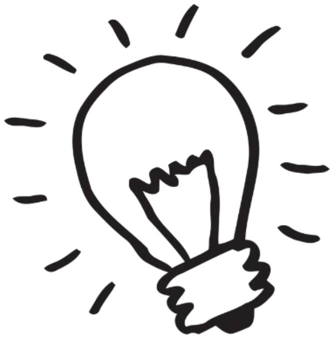
Nucleation barrier for CsOH (tentative results)

$$\Delta\phi(N)/kT$$



- Vapour density 10^{-6} Å^{-3} , temperature 1000 K
- Based on empirical potentials for Cs, O and H

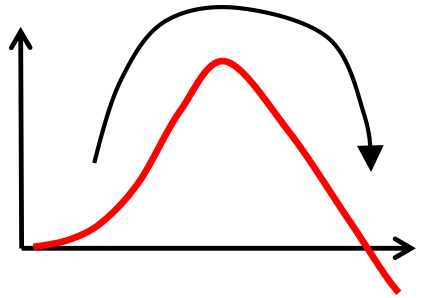
Other methods for computing free energy are available!



- Harmonic cluster model
  - Vehkamäki, etc
- Umbrella sampling Monte Carlo
  - ten Wolde, Frenkel, Chen, Siepmann, Nellas, etc
- Thermodynamic integration
  - Hale, Kathmann, etc


ARE WE THERE YET !?!
MATT GROENING

THE PLAN



1. The long history of nucleation theory
2. What is the *nucleation barrier* made of?
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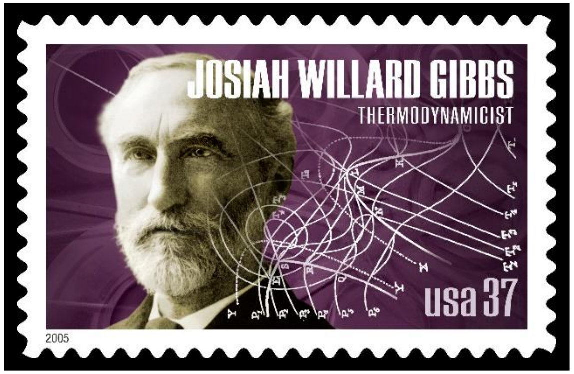
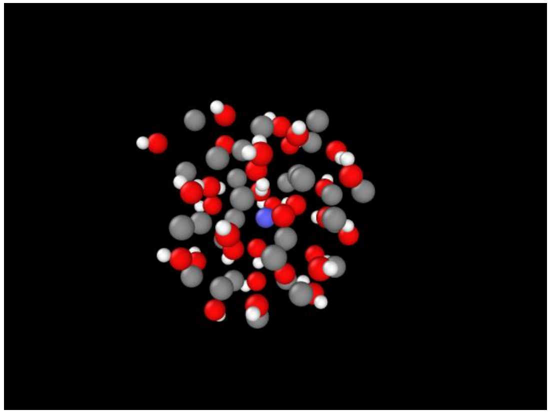
4. **Entropy production in nucleation**



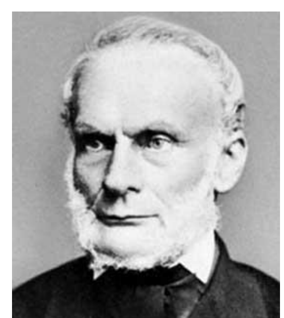



Caution: Entropy

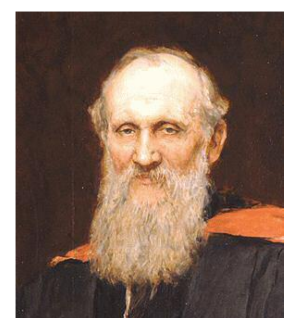
Part 4: Entropy and the nucleation process

- Component of the nucleation barrier
- Expensive to compute
- ‘Arrow of time’

Carnot



Clausius



Kelvin

Boltzmann

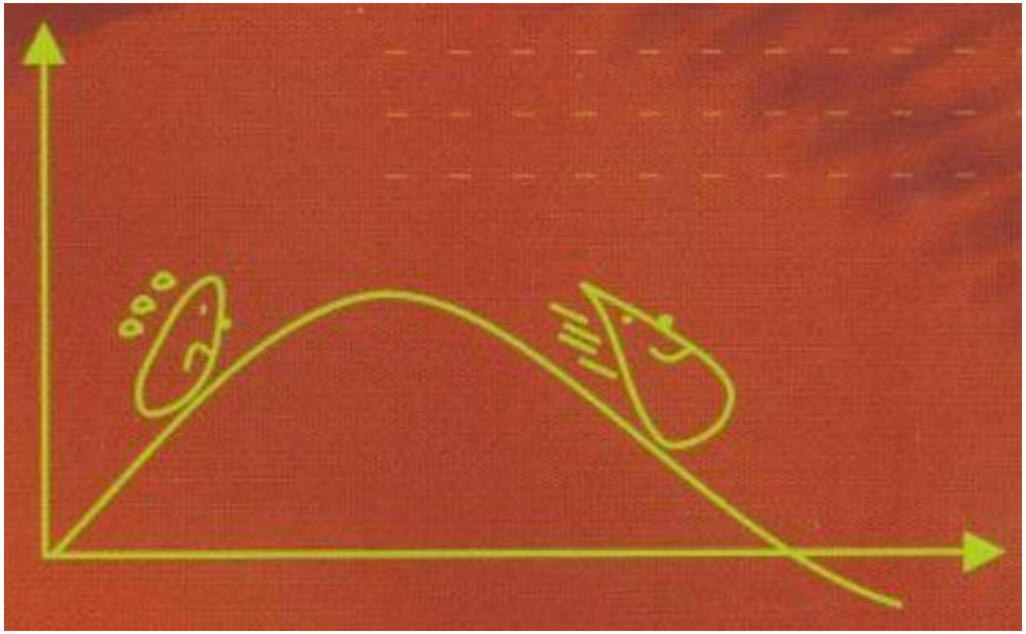
Second law of thermodynamics

Die Availabilitie der System strebt einem **Minimum** zu (after Clausius 1865)

$$\Delta S_{\mathrm{world}} = -\Delta A_{\mathrm{system}} / T \geq 0$$

Is the second law broken during nucleation?

- How can a cluster climb over an availability barrier?



size N in molecules

Vehkamäki: *Classical nucleation theory in multicomponent systems*, Springer 2006

A warning:

… if your theory is found to be against the second law of thermodynamics…

Arthur Eddington

***The Nature of the Physical World* (1928)**

A warning:

… if your theory is found to be against the second law of thermodynamics I can give you no hope…

Arthur Eddington

***The Nature of the Physical World* (1928)**

A warning:

… if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

Arthur Eddington

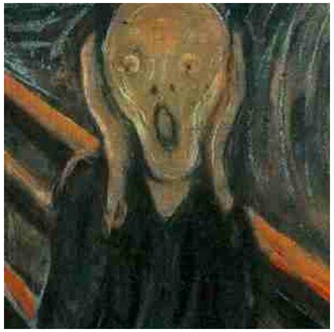
***The Nature of the Physical World* (1928)**

Is the second law broken during nucleation?

Remember Betteridge’s law!

No

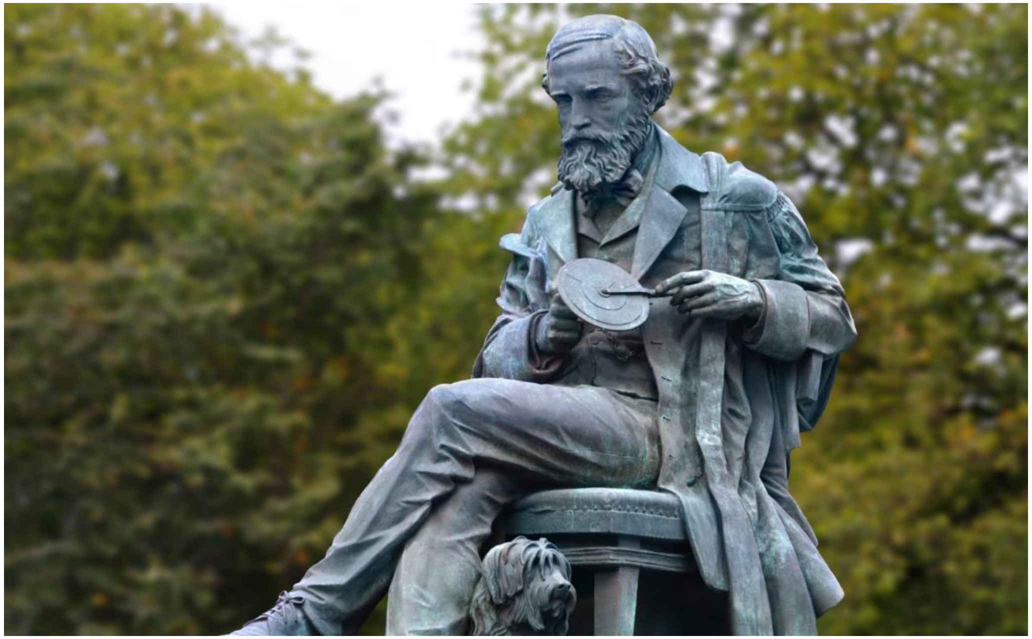
…. but ….



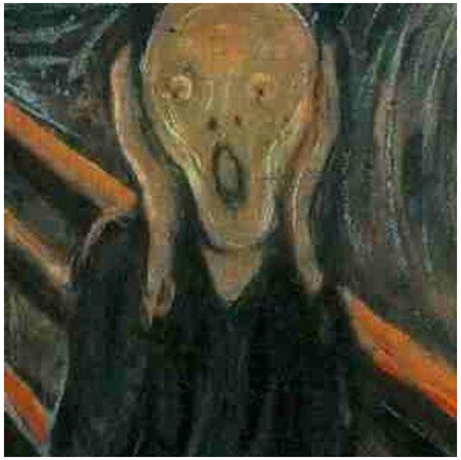
- There **are** negative fluctuations in entropy
  - but **not** associated with barrier-hopping
- Let us consider the modern understanding of the second law

James Clerk Maxwell >150 years ago

…the second law is continually being violated…. in any sufficiently small group of molecules …



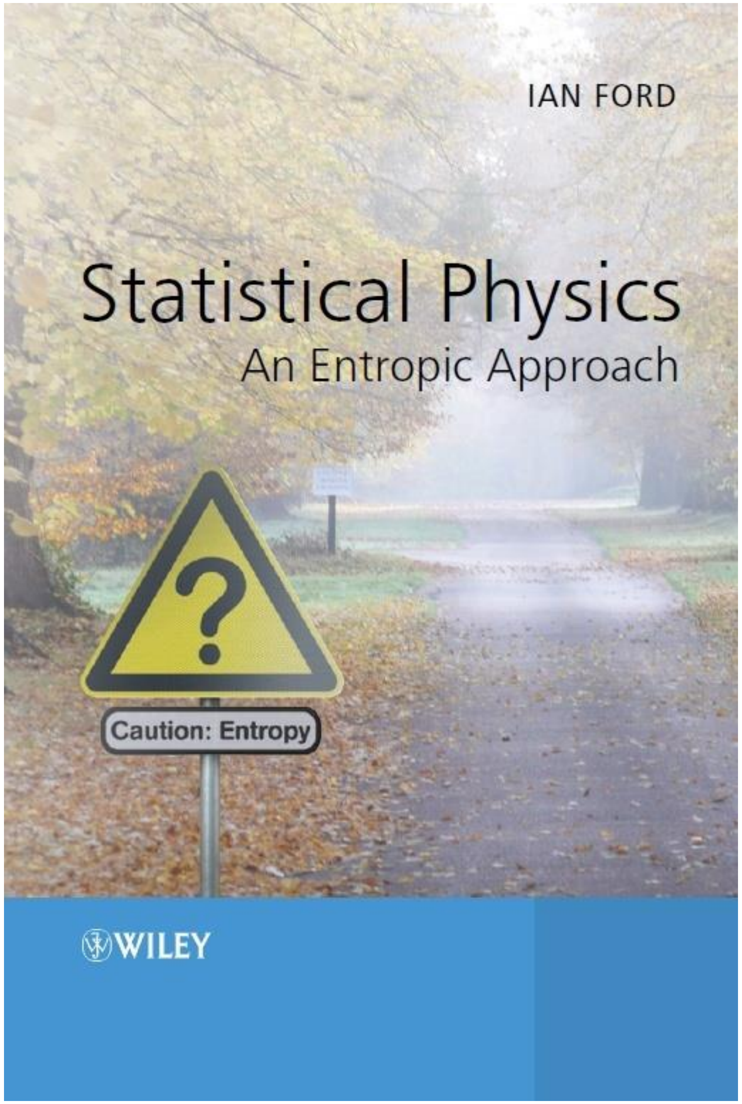
Apparent breakage of the second law



- For small systems, we must expect the unexpected
- ‘Fluctuation relations’
  - quantify the extent to which the second law can be broken

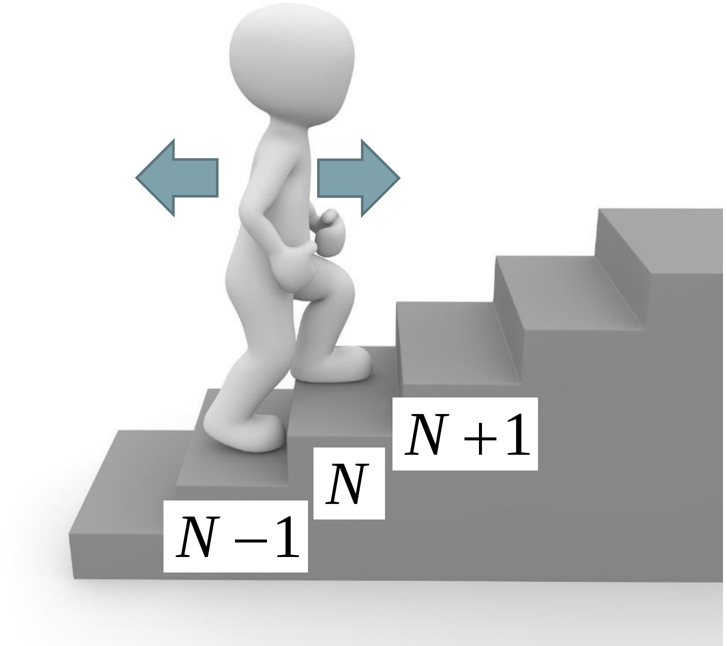
Advertising alert!

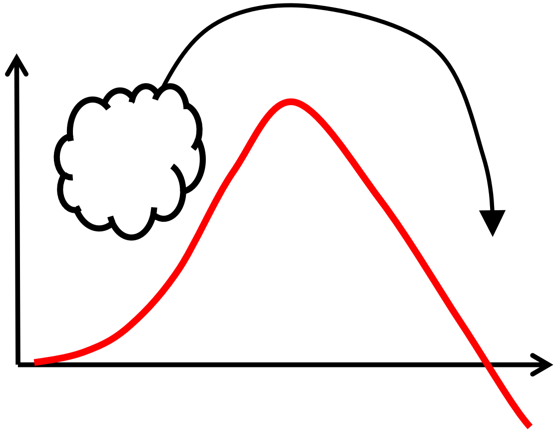
- Ford, *Statistical Physics: an entropic approach* (Wiley, 2013)



Nucleation and the second law

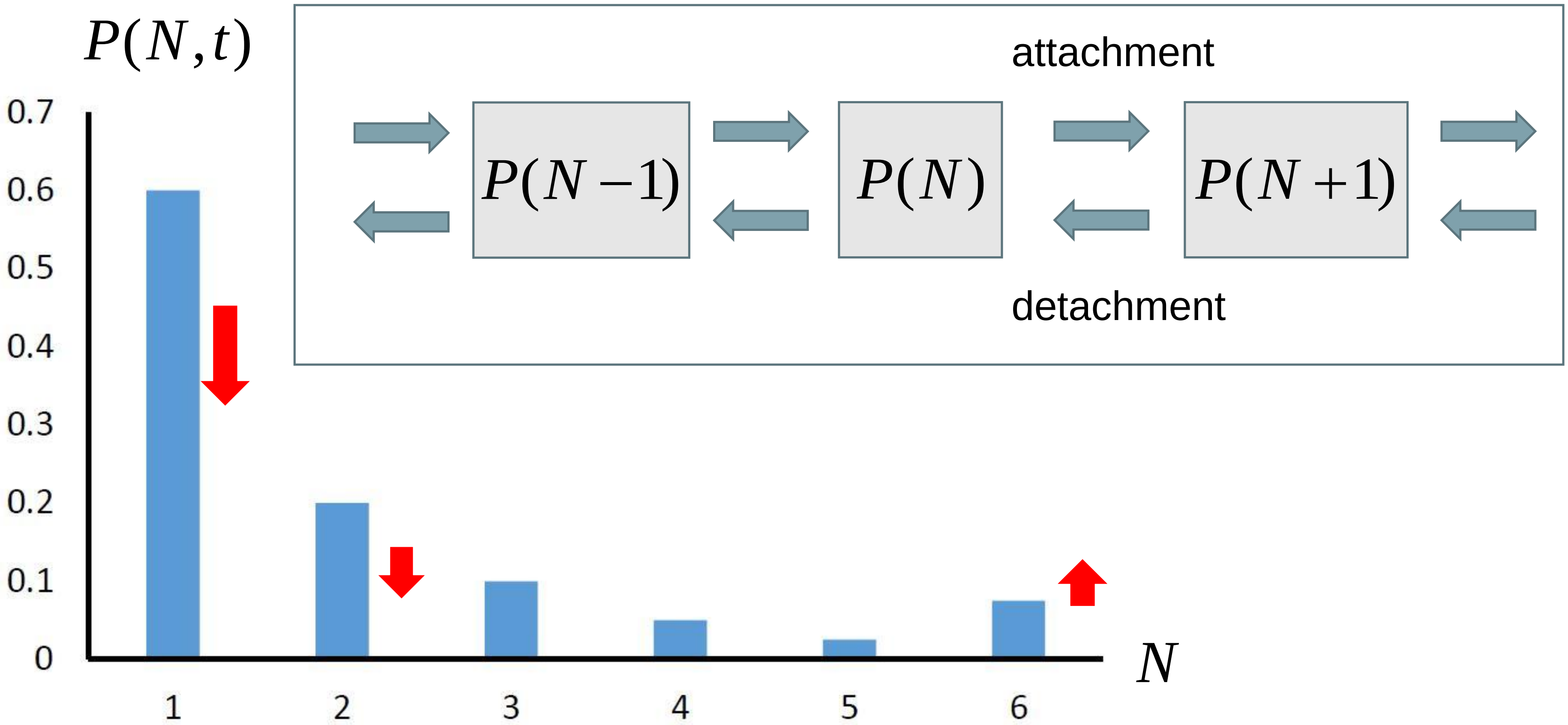
- Climbing the barrier is not the only contribution to total entropy production
- Further contribution from ***uncertainty*** in the size of the cluster





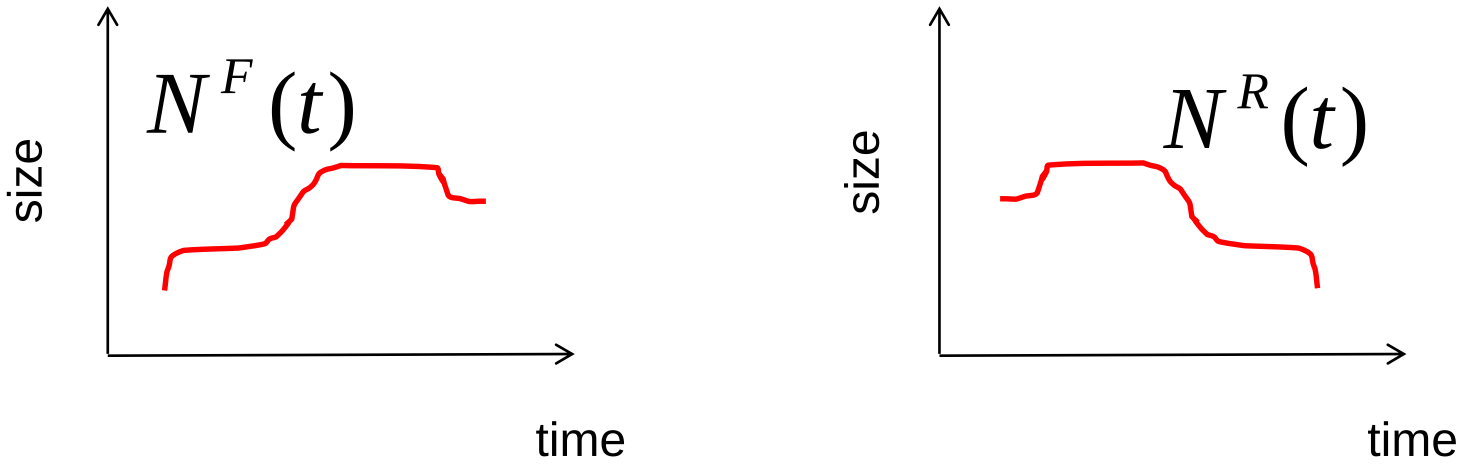
Master equations

- Probability $P(N,t)$ that a cluster assumes size N



Development of stochastic thermodynamics

- based on comparing probabilities of forward and backward dynamics



Definition of entropy production:

$$\Delta s_{\mathrm{tot}} = k \ln\left(\frac{\mathrm{prob(forward\ trajectory)}}{\mathrm{prob(reverse\ trajectory)}}\right)$$

Sekimoto, Seifert, etc

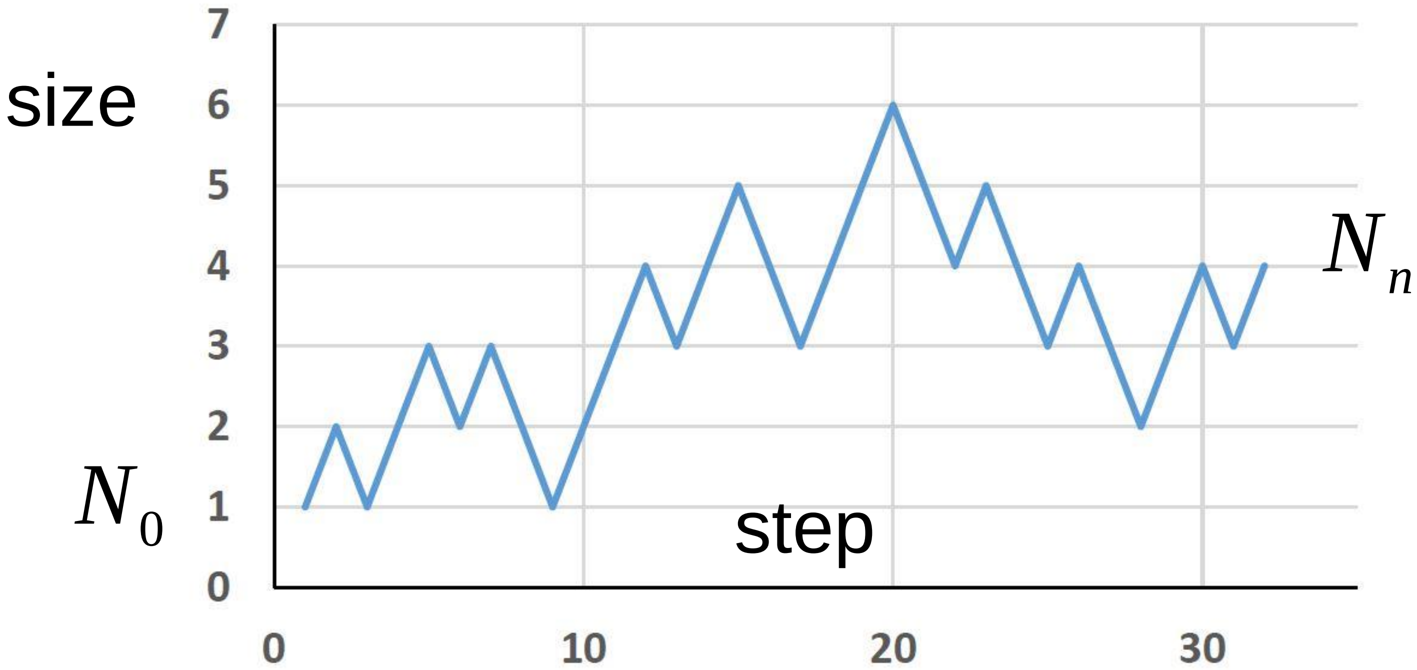
trajectories with positive and negative Δs_{tot}

and a **second law**

$$\Delta S_{\mathrm{tot}} = \langle \Delta s_{\mathrm{tot}} \rangle \geq 0$$

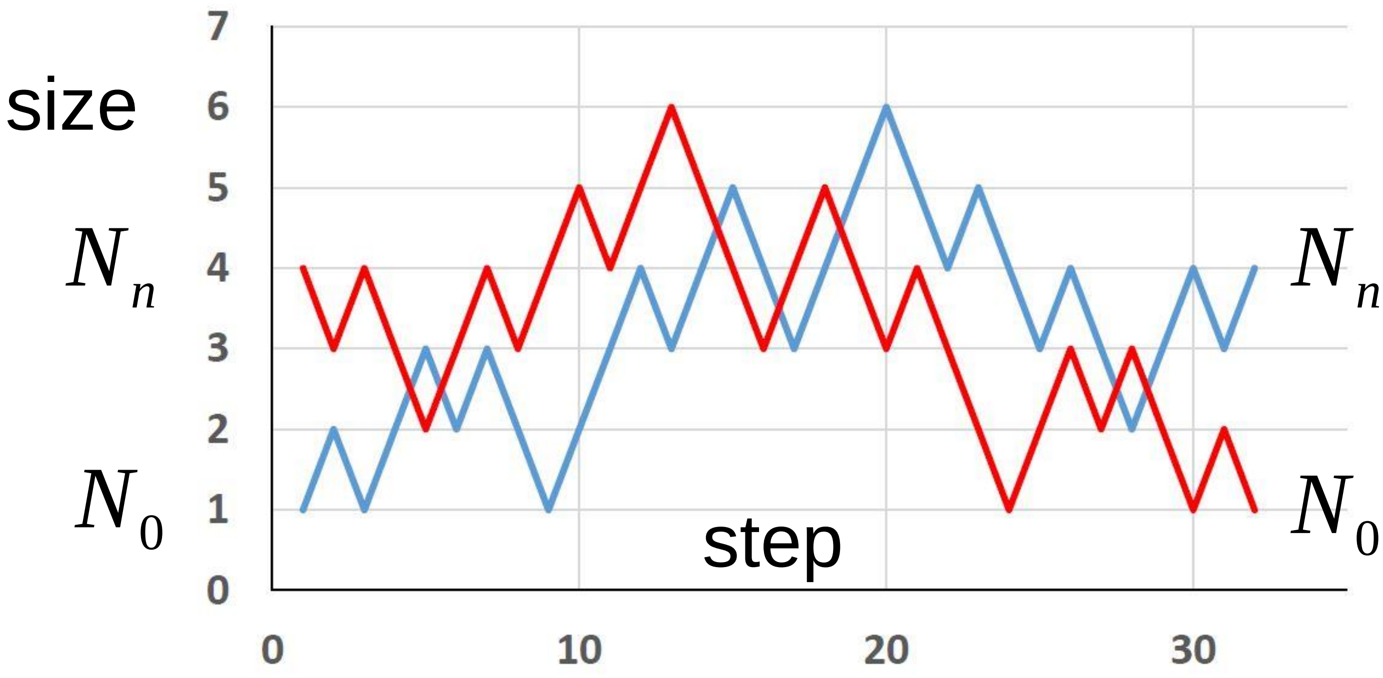
(brackets denote averaging over trajectories)

Forward and backward cluster trajectories and their probabilities



$$\text{prob(forward)} = \mathrm{P}(N_0 \to N_1 \cdots \to N_n)$$

Forward and backward cluster trajectories and their probabilities



$$\text{prob(forward)} = \mathrm{P}(N_0 \to N_1 \cdots \to N_n)$$

$$\text{prob(backward)} = \mathrm{P}(N_n \cdots \to N_1 \to N_0)$$

Entropy production for a nucleating cluster

$$\Delta s_{\text{tot}} = k \ln\left(\frac{\text{prob(forward trajectory)}}{\text{prob(backward trajectory)}}\right)$$

$$\Rightarrow \quad \boxed{\Delta s_{\text{tot}}(t) = -\Delta A(N)/T +} \;\cdots$$

Entropy production for a nucleating cluster

$$\Delta s_{\mathrm{tot}} = k \ln\left(\frac{\text{prob(forward trajectory)}}{\text{prob(backward trajectory)}}\right)$$

$$\Delta s_{\mathrm{tot}}(t) = -\Delta A(N)/T + \Delta\left[-k \ln P(N,t)\right]$$

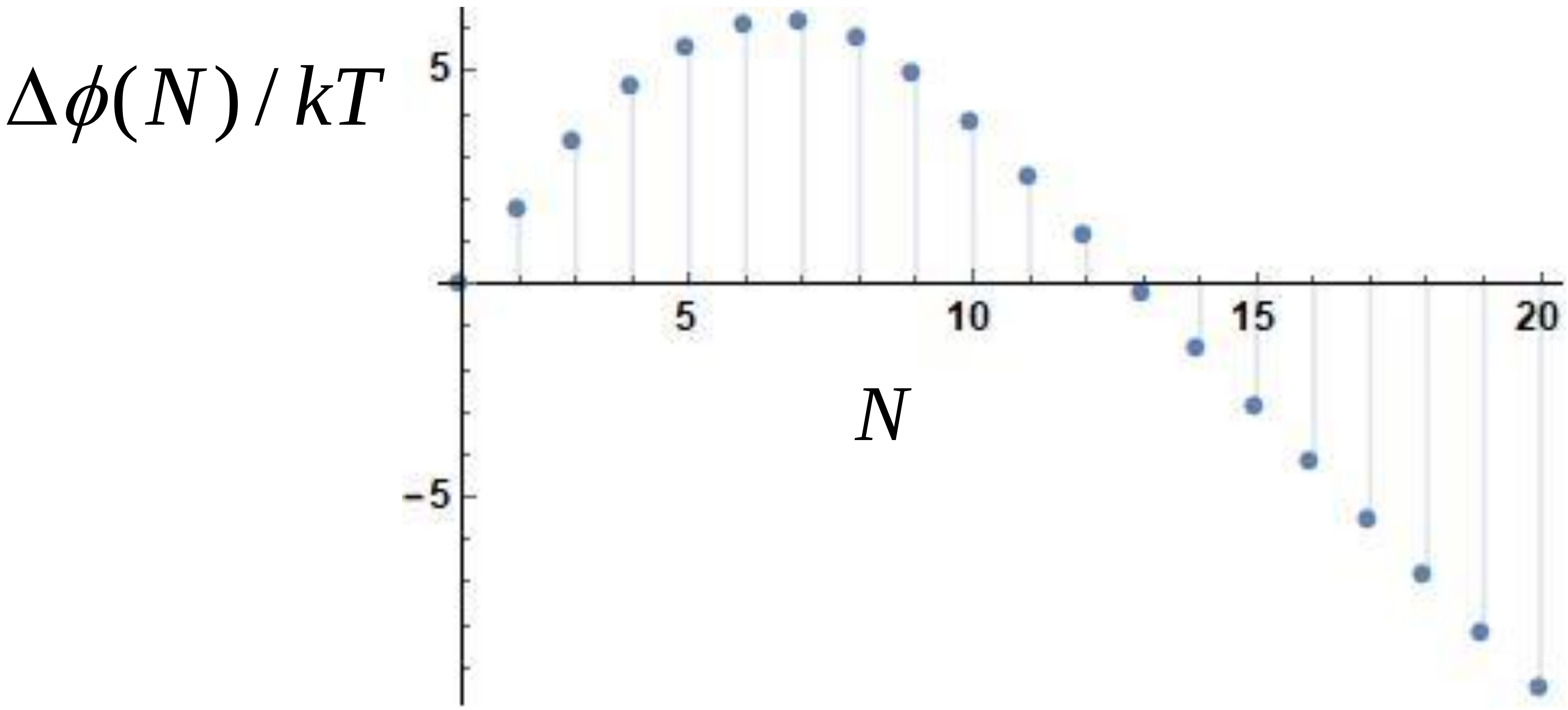
Interpreted as the change in *stochastic entropy* of the **environment**

Change in *stochastic entropy* of the **cluster**

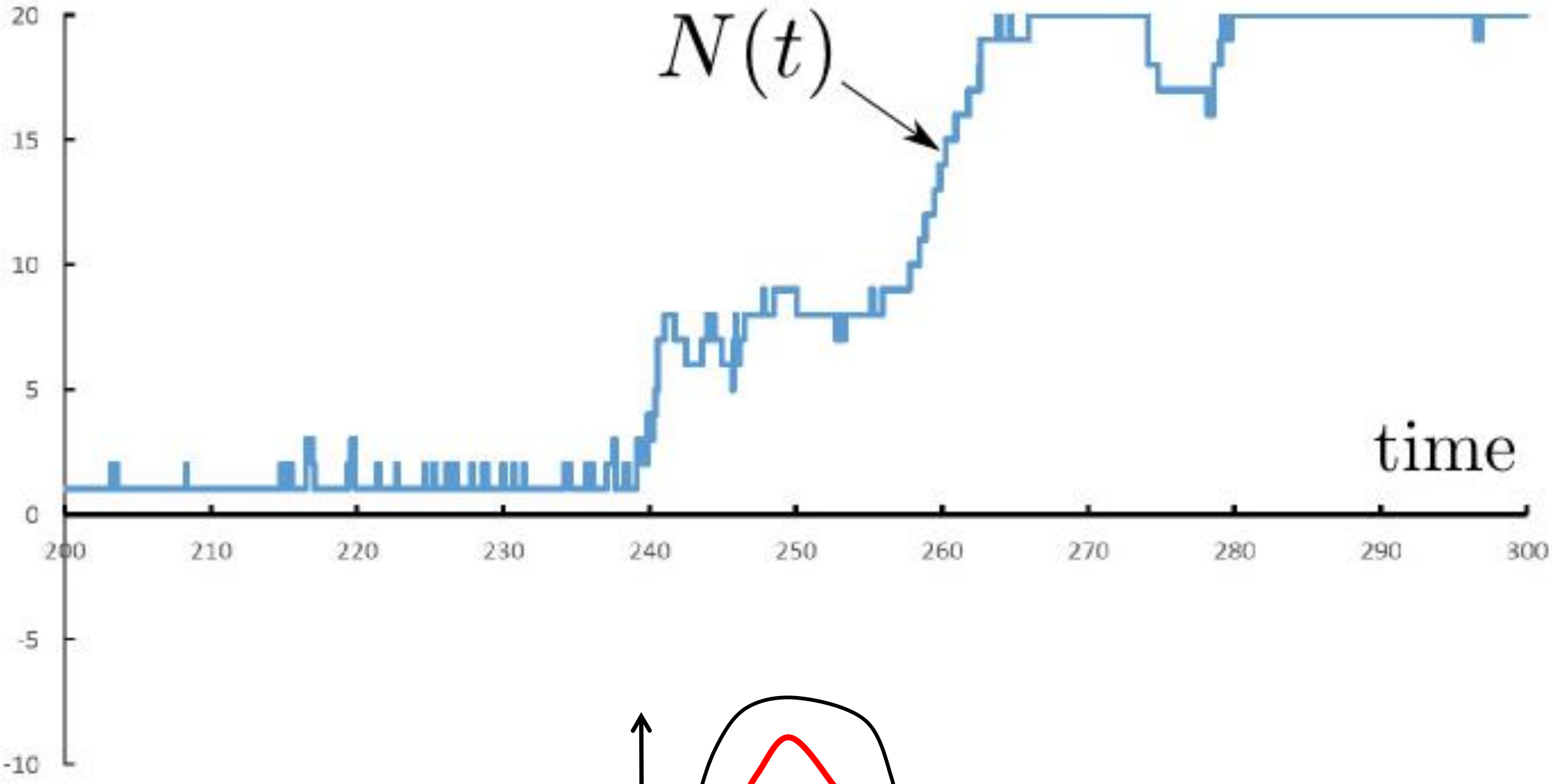
[Or change in the 'surprisal']

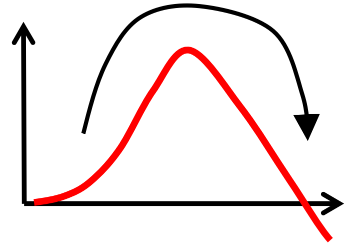
I.J. Ford and R.E. Spinney, Phys. Rev. E 86 (2012) 021127.

Toy model: nucleation barrier



Entropy production of a nucleation event





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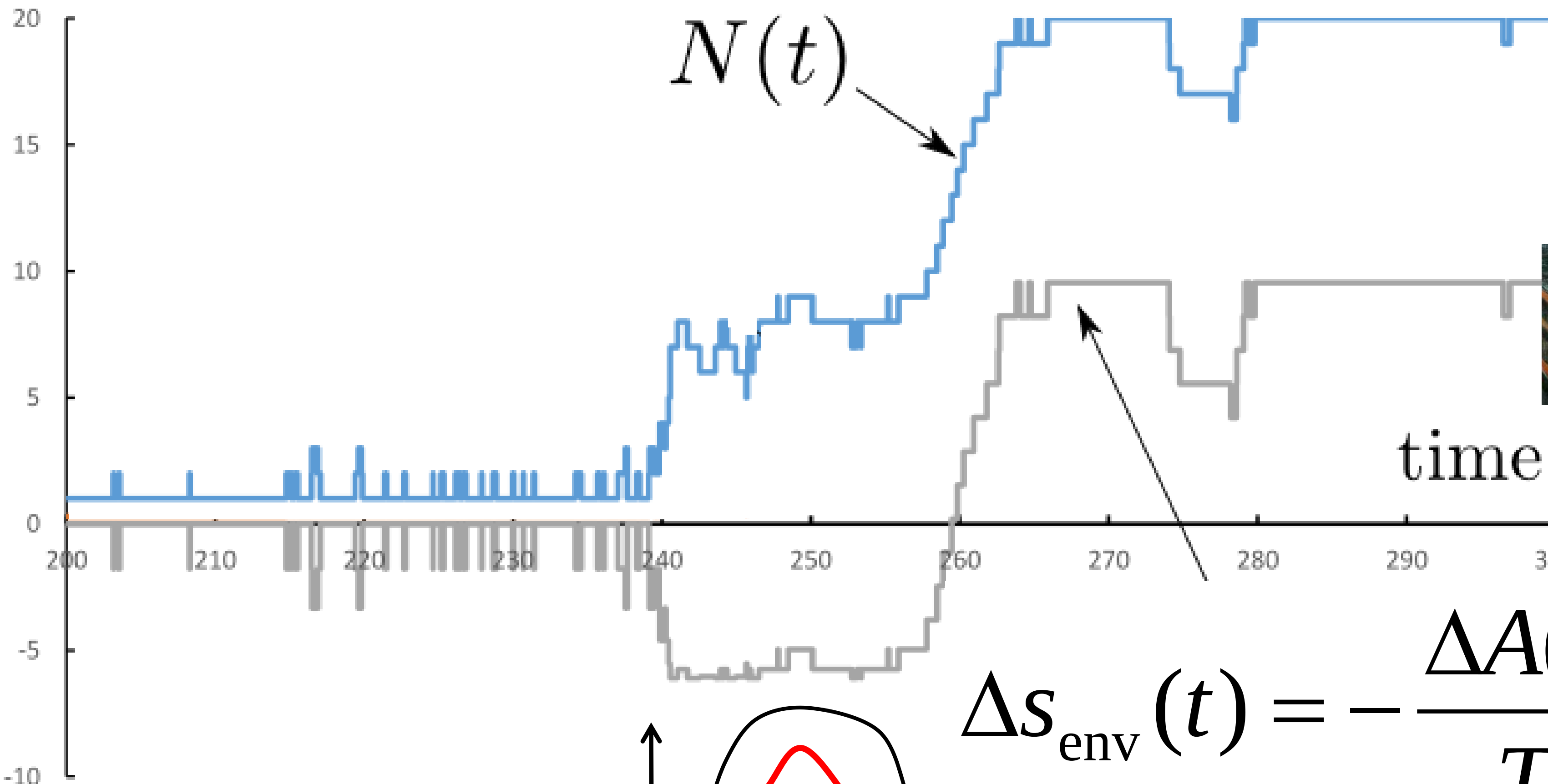
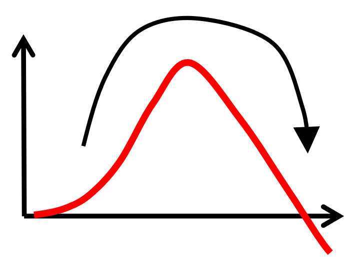
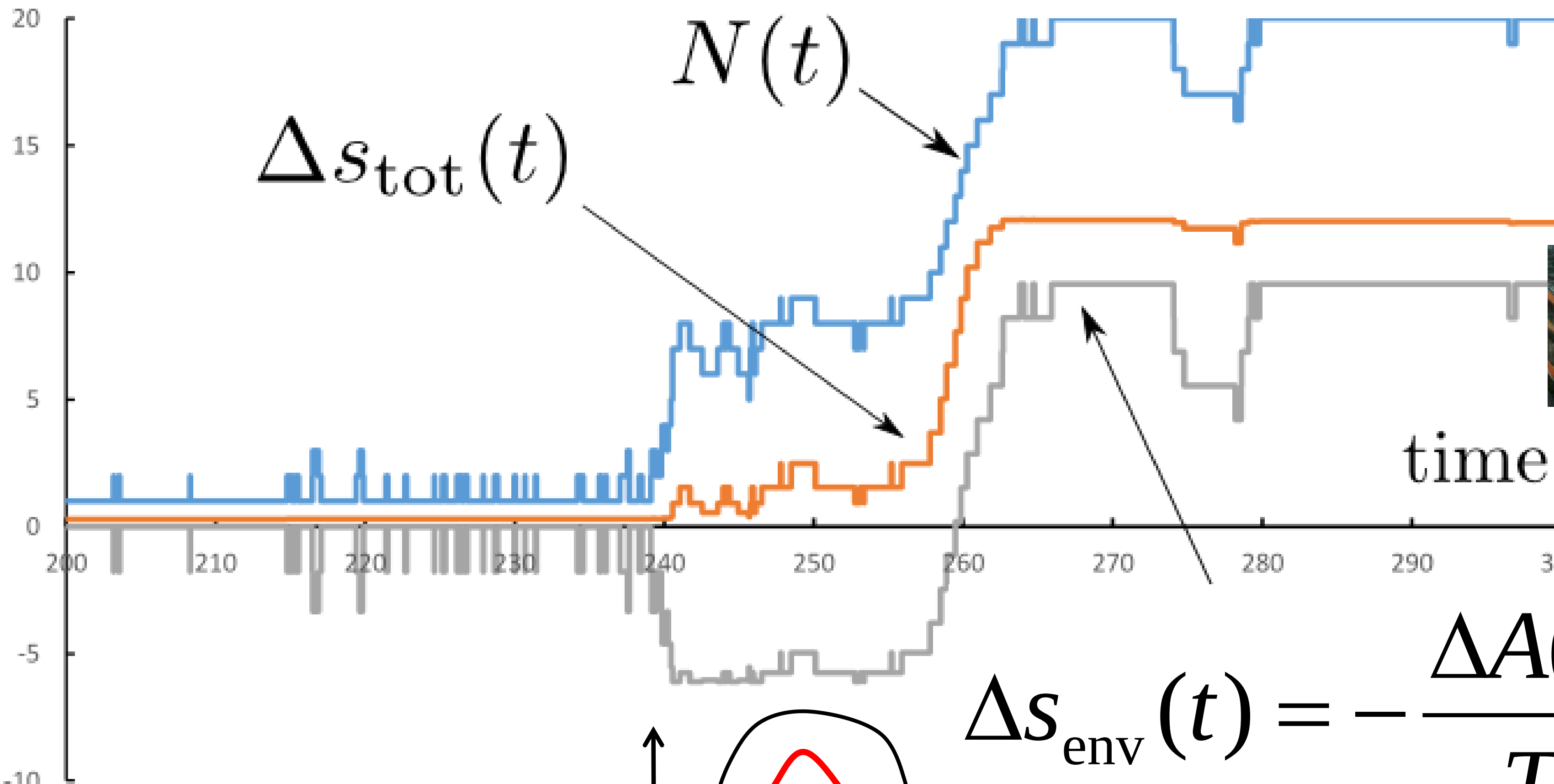
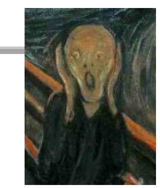


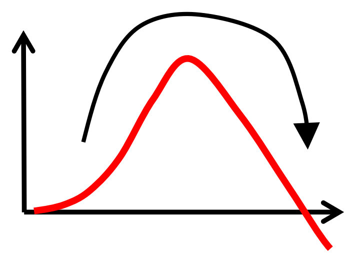


$$\Delta s_{\mathrm{env}}(t) = -\frac{\Delta A(t)}{T}$$

Entropy production of a nucleation event

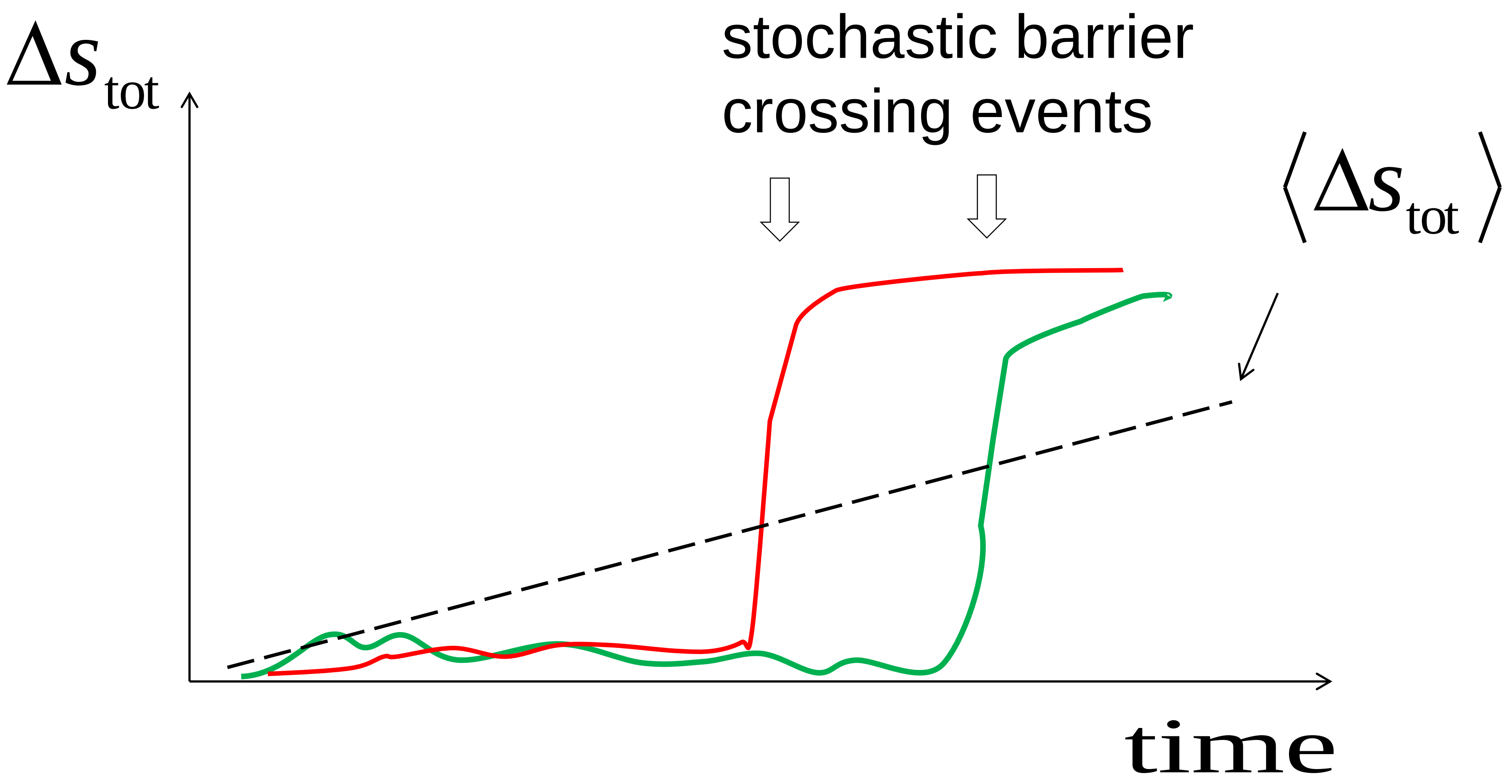






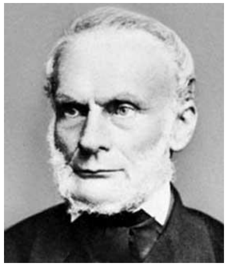
$$\Delta s_{\mathrm{env}}(t) = -\frac{\Delta A(t)}{T}$$

Stochastic entropy production and its average

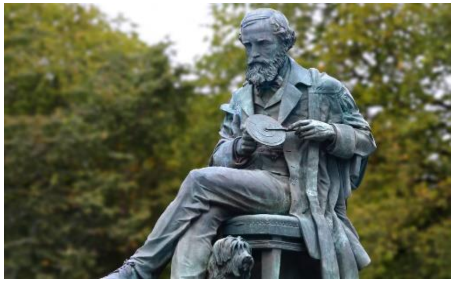


The second law survives
(as a statistical expectation)

- Barrier crossing involves
  - an increase in **availability potential**
    - a <u>decrease</u> in entropy of the world
  - and a 'surprising' fluctuation in cluster size
    - larger increase in entropy
  - plus minor fluctuations in total entropy



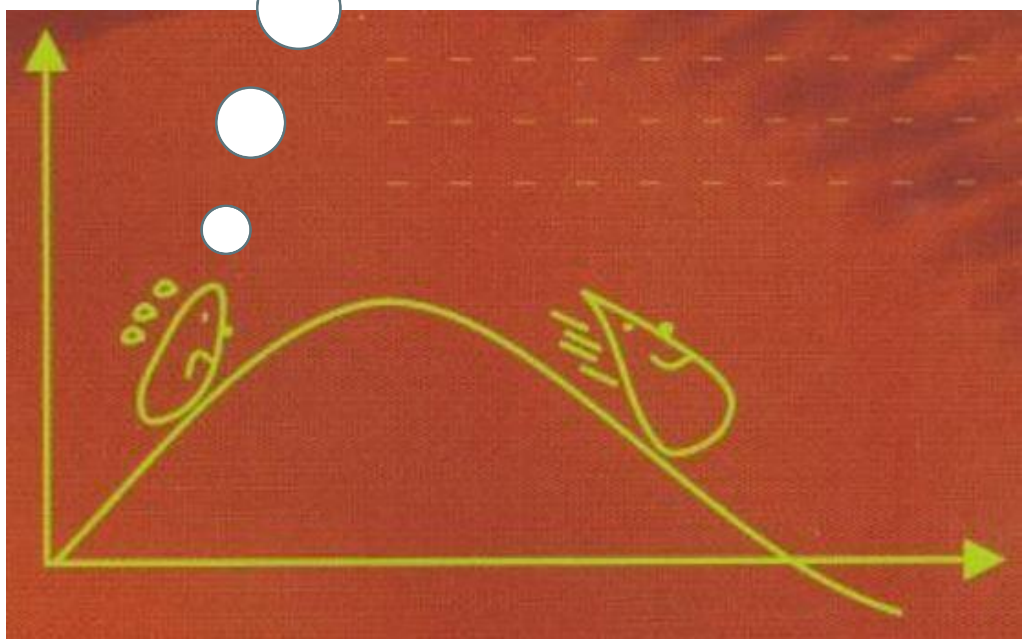
Clausius and Maxwell are both happy



The picture:

I'm surprised to be doing this…..

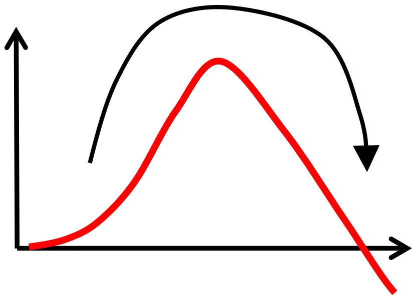
$\Delta\phi$



size N in molecules

Vehkamäki: *Classical nucleation theory in multicomponent systems*, Springer 2006

THE PLAN



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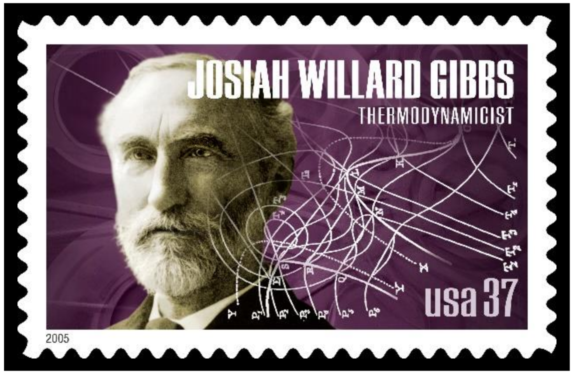

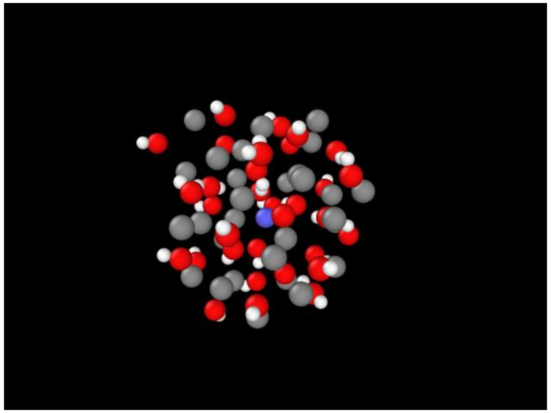

You have reached your destination

Where are we?…

You have reached your destination

- Status of the theory of aerosol nucleation?
  - a variety of approaches
  - my favourite: statistical mechanics of single clusters
- Can we account for experimental nucleation rates?
  - some successes where high quality data available
  - molecular force fields needed, calculations are expensive
- What is nucleation theory for?
  - a predictive tool
  - interpretation of experimental data (e.g. nucleation theorems)
  - framework for thinking about barrier crossing

Thanks for listening!