Radboud Universiteit

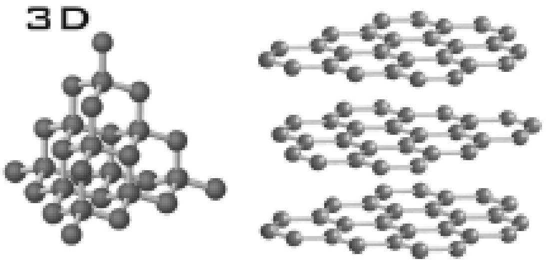
Hydrogen on graphene

Mikhail Katsnelson

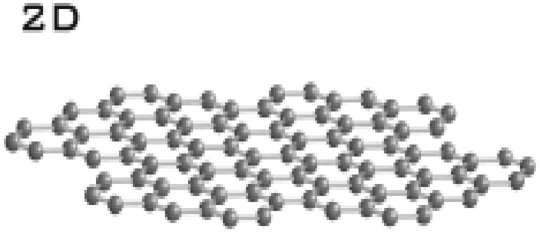
Thanks to Andre Geim, Danil Boukhvalov, Shengjun Yuan,
Sasha Lichtenstein, Tim Wehling and other collaborators

Allotropes of Carbon

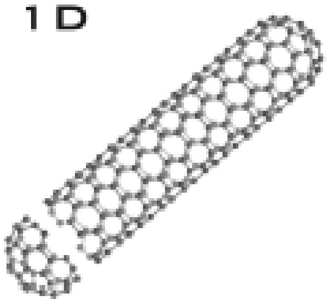
Diamond, Graphite



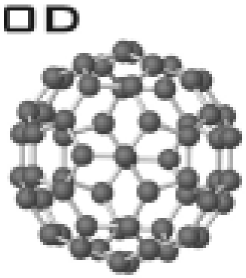
Graphene: prototype truly 2D crystal



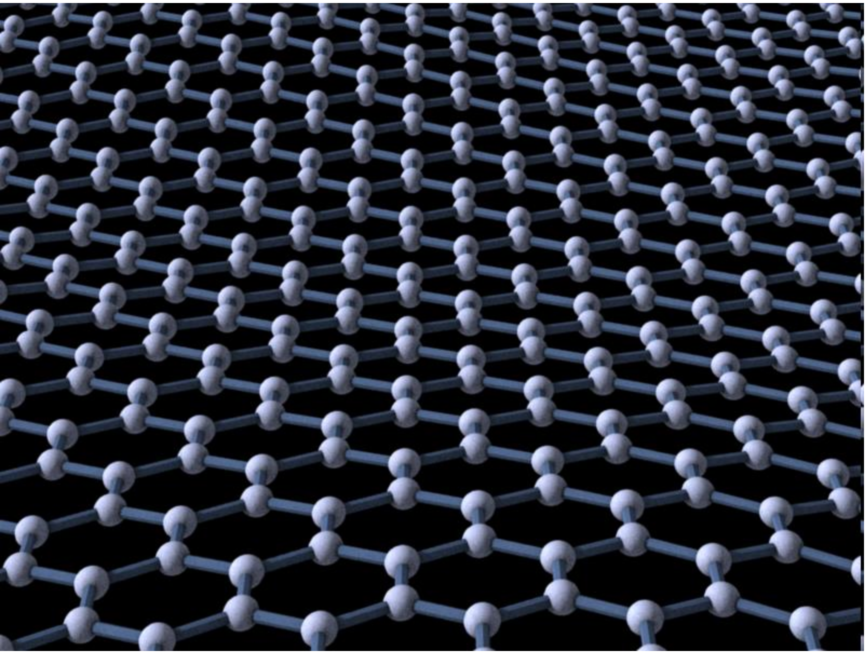
Nanotubes

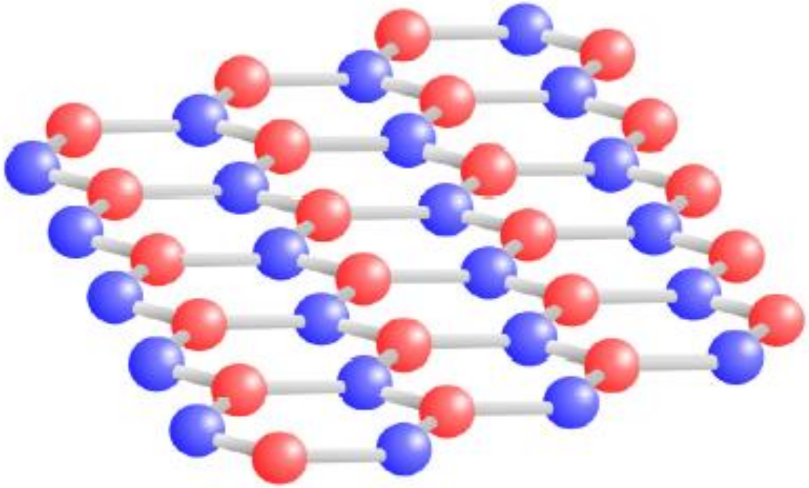


Fullerenes



Honeycomb lattice





Two equivalent sublattices, A and B (pseudospin)

Outline

1. Single H atom on graphene and randomly distributed H atoms
2. Fully hydrogenated graphene: graphane
3. Single-side hydrogenated graphene
4. Penetration of protons through graphene
5. Dissociation of molecular hydrogen on graphene
6. The role of ripples

Single H atom or pairs of atoms

D. W. Boukhvalov, MIK, A. I. Lichtenstein, Phys. Rev. B 77, 035427 (2008)

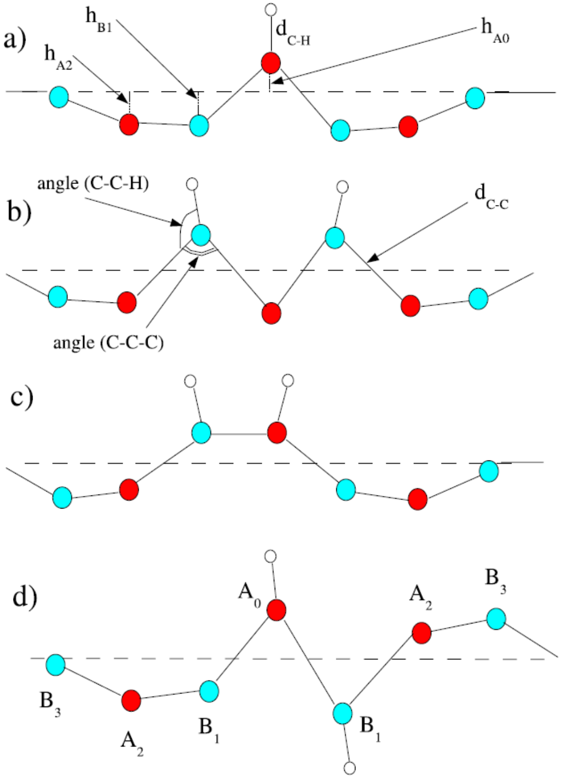


FIG. 3. (Color online) Picture of local distortions of graphene at chemisorption of (a) single hydrogen atom (A_0), (b) two hydrogen atoms bonded with carbon atoms from the same sublattice (A_0-A_2), (c) two hydrogen atoms bonded with neighboring carbon atoms from the same side of graphene sheet (A_0-B_1), and (d) two hydrogen atoms bonded with neighboring carbon atoms from both sides of graphene sheet (A_0-B_1'). Red and blue circles are carbon atoms from two sublattices and white circles are hydrogen atoms.

Atomic distortions are important

For two atoms: more favorable to sit in different sublattices, the most favorable is two-side

TABLE I. Dependence of magnetic moments M (in μ_B), chemisorption energies E_{chem} (in eV), and geometrical parameters (see Fig. 3), in deg. and Å, on configuration of hydrogen (see Fig. 3); d are interatomic distances and h are heights of atoms from graphene plane.

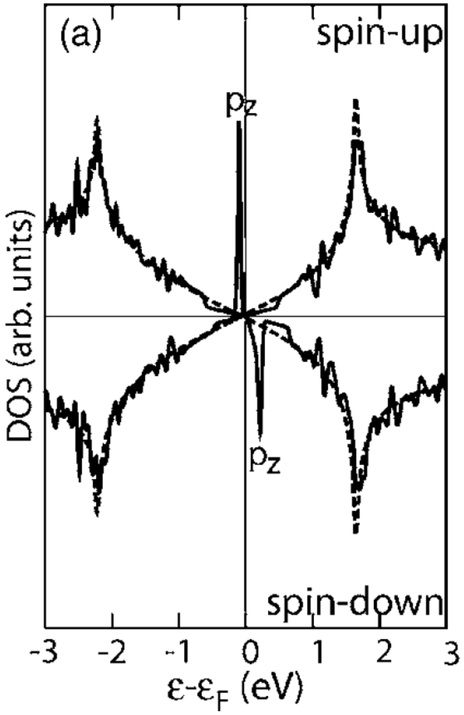
Configuration	M	E_{chem}	h_{A_0}	h_{B_1}	h_{A_2}	Angle (C-C-H)	Angle (C-C-C)	$d_{C—H}$	$d_{C—C}$
A_0	1.0	1.441	0.257	−0.047	−0.036	101.3	115.4	1.22	1.496
A_0-A_2	2.0	1.406	0.285	−0.040	−0.096	102.7	116.6	1.132	1.483
A_0-B_1	0.0	0.909	0.364	−0.088	−0.069	102.2	117.5	1.077	1.491
A_0-B_1'	0.0	0.540	0.298	−0.027	−0.035	105.1	106.7	1.112	1.512

Single H atom: electronic structure

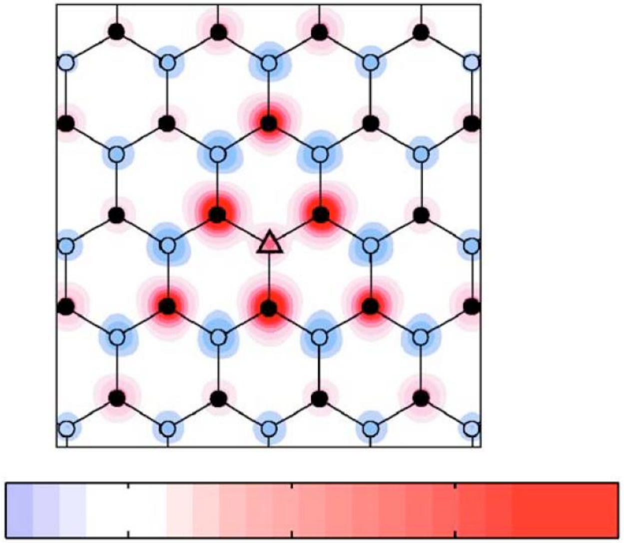
PHYSICAL REVIEW B **75**, 125408 (2007)

Defect-induced magnetism in graphene

Oleg V. Yazyev* and Lothar Helm



Midgap states, local magnetic moments are predicted



Spin-density projection around H atom

Very similar to eliminating carbon atom

Single H atom: electronic structure II

PRL **105,** 056802 (2010) PHYSICAL REVIEW LETTERS

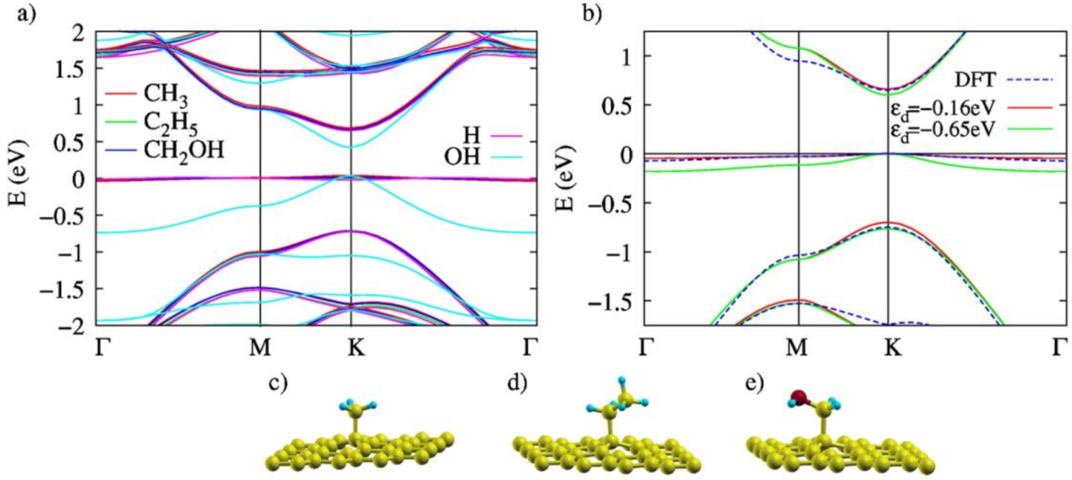
Resonant Scattering by Realistic Impurities in Graphene

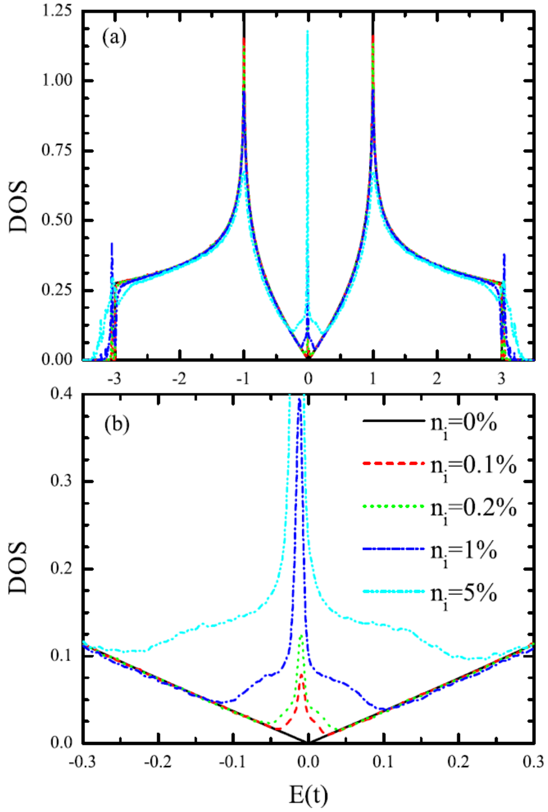
T. O. Wehling,[1,*] S. Yuan,[2] A. I. Lichtenstein,[1] A. K. Geim,[3] and M. I. Katsnelson[2]

Effective single-band model

$$\hat{H} = -t\sum_{\langle i,j\rangle} c_i^\dagger c_j \qquad \hat{H}_{\mathrm{imp}} = \epsilon_d d^\dagger d \qquad \hat{V} = V c_0^\dagger d + \mathrm{H.c.}$$

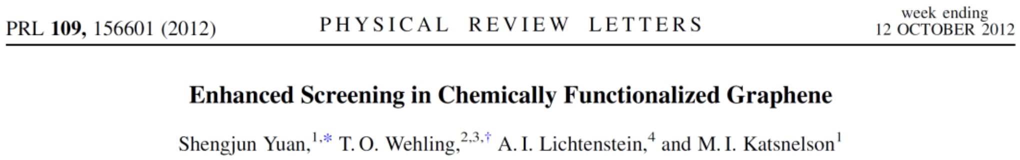
$$V \approx 2t = 5.2\ \mathrm{eV\ and}\ \epsilon_d \approx -t/16 = -0.16\ \mathrm{eV}$$





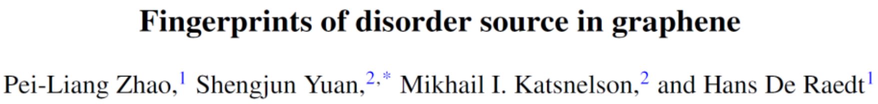
Electronic structure is very similar for H and for univalent hydrocarbon groups

Finite concentration: single-electron theory


PRL **109,** 156601 (2012) PHYSICAL REVIEW LETTERS week ending 12 OCTOBER 2012

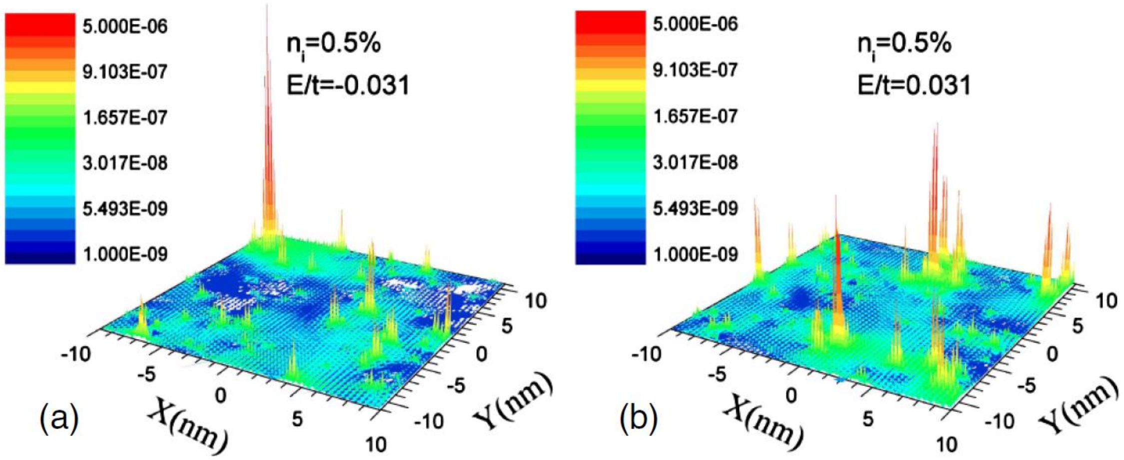
Enhanced Screening in Chemically Functionalized Graphene

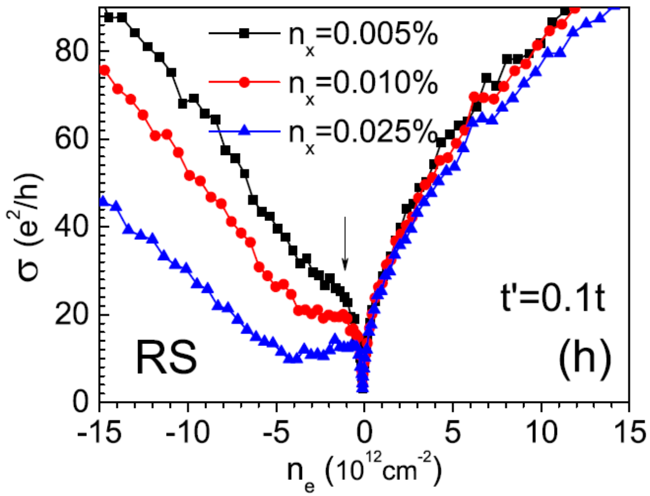
Shengjun Yuan,[1,*] T. O. Wehling,[2,3,†] A. I. Lichtenstein,[4] and M. I. Katsnelson[1]

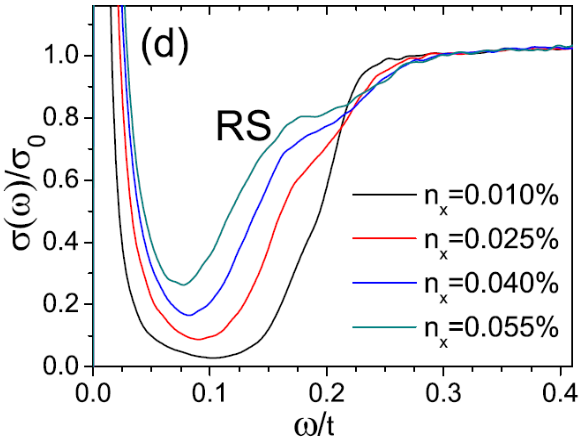

Fingerprints of disorder source in graphene

Pei-Liang Zhao,[1] Shengjun Yuan,[2,*] Mikhail I. Katsnelson,[2] and Hans De Raedt[1]


PHYSICAL REVIEW B **92**, 045437 (2015)







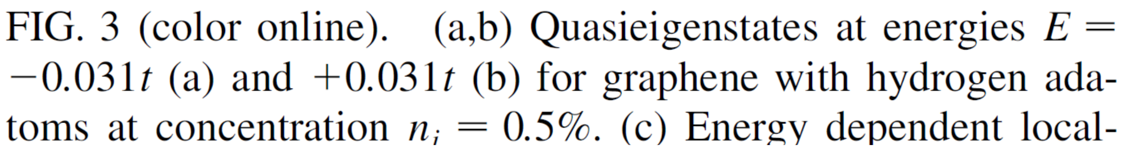
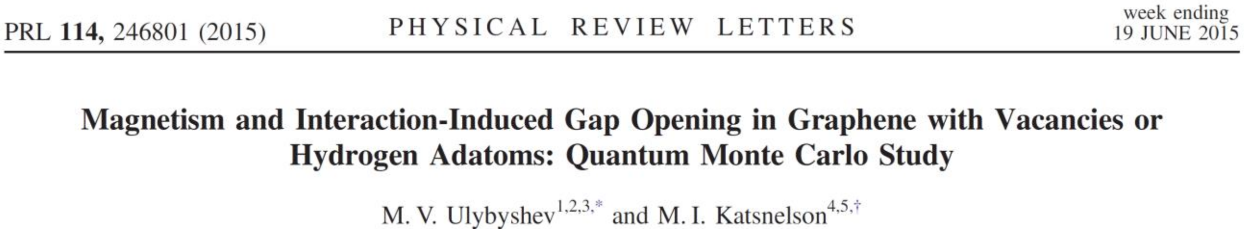


FIG. 3 (color online). (a,b) Quasieigenstates at energies $E = -0.031t$ (a) and $+0.031t$ (b) for graphene with hydrogen adatoms at concentration $n_i = 0.5\%$. (c) Energy dependent local-

Finite concentration: many-body effects

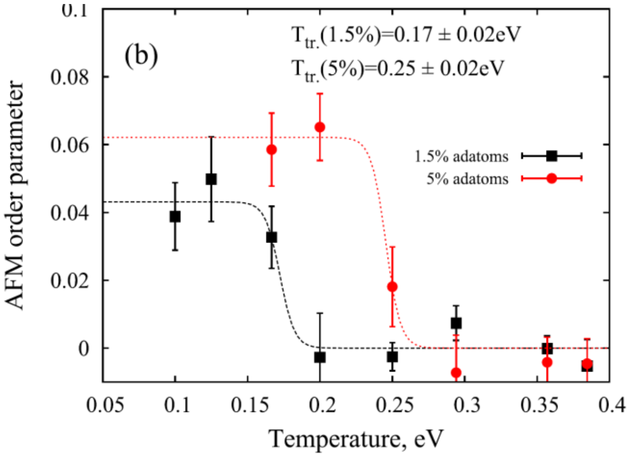


PRL **114**, 246801 (2015) PHYSICAL REVIEW LETTERS week ending 19 JUNE 2015

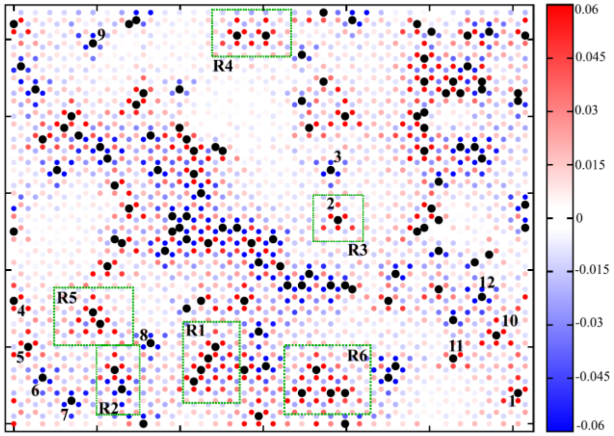
Magnetism and Interaction-Induced Gap Opening in Graphene with Vacancies or Hydrogen Adatoms: Quantum Monte Carlo Study

M. V. Ulybyshev[1,2,3,*] and M. I. Katsnelson[4,5,†]

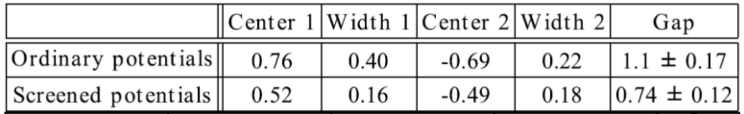
Lattice QMC calculations; two main effects: energy gap formation and strong antiferromagnetic correlations between induced local moments



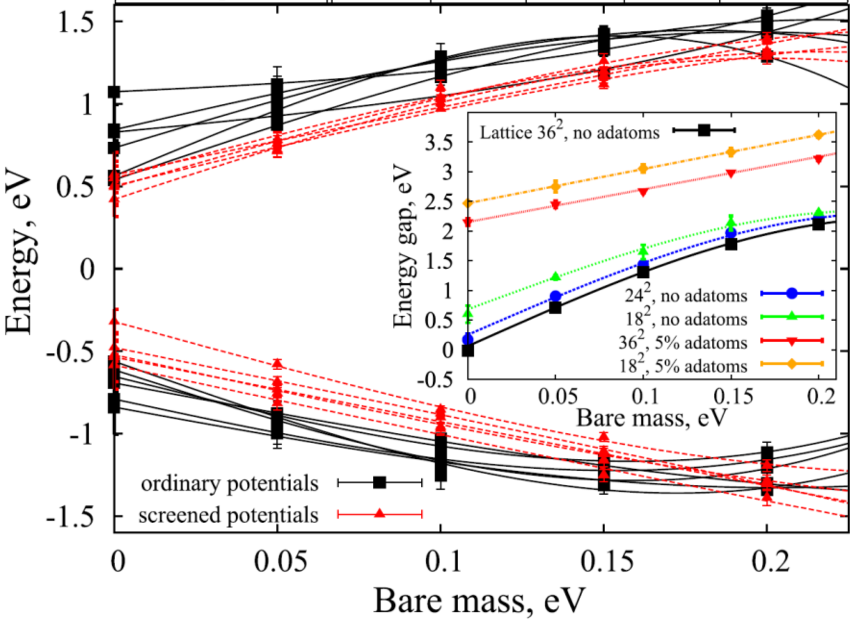
AFM correlations till very high *T*



Average spin distribution



	Center 1	Width 1	Center 2	Width 2	Gap
Ordinary potentials	0.76	0.40	-0.69	0.22	1.1 ± 0.17
Screened potentials	0.52	0.16	-0.49	0.18	0.74 ± 0.12



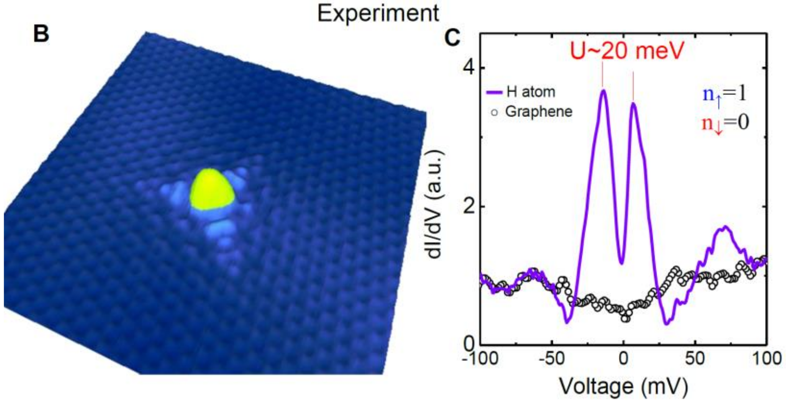
Energy gap opening (spontaneous in the limit zero bare mass)

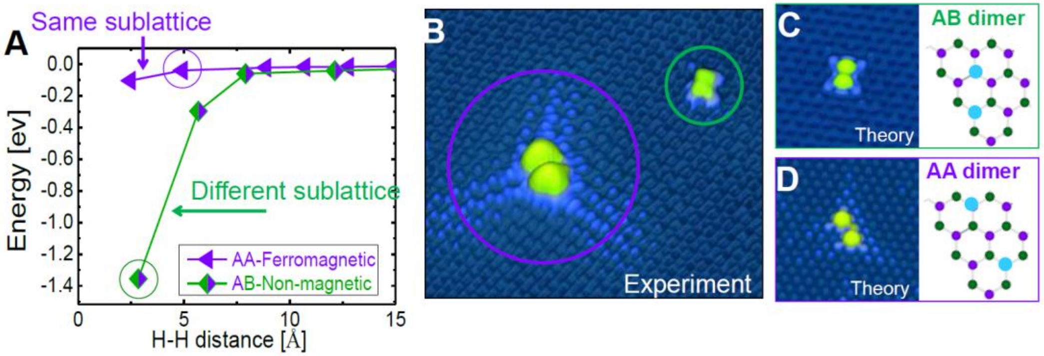
Several H atoms: experiment

Atomic-scale control of graphene magnetism using hydrogen atoms

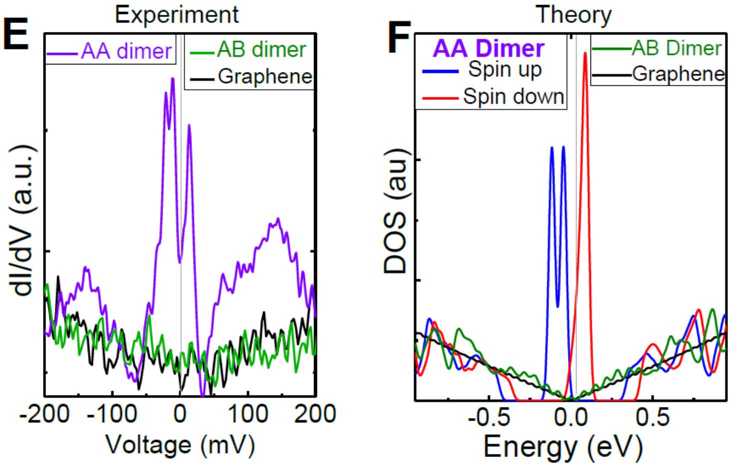
Authors: H. González-Herrero[1], J. M. Gómez-Rodríguez[1,2,3], P. Mallet[4,5], M. Moaied[1,6], J. J. Palacios[1,2,3], C. Salgado[1], M. M. Ugeda[7,8], J.Y. Veuillen[4,5], F. Yndurain[1,2,3] and I. Brihuega[1,2,3]

Science 352, 437 (2016)





Spin-split midgap states for single H atom on graphene



One can control graphene magnetism adding or deleting H atoms by STM tip

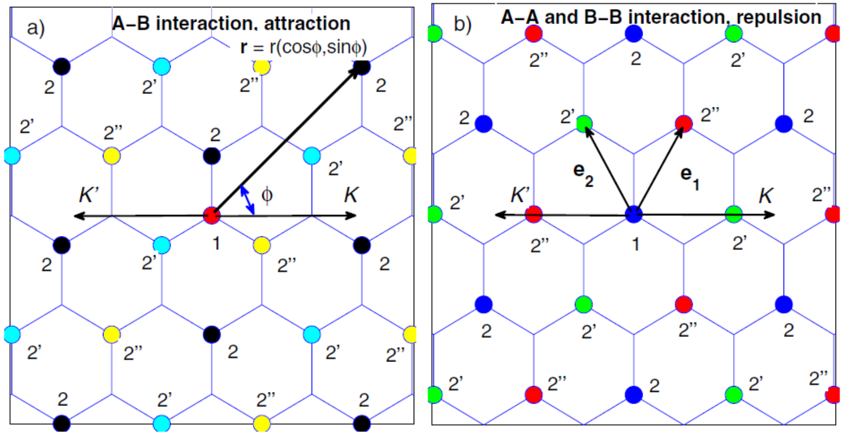
FM interaction between AA atoms and AFM between AB atoms

Interaction at large distances

PRL **103,** 016806 (2009) PHYSICAL REVIEW LETTERS week ending 3 JULY 2009

Long-Range Interaction between Adatoms in Graphene

Andrei V. Shytov,[1] Dmitry A. Abanin,[2] and Leonid S. Levitov[3]



Two resonant scatterers

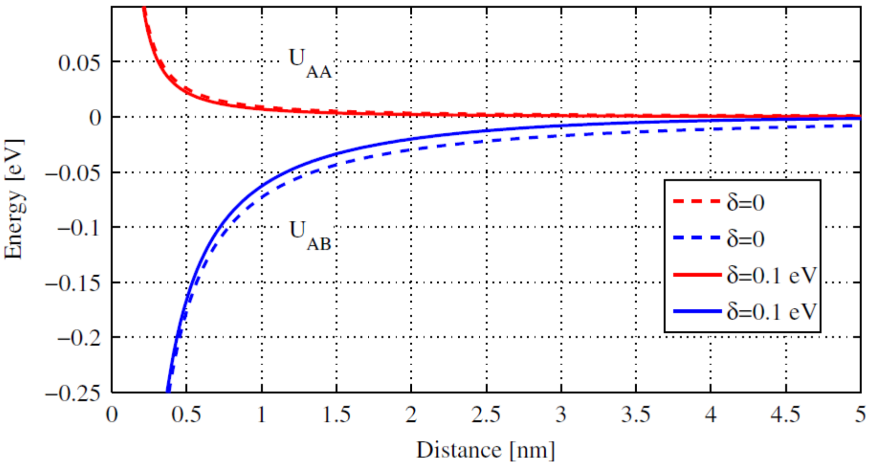
$$\Omega = -T\sum_{\varepsilon_n}\mathrm{Tr}\ln(1 - T_1 G_{12} T_2 G_{21})$$

$$T_0(i\varepsilon) = \frac{\pi v_0^2}{i\varepsilon\ln(W/|\varepsilon|) + \delta}, \qquad |\delta| \ll W \approx 3t_0$$

$$U_{AB}(\tilde{a} \lesssim r \ll \hbar v_0/\delta) \approx -\frac{\hbar v_0 |\sin(\mathbf{Kr} + \phi)|}{r\log(r/\tilde{a})}$$

$$U_{AA}(\tilde{a} \lesssim r \ll \hbar v_0/\delta) \approx \frac{\pi\hbar v_0}{4r\log^2(r/\tilde{a})}\cos^2(\mathbf{Kr})$$

$$\tilde{a} = \hbar v_0/W$$



Graphane: two-side hydrogenated graphene

Graphane: fully hydrogenated graphene CH

Science **323**, 610 (2009)

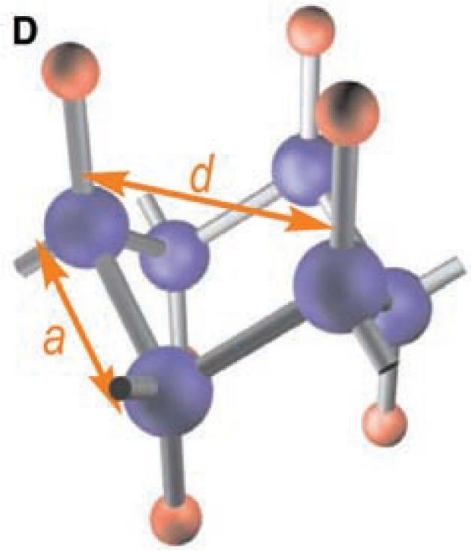
Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane

D. C. Elias,[1*] R. R. Nair,[1*] T. M. G. Mohiuddin,[1] S. V. Morozov,[2] P. Blake,[3] M. P. Halsall,[1] A. C. Ferrari,[4] D. W. Boukhvalov,[5] M. I. Katsnelson,[5] A. K. Geim,[1,3] K. S. Novoselov[1]†

Evidences: gap formation, Raman spectra…

Chemical stability is quite low (contrary to CF)

Electronic structure

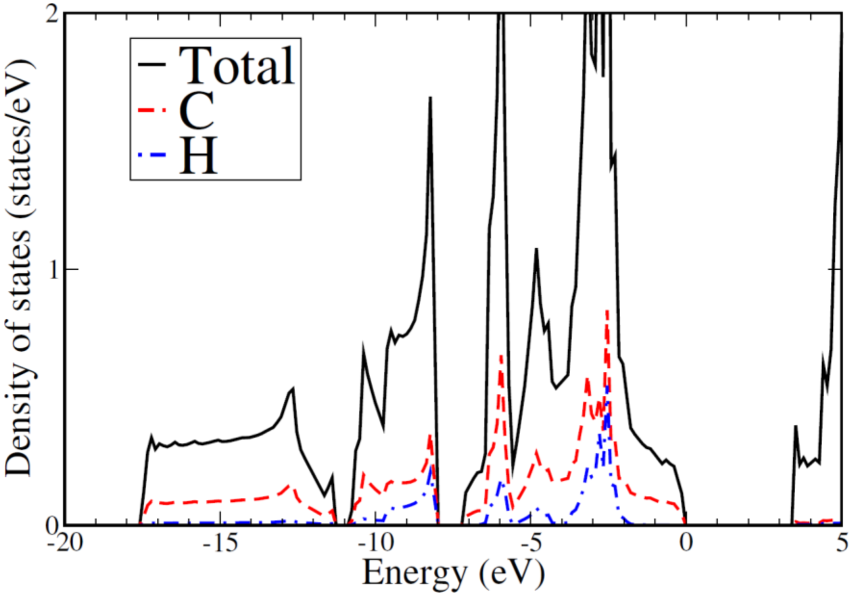


Schematic structure

PHYSICAL REVIEW B **79**, 245117 (2009)

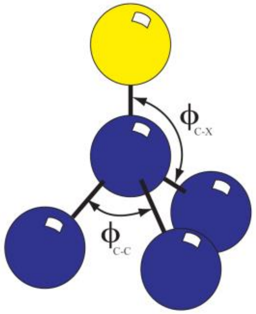
Accurate electronic band gap of pure and functionalized graphene from GW calculations

S. Lebègue,[1] M. Klintenberg,[2] O. Eriksson,[2] and M. I. Katsnelson[3]



Gap about 5 eV

Stability of various CX compounds



PHYSICAL REVIEW B **81**, 085433 (2010)

Theoretical analysis of the chemical bonding and electronic structure of graphene interacting with Group IA and Group VIIA elements

M. Klintenberg,[1,*] S. Lebègue,[2] M. I. Katsnelson,[3] and O. Eriksson[1]

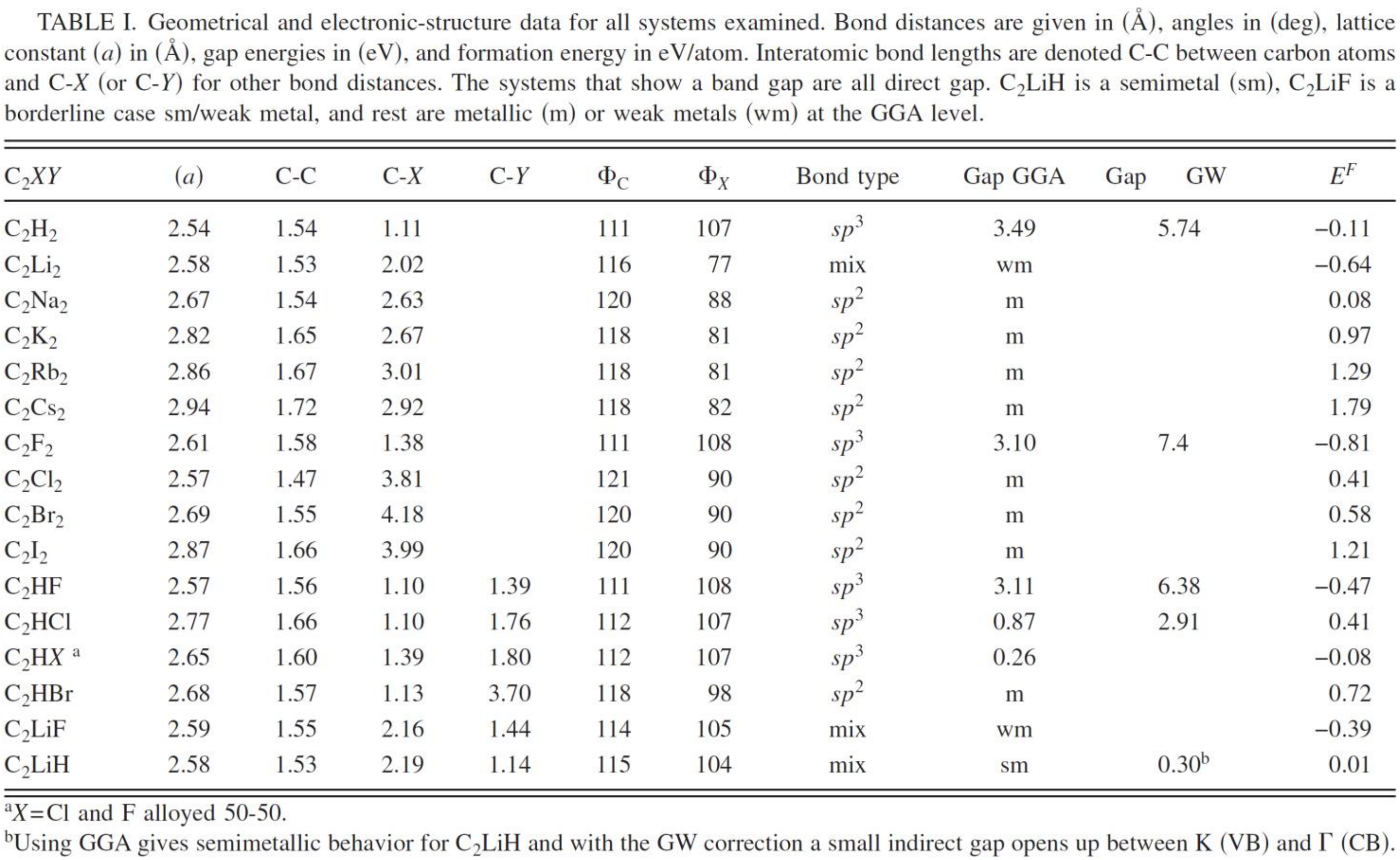


TABLE I. Geometrical and electronic-structure data for all systems examined. Bond distances are given in (Å), angles in (deg), lattice constant (a) in (Å), gap energies in (eV), and formation energy in eV/atom. Interatomic bond lengths are denoted C-C between carbon atoms and C-X (or C-Y) for other bond distances. The systems that show a band gap are all direct gap. C_2LiH is a semimetal (sm), C_2LiF is a borderline case sm/weak metal, and rest are metallic (m) or weak metals (wm) at the GGA level.

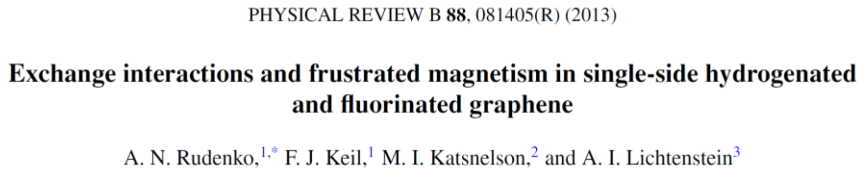
C_2XY	(a)	C-C	C-X	C-Y	Φ_C	Φ_X	Bond type	Gap GGA	Gap GW	E^F
C_2H_2	2.54	1.54	1.11		111	107	sp^3	3.49	5.74	−0.11
C_2Li_2	2.58	1.53	2.02		116	77	mix	wm		−0.64
C_2Na_2	2.67	1.54	2.63		120	88	sp^2	m		0.08
C_2K_2	2.82	1.65	2.67		118	81	sp^2	m		0.97
C_2Rb_2	2.86	1.67	3.01		118	81	sp^2	m		1.29
C_2Cs_2	2.94	1.72	2.92		118	82	sp^2	m		1.79
C_2F_2	2.61	1.58	1.38		111	108	sp^3	3.10	7.4	−0.81
C_2Cl_2	2.57	1.47	3.81		121	90	sp^2	m		0.41
C_2Br_2	2.69	1.55	4.18		120	90	sp^2	m		0.58
C_2I_2	2.87	1.66	3.99		120	90	sp^2	m		1.21
C_2HF	2.57	1.56	1.10	1.39	111	108	sp^3	3.11	6.38	−0.47
C_2HCl	2.77	1.66	1.10	1.76	112	107	sp^3	0.87	2.91	0.41
C_2HX [a]	2.65	1.60	1.39	1.80	112	107	sp^3	0.26		−0.08
C_2HBr	2.68	1.57	1.13	3.70	118	98	sp^2	m		0.72
C_2LiF	2.59	1.55	2.16	1.44	114	105	mix	wm		−0.39
C_2LiH	2.58	1.53	2.19	1.14	115	104	mix	sm	0.30[b]	0.01

[a] X=Cl and F alloyed 50-50.

[b] Using GGA gives semimetallic behavior for C_2LiH and with the GW correction a small indirect gap opens up between K (VB) and Γ (CB).

Chemical bond with H is much weaker than with F or Li

Single-side hydrogenated graphene



PHYSICAL REVIEW B **88**, 081405(R) (2013)

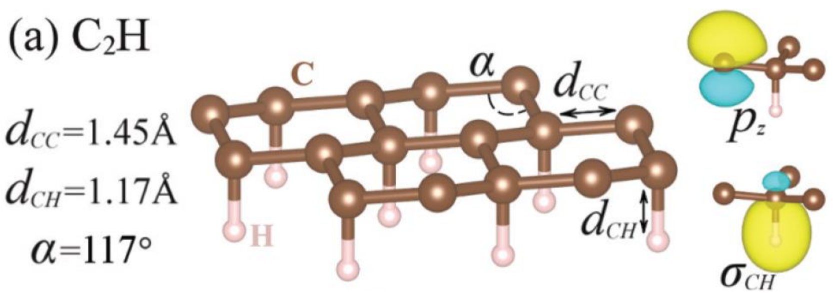
Exchange interactions and frustrated magnetism in single-side hydrogenated and fluorinated graphene

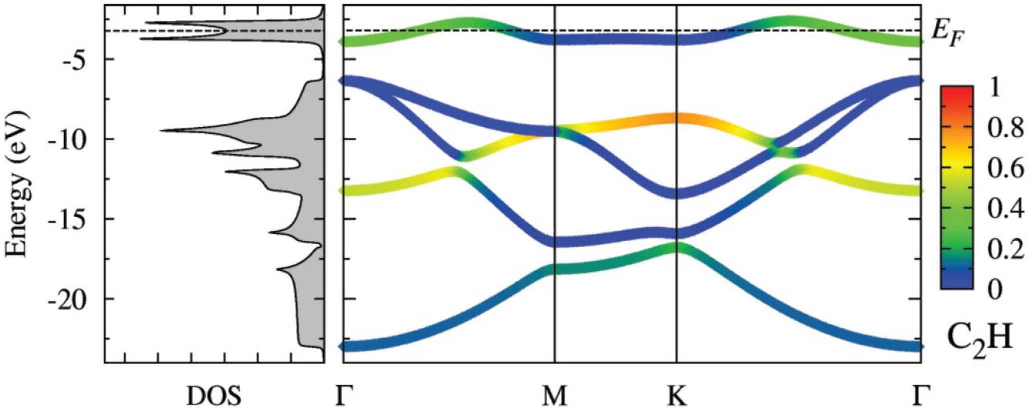
A. N. Rudenko,[1,*] F. J. Keil,[1] M. I. Katsnelson,[2] and A. I. Lichtenstein[3]

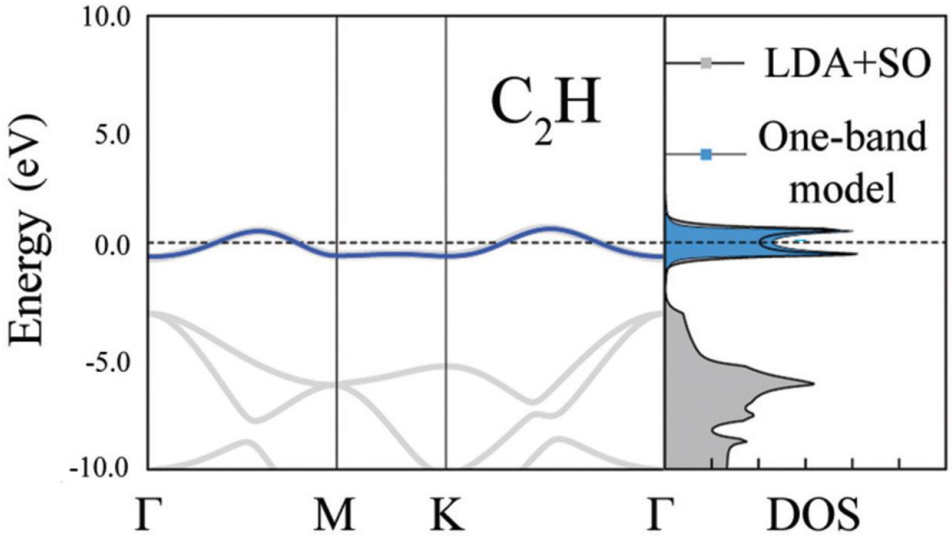
PHYSICAL REVIEW B **94**, 214411 (2016)

Role of direct exchange and Dzyaloshinskii-Moriya interactions in magnetic properties of graphene derivatives: C_2F and C_2H

V. V. Mazurenko,[1] A. N. Rudenko,[1,2] S. A. Nikolaev,[1] D. S. Medvedeva,[1] A. I. Lichtenstein,[1,3] and M. I. Katsnelson[1,2]







"Impurity" band well separated from other bands

Strong electron correlations within this Band

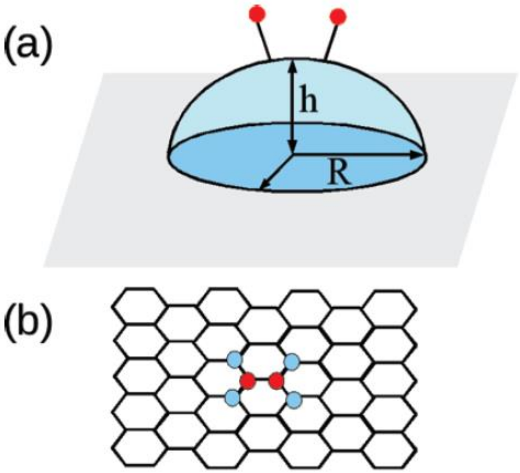
Frustrated magnetic interactions, competition between FM and spin spiral states

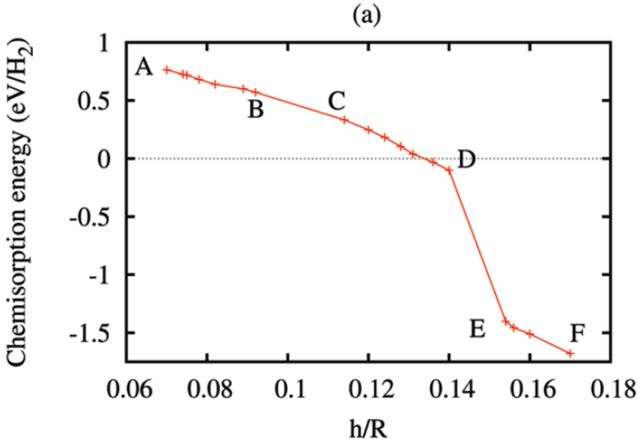
Curvature is crucially important!

Enhancement of Chemical Activity in Corrugated Graphene

Danil W. Boukhvalov* and Mikhail I. Katsnelson†

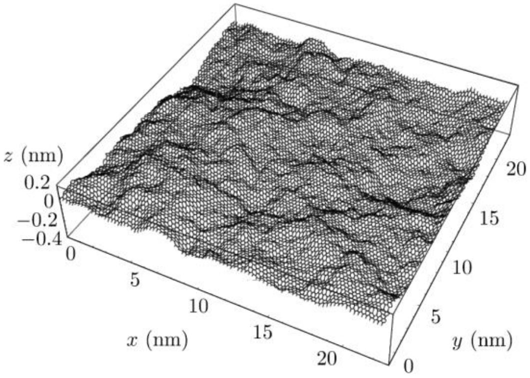
J. Phys. Chem. C **2009,** *113,* 14176–14178



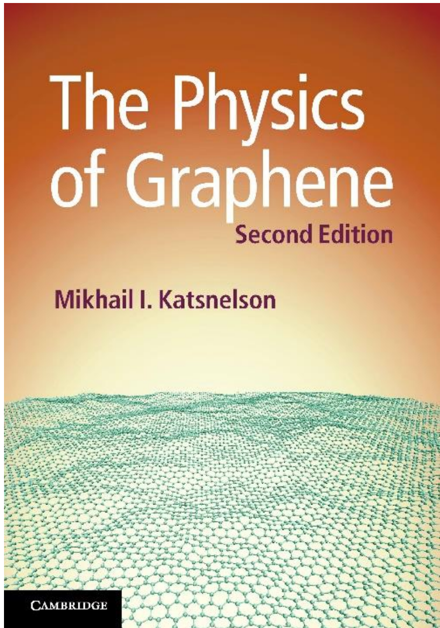


Graphene is curved due to thermal fluctuations (or due to roughness of substrate)

A.Fasolino, J. H. Los, MIK, Intrinsic ripples in graphene, Nat. Mater. 6, 858 (2007)



Graphene at room temperature

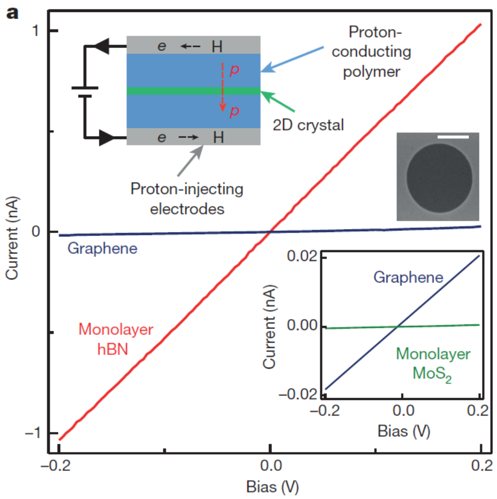


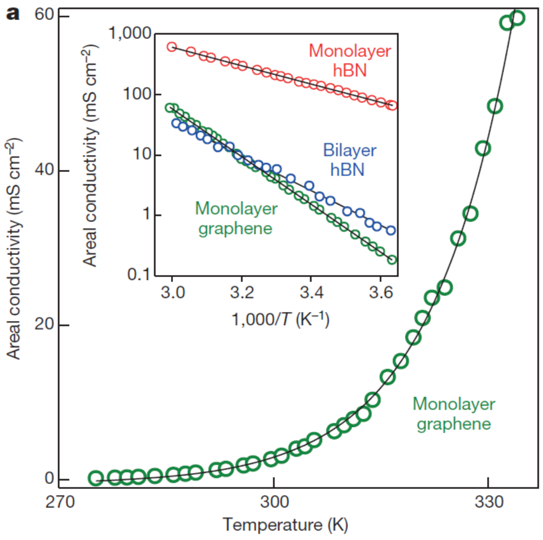
Proton permeation through graphene and hBN

Proton transport through one-atom-thick crystals

2014 | VOL 516 | NATURE | 227

S. Hu[1,2], M. Lozada-Hidalgo[1], F. C. Wang[3], A. Mishchenko[1], F. Schedin[2], R. R. Nair[1], E. W. Hill[2], D. W. Boukhvalov[4],
M. I. Katsnelson[4], R. A. W. Dryfe[5], I. V. Grigorieva[1], H. A. Wu[3] & A. K. Geim[1,2]





The transport barrier heights E for different 2D crystals are obtained by measuring σ as a function of temperature T (Fig. 2a), revealing that proton conductivities exhibit Arrhenius-type behaviour, $\exp(-E/k_BT)$, where k_B is the Boltzmann constant. We note that the conductivity of Nafion contributes little to the overall value of S, and changes only by a factor of two over the T range examined (Extended Data Fig. 8). The data in Fig. 2a yield $E = 0.78 \pm 0.03$, 0.61 ± 0.04 and 0.3 ± 0.02 eV for graphene, bilayer hBN and monolayer hBN, respectively. Measurements on different devices give values that are reproducible within our experimental accuracy of ~10% (Extended Data Fig. 4). This is consistent with the high reproducibility of σ found for different devices (Fig. 1b) because otherwise different E values should yield hugely different σ values at a given T.

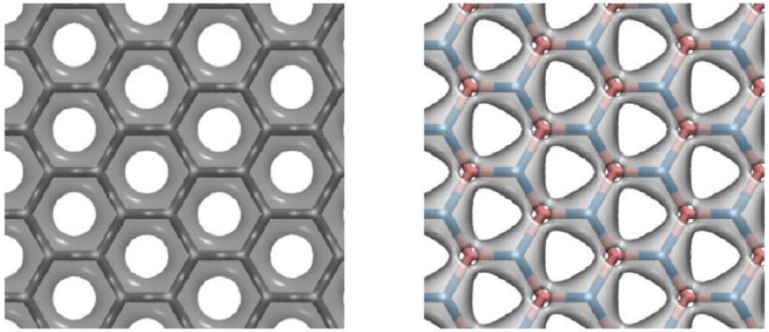
The barrier to proton transport through graphene we have determined is notably lower than the 1.2–2.2 eV found in *ab initio* molecular dynamics simulations and calculations using the climbing-image nudged elastic band method[4–6], which would result in proton conductivities millions of times smaller and undetectable in our experiments. We have reproduced the earlier barrier calculations for graphene and extended them to monolayer hBN (‘Theoretical analysis of proton transport through 2D crystals’ in Methods), obtaining values of $E = 1.25$–1.40 eV for graphene, in agreement with refs 4, 5, and ~0.7 eV for monolayer hBN. The disagreement between experiment and theory in the absolute value of E is perhaps not surprising given the complex nature of possible transport pathways and the sensitivity of the calculations to pseudopotentials, the exchange correlation functional and so on. The difference might also arise because protons in Nafion and water move along hydrogen bonds[25] rather than in vacuum as assumed by theory so far.

Proton permeation through graphene and hBN II

Strong disagreement between theory and experiment

Density functional based simulations of proton permeation of graphene and hexagonal boron nitride†

J. M. H. Kroes,* A. Fasolino and M. I. Katsnelson



(a) graphene **(b)** h-BN

Fig. 1 Electron density clouds at an isovalue of 0.1 e$^-$ Bohr^{-3} for mono-layer graphene (a) and h-BN (b) with B (N) in pink (blue).

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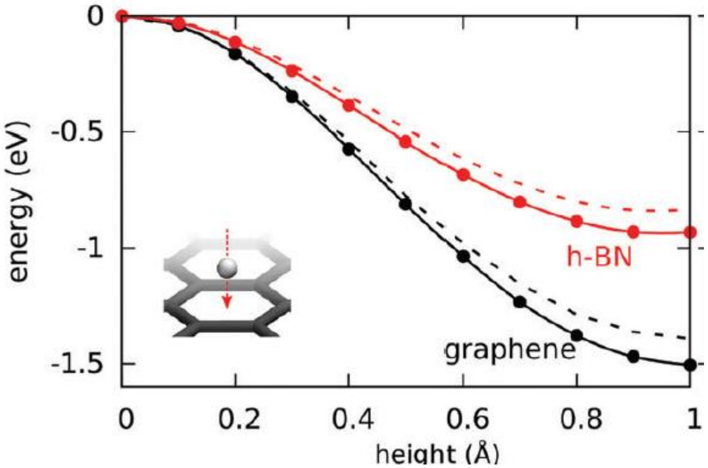
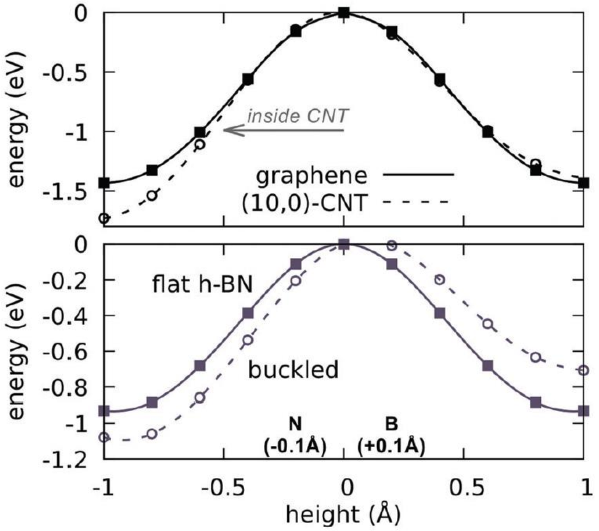


Curvature does not help, solvent does not help…
Experimentalists insist: no holes etc.

The problem remains open

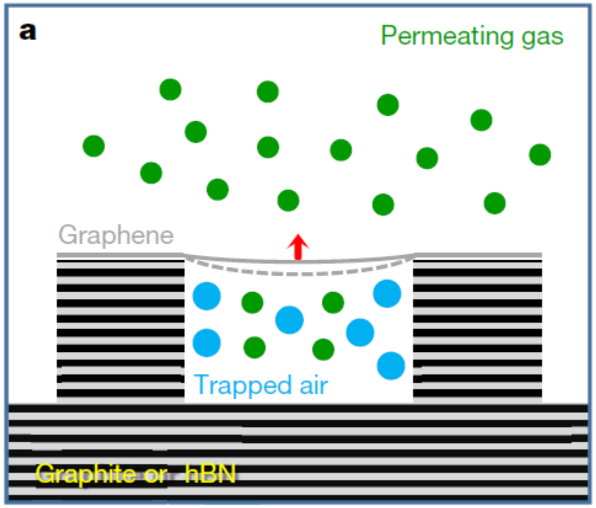


Decomposition of molecular hydrogen

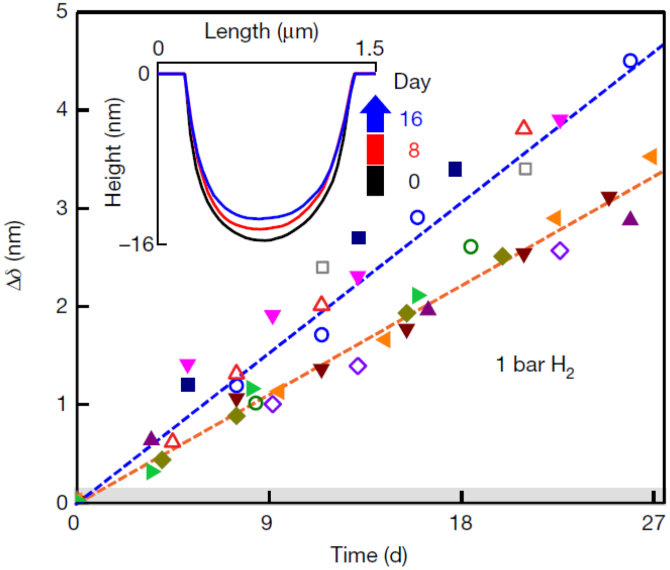
Limits on gas impermeability of graphene

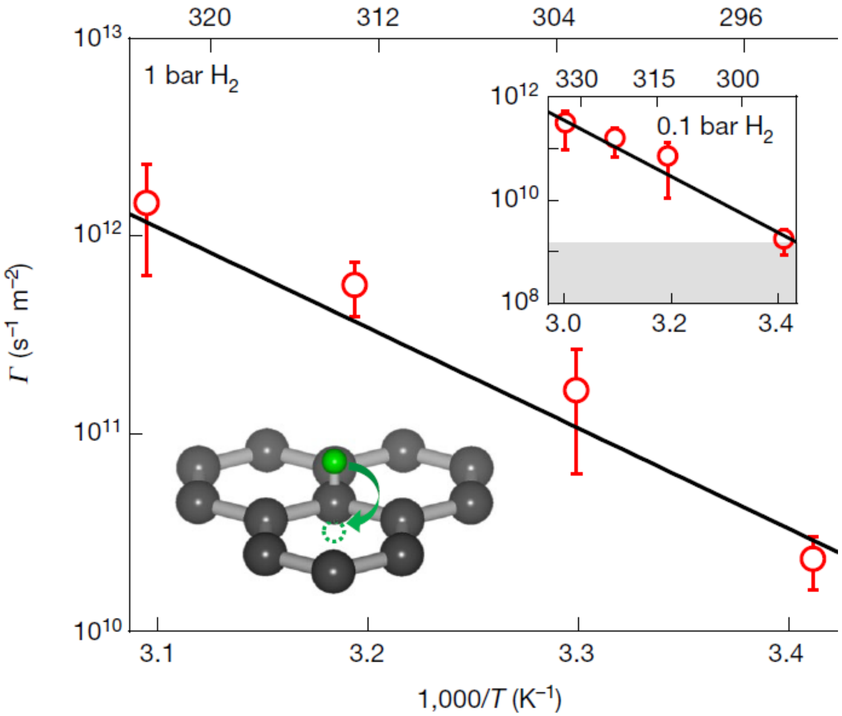
Nature | Vol 579 | 12 March 2020 | **229**

P. Z. Sun[1,2], Q. Yang[1,2], W. J. Kuang[1], Y. V. Stebunov[1,2], W. Q. Xiong[3], J. Yu[4], R. R. Nair[2], M. I. Katsnelson[4], S. J. Yuan[3,4]✉, I. V. Grigorieva[1], M. Lozada-Hidalgo[1], F. C. Wang[1,2,5] & A. K. Geim[1,2]✉



Graphene is impermeable for any gases including He but excluding molecular hydrogen

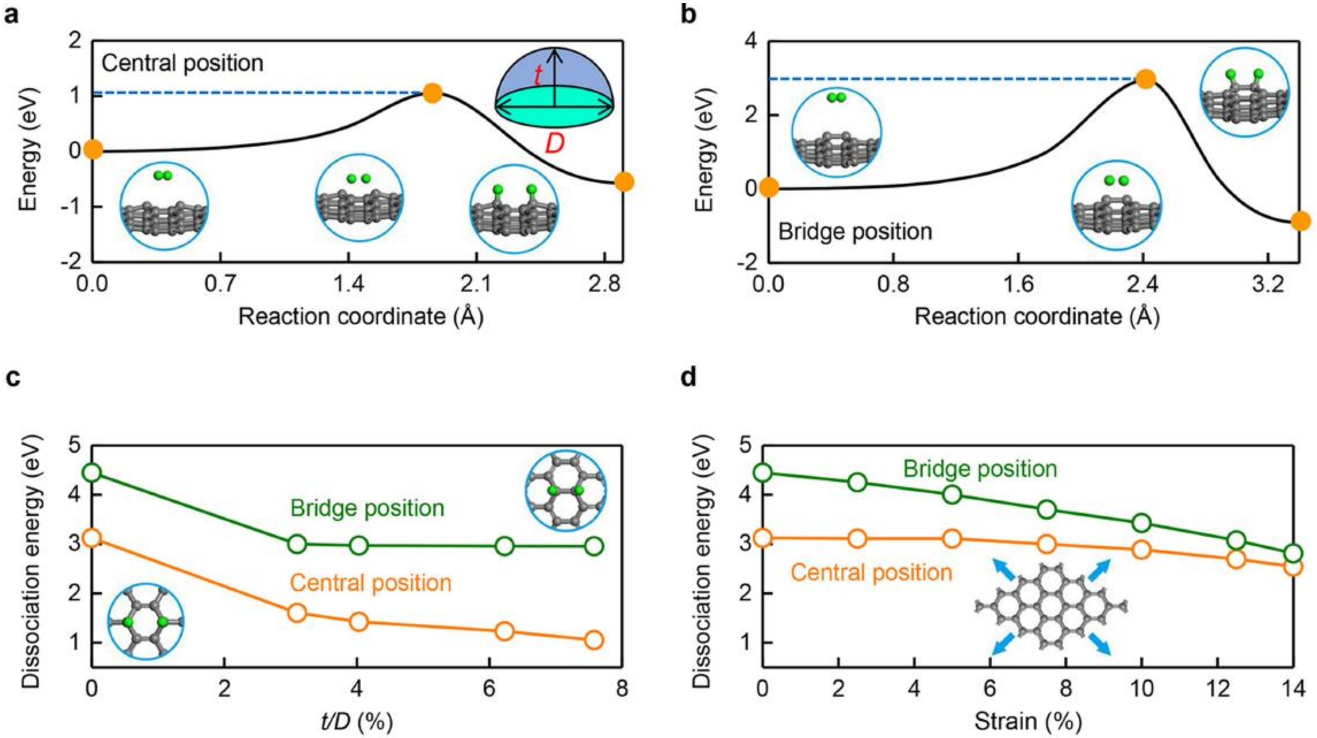




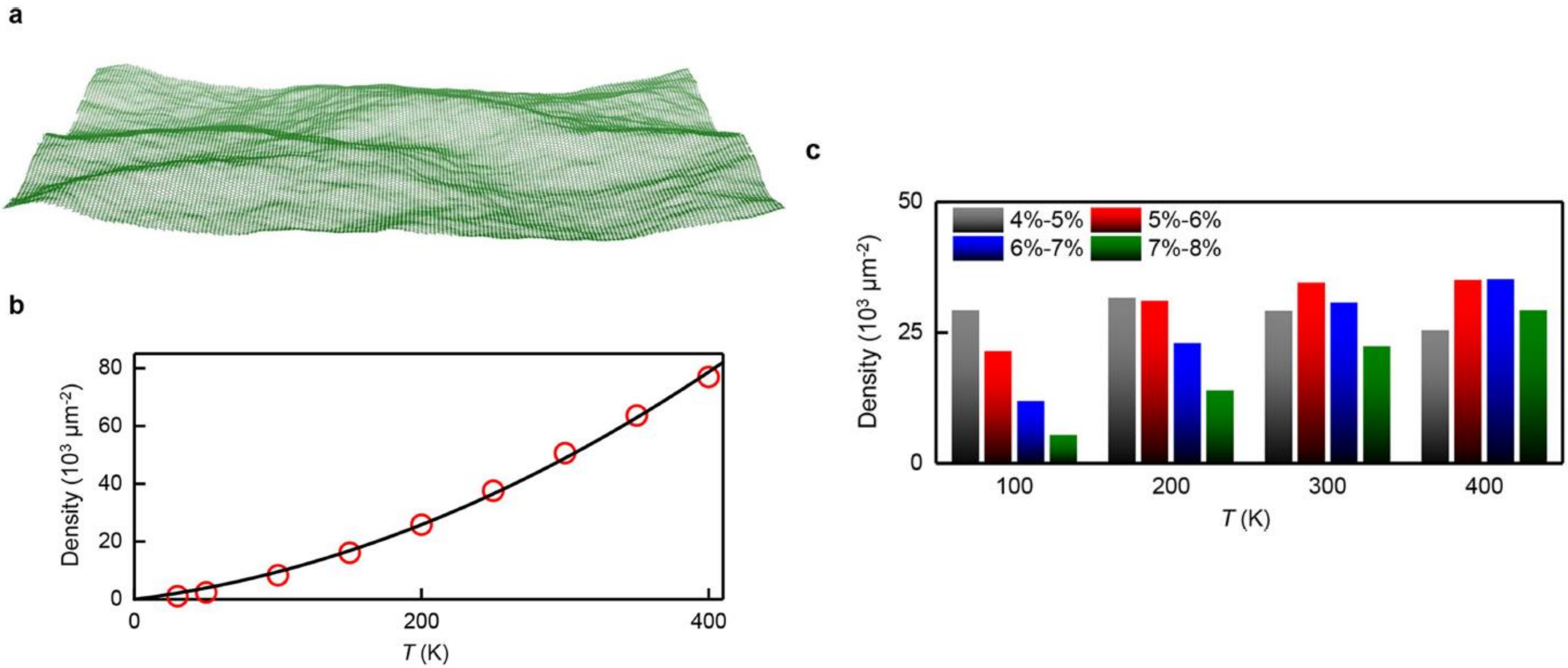
@RT

Decomposition of molecular hydrogen II

The only option which one can imagine: decomposition of H2 into two atoms and permeation of atoms; the role of ripples is decisive!



Decomposition of molecular hydrogen III



Extended Data Fig. 7 | Intrinsic (dynamic) ripples in graphene at different temperatures. **a**, Typical snapshot of graphene membrane at 300 K using molecular dynamics simulations. **b**, Density of ripples with $t/D \geq 7\%$ (most chemically active). Symbols are the calculations for different T. Solid curve is a guide to the eye. **c**, Statistical distribution of intrinsic ripples with different t/D.

It seems that we have enough of ripples

Distribution of ripples at finite temperatures

Distribution of ripples in graphene membranes

PHYSICAL REVIEW B **106**, 045418 (2022)

Jin Yu,[1,2,3] Mikhail I. Katsnelson,[2] Tianzhong Zhang,[1] and Shengjun Yuan[4,2,]

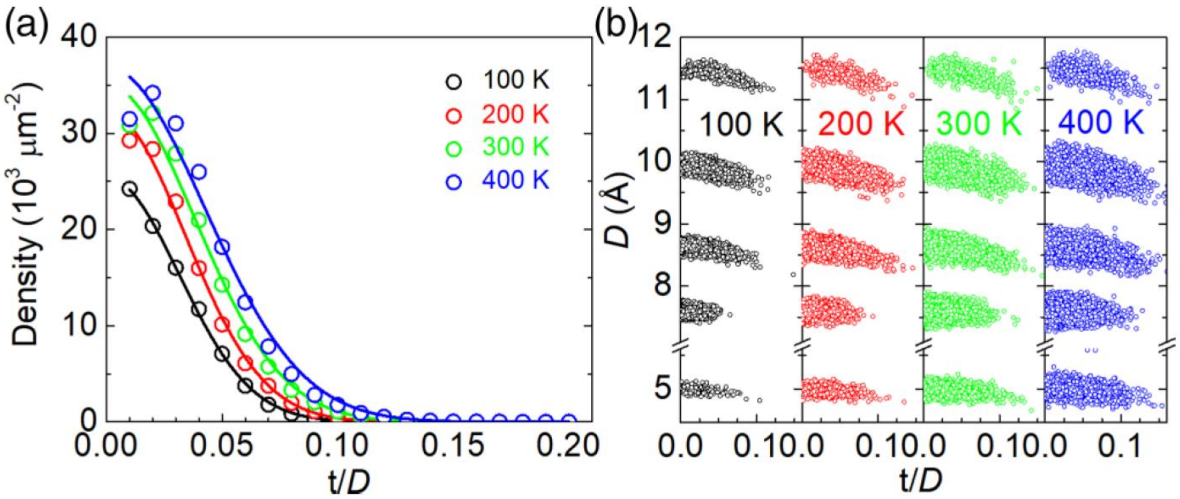


FIG. 2. (a) Ripple density and (b) size D as a function of t/D in graphene membrane with the circlelike model. The circles are statistical data from MD simulations and the solid lines are fit results using Eq. (2). Black, red, green, and blue represent for 100, 200, 300, and 400 K, respectively.

t ripple height, D diameter

@RT a lot of ripples with quite high curvature (important for chemistry!)

$$P(t, D) = A \exp\left[-C \frac{\kappa}{k_B T}\left(\frac{t}{D}\right)^2\right]$$

$$\frac{\kappa}{k_B T} \approx 40 \quad \text{@RT}$$

	t/D_{ave}	
T	A	C
100 K	47.76	28.12
200 K	72.89	67.40
300 K	99.14	112.79
400 K	120.57	156.01

To conclude

A very rich and interesting physics and chemistry

Not too strong bonding; reversible hydrogenation
(may be interesting for hydrogen storage?)

Resonant electron scatterer: midgap states, magnetic moments, strong effect on electron mobility

At finite concentrations: gap opening and semimetal-insulator transition

Proton permeation: still unsolved problem

Permeation of H_2 due to its dissociation

Crucial role of thermally induced ripples and curvature in general