Classical Theories of nucleation
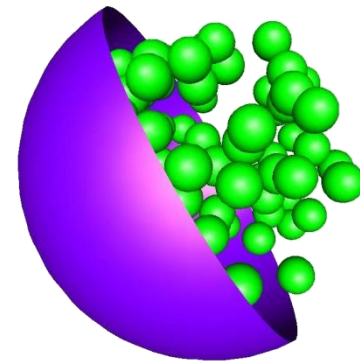
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Outline

- **Introduction**
- **Classical Nucleation Theory of Homogenous condensation**
  - Kinetics of nucleation
  - Thermodynamics of nucleation
- **Bubble formation**
- **Nucleation in condensed phases**
- **Heterogeneous nucleation**
- **How good is CNT?**
- **Limitations of CNT**
- **Quick tour of recent developments**

What is nucleation?

Nucleation is the first and crucial step in many phase transitions
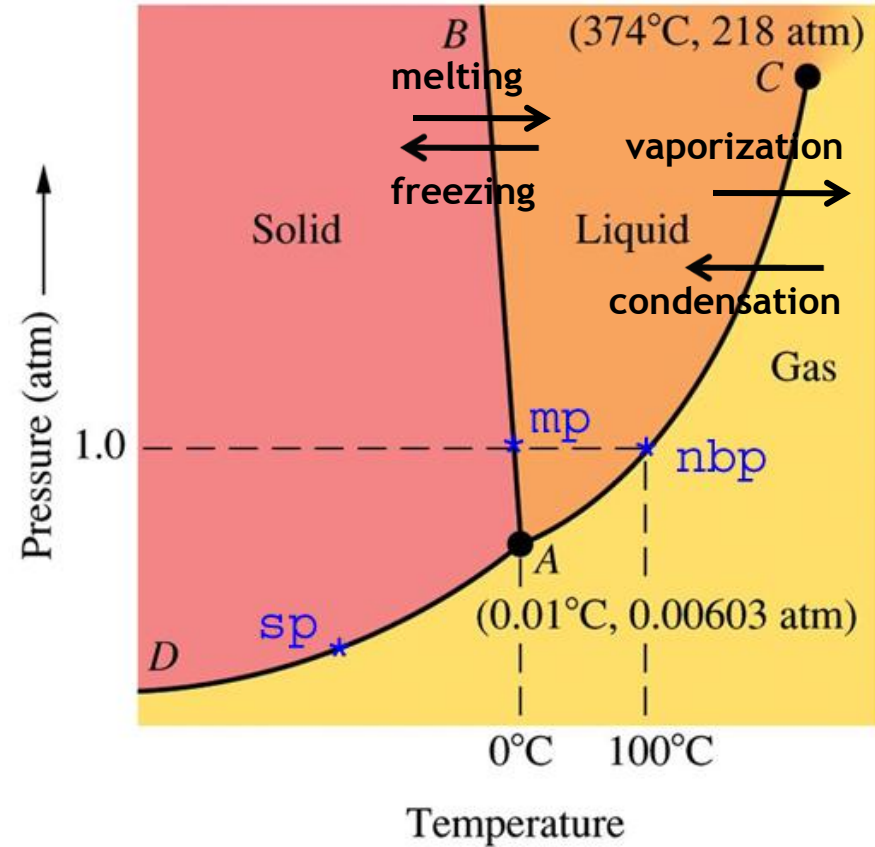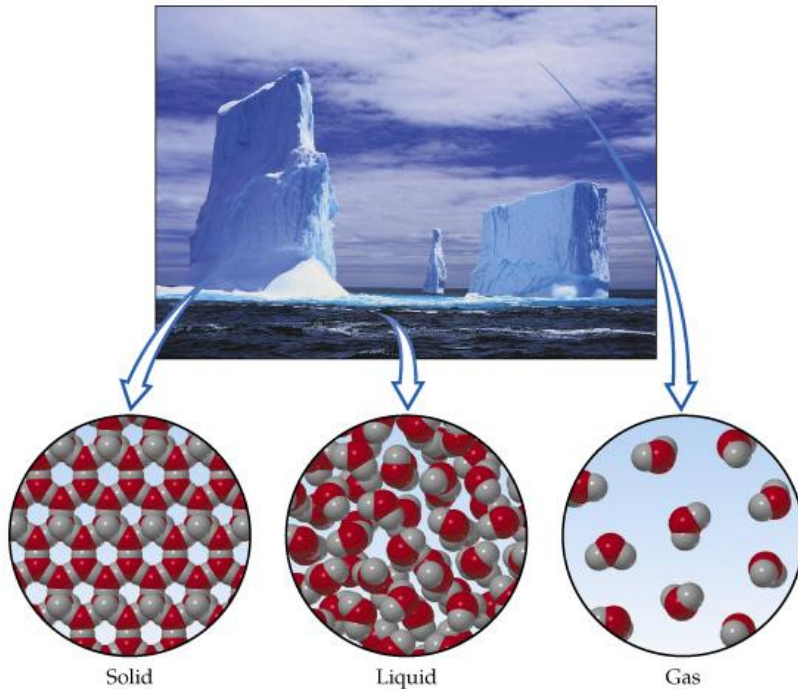
Phase transitions and metastability
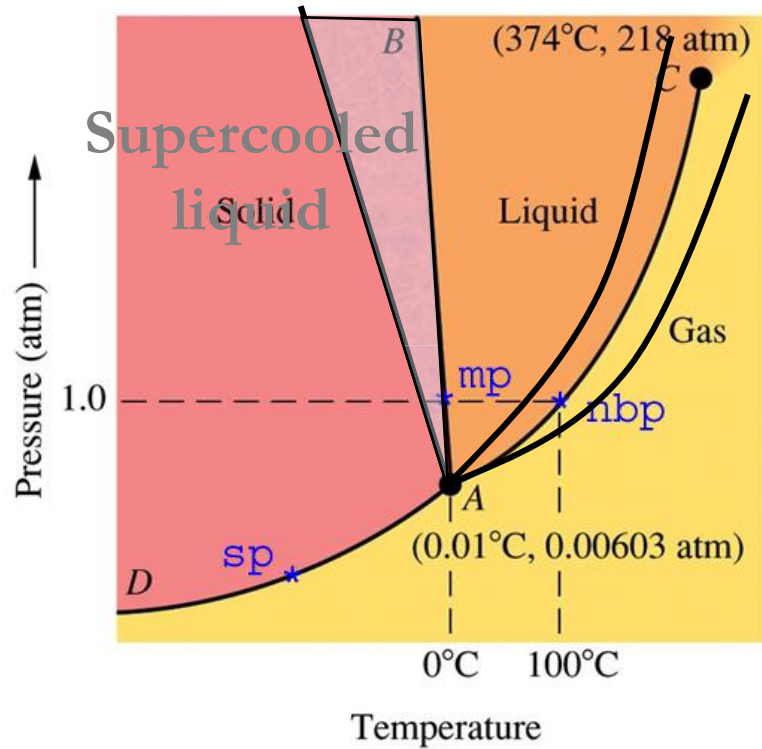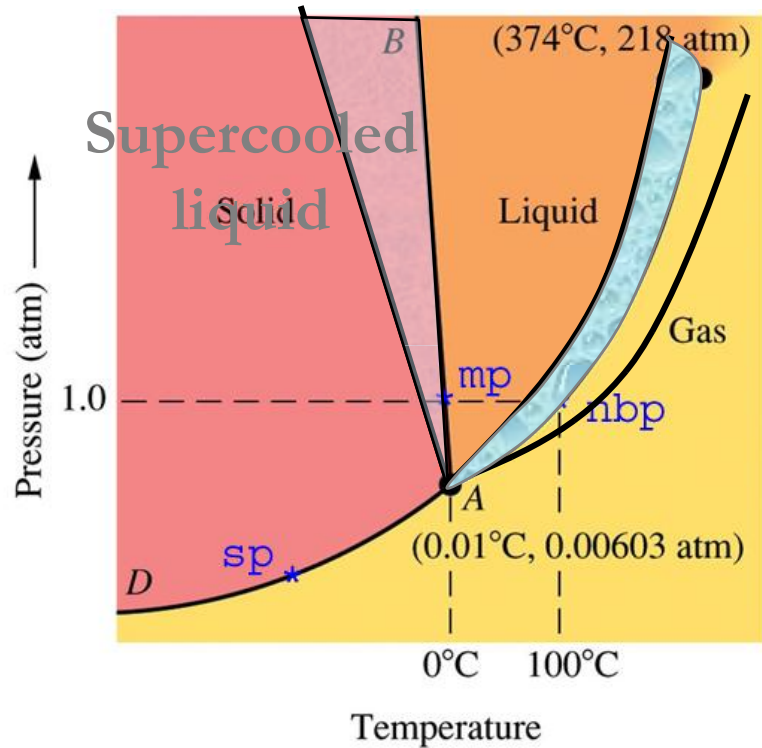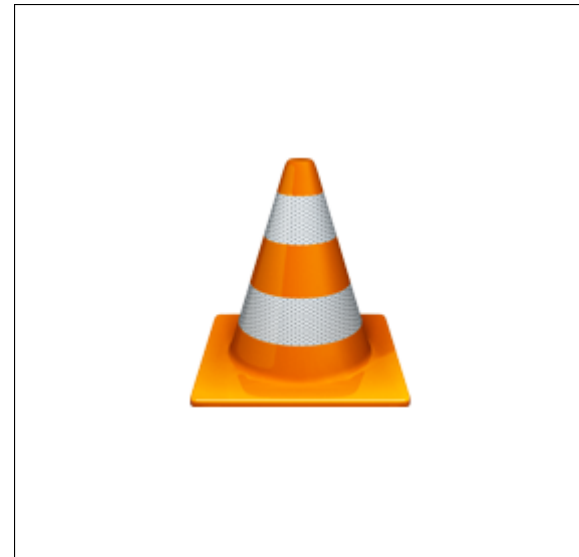
Phase transitions and metastability

Supersaturated vapor

Supercooled liquid

Liquid nucleation

Crystal nucleation

Why is nucleation important?

Nucleation is an activated process that controls most phase transitions
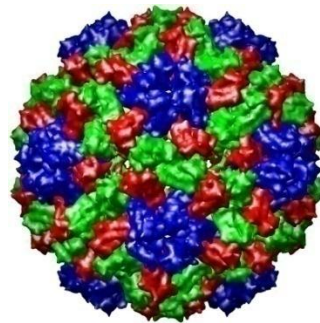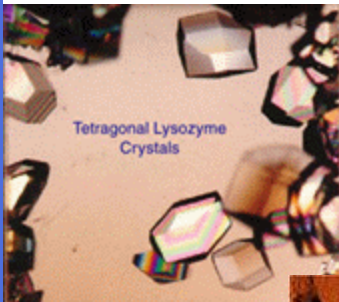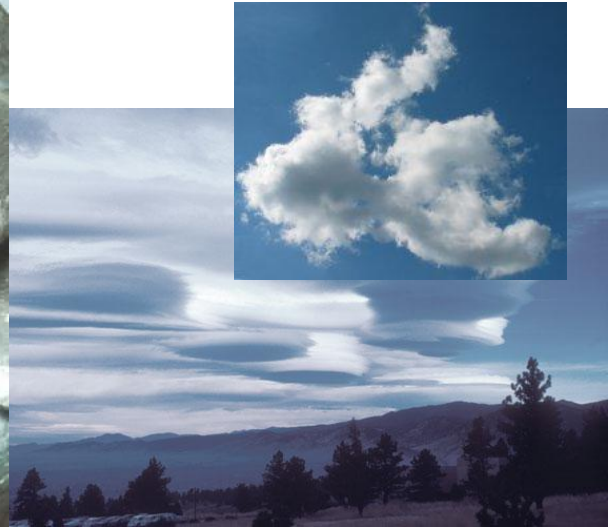
Introduction: phase transitions in a van der Waals fluid

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T < 0$$
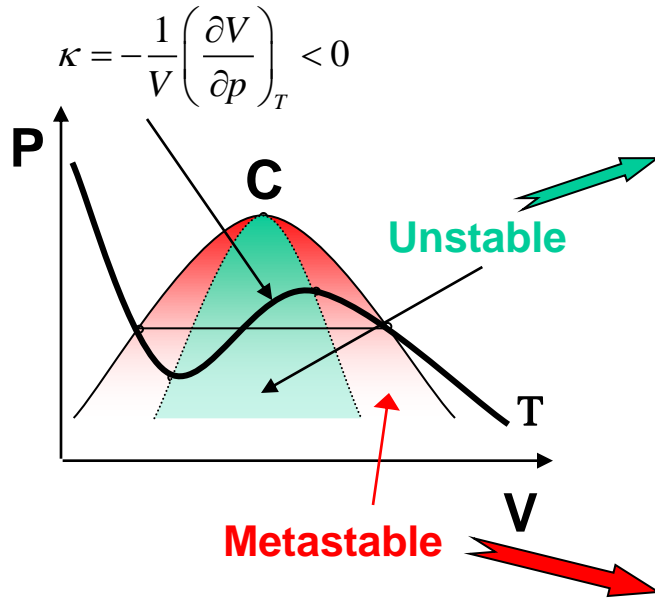
Spinodal Decomposition

Unstable

Metastable
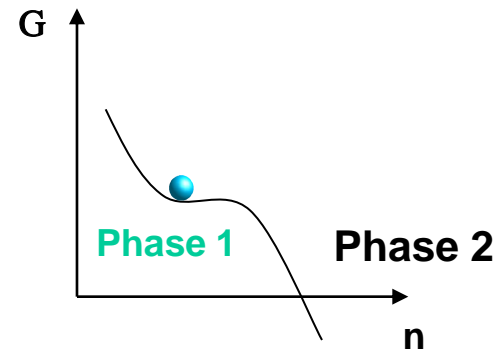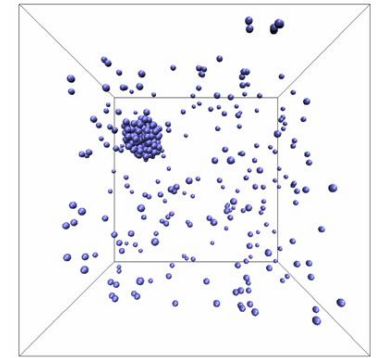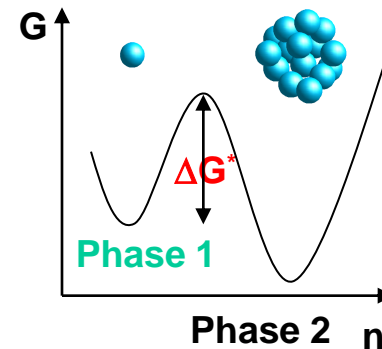
Nucleation

- Supersaturation: $S = p/p_{eq}$
- Nucleation Barrier: ΔG^*
- Critical size: n^*
- Nucleatíon Rate: **J**

Simplest example of a nucleation process: condensation of a vapor

- **Nucleation:** Initial mechanism that explains the formation of the first embryos of the new phase

- ## Work of cluster formation

$$\Delta G_{CNT}(n) = -\Delta\mu\, n + \sigma A(n)$$

n ⬌

ΔG — Surface term — Nucleation barrier — ΔG* — n* — n — Volume term
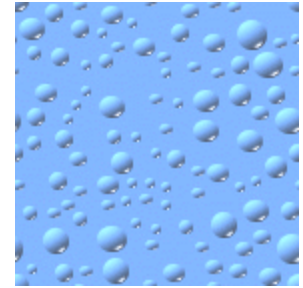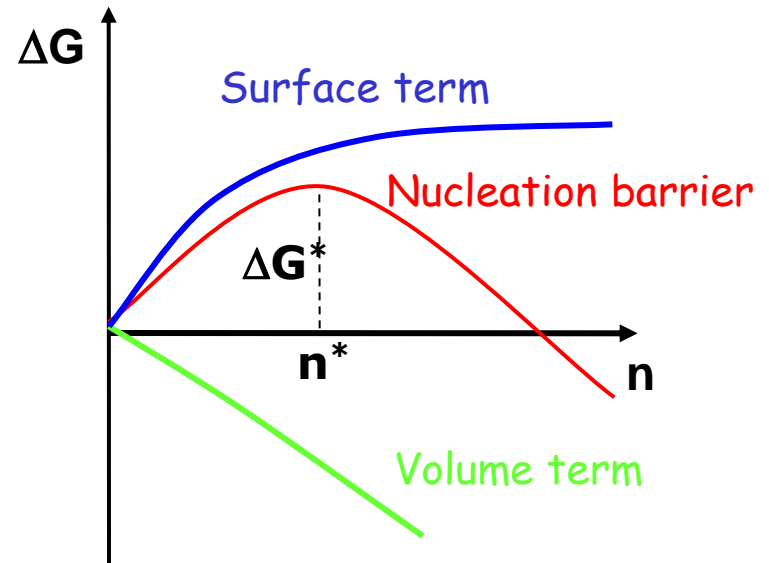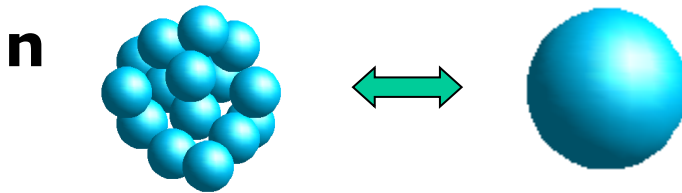
- ## Classification:
  - Homogeneous
  - Heterogeneous
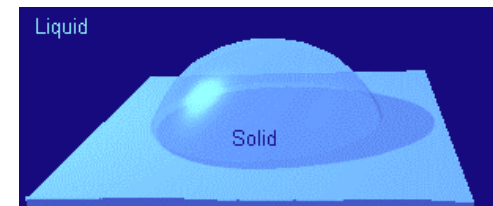
Nucleation Kinetics

- Growth of clusters is modeled as a series of chemical reactions

i

$$f(i,t) \underset{\alpha(i+1,t)}{\overset{\beta(i,t)}{\rightleftharpoons}} f(i+1,t)$$

β

α
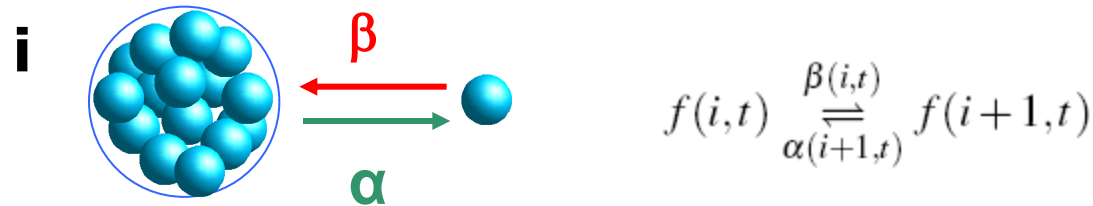
- Assumptions:
  - Clusters grow/decay by the addition of **individual** molecules
  - No memory
  - Isothermal conditions

- Master equation of the evolution of clusters:

$$\frac{\partial f(i,t)}{\partial t} = \beta(i-1,t)f(i-1,t) - \alpha(i,t)f(i,t) - \beta(i,t)f(i1,t) + \alpha(i+1,t)f(i+1,t)$$

f(i,t)= concentration of clusters containing i molecules at time t

$\alpha(i,t)$= rate of detachment of individual molecules from a cluster of size i

$\beta(i,t)$ = rate of attachment of individual molecules to a cluster of size i

Nucleation kinetics (2)

Master equation:

$$\frac{\partial f(i,t)}{\partial t} = \beta(i-1,t)f(i-1,t) - \alpha(i,t)f(i,t) - \beta(i,t)f(i1,t) + \alpha(i+1,t)f(i+1,t)$$

Current:

$$J(i+\frac{1}{2},t) = \beta(i,t)f(i,t) - \alpha(i+1,t)f(i+1,t)$$

i ⟵ i+1
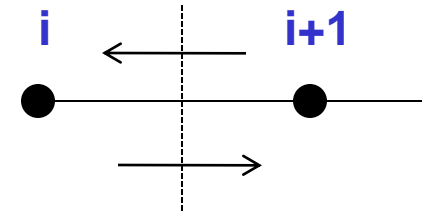
$$\frac{\partial f(i,t)}{\partial t} = J(i-\frac{1}{2},t) - J(i+\frac{1}{2},t)$$

Steady state nucleation rate J:

$$\frac{\partial f(i,t)}{\partial t} = 0 = J(i-\frac{1}{2},t) - J(i+\frac{1}{2},t)$$

$$J(i\pm\frac{1}{2},t) = J \qquad J = \text{steady state nucleation rate}$$

J does not depend on time and is the same for all sizes

Kinetic theory of nucleation

$$J = \beta(i)f(i) - \alpha(i+1)f(i+1)$$

- Condensation rate can be evaluated from kinetic theory

$$\beta(i) = \frac{p}{\sqrt{2\pi m_1 k_B T}} \quad A(n) = \frac{p}{\sqrt{2\pi m_1 k_B T}} s_1 n^{2/3}$$

- … but the evaporation rate not!

To circunvent this problem, one resorts to the so-called constrained equilibrium hypothesis

"Constrained" equilibrium

N(i)= constrained equilibrium distribution, that satisfies:

$$J(i) = 0 \ for \ all \ i$$

N(i) is then the equilibrium cluster distribution

$$P(i) \approx \frac{N(i)}{N} \approx e^{\frac{-\Delta G(i)}{kT}}$$

$$N(i) \sim N_1 e^{\frac{-\Delta G(i)}{kT}}$$
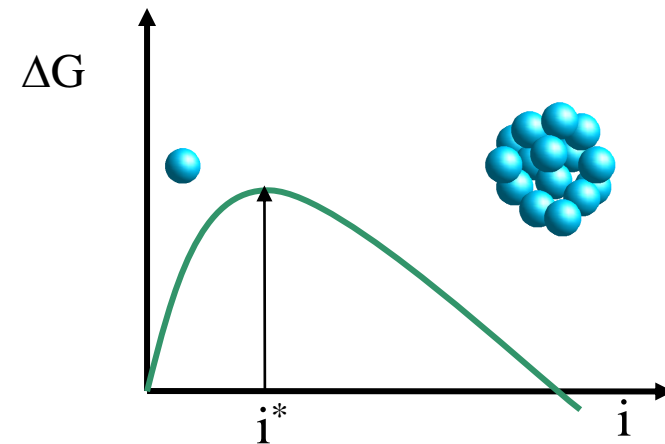
Steady state rate $\qquad J = \beta(i) f(i) - \alpha(i+1) f(i+1)$

Using N(i) one gets:

$$J(i) = 0 \ for \ all \ i \quad \Longrightarrow \quad \beta(i)N(i) = \alpha(i+1)N(i+1)$$

$$\alpha(i+1) = \bar{\beta}(i)\frac{N(i)}{N(i+1)} \quad \Longrightarrow \quad J = \beta(i)N(i)\left[\frac{f(i)}{N(i)} - \frac{f(i+1)}{N(i+1)}\right]$$

Kinetics of nucleation (4)

$$\frac{J}{\beta(i)N(i)} = \frac{f(i)}{N(i)} - \frac{f(i+1)}{N(i+1)}$$

Summing up over all cluster sizes:

$$\sum_{i=1}^{i_b-1}\left[\frac{f(i)}{N(i)} - \frac{f(i+1)}{N(i+1)}\right] = \frac{f(1)}{N(1)} - \frac{f(2)}{N(2)} + \frac{f(2)}{N(2)} - \frac{f(3)}{N(3)} + ... - \frac{f(i_b)}{N(i_b)}$$

$$\sum_{i=1}^{i_b-1}\frac{J}{\beta(i)N(i)} = \frac{f(1)}{N(1)} - \frac{f(i_b)}{N(i_b)}$$

Boundary conditions: $\qquad \dfrac{f(1)}{N(1)} = 1 \qquad\qquad \dfrac{f(i_b)}{N(i_b)} = 0$

$$\sum_{i=1}^{i_b-1}\frac{J}{\beta(i)N(i)} = 1 \implies \boxed{J = \left[\sum_{i=1}^{i_b-1}\frac{1}{\beta(i)N(i)}\right]^{-1}} \qquad N(i) \sim N_1 e^{\frac{-\Delta G(i)}{kT}}$$

So now it is a matter of calculating the work of formation of a cluster of i molecules

Nucleation rate

$$J = \left[\sum_{i=1}^{i_b-1} \frac{1}{\beta(i)N(i)} \right]^{-1}$$

ΔG

Nucleation Barrier

**ΔG*

n* **n**

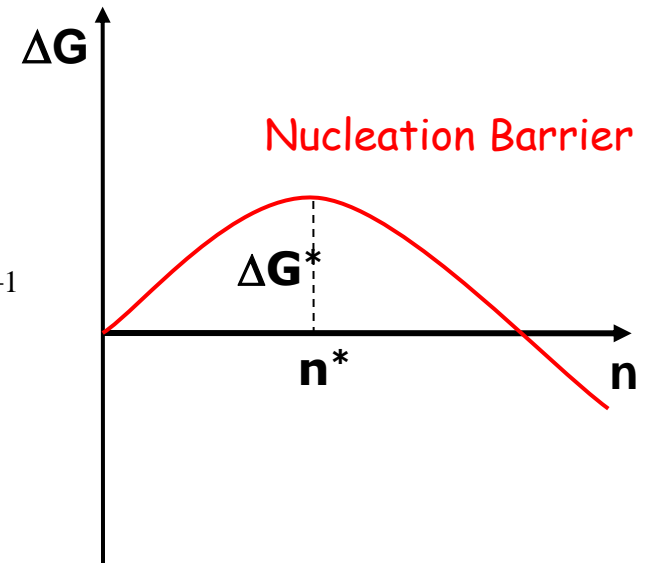**Continuous approx.:**

$$J \approx N_1 \left[\int_{i=1}^{i_b-1} \frac{di}{\beta(i)e^{-\frac{\Delta G(i)}{k_B T}}} \right]^{-1}$$

Steepest descent:

$$\Delta G(i) \approx \Delta G(i^*) + \frac{1}{2} \left. \frac{d^2 \Delta G(i)}{di^2} \right|_{i^*} (i - i^*)^2 + ...$$

$$J = N_1 \beta(i^*) Z e^{-\frac{\Delta G^*}{k_B T}}$$

Zeldovich factor

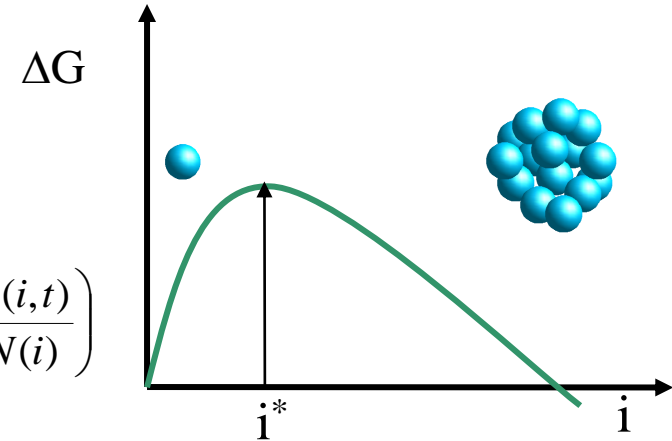$$Z = \sqrt{\frac{|\Delta G''(i^*)|}{2\pi k_B T}}$$

Continuous approximation to the master equation

$$\frac{\partial f(i,t)}{\partial t} = J(i - \frac{1}{2}, t) - J(i + \frac{1}{2}, t) = -\frac{\partial J(i,t)}{\partial i}$$

$$J(i+1/2,t) = \beta(i)N(i)\left(\frac{f(i,t)}{N(i)} - \frac{f(i+1,t)}{N(i+1)}\right) \approx \beta(i)N(i)\frac{\partial}{\partial i}\left(\frac{f(i,t)}{N(i)}\right)$$

$$\frac{\partial f(i,t)}{\partial t} = -\frac{\partial J(i,t)}{\partial i} = \frac{\partial}{\partial i}\left(\beta(i)N(i)\frac{\partial}{\partial i}\left(\frac{f(i,t)}{N(i)}\right)\right)$$

$$\frac{\partial f(i,t)}{\partial t} = \frac{\partial}{\partial i}\left(\beta(i)e^{-\frac{\Delta G(i)}{kT}}\frac{\partial}{\partial i}\left(f(i,t)e^{\frac{\Delta G(i)}{kT}}\right)\right)$$

Fokker-Planck eq. for nucleation

$$J = N_1\beta(i^*)Ze^{-\frac{\Delta G^*}{k_B T}}$$

Nucleation rate (i.e. Kramers rate, transition state rate, Arrenhius...)

ΔG

i^* i

Simplified thermodynamics of cluster formation

- Quick review of thermodynamics *a la* Callen:

$$U(S,V,N) = TS + \mu N - pV.$$

$$dU = TdS + \mu dN - pdV$$

Gibbs-Duhem eq.
$$0 = -SdT - Nd\mu + Vdp$$

**Thermodynamic potentials:**

$$G(p,T,N) = U - TS + pV = \mu N$$
$$dG = \mu dN - SdT + Vdp$$

$$\Omega(\mu,V,T) = -pV$$
$$d\Omega = -Nd\mu - SdT - pdV$$

Abraham's book

CNT assumptions

- The (drastic) assumptions of CNT are:
  - Thermodynamics can be applied to unstable objects of molecular dimensions
  - Homogenous phases up to the interface
  - The interface is perfectly sharp
  - The densities are the same as in the bulk phases
  - The surface tension is the same

  as the bulk flat interface
  - Spherical drop
  - Ideal vapor
  - Incompressible liquid
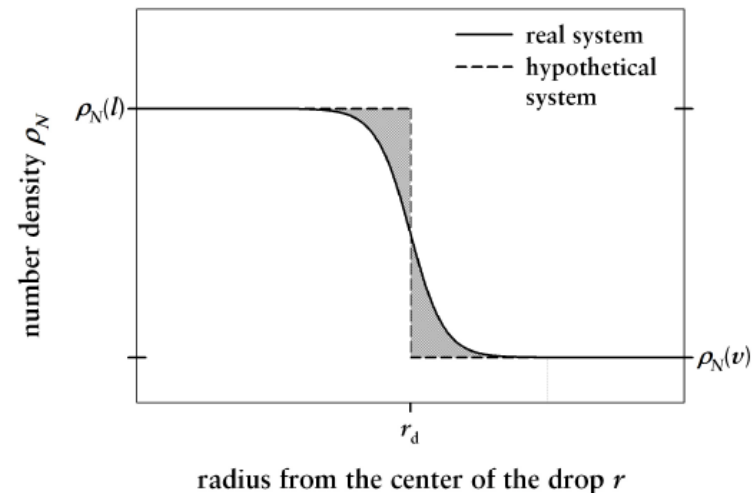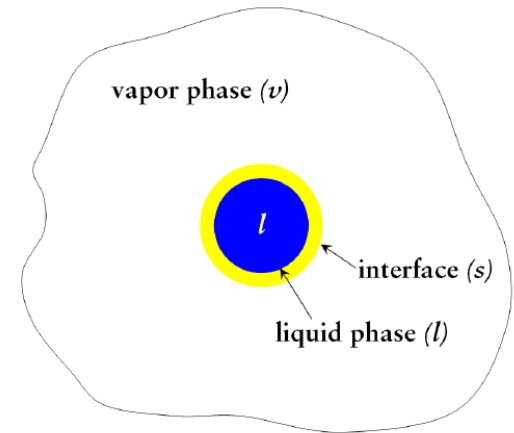
A hypothetical vapor+drop system

Total number of particles and energy:

$$N = N_v + N_l + N_s$$

$$U = U_v + U_l + U_s$$

Surface quantities are defined as "excesses":

$$U_s = U - U_v - U_l$$

For each phase:

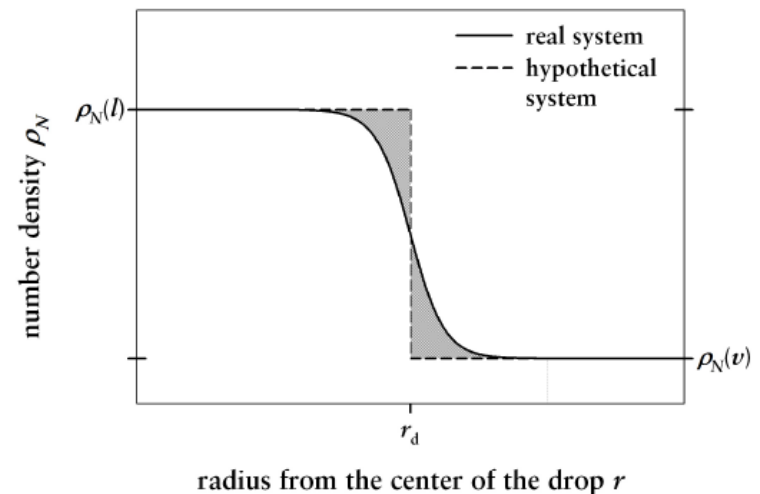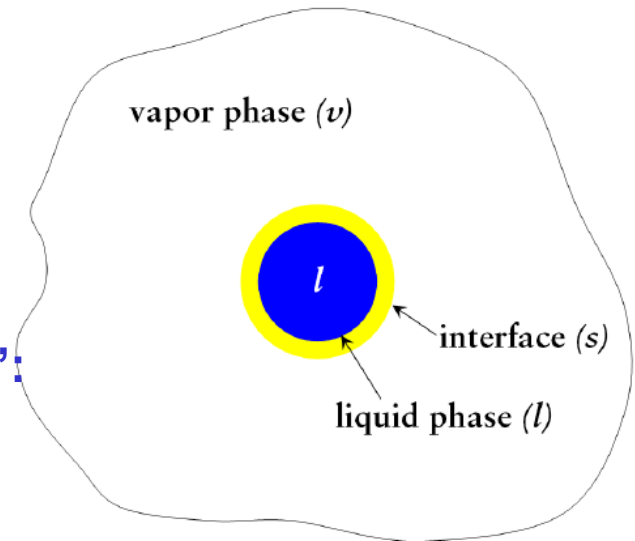$$U_v(r) = T_v S_v(r) + \mu_v N_v(r) - p_v V_v(r)$$

$$U_l(r) = T_l S_l(r) + \mu_l N_l(r) - p_l V_l(r)$$

$$U_s(r) = T_s S_s(r) + \mu_s N_s(r) + \gamma A(r)$$

where:

$$-p_i = \left(\frac{\partial U_i(r)}{\partial V_i}\right)_{S_i, N_i} \qquad T_i = \left(\frac{\partial U_i(r)}{\partial S}\right)_{V_i, N_i}$$

$$\gamma = \left(\frac{\partial U_s(r)}{\partial A}\right)_{S_s, N_s} \qquad \mu_i = \left(\frac{\partial U_i(r)}{\partial N_i}\right)_{S_i, V_i}$$

vapor phase (v)

l

interface (s)

liquid phase (l)

real system
---- hypothetical system

$\rho_N(l)$

number density ρ_N

$\rho_N(v)$

r_d

radius from the center of the drop r

Generalized Laplace equation

- Critical nucleus= drop at (unstable) equilibrium with the vapor

Equilibrium conditions:

$$\mu_v = \mu_l = \mu_s \equiv \mu$$

$$T_v = T_l = T_s \equiv T$$

$$
\begin{aligned}
U &= U_v + U_l + U_s \\
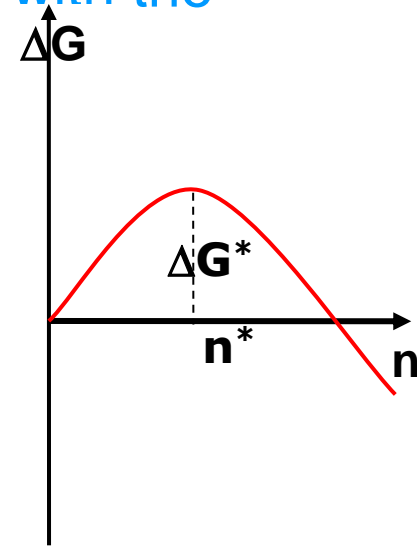&= -p_v V_v(r) - p_l V_l(r) + \gamma A(r) + TS + \mu N
\end{aligned}
$$

$$dU = -p_v dV_v(r) - p_l dV_l(r) + \gamma dA(r) + A\left[\frac{\partial \gamma}{\partial r}\right] dr$$

$$-dV_v = dV_l = A dr$$

$$\boxed{p_l - p_v = \frac{2\gamma}{r} + \left[\frac{\partial \gamma}{\partial r}\right]}$$

For the **"surface of tension"**

$$\left[\frac{\partial \gamma}{\partial r}\right] = 0 \qquad \Longrightarrow \qquad p_l - p_v = \frac{2\gamma_s}{r_s}$$

Δ**G**

Δ**G***

n*

n

Generalized Kelvin equation

- At equilibrium: $\mu_l(p_l) = \mu_v(p_v)$

Gibbs-Duhem eq: $SdT - Vdp + Nd\mu = 0$

Ideal gas:

$$d\mu_v = \frac{k_B T}{p} dp$$

$$\boxed{\mu_l(p_{sat}) = \mu_v(p_{sat})}$$

Incompressible fluid:

$$d\mu_l = v_l dp$$

$$\mu_v(p_v) - \mu_v(p_{sat}) = kT \ln \frac{p_v}{p_{sat}}$$

$$\mu_l(p_l) - \mu_l(p_{sat}) = v_l(p_l - p_{sat})$$

$$k_B T \ln S_p = v_l(p_l - p_{sat})$$

$$\boxed{S = \frac{p}{p_{sat}}}$$

$$k_B T \ln S_p = \left(\frac{2\gamma}{r^*} + \left[\frac{\partial \gamma}{\partial r} \right]_{r=r^*} \right) v_l + v_l(p_v - p_{sat})$$
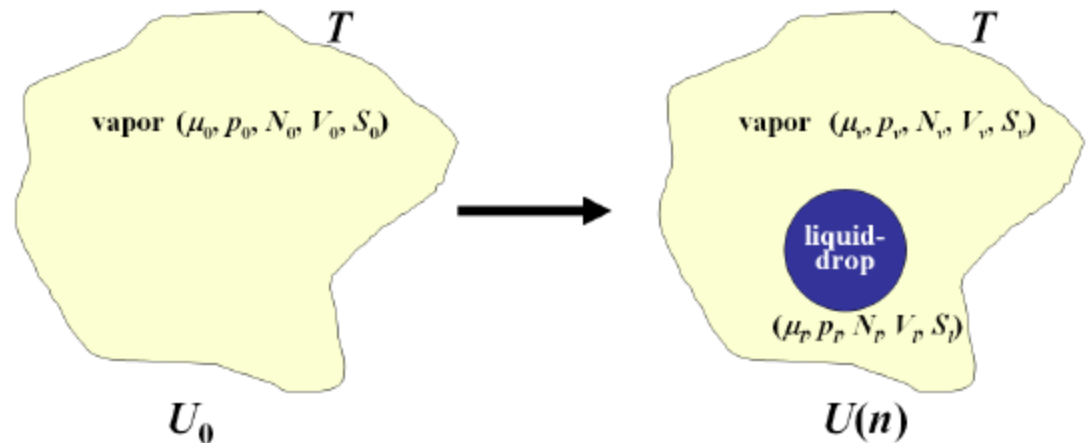
$$r_s^* = \frac{2\gamma_s v_l}{k_B T \ln S_p}$$

For the "surface of tension"

Work of cluster formation

Work of formation= difference between the free energy of drop+vapor and that of a pure vapor at the same conditions

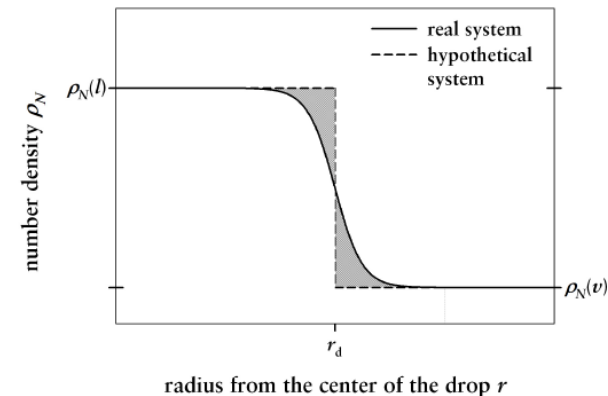**In general, it depends on the constraints. At cte N,p,T**

vapor $(\mu_0, p_0, N_0, V_0, S_0)$

T

U_0

vapor $(\mu_v, p_v, N_v, V_v, S_v)$

liquid-drop

$(\mu_l, p_l, N_l, V_l, S_l)$

T

$U(n)$

$$\Delta G = \Delta U - T\Delta S + p\Delta V$$
$$= (p - p_l)V_l + \gamma A(r) + (\mu_l - \mu_v)N_l + (\mu_s - \mu_v)N_s$$

Equimolar:

$$N_s = 0$$

$$\boxed{\Delta G = (p - p_l)V_{l,e.} + \gamma_e A_e + (\mu_l(p_l) - \mu_v(p))n}$$

Incompressible drop:

$$\mu_l(p_l) - \mu_l(p_v) = v_l(p_l - p_v)$$

$$\boxed{\Delta G = \gamma_e A_e + (\mu_l(p_v) - \mu_v(p_v))n}$$

number density ρ_N

$\rho_N(l)$

$\rho_N(v)$

r_d

—— real system
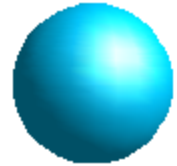---- hypothetical system

radius from the center of the drop r

Work of cluster formation in CNT
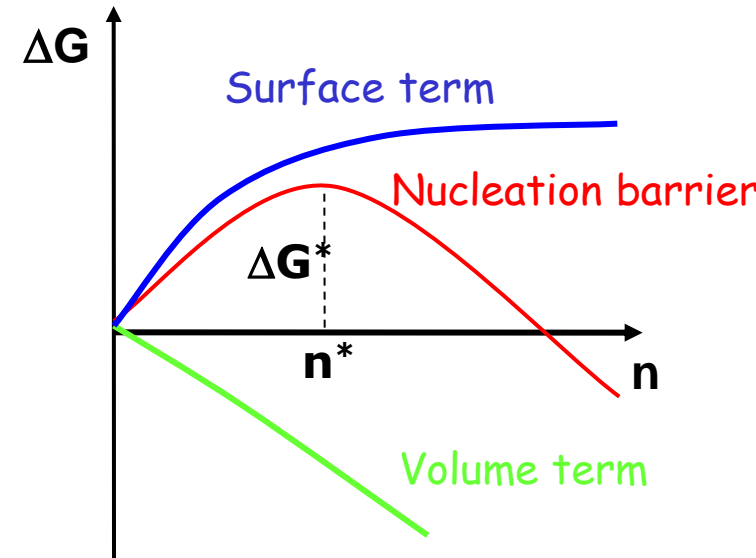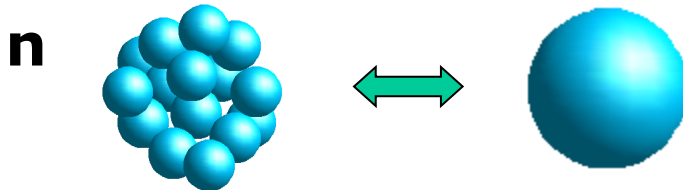
- Assumptions:
  - Spherical drop

$$V_l = \frac{4\pi r^3}{3} = nv_l \qquad r = \left(\frac{3v_l}{4\pi}\right)^{1/3} n^{1/3}$$

$$A(n) = 4\pi r^2 = \left(36\pi v_l^2\right)^{1/3} n^{2/3} = s_1 n^{2/3}$$

  - Incompressibility
  - Sharp interface
  - Same surface tension as the bulk flat liquid

$$\Delta G_{CNT}(n) = -\Delta\mu\, n + \gamma s_1 n^{2/3}$$

n

Nucleation barrier and critical cluster size

$$\Delta G(n) = -\Delta\mu n + s_1\gamma\left(n^*\right)^{2/3}$$
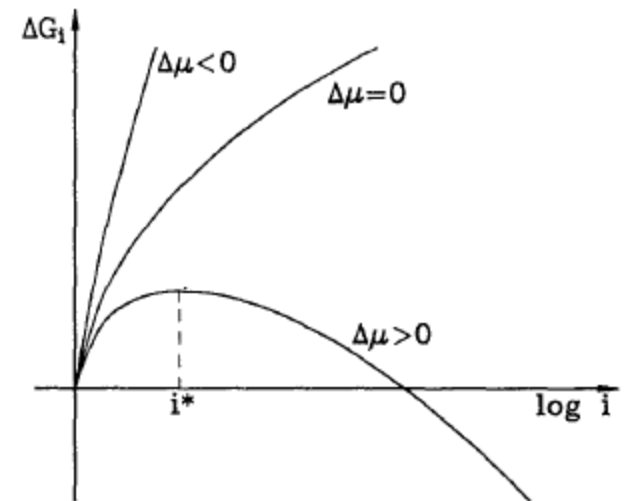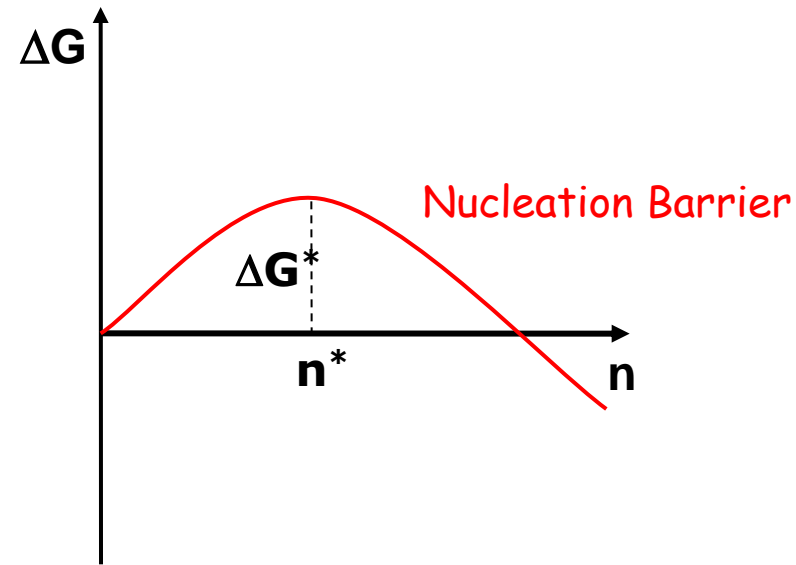
- Critical cluster size:

$$\left.\frac{\partial\Delta G}{\partial n}\right|_{n^*} = 0 \qquad -\Delta\mu + \frac{2}{3}s_1\gamma\left(n^*\right)^{-1/3} = 0$$

$$n^* = \frac{32\pi}{3}\frac{v_l^2\gamma^3}{\Delta\mu^3}$$

- Height of the nucleation barrier:

$$\Delta G^* = \frac{16\pi}{3}\frac{v_l^2\gamma^3}{\Delta\mu^2} = \Delta G(n^*)$$

CNT for condensation of an ideal vapor

- Gibbs-Duhem equation $\quad SdT - Vdp + Nd\mu = 0$

$$d\mu = \frac{V}{N}dp$$

Ideal gas:

$$d\mu_v = \frac{k_B T}{p}dp$$

$$\mu_v(p_v) - \mu_v(p_{sat}) = kT \ln \frac{p_v}{p_{sat}}$$

Incompressible fluid:

$$d\mu_l = v_l dp$$

$$\boxed{\mu_l(p_{sat}) = \mu_v(p_{sat})}$$

$$\mu_l(p_v) - \mu_l(p_{sat}) = v_l(p_v - p_{sat})$$

$$\mu_l(p_v) - \mu_l(p_v) = v_l(p_v - p_{sat}) - k_B T \ln S_p$$

$$\Delta\mu \cong k_B T \ln S$$

$$\boxed{S = \frac{p}{p_{sat}}}$$

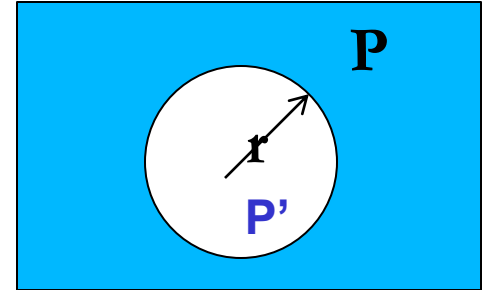$$\Delta G^* = \frac{16\pi}{3}\frac{v_l^2 \gamma^3}{(kT \ln S)^2}$$

$$n^* = \frac{32\pi}{3}\frac{v_l^2 \gamma^3}{(kT \ln S)^3}$$

$$J = v_l\left(\frac{p}{kT}\right)^2 \sqrt{\frac{2\gamma}{\pi m}} \exp\left(-\frac{16\pi}{3kT}\frac{v_l^2 \gamma^3}{(kT \ln S)^2}\right)$$

Bubble nucleation

- Work of formation of a bubble

$$\Delta G(r, P') = 4\pi r^2 \gamma - \frac{4\pi r^3}{3}(P' - P) + \frac{4\pi r^3}{3} P' \ln \frac{P'}{P_{sat}}$$
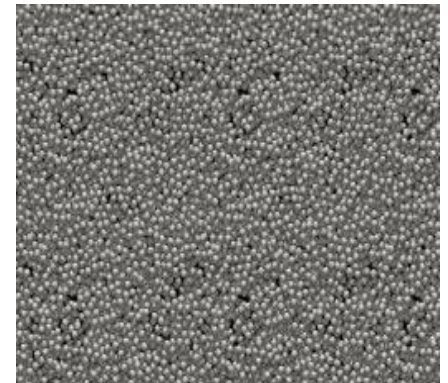

- Assumptions:
  - Vapor in the bubble is in thermodynamic equilibrium.

  $$P' = P_{sat}$$

  - And mechanic equilibrium

  $$P' - P = \frac{2\gamma}{r*}$$

$$r* = \frac{2\gamma}{\Delta P}$$

$$\Delta G* = \frac{4\pi \gamma r^{*2}}{3} = \frac{16\pi \gamma^3}{3(\Delta P)^2}$$

Nucleation in condensed phases

- Crystal nucleation in undercooled liquids

$$n* = \frac{32\pi}{3} \frac{v_l^2 \gamma^3}{\Delta\mu^3}$$

$$\Delta G* = \frac{16\pi}{3} \frac{v_l^2 \gamma^3}{\Delta\mu^2}$$

$$\Delta\mu \approx \frac{(T_m - T)h_f}{T_m}$$

$h_f =$ **enthalpy of fussion per molecule**

$$\beta = \upsilon_0 a_0 n^{2/3} e^{-E_0/k_B T} \longleftarrow \text{activation energy}$$
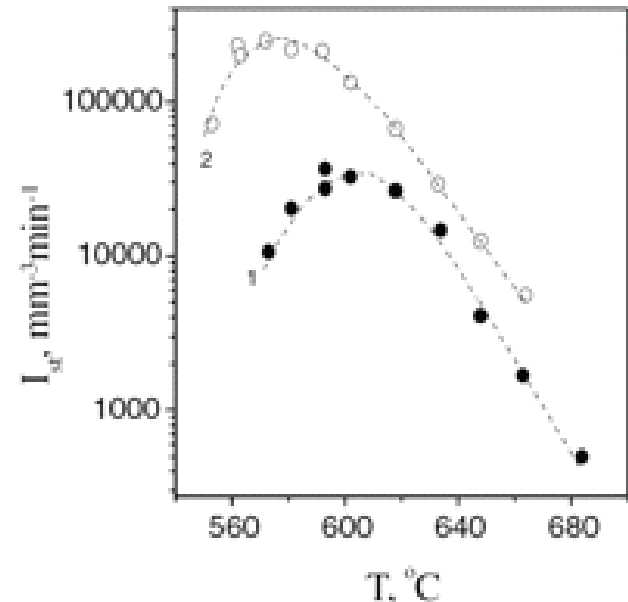
vibration frequency

# of surface sites

Very often the prefactor is assumed to be proportional to bulk diffusivity

$$\beta \approx \frac{6D}{\lambda^2} s_1 n^{2/3}$$

$$J = N_1 \frac{24 D n^{2/3}}{\lambda^2} Z e^{-\frac{\Delta G^*}{k_B T}}$$

Nucleation in supersaturated solutions

$$\Delta\mu = k_B T \ln S = k_B T \ln \frac{C}{C_{sat}} \qquad\qquad \beta^* = (48\pi^2 v_1)^{1/3} DC n^{*1/3}$$
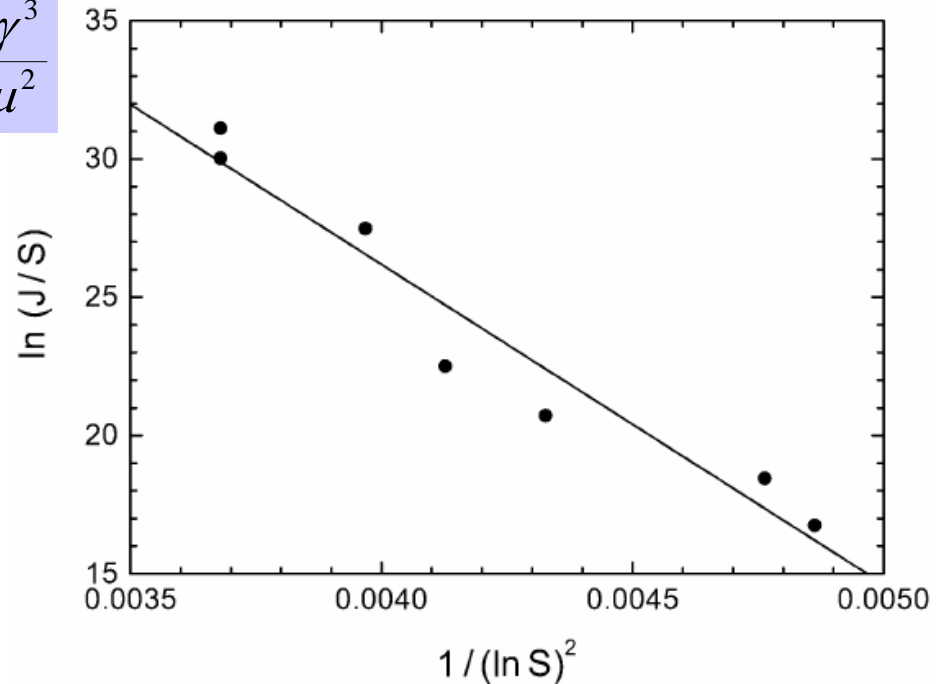
$$n^* = \frac{32\pi}{3} \frac{v_l^2 \gamma^3}{\Delta\mu^3} \qquad\qquad \Delta G^* = \frac{16\pi}{3} \frac{v_l^2 \gamma^3}{\Delta\mu^2}$$
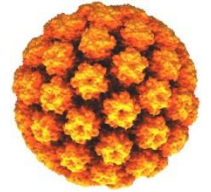
$$J(S) = AS \exp(-B/\ln^2 S)$$

$$B = 16\pi \upsilon_0^2 \gamma_{ef}^3 / 3(kT)^3$$

Nucleation experiments are used to estimate Surface tensions
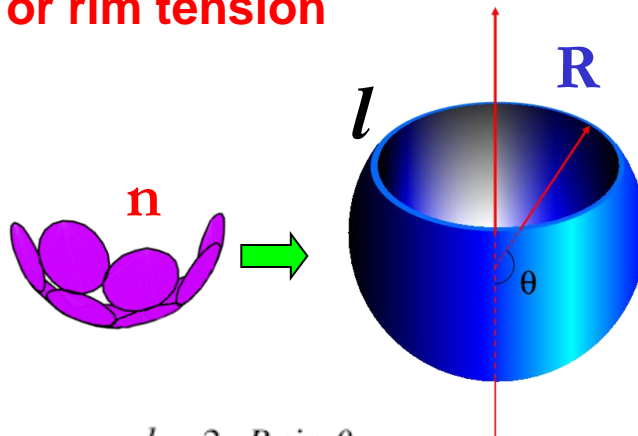
Classical Nucleation Theory of Viral Capsid Self-Assembly

• **Free energy of formation** of a partially formed capsid

$$\Delta G(n) = n\Delta\mu + \sigma l$$

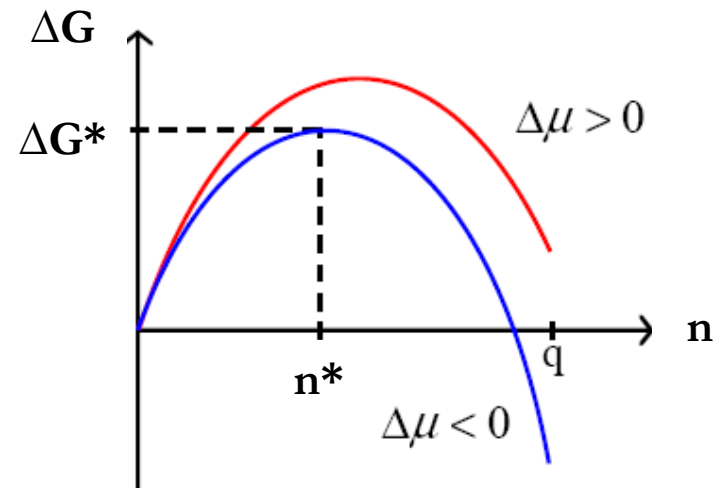$\Delta\mu$: **chemical potential difference**

σ: **line or rim tension**

$$l = 2\pi R \sin\theta$$

$$n = q(1 - \cos\theta)/2$$

$$l = \frac{4\pi R}{q}\sqrt{n(q-n)}.$$

Intermediates supressed by rim tension!

$$\Delta G(n) = n\Delta\mu + a\sqrt{n(q-n)}$$

$$a = \frac{4\pi R\sigma}{q}$$

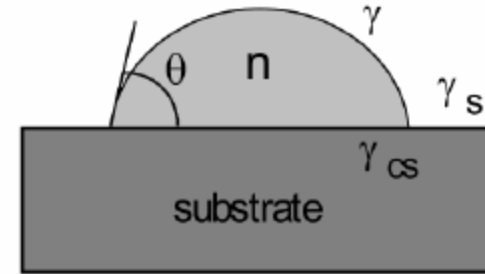Zandi et al, Biophys. J **90**, 1939 (2006)

Heterogeneous nucleation

$$\Delta G_{het} = -\frac{V_{cap}}{v_l}\Delta\mu + A_{cap}\gamma + \pi(R\sin\theta)^2(\gamma_{ls}-\gamma_{gs})$$

$$V_{cap} = \frac{4\pi R^3}{3}v(\theta) \qquad A_{cap} = 4\pi R^2 s(\theta)$$

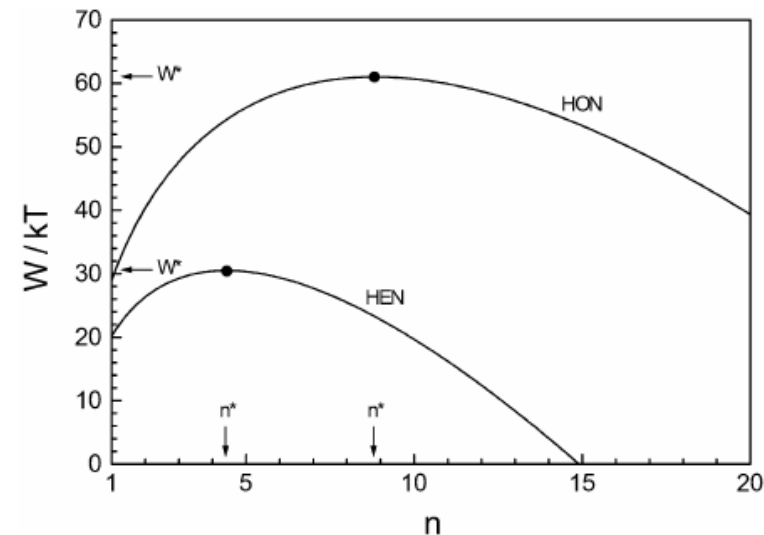$$s(\theta) = \frac{(1-\cos\theta)}{2} \qquad v(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

Young's equation: $\cos\theta = \dfrac{\gamma_{gs}-\gamma_{ls}}{\gamma_{gl}}$

$$\Delta G_{het}(R) = \Delta G_{hom}(R)v(\theta)$$

$$\Delta G_{het}^* = \Delta G_{hom}^* v(\theta) \qquad n_{het}^* = n_{hom}^* v(\theta)$$

Heterogenous nucleation is always more favourable

Nucleation Theorem

$$\left(\frac{\partial \Delta G^*}{\partial \Delta \mu} \right)_{V,T} = -\Delta n^*$$

D. Kashchiev, J. Chem. Phys. **76**, 5098 (1982)

R.K. Bowles, et al J.Chem. Phys. **115**, 1853 (2001)

T.L. Hill, J. Chem. Phys. **36**, 3182 (1962)

Independent of the theory!

Experimental importance:

It allows the evaluation of the critical cluster size directly from experiments
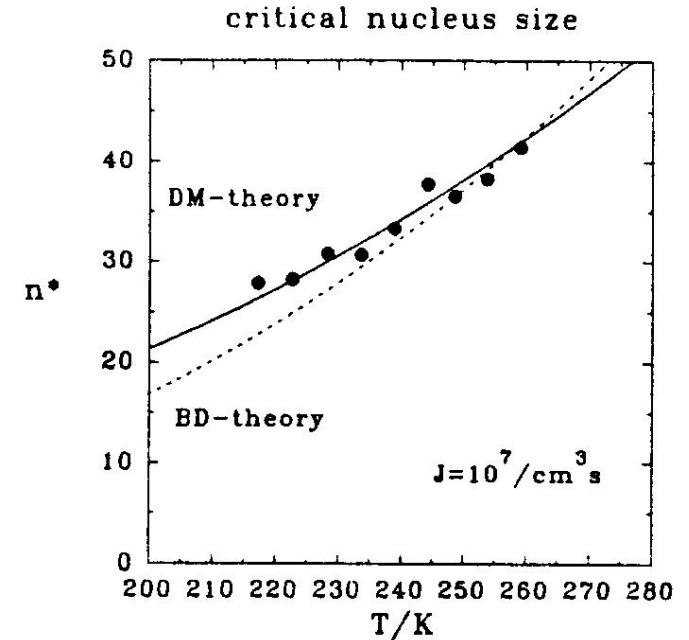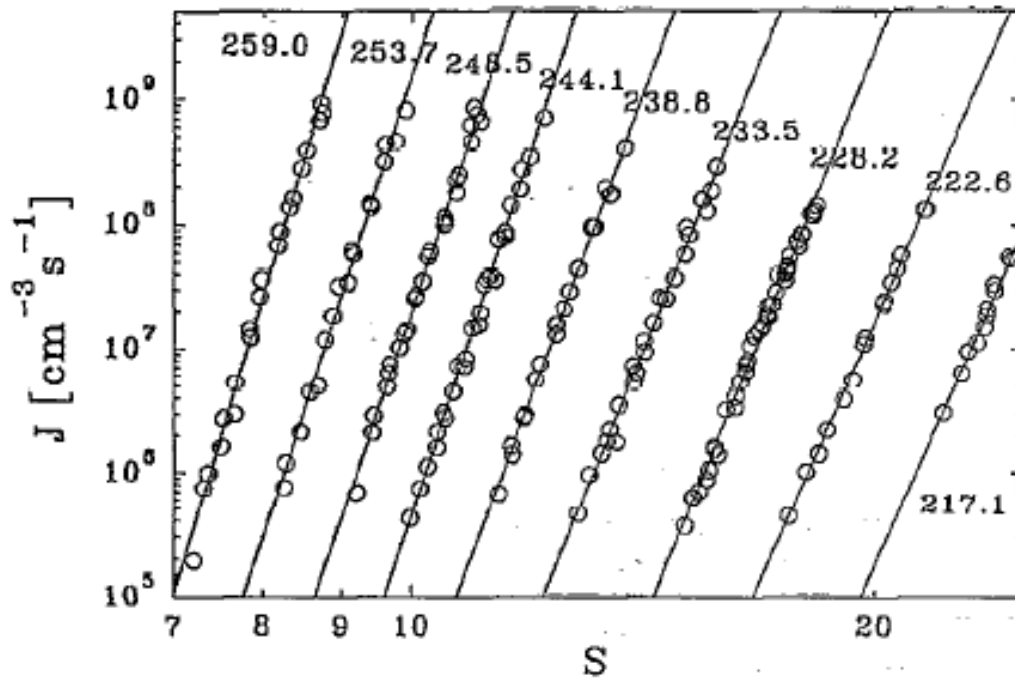
$$J = K e^{-\Delta G^*/k_B T}$$

$$\Delta G^*/k_B T = -\ln J + \ln K$$

$$\left(\frac{\partial \Delta G^*}{\partial \Delta \mu} \right)_T = -\frac{\partial \ln J}{\partial \ln S} + \frac{\partial \ln K}{\partial \ln S}$$

$$\frac{\partial \ln J}{\partial \ln S} = n^* + \frac{\partial \ln K}{\partial \ln S} \qquad \Longrightarrow \qquad \frac{\partial \ln J}{\partial \ln S} \approx n^*$$
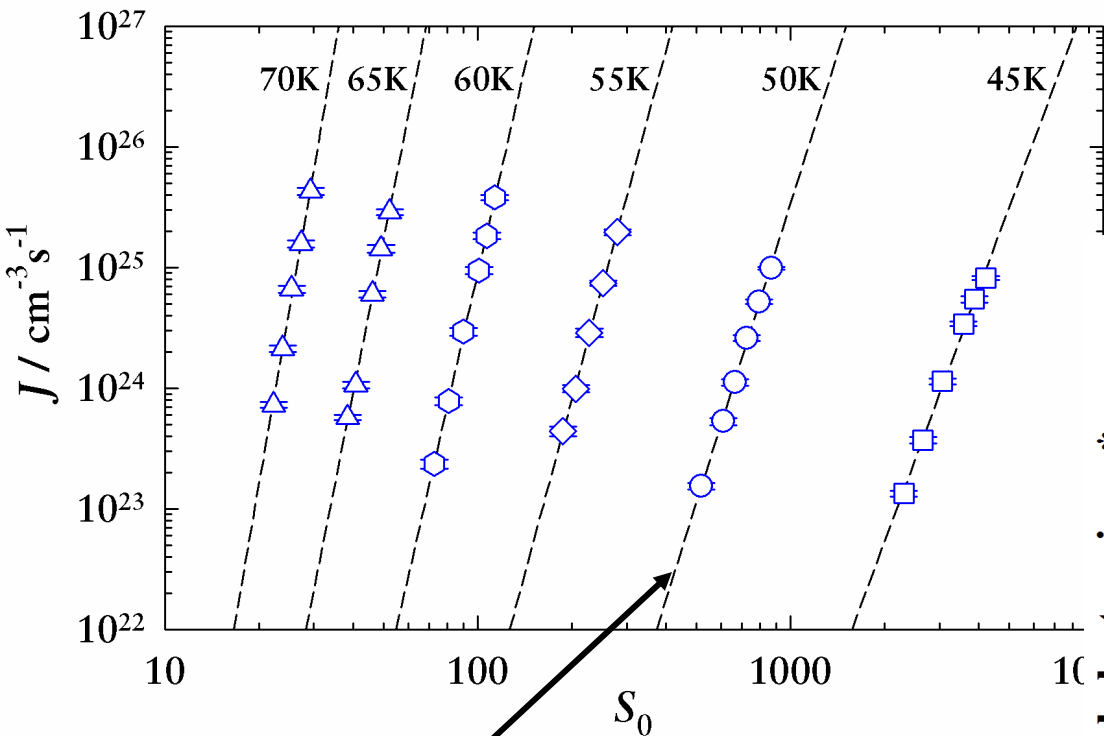
Nucleation theorem in action

- Water condensation experiments in an expansion chamber
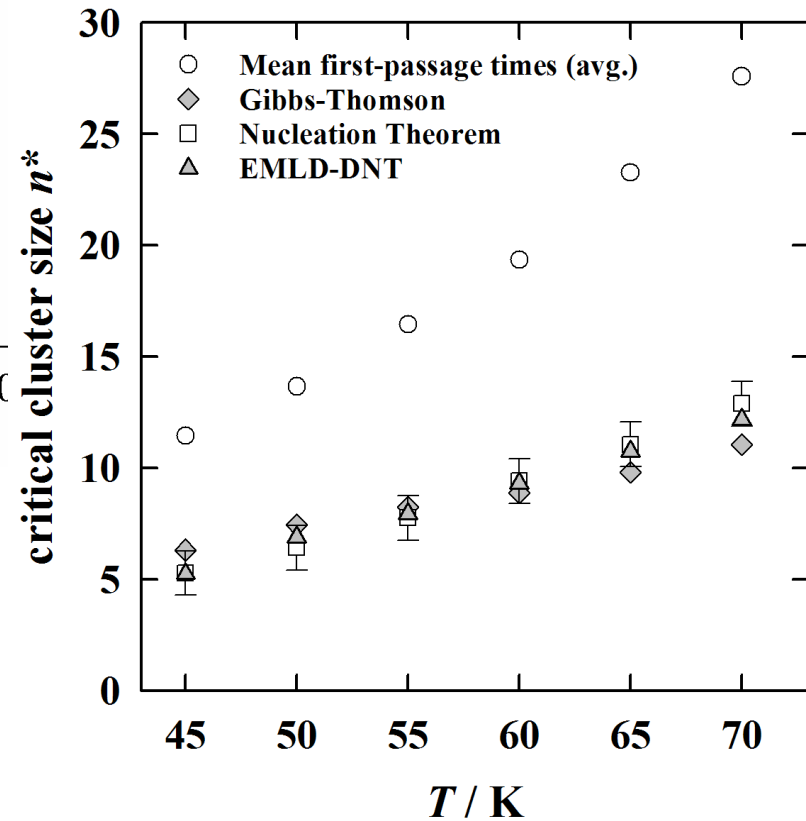

(Viisanen *et al.* 1993)
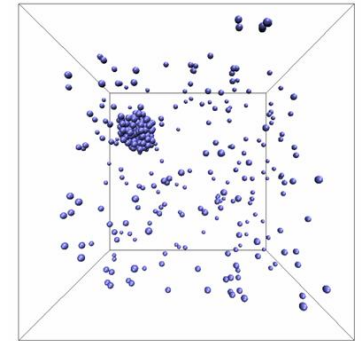
$$\frac{\partial \ln J}{\partial \ln S} \approx n^*$$

Nucleation theorem in action (2)

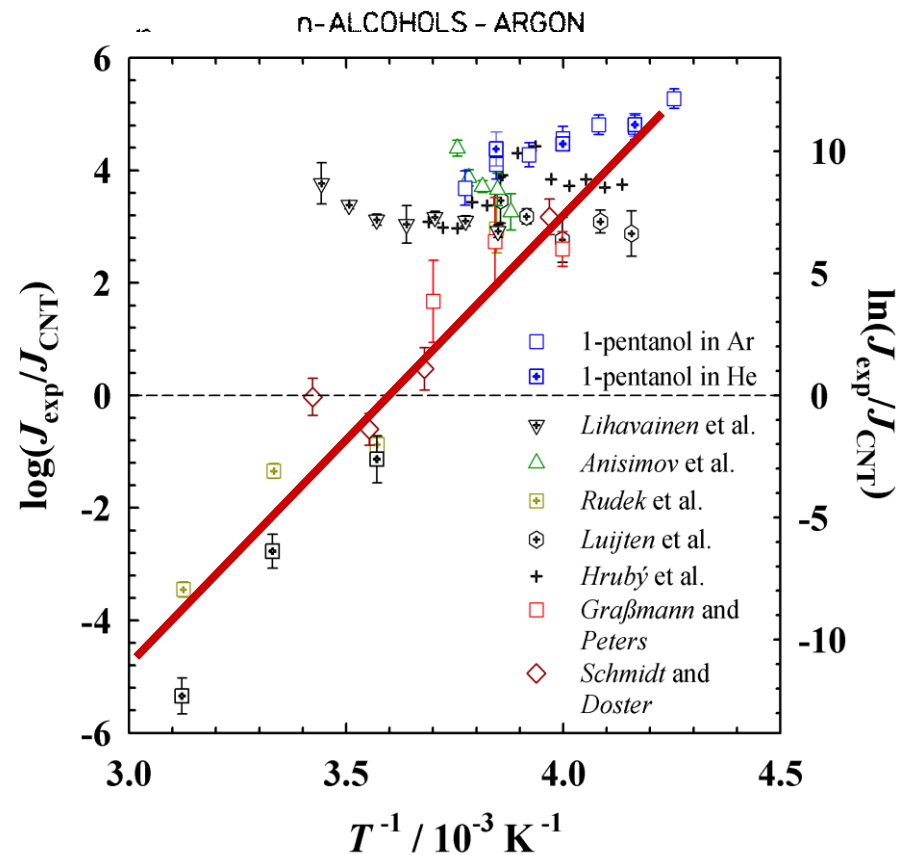$$n_{NT}^* \approx \frac{\partial \ln J}{\partial \ln S}$$

Nucleation Theorem

Kashchiev, J. Chem. Phys. 76, 5098 (1982).
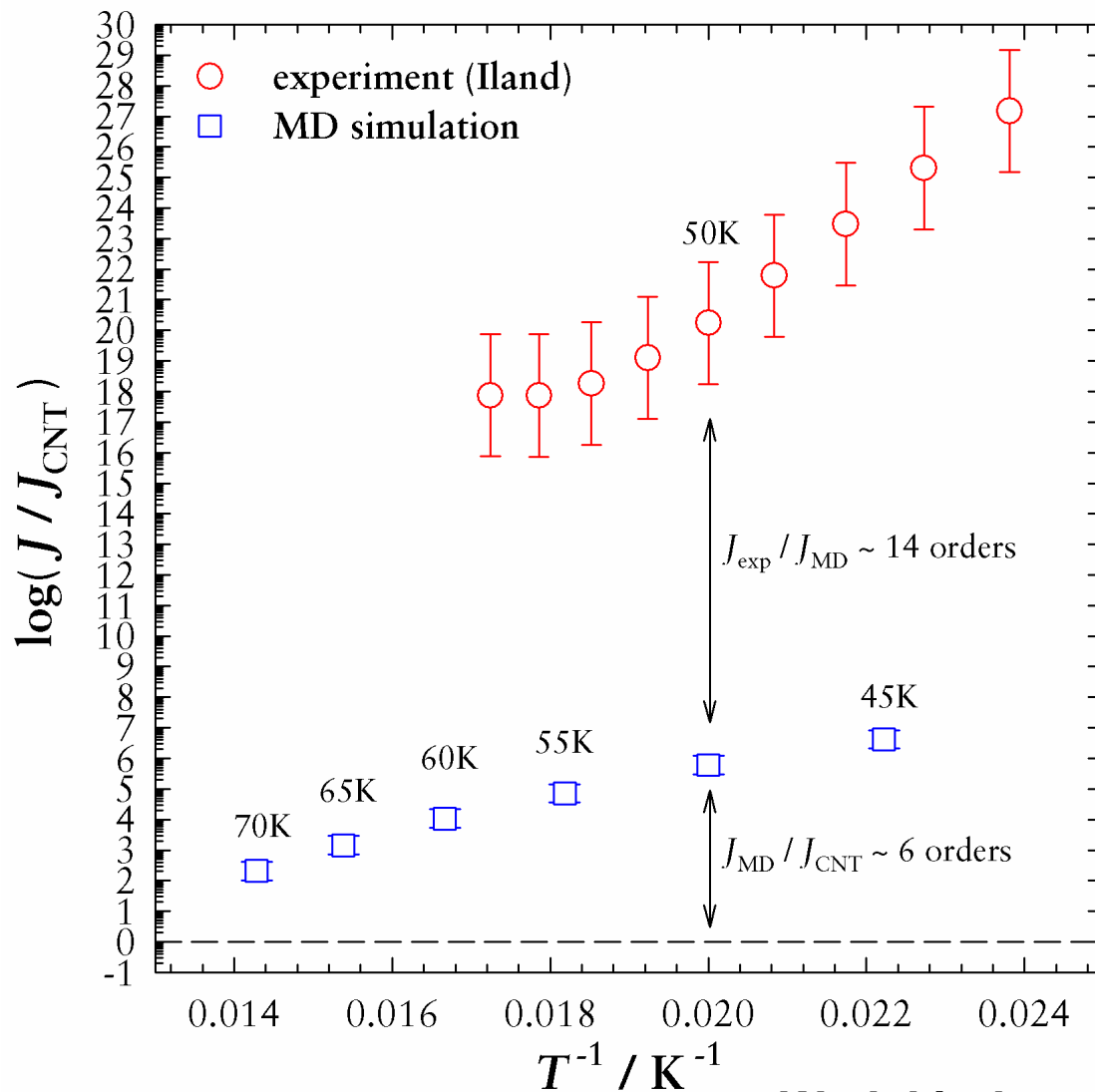R.K. Bowles et al. J.Chem. Phys. **115**, 1853 (2001).

Comparison with condensation experiments

- CNT has serious problems:

  - Wrong T dependence of nucleation rates:
    - J_{CNT} too high at high T
    - J_{CNT} too low at low T

  - Discrepancies reach several orders of magnitude !!!

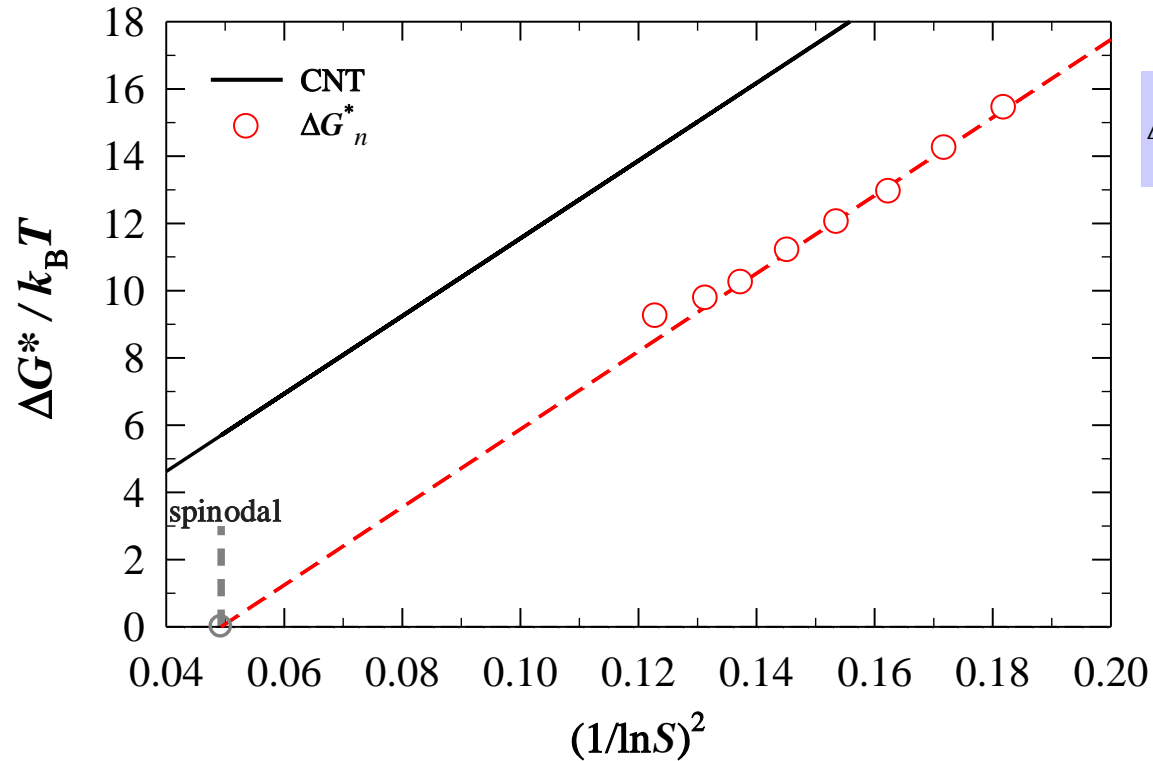# Comparison between CNT, simulation and experiment for argon condensation
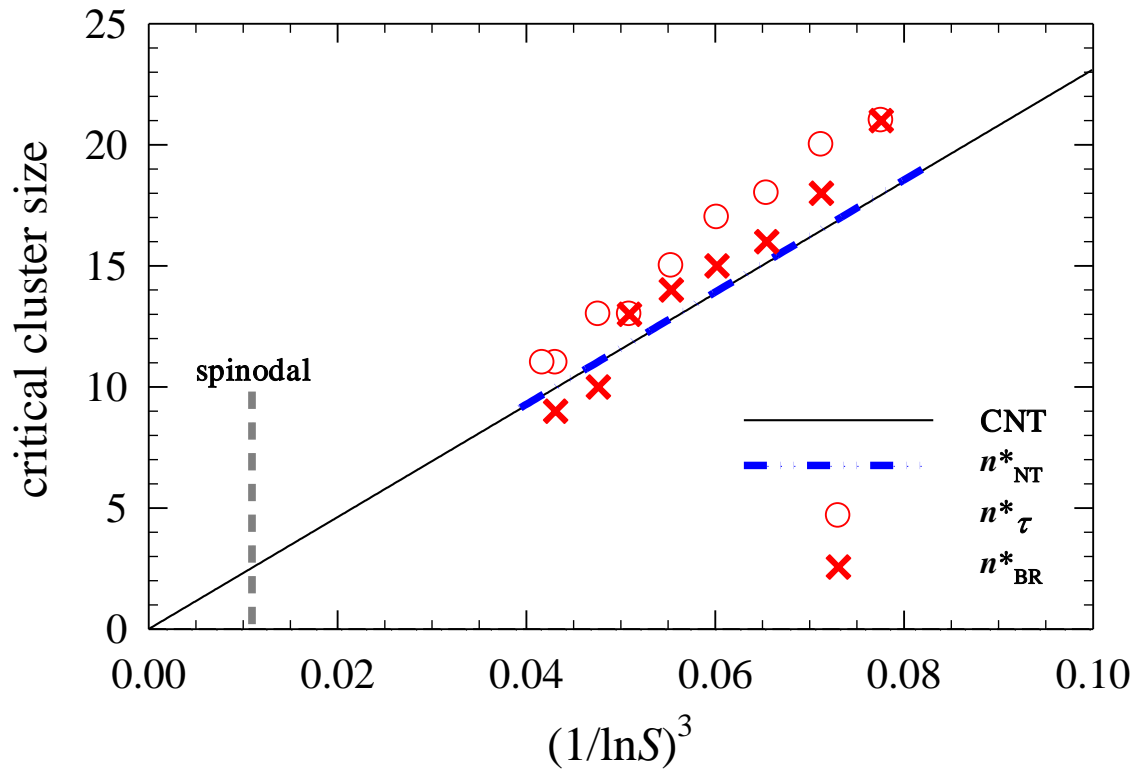

Wedekind et al, JCP (2007)

Nucleation Barrier Height: only wrong by a constat!

$$\Delta G_{CNT}^{*} = \frac{16\pi}{3} \frac{v_l^2 \gamma^3}{(kT \ln S)^2}$$

$$\Delta G(n^*) = \Delta G_{CNT}(n^*) + D(T)$$

Critical cluster size OK!

$$n* = \frac{32\pi}{3} \frac{v_l^2 \gamma^3}{(kT \ln S)^3}$$

CNT prediction is surprinsingly good

Pros/Cons of CNT

- **Positive points:**
    - Uses bulk thermodynamic measurable quantities
    - Simple numerical predictions
    - Predicts critical cluster sizes welll
    - Seems to mispredict the barrier just by a T-dependent constant

- **Disadvantages:**
    - No spinodal

    (the nucleation barrier is always

    finite)

    - Capillarity approximation
    - Ignores all contributions beyond surface and volume
    - Bad predictions compared to experiments and simulation
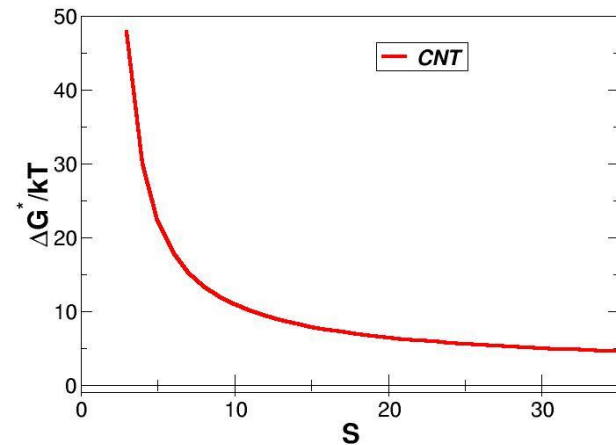
Recent theoretical developments

- **Phenomenological theories**
  - Aim to correct the nucleation barrier

- **Kinetic theories**
  - Focus on evaluating $\alpha(i)$

- **Molecular theories (Reiss et al…)**
  - Rigorous molecular description of cluster using statistical mechanics–linked to simulations

- **Density functional and field theories**
  - Overcome the capillarity approximation

Phenomenological theories

- **Fisher's droplet**

M.E. Fisher, Rep. Prog. Phys. **30**, 615 (1967)

  – Aims to correct the nucleation barrier by accounting for more terms beyond surface and volume

$$\frac{\Delta G(n)}{k_B T} = -n \ln S + \kappa_n \theta n^\gamma + \tau \ln n + \ln(V q_0)$$

  – Dillmann&Meyer $\kappa_n = 1 + \alpha_1 n^{-1/3} + \alpha_2 n^{-2/3}$

A. Dillmann and G.E.A. Meier, J. Chem. Phys. **94**, 3872 (1991)

I.J. Ford, A. Laaksonen, and M. Kulmala, J. Chem. Phys. **93**, 764 (1993)

- **Self-consistent theories**

  – Impose (somewhat artificially) that ΔG(n=1)=0

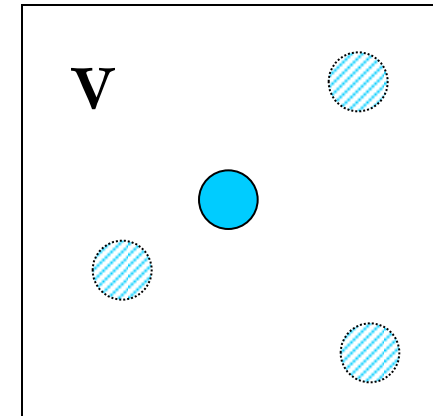$$\Delta G_{SCT}(n) = \Delta G_{CNT}(n) - \Delta G_{CNT}(1)$$

S.L. Girshick and C-P Chiu, J. Chem. Phys. **93**, 1273 (1990)

Translational and rotational contributions

- Another mesoscopic aspect:
  - Translational-Rotational paradox

Lothe&Pound (1962)

$$\Delta G_{CNT} + \Delta G_{trans} + \Delta G_{rot} \implies J \approx J_{CNT} 10^{17}$$

V
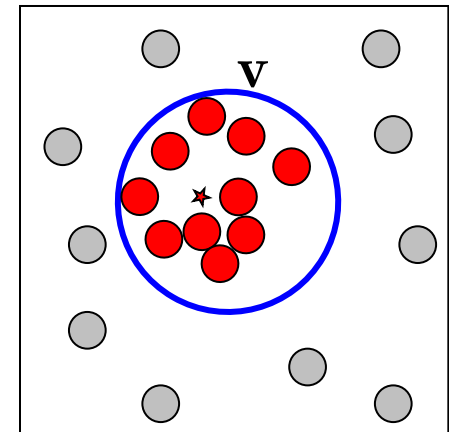
- Mesoscopic interpretation in terms of the volume scale

Lothe&Pound

$$\Delta G_{LP} = -k_B T \ln \frac{V}{\Lambda^3}$$

$$\Delta G = -k_B T \ln \frac{V}{v_{car}}$$

Reiss&Kegel&Katz

$$\Delta G_{RKK} = -k_B T \ln \frac{V}{\sqrt{k_B T \kappa v(n)}}$$

v

H. Reiss, W.K. Kegel, and J.L. Katz, Phys. Rev. Lett. **78**, 4506 (1997)

Phenomenological theories (2)

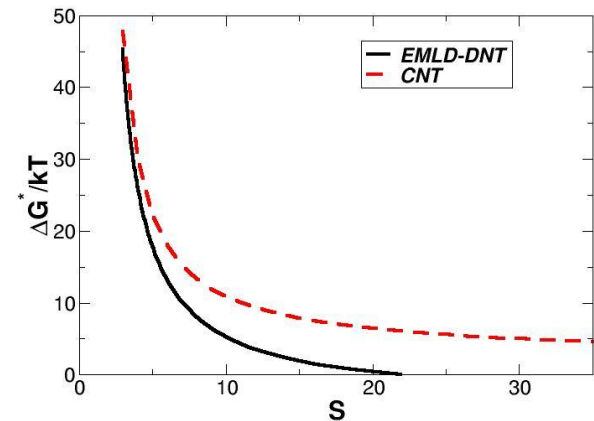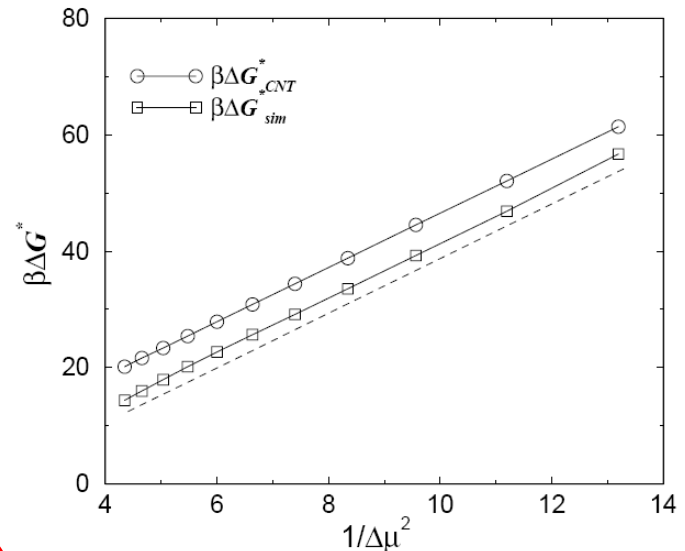- Scaling relations: n* well predicted by CNT+ Nucleat. theorem

$$n^* = C(T)\Delta\mu^{-3},$$
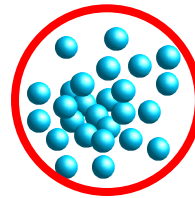
$$\Delta G^* - \Delta G^*_{CNT} = -D(T)$$

R. McGraw and A. Laaksonen, Phys. Rev. Lett. **76**, 2754 (1996

- EMLD-DNT:
  - A physical cluster that incorporates fluctuations and translation
  - Accounts for the spinodal and seem to correct the wrong T-dependence

Reguera, D.; Reiss, H. *J. Phys Chem. B* **2004**, *108*, 19831
Reguera, D.; Reiss, H. *Phys. Rev. Lett.* **2004**, *93*, 165701.

Kinetic theories

- **Aim at calculating α(i)**
  - General drawback: rates are extremely sensitive to the details of the potential and to an accurate evaluation of α(i)

- **Ruckenstein & coworkers**
  - α(i) obtained as the MFPT of escape of a monomer from the effective potential generated by all cluster's molecules

E. Ruckenstein, Y.S. Djikaev / *Advances in Colloid and Interface Science* 118 (2005) 51–72
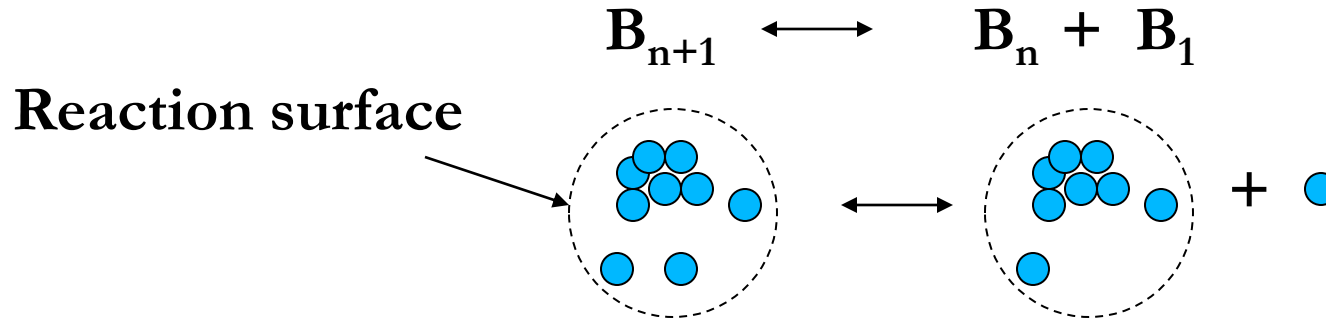
- **Dynamical nucleation theory**
  - Uses VTST to obtain α(i) considering the evaporation event as a chemical reaction

Schenter, G. K.; Kathmann, S. M.; Garrett, B. C. *Phys. Rev. Lett.* **1999**, *82*, 3484

VTST and DNT

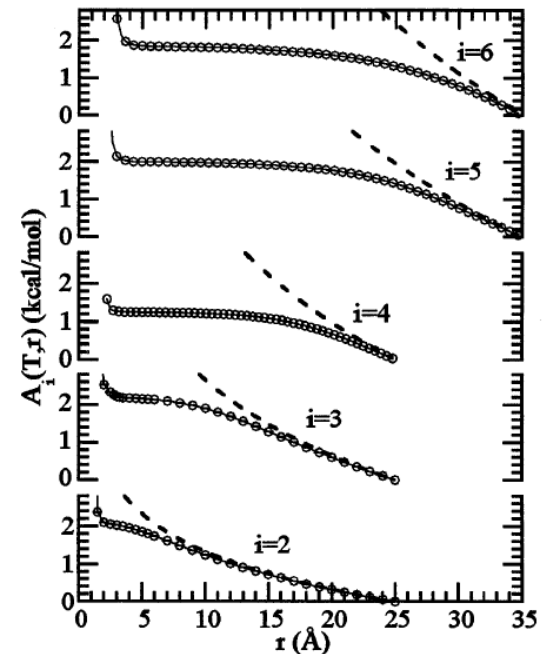- **DNT**: Evaporation as a **reaction**

(Schenter, Kathmann, Garrett PRL'99)

$$B_{n+1} \longleftrightarrow B_n + B_1$$

Reaction surface

- **VTST**: V that minimizes the reaction

  (evaporation) rate

$$\alpha_i^{\text{VTST}}(T) = -\left(\frac{1}{2\pi m k_B T}\right)^{1/2} \frac{d}{dr} A_i(T, r)\bigg|_{r=r_i^{\ddagger}}$$

$$= \frac{\bar{c}}{4}\left[4\pi(r_i^{\ddagger})^2\right]\frac{P_i^{\text{int}}}{k_B T},$$

- **DNT**: nice idea but very requires expensive

simulations…

Density functional theory

- Free energy of a drop is assumed to be a functional of the density profile ρ(r)

$$\delta \Omega_V [\rho(r)]/\delta\rho(r) = 0 \qquad \text{at } \rho(r) = \rho_{eq}(r)$$

R. Evans, Adv. Phys. **28**, 143 (1979)

  - Disadvantages:
    - No info about kinetics
    - Results depend on the functional used
    - The square gradient approximation predicts n* →∞ at the spinodal
  - Advantages:
    - Results qualitatively good
    - Removes capillarity approximation

- Cahn&Hilliard :

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

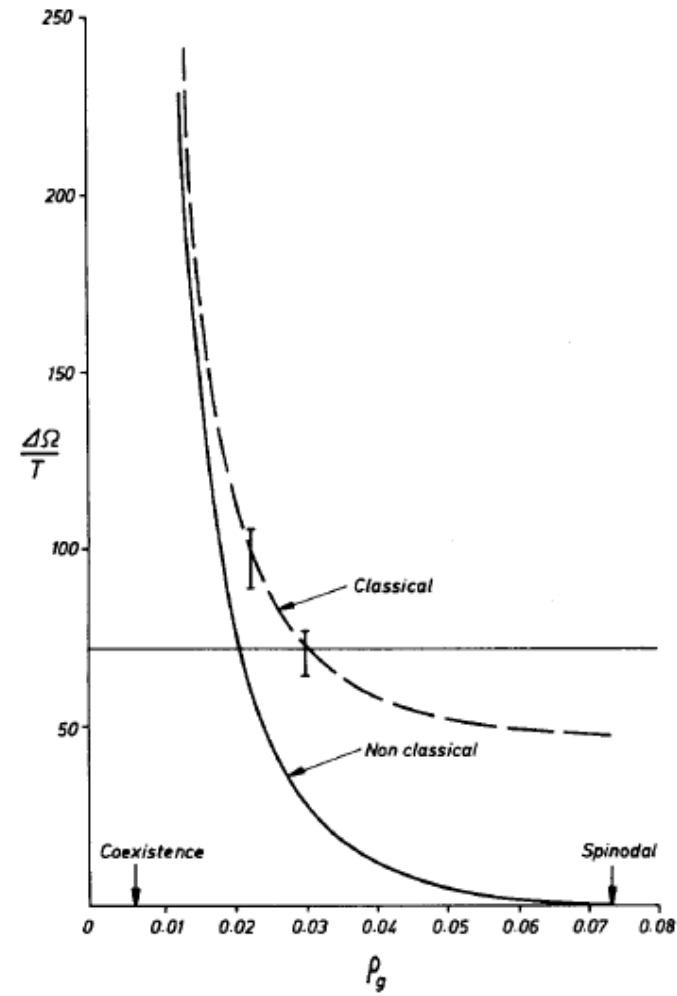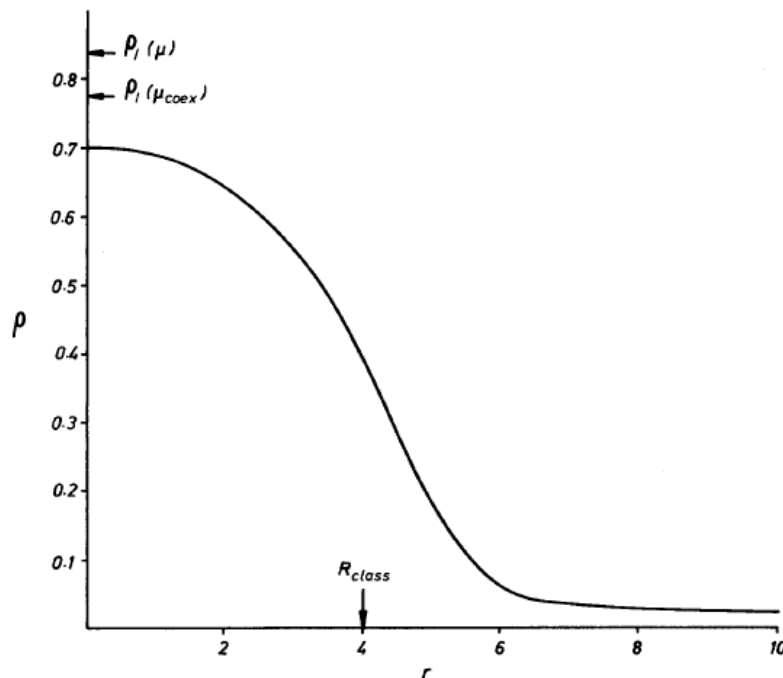J.W. Cahn and J.E. Hilliard, J. Chem. Phys. **28**, 258 (1958)

Density functional theory (2)

- Oxtoby& coworkers

$$\Omega\left[\rho(\mathbf{r})\right] = \int d\mathbf{r}\left\{f_h\left[\rho(\mathbf{r})\right] - \mu\rho(\mathbf{r})\right\} + \int\int d\mathbf{r}d\mathbf{r}'\phi_{att}(\left|\mathbf{r} - \mathbf{r}'\right|)\rho(\mathbf{r})\rho(\mathbf{r}')$$

$$\mu_{h}(\rho(\mathbf{r})) = \mu - \int d\mathbf{r}'\ \rho(\mathbf{r}')\phi_{att}\left(\left|\mathbf{r} - \mathbf{r}'\right|\right)$$

Summary

- Nucleation is a very fundamental problem still not fully understood

- CNT is still the most widely used theory despite its limitations and the fact that mispredicts the nucleation rates by several orders of magnitude

- CNT seems to predict n* correctly, but mispredicts ΔG^* by a (temperature-dependent) constant

- More work is necessary to be able to predict accurately nucleation rates!