Crystal Growth: Physics, Technology and Modeling

Stanisław Krukowski & Michał Leszczyński
Institute of High Pressure Physics PAS
01-142 Warsaw, Sokołowska 29/37
e-mail: stach@unipress.waw.pl, mike@unipress.waw.pl

Zbigniew Żytkiewicz
Institute of Physics PAS
02-668 Warsaw, Al. Lotników 32/46
E-mail: zytkie@ifpan.edu.pl

Lecture 5. Thermodynamics of growth processes

http://w3.unipress.waw.pl/~stach/cg-2022-23/

Equilibrium

Equilibrium - extent

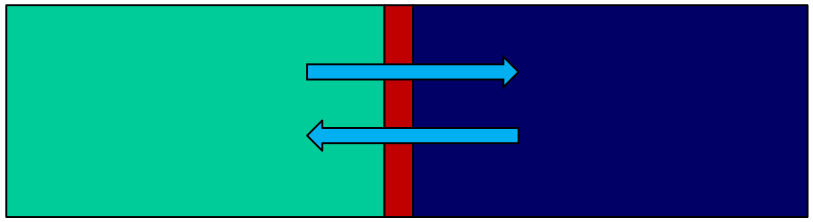
- **Between different phases**

- **Inside single phase:**
  - **spatial – local equilibrium**
  - **degrees of freedom – partial equilibrium**

Equilibrium - type

- **mechanical**
- **thermal**
- **chemical**

Phase equilibrium - fluxes



$$\vec{g} \equiv \frac{\Delta G\, \vec{n}}{\Delta S\, \Delta t}$$ **Flux**

$\vec{n}$ **= unit vector, normal to the surface**

- **Two phase state, stationary, i.e. time independent, such that introduction of barriers does not enforce any change**

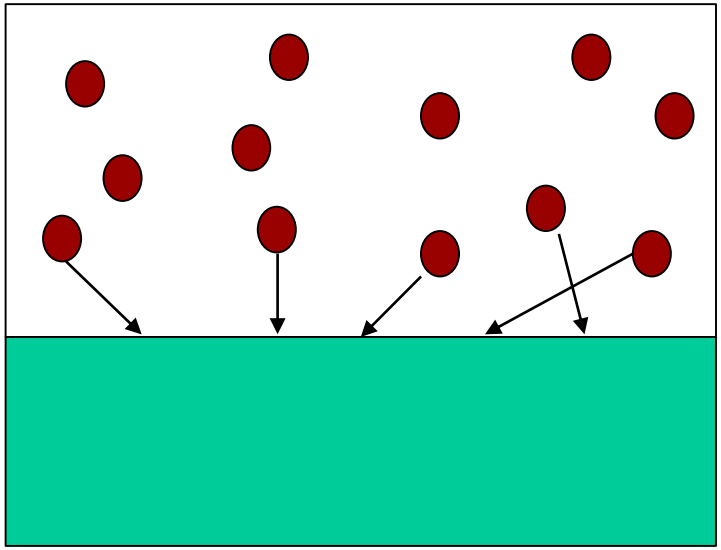
- **Flux – vectorial quantity $\vec{g}$ indicating amount of physical quantity (conserved - ΔG) transported across unit of surface (ΔS) in the unit of time (Δt)**

- **Two phase state, stationary, i.e. time independent: fluxes are balanced**

  - mechanical → momentum flux
  - thermal → energy flux
  - chemical → mass flux

Fluxes - balance

- **Two phases – solid and vapor**



- **Molecule flux *I* (number of molecules arriving at the unit area of the surface in the unit of time**

$$I = \frac{p}{\sqrt{2\pi mkT}}$$

Ideal gas – equilibrium and transport properties

- **Equation of state**

$$pV = nkT \qquad p = nkT \qquad k = 1.3800648 \times 10^{-23}\ J/K$$

- **Mean free path λ and mean free flight time τ, thermal velocity <v>**

$$\lambda = \frac{1}{\sqrt{2}n\sigma} \qquad \tau = \frac{\lambda}{< v >} \qquad < v > = \sqrt{\frac{3kT}{m}}$$

- **Average molecular flux – does not depend on transport properties**

$$I = \frac{p}{\sqrt{2\pi mkT}} = n\sqrt{\frac{kT}{2\pi m}}$$

Standard and normal conditions (IUPAC & NIST)

- **Standard conditions (to 1982)**

$T = 273.15\ K$ $p = 1$ atm = 101325 Pa

- **Standard conditions (to 1982)**

$T = 273.15\ K$ $p = 1$ bar = 100000 Pa

- **Normal conditions**

$T = 293.15\ K$ $p = 1$ atm = 101325 Pa

Ideal gas - numbers

- **Density** n

$$n = 2.687 \times 10^{19}\ cm^{-3}$$

- **Average thermal velocity** $\langle v \rangle$ **at** $T = 300\ K$

$$\langle v \rangle = \sqrt{\frac{3kT}{m}} = 512\ m/s$$

- **Mean free path** λ **and mean free flight time** τ

$$\lambda = \frac{1}{\sqrt{2}\, n\, \sigma} = 3 \times 10^{-6}\ m \qquad \tau = \frac{\lambda}{\langle v \rangle} = 5.6 \times 10^{-9}\ s$$

Molecule size - $d = 2R \sim 10^{-10} m$

Total scattering crossection- $\sigma = \pi R^2 \sim 10^{-20} m^2$

Surface geometry

- **GaN density (molecules)** n_{GaN}

$$n_{GaN} = 4.3 \times 10^{22}\ cm^{-3}$$

- **GaN molar volume** v_{GaN}

$$v_{GaN} = 2.3 \times 10^{-23}\ cm^{3}$$

- **GaN surface atom density** η_{GaN}

$$\eta_{GaN} = n_{GaN}^{2/3} = 8.671 \times 10^{14}\ cm^{-2} \qquad \eta_{GaN} = \frac{4}{3a^2\sqrt{3}} = 7.611 \times 10^{14}\ cm^{-2}$$

- **GaN surface area for single site (0001)surface** η_{GaN}

$$\varsigma_{GaN} = v_{GaN}^{2/3} = 1.145 \times 10^{-15}\ cm^{2} \qquad \varsigma_{GaN} = \frac{3a^2\sqrt{3}}{4} = 1.314 \times 10^{-15}\ cm^{2}$$

GaN lattice constant – a =3.1890 Å

Fluxes & surface equilibrium

- **Average molecular flux** I

$$I = \frac{p}{\sqrt{2\pi mkT}} = 2.785 \times 10^{23}\, s^{-1} cm^{-2}$$

- **Site impact frequency** ν

$$\nu = I\varsigma_{GaN} = 3.788 \times 10^{8}\, s^{-1}$$

- **Adsorption rate** r

$$r = \nu\sigma = I\varsigma_{GaN}\sigma$$

σ – sticking coefficient i.e. probability of attachment $(0 \leq \sigma \leq 1)$

Sticking coefficient

- **Sticking coefficient – probability of transition *P* from initial (*I* - vapor) to final (F - surface attached) state**

$$\sigma \equiv P\,(I \longrightarrow F)$$

- **Probability of transition *P* is calculated using notion of transition state *T***

- **Transition state *T***

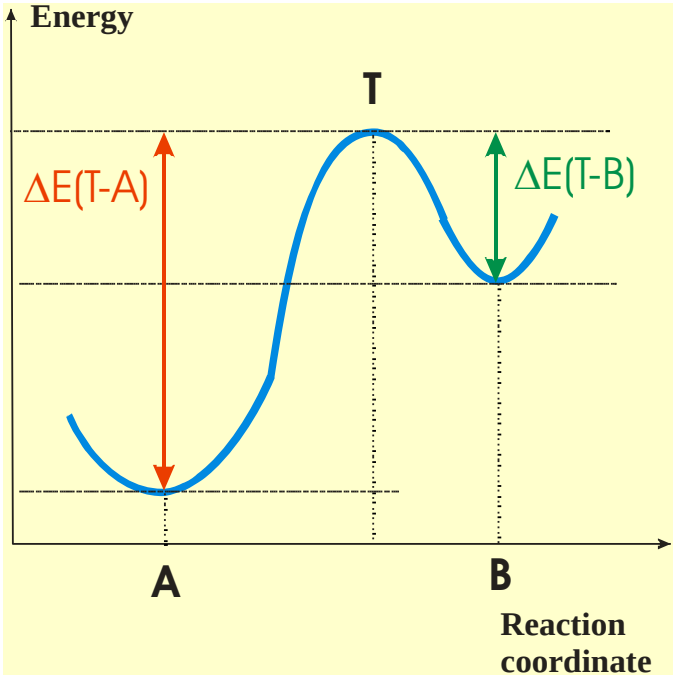
  - **No return from Transition state (T) to Initial state (I)**

  - **Energy higher than initial state**

  - **Energy landscape – saddle point**

Transition state – time evolution of the system

- **Time evolution chemical kinetics approach**



- **Energy barriers**

- A → B transition

$$\Delta E(T - A) = E(T) - E(E)$$

- B → A transition

$$\Delta E(T - B) = E(T) - E(B)$$

Energy – total energy of the system in adiabatic approximation

Transition state –probability of arrival

Tolman principle

- **Probability of the system in a given macro state is proportional to the volume of the phase space Q compatible with this macro state**

- **For reaction coordinate – the relative probability is:**

$$\frac{P(T)}{P(A)} = \frac{Q(T)}{Q(A)} exp\left[-\frac{F(T)-F(A)}{kT}\right]$$

Q(T) , Q(A) statistical sums over remaining degrees of freedom in states T and A

- **Free energy of the system of the temperature T:**

$$F = -kB\ lnQ = -kT\ ln(Q_{tr}Q_{viv}Q_{rot})$$

Transition state –Arrhenius principle

- **Absence of strong coupling (energy coupling on Hamiltonian level)**

$$\frac{P(T)}{P(A)} = exp\left[-\frac{F(T)-F(A)}{kT}\right]$$

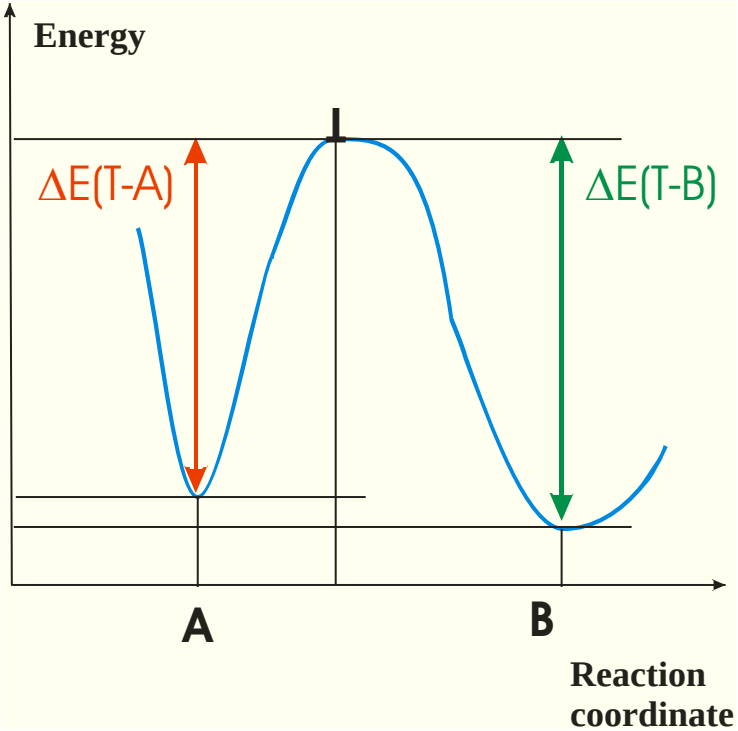
$$\frac{P(T)}{P(A)} = exp\left[\frac{S(T)-S(A)}{k}\right] exp\left[-\frac{E(T)-E(A)}{kT}\right]$$

- **No entropy difference:**

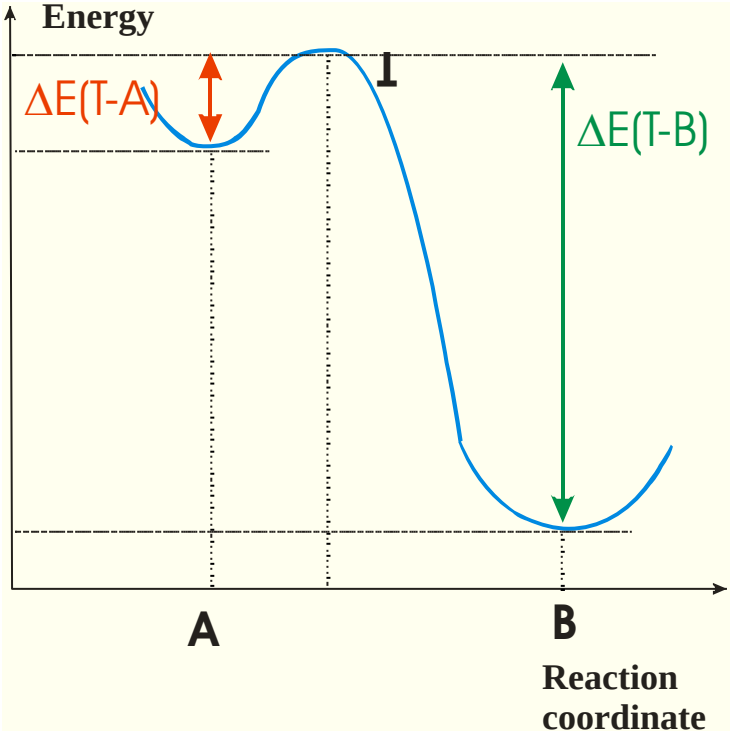
$$\frac{P(T)}{P(A)} \cong exp\left[-\frac{E(T)-E(A)}{kT}\right] = exp\left[-\frac{\Delta E}{kT}\right]$$

Energetic properties of the growth models

- **Dynamic models**



- **Kinetic models**



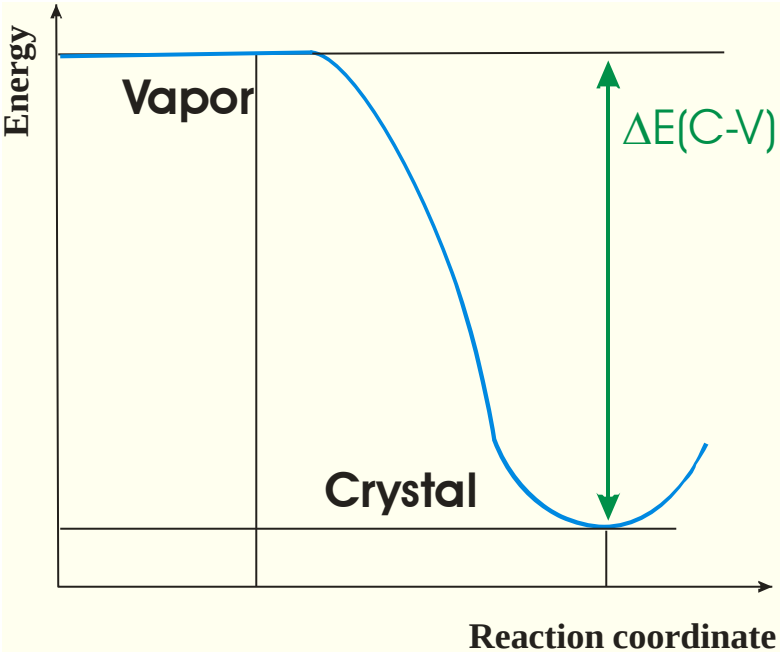
$$r = \nu P(I \longrightarrow F) = \nu \exp\left[-\frac{\Delta E}{kT}\right]$$

Growth models

- **Dynamic models**
  - **Transition forward and backward have comparable probability**
  - **Both direction are important**
  - **Existence of equilibrium state**

- **Kinetic models**
  - **Probabilities are drastically different**
  - **Alternatively – blocking of some transition is enforced**
  - **Absence of equilibrium state**

Vapor – crystal growth models



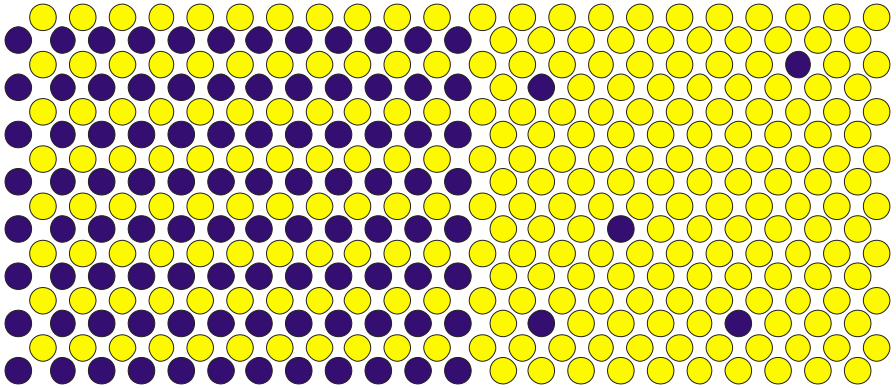
- **Deposition at the single site (v → c)**

$$r = I\varsigma = \frac{p\varsigma}{\sqrt{2\pi mkT}} = n\varsigma\sqrt{\frac{kT}{2\pi m}}$$

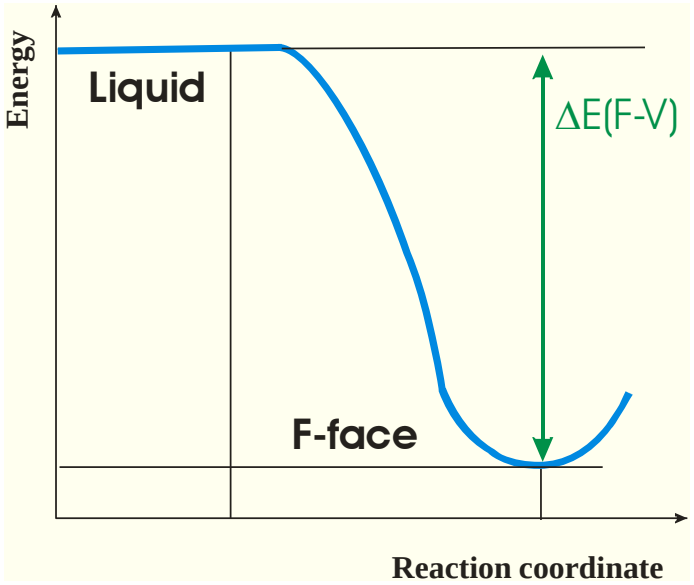
- **Sublimation (c → v)**

$$r = \nu \exp\left[-\frac{\Delta E(C-V)}{kT}\right]$$

Liquid – crystal growth models



- **Diffusion**
- **Crystallization (l → c)**



- **Dissolution (c → l)**

$$r = \nu \exp\left[-\frac{\Delta E(C-L)}{kT}\right]$$

Growth dynamics – deviation from equilibrium

- **Equilibrium**
  - **Dynamical** $p_v = p_l = p_{eq}$
  - **Thermal** $T_v = T_l = T_{eq}$
  - **Chemical** $\mu_v = \mu_l = \mu_{eq}$
- **Deviation from equilibrium**
  - **Supersonic**
  - **Supercooling** $\Delta\tau = \frac{T_{l,v} - T_{eq}}{T_{eq}}$
  - **Supersaturation** $\Delta\mu = \frac{\mu_{l,v} - \mu_{eq}}{kT}$

Supersaturation σ in ideal systems

- **Ideal gas**

$$\sigma = \frac{\Delta\mu}{kT} = ln\left(\frac{p}{p_{eq}}\right) = ln\left(1 - \frac{p - p_{eq}}{p_{eq}}\right) \cong \frac{p - p_{eq}}{p_{eq}}$$

- **Ideal solution**

$$\sigma = \frac{\Delta\mu}{kT} = ln\left(\frac{x}{x_{eq}}\right) = ln\left(1 - \frac{x - x_{eq}}{x_{eq}}\right) \cong \frac{x - x_{eq}}{x_{eq}}$$

Dynamic processes - metastable states – nucleation barriers

- **Some systems remain in mother state under supersaturation – energy barriers (height of the transition state)**
- **Transition – probability of attainment of transition state**
- **Nucleation theory – transition state is nucleus of the new phase (solid) of sufficiently large size**
- **Isotropic case – finite size system is represented by the sphere of the radius R. The energy barrier (energy of the nucleus is):**

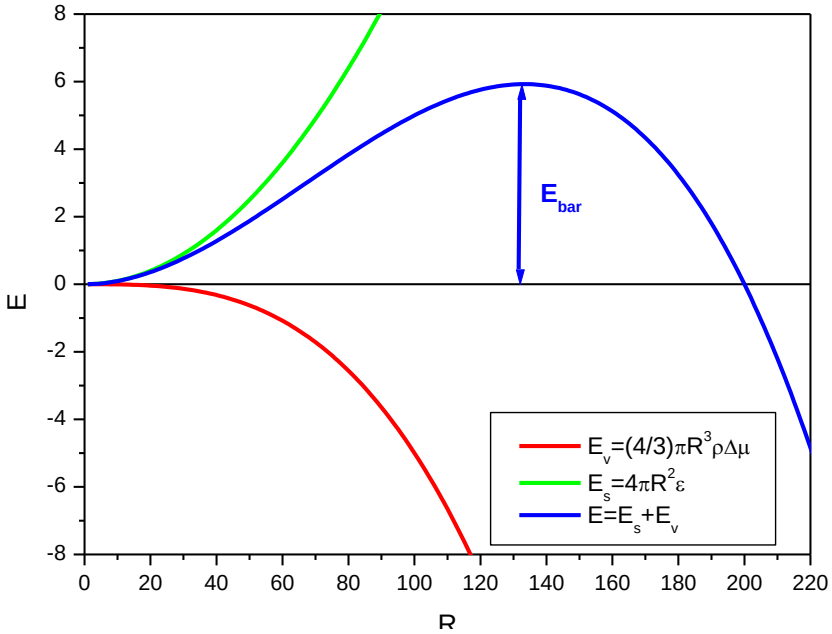
$$\Delta E = \frac{4\pi R^3 \rho\, \Delta\mu}{3} + 4\pi R^2\, \gamma$$

$\Delta\mu = -\sigma < 0$ **– volume term is negative**

$\gamma > 0$ **– surface term is positive**

Nucleation barriers - size

$$\Delta E = \frac{4\pi R^3 \rho\, \Delta\mu}{3} + 4\pi R^2\, \gamma$$



Surface term dominates for small R

Volume term dominates for large R

Nucleation critical radius

$$R_{crit} = \frac{2\,\gamma}{\rho\,|\Delta\mu|} = \frac{2\,\gamma}{\rho k T \sigma}$$

Energy barrier - energy at critical radius

$$\Delta E = \frac{16\pi\gamma^{\,3}}{3\rho^2(\Delta\mu)^2} = \frac{16\pi\gamma^{\,3}}{3\rho^2(kT\sigma)^2}$$

Nucleation types

- **Heterogeneous nucleation – process in which the energy barrier is lowered due to existence of other factors (third phase, etc.)**
- **Homogenous nucleation – process with standard energy barrier**

Nucleation rate r_{nucl}

$$r_{nucl} = \nu N_s P(R_{crit})$$

Probability of critical nucleus $P(R_{crit})$

$$P(R_{crit}) = exp\left[-\frac{\Delta E_{crit}}{kT}\right] = exp\left[-\frac{16\pi\gamma^3}{3\rho^2(\Delta\mu)^2 kT}\right]$$

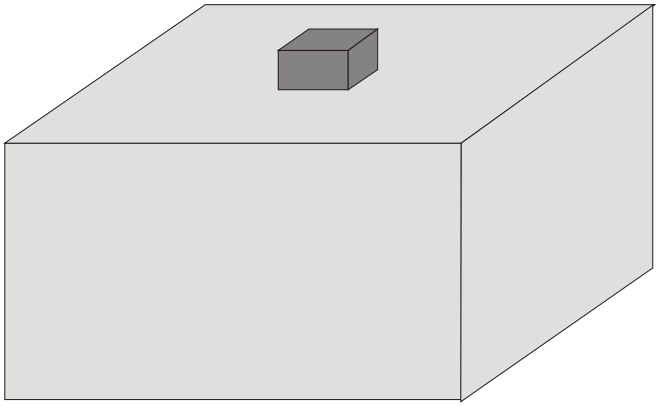
Number of sites at the surface N_s

$$N_s = \frac{4\pi R_{crit}^3 \rho_s}{3}$$

Attempt frequency ν

Crystal growth rate – nucleation controlled

- **Crystals may be controlled by creation of new atomic layers – via 2-d nucleation**



$$r_{nucl} = \nu N_L P(R_{crit}) = \nu N_L exp\left(-\frac{\Delta E_{crit}}{kT}\right)$$

Number of sites at the Edge - N_L

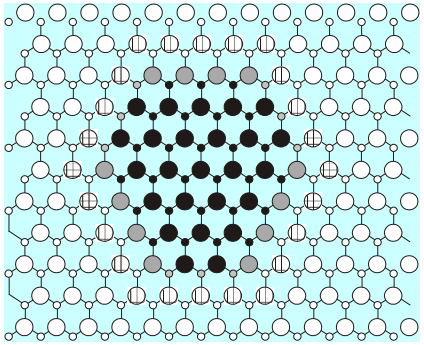
$$N_L = \frac{L}{a}$$

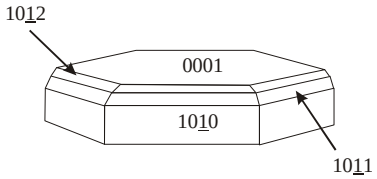
Edge length - L

Lattice constant - a

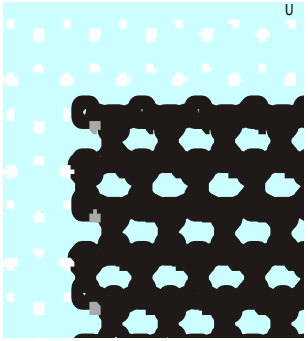
Edge energy for lattice constant – energy of broken bond - ϕ

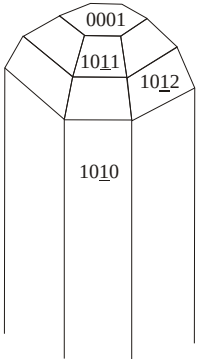
2-d nucleation on GaN(0001) & GaN(10-10) surfaces



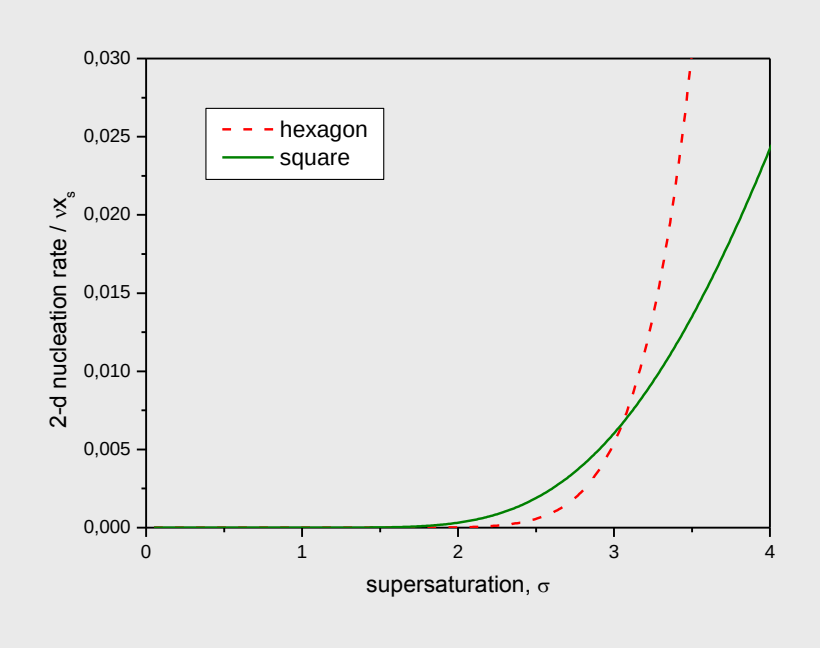


$$I = \nu\left(\frac{6\phi}{|\Delta\mu|} + 6\right) exp\left[-\frac{1}{kT}\left(\frac{3\phi^2}{|\Delta\mu|} - \frac{3|\Delta\mu|}{4}\right)\right]$$





$$I = \nu\left(\frac{4\phi}{|\Delta\mu|} - 1\right) exp\left[-\frac{1}{kT}\left(\frac{2\phi^2}{|\Delta\mu|} - \frac{|\Delta\mu|}{8}\right)\right]$$



- **Growth anisotropy, i.e. different rates leading to different shapes**
- **Acceleration of the growth along [0001] direction for high supersaturation**

Kinetic process – diffusion

Kinetic process – diffusion, i.e. random motion of the species (atoms or molecules):

- **Mean (averaged over many jumps) translation is zero**
- **Correlation of the direction of the two consecutive jumps is zero (Markov process, i.e. process with no memory)**

Diffusion types:

- **Free – jumps directions and lengths are purely random**
- **Lattice – jumps between lattice sites**

Free diffusion in the vapor

- **Mean average translation is zero (no convection)**
- **Correlation of the direction of the two consecutive jumps is zero (Markov process, i.e. process with no memory)**

- **Mean free path** $\lambda = \frac{1}{\sqrt{2}\, n\, \sigma}$
- **Mean free flight time** $\tau = \frac{\lambda}{\langle v \rangle}$
- **Average thermal velocity** $\langle v \rangle = \sqrt{\frac{3kT}{m}}$

Total scattering crossection - σ

Lattice diffusion

- **Species localized in lattice sites**
- **Correlation of the direction of the two consecutive jumps is zero (Markov process, i.e. process with no memory)**
- **The rate r is given by**

$$r = \nu P(i \longrightarrow f)$$

Attempt frequency ν

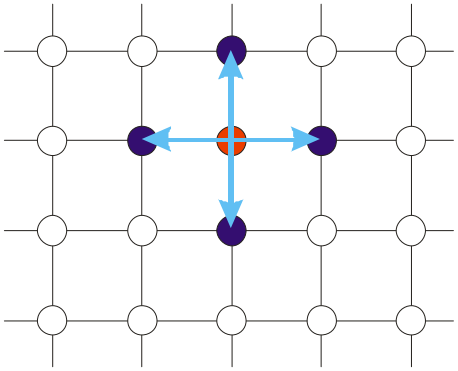
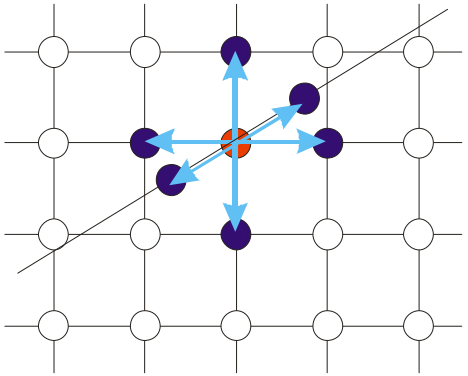
- **Jump probability**

$$P(i \longrightarrow f) = \frac{1}{C} exp\left[-\frac{\Delta E_{diff}}{kT}\right]$$

Normalization constant C depends on lattice type and space dimension (lattice geometry)

Lattice diffusion – dimension of the space

- **Simple cubic lattice**

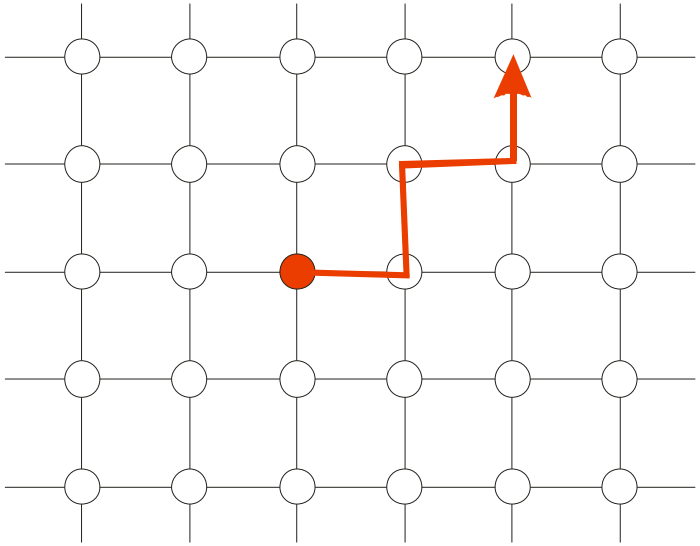
d = 1	d = 2	d = 3
		
C = 2	C = 4	C = 6

- **Probability of jump in specific direction** $P(i \rightarrow f)$

$$P(i \rightarrow f) = \frac{1}{C} \, exp\left[-\frac{\Delta E_{diff}}{kT}\right]$$

Displacement in time (tracer diffusion)

- **Simple cubic lattice**



- **Translation vector – vectorial sum of the consecutive jumps**
- **Square of the passed distance (distance difference between position at zero & n jump or sum of the n consecutive jumps**

$$\left(\Delta r_{diff}(t)\right)^2 = [\vec{r}(t) - \vec{r}(0)]^2 = \sum_{i=1}^{n} \vec{a}_i \cdot \sum_{i=1}^{n} \vec{a}_i$$

- **Number of jumps**

$$n = \frac{t}{\tau_o} = t\,\nu$$

Distance (tracer diffusion)

- **Square of the diffusion length**

$$\left(\Delta r_{diff}(t)\right)^2 = \sum_{i=1}^{n(t)} \vec{a}_i \cdot \sum_{i=1}^{n(t)} \vec{a}_i = \sum_{\substack{i=1,j=1 \\ i \neq j}}^{n(t)} \vec{a}_i \cdot \vec{a}_j + \sum_{i=1}^{n(t)} (\vec{a}_i)^2$$

- **Ensemble average – over many realizations of the jump paths**

$$\left\langle \left(\Delta r_{diff}(t)\right)^2 \right\rangle = \sum_{\substack{i=1,j=1 \\ i \neq j}}^{n(t)} \langle \vec{a}_i \cdot \vec{a}_j \rangle + \sum_{i=1}^{n(t)} \langle (\vec{a}_i)^2 \rangle$$

- **Markov process – no correlation between consecutive jumps**

$$\langle \vec{a}_i \cdot \vec{a}_j \rangle = 0$$

- **Square length is constant**

$$(\vec{a}_i)^2 = a^2$$

Mean square displacement in time (tracer diffusion)

- **Square of the diffusion length in time**

$$\left\langle \left(\Delta r_{diff}(t) \right)^2 \right\rangle = n(t) a^2 P\left(\Delta E_{diff}\right)$$

- **Number of jumps**

$$n(t) = \frac{t}{\tau_o} = t\,\nu$$

- **Probability of jump** $P\left(\Delta E_{diff}\right)$

$$P\left(\Delta E_{diff}\right) = exp\left[-\frac{\Delta E_{diff}}{kT}\right]$$

- **Distance in tracer diffusion**

$$\left\langle \left(\Delta r_{diff}(t) \right)^2 \right\rangle = n(t) a^2 exp\left[-\frac{\Delta E_{diff}}{kT}\right] = \frac{a^2 t}{\tau_o} exp\left[-\frac{\Delta E_{diff}}{kT}\right]$$

Tracer diffusion

- **Tracer diffusion on surface (d = 2)**

$$\left\langle \left(\Delta r_{diff}(t) \right)^2 \right\rangle = 2dDt = 4D_{sur}t$$

- **Jumps distance**

$$\left\langle \left(\Delta r_{diff}(t) \right)^2 \right\rangle = a^2 \nu t \, exp\left[-\frac{\Delta E_{diff}}{kT} \right]$$

- **Diffusion in d = 2 systems**

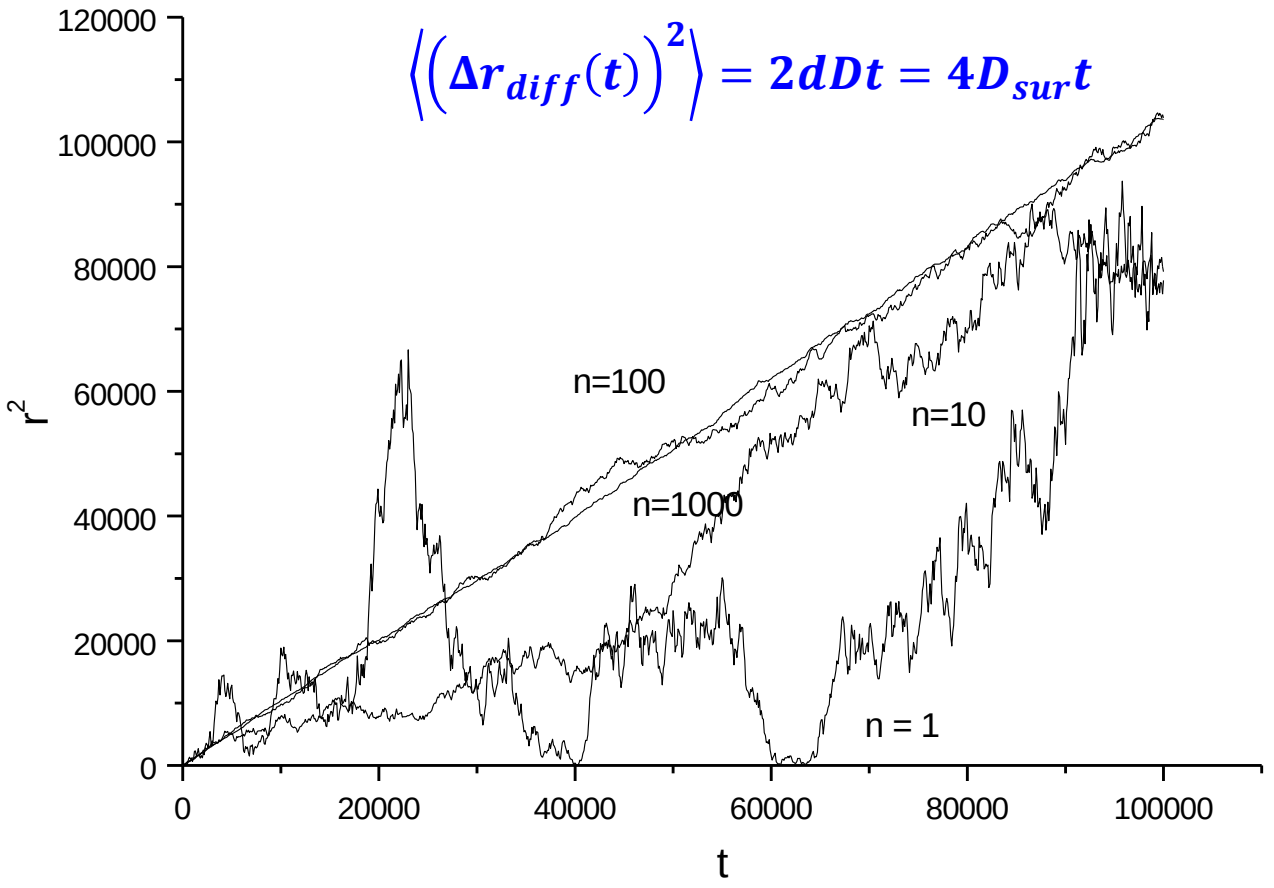
$$D = \frac{a^2 \nu}{2d} exp\left[-\frac{\Delta E_{diff}}{kT} \right]$$

- **Diffusion on surface**

$$D_{sur} = \frac{a^2 \nu}{4} exp\left[-\frac{\Delta E_{diff}}{kT} \right]$$

Tracer diffusion in square lattice

- **Averaging over defined number of realizations**

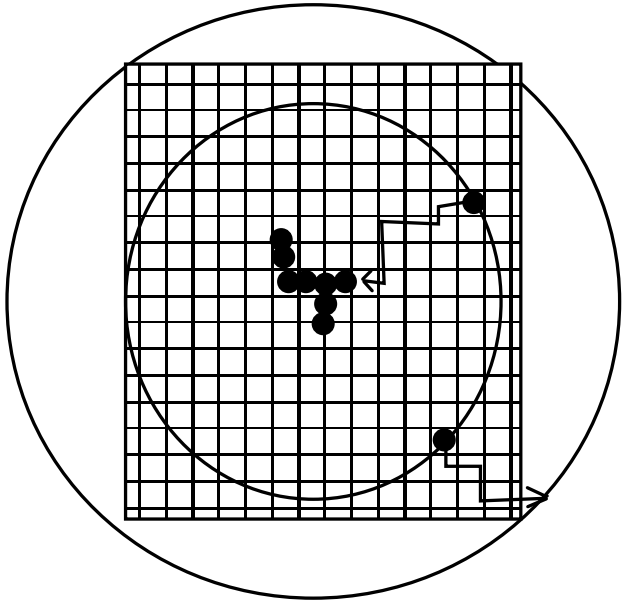


- **Linear dependence is attained in large number of realizations**

Purely kinetic growth model – diffusion limited aggregation (DLA)

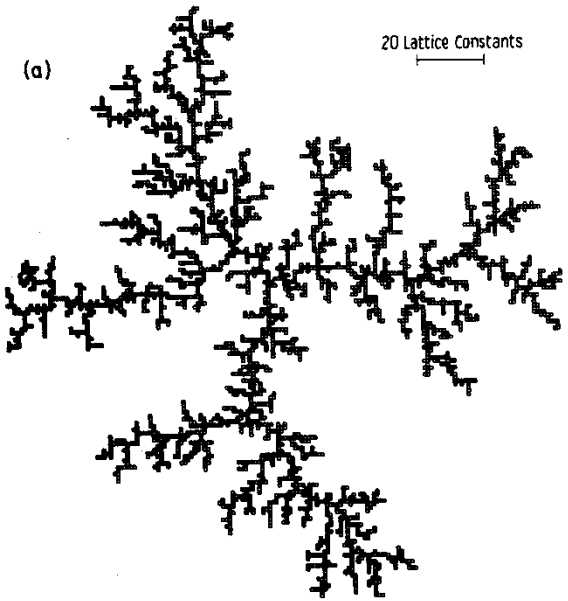
- **Molecule start at far distance**
- **Random jump direction at square lattice**
- **At contact the molecule is irreversibly included**

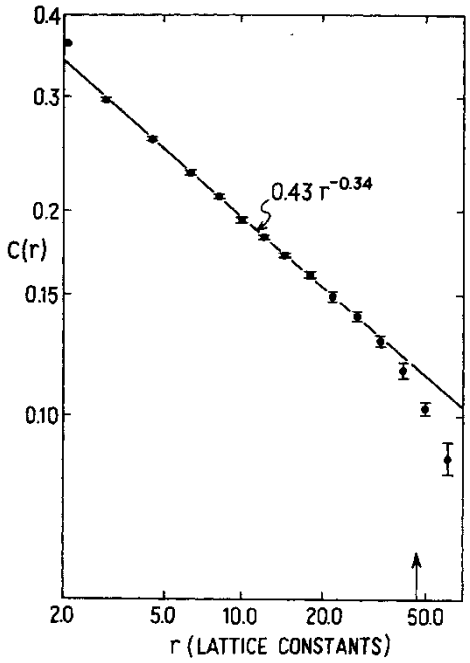
- **Above process is called Diffusion Limited Aggregation**

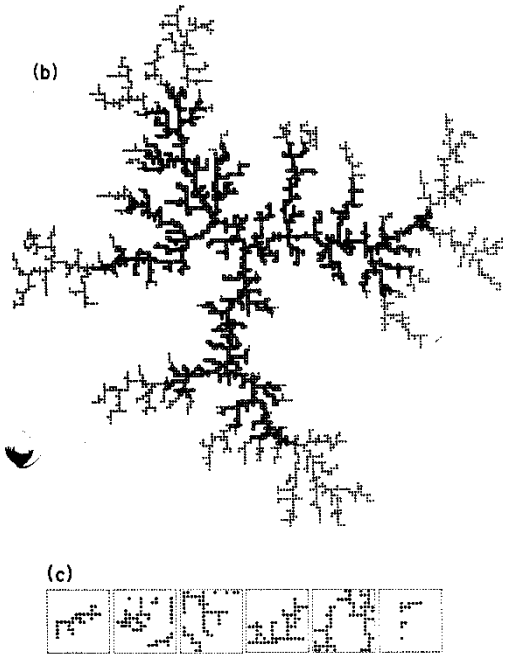


T. A. Witten Jr. & L.M. Sander Phys. Rev. Lett. 47 (1981) 1400

DLA – growth of fractal objects







- **Correlation function**

$$C(r) = \frac{1}{N}\sum_{r'} \rho(r')\rho(r+r')$$

$$C(r) \sim r^{2-D}$$

- **Geometric dimensionality (Hausdorff)**

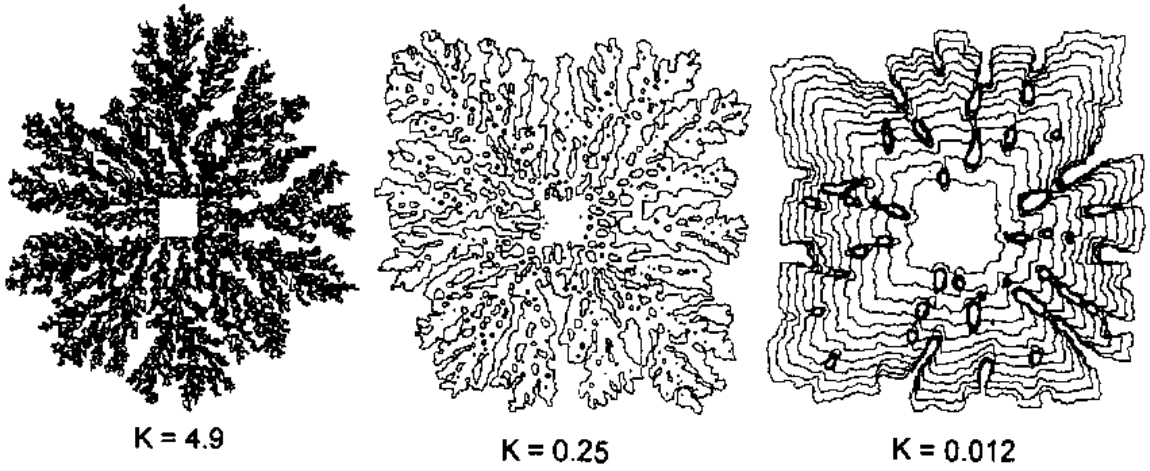
$$C(r) \sim r^{-0.343 \mp 0.004}$$

$$D = 1.695 \mp 0.002$$

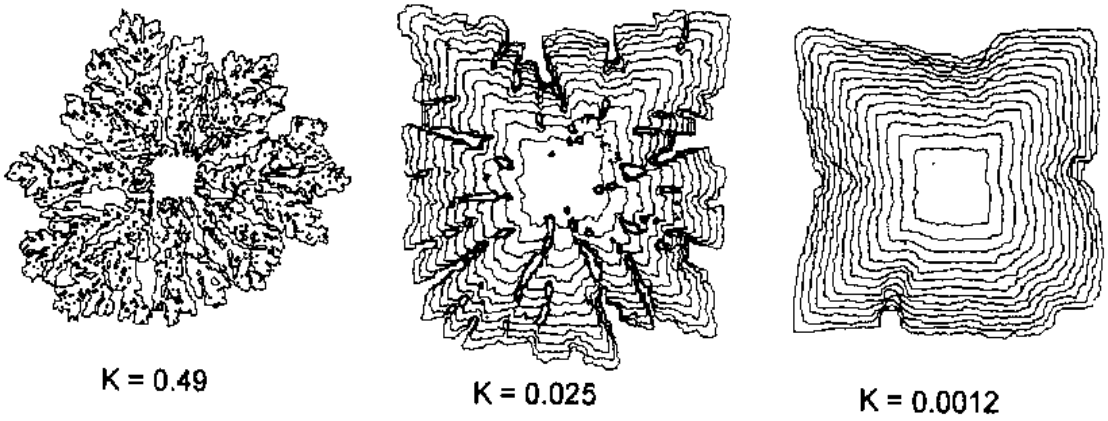
T. A. Witten Jr. & L.M. Sander Phys. Rev. Lett. 47 (1981) 1400

Combined model – transition from fractal to crystal growth

Dense fractal



- **Shape – 1000 atoms**

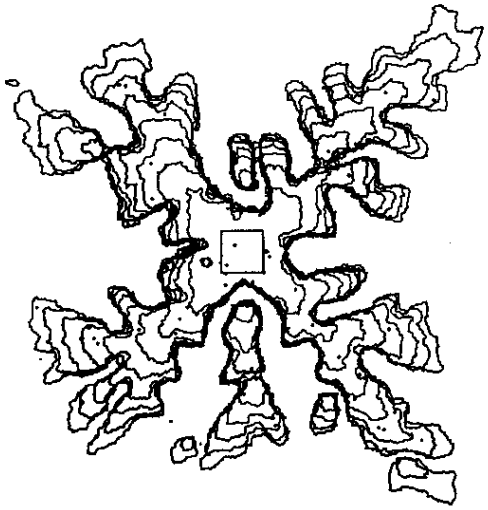


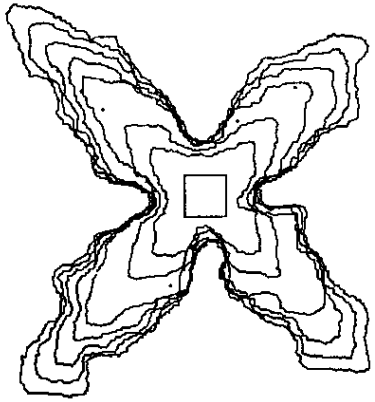
Crystal

$$K = (1+\sigma)\, exp\left[-\frac{2\phi + \Delta E_{bar}}{kT}\right]$$

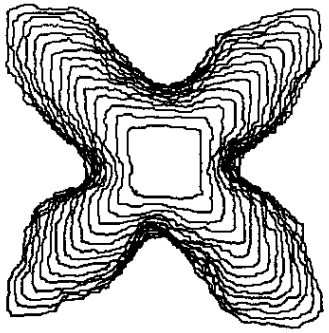
S. Krukowski J.C. Tedenac, J. Cryst. Growth160 (1996) 167

Combined model – transition from fractal to crystal growth

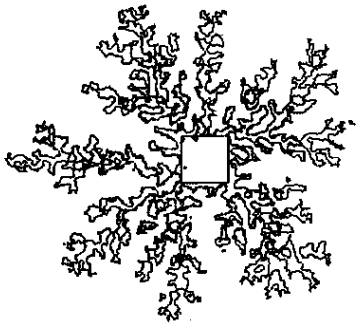


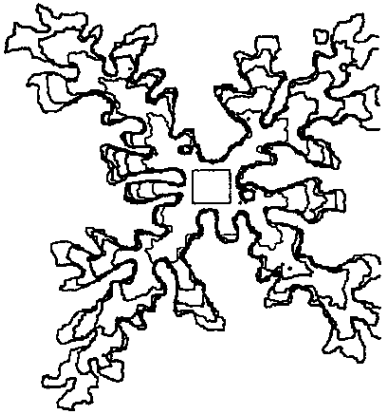


Needle crystal

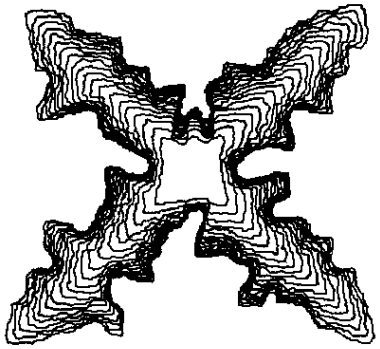


Fractal





Dendrite



S. Krukowski J.C. Tedenac, J. Cryst. Growth 203 (1999) 269

Literature

Nucleation

- **J. B. Zeldovich, Acta Physicochim. USSR 18 (1943) 1**

Diffusion

- **G. Ehrlich & K. Stolt, Ann. Rev. Phys. Chem. 31 (1980) 603**
- **G.L. Kellog, T.T. Tsong& P. Cowan, Surf. Sci. 70 (1978) 485**
- **R. Gomer, Rep. Prog. Phys. 53 (1990) 917**
- **W. Schommers, P. Von Blanckenhagen, Structure and Dynamics of Surfaces II, Ch. 3.2, Springer 1987.**

Fractals

- **B. Mandelbrot, Fractal Geometry of Nature, 1982**