Dislocations in graphene

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In collaboration with:

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Symposium on Multiscale Dislocation Dynamics

UCSD, La Jolla, January 16-17, 2010

Graphene

Andre K. Geim
School of Physics
& Astronomy
Manchester University

- 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*
- Exceptional properties!

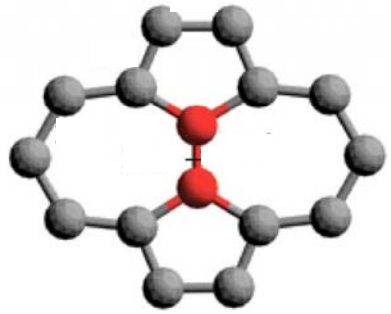
Graphene and defects

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

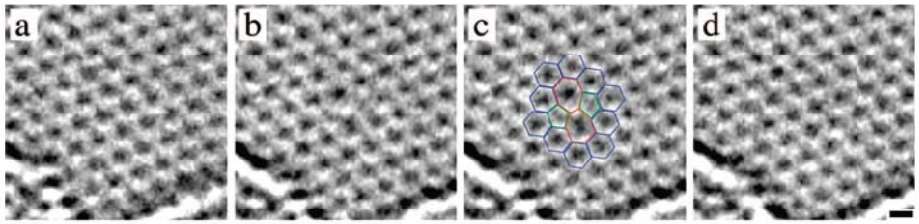


Stone-Wales defect

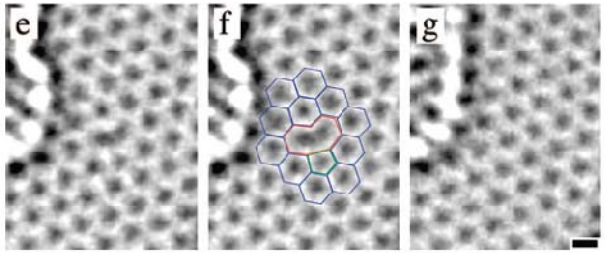
Direct Imaging of Lattice Atoms and Topological Defects in Graphene Membranes

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

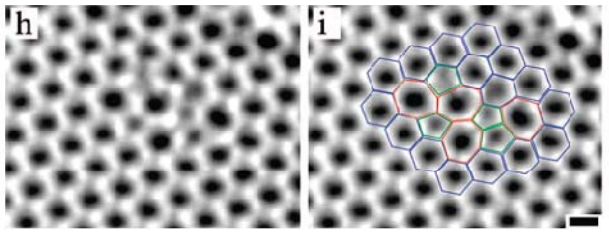
Jannik C. Meyer,† C. Kisielowski,‡ R. Erni,‡ Marta D. Rossell,‡ M. F. Crommie,† and A. Zettl*,†

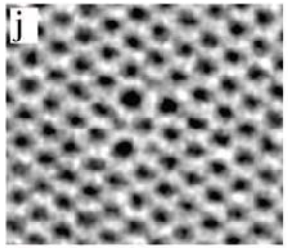


Stone-Wales defect

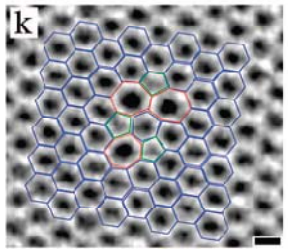


vacancy





heptagons and pentagons



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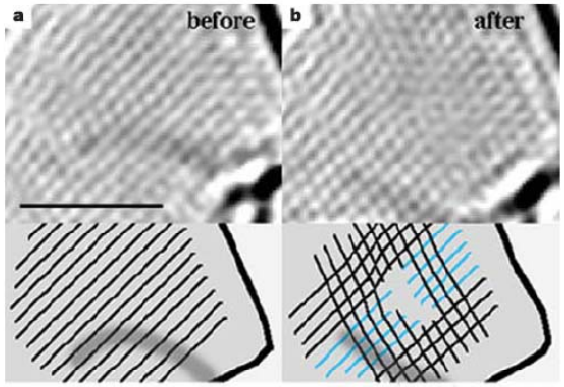
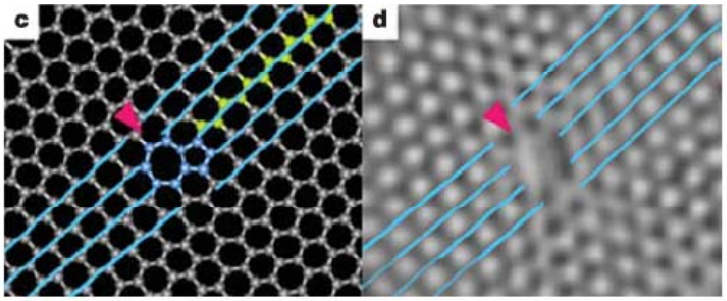
Graphene and defects

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





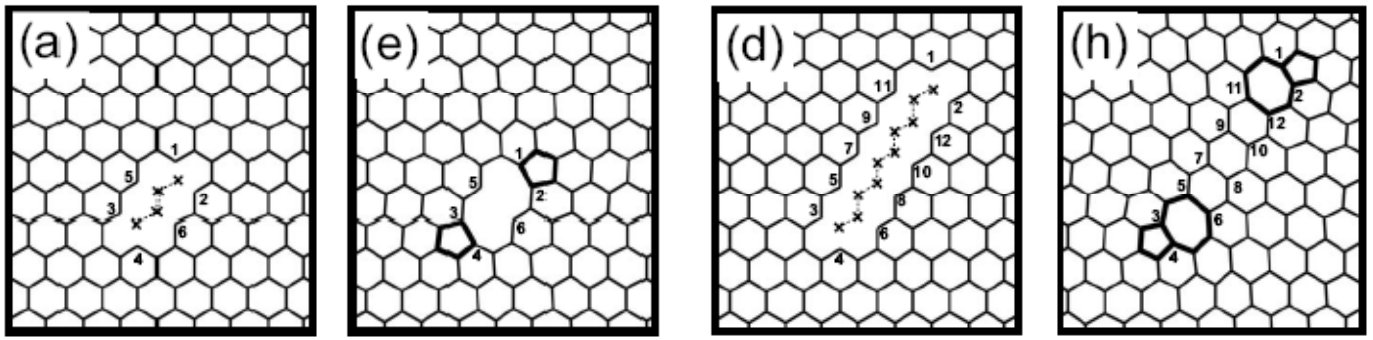
edge dislocation
(missing zig-zag chain)

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]



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Graphene and defects

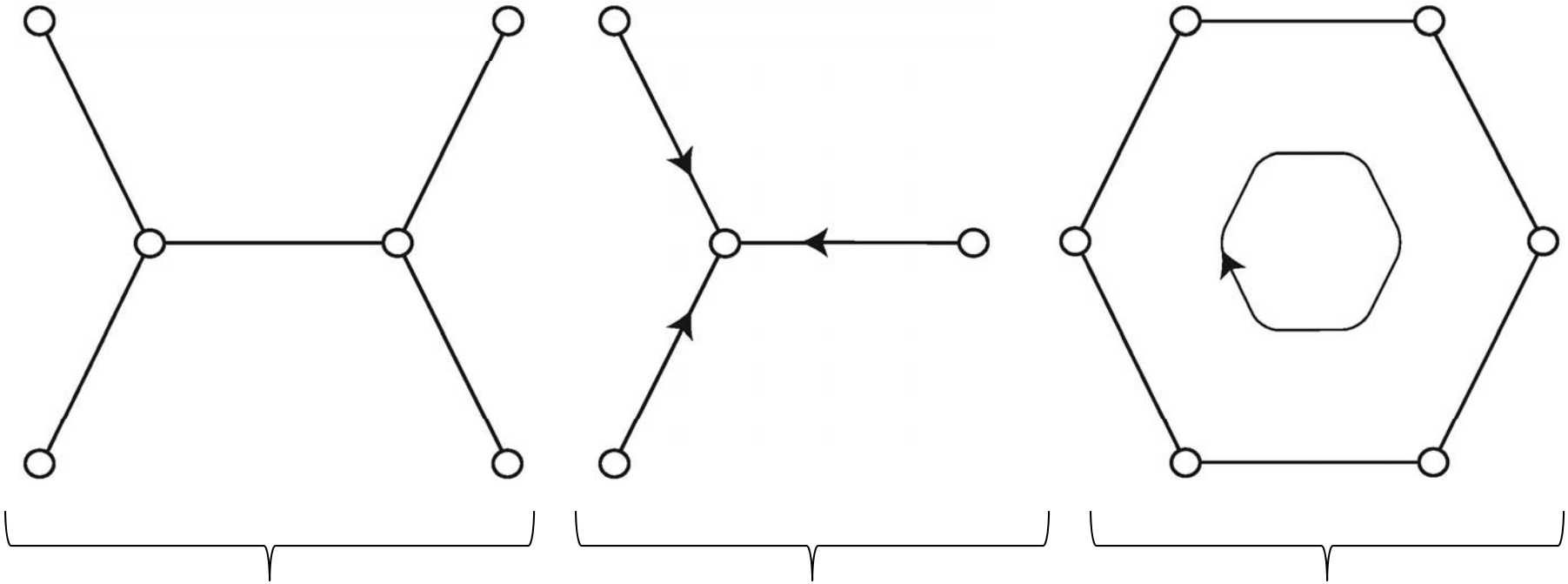
- Main issues of interest:
  - *Properties of individual defects: Core structure, core energies, limiting behaviors (dilute, continuum…)*
  - *Equilibrium properties of defect ensembles: Free energy, critical temperature for spontaneous defect nucleation*
- Majority of studies to date computational:
  - *Ab initio: Restricted to small cells, difficult to extract thermodynamic properties…*
  - *Molecular dynamics: Predictiveness limited by empirical potentials, cell size, time step…*
- Defect densities at critical temperature small, not accessible to direct simulation?
- Mixed continuum-atomistic:
  - *Ertekin E., Chrzan D.C., Daw M.S., Phys. Rev. B,* ***79****(15) 155421, 2009; Phil. Mag. Let.,* ***88****(2) 159-167 2008.*

In this work: Discrete lattice elasticity, discrete defects

Graphene and defects

- Our approach:
  - *Discrete elasticity of graphene lattice*
  - *Discrete dislocations as eigendeformations*
  - *Discrete Fourier transform, closed-form solutions*
  - *Limit of dilute dislocations, continuum limit*
  - *Equilibrium statistical mechanics, mean field*
- Results to date:
  - *Closed-form solutions: Dipoles, quadrupoles…*
  - *Verification & Validation: Core structures, core energies, dynamic stability*
  - *Rigorous mathematical limits: Dilute/continuum, prelogarithmic energy factors*
  - *Equilibrium properties: Critical temperature, scaling (in progress)*

Graphene – Differential cell complex



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

The oriented cells of graphene

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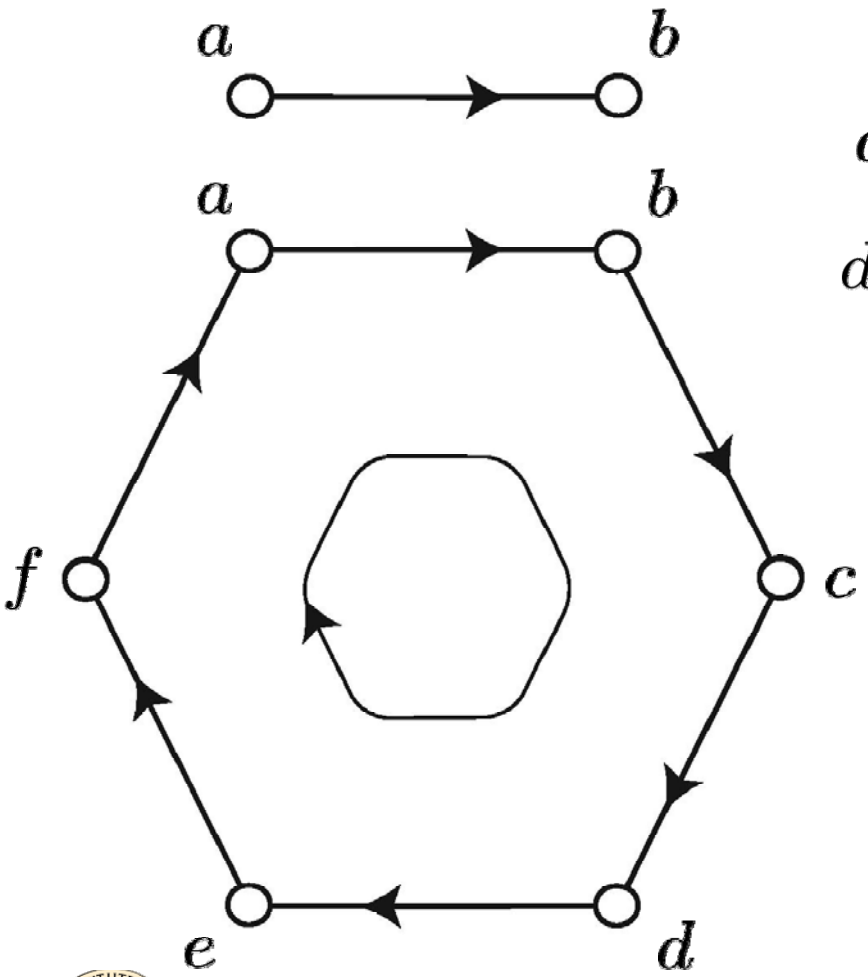
Graphene – Differential cell complex



- Differential operator:

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

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

- Codifferential operator:

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

- Fundamental property:

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

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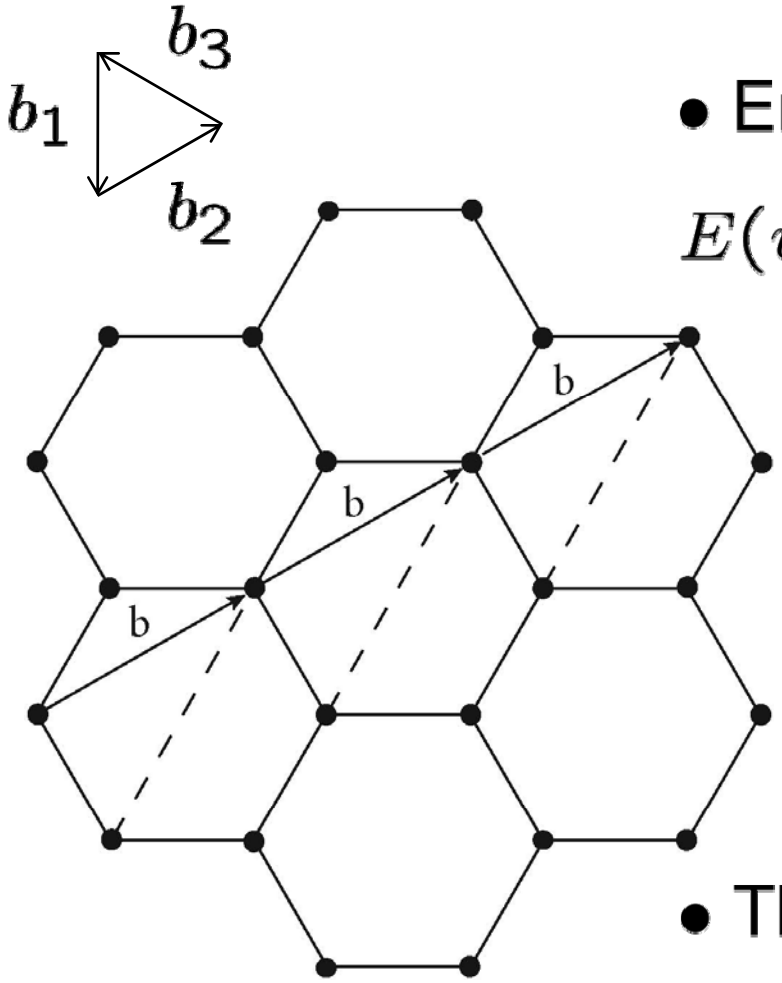
Graphene – Discrete dislocations



lattice-preserving shear deformation

- 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:

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

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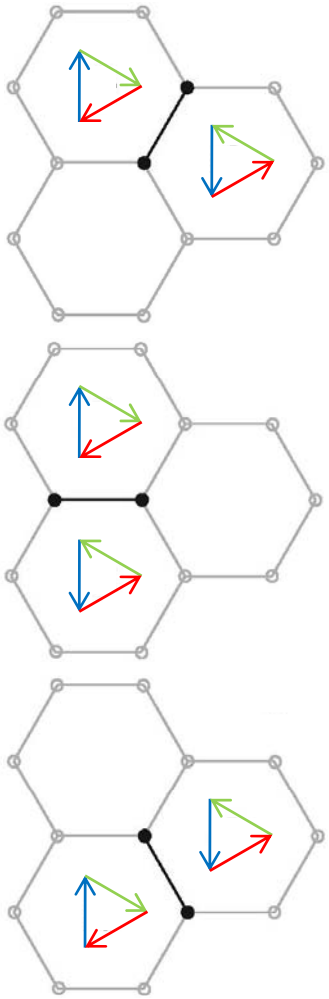
Graphene – Discrete dislocations



basis for graphene dislocations

- Energy of defective graphene:

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

- Displacement equilibrium problem:

$$E(\beta) = \min_u E(u,\beta)$$

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

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

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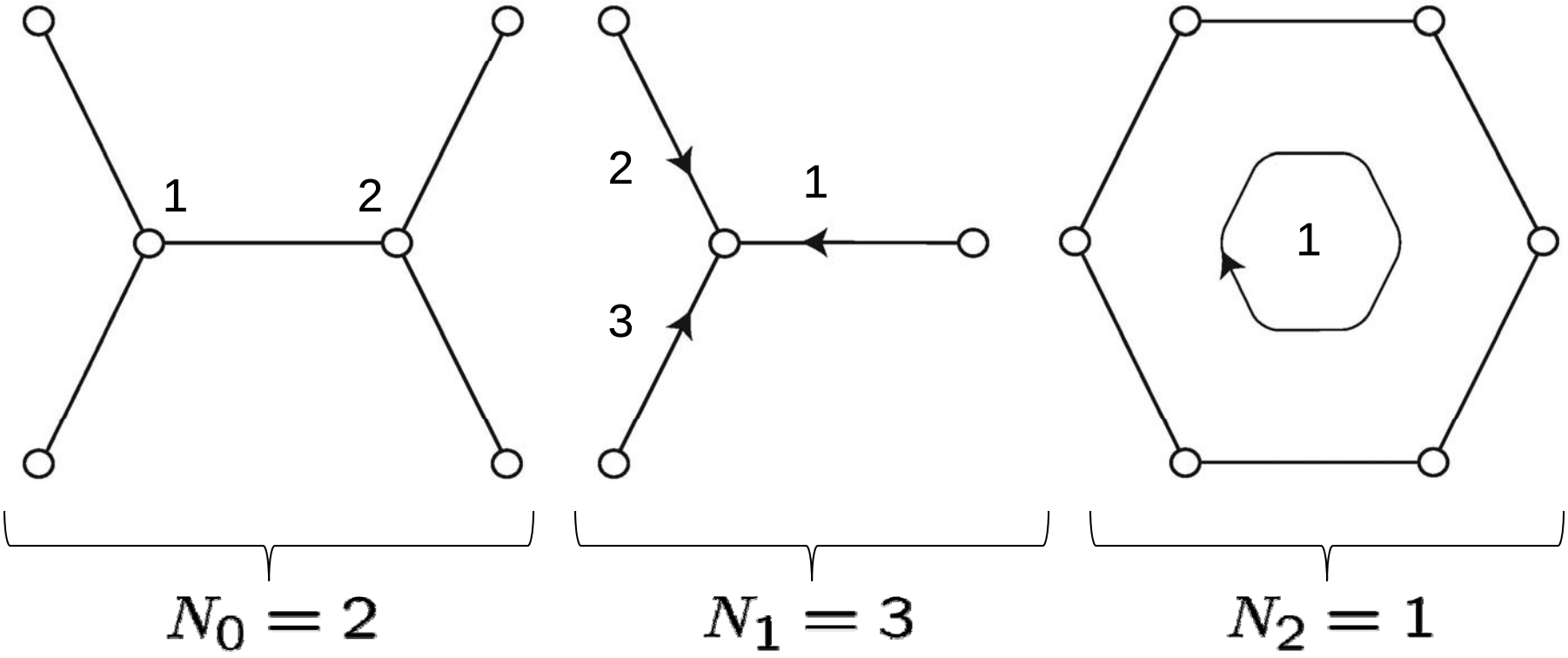
Graphene – Discrete Fourier Transform



Classification of cells by type

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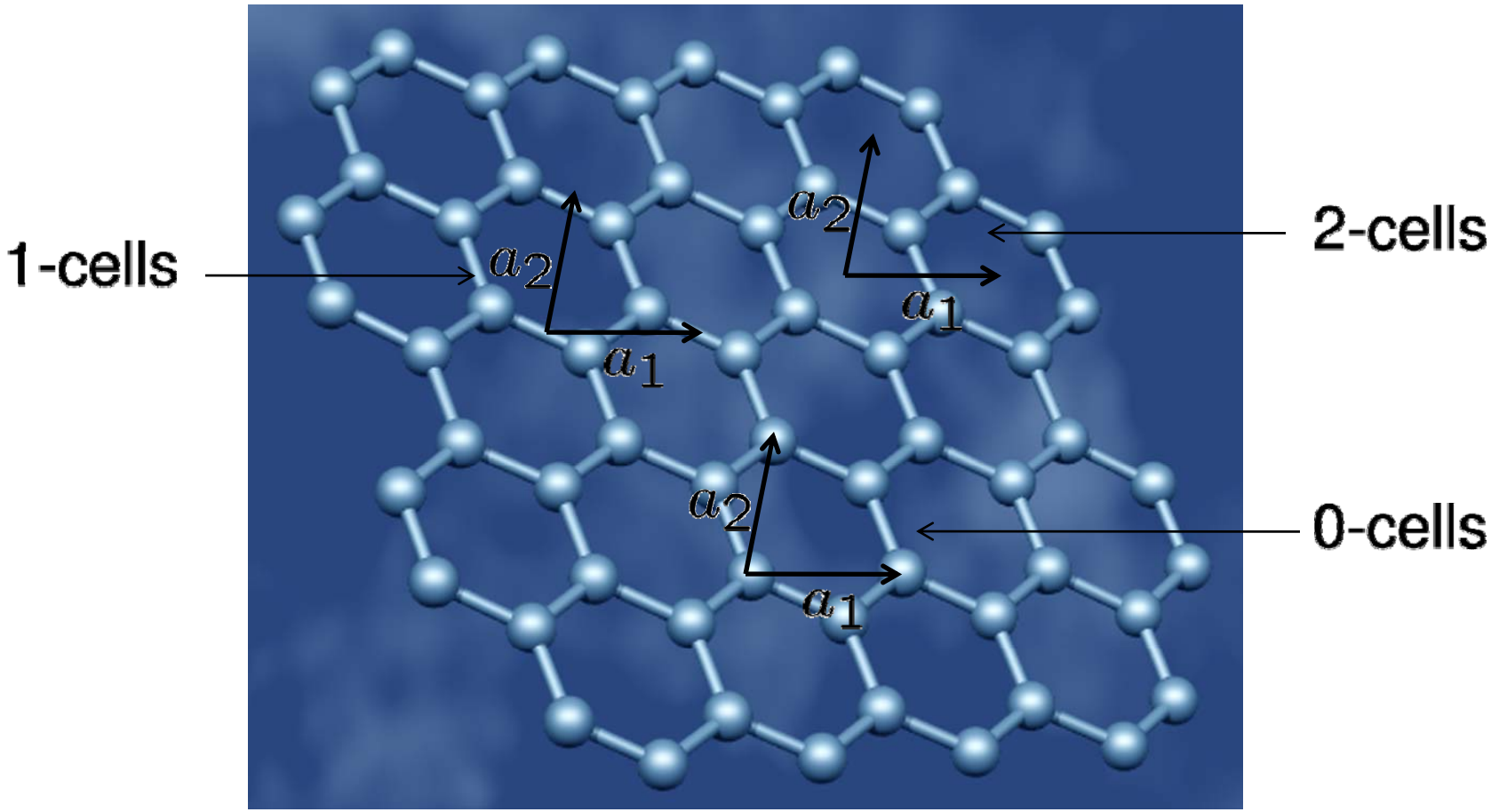
Graphene – Discrete Fourier Transform



cells of same type define
simple Bravais lattices

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Graphene - Discrete Fourier transform

- Discrete Fourier Transform:

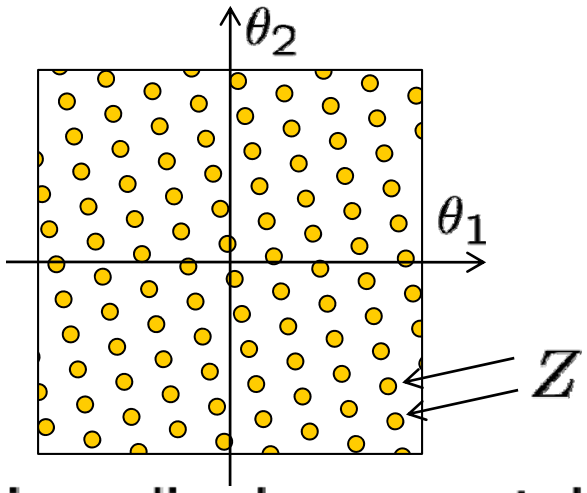
$$\hat{\alpha}(\theta) = \sum_{l \in \mathbb{Z}^2} \alpha(l) \mathrm{e}^{-i\theta \cdot l}, \quad \theta \in [-\pi, \pi]^2$$

- For given discrete dislocation density:

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

- Explicit expressions for $\hat{\Gamma}(\theta)$
- Periodic densities: $E(\alpha) =$

$$\frac{1}{|Z|} \sum_{\Theta \in Z} \frac{1}{2} \langle \hat{\Gamma}(\Theta) \hat{\alpha}(\Theta), \hat{\alpha}^*(\Theta) \rangle$$



- Closed form expressions for energies, displacements!

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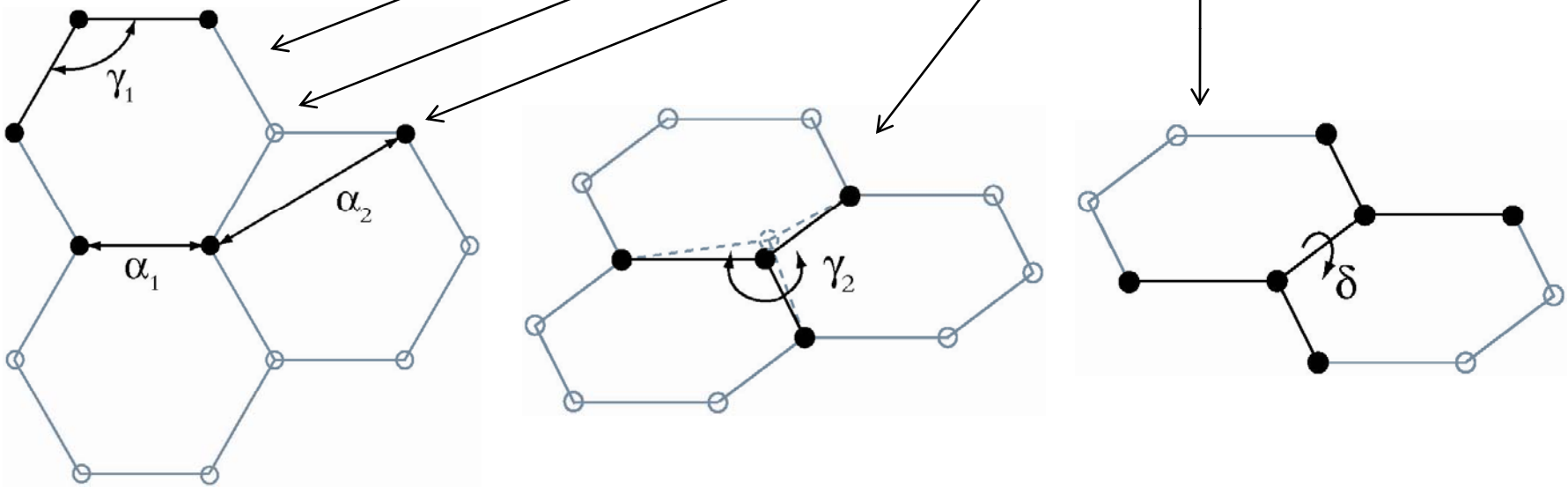
Graphene – Force constants

- ASOIO Potential:

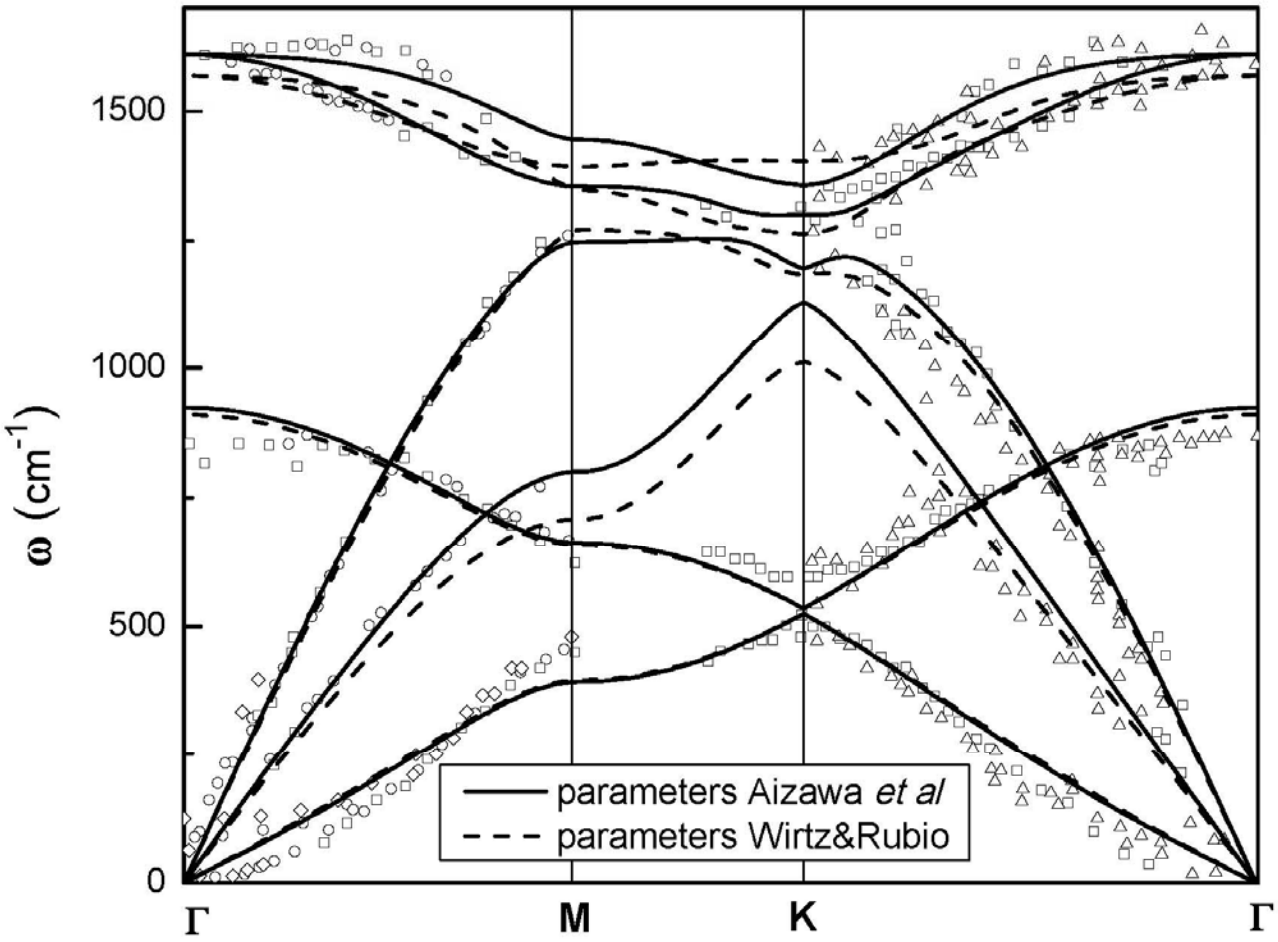
interaction with substrate

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



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))

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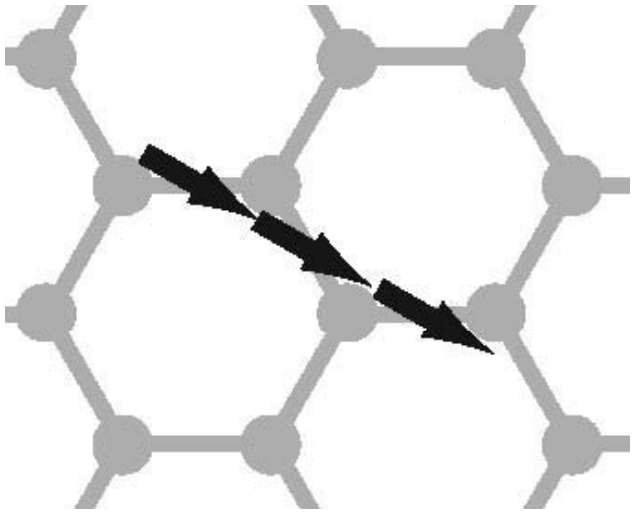
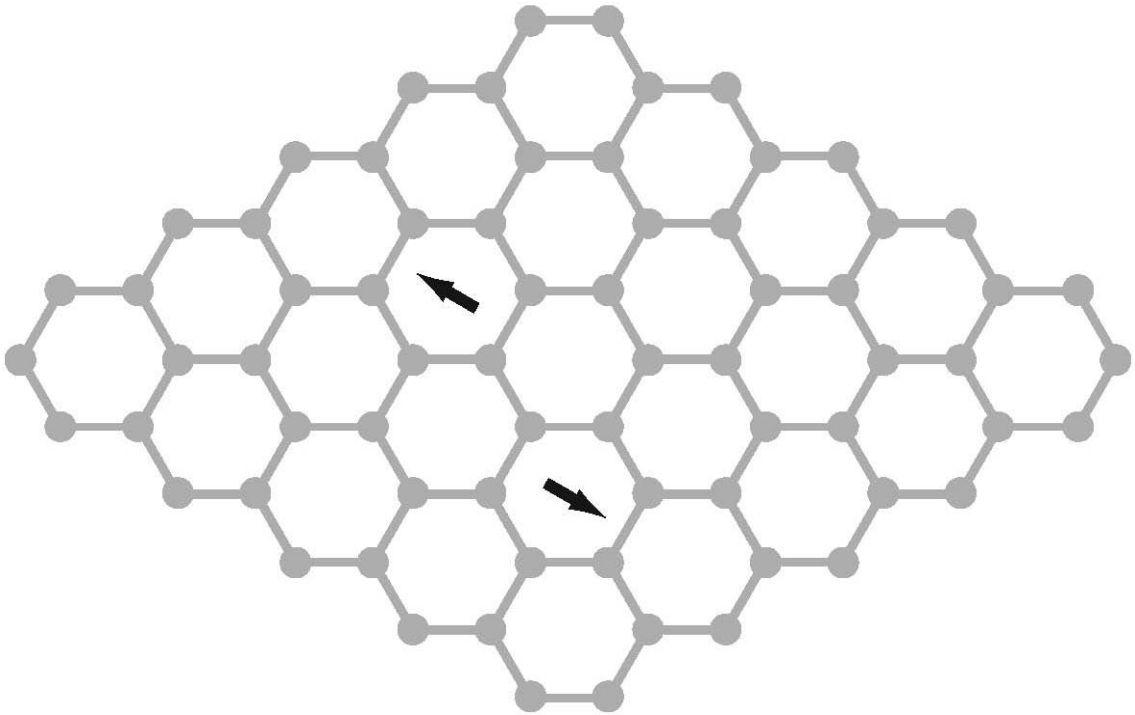
Graphene – Dislocation dipoles



close-up of
eigendeformations



dislocation dipole in unit cell

Periodic arrangement of dislocation dipoles

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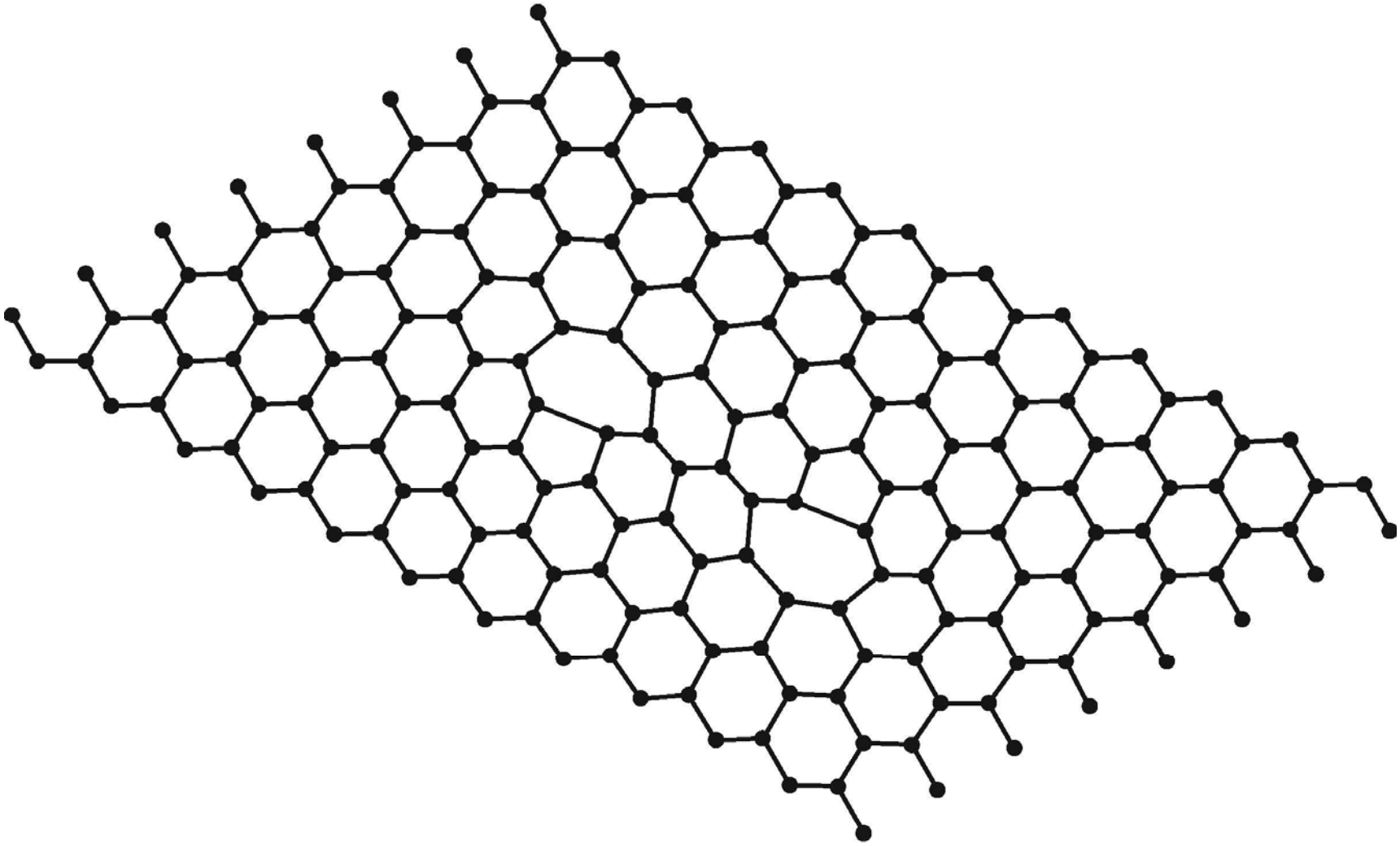
Graphene – Dislocation dipoles



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

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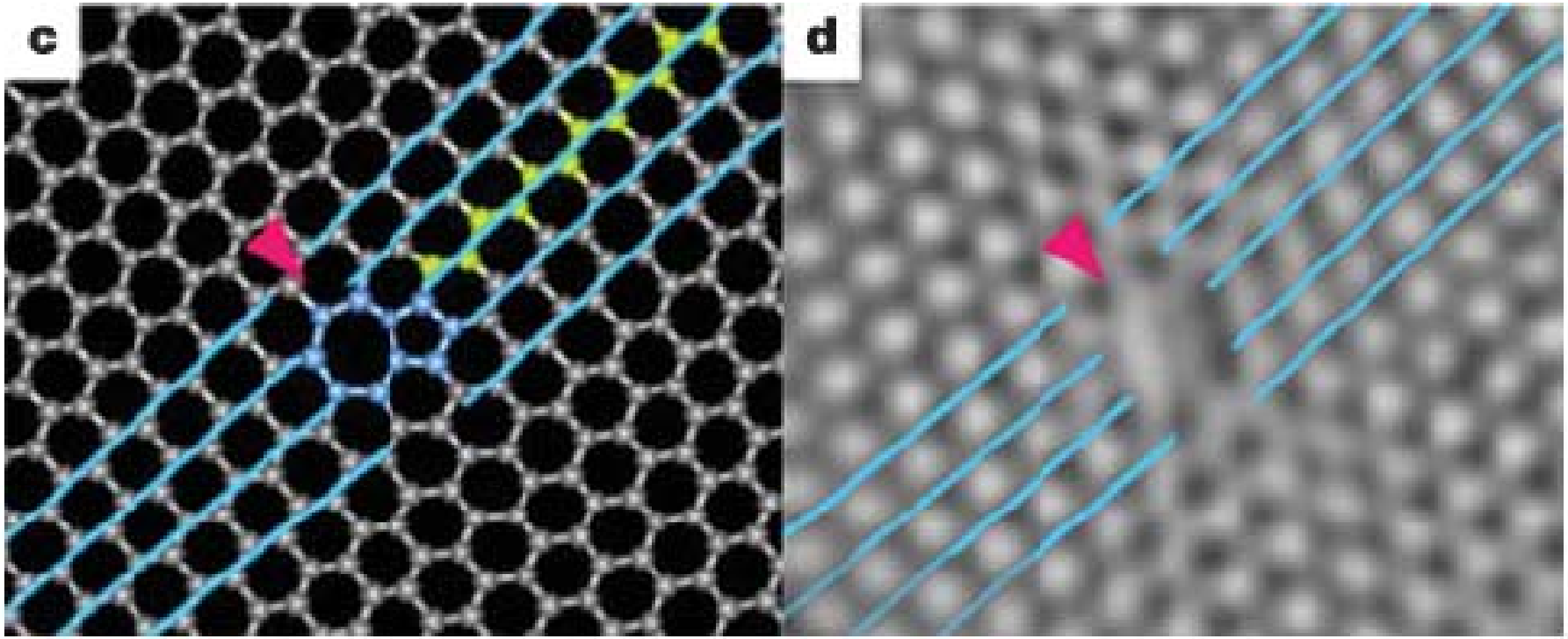
Graphene – Dislocation dipoles



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)

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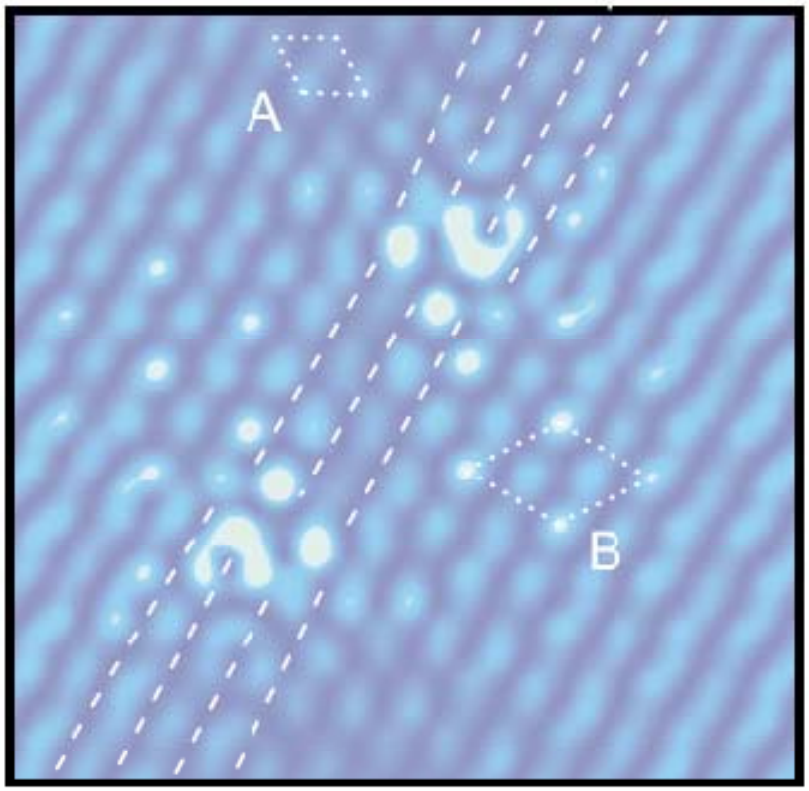
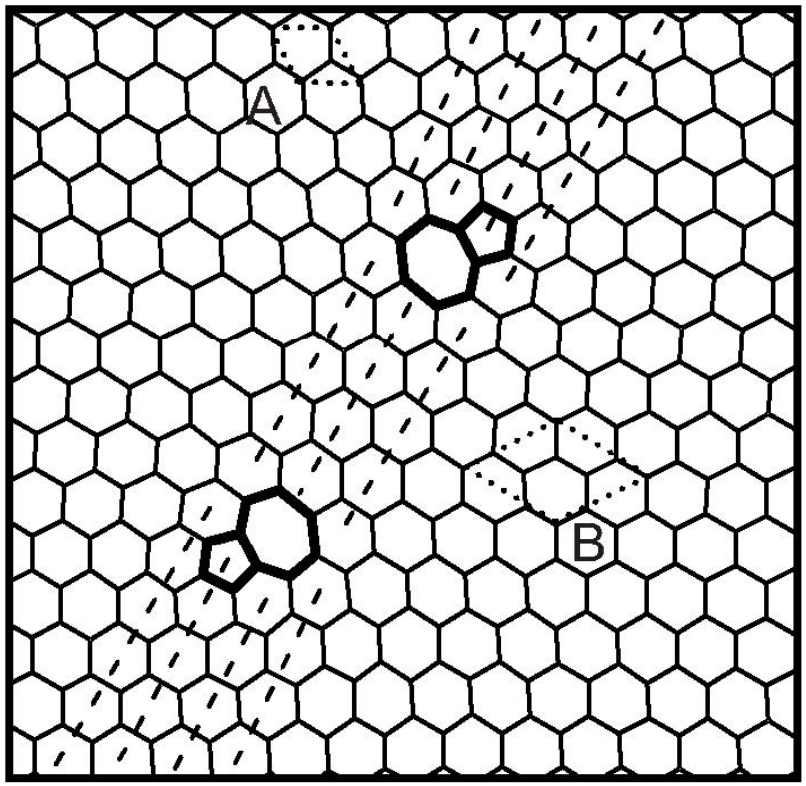
Graphene – Dislocation dipoles



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)

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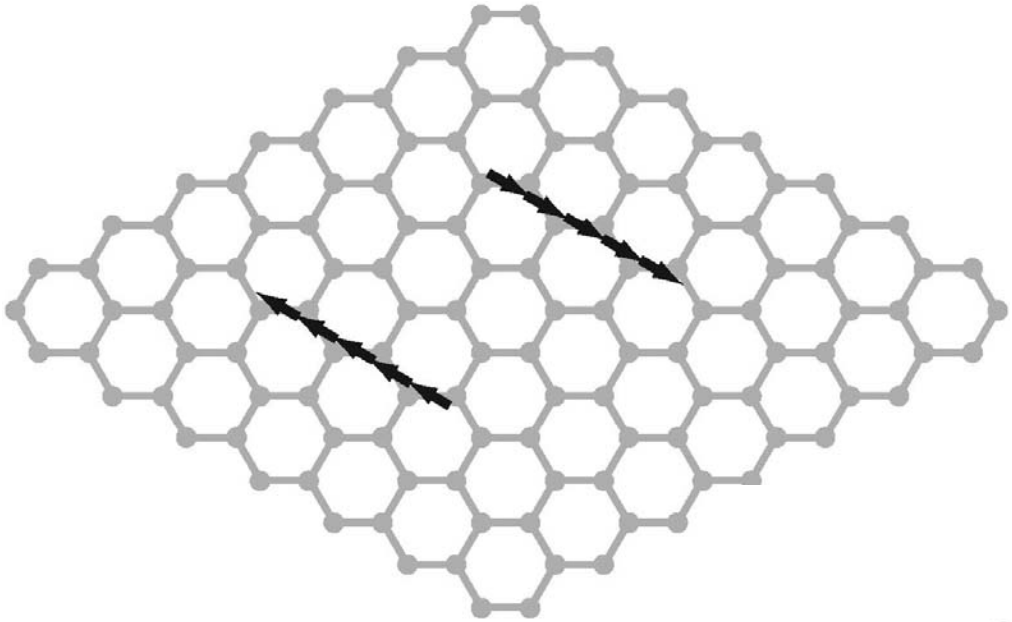
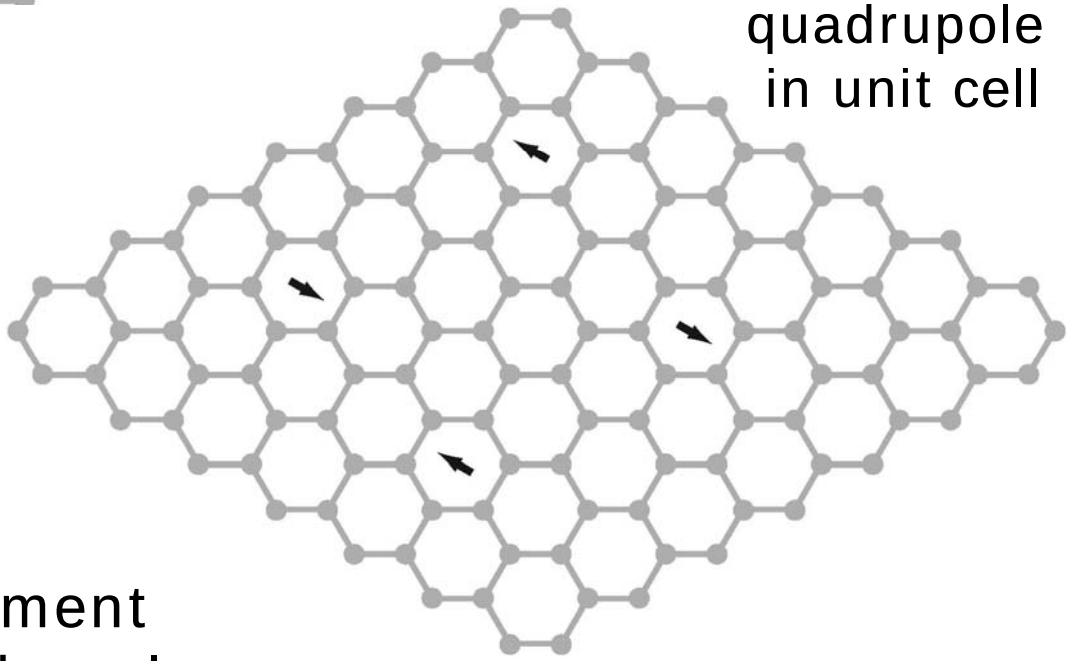
Graphene – Dislocation quadrupoles



eigendeformations
defining a quadrupole

quadrupole
in unit cell



periodic arrangement
of dislocation quadrupoles

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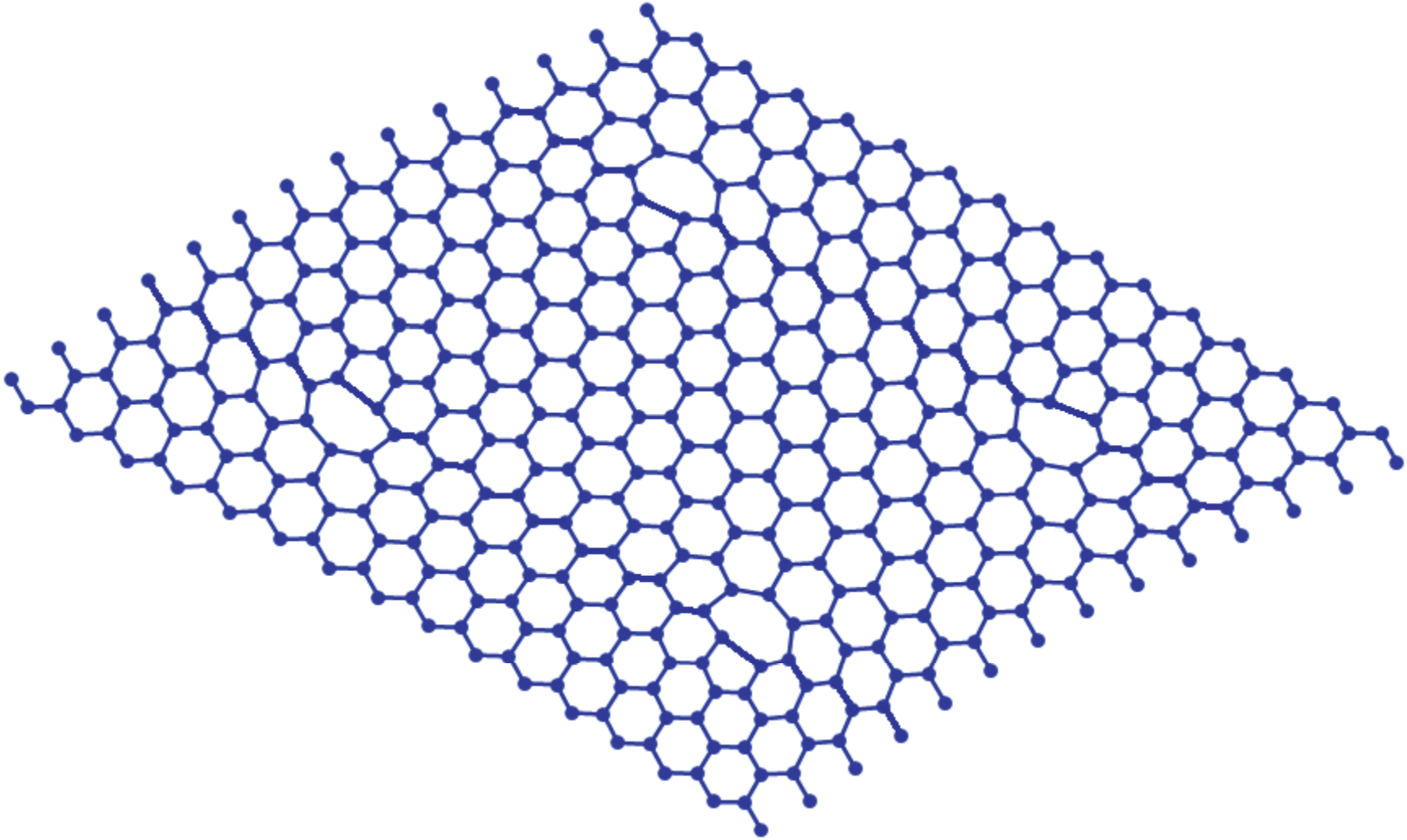
Graphene – Dislocation quadrupoles



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

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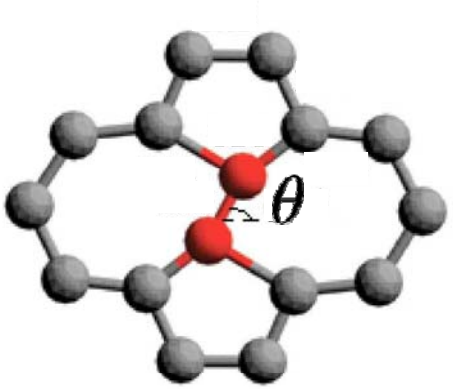
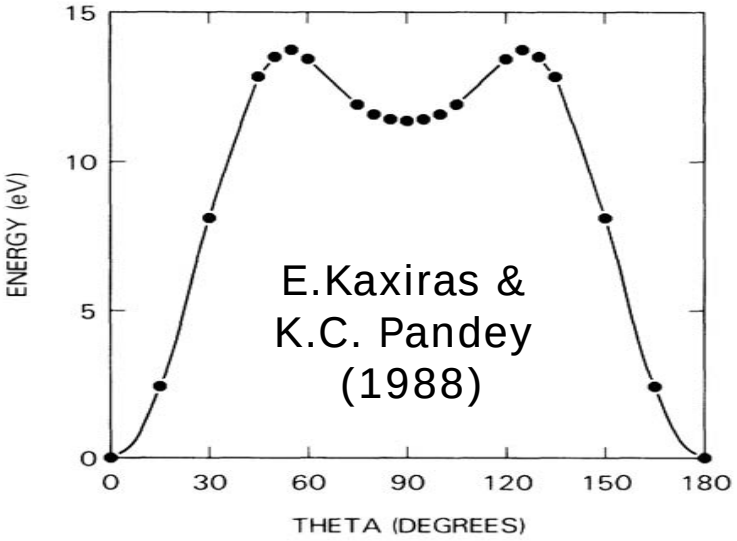
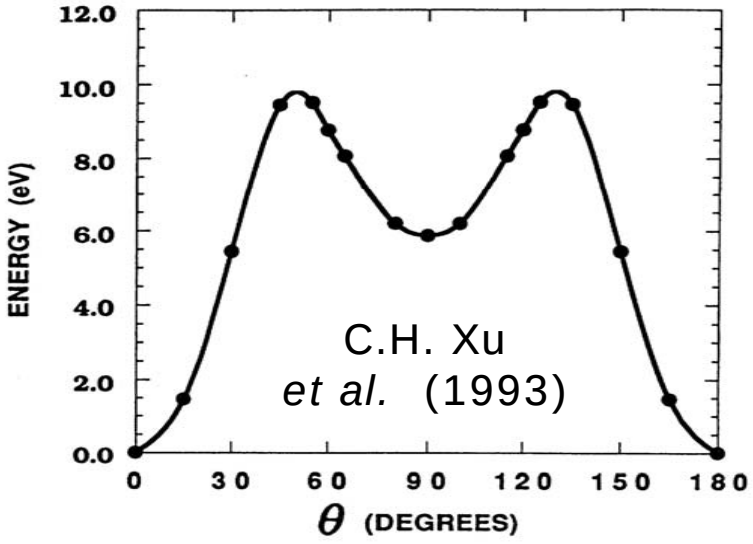
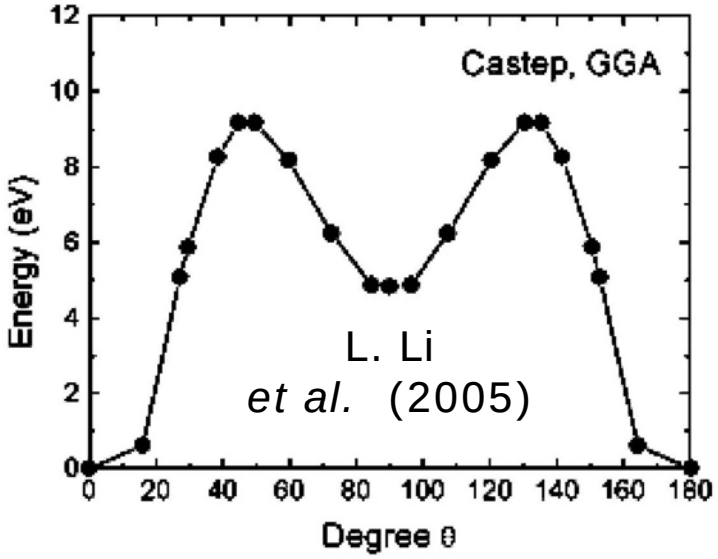
Graphene – Dislocation cores



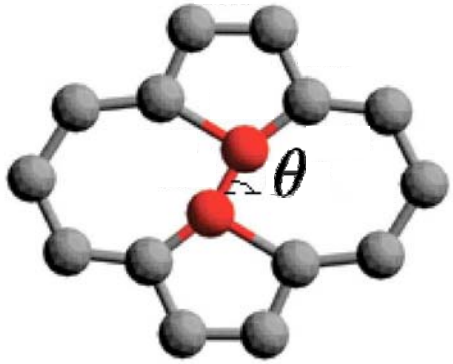
bond rotation angle







Graphene – Dislocation cores

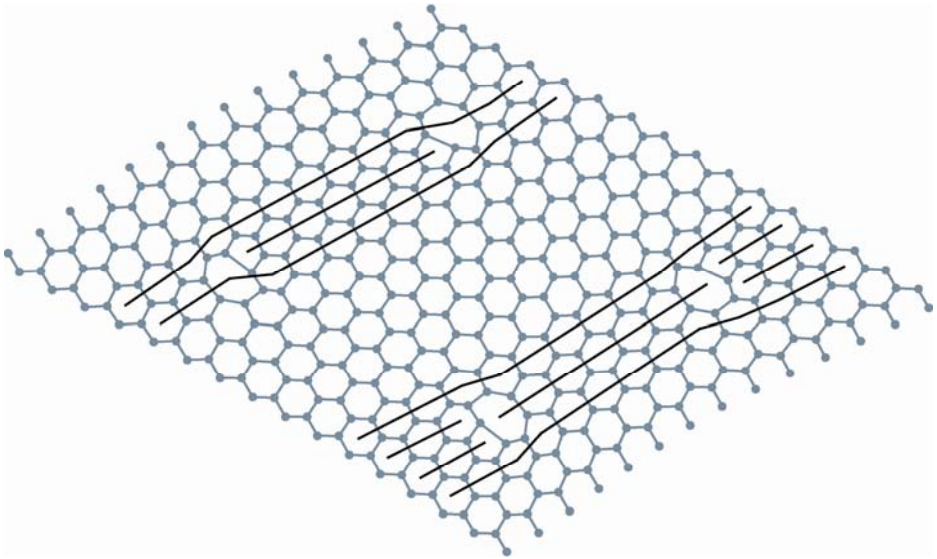


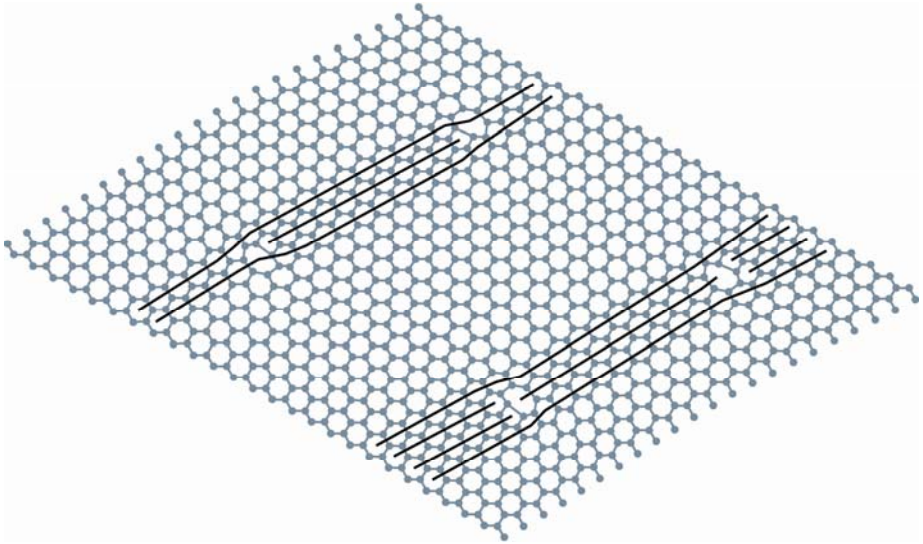
bond rotation angle

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
- Dynamic stability of core structures?

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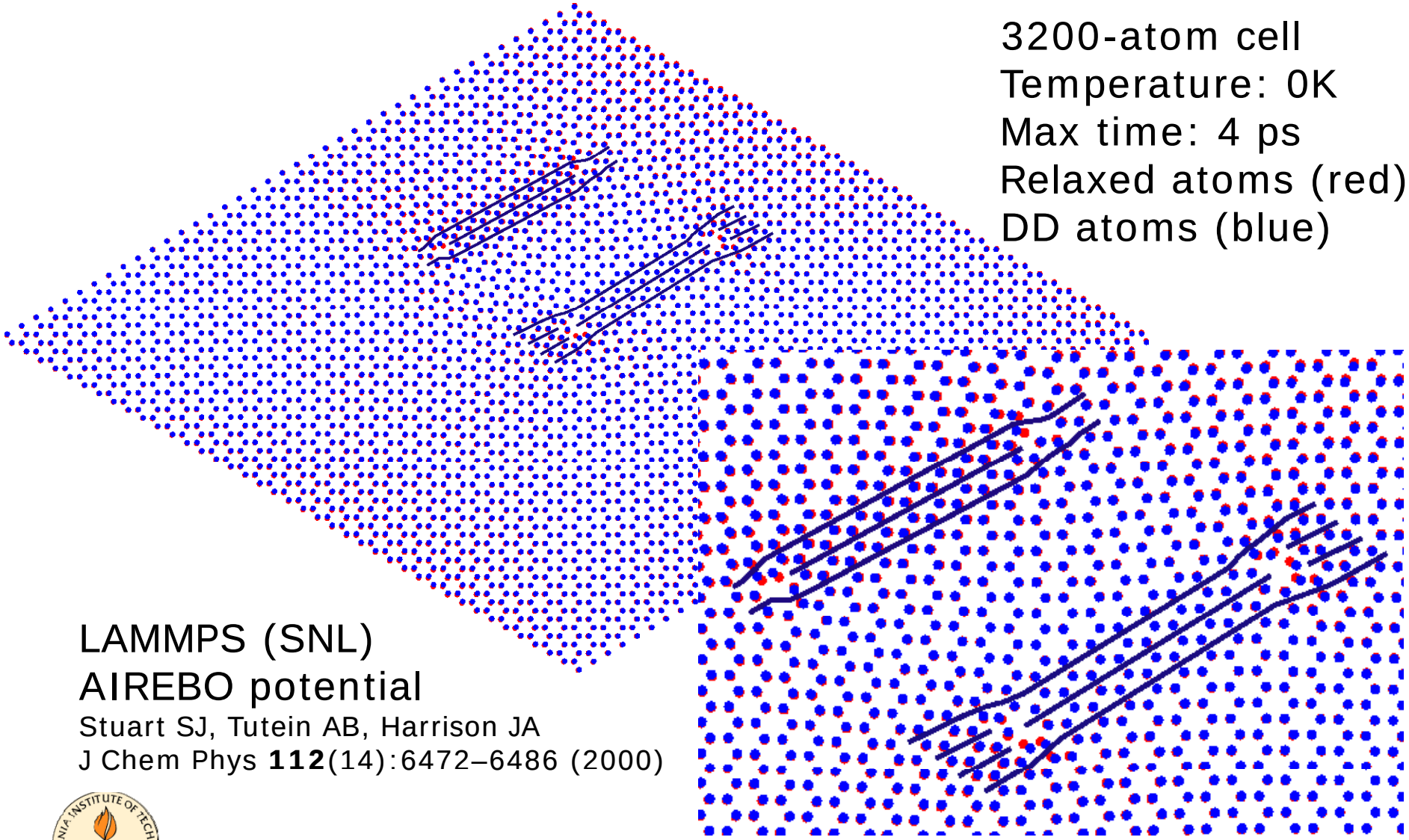
Graphene – Dislocation core stability



3200-atom cell
Temperature: 0K
Max time: 4 ps
Relaxed atoms (red)
DD atoms (blue)

LAMMPS (SNL)
AIREBO potential
Stuart SJ, Tutein AB, Harrison JA
J Chem Phys **112**(14):6472–6486 (2000)

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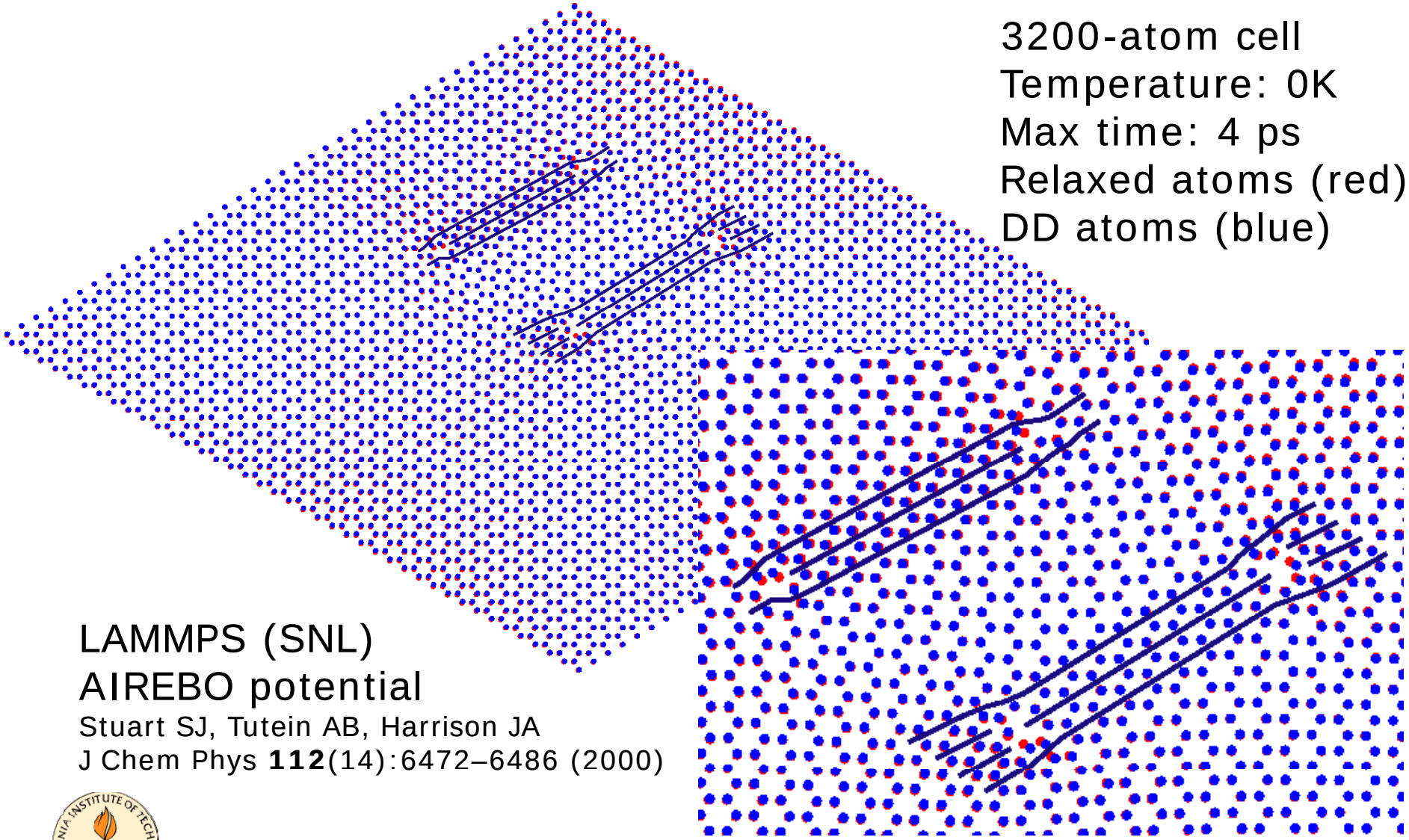
Graphene – Dislocation core stability



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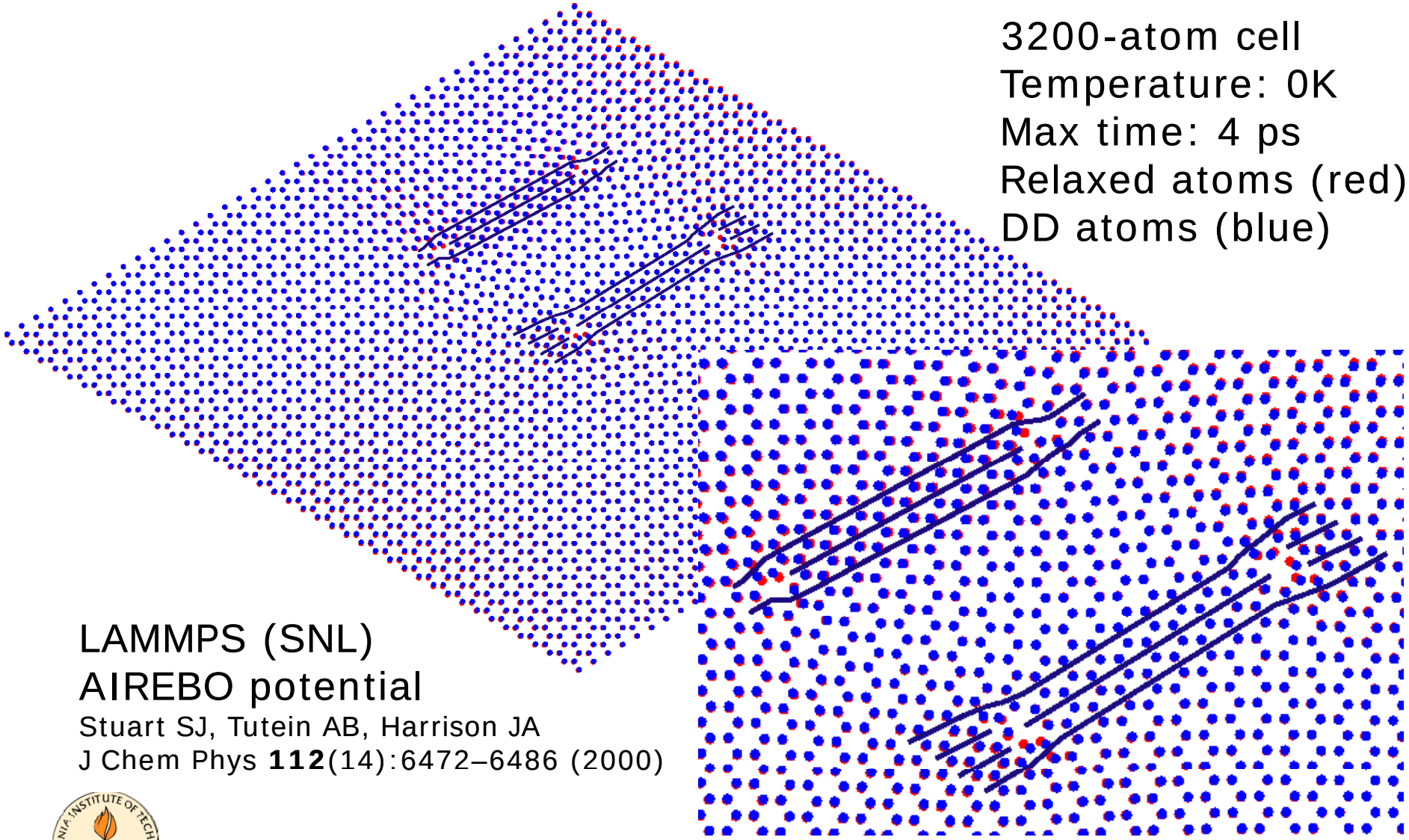
Graphene – Dislocation core stability



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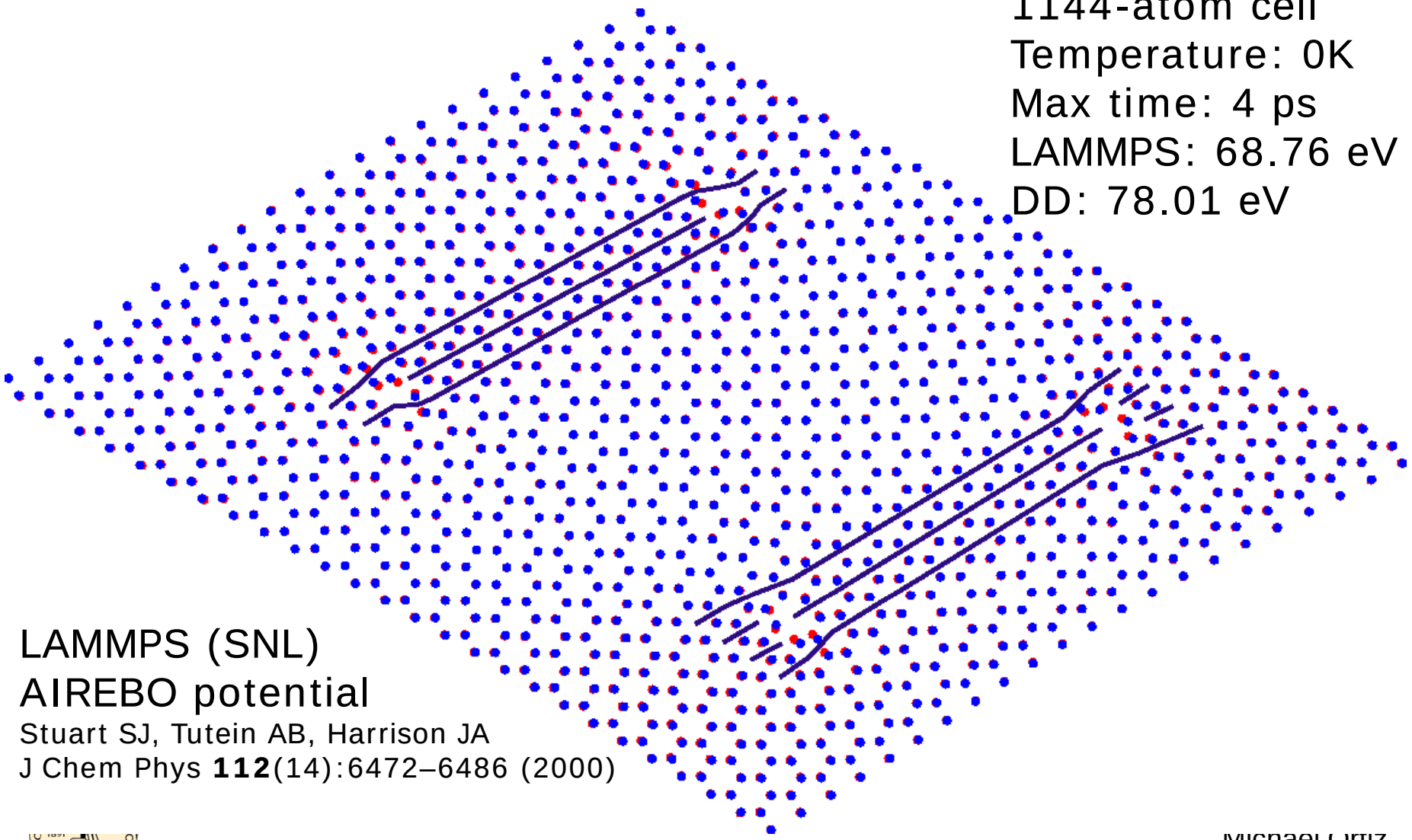
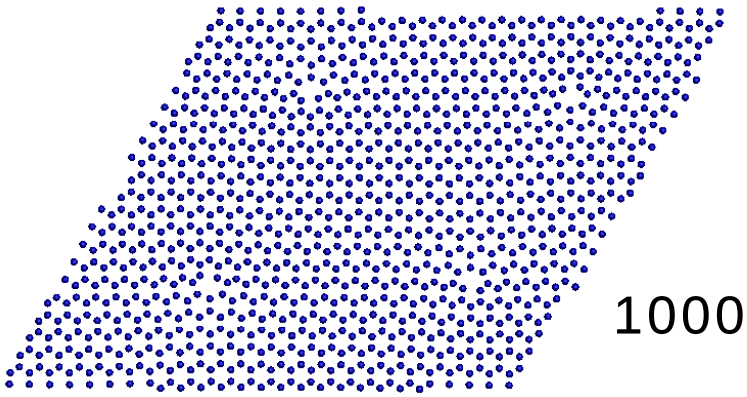


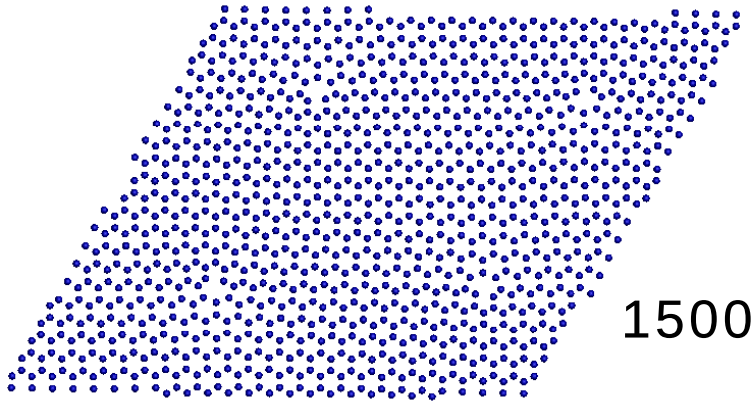
1144-atom cell
Temperature: 0K
Max time: 4 ps
LAMMPS: 68.76 eV
DD: 78.01 eV

LAMMPS (SNL)
AIREBO potential
Stuart SJ, Tutein AB, Harrison JA
J Chem Phys **112**(14):6472–6486 (2000)

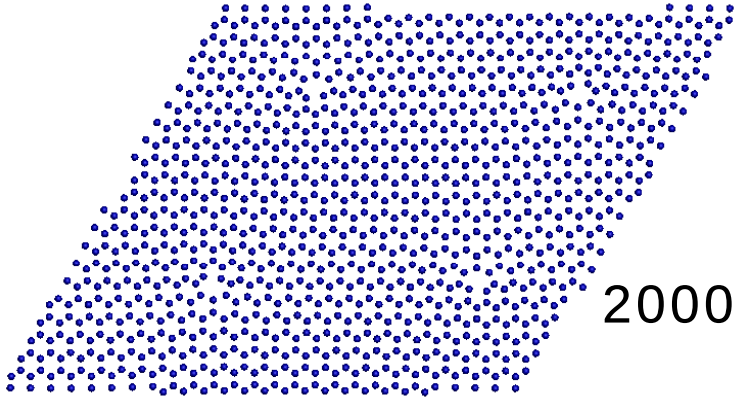
Graphene – Dislocation core stability



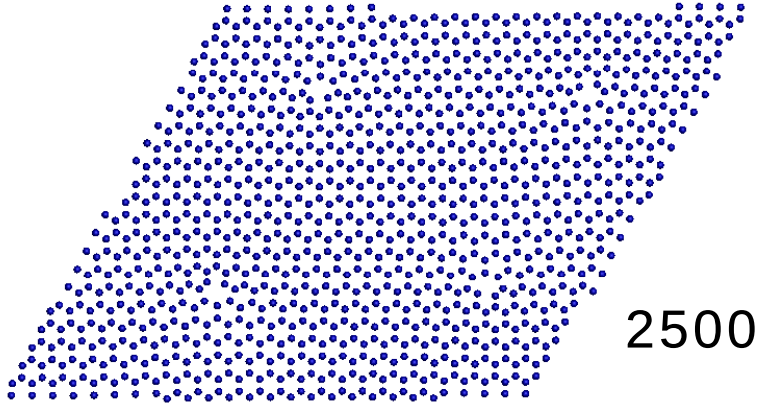
1000 K



1500 K



2000 K



2500 K

LAMMPS (SNL) AIREBO potential, 1144-atom cell

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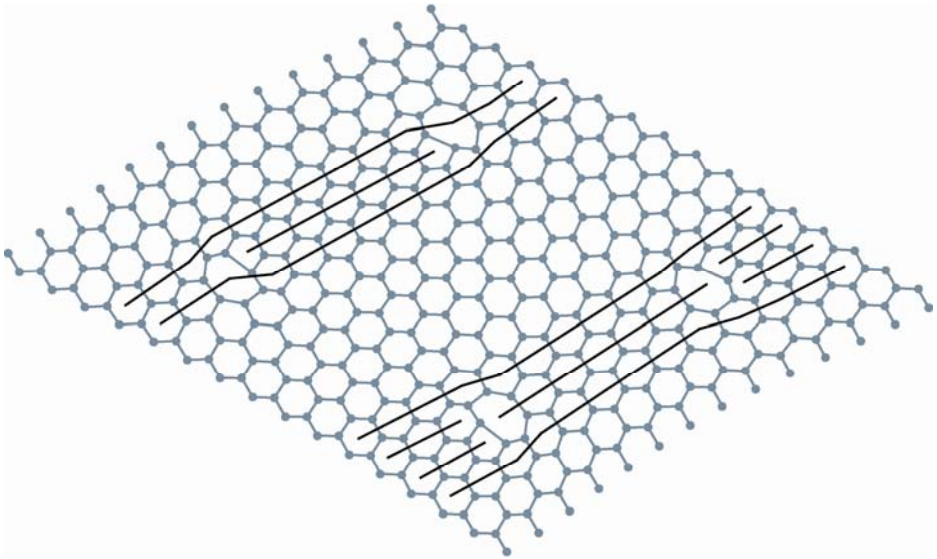
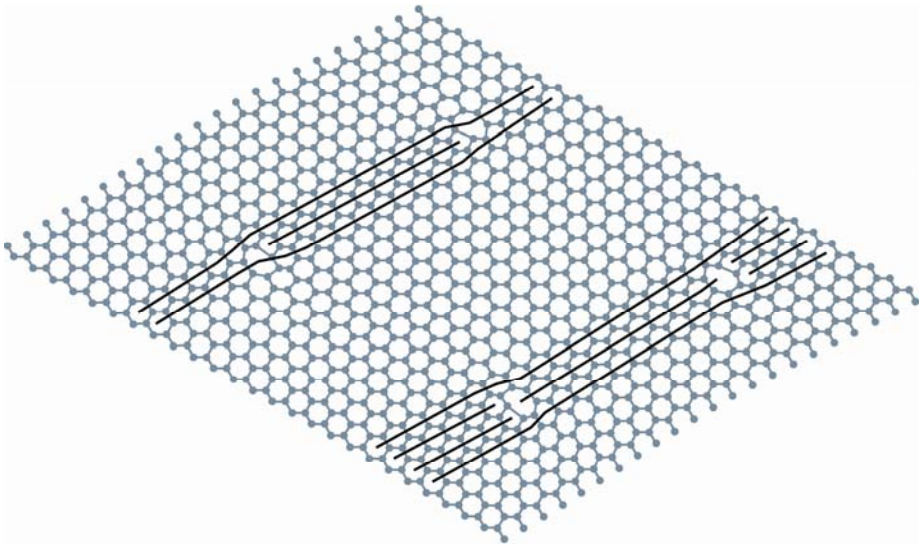
Graphene – Dislocation cores





- Dislocation cores predicted by the discrete-dislocation are stable with respect to fully non-linear AIREBO potential
- Dislocation cores appear stable up to high temperatures (2500 K)
- Spontaneous nucleation, critical behavior?

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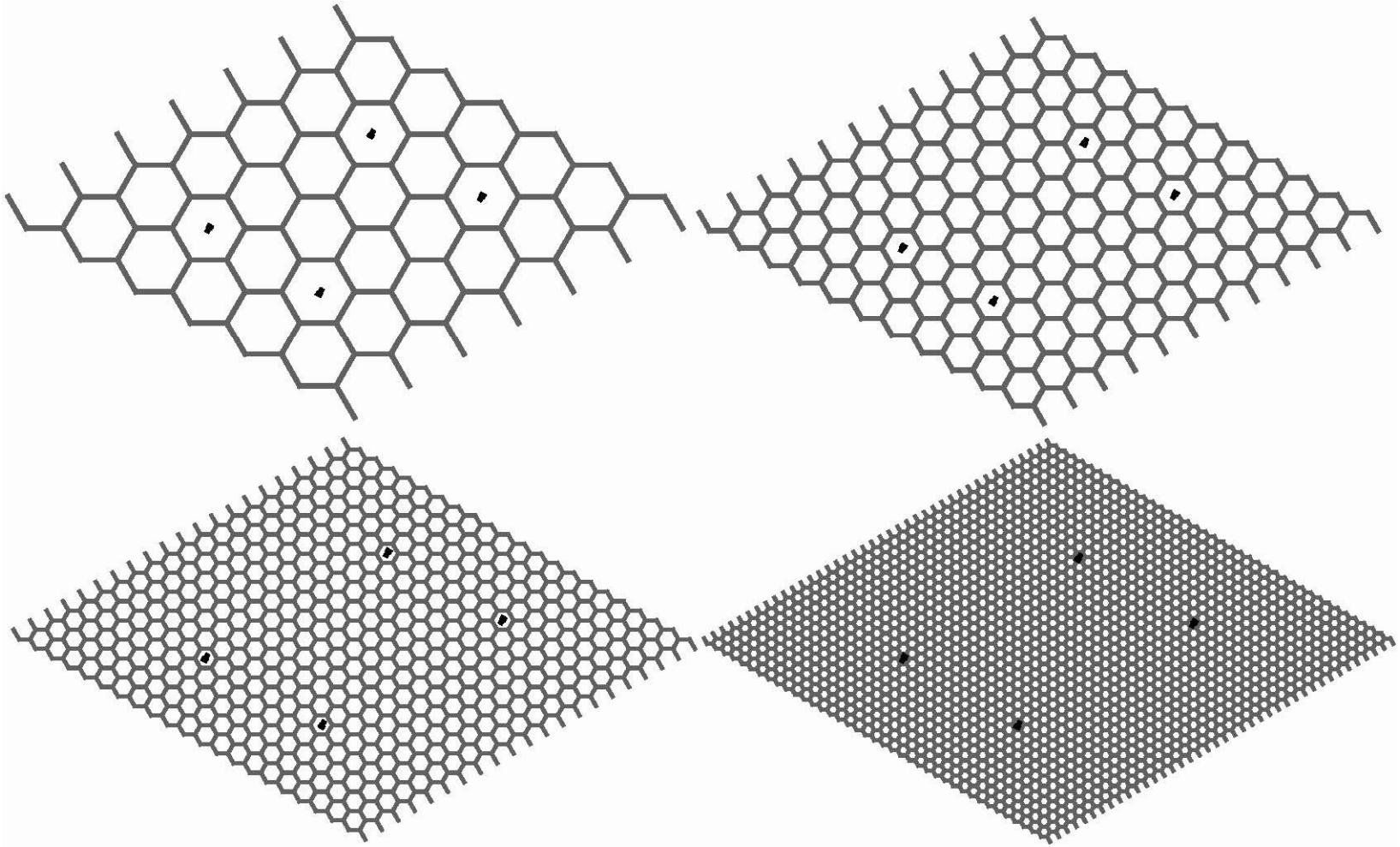
Graphene – Dilute/continuum limits



Limit of dilute dislocation densities
(equivalently, continuum limit)

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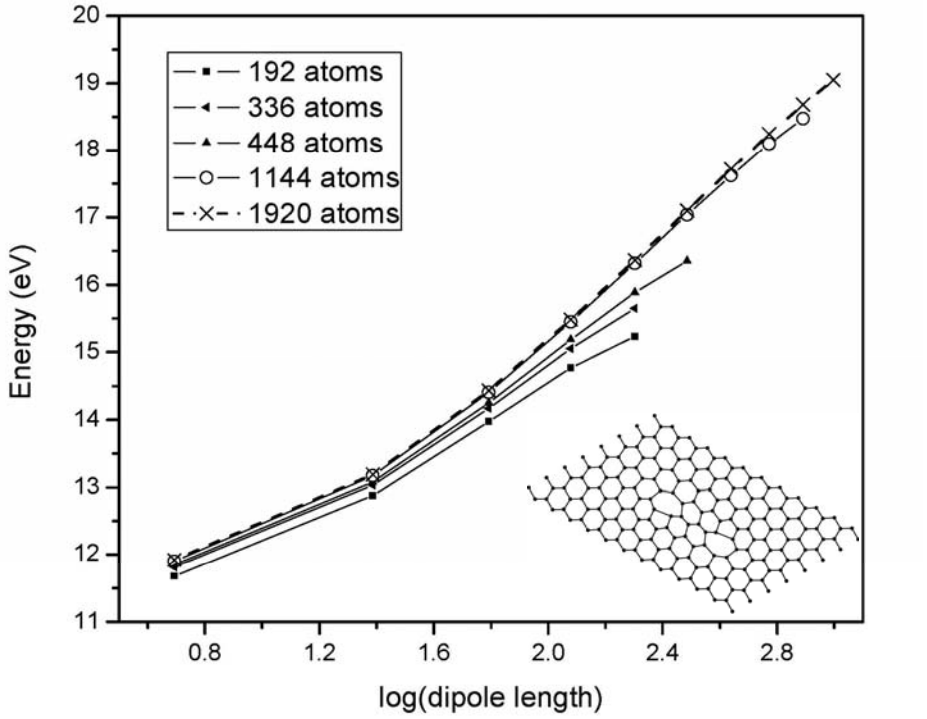
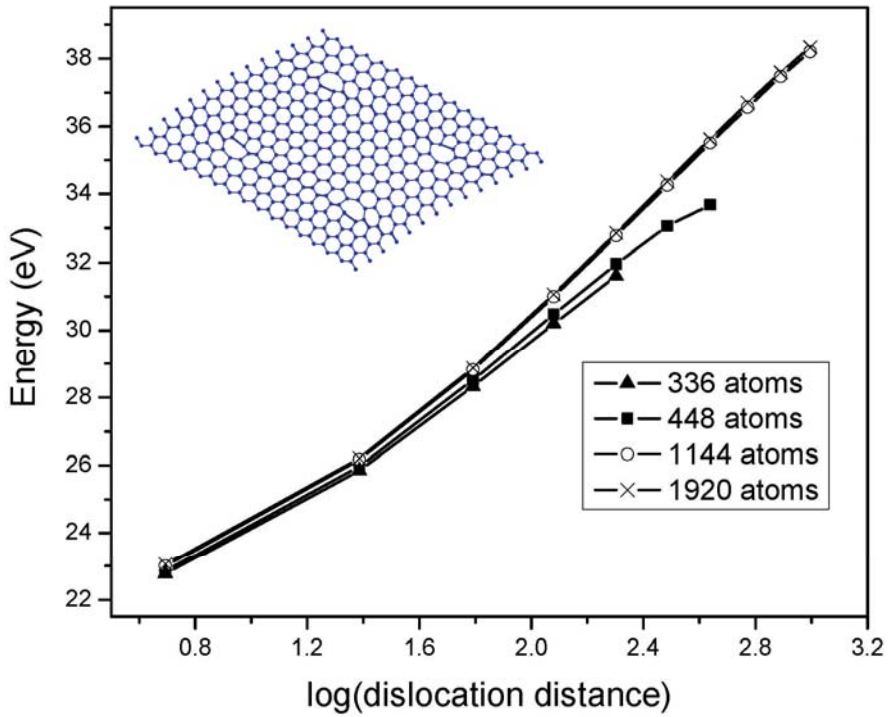
Graphene – Dilute/continuum limits





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

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

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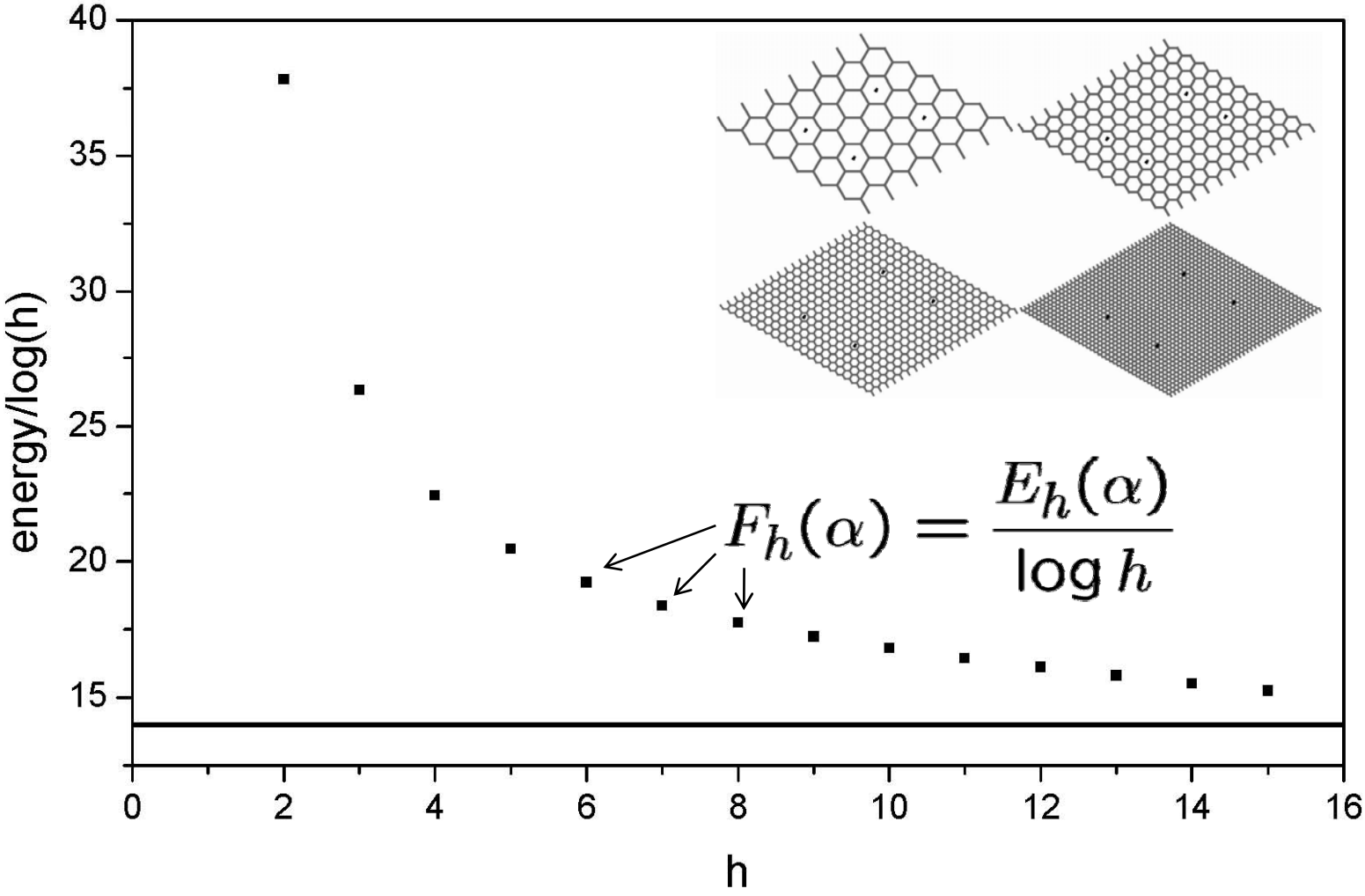
Graphene – Dilute/continuum limits



Energy sequence is decreasing!

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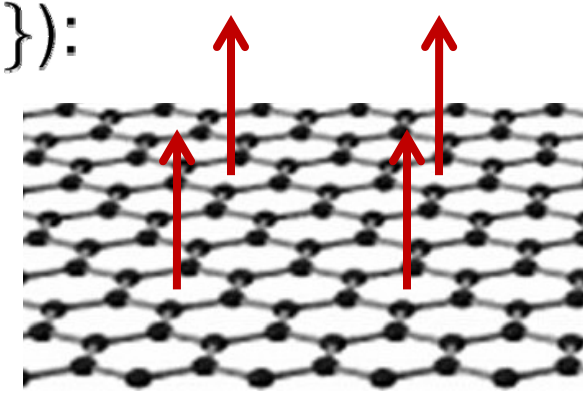
Graphene – Dilute/continuum limits

- Limiting energy ($s(l) \in \{-1, 0, 1\}$):

$$E_0 = \frac{1}{2} K b^2 \log \frac{R}{b} \sum_{l \in \mathbb{Z}^2} |s(l)|$$

(line-tension approximation)



- Non-interaction three-state Potts, triangular lattice!
- Application to mean-field analysis (in progress):

$$\text{Free energy} \equiv F \sim \min_K \left(F_0 + \langle E - E_0 \rangle_0 \right)$$

where $\langle \cdot \rangle_0 \equiv$ average in E_0-ensemble.

- Spontaneous dislocation nucleation near melting

Dislocations in graphene

Thank you!