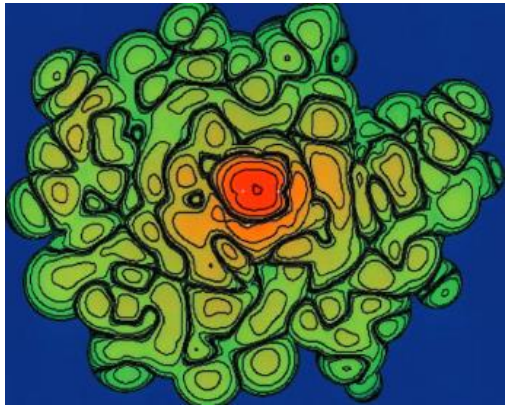
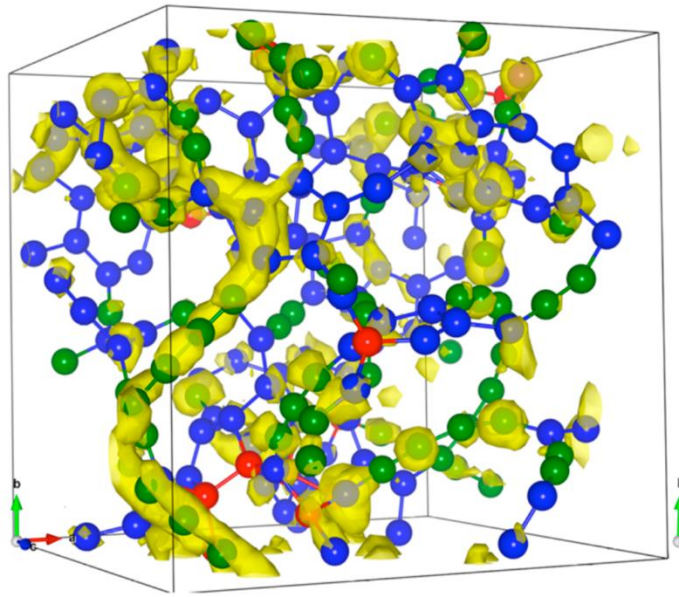
Synthetic graphite: a story 130 years in the telling

David Drabold, Ohio University





Roadmap

- *Ab initio* modeling and Machine-Learning Oxbridge GAP potential
- Graphitization history and direct simulations
- Baby steps toward graphitizing coal

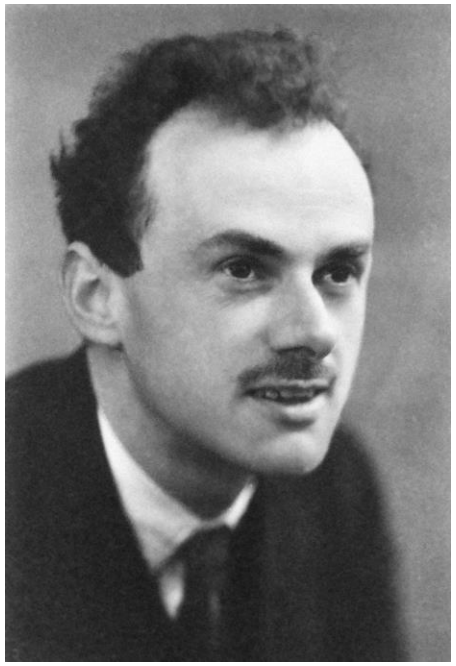
Atomistic simulation of materials

- Goal: prediction, understanding, optimization
- Central problem: how to obtain accurate and efficient force estimates.
- Big picture:
  - Input: force laws and initial conditions
  - Output: structure, vibrations, electronic, optical, magnetic, transport

Interatomic interactions

- Q. How do we compute generally applicable and accurate interactions?
- A: Grapple with the chemistry -- quantum mechanics.

This is best done with ***Density Functional Theory*** (Dirac, Fermi, Slater, Kohn [Nobel Prize, Chemistry, 1998]).



The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved. -- Dirac

Machine Learning for interatomic interactions

- Pick a material, say C or a-SiO_2. How many millions of computer core hours have been spent, a paper published, and the simulation data **deleted**?
- Suppose that we try to build a database of the all the atomistic information we obtained.
  - Q: Can we use this data to predict interatomic interactions for new simulations of the same material?
  - A: Conceptually, YES -- because the potential is a continuous function of the coordinates — so it is effectively a **difficult interpolation problem!**

One highly successful ML approach

- **Csányi, Bartok and Deringer (and others)** have pioneered a successful new approach: "Gaussian Approximation Potential" (GAP).
- Train from accurate DFT compuations.
- Beautiful and graceful mathematical framework.

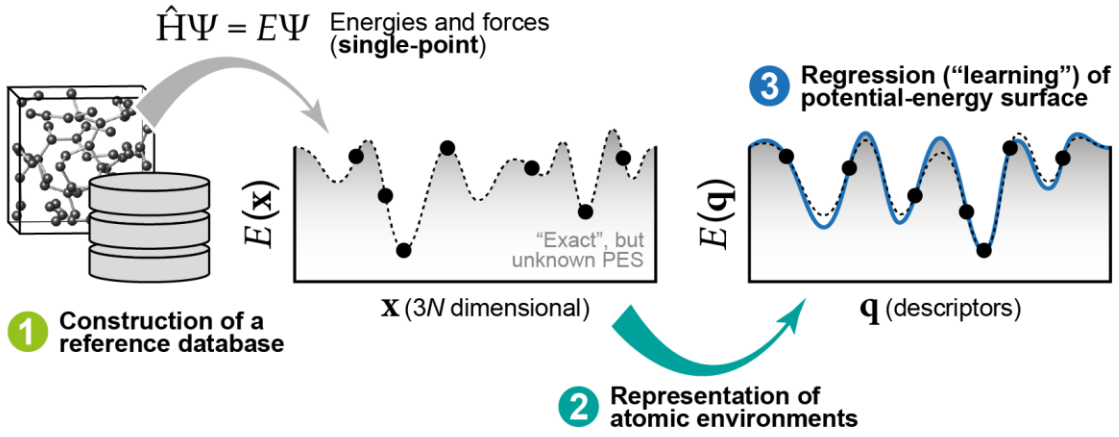
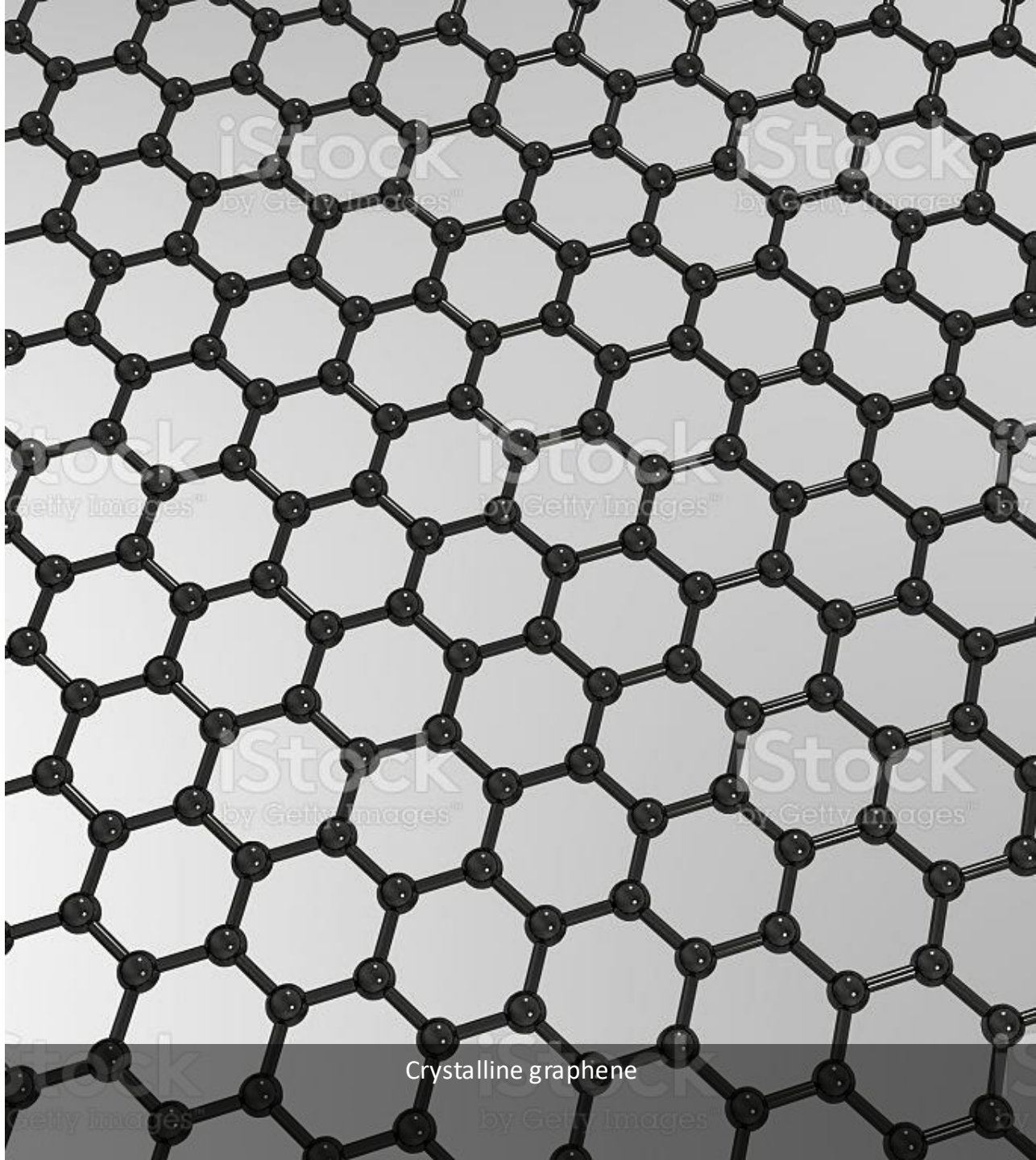


Figure: thanks to V. Deringer, Oxford

Ex: Deringer, Caro and Csányi, Adv. Mats. 31 1902765 (2019)

Graphite

- Graphite is essential material, used for anode of Li-ion batteries (each Tesla model S requires 54 kg of graphite).
- Graphite consists of layers of graphene (regular hexagons of carbon atoms as shown)



Crystalline graphene

Graphitization

- Background: we work on carbonaceous (coal-derived) materials – for construction and technological applications with Profs. J. Trembly and Y. Al-Majali (Ohio: Mechanical Engineering).
- Question: *Can we make synthetic graphite from other carbon materials*? **Experimentally** it is known that annealing carbon rich materials near 3000K leads to somewhat graphitic materials.

Synthetic graphite is as old as the hills

J. Am. Chem. Ind. (1931)

AMERICAN CHEMICAL INDUSTRIES

Acheson Oildag Company

TWENTY-THREE years ago the Acheson Oildag Company started operations at Niagara Falls, N. Y. It was formed for the purpose of producing commercially the final product obtained by Edward Goodrich Acheson in a now famous series of closely related experiments.

In 1891, after having succeeded in effecting the large-scale production of silicon carbide, "Carborundum," Acheson sought to produce a still harder abrasive by subjecting the same elements to a higher temperature for a longer period of time. Practice did not bear out his theory, however, as the silicon volatilized under these conditions, leaving the carbon in the form of an extremely unctuous graphite of very high purity. Further work showed the preliminary formation of silicon carbide to be unnecessary in the production of artificial graphite and that any form of carbon, when subjected to the proper temperature conditions, could be converted into the graphitic form. This little high-temperature experiment was important, nevertheless, as it resulted in the organization of the Acheson Graphite Company.

E. G. Acheson, Chairman
Board of Directors

Acheson next sought to utilize the graphite he was producing in competition with Nature. The crucible trade was then consuming most of the graphite being mined, so Acheson decided to engage in the manufacture of crucibles. In this connection he did considerable work on clays, which he hoped to employ as binders. In the course of his experiments he noted that certain clays, though of similar composition, varied greatly in plasticity. Since sedimentary clays were generally more plastic than the residual type, Acheson attributed this difference to some effect exerted by the water responsible for the transfer of the sedimentary clays from their original beds. Working on the belief that this change was brought about by organic matter leached from the fertile regions through which the streams flowed he improved the plasticity of clay bodies by treating them with aqueous extracts of straw.

Searching the literature to see if anyone had discovered this effect before him, Acheson found but one reference to a similar use of straw. This was in Exodus 5:7–19, wherein is described the brick-making operations of the Egyptians. Feeling that the Egyptians used the straw to render the clay more plastic rather than as a fibrous binder, Acheson called his treated product "Egyptianized clay."

The then newly invented ultra-microscope revealed that the increase in plasticity was due to a reduction in the particle size of the clay. Jerome Alexander was in possession of one of these instruments and showed Acheson that by his deflocculation process he had unquestionably produced particles of colloidal dimensions.

Knowing his manufactured graphite to be far superior to the natural product for lubrication purposes because of its freedom

Miss Harris, for five years was with the Acheson Oildag company and at the time of her resignation was assistant treasurer. She was very popular with her associates, who remembered her with a handsome wedding gift. Pre-nuptial

Leona Mae Harris
ca. 1920

Port Huron (MI) Times-Herald 24 Mar 1919. p. 2

Acheson/Castner graphitization process. *Very* high temperature annealing process.

Wikipedia: …**Process is run for approximately 20 hours at 200 V with a starting current of 300 A (60 kW) for a furnace approximately 9 meters long by 35 cm in width and 45 cm in depth,** and the resistance drops as the carbon heats … causing the current to increase. **"Heat" to T near 3000 K**. Cool down takes weeks.

Fun fact: First Acheson plant at Niagara Falls soon after initial hydro power there in 1893.

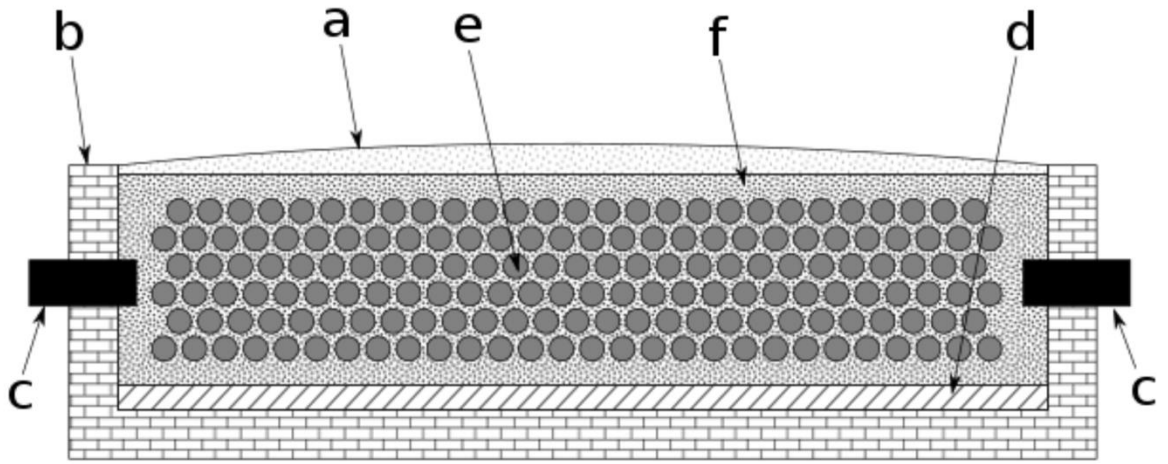


Diagram of a resistive Acheson furnace for producing electrode rods formed from powdered coke mixed with silica clay:
a – mixture of coke and sand,
b – bricks,
c – carbon electrodes,
d – refractory material,
e – rods to graphitize,
f – granulated coke

Approach to graphitization simulation

- Use plane wave DFT (VASP) and density around 2.4 gm/cc, anneal at 3000K.
- Next, use Deringer/Csanyi carbon GAP – *trained by VASP/DFT.*
- Checked Van der Waals corrected DFT, no significant change.
- Traditional empirical potentials: Tersoff and REAX-FF give qualitatively incorrect results.

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 1 1 JANUARY 1993-I

***Ab initio* molecular dynamics for liquid metals**

G. Kresse and J. Hafner
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(Received 8 July 1992; revised manuscript received 9 October 1992)

PHYSICAL REVIEW B **95**, 094203 (2017)

Machine learning based interatomic potential for amorphous carbon

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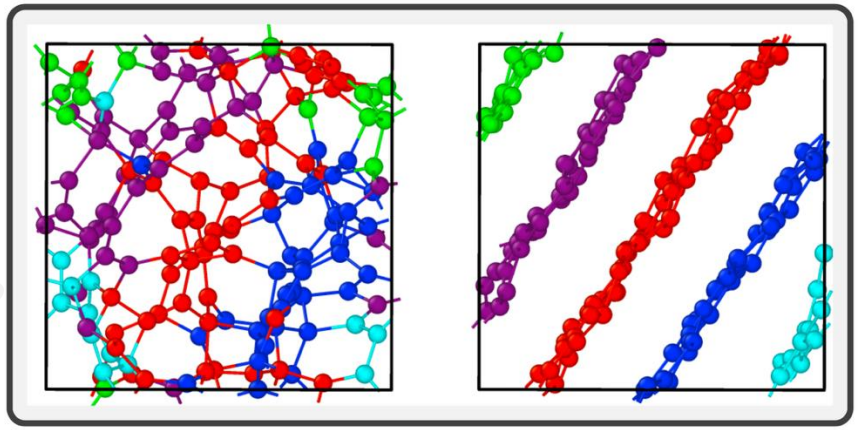
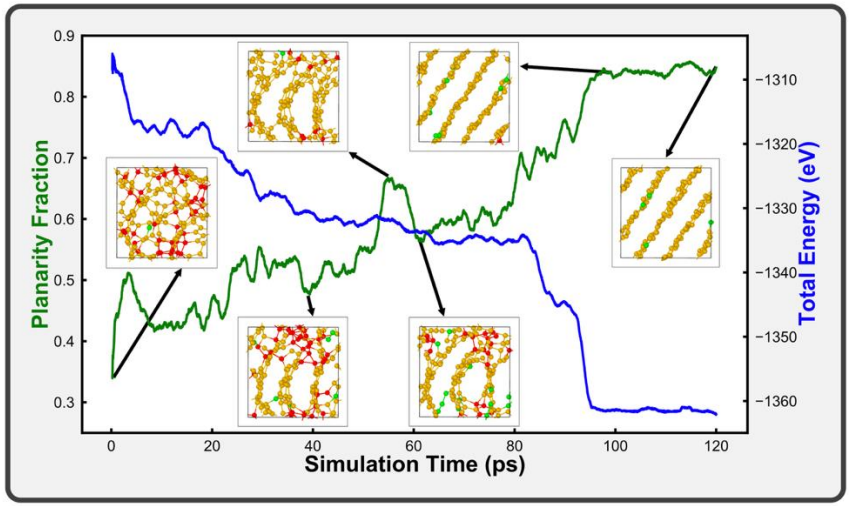
(Received 9 November 2016; published 3 March 2017)

The system layers in under 100 ps!

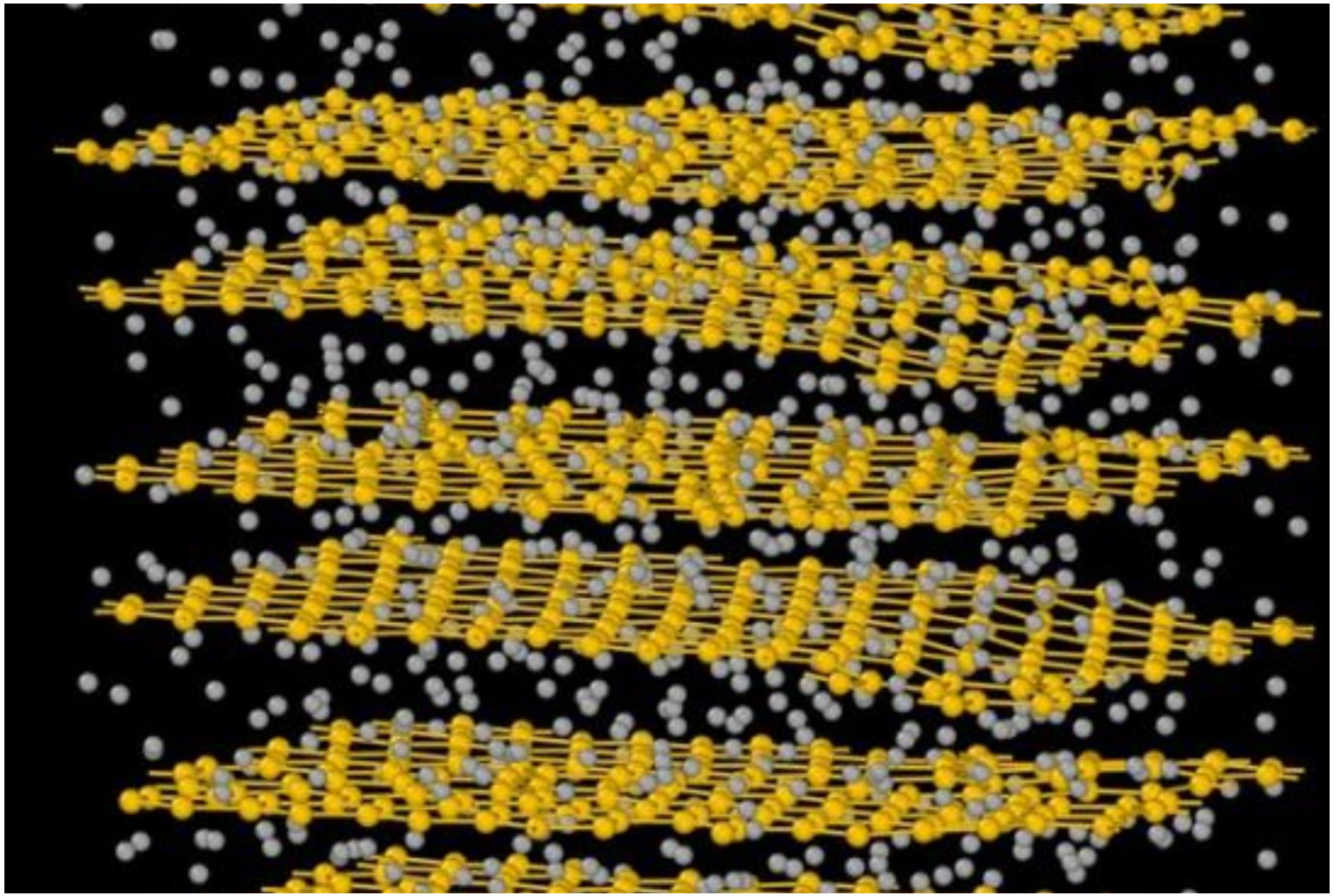
- “Cook” amorphous carbon with plane wave DFT – VASP and 160 atoms.
- It layers!





Ab initio simulation of amorphous graphite, Phys. Rev. Lett. **128** 236402 (2022); Atomistic nature of amorphous graphite, Phys. Chem. Glasses: Eur. J. of Glass Sci. and Tech. Part B **64** 16 (2023).

1000-atom GAP model (gold, relaxed after layering). Random (grey) starting conformation.

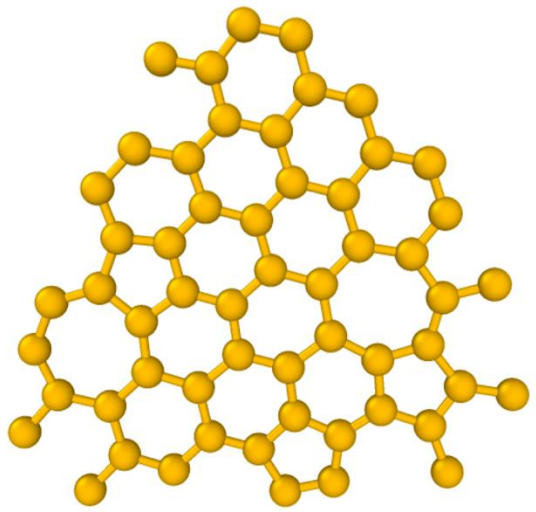


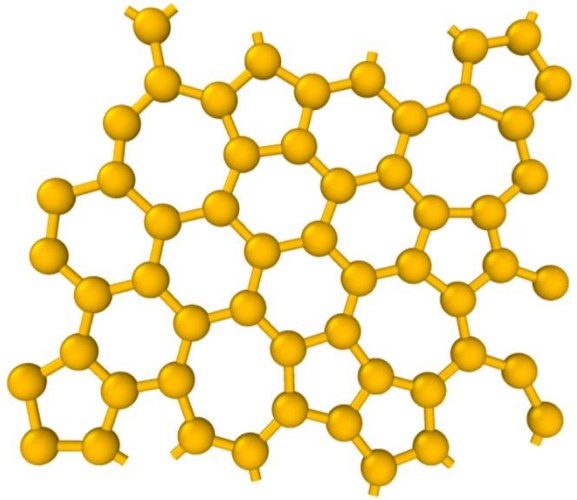
What's in the planes?

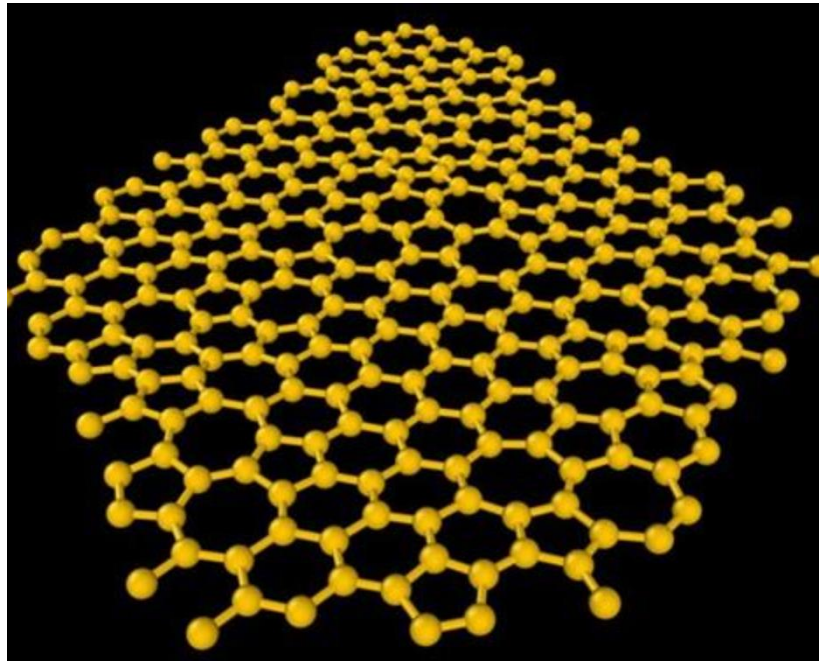
- Amorphous **GRAPHENE**: sp^2 carbon with topological (ring) disorder!

Above: VASP (plane-wave DFT, below ML GAP potential).

It works for *random* initial coordinates.







Dynamical simulation of layering.

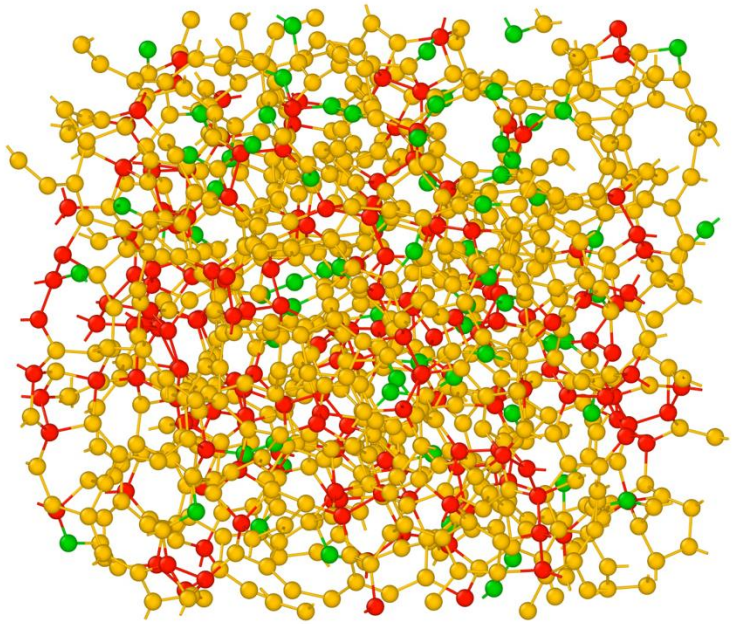
- 520, 1000 atoms, random coordinates near graphite density. Both using GAP.
- Constant-T simulation at T=3000K

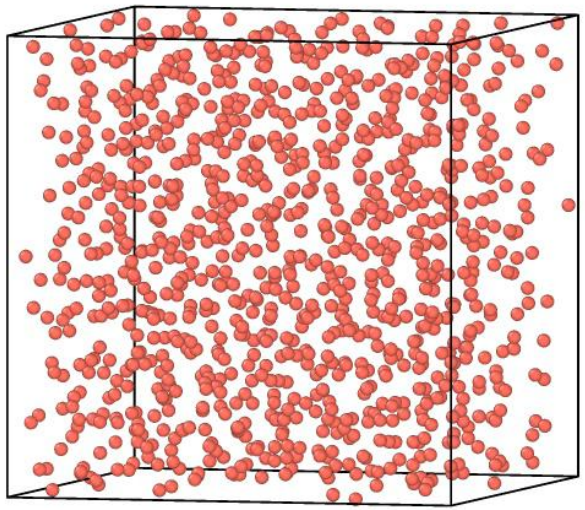
Colors:

Green: sp (two-fold) atoms

Yellow: sp^2 (three-fold, graphene-like)

Red: sp^3 (four-fold, diamondlike)





Space-projected conductivity

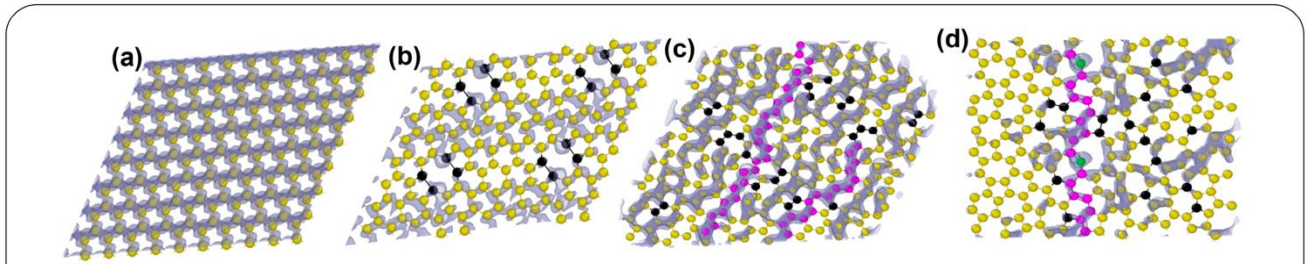


FIG. 5: SPC results (grey isosurface) for (a) an ideal graphene layer, (b) a graphene layer with 2 vacancies, (c) M1, and (d) M2. Atoms in pink in (c) and (d) show atoms forming conduction paths in the spatial grid, while atoms in black are border atoms where one or both neighboring rings are non-hexagon rings. Green colored atoms in (d) are consistent for SP atoms in M2.

Fact: odd-membered rings reduce electronic conduction

Space-projected conductivity and spectral properties of the conduction matrix, in “Form and Function of Disorder”, Physica Status Solidi B 2000438 (2020).

Comments

- We don’t get graphite – *we get flat layers of amorphous graphene*!
- Repeated many times, for densities from 2.2 gm/cc—2.8 gm/cc layering occurs. Often very flat, sometimes “undulating”. Takes *ca*. 100 ps (1 ps = 10^{-12} s) to layer.
- Occurs even for **random** starting conformations.
- Carried out with up to 2000 atoms.
- Graphite has preferred stacking. This stuff is disordered so no exact registry.
- Electrical conductivity influenced (reduced) by ring disorder.
- Physicist summary: a special disorder-order transition with long-range order (planes and galleries) but topological disorder in the planes.

Periodic boundary conditions and symmetry

- Non-cubic supercells produce layering with multiple crystallites and grain boundaries.
- So – consider a simulation with **open** BC. Fill sphere with carbon atoms randomly distributed at 2.44 gm/cm^3, Use GAP potential and anneal at 3000K. Consider 60, 300, 540, 840, 1374,2160 and 3774 atoms in the sphere.

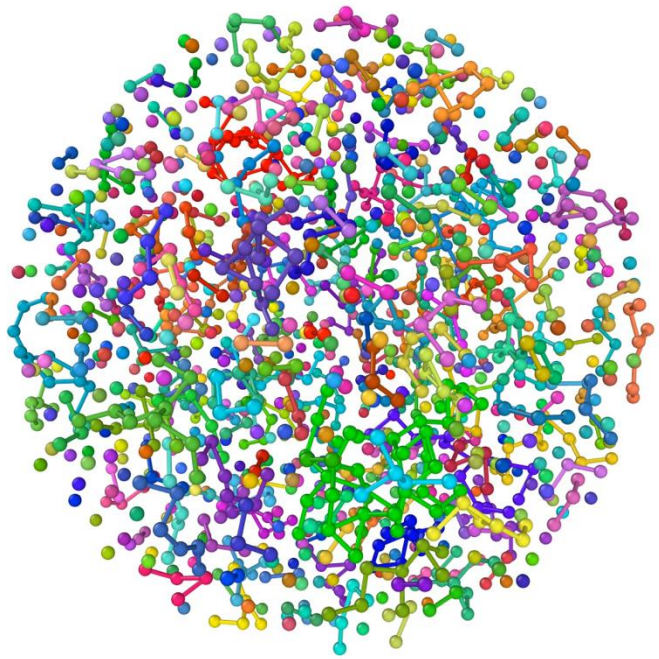
- Result: Multilayer fullerenes!

			layer Size [number of atoms]			
Model	τ[ps]	Layers	s_1	s_2	s_3	s_4
BO_{60}	41	one	60	-	-	-
BO_{300}	99	two	76	224	-	-
BO_{540}	104	two	174	366	-	-
BO_{840}	119	three	25	282	533	-
BO_{1374}	109	three	158	456	760	-
BO_{2160}	113	three	189	799	1172	-
BO_{3774}	131	four	316	572	1210	1676

Growing onions

1374 atom simulation, 3000K. *Layers fully formed after 110 ps.*

158/456/760 atoms per shell

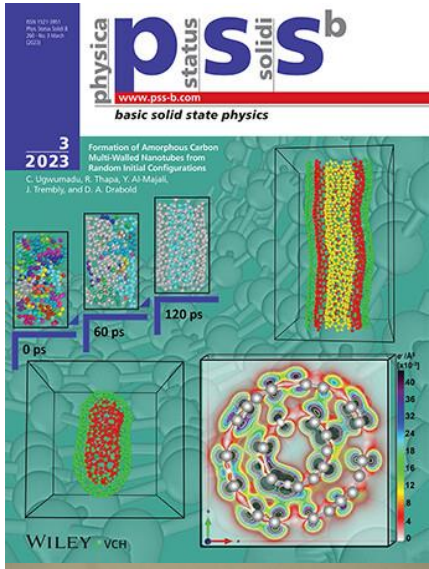


Multi-shell fullerene “Bucky Onion” structures

- Once again, for a suitable density and temperature window, carbon layers.
- No sp or sp^3 atoms – nothing but sp^2 at 3000K. Lots of ring defects, yet despite “no graphite registry” it still binds.
- Shell formation proceeds *from the surface in.*
- We checked GAP with VASP and SIESTA (DFT methods). VASP is inconvenient for this problem. GAP is a real space method -- ideal for molecules.

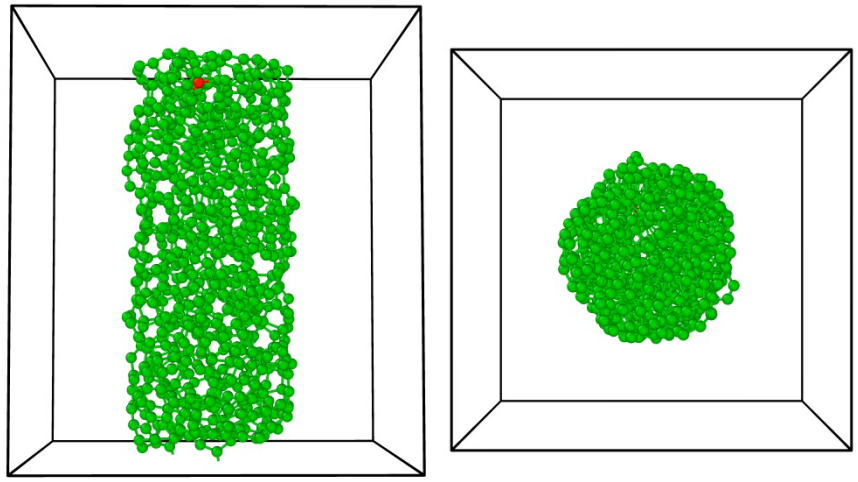
Multi-wall Nanotubes

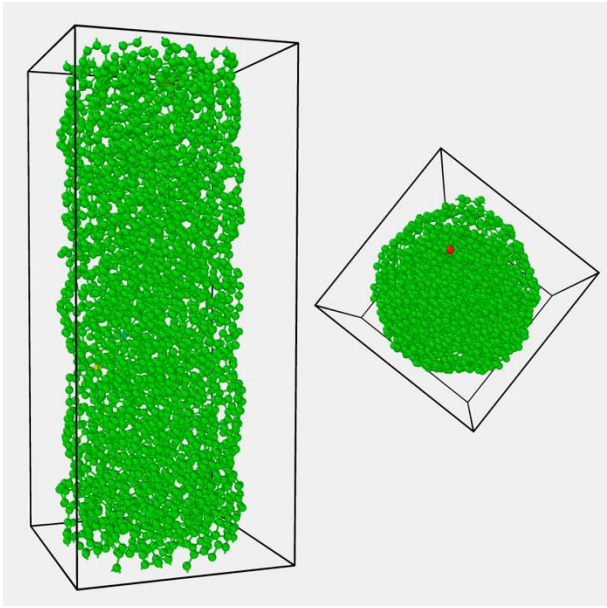
- Undertake the same approach but with cylindrical symmetry (periodic boundary conditions in one dimension).
- Random initial coordinates in a cylinder at density near graphite.
- Anneal at 3000K.
- Get nanotubes! (Not really this easy, subtleties of aspect ratios *etc*.).



C. Ugwumadu *et al*., Physica Status Solidi B, 2200527 (2023)

Nanotube Formation





Left: 840 atom simulation, 3000K.
Layers fully formed at 181 ps.

290/550 atoms in capped tube “capsule”.

3000 atom simulation, 3000K.
Layers fully formed at 205 ps.

164/541/986/1309 atoms in four hollow tubes.

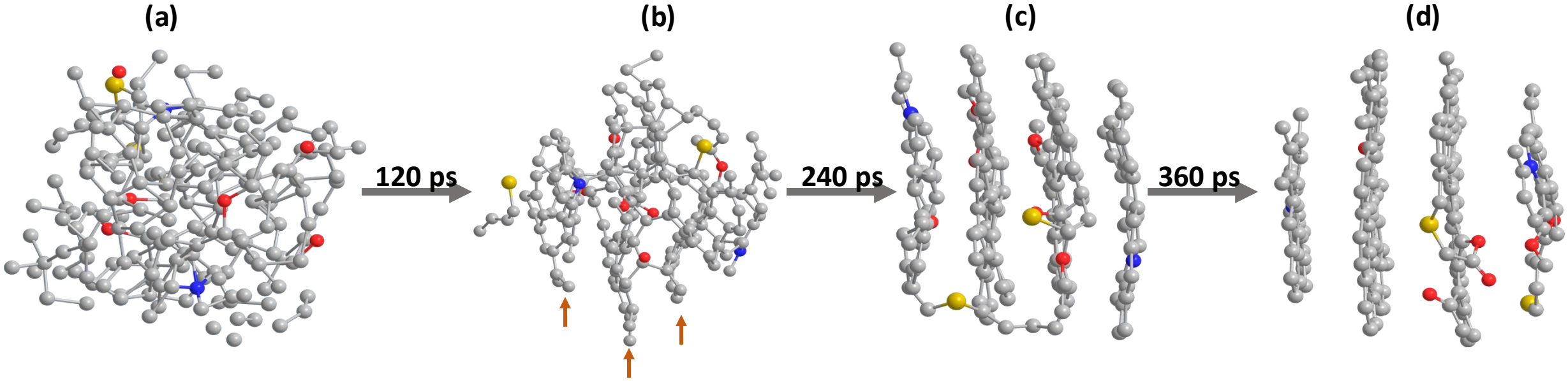
Discussion

- In significant temperature/density window carbon layers, we directly simulate the layering process in open and periodic systems.
- Unusual to see such a disorder-order transition from direct MD simulation.
- The interlayer interaction in the simulations is **not** primarily Van der Waals – dispersive forces are not included in our DFT (LDA or PBE) simulations!
- The cohesion accrues from Kohn-Sham states built from delocalized π orbitals near the Fermi level extending into the galleries (regions between planes). A kind of “weak metallic binding” results.
- If one includes VdW corrections, the layering still occurs.

Steps toward graphitization of coal

- Model effects of primary “coal impurities”: N, O, S… on layering and other properties.
- As in earlier work with elemental C, start with random model including 5% and 10% impurities
- Note – we leave out H (for now).

”Coal” to “Graphite” in a nutshell: **5% non-carbon** (190C, 6 O, 2N, 2S) [VASP] density=2.4 gm/cc. T=3000K. *sans* hydrogen.



Grey, carbon, red: oxygen, blue: nitrogen, yellow: sulfur

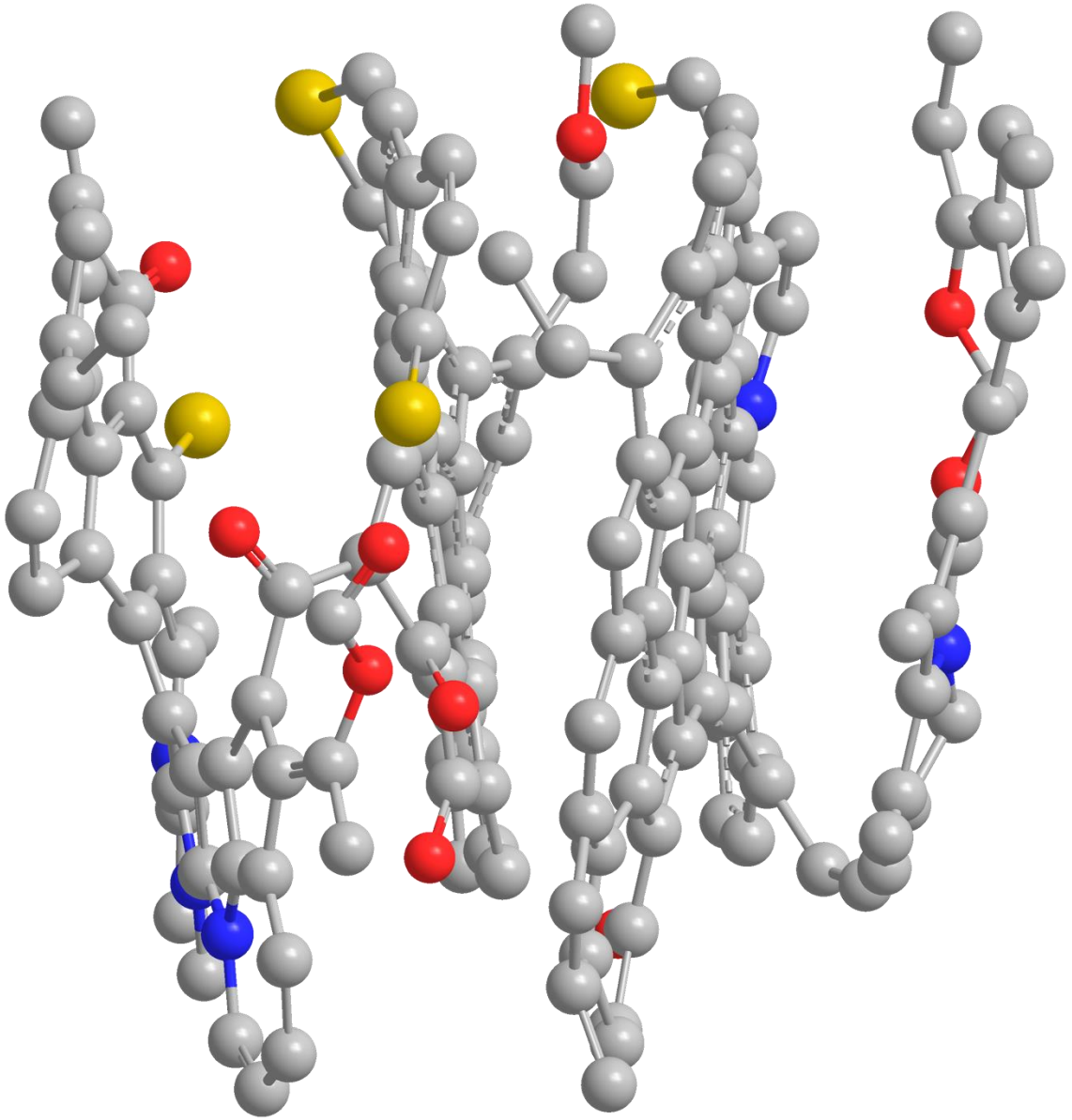
C. Ugwumadu *et al.* IOP Nanotechnology https://iopscience.iop.org/article/10.1088/1361-6528/ad1058

5% impurity simulation: comments

- Even with 5% impurities there is a strong proclivity to layer on a *ca*. 0.5 ns time scale.
- Nitrogen substitutes happily into sp^2 rings, ruins electrical conductivity.
- **O and S are big trouble**: they **break ring connectivity**, **decrease planarity**, and **electrical conductivity**.

10% impurities: weak/inadequate layering

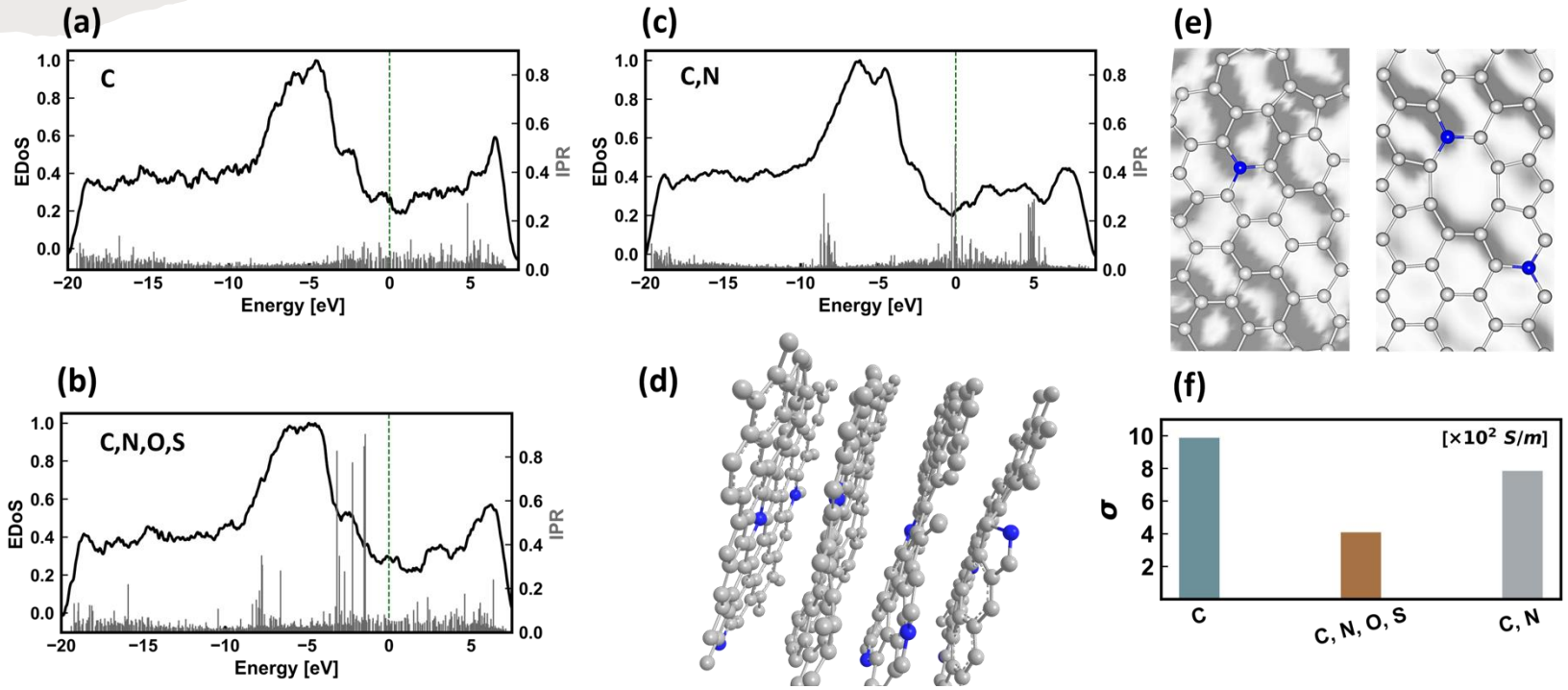
N: substitutional in planes; O, S highly disruptive



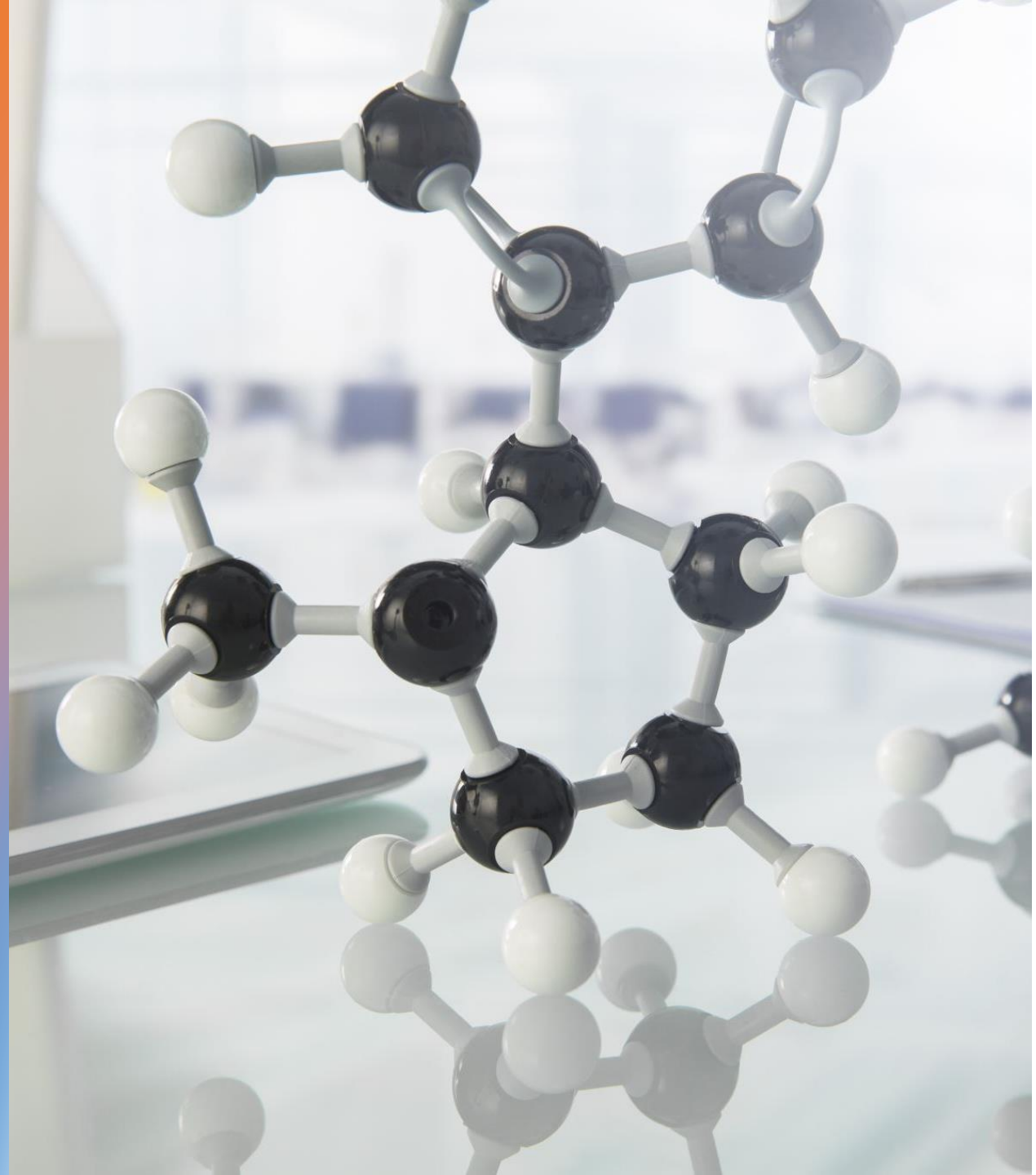
Grey, carbon, red: oxygen, blue: nitrogen, yellow: sulfur

Attempted graphitization – the movie!
(T=3000K)

Electronic structure and space-projected conductivity



Note: (d) and (e), N impurities only.



Overall conclusions

- There is some evidence that amorphous graphite might exist, we determined the mechanism of cohesion, and we computed the electronic properties.
- We find that similar processes apply in open systems, leading to bucky onions and multiwall nanotubes.
- We have begun to understand the challenge of graphitizing coal.

Collaborators

- Students: Rajendra Thapa and Chinonso Ugwumadu
- GAP potential: V. Deringer, G. Csanyi (Oxford/Cambridge)
- Carbon: J. Trembly [*et* group] (Ohio), Keerti Kappagantula (PNNL), M. Thorpe (ASU), B. Bhattarai and K. Subedi (Los Alamos)

Machine-Learning interatomic potentials

For a given configuration encountered:

- Identify local bonding environment in some form including all effects of “rotation” etc.
- Compare current configuration with what is in the database. Need a metric on the space of configurations.
- Determine whether existing database is adequate to provide energy, forces etc. from “interpolation”.
  - If adequate, take a time step with the “inferred” forces.
  - If not, **learn on the fly** – do a new quantum calculation on the configuration and add it to the database. Use the computed forces to take a time step

History II: DFT/*Ab initio* MD in a slide

$$\{\frac{-\hbar^2}{2m}\nabla^2 + V_{ext}(x) + V_{Hartree}(\rho[x]) + V_{xc}(\rho[x])\}\psi_i = \lambda\psi_i$$

Pick a representation, diagonalize (obtain $\{\psi\}$),
compute the density matrix $\rho_{\mu\nu}$. Then:

$$E_{bs} = Tr(\rho H)$$
$$n(\vec{R}) = < \vec{R} \mid \hat{\rho} \mid \vec{R} >$$
$$F_{bs}^{\alpha} = -\nabla_{\alpha} E_{bs}$$

Practical but computationally expensive: cubic or worse size scaling

Electronic structure:

Slices through a gallery:

Delocalized electron gas in the galleries between layers – main interlayer glue of a-graphite.

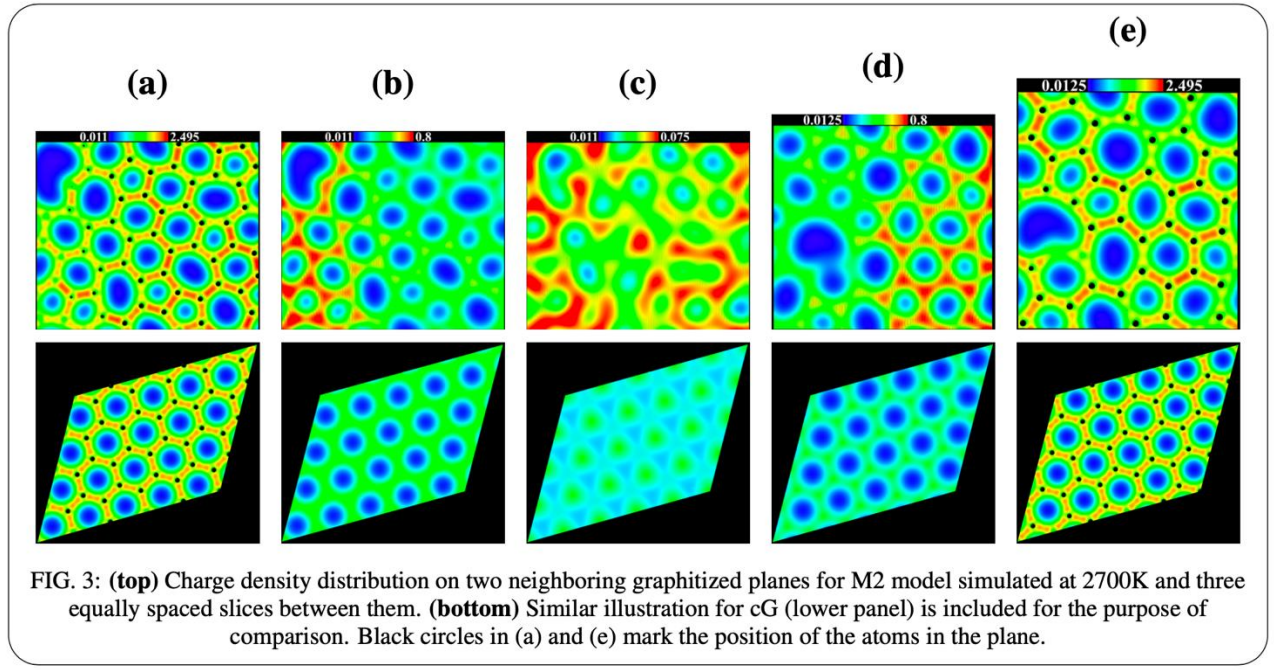


FIG. 3: **(top)** Charge density distribution on two neighboring graphitized planes for M2 model simulated at 2700K and three equally spaced slices between them. **(bottom)** Similar illustration for cG (lower panel) is included for the purpose of comparison. Black circles in (a) and (e) mark the position of the atoms in the plane.