Long-range potentials with the Ewalds image technique

Riccardo Fantoni

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Suppose the bare potential in infinite d dimensional space is $v(r)$. Let us define the Fourier transform by

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

Then its inverse is

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

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 it converge we also add a uniform background of the same density (Ω =volume) of opposite charge. Thus the "image pair-potential" is equal to

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

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

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

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

Because both sums are so poorly convergent, we make the division into $k-$space and $r-$space; taking the long-range part into $k-$space. We write

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

and equivalently (since Fourier transform is linear)

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

Then the image pair-potential is written as

$$v_I(r) = \sum_{\mathbf{L}} v_s(|\mathbf{r}+\mathbf{L}|) + \frac{1}{\Omega}\sum_{\mathbf{k}} \tilde{v}_{l\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{\Omega}\tilde{v}_0 \ . \tag{7}$$

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 pair-potential $q_i q_j v(r_{ij})$. The image potential energy for the $N-$particle system is

$$V_I = \sum_{i<j} q_i q_j v_I(r_{ij}) + \sum_i q_i^2 v_M \ , \tag{8}$$

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 pair-potential. Hence

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

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

$$V_I = \sum_{i<j}\sum_{\mathbf{L}} q_i q_j v_s(|\mathbf{r}_{ij}+\mathbf{L}|) + \frac{1}{\Omega}{\sum_{\mathbf{k}}}' \tilde{v}_{l\mathbf{k}} \sum_{i<j} q_i q_j e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} - \frac{1}{\Omega}\sum_{i<j}\tilde{v}_{s0} q_i q_j + \sum_i q_i^2 v_M \ , \tag{10}$$

$$v_M = \frac{1}{2}\left[\sum_{\mathbf{L}} v_s(|\mathbf{L}|) + \frac{1}{\Omega}{\sum_{\mathbf{k}}}' \tilde{v}_{l\mathbf{k}} - \frac{1}{\Omega}\tilde{v}_{s0} - v(0)\right] \ , \tag{11}$$

or,

$$V_I = \sum_{i<j}\sum_{\mathbf{L}} q_i q_j v_s(|\mathbf{r}_{ij}+\mathbf{L}|) + \frac{1}{2\Omega}{\sum_{\mathbf{k}}}' \tilde{v}_{l\mathbf{k}} |\rho_{\mathbf{k}}|^2 + \frac{1}{2}\sum_i q_i^2 v_c - \frac{1}{2\Omega}\tilde{v}_{s0}\left[\sum_i q_i\right]^2 \ , \tag{12}$$

where

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

$$|\rho_{\mathbf{k}}|^2 = \sum_i q_i^2 + 2\sum_{i<j} q_i q_j \cos(\mathbf{k}\cdot\mathbf{r}_{ij}) \ , \tag{14}$$

$$v_c = \lim_{\mathbf{r}\to 0}\left[\sum_{\mathbf{L}} v_s(|\mathbf{r}+\mathbf{L}|) - v(r)\right] \ . \tag{15}$$

Now we give the standard forms for the breakup which is done with a Gaussian charge distribution. α is a free parameter related to the width of the distribution. It gives nice

analytic results but is not necessarily optimal. See the paper by Natoli and Ceperley (J. Comp. Phys. 1994).

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

$$v_s(r) = \frac{\Gamma(\nu, (\alpha r)^2)}{\Gamma(\nu) r^n} , \tag{16}$$

$$\tilde{v}_{l\mathbf{k}} = \frac{\pi^{d/2}(2/k)^{2\mu}\Gamma(\mu, (k/2\alpha)^2)}{\Gamma(\nu)} , \tag{17}$$

$$\tilde{v}_{s0} = \frac{\pi^{d/2}}{\Gamma(\nu)\mu\alpha^{2\mu}} , \tag{18}$$

$$v_c = -\frac{\alpha^n}{\nu\Gamma(\nu)} , \tag{19}$$

where $\Gamma(a, z)$ is the incomplete gamma function (see Abramowitz and Stegun) and $\nu = n/2$ and $\mu = (d - n)/2$.

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

$$v_s(r) = \mathrm{erfc}(\alpha r)/r , \tag{20}$$

$$\tilde{v}_{l\mathbf{k}} = \frac{4\pi e^{-(k/2\alpha)^2}}{k^2} \tag{21}$$

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

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

One usually chooses α so that the short-ranged potential is nearly zero at the edge of the box $(\pm L/2, \pm L/2, \pm L/2)$ and then increases the number of $\mathbf{k}$ points until convergence is achieved.