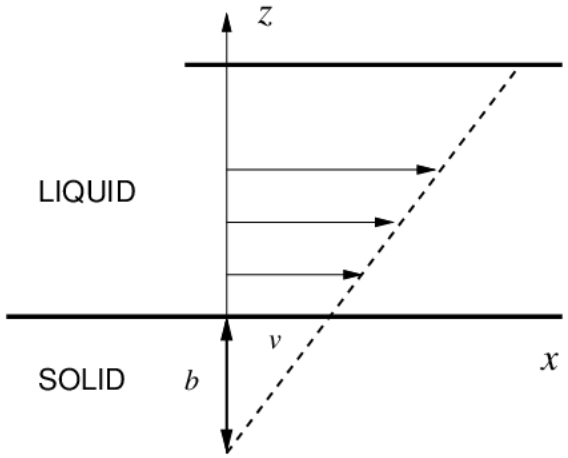
Combined First-Principles and Classical Modeling of hBN-Water Interfaces:

How Surface Roughness and Defects Modulate Wettability and Friction



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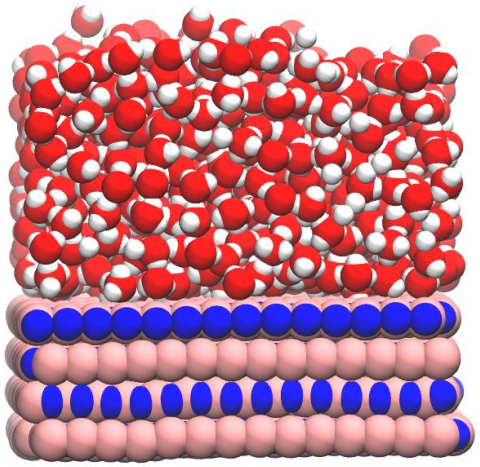
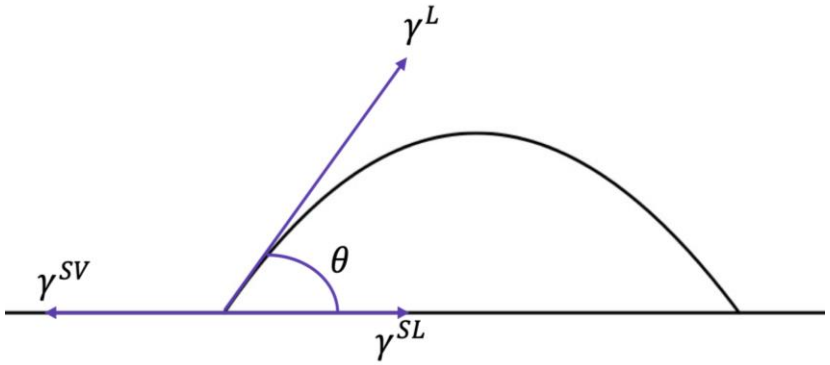
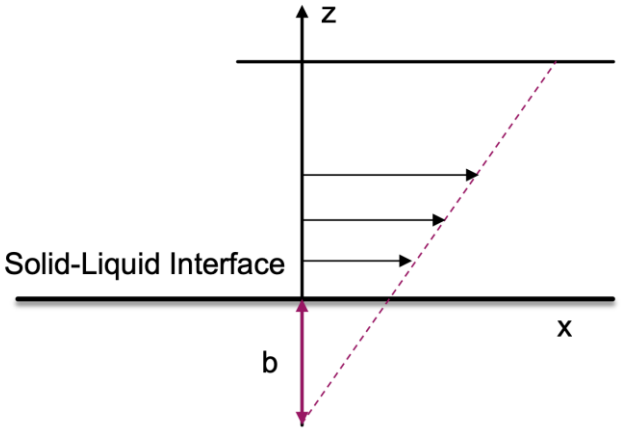


Introduction to solid-liquid interfaces

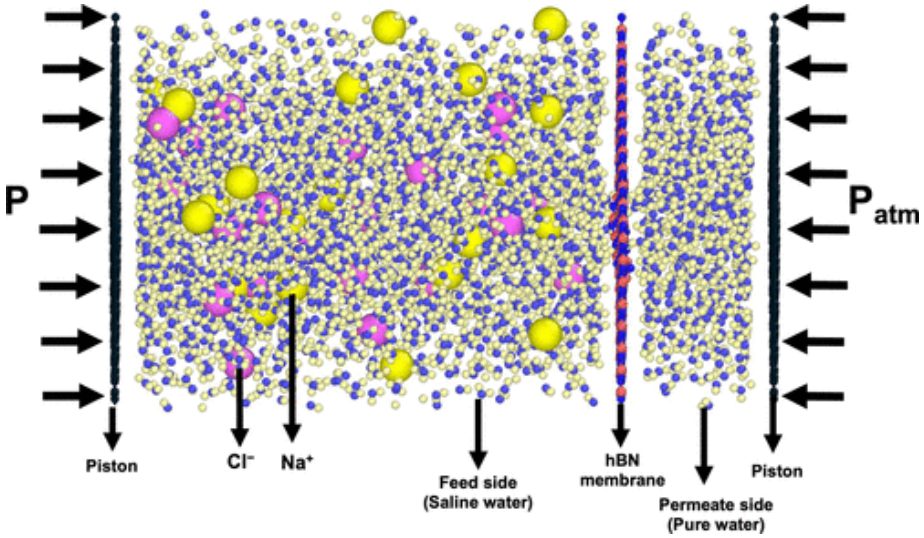
- Wettability is the tendency of a fluid to spread on to a solid surface.
- Lower contact angle (≤90°) signifies greater wettability, whereas higher contact angle (≥90°) indicates lower wettability.
- Slip length is the distance from the boundary where the linearly extrapolated fluid velocity profile vanishes.





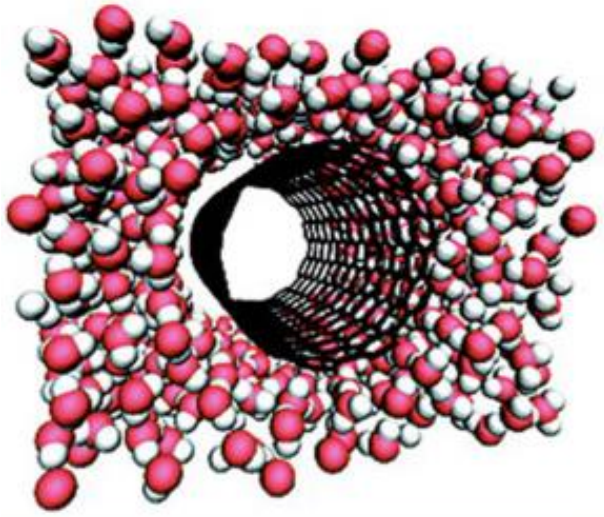
Motivation

- Two-dimensional materials are ultrathin nanomaterials with unique characteristics
  - High surface-to-volume ratio
  - High mechanical strength
  - Adjustable chemical functionality



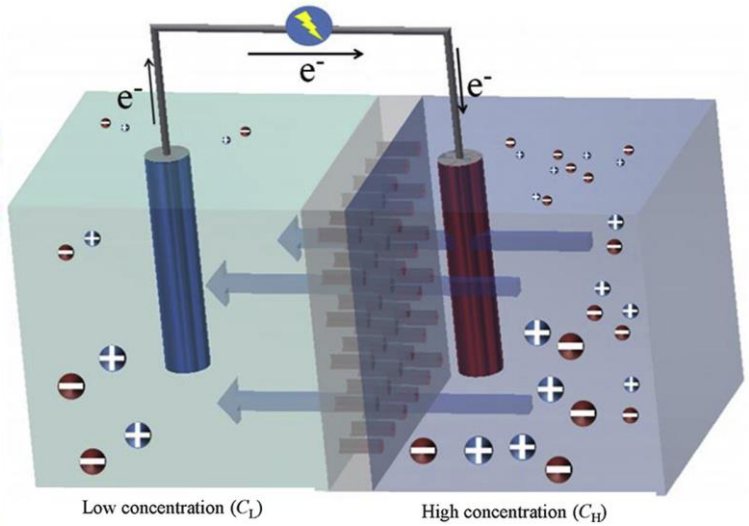
Water desalination

Sharma et al. J. Phys. Chem. B 2022, 126, 6, 1284–1300



Nanofluidics

Falk et al. Langmuir, 2012, 14261-14272.



Osmotic Energy Harvesting

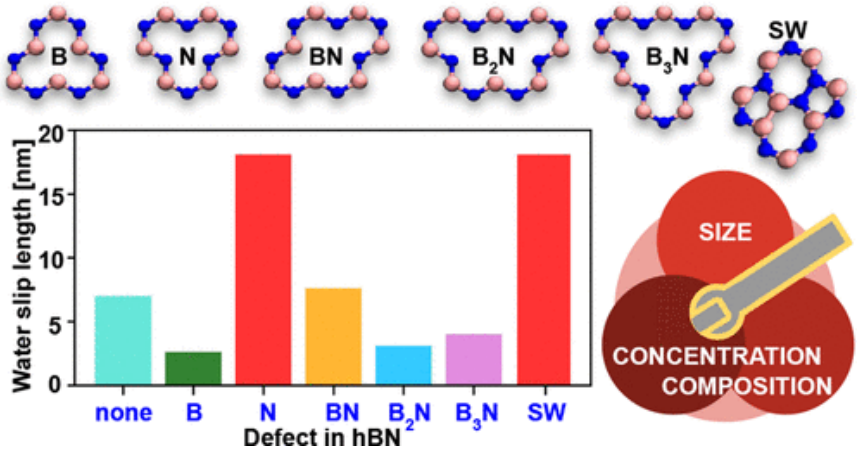
Haider et al. Materials Today Energy, 2022, 100909

Problem description

- Researchers are investigating the properties such as wettability, frictional, mechanical strength etc. of 2D materials.

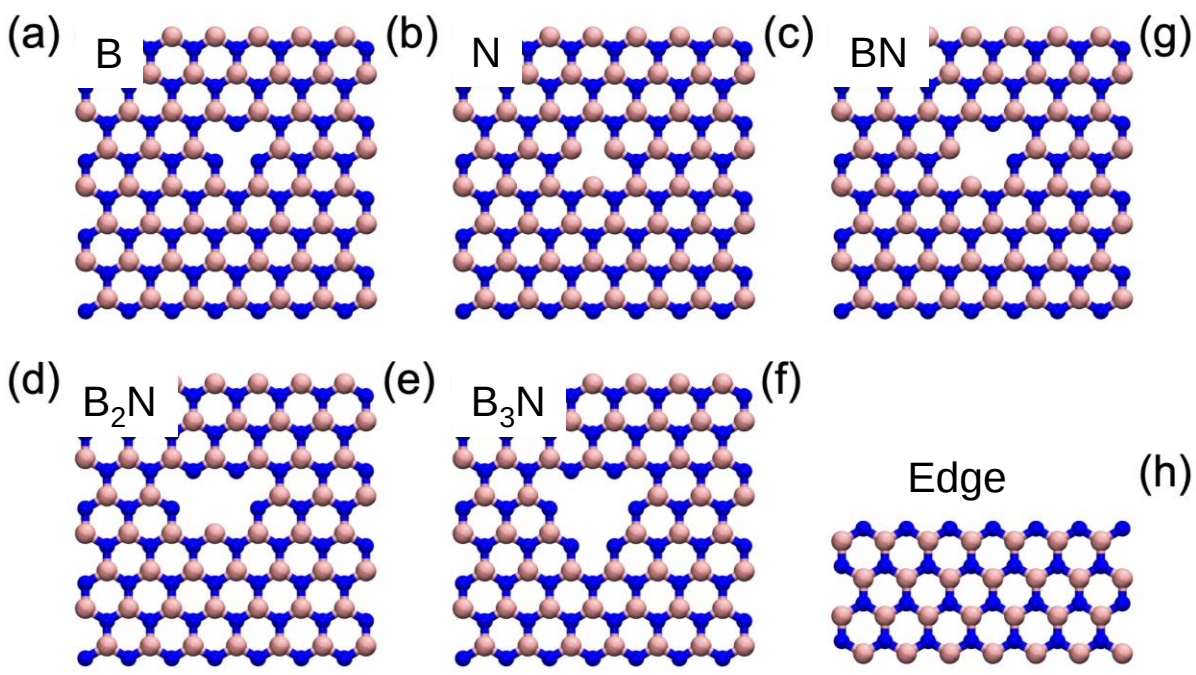
- In the real world, 2D materials may contain defects such as vacancy defects.

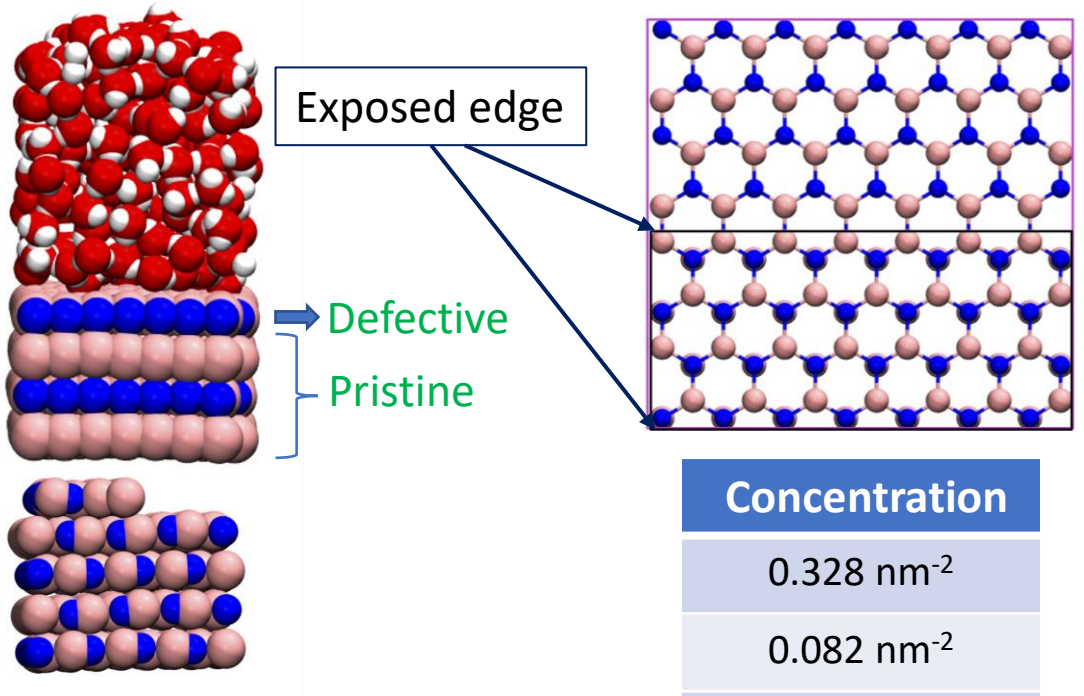
- The effect of defects on the wettability and friction of hBN surfaces is recently gaining attention.
  - Seal and Govind Rajan reported friction coefficient on a hBN surface containing defects
  - Verma et al. reported the water contact angle on a hBN surface containing defects.



Verma *et al. Phys. Chem. Chem. Phys.* **2021**, *23* (18), 10822–10834.
Seal and Govind Rajan, *Nano Letters* (2021), 21, 19, 8008–8016.

System Descriptions





Concentration
0.328 nm^{-2}
0.082 nm^{-2}
0.116 nm/nm^2
0.058 nm/nm^2

These defects were observed experimentally under TEM imaging. [1]

[1]Park et al. small, 2021, 17(23), 2100693
Humphrey et al. J Mol Graph. 1996,14(1):33-8, 27-8.

Approach

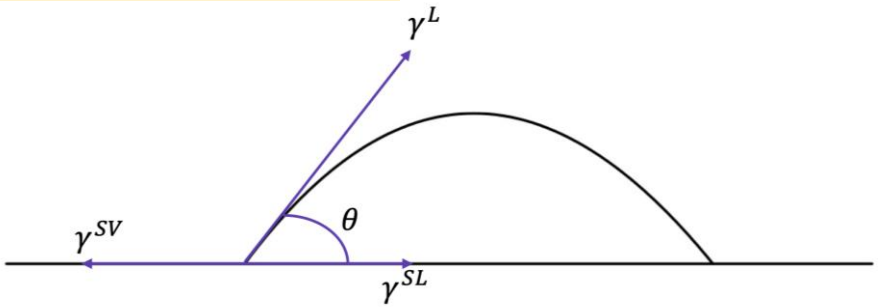
- The Young–Dupre equation relates the contact angle (θ) and surface tension of the liquid (γ_L)

$$W_{ad} = \gamma_L(1 + cos\theta)$$

Work of adhesion can be computed using free energy perturbation method

Surface tension:

$$\gamma_L = \frac{L_{normal}}{2}\left[\langle P_{normal}\rangle - \langle P_{tangential}\rangle\right]$$



- Slip length can be found using

$$b = {}^{\eta}/_{\lambda}$$

- Friction coefficient can be found using Green-Kubo relation

$$\lambda = \lim_{t\to\infty} \frac{1}{2Ak_BT} \int_0^t \langle F(t')F(0)\rangle dt'$$

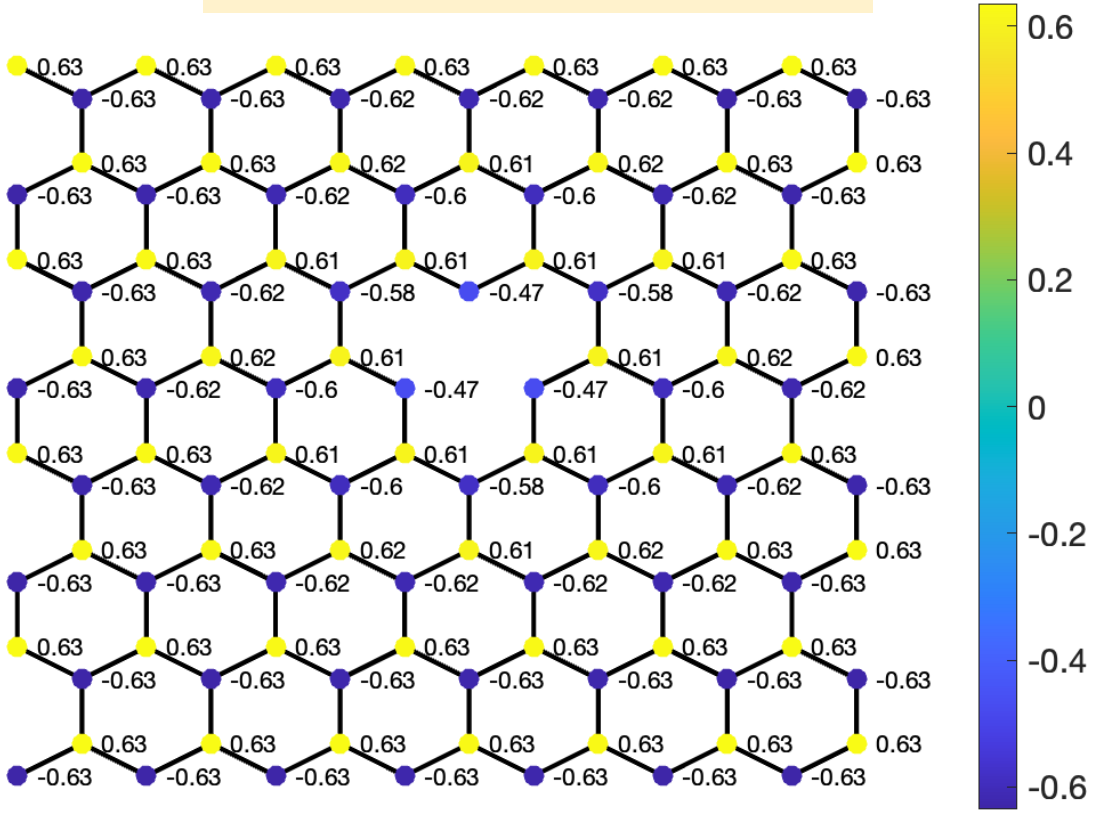
Bocquet and Barrat, J. Chem. Phys. 2013, **139**, 044704.
Kirkwood et al. J. Chem. Phys. 1949, 17, 338−343.

Modeling details

- Molecular dynamics (MD) simulation using LAMMPS
- Force field: Govind Rajan *et al*.
- NVT ensemble, Nose-Hoover Thermostat (298.15 K)

- Density functional theory (DFT) using cp2k to compute partial charges
- Partial charges: DDAP scheme proposed by Blöchl

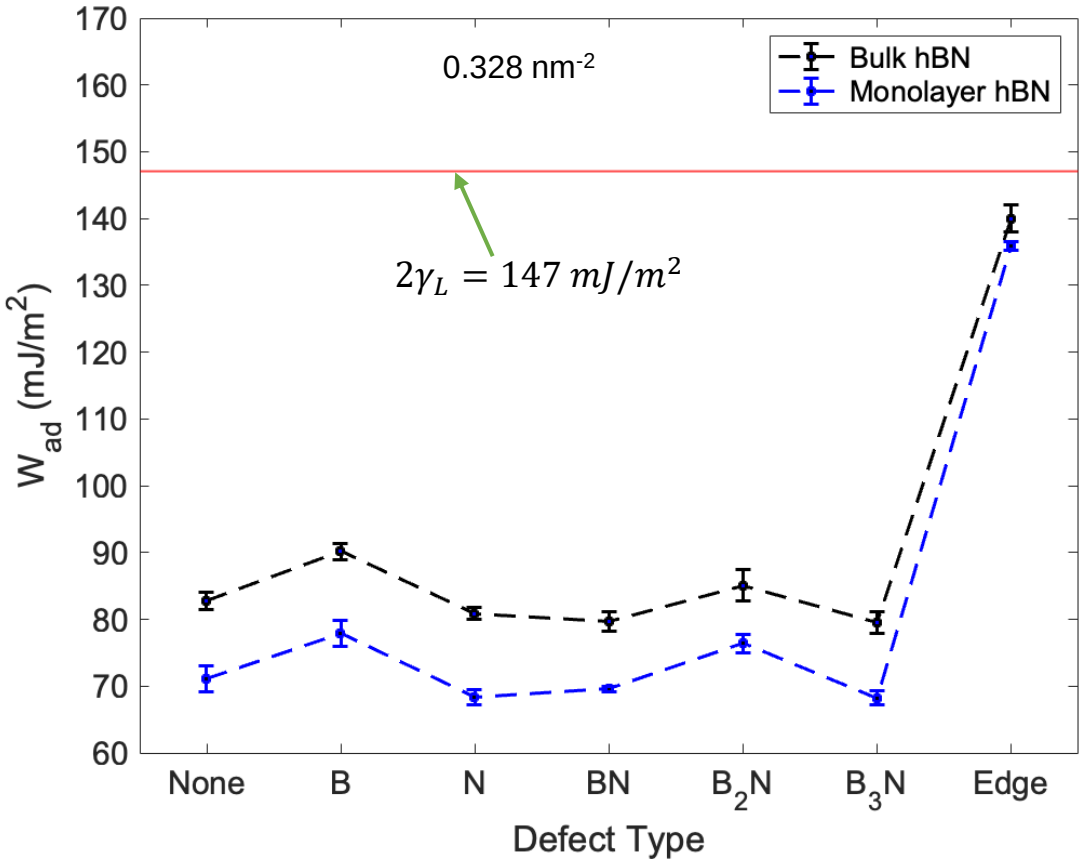
Pristine Layers
B: +0.907*e*, N: -0.907*e*

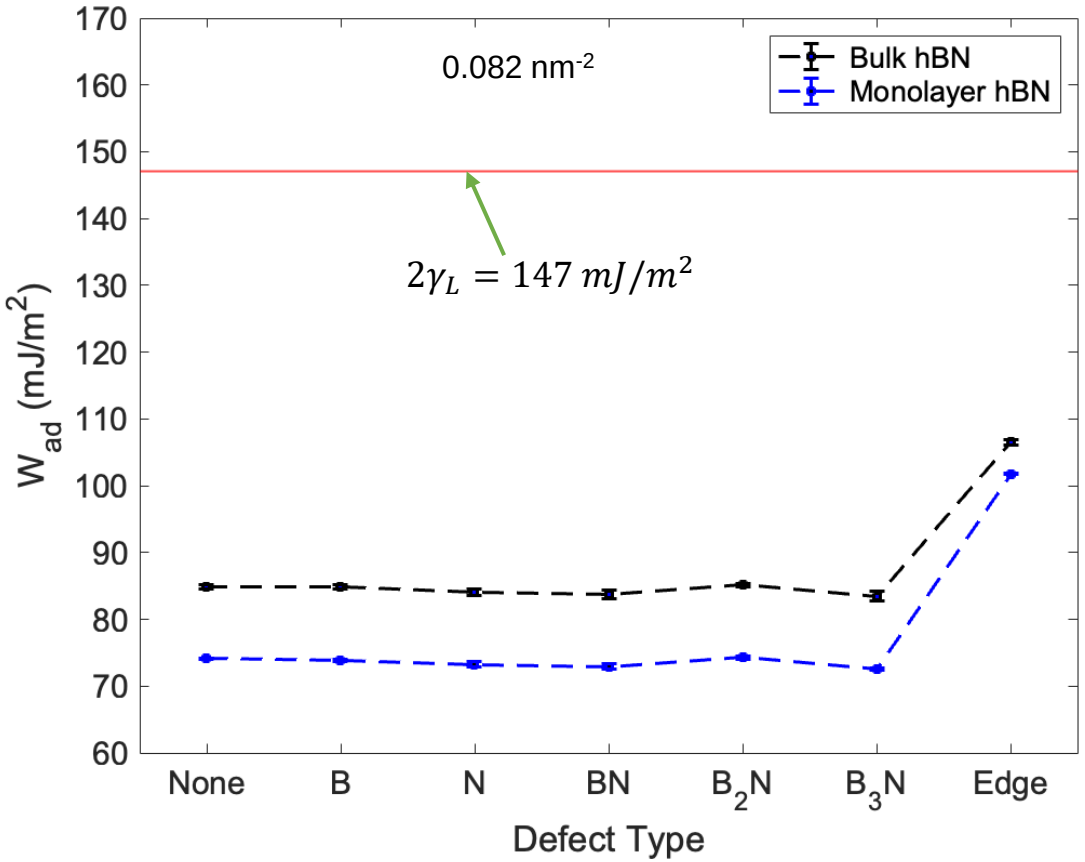


Partial charge distribution (in elementary charge units (*e*)) calculated using the DDAP scheme for hBN with B vacancy

Govind rajan et. al, J. Phys. Chem. Lett. 2018, 9, 1584−1591.
P. E. Blöchl, J. Chem. Phys. **103**, 7422 (1995).

Work of adhesion for various concentrations

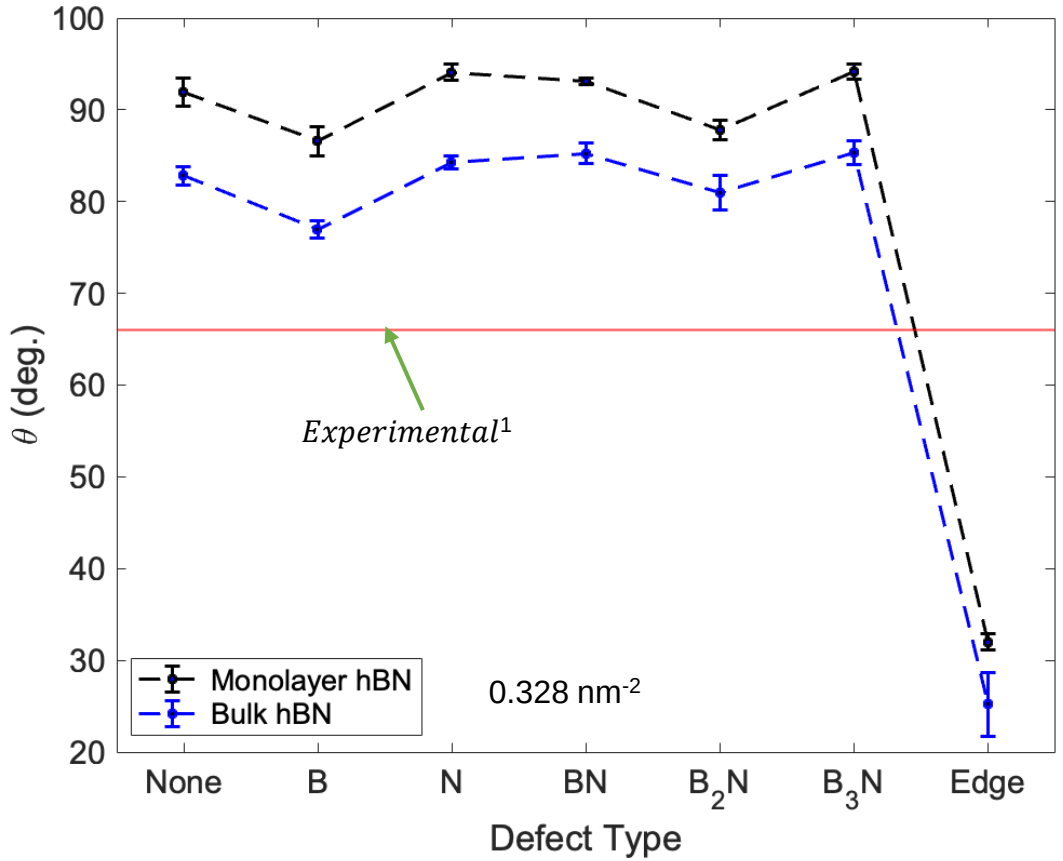


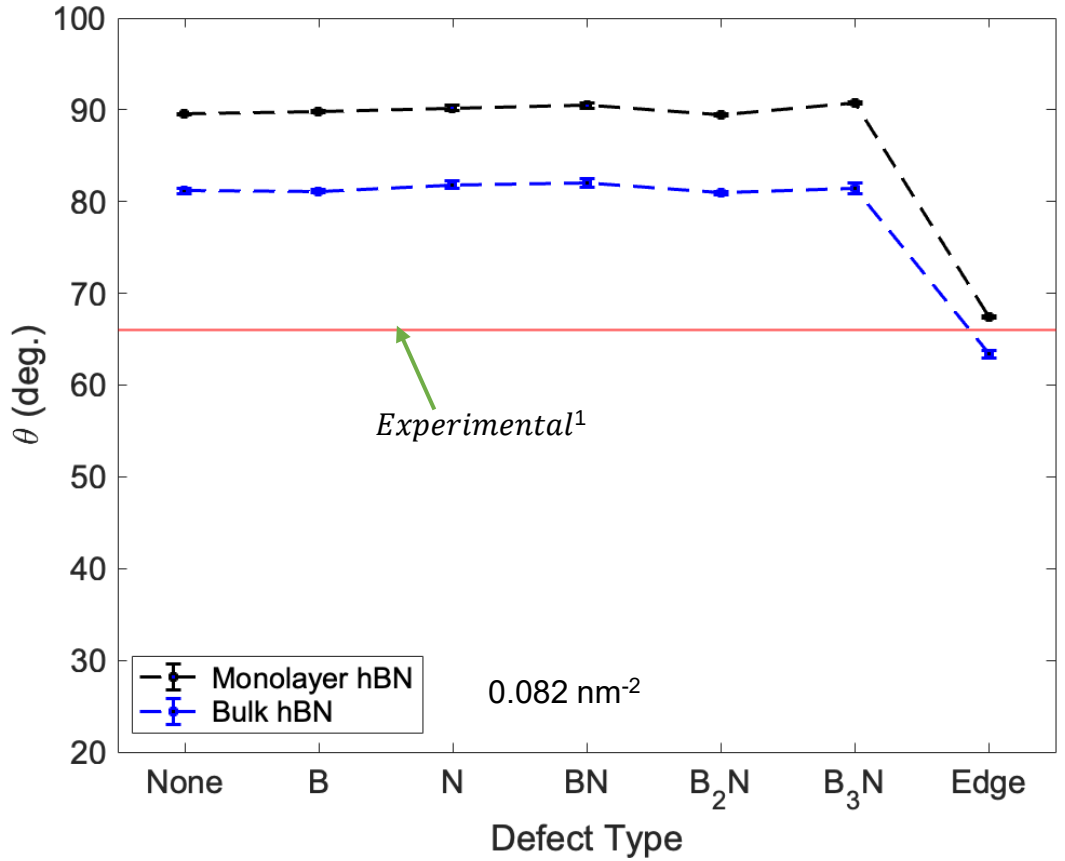


- hBN with exposed edges shows higher work of adhesion.
- At lower concentrations, the charges on each B and N atom are closer to bulk charges.

Verma and Govind Rajan, In preparation.

Water contact angle (WCA)



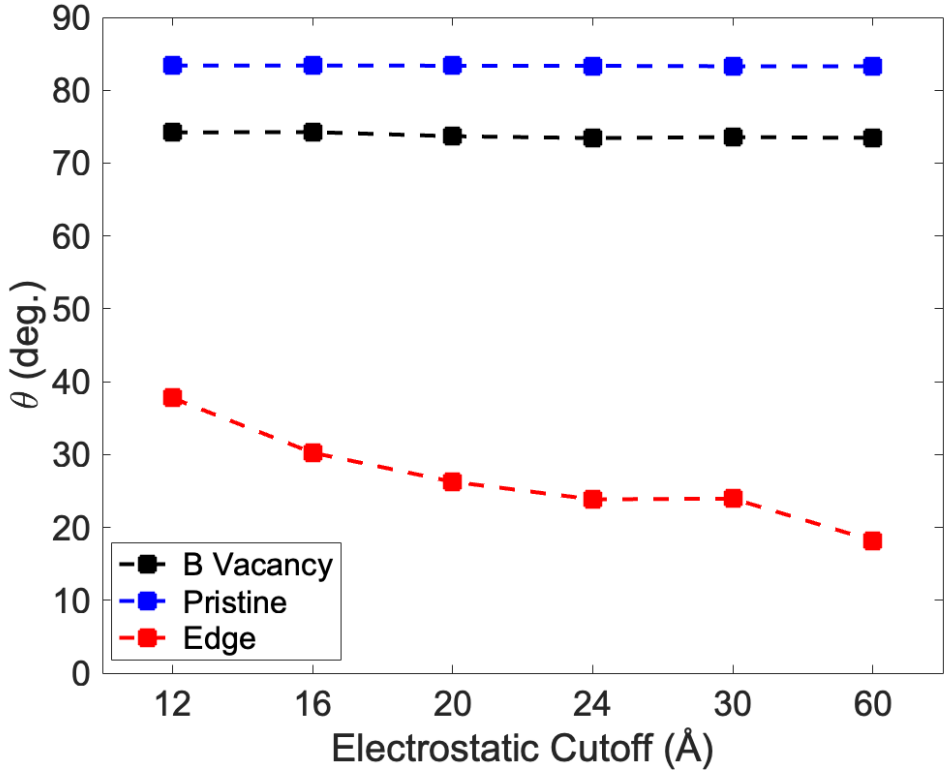


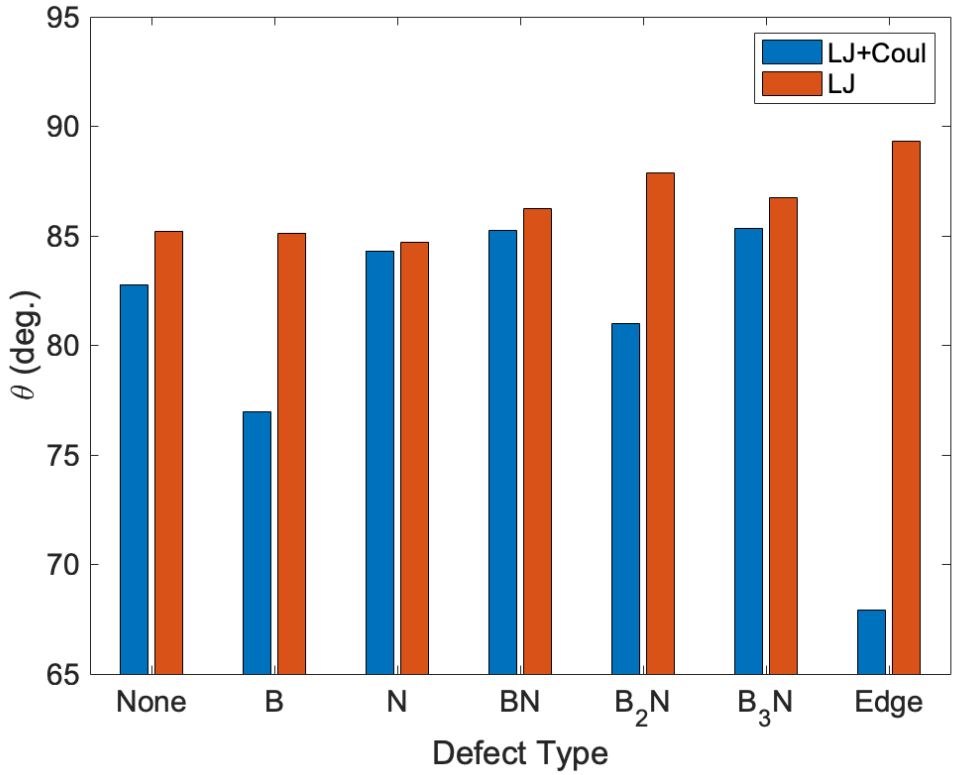
- Defect at a concentration equal to 0.082 nm^{-2} no longer affect the wetting properties of hBN surfaces.
- The hBN with monolayer roughness shows a WCA (63.4°) which is very close to experimental WCA (66°). [2]

[1]Li et al. Adv. Funct. Mater. 2017, 27, 1603181 [2]Verma and Govind Rajan, In preparation.

Understanding the wetting properties of hBN using interfacial interactions

- To understand the role of the electrostatic interaction, we must consider both short-range and long-range electrostatic interaction.





Verma and Govind Rajan, In preparation.

Friction coefficient and water slip length

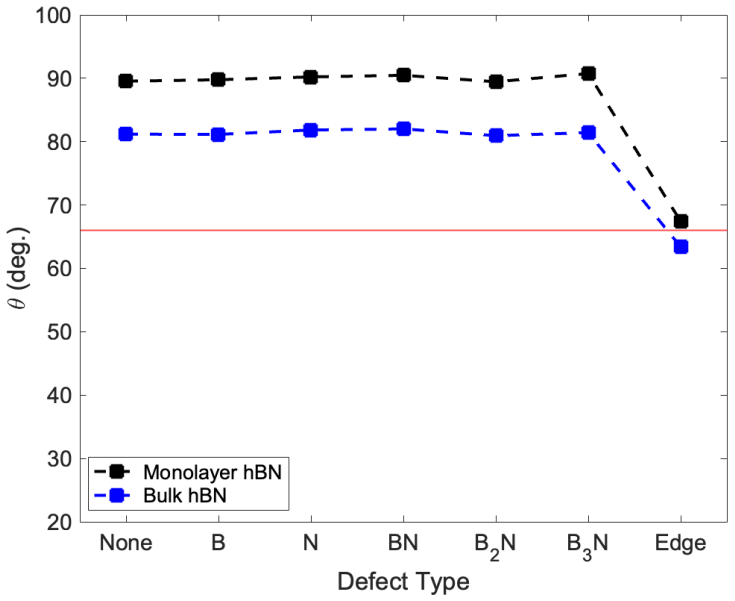
- The experimental value of water slip length is 1 nm.[1]
- We computed water slip length of 1.8 nm with monolayer roughness hBN. [2]
- The monolayer roughness is very important in explaining the interfacial properties of hBN.

$$b = {}^{\eta}/_{\lambda}\,, (\eta = 1.32 \text{ mPa s})$$ [3]

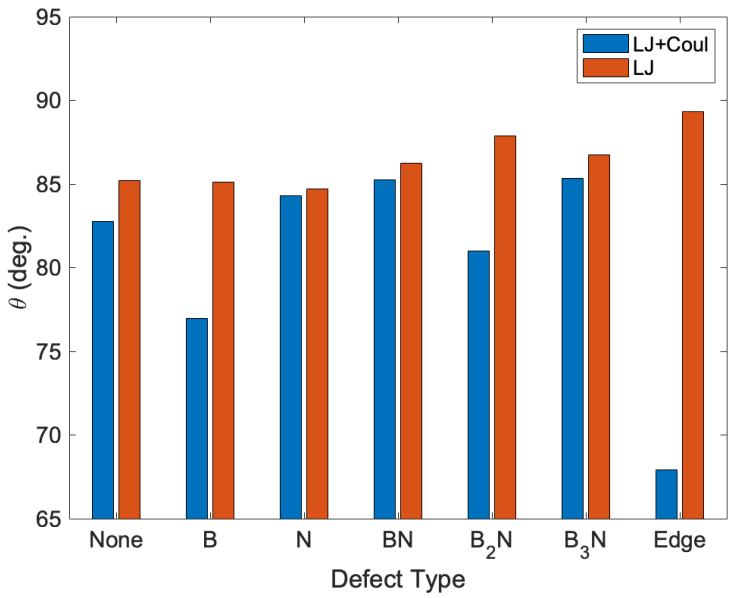
hBN configuration	Friction coefficient ($10^5 Ns/m^3$)	Slip length (nm)
Pristine hBN [4]	1.7 ± 0.2	7.7
Edge (0.116 nm/nm^2)	7.2 ± 0.3	1.8
Edge (0.058 nm/nm^2)	3.3 ± 0.7	4.0

[1]Keerthi et al. Nat Commun, 2021, 12, 3092.
[2]Verma and Govind Rajan, In preparation.
[3]Seal and Govind Rajan, *Nano Letters,* 2021, 8008-8016.
[4]Govind Rajan et al. *Nano Letters,* 2019, 1539-1551.

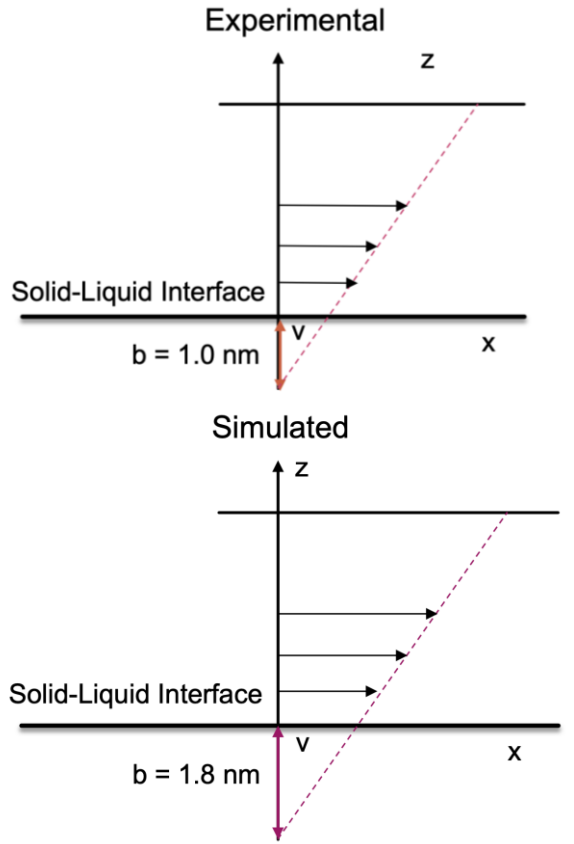
Conclusions



Simulated WCA of 63.4° very close to experimental WCA of 66°; lower vacancy concentration does not affect wettability of hBN



Electrostatic interactions between water and hBN depend on defect type



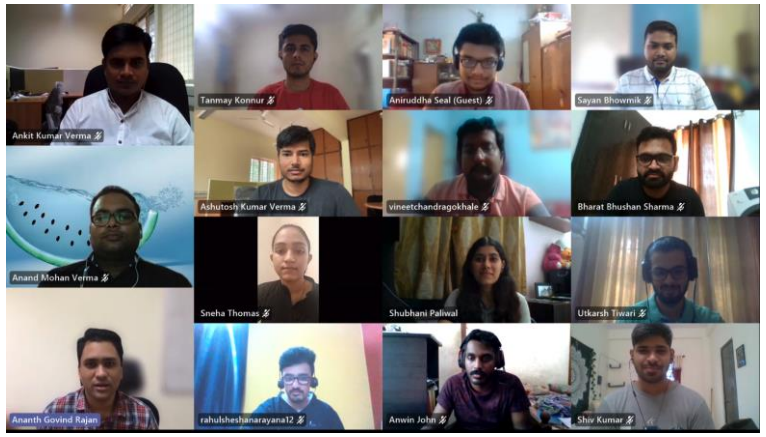
The estimate of 1.8 nm is closest to the experimental measurement of 1 nm

Acknowledgement

Prof. Ananth Govind Rajan

NATIONAL SUPERCOMPUTING MISSION

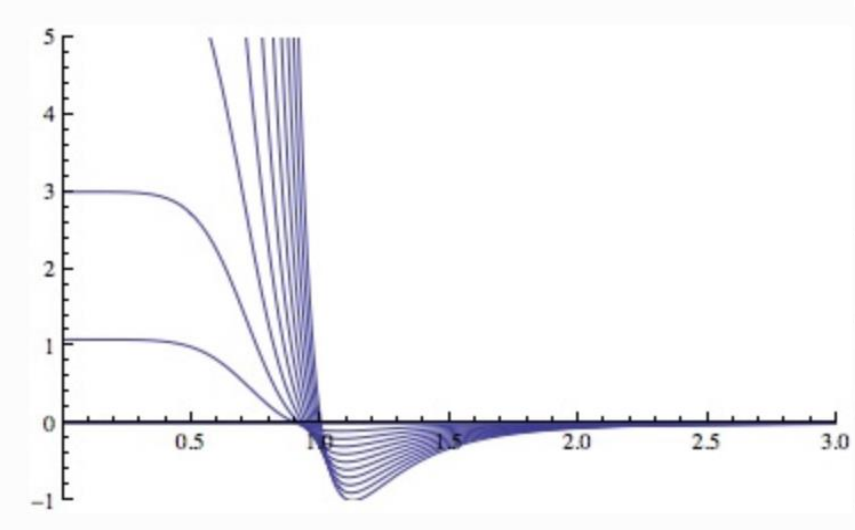
INDIAN INSTITUTE OF SCIENCE SERC

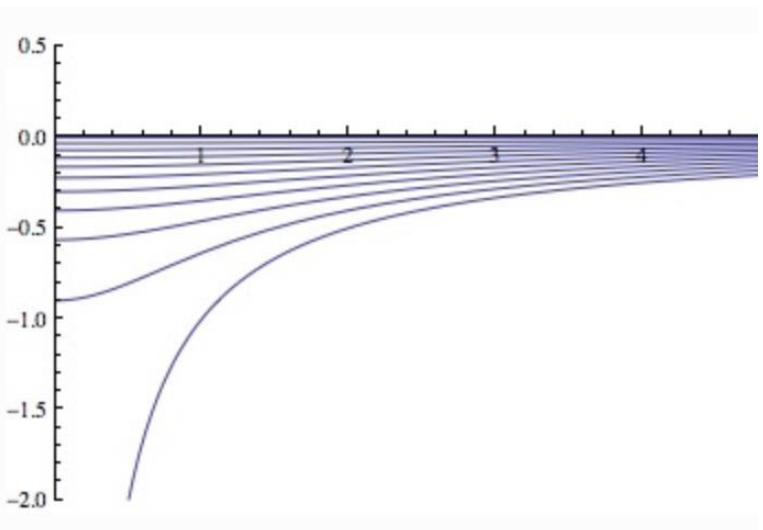


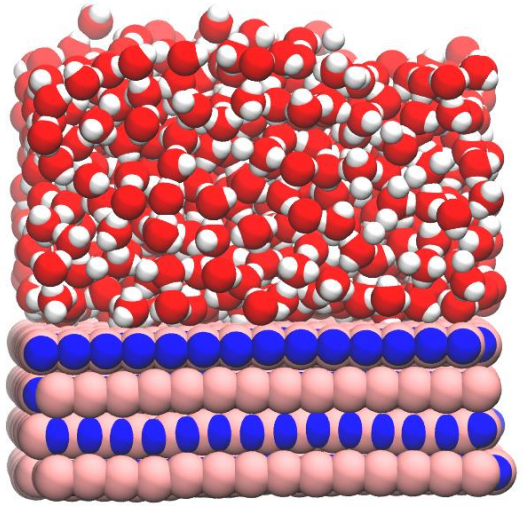
Thank You

Soft core potential

- Soft core potential can be used to calculate free energy change.
- n = 1, α_{LJ}=0.5, α_C=10 Å^2
- $E = \lambda^n 4\epsilon \left\{ \frac{1}{\left[\alpha_{LJ}(1-\lambda)^2+\left(\frac{r}{\sigma}\right)^6\right]^2} - \frac{1}{\alpha_{LJ}(1-\lambda)^2+\left(\frac{r}{\sigma}\right)^6} \right\} \quad r < r_c$
- $E = \lambda^n \frac{c q_i q_j}{\epsilon[\alpha_C(1-\lambda)^2+r^2]^{1/2}} \quad r < r_c$







https://docs.lammps.org/_images/lj_soft.jpg

Work of Adhesion

System	W_{ad} on bulk hBN (mJ/m^2)		W_{ad} on monolayer hBN (mJ/m^2)	
	0.328 nm^{-2}	0.082 nm^{-2}	0.328 nm^{-2}	0.082 nm^{-2}
Pristine	82.80	84.84	71.11	74.15
B vacancy	90.16	84.88	77.92	73.85
N vacancy	80.85	84.00	68.31	73.28
BN vacancy	79.67	83.79	69.57	72.95
B_2N vacancy	85.09	85.22	76.37	74.29
B_3N vacancy	79.54	83.43	68.21	72.60
Exposed edge	131.16	101	126.56	95.39

Water Contact Angle

System	WCA on bulk hBN (°)		WCA on monolayer hBN (°)	
	0.328 nm^{-2}	0.082 nm^{-2}	0.328 nm^{-2}	0.082 nm^{-2}
Pristine	82.8	81.2	91.9	89.54
B vacancy	76.9	81.2	86.6	89.8
N vacancy	84.3	81.8	94.1	90.2
BN vacancy	85.2	82.0	93.1	90.5
B_2N vacancy	80.9	80.9	87.8	89.4
B_3N vacancy	85.3	82.3	94.2	90.7
Exposed edge	38.5	68.1	43.9	72.7

WCA using various force field for pristine hBN

	DREIDING	Wu et al.	Hilder et al.	Garnier et al.	Govind Rajan et al.
σ_{BO}(Å)	3.310		3.2720	3.3068	3.237
σ_{NO}(Å)	3.266		3.1908	3.2644	3.192
σ_{BM}(Å)		3.322			
σ_{NM}(Å)		3.278			
ε_{BO}(kcal/mol)	0.1414		0.0955	0.14146	0.1208
ε_{NO}(kcal/mol)	0.1748		0.2069	0.17475	0.0999
ε_{BM}(kcal/mol)		0.0981			
ε_{NM}(kcal/mol)		0.1213			
$\theta(°)$	15.4 ± 5.1	76.2 ± 0.3	42.6 ± 0.5	19.2 ± 2.2	81.2 ± 0.5

- None of the other force fields for hBN can reproduce quantitatively the experimentally measured WCA on hBN, when modeling the hBN surface as a pristine layer.
- In combination with the TIP4P/Ice water model, Govind Rajan force field was shown to predict water-hBN binding energies in exceptional agreement with reference-quality quantum Monte Carlo (QMC) calculations carried out by the Michaelides group.

Surface tension

- The surface tension γ is calculated by estimating the change in the Helmholtz free energy A upon a change in the interfacial area a.
- $\gamma = \left(\frac{\partial A}{\partial a}\right)_{N,V,T} \cong \left(\frac{\Delta A}{\Delta a}\right)_{N,V,T}$
- Surface tension can be theoretically predicted using molecular simulations
  - Free-energy perturbation
  - Test-area method
  - Bennett's method

J. Chem. Phys. **127**, 174709 (2007); https://doi.org/10.1063/1.2795698

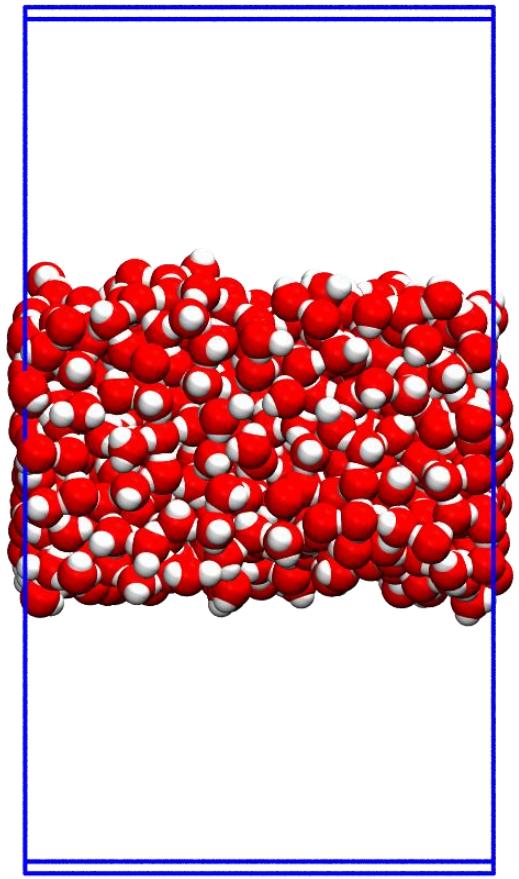
Surface tension

- The surface tensions of water are calculated according to

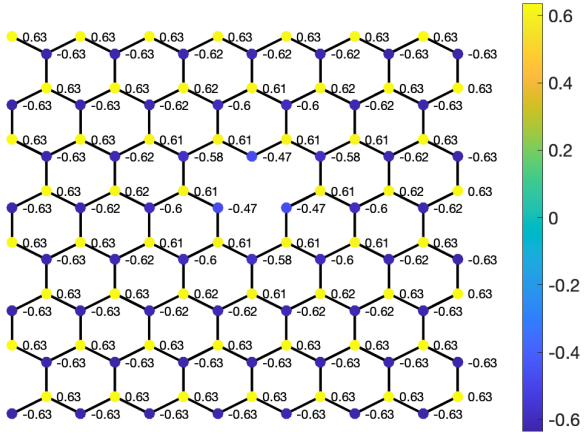
$$\gamma_L = \frac{L_z}{2}\left[\langle P_{zz}\rangle - \frac{1}{2}\left(\langle P_{xx}\rangle + \langle P_{yy}\rangle\right)\right]$$

Where a liquid interface is perpendicular to the z-direction, L_Z is the length of the simulation box in the z-direction, P_{zz} is the pressure of the liquid in the normal z-direction, P_{xx} and P_{yy} are the pressure in the tangential direction.

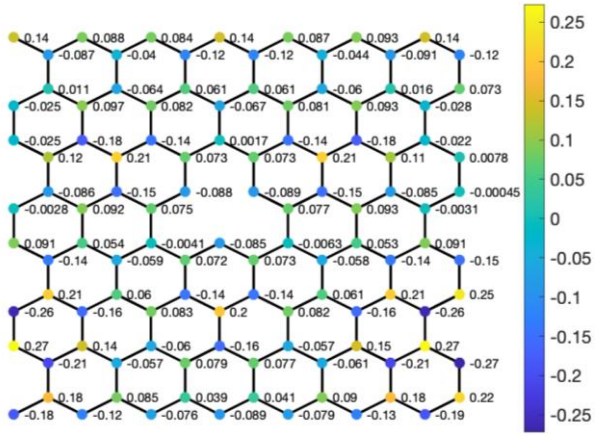
Water Model	Surface Tension (C. Vega and E.)	Surface Tension(this work) (mJ/m^2)
TIP4P	59.0±0.9	49.67±0.4
TIP4P/2005	69.3±0.9	62.95±0.6
TIP4P/Ice	80.1±0.7	73.56±0.8



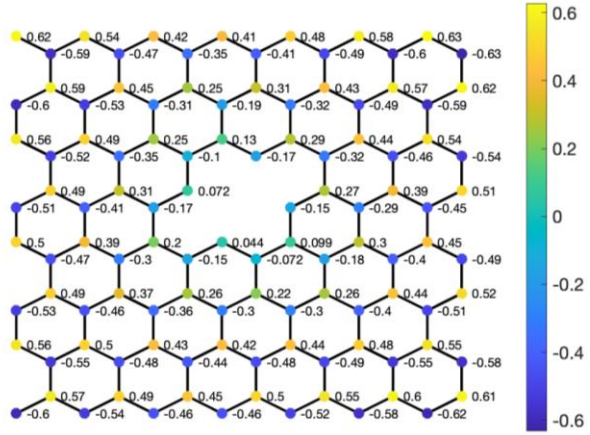
Charge distributions on hBN sheet containing defects



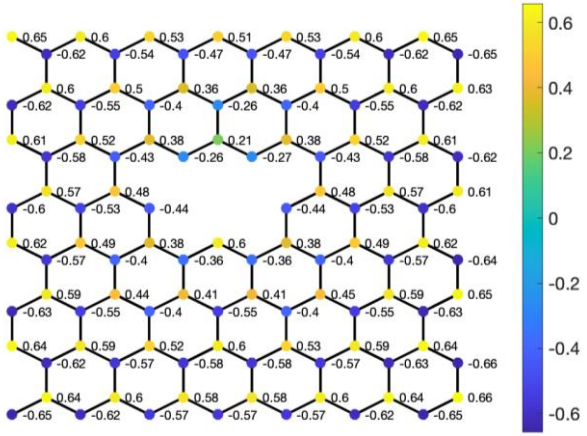
B vacancy



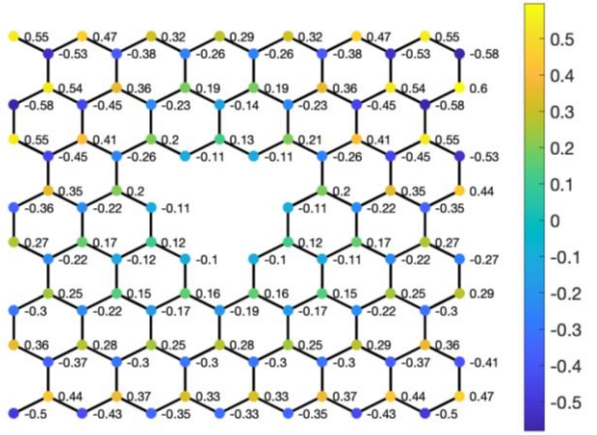
N vacancy



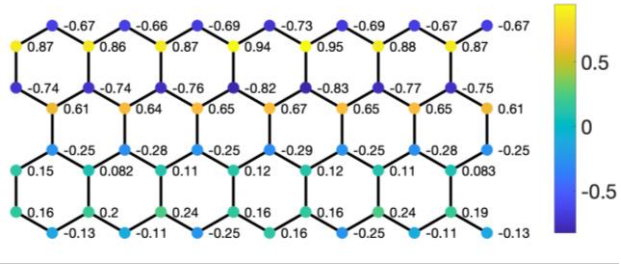
BN vacancy



B_2N vacancy



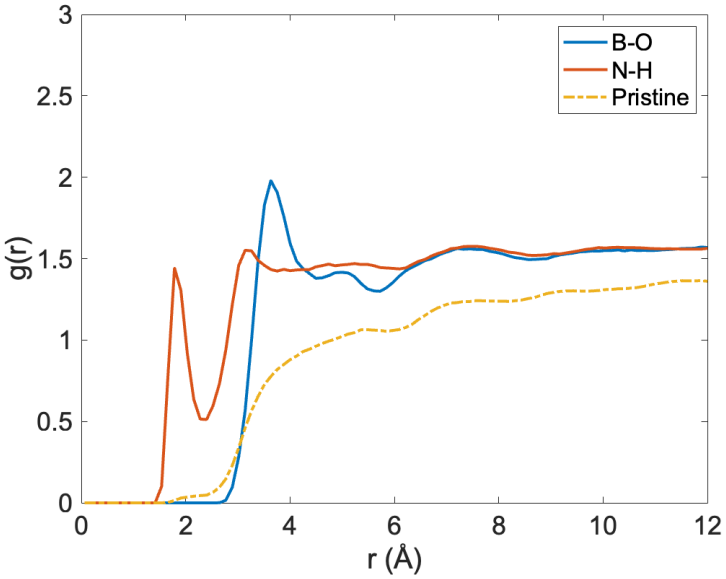
B_3N vacancy



Edge defect

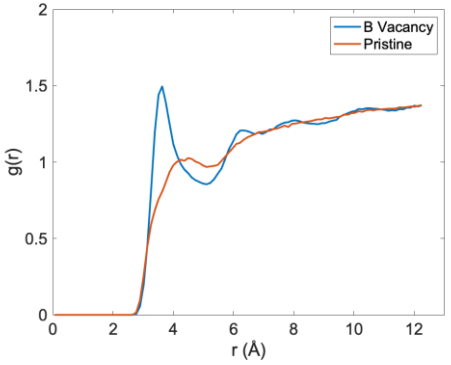
Radial distribution function

- To see the effect of the defects on the RDF, we computed RDF for the B and N atoms at the rim of the pores instead of all B and N atoms.
- The zigzag edges are terminated either on N or B atoms. Thus, each zigzag edge of an hBN nanosheet is charged either positively (B-terminated edge) or negatively (N-terminated edge).
- In the case of edge defects, the radial distribution function (RDF) has a sharp peak for B-O and N-H.
- H atoms interact with N atoms and come closer. Subsequently, O atoms also come closer to the surface

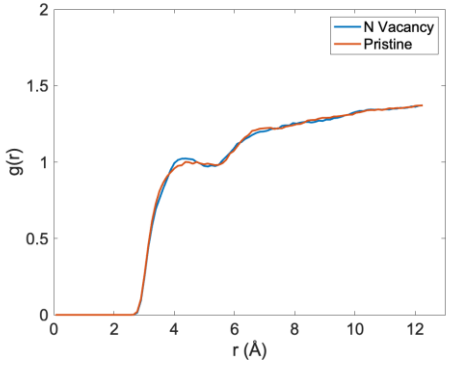


Radial distribution function (B-O, N-H)

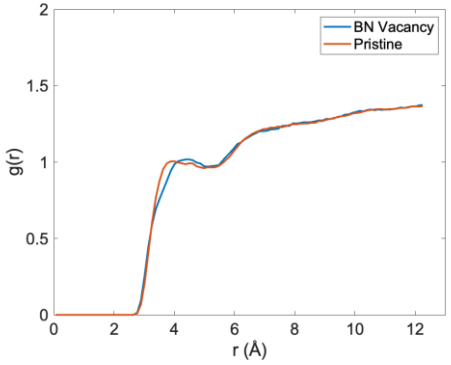
B vacancy



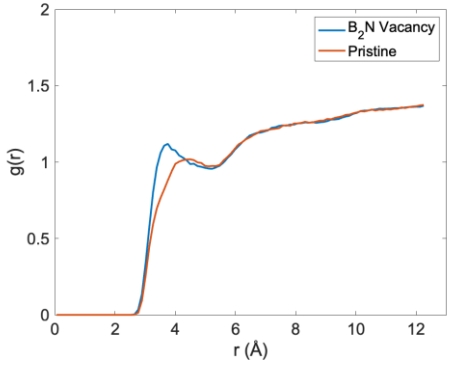
N vacancy



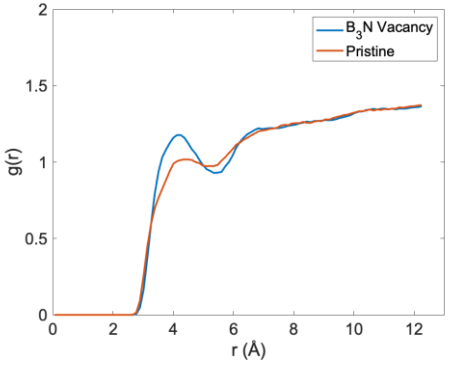
BN vacancy

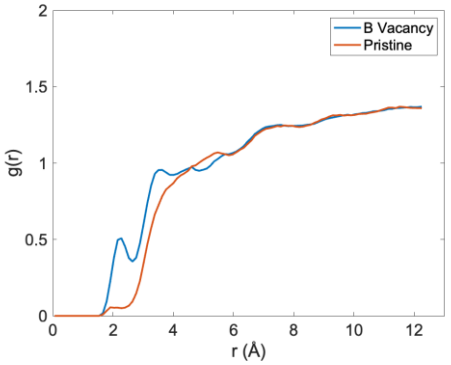


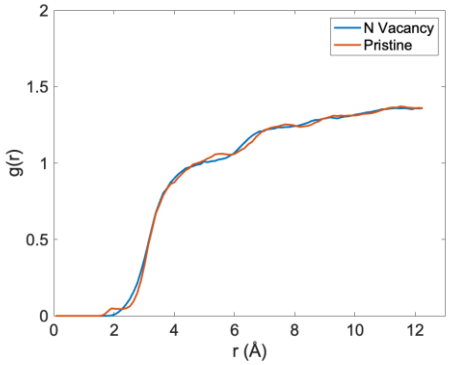
B_2N vacancy

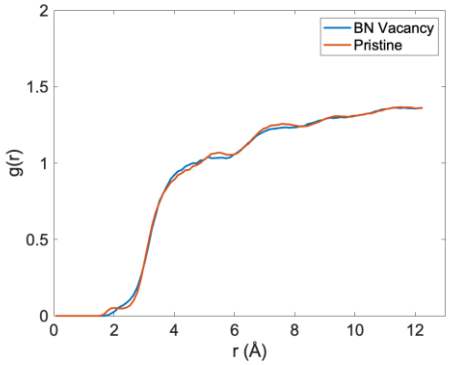


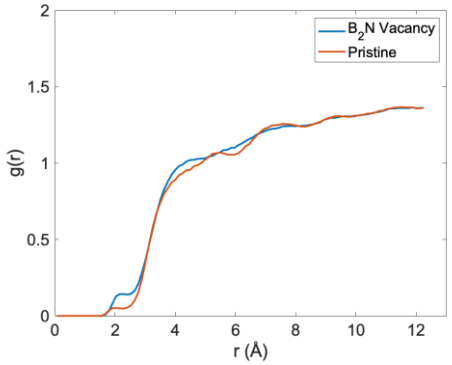
B_3N vacancy

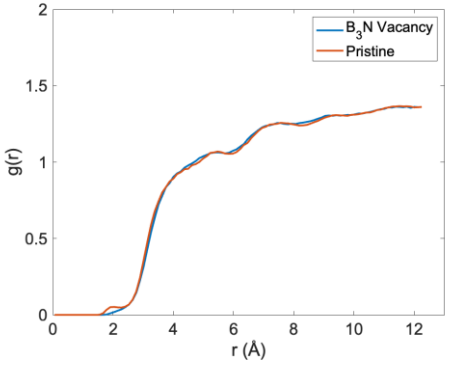




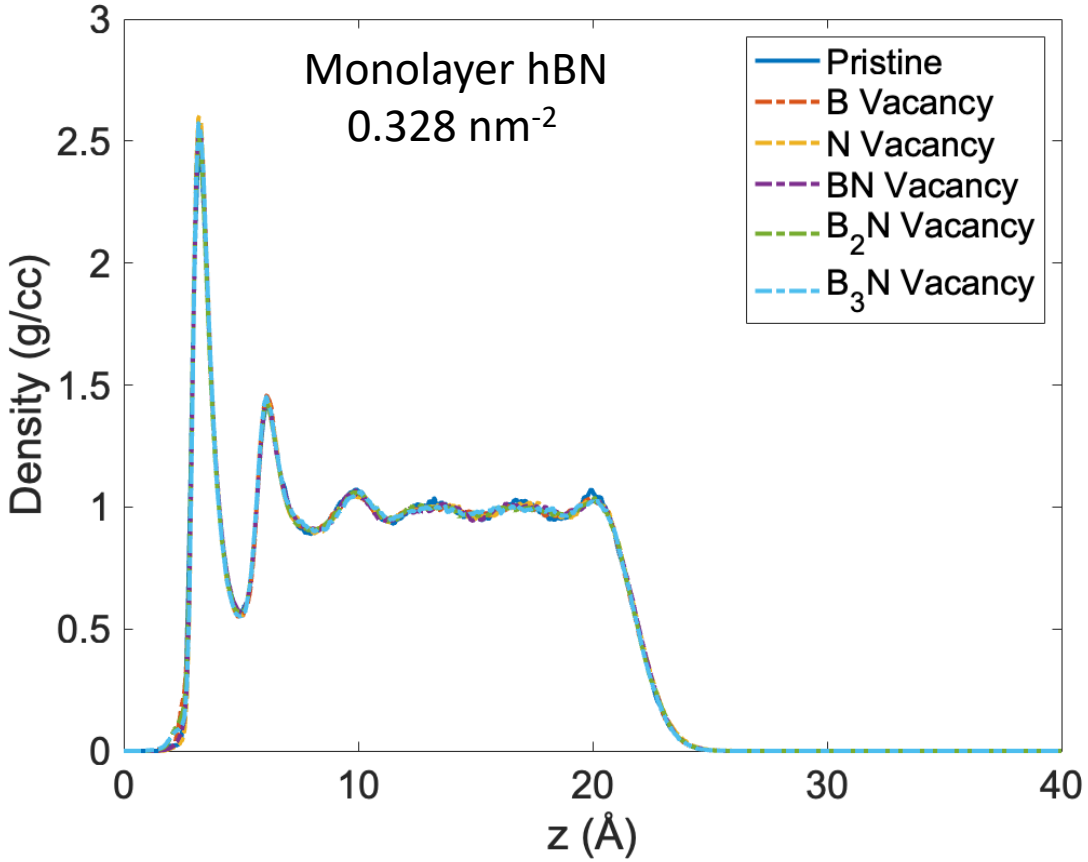


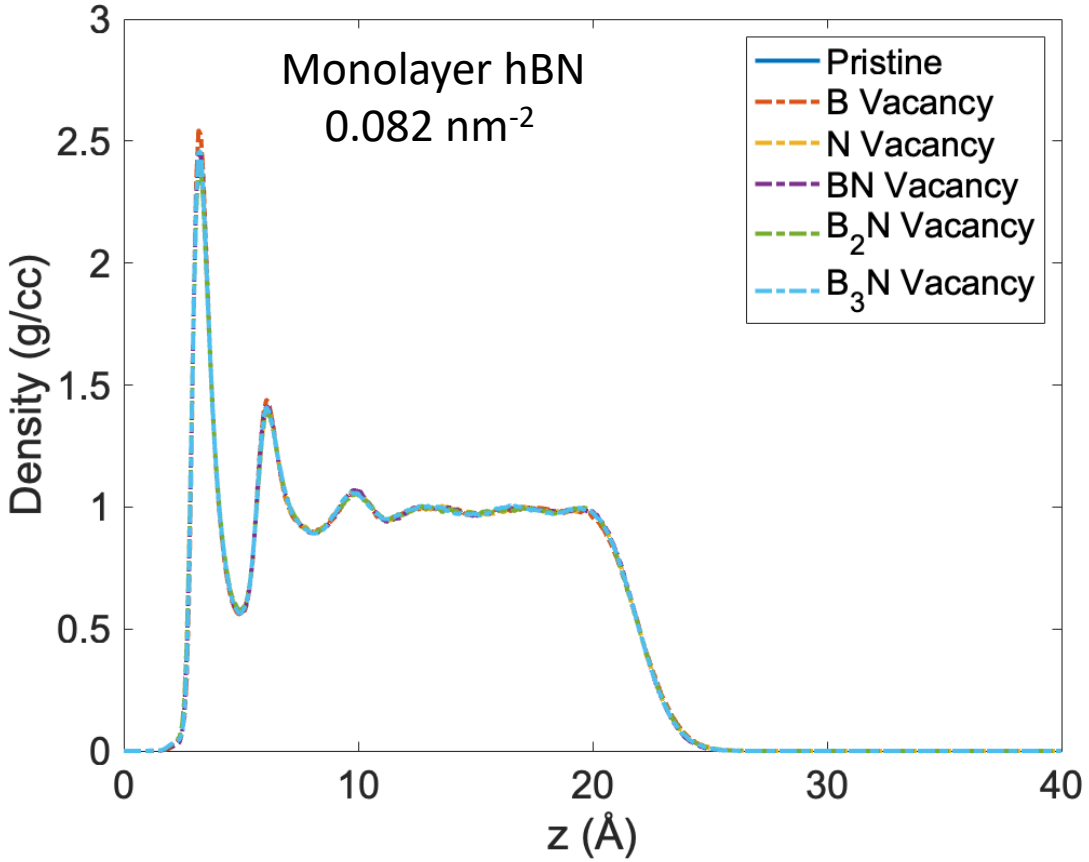






Water density profile





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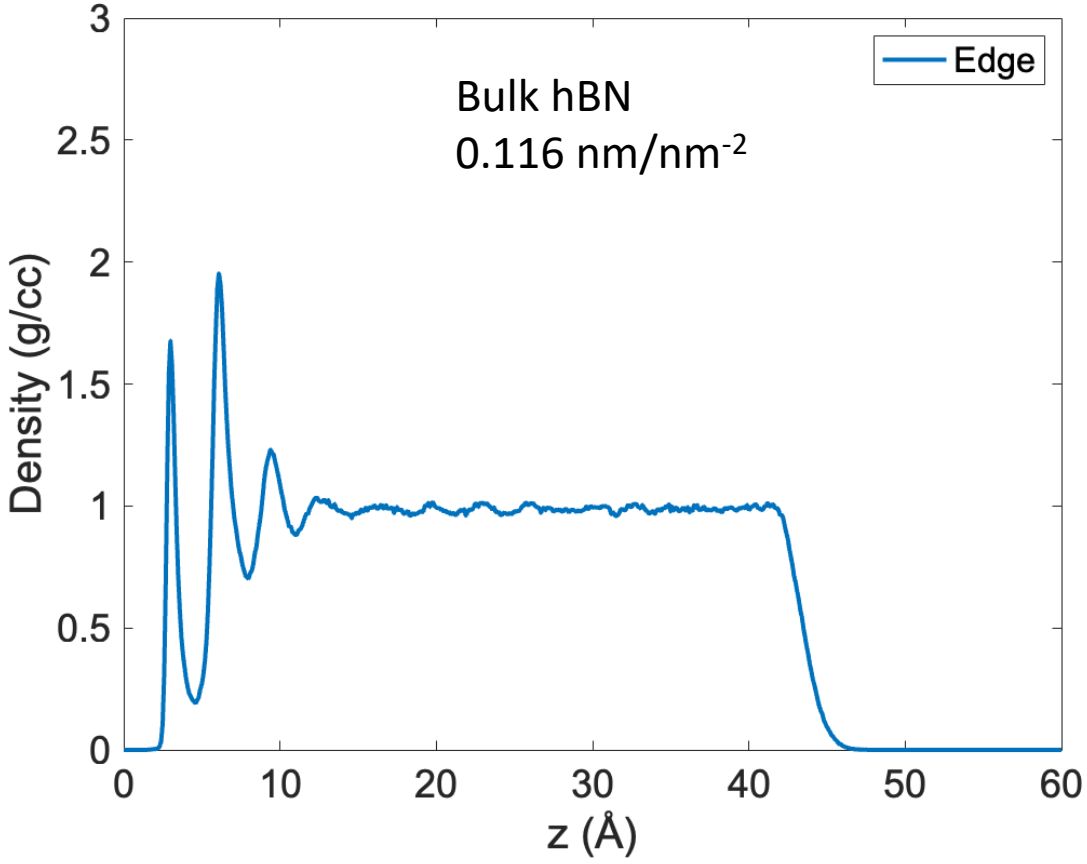

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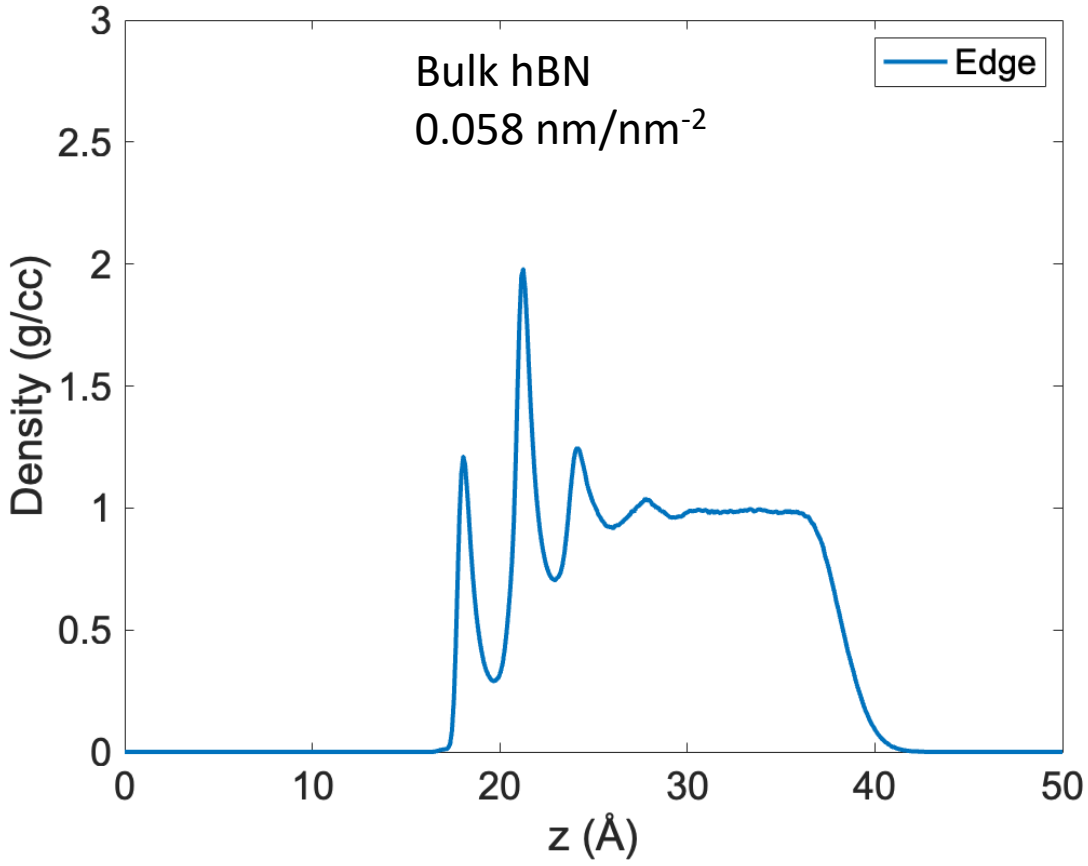

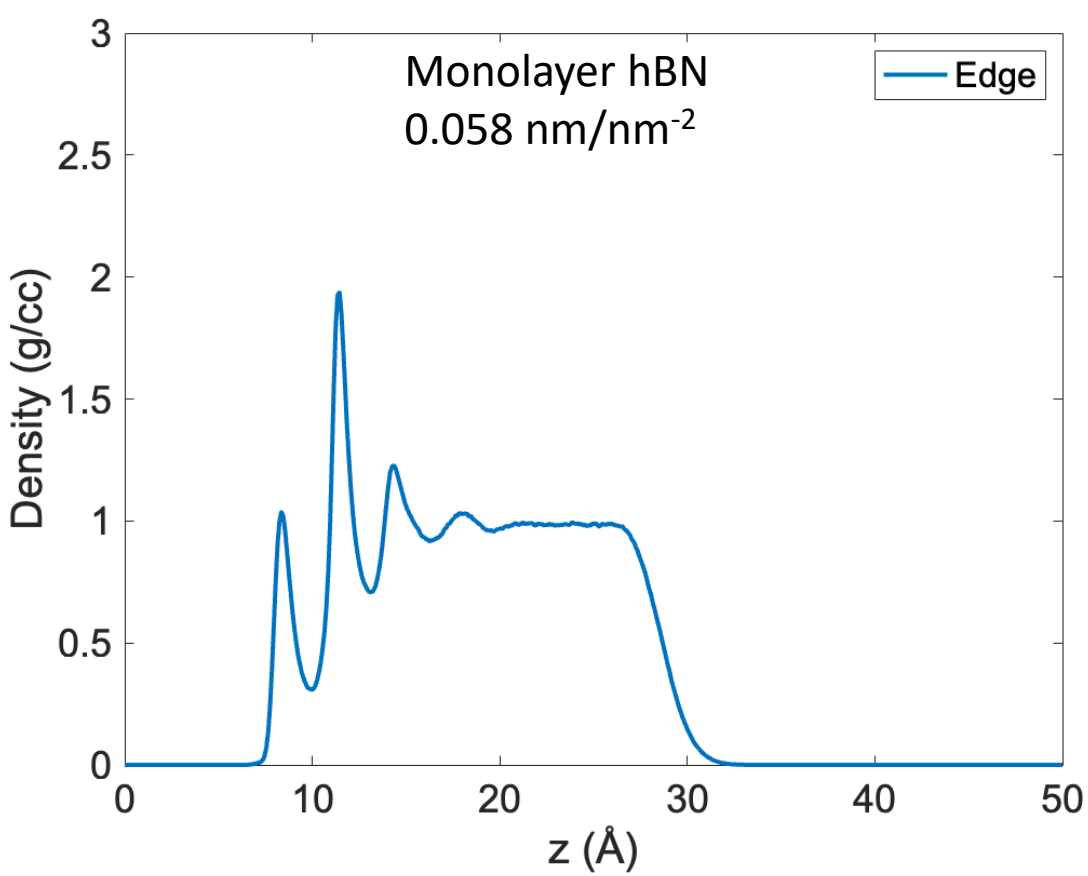

Green-Kubo plots