

Notes on formation of 2D heterostructures

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1 Strain calculations

Calculations have been performed for monolayers under compressive and tensile strain. These are obtained by compressing/stretching the in-plane lattice parameter and then by relaxing the atomic coordinates (but not the cell parameters). The total energy, $E(a)$, is then plotted as a function of the in-plane lattice parameter, a , with respect to that of the system at the equilibrium lattice constant, $E(a_0)$. An example for MoS₂ monolayers is presented in Fig. 1. For all the 2D materials

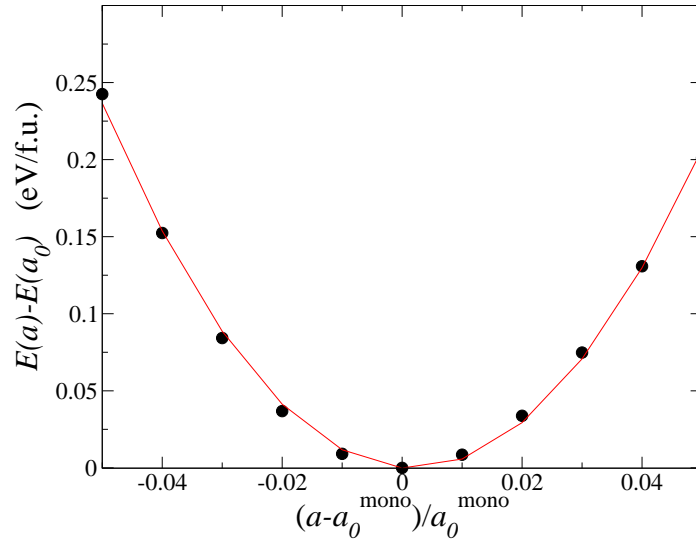


Figure 1: Total energy as a function of the lattice constant, a , for MoS₂ monolayers. Here a_0^{mono} is the equilibrium lattice constant for the monolayer. DFT data are the black dots while the red solid line represent a quadratic fit.

investigated it appears that a quadratic fit of ΔE reproduces well the DFT results, i.e. we have found

$$E(a) - E(a_0) = \Delta E(\delta a) = \alpha(\delta a)^2, \quad (1)$$

where $\delta a = (a - a_0^{\text{mono}})/a_0^{\text{mono}}$. As such the strain energy per unit area $\Delta E(\delta a)/\beta a^2 = \delta E(\delta a)$ associated to the monolayer is

$$\delta E(\delta a) = \frac{\alpha}{\beta(a_0^{\text{mono}})^2} \delta a^2 = \alpha_S \delta a^2, \quad (2)$$

where β is a geometry factor depending on the 2D unit cell (for the hexagonal lattice $\beta = \sqrt{3}$).

In the next table we report, α , α_S , the in-plane lattice parameters (as obtained by fully relaxed DFT) for both the bulk and monolayer phase, and the bulk binding energy for a number of 2D materials. We also report the same quantities as extracted from previously published data (both experimental and theoretical).

Table 1: Structural parameters for bulk and monolayer structures as calculated with the TS van der Waals function (based on GGA - PBE). Here we report: the in-plane lattice parameter for bulk, a_0^{bulk} , and monolayer, a_0^{mono} , (in Å); $\delta a_0 = \frac{a_0^{\text{bulk}} - a_0^{\text{mono}}}{a_0^{\text{mono}}}$ (in %); the quadratic coefficient of the strain vs lattice parameter curve, α , (in eV/f.u.); the strain energy per unit area, α_S , (in meV/Å²); and the calculated binding energy per unit area for bulk, $E_{\text{bind}}^{\text{bulk}}$, and bilayers, $E_{\text{bind}}^{\text{bil}}$ (in meV/Å²).

Material	a_0^{bulk}	a_0^{mono}	δa_0	α	α_S	$E_{\text{bind}}^{\text{bulk}}$	$E_{\text{bind}}^{\text{bil}}$
MoS ₂	3.158	3.160	-0.06	88.26	10,210	35.26	21.43
MoSe ₂	3.296	3.291	0.15	79.63	8,490	34.32	20.86
WS ₂	3.164	3.166	-0.06	96.01	11,060	32.25	19.60
WSe ₂	3.293	3.294	-0.03	84.25	8,970	28.93	17.59
SnS ₂	3.698	3.694	0.1	62.69	5,300	16.99	10.33
SnSe ₂	3.882	3.748	3.53	23.99	1,970	18.13	11.02
NbSe ₂	3.442	3.447	-0.14	78.64	7,640	37.34	22.70
GeI ₂	4.263	4.167	2.3	30.91	2,060	12.24	7.44
BN	2.504	2.508	-0.15	120.89	22,190	29.46	17.91
C		2.463	-0.15	136.89		30.05	18.27

Table 2: Published data. Here we report: the in-plane experimental lattice parameter for bulk materials, $a_0^{\text{bulk-exp}}$, (in Å); the out of plane experimental lattice parameter, $c_0^{\text{bulk-exp}}$, (in Å); the calculated GGA-PBE in-plane lattice parameter for monolayers, $a_0^{\text{mono-GGA}}$, (in Å); $\delta a_0^{\text{GGA}} = \frac{a_0^{\text{bulk}} - a_0^{\text{mono-LDA}}}{a_0^{\text{mono-GGA}}}$ (in %); $\delta a_0^{2\text{H-3R}} = \frac{a_0^{2\text{H}} - a_0^{3\text{R}}}{a_0^{2\text{H}}}$ (in %); $E_{\text{bind}}^{\text{bulk}}$, (in meV/Å²), as calculated from RPA. Experimental value are from the Crystallography Open Database [1], GGA data from [2], binding energies from [3].

Material	$a_0^{\text{bulk-exp}}$	$c_0^{\text{bulk-exp}}$	$\delta a_0^{2\text{H-3R}}$	$a_0^{\text{mono-GGA}}$	δa_0^{GGA}	$E_{\text{bind}}^{\text{bulk}}$
MoS ₂ 2H	3.14	12.53		3.184	-1.38	20.53
MoS ₂ 3R	3.16	18.45 (12.3)	-0.63	3.184	-0.75	
MoSe ₂ 2H	3.288	12.9		3.32	-0.96	19.63
MoSe ₂ 3R	3.292	19.39 (12.93)	-0.12	3.32	-0.84	
WS ₂ 2H	3.153	12.32		3.186	-1.03	20.24
WS ₂ 3R	3.158	18.49 (12.33)	-0.15	3.186	-0.87	
WSe ₂ 2H	3.282	12.96		3.319	-1.11	19.98
SnS ₂ 1T	3.62	5.85 (11.7)		3.696	-2.05	22.43 (VV10)
SnSe ₂ 1T	3.81	6.14 (12.28)		3.863	-1.37	23.41 (VV10)
NbS ₂ 1T	3.42	5.938 (11.88)		3.372	1.42	
NbS ₂ 2R	3.33	17.8 (11.87)	2.7	3.344	-0.41	17.58
NbSe ₂ 2H	3.442	12.54		3.471	-0.83	19.57
NbSe ₂ 3R	3.45	18.88 (12.59)	-0.23	3.471	-0.57	
TiS ₂ 1T	3.397-4.412	5.695 (11.39)		3.415	-0.5	18.88
TiSe ₂ 1T	3.533	5.995 (11.99)		3.536	-0.08	17.39

A few considerations can be made at this point:

1. There is always some level on strain when forming heterostructures, even if these are made of the same material. For instance the in-plane lattice constants of the 2H and 3R polymorphs of 2D transition metal dichalcogenides differ by 0.1-0.5%.
2. The binding energy per unit area seems rather insensitive to the chemical composition with values around $20 \text{ meV}/\text{\AA}^2$. This is particularly true for XS_2 and XSe_2 with X a transition metal. More spread is present when looking at other classes, e.g. GeI_2 .
3. In general the in-plane lattice constant of a bulk layered material seems to be under a small compressive strain with respect to that of the isolated monolayer. This result, however, needs to be taken with care since no experimental determination of the in-plane lattice constant for monolayers is available.

2 van der Waals bonding between layers

The free energy (per unit area) associated to the van der Waals interaction between two planes at a distance d can be obtained by integrating the $1/r^6$ London potential over all the atoms on the surfaces, and reads

$$E_{\text{bind}} = -\frac{A}{12\pi}d^{-2}, \quad (3)$$

where A is the Hamaker constant,

$$A = \pi^2 C \rho_1 \rho_2. \quad (4)$$

Here ρ_i is the number of atoms per unit volume in the i -th plane and C is the London r^{-6} coefficient. The Hamaker constant can be re-written in terms of the macroscopic properties of the two surfaces by using McLachlan's expression for the van der Waals free energy [4]. This is

$$A \approx \frac{3}{4}k_{\text{B}}T \left(\frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + \epsilon_0} \right) \left(\frac{\epsilon_2 - \epsilon_0}{\epsilon_2 + \epsilon_0} \right) + \frac{3h}{4\pi} \int_{\nu_1}^{\infty} \left(\frac{\epsilon_1(i\nu) - \epsilon_0}{\epsilon_1(i\nu) + \epsilon_0} \right) \left(\frac{\epsilon_2(i\nu) - \epsilon_0}{\epsilon_2(i\nu) + \epsilon_0} \right) d\nu, \quad (5)$$

where ϵ are the static dielectric constants (ϵ_0 is the vacuum one), $\epsilon(i\nu)$ are the value of ϵ at imaginary frequency and $\nu_n = (2\pi k_{\text{B}}T/h)n$. Finally, by approximating the dielectric function as

$$\epsilon(\nu) = 1 + \frac{\text{constant}}{1 - i\nu/\nu_{\text{rot}}} + \frac{\text{constant}}{1 - \nu^2/\nu_{\text{e}}^2}, \quad (6)$$

with ν_{rot} being the molecular rotation relaxation frequency and ν_{e} is the main electronic absorption frequency in the UV, we can write

$$A \approx \frac{3}{4}k_{\text{B}}T \left(\frac{\epsilon_1 - 1}{\epsilon_1 + 1} \right) \left(\frac{\epsilon_2 - 1}{\epsilon_2 + 1} \right) + \frac{3h\nu_{\text{e}}}{8\sqrt{2}} \frac{(n_1^2 - 1)(n_2^2 - 1)}{(n_1^2 + 1)^{1/2}(n_2^2 + 1)^{1/2}[(n_1^2 + 1)^{1/2} + (n_2^2 + 1)^{1/2}]}, \quad (7)$$

where n is the refractive index of the medium in the visible. Note that, in general, the static contribution to the Hamaker constant has the form $A_{\text{stat}} \propto f(\epsilon_1)f(\epsilon_2)$, with $f(\epsilon) = \left(\frac{\epsilon-1}{\epsilon+1} \right)$, and it can be extracted from the binding energy of the bulk 2D materials, since for bulk it is $E_{\text{bind}} \propto f(\epsilon)^2$.

Let us now relate the calculated binding energies for bulk to the one expected for bi-layers (assuming that van der Waals forces are additive). The binding energy (per layer) of a bulk

layered compound is given by summing up all the pair-wise energy contributions to all the planes, namely

$$E_{\text{bind}}^{\text{bulk}} = -\frac{A}{12\pi} \frac{1}{d^2} \sum_{n=1}^{\infty} \frac{1}{n^2} = -\frac{A}{12\pi} \frac{1}{d^2} \zeta(2), \quad (8)$$

where we have used the sum rule for the p-series, $\sum_{n=1}^{\infty} \frac{1}{n^p} = \zeta(p)$, with $\zeta(p)$ being the Riemann zeta function calculated at p . In our case we have $\zeta(2) = \pi^2/6 \approx 1.645$, so that we conclude

$$E_{\text{bind}}^{\text{bil}} = E_{\text{bind}}^{\text{bulk}}/1.645. \quad (9)$$

The calculated binding energies for bilayers are reported also in Table 1.

3 Evaluation of the maximum strain sustainable by a bi-layer

Let us now evaluate the maximum strain sustainable by the layers of a bi-layer made of different materials, e.g. WS_2/MoS_2 . Let us suppose that the bi-layer is made of materials with monolayer in-plane lattice constants a_1 and a_2 , and that the bi-layer has a lattice constant a . Then the condition for the bi-layer to form is that

$$E_{\text{bind}}^{\text{bil}} > \alpha_{\text{S1}}(\delta a_1)^2 + \alpha_{\text{S2}}(\delta a_2)^2, \quad (10)$$

where α_{S} and δa has been defined before in section 1. Explicitly, this writes

$$E_{\text{bind}}^{\text{bil}} > \alpha_{\text{S1}} \left(\frac{a - a_1}{a_1} \right)^2 + \alpha_{\text{S2}} \left(\frac{a - a_2}{a_2} \right)^2. \quad (11)$$

If $a_1 = a_2$ the equation is satisfied for $a = a_1 = a_2$. If $a_1 \neq a_2$ then the minimal condition to form the bi-layer is

$$E_{\text{bind}}^{\text{bil}} = \alpha_{\text{S1}}(\delta a_1)^2 + \alpha_{\text{S2}}(\delta a_2)^2, \quad (12)$$

namely when all the binding energy is compensated by the strain induced on the layers. The equation (12) is solved for

$$a = \frac{a_1 a_2}{\alpha_{\text{S1}} a_2^2 + \alpha_{\text{S2}} a_1^2} \left[(\alpha_{\text{S1}} a_2 + \alpha_{\text{S2}} a_1) \pm \sqrt{(\alpha_{\text{S1}} a_2 + \alpha_{\text{S2}} a_1)^2 - (\alpha_{\text{S1}} a_2^2 + \alpha_{\text{S2}} a_1^2)(\alpha_{\text{S1}} + \alpha_{\text{S2}} - E_{\text{bind}}^{\text{bil}})} \right]. \quad (13)$$

In figure 2 we graphically display equation (10) for the case of MoS_2 and WSe_2 . The figure helps in understanding the potential formation of such heterostructure. The red and black parabolas are the $\delta E(\delta a)$ curves for WSe_2 and MoS_2 respectively, while the blue one is the sum of them, namely the strain energy for the two layers. Such curve has a minimum at $a_{\text{MoS}_2+\text{WSe}_2}$, which represents the common lattice constant for the commensurate heterostructure (same unit cell for MoS_2 and WSe_2) with minimal strain energy. At such minimum the total strain energy is less than the binding energy of both MoS_2 and WSe_2 bi-layers. Since it is expected that the van der Waals contribution to the binding energy of the $\text{MoS}_2/\text{WSe}_2$ bi-layer will be similar to that of either MoS_2 and WSe_2 bi-layers (horizontal lines), we can conclude that the van der Waals forces are enough to compensate for the strain, i.e. the $\text{MoS}_2/\text{WSe}_2$ bi-layer can bind at the $a_{\text{MoS}_2+\text{WSe}_2}$ lattice parameter. The total binding energy for the $\text{MoS}_2/\text{WSe}_2$ bi-layer is then simply obtained as the van der Waals contribution minus the elastic one at the minimum strain. We can then estimate such binding energy by simply using the MoS_2 and WSe_2 van der Waals binding energies for bi-layers. For the $\text{MoS}_2/\text{WSe}_2$ bilayer we obtain a lattice parameter $a_{\text{MoS}_2+\text{WSe}_2} = 3.22 \text{ \AA}$, meaning that MoS_2 is under

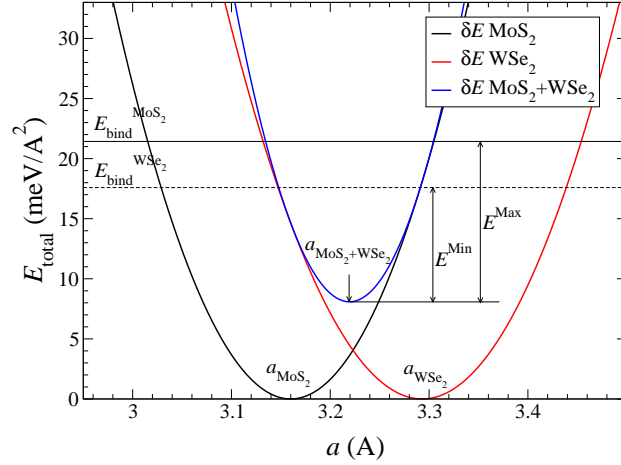


Figure 2: Binding curves for an hypothetical commensurate MoS₂/WSe₂ bi-layer. In this case the total elastic cost (blue line) is lower than the binding energy of either MoS₂ and WSe₂ bi-layers. As such we expect the bi-layer to form with a lattice constant $a_{\text{MoS}_2+\text{WSe}_2}$ and a total binding energy in between E^{Min} and E^{Max} .

a tensile strain of 1.86%, while WSe₂ is under a compressive one of 2.26%. The total estimated binding energy is then in between 9.5 meV/Å² and 13.34 meV/Å².

In figure 3 we present a second example for SnS₂/GeI₂. In this case the total elastic energy is significantly larger than the van der Waals binding energy of any of the two layers. As a consequence a commensurate SnS₂/GeI₂ cannot be formed. Note that this does not exclude the formation of bi-layers with a unit cell comprising more than one primitive cell of the monolayer.

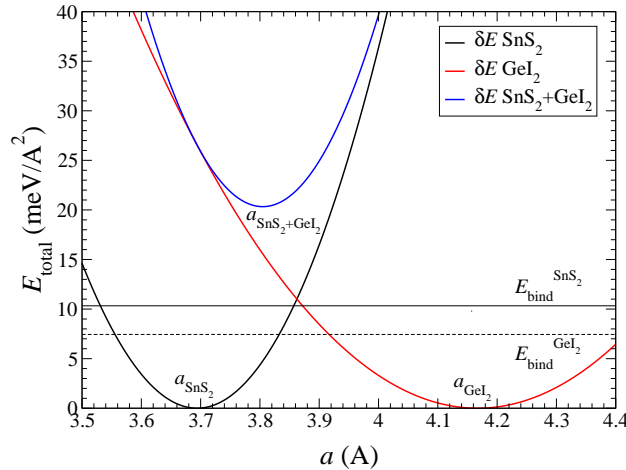


Figure 3: Binding curves for an hypothetical commensurate SnS₂/GeI₂ bi-layer. In this case the total elastic cost (blue line) is higher than the binding energy of either SnS₂ and GeI₂ bi-layers. As such we expect the bi-layer not to form.

References

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