Coulomb interaction in periodic wire geometry

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This is mainly mathematical and about the precise form of the Coulomb interaction in a periodic supercell appropriate for one-dimension (wire, nanotube, polymer, etc.) calculations. The periodic direction is z and the unit cell is of length L, and the vacuum separated periodic copies in the xy plane whose area is being increased to achieve convergence. The area of the unit cell is A in the xy plane so the cell volume is $\Omega = AL$. In what follows, we will mainly focus on a square lattice in the xy plane so $A = a^2$. The reciprocal vectors in the xy plane are called $G_{xy} = 2\pi(n,m)/a$ for integer pairs (n,m), the position vector projection in the xy plane is r_{xy}, and the reciprocal vectors along z are $G_z = 2\pi j/L$ for integer j. We will often shorten the length of r_{xy} as r so $r = |r_{xy}| = \sqrt{x^2+y^2}$.

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 wire geometry.

So we separate out the $G_z = 0$ long-range part of the sum from the rest:

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

The first part is the long-range part average over the z direction ($G_z = 0$) 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

$$\int \frac{d^2q}{(2\pi)^2} \frac{e^{iq\cdot r_{xy}}}{q^2 + G_z^2} = \int_0^\infty \frac{dq}{2\pi} \frac{qJ_0(qr)}{q^2 + G_z^2} = \frac{K_0(|G_z|r)}{2\pi}.$$

The modified Bessel function $K_0(z)$ has these properties (among others):

$$\begin{aligned}
K_0(z) &= \int_0^\infty \frac{du\cos(zu)}{\sqrt{1+u^2}} = \int_0^\infty du \exp(-z\cosh u) = \int_0^\infty du \cos(z\sinh u) \\
K_0(z) &= -\ln(z/2) + \gamma + O(z^2) \qquad \text{for small } z \\
K_0(z) &= \sqrt{\frac{\pi}{2z}}\, e^{-z} \left(1 - \frac{1}{8z} + O(z^{-2})\right)
\end{aligned}$$

The last property is the useful one as it shows that $K_0(z)$ decays exponentially for large arguments. The second fact we use is that for any two-dimensional sampling of a Fourier transform we get a periodized function in real space:

$$\text{if } f(r_{xy}) = \int \frac{d^2q}{(2\pi)^2} \tilde{f}(q) e^{iq\cdot r_{xy}} \text{ then } \sum_{n,m} \tilde{f}\left(\frac{2\pi(n,m)}{a}\right) e^{2\pi i(nx+my)/a} = a^2 \sum_{j,k} f(x-ja, y-ka)$$

This means that the short range part is

$$V_s(x,y,z) = \sum_{G_z\neq 0} \frac{2e^{iG_z z}}{L} \sum_{j,k} K_0\left(|G_z|\sqrt{(x-ja)^2 + (y-ka)^2}\right) \tag{3}$$

As long as $a \gg L$ and the r of interest does not get as large as a (i.e. r is not deep in the vacuum region and $r \ll a$), only the $j = k = 0$ term contributes to exponential precision so

$$V_s(r_{xy}, z) \approx \sum_{G_z\neq 0} \frac{2e^{iG_z z} K_0(|G_z| r_{xy})}{L}$$

The error is $\sim e^{-a|G_z|} \sim e^{-2\pi a/L}$. This is some periodic function in z that is highly localized within L going away into the vacuum in the xy plane: charge modulations of wave vector G_z along the wire plane give a Coulomb potential that decays exponentially into the vacuum with decay length $1/|G_z|$. For non-zero r_{xy}, this is finite and converges quickly over G_z.

The long-range part is more problematic:

$$V_l(x,y) = \sum_{G_{xy}\neq 0} \frac{4\pi e^{iG_{xy}\cdot r_{xy}}}{ALG_{xy}^2}.$$

We can't use the above technique of a periodized function since $G_{xy} = 0$ is missing from the sum. We also can't add it in since it is infinite. It is temping to use a screened interaction which does allow us to do the sums

$$\begin{aligned} V_l^\lambda(x,y) &= \sum_{G_{xy}} \frac{4\pi e^{iG_{xy}\cdot r_{xy}}}{AL(\lambda^2+G_{xy}^2)} - \frac{4\pi}{AL\lambda^2} \\ &= \frac{2}{L}\sum_{j,k} K_0\left(\lambda\sqrt{(x-ja)^2+(y-ka)^2}\right) - \frac{4\pi}{AL\lambda^2} \end{aligned}$$

and then carefully take $\lambda \to 0$. This is of course fine in principle, but in practice for small λ we have sums of periodic copies of logarithmic potentials which is poorly convergent and not easy to deal with analytically; in fact, some part of the sum over the K_0 must cancel the $-1/\lambda^2$ divergence in the last term.

Below, we will try to do the sum directly and largely succeed. But before that, since we are mainly concerned with the $r/a \ll 1$ region, let's make a simple approximation to see what the answer might look like. Instead of woking with a square symmetry, let's try to make things as circular as possible since then we will only have a radial problem. So we will solve the problem inside of a circle of radius R where $\pi R^2 = a^2$, we will assume $V_l(r)$ only depends on r, and if all goes well $V_l'(R) = 0$ at the boundary so we can "connect" this answer to the other circles. This problem can be solved in many ways, but we can use electrostatics to skip many steps. We have a line charge with $1/L$ charge per unit length at $r = 0$ and then a smooth uniform distribution of charge of density $1/La^2 = 1/(L\pi R^2)$. The total charge inside a circle of radius r must relate to the electric field $E(r)$ via

$$2\pi r E(r) = \frac{4\pi}{L}\left(1 - \pi r^2/(\pi R^2)\right] \to E(r) = 2/r - 2r/R^2$$

We have $E(R) = 0$ as needed. Solving $V_l' = -E$ gives

$$V_l(r) = -\frac{2}{L}\ln r + (r/R)^2/L + \phi_0$$

The constant ϕ_0 is determined by making the average of $V_l(r)$ zero over the circle

$$\int_0^R 2\pi r dr V_l(r) = 0$$

This gives $L\phi_0 = 2\ln R - 3/2$. So all together

$$V_l(r) = \frac{1}{L}\cdot\left(-2\ln(r/R) + r^2/R^2 - 3/2\right)$$

We now rewrite this in terms of the basic length a via $R = a/\sqrt{\pi}$

$$\begin{aligned} V_l(r) &= \frac{1}{L}\cdot\left(-2\ln(r/a) - 2\ln\sqrt{\pi} + \pi r^2/a^2 - 3/2\right) \\ &= \frac{1}{L}\cdot\left(-2\ln(r/a) - 2.6447 + \pi(r/a)^2\right) \end{aligned}$$

where we take this seriously only for $r < R$. The main point is that we've extracted the logarithmic part, the constant part, and subleading quadratic part that goes to zero as

$a \to \infty$. There are no terms linear in r as expected from basic electrostatics. We keep this form in mind below.

Let us attempt to perform the sum directly to the extent possible:

$$V_l(x,y) = \sum_{G_{xy}\neq 0} \frac{4\pi e^{iG_{xy}\cdot r_{xy}}}{ALG_{xy}^2} = \frac{1}{L\pi}\sum_{n,m}{}' \frac{\exp(2\pi i(nx+my)/a)}{n^2+m^2}$$

where the prime means we exclude $n = m = 0$. This periodic function obeys the following properties

$$\nabla^2 V_l''(x,y) = -4\pi\left(\sum_{j,k}\delta(x-ja)\delta(y-ka) - \frac{1}{a^2}\right)$$

$$\int_0^a dx \int_0^a dy\; V_l(x,y) = 0 \quad , \quad V_l(x+ja, y+ma) = V_l(x,y)\,.$$

We are only interested in the fundamental region $0 < x, y < a$. Rather than trying to solve this differential equation, we will do the sum using known infinite functional series.

First, to make the expressions shorter, we define scaled versions of x and y as

$$(u,v) = \frac{2\pi}{a}(x,y)$$

and we split off the $n = 0$ terms off from the rest

$$\begin{aligned} V_l &= \frac{1}{L\pi}\sum_{n,m}{}' \frac{e^{inu}e^{imv}}{n^2+m^2} = \frac{1}{L\pi}\sum_{m\neq 0}\frac{e^{imv}}{m^2} + \frac{1}{L\pi}\sum_{n\neq 0} e^{inu}\sum_m \frac{e^{imv}}{m^2+n^2} \\ &= \frac{1}{L\pi}\sum_{m\neq 0}\frac{\cos(mv)}{m^2} + \frac{1}{L\pi}\sum_{n\neq 0}\cos(nu)\sum_m \frac{\cos(mv)}{m^2+n^2}\,. \end{aligned}$$

where we used the fact that the sums are real so we can take the real part of the exponentials as needed. We use the known sums from Gradshteyn-Rhyzhik p. 48 (#3 and #9)

$$\sum_{m=1}^{\infty}\frac{\cos(m\alpha)}{m^2} = \frac{\pi^2}{6} - \frac{\pi\alpha}{2} + \frac{\alpha^2}{4} \qquad \text{for } 0 \le \alpha \le 2\pi$$

and the much more powerful

$$\sum_{m=-\infty}^{\infty}\frac{\cos(m\alpha)}{(m-\beta)^2+\gamma^2} = \frac{\pi}{\gamma}\frac{e^{i\beta(\alpha-2\pi)}\sinh(\gamma\alpha) + e^{i\beta\alpha}\sinh(\gamma(2\pi-\alpha))}{\cosh(2\pi\gamma) - \cos(2\pi\beta)} \quad \text{for } 0 \le \alpha \le 2\pi\,.$$

(The first sum can actually be derived from the more general second one.)

Using them, we have

$$V_l = \frac{2}{L\pi}\left(\frac{\pi^2}{6} - \frac{\pi v}{2} + \frac{v^2}{4}\right) + \frac{1}{L}\sum_{n\neq 0}\frac{\cos(nu)}{n}\cdot\frac{\sinh(nv)+\sinh(2\pi n - nv)}{\cosh(2\pi n) - 1}$$

We now use elementary results that $\sinh a + \sinh b = 2\sinh([a+b]/2)\cosh([a-b]/2)$ and $\cosh(2a) = 2\sinh^2 a + 1$ to get

$$V_l \;=\; \frac{1}{L}\left(\frac{\pi}{3} - v + \frac{v^2}{2\pi}\right) + \frac{2}{L}\sum_{n=1}^{\infty}\frac{\cos(nu)}{n}\cdot\frac{\cosh(n(\pi - v))}{\sinh(n\pi)}$$

The term

$$\frac{\cosh(n(\pi - v))}{\sinh(n\pi)}$$

rapidly approaches e^{-nv} as n gets large (for $|v| < \pi$). We can add and subtract this to get

$$V_l \;=\; \frac{1}{L}\left(\frac{\pi}{3} - v + \frac{v^2}{2\pi}\right) + \frac{2}{L}\sum_{n=1}^{\infty}\frac{\cos(nu)}{n}e^{-nv} + \frac{2}{L}\sum_{n=1}^{\infty}\frac{\cos(nu)}{n}\cdot\left[\frac{\cosh(n(\pi - v))}{\sinh(n\pi)} - e^{-nv}\right]$$

The first infinite sum is actually known: Gradshteyn-Rhyzhik p. 49 (#2)

$$\sum_{n=1}^{\infty}\frac{p^n\cos(n\alpha)}{n} = -\frac{1}{2}\ln\left(1 - 2p\cos\alpha + p^2\right) \qquad \text{for } 0 < \alpha < 2\pi \ ,\ p^2 \le 1$$

In our case $p = e^{-v}$ so we get

$$\begin{aligned} V_l \;=\;& \frac{1}{L}\left(\frac{\pi}{3} - v + \frac{v^2}{2\pi}\right) - \frac{1}{L}\ln\left(1 - 2e^{-v}\cos u + e^{-2v}\right) \\ &+ \frac{2}{L}\sum_{n=1}^{\infty}\frac{\cos(nu)}{n}\cdot\left[\frac{\cosh(n(\pi - v))}{\sinh(n\pi)} - e^{-nv}\right] \end{aligned}$$

This expression is very useful for numerically computing V_l because the sum is rapidly convergent for any value of u and v. The linear term in v seems strange since the original expression seems even in u, v as it is based on cosines. We will see below that it is actually canceled by a part of the logarithm for small v and u.

To see what this means for small u and v, we just series expand everything. Doing the expansion by hand (i.e. Mathematica) gives

$$\begin{aligned} V_l \;=\;& \frac{1}{L}\left(\frac{\pi}{3} - v + \frac{v^2}{2\pi}\right) + \frac{1}{L}\Big(- \ln(u^2 + v^2) + v + u^2/12 - v^2/12 + \cdots\Big) \\ &+ \frac{1}{L}\sum_{n=1}^{\infty}[\coth(n\pi) - 1]\cdot\left[\frac{2}{n} - nu^2 + nv^2 + \cdots\right] \end{aligned}$$

The numerical sums needed are

$$\sum_{n=1}^{\infty}[\coth(n\pi) - 1]\cdot\frac{2}{n} = 0.00749072979907$$

and

$$\sum_{n=1}^{\infty}[\coth(n\pi) - 1]\cdot n = 0.00375586178739 \approx \frac{1}{12} - \frac{1}{4\pi}$$

and plugging in gives

$$V_l = \frac{1}{L}\Big(- \ln(u^2 + v^2) + 1.0546883 + (1/(4\pi))(u^2 + v^2) + \cdots \Big)$$

Converting back to actual units with $u^2 + v^2 = (2\pi/a)^2 r^2$ we have

$$\begin{aligned} V_l &= \frac{1}{L}\Big(- 2\ln(r/a) - 2\ln(2\pi) + 1.0546883 + \pi(r/a)^2 + \cdots \Big) \\ &= \frac{1}{L}\Big(- 2\ln(r/a) - 2.6210658 + \pi(r/a)^2 + \cdots \Big) \end{aligned}$$

Notice how similar this is to very high precision to the much easier result obtained by the circular model. The constant is quite close but of course not exactly the same.