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"Classical Nucleation Theory: An Overview"

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CLASSICAL NUCLEATION THEORY
AN OVERVIEW

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1.) INTRODUCTION

- **Solidification is a First Order Phase Transition with a Discontinuity in the Density**
- **Melt can be undercooled below Melting Temperature T_M**
- **Crystalline Phase is formed via Nucleation Process**
- **Nuclei must overcome Nucleation Barrier due to Interface Tension**

1.1) Homogeneous Nucleation

Gibb's Free Enthalpy G_d of a droplet with Volume V and Surface A:

$$G_d = -\int_V dV\,\Delta G + \int_A df\,\sigma$$

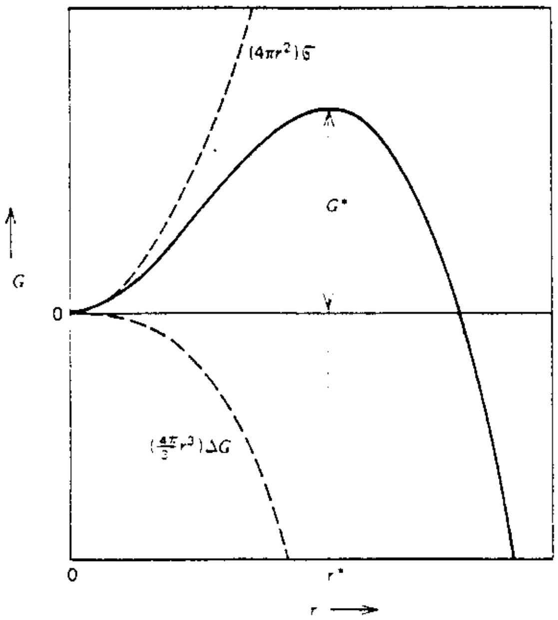
ΔG: Difference in Gibb's free molar enthalpies of liquid and solid phase
σ: Interface Tension between Solid and Liquid

Spherical Droplets, Radius r:

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

Homogeneous Nucleation (cont'd)

Nucleation Barrier, Critical Nucleus



On the average, droplets with

$r < r^*$ shrink
$r > r^*$ grow

Critical Nucleus:

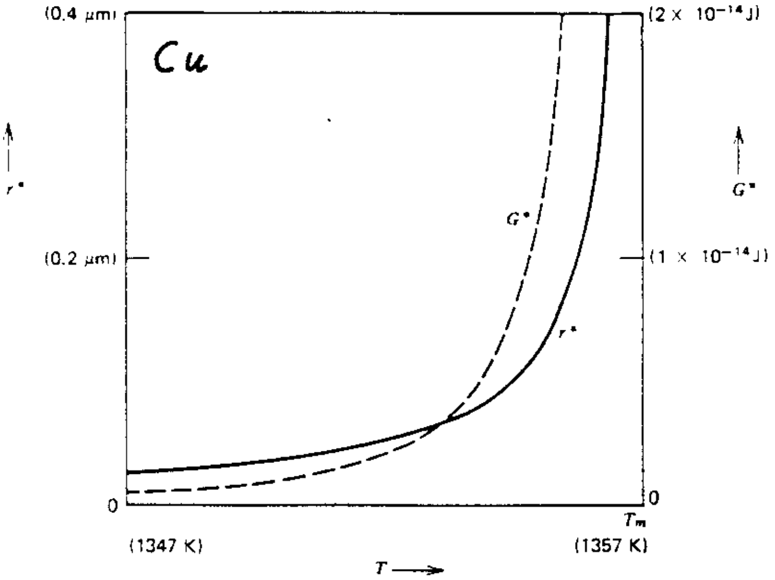
$$r = r^* = \frac{2\sigma}{\Delta G}$$

Activation Barrier:

$$G^* = G_d(r^*) = \frac{16\pi}{3}\frac{\sigma^3}{\Delta G^2}$$

Homogeneous Nucleation (cont'd)

Nucleation Barrier, Critical Nucleus: Temperature Dependence



Undercooling: $\Delta T \;=\; T_M \;-\; T$

$\sigma(\Delta T) \;\approx\; \sigma(0) \qquad \Delta G\,(\,\Delta T\,) \;\approx\; \Delta S(0)\,\Delta T$

Hence,

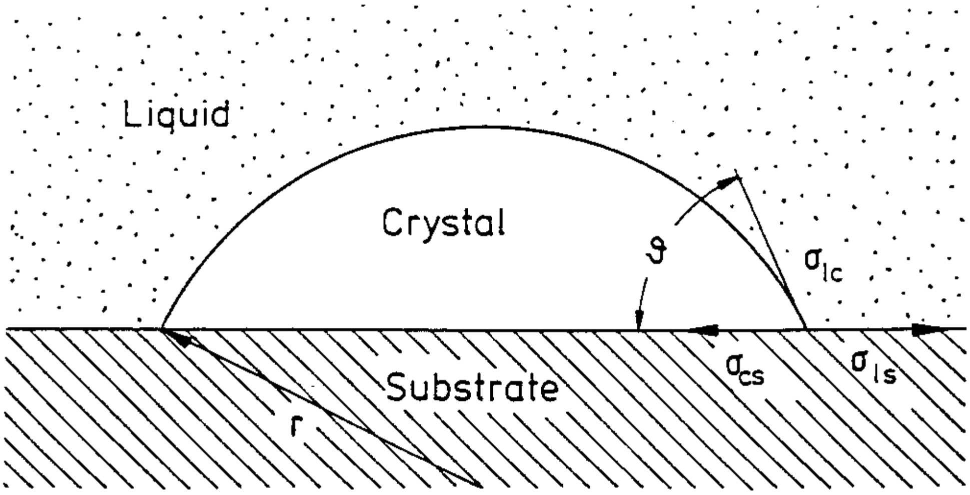
$$r^{*}(\Delta T) \;=\; \frac{2\sigma(0)}{\Delta S(0)}\,\frac{1}{\Delta T}$$

$$G^{*}(\Delta T) \;=\; \frac{16\pi}{3}\,\frac{(\sigma(0))^{3}}{(\Delta S(0))^{2}}\,\frac{1}{(\Delta T)^{2}}$$

1.2) Heterogeneous Nucleation

- Homogeneous Nucleation is intrinsic process and always present
- Heterogeneous Nucleation occurs if impurities exist in the melt or at its surface
- Heterogeneous Nucleation has lower nucleation barrier, if nucleus wets impurity

Spherical Cap Model



Force Balance: $\sigma_{ls} = \sigma_{cs} + \cos\vartheta\,\sigma_{lc}$

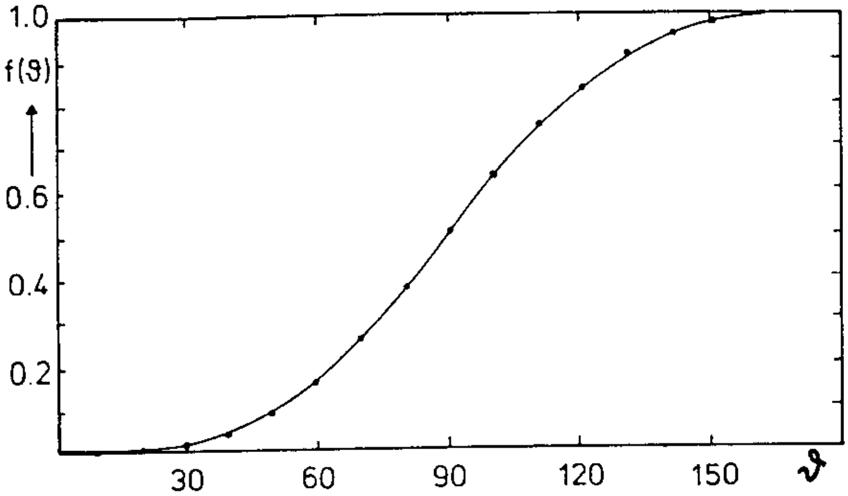
Gibb's Energy of Cap:

$$G_{\mathrm{Het}} = -\int_{\mathrm{cap}} dV\,\Delta G + \int_{\mathrm{cap}} df\,\sigma_{lc} + \int_{\mathrm{base}} df\,(\sigma_{cs} - \sigma_{ls})$$

Heterogeneous Nucleation (cont'd)

$$G_{\mathrm{Het}} = G_{\mathrm{Hom}}\, f(\vartheta)$$

$$f(\vartheta) = \frac{1}{4}\left(2 - 3\cos\vartheta + \cos^3\vartheta\right)$$



⇒ For complete wetting ($\vartheta = 0$), there is no nucleation barrier

⇒ For complete non-wetting ($\vartheta = \pi$), there is no barrier reduction: $G_{\mathrm{Het}} = G_{\mathrm{Hom}}$

⇒ Generally:

$$r^*_{\mathrm{Het}} = r^*_{\mathrm{Hom}} = \frac{2\sigma}{\Delta G}$$

$$G^*_{\mathrm{Het}} = G^*_{\mathrm{Hom}} f(\vartheta) \leq G^*_{\mathrm{Hom}}$$

2. NUCLEATION KINETICS

In Undercooling and Solidification Experiments, two quantities are of central importance:

- The Cluster Distribution $N(n)$
- The Nucleation Rate I

The latter determines the Kinetics of Nucleation.

2.1) The Volmer - Weber - Theory

Equilibrium Cluster Distribution:

$$N(n) \sim N_1 \exp\left(-\frac{E(n)}{kT}\right)$$

$$E(n) = -\Delta G\, V_a\, n + \sigma\,(4\pi)^{1/3}(3V_a)^{2/3} n^{2/3}$$

$$\Rightarrow \lim_{n\to\infty} N(n) = \infty \quad \text{for} \quad \Delta G > 0$$

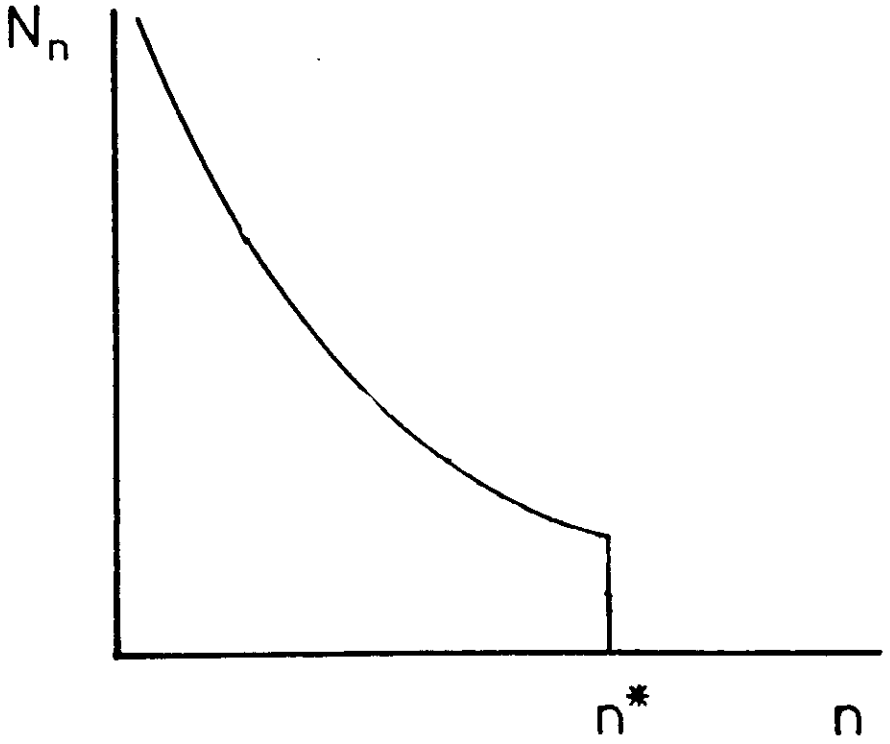
⇒ In equilibrium, only the infinite cluster, i.e. the solidified crystal exists.

⇒ Consider only clusters with $n \le n^*$

$$N(n) = \begin{cases} N_1 \exp\left(-\dfrac{E(n)}{kT}\right) & n \le n^* \\ 0 & n > n^* \end{cases}$$

Volmer-Weber-Theory (cont'd)

Cluster Distribution Function



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Volmer-Weber-Theory (cont'd)

The Nucleation Rate

Addition of one atom to a critical nucleus gives rise to nucleation

$$\Rightarrow I = 4\pi(r^*)^2 \, D(T) \, N(n^*)$$

$D(T)$ = atomic diffusion constant

The diffusion constant may be replaced by the viscosity η, using the Einstein relation:

$$D(T) = \frac{kT}{6\pi (V_a)^{1/3}} \frac{1}{\eta(T)}$$

Heterogeneous Nucleation:

$$N(n^*) = N_{\text{Het}} \exp\left(- \frac{E(n^*) \, f(\vartheta)}{kT}\right)$$

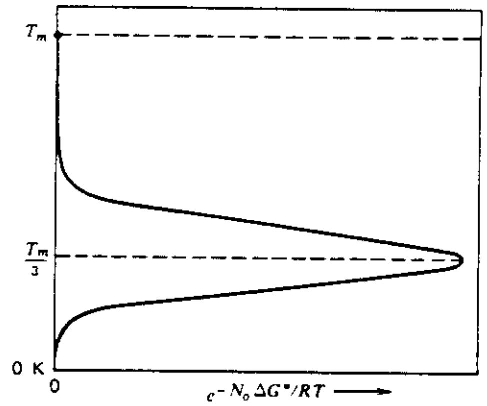
Volmer-Weber-Theory (cont'd)

Temperature Dependence

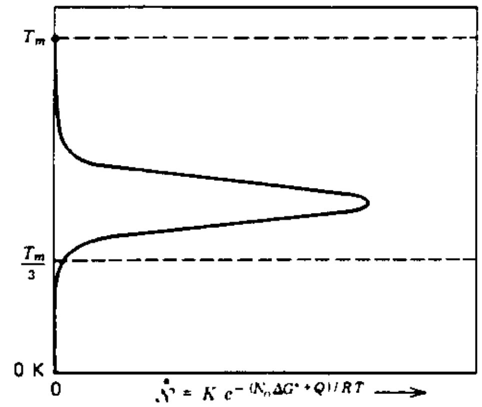
$$N(n^*) \;=\; N_1 \exp\left\{ -\frac{16\pi}{3}\,\frac{\sigma^3}{\Delta S^2}\,\frac{1}{kT\,(T_M - T)^2} \right\}$$

⇒ Number of critical nuclei vanishes for $T = 0$, $T = T_M$

⇒ Number of critical nuclei has a maximum for $T = T_M/3$



With $D(T) = D_0\, e^{-A/kT}$, the maximum is shifted to higher temperatures:



2.2) Nucleation as Chemical Reaction

Consider cluster of n atoms as chemical species A_n

$$\mathbf{A}_1 + \mathbf{A}_{n-1} \underset{k_n^-}{\overset{k_{n-1}^+}{\leftrightarrow}} \mathbf{A}_n$$

Rate Constants

$$\frac{k_{n-1}^+}{k_n^-} = \exp\left\{ -\frac{E(n) - E(n-1)}{kT} \right\}$$

Reaction Fluxes

$$J_n = k_{n-1}^+ c_{n-1} - k_n^- c_n$$

Rate Equations

$$\frac{dc_n}{dt} = J_n - J_{n+1}$$

The Nucleation Kinetics are known, once these equations, subject to appropriate boundary conditions, are solved.

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Nucleation as Chemical Reaction (cont'd)

The Equilibrium Solution

Equilibrium : $\frac{dc_n}{dt} = 0$ and $J_n = 0$

$$\Rightarrow \quad N(n) = \frac{k_{n-1}^{+}}{k_n^{-}} N(n-1)$$

$$\Rightarrow \quad N(n^*) = \prod_{i=1}^{n^*-1} \frac{k_{i-1}^{+}}{k_i^{-}} N_1$$

$$= \exp\left\{ -\frac{E(n^*)}{kT} \right\} N_1$$

Truncating the reaction chain at $n = n^*$
$\Leftrightarrow \quad k_{n^*}^{-} = 0 \quad \forall \; n > n^* + 1$
one obtains:

$$I = k_{n^*}^{+} N_1 \exp\left\{ -\frac{E(n^*)}{kT} \right\}$$

i.e. the Volmer-Weber result.

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Nucleation as Chemical Reaction (cont'd)

The Steady State Solution

In the steady state,

$$\frac{dc_n}{dt} = 0 \quad \text{however} \quad J_n = J_{n+1} = J_0 \neq 0$$

J_0 is the net flux through all reactions and therefore:

$$J_0 = I$$

The steady state concentrations $\tilde{c}_n$ can be obtained by using the equlibrium solutions $N(n)$ to eliminate k^-

$$\frac{J_0}{k^+_{n-1}\, N(n-1)} = \left(\frac{\tilde{c}_{n-1}}{N(n-1)} - \frac{\tilde{c}_n}{N(n)} \right)$$

Boundary Conditions:

$$\tilde{c}_1 = N_1 \quad \text{and} \quad \tilde{c}_M = 0 \quad M \gg n^*$$

Summing from 1 to M:

$$\frac{J_0}{\sum\limits_{i=1}^{M} \frac{1}{k_i^+\, N(i)}} = 1$$

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Nucleation as Chemical Reaction (cont'd)

The Steady State Solution (cont'd)

The sum can be evaluated making following approximations:

1. Expand N(i) around its minimum at $i = n^*$ to second order
2. Replace k_i^+ by $k_{n^*}^+$
3. Replace sum by integral
4. Extend limits of integration to $\pm\ \infty$

$\Rightarrow$

$$J_0 = I = Z\ k_{n^*}^+\ N_1\ \exp\left\{ -\frac{E(n^*)}{kT} \right\}$$

Z is the so-called Zeldovich-Factor:

$$Z = \int_{-\infty}^{+\infty} dx\ \exp\left\{ -\frac{E''(n^*)\, x^2}{kT} \right\} = \sqrt{\frac{\Delta G V_a}{6\pi kT\, n^*}}$$

Above result has been first obtained by Becker and Döring, and later by Zeldovich and Frenkel.

Nucleation as Chemical Reaction (cont'd)

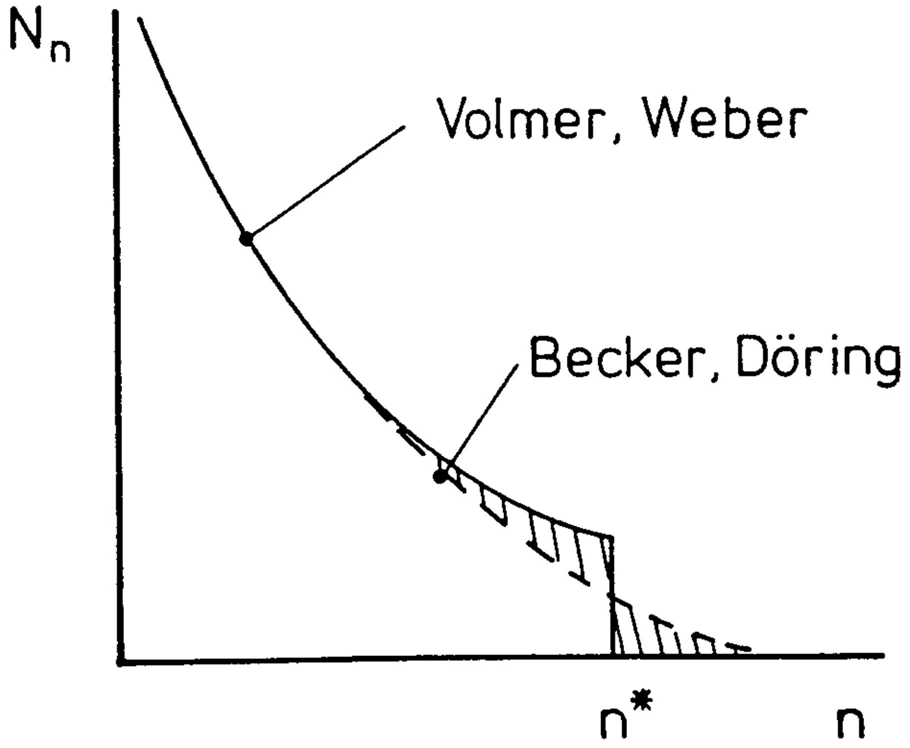
The Steady State Solution (cont'd)

As compared with the Volmer-Weber Theory, the nucleation rate is reduced by the Zeldovich factor.

Reason:

Postcritical nuclei with $n > n^*$ are allowed to decay

Once J_0 is known, the cluster distribution $\tilde{c}_n$ can be calculated.



3.) CONCLUSION

3.1) Summary

- Classical Nucleation Theory can be extended to include
  - binary alloys
  - non steady state solutions (time lag)
  - non spherical nuclei (anisotropy)

- Classical Nucleation Theory is
  - a mean value theory (no fluctuations)
  - a macroscopic theory (use of σ)
  - an isothermal theory ($T = \text{const}$)

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3.2) BIBLIOGRAPHY

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