Impurity-induced step patterns in vapor and solution growth: From step bunches to Supersteps

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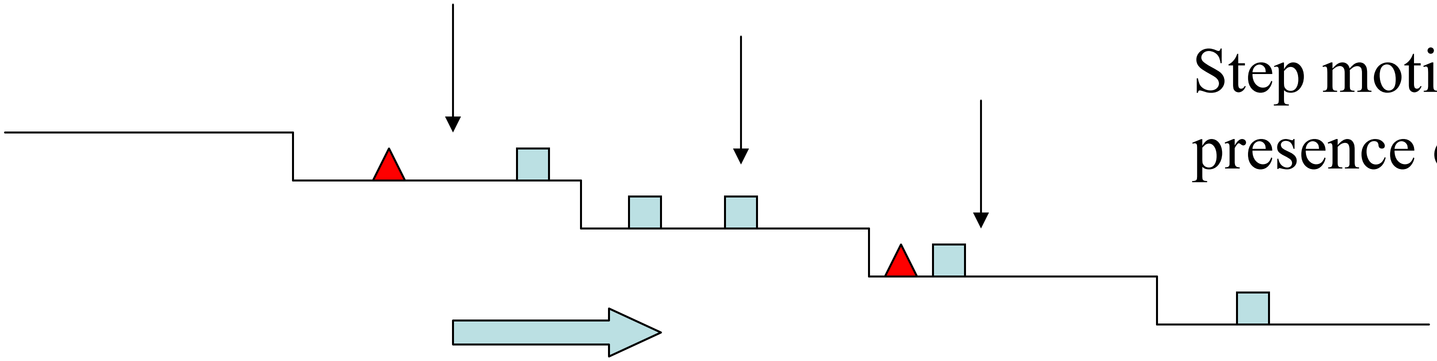
Impurities in vapor and solution growth



Step motion in the presence of impurities

- Change in Morphology, step flow rate on the crystal surface

  Recent Examples: Mg in Calcite growth, Fe in KDP (KH_2PO_4)

- Impurities can serve as nucleation sites

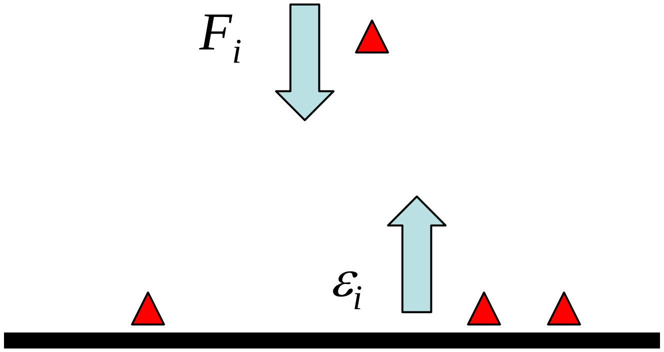
  Acceleration of Calcite Kinetics by Abalone Nacre Proteins

- Change bulk properties of the crystal

  Impurities in KDP crystals can dramatically affect laser properties

We focus on impurities that inhibit step motion

Simple Langmuir description of impurity adsorption



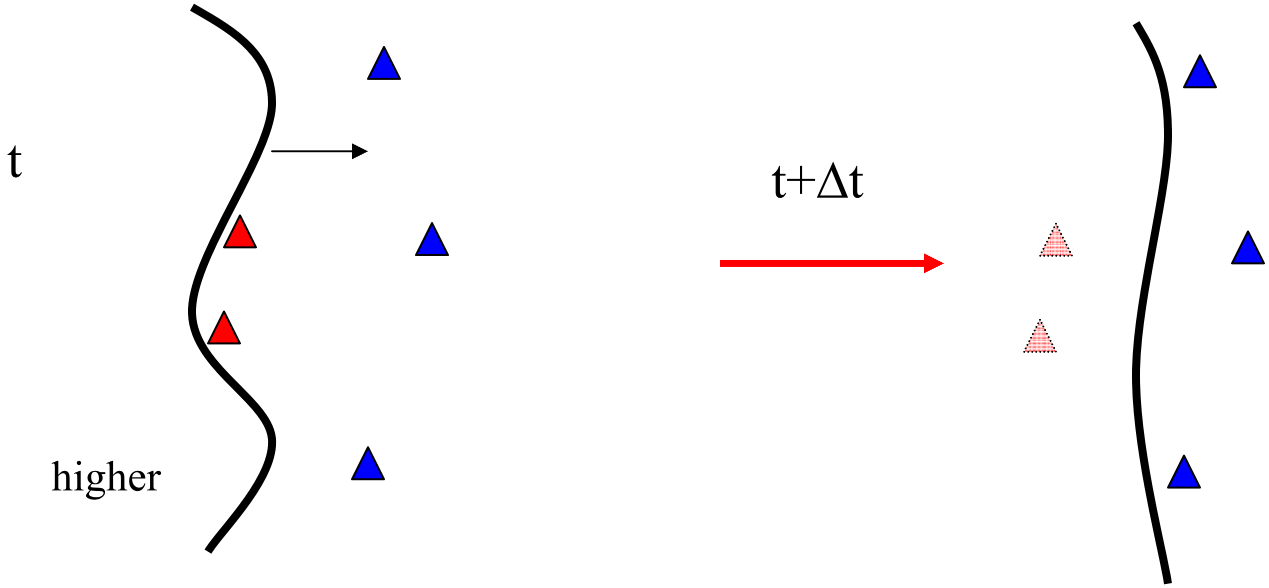
$$\frac{dc_i}{dt} = F_i(1-c_i) - \varepsilon_i c_i = F_i - (\varepsilon_i + F_i)c_i$$

$$\bar{c}_i \equiv \frac{F_i}{\varepsilon_i + F_i}$$

$$c_i(t) = \bar{c}_i(1 - e^{-(\varepsilon_i + F_i)t})$$

Filling time $\tau_i = (\varepsilon_i + F_i)^{-1}$

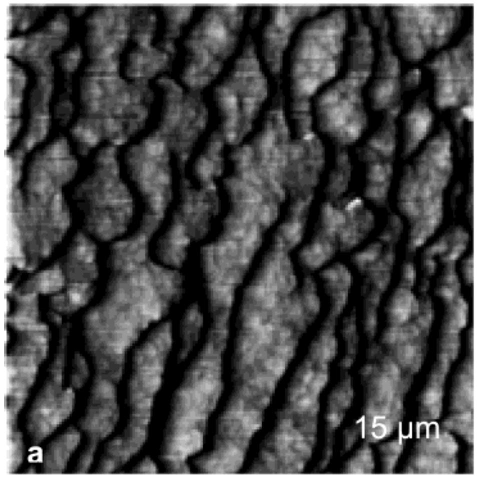
Impurities impede local step motion but are covered (or dislodged) by advancing step



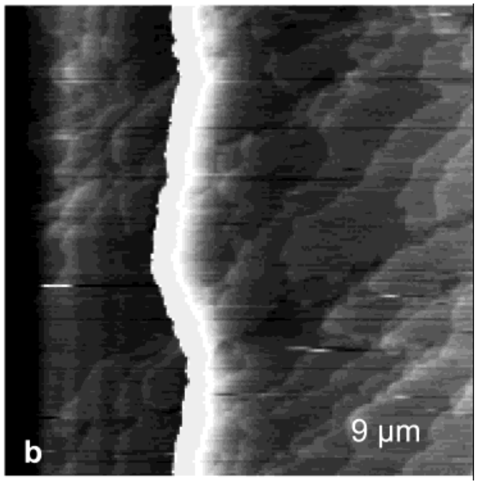
Experiments on KH_2PO_4 (KDP) crystals grown in solution (stirred)

T.A. Land, T.L. Martin, G.T.R. Palmore, S.Potapenko and J.J. De Yoreo

Nature, **399**, 442 (1999)



Dead zone



Macrostep motion

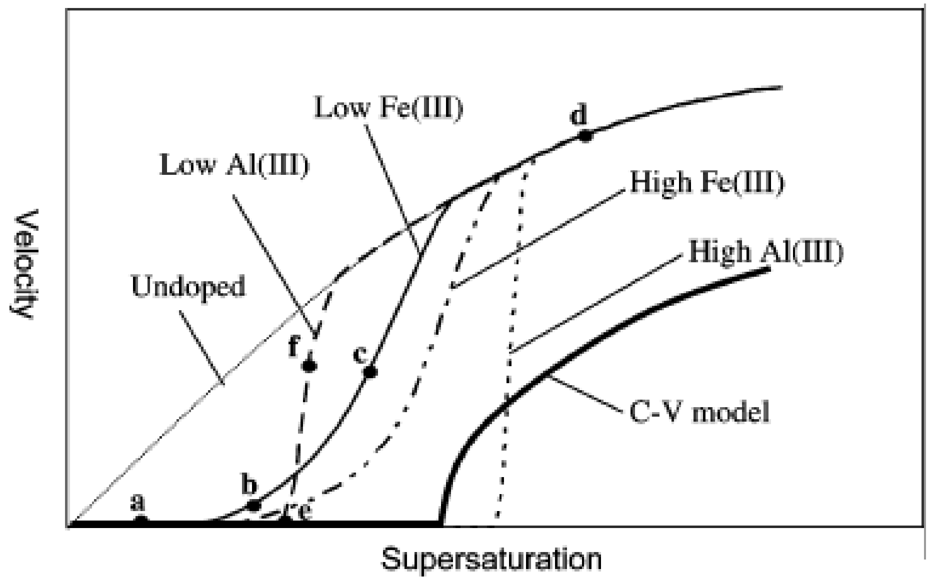
Small amount of Fe, Al, Cr impurities can completely stop growth of crystal.

Recovery occurs by motion of large bunches of steps (10-30steps) called **macrosteps**

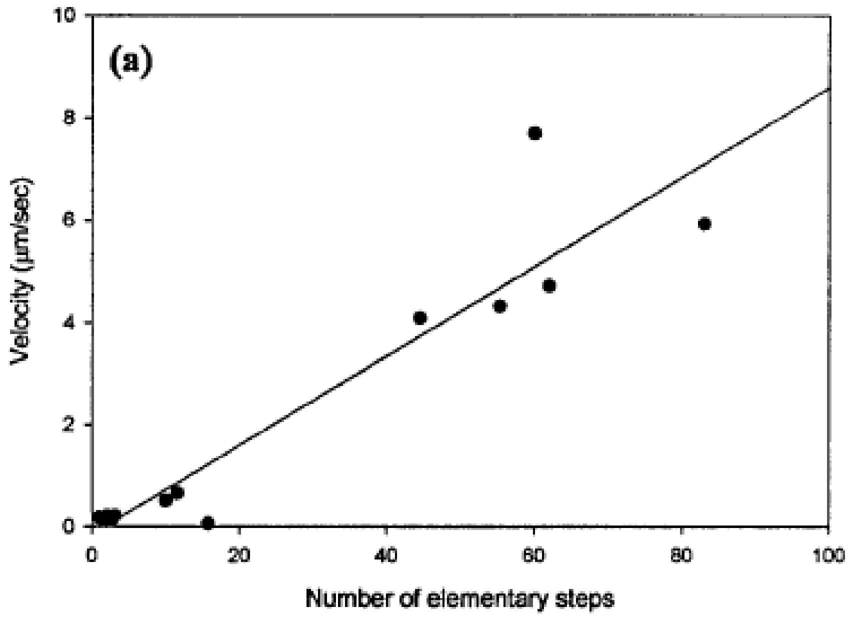
With Cr(III) and Al(III), **supersteps** (40-100 steps)

Phys. Rev. Lett. **93**, 216130 (2004)

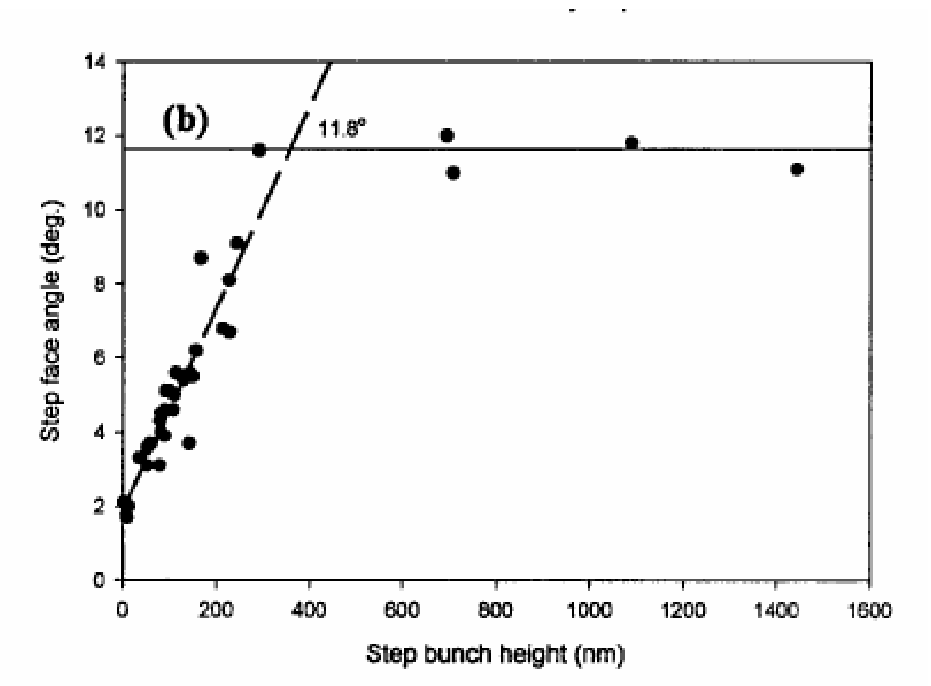
Impurities embedded



Bunch velocity



Step face angle

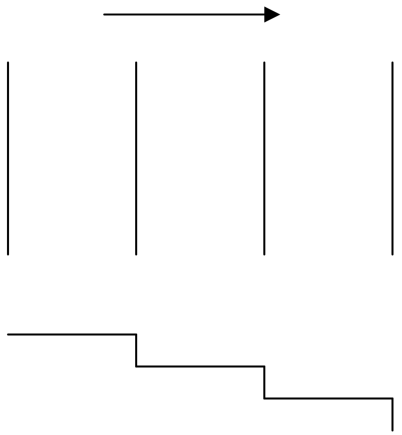


Velocity of a step bunch proportional to the number of steps in the bunch.

This is only valid for a small range of supersaturations

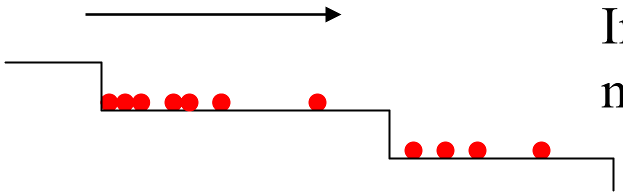
Superstep and macrostep bunches move together

Frank Model - 1958



Uniform Step Train moving with constant velocity unstable to step bunching in the presence of impurity flux

1. Impurities stick to the surface
2. Impurities impede steps
3. **Steps cover impurities**



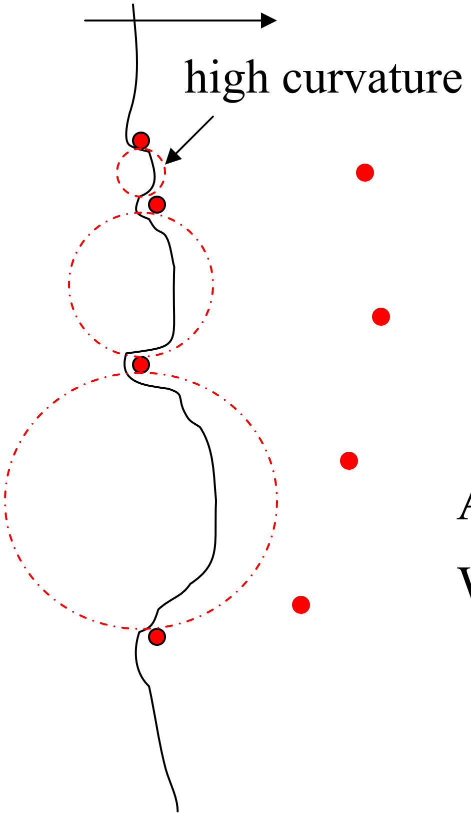
Impurity concentration profile caused by motion makes uniform step train unstable

Dynamics of impurity adsorption drives bunching

1-D model, no curvature effects, step repulsions ignored (no overhangs permitted)

Growth slows down as bunches form and more impurities are adsorbed

Cabrera-Vermilea (CV) Model - 1958



1. Impurities stick on surface
2. If impurities are far apart on average step can squeeze between them
3. If impurities are too close to each other, they pin steps and stop motion

Average impurity spacing $d \sim 1/C_i^{1/2}$

When critical nucleus $\rho_c > d/2$ step pinned

$$\rho_c = \frac{\gamma \Omega}{kT \ln(1+\sigma)}$$

Step velocity as a function of supersaturation and impurity concentration has threshold:

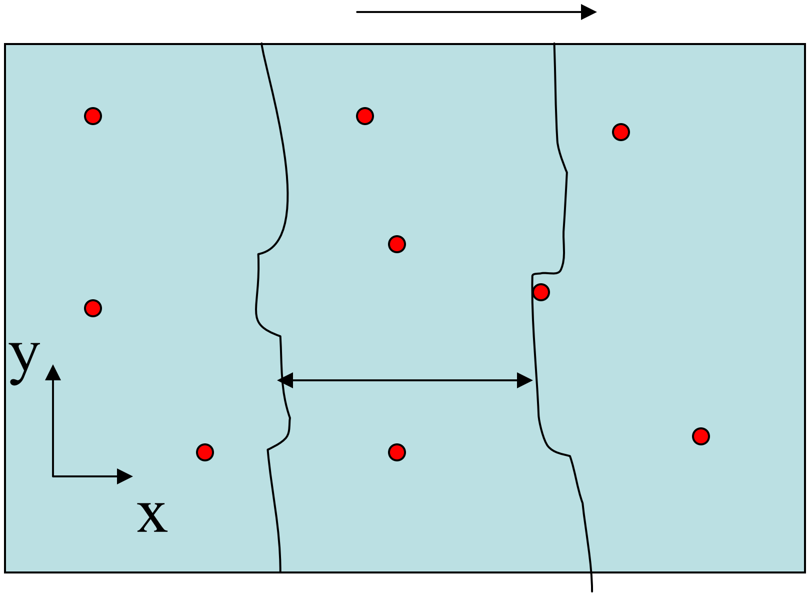
$$v = 0 \qquad \sigma < \sigma_{th}$$

$$v = v_0 \left(1 - \frac{2\rho_c}{d}\right)^{1/2} \qquad \sigma > \sigma_{th}$$

Pinning related to impurity spacing through curvature; v_0 is growth rate in absence of impurities

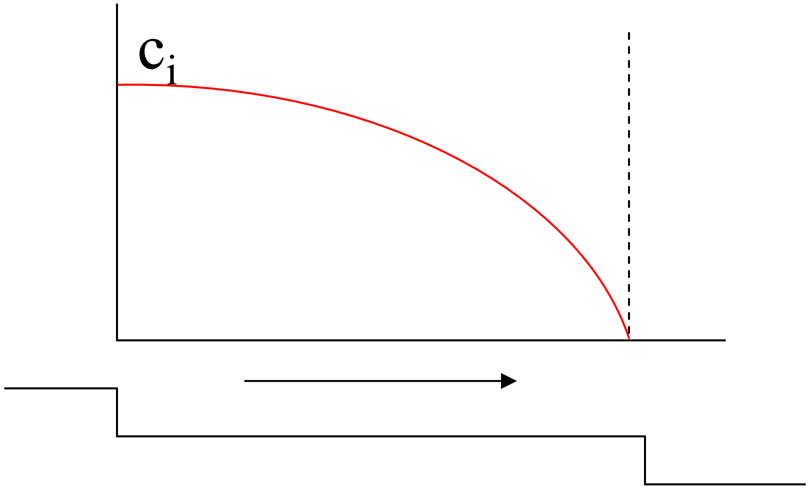
New mesoscopic 2-D Monte-Carlo Model

- Generalization of Kandel-Weeks model (1994); Combines ideas from Frank and CV models
- Main component growth treated effectively like simplest BCF model with diffusion length l_d
- Impurity treated as discrete particles on a square lattice with spacing a_i
- Impurity flux F_i to unoccupied sites; evaporate from the surface with rate $1/\tau_i$



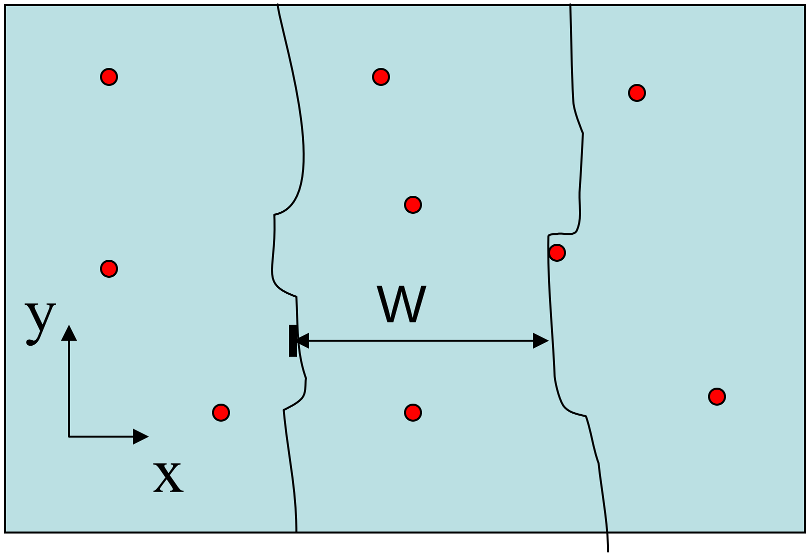
Covered impurity removed

Impurity profile between steps



New Model- Monte Carlo Scheme

1. Impurity sweep
2. Step flow sweep – Attempt to move step segments of length a_i with an acceptance-rejection criteria based on Metropolis scheme.
3. Energy is due to line-tension, step repulsions, and extra impurity energy penalty E_i if step tries to cover impurity



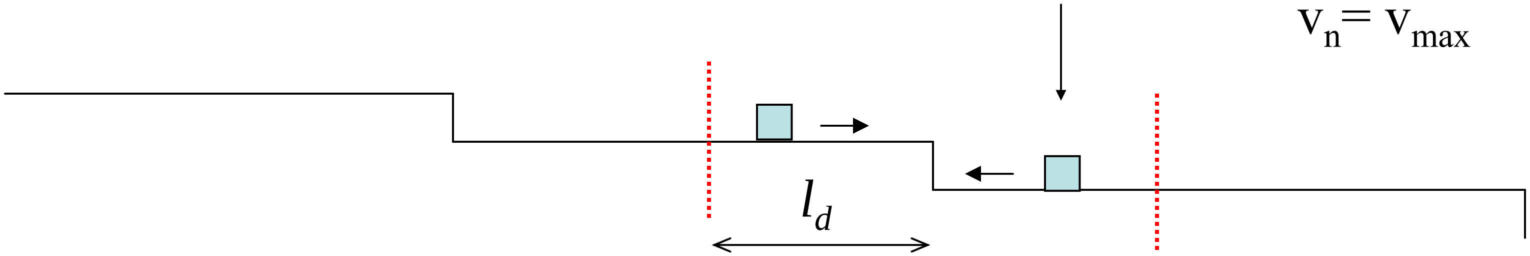
$$E(\{X_n\}) = \sum_{y,n}\left[\gamma\left(X_n(y+1)-X_n(y)\right)^2 + \sum_{n'} G\left(\frac{1}{\left(X_n(y)-X_{n'}(y)\right)^2}\right)\right]$$

$$P_{Trial-Backward} = \frac{1-A}{2} \qquad P_{Trial-Forward} = \frac{1+A}{2} - A\exp\left(-\frac{W}{l_d}\right)$$

$$P_{acc} = \min\left[1, \exp\left(-\frac{\Delta E + \boxed{E_i}}{kT}\right)\right]$$ in presence of impurity

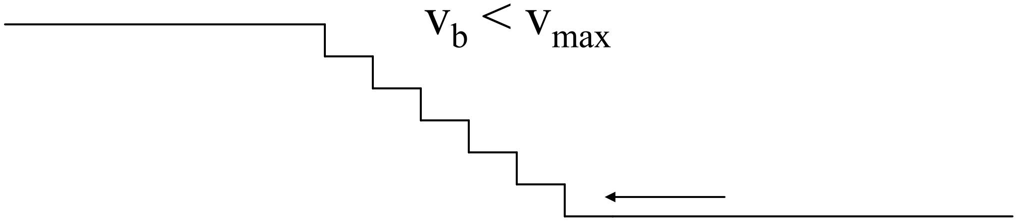
Negative curvature (like CV model) and repulsive force from step behind increases probability of forward move; Impurity decreases probability

Diffusion length important in vapor growth of pure component


$v_n = v_{max}$

Bunch with $w_b < l_d$ has smaller velocity; bunch not stable

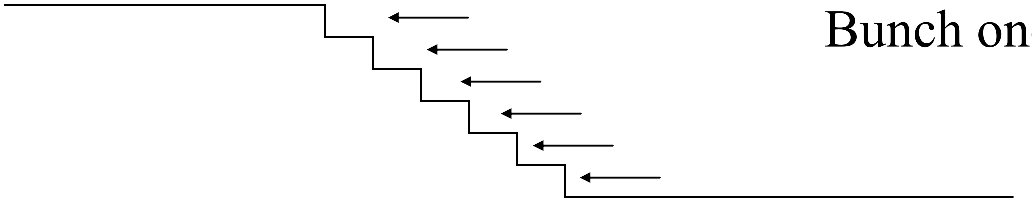
$v_b < v_{max}$



$v_1 > v_b$

Solution growth: step velocity independent of terrace width

$v_b = v_{max}$



Bunch once formed can stay together!

$v_1 = v_b = v_{max}$

$l_d = 10$ $A = 0.15$ (moderate) $\gamma = 0.5$ (moderate); [$F_i = 0.00001$ $\varepsilon_i = 0.00004$ $E_i = 4.5$ $G = 1$ for all]

Show Movie 1

$l_d = 10$ $A = 0.9$ (very large) $\gamma = 0.1$ (Low Line Tension)

Show Movie 2

Observations from these results for vapor growth

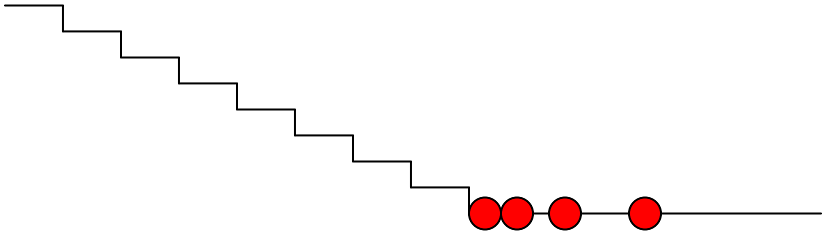
1. Bunching occurs with initial pairing, followed by slow coarsening

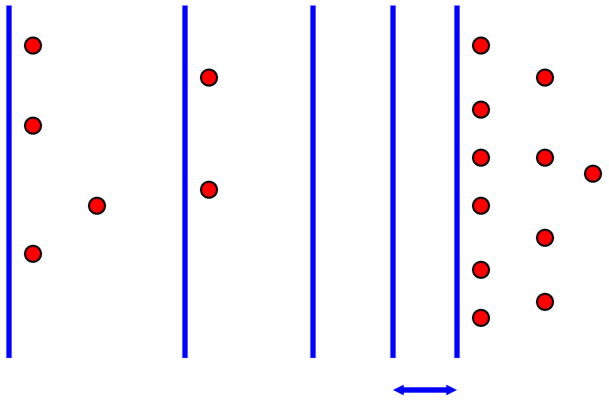
2. Bunches move slower than single steps because of narrow terraces within a bunch with widths smaller that the diffusion length

3. Step repulsions have little effect on growth rate

How can supersteps move faster than individual steps in solution growth?

Step Repulsions can be effective in solution growth





Larger bunches have narrower terraces, and fewer impurities

Driving force independent of terrace width: All steps want to move forward except for the bottom step of a bunch

Repulsions from steps behind can help push first step forward past impurities

In a large bunch, the bunch is tighter and the repulsions are greater.

Supersteps self-assmmble when impurities greatly impede motion of individual steps

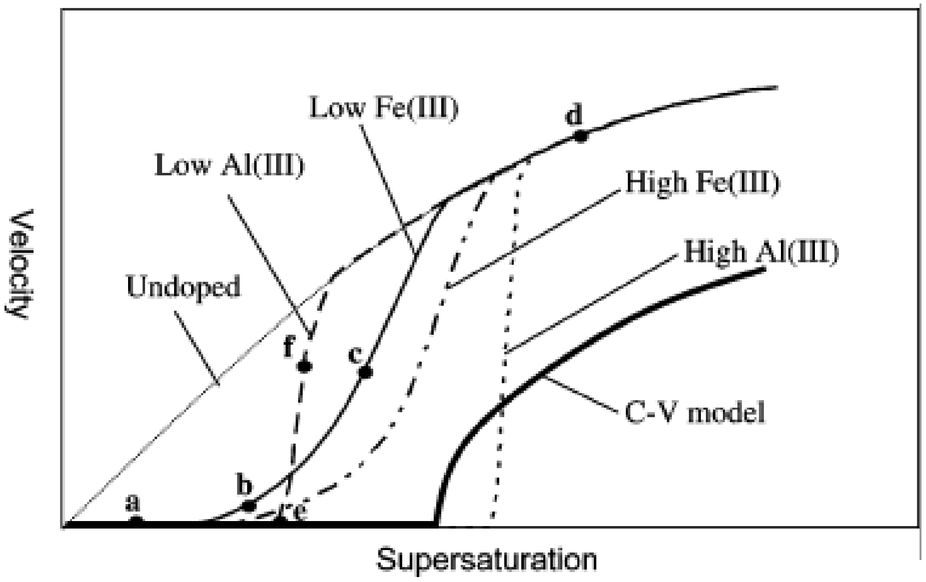
$l_d = 0$ $A = 0.10$ (small) $\gamma = 0.5$ (moderate) Dead Zone

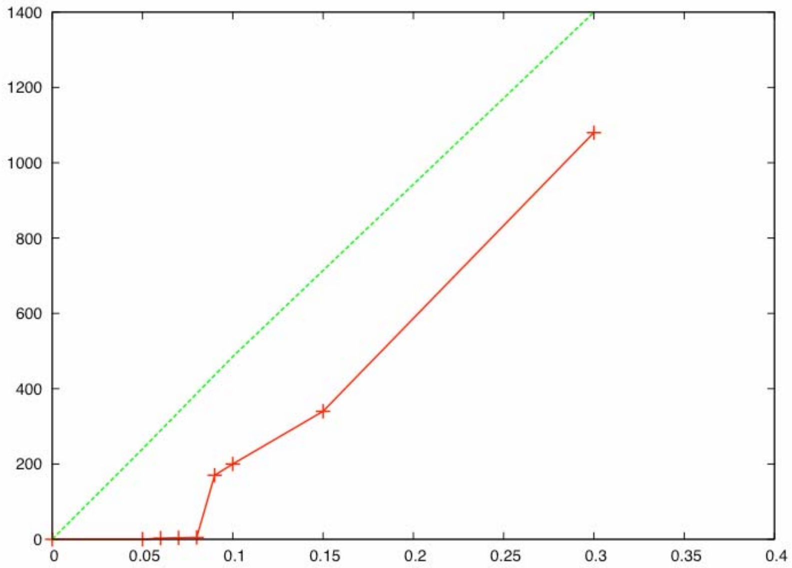
Show Movie 3

$l_d = 0$ $A = 0.15$ (small) $\gamma = 0.5$ (moderate) Macrostep formation

Show Movie 4

Velocity against driving force





We recover experimental trends along with superstep effect !!

Conclusions

Impurity induced step retardation can explain both step bunching and the very fast motion of step bunches

The constant driving force independent of terrace width in solution growth is a crucial feature that allows large bunches to move together.

Repulsions are effective in helping the bunch move rapidly only when the first step is sufficiently pinned by impurities.

The new impurity model is very general and can explain existence of different regimes in different systems.

- vapor growth – bunching and slow coarsening.
- solution growth – dead zone and superstep formation