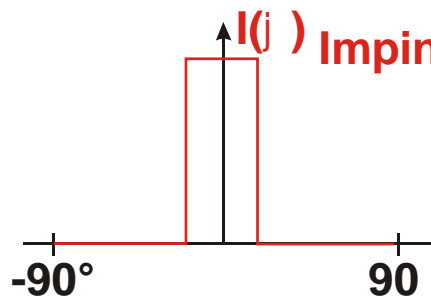
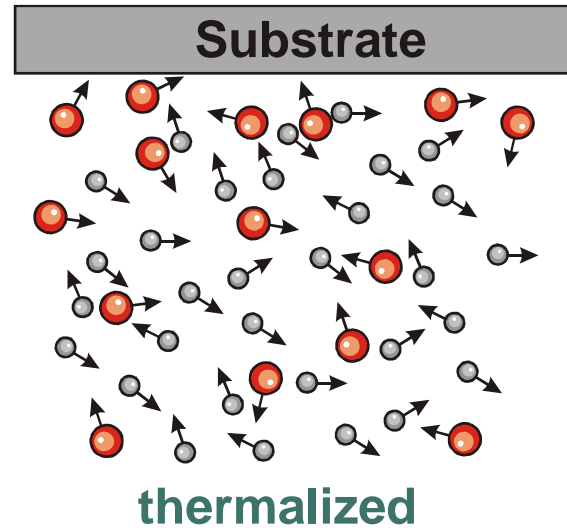
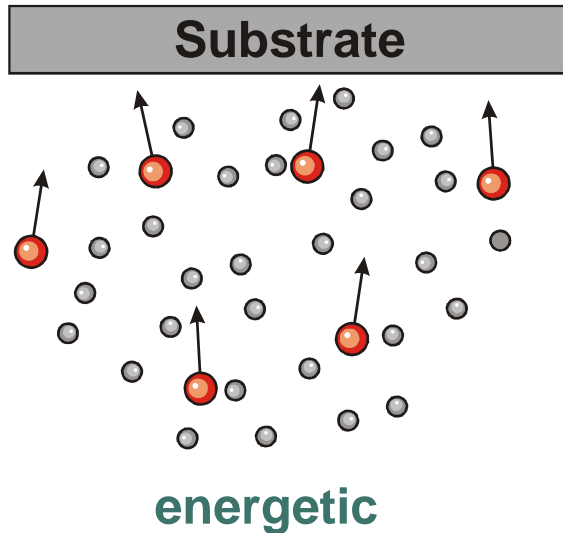
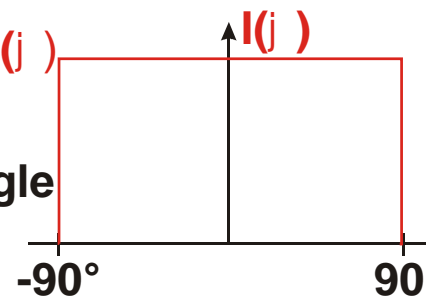


# Repetition: Gas Phase Scattering

As a result of collisions in the gas phase two **limiting cases** can be distinguished:

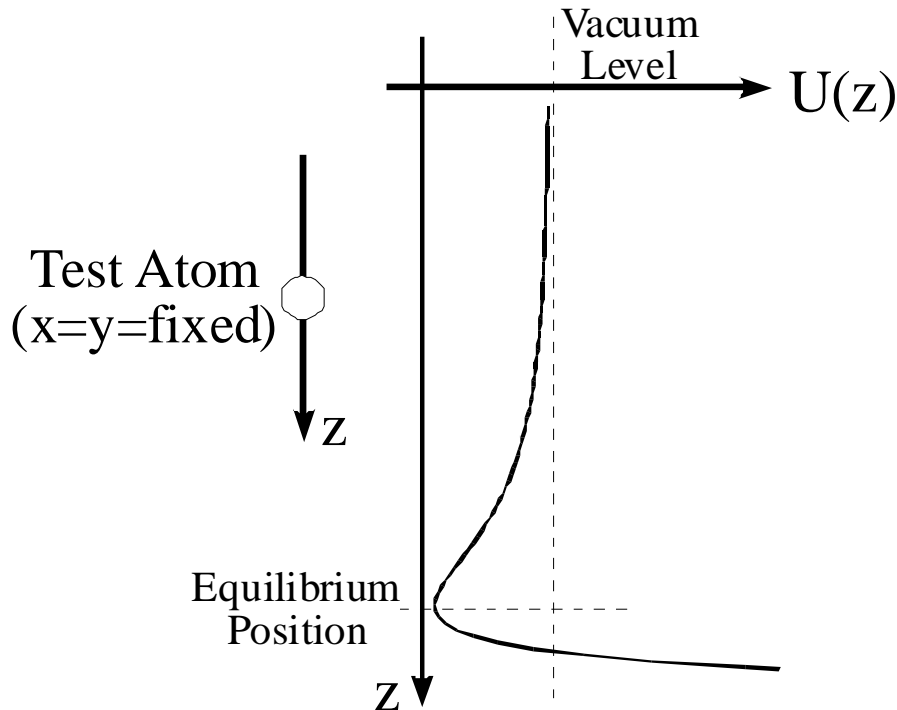


collimated



isotrope

# Repetition: Potential Energy Surfaces



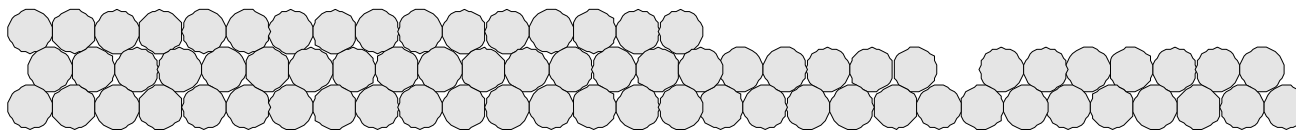
## Interaction Surface/Test Atom Described by Model Potentials

### Pair Potentials:

- Lennard Jones
- Morse

### Many Body Potentials:

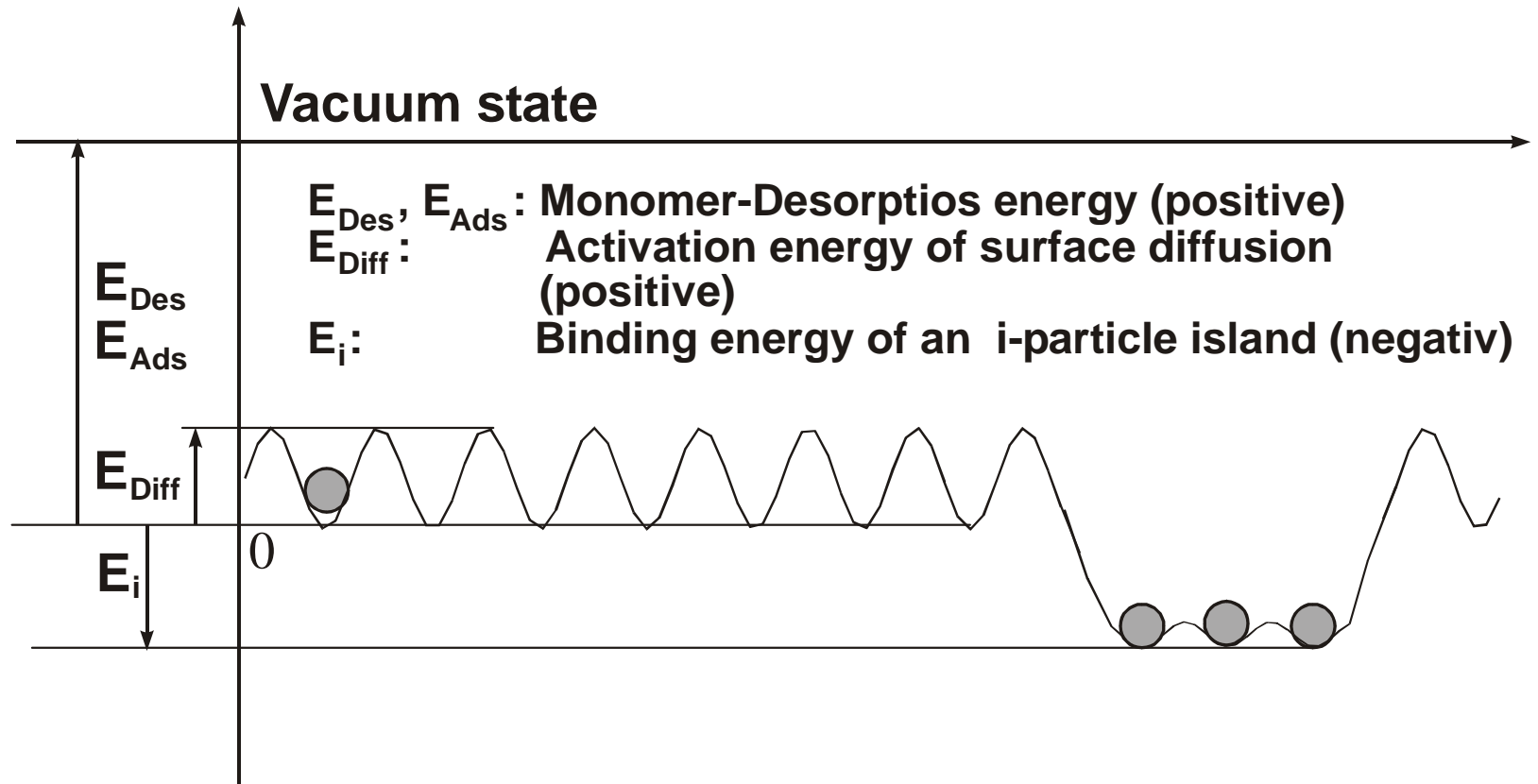
- Embedded Atom
- Sutton Chen
- Tight Binding



Topmost Atomic Layers (Side View)

# Repetition: Binding Energies

## Important binding energies



# Repetition: Time Scales

## Lattice vibrations:

$$\nu_0 \cong 5 \cdot 10^{12} \text{ Hz}$$

$$T_S = 300 \text{ K}$$

$$k_B = 1,38 \cdot 10^{-23} \text{ J/K}$$

## Surface diffusion:

$$\nu_{\text{Diff}} = \nu_0 \cdot e^{-\frac{E_{\text{Diff}}}{k_B T_S}}$$

$$E_{\text{Diff}} = 0,2 \text{ eV} = 3,2 \cdot 10^{-20} \text{ J}$$

$$\nu_{\text{Diff}} = 2,2 \cdot 10^9 \text{ Hz}$$

$$\tau_{\text{Diff}} = \nu_{\text{Diff}}^{-1} = 0.5 \text{ ns}$$

## Desorption:

$$\nu_{\text{Des}} = \nu_0 \cdot e^{-\frac{E_{\text{Des}}}{k_B T_S}}$$

$$E_{\text{Des}} = 2 \text{ eV} = 3,2 \cdot 10^{-19} \text{ J}$$

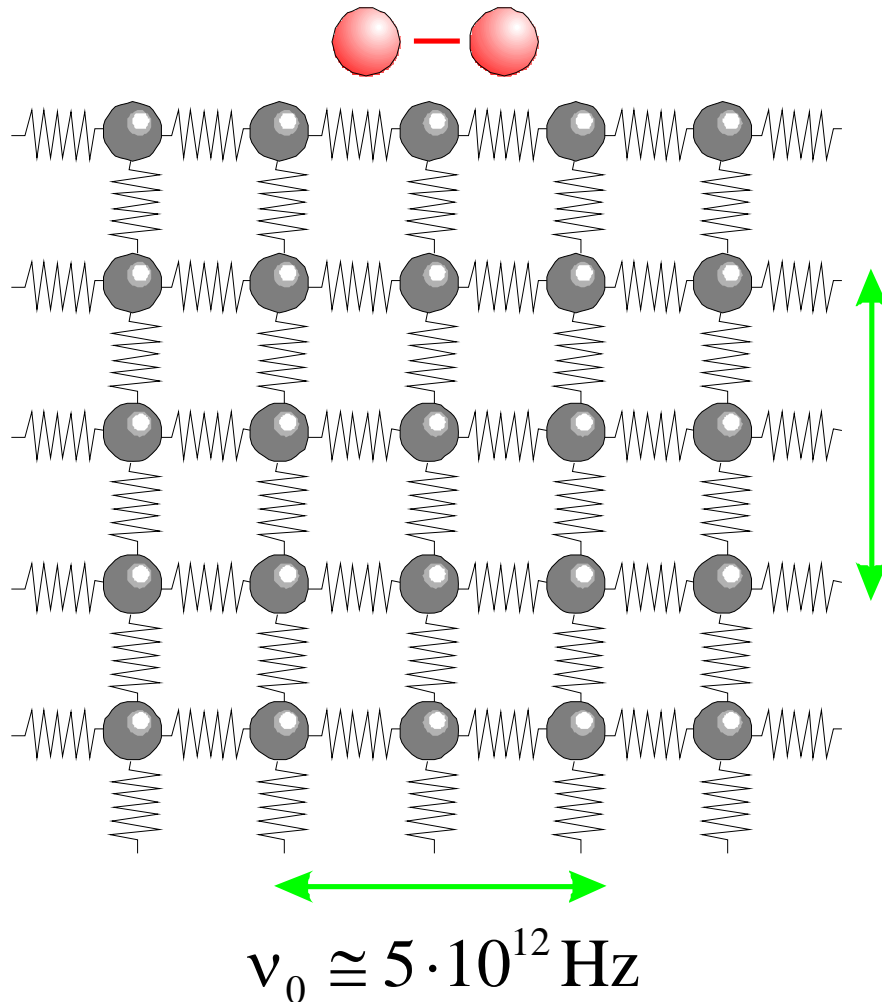
$$\nu_{\text{Des}} = 1,2 \cdot 10^{-21} \text{ Hz (!)}$$

$$\tau_{\text{Des}} = \nu_{\text{Des}}^{-1} = 10^{13} \text{ a}$$

# Repetition: Condensation Regimes

- **Complete condensation:**  
Each impinging particle remains on the surface because of the extremely low desorption frequency.  
**Prerequisite:  $T_s <$**
- **Incomplete condensation:**  
Particles can desorb, an adsorption/desorption-equilibrium is created ein (see later).  
**Prerequisite:  $T_s >$**

# Elementary Processes: Nucleation



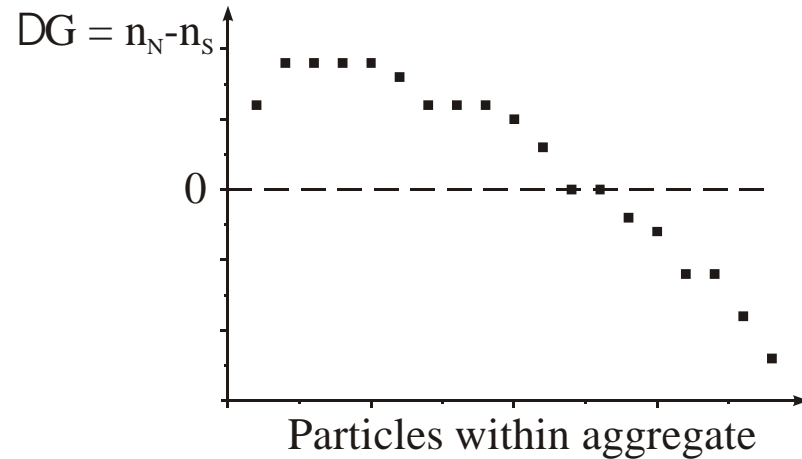
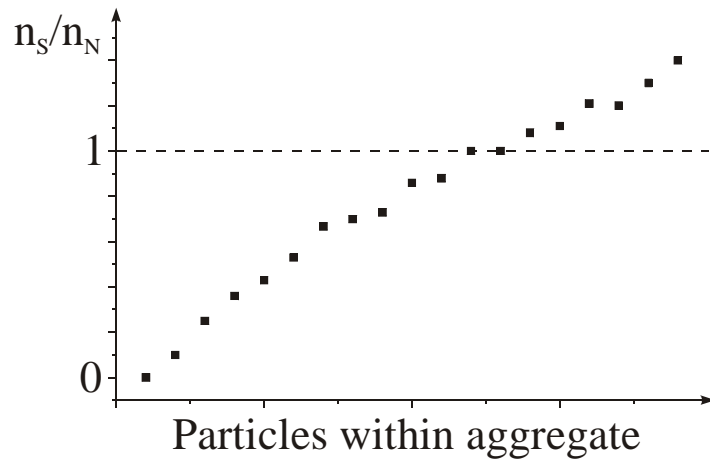
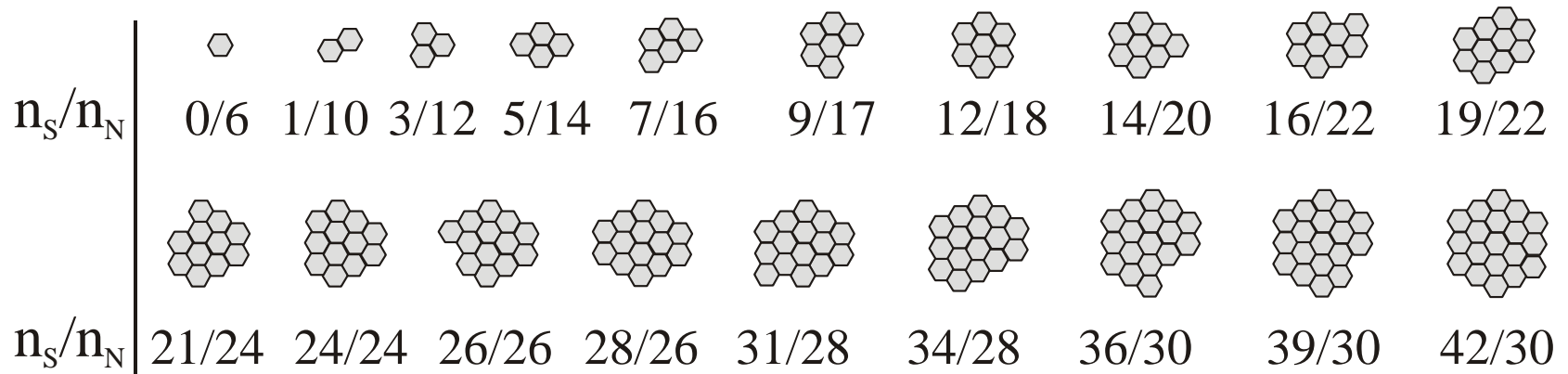
**Nucleation frequency:**

$$\nu_{\text{Nucl}} = \nu_0 \cdot e^{-\frac{\Delta G}{k_B T_S}}$$

**What is  $\Delta G$ ?**

# Nucleation: Many Particle Aggregates

## 2D-aggregates - hexagonal coordination



# Nucleation: Continuum Approximation

## Droplet-model: basics

Phase transition vapor (D)/solid (K):

$$\Delta G = G_K - G_D < 0 \Rightarrow \text{Solid state stable}$$

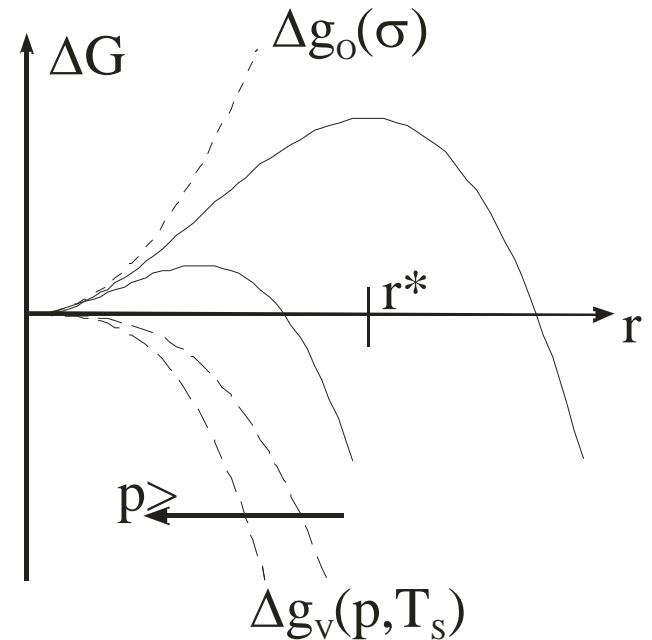
$$\Delta G = \Delta G(\sigma, p, T_s, r) = \Delta g_o(\sigma, r) + \Delta g_v(p, T_s, r)$$

$r$  = Droplet radius

$p$  = Pressure outside the droplet  
(larger than equilibrium  
vapor pressure)

$T_s$  = (Substrate) Temperature

$\sigma$  = surface energy of the droplet



$$\Delta G = \sigma r^2 + \Delta G_v(p, T_s) r^3$$



# Thermodynamic Interpretation of $\Delta G$

From the thermodynamic point of view  
**nucleation** is a

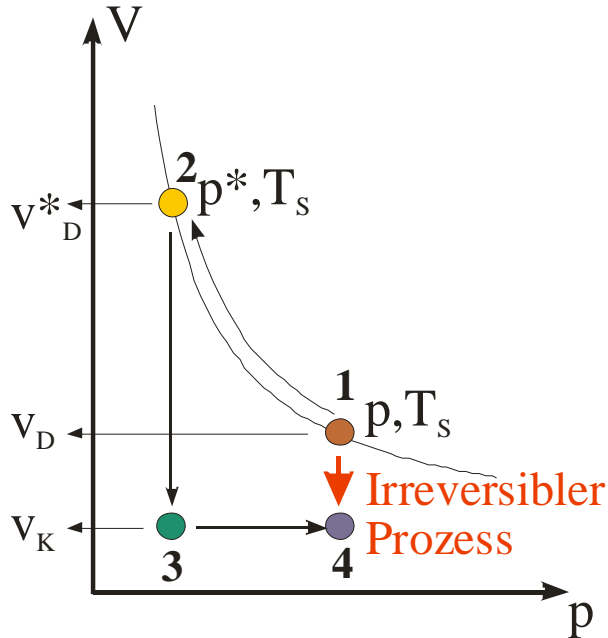
- **Isothermal**
- **Isobaric**

process, because it proceeds at constant substrate temperature,  $T_s$ , and constant supersaturation pressure,  $p$ . The **thermodynamic potential** to describe this type of process is **Gibbs' free enthalpy,  $G$** .

$$G = U - TS + pV$$

# Thermodynamic Calculation of $\Delta G_V$

The volume contribution to  $G$ ,  $\Delta G_V$ , can be calculated:



- 1: supersaturated vapor
- 2: reversible sublimation/desublimation
- 3: isobar volume reduction
- 4: Condensate

$$G = U - TS + pV$$

$$d'Q = dU - d'A = dU + pdV$$

$$\Delta S = d'Q/T_s$$

$$\Delta G = G_K - G_D < 0$$

$$\Delta G = U_K - U_D + p^*v_K - pv_D - T_s(S_K - S_D) = \boxed{pv_D = p^*v_D^*}$$

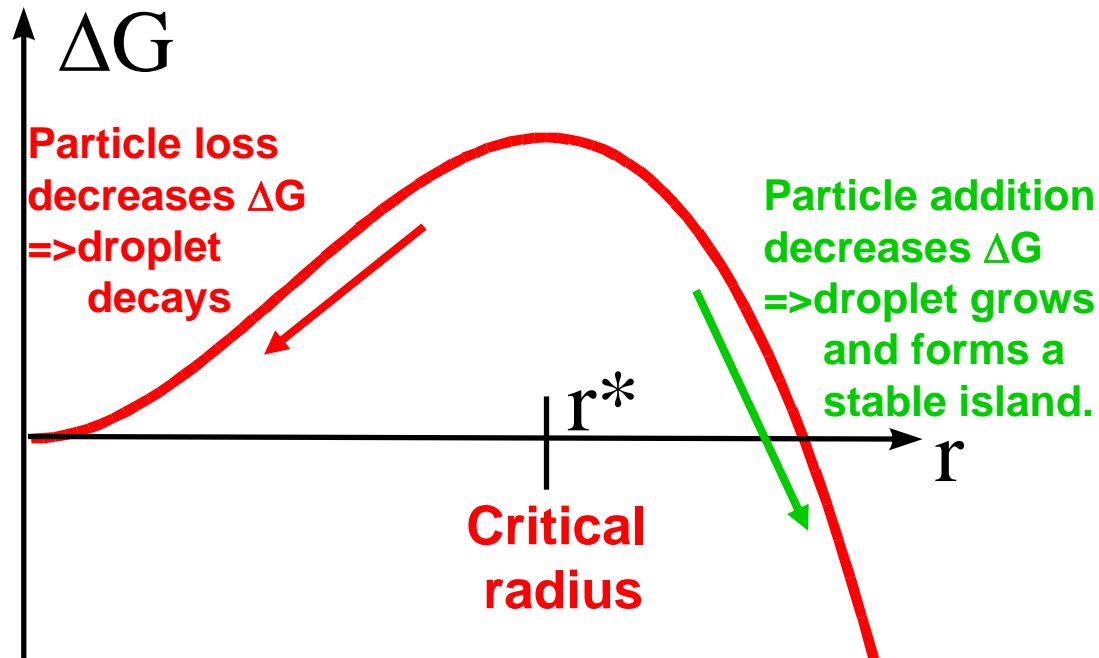
$$= \Delta U + p^*v_K - p^*v_D^* - T_s \Delta S$$

$$\Delta S = \frac{1}{T_s} \left( \Delta U + p^*v_K - p^*v_D^* + \int_{v_D}^{v^*} pdV \right)$$

$$\Delta G = - \int_{v_D}^{v^*} pdV = -RT_s \int_{v_D}^{v^*} \frac{dV}{V} = -RT \ln \frac{v^*}{v_D} = -RT \ln \frac{p}{p^*}$$

$$\boxed{\Delta G_V} = \frac{\Delta G}{V} = \frac{RT}{N_L V_{\text{Atom}}} \ln \frac{R_{\text{des}}}{R} = \frac{k_B T_s}{V_{\text{Atom}}} \ln \frac{R_{\text{des}}}{R}$$

# Interpretation of $\Delta G$



$$\Delta G = \sigma r^2 + \Delta G_V(p, T_S) r^3$$

$$\Delta G_V(p, T_S) = -\frac{k_B T_S}{V_{\text{Atom}}} \ln\left(\frac{p}{p^*}\right) = \frac{k_B T_S}{V_{\text{Atom}}} \ln\left(\frac{R_{\text{Des}}}{R}\right)$$

# Nucleation: The Isolated Nucleus

## Assumptions:

- **Only one aggregate present**
- **Adsorption/desorption-equilibrium**

## What is "Adsorption/desorption-equilibrium" ?

**The number of single atoms ("monomers") at the substrate surface is limited by desorption processes and remains constant in the temporal average.**

# Adsorption/Desorption-Equilibrium

$$\frac{dn_1}{dt} = R - \nu_0 \cdot n_1 \cdot e^{-\frac{E_{\text{Des}}}{k_B T_S}} = 0$$

$$n_1 = R \cdot \nu_0^{-1} \cdot e^{\frac{E_{\text{Des}}}{k_B T_S}}$$

$n_1$  = Monomer number [ $\text{m}^{-2}$ ]

$R$  = Deposition rate [ $\text{m}^{-2}\text{s}^{-1}$ ]

$\nu_0$  = Phonon frequency [ $\text{s}^{-1}$ ]

# Isolated Nucleus: Droplet-Model

## Model assumptions:

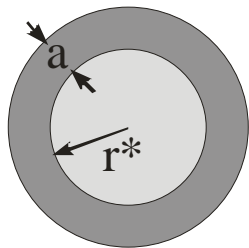
### Adsorption/desorption-eq.:

$$\frac{dn_1}{dt} = 0 = R - n_1 v_0 \exp\left(-\frac{E_{\text{Des}}}{k_B T_S}\right)$$

$$n_1 = R v_0^{-1} \exp\left(\frac{E_{\text{Des}}}{k_B T_S}\right)$$

### Supply of monomers to the critical nucleus:

Surface diffusion from capture zone, with area  $2\pi r^* a$



$$U^* = 2\pi r^*$$

$$v_{\text{Diff}} = v_0 \cdot \exp\left(-\frac{E_{\text{Diff}}}{k_B T_S}\right)$$

### Number of droplets with radius $r$ :

$$n(r) = n_1 \exp\left(-\frac{\Delta G(r)}{k_B T_S}\right)$$

### Nucleation rate of critical nuclei (radius $r^*$ ):

$$I[\text{m}^{-2}\text{s}^{-1}] = U^* a \cdot n_1 \cdot v_0 \cdot \exp\left(-\frac{E_{\text{Diff}}}{k_B T_S}\right) \cdot n_1 \exp\left(-\frac{\Delta G^*}{k_B T_S}\right)$$

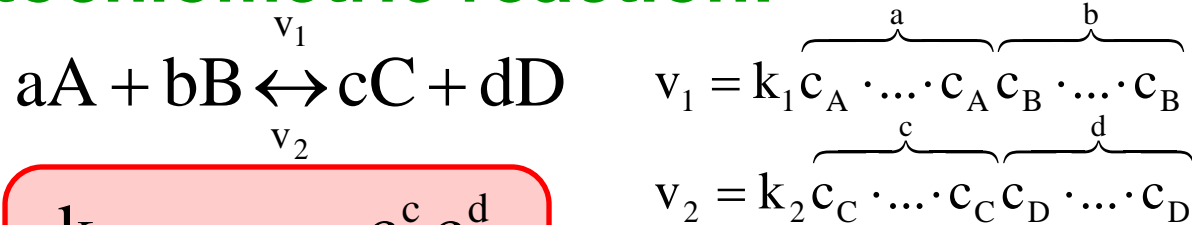
### Taking into account the adsorption/desorption equilibrium:

$$I[\text{m}^{-2}\text{s}^{-1}] = U^* a \cdot n_1 \cdot R \cdot \exp\left(\frac{E_{\text{Des}} - E_{\text{Diff}} - \Delta G^*}{k_B T_S}\right)$$

$$= U^* a \cdot v_0^{-1} \cdot R^2 \cdot \exp\left(\frac{2 \cdot E_{\text{Des}} - E_{\text{Diff}} - \Delta G^*}{k_B T_S}\right)$$

# Particle-Model: Mass Action Law (MWG)

## Stoichiometric reaction:



$$\frac{k_1}{k_2} = K_c = \frac{c_C^c c_D^d}{c_A^a c_B^b}$$

$k_{1,2}$  = Proportionality constants

$c_i$  = Concentrations

$K_c$  = Reaction constant

$K_c$  is connected to the energy  $\Delta E$  which is set free or consumed by the reaction:

$$\Delta E = -k_B T \ln K_c$$

# Mass Action Law and Particle-Model

**i single particles form i-particle aggregate:**

$$c_1 \equiv n_1 / N_0 = i \cdot 1$$

$$c_i \equiv n_i / N_0 = 1$$

$$\frac{n_i}{N_0} / \left( \frac{n_1}{N_0} \right)^i = K_c = \exp \left[ - \frac{\Delta E}{k_B T_S} \right] = \exp \left[ \frac{E_i}{k_B T_S} \right]$$

**$N_0$  = Number of available adsorption sites**

**$E_i$  =  $-\Delta E$  = Energy gain in the case of formation of a i-particle Aggregate**



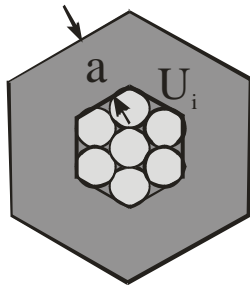
# Isolated Nucleus: Particle Model

## Model assumptions:

**Adsorption/desorption-eq.:**

**Supply of monomers to the critical nucleus:**

Surface diffusion from capture zone, with area  $U_i a$



**Mass action law valid for the formation of a  $i$ -aggregate:**

$i$  monomers  $\rightleftharpoons$  1  $i$ -aggregate

$$\left(\frac{n_1}{N_0}\right)^{-i} \left(\frac{n_i}{N_0}\right) = \exp\left(\frac{E_i}{k_B T_S}\right)$$

**Number of  $i$ -particle aggregates:**

$$n_i = N_0 \left(\frac{n_1}{N_0}\right)^i \exp\left(\frac{E_i}{k_B T_S}\right)$$

**Nucleation rate of  $i+1$ -aggregates:**

$$I_{i+1}[\text{m}^{-2}\text{s}^{-1}] = n_i \cdot U_i \cdot a \cdot n_1 \cdot v_0 \cdot \exp\left(-\frac{E_{\text{Diff}}}{k_B T_S}\right)$$

**Taking into account the adsorption/desorption equilibrium:**

$$I_{i+1}[\text{m}^{-2}\text{s}^{-1}] = U_i \cdot a \cdot R \cdot N_0 \left(\frac{R}{v_0 N_0}\right)^i \exp\left(\frac{(i+1)E_{\text{Des}} + E_i - E_{\text{Diff}}}{k_B T_S}\right)$$

# Nucleation Rates: Interpretation

Simple nucleation theory yields nucleation rates  $I$  of the form:

$$I[\text{m}^{-2}\text{s}^{-1}] \cong A \cdot R^p e^{\frac{E}{k_B T_S}}$$

**Droplet-model:**

**$E=E(\Delta G^*) \Rightarrow$  unambiguous**

**Particle-model:**

**$E=E(i, E_i) \Rightarrow$  ambiguous**

# Rate Equations

General  $\longrightarrow$  Simplified

$$\frac{dn_1}{dt} = R - \frac{n_1}{\tau_{\text{Des}}} - 2U_1 - \sum_{j=2}^{\infty} U_j$$

$$\frac{dn_j}{dt} = U_{j-1} - U_j$$

$R$  = Deposition Rate

$\tau_{\text{Des}}$  = Monomer Re-evaporation time

$n_1$  = Monomer density

$n_i$  = Density of  $i$ -particle-aggregates

$U_i$  = Monomer capture rates  
of  $i$ -particle aggregates

$$\frac{dn_1}{dt} = R - \frac{n_1}{\tau_{\text{Des}}} - \frac{d(n_x w_x)}{dt}$$

$$\frac{dn_j}{dt} = 0 \quad (2 \leq j \leq i)$$

$$\frac{dn_x}{dt} = U_i - U_c - U_m$$

$$n_x = \sum_{j=i+1}^{\infty} n_j = \text{Number of stable islands}$$

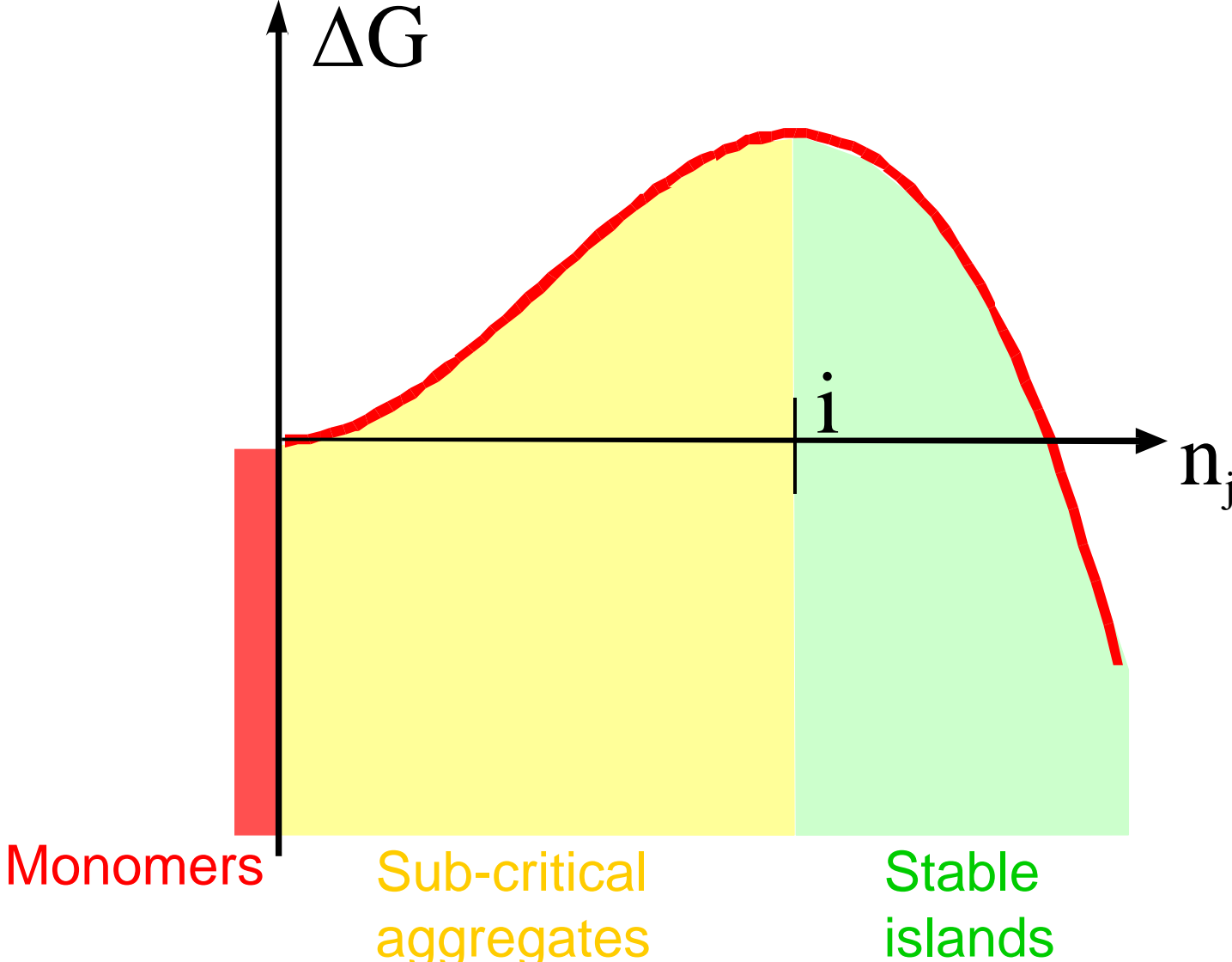
$w_x$  = Mean number of atoms in stable island

$U_i$  = Island generation, monomer capture

$U_c$  = Island annihilation, growth-coalescence

$U_m$  = Island annihilation, mobility-coalescence

# Aggregate Types



# Rate Equations: Solutions

## Incomplete condensation

### 2d-growth

$$n_x(R, T_s, Z, i) = K \cdot \eta(Z) \cdot \Omega^{-2/3} \cdot \left( \frac{R}{N_0 v_B} \right)^i \cdot \exp \left[ \frac{1}{k_B T_s} (E_i + (i+1)E_{Des} - E_{Diff}) \right]$$

### 3d-growth

$$n_x(R, T_s, Z, i) = K \cdot \eta(Z) \cdot \Omega^{-2/3} \cdot \left( \frac{R}{N_0 v_0} \right)^{\frac{2i}{3}} \cdot \exp \left[ \frac{2}{3k_B T_s} (E_i + (i+1)E_{Des} - E_{Diff}) \right]$$

## Complete condensation

### 2d-growth

$$n_x(R, T_s, Z, i) = K \cdot \eta(Z) \cdot \Omega^{-\frac{2}{3(i+2)}} \cdot N_0^{\frac{i+1}{3(i+2)}} \cdot \left( \frac{R}{N_0 v_0} \right)^{\frac{i}{i+2}} \cdot \exp \left[ \frac{1}{k_B T_s} \frac{1}{i+2} (E_i + iE_{Diff}) \right]$$

### 3d-growth

$$n_x(R, T_s, Z, i) = K \cdot \eta(Z) \cdot \Omega^{-\frac{2}{2i+5}} \cdot N_0^{\frac{2(i+1)}{2i+5}} \cdot \left( \frac{R}{N_0 v_0} \right)^{\frac{2i}{2i+5}} \cdot \exp \left[ \frac{1}{k_B T_s} \frac{2}{2i+5} (E_i + iE_{Diff}) \right]$$

$$K = K(\alpha, s_i, C_i) \quad K \cdot \eta(z) \cong 1 \text{ for } Z < 10\%$$

# Island Densities: Interpretation

**Rate equations yield island densities  $n_x$  of the form:**

$$n_x [\text{m}^{-2}] \cong A \cdot \left( \frac{R}{v_0} \right)^p e^{-\frac{E}{k_B T_S}}$$

**The exponent  $p$  is not necessarily an integer and is a function of the size of the critical nucleus,  $i$ .**

# Observable: Island Density $n_x$

**The solution of the rate equations allow the prediction or the determination of the**

- **Size of the critical nucleus**
- **Condensation regime**
- **Growth mode (2d/3d)**
- **Dependence of  $n_x$  on  $T_S$**
- **Dependence of  $n_x$  on  $R$**

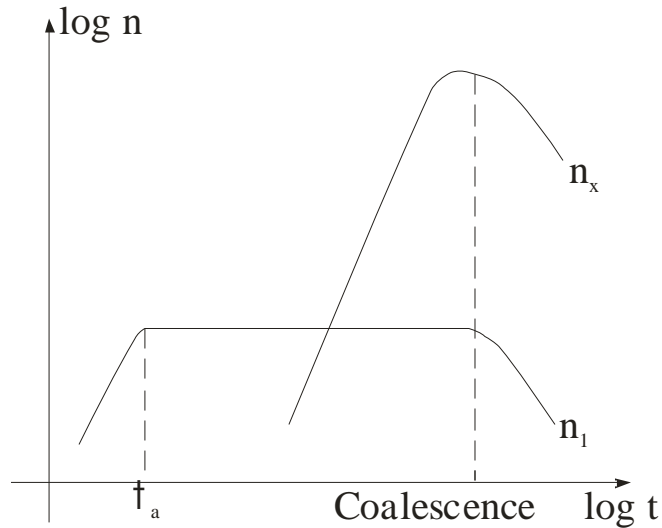
**by the observation of  $n_x$  for selectes  $T_S$  and  $R$ .**

# Rate Equations: General Solution

## Incomplete condensation

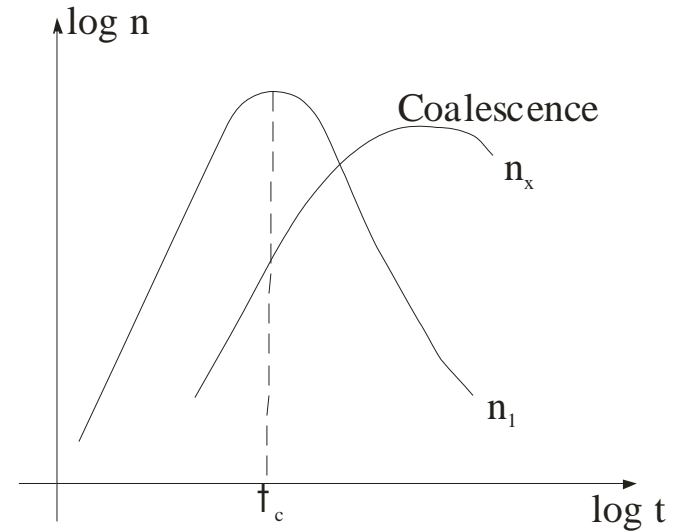
$$\frac{dn_1}{dt} = 0 = R - \frac{n_1}{\tau_a}$$

$$\frac{d(n_x w_x)}{dt} \cong 0$$



## Complete condensation

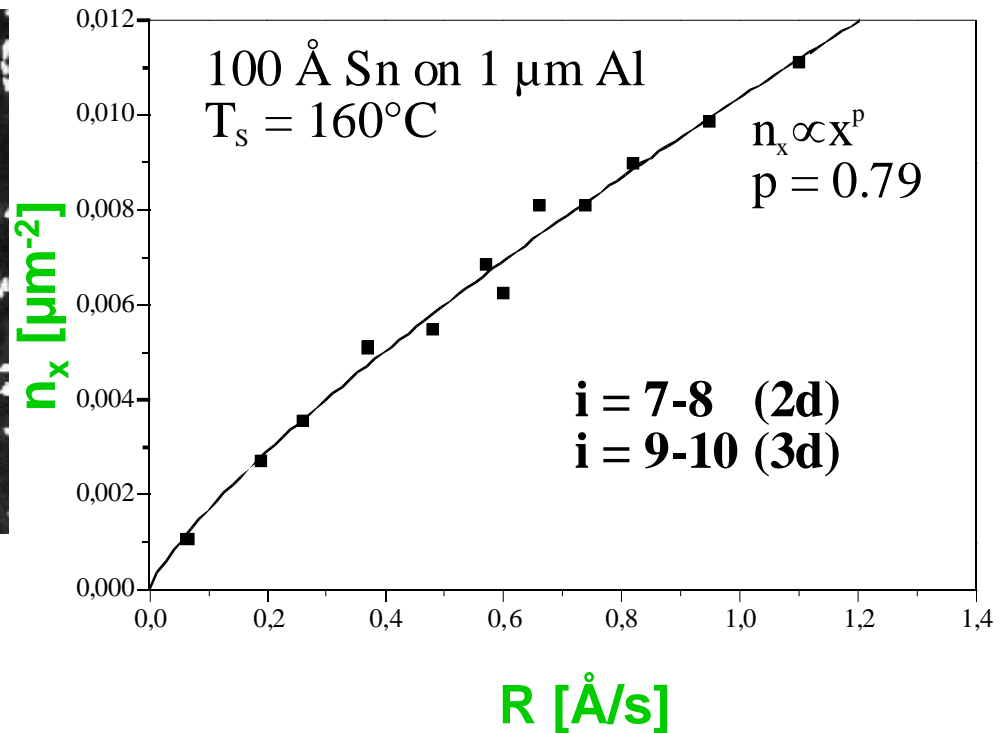
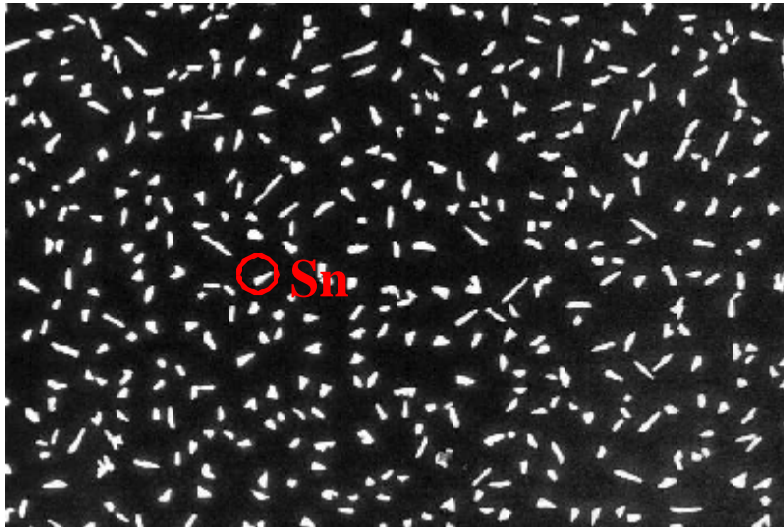
$$\frac{dn_1}{dt} = R - \frac{d(n_x w_x)}{dt}$$





# Example: Determination of Critical Nucleus Size

## Sn on polycrystalline Al:

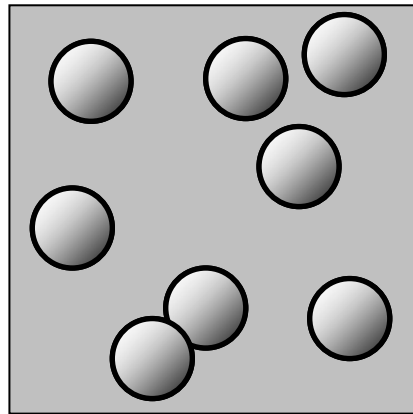


The variation of the deposition rate  $R$  at constant substrate temperature  $T_s$  allows the determination of the critical particle number in the critical nucleus,  $i$

The condensation regime can be noted due to the "fractional power law", i. e.  $p < 1$ .

# Nucleation Scenarios

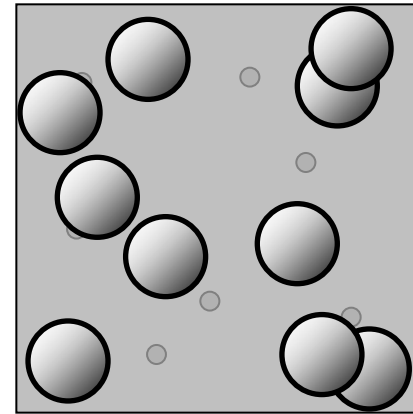
## Heterogenous nucleation



■ Substrate  
● Defect

$$T_1$$
$$T_2 > T_1$$

## Homogenous nucleation



■ Substrate  
● Defect

$$T_1$$
$$T_2 > T_1$$

# Limits of Rate Equations

**Rate equations allow no statement about**

- **the shape of stable islands**
- **the size distribution of stable islands**
- **the influence of defects on nucleation**

**because they represent a "mean field theory", i. e. they neglect the influence of correlations within the island distribution or of special island shapes on the local monomer density.**

# Kinetic Monte Carlo Simulation I

**Kinetic Monte Carlo (KMC) simulations allow the determination of**

- **the shape of the stable islands**
- **the size distribution of stable islands**
- **the influence of defects on nucleation**

**they only use the elementary processes of film growth (deposition, surface diffusion, desorption, particle bonding) as input for the simulation of film growth.**

# Kinetic Monte Carlo Simulaion II

- **Definition of event types**
- **Definition of relative event probabilities ("conditional probabilities")**
- **Choice of a particle for the execution of the event**
- **Determination of the time interval between specific events**

**Advantage:** each chosen event changes the system


**Disadvantage:** not all event types are known a priori; algorithm is memory consuming

# KMC: Principle I


## Particle configurations and event types:

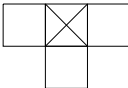
$$E_{\text{Diff}} = 0.4 \text{ eV}$$

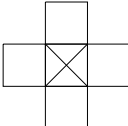
$$E_{\text{b}} = 0.2 \text{ eV}$$


$$v_1 = v_0 \exp[-(E_{\text{Diff}} / k_{\text{B}} T_{\text{S}})] \equiv 1$$


$$v_2 = v_0 \exp[-(E_{\text{Diff}} + E_{\text{b}}) / k_{\text{B}} T_{\text{S}}] \equiv 0,02v_1$$

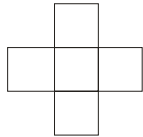

$$v_3 = v_0 \exp[-(E_{\text{Diff}} + 2E_{\text{b}}) / k_{\text{B}} T_{\text{S}}] \equiv 4 \cdot 10^{-4} v_1$$


$$v_5 = v_0 \exp[-(E_{\text{Diff}} + 3E_{\text{b}}) / k_{\text{B}} T_{\text{S}}] \equiv 9 \cdot 10^{-6} v_1$$


$$v_5 = v_0 \exp[-(E_{\text{Diff}} + 4E_{\text{b}}) / k_{\text{B}} T_{\text{S}}] \equiv 2 \cdot 10^{-7} v_1$$

# KMC: Principle II

## Conditional probabilities



□ **Event types:**

Deposition:  $1 \times 1,5 \cdot 10^{-3}$

Monomer-diff.:  $1 \times 1$

Dimer-diff.:  $4 \times 0,02$

Pentamer-diff.:  $1 \times 10^{-7}$

**Normalization to ]0,1]**



# KMC: Principle III

## Time step:

$$\Delta t_{\text{event}} = - \left\{ R + v_0 \left( \sum_n n_n \exp \left[ - (E_{\text{Diff}} + nE_b) / (k_B T_S) \right] \right) \right\}^{-1} \ln r$$

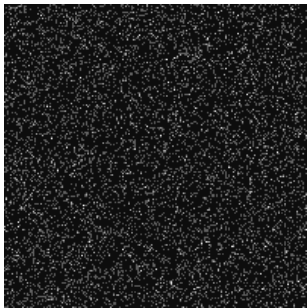
**$r$  ... Random number  $[0,1[$**

**$n_n$  ... Number of monomers with  $n$  nearest neighbors**

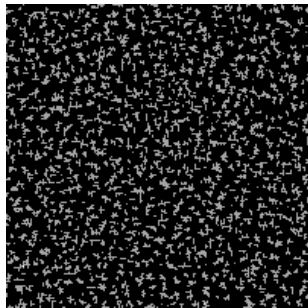


# KMC – Results and Trends I

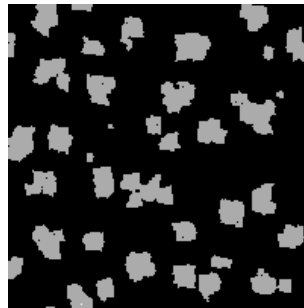
## Variation of substrate temperature $T_s$



$T_s=10K$



300K



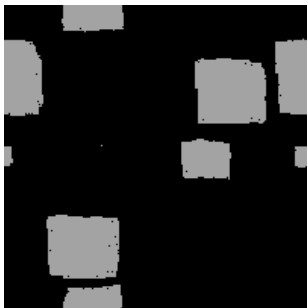
600K



700K

$R=1ML/s$   
 $E_{Diff}=0.5 eV$   
 $E_{Des}=1 eV$   
 $E_b=0.5 eV$

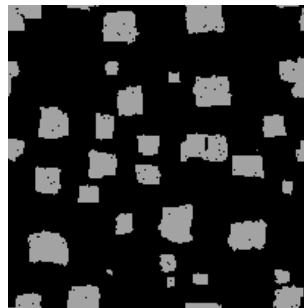
## Variation of deposition rate $R$



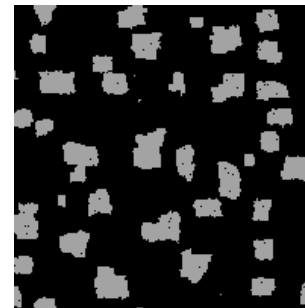
$R=0.5 ML/s$



1ML/s



5 ML/s



10 ML/s

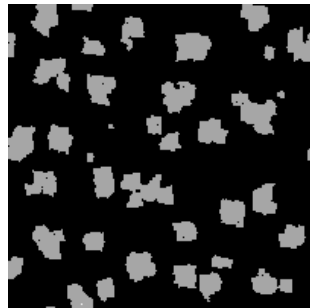
$T_s=700 K$   
 $E_{Diff}=0.5 eV$   
 $E_{Des}=1 eV$   
 $E_b=0.5 eV$

# KMC – Results and Trends II

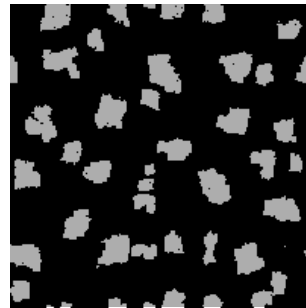
## Variation of desorption energy $E_{Des}$



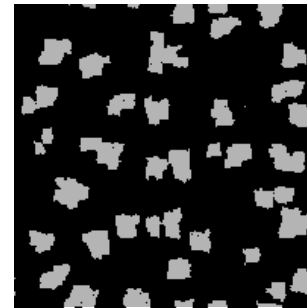
$E_{Des}=0.8$  eV



1 eV



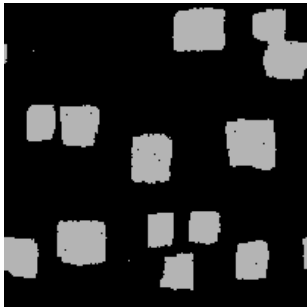
1.5 eV



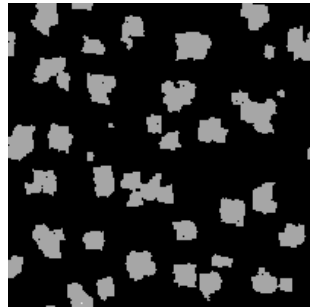
5 eV

$T_S=600$  K  
 $R=1$  ML/s  
 $E_{Diff}=0.5$  eV  
 $E_b=0.5$  eV

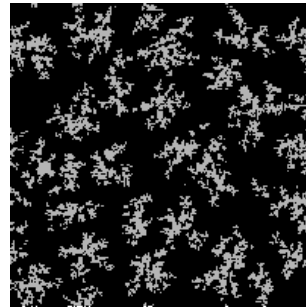
## Variation lateral bond energy $E_b$



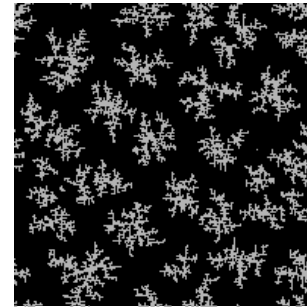
$E_{Lat}=0.3$  eV



0.5 eV



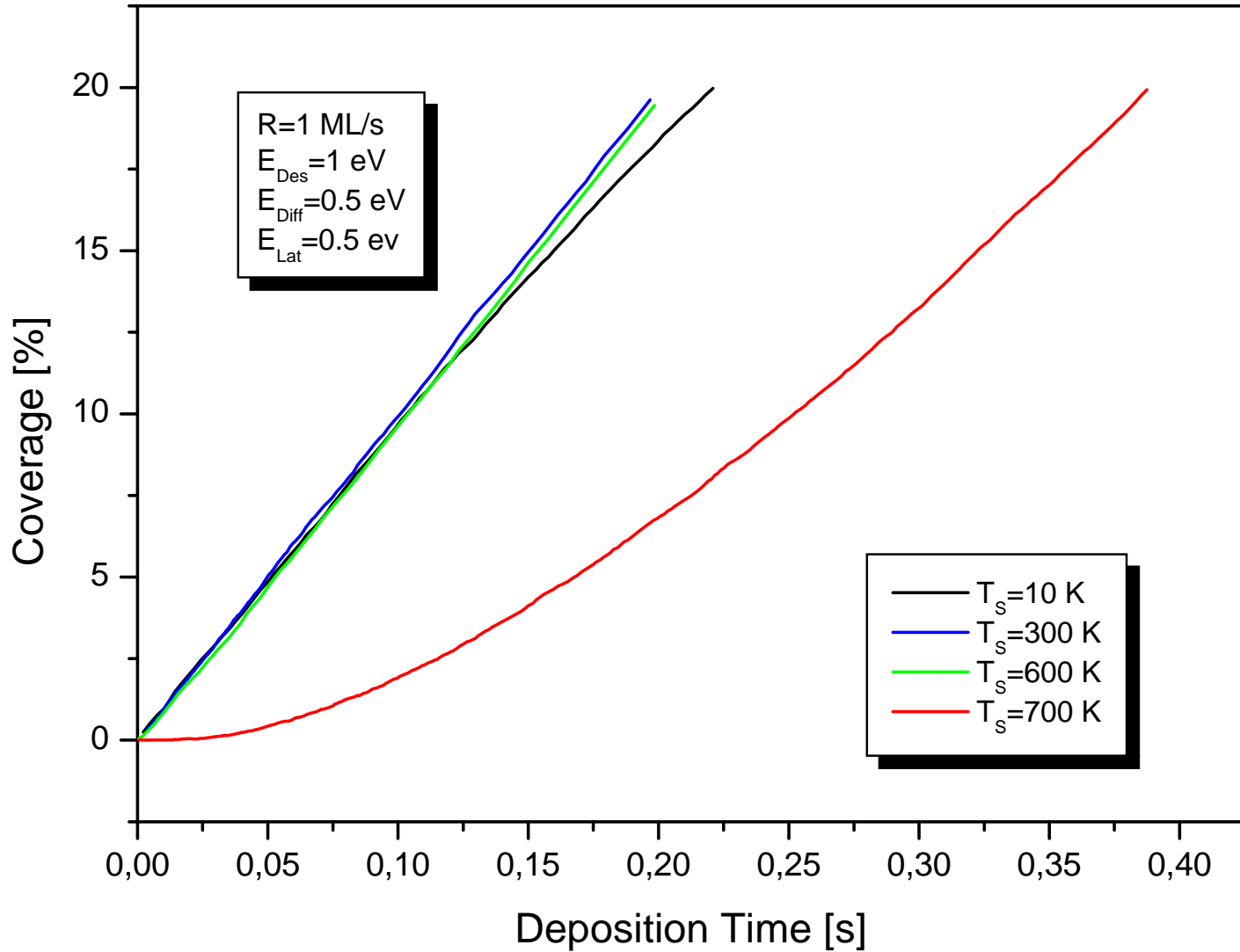
0.7 eV



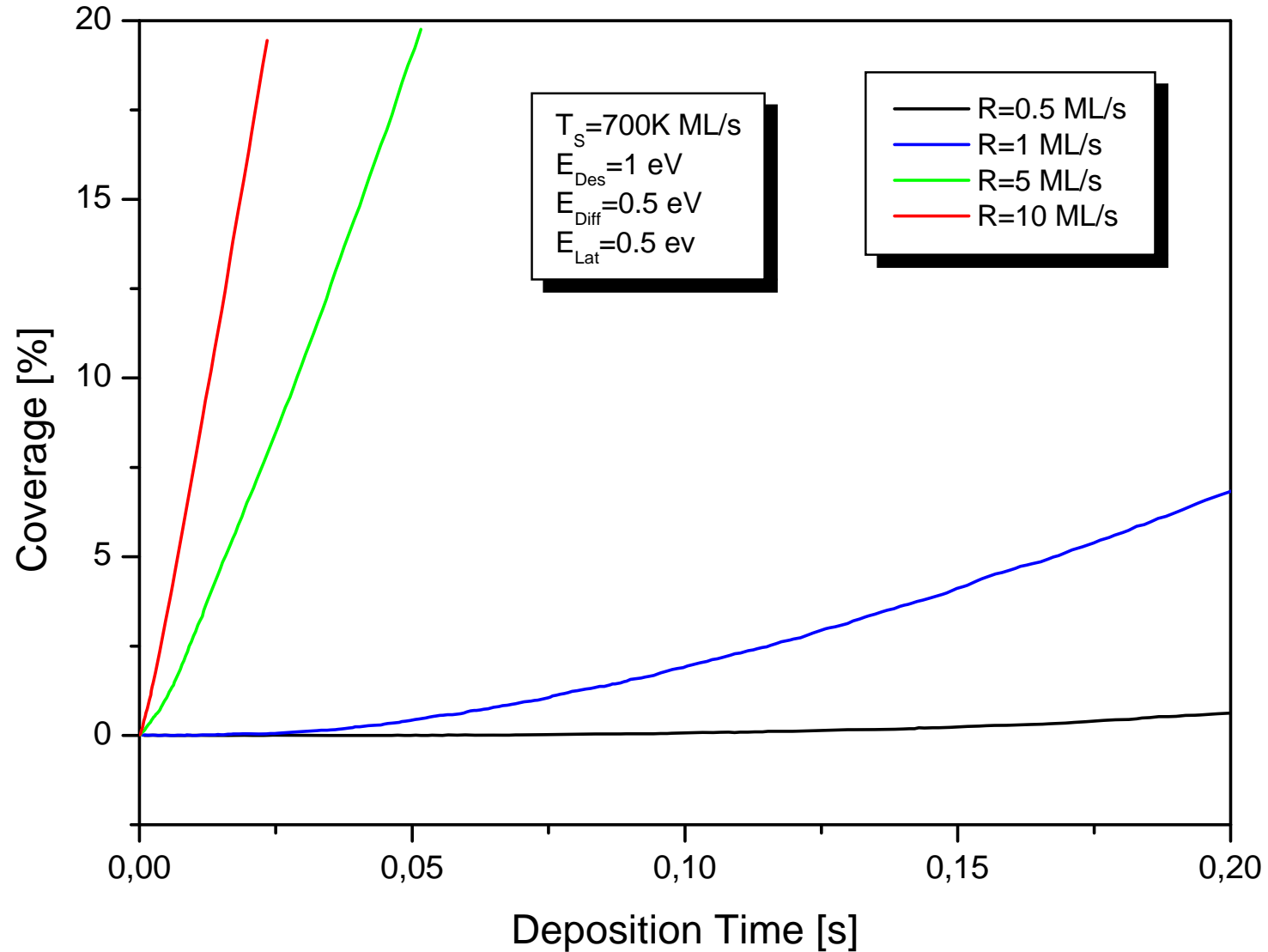
1.5 eV

$T_S=600$  K  
 $R=1$  ML/s  
 $E_{Diff}=0.5$  eV  
 $E_{Des}=1$  eV

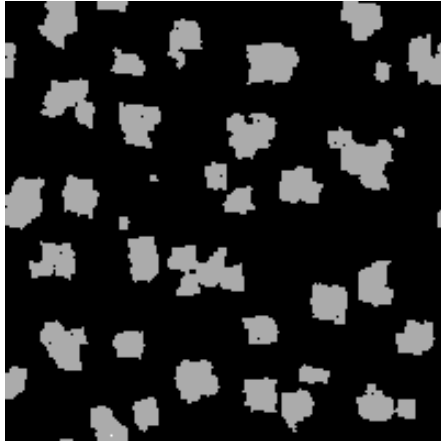
# KMC – Temperature Variation



# KMC – Rate Variation



# KMC – Island Size Distributions



$T_s=600K$



$T_s=700K$

