Coulomb interaction in periodic slab geometry

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This is mainly mathematical and about the precise form of the Coulomb interaction in a periodic supercell appropriate for slab or sheet calculations where on direction z is of length L and is being converged to large values of vacuum separation between periodic copies along z. In the xy plane, the unit cell has area A and along z it has length L for a volume $\Omega = AL$. The reciprocal vectors in the xy plane are called G_{xy}, the position vector projection in the xy plane is r_{xy}, and the reciprocal vectors along z are $G_z = 2\pi n/L$ for integer n.

In any periodic supercell, the Coulomb interaction is made periodic and the divergence at zero wave vector is removed by actually using the interaction function

$$V_c(r-r') = \sum_{G\neq 0} \frac{4\pi}{\Omega |G|^2} e^{iG\cdot(r-r')} \tag{1}$$

where this function obeys the key properties

$$\begin{aligned} \nabla^2 V_c(r) &= -4\pi \sum_R \delta(r-R) && \text{Poisson equation} \\ V_c(r+R) &= V_c(r) && \text{Periodic} \\ \int_\Omega dr\, V_c(r) &= 0 && \text{Zero average} \end{aligned}$$

We want to find the form of this function for a slab geometry.

So we separate out the xy sum from the z sum to get

$$V_c(r) = \sum_{G_z\neq 0} \frac{4\pi e^{iG_z z}}{ALG_z^2} + \sum_{G_{xy}\neq 0} \frac{4\pi e^{iG_{xy}\cdot r_{xy}}}{AL} \sum_{G_z} \frac{e^{iG_z z}}{G_{xy}^2 + G_z^2} = V_l(z) + V_s(r_{xy}, z) \tag{2}$$

The first part is the long-range part average over the xy cell (i.e. $G_{xy} = 0$) and the second part is the short-ranged part. For the short-ranged part, we use the following two facts: first, we have the following continuous Fourier transform

$$\int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{e^{iqz}}{G_{xy}^2 + q^2} = \frac{e^{-|z||G_{xy}|}}{2|G_{xy}|},$$

and second, for any one-dimensional discrete sampling of a Fourier transform we get a periodized function in real space:

$$\text{if } f(z) = \int_{-\infty}^{\infty} \frac{dq}{2\pi} \tilde{f}(q) e^{iqz} \quad \text{then} \quad \sum_n \tilde{f}\left(\frac{2\pi n}{L}\right) e^{2\pi i n z/L} = L \sum_m f(z - Lm)\,.$$

This means that the short range part is

$$V_s(r_{xy}, z) = \sum_{G_{xy}\neq 0} \frac{4\pi e^{iG_{xy}\cdot r_{xy}}}{AL} \sum_{G_z} \frac{e^{iG_z z}}{G_{xy}^2 + G_z^2} = \sum_{G_{xy}\neq 0} \frac{2\pi e^{iG_{xy}\cdot r_{xy}}}{A|G_{xy}|} \sum_m e^{-|z-mL||G_{xy}|} \tag{3}$$

As long as L is much larger than the xy lattice spacing and the z of interest does not get as large as L (i.e. z is not deep in the vacuum region), only the $m = 0$ term contributes to exponential precision so

$$V_s(r_{xy}, z) \approx \sum_{G_{xy}\neq 0} \frac{2\pi e^{iG_{xy}\cdot r_{xy}}}{A|G_{xy}|} e^{-|z||G_{xy}|}$$

The error is $\sim e^{-L|G_{xy}|} \sim e^{-2\pi L/a_{xy}}$ where a_{xy} is the length of the xy lattice vector(s). This is some periodic function in r_{xy} that is highly localized within a few a_{xy} in the z direction going into the vacuum: charge modulations of wave vector G_{xy} in the plane give a Coulomb potential that decays exponentially into the vacuum with decay length $1/|G_{xy}|$.

The long-range part is more problematic:

$$V_l(z) = \sum_{G_z\neq 0} \frac{4\pi e^{iG_z z}}{ALG_z^2} = \frac{L}{A\pi} \sum_{n\neq 0} \frac{e^{2\pi i n z/L}}{n^2}$$

This function obeys the following properties

$$V_l''(z) = -\frac{4\pi}{AL}\left(L\sum_m \delta(z - mL) - 1\right) \quad , \quad \int_0^L V_l(z) = 0 \quad , \quad V_l(z + L) = V_l(z)\,.$$

We are only interested in the fundamental region $0 < z < L$. The first relation says that $V_l(z)$ will be parabolic in the region with curvature $4\pi/AL$:

$$V_l(z) = a + bz + \frac{2\pi z^2}{AL}$$

Ensuring periodicity $V(0) = V(L)$ gives us the value of $b = -2\pi/A$. There are two methods to determine a. One is to enforce the zero average

$$0 = \int_0^L dz\, V_l(z) = \int_0^L dz\, (a - 2\pi z/A + 2\pi z^2/(AL))$$

The other is to directly compute $V(0)$ as

$$V(0) = \frac{L}{\pi A} \sum_{n\neq 0} \frac{1}{n^2} = \frac{2L}{\pi A} \sum_{n=1}^{\infty} \frac{1}{n^2}$$

where the infinite sum was shown first by Euler to be $\pi^2/6$. Either way gives $a = L\pi/(3A)$. Thus we have found that

$$V_l(z) = \frac{L\pi}{3A} - \frac{2\pi z}{A} + \frac{2\pi z^2}{AL}\,. \tag{4}$$

Therefore, the final expression is for $0 < z < L$

$$V_c(r) = \frac{L\pi}{3A} - \frac{2\pi z}{A} + \frac{2\pi z^2}{AL} + \sum_{G_{xy}\neq 0} \frac{2\pi e^{iG_{xy}\cdot r_{xy}}}{A|G_{xy}|} \sum_m e^{-|z-mL||G_{xy}|} \tag{5}$$

What this result means is the following: we would like to extract converged results for $L \to \infty$ involving integrals over $V_c(r - r')$. The short-ranged part is very well behaved. The long-ranged part has three components but only one is the physical one we want: the middle $-2\pi z/A$ which is the potential due to a sheet of charge with unit surface areal charge density. The last one scales as $1/L$ so it no problem, but first diverges. Thus if our integrals are over non-neutral distributions, this term will contribute and our results will be formally infinite. In practice, we will have to fit this term out and separate out the L independent component.

This diverging term only exists because we are enforcing that the integral of $V_c(r)$ over a unit cell is zero. It would be "nice" to only work with the physical $-2\pi z/A$ term but this one is not periodic.

Incomplete for now...

We can try to see how dielectric screening may modify these consideration in the simplest approximation. We will focus on the long-range part where $G_{xy} = 0$. So we have a single sheet of charge at $z = 0$ as our free charge. The dielectric is linear, homogenous, and extends over the range $-a < z < b$ where $a, b > 0$. For convenience we work with $-L/2 < z < L/2$ for this particular case as our periodic unit cell. The potential, electric, and displacement fields obey

$$\frac{dD(z)}{dz} = 4\pi\rho_{free} = \frac{4\pi}{A}\left[\sum_{m=-\infty}^{\infty}\delta(z - mL) - 1/L\right]\ ,\ E(z) = \frac{D(z)}{\epsilon(z)}\ ,\ \frac{d\phi(z)}{dz} = -E(z)$$

where

$$\epsilon(z) = \begin{cases} 1 & -L/2 < z < -a \\ \epsilon_0 & -a < z < b \\ 1 & b < z < L/2 \end{cases}$$

and all quantities are periodic with period L. Solving for $D(z)$ is easy as it is just the bare Coulomb problem:

$$D(z) = D_0 + \frac{2\pi|z|}{A} - \frac{2\pi z^2}{AL} \qquad \text{for } -L/2 < z < L/2$$

... to be continued ...