Ewald Sum (derivation taken from Daan Frenkel and Berend Smit "Understanding Molecular Simulations", appendix B)

We write electrostatic energy as

$$U = \frac{1}{2}\sum_{i,j.n} \frac{q_i q_j}{\left| r_i - r_j + nL \right|} \tag{1}$$

where the $\frac{1}{2}$ in front of the sum is to avoid double counting. The charges on the atoms are q_i and q_j respectively, r_i and r_j the coordinates of atoms and nL a displacement vector for different boxes. In three dimensions *L* includes the lattice vectors while *n* is an integer vector that determine the number of displacements in that direction. The sum is extended for all atoms within a box and for all interactions between the prime box and other boxes.

We define the electric potential $\phi(r)$ as the electrostatic energy an atom with charge +1 will feel if place at coordinate *r*. We have

$$\phi(r) = \sum_{i,n} \frac{q_i}{\left| r_i - r + nL \right|} \tag{2}$$

In particular and in connection with the above equation we define the electric potential at position r_i, a position that coincide with the location of atom *i*, in the absence of atom *i*.

$$\phi(r_i) = \sum_{j,n}{}' \frac{q_j}{\left| r_i - r_j + nL \right|} \tag{3}$$

where the prime on the sum is to exclude atom *i* (in the primary box) from the calculations of the potential. With the above definition we can write the total energy as

$$U = \frac{1}{2}\sum_i q_i \phi(r_i) \tag{4}$$

With the above notation, it is clear that the calculation of the electric potential (for all *r*) is the most difficult part of the electrostatic energy calculations. The last summation is scalar product and can be computed by *N* operations. In contrast the calculation of the electric potential (at *N* different locations -- $\phi(r_i) \quad i = 1,..,N$) is proportional to N^2. It therefore makes sense for us to focus for a while on the calculation of the electric potential.

The difficulty in computing something like electric potential is a slow decay rate of the interaction as a function of r, which means that we have to include many terms in the sum of equation (3). In the Ewald sum we split the charge to one component that decays rapidly as a function of a distance and another component that has small contributions at short distance and is dominated by a long-range term. Summation of the long-range term is done in Fourier space, as described below. But first to the charge splitting: Instead of having a simple charge q_i at the Cartesian position r_i. We write

$$\rho\left(r\right)=\sum_i q_i\left(\delta\left(r-r_i\right)-\left(\frac{\alpha}{\pi}\right)^{3/2}\exp\left(-\alpha\left(r-r_i\right)^2\right)\right)+q_i\left(\frac{\alpha}{\pi}\right)^{3/2}\exp\left(-\alpha\left(r-r_i\right)^2\right)=$$

$$\sum_i \rho_{i-long}+\rho_{i-short}= \tag{5}$$

Consider now distances that are significantly larger than the range of the Gaussian $\left(r^2 \gg 1/\alpha\right)$. At these distances we expect $\rho_{i-short}$ to make little contribution. The charge at the original is screened by the opposite charge cloud (the Gaussian) which at large distances cancel each other to give zero. On the other hand at large distances the second term (in which a Gaussian is replacing the point charge) is behaving like a point charge. A well known result from electrostatic is that spherically symmetric distribution of charges acts like a point charge if considered at distances sufficiently far such that the charge density decay to zero at the position, r, in which we compute the electric potential $\phi\left(r\right)$. On the other hand if the distances are significantly shorter ($r^2 \ll \alpha$), then the effective charge for the calculation of the electric potential at the short distances is smaller and with significantly smaller contribution than the fixed point charge.

These qualitative arguments suggest separating the calculations of the electrostatic potential into two parts. Consider first the long-range part (a system with a charge density which is a sum of Gaussians). We denote the charge density by $\rho_{long}\left(r\right)$ and have

$$\rho_{long}\left(r\right)=\sum_{j,N} q_j\left(\frac{\alpha}{\pi}\right)^{3/2}\exp\left(-\alpha\left|r-\left(r_j+nL\right)\right|^2\right) \tag{7}$$

Now we consider the Poisson equation for the above charge density

$$\nabla^2\phi_{long}\left(r\right)=-4\pi\rho_{long}\left(r\right) \tag{8}$$

A distraction: the Poisson equation

For those who did not learn electrostatic before and equation (8) looks like it just landed from Mars, here is a quick argument, based on the well-known Gauss (or Green) Theorem relating a surface integral to volume integral.

Gauss theorem: For a vector field F (for every point in three-dimension, *r*, $F\left(r\right)$ is a vector of rank 3) we have

$$\int_S F\cdot dS=\int_V\left(\nabla\cdot F\right)dV$$

where the *S* integral is over a surface area that enclose a volume *V*. The surface element, *dS,* is a vector pointing in the direction perpendicular to the surface (element) with a norm: the area of the surface element. The scalar product of the “del” operator and the vector field F means $\nabla \cdot F = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}$ and the last integration is over the volume V. Consider the electric field generated from the electric potential as $F = -\nabla \phi$, we have

$$\int_S \left(-\nabla \phi\right) \cdot dS = \int_V \left(-\nabla^2 \phi\right) dV$$

Writing the explicit point charge expression we have at our disposal for the electric potential, we consider the surface integral. Specifically

$$\int_S \left(-\nabla \phi\right) dS = \int_S \sum_i \frac{q_i}{r_i^2}\left(e \cdot dS\right) = \sum_i q_i \int_S \frac{1}{r_i} r_i^2 \sin\left(\theta\right) d\theta d\varphi = 4\pi \sum_i q_i$$

We have performed the surface integral using spheres. The last summation can be converted into a volume integral using the charge density. The sum over all charges is the same as an integral over the spatial charge density.

$$4\pi \sum_i q_i = 4\pi \int_V \sum_i q_i \delta\left(r - r_i\right) dV = 4\pi \int_V \rho\left(r\right) dV = \int_V \left(-\nabla^2 \phi\right) dV$$

and in summary we obtain the Poisson equation

$$\nabla^2 \phi = -4\pi\rho$$

End of distraction

A spatial Fourier transform of the Poisson equation gives:

$$k^2 \tilde{\phi}_{long}\left(k\right) = 4\pi \tilde{\rho}_{long}\left(k\right)$$

where we used the notation $\tilde{G}\left(k\right)$ is the Fourier transform of $G\left(r\right)$

$$\tilde{G}\left(k\right) = \frac{1}{V}\int_V \exp\left(-ikr\right) G\left(r\right) dV$$

We have for the charge density (using also he symmetry of the box)

$$\tilde{\rho}_{long}\left(k\right) = \frac{1}{V}\int_V \exp\left(-ikr\right) \rho_{long}\left(r\right) dV = \frac{1}{V}\sum_j q_j \exp\left(-ikr\right) \exp\left(-k^2/4\alpha\right)$$

Substituting back in the Poisson equation, we obtain

$$\tilde{\phi}_{long}\left(k\right) = \frac{4\pi}{k^2 V}\sum_{j=1}^{N} q_j \exp\left(-ikr_j\right) \exp\left(-k^2/4\alpha\right)$$

And now we need to Fourier transform backward

$$\phi_{long}\left(r\right) = \sum_k \exp\left(ikr\right) \tilde{\phi}_{long}\left(k\right) = \frac{1}{V}\sum_k \sum_j \frac{4\pi q_j}{k^2} \exp\left(ik\left(r - r_j\right)\right) \exp\left(-k^2/4\alpha\right)$$

Finally the contribution of long range interactions to the electrostatic energy

$$U = \frac{1}{2}\sum_i q_i \phi_{long}\left(r_i\right) = \frac{1}{2}\sum_{i,j} \frac{4\pi q_i q_j}{V k^2} \exp\left[ik\left(r_i - r_j\right)\right] \exp\left(-k^2/4\alpha\right)$$

Using the definition of the TRUE charge density

$$\tilde{\rho}\left(k\right) = \frac{1}{V}\sum_i q_i \int_V \delta\left(r - r_i\right) \exp\left(-ikr\right) = \frac{1}{V}\sum_i q_i \exp\left(ikr_i\right)$$

We can write the expression for the electrostatic energy in a slightly more compact form

$$U = \frac{V}{2}\sum_k \frac{4\pi}{k^2}\left|\tilde{\rho}(k)\right|^2 \exp\left(-k^2/4\alpha\right)$$

self energy

In the calculations of the long-range interactions and the electric potential we computed also the interaction of the charge with itself (we computed the electric potential at site *i* using a Gaussian charge density and then computed in the formula above the interaction energy include a point charge at site *i*). This is wrong. We therefore need to subtract from the electric energy the contribution of the self energy – i.e. the charge interacting with self). The self energy is

$$U_{self} = \frac{1}{2}\sum_i q_i \phi_{self}\left(r_i\right)$$

The self potential that w eintroduces is coming from a Gaussian centered at r_i. Since it interacts with a particle at the same location, we can take the point charge and the Gaussian to be centered at the origin. We need to solve the Poisson equation for a Gaussian charge density centered at the origin to figure out what is the self electric-potential, we have

$$-\frac{1}{r}\frac{\partial^2\left(r\phi_{gauss}\right)}{\partial r^2} = 4\pi\rho_{Gauss} \qquad \rho_{Gauss} = q_i\left(\frac{\alpha}{\pi}\right)^{3/2}\exp\left(-\alpha r^2\right)$$

This can be solved exactly to give

$$\phi_{Gauss} = q_i \cdot erf\left(\sqrt{\alpha}r\right)$$

and where the correction is needed ($r = 0$), we have $\phi_{Gauss}\left(r=0\right) = 2q_i\left(\frac{\alpha}{\pi}\right)^{1/2}$

The self energy is then

$$U = \left(\frac{\alpha}{\pi}\right)^{1/2}\sum_i q_i^2$$

Short range

The above discussing prepared us for the calculation of the short-term part. We can write down the electric potential induced by a Gaussian charge density at the origin.

We have

$$\phi_{short}\left(r\right) = \frac{q_i}{r} - \frac{q_i}{r}erf\left(\sqrt{\alpha}r\right) = \frac{q_i}{r}erfc\left(\sqrt{\alpha}r\right)$$

The short range electrostatic energy is therefore

$$U_{short} = \frac{1}{2}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}}\exp\left(\sqrt{\alpha}r_{ij}\right)$$

And the whole

$$U = \frac{V}{2}\sum_{k}\frac{4\pi}{k^{2}}\left|\tilde{\rho}\left(k\right)\right|^{2}\exp\left(-k^{2}/4\alpha\right)-\left(\frac{\alpha}{\pi}\right)^{1/2}\sum_{i}q_{i}^{2}+\frac{1}{2}\sum_{i\neq j}\frac{q_{i}q_{j}}{r_{ij}}\exp\left(\sqrt{\alpha}r_{ij}\right)$$