NANOPHYSIQUE
INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch. 4 : Crystal Growth

James Lutsko

Lecture 5, 2022-2023

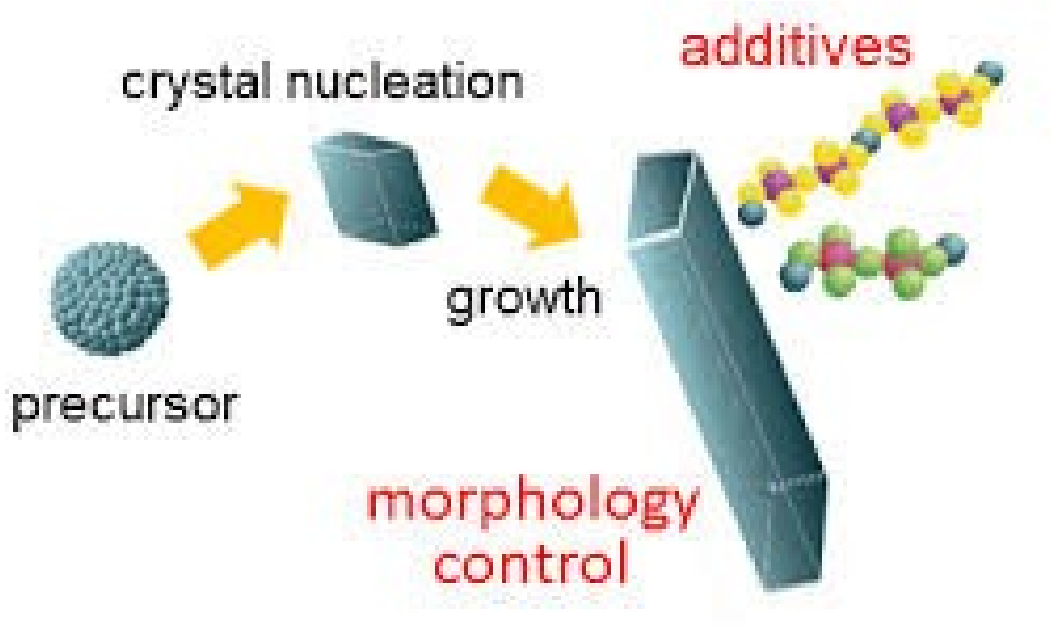
Crystal Growth

- Crystal growth mechanisms
- Simulations of crystal growth: the SOS model
  - Impurities and step blocking
  - Macrosteps
- Simulations of crystal growth: including fluid transport
  - Density profiles
  - Macrosteps
  - Islands

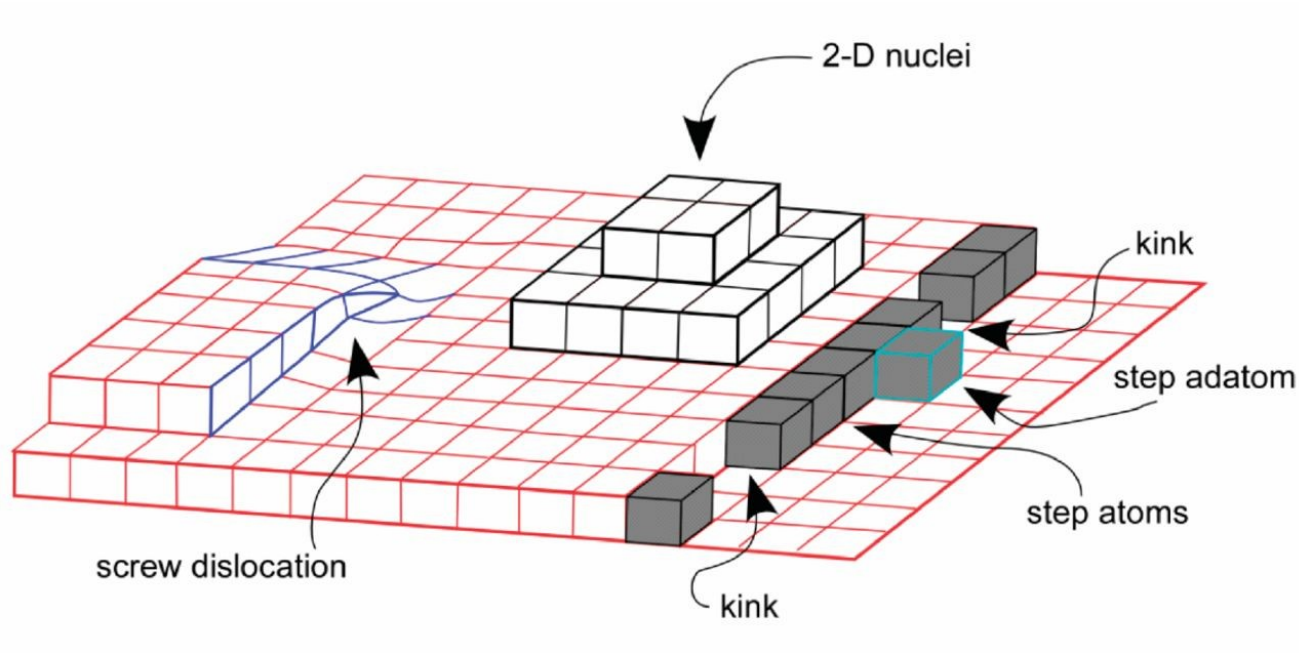
Crystal Growth

- Crystal growth mechanisms
- Simulations of crystal growth: the SOS model
  - Impurities and step blocking
  - Macrosteps
- Simulations of crystal growth: including fluid transport
  - Density profiles
  - Macrosteps
  - Islands

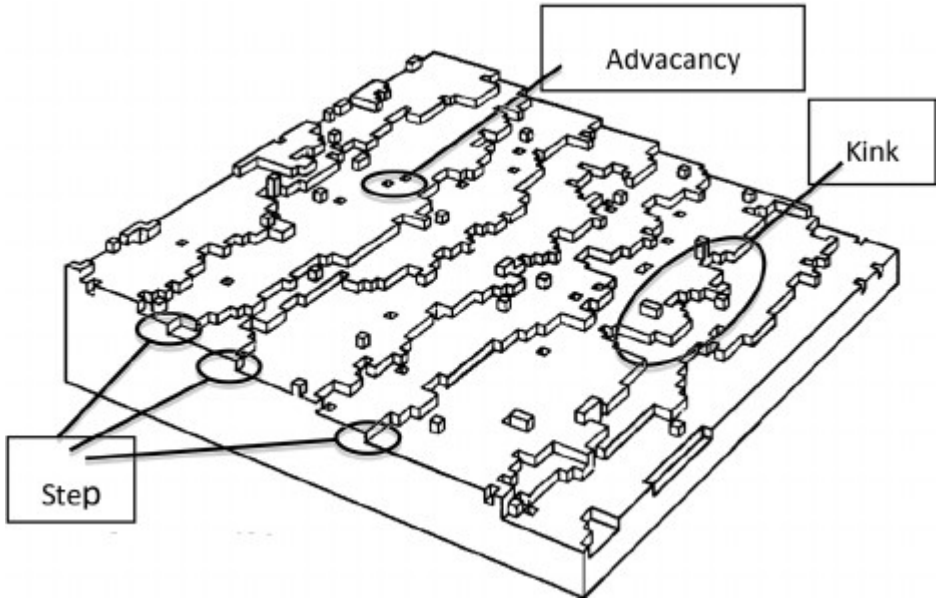
How crystals form

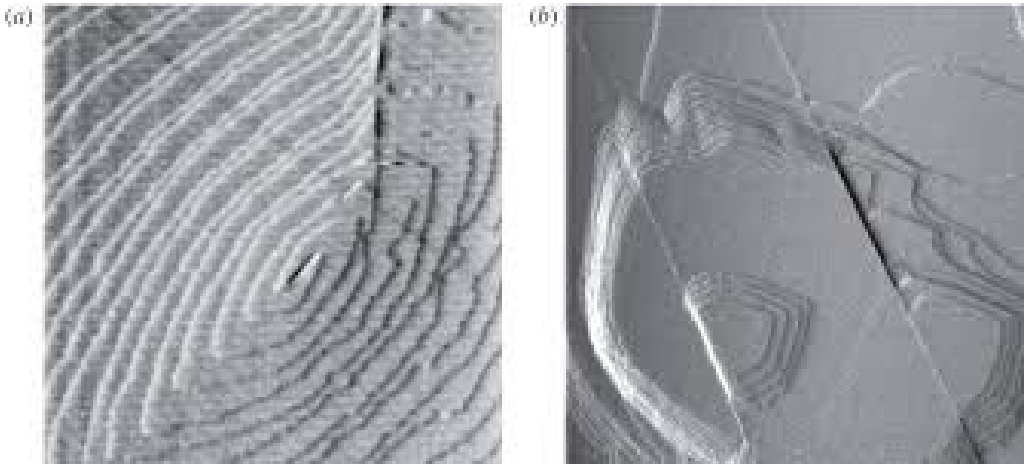


How crystals grow



How crystals grow





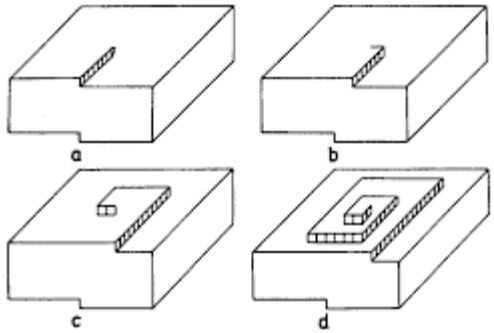
Motivation: The importance of understanding the effect of impurities on crystallization

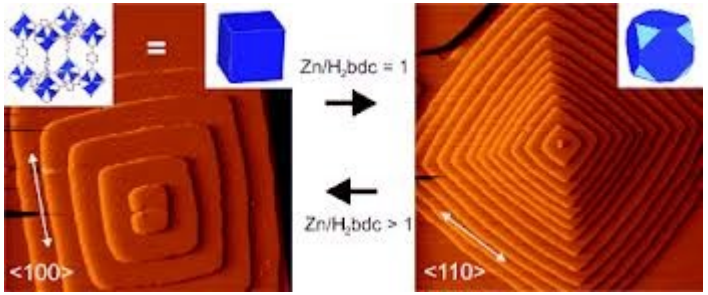
- Many applications require high-quality crystals (e.g. for Xray diffraction) and impurities can spoil crystal quality

- Other applications require the suppression of crystallization and adding the right impurities can be beneficial (*but what are the right impurities?)*

- In some cases, impurities are used to control crystallization (e.g. in biomineralization).

Crystal growth from solution

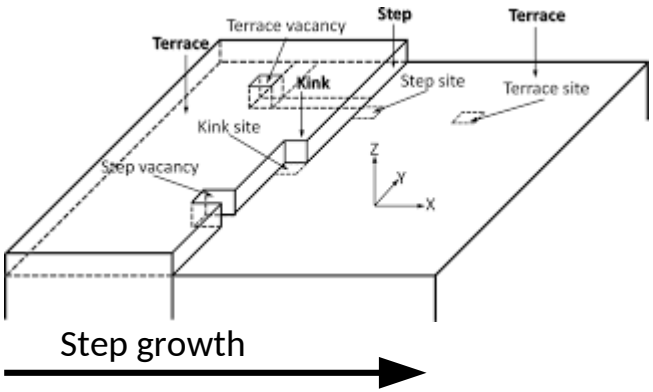




- Defects – such as spiral dislocations – give rise to steps

- At higher supersaturations, 2D nucleation of islands also occurs

Crystal growth from (pure) solution



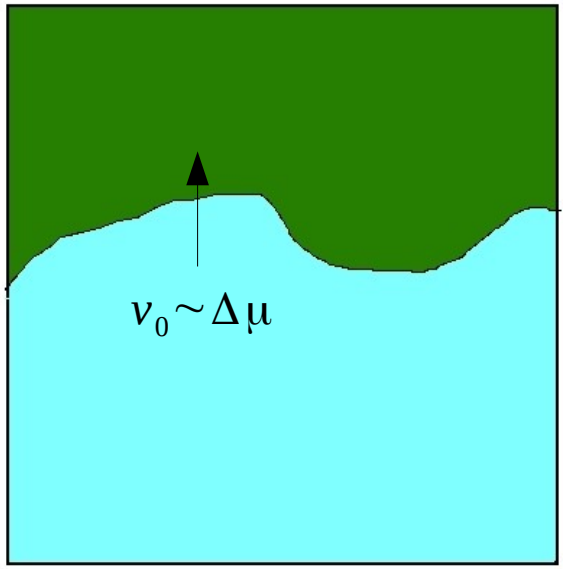
- Bond counting: in cubic solid, each molecule has 6 neighbors and therefore has total binding energy -3ϵ

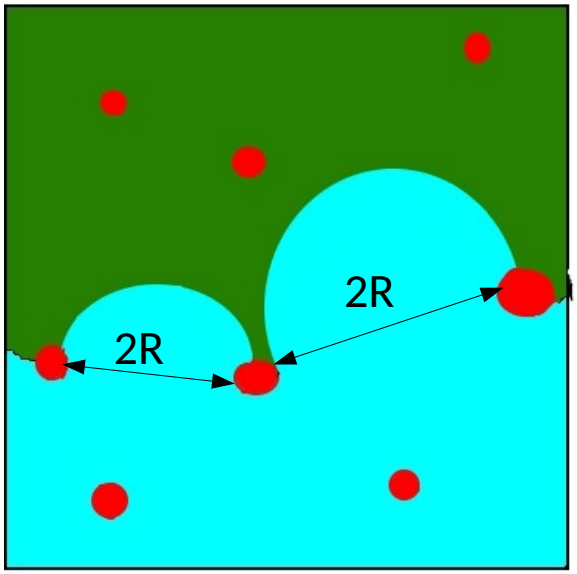
- Equilibrium chemical potential (e.g. energy of a molecule in solution) is therefore $\mu_{eq} = -3\epsilon$

- Molecules preferentially attach at kink sites where they can form three bonds: $\Delta E = -3\epsilon - \mu = -(\mu - \mu_{eq}) = -\Delta\mu$

- To start a new line, a stable kink must nucleate.

Crystal growth with impurities: The Cabrera-Vermilyea model





Gibbs-Thompson: effective chemical potential on a curved boundary is

$$\Delta\mu_{eff} = \Delta\mu\left(1 - R_c/R\right)$$

where R_c is critical radius for 2D nucleation.

CV criterion for step pinning:

$$R < R_c \Rightarrow \Delta\mu_{eff} < 0 \Rightarrow \text{pinning}$$

CV model for step velocity:

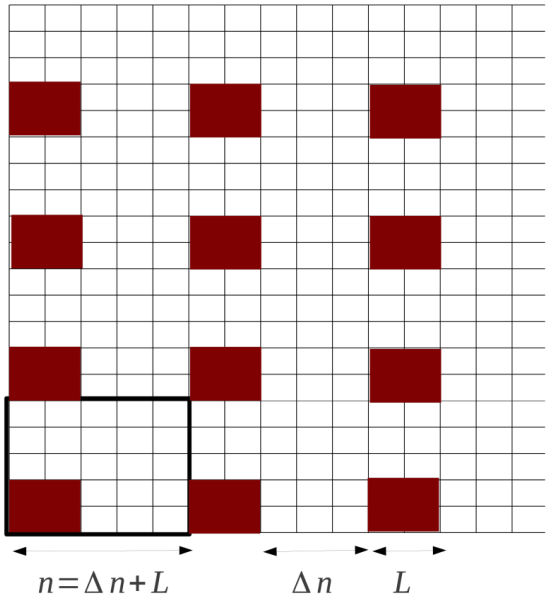
$$v = \sqrt{v_0 \times v_0\left(1 - R_c/R\right)} = v_0\sqrt{1 - R_c/R}$$

Crystal Growth

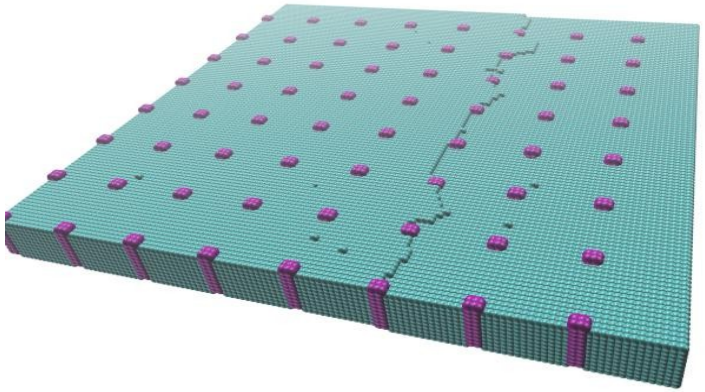
- Crystal growth mechanisms
- Simulations of crystal growth: the SOS model
  - Impurities and step blocking
  - Macrosteps
- Simulations of crystal growth: including fluid transport
  - Density profiles
  - Macrosteps
  - Islands and flow

Kinetic Monte Carlo simulations

Impurities: molecules with different bond energy that differs from the growth units (e.g., zero in horizontal plane).



Impurities can be ***static*** or ***dynamic***



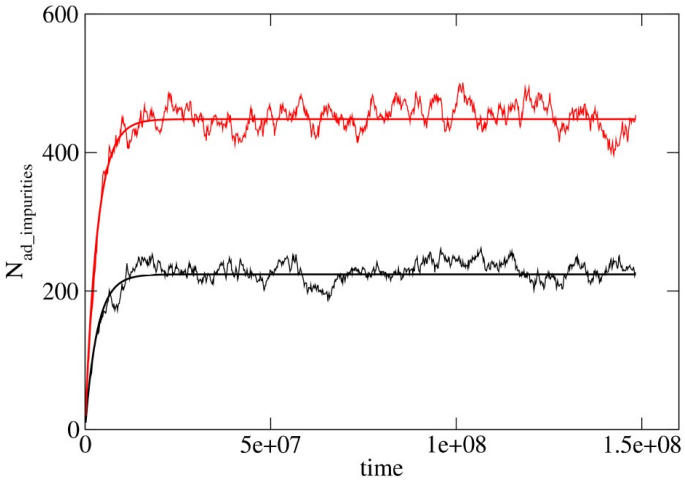
- Molecules land on surface with frequency $\nu_0 e^{\mu/k_B T}$

- Molecules leave surface with frequency $\nu_0 e^{E/k_B T}$

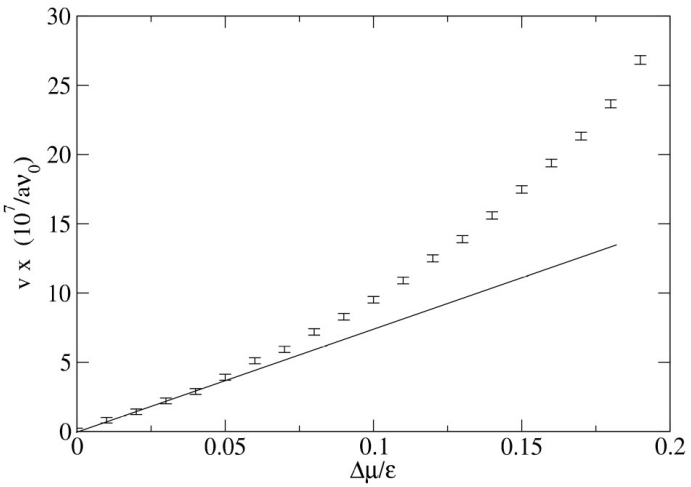
- Diffusive moves also possible

Equilibrium & Normal Growth

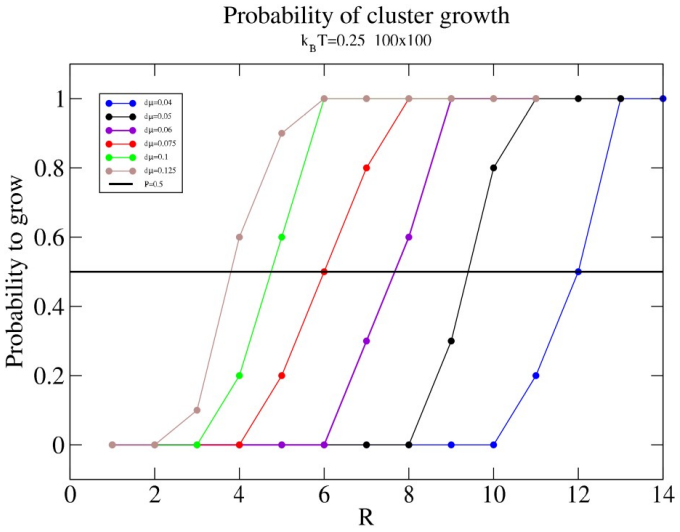
Equilibration

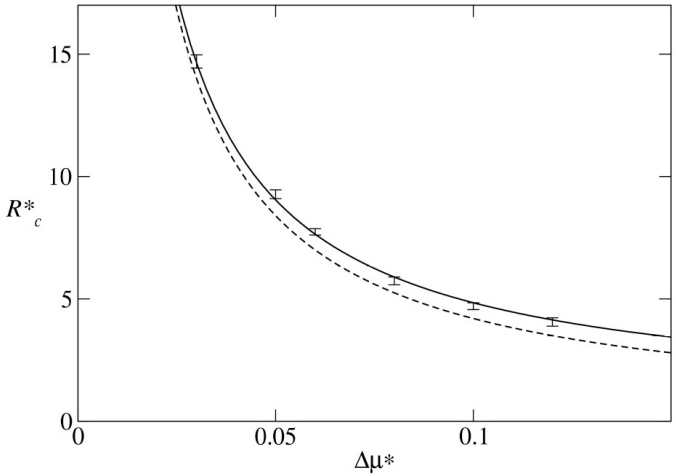


$k_B T = 0.25\,\epsilon$



Empirical Critical Radius

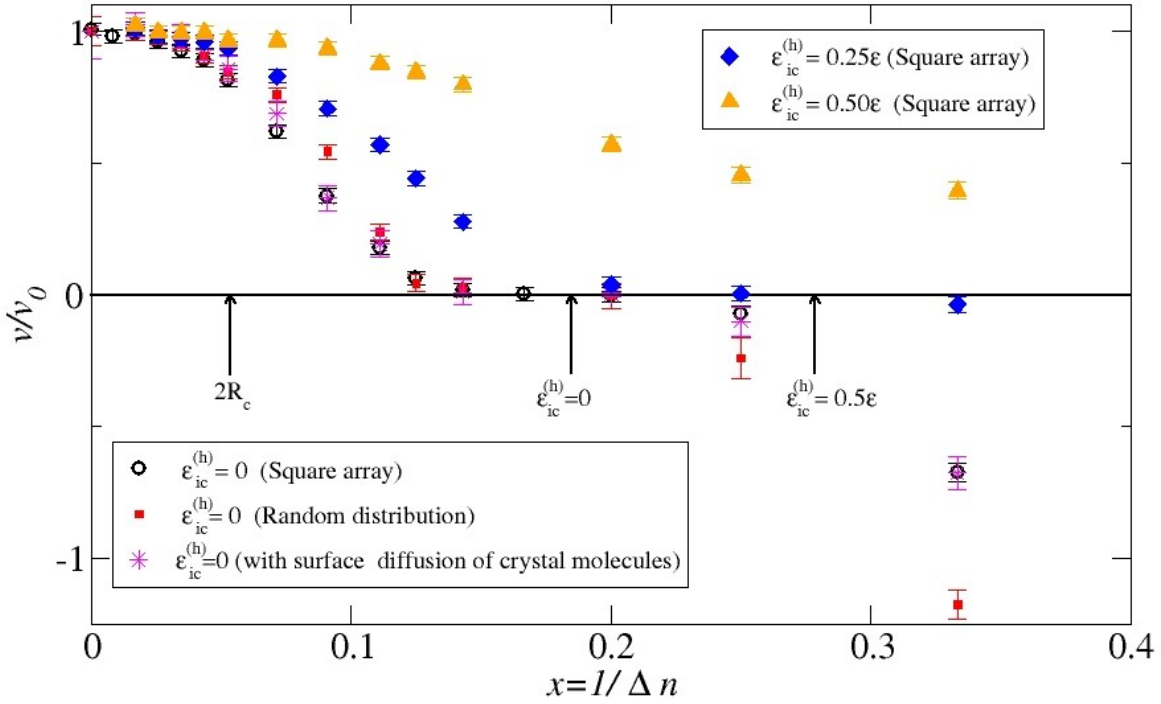




Protocol:

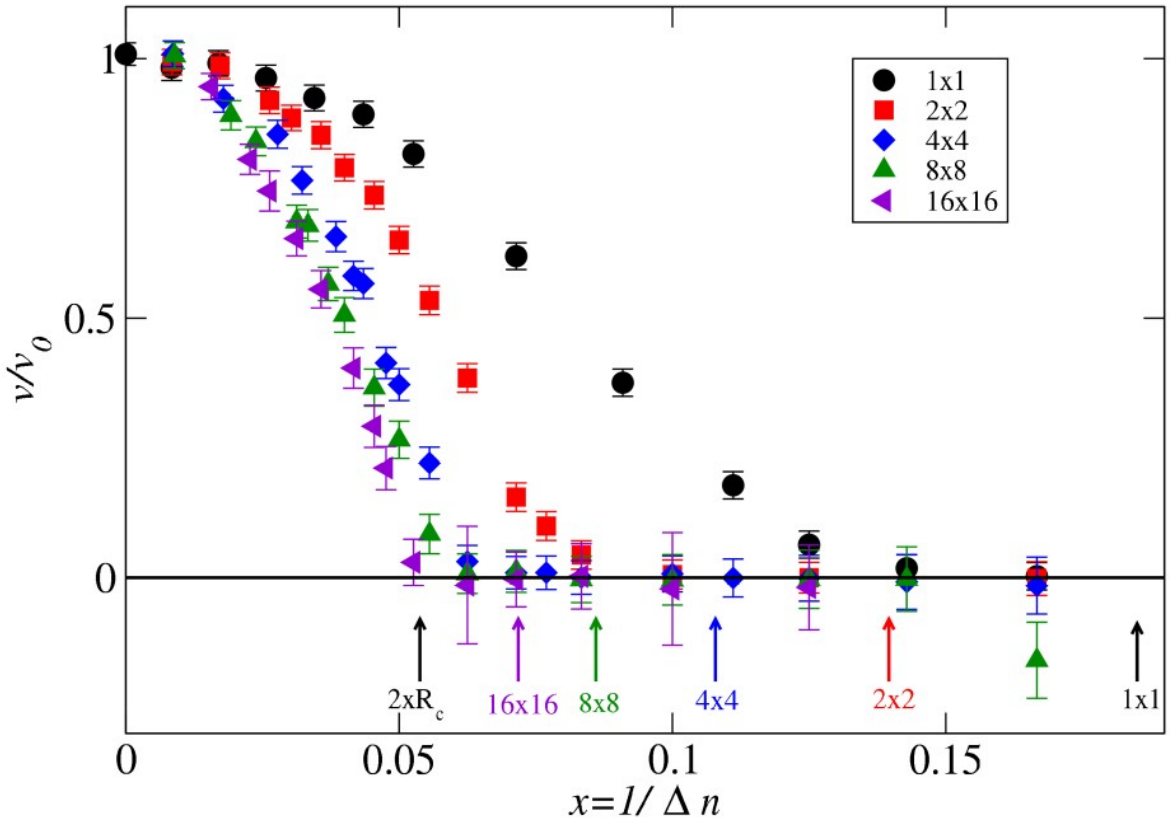
- Start with cluster of given size
- Run until cluster either evaporates or grows above threshold
- Repeat N (~100) times to get probability of cluster growth
- P=0.5 determines critical radius

Test of CV: small impurities



- Pinning does not occur anywhere near the CV threshhold.
- Energetics of the impurities also affects pinning.

Test of CV: larger impurities



- Size of impurities is very important
- Large impurities seem to approach CV prediction.

Beyond CV: the physical basis of step pinning

- It is certainly true that above the CV threshhold, steps are not pinned.

$$\Delta n > 2R_c \Longrightarrow \text{No pinning}$$

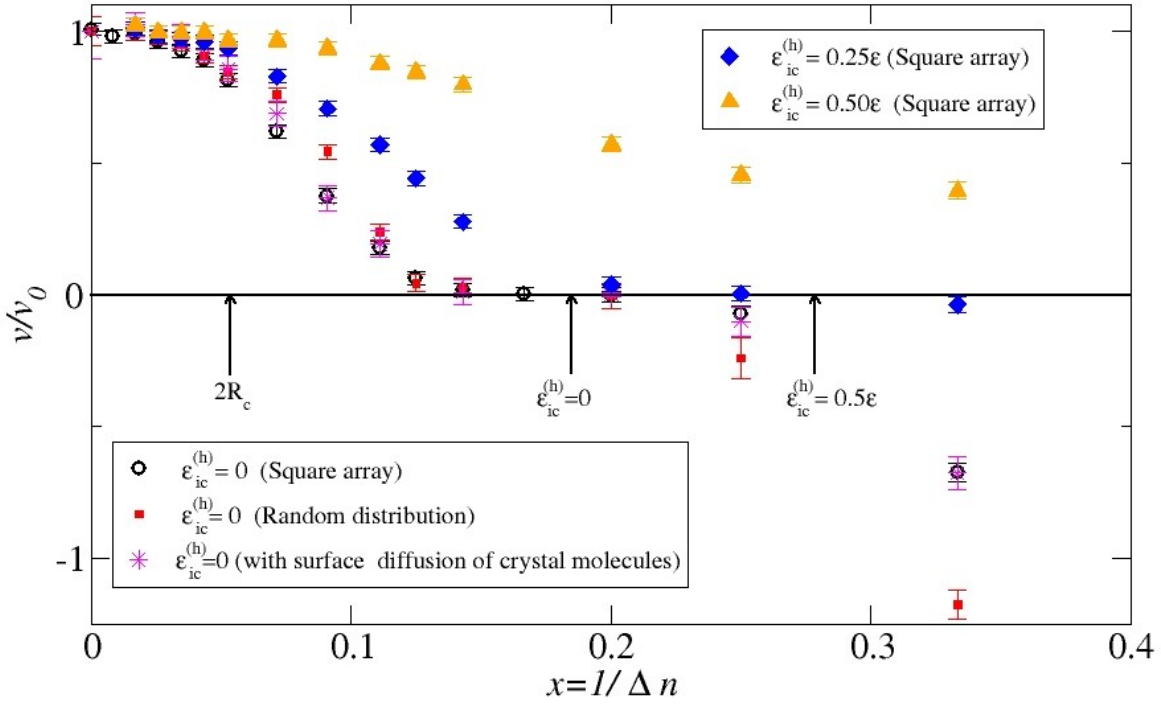
- Step growth is always favored when the free energy of the system (solution plus crystal) is lowered by adding a layer to the crystal. Conversely, it will not occur if adding a layer raises the free energy.

$$F(N+1 \text{ layers}; \Delta n) > F(N \text{ layers}; \Delta n) \Longrightarrow \text{pinning}$$

$$\Delta n < L \times \left(\sqrt{1+4\gamma/(L\Delta\mu)} - 1\right) \underset{L\to\infty}{\Rightarrow} 2\gamma/\Delta\mu = 2R_c$$

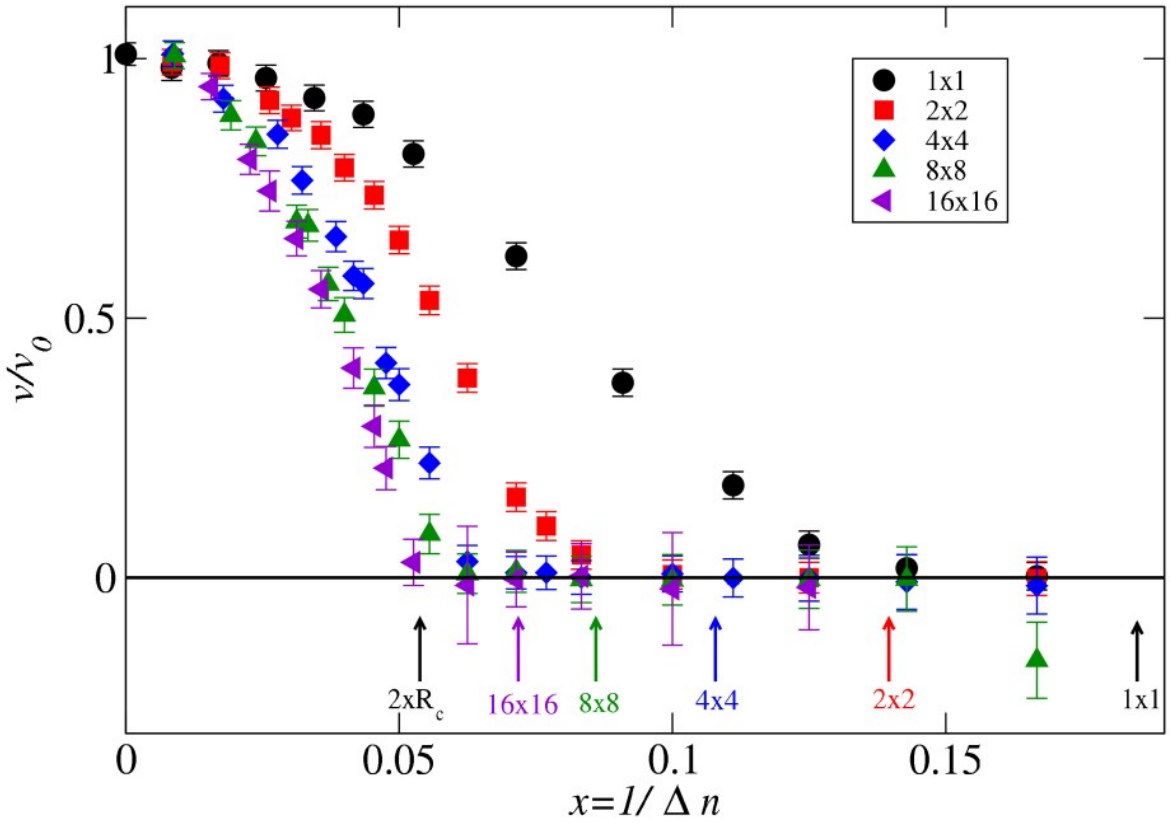
- In between these threshholds, “pinning” is a question of time scales.

Test of CV: small impurities



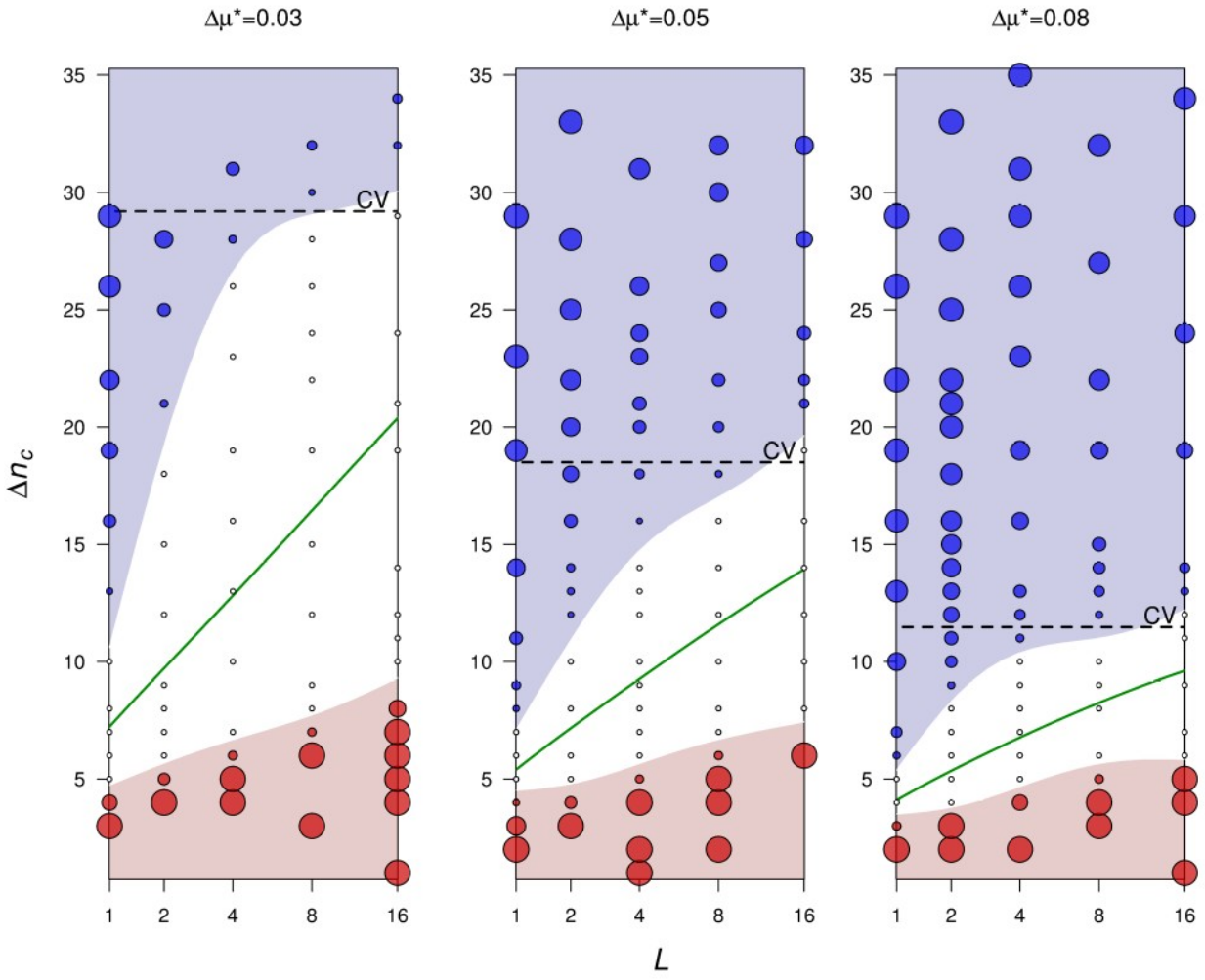
- Pinning does not occur anywhere near the CV threshhold.
- Energetics of the impurities also affects pinning.

Test of CV: larger impurities

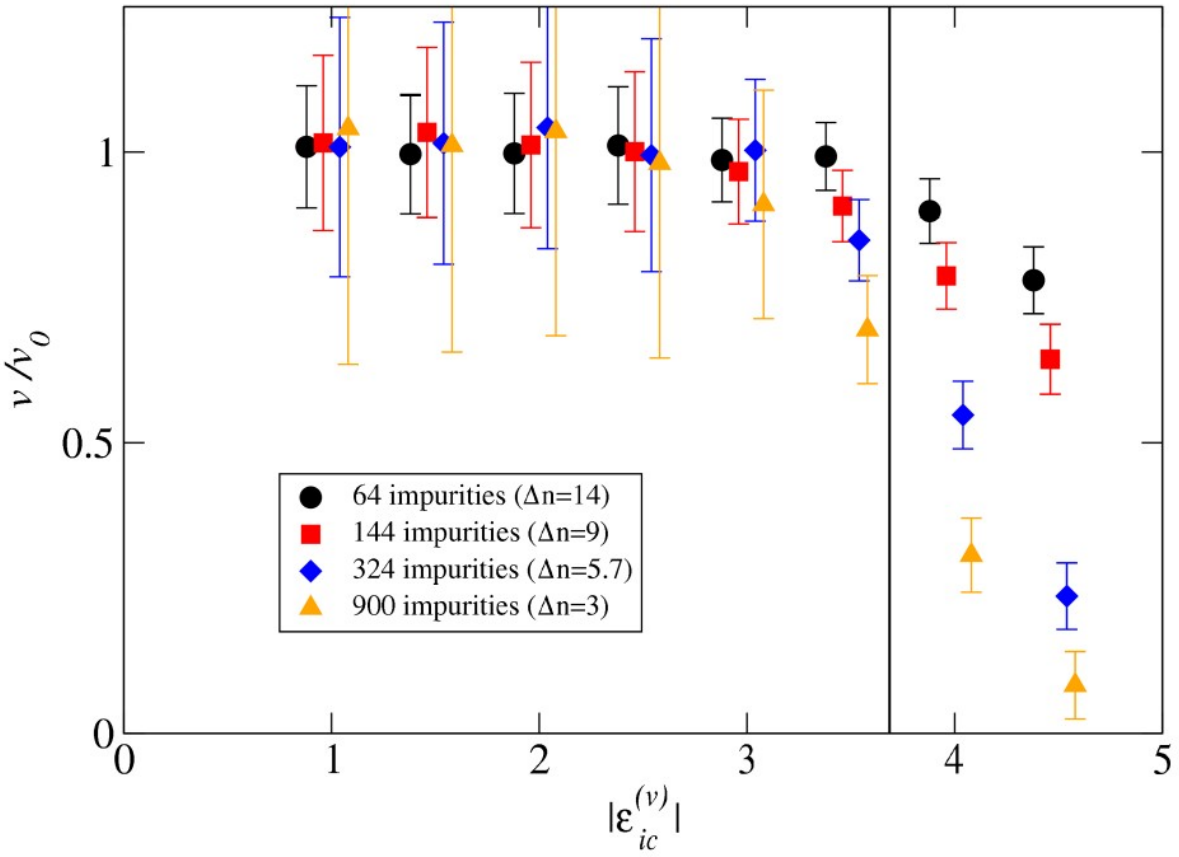


- Size of impurities is very important
- Large impurities seem to approach CV prediction.

Putting it all together



Dynamic impurities



- Long residency times required for impurities to block step growth