\[ J_0 = Z_1 \sum_{n=1}^{N-1} \left( \frac{1}{\omega_n} \frac{\omega_2^- \omega_3^- \ldots \omega_n^-}{\omega_1^+ \omega_2^+ \ldots \omega_{n-1}^+} \right) \approx \frac{1}{\omega^*} \frac{1}{\Gamma} \exp \left( \frac{\Delta G^*}{kT} \right) \]

\[ \Delta G^* = -n^* \Delta \mu + \Phi^* \]

\[ J_0 = \omega^* \Gamma N_0 \exp \left( -\frac{\Phi^*}{kT} \right) \exp \left( n^* \frac{\Delta \mu}{kT} \right) \]
Classical extreme
ELECTROCHEMICAL NUCLEATION OF Hg ON Pt

Ivan Markov, Bulgarian Academy of Sciences
NUCLEATION RATE AS A FUNCTION OF $R$ AND $T$

$\omega_n^+ = ? \quad \omega_n^- = ?$

On (111) surface of fcc crystal:

In the capillary approach

$$\omega_n^+ = P_n D_s \text{grad} n_s \simeq P_n D_s \frac{n_s}{a} = D_s n_s \frac{P_n}{a}$$

$P_n$ - cluster perimeter

$\frac{P_n}{a}$ - number of lateral unsaturated bonds

In the atomistic approach

$$\omega_n^+ = \alpha_n D_s n_s$$

$\alpha_n$ is the number of ways an adatom joins the critical nucleus to produce a stable cluster

$n^* = 2, \alpha_2 = 6$
\[ \omega_n^- = \beta_n \nu \exp \left( \frac{E_n - E_{n-1} + E_{sd}}{kT} \right) \]

- \( E_n \) - energy to disintegrate a cluster of \( n \) atoms into single atoms
- \( E_n - E_{n-1} \) - energy of detachment of an atom from a cluster of size \( n \)
- \( \beta \) - number of ways of detachment of an atom from a cluster of size \( n \)

\( \beta_3 = 6 \)

\[ \alpha_n = \beta_{n+1} \]

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\[ J_0 = \omega_1^+ n_s \left[ 1 + \frac{\omega_2^-}{\omega_2^+} + \frac{\omega_2^+ \omega_3^-}{\omega_2^+ \omega_3^+} + \frac{\omega_2^+ \omega_3^- \omega_4^-}{\omega_2^+ \omega_3^+ \omega_4^+} \cdots \right]^{-1} \]

1. \( n^* = 1, \quad 1 \gg \frac{\omega_2^-}{\omega_2^+} \gg \frac{\omega_2^+ \omega_3^-}{\omega_2^+ \omega_3^+} \gg \frac{\omega_2^+ \omega_3^- \omega_4^-}{\omega_2^+ \omega_3^+ \omega_4^+} \)

\[ J_0 = \omega_1^+ n_s = \alpha_1 D_s n_s^2 \]

\[ D_s = a^2 \nu \exp \left( -\frac{E_{sd}}{kT} \right) \]

\[ n_s = R \tau_s = \frac{R}{\nu} \exp \left( \frac{E_{des}}{kT} \right) \]

\[ J_0 = \alpha_1 \frac{R}{\nu N_0} \exp \left( \frac{2E_{des} - E_{sd}}{kT} \right) \left( N_0 \approx \frac{1}{a^2} \right) \]
2. \( n^* = 2, 1 \ll \frac{\omega_2^-}{\omega_2^+} \gg \frac{\omega_2^- \omega_3^-}{\omega_2^+ \omega_3^+} \gg \frac{\omega_2^- \omega_3^- \omega_4^-}{\omega_2^+ \omega_3^+ \omega_4^+} \ldots \)

\[
J_0 = \omega_1^+ n_s \frac{\omega_2^-}{\omega_2^+} \left( \frac{\omega_2^-}{\omega_2^+} = \frac{\alpha_2 D_s n_s}{\alpha_1 \nu} \exp \left( \frac{E_2 + E_{sd}}{kT} \right) \right) \]

\[
J_0 = \alpha_2 \frac{R^3}{\nu^2 N_0^2} \exp \left( \frac{3E_{des} - E_{sd}}{kT} \right) \exp \left( \frac{E_2}{kT} \right) \]

In the general case:

\[
J_0 = \alpha^* R \left( \frac{R}{\nu N_0} \right)^{n^*} \exp \left( \frac{(n^* + 1)E_{des} - E_{sd}}{kT} \right) \exp \left( \frac{E^*}{kT} \right) \]

In terms of adatom concentration

\[
J_0 = \alpha^* D_s \frac{n_s^{n^*+1}}{N_0^{n^*-1}} \exp \left( \frac{E^*}{kT} \right) \]

\( \text{Si(001)} \)

\( R = 1 \times 10^{13} \text{ cm}^{-2} \text{sec}^{-1} \)

\( T = 800 \text{ K} \)

\( E_{des} = 2 \text{ eV} \)

\( E_{sd} = 0.6 \text{ eV} \)

\( N_0 = 6.78 \times 10^{14} \text{ cm}^{-2} \)

\( n^* = 1 \)

\( J_0 \approx 3 \times 10^8 \text{ cm}^{-2} \text{sec}^{-1} \)
TRANSIENT NUCLEATION
VAPOR DEPOSITION IN CLEAN MEDIUM

CURVES NUCLEUS DENSITY VS TIME
Cu on Ni(001) under clean conditions
Ivan Markov, Bulgarian Academy of Sciences
Deposition of Ge on Pb precovered Si(001) (Tien T. Tsong PRL (1998))

Ivan Markov, Bulgarian Academy of Sciences
GENERAL PROBLEM

\[
\frac{dZ(n, t)}{dt} = [\omega^+(n - 1)Z(n - 1, t) - \omega^-(n)Z(n, t)]
- [\omega^+(n)Z(n, t) - \omega^-(n + 1)Z(n + 1, t)]
\]

\(Z(n, t)\) - the concentration is a continuous function of size \(n\)

\(J(n, t) = \omega^+(n - 1)Z(n - 1, t) - \omega^-(n)Z(n, t)\)

\[
\frac{dZ(n, t)}{dt} = J(n, t) - J(n - 1, t)
\]

or

\[
\frac{dZ(n, t)}{dt} = -\frac{dJ(n, t)}{dt}
\]

The expression of the detailed balance reads

\(\omega^+(n - 1)N(n - 1) = \omega^-(n)N(n)\)

or

\(\omega^-(n) = \omega^+(n - 1)\frac{N(n - 1)}{N(n)}\)
\[ J(n,t) = \omega^+(n-1)N(n-1) \left( \frac{Z(n-1,t)}{N(n-1)} - \frac{Z(n,t)}{N(n)} \right) \]

or

\[ J(n,t) = -\omega^+(n)N(n) \frac{d}{dn} \left( \frac{Z(n,t)}{N(n)} \right) \]

\[ \frac{dZ(n,t)}{dt} = \frac{d}{dn} \left[ \omega^+(n)N(n) \frac{d}{dn} \left( \frac{Z(n,t)}{N(n)} \right) \right] \]

\[ \frac{d}{dt} \left( \frac{dZ(n,t)}{N(n)} \right) = \omega^+(n) \frac{d^2}{dn^2} \left( \frac{dZ(n,t)}{N(n)} \right) + \left( \frac{d\omega^+(n)}{dn} - \frac{\omega^+(n) d\Delta G(n)}{kT} \frac{d}{dn} \right) \frac{d}{dn} \left( \frac{Z(n,t)}{N(n)} \right) \]

In the vicinity of the critical size:

\[ \omega^+(n) \approx \omega^+(n^*) = \text{const, } \Delta G(n^*) = \text{max, and hence} \]

\[ \frac{d}{dt} \left( \frac{dZ(n,t)}{N(n)} \right) = \omega^+(n) \frac{d^2}{dn^2} \left( \frac{dZ(n,t)}{N(n)} \right) \]

the nucleation process is governed by the familiar diffusion equation in which the diffusion coefficient is replaced by the rate constant \( \omega^* \), and which reflects the random character of the growth process. The latter reflects the random attachment and detachment of atoms to and from the growing clusters. Thus, the growth of the cluster takes place as a "diffusion process" in the space of size \( n \).

That is why we say that the nucleation is a random process.

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SOLUTION OF THE “DIFFUSION EQUATION

BOUNDARY CONDITIONS:

\( t = 0, \quad Z(1,0) = N(1), \quad Z(n \geq 2,0) = 0 \)

\( t = t, \quad Z(1,t) = N(1), \quad Z(N,t) = 0 \)

\[
\frac{Z(n,t)}{N(n)} = \frac{1}{2} - \frac{n - n^*}{\Delta n^*} - \frac{2}{\pi} \sum_{i=1}^{\infty} \frac{1}{i} \sin \left( i \pi \frac{n - n^*}{\Delta n^*} + \frac{i \pi}{2} \right) \exp \left( - \frac{i^2 \pi \omega^* t}{16 \Delta n^*^2} \right)
\]

\( n = n^* \rightarrow Z(n^*) = \frac{1}{2} N(n^*) \)
\[ J(t) = J_0 \left[ 1 + 2 \sum_{i=1}^{\infty} (-1)^i \exp\left(-i^2 \frac{t}{\tau}\right) \right] \]

\[ \tau = \frac{4(\Delta n^*)^2}{\pi \omega * \Gamma^2} = \frac{16}{\pi^2 \omega * \Gamma^2} \]

\[ N(t) = \int_{0}^{t} J(t) \, dt \]

\[ N(t) = J_0 \tau \left[ \frac{t}{\tau} + \frac{\pi^2}{6} - 2 \sum_{i=1}^{\infty} \frac{(-1)^i}{i^2} \exp\left(-i^2 \frac{t}{\tau}\right) \right] \]
NUCLEATION IN VAPOR:

\[ \tau = \frac{16}{\pi} \sqrt{\frac{m}{kT}} \frac{\sigma}{P[\ln(P/P_\infty)]^2} \]

Nucleation of water:

\[ T = 300K, \sigma = 75.2 \text{ erg cm}^{-2}, m = 3.10^{-23} \text{ g}, \]

\[ P_\infty = 20 \text{ torr}, \ P / P_\infty = 4, \]

\[ \tau \approx 10^{-11} \text{ sec} \]
NUCLEATION IN SOLUTION

\[ \tau = \frac{16}{\pi} \frac{\sigma}{kT \nu a} \left[ \ln(C / C_{\infty}) \right]^2 \exp\left( \frac{\Delta U}{kT} \right) \]

Nucleation of BaSO₄

\[ T = 300 K, \quad \sigma = 116 \text{ erg cm}^{-2}, \quad \Delta U = 7000 \text{ cal mol}^{-1}, \]
\[ C_{\infty} = 1.10^{-5} \text{ mol l}^{-1} = 6.10^{15} \text{ molecules cm}^{-3}, \]
\[ C / C_{\infty} = 1000, \quad \nu = 1.10^{13} \text{ sec}^{-1}, \quad a = 4.10^{-8} \text{ cm}, \]

\[ \tau \approx 1.10^{-3} \text{ sec} \]

Nucleation of PbSO₄:

\[ \sigma = 100 \text{ erg cm}^{-2}, \quad \Delta U = 14500 \text{ cal mol}^{-1}, \]
\[ C_{\infty} = 8.5.10^{16} \text{ molecules cm}^{-3}, \quad C / C_{\infty} = 28, \]

\[ \tau \approx 30 \text{ sec} \]
NUCLEATION IN LIQUIDS (MELTS):
\[
\tau = \frac{16 \sigma k T \nu_c}{\pi \Delta s_m^2 \Delta T^2 v_a} \exp \left( \frac{\Delta U}{k T} \right)
\]

Nucleation of metals: Ag
\[
\sigma = 150 \text{ erg cm}^{-2}, \quad \nu_c = 5.10^{-22} \text{ cm}^3,
\]
\[
\Delta s_m = 2.19 \text{ cal/K mol} = 1.52.10^{-16} \text{ erg/K},
\]
\[
\nu = 1.10^{13} \text{ sec}^{-1}, \quad T = 1230 \text{ K}, \quad \Delta T = 5 \text{K},
\]

\[
\tau \approx 1.10^{-6} \text{ sec}
\]

NUCLEATION IN GLASS - FORMING MELTS: SiO_2, GeO_2
\[
\Delta U \approx 100 - 150 \text{ kcal/mol}
\]

\[
\tau \approx 1.10^5 \text{ sec} = 24 \text{ hours}
\]

The solidification takes place in a transient regime. The steady state is never reached.

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HETEROGENEOUS NUCLEATION

\[ \tau = 17 \left[ \frac{m}{k^3 T^3} \frac{\phi(\theta)}{\sin \theta} \frac{\sigma^2 v_l}{aP[\ln(P / P_{\infty})]^3} \exp \left( -\frac{E_{des} - E_{sd}}{kT} \right) \right] \]

Having in mind that \( r^* = \frac{2\sigma v_l}{kT \ln(P / P_{\infty})} \)

\[ \frac{\tau(\text{het})}{\tau(\text{hom})} = \frac{\pi}{2} \frac{r^*}{a} \frac{\phi(\theta)}{\sin \theta} \exp \left( -\frac{E_{des} - E_{sd}}{kT} \right) \]

\( \tau(\text{het}) << \tau(\text{hom}) \)
\[ F(x) = \frac{N(t)}{J_0 \tau}, \quad x = \frac{t}{\tau} \]

\[ F(x) = x + \frac{\pi^2}{6} - 2\sum_{i=1}^{\infty} \frac{(-1)^i}{i^2} \exp(-i^2 x) \]
MASS CRYSTALLIZATION AND SATURATION
NUCLEUS DENSITY

1. **IN MELTS** (polymers, glasses, alloys) - determine the crystalline dispersion and in turn the mechanical properties.

2. **ON SUBSTRATES** - (semiconducor and magnetic films) - determine the electrical, magnetic, mechanical (defect structure) properties of thin films.

3. **2D NUCLEATION** - determine the kinetics of growth of crystals and thin epitaxial films.

**REASONS FOR SATURATION BEHAVIOR:**

1. Availability of defect sites, impurities, etc. in the system.

2. Formation of zones around the growing nuclei where the nucleation is inhibited (soft impingement in solidification, denuded zones in thin film growth).

3. Ostwald’s ripening (coarsening), coalescence.

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NUCLEATION ON DEFECT SITES

1. ONE AND THE SAME ACTIVITY OF THE DEFECT SITES

\[ \phi(\theta) = \text{const and the critical supersaturation } \Delta \mu_c = \text{const} \]

RANDOM DISTRIBUTION OF THE DEFECT SITES

\[
\frac{dN}{dt} = J'_0 (N_D - N)
\]

\( J'_0 \) - steady state nucleation rate per site (sec\(^{-1}\))

\( N_D \) - density of defect sites

\( N \) - nucleus density

\( t = 0, \ N = 0 \)

\[ N = N_D \left[1 - \exp(-J'_0 t)\right] \]

\( t \to \infty, \ N \to N_D \)
2. ARBITRARY ACTIVITY DISTRIBUTION OF THE DEFECT SITES

\[ \phi(\theta) \neq 0, \text{ and of the critical supersaturation } \Delta \mu_c \]

\[ N = \int_{0}^{\Delta \mu} N_D(\Delta \mu_c) \left[ 1 - \exp \left[ J'_0(\Delta \mu_c) t \right] \right] d\Delta \mu_c \]

\[ J = J(t) \text{ and } \theta = const \]

\[ N = N_D \left[ 1 - \exp \left( -\int_{0}^{t} J(t) dt \right) \right] \]

In the general case, increasing the supersaturation new defect sites with lower critical supersaturation take part into the nucleation process. The increase of the saturation nucleus density with the supersaturation is thus a mixture of two effects: (i) the increase of the nucleation rate \( J'_0(\Delta \mu_c) \), and (ii) the increase of the \( N_D(\Delta \mu_c) \), with the supersaturation.
Zones around Hg droplet on a Pt sphere and Ag crystallites electrodeposited on conducting glass.

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NUCLEATION EXCLUSION ZONES IN MELTS

IF THE HEAT CONDUCTIVITY OF THE MELT IS LOW, THE LATENT HEAT OF CRYSTALLIZATION IS ACCUMULATED AND THE TEMPERATURE AT THE INTERFACE IS CLOSE TO THE MELTING POINT. A ZONE WITH A SMALL UNDERCOOLING $T_m - T_i$ IS FORMED AROUND THE GROWING CRYSTALLITES IN WHICH THE NUCLEATION IS ARRESTED:

HEAT FLOW CONTROL - SOFT IMPINGEMENT

IF THE HEAT CONDUCTIVITY OF THE MELT IS HIGH, THE LATENT HEAT OF CRYSTALLIZATION IS RAPIDLY TAKEN AWAY. THE INTERFACIAL TEMPERATURE IS FAR FROM THE MELTING POINT. THE UNDERCOOLING IS LARGE AND THE TEMPERATURE GRADIENT IS CONCENTRATED IN A THIN REGION AROUND THE CRYSTAL. THE CRYSTAL ITSELF PLAYS THE ROLE OF EXCLUSION ZONE:

INTERFACE CONTROL - HARD IMPINGEMENT

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Δμ - supersaturation in the system

Δμ_{cr} - critical supersaturation

r_c - radius of the nucleation exclusion zone

Zones can be 3D (in melts), 2D (on surfaces) or 1D (at steps).
CALCULATION OF CRYSTALLIZED FRACTION

PROBABILISTIC APPROACH OF KOLMOGOROV

$V, T$

$V$ - volume of the supersaturated phase

$v(\bar{n}, t)$ - rate of growth of the nucleation exclusion zone function of the direction $\bar{n}$ and the time $t$

$v(\bar{n}, t) = c(\bar{n}) k(t)$

$c^3 = \frac{1}{4\pi} \int_{S} c^3(\bar{n}) d\sigma \rightarrow$ isotropic rate

The volume of the nucleation exclusion zone is

$V'(t', t) = \frac{4\pi c^3}{3} \left[ \int_{t'}^{t} k(\tau - t') d\tau \right]^3$

$t'$ - time of nucleus formation

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\[
\frac{dN}{dt} = J_0 \Theta(t)
\]

\(\Theta(t)\) - fraction of the volume uncovered by nucleation exclusion zones.

\[
N(t) = J_0 \int_0^t \Theta(t) dt
\]

\[
\xi(t) = \frac{V_c}{V} = 1 - \Theta(t)
\]

where \(V_c\) is the crystallized volume.

Thus the nucleus density \(N(t)\) as a function of time and the kinetics of mass crystallization \(\xi(t)\) are interconnected. Once we know \(\xi(t)\) we can easily compute \(N(t)\).
The fraction $\Theta(t)$ is equal to the probability to find an arbitrary chosen point $P$ at a moment $t$ outside of a nucleation exclusion zone. The probability $1 - \Theta(t)$ the point $P$ to be inside a zone is equivalent to the formation of a nucleus at a moment $t' < t$ at a point $P'$ smaller than the distance

$$r(t', t) = c \int_{t'}^{t} k(\tau - t') d\tau$$
The probability of formation of at least one nucleus in the time interval $\Delta t' = t - t'$ at a distance smaller than $r$ is

$$J_0 V'(t', t) \Delta t'$$

The probability of no nucleus formation is

$$1 - J_0 V'(t', t) \Delta t'$$

The probability the point $P$ to be outside the volume $V'(t', t)$ at a moment $t$ from the beginning of the crystallization is

$$\Theta(t) = \prod_{i=1}^{s} \left(1 - J_0 V'(t_i) \Delta t' \right)$$

where $t_i = i \Delta t'$ and $t = s \Delta t'$.

$$\ln \Theta(t) = \sum_{i=1}^{s} \ln [1 - J_0 V'(t_i) \Delta t'] \approx - \sum_{i=1}^{s} J_0 V'(t_i) \Delta t' \approx - J_0 \int_{0}^{t} V'(t') dt'$$

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\[ \Theta(t) = \exp \left( -J_0 \int_0^t V'(t')dt' \right) \]

\[ N(t) = J_0 \int_0^t \exp \left( -J_0 \int_0^{\tau} V'(t')dt' \right) d\tau \]

Assuming a constant growth rate \( k(t) = 1 \)

\[ V' = \frac{4\pi c^3}{3} (t - t')^3 \]

\[ N(t) = J_0 \int_0^t \exp \left( -\frac{\pi}{3} J_0 c^3 \tau^4 \right) d\tau \]

The saturation nucleus density is obtained from the condition \( t \to \infty \)

\[ N_S = 0.9 \left( \frac{J_0}{c} \right)^{3/4} \]

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KINETICS OF MASS CRYSTALLIZATION

\[ \xi = 1 - \exp\left( -\frac{\pi}{3} J_0 c^3 \tau^4 \right) \]

If the nucleation take place in a short interval in the beginning of crystallization, i.e. \( t = 0, \ N = N_s \), one obtains

\[ \xi = 1 - \exp\left[ -N_s V'(t') \right] = 1 - \exp\left( -\frac{4}{3} \pi N_s c^3 t^3 \right) \]

In the case of nucleation on a surface we replace the volume \( V'(t') \) by the area \( S'(t') \) of the nucleation exclusion zone

\[ S'(t') = \pi c^2 \left( \int_{t'}^t k(\tau - t')d\tau \right)^2 \]

and with a constant growth rate \( k(t) = 1 \) one obtains

\[ \xi = \frac{S_c}{S} = 1 - \exp\left( -\frac{\pi}{3} J_0 c^2 t^3 \right) \]
\[ \xi = 1 - \exp(-kt^n) \]
Nucleation and growth of CoSi$_2$ in amorphous thin film of Co-Si alloy

Ivan Markov, Bulgarian Academy of Sciences
INTERPRETATION OF DATA

THE LOG-LOG PLOT

\[ n = 4 - \text{progressive 3D nucleation, linear growth} \]
\[ n = 3 - \text{3D instantaneous nucleation, linear growth} \]
\[ 2D \text{progressive nucleation, linear growth} \]
\[ n = 2 - 2D \text{progressive nucleation, } \sqrt{t} \text{ growth.} \]


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