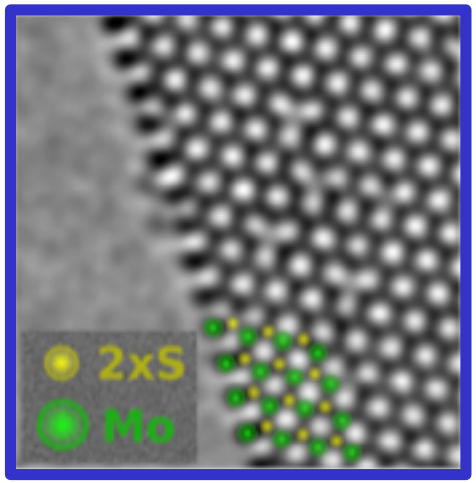
Defects in Crystalline Solids: the Basics



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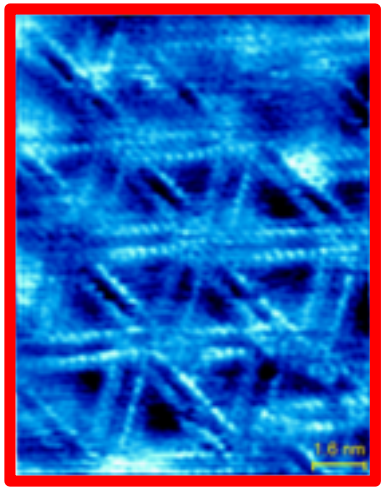
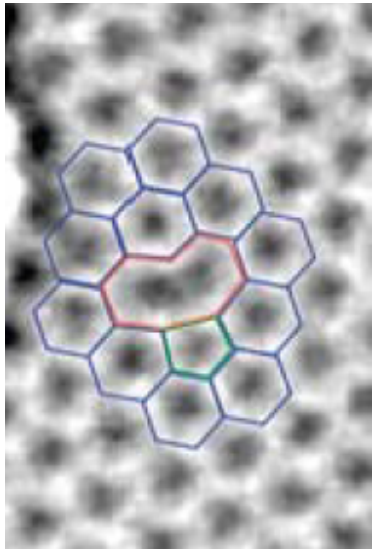
National University of Science and Technology "MISIS", Russian Federation

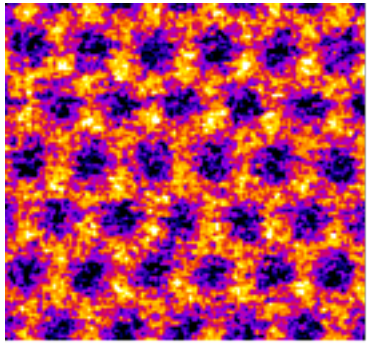


Outline of the tutorial lecture

1. Introduction: Why do we care about defects in crystalline solids?
2. What we already know: defects in bulk systems, their classification and origin.
3. Basic formula for defect concentration at thermodynamic equilibrium;
4. Overview of experimental techniques for defect identification
5. Overview of frequently used atomistic approaches to get insights into defect behavior
6. Defects in two-dimensional materials: Why interesting?



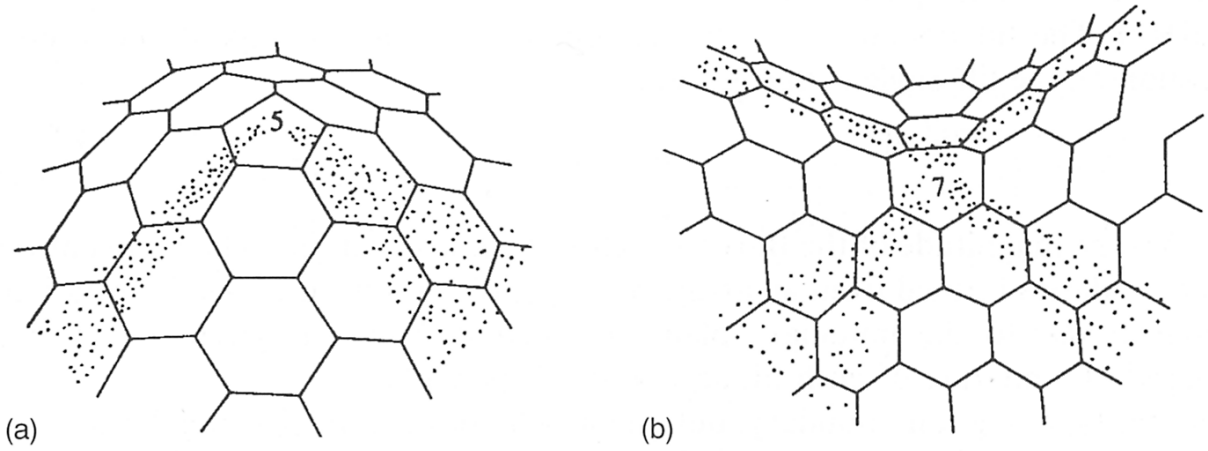
Courtesy of J. Meyer



Courtesy of K. Suenaga

Some basics of defects in solids:

Repetitio est mater studiorum

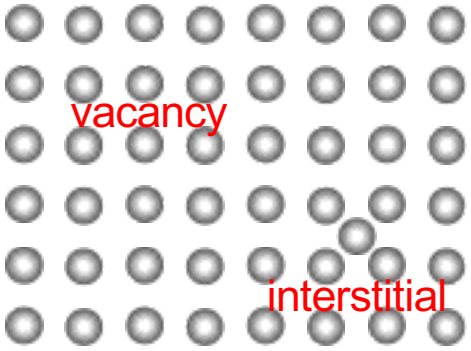


Defects in crystalline solids

What are defects?

In general, structural imperfection in a crystal, deviation from the perfect order (periodicity)

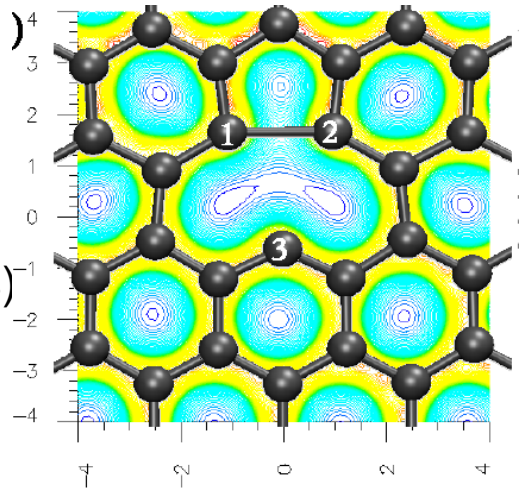
Note that defects can also be defined in amorphous systems and quasicrystals — beyond the scope of the lecture



Why do we care about defect?

They frequently govern materials properties:

- Mechanical (e.g. dislocations in metals)
- Electronic (e.g. dopant atoms in semiconductors)
- Optical (e.g., color centers in wide-gap semiconductors)
- Magnetic (impurity atoms; coordination defect)
- Also responsible for diffusion of atoms in the solid, etc.



Ashcroft-Mermin: "Like human defects, those of crystals come in a seemingly endless variety, many dreary and depressing, and a few fascinating."

Defect (more thorough) definition

A structural defect is a configuration in which an atom (or group of atoms) does not satisfy the structure rules pertaining to the ideal reference system or material.

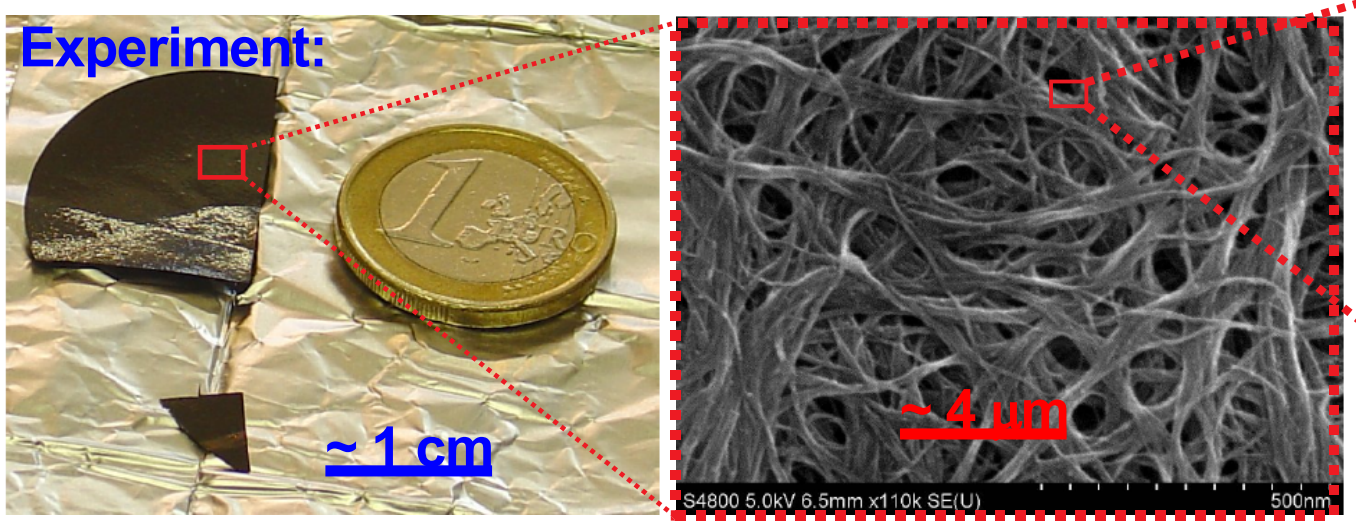
Are defects in solids really the "bad" guys?

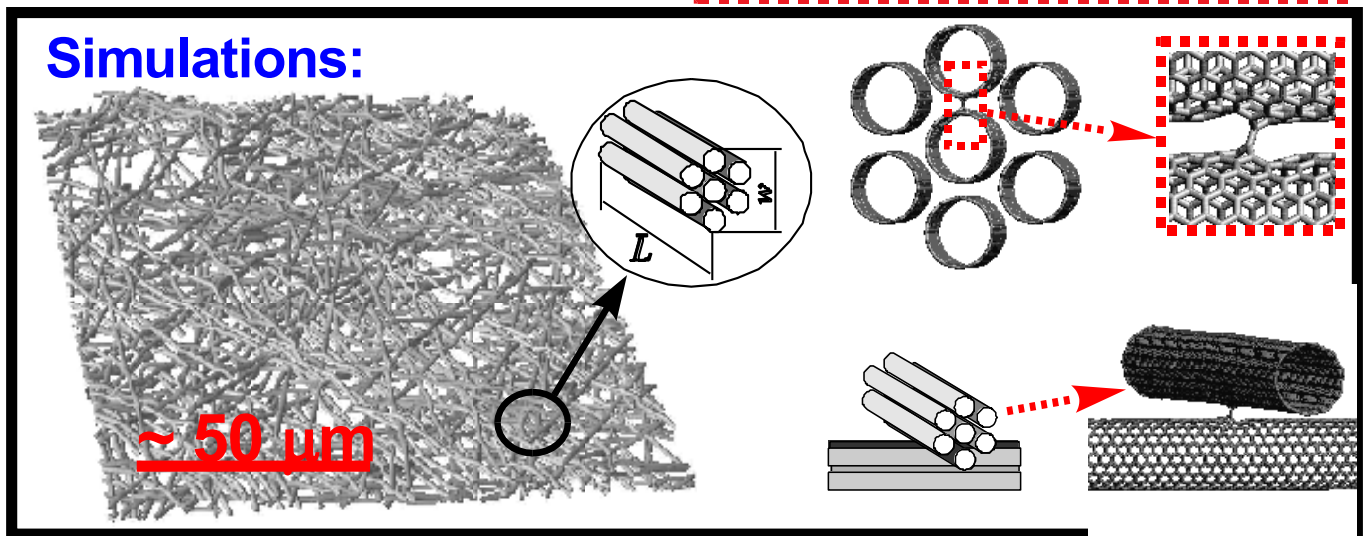
- Deterioration of mechanical properties
- Break down of electronic devices
- Non-radiative transitions
- Undesirable magnetism

- Improvement of mechanical properties in some systems
- Doping
- Providing bright colors
- Pinning of magnetic vortices in type II superconductors

Example of when the defects strengthen the material

Mechanical properties of carbon nanotube paper



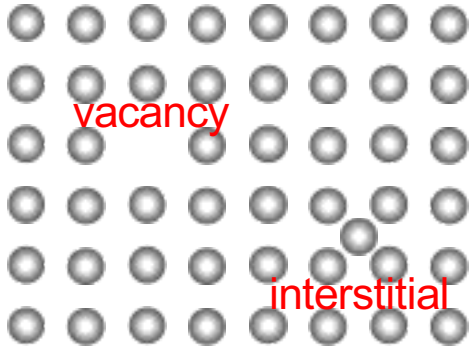


The continuum theory model with parameters derived from atomistic simulations

J. Åström *et al.*, PRL 93 (2004) 215503.

Classification of defects in crystalline solids

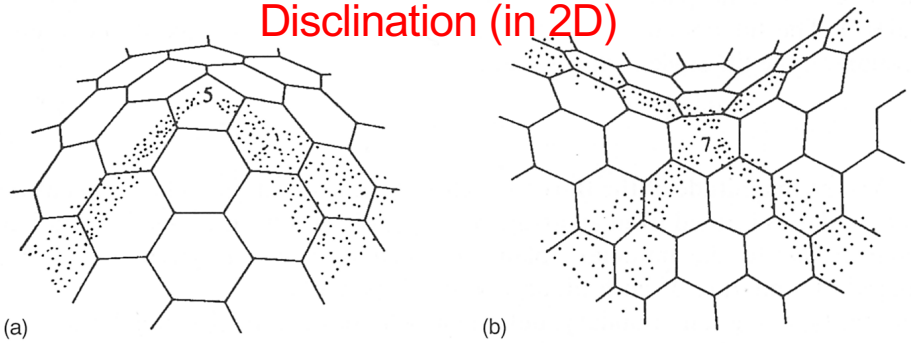
➢ How can we classify them?



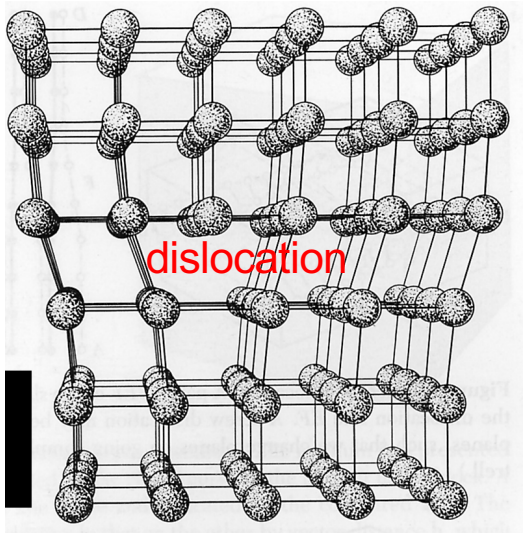
According to their dimensionality:

- Point defects (e.g. vacancies) 0D defects
- Linear defects (e.g. dislocations) 1D defects
- Planar defects (grain boundaries) 2D defects
- Volume defects (voids) 3D defects

Disclination (in 2D)



Note that in 2D systems 2D and 3D defects do not exist

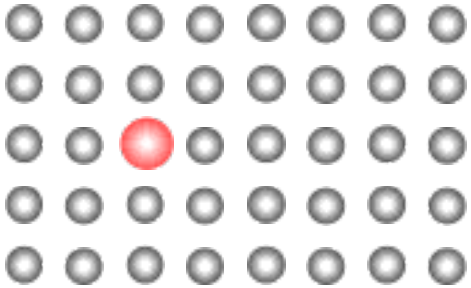


According to their origin:

- Native (pre-existing in the sample)
- Irradiation- (or, e.g., chemical-treatment)-induced

Classification of defects in crystalline solids

How can we classify them?

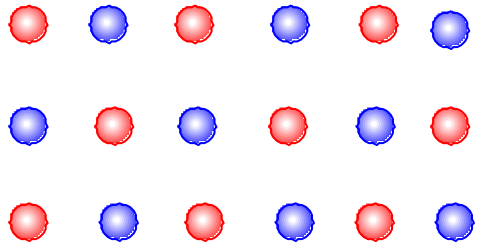


According to their thermodynamics (concentration):

- In thermodynamic equilibrium (relevant to point defects only)
- Non-equilibrium (e.g. irradiation-induced defects)

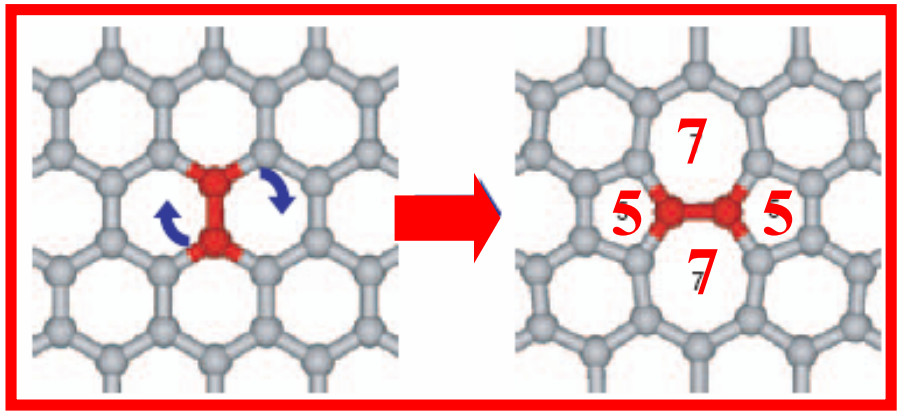
According to sample chemical content (elemental solids, compounds):

- Intrinsic (e.g., vacancies, interstitials)
- Extrinsic (impurity atoms)
- Antisites (in compound solids)
- Chemically equivalent: isotopes (vibrational properties)



According to the local number of atoms:

- Missing/extra atoms (e.g., vacancies, interstitials)
- Wigner defects, e.g., Stone-Wales defects in graphene, rotational defects in TMDs, metastable I-V complexes in Si or graphite
- Topological defect



Energetics of point defects in monatomic solids

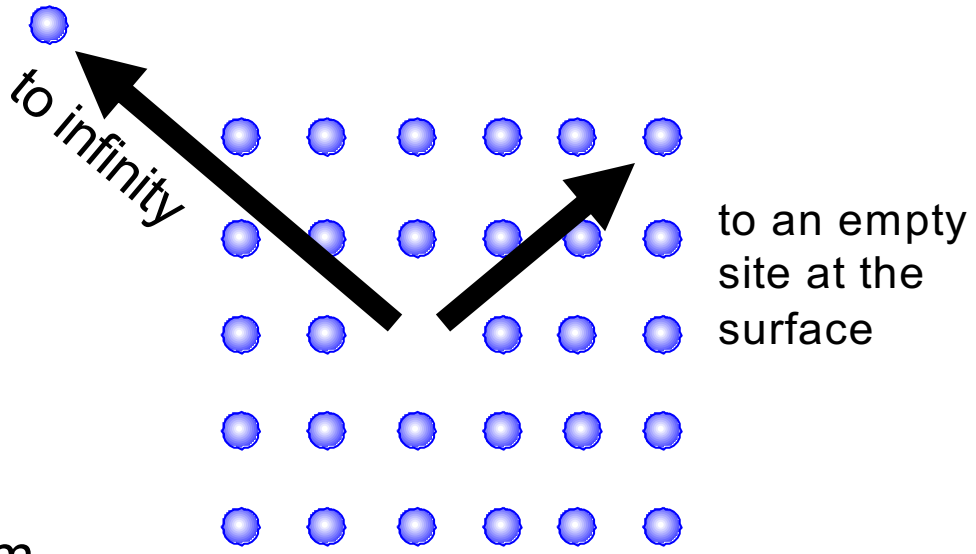
Schottky defect

formation energy:

$E_f = E(N-1) + E(1) - E(N)$

$E_f = E(N-1) + E(N)/N - E(N)$

$E_f > 0$!!! N is the number of atoms in the system



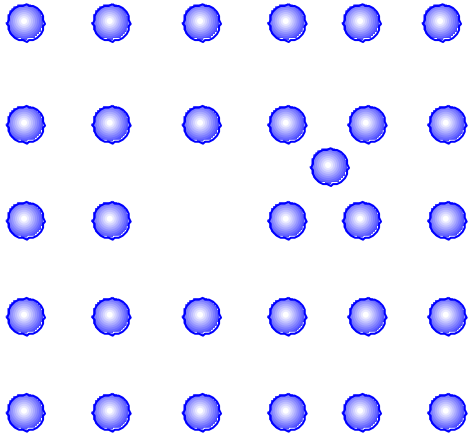
Frenkel defect

formation energy:

$E_f = E(N \text{ with iv pair}) - E(N)$

$E_f = E_f(vac) + E_f(inter)$

$E_f > 0$!!!

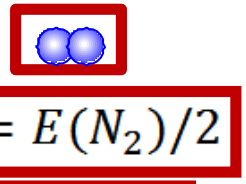


Formation energies of some point defects

- In general, let's define formation energy of an electrically neutral point defect (vacancy/interstitial) as :

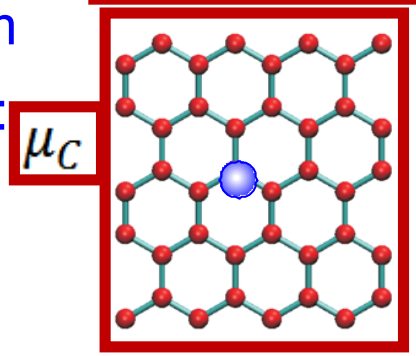
$$E_f = E_{tot}(\text{with defect}) - E_{tot}(\text{without defect}) \pm \mu$$

where μ is chemical potential of the missing/extra atom



- For substitutional impurities (e.g., N atom in graphene):

$$E_f = E_{tot}(\text{with defect}) + \mu_C - E_{tot}(\text{without defect}) - \mu_N$$

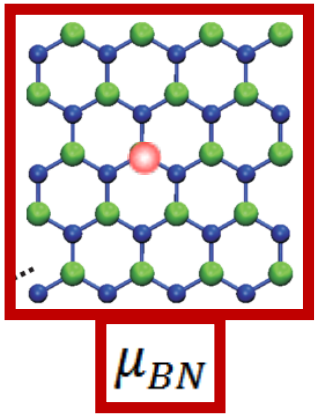


- For defects in compounds (e.g. C impurity in BN) another condition should be met:

$$\mu_N + \mu_B = \mu_{BN}$$

$$E_f = E_{tot}(\text{with defect}) + \mu_N - E_{tot}(\text{without defect}) - \mu_C$$

$$E_f = E_{tot}(\text{with defect}) + \mu_{BN} - \mu_B - E_{tot}(\text{without defect}) - \mu_C$$



So called, N-rich and B-rich conditions;

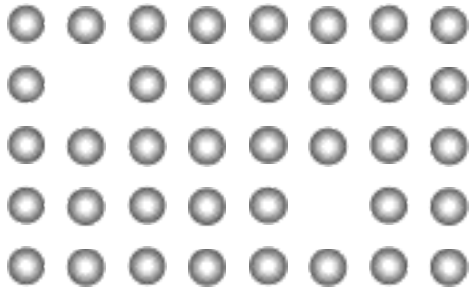
In general, E_f is a function of chemical potentials (choose ones matching the experimental situation)

Where do defects come from?

- Defect formation energy is positive: **it costs energy** to create a defect;

  Why do we have then defects in solids ***at finite temperatures***?

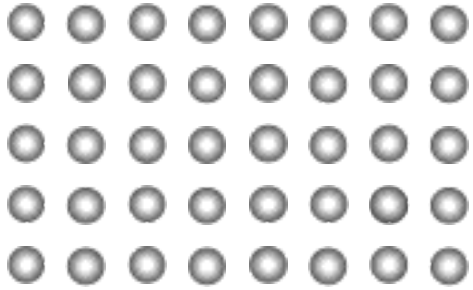
- Assume:
  - vacancy concentration is low (defects do not interact)
  - T = const
  - P = const



- The Gibbs free energy of the crystal:

$G = G0 + nEf - TS$, where

$G0$ = Gibbs energy of the ideal crystal;
n = defect concentration; $n = Nv/N$
$Ef > 0$ = energy required to create a vacancy
S = configurational entropy



$$S = k_B \ln \frac{N!}{(N - N_v)! N_v!}$$

Where do defects come from?

The Gibbs free energy of the crystal:

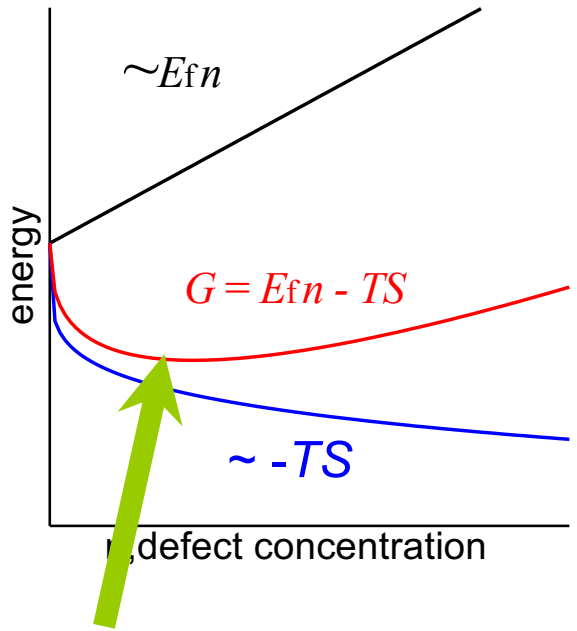
$$G = G0 + nEf - TS$$

At thermodynamic equilibrium:

$$\partial G/\partial n = 0$$

$$Ef - T\partial S/\partial n = 0 \qquad n = Nv/N;\ Nv << N$$

$$S = k_B \ln \frac{N!}{(N-N_v)!N_v!} \qquad \ln x! \approx x \ln x - x, \quad x \to \infty$$



$$n = N_v / N_L = \exp\left(-E_f / k_B T\right)$$

- Entropy gives rise to appearance of point defects at finite temperatures
- Synthetic materials (or e.g., subjected to irradiation) concentration of defects may be different from equilibrium

Typical defect formation energies in bulk solids

Material	Δh_f *(eV)*	$\Delta s_f / k_B$
Vacancies		
Al	0.75	2.4
Cu	1.18	1.6–3.0
Ag	1.09	$\simeq$ 1.5
Au	0.94	1.0
Schottky defects		
NaCl	2.44	9.8
NaI	2.00	7.6
KCl	2.54	9.0
KBr	2.53	10.3
Frenkel defects		
AgCl	1.45–1.55	5.4–12.2
AgBr	1.13–1.28	6.6–12.2

Al: melting Tm = 933K

T = 300K, n = 3 10^{-12}

T = 800K, n = 2 10^{-4}

exp(2.4) ≈ 10 (prefactor)

$$n = N_v / N_L = \exp\left(-\Delta h_f / k_B T + \Delta s_f / k_B\right)$$

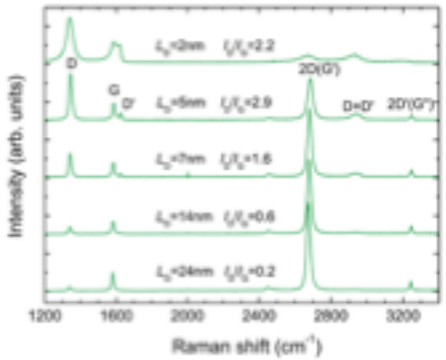
Small exercise

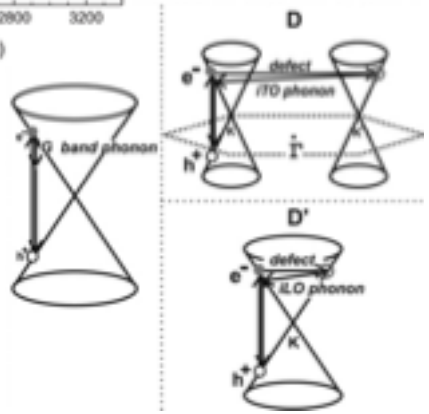
SW defect in graphene, E_f = 4-5 eV

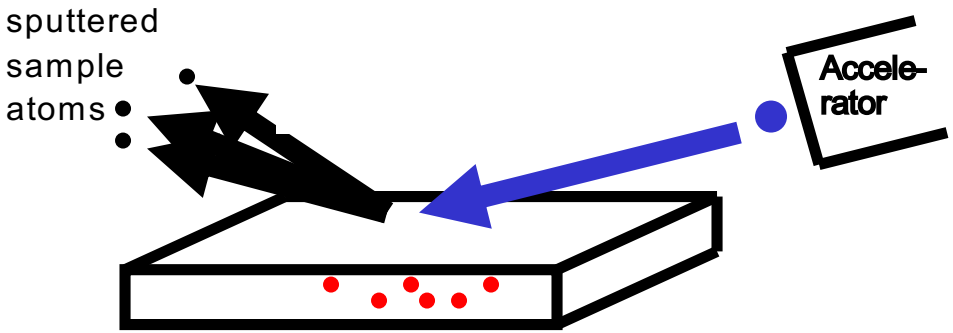
How many defects at 300K?

Experimental methods used to detect and characterize defects in materials

(also elemental analysis techniques to detect impurities)







Methods of defect characterization (an overview)

- **Indirect methods:**
  - Optical spectroscopy
    Main idea: detection of optical transitions associated with defects
  - Electron paramagnetic resonance
    Main idea: detection of localized electron magnetic moments
  - Raman spectroscopy
    Main idea: detection of new phonon modes associated with defects

finite defect concentration required

  - X-ray absorption spectroscopy and related methods (XAFS,XANES)
    Main idea: probing the electronic states associated with defects by exciting core electrons
  - Positron annihilation spectroscopy (does not work for 2D materials)
    Main idea: *a positron gets stuck on the vacancy;we detect the photons which appear upon its annihilation with an electron*
- **Direct methods:**
  - Scanning probe microscopy
    Main idea: getting an image of a particular defect *on the surface*
  - Transmission electron microscopy
    Main idea: getting an image of a particular defect in a thin slice

Detection of individual defects is possible

Electron spin (paramagnetic) resonance (ESR/EPR)

- Assume we have unpaired localized electrons
- Example: dangling bond at atoms near vacancies in semiconductors

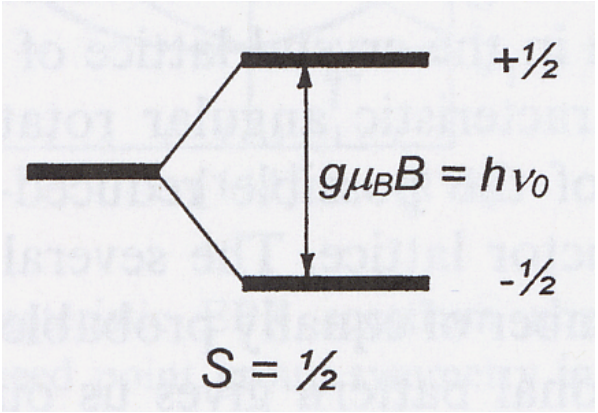
The main idea: We can detect the magnetic moment associated with the spin of the unpaired electron

- Let's apply a steady magnetic field B0

$$E = E_0 + m_s g_e \mu_B B_0$$

$m_s = \pm 1/2; \quad g_e \approx 2$ (the Lande Factor)

$\mu_B = e\hbar / 2m_e$ (the Bohr magneton)



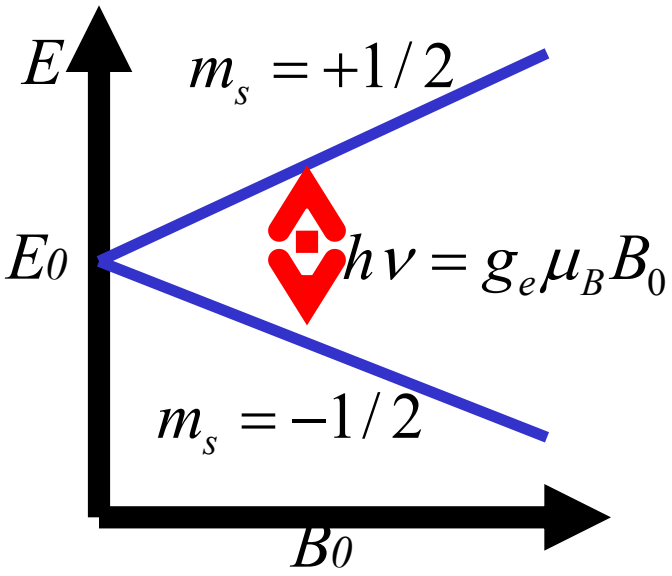
Electron spin (paramagnetic) resonance (ESR/EPR)

- Let's apply alternating EM field B_1 of frequency ν perpendicular to B_0
- If $h\nu = g_e \mu_B B_0$

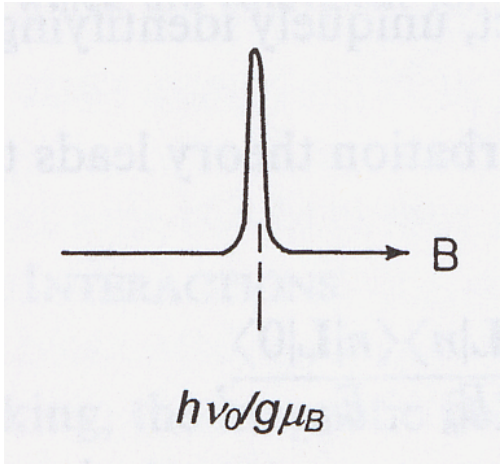
  we will have absorption!

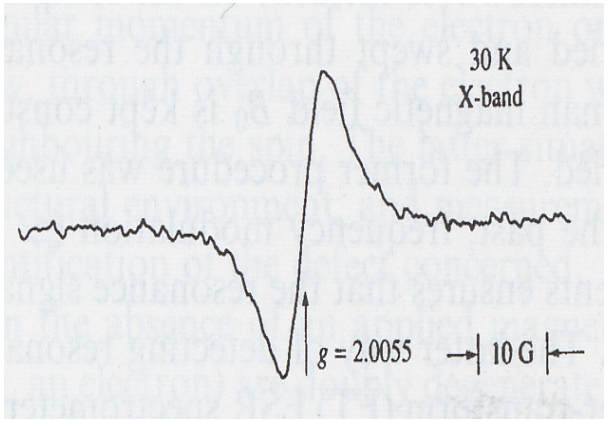
$B_0 \sim 0.3$ T

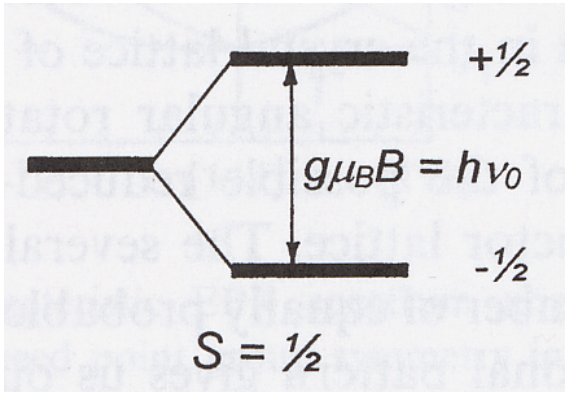
$\nu \sim 9$ GHz (microwave region)



adsorption peak its derivative (with opposite sign)



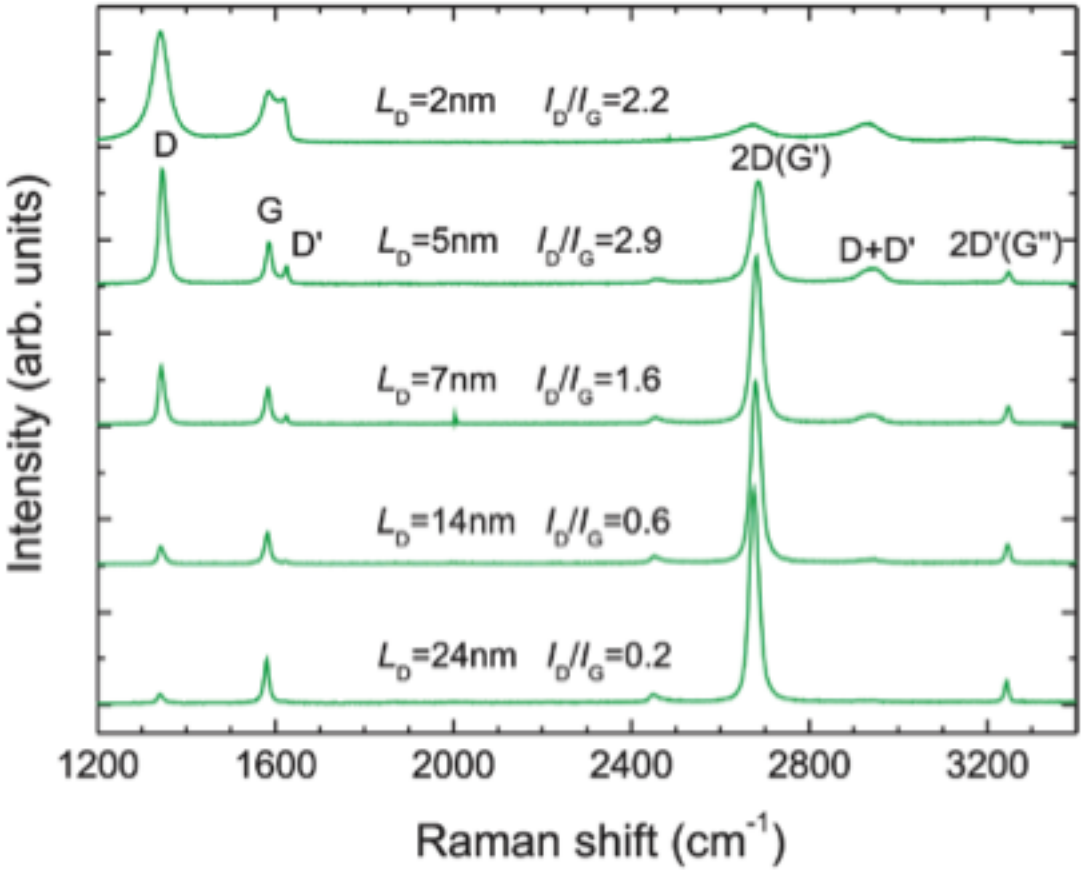


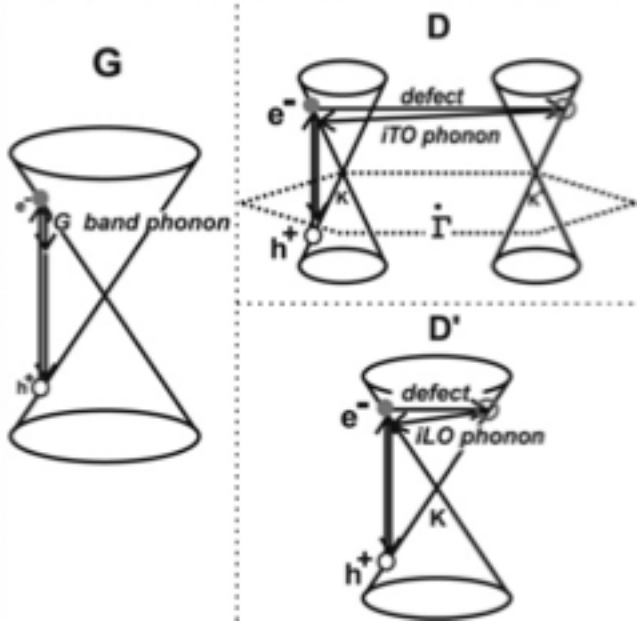


Spectroscopic methods of defect detection

Raman spectroscopy

- New peaks due to defects observed in Raman spectra; the associated processes are not allowed in pristine graphene





- Non-destructive technique;
- Information is integrated over a macroscopic (~ μm) area;
- Not in all materials new peaks appear

Concado et al.,
Nano Lett. 11 (2011) 3190

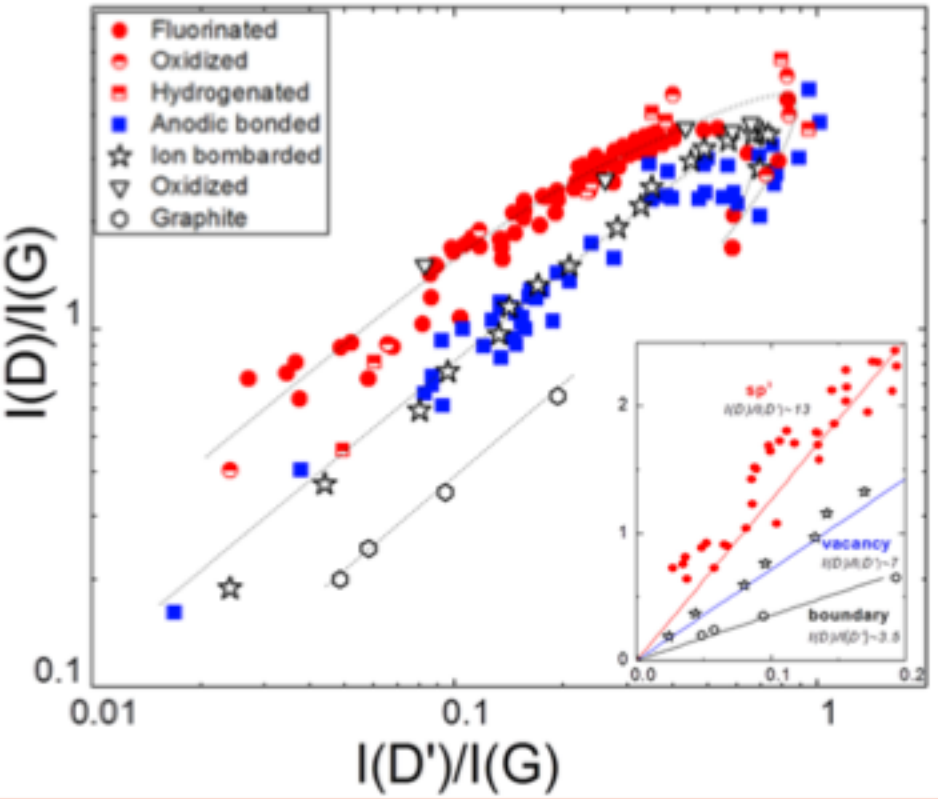
Spectroscopic meth

- Raman spectroscopy

NANO LETTERS

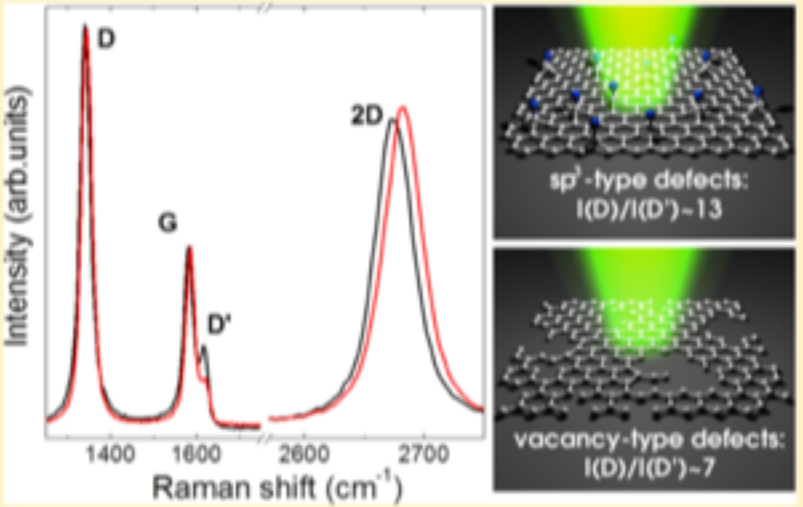
Probing the Nature of Defects in

Axel Eckmann,[†] Alexandre Felten,[‡,§] Artem Mishc
Kostya S. Novoselov,[∥] and Cinzia Casiraghi*[,†,‡]

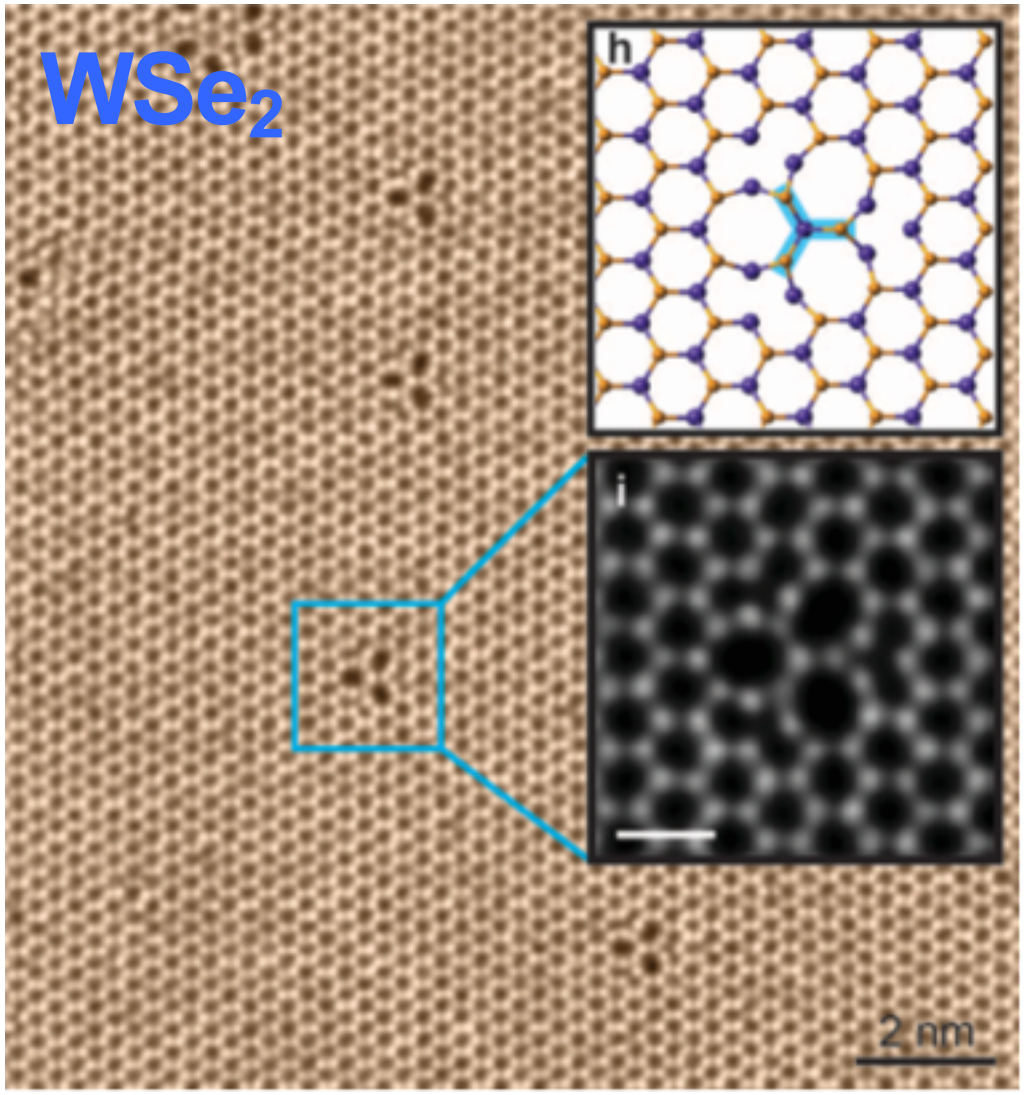


ABSTRACT: Raman spectroscopy is able to probe disorder in graphene through defect-activated peaks. It is of great interest to link these features to the nature of disorder. Here we present a detailed analysis of the Raman spectra of graphene containing different type of defects. We found that the intensity ratio of the D and D′ peak is maximum (~13) for sp^3-defects, it decreases for vacancy-like defects (~7), and it reaches a minimum for boundaries in graphite (~3.5). This makes Raman Spectroscopy a powerful tool to fully characterize graphene.

In principle, even identification of defect types is possible.

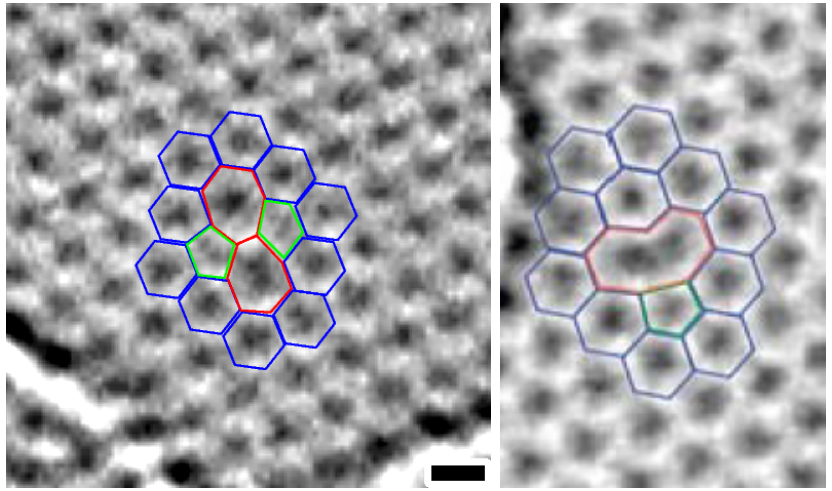


Transmission electron microscopy



Courtesy of K. Suenaga

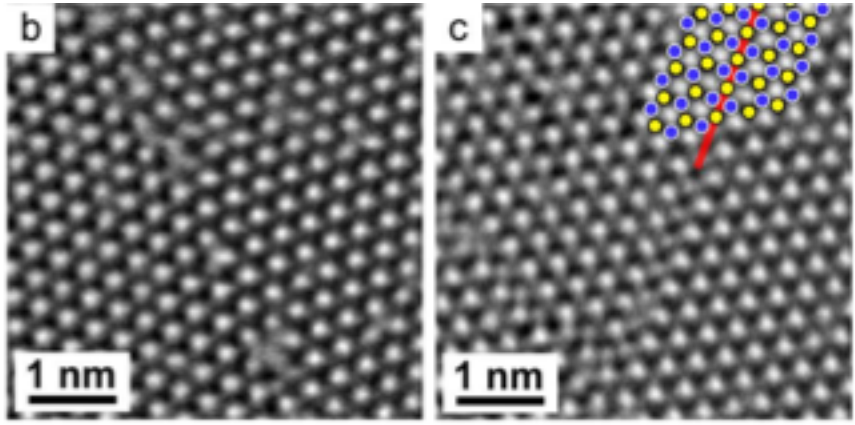
graphene



Courtesy of J. Meyer

MoSe2

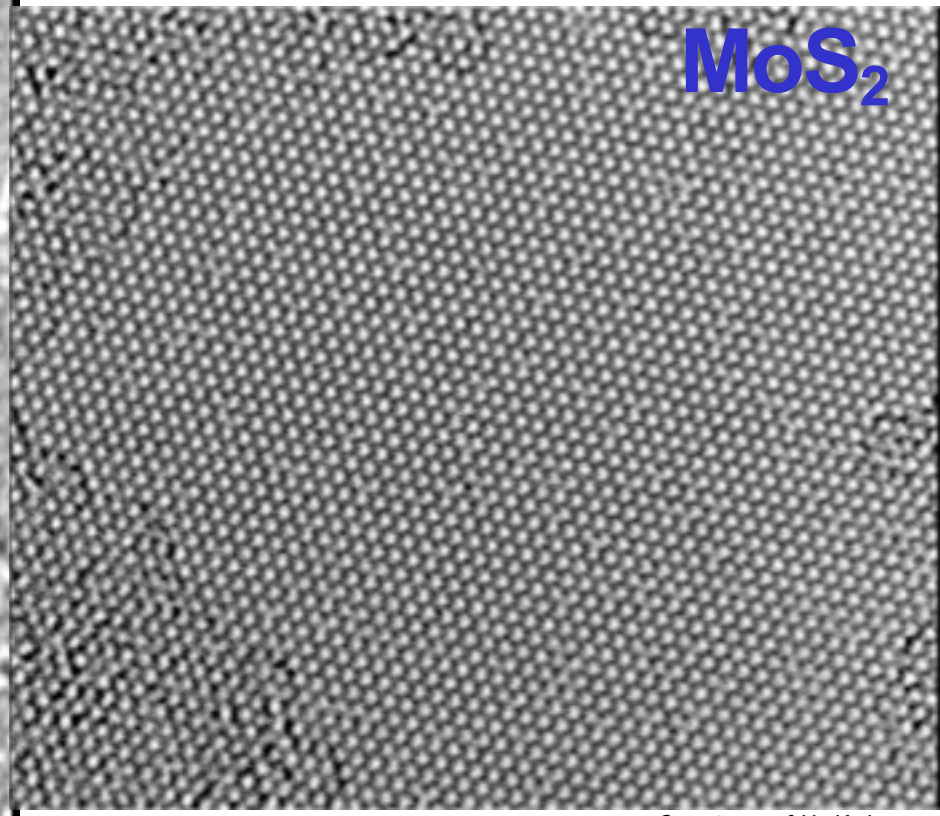
Courtesy of U. Kaiser



Seeing is believing … (many more examples later on)

Courtesy of J. Meyer

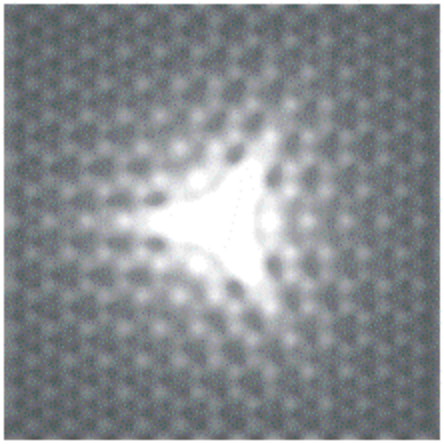
'Direct' pictures of defects in graphene and other 2D materials (TEM, STM, etc.)



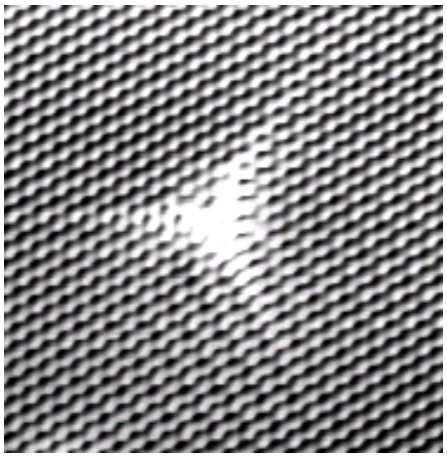
Courtesy of U. Kaiser

STM imaging of surface defects

- Vacancy in graphite:
  - The defect size on the image is much larger than the actual size.
  - The vacancy appears as protrusion!

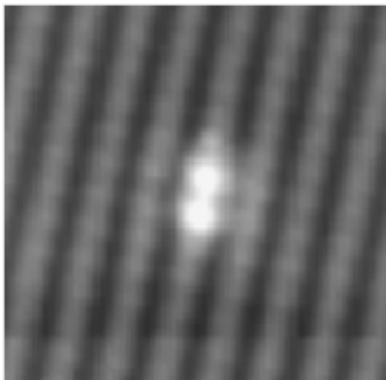


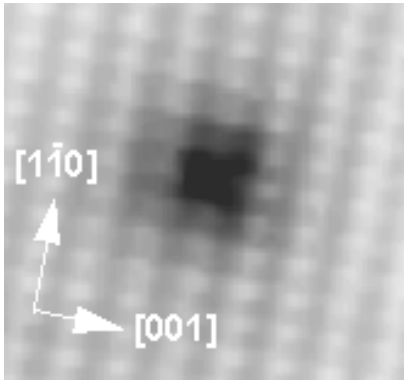
simulations



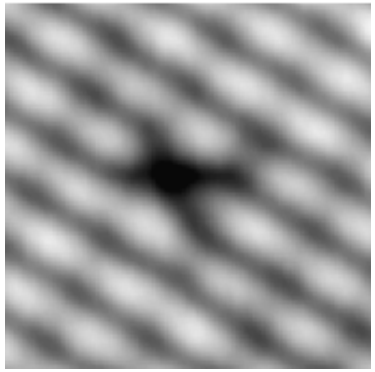
experiments

- Vacancy in GaAs



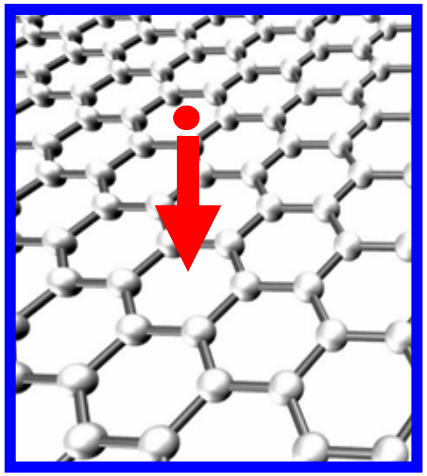


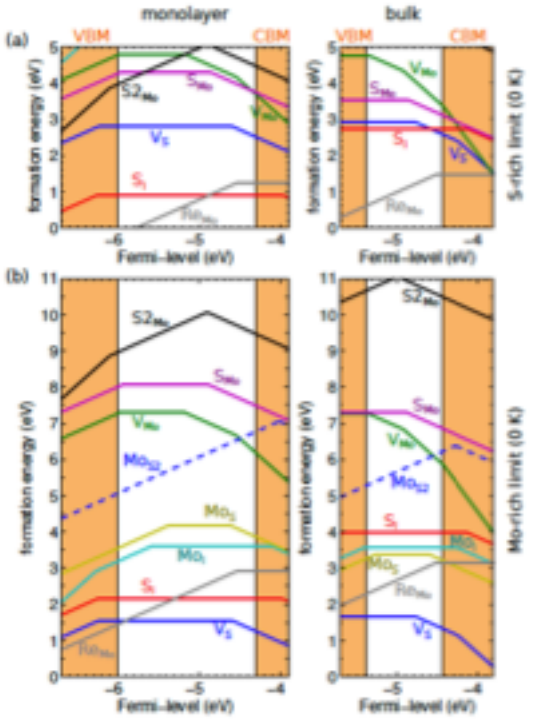
- Vacancy in GaP



We can detect point defects! (and surely line defects)

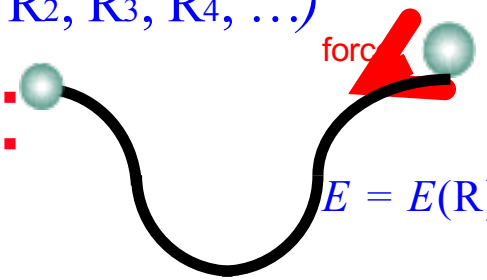
Computational methods used to describe atomic structure of defects, their effects on materials properties, as well as defect production under irradiation





Assume we know how the atoms interact, i.e., we know the energy of the system as a function of atomic coordinates: $E = E(R_1, R_2, R_3, R_4, \ldots)$

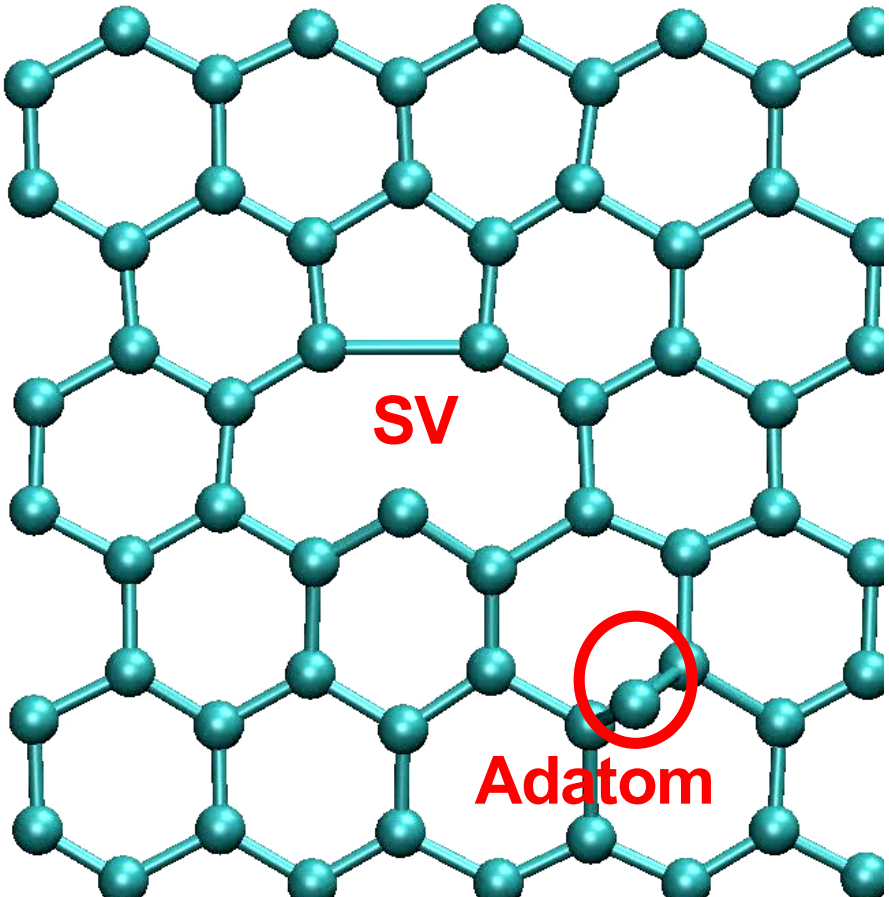
What we would like to do:



- Find the equilibrium positions of the atoms corresponding to the absolute minimum of energy (the structure)
- Compare the relative energies of several atomic configurations (conformations)
- Calculate the properties (mechanical/ electronic/magnetic) of the system
- Model the dynamical behavior of the system at finite temperatures (molecular dynamics)

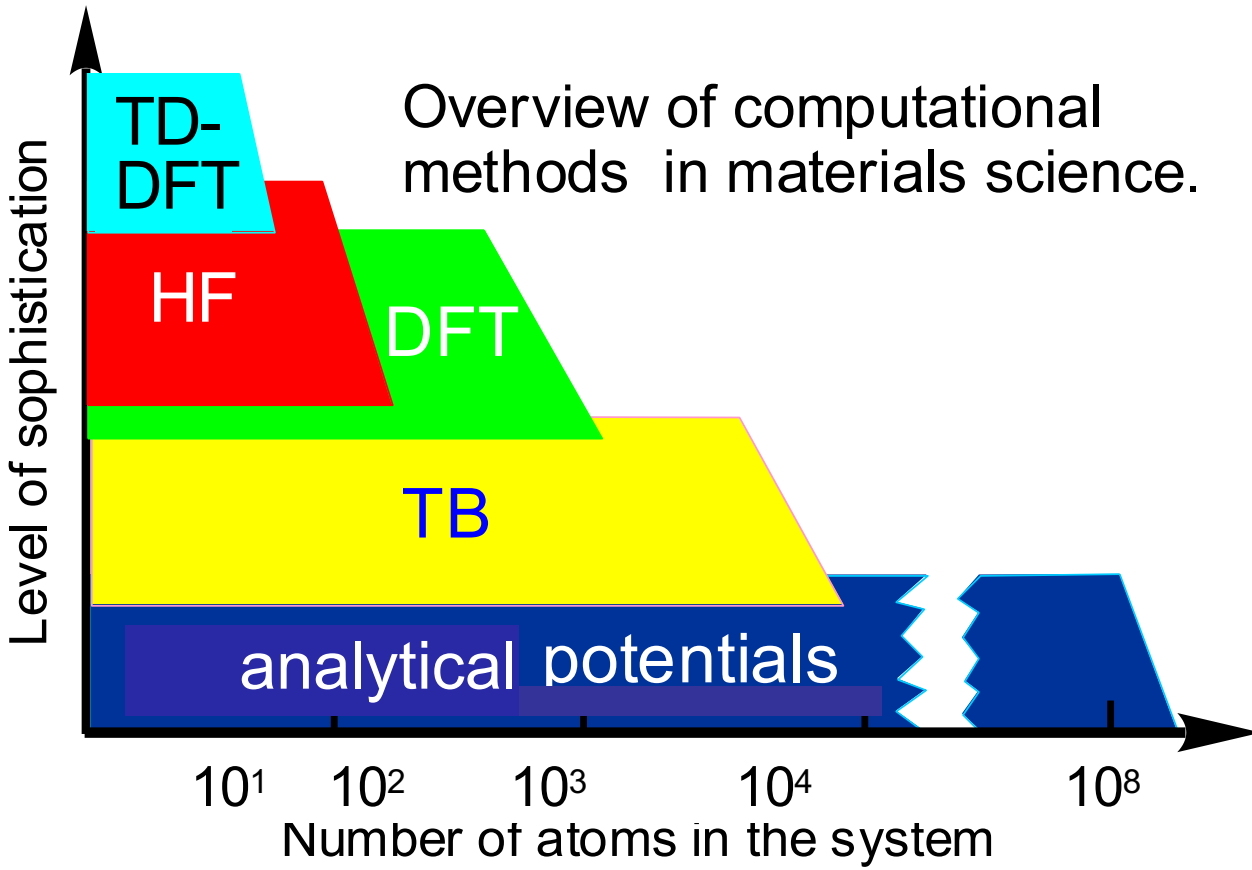
$$m_i \frac{\partial^2}{\partial t^2} R_i = -\frac{\partial}{\partial R_i} E(R_1, R_2, \ldots, R_i, \ldots . R_N)$$

- Calculate thermodynamic properties making use of statistical mechanics



Atomistic simulations: accuracy vs efficiency

- Time-dependent density-functional-theory methods (beyond Born-Oppenheimer approximation)
- Density-functional-theory methods
- Tight-binding methods
- Molecular dynamics with analytical potentials
- Kinetic Monte-Carlo methods



Always a compromise between the computational efficiency and the accuracy

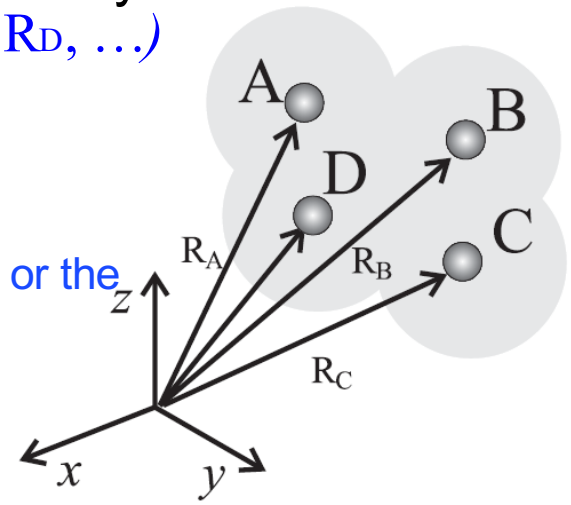
Internal (potential) energy as a function of atom positions

Atomistic simulations: we need to know the energy of the system as a function of atomic coordinates: $E = E(R_A, R_B, R_C, R_D, \ldots)$

- Empirical (analytical) potentials: E is an analytical function of atom coordinates

  Parameters are normally chosen to match the experiments or the results of more accurate calculations

$$\mathcal{U}(\mathbf{r}) = \sum_{ij} \left\{ De^{-2\alpha(r_{ij}-r_0)} - 2De^{-\alpha(r_{ij}-r_0)} \right\}$$



- Semi-empirical (tight-binding) methods:

$$\mathbf{H}\Psi = E\Psi$$

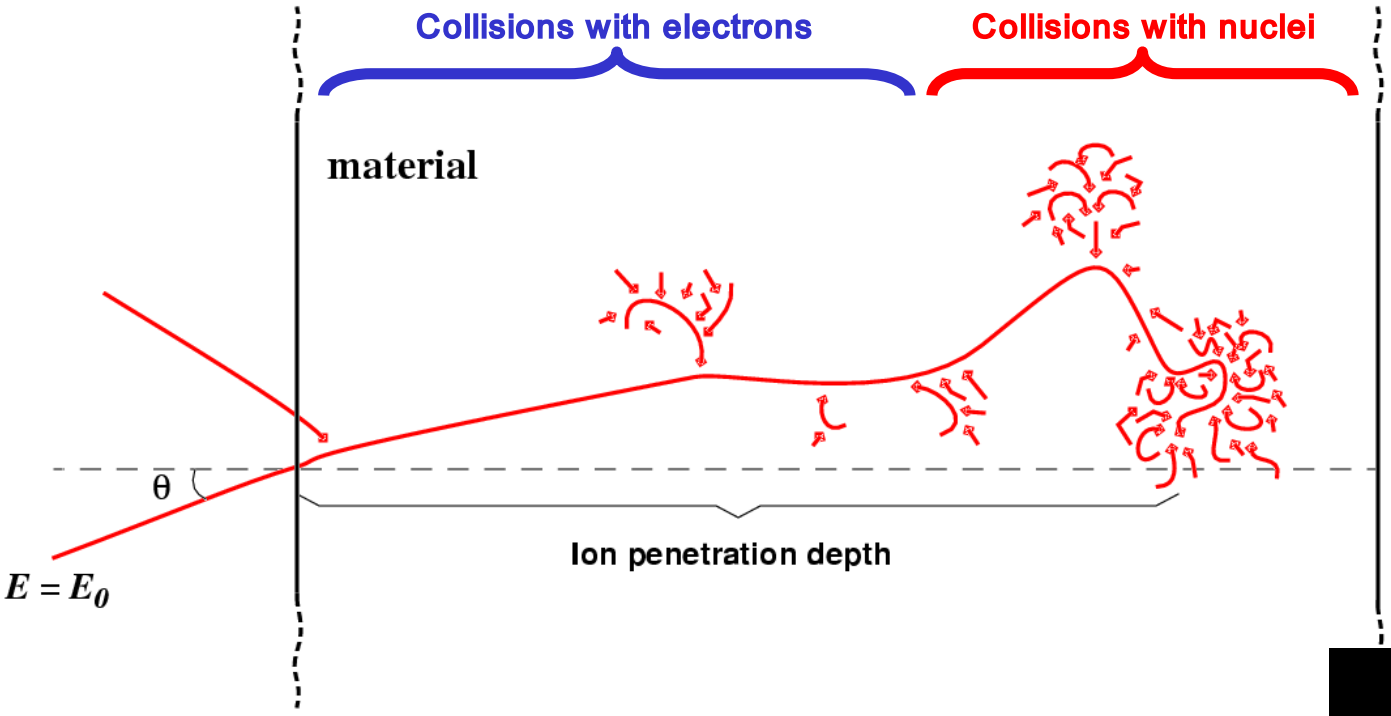
Parameters of the Hamiltonian are chosen in such a way that the results of calculations match the experiments or ab inito calculations

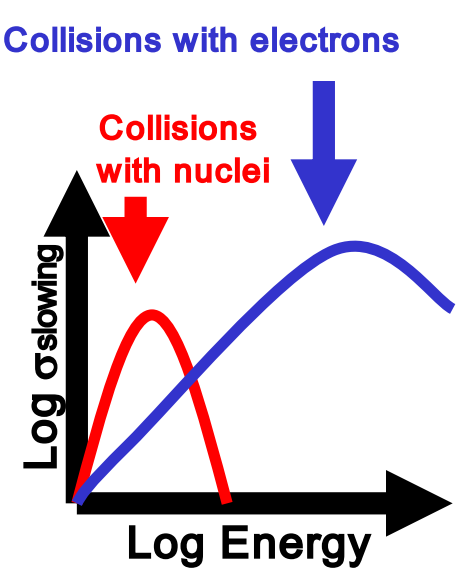
- First-principles (ab initio) methods:

$$\mathbf{H}\Psi = E\Psi$$

No information from experiments is required: The Schrödinger equation is solved using some approximations (the same for all the materials).

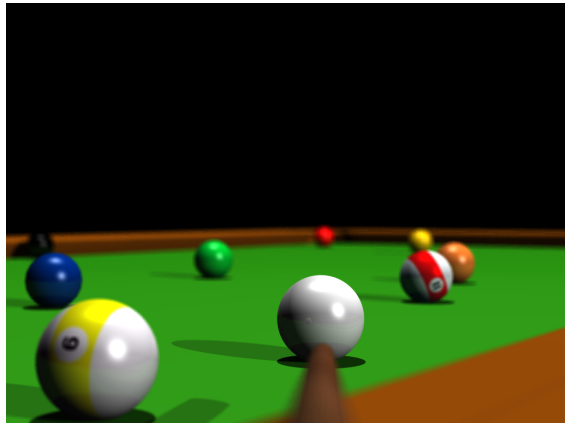
Schematic illustration of ion slowing-down





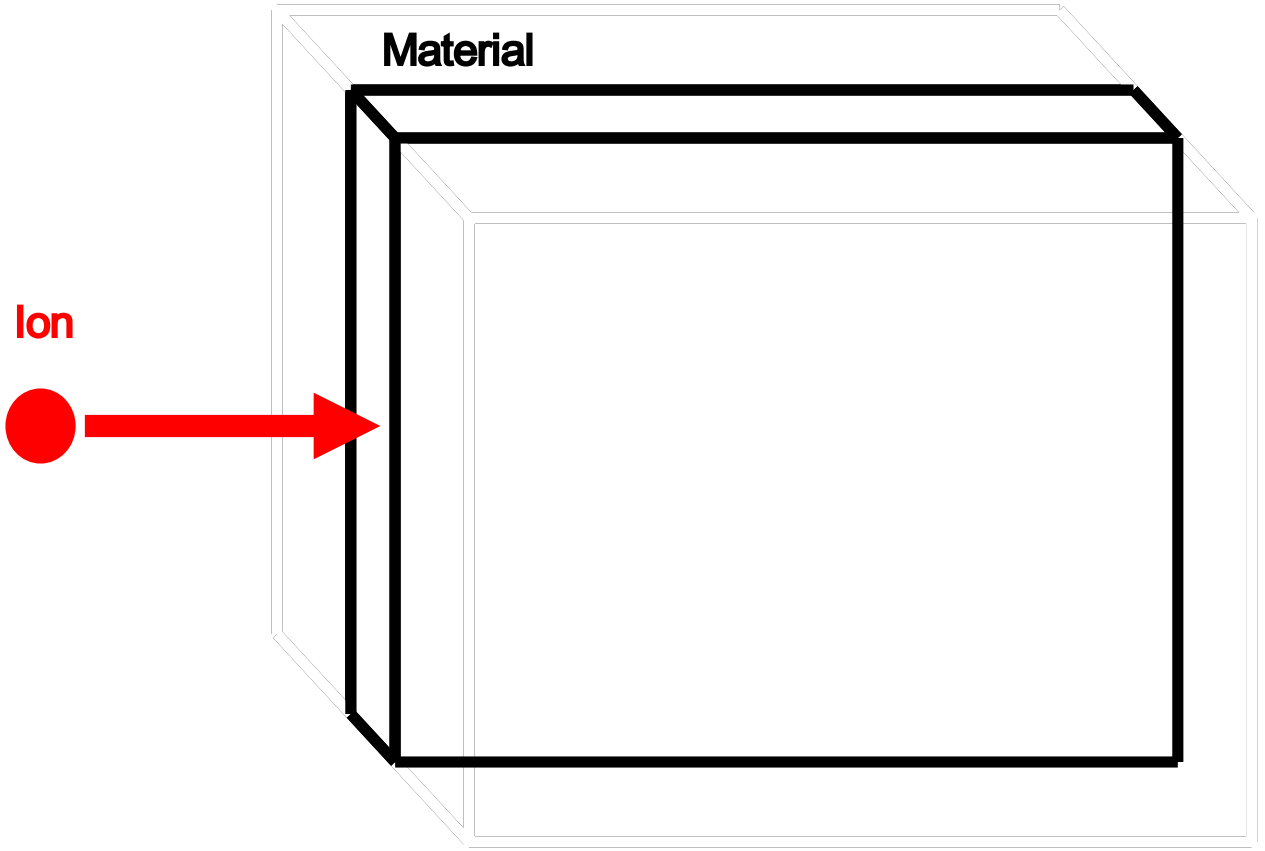
Simulations:

- Collisions with nuclei: MD on the BO surface
- Collisions with electrons: Time dependent DFT
- Both: MD beyond BO approximation (TD-DFT combined with MD for the atoms)



An irradiation event: animation view

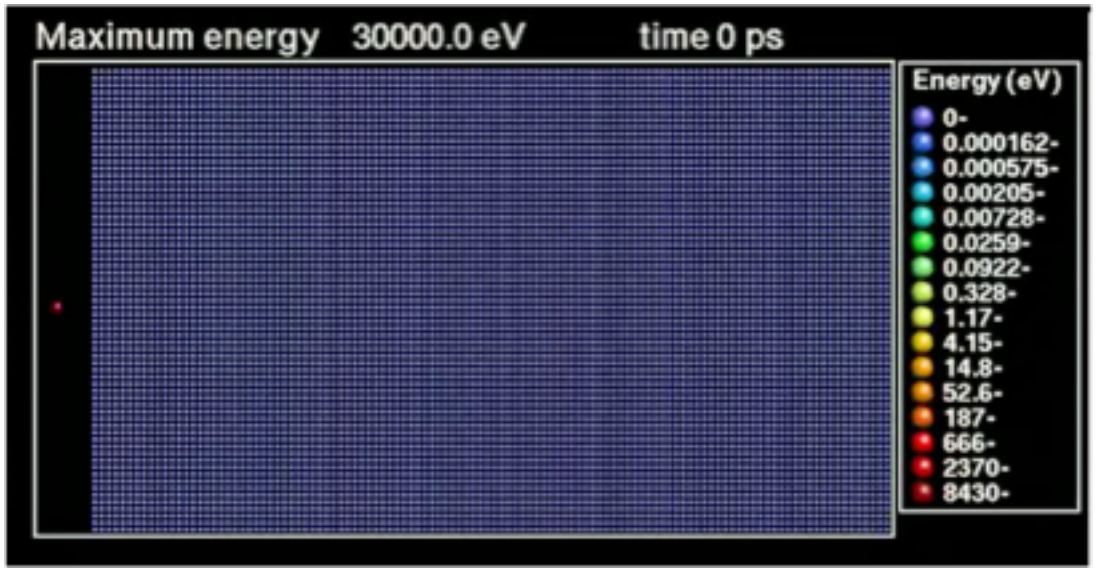
- An atom-level computer simulation can make it much clearer what the process really looks like



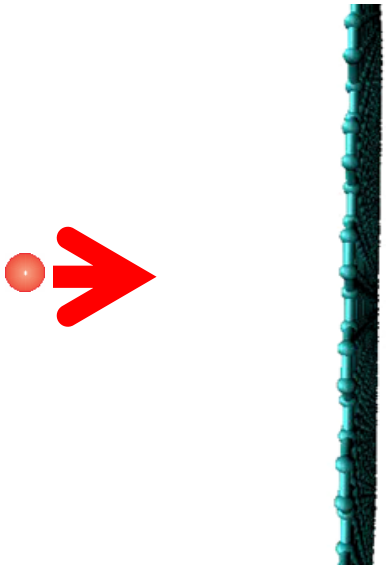
2D materials under ion irradiation

Bulk systems

Animation by K. Nordlund, U. Helsinki



2D materials (free standing)

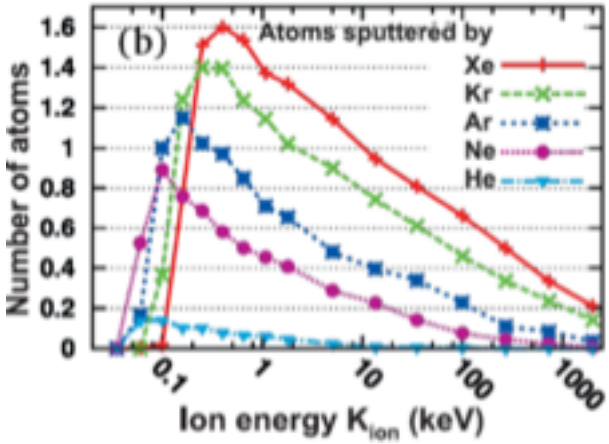


2D materials (free standing)

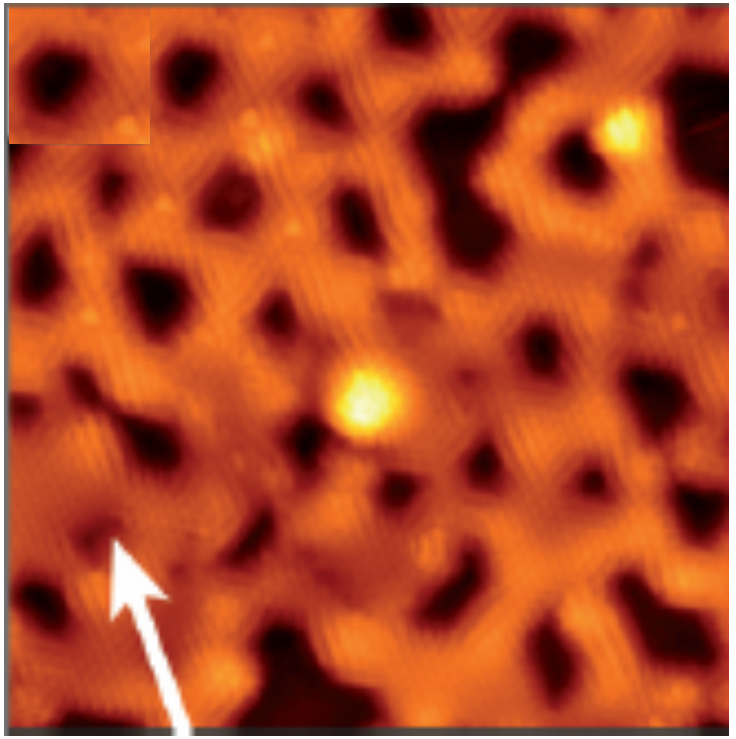
- No collisional cascades
- Curve # of defects vs ion energy has a maximum

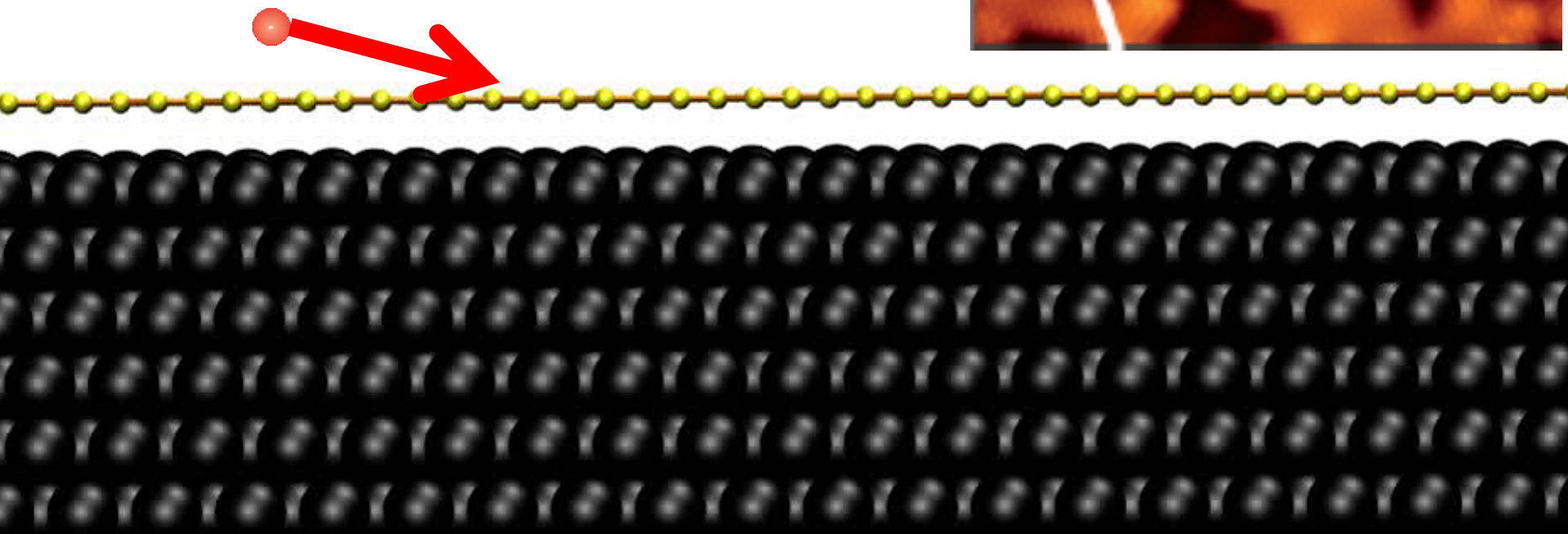
  O. Lehtinen et al., Phys. Rev. B 81 (2010) 153401.

- Possibility to study the single interaction between the ion and target atoms



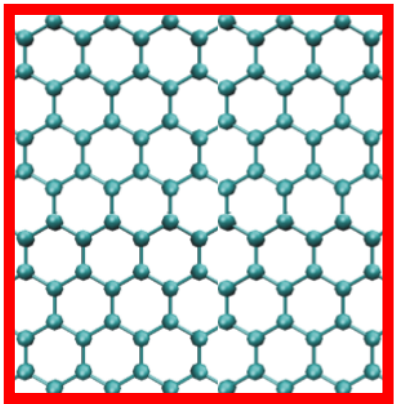
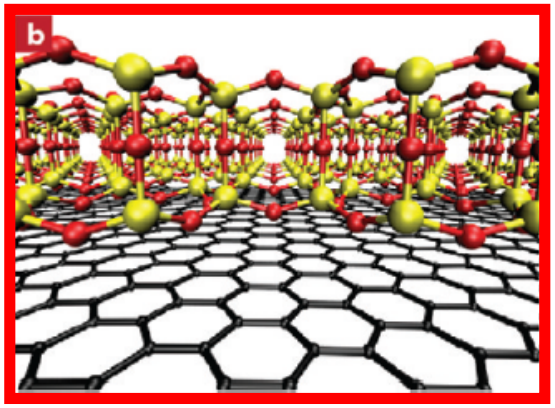
Graphene under ion irradiation

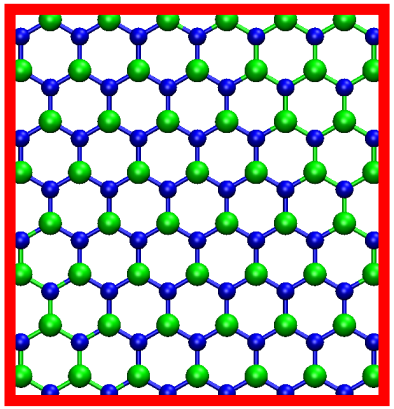
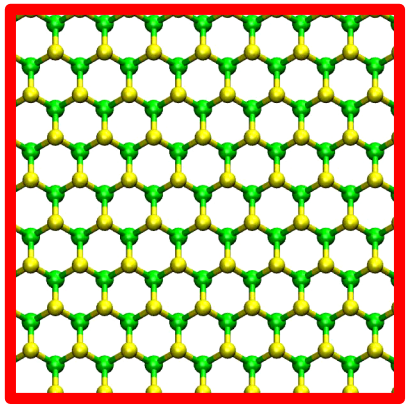




Why do we care about defects in 2D systems?

(Such as graphene, BN, transition metal dichalcogenides, etc.)

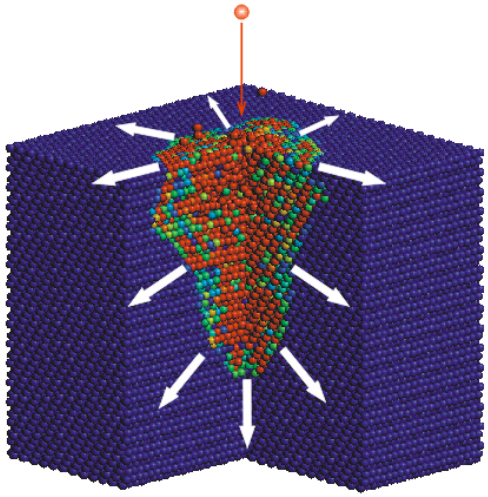



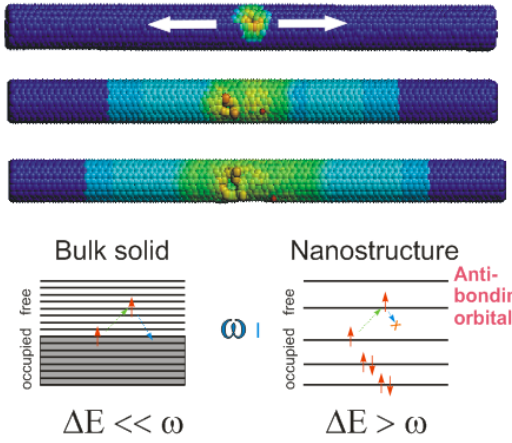
- Defects (point and line defects) are ubiquitous; The thermodynamics is responsible for defect appearance at finite temperatures;
- Man-made materials (e.g., CVD-grown) may be not in equilibrium;
- As 2D materials have 'surface' only, effects of the environment are strong!
- Defects can be created by ion and electron irradiation;
- Defects affect material properties and may be beneficial;

For an overview see AVK and F. Banhart, Nature Mater. 6 (2007) 723-733.
AVK and K. Nordlund, Appl. Phys. Rev. 107 (2010) 071301.

Irradiation of systems with reduced dimensionality: fundamental aspects

- Exciting new physics

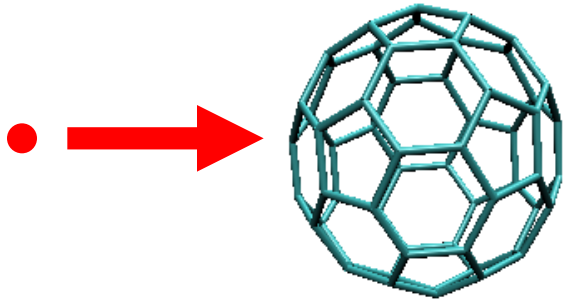




- Energy conversion mechanism from the projectile to atomic stochastic motion is different from that in bulk solids due to nano-scale system size
- Large surface area
- Only a small amount of energy of the projectile is deposited into the system, but this may give rise high local temperature

Example: 30 eV transferred to a C atom

in C_{60} would rise “temperature” up to ~ 2000K



- All of the above is relevant to graphene: production of defects in a 2D material

Conclusions

- Defects are important and frequently govern material properties
- Defects can be useful or have detrimental effects
- There are many techniques to identify defects
- Simulations provide lots of insight into the structure and properties of the materials with defects

Thank you for your attention!