Assignment 3 Solutions

Electrostatic energy of a crystal

Here are the first 6 approximations (in units of U), extending to ions at distance $3a$:

$$\begin{aligned}
-2.000000 &= \frac{1}{2}\left(-\frac{4}{1}\right) \\
-0.585786 &= \frac{1}{2}\left(-\frac{4}{1}+\frac{4}{\sqrt{2}}\right) \\
0.414214 &= \frac{1}{2}\left(-\frac{4}{1}+\frac{4}{\sqrt{2}}+\frac{4}{2}\right) \\
-1.374641 &= \frac{1}{2}\left(-\frac{4}{1}+\frac{4}{\sqrt{2}}+\frac{4}{2}-\frac{8}{\sqrt{5}}\right) \\
-0.667534 &= \frac{1}{2}\left(-\frac{4}{1}+\frac{4}{\sqrt{2}}+\frac{4}{2}-\frac{8}{\sqrt{5}}+\frac{4}{\sqrt{8}}\right) \\
-1.334201 &= \frac{1}{2}\left(-\frac{4}{1}+\frac{4}{\sqrt{2}}+\frac{4}{2}-\frac{8}{\sqrt{5}}+\frac{4}{\sqrt{8}}-\frac{4}{3}\right)
\end{aligned}$$

As you can see, convergence is very poor. Though negative energy (crystal stability) prevails, it seems hard to estimate the infinite crystal value even to within a factor of two.

Let's try the "molecule" approach:

The internal energy is a sum of six terms:

$$U_{00}/U = -4 + \frac{2}{\sqrt{2}} = -2.58579$$

All molecule-pair terms are sums of 4×4 terms. Here is the first one:

$$U_{20}/U = -2 + \frac{2}{\sqrt{2}} + \frac{4}{2} - \frac{4}{\sqrt{5}} - \frac{2}{3} + \frac{2}{\sqrt{10}} = -0.408852$$

It was easy to write a *Mathematica* function for computing these. Here are the first few beyond the first:

$$U_{22}/U = +0.0912234$$

$$U_{40}/U = -0.0121214$$

$$U_{42}/U = +0.0028098$$

Notice how rapidly these terms become small — the energy between electrically neutral objects (molecules). The sequence of approximations now looks like this:

$$
\begin{aligned}
-2.58579 &= U_{00}/U \\
-3.40349 &= (U_{00} + (4/2)U_{20})/U \\
-3.22104 &= (U_{00} + (4/2)U_{20} + (4/2)U_{22})/U \\
-3.24529 &= (U_{00} + (4/2)U_{20} + (4/2)U_{22} + (4/2)U_{40})/U \\
-3.23405 &= (U_{00} + (4/2)U_{20} + (4/2)U_{22} + (4/2)U_{40} + (8/2)U_{42})/U
\end{aligned}
$$

This is converging nicely, already better than a 1% estimate! Dividing by 4 to get the energy per ion:

$$-0.808512\, U$$

This is what the earlier attempt tried (unsuccessfully) to find.

According to Wikipedia, the repeat distance ("lattice constant") in a 3D NaCl crystal is 5.64 Å, so the distance between ions is $a = 5.64/2$ Å$= 2.82 \times 10^{-10}$ m. Plugging in the physical constants,

$$U = K\,\frac{e^2}{a} = 8.2 \times 10^{-19}\ \text{J}.$$

One mole of NaCl has $2N_A$ ions, where N_A is Avogadro's number. Remembering to use -0.874 for the 3D sum instead of the -0.8085 we calculated earlier, the energy per mole of NaCl is

$$-0.874(2N_A)U = -8.6 \times 10^5\ \text{J/mole}.$$

Electrostatics in a spherical world

By symmetry, the electric field of a point charge at the north pole of sphere-world has the form

$$\mathbf{E} = E(\theta)\hat{\theta},$$

where $\hat{\theta}$ is the unit vector tangent to the line of longitude and directed toward increasing θ (the south pole). For the curve $\mathcal{C}$ of constant latitude, the "surface" element in Gauss's law is

$$d\mathbf{a} = d\ell\,\hat{\theta}$$

since $\hat{\theta}$ is the outward normal to $\mathcal{C}$ and the magnitude of $d\mathbf{a}$ is a *line* element $d\ell$ on the line of latitude. By spherical geometry the radius of the circle of constant latitude is $R\sin\theta$. The circumference of this circle is therefore

$$\oint_{\mathcal{C}} d\ell = 2\pi R\sin\theta.$$

By Gauss's law,

$$\begin{aligned} \oint_{\mathcal{C}} \mathbf{E} \cdot d\mathbf{a} &= E(\theta) \oint_{\mathcal{C}} d\ell = E(\theta) 2\pi R \sin\theta \\ &= q/\epsilon' \end{aligned}$$

From this we can solve for the magnitude of the electric field:

$$E(\theta) = \frac{1}{2\pi\epsilon'} \frac{q}{R\sin\theta} \ .$$

The electric field diverges at $\theta = 0$ as it should because there is a point source at the north pole. But notice that $E(\theta)$ also diverges at $\theta = \pi$ and the field lines there (with direction $\hat{\theta}$) are pointing toward the south pole. This shows we cannot have a point source at the north pole without a matching point sink (charge $-q$) at the south pole. Sphere-world is always charge neutral!

Without loss of generality we will place q_1 at the north pole ($\theta = 0$). The energy U_{12} will then depend only on the latitude (θ) of q_2, since moving q_2 along a line of latitude involves no work ($\mathbf{E}$ and the line element $d\ell\hat{\phi}$ are perpendicular). We therefore need consider only paths along a line of longitude, and we choose to start the path at $\theta = \pi/2$, where U_{12} is defined to be zero:

$$U_{12}(\theta) - 0 = -\int_{\text{path}} \mathbf{F} \cdot d\ell\hat{\theta} \ .$$

From the earlier electric field calculation we know

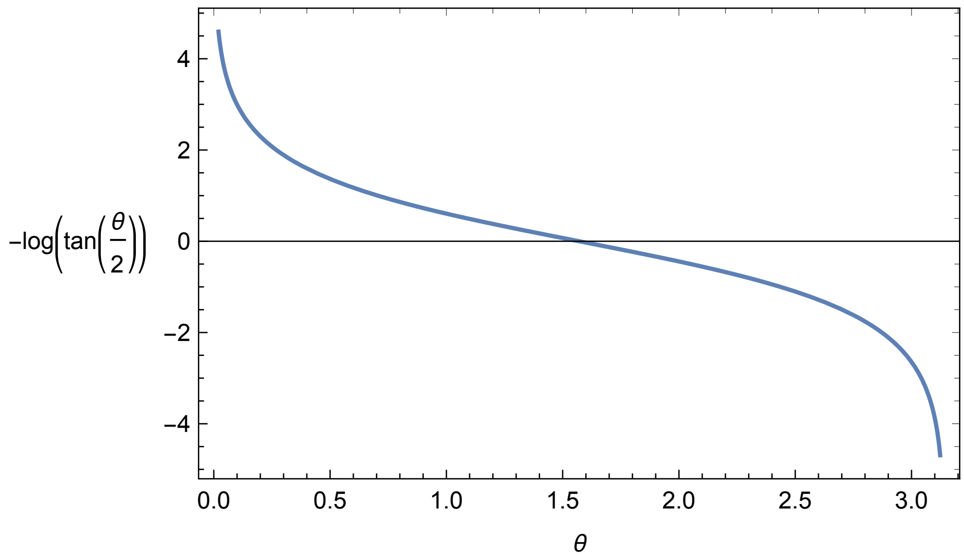
$$\mathbf{F} = q_2\,\mathbf{E} = \frac{q_2 q_1}{2\pi\epsilon'\, R\sin\theta}\ \hat{\theta},$$

and the element of arc length (along the line of longitude) is

$$d\ell = R\,d\theta.$$

Plugging these into the work integral we get

$$\begin{aligned} U_{12} &= -\frac{q_2 q_1}{2\pi\epsilon'} \int_{\pi/2}^{\theta} \frac{d\theta'}{\sin\theta'} \\ &= -\frac{q_2 q_1}{2\pi\epsilon'} \log(\tan(\theta/2)) \ . \end{aligned}$$



To understand this energy plot, remember that it describes *four* point charges: q_1 at the north pole, $-q_1$ at the south pole, q_2 at $\phi = 0$ and θ, and $-q_2$ at $\phi = \pi$ and $\pi - \theta$ (opposite q_2 on the sphere). When q_1 and q_2 have the same sign, and θ is close to zero, then two pairs of like charges are close together and the energy diverges positively. On the other hand, if θ is close to π, then two pairs of unlike charges are close together and the energy diverges negatively.