Nucleation of First-Order Phase Transitions

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Funding

National Science Foundation
WHERE DISCOVERIES BEGIN

NASA

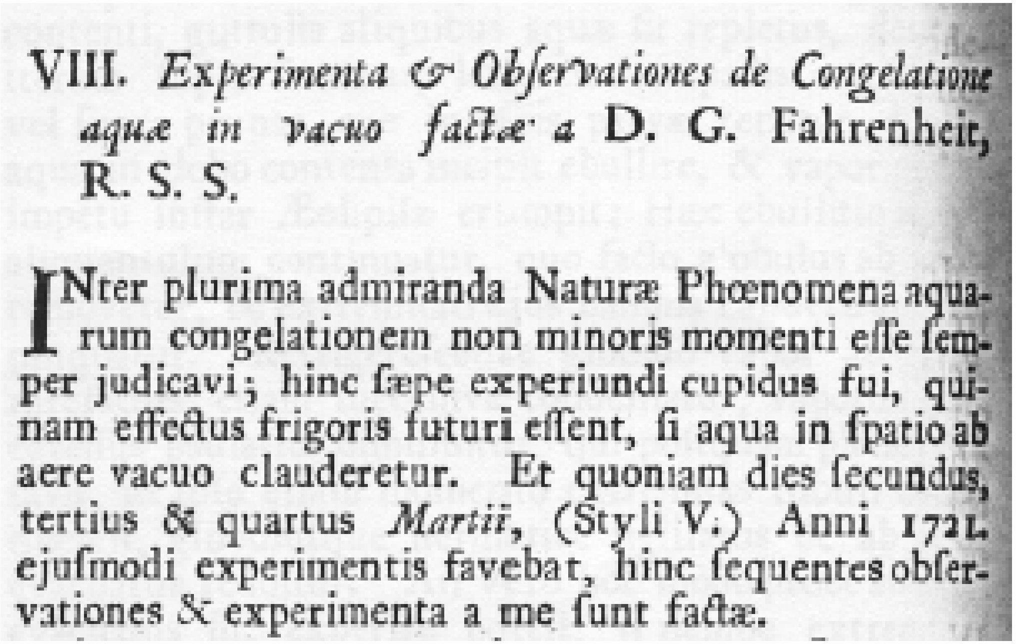
Outline of Talk

- Introduction
- Nucleation Models
  - Classical Theory
  - Fits of Classical Theory
    - Liquid data
    - Glasses
      - Steady-State
      - Time-Dependent
- Beyond the Classical Theory
  - Diffuse Interface Theory
  - Density Functional Theory
  - Fits to liquid and glass data
- Coupled Processes
  - Coupled interfacial/diffusive fluxes
  - Coupled phase transitions
- Conclusions

Gabriel Fahrenheit (1686 – 1736)

In 1724, he reported the supercooling of water, i.e. water remaining a liquid below 32°F (0°C, the freezing point)

D.G. Fahrenheit, Proc. Roy. Soc. London **33**, 78 (1724)



VIII. *Experimenta & Obſervationes de Congelatione aquæ in vacuo factæ* a D. G. Fahrenheit, R. S. S.

INter plurima admiranda Naturæ Phœnomena aquarum congelationem non minoris momenti eſſe ſemper judicavi; hinc ſæpe experiundi cupidus fui, quinam effectus frigoris futuri eſſent, ſi aqua in ſpatio ab aere vacuo clauderetur. Et quoniam dies ſecundus, tertius & quartus *Martii*, (Styli V.) Anni 1721. ejuſmodi experimentis favebat, hinc ſequentes obſervationes & experimenta a me ſunt factæ.

⇒ ***Existence of a barrier to crystallization***

- the Nucleation Barrier -

Nucleation

- First step in most first order phase transitions (such as freezing of water)
- Homogeneous Nucleation
  - Atomistic view
    - Small nuclei of new phase form by chance aggregation
    - Stochastic in time and space (nuclei grow and shrink)
    - When larger than a “critical size” biased to grow
  - Nuclei increase with
    - Larger driving free energy - decreased temperature for liquid crystallization
    - Decreased nucleation barrier
  - Theories
    - Classical Theory
    - Diffuse Interface Theories
    - Density Functional Theories
- Heterogeneous Nucleation
  - Stochastic in time but not in space
  - Nucleation barrier lowered by impurities, container walls, etc.
  - Most common type of nucleation
  - Practical importance
    - Seeding of clouds
    - Grain refinement (i.e. smaller grain sizes) in crystallized materials
    - e.g. Corning ware- fine grained ceramic

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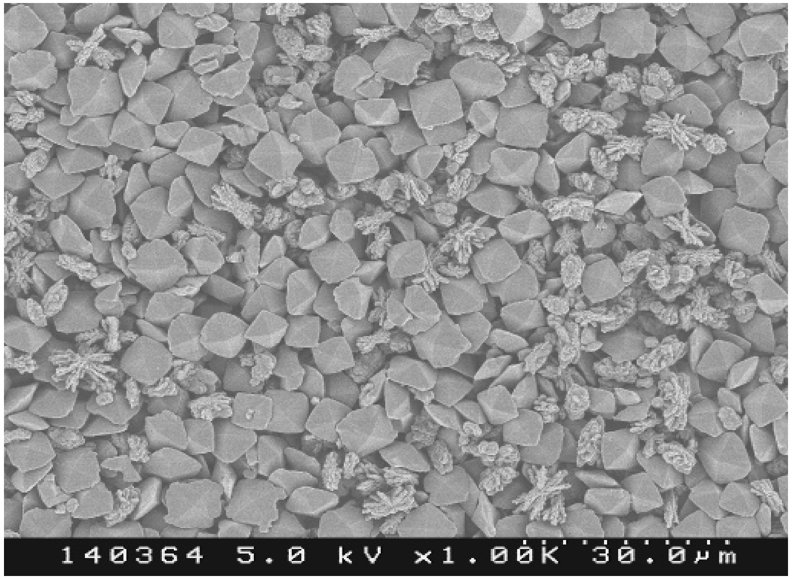
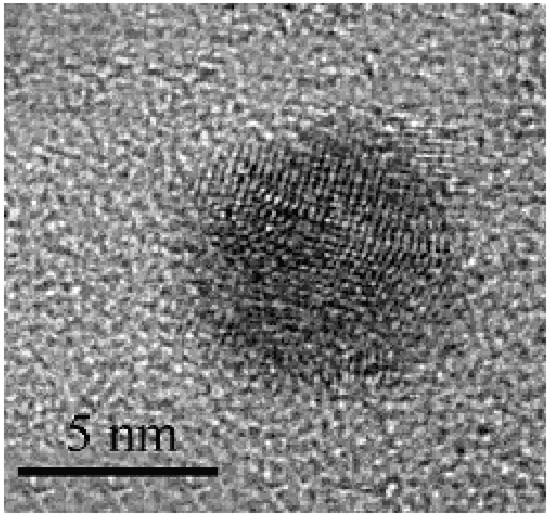
Nucleation in Medicine



urinary stones

Nanobiotechnology



Au Nanoparticles Alfalfa plants
J. L. Gardea-Torresdey et al.
Nano Letters, ***2***, 397 (2002)

Nucleation in Cosmology

A First Order Phase Transition from Inflationary to Big Bang Universe
GERALD HORWITZ
Annals of the New York Academy of Sciences
Volume 470, Issue Twelfth , Pages380 - 380
1986 The New York Academy of Sciences

Anti-Nucleation/Growth Agents

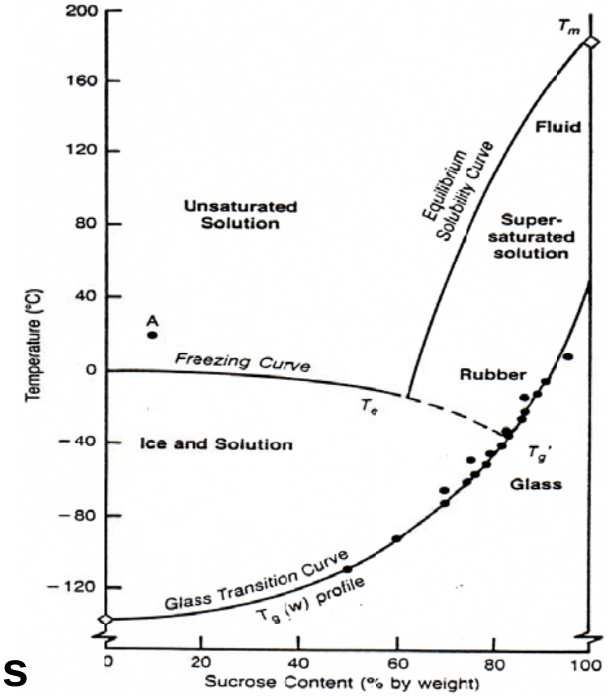
Dissostichus mawsoni
the Antarctic toothfish

- Melting temperature of blood = - 0.8°C
- Water temperature = -1.9°C
- Antifreeze glycoproteins
- Poison growth sites

Nucleation Promotion Agents

Northern Wood Frog
Rana sylvatica

- **only frog that lives north of Artic Circle**
- **in winter completely solid, 65% ice**
- **Ice nucleating agent**
  - **- promotes freezing outside cell**
  - **- draws water from cells by osmosis**
  - **- cells congeal into glass**



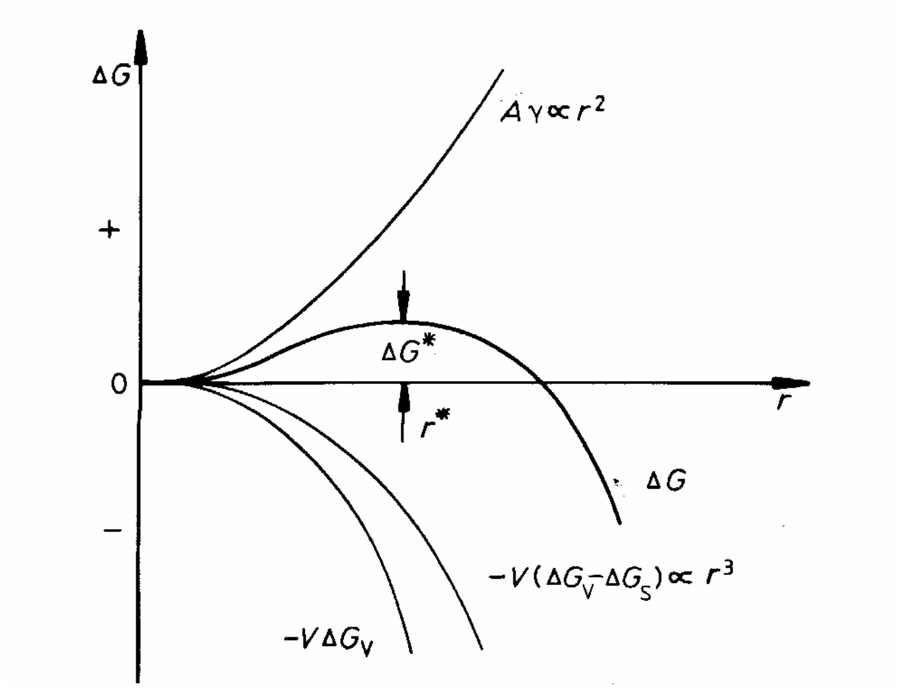
THE CLASSICAL THEORY OF HOMOGENEOUS NUCLEATION

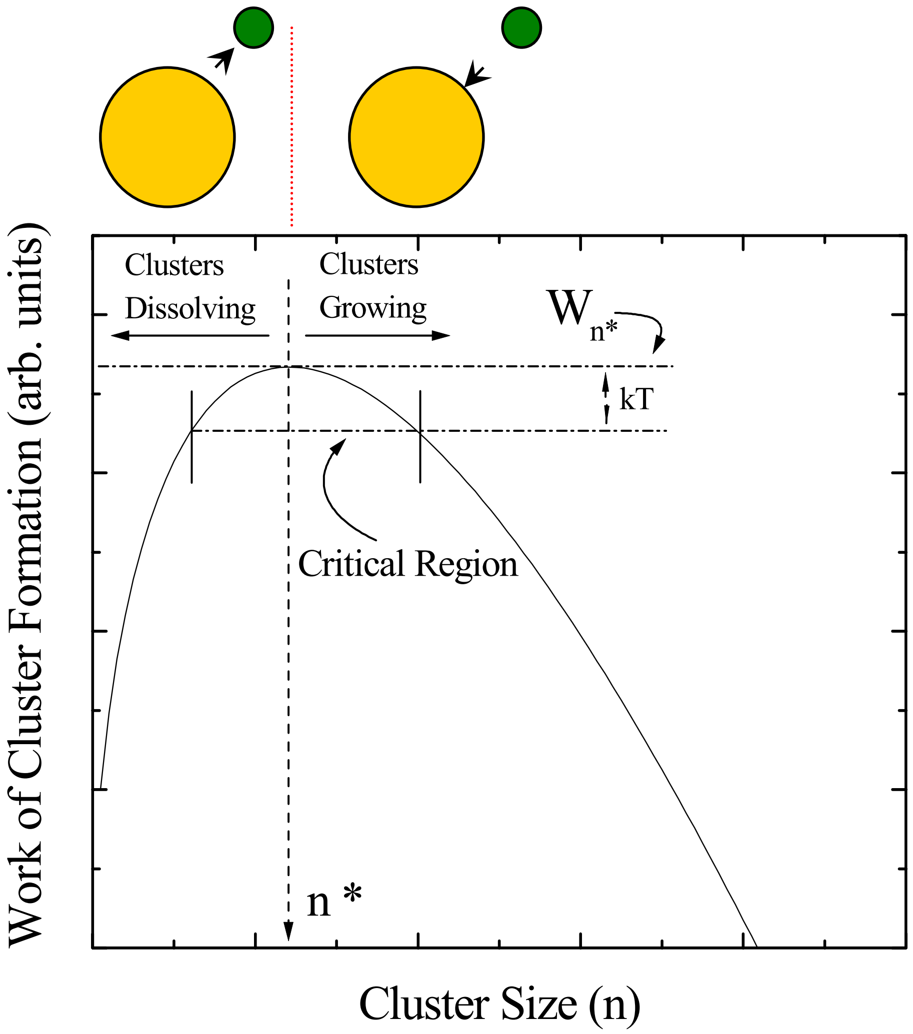
$$W_{\min} = \boxed{\frac{4\pi}{3} r^{3} \left(\delta\mu / \bar{\mathrm{v}}\right)} + \boxed{4\pi r^{2} \sigma}$$

Driving free Energy

Surface Energy Barrier

$$W_{\min} = \boxed{n\,\delta\mu} + \boxed{\kappa\, n^{2/3} \sigma}$$





Josiah Willard Gibbs (1839 -1903)

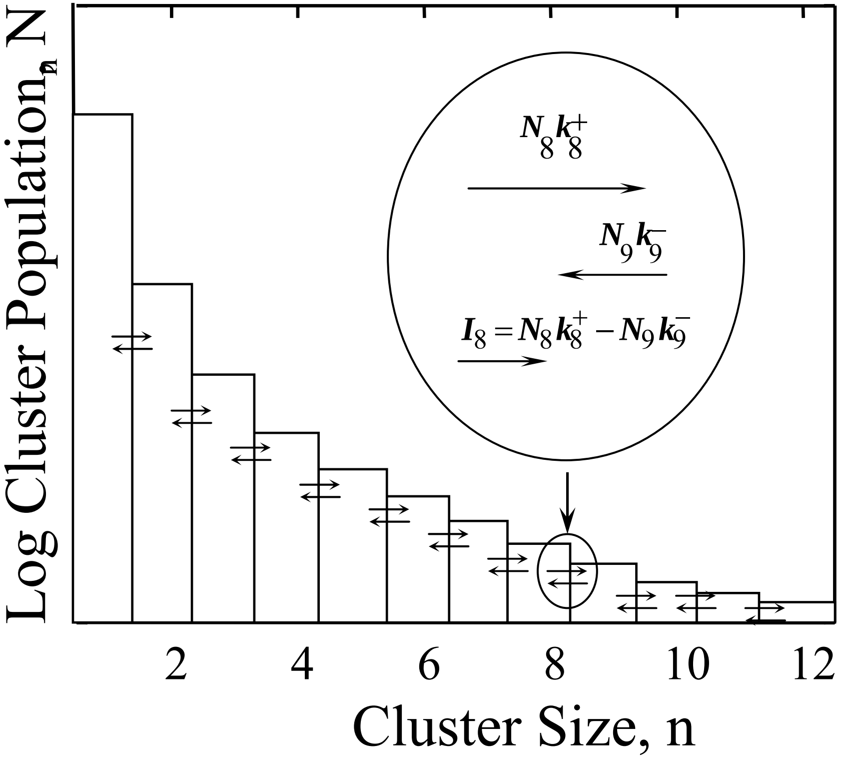
Probability Of fluctuation

$$P \propto \exp\left(-\frac{W_{\min}}{kT}\right)$$

Kinetic Model for Homogeneous Nucleation (Volmer and Weber - 1926)

- Single atom attachment or detachment
- **Nucleation rate is a function of the time and cluster size**

$$I_{n,t} = N_{n,t}\, k_n^{+} - N_{n+1}\, k_{n+1}^{-}$$



$$\begin{aligned}\frac{\partial N(n,t)}{\partial t} &= N(n-1,t)\,k^{+}(n-1)\\ &\quad - N(n,t)\big(k^{+}(n)+k^{-}(n)\big)\\ &\quad + N(n+1,t)\,k^{-}(n+1)\end{aligned}$$

$$\Rightarrow \frac{\partial N(n,t)}{\partial t} = \frac{\partial}{\partial n}\left(k^{+}(n)\,N^{\mathrm{eq}}(n)\frac{\partial}{\partial n}\left(\frac{N(n,t)}{N^{\mathrm{eq}}(n)}\right)\right)$$ - Zeldovich-Frenkel Equation

Calculation of Interfacial Rates

Vapor – *forward rate is simply the number of collisions between free monomer and cluster multiplied by the probability that the monomer is incorporated into cluster*

Solid – *(D. Turnbull and J. C. Fisher, J. Chem. Phys.* ***17,*** *71 (1949)). assumed an activated process for incorporation of monomer into cluster*

$$k_n^+ = 4n^{2/3} \; \gamma \; \exp\left(-\frac{\delta g_n}{2kT} \right)$$

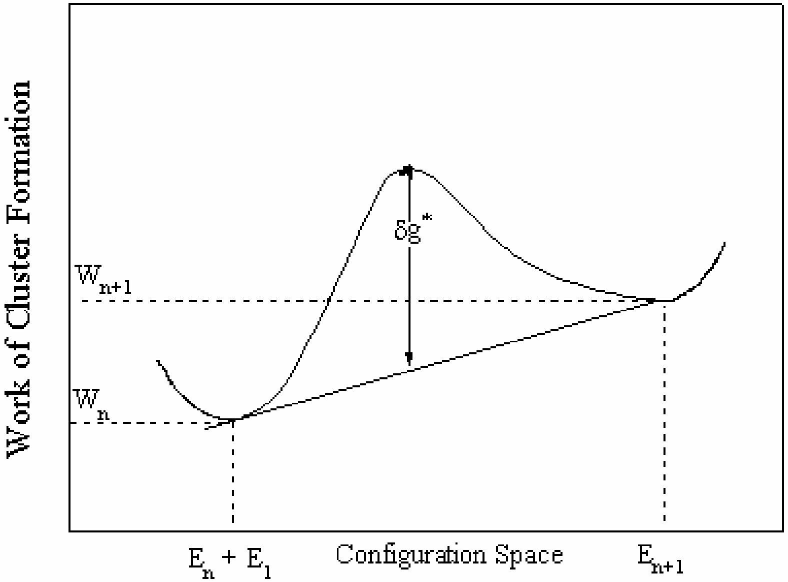
number of attachment sites

jump frequency

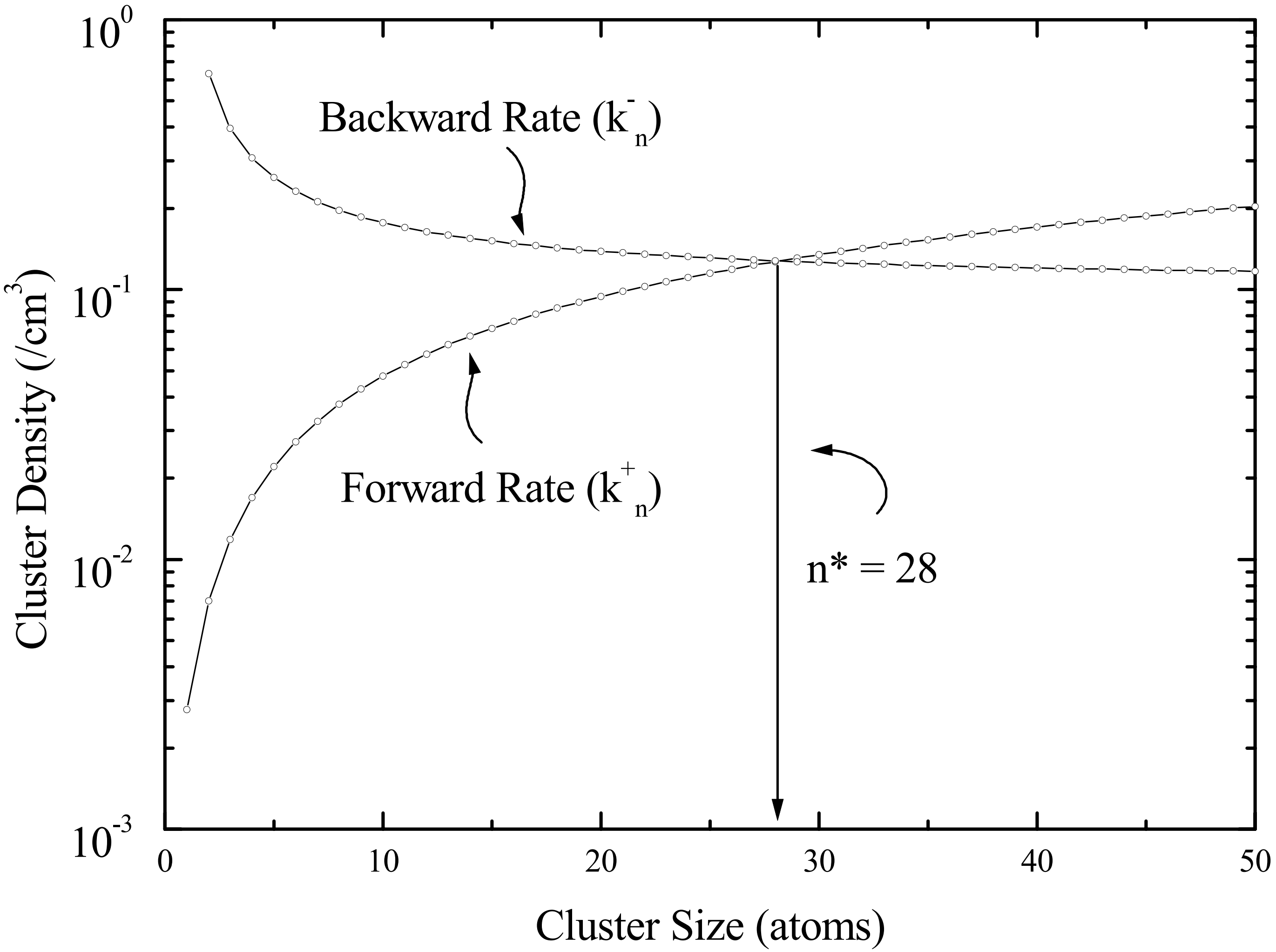
biasing term

$$\delta g_n = \frac{W_{n+1} - W_n}{2}$$

$$\gamma = \frac{6D}{\lambda^2}$$



Comparison of Forward and Backward Rates



Becker-Döring Treatment

- Detailed balance

$$k^-(n+1) = k^+(n)\frac{N^{\mathrm{eq}}(n)}{N^{\mathrm{eq}}(n+1)} \quad \Rightarrow \quad I^{\mathrm{st}} = N^{\mathrm{eq}}(n)k^+(n)\left(\frac{N^{\mathrm{st}}(n)}{N^{\mathrm{eq}}(n)} - \frac{N^{\mathrm{st}}(n+1)}{N^{\mathrm{eq}}(n+1)}\right)$$

- Boundary conditions

$$N^{\mathrm{st}}(n) \to N^{\mathrm{eq}}(n) \ \text{as} \ n \to 0$$

$$N^{\mathrm{st}}(n) \to 0 \qquad \text{as} \ n \to \infty$$

$$\Rightarrow \qquad I^{\mathrm{st}} = \left(\sum_{n=\tilde{\mathrm{u}}}^{\tilde{\mathrm{v}}} \frac{1}{N^{\mathrm{eq}}(n)k^+(n)}\right)^{-1}$$

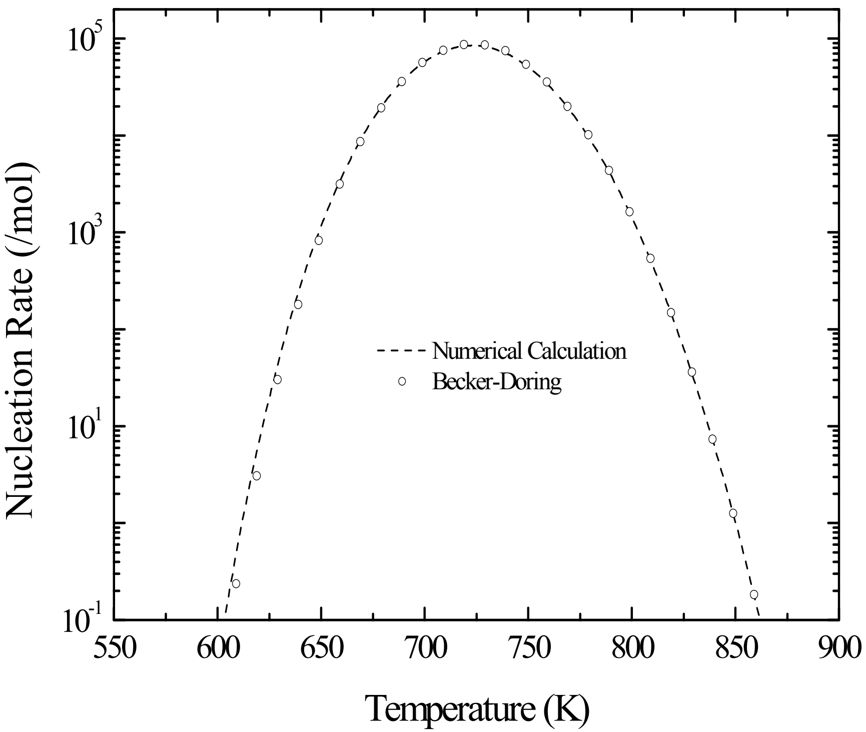
- Solve for steady state rate
  - Replace k⁺(n) by k⁺(n*)
  - Expand W(n) about W(n*)
  - Change sum to integral

$$\sum_{n=\tilde{\mathrm{u}}}^{\tilde{\mathrm{v}}} \frac{1}{N^{\mathrm{eq}}(n)} = \frac{1}{N_{\mathrm{A}}}\exp\frac{W(n^*)}{k_{\mathrm{B}}T}\int_{-\infty}^{\infty} \mathrm{d}\hat{\xi}\exp\left(-\frac{W(n^*)\hat{\xi}^2}{3n^{*2}k_{\mathrm{B}}T}\right)$$

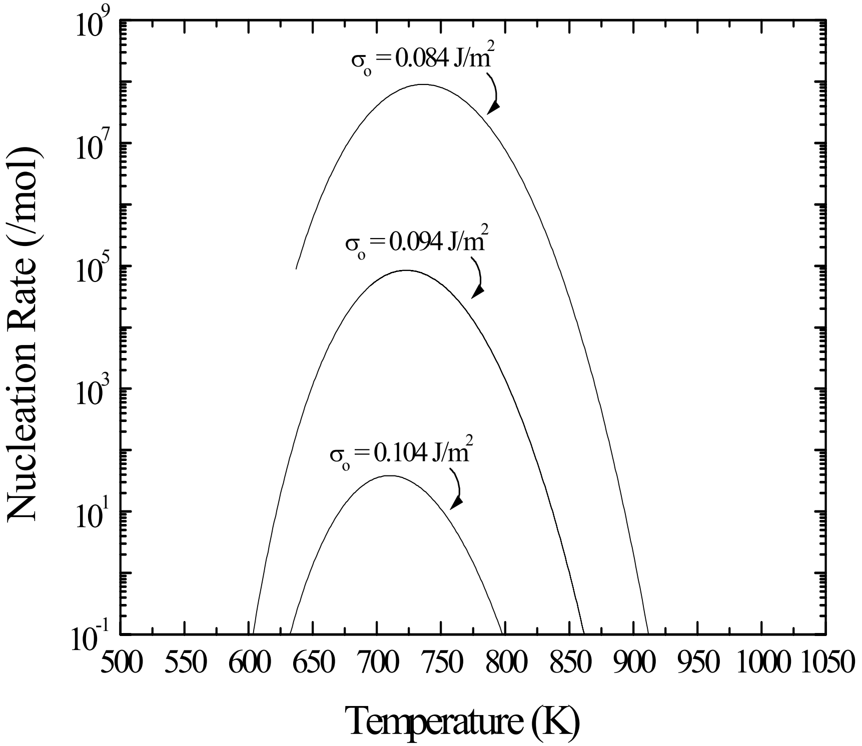
$$\simeq \frac{1}{N_{\mathrm{A}}}\exp\left(\frac{W(n^*)}{k_{\mathrm{B}}T}\right)\left(\frac{3\pi k_{\mathrm{B}}T}{W(n^*)}\right)^{1/2} n^*$$

$$I^{\mathrm{st}} = N^{\mathrm{eq}}(n^*)k^+(n^*)Z \qquad where \quad Z = \left(\frac{|\Delta\mu|}{6\pi k_{\mathrm{B}}Tn^*}\right)^{1/2} \ - \ Zeldovich \quad factor$$

Steady-State Nucleation Rate in Crystallization



- Becker-Döring expression and numerical calculation agree quantitatively
- Rate increases at high temperatures due to increasing driving free energy
- Rate Decreases at low temperatures due to decreasing mobility

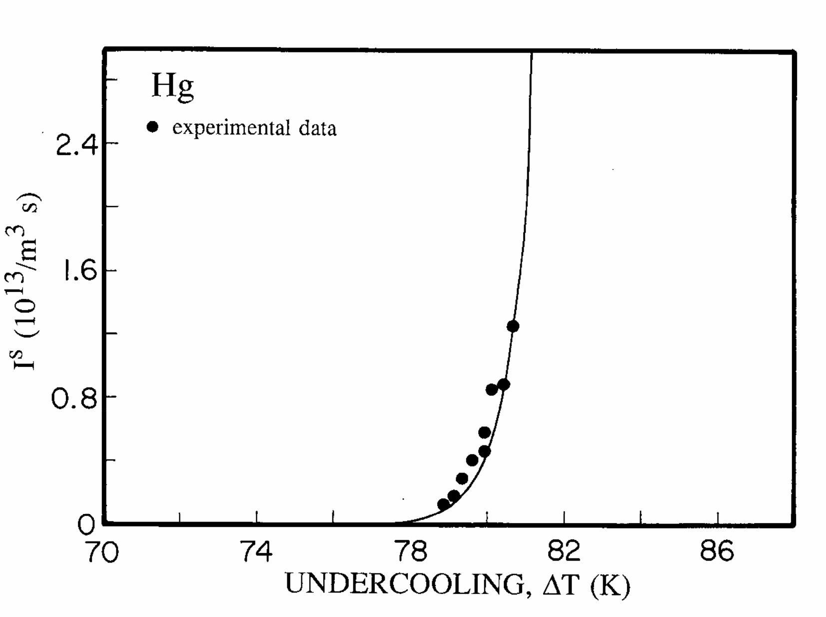


- Numerical calculations of rates
- Magnitude of rate is extremely sensitive to the values of interfacial free energy
- Values of σ are NOT the same as those from macroscopic measurements
- Key problem with classical theory - σ are only obtained from fits to nucleation data

LIQUID
EXPERIMENTAL
MEASUREMENTS

Maximum undercooling studies

(Based on strong T dependence of I)

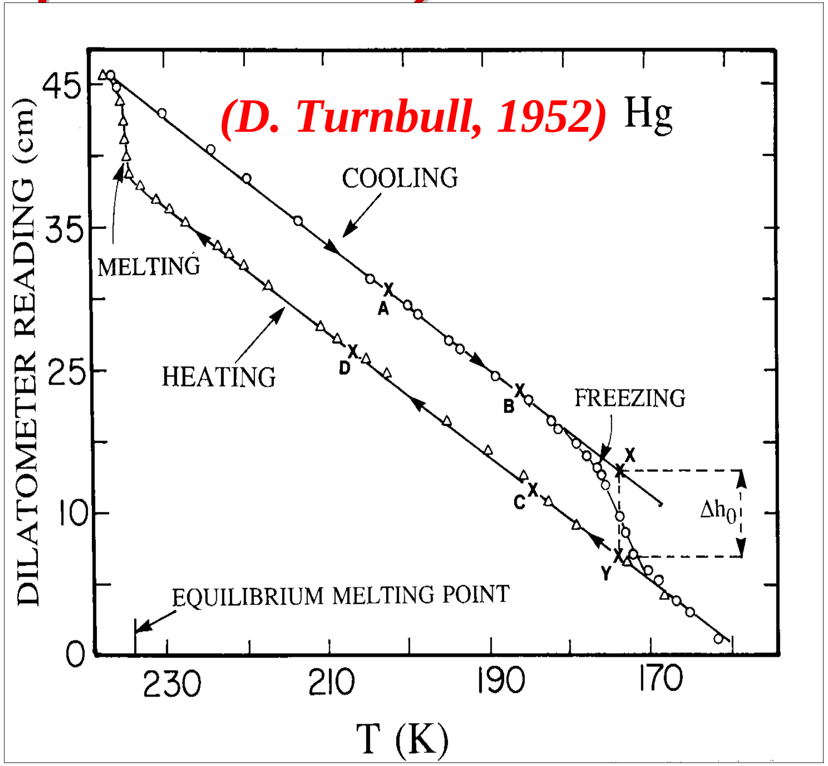


Probability of droplet having no nuclei given N nuclei per mole

$$x = \exp\left(-vN\right)$$

$$x = \exp\left(-\frac{v}{Q}\int_{T_m}^{T_u} I^s(T)\,dT\right)$$

where, v is the droplet volume and Q is the cooling rate



(D. Turnbull, 1952)

- Reduced Undercooling

  $\Delta T_r = \Delta T / T_m$

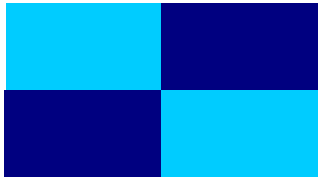
  – T_m melting temperature

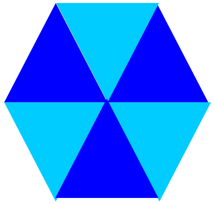
  – ΔT (T_m-T_n)

- For Hg, $\Delta T_r \approx 0.3$
- All metals undercool with $\Delta T_r \approx 0.2$

Why can Liquid Metals be Supercooled?

- Turnbull’s experimental results were met with surprise
- Based on densities and coordination numbers, it was believed that the liquid/crystal atomic structures were similar
- Allowed rotational symmetries for crystals (consider 2d tiling)


2-fold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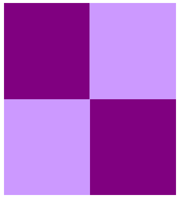
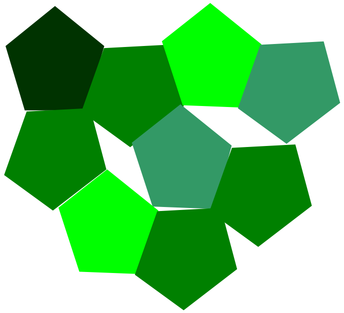
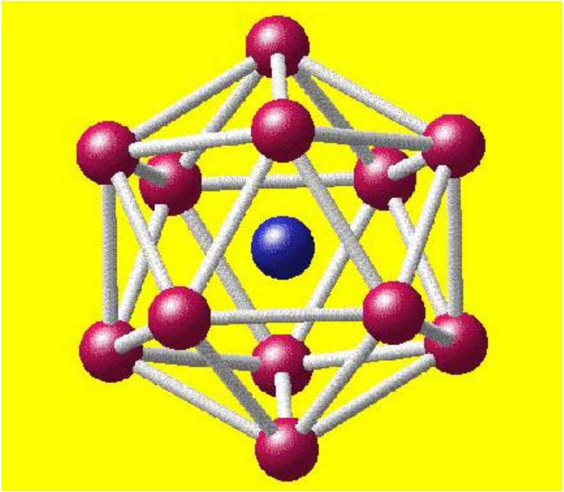

4-fold


6-fold


5-fold

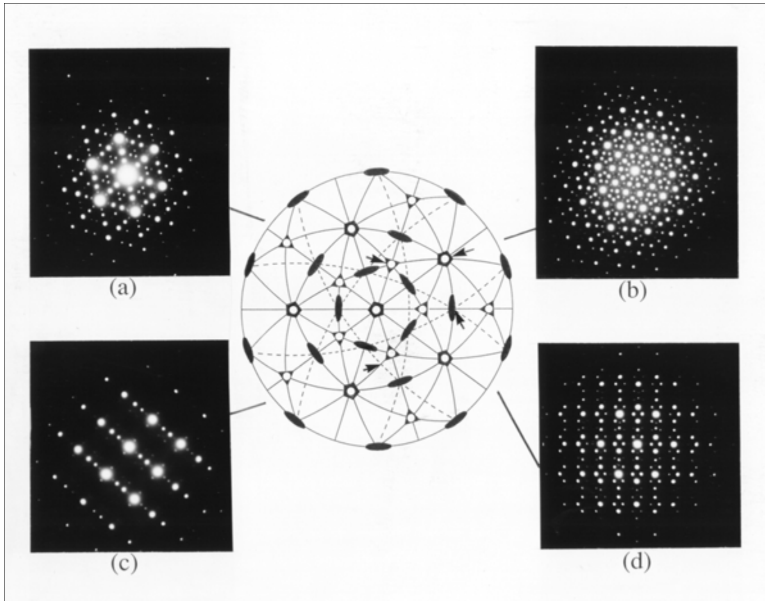
Frank’s hypothesis

The atoms in a metallic liquid are arranged in the form of an icosahedron



Nucleation of an ordered crystal requires that the icosahedral order be destroyed

Nucleation of the icosahedral phase (i-phase) from AlCuV Metallic Glass



- I-phase – extended icosahedral order
- Fit to classical theory of nucleation
- Very small interfacial free energy

$$\boxed{\sigma_{i/g} < 0.1\ \sigma_{xtl/l}(Al)}$$

- Local structures of i-phase and glass are very similar

J. C. Holzer & K. F. Kelton, Acta. Metall., **39**, 1883-43 (1991)

Nucleation of i-phase in Undercooled Liquid

D. Holland-Moritz, Int. J. Non-Eq. Processing, **11**, 169-199 (1998).

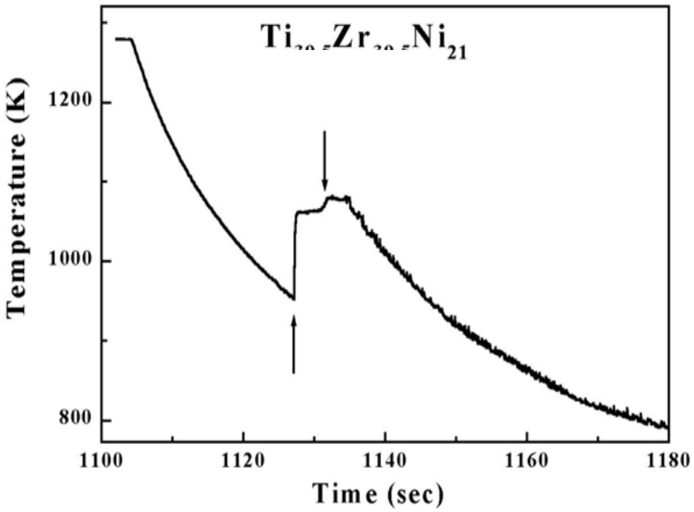
- rf-levitation studies of i-phase and related phases (crystal approximants)

- **Icosahedral Phase**
  - ✍ $Al_{60}Cu_{34}Fe_{6}$
    $\Delta T^{I} \approx 100K$ ⇨ $\Delta T^{I}/T_{L} \approx 0.1$
  - ✍ $Al_{58}Cu_{34}Fe_{8}$
  - ✍ Al- Pd - Mn
    $\Delta T^{I} \approx 125K$ ⇨ $\Delta T^{I}/T_{L} \approx 0.11$

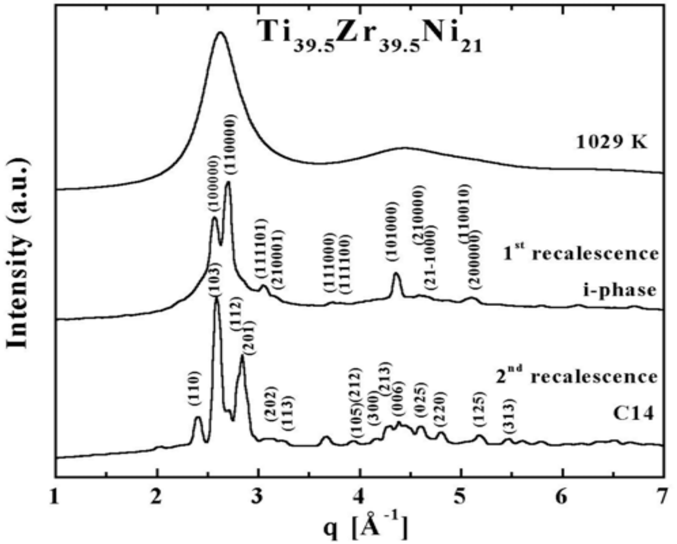
- **Crystal Approximants**
  - ✍ λ - $Al_{13}Fe_{4}$ ⇨ $\Delta T^{\lambda}/T_{L} \approx 0.12$
  - ✍ μ - $Al_{5}Fe_{2}$ ⇨ $\Delta T^{\mu}/T_{L} \approx 0.15$

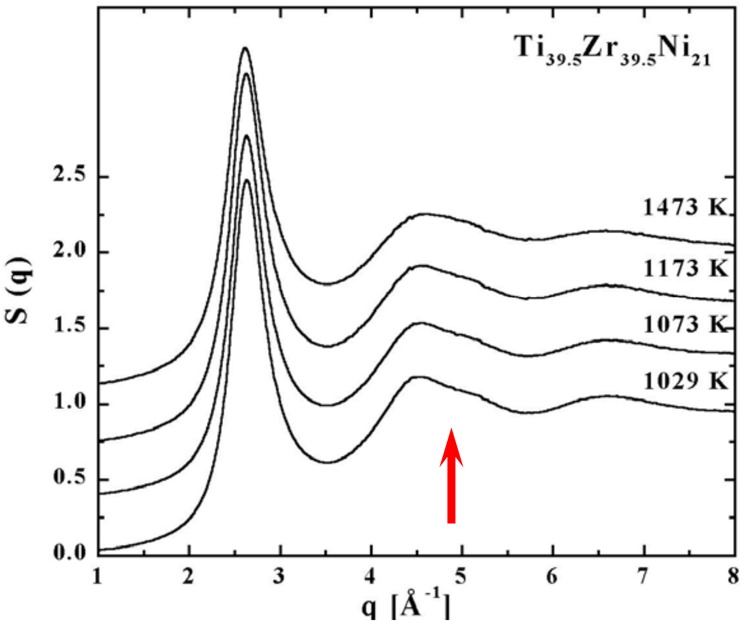
- **Crystal Phases**
  - ✍ β(AlCuCo) - (CsCl Structure)
    ⇨ $\Delta T^{\beta}/T_{L} \approx 0.25$

Icosahedral Ordering in a $Ti_{39.5}Zr_{39.5}Ni_{21}$ Liquid and Nucleation



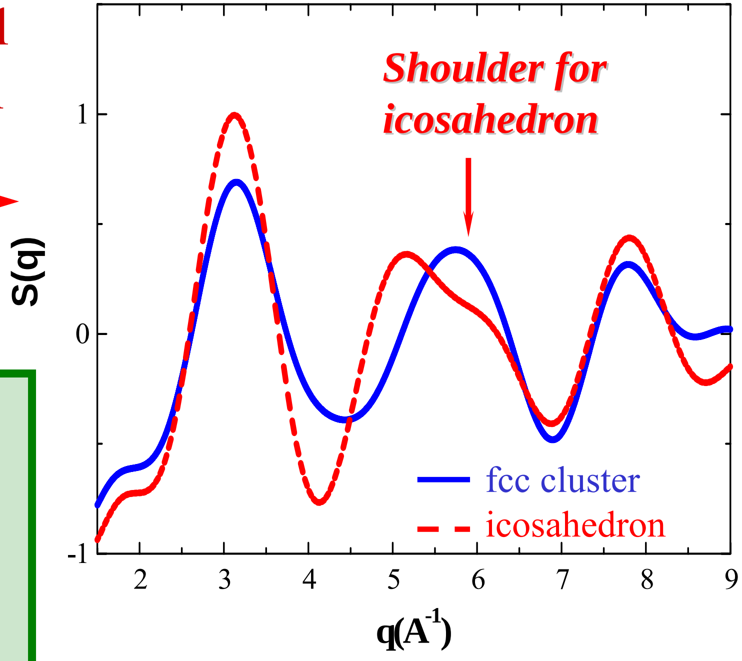
Recalescence to metastable quasicrystal





Icosahedral ordering in liquid

Ordering lowers nucleation barrier



Shoulder for icosahedron

K. F.Kelton, et a. *Phys. Rev. Lett*, **90**, 195504 (2003)

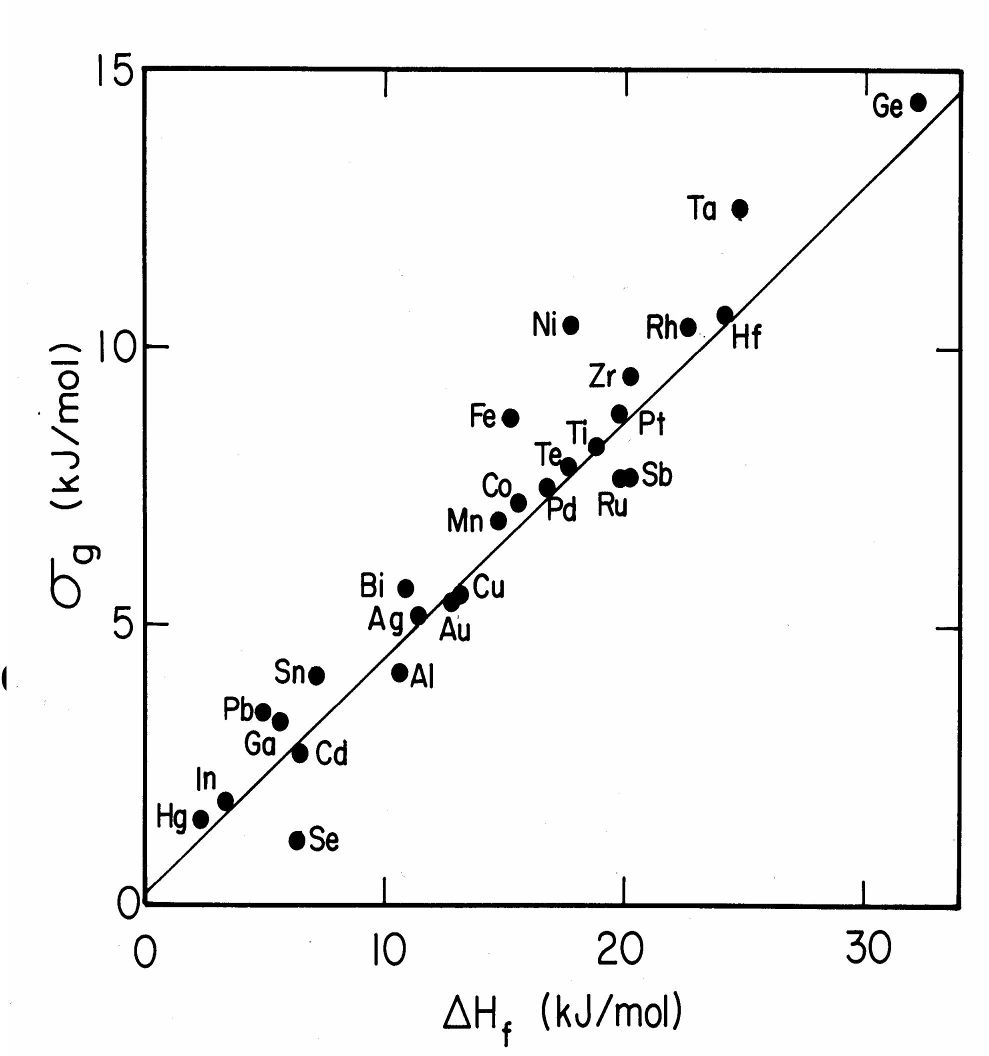
Maximum Undercooling Data

$$I^{S} = A^{*}\, exp\left[-\frac{16\pi}{3k_{B}T}\frac{\sigma^{3}}{\Delta G_{V}^{2}}\right]$$

- Minimize Heterogeneous Nucleation
- Assume constant atomic mobility (taken at the melting temperature)
- Driving free energy assumed t scale with undercooling

  $\Delta G_v = \Delta H_f\, \Delta T_/T_m$

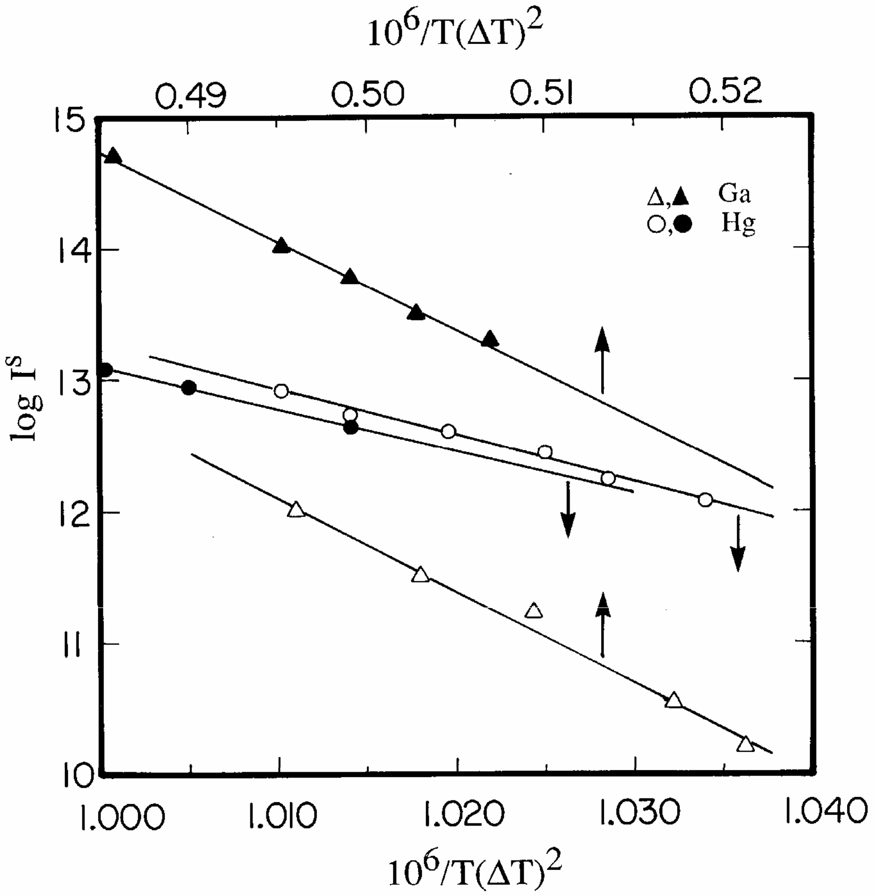
- Surface energy scales linearly with enthalpy of fusion



K. F. Kelton
Solid State Physics **45** (1991)

Fits to $I^s(T)$

System	σ(J/m^2)	Log A* (/m^{3}s) EXPERIMENTAL
Hg	0.031	48.1
$C_{17}H_{36}$	0.0072	36.5 ± 2
$C_{18}H_{38}$	0.0096	37.3 ± 2
$C_{24}H_{50}$	0.0082	30 ± 4
H_2O	0.032	52.5



$$I^s = A^* \exp\left(-\frac{16\pi}{3k_BT}\,\frac{\sigma^3}{\Delta H_f^2\,\Delta T_r^2}\right)$$

$$\ln(I^S) = \ln A^* - \left(\frac{16\pi}{3k_BT}\,\frac{\sigma^3\,T_m^2}{\Delta H_f^2}\right)\frac{1}{\Delta T^2}$$

Hg : log A* (theory) = 41

$\sigma = \sigma_o T$

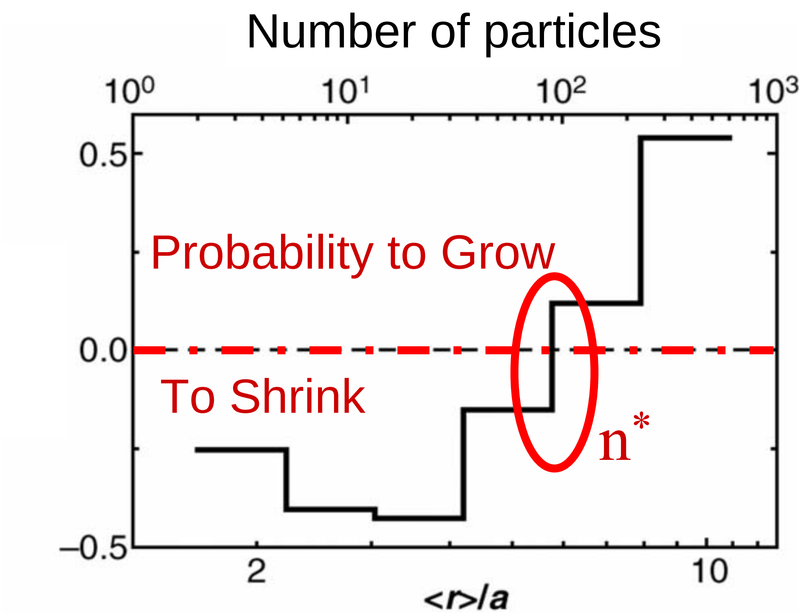
$\Rightarrow d\sigma/dT > 0$

K. F. Kelton
Solid State Physics **45** (1991)

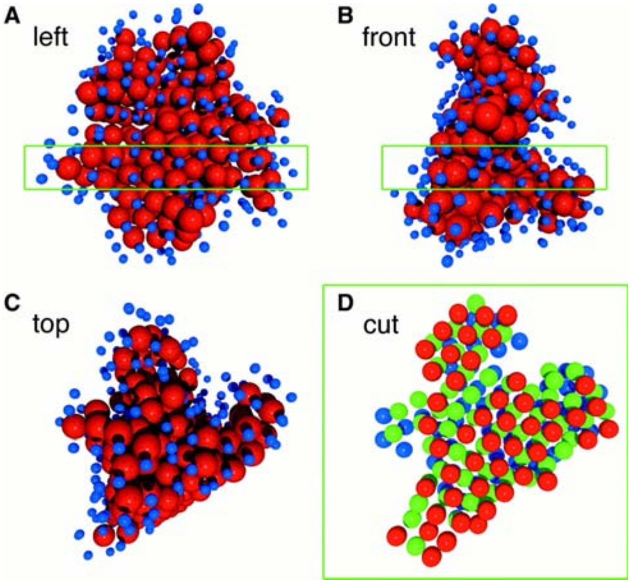
Crystallization in Colloidal Suspensions

- Suspensions of solid particles in liquid
- Particle interactions can be adjusted to more accurately fit computer simulations or theoretical models
- Structure and nucleation in of colloid suspension in shear melted liquid can be measured by light scatting
- Good agreement found (see C. Sinn, A. Heymann, A. Stipp & T. Palberg, “Solidification kinetics of hard-sphere colloidal suspensions,” *Prog. Coll. Polym. Sci.* **118**, 266–275 (2001)).

Proof of Statistical Fluctuation



Diffuse Interface – Not Compact



U. Gasser et al. *Science,* **292**, 258–262 (2001).

GLASSES

Quantitative nucleation rate measurements in glasses

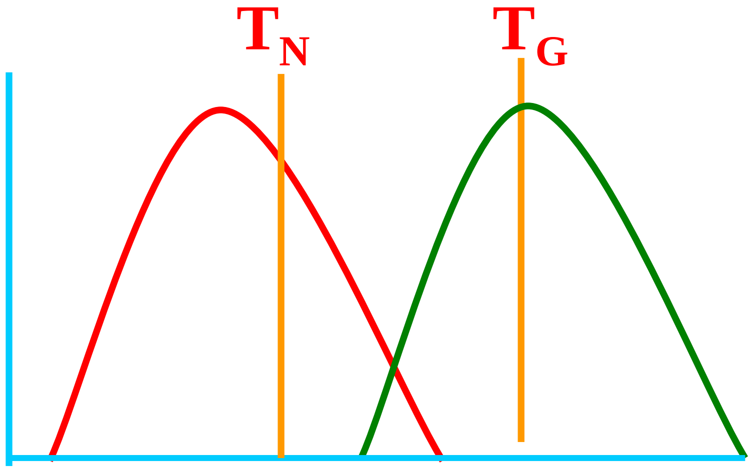
- Two-step annealing treatments

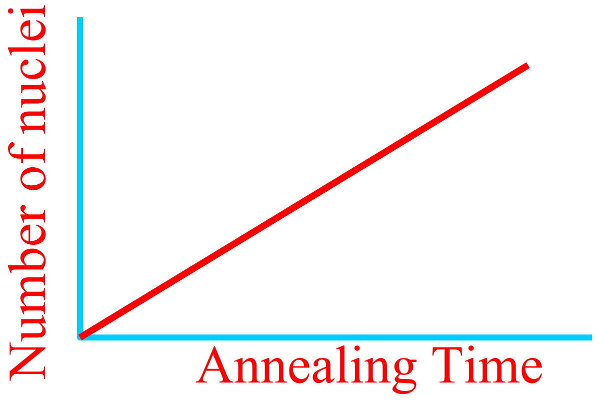
  — Nucleation Rate

  — Growth Velocity

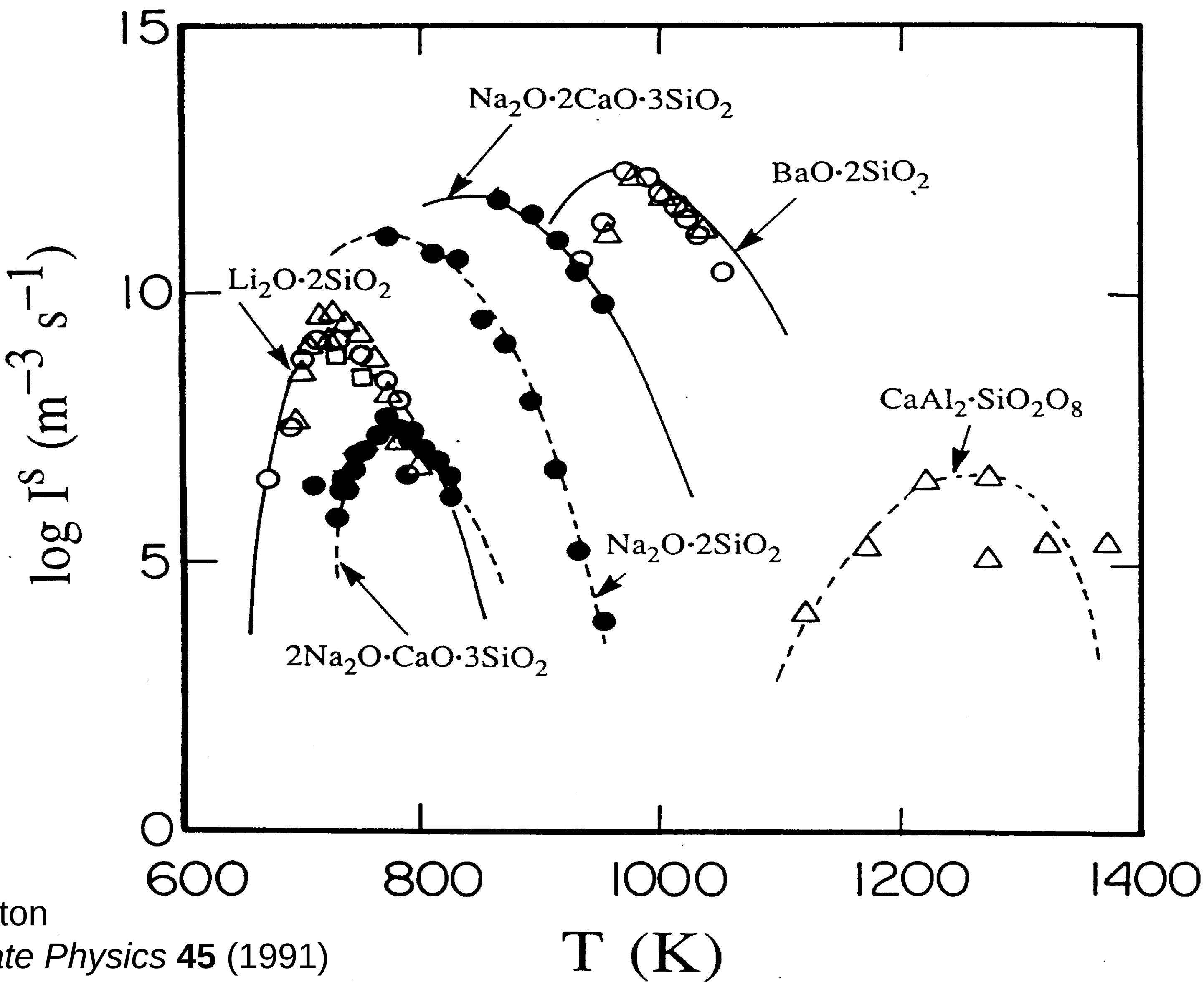
- Count nuclei directly
  - Optical microscopy
  - SEM or TEM

- $$N = \int_0^t I(t)\,dt = I^S t$$





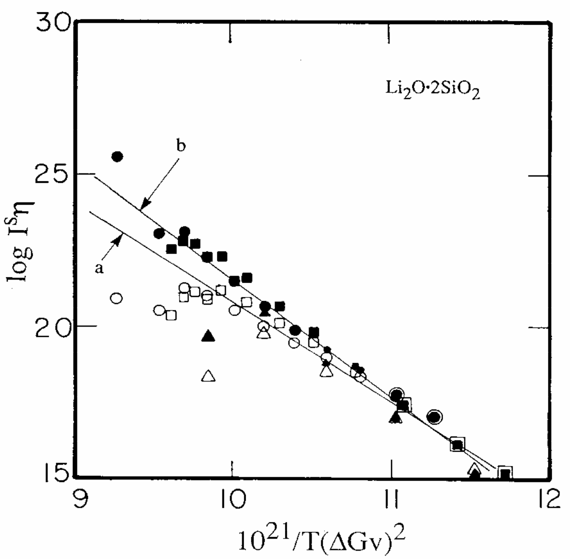
Homogeneous nucleation in polymorphically crystallizing silicate glasses



K. F. Kelton
Solid State Physics **45** (1991)

Fits to Glass Crystallization Data

$$\mathrm{I} = \frac{\mathcal{A}}{\eta} \exp\left[-\frac{16\pi}{3k_B} \frac{\sigma^3}{T\Delta G_v^2} \right] \quad \Rightarrow \quad \ln(I\eta) = \ln\mathcal{A} - \frac{16\pi}{3k_B} \frac{\sigma^3}{T\Delta G_v^2}$$



K. F. Kelton
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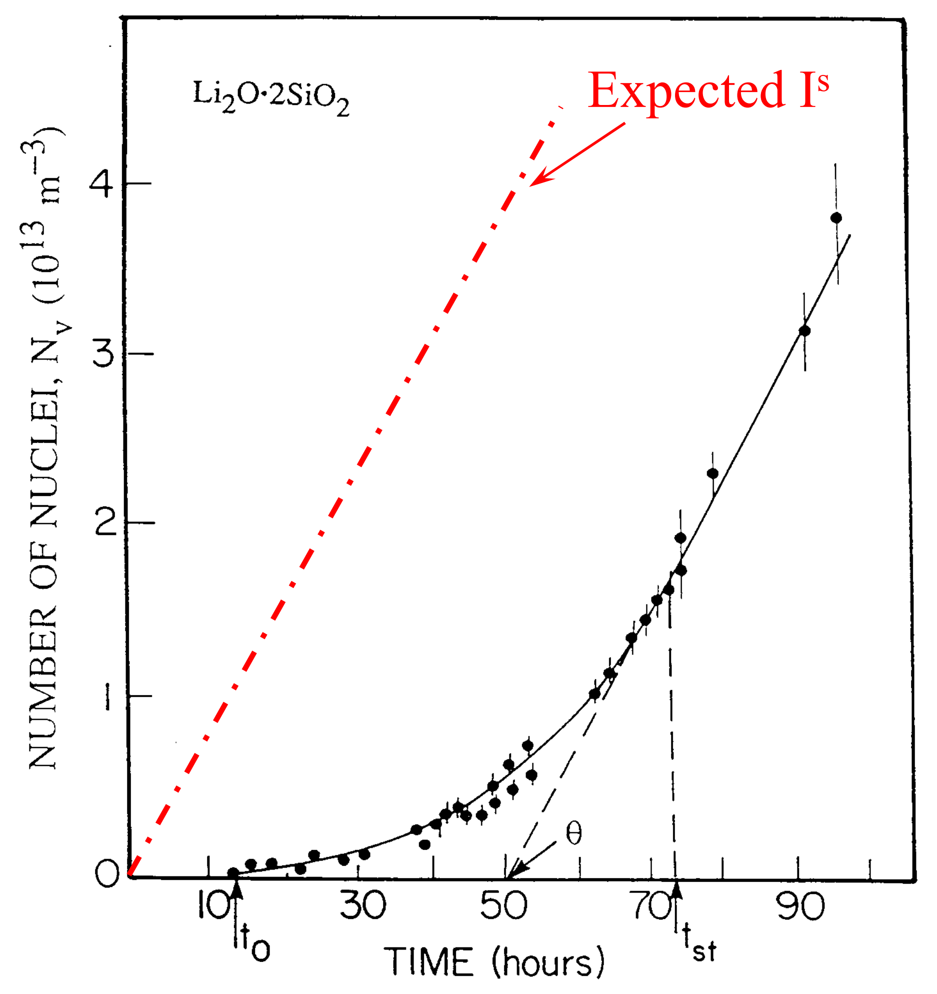
THEORETICAL		CALCULATED					
				$\sigma = \sigma_o + \sigma_1 T$			
	$\mathcal{A}$	$\mathcal{A}$				$\sigma(T_{max})$	(J/m^2K)
Glass	(Pa/m^3)	(Pa/m^3)	$\sigma(J/m^2)$	$\sigma_o(J/m^2)$	$\sigma_1(J/m^2)$	Kelton	James
$Li_2O.2SiO_2$	$10^{33.0}$	$10^{53.2}$	0.139	0.138	2.1×10^{-5}	0.153	0.143
		$10^{60.1}$	0.147	0.125	3.7×10^{-5}	0.152	0.147
$Na_2O.2CaO.3SiO_2$	$10^{32.6}$	$10^{60.8}$	0.131	0.103	3.1×10^{-5}	0.130	0.108
$BaO.2SiO_2$	$10^{32.9}$	$10^{55.3}$	0.100	0.077	2.8×10^{-5}	0.104	0.101

TIME-DEPENDENT NUCLEATION IN GLASSES

Time-dependent nucleation

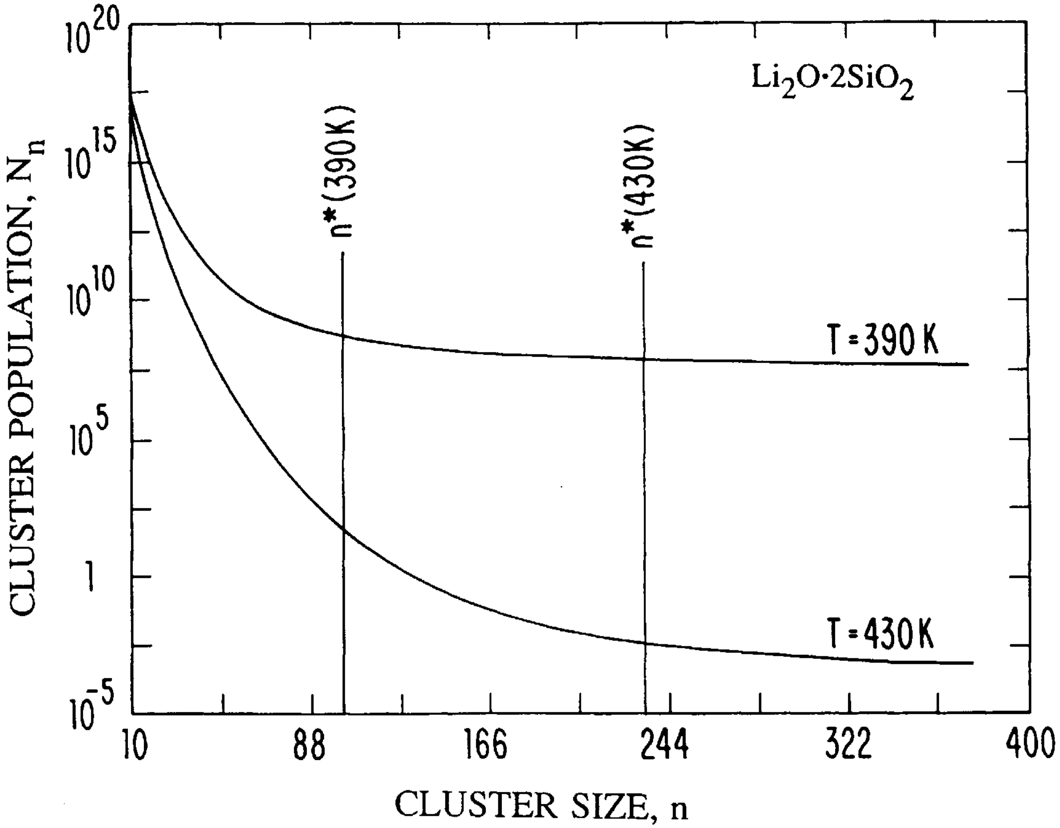
- Polymorphic Crystallization - no change in composition
- Nucleation in $Li_2O{\cdot}2SiO_2$ glass
- Due to change in cluster distribution toward steady-state distribution at annealing temperature

$$N_v = I^s(t-\theta)\ , \qquad for\ t >>$$



V. M. Fokin, A. M. Kalinina and V. N. Filipovich, J. Cryst. Growth, **52**, 115 (1981)

Origin of Time-Dependent Nucleation Rates



- I (n*) ~ $N^e(n^*)$ * $k^+(n^*)$
- Cluster distribution inherited from rapid quench to produce glass is characteristic of that from higher temperature
- Initially, $N^e(n^*)$ is lower than steady-state density at annealing temperature
- Nucleation rate increases as quenched cluster distribution relaxes to steady-state one at annealing temperature

Fits to Transient Data

Zeldovich-Frenkel equation

$$\frac{\partial N_{n,t}}{\partial t} = \frac{\partial}{\partial n}\left[k_n^+ N_n^e \frac{\partial}{\partial n}\left(\frac{N_{n,t}}{N_n^e}\right)\right]$$

Diffusion equation in size space

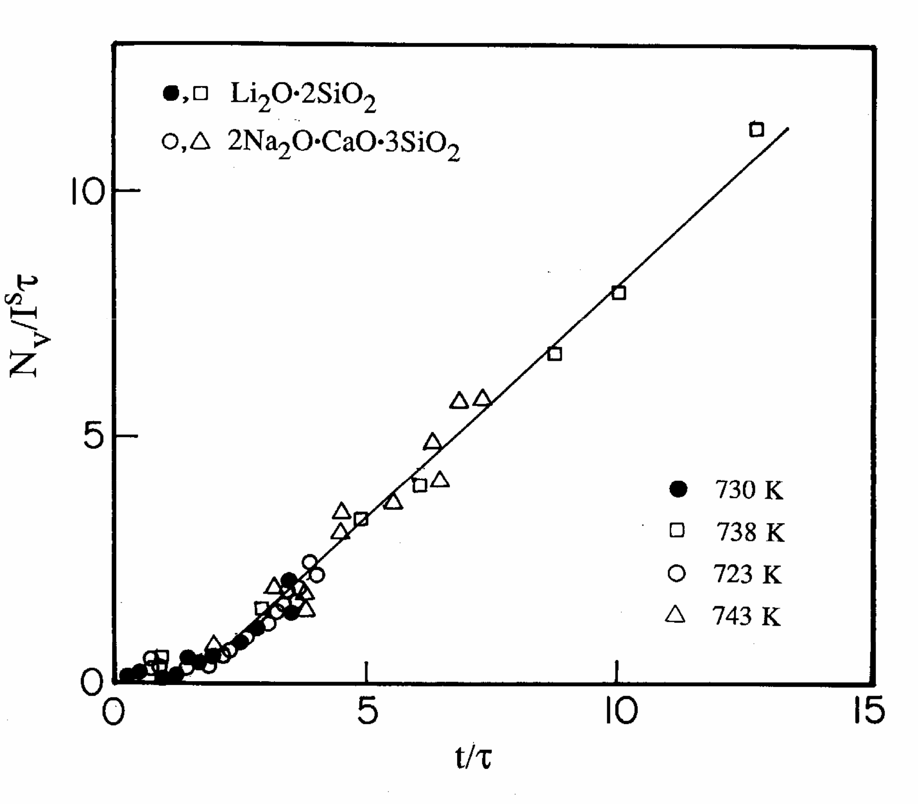
$$\left(\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial C}{\partial x}\right]\right)$$ Fick's law

Kashchiev's solution - I(t)

1. $k_n^+ \rightarrow k_{n*}^+$

2. $W_n \simeq W_{n*} + \frac{1}{2}\left.\frac{\partial^2 W_n}{\partial n^2}\right|_{n=n*} (n - n*)^2$

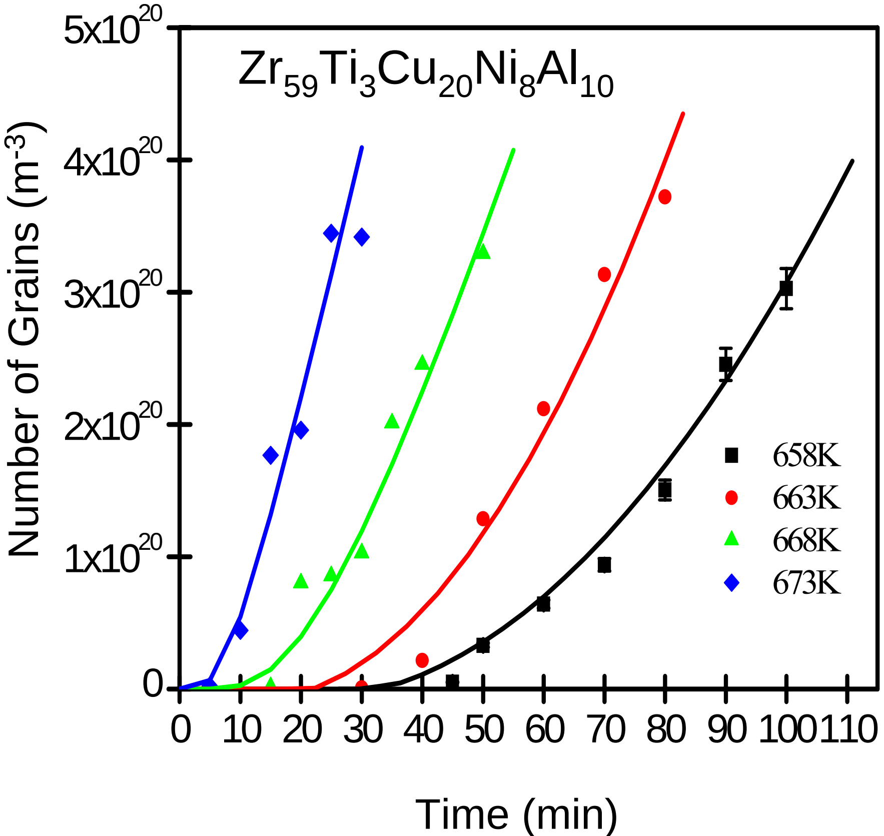
$$\boxed{\begin{gathered} I_{n*,t} = I^s\left[1 + 2\sum_{m=1}^{\infty}(-1)^m \exp\left(-\frac{m^2 t}{\tau_K}\right)\right] \\ \tau_K = -\frac{24 k_B T n*}{\pi^2 k_{n*}^+ \Delta\mu} = \frac{4}{\pi^3 k_{n*}^+ Z^2} \qquad \theta = \frac{\pi^2 \tau}{6} \end{gathered}}$$

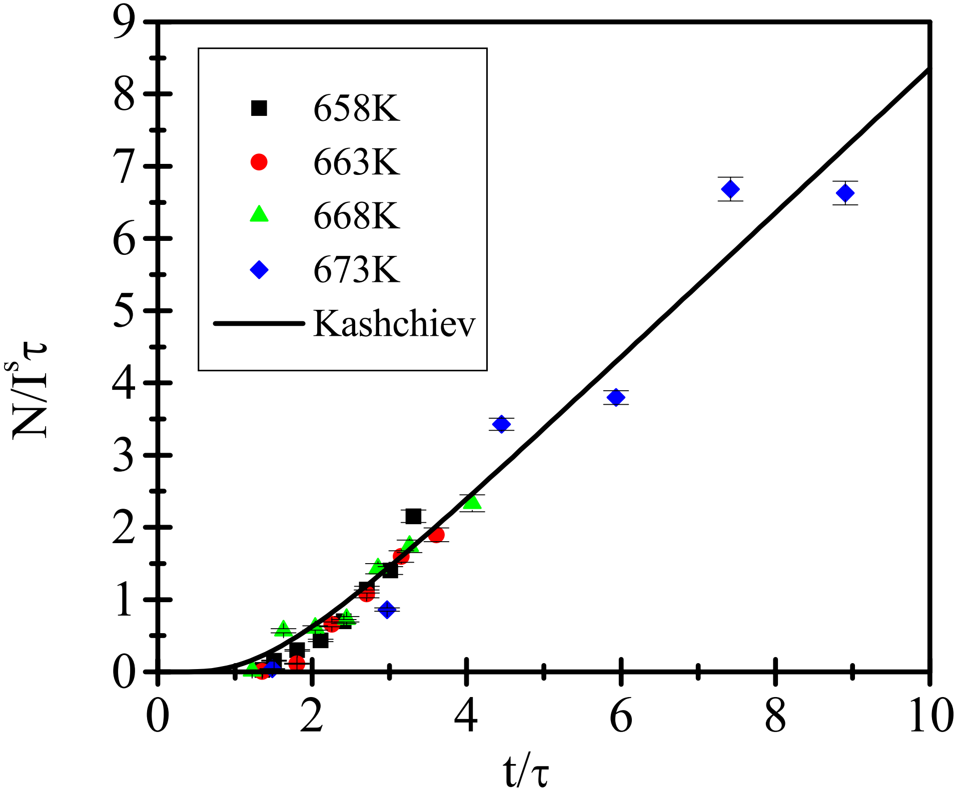


Scaling

D. Kashchiev, *Surface Science* **14**, 209–220 (1969)

Icosahedral Order in Metallic Glasses





Fit to time-dependent nucleation data using

- measured viscosity
- calculated driving free energy from enthalpy
- and measured specific heats

$\sigma = 0.006 \pm 0.002$ J/m^2

Additional evidence for significant short-range icosahedral order in glass

Y. Shen, T. H. Kim, A. Gangopadhyay, K. F. Kelton PRL, Feb. 2009

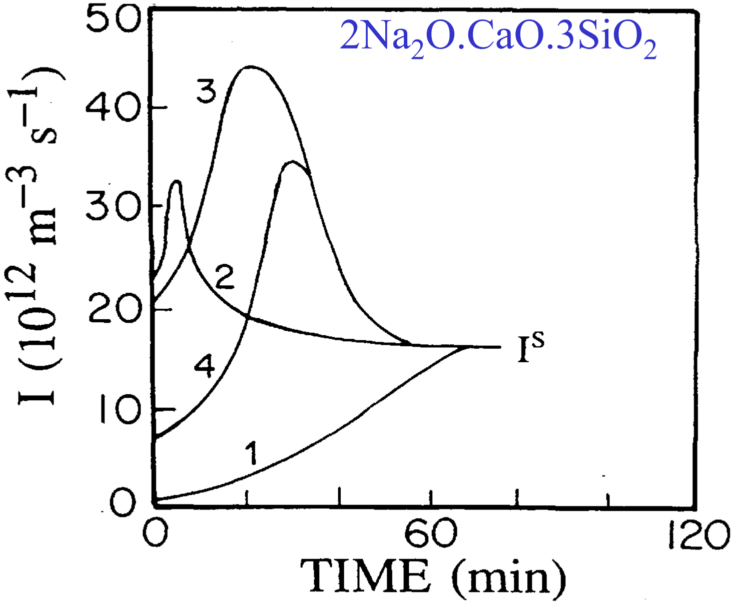
Examine kinetic model for nucleation

Multi-Step Annealing Experiment

A. M. Kalinina et al., JNCS, 38, (1980)

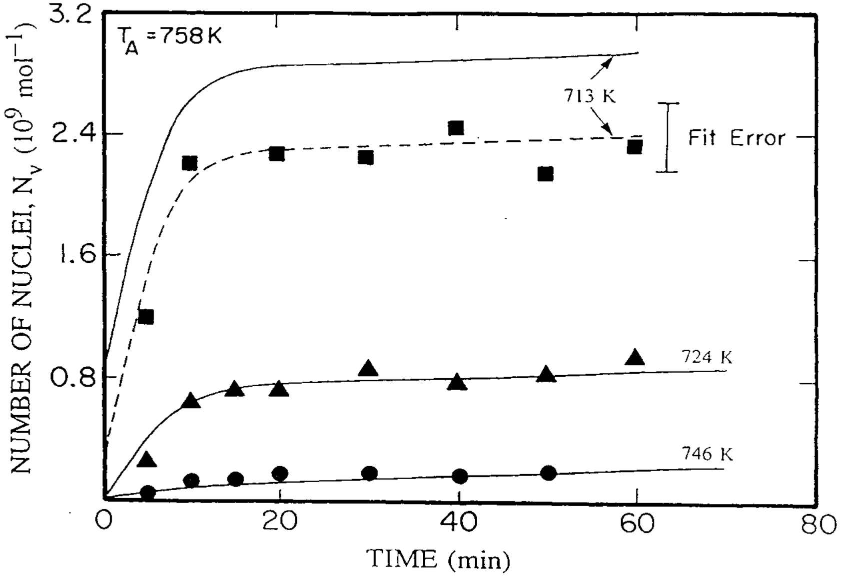
- Quench Glass
- Preanneal at (one):
  1. As-quenched
  2. 4h at 743K
  3. 3h at 733K
  4. 65h at 723K
- 753K anneal

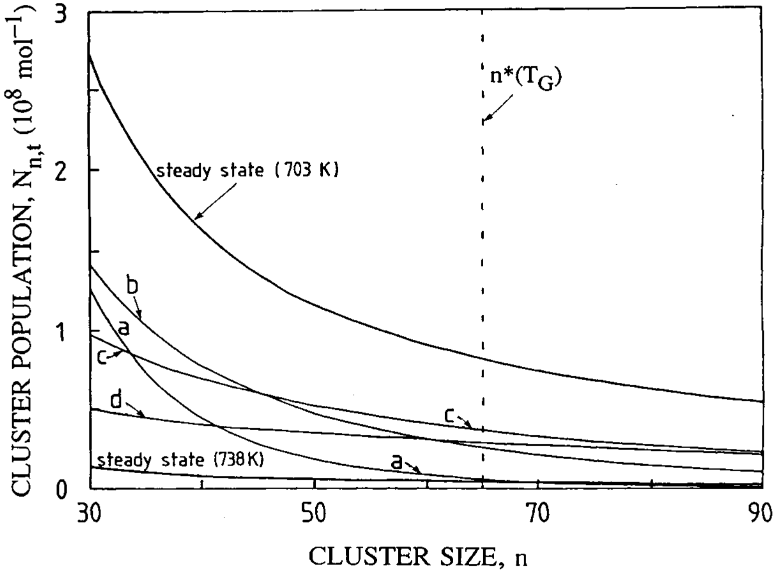
Growth at 899K



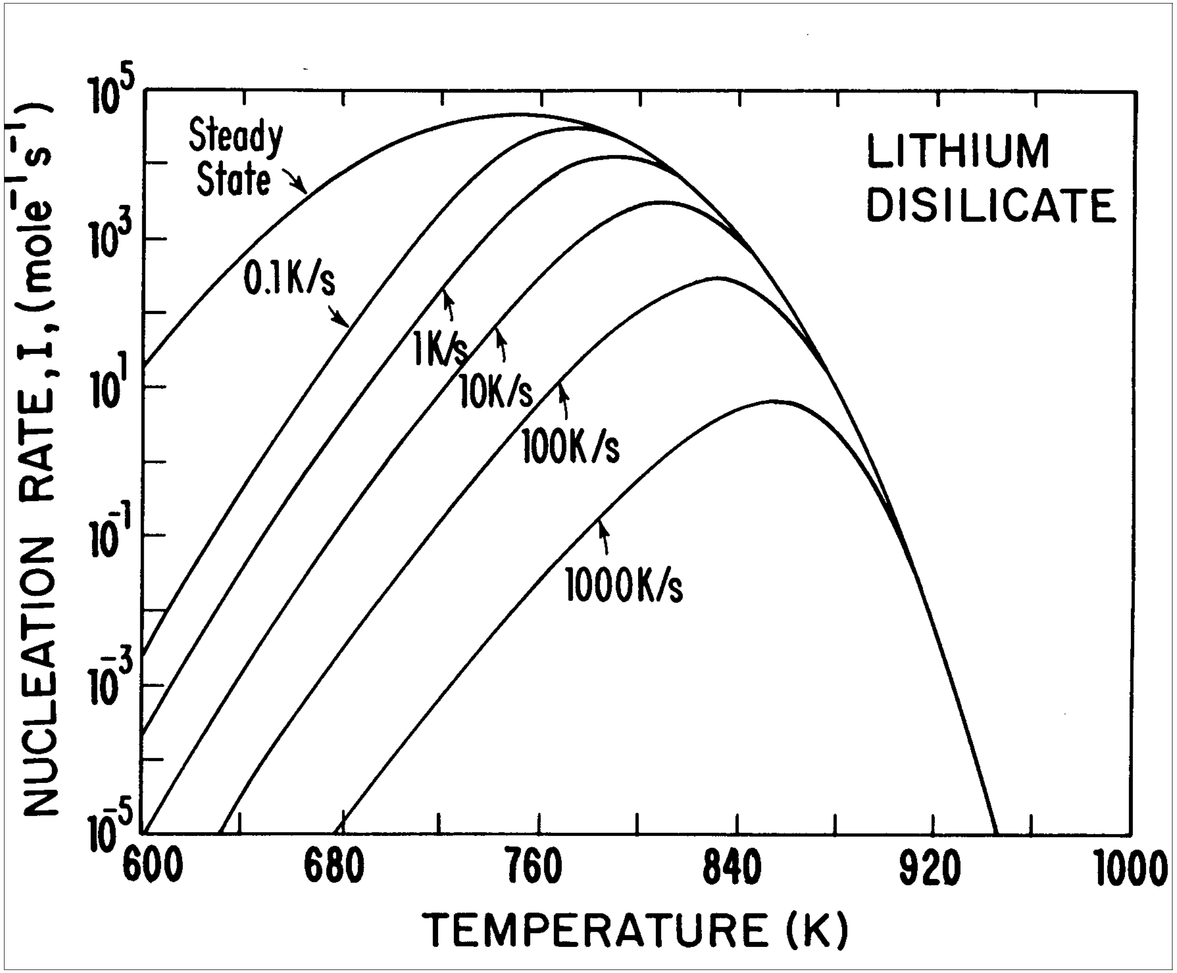
Calculated

K. F. Kelton and A. L. Greer, Phys. Rev. B., 38 (1988)





Nucleation Rate During a Rapid Quench



- Nucleation rate drops far below steady-state rate
- Temperature of departure from steady state rate increases with quench rate
- Important for glass formation in early metallic glasses (Fe-B)

Classical Theory Scoresheet

Successes

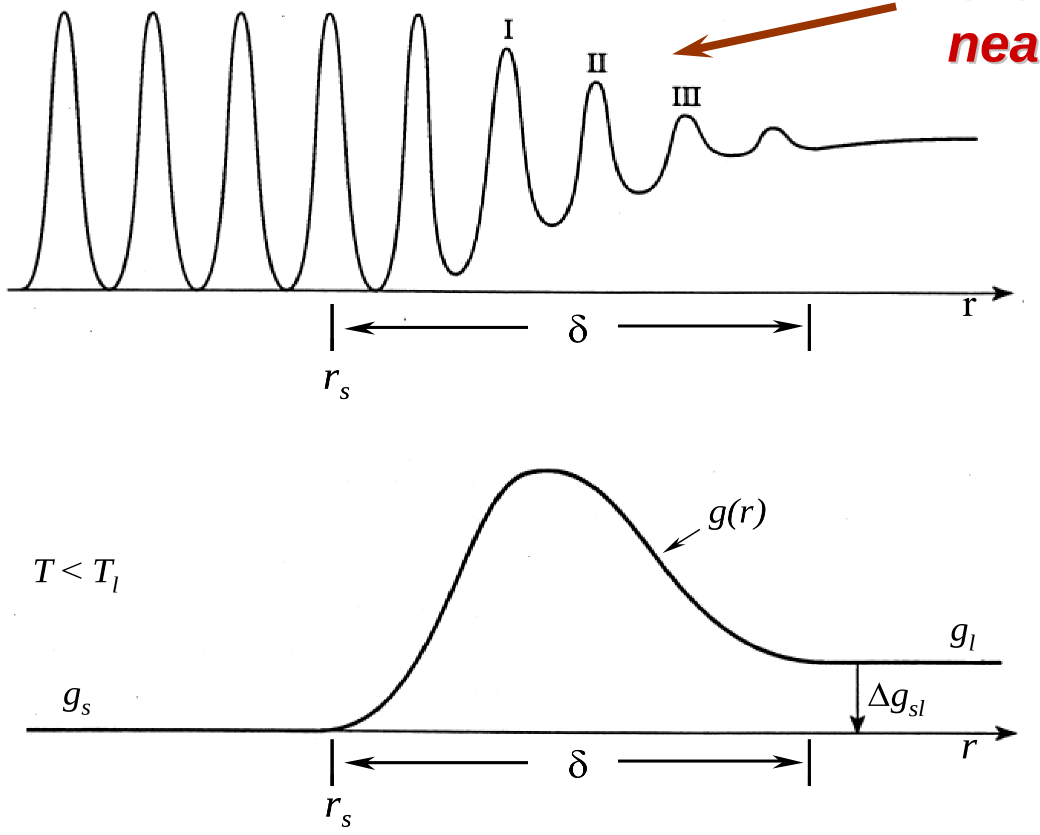
- Observed critical undercooling for liquids is predicted
- Effective interfacial energies, σ, evaluated from nucleation rates scale with the enthalpy of fusion as expected
- Predicted linear dependence between $\log(I\acute{\eta})$ and $(T\Delta G^2_v)^{-1}$ observed over a wide temperature range in liquids and glasses
- Explains both the time and temperature dependence of the nucleation rate in glasses and atom fraction dependence for colloidal liquids

Problems

- Nucleation prefactor, A* is generally orders of magnitude larger than is predicted theoretically
- Computer simulations show that the capillarity approximation, *i.e.* separating work of cluster formation into a bulk and an isotropic interfacial component, is meaningless when the cluster size is of the same order as the interfacial thickness
- Nucleation studies in colloidal suspensions and in computer simulations show that the interface is not sharp
- Use of bulk thermodynamic quantities for clusters containing tens of atoms is questionable!

Diffuse Interface

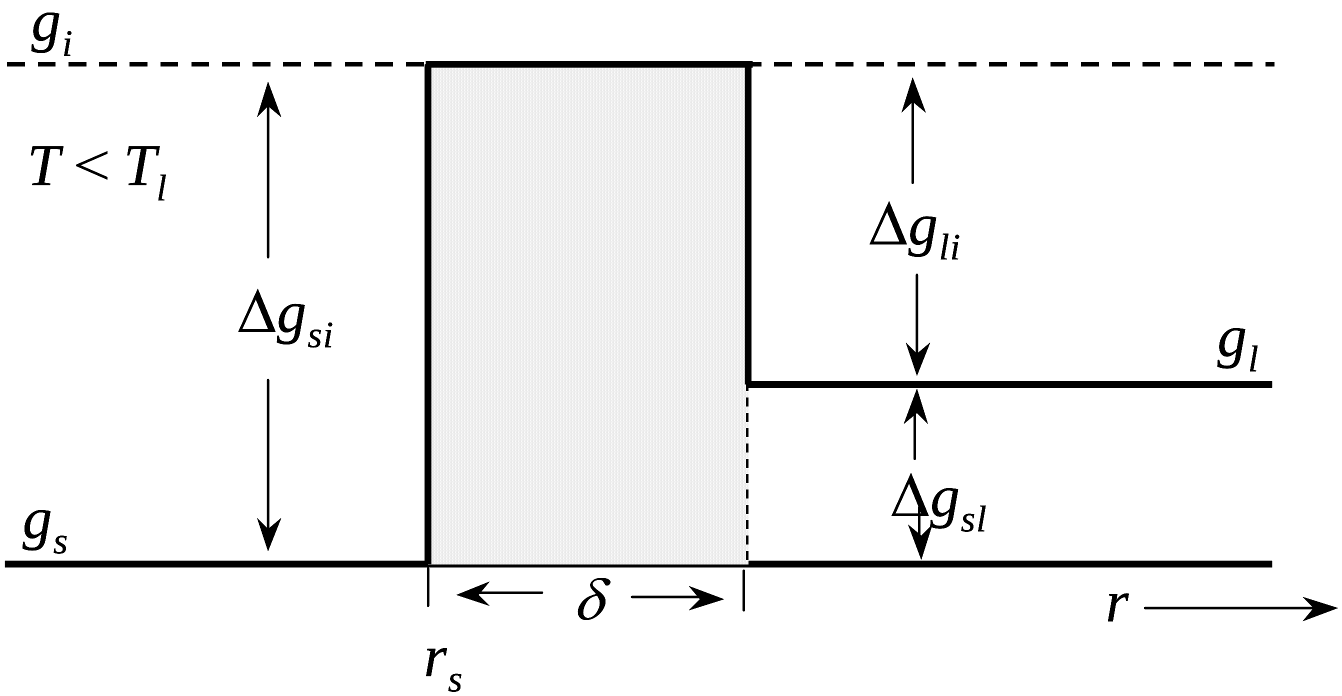
(Colloid Nucleation and Computer Simulation Studies)



Ordering of liquid near interface

$$W\left(r_{\mathrm{s}}\right)=4\pi\int_{0}^{\infty}\left(g\left(r\right)-g_{1}\right)r^{2}\,\mathrm{d}r \quad \textit{and} \quad \left.\frac{\mathrm{d}W\left(r_{\mathrm{s}}\right)}{\mathrm{d}r_{\mathrm{s}}}\right|_{r_{\mathrm{s}}=r_{\mathrm{s}}^{*}}=0$$

Diffuse Interface Model



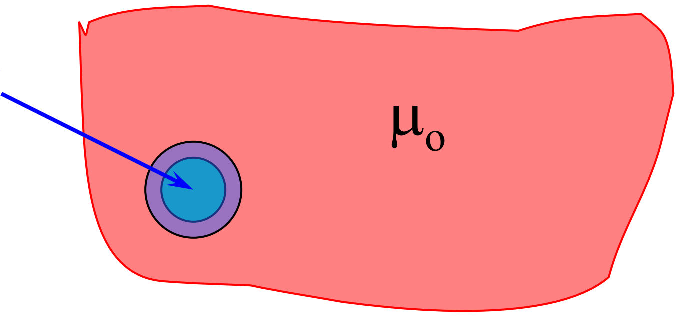
- F. Spaepen (*Solid State Physics*, , 1994)
- L. Gránásy (*J. Non-Cryst. Sol.* **162**, 301–303 (1993))

- Key Results:
  - Critical work and critical radii are functions of the interfacial width
  - Predicts that ordering near interface gives $d\sigma/dT > 0$ – opposite to that expected for a free energy ($\sigma = \Delta h - T\,\Delta s$), <u>but</u> in agreement with experimental nucleation data.

Density Functional Theory (DFT)

$$G[\rho(r)] = \int_V g\big(\rho(\mathbf{r})\big)\, d\mathbf{r}$$

Fluctuation to new phase



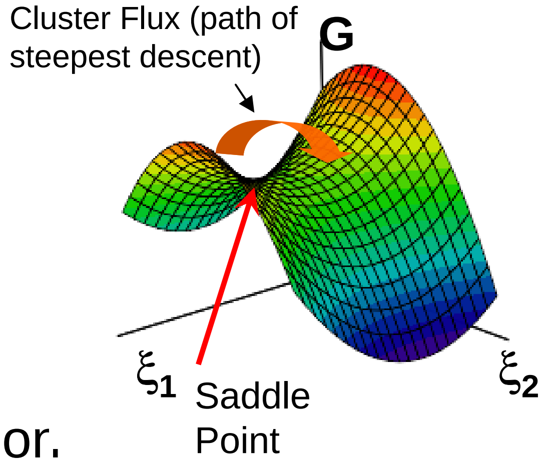
New work of cluster formation

$$W[\rho(\mathbf{r})] = \int_V \Big\{ \big(g(\rho(\mathbf{r})) - \mu_o \rho(\mathbf{r})\big) \Big\} d\mathbf{r}$$

- Does not rely on any assumed dividing surface
- Does not require introduction of interfacial energy
- Solve for saddle-point configuration
- Corresponds to critical size

$$\big(\delta W[\rho(\mathbf{r})]\big)_{\rho(\mathbf{r})=\rho^*(\mathbf{r})} = 0$$

- Analogous to d*G*/d*r* = 0 for *r*=*r**
- Solve for density profile ($\rho^*(\mathbf{r})$) using Euler's equatior.

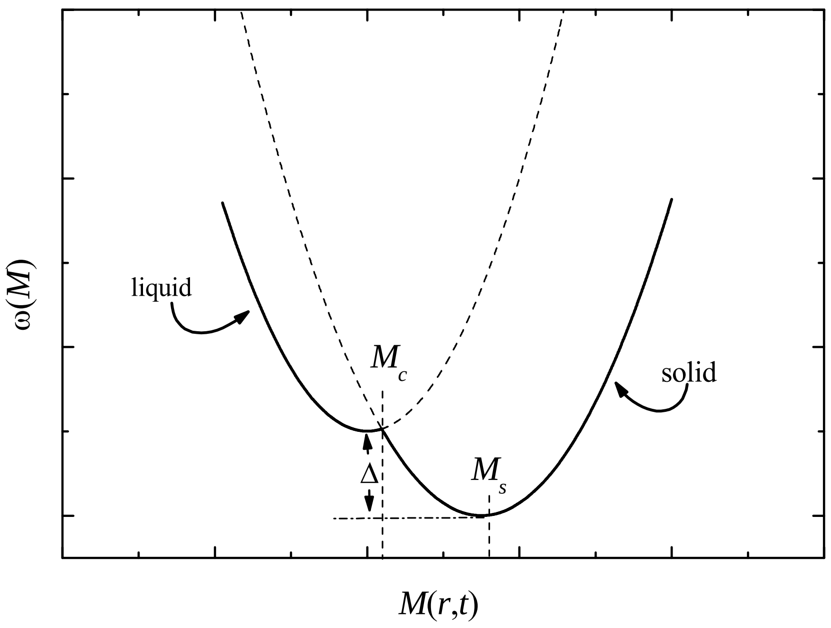


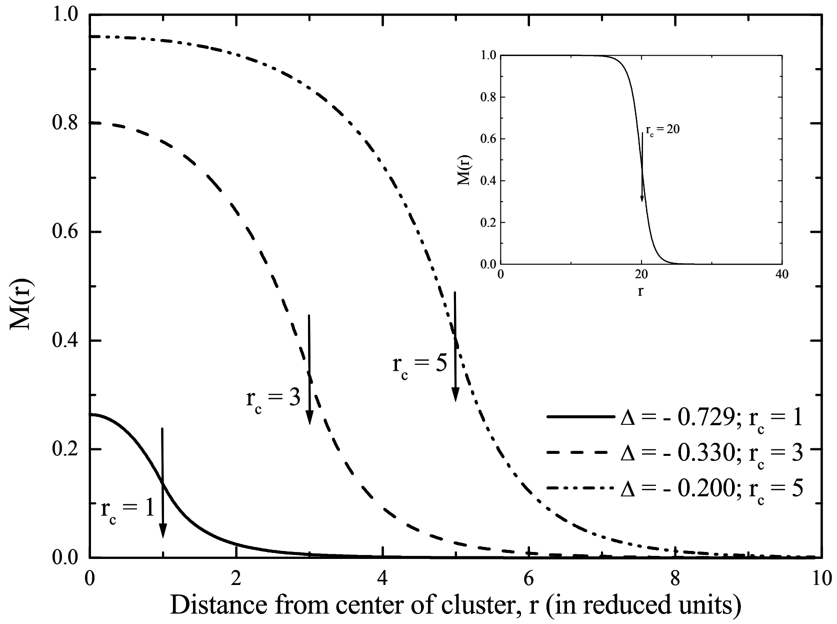
- Determine W* from $W^* = \int_V \Big\{ \big(g(\rho^*(\mathbf{r})) - \mu_o \rho^*(\mathbf{r})\big) \Big\} d\mathbf{r}$

- Most treatments assume square gradient approximation (Cahn-Hilliard)

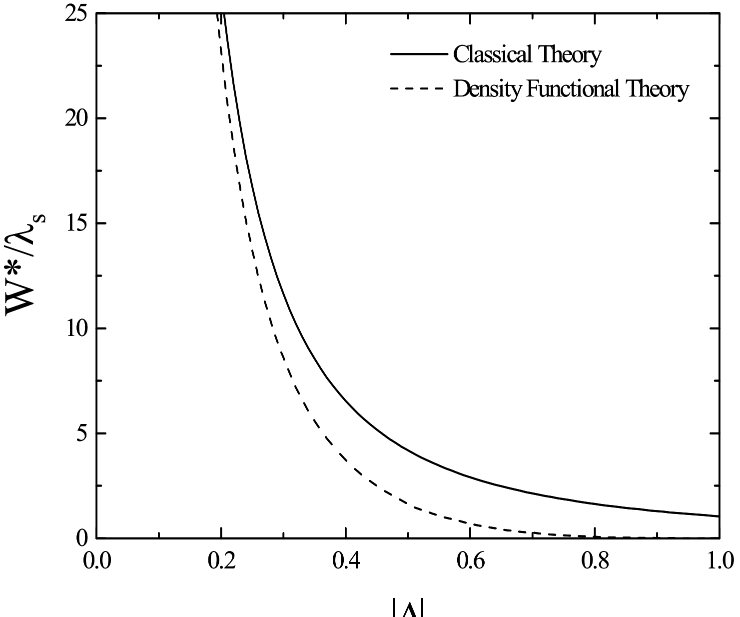
$$g\big(\rho(r)\big) = g_o(\overline{\rho}) + \kappa(\nabla\rho)^2 + \ldots$$

Simple Single Order Parameter DF Treatment





- Single order parameter - difference in liquid and solid
- Free energy functional in terms of order parameter
- Deep undercoolings, order parameter never reaches that of bulk solid
- Smaller work of cluster formation than predicted from Classical Theory



Bagdassarian & Oxtoby*J. Chem. Phys.* **100**, 2139–2148 (1994).

FITS OF LIQUID AND GLASS NUCLEATION DATA TO NON-CLASSICAL THEORIES

Fits of Data to Non-Classical Theories

$$I^{s} = \mathcal{A}^{*} \exp\left(-\chi(T)^{3} \frac{W^{*}_{CNT}}{kT} \right) \quad \Rightarrow \quad \ln\left(\frac{I^{s}}{A^{*}} \right) = -\chi(T)^{3} \frac{16\pi}{3kT} \frac{\sigma^{3}_{CNT}}{\delta\mu^{2}}$$

$$\text{where} \quad \chi(T) = W^{*}_{NC} / W^{*}_{CNT}$$

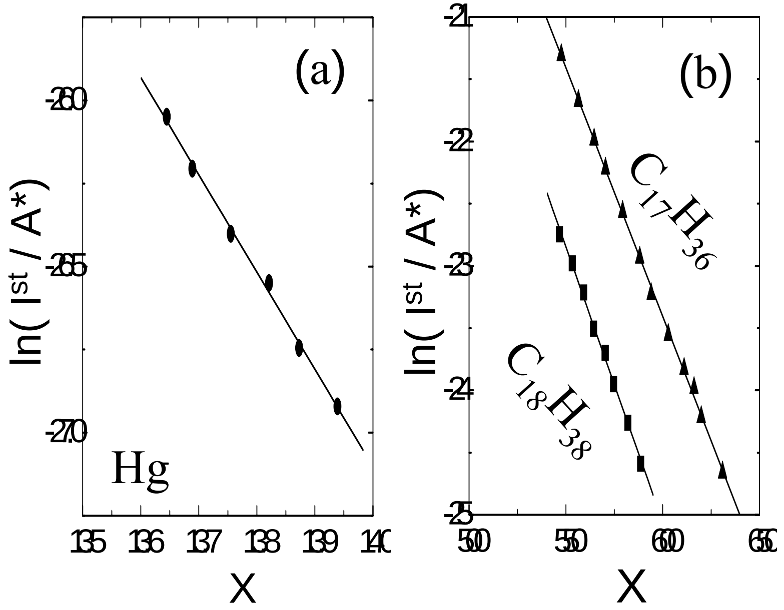
Fitting Procedure

- Assume expected value for $\mathcal{A}^*$
- Plot ln($I^s/\mathcal{A}^*$), where I^s are the measured values for the steady-state nucleation rate, as a function of $X=\chi^3(T)\delta\mu^{-2}T^{-1}$
- Expect
  - straight line with slope proportional to σ^3
  - intercept at origin
- Use measured intercept to differentiate between predictions of models

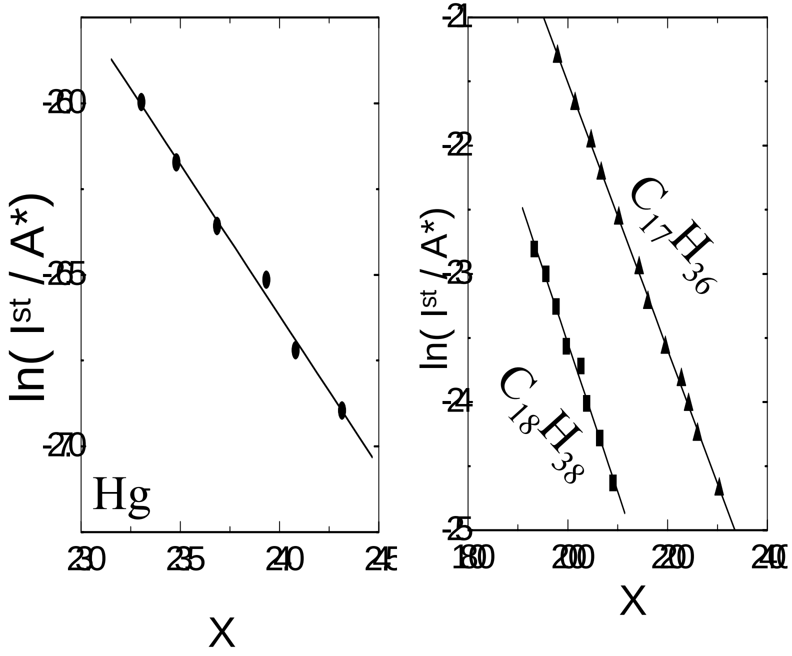
Model	Acronym
Self-consistent CNT	SCCT
Phenomenological diffuse interface theory	DIT
Perturbative DF	PDFA
Semi-empirical DF	SDFA
Modified-weighted DF	MWDA
Ginzburg-Landau free energy used in Cahn-Hilliard model	GLCH

Fits to Liquid Undercooling Data

Classical Theory



Phenomenological Diffuse Interface Theory

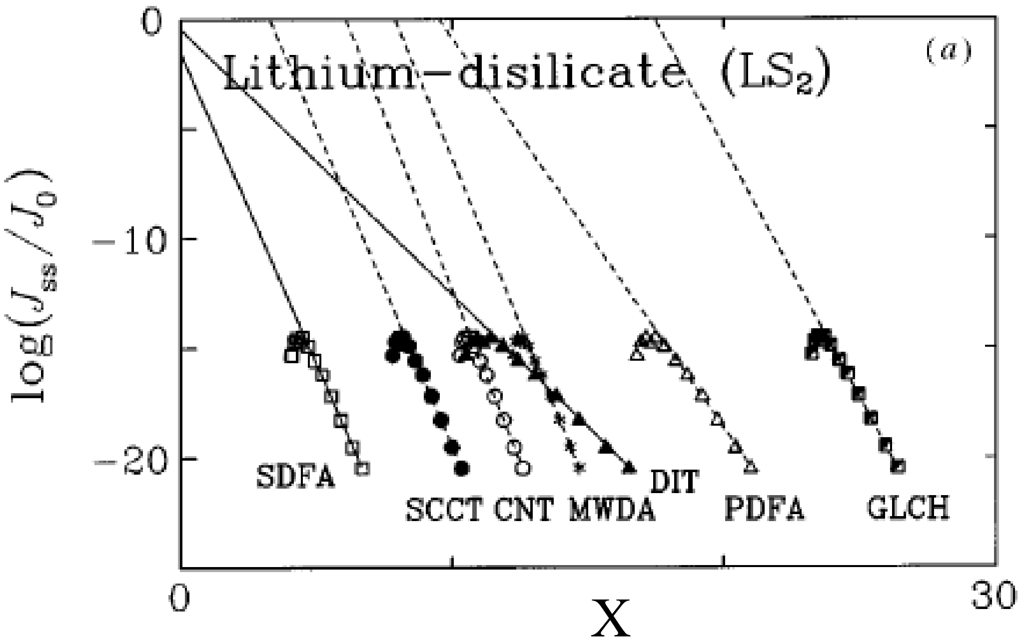


Intercept Values and Errors Obtained by Fitting Experimental Nucleation Data*

Glass	CNT	SCCT	DIF	SDFA	PDFA	MWDA
$C_{17}H_{36}$	0.6 ± 0.8	-1.5 ± 0.7	-0.7 ± 0.8	-0.5 ± 1.9	2.0 ± 0.8	0.5 ± 0.8
$C_{18}H_{38}$	1.5 ± 1.6	-1.3 ± 1.4	-0.2 ± 1.5	0.6 ± 1.5	2.9 ± 1.7	1.4 ± 1.6
Hg	14.3 ± 4.0	11.3 ± 3.7	5.7 ± 2.1	-8.9 ± 1.7	17.0 ± 4.2	20.1 ± 4.5

*From [Granasy, 1997 #1525]

Fits to Glass Crystallization Data



Intercept Values and Errors Obtained by Fitting Experimental Nucleation Data*

Glass	**CNT**	**SCCT**	**DIF**	**SDFA**	**PDFA**	**MWDA**	**GLCH**	**log x_c**
LS_2	19 ± 4	10 ± 4	-0.5 ± 2.0	-1.5 ± 1.9	15 ± 4	24 ± 5	40 ± 8	
BS_2	24 ± 5	28 ± 5	-0.7 ± 2.3	-4.9 ± 1.9	22 ± 5	30 ± 7	49 ± 10	-12.2
N_2CS_3	125 ± 66	92 ± 52	-0.5 ± 3.1	0.8 ± 2.6	71 ± 27	180 ± 92	-410 ± 328	
NC_2S_3	56 ± 18	40 ± 19	-2.9 ± 5.5	-9.2 ± 1.8	49 ± 15	72 ± 25	156 ± 94	-12.5
CS	178 ± 64	157 ± 59	-3.6 ± 4.8	-13 ± 2	165 ± 57	263 ± 123	1837	-17.2
NS	257	194 ± 165	-10 ± 3	-13 ± 2	92 ± 67	138 ± 104	-108 ± 65	
LB_2	581	472	-13± 3	-17 ± 2	-336	202	-96 ± 81	-16.6
CAS_2	-15± 4	-18± 3	-17± 2	-17± 2	15±4	-14±4	-13±6	

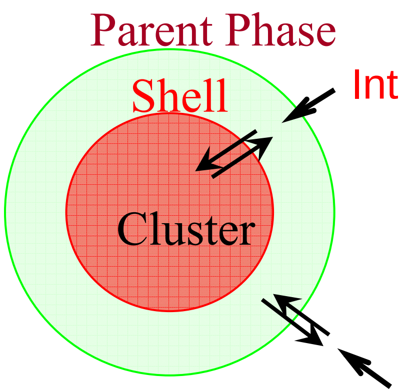
*From [Granasy, 1998 #1430]. Glasses: $Li_2O.2SiO_2$ (LS_2), $BaO.2SiO_2$ (BS_2), $2Na_2O.CaO.3SiO_2$ (N_2CS_3), $Na_2O.2CaO.3SiO_2$ (NC_2S_3), $CaO.SiO_2$ (CS), $Na_2O.SiO_2$ (NS), $Li_2O.2B_2O_3$ (LB_2) and $CaO.Al_2O_3.2SiO_2$ (CAS_2).

COUPLED INTERFACE AND DIFFUSIVE FLUXES

COUPLED-FLUX
(OR LINKED FLUX)
MODEL FOR NUCLEATION

Coupled-flux nucleation

K. F. Kelton, Acta Mater. 48, (2000)



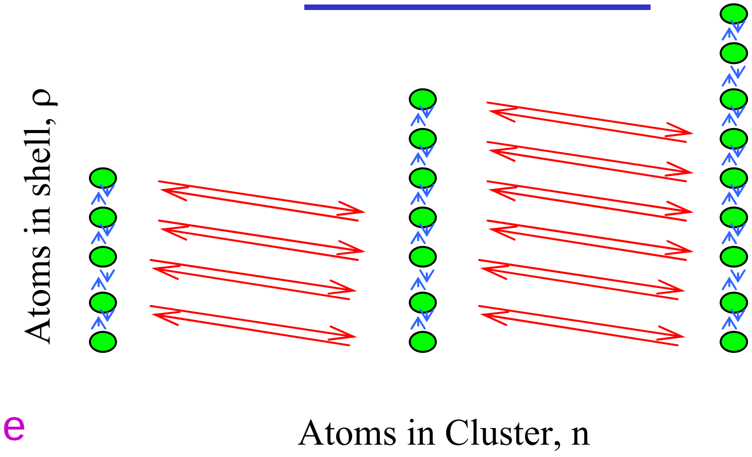
Interface Attachment Rates

$k^{+}(n,\rho)$ and $k^{-}(n,\rho)$

Shell-Parent Phase Exchange

$\alpha(n,\rho)$ and $\beta(n,\rho)$

Kinetic Model



Thermodynamic Model

$$N(n,\rho) = N_o \exp\left(-\frac{W_n}{kT}\right) P\{\rho\}$$

Gibbs Term

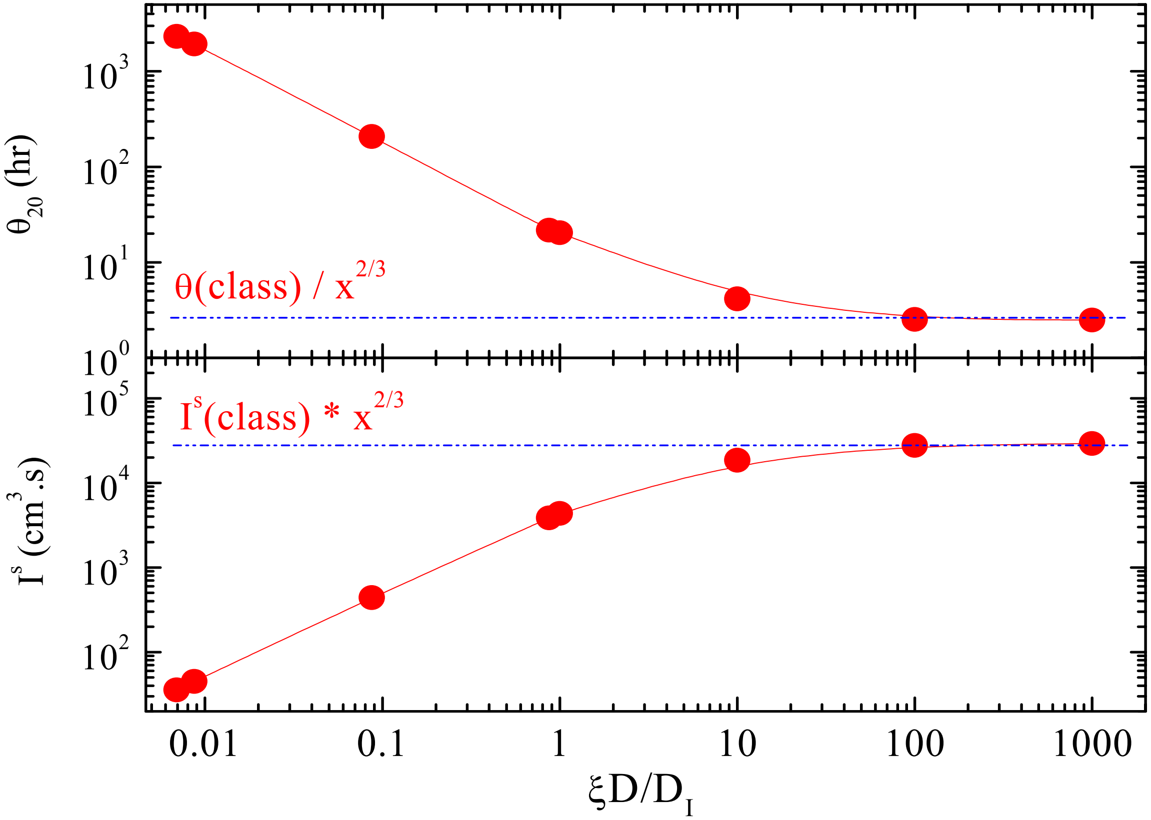
Configuration entropy from inclusion of shell

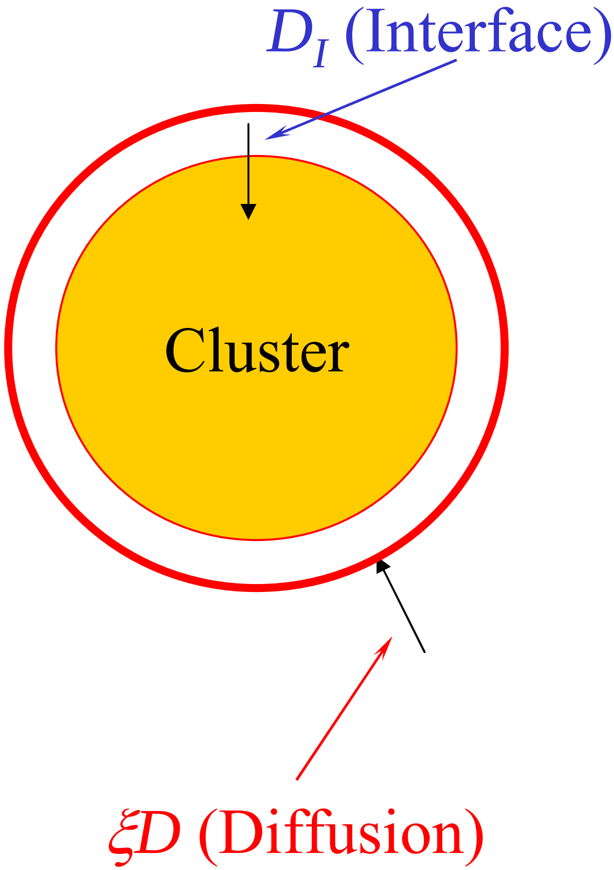
- **Key Prediction** – Enhanced solute concentration in parent phase near precipitate
- Supported by Kinetic Monte-Carlo Lattice Gas calculations

  J. Diao, R. Salazar, K. F. Kelton, L. D. Gelb
- Possible explanation of nanocrystal formation (glass devitrification)

  *K. F. Kelton, Phil. Mag. Lett., **77**, 337 (1998)*

Dependence on Relative Rates (Interface vs Diffusion)





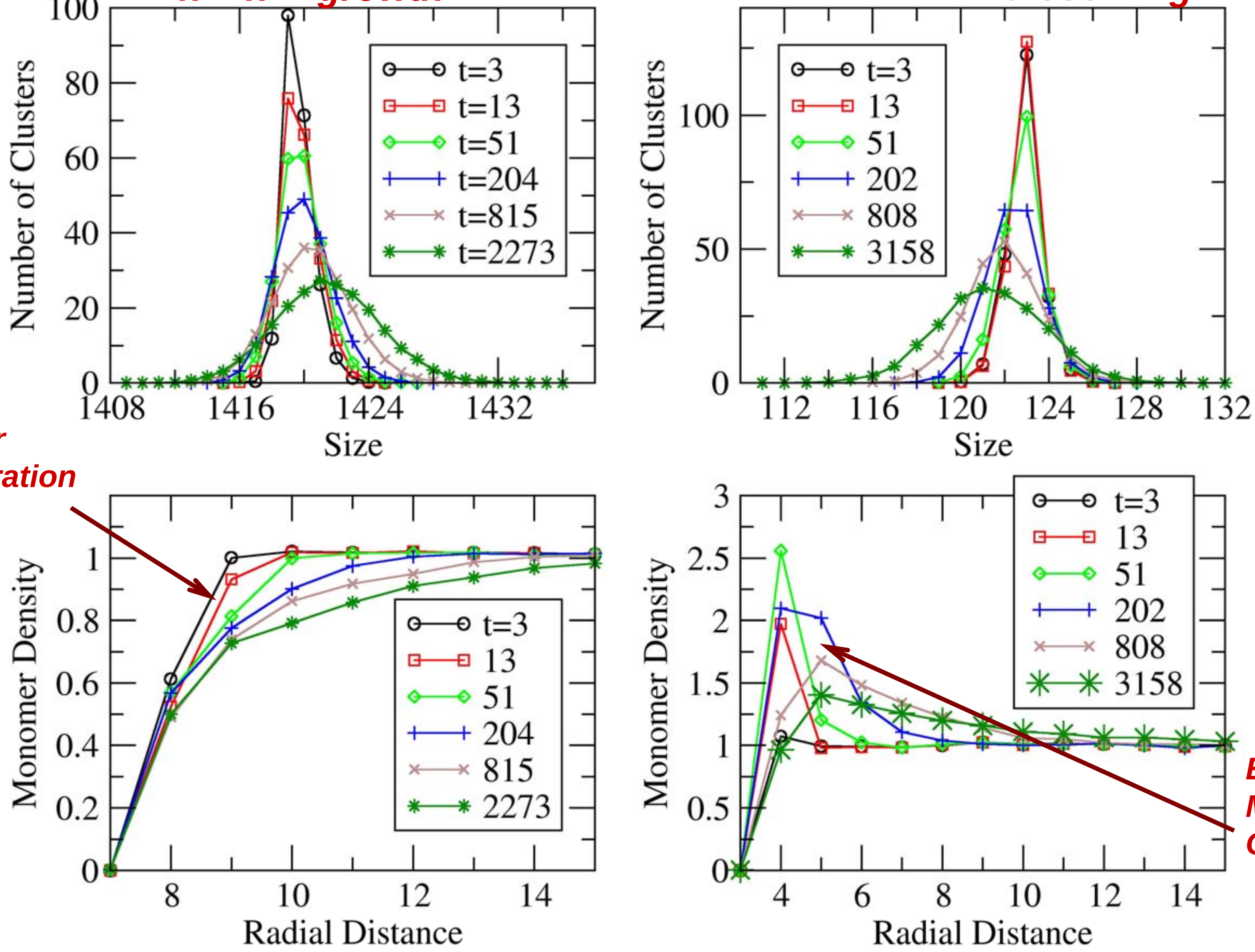
D_I (Interface)

Cluster

ξD (Diffusion)

- As diffusion becomes more important – nucleation rate drops and induction time increases sharply
- With increasing diffusion rate - approaches classical theory prediction since always correct atoms at the cluster interface

Kinetic Monte-Carlo Lattice Gas Calculations



n > n - growth*

n < n - dissolving*

Depleted Monomer Concentration

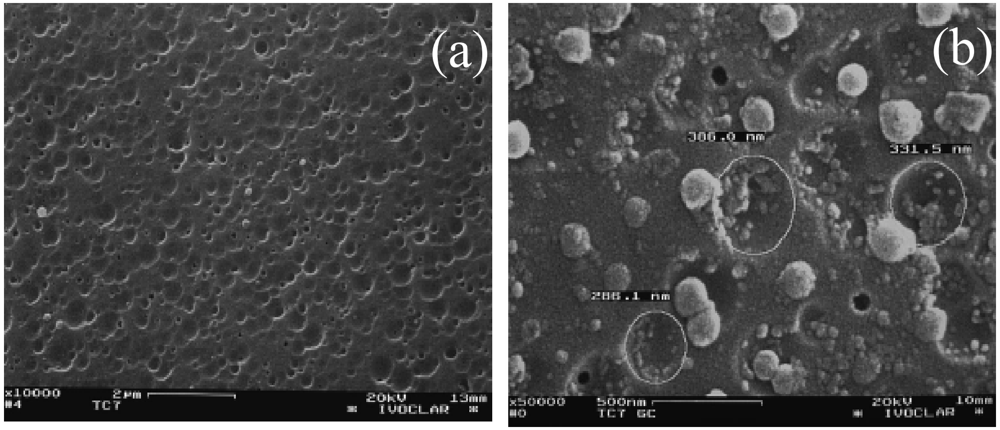
Enhanced Monomer Concentration

H. Diao, R. Salazar, K.F. Kelton & L.D. Gelb
Acta Mater. ***56****, 2585–2591 (2008).*

Supports Coupled-Flux Prediction

COUPLING OF PHASE TRANSITIONS – POSSIBLY OF DIFFERENT ORDER – TO THE NUCLEATION BARRIER

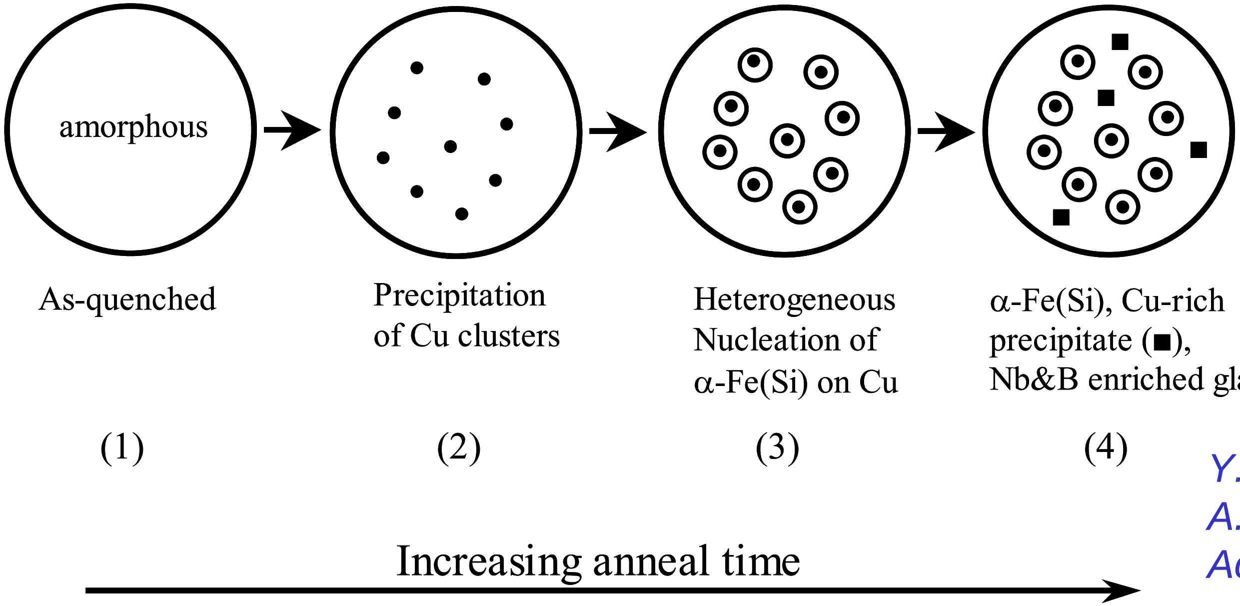
Phase Separation catalyzes nucleation



- Phase separation into $CaO.P_2O_5$ rich regions
- Catalyzes crystallization

SEM of phase separated $(SiO_2)_{61.5}(Al_2O_3)_{9.4}(Na_2O)_{9.2}(K_2O)_{7.7}$-$(CaO)_6(ZrO_2)_{0.5}(TiO_2)_{0.2}(P_2O_5)_{1.9}(CeO_2)_{0.3}(Li_2O)_{0.5}(B_2O_3)_{0.3}F_{2.5}$ glass

Nano-precipitation – catalyzes nucleation



As-quenched (1)

Precipitation of Cu clusters (2)

Heterogeneous Nucleation of α-Fe(Si) on Cu (3)

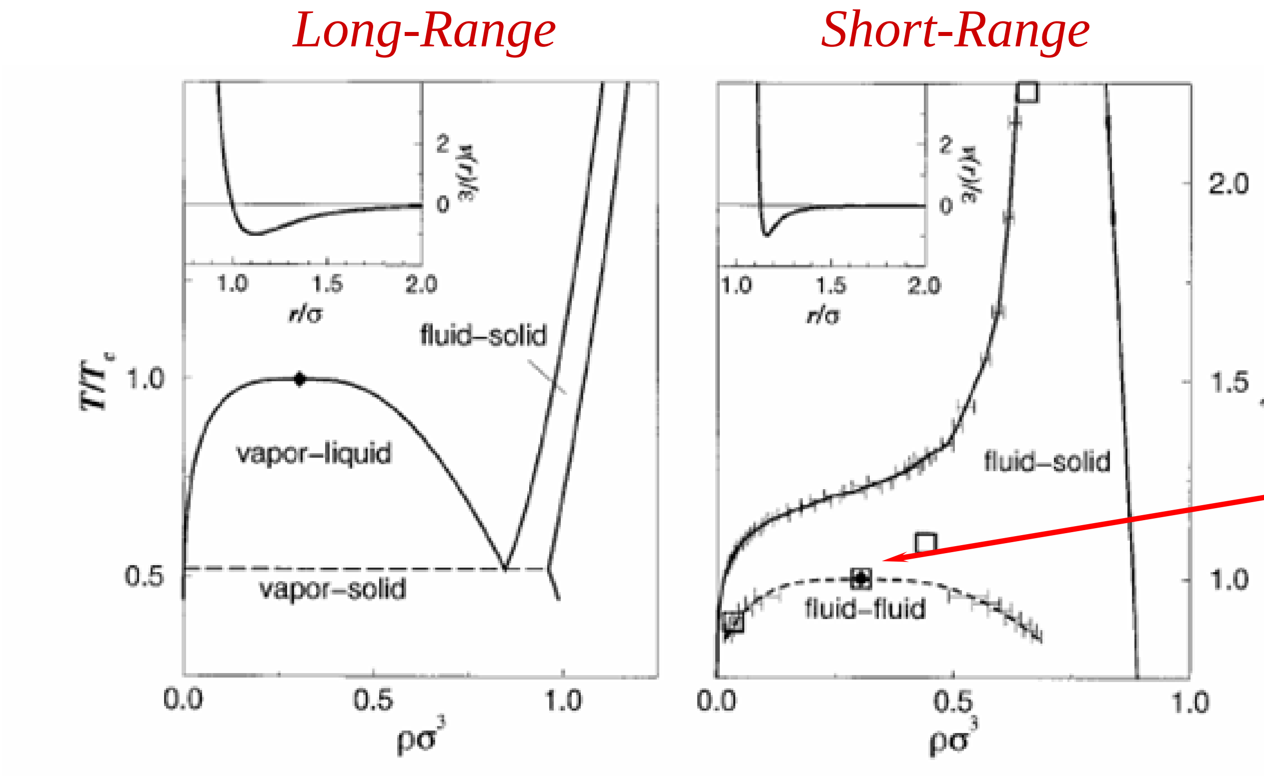
α-Fe(Si), Cu-rich precipitate (■), Nb&B enriched glass (4)

Increasing anneal time

FINEMET Metallic Glasses

*Y. Q. Wu, T. Bitoh, K. Hono, A. Makino, A. Inoue, Acta Mater. **49** (2001) 4069*

Molecular Dynamics Calculations for Colloidal Suspension

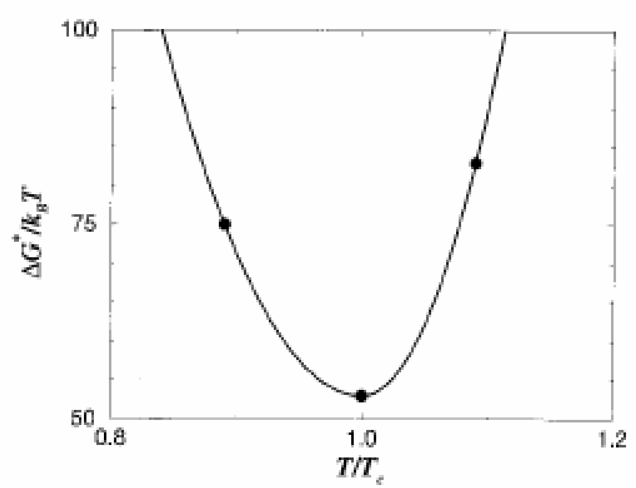

Long-Range

Short-Range

Pieter Rein ten Wolde & Daan Frenkel, Science, Vol. 277, 1975-78 (1997)

Metastable Critical Point

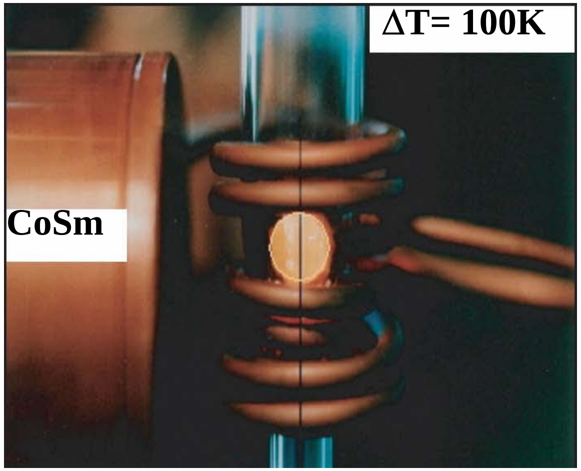
Enormous decrease in nucleation barrier !

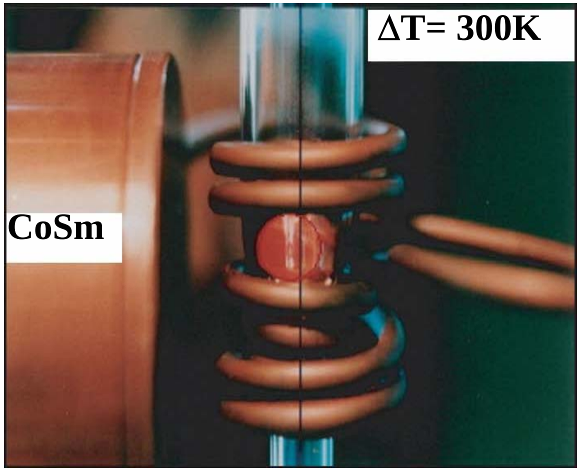


- dilute colloidal liquid (analogous to vapor phase)
- dense colloidal fluid (analogous to liquid)
- colloidal crystal phase

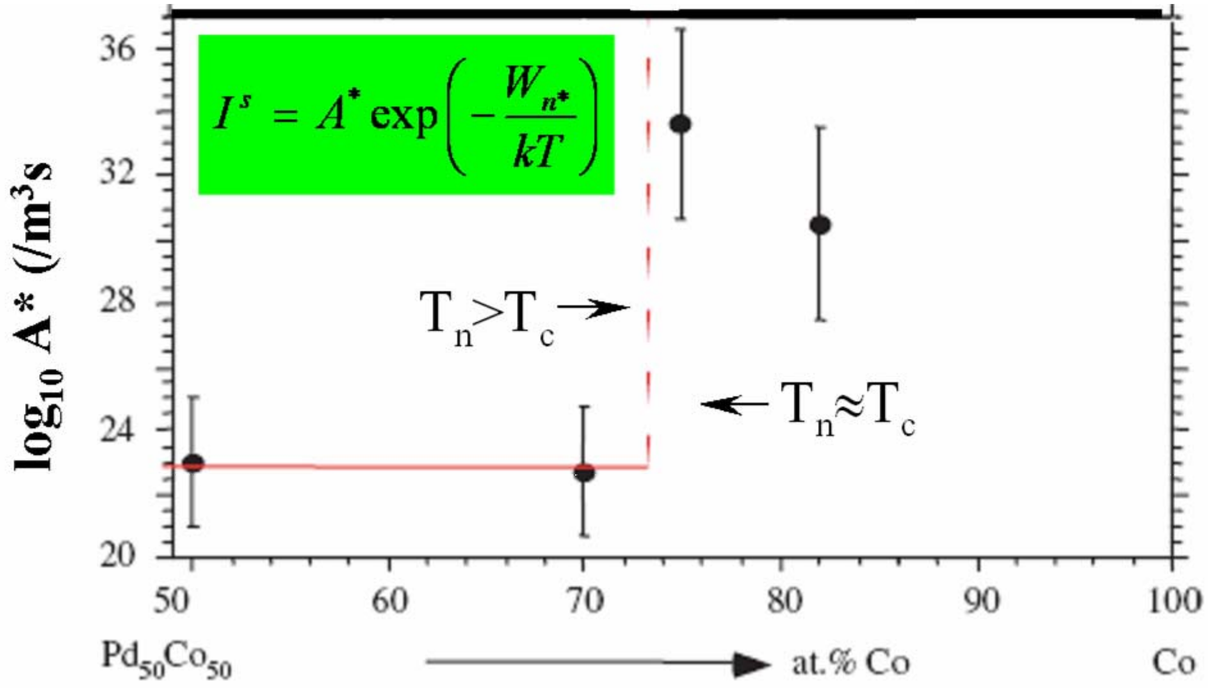
Coupling with Magnetic Ordering

D. Herlach *et al.* - Phil. Trans. Roy. Soc. **361**, 497 (2003)





Undercooling is limited by onset of magnetic ordering, just above T_c in undercooled Co-based liquids



Summary and Conclusions

- Nucleation is stochastic
- Classical Theory of Nucleation
  - Explains dependence of steady-state rate on driving free energy (supercooling in liquids)
  - Quantitatively explains time-dependent nucleation behavior
  - Interfacial free energy provides measure of nucleation barrier – indicates structural and chemical differences in initial and new phases
  - But, predicts incorrect pre-term (sometimes by orders of magnitude)
  - And, Capillarity assumption incorrect for small clusters
- Beyond the Classical Theory
  - Phenomenological diffuse interface theory
  - Density Functional Theories
- Importance of coupled processes in nucleation
  - Coupled interface/diffusive fluxes
  - Coupled phase transitions – density functional theories likely better theoretical approach
- **The role of nucleation in glass formation and stability can be very complex**

Nucleation in Condensed Matter

Applications in Materials and Biology

K. F. Kelton
A. L. Greer

In Nucleation in Condensed Matter, key theoretical models for nucleation are developed and experimental data are used to discuss their range of validity. A central aim of this book is to enable the reader, when faced with a phenomenon in which nucleation appears to play a role, to determine whether nucleation is indeed important and to develop a quantitative and predictive description of the nucleation behavior. The third section of the book examines nucleation processes in practical situations, ranging from solid-state precipitation to nucleation in biological systems and in food and drink. Nucleation in Condensed Matter is a key reference for an advanced materials course in phase transformations. It is also an essential reference for researchers in the field.

- Unified treatments of theories, experimental evaluations and application case studies
- Derivations of key models
- Detailed discussion of experimental measurements
- Examples of nucleation in diverse systems

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Applications in Materials and Biology

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