## Supplemental Information: Missing links towards understanding equilibrium shapes of hexagonal boron nitride: algorithm, hydrogen passivation, and temperature effects

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## I. Comparison of our results, previous method and studies



**Fig.S1**. Total edge energies  $({}^{E}_{tri} - n_{N}\mu_{N} - n_{B}\mu_{B})$  as a function of the sizes of bare triangular clusters, with linear fittings.

To obtain the exact value for comparison, here we strictly followed the algorithm proposed in ref.1, 2, and we did a linear fitting for the edge formation energies of the bare clusters as a function of cluster sizes. Here, the formation energy is defined as  $(E_{tri} - n_N \mu_N - n_B \mu_B)$ , where  $E_{tri}$  is the total energy of each bare cluster. The cluster sizes range from m=2 to m=10, as shown in

**Fig.S1**. The accuracy of this method can also be estimated through Eq. (4), where  $\hat{\mu}_{H_N}$  and  $\hat{\mu}_{H_B}$  can be obtained via the ribbon models as shown in Fig.1(b), namely, subtracting the total energy by the chemical potentials of B and N atoms as well as the obtained  $\gamma_N$  or  $\gamma_B$  by the bare cluster method. Previous error estimation by using the sum of formation energies of two conjugated edges, obtained from a ribbon with both bare edges, is problematic, because of large interactions and unphysical charge transfer between these edges. The two N atoms, as shown in the red circle in **Fig.1(e)**, form bonds after relaxation, with the interatomic distance shrinks from ~2.5 Å to ~1.6 Å. However, for B terminated edges, no significant reconstruction is observed. Therefore, the difference of the computing error between these two edges is due to the significant reconstruction of N-N dimers near the corner. Such reconstructions can help satisfy ECM for anion terminated edge, but no cation terminated edges. This can be confirmed by the 0.28 Bohr magneton difference of the magnetic moments on the edge N atoms, between the bare cluster edges and the asymmetric ribbon models like that shown in **Fig.1(c)**. This can be clearly demonstrated by a detailed comparisons of their spin charge densities, which are shown below.



**Fig.S2.** Illustrations of the spin charge density for (a) N-terminated bare triangular cluster; (b) B-terminated bare triangular cluster; (c) N-edged ribbon, and the bottom passivated with H; (d) B-edged ribbon, and the bottom passivated with H. Nitrogen, boron and hydrogen atoms are denoted as silver, green, light pink balls. The yellow charge density represents the majority spin, and blue represents the minority spin. In (a) and (b), N atoms and B atoms are numbered with the labels of N1~N15, B1~B10 and N1~N10, B1~B15, respectively.

Here we calculated and presented the spin charge density of the N-terminated zigzag (ZZN) edge and the B-terminated zigzag (ZZB) edge on bare triangular clusters and ribbon models, as shown in **Fig. S2**. For ZZN edge, because of the corner distortions, the spin polarized states (pure magnetic moments on atoms) on the distorted N atoms (like N2 shown in **Fig. S2(a)**) are smaller than that on the ribbon model as shown in **Fig. S2(c)**. Therefore, bare clusters with larger size are required to minimize the impact of corner distortion. This is the direct indication on the physical origin of the low accuracy of bare cluster method. For ZZB edges, without the corner distortions, spin charge densities on the bare clusters or on the ribbon are similar, as shown in **Fig. S2(b)** and **Fig. S2(d)**. As the result, the absolute formation energies of ZZB edge obtained by both methods are very close. Also, according to **Fig. S2(c)** and **Fig. S2(d)**, with the bottom passivated by H, no significant charge transfer should exist.

Here we compared our results of H-passivated edge formation energies under finite temperature and pressure with the ones in previous work. And based on these quantities, the comparison of equilibrium shapes is also discussed.

First, for the formation energies of H-passivated edges under finite temperature and pressure, a qualitative comparison can be made. Set the crossing point of ZZBH and ZZNH as a reference point, our results show that the formation energy of ARMH is larger than this point (as shown in Fig.3(red lines)), while previous work indicated that it was smaller (see ref. 3, Fig.3(h)). The schematic diagram is shown in Fig.S3. The reason of such difference should be attributed to the

problematic algorithm applied in previous work. As we showed in this paper (Table 1), the systematic error of previous method is up to 3.43%, and especially for ZZN edge, the error is up to around 0.08 eV/Å. Further, in early works, an asymmetric slab was used to calculate the H-passivated edges (such as, see ref. 3 Electronic Supplementary Information, Fig.S1(d)). As a result, the systematic error of the bare cluster method would enter the final results of the formation energy of H-passivated edges. Such kind of error accumulation would lead to a large error in the estimation of the energy of the crossing point. Our estimation suggests that the error of the crossing point could be as large as 65% at absolute zero, and it could be still at least 15% when considering the case under finite temperature and pressure.



Fig.S3. Schematic diagram of the results comparison of ours and previous ones, qualitatively.

Additionally, although the temperature and pressure settings for considering the chemical potential of hydrogen are slightly different between the previous work and ours, even considering the case at absolute zero, our results showed that the H-passivated armchair edge cannot have a much lower formation energy than the crossing point, as shown in Fig.3 (the blue lines). Therefore, when the finite temperature and pressure effects are taken into consideration, the armchair edge can only have larger formation energy that perfectly explains why armchair edge and armchair-terminated hexagons are unlikely to be observed in experiments.

Then, based on these edge formation energies, for the predicted equilibrium shapes, our results showed a shape transition process from triangles, to truncated triangles, then to zigzag-terminated hexagons, which is well consistent with experiments (as shown in Fig.4). While in previous work (see ref. 3 Fig.4 (d)~(f)), experimentally observed truncated triangles are missed, and they predicted that the hexagon is terminated by armchair edges, without a complete shape transition obtained.

Table S1. Energies for boron allotropes. (eV/atom)		
Allotropes	Е	
B <sub>1</sub>	-4.979	
$B_2$	-5.999	

**II. Boron allotropes summary for the chemical potential settings Table S1** Energies for boron allotropes (eV/atom)

B <sub>12</sub>	-6.143
$B_{45}$	-6.485
$\mathbf{B}_{50}$	-6.479

## **III.** Algorithm applicability testing on graphene and MoS<sub>2</sub>

Here we took graphene zigzag edges as an example to confirm the accuracy of our method, because for graphene we can construct a symmetric ribbon, as shown in **Fig.S4 (a)**, to obtain edge formation energy directly, so that we are able to regard this value as a reference to obtain the accuracy of our method. At this stage, the absolute zigzag edge formation energy of graphene can be expressed as:

$$\gamma_G = \frac{1}{2l} (E_{tot} - n_C \mu_C).(S1)$$

Here, l is the length of the edge,  $E_{tot}$  is the total energy of this ribbon model,  $n_c$  is the number of carbon (C) atoms in this ribbon, and  $\mu_c$  is the chemical potential of C.

Moreover, for our passivation scheme, we use hydrogen atoms to passivate graphene zigzag edges to maintain an insulating ground state. Similar to the calculations conducted on h-BN, we also calculated a set of triangular clusters, as shown in **Fig.S4 (b)**, to obtain the pseudo chemical potential of the passivated hydrogen atoms, by a polynomial fitting as shown in **Fig.S5**, where the fitting treated the total energy of clusters as a function of cluster size. The total energy of the set of triangular clusters can be expressed as:

$$E_{G}^{cluster} = N_{G}^{2} \mu_{C} + (3N_{G} - 6)\hat{\mu}_{H_{C}} + 6\hat{\mu}_{H_{C}}^{corner}, (S2)$$

where  ${}^{N_{G}}$  denotes the cluster size, from 2 to 7 in our calculations, which in the case of Fig. S3(b) equals seven.  $\hat{\mu}_{H_{C}}$  is the pseudo chemical potential of hydrogen atoms, and  $\hat{\mu}_{H_{N}}^{corner}$  is the pseudo-chemical potential of H at the corner of the cluster.

Therefore, we can calculate the absolute edge formation energy by using the ribbon model shown in **Fig.S4 (c)**, through:

$$\gamma_{edgeG} = \frac{1}{l} \Big( E_{tot}^{H} - n_{C} \mu_{C} - n_{H_{C}} \hat{\mu}_{H_{C}} \Big). (S3)$$

Here,  $E_{tot}^{H}$  is the total energy of the ribbon model (**Fig.S4 (c)**),  $n_{H_{C}}$  is the number of hydrogen atoms in this ribbon.



Fig.S4. (a) An illustration of graphene ribbon with two equivalent zigzag edges. (b) An example

of triangular cluster of graphene with  $C_{49}H_{21}$ , fully-passivated by hydrogen atoms. (c) An illustration of graphene ribbon with one of the two zigzag edges passivated by hydrogen atoms.



Fig.S5. Polynomial fitting of fully-passivated graphene triangular clusters.

Then we can directly compare the two values calculated by different methods to estimate the accuracy. As shown in **Table. S2**, the difference is within 0.0007 eV/Å, which indicates that our passivation scheme is a rather accurate method.



![](_page_5_Figure_0.jpeg)

**Fig.S6.** (a) An illustration of MoS<sub>2</sub> ribbon with two inequivalent zigzag edges, one terminated with Mo atoms (**ZZM**), and the other with S atoms (**ZZS**). (b) An example of triangular cluster of MoS<sub>2</sub> with Mo<sub>28</sub>S<sub>66</sub>H<sub>m6</sub>H<sub>S36</sub>, terminated by S atoms and fully-passivated by pseudo-hydrogen atoms. (c) An example of triangular cluster of MoS<sub>2</sub> with Mo<sub>36</sub>S<sub>56</sub>H<sub>m48</sub>, terminated by Mo atoms and fully-passivated by pseudo-hydrogen atoms. (d)(e) Illustrations of MoS<sub>2</sub> ribbons with one of the two zigzag edges passivated by pseudo-hydrogen atoms. These models are used to calculate the absolute formation energies of corresponding edges. (f) An illustration of MoS<sub>2</sub> ribbon with two inequivalent zigzag edges passivated with corresponding pseudo-hydrogen atoms. This model is used for the estimation of the self-consistent accuracy. Here, Mo atoms, S atoms, pseudo-hydrogen atoms with 0.66*e* (H<sub>S</sub>) and pseudo-hydrogen atoms with 1.33*e* (H<sub>m</sub>) are denoted as balls in light purple, yellow, black and red, respectively.

Our method is a general approach and can be applied to other 2D or quasi-2D materials. Here we took MoS<sub>2</sub> as an example to show the applicability of our method. For MoS<sub>2</sub>, it is difficult to obtain the absolute formation energy of the polar edges as shown in **Fig.S6 (a)**. Therefore, by applying our passivation scheme, similar to the computational process of h-BN, we are able to solve this problem. The general procedures of computation can be described as follows. We can first obtain the pseudo chemical potential of the passivated atoms. Here, by electron counting analysis, we passivated the S-edge (ZZS) by pseudo hydrogen with 0.66e and passivated the Moedge (ZZM) by pseudo hydrogen with 1.33e. The pseudo chemical potentials of the passivated pseudo hydrogen atoms can be obtained by the sets of triangular clusters, as shown in **Fig.S6 (b)** and **(c)**, through polynomial fittings as shown in **Fig.S7**, where the fitting treated the total energy of clusters as a function of cluster size. The total energy of the set of triangular clusters, as shown in **Fig.S6(b)**, can be expressed as:

 $E^{cluster}_{S} = \frac{N_{mos}^{2} - N_{mos}}{2} \mu_{Mo} + \frac{N_{mos}^{2} + N_{mos} - 6}{2} (E_{mos} - \mu_{Mo}) + (3N_{mos} - 6)\hat{\mu}_{H_{S}} + 6\hat{\mu}_{H_{m}}^{corner}, (S4)$ Where  $E_{mos}$  is the total energy per formula of bulk MoS<sub>2</sub> material,  $N_{mos}$  denotes the cluster size, from 3 to 9 in our calculations, which in the case of **Fig. S6(b)** equals eight.  $\hat{\mu}_{H_{C}}$  is the pseudo chemical potential of hydrogen atoms,  $\hat{\mu}_{H_{S}}$  is the pseudo chemical potential of corresponding pseudo hydrogen atoms on the edge, and  $\hat{\mu}_{H_{Mo}}^{corner}$  is the pseudo-chemical potential of H at the corner of the cluster. Additionally, the total energy of the set of triangular clusters, as shown in **Fig.S6(c)**, can be expressed as:

$$E_{Mo}^{cluster} = \frac{N_{mos}^{2} + N_{mos}}{2} \mu_{Mo} + \frac{N_{mos}^{2} - N_{mos}}{2} (E_{mos} - \mu_{Mo}) + (6N_{mos} - 12)\hat{\mu}_{H_{m}} + 12\hat{\mu}_{H_{m}}^{C4} (S5)$$

where,  ${}^{\mu}_{H_m}$  are the pseudo chemical potential of corresponding pseudo hydrogen atoms on the edge, and  $\hat{\mu}_{H_m}^{C4}$  is the pseudo-chemical potential of H at the corner of the cluster.

Finally, by using the obtained pseudo chemical potentials of pseudo hydrogen atoms, we can calculate the absolute edge formation energies through the ribbon models as shown in Figs.S6 (d) and (e), i.e.,

$$\gamma_{edge}^{ZZM} = \frac{1}{l} \Big( E_{tot}^{ZZM} - n_{Mo} \mu_{Mo} - n_{S} \mu_{S} - n_{H_{S}} \hat{\mu}_{H_{S}} \Big), (S6)$$

and,

$$\gamma_{edge}^{ZZS} = \frac{1}{l} \Big( E_{tot}^{ZZS} - n_{Mo} \mu_{Mo} - n_{S} \mu_{S} - n_{H_{m}} \hat{\mu}_{H_{m}} \Big), (S7)$$

Here,  $E_{tot}^{ZZS}$  and  $E_{tot}^{ZZM}$  are the total energy of the ribbon models (**Figs.S5(d)&(e)**),  $n_{Mo}$  and  $n_{S}$  are the number of Mo and S atoms in these ribbons. The calculated results are shown in Table. S2.

Under Mo-rich condition, ZZM is slightly more stable than ZZS. To estimate this computational accuracy, similarly, we used the ribbon model as shown in Fig.S5 (f) to calculate the selfconsistent accuracy, as that in h-BN case. The accuracy is within 0.0013 eV/Å, which is in the typical order of our passivation scheme, as compared with that of graphene and h-BN. These results proved that our method can be regarded a general approach in the field of edge stability calculations of 2D or quasi-2D materials.

![](_page_6_Figure_10.jpeg)

Fig.S7. Polynomial fittings of fully-passivated MoS<sub>2</sub> triangular clusters.

**Table. S2.** Calculated absolute edge formation energies for graphene zigzag edges and  $MoS_2$  asymmetric edges. The values of  $MoS_2$  edges are calculated at the condition of Mo-rich. Unit is in eV/Å.

	Passivation scheme	Symmetric ribbon	Accuracy
Graphene edge	2.9345	2.9338	0.0007
	MoS <sub>2</sub> ZZM	MoS <sub>2</sub> ZZS	Accuracy
Edge energies (Mo- rich)	0.7065	0.7206	0.0013

## IV. Polar plot of h-BN edges under different conditions

![](_page_7_Figure_3.jpeg)

**Fig.S8.** Polar plots of edge formation energies of h-BN monolayers at different  $\Delta \mu_N$  for (a) bare

edges; (b) H-passivated edges at T = 0 K; (c) H-passivated edges at T = 1300 K. The 0° edge is chosen to be the armchair edge. The standard practice of interpolations, applied elsewhere<sup>4</sup>, is conducted here for high index edges.

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