Long-range potentials with the Ewald image technique.

There is a problem in using long-range potentials in periodic boundaries; how do you deal with the potential that leaks across the boundaries? Suppose the bare potential in infinite space is $v(r)$. Let us define the Fourier transform by:

$$\tilde{v}_{\mathbf{k}} = \int_{-\infty}^{\infty} d^D\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} v(r). \tag{1}$$

Here D is the dimensionality of space. Then its inverse is:

$$v(r) = \frac{1}{(2\pi)^D} \int_{-\infty}^{\infty} d^D\mathbf{k} e^{i\mathbf{k}\mathbf{r}} \tilde{v}_{\mathbf{k}} \tag{2}$$

Now let us find the energy of a single particle interacting with an infinite rectangular lattice of another particle a distance $\mathbf{r}$ away. To make the sum converge for a long-range potential, we also add a uniform background of the same density ($1/volume = 1/\Omega$) of opposite charge. Thus, the *image potential* is equal to

$$v_I(\mathbf{r}) = \sum_{\mathbf{L}} v(\mathbf{r}+\mathbf{L}) - \tilde{v}_0/\Omega. \tag{3}$$

The $\mathbf{L}$ sum is over the Bravais lattice of the simulation cell $\mathbf{L} = (m_x L_x, ..)$ where $m_x, m_y ...$ range over all positive and negative integers. The second term is the background. Converting this to k-space using the Poisson sum formula:

$$v_I(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{k}}{}' \tilde{v}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} \tag{4}$$

where the prime indicates that we omit the $\mathbf{k} = 0$ term; it cancels out with the background. The k-sum is over reciprocal lattice vectors of the simulation box: $\mathbf{k} = (2\pi n_x/L_x, ..)$.

Because both sums are so poorly convergent, we use both k-space and r-space; taking the long-range part into k-space and the short-range part in r-space. We write:

$$v(r) = v_s(r) + v_l(r) \tag{5}$$

(For the moment this division is arbitrary.) Since Fourier transforms are linear:

$$\tilde{v}_{\mathbf{k}} = \tilde{v}_{s\mathbf{k}} + \tilde{v}_{l\mathbf{k}} \tag{6}$$

Then the image potential is written:

$$v_I(\mathbf{r}) = \sum_{\mathbf{L}} v_s(|\mathbf{r}+\mathbf{L}|) + \frac{1}{\Omega} \sum_{\mathbf{k}} \tilde{v}_{l\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} \tag{7}$$

where the background requires $\tilde{v}_{l0} = -\tilde{v}_{s0}$.

Now let us work with N particles of charge q_i in a periodic box and let us compute the total potential energy of the unit cell. Particles i and j are assumed to interact with a potential of $q_i q_j v(r_{ij})$. The image potential for the N-particle system is:

$$V_I = \sum_{i<j} q_i q_j v_I(\mathbf{r}_{ij}) + \sum_{i=1}^{N} q_i^2 v_M \tag{8}$$

where v_M is the interaction of a particle with its own images; it is a Madelung constant for particle i interacting with the perfect lattice of the simulation cell. If this term were not present, particle i would only see $N-1$ particles in the surrounding cells instead of N. We can find its value by considering the limit as two particles get close together with the image potential.

$$v_M = \frac{1}{2} \lim_{\mathbf{r}\to 0} [v_I(\mathbf{r}) - v(\mathbf{r})] \tag{9}$$

Now we substitute the split up image potential and collect all the terms together:

$$V_I = \sum_{i<j} q_i q_j v_s(r_{ij}) + \frac{1}{2\Omega} \sum_{\mathbf{k}} {}' \tilde{v}_{lk} |\rho_{\mathbf{k}}|^2 + const. + dipole \tag{10}$$

where:

$$const. = \frac{\sum_i q_i^2 v_c}{2} - \frac{\tilde{v}_{s0} [\sum_i q_i]^2}{2\Omega} \tag{11}$$

$$v_c = \lim_{r\to 0} (v_s(r) - v(r)) \tag{12}$$

$$\rho_{\mathbf{k}} = \sum_i q_i e^{i\mathbf{k}\mathbf{r}} \tag{13}$$

The second term of the constant only appears if the system has an imbalanced charge of particles. (The background really balances out the charge, examples are the one-component plasma or jellium.)

The dipole term comes from how the infinite sums are finally dealt with for a macroscopic sample. It is only appropriate to use this term if the charge is localized in the sense that you can define a dipole moment (for example if the system consists of positive and negative charges bound together.)

$$dipole = \frac{2\pi}{(2\epsilon + 1)\Omega} |\sum_i q_i \mathbf{r}_i|^2 \tag{14}$$

where ϵ is the dielectric constant of the surrounding media; it would be infinite if the simulation systems is in contact with a metal so that surface charges cannot accumulate and unity for a vacuum.

Now we give the standard forms for the breakup which is done with a Gaussian charge distribution. It gives nice analytic results but is not necessarily

optimal. (See the paper by Natoli and Ceperley, J. Comp. Phys. **117**, 171 (1994.)

For an interaction that goes as $v(r) = r^{-n}$ the needed functions are:

$$v_s(r) = \frac{\Gamma(\nu, (\kappa r)^2)}{\Gamma(\nu) r^n} \tag{15}$$

$$v_{lk} = \frac{\pi^{D/2}(2/k)^{2\mu}\Gamma(\mu, (k/(2\kappa))^2)}{\Gamma(\nu)} \tag{16}$$

$$\tilde{v}_{s0} = \frac{\mu\pi^{D/2}}{\Gamma(\nu)\kappa^{2\mu}} \tag{17}$$

$$v_c = -\frac{\kappa^n}{\nu\Gamma(\nu)} \tag{18}$$

where $\Gamma(x, a)$ is the incomplete gamma function (see Abramowitz and Stegan) and $\nu = n/2$ and $\mu = (D - n)/2$. A free parameter κ appears that is related to the width of the distribution. For large arguments the short-ranged potential drops off exponentially fast:

$$v_s(r) \propto e^{-(\kappa r)^2}/r^2 \tag{19}$$

Specializing for the usual case of the Coulomb interaction (n=1) in three dimensions $D = 3$ we get:

$$v_s(r) = erfc(\kappa r)/r \tag{20}$$

$$v_{lk} = \frac{4\pi e^{-(k/(2\kappa))^2}}{k^2} \tag{21}$$

$$\tilde{v}_{s0} = \frac{\pi}{\kappa^2} \tag{22}$$

$$v_c = -\frac{2\kappa}{\sqrt{\pi}} \tag{23}$$

One usually chooses κ so that the short-ranged potential is zero at the edge of the box (at $L/2$) and we can use the minimum imae convention and then increase the number of $\mathbf{k}$ points until convergence is achieved. The optimal value of κ to get high accuracy in the Ewald sum is:

$$\kappa^* = \sqrt{\pi}/L \tag{24}$$