Dislocations in graphene

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Workshop on PDEs and Materials
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Graphene

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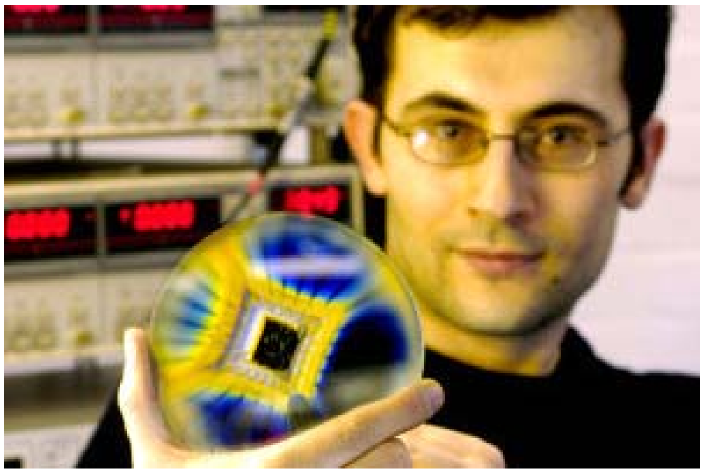
- First fabricated by Novoselov, K.S., *et al*. "Electric field effect in atomically thin carbon films" Science, 306 (2004) pp. 666-669
- One-atom thick free-standing carbon sheet
- Stable under ambient conditions
- 2D crystal arranged in a chicken-wire or honeycomb lattice
- Fabricated by:
  - *Mechanical cleavage of graphite (manually, ultrasonic)*
  - *Epitaxial growth followed by chemical etching*

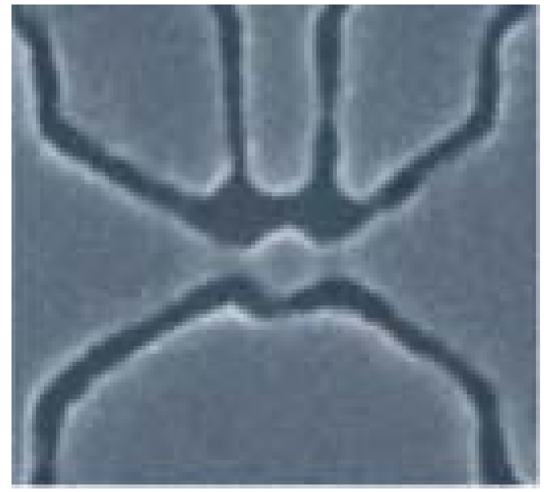
Graphene

- A.K. Geim, "Graphene: Status and Prospects", *Science*, **324** (2009) pp. 1530-1534:
  - *Graphene is a wonder material*
  - *Thinnest known material in the universe and the strongest ever measured*
  - *Its charge carriers exhibit giant intrinsic mobility, have zero effective mass, and can travel for micrometers without scattering at room temperature.*
  - *Can sustain current densities six orders of magnitude higher than that of copper*
  - *Shows record thermal conductivity and stiffness, is impermeable to gases*
  - *Electron transport in graphene is described by a (relativistic-quantum) Dirac-like equation*

Graphene - Applications



“Graphene used to create world's smallest transistor. Graphene can be carved into tiny electronic circuits with individual transistors having a size not much larger than that of a molecule”



Graphene-based single-electron transistor. Device with the central island of 250 nm in diameter and distant side gates; high resolution lithography allows features down to 10 nm (Ponomarenko, L.A., et al., “Chaotic Dirac Billiard in Graphene Quantum Dots,” *Science,* **320** (2008) pp. 356-358)

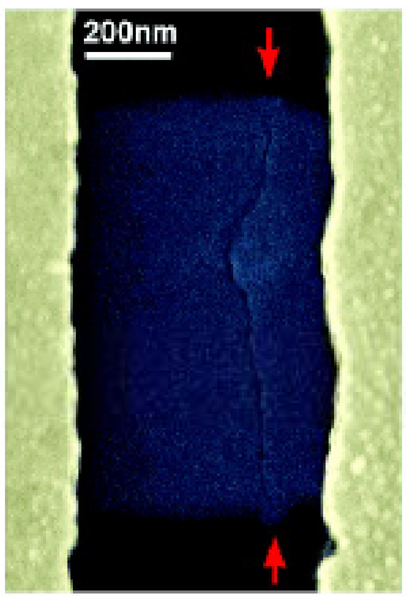
http://www.manchester.ac.uk/aboutus/news/

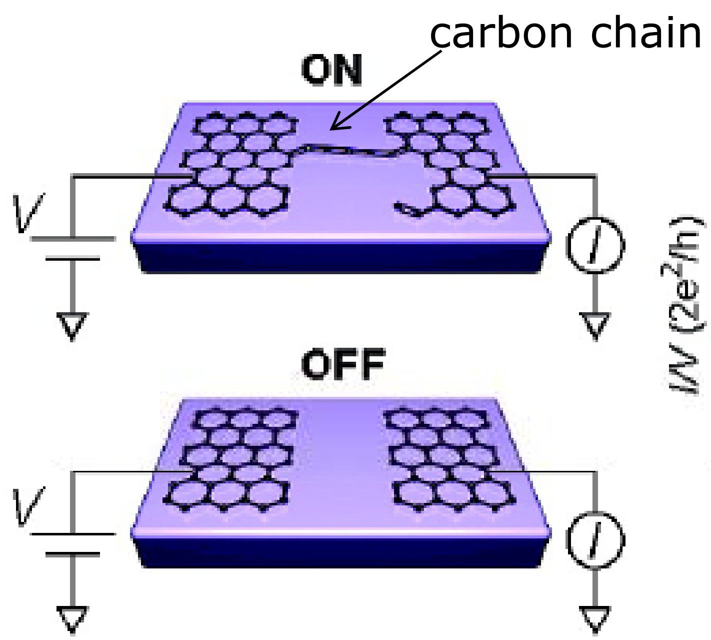
Graphene - Applications

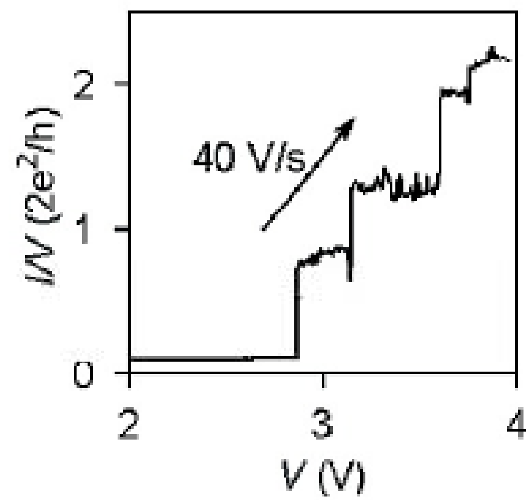
Graphene-Based Atomic-Scale Switches

Brian Standley,† Wenzhong Bao,‡ Hang Zhang,‡ Jehoshua Bruck,§ Chun Ning Lau,‡ and Marc Bockrath*,†

NANO LETTERS
2008
Vol. 8, No. 10
3345-3349







nonvolatile memory element
based on graphene break junctions

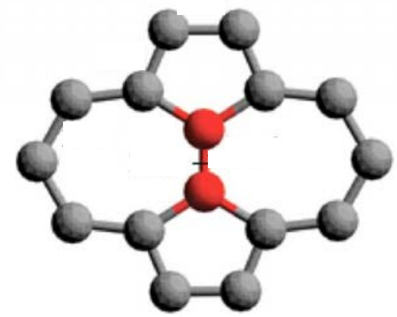
Graphene and defects

THEORETICAL STUDIES OF ICOSAHEDRAL C_{60} AND SOME RELATED SPECIES

A.J. STONE and D.J. WALES

University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, UK

Received 1 May 1986; in final form 23 May 1986

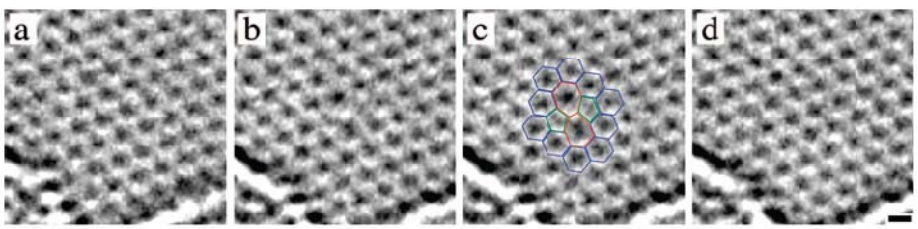


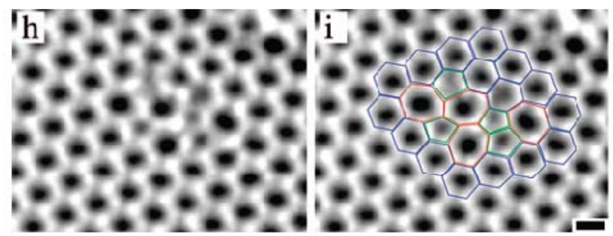
Stone-Wales defect

Direct Imaging of Lattice Atoms and Topological Defects in Graphene Membranes

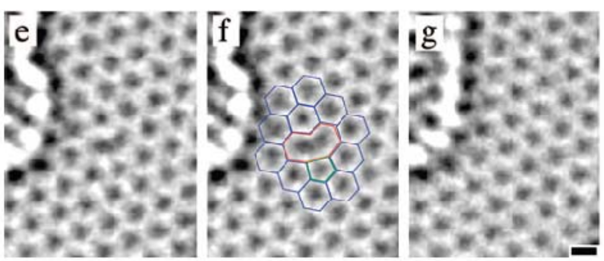
NANO LETTERS
2008
Vol. 8, No. 11
3582-3586

Jannik C. Meyer,[†] C. Kisielowski,[‡] R. Erni,[‡] Marta D. Rossell,[‡] M. F. Crommie,[†] and A. Zettl[*,†]

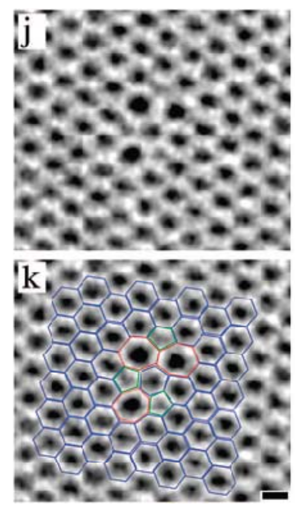




Stone-Wales defect



vacancy



heptagons
and pentagons

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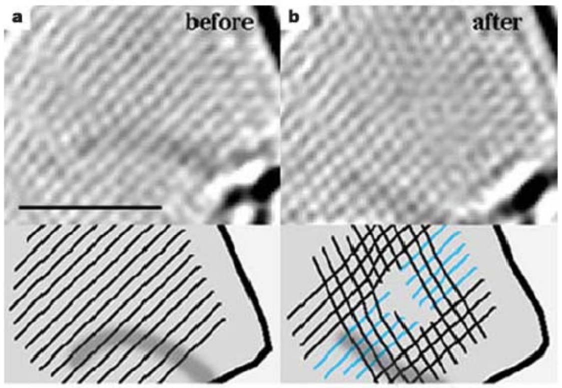
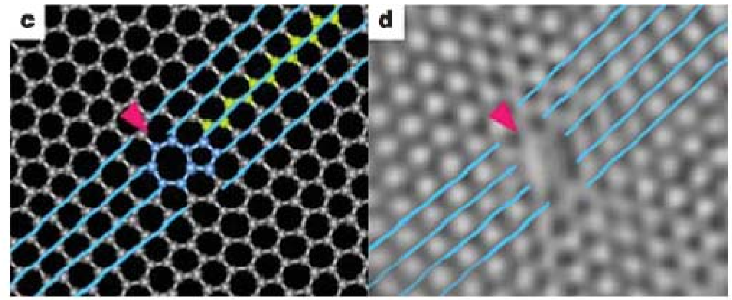
Graphene and defects

Direct evidence for atomic defects in graphene layers

Ayako Hashimoto[1], Kazu Suenaga[1], Alexandre Gloter[1,2], Koki Urita[1,3] & Sumio Iijima[1]

NATURE | VOL 430 | 19 AUGUST 2004 | www.nature.com/nature





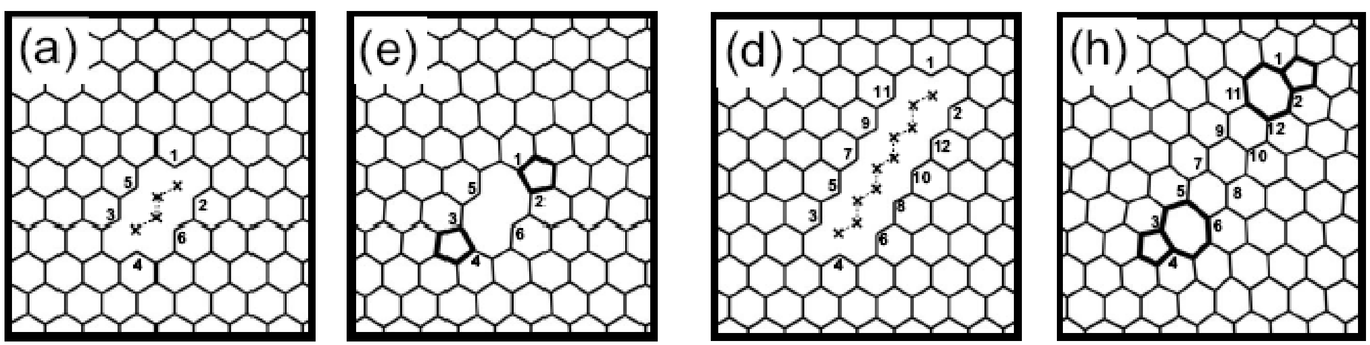
edge dislocation
(missing zig-zag chain)

topological defects induced
by electron-beam irradiation

PHYSICAL REVIEW B 78, 165403 (2008)

Stability of dislocation defect with two pentagon-heptagon pairs in graphene

Byoung Wook Jeong,[1] Jisoon Ihm,[1] and Gun-Do Lee[2]



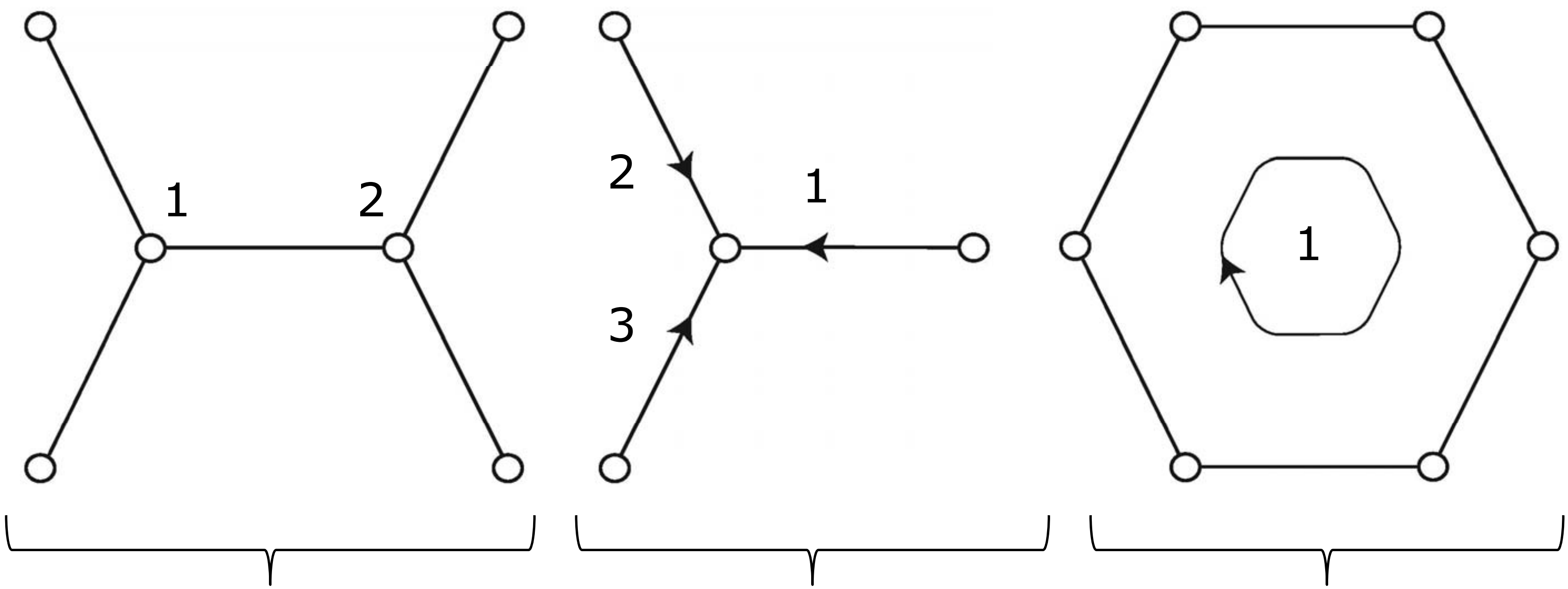
Graphene and defects

- Majority of studies to date computational:
  - *Ab initio: Restricted to small cells, difficult to extract thermodynamic properties…*
  - *Molecular dynamics: Predictiveness limited by empirical potentials, cell size, time step…*
  - *Mixed continuum atomistic: Ad hoc, patchwork…*
- Main issues of interest:
  - *Properties of individual defects: Core structure, core energies, limiting behaviors (dilute, continuum…)*
  - *Equilibrium properties of defect ensembles: Free energy, critical temperature for spontaneous defect nucleation*
- Defect densities at critical temperature small, not accessible to direct simulation!

Graphene and defects

- Our approach:
  - *Graphene lattice as differential complex*
  - *Defects as eigendeformations*
  - *Formal asymptotics and/or Γ-convergence*
  - *Equilibrium statistical mechanics*
- Results to date:
  - *Dislocation core structures, validation*
  - *Core energies, prelogarithmic energy factors*
  - *Continuum and dilute limits of stored energies:*
    - *Direct numerical simulation*
    - *Formal asymptotics*
    - *Γ-convergence (in progress)*
  - *Critical temperature, scaling (in progress)*

Graphene – Differential cell complex



$E_0 = \{0\text{-cells}\}$ $E_1 = \{1\text{-cells}\}$ $E_2 = \{2\text{-cells}\}$

the oriented cells of graphene
classification by type

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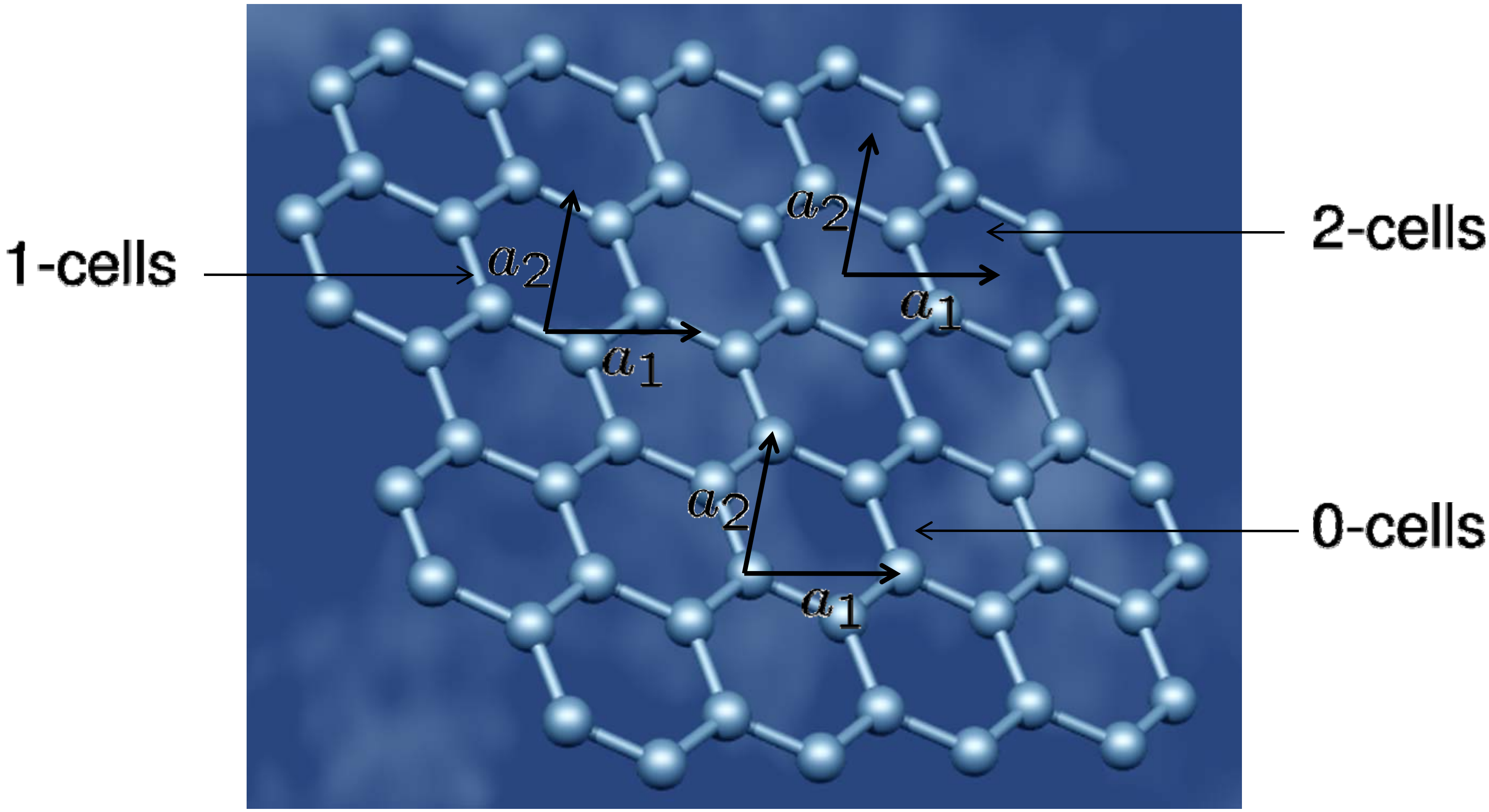
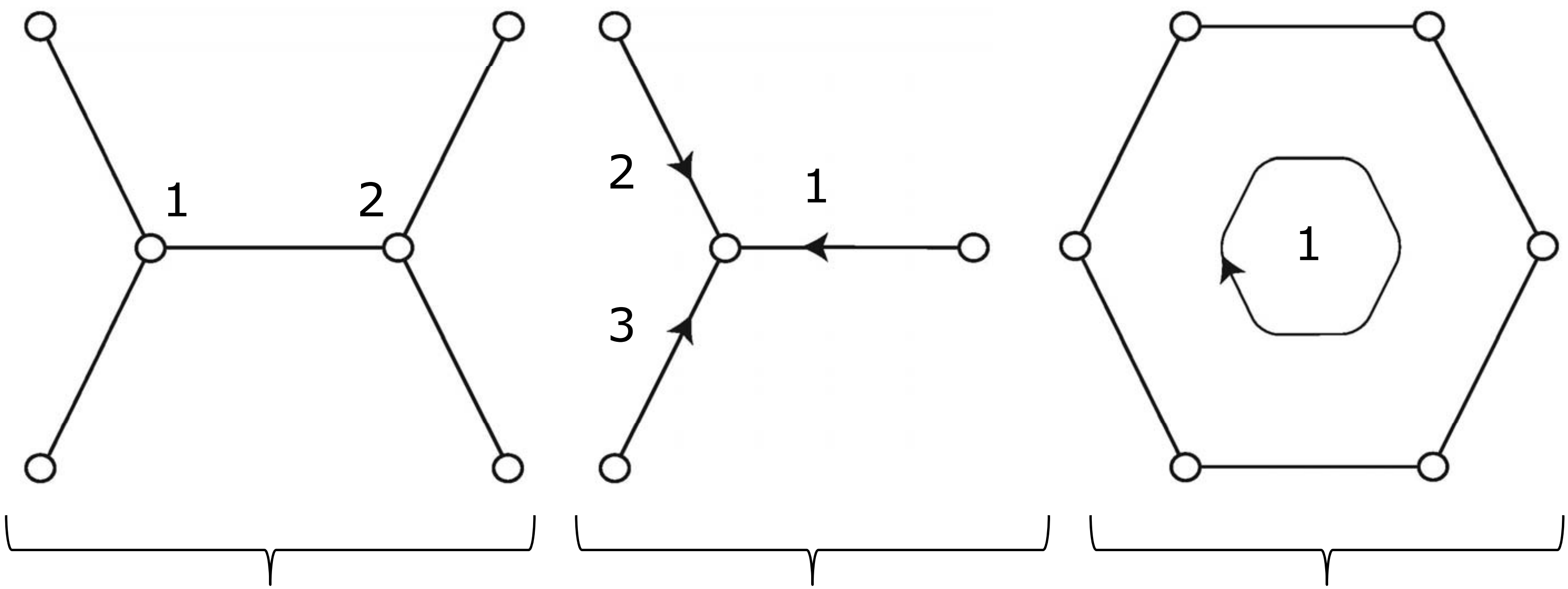
Graphene – Differential cell complex



cells of same type define
simple Bravais lattices

Graphene – Differential cell complex

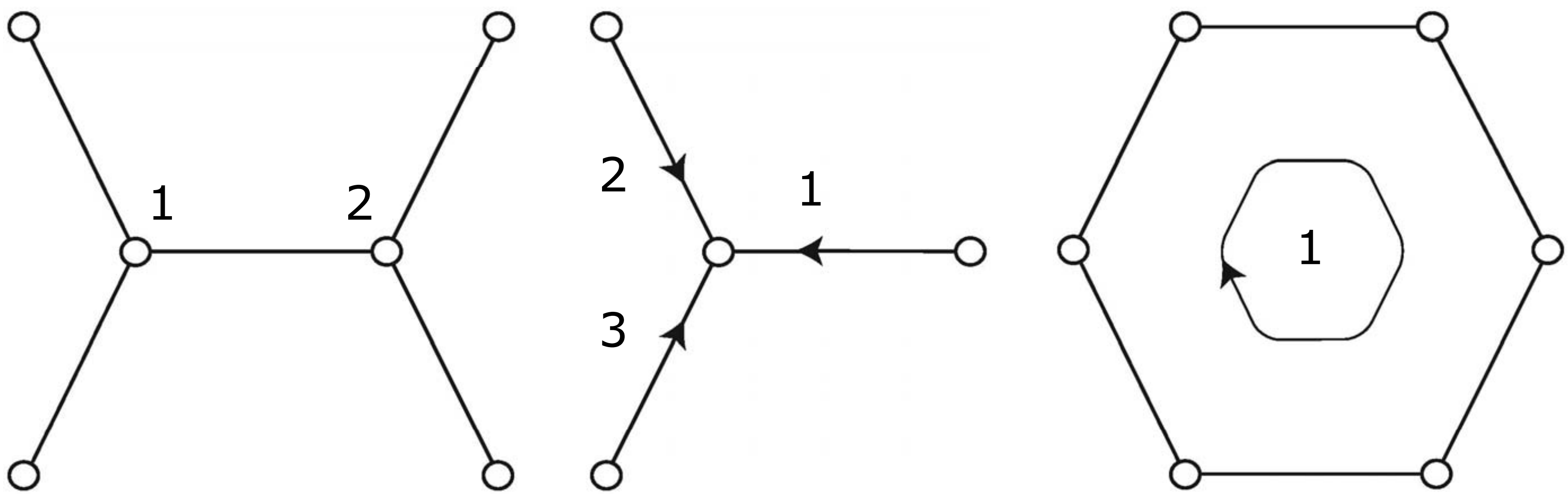


$$N_0 = 2 \qquad N_1 = 3 \qquad N_2 = 1$$

$$E_p = \{e_p(l,\alpha),\ l \in \mathbb{Z}^2,\ \alpha = 1, \dots, N_p\}$$

the Bravais lattices of cells of same type

Graphene – Differential cell complex



discrete p-forms: $\Omega^p = \{\omega_p : E_p \to \mathbb{R}^m\}$

discrete p-currents: $\Omega_p = \{\Lambda^p : E_p \to \mathbb{R}^m\}$

duality pairing: $\langle \Lambda^p, \omega_p \rangle = \sum_{\alpha=1}^{N_p} \sum_{l \in \mathbb{Z}^2} \Lambda^p(l,\alpha) \cdot \omega_p(l,\alpha)$

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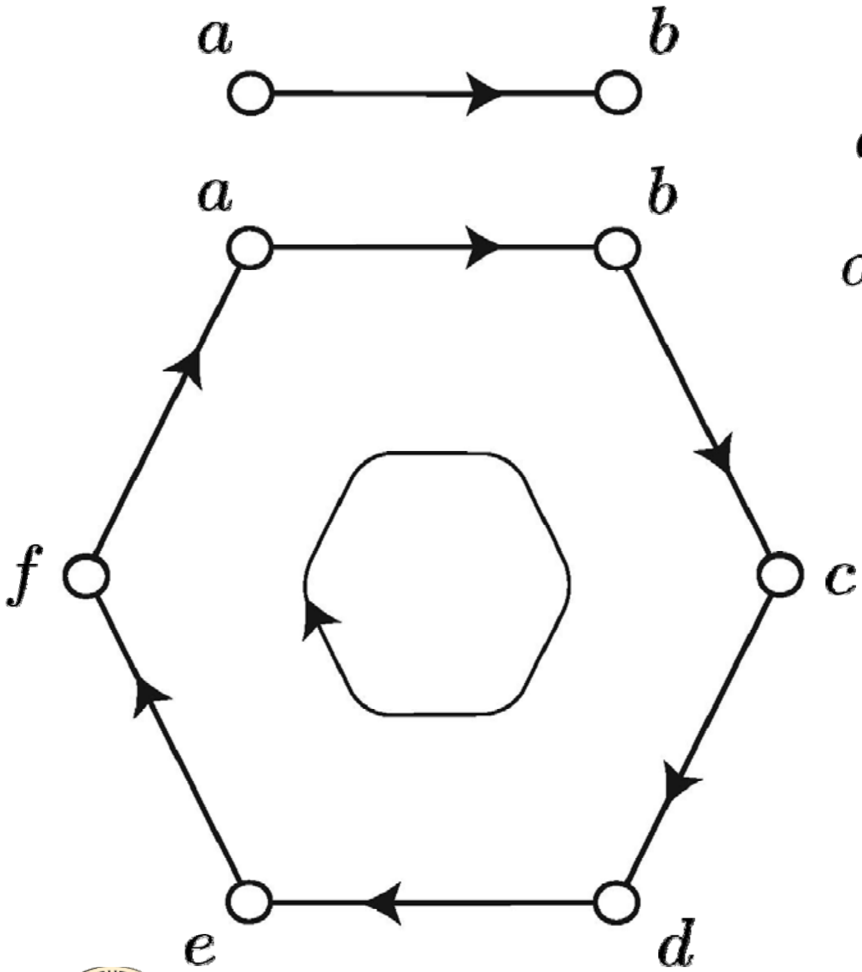
Graphene – Differential cell complex



- Differential operator:

$$d\omega(e_{ab}) = \omega(e_b) - \omega(e_a)$$

$$d\omega(e_{abcdef}) = \omega(e_{ab}) + \omega(e_{bc}) + \omega(e_{cd}) + \omega(e_{de}) + \omega(e_{ef}) + \omega(e_{fa})$$

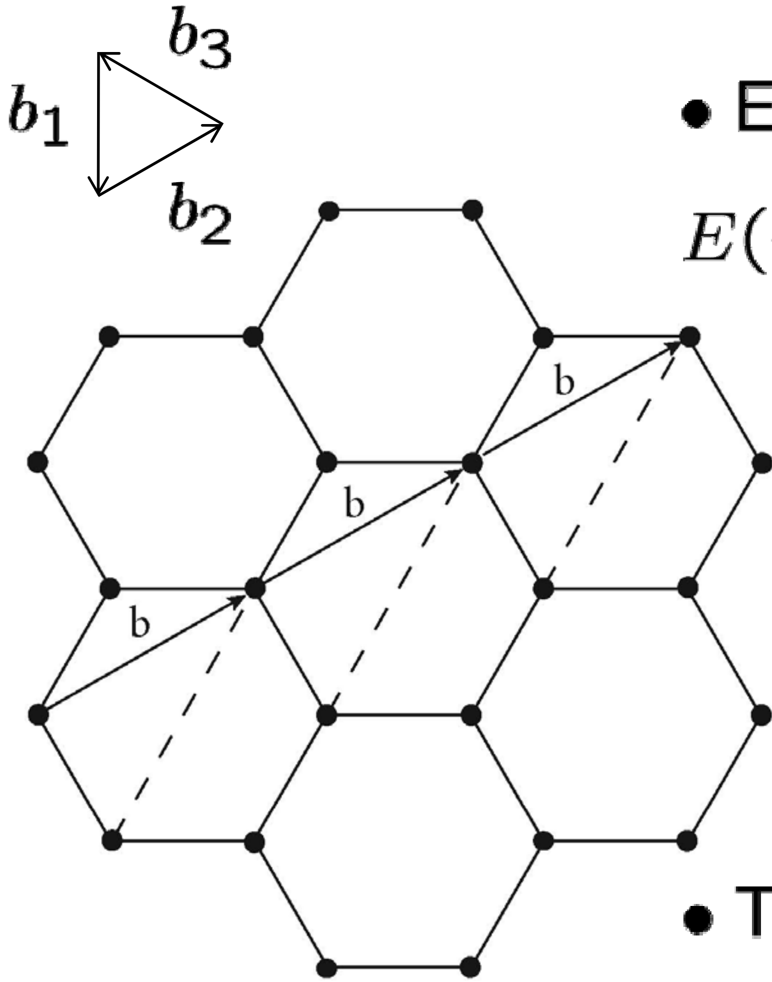
- Codifferential operator:

$$\langle \Lambda, d\omega \rangle = \langle \delta\Lambda, \omega \rangle$$

- Fundamental property:

$$d^2 = 0, \quad \delta^2 = 0$$

Graphene – Discrete dislocations



- Energy of defective graphene:

$$E(u,\beta) = \frac{1}{2}\langle \Psi * (du-\beta), (du-\beta)\rangle$$

$\Psi \equiv$ bondwise force constants

$\Omega^0 \ni u \equiv$ displacement field

$\Omega^1 \ni du \equiv$ bond deformation

$\Omega^1 \ni \beta \equiv$ eigendeformations

- Three lattice-preserving shears:

$$\beta(e_1) \in b_1\mathbb{Z} + b_2\mathbb{Z} + b_3\mathbb{Z}$$

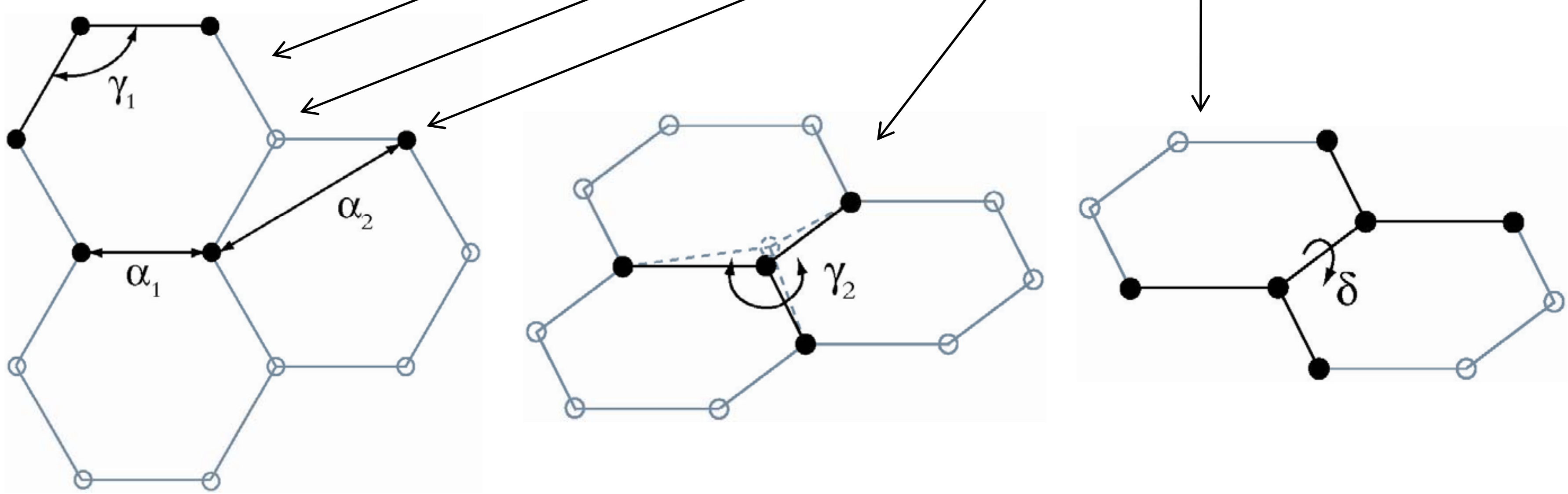
lattice-preserving shear deformation

Graphene – Force constants

- ASOIO Potential:

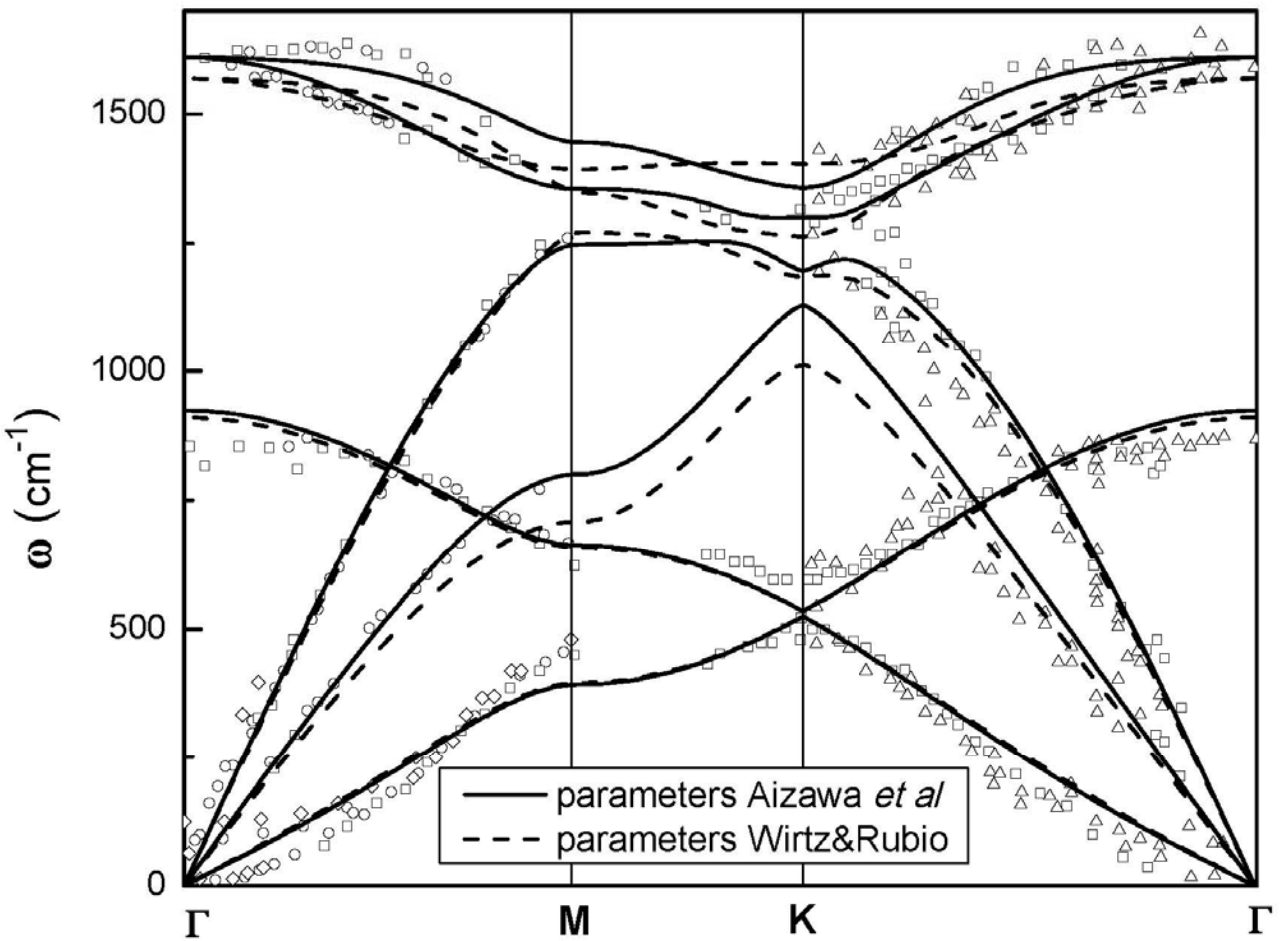
interaction with substrate

$$E(u) = V_1 + V_2 + V_3 + V_4 + V_5 + V_6$$



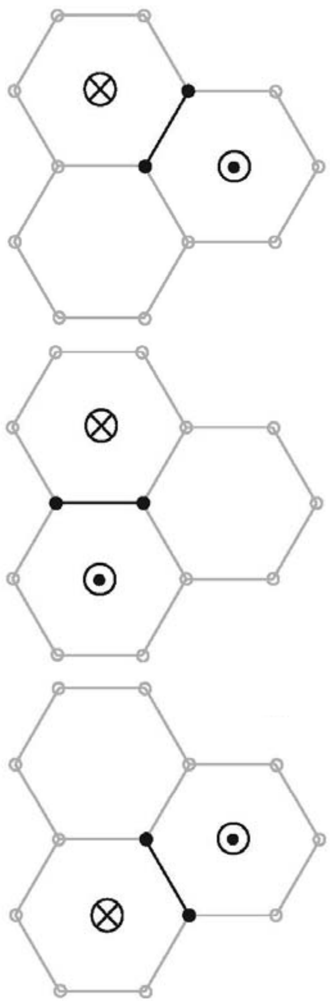
Aizawa, T. et al., "Bond Softening in Monolayer Graphite Formed on Transition-Metal Carbide Surfaces" Phys. Rev. B, **42**(18) (1990) pp. 11469--11478

Graphene – Force constants



Phonon-dispersion curves computed from ASOIO potential (Aizawa *et al*. (1990) and by Wirtz & Rubio (2004))

Graphene – Discrete dislocations



basis for graphene dislocations

- Energy of defective graphene:

$$E(u,\beta) = \frac{1}{2}\langle \Psi * (du - \beta), (du - \beta)\rangle$$

- Displacement equilibrium problem:

$$\delta\Psi * du \equiv \boxed{Au = f} \equiv \delta\Psi\beta$$

- Note: inf $E(u,\beta) = 0$ if $\beta = dv$
- Discrete dislocation density: $\boxed{\alpha = d\beta}$
- Hodge: $\alpha = 0$ iff $\beta = dv$
- Stored energy depends on α:

$$E(\alpha) = \inf\{E(u,\beta),\ d\beta = \alpha\}$$

Graphene - Discrete Fourier transform

- Discrete Fourier Transform: $\hat{f}(\theta) = \sum_{l \in \mathbb{Z}^2} f(l) \mathrm{e}^{-i\theta \cdot l}$
- Inverse: $f(l) = \dfrac{1}{(2\pi)^2} \displaystyle\int_{[-\pi,\pi]^2} \hat{f}(\theta) \mathrm{e}^{i\theta \cdot l} \, d\theta$
- Convolution theorem: $\widehat{f * g} = \hat{f}\hat{g}$
- Parseval identity: $\langle f, g \rangle = \dfrac{1}{(2\pi)^2} \displaystyle\int_{[-\pi,\pi]^2} \hat{f}(\theta) \hat{g}^*(\theta) \, d\theta$
- Differential operator: $\widehat{d\omega}(\theta) = Q(\theta)\hat{\omega}(\theta)$

$$Q_1(\theta) = \begin{pmatrix} 1 & -\mathrm{e}^{i\theta_2} \\ 1 & -1 \\ 1 & -\mathrm{e}^{-i\theta_3} \end{pmatrix}, \quad \theta_3 = \theta_1 - \theta_2$$

$$Q_2(\theta) = \left(\mathrm{e}^{i\theta_3} - 1, 1 - \mathrm{e}^{i\theta_1}, \mathrm{e}^{i\theta_1} - \mathrm{e}^{i\theta_3} \right)$$

Graphene - Discrete Fourier transform

- For given eigendeformations: $\hat{u}(\theta) = -\hat{\Phi}^{-1} Q_1^T \hat{\Psi} \hat{\beta}$

  where: $\hat{\Phi}(\theta) = Q_1^T(\theta)\hat{\Psi}(\theta)Q_1^*(\theta)$

- For given discrete dislocation density:

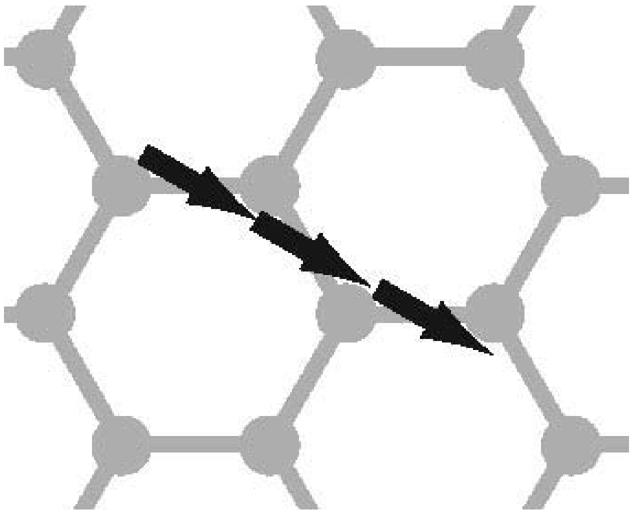
$$E(\alpha) = \frac{1}{(2\pi)^2} \int_{[-\pi,\pi]^2} \frac{1}{2} \langle \hat{\Gamma}(\theta)\hat{\alpha}(\theta), \hat{\alpha}^*(\theta) \rangle \, d\theta$$

$$\hat{\Gamma}(\theta) = \hat{\Delta}^{-T}(Q_2^* \hat{\Psi} Q_2^T - Q_2^* \hat{\Psi} Q_1^* \hat{\Phi}^{-1} Q_1^T \hat{\Psi} Q_2^T) \hat{\Delta}^{-1}$$

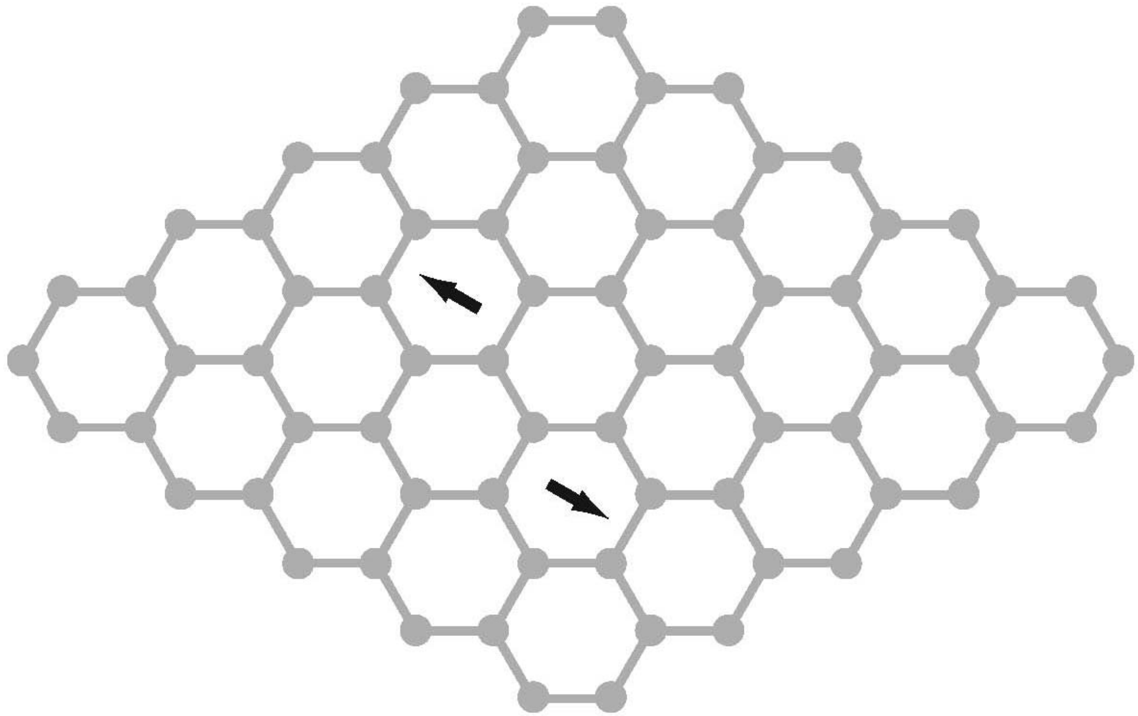
$$\hat{\Delta}(\theta) = 2(3 - \cos\theta_1 - \cos\theta_2 - \cos\theta_3)$$

- Periodic case: Integrals reduce to finite sums

Graphene – Dislocation dipoles



close-up of
eigendeformations



dislocation dipole in unit cell

Periodic arrangement of dislocation dipoles

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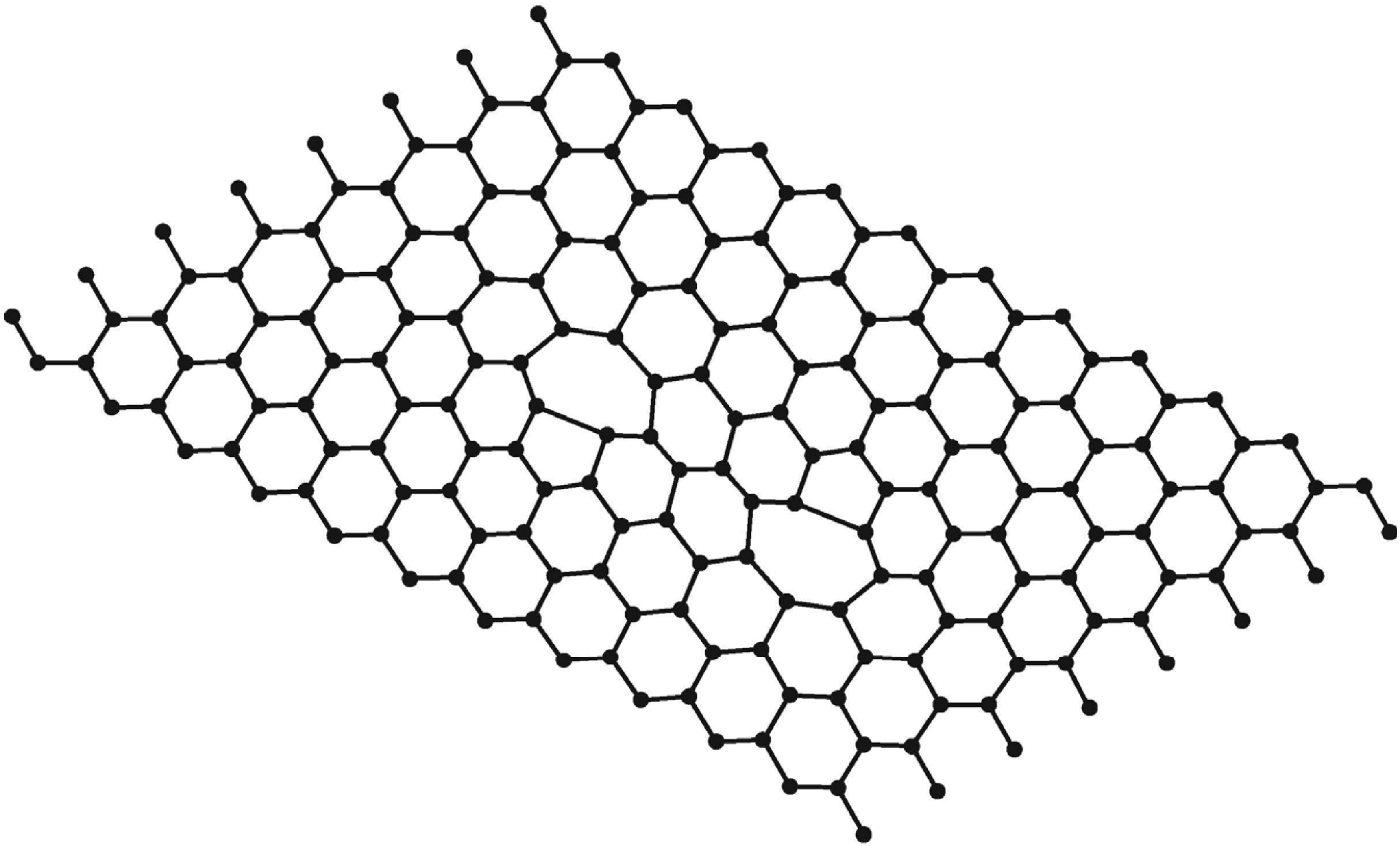
Graphene – Dislocation dipoles



Discrete dipole core structure in ASOIO graphene, exhibiting dissociated pentagon-heptagon ring (5-7-7-5)

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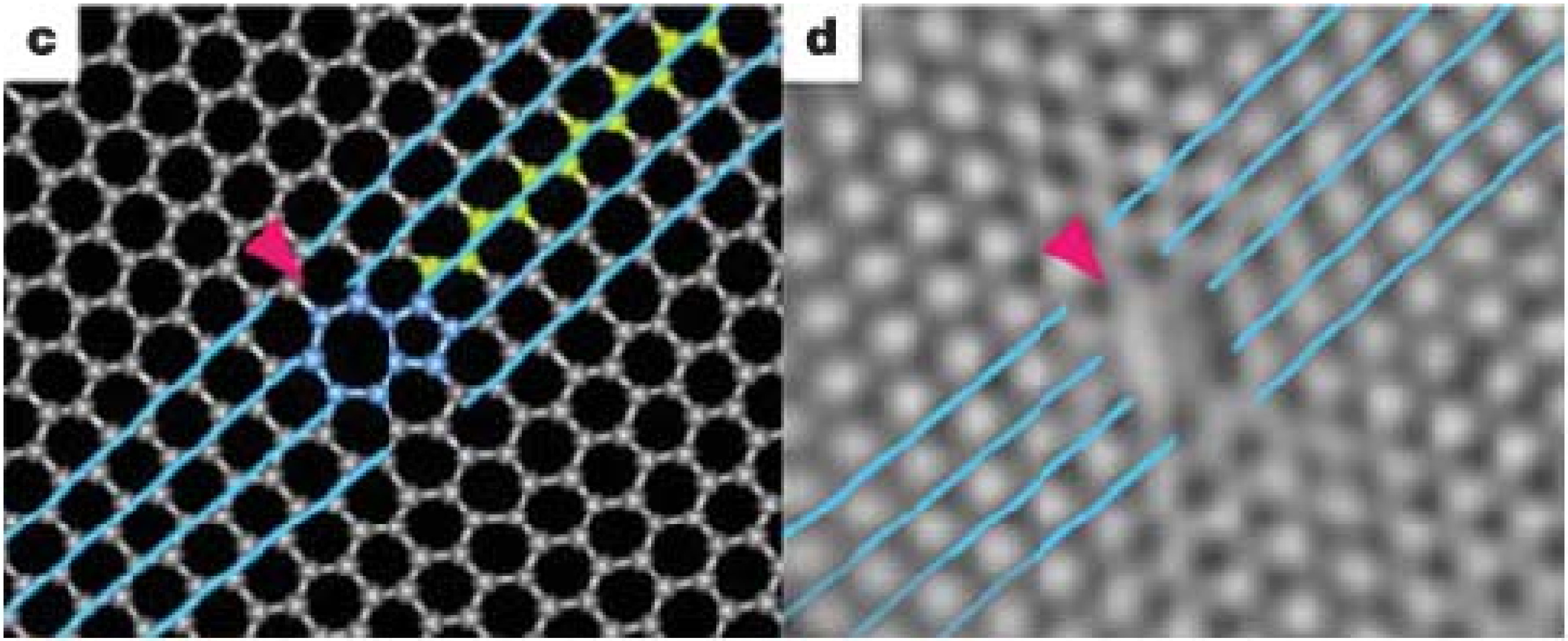
Graphene – Dislocation dipoles

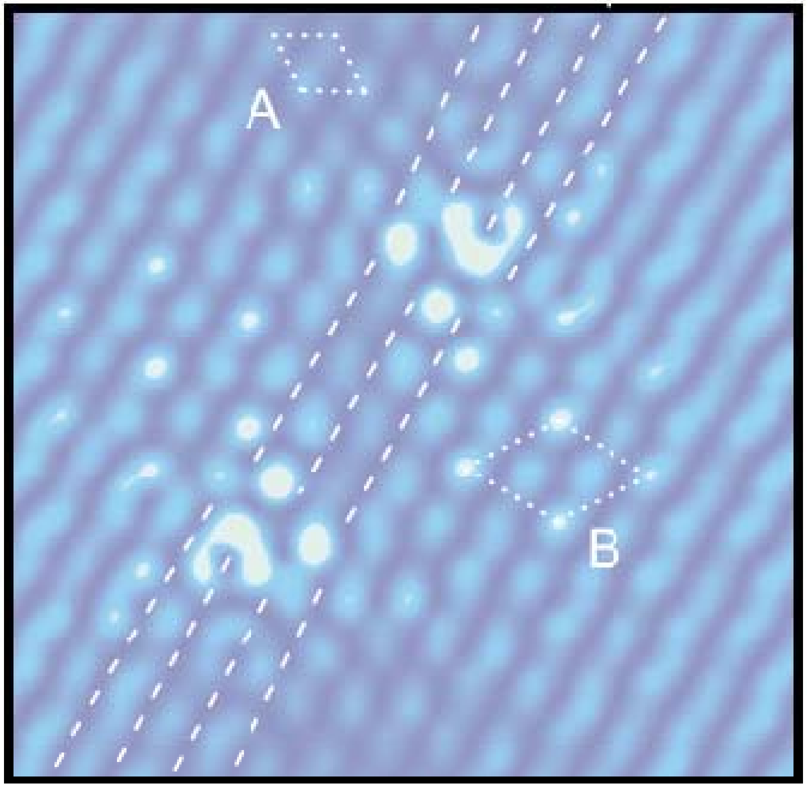


pentagon–heptagon pair
in the graphitic network

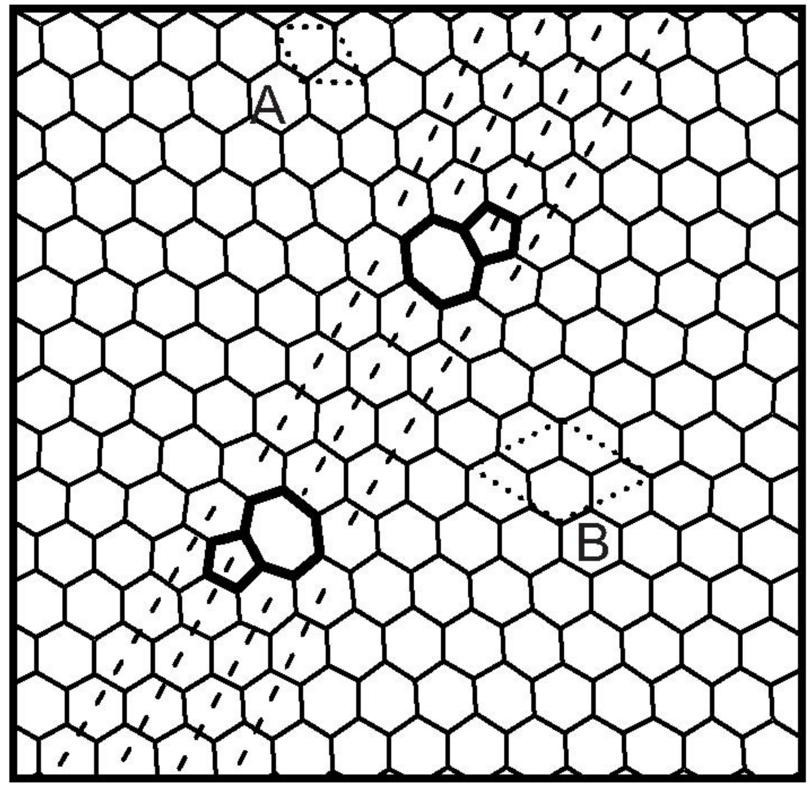
simulated HR-TEM image

In situ observation of a dislocation in a graphene layer
(Hasimoto *et al.* "Direct evidence for atomic defects in graphene layers", Letters to Nature, **430** (2004) pp.870-873)

Graphene – Dislocation dipoles



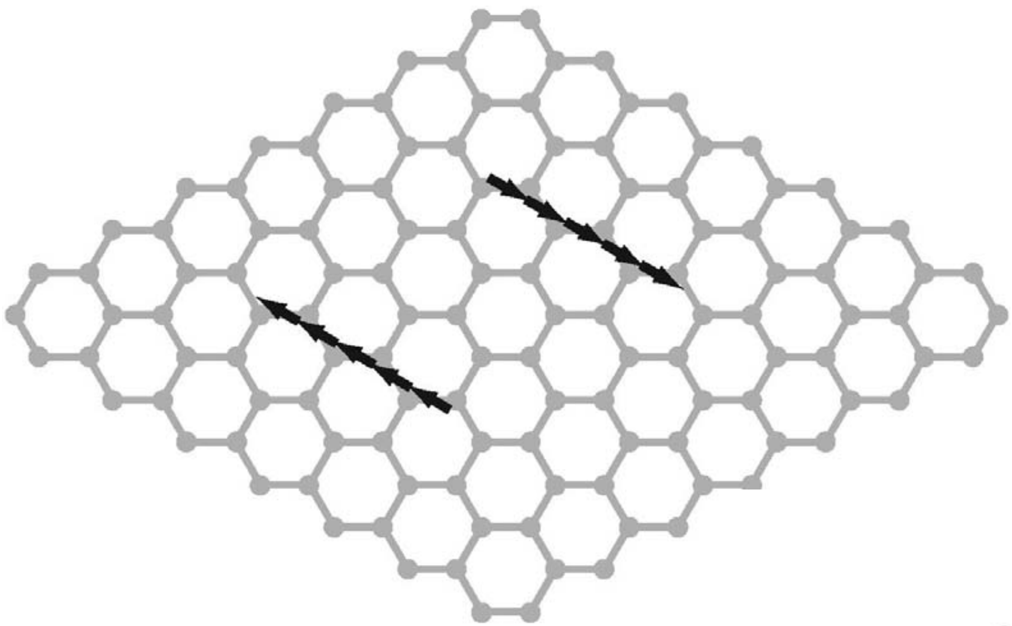
Simulated STM image (DFT)



Atomic structure

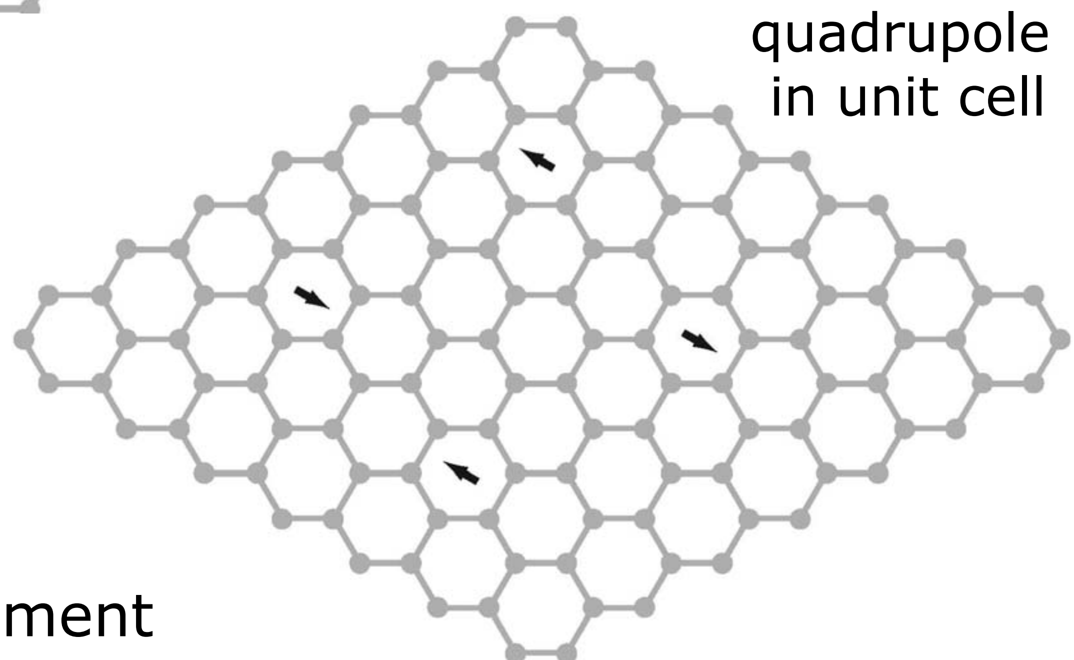
Jeong, B.W. et al., Stability of dislocation defect with two pentagon-heptagon pairs in graphene, Phys. Rev. B, **78**, 165403 (2008)

Graphene – Dislocation quadrupoles



eigendeformations
defining a quadrupole

quadrupole
in unit cell



periodic arrangement
of dislocation quadrupoles

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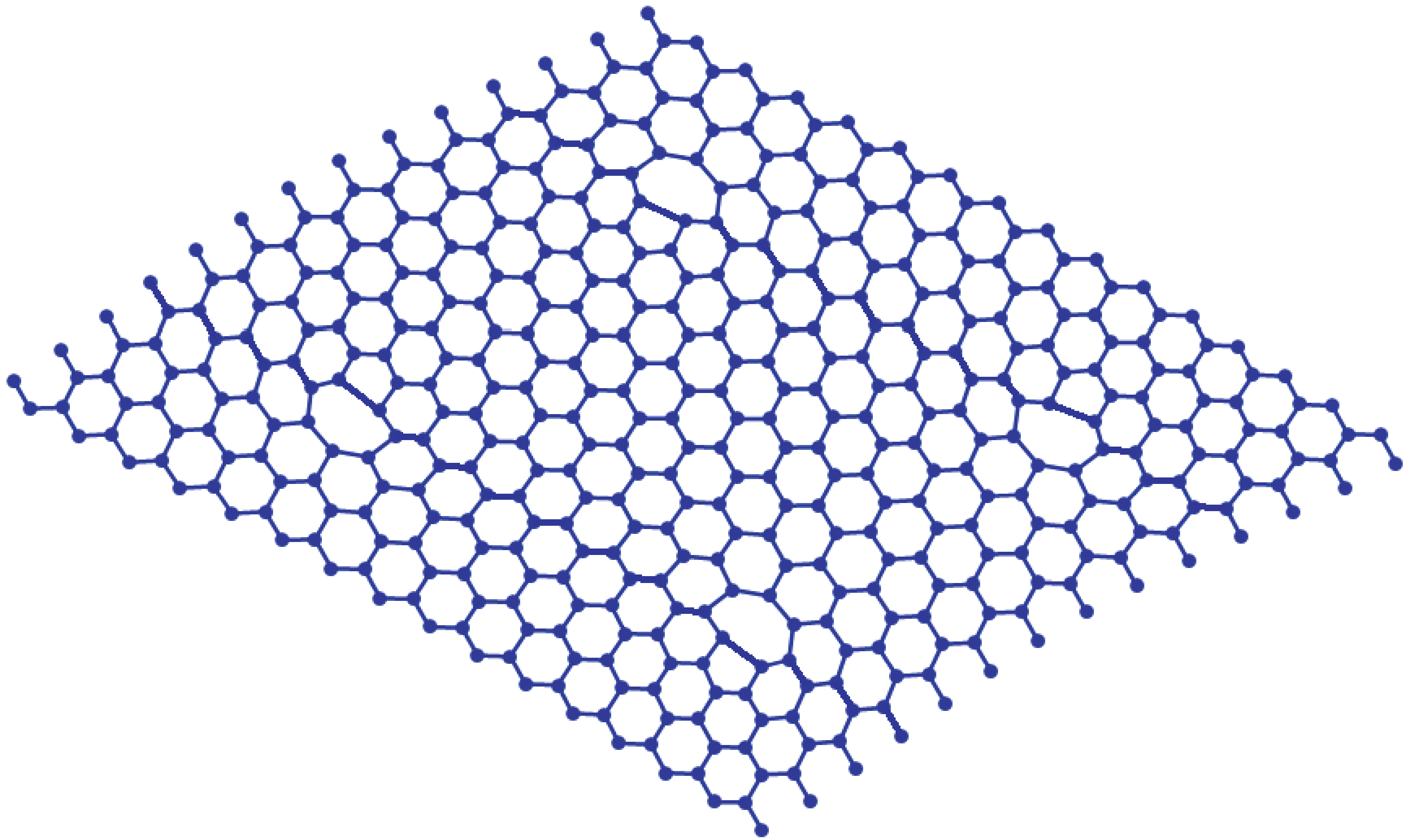
Graphene – Dislocation quadrupoles



Discrete quadrupole core structure in ASOIO graphene, exhibiting dissociated pentagon-heptagon ring (5-7-7-5)

Michael Ortiz
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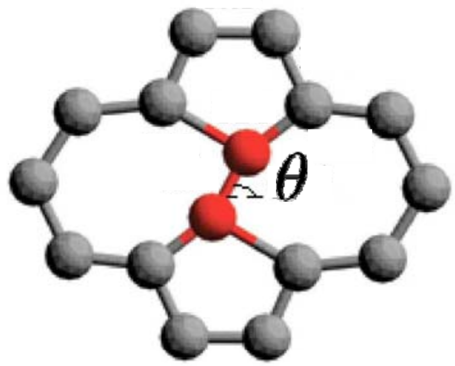
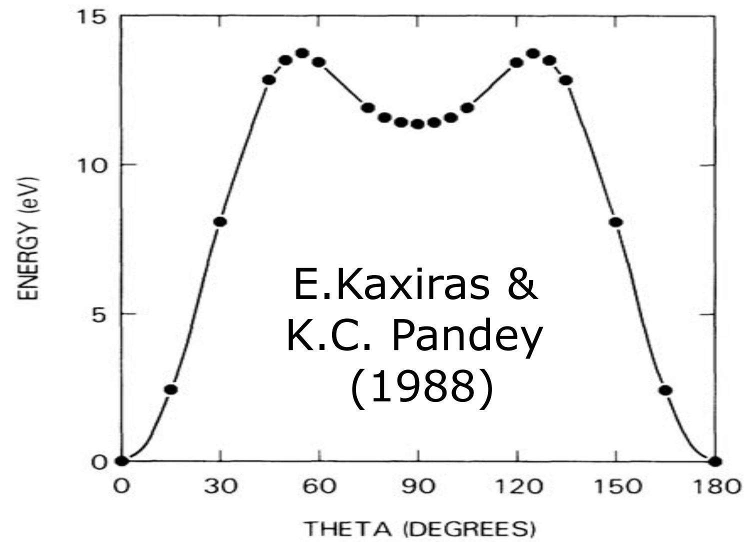
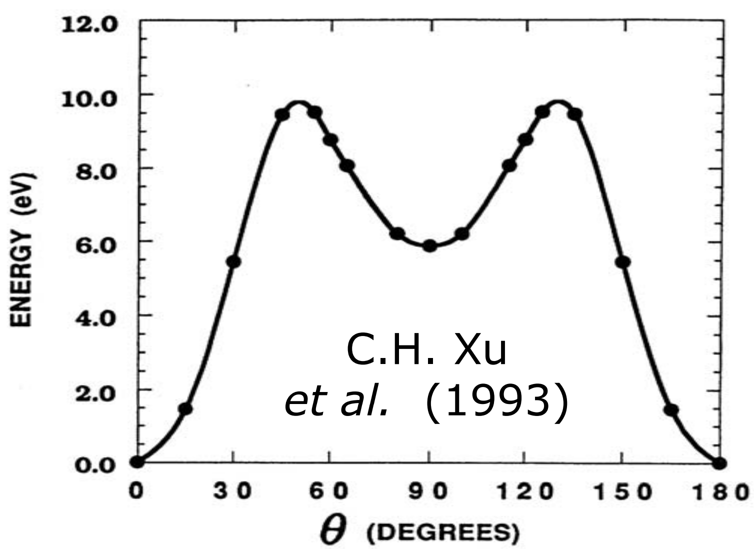
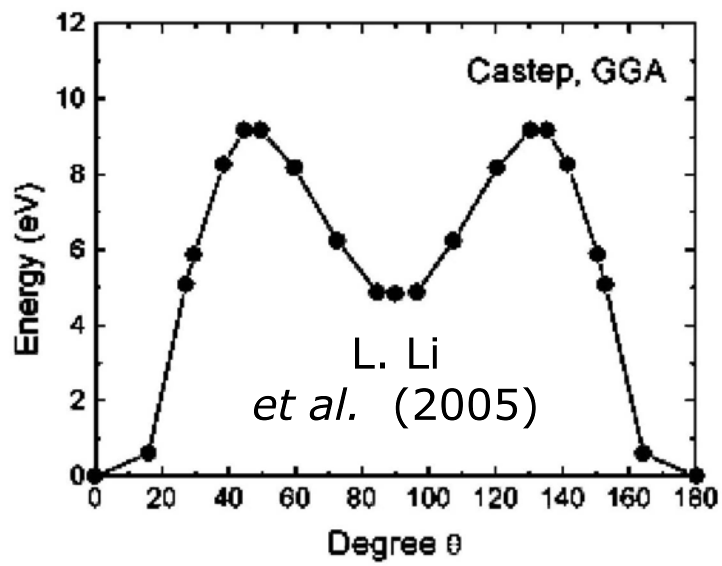
Graphene – Dislocation cores



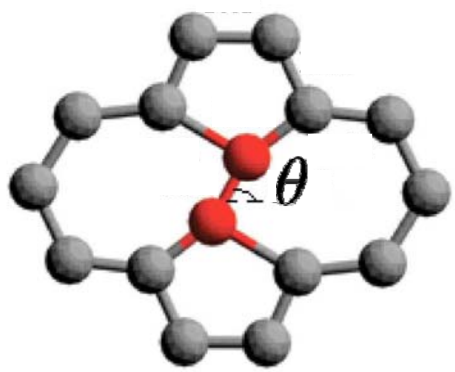
bond rotation angle







Graphene – Dislocation cores

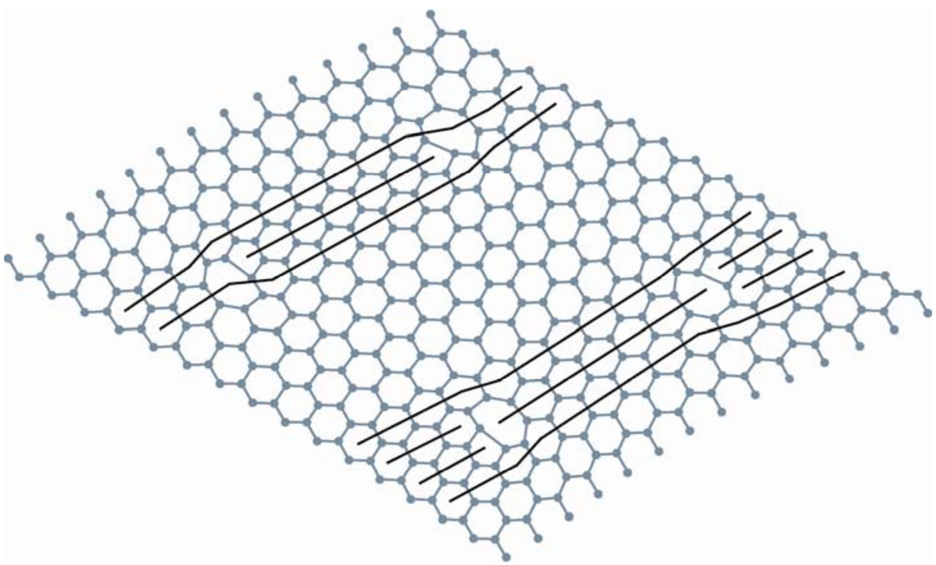


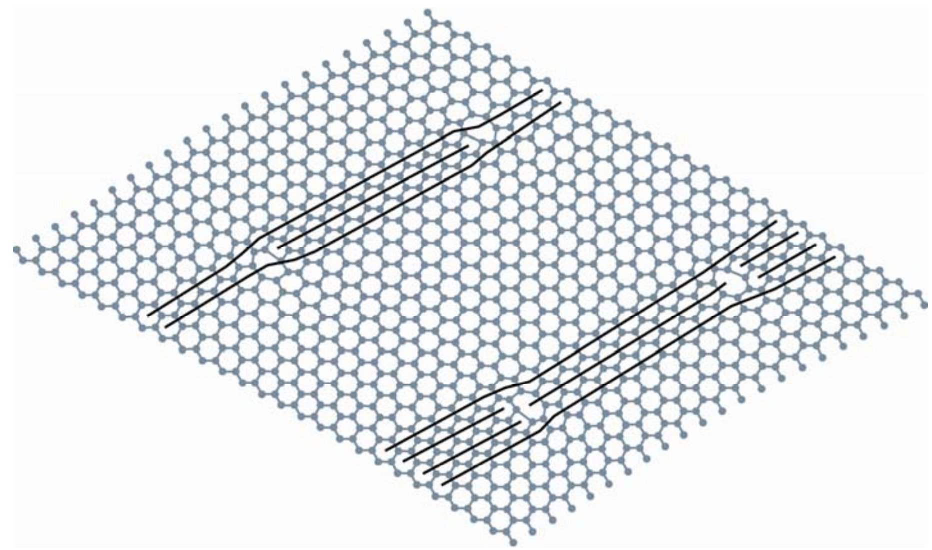
bond rotation angle

Summary of bond angles and formation energies at transition state computed from firs-principles calculations

Study	Formation angle	Formation energy
Ariza & MO	52 degrees	11.92 eV
Li et al. (2005)	45 degrees	9.2 eV
Kaxiras & Pandy (1988)	55 degrees	14.0 eV
Xu et al. (1993)	50 degrees	9.8 eV
Los et al. (2005)	50 degrees	8.0 eV
Meyer et al. (2008)	-	< 15.6 eV

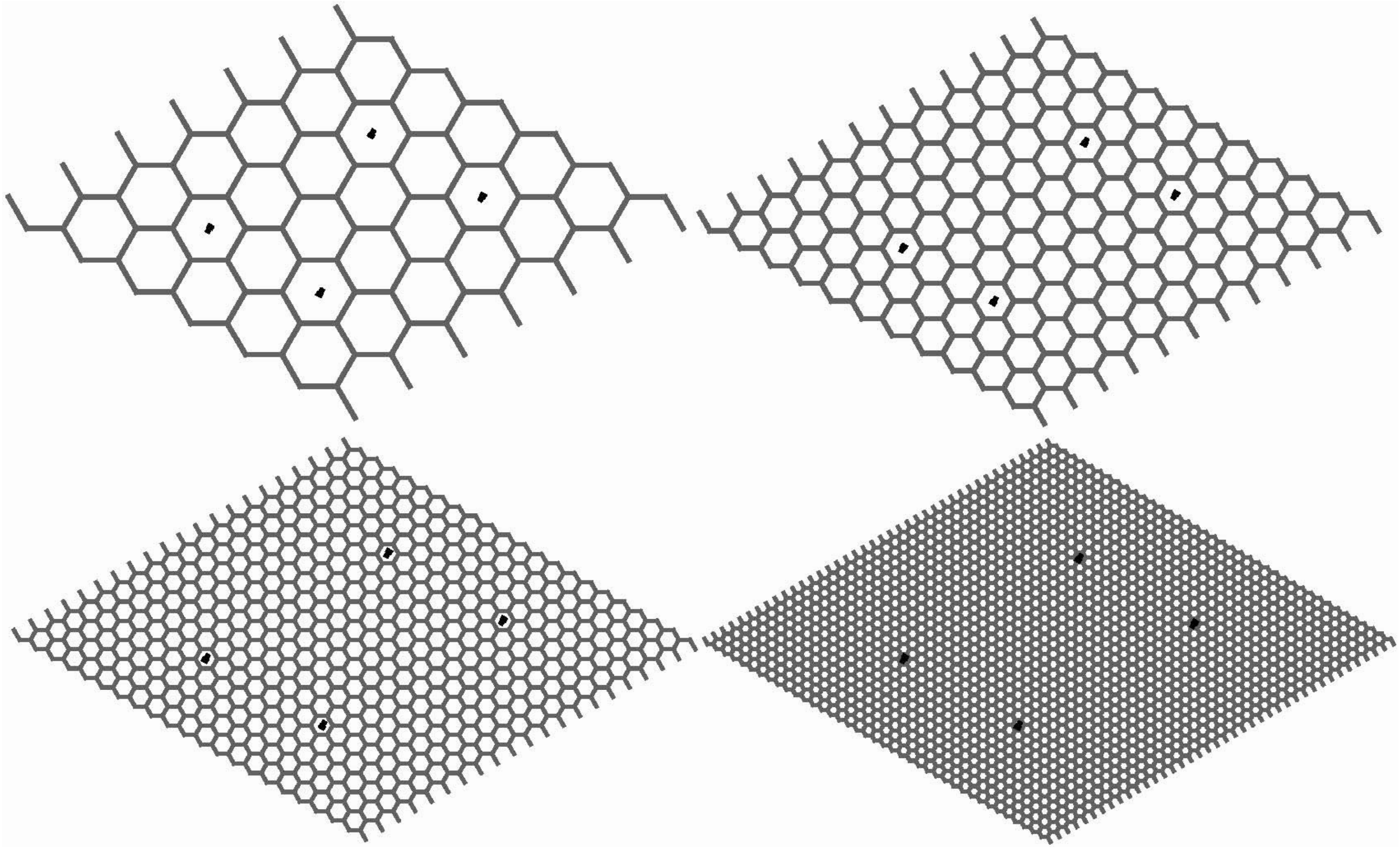
Graphene – Dislocation cores





- Discrete-dislocation model predicts 5-7 dislocation core structures, in agreement with observation and first-principles calculations
- Predicted unstable transition configuration and formation energies are in the range of first-principles calculations

Graphene – Dilute/continuum limits



Limit of dilute dislocation densities
(equivalently, continuum limit)

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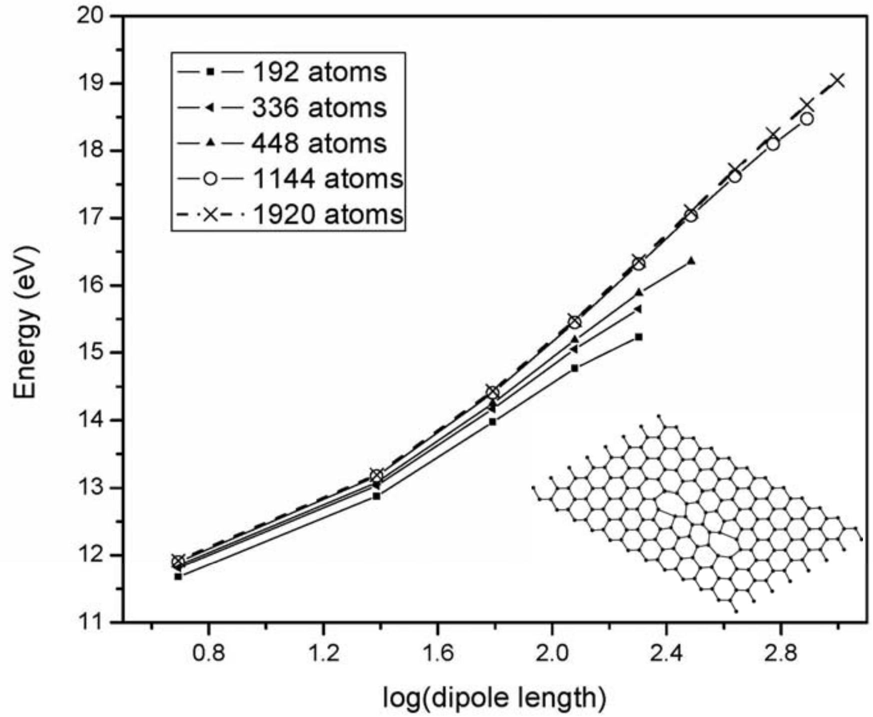
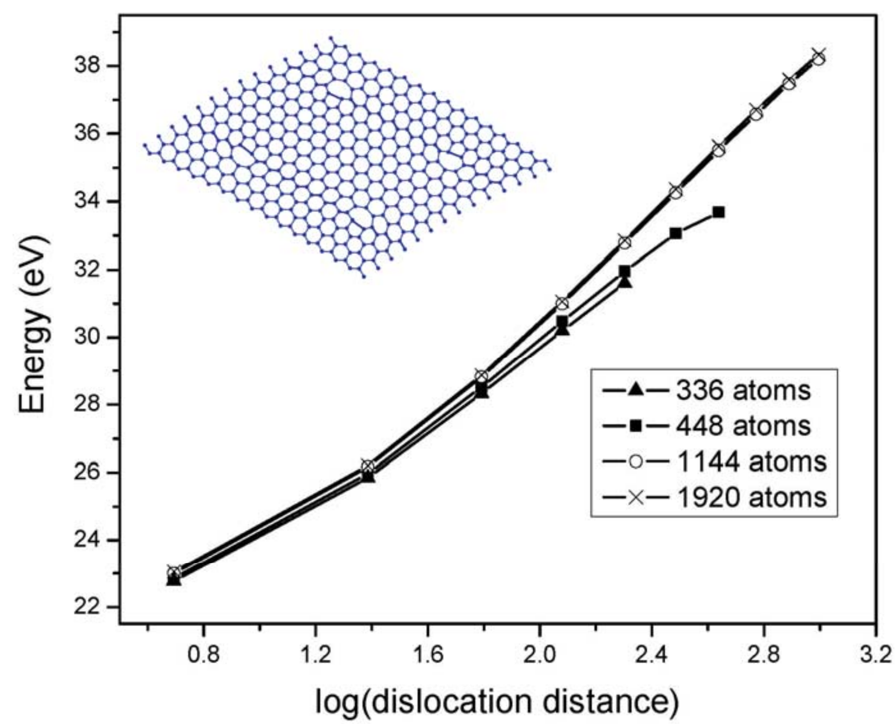
Graphene – Dilute/continuum limits





$$E = (23.07255\ \text{eV}) + (6.80\ \text{eV})\ \log h$$

Energy of periodic dislocation densities in ASOIO graphene as a function of dislocation separation and unit-cell size.

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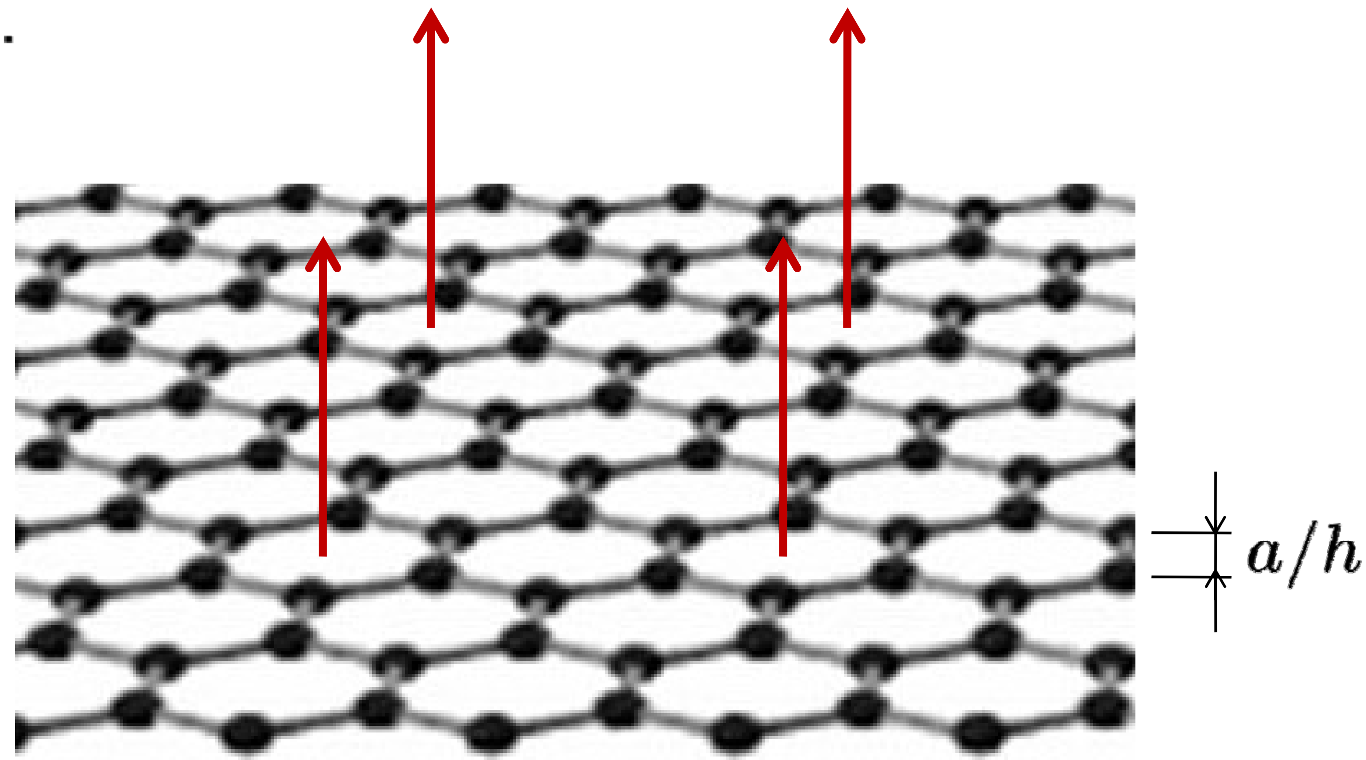
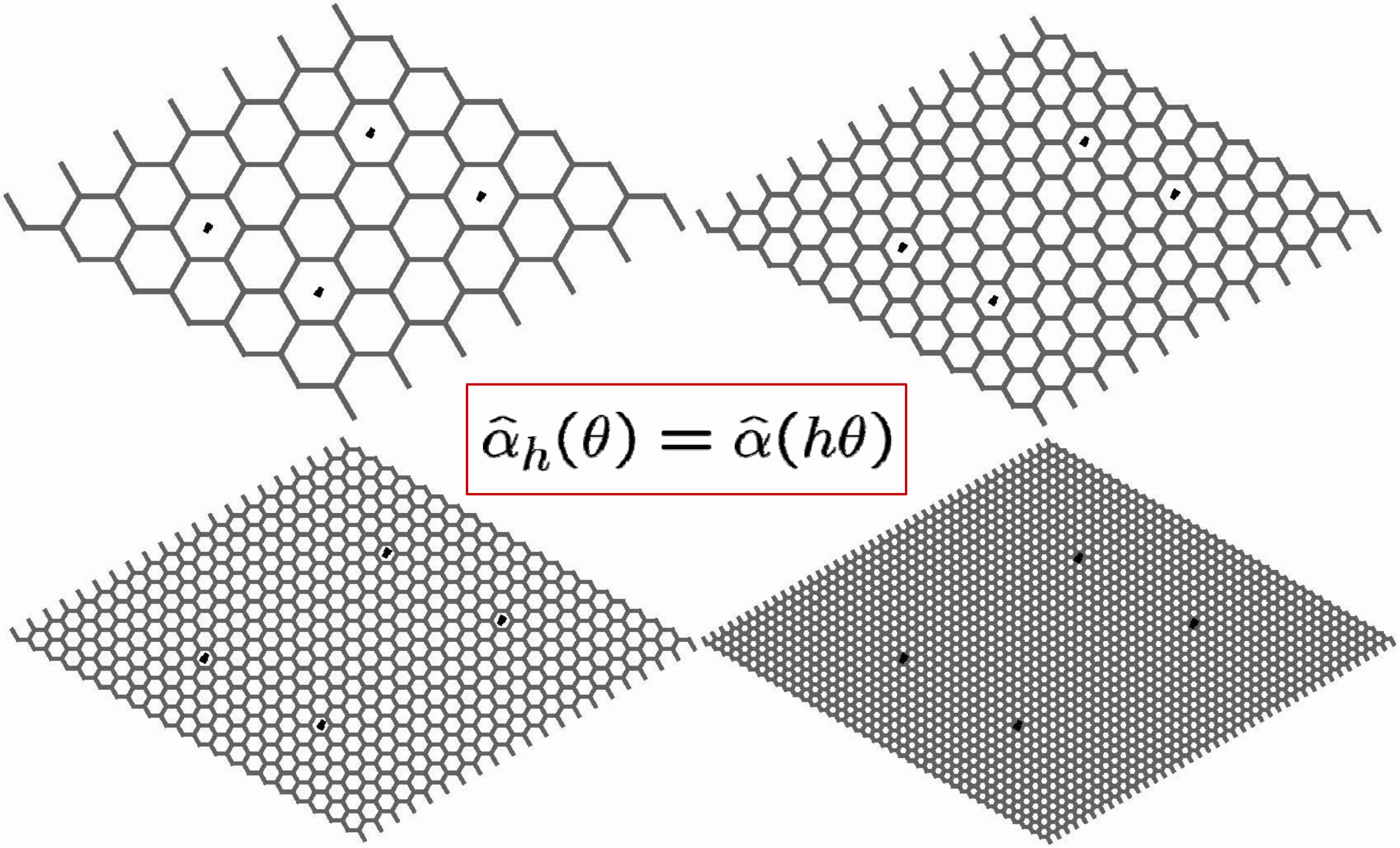
Graphene – Dilute/continuum limits

- Identify discrete dislocation densities with measures whose Fourier transform is $[-h\pi, h\pi]^2$-periodic for some $h \in \mathbb{N}_+$.



$\hat{\alpha}(\theta)$ is $[-h\pi, h\pi]^2$-periodic!

Graphene – Dilute/continuum limits



$$\widehat{\alpha}_h(\theta) = \widehat{\alpha}(h\theta)$$

Sequence of scaled dislocation densities

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Graphene – Dilute/continuum limits

- Define the sequence of energies:

$$E_h(\alpha) = \begin{cases} E(\alpha_h), & \text{if } \hat{\alpha} \text{ is } [-h\pi, h\pi]^2 - \text{periodic}, \\ +\infty, & \text{otherwise.} \end{cases}$$

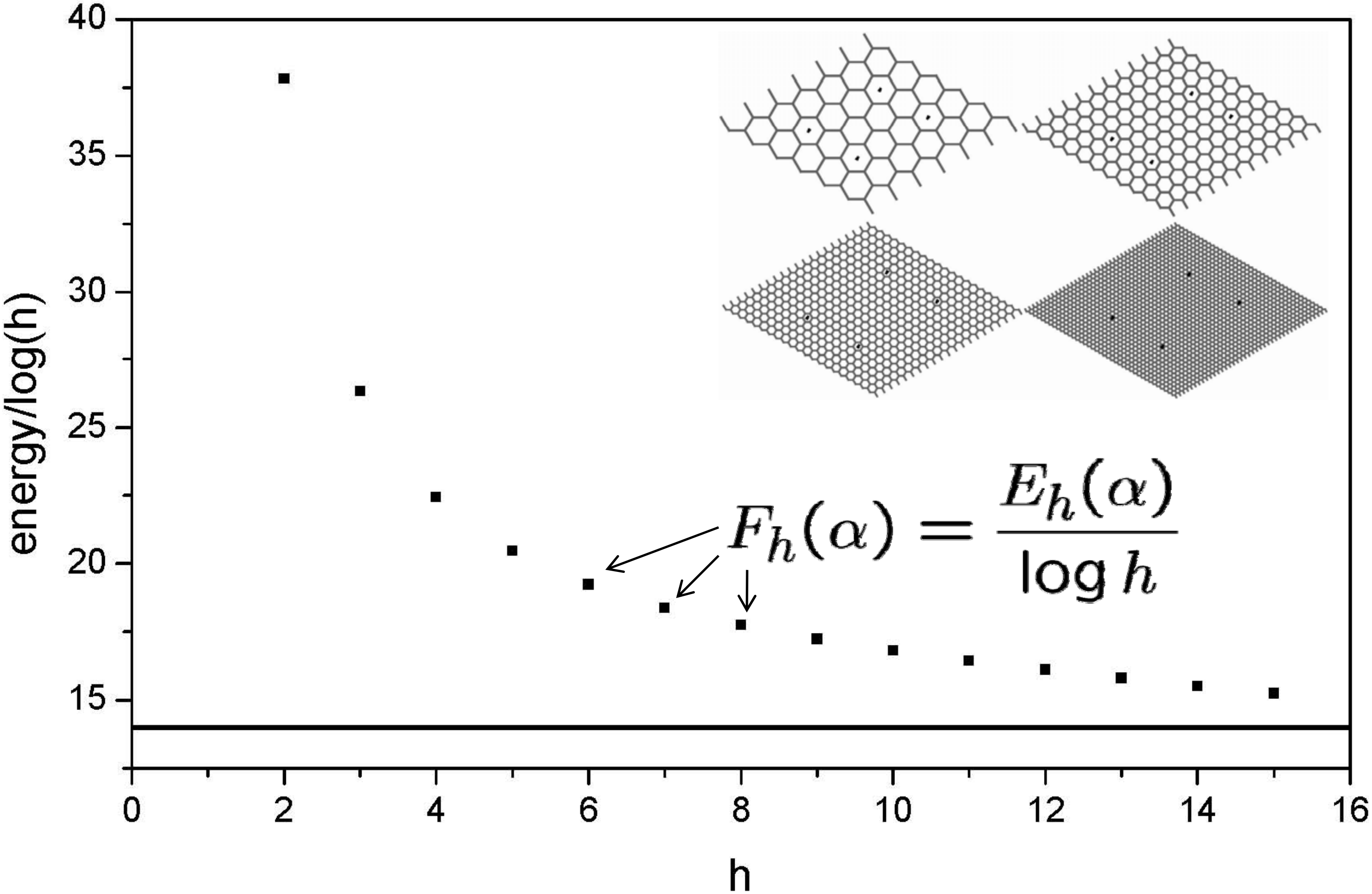
- Pointwise limit: $F(\alpha) \equiv \lim_{h\to\infty} \frac{E_h(\alpha)}{\log h} =$

$$\begin{cases} \langle K\alpha, \alpha\rangle_{l^2(\mathbb{Z}^2)}, & \text{if } \hat{\alpha} \text{ is } [-k\pi, k\pi]^2 - \text{periodic}, \\ +\infty, & \text{otherwise.} \end{cases}$$

where $K \equiv$ LE prelogarithmic energy factor

- Pointwise limit: Sum of dislocation core energies!
- Γ-limit of the sequence?

Graphene – Dilute/continuum limits



Energy sequence is decreasing!

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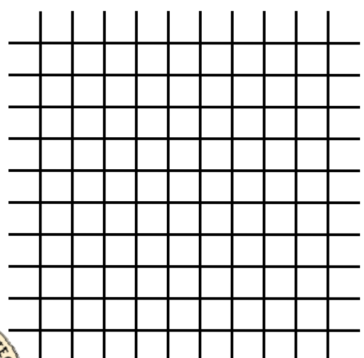
Graphene – Dilute/continuum limits

Proposition [Dal Maso (1993), Prop. 5.7]*If F_h is a decreasing sequence converging to F pointwise, then F_h Γ-converges to the relaxation* $\mathrm{sc}^- F$ *of F.*

Question: What is the relaxation of the pointwise limit?

M. Ponsiglione: Square lattice, screw (scalar) dislocations, energy proportional to total mass of dislocation.

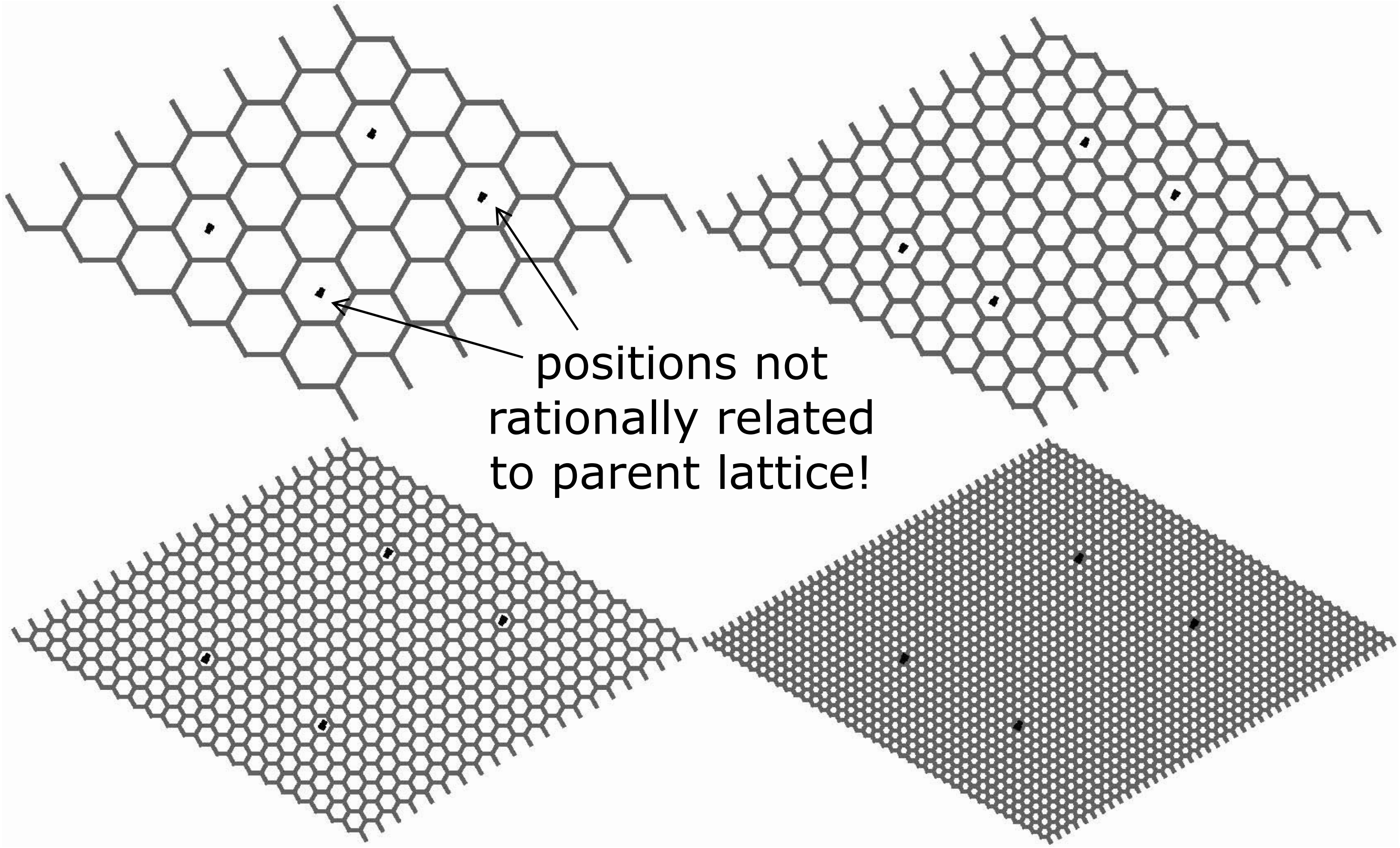


$$\mathrm{sc}^- F(\alpha) = C|\alpha|$$

↑ total dislocation mass!

Garroni & Leoni: Related 2D result

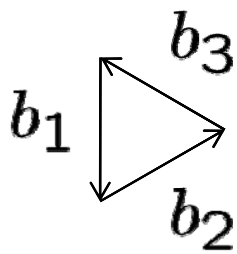
Graphene – Dilute/continuum limits

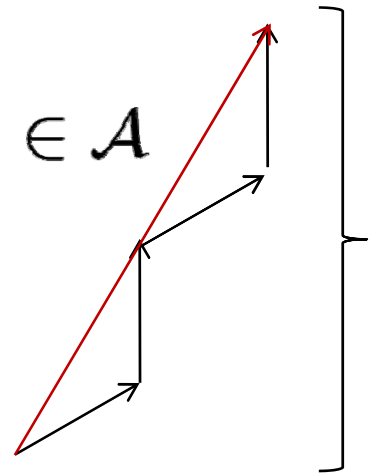


Extend limit to $\widehat{\alpha}(\theta)$ $[-a\pi, b\pi]^2$-periodic by density

Graphene – Dilute/continuum limits

- Recall: $\alpha(l) \in b_1\mathbb{Z} + b_2\mathbb{Z} + b_3\mathbb{Z} \equiv \mathcal{A}$
- Decompose dislocations locally:





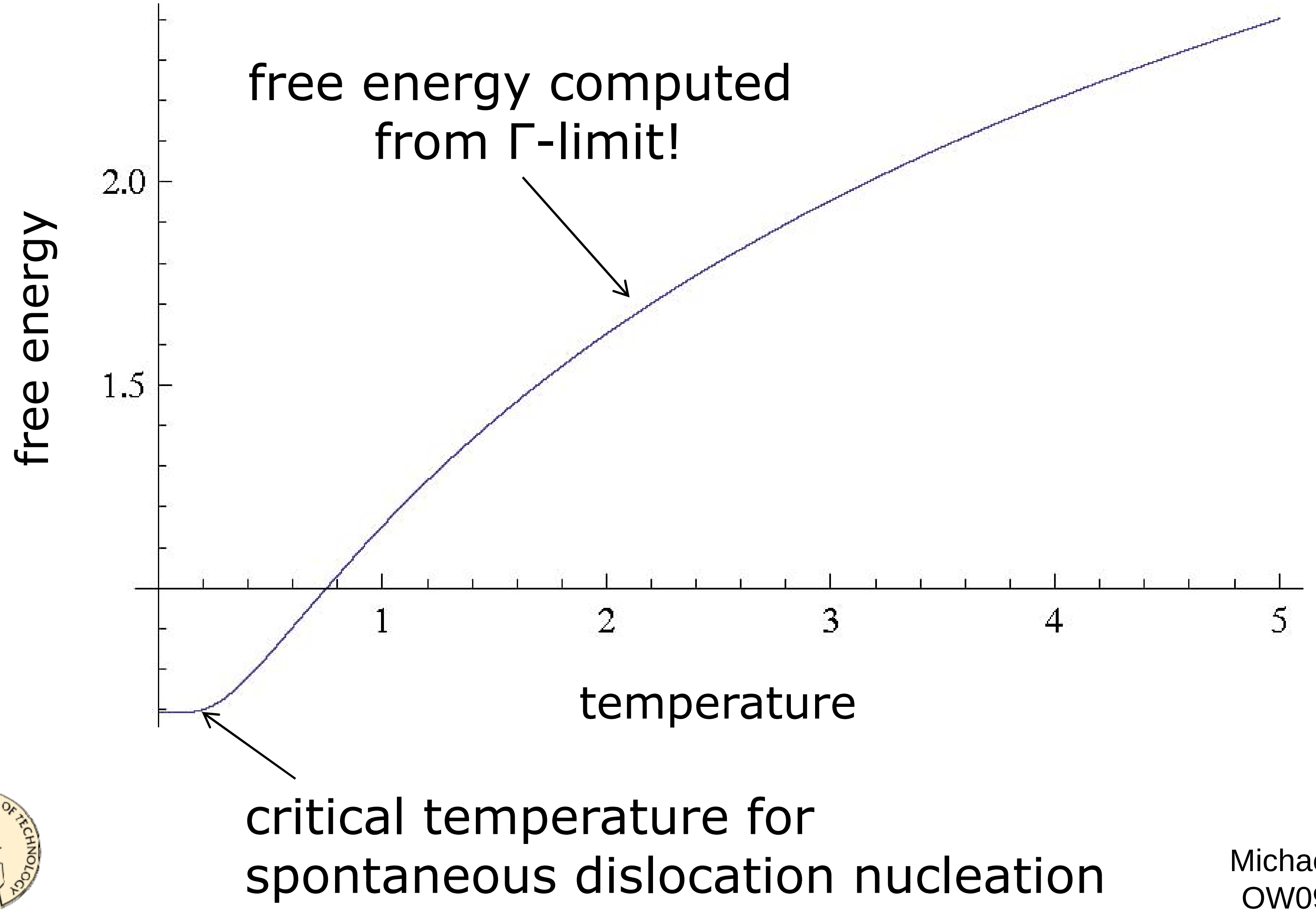
path in $\mathcal{A}$
of unit
dislocations

hom. of degree 1:
line tension!

- Optimize decomposition:

$$\mathrm{sc}^{-}F \sim \sum_{l\in\mathbb{Z}^2} \left[\min_{\text{paths to } \alpha(l)} \left(\sum_{b\in\text{path to } \alpha(l)} \frac{1}{2}\langle Kb, b\rangle \right) \right]$$

Graphene – Free energy of defects



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Dislocations in graphene

Thank you!