

Crystal Growth: Physics, Technology and Modeling

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Lecture 5. Thermodynamics of growth processes

<http://www.unipress.waw.pl/~stach/cg-2021-22>

Equilibrium

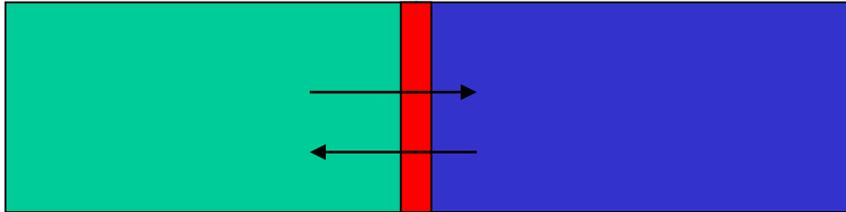
Equilibrium:

- between different phases
- inside phase:
 - i/ spatial – local equilibrium
 - ii/ different degrees of freedom – partial equilibrium

Equilibrium:

- mechanical
- thermal
- chemical

Phase equilibrium



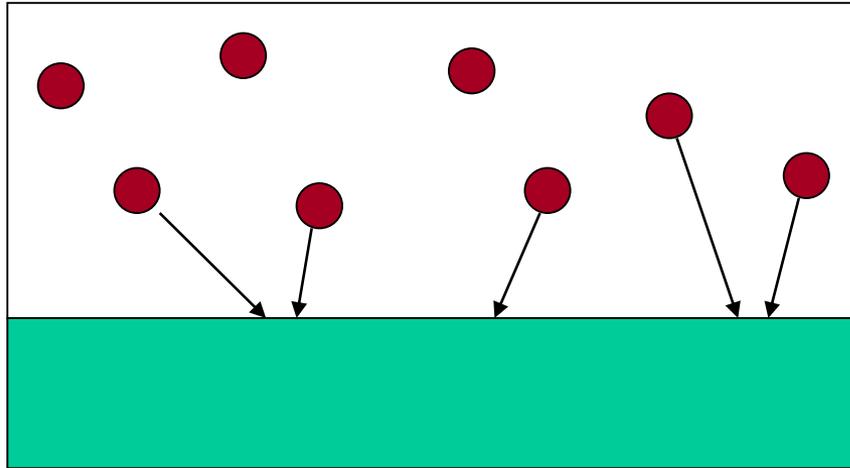
$$\vec{g} = \frac{\Delta G \vec{n}}{\Delta S \Delta t}$$

\vec{n} – unit vector normal to the surface

- Two phase state, stationary, i.e. time independent , such that introduction of the barriers does not introduce any change.
- Flux – amount on physical quantity (conserved - stream) transported across unit of surface in the unit of time.
- Two phase state, stationary, i.e. time independent , such that fluxed are balanced:
 - mechanical \rightarrow momentum flux
 - thermal \rightarrow energy flux
 - chemical \rightarrow mass flux

Fluxes – equilibrium

- **Two phases: solid and vapor**



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

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

Ideal gas – equilibrium and transport properties

- Equation of state

$$pV = NkT \quad p = nkT \quad k = 1.3800648 \times 10^{-23} \frac{J}{K}$$

- Mean free path λ and mean free time τ

$$\lambda = \frac{1}{\sqrt{2}n\sigma} \quad \tau = \frac{\lambda}{\langle v \rangle} \quad \langle v \rangle = \sqrt{\frac{3kT}{m}}$$

σ - total scattering crosssection

- Average mass 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)

$$T = 273.15K$$

$$p = 1 \text{ atm} = 101325 \text{ Pa}$$

- Standard conditions (after 1982)

$$T = 273.15K$$

$$p = 1 \text{ bar} = 10^5 \text{ Pa}$$

- Normal conditions

$$T = 293.15K$$

$$p = 1 \text{ atm} = 101325 \text{ Pa}$$

Ideal gas - number

- **Density**

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

- **Average thermal velocity at 300K**

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

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

$$\lambda = \frac{1}{\sqrt{2}n\sigma} = 3 \times 10^{-6} \text{ m}$$

$$\tau = \frac{\lambda}{\langle v \rangle} = 5.6 \times 10^{-9} \text{ s}$$

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 (GaN molecules)

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

- GaN molar volume GaN

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

- GaN surface atom (sites) density – average & GaN(0001)

$$\eta = n^{2/3} = 8.671 \times 10^{14} \text{ cm}^{-2} \quad \eta = \frac{4}{3a^2\sqrt{3}} = 7.612 \times 10^{14} \text{ cm}^{-2}$$

- GaN surface for single atom (site) – average & GaN(0001)

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

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

Fluxes & surface equilibrium

- Average molecule flux (normal conditions):

$$I = \frac{p}{\sqrt{2\pi m k T}} = 2.875 \times 10^{23} \text{ cm}^{-2} \text{ s}^{-1}$$

- Site molecule impact frequency

$$\nu = I \cdot \sigma = 3.778 \times 10^8 \text{ s}^{-1}$$

- Adsorption – flux and sticking coefficient

$$R = \zeta \cdot \nu \cdot \sigma = I \cdot \sigma$$

- Adsorption rate – frequency and sticking coefficient

$$r = \nu \cdot \sigma$$

σ – sticking coefficient, probability of attachment ($0 \leq \sigma \leq 1$)

Sticking coefficient

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

$$\sigma = P(i \rightarrow f)$$

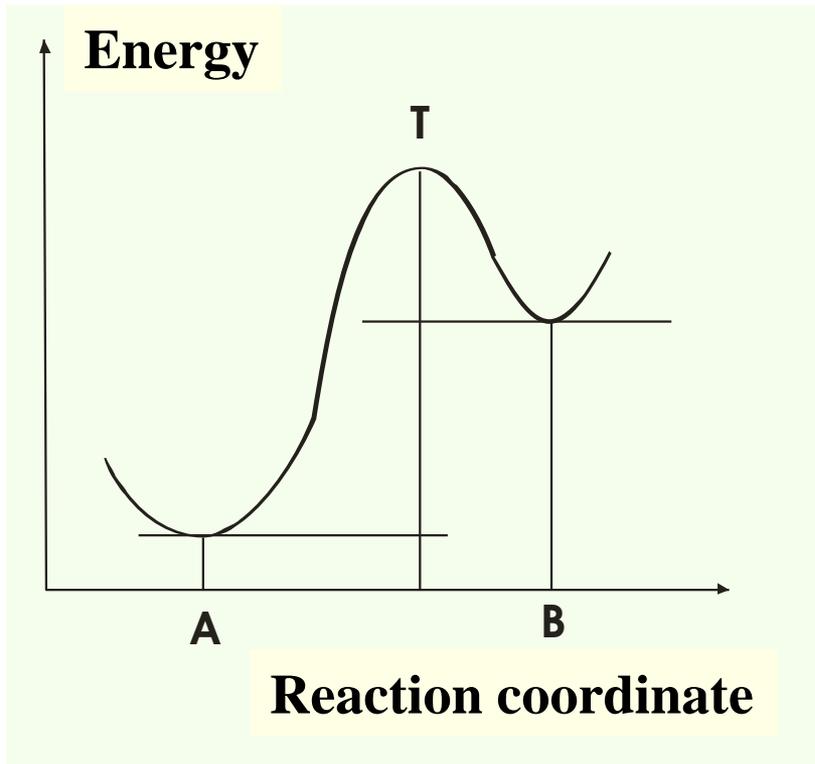
- **Probability of transition is calculated using transition state theory.**

Transition state T has

- **energy higher than initial state**
- **energy landscape – saddle point**
- **no return from T to initial state.**

Transition state – time evolution of the system

- **Time evolution – chemical kinetic approach:**



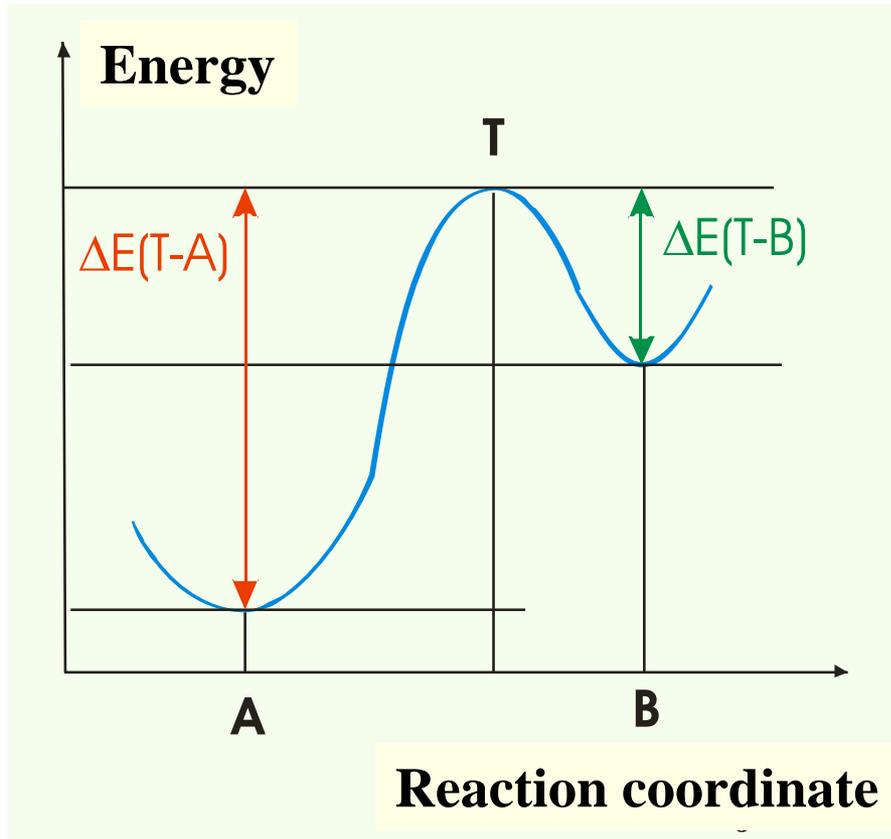
Energy barriers:

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

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

Transition state – energy barriers

- Time evolution of the system:



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 the arrival

- Free energy of the system having temperature T:

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

Tolman principle

- Probability of the system in a given macro state is proportional to the volume of the phase space Q compatible with the macrostate.
- For reaction coordinate – the relative probability is therefore

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

Q(T) & Q(A) – statistical sums over the remaining degrees of freedom

Transition state – Arrhenius principle

- **No strong coupling to remaining degrees of freedom (dynamic – interaction Hamiltonian $\rightarrow Q(T)=Q(A)$)**

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

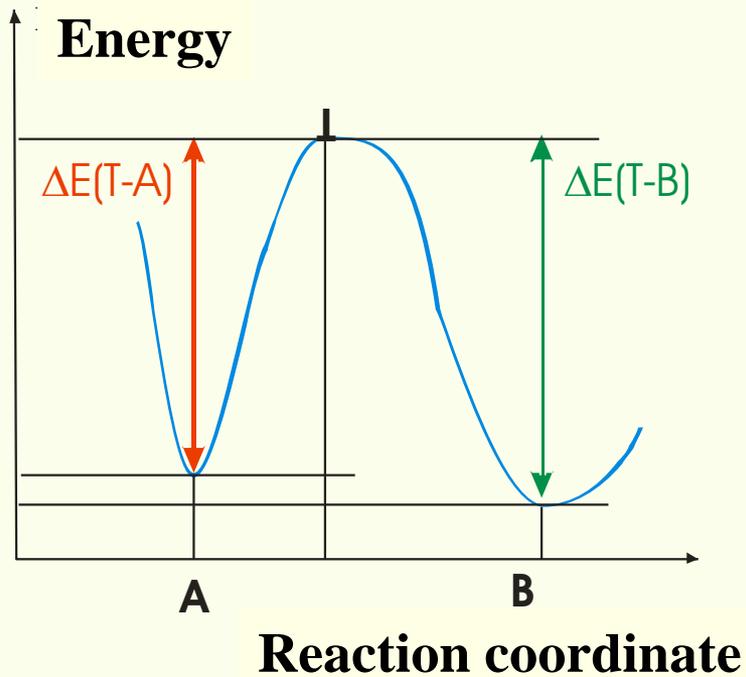
$$\frac{P(T)}{P(A)} = \exp \left[\frac{S(T) - S(A)}{k} \right] \exp \left[-\frac{E(T) - E(A)}{kT} \right]$$

- **In case of comparable entropies (no system reconstruction) Arrhenius relations holds:**

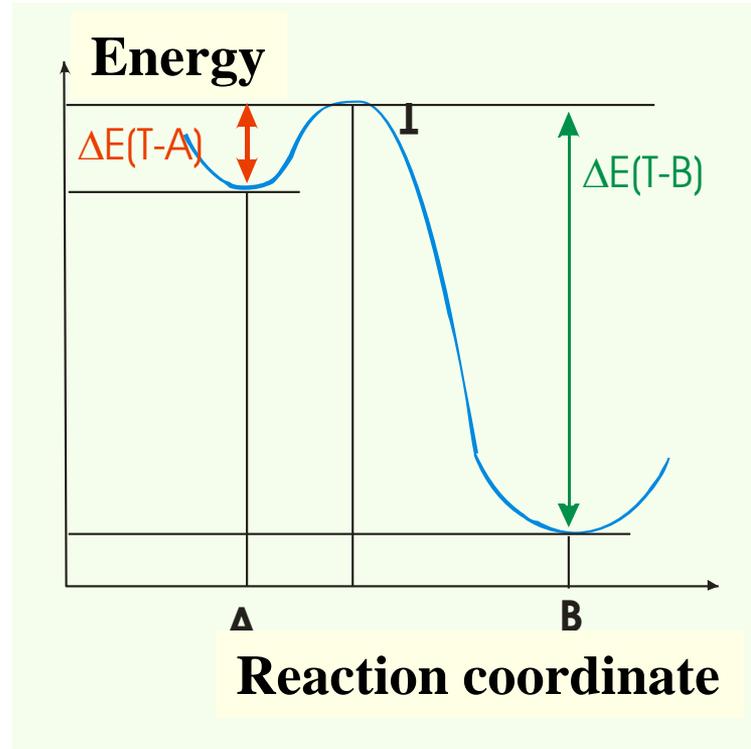
$$\frac{P(T)}{P(A)} \cong \exp \left[-\frac{E(T) - E(A)}{kT} \right] = \exp \left[-\frac{\Delta E}{kT} \right]$$

Energetic properties of growth models

Dynamic models



Kinetic models



$$R = \nu P(i \rightarrow f) = \nu \exp \left[-\frac{\Delta E}{kT} \right]$$

Growth models

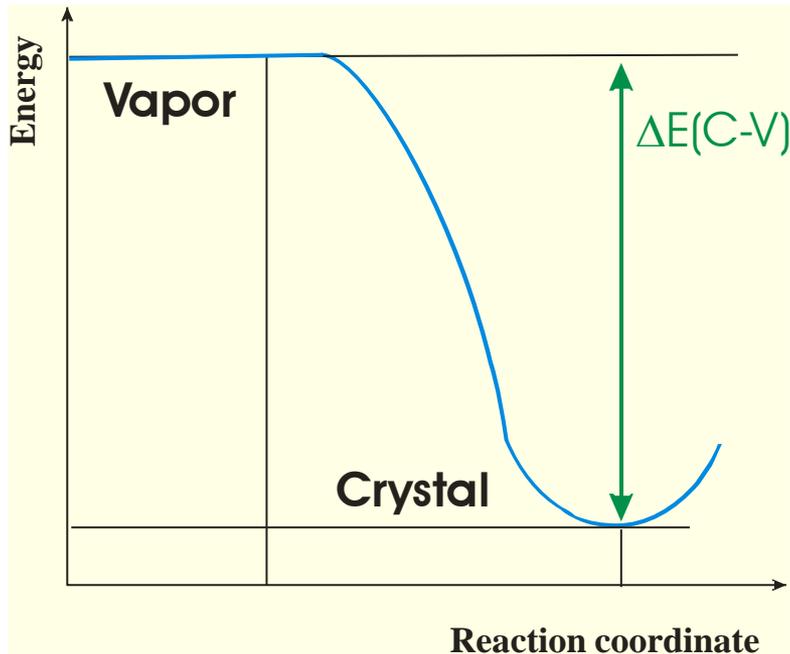
Dynamic models

- **Transitions forward and backward have comparable probability**
- **Both directions are important**
- **Equilibrium state exists**

Kinetic models

- **Probabilities are drastically different**
- **Alternatively, blockage of configurational or other type exists**
- **Equilibrium state is absent**

Vapor-crystal dynamic model



- Deposition for single site ($v \rightarrow c$)

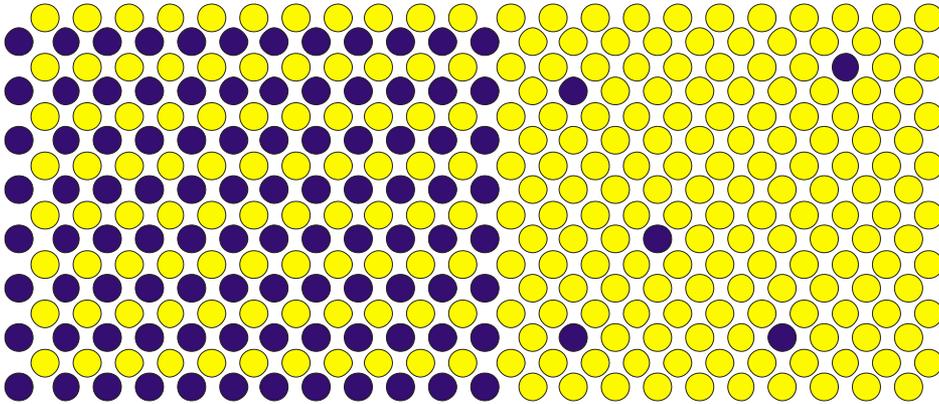
$$R = I\zeta = \frac{p\zeta}{\sqrt{2\pi mkT}} = n\zeta \sqrt{\frac{kT}{2\pi m}}$$

- Sublimation ($c \rightarrow v$)

$$R = \nu^* \exp\left[-\frac{\Delta E(K-G)}{k_B T}\right]$$

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

Liquid-crystal dynamic model

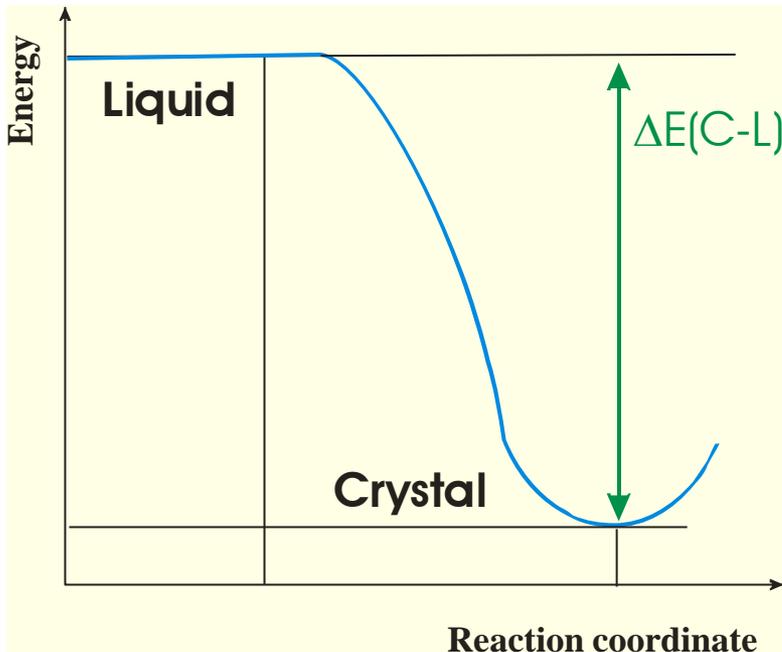


- **Diffusion**
- **Crystallization**

$$R = v$$

- **Dissolution**

$$R = v^* \exp\left[-\frac{\Delta E(K - C)}{k_B T}\right]$$



Thermodynamics of growth

Growth – deviation from equilibrium

Equilibrium:

- Dynamical

$$p_g = p_l = p_{eq}$$

- Thermal

$$T_g = T_l = T_{eq}$$

- Chemical

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

Deviation from equilibrium:

- Special processes

- Supercooling

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

- Supersaturation

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

Supersaturation 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

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

Under relatively low supersaturation the system is in metastable state – transition to stable state occurs via nucleation

Metastable states – nucleation barriers

Chemical potential of the solid is lower → transition to solid state.

Transition – creation of the finite size solid – surface energy density γ

Isotropic approximation – finite size system represented by the sphere of the radius R . The energy change is equal to

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

$\Delta\mu < 0$ – volume term is negative

$\gamma > 0$ – surface term is positive

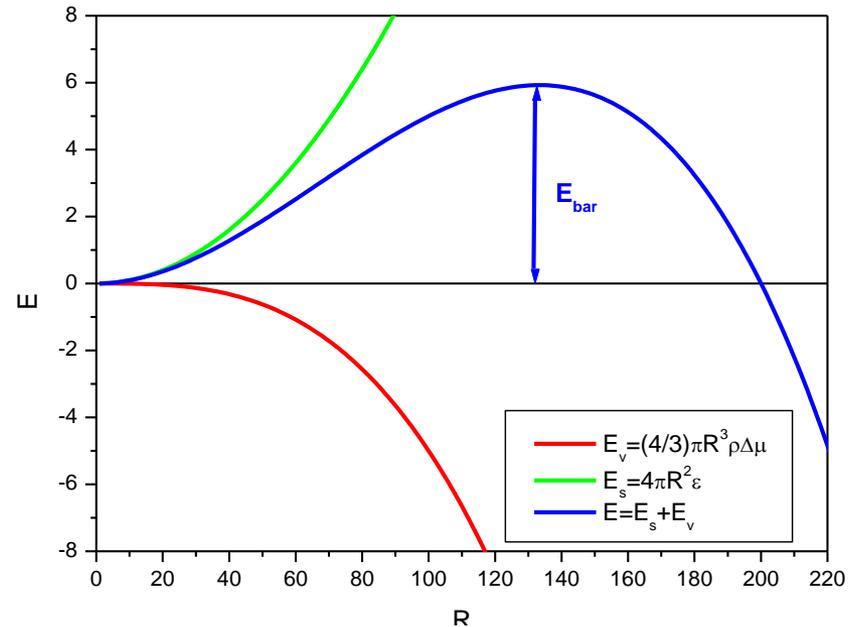
Nucleation barrier - size

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

Surface term dominates for low R,
volume term for large R.

Maximum energy radius is called
nucleation critical radius R_{crit} :

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



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

Both critical parameters become very large for low supersaturation σ .

Homogenous nucleation rate

Creation of new phase without contribution from the other bodies is called homogenous nucleation. Its rate is calculated by the rate of flow over critical nucleation radius. This is equal to the attempt frequency ν multiplied by number of sites at which the process goes N_s and the probability of attaining the state of nucleation barrier energy P (Zeldovich 1943)

$$r = \nu N_s P = \nu N_s \exp \left[-\frac{\Delta E_{crit}}{kT} \right]$$

Denote the density of the molecules at the nucleus edge by ρ_s . The rate is

$$r = \frac{16\pi\gamma^2\nu\rho_s}{\rho^2(\Delta\mu)^2} \exp \left[-\frac{16\pi\gamma^2}{3\rho^2kT(\Delta\mu)^2} \right]$$

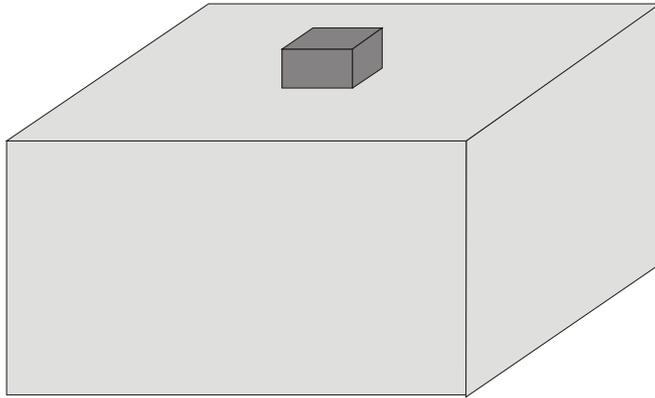
For low supersaturations the rates are extremely small – the time of the creation of single critical nucleus is comparable with the time of Universe existence

Crystal growth – 2-d nucleation rate

Growth of crystals proceeds via:

i/ structural defects (dislocations) acting as step sources

ii/ nucleation of new layers (2-d nucleation)

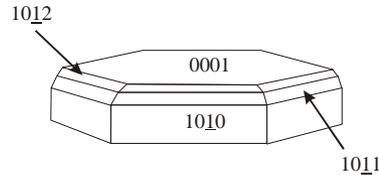
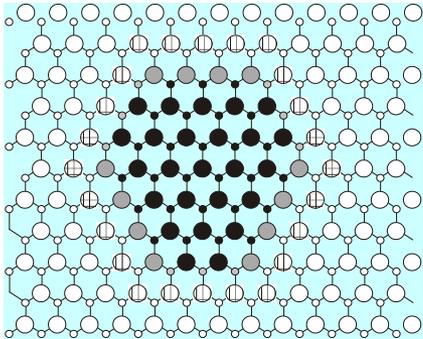


$$r = \nu N_L P = \nu N_L \exp \left[-\frac{\Delta E_{crit}}{kT} \right]$$

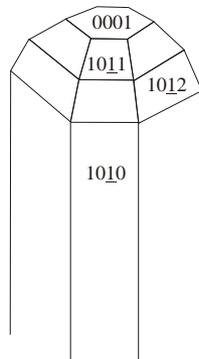
N_L – number of sites at the edge

Unit of length of the edge energy density is ϕ . This is generally denoted as the energy of broken bond.

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



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



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

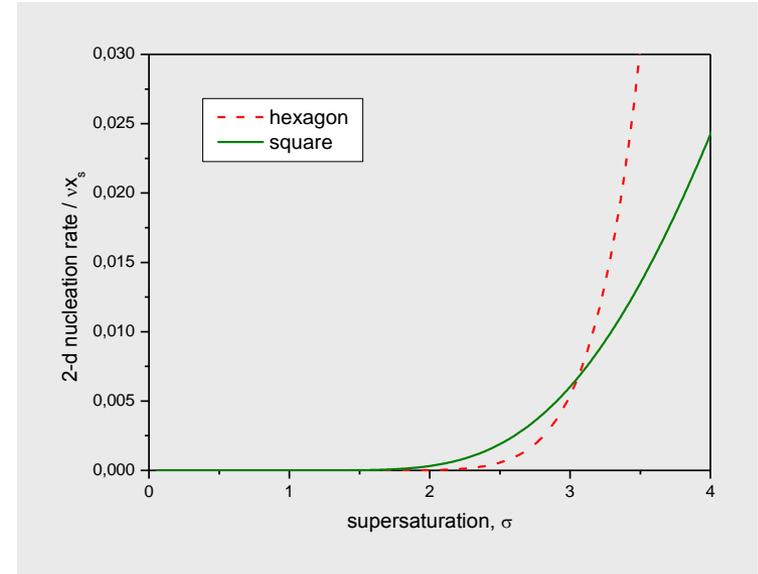


Diagram recovers:

- Growth anisotropy
- Acceleration of the growth along (0001) direction for high supersaturation

x_1 – thickness of the single layer

Diffusion

Diffusion is disordered, random motion of the atoms (molecules) of the following properties:

- **Mean (averaged over many jumps) translation is zero**
- **Correlation of the directions of the two consecutive jumps is zero (Markov process)**

Diffusion types:

- **Free – directions and the length of the jumps are not prescribed**
- **Lattice – jumps between lattice sites**

Lattice diffusion

Lattice diffusion:

- Molecules are localized in lattice sites
- Two consecutive jumps correlation is zero (Markov process)
- The rate is given by:

$$R_{dif} = \nu P(i \rightarrow f) \quad \nu = \tau_o^{-1} - \text{attempt frequency (inverse of time)}$$

- Probability P is

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

C – normalization constant (depends on the lattice type and dimension)

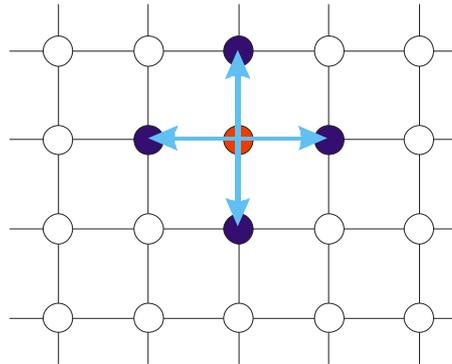
Lattice diffusion - dimensionality

Dimensional properties (regular lattice) :

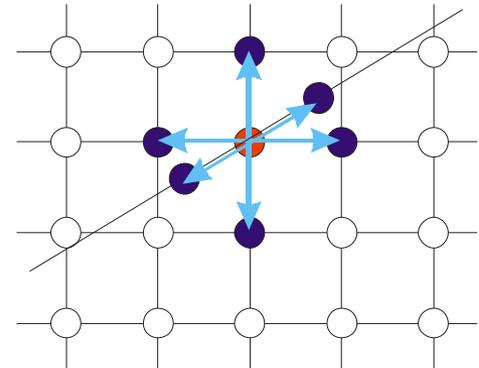
• $d = 1$



• $d = 2$



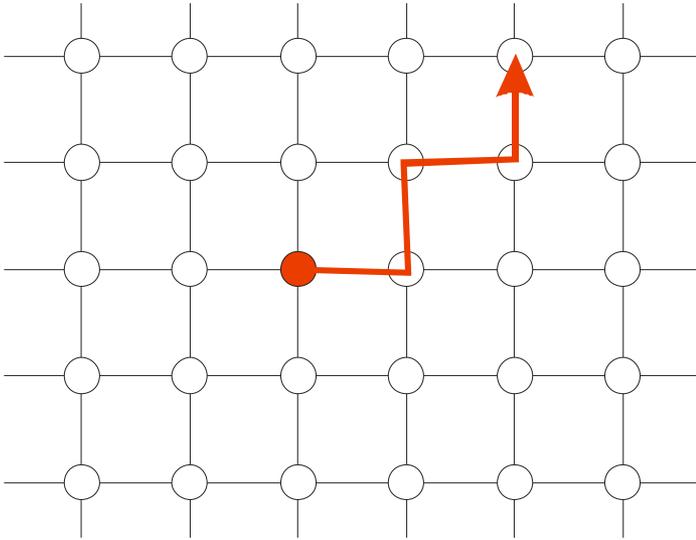
• $d = 3$



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

d – lattice dimensionality

Diffusion – mean square displacement in time (tracer diffusion)



- **Translation vector – is vectorial sum of the consecutive jumps**
- **Square of the distance traveled :**

$$(\Delta\vec{r})^2(t) = [\vec{r}(n) - \vec{r}(0)]^2 = \sum_{i=1}^n \vec{a}_i \sum_{j=1}^n \vec{a}_j$$

- **The time determines the number of the jumps**

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

Diffusion – average distance travelled in time at surface

- Ensemble average
- No correlation of the consecutive jumps

$$(\Delta\vec{r})^2(t) = \sum_{i=1}^{n(t)} \vec{a}_i \sum_{j=1}^{n(t)} \vec{a}_j = \sum_{i=1, j=1}^{n(t)} \vec{a}_i \vec{a}_j + \sum_{i=1}^{n(t)} (a_i)^2 = n(t)a^2 = \frac{a^2 t P}{\tau_o}$$

- Number of steps and probability P

$$n(t)P = \frac{tP}{\tau_o} = t\nu P \quad P(i \rightarrow f) = \exp\left[-\frac{\Delta E_{dif}}{kT}\right]$$

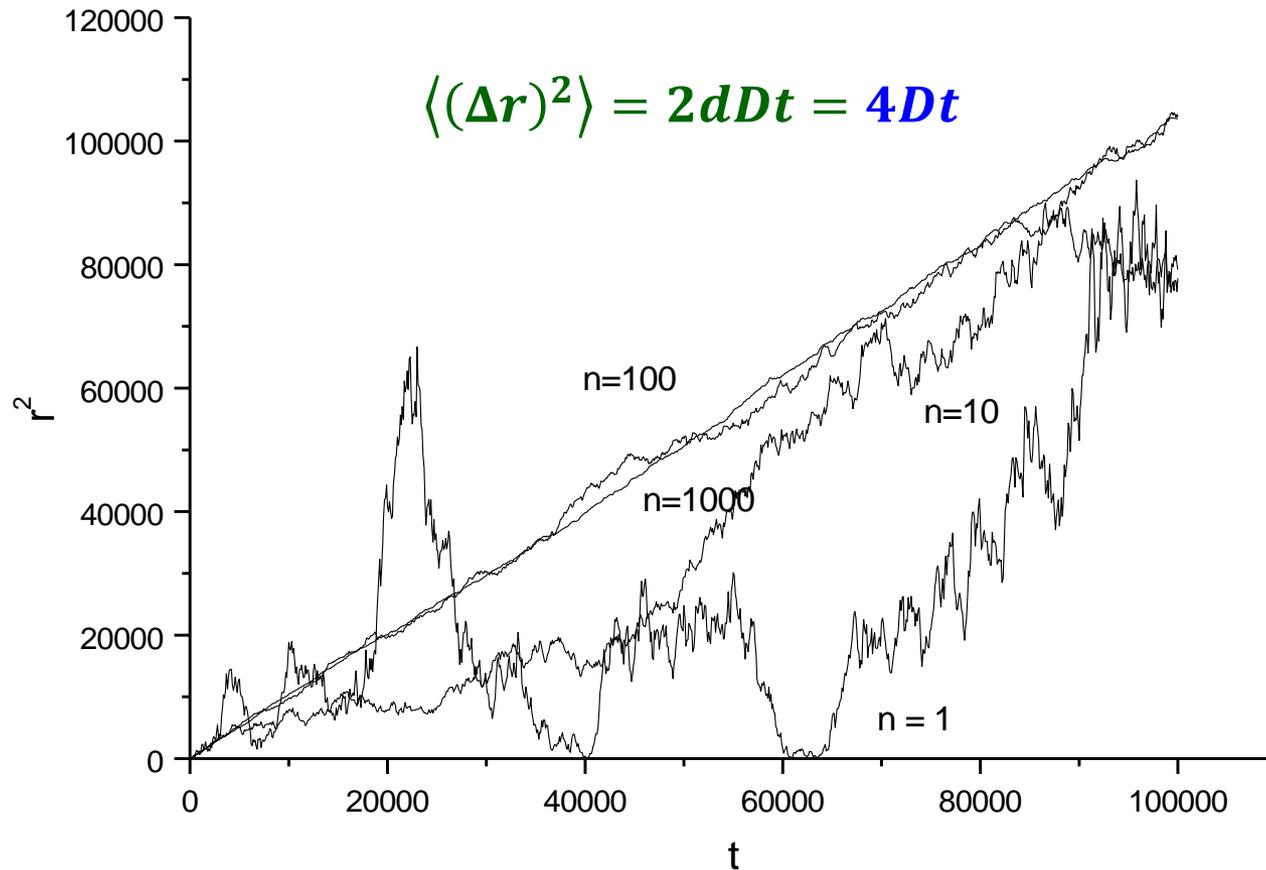
- Distance

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

- Diffusion definition (2-d): $\langle(\Delta r)^2\rangle = 2dDt = 4D_{sur}t$

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

Diffusion – ensemble average

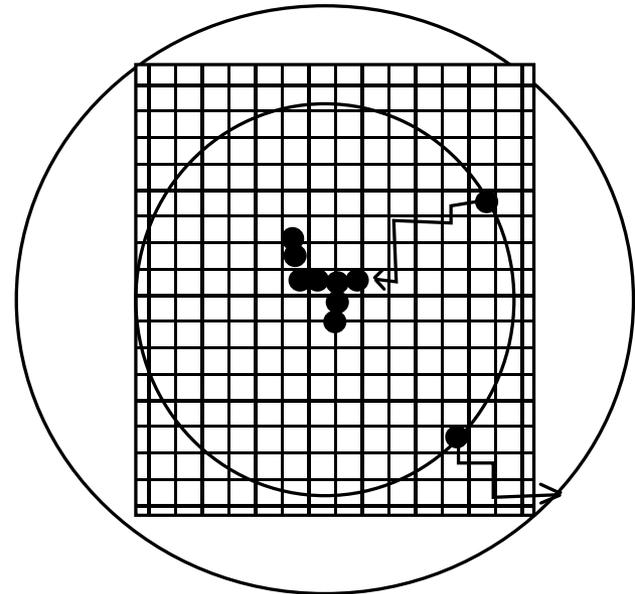


- **Linear dependence is identified for large ensemble only**

Kinetic model - Diffusion Limited Aggregation (DLA)

The following process is called **Diffusion Limited Aggregation (DLA)** :

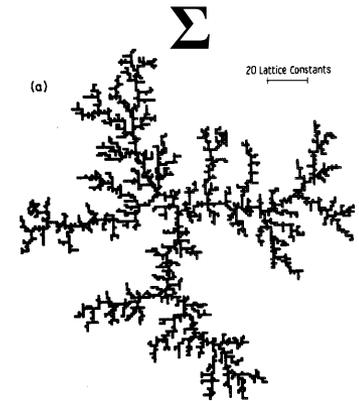
- **Molecule start at far distance**
- **Random direction**
- **At contact molecule is included into the growing nucleus irreversibly**



Fractals

- Volume estimate V of the object Σ via coverage by minimal number of spheres Ω such that

$$\Sigma \in \bigcup_{i=1}^{N(l)} \Omega_i \quad V_d(l) = CN(l)l^d$$



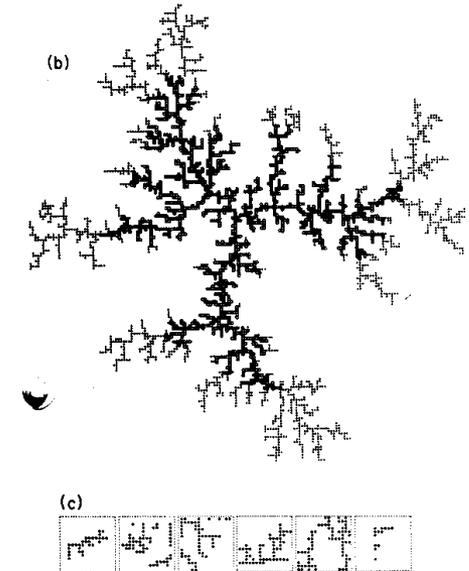
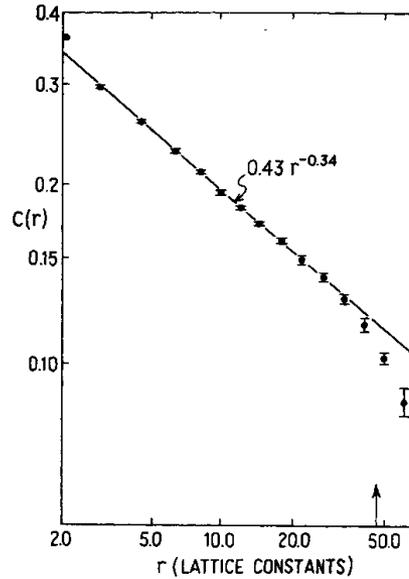
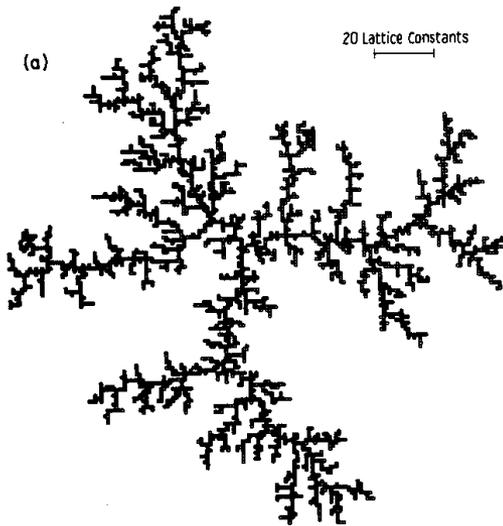
- Hausdorff measure F of the object Σ via coverage by minimal number of spheres Ω such that

$$F = N(l)l^D \quad \longrightarrow \quad D = \lim_{l \rightarrow 0} \frac{\ln[N(l)]}{\ln[l]}$$

measure F is independent of the size l if D is the Hausdorff (Hausdorff – Besicovitch) dimension D .

- Object Σ is fractal (fractional dimension) if D is noninteger numer (B. Mandelbrot 1975)

DLE → growth of fractals



Correlation function:

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

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

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

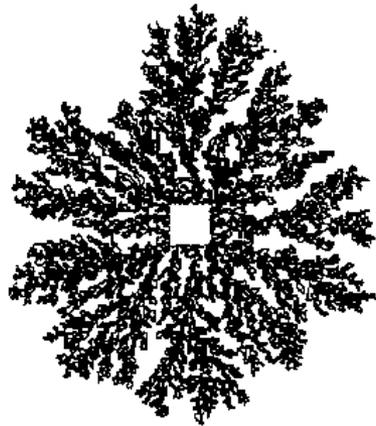


$$D \sim 1.657$$

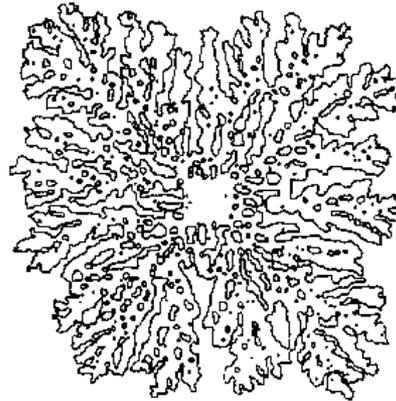
$$\underline{D = 1.695 \pm 0.002}$$

Simulation results

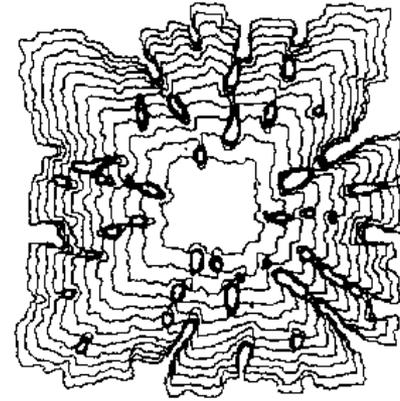
Kinetic model – transition from fractal to crystal growth



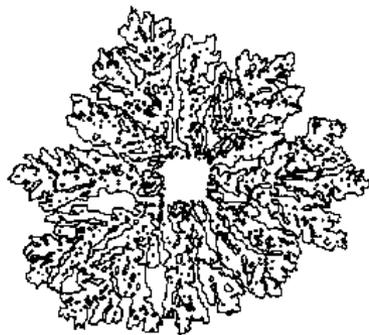
$K = 4.9$



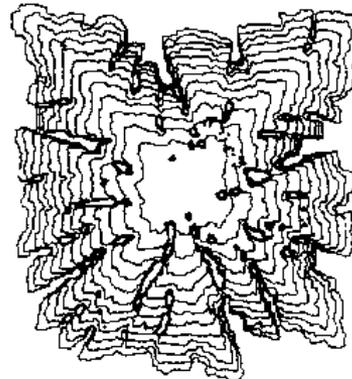
$K = 0.25$



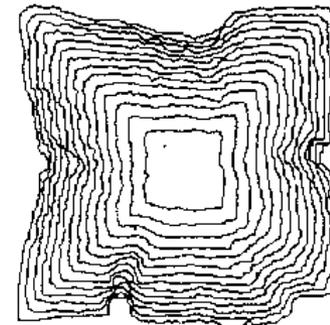
$K = 0.012$



$K = 0.49$



$K = 0.025$



$K = 0.0012$

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

Free diffusion in the vapor

Free diffusion is disordered, random motion of the atoms (molecules) of the following properties

- Mean average translation is zero
- No correlation of the consecutive flights direction
- Mean free path λ and mean free time τ and average thermal velocity $\langle v \rangle$

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

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

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

σ - total scattering crosssection

Literature

Nucleation

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

Diffusion

- **G. Ehrlich & K. Stolt, Ann. Rev. Phys. Chem. 31 (1980) 603**
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Fractals

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