Convergence tests for the cluster DFT calculations

1. Convergence with respect to basis set.

Test calculations for basis set convergence have been performed using the PBE functional for a 72 atoms zigzag *h*-BN dimmer. A set of three Gaussian basis sets with increasing size and diffuseness has been used including the 3-21G, 6-31G**, and 6-311++G(3df,3pd). At an interlayer distance of 3.3 Å the difference between the total energy calculated using the 6-31G** and the 6-311++G(3df,3pd) basis sets is ~1.3 meV/atom. When looking at the different energy components at that interlayer distance the exchange-correlation energy is converged down to ~1.2 meV/atom. The electrostatic and kinetic energies are less converged (~8 and ~10.6 meV/atom, respectively) although, as mentioned above, their overall contribution to the total energy is well converged. The following figure shows the convergence of the different energy terms as function of interlayer distance with respect to the basis set used. As can be seen, for the purpose of estimating the role of the different energy components for the interlayer binding the 6-31G** basis set results are satisfying.

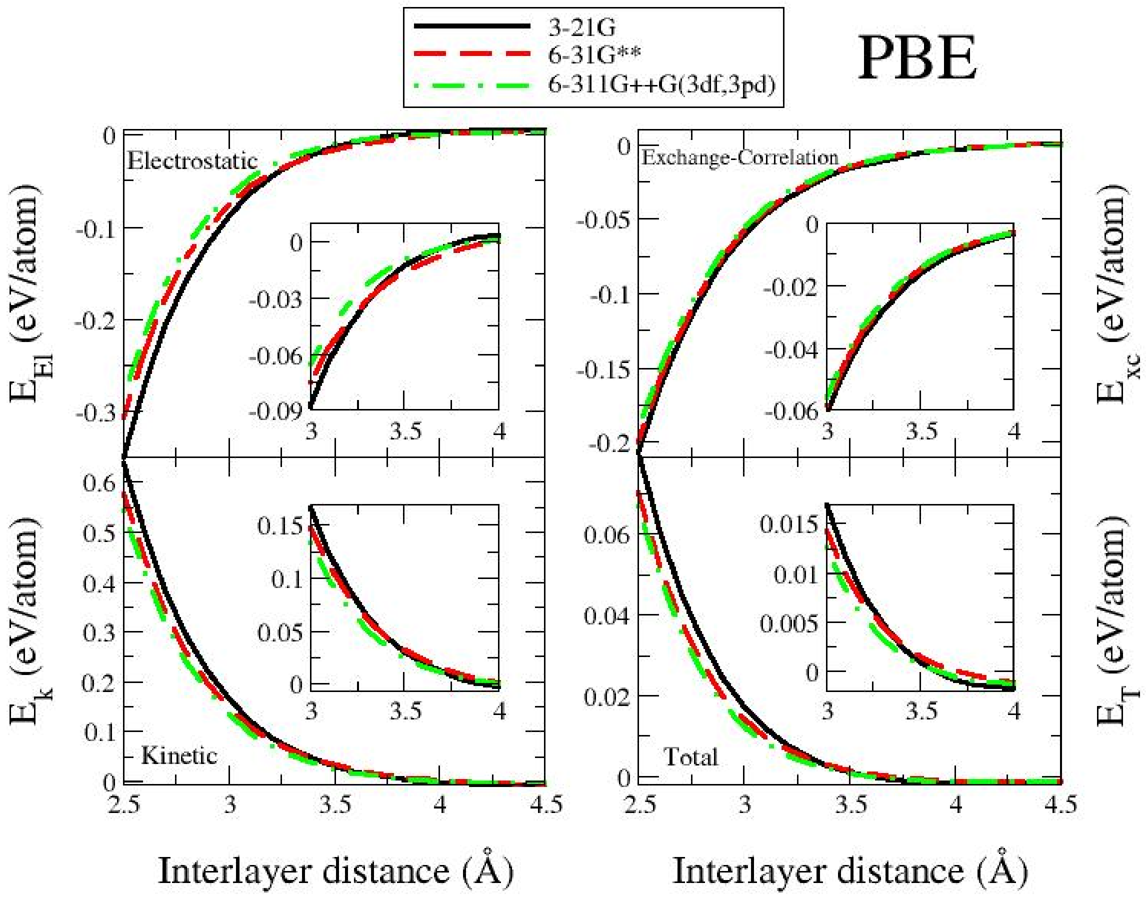

Fig. S1: Basis set convergence tests for the cluster DFT calculations. Electrostatic (upper left panel), exchange correlation (upper right panel), kinetic (lower left panel), and total (lower right panel) energies as a function of the interlayer distance of a 72 atoms zigzag *h*-BN dimmer calculated using the PBE functional and the 3-21G (solid black line), 6-31G** (dashed red line), and the 6-311++G(3df,3pd) (dashed-dotted green line) basis sets. Insets: zoom in on the region of physically relevant interlayer distances.

2. <u>Convergence with respect to the size and shape of the cluster</u>

To test for convergence of the results with respect to the shape and size of the finite bilayer flakes used, calculations of the different energy components as a function of the interlayer distance for armchair and zigzag flakes of increasing size have been performed. Fig. S2 presents images of some of the flakes used in the present study.

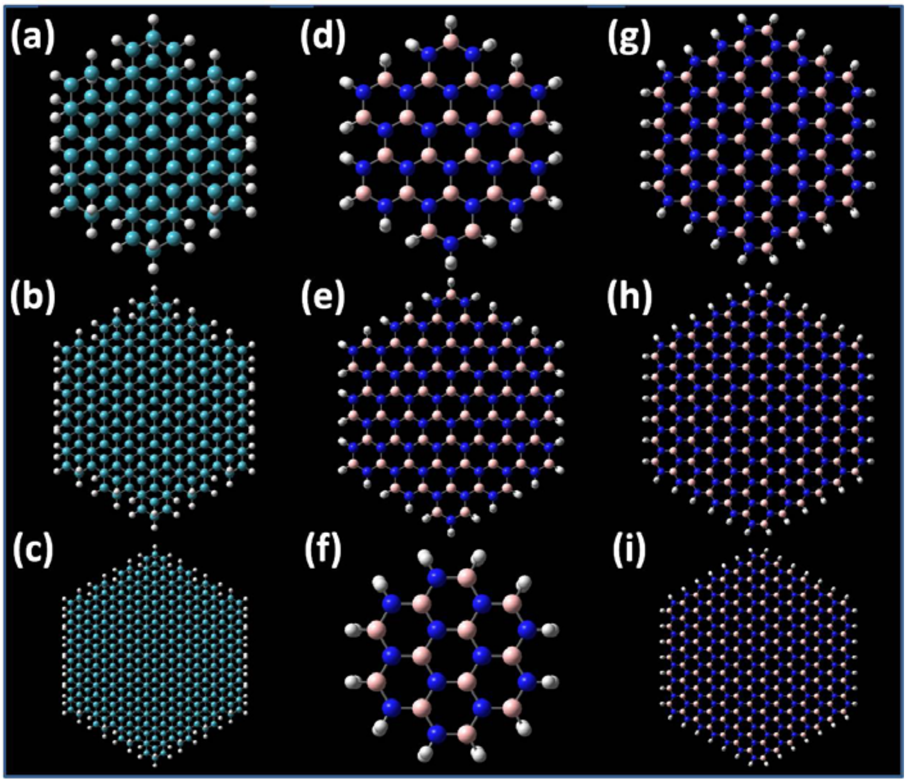

Fig. S2: Images of some of the hydrogen terminated dimmer hexagonal flakes used in the present study: (a) 120 atoms armchair graphene dimmer, (b) 288 atoms armchair graphene dimmer, (c) 528 atoms armchair graphene dimmer, (d) 120 atoms armchair *h*-BN dimmer, (e) 288 atoms armchair *h*-BN dimmer, (f) 72 atoms zigzag *h*-BN dimmer, (g) 240 atoms zigzag *h*-BN dimmer, (h) 504 atoms zigzag *h*-BN dimmer, and (i) 672 atoms zigzag *h*-BN dimmer. Cyan, blue, pink and grey spheres represent carbon, nitrogen, boron, and hydrogen atoms, respectively.

All calculations have been performed using the PBE/6-31G** level of theory. At 3.3 Å the total, electrostatic, exchange-correlation, and kinetic energies of the zigzag *h*-BN dimmer consisting of 672 atoms are converged down to 0.2, 1.4, 0.5, 2.1 meV/atom, respectively. For the armchair graphene dimmer consisting of 528 atoms at the same interlayer distance the total, electrostatic, exchange-correlation, and kinetic energies are converged down to 0.2, 2.5, 1.7, 4.4 meV/atom, respectively.

Figs. S3 and S4 present the convergence of the interlayer dependence of the different energy components as a function of flake size for bilayer graphene and *h*-BN, respectively. As can be seen, for all practical purposes the results of the largest cluster sizes are well converged showing only marginal edge effects.

Fig. S5 compares the interlayer dependence of the different energy components of two armchair and one zigzag *h*-BN dimmers showing that the converged results are independent of the shape of the flakes used in the calculations.

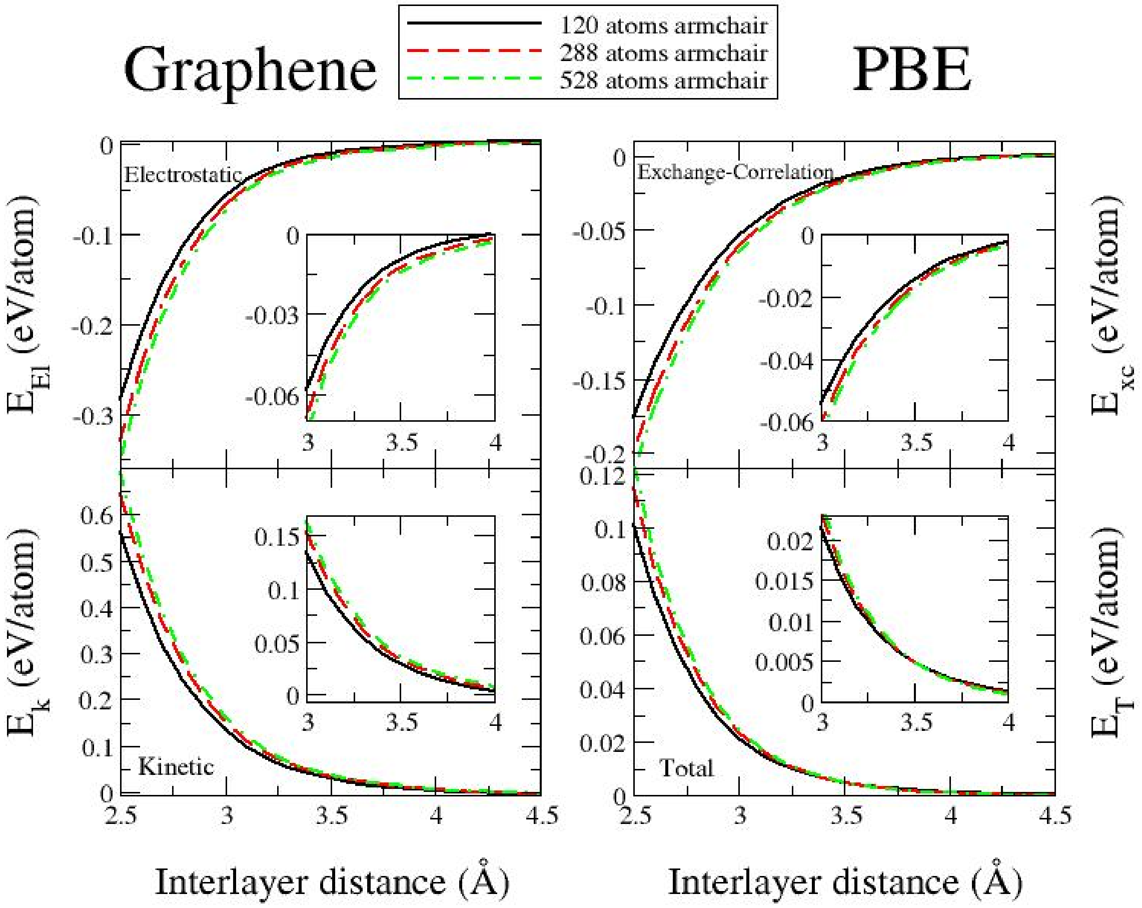

Fig. S3: Convergence of the interlayer dependence of the electrostatic (upper left), exchange-correlation (upper right), kinetic (lower left), and total (lower right) energies with respect to the size of the armchair graphene flakes. Solid black, dashed red, and dashed-dashed-dotted green curves represent results for the 120, 288, and 528 atoms graphene dimmer flakes.

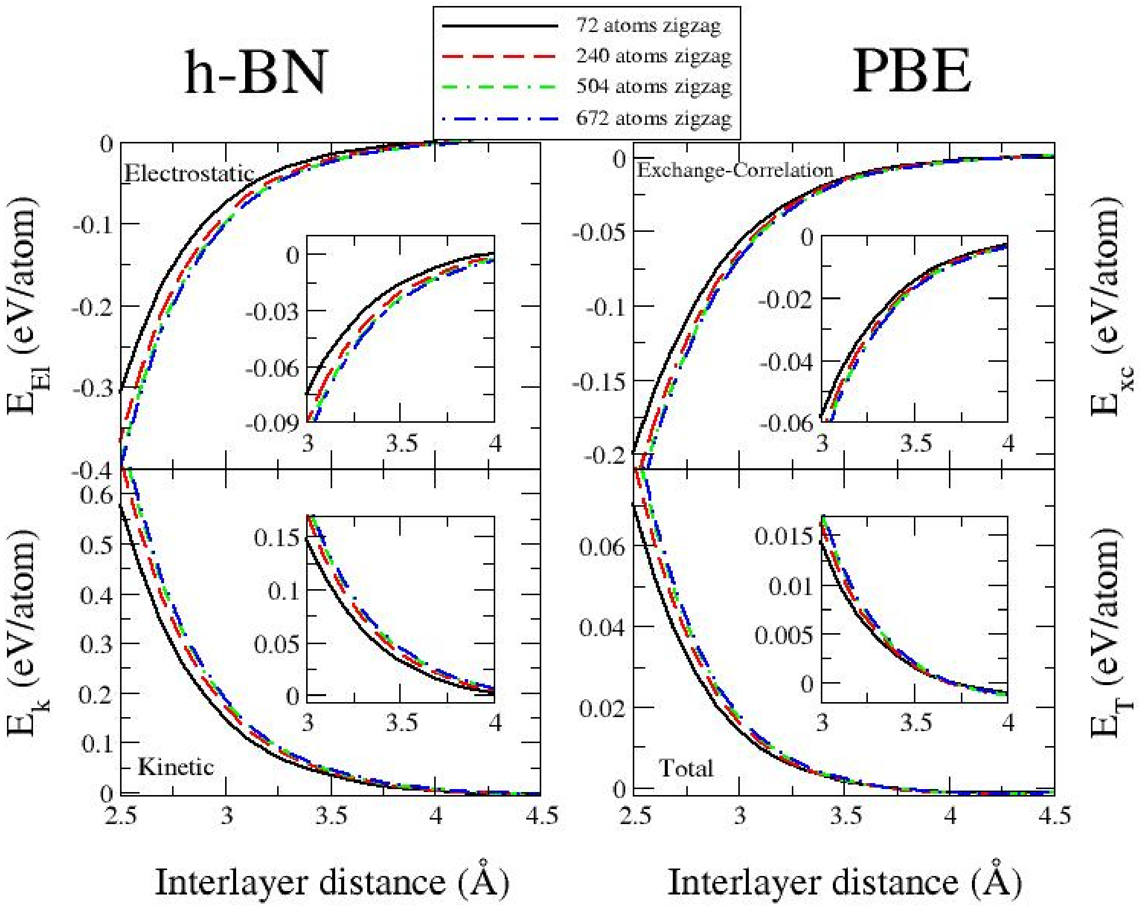

Fig. S4: Convergence of the interlayer dependence of the electrostatic (upper left), exchange-correlation (upper right), kinetic (lower left), and total (lower right) energies with respect to the size of the zigzag *h*-BN flakes. Solid black, dashed red, dashed-dashed-dotted green, and dashed-dotted blue curves represent results for the 72, 240, 504, and 672 atoms *h*-BN dimmer flakes.

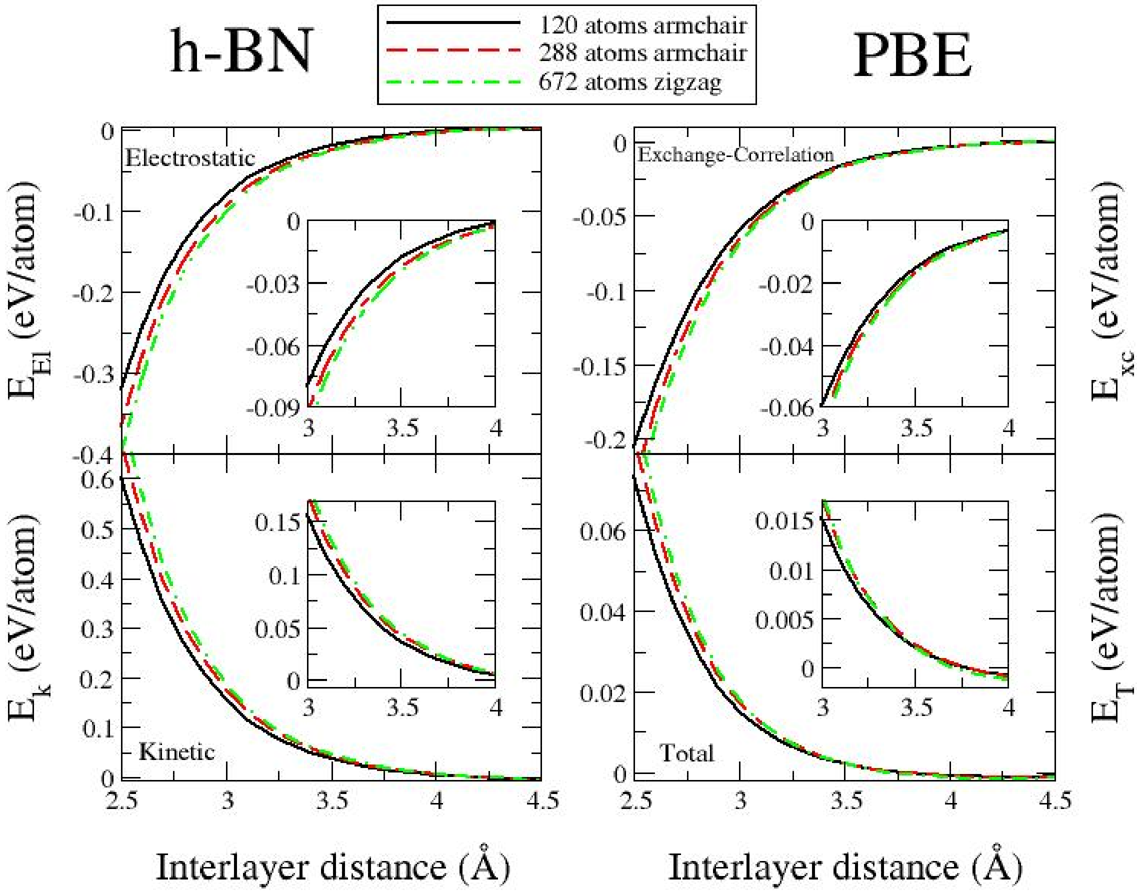

Fig. S5: Convergence of the interlayer dependence of the electrostatic (upper left), exchange-correlation (upper right), kinetic (lower left), and total (lower right) energies with respect to the shape of the *h*-BN flakes. Solid black, dashed red, and dashed-dashed-dotted green curves represent results for the 120 atoms armchair, 288 atoms armchair, and 672 atoms zigzag *h*-BN dimmer flakes.

The Ewald summation method for the Coulomb potential of a two dimensional (2D) periodic slab of point charges

We are interested in calculating the electrostatic potential induced by a slab of charged particles which is periodic in two directions and finite in the third direction. For simplicity we consider a rectangular unit-cell such that the periodic directions are aligned along the X and Y axes with translational vectors $\vec{a}_x = (T_x, 0, 0)$ and $\vec{a}_y = (0, T_y, 0)$. The unit cell is assumed to contain d charged particles located at positions $\vec{r}_i = (x_i, y_i, z_i);\ i = 1, 2, \ldots, d$ and to be charge neutral such that:

$$\text{(S1)} \qquad \sum_{i=1}^{d} q_i = 0$$

The location of a general atom in the slab is then given by the following expression:

$$\text{(S2)} \qquad \vec{r}_{i,n,m} = \vec{r}_i + n\vec{a}_x + m\vec{a}_y = (x_i + nT_x, y_i + mT_y, z_i);\ i = 1, 2, \ldots, d\ ;\ n_1, n_2 = 0, \pm 1, \pm 2, \cdots, \pm\infty$$

With these definitions we may write the general expression for the electrostatic potential at point $\vec{r} = (x, y, z) \neq \vec{r}_{i,n,m}$ due to the infinite 2D-periodic slab as:

$$\text{(S3)} \quad \varphi(\vec{r}) = \varphi(x, y, z) = \sum_{i=1}^{d} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{q_i}{\left|\vec{r} - \vec{r}_{i,n,m}\right|} = \sum_{i=1}^{d} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{q_i}{\sqrt{(x - x_i - nT_x)^2 + (y - y_i - mT_y)^2 + (z - z_i)^2}}$$

The potential $\varphi(\vec{r})$ is a periodic function in the X and Y directions with a period of $T_x = |\vec{a}_x|$ along the X direction and a period of $T_y = |\vec{a}_y|$ along the Y direction. This can be easily demonstrated as follows:

$$\text{(S4)} \quad \begin{aligned} \varphi(x + pT_x, y, z) &= \sum_{i=1}^{d} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{q_i}{\left[(x + pT_x - x_i - nT_x)^2 + (y - y_i - mT_y)^2 + (z - z_i)^2\right]^{1/2}} = \\ &= \sum_{i=1}^{d} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{q_i}{\left[(x - x_i - (n-p)T_x)^2 + (y - y_i - mT_y)^2 + (z - z_i)^2\right]^{1/2}} \underset{l=n-p}{=} \\ &= \sum_{i=1}^{d} \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{q_i}{\left[(x - x_i - lT_x)^2 + (y - y_i - mT_y)^2 + (z - z_i)^2\right]^{1/2}} = \varphi(x, y, z) \end{aligned}$$

where p is an integer number and the equality leading from the second to the third line uses the fact the summation over the index n covers the infinite range of integer numbers from $-\infty$ to $+\infty$. Similar arguments may be used to prove the periodicity in the y direction.

We can now define the potential arising at point $\vec{r}$ due to one of the particles in the unit cell and its periodic images:

(S5)
$$\varphi_i(\vec r)=\varphi_i(x,y,z)=\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\frac{q_i}{\sqrt{(x-x_i-nT_x)^2+(y-y_i-mT_y)^2+(z-z_i)^2}}=$$
$$=q_i\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\frac{1}{\sqrt{(x-x_i-nT_x)^2+(y-y_i-mT_y)^2+(z-z_i)^2}}$$

such that

(S6) $$\varphi(\vec r)=\sum_{i=1}^{d}\varphi_i(\vec r)$$

The sum appearing in Eq. (5) is divergent while the sum appearing in Eq. (3) is conditionally convergent provided that the unit cell is charge neutral (Eq. (1)). In order to evaluate the sum $\varphi(\vec r)$ we utilize the Ewald summation method which splits the conditionally convergent sum into two absolutely (fast) converging sums. This is achieved by splitting the singular and long-range Coulomb potential into a singular short-range part, which can be readily evaluated in real-space, and a non-singular long-range part which is evaluated in reciprocal space. To this end, we notice that, similar to $\varphi(\vec r)$, $\varphi_i(\vec r)$ is also a periodic function in the X and Y directions with the same periodicity (the proof follow the same lines as the proof for $\varphi(\vec r)$).

We now recall that a periodic function $f(x)=f(x+nT);\, n=0,\pm1,\pm2,\ldots$ can be expanded in a Fourier series of the form:

(S7) $$f(x)=\sum_{m=-\infty}^{\infty}\hat f(m)e^{2\pi imx/T}\quad;\quad \hat f(m)=\frac{1}{T}\int_{-T/2}^{T/2}f(x)e^{-2\pi imx/T}dx$$

Defining $k_x=0\,,\pm2\pi/T\,,\pm4\pi/T\,,\ldots$ the expansion can be rewritten in the following form:

(S8) $$f(x)=\sum_{k_x}\hat f(k_x)e^{ik_xx}\quad;\quad \hat f(k_x)=\frac{1}{T}\int_{-T/2}^{T/2}f(x)e^{-ik_xx}dx\quad;\quad k_x=0\,,\pm2\pi/T\,,\pm4\pi/T\,,\ldots$$

Similarly, for a two-dimensional (2D) periodic function which obeys $f(x,y)=f(x+nT_x,y+mT_y)\quad;\quad n,m=0,\pm1,\pm2,\ldots$ one has:

(S9)
$$f(x,y)=\sum_{k_x}\sum_{k_y}\hat f(k_x,k_y)e^{i(k_xx+k_yy)}=\sum_{k_x}\sum_{k_y}\hat f(\vec\kappa)e^{i\vec\kappa\cdot\vec\rho}$$
$$\hat f(\vec\kappa)=\frac{1}{T_x}\frac{1}{T_y}\int_{-T_x/2}^{T_x/2}dx\int_{-T_y/2}^{T_y/2}dy\; f(x,y)e^{-i\vec\kappa\cdot\vec\rho}$$

With

(S10)
$$\vec\rho=(x,y);\,\vec\kappa=(k_x,k_y)$$
$$k_x=0\,,\pm2\pi/T_x\,,\pm4\pi/T_x\,,\ldots$$
$$k_y=0\,,\pm2\pi/T_y\,,\pm4\pi/T_y\,,\ldots$$

It is now possible to expand $\varphi_i(\vec{r})$ as a 2D Fourier series of the form:

(S11) $$\varphi_i(\vec{r}) = \sum_{k_x}\sum_{k_y}\hat{\varphi}_i(\vec{\kappa}, z)e^{i\vec{\kappa}\cdot\vec{\rho}}$$

With the Fourier coefficients given by:

(S12) $$\hat{\varphi}_i(\vec{\kappa}, z) = \frac{1}{T_xT_y}\int_{-T_x/2}^{T_x/2}dx\int_{-T_y/2}^{T_y/2}dy\varphi_i(\vec{r})e^{-i\vec{\kappa}\cdot\vec{\rho}} =$$
$$= \frac{q_i}{T_xT_y}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\int_{-T_x/2}^{T_x/2}dx\int_{-T_y/2}^{T_y/2}dy\frac{1}{\sqrt{(x-x_i-nT_x)^2+(y-y_i-mT_y)^2+(z-z_i)^2}}e^{-i(k_xx+k_yy)}$$

Defining new variables:

(S13) $$\begin{cases}\tilde{x} = x - x_i - nT_x\\ \tilde{y} = y - y_i - mT_y\\ \tilde{z} = z - z_i\end{cases} \Rightarrow \begin{cases}d\tilde{x} = dx\\ d\tilde{y} = dy\\ d\tilde{z} = dz\end{cases} ; \begin{cases}x = \tilde{x} + x_i + nT_x\\ y = \tilde{y} + y_i + mT_y\\ z = \tilde{z} + z_i\end{cases}$$

We can rewrite the integral as:

(S14) $$\hat{\varphi}_i(\vec{\kappa}, \tilde{z}) = \frac{q_i}{T_xT_y}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\int_{-T_x/2-x_i-nT_x}^{T_x/2-x_i-nT_x}d\tilde{x}\int_{-T_y/2-y_i-mT_y}^{T_y/2-y_i-mT_y}d\tilde{y}\frac{1}{\sqrt{\tilde{x}^2+\tilde{y}^2+\tilde{z}^2}}e^{-i\left[k_x(\tilde{x}+x_i+nT_x)+k_y(\tilde{y}+y_i+mT_y)\right]} =$$
$$= \frac{q_i}{T_xT_y}e^{-i(k_xx_i+k_yy_i)}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\int_{-T_x/2-x_i-nT_x}^{T_x/2-x_i-nT_x}d\tilde{x}\int_{-T_y/2-y_i-mT_y}^{T_y/2-y_i-mT_y}d\tilde{y}\frac{1}{\sqrt{\tilde{x}^2+\tilde{y}^2+\tilde{z}^2}}e^{-i(k_x\tilde{x}+k_y\tilde{y})}e^{-i(k_xnT_x+k_ymT_y)}$$

Noticing that $e^{-i(k_xnT_x+k_ymT_y)} = e^{-i\left(\frac{2\pi p}{T_x}nT_x+\frac{2\pi q}{T_y}mT_y\right)} = e^{-2\pi i(pn+qm)} = 1;\ p,q,n,m = 0,\pm1,\pm2,\ldots$ and defining $\vec{\rho}_i = (x_i, y_i)$ and $\vec{\tilde{\rho}} = (\tilde{x}, \tilde{y})$ we obtain:

(S15) $$\hat{\varphi}_i(\vec{\kappa}, \tilde{z}) = \frac{q_i}{T_xT_y}e^{-i\vec{\kappa}\cdot\vec{\rho}_i}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\int_{-T_x/2-x_i-nT_x}^{T_x/2-x_i-nT_x}d\tilde{x}\int_{-T_y/2-y_i-mT_y}^{T_y/2-y_i-mT_y}d\tilde{y}\frac{1}{\sqrt{\tilde{x}^2+\tilde{y}^2+\tilde{z}^2}}e^{-i\vec{\kappa}\cdot\vec{\tilde{\rho}}} =$$
$$= \frac{q_i}{T_xT_y}e^{-i\vec{\kappa}\cdot\vec{\rho}_i}\sum_{n=-\infty}^{\infty}\int_{-T_x/2-x_i-nT_x}^{T_x/2-x_i-nT_x}d\tilde{x}\sum_{m=-\infty}^{\infty}\int_{-T_y/2-y_i-mT_y}^{T_y/2-y_i-mT_y}d\tilde{y}\frac{1}{\sqrt{\tilde{x}^2+\tilde{y}^2+\tilde{z}^2}}e^{-i\vec{\kappa}\cdot\vec{\tilde{\rho}}}$$

In Eq. (15) both integrations are performed over finite segments. The summation shifts the segments in a consecutive manner such that the sum of all segmental integrals can be replaced by an integral over the full range:

(S16) $$\sum_{n=-\infty}^{\infty}\int_{-T_x/2-x_i-nT_x}^{T_x/2-x_i-nT_x}d\tilde{x} = \cdots + \int_{-3T_x/2-x_i}^{-T_x/2-x_i}d\tilde{x} + \int_{-T_x/2-x_i}^{T_x/2-x_i}d\tilde{x} + \int_{T_x/2-x_i}^{3T_x/2-x_i}d\tilde{x} + \cdots = \int_{-\infty}^{\infty}d\tilde{x}$$

Here, we have displayed the terms with $n = 1,0,-1$, respectively. Similarly, we obtain $\sum_{m=-\infty}^{\infty} \int_{-T_y/2-y_i-mT_y}^{T_y/2-y_i-mT_y} d\tilde{y} = \int_{-\infty}^{\infty} d\tilde{y}$ such that $\hat{\varphi}(\vec{\kappa},\tilde{z})$ is given by:

$$\hat{\varphi}_i(\vec{\kappa},\tilde{z}) = \frac{q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_{-\infty}^{\infty} d\tilde{x} \int_{-\infty}^{\infty} d\tilde{y} \frac{1}{\sqrt{\tilde{x}^2 + \tilde{y}^2 + \tilde{z}^2}} e^{-i\vec{\kappa}\cdot\tilde{\vec{\rho}}} \tag{S17}$$

The evaluation of the remaining double integrals is performed by transforming to a polar coordinate system such that:

$$\begin{cases} \tilde{\rho} = \left|\tilde{\vec{\rho}}\right| = \sqrt{\tilde{x}^2 + \tilde{y}^2} \\ \tilde{\theta} = arctg\left(\dfrac{\tilde{y}}{\tilde{x}}\right) \end{cases} \quad ; \quad \begin{cases} \tilde{x} = \tilde{\rho}\cos(\tilde{\theta}) \\ \tilde{y} = \tilde{\rho}\sin(\tilde{\theta}) \end{cases} \tag{S18}$$

and

$$\begin{aligned} \hat{\varphi}_i(\vec{\kappa},\tilde{z}) &= \frac{q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_0^{\infty} \frac{\tilde{\rho}}{\sqrt{\tilde{\rho}^2 + \tilde{z}^2}} d\tilde{\rho} \int_0^{2\pi} d\tilde{\theta} e^{-i\left(k_x\tilde{\rho}\cos\tilde{\theta} + k_y\tilde{\rho}\sin\tilde{\theta}\right)} = \\ &= \frac{q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_0^{\infty} \frac{\tilde{\rho}}{\sqrt{\tilde{\rho}^2 + \tilde{z}^2}} d\tilde{\rho} \int_0^{2\pi} d\tilde{\theta} e^{-i\left(k_x\cos\tilde{\theta} + k_y\sin\tilde{\theta}\right)\tilde{\rho}} \end{aligned} \tag{S19}$$

We may now also transform $\vec{\kappa}$ to its polar representation

$$\begin{cases} \kappa = |\vec{\kappa}| = \sqrt{k_x^{\ 2} + k_y^{\ 2}} \\ \eta = arctg\left(\dfrac{k_y}{k_x}\right) \end{cases} \quad ; \quad \begin{cases} k_x = \kappa\cos(\eta) \\ k_y = \kappa\sin(\eta) \end{cases} \tag{S20}$$

to obtain:

$$\begin{aligned} \hat{\varphi}_i(\vec{\kappa},\tilde{z}) &= \frac{q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_0^{\infty} \frac{\tilde{\rho}}{\sqrt{\tilde{\rho}^2 + \tilde{z}^2}} d\tilde{\rho} \int_0^{2\pi} d\tilde{\theta} e^{-i\left(\cos\eta\cos\tilde{\theta} + \sin\eta\sin\tilde{\theta}\right)\kappa\tilde{\rho}} = \\ &= \frac{q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_0^{\infty} \frac{\tilde{\rho}}{\sqrt{\tilde{\rho}^2 + \tilde{z}^2}} d\tilde{\rho} \int_0^{2\pi} d\tilde{\theta} e^{-i\kappa\tilde{\rho}\cos(\tilde{\theta}-\eta)} \end{aligned} \tag{S21}$$

By changing variables such that $\alpha = \tilde{\theta} - \eta$; $d\alpha = d\tilde{\theta}$ we can write:

$$\hat{\varphi}_i(\vec{\kappa},\tilde{z}) = \frac{q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_0^{\infty} \frac{\tilde{\rho}}{\left[\tilde{\rho}^2 + \tilde{z}^2\right]^{1/2}} d\tilde{\rho} \int_{-\eta}^{2\pi-\eta} e^{-i\kappa\tilde{\rho}\cos\alpha} d\alpha \tag{S22}$$

Since the cosine function is periodic and the angular integration is performed over a full period of 2π we may write:

(S23) $$\int_{-\eta}^{2\pi-\eta} e^{-i\kappa\tilde{\rho}\cos\alpha}\, d\alpha = \int_{0}^{2\pi} e^{-i\kappa\tilde{\rho}\cos\alpha}\, d\alpha = 2\pi J_0\left(\left|\kappa\tilde{\rho}\right|\right) = 2\pi J_0\left(\kappa\tilde{\rho}\right)$$

where $J_0(x)$ is the zeroth order Bessel function of the first kind, and the last equality results from the fact that κ and $\tilde{\rho}$ are positive norms of the corresponding vectors. With this we can write:

(S24) $$\begin{aligned}\hat{\varphi}_i(\vec{\kappa},\tilde{z}) &= \frac{2\pi q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_0^\infty \frac{\tilde{\rho} J_0(\kappa\tilde{\rho})}{\sqrt{\tilde{\rho}^2+\tilde{z}^2}}\, d\tilde{\rho} = \frac{2\pi q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_0^\infty \frac{(R/\kappa) J_0(R)}{\left[R^2/\kappa^2+\tilde{z}^2\right]^{1/2}} \frac{dR}{\kappa} = \\ &= \frac{2\pi q_i}{T_x T_y} \frac{e^{-i\vec{\kappa}\cdot\vec{\rho}_i}}{\kappa} \int_0^\infty \frac{R J_0(R)}{\left[R^2+(\tilde{z}\kappa)^2\right]^{1/2}}\, dR = \frac{2\pi q_i}{T_x T_y} \frac{e^{-i\vec{\kappa}\cdot\vec{\rho}_i}}{\kappa} e^{-\kappa|\tilde{z}|}\end{aligned}$$

where we have set $R = \kappa\tilde{\rho}$; $dR = \kappa d\tilde{\rho}$. Since, $\tilde{z} = z - z_i$ we can finally write:

(S25) $$\hat{\varphi}_i(\vec{\kappa},z) = \frac{2\pi q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \frac{e^{-\kappa|z-z_i|}}{\kappa}$$

In order to construct fully convergent lattice sums, we now use the following integral identity to split the $1/\kappa$ into two ranges:

(S26) $$\frac{e^{-\kappa|z|}}{\kappa} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt = \frac{2}{\sqrt{\pi}} \int_0^\lambda e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt + \frac{2}{\sqrt{\pi}} \int_\lambda^\infty e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt$$

Using this we obtain:

(S27) $$\begin{aligned}\hat{\varphi}_i(\vec{\kappa},z) &= \frac{2\pi q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \left[\frac{2}{\sqrt{\pi}} \int_0^\lambda e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt + \frac{2}{\sqrt{\pi}} \int_\lambda^\infty e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt\right] = \\ &= \frac{4\sqrt{\pi} q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_0^\lambda e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt + \frac{4\sqrt{\pi} q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \int_\lambda^\infty e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt = \hat{\varphi}_i^S(\vec{\kappa},z) + \hat{\varphi}_i^L(\vec{\kappa},z)\end{aligned}$$

Where the short (S) and long (L) range contributions to $\hat{\varphi}_i(\vec{\kappa},z)$ have been defined as:

(S28) $$\begin{cases}\hat{\varphi}_i^S(\vec{\kappa},z) = \dfrac{4\sqrt{\pi} q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \displaystyle\int_0^\lambda e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt \\ \hat{\varphi}_i^L(\vec{\kappa},z) = \dfrac{4\sqrt{\pi} q_i}{T_x T_y} e^{-i\vec{\kappa}\cdot\vec{\rho}_i} \displaystyle\int_\lambda^\infty e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt\end{cases}$$

The full potential can be now written as:

(S29) $$\varphi(\vec{\kappa},z) = \sum_{i=1}^d \varphi_i(\vec{\kappa},z) = \sum_{i=1}^d \left[\hat{\varphi}_i^S(\vec{\kappa},z) + \hat{\varphi}_i^L(\vec{\kappa},z)\right] = \sum_{i=1}^d \hat{\varphi}_i^S(\vec{\kappa},z) + \sum_{i=1}^d \hat{\varphi}_i^L(\vec{\kappa},z) = \varphi^S(\vec{\kappa},z) + \varphi^L(\vec{\kappa},z)$$

The long range term

The long range term, $\varphi^L(\vec{r})$, is absolutely convergent in reciprocal space and thus it is first summed in reciprocal space and then transformed back to real space. When evaluating the relevant integrals one needs to separately treat the cases where $\kappa > 0$ and $\kappa = 0$:

$\kappa > 0$

For $\kappa > 0$ the long-range integral is given by:

(S30) $$\int_{\lambda}^{\infty} e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt = \frac{\sqrt{\pi}}{4\kappa}\left[e^{\kappa|z-z_i|} erfc\left(\lambda\kappa + \frac{|z-z_i|}{2\lambda}\right) + e^{-\kappa|z-z_i|} erfc\left(\lambda\kappa - \frac{|z-z_i|}{2\lambda}\right)\right]$$

And thus:

(S31) $$\varphi^L(\vec{\kappa} > 0, z) = \sum_{i=1}^{d} \hat{\varphi}_i^L(\vec{\kappa}, z) = \frac{4\sqrt{\pi}}{T_x T_y}\sum_{i=1}^{4} q_i \int_{\lambda}^{\infty} e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt e^{-i\vec{\kappa}\cdot\vec{\rho}_i} =$$
$$= \frac{\pi}{T_x T_y \kappa}\sum_{i=1}^{d}\left[e^{\kappa|z-z_i|} erfc\left(\lambda\kappa + \frac{|z-z_i|}{2\lambda}\right) + e^{-\kappa|z-z_i|} erfc\left(\lambda\kappa - \frac{|z-z_i|}{2\lambda}\right)\right] q_i e^{-i\vec{\kappa}\cdot\vec{\rho}_i}$$

$\kappa = 0$

For $\kappa = 0$ the integral is divergent. Nevertheless, it can be written as a sum of a converging integral and a constant (not depending on i) divergent part as follows:

(S32) $$\int_{\lambda}^{\infty} e^{-\kappa^2 t^2 - |z-z_i|^2/(4t^2)} dt \underset{\kappa=0}{\rightarrow} \int_{\lambda}^{\infty} e^{-|z-z_i|^2/(4t^2)} dt = \int_{\lambda}^{\infty}\left[e^{-|z-z_i|^2/(4t^2)} - 1\right] dt + \int_{\lambda}^{\infty} dt =$$
$$= \lambda - \lambda e^{-\frac{|z-z_i|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z-z_i| erf\left(\frac{|z-z_i|}{2\lambda}\right) + \int_{\lambda}^{\infty} dt$$

with this we obtain:

(S33) $$\varphi^L(\vec{\kappa} = 0, z) = \sum_{i=1}^{d} \hat{\varphi}_i^L(\vec{\kappa} = 0, z) = \frac{4\sqrt{\pi}}{T_x T_y}\sum_{i=1}^{4} q_i \int_{\lambda}^{\infty} e^{-|z-z_i|^2/(4t^2)} dt =$$
$$= \frac{4\sqrt{\pi}}{T_x T_y}\sum_{i=1}^{d} q_i \left[\lambda - \lambda e^{-\frac{|z-z_i|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z-z_i| erf\left(\frac{|z-z_i|}{2\lambda}\right) + \int_{\lambda}^{\infty} dt\right] =$$
$$= \frac{4\sqrt{\pi}}{T_x T_y}\sum_{i=1}^{d}\left[-\lambda e^{-\frac{|z-z_i|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z-z_i| erf\left(\frac{|z-z_i|}{2\lambda}\right)\right] q_i + \sum_{i=1}^{4}\left[\left(\lambda + \int_{\lambda}^{\infty} dt\right) q_i\right] =$$
$$= \frac{4\sqrt{\pi}}{T_x T_y}\sum_{i=1}^{d}\left[-\lambda e^{-\frac{|z-z_i|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z-z_i| erf\left(\frac{|z-z_i|}{2\lambda}\right)\right] q_i + \left(\lambda + \int_{\lambda}^{\infty} dt\right)\sum_{i=1}^{4} q_i$$

Since we treat charge neutral unit-cells such that $\sum_{i=1}^{d} q_i = 0$ (Eq. (1)) the divergent term falls and we are left with:

(S34) $$\varphi^L(\vec{\kappa}=0,z) = \frac{4\sqrt{\pi}}{T_x T_y}\sum_{i=1}^{d}\left[-\lambda e^{-\frac{|z-z_i|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z-z_i| erf\left(\frac{|z-z_i|}{2\lambda}\right)\right] q_i$$

We can now back-transform to real space:

(S35) $$\boxed{\begin{aligned}&\varphi^L(\vec{r}) = \sum_{k_x}\sum_{k_y}\hat{\varphi}^L(\vec{\kappa},z)e^{i\vec{\kappa}\cdot\vec{\rho}} = \frac{4\sqrt{\pi}}{T_x T_y}\sum_{i=1}^{d}\left[-\lambda e^{-\frac{|z-z_i|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z-z_i| erf\left(\frac{|z-z_i|}{2\lambda}\right)\right] q_i + \\ &+ \frac{\pi}{T_x T_y}\sum_{k_x}\sum_{k_y}{}^{*}\frac{1}{\sqrt{k_x^2+k_y^2}}\times \\ &\sum_{i=1}^{d}\left[e^{\sqrt{k_x^2+k_y^2}|z-z_i|} erfc\left(\lambda\sqrt{k_x^2+k_y^2} + \frac{|z-z_i|}{2\lambda}\right) + e^{-\sqrt{k_x^2+k_y^2}|z-z_i|} erfc\left(\lambda\sqrt{k_x^2+k_y^2} - \frac{|z-z_i|}{2\lambda}\right)\right] q_i e^{i[k_x(x-x_i)+k_y(y-y_i)]}\end{aligned}}$$

Where $k_x = 0, \pm 2\pi/T_x, \pm 4\pi/T_x, \ldots$ and $k_y = 0, \pm 2\pi/T_y, \pm 4\pi/T_y, \ldots$ and the star sign indicates that we the term with $k_x = k_y = 0$ is excluded from the sum. This can be explicitly written as:

(S36) $$\boxed{\begin{aligned}&\varphi^L(\vec{r}) = \frac{4\sqrt{\pi}}{T_x T_y}\sum_{i=1}^{d}\left[-\lambda e^{-\frac{|z-z_i|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z-z_i| erf\left(\frac{|z-z_i|}{2\lambda}\right)\right] q_i + \frac{1}{2}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}{}^{*}\frac{1}{\sqrt{n^2T_y^2+m^2T_x^2}}\times \\ &\sum_{i=1}^{d}\left[e^{2\pi\sqrt{(n/T_x)^2+(m/T_y)^2}|z-z_i|} erfc\left(2\pi\lambda\sqrt{(n/T_x)^2+(m/T_y)^2} + \frac{|z-z_i|}{2\lambda}\right) + \right. \\ &\left. e^{-2\pi\sqrt{(n/T_x)^2+(m/T_y)^2}|z-z_i|} erfc\left(2\pi\lambda\sqrt{(n/T_x)^2+(m/T_y)^2} - \frac{|z-z_i|}{2\lambda}\right)\right] q_i e^{2\pi i[(n/T_x)(x-x_i)+(m/T_y)(y-y_i)]}\end{aligned}}$$

The short range term

The short range term, $\varphi^S(\vec{r})$, is first back-transformed to real space (where it is absolutely convergent) and then summed.

(S37)
$$\varphi^S(\vec{r})=\sum_{k_x}\sum_{k_y}\hat{\varphi}^S(\vec{\kappa},z)e^{i\vec{\kappa}\cdot\vec{\rho}}=\sum_{k_x}\sum_{k_y}\left[\frac{4\sqrt{\pi}}{T_xT_y}\sum_{i=1}^{d}q_i e^{-i\vec{\kappa}\cdot\vec{\rho}_i}\int_0^{\lambda}e^{-\kappa^2t^2-|z-z_i|^2/(4t^2)}dt\right]e^{i\vec{\kappa}\cdot\vec{\rho}}=$$
$$=\frac{4\sqrt{\pi}}{T_xT_y}\sum_{k_x}\sum_{k_y}\sum_{i=1}^{d}q_i e^{i\vec{\kappa}\cdot(\vec{\rho}-\vec{\rho}_i)}\int_0^{\lambda}e^{-\kappa^2t^2-|z-z_i|^2/(4t^2)}dt=\frac{4\sqrt{\pi}}{T_xT_y}\sum_{i=1}^{d}q_i\int_0^{\lambda}\left[\sum_{k_x}\sum_{k_y}e^{-\kappa^2t^2}e^{i\vec{\kappa}\cdot(\vec{\rho}-\vec{\rho}_i)}\right]e^{-|z-z_i|^2/(4t^2)}dt=$$
$$=\frac{4\sqrt{\pi}}{T_xT_y}\sum_{i=1}^{d}q_i\int_0^{\lambda}\left[\sum_{k_x}\sum_{k_y}e^{-(k_x^2+k_y^2)t^2}e^{i[k_x(x-x_i)+k_y(y-y_i)]}\right]e^{-|z-z_i|^2/(4t^2)}dt=$$
$$=4\sqrt{\pi}\sum_{i=1}^{d}q_i\int_0^{\lambda}\left[\left(\frac{1}{T_x}\sum_{k_x}e^{-k_x^2t^2}e^{ik_x(x-x_i)}\right)\left(\frac{1}{T_y}\sum_{k_y}e^{-k_y^2t^2}e^{ik_y(y-y_i)}\right)\right]e^{-|z-z_i|^2/(4t^2)}dt$$

According to Poisson's summation formula (see proof below) we may write

(S38)
$$\sum_{n=-\infty}^{\infty}f(x+nT)=\frac{1}{T}\sum_{m=-\infty}^{\infty}\hat{f}(m)e^{2\pi imx/T}\quad;\quad\hat{f}(m)=\int_{-\infty}^{\infty}f(x)e^{-2\pi imx/T}dx$$

and applying to one of the sums above we obtain:

(S39)
$$\frac{1}{T_x}\sum_{k_x}e^{-k_x^2t^2}e^{ik_x(x-x_i)}=\frac{1}{T_x}\sum_{m=-\infty}^{\infty}\left[e^{-(2\pi m/T_x)^2t^2}e^{-2\pi imx_i/T_x}\right]e^{2\pi imx/T_x}$$

where we can identify $\hat{f}(m)=e^{-(2\pi m/T_x)^2t^2}e^{-2\pi imx_i/T_x}$. Owing to the following relation $\int_{-\infty}^{\infty}\left[\frac{1}{2\sqrt{\pi}t}e^{-(x-x_i)^2/(4t^2)}\right]e^{-2\pi imx/T_x}dx=e^{-(4\pi^2m^2t^2/T_x^2)}e^{-(2\pi imx_i/T_x)}=\hat{f}(m)$ we find that $f(x)=\frac{1}{2\sqrt{\pi}t}e^{-(x-x_i)^2/(4t^2)}$.

Thus using Poisson's formula (Eq. (38)) we obtain:

(S40)
$$\frac{1}{T_x}\sum_{k_x}e^{-k_x^2t^2}e^{ik_x(x-x_i)}=\frac{1}{T_x}\sum_{m=-\infty}^{\infty}\left[e^{-(2\pi m/T_x)^2t^2}e^{-2\pi imx_i/T_x}\right]e^{2\pi imx/T_x}=\sum_{n=-\infty}^{\infty}\frac{1}{2\sqrt{\pi}t}e^{-(x+nT_x-x_i)^2/(4t^2)}$$

Using this we can now write

$$\varphi^S(\vec{r}) = 4\sqrt{\pi}\sum_{i=1}^{d} q_i \int_0^{\lambda}\left[\left(\frac{1}{T_x}\sum_{k_x} e^{-k_x^2t^2} e^{ik_x(x-x_i)}\right)\left(\frac{1}{T_y}\sum_{k_y} e^{-k_y^2t^2} e^{ik_y(y-y_i)}\right)\right] e^{-|z-z_i|^2/(4t^2)} dt =$$

$$= 4\sqrt{\pi}\sum_{i=1}^{d} q_i \int_0^{\lambda}\left[\left(\sum_{n=-\infty}^{\infty}\frac{1}{2\sqrt{\pi}t} e^{-(x+nT_x-x_i)^2/(4t^2)}\right)\left(\sum_{m=-\infty}^{\infty}\frac{1}{2\sqrt{\pi}t} e^{-(y+mT_y-y_i)^2/(4t^2)}\right)\right] e^{-|z-z_i|^2/(4t^2)} dt =$$

(S41) $$= \frac{1}{\sqrt{\pi}}\sum_{i=1}^{d} q_i \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\int_0^{\lambda}\frac{e^{-\left[(x+nT_x-x_i)^2+(y+mT_y-y_i)^2+|z-z_i|^2\right]/(4t^2)}}{t^2} dt =$$

$$= \frac{1}{\sqrt{\pi}}\sum_{i=1}^{d} q_i \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sqrt{\pi}\,\frac{erfc\left(\sqrt{(x+nT_x-x_i)^2+(y+mT_y-y_i)^2+|z-z_i|^2}\Big/(2\lambda)\right)}{\sqrt{(x+nT_x-x_i)^2+(y+mT_y-y_i)^2+|z-z_i|^2}} =$$

$$= \sum_{i=1}^{d} q_i \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\frac{erfc\left(\sqrt{(x+nT_x-x_i)^2+(y+mT_y-y_i)^2+|z-z_i|^2}\Big/(2\lambda)\right)}{\sqrt{(x+nT_x-x_i)^2+(y+mT_y-y_i)^2+|z-z_i|^2}}$$

So that

(S42) $$\boxed{\varphi^S(\vec{r}) = \sum_{i=1}^{d} q_i \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\frac{erfc\left(\sqrt{(x+nT_x-x_i)^2+(y+mT_y-y_i)^2+|z-z_i|^2}\Big/(2\lambda)\right)}{\sqrt{(x+nT_x-x_i)^2+(y+mT_y-y_i)^2+|z-z_i|^2}}}$$

The Ewald method for partially charged atomic centers in *h*-BN

Using the method described above, we can now write explicit expressions for calculating the electrostatic potential above a single layer of hexagonal boron nitride (*h*-BN). As explained above, we consider a rectangular unit-cell of the *h*-BN layer (see Fig. S1) with translational vectors $\vec{a}_x = \sqrt{3}a(1,0,0)$ and $\vec{a}_y = 3a(0,1,0)$, x-periodicity of $T_x = |\vec{a}_x| = \sqrt{3}a$ and y-periodicity of $T_y = |\vec{a}_y| = 3a$, a being the B-N bond length.

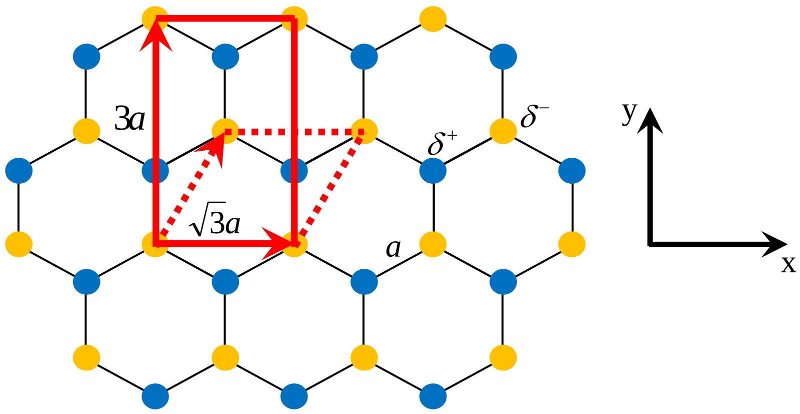

Fig. S6: Illustration of the unit cell used for the Ewald summation of the electrostatic potential above a two dimensional layer of pristine hexagonal boron nitride. Blue and orange circles represent boron and nitrogen atoms, respectively. Dashed red line shows the minimal (non-Cartesian) unit-cell consisting of two atoms while the full red line shows the rectangular Cartesian four atom unit-cell used in the calculations presented in the present study. a and δ stand for the B-N bond length and partial charge on each atomic site, respectively (see main text for more details).

Without loss of generality we assume that the *h*-BN sheet is located in the XY-plane with Z=0 and calculate the electrostatic potential generated by the 2D sheet at a general point $\vec{r} = (x, y, z \neq 0)$. The rectangular unit cell includes $d = 4$ atoms located at the following positions:

$$\vec{r}_1 = (0,0,0) \quad ; \quad \vec{r}_2 = (0,1,0)a \quad ; \quad \vec{r}_3 = \frac{1}{2}\left(\sqrt{3},3,0\right)a \quad ; \quad \vec{r}_4 = \frac{1}{2}\left(\sqrt{3},5,0\right)a \tag{S43}$$

and bearing the following charges:

$$q_1 = \delta^- = -\delta \quad ; \quad q_2 = \delta^+ = +\delta \quad ; \quad q_3 = \delta^- = -\delta \quad ; \quad q_4 = \delta^+ = +\delta\,. \tag{S44}$$

such that it is charge neutral:

$$\sum_{i=0}^{d} q_i = 0\,. \tag{S45}$$

The long range term

The long range term appearing in Eq. (36) is composed of two terms, one resulting from the case where κ=0 and the other with κ>0.

Since $z_i = 0$ (Eq. (43)) and the unit cell is neutral (Eq. (45)) the term with κ=0 vanishes

(S46) $$\frac{4\sqrt{\pi}}{3\sqrt{3}a^2}\sum_{i=1}^{4}\left[-\lambda e^{-\frac{|z-z_i|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z-z_i|erf\left(\frac{|z-z_i|}{2\lambda}\right)\right]q_i = \frac{4\sqrt{\pi}}{3\sqrt{3}a^2}\left[-\lambda e^{-\frac{|z|^2}{4\lambda^2}} - \frac{1}{2}\sqrt{\pi}|z|erf\left(\frac{|z|}{2\lambda}\right)\right]\sum_{i=1}^{4}q_i = 0$$

Therefore, for the long range contribution to the potential we are left with the κ>0 term:

(S47) $$\varphi^L(\vec{r}) = \frac{1}{2}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}{}^{*}\frac{1}{a\sqrt{9n^2+3m^2}}\left[e^{(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}+\frac{|z|}{2\lambda}\right)+ e^{-(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}-\frac{|z|}{2\lambda}\right)\right]\sum_{i=1}^{4}q_i e^{2\pi i\left[\sqrt{3}n(x-x_i)+m(y-y_i)\right]/(3a)}$$

This sum can be rewritten as a sum of three terms: (i) a term with $n = 0$ and $m \neq 0$, (ii) a term with $n \neq 0$ and $m = 0$, and (iii) a term with $n \neq 0$ and $m \neq 0$. Furthermore, we can limit the sums to the range $0,1,\ldots,\infty$ by collecting the terms with corresponding positive and negative indices: $\pm m$ and $\pm n$.

$\underline{m \neq n = 0}$

$$\varphi^L_{m\neq n=0}(\vec{r}) = \frac{1}{2}\sum_{m=-\infty}^{\infty}{}'\frac{1}{\sqrt{3}a|m|}\left[e^{(2\pi|m|/(3a))|z|}erfc\left((2\pi|m|\lambda/(3a))+\frac{|z|}{2\lambda}\right)+e^{-(2\pi|m|/(3a))|z|}erfc\left((2\pi|m|\lambda/(3a))-\frac{|z|}{2\lambda}\right)\right]\times \sum_{i=1}^{4}q_i e^{2\pi i m(y-y_i)/(3a)} =$$

$$= \frac{1}{2\sqrt{3}a}\sum_{m=1}^{\infty}\frac{1}{m}\left[e^{(2\pi m/(3a))|z|}erfc\left((2\pi m\lambda/(3a))+\frac{|z|}{2\lambda}\right)+e^{-(2\pi m/(3a))|z|}erfc\left((2\pi m\lambda/(3a))-\frac{|z|}{2\lambda}\right)\right]\times \sum_{i=1}^{4}q_i\left[e^{2\pi i m(y-y_i)/(3a)}+e^{-2\pi i m(y-y_i)/(3a)}\right]=$$

$$= \frac{1}{\sqrt{3}a}\sum_{m=1}^{\infty}\frac{1}{m}\left[e^{(2\pi m/(3a))|z|}erfc\left((2\pi m\lambda/(3a))+\frac{|z|}{2\lambda}\right)+e^{-(2\pi m/(3a))|z|}erfc\left((2\pi m\lambda/(3a))-\frac{|z|}{2\lambda}\right)\right]\times \sum_{i=1}^{4}q_i\cos[2\pi m(y-y_i)/(3a)]$$

So that

(S48) $$\varphi^L_{m\neq n=0}(\vec{r}) = \frac{1}{\sqrt{3}a}\sum_{m=1}^{\infty}\frac{1}{m}\left[e^{(2\pi m/(3a))|z|}erfc\left((2\pi m\lambda/(3a))+\frac{|z|}{2\lambda}\right)+e^{-(2\pi m/(3a))|z|}erfc\left((2\pi m\lambda/(3a))-\frac{|z|}{2\lambda}\right)\right]\times \sum_{i=1}^{4}q_i\cos[2\pi m(y-y_i)/(3a)]$$

$\underline{n \neq m = 0}$

$$\varphi^L_{n\neq m=0}(\vec{r}) = \frac{1}{2}\sum_{n=-\infty}^{\infty}{}' \frac{1}{3a|n|}\left[e^{\left(2\pi|n|/\left(\sqrt{3}a\right)\right)|z|} erfc\left(\left(2\pi|n|\lambda/\left(\sqrt{3}a\right)\right) + \frac{|z|}{2\lambda}\right) + \right.$$

$$\left. + e^{-\left(2\pi|n|/\left(\sqrt{3}a\right)\right)|z|} erfc\left(\left(2\pi|n|\lambda/\left(\sqrt{3}a\right)\right) - \frac{|z|}{2\lambda}\right)\right] \sum_{i=1}^{4} q_i e^{2\pi i n (x-x_i)/\left(\sqrt{3}a\right)} =$$

$$= \frac{1}{6a}\sum_{n=1}^{\infty}\frac{1}{n}\left[e^{\left(2\pi n/\left(\sqrt{3}a\right)\right)|z|} erfc\left(\left(2\pi n\lambda/\left(\sqrt{3}a\right)\right) + \frac{|z|}{2\lambda}\right) + \right.$$

$$\left. + e^{-\left(2\pi n/\left(\sqrt{3}a\right)\right)|z|} erfc\left(\left(2\pi n\lambda/\left(\sqrt{3}a\right)\right) - \frac{|z|}{2\lambda}\right)\right] \sum_{i=1}^{4} q_i \left[e^{2\pi i n (x-x_i)/\left(\sqrt{3}a\right)} + e^{-2\pi i n (x-x_i)/\left(\sqrt{3}a\right)} \right] =$$

$$= \frac{1}{3a}\sum_{n=1}^{\infty}\frac{1}{n}\left[e^{\left(2\pi n/\left(\sqrt{3}a\right)\right)|z|} erfc\left(\left(2\pi n\lambda/\left(\sqrt{3}a\right)\right) + \frac{|z|}{2\lambda}\right) + \right.$$

$$\left. + e^{-\left(2\pi n/\left(\sqrt{3}a\right)\right)|z|} erfc\left(\left(2\pi n\lambda/\left(\sqrt{3}a\right)\right) - \frac{|z|}{2\lambda}\right)\right] \sum_{i=1}^{4} q_i \cos\left(2\pi n (x-x_i)/\left(\sqrt{3}a\right)\right)$$

So that

$$\varphi^L_{n\neq m=0}(\vec{r}) = \frac{1}{3a}\sum_{n=1}^{\infty}\frac{1}{n}\left[e^{\left(2\pi n/\left(\sqrt{3}a\right)\right)|z|} erfc\left(\left(2\pi n\lambda/\left(\sqrt{3}a\right)\right) + \frac{|z|}{2\lambda}\right) + \right.$$

$$\left. + e^{-\left(2\pi n/\left(\sqrt{3}a\right)\right)|z|} erfc\left(\left(2\pi n\lambda/\left(\sqrt{3}a\right)\right) - \frac{|z|}{2\lambda}\right)\right] \sum_{i=1}^{4} q_i \cos\left(2\pi n (x-x_i)/\left(\sqrt{3}a\right)\right) \quad \text{(S49)}$$

$\underline{n \neq 0\,;\, m \neq 0}$

$$\varphi^L(\vec{r}) = \frac{1}{2}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}{}^{*} \frac{1}{a\sqrt{9n^2+3m^2}}\left[e^{(2\pi/(3a))\sqrt{3n^2+m^2}\,|z|} erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2} + \frac{|z|}{2\lambda}\right) + \right.$$

$$\left. e^{-(2\pi/(3a))\sqrt{3n^2+m^2}\,|z|} erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2} - \frac{|z|}{2\lambda}\right)\right] \sum_{i=1}^{4} q_i e^{2\pi i\left[\sqrt{3}n(x-x_i)+m(y-y_i)\right]/(3a)} =$$

$$= \frac{1}{2}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \frac{1}{a\sqrt{9n^2+3m^2}}\left[e^{(2\pi/(3a))\sqrt{3n^2+m^2}\,|z|} erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2} + \frac{|z|}{2\lambda}\right) + \right.$$

$$\left. e^{-(2\pi/(3a))\sqrt{3n^2+m^2}\,|z|} erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2} - \frac{|z|}{2\lambda}\right)\right] \times$$

$$\sum_{i=1}^{4} q_i \left[e^{2\pi i\left[\sqrt{3}n(x-x_i)+m(y-y_i)\right]/(3a)} + e^{-2\pi i\left[\sqrt{3}n(x-x_i)+m(y-y_i)\right]/(3a)} + e^{2\pi i\left[\sqrt{3}n(x-x_i)-m(y-y_i)\right]/(3a)} + e^{-2\pi i\left[\sqrt{3}n(x-x_i)-m(y-y_i)\right]/(3a)} \right] =$$

$$= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\frac{1}{a\sqrt{9n^2+3m^2}}\left[e^{(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}+\frac{|z|}{2\lambda}\right)+\right.$$
$$\left.e^{-(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}-\frac{|z|}{2\lambda}\right)\right]\times$$
$$\sum_{i=1}^{4}q_i\left[\cos\left(2\pi\left[\sqrt{3}n(x-x_i)+m(y-y_i)\right]/(3a)\right)+\cos\left(2\pi\left[\sqrt{3}n(x-x_i)-m(y-y_i)\right]/(3a)\right)\right]=$$
$$= \frac{2}{a}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\frac{1}{\sqrt{9n^2+3m^2}}\left[e^{(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}+\frac{|z|}{2\lambda}\right)+\right.$$
$$\left.e^{-(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}-\frac{|z|}{2\lambda}\right)\right]\sum_{i=1}^{4}q_i\cos\left[2\pi n(x-x_i)/\left(\sqrt{3}a\right)\right]\cos\left[2\pi m(y-y_i)/(3a)\right]$$

so that

$$\varphi^L_{n\neq 0,m\neq 0}(\vec{r}) = \frac{2}{a}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\frac{1}{\sqrt{9n^2+3m^2}}\left[e^{(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}+\frac{|z|}{2\lambda}\right)+\right.$$
$$\left.e^{-(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}-\frac{|z|}{2\lambda}\right)\right]\sum_{i=1}^{4}q_i\cos\left[2\pi n(x-x_i)/\left(\sqrt{3}a\right)\right]\cos\left[2\pi m(y-y_i)/(3a)\right] \quad \text{(S50)}$$

Summing up all the long-range terms (Eqs. (48), (49), and (50)) we obtain:

$$\boxed{\begin{aligned}&\varphi^L(\vec{r}) = \frac{2}{a}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\frac{1}{\sqrt{9n^2+3m^2}}\left[e^{(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}+\frac{|z|}{2\lambda}\right)+\right.\\&\left.e^{-(2\pi/(3a))\sqrt{3n^2+m^2}|z|}erfc\left((2\pi\lambda/(3a))\sqrt{3n^2+m^2}-\frac{|z|}{2\lambda}\right)\right]\sum_{i=1}^{4}q_i\cos\left[2\pi n(x-x_i)/\left(\sqrt{3}a\right)\right]\cos\left[2\pi m(y-y_i)/(3a)\right]+\\&\frac{1}{\sqrt{3}a}\sum_{m=1}^{\infty}\frac{1}{m}\left[e^{(2\pi m/(3a))|z|}erfc\left((2\pi m\lambda/(3a))+\frac{|z|}{2\lambda}\right)+e^{-(2\pi m/(3a))|z|}erfc\left((2\pi m\lambda/(3a))-\frac{|z|}{2\lambda}\right)\right]\times\\&\sum_{i=1}^{4}q_i\cos\left[2\pi m(y-y_i)/(3a)\right]+\\&\frac{1}{3a}\sum_{n=1}^{\infty}\frac{1}{n}\left[e^{\left(2\pi n/\left(\sqrt{3}a\right)\right)|z|}erfc\left(\left(2\pi n\lambda/\left(\sqrt{3}a\right)\right)+\frac{|z|}{2\lambda}\right)+e^{-\left(2\pi n/\left(\sqrt{3}a\right)\right)|z|}erfc\left(\left(2\pi n\lambda/\left(\sqrt{3}a\right)\right)-\frac{|z|}{2\lambda}\right)\right]\times\\&\sum_{i=1}^{4}q_i\cos\left(2\pi n(x-x_i)/\left(\sqrt{3}a\right)\right)\end{aligned}} \quad \text{(S51)}$$

The short range term

For the short range term we obtain (see Eq. 42):

(S52) $$\boxed{\varphi^S(\vec{r}) = \sum_{i=1}^{4} q_i \sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} \frac{erfc\left(\sqrt{\left(x+n\sqrt{3}a-x_i\right)^2+\left(y+3ma-y_i\right)^2+z^2}\Big/(2\lambda)\right)}{\sqrt{\left(x+n\sqrt{3}a-x_i\right)^2+\left(y+3ma-y_i\right)^2+z^2}}}$$

Proof of Poisson's summation formula (Eq. 38):

We define a function

(S53) $$h(x) = \sum_{n=-\infty}^{\infty} f(x+nT)$$

which is T-periodic $\left(h(x+mT) = \sum_{n=-\infty}^{\infty} f[x+(n+m)T] \underset{l\equiv n+m}{=} \sum_{l=-\infty}^{\infty} f(x+lT) = h(x) \right)$ and can therefore be expanded in a Fourier series such that:

(S54) $$h(x) = \sum_{n=-\infty}^{\infty} f(x+nT) = \sum_{m=-\infty}^{\infty} \hat{h}(m) e^{2\pi i m x/T}$$

With

(S55) $$\hat{h}(m) = \frac{1}{T}\int_{-T/2}^{T/2} h(x)e^{-2\pi i m x/T}dx = \frac{1}{T}\int_{-T/2}^{T/2}\sum_{n=-\infty}^{\infty} f(x+nT)e^{-2\pi i m x/T}dx = \frac{1}{T}\sum_{n=-\infty}^{\infty}\int_{-T/2}^{T/2} f(x+nT)e^{-2\pi i m x/T}dx =$$
$$\underset{\tilde{x}=x+nT}{=} \frac{1}{T}\sum_{n=-\infty}^{\infty}\int_{-T/2+nT}^{T/2+nT} f(\tilde{x})e^{-2\pi i m(\tilde{x}-nT)/T}d\tilde{x} = \frac{1}{T}\int_{-\infty}^{\infty} f(\tilde{x})e^{-2\pi i m\tilde{x}/T}e^{2\pi i m n}d\tilde{x} \underset{\tilde{x}=x}{=} \frac{1}{T}\int_{-\infty}^{\infty} f(x)e^{-2\pi i m x/T}dx$$

Here, similar to Eq. (16) we have used the relation:

(S56) $$\sum_{n=-\infty}^{\infty}\int_{-T/2+nT}^{T/2+nT} d\tilde{x} = \cdots + \int_{-3T/2}^{-T/2} d\tilde{x} + \int_{-T/2}^{T/2} d\tilde{x} + \int_{T/2}^{3T/2} d\tilde{x} + \cdots = \int_{-\infty}^{\infty} d\tilde{x}$$

The total interlayer Coulomb energy due to interactions between partially charged atomic centers of an infinite *h*-BN bilayer

Consider a *h*-BN bilayer of finite size consisting of N unit cells stacked in parallel exactly on top of each other in the AA' stacking mode with an interlayer distance R. The intra-layer monopolar Coulomb interactions within each layer are independent of R and are therefore not considered. We are interested in calculating the interlayer monopolar interaction energy given by (in atomic units):

$$\text{(S57)} \qquad E_N^{1,2;El} = \sum_{i=1}^{N}\sum_{d=1}^{2}\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{q_{i,d}^{(1)}q_{j,e}^{(2)}}{r_{i,d;j,e}}$$

Where the sums over i and j run over all unit cells in layers 1 and 2, respectively, and the sums over d and e run over the two atoms within each unit cell of the corresponding layer. $q_{i,d}^{(1)}$ is the formal charge on atom d of unit cell i in layer 1, $q_{j,e}^{(2)}$ is the formal charge on atom e of unit cell j in layer 2, and $r_{i,d;j,e}$ is the distance between these two atoms. We may rewrite this sum as follows:

$$\text{(S58)} \qquad E_N^{1,2;El} = \sum_{i=1}^{N}\sum_{d=1}^{2}q_{i,d}^{(1)}\left(\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{q_{j,e}^{(2)}}{r_{i,d;j,e}}\right) = \sum_{i=1}^{N}\sum_{d=1}^{2}q_{i,d}^{(1)}\phi_{i,d}^{(2)}$$

Where $\phi_{i,d}^{(2)} = \left(\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{q_{j,e}^{(2)}}{r_{i,d;j,e}}\right)$ is the monopolar electrostatic potential experienced by particle d in unit cell i of layer 1 due to all the atomic formal charges in layer two.

As the limit of an infinite bilayer will be taken it is desired to normalize the energy by the total number of atoms $4N$:

$$\text{(S59)} \qquad \bar{E}_N^{1,2;El} = \frac{1}{4N}\sum_{i=1}^{N}\sum_{d=1}^{2}q_{i,d}^{(1)}\phi_{i,d}^{(2)}$$

When the limit $N \to \infty$ is taken all unit cells of layer 1 become equivalent both in terms of their atomic charges and in terms of the electrostatic potential they experience due to layer 2. Therefore, one may replace the general cell index i by any cell index, say 1, and write $\sum_{d=1}^{2}q_{i,d}^{(1)}\phi_{i,d}^{(2)} \xrightarrow[N\to\infty]{} \sum_{d=1}^{2}q_{1,d}^{(1)}\phi_{1,d}^{(2)}$ .With this we may write the total energy per atom in the limit of an infinite bilayer as:

$$\text{(S60)} \qquad \bar{E}_{N\to\infty}^{1,2;El} = \frac{1}{4N}\sum_{i=1}^{N}\sum_{d=1}^{2}q_{1,d}^{(1)}\phi_{1,d}^{(2)} = \frac{1}{4N}\sum_{d=1}^{2}q_{1,d}^{(1)}\phi_{1,d}^{(2)}\sum_{i=1}^{N}1 = \frac{1}{4N}N\sum_{d=1}^{2}q_{1,d}^{(1)}\phi_{1,d}^{(2)} = \frac{1}{4}\sum_{d=1}^{2}q_{1,d}^{(1)}\phi_{1,d}^{(2)}$$

or:

$$\text{(S61)} \qquad \bar{E}_{N\to\infty}^{1,2;El} = \frac{1}{4}\sum_{d=1}^{2}q_{1,d}^{(1)}\phi_{1,d}^{(2)} \quad ; \quad \phi_{i,d}^{(2)} = \left(\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{q_{j,e}^{(2)}}{r_{i,d;j,e}}\right)$$

Furthermore, due to the lattice symmetry of the AA' stacked *h*-BN bilayer the potential experience by the two atoms within each unit cell is equal in magnitude and opposite in sign. Since the formal charges of the two atoms in the unit cell are opposite in sign as well the monopolar electrostatic energy they contribute is equal resulting in the following final expression for the total energy per atom of the infinite bilayer *h*-BN system:

$$\text{(S62)} \qquad \overline{E}^{1,2;El}_{N\to\infty} = \frac{1}{2} q^{(1)}_{1,1}\phi^{(2)}_{1,1} \quad ; \quad \phi^{(2)}_{i,d} = \left(\sum_{j=1}^{N} \sum_{e=1}^{2} \frac{q^{(2)}_{j,e}}{r_{i,d;j,e}} \right)$$

Namely, the total monopolar electrostatic energy per atom of the infinite bilayer *h*-BN system equals half the energy of a charge placed above a lattice site of a single infinite *h*-BN layer. The monopolar electrostatic potential, $\phi^{(2)}_{i,d}$, may be calculated using the Ewald summation method described above.

The total interlayer vdW energy of infinite bilayer graphene and *h*-BN

Consider a finite sized *h*-BN or graphene bilayer consisting of *N* unit cells stacked in parallel exactly on top of each other in the AA' stacking mode with an interlayer distance *R*. The intra-layer vdW interactions within each layer are independent of *R* and are therefore not considered. We are interested in calculating the interlayer vdW energy given by:

$$E_N^{1,2;vdW} = \sum_{i=1}^{N}\sum_{d=1}^{2}\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{i,d;j,e}}{r_{i,d;j,e}^{6}} \tag{S63}$$

where the sums over *i* and *j* run over all unit cells in layers 1 and 2, respectively, and the sums over *d* and *e* run over the two atoms within each unit cell of the corresponding layer. $c_6^{i,d;j,e}$ is the appropriate c_6 coefficient between atom *d* of unit cell *i* in layer 1 and atom *e* of unit cell *j* in layer 2 and $r_{i,d;j,e}$ is the distance between these two atoms.

As the limit of an infinite bilayer will be taken it is desired to normalize the energy by the number of atoms, 4*N*. Thus, the total vdW energy per atom is given by:

$$\overline{E}_N^{1,2;vdW} = \frac{1}{4N}\sum_{i=1}^{N}\sum_{d=1}^{2}\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{i,d;j,e}}{r_{i,d;j,e}^{6}} \tag{S64}$$

where the bar designates energy per atom. In the above expression the term $\sum_{d=1}^{2}\left(\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{i,d;j,e}}{r_{i,d;j,e}^{6}}\right)$ is the vdW interaction energy of unit cell *i* in layer 1 with all the atoms in layer 2. When the limit $N\to\infty$ is taken all unit cells in layer 1 become equivalent in terms of their chemical environment (and thus also in terms of their C_6 coefficients) and also in terms of their interaction with the infinite layer 2. Therefore one may replace the general cell index *i* by any cell index, say 1, and write $\sum_{d=1}^{2}\left(\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{i,d;j,e}}{r_{i,d;j,e}^{6}}\right)\xrightarrow[N\to\infty]{}\sum_{d=1}^{2}\left(\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{1,d;j,e}}{r_{1,d;j,e}^{6}}\right)$. With this we may write the total energy per atom in the limit of an infinite bilayer as:

$$\begin{aligned}\overline{E}_{N\to\infty}^{1,2;vdW} &= \frac{1}{4N}\sum_{i=1}^{N}\sum_{d=1}^{2}\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{1,d;j,e}}{r_{1,d;j,e}^{6}} = \frac{1}{4N}\sum_{d=1}^{2}\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{1,d;j,e}}{r_{1,d;j,e}^{6}}\sum_{i=1}^{N}1 = \\ &= \frac{1}{4N}N\sum_{d=1}^{2}\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{1,d;j,e}}{r_{1,d;j,e}^{6}} = \frac{1}{4}\sum_{d=1}^{2}\sum_{j=1}^{N}\sum_{e=1}^{2}\frac{c_6^{1,d;j,e}}{r_{1,d;j,e}^{6}}\end{aligned} \tag{S65}$$

or:

$$\boxed{E_\infty^{vdW} = \frac{1}{4}\sum_{d=1}^{2}\left(\sum_{j=1}^{\infty}\sum_{e=1}^{2}\frac{c_6^{1,d;j,e}}{r_{1,d;j,e}^{6}}\right)} \tag{S66}$$

Namely, the total vdW energy per atom of the infinite bilayer *h*-BN or graphene systems equals a quarter of the vdW energy of a single unit cell placed above a single infinite layer of the corresponding material. As the vdW energy decays as $1/r^6$ this sum is absolutely convergent and one may use a finite flake to represent the infinite lower layer and converge the results with respect to the dimensions of the flake.