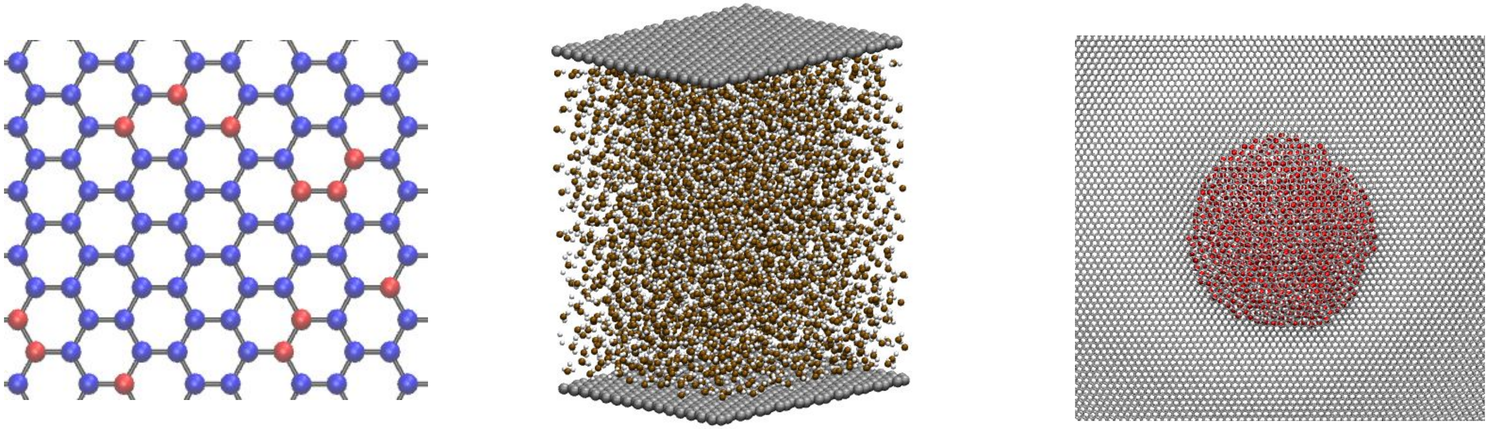
Thermo-mechanical properties of carbon nanostructures: MD approach



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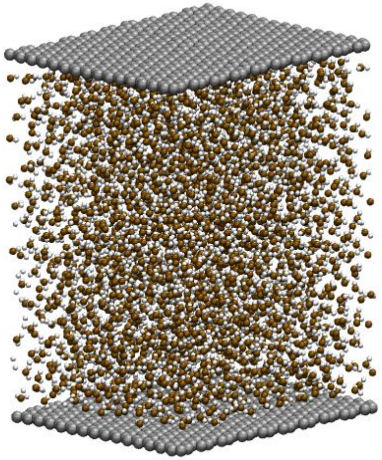
Outline:

I. MD simulation
II. Graphene Nanobubbles
III. Nitrogen-doped graphene



I. MD simulation

Molecular Dynamics simulations

❑ Molecular dynamics simulation (MD) is a technique for computing the **equilibrium and transport** properties of a **classical** many body system. CLASSICAL means that nuclear motion of the particles obeys the Newtonian mechanics.

❑ MD is in many aspects very **similar to real experiment**.
1-we prepare a sample of the material that we wish to study.
2-we connect this sample to a measuring instrument e.g. a thermostat, barostat, etc.
3-Finally, we measure the properties of interest during a certain time interval.

❑Force field (FF), as (semi-) **empirical level of approximation**, is a mathematical expression describing the particles various **interactions**.

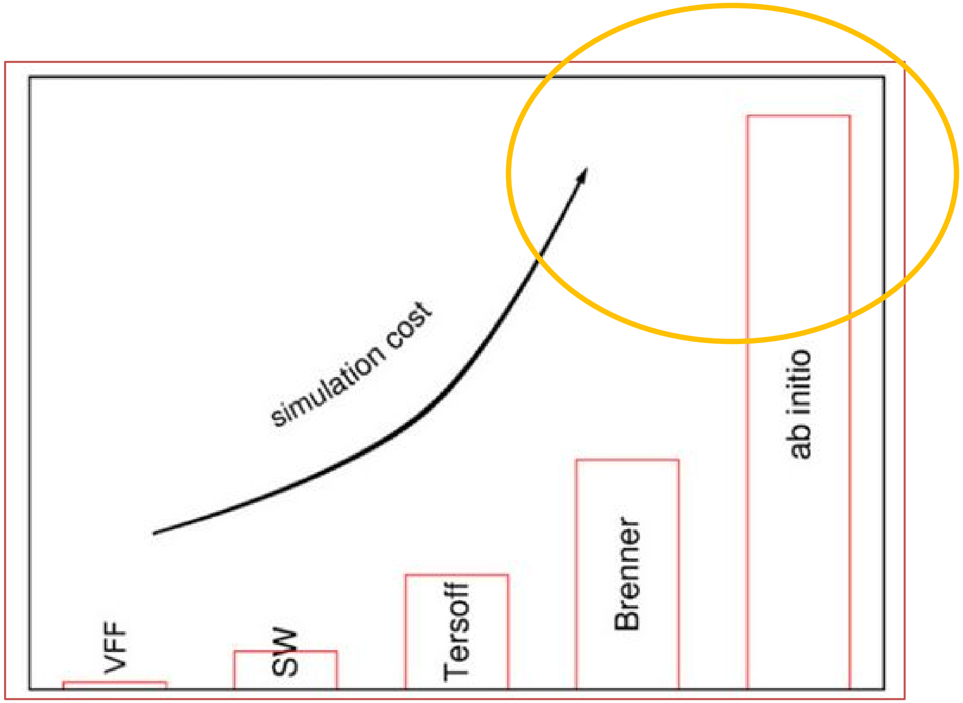
❑The FF is key to obtain a computationally **fast** and physically **correct** MD.

(Classical) MD: pros and cons

- ❑Not as **accurate** as first principle methods such as DFT, QMC, TB.

- ❑Computationally **efficient** (noticeably less CPU and memory usage) than ab-initio methods capable of simulating millions of atom.

- ❑Packages: **LAMMPS**, GROMACS, NAMD, DL_POLY
  Hybrid MM/MD: CPMD (e.g. Ion channel)

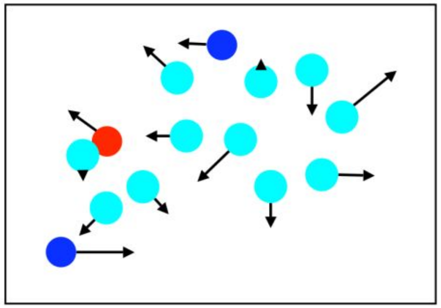


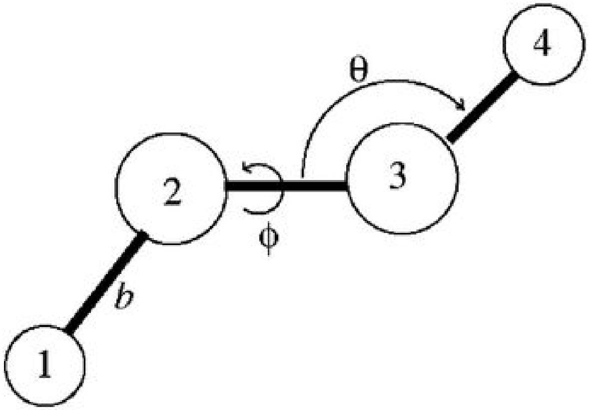
Force Fields

- OPLS [1], AMBER, CHARMM, GROMOS

$$V(r) = \boxed{\sum_{bonds} k_b(b-b_0)^2 + \sum_{angles} k_\theta(\theta-\theta_0)^2 + \sum_{torsions} k_\phi[\cos(n\phi+\delta)+1]}$$

$$\boxed{+ \sum_{\substack{nonbond\\pairs}} \left[\frac{q_iq_j}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}}\right]}$$





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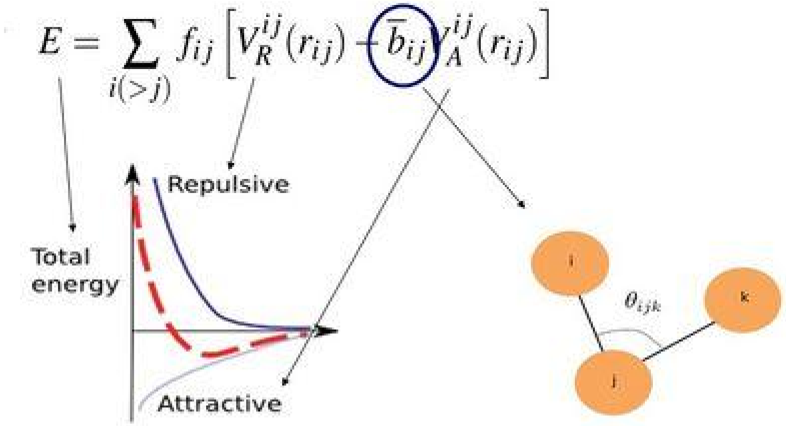
1. Jorgensen, W. L.; Madura, J. D.; Swenson, C. J. Optimized intermolecular potential functions for liquid hydrocarbons. J. Am. Chem. Soc. 1984 , 106 , 6638-6646.

Reactive bond-order Force Fields

❑Tersoff , airebo [1], Reax[2]

❑This type of FFs allows **bond making and breaking** with appropriate changes in atomic hybridization.

❑Chemical binding energy E can be simply written as a sum over nearest neighbours in the form of

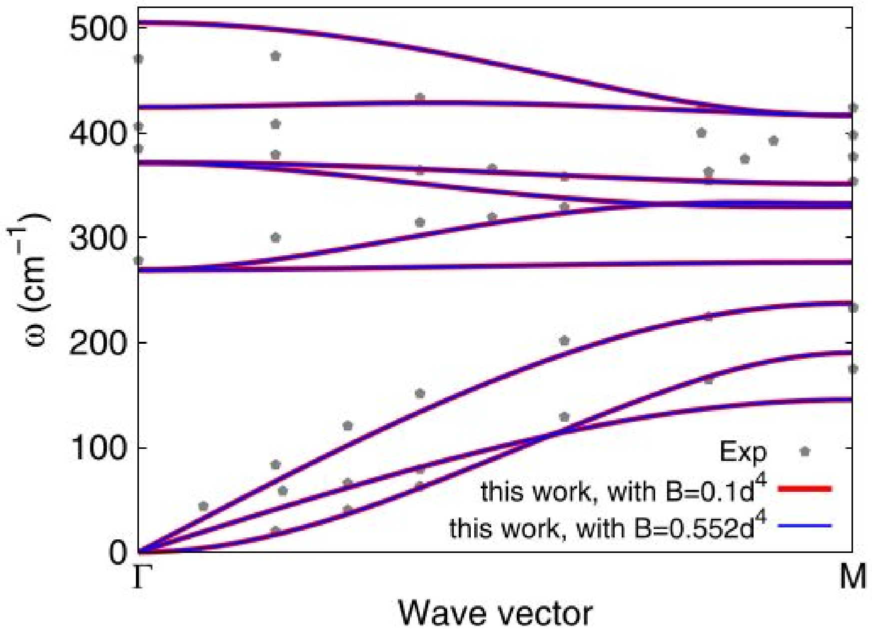


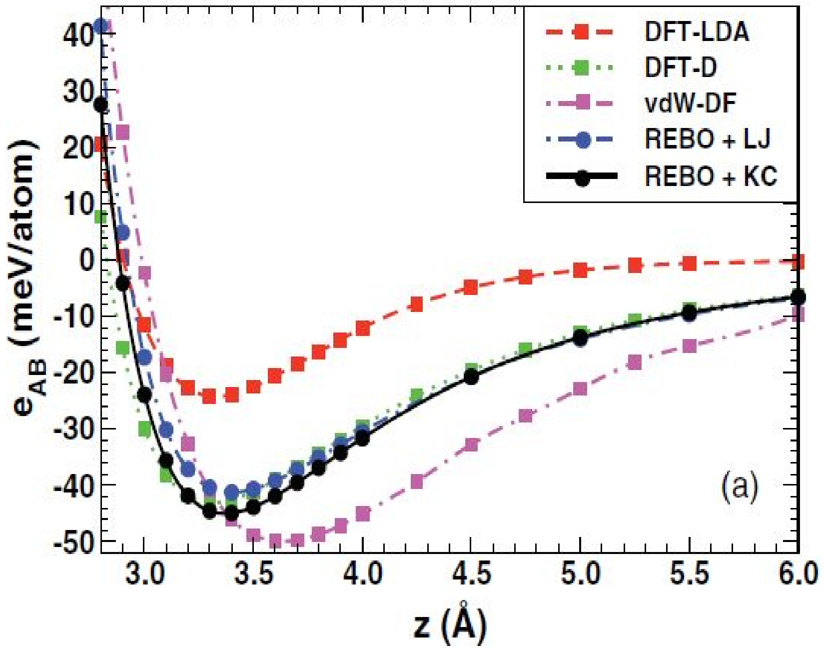
$$E = \sum_{i(>j)} f_{ij}\left[V_R^{ij}(r_{ij}) - \boxed{\bar{b}_{ij}} V_A^{ij}(r_{ij})\right]$$

1. Stuart, S. J.; Tutein, A. B.; Harrison, J. A. A reactive potential for hydrocarbons with intermolecular interactions. J. Phys. Chem. A 2000 , 112 , 6472-6486.
2. Van Duin, A. C.; Dasgupta, S.; Lorant, F.; Goddard, W. A. ReaxFF: a reactive force feld for hydrocarbons. J. Phys. Chem. A 2001 , 105 , 9396-9409.

FF parametrizations

❑ Experiment [1]: X-ray and electron diffraction, neutron scattering
❑ First principle [2]: DFT, quantum mechanical calculations





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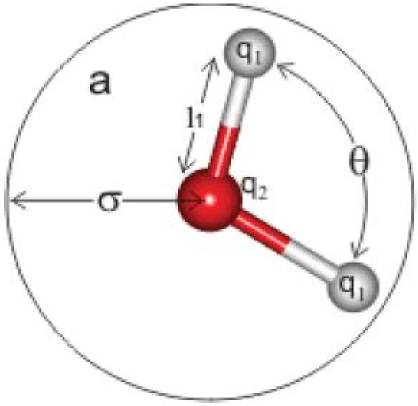
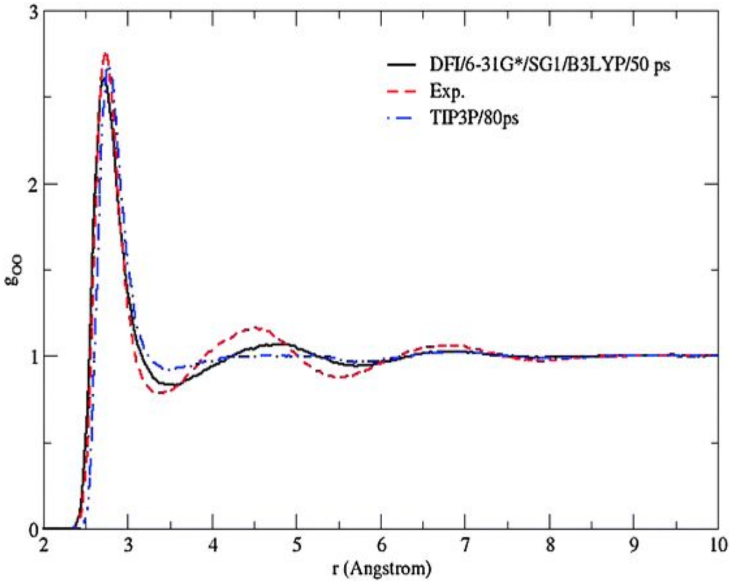
1. Jiang, Jin-Wu. "Parametrization of Stillinger–Weber potential based on valence force field model: application to single-layer MoS2 and black phosphorus." *Nanotechnology* 26.31 (2015): 315706.
2. Reguzzoni, M., et al. "Potential energy surface for graphene on graphene: Ab initio derivation, analytical description, and microscopic interpretation."*Physical Review B* 86.24 (2012): 245434.

Water models

Different models are useful to successfully predict the physical properties of water. Generally, each model is to fit well with one particular properties.



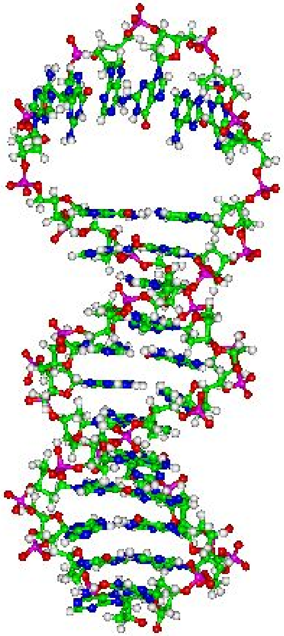
$$\sum_{bonds} K_b(b-b_o)^2 + \sum_{angles} K_\theta(\theta-\theta_o)^2 + \sum_{onbonded} \frac{q_i q_j}{4\pi D r_{ij}} + \varepsilon_{ij}\left[\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{6}\right]$$

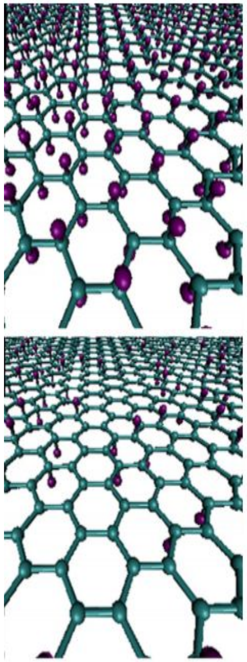


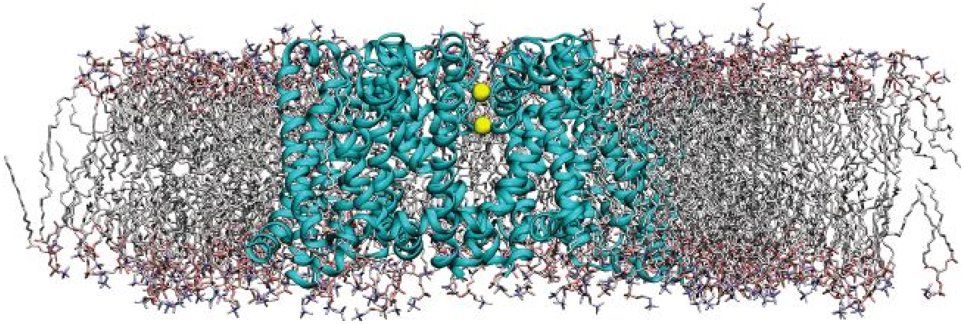
model			thermodynamic		
name	date	$n_{cen}{}^b$	T (K)	U_{pot} (kcal mol^{-1})	C_V (cal mol^{-1} K^{-1})
F3C[c]		3	298	−9.6	26(20)
(σ)[c]			(5)	(0.05)	(1.6)
expt			298	−9.9	18
RCF	1978[29]	3	302	−9.5	
TIP3P	1980[23,27]	3	298	−9.9	17
SPC	1981[22,27]	3	298	−10.2	23
SPCE	1987[28]	3	300	−10.8	

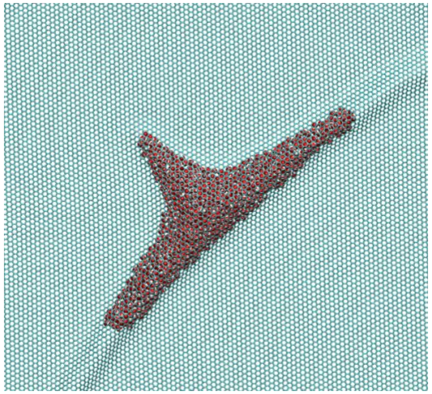
MD applications

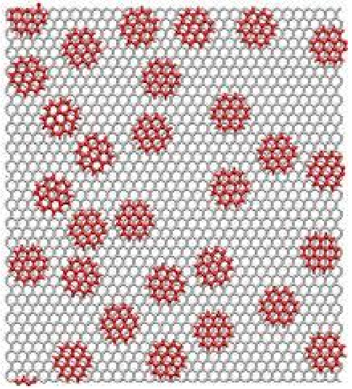
- Biophysics: DNA and protein folding e.g. ion channel, membrane
- Soft condensed matter: ordered phase of Liquid crystals, critical phenomena
- Solid state: elasticity, structure, (intrinsic) out-of-plane fluctuation, friction, viscosity

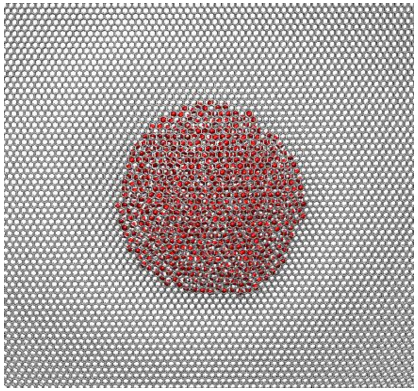










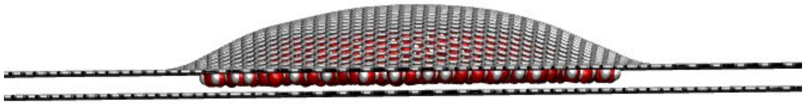


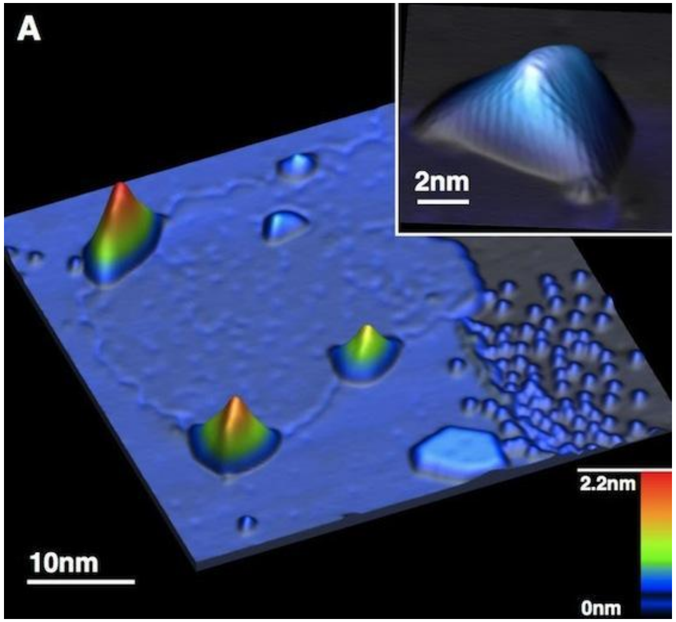
II. Graphene nanobubble

Nanobubbles

When placing a graphene membrane on a substrate, some molecules may be trapped underneath to form a **bump shape** which known as nanobubbles (NB).

NB is result of a **competition between the adhesion and the elasticity** of the substrate and the cover.





height ~ 0.3 nm to a few micron
diameter ~ 0.1 to 100nm
(semi-) circular, triangular, diamond

Levy, N., et al. "Strain-induced pseudo–magnetic fields greater than 300 tesla in graphene nanobubbles." *Science* 329.5991 (2010): 544-547.
Zabel, Jakob, et al. "Raman spectroscopy of graphene and bilayer under biaxial strain: bubbles and balloons." *Nano letters* 12.2 (2012): 617-621.

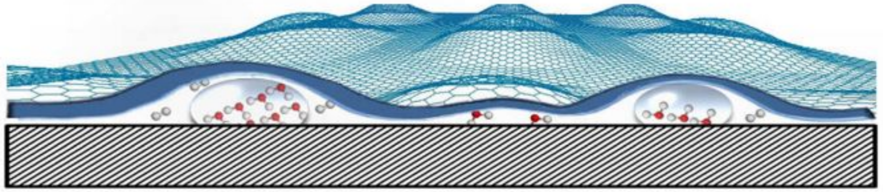
Potential applications

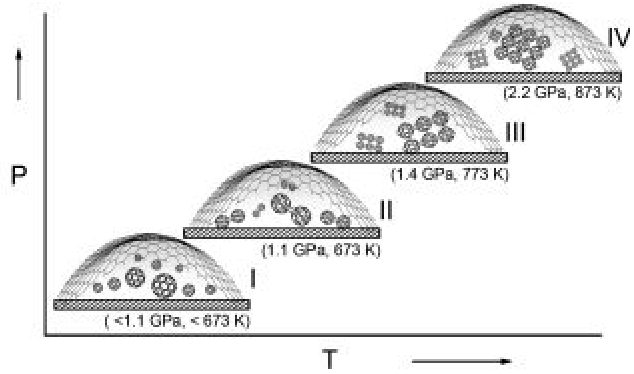
- Well-controlled pressurization method that used as **hydrothermal anvil cell** and quite suitable for observing high-pressure chemistry [1].

- **Imaging agent** to directly observe the chemical reactions [2].
- Enabling an **AFM study of the first water adlayer** on mica.

- Controllable curvature of NG by applying an external electric field which may be uses as **optical lenses** with variable focal length.

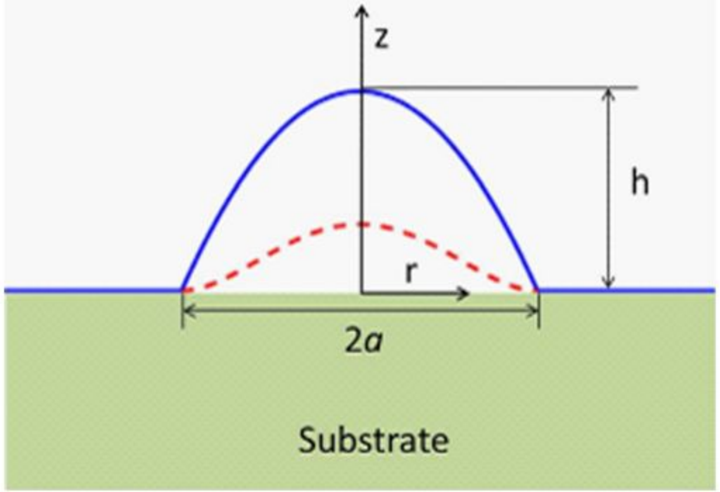
- NG induces enormous **pseudo-magnetic fields** greater than 300T [3].





1. Lim, Candy Haley Yi Xuan, et al. "A hydrothermal anvil made of graphene nanobubbles on diamond." *Nature communications* 4 (2013): 1556.
2. Lim, Candy Haley Yi Xuan, Milos Nesladek, and Kian Ping Loh. "Observing High-Pressure Chemistry in Graphene Bubbles." *Angewandte Chemie International Edition* 53.1 (2014): 215-219.
3. Levy, N., et al. "Strain-induced pseudo–magnetic fields greater than 300 tesla in graphene nanobubbles." *Science* 329.5991 (2010): 544-547.

Mechanical analysis of circular Nanobubbles



$$U(r) = \frac{E_{2D}}{2(1-\nu^2)}(\varepsilon_r^2 + 2\nu\varepsilon_r\varepsilon_\theta + \varepsilon_\theta^2)$$

$$\Pi(a,h,u_0) = 2\pi\int_0^a U(r)rdr - 2\pi(p-p_0)\int_0^a z(r)rdr$$

$$\frac{\partial\Pi}{\partial u_0} = \frac{\partial\Pi}{\partial h} = 0$$

$$h = \left[\frac{\phi(\nu)(p-p_0)a^4}{E_{2D}}\right]^{\frac{1}{3}}$$

$$u_0 = \left[\frac{\psi(\nu)(p-p_0)^2a^5}{E_{2D}^2}\right]^{\frac{1}{3}}$$

$$\boxed{p = \frac{E_{2D}h^3}{\phi a^4} + p_0}$$

Membrane theory:

$$z(r) = h\left(1 - \frac{r^2}{a^2}\right)$$

$$u(r) = u_0\frac{r}{a}\left(1 - \frac{r}{a}\right)$$

$$\varepsilon_r(r) = \frac{u_0}{a}\left(1 - \frac{2r}{a}\right) + \frac{2h^2r^2}{a^4}$$

$$\varepsilon_\theta(r) = \frac{u_0}{a}\left(1 - \frac{r}{a}\right)$$

Non-linear plate model

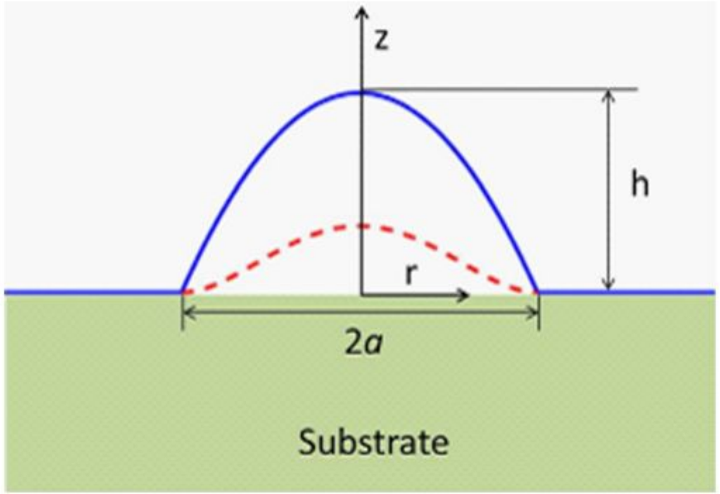
$$U_\mathrm{s}(r) = \frac{E_\mathrm{2D}}{2(1-\nu^2)}(\varepsilon_r^2 + 2\nu\varepsilon_r\varepsilon_\theta + \varepsilon_\theta^2)$$

$$U_b(r) = \frac{D}{2}\left[\left(\frac{d^2z}{dr^2}\right)^2 + \frac{1}{r^2}\left(\frac{dz}{dr}\right)^2 + \frac{2\nu}{r}\frac{dz}{dr}\frac{d^2z}{dr^2}\right]$$

$$\begin{aligned}\Pi(a,h,c_1,c_2) = {} & 2\pi\int_0^a [U_s(r) + U_b(r)]r\,dr \\ & - 2\pi(p-p_0)\int_0^a z(r)r\,dr\end{aligned}$$

$$\frac{\partial\Pi}{\partial \mathrm{c}_1} = \frac{\partial\Pi}{\partial \mathrm{c}_2} = 0 \qquad \frac{\partial\Pi}{\partial \mathrm{h}} = 0$$

$$\boxed{p = 64\eta\frac{E_\mathrm{2D}h^3}{a^4} + 64\frac{Dh}{a^4} + p_0}$$



$$z(r) = h\left(1 - \frac{r^2}{a^2}\right)^2$$

$$u(r) = r(a-r)(\mathrm{c}_1 + \mathrm{c}_2 r)$$

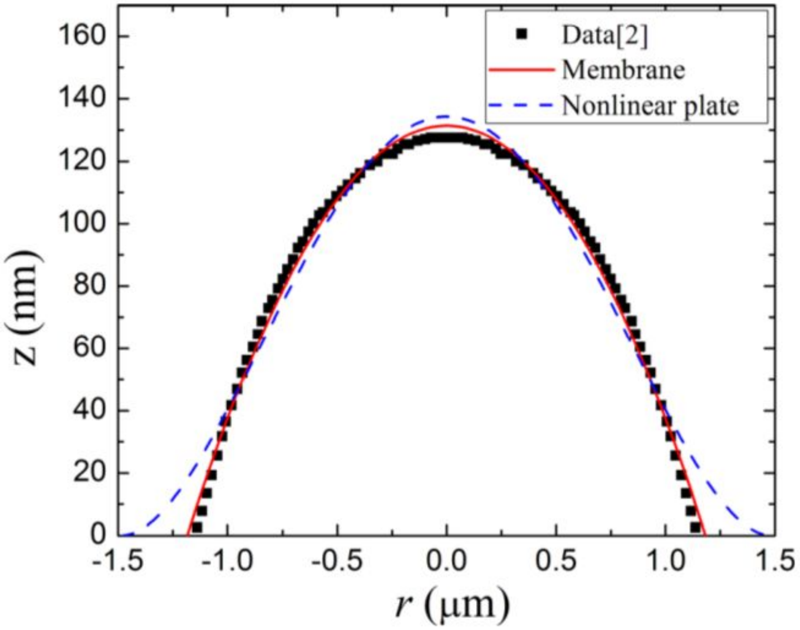
$$\varepsilon_\theta = (a-r)(\mathrm{c}_1 + \mathrm{c}_2 r)$$

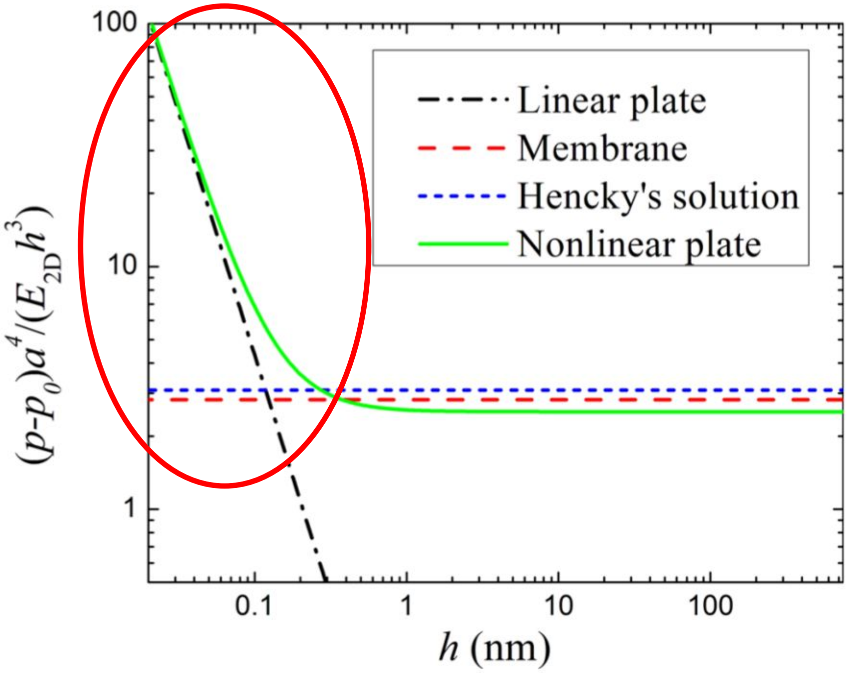
$$\begin{aligned}\varepsilon_r = {} & \mathrm{c}_1(a-2r) + \mathrm{c}_2 r(2a-3r) \\ & + \frac{8h^2r^2(a^2-r^2)^2}{a^8}\end{aligned}$$

- The theory of elasticity is sufficient for large size bubble. However, It fails to give a correct result for **small-size nanobubbles**.

- The type of trapped **material** is not taken into account (ideal gas assumption).

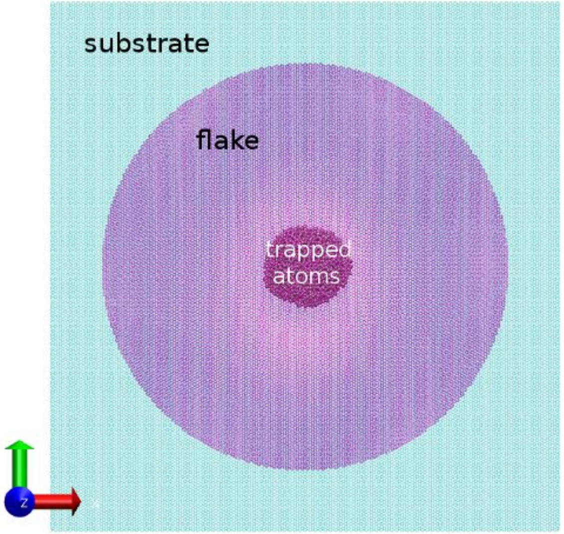
- The **structure** of trapped atoms within the nanobubble is not considered.





Yue, Kaimin, et al. "Analytical methods for the mechanics of graphene bubbles." *Journal of Applied Physics* 112.8 (2012): 083512.
Wang, Peng, et al. "Numerical analysis of circular graphene bubbles." *Journal of Applied Mechanics* 80.4 (2013): 040905.
Khestanova, E.; Guinea, F.; Fumagalli, L.; Geim, A.; Grigorieva, I. Graphene bubbles on a substrate: universal shape and van der Waals pressure. Nature. Comm. 2016 , 7 , 12587.

MD methods



- ❑Two relatively large (square) graphane flakes (each layer was ~70k atoms, 50nmx50nm)

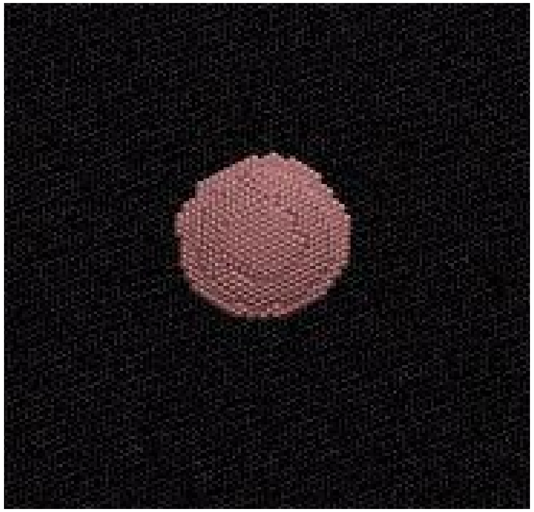
- ❑Helium, water, ethanol, hexadecane, NaCl as trapped substances (~3k)

- ❑Hybrid/overlay usage of appropriate potentials airebo (reaxFF), TIP3P, OPLS, EIM, LJ.

- ❑Interested properties:
  topography, line profile,
  phase, pressure, density, RDF
  radial and angular stress (strain)

$$P_{vdW} = - < \frac{Tr(\sigma)}{3V_b} >$$

$$\rho = < \frac{N m_u}{N_A V_b} >$$



Tsai, D. The virial theorem and stress calculation in molecular dynamics. J. Chem. Phys. 1979 , 70 , 1375-1382.

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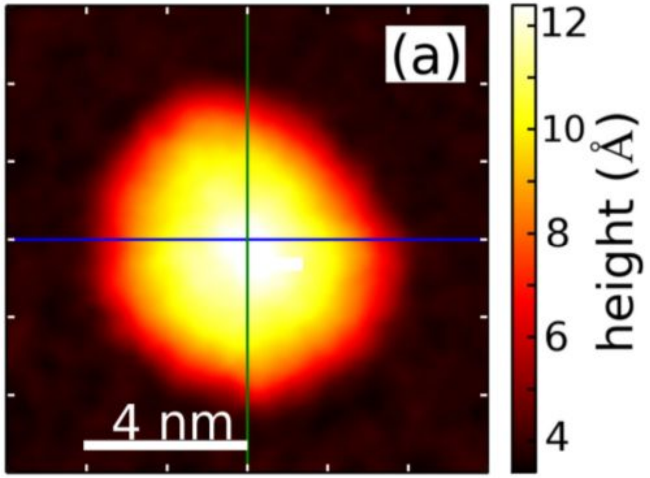
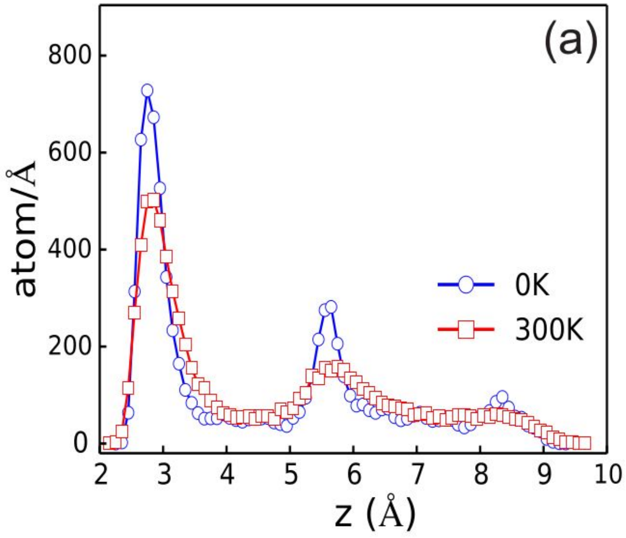
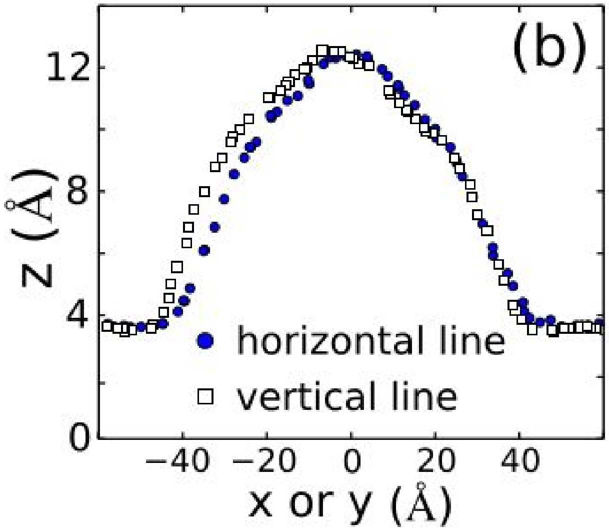
Water nanobubble

The **semicircular** water bubble is immobile in the presence of temperature fluctuations at room temperature, and molecules exhibits an **amorphous** structure with ρ =**0.9 gr/cm3** and P=**0.93 GPa**.



Density profile across z-axis indicates **layered** structure even at ambient condition.



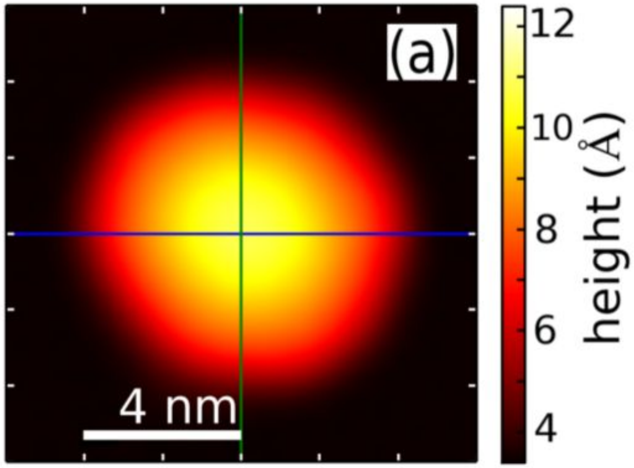


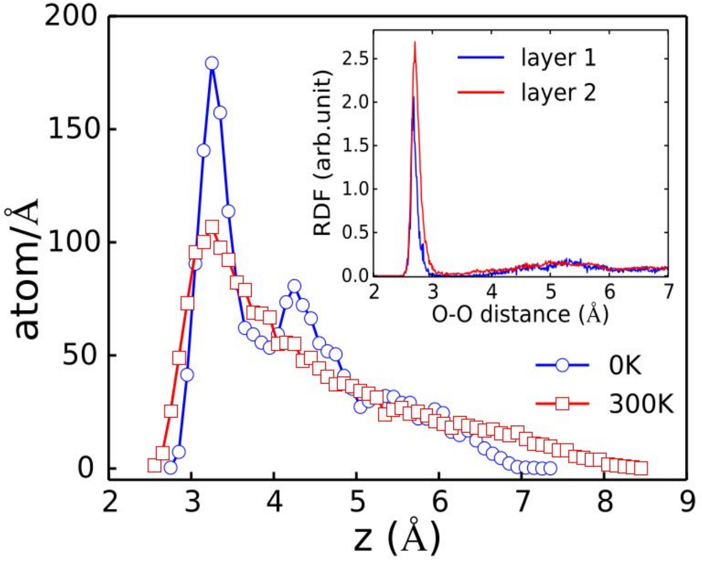
Finney, J.; Hallbrucker, A.; Kohl, I.; Soper, A.; Bowron, D. Structures of high and low density amorphous ice by neutron diffraction. Phys. Rev. Lett. 2002 , 88 , 225503.

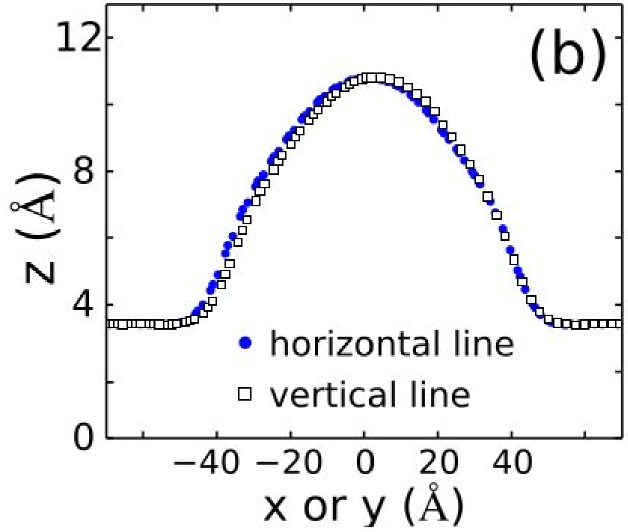
Ethanol nanobubble

We found very good **agreement** between our MD results for hydrocarbon bubbles and the predictions from **theory of elasticity**.

20% **larger viscosity** than water (1.2 mPa.s). The estimated density and pressure are **ρ =0.520 gr/cm3 and P=0.49 GPa**. plus the **experimentally reported liquid phase** of bulk ethanol under 1 GPa pressure from dielectric spectroscopy.



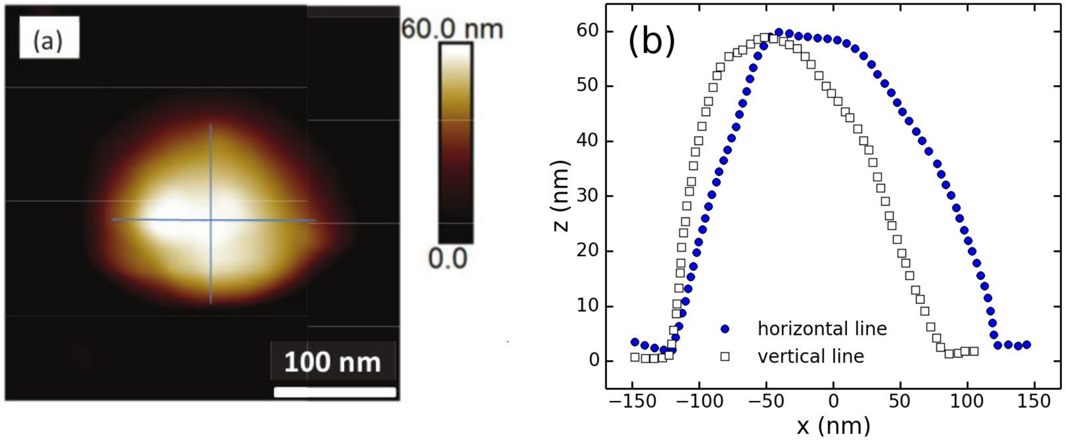




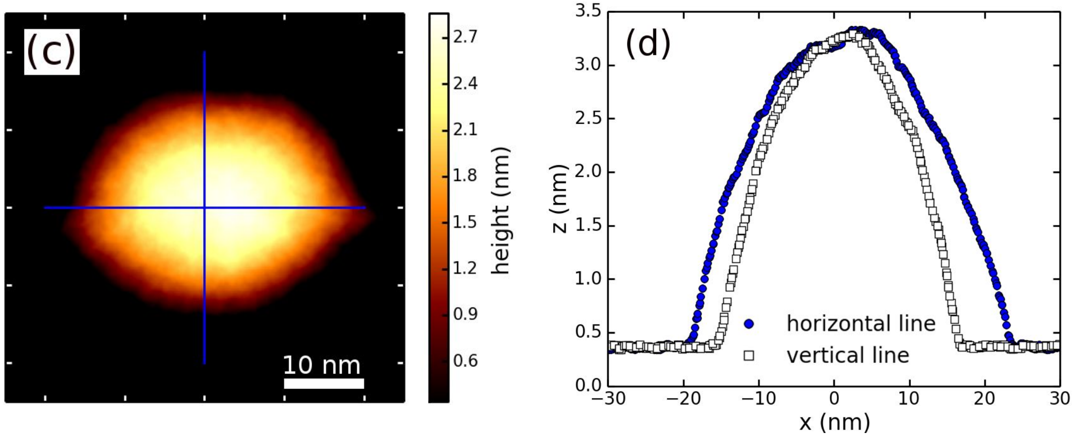
Khestanova, E.; Guinea, F.; Fumagalli, L.; Geim, A.; Grigorieva, I. Graphene bubbles on a substrate: universal shape and van der Waals pressure. Nature. Comm. 2016 , 7 , 12587.

Large water bubble

AFM image of water bubble and corresponding profiles along two perpendicular lines.



We performed a huge MD simulations for a larger water bubble with the size of 35 nm



both AFM image and MD data confirm the **non-circular** shape for the water bubble

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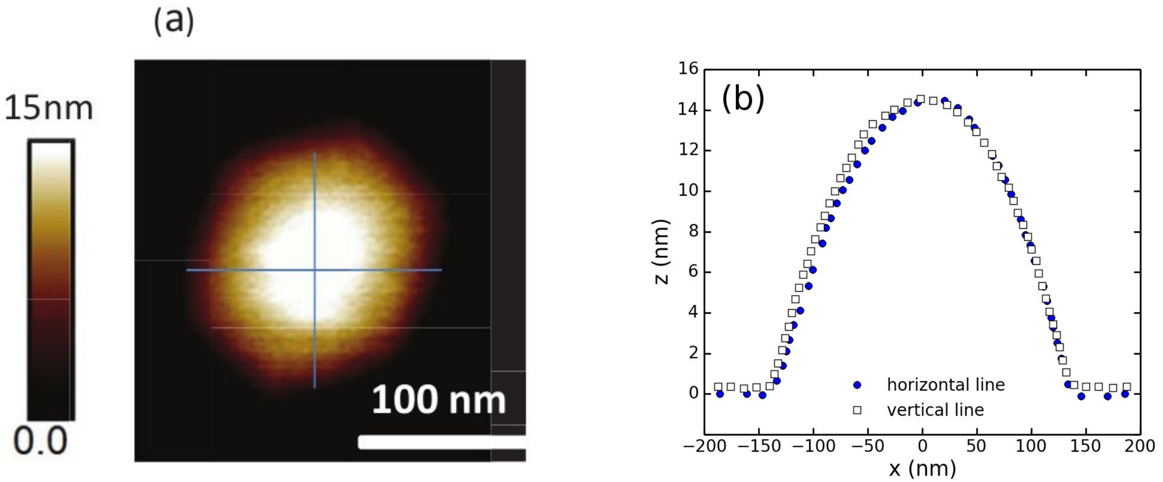
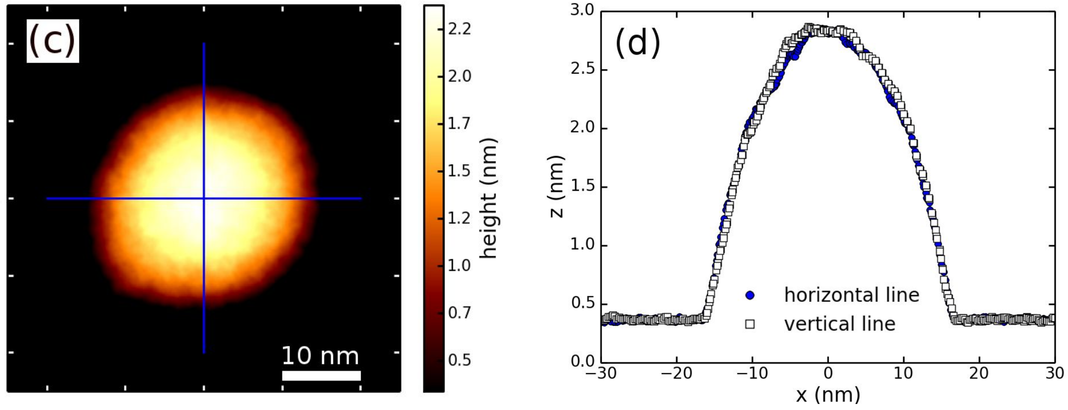
Large ethanol bubble

we depict AFM image of hydrocarbon bubble (likely are filled by small hydrocarbons) and corresponding profiles along two perpendicular lines.



The MD results for a large ethanol bubble is shown (R 30 nm).



AFM images nicely show **circular** shape which is in agreement with our MD results.

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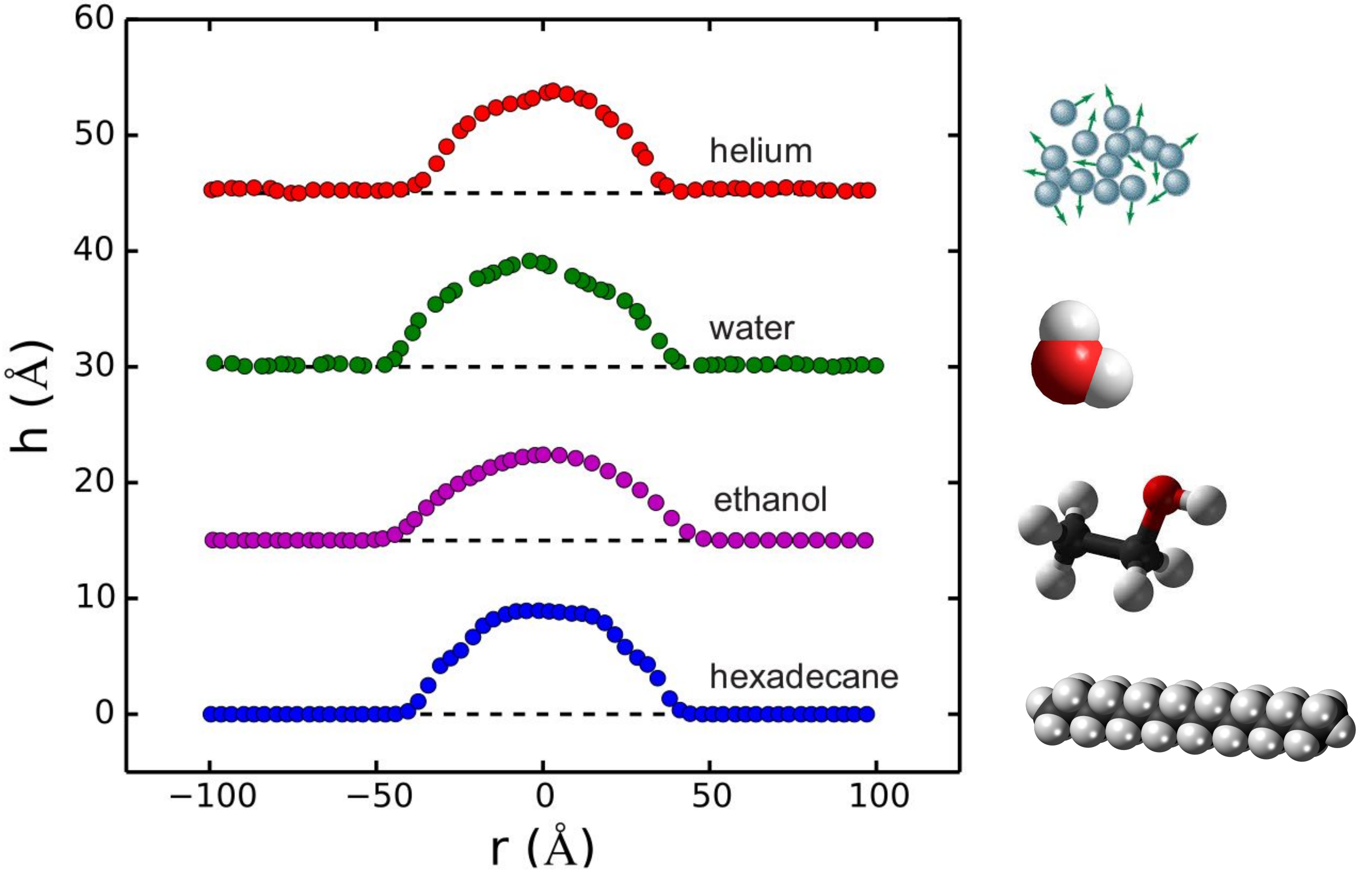
School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK

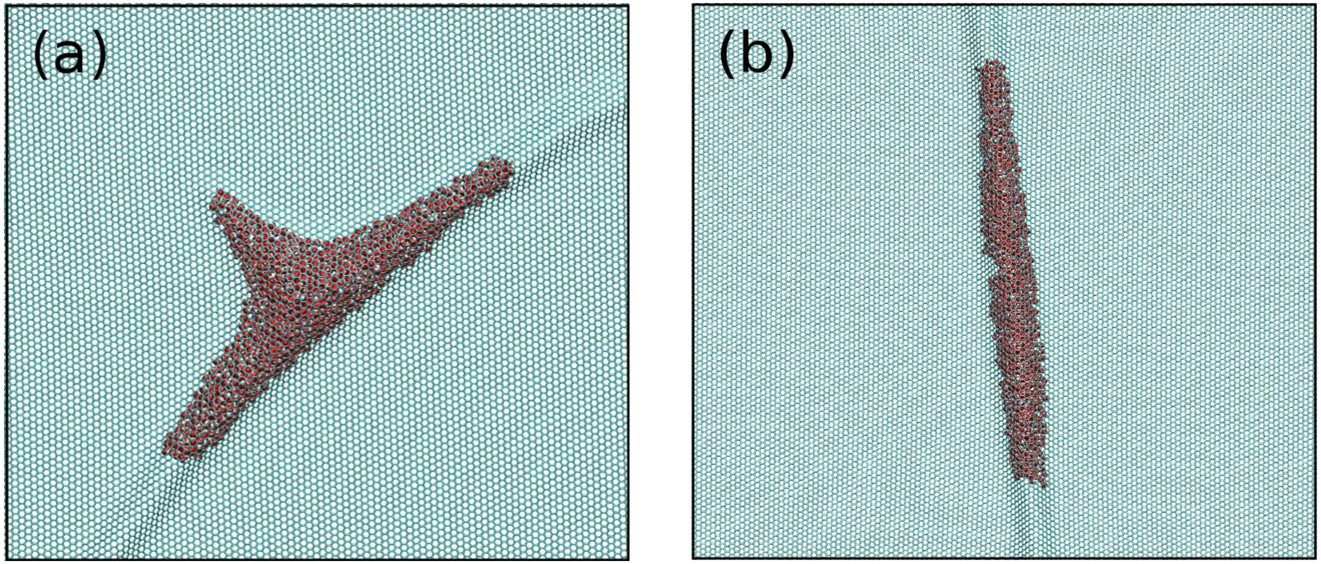
Comparing nanobubbles



Boundary stresses

We found that the bubble subjected to **triaxial and biaxial stresses forms trigonal and linear wrinkles** [1].

As result, it is concluded that not only the trapped substance, but also the **boundary stresses** can fundamentally changes the shape of bubble.

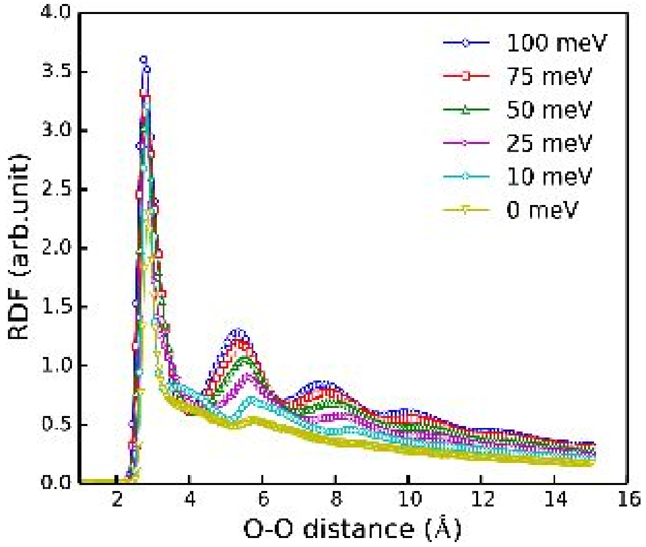


1. Neek-Amal, M.; Covaci, L.; Shakouri, K.; Peeters, F. Electronic structure of a hexagonal graphene ake subjected to triaxial Stress. Phys. Rev. B 2013 , 88 , 115428

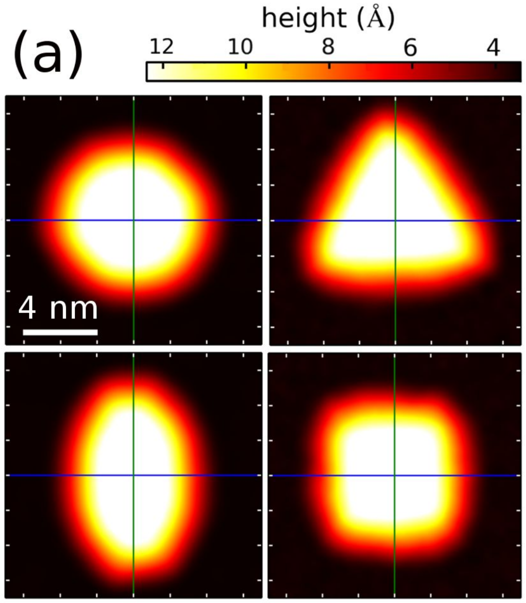
Square ice

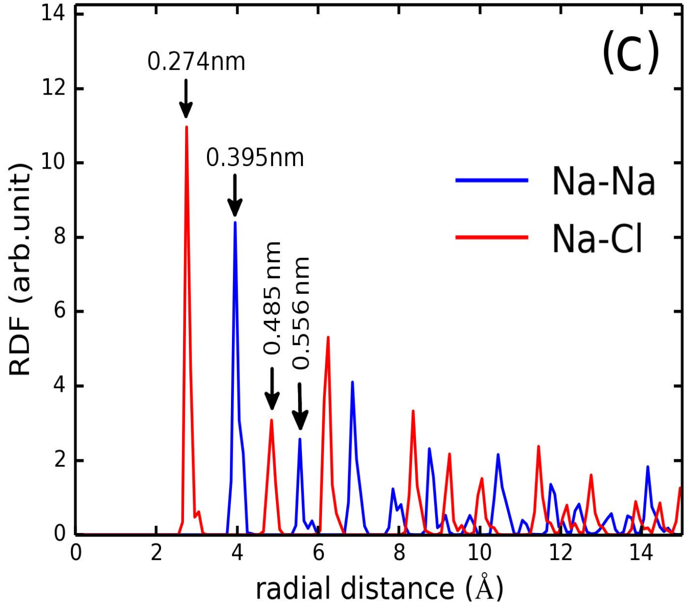
using an extra Lennard-Jones (LJ) interaction between layers we were able to **elucidate the effects of adhesion**.

We found that the second and third peaks become more pronounced when the adhesion energy increases. However, we **did not obtain square ice** structure.



In case of NaCl bubble, the first peak appears at 2.74 Å which is close to reported value (2.8 Å) in Ref [1] for square ice.





1. Algara-Siller, G.; Lehtinen, O.; Wang, F.; Nair, R.; Kaiser, U.; Wu, H.; Geim, A.; Grigorieva, I. Square ice in graphene nanocapillaries. Nature (London) 2015 , 519 , 443-445.

Summary (1)

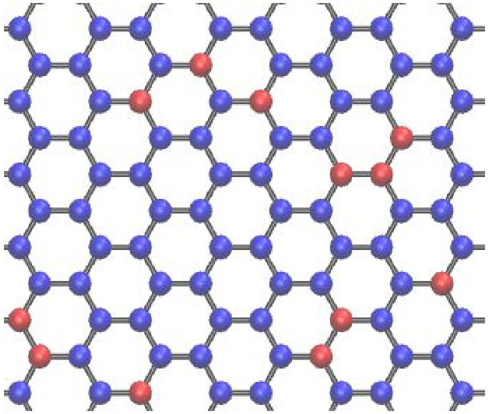
- Significant differences in the microscopic details of the bubbles were found for different trapped substances.

- Nanobubbles filled with small hydrocarbons (e.g. ethanol) is more relevant to AFM images and the reported pressure and geomery based on the theory of elasticity.

- We found that boundary stress causes the formation of wrinkles and can basically change the shape of water nanobubbles.

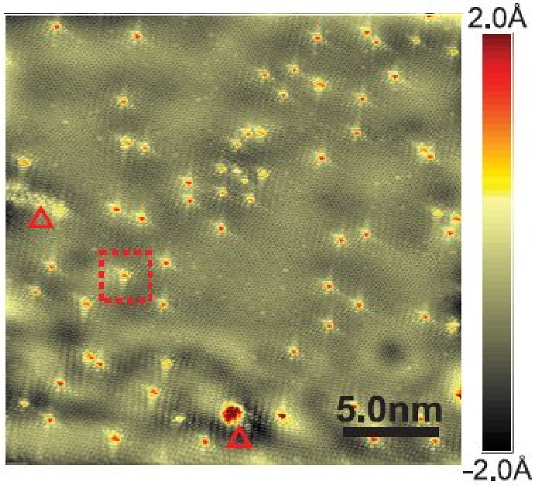
- Long hydrocarbons (e.g. hexadecane) forms likely a flat bubble.

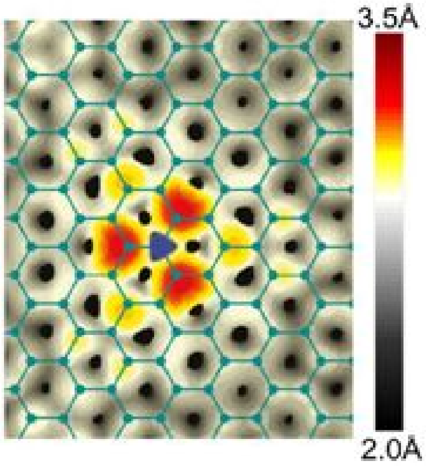
- The pressure inside the bubble can be tuned by changing the adhesion energy which results in an ordered phase of the trapped substance (i.e. amorphous-ice).



III. N-doped Graphene

Motivations:





❑ Substitutional (N) doping is an effective way to intrinsically **modify the properties** of carbon based materials.

❑ In recent years, several **experimental techniques**, e.g. CVD and ammonia heat-treatment processes, have been developed to fabricate nitrogen-doped graphene (NG) sheet [1,2].

❑ **First principle** calculations also have been performed to investigate the geometry and electronic structure of doped graphene sheet [3].

❑ N-doping enhances the biocompatibility of carbon nanomaterials and therefore is favorable for **biosensing applications**. Enhanced Raman scattering to efficiently probe organic molecules on NG sheet [4].

1. Zhao, Liuyan, et al. "Visualizing individual nitrogen dopants in monolayer graphene." *Science* 333.6045 (2011): 999-1003.
2. Iyer, Ganjigunte RS, et al. "Nanoscale imaging of freestanding nitrogen doped single layer graphene." *Nanoscale* 7.6 (2015): 289-2294.
3. Rani, Pooja, and V. K. Jindal. "Designing band gap of graphene by B and N dopant atoms." *RSC Advances* 3.3 (2013): 802-812.
4. Lv, Ruitao, et al. "Nitrogen-doped graphene: beyond single substitution and enhanced molecular sensing." *Scientific reports* 2 (2012).

MD methods

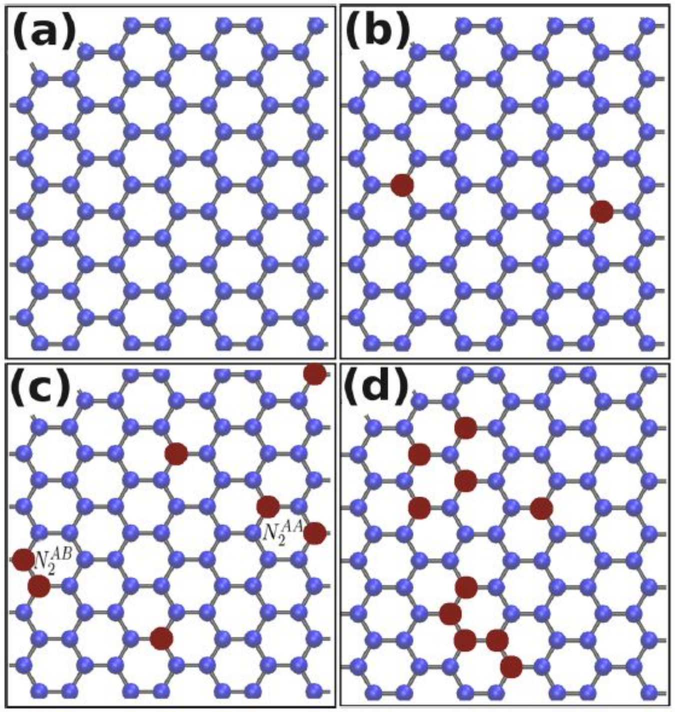
❑Total atoms 11k, 18nmx18nm

❑N atoms **randomly distributed** over graphene sheet by simply substituting carbon with nitrogen.

❑**ReaxFF** as bond-order reactive potential [1]

❑stress and strain calculated from stress tensor [2]

❑Interested properties:
structural: line-profile, bond length, etc.
energy: formation energy
mechanical: Young modulus, poisson ratio, (ultimate) stress/strain



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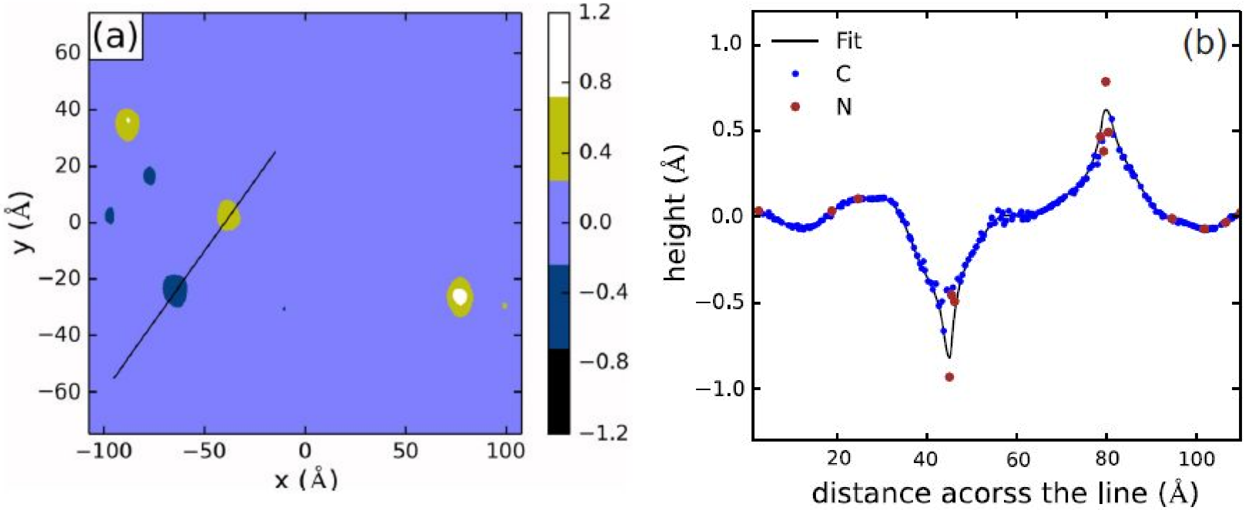
1. Van Duin, A. C.; Dasgupta, S.; Lorant, F.; Goddard, W. A. ReaxFF: a reactive force feld for hydrocarbons. J. Phys. Chem. A 2001 , 105 , 9396-9409.
2. Tsai, D. The virial theorem and stress calculation in molecular dynamics. J. Chem. Phys. 1979 , 70 , 1375-1382.

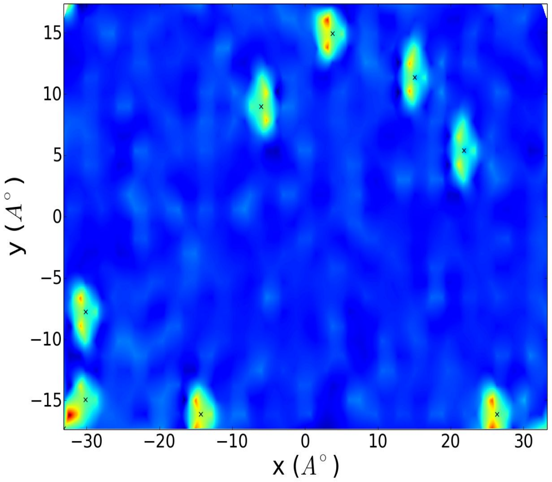
Structural deformations

A typical height distribution of doped graphene with 5% nitrogen concentration and the height profile across two typical N clusters.

Our results for the average peak height for a single dopant (~1.0 Å) is in good agreement with the STM images [1].

The bond lengths slightly depend on the dopant configuration. On average, they are calculated as: C-C: 1.43 Å C-N : 1.37 Å N-N : 1.57 Å





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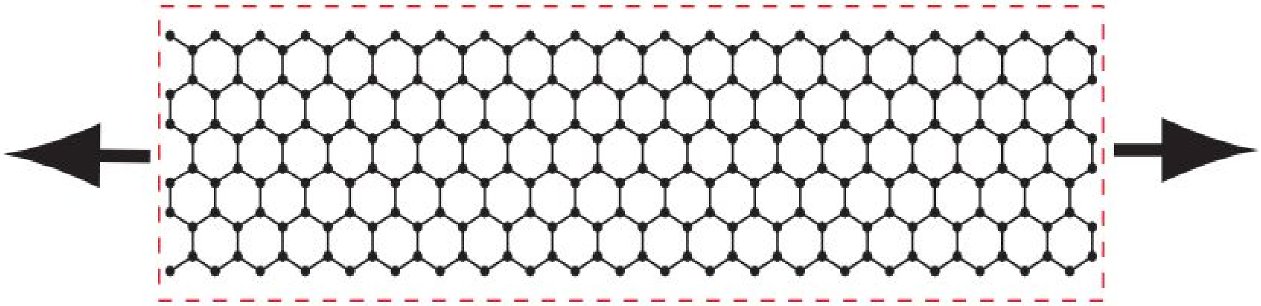
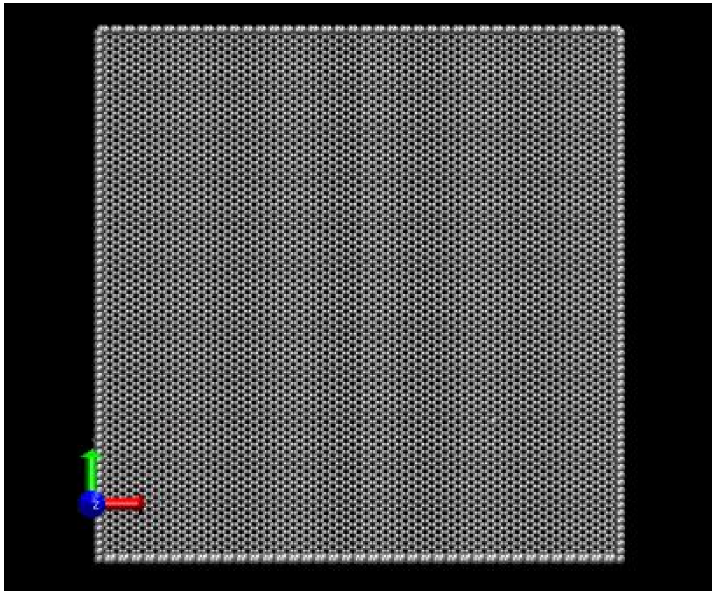
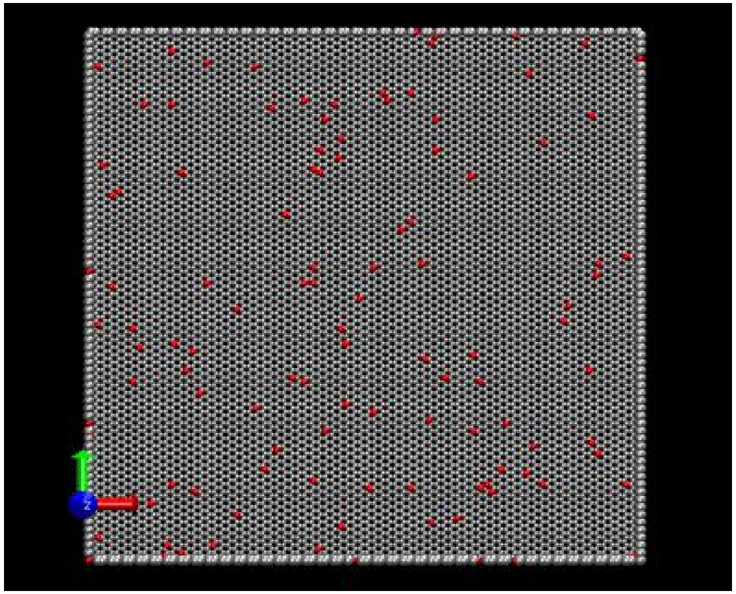
1. Zhao, Liuyan, et al. "Visualizing individual nitrogen dopants in monolayer graphene." *Science* 333.6045 (2011): 999-1003.

Mechanical properties



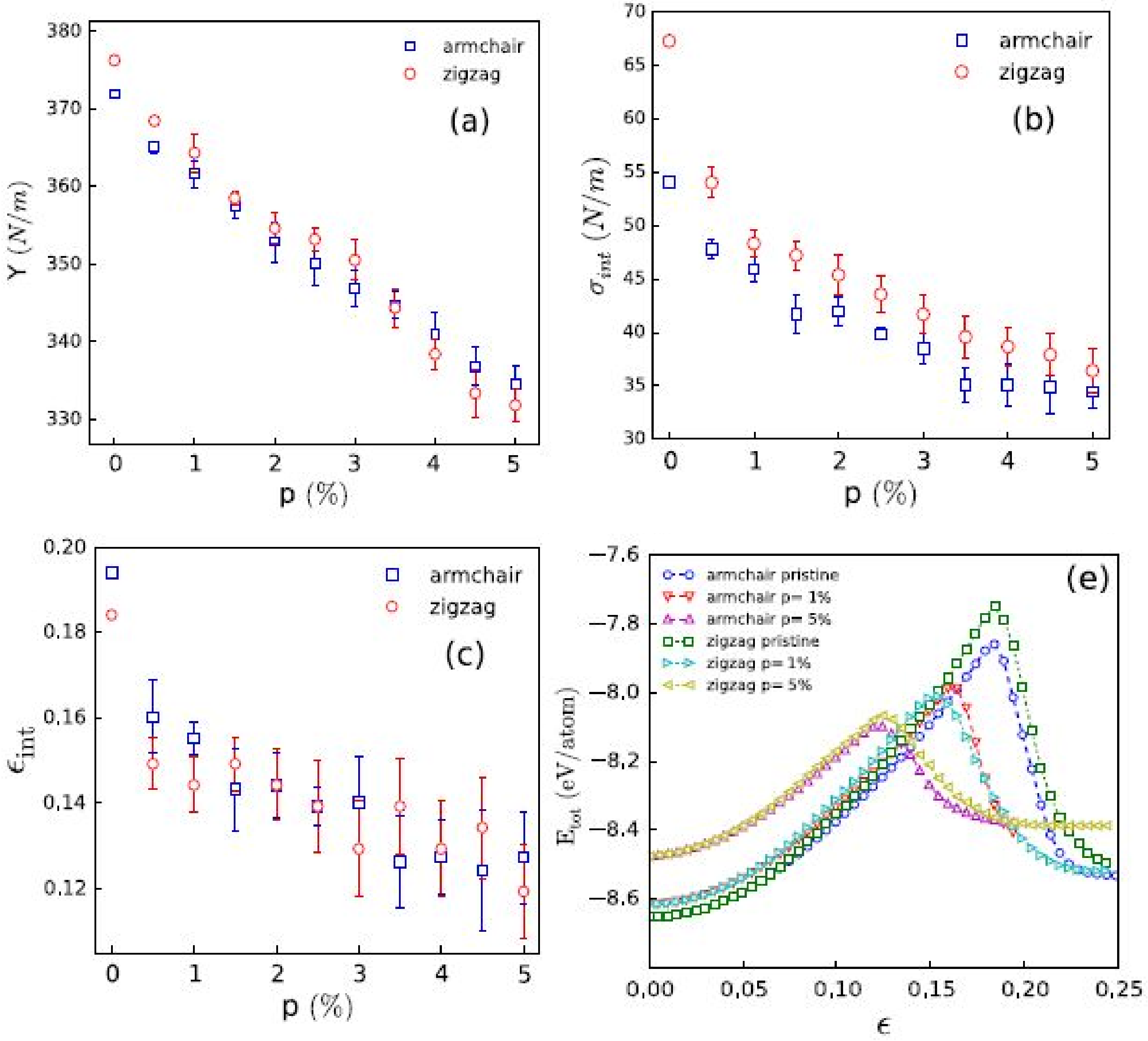


Pristine graphene

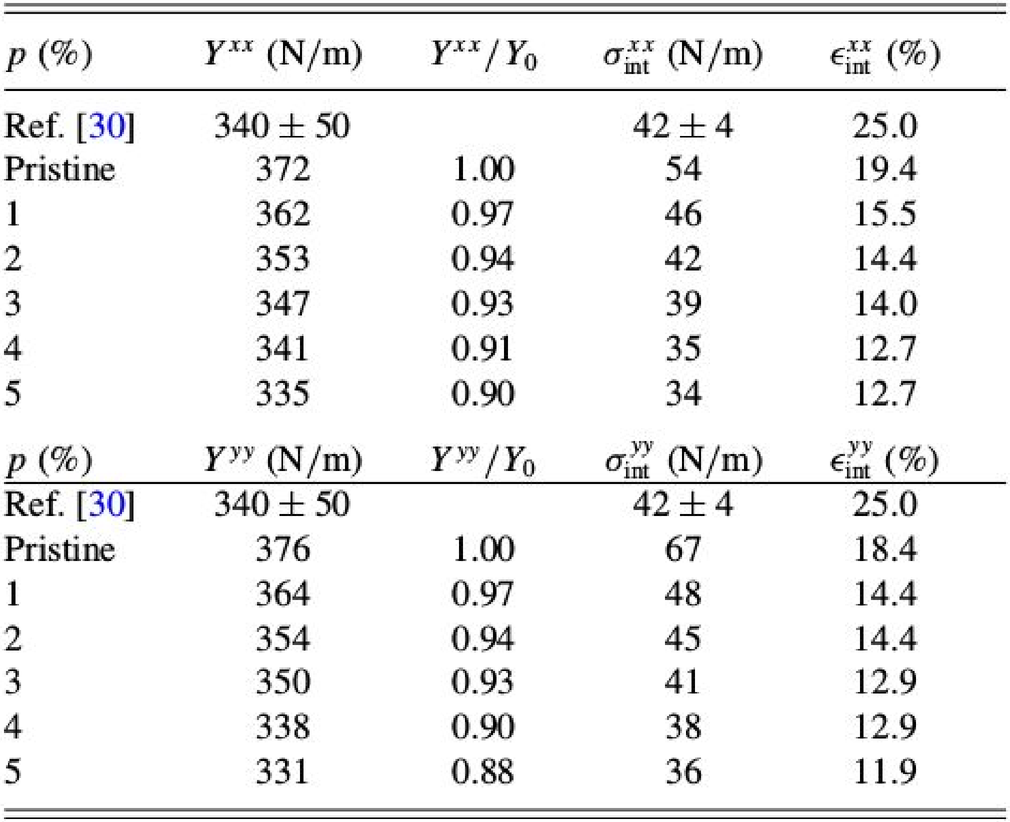


1% N-doped graphene

Mechanical properties



Mechanical properties



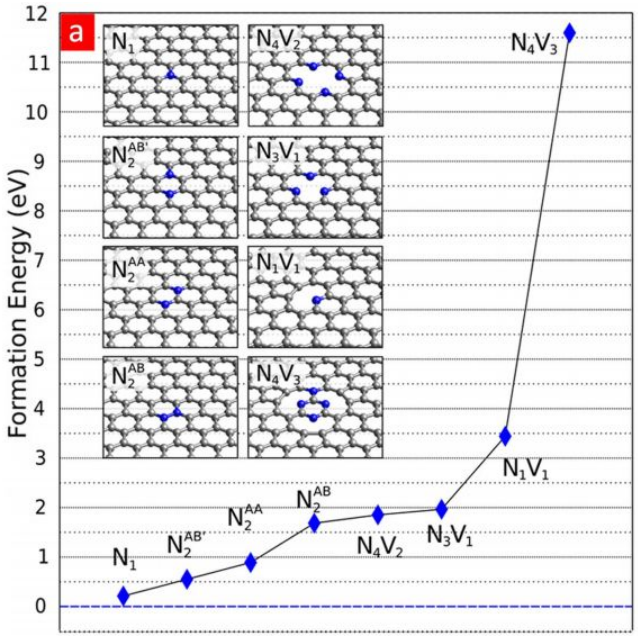
p (%)	Y^{xx} (N/m)	Y^{xx}/Y_0	$\sigma_{\mathrm{int}}^{xx}$ (N/m)	$\epsilon_{\mathrm{int}}^{xx}$ (%)
Ref. [30]	340 ± 50		42 ± 4	25.0
Pristine	372	1.00	54	19.4
1	362	0.97	46	15.5
2	353	0.94	42	14.4
3	347	0.93	39	14.0
4	341	0.91	35	12.7
5	335	0.90	34	12.7

p (%)	Y^{yy} (N/m)	Y^{yy}/Y_0	$\sigma_{\mathrm{int}}^{yy}$ (N/m)	$\epsilon_{\mathrm{int}}^{yy}$ (%)
Ref. [30]	340 ± 50		42 ± 4	25.0
Pristine	376	1.00	67	18.4
1	364	0.97	48	14.4
2	354	0.94	45	14.4
3	350	0.93	41	12.9
4	338	0.90	38	12.9
5	331	0.88	36	11.9

Formation Energies

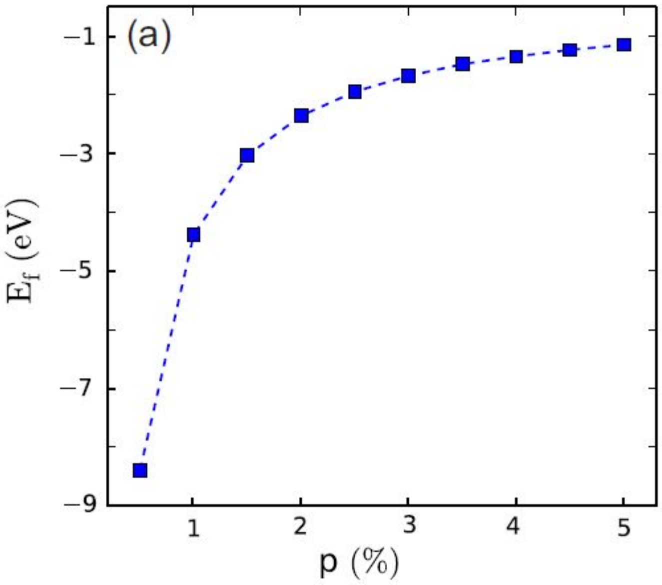
In agreement with the ab-initio calculations, formation energies for different types N-doped graphene conforms the **stability** of nitrogen atoms in substitution.

The ab-initio computed formation energies for different N-dopant configurations on NG sheet [1].



Reference of formation energy is binding energies for pristine graphene and a free N2 molecule.

$$E_f = [E_{\rm NG} - n_{\rm C}\varepsilon_{\rm C} - n_{\rm N}\varepsilon_{\rm N}]/n_{\rm N}$$



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1. Lv, Ruitao, et al. "Nitrogen-doped graphene: beyond single substitution and enhanced molecular sensing." *Scientific reports* 2 (2012).

Local dipole moments

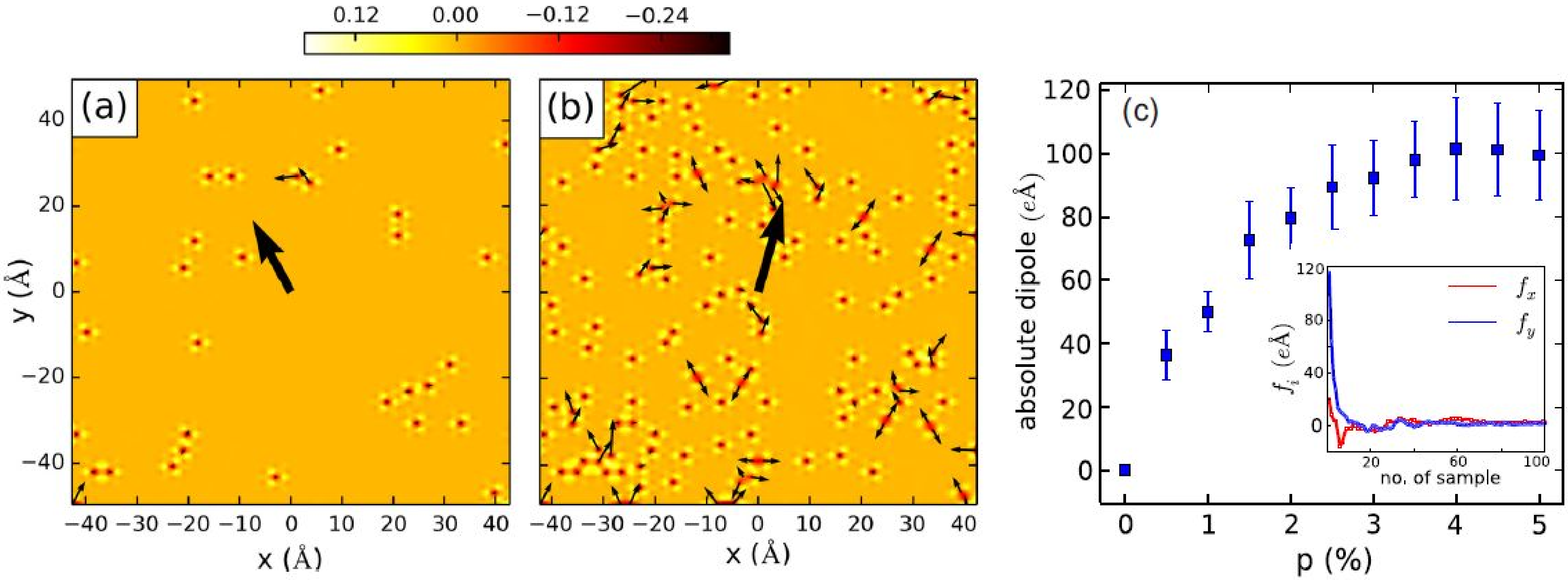

FIG. 2. Density plot of the charge distribution of doped graphene with (a) 1% and (b) 5% nitrogen doping. Small arrows indicate the local dipoles, and the thick arrow corresponds to the net dipole. The color scale is in units of the elementary charge. (c) Absolute value of the net dipole as function of the N-dopant concentration. The inset indicates vanishing of the total dipole when we average over many samples, where f_x and f_y are the x and y components of the total dipole of n_s samples.

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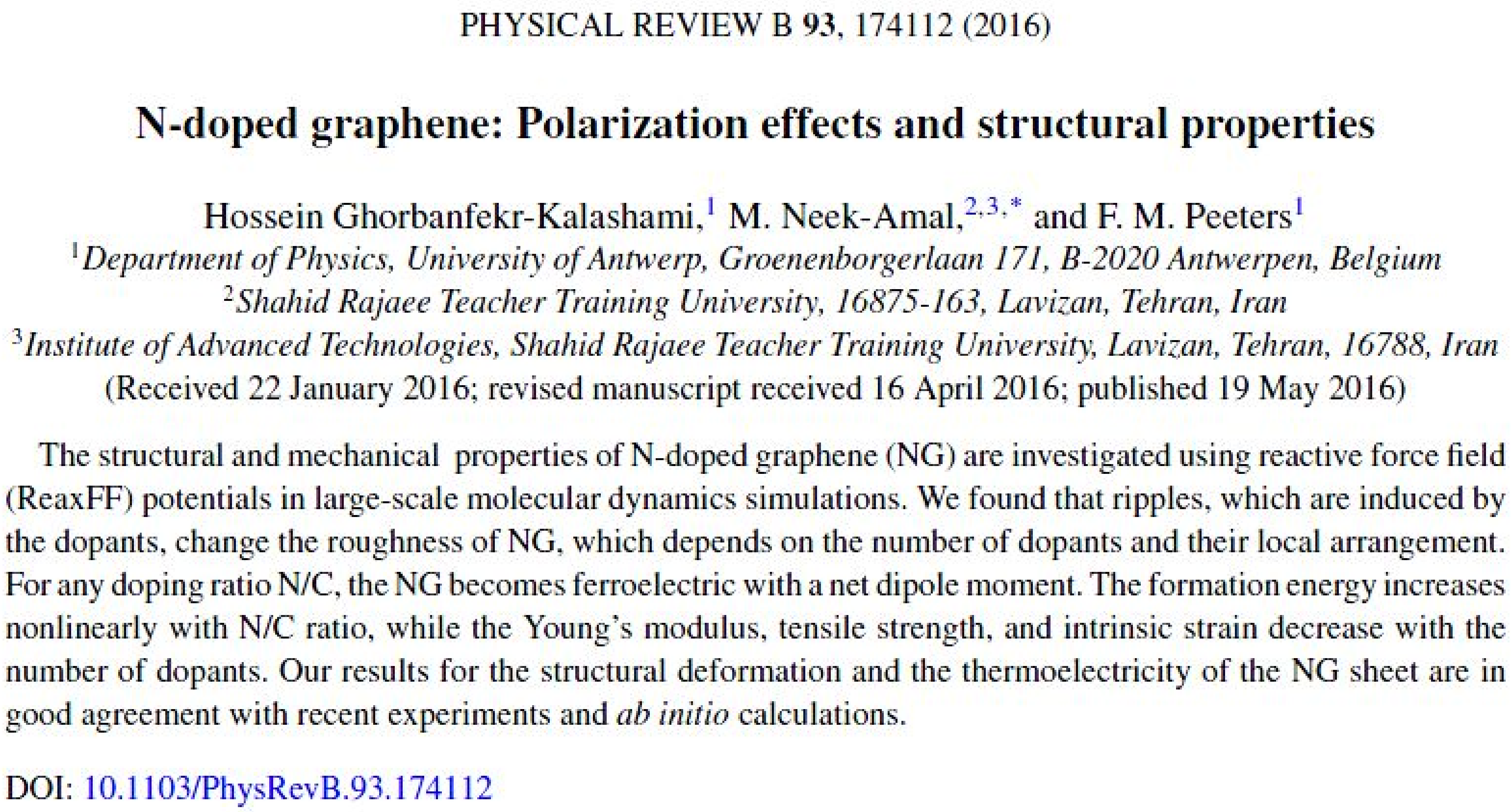

PHYSICAL REVIEW B **93**, 174112 (2016)

N-doped graphene: Polarization effects and structural properties

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The structural and mechanical properties of N-doped graphene (NG) are investigated using reactive force field (ReaxFF) potentials in large-scale molecular dynamics simulations. We found that ripples, which are induced by the dopants, change the roughness of NG, which depends on the number of dopants and their local arrangement. For any doping ratio N/C, the NG becomes ferroelectric with a net dipole moment. The formation energy increases nonlinearly with N/C ratio, while the Young's modulus, tensile strength, and intrinsic strain decrease with the number of dopants. Our results for the structural deformation and the thermoelectricity of the NG sheet are in good agreement with recent experiments and *ab initio* calculations.

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Summary (2)

- We found that the roughness of the NG systems is sensitive to the dopant concentration.

- The major contribution to the ripples is from the nitrogen cluster formation in the graphene layer.

- The graphene layer is mechanically weaker when doped with nitrogen, resulting in a decrease of the Young’s modulus, poisson ratio, and the breaking stress/strain.

- The formation energy increases as a function of the number of dopants, which results in a decrease in the stability of the nitrogen-doped graphene.