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Defect Migration in the Presence of Diffusing Impurities

The Physics of Dirt

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Defects

- Many properties controlled not by perfection, but by deviations from perfection
- Defects - Properties

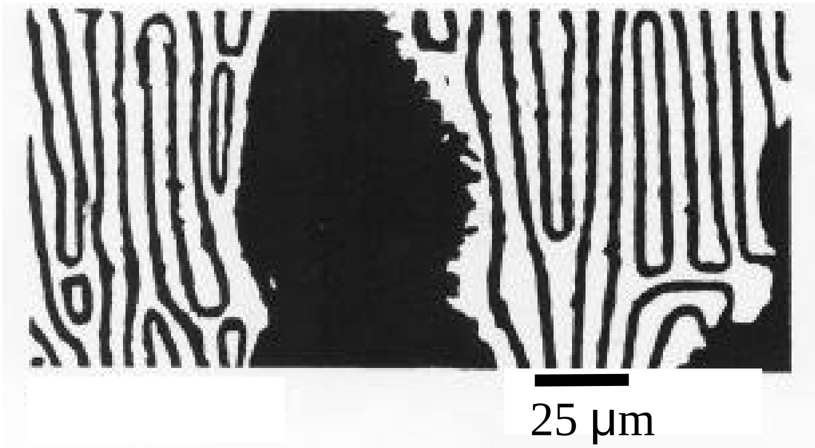
Dislocations	Plastic Deformation
Ferroelectric Domain Walls	Hysteresis
Grain Boundaries	Strength
Magnetic Domain Walls	Switching behavior

- In many applications, defect migration is key
- Defect migration

  Intrinsic Mobility
  Extrinsic Mobility

- Extrinsic mobility - defect/impurity interactions

Domain Walls

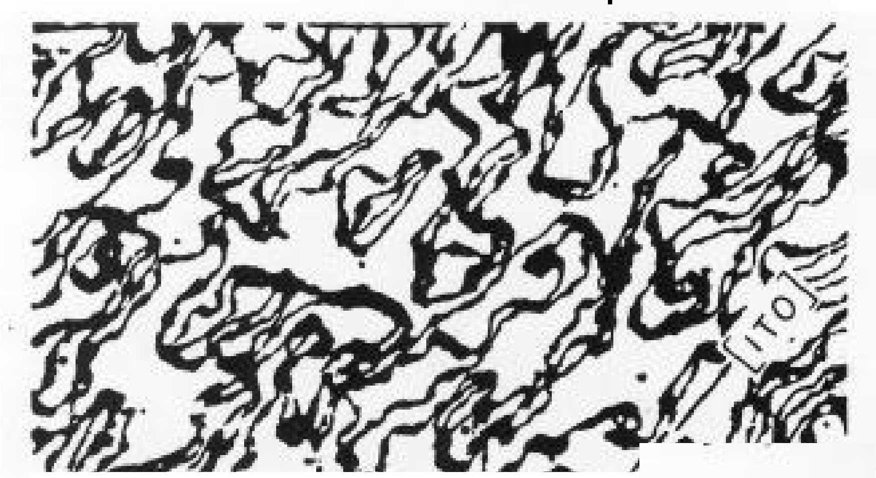


Ferromagnetic domain walls

$Co_3B_7O_{13}Br$

Alvarez, et al.

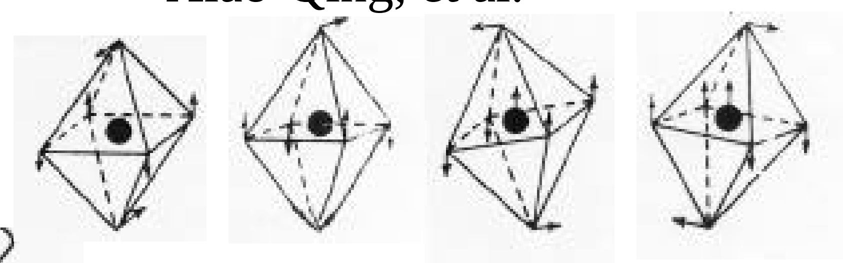
Polarization ↓ ↑

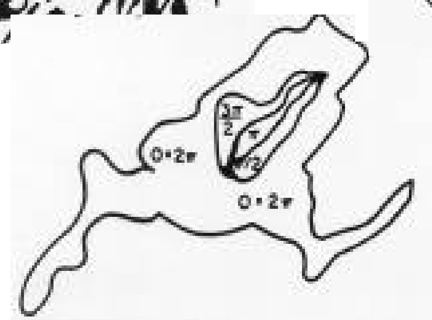


Ferroelectric domain walls

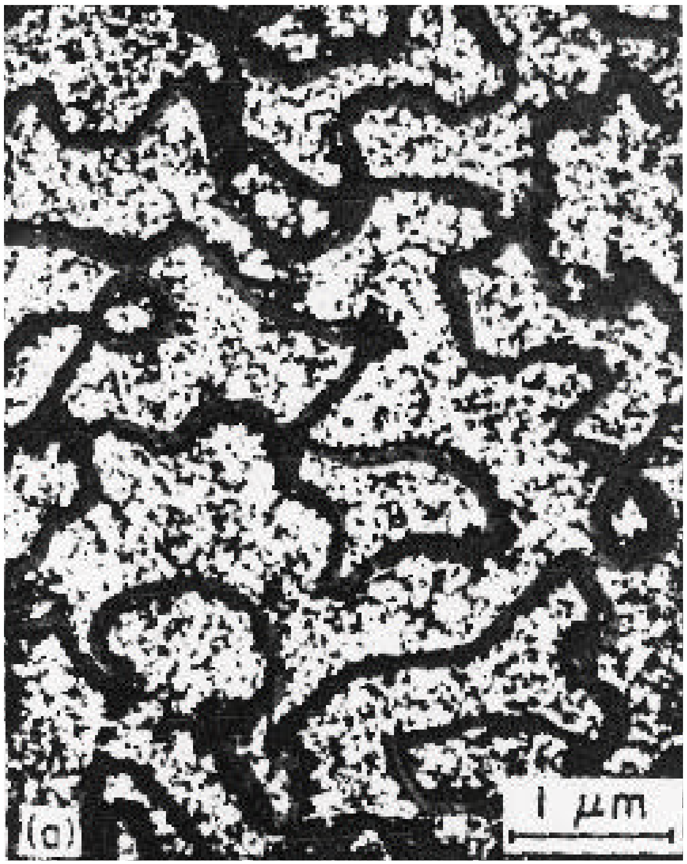
$Ba_2NaNb_5O_{15}$

Xiao-Qing, et al.





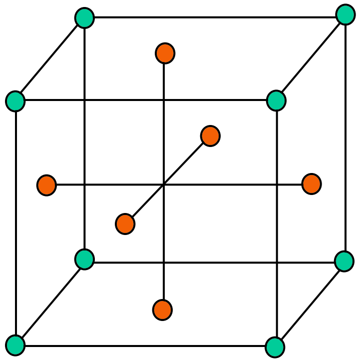
Domain Walls



Anti-phase Boundaries

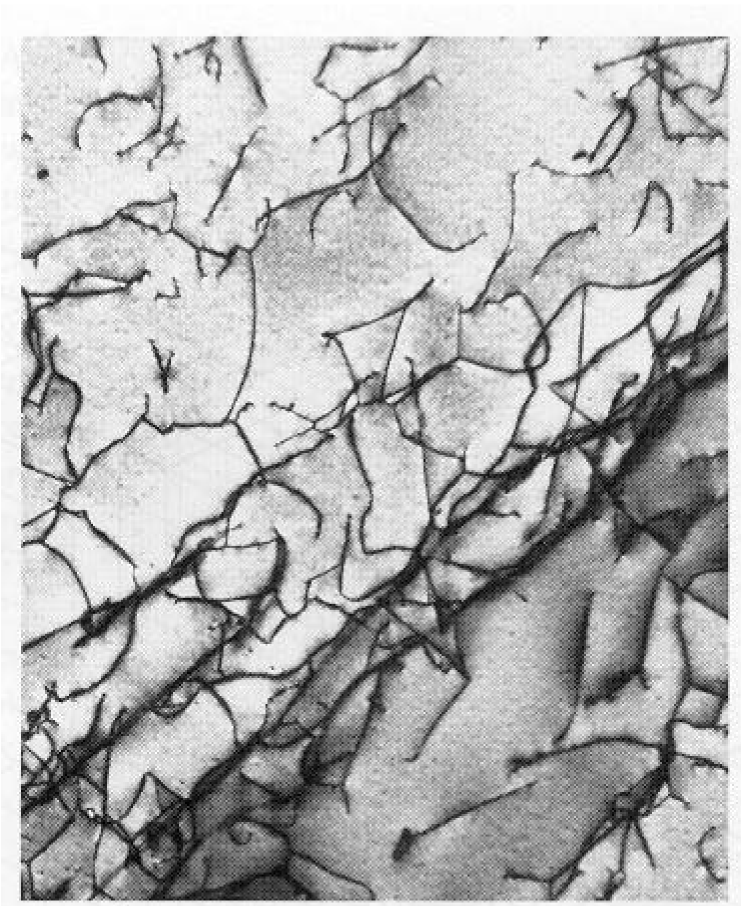
Fe-23%Al

Allen, Cahn

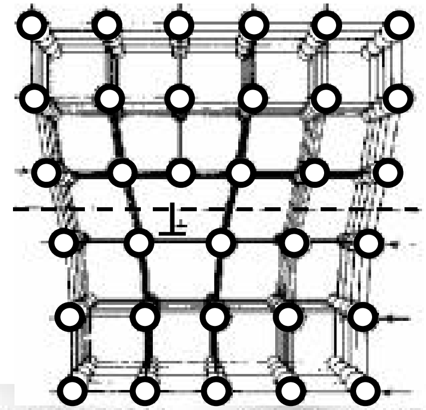


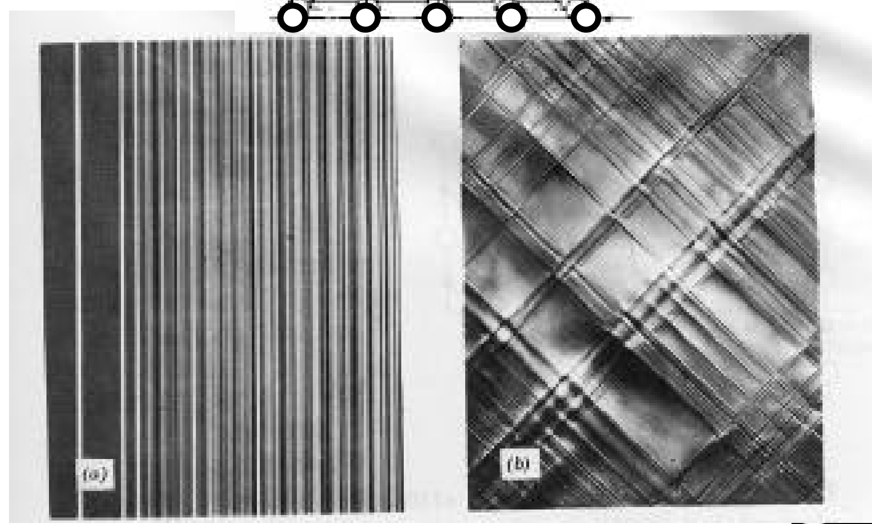
Line Defects - Dislocations

Dislocations - carriers of deformation



TEM Micrograph of a Ti-alloy
Plichta



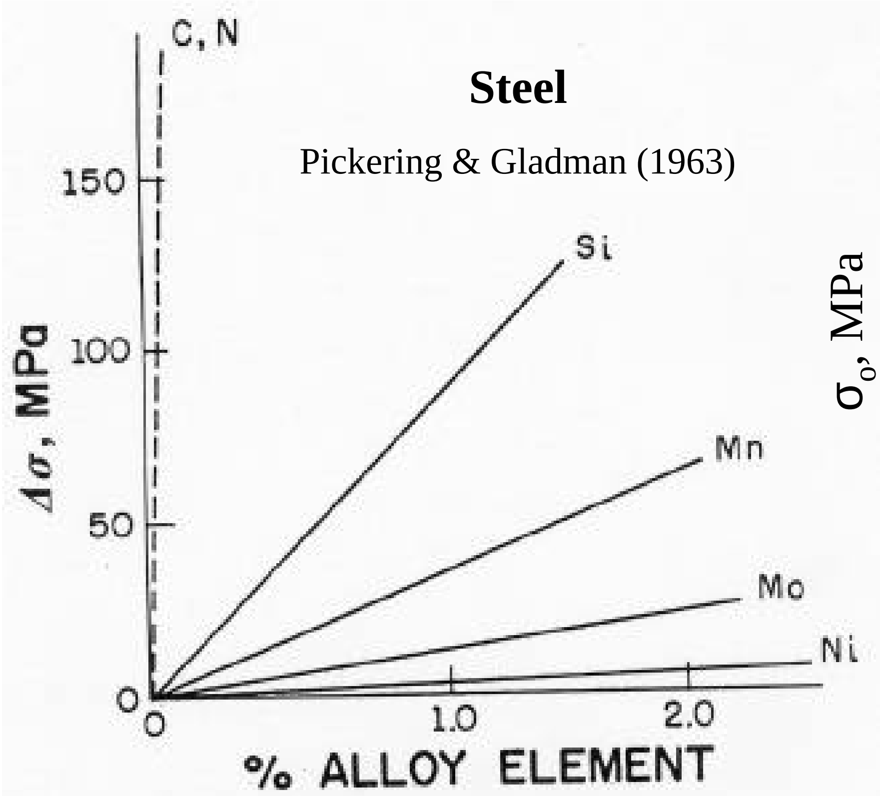


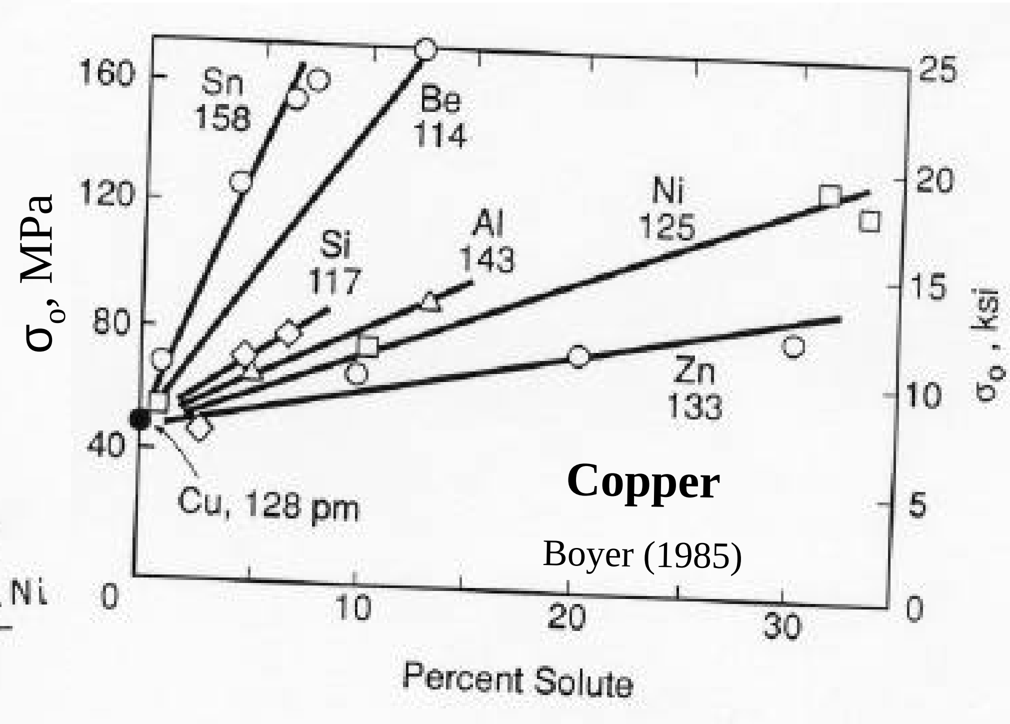
Surface markings on MgO Crystal
Johnson, Stokes, Li

Implications of Defect/Impurity Interactions

- Large activation energies for defect migration
- Thresholds for defect migration
- Dislocation-impurity interactions often control yield/flow behavior in metals
- Portevin-Lechatelier effect - serrated flow
- Development of crystallographic texture
  - Deformation
  - Recrystallization, grain growth
- Hysteresis
- Ferroelectric fatigue

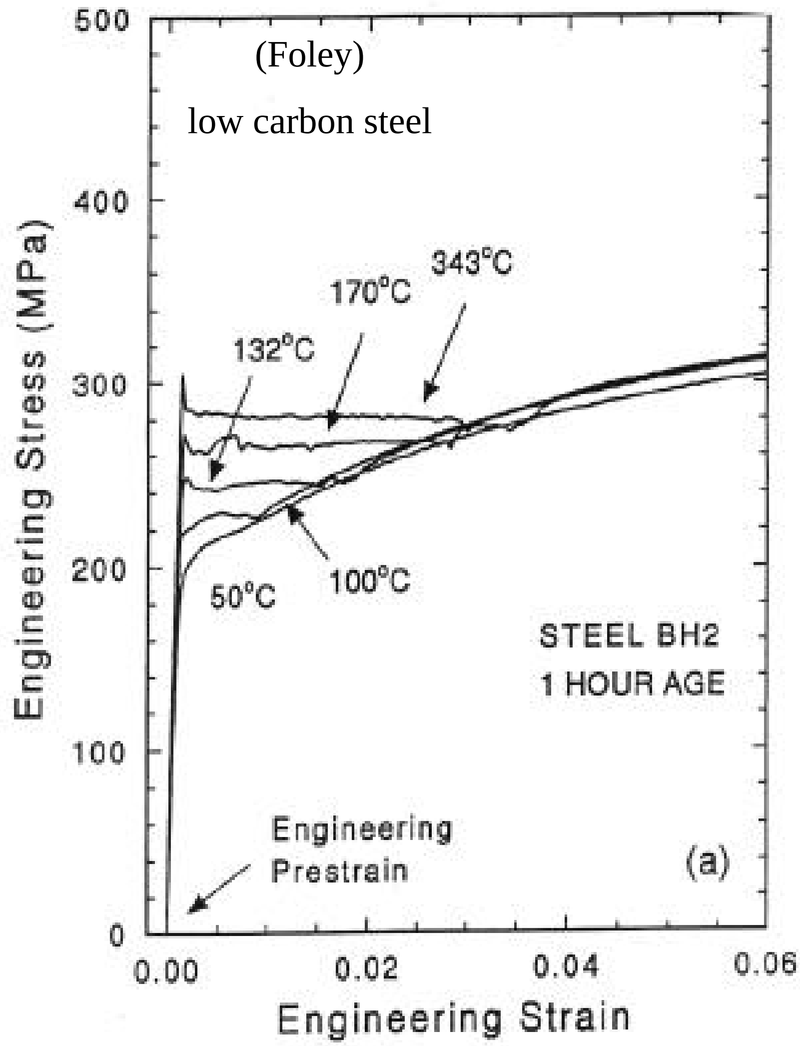
Effect of Solute on the Yield Strength of Metals





- Alloying commonly increases the yield strength
- Interstitials commonly more potent than substitutionals

Portevin-Lechatelier Effect in Metals



- Serrated yield
- Yield strength increases with temperature
- Only occurs under conditions where mobile solute is present

General Continuum Theory

- Steady-state motion of defect (grain boundary/dislocation) + diffusing impurities

- Early analyses

  Lücke & Detert (1957), Cottrell (1958), Cahn (1962), Lücke & Stüwe (1963, 1971), Yoshinaga & Morozumi (1971), Westengen & Ryum (1978), Fukuyama & Lee (1978), Takeuchi and Argon (1979), Nakanishi (1979), Fuentes-Samaniego et al. (1984), James & Barnett (1986), Hillert (1999) + ….

- Diffusion in frame that moves with defect

$$J = -\frac{DC}{kT}\frac{d\mu}{dx} - V\left(C - C_\infty\right) = -D\frac{dC}{dx} - \frac{DC}{kT}\frac{dE}{dx} - V\left(C - C_\infty\right)$$

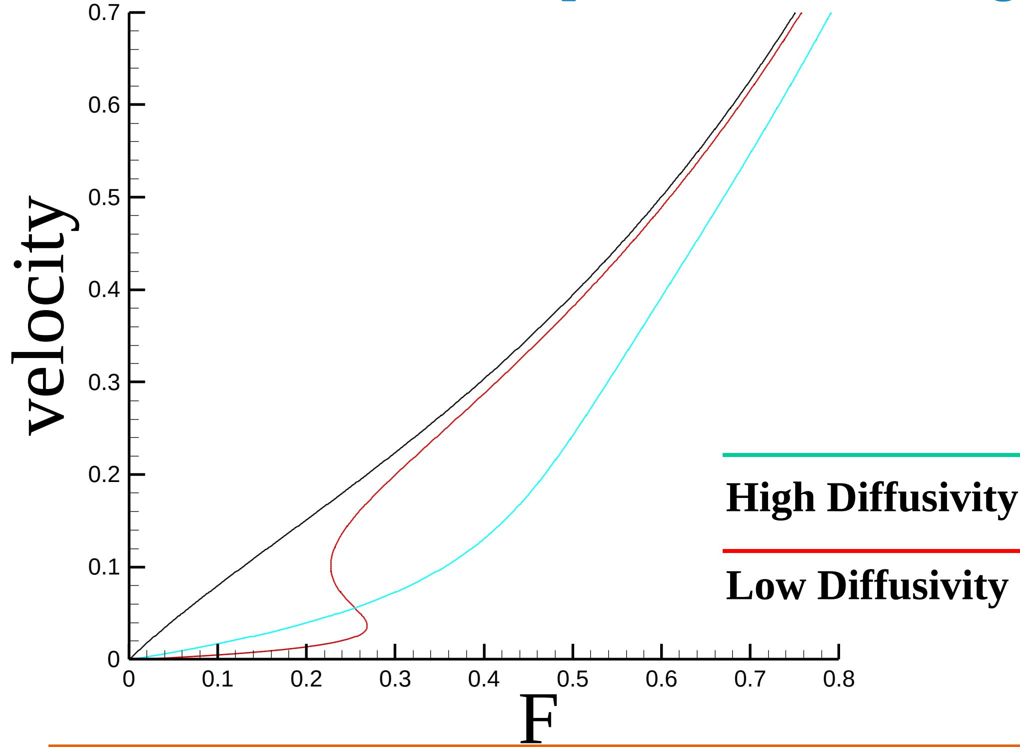
  where E(x) is the interaction between impurity & defect

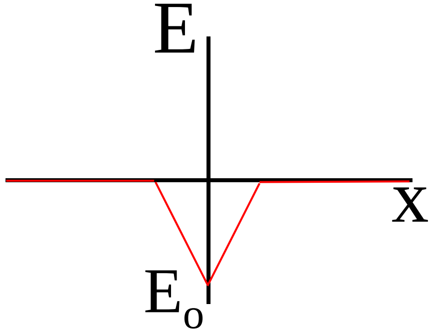
- Driving force necessary to move defect w/velocity V

$$F = F_o(V) + F_i(V)$$

Theoretical Analysis

- **Impurities create a drag force on moving defect** $F_i = -n\oint_{-\infty}^{+\infty} C(x)\frac{dE}{dx}dx$
- **Driving force necessary to move defect w/velocity V:** $F = F_o(V) + F_i(V)$
- **Assume interaction profile is short-ranged/triangular well**





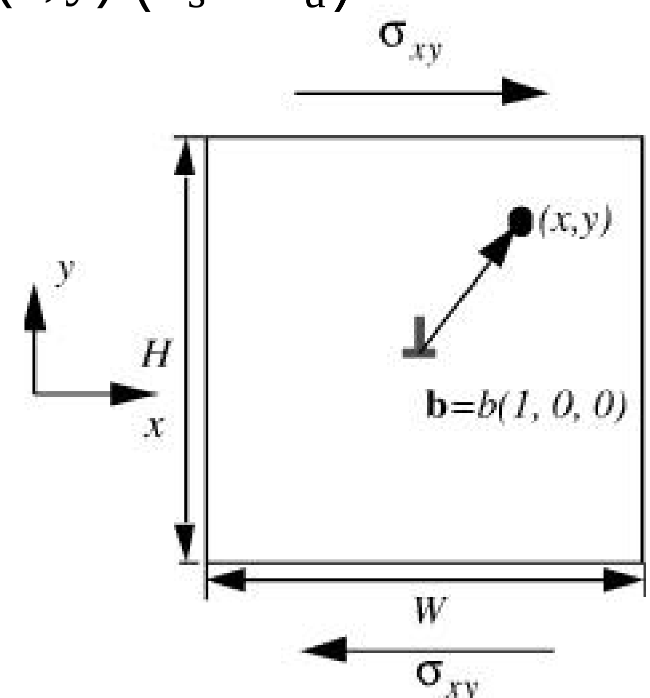
Model

- **Interaction energy**

$$E_s(x,y) = p(x,y)\,\delta V = p(x,y)\,(V_s - V_a)$$

- **Work done by external stress**

$$E_\sigma = \sigma b\,\Delta x$$



- **Normalization**
  - **Length** **b**
  - **Energy** $\mathbf{Gb^2}$
  - **Stress** **G**
  - **Time** **1/Γ**

- **Dynamics**
  - **Solute diffusion in the stress field of the dislocation**
  - **Dislocation glides**

Assumptions

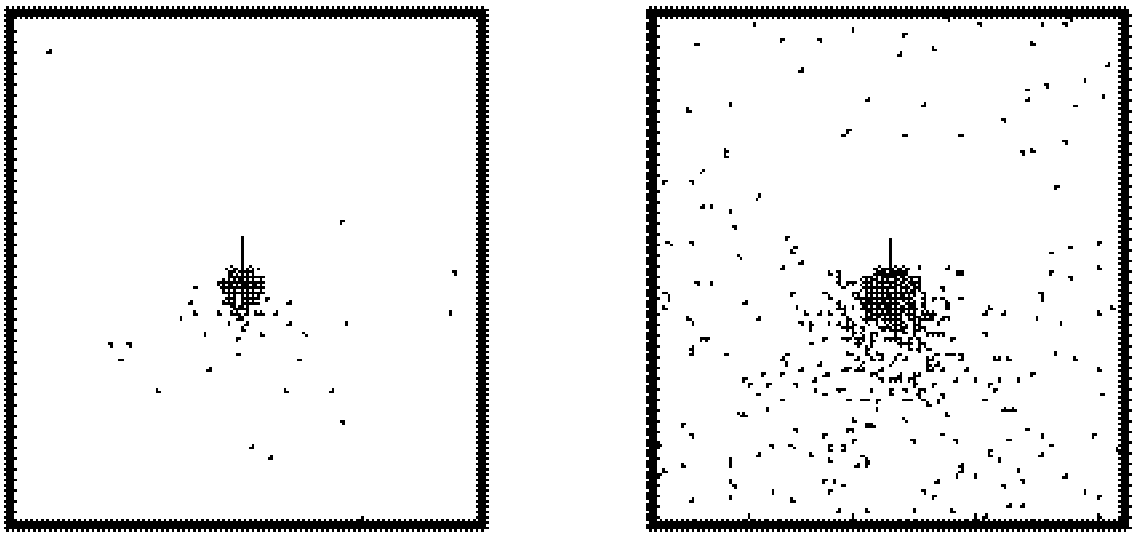
- Solute misfit
  - Dilatational misfit only
  - No solute-solute interactions
- Dislocation does not climb
- Only one slip plane
- Periodic boundary conditions
  - Dislocation stress field (array)
  - Dislocation motion
- Dislocation-solute interaction cut-off when both occupy the same site
- Only one solute can occupy a site at any time

Simulation Algorithm

- **Place impurities and dislocation randomly on a fixed lattice**
- **Attempt to move dislocation or impurity**
  - **Dislocation and impurity have different mobility**
  - **Probability of choosing dislocation = 1/R**
    where $\mathbf{R=1+N_i\,(M_i/M_d)}$
  - **Generate a random number P in [0,R)**
  - **If P>1, attempt to move a impurity, else attempt to move dislocation**
- **Motion**
  - **If dislocation is chosen, attempt to move left or right**
  - **If impurity is chosen, attempt to move to any nearest neighbor site**
- **Acceptance criteria**
  - **Generate a random number Q in [0,1)**
  - **If $\mathbf{Q < \exp(-\Delta E/kT)}$, accept the move, otherwise reject it**

Impurity Distribution: no applied stress

$$\frac{Gb\Delta V(1+\nu)}{3H(1-\nu)kT} = 200$$



$C_0 = 1\%$ $C_0 = 5\%$

- **Condensed impurity cloud forms near core at all concentrations**
- **Dilute (Cottrell) cloud also forms**

Impurity Distribution: analytical & simulation

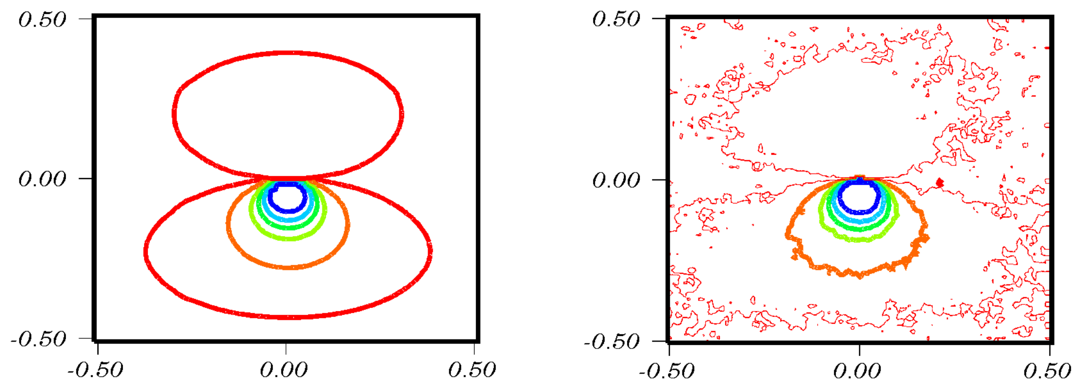
No site-exclusion
Boltzmann

$$c = c_o \exp\left[\frac{-p\,\delta V}{kT}\right]$$

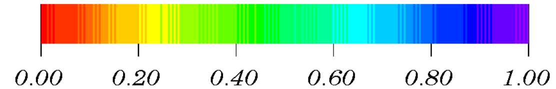
Site exclusion
Fermi-Dirac

$$c = \frac{1}{1 + \left(\frac{1 - c_o}{c_o}\right)\exp\left[\frac{p\,\delta V}{kT}\right]}$$

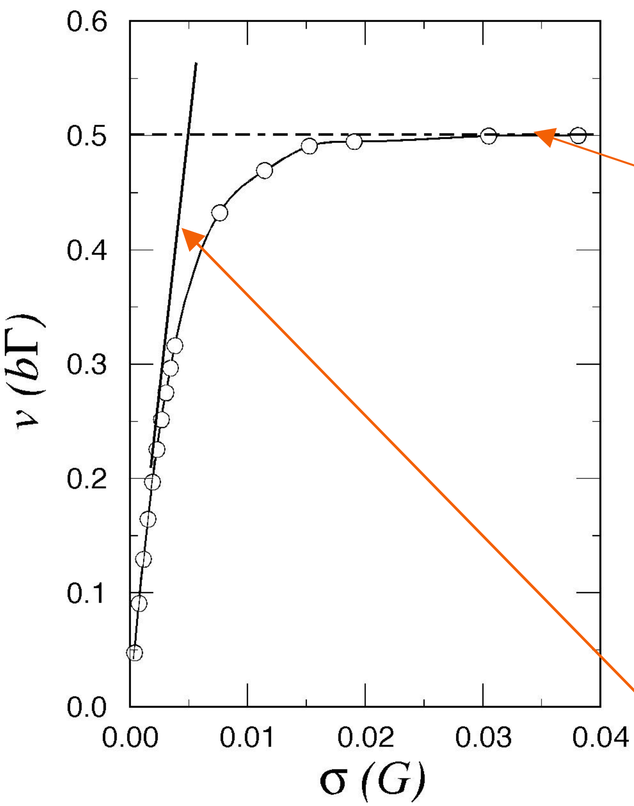
C_0=5%



Site exclusion analysis ***Simulation***



Intrinsic Dislocation Velocity: no impurities



- **Saturation velocity**
  - **Attempt frequency = Γ**
  - **Maximum displacement per attempt = b**
  - **Maximum velocity = bΓ/2**
- **Initial slope**
  - **Dislocation mobility**

$$M = \frac{D}{kT} = \frac{1}{2}\frac{\Gamma a^2}{kT}$$

  - **Dislocation velocity**

$$v = MF$$

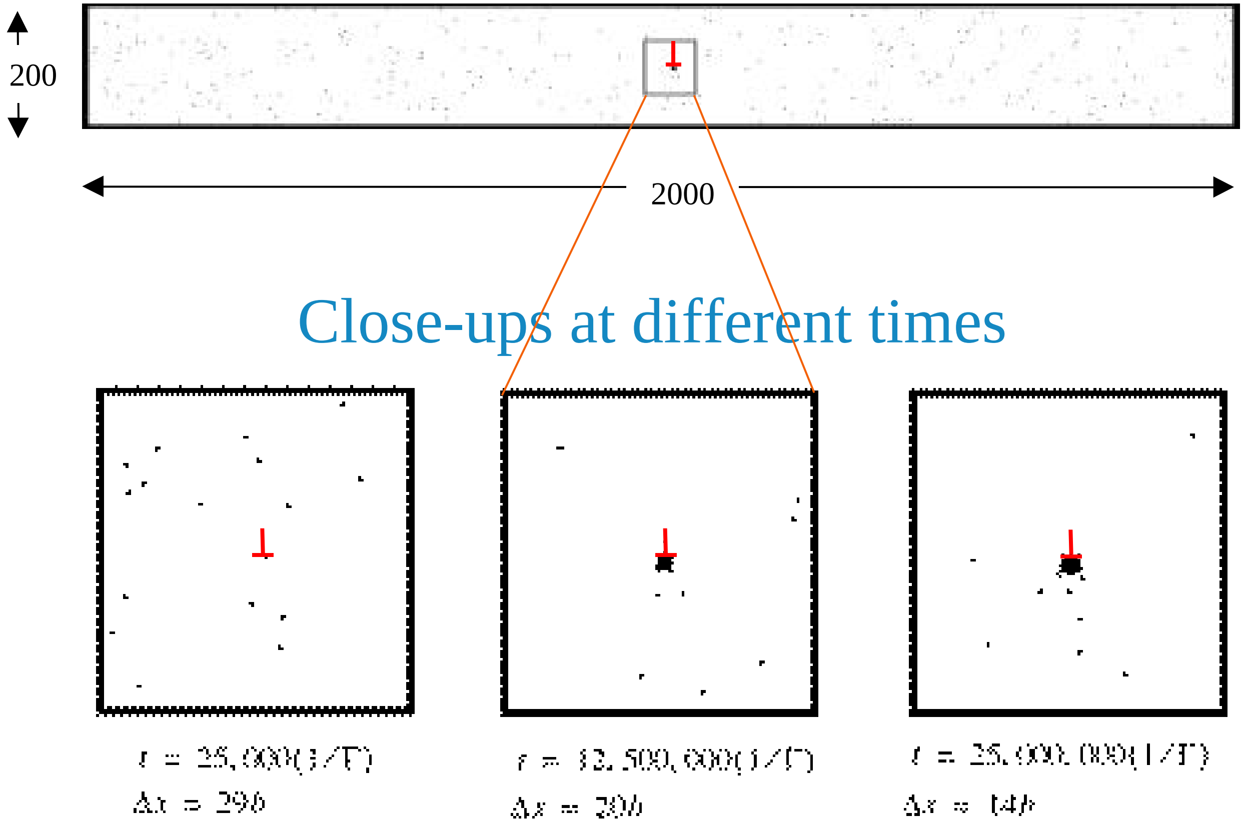
$$= \left(\frac{1}{2}\frac{\Gamma a^2}{kT}\right)(\sigma b)$$

  - **Here, a = b**

$$\frac{v}{(b\Gamma)} = \left(\frac{1}{2}\frac{Gb^2}{kT}\right)\frac{\sigma}{(G)}$$

Impurity Profile: small stress

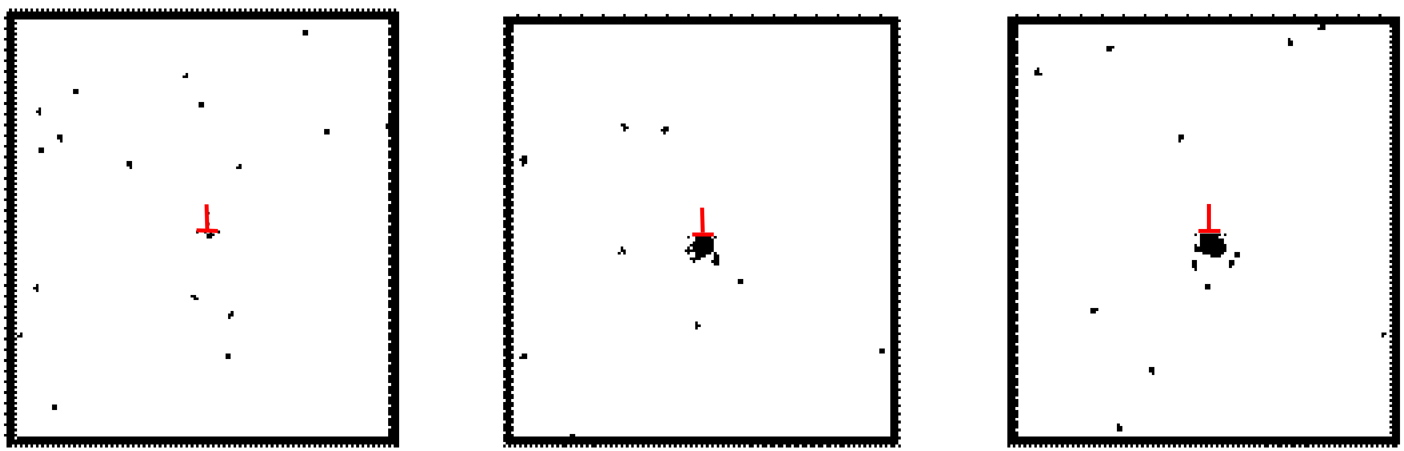
$\sigma = 3.3\mathrm{x}10^{-4}\ G \quad C_o = 7.5\mathrm{x}10^{-4}$



- **Condensed cloud is forms**
- **Dislocation captured by impurities**

Impurity Profile: high stress

$\sigma = 2.0\text{x}10^{-2}$ G $C_o = 7.5\text{x}10^{-4}$



$t = 25,000(1/\Gamma)$ $\Delta x = 843b$

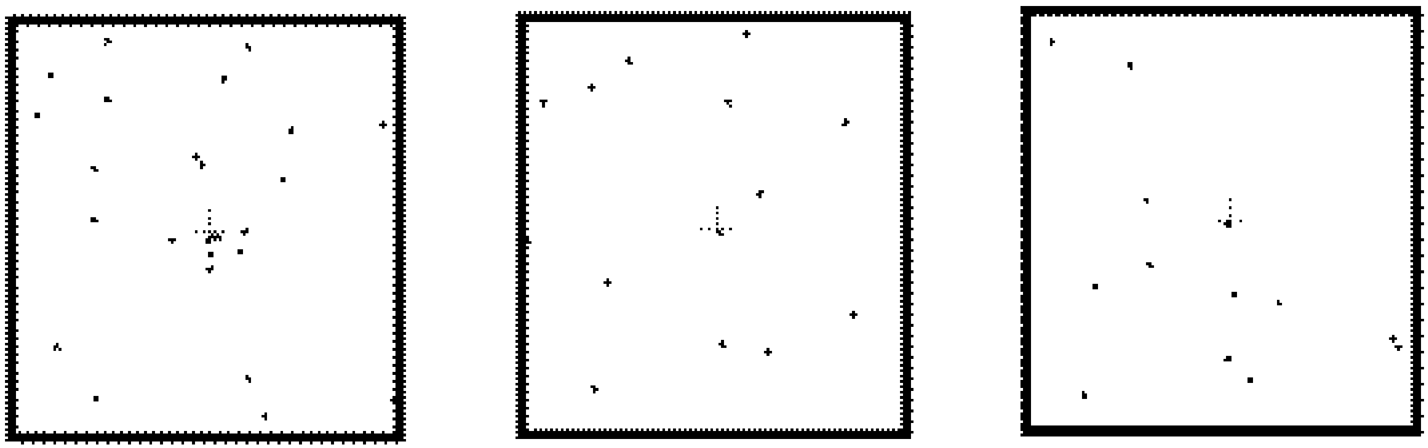
$t = 12,500,000(1/\Gamma)$ $\Delta x = 2792b$

$t = 25,000,000(1/\Gamma)$ $\Delta x = 2931b$

- Condensed cloud is forms
- Dislocation initially moves large distance
- Dislocation eventually captured by impurities

Solute Profile w/slightly higher stress

$\sigma = 3.2\text{x}10^{-2}$ G $C_o=7.5\text{x}10^{-4}$



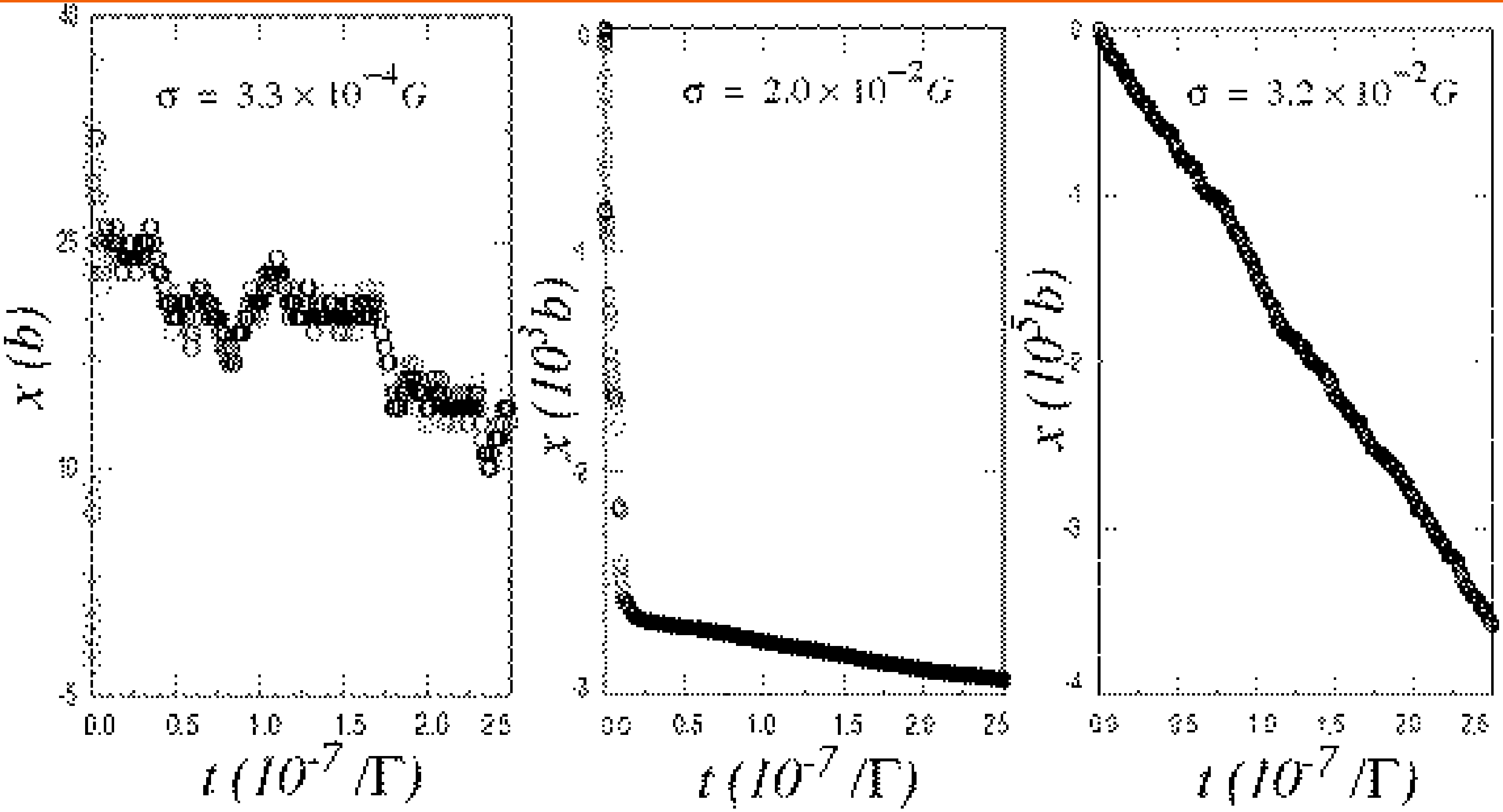
$t = 25,000(1/\Gamma)$ $\Delta x = 748b$

$t = 12,500,000(1/\Gamma)$ $\Delta x = 187607b$

$t = 25,000,000(1/\Gamma)$ $\Delta x = 358387b$

- Dislocation interacts with solute
- Dislocation temporarily gets stuck on solutes, but pulls free
- Dislocation continues to move

Dislocation Position History



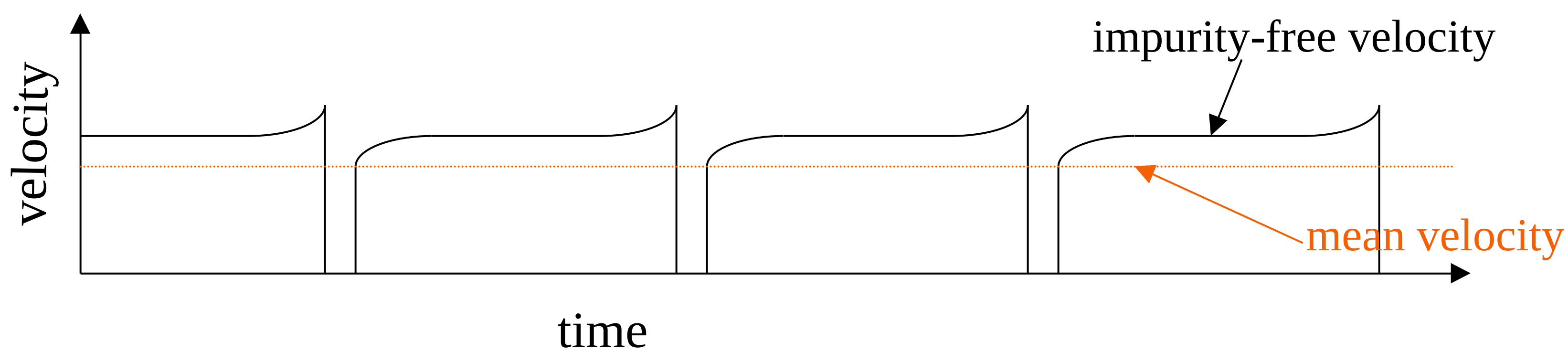
$C_o = 7.5 \times 10^{-4}$

- At low stress, dislocation moves very slowly
- At high stress, dislocation moves rapidly, then a transition to slow motion
- At the highest stress, dislocation motion is nearly constant

High Velocity Branch

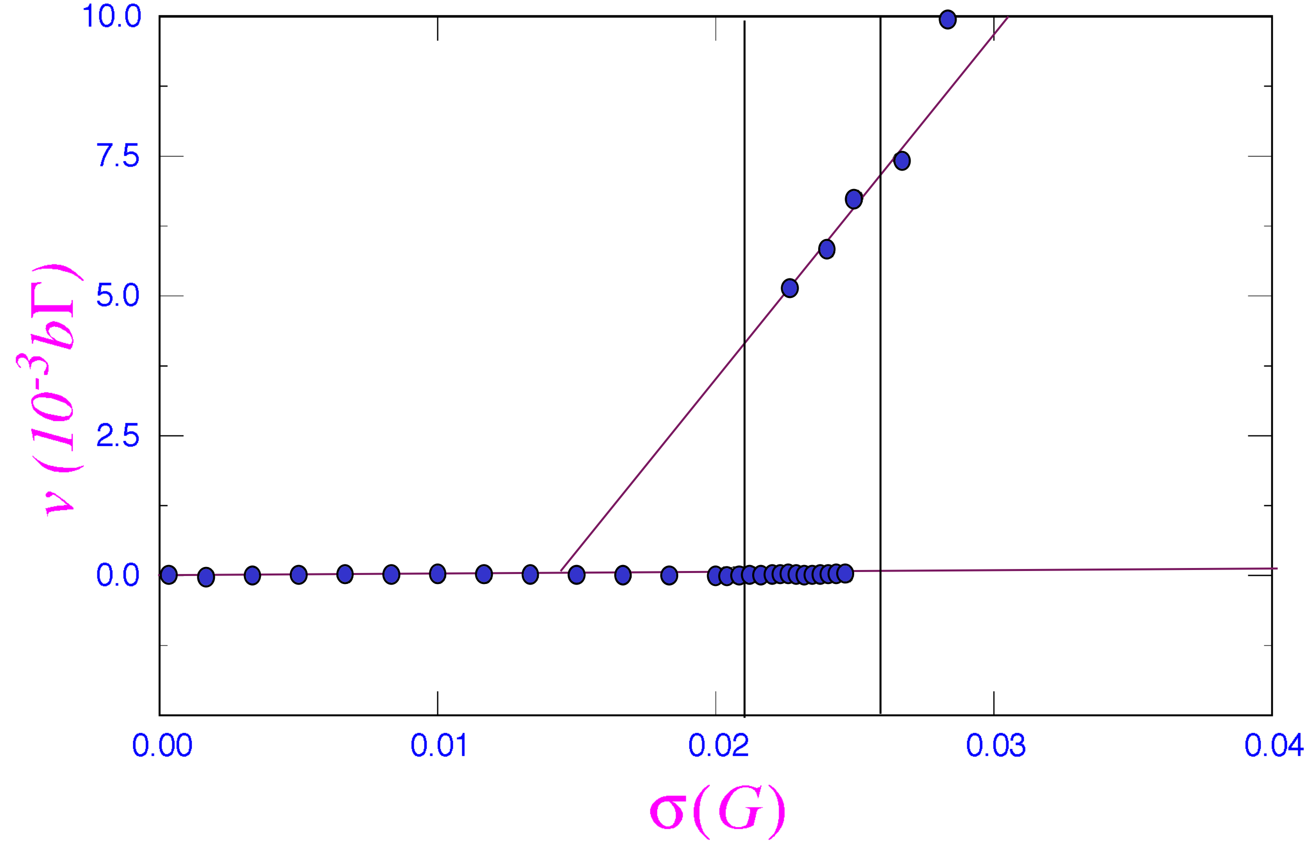
If the dislocation does not drag impurities at high velocity, why is the velocity lower than when no impurities are present?

- **Dislocation still encounters impurity atoms at or near the slip plane**
  - **Stochastically, these atoms yield no net force**
  - **Dislocation must escape from impurities**



- **Dislocation trapping & escape decrease dislocation velocity**
  - **Not in continuum theories**

Velocity Transition

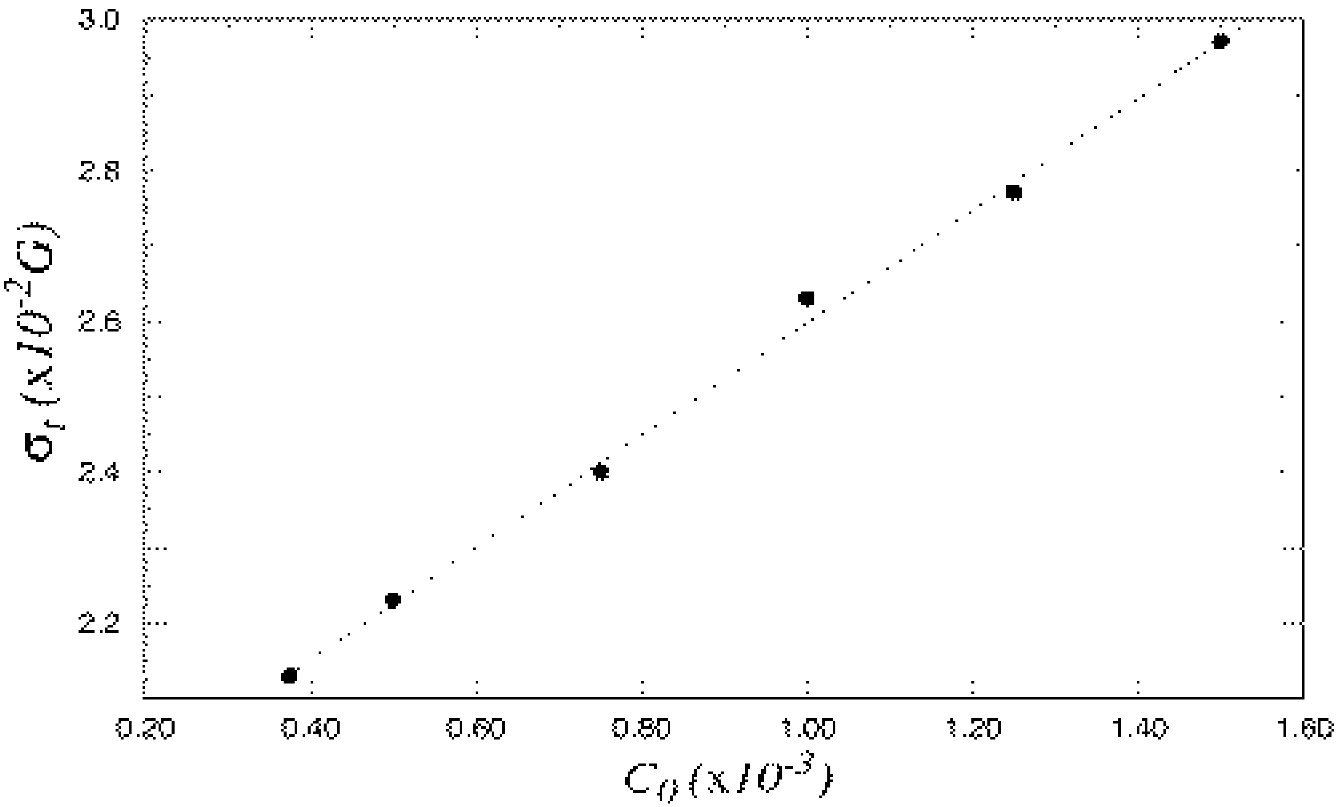


C_o=7.5x10^{-4}

- **Abrupt change in mobility**
- **Two distinct mobility branches (overlap is small)**
- **Dislocation jumps back and forth at fixed stress!**

Concentration Dependence of Threshold

ΔV= 0.5 b^2



- **Near linear dependence of threshold on bulk impurity concentration**
- **Caveat: relatively small range of stress**

Which part of the impurity cloud matters?

- **The retarding force on the dislocation is**

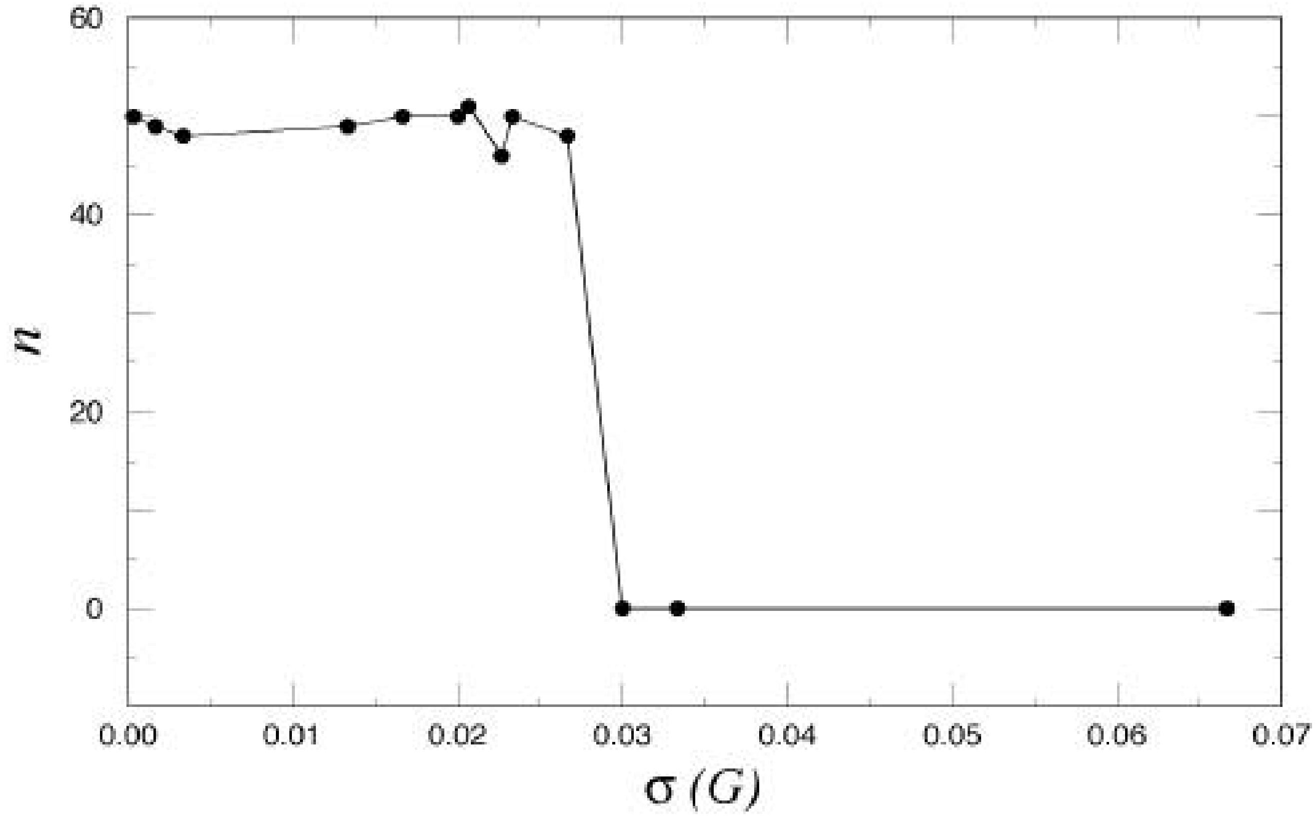
$$F = \int\int c(r,\theta)\left[-\frac{\partial E(r,\theta)}{\partial r}\right] r\,dr\,d\theta$$

- **Far from the dislocation, c decays like exp(-1/r) and $\partial E/\partial r$ decays as $1/r^2$**
  - **The argument of the integral decays rapidly with increasing r**
  - **This implies that the impurity near the dislocation dominates the interaction**

- **Near the dislocation, the impurity concentration is constant and $\partial E/\partial r$ decays as $1/r^2$**
  - **This leads to a force that grows logarithmically with the size of the condensed cloud**
  - **This force is insensitive to the details around the core, provided that the condensed cloud is much larger than the core size**

The impurity drag on the dislocation is dominated by the size of the condensed cloud

Size of the Condensed Cloud



$C_o = 7.5 \times 10^{-4}$

- **Size of condensed cloud changes when velocity changes**
- **Little effect of jump in mobility on impurity cloud**

Conclusions: dislocations

- Discrete, MC model that self-consistently determines dislocation velocity and impurity profile
- A condensed cloud of impurities forms at low dislocation velocities
- Dislocation moves at low velocities by dragging impurity cloud
- The retarding force is dominated by the condensed cloud
- At high velocity the dislocation does not drag a cloud, but moves more slowly than in the absence of impurities
  - In this limit, the dislocation moves by thermal activation out of impurity traps
- At intermediate driving forces, the dislocation mobility can be multivalued
  - Moving dislocation can jump back and forth between these branches at fixed driving force

Problems & Solutions

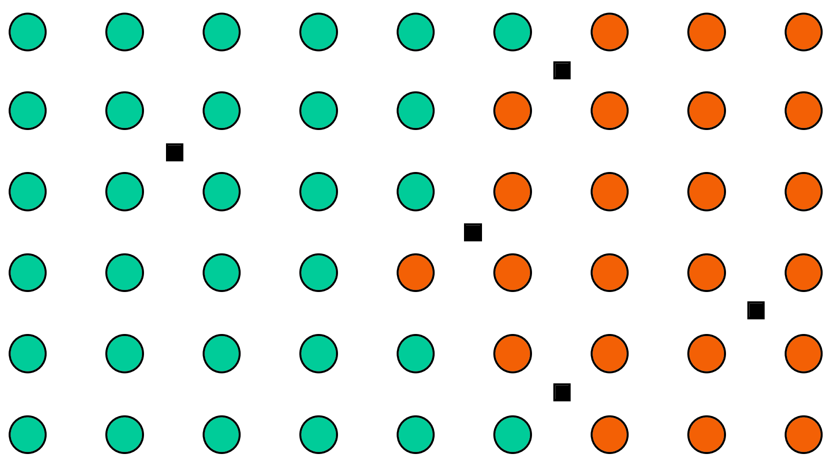
- Dislocations are flexible lines **not** points - dimensionality
- Solute profile is strongly localized at core - continuum vs. discrete

- Go to higher dimension (2 or 3)
- Simplifications
  - ♦ Long range interactions ⇔ line tension model + core interaction
  - ♦ Better model for interface/boundary

Simulation Model

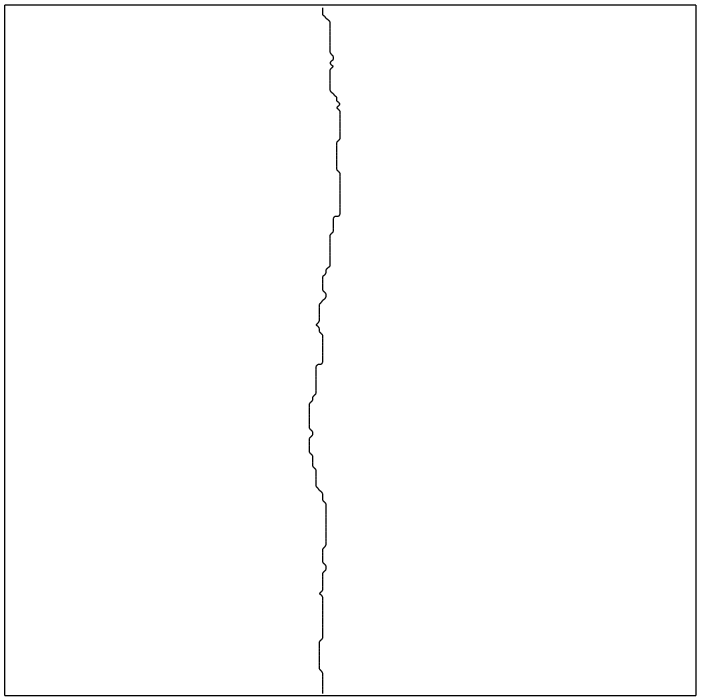
- 2-d, boundary is a line
- Ising model + diffusing interstitial impurities
- Drive with field
- Site exclusion, short range interactions

$$E_{ss} = -(J/2)\, \Sigma_{ij}\, s_i\, s_j + H\, \Sigma_i\, s_i - (E_o/2)\, \Sigma_i\, \theta_i\, |\Sigma_j s_j| + \varphi \Sigma_{ij}\, \theta_i\, \theta_j$$



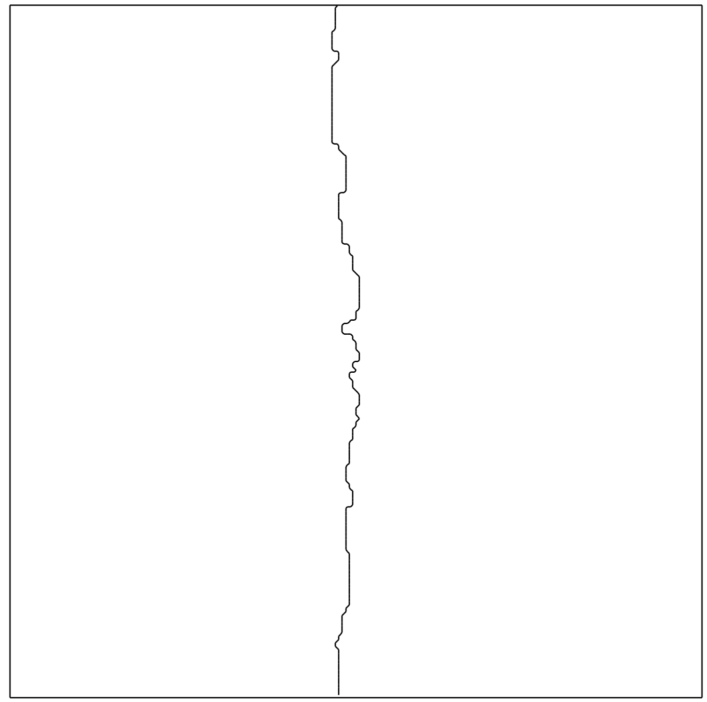
Migration: no impurities

Low Field



|H|=0.01

High Field

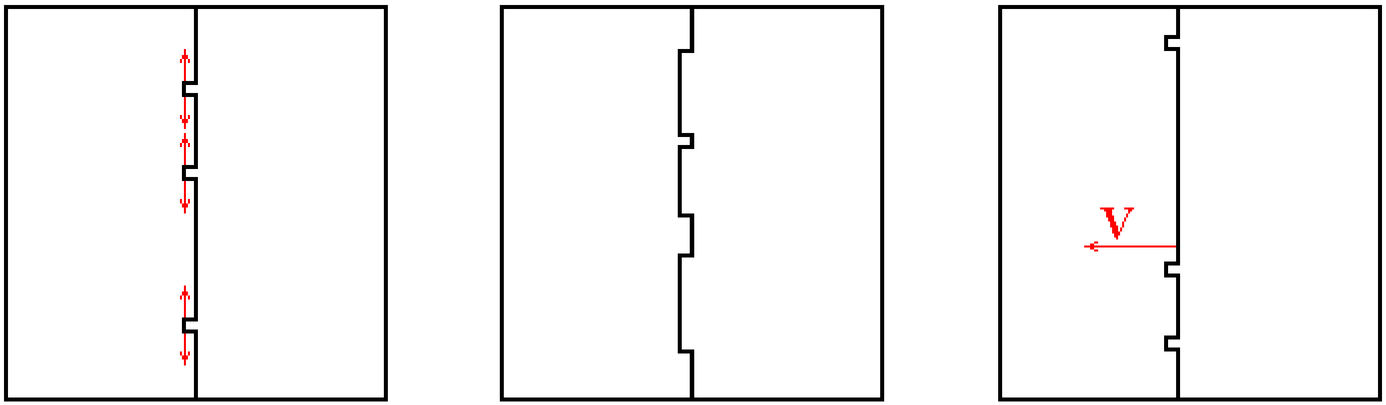


|H|=0.10

- Defect move by double kink nucleation and propagation

Kink Model for Defect Migration

migration sequence w/o impurities



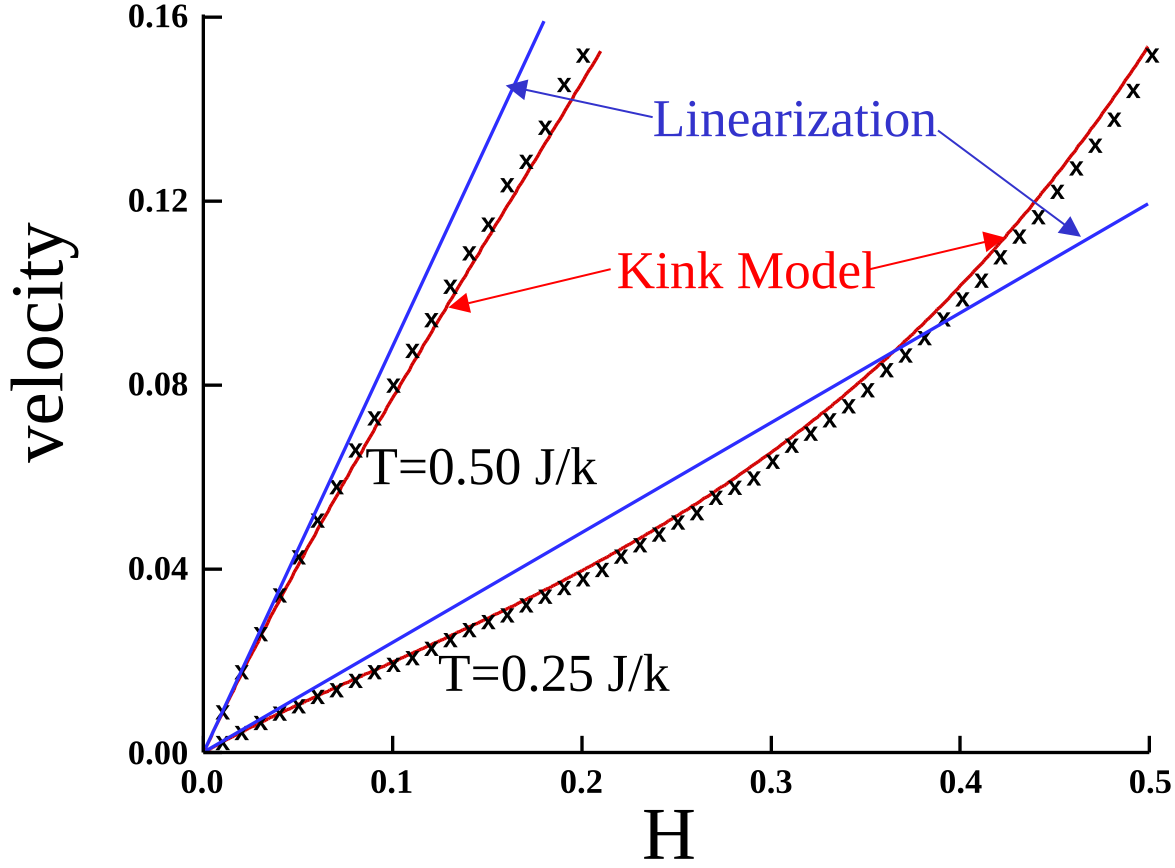
Double kink nucleation rate: $w_{dk} = e^{-(4J-2H)/kT}$

Kink migration velocity: $V_y^0 \,(1 - w_k)$, where $w_k = e^{-2H/kT}$

Boundary velocity:

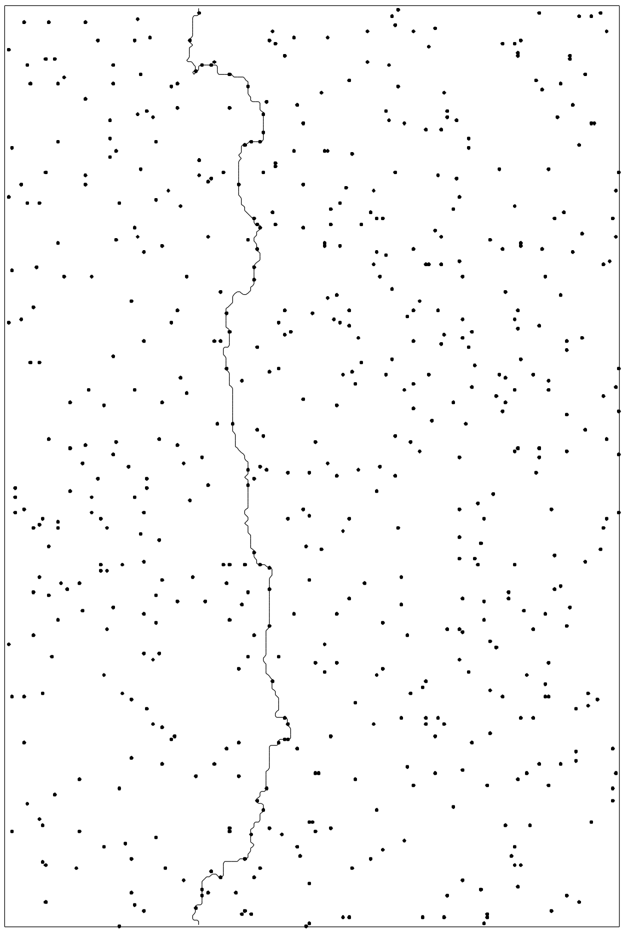
$$V = (1 - w_k)\sqrt{\frac{4}{3}\,\frac{w_{dk}}{1 - w_k/2}} \approx 4\sqrt{\frac{2}{3}}\; e^{-2J/kT}\,\frac{1}{kT}\,H$$

Kink Model/Simulation Comparison

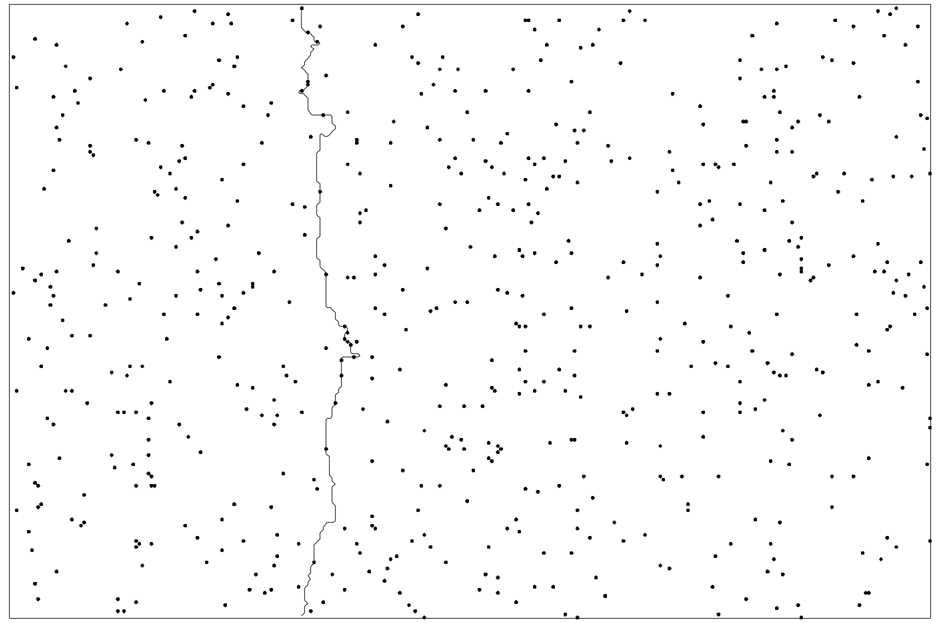


- Excellent agreement between kink model and simulation
- Linearization is satisfactory only at very small driving forces

Boundary Migration: static impurities



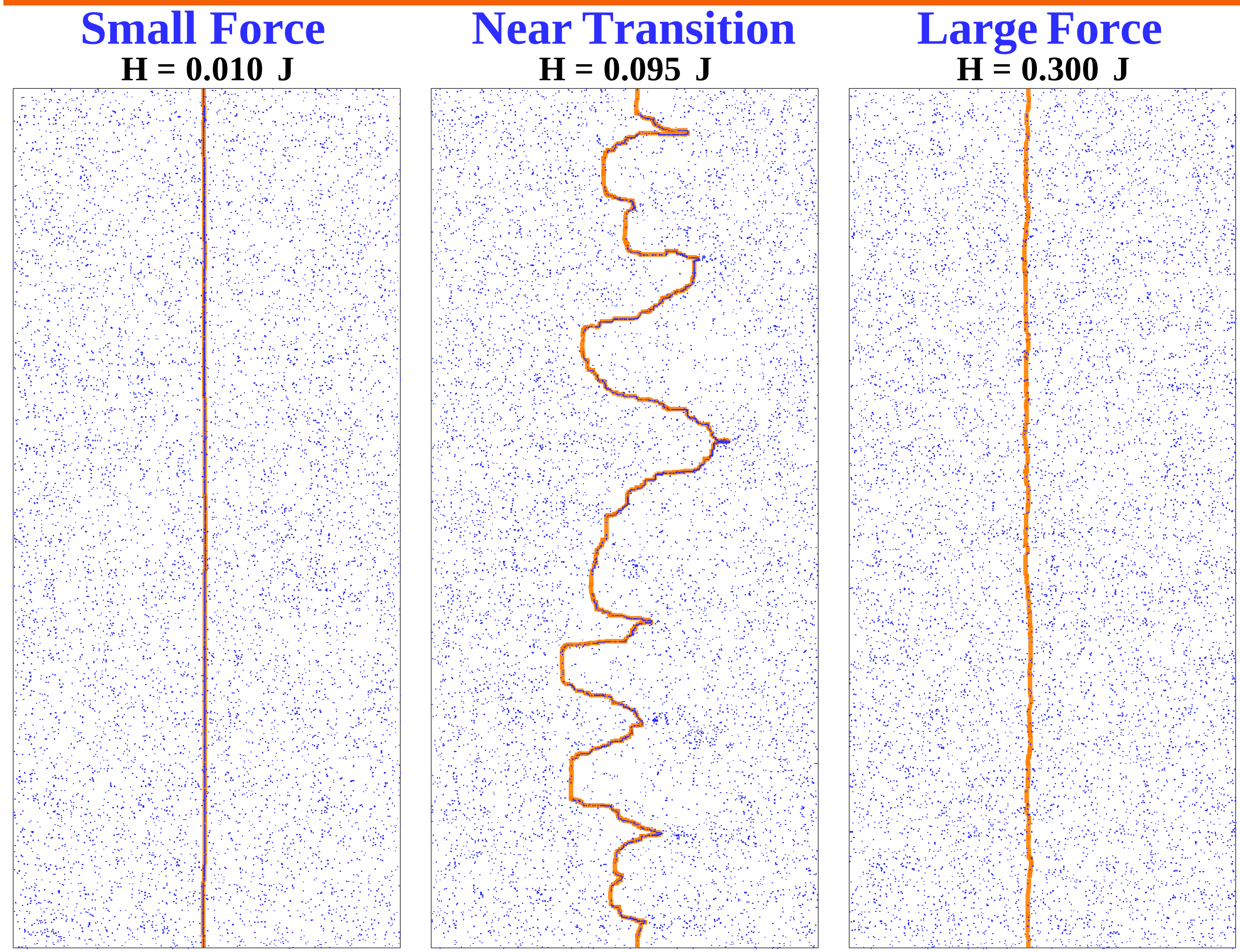
Low Field |H|=0.01



High Field |H|=0.10

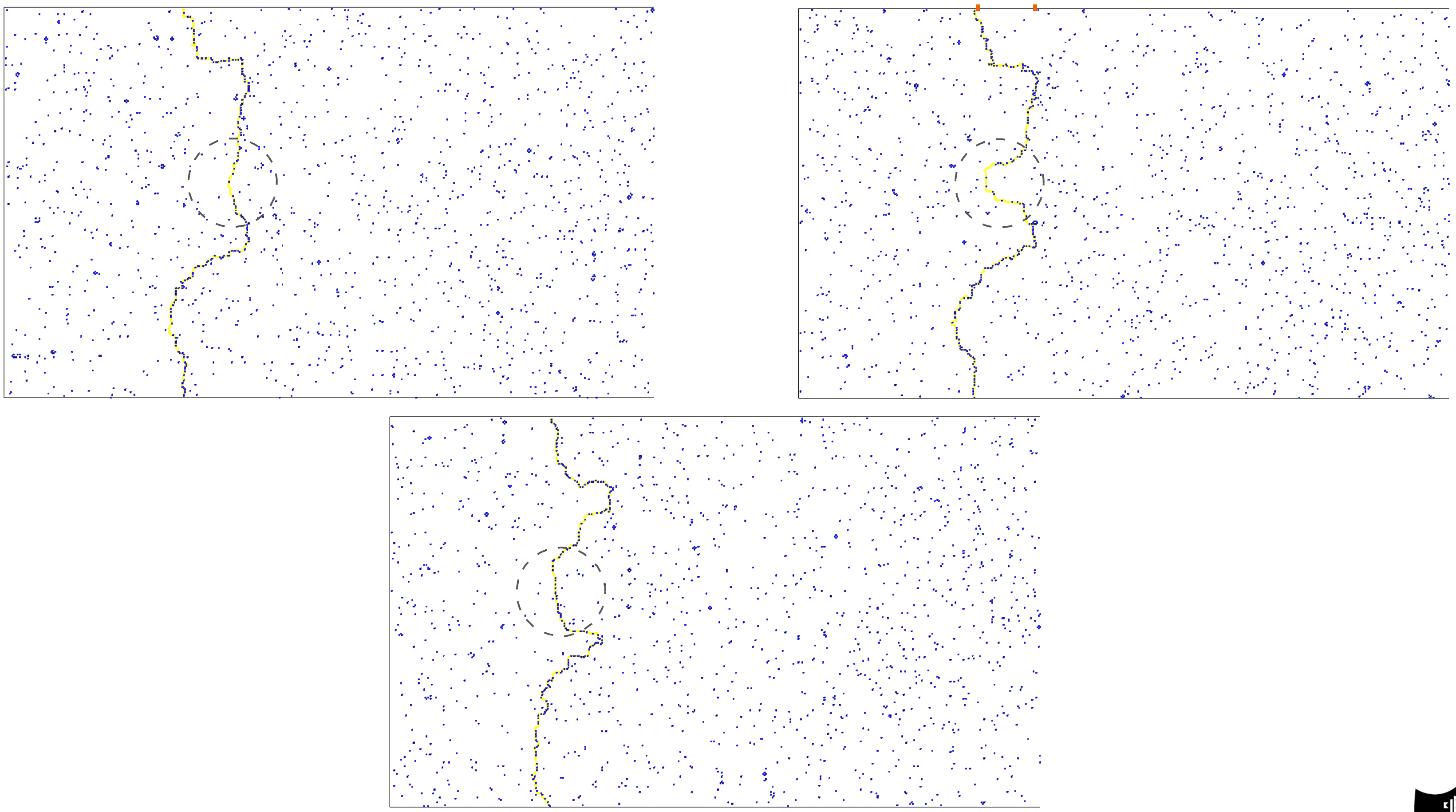
C=0.01

Boundary Migration: diffusing impurities



$\varphi = 0$ J
$E_0 = -1.63$ J
$T = 0.25$ J/k
$C_\infty = 0.010$
$D = 0.0916\ a^2/\tau$

Boundary Profile Evolution

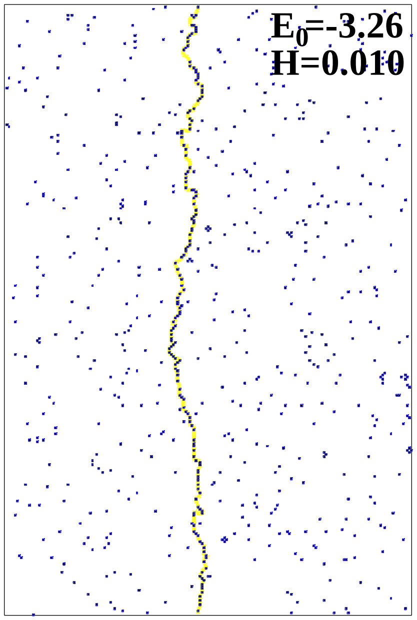


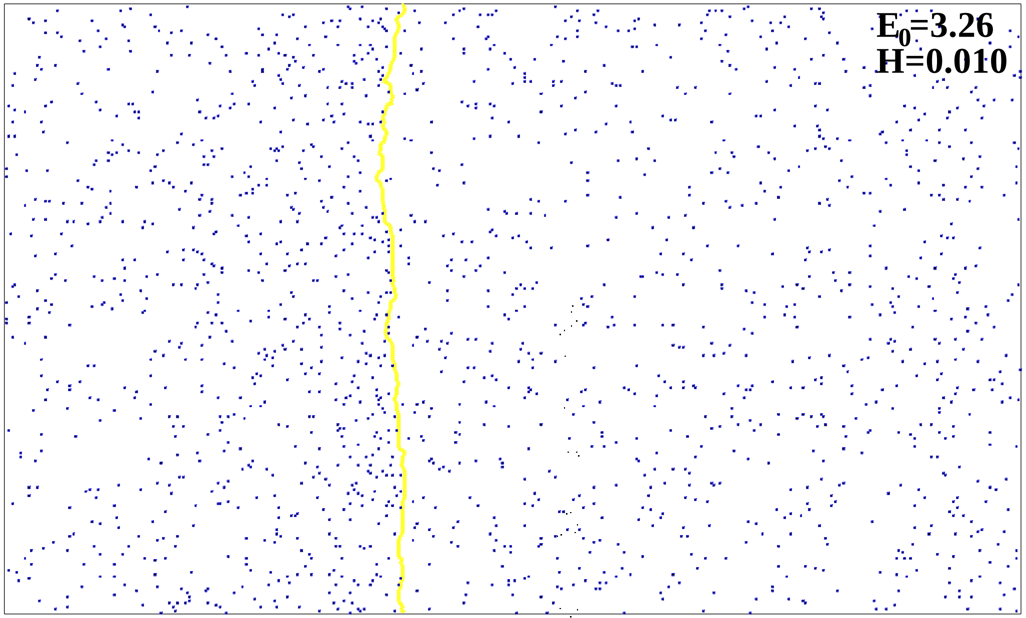
- Boundary bulges forward where local impurity concentration is low
- High curvature near "corners" pulls boundary away from impurities

Boundary Migration: sign of interaction

D=0.0916
C=0.010

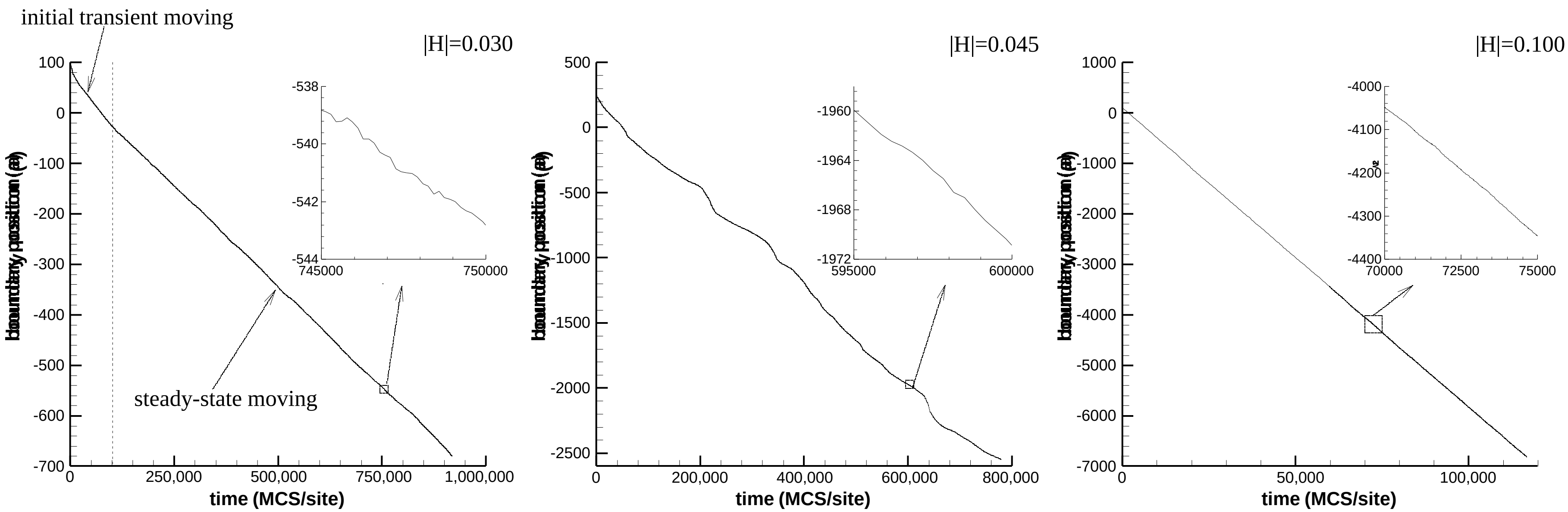
Small Driving Force





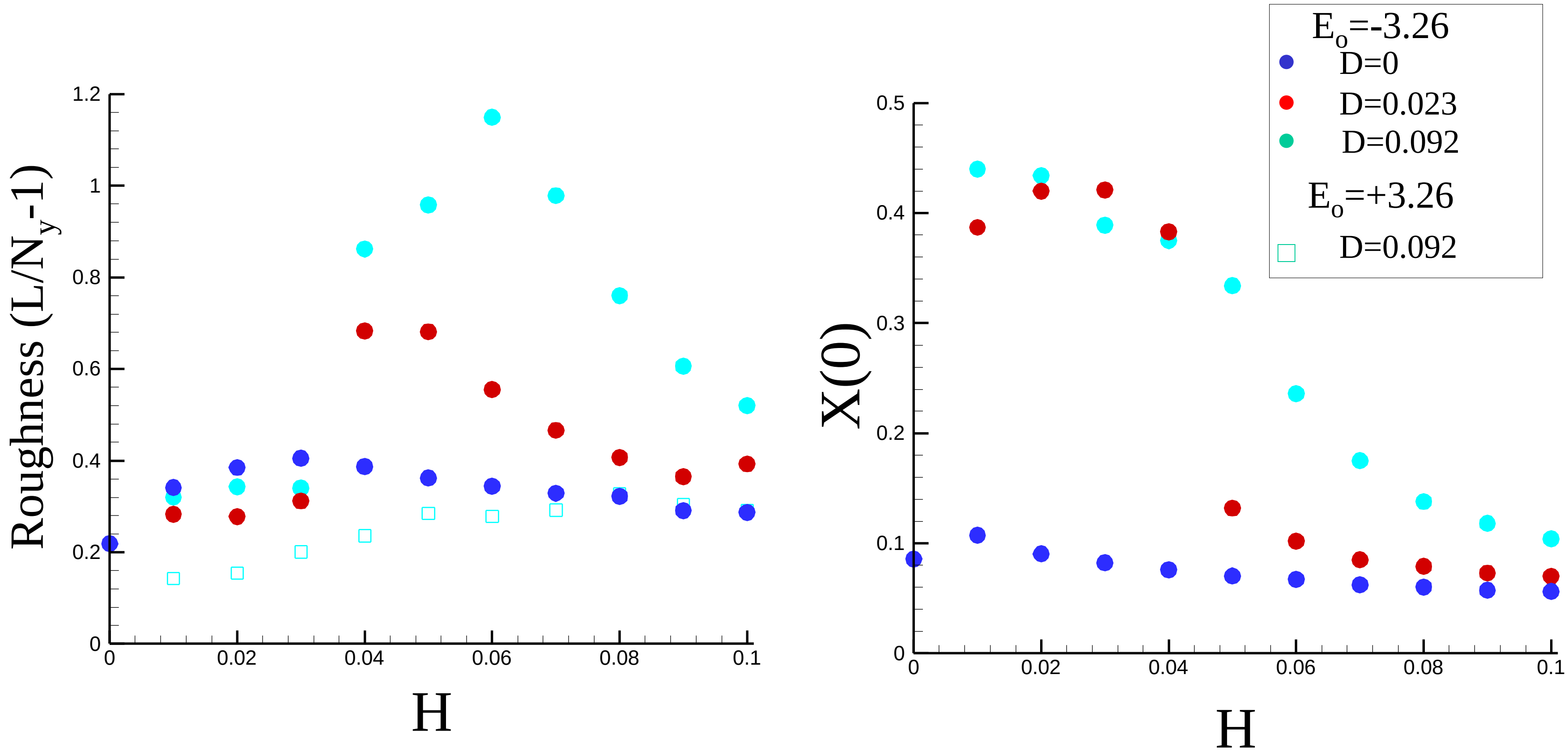
Boundary Displacement

$D=0.0916 \quad C=0.010 \quad E_o=-3.26$



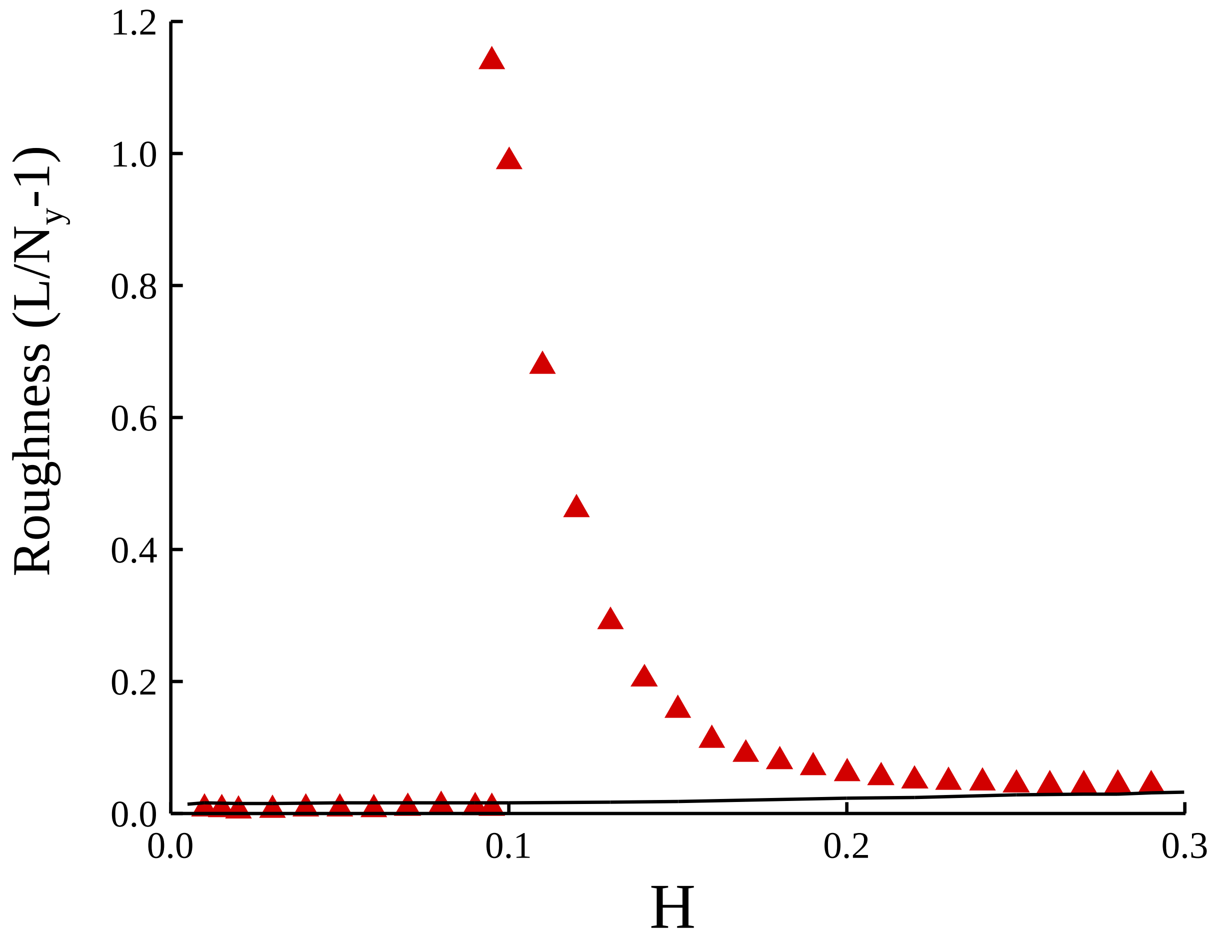
- Small scale fluctuations away from constant velocity line
- Intermediate driving forces - fluctuations are observed on large scale
- Simulation cell size never adequate for intermediate driving forces

Boundary Roughness & Segregation



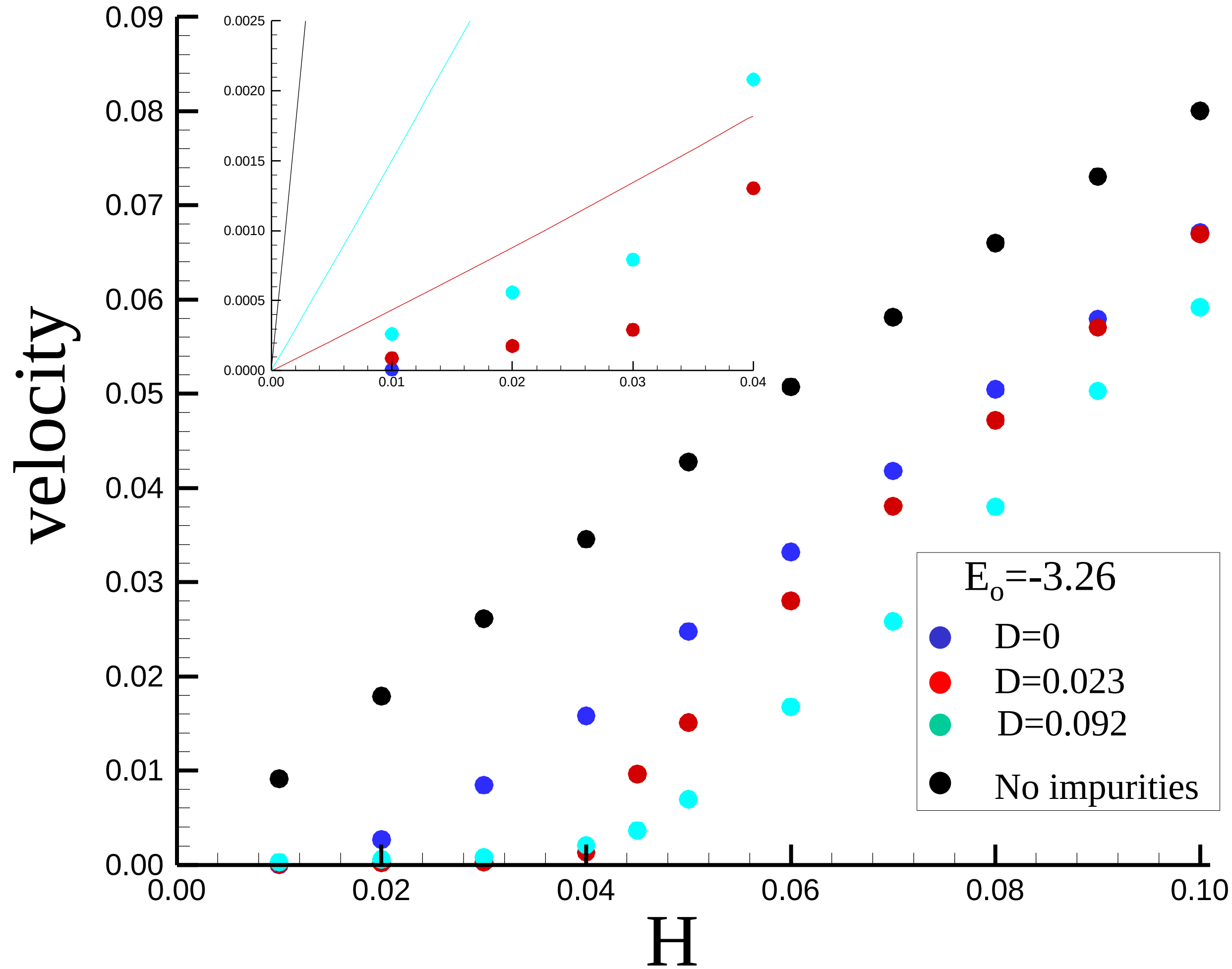
- Roughness shows a peak (jump) when D≠0 and attractive impurities
- Segregation initially increases with increasing driving force, then decreases rapidly near peak roughness

Boundary Roughness at Lower T



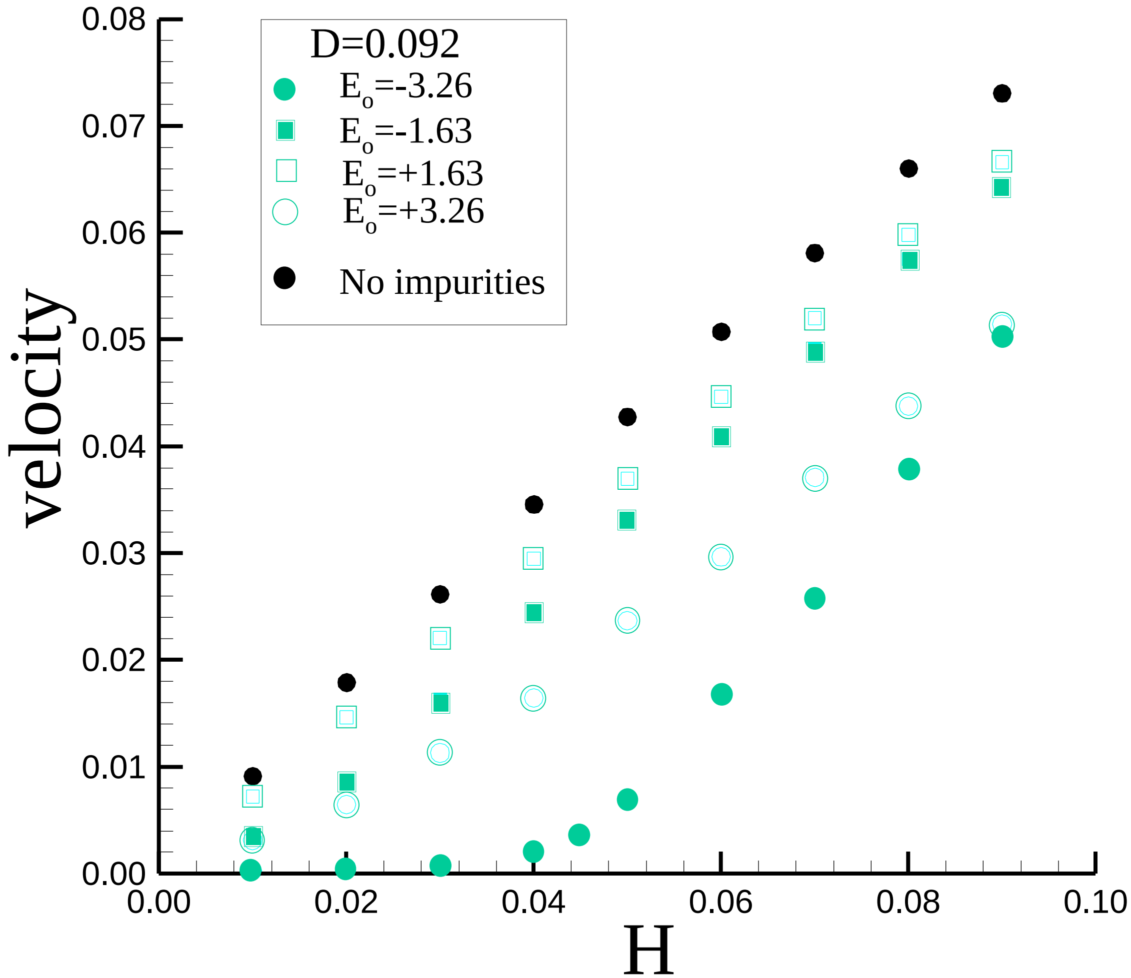
- Jump in roughness can be very sharp when segregation is strong

Boundary Velocity: effect of diffusivity



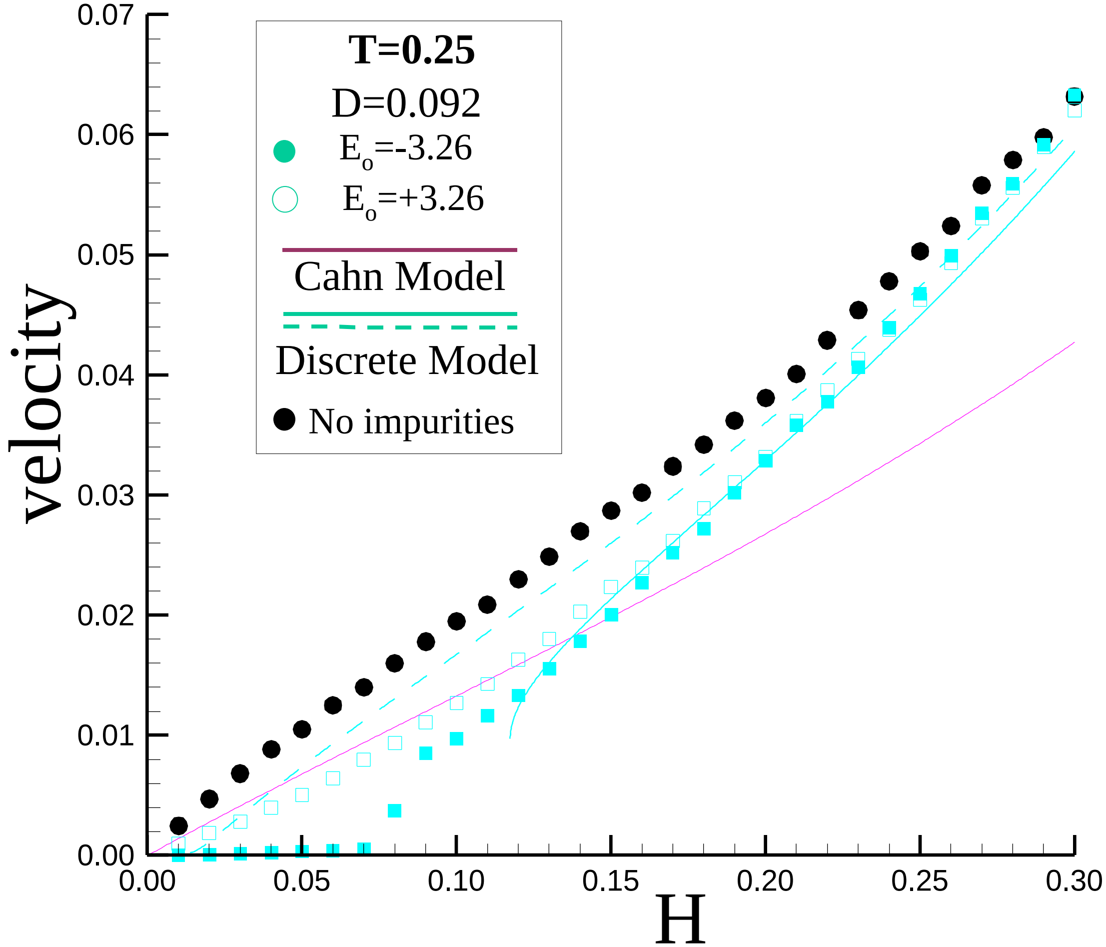
- Large driving force: D ⇑, V ⇓ and threshold ⇑
- Small driving force: D ⇑, V ⇑, poor agreement with theory

Boundary Velocity: interaction strength/sign



- +/- interactions are not equivalent
- Attraction - more pronounced transition

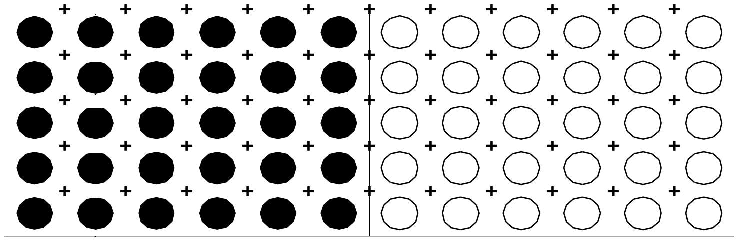
Boundary Velocity: lower temperature



- Lowering T at fixed D (i.e., only change in thermal activation)
- Lower velocities, transition at larger driving force
- Poor agreement with analytical theory, especially at large driving forces

A Discrete Model for Boundary Motion

- Classical theory treats boundary and impurity field as a continuum
- In nature & simulation - both are discrete
- Retain simplicity of 1-d, but consider impurity flux and local interactions on each distinct impurity plane

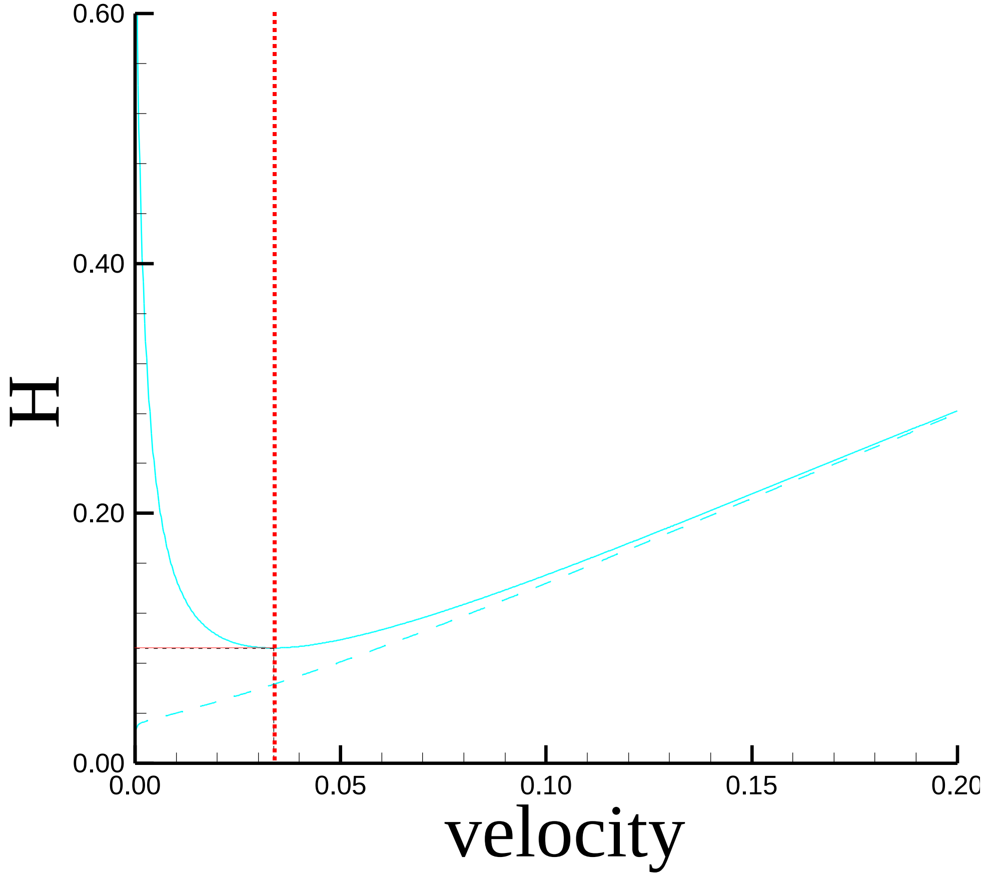


i=0

$$X(i) = \begin{cases} \dfrac{VX_o + \frac{D}{a}X(i-1)}{V + \frac{D}{a}} = X_o & i<0 \\[2ex] \dfrac{\left(V + \frac{D}{a}e^{-\Delta E/kT}\right)X_o}{V + \frac{D}{a} - \frac{D}{a}\frac{X_o}{X_s}\left(1 - e^{-\Delta E/kT}\right)} & i=0 \\[2ex] \dfrac{VX_o + \frac{D}{a}X(0)}{V + \frac{D}{a} - \frac{D}{a}\frac{X_s - X(0)}{X_s}\left(1 - e^{-\Delta E/kT}\right)} & i=1 \end{cases}$$

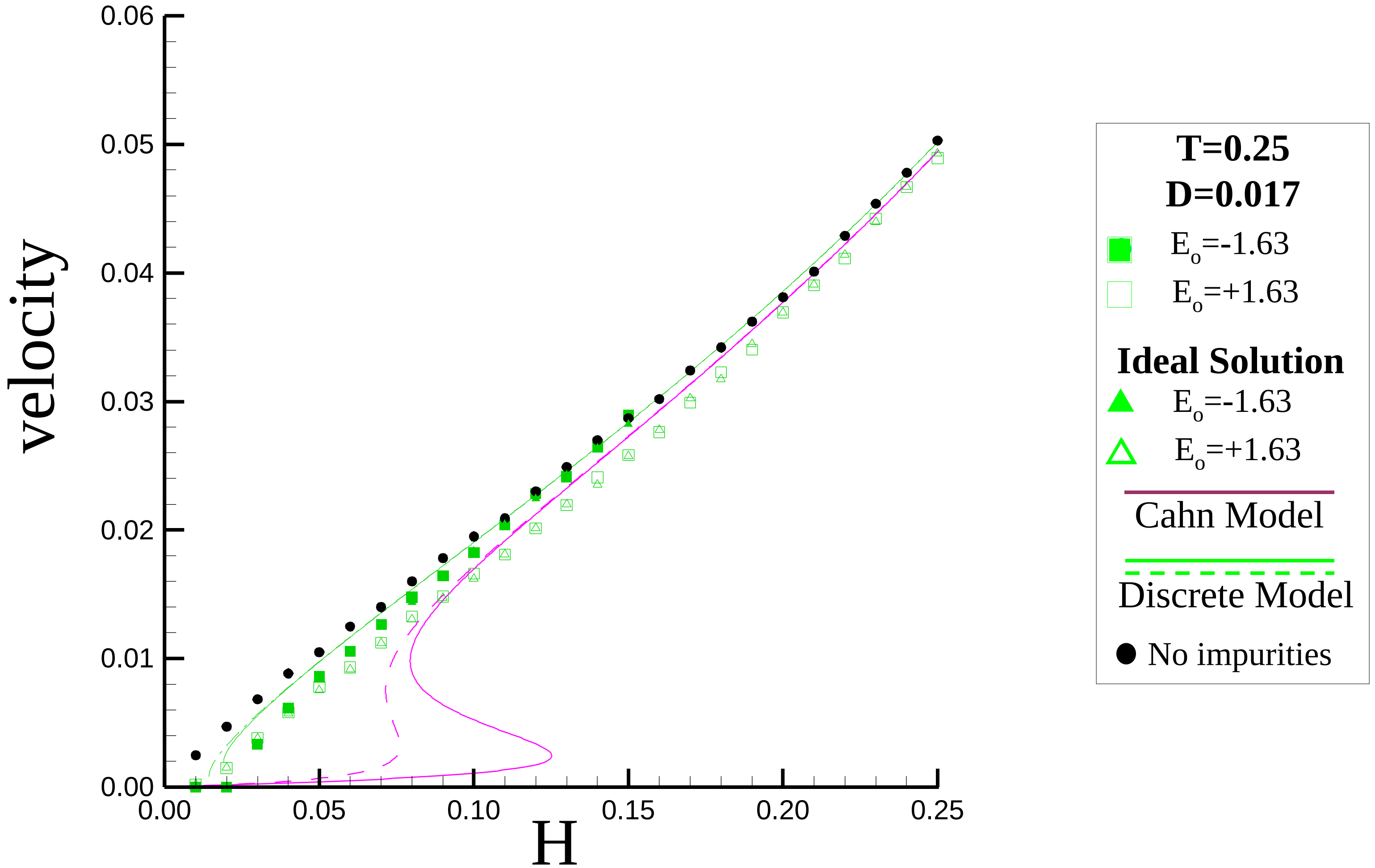
- Use concentration profile to determine drag force à la Cahn

Discrete Model Prediction



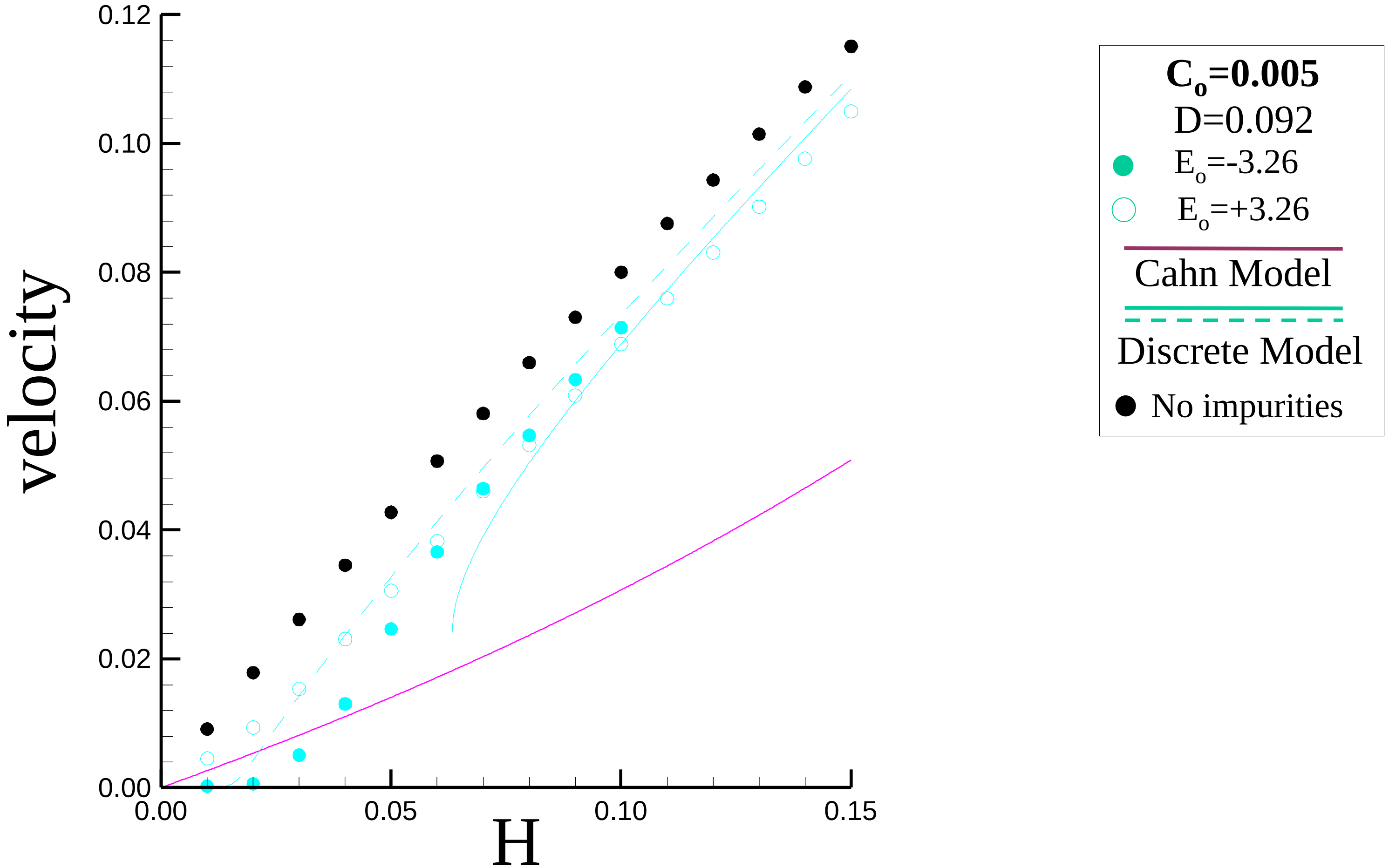
- Valid only at high velocity - abrupt transition at critical driving force
- As D$\rightarrow$0, critical driving force still exists and is finite

Boundary Velocity: lower T and D + ideal sol'n



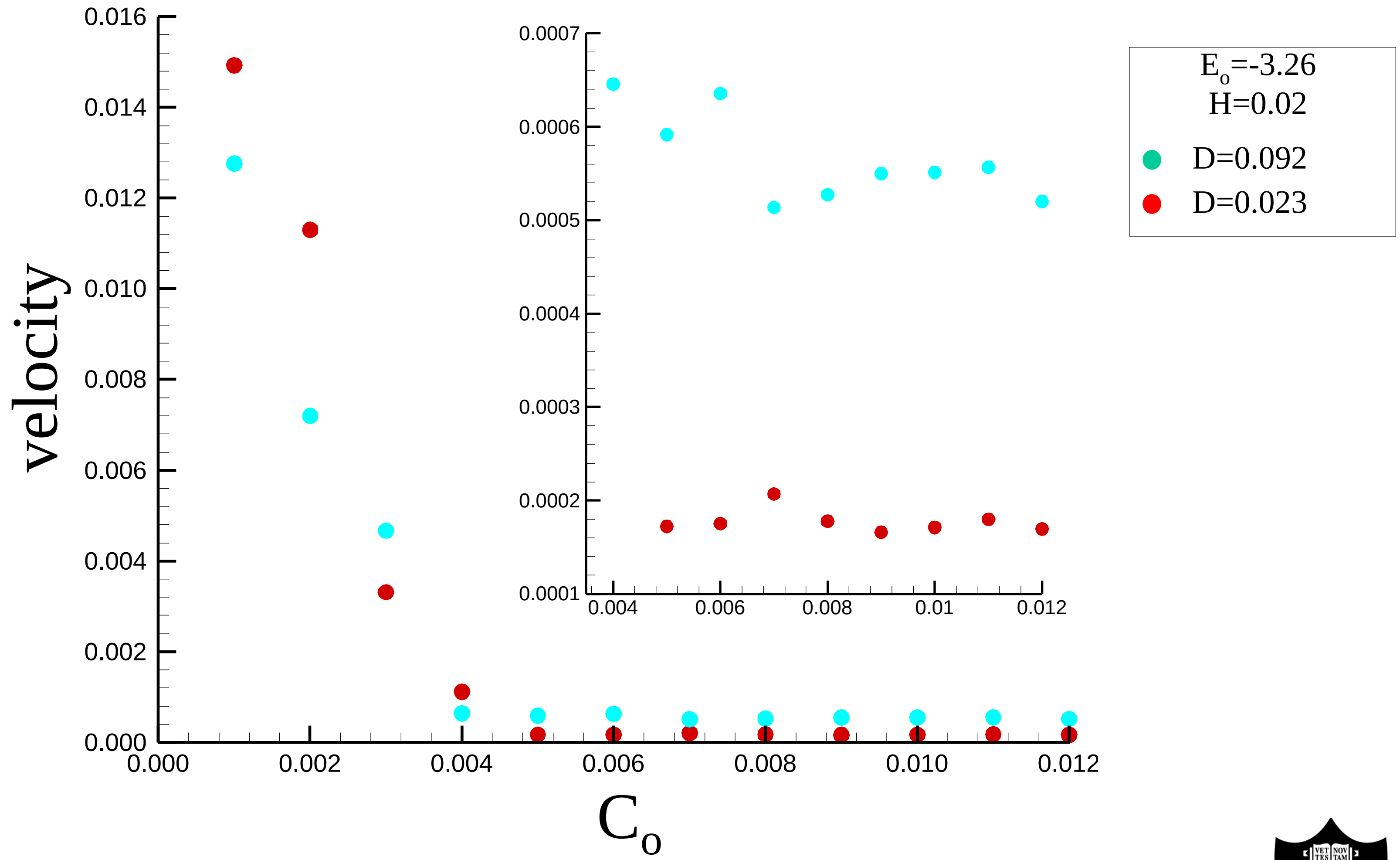
- Cahn model vastly overestimates transition, discrete model does well
- Discrepancy not due to assumptions about solution thermodynamics

Boundary Velocity: lower bulk concentration



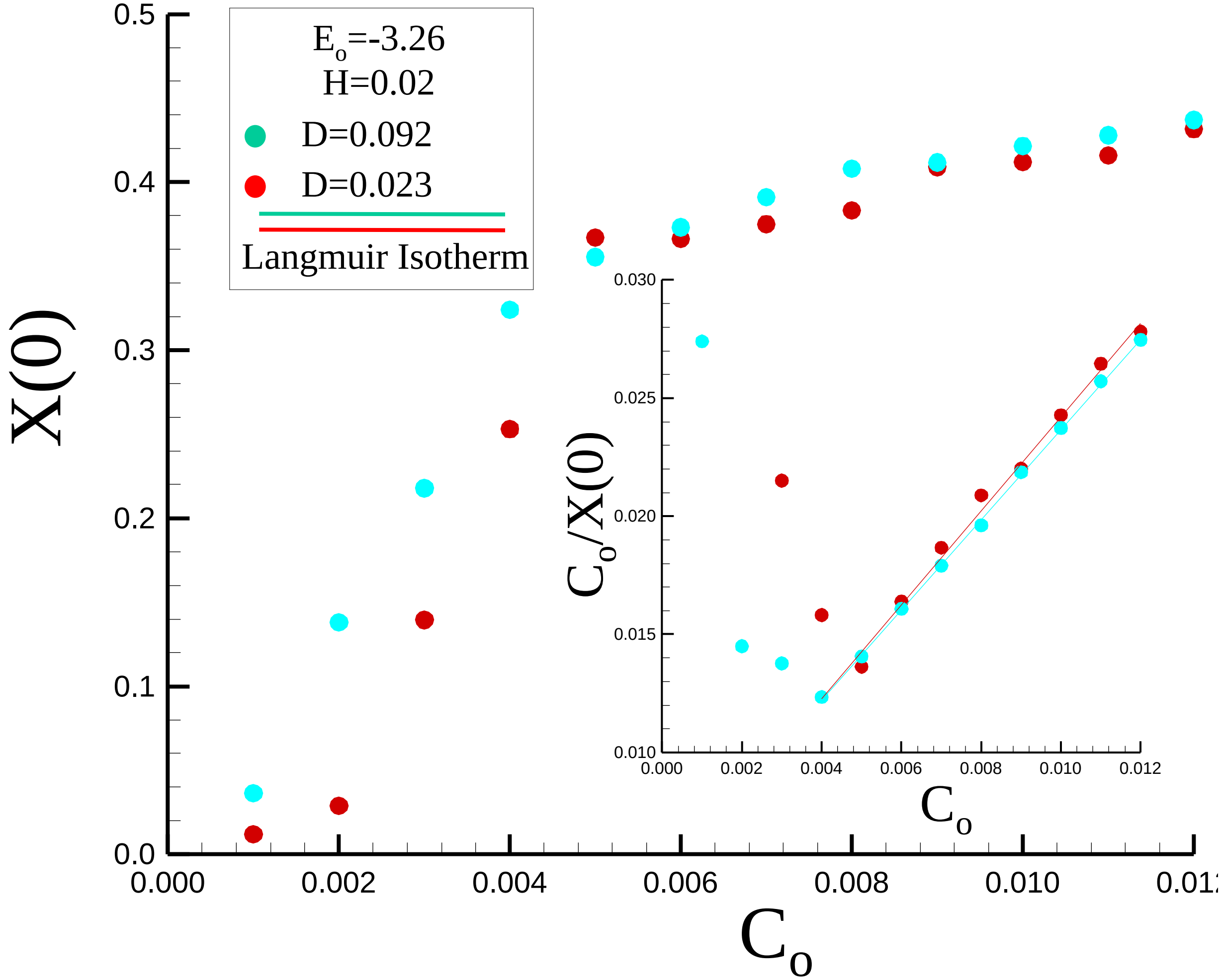
- Lower impurty concentration results in larger velocities; transition still exists
- Neither Cahn’s model not discrete model do well, but discrete does better

Boundary Velocity: effect of bulk concentration



- Velocity nearly impurity concentration independent when boundary is saturated
- Velocity transition with concentration parallels transition with driving force

Boundary Composition: effect of C_o



Langmuir isotherm:

$$X(0) = \frac{X_s b C_o}{1 + b C_o}$$

- Asymptotic boundary composition is X_s=0.5
- Langmuir isotherm works in regime where velocity is small

Kink Model w/impurities

Kink model where concentration is from discrete model & formation and migration energies are (strongly) modified by the impurities

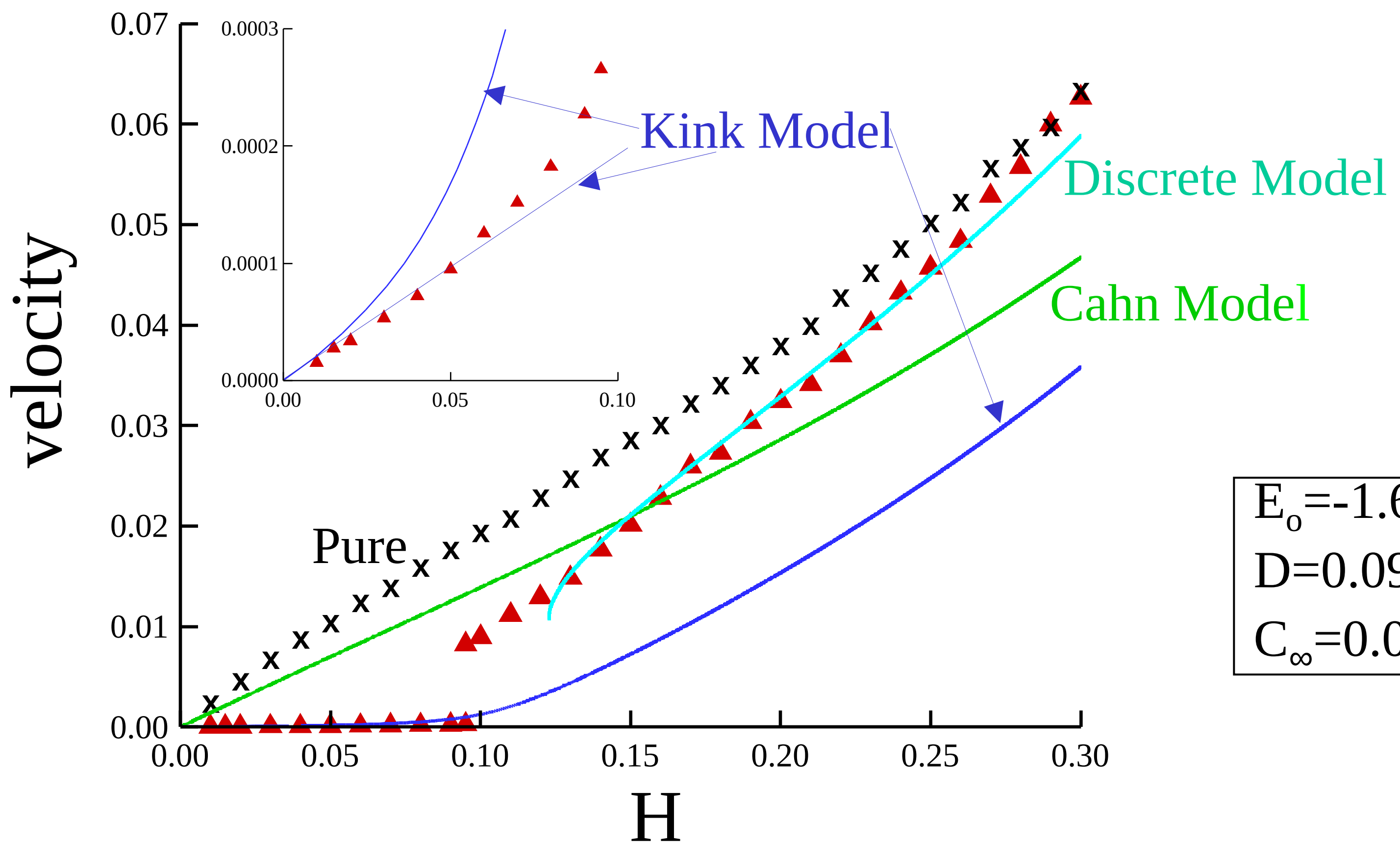
Boundary velocity w/o impurities: $V^0 = 4\sqrt{\frac{2}{3}}\, e^{-E_{dk}/2kT} \frac{D_k}{kT} F = M^0 F$

Boundary velocity w/impurities: $V = V^0 \dfrac{1 - X_0 + X_0 e^{E_0/2kT}}{X_0 \frac{4D_k}{D} + 1 - X_0}$

Boundary mobility: $M \approx M^0 \dfrac{D}{4D_k} e^{E_0/2kT}$ at low T

- **When bulk impurity concentration is large, $V \neq f(C_\infty)$**
- **Activation energy** $\Delta H = \frac{1}{2} E_{dk} + E_D - \frac{1}{2} E_0$

Kink Model/Simulation Comparison



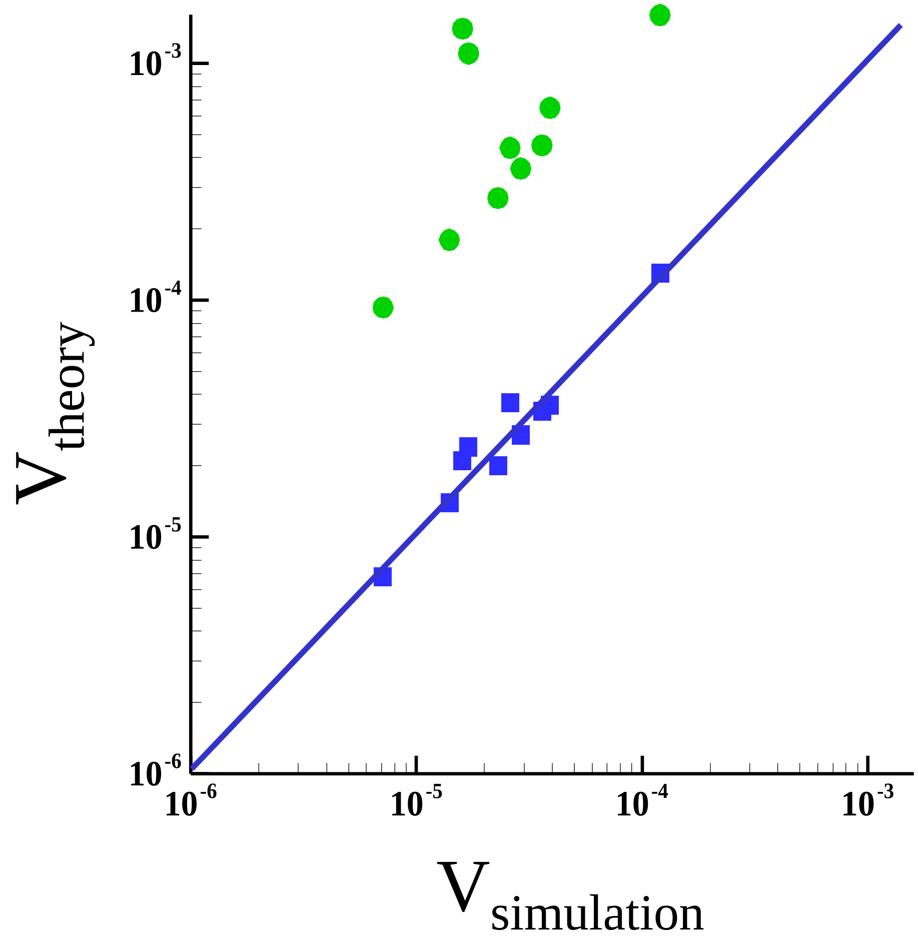
E_o=-1.63J

D=0.0916 a^2/MCS

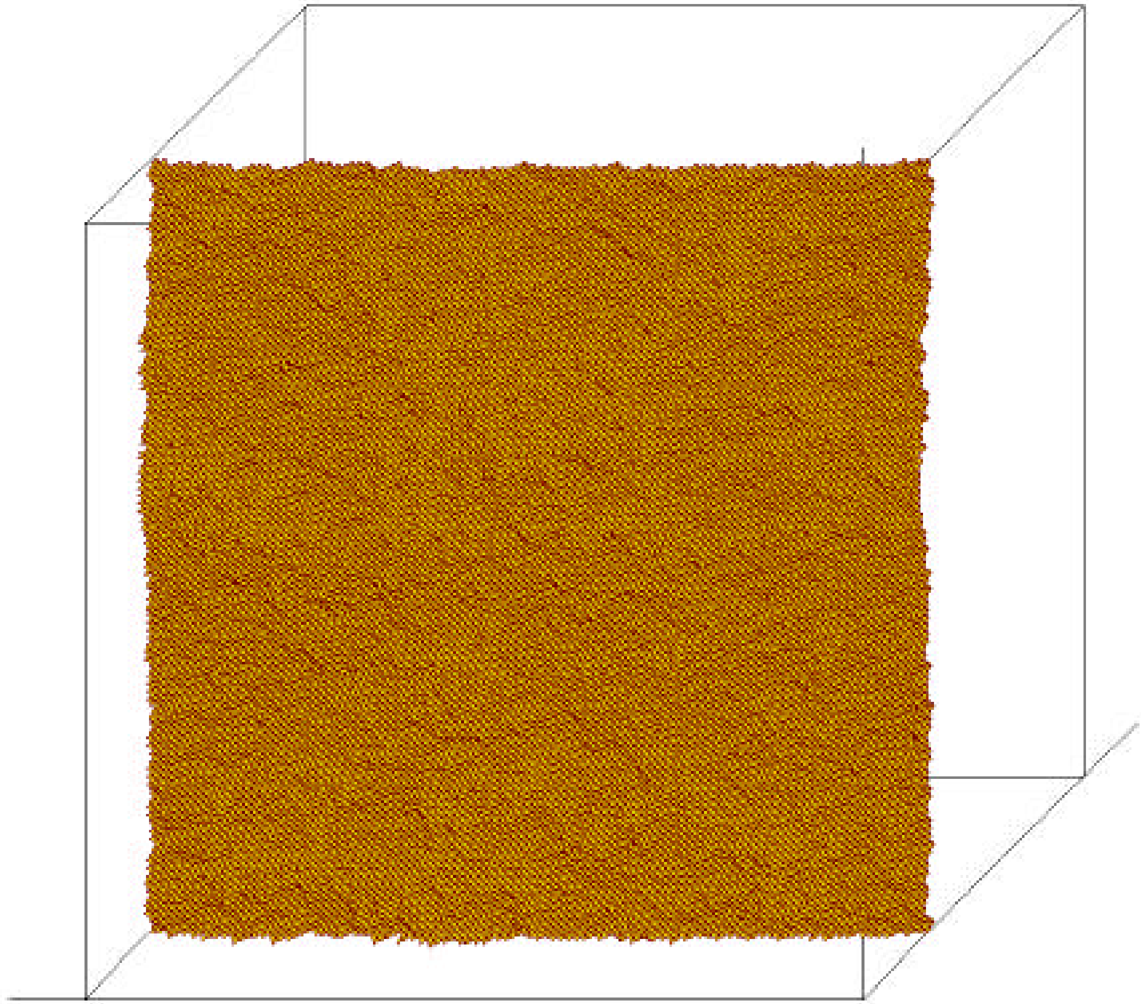
C_∞=0.01

- Discrete model works well at large driving forces, shows transition
- Kink model works for very small driving forces - mobility

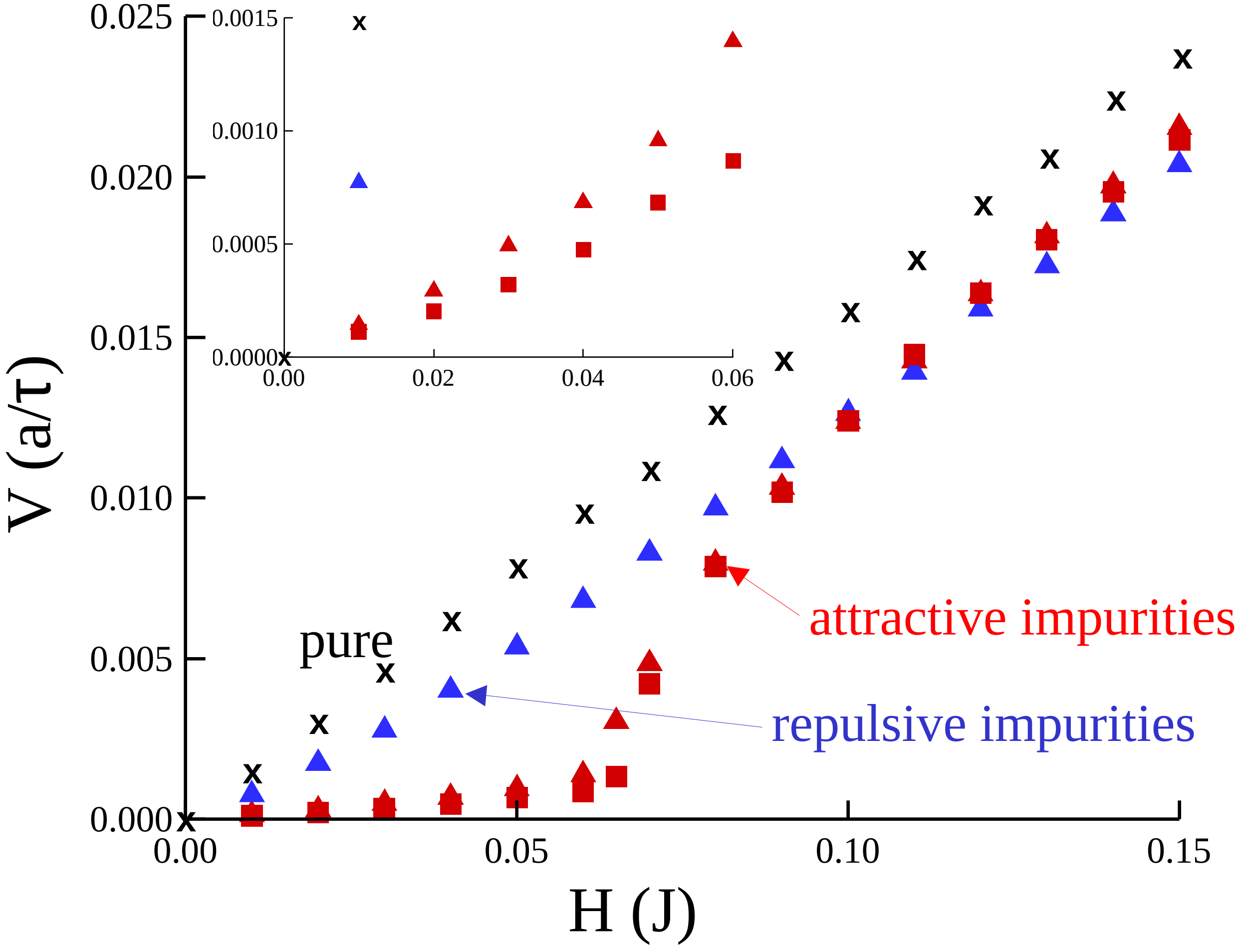
Kink Model/Simulation Comparison



3-d Simulation w/Diffusing Impurities



Velocity vs. Driving Force: 3-d



Omnium Gatherum: dislocations

- Straight dislocations w/elastic interactions between impurities & ⊥
- Saturated & Quasi-Static impurity regimes
- Diffuse Cottrell atmosphere **plus** condensed cloud
- Saturated regime - condensed cloud is near equilibrium & controls motion
- Multiple dislocations
  - some saturated, some not
  - ⊥ interact with other ⊥ **and** their impurity clouds
  - mobilities for dislocation dynamics
    - dressed-dressed
    - dressed-naked
    - naked-naked

Work with Y. Wang, C. Deo, J. Rickman, R. LeSar, V. Bulatov

Conclusions: boundaries

- Two migration regimes: impurity drag & quasi-static impurity
- Impurity drag: D $\Uparrow$, V $\Uparrow$, poor boundary is saturated
- Quasi-static impurity: D $\Uparrow$, V $\Downarrow$ and threshold $\Uparrow$
- Force-velocity relation is very sensitive to sign of interaction
- Boundary segments, where local concentration is small,

  preferentially escape - different segments in different regimes
- Continuum model: poor quantitative results, qualitative results in both
- Discreteness is key (purely continuum models cannot work)
- Boundary flexibility is important (finite line tension/ dimensionality)
- Site saturation can be important