Epitaxial Growth of Nanostructures

M. Ceriotti - MSE304

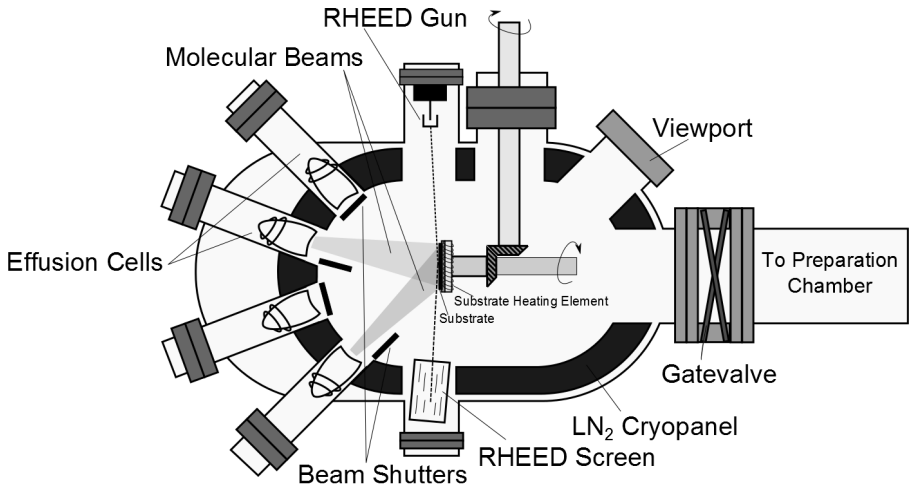
EPFL

Outline

- The role of kinetics in the growth of materials:
  - Diffusion Limited Aggregation
- Molecular beam epitaxy
- Modes of epitaxial growth (Howe, Section 7.2)

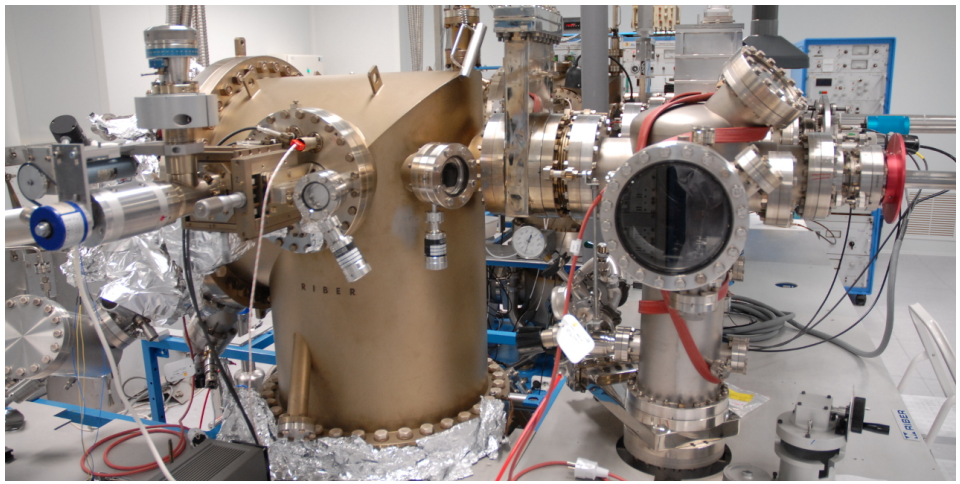
Thin-film Technology

- 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



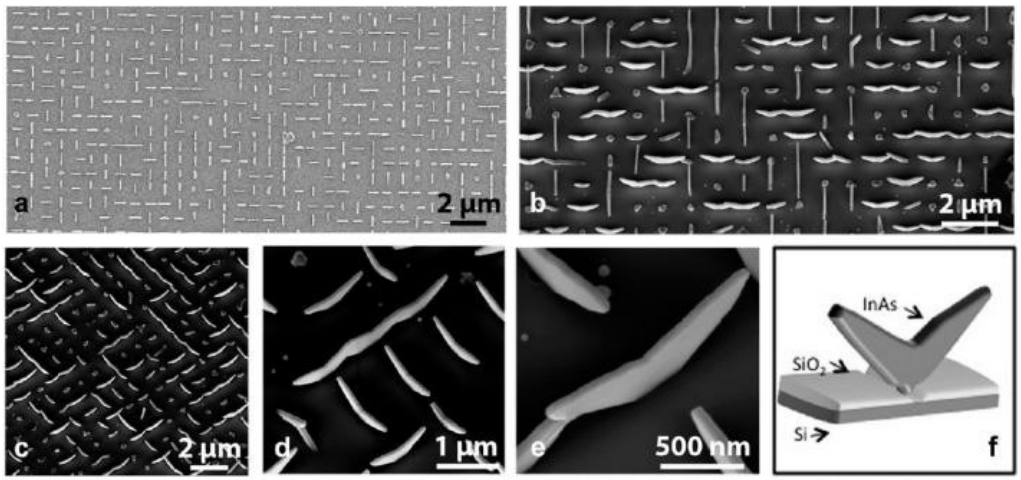
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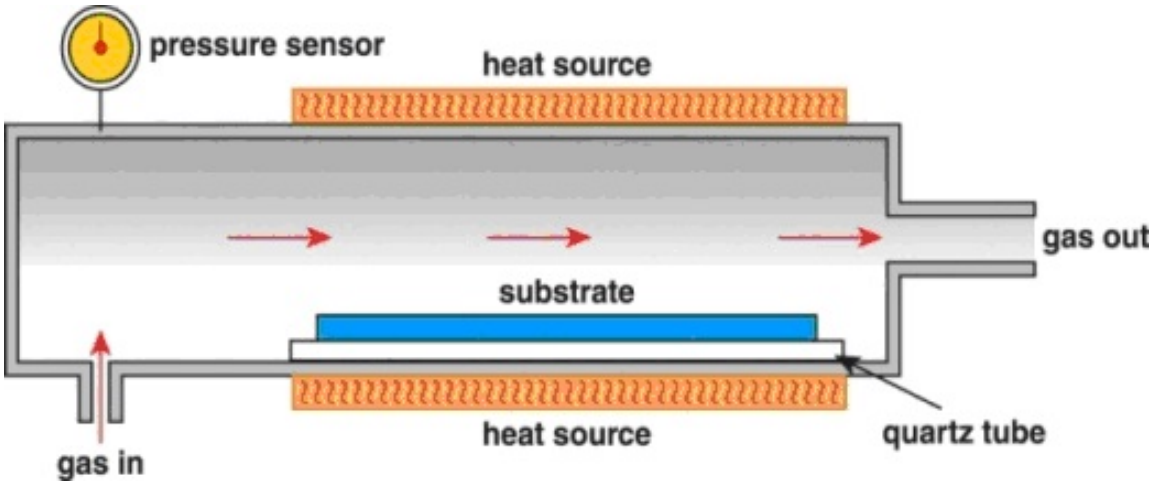
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V-shaped GaAs nanomembranes grown on Si(001). [Conesa-Boj et al., ACS Nano, 2012]

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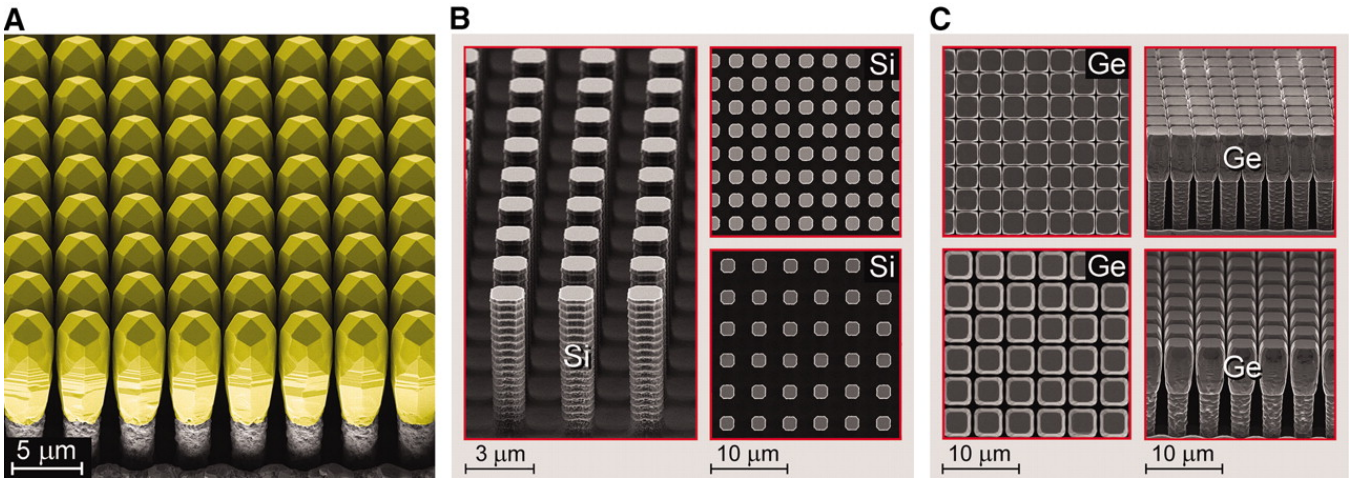
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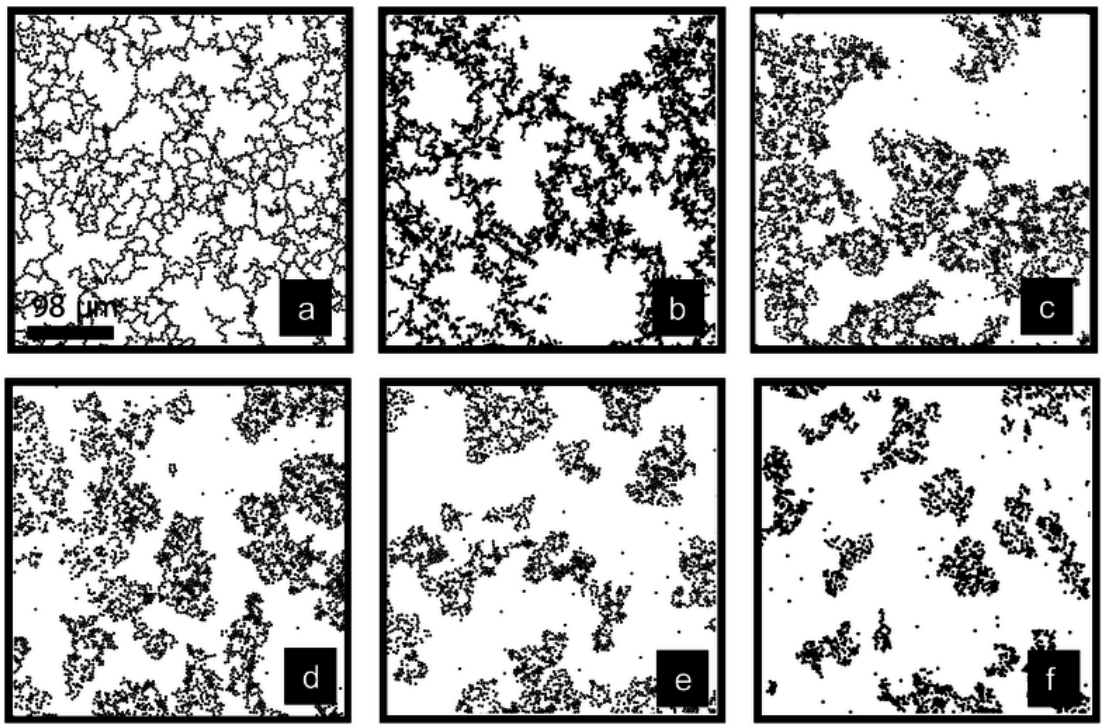
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Strain-free Ge nanopillars grown by PECVD. [Falub et al., Science, 2012]

Diffusion-Limited Aggregation

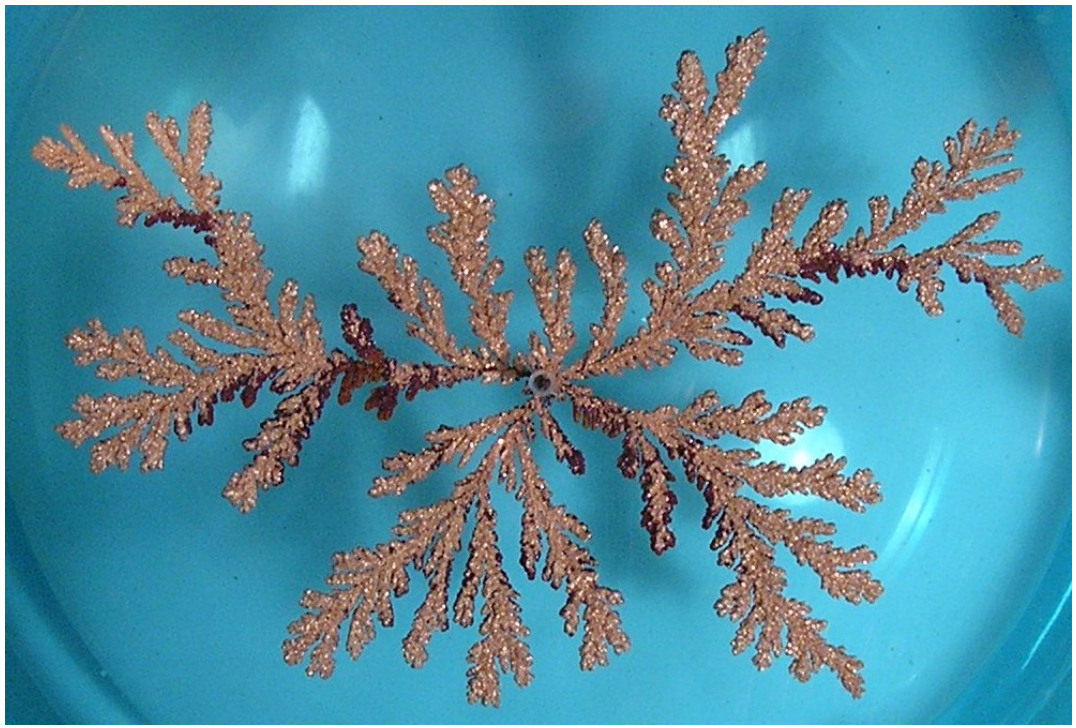
- Growth regimes discussed this far assume local equilibration between atom attachments
- The opposite case is a “stick where you hit” grow mode - strongly out of equilibrium structure
- Diffusion-limited aggregation



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

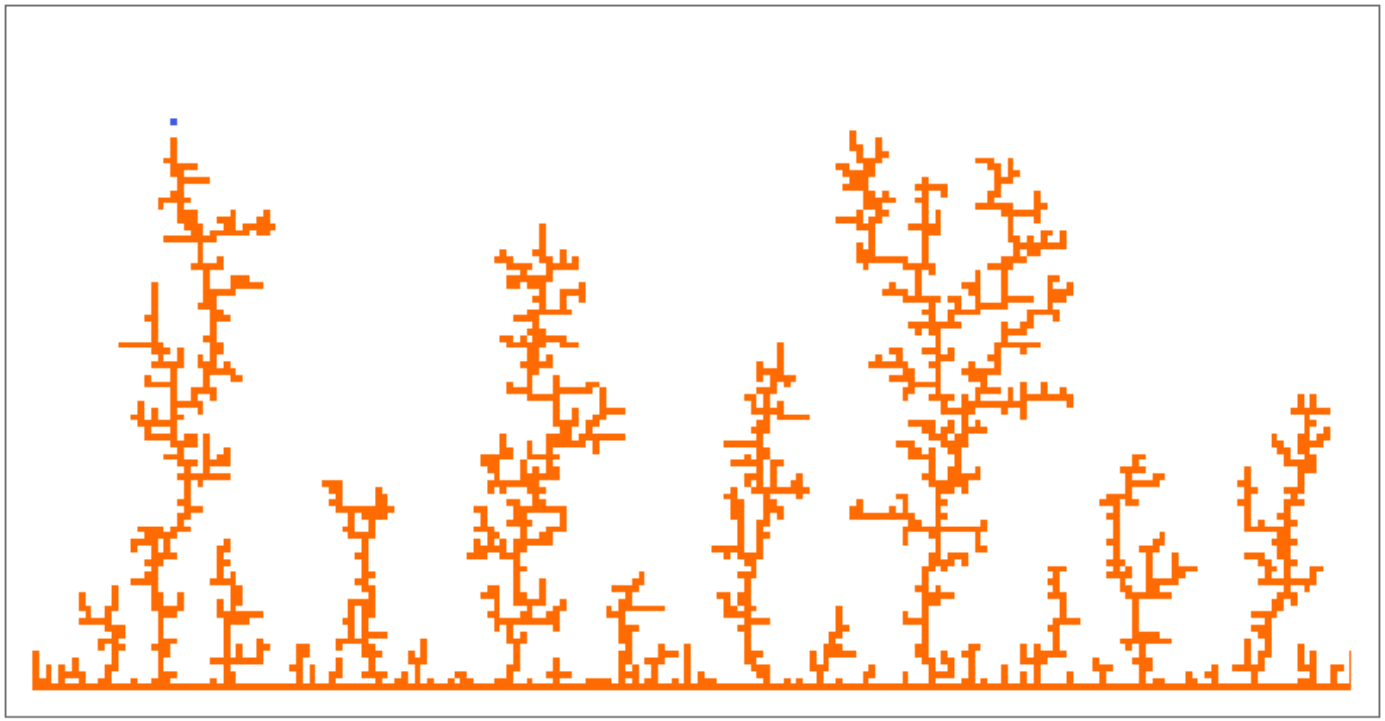
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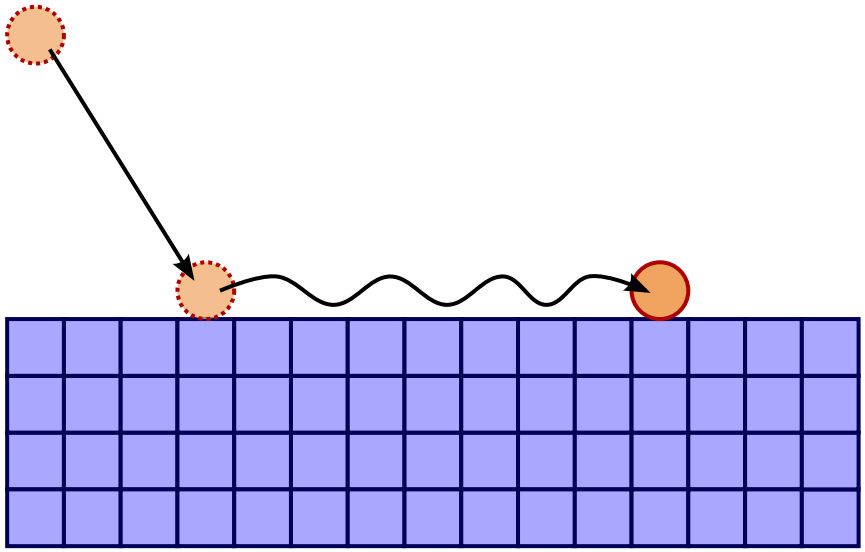
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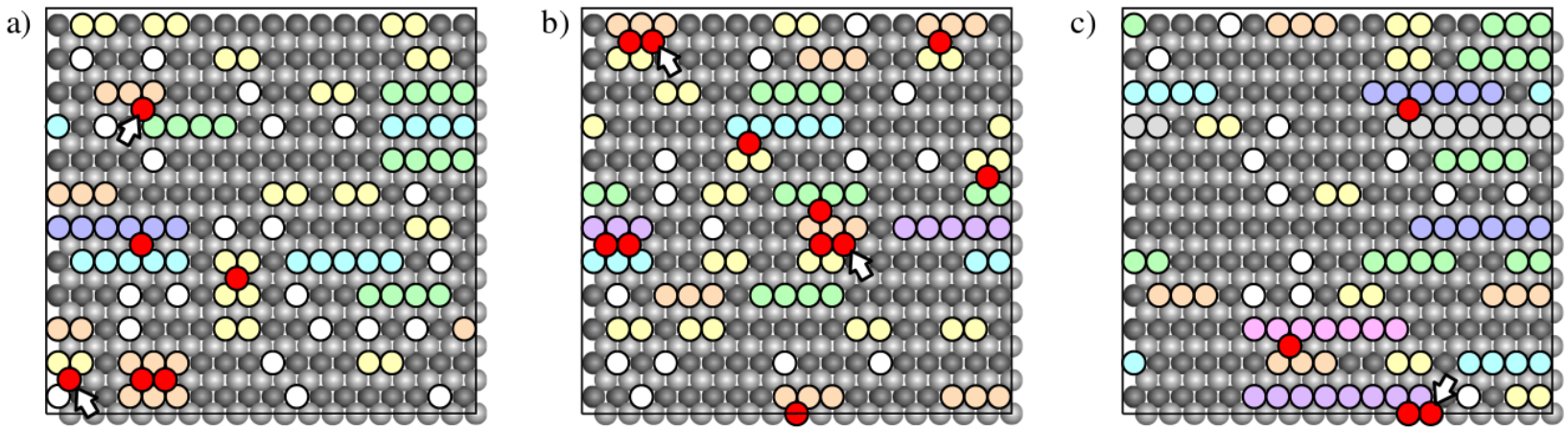
Modes of Epitaxial Growth

- Assume first that each deposited atom reaches (local) thermodynamic equilibrium
- Depending on the interaction between the substrate α and the film β we can have
  - Franck-Van Der Merwe growth (layer-by-layer)
  - Volmer-Weber growth (3D Islands)
  - Stranski-Krastanov growth (2D + 3D)



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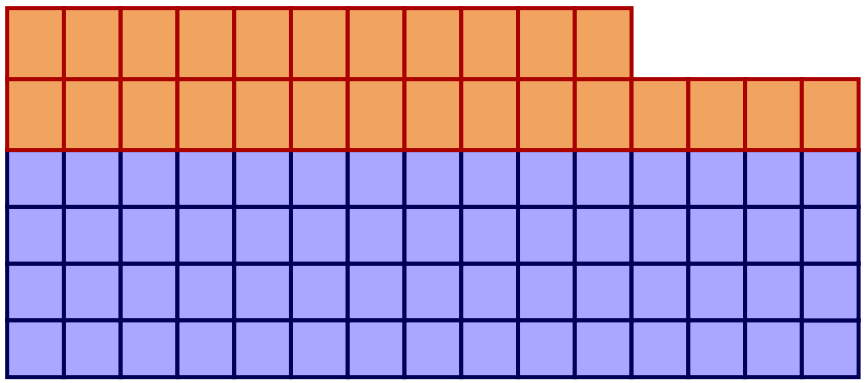


Transient mobility at Ag(110). [Ceriotti, Ferrando, Montalenti, Nanotechnology, 2006]

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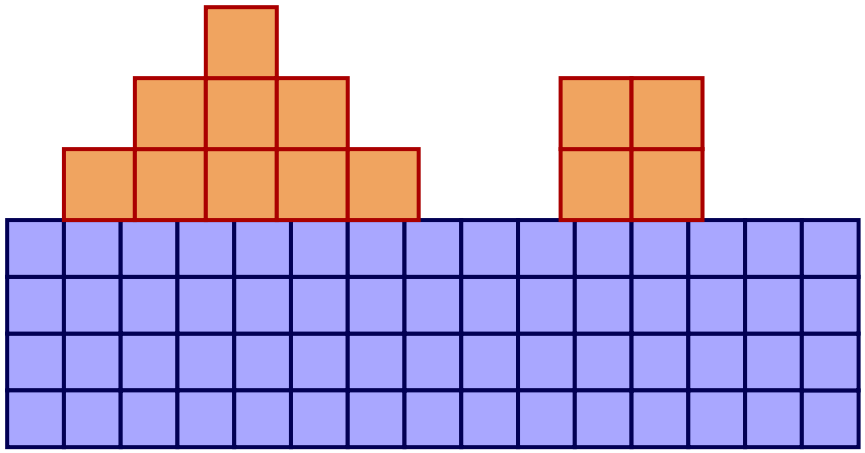
Frank-Van der Merwe



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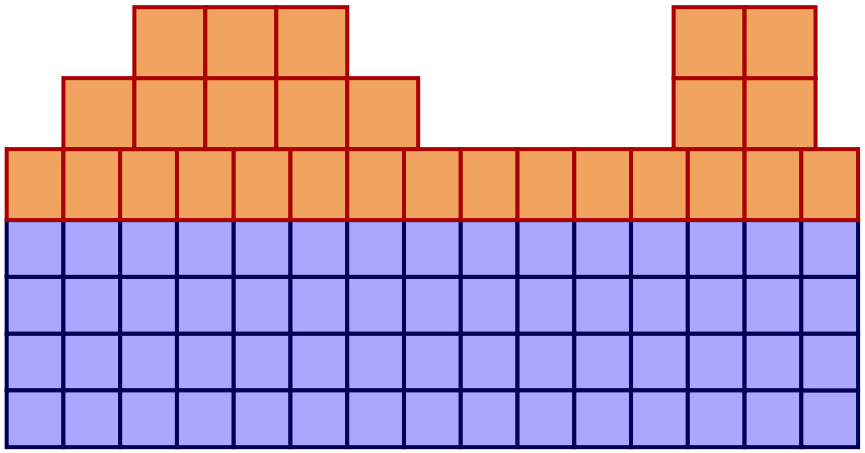
Volmer-Weber



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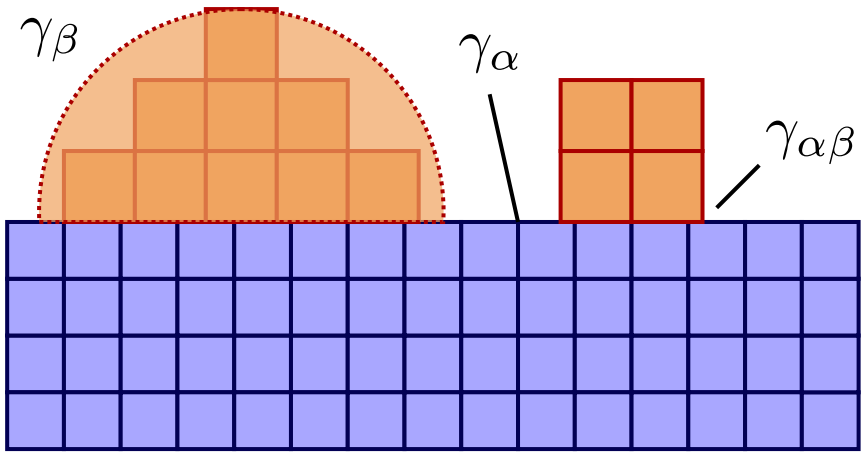
Stranski-Krastanov



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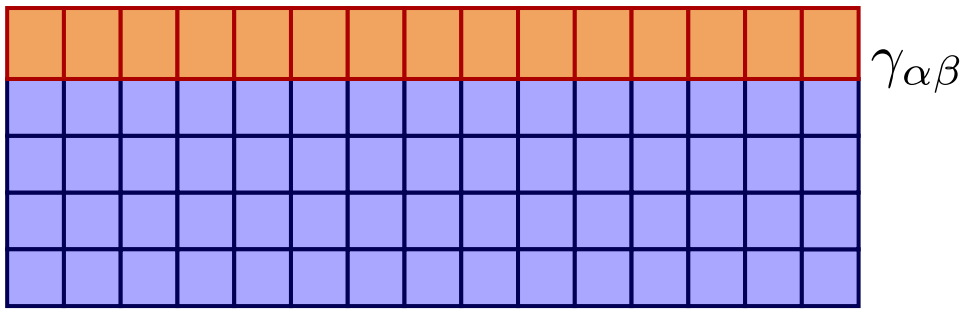
Macroscopic Thermodynamics Description

- 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 $\gamma_{\beta\varepsilon} + \gamma_\beta > \gamma_\varepsilon$



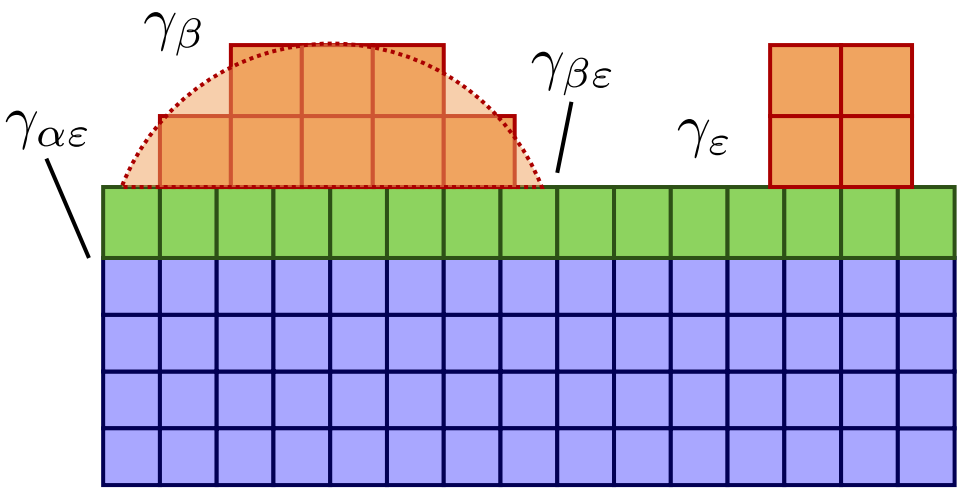
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Balancing Strain and Surface Energies

- For simplicity we will compare (strained) FM and VW growth modes
  - The strained film (thickness L) is associated with an elastic energy per unit area $E_{el} = C\delta^2 L$

$$\underbrace{\gamma_{\alpha\beta} + \gamma_{\beta}}_{\text{"chemical" surface terms}} + \underbrace{C\delta^2 L}_{\text{elastic strain energy}} \qquad \delta = (a_\beta - a_\alpha)/a_\beta$$

  - Assume that the clusters relax by misfit dislocations (so the interface energy is $\gamma_{\alpha\beta} + \gamma_{\delta}$) and make the simplifying assumption that $\gamma_\alpha = \gamma_{\alpha\beta} + \gamma_\delta$ (implies hemispherical cluster shapes $\theta = \pi/2$)
  - Mass balance implies that
  - The two configurations are energetically equivalent when

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$$\underbrace{3\frac{L}{r}\gamma_{\beta}}_{\text{cluster surface}} + \underbrace{\gamma_{\alpha}}_{\text{substrate}}$$

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$$\gamma_{\alpha\beta} + \gamma_{\beta} + C\delta^2 L = 3\frac{L}{r}\gamma_{\beta} + \gamma_{\alpha}$$

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$$\frac{3\gamma_{\beta}}{C\delta^2 + (\gamma_{\beta} - \gamma_{\delta})/L} = r, \quad \text{or} \quad \frac{\gamma_{\beta} - \gamma_{\delta}}{3(\gamma_{\beta}/r) - C\delta^2} = L$$