EPFL
École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering
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SuNMiL
Supramolecular NanoMaterials and Interfaces Laboratory

Heterophase Interfaces and Thin Films
Lesson 12

MSE 304

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桑缪 썬밀 सानमिल ΣouNMιΛ سنمل CaHMПЛ

Key Topics in the Previous Class

Described solid - solid interfaces

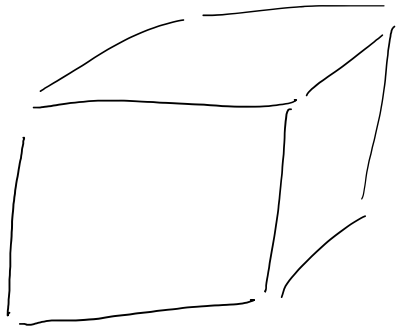
crystallography

energetics

-> solid - solid interface -> $\gamma_{ss} \simeq n_{bb} \cdot \varepsilon_{bb} + \bar{I}_{el}$

Slip Planes in a Crystal Structure

how do dislocations move?



{1,1,1} → 1,1,1 ; 1,1,$\bar{1}$; 1,$\bar{1}$,1 ; 1,$\bar{1}$,$\bar{1}$; $\bar{1}$,1,$\bar{1}$; $\bar{1}$,$\bar{1}$,1 ; $\bar{1}$,$\bar{1}$,$\bar{1}$

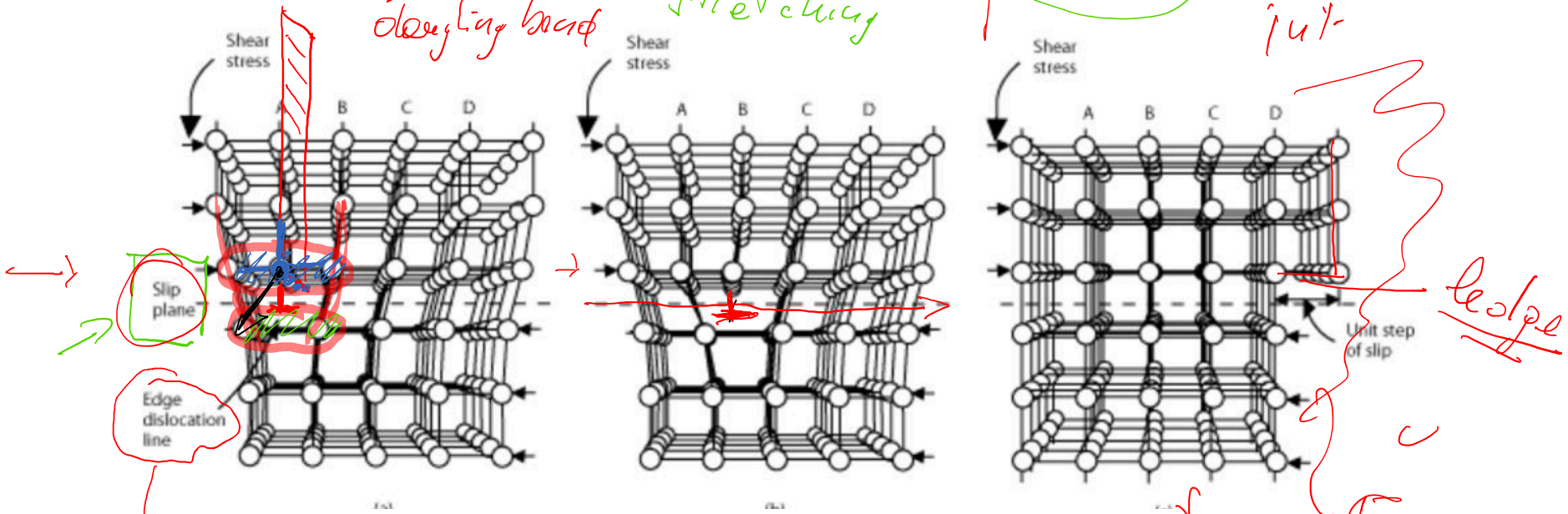
(u,v,w) ← crystallographic plane

density of a plane depends on u,v,w

slip plane the highest density plane

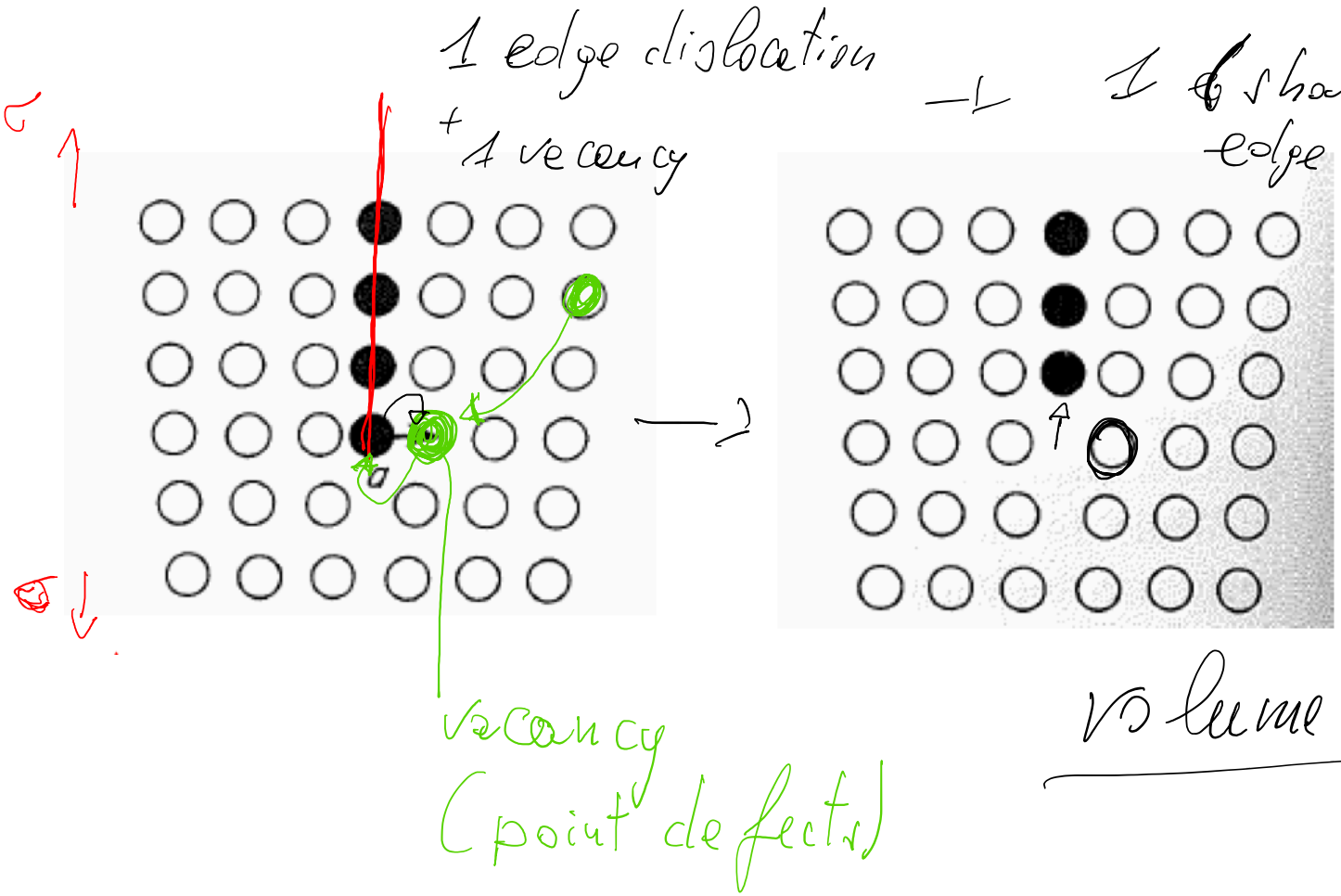
fcc (1,1,1) → {1,1,1}

Glide Motion of Dislocations



Edge or line dislocation (or a dislocation that has an edge character)

Climb Motion for Dislocations



Glide and Climb Motion for Dislocations

$\vec{l}$ vector in the plane of the dislocation

$\vec{t}$ ⊥ dislocation movement

Glide vs. Climb

Glide/slip: *conservative movement within the slip plane*

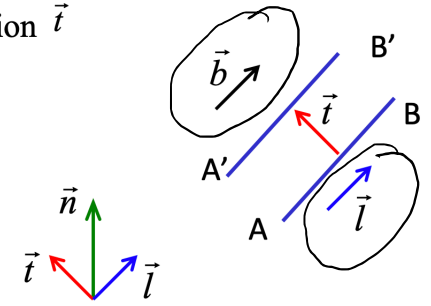
Climb: *non-conservative movement away from the slip plane*

let's consider a dislocation AB that moves to A'B' in the direction $\vec{t}$

$\vec{n} = \vec{l} \times \vec{t}$ - surface normal

$\vec{b} \cdot \vec{n} = 0$ - conservative motion, glide

$\left.\begin{array}{l} \vec{b} \cdot \vec{n} > 0 \text{ - addition of material} \\ \vec{b} \cdot \vec{n} < 0 \text{ - removal of material} \end{array}\right\}$ climb



$\vec{n} \cdot \vec{b} = \vec{l} \times \vec{t}$

Glide and Climb Motion of Dislocations

Glide vs. Climb

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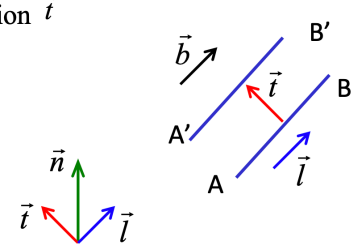
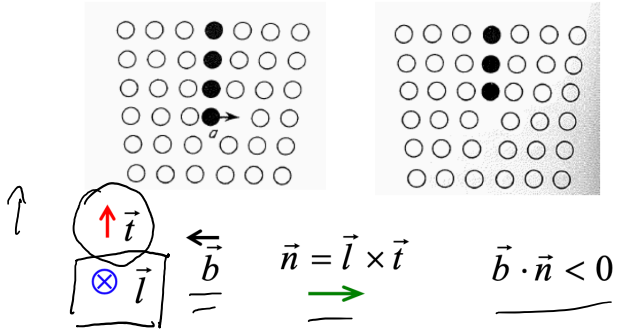
} climb



example:



- positive climb
  crystal shrinks in direction parallel to slip plane
  results from compressive strain

in general, volume change due to climb is

$$\Delta V = \vec{b} \cdot \vec{l} \times \vec{t} = \vec{b} \times \vec{l} \cdot \vec{t}$$

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Glissile and Sessile Interfaces

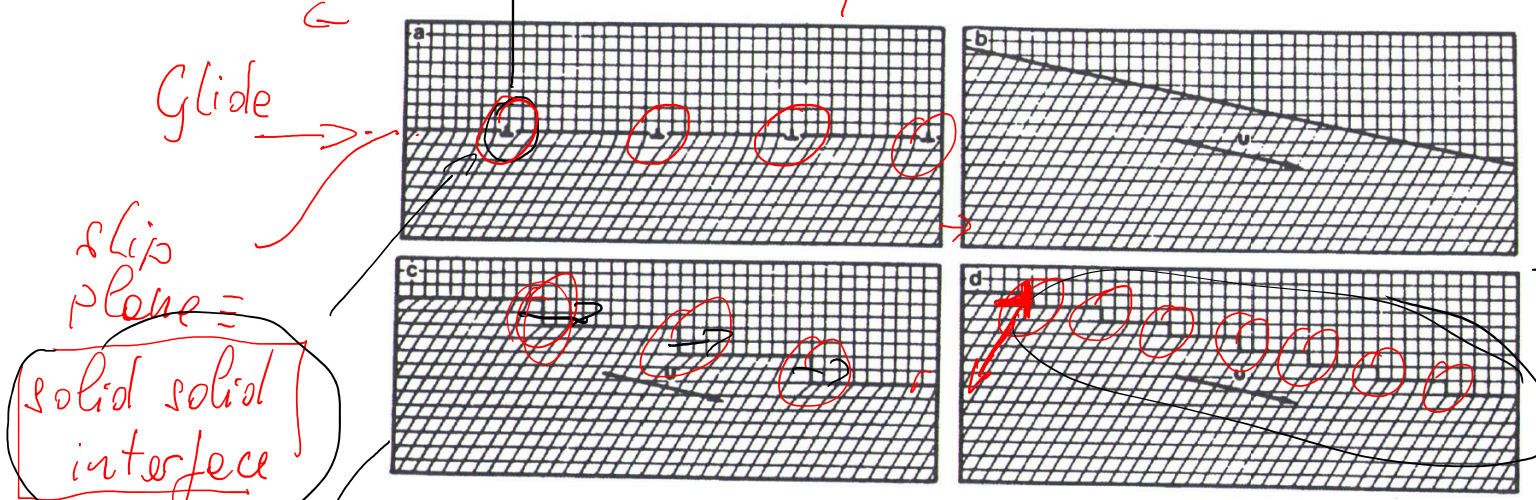

Figure 14.39. Possible interfaces for a transformation described by a shear e_{12} coupled with an expansion e_{11} in the shear plane. (a) The expansion is accommodated by a set of perfect lattice (misfit) dislocations. (b) The interface lies along an invariant line **u** and no dislocations are necessary. (c) The invariant line is resolved onto every other close-packed plane as in the f.c.c.–h.c.p. transformation where each ledge is an $a/6<112>$ partial dislocation. (d) The invariant line is resolved onto every close-packed plane as in an f.c.c.–b.c.c. transformation where each ledge contains an $a/12<112>$ partial dislocation. Reprinted with permission from [153] by Elsevier Science Ltd., Oxford, England.

SESSILE INTERFACE can move only by a climb of its interfacial (misfit) dislocation

climb

Glide

slip plane = solid solid interface

GLISSILE can move by a glide motion of its interfacial dislocation into the bulk

Glide → move solid-solid interface

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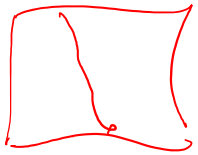
Glissile and Sessile Interfaces



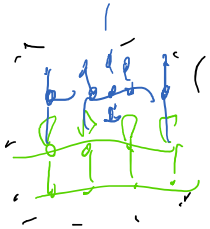
movement of interface a key mechanical property determinant for a material hardening

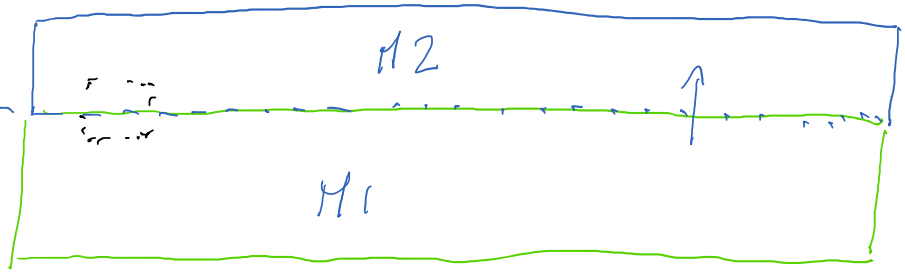
required two sliding of point defects

Glide motion is always faster than a climb

Glissile interface moves faster than a sessile interface

Thin Films in Modern Technology





interfacial electronic behavior

band structure of M2

band structure of M1

band structure → bonding in a perfect crystal → electronic behaviour of the material

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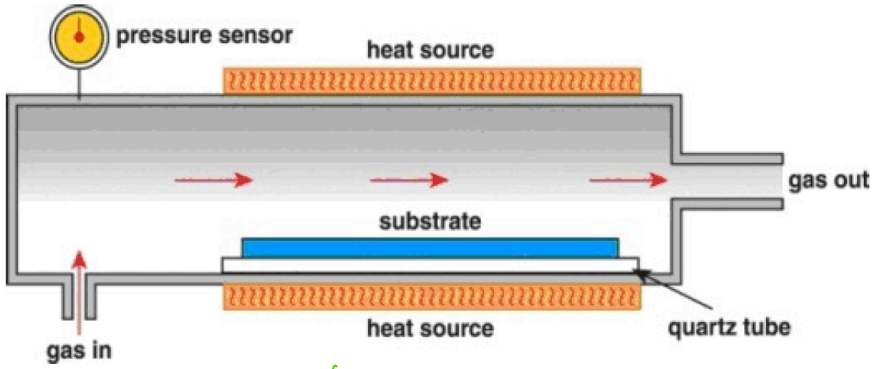
Thin Films in Modern Technology

- Growth of thin films of materials allows extreme control of the structure of matter at the nano-scale
- On the lab. scale: molecular beam epitaxy (MBE)
  - Extremely "clean" conditions, exquisite control of all parameters
  - Batch operation, extremely slow, ultra-high vacuum
- On the industrial level: chemical vapor deposition (CVD)
  - "Dirtier" operation, but much simpler to operate

in vacuum



substrate

start a substrate with a know surface (know crystallography)

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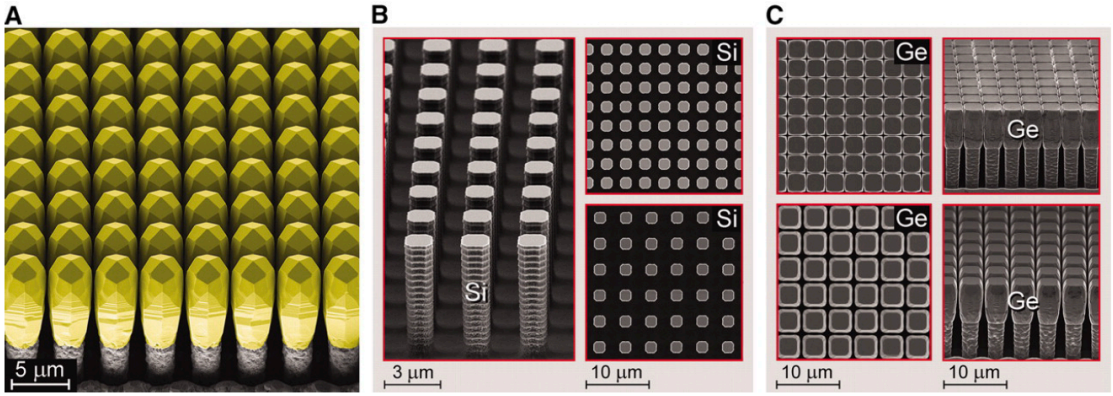
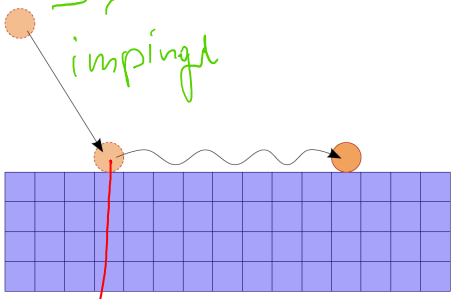
Thin Films – Morphology Control

columns, pillars, nanowires



Strain-free Ge nanopillars grown by PECVD. [Falub et al., Science, 2012]

Growth Models for Thin Films



atom MBE
molecule that decompose CVD
impingt

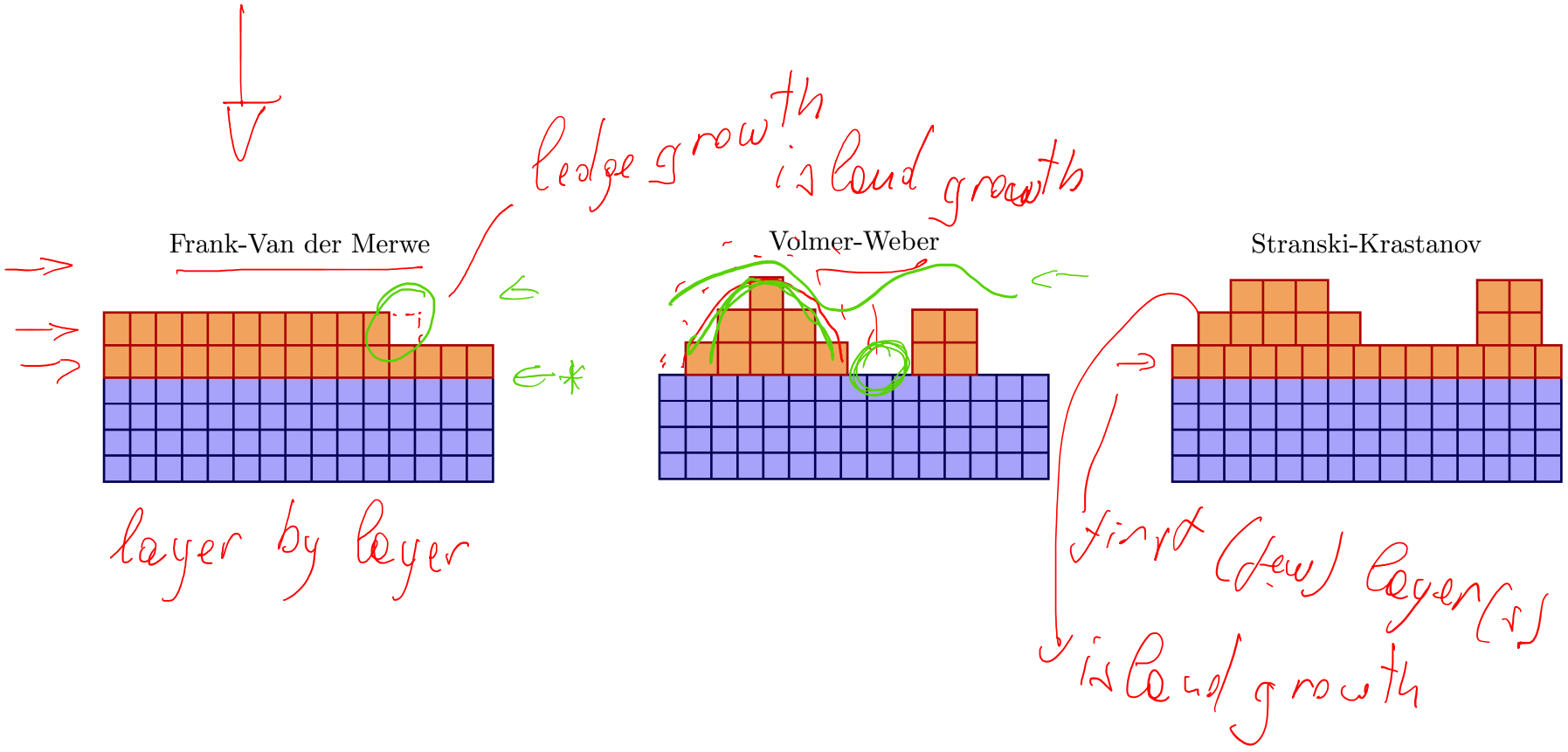
2 extreme case

(1)

→ an adatom can freely move up to its equilibrium position

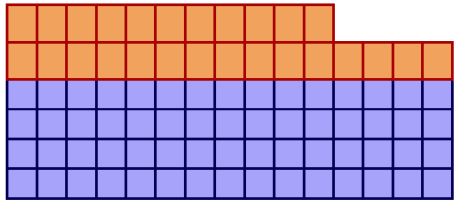
→ any adatoms is kinetically trapped

Growth Models for Thin Films



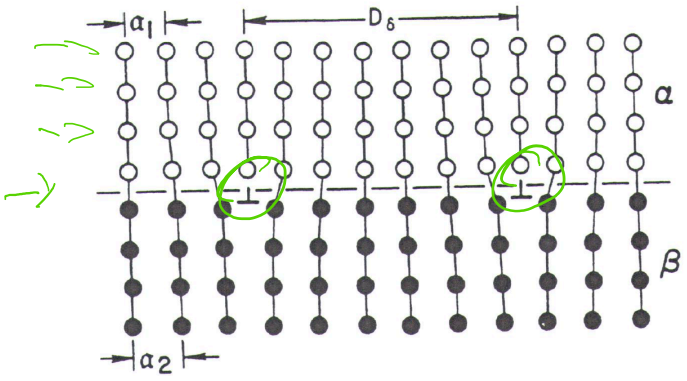
Growth Models for Thin Films

Frank-Van der Merwe



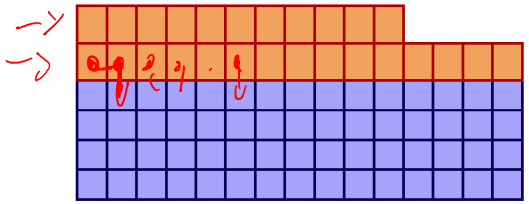
δ is small

no difference in crystallographic dimension and symmetry $\Rightarrow \delta = 0$



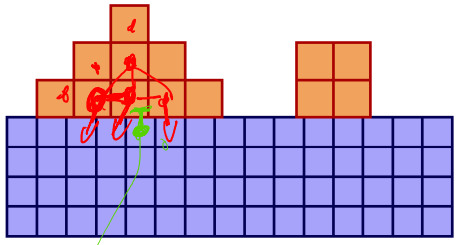
Growth Models for Thin Films: First Explanation

Frank-Van der Merwe



adatoms prefer to bond to substrate atoms more that to themselves

Volmer-Weber



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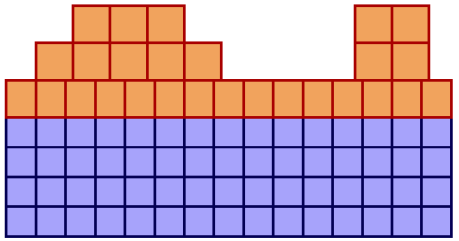
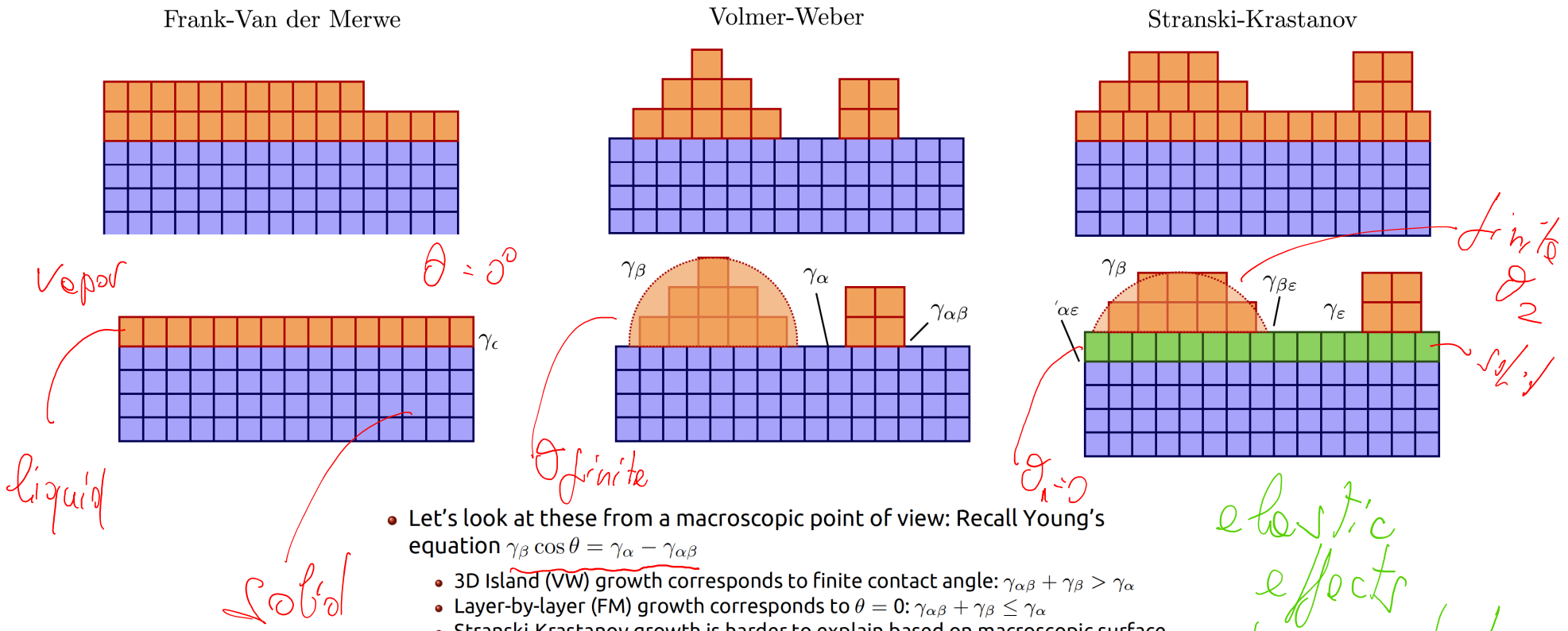
Stranski-Krastanov

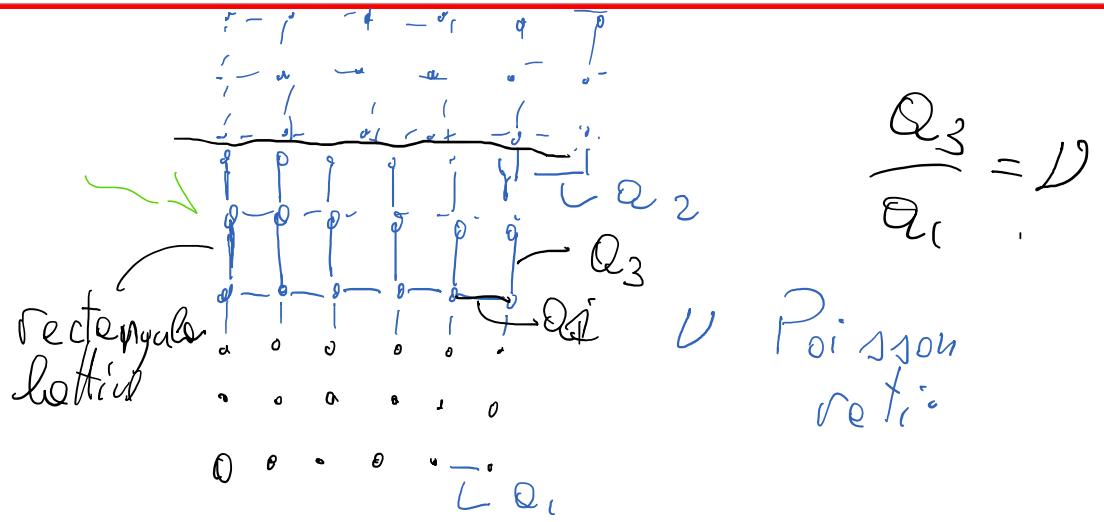


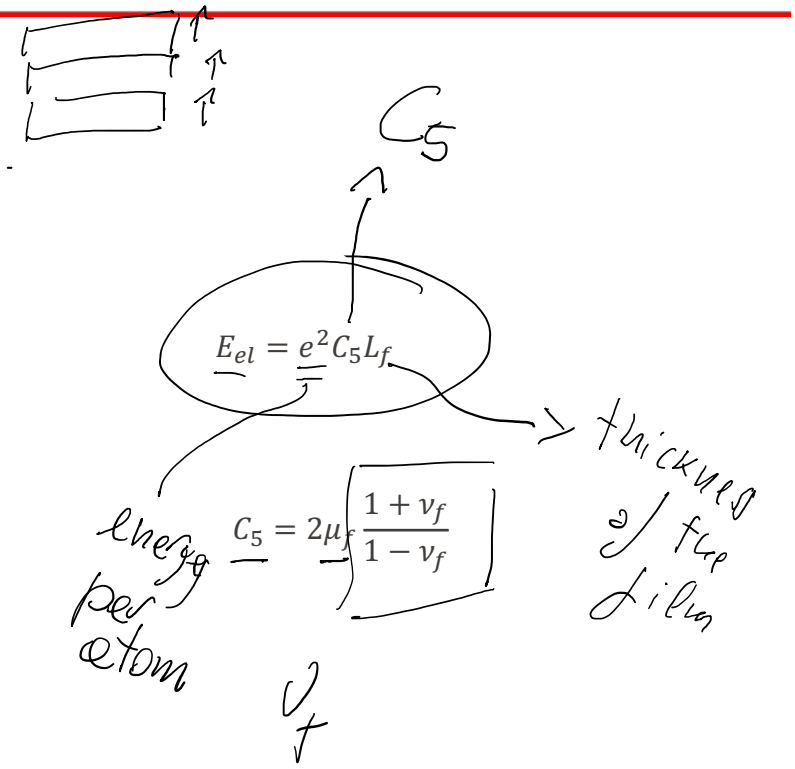
Growth Models for Thin Films: Second Explanation

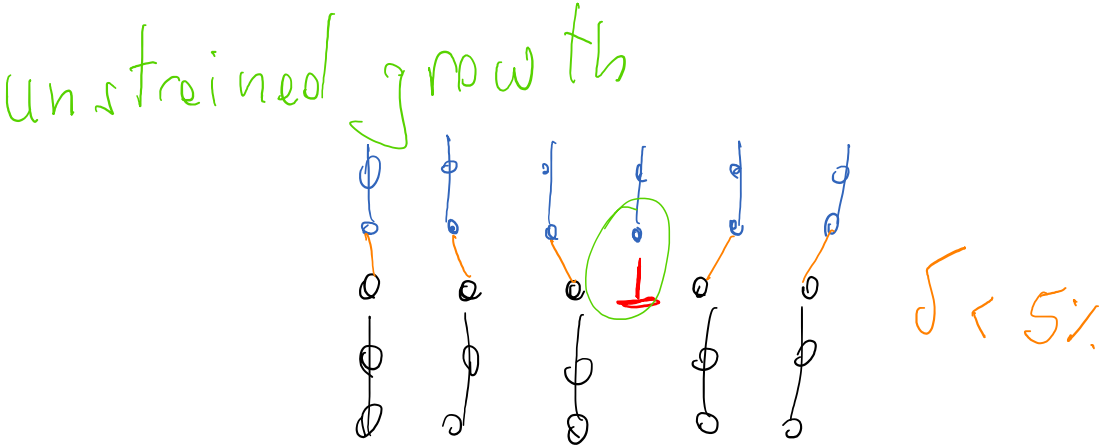


- Let's look at these from a macroscopic point of view: Recall Young's equation $\gamma_\beta \cos\theta = \gamma_\alpha - \gamma_{\alpha\beta}$
  - 3D Island (VW) growth corresponds to finite contact angle: $\gamma_{\alpha\beta} + \gamma_\beta > \gamma_\alpha$
  - Layer-by-layer (FM) growth corresponds to $\theta = 0$: $\gamma_{\alpha\beta} + \gamma_\beta \leq \gamma_\alpha$
  - Stranski-Krastanov growth is harder to explain based on macroscopic surface energies. If we consider the strained film as a different material ε, it must be that $\gamma_{\alpha\varepsilon} + \gamma_\varepsilon \leq \gamma_\alpha$, and $\gamma_{\beta\varepsilon} + \gamma_\beta > \gamma_\varepsilon$

Strained and Unstrained Growth







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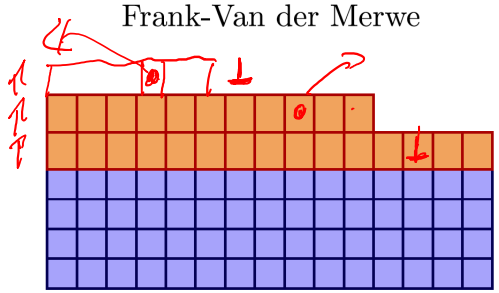
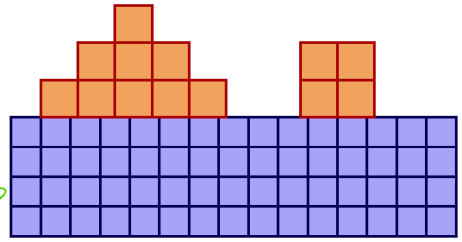
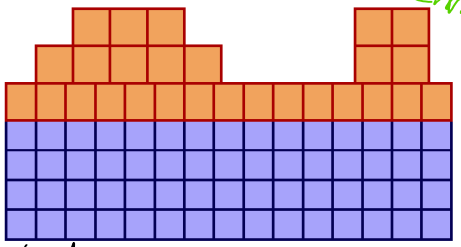
Growth Models for Thin Films: Third Explanation







$$\mu(n) = \mu_\infty + [\varphi_a - \varphi'_a(n) + \varepsilon_d(n) + \varepsilon_e(n)]$$

$\frac{d\mu}{dn} > 0$

$\frac{d\mu}{dn} < 0$

per atom
- $\varepsilon_d(n)$ energy of the dislocations
- $\varepsilon_e(n)$ elastic energy

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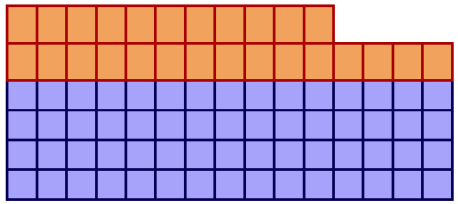
Growth Models for Thin Films: Third Explanation

Frank-Van der Merwe



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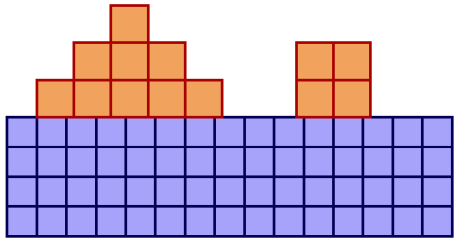
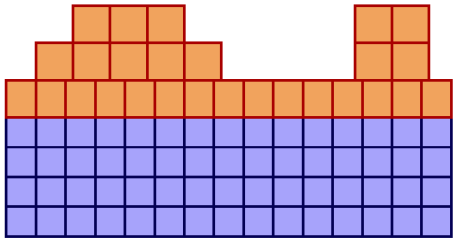
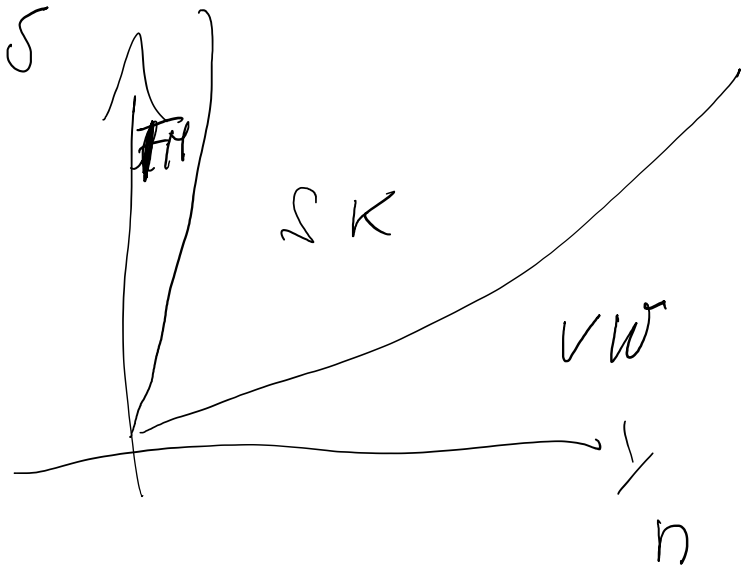


Stranski-Krastanov





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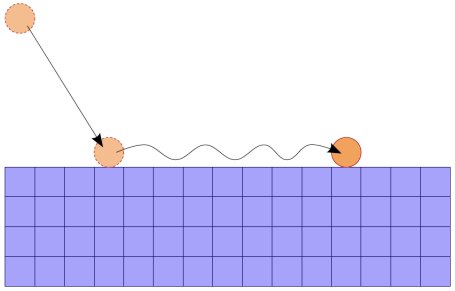
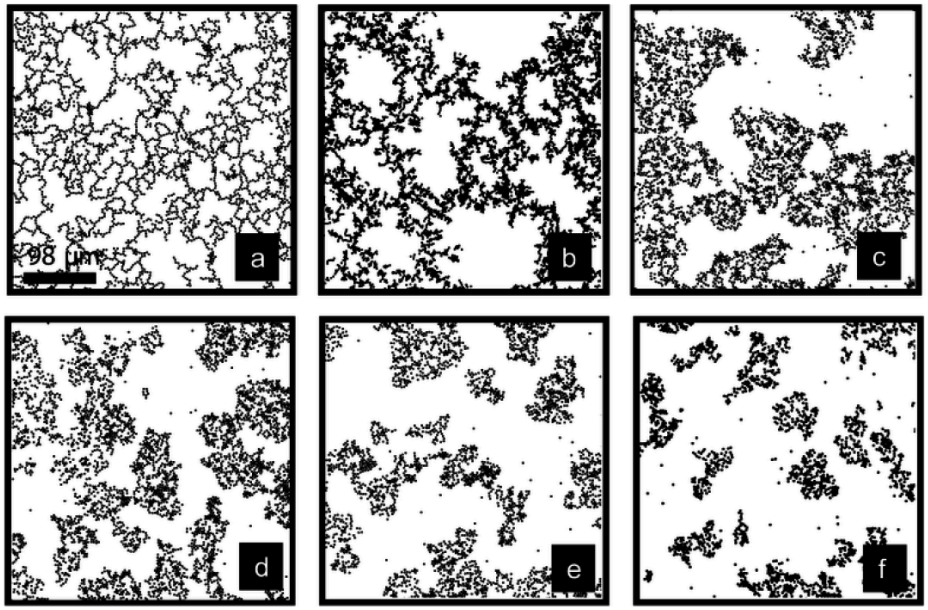
Growth Models for Thin Films



#2 atoms are stuck

Diffusion Limited Aggregation

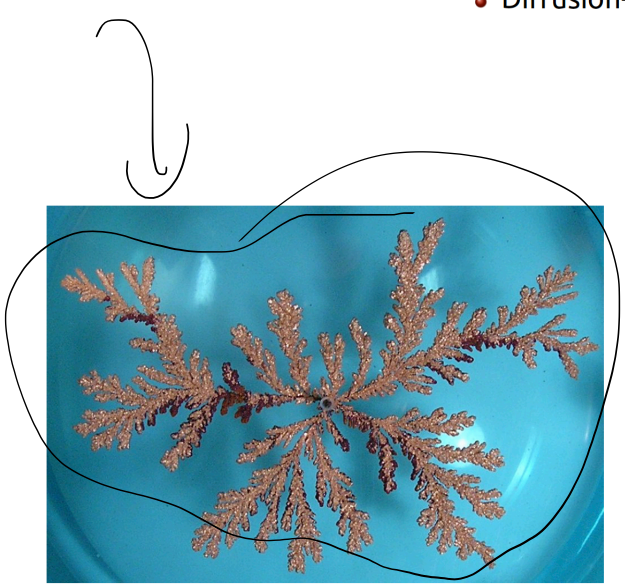
DLA



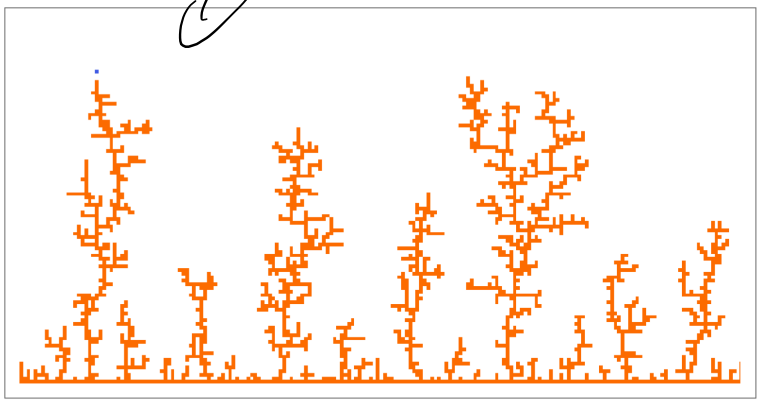
Flow-induced aggregation of colloids. [Massachaele et al., Soft Matter, 2011]

Diffusion Limited Aggregation

- Growth regimes discussed this far assume local equilibration between atom attachments
- The opposite case is a "stick where you hit" grow mode - strongly out of equilibrium structure
- Diffusion-limited aggregation



snow flakes dendrimer



columnar

Conclusions

interface movement depends on the nature of the interfacial dislocations

mechanical properties

↳ can control thin film growth

electronic properties