Winter 1-1-2008

Lecture 9, Part 1: Nucleation, growth and transparent glass-ceramics - Nucleation theory in glass

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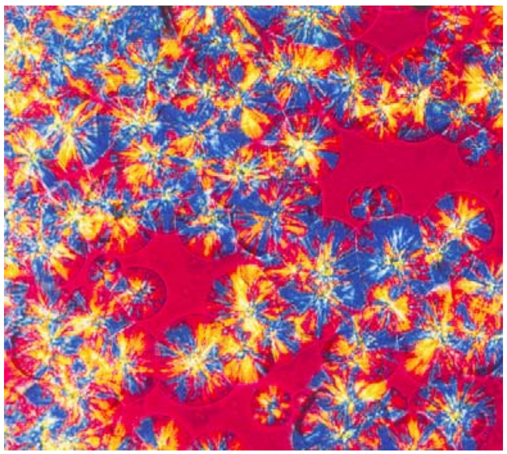
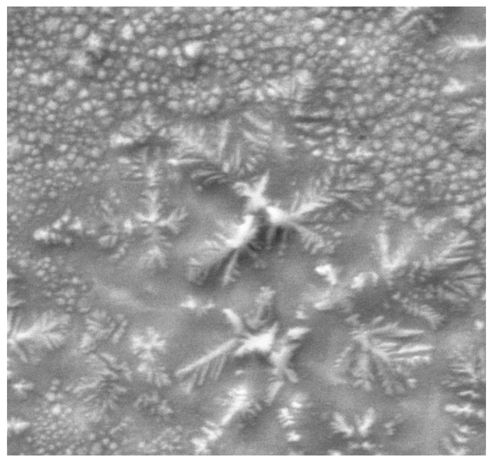
Crystal Nucleation in…

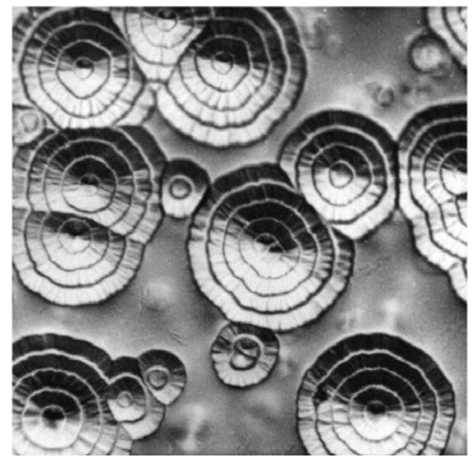
POLYMER	METALLIC	& INORGANIC GLASSES



Polypropilene



$Zr_{55}Cu_{30}Ni_5Al_{10}$



$Na_2O{\cdot}2CaO{\cdot}3SiO_2$

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Vitreous Materials Laboratory
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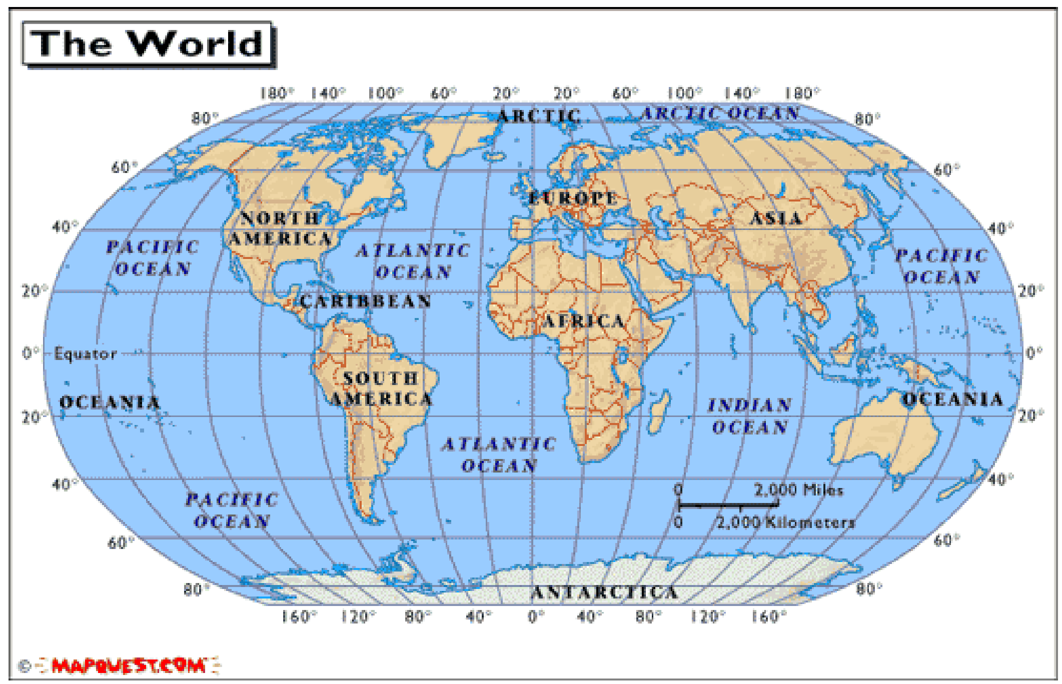
LaMaV

Vitreous Materials Lab., Fed. Univ. São Carlos

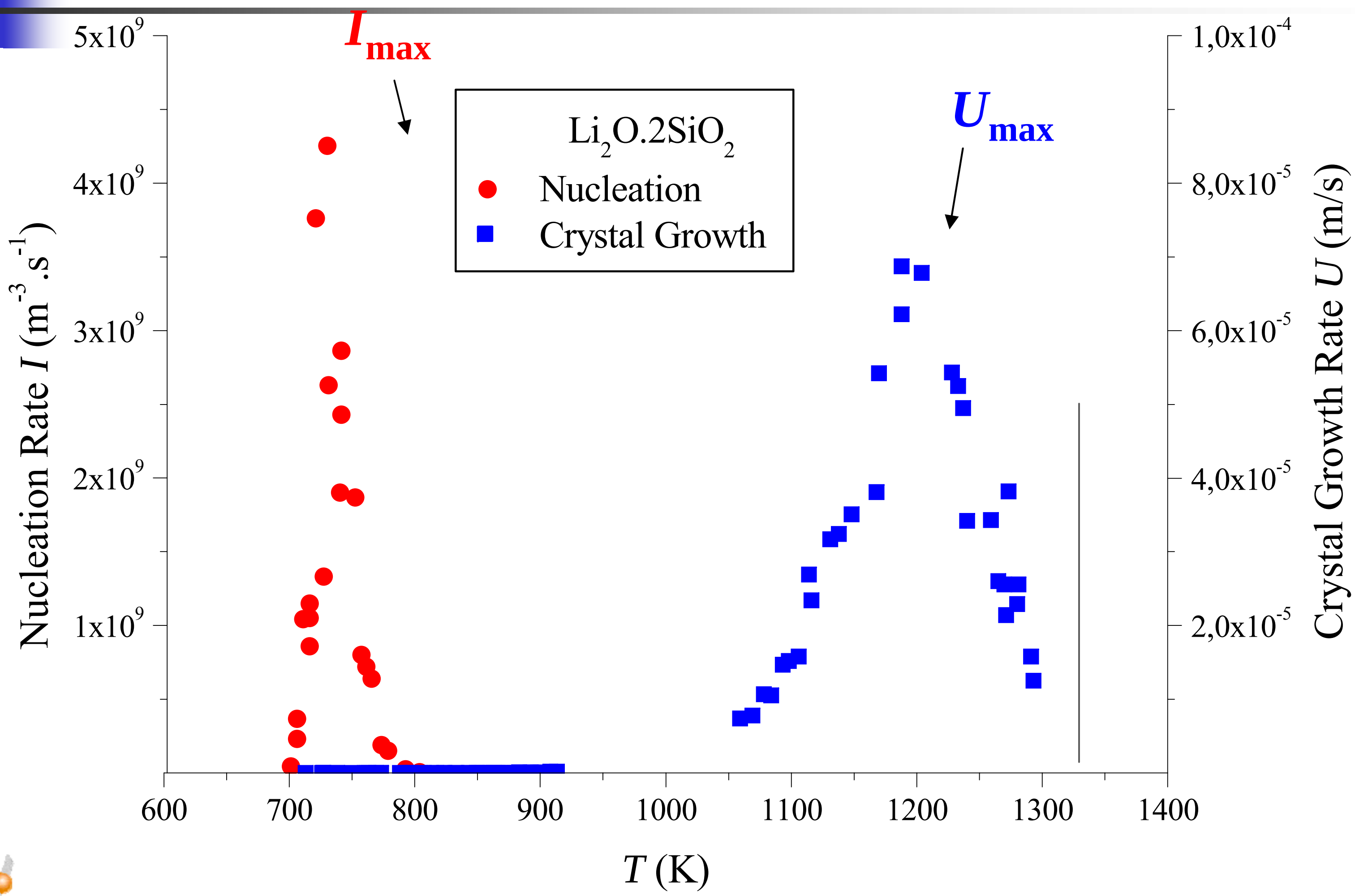


LaMaV

Objective

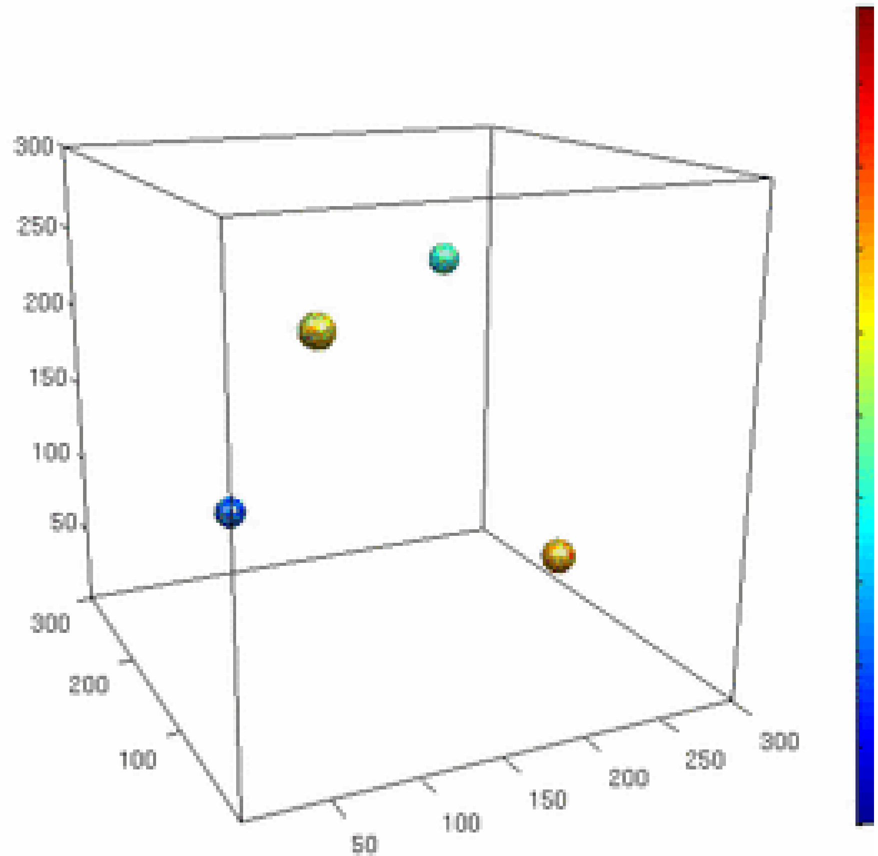
To discuss the validity and utility of the CNT using relevant findings on crystal nucleation in deeply undercooled liquids reported in the last 50 years…

Crystal nucleation and growth rate curves



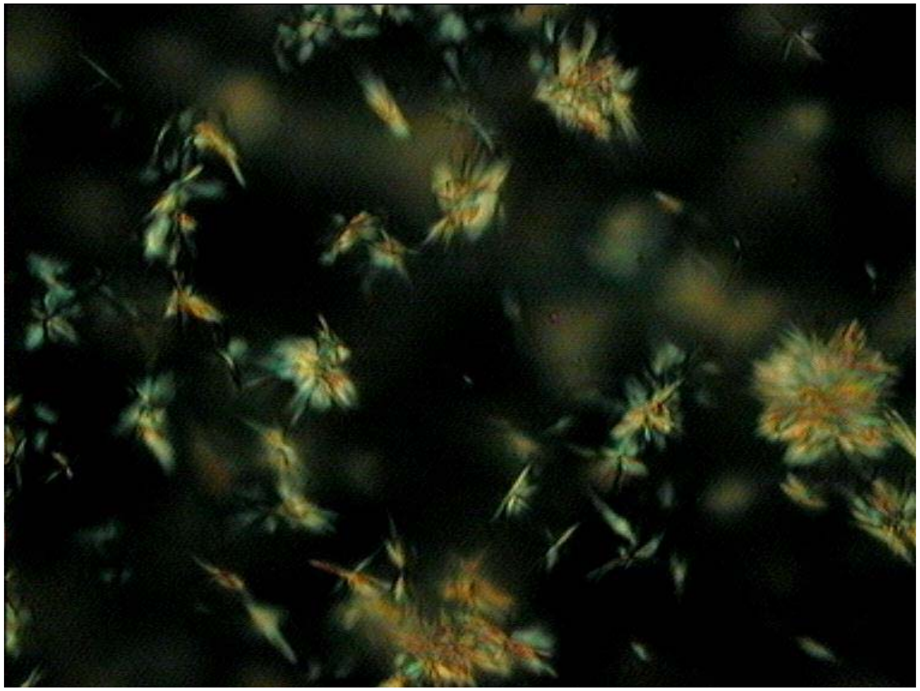
Simulation of nucleation and growth

T. Pusztai, G. Bortel, L. Gránásy, *Europhys. Lett.* **71** (2005)

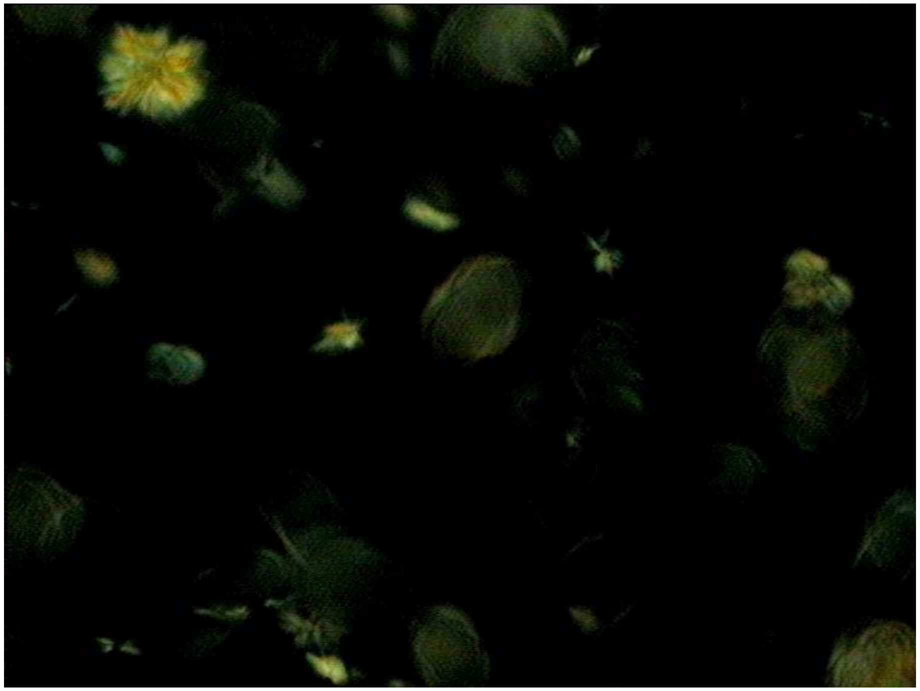


Courtesy of László Gránásy

Real nucleation and growth in PDMS



$63°C$, ΔT=6min. **Surface nucleation**



$63°C$, ΔT=4min. **Internal nucleation**

Outline

i) The CNT: Theory and tests in the last 50 years

a) the diffusion mechanism ?

b) surface energy = $f\,(T, \mathrm{size})$?

c) metastable phases ?

d) what is next ?

ii) How useful is CNT to the understanding of glass-formation and to the development of GC ?

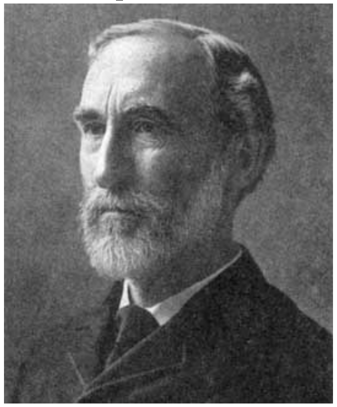
Importance and motivation

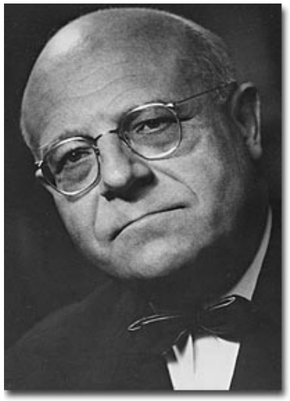
- If crystallization is averted on the cooling path any liquid can vitrify to a glass;
- The development of useful glass-ceramics with designed micro/nano structures...

CNT

Theory and tests in the last 50 years

CNT Researchers Gallery


Josiah W. Gibbs

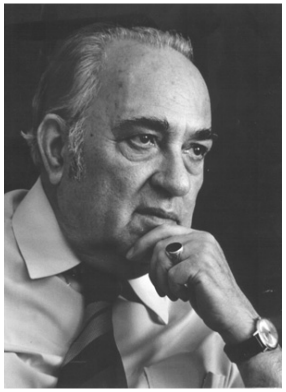

Iwan Stranski

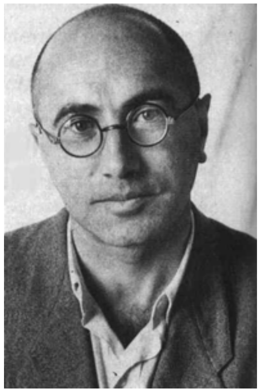

Gustav Tammann


Yakov Frenkel


Ladislau Farkas


Max Volmer


Rostislav Kaischew

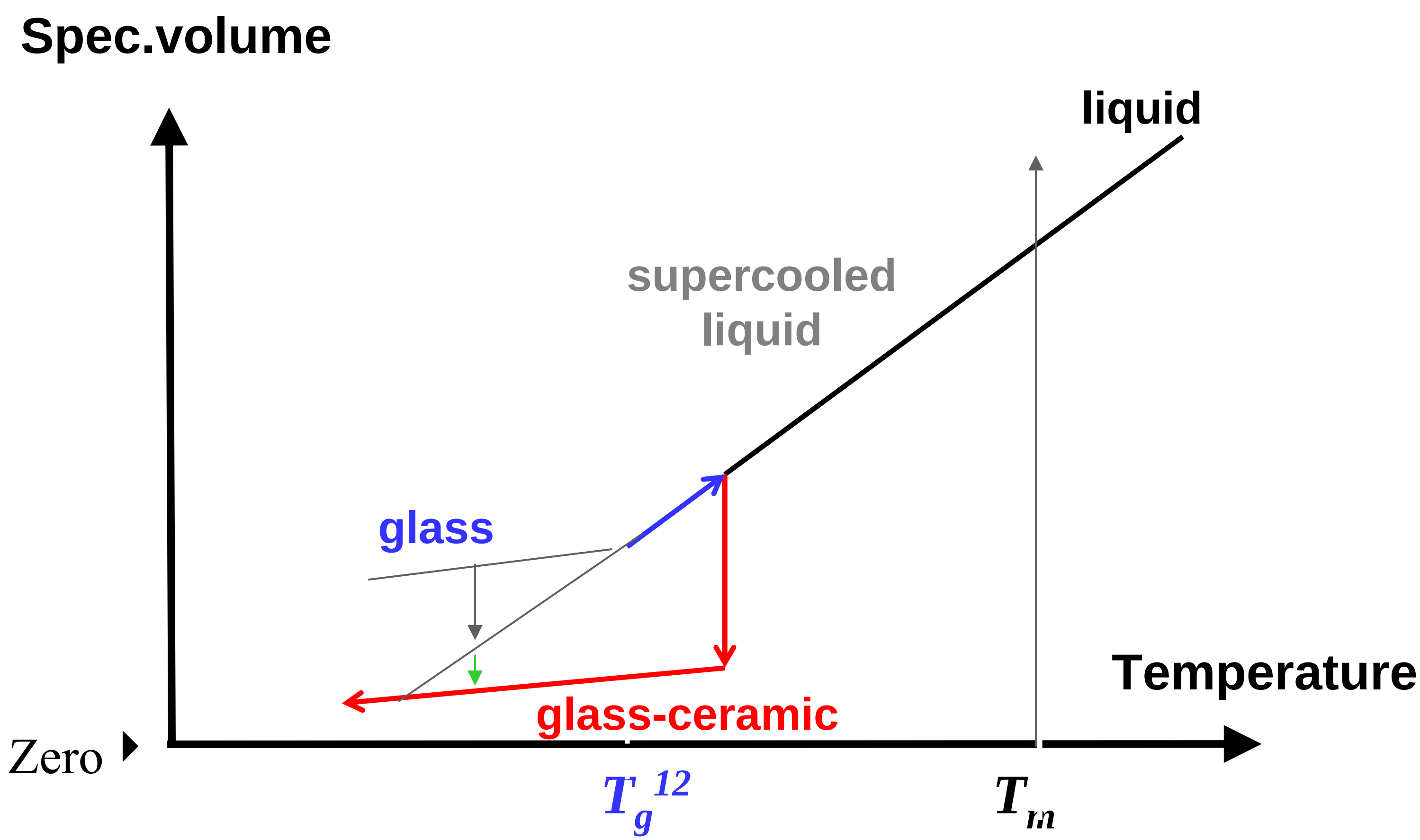

Yakov Zeldovich


Richard Becker


David Turnbull

Undercooling viscous liquids followed by isothermal crystallization

Treatment of glasses at deep undercoolings – direct measurement of *I*



Types of nucleation

- **Homogeneous***:* spontaneous formation from the melt; any volume element of the undercooled liquid is equally prone to nucleation;

- **Heterogeneous**: nuclei form preferentially on a 'foreign' surface: solid impurities, crucible walls, bubbles, seeds, etc.

CNT: Critical Nucleus Size

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \sigma$$

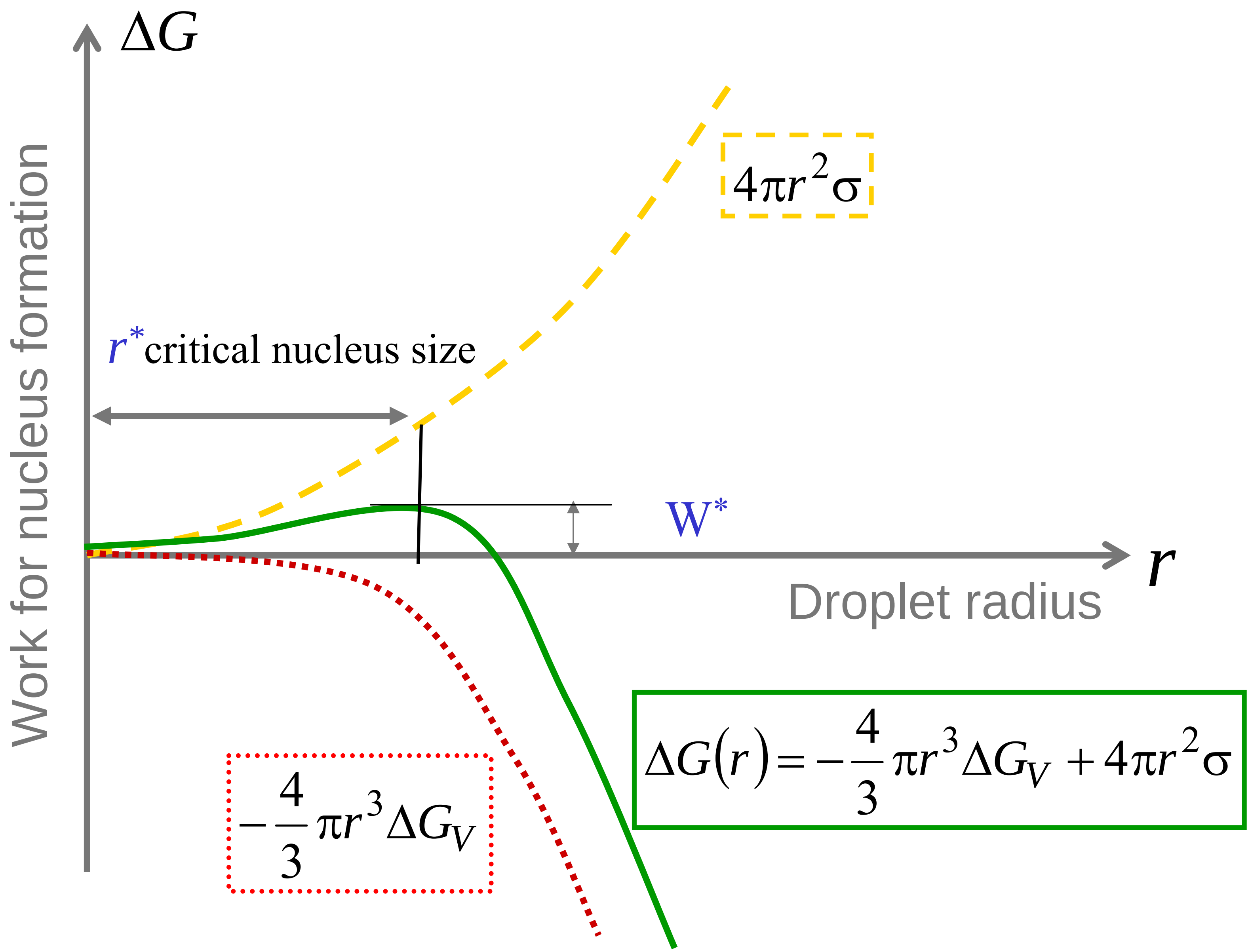
$$\frac{\partial \Delta G}{\partial r} = -4\pi r^2 \Delta G_V + 8\pi r \sigma$$

$$\frac{\partial \Delta G}{\partial r} = 0, \quad \text{so} \quad r_{\text{critical}} = \frac{2\sigma}{\Delta G_V} = r^*$$

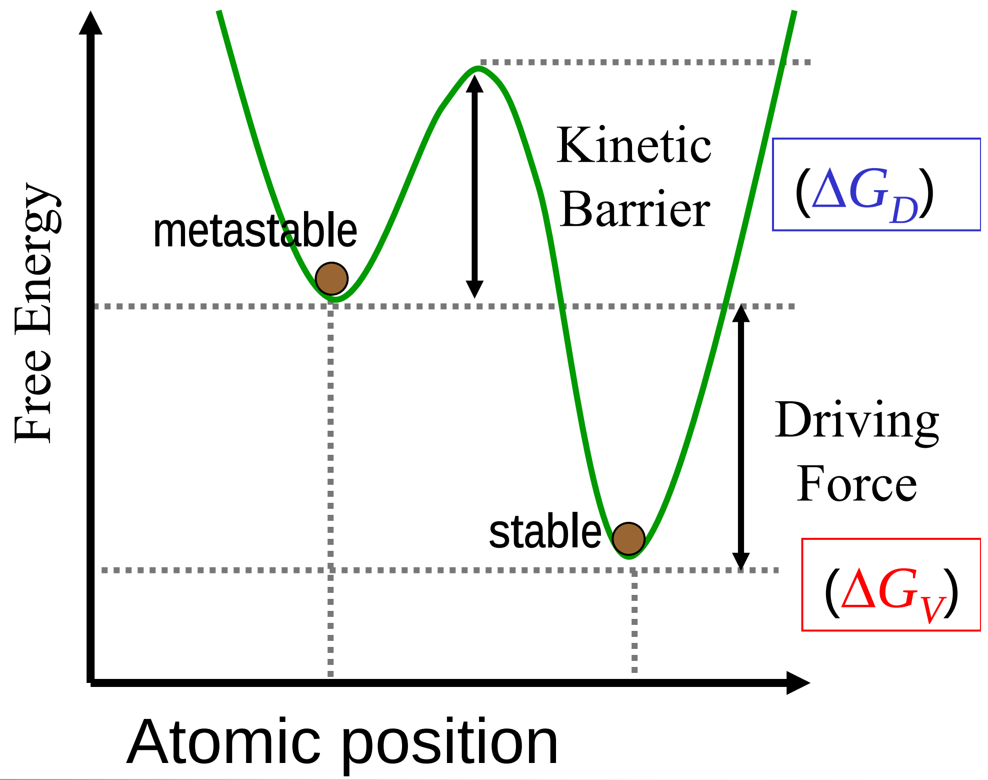
$$\Delta G^*_{\text{critical}} = \frac{16\pi\sigma^3}{3(\Delta G_V)^2} = \Delta G^*$$

W*

Work of Formation of a Spherical Nucleus, W*



CNT



Free Energy
metastable
Kinetic Barrier
(ΔG_D)
Driving Force
stable
(ΔG_V)
Atomic position

CNT: Expression and main assumptions

- Homogeneous nucleation of the stable phase
- Driving force = that of a stress free macroscopic crystal; $\Delta G(T) = \Delta G_0(T)$
- Interfacial energy = independent of nucleus size (R) and temperature, $\sigma = \sigma_0$

$$I \approx \nu_0 \, \mathbf{exp}\left(-\frac{\Delta G_D}{k_B T}\right) n_V \, \mathbf{exp}\left(-\frac{W^*}{k_B T}\right) \quad [\mathrm{m^{-3}.s^{-1}}]$$

D/λ^2

Transport **Thermodynamic**

If molecular rearrangements controlled by viscous flow & the SE eq. is valid

$$D \approx \frac{k_B T}{3\pi\lambda\eta}$$

$$W^* = \frac{K\sigma_0^3}{\Delta G_V^2}$$

$\sigma \neq \sigma(R,T)$

$\Delta G(T) \neq \Delta G(R,T)$

- Let us then test CNT's predicting power

Peter James

CNT test

$$I = K_1 \frac{T}{\eta} \exp\left(-\frac{W^*}{k_B T}\right) \qquad W^* = \frac{K\sigma_0^3}{\Delta G_V^2}$$

Using experimental $\boldsymbol{I(T)}$, $\eta(T)$ and $\boldsymbol{\Delta G_v (T)}$

$\ln (I.\eta/T)$ *vs.* $1/(T.\Delta G_v^2)$ **should give a straight line:**

Intercept = K_1

Slope = σ_0 **(unknown)** $\sigma_0 \sim \alpha.\Delta H_m$

P. F. James: *Advances in Ceramics* **4** (1982)

Parameters needed to test CNT

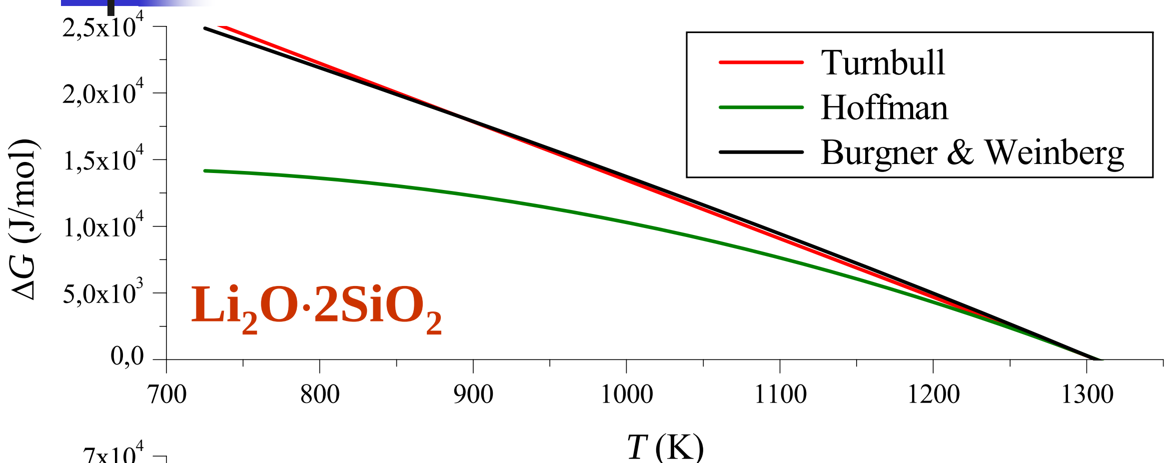
- **Viscosity (T) & I(T)**

... in the same temperature range using a glass of the same batch/ melting operation!

- **Deltha G (T) – measured or calculated** (see next slide)

Thermodynamic driving force

John Hoffman

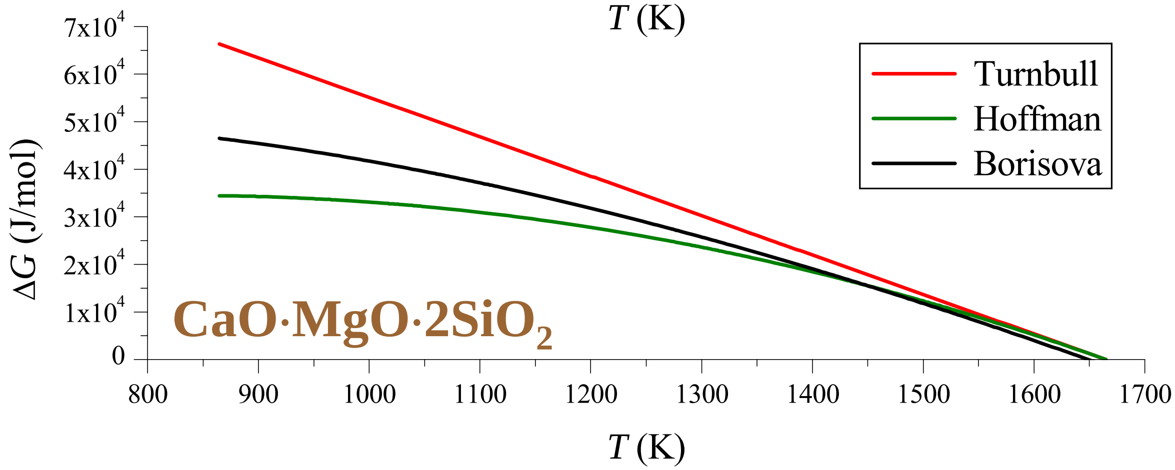


Turnbull

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}$$

Hoffman

$$\Delta G = \frac{\Delta H_m \Delta T T}{T_m^2}$$



Comparison of measured Gibbs free energies ΔG and approximations of Turnbull and Hoffman for L_2S and diopside in wide range of temperatures.

The expressions of Turnbull and Hoffmann bound the experimental ΔG

Tests of CNT

David Turnbull

<u>Homogeneous</u> nucleation in supercooled liquid metals

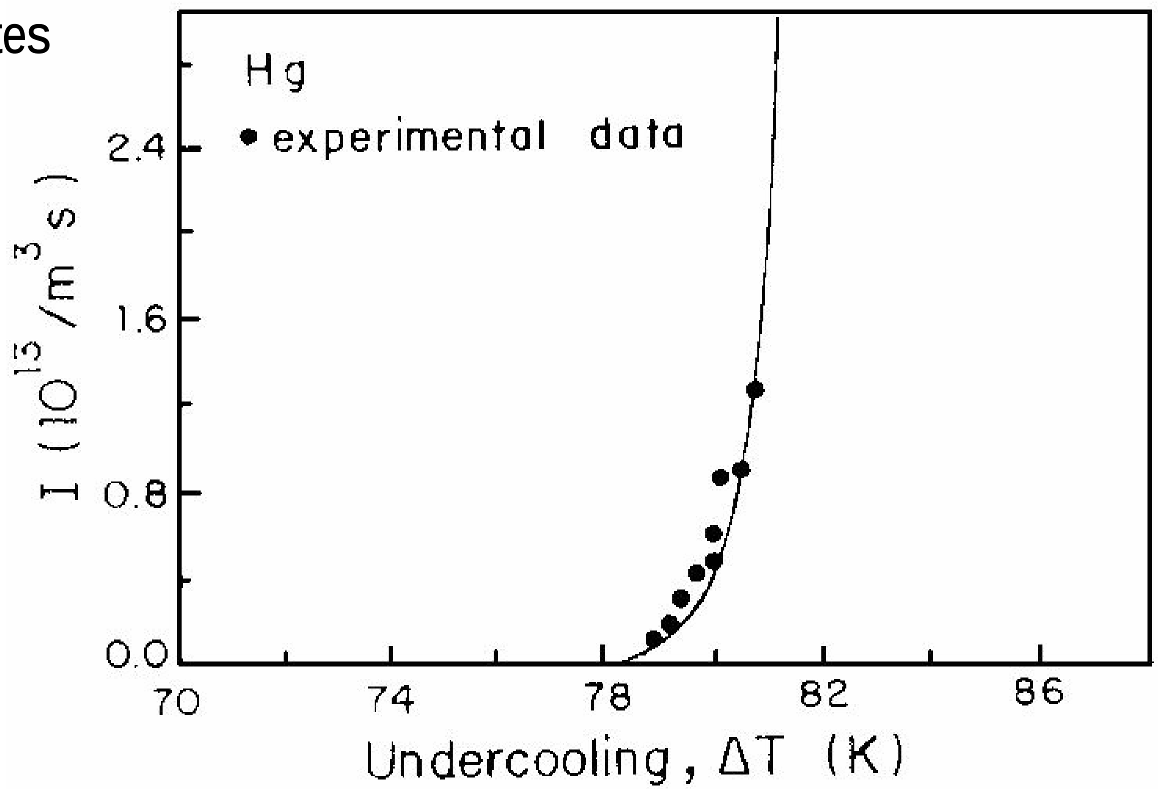
1948-50: Vonnegut, Turnbull and others: *droplet* technique for liquid metals.

The maximum undercoolings and crystal growth rates were measured and then the nucleation rates were estimated.

Liquid metals (1950's)

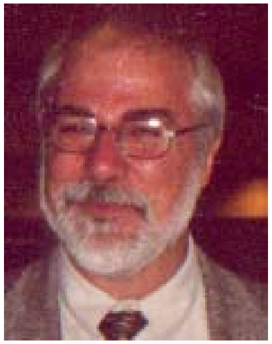
Homogeneous nucleation rates in liquid mercury.

only 2 ºC!



D. Turnbull, *J. Chem. Phys.* **20** (1952)

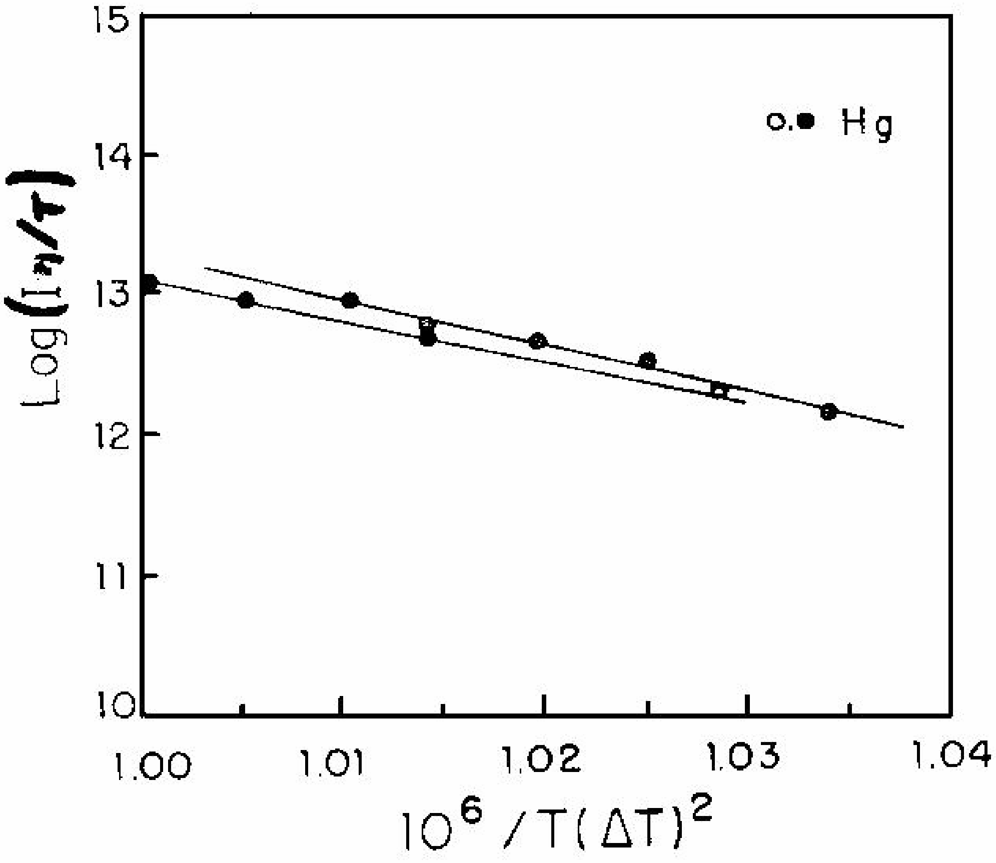
Kenneth Kelton



Liquid metals (1950's)

Straight lines:

Pre-exponential 7 o.m. higher than predicted

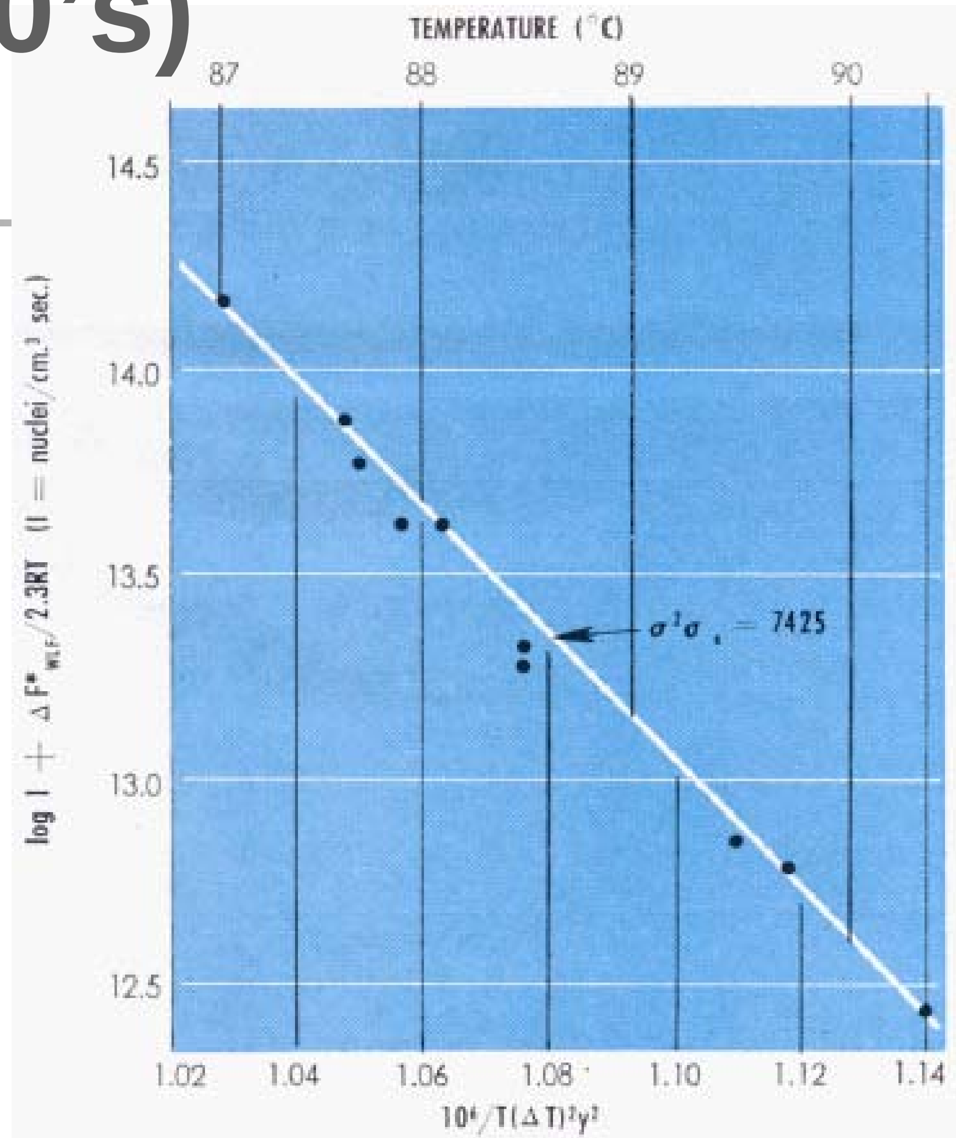


K. Kelton, *Sol. State Phys*. **45** (1991)

Homogeneous nucleation rate in polyethylene.

Polymers (1960's)

Increased to 3 ºC!



Droplet **technique: isothermal nucleation rates of unfractionated linear polyethylene**

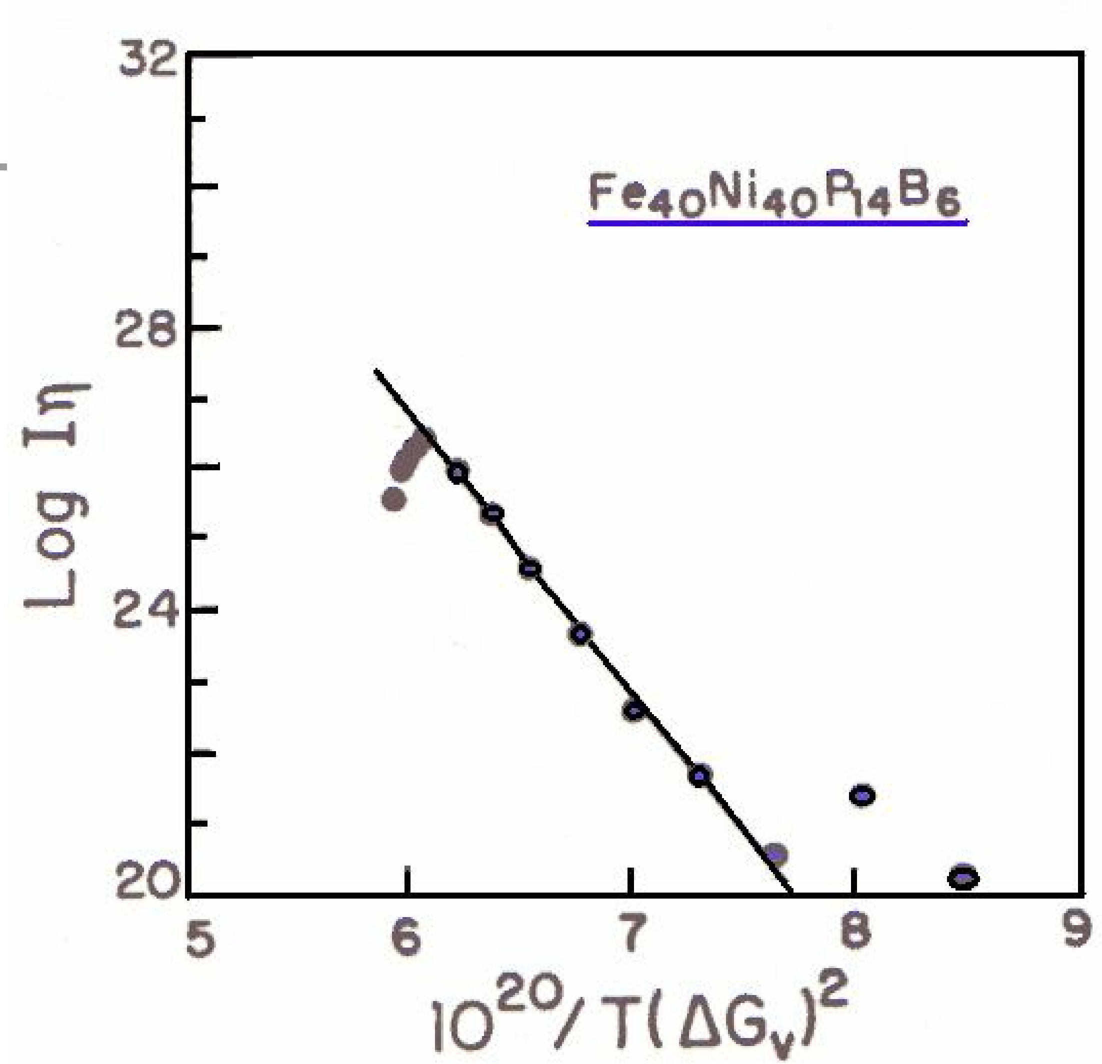
The pre-exponential constant was 12 orders of magnitude larger than the theoretical value

F. Gornick, J. D. Hoffman, *Ind. Eng. Chem.* **58** (1966)

Glassy metallic alloys (1970-80's)

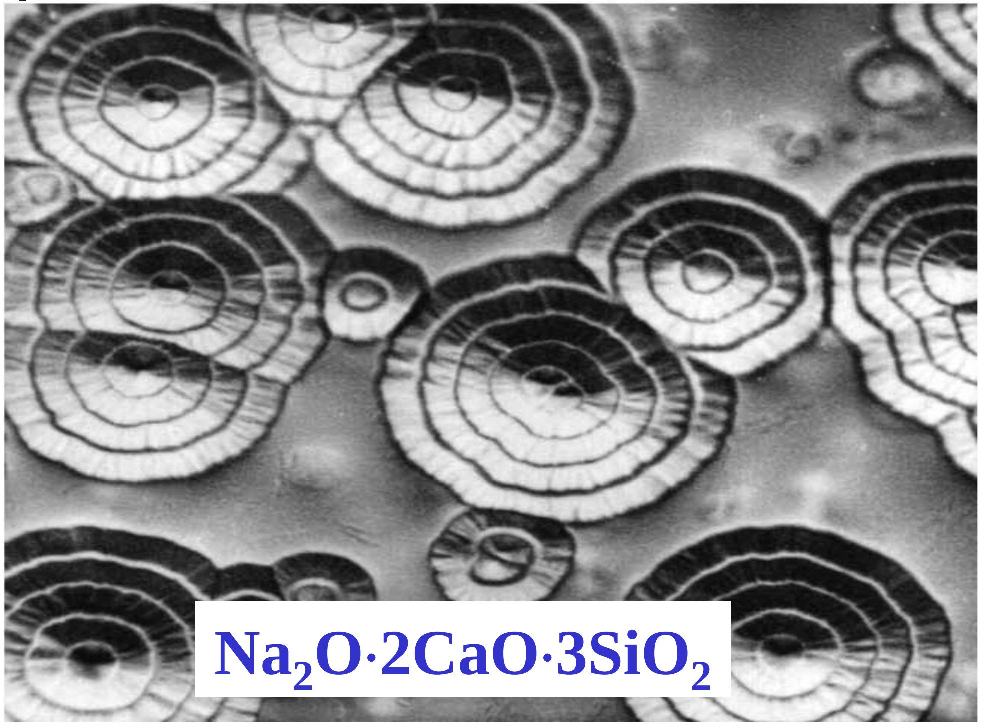
$Fe_{40}Ni_{40}P_{14}B_{6}$,

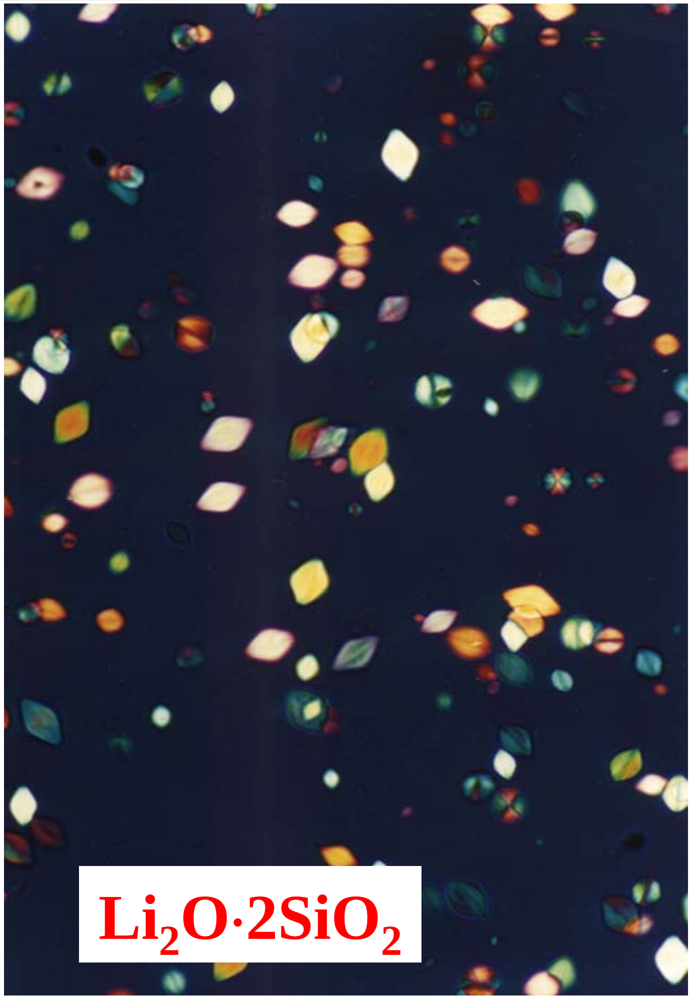
The linear portion with σ_0 gives pre-exponential factor 20 o.m. larger than predicted.



R. S. Tiwary, J. C. Claus, M. Vonheimendhal, *Mat. Sci. Eng*. **55** (1982)

Homogeneous Nucleation in Stoichiometric Silicate Glasses



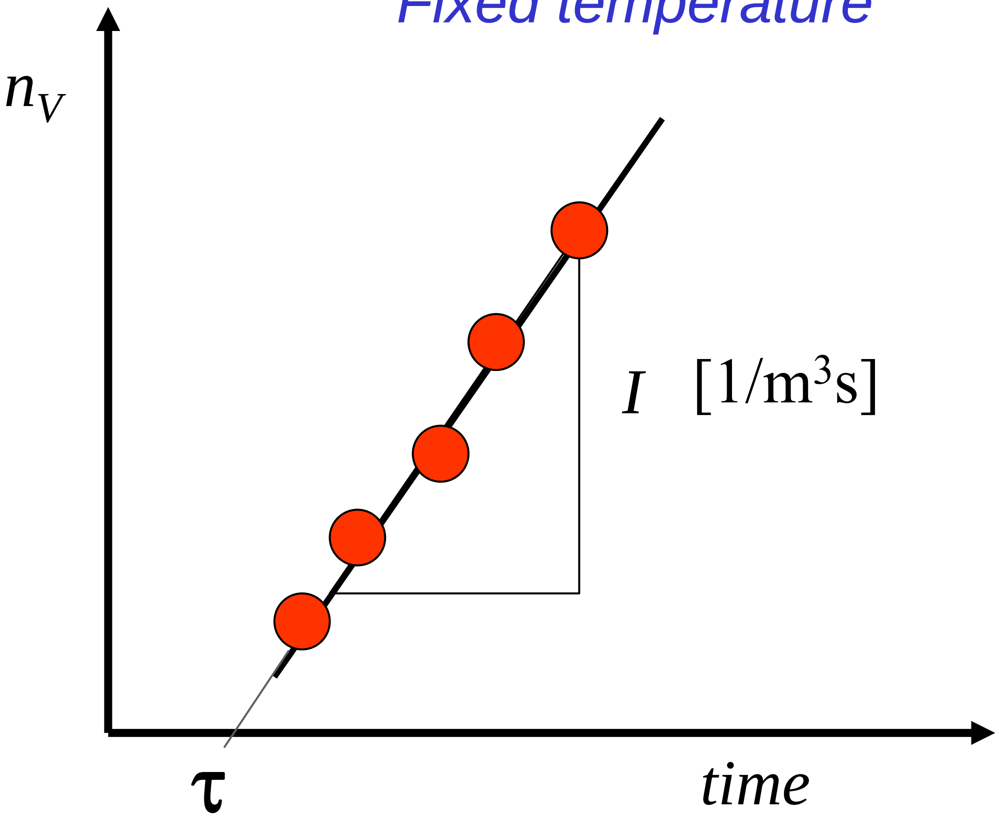


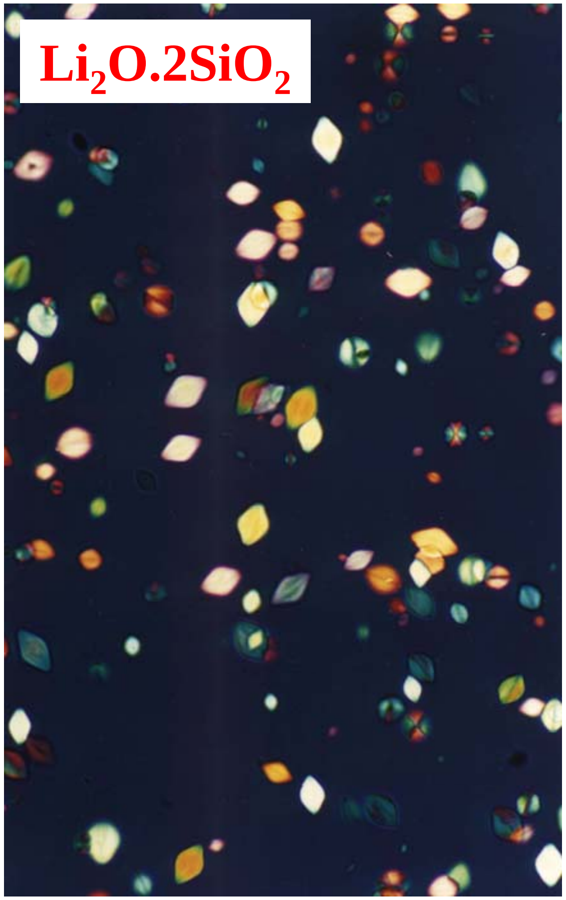
Very few silicate glasses spontaneously display internal homogeneous nucleation (+ surface)

Measurement of nucleation rates

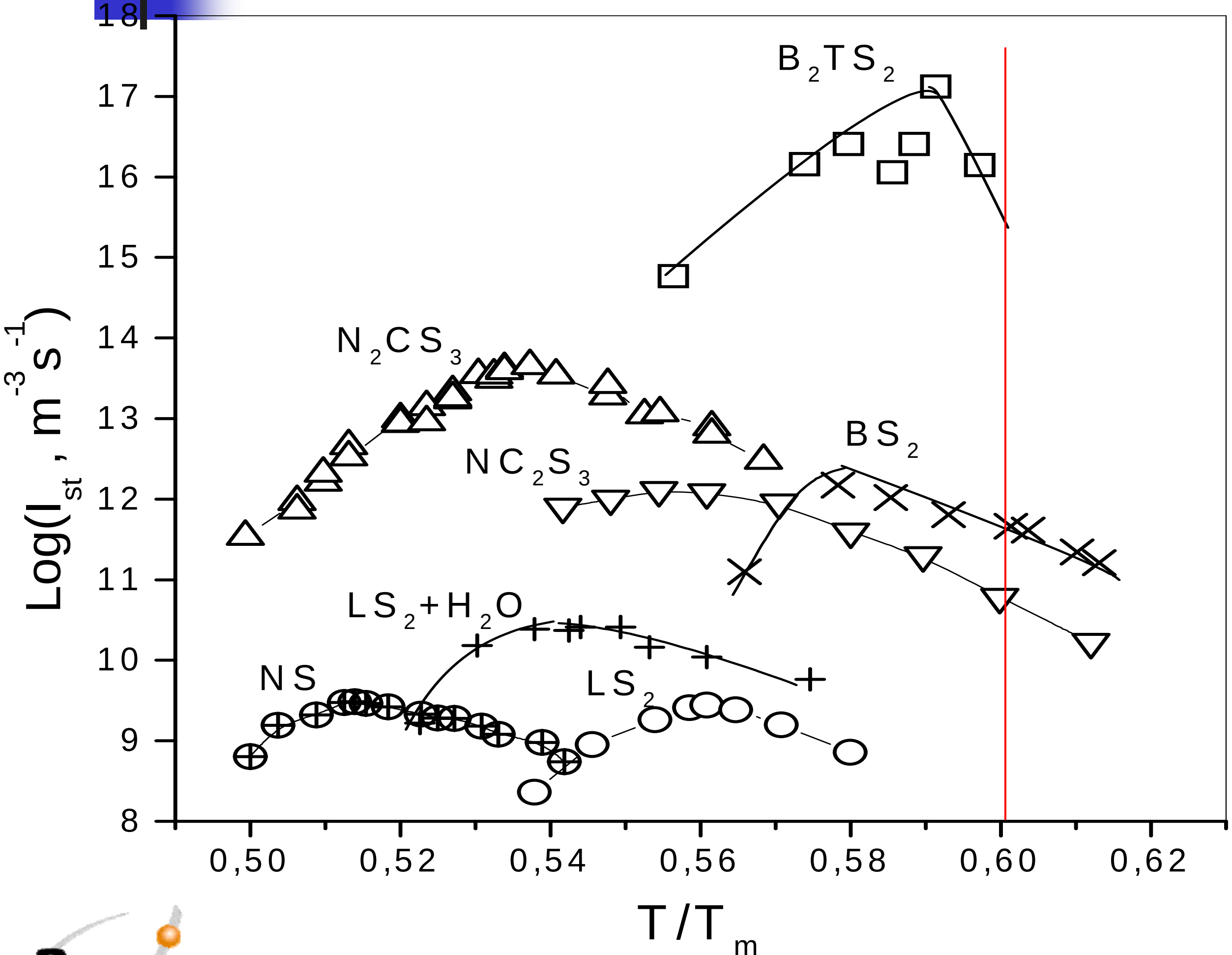
number of crystals per unity volume n_V

Fixed temperature





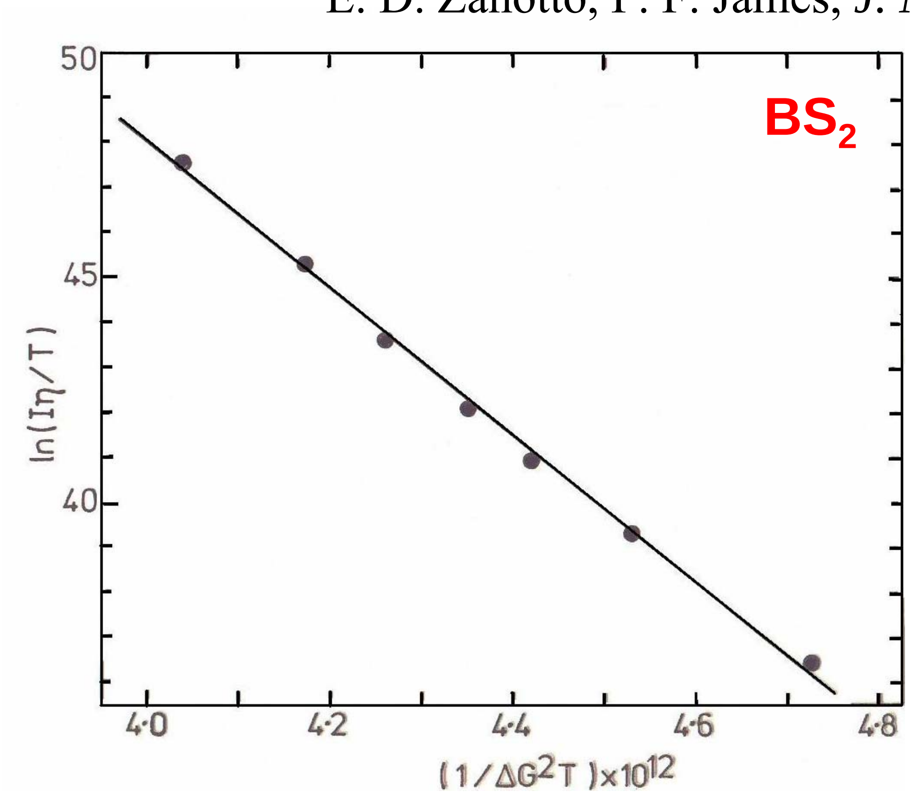
Deeply Undercooled Oxide Glasses (1970-2000's)



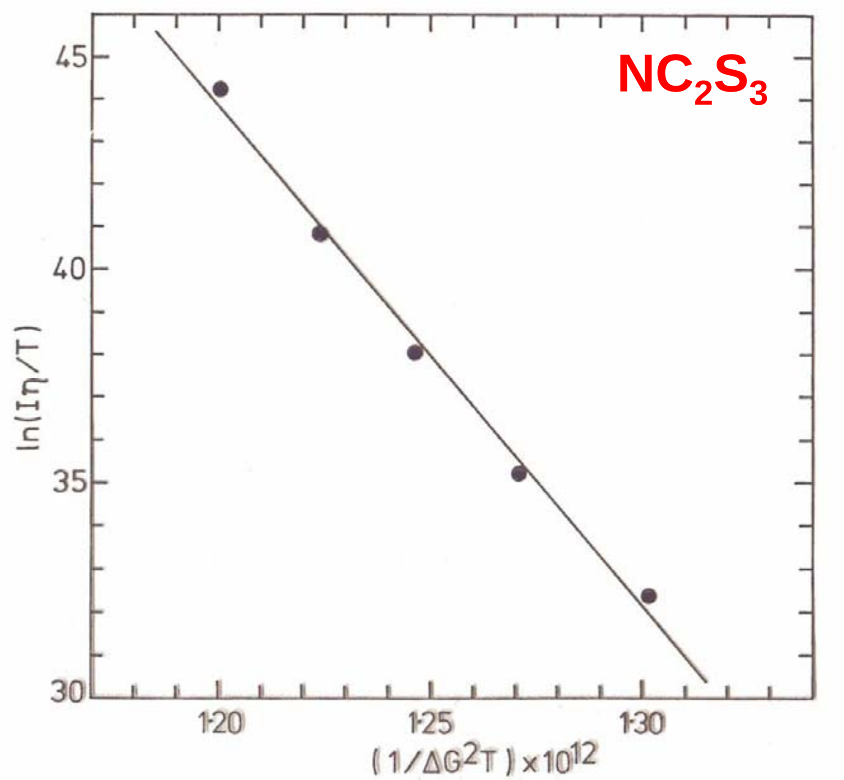
Fokin, Kalinina & Filipovich; Neilson & Weinberg; Rowlands, Gonzalez-Oliver, Ito, Zanotto & James; Hishinuma&Uhlmann and others have tested CNT using direct measurements of homogeneous nucleation rates in glasses in wide temperature ranges.

Testing CNT for Oxide Glasses

G. F. Neilson, M. C. Weinberg, *J. Non-Cryst. Solids* **34** (1979)
P. F. James, E. G. Rowlands, *Phys. Chem. Glasses* **20** (1979)
C. J. R. Gonzalez-Oliver, P. F. James, *J. Non-Cryst. Solids* **38-39** (1980)
E. D. Zanotto, P. F. James, *J. Non-Cryst. Solids* **104** (1988)

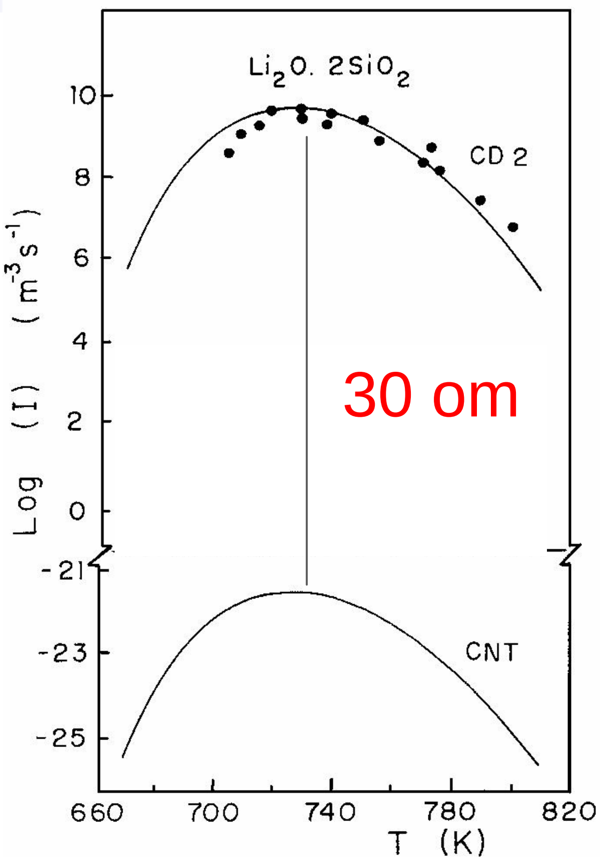


ln($I\ \eta/T$) vs.($1/\Delta G^2 T$) for BS_2.



ln($I\ \eta/T$) vs. ($1/\Delta G^2 T$) for NC_2S_3.

Results for LS2 glass



S. Manrich, E. D. Zanotto, *Cerâmica* **41** (1995).

Results

Varying ΔG_V

$$\sigma = \frac{\alpha \Delta H_m}{\sqrt[3]{N_A V_m^2}}$$

Silicate Glasses	α Turnb ΔC_p^{exp}	Discrepancy in I_{max} (o. m.)
BS_2	0.51- 0.56	13 - 32
LS_2	0.44 - 0.48	16 - 36
NC_2S_3	0.39 - 0.41	15 - 55
N_2CS_3	0.43 - 0.47	25 - 55
B_2TS_2	0.40 - ?	26 - ?

Reduced surface energy, α , was fit to give the best T dependence.

Summary

- **With a constant σ_0 , CNT describes the temperature dependence, but <u>not</u> the magnitude of $I(T)$.**

- **Possible problems: diffusion mechanism (breakdown of the SE?), size and temperature dependent surface energy, metastable phase formation, effect of elastic stresses, etc…?**