

# Crystal Growth: Physics, Technology and Modeling

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## Lecture 5. Thermodynamics of growth processes

<http://www.unipress.waw.pl/~stach/cg-2024-25>

# Equilibrium

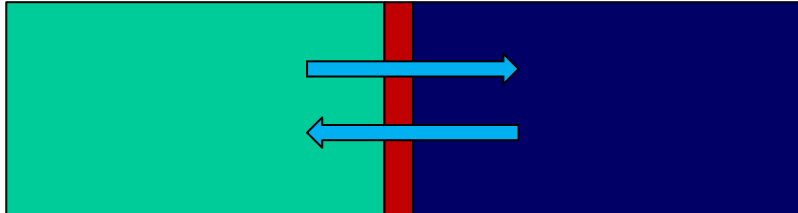
## Equilibrium - extent

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

## Equilibrium - type

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

## Phase equilibrium - fluxes



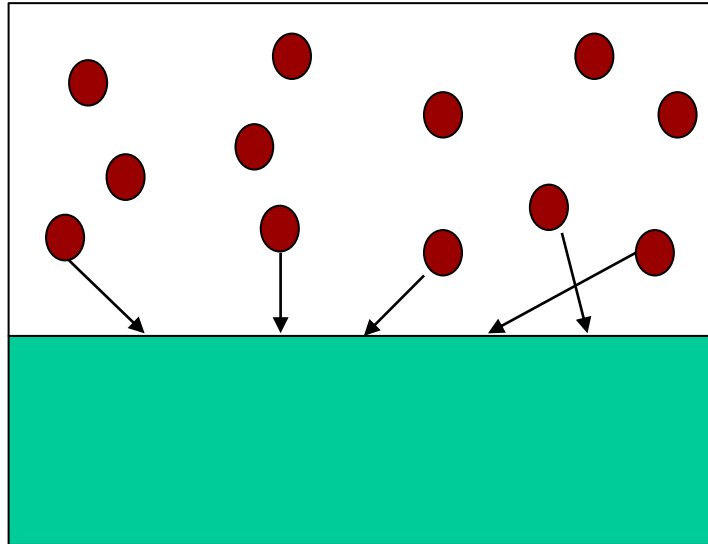
$$\vec{g} \equiv \frac{\Delta G \vec{n}}{\Delta S \Delta t} \quad \text{Flux}$$

$\vec{n}$  = 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 -  $\Delta G$ ) transported across unit of surface ( $\Delta S$ ) in the unit of time ( $\Delta t$ )
- Two phase state, stationary, i.e. time independent: fluxes are balanced
  - mechanical  $\rightarrow$  momentum flux
  - thermal  $\rightarrow$  energy flux
  - chemical  $\rightarrow$  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

$$pV = nkT$$

$$p = nkT$$

$$k = 1.3800648 \times 10^{-23} \text{ J/K}$$

- Mean free path  $\lambda$  and mean free flight time  $\tau$ , thermal velocity  $\langle v \rangle$

$$\lambda = \frac{1}{\sqrt{2}n\sigma}$$

$$\tau = \frac{\lambda}{\langle v \rangle}$$

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

- 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)**

$$T = 273.15 \text{ K}$$

$$p = 1 \text{ atm} = 101325 \text{ Pa} = 101325 \text{ N/m}^2$$

- **Standard conditions (from 1982)**

$$T = 273.15 \text{ K}$$

$$p = 1 \text{ bar} = 100000 \text{ Pa} = 100000 \text{ N/m}^2$$

- **Normal conditions**

$$T = 293.15 \text{ K}$$

$$p = 1 \text{ atm} = 101325 \text{ Pa} = 101325 \text{ N/m}^2$$

## Ideal gas - numbers

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

- Average thermal velocity  $\langle v \rangle$  at  $T = 300 \text{ K}$

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

- Mean free path  $\lambda$  and mean free flight time  $\tau$

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

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

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

## Surface geometry

- GaN density (Ga-N molecules – in fact pairs of atoms)  $n_{GaN}$

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

- GaN molar volume  $v_{GaN}$

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

- GaN surface atom density  $\eta_{GaN}$

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

- GaN surface area for single site (0001) surface  $\zeta_{GaN}$

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

**GaN lattice constant:  $a = 3.1890 \text{ \AA}$**



## Fluxes & surface equilibrium

- Average molecular flux  $I$

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

- Site impact frequency  $\nu$

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

- Adsorption rate  $r$

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

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

## Sticking coefficient

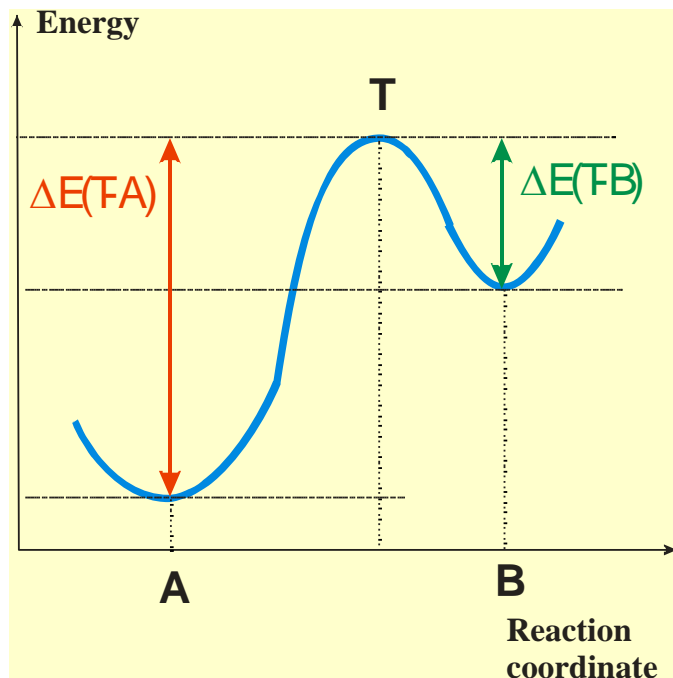
- **Sticking coefficient – probability of transition  $P$  from initial ( $I$  - vapor) to final ( $F$  - surface attached) state**

$$\sigma \equiv P (I \rightarrow F)$$

- **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**

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

- **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:

$$F = -k_B \ln Q = -kT \ln(Q_{tr} Q_{vib} Q_{rot})$$

## Transition state – Arrhenius law

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

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

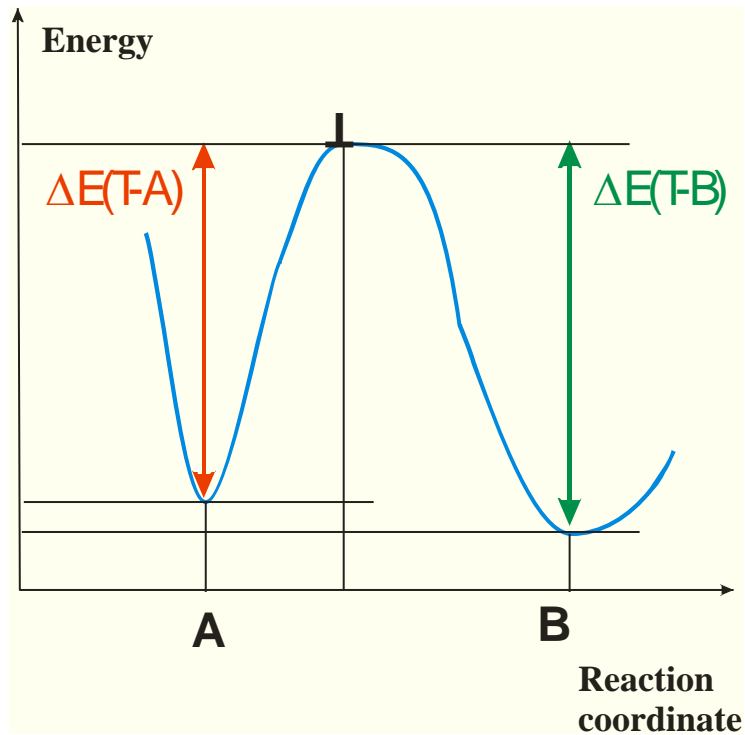
$$\frac{P(T)}{P(A)} = \exp \left[ \frac{S(T) - S(A)}{k} \right] \exp \left[ -\frac{E(T) - E(A)}{kT} \right]$$

- **No entropy difference:**

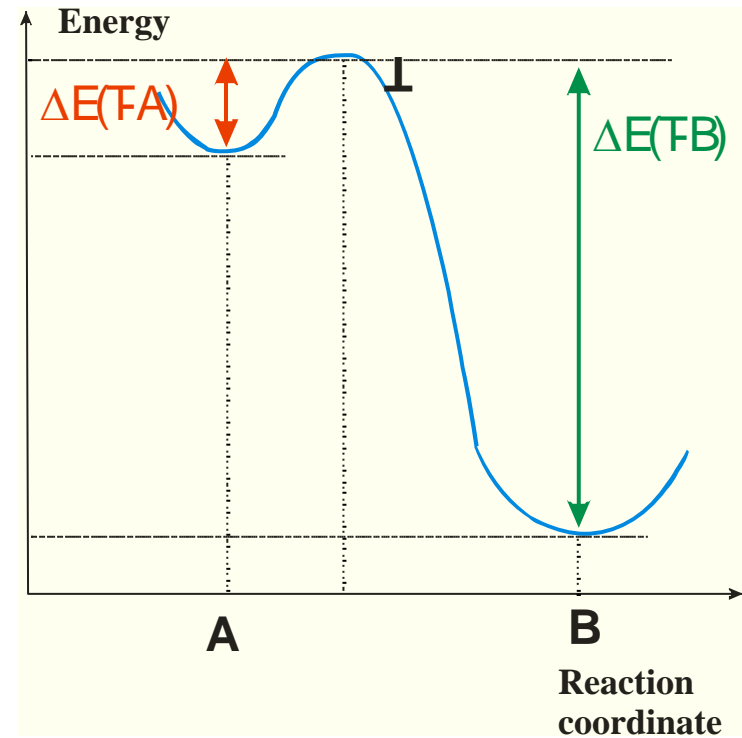
$$\frac{P(T)}{P(A)} \cong \exp \left[ -\frac{E(T) - E(A)}{kT} \right] = \exp \left[ -\frac{\Delta E}{kT} \right]$$

# Energetic properties of the growth models

- Dynamic models



- Kinetic models

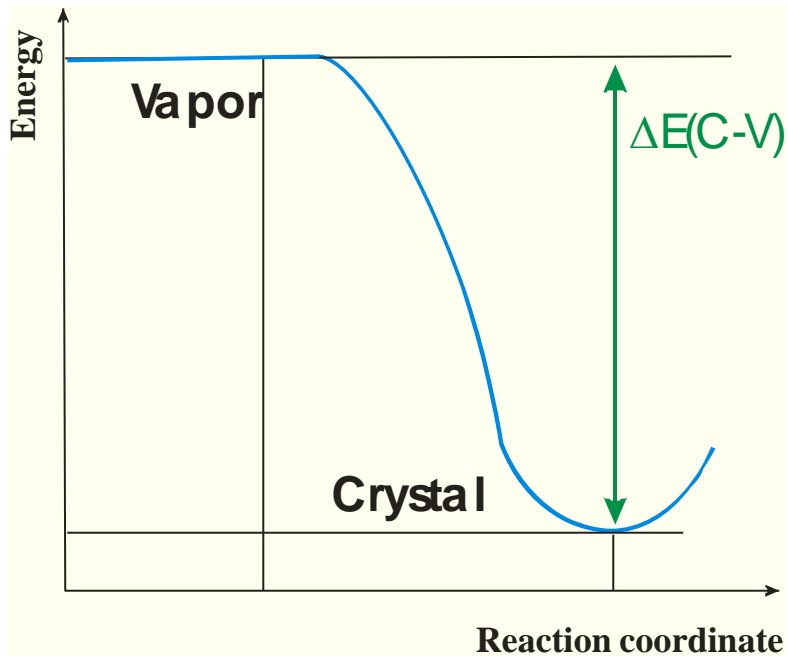


$$r = \nu P(I \rightarrow F) = \nu \exp \left[ -\frac{\Delta E}{kT} \right]$$

# 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 ( $v \rightarrow c$ )

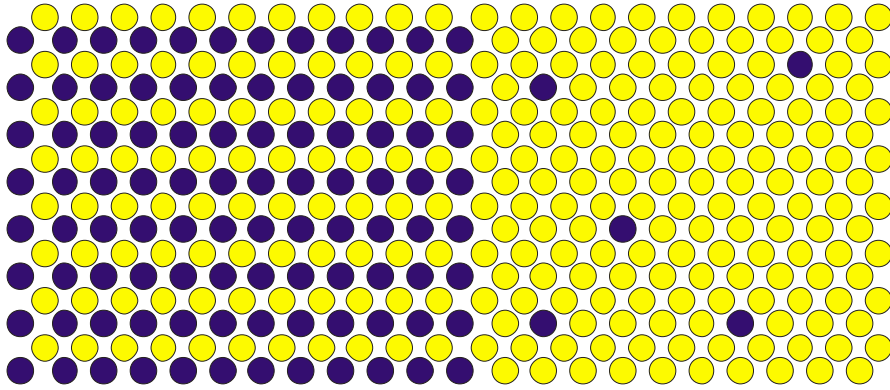
$$r = I \zeta = \frac{p \zeta}{\sqrt{2\pi m k T}} = n \zeta \sqrt{\frac{k T}{2\pi m}}$$

- Sublimation ( $c \rightarrow v$ )

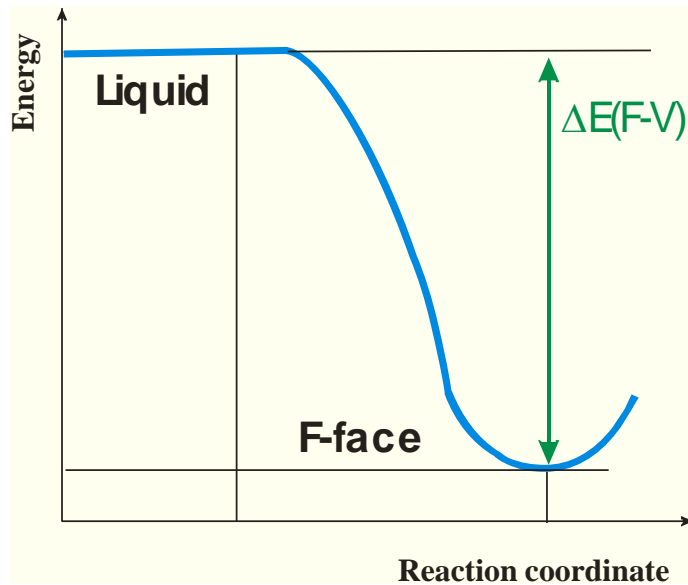
$$r = v \exp\left[-\frac{\Delta E(C - V)}{k T}\right]$$



# Liquid – crystal growth models



- Diffusion
- Crystallization (l → c)



- Dissolution (c → l)

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

# Growth dynamics – deviation from equilibrium

- **Equilibrium**

- **Dynamical**

- **Thermal**

- **Chemical**

$$p_v = p_l = p_{eq}$$

$$T_v = T_l = T_{eq}$$

$$\mu_v = \mu_l = \mu_{eq}$$

- **Deviation from equilibrium**

- **Supersonic**

- **Supercooling**

- **Supersaturation**

$$\Delta\tau = \frac{T_{l,v} - T_{eq}}{T_{eq}}$$

$$\Delta\mu = \frac{\mu_{l,v} - \mu_{eq}}{kT}$$

## Supersaturation $\sigma$ 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

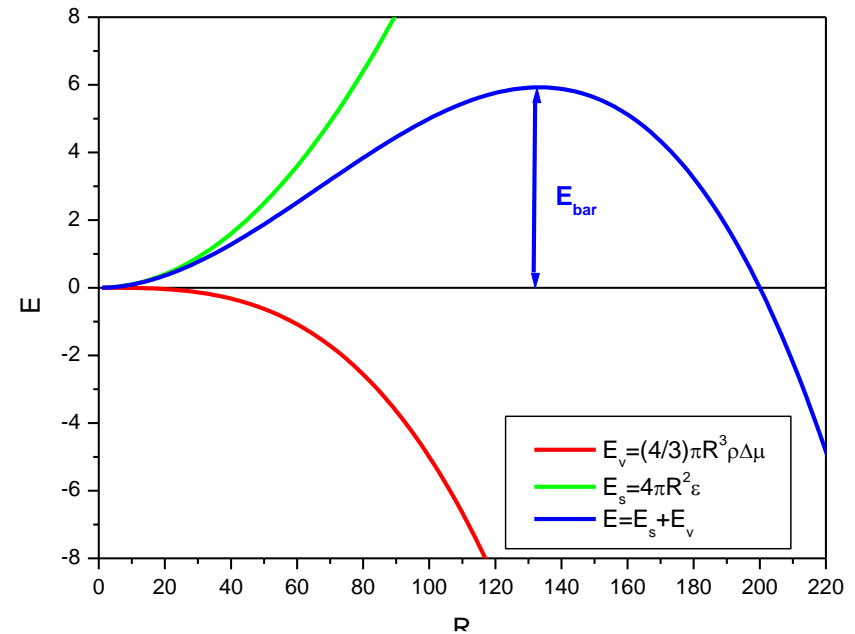
$$\Delta E = \frac{4\pi R^3 \rho \Delta\mu}{3} + 4\pi R^2 \gamma$$

Surface term dominates for small R

Volume term dominates for large R

Nucleation critical radius

$$R_{crit} = \frac{2\gamma}{\rho |\Delta\mu|} = \frac{2\gamma}{\rho kT\sigma}$$



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  $P(R_{crit})$

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

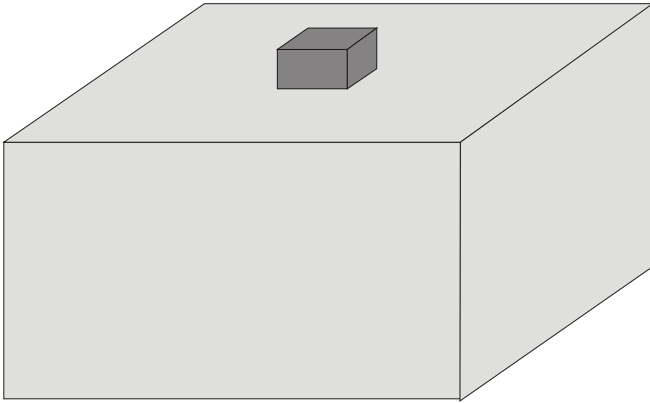
Number of sites at the surface  $N_s$

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

Attempt frequency  $\nu$

## 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 -  $N_L$

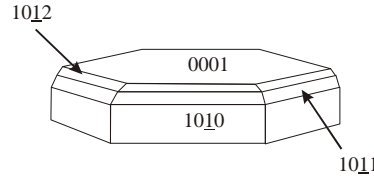
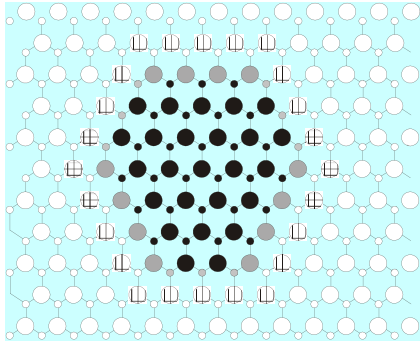
$$N_L = \frac{L}{a}$$

Edge length -  $L$

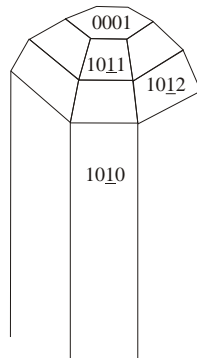
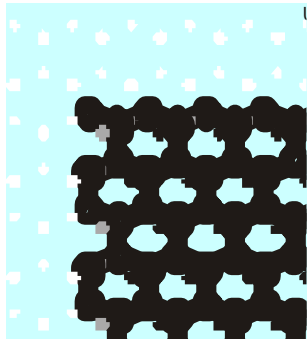
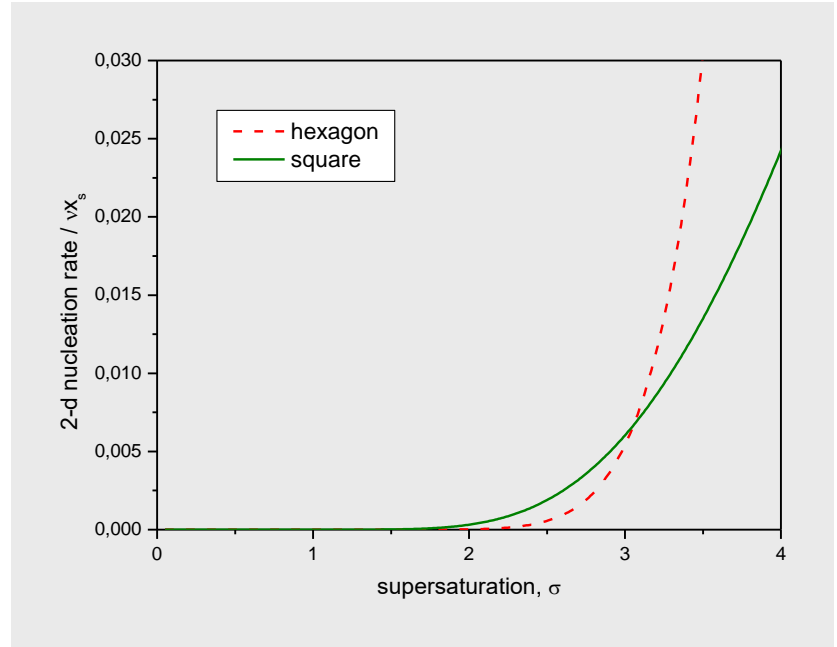
Lattice constant -  $a$

Edge energy for lattice constant  
– energy of broken bond -  $\phi$

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



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



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

- **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
- Mean free flight time
- Average thermal velocity

$$\lambda = \frac{1}{\sqrt{2} n \sigma}$$

$$\tau = \frac{\lambda}{\langle v \rangle}$$

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

**Total scattering crosssection (the same symbol as superaturation) -  $\sigma$**

## 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

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

Attempt frequency  $\nu$

- Jump probability

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

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

# Lattice diffusion – dimension of the space

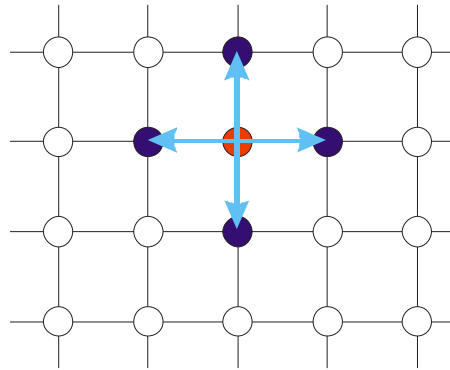
- Simple cubic lattice

- $d = 1$



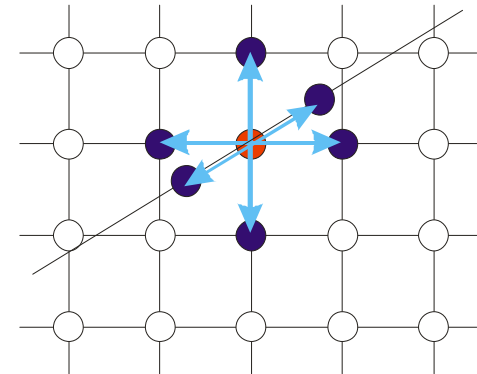
- $C = 2$

- $d = 2$



- $C = 4$

- $d = 3$



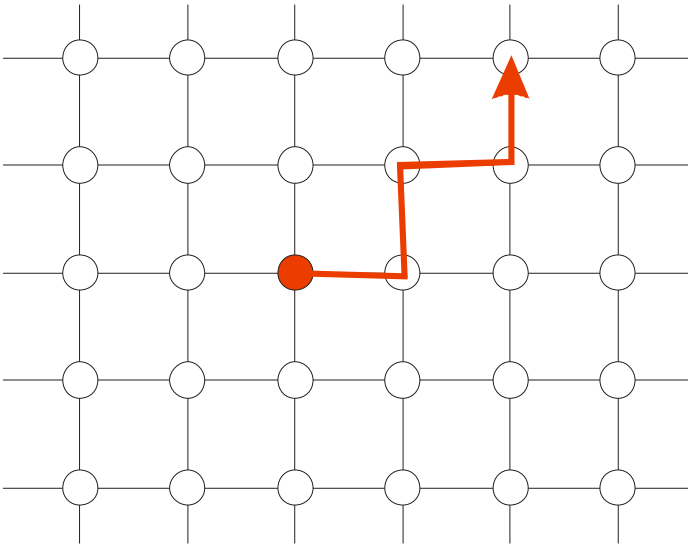
- $C = 6$

- 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**

$$n = \frac{t}{\tau_0} = t \nu$$

## 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**

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

- **Number of jumps**

$$n(t) = \frac{t}{\tau_0} = t \nu$$

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

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

- **Distance in tracer diffusion**

$$\left\langle \left( \Delta r_{diff}(t) \right)^2 \right\rangle = n(t) a^2 \exp \left[ -\frac{\Delta E_{diff}}{kT} \right] = \frac{a^2 t}{\tau_0} \exp \left[ -\frac{\Delta E_{diff}}{kT} \right]$$

## 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**

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

- **Diffusion in  $d = 2$  systems**

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

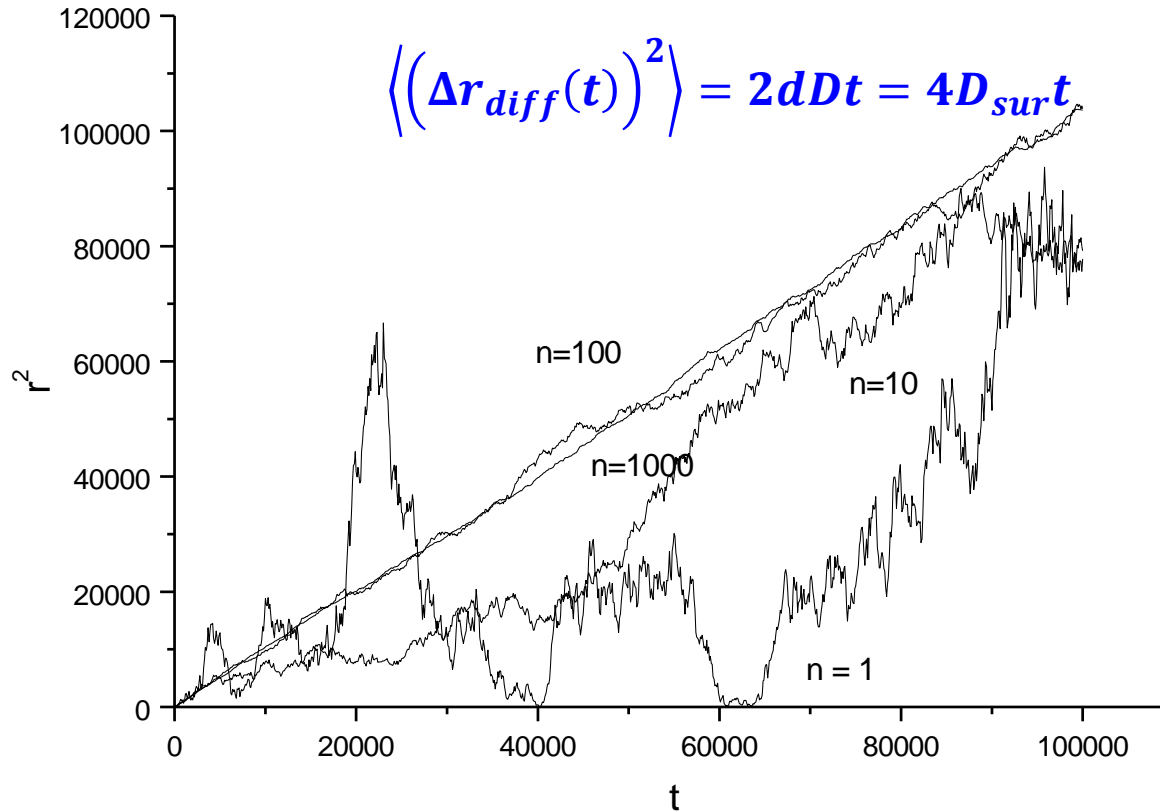
- **Diffusion on surface**

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



# Tracer diffusion in square lattice

- **Averaging over defined number of realizations**

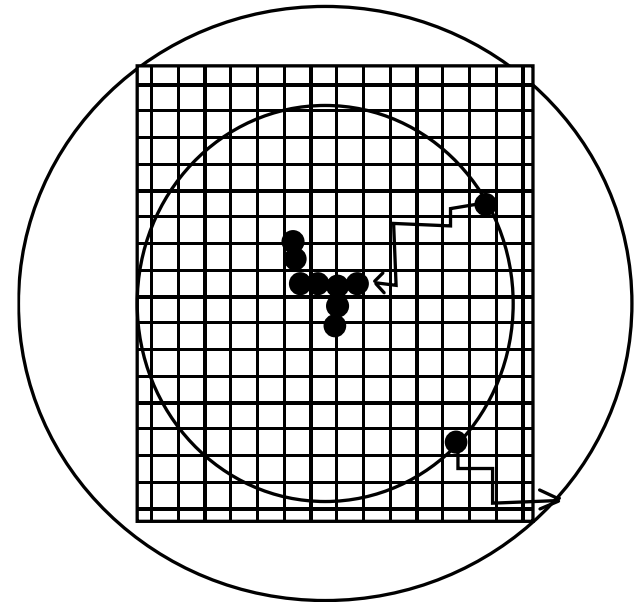


- **Linear dependence is attained in large number of realizations**

*S. Krukowski L. A. Turski, Phys. Lett. 175 (1993) 349*

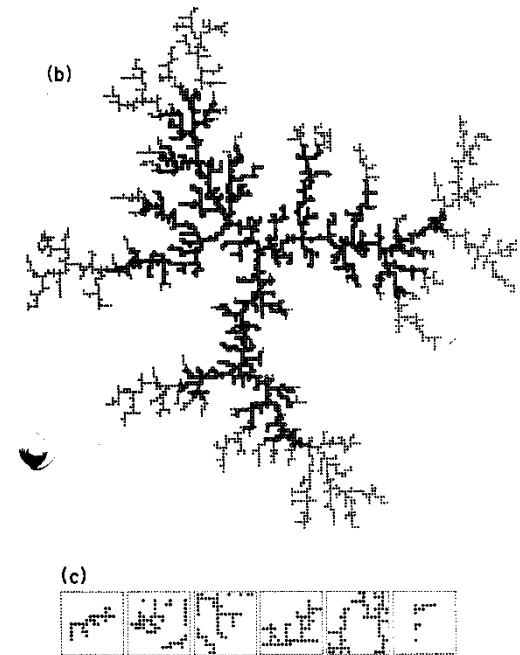
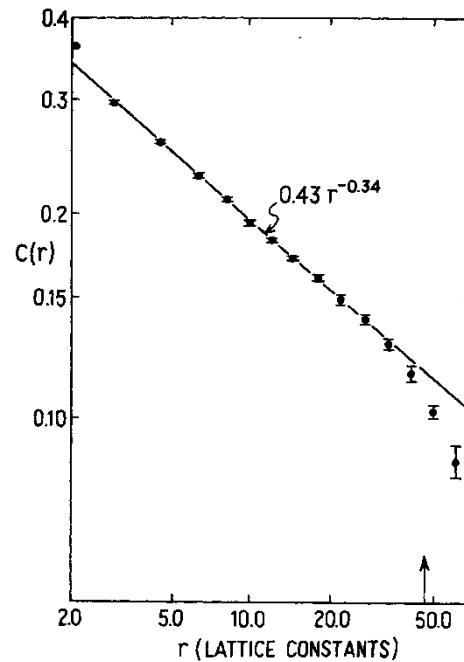
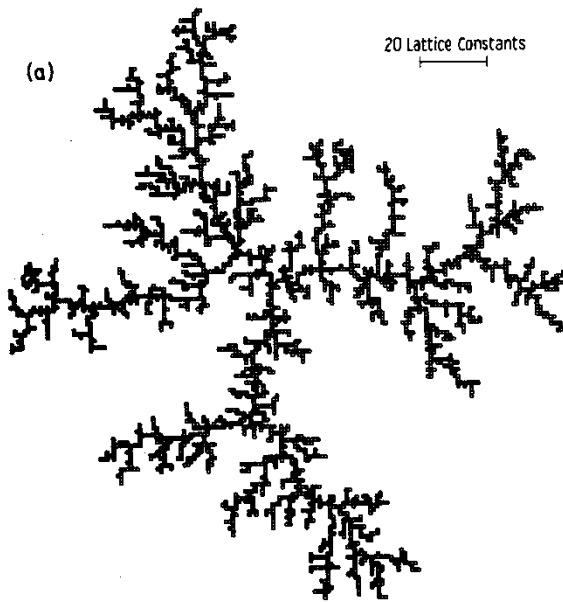
# Purely kinetic growth model – diffusion limited aggregation (DLA)

- 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)

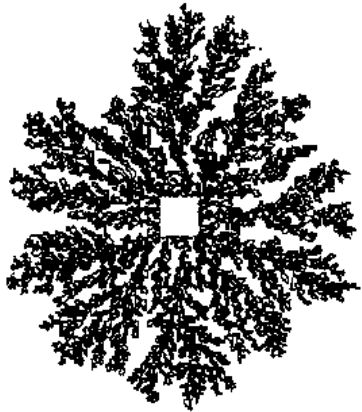
$$C(r) \sim r^{-0.343 \mp 0.004}$$

$$D = 1.695 \mp 0.002$$

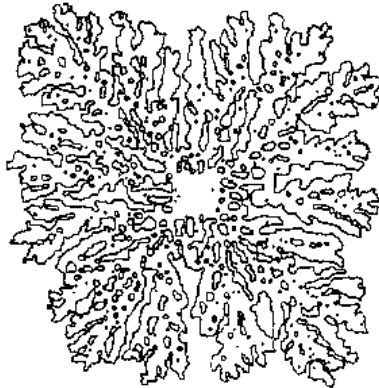
*T. A. Witten Jr. & L.M. Sander Phys. Rev. Lett. 47 (1981) 1400*

# Combined model – transition from fractal to crystal growth

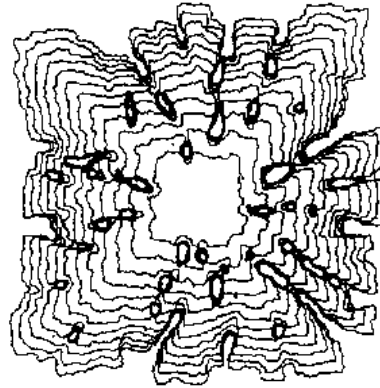
## Dense fractal



K = 4.9

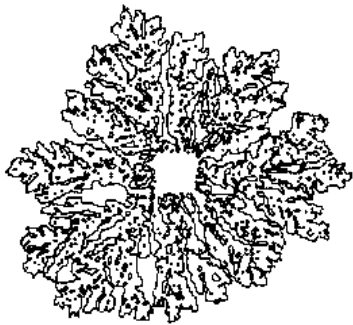


K = 0.25

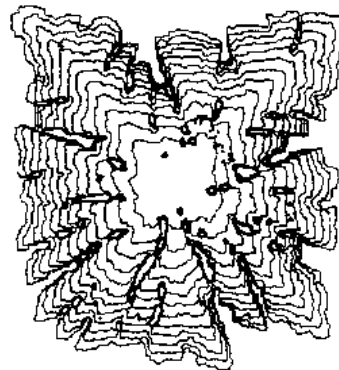


K = 0.012

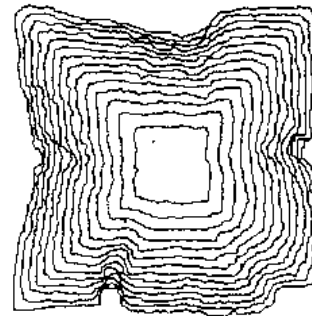
- Shape – 1000 atoms



K = 0.49



K = 0.025



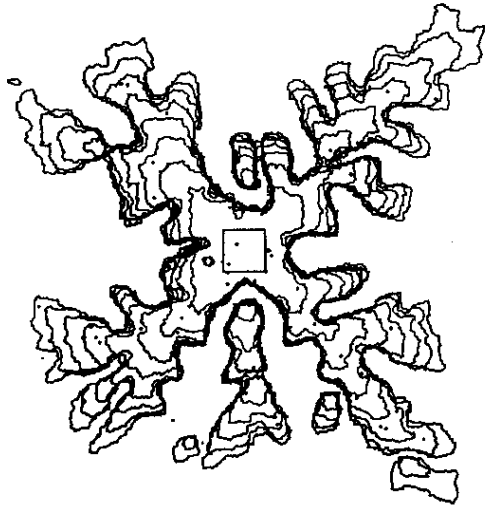
K = 0.0012

## Crystal

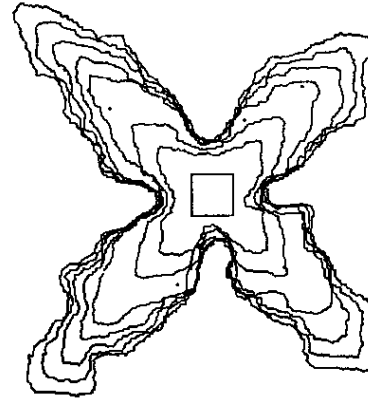
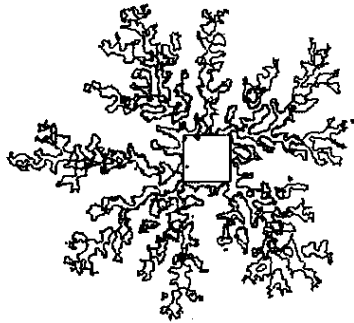
$$K = (1 + \sigma) \exp \left[ -\frac{2\phi + \Delta E_{bar}}{kT} \right]$$

*S. Krukowski J.C. Tedenac, J. Cryst. Growth 160 (1996) 167*

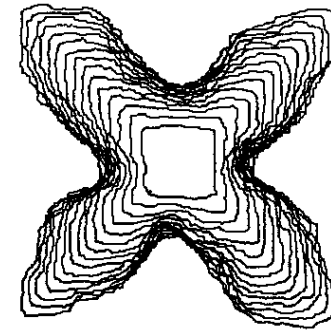
# Combined model – transition from fractal to crystal growth



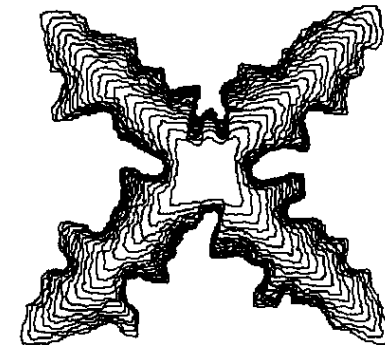
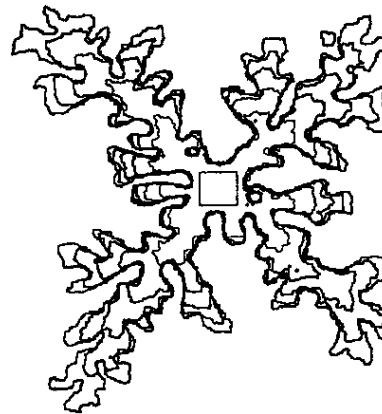
Fractal



Needle crystal



Dendrite



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

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