Particle Formation: Theory of Nucleation and Systems

theories:

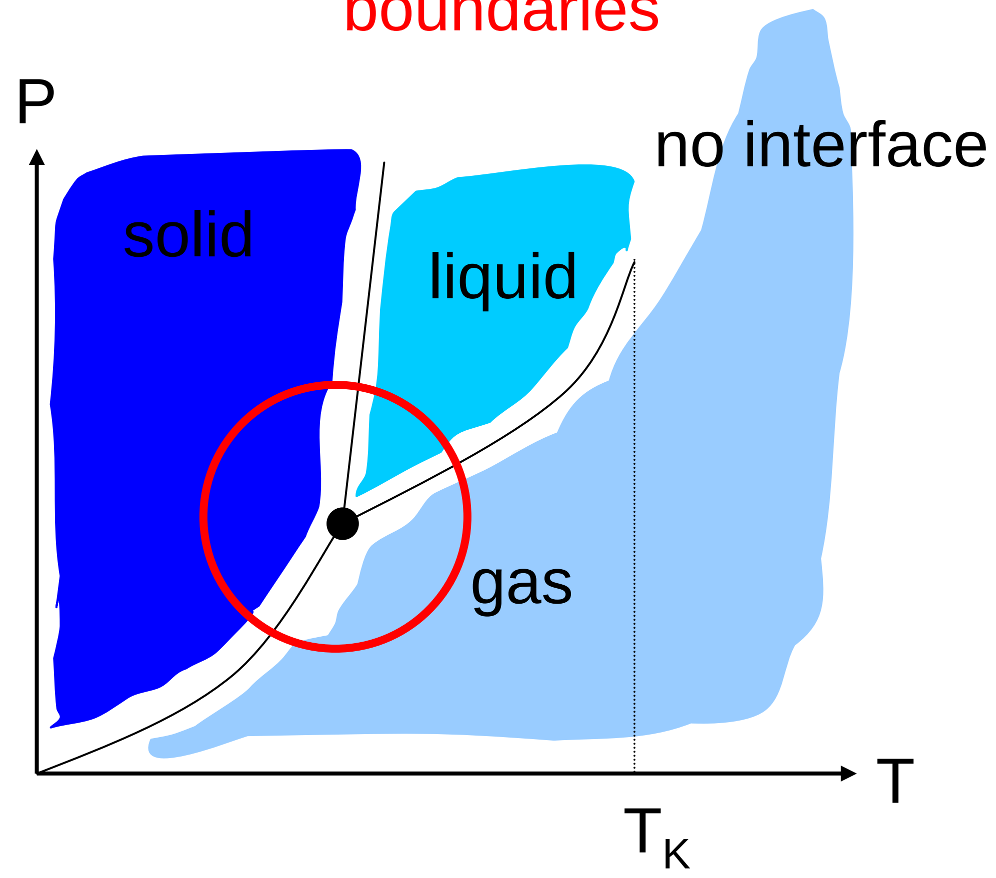
- classical nucleation theory
- density functional theory
- computer simulations

systems:

- clouds, rain, and snow
- crystallization
- boiling and condensation
- stone formation
- emulsion polymerization

What means Nucleation?

crossing the phase boundaries



first order phase transition

Nucleation - Definition

crossing phase boundaries

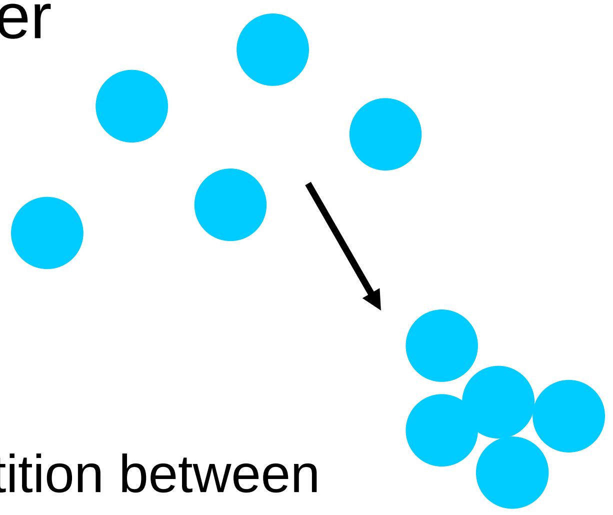
↓

Nucleation Prerequisite: to bring the system temporary into a thermodynamic unstable state

nucleation may be defined as the first irreversible formation of a nucleus of the new (equilibrium) phase

a nucleus or a cluster is a small ensemble of molecules / atoms of the new phase

Some Remarks (Key Points)



→ one molecule cannot form a cluster

→ matter can exist in different phases
at different conditions (T, P)

→ phase transitions are abrupt

→ what phase exists depends on a competition between
minimizing energy and maximizing entropy

→ if a small number of molecules start to aggregate into a
small cluster they loose position entropy; the loss of potential
energy is less due to the high fraction of surface molecules

→ cluster formation costs net entropy

Nucleation Theories

→ phenomenological approaches

effort is concentrated, on obtaining the free energy of the formation of small clusters by using macroscopic quantities (surface tension, density);
classical nucleation theory is the most popular example

→ kinetic approaches

Calculating nucleation rates without any need to estimate cluster formation energies

→ microscopic (molecular) approaches

First-principle models for cluster structure and free energy of cluster formation as for instance computer simulations and density functional theories

Classical Nucleation Theory (CNT)

The understanding of nucleation theory has been dominated for almost 70 years by CNT

<u>Volmer, Weber 1925</u>

[M. Volmer, A. Weber Z. Physikal. Chemie 119, 277 (1925)]

<u>Becker, Döring 1935</u>

[R. Becker, W. Döring Ann. Phys. 24, 719 (1935)]

<u>Frenkel 1939</u>

[J. Frenkel J. Chem. Phys. 7, 538 (1939)]

<u>Zeldovich 1943</u>

[J. B. Zeldovich Acta Physicochimica USSR 18, 1 (1943)]

Nucleus Formation

a homogeneous system becomes heterogeneous → formation of a bulky new face and of an interface

driving force (affinity) of a transformation (ϕ) from 1 to 2

$$\boxed{\phi = -\Delta G / \Delta n = \mu_1 - \mu_2}$$

$\phi < 0$ → thermodynamically impossible process

$\phi > 0$ → spontaneous process

$\phi = 0$ → equilibrium

→ energy gain (new bulk phase 2):

$$\Delta G_{bulk} = -n \cdot \phi$$

→ energy cost (interface between 1 and 2):

$$\Delta G_{surface} = \sigma \cdot A$$

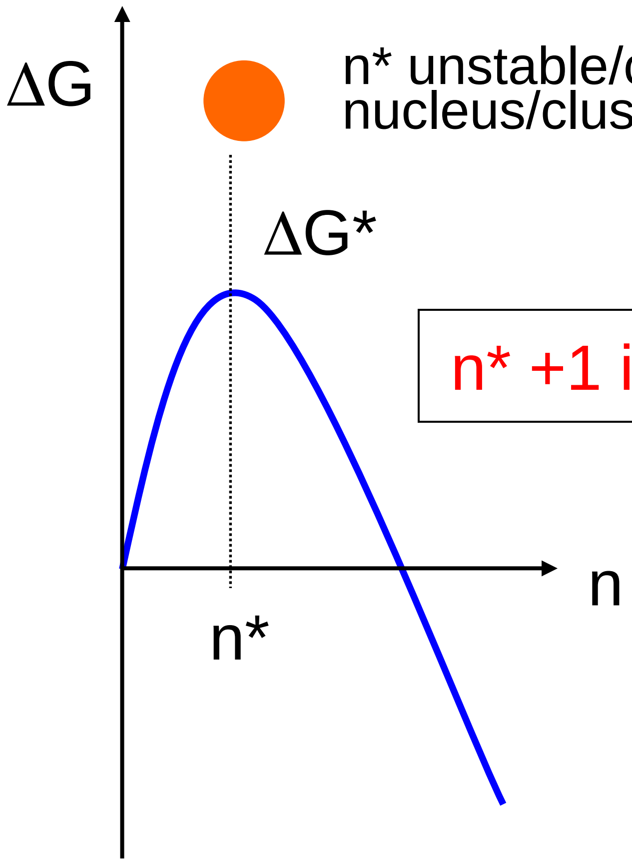
nucleus = cluster

free energy of nucleus formation:

$$\Delta G = -n \cdot \phi + \sigma \cdot A = -n \cdot \phi + n^{2/3} \cdot \psi \qquad \psi > 0$$

Nucleation Barrier (qualitative illustration)

$$\Delta G = -n \cdot \phi + \sigma \cdot A = -n \cdot \phi + n^{2/3} \cdot \psi$$



n* unstable/critical nucleus/cluster

n* +1 is stable

some simple mathematics

$$\frac{d\Delta G}{dn} = 0 \qquad n = n^* = \left(\frac{2\phi}{3\psi}\right)^3$$

$$\Delta G^* = \frac{4 \cdot \psi^3}{27 \cdot \phi^2}$$

$$\frac{d^2\Delta G}{dn^2}\bigg|_{n=n^*} < 0$$

the equilibrium is unstable

the asterisk defines critical values

Some Critical Values

$$\Delta G = -\phi \cdot n + \sigma \cdot A$$

$$n = \frac{V}{v}$$

$$R = \frac{3 \cdot V}{A}$$

$$R^* = \frac{2 \cdot \sigma \cdot v}{\phi}$$

$$\frac{d\Delta G}{dn} = -\phi + \frac{2 \cdot \sigma \cdot v}{R}$$

Definition of a radius
for any body

W. Thomson (1870)

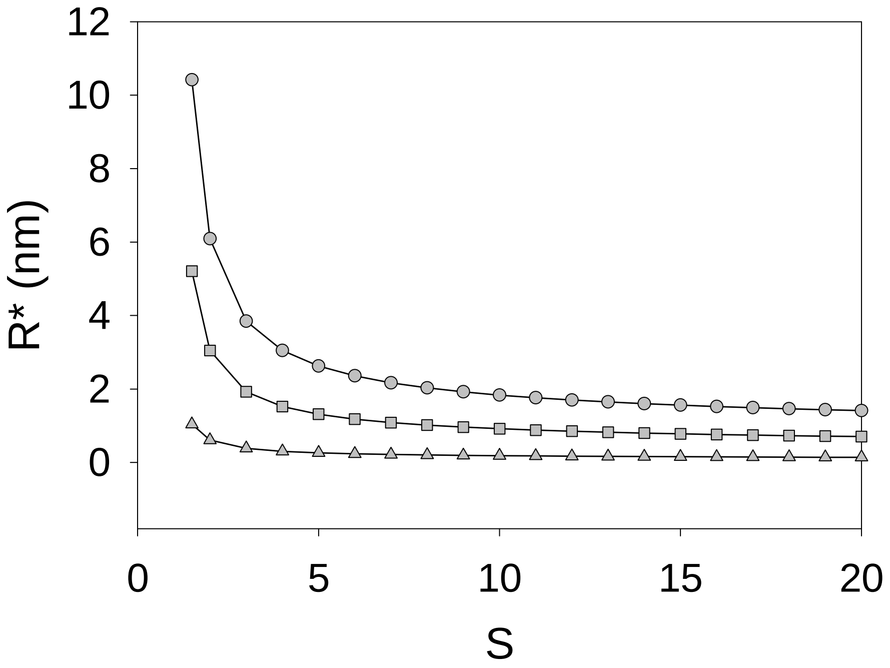
$$n^* = \frac{A^* \cdot R^*}{3 \cdot v} = \frac{2 \cdot \sigma \cdot A^*}{3 \cdot \phi}$$

$$\Delta G^* = \frac{\sigma \cdot A^*}{3}$$

Gibbs (1877)

$$\Delta G^* = \frac{\sigma^* \cdot V^*}{R^*} = \frac{n^* \cdot \phi}{2}$$

Some Calculations: Sizes of the Critical Nucleus



radius of particles capable of the unstable phase equilibrium

$$R^* = \frac{2 \cdot \sigma \cdot v}{\phi} \qquad \phi = k_B T \ln S$$

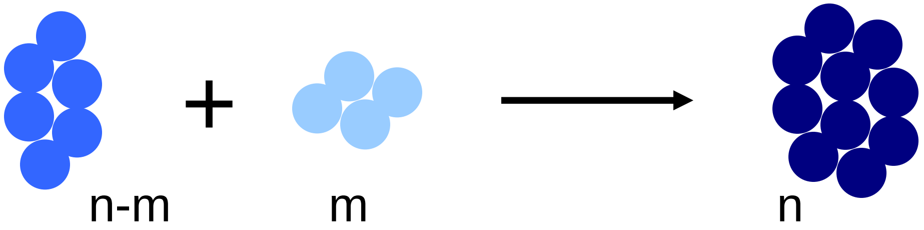
Gibbs-Thomson equation

$v = 10^{-28}$ m^3, T = 343.15 K,
k_B = 1.38 10^{-23} J/K

→ At a given S only nuclei of one particular size are in equilibrium with the (mother) phase

Nucleation Rate Via Cluster Collision

Collision frequency (f_c) of clusters of different size



$$f_c \propto \exp\left(\phi\cdot(n-m)-\psi\cdot(n-m)^{2/3}\right)\times\exp\left(\phi\cdot m-\psi\cdot m^{2/3}\right)$$

$f_c \propto \exp(\phi\cdot n)\times\exp(-\psi\cdot f(m))$ → <u>collision characterized through m</u>

$$f(m)=m^{2/3}+(n-m)^{2/3}$$

f(m) has a maximum at:

$$m=n^{*}/2$$

→ f_c is minimum

f_c maximum at minimum f(m)

$$m=1$$

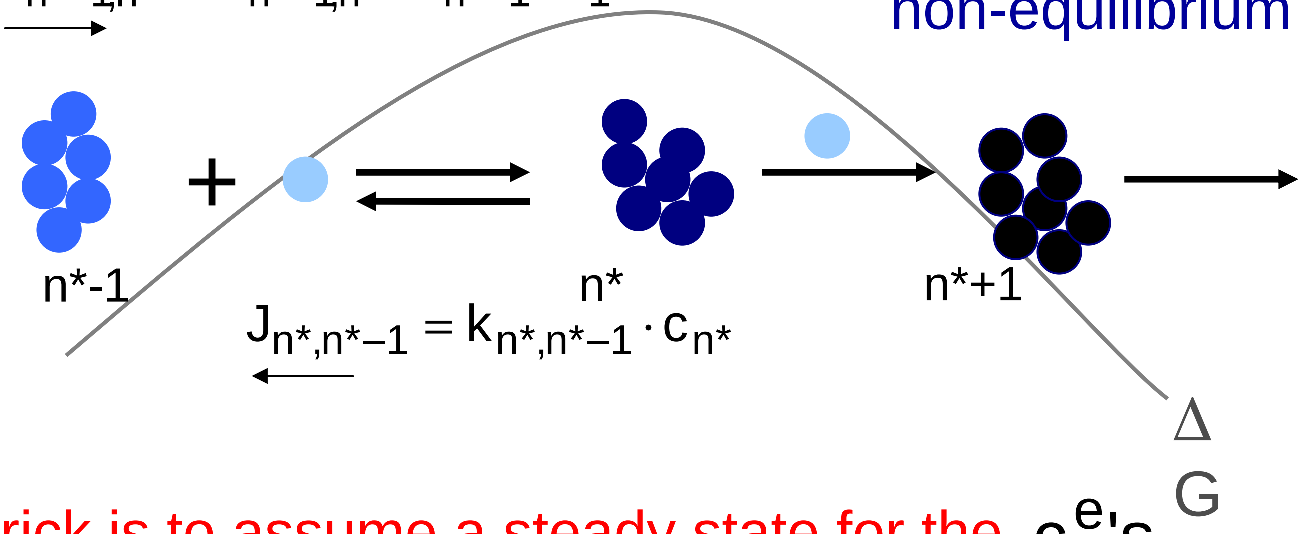
$$m=n^{*}-1 \quad (\Rightarrow n^{*}=m+1)$$

Clusters are built in small steps and not by a combination of equal parts

A Nucleation Rate (J) Equation

$$\underset{\longrightarrow}{J_{n^*-1,n^*}} = k_{n^*-1,n^*} \cdot c_{n^*-1} \cdot c_1$$

non-equilibrium process



stable nucleus growth

$$\underset{\longleftarrow}{J_{n^*,n^*-1}} = k_{n^*,n^*-1} \cdot c_{n^*}$$

The trick is to assume a steady state for the c_n^e's so that they do not change with time

$$\underline{J^e_{n^*,n^*-1} = k_{n^*,n^*-1} \cdot c^e_{n^*}} = J^e_{n^*-1,n^*}$$

with the equation for c_n

$$\boxed{J = k_{nuc} \cdot \frac{1}{v_0} \cdot \exp\left(\left(n^* \cdot \phi - n^{*2/3} \cdot \psi\right)/k_B T\right) = PEF \cdot \exp(-\Delta G^* / k_B T)}$$

PEF - pre-exponential factor

Some Remarks

Volmer and **Weber** gave the first expression for J

[M. Volmer, A. Weber Z. Physikal. Chemie 119, 277 (1925)]

$$J \propto \exp(-\Delta G^* / k_B T)$$

They assumed J is proportional to a Boltzmann factor and set $W^* = \Delta G^*$

The PEF was provided by **Farkas** (kinetic factor)

[L. Farkas Z. Physikal. Chemie 125, 236 (1927)]

equilibrium reactions

every collision of molecules is a potential start toward nucleus formation

every molecule that collides with a growing nucleus sticks to it

CNT Nucleation Rate

$$\boxed{J = Z \cdot \varphi \cdot a^* \cdot c_1 \cdot \exp(-\Delta G^* / k_B T)}$$

$$Z = \left(\frac{\Delta G^*}{k_B T} \cdot \frac{1}{3\pi (n^*)^2} \right)^{1/2}$$

$$\varphi = \frac{\eta \cdot k_B \cdot T}{V} \cdot \frac{1}{(2\mu \cdot k_B T)^{1/2}}$$

$$a^* = (36\pi \cdot v^2)^{1/3} \cdot n^{*2/3}$$

μ - mass of the molecules impinge the cluster

η - molecules in the reaction volume V

Some Remarks on CNT

CNT is based on the continuums thermodynamics treatment of clusters by imposing the the capillarity approximation which means that small clusters are considered to have the same properties as the bulk material

phase equilibria involving spatial scales which are large compared to molecular sizes have long been studied with continuum thermodynamics

continuums thermodynamic requires a large, representative ensemble and a well defined surface

critical clusters can contain only a few tens of molecules - the validity of the continuums thermodynamics is doubtful

however, CNT describes experimental data

Theories Beyond CNT

modifications of CNT

correction factors in the capillarity approximation

$$\Delta G = -n \cdot \phi + \sigma \cdot A = -n \cdot \phi + n^{2/3} \cdot \psi$$

→ consideration of translational and rotational degrees of freedom of a cluster

J. Lothe, G.M. Pound J. Chem. Phys. 36, 2080 (1962)
H. Reiss, J. L. Katz, E.R. Cohen J. Chem. Phys. 48, 5553 (1968)
H. Reiss J. Stat. Phys. 2, 83 (1970)
V. Ruth, J.P. Hirth, G.M. Pound J. Chem. Phys. 88, 7079 (1988)

→ consideration of the partial pressure of the cluster which is considered as a molecule by a factor 1/S in PEF

W.G. Courtney J. Chem. Phys. 35, 2249 (1961)
M. Blander, J.L. Katz J. Stat. Phys. 4, 55 (1972)
S.L. Girshick, C.P. Chiu J. Chem. Phys. 93, 1273 (1990)
S.L. Girshick J. Chem. Phys. 94, 826 (1991)

Theories Beyond CNT, continued-1

modifications of CNT

→ **Dillmann-Meier** theory: consideration of curvature dependence of σ, of additional degrees of freedom, and a demand for thermodynamic consistency

A. Dillmann, G.E.A. Meier Chem. Phys. Lett.160, 71 (1989)
A. Dillmann, G.E.A. Meier J. Chem. Phys. 94, 3872 (1991)
I.J. Ford, A. Laaksonen, M. Kulmala J. Chem. Phys. 99, 764 (1993)

$$\Delta G/k_B T = \kappa(n) \cdot n^{2/3} \cdot \psi' + \tau \underline{\cdot \ln(n) - \ln(q_0 \cdot V) - n} \cdot \phi'$$

$\kappa(n)$ - size dependence of σ

differences between the molecular structure of a free cluster and a group of the same number of particles in the new phase bulk material; τ and q_0 are chosen to fit both the critical density and pressure

Theories Beyond CNT, continued-2

microscopic approaches ⟶ density functional theory

density functional theory (DFT): any nucleating system has an inhomogeneous structure; the free energy of the nonuniform system is a unique functional of the average density whose minima determine the thermodynamically states at a given temperature

Cahn & Hillard: the first DFT calculation of nucleation;

$$\Omega[\rho(r)] = \int dr \left\{ f_h[\rho(r)] - \mu\rho(r) + k[\nabla\rho(r)]^2 \right\}$$

$\rho(r)$ - average density

μ - chemical potential

f_h - free energy per volume of a homogeneous system

$k[\nabla\rho(r)]^2$ - nonlocal contributions to f_h

$\Delta\Omega^*$ - free energy cost of the nucleus

$\Omega[\rho(r)]$ - grand potential

J.W. Cahn, J.E. Hillard J. Chem. Phys. 31, 688 (1959)

Kinetic Nucleation Theory

a nucleation theory without the constrained equilibrium of the CNT at S > 1 but with a stable equilibrium at S = 1

J.L. Katz, H. Weidersich J. Coll. Interface Sci. 61, 351 (1977)
J.L. Katz, M.D. Donohue Adv. Chem. Phys. 40, 137 (1979)
S.L. Girshick, C.-P. Chiu J. Chem. Phys. 93, 1273 (1990)

$$C_1 + C_{n-1} \leftrightarrow C_n$$ condensation ⟷ evaporation

$$J_n = \xi \cdot a_{n-1} \cdot C_{n-1} - E_n \cdot C_n$$ rate

$$\xi = \left(\frac{k_B T}{2 \cdot \pi \cdot m_1} \right)^{1/2} \cdot C_1$$

monomer flux to the surface from ideal gas kinetic theory

$$E_n = \xi^e \cdot a_{n-1} \cdot \frac{C_{n-1}^e}{C_n^e}$$

monomer evaporation coefficient from equilibrium $J_n = 0$; e denotes equilibrium

Kinetic Nucleation Theory, continued-1

$$\frac{J_n}{\xi \cdot a_{n-1} \cdot C^e_{n-1}} = \frac{C_{n-1}}{C^e_{n-1}} - \frac{\xi^e}{\xi} \cdot \frac{C_n}{C^e_n}$$

some mathematics

$$\frac{\xi}{\xi^e} = \frac{C_1}{C^e_1} = S$$

$$C^e_n = N \cdot \exp(-\frac{\Delta G(n)}{k_B T})$$

$J = \left[\frac{H``(n^*)}{2 \cdot \pi}\right]^{1/2} \exp(H(n^*)$

$$H(n) = \ln(\xi \cdot a_n \cdot C^e_n \cdot S^n)$$

$$J = \left[\frac{H``(n^*)}{2 \cdot \pi}\right]^{1/2} \exp(H(n^*)$$

nucleation rate in form of an error function

Kinetic Nucleation Theory, continued-2

$$C_n^e = N \cdot \exp\left(-\frac{\Delta G(n)}{k_B T}\right)$$

Boltzmann statistics for equilibrium cluster distribution; N - normalization constant

ΔG - Gibbs free energy of n-mer formation in the equilibrium state

ΔG from CNT $$\frac{\Delta G}{k_B T} = \Omega \cdot n^{2/3} - n \cdot \ln S \qquad \Omega = \frac{\sigma \cdot a_1}{k_B T}$$

n = 1: the equations are not satisfied; CNT is internally inconsistent; but this is not a big problem as n is only needed around n*

stable equilibrium (S =1) $$\frac{\Delta G}{k_B T} = \Omega \cdot n^{2/3} \qquad n^* \Leftarrow \frac{dH(n)}{dn} = 0$$

$$n^* = \left(\frac{2 \cdot \Omega}{3 \cdot \ln S}\right)^3 \qquad J = \frac{N \cdot \xi \cdot a_1}{3} \cdot \left(\frac{\Omega}{\pi}\right)^{1/2} \exp\left(-\frac{4 \cdot \Omega^3}{27 \cdot (\ln S)^2}\right)$$

identical results with CNT

Kinetic Nucleation Theory, continued-3

$$\frac{\Delta G}{k_B T} = \Omega \cdot \left(n^{2/3} - 1\right)$$

some mathematics

$$C_n^e = N \cdot \exp(-\Omega(n^{2/3} - 1))$$

$$J = \left[\frac{H``(n^*)}{2 \cdot \pi}\right]^{1/2} \exp(H(n^*)$$

$$J_{kin} = v \cdot \left(\frac{2\sigma}{\pi \cdot m}\right)^{1/2} \cdot C_{S1}^2 \cdot S \cdot \exp\left(\Omega - \frac{4 \cdot \Omega^3}{27 \cdot (\ln S)^2}\right)$$

$$J_{CNT} = v \cdot \left(\frac{2\sigma}{\pi \cdot m}\right)^{1/2} \cdot C_{S1}^2 \cdot S^2 \cdot \exp\left(-\frac{4 \cdot \Omega^3}{27 \cdot (\ln S)^2}\right)$$

$$\Rightarrow \quad \frac{J_{kin}}{J_{CNT}} = \frac{\exp \Omega}{S}$$

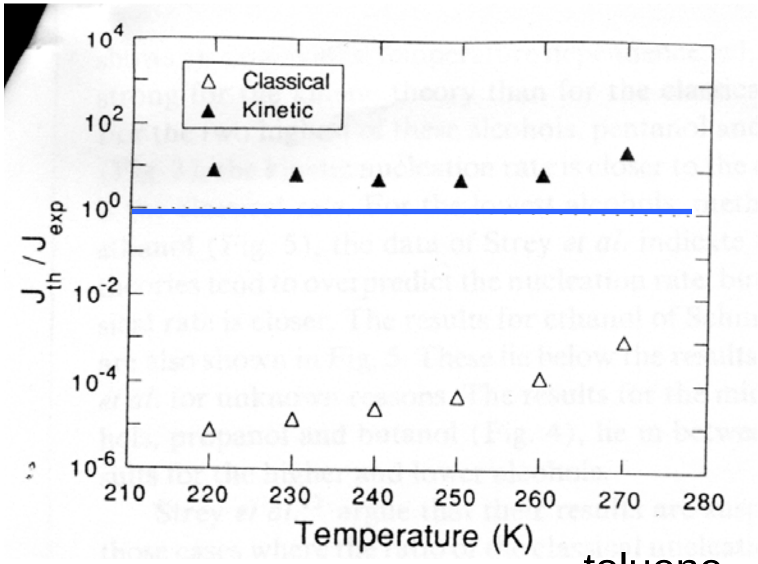
Kinetic Nucleation Theory, continued-4

$$\frac{J_{kin}}{J_{CNT}} = \frac{\exp\Omega}{S}$$

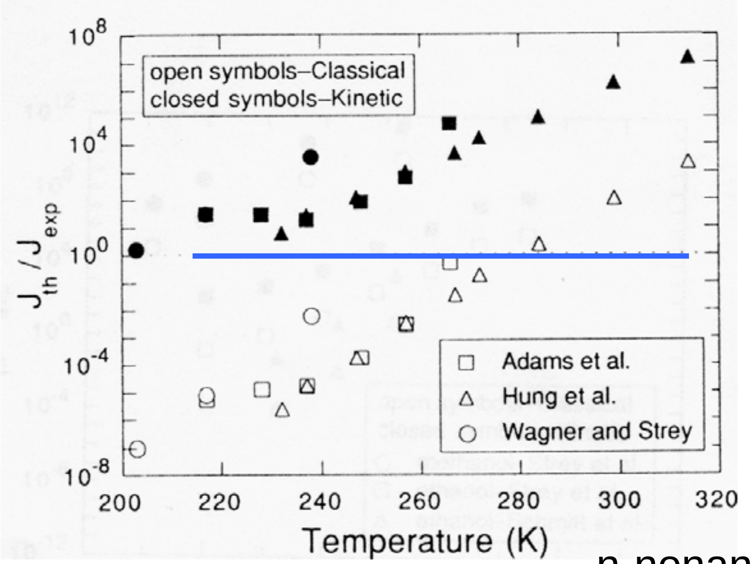
Ω - dimensionless, temperature-dependent surface tension

$\exp\Omega$ - is an often large and temperature-dependent correction to the CNT

some examples:



toluene



n-nonane

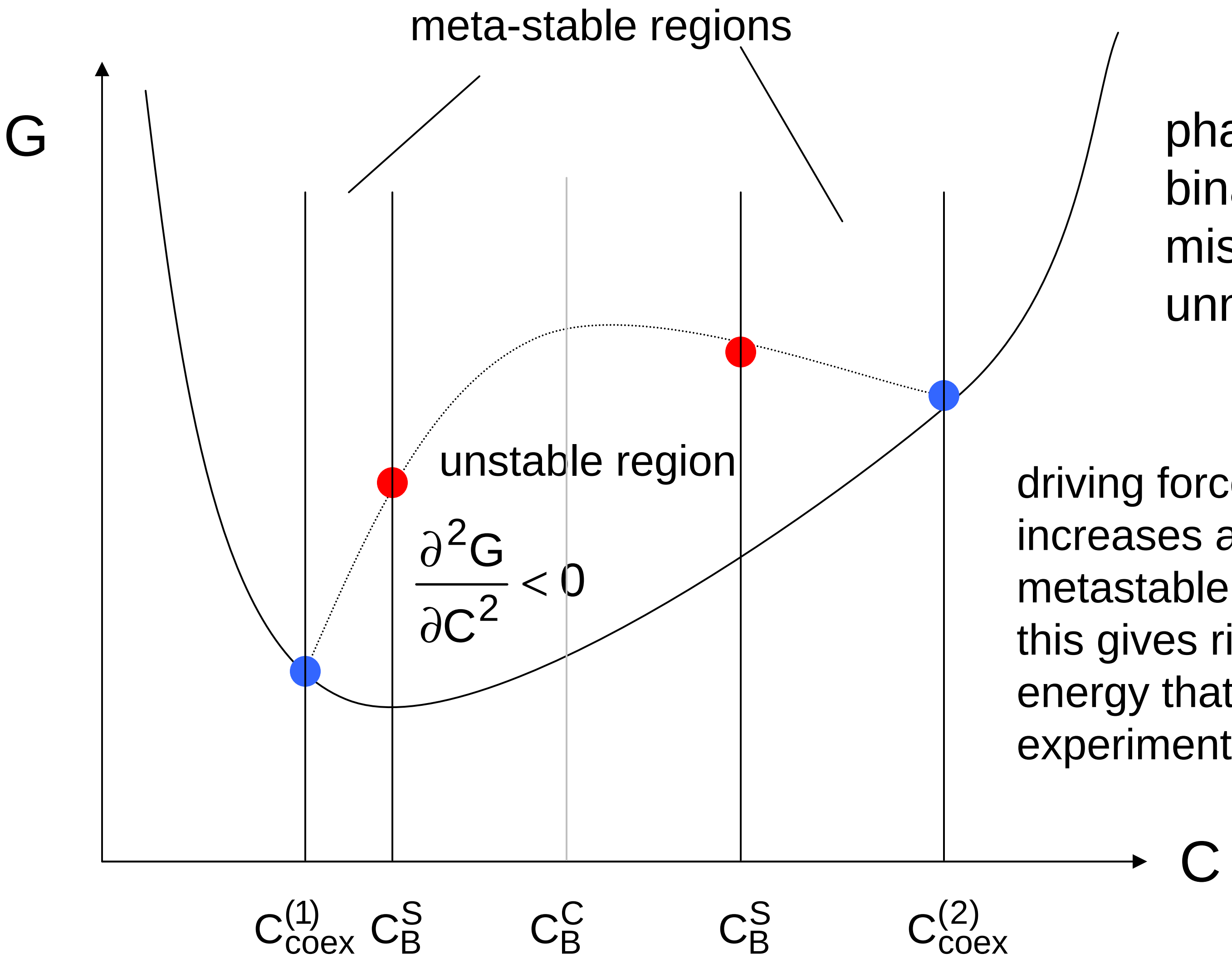
Spinodal Decomposition

→ For reasons of entropy the single phase of a (solid) solution with a given composition is thermodynamically stable only at elevated temperatures or low concentrations. At lower temperatures or higher concentrations the free energy of the system is lowered through demixing or decomposition or phase separation or nucleation into two phases.
These terms basically describe the same physical fact.

→ The spinodal curve has a meaning for the initial homogeneous state and controls the early stages of phase separation.

Material Science and Technology, R. W. Cahn, P. Haasen, E.J. Kramer (editors), Volume 5 „Phase Transformation in Materiáls“, Pter Haasen (voleme editor), VCH, 1991

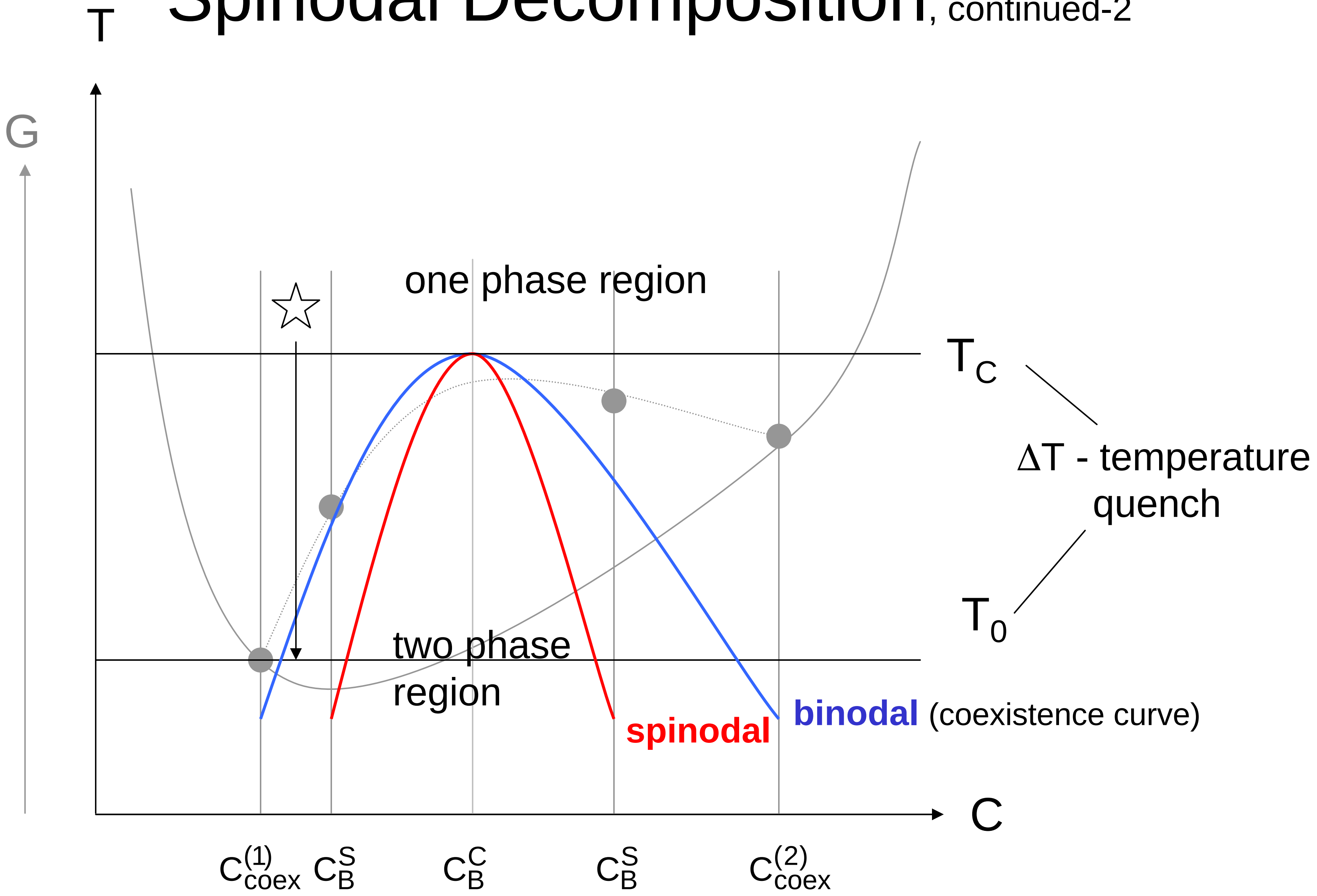
Spinodal Decomposition, contiunued-1



phase diagram of a binary mixture with a miscibility gap of unmixing

driving force for the transition increases as the unstabel / metastable region is penetrated; this gives rise to activation free energy that depends strongly on experimental conditions

Spinodal Decomposition, continued-2



Binary Nucleation

more than one component nucleate

binary Gibbs-Thomson equation

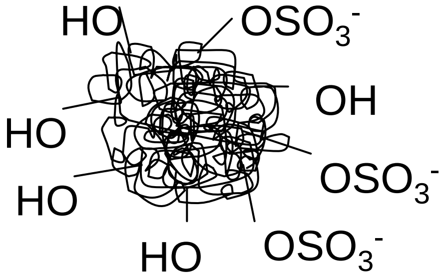
$$\Delta\mu_i = -\frac{2\sigma \cdot v_i}{R}$$

σ - for a binary cluster???

σ_A and σ_B for both components?

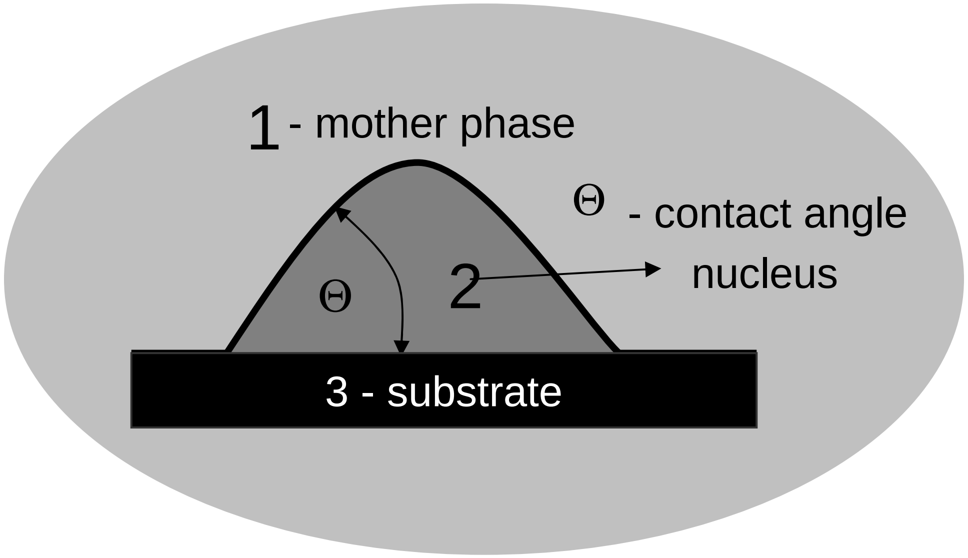
microscopic and macroscopic σ

Binary or multiple nucleation is important for many processes like cloud formation and emulsion polymerization



Heterogeneous Nucleation, continued-1

promotion of nucleation by insoluble particles / interfaces



$$f(m) = (2+m)\cdot\frac{1}{4}\cdot(1-m)^2$$

$$m = \cos\Theta = \frac{\sigma_{31} - \sigma_{32}}{\sigma_{21}}$$

$$\Delta G^*{}_{\mathrm{het}} = \Delta G^*{}_{\mathrm{hom}} \cdot f(m)$$

heterogeneous: Θ = 0° → m = 1 → f(m) = 0

Θ = 180° → m = -1 → f(m) = 1 **homogeneous**

Heterogeneous Nucleation, continued-2

the description of the interaction between substrate and nucleus using a single parameter [f(m)] (Young-equation) is very crude, but there are no theoretic developments in a more microscopic direction

this situation does not reflect the importance of heterogeneous nucleation in our world where interfaces are almost always present (dust particles in atmospheric nucleation, reactor walls in crystallizations, precipitations, and polymerizations, etc.)

Ion-Induced Nucleation

- another kind of nucleation which is not yet well understood on the basic level
- classical expression for the free energy to form a critical nucleus of radius R around an ion of radius R_i is:

$$\Delta G^*_{ii} = \Delta G^*_{hom} + \frac{e^2}{8\varepsilon\varepsilon_0} \cdot \left(\frac{1}{R_i} - \frac{1}{R} \right) \cdot \left(1 - \frac{1}{\varepsilon} \right)$$

e - unit charge ε_0 - vacuum permittivity

ε - relative dielectric constant of the nucleus

- the classical theory does not predict differences due to ion polarity
- but it is known since 100 years that water vapor nucleates much more readily around negative ions than positive ones

C.T.R. Wilson Philos. Trans. A 193, 289 (1899)

Ion-Induced Nucleation, continued

Fletcher: the polarity preference is attributed to the surface orientation of polar molecules

N.H. Fletcher „The Physics of Rainclouds“, Cambridge University Press (1962)

Rabeony & Mirabel: studied substances with dipole moments ranging from 0 to 1.8 debye; they found that all substances (including water) showed a polarity preference in the presence of an electric field, but not when the field was absent

H. Rabeony, P. Mirabel J. Phys. Chem. 91, 1815 (1987)

Adachi, Okuyama & Seinfeld: used a unipolar ion stream mixed with dibutylphthalate (DBP) vapor with no electric field present; they found a clear positive sign preference and a strong dependence on the ion size

M. Adachi, K. Okuyama, J.H. Seinfeld J. Aerosol.Sci. 23, 327 (1992)

Experiments

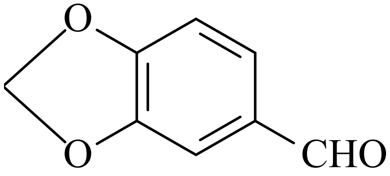
- nucleation experiments are not easy to carry out and the results are not easy to predict

$$J \propto \exp(-\Delta G^* / k_B T)$$

- this exponential dependence makes nucleation very prone to even slight changes in the experimental conditions
- the direct experimental observation of nucleation is a hard task as the critical nucleus is pretty small (n < 100)
- induction time statistics is a fundamental problem in nucleation experiments
- in comparison to the number of existing molecules the nucleus formation is a rare event

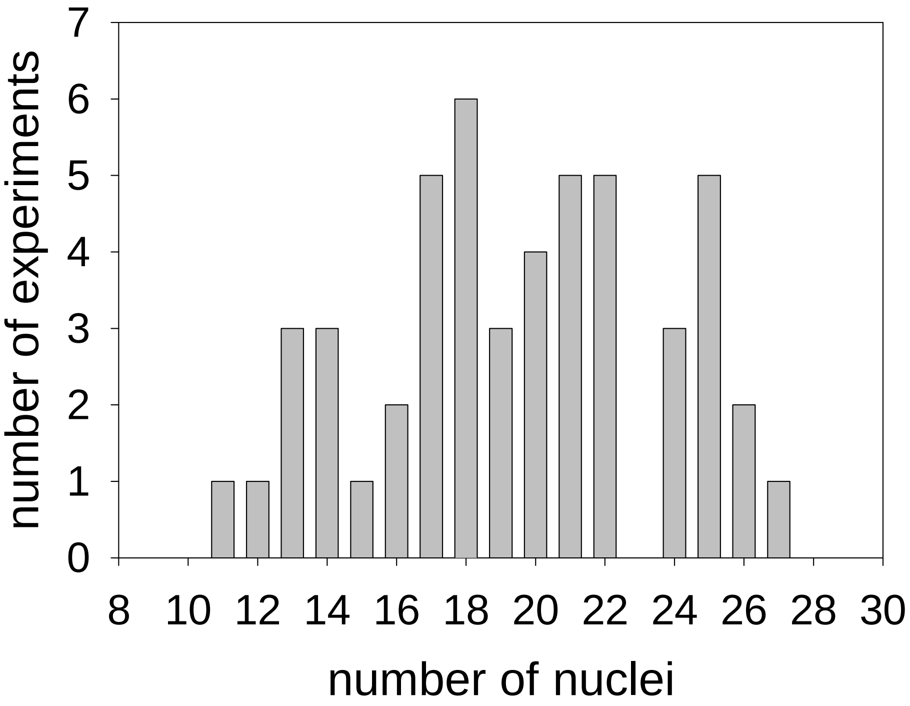
Statistics of Nucleation

that nucleation is like a game of dice is known for almost hundred years



piperonal F_P = 37°C

a melt at 50°C was supercooled to 25°C for and kept for 30 seconds then brought in a bath at 35°C to count the nuclei



→ the larger the amount of piperonal the less the statistical scatter

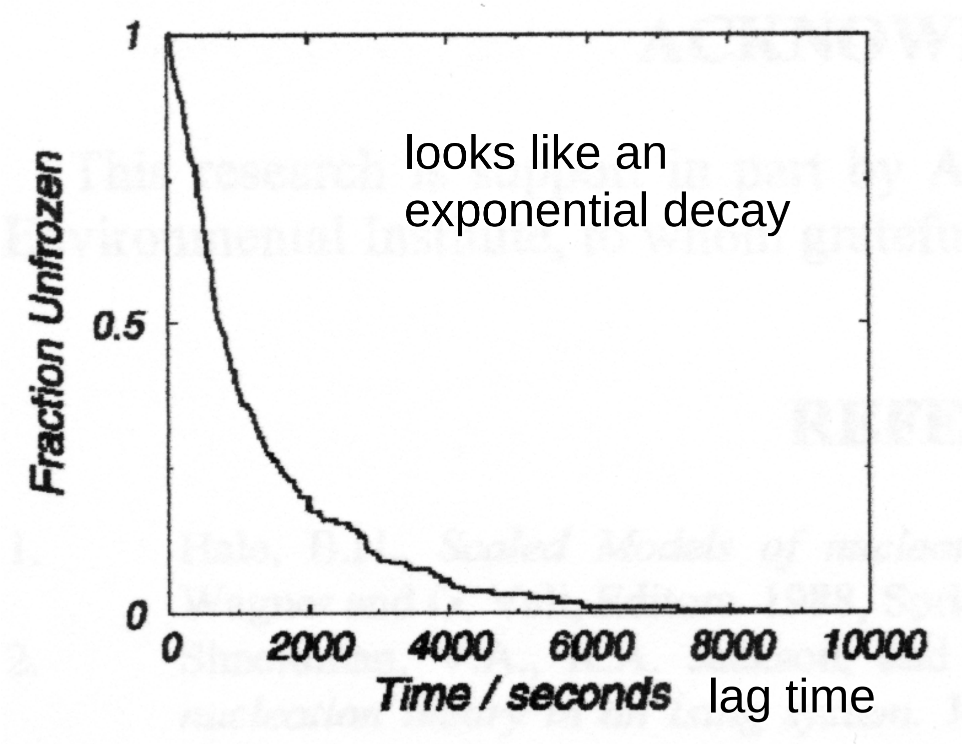
G. Tammann „Aggregatzustände“ Verlag von Leopold Voss, Leipzig, 1922, p 237

Statistics of Nucleation, continued

freezing of water

A single sample of water is repeatedly cooled to a fixed supercooling point; the sample is held there until a freeze occurs; the time it takes is called lag time or induction time (τ)

Up to 500 repeats (N_0) to generate unambiguous statistics for nucleation



looks like an exponential decay

lag time

$$N(t) = N_0 \cdot \exp(-k \cdot t)$$

$k \equiv 1/\langle \tau \rangle$ → statistical nucleation rate constant

A. Heneghan, A.D.J. Haymet „Nucleation of pure and AgI seeded supercooled water using an automated lag time apparatus“ in AIP Conference Proceedings 534, 439 (2000)

Statistics of Nucleation, remarks

- nucleation as the passing of a system from a metastable into a stable state is of random nature
- in the case of supersaturated solutions random fluctuations of the solute concentration can trigger the nucleation process
- the random nature is the reason that an induction or lag time is observed in nucleation processes
- Knowledge of statistics in the study of random phenomena is absolutely necessary (e.g. to repeat the experiments many times under precisely the same conditions)
- this is important to draw reliable conclusions

Nucleation Models - A Comparison

SCCT - self consistent classical theory corrects for the nonzero free energy of the monomers via subtracting the free energy of the monomer from all cluster sizes

DIT - diffuse interface theory considers a strongly curvature dependent surface tension related to a characteristic interface thickness

DFT - density functional theory incorporates molecular interaction potential explicitly; the radial density profile of the critical fluctuation is determined by finding the extremum of the of the free energy functional via variational methods

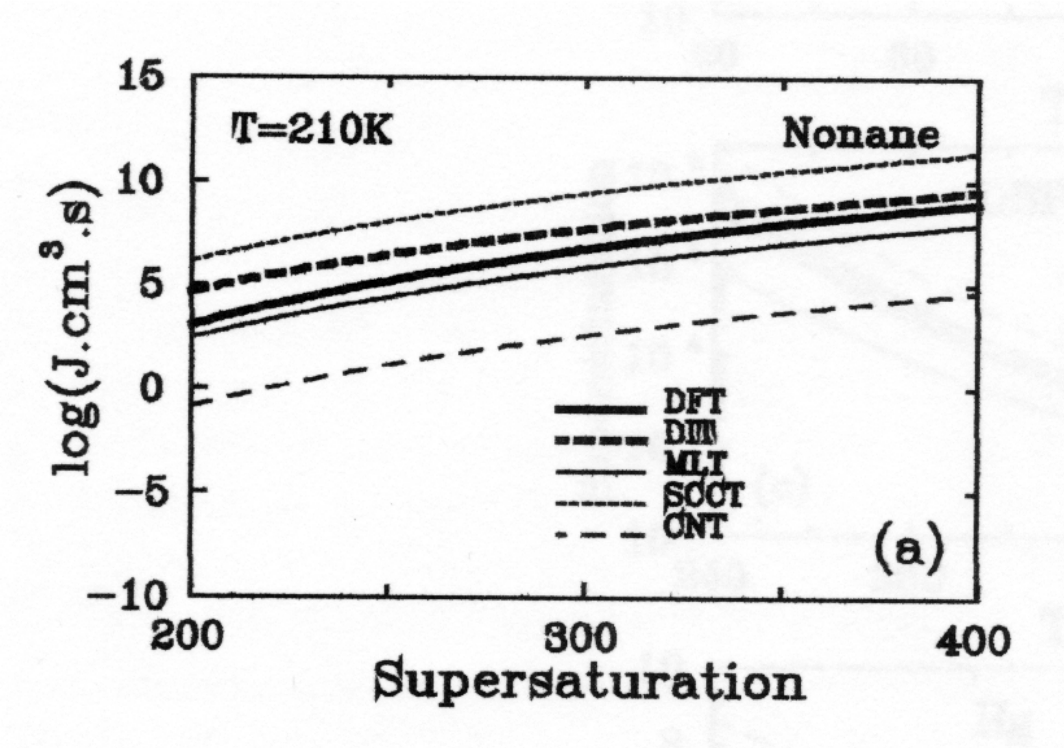
MLT - a DFT related scaling theory; the curvature dependence of the surface tension is related to the number of molecules in the classical drop at the spinodal (Yukawa type perturbative attraction)

CNT - classical nucleation theory; constrained equilibrium

Nucleation Models - A Comparison, continued

the problem with nucleation models:

O_{FF} - orders of magnitude "off" from experiment

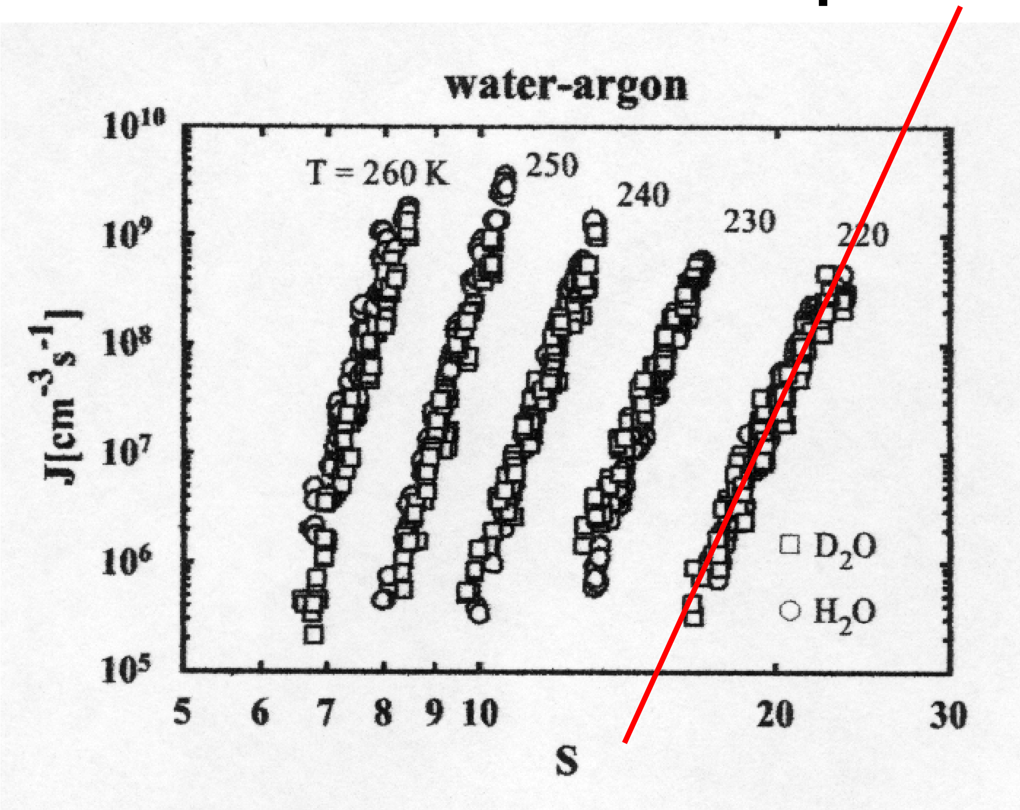


Model	O_{FF}
CNT	4.13
DFT	2.3
MLT	1.9
SCCT	1.73
DIT	1.27

a difference of 7 orders of magnitude

L. Gránásy „Comparison of Modern Theories of Vapor Condensation“ in AIP Conference Proceedings 534, 209 (2000)

Nucleation Experiments, an example



$$n^* = \frac{d(k_B T \cdot \ln J)}{d\phi}$$

n*: 20 - 40

$$n^* = \frac{32 \cdot \pi \cdot v^2 \cdot \sigma^3}{3 \cdot \phi^3}$$

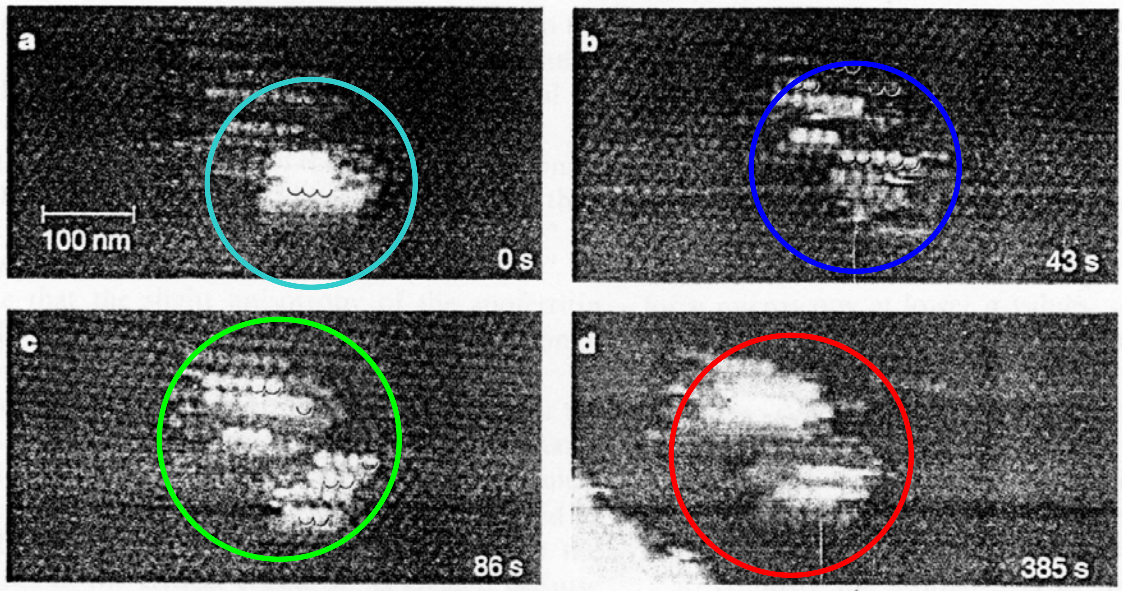
macroscopic σ - values

The nucleation rate of D_2O at the same absolute vapor pressure is 2500 times higher than that of H_2O; but at the same T and S the rates are identical

J. Wölk, Y. Viisanen, R. Strey „Homogeneous Nucleation Rates for Water“ in AIP Conference Proceedings 534, 439 (2000)

Catching Crystals at Birth, brand new results-1

the earliest stages of crystallization are nucleation processes



changes in C_n

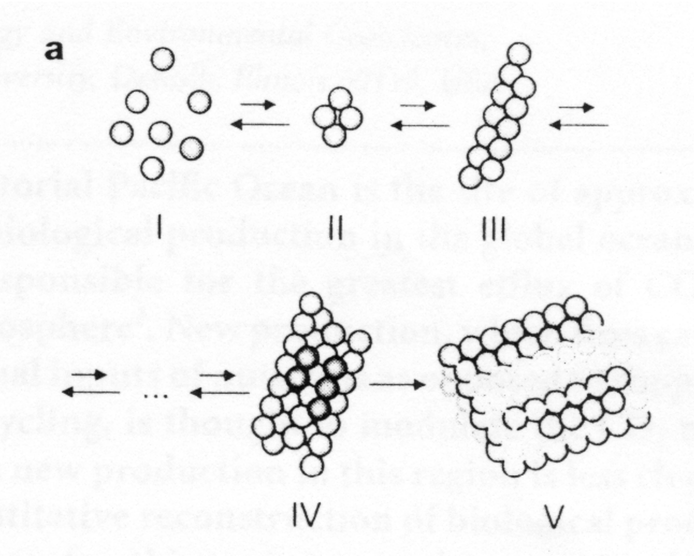
near-critical size cluster of an apoferritin crystal at (ϕ = 1.1)
AFM picture; glass plate covered with a monolayer of

S.-T, Yau, P.G. Velikov Nature 406, 494 (2000) and D.W. Oxtoby Nature 406, 464 (2000)

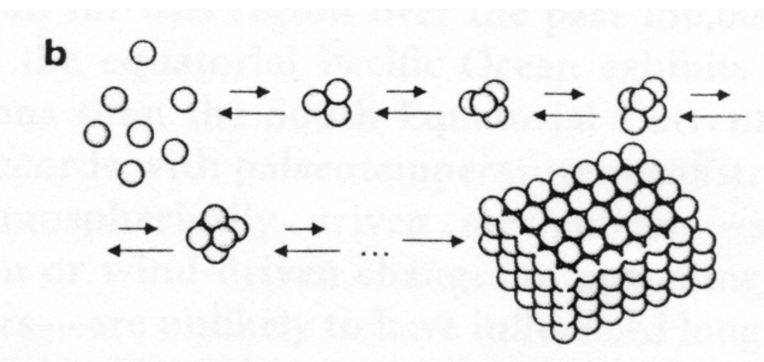
Catching Crystals at Birth, brand new results-2

nucleation pathways

nucleation via a
planar critical cluster:



nucleation via a
compact critical cluster:



The Attempt of a Summary

→ many systems where nucleation is an important step

→ in general: nucleation is a phase transformation which may take place via density fluctuations

→ many theories of nucleation which are able to describe experimental results well in (a) particular case(s)

→ CNT describes basic principle of nucleation processes and is successfully used in many cases

→ the experimental investigation of the nucleation (critical nucleus) is a hard task and still today a challenge for almost all systems