Phase Field Crystal Modeling of Material Structures and Dynamics: Theory, Applications, and Challenges

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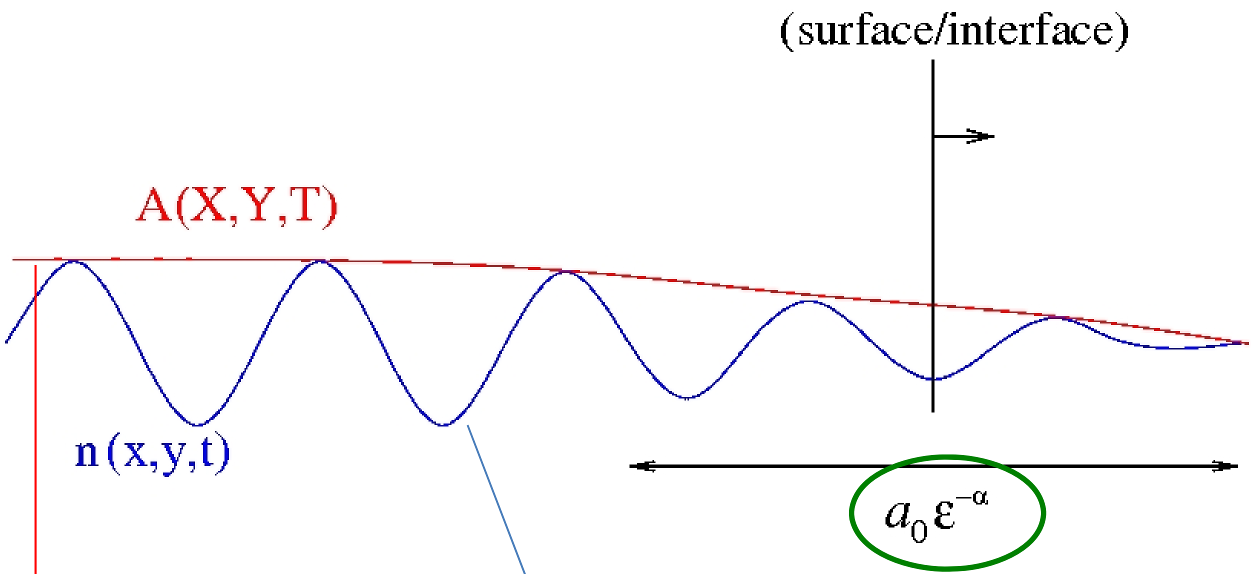
Workshop on "New algorithms for exploring structure and dynamics of interfaces",
UBC, Vancouver, Canada (July 31, 2017)

- Fundamental scales in a crystalline/ordered system:



Microscopic (“*fast*” scales): crystalline lattice, atomic resolution
characteristic length scales vs. symmetry

Mesoscopic (“*slow*” scales): structural amplitudes/envelopes,
nanopatterns, grains, etc.

In theoretical modeling: **Can these two types of scales be separated?**

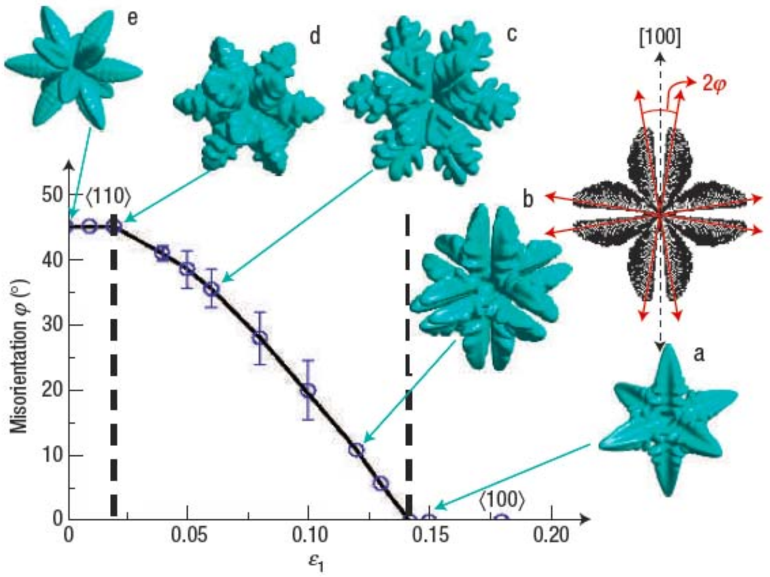
Coupling between different scales: ***Need multiple-scale modeling***

Theoretical Modeling of Material Structure and Dynamics

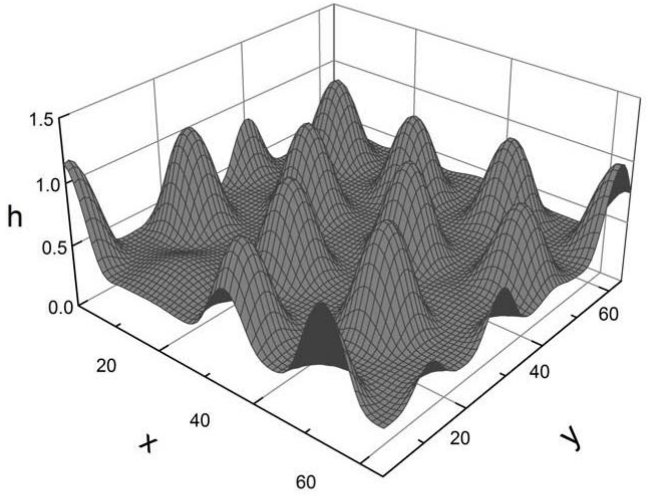
➢ Continuum approach

For example,

- Phase field method
- Continuum elasticity theory



T. Haxhimali et al., Nat. Mater. 5, 660 (2006)



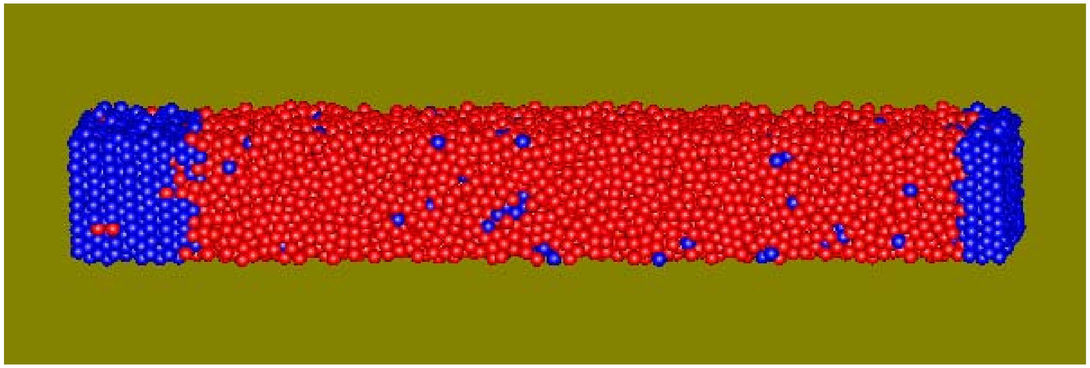
C.G. Gamage and Z.-F. Huang, PRE 87, 022408 (2013)

Capture *long-wavelength* behavior but not crystalline details
(What is missing in continuum theory: discrete nature of lattice)

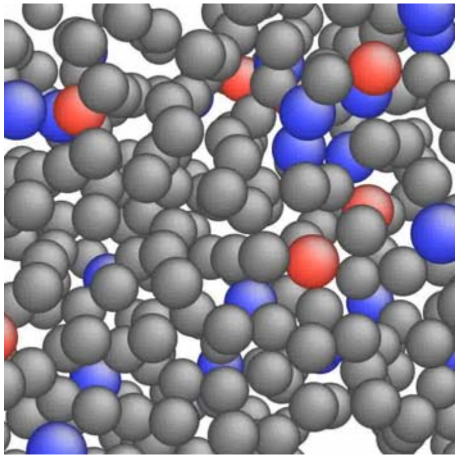
Theoretical Modeling of Material Structure and Dynamics

➢ Atomistic simulation

- E.g., Molecular dynamics or Monte-Carlo simulations
- Capture *microscopic details of crystalline structure*
- Usually computationally challenging for large systems (for both spatial and time scales)
- New development of algorithms and techniques (this workshop)



J.J. Hoyt et al., Acta Mater. 47, 3181 (1999): Ni solid-liquid

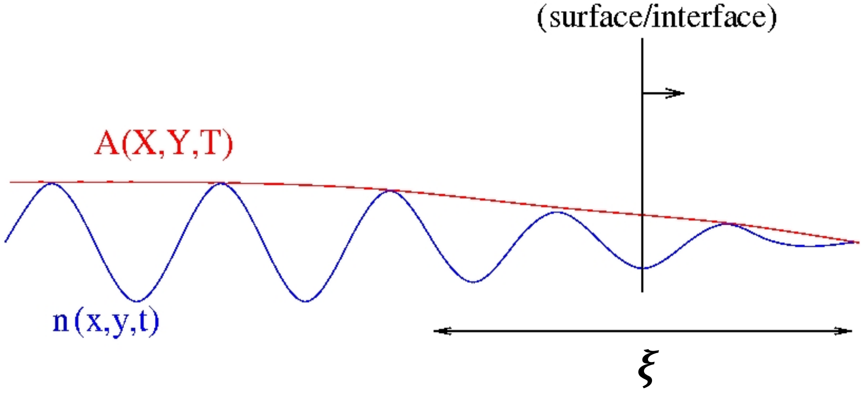


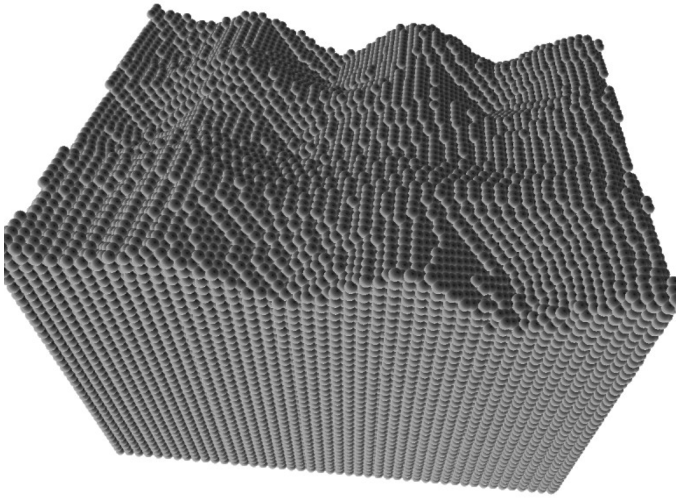
Ni-Al-W alloy (liquid diffusion)
Woodward et al. JAP 2010

Theoretical Modeling of Material Structure and Dynamics

Mesoscopic/Microscopic description

- **Phase field crystal (PFC) model**: incorporates **microscopic** length scale of *crystalline structures* and ***diffusive*** time scales
- Developed from classical density functional theory (CDFT)
- **Amplitude equation formalism:**
  for "***slow***"/**mesoscopic**-scale profile of surfaces/interfaces or defects
- **Coupling between different scales**

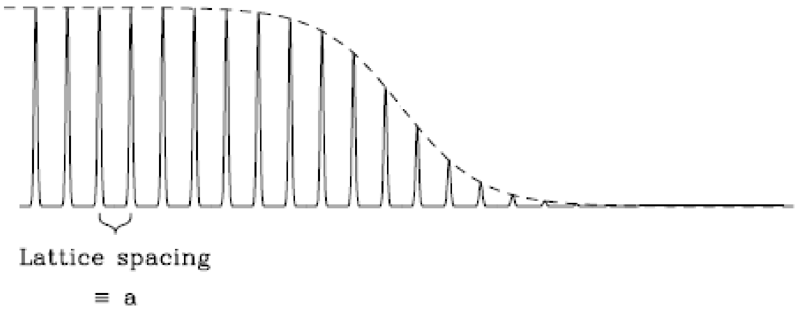




Note: 2 different scales (PFC bcc)

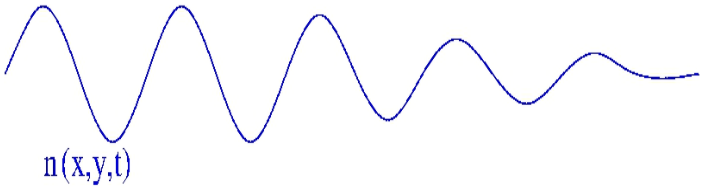
Why PFC? (advantages *and disadvantages*)

- CDFT

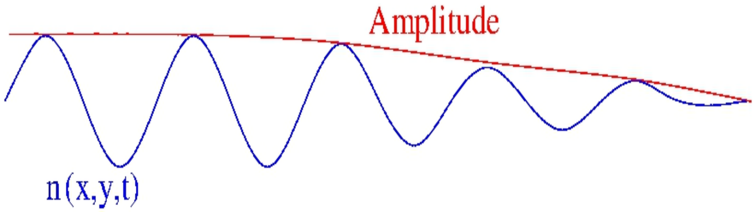


spatial resolution: dx ~ *a*/100 ~ 10^{-2} Å

- PFC (a periodic continuum-field theory)



spatial resolution: dx ~ *a*/10 ~ 10^{-1} Å



Dynamics

MD: atomic vibration scale

PFC: time average (or coarse-graining) scale → diffusive time scale
(orders of magnitude larger than traditional/typical MD scale)

However, there are lots of challenges (No free lunch!)
(to be discussed later)

Phase Field Crystal (PFC) model: Basic theory

- From classical density functional theory (CDFT) of freezing

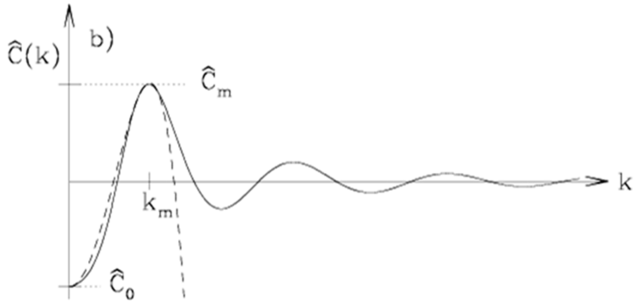
$$F/k_BT = \int d\vec{r}\,\left[\rho\ln(\rho/\rho_l)-\delta\rho\right] - \frac{1}{2!}\int d\vec{r}_1 d\vec{r}_2\,\delta\rho(\vec{r}_1)\,C^{(2)}(\vec{r}_1-\vec{r}_2)\,\delta\rho(\vec{r}_2)$$

$$-\frac{1}{3!}\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3\,C^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,\delta\rho(\vec{r}_1)\,\delta\rho(\vec{r}_2)\,\delta\rho(\vec{r}_3) + \cdots$$

(ρ: *atomic number density*, ρ_l: reference-state density)

- Expand around an *atomic density variation field*

$$n(\vec{r},t) = (\rho-\rho_l)/\rho_l$$



- **PFC Dynamics (relaxational)**

$$\partial n/\partial t = \Gamma\nabla^2\delta F/\delta n + \nabla\cdot\vec{\eta}$$

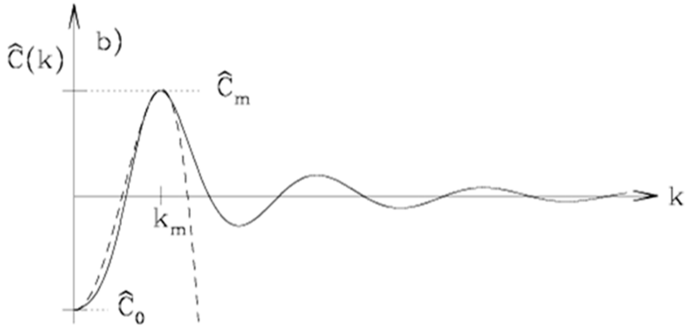
$$\partial n/\partial t = \Gamma\nabla^2\left[-\rho_l\int d\vec{r}\,'C_2(\vec{r}-\vec{r}\,')n(\vec{r}\,') + n + \tau n^2 + v n^3\right] + \nabla\cdot\vec{\eta}$$

PFC model equation (general form)

- Original (simplest) PFC model

Expand *the correlation function* in Fourier space

$$\hat{C} = -\hat{C}_0 + \hat{C}_2 q^2 - \hat{C}_4 q^4 + \cdots$$



PFC relaxational dynamics (after rescaling)

$$\partial n / \partial t = \nabla^2 \left[-\varepsilon n + \underline{(\nabla^2 + q_0^2)^2} n - g n^2 + n^3 \right] + \nabla \cdot \vec{\eta}$$

ε: *reduced temperature*; q_0=1 after rescaling via lattice spacing;
$g = (3/B^x)^{1/2}/2$; B^x: proportional to *bulk modulus*; η: noise

(For more details, see K.R. Elder *et al*., PRL02, PRE04, PRB07; Huang & Elder, PRL08)

Note: here only 1 microscopic length scale (q_0), plus diffusive time scale

➢ Some development of PFC-type models:

- *Structural PFC* (XPFC): (See e.g., the work of McGill/McMaster and UBC groups in PRL2010, PRE2011, PRB2013)

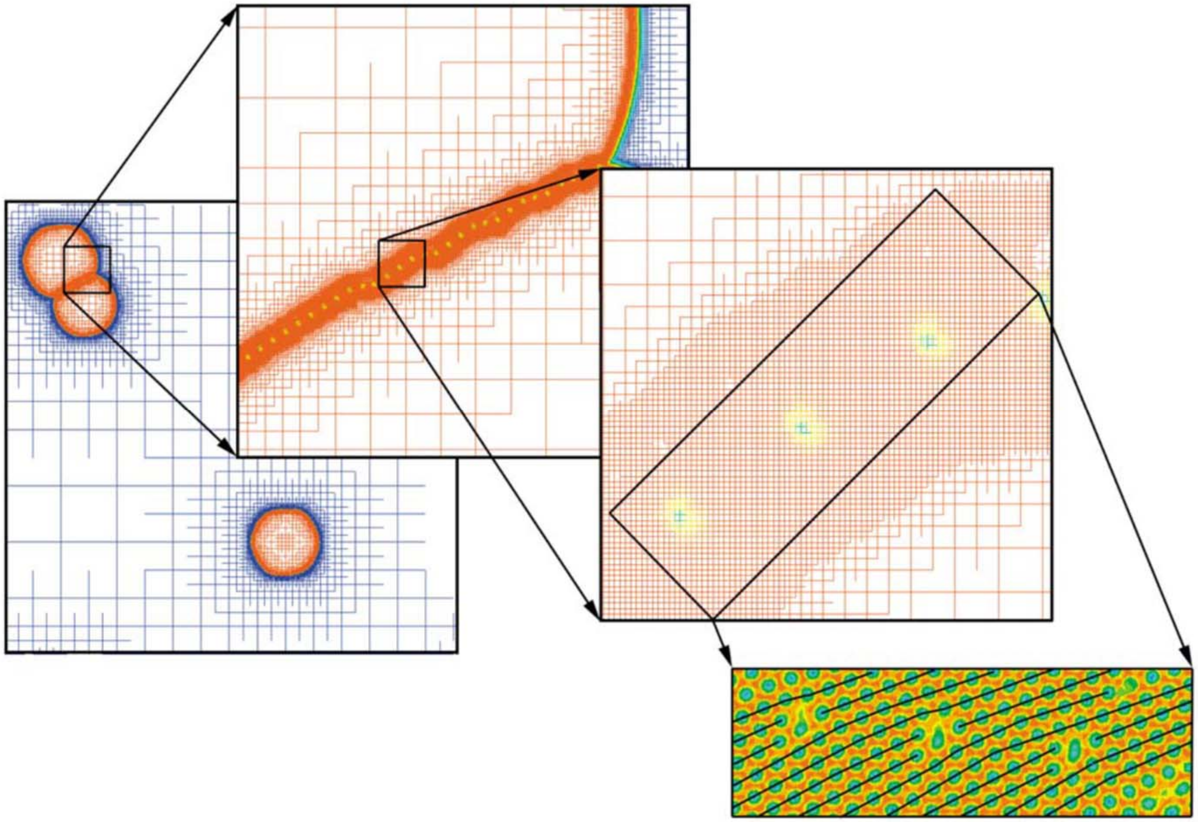
  The peaks of CDFT 2-point correlation functions (in Fourier space)

  → Gaussian-type fitting (different from the *q*-polynomial fitting described above in the original PFC model)

  → PFC-type modeling of 2D (hex, square) and 3D (bcc, fcc, hcp, simple cubic, diamond (Chan et al. PRE2015)) structures

- *Wave-mode PFC*: fast dynamics with elastic interaction
- *Multi-component PFC* (e.g., for binary and ternary alloys)
- *Vapor-Liquid-Solid PFC* (Schwalbach *et al*. PRE2013; Kocher/Provatas PRL2015)
- *Multi-mode PFC* (PRL2013, PRL2016; to be discussed later)
- Angle-dependent PFC (Seymour/Provatas PRB2016, Alster et al. arXiv2017, Wang/Liu/Huang 2017)
- Many others ……

Multiple-scale nature of materials:

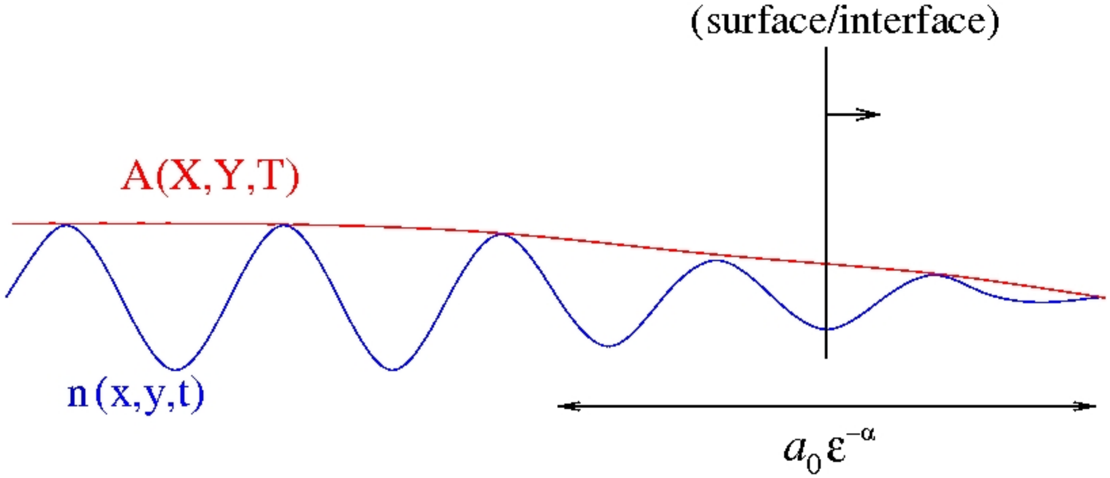


Multiple length scales: micrometer ↔ nanometer ↔ atomistic

(Athreya, Goldenfeld, Dantzig, Greenwood, and Provatas, PRE 2007)

How to study the *meso* ("*slow*") scales? Amplitude Formalism

Scale separation! (*adiabatic*)



- *Standard multiple-scale approach (or singular perturbation)*:

  for slowly varying **complex** amplitudes/envelopes

$$n = n_0(X,Y,T) + \sum_{j=1}^{3} A_j(X,Y,T) e^{i\boldsymbol{q}_j^0 \cdot \boldsymbol{r}} + \text{c.c.} \quad (A_j = |A_j| e^{i\varphi_j})$$

Separate "*fast*" (*x*, *y*, *t*) and "*slow*" **scales** (*X*, *Y*, *T*)

$$X = \epsilon^{1/2} x, \quad Y = \epsilon^{1/2} y, \quad T = \epsilon t$$

Beyond the traditional Phase Field models: *incorporate elasticity/plasticity*

Amplitude Equation Formalism

- Amplitude Equations (with ***scale separation***)

$$\partial A_j/\partial t = -q_0^2 \delta \mathcal{F}/\delta A_j^*,$$
$$\partial n_0/\partial t = \nabla^2 \delta \mathcal{F}/\delta n_0,$$

$F(A_j, A_j^*, n_0)$: Effective free energy (a Lyapunov functional)
rotational invariance (*multi-grain orientations; polycrystals*)
in small-deformation limit, reduced to continuum elasticity

- Similar procedure for alloys: the *atomic density* and *concentration* fields

$$n = (\rho - \rho_l)/\rho_l$$
$$\psi = (\rho_A - \rho_B)/\rho \qquad (\text{with } \rho = \rho_A + \rho_B)$$

(n: scale separation to A_j and n_0; ψ: slow-varying variable)

- Many applications: *solidification, islands/quantum dots growth during epitaxy, surface segregation, grain boundaries, surface ordering, ……*

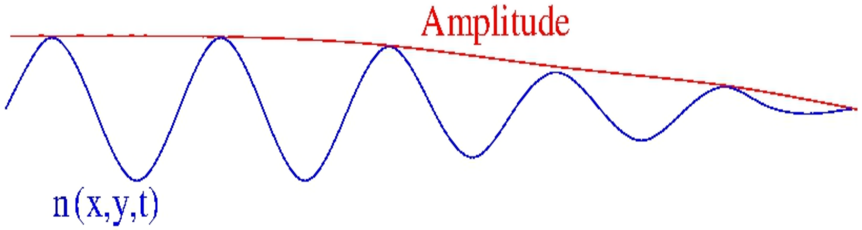
- Some advantages of amplitude equation representation

Computational:

Larger spatial scales (mesoscopic)
More numerically "stable" and "controllable"
Adaptive mesh refinement method applicable

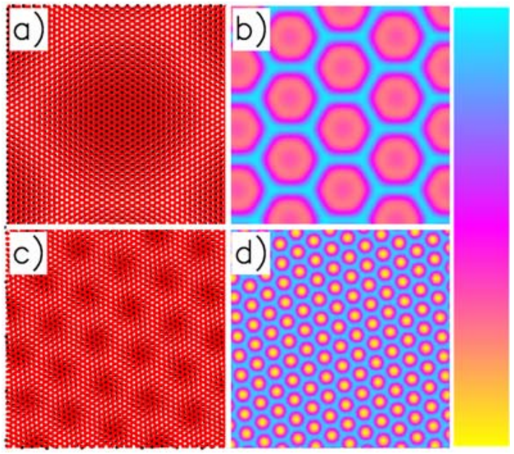
Analytical:

Connection to continuum approaches
Phase field model, continuum elasticity theory
Some analytical results available
Perturbation methods



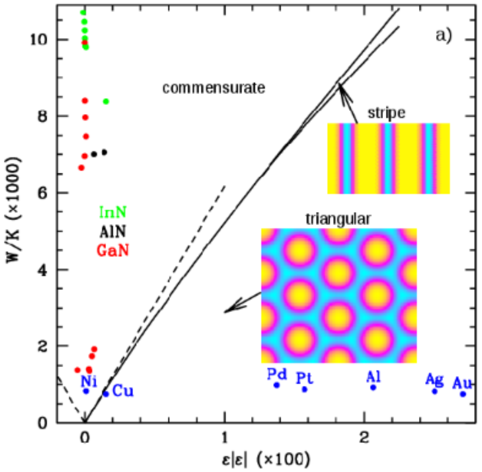
Example: Graphene Moiré patterns on metallic surfaces

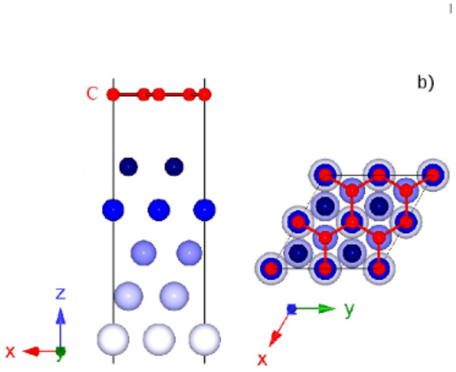
– Application of amplitude PFC: *Effect of film-substrate misorientation θ*



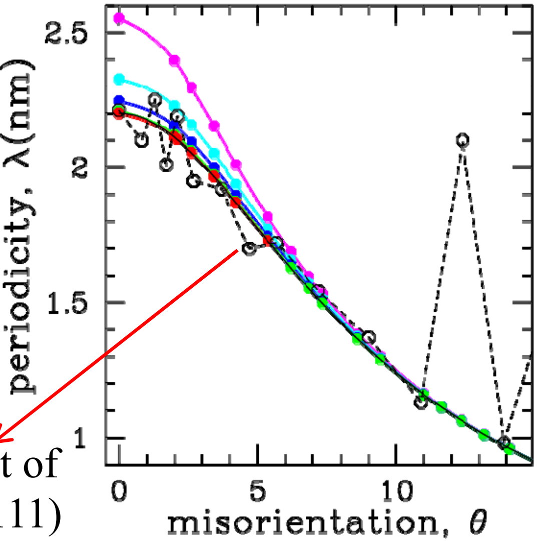
θ = 0

θ = 5.36º

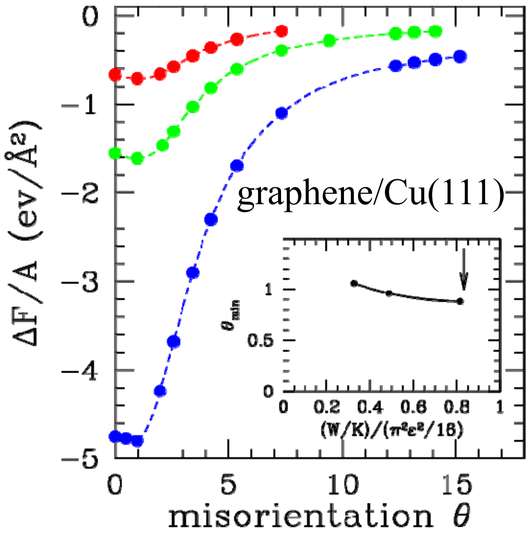




film-substrate adhesion: First-principles DFT



o: Experiment of graphene/Pt(111)



Largest system size: up to 19.6 μm × 33.9 μm (~2.5×10^{10} equivalent atomic sites; for *θ* = 0.497º on Cu(111))

(M. Smirman, D. Taha, A.K. Singh, Z.-F. Huang, K.R. Elder, PRB 2017)

Some recent advances and ongoing challenges

Sample topics:

- Control of crystalline symmetries and structure chirality
  Challenges: competition among length scales; bonding angle control
- Structure and dynamics of graphene-type 2D materials
  Challenges: matching to real materials; out-of-plane 3D deformation
- Coupling between micro and meso scales (surface or interface pinning)
  Challenges: Extension to general cases; defect dynamics with Peierls barrier
- Time scales: diffusional dynamics vs. mechanical/elastic relaxation
  Challenges: slow vs. fast; lack of instantaneous mechanical equilibrium
- Atomic density localization and vacancy
  Challenges: conservation of density vs. maxima (sites); vacancy dynamics
- Hydrodynamic coupling (Challenges: micro vs. hydrodynamic/meso scales)
- Others ……

Topic I: Control of crystalline symmetries and structure chirality

- What determines the crystal structure of a material system?

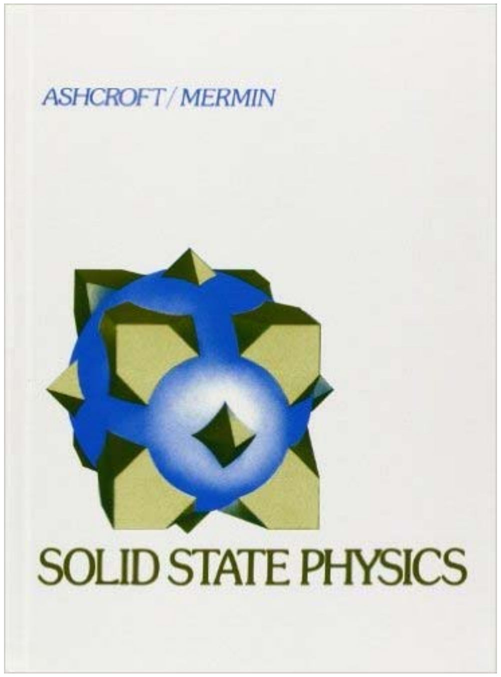
  not just symmetry and space group;

  interatomic interaction?

- But why materials with different types of interaction can have same structure and symmetry?

  e.g., solids, soft matter (colloids, copolymers), ultracold atoms

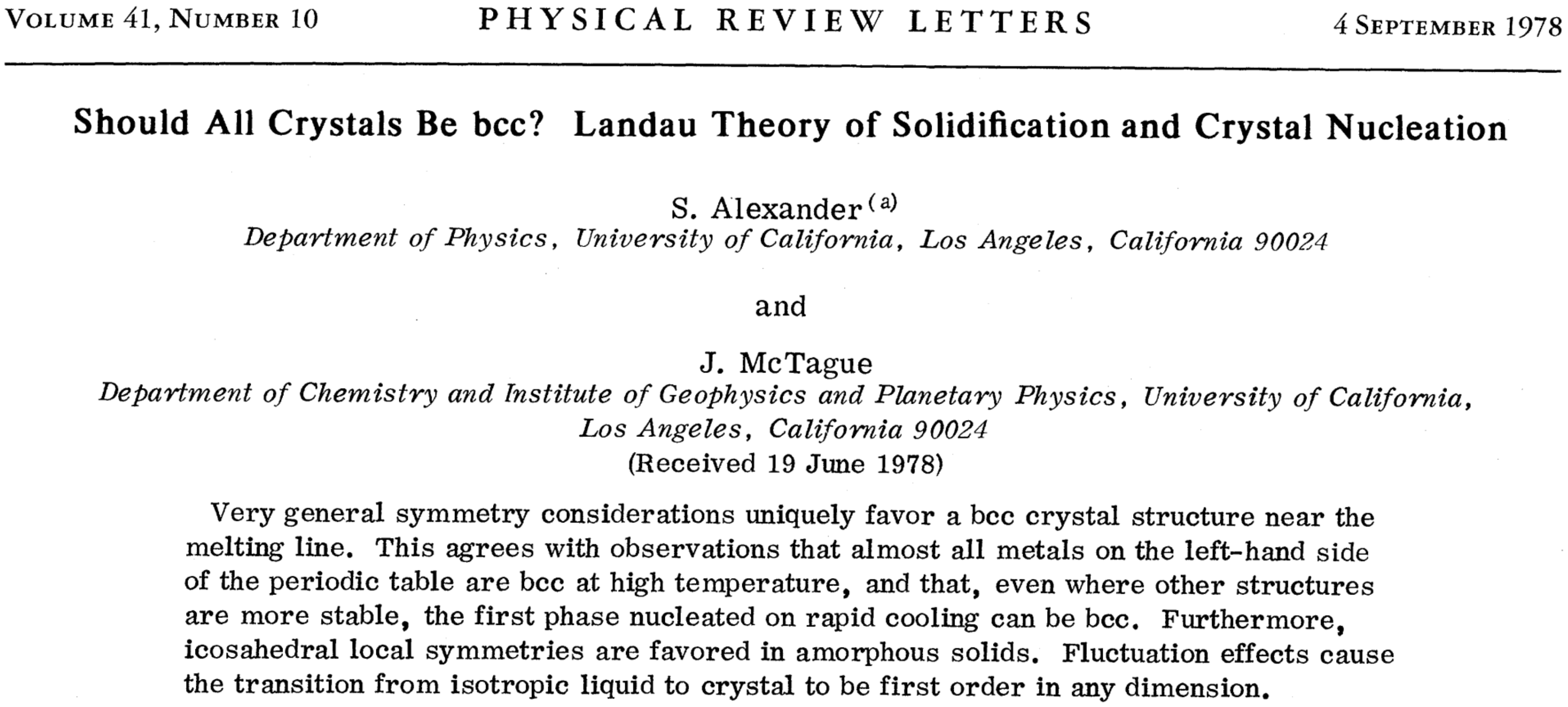
- Why a same type of material can have different crystal symmetries?



- What did standard textbooks say about this? *Almost none*

- *Alexander-McTague analysis of crystallization*

  (PRL78; see also Chaikin&Lubensky's book)



VOLUME 41, NUMBER 10 PHYSICAL REVIEW LETTERS 4 SEPTEMBER 1978

Should All Crystals Be bcc? Landau Theory of Solidification and Crystal Nucleation

S. Alexander[a]
Department of Physics, University of California, Los Angeles, California 90024

and

J. McTague
Department of Chemistry and Institute of Geophysics and Planetary Physics, University of California,
Los Angeles, California 90024

(Received 19 June 1978)

Very general symmetry considerations uniquely favor a bcc crystal structure near the melting line. This agrees with observations that almost all metals on the left-hand side of the periodic table are bcc at high temperature, and that, even where other structures are more stable, the first phase nucleated on rapid cooling can be bcc. Furthermore, icosahedral local symmetries are favored in amorphous solids. Fluctuation effects cause the transition from isotropic liquid to crystal to be first order in any dimension.

- Use the Alexander-McTague analysis of crystallization (PRL78):

The favored crystalline state is determined by the largest contribution of the cubic term in free energy expansion of atomic number density n:

$$F = \int dr\left(an^2 + bn^3 + cn^4 + \cdots\right)$$

$$n = n_0 + \sum_{\vec{q}} A_{\vec{q}} e^{i\vec{q}\cdot\vec{r}}, \quad \vec{q} = l\vec{k}_1 + m\vec{k}_2$$ (the reciprocal lattice vectors)

⇒ Triads of density waves with closed-loop wave vectors

$$\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = 0$$

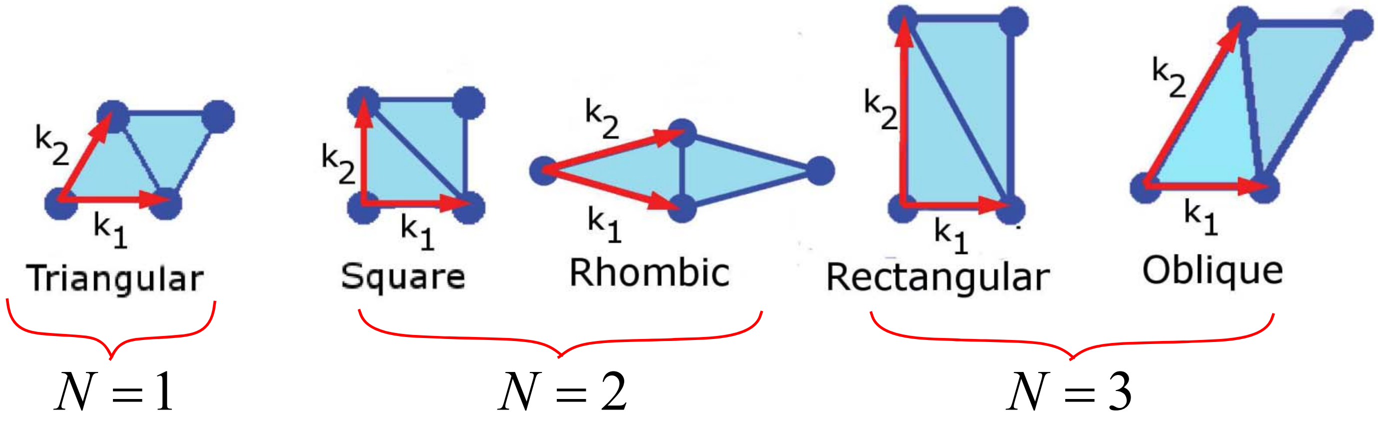
⇒ Close to melting, bcc is always favored in 3D and triangular in 2D

Sounds not right? Why?

In Alexander-McTague analysis, only ***1 mode*** *is considered*

- **Three modes** are needed to produce all five 2D Bravais lattices

Why?



Triads of density waves with closed-loop wave vectors (*resonant condition*)

$$\vec{k}_1 + \vec{k}_2 + \vec{k}_3 = 0$$

Within each mode: same magnitude of wave vector **k**

Multi-mode Phase Field Crystal (PFC) model

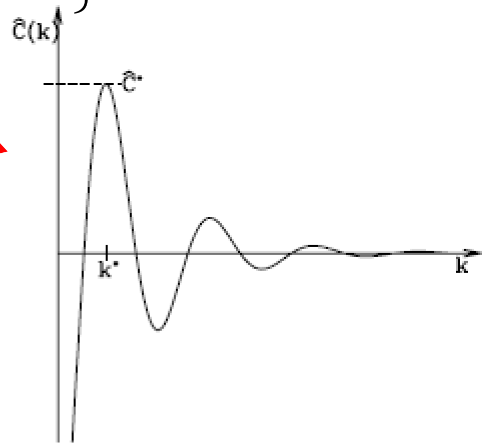
- Crystalline systems with N competing microscopic length scales

$$F[n]=\int d\mathbf{r}\left\{\frac{1}{2}n\prod_{i=0}^{N-1}\left[\underline{(\nabla^2+Q_i^2)^2+b_i}\right]n-\frac{\varepsilon}{2}n^2-\frac{g}{3}n^3+\frac{1}{4}n^4\right\}$$

(i) N modes (N peaks in $\hat{C}(q)$);

(ii) Isotropic and rotational invariance

b_i: tune the excitation level of each mode

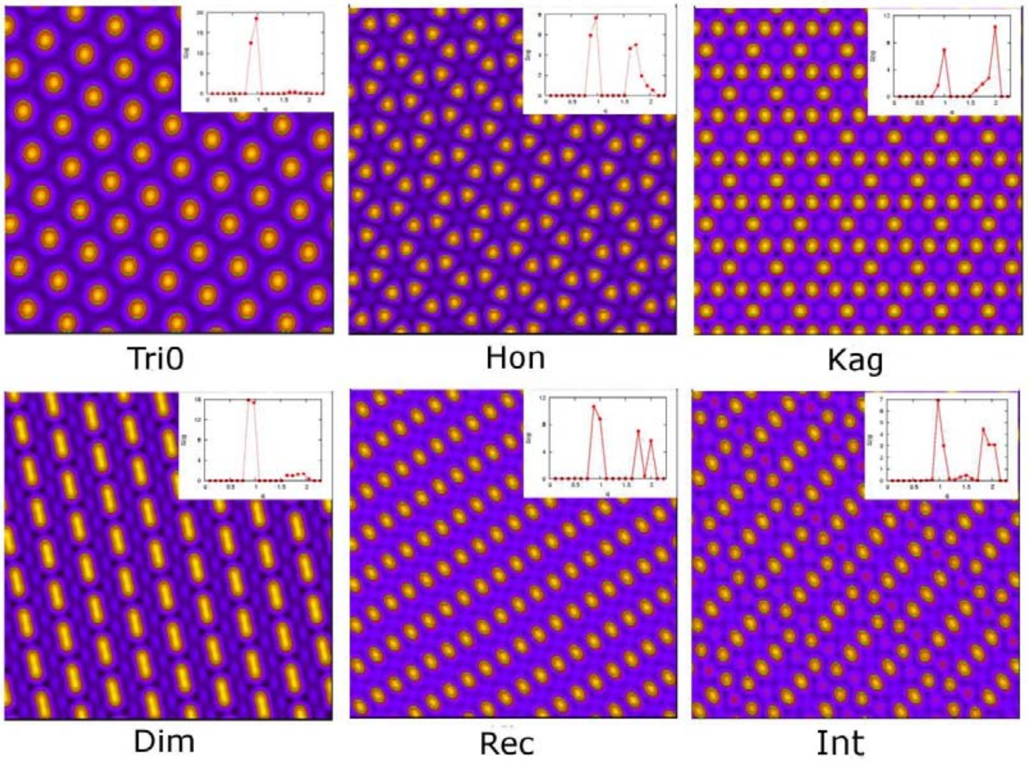


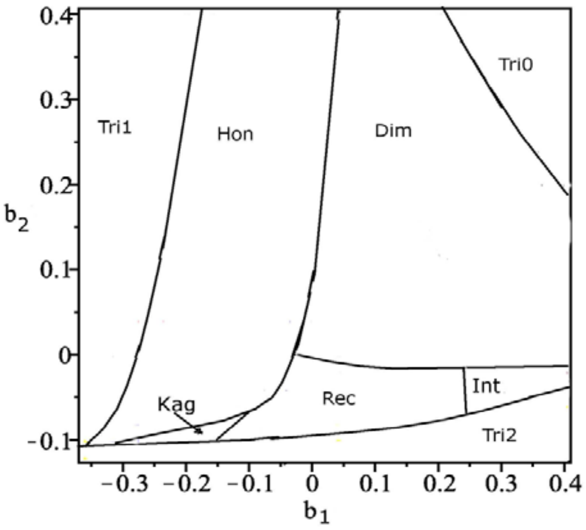
- PFC Dynamics

$$\partial n/\partial t=\nabla^2\left[-\varepsilon n+\prod_{i=0}^{N-1}\left[(\nabla^2+Q_i^2)^2+b_i\right]n-gn^2+n^3\right]$$

- ***Minimum*** *number of modes (length-scales) needed for determining complex crystal structures:* ***N=3 in 2D***

- Example of Triangular-series:
  $Q_i = 1, \sqrt{3}, 2$ (the first 3 shortest reciprocal vectors for triangular)

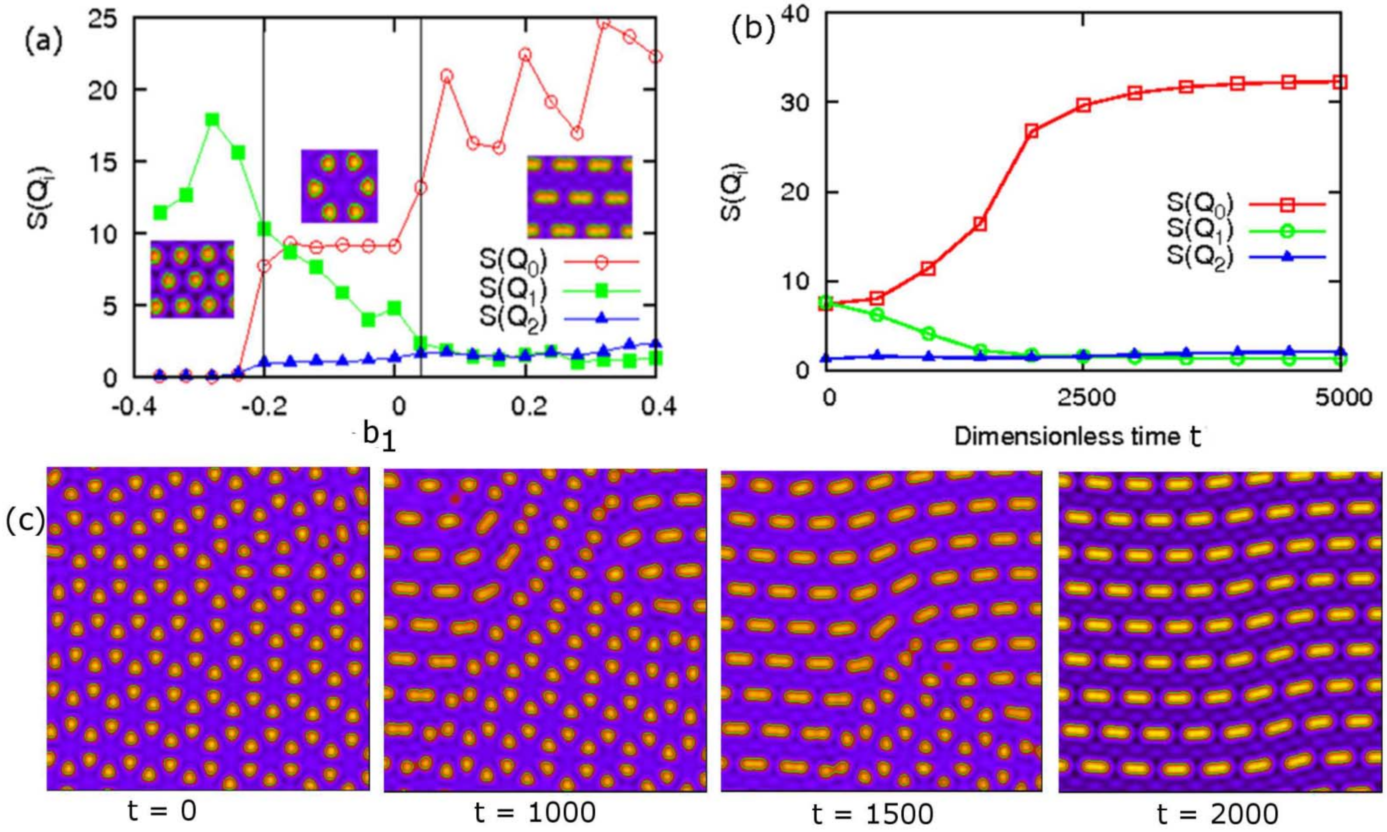




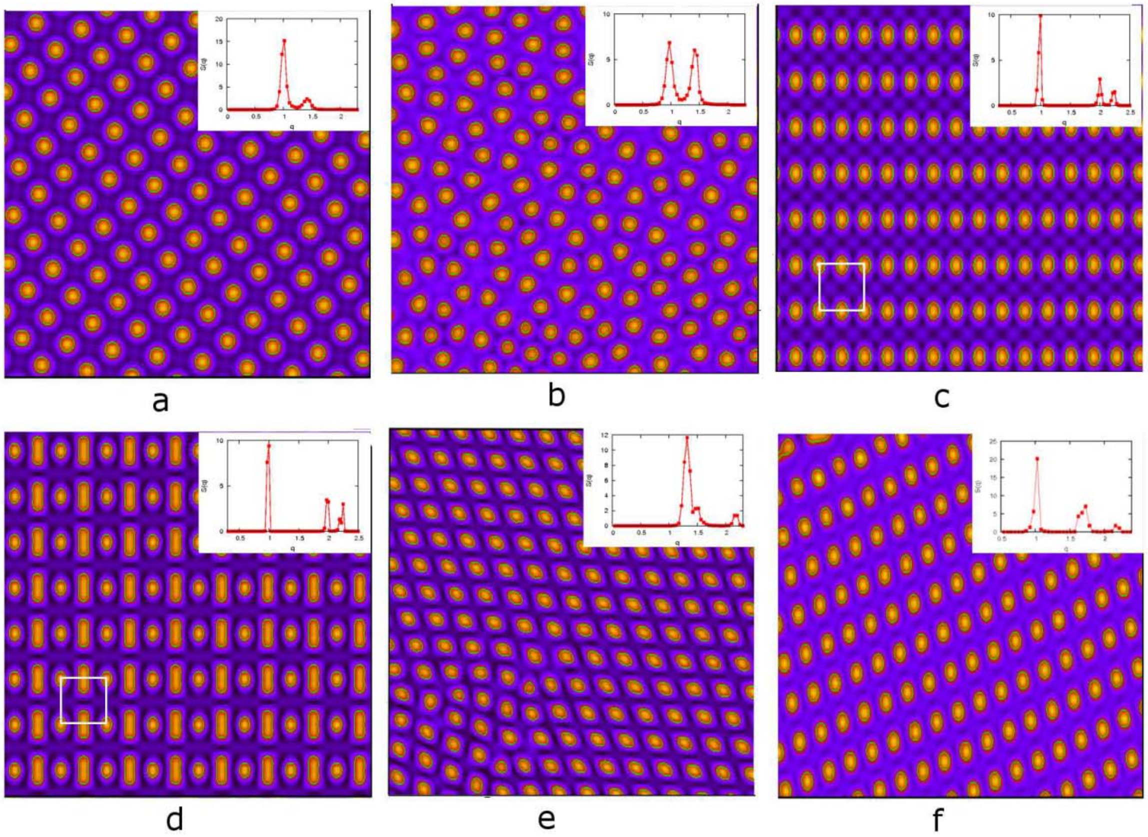
Complex phase behavior due to competition between different modes (different *microscopic length scales*)

S.K. Mkhonta, K.R. Elder, and Z.-F. Huang, PRL **111**, 035501 (2013)

➢ Dynamics of Phase Transformation

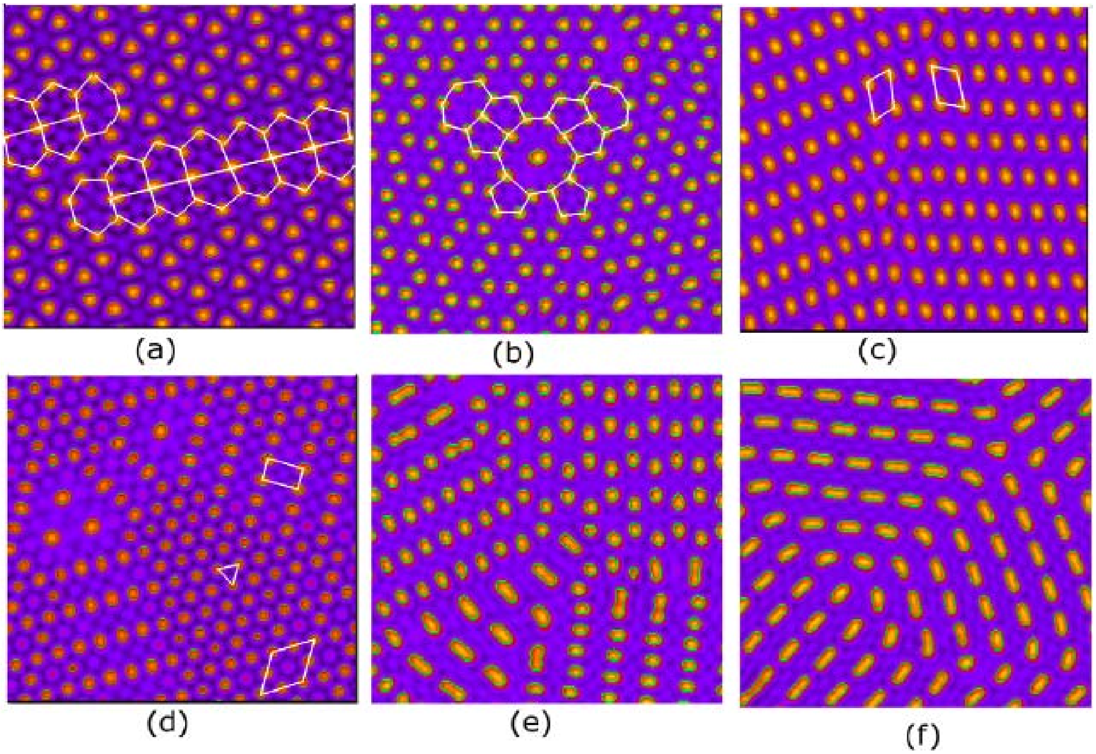


- Some other examples of 2D phases (different Q_i ratios)

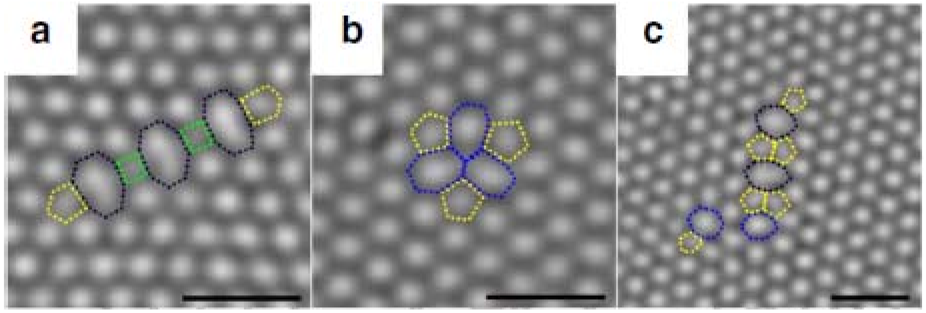


(a) square; (b) pentagon-hexagon; (c) rectangular;
(d) dimer-square; (e) rhombic; (f) oblique

➢ Defects and phase coexistence



(a),(b): defects in honeycomb structures; (c): grain boundary in oblique phase; (d),(e): phase coexistence and defects; (f): disclination in dimer phase



TEM image of graphene

(Robertson *et al*., Nature Commun. 2012)

What else? Can we control chirality of structure/pattern?

- ***Chirality***: *An object or system is chiral if it is distinguishable from its mirror image (by translation and rotation; lack of symmetry axes)*

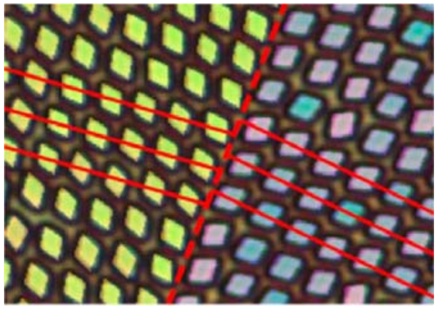
- *Chiral systems: natural for systems with chiral components (e.g., single-handed molecules like DNA) and anisotropic interactions*

- *How about systems composed of* ***achiral building blocks*** *and/or governed by* ***isotropic interactions****?*

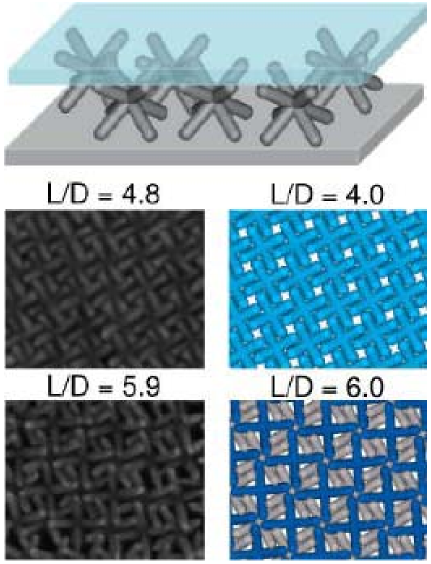
e.g., some colloidal or nanocrystal systems with achiral shaped particles,

excluded volume effect

or steric interaction



(K. Zhao & T.G. Mason, J. Am. Chem. Soc. 2013)



(Qi *et al*. Nano Lett. 2012)

- Use similar approach of multi-mode PFC

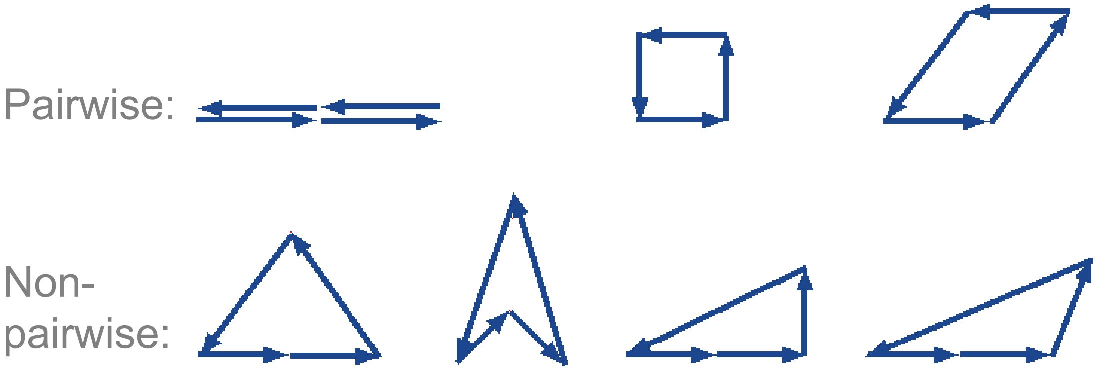
$$F[n] = \int d\mathbf{r} \left\{ \frac{\lambda}{2} n \prod_{i=0}^{N-1} \left[(\nabla^2 + Q_i^2)^2 + b_i \right] n - \frac{\varepsilon}{2} n^2 - \frac{g}{3} n^3 + \frac{1}{4} n^4 \right\}$$

Isotropy and rotationally invariant

Resonant conditions

For cubic term: $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = 0$

For quartic term: $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4 = 0$



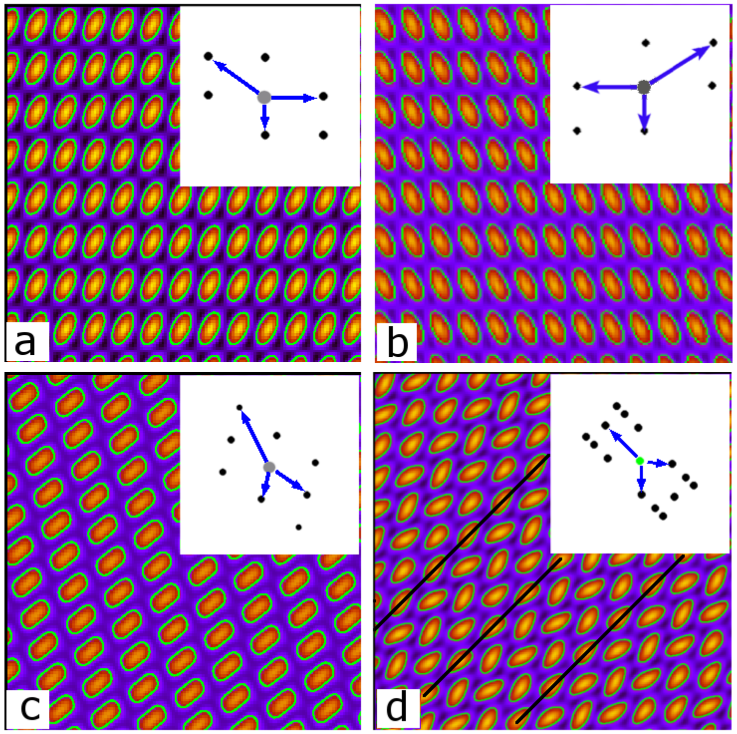
- *Q_i (length scale) ratio → base lattice symmetry*
- *Nonlinear coupling → resonant density wave vectors*

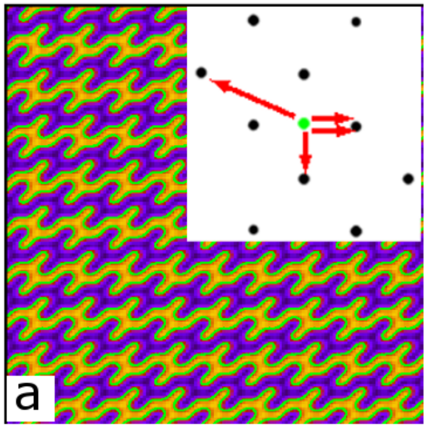
- Emergence of 2D chirality from isotropic interactions of 3 length scales

  (a) Misalignment of building blocks from lattice symmetry axes
  (both the particle/block and the lattice are achiral; e.g., (a), (b))

  (b) Chirality of lattice itself (e.g., (c): oblique)

  (c) Chiral superlattices
  (the constituent layer/motif is chiral)

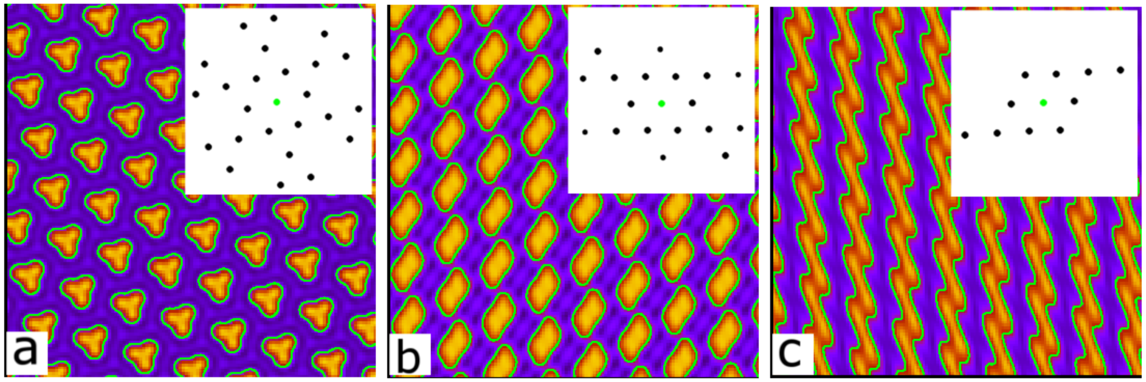




(*Frieze group p211*)

S.K. Mkhonta, K.R. Elder, and Z.-F. Huang, PRL **116**, 205502 (2016)

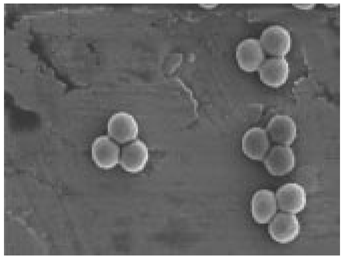
- *Another example* ($Q_i = 1, \sqrt{3}, \sqrt{7}$ of triangular base lattice)



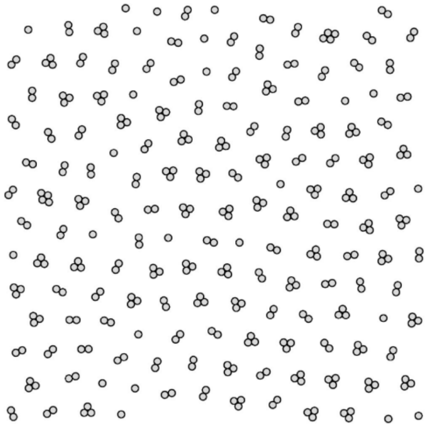
(achiral (*p31m*); soft) (chiral (*p2*); hard) (chiral; hard)

(*weaker cubic coupling*)

Compared to colloid experiments and MC simulations



(unit of small clusters; V.N. Manoharan, M.T. Elsesser, & D.J. Pine, Science 2003)

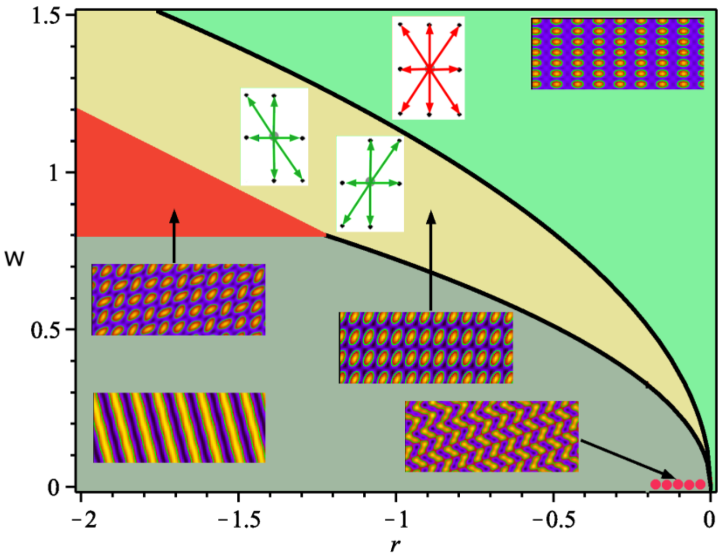


(M. Rechtsman, F. Stillinger, and S. Torquato, PRE 2006)

- *Elastic properties*

For chiral rectangular

$$E_{el} = \frac{1}{2}C_{11}u_{xx}^2 + \frac{1}{2}C_{22}u_{yy}^2 + C_{12}u_{xx}u_{yy} + 2C_{44}u_{xy}^2$$
$$\underline{+2C_{14}u_{xx}u_{xy} + 2C_{24}u_{yy}u_{xy}}$$



Chiral elastic constants C_{14} *and* C_{24}

- *>0 (<0) for right- (left-) handed state*
- *Enantioselectivity and control of homochirality*

  e.g., a simple shear → shrinking of one enantiomorph but expanding of the other → handedness selection (elastically)

- *Other applications …*

S.K. Mkhonta, K.R. Elder, and Z.-F. Huang, PRL **116**, 205502 (2016)

- Challenges

- How about 3D? Where is the bonding angle control (2D/3D)?
- All the above are essentially for isotropic interactions
- Anisotropic interaction vs. rotational invariance?

Some new development of angle-dependent PFC models:

- Models based on infinite series of C_3 expansion
  - 2D: $C_3(\vec{r}_1,\vec{r}_2)=\sum_i C_s^{(i)}(\vec{r}_1)C_s^{(i)}(\vec{r}_2)=C_r(r_1)C_r(r_2)\cos\left[m(\theta_2-\theta_1)\right]$
    (M. Seymour and N. Provatas, PRB 2016)
  - 3D/2D: based on spherical harmonics
    (E. Alster, D. Montiel, K. Thornton, and P.W. Voorhees, arXiv 2017)
- Model based on finite-order expansion of C_3 and C_4
  (Z. Wang, Z. Liu, and Z.-F. Huang, to be published)

- *All show angle dependence while maintaining rotational invariance of free energy functional*

Some recent advances and ongoing challenges

Sample topics:

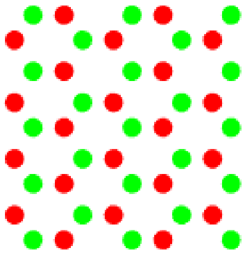
- Control of crystalline symmetries and structure chirality
  Challenges: competition among length scales; bonding angle control
- Topic II: Structure and dynamics of graphene-type 2D materials
  Challenges: matching to real materials; out-of-plane 3D deformation
- Coupling between micro and meso scales (surface or interface pinning)
  Challenges: Extension to general cases; defect dynamics with Peierls barrier
- Time scales: diffusional dynamics vs. mechanical/elastic relaxation
  Challenges: slow vs. fast; lack of instantaneous mechanical equilibrium
- Atomic density localization and vacancy
  Challenges: conservation of density vs. maxima (sites); vacancy dynamics
- Hydrodynamic coupling (Challenges: micro vs. hydrodynamic/meso scales)
- Others ……

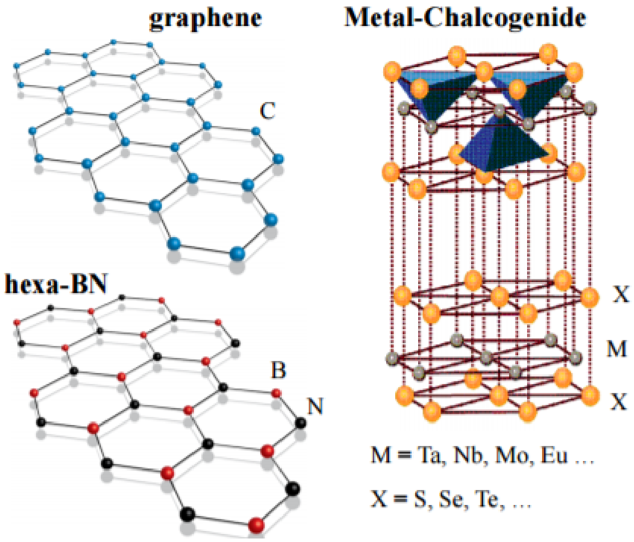
Topic II: Structure and dynamics of graphene-type 2D materials

- Characteristics of binary hexagonal 2D materials (e.g., *h*-BN and TMDs) (*compared to single-component 2D materials like graphene*)

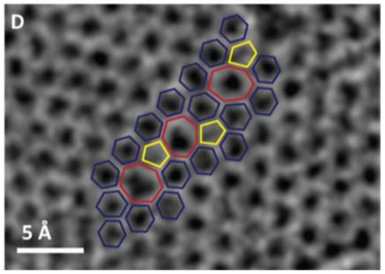
Breaking of inversion symmetry

in binary honeycomb lattice

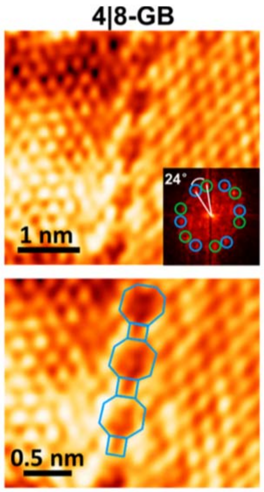




- Topological defects (*grain boundaries and dislocations*)



(*h*-BN 5|7 GB; A.L. Gibb *et al*. JACS 2013)

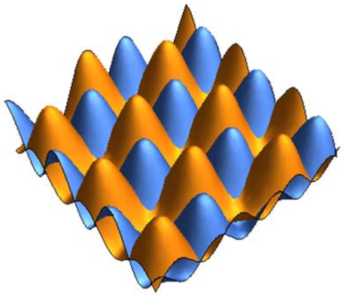


(Q. Li *et al.* Nano Lett. 2015)

- 60° *inversion domain boundaries* (due to inversion symmetry breaking)
- *Effects on electronic properties*
- *Atomistic methods (e.g., DFT, MD):* limited length and time scales; preconstructed defect cores

➢ Binary PFC model with sublattice ordering

(n_A, n_B: atomic number density variations)

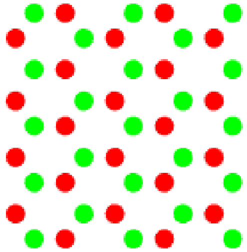


$$F = \int d\vec{r} \left\{ \underbrace{-\frac{1}{2}\varepsilon_A n_A^2 + \frac{1}{2} n_A \left(\nabla^2 + q_A^2\right)^2 n_A - \frac{1}{3} g_A n_A^3 + \frac{1}{4} n_A^4}_{\text{For component A}} \right.$$

$$\underbrace{-\frac{1}{2}\varepsilon_B n_B^2 + \frac{\beta_B}{2} n_B \left(\nabla^2 + q_B^2\right)^2 n_B - \frac{1}{3} g_B n_B^3 + \frac{v}{4} n_B^4}_{\text{For component B}}$$

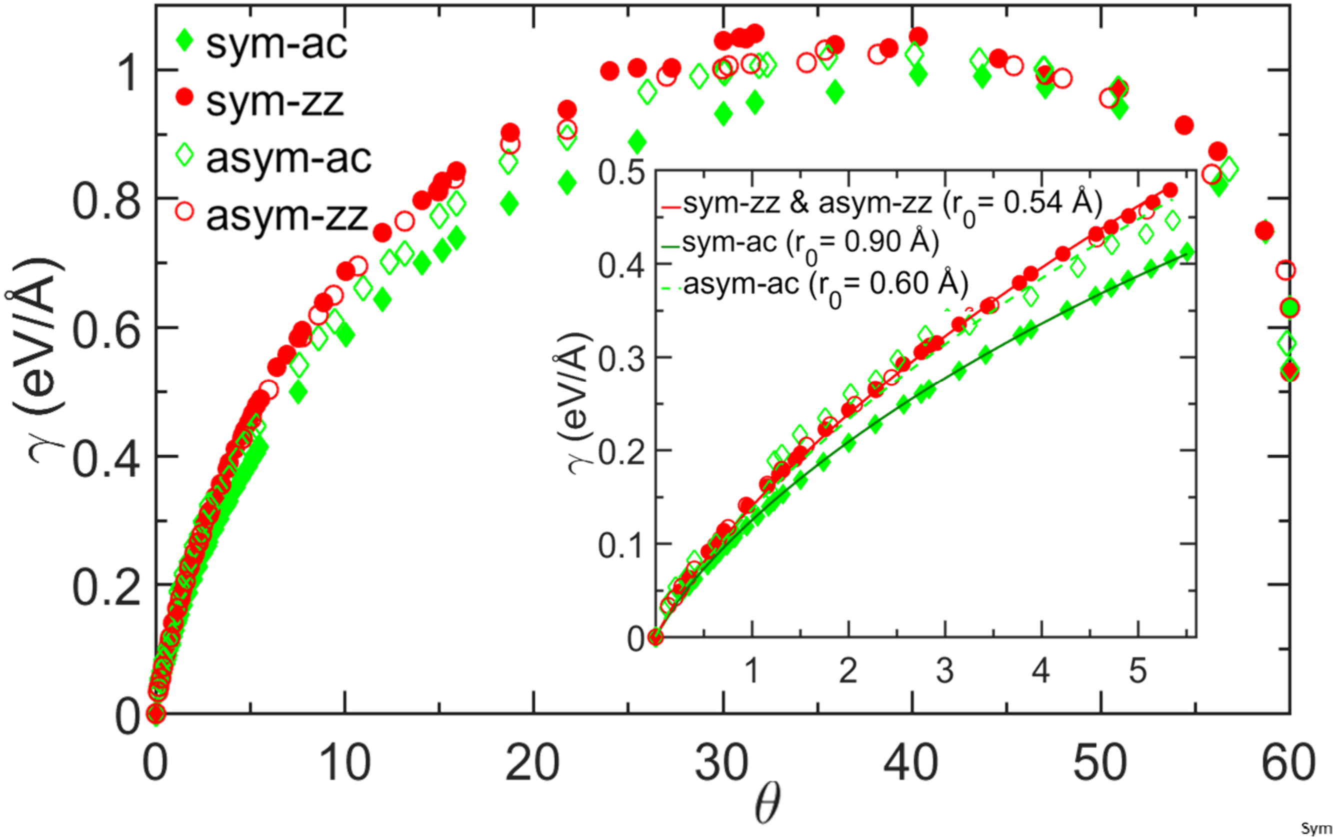
$$\left. \underbrace{+\alpha_{AB} n_A n_B + \beta_{AB} n_{AB} \left(\nabla^2 + q_{AB}^2\right)^2 n_B + \frac{w}{2} n_A^2 n_B + \frac{u}{2} n_A n_B^2)}_{\textit{For A/B coupling}} \right\}$$

- α_{AB}: favor A(B) minima on B(A) maxima;
  prevent A/B maxima (atomic sites) overlap
- w, u: allow A/B minima overlap,
  but not necessarily B(A) maxima on A(B) minima;
  important for honeycomb stabilization (*ring-center vacancy*)



- *Dynamics*: conserved $\partial n_{A(B)} / \partial t = \nabla^2 \delta F / \delta n_{A(B)}$
  non-conserved $\partial n_{A(B)} / \partial t = -\delta F / \delta n_{A(B)} + \mu_{A(B)}$

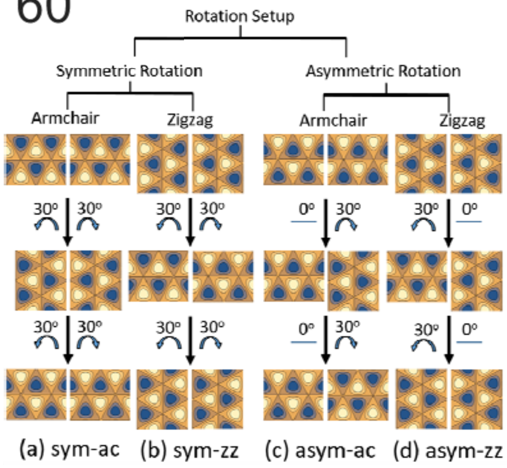
➢ Grain boundary structures and energies: PFC modeling of *h*-BN



- *At small misorientation angles:*
  well fitted to the Read-Shockley equation

$$\gamma = \frac{bY_2}{8\pi}\theta\left[1+\ln(b/r_0)-\ln(2\pi\theta)\right]$$

D. Taha, S.K. Mkhonta, K.R. Elder, Z.-F. Huang, PRL **118**, 255501 (2017)



- Some advantages of PFC GBs study
  - *Being able to access large system sizes and diffusive time scales* (up to 0.9 µm × 0.3 µm, with 9.1×10^6 equivalent atomic sites)
  - *Without any predetermined setup of defect cores* (important for identifying complex defect structures)
  - *Across the full range of GB misorientations* (both structures and energies)

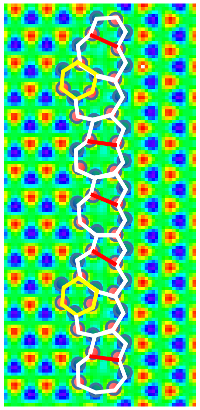
Sample results for special angles:

$\theta = 30^{\circ}$ (armchair/zigzag)

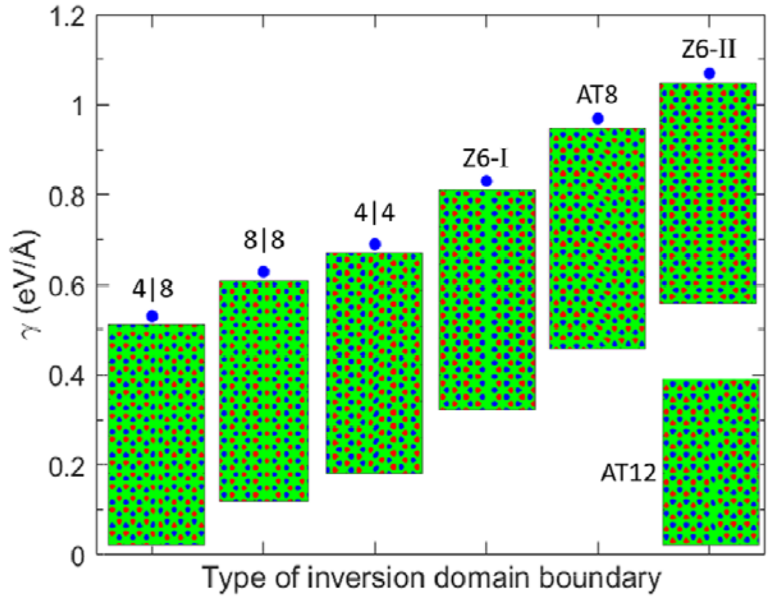
graphene: *7|5|7 fly-heads*

(MD; by Y. Liu, B.I. Yakobson, Nano Lett. 2010)

PFC h-BN: *7|6|8 fly-heads*



$\theta = 60^{\circ}$ (inversion domain boundaries)

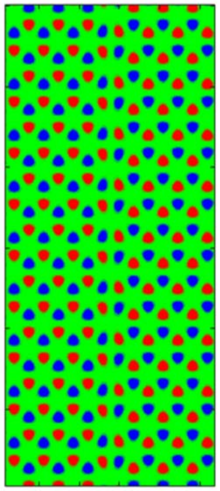


How reliable are these PFC results of defect core structures?

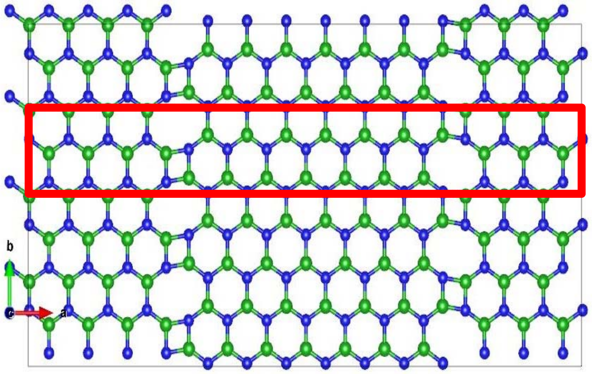
- *Reminder of the PFC model used:*
  a long-wavelength theory (short-wavelength behavior?); no real atomic bonds

- Combination with first-principles DFT calculations (ongoing)
  (*using PFC result as initial configuration; ongoing collaboration with the DFT group in Tsinghua Physics (W.H. Duan and Y. Li)*)

60º IDB of *h*-BN: 4|8 structure

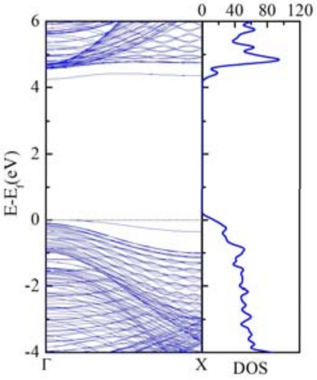


PFC
(γ = 0.53 eV/Å)

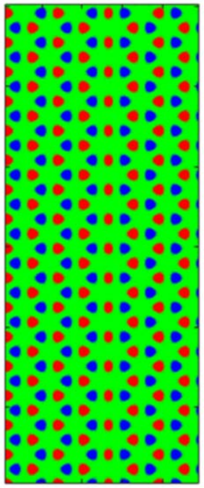


DFT: tilted 4|8
(γ = 0.43 eV/Å
band gap 4.25eV)

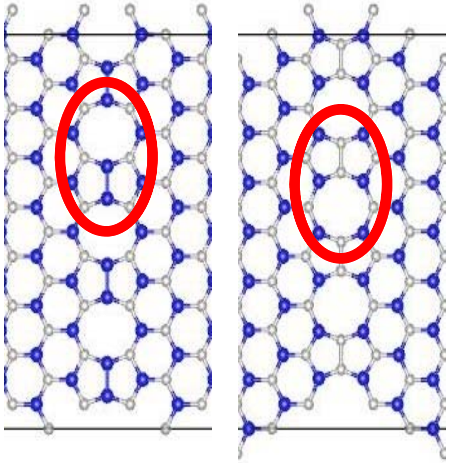
Consistent with previous DFT work (Liu, Zou, Yakobson, ACS Nano 2012; Li *et al*. Nano Lett 2015)



8|8 structure



PFC

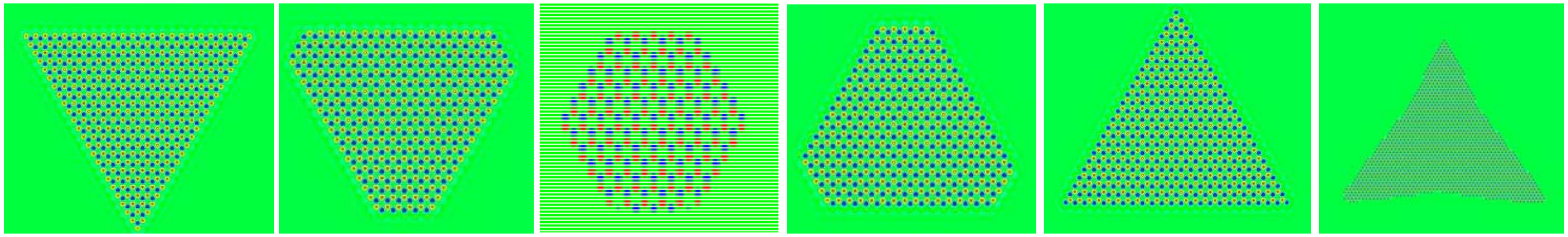


DFT: 8|8 → 5|5|8
(*avoid unsaturated bonds; but form B-B or N-N homoelemental bonds*)

(5|5|8 observed in DFT result of Li *et al*. ACS Nano 2012)

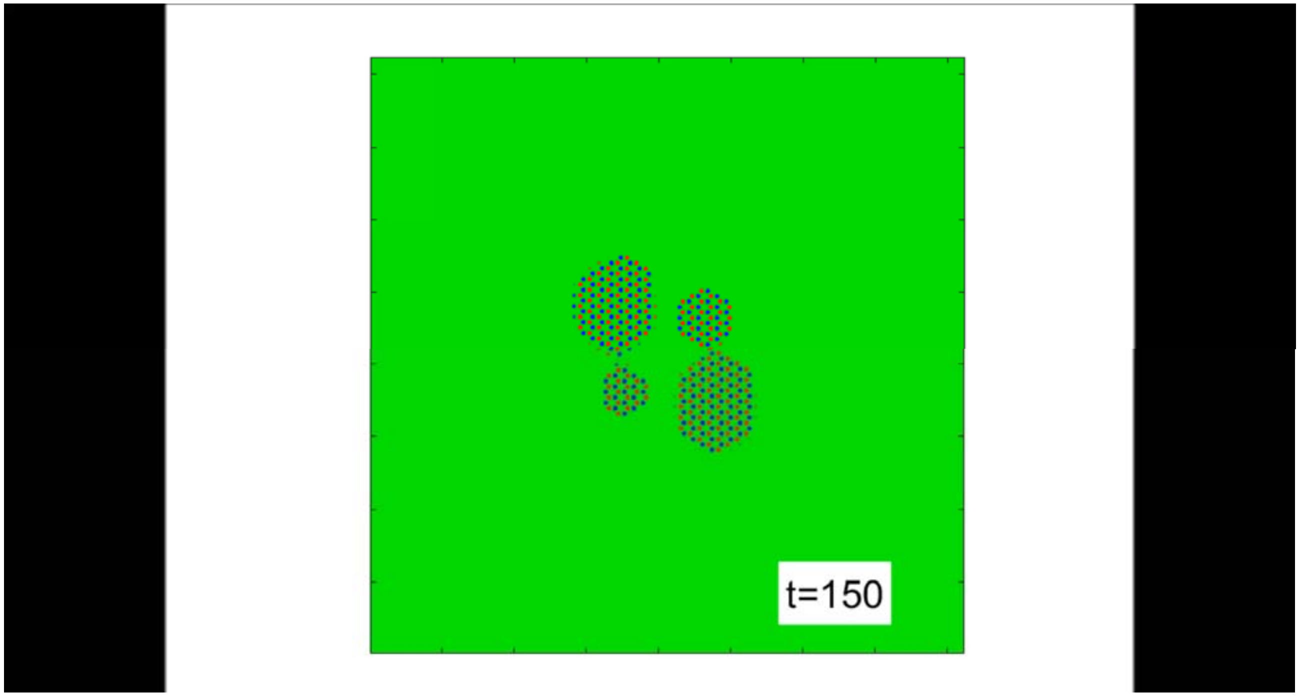
Grain growth and collective dynamics of inversion domains

- Control of grain shape: via chemical potential μ_A vs. μ_B
  (*triangle* $\rightarrow$ *truncated triangle* $\rightarrow$ *hexagon, with zigzag edges*)



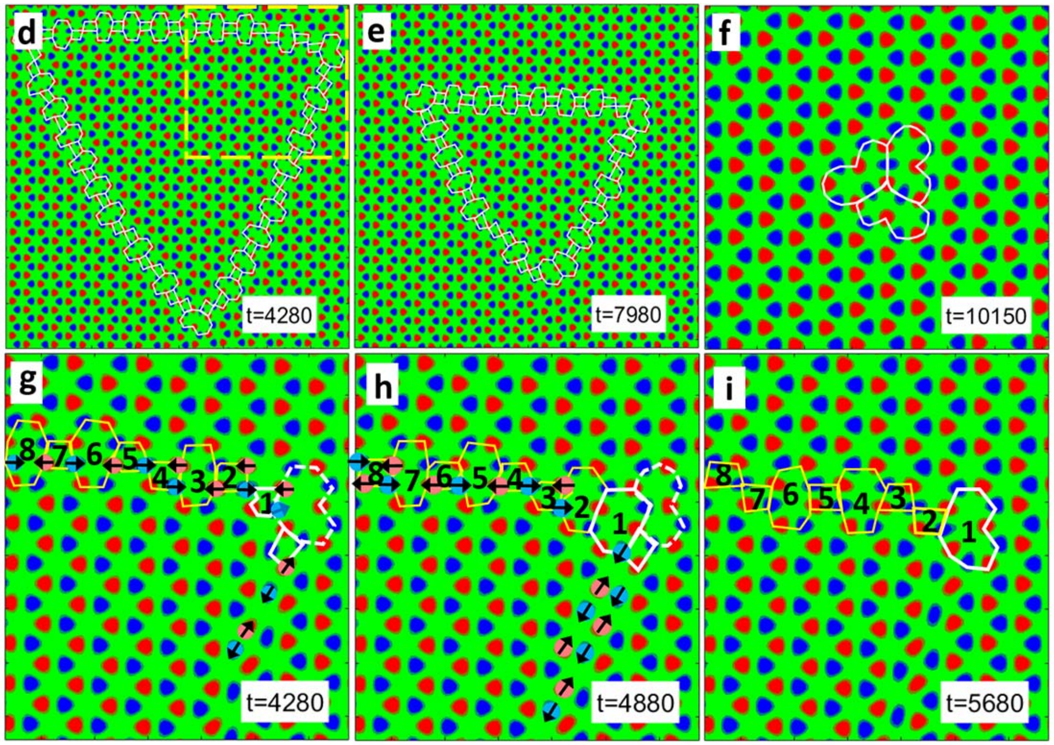
$\mu_A > \mu_B$ $\mu_A = \mu_B$ $\mu_A < \mu_B$

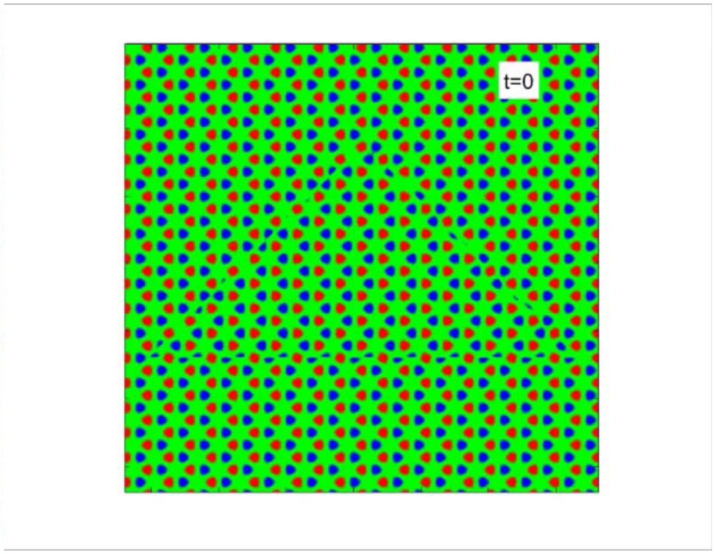
- Grain growth dynamics (for 60º inversion domains)

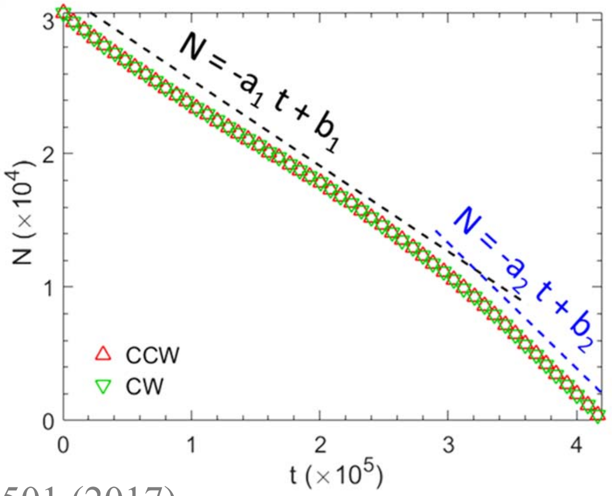


- Collective dynamics

  shape transformation of defect core rings mediated via heart-shaped junctions





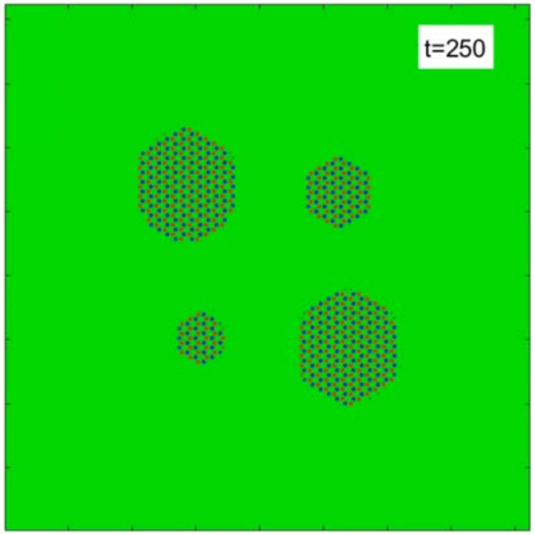


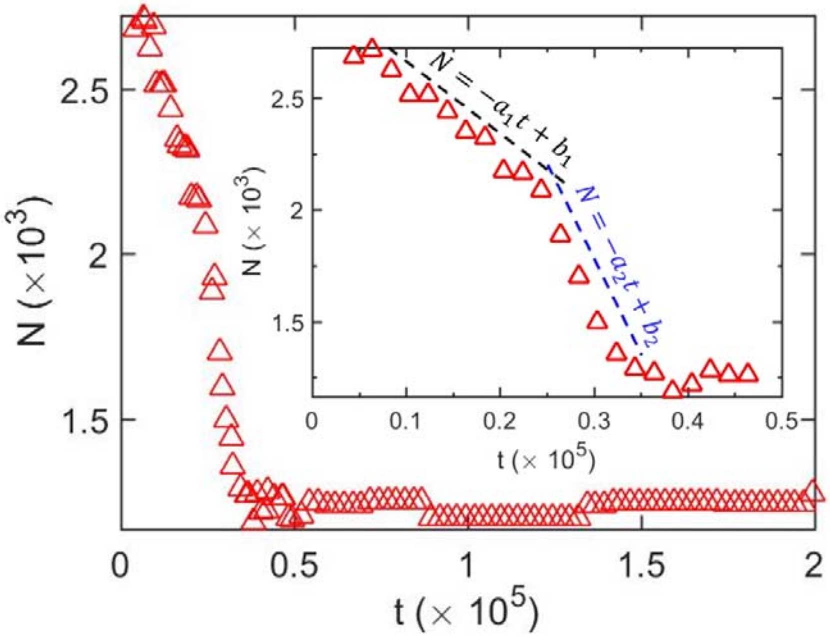
- *Boundary motion: rigid and diffusionless*
- *Grain area shrinking:* $N \sim t$ *(2 linear regimes)*

  → *Grain size* $L \propto t^{\alpha}$, *with* $\alpha = 1/2$

D. Taha, S.K. Mkhonta, K.R. Elder, and Z.-F. Huang, PRL **118**, 255501 (2017)

- *Why the growth exponent* $\alpha = 1/2$? (same as classical curvature-driven growth)
- *Here: straight or weakly curved grain boundaries* (rigid, diffusionless motion)
- Cases of grain growth slowing-down and stagnation? Yes, but still $\alpha = 1/2$





Then what are the growth mechanisms (for inversion domains)?

- *Any grain rotation, translation, or shear-induced deformation?*

  No. Different from the Cahn-Taylor mechanism (normal & tangential motions)

  60º GB: No lattice sites mismatch (always lattice plane continuity);
  due to inversion symmetry breaking in binary lattice

➢ Challenges

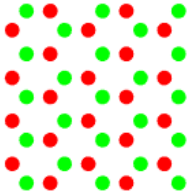
- 3D vs 2D: out-of-plane deformations in 2D materials
  - – Current PFC modeling of 2D materials: planar monolayer (epitaxy)
  - – Need new development of PFC models for 2D layered materials

    Effectively 3D models (for graphene, *h*-BN, MoS_2, ……)

    Allow vertical corrugation/buckling and relaxation of monolayers

    GBs and defects: important for small angles

- Matching to real materials

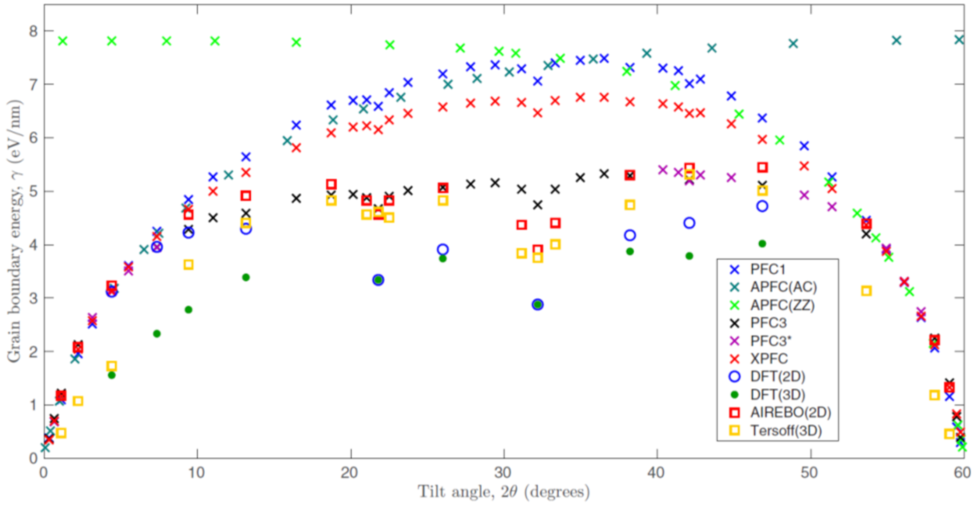


  - – Model construction of the above binary PFC is based on
    - *Crystalline symmetry (including lattice length scales)*
    - *A characteristic of binary compounds: the heteroelemental A-B neighboring is energetically favored as compared to homoelemental A-A or B-B ones*
  - – Model parameters: *phenomenological and dimensionless*

How to match the model to real materials?

– Model parameterization:

- *In principle, determine the model parameters by fitting the direct correlation functions of classical DFT (e.g., from MD data)*
- *For 2D materials:* availability and consistency of atomistic data?



Example: discrepancy in atomistic calculations of graphene GBs (*MD (AIREBO vs Tersoff potential), DFT*)

(P. Hirvonen *et al*. PRB 2016)

- *Current effort of model parameterization to h-BN:*

  Length scale: 1 PFC unit = 0.342 Å (from *h*-BN lattice constant)

  Energy scale: 1 PFC unit = 2.74 eV (from *h*-BN elastic modulus)

- *More rigorous parameterization process?*

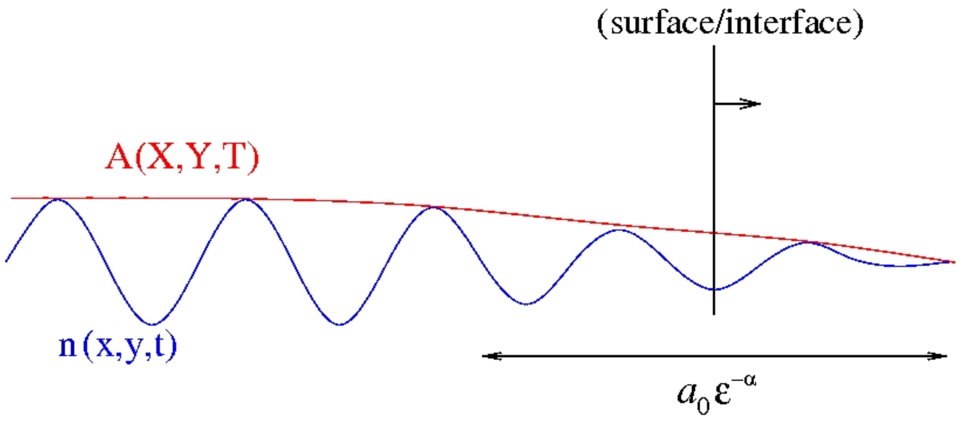
Some recent advances and ongoing challenges

Sample topics:

- Control of crystalline symmetries and structure chirality
  Challenges: competition among length scales; bonding angle control
- Structure and dynamics of graphene-type 2D materials
  Challenges: matching to real materials; out-of-plane 3D deformation
- Topic III: Coupling between micro & meso scales (surface/interface pinning)
  Challenges: Extension to general cases; defect dynamics with Peierls barrier
- Time scales: diffusional dynamics vs. mechanical/elastic relaxation
  Challenges: slow vs. fast; lack of instantaneous mechanical equilibrium
- Atomic density localization and vacancy
  Challenges: conservation of density vs. maxima (sites); vacancy dynamics
- Hydrodynamic coupling (Challenges: micro vs. hydrodynamic/meso scales)
- Others ……

Reminder: Amplitude equation formalism

Scale separation! (*adiabatic*)



- *Standard multiple-scale approach (or singular perturbation)*:

  for slowly varying ***complex*** amplitudes/envelopes

$$n = n_0(X,Y,T) + \sum_{j=1}^{3} A_j(X,Y,T) e^{i\boldsymbol{q}_j^0 \cdot \boldsymbol{r}} + \text{c.c.} \qquad (A_j = |A_j| e^{i\varphi_j})$$

Separate "*fast*" (*x*, *y*, *t*) and "*slow*" **scales** (*X*, *Y*, *T*)

$$X = \epsilon^{1/2} x, \quad Y = \epsilon^{1/2} y, \quad T = \epsilon t$$

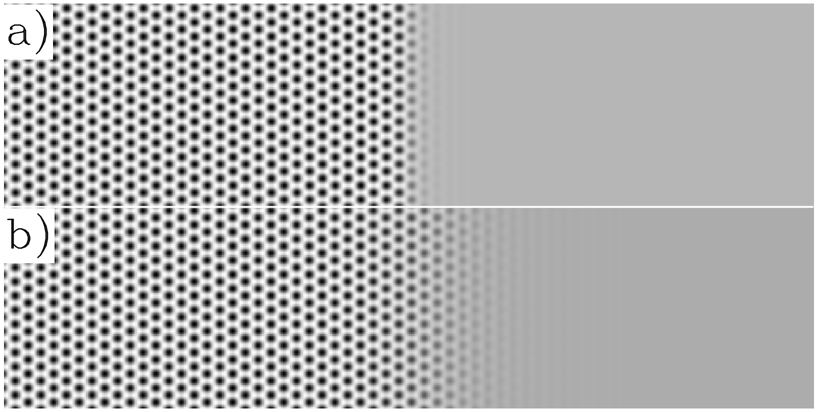
→ *Amplitude Equations* (*single-component*)

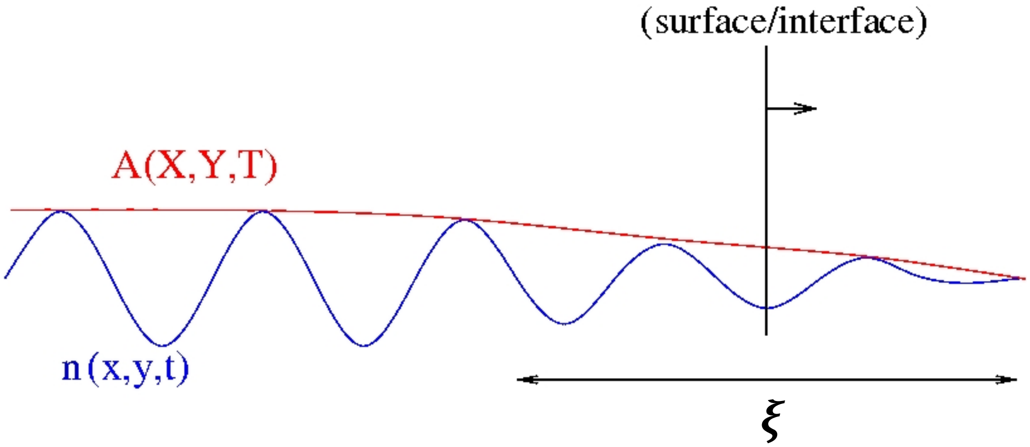
$$\partial A_j / \partial t = -q_0^2 \delta \mathcal{F} / \delta A_j^*,$$

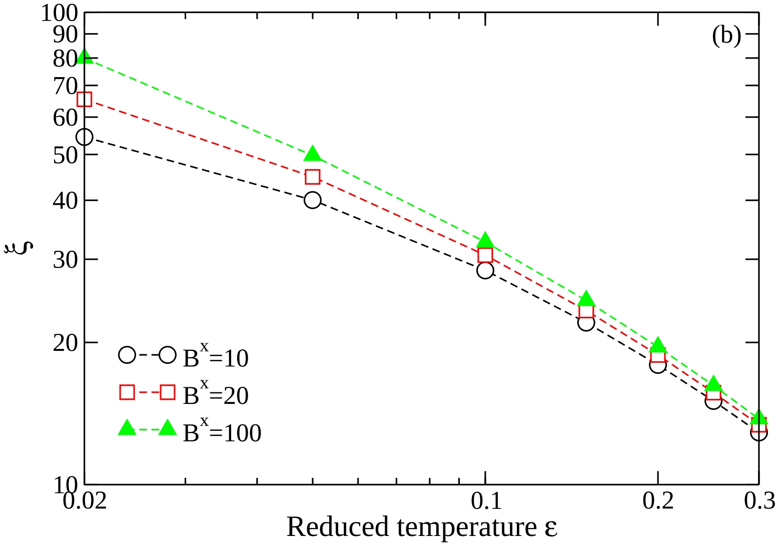
$$\partial n_0 / \partial t = \nabla^2 \delta \mathcal{F} / \delta n_0,$$

Back to some fundamentals:

Solid Liquid







High T (*diffuse*) → Low T (*sharp*)

$\xi >> a_0$: The Phase-Field limit

→ fast/slow scale separation

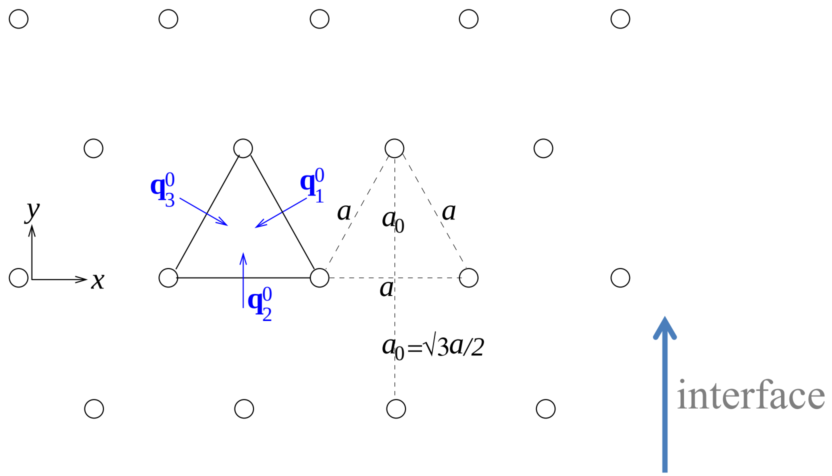
(Note: atomic layer spacing $a_0 = 2\pi/q_0 \sim 6.28$)

Nonadiabatic Effects

- Lower temperature → larger ε → sharper surface/interface

→ **Scale coupling** between *slowly varying* amplitudes and the underlying "*fast*" periodic crystal structure

→ ***Nonadiabatic corrections***



$$\partial A_1/\partial t = -q_0^2\delta\mathcal{F}/\delta A_1^* + \underbrace{\frac{1}{\lambda_0}\int_y^{y+\lambda_0} dy' 3q_0^2\left[2(g-3n_0)A_1A_2^* - 3(A_1^2A_3 + A_2^{*2}A_3^*)\right]}_{\text{“slow”}}\underbrace{e^{-iq_0y'}}_{\text{“fast”}}$$

(Note: A_j (j=1,2,3) and n_0 are of "slow" scales ($\varepsilon^{1/2}x$, $\varepsilon^{1/2}y$, εt).
If no scale coupling, the nonadiabatic term = 0.)

Z.-F. Huang, PRE **87**, 012401 (2013)

- How about binary alloys?

(n: atomic number density; ψ: alloy concentration field)

$$\partial n / \partial t = \nabla^2 \frac{\delta F}{\delta n} + m \nabla^2 \frac{\delta F}{\delta \psi}$$

$$\partial \psi / \partial t = m \nabla^2 \frac{\delta F}{\delta n} + \nabla^2 \frac{\delta F}{\delta \psi}$$

$$m = \frac{M_A - M_B}{M_A + M_B}$$

$$(note: when\ M_A = M_B,\ m = 0)$$

(K.R. Elder et al. PRB 2007; Z.-F. Huang, K.R. Elder, and N. Provatas, PRE 2010; K.R. Elder, Z.-F. Huang, and N. Provatas, PRE 2010)

where

$$\begin{aligned} F = \int d\vec{r} \Big\{ & \underline{-\frac{1}{2}\varepsilon n^2 + \frac{1}{2} n \left(\nabla^2 + q_0^2\right)^2 n + \frac{1}{3} g_2 n^3 + \frac{1}{4} n^4} \\ & \underline{+ \frac{1}{2}\left(w_0 + 2v_1 n + g n^2\right)\psi^2 + \frac{1}{4} u_0 \psi^4 + \frac{1}{2} K_0 |\nabla \psi|^2} \\ & \underline{+ 2\alpha n \left(\nabla^2 + \nabla^4\right)(n\psi)} \Big\} \end{aligned}$$

like single-component case

Cahn-Hilliard ψ^4 free energy coupled to atomic density *n*

Compositional strain and coupling

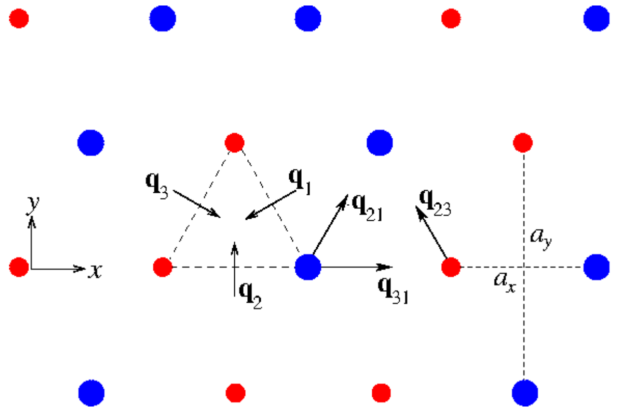
➢ Nonadiabatic Effects in Alloys

- Meso-micro scale coupling and pinning
- For amplitudes A_j: similar to single-component case
- *Additional effect from alloy concentration field*

“slow”

$$\frac{\partial\psi}{\partial t} = m\nabla^2\frac{\delta F}{\delta n_0} + \nabla^2\frac{\delta F}{\delta\psi} - \frac{1}{a_x a_y}\int_x^{x\pm a_x} dx' \int_y^{y+a_y} dy' \Big[\overbrace{(mf_{p_0} + f'_{p_0})}\underline{e^{i\vec{q}_{13}\cdot\vec{r}\,'}} + \overbrace{(mf_{p_1} + f'_{p_1})}\underline{e^{i\vec{q}_{12}\cdot\vec{r}\,'}} + \overbrace{(mf_{p_3} + f'_{p_3})}\underline{e^{i\vec{q}_{32}\cdot\vec{r}\,'}} + \text{c.c.} \Big]$$

“fast”

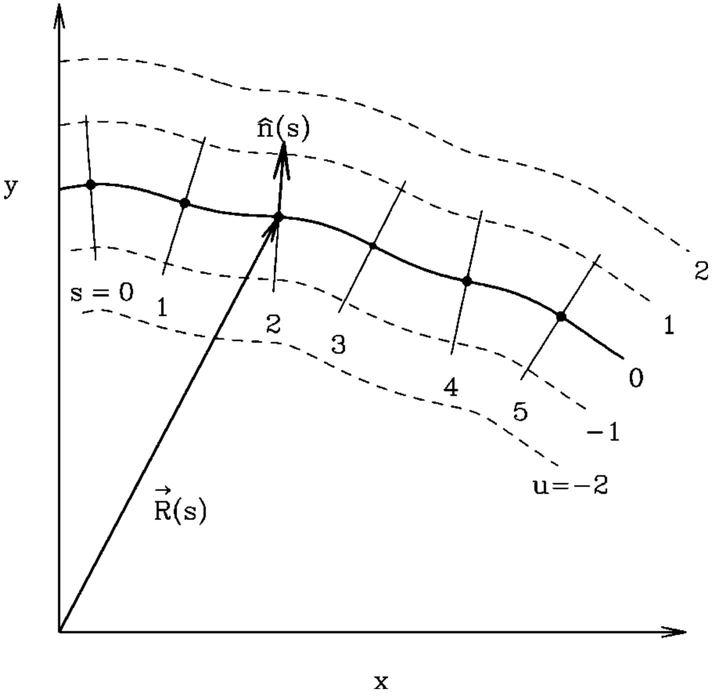


Note: A_j (j=1,2,3), n_0 and ψ are of “slow” scales; $f_{pi} = f_{pi}(A_j, n_0)$, $f_{pi}' = f_{pi}'(A_j, \psi)$

Z.-F. Huang, PRE **93**, 022803 (2016)

- Further coarse-graining → Interface equations of motion

Use local curvilinear coordinate (*u, s*)



$$\hat{n} = \hat{x}\sin\theta + \hat{y}\cos\theta, \qquad \hat{t} = \partial\hat{n}/\partial\theta$$

$$local\ curvature: \ \kappa = \nabla\cdot\hat{n} = \partial\theta/\partial s$$

normal velocity of interface:

$$v_n = -\partial u/\partial t \simeq \partial h/\partial t/[1+(\partial_x h)^2]^{1/2}$$

($h(x,t)$: *surface height*)

➢ Interface equations of motion

- ***A generalized Gibbs-Thomson relation:***

Lattice pinning: scale coupling effect

$$\underline{\mu_k^{-1}(\theta,m)v_n = -\Delta - (\gamma+\gamma'')\kappa} - p_0(\theta)\sin(qh_n+\varphi) + \eta_v$$

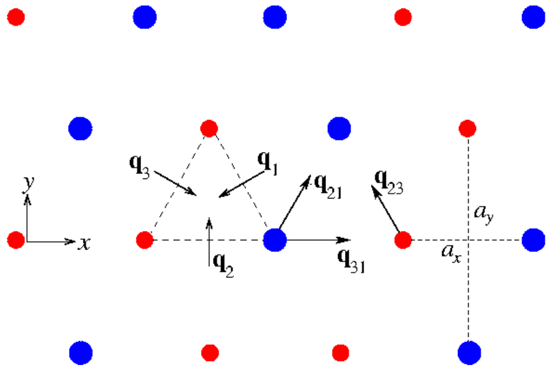
noise

Surface/interface energy

Kinetic coefficient

Interface supersaturation

(thermodynamic driving force, by e.g., *external flux*)



Note: all of μ_k, γ, p_0 and φ are anisotropic!

From the generalized Gibbs-Thomson relation, set $\zeta_0 = 1/\mu_k$, $\lambda = -\Delta$, $\sigma = \gamma+\gamma''$

$$\zeta_0 v_n = \lambda - \sigma\kappa - p_0 \sin(q_0 h + \varphi) + \eta_v$$

use $v_n = -\partial u/\partial t \simeq \partial h/\partial t/[1+(\partial_x h)^2]^{1/2}$ (*h: interface height*)

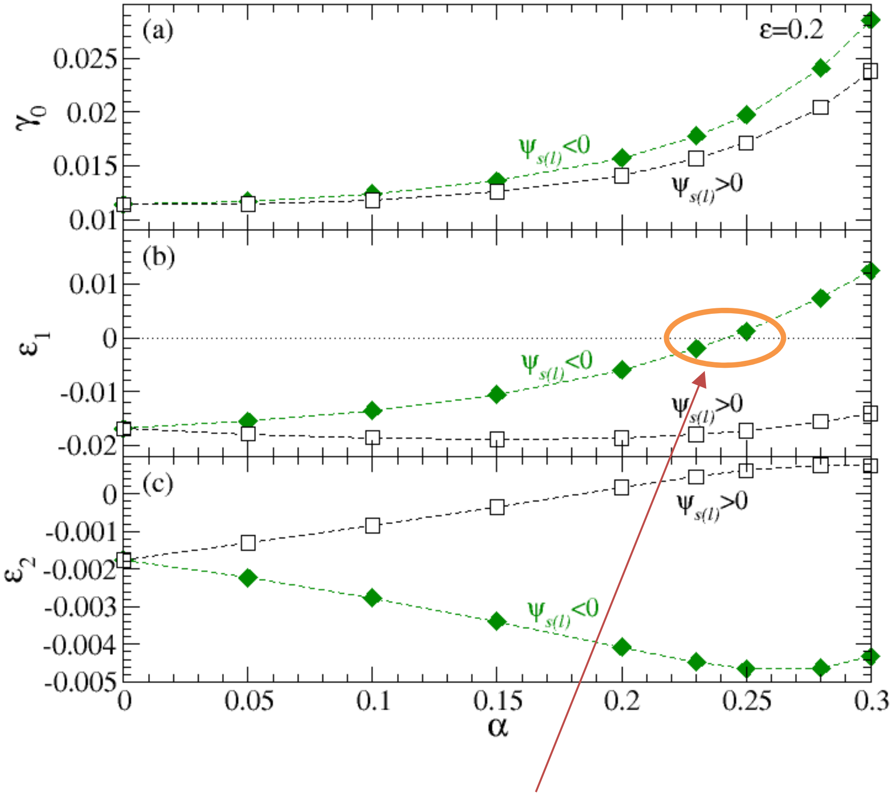
⇒ A driven <u>sine-Gordon</u> equation

$$\zeta_0 \partial h/\partial t = F_0 + \overbrace{\sigma\nabla^2 h} + \frac{\lambda}{2}|\nabla h|^2 - \overbrace{p_0 \sin(q_0 h + \varphi)} + \eta_v$$

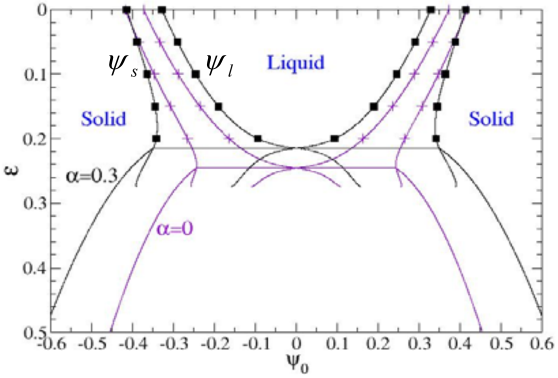
(Hwa-Kardar-Paczuski equation, or Nozieres-Gallet plus KPZ nonlinearity)

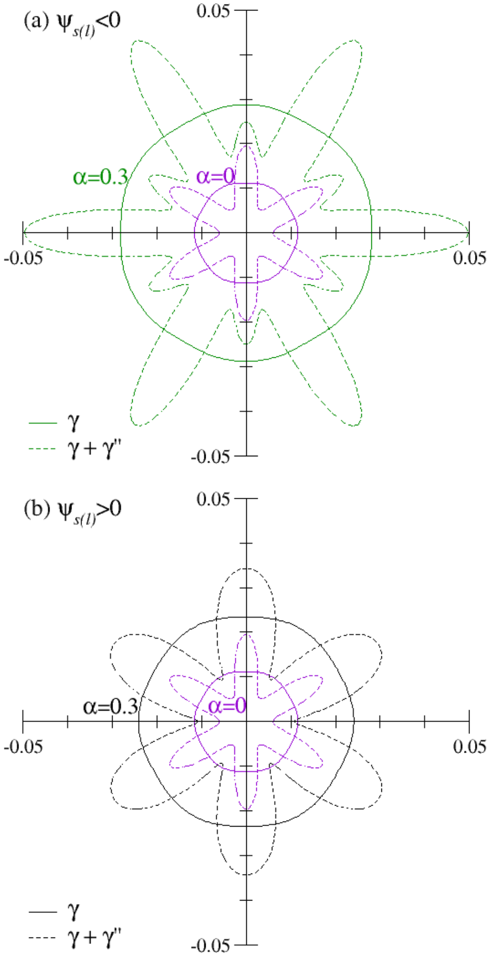
- Anisotropy of solid-liquid interfacial energy

$$\gamma = \gamma_0 (1 + \varepsilon_1 \cos 6\theta + \varepsilon_2 \cos^2 6\theta + \ldots)$$



- Reversal of γ anisotropy (at large enough α): *Shape change of polar plots* (*30° rotation*)
- Important effect of alloy compositional strain and interface stresses





- Effect of alloy compositional strain

Positive vs negative branches of solidus-liquidus lines (for $\alpha > 0$):

$\psi_{s(l)} < 0$: *at interface* $\psi > \psi_s$

→ *surface enrichment of larger atom A*

→ *compressive interface stress*

$\psi_{s(l)} > 0$: *at interface* $\psi < \psi_s$

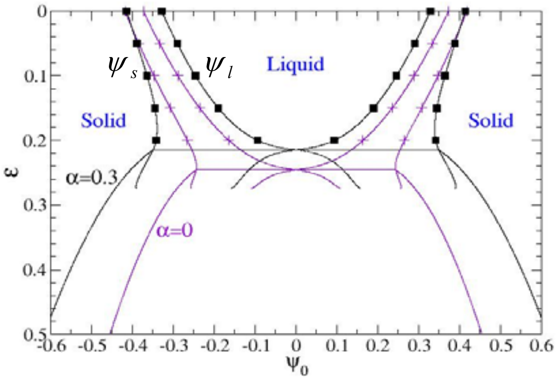
→ *surface enrichment of smaller atom B*

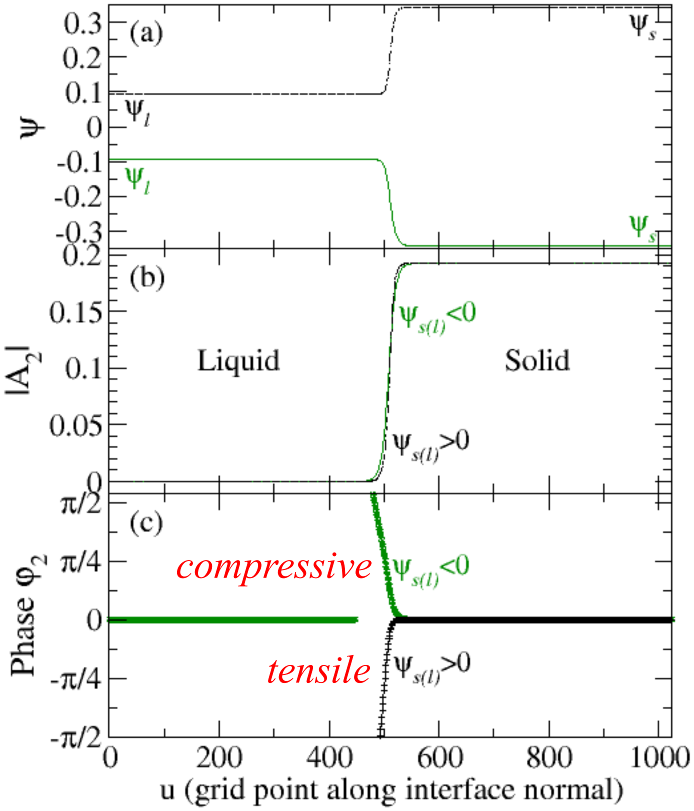
→ *tensile interface stress*

(note: $\alpha > 0$ larger A, smaller B; $\psi = (\rho_A - \rho_B)/\rho$)

⟶ Interface preferential segregation and compositionally induced interface stresses

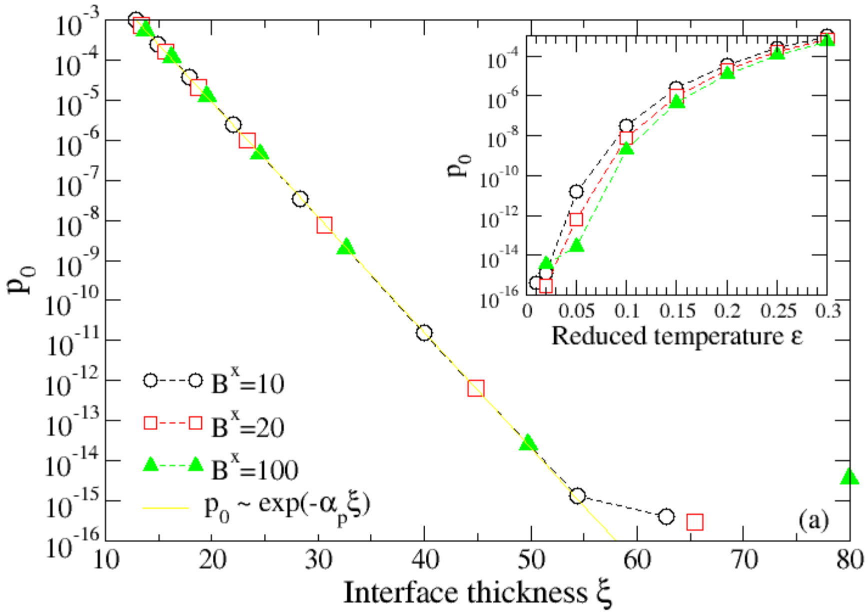
Meso-meso coupling between structural and concentration profiles





- Scaling of lattice pinning strength (micro-meso scale coupling)

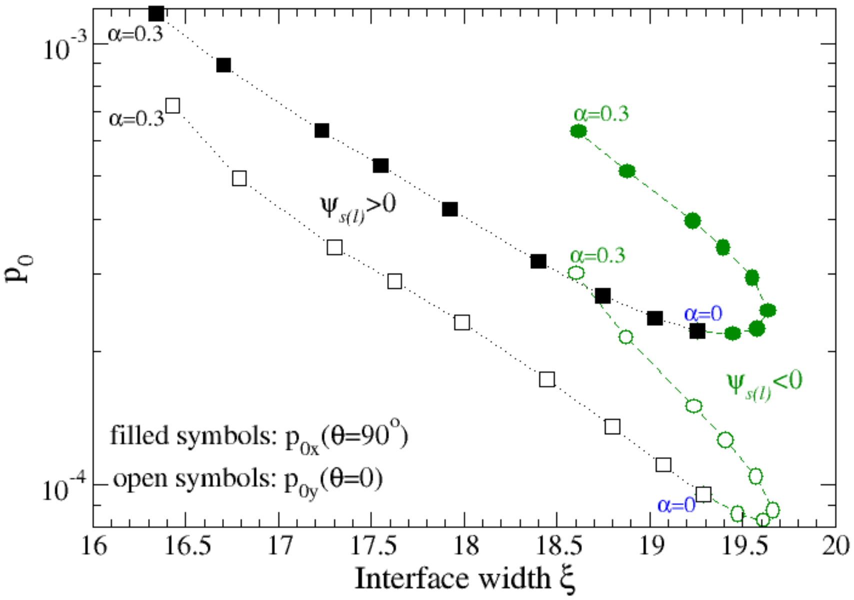
Single-component



$$p_0 \sim e^{-\alpha_p \xi} \quad (\alpha_p = 0.6620 \pm 0.0008)$$

Z.-F. Huang, PRE **87**, 012401 (2013)

Binary alloy



- Anisotropic, hysteresis-type behavior
- Asymmetric effect of nonzero α (*compositional strain*) and interface preferential segregation

Z.-F. Huang, PRE **93**, 022803 (2016)

Application: *Liquid/Solid Front Motion*

- Continuous growth mode ($|F_0| > p_0$, *e.g.*, small ε and high temperature)

  Exact solution (1D):

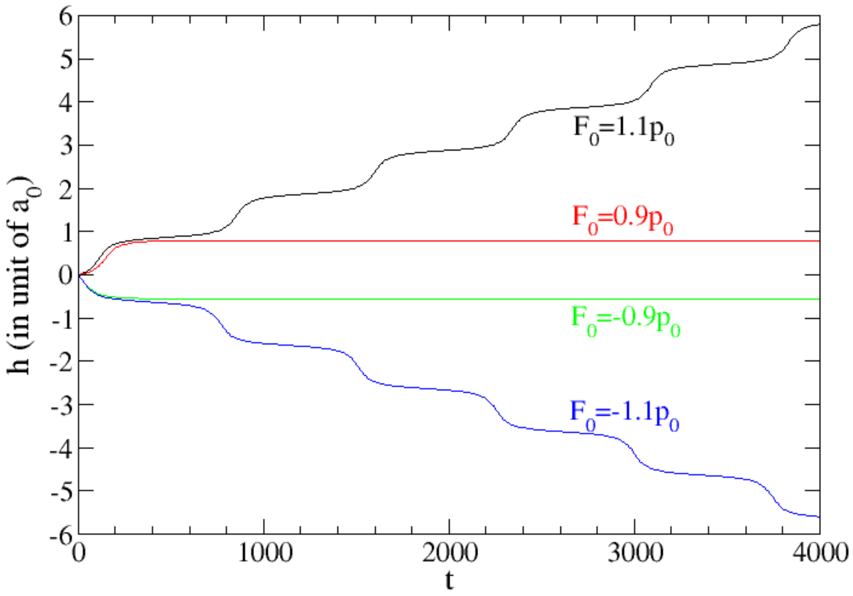
  $$y_h = \{2\arctan[\beta\tan(q_0(v_0^2 - p^2/\zeta^2)^{1/2}t/2 + \tau_0)] - \varphi_0\}/q_0$$

  Front motion by "jumps" of distance a_0, exactly one atomic layer spacing!

- Activated/nucleated growth mode ($|F_0| < p_0$, *e.g.*, large ε and low temperature)

  Exact solution also available

  The front is ***locked/pinned*** by the underlying crystalline potential



(consistent with crystal growth theory of Cahn (J.W. Cahn, Acta Metall. 1960, 1964))

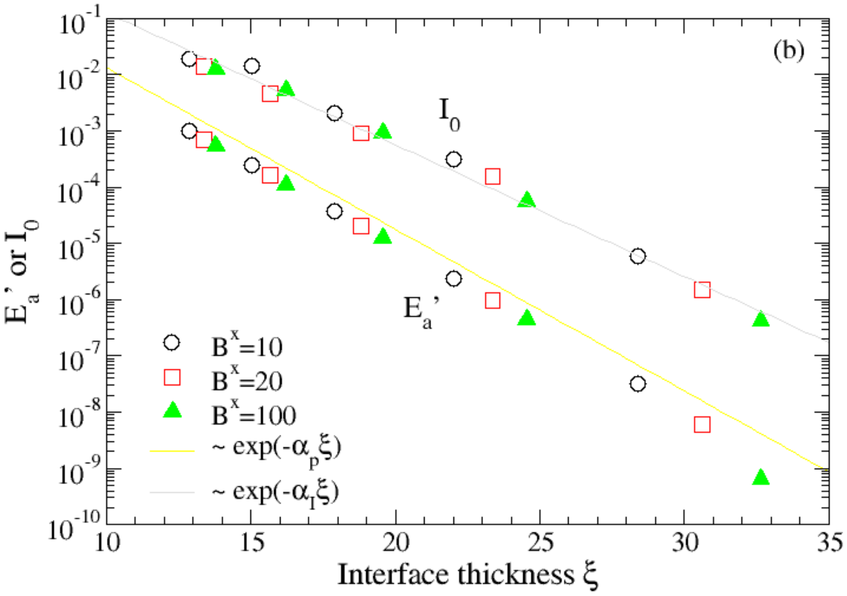
- Activated/nucleated growth mode
  ($|F_0| < p_0$, *e.g.*, large ε and low temperature)

Thermal noise/fluctuations important → ***A stochastic, escape problem***

→ An activated, thermal nucleation process (Kramers' escape rate)

$$I = I_0 e^{-E_a/k_B T}$$

(Note: *not exactly Arrhenius*, due to $I_0(\mathrm{T})$ and $E_a(T)$.)



The prefactor

$$I_0 = (p_0^2 - F_0^2)^{1/2}/\zeta_0$$

Activation energy

$$E_a = \frac{2}{\vartheta q_0^3 \Gamma_0}\left[\left(p_0^2 - F_0^2\right)^{1/2} - |F_0| \arccos\left(|F_0|/p_0\right)\right]$$

(Z.-F. Huang, PRE **87**, 012401 (2013))

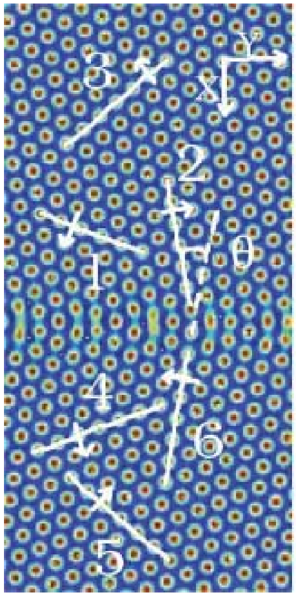
Challenges

- Extension to general scenarios
  - Various types of complex interfaces (not limited to the simplified configuration studied above)
  - Both 2D and 3D (*pure, alloying, or sublattice-ordered materials*)

- Defect dynamics with Peierls barrier
  - Example: grain boundary motion

$$\dot{y}_{\mathrm{gb}} = [f_0(\epsilon) - p(\epsilon)\sin(2q_0 y_{\mathrm{gb}}\sin(\theta/2) + \varphi_0)]/\zeta(\epsilon)$$

    - $p(\varepsilon)$: *pinning force, due to fast/slow scale coupling*
    - *At low* T (with $p > f_0$), *defects will be locked/pinned by lattice structure* (*Peierls force*); *thermally activated motion*
    - *Related to GB roughening*
  - Relation to grain growth dynamics and stagnation



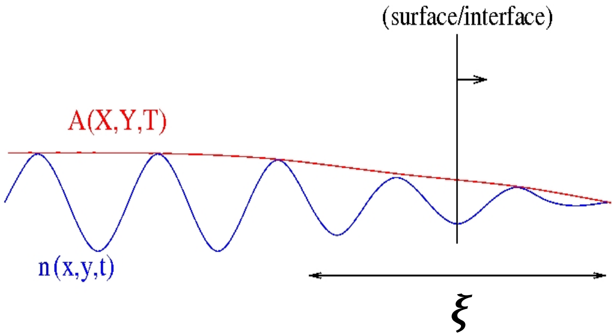
Summary

Multiple-scale modeling for *nonequilibrium* complex systems

- Across different scales: *Microscopic*
  Mesoscopic
  Continuum/hydrodynamic
- Main feature/motivation: *Maintain the efficiency advantage of continuum approach through coarse-graining processes, while at the same time incorporating significant effects of detailed crystalline structures*.
- ***PFC method:*** Essentially a continuum field theory; long wavelength, coarse-grained; a wide range of applications; advantages & disadvantages

  Challenges

  - *Micro vs. Meso scales and coupling; reliability of short-wavelength behavior*
  - *Matching to real materials*
  - ……



- Further development of the theory; Combination with atomistic methods

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