Recent advances in Phase-Field Crystal modeling of heterogeneous crystal nucleation

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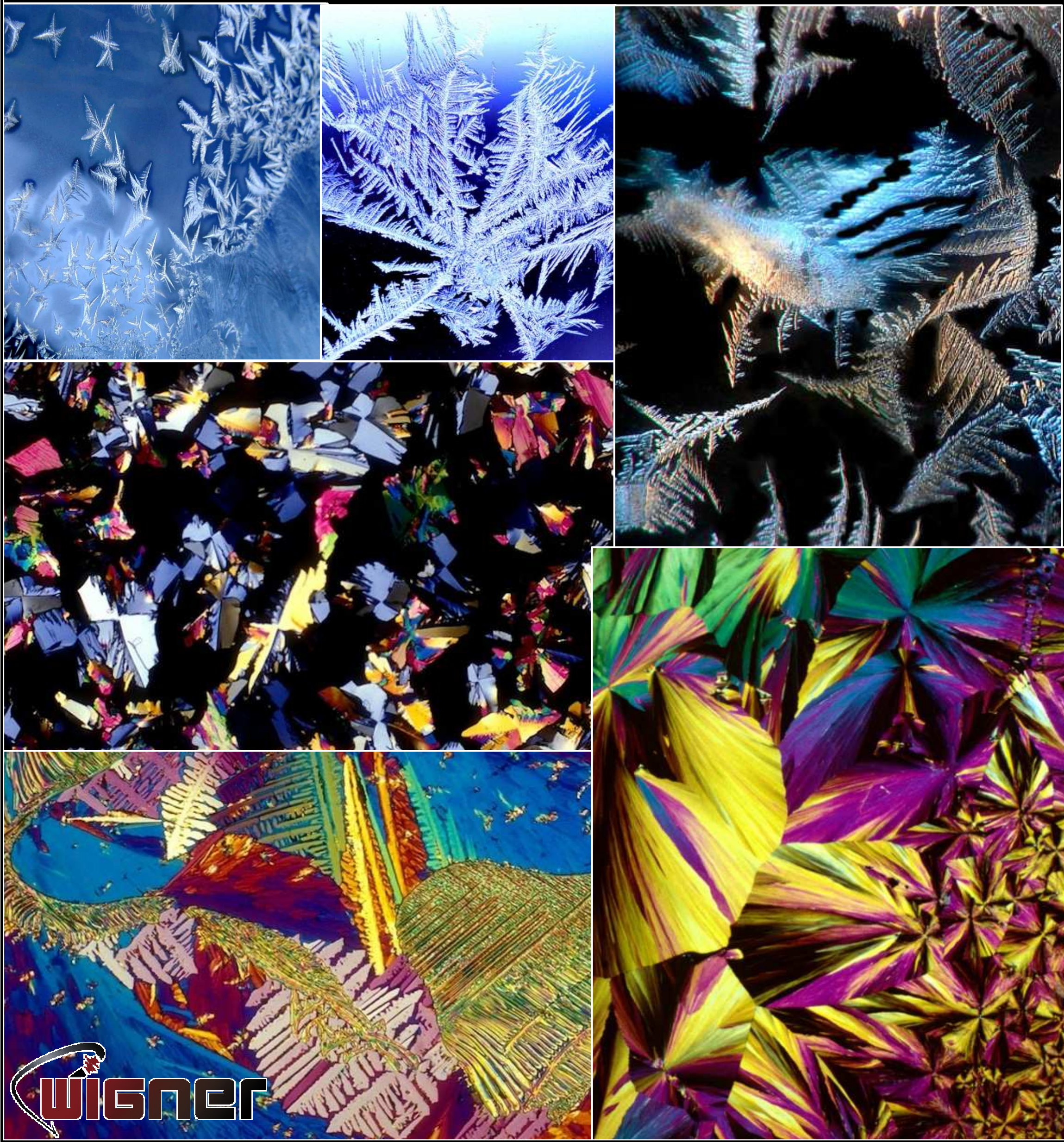
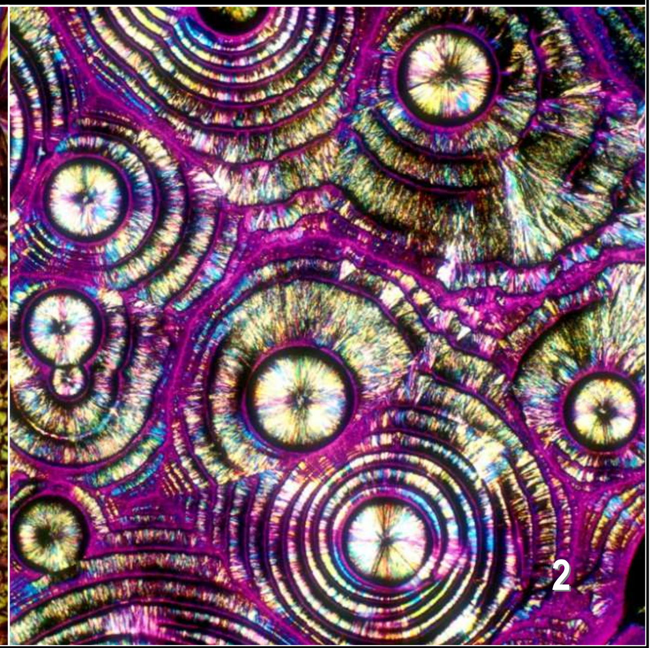
I. Introduction: Complex polycrystalline structures



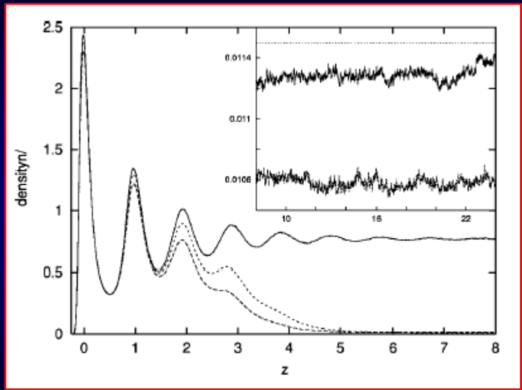
Complex patterns evolve due to the interplay of **nucleation** and **growth**.

Usually **heterogeneous nucleation**, during which crystallization is assisted by foreign walls or particles



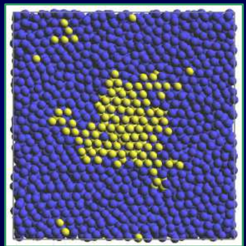
MD/MC Results:

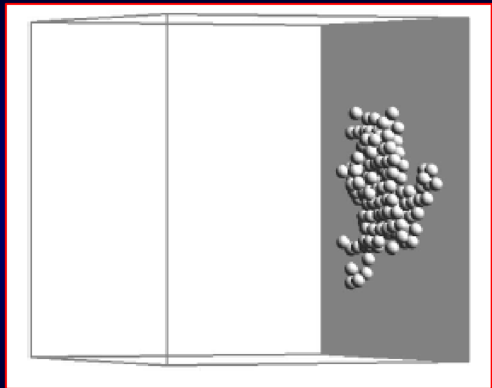
(a) Unstructured walls cause liquid ordering:



(e.g.: Toxwaerd 2002)

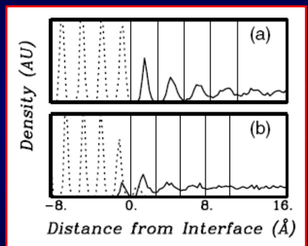
(b) Unstructured wall: HS (111) nearly wets it

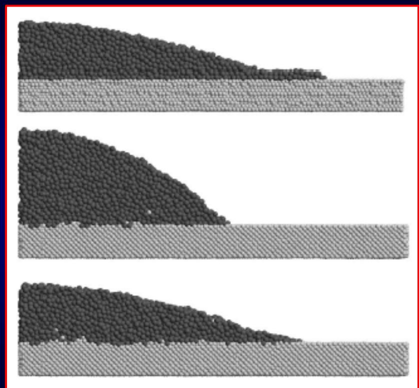




(Auer & Frenkel, PRL 2003)

(c) Liquid ordering at cryst. wall vs orientation:





(Webb & al., PRL 2003)

MD/MC:
the liquid orders at the substrate-liquid interface, which may either help or suppress crystallization depending on the closeness of the ordered liquid structure to that of the crystalline phase.

II. The Phase-Field Crystal Approach: a Simple Dynamical Density Functional Theory

(K. R. Elder *et al.*, PRL, 2002)

The Phase-Field Crystal Model (K.R. Elder et al. PRL 2002)

Classical density functional theory (RY: The free energy is Taylor expanded)

$$\frac{\mathcal{F}}{k_B T} = \int d\vec{r}[\rho(\vec{r})\ln(\rho(\vec{r})/\rho_\ell) - \delta\rho(\vec{r})] - \frac{1}{2}\int d\vec{r}\, d\vec{r}'\, \delta\rho(\vec{r}) C_2(\vec{r},\vec{r}')\, \delta\rho(\vec{r}') + \cdots ,$$

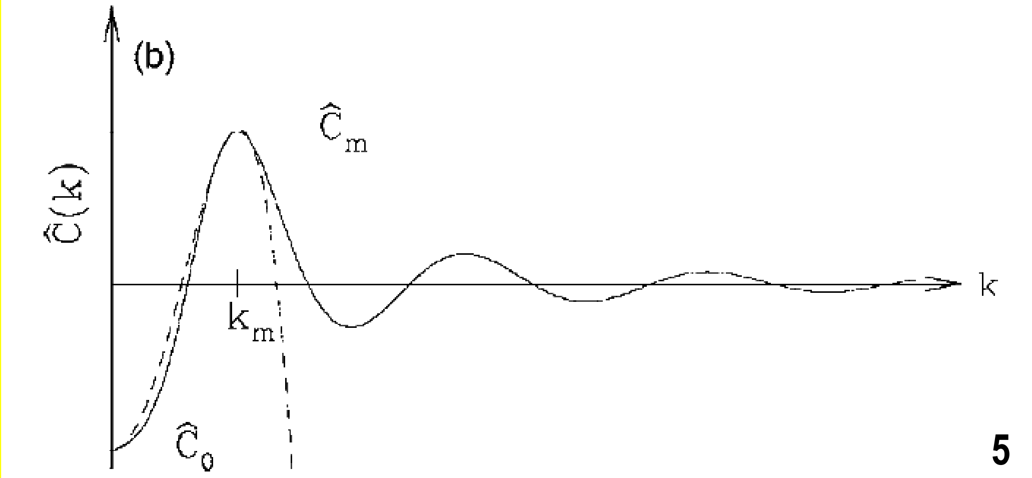
Reference: homogeneous liquid (ℓ)
ρ : time-averaged particle density (number density)
$\delta\rho = \rho - \rho_\ell$
C_2: two-particle direct correlation function: $C_2(k) = 1 - 1/S(k)$

PFC: The two-particle dir. correlation function is Taylor expanded up to 4th order in Fourier space
Physics: in the 3 exp. coeffs. related to the compressibility, bulk modulus and lattice const.

Free energy functional:

Brazovskii/Swift-Hohenberg form:

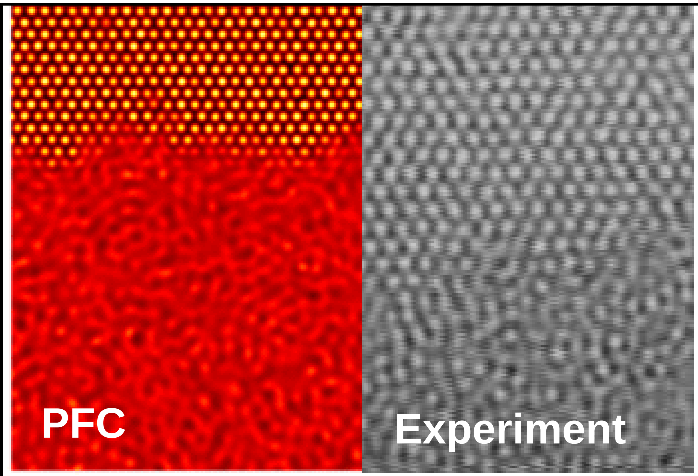
$$\Delta\tilde{F} = \int d\tilde{\mathbf{r}} \left\{ \frac{\psi}{2}\left[r + (1+\tilde{\nabla}^2)^2\right]\psi + \frac{\psi^4}{4} \right\}$$



Euler-Lagrange eq. (ELE)
(extremes of free energy)

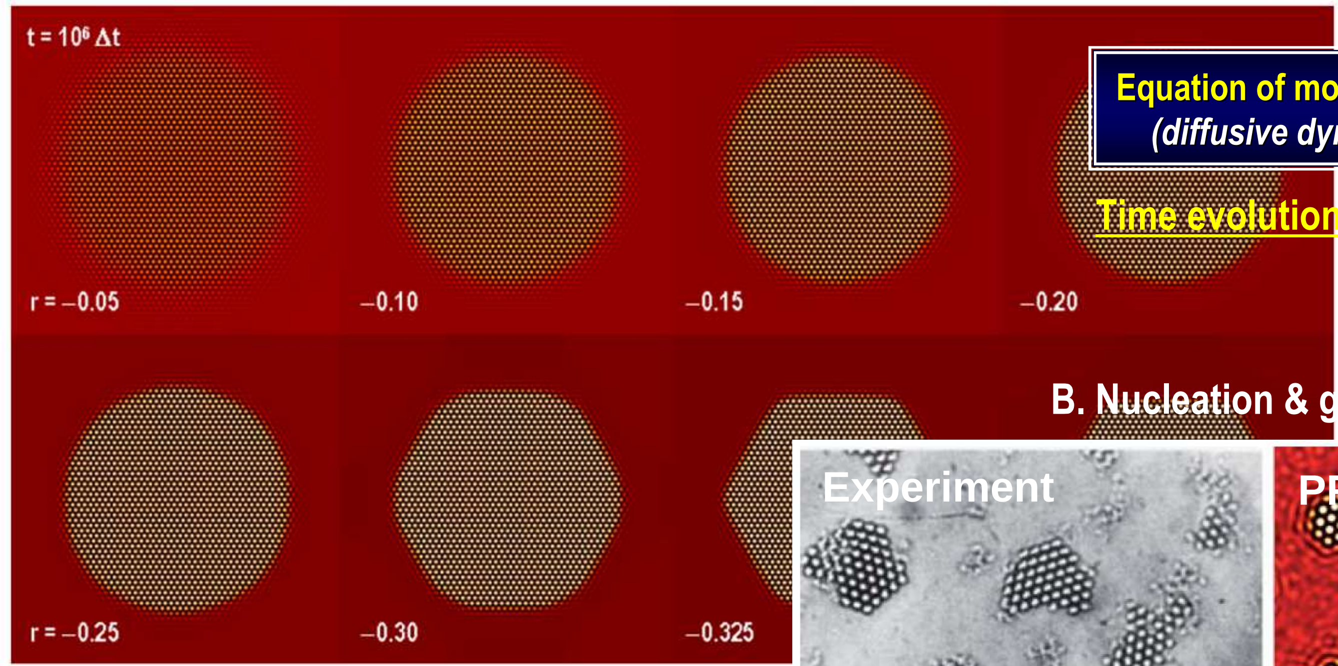
$$\frac{\delta \Delta \tilde{F}}{\delta \psi} = \left.\frac{\delta \Delta \tilde{F}}{\delta \psi}\right|_{\psi_0}$$

Equilibrium properties:
- phase diagram
- interface free energies
- nucleation barrier, etc.



A. Crystal-liquid interface

Equilibrium shapes. Parameter *r* regulates anisotropy.

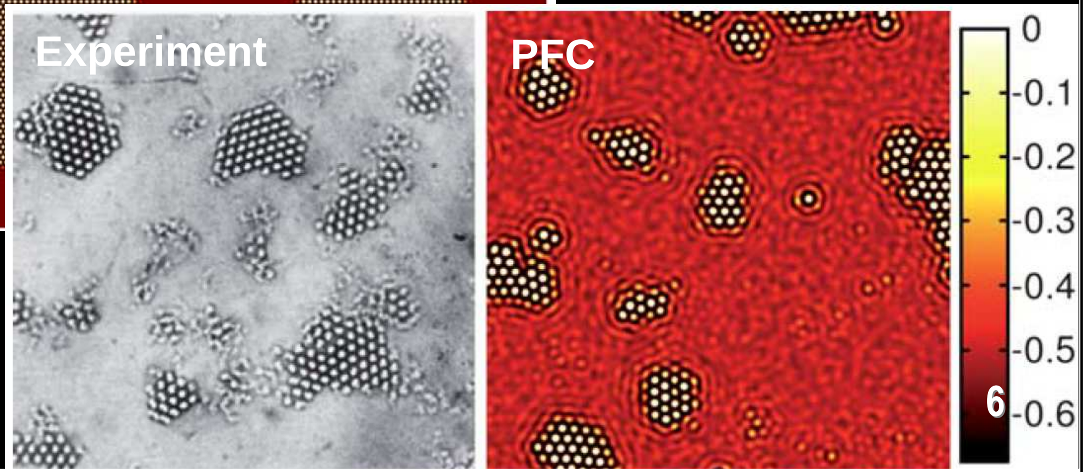


Equation of motion (EOM):
(diffusive dynamics - colloids)

Time evolution:

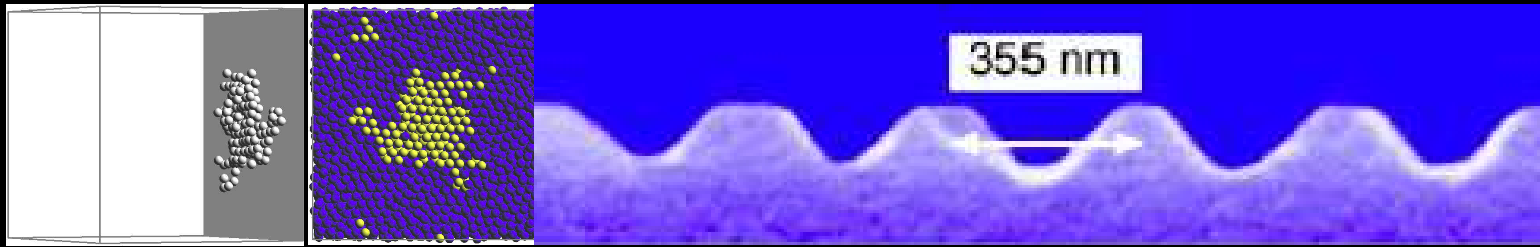
$$\frac{\partial \psi}{\partial \tilde{t}} = \tilde{\nabla}\left\{\tilde{\nabla}\frac{\delta \Delta \tilde{F}}{\delta \psi} + \zeta\right\}$$

B. Nucleation & growth in colloids

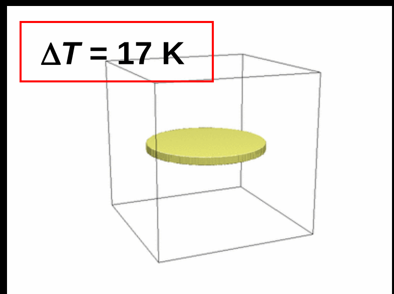


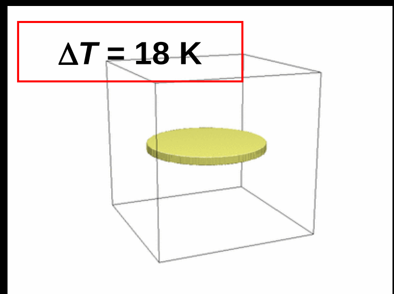
III. PFC Results for Heterogeneous Nucleation

A. Crystallization induced by flat & modulated surfaces?



B. Particle-induced freezing?



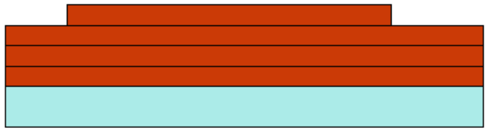


A. Crystallization on flat/modulated surfaces in 2D

A.1: Crystallization on flat walls:

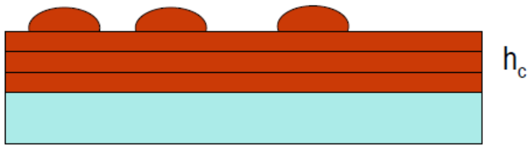
Three Growth Modes in Heteroepitaxy (A/B)
(Bauer, 1958)

(a) 2D or layer-by-layer
(Frank - Van der Merwe)



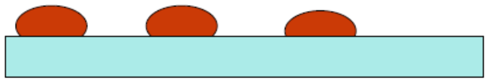
$\Delta\gamma = \gamma_o + \gamma_i - \gamma_s < 0$

(b) 2D followed by 3D islanding
(Stranski - Krastanov)



$\Delta\gamma \sim 0$

(c) 3D islanding
(Volmer - Weber)



$\Delta\gamma > 0$

γ_0 – free energy of crystal – liquid interface
γ_i – free energy of crystal – substrate interface
γ_s – free energy of substrate – liquid interface

Substrate in PFC:

Extra term added to free energy density:

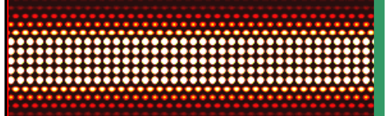
$$f_{PFC} + V(\underline{r})\,\psi(\underline{r})$$

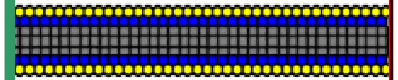
$$\text{Potential: } V(\mathbf{r}) = [V_0 - V_1 S(a_s, \mathbf{r})]\,h(\mathbf{r})$$

V_0 and V_1 – constants
$S(a_s, \underline{r})$ – SM approximant
$h(\underline{r})$ – envelop function

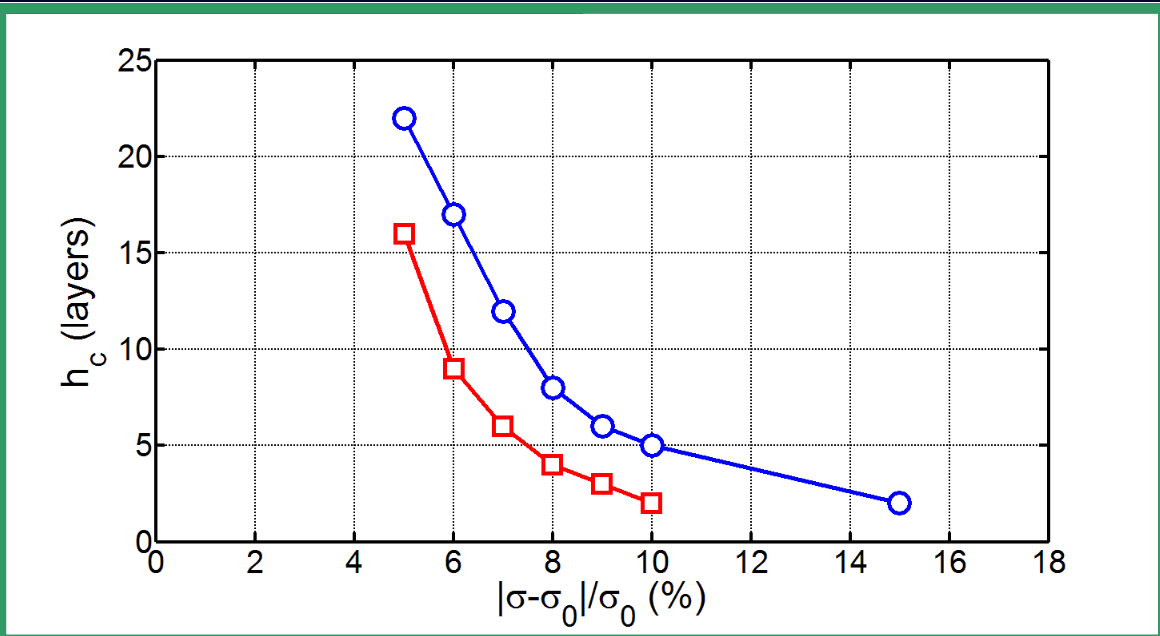
(a) Crystallization on flat walls in cooling (EOM): $\psi_0 = -0.25$; $\varepsilon = 0.1 - 0.1875$ (diffuse SL interface)

$a_s/\sigma = 1.00$



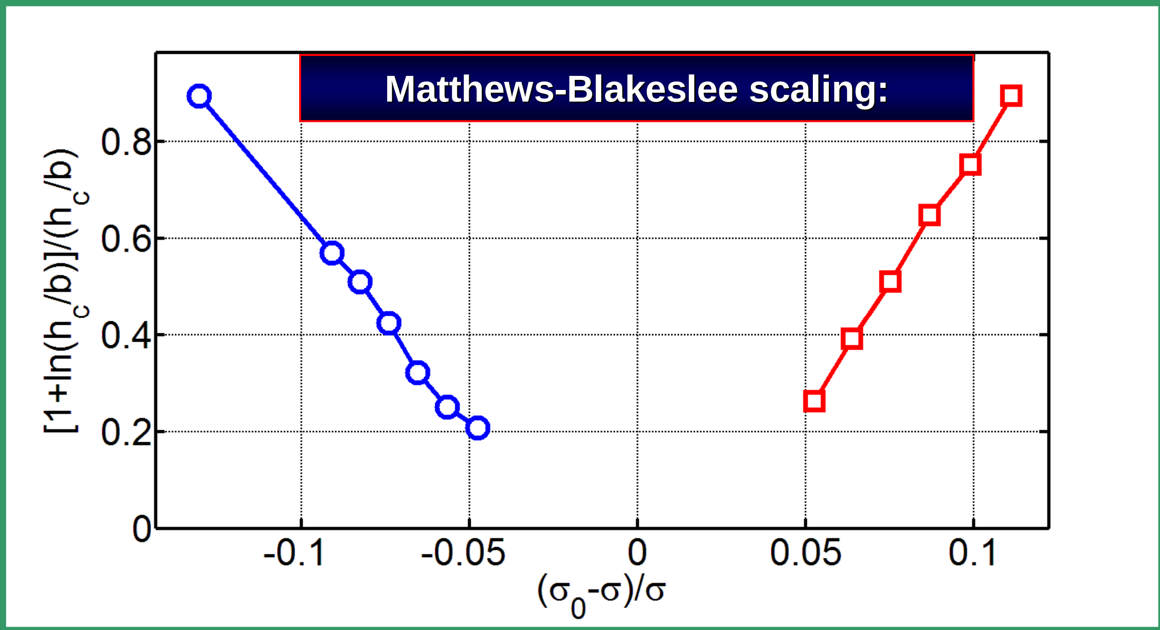


Layer-by-layer
(Frank – van der Meerwe)

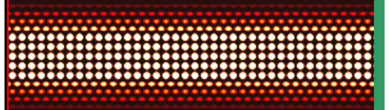


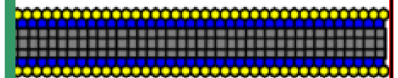
$\varepsilon \approx 0.1 - 0.2$
metal-like

ue; 6 : yellow; 7 : red



$a_s/\sigma = 1.07$

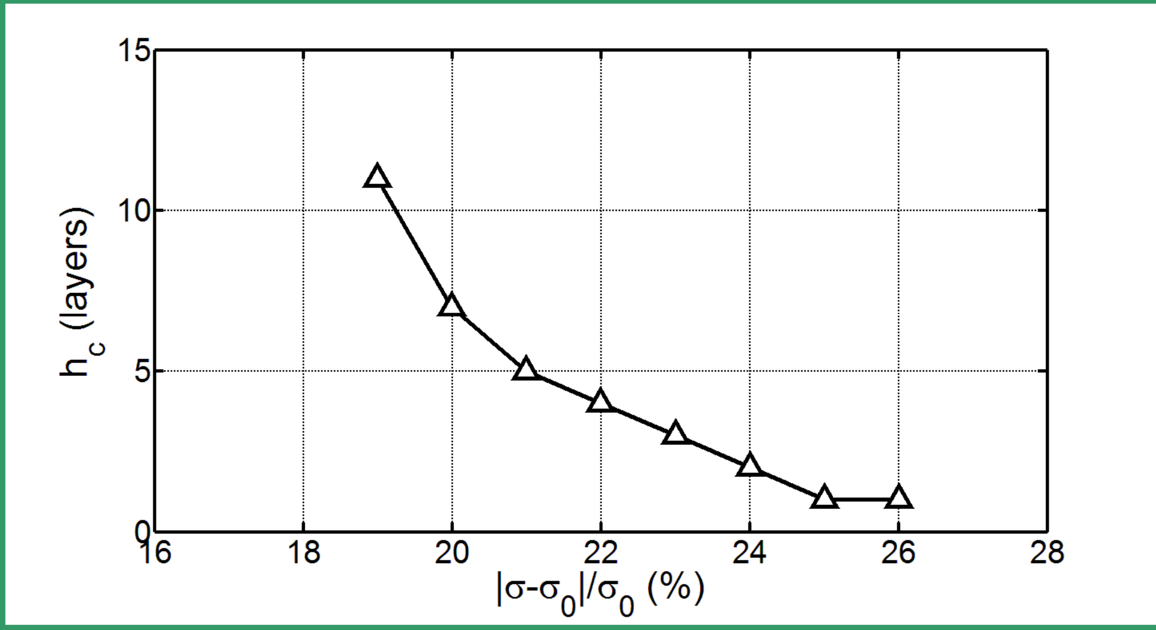




Layer-by-layer follov
(Stranski-Krastanov, Asarc

(b) Crystallization on flat walls in cooling (EOM): $\psi_0 = -0.5$; $\varepsilon = 0.4 - 0.75$ (faceted SL interface)

$a_s/\sigma = 1.00$

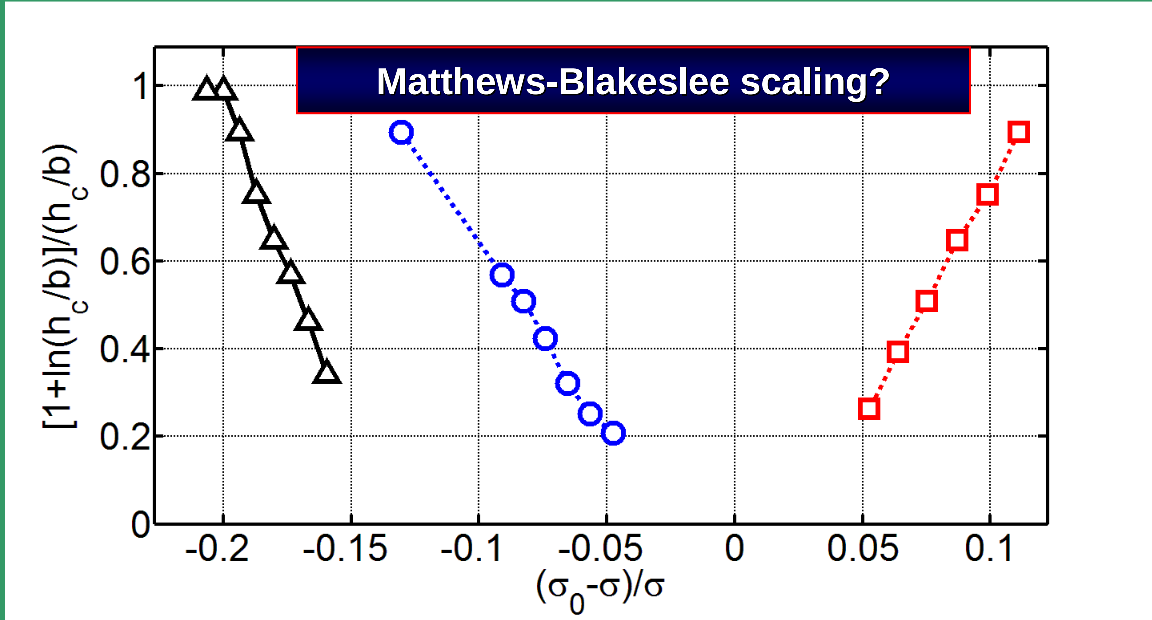


Layer-by-layer
(Frank – van der Meerwe)

$\varepsilon \approx 0.4 - 0.8$
covalent

ue; 6 : yellow; 7 : red

$a_s/\sigma = 1.19$



Layer-by-layer follov
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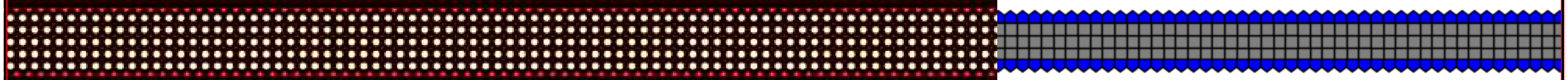
Crystallization on flat walls in cooling (EOM): $\psi_0 = -0.5$; $\varepsilon = 0.4 - 0.75$



$a_s/\sigma = 1.2$ EOM $\zeta = 0.0$

$a_s/\sigma = 1.2$ EOM $\zeta = 1.0$

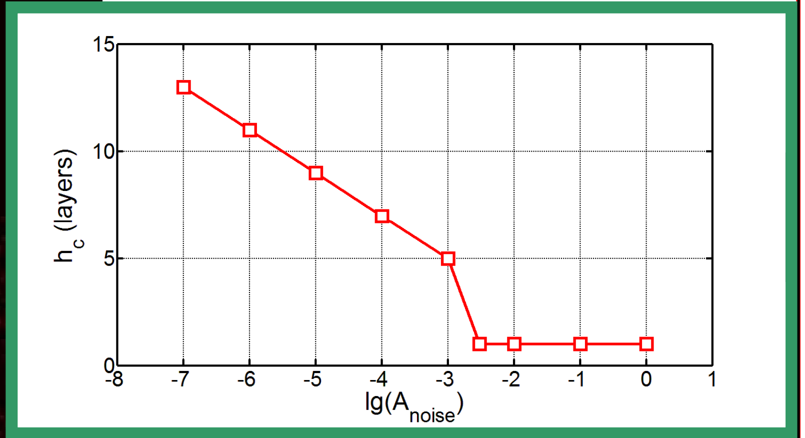
Observations:

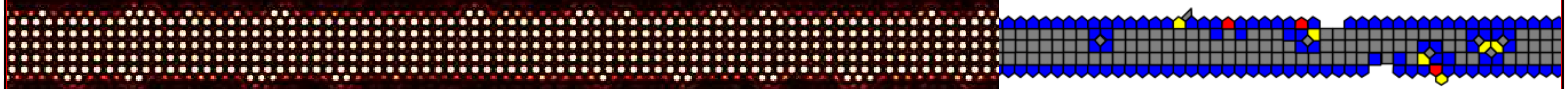
Without noise:

- First pseudomorphic solid forms;
- Beyond critical thickness (h_c) misfit dislocations form that release elastic strain energy.

With noise:

- Periodic defect structure in the first layer from the beginning



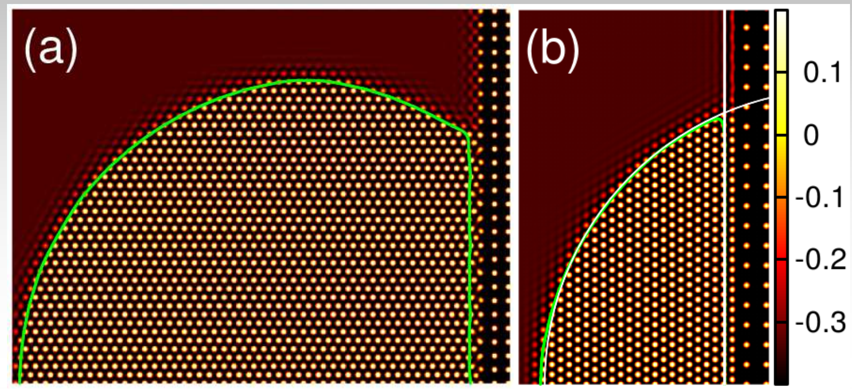


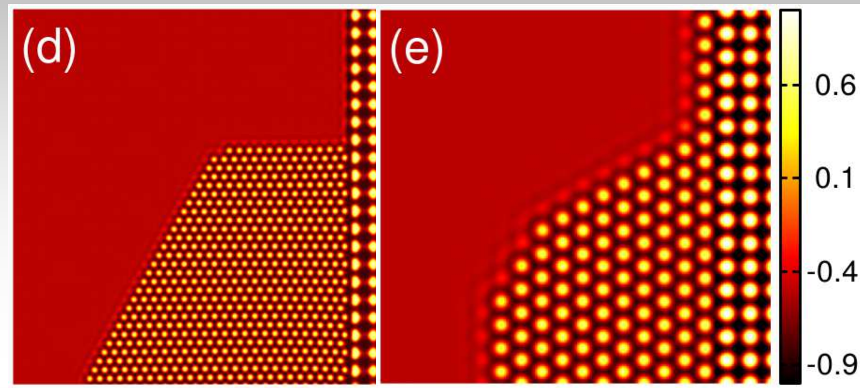
A.2: Island formation (heterogeneous nucleation) on flat interfaces (ELE): (Volmer-Weber)

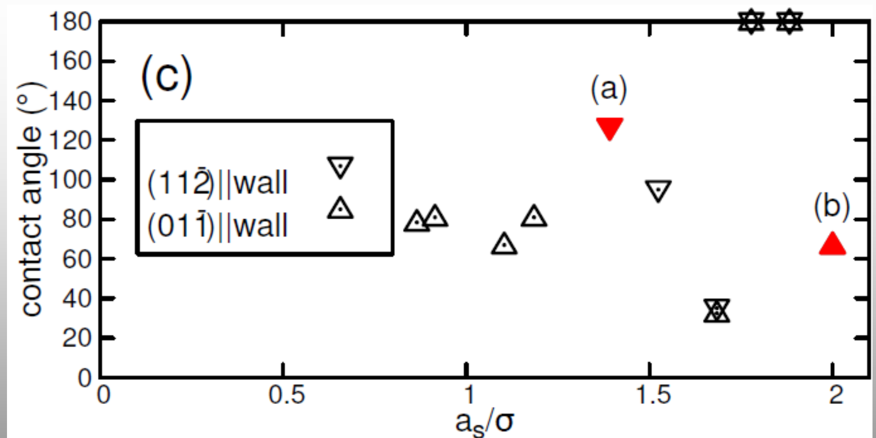
$$\text{Potential}: \quad V(\mathbf{r}) = \left[V_0 - V_1 S(a_s, \mathbf{r})\right] h(\mathbf{r})$$

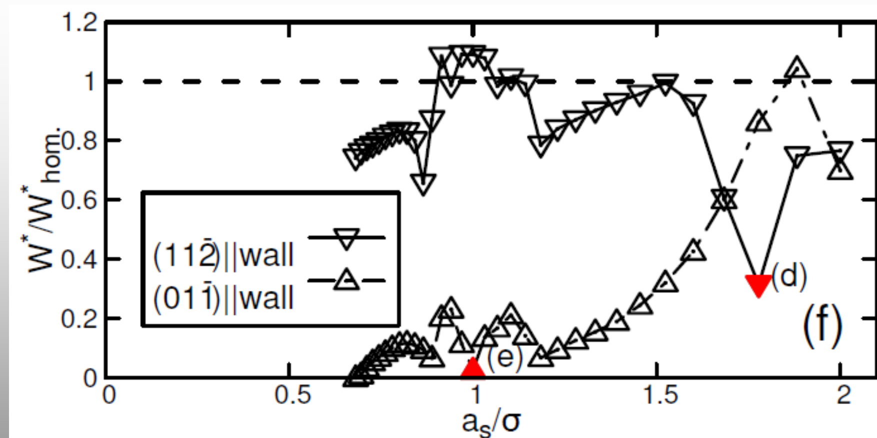
Nearly isotropic ($r = -0.25$) ; $\psi_0 = -0.341$, $V_0 = V_1 = 0.5$

Faceted ($r = -0.5$) ; $\psi_0 = -0.51415$, $V_0 = 0$, $V_1 = 0.65$







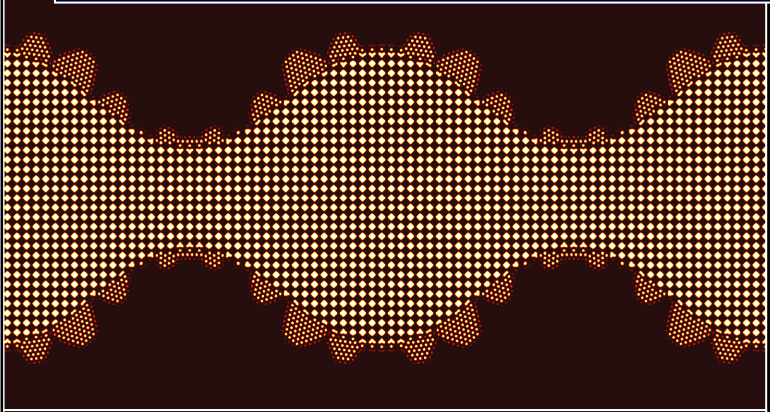


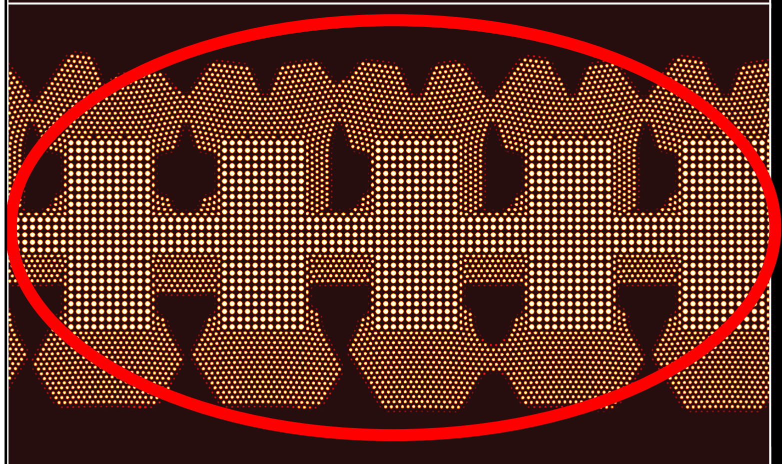
Tóth et al. PRL (2012).

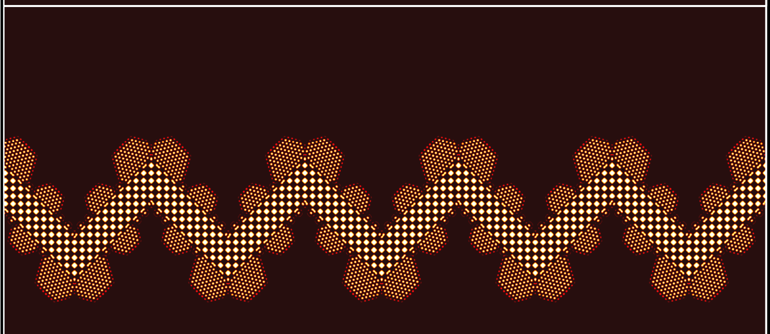
Contact angle (ϑ) and barrier height (W^*) are nonmonotonic functions of a_s

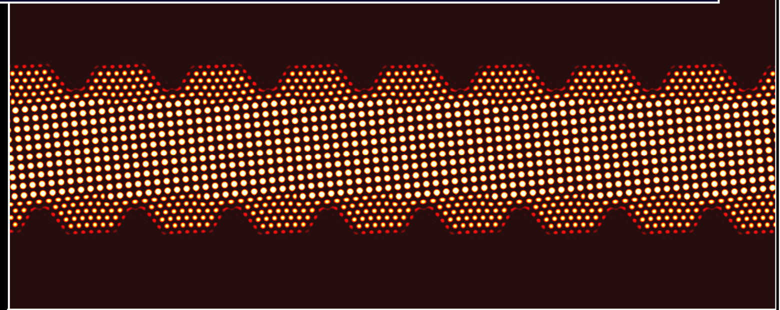
WIGNER

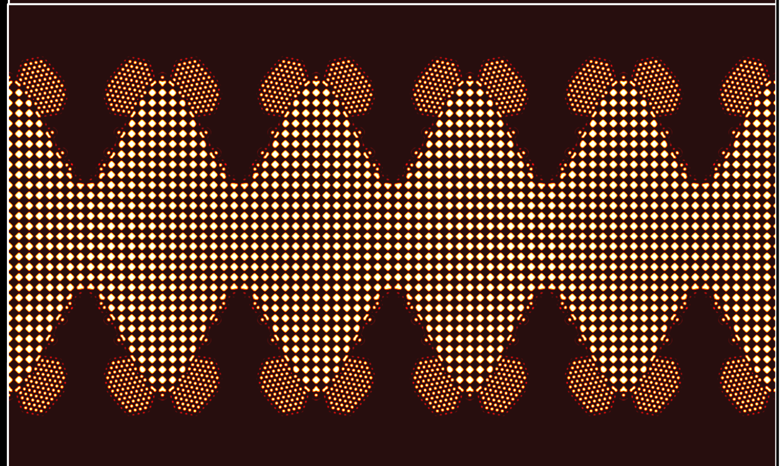
A.3: Heteroepitaxy on various substrate configurations: (a_s/σ = 1.2; ψ_0 = -0.5; ; ε = 0.4 – 0.75)

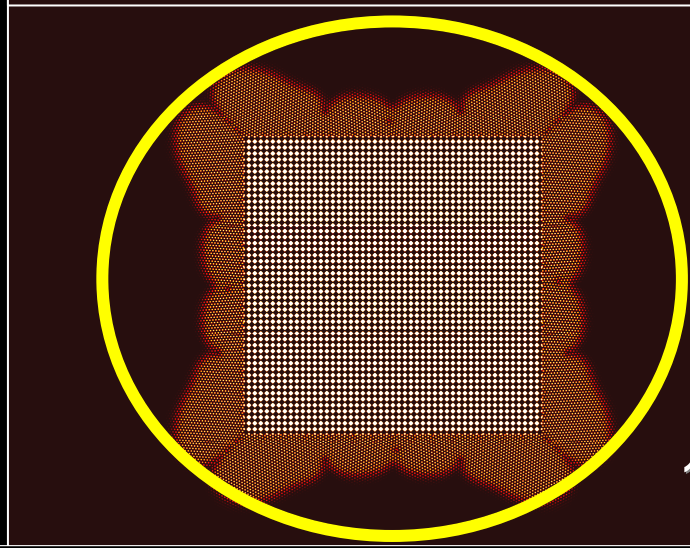












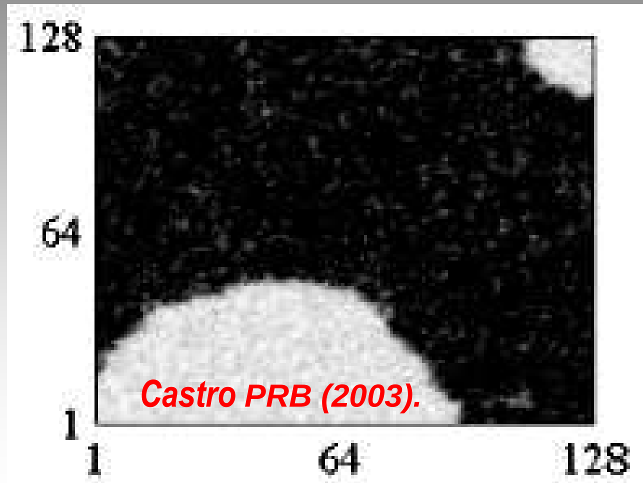
Various shapes:

- sinus & rectangular grooves,
- saw-tooth,
- atomic-scale steps,
- square,

etc.

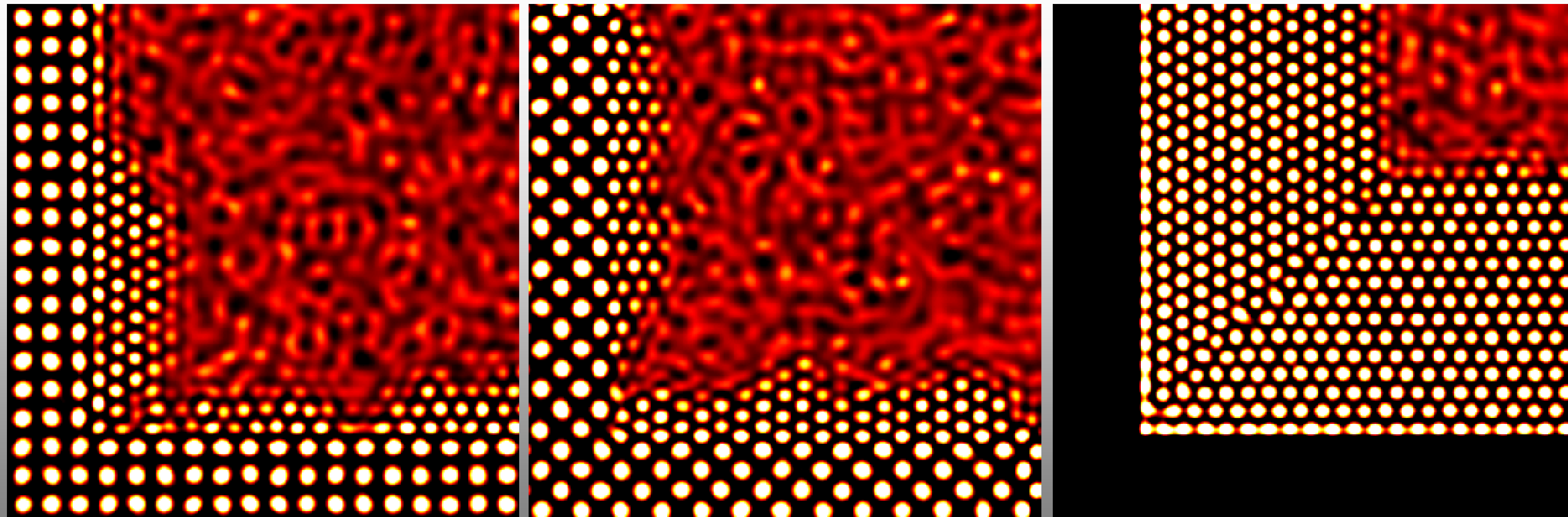
A.4: Heterogeneous nucleation in rectangular corner (EOM):

(a) Conventional PF & CNT: The corner is preferable.



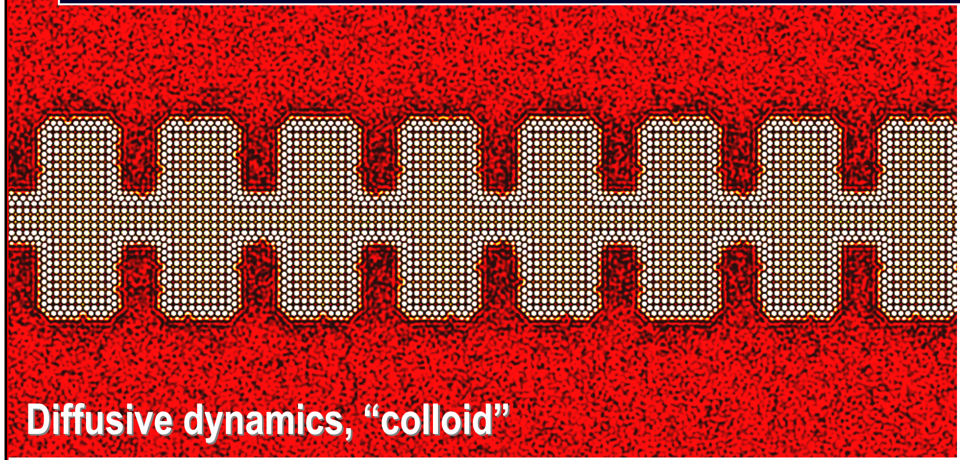
(b) PFC: This corner is NOT preferable!!!

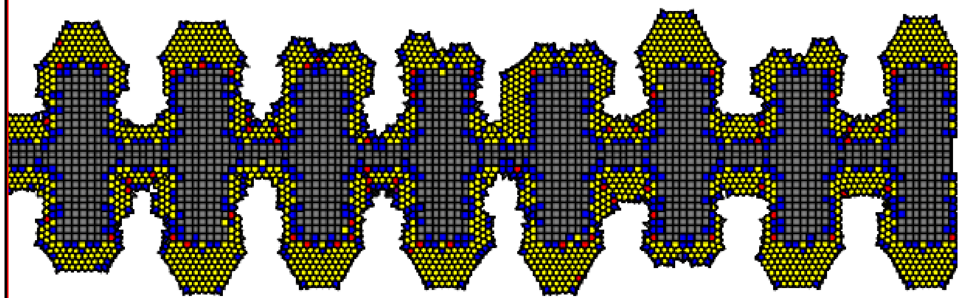
$r = -0.25$
$\psi_0 = -0.32$
$\alpha = 0.1$
$a_s/\sigma = 1.39$

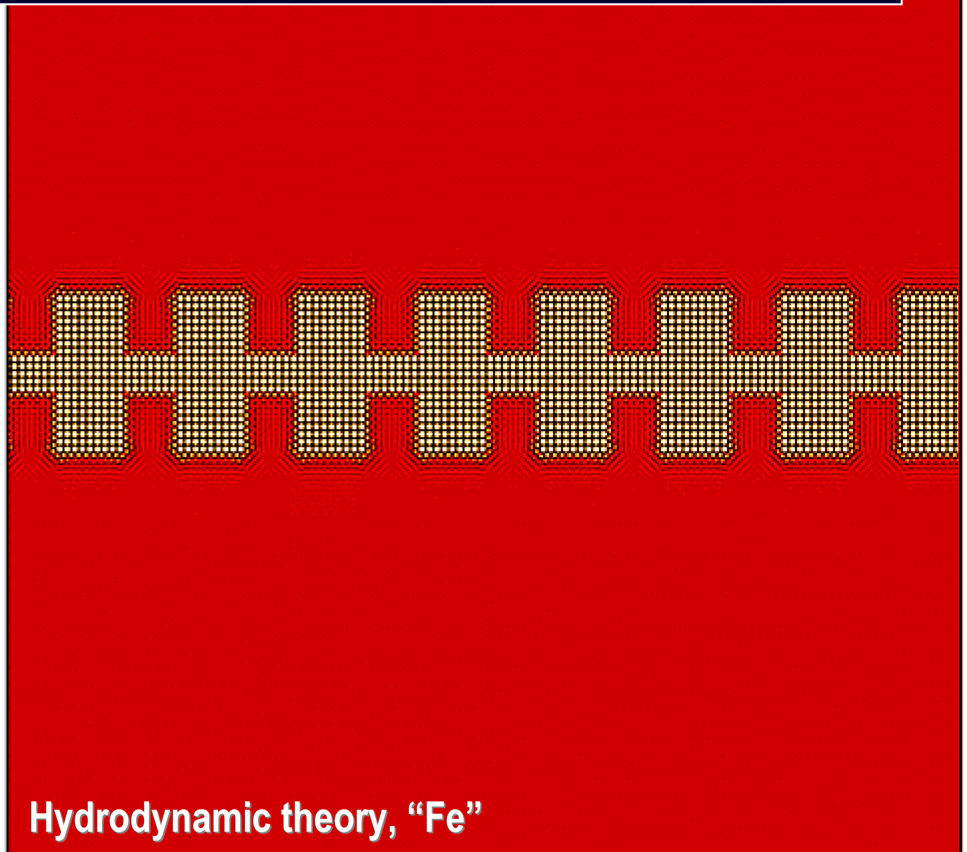


Gránásy et al. Philos. Mag. (2011).

A.5: Rectangular grooves: Isothermal freezing of “colloidal” and “metallic” liquids in PFC:







Observations:

I. Diffusive dynamics:

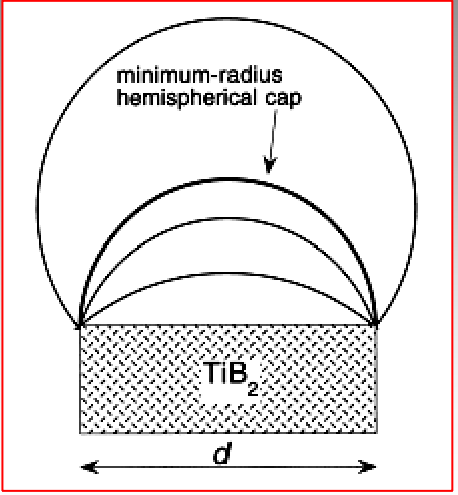
- Depletion zone
- Faceted crystals all the time

II. Hydrodynamic theory:

- No depletion zone
- Small anisotropy
- Capillary waves

wigner

B. Particle-induced freezing in 2D & 3D:

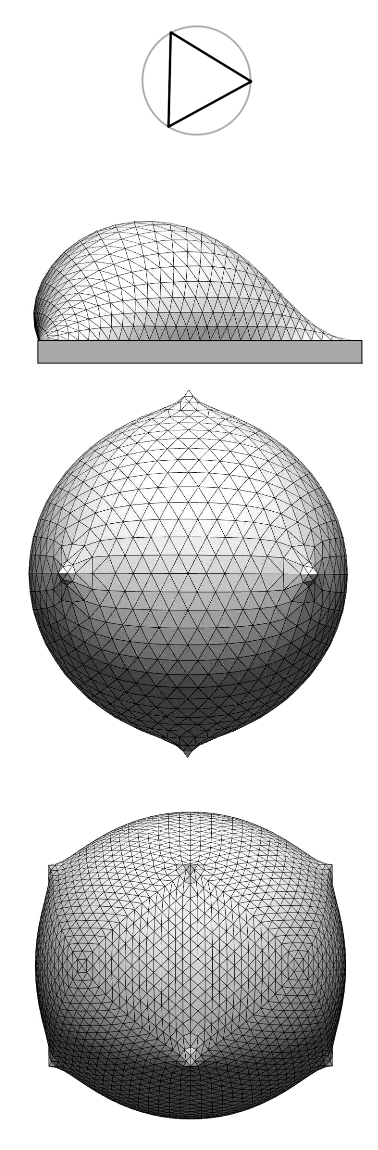


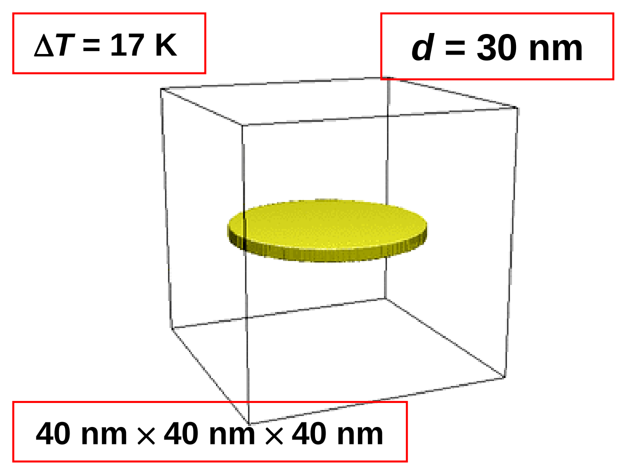
(Greer et al., Acta Mater., 2002)

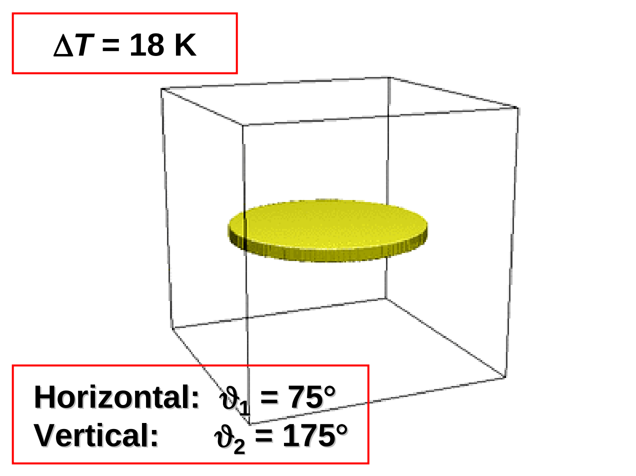
- Cylindrical particles ~ wet by the crystal on top/bottom, not on sides;
  (e.g., Al + Al-Ti-B inoculant → Ti_2B particles with $AlTi_3$ coating on {0001} faces different contact angles on different faces)
- Free growth for

$$\Delta T > \Delta T_c = \frac{4\gamma_{SL} T_m}{L d}$$

- PFT simulations → $\Delta T_c \propto 1/d$; $\Delta T_c <$ classical

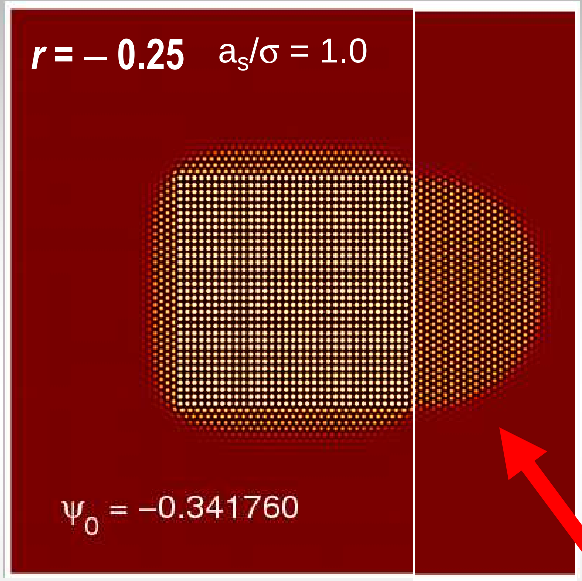


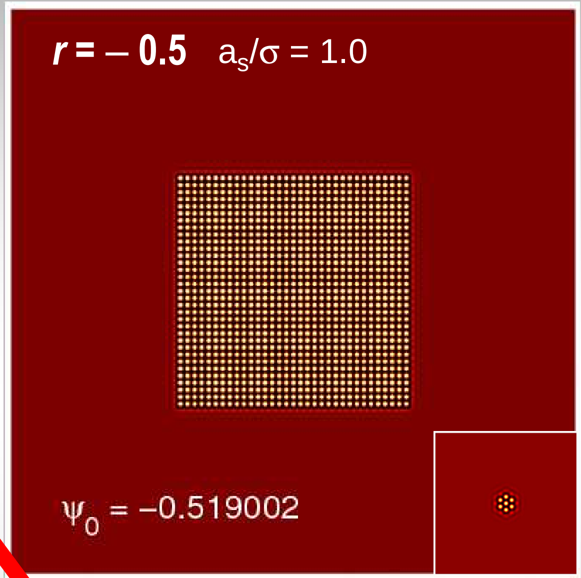




B.1 Free-growth limited mode of particle induced freezing in 2D (ELE)

EL solutions for increasing driving force:





Results:

- Small anisotropy: Greer's model OK
- Faceted: free-growth at a much larger driving force

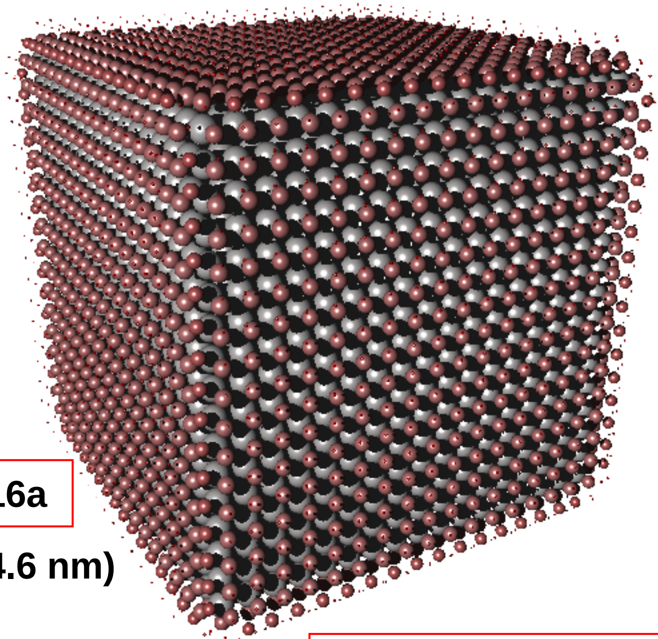
Tóth et al. PRL (2012)

Homogeneous nuclei at the critical driving force

B.2 Free-growth limited mode of particle induced freezing in 3D (ELE)

$r = -0.25$

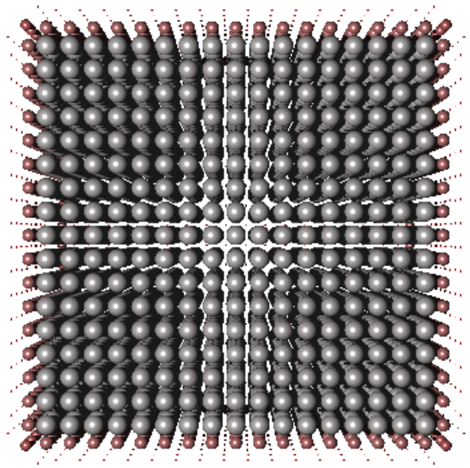
SC substrate
Cubic shape
$a_s/a_{BCC} = 1$



L = 16a

(L ~ 4.6 nm)

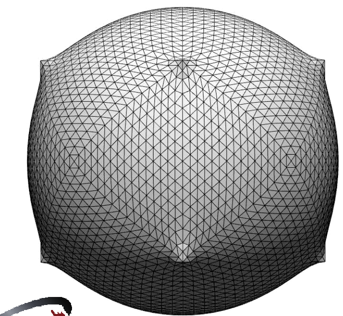
$\psi_0 = -0.3540$



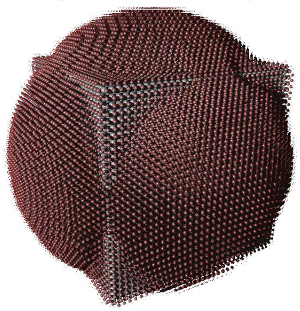
Tóth et al. PRL (2012)

$\psi_0 = -0.3540$

256 × 256 × 256 grid

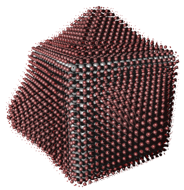


(L ~ 9.2 nm)



L = 32a

(L ~4 .6 nm)

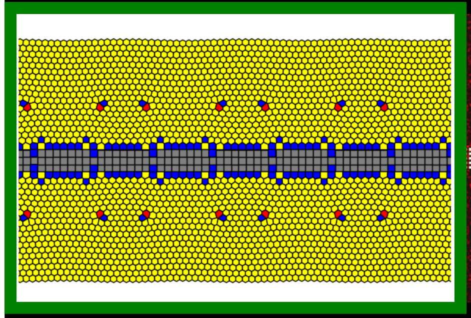


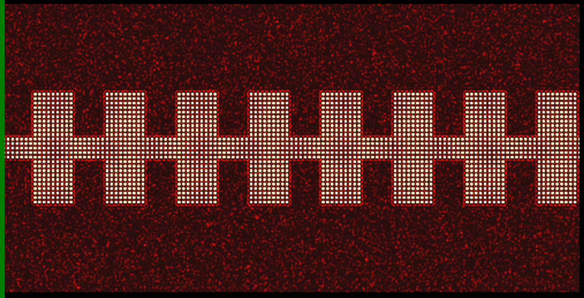
L = 16a

The critical shape preceding free growth depends on size!

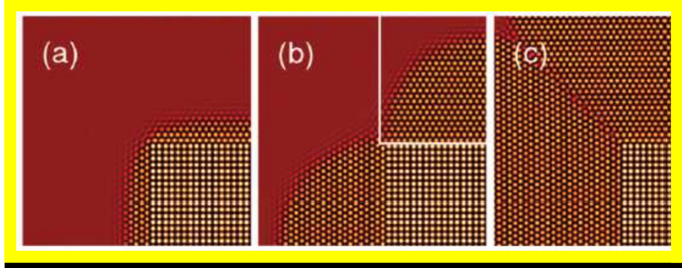
IV. Summary:

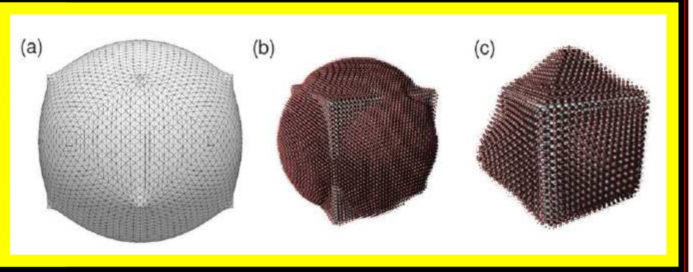
A. Nucleation on walls:
- Epitaxial growth for $a_s = \sigma$
- Surface spinodal for $a_s \neq \sigma$
- Three modes of heteroepitaxy
  (Asaro-Tiller-Grinfeld instability)





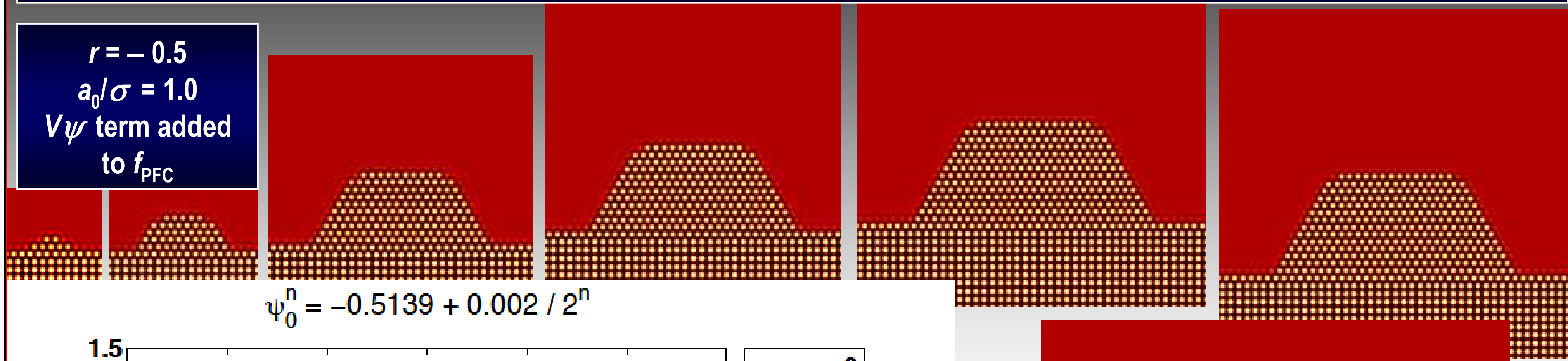
B. Particle induced freezing:
- Works for small ε
- Does not work for large ε
- Size dependent critical shape
- Non-monotonic dependence of barrier & contact angle on lattice mismatch

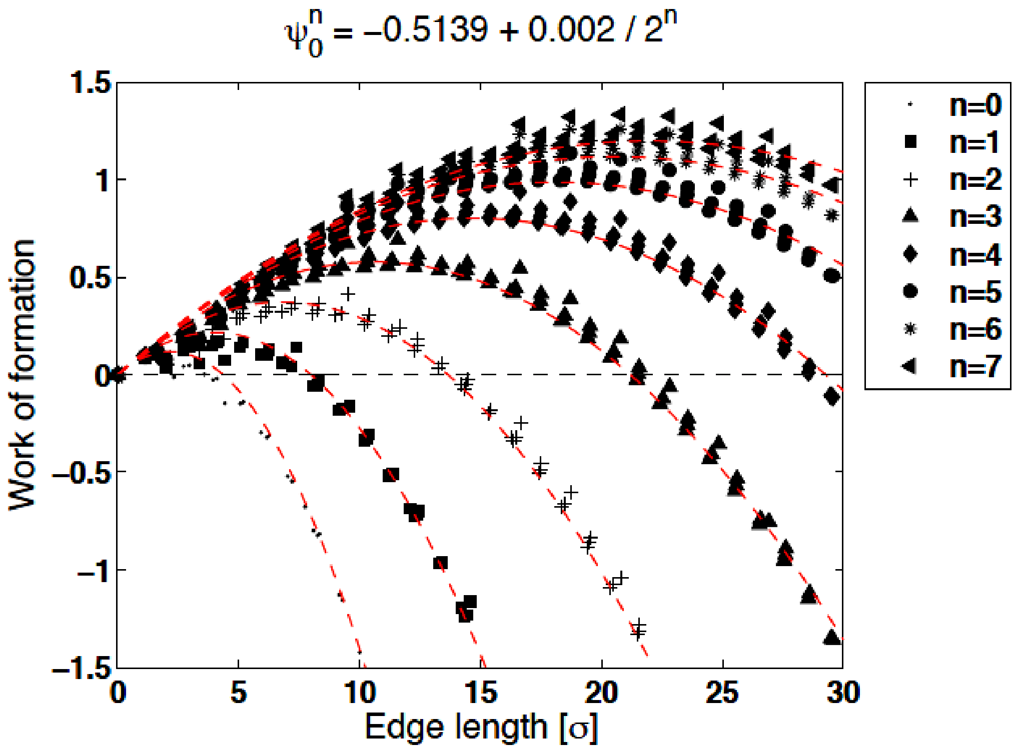


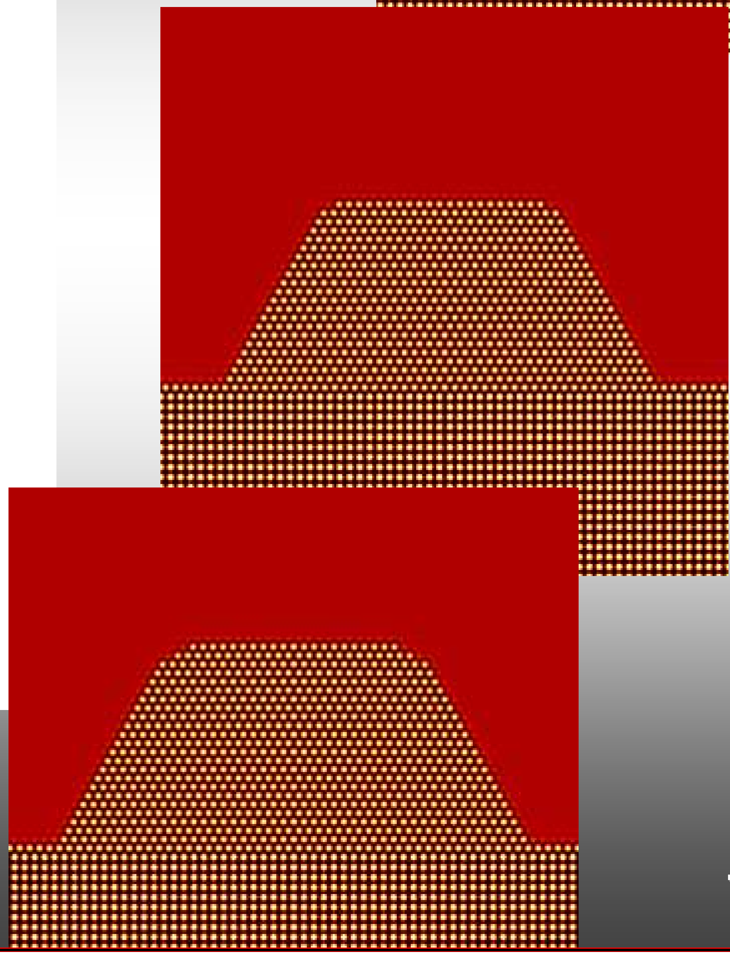


Heterogeneous crystal nuclei in 2D (EL equation): (Tóth *et al.*, J. Phys.: Condens. Matter 22, art. no. 364101 (2010))

$r = -0.5$
$a_0/\sigma = 1.0$
$V\psi$ term added to f_{PFC}







Results:
- Adsorbed monolayer !
- Contact angle: 60 °, determined by crystal structure

+1

Hydrodynamic theory of freezing (Tóth *et al.*, J. Phys.: Condens. Matter 27, art. no. 055001 (2014))

Fluctuating Nonlinear Hydrodynamics

Following L. D. **Landau** & E. M. **Lifshitz** (1959)

Navier-Stokes: $$\frac{\partial \mathbf{p}}{\partial t} + \nabla \cdot (\mathbf{v} \otimes \mathbf{p}) = \nabla \cdot [\mathbb{R}(\rho) + \mathbb{D}(\mathbf{v}) + \mathbb{S}]$$

continuity: $$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{p} = 0$$

- Variables: $\rho(\mathbf{r}, t)$ (mass density) and $\mathbf{p}(\mathbf{r}, t)$ (momentum density), $\mathbf{v} = \mathbf{p}/\rho$
- $\mathbb{R}(\rho)$: reversible stress tensor (to be defined on thermodynamical basis)
- $\mathbb{D}(\mathbf{v})$: dissipative stress tensor, $\mathbb{D} = \mu_S[(\nabla \otimes \mathbf{v}) + (\nabla \otimes \mathbf{v})^T] + \mu_B(\nabla \cdot \mathbf{v})$
- $\mathbb{S}$: Stochastic momentum noise with the correlator[2]:

$$\langle S_{ij}(\mathbf{r}, t) S_{kl}(\mathbf{r}', t') \rangle = (2 k_B T \mu_S) \left[(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}) + \left(\frac{\mu_B}{\mu_S} - \frac{2}{3} \right) \delta_{ij}\delta_{kl} \right] \delta_{\mathbf{r},\mathbf{r}'} \delta_{t,t'}$$

Problems related to applying $F[\rho]$ of a CDFT of freezing in the Navier-Stokes equation

Main problem: The crystal is represented by lattice periodic field distribution!
$\Rightarrow \mathbf{v} = \mathbf{p}/\rho$ is **singular** & generates **spurious interatomic flows** - UNPHYSICAL

From the viewpoint of *scales*...

The validity limit of the Navier-Stokes is approx. 100× effective molecular diameter...
(... below which the definition of **the continuum velocity field** fails.)

Scale separation

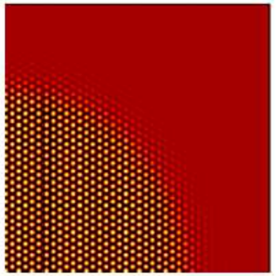
Coarse-graining (CG):

$\hat{\mathbf{v}} = \hat{\mathbf{p}}/\hat{\rho}$

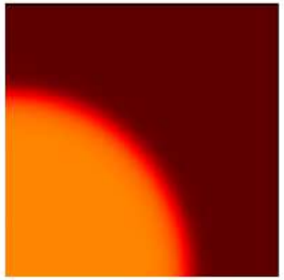
Apply $\nabla(\hat{\mathbf{v}} \otimes \mathbf{p})$ and $\mathbb{D}(\hat{\mathbf{v}})$ in the Navier-Stokes

and

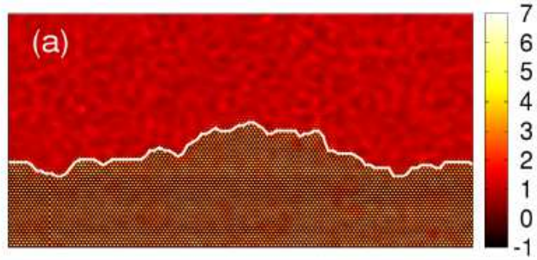
$\nabla \cdot \mathbb{R} = -\rho_0 \cdot \nabla \frac{\delta F[\rho]}{\delta \rho}$



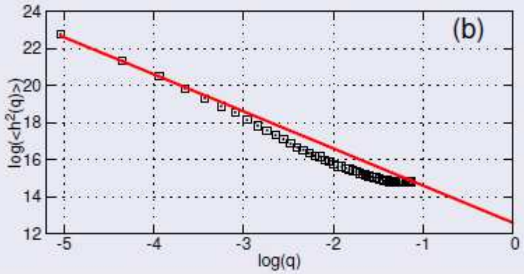
$\xrightarrow{CG}$



Fluctuating crystal-liquid front



Capillary wave spectrum



Crystalline anisotropy

CW theory: $\langle |h(q)|^2 \rangle = (k_B T)/(q^2 \tilde{\gamma} L)$

Stiffness: $\tilde{\gamma} = \gamma(\theta) + \gamma''(\theta)$

For 6fold symmetry the estimation is

$\epsilon \approx |(\tilde{\gamma}_{max} - \tilde{\gamma}_{min})/(\tilde{\gamma}_{max} + \tilde{\gamma}_{min})|/35$

$\Rightarrow \epsilon \lesssim 0.002$ (reasonable in PFC)

+2