

## 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:

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

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

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

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 ( $1/\text{volume} = 1/\Omega$ ) of opposite charge. Thus, the *image potential* is equal to

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

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:

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

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:

$$v(r) = v_s(r) + v_l(r) \quad (5)$$

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

$$\tilde{v}_{\mathbf{k}} = \tilde{v}_{s\mathbf{k}} + \tilde{v}_{l\mathbf{k}} \quad (6)$$

Then the image potential is written:

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

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:

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

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.

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

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

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

where:

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

$$v_c = \lim_{r \rightarrow 0} (v_s(r) - v(r)) \quad (12)$$

$$\rho_{\mathbf{k}} = \sum_i q_i e^{i\mathbf{k}\mathbf{r}} \quad (13)$$

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.)

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

where  $\epsilon$  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:

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

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

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

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

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  $\kappa$  appears that is related to the width of the distribution. For large arguments the short-ranged potential drops off exponentially fast:

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

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

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

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

$$\tilde{v}_{s0} = \frac{\pi}{\kappa^2} \quad (22)$$

$$v_c = -\frac{2\kappa}{\sqrt{\pi}} \quad (23)$$

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

$$\kappa^* = \sqrt{\pi}/L \quad (24)$$

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