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why not change the world?®

Large-scale Atomistic Computations of the Phonons in Twisted Bilayer Graphene

Michael Lamparski | 07/21/20

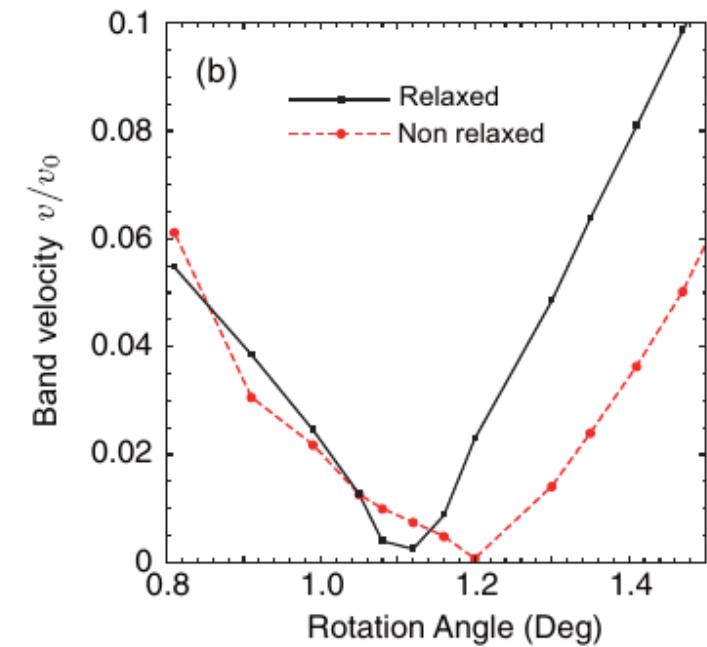
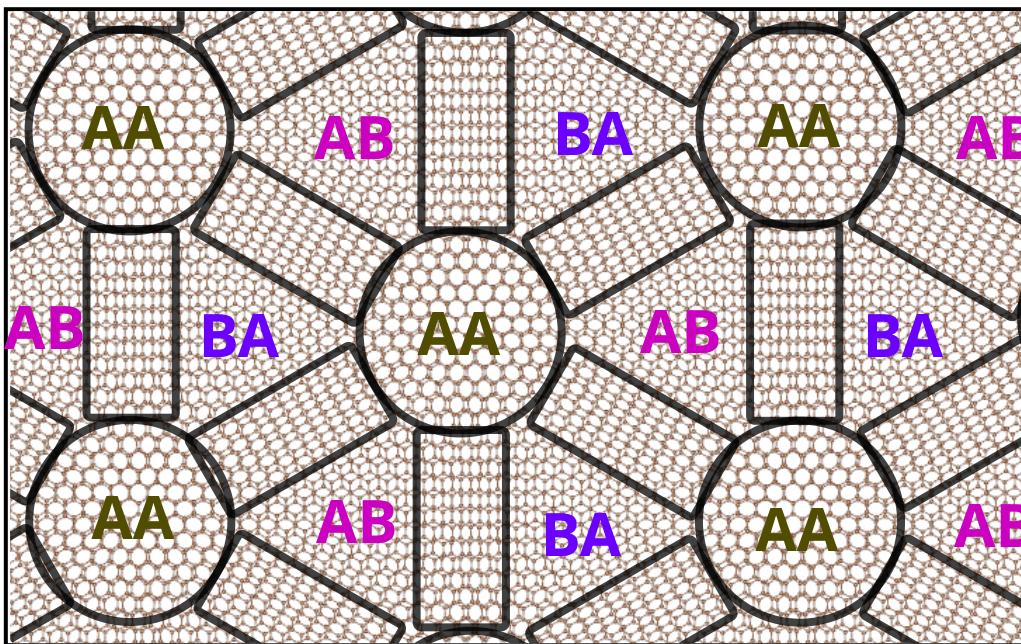
Motivation

- What is twisted bilayer graphene?
 - Two layers of graphene...
 - ...with a twist.
- Potential applications in electronics.
- Magic angle?



Motivation

- Structural relaxation known to play crucial role in electronic properties.



Nam and Koshino, Phys. Rev. B, 7 075311 (2017)

- What about phonons?
- Relaxation calls for **atomistic computations!**



Goals

- Goal:
 - Study of **phonons** at **many twist angles** with **relaxation** accounted for.
 - Not just at magic angle.
 - Did **all angles that produce cells under 20k atoms**. (692 structures)
- Explore the question of mapping Raman spectra to angle.
- Discover new physics!



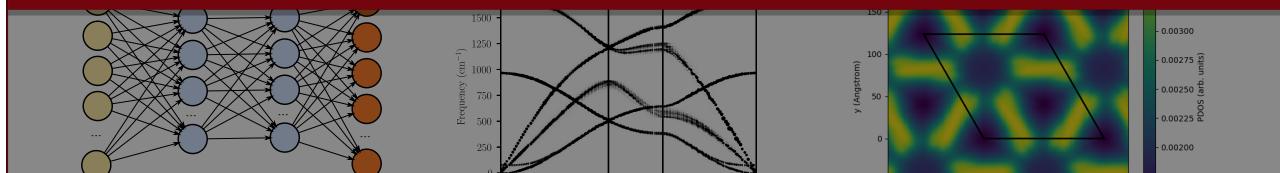
1. Introduction



2. Database Generation



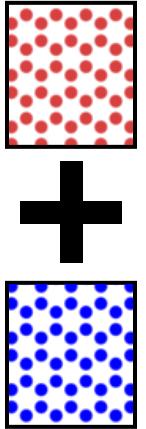
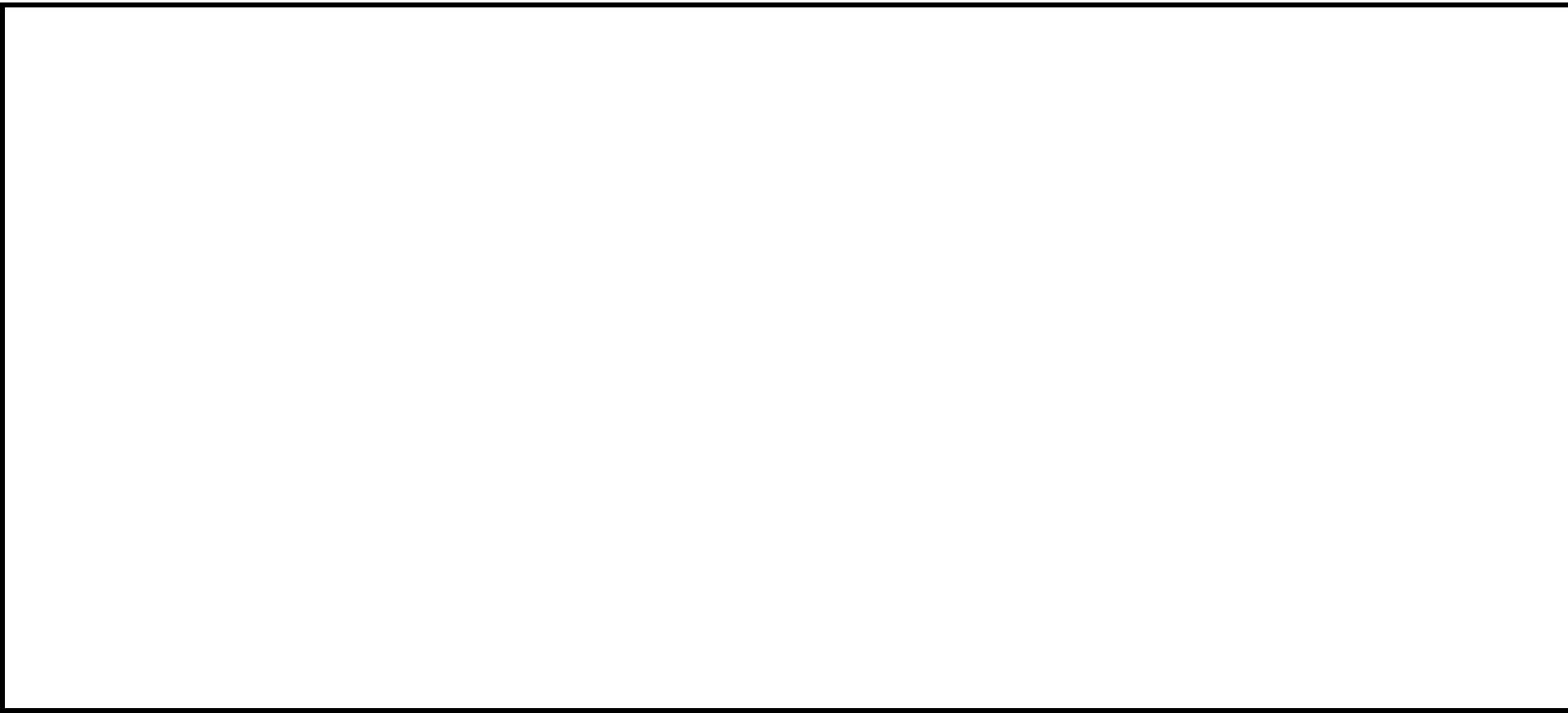
3. Analysis



4. Outcomes



Moiré patterns

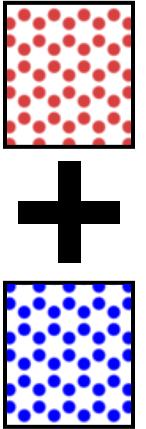
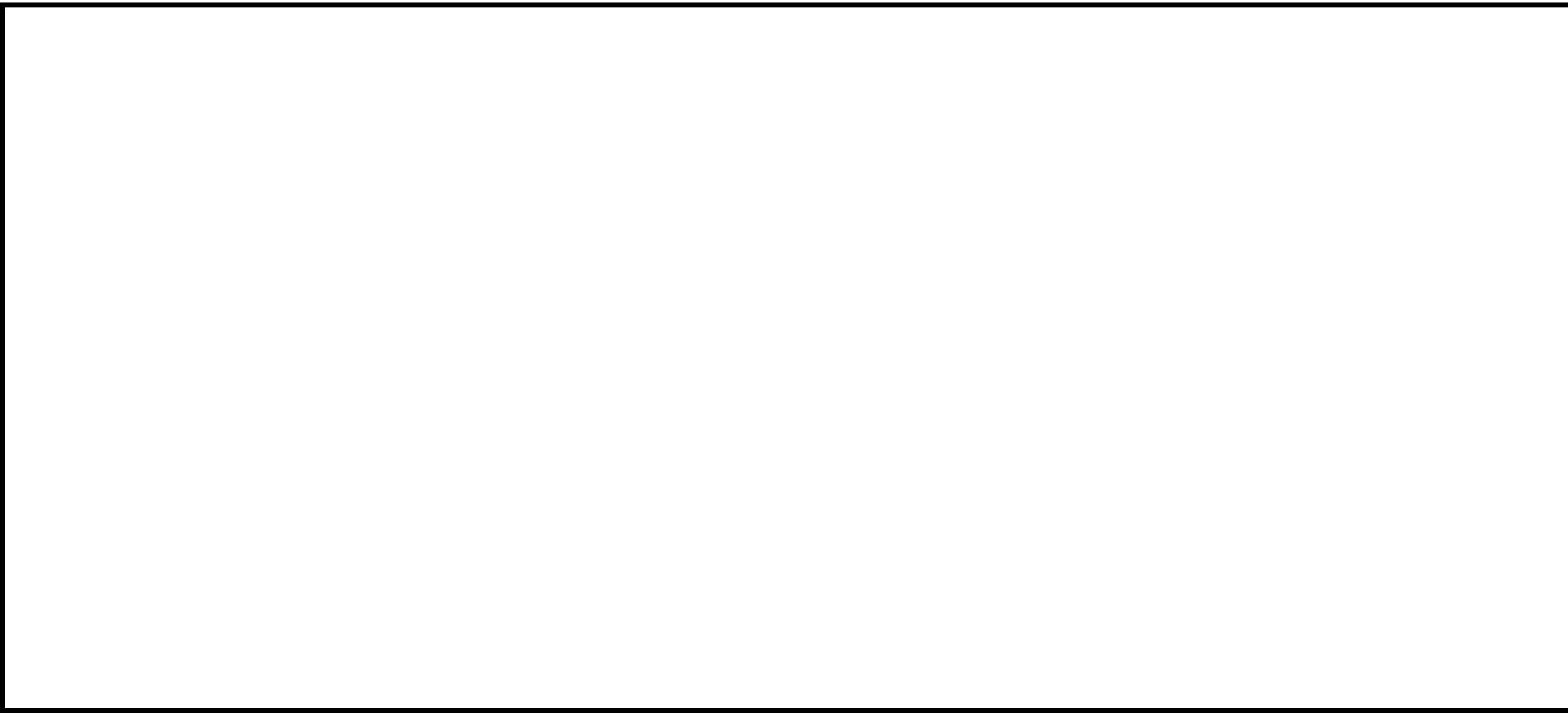


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6 . 1

Moiré patterns

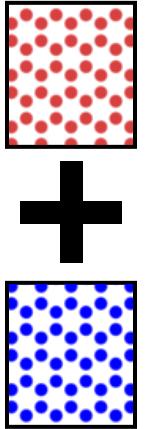
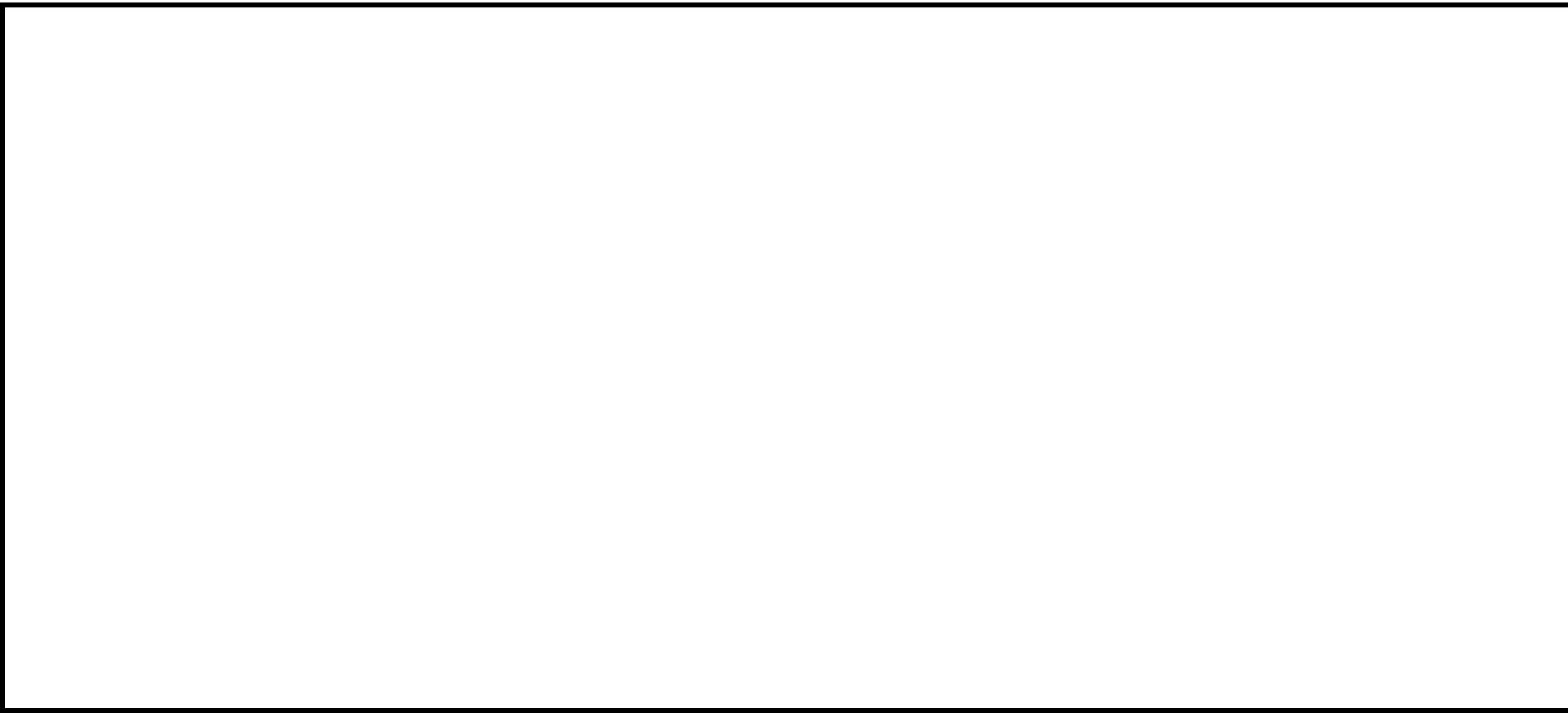


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6 . 2

Moiré patterns



Commensurate cell twist angles via number theory

- Relaxation requires periodic boundary conditions.
- **Not all twist angles** generate a periodic structure!
- How to enumerate those that do?
- Already known two-integer parameterization:

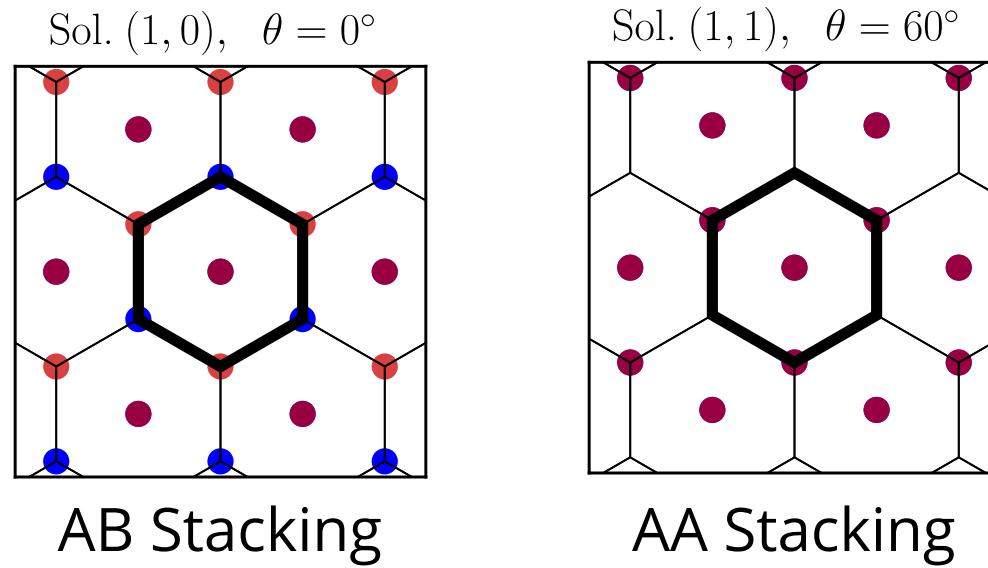
$$\theta_{uv} = \cos^{-1} \frac{3u^2 - v^2}{3u^2 + v^2} \quad \begin{array}{l} u \geq v \geq 0 \\ \gcd(u, v) = 1 \end{array}$$

(**aside:** only **square** and **hexagonal crystal systems** admit any interesting commensurate cells from pure rotation)



Generating commensurate cells

$$\gcd(1, 0) = 1$$
$$\gcd(1, 1) = 1$$

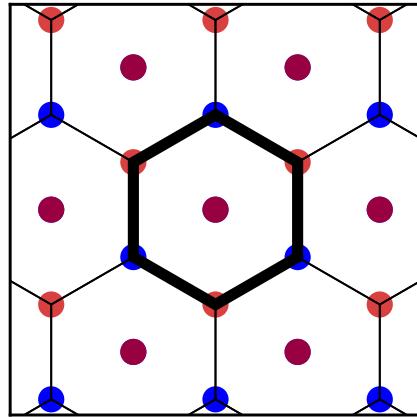


Generating commensurate cells

$$\begin{aligned}\gcd(1, 0) &= 1 \\ \gcd(1, 1) &= 1\end{aligned}$$

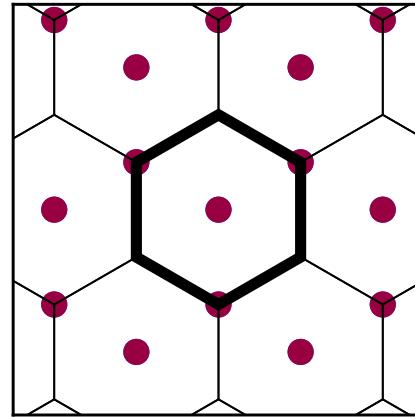
$$\begin{aligned}\gcd(2, 0) &= 0 \\ \gcd(2, 1) &= 1 \\ \gcd(2, 2) &= 2\end{aligned}$$

Sol. (1, 0), $\theta = 0^\circ$



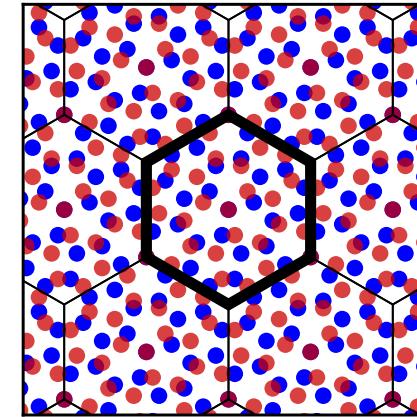
AB Stacking

Sol. (1, 1), $\theta = 60^\circ$

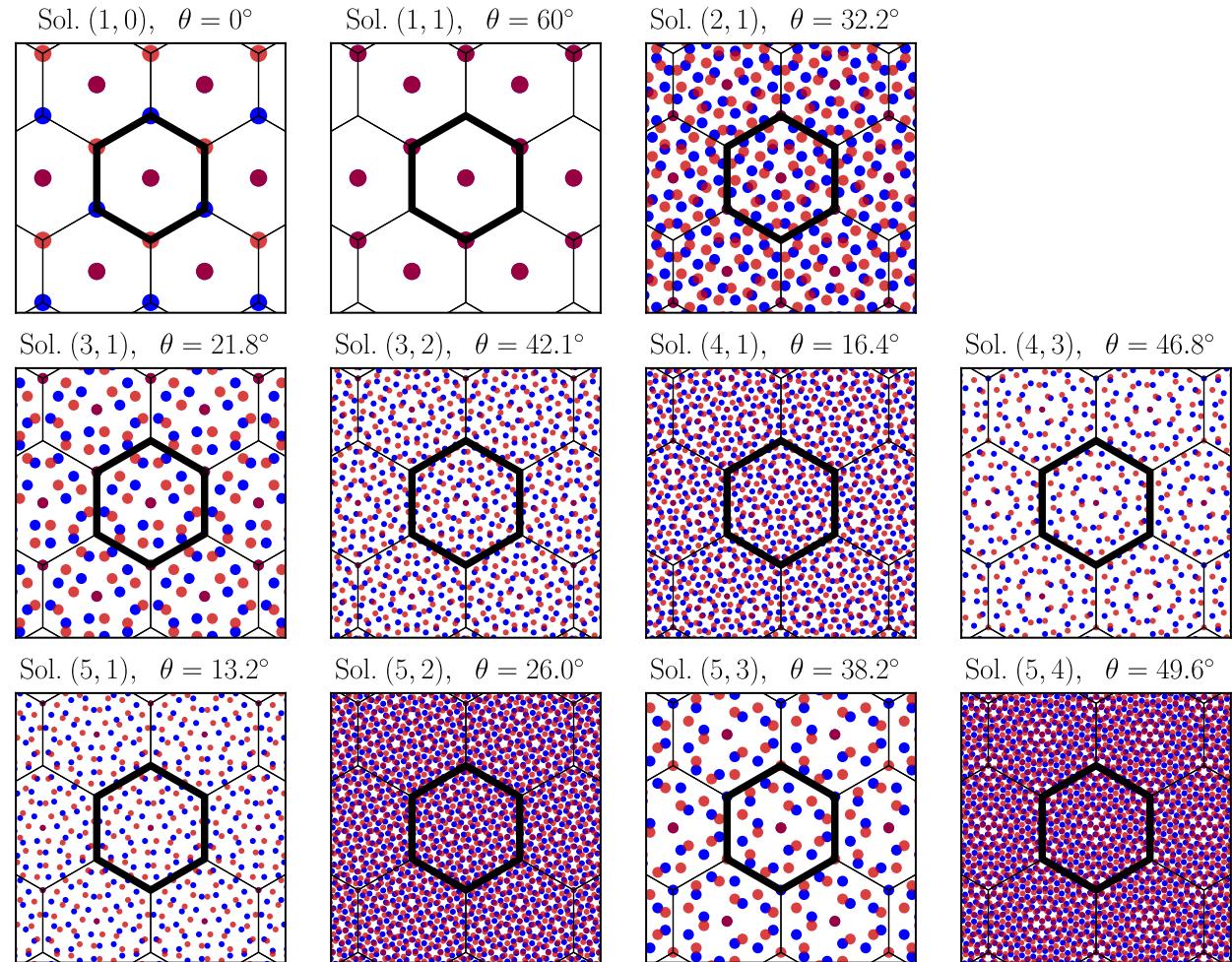


AA Stacking

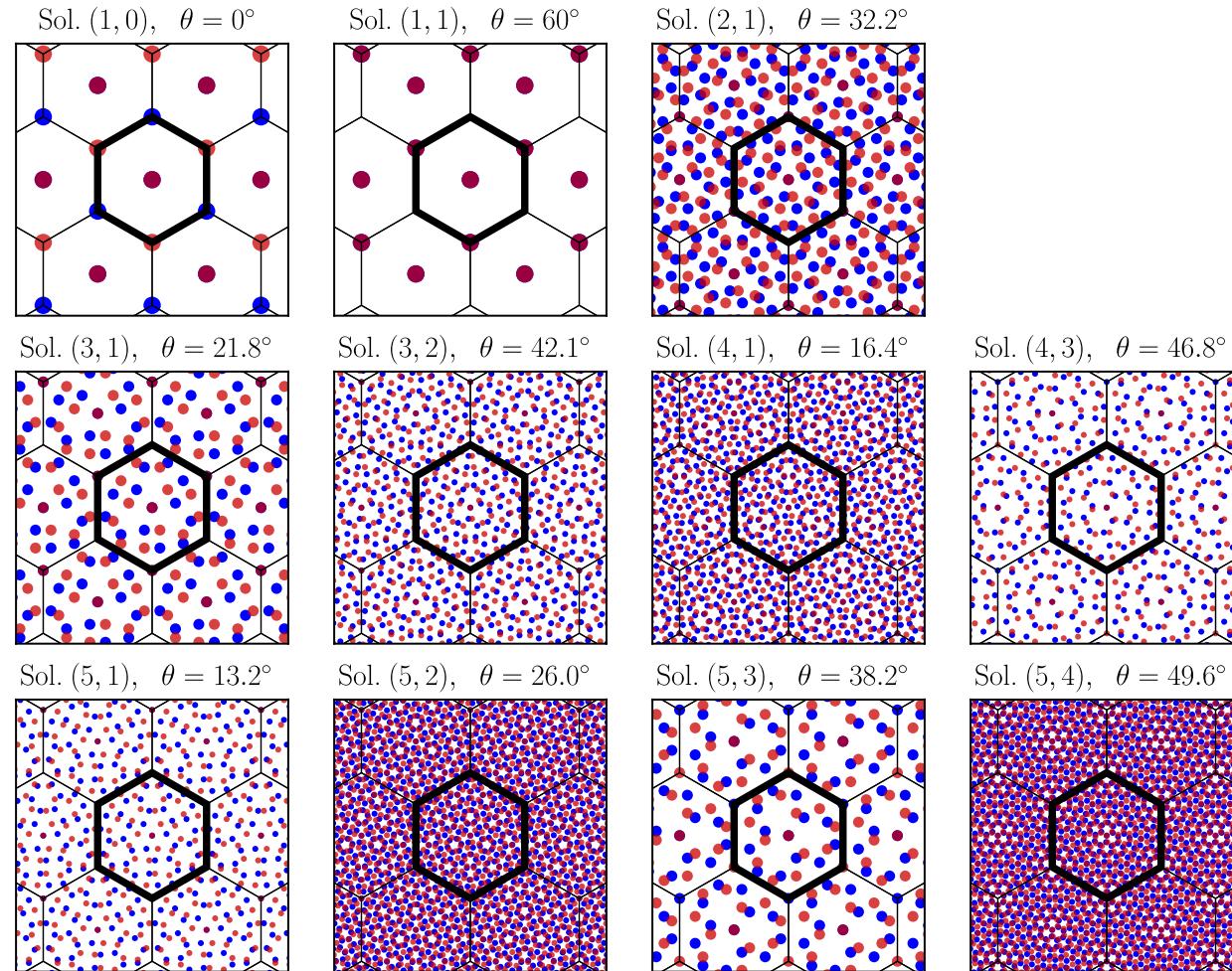
Sol. (2, 1), $\theta = 32.2^\circ$



Generating commensurate cells



Generating commensurate cells



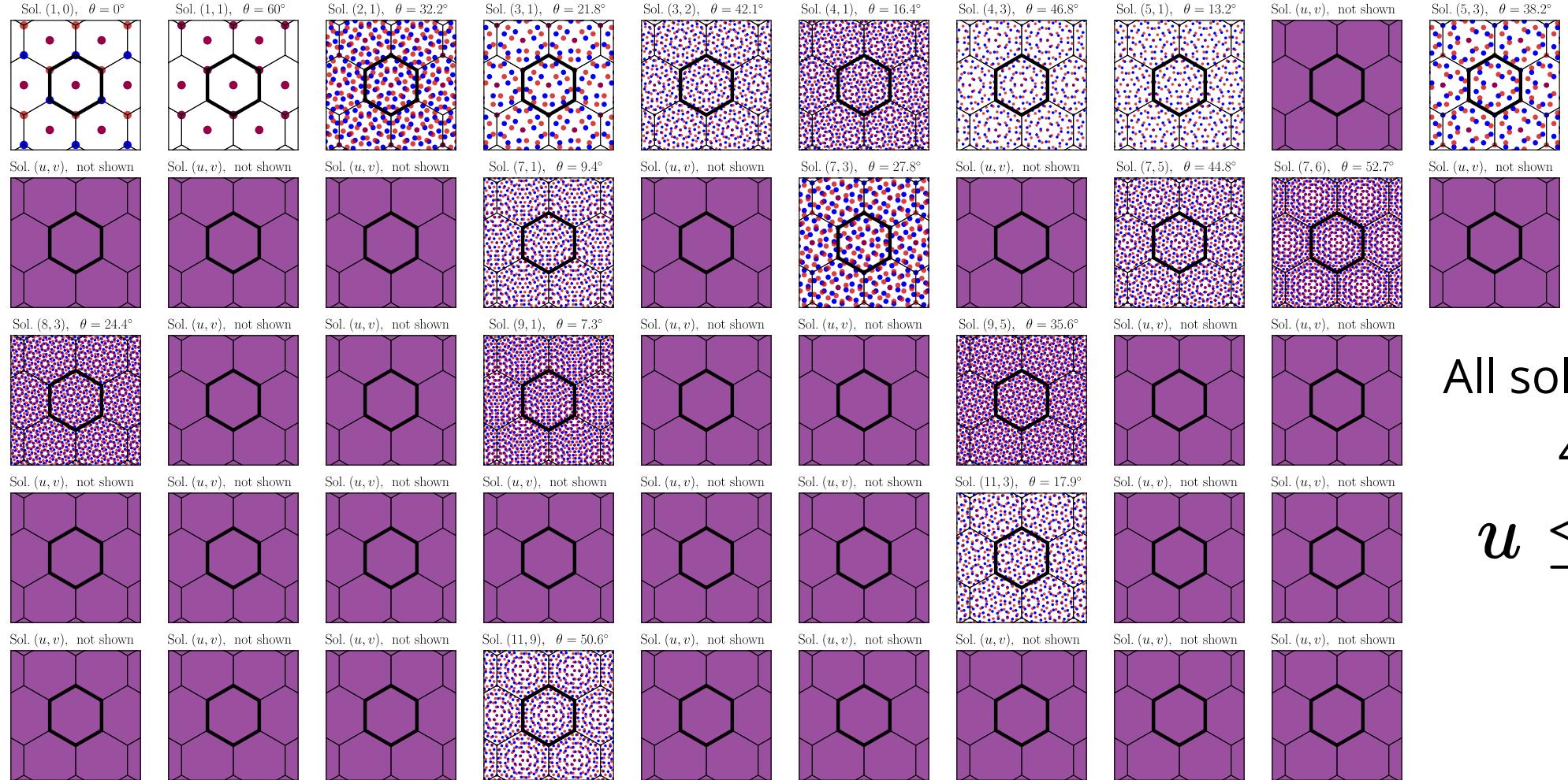
All solutions under
40 cells?

$$u^2 \leq 4N$$

$$u \leq 12.649$$



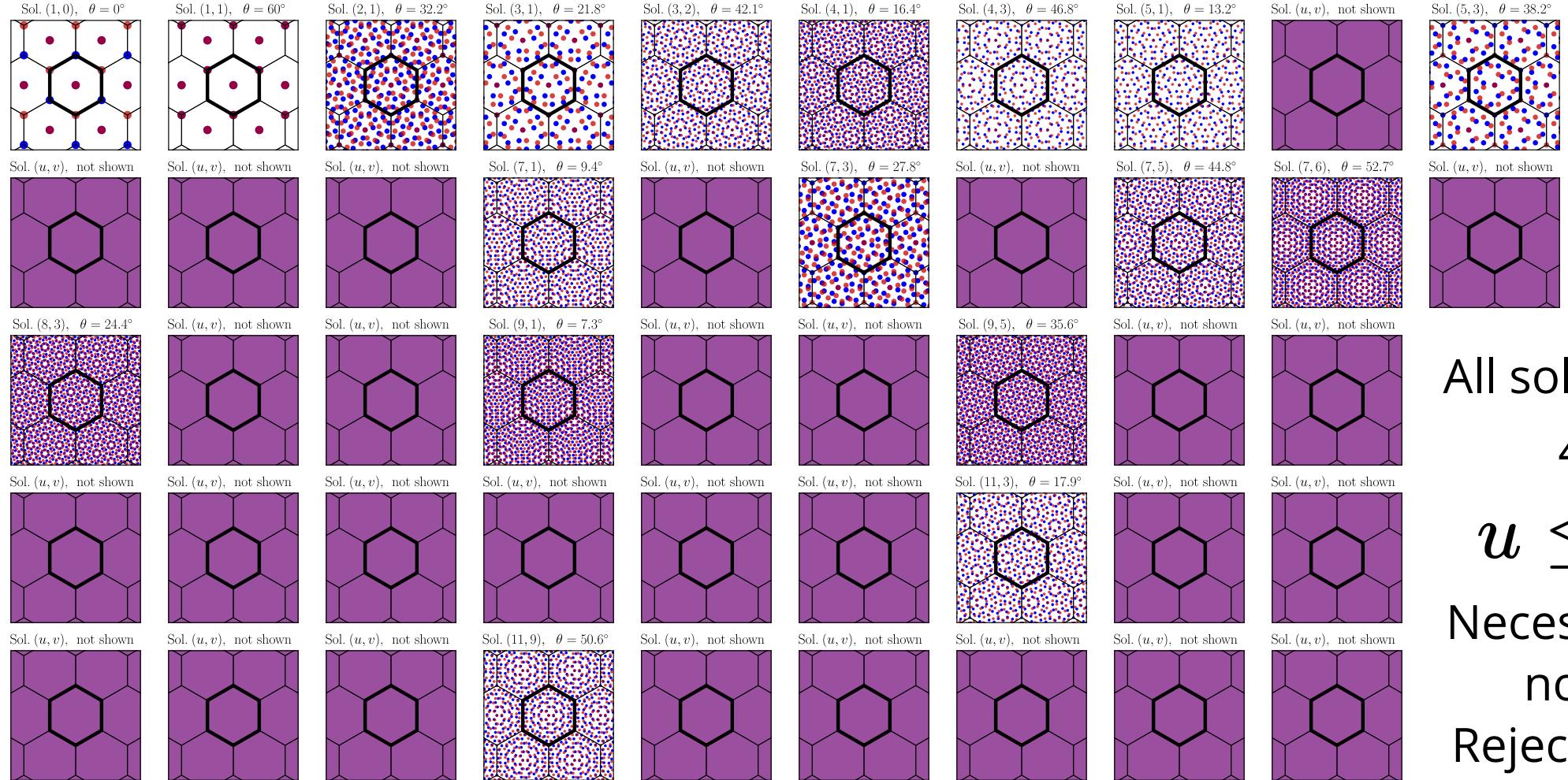
Generating commensurate cells



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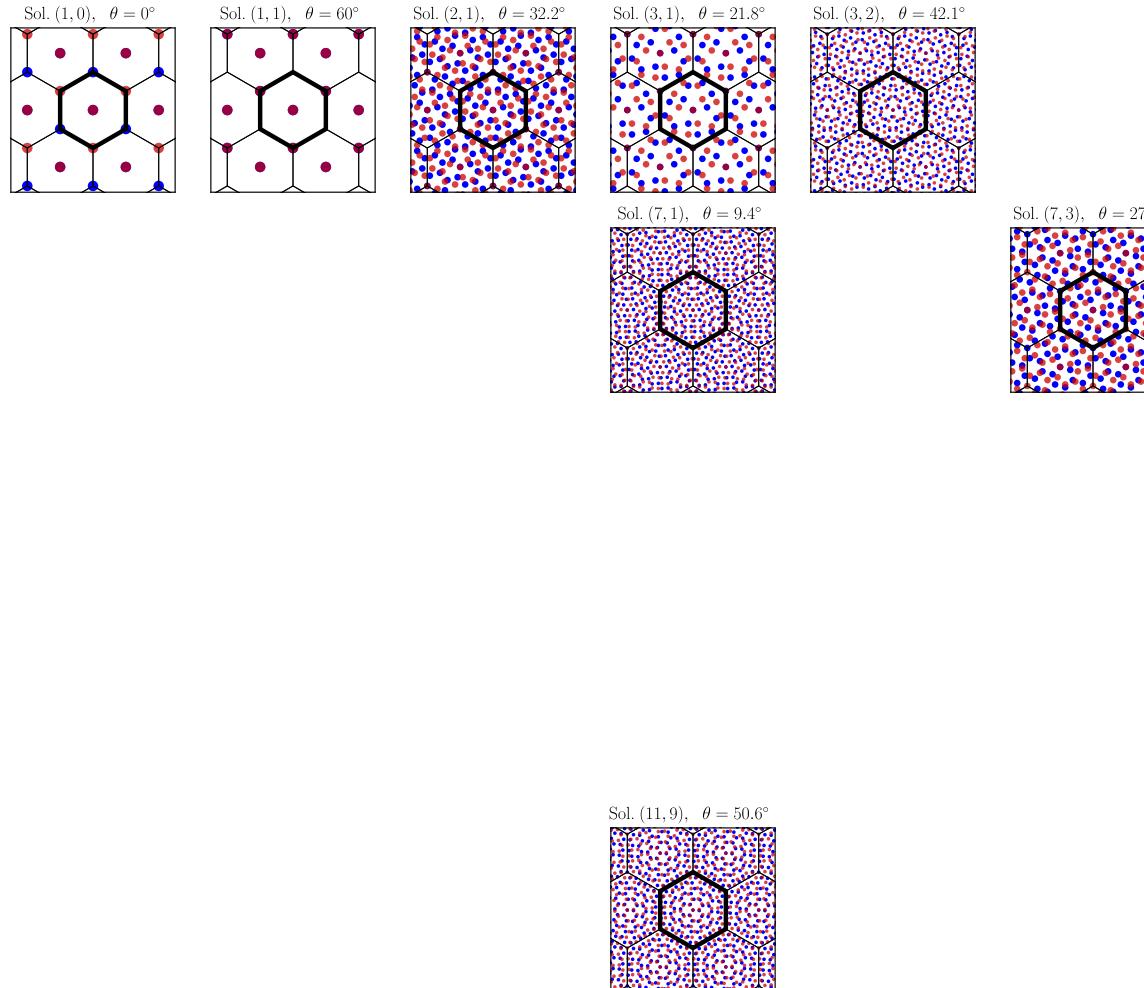
Generating commensurate cells



All solutions under
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 $u \leq 12.649$
Necessary condition,
not sufficient.
Reject the bad ones!



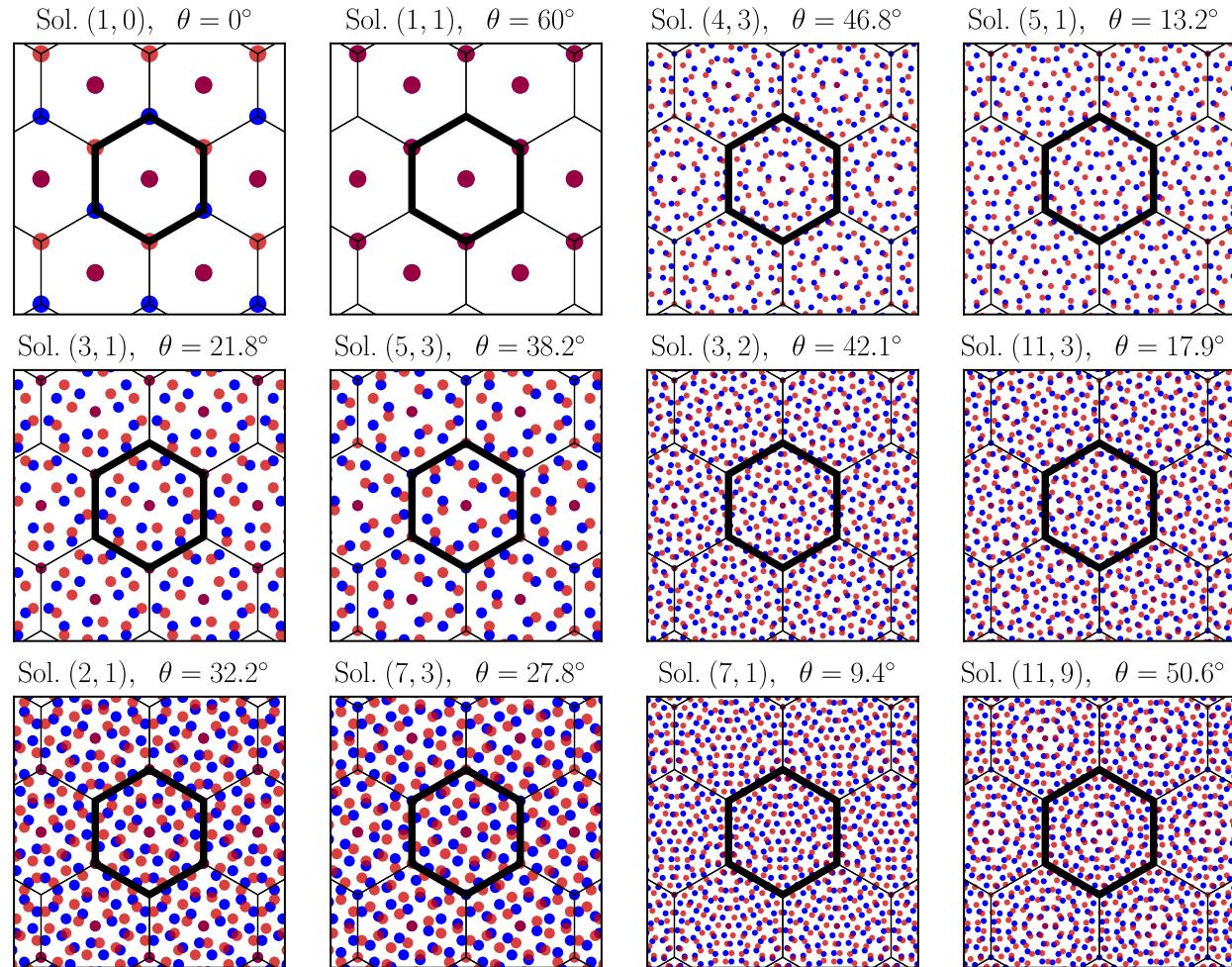
Generating commensurate cells



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Necessary condition,
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Generating commensurate cells



- Go big or go home: **Classical force field**
- Second-generation **REBO** [1]
 - Versatile at modeling geometry of hydrocarbons.
 - Anticipating **other applications**:

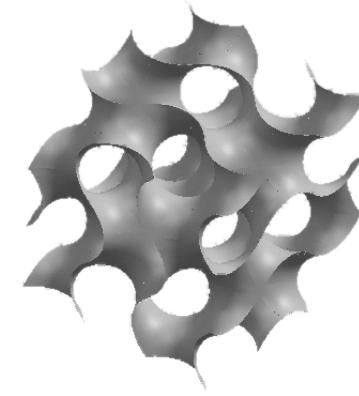
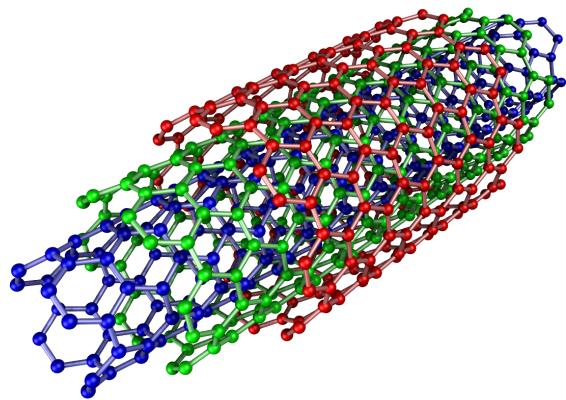
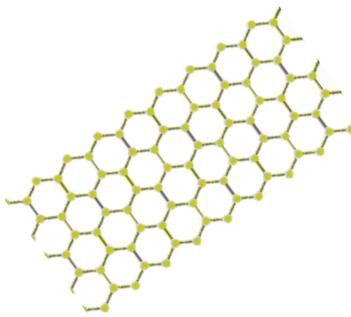


Image credit: Multiwalled carbon nanotube by Eric Weiser, licensed under CC BY SA 3.0.

[1] D. W. Brenner et al, J. Phys.: Condens. Matter, **14** 783 (2002)

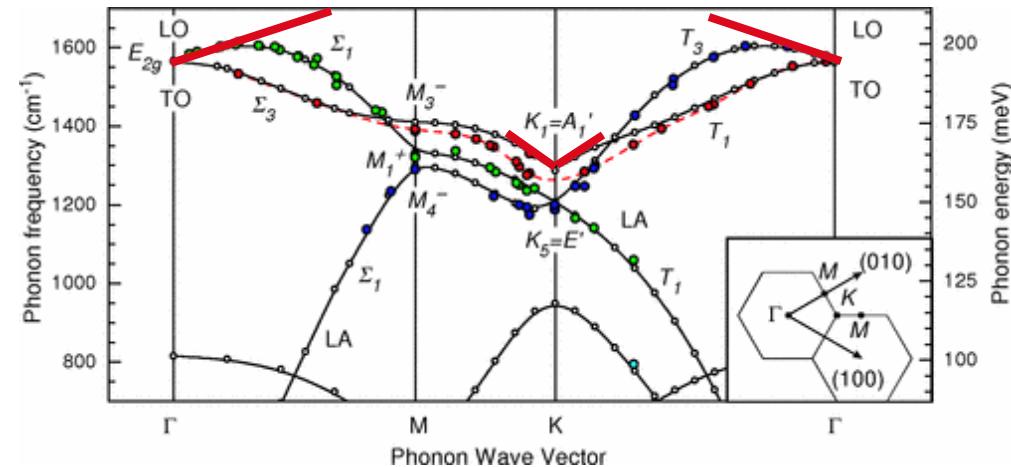


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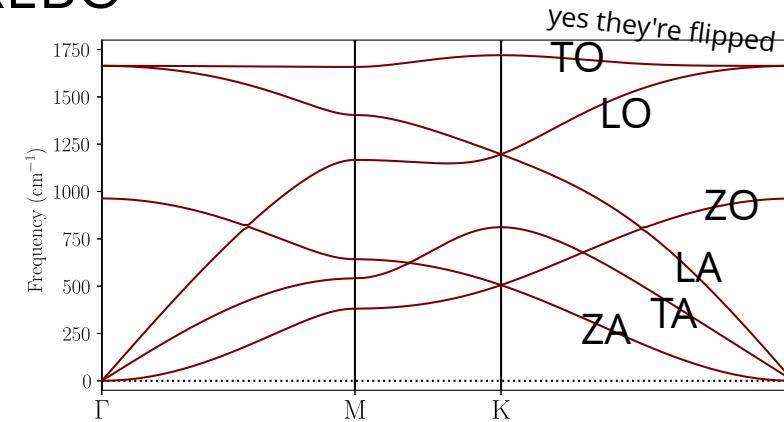
Large-scale atomistic computations of
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- So how are REBO's phonons?
- Out of plane: alright.
- In-plane modes...
 - Lack of **Kohn anomalies**
 - **TO/LO modes** pretty off
- Careful with high frequencies!
 - Gamma point okay...

DFT & XRD data [1]



REBO

[1] J. Maultzsch et al, Phys. Rev. Lett. **92**, 075501 (2004).

- REBO only for covalent bonds.
- What about van der Waals?

AIREBO (Lennard-Jones) [1]

$$V(r) = 4\epsilon \left[-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12} \right]$$

[1] S. J. Stuart, J. Chem. Phys. **112**, 6472 (2000)

[2] A. N. Kolmogorov, and V. H. Crespi, Phys. Rev. B **71**, 235415 (2005)



- REBO only for covalent bonds.
- What about van der Waals?

AIREBO (Lennard-Jones) [1]

$$V_{\text{LJ}} = V_{\text{LJ}}(r)$$

Fundamentally cannot
fit both in-plane corrugation
and out-of-plane compressibility

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Kolmogorov-Crespi [2]

$$V_{\text{KC}} = V_{\text{KC}}(\mathbf{r}_{ij}, \hat{\mathbf{n}}_i, \hat{\mathbf{n}}_j)$$

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z-axis seems
reasonable, right?

[1] S. J. Stuart, J. Chem. Phys. **112**, 6472 (2000)

[2] A. N. Kolmogorov, and V. H. Crespi, Phys. Rev. B **71**, 235415 (2005)



Phonons in the harmonic approximation

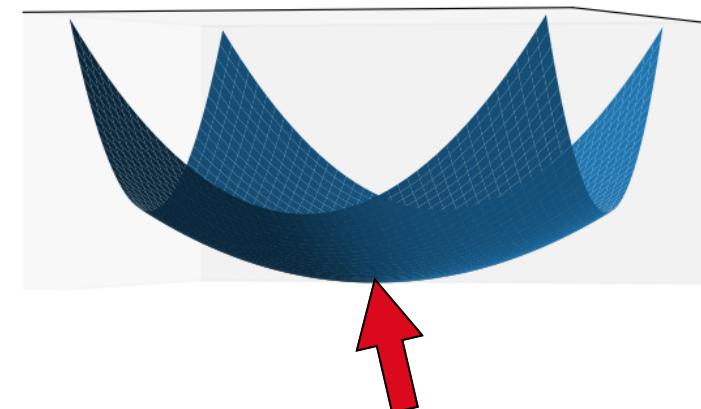
- Perform structural relaxation!
- With structure now at a local minimum of potential energy:

$$V(x) = V(x_0) + \cancel{\frac{dV(x)}{dx} \Big|_{x_0}^x (x - x_0)} + \frac{1}{2!} \left. \frac{d^2V(x)}{dx^2} \right|_{x_0}^x (x - x_0)^2 + \dots$$

$$V(u) = V(0) + \frac{1}{2!} \left. \frac{d^2V(u)}{du^2} \right|_0^u u^2 + \dots \quad \leftarrow (u \equiv x - x_0)$$

$$3D: \quad V(\mathbf{u}) = V(\mathbf{0}) + \frac{1}{2} \mathbf{u}^T \boldsymbol{\Phi} \mathbf{u} + \dots$$

- System of $3n$ coupled **harmonic oscillators**.



Phonons in the harmonic approximation

$$V(\mathbf{u}) = V(\mathbf{0}) + \frac{1}{2} \mathbf{u}^T \Phi \mathbf{u} + \dots$$

- System of $3n$ coupled **harmonic oscillators**.
- Diagonalize $3n \times 3n$ **dynamical matrix** at some \mathbf{q} :

$$\mathbf{D}_{a,b}(\mathbf{q}) = \frac{1}{\sqrt{m_a m_b}} \sum_l \Phi_{a0,bl} e^{i(\mathbf{q} \cdot [\mathbf{x}_{bl} - \mathbf{x}_{a0}])}$$

eigensolutions:
$$\boxed{\mathbf{D}_{a,b}(\mathbf{q}) \mathbf{v}_{\mathbf{q}i} = \varepsilon_{\mathbf{q}i} \mathbf{v}_{\mathbf{q}i}}$$

$$\omega_{\mathbf{q}i} \propto \sqrt{\varepsilon_{\mathbf{q}i}}$$

- Displacements periodic (in time and space):

$$\mathbf{u}_{\mathbf{q}i;al}(t) = A_{\mathbf{q}i} m_i^{-1/2} \mathbf{v}_{\mathbf{q}i} \exp [i(\mathbf{q} \cdot \mathbf{x}_{al} - \omega_{\mathbf{q}i} t)]$$

- Let's try a simple system.

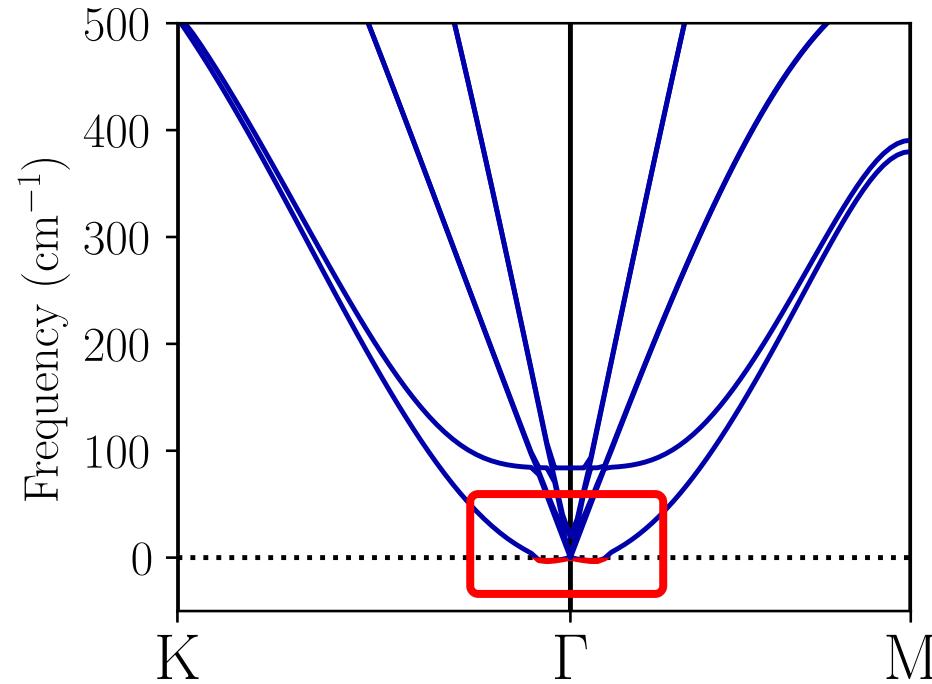


z normals insufficient for bilayer graphene

AB-stacked bilayer graphene

$$\omega_{\mathbf{q}i} \propto \sqrt{\varepsilon_{\mathbf{q}i}}$$

$$\mathbf{u}_{\mathbf{q}i}(t) = e^{-i\omega_{\mathbf{q}i}t} \mathbf{u}_{\mathbf{q}i}(0)$$



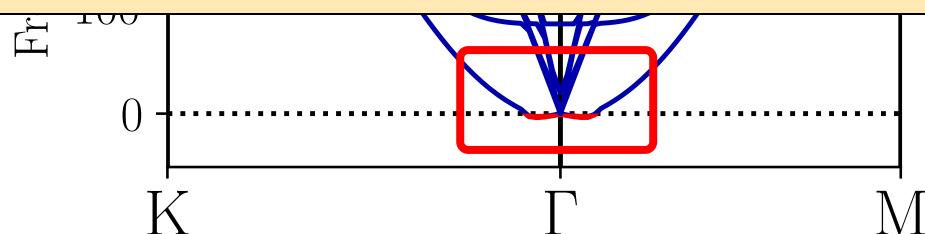
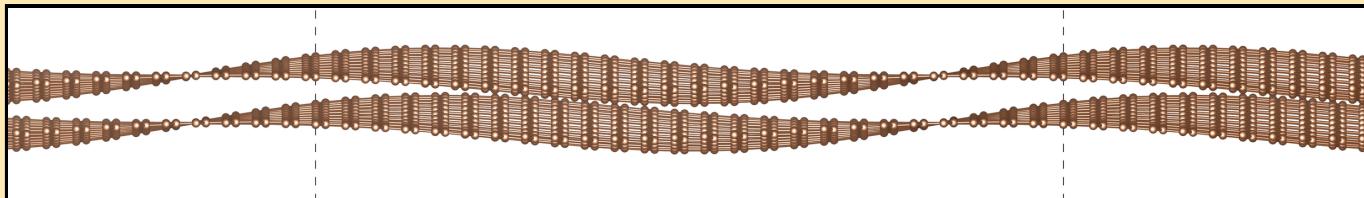
z normals insufficient for bilayer graphene

AB-stacked bilayer graphene

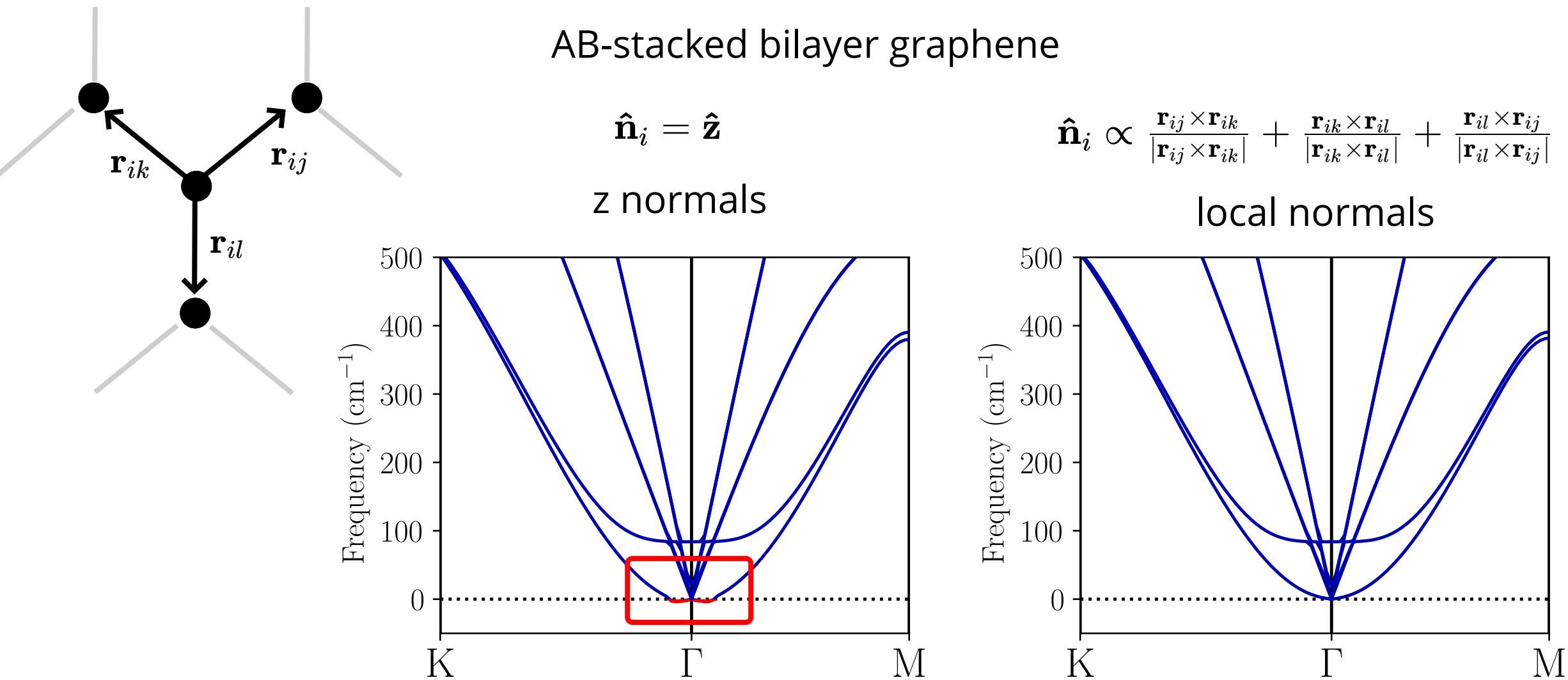
$$\omega_{qi} \propto \sqrt{\varepsilon_{qi}}$$

$$\mathbf{u}_{\alpha i}(t) = e^{-i\omega_{qi}t} \mathbf{u}_{\alpha i}(0)$$

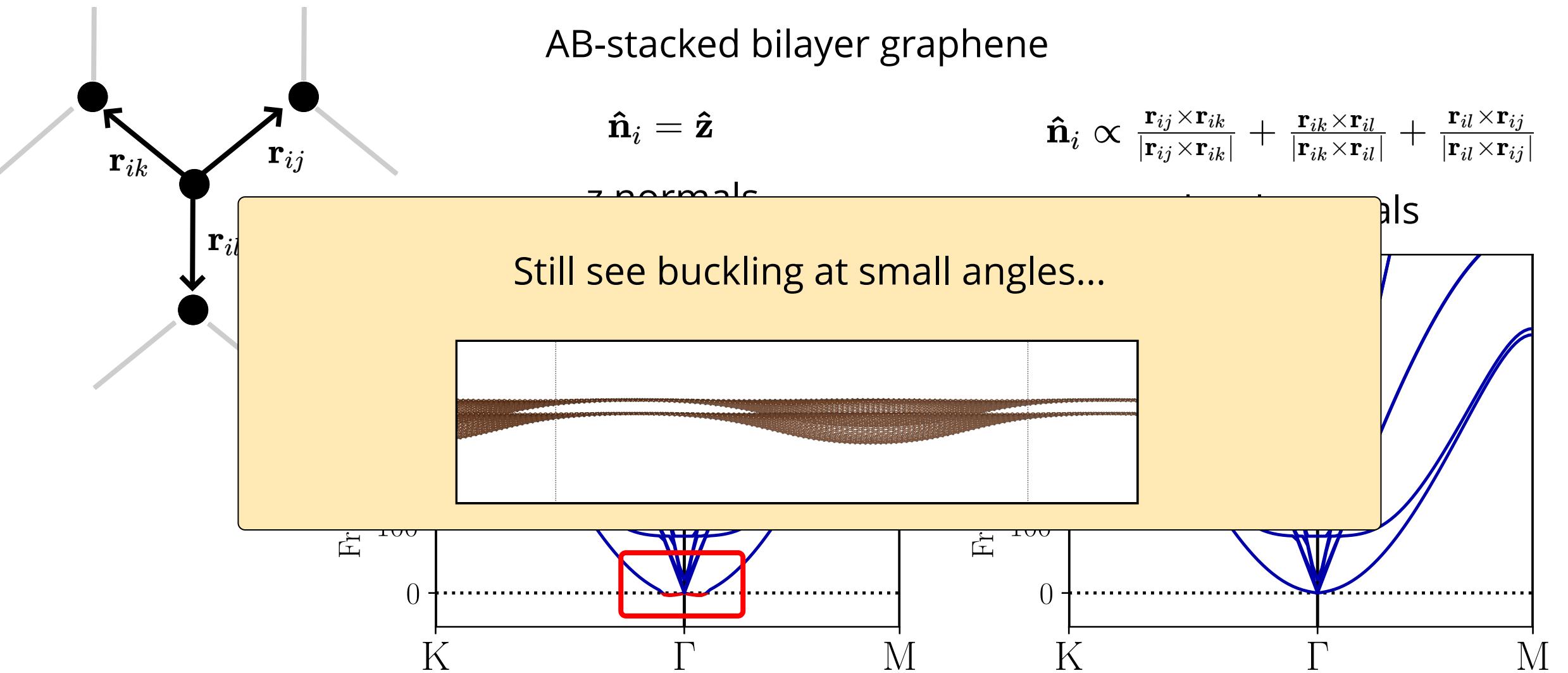
Implies pristine, AB-stacked graphene **will buckle** to reduce potential energy whenever a **large enough supercell** is taken...!?



z normals insufficient for bilayer graphene

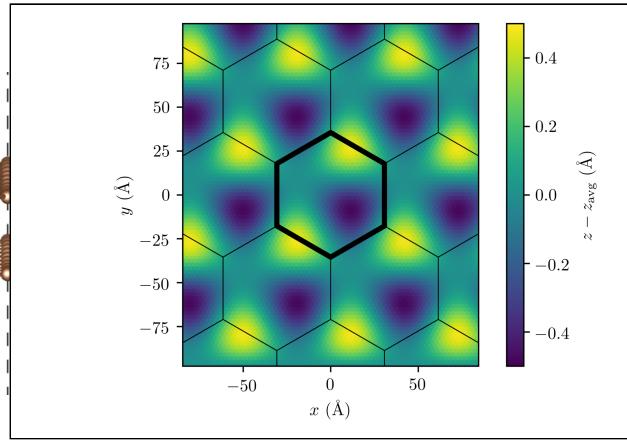
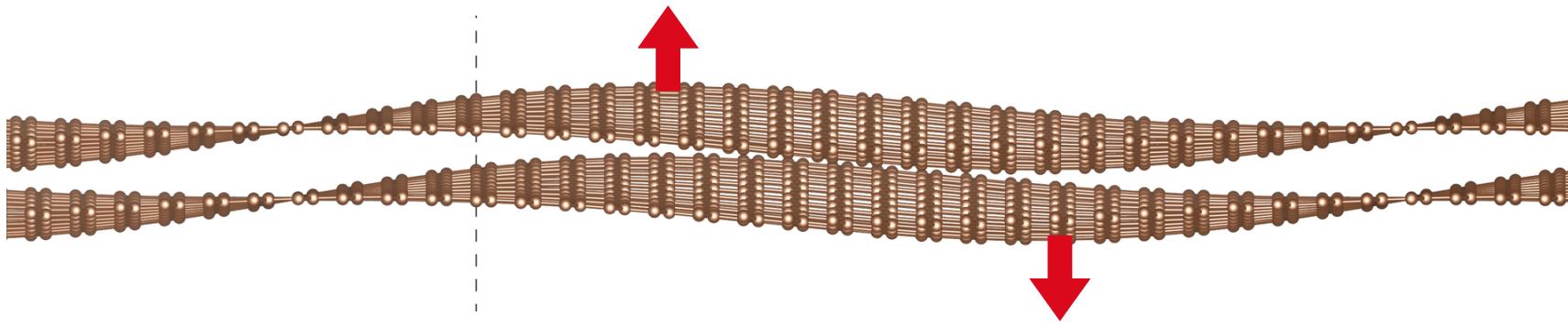


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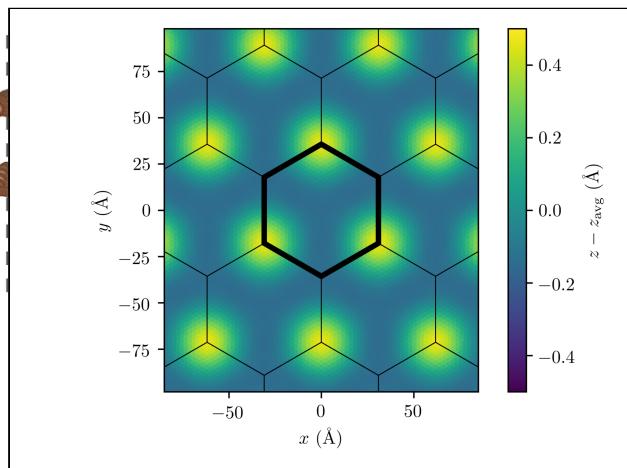
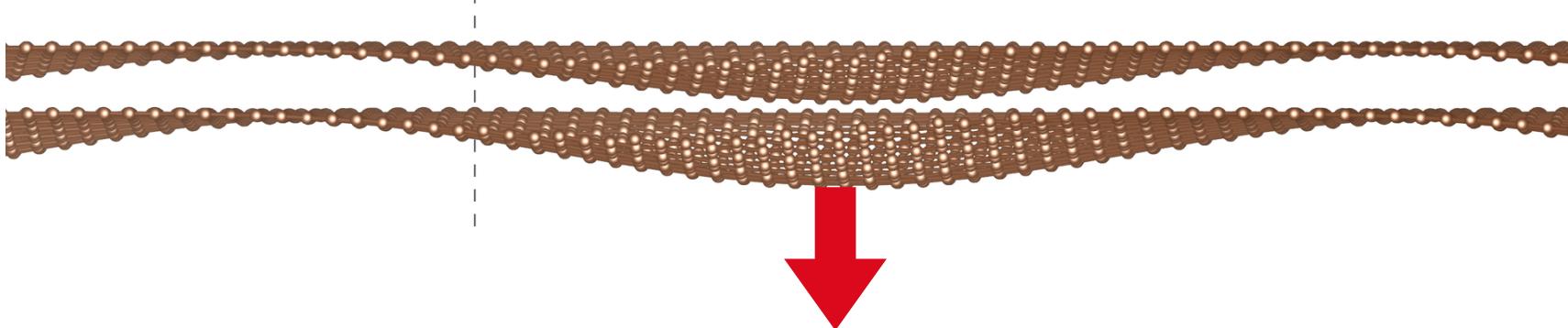


z normals insufficient for bilayer graphene

AB graphene supercell (z normals)

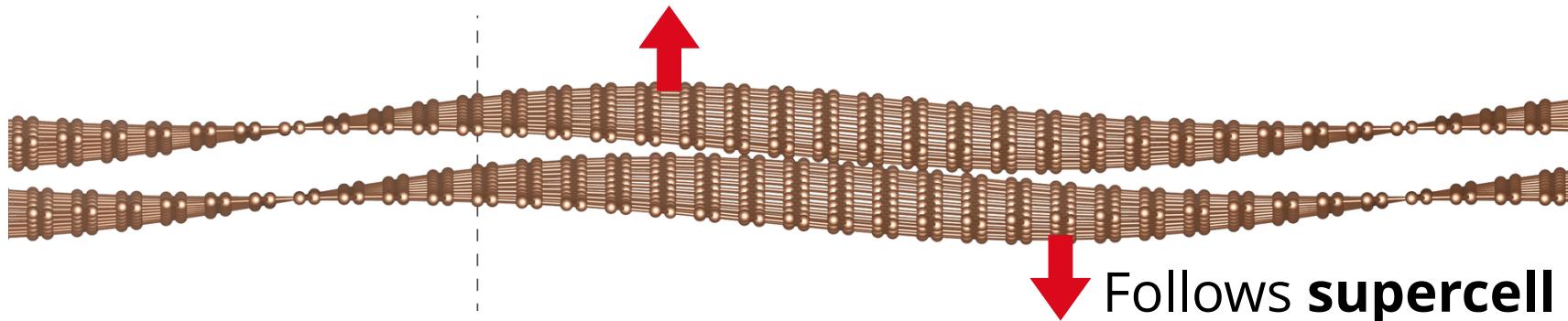


Small angle (local normals)



z normals insufficient for bilayer graphene

AB graphene supercell (z normals)



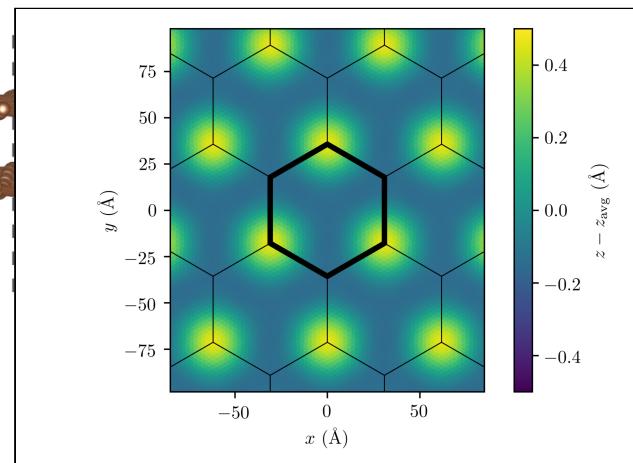
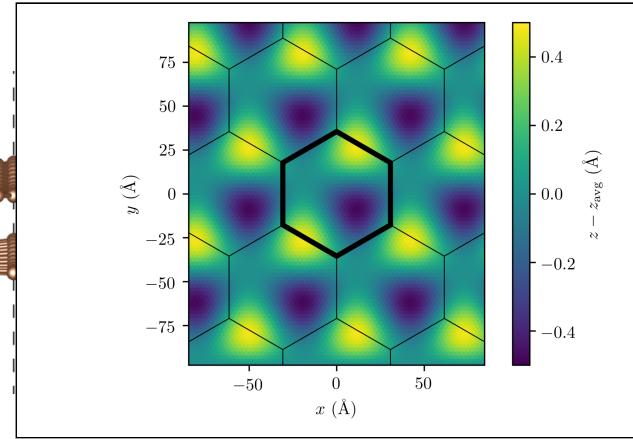
Small angle (local normals)



Follows **supercell**
lattice (arbitrary)

Follows **moiré**
lattice (physical)

Still worth some caution
(heavily impacts corrugation)
AA
region



Lattice optimization

- Is buckling due to strain? Try **relaxing system scale**:
- With PBCs, requires derivatives with respect to displacement vectors:

$$\mathbf{r}_{ij} = \mathbf{x}_j - \mathbf{x}_i$$

$$V = V(\mathbf{r}_{12}, \mathbf{r}_{13}, \dots, \mathbf{r}_{(n-1)n})$$

$$\mathbf{r}_{ij}^T \rightarrow (\mathbf{f}_j - \mathbf{f}_i)^T \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Optimize **3N + 1** parameters

- Buckling **still occurs**.
- Lattice param only shrinks **after** buckling!!



Lattice optimization

- Is buckling due to strain? Try **relaxing system scale**:
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$$\mathbf{r}_{ij}^T \rightarrow (\mathbf{f}_j - \mathbf{f}_i)^T \begin{bmatrix} \alpha & \beta & 0 \\ \gamma & \delta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

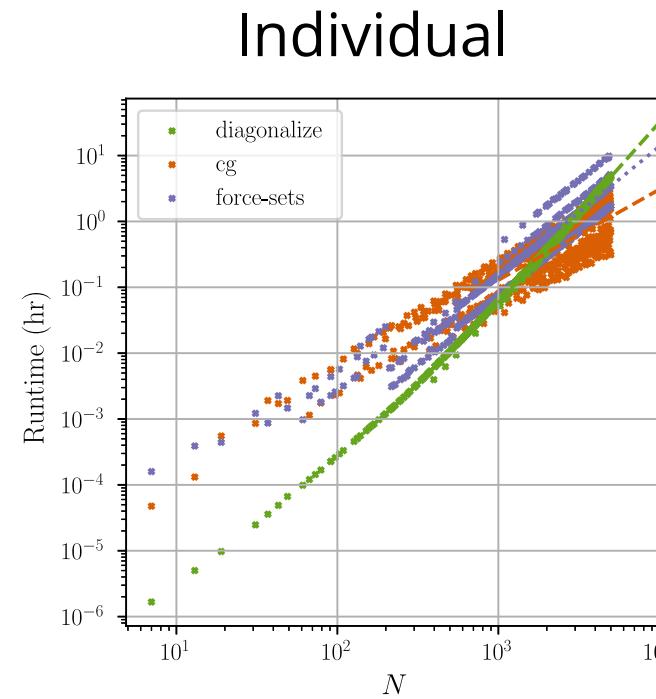
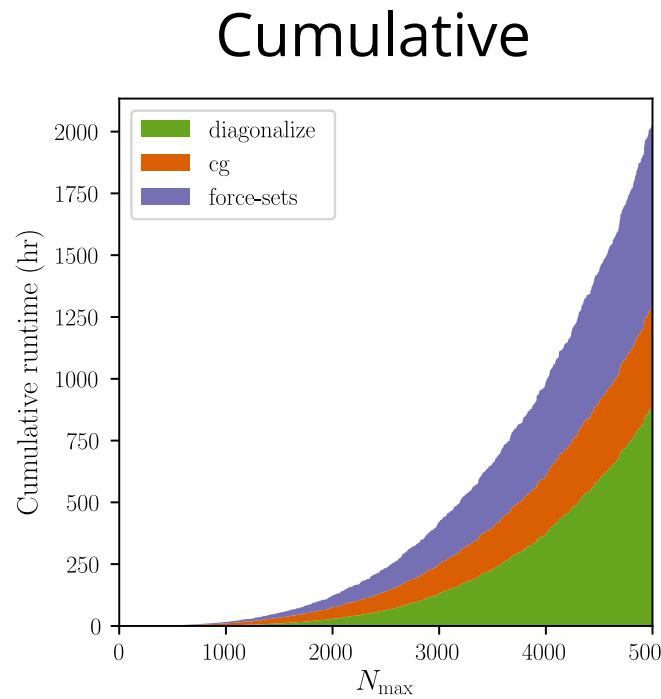
Optimize **3N + 4** parameters

- Buckling **still occurs**.
- Lattice param only shrinks **after** buckling!!
- Same deal when considering **anisotropic strain**.



Computational requirements

- Quadratic memory requirements for diagonalization — **limiting factor!!**
- Also note **current runtime costs**:



$$T \propto N^{2.74}$$

$$T \propto N^2$$

$$T \propto N^{1.38}$$

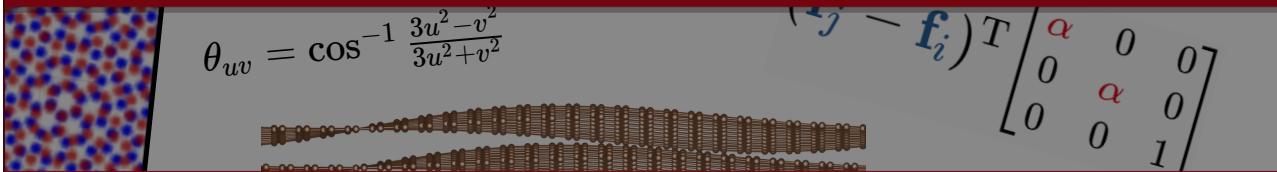
diagonalization
force sets
relaxation



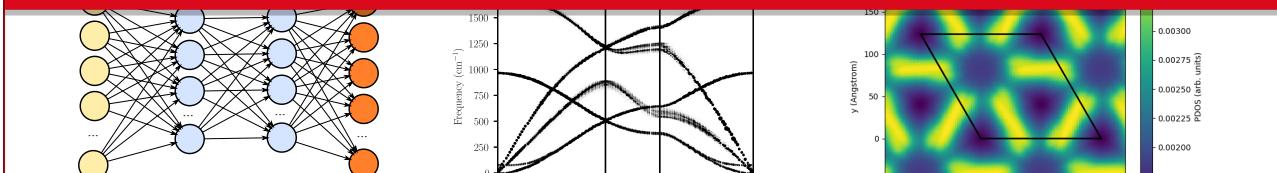
1. Introduction



2. Database Generation



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4. Outcomes



Machine learning the phonon database

- Many effects of twist angle **on** Raman spectra known...
 - ...some restricted to small angle regions...
 - ...some dependent on laser frequency...
- ...let's predict twist angle **from** Raman spectra!
- Best model?
 - A complicated **fitting problem**...
- Sounds like a job for.....!

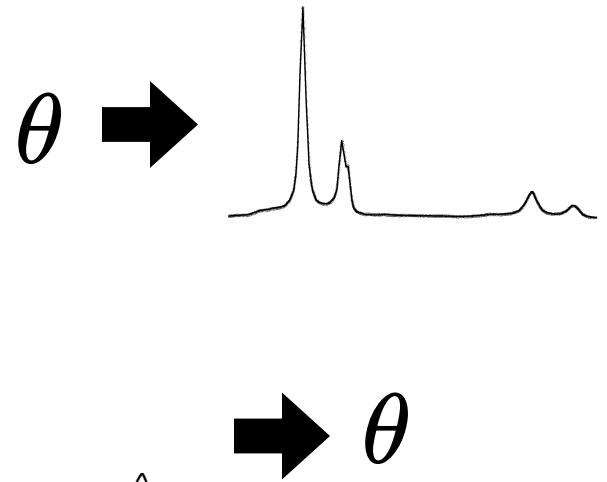


Image credit: Raman spectrum: Modified from work by Felix Rosenberg, Emanuel Ionescu, Norbert Nicoloso and Ralf Riedel / CC BY



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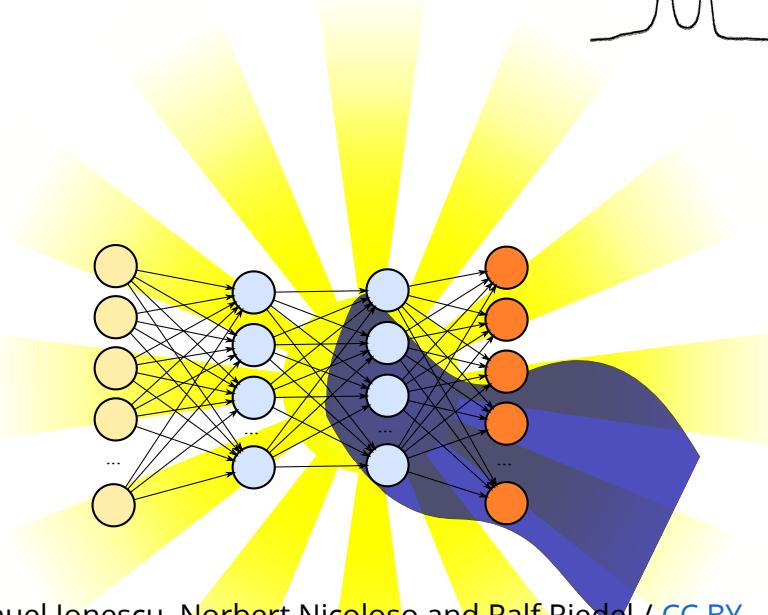
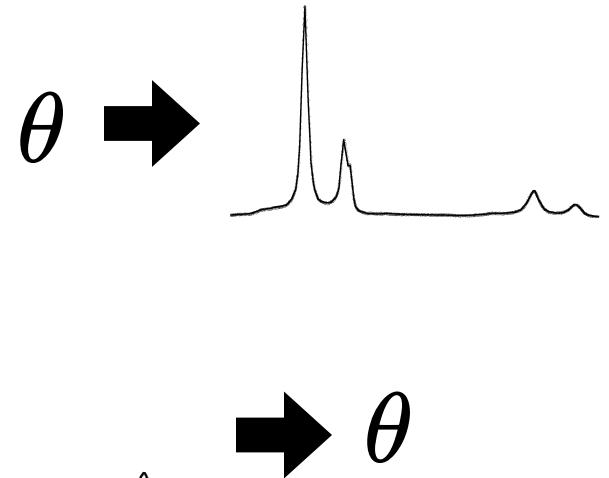


Image credit: Raman spectrum: Modified from work by Felix Rosenberg, Emanuel Ionescu, Norbert Nicoloso and Ralf Riedel / CC BY

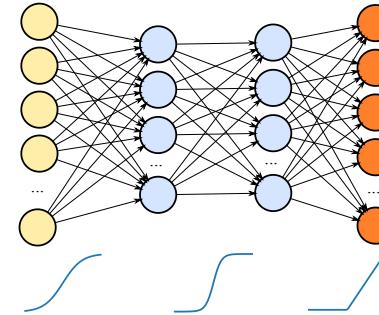
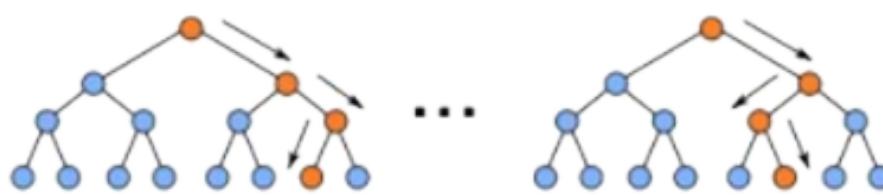


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Large-scale atomistic computations of
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Machine learning the phonon database

- Machine learning has models for fitting **nonlinear functions**.



- Natalya Sheremetyeva: ML models trained on data set explain on average 98% of the data variance.
- **Promising proof-of-concept:**
 - **Robustness to noise** demonstrated.
 - **Similar challenges to** experimental data.
 - Experimental data could be **easier to learn** by comparison.

N. Sheremetyeva, M. Lamparski, C. Daniels, B. Van Troeye, and V. Meunier. *Machine-learning models for raman spectra analysis of twisted bilayer graphene*. Accepted in Carbon (2020).

Image credit: Random forest: Modified from work by Venkata Jagannath / [CC BY-SA 4.0](#)



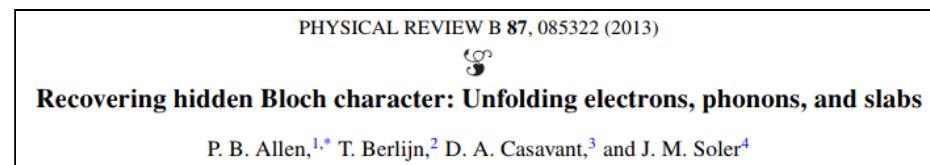
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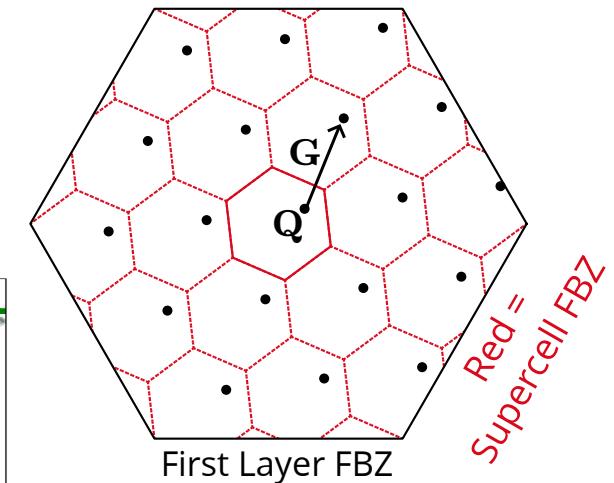
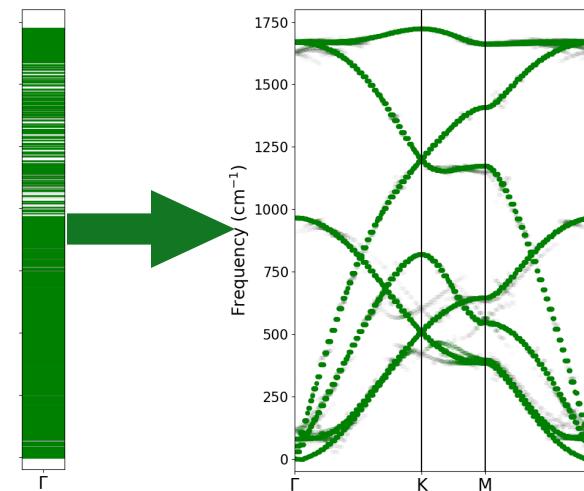
Unfolding phonons — overview

- To compare different angles, unfold onto a **common FBZ** (the first layer!)
- Any bloch function Ψ of wavevector \mathbf{Q} (in supercell FBZ) can be decomposed into parts with wavevector $\mathbf{Q} + \mathbf{G}$ (in primitive FBZ)

$$\langle \Psi | \hat{P}(\mathbf{Q} \rightarrow \mathbf{Q} + \mathbf{G}) | \Psi \rangle = \frac{1}{N} \sum_{i=1}^N \langle \Psi | \hat{T}(\mathbf{r}_i) | \Psi \rangle e^{i(\mathbf{Q}+\mathbf{G}) \cdot \mathbf{r}_i}$$

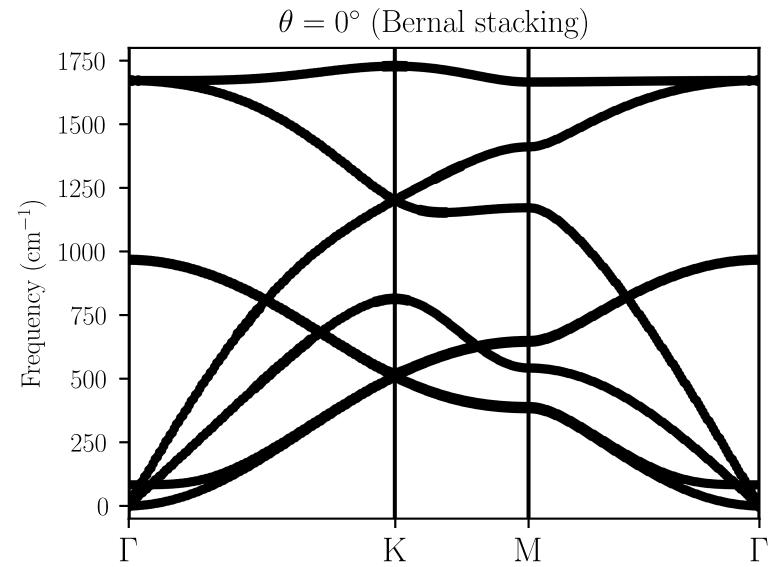


- **Practical concern:** Use a **perfect supercell approximation** so that the $\langle T(r) \rangle$ are not trivial.

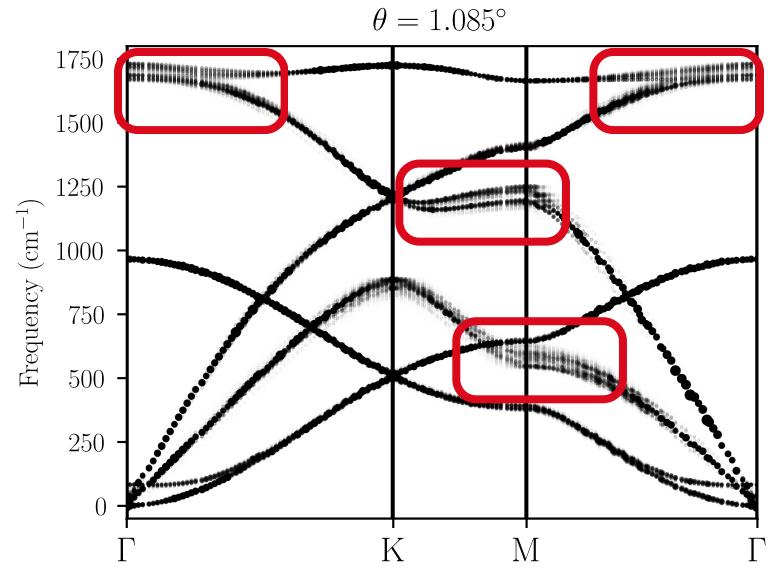


Unfolding phonons — band structures

AB graphene



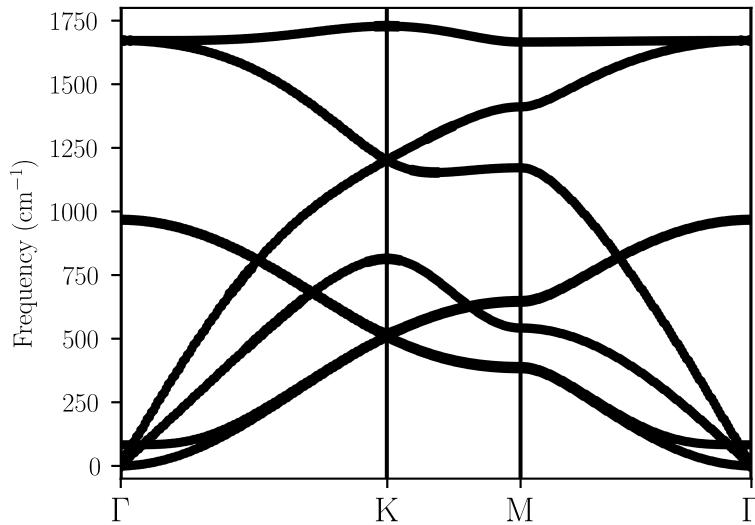
Magic angle



Unfolding phonons — band structures

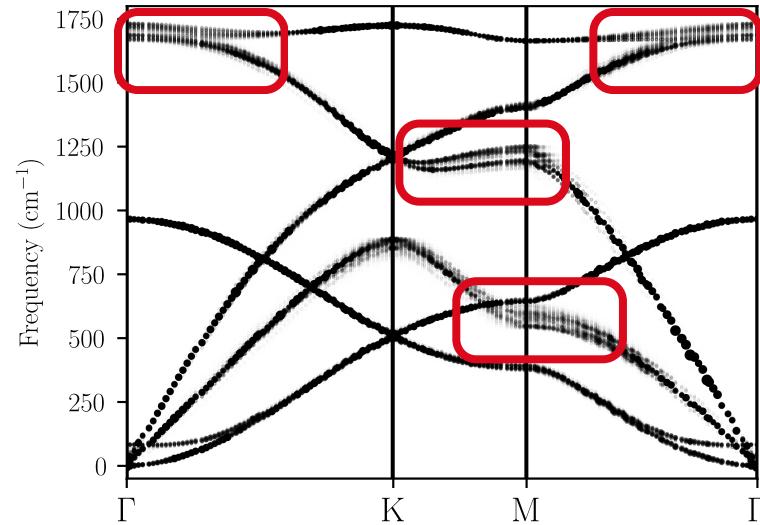
AB graphene

$\theta = 0^\circ$ (Bernal stacking)



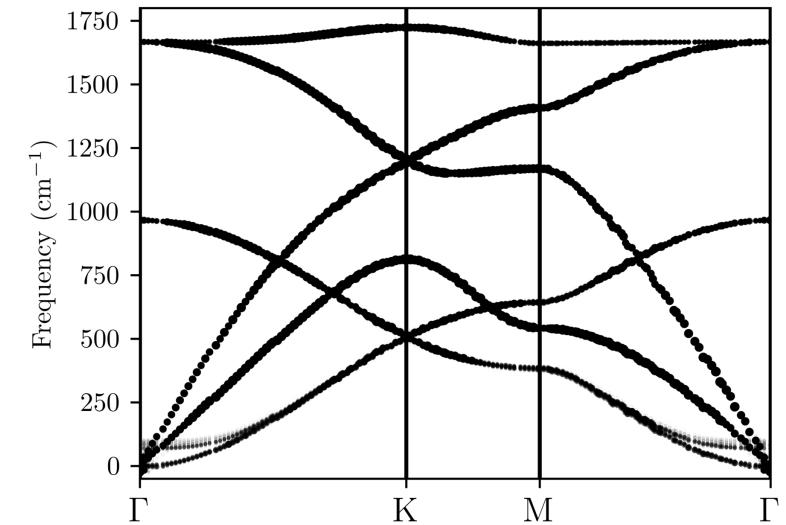
Magic angle

$\theta = 1.085^\circ$



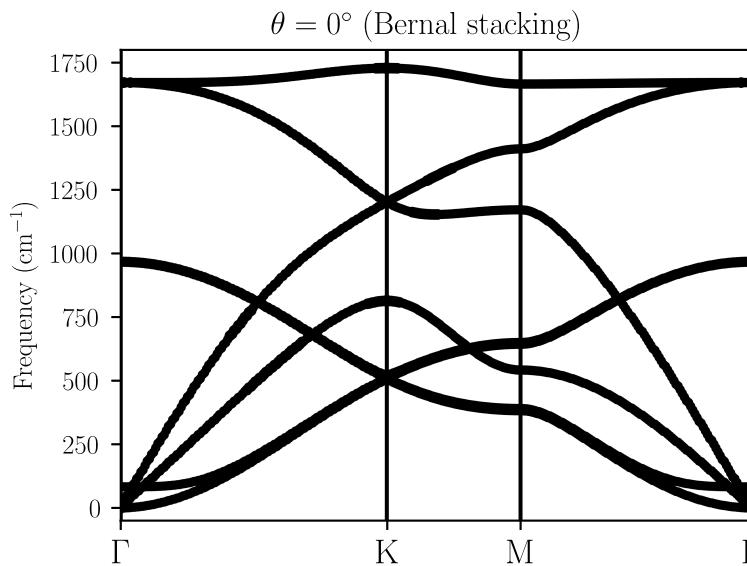
Unrelaxed

$\theta = 1.085^\circ$ (unrelaxed)

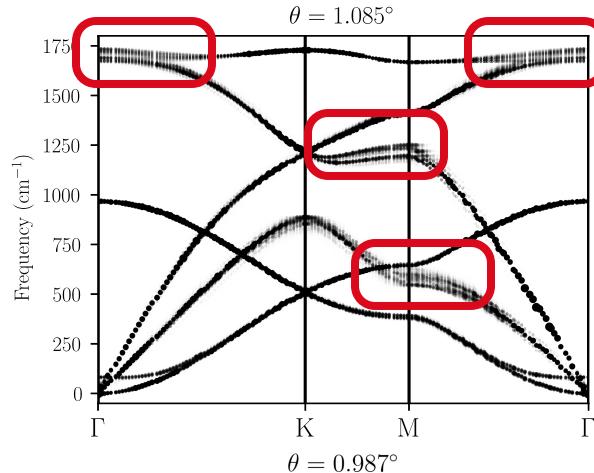


Unfolding phonons — band structures

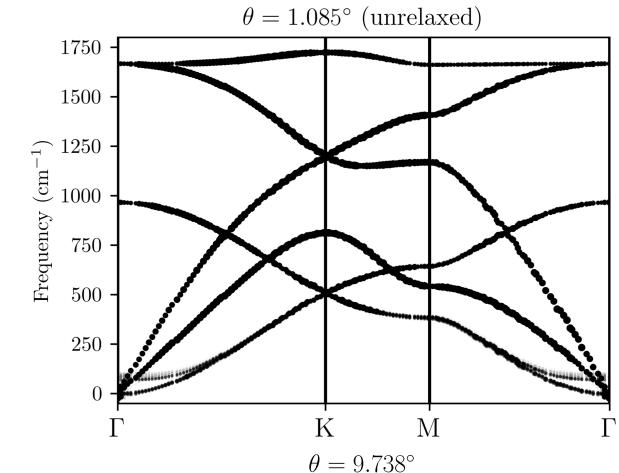
AB graphene



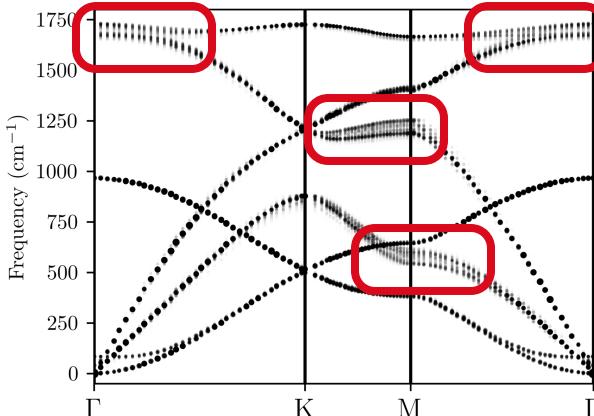
Magic angle



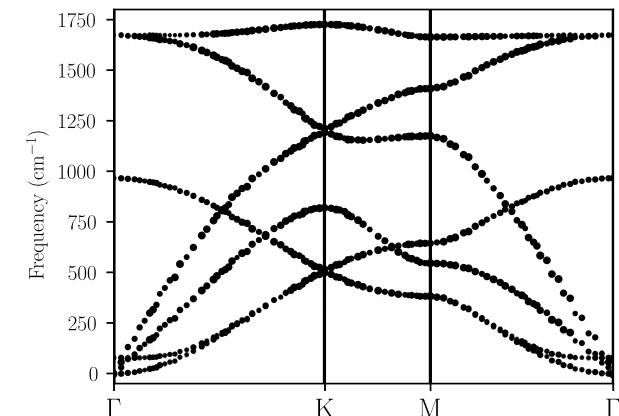
Unrelaxed



Smaller angle

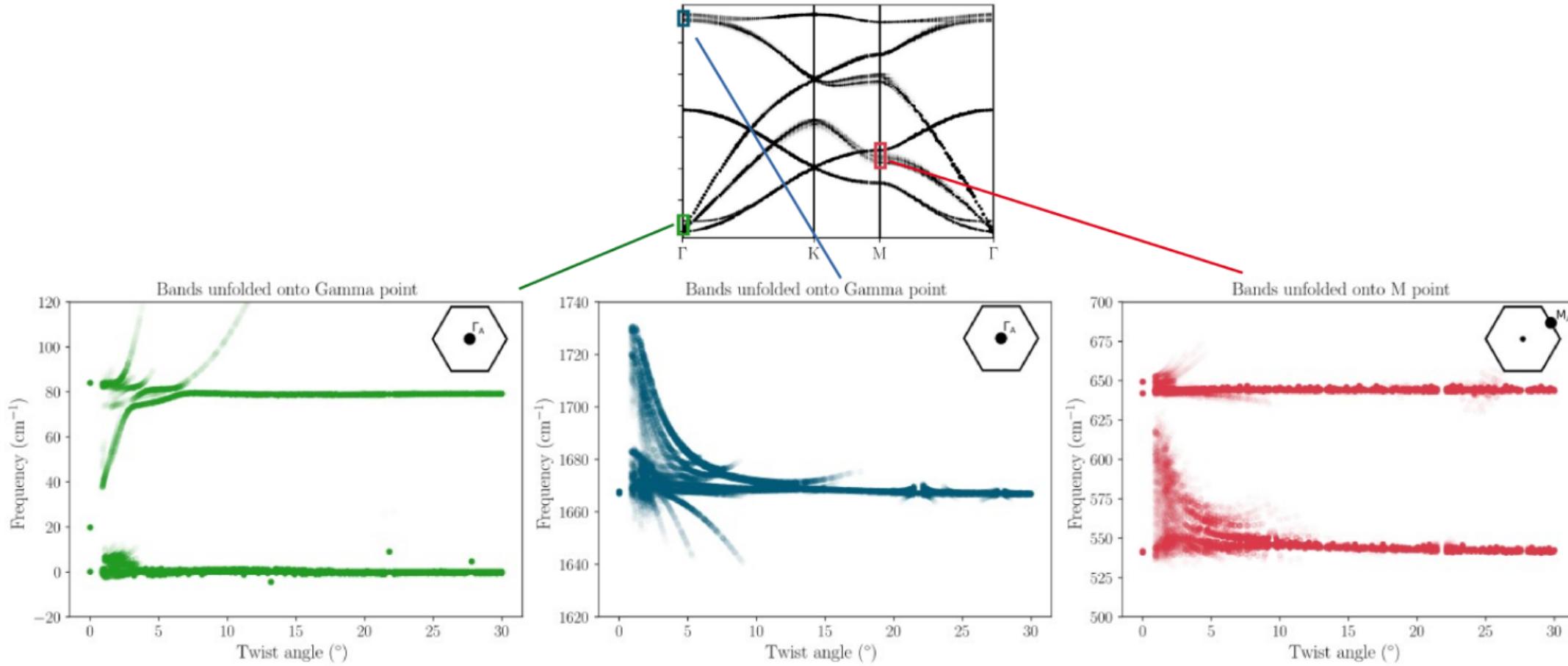


Large angle



Unfolding phonons — splitting predicted

- We can trace its evolution with respect to angle:



M. Lamparski, B. Van Troeye, and V. Meunier. Soliton signature in the phonon spectrum of twisted bilayer graphene, 2D Materials, 7 025050 (2020).



Rensselaer

Large-scale atomistic computations of
the phonons in twisted bilayer graphene

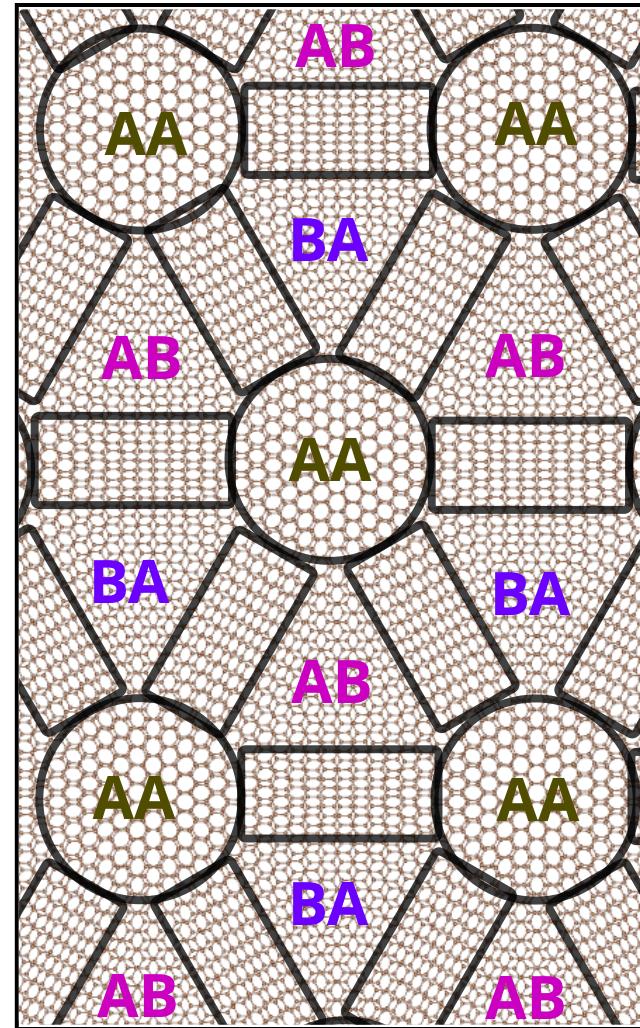
Unfolding phonons — splitting explained

- **Frenkel-Kontorova model:** Simple model for a **harmonic chain** in the presence of a **periodic potential**.
("fixed substrate")

$$V = A \sum_i \frac{1}{2} (x_{i-1} - x_i - a_0)^2$$

$$+ B \sum_i \cos\left(\frac{2\pi x_i}{s}\right)$$

- Solutions include not just **phonons**, but also topological defects known as **solitons**.

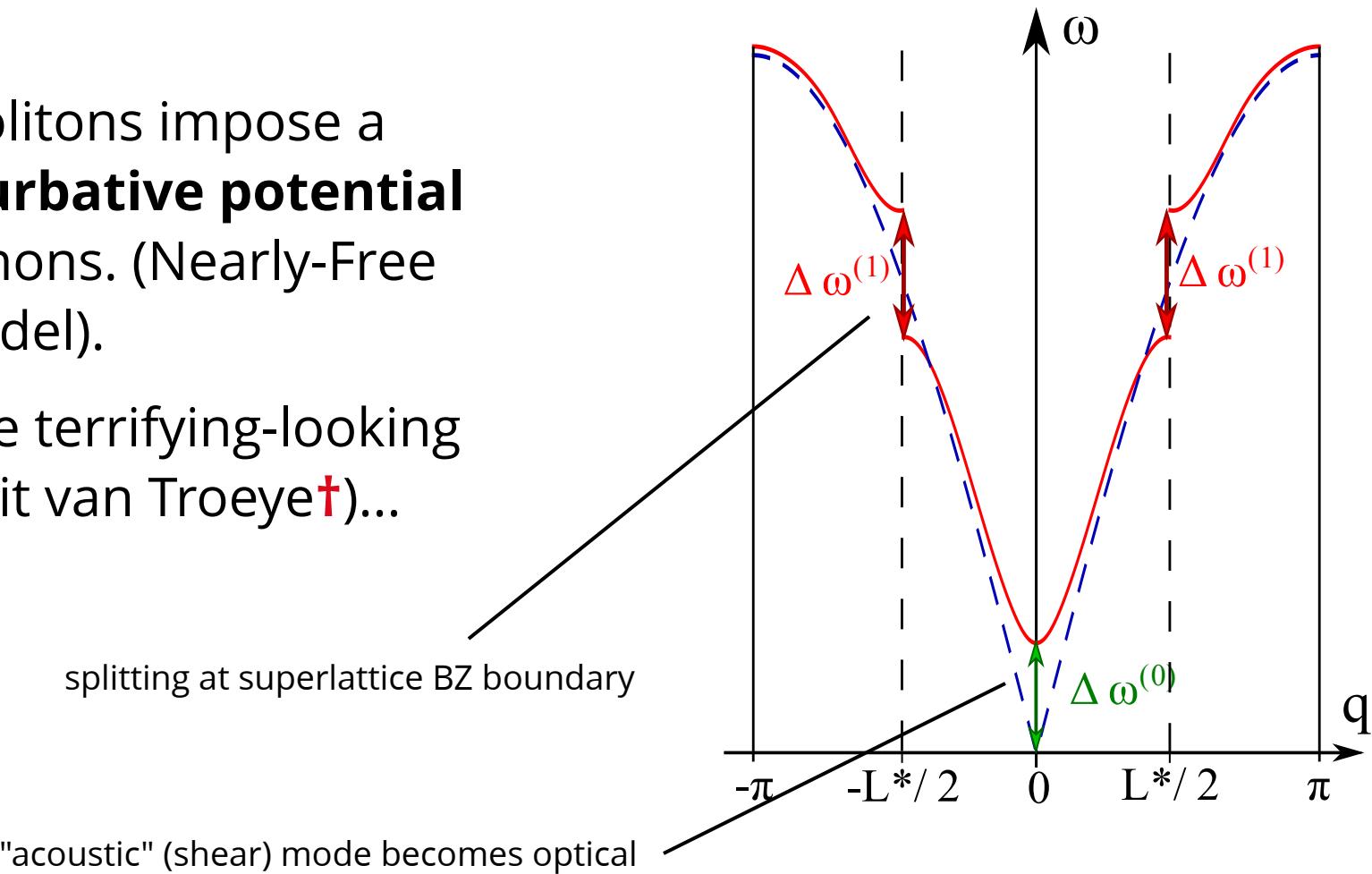


M. Lamparski, B. Van Troeye, and V. Meunier. Soliton signature in the phonon spectrum of twisted bilayer graphene, 2D Materials, 7 025050 (2020).



Unfolding phonons — splitting explained

- Let these solitons impose a **weak perturbative potential** on the phonons. (Nearly-Free Phonon model).
- ...after some terrifying-looking math (Benoit van Troeyet[†])...

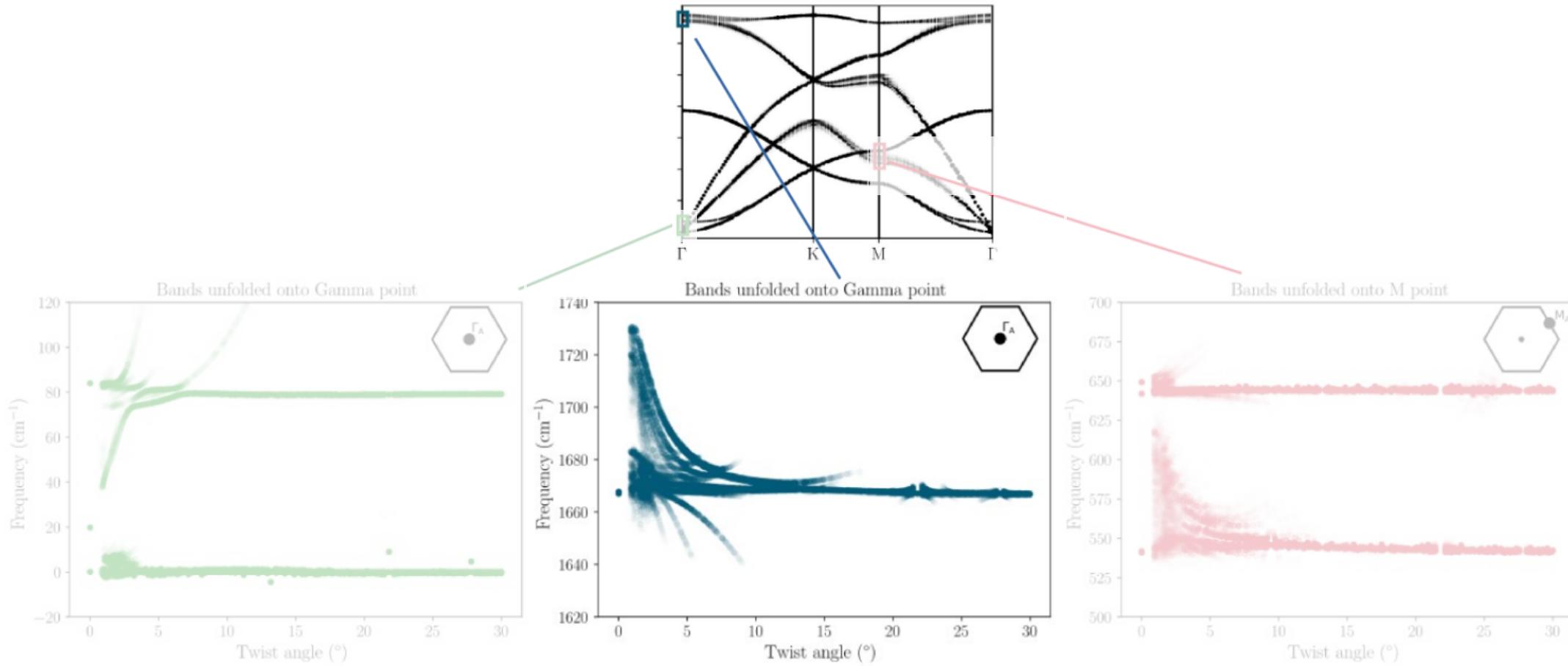


[†] Currently undergoing peer review at Phys Review B



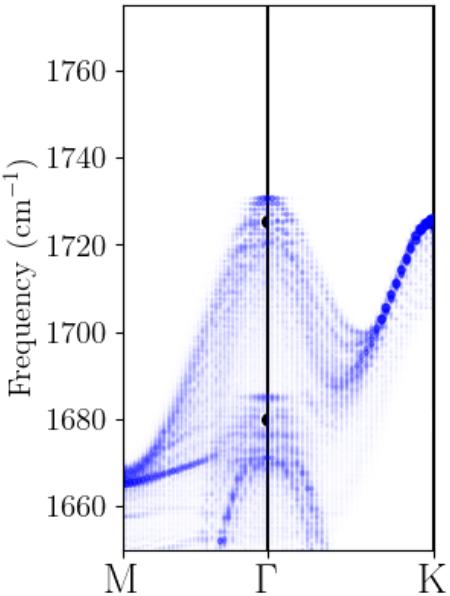
Unfolding phonons — splitting observed??

- Mode responsible for the **G peak** in the Raman spectrum of graphene...



Unfolding phonons — splitting observed??

- Jorio: We see **localized variations** in G peak frequency, **higher along AB/BA domain walls** (solitons!). †
- If we compute PDOS at the upper and lower parts of our split G band...



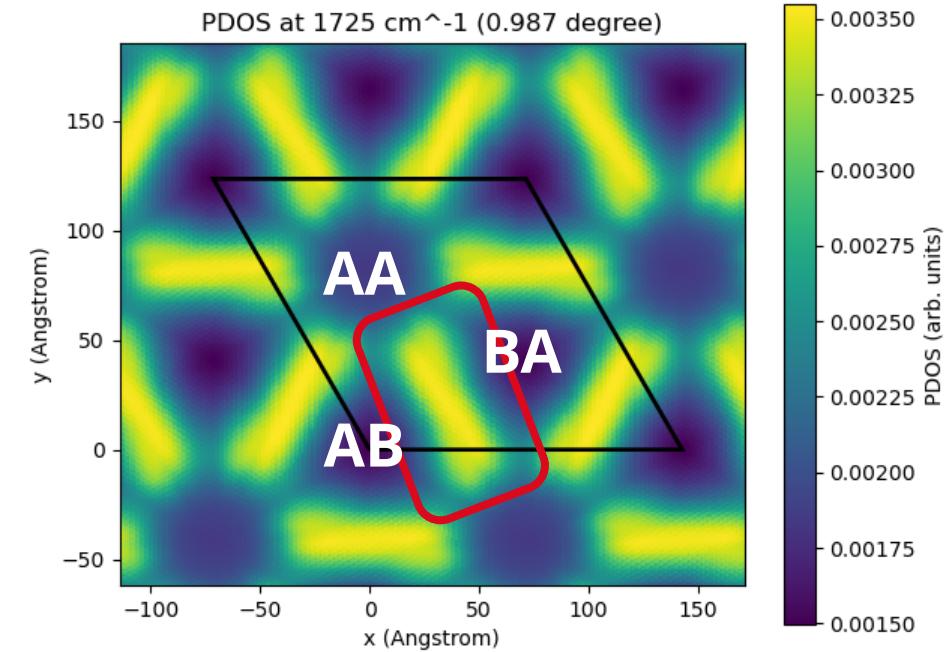
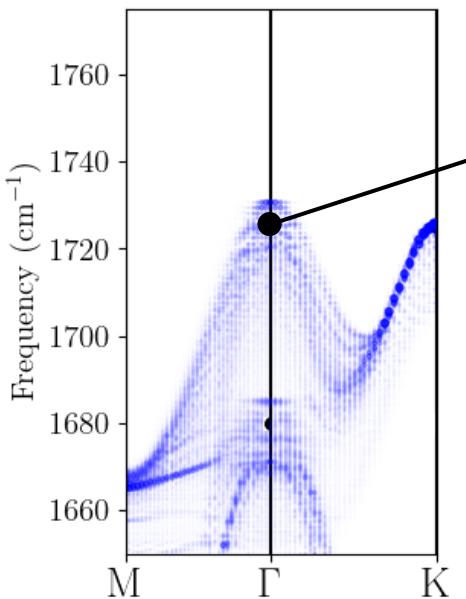
- Massive collaboration!

† Currently undergoing peer review at Nature...!



Unfolding phonons — splitting observed??

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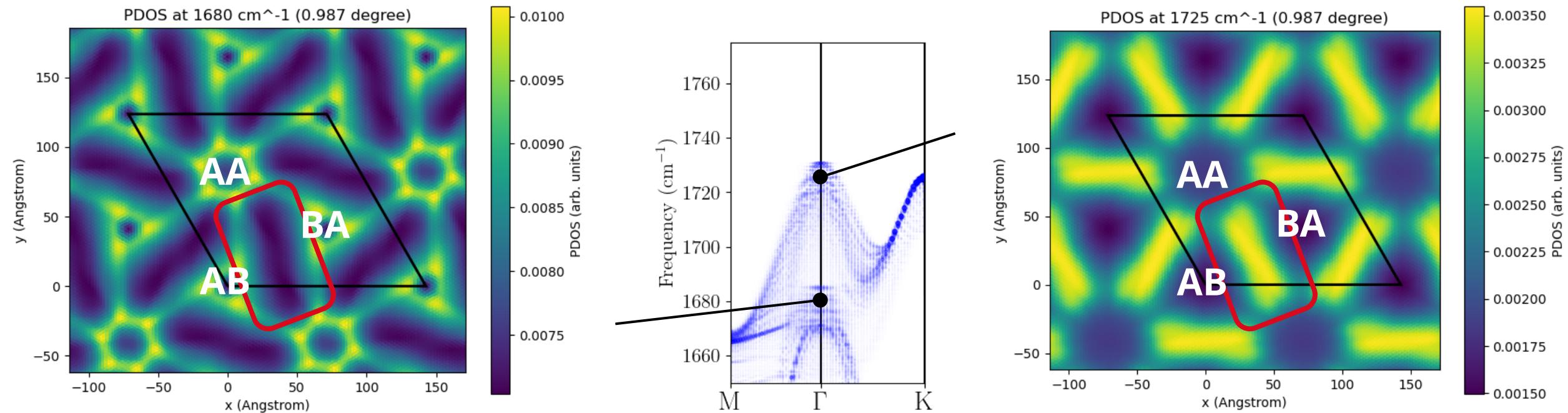
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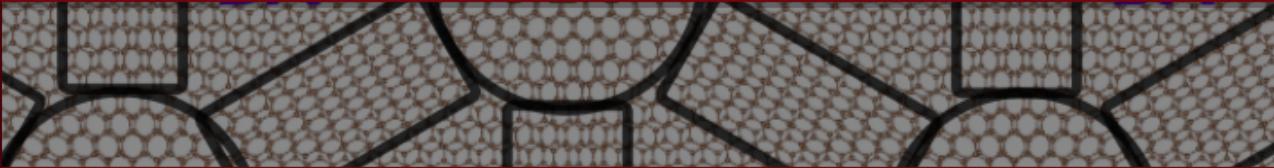


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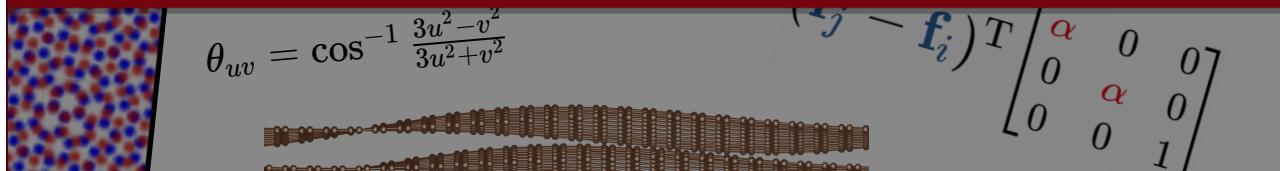
† Currently undergoing peer review at Nature...!



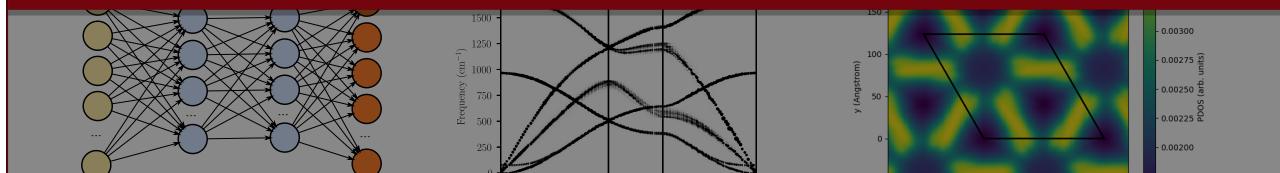
1. Introduction



2. Database Generation



3. Analysis

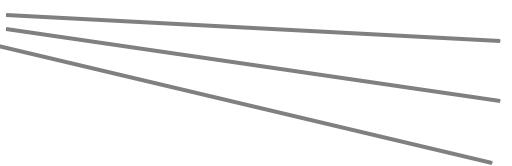


4. Outcomes



The Big Deal (TM)

- More than just a computation.
- **Tough problems require tough solutions.**
 - Initially used (and contributed to) Phonopy and LAMMPS
 - Performance demanded **integrated solution**
 - Needed:
 - Local normals
 - Sparse dynamical matrices
 - Phonons away from gamma (sometimes)
 - Now use **own code**



| |
|---|
| ↳ optimize POSCAR writing ✓ |
| #61 by ExpHP was merged on Jan 29, 2018 |
| ↳ optimize sp2_map generation ✓ |
| #60 by ExpHP was merged on Jan 29, 2018 |
| ↳ optimize get_smallest_vectors once more with numpy broadcasting and C ✓ |
| #50 by ExpHP was merged on Aug 17, 2017 |
| ↳ use `compute_permutation` in `distribute_fc2` ✓ |
| #48 by ExpHP was merged on Aug 14, 2017 |
| ↳ add compute_permutation C function ✓ |
| #47 by ExpHP was merged on Aug 13, 2017 |
| ↳ Fix O(n^3) scaling in get_smallest_vectors ✓ |
| #46 by ExpHP was merged on Aug 12, 2017 |
| ↳ Optimize `get_equivalent_smallest_vectors` (also, bugfix for HDF5 in python3) ✓ |
| #41 by ExpHP was merged on Apr 8, 2017 |

Phonons
Optimization
REBO+KC

Phonopy: <https://phonopy.github.io/phonopy/>
LAMMPS: <https://lammps.sandia.gov/>



Unfolding phonons — going public

- Unfolding particularly tricky:
 - Bloch phases arising in various places.
 - Necessary to **coalesce degenerate kets** to reduce data and plot size.
 - Smaller structures might want to sample **more Q points**.
 - Even trickier without supercell approximation...
- Band unfolding also useful for electrons.
- New script **unfold.py** won't be hard to adapt to other problems,
let's share it!



Publications

Published

- W. M. Parkin, A. Balan, L. Liang, P. M. Das, **M. Lamparski**, C. H. Naylor, J. A. Rodriguez-Manzo, A. T. C. Johnson, V. Meunier, and M. Drndic. *Raman Shifts in Electron-Irradiated Monolayer MoS₂*. ACS Nano **10**, 4134 (2016), ISSN 1936-0851.
- R. Garg, S. K. Rastogi, **M. Lamparski**, S. C. de la Barrera, G. T. Pace, N. T. Nuhfer, B. M. Hunt, V. Meunier, and T. Cohen-Karni. *Nanowire-Mesh-Templated Growth of Out-of-Plane Three-Dimensional Fuzzy Graphene*. ACS Nano **11**, 6301 (2017), ISSN 1936-0851.
- A. Yoshimura, **M. Lamparski**, N. Kharche, and V. Meunier. *First-principles simulation of local response in transition metal dichalcogenides under electron irradiation*. Nanoscale **10**, 2388 (2018).
- D. San Roman, D. Krishnamurthy, R. Garg, H. Hafiz, **M. Lamparski**, N. T. Nuhfer, V. Meunier, V. Viswanathan, and T. Cohen-Karni. *Engineering Three-Dimensional (3D) Out-of-Plane Graphene Edge Sites for Highly Selective Two-Electron Oxygen Reduction Electrocatalysis*. ACS Catalysis pp. 1993–2008 (2020).
- **M. Lamparski**, B. Van Troeye, and V. Meunier. *Soliton signature in the phonon spectrum of twisted bilayer graphene*. 2D Materials **7**, 025050 (2020).

Submitted

- N. Sheremeteva, M. Lamparski, C. Daniels, B. Van Troeye, V. Meunier, *Machine-learning models for Raman spectra analysis of twisted bilayer graphene*. <https://arxiv.org/abs/2007.03839>. Accepted to Carbon.
- B. Van Troeye, **M. Lamparski**, N. Sheremeteva, V. Meunier. *Nearly-Free Phonons in a weak soliton potential and the case of twisted bilayer graphene*. In peer review at Physical Review B.
- Andreij C. Gadelha, ..., B. Van Troeye, **M. Lamparski**, V. Meunier, ..., and A. Jorio. *Lattice dynamics localization in low-angle twisted bilayer graphene*. <https://arxiv.org/abs/2006.09482>. In peer review at Nature?!



Thanks

Committee

Vincent
Meunier



Humberto
Terrones

Shengbai
Zhang



Yunfeng
Shi



Rensselaer

Colleagues

Colin Daniels, Anthony Yoshimura, Andrew Cupo, Natalya Sheremetyeva
Liangbo Liang, Damien Tristant, Benoit van Troeye



Collaborators



Carnegie
Mellon
University



Software/Libs

NumPy



Spglib



Phonopy



DF-TB



reveal.js



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Large-scale atomistic computations of
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