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Atmospheric particle formation

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- Heterogeneous nucleation and activation
- Why do we care?

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Nucleation

Basic concepts and theory

What is nucleation?

- Formation of microscopic regions of **stable phase** within a **metastable mother phase**

Examples:

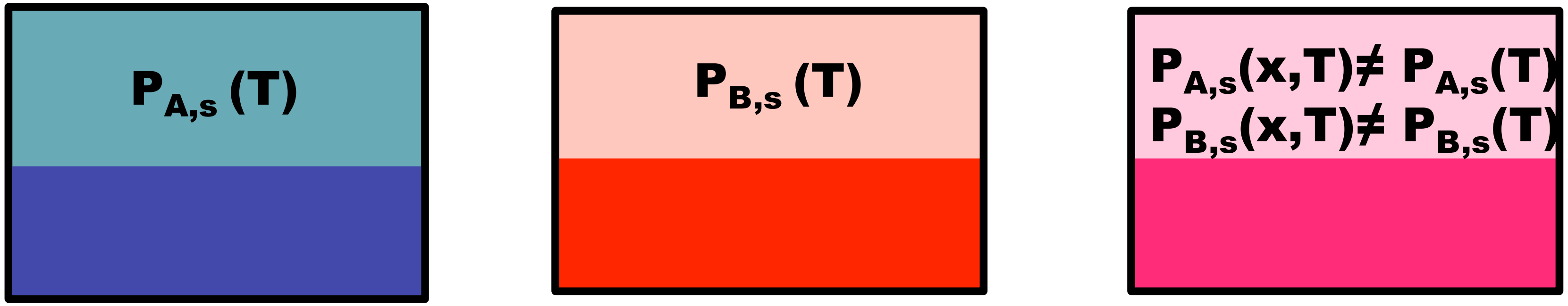
Metastable mother phase:	**Stable phase**:
supercooled liquid	ice crystals
supersaturated vapour	liquid droplets
supersaturated salt solution	salt crystals in the liquid
quark-gluon plasma	hadron matter
scattered cars on a road	a traffic jam

Example: Supercooled water

- Freezing point of bulk water is 0°C
- NOTE: Small clusters can have a lower freezing point
- Bulk water can stay liquid almost down to -42 °C (at P=1atm)
- Needs to be free on impurities and gas bubbles

- Cloud droplets (stratiform, cumulus)
  - Can freeze when hitting airplanes
  - Freezing rain – car windscreens – black ice
- Freezing can be initiated by
  - adding impurities, crystallization seeds
  - adding ice
  - shaking

Saturation vapour pressure



$P_{A,s}(T)$

$P_{B,s}(T)$

$P_{A,s}(x,T) \neq P_{A,s}(T)$

$P_{B,s}(x,T) \neq P_{B,s}(T)$

pure A

pure B

mixture of A and B
mole fraction x

Saturation vapour pressure is a property of the LIQUID
- **increases exponentially with temperature**
- **depends on liquid composition**

Above a liquid pool:

- **if the vapour pressure is higher than P_s, vapour condenses**
- **if the vapour pressure is lower than P_s, liquid evaporated**

- **Wet laundry dries faster in warm air**
- **Skin gets dry in the winter**
- **Breathing in the winter forms mist**

Saturation ratio measures the driving force for gas-liquid transition

$$S = \frac{P_i}{P_{i,s}(x,T)}$$

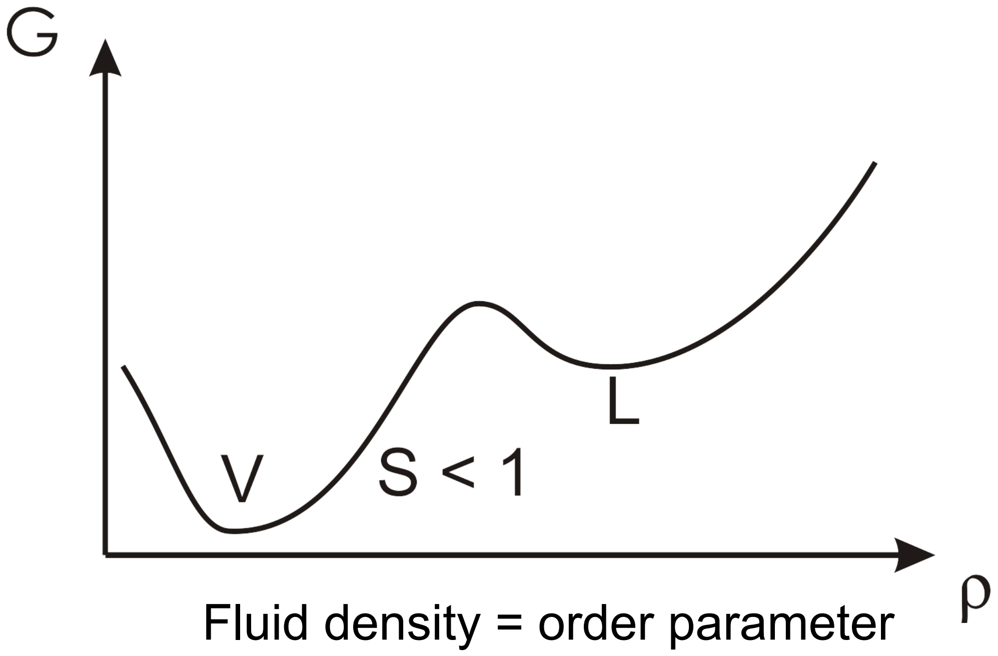
Saturation vapour pressure over a flat surface of a liquid mixture

$$P_{i,s}(x,T) = \Gamma_i(x,T) \cdot x_i \cdot P_{i,pure}(T)$$

Activity coefficient measures how much more/less molecule A likes molecule B than another molecule A

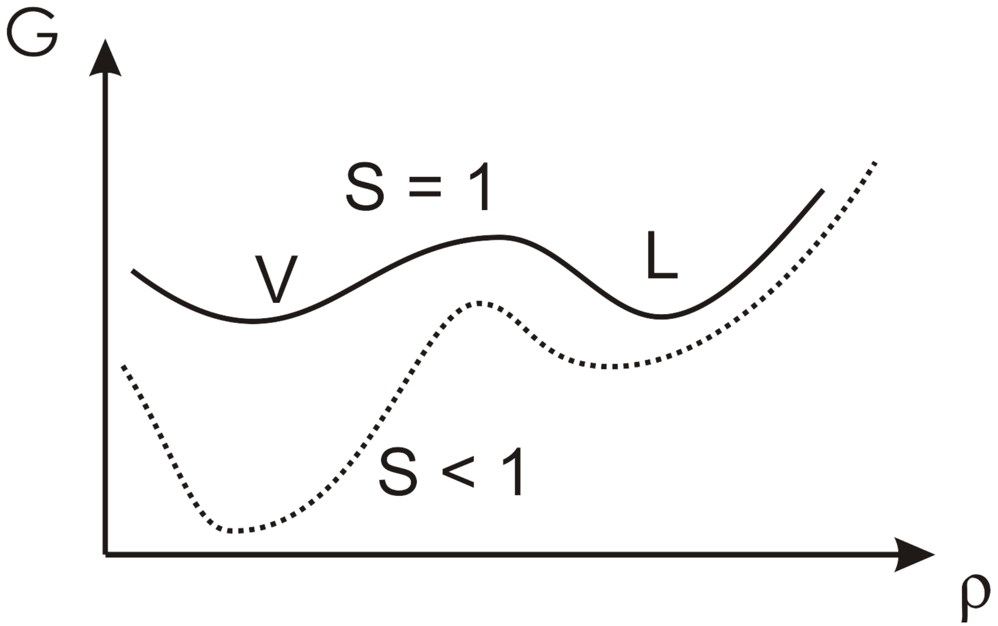
x_i is the mole fraction of component i

Why do we get trapped to the metastable state?

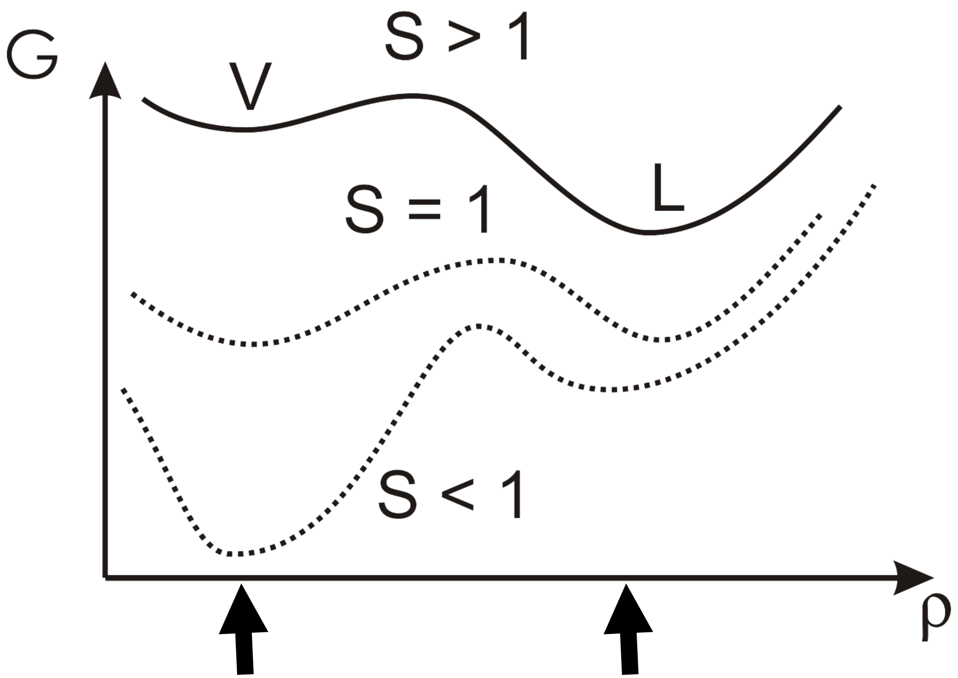


- G is the free-energy of the system - we return to this later

Why do we get trapped to the metastable state?

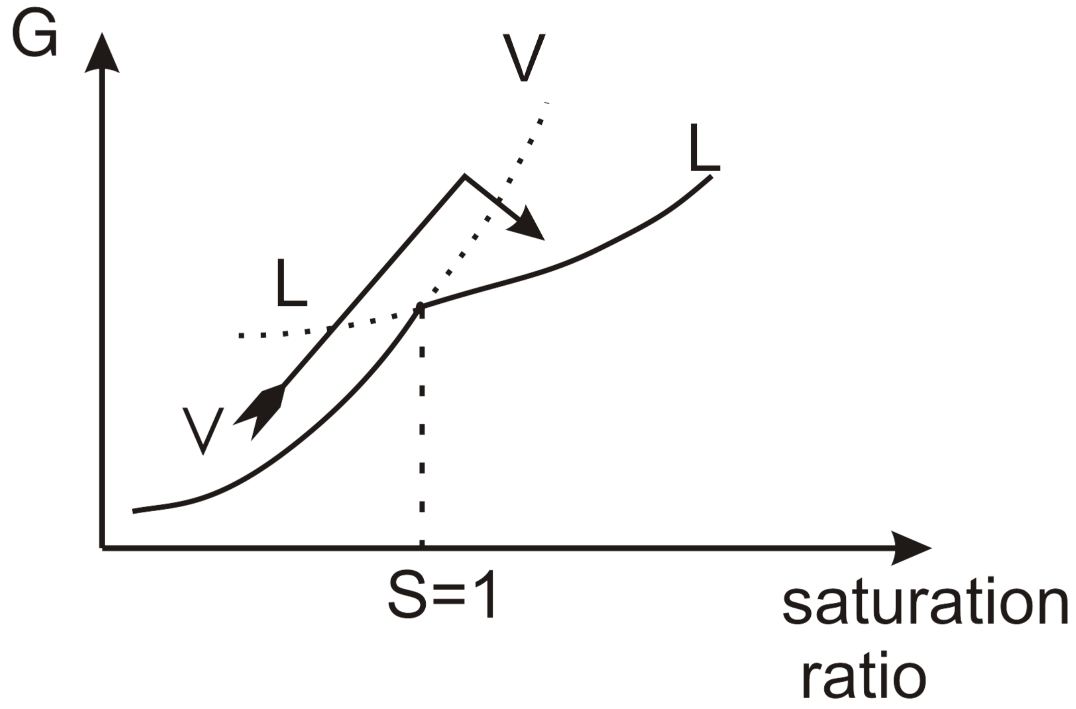


Why do we get trapped to the metastable state?

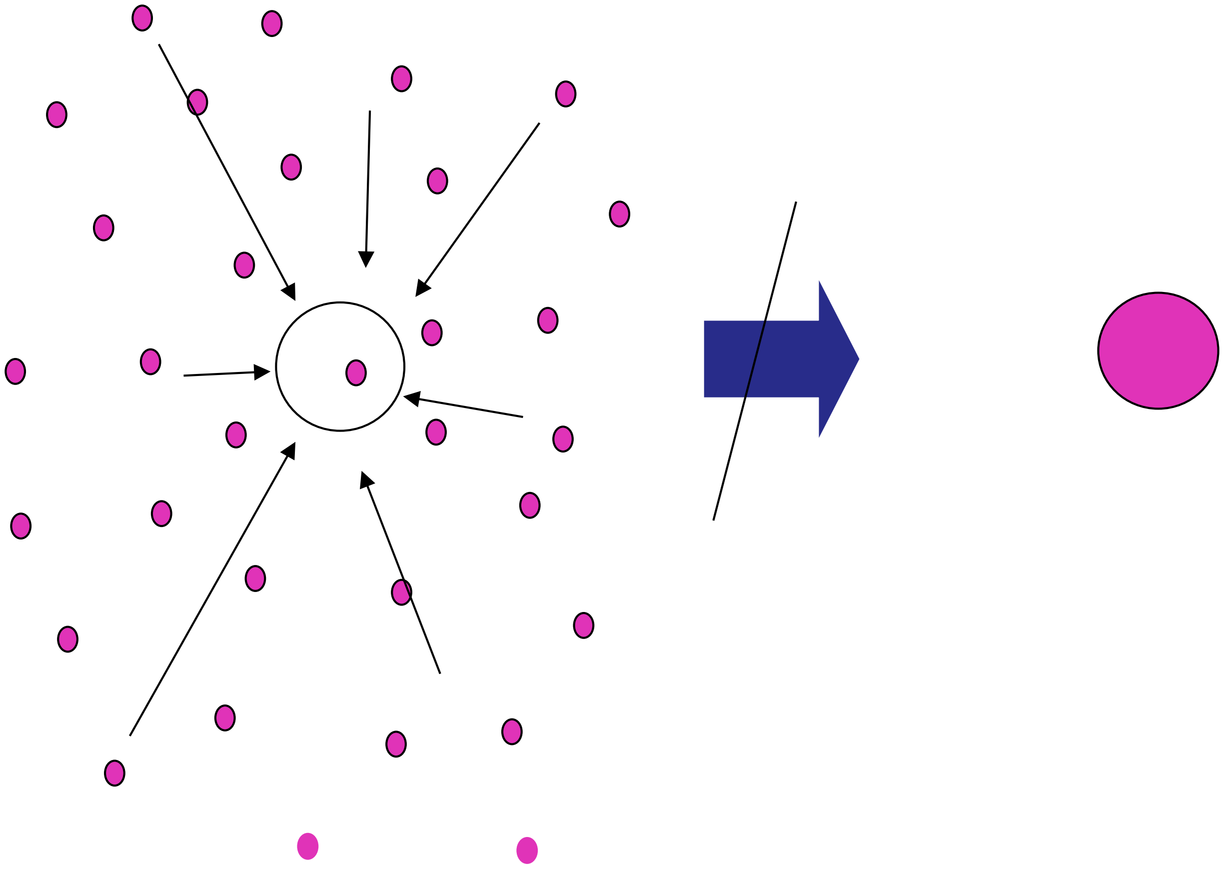


- First order phase transition:
  - **discontinuity (=jump)in the density**
  - energetic barrier
  - latent heat
  - nucleation

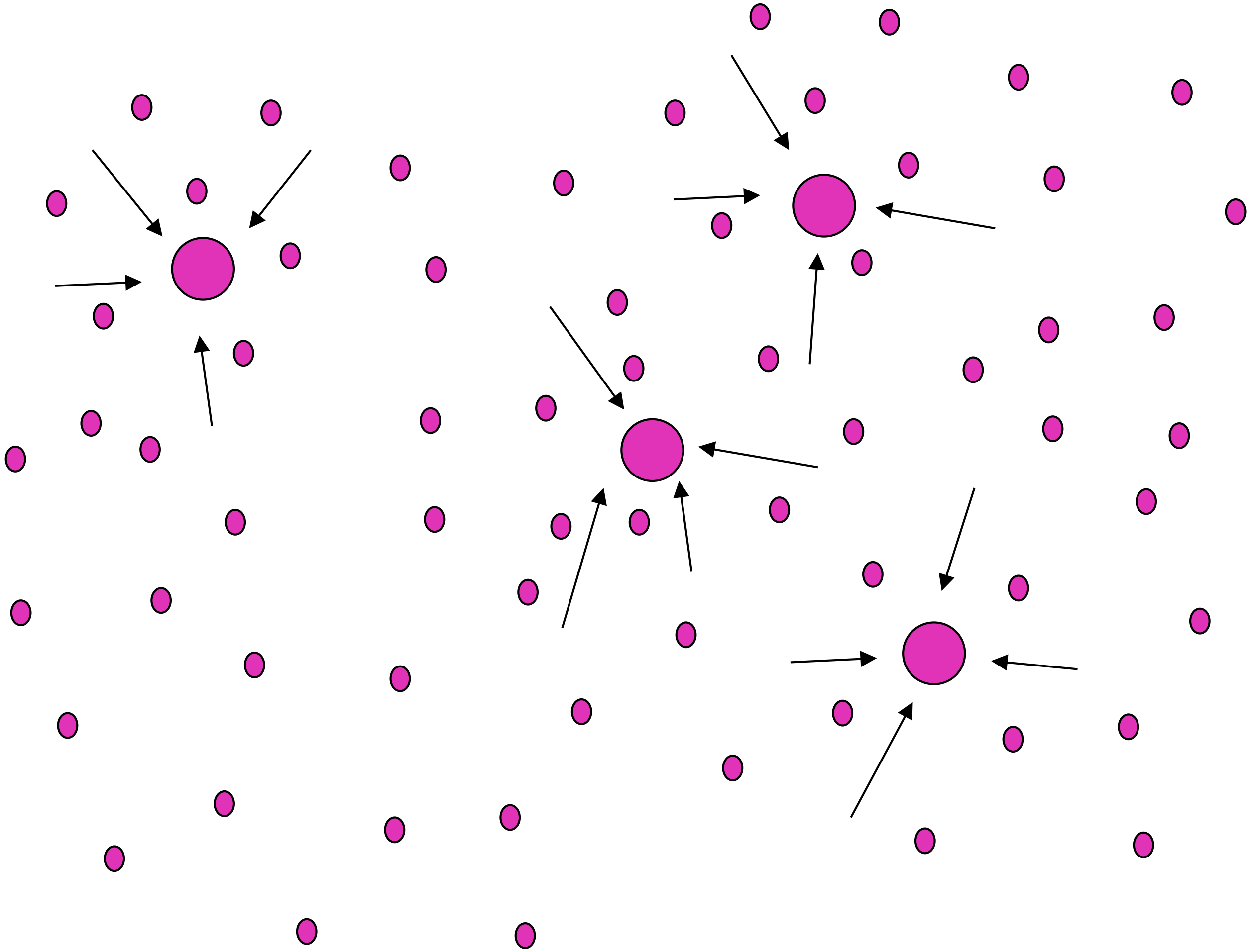
Nucleation moves the system from metastable (V) to stable state (L)



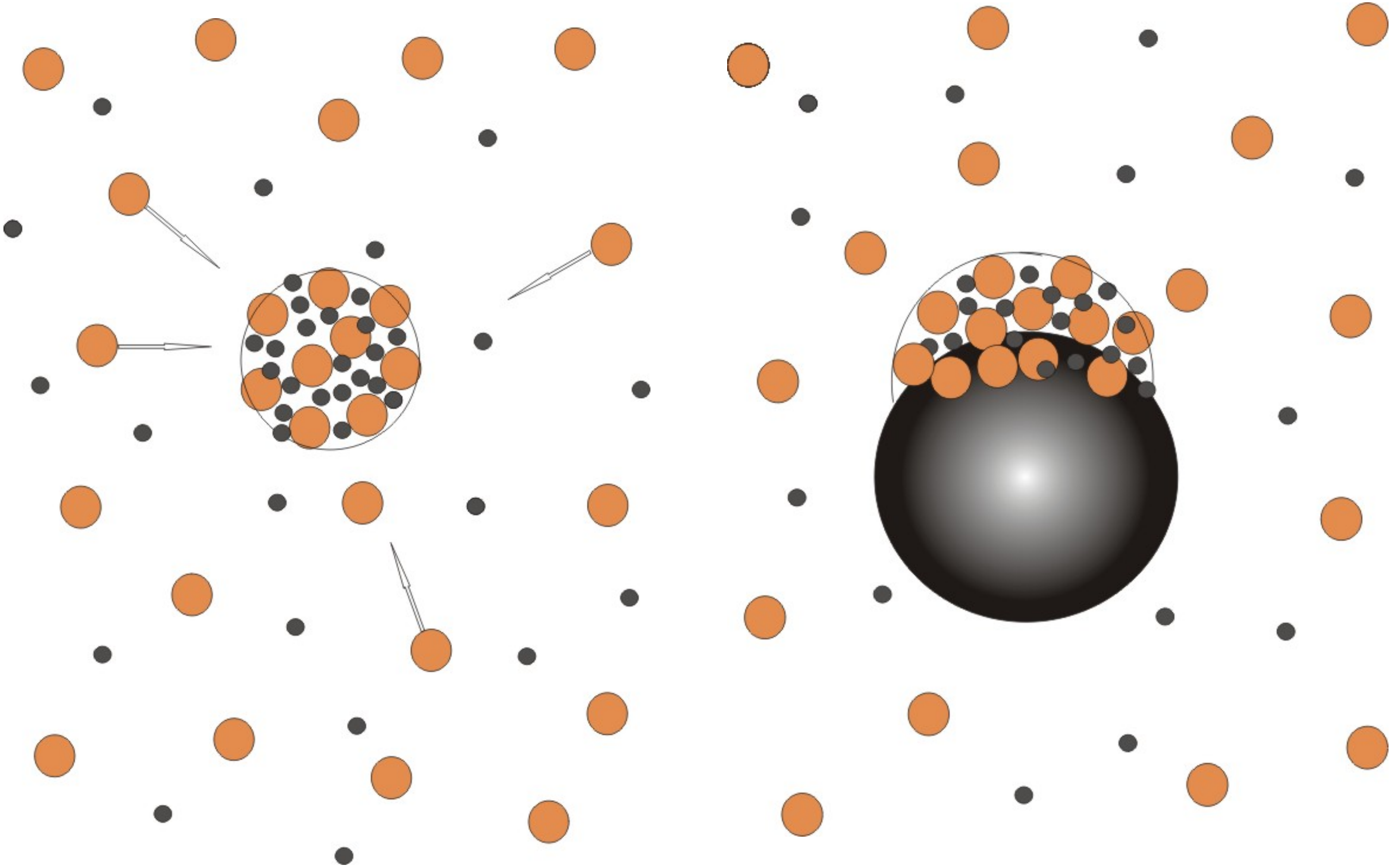
Another view: global phase transition can not occur instantaneously



Local clustering centres



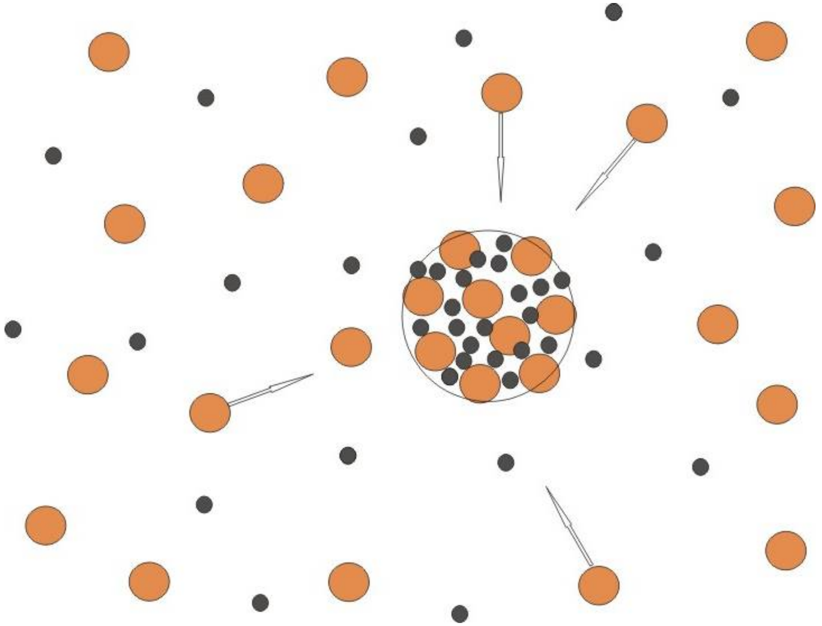
Homogeneous vs. heterogeneous nucleation



One component versus multicomponent nucleation

- Number of components in the nucleating vapour
- Unary –one component (H_2O)
- Binary- two components (H_2SO_4 +H_20)
- Ternary –three components (NH_3+H_2SO_4 +H_20)

- Can be homogenous or heterogeneous (or ion induced)



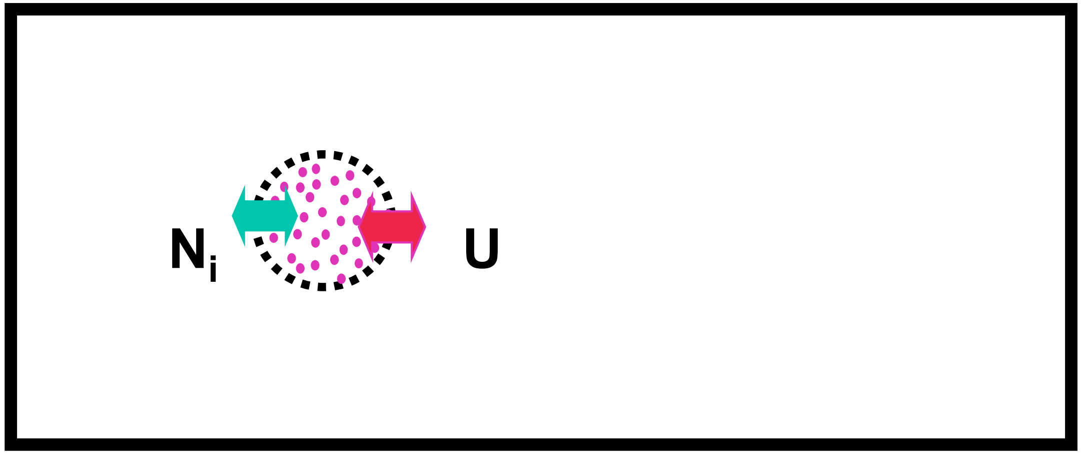
Free-energy

- Second law of thermodynamics: in an **isolated system equilibrium** state is found by finding a **maximum of entropy –** energy U is fixed

- If we want to keep pressure, temperature of chemical potential constant, the system is not isolated: it exchanges energy and/or particles with the environment
  - Heat (energy) to keep temperature constant
  - Volume work (energy) to keep pressure constant
  - Particles (and energy with them) to keep chemical potential constant

…free energy continued

- To use the second law of thermodynamics we study the **total entropy: system+ environment**
  - Assume system small, environment huge →
  - Pressure P_e, temperature T_e and chemical potential $\mu_{i,e}$ of the environment stay constant
- **Maximising the total entropy** mathematically equivalent to **minimising a free energy**



Which free energy to use?

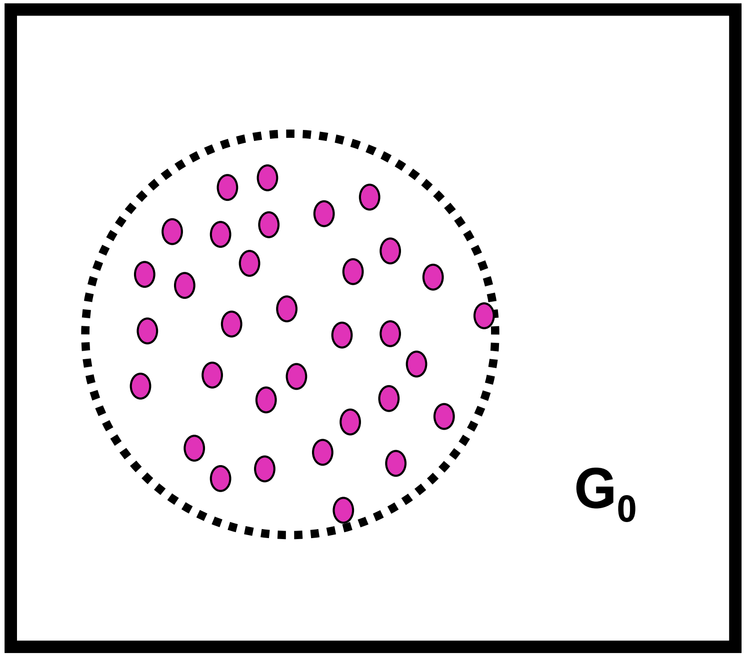
- Depends of which parameters are kept constant in the atmosphere or laboratory
- If the number of molecules in the vapour does not practically change due to cluster formation all the following are equivalent
  - Gibbs free energy (pressure, temperature, number of molecules)
  - Grand potential (temperature, chemical potential, volume)
  - Helmholtz free energy (temperature, volume, number of molecules)
- The historically standard choice is Gibbs free energy G

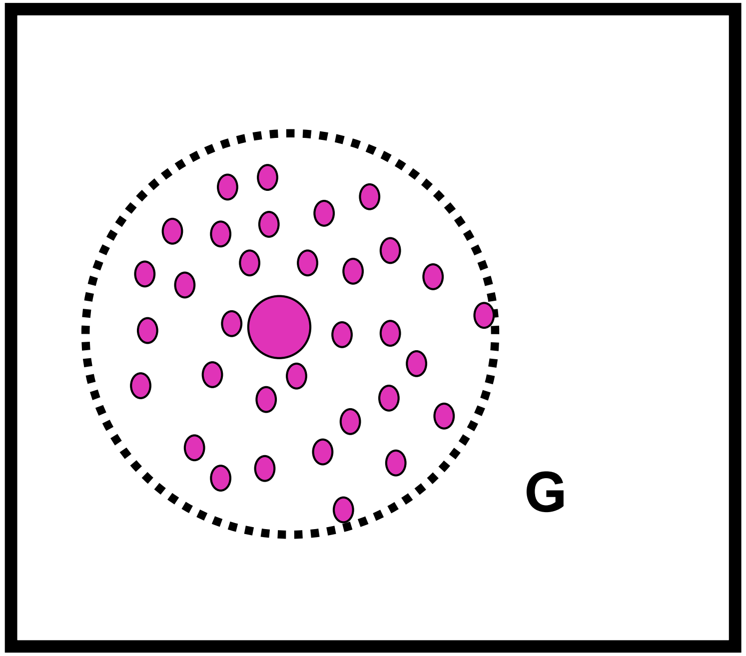
$$G=U-T_eS-P_eV$$

- Note connection to mechanics: if entropy is constant, we must minimize energy!

We use $\Delta G=G-G_0$ instead of G

- the difference in free energy between
  - the initial state (supersaturated vapour) and
  - the final state (cluster in a supersaturated vapour)
- G_0 is just a constant, does not affect the search of the minimum
- makes the formulae simpler **$\Delta G =- N kT \ln S+ A\sigma$**





Microscopic explanations for

- **Pressure**

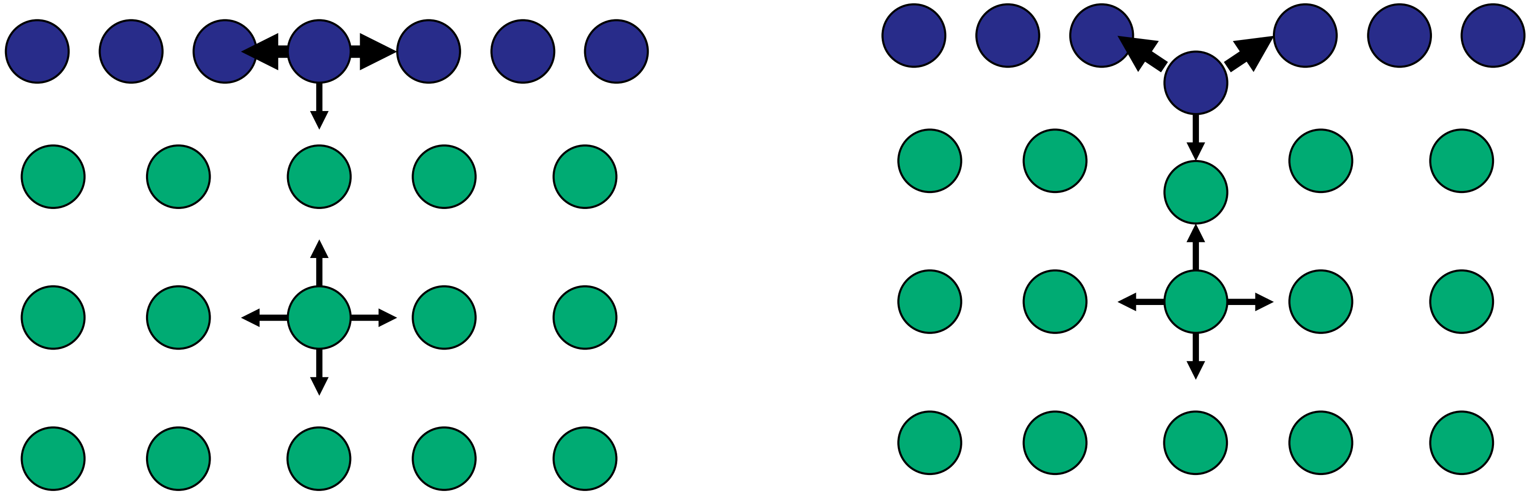
$$P = -\left(\frac{\partial U}{\partial V}\right)_{N_i,\mathbf{S},A}$$

  - Thermodynamic vs. mechanical pressure
  - Molecules moving due to thermal motion- drumming the walls

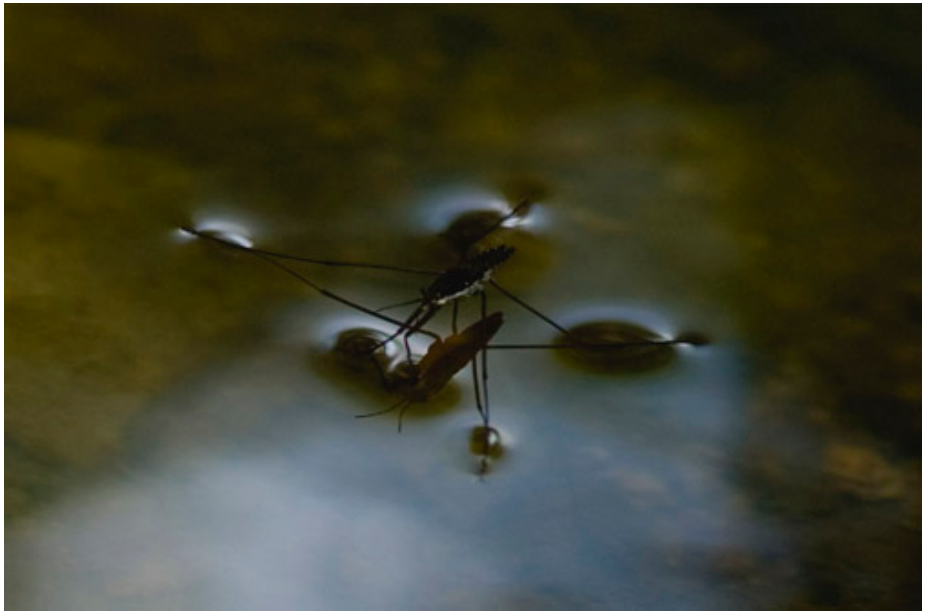
$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{N_{j\neq i},V,\mathbf{S},A}$$

- **Chemical potential**
  - Energy that one molecules gain when inserted to the gas/liquid/solid
    - Kinetic energy due to thermal motion, depends on T
    - Potential energy due to interactions, depends on how close to other molecules and thus on P, T

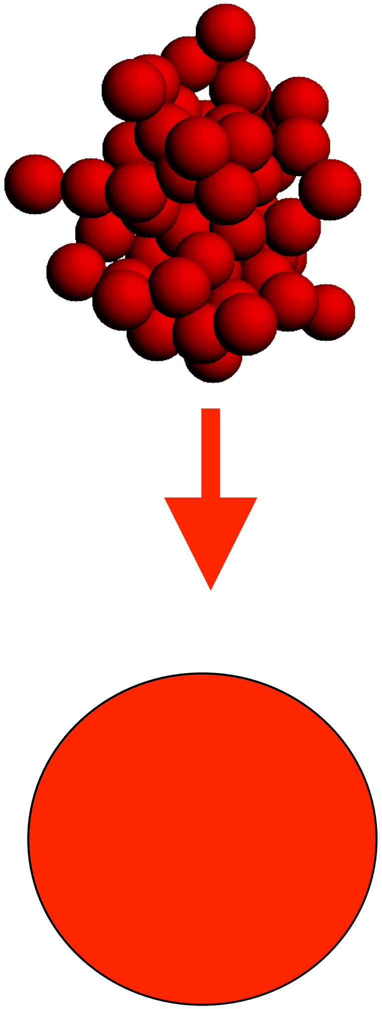
Surface tension from molecular point of view



$$\sigma = \left(\frac{\partial U}{\partial A}\right)_{N_i,V,S}$$



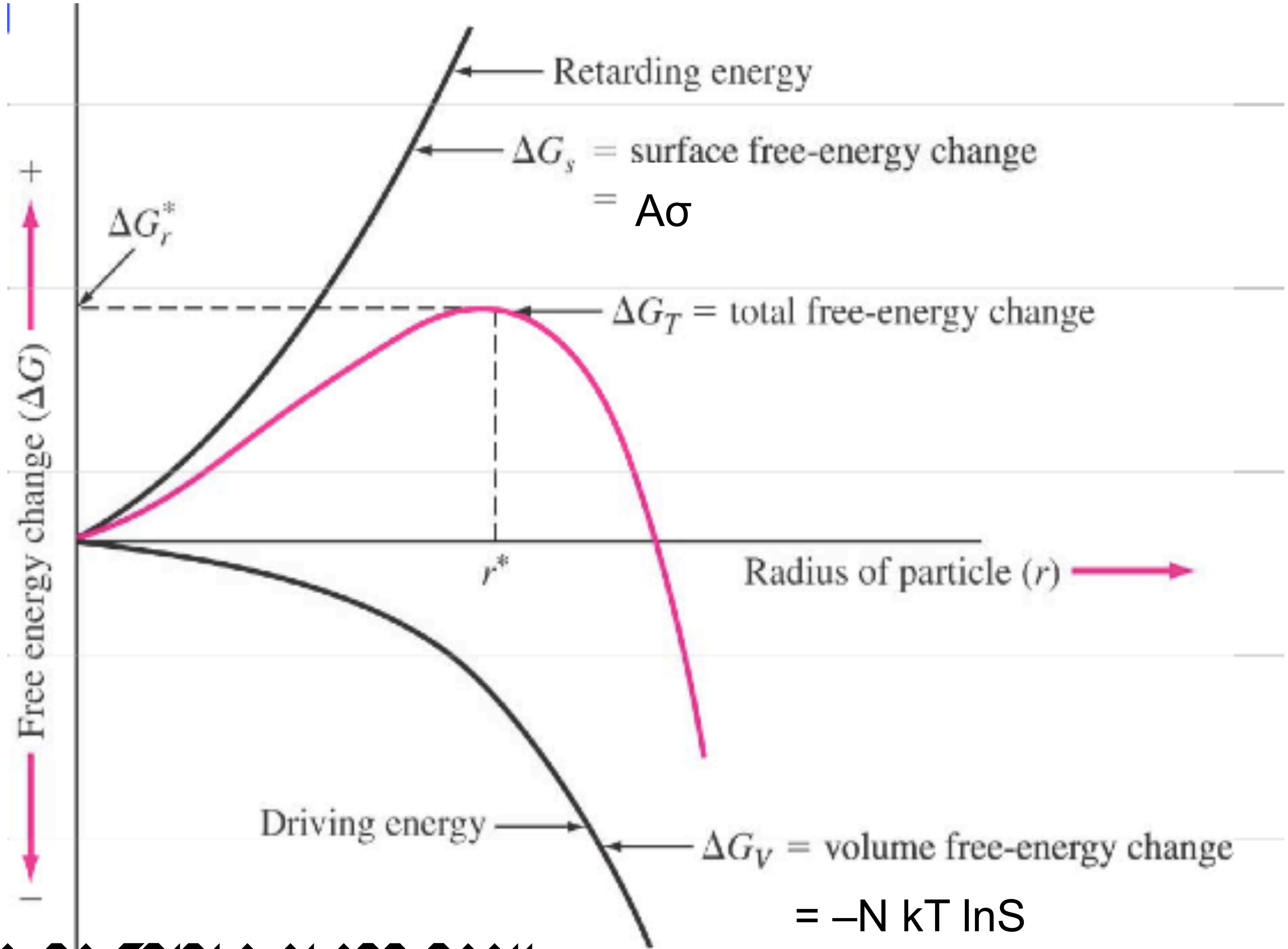
Classical Nucleation Theory = CNT



$\Delta G = - N kT \ln S + A\sigma$

$N kT \ln S \sim N \sim r^3$

$A\sigma \sim N^{2/3} \sim r^2$



AC⚡DC TRIPLE ChORD ROCK:

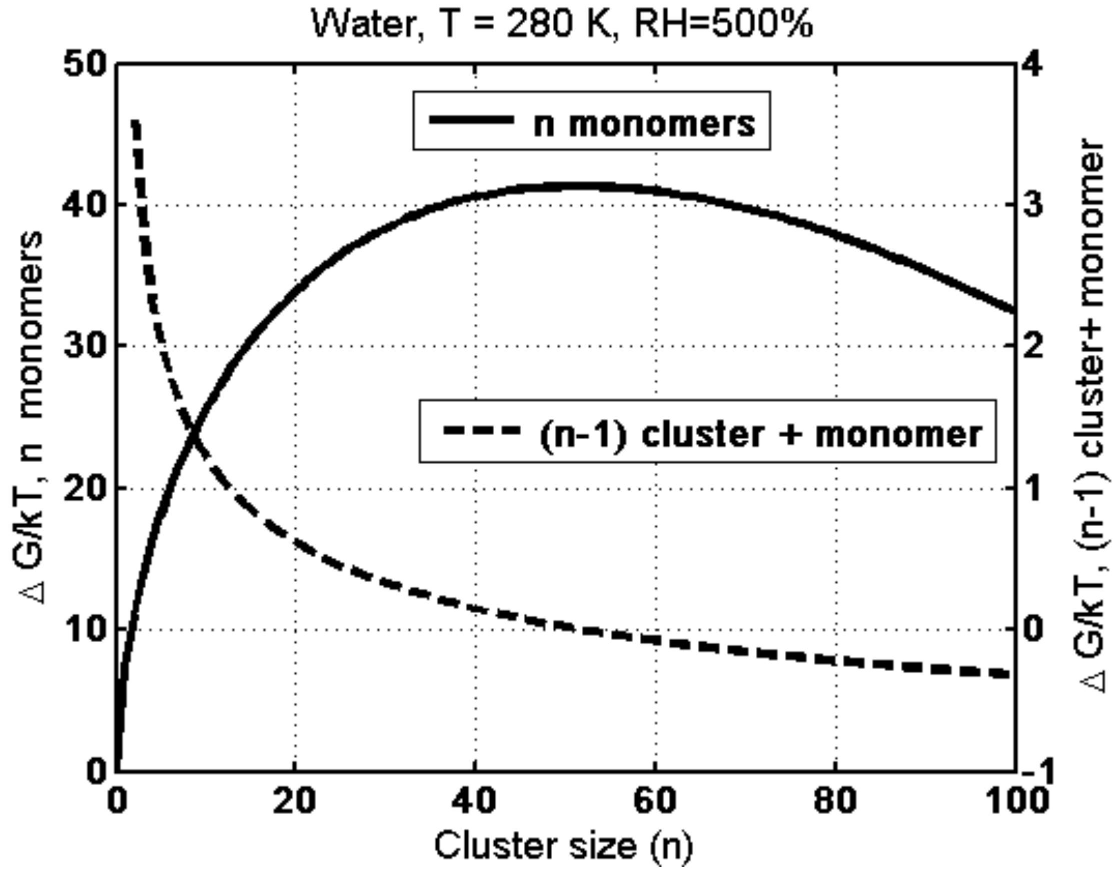
R⚡R^2⚡R^3

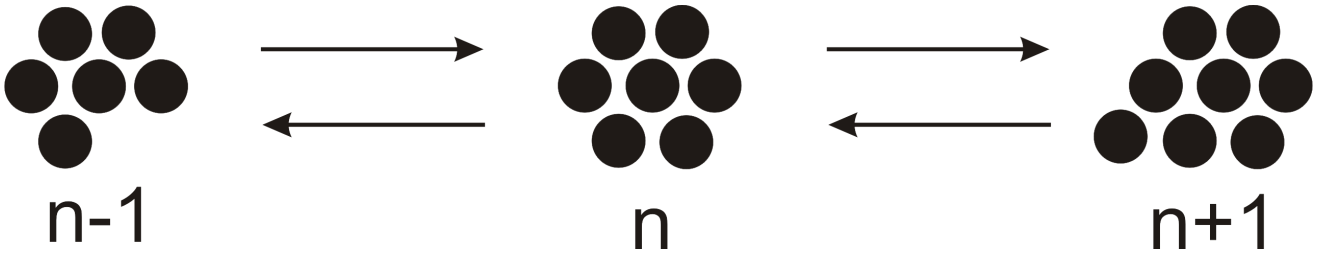
$\Delta G = -N kT \ln S + A\sigma$

Surface formation costs energy

- When S>1 the molecules would rather be in bulk liquid than in bulk vapour **$-N kT \ln S<0$**
- When you form an area of a new phase you must generate a surface between the phases **$A\sigma>0$**
- The molecules of the surface have a different environment than those in the bulk phases- their contribution to the energy is different → surface tension **σ**

Addition of a monomer becomes favourable at the critical size

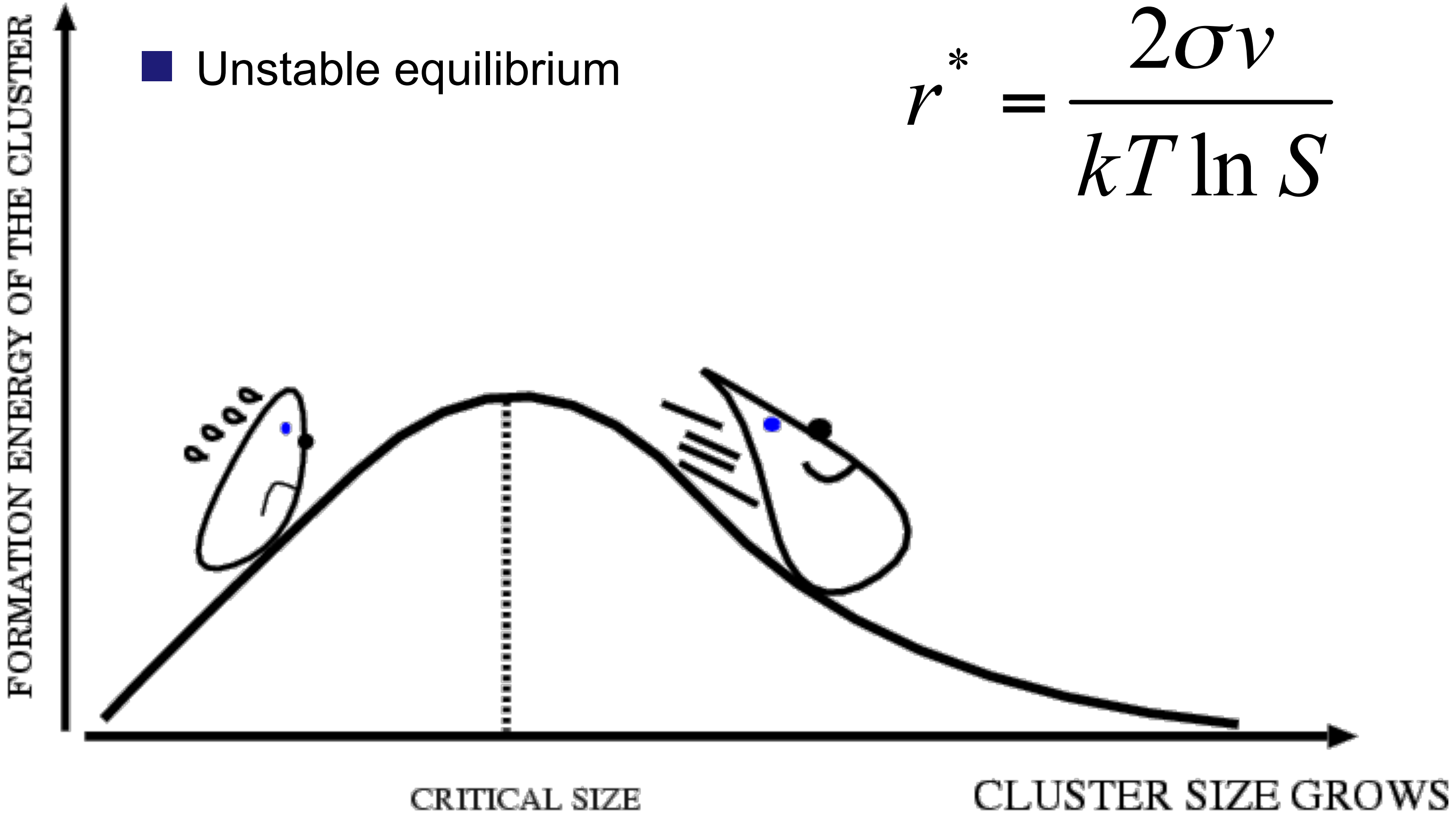




We looked for a minimum in free energy- found a maximum

- Unstable equilibrium

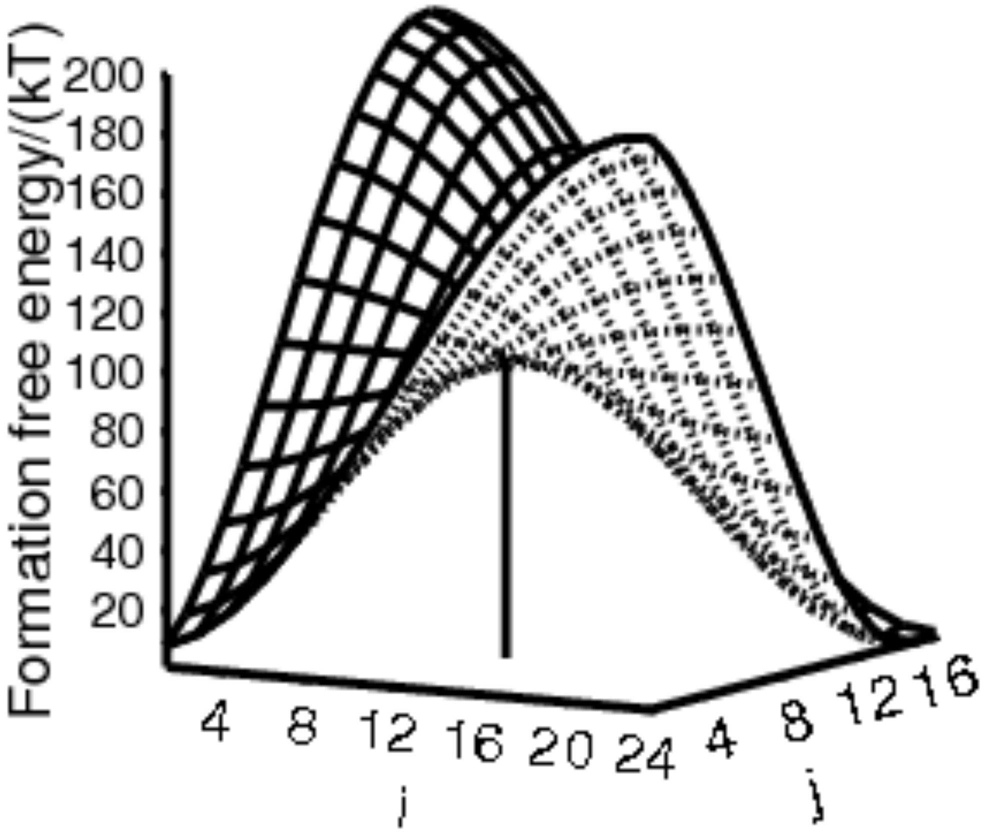
$$r^* = \frac{2\sigma v}{kT \ln S}$$



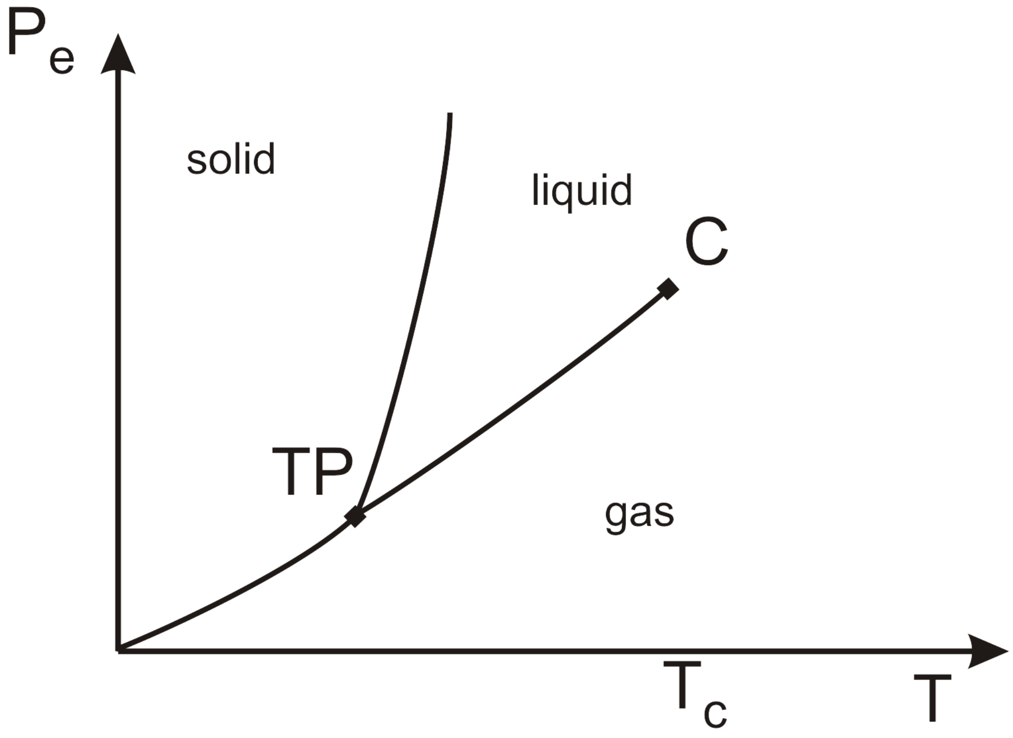
$$N^* = \rho/m\ 4/3\pi\ r^{*3}$$

Multicomponent free energy surface-critical cluster at the saddle point

- Maximum in one direction, minimum in all the other directions



Critical point ≠ critical cluster



Nucleation rate J

- Number of critical clusters formed per unit volume per unit time

[J]= 1/(cm^{3}s), 1/(m^{3}s)

$$J = K^* \times Z \times \underbrace{C_{monomers} \exp(-\Delta G^* / kT)}_{\text{Number of critical clusters in a supersaturated equilibrium vapour}}$$

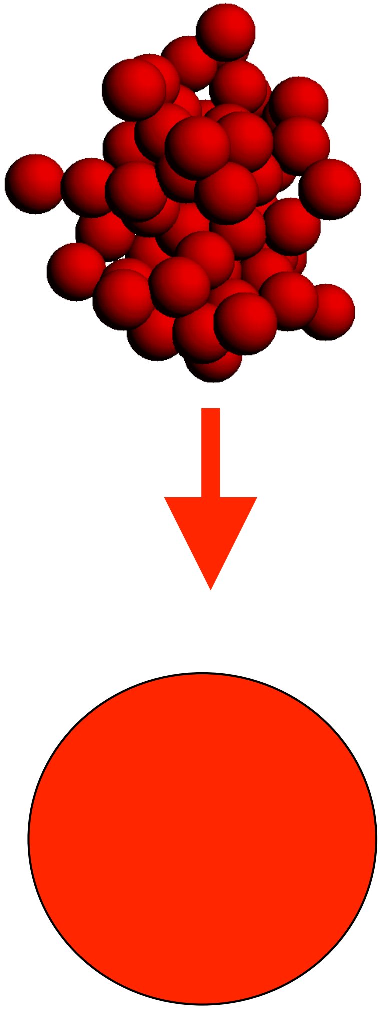
Collision rate of monomers to critical cluster

Zeldovich factor:

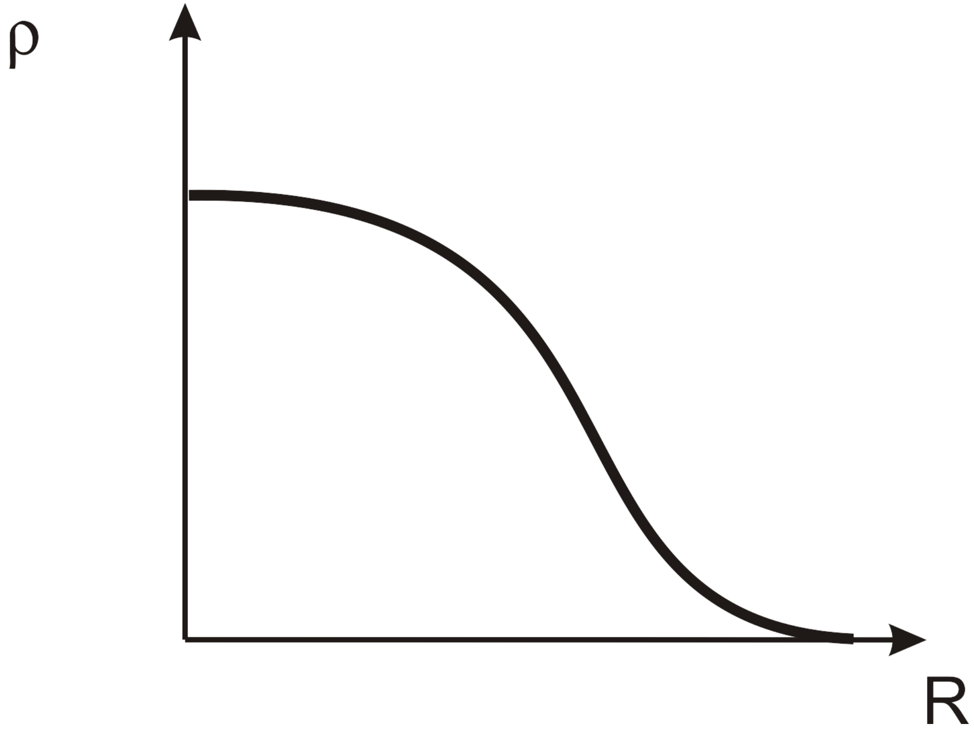
-½:number of cluster differs from supersaturated equilibrium

-~1/10: part of overcritical clusters break up

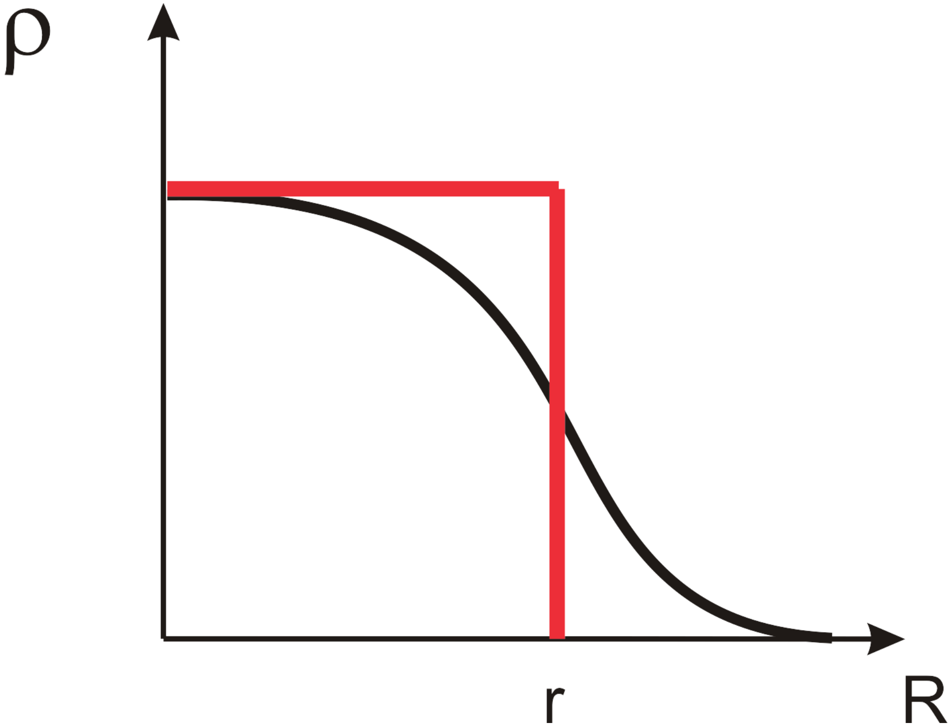
Classical Nucleation Theory - assumptions



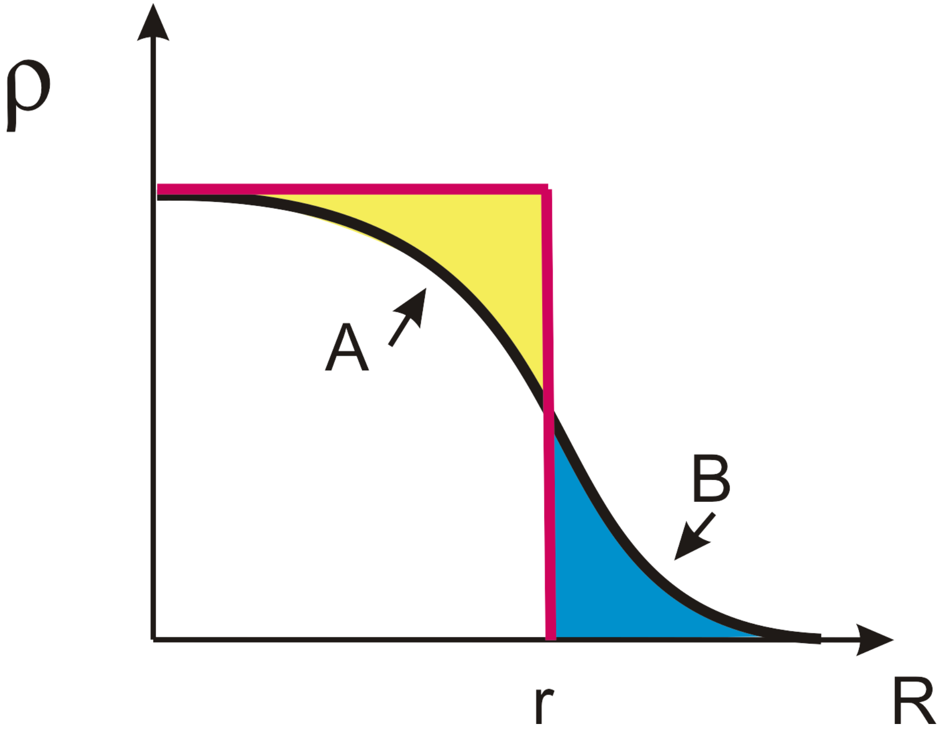
Real density profile of a spherical droplet



CNT model profile



Error in the number of molecules in the cluster zero if yellow area= blue area
➔ equimolar surface

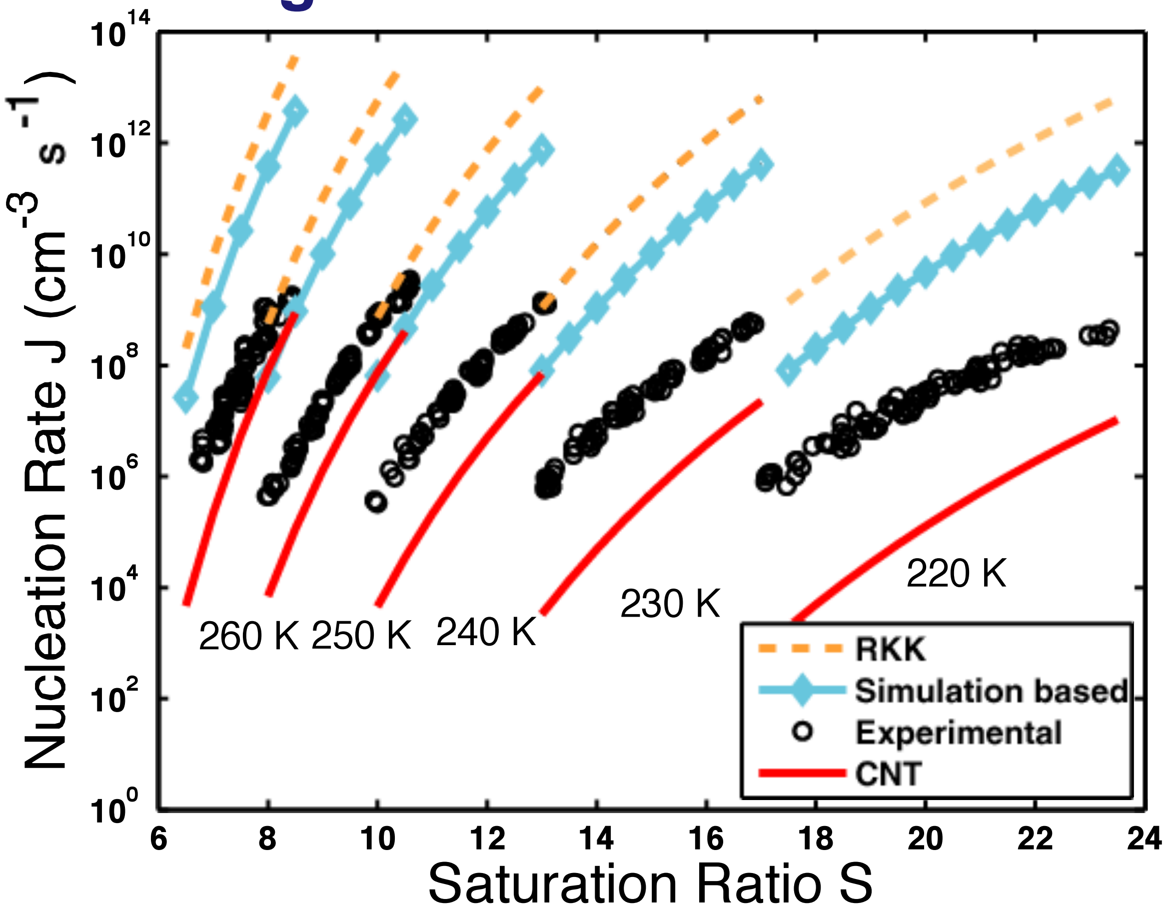


Assumptions of CNT

- ideal gas
- ideal mixture of gases
- incompressible liquid
- pressure and composition of vapour do not change due to nucleation (clusters have small amount of molecules compared to the whole vapour)
- exchange between surface and bulk liquid much faster than between gas and surface/bulk
- average volume in liquid << average volume in gas

- volume of the droplet calculated from bulk liquid density
- flat surface surface tension
- two dividing surfaces coincide- surface of tension (related to measured surface tension) and equimolar surface

Comparison with experiments: Nucleation rates for homogeneous nucleation of water



Experiments by Wölk et al

- CNT gives
  - ~correct S dependence of nucleation rate
  - wrong T dependence of nucleation rate

Nucleation theorems 1

- General results, not dependent on the validity of CNT
- S - dependence of nucleation rate gives critical cluster size

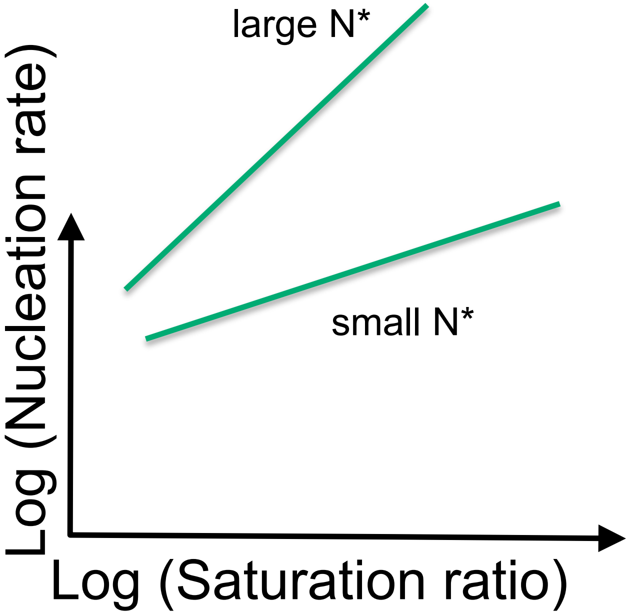
$$\left(\frac{\partial \ln J}{\partial \ln S}\right)_T = N^*(+\varepsilon)$$

- J= $\alpha \times S^{N^*}$ ➔ lnJ= lnα+ N*lnS
- Just like chemical reaction rate

  A+B+C➔ product

  J= k×[A]×[B]×[C]
- Correct S dependence:

  CNT gives correct N*



Nucleation theorems 2

- T - dependence of nucleation rate gives critical cluster energy

$$\left(\frac{\partial \ln J}{\partial T}\right)_S = \frac{\Delta U^* + \alpha}{kT^2}$$

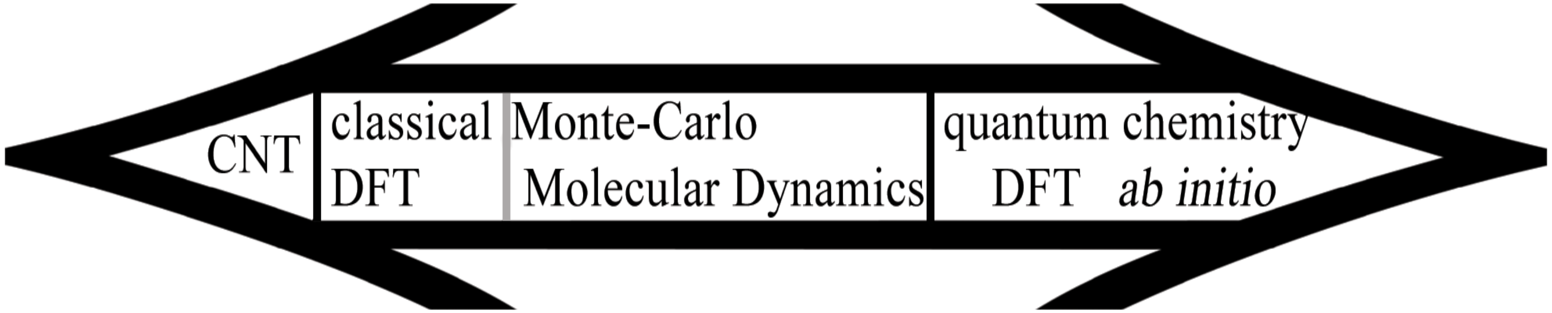
ΔU* compared to pure bulk liquid

- CNT gives wrong ΔU*→ wrong ΔG*

Comparison of methods for calculating formation free energies for clusters

- Computationally cheap
  - Large clusters
- Inaccurate molecular interaction energies

- Computationally demanding
  - Only small clusters
- Very accurate molecular interaction energies



- Advanced and accurate statistical sampling
- Much empirical data needed
  - System-specific

- Very primitive and approximate statistical sampling
- Little or no empirical data needed
  - Can be used to study any system