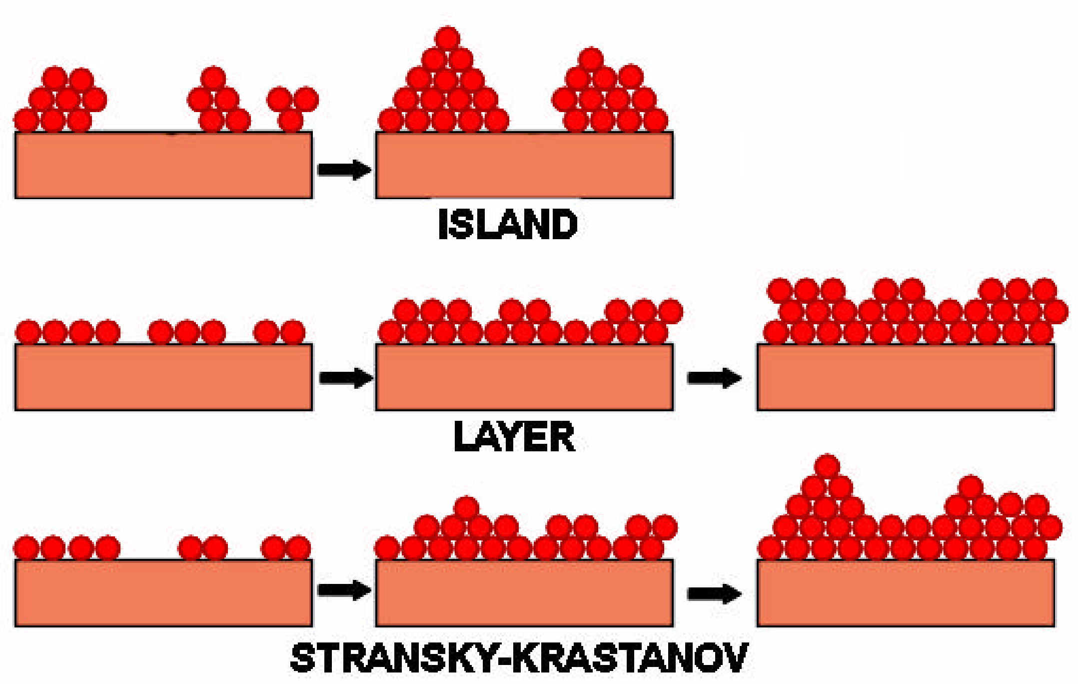
Substrate Surfaces & Thin-Film Nucleation

Basic modes of thin-film growth

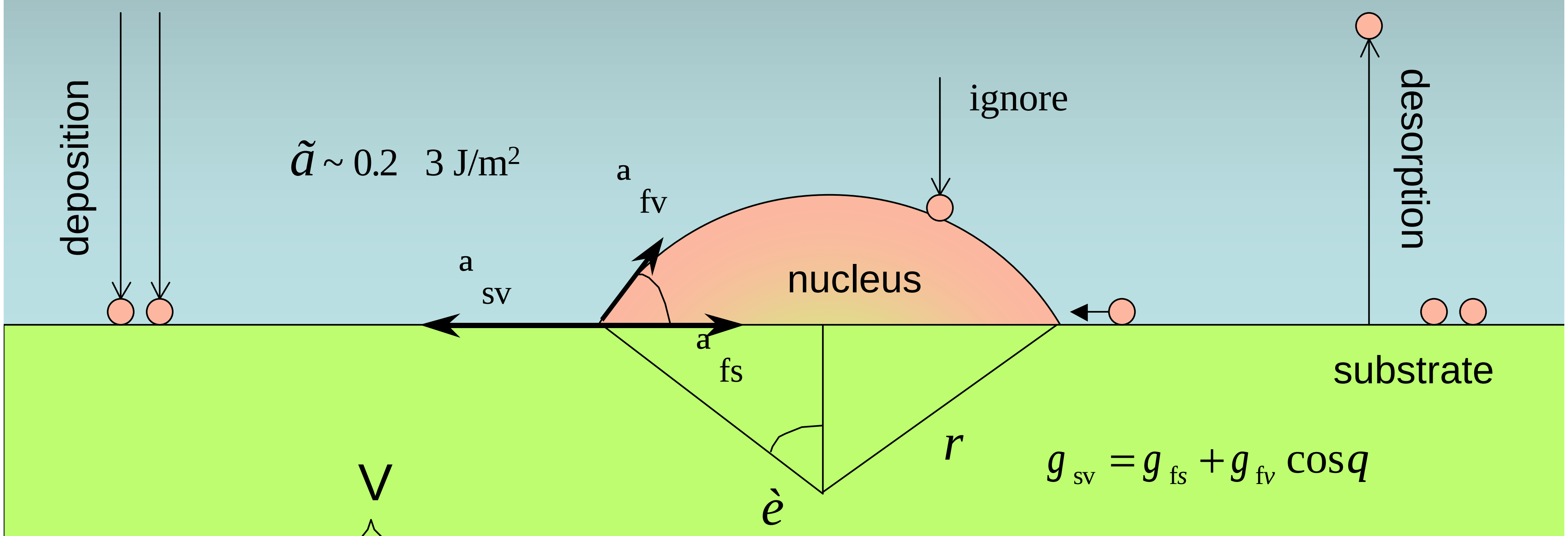


Thermodynamics of Thin-Film Nucleation

Issues addressed:

- conditions for stability of thin-film
- role of surface energies
- energies involved in nuclei formation
- thermodynamics of different modes
- influence of deposition rate & *T*

Thermodynamics of Thin-Film Nucleation



$$\Delta G(r) = \overbrace{\frac{ð}{3}(2 - 3\cos q + \cos^3 q)\, r^3}^{V} \Delta G_V +$$

$$+ \overbrace{2ð\,(1 - \cos q)\, r^2}^{S_{fv}} g_{fv} + \overbrace{ð \sin^2 q\, r^2}^{S_{fs}} (g_{fs} - g_{sv})$$

Thermodynamics of Thin-Film Nucleation

$$\Delta G_V = \frac{k_B T}{\Omega}\ln\frac{P_S}{P_V} = \frac{k_B T}{\Omega}\ln(1+ss)$$

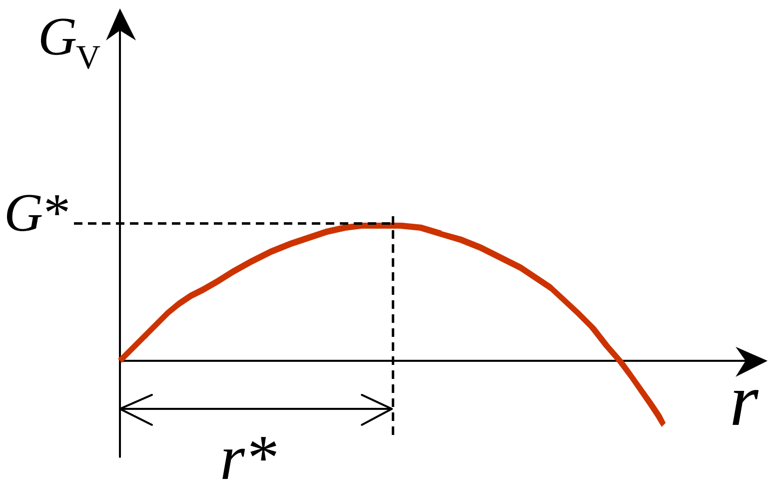
$$ss \equiv \frac{P_V}{P_S} - 1 \quad (\text{supersaturation})$$

If *ss*=0 $G_V = 0$ and nucleation impossible

$$\Delta G(r) = \overbrace{\frac{\eth}{3}(2-3\cos q + \cos^3 q)\, r^3}^{\text{V}} \Delta G_V + \overbrace{2\eth\,(1-\cos q)\, r^2}^{S_{fv}} g_{fv} + \overbrace{\eth \sin^2 q\, r^2}^{S_{fs}} (g_{fs} - g_{sv})$$

$$\frac{d}{dr}\Delta G(r) = 0 \rightarrow$$

$$r^* = \frac{-2(S_{fv} g_{fv} + S_{fs}(g_{fs} - g_{sv}))}{3V\Delta G_V}$$



$$\Delta G^* = \Delta G(r^*) = \frac{16\eth g_{fv}^3}{3(\Delta G_V)^2}\overbrace{\left(\frac{2-3\cos q + \cos^3 q}{4}\right)}^{\textit{wetting factor}}$$

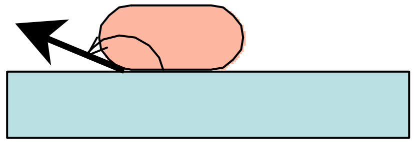
density of stable nuclei: $$N^* = n_S \exp\left(-\frac{\Delta G^*}{k_B T}\right)$$

n_S - density of all nuclei

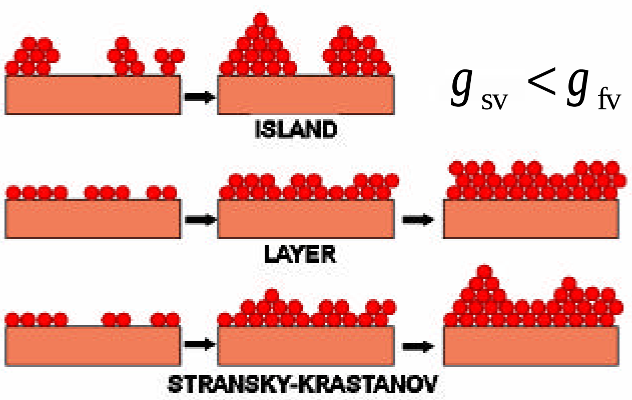
Thermodynamics of Thin-Film Nucleation

$$\cos q = \frac{g_{sv} - g_{fs}}{g_{fv}}$$

metals on dielectrics



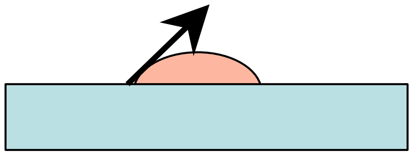
no wetting



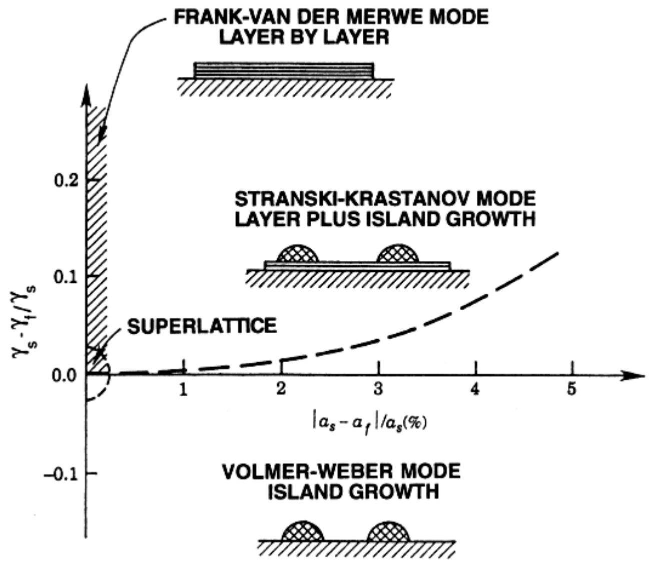
$$g_{sv} < g_{fv} + g_{fs}; \quad q > 90^\circ$$

$$g_{sv} \begin{Bmatrix} \geq \\ > \end{Bmatrix} (g_{fv} + g_{fs}); \quad q < 90^\circ$$

misfit



wetting



In general, materials with low surface energy will wet substrates with a higher surface energy

autoepitaxy: $\tilde{a}_{fs}=0$

Thermodynamics of Thin-Film Nucleation

Dependence on Substrate T and Deposition rate

$$\dot{R} \propto P_{\mathrm{V}}$$

equilib. evap. rate from the nucleus at the substr.T

$$\Delta G_{\mathrm{V}} = -\frac{k_{\mathrm{B}}T}{\Omega}\ln\frac{\dot{R}}{\dot{R}_e}$$

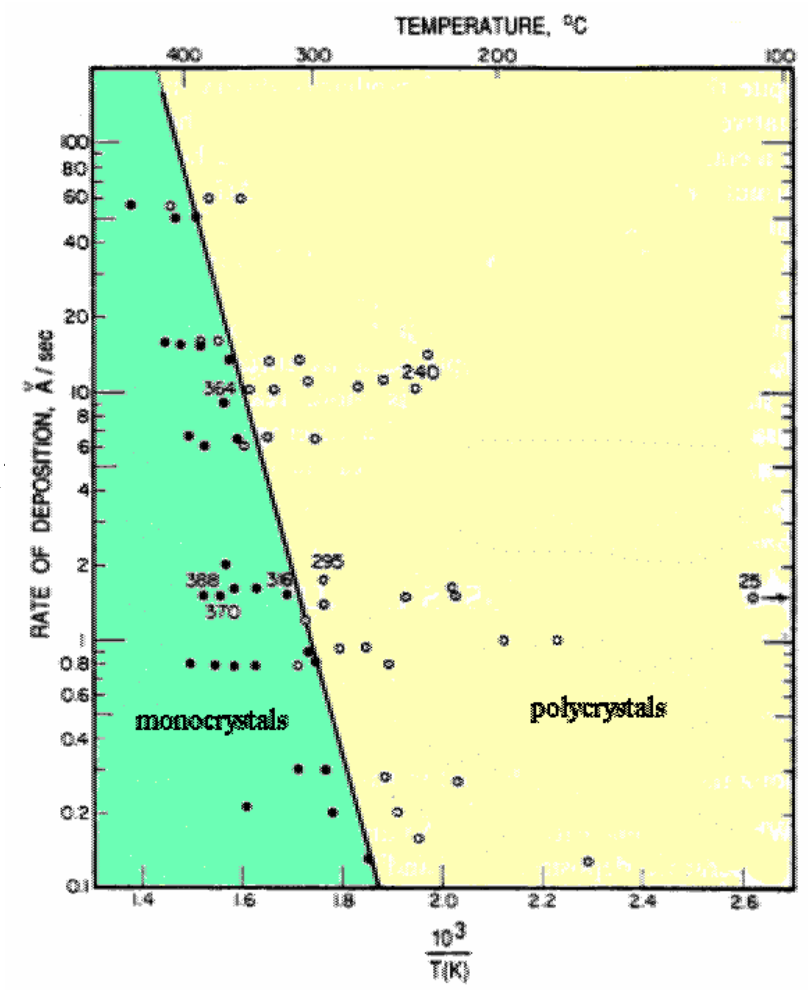
$$\left.\frac{\partial r^*}{\partial T}\right|_{\dot{R}} = \frac{\partial}{\partial T}\left(\frac{-2(S_{\mathrm{fv}}g_{\mathrm{fv}} + S_{\mathrm{fs}}(g_{\mathrm{fs}} - g_{\mathrm{sv}}))}{3V\Delta G_{\mathrm{V}}}\right) > 0$$

for $|\Delta G_{\mathrm{V}}| << 1.6\cdot 10^{10}\ \mathrm{J/m^3}, g_{\mathrm{fv}} = 1\,\mathrm{J/m^2}, \partial g_{\mathrm{fv}}/\partial T \approx -0.05\,\mathrm{mJ/m}$

$\partial\Delta G_{\mathrm{V}}/\partial T \approx 8\cdot 10^{6}\ \mathrm{J/m^3K}$

$$\left.\frac{\partial r^*}{\partial \dot{R}}\right|_{T} = \frac{\partial r^*}{\partial\Delta G_{\mathrm{V}}}\frac{\partial\Delta G_{\mathrm{V}}}{\partial\dot{R}} = \left(-\frac{\partial r^*}{\partial\Delta G_{\mathrm{V}}}\right)\left(-\frac{k_{\mathrm{B}}T}{\Omega\dot{R}}\right) < 0$$

$$\left.\frac{\partial\Delta G^*}{\partial\dot{R}}\right|_{T} < 0 \qquad \left.\frac{\partial\Delta G^*}{\partial T}\right|_{\dot{R}} < 0$$



Cu films on (111) NaCl

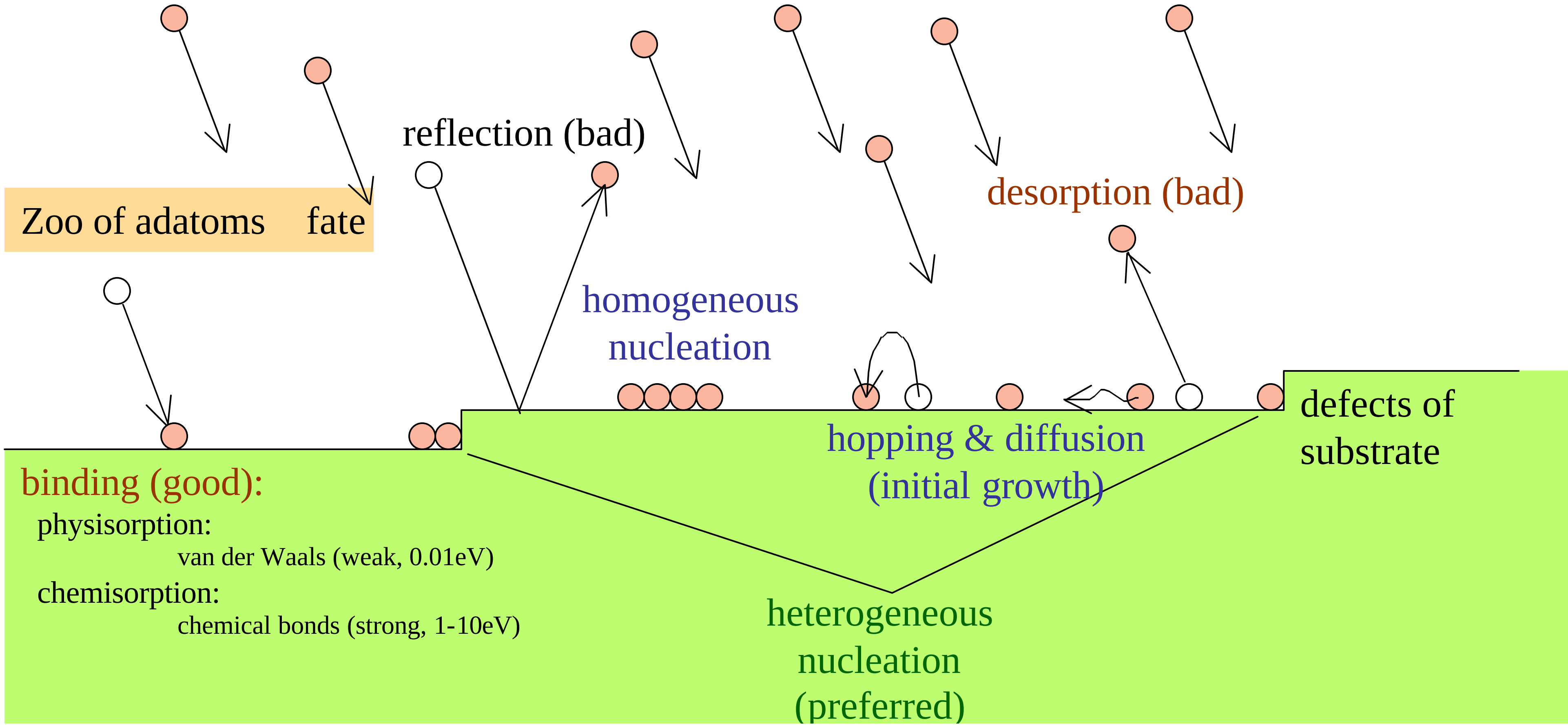
Kinetics of Thin-Film Nucleation

Issues addressed:

nucleation rate $\tilde{N}$ and its dependence on
t, T, $\dot{R}$, film itself and substrate

development of film growth and coalescence of nuclei

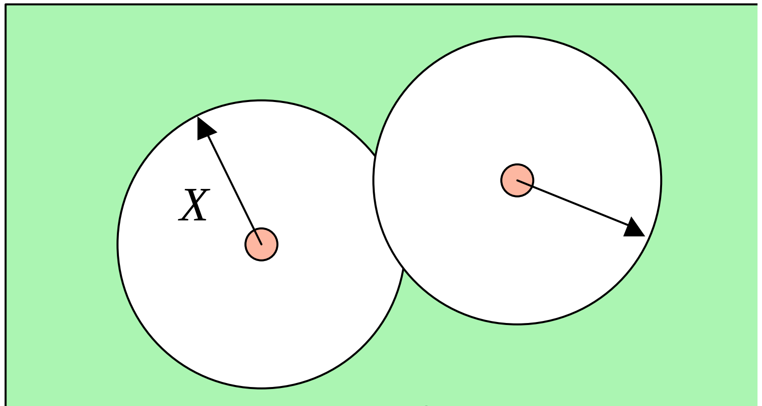
t-dep. of the growth and coalescence of nuclei



Kinetics of Thin-Film Nucleation

diffusion is determined by:

E_{diff} energy barrier for diffusion
T_{s} temperature of substrate
vibrational frequency of an adatom í
(attempt frequency)



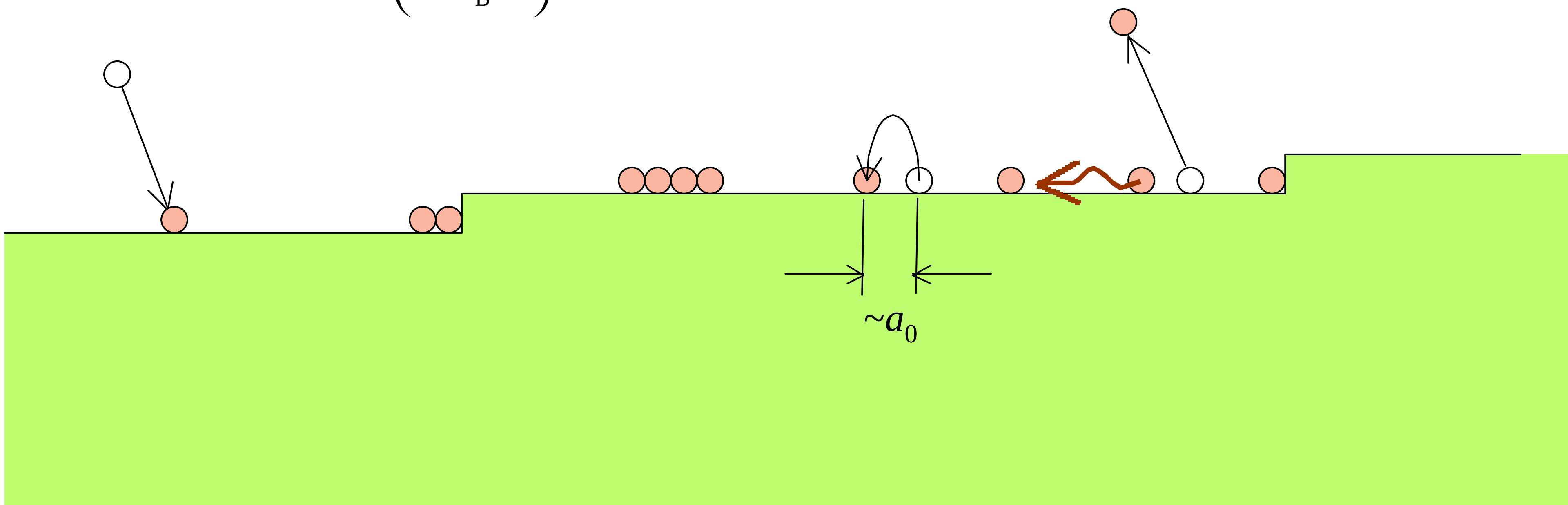
cluster can be formed in overlap region

frequency of surface jumps $\boldsymbol{n}_{\mathrm{J}} = \boldsymbol{n} \exp\left(-\frac{E_{\mathrm{diff}}}{k_{\mathrm{B}}T}\right)$

$$X \sim \sqrt{t_{\mathrm{S}} D_{\mathrm{S}}} = a_0 \exp\left(\frac{E_{\mathrm{des}} - E_{\mathrm{diff}}}{2k_{\mathrm{B}}T}\right)$$

surface diffusion coefficient

$$D_{\mathrm{S}} \sim a_0^2 \boldsymbol{n} \exp\left(-\frac{E_{\mathrm{diff}}}{k_{\mathrm{B}}T}\right)$$



Kinetics of Thin-Film Nucleation

desorption is determined by:

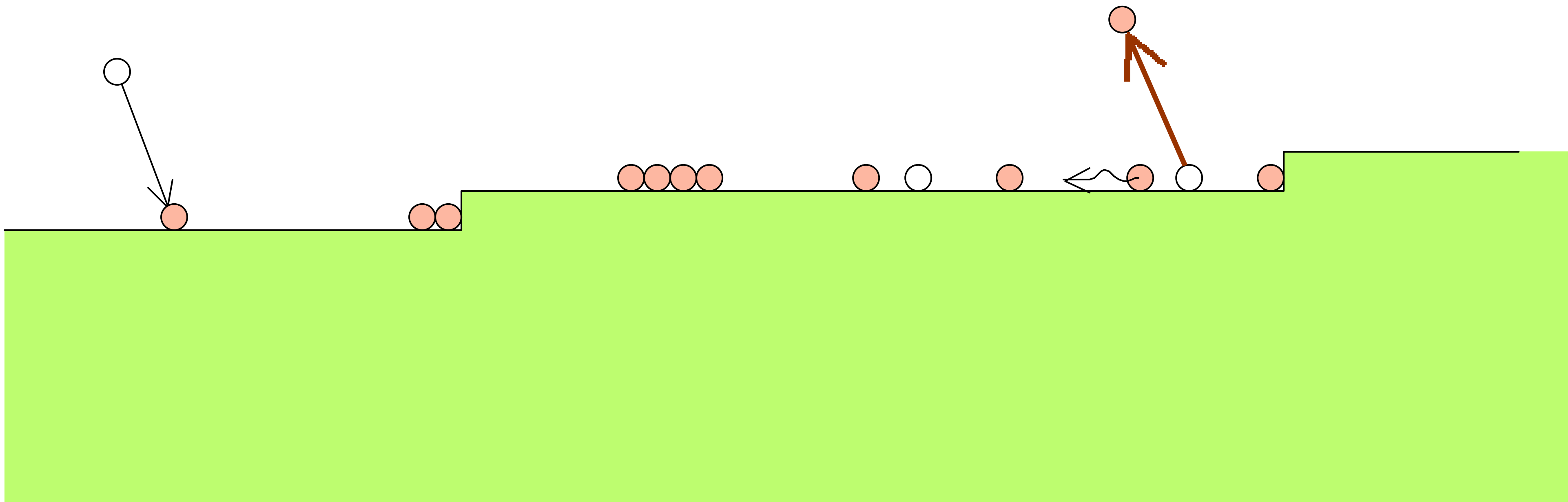
E_{des} energy barrier for desorption

T_s temperature of substrate

vibrational frequency of an adatom í

(attempt frequency)

life time of desorbing adatoms $$t_S = \frac{1}{n}\exp\left(\frac{E_{des}}{k_B T}\right)$$

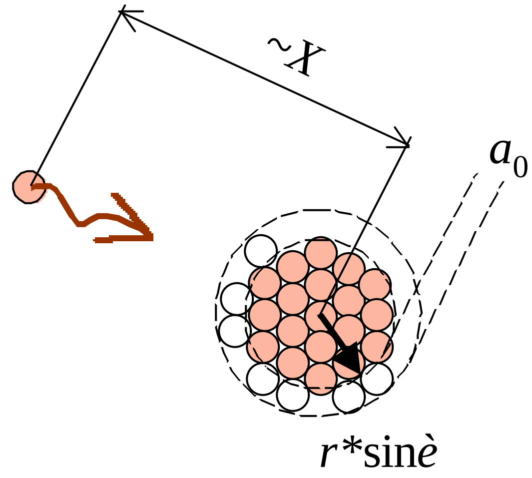


Kinetics of Thin-Film Nucleation

Nucleation rate

critical area $A^* \approx (2\text{ð}r^* \sin q)\, a_0$

$$\dot{N} = N^* \cdot A^* \cdot w \quad (\mathrm{cm}^{-2}\,\mathrm{s})$$



$$N^* = n_S \exp\left(-\frac{\Delta G^*}{k_B T}\right)$$

equilibrium concentration of *stable* nuclei

impingement rate onto nucleus

$$w = \Phi\, t_S\, n_J$$

$$n_J = n \exp\left(-\frac{E_{\mathrm{diff}}}{k_B T}\right)$$

$$t_S = \frac{1}{n} \exp\left(\frac{E_{\mathrm{des}}}{k_B T}\right)$$

$$f(v_x) = \frac{1}{n}\frac{\mathrm{d}n_x}{\mathrm{d}v_x} = \sqrt{\frac{M}{2\text{ð}RT}} \cdot \exp\left(-\frac{Mv_x^2}{2RT}\right)$$ Maxwell-Boltzmann

$$P = \frac{n}{N_A} RT$$

$$\Phi = \int_0^\infty v_x \mathrm{d}n_x = \int_0^\infty n\, f(v_x)\, \mathrm{d}v_x = n\sqrt{\frac{M}{2\text{ð}RT}} \cdot \int_0^\infty v_x \exp\left(-\frac{Mv_x^2}{2RT}\right) \mathrm{d}v_x = n\sqrt{\frac{RT}{2\text{ð}M}} = \frac{PN_A}{\sqrt{2\text{ð}RMT}}$$

(absorption flux from vapor)

the perfect gas law

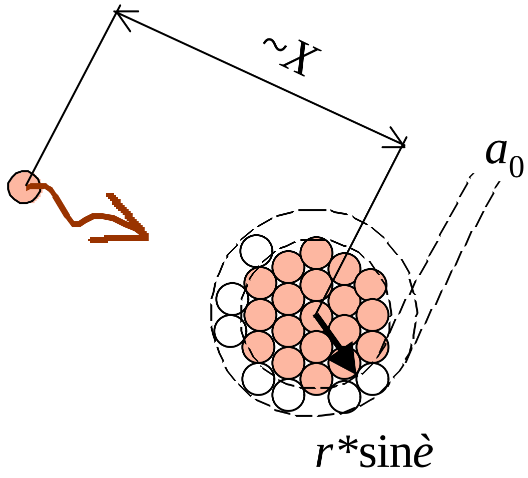
$$\dot{N} = (2p\, r^* \sin q)\, a_0 \frac{PN_A}{\sqrt{2\text{ð}RMT}}\, n \exp\left(\frac{E_{\mathrm{des}} - E_{\mathrm{diff}} - \Delta G^*}{k_B T}\right)$$

Kinetics of Thin-Film Nucleation

Atomistic Nucleation Model

Walton-Rhodin Theory

treats clusters of atoms as molecules rather than solid caps
considers the bonds between atoms
is similar to the capillarity model



E_{i*} - energy to break/form a critical cluster of i* atoms
N_{i*} - density of critical nuclei
N_1 density of single adatoms
n_0 density of adsorption cites

"Chemical" reaction: $iA=A_i$

$$\Delta G_i^* = E_i^* + k_B T \ln\left(\frac{N_1^{i*}}{N_i^*}\right)$$

Critical free energy to form nucleus ("molecule")
(chemical equilibrium between clusters and monomers)

$$n_J = n \exp\left(-\frac{E_{\text{diff}}}{k_B T}\right)$$

$$N_1 = \dot{R} t_S = \frac{\dot{R}}{n} \exp\left(\frac{E_{\text{des}}}{k_B T}\right)$$

$$t_S = \frac{1}{n} \exp\left(\frac{E_{\text{des}}}{k_B T}\right)$$

$$\dot{R} X^2 = a_0^2 \exp\left(\frac{E_{\text{des}} - E_{\text{diff}}}{k_B T}\right)$$

$$X \sim \sqrt{t_S D_S} = a_0 \exp\left(\frac{E_{\text{des}} - E_{\text{diff}}}{2 k_B T}\right)$$

$$\dot{N}_{i*} = \dot{R} a_0^2 n_0 \left(\frac{\dot{R}}{n_0 n}\right)^{i*} \exp\left(\frac{(i^* + 1)E_{\text{des}} - E_{\text{diff}} + E_{i*}}{k_B T}\right)$$

Law of Mass Action **(Waage & Guldberg 1867)**

aA + bB + ...   xX + yY + ...

[forward rate] k_1 $[A]^a$ $[B]^b$ ···

[reverse rate] k_{-1} $[X]^x$ $[Y]^y$ ···

in equilibrium, $k_1 [A]^a [B]^b \cdots = k_{-1} [X]^x [Y]^y \cdots$

$H_2 + I_2$ 2HI;

the direct reaction results from collision of H_2 and I_2 molecules =>
reaction rate is proportional to the number of such collisions;
the number of collisions is proportional to density of H_2 and I_2;
the density is proportional to pressure =>

the reaction rate is proportional to the partial pressures of H_2 and I_2 :

$$k_1 P_{H_2} P_{I_2}$$

similarly, the reverse reaction rate is proportional to the number of collisions between HI molecules => the reaction rate is

$$k_{-1} P_{HI}^2$$

in equilibrium $k_1 P_{H_2} P_{I_2} = k_{-1} P_{HI}^2$

we define the constant of equilibrium as

$$K(T) = k_{-1} / k_1 = P_{H_2} P_{I_2} / P_{HI}^2$$

ÄG = ÄG^0 + RT ln$K$,

Kinetics of Thin-Film Nucleation

Atomistic Nucleation Model (continued)

$$\dot{N}_{i^*} = \dot{R} a_0^2 n_0 \left(\frac{\dot{R}}{n_0 n}\right)^{i^*} \exp\left(\frac{(i^*+1)E_{\mathrm{des}} - E_{\mathrm{diff}} + E_{i^*}}{k_{\mathrm{B}} T}\right)$$

$$\dot{N}_{i^*=1} = \dot{N}_{i^*=2}$$

$$T_{1\to 2} = -\frac{E_{\mathrm{des}} + E_2}{k_{\mathrm{B}} \ln\left(\frac{\dot{R}}{nn}\right)}$$

$$\dot{R} = n_0 n \exp\left(-\frac{E_{\mathrm{des}} + E_2}{k_{\mathrm{B}} T_{1\to 2}}\right)$$

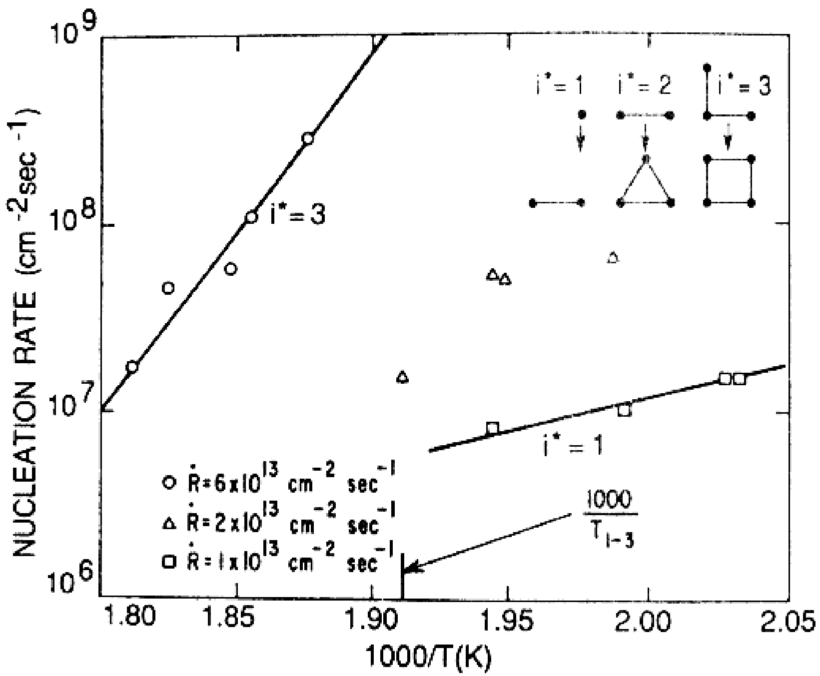


Figure 7-14 Nucleation rate of Ag on (100) NaCl as a function of temperature. Data for three different deposition rates are plotted. Also shown are smallest stable epitaxial clusters corresponding to critical nuclei. (From Ref. 21.)

Kinetics of Thin-Film Nucleation

Kinetic Nucleation Model

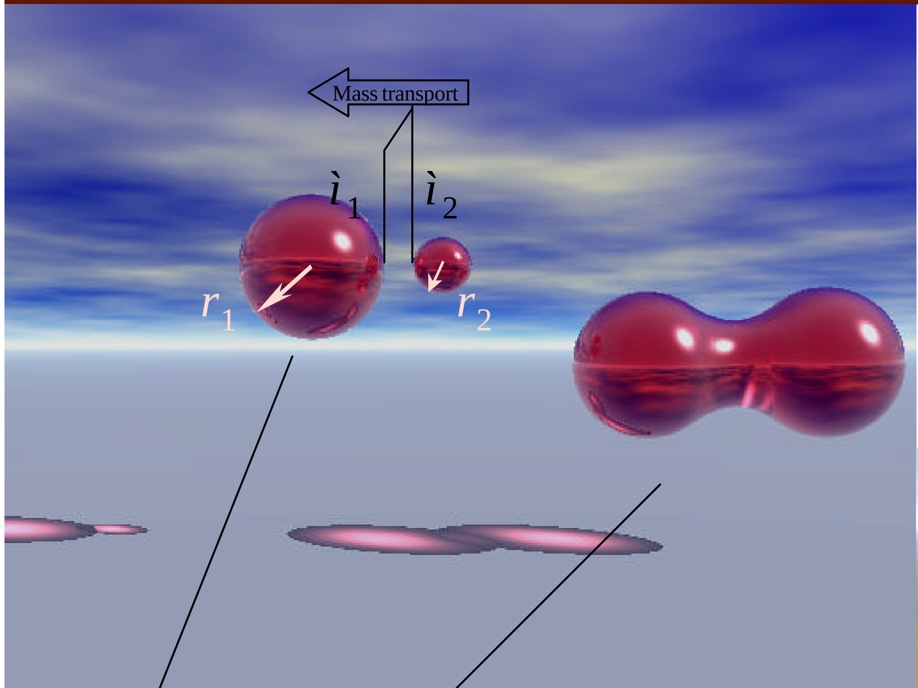
$$\frac{\mathrm{d}}{\mathrm{d}t} N_1 = \dot{R} - \frac{N_1}{t_{\mathrm{S}}} - K_1 N_1 - N_1 \sum_{i=2}^{\infty} K_i N_i$$

$$\frac{\mathrm{d}}{\mathrm{d}t} N_i = K_{i-1} N_1 N_{i-1} - K_i N_1 N_i$$

$$N_{\mathrm{S}} = A n_0 \left(\frac{\dot{R}}{n_0 t} \right)^p \exp\left(\frac{E}{k_{\mathrm{B}} T} \right)$$

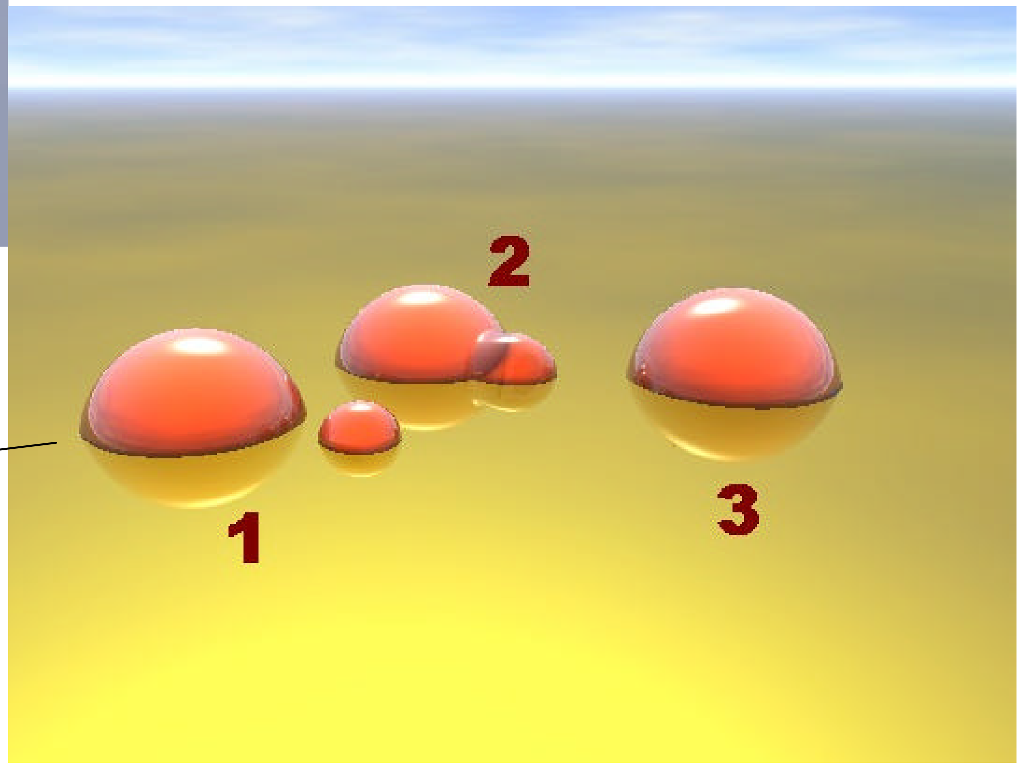
Kinetics of Thin-Film Nucleation

Cluster Coalescence and Depletion



$$\mu_i = \frac{dG}{dn_i} = \frac{d(4\pi r_i^2 \gamma)}{d(4\pi r_i^3 / 3\Omega)} =$$

$$= \frac{(8\pi r_i \gamma)dr_i}{(4\pi r_i^2 / 3\Omega)dr_i} = \frac{2\Omega\gamma}{r_i}$$



Ostwald rippening (large islands grow at the expence of the smaller ones)

Sintering

Cluster migration

Grain size