Aalto University
School of Science

MSP Group

Multi-Scale Modeling of Graphene from Nano to Micron Scales

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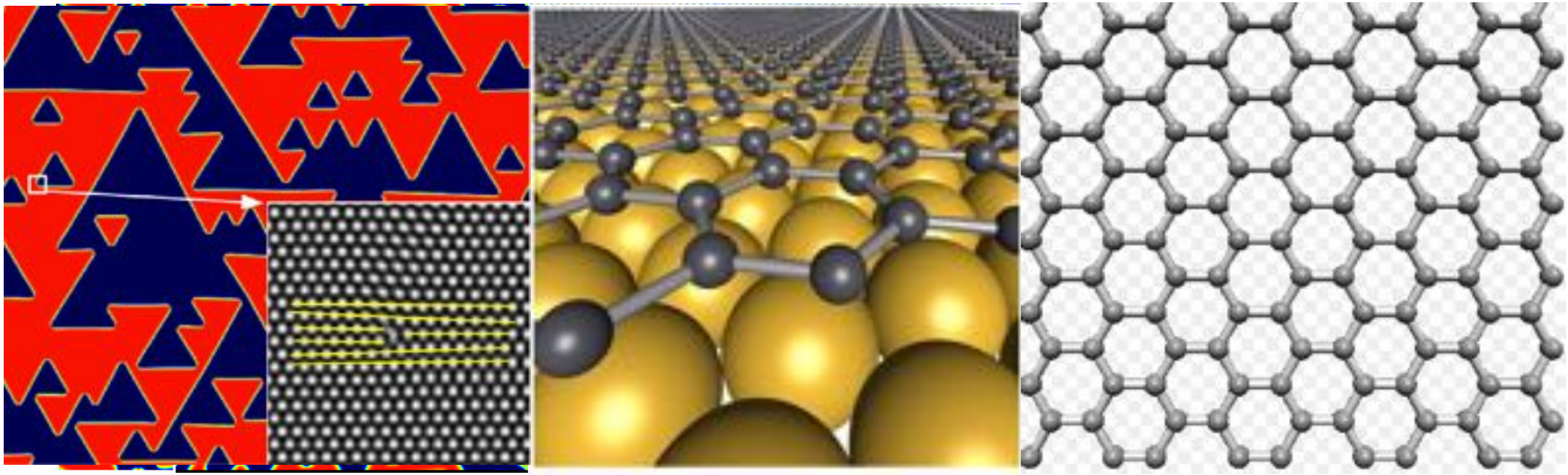
Department of Mathematical Sciences & Physics at Loughborough University, UK



[K.R. Elder *et al.*, PRL (2012); PRB (2013); JCP (2016); P. Hirvonen *et al.*, PRB (2016); Sci. Rep. (2017); Z. Fan *et al.*, PRB (2017), Nano Lett. (2017); K. Azizi *et al.*, Carbon (2017)]

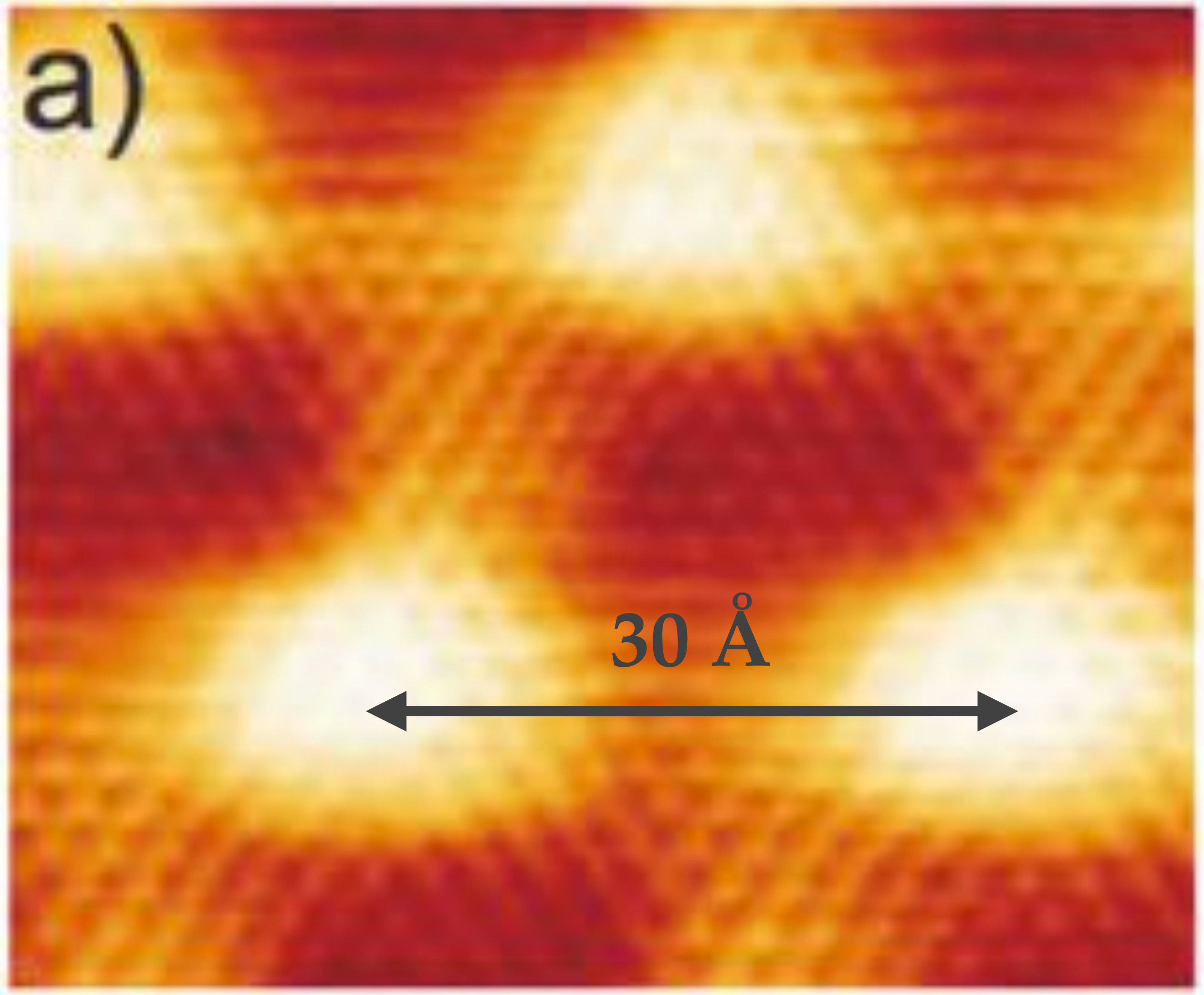
TiTiTyy 26.10.2017

Outline of the Talk

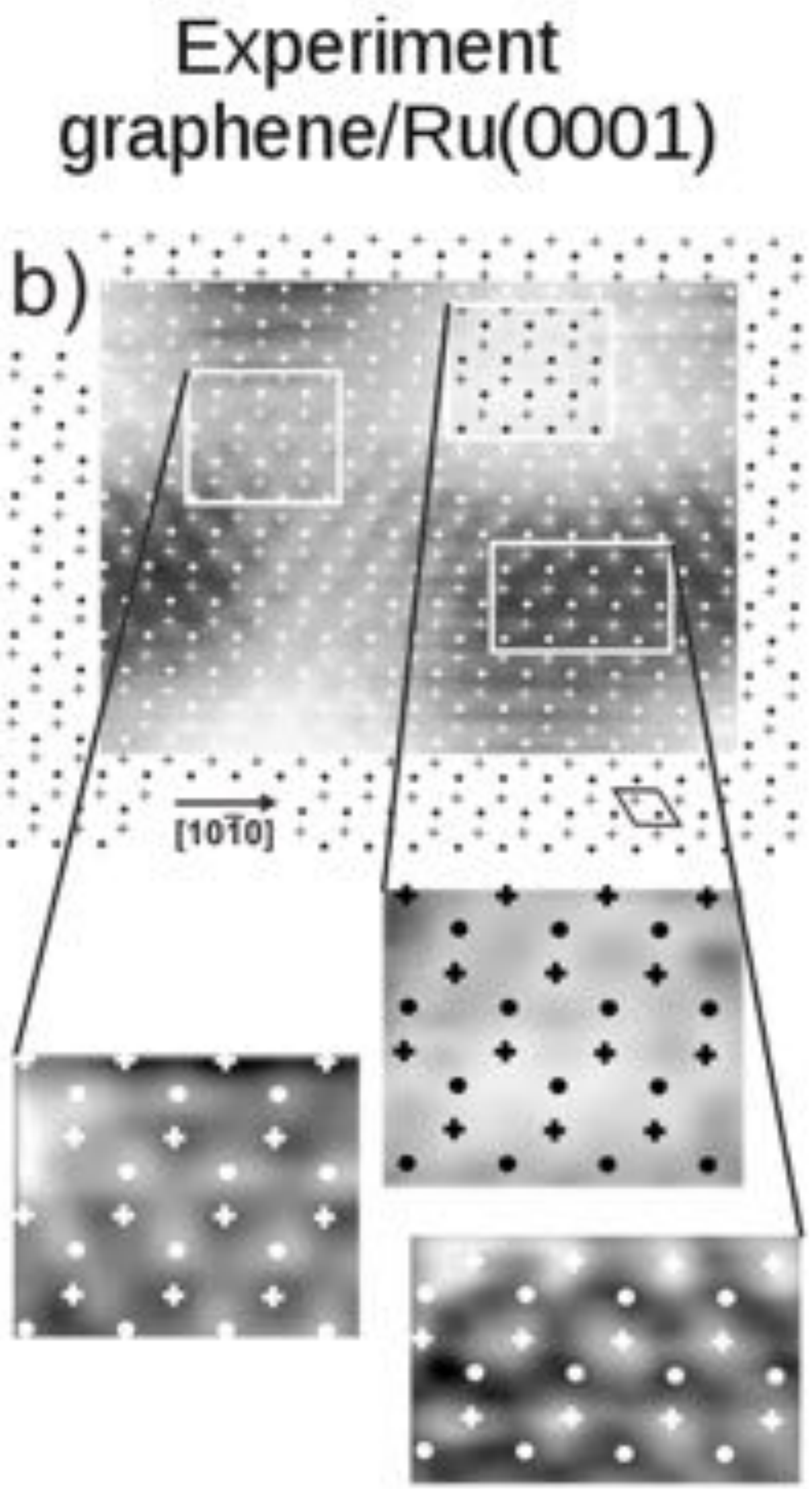
- Introduction to Graphene and Modeling Methods
- Phase Field Crystal Model
- Multi-Scale Modeling Strategy for Graphene
- Large Multigrain Flakes
- Heat Conduction in Graphene
- Summary and Conclusions

Introduction

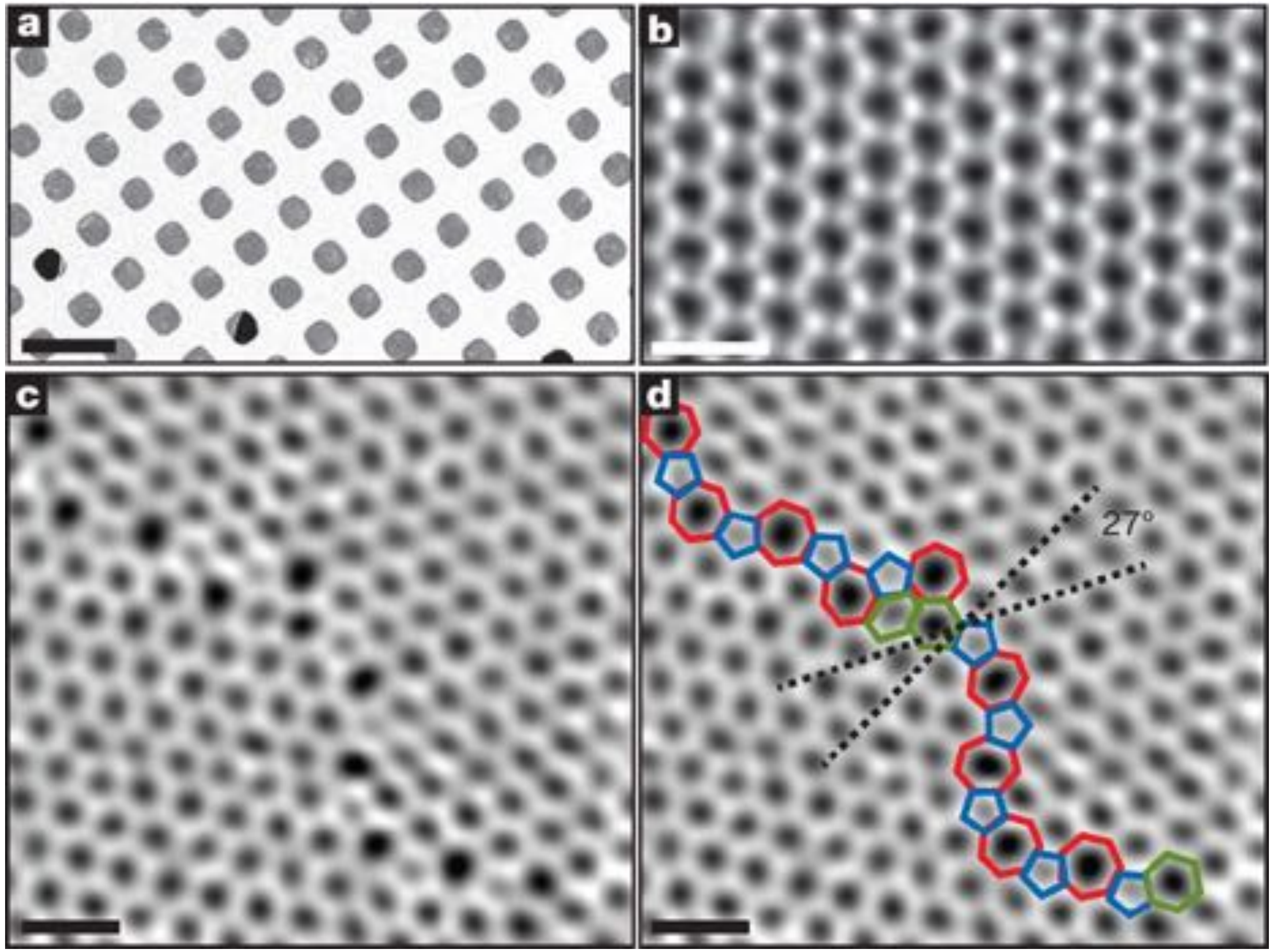
- Graphene is often grown on metal surfaces to achieve epitaxial configurations (usually under tensile stress)



[S. Marchini *et al.*, PRB **76**, 075429 (2006)]

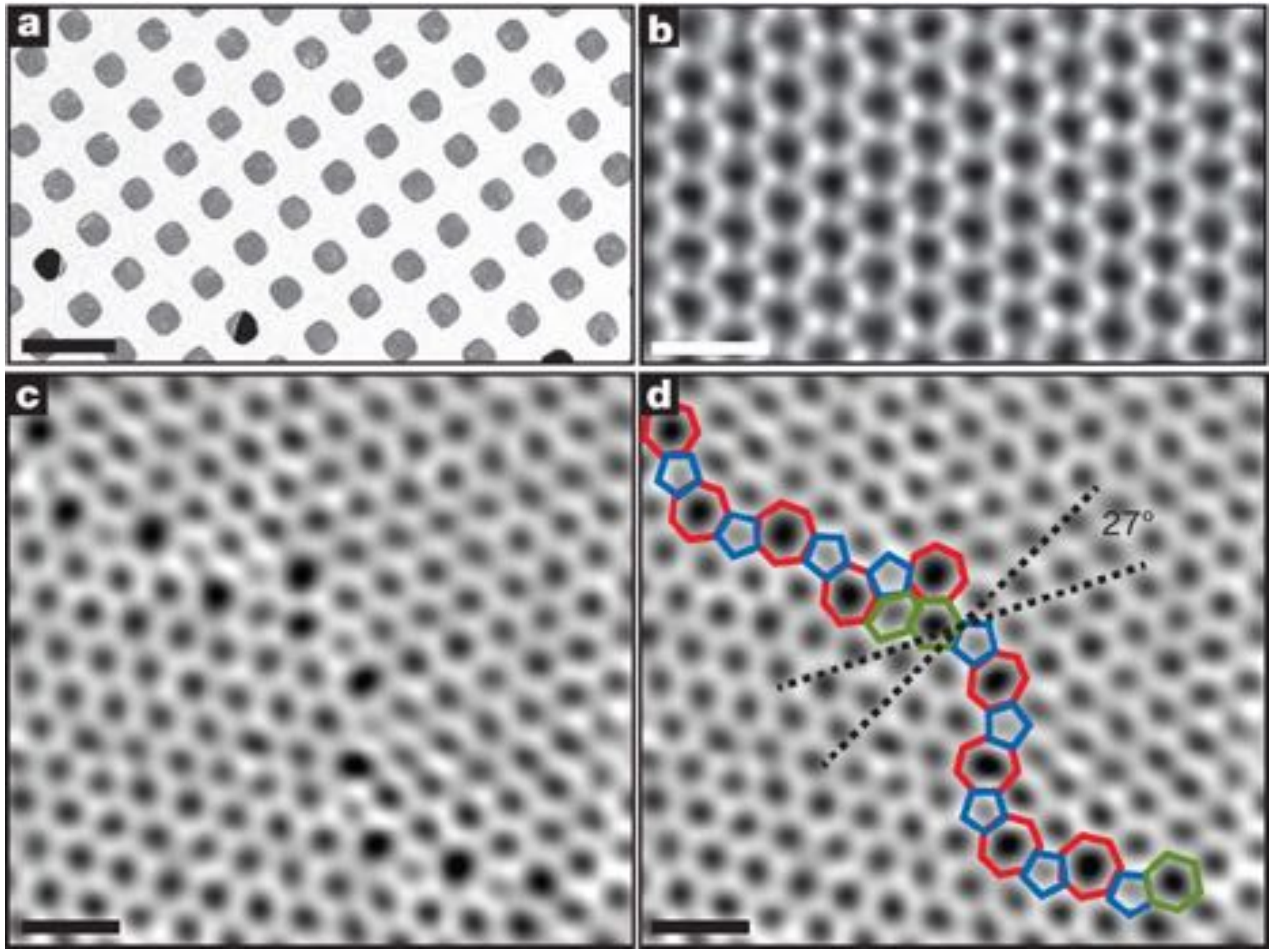


Introduction



High resolution electron microscopy of graphene flakes
[Huang *et al.*, Nature **469**, 389 (2011)]

Introduction



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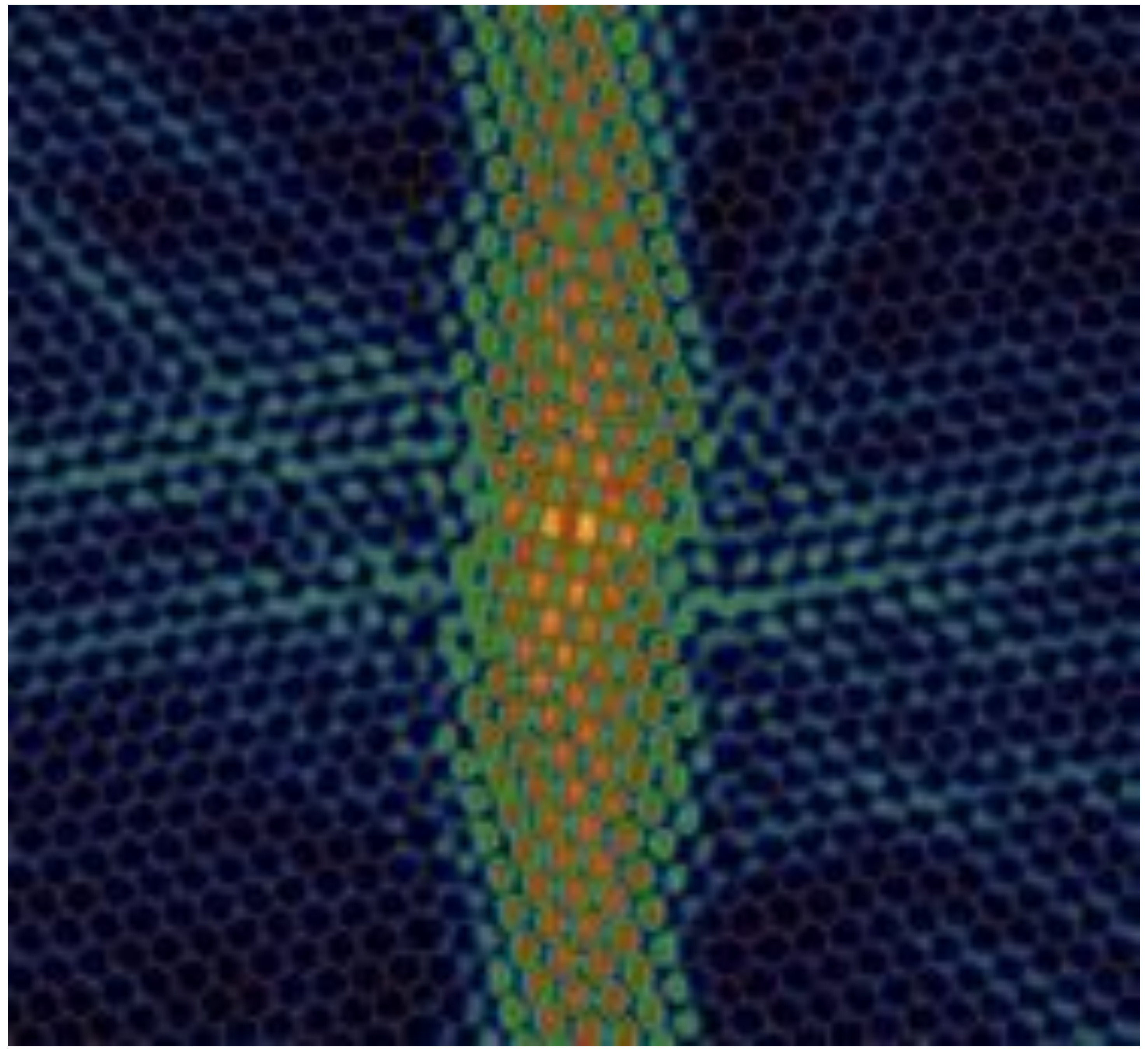
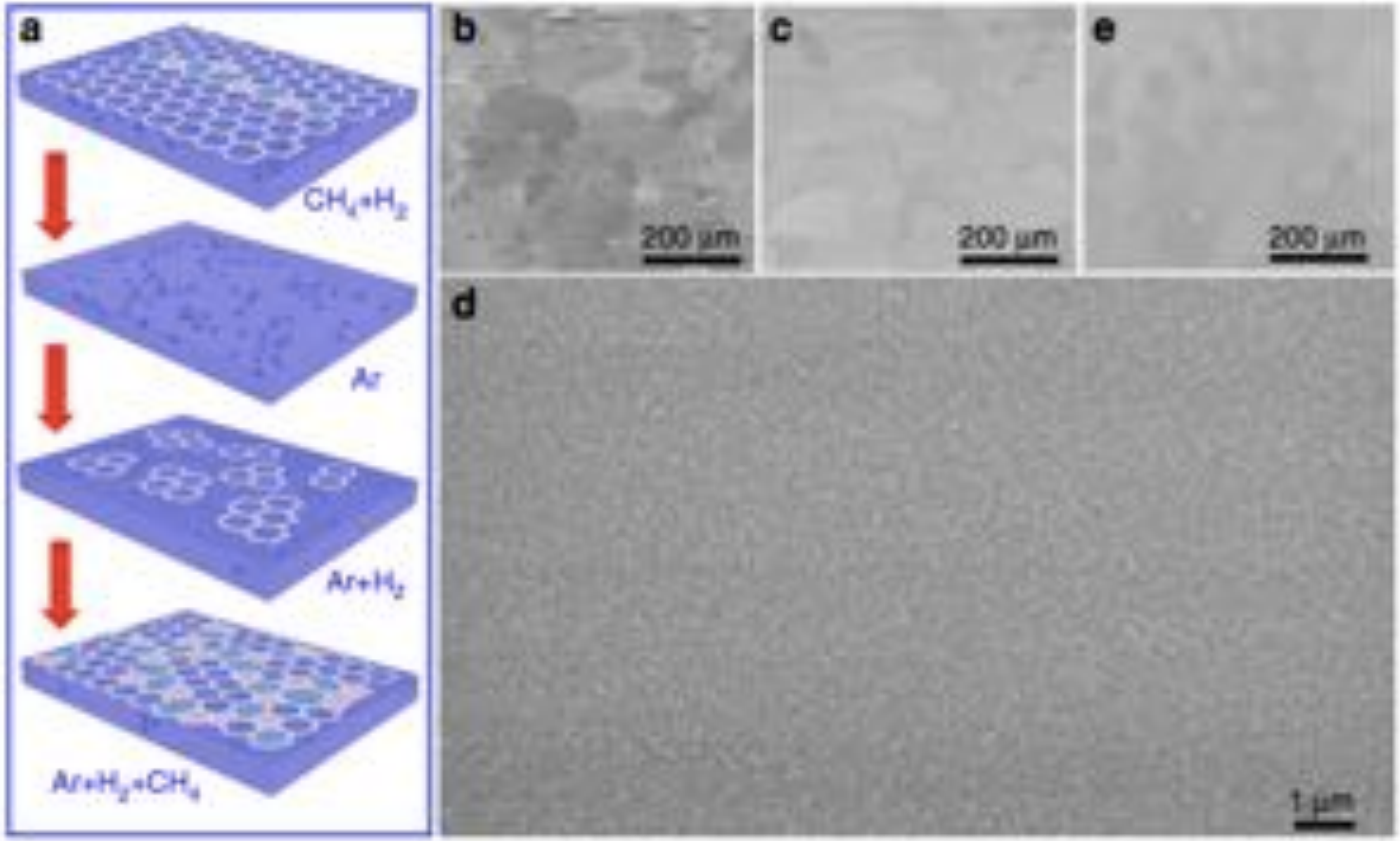


Photonic wave guide between grain boundaries
[Mark *et al.*, J. Nanophoton. **6**, 061718 (2012)]

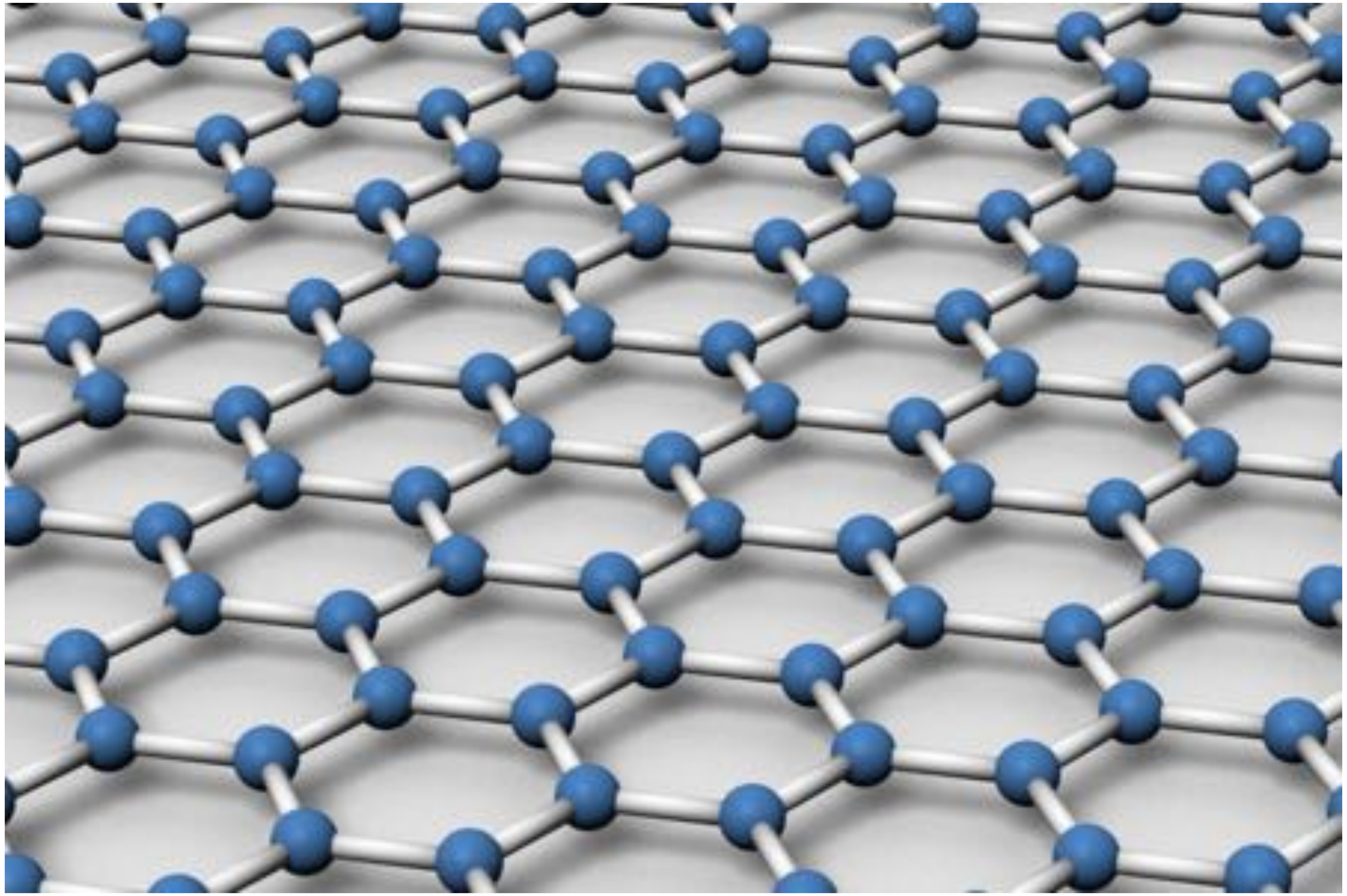
Introduction

- Controlled growth of grains can now be achieved with modified chemical vapour deposition

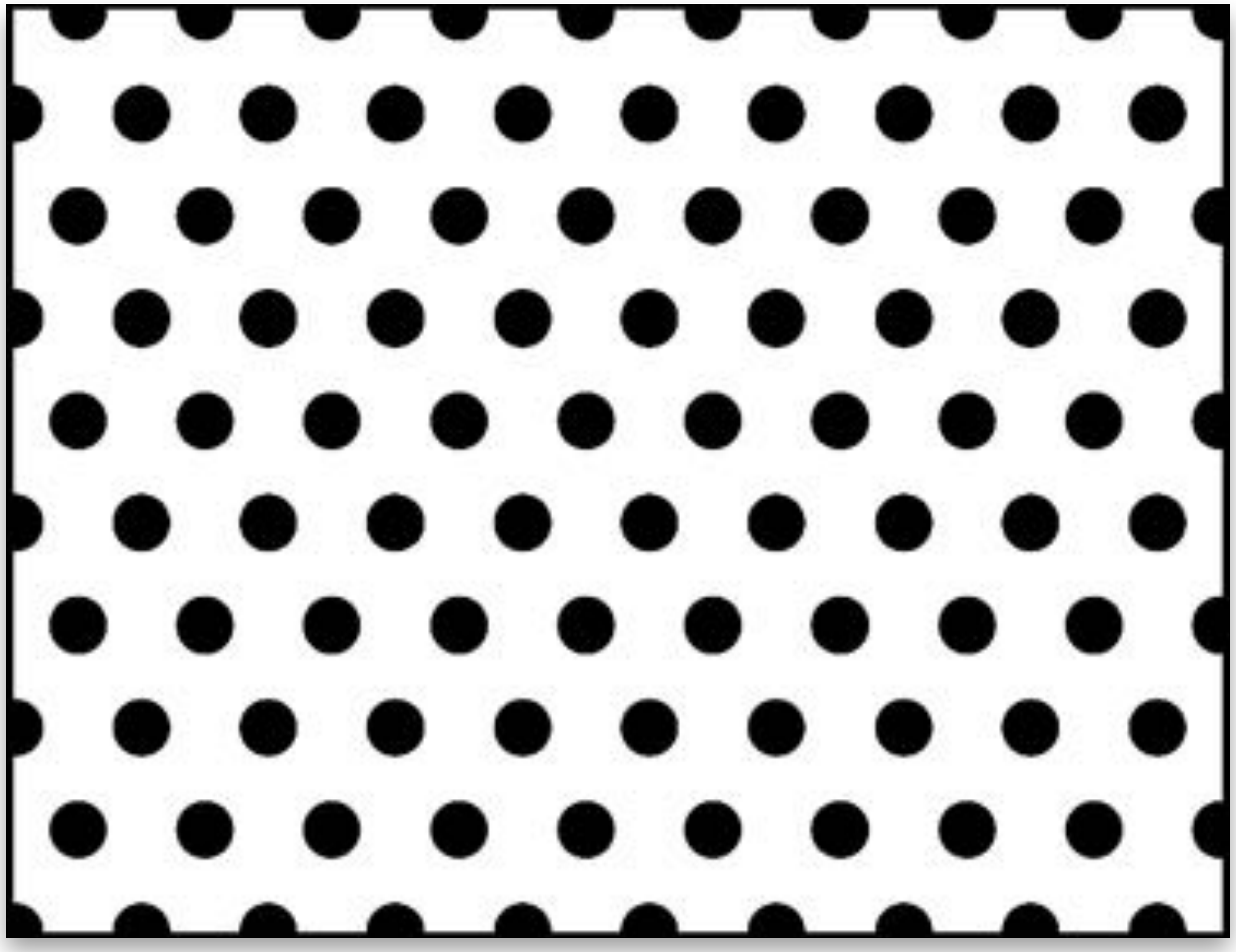


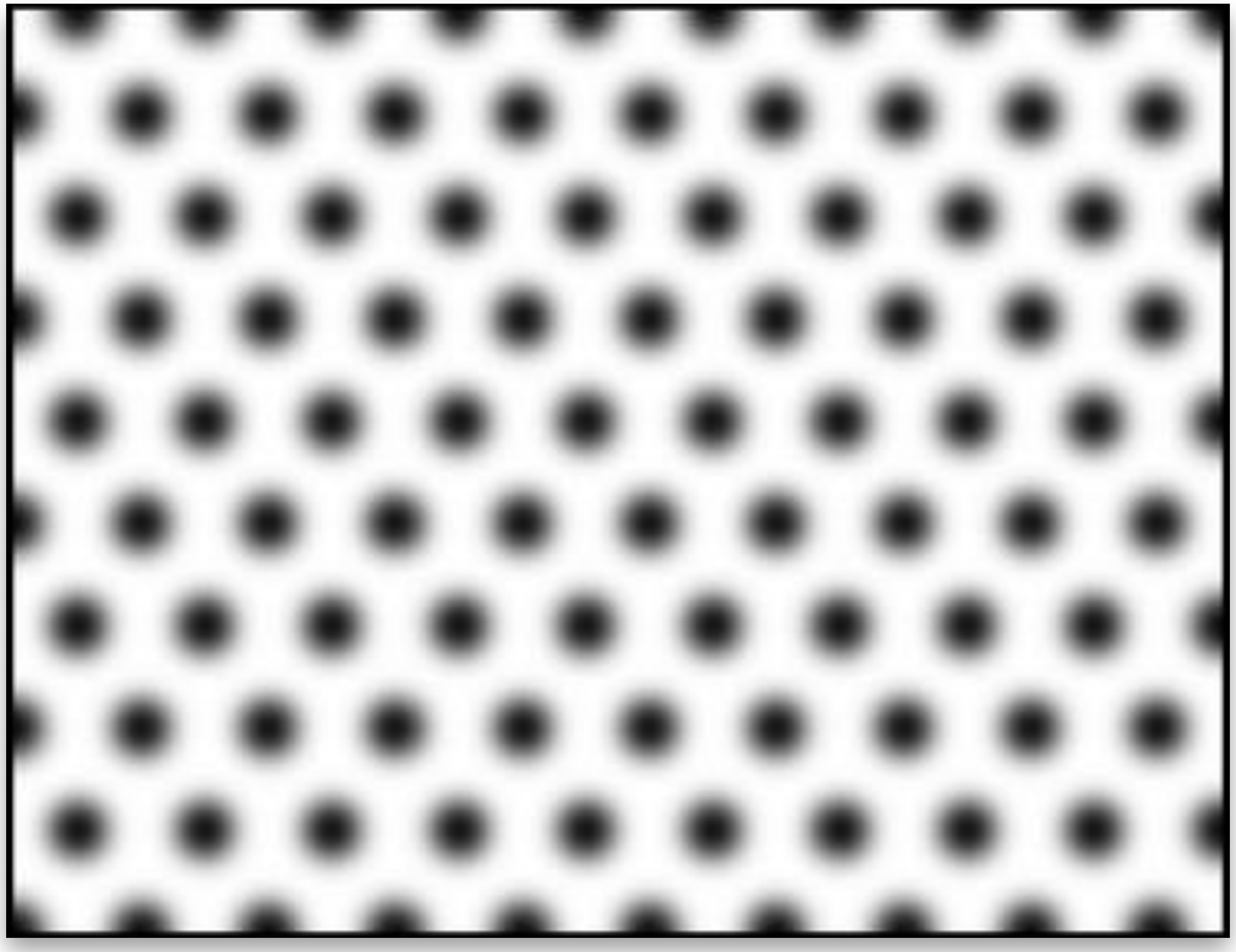
[T. Ma *et al.*, Nat. Comm. **8**, 14486 (2017)]

Modeling Graphene



Phase Field Crystal (PFC) Model[1]





Atomistic description: $n(\mathbf{r}) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j)$

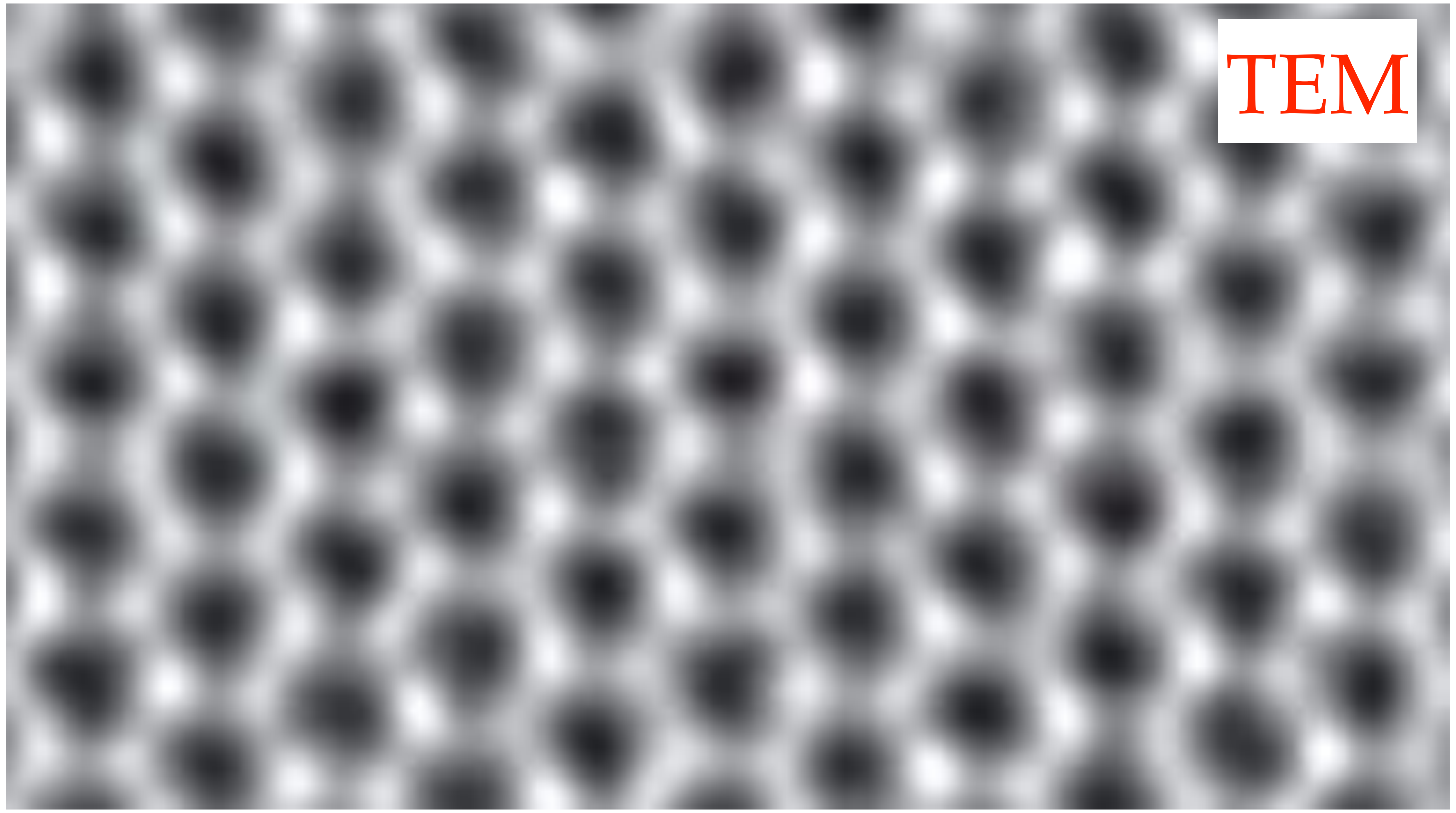
Statistical description: $n(\mathbf{r}) = \left\langle \sum_j \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle$

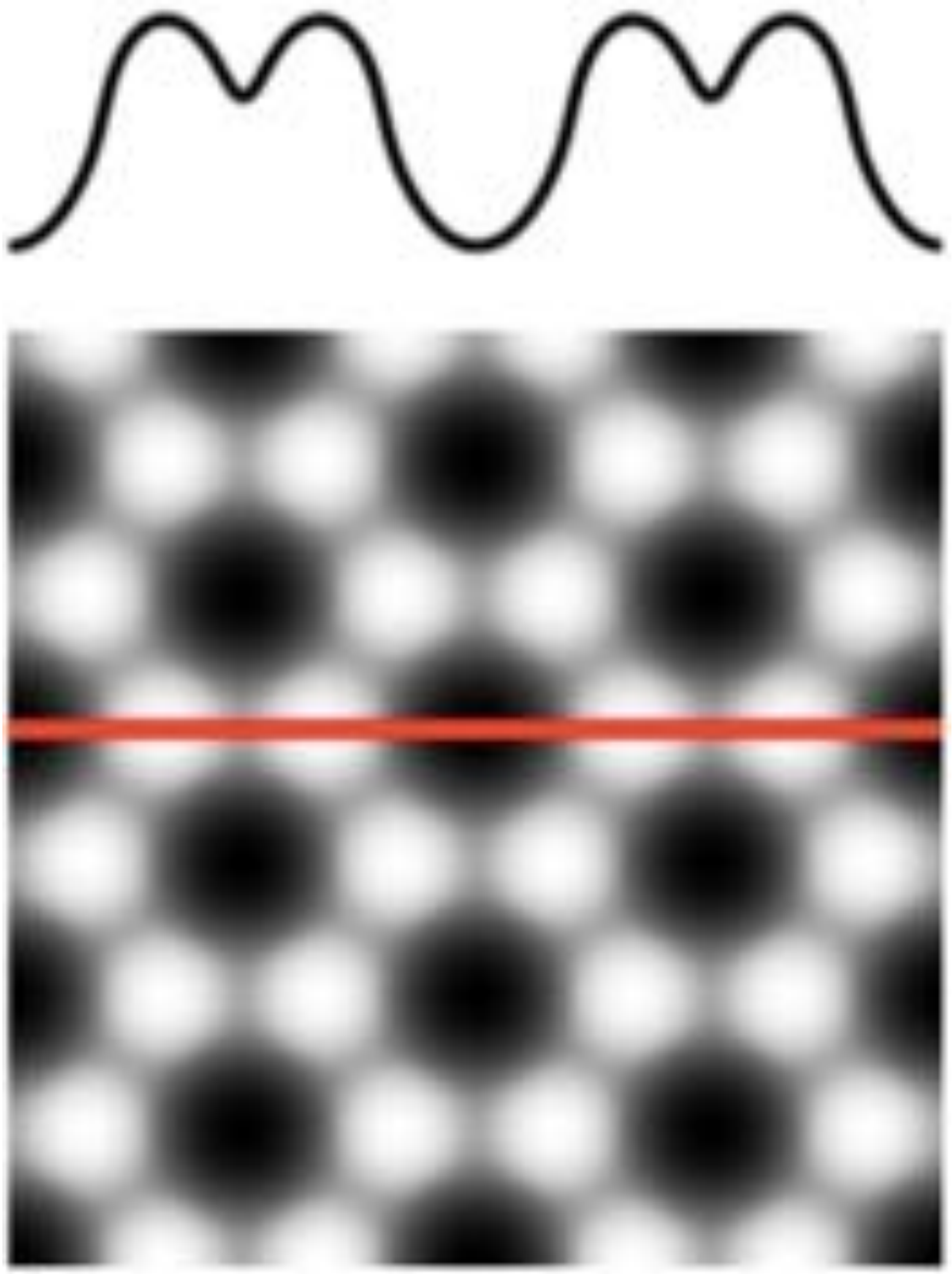
[1]K. Elder *et al.* PRL **88**, 245701 (2002)

PFC Free Energy

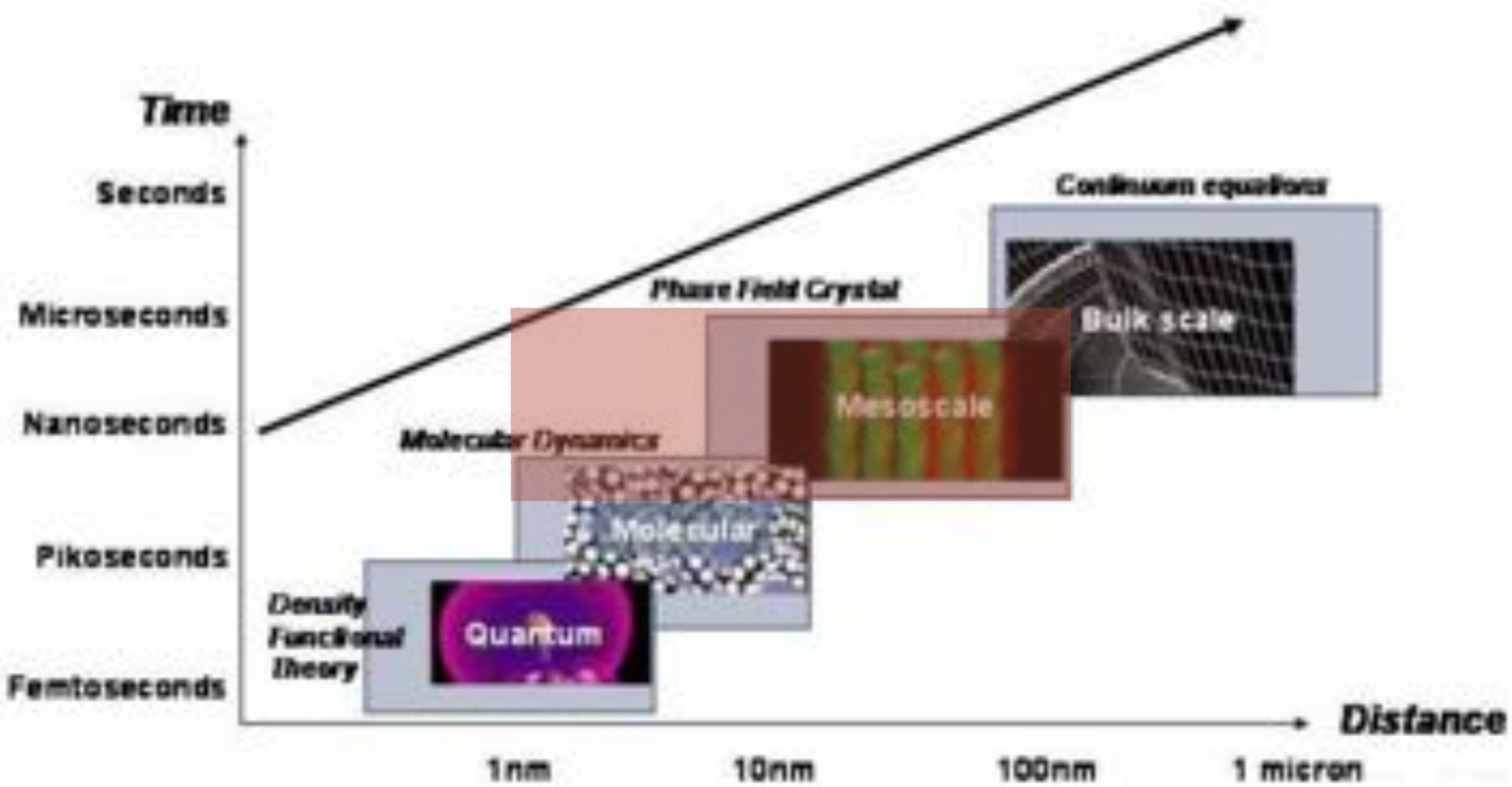
$$F\left[n(\mathbf{r},t)\right] = \int d\mathbf{r}\left[\frac{\Delta B}{2}n^2 + \frac{B^x}{2}n(1+\nabla^2)^2 n - \frac{\tau}{3}n^3 + \frac{\nu}{4}n^4\right]$$

- *Graphene (honeycomb) ground state*





Modeling Scales



PFC Free Energy

$$F\left[n(\mathbf{r},t)\right] = \int d\mathbf{r} \left[\frac{\Delta B}{2} n^2 + \frac{B^x}{2} n(1+\nabla^2)^2 n - \frac{\tau}{3} n^3 + \frac{\nu}{4} n^4 \right]$$

- Describes the energy of the system as functional of the atomistic number density field - *liquid and crystalline ground states (and coexistence)*
- Contains *topological defects and elastic excitations*
- Can be derived from classical DFT [Elder & Grant (2004), Jaatinen & T.A-N. (2010)]
- Usually coupled to dissipative dynamics in time

$$\frac{\partial n}{\partial t} = -\frac{\delta F[n]}{\delta n}$$

[Swift & Hohenberg (1977), Elder *et al.* (2002)]

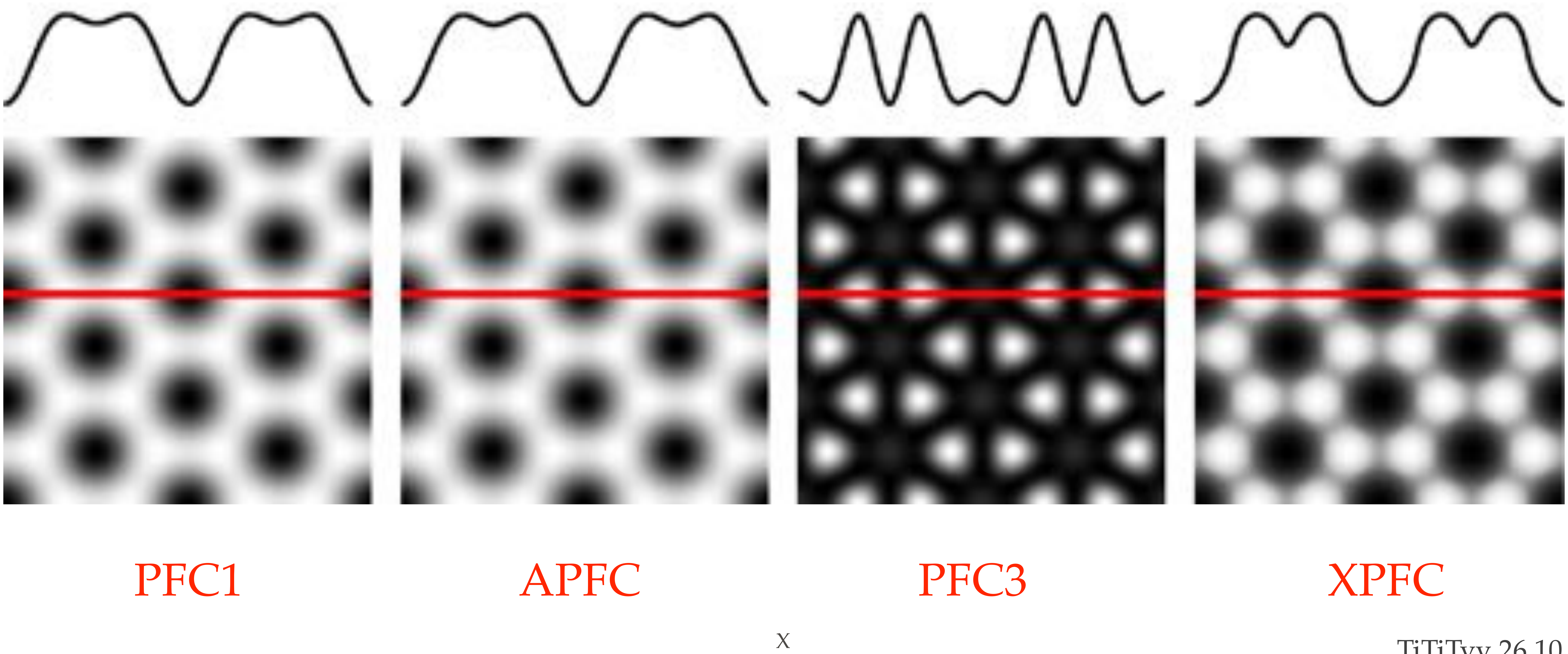
Multi-Scale Modeling Strategy for Graphene

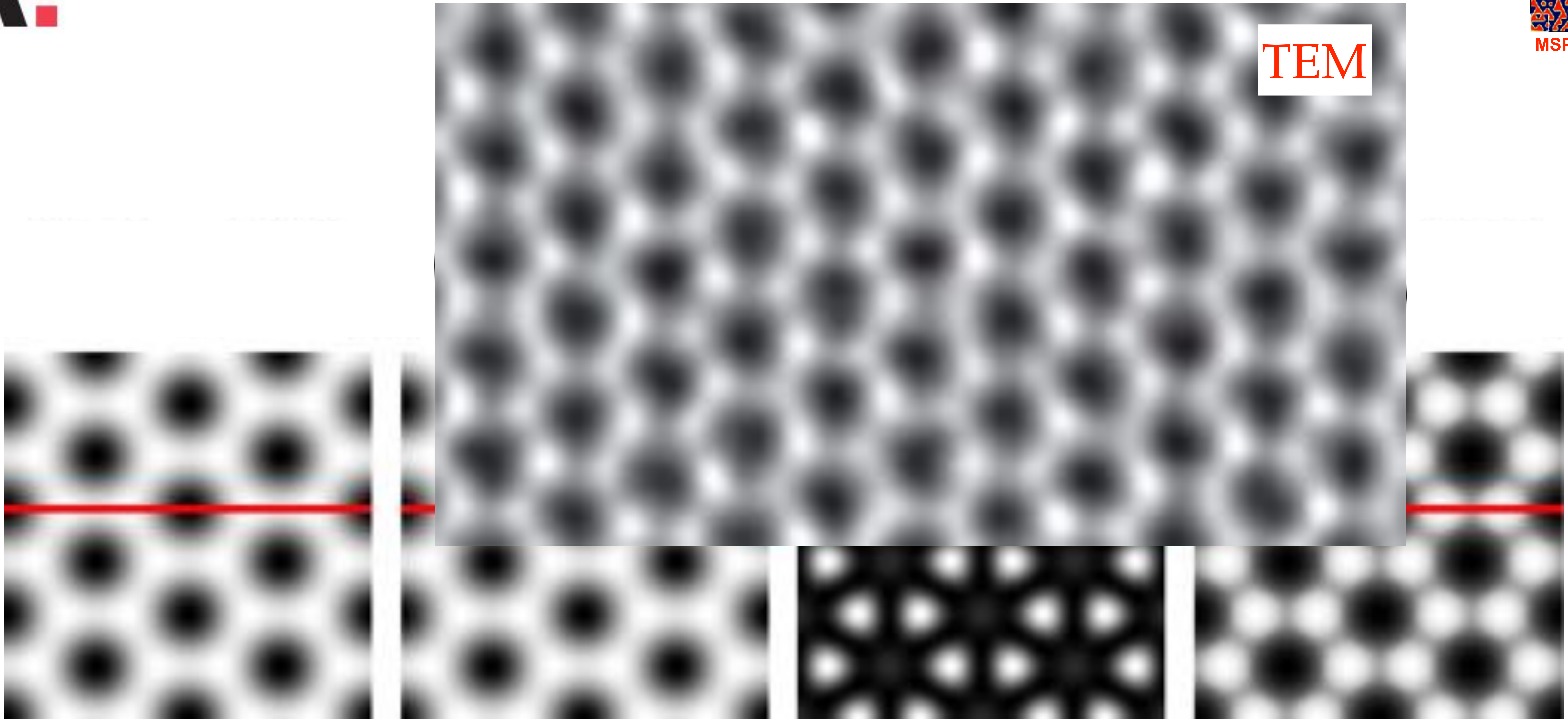
- Use PFC to generate 2D grain boundary configurations
- Input to all-electron QM-DFT calculations for grain boundary energy and use these to fix energy scale in PFC
- Generate large-scale, multi-grain PFC samples as input to MD to relax for further calculations (e.g. heat conduction and electric conductivity)

Methodology III: 2D PFC Models

- PFC1: Standard PFC (412 - 41 600 atoms)
- APFC: Amplitude expansion of PFC1 (1 140 - 5 900 000 atoms)
- PFC3: Three-mode PFC model (412 - 41 600 atoms)
- XPFC: PFC model with two and three-body interactions (412 - 166 400 atoms) [M. Seymour and N. Provatas, PRB **93**, 035447 (2016)]

PFC Density Fields





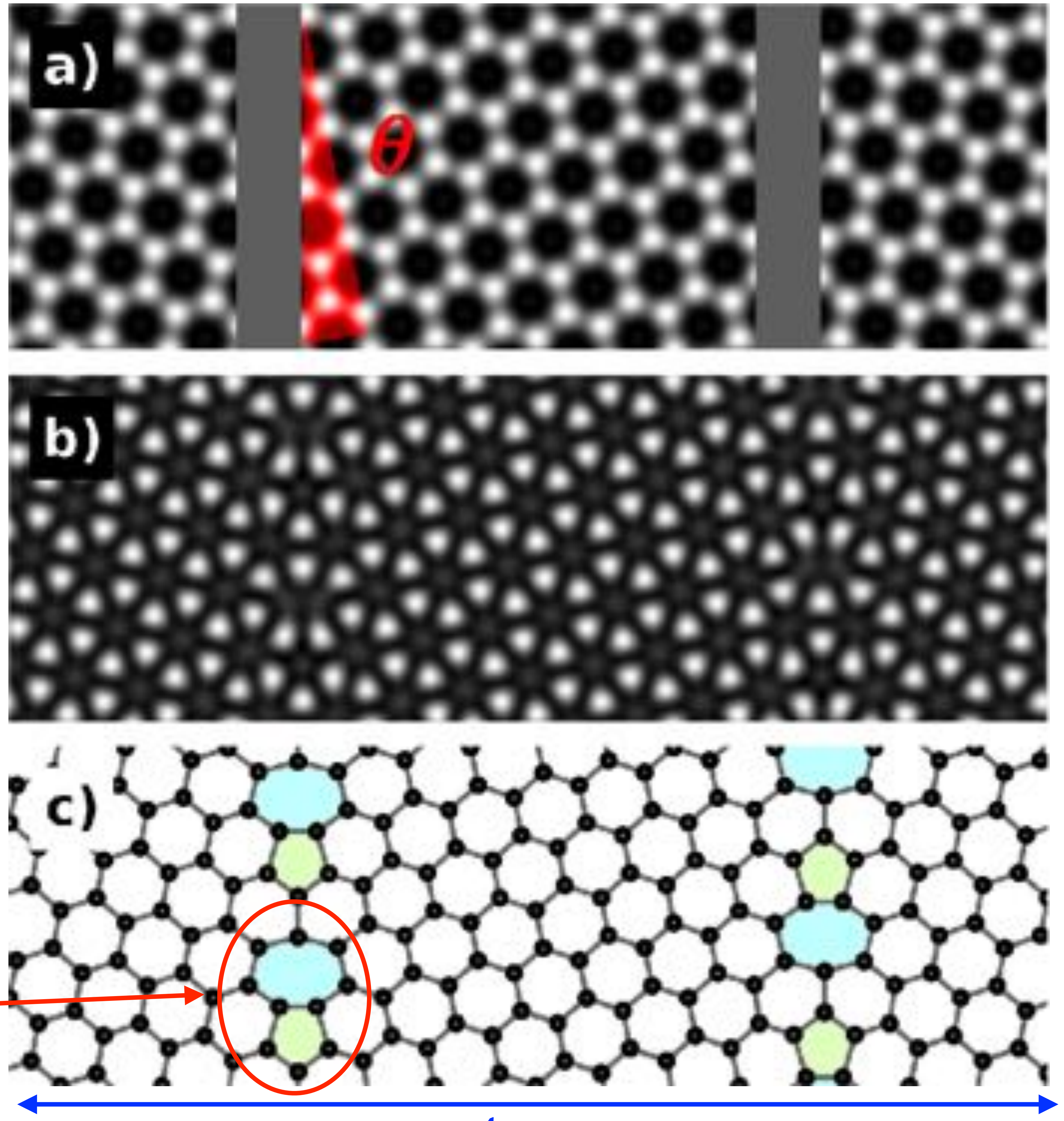
PFC1 APFC PFC3 XPFC

X

X

Step 1: Creating PFC Grain Boundaries

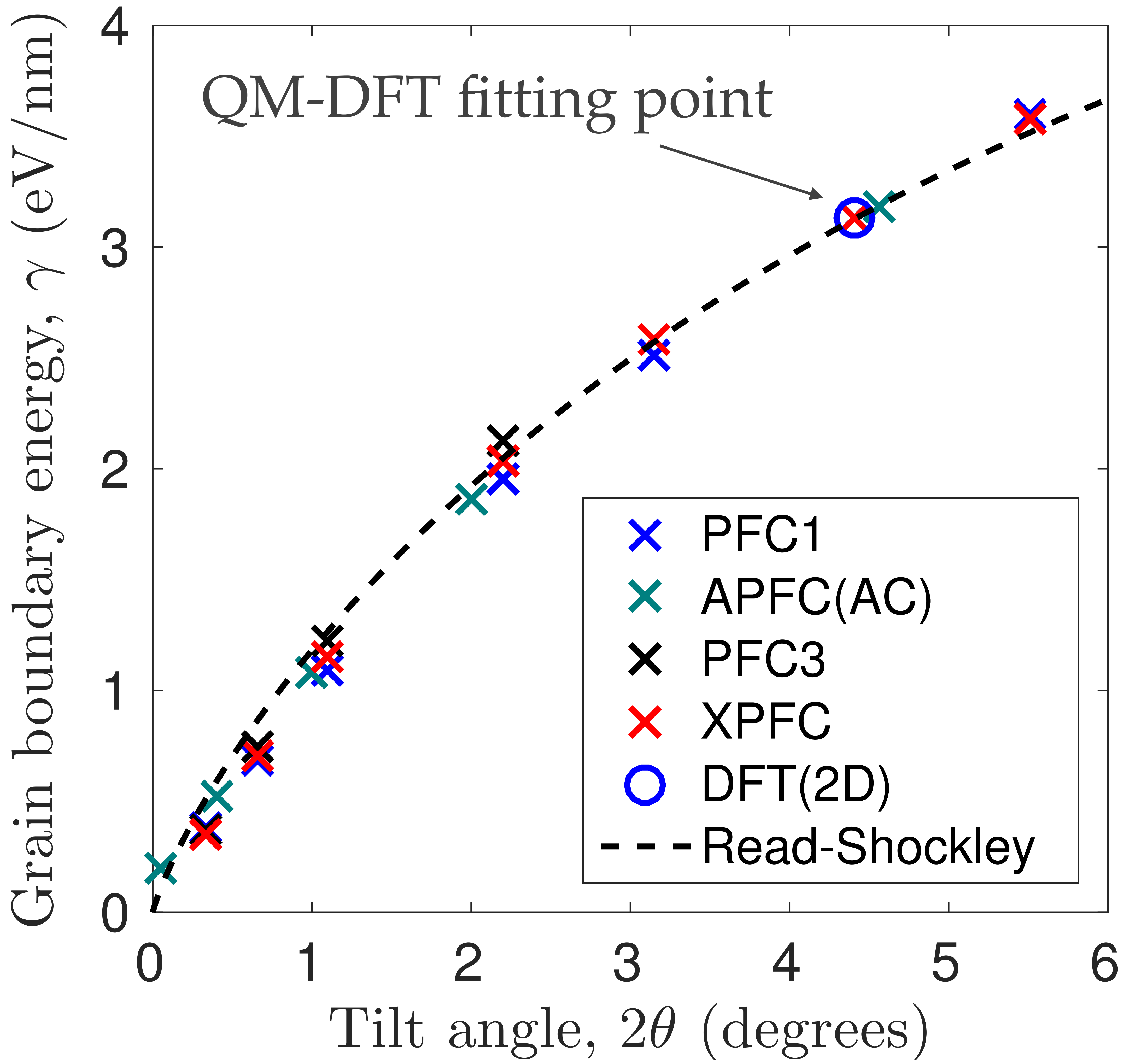
- Bicrystalline layout (with two GBs) and periodic boundaries
- Finite size effects eliminated (system sizes > 10 nm)
- Atomic positions used as input for QM-DFT and MD relaxation



Step 2: Fitting to QM-DFT

- Small-angle GB limit $2\theta \approx 4.6^\circ$ used to set energy scales in PFC models
- Read-Shockley equation in small GB angle limit:

$$\gamma = \frac{bY_{2D}}{8\pi}\theta\left(\frac{3}{2} - \ln(2\pi\theta)\right)$$



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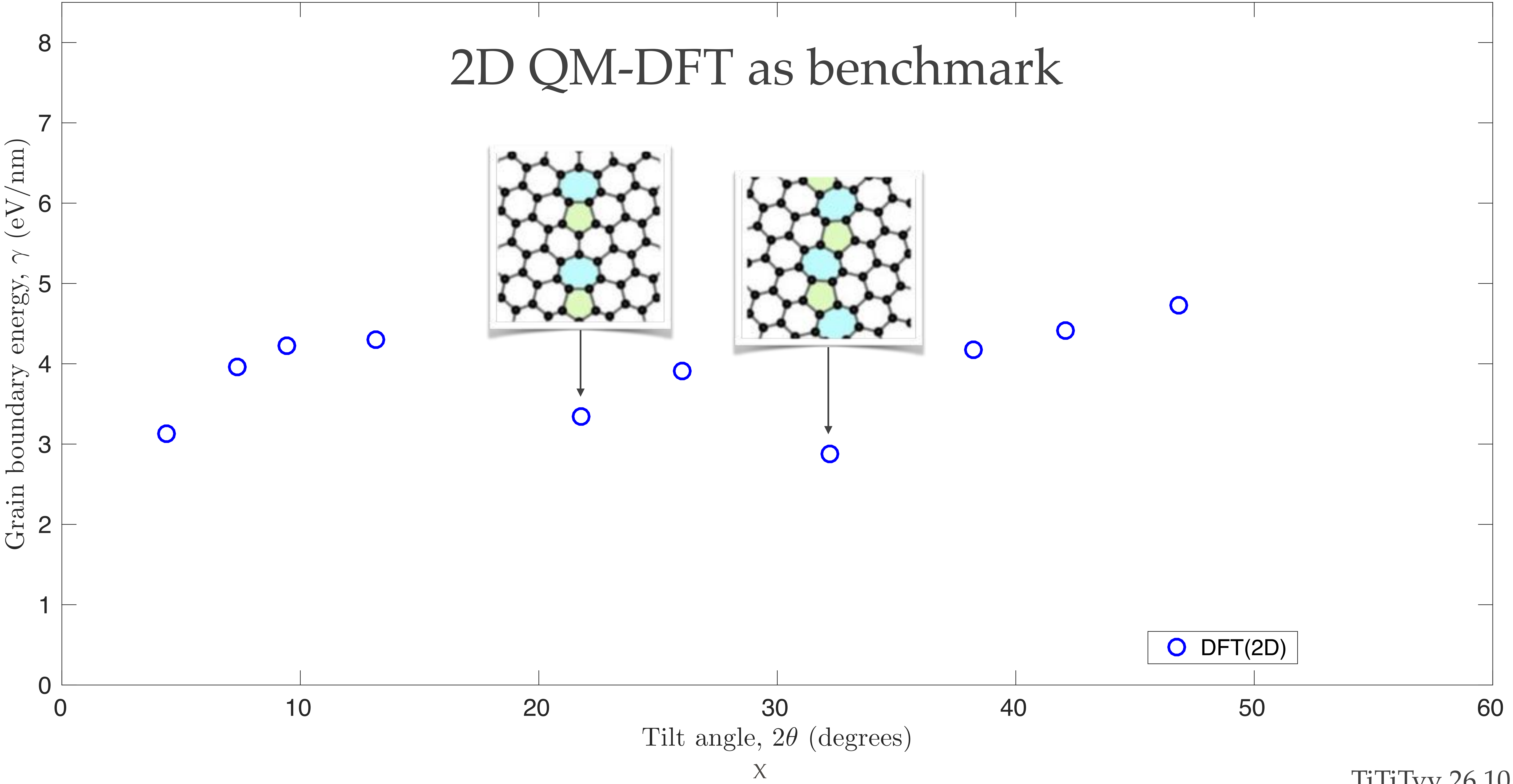
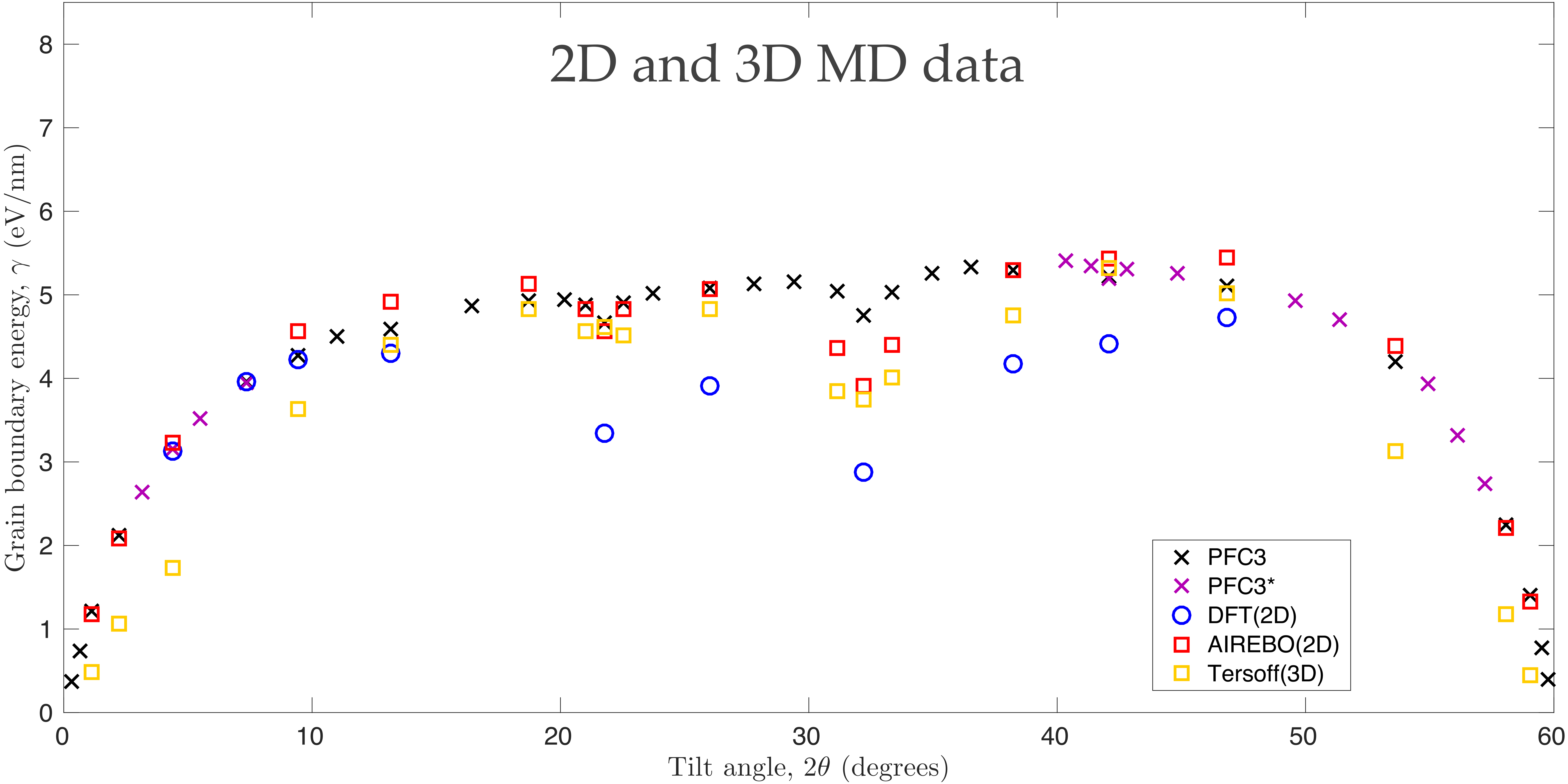
Step 3: Grain Boundary Energies

2D QM-DFT as benchmark



2D and 3D MD data



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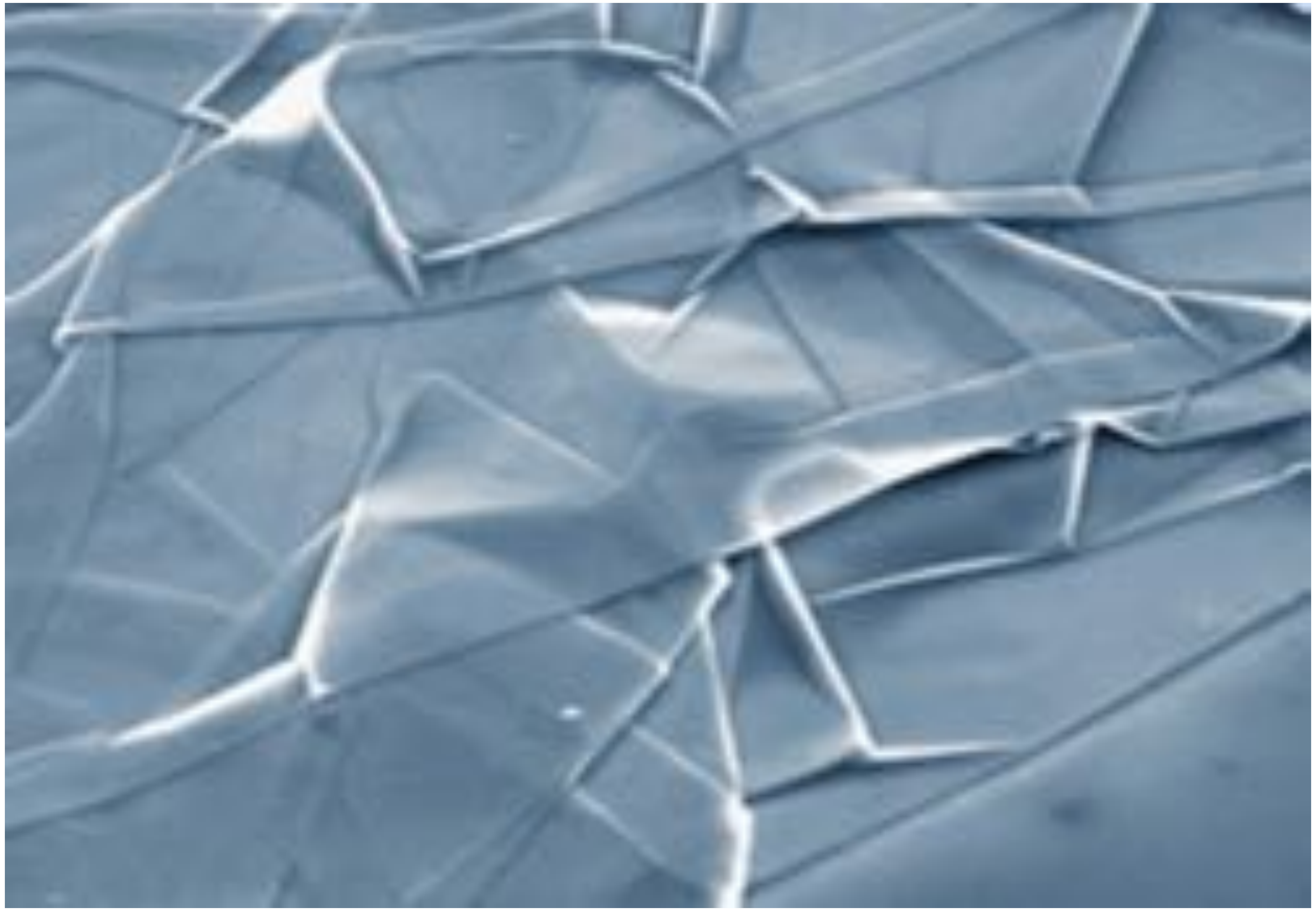
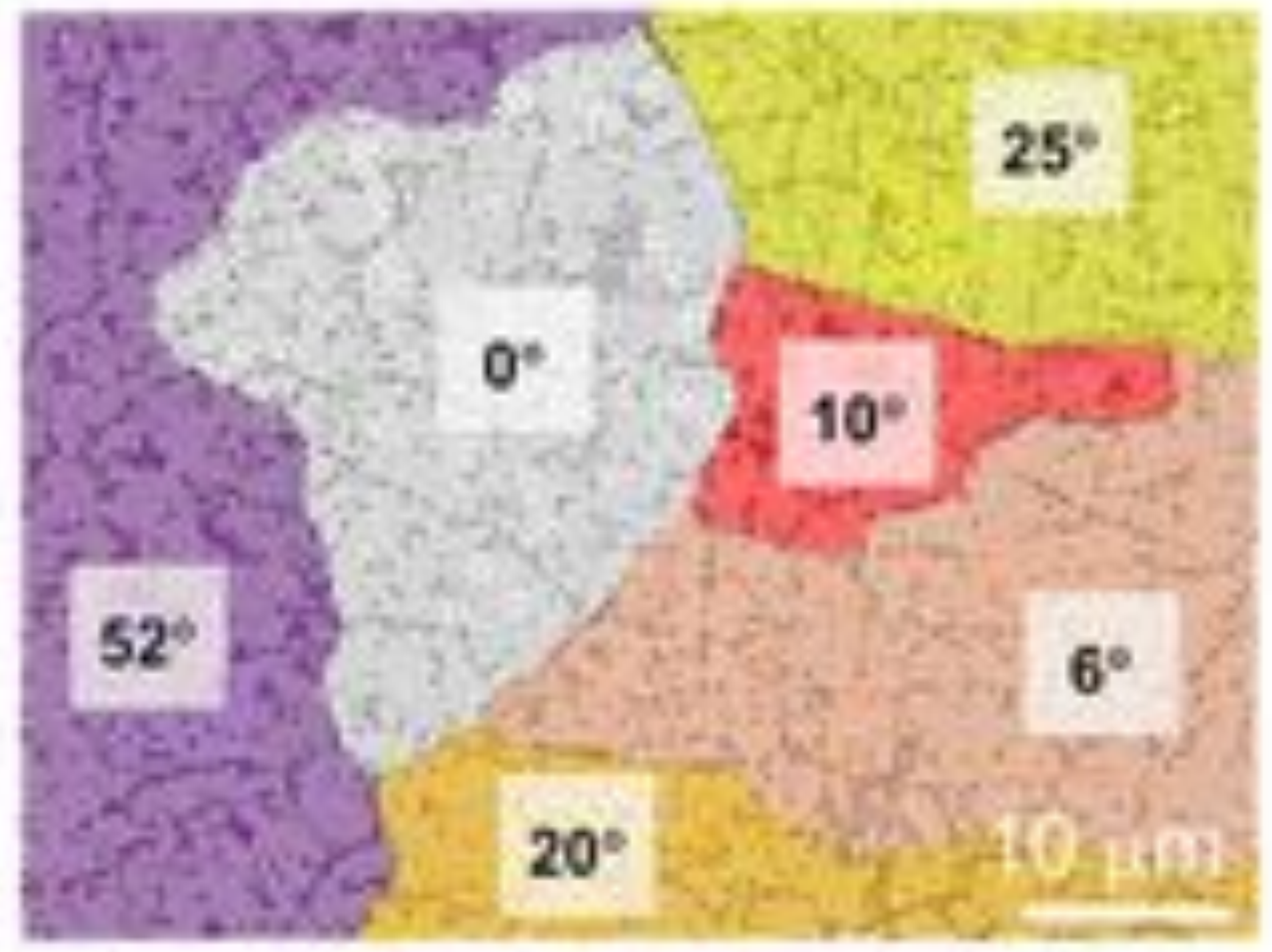
Large Multigrain Flakes



Large Multigrain Flakes

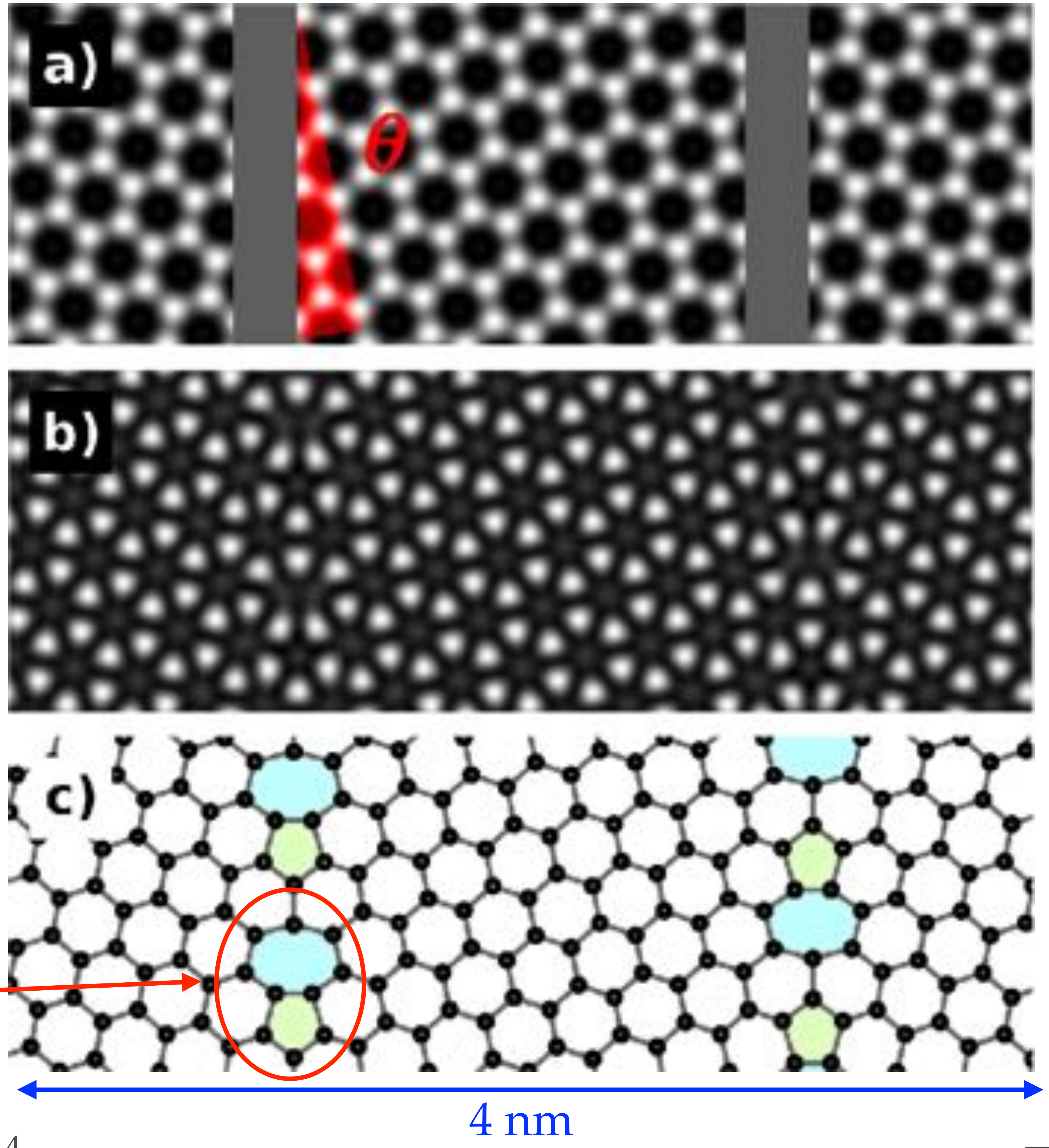
- Large, relaxed multigrain samples can be used to study e.g. heat and electrical conduction
- *Strategy:* Generate large samples with PFC1 and relax with MD (optimized Tersoff potential used here)



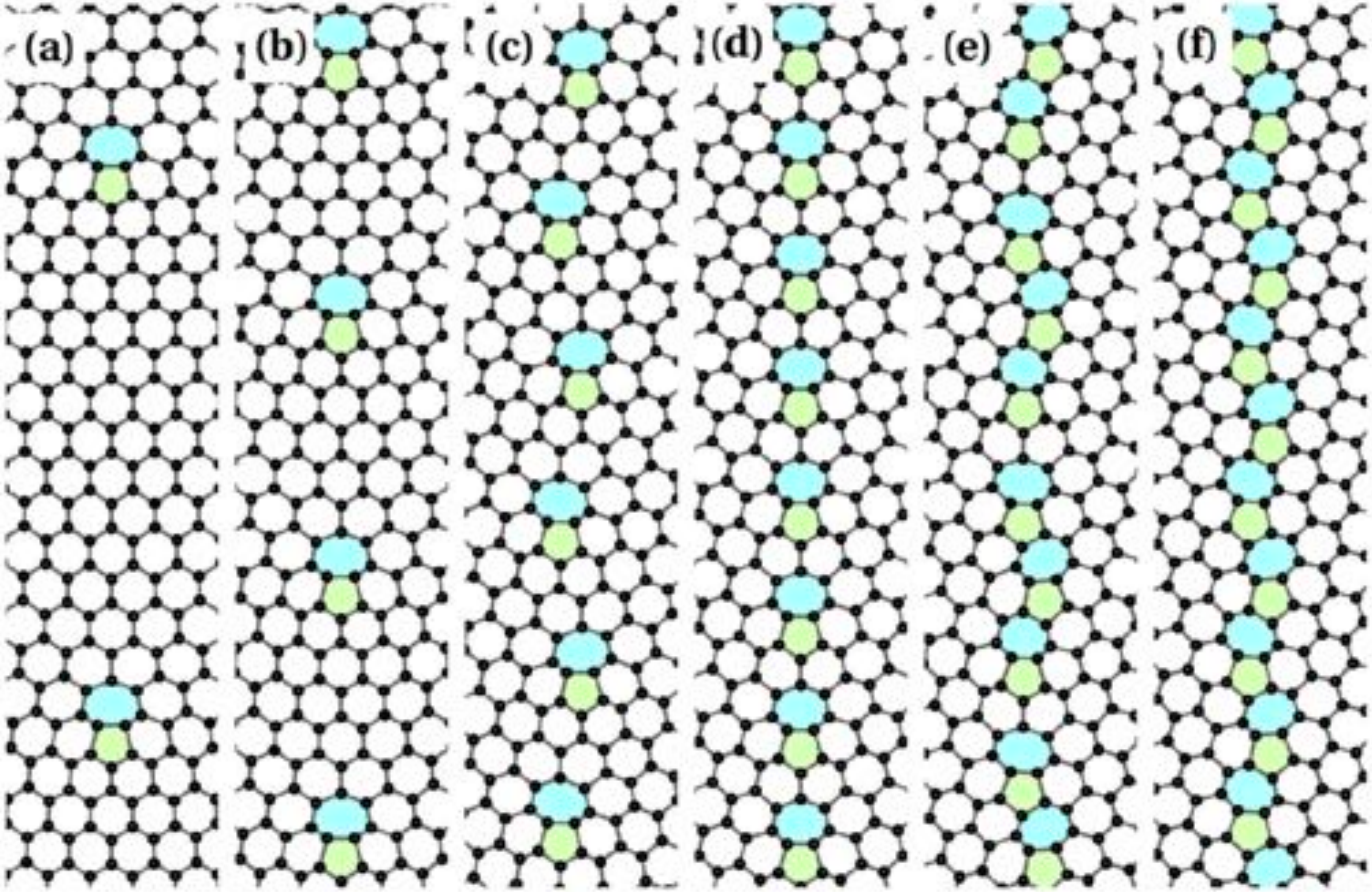
[H. Ago *et al.*, ACS Nano **10**, 3233 (2016)]

Graphene Grain Boundaries

- Bicrystalline samples are generated by having two grain boundaries with periodic boundary conditions

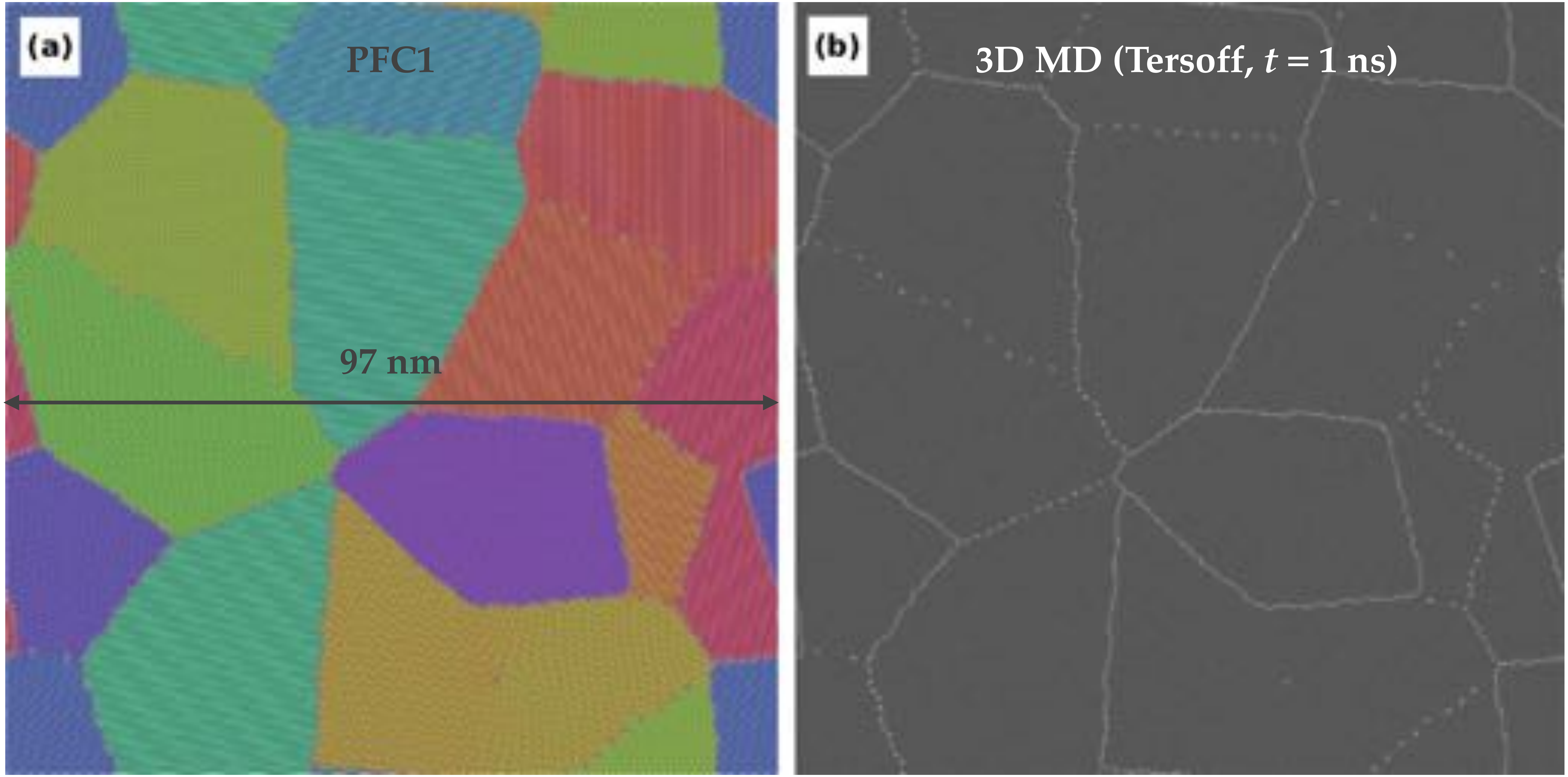


Graphene Grain Boundaries



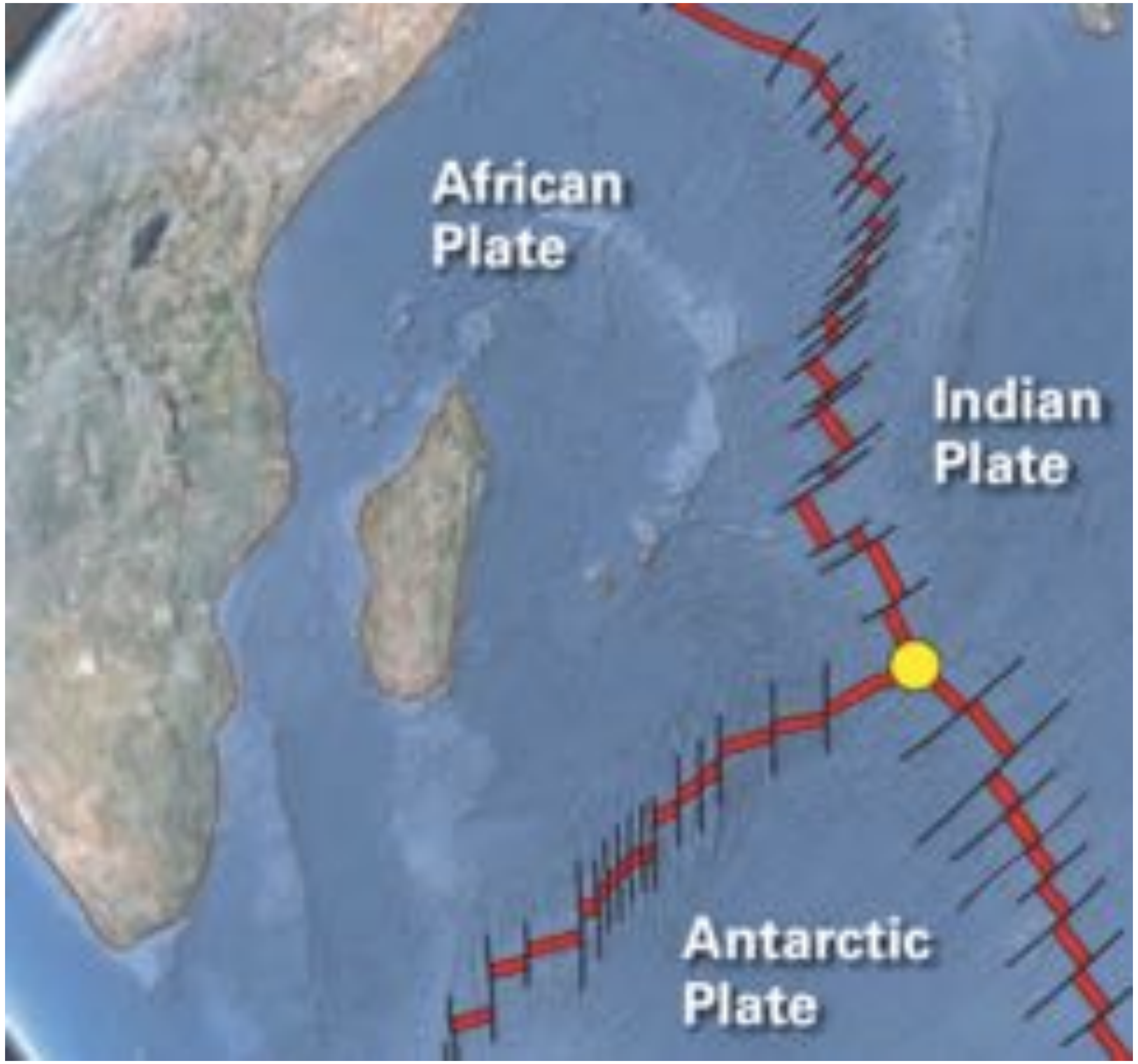
2θ 4.4° 9.4° 16.4° 21.8° 27.8° 32.2°

Large Multigrain Flakes



Large Multigrain Flakes

Triple Junctions



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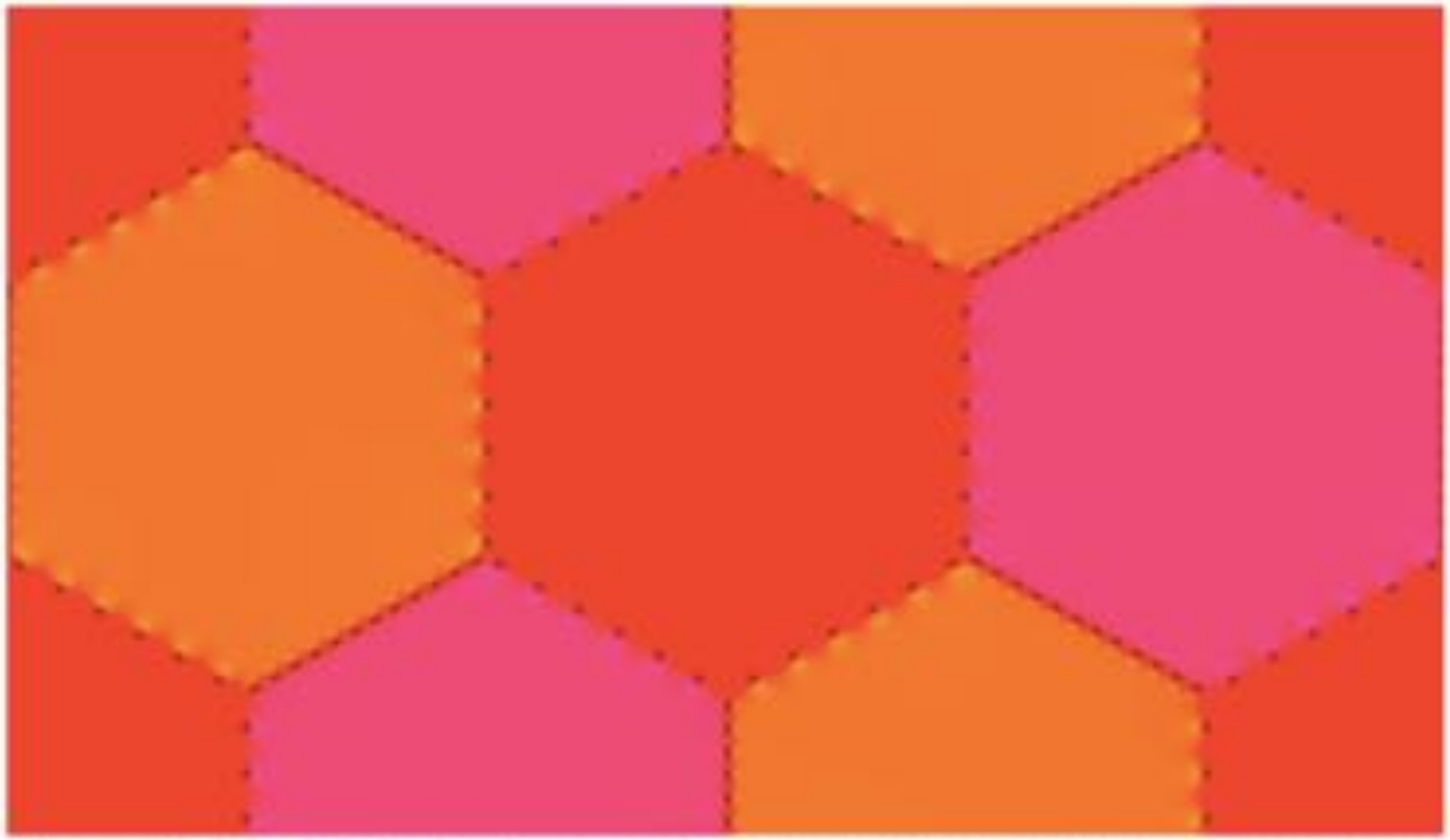
Triple Junctions in Graphene



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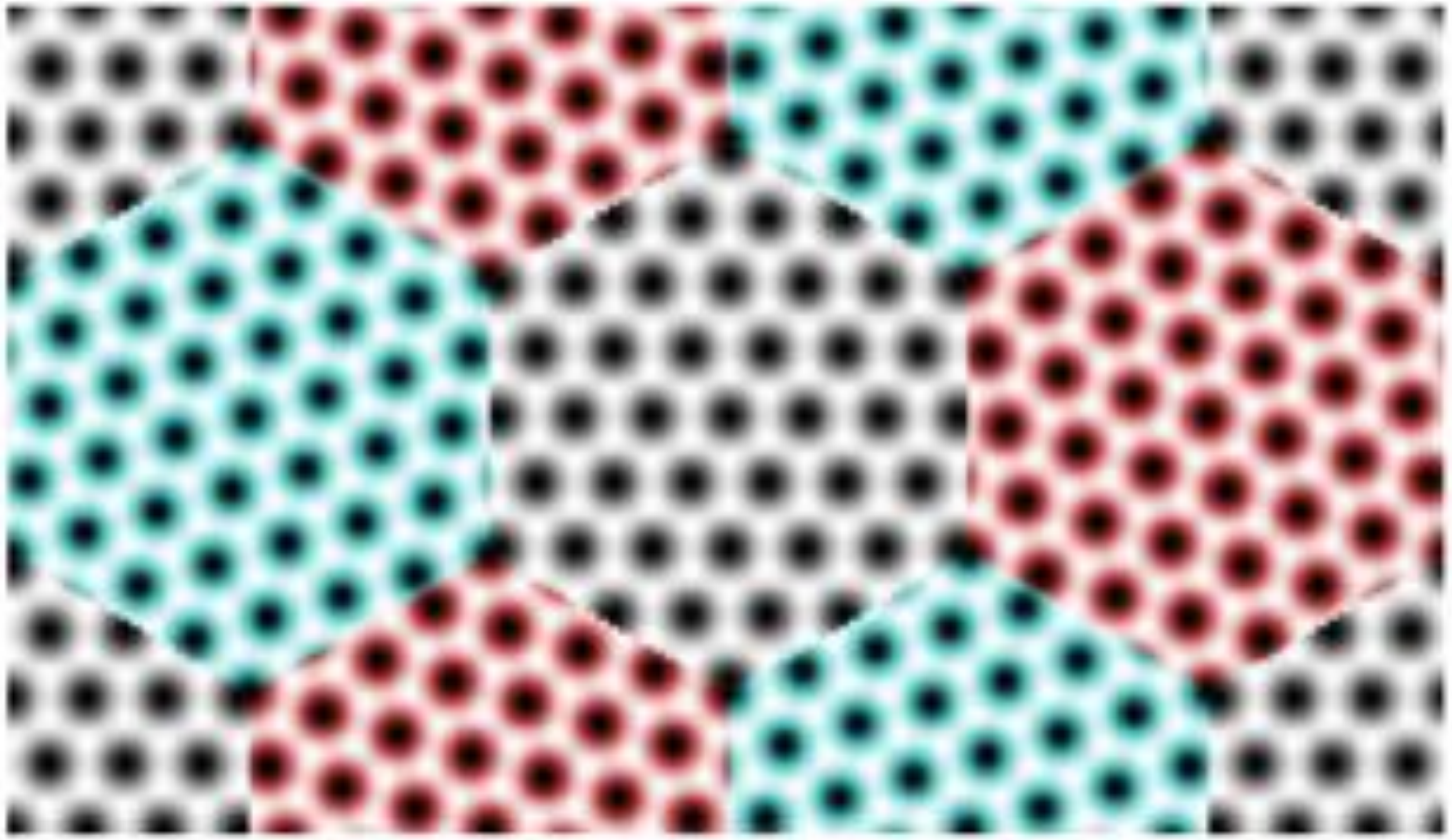
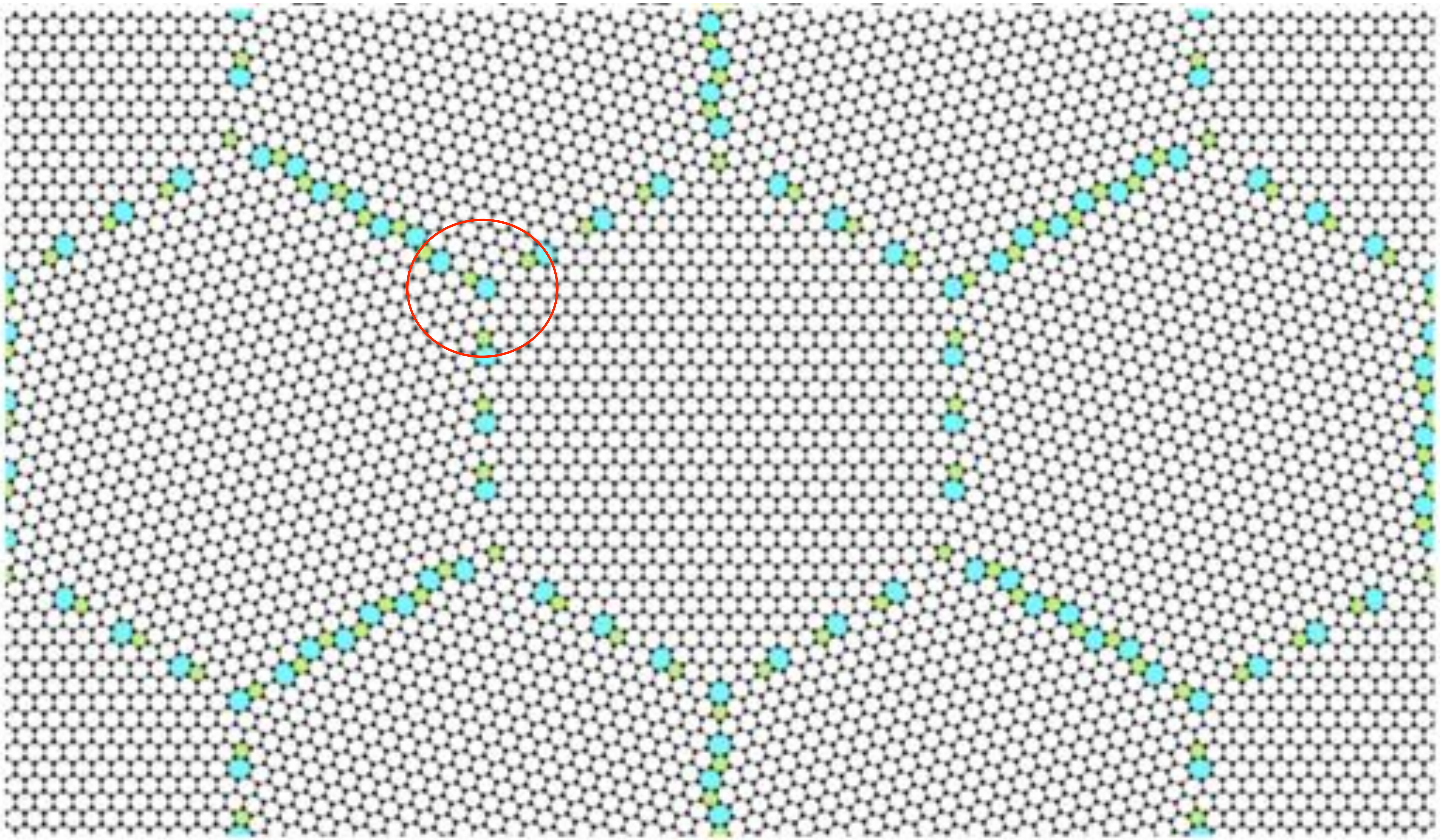
Triple Junctions in Graphene



- Total energy of the system $F = f_{\mathrm{s}}A + f_{\mathrm{L}}L + f_{\mathrm{p}}N$

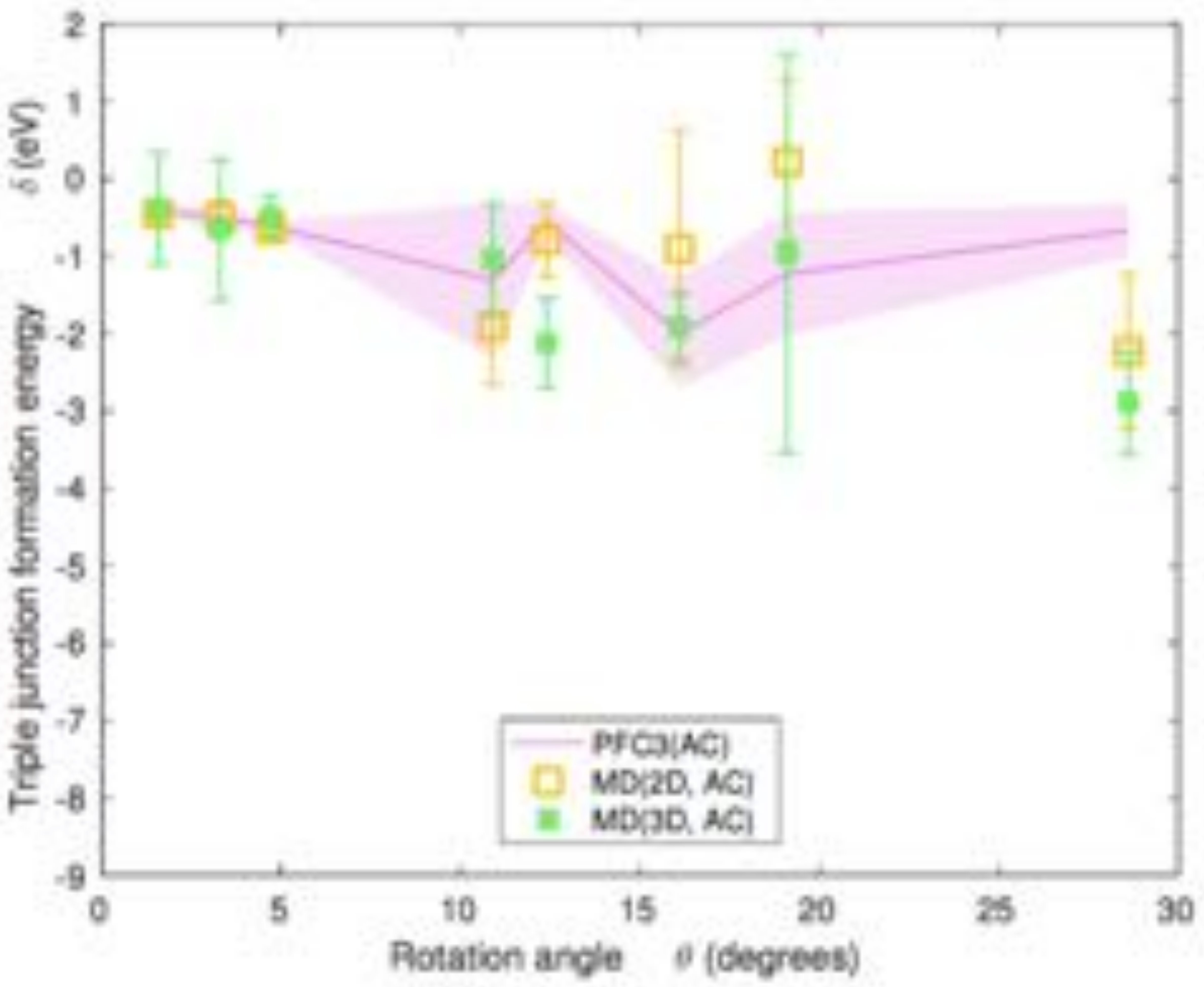
Triple Junctions in Graphene



Total energy of the system $F = f_s A + f_L L + f_p N$

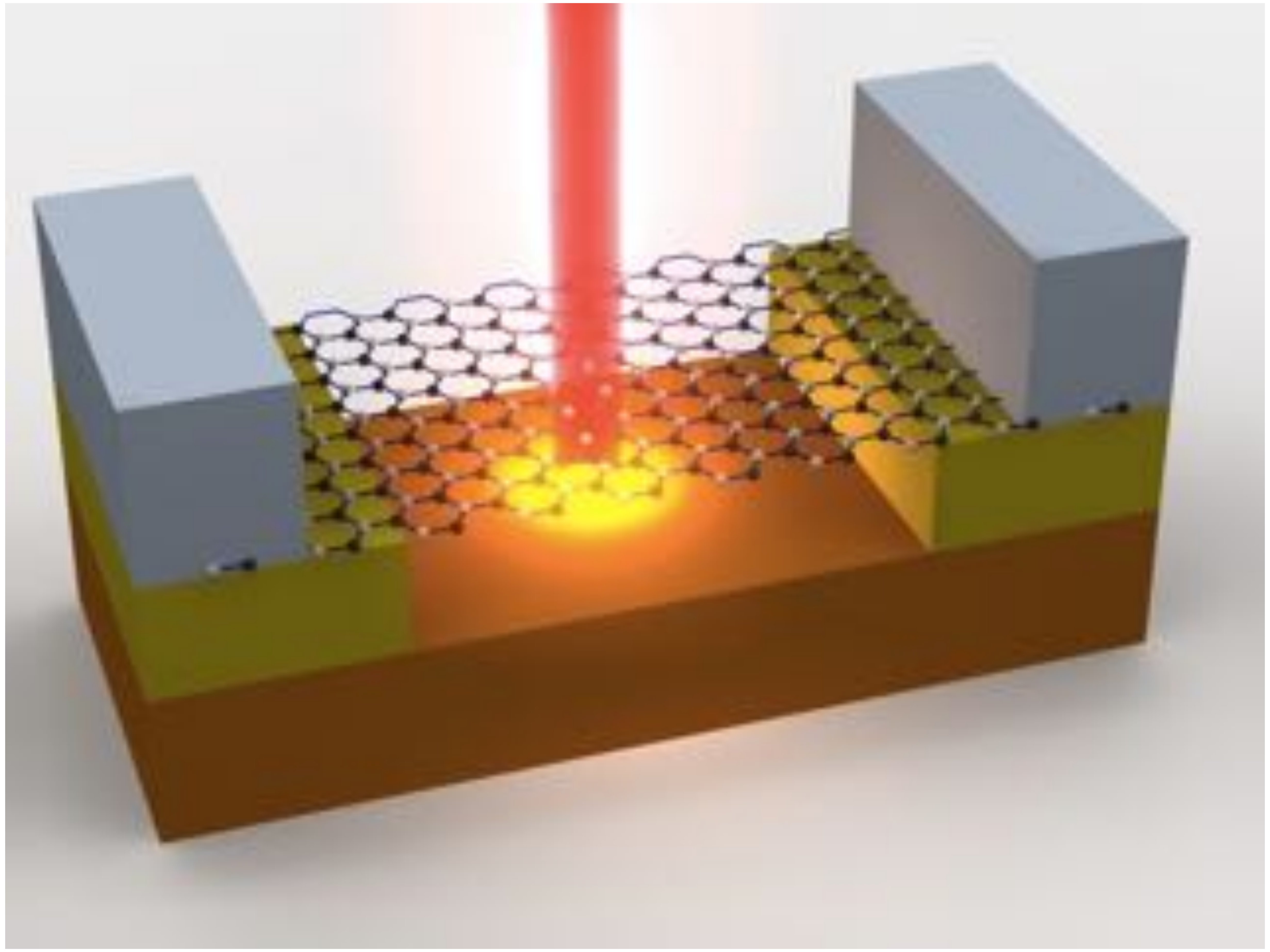
X

Triple Junctions in Graphene



- For most orientations, the triple junction formation energies are *negative*
- Grain boundary energies are 1-5 eV / nm i.e. (at least two) orders of magnitude larger and dominate the total energy

Heat Conduction in Graphene



[Z. Fan, L.F.C. Pereira, P. Hirvonen, M.M. Ervasti, K.R. Elder, D. Donadio, T. Ala-Nissila, and A. Harju, Phys. Rev. B **95**, 144309 (2017); Nano Letters 7b1072 (2017); K. Azizi, P. Hirvonen, Z. Fan, A. Harju, K.R. Elder, T. Ala-Nissila, and S. M. Vaez-Allaei, Carbon **125**, 384 (2017)]

Heat Conduction in Graphene

- Heat conductivity in and out-of plane can be calculated from the heat (energy) flow autocorrelation function

$$\kappa_{\mu\nu}(t) = \frac{1}{k_B T^2 V} \int_0^t dt' C_{\mu\nu}(t')$$

where

$$C_{\mu\nu}(t) = \langle J_\mu(0) J_\nu(t) \rangle$$

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where

$$C_{\mu\nu}^{\text{in/out}}(t) = \langle J_\mu^{\text{in/out}}(0) J_\nu^{\text{in/out}}(t) \rangle$$

and

$$\boldsymbol{J}^{\text{in}} = \sum_i \sum_{j \neq i} \boldsymbol{r}_{ij} \left(\frac{\partial U_j}{\partial x_{ji}} v_{xi} + \frac{\partial U_j}{\partial y_{ji}} v_{yi} \right), \quad \boldsymbol{J}^{\text{out}} = \sum_i \sum_{j \neq i} \boldsymbol{r}_{ij} \left(\frac{\partial U_j}{\partial z_{ji}} v_{zi} \right)$$

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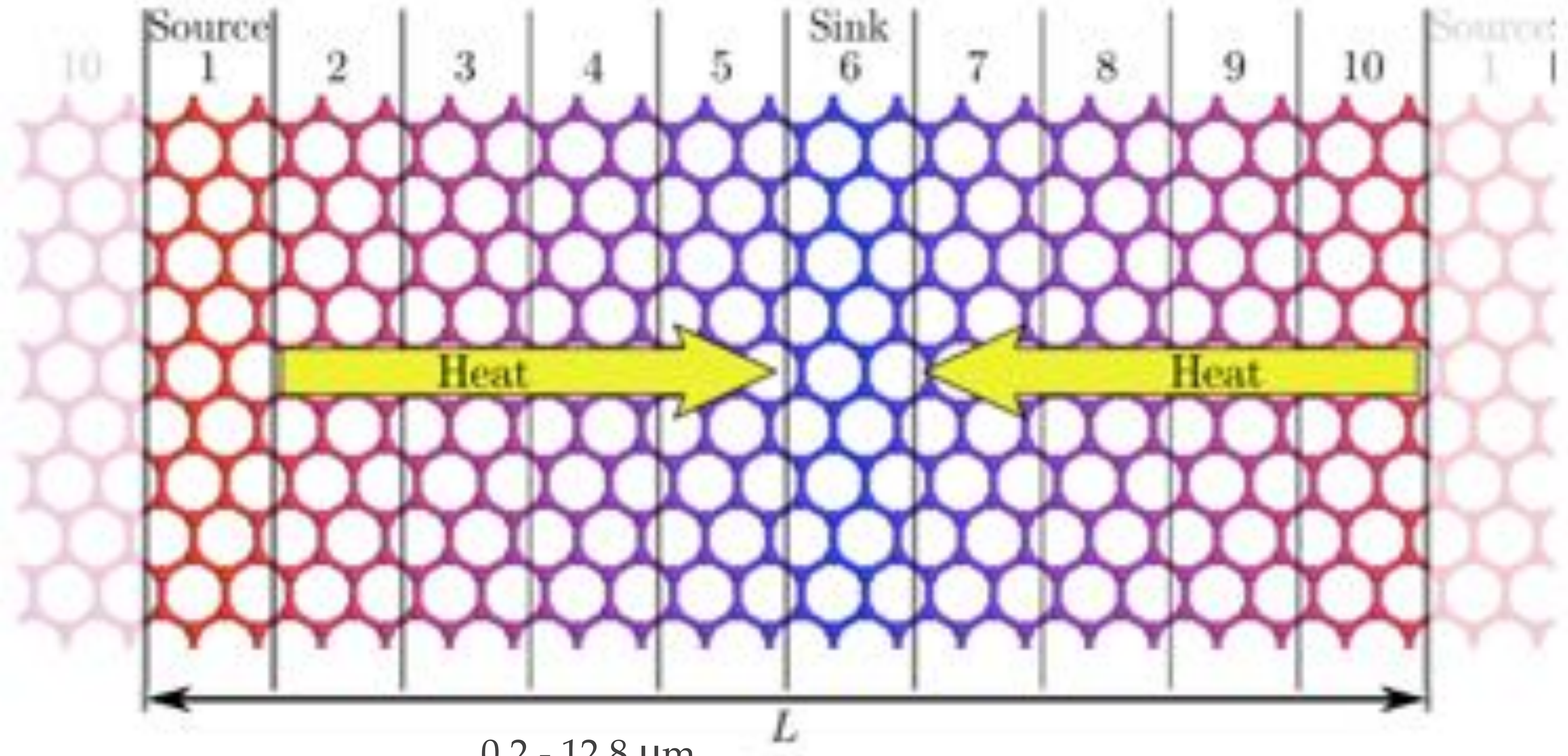
Heat Conduction in Graphene

- … or from Fourier's law by setting an external thermal gradient

10 nm

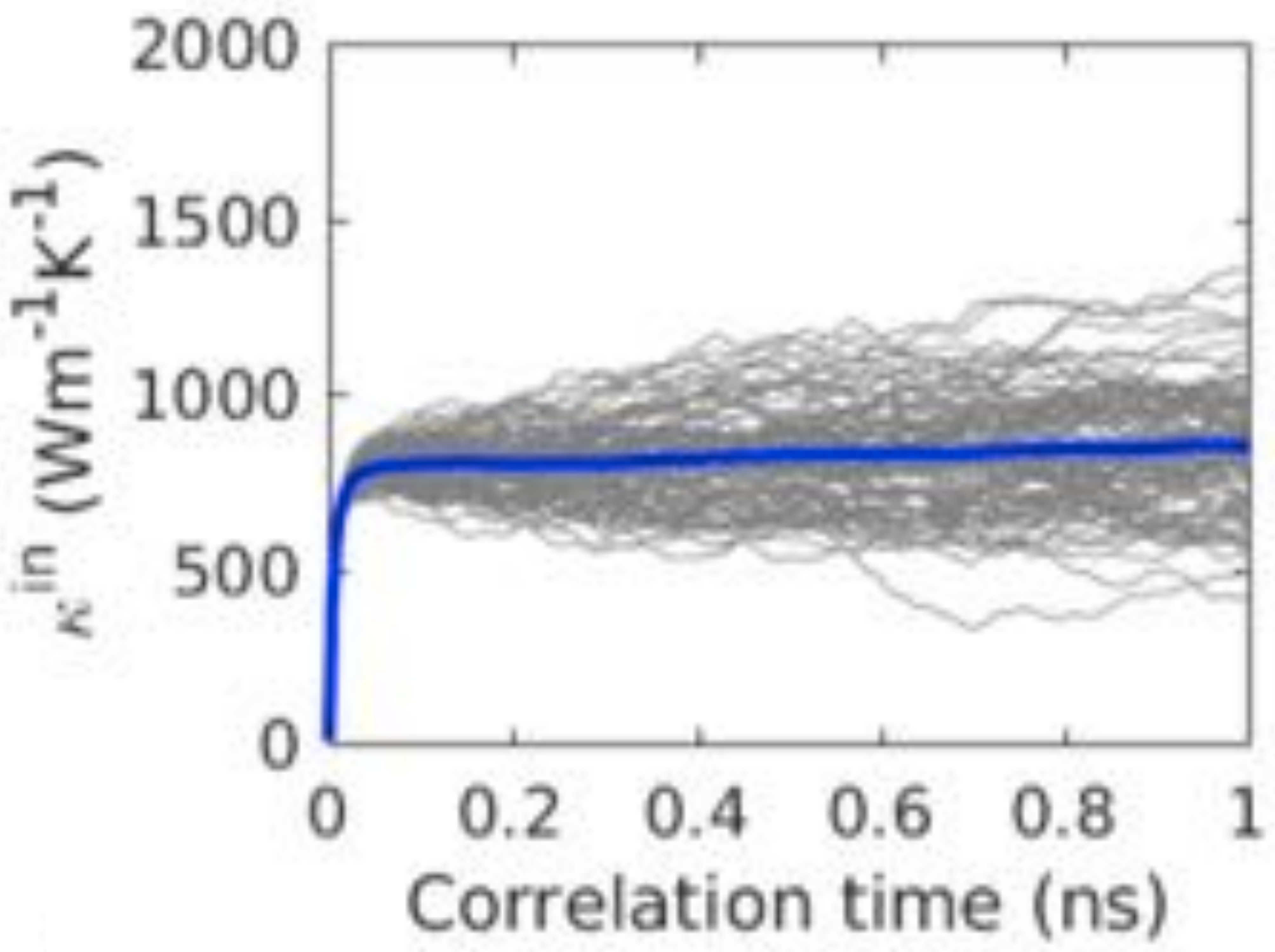


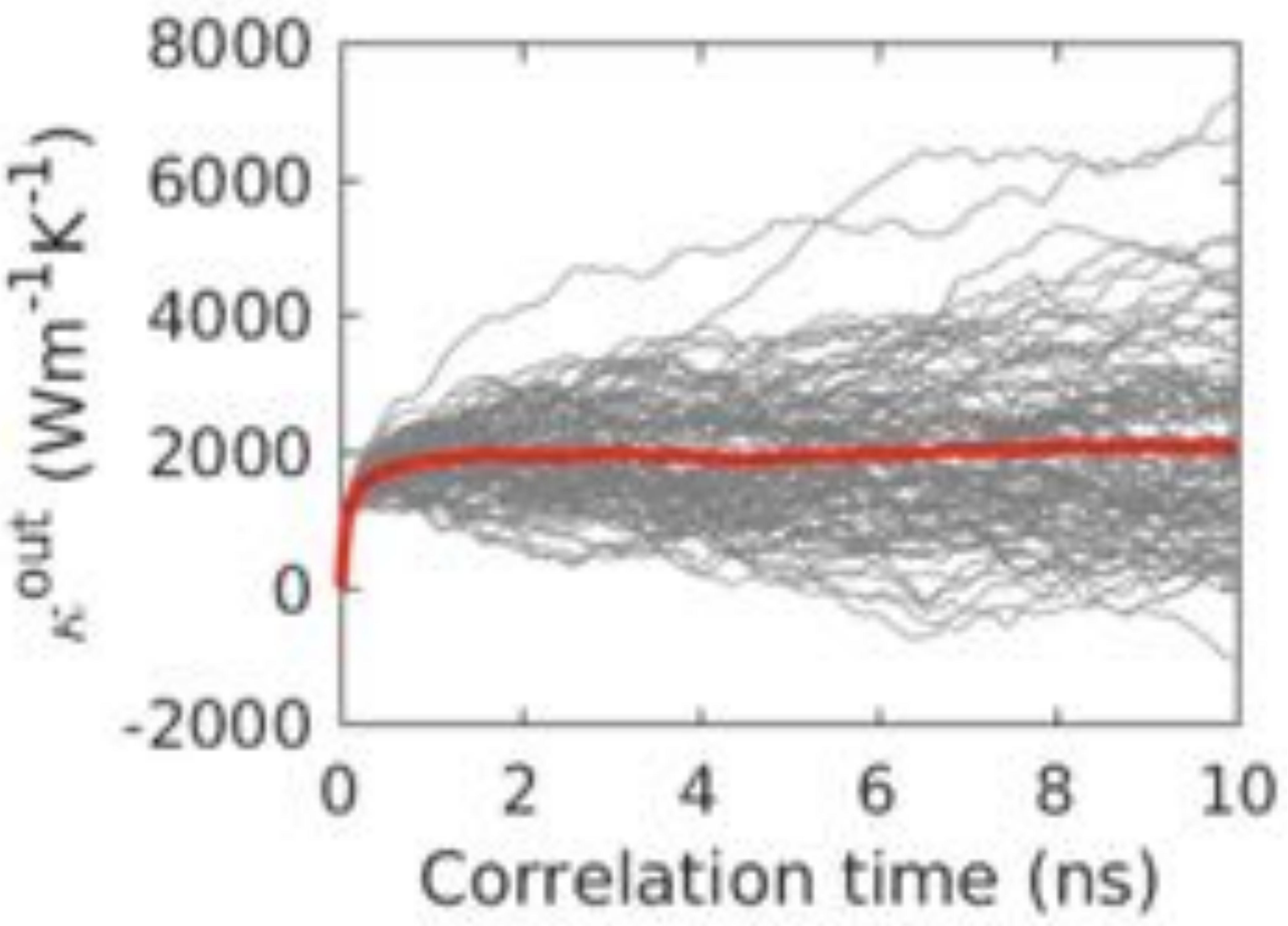
0.2 - 12.8 μm

$$\kappa(L) = \frac{Q^{ext}/2}{S|\nabla T|}$$

Heat Conduction in Pristine Graphene

- The *out-of-plane component converges much slower* than the in-plane one





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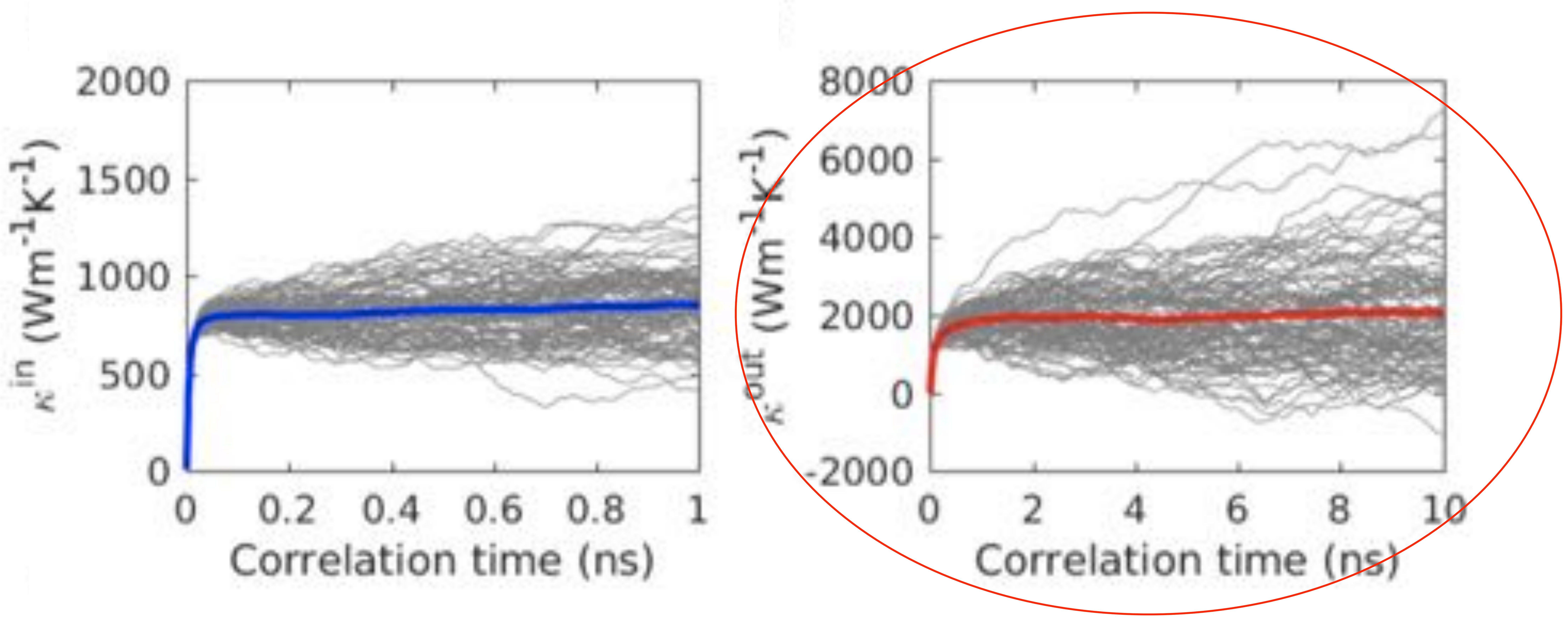

Heat Conduction in Pristine Graphene

- For pristine graphene we find at $T = 300$ K (MD with opt. Tersoff)

$$\kappa_0^{\text{in}} \approx 800 \ \text{Wm}^{-1}\text{K}^{-1} \ \text{and} \ \kappa_0^{\text{out}} \approx 2\ 100 \ \text{Wm}^{-1}\text{K}^{-1}$$

$$\kappa_0 = \kappa_0^{\text{in}} + \kappa_0^{\text{out}} = 2\ 900 \ \text{Wm}^{-1}\text{K}^{-1}$$

Experimentally $\kappa_0 \approx 1500 - 2500 \ \text{Wm}^{-1}\text{K}^{-1}$

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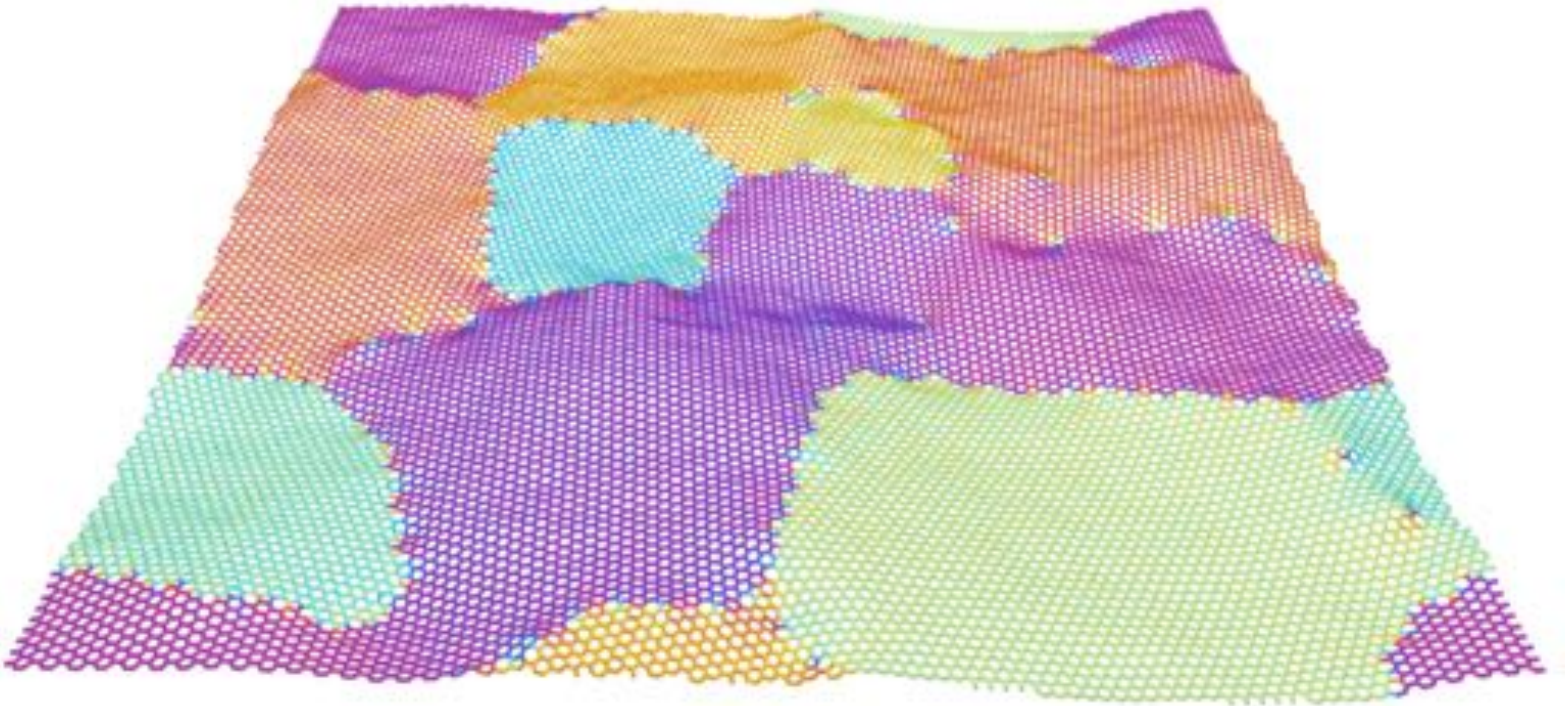
Experimentally $\kappa_0 \approx 1500 - 2500 \ \text{Wm}^{-1}\text{K}^{-1}$

- For uniaxially strained graphene the out-of-plane component diverges for 2% strain

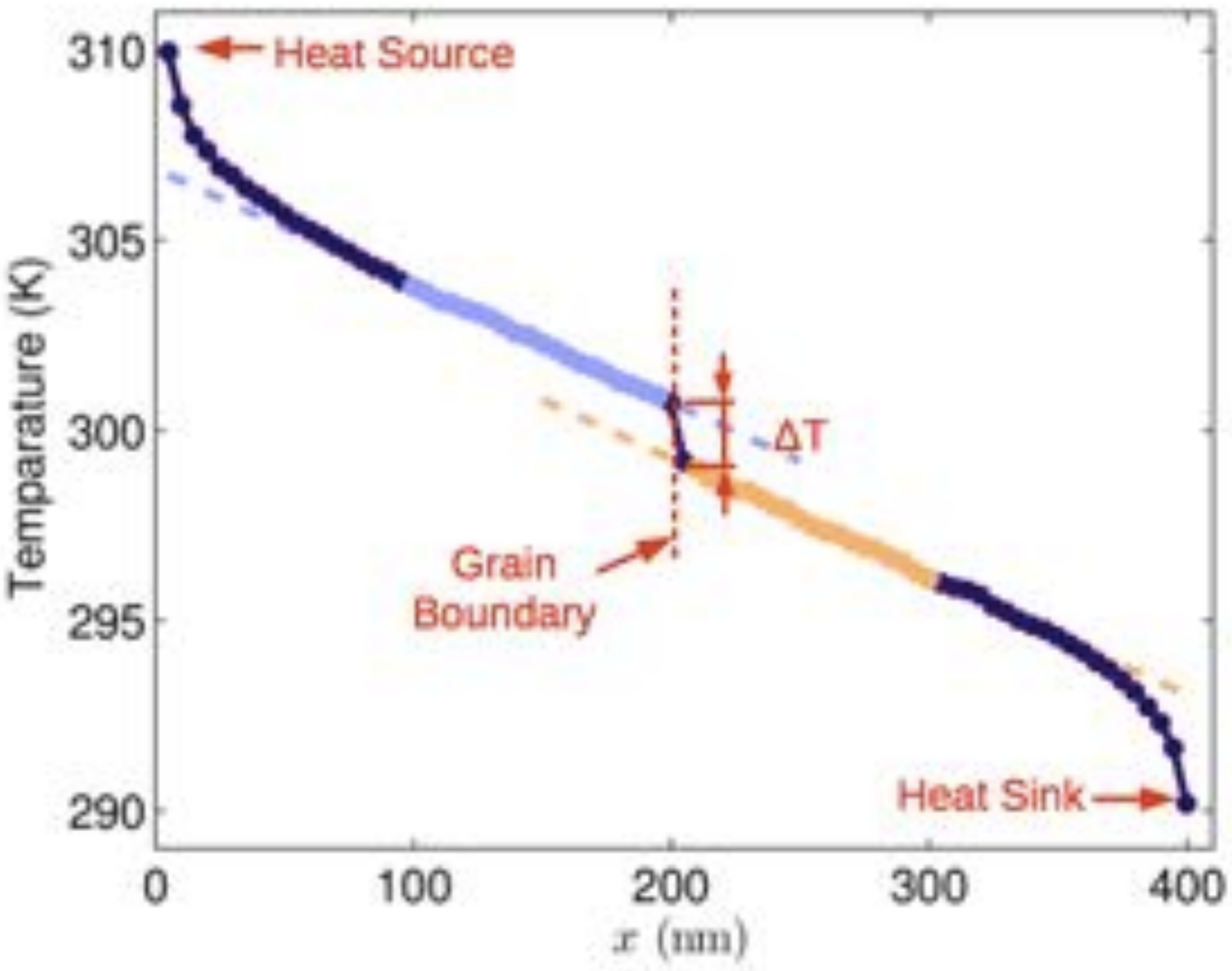
Heat Conduction in Multigrain Flakes



Heat Conduction in Multigrain Flakes

- Heat flow across an interface is characterised by *Kapitza conductance*

$$Q = G\Delta T$$



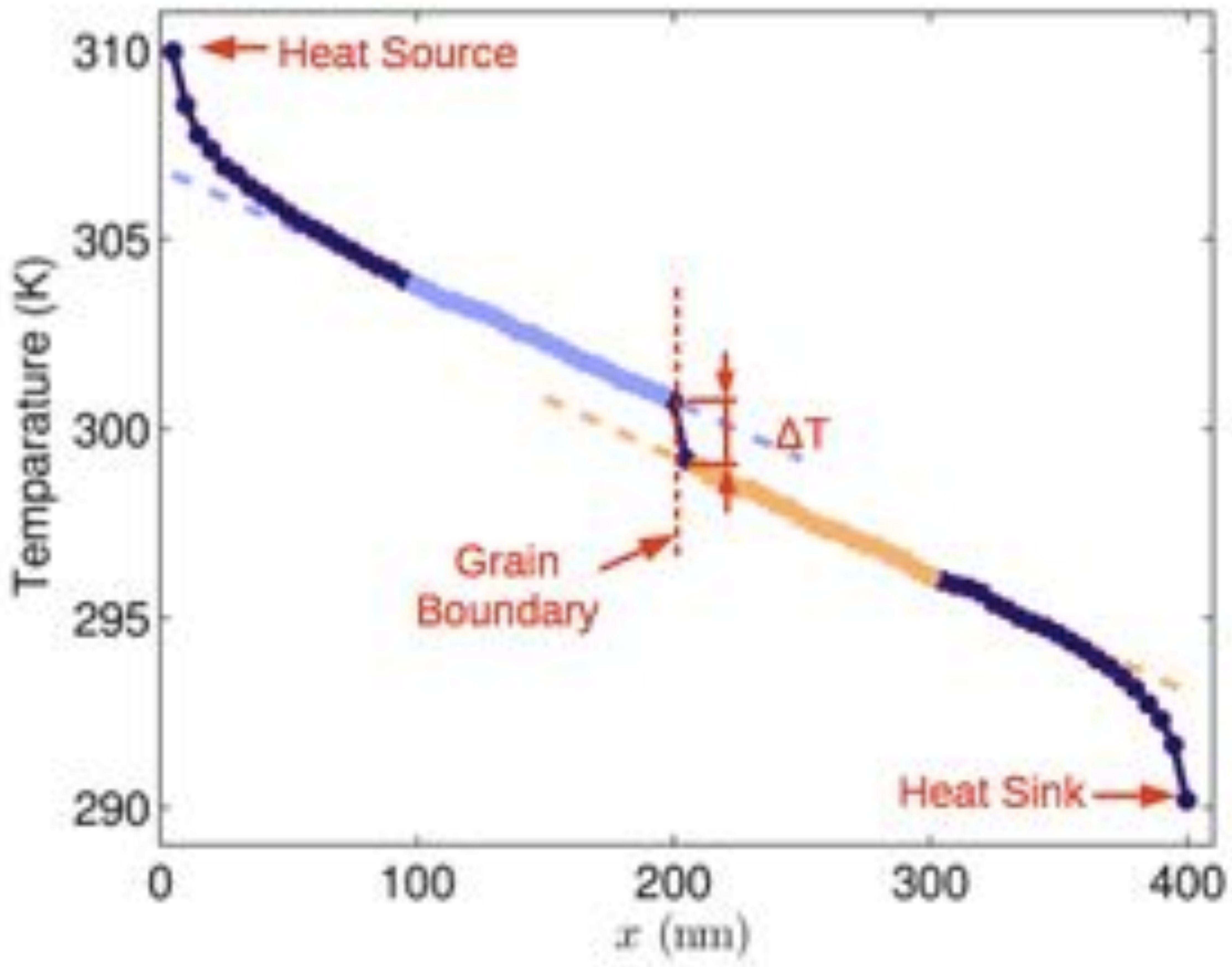
Heat Conduction in Multigrain Flakes

- Heat flow across an interface is characterised by *Kapitza conductance*

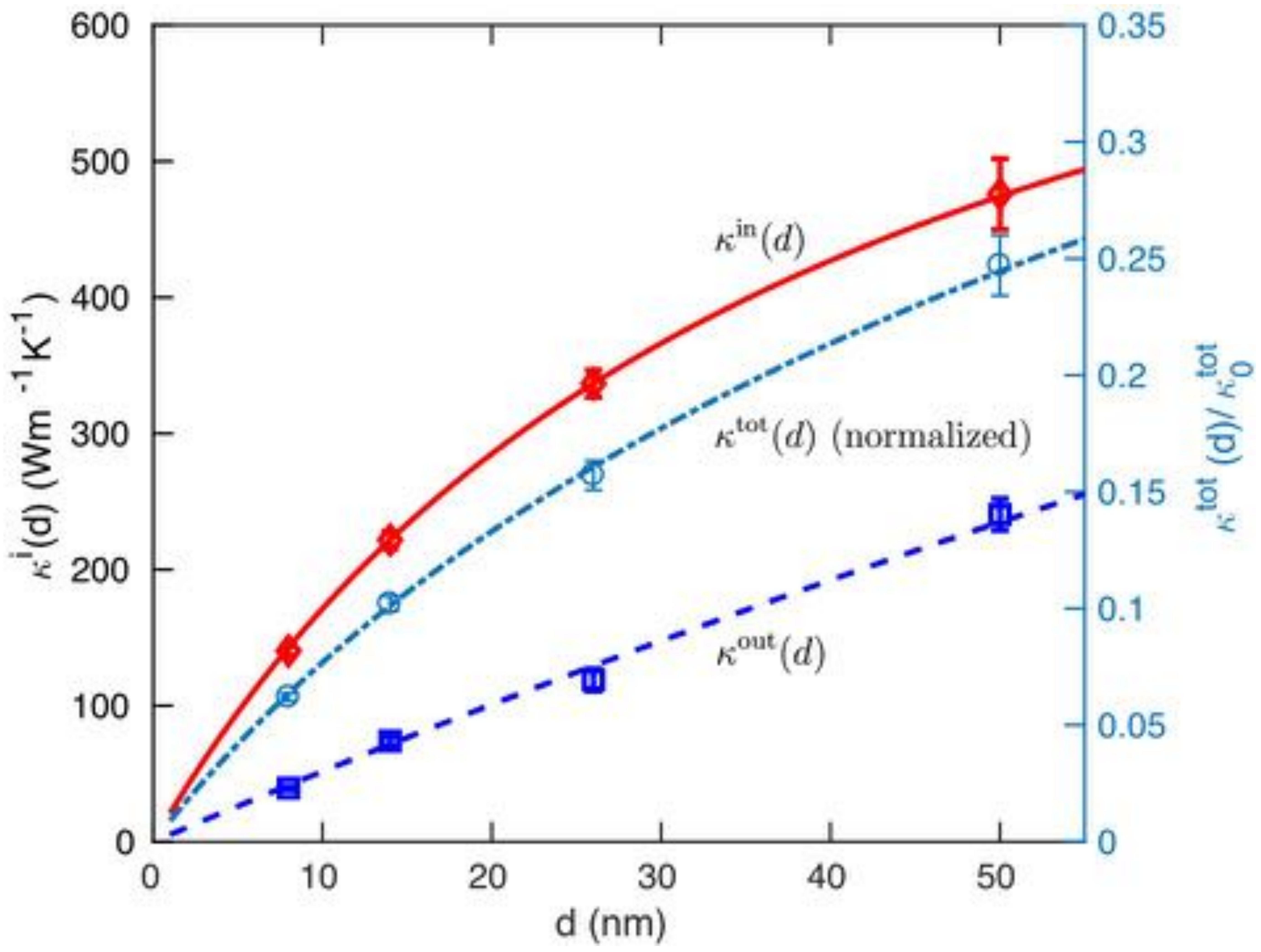
$$Q = G\Delta T$$

- The *Kapitza length L* equals the thickness of the material of thermal conductivity κ that provides the same change in temperature as a given interface

$$L^i = \kappa^i / G^i \quad (i = \text{in, out})$$

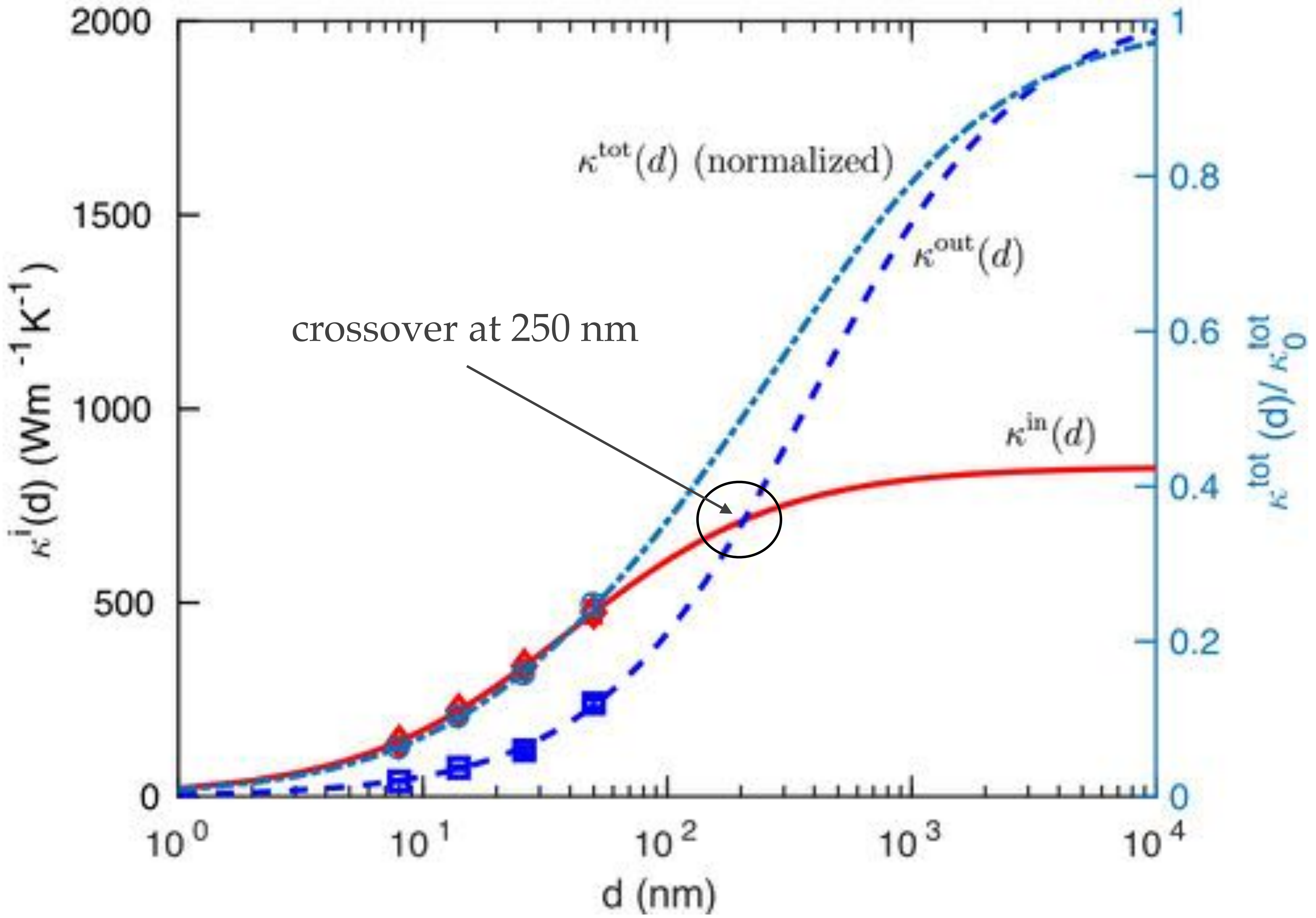


Heat Conduction in Multigrain Flakes



- Heat conductivity out of plane is *strongly suppressed* by grains

Heat Conduction in Multigrain Flakes



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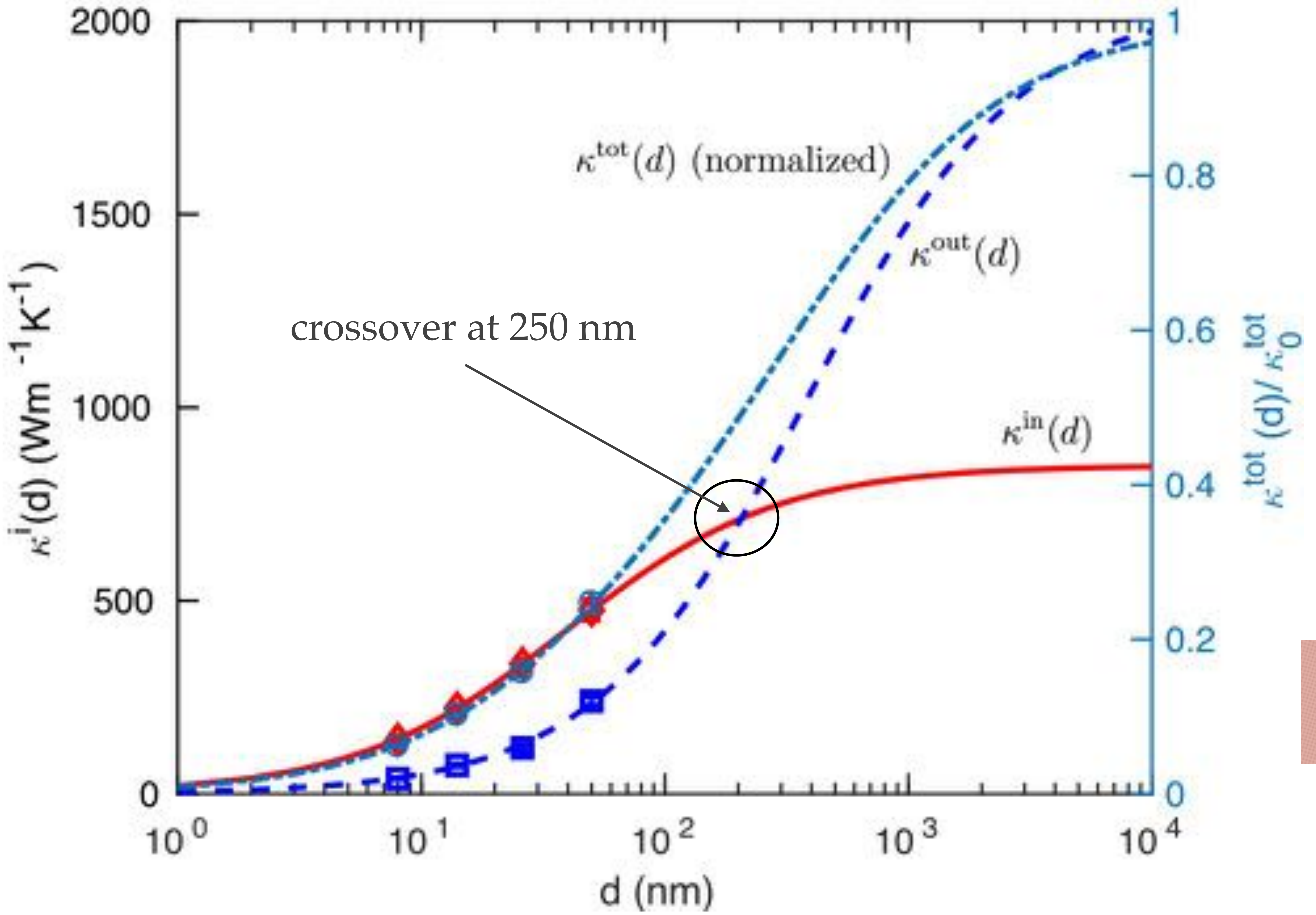
Heat Conduction in Multigrain Flakes



- Heat conductivity out of plane is *strongly suppressed* by grains
- The Kapitza length L for out of plane is an *order of magnitude larger* than that of the in-plane

$$L^{out} \approx 400 \text{ nm} \gg L^{in} \approx 40 \text{ nm}$$

Heat Conduction in Multigrain Flakes

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ARTICLE

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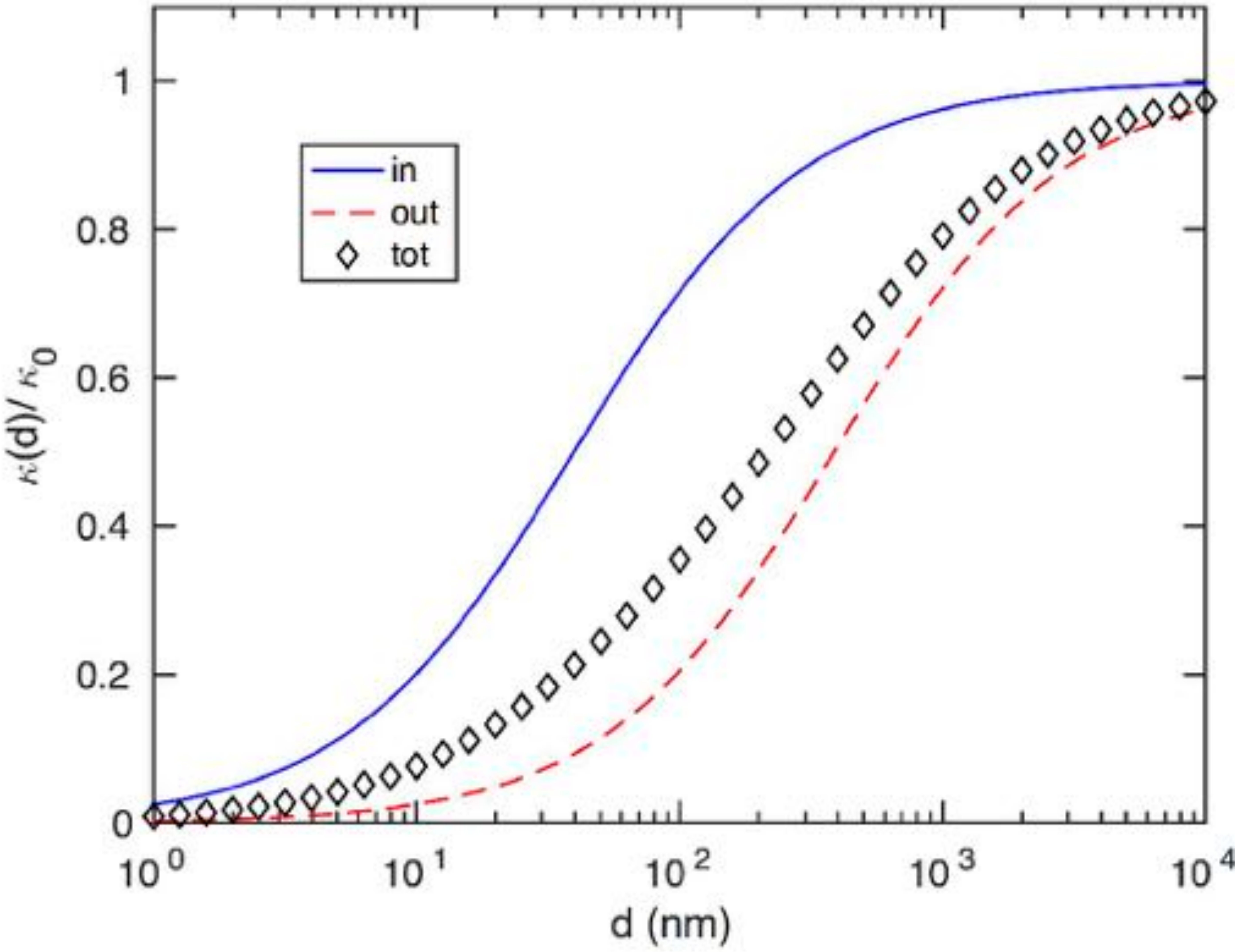
Tailoring the thermal and electrical transport properties of graphene films by grain size engineering

Teng Ma[1], Zhibo Liu[1], Jinxiu Wen[2], Yang Gao[1], Xibiao Ren[3], Huanjun Chen[2], Chuanhong Jin[3], Xiu-Liang Ma[1], Ningsheng Xu[2], Hui-Ming Cheng[1] & Wencai Ren[1]

Heat Conduction in Multigrain Flakes



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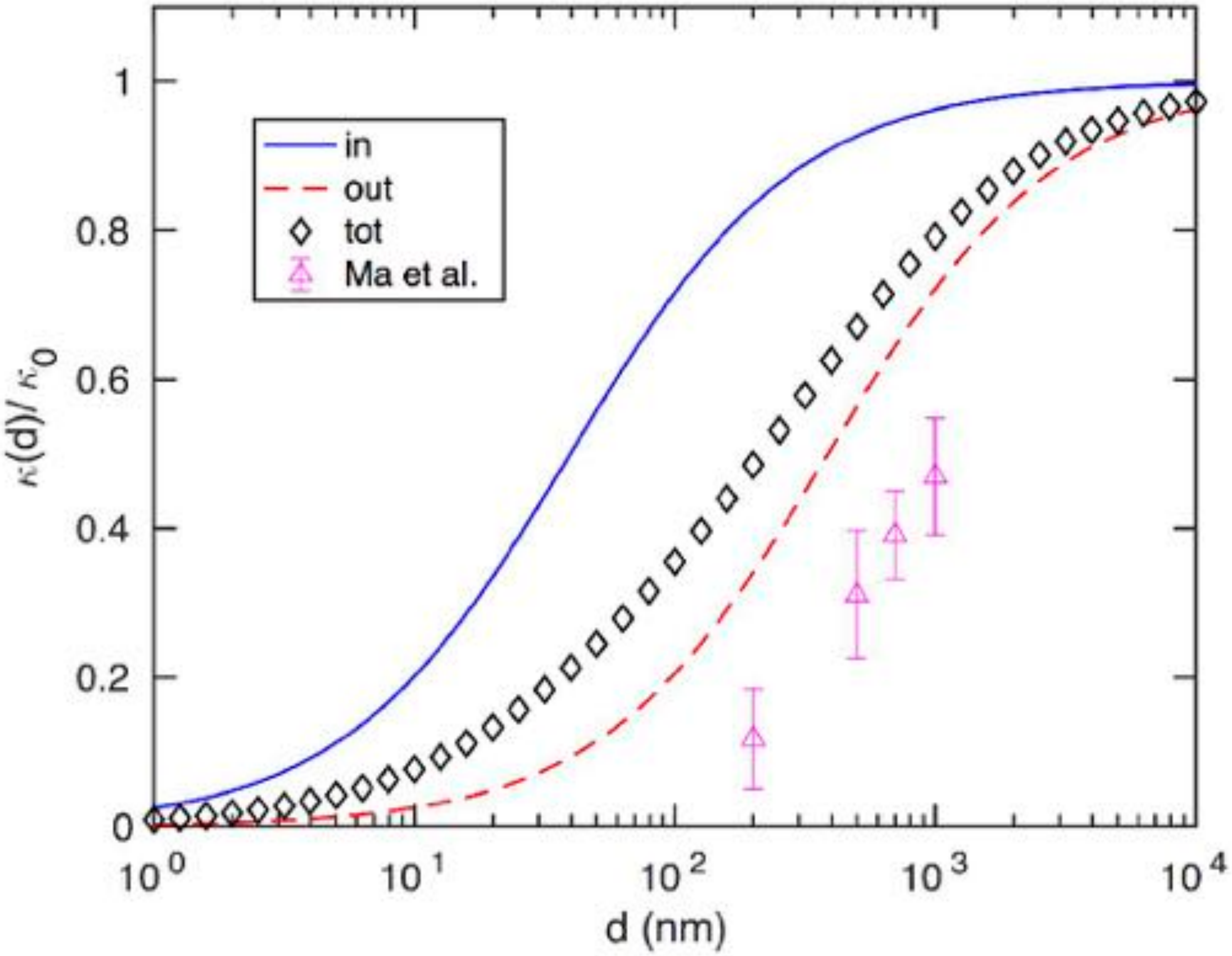
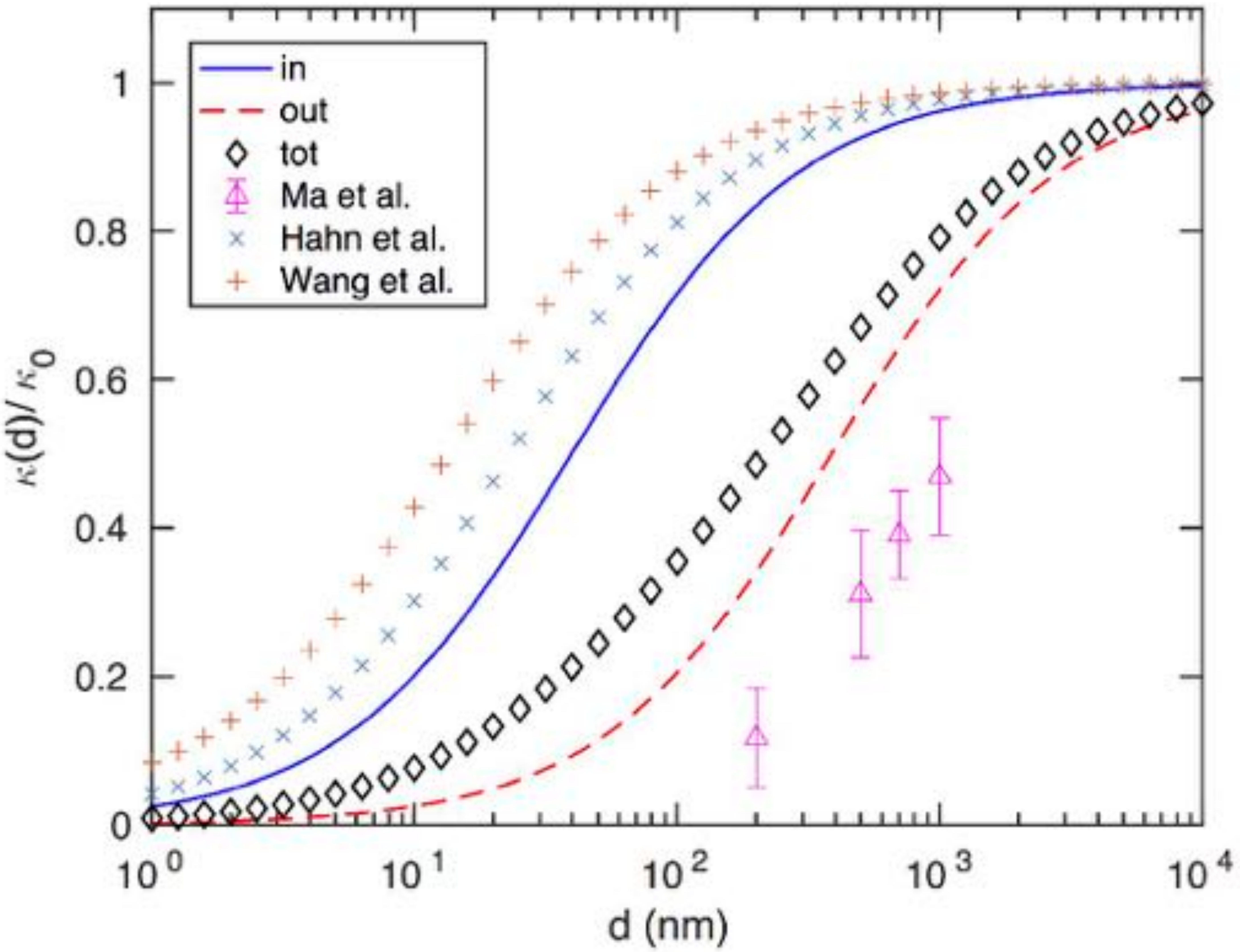


Heat Conduction in Multigrain Flakes

[Y. Wang *et al.*, J. Mater. Res. **29**, 362 (2014)]

[K.R. Hahn *et al.*, Carbon **96**, 429 (2016)]



Heat Conduction in Multigrain Flakes

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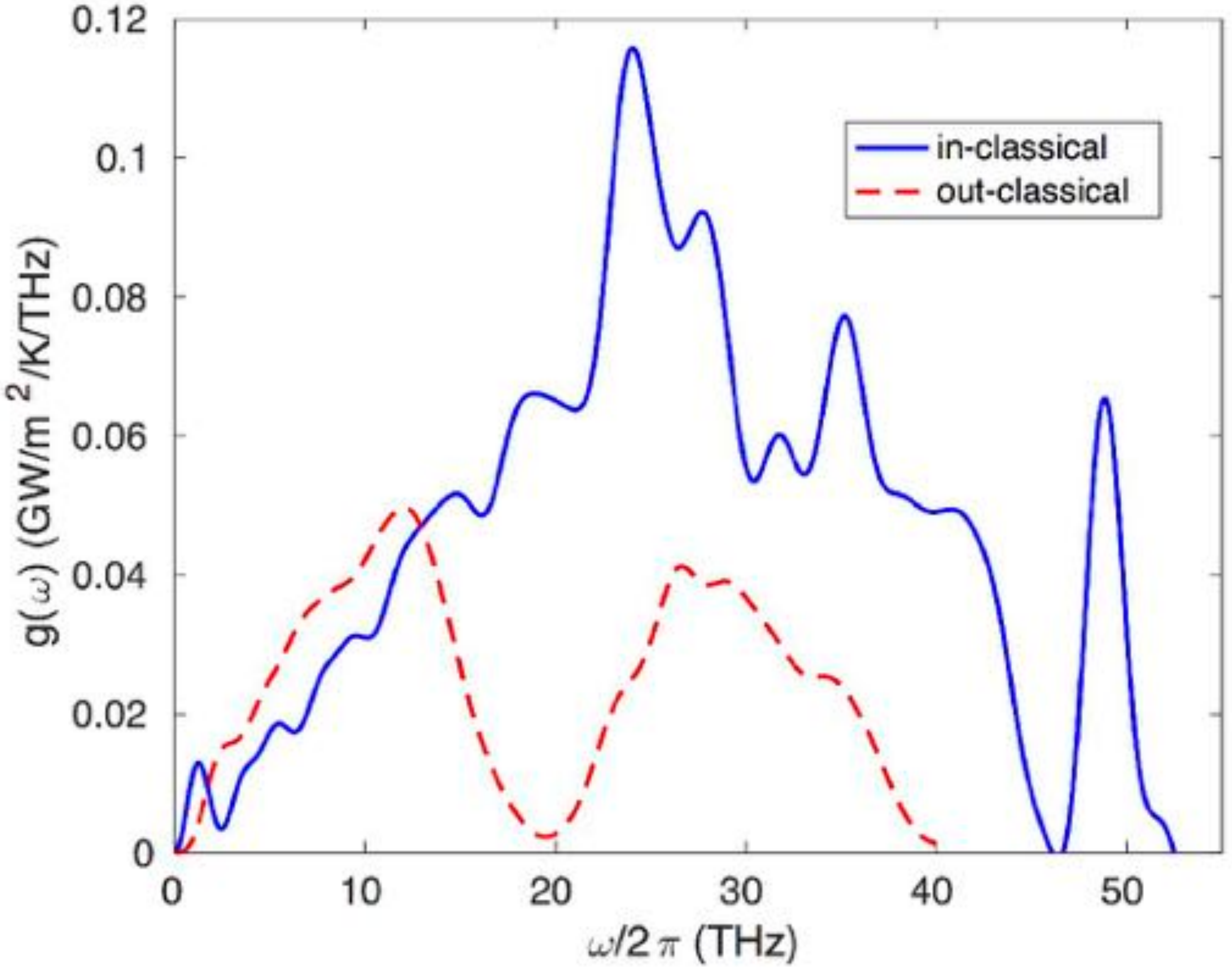
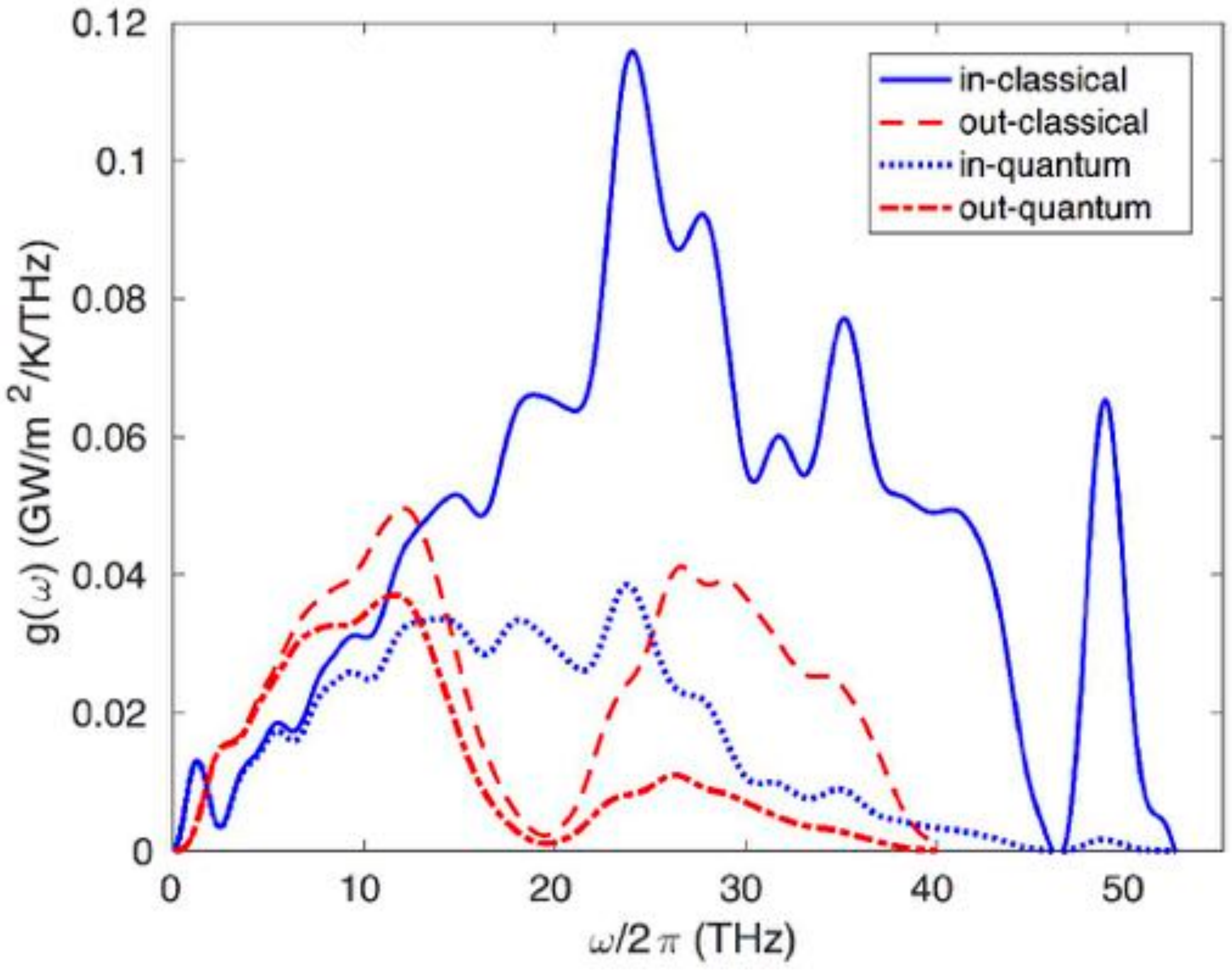


- Spectral conductance

$$g_{A\to B}^{\text{in/out}}(\omega) = \frac{q_{A\to B}^{\text{in/out}}(\omega)}{S|\Delta T|}$$

[K. Sääskilahti *et al.*, AIP Adv. **6**, 12190 (2016)]

Heat Conduction in Multigrain Flakes



- Spectral conductance

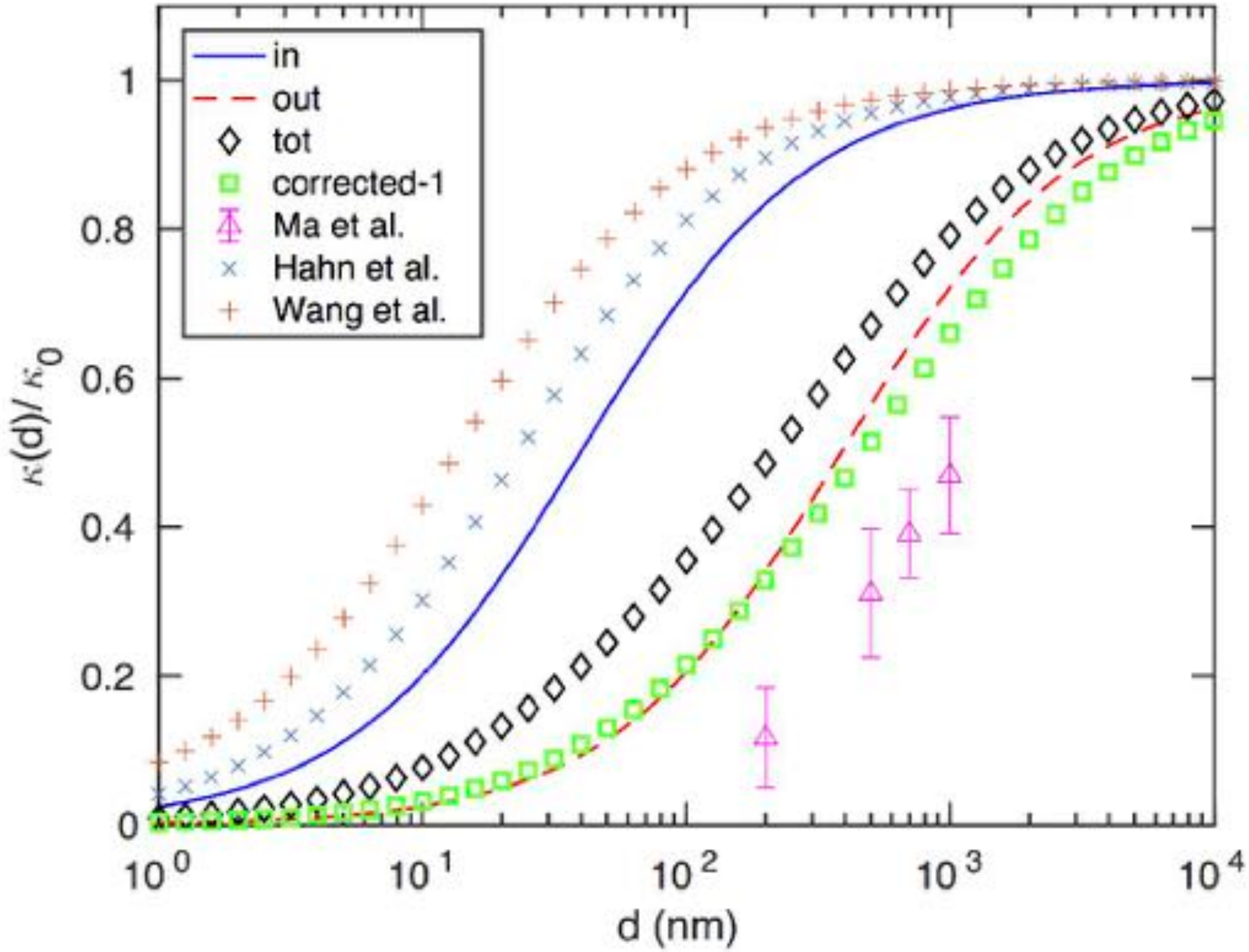
$$g^{\text{in/out}}_{A\to B}(\omega) = \frac{q^{\text{in/out}}_{A\to B}(\omega)}{S|\Delta T|}$$

[K. Sääskilahti *et al.*, AIP Adv. **6**, 12190 (2016)]

- Quantum corrected by Bose-Einstein factor

$$L^{\text{in}} \approx 120 \text{ nm and } L^{\text{out}} \approx 800 \text{ nm}$$

Heat Conduction in Multigrain Flakes



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Heat Conduction in Pristine Graphene

- For pristine graphene we find at $T = 300$ K (MD with opt. Tersoff)

$$\kappa_0^{\text{in}} \approx 800 \ \text{Wm}^{-1}\text{K}^{-1} \ \text{and} \ \kappa_0^{\text{out}} \approx 2\ 100 \ \text{Wm}^{-1}\text{K}^{-1}$$

$$\kappa_0 = \kappa_0^{\text{in}} + \kappa_0^{\text{out}} = 2\ 900 \ \text{Wm}^{-1}\text{K}^{-1}$$

Experimentally $\kappa_0 \approx 1500 - 2500 \ \text{Wm}^{-1}\text{K}^{-1}$

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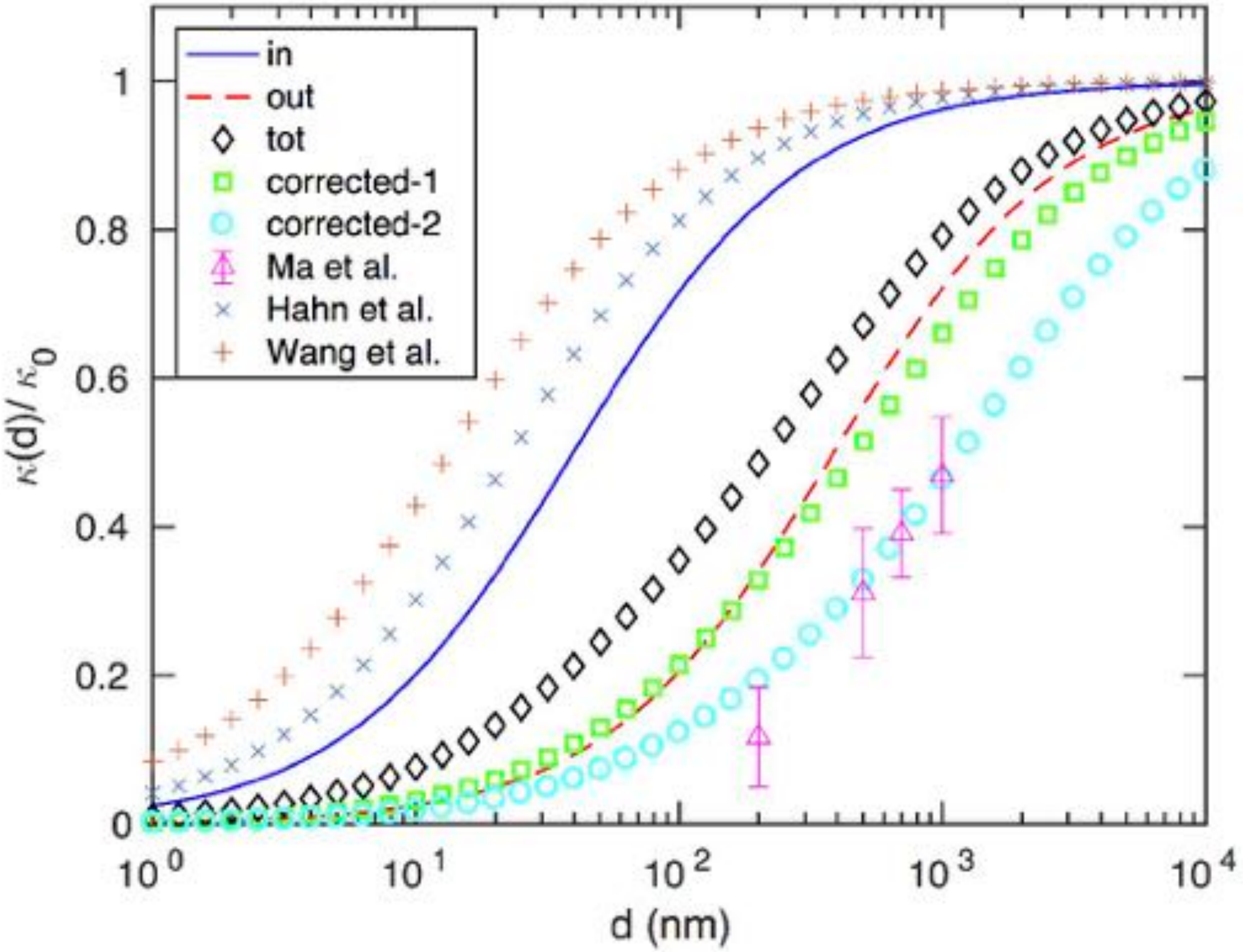
Recent lattice dynamics calculations give 5 450 W/mK [Y. Kuang *et al.*, Int. J. Heat Mass Transfer **101**, 772 (2016)]

Heat Conduction in Multigrain Flakes



- Final estimates for the Kapitza lengths

$L^{\text{in}} \approx 0.12\ \mu\text{m}$ and $L^{\text{out}} \approx 2\ \mu\text{m}$

Summary and Conclusions

- Phase-field crystal models can be employed for a *quantitative description* of 2D grain boundaries in graphene by proper fitting of the elastic properties
- PFC models produce realistic 5|7 grain boundaries in most cases
- Large multigrain samples (microns in linear size) can be generated for MD relaxation in 3D and used for further investigations (thermal, mechanical and transport properties) - *thermal transport is controlled by flexural modes in pristine graphene and strongly affected by grains*
- *Quantum corrections need to be taken into account* both for pristine and multigrain graphene (because of high Debye temperature)

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