Ewald summation

Volodymyr P. Sergiievskyi

July 5, 2014

1 Charge splitting

The task is to compute the coulomb potential in a periodic boundary conditions.

$$U = \frac{1}{2}\sum_i \sum_{j\neq i} \frac{q_i q_j}{r_{ij}} + \frac{1}{2}\sum_{\mathbf{n}\neq 0}\sum_i \sum_j \frac{q_i q_j}{r_{ij} + \mathbf{n}\circ\mathbf{L}} \tag{1}$$

where $\mathbf{n} \equiv (n_x, n_y, n_z) \in \mathbb{Z}^3$, $\mathbf{L} \equiv (L_x, L_y, L_z)$ is the size of the simulation box [1]. The symbol $\circ$ represents the Hadamard (pointwise) product: $\mathbf{n}\circ\mathbf{L} = (n_x L_x, n_y L_y, n_z L_z)$.

Energy can be rewritten in terms of potential:

$$U = \sum_i q_i \phi_i(\mathbf{r}_i) \tag{2}$$

where $\phi_i(\mathbf{r})$ is the potential, created by all the charges except the charge i:

$$\phi_i(\mathbf{r}) = \sum_{j\neq i} \frac{q_j}{r_{ij}} + \sum_{\mathbf{n}\neq 0}\sum_j \frac{q_j}{|\mathbf{r}_{ij} + \mathbf{n}\circ\mathbf{L}|} \tag{3}$$

Because the sum is converging only conditionally, the following technique is used for the calculation: charges are splited into two parts.

1. The first part is the charges, screened with the gaussiansof opposite sign
2. The second part are the gaussians, to compensate ones added for the screening

This is represented in Figure 1. Mathematically, initial distributions of the point charges can be represented as a sum of delta-functions. Thenm split can be written numerically as follows:

$$\rho(\mathbf{r}) \equiv \sum_{\mathbf{n}}\sum q_i \delta(\mathbf{r} - \mathbf{r_i} - \mathbf{n}\circ\mathbf{L}) = \rho_0(\mathbf{r}) + \rho_1(\mathbf{r}) \tag{4}$$

where

$$\rho_0(\mathbf{r}) \equiv \sum_{\mathbf{n}}\sum_i q_i \left(\delta(\mathbf{r} - \mathbf{r}_i - \mathbf{n}\circ\mathbf{L}) - \left(\frac{\alpha^2}{\pi}\right)^{3/2} e^{-\alpha^2(\mathbf{r}-\mathbf{r}_i)^2} \right) \tag{5}$$

and

$$\rho_1(\mathbf{r}) \equiv \sum_{\mathbf{n}}\sum_i \left(\frac{\alpha^2}{\pi}\right)^{3/2} q_i e^{-\alpha^2(\mathbf{r}-\mathbf{r}_i-\mathbf{n}\circ\mathbf{L})^2} \tag{6}$$

[1] Here and below the atomic units are used, such that $4\pi\epsilon_0 \equiv 1$ in coulomb law

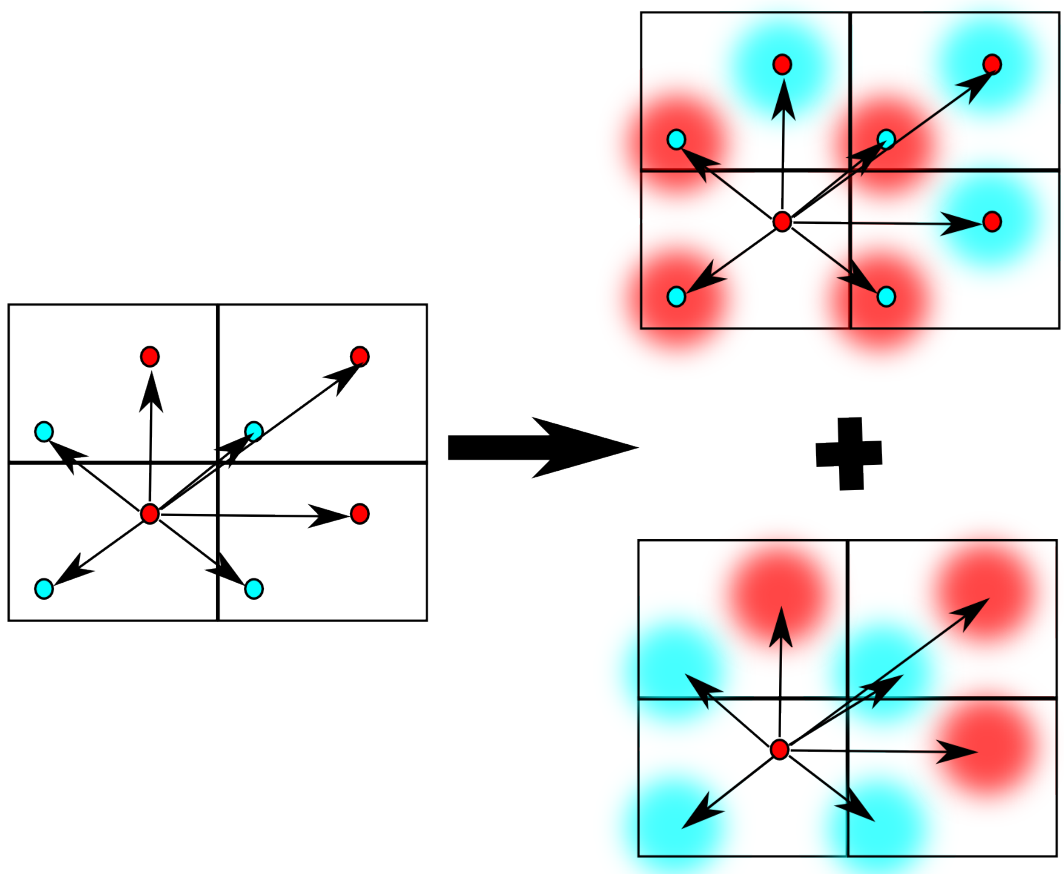

Figure 1: Ewald sum decomposition: point charge interactions are replaced by sum of two interactions: point charges with screened charges and pont charges with complementary gaussians

2 Potential of a gaussian charge

To calculate the potential of the charge distributions we can use the Poisson equation:

$$-\nabla^2\phi(\mathbf{r}) = 4\pi\rho(\mathbf{r}) \tag{7}$$

Let's calculate the potential of the gaussian charge distribution distributed around the origin:

$$\rho_G(\mathbf{r}) \equiv q\left(\frac{\alpha^2}{\pi}\right)^{3/2} e^{-\alpha^2 r^2} \tag{8}$$

Because the system in this case is spherically symmetric, we can use the spherical coordinates:

$$\nabla^2\phi_G \equiv \frac{1}{r}\frac{\partial^2(r\phi_G)}{\partial r^2} \tag{9}$$

which gives the following equation:

$$-\frac{\partial^2(r\phi_G)}{\partial r^2} = 4\pi r q\left(\frac{\alpha^2}{\pi}\right)^{3/2} e^{-\alpha^2 r^2} \tag{10}$$

Taking $\int_\infty^R dr$ of both parts we find:

$$-\left.\frac{\partial(r\phi_G)}{\partial r}\right|_0^R = -2q\pi\left(\frac{\alpha^2}{\pi}\right)^{3/2}\frac{1}{\alpha^2}\int_\infty^R e^{-\alpha^2 r^2}(-2r\alpha^2)dr \tag{11}$$

Using that $\partial\phi_G/\partial r(\infty) = 0$ and $2r\alpha^2 dr \equiv d(-\alpha^2 r^2)$ we have

$$\frac{\partial(R\phi_G)}{\partial r} = 2q\left(\frac{\alpha^2}{\pi}\right)^{1/2} e^{-\alpha^2 R^2} \tag{12}$$

Changing $r \to R$ and taking the integral $\int_0^R dr$ of both parts we have

$$R\phi_G(R) - 0\phi_G(0) = q\mathrm{erf}(\alpha R) \tag{13}$$

where $\mathrm{erf}(x) \equiv \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt$ is a Gauss error function. This gives the following potential:

$$\phi_G(\mathbf{r}) = \frac{q}{|\mathbf{r}|}\mathrm{erf}(\alpha|\mathbf{r}|) \tag{14}$$

3 Energy of the screened charges (real-part sum)

The potential of sum of charges is sum of the potentials of the single charges. For the single screened charge we have:

$$\rho_i^0(\mathbf{r}) = q_i\left(\delta(\mathbf{r}-\mathbf{r}_i) - \left(\frac{\alpha^2}{\pi}\right)^{3/2} e^{-\alpha^2(\mathbf{r}-\mathbf{r}_i)^2}\right) \tag{15}$$

The potential for this charge will be

$$\phi(\mathbf{r};\mathbf{r}_i,q_i) = \frac{q_i}{\mathbf{r}-\mathbf{r}_i} - \frac{q_i}{\mathbf{r}-\mathbf{r}_i}\mathrm{erf}(\alpha(\mathbf{r}-\mathbf{r}_i)) \equiv \frac{q_i}{\mathbf{r}-\mathbf{r}_i}\mathrm{erfc}(\alpha(\mathbf{r}-\mathbf{r}_i)) \tag{16}$$

Then the potential of all charges except the i-th one can be written as follows:

$$\phi_i^0(\mathbf{r}) \equiv \sum_{j\neq i} \psi(\mathbf{r};\mathbf{r}_j,q_j) + \sum_{\mathbf{n}\neq 0}\sum_j \psi(\mathbf{r};\mathbf{r}_j+\mathbf{n}\circ\mathbf{L},q_j) \tag{17}$$

$$= \sum_{j\neq i} \frac{q_j}{|\mathbf{r}-\mathbf{r}_j|}\mathrm{erfc}(\alpha(\mathbf{r}-\mathbf{r}_j)) + \sum_{\mathbf{n}\neq 0}\sum_j \frac{q_j}{|\mathbf{r}-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L}|}\mathrm{erfc}(\alpha(\mathbf{r}-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L})) \tag{18}$$

The energy of interaction of charges in the simulation box with this field can be written as follows:

$$U_0 \equiv \frac{1}{2}\sum_i q_i\phi_i^0(\mathbf{r}_i) = \frac{1}{2}\sum_i\sum_{j\neq i}\frac{q_iq_j}{r_{ij}}\mathrm{erfc}(\alpha r_{ij}) + \frac{1}{2}\sum_{\mathbf{n}\neq 0}\sum_i\sum_j \frac{q_iq_j}{|\mathbf{r}_i-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L}|}\mathrm{erfc}(\alpha(\mathbf{r}_i-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L})) \tag{19}$$

In principle, the sum is taken for infinite number of box replications $\mathbf{n} = (n_x, n_y, n_z)$ where $n_x, n_y, n_z = 0, 1\ldots\infty$. However, $\mathrm{erfc}(x)$ decays fast, so the sum can be truncated after some number of replications. For example, the sum can be taken only for $\mathbf{n}$ where $n_x^2+n_y^2+n_z^2 < n_{max}^2$ with n_{max}=3 or 4.

4 Interaction of the charges with gaussians (fourier space sum)

4.1 Basis set

Smooth functions, defined in volume $V = L_x \times L_y \times L_z$ can be represented in a Fourier form:

$$f(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{m}} \hat{f}(\mathbf{k_m})e^{i\mathbf{k_m r}} \tag{20}$$

where $\mathbf{m} \equiv (m_x, m_y, m_z) \in \mathbb{Z}^3$ and $\mathbf{k_m} \equiv (k^x_{\mathbf{m}}, k^y_{\mathbf{m}}, k^z_{\mathbf{m}}) \equiv \left(\frac{2\pi m_x}{L_x}, \frac{2\pi m_y}{L_y}, \frac{2\pi m_z}{L_z}\right)$

To prove it, we check that the system $\{e^{i\mathbf{k_m r}} : \mathbf{m} \in \mathbb{Z}^3, \mathbf{r} \in V\}$ is orthonormal with respect to the following scalar product:

$$\langle a(\mathbf{r}), b(\mathbf{r})\rangle \equiv \frac{1}{V}\int_V a(\mathbf{r})\overline{b(\mathbf{r})}d\mathbf{r} \tag{21}$$

where $\overline{x}$ means complex conjugation.

Indeed

$$\langle e^{i\mathbf{k_{m_1}}}, e^{i\mathbf{k_{m_2}}}\rangle = \frac{1}{V}\int_V e^{i(\mathbf{k_{m_1}}-\mathbf{k_{m_2}})\mathbf{r}}d\mathbf{r} = \tag{22}$$

$$\frac{1}{V}\int_0^{L_x} e^{i(k^x_{\mathbf{m_1}}-k^x_{\mathbf{m_2}})x}dx \int_0^{L_y} e^{i(k^y_{\mathbf{m_1}}-k^y_{\mathbf{m_2}})y}dy \int_0^{L_z} e^{i(k^z_{\mathbf{m_1}}-k^z_{\mathbf{m_2}})z}dz \tag{23}$$

Let's calculate the first multiplier. If $k^x_{\mathbf{m_1}} = k^x_{\mathbf{m_2}}$ we have $\int_0^{L_x} 1dx = L_x$. Otherwise

$$\int_0^{L_x} e^{i(k^x_{\mathbf{m_1}}-k^x_{\mathbf{m_2}})x}dx = \frac{1}{i(k^x_{\mathbf{m_1}}-k^x_{\mathbf{m_2}})}(e^{i(k^x_{\mathbf{m_1}}-k^x_{\mathbf{m_2}})L_x} - e^0) \tag{24}$$

Considering the definition of $k_{\mathbf{m}}$ we have:

$$e^{i(k^x_{\mathbf{m_1}}-k^x_{\mathbf{m_2}})L_x} = e^{\frac{2\pi i}{L_x}(m^x_1-m^x_2)L_x} = \cos(2\pi(m^x_1-m^x_2)) + i\sin(2\pi(m^x_1-m^x_2)) = 1 \tag{25}$$

Thus,

$$\int\limits_0^{L_x} e^{i(k^x_{\mathbf{m_1}}-k^x_{\mathbf{m_2}})x}dx = L_x\delta_{m^x_1,m^x_2} \tag{26}$$

And in general

$$\frac{1}{V}\int_V e^{i(\mathbf{k_{m_1}}-\mathbf{k_{m_2}})\mathbf{r}}d\mathbf{r} = \delta_{\mathbf{m_1 m_2}} \tag{27}$$

So, $\{e^{i\mathbf{k_m r}} : \mathbf{m}\in\mathbb{Z}^3, \mathbf{r}\in V\}$ is the basis in volume V.

4.2 Fourier representation of gaussian densities

We consider the Fourier representation of the gaussian density (6):

$$\rho_1(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{m}}\hat{\rho}_1(\mathbf{k_m})e^{i\mathbf{k_m r}} \tag{28}$$

To find a particular coefficient $\hat{\rho}_1(\mathbf{k_{m_0}})$ we can multiply both parts by $e^{-i\mathbf{k_{m_0}r}}$ and integrate over $\mathbf{r}$. Using the definition of scalar product we have:

$$\frac{1}{V}\int\rho_1(\mathbf{r})e^{-i\mathbf{k_{m_0}r}}d\mathbf{r} = \frac{1}{V}\sum_{\mathbf{m}}\hat{f}(\mathbf{k_m})\langle e^{i\mathbf{k_m}^2\mathbf{r}}, e^{i\mathbf{k_m r}}\rangle \tag{29}$$

Considering the orthonomality of the basis set (27) and equality

$$\sum_{\mathbf{m}}\hat{\rho}_1(\mathbf{k_m})\delta_{\mathbf{mm_0}} = \hat{\rho}_1(\mathbf{k_{m_0}}) \tag{30}$$

we have

$$\hat{\rho}_1(\mathbf{k_{m_0}}) = \int\rho_1(\mathbf{r})e^{-i\mathbf{k_{m_0}r}}d\mathbf{r} \tag{31}$$

Using the density (6) we have:

$$\rho_1(\mathbf{k_m}) = \int_V e^{-i\mathbf{k_m r}}\sum_{\mathbf{n}}\sum_j\left(\frac{\alpha^2}{\pi}\right)^{3/2}q_j e^{-\alpha^2(\mathbf{r}-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L})^2}d\mathbf{r} = \int_V\sum_{\mathbf{n}}\left(\frac{\alpha^2}{\pi}\right)^{3/2}e^{-i\mathbf{k_m r}}\sum_j q_j e^{-\alpha^2(\mathbf{r}-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L})^2}d\mathbf{r} \tag{32}$$

Changing the integration variable to $\mathbf{r}'$, such that $\mathbf{r}\equiv\mathbf{r}'+\mathbf{n}\circ\mathbf{L}$ we have $d\mathbf{r}=d\mathbf{r}'$, $\mathbf{r}-\mathbf{r}'-\mathbf{n}\circ\mathbf{L} = \mathbf{r}'-\mathbf{r_j}$, $\int_V d\mathbf{r} = \int_{V-\mathbf{n}\circ\mathbf{L}}d\mathbf{r}'$. This gives the following representation:

$$\hat{\rho}_1(\mathbf{k_m}) = \sum_{\mathbf{n}}\int_{V-\mathbf{n}\circ\mathbf{L}}\left(\frac{\alpha^2}{\pi}\right)^{3/2}e^{-i\mathbf{k_m r}'}e^{-i\mathbf{k_m}(\mathbf{n}\circ\mathbf{L})}\sum_j q_j e^{-\alpha^2(\mathbf{r}'-\mathbf{r}_j)^2}d\mathbf{r}' \tag{33}$$

Now, we can see, that $e^{-i\mathbf{k_m}(\mathbf{n}\circ\mathbf{L})} = 1$. Indeed,

$$e^{-i\mathbf{k_m}(\mathbf{n}\circ\mathbf{L})} = e^{-i\frac{2\pi m_x}{L_x}n_xL_x}e^{-i\frac{2\pi m_y}{L_y}n_yL_y}e^{-i\frac{2\pi m_z}{L_z}n_zL_z} \tag{34}$$

and $e^{-i2\pi mn} = \cos(2\pi mn) - i\sin(2\pi mn) = 1$

In that case the term under the integral does not depend on $\mathbf{n}$, and we can charge $\sum_{\mathbf{n}} \int_{V-\mathbf{n}\circ\mathbf{L}}$ to $\int_{\mathbb{R}^3}$:

$$\hat{\rho}_1(\mathbf{k_m}) = \sum_j q_j \left(\frac{\alpha^2}{\pi}\right)^{3/2} \int_{\mathbb{R}^3} e^{-i\mathbf{k_m}\mathbf{r}'} e^{-\alpha^2(\mathbf{r}'-\mathbf{r}_j)^2} d\mathbf{r}' \tag{35}$$

This in turn can be rewritten in a following form:

$$\hat{\rho}_1(\mathbf{k_m}) = \sum_j q_j \left(\frac{\alpha^2}{\pi}\right)^{3/2} \int_{\mathbb{R}^3} e^{-\alpha^2(\mathbf{r}'-\mathbf{r}_j)^2 - i\mathbf{k_m}(\mathbf{r}-\mathbf{r_j})} e^{-i\mathbf{k_m}\mathbf{r_j}} d(\mathbf{r}' - \mathbf{r_j}) = \sum_j q_j e^{-i\mathbf{k_m}\mathbf{r_j}} \hat{G}_\alpha(\mathbf{k_m}) \tag{36}$$

where

$$\hat{G}_\alpha(\mathbf{k_m}) = \left(\frac{\alpha^2}{\pi}\right)^{3/2} \int_{\mathbb{R}^3} e^{-\alpha^2\mathbf{r}^2} e^{-i\mathbf{k_m}\mathbf{r}} d\mathbf{r} \tag{37}$$

is a Fourier transformed Gaussian function. The three-dimensional transformation is product of 1-d transformations:

$$\hat{G}_\alpha(\mathbf{k_m}) = \left(\frac{\alpha^2}{\pi}\right)^{3/2} \int\limits_{-\infty}^{\infty} e^{-\alpha^2x^2} e^{-ik^x_{\mathbf{m}}x} dx \int\limits_{-\infty}^{\infty} e^{-\alpha^2y^2} e^{-ik^y_{\mathbf{m}}y} dy \int\limits_{-\infty}^{\infty} e^{-\alpha^2z^2} e^{-ik^z_{\mathbf{m}}z} dz \tag{38}$$

In the x direction we have:

$$\int\limits_{-\infty}^{\infty} e^{-\alpha^2x^2} e^{-ik^x_{\mathbf{m}}x} dx = \int\limits_{-\infty}^{\infty} e^{-\alpha^2(x^2 + 2\frac{ik^x_{\mathbf{m}}}{2\alpha^2}x + \frac{i^2(k^x_{\mathbf{m}})^2}{4\alpha^4}) + \alpha^2\frac{i^2(k^x_{\mathbf{m}})^2}{4\alpha^4}} dx \tag{39}$$

$$= e^{-\frac{(k^x_{\mathbf{m}})^2}{4\alpha^2}} \frac{1}{\alpha} \int\limits_{-\infty}^{\infty} e^{-\alpha^2(x+\frac{ik^x_{\mathbf{m}}}{2\alpha^2})^2} d\alpha(x - \frac{ik^x_{\mathbf{m}}}{2\alpha^2}) = e^{-\frac{(k^x_{\mathbf{m}})^2}{4\alpha^2}} \sqrt{\frac{\pi}{\alpha^2}} \tag{40}$$

where we used the Gaussian integral value: $\int_{-\infty}^{\infty} e^{-t^2} dt = \sqrt{\pi}$

This gives the following value for the Fourier transformed Gaussian:

$$\hat{G}_\alpha(\mathbf{k_m}) = e^{-\frac{(k^x_{\mathbf{m}})^2}{4\alpha^2}} e^{-\frac{(k^y_{\mathbf{m}})^2}{4\alpha^2}} e^{-\frac{(k^z_{\mathbf{m}})^2}{4\alpha^2}} = e^{-\frac{|\mathbf{k_m}|^2}{4\alpha^2}} \tag{41}$$

and

$$\hat{\rho}_1(\mathbf{k_m}) = \sum_j q_j e^{-i\mathbf{k_m}\mathbf{r_j}} e^{-\frac{|\mathbf{k_m}|^2}{4\alpha^2}} \tag{42}$$

4.3 Poisson equation in a Fourier space

Let's write the Fourier representations of charge and potential functions:

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{p}} \hat{\rho}(\mathbf{k_p}) e^{i\mathbf{k_p}\mathbf{r}} \tag{43}$$

$$\phi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{s}} \hat{\phi}(\mathbf{k_s}) e^{i\mathbf{k_s}\mathbf{r}} = \frac{1}{V} \sum_{s_x, s_y, s_z} \hat{\phi}(\mathbf{k_s}) e^{ik^x_{\mathbf{s}}x} e^{ik^y_{\mathbf{s}}y} e^{ik^z_{\mathbf{s}}z} \tag{44}$$

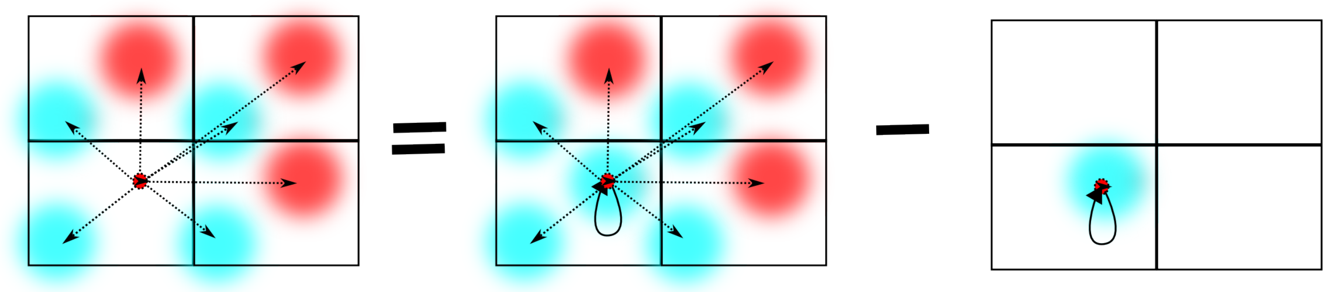

Figure 2: Potential acting on some specific charge can be represented as a difference of the total potential of all gaussians and self-interaction potential.

Laplacian operator ∇^2 can be rewritten as a sum:

$$\nabla^2\phi(\mathbf{r}) = \frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2} \tag{45}$$

Then, the x summand is

$$\frac{\partial^2}{\partial x^2}\sum_{s_x,s_y,s_z}\hat{\phi}(\mathbf{k_s})e^{ik_\mathbf{s}^x x}e^{ik_\mathbf{s}^y y}e^{ik_\mathbf{s}^z z} = \sum_{s_x,s_y,s_z} i^2(k_\mathbf{s}^x)^2)\hat{\phi}(\mathbf{k_s})e^{ik_\mathbf{s}^x x}e^{ik_\mathbf{s}^y y}e^{ik_\mathbf{s}^z z} \tag{46}$$

The derivatives over y and z are analogous. Thus, the expression for the Laplacian is:

$$\nabla^2\phi(\mathbf{r}) = \sum_{s_x,s_y,s_z} i^2((k_\mathbf{s}^x)^2 + (k_\mathbf{s}^y)^2 + (k_\mathbf{s}^z)^2)\hat{\phi}(\mathbf{k_s})e^{i\mathbf{k_s}\mathbf{r}} = -\sum_\mathbf{s}|\mathbf{k_s}|^2\hat{\phi}(\mathbf{k_s})e^{i\mathbf{k_s}\mathbf{r}} \tag{47}$$

Inserting this into the Poisson equation we have:

$$\sum_\mathbf{s}|\mathbf{k_s}|^2\hat{\phi}(\mathbf{k_s})e^{i\mathbf{k_s}\mathbf{r}} = 4\pi\sum_\mathbf{p}\hat{\rho}(\mathbf{k_p})e^{i\mathbf{k_p}\mathbf{r}} \tag{48}$$

Multiplying both parts by $e^{-i\mathbf{k_m}\mathbf{r}}$, integrating over V and using the orthogonality $1/V\int_V e^{-i\mathbf{k_p}\mathbf{r}}e^{-i\mathbf{k_m}\mathbf{r}}d\mathbf{r} = \delta_\mathbf{mp}$ we have:

$$|\mathbf{k_m}|^2\hat{\phi}(\mathbf{k_m}) = 4\pi\hat{\rho}(\mathbf{k_m}) \tag{49}$$

and

$$\hat{\phi}(\mathbf{k_m}) = \frac{4\pi}{|\mathbf{k_m}|^2}\hat{\rho}(\mathbf{k_m}) \tag{50}$$

4.4 Gaussian interaction energy

Now, we can compute the total potential $\phi^1_{tot}(\mathbf{r})$ of all gaussian densities. To do this, we insert the gaussian density representation in k-space (42) into the Poisson equation (50):

$$\hat{\phi}^1_{tot}(\mathbf{k_m}) = \frac{4\pi}{|\mathbf{k_m}|^2}\sum_j q_j e^{-i\mathbf{k_m}\mathbf{r_j}}e^{-\frac{|\mathbf{k_m}|^2}{4\alpha^2}} \tag{51}$$

which gives the following potential in $\mathbf{r}$-space:

$$\phi^1_{tot}(\mathbf{r}) = \frac{1}{V}\sum_\mathbf{m}\hat{\phi}^1_{tot}(\mathbf{k_m})e^{i\mathbf{k_m}\mathbf{r}} = \frac{1}{V}\hat{\phi}^1_{tot}(\mathbf{k}=0) + \frac{1}{V}\sum_{\mathbf{m}\neq 0}\frac{4\pi}{|\mathbf{k_m}|^2}\sum_j q_j e^{i\mathbf{k_m}(\mathbf{r}-\mathbf{r_j})}e^{-\frac{|\mathbf{k_m}|^2}{4\alpha^2}} \tag{52}$$

The value at $\mathbf{k} = 0$ should be computed separately. The case $\hat{\phi}^1_{tot}(\mathbf{k} = 0) = 0$ corresponds to the metallic media which surrounds the macroscopic simulation box.

The potential energy can be computed as follows:

$$U_1 = \frac{1}{2} \sum_s \phi^1_s(\mathbf{r}_s) q_s \tag{53}$$

where

$$\phi^1_s(\mathbf{r}_s) \equiv \phi^1_{tot}(\mathbf{r}_s) - \phi^s_G(\mathbf{r}_s) \tag{54}$$

is the potential, created by all the charges except the charge s, and $\phi^s_G(\mathbf{r}_s)$ is a "self-interaction" of point charge s with the gaussian which represents this charge (see Figure 2).

Potential of one gaussian was computed before (eq. (14)). We only shift it to the position $\mathbf{r_s}$

$$\phi^s_G(\mathbf{r}) = \frac{q_s}{|\mathbf{r} - \mathbf{r_s}|} \mathrm{erf}(\alpha |\mathbf{r} - \mathbf{r_s}|) \tag{55}$$

To compute the energy, we need the potential at point $\mathbf{r_s}$:

$$\phi^s_G(\mathbf{r_s}) = q_s \lim_{|\mathbf{r} - \mathbf{r_s}| \to 0} \frac{\mathrm{erf}(\alpha |\mathbf{r} - \mathbf{r_s}|)}{|\mathbf{r} - \mathbf{r_s}|} \tag{56}$$

Defining $R \equiv |\mathbf{r} - \mathbf{r_s}|$ and using the definition of erf function we can expand it into the Taylor series:

$$\mathrm{erf}(R) = \frac{2}{\sqrt{\pi}} \int_0^R e^{-t^2} dt = \frac{2}{\sqrt{\pi}} \int_0^R (1 - t^2 + \dots) dt = \frac{2}{\sqrt{\pi}} R + o(R^2) \tag{57}$$

This gives $\mathrm{erf}(\alpha R) \approx 2\sqrt{\frac{\alpha^2}{\pi}} R$ and

$$\phi^s_G(\mathbf{r_s}) = q_s \lim_{R \to 0} \frac{\mathrm{erf}(\alpha R)}{R} = 2 q_s \sqrt{\frac{\alpha^2}{\pi}} \tag{58}$$

Inserting this into expression for the potential energy (53) we have:

$$U_1 = \frac{1}{2} \sum_s \phi^1_{tot}(\mathbf{r}_s) q_s - \frac{1}{2} \sum_s \phi^s_G(\mathbf{r_s}) q_s \tag{59}$$

$$= \frac{1}{V} \hat{\phi}^1_{tot}(\mathbf{k} = \mathbf{0}) \frac{1}{2} \sum_s q_s + \frac{1}{2} \sum_{\mathbf{m} \neq 0} \frac{4\pi}{|\mathbf{k_m}|^2} \frac{1}{V} \sum_j \sum_s q_j q_s e^{i \mathbf{k_m} \mathbf{r}_{js}} e^{-\frac{|\mathbf{k_m}|^2}{4\alpha^2}} - \frac{1}{2} \sum_s 2 q_s^2 \sqrt{\frac{\alpha^2}{\pi}} \tag{60}$$

Assuming $\phi^1_{tot}(\mathbf{k} = 0) < \infty$, and adding this sum to the real-space sum (19)we have :

$$U = U_0 + U_1 = \tag{61}$$

$$\frac{1}{2V} \sum_{\mathbf{m} \neq 0} \frac{4\pi}{|\mathbf{k_m}|^2} \sum_j \sum_s q_j q_s e^{i \mathbf{k_m} \mathbf{r}_{js}} e^{-\frac{|\mathbf{k_m}|^2}{4\alpha^2}} - \sqrt{\frac{\alpha^2}{\pi}} \sum_s q_s^2 \tag{62}$$

$$+ \frac{1}{2} \sum_s \sum_{j \neq s} \frac{q_s q_j}{r_{sj}} \mathrm{erfc}(\alpha r_{sj}) + \frac{1}{2} \sum_{\mathbf{n} \neq 0} \sum_s \sum_j \frac{q_s q_j}{|\mathbf{r}_s - \mathbf{r}_j - \mathbf{n} \circ \mathbf{L}|} \mathrm{erfc}(\alpha (\mathbf{r}_s - \mathbf{r}_j - \mathbf{n} \circ \mathbf{L})) \tag{63}$$

Note, we can also change $e^{i \mathbf{k_m} \mathbf{r}_{js}}$ to $\cos(\mathbf{k_m} \mathbf{r}_{js})$ in the first summand, because $i \sin(\dots)$ is odd, and thus vanishes in sum of terms with $\mathbf{m}$ and $-\mathbf{m}$. This makes the sum consistent with Ref. [1].

5 Ewald Sums Generalization for $1/r^w$ potentials

5.1 Patterson function

With some modifications one can apply the Ewald technique not only to the $1/r$ Coulomb potentialsm but also to a general potentials $1/r^w$ for arbitrary m. In this section the methods given in [2] and [3] is described with small modifications.

So, let we need to calculate the Lattice energy

$$S = \frac{1}{2} \sum_{\substack{j,s,\mathbf{n} \\ \mathbf{r}_j \neq \mathbf{r}_s + \mathbf{n} \circ \mathbf{L}}} \frac{A_{js}}{|\mathbf{r}_j - \mathbf{r}_s + \mathbf{n} \circ \mathbf{L}|^w} \tag{64}$$

where $\mathbf{r}_j$, $\mathbf{r}_s$ are the particle positions, $\mathbf{L} \equiv (L_x, L_y, L_z)$ is the box size, $\mathbf{n} \equiv (n_x, n_y, n_z) \in \mathbb{Z}^3$ is the index of the box replica, $\mathbf{n} \circ \mathbf{L} = (n_x L_x, n_y L_y, n_z L_z)$ is the point-wise multiplication.

To avoid the sum divergence due to infinite singularities, we can rewrite the sum in a following way:

$$S = \frac{1}{2} \sum_{\substack{j,s,\mathbf{n} \\ r_{js;\mathbf{n}} \neq 0}} \frac{A_{js} \phi(r_{js;\mathbf{n}})}{r^w_{js;\mathbf{n}}} + \frac{1}{2} \sum_{\substack{j,s,\mathbf{n} \\ r_{js;\mathbf{n}} \neq 0}} \frac{A_{js}(1 - \phi(r_{js;\mathbf{n}}))}{r^w_{js;\mathbf{n}}} \tag{65}$$

where $r_{js;\mathbf{n}} \equiv |\mathbf{r}_j - \mathbf{r}_s + \mathbf{n} \circ \mathbf{L}|$, $\phi(r)$ is a smooth decaying function, such that $\phi(0) = 1$, $\phi(\infty) = 0$

The sum can be represented in the integral form. To do it, first let's assume that the space is descritized in such a way, that atoms can have only positions in the grid points. The number of grid points in the box of volume V is $N_x \times N_y \times N_z$. Increasing N_x, N_y, N_z we can locate atoms with any necessary accuracy, so this assumption is not a big limitation of generality.

Now, we consider the Patterson function

$$P(\mathbf{r}) = \frac{1}{V} \sum_{js} \sum_{m_x, m_y, m_z = 0}^{N_x, N_y, N_z} F_2(\mathbf{k}_\mathbf{m}) e^{i \mathbf{k}_\mathbf{m} \mathbf{r}} = \frac{1}{V} \sum_{js} A_{js} \sum_{m_x, m_y, m_z = 0}^{N_x, N_y, N_z} \exp(2\pi i (\mathbf{m} \div \mathbf{L}) \cdot (\mathbf{r} + \mathbf{r}_s - \mathbf{r}_j)) \tag{66}$$

where $\mathbf{m} \equiv (m_x, m_y, m_z)$, $\mathbf{L} \equiv (L_x, L_y, L_z)$,

$$F_2(\mathbf{k}_\mathbf{m}) = \sum_{js} A_{js} \exp(\mathbf{k}_\mathbf{m} (\mathbf{r}_s - \mathbf{r}_j)) \tag{67}$$

, $\mathbf{k}_\mathbf{m} \equiv 2\pi \mathbf{m} \div \mathbf{L}$, $\div$ is a point-wise division, i.e. $\mathbf{m} \div \mathbf{L} = (m_x/L_x, m_y/L_y, m_z/L_z)$. We consider the case when the particle positions are sticked to the grid points, i.e.

$$\mathbf{r} \equiv \mathbf{p} \circ \mathbf{L} \div \mathbf{N} \qquad \mathbf{r}_j \equiv \mathbf{p}_j \circ \mathbf{L} \div \mathbf{N} \tag{68}$$

where $\mathbf{p}, \mathbf{p}_j \in \mathbb{Z}^3$, $\mathbf{N} \equiv (N_x, N_y, N_z)$. Considering the case $N_x, N_y, N_z \to \infty$ we have

$$\frac{1}{N_x} \sum_{m_x = 0}^{N_x} \exp(2\pi i \frac{m_x}{L_x} \frac{p^x + p^x_s - p^x_j}{N_x} L_x) = \frac{1}{N_x} \sum_{m_x = 0}^{N_x} \exp(2\pi i \frac{m_x}{N_x} \Delta p^x) \tag{69}$$

where $\Delta p_x \equiv p^x + p^x_s - p^x_j$.

We consider the case $N_x \to \infty$. Then, there are two cases:

1. $\Delta p^x = n_x N_x$, $n_x \in \mathbb{Z}$

2. $\Delta p^x \neq n_x N_x$

In the first case we have

$$\exp(2\pi i \frac{m_x}{N_x} N_x M) = \exp(2\pi i m_x n_x) = 1 \tag{70}$$

and

$$N_x \frac{1}{N_x} \sum_{m_x=0}^{N_x} \exp(2\pi i \frac{m_x}{N_x} \Delta p^x) = N_x \tag{71}$$

In the second case if $N_x \to \infty$ the sum above can be rewritten in a terms of integral, i.e.:

$$N_x \frac{1}{N_x} \sum_{m_x=0}^{N_x} \exp(2\pi i \frac{m_x}{N_x} \Delta p^x) \to N_x \int_0^1 \exp(2\pi i t \Delta p^x) dt = \frac{N_x}{2\pi i \Delta p^x} (\exp(2\pi i \Delta p^x) - \exp(0)) = 0 \tag{72}$$

The first case is equivalent to the following:

$$\Delta p^x = p^x + p^x_s - p^x_j = n_x N_x \Rightarrow \frac{p^x + p^x_s - p^x_j}{N_x} L_x = x + x_s - x_j = n_x L_x \tag{73}$$

The same in three dimensions:

$$\mathbf{r} + \mathbf{r}_s - \mathbf{r}_j = \mathbf{n} \circ \mathbf{L} \tag{74}$$

Then, the two above cases can be summarized in a following formula:

$$\sum_{\mathbf{m}=0}^{\mathbf{N}} \exp(2\pi(\mathbf{m} \div \mathbf{L}) \cdot (\mathbf{r} + \mathbf{r}_s - \mathbf{r}_j) = N_x N_y N_z \sum_{\mathbf{n} \in \mathbb{Z}^3} \zeta(\mathbf{r} + \mathbf{r}_s - \mathbf{r}_j - \mathbf{n} \circ \mathbf{L}) \tag{75}$$

where $\zeta(\mathbf{r})$ for $\mathbf{r} \equiv \mathbf{p} \circ \mathbf{L} \div \mathbf{N}$ is defined in a following way:

$$\zeta(\mathbf{r}) = \zeta(\mathbf{p} \circ \mathbf{L} \div \mathbf{N}) = \delta_{p_x} \delta_{p_y} \delta_{p_z} \tag{76}$$

This gives the following expression for $P(r)$:

$$P(\mathbf{r}) = \frac{N_x N_y N_z}{V} \sum_{js} A_j s \sum_{\mathbf{n} \in \mathbb{Z}^3} \zeta(\mathbf{r} + \mathbf{r}_s - \mathbf{r}_j - \mathbf{n} \circ \mathbf{L}) \tag{77}$$

5.2 Integral representation

The sum (65) can be rewritten in a following form:

$$S = \frac{1}{2} \int_{\mathbb{R}^3} (P(\mathbf{r}) - \zeta(\mathbf{r}) P(\mathbf{r})) \frac{\phi(|\mathbf{r}|)}{|\mathbf{r}|^w} d\mathbf{r} + \frac{1}{2} \int_{\mathbb{R}^3} (P(\mathbf{r}) - \zeta(\mathbf{r}) P(\mathbf{r})) \frac{1 - \phi(|\mathbf{r}|)}{|\mathbf{r}|^w} d\mathbf{r} \tag{78}$$

where $\zeta(r) \equiv \delta(r)/\delta(0)$

Indeed

$$S = 1/2(\int \frac{P - \zeta P)\phi}{r^w} + \int \frac{(P - \zeta P)1}{r^w} - \int \frac{(P - \zeta P)1}{r^w}) = 1/2 \int \frac{P}{r^w} - 1/2 \int \frac{\zeta P}{r^w} \tag{79}$$

The first summand is

$$\frac{1}{2}\int \frac{P(\mathbf{r})}{|\mathbf{r}|^w}d\mathbf{r} = \frac{1}{2}\frac{N_xN_yN_z}{V}\sum_{js}\sum_{\mathbf{n}} A_{js}\int_{\mathbb{R}^3}\frac{\zeta(\mathbf{r}+\mathbf{r}_s-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L})}{|\mathbf{r}|^w} \tag{80}$$

We have the discrete grid in the real space. Thus, the integral over the whole space can be rewritten in a form of sum. In that case the number of grid points in the box of volume $V = L_xL_yL_z$ is $\mathbf{N} = (N_x, N_y, N_z)$, thus grid step is $V/N_xN_yN_z$. The sum then is rewritten as follows:

$$S = \frac{1}{2}\frac{N_xN_yN_z}{V}\sum_{js}\sum_{\mathbf{n}} A_{js}\sum_{\mathbf{p}=-\infty}^{\infty}\frac{\zeta(\mathbf{r}+\mathbf{r}_s-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L})}{|\mathbf{r}|^w}\frac{V}{N_xN_yN_z} = \frac{1}{2}\sum_{js}\sum_{\mathbf{n}}\frac{A_{js}}{|\mathbf{r}_j-\mathbf{r}_s+\mathbf{n}\circ\mathbf{L}|^w} \tag{81}$$

there the sum is taken over all j and s, including self interaction ($j = s$, $\mathbf{n} = 0$).

The second summand is responsible for the self-interactions:

$$\frac{1}{2}\int_{\mathbf{R}^3}\zeta(\mathbf{r})\frac{P(\mathbf{r})}{r^w}d\mathbf{r} = \frac{1}{2}\sum_{js}\sum_{\mathbf{n}}\frac{A_{js}}{|\mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}|^w}\zeta(\mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}) \tag{82}$$

Because all atoms are inside the box, $\zeta(\mathbf{r}_s - \mathbf{r}_j + \mathbf{n}\circ\mathbf{L})$ is non-zero only when $\mathbf{n} = 0$ and $s = j$. Thus, the second summand is

$$\frac{1}{2}\sum_{js}\sum_{\mathbf{n}}\frac{A_{js}}{|\mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}|^w}\delta_{js}\delta_{n_x}\delta_{n_y}\delta_{n_z} \tag{83}$$

Combining both summands we have

$$S = \frac{1}{2}\int_{\mathbb{R}^3}(P(\mathbf{r})-\zeta(\mathbf{r})P(\mathbf{r}))\frac{1}{|\mathbf{r}|^w}d\mathbf{r} = \frac{1}{2}\sum_{\substack{js\mathbf{n}\\ \mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}\neq 0}}\frac{A_{js}}{|\mathbf{r}_j-\mathbf{r}_s+\mathbf{n}\circ\mathbf{L}|^w} \tag{84}$$

5.3 Parseval theorem

As it was shown, the sum (65) can be splitted into several parts. Indeed, in expresion (65) we see that

$$S = S_1 + S_2 \tag{85}$$

where

$$S_1 = \sum_{\mathbf{n}}\sum_{\substack{js\\ \mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}\neq 0}}\frac{A_{sj}\phi(|\mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}|)}{|\mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}|^w} \tag{86}$$

$$S_2 = \sum_{\mathbf{n}}\sum_{\substack{js\\ \mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}\neq 0}}\frac{A_{sj}(1-\phi(|\mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}|))}{|\mathbf{r}_s-\mathbf{r}_j+\mathbf{n}\circ\mathbf{L}|^w} \tag{87}$$

The function $\phi(r)$ decays to zero, thus the sum S_1 can be computed directly in real space. The second sum S_2 can be represented using the Petterson function (66):

$$S_2 = \frac{1}{2}\int_{\mathbb{R}^3}(P(\mathbf{r})-\zeta(\mathbf{r})P(\mathbf{r}))\frac{1-\phi(\mathbf{r})}{|\mathbf{r}|^w}d\mathbf{r} = I_{21} - I_{22} \tag{88}$$

where

$$I_{21} = \frac{1}{2}\int_{\mathbb{R}^3} P(\mathbf{r})\frac{1-\phi(\mathbf{r})}{|\mathbf{r}|^w}d\mathbf{r} \tag{89}$$

$$I_{22} = \frac{1}{2}\int_{\mathbb{R}^3} \zeta(\mathbf{r})P(\mathbf{r})\frac{1-\phi(\mathbf{r})}{|\mathbf{r}|^w}d\mathbf{r} \tag{90}$$

The second integral I_{22} can be also calculated directly. In assumption of discrete particle positions and using the representation (77) we have

$$I_{22} = \frac{1}{2}\sum_{\mathbf{p}}\frac{N_xN_yN_z}{V}\sum_{js}A_{js}\zeta(\mathbf{p})\sum_{\mathbf{n}}\zeta(\mathbf{r}+\mathbf{r}_s-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L})\frac{1-\phi(\mathbf{r})}{|\mathbf{r}|^w}\frac{V}{N_xN_yN_z} \tag{91}$$

Again, $\zeta(\mathbf{r})\zeta(\mathbf{r}+\mathbf{r}_s-\mathbf{r}_j-\mathbf{n}\circ\mathbf{L}) = \delta_{sj}\delta_{n_x}\delta_{n_y}\delta_{n_z}$ which gives

$$I_{22} = \frac{1}{2}\sum_j A_{jj}\lim_{\mathbf{r}_s\to\mathbf{r}_j}\frac{1-\phi(|\mathbf{r}_s-\mathbf{r}_j|)}{|\mathbf{r}_s-\mathbf{r}_j|^w} \tag{92}$$

For the first integral I_{21} we can use the Parseval's theorem. Let's use the following definitions of the direct and inverse continous Fourier transformations:

$$FT_3[f(\mathbf{r})](\mathbf{h}) \equiv \tilde{f}(\mathbf{h}) = \int_{\mathbb{R}^3} f(\mathbf{r})\exp(2\pi i\mathbf{h}\cdot\mathbf{r})d\mathbf{r} \tag{93}$$

$$IFT_3[\tilde{f}(\mathbf{h})](\mathbf{r}) \equiv f(\mathbf{r}) = \int_{\mathbb{R}^3} \tilde{f}(\mathbf{h})\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})d\mathbf{h} \tag{94}$$

The reason, why we are using exactly these definitions is that the same definitions are used in Ref. [4], where results for the particular useful for us ϕ-functions are discussed.

Then Parseval's theorem can be written in a following way:

$$\int_{\mathbb{R}^3} f(\mathbf{r})\overline{g(\mathbf{r})}d\mathbf{r} = \int_{\mathbb{R}^3}\tilde{f}(\mathbf{h})\overline{\tilde{g}(\mathbf{h})}d\mathbf{h} \tag{95}$$

Indeed, using the definitions above

$$\int f(\mathbf{r})\overline{g(\mathbf{r})}d\mathbf{r} = \int d\mathbf{r}\int d\mathbf{h}_1\tilde{f}(\mathbf{h}_1)\exp(-2\pi\mathbf{h}_1\cdot\mathbf{r})\overline{\int d\mathbf{h}_2\tilde{g}(\mathbf{h}_2)\exp(-2\pi\mathbf{h}_2\cdot\mathbf{r})} \tag{96}$$

$$= \iint d\mathbf{h}_1 d\mathbf{h}_2\tilde{f}(\mathbf{h}_1)\overline{\tilde{g}(\mathbf{h}_2)}\int\exp(2\pi i(\mathbf{h}_2-\mathbf{h}_1)\cdot\mathbf{r})d\mathbf{r} \tag{97}$$

$$= \iint d\mathbf{h}_1 d\mathbf{h}_2\tilde{f}(\mathbf{h}_1)\overline{\tilde{g}(\mathbf{h}_2)}\delta(\mathbf{h}_2-\mathbf{h}_1) = \int\tilde{f}(\mathbf{h})\overline{\tilde{g}(\mathbf{h})}d\mathbf{h} \tag{98}$$

Using this relation for the integral I_{21} (89) we have

$$I_{21} = \int_{\mathbb{R}^3} P(\mathbf{r})\frac{1-\phi(|\mathbf{r}|}{|\mathbf{r}|^w}d\mathbf{r} = \int_{\mathbb{R}^3}\tilde{P}(\mathbf{h})FT_3\left[\frac{1-\phi(|\mathbf{r}|}{|\mathbf{r}|^w}\right](\mathbf{h})d\mathbf{h} \tag{99}$$

We can calculate the continuous Fourier transformation of the Petterson function $\tilde{P}(\mathbf{h})$. Using the definition (66) we have

$$\tilde{P}(\mathbf{h}) = \int_{\mathbb{R}^3} P(\mathbf{r})\exp(2\pi\mathbf{h}\cdot\mathbf{r})d\mathbf{r} \tag{100}$$

$$= \frac{1}{V} \sum_{js} A_{js} \sum_{\mathbf{m}} \int_{\mathbb{R}^3} \exp(2\pi i(\mathbf{m} \div \mathbf{L}) \cdot (\mathbf{r} + \mathbf{r}_s - \mathbf{r}_j)) \tag{101}$$

$$= \frac{1}{V} \sum_{js} A_{js} \sum_{\mathbf{m}} \exp(2\pi i(\mathbf{m} \div \mathbf{L}) \cdot (\mathbf{r}_s - \mathbf{r}_j)) \int_{\mathbb{R}^3} \exp(2\pi i((\mathbf{m} \div \mathbf{L}) + \mathbf{h}) \cdot \mathbf{r}) d\mathbf{r} \tag{102}$$

$$= \frac{1}{V} \sum_{js} A_{js} \sum_{\mathbf{m}} \delta((\mathbf{m} \div \mathbf{L}) + \mathbf{h}) \exp(2\pi i(\mathbf{m} \div \mathbf{L}) \cdot (\mathbf{r}_s - \mathbf{r}_j)) \tag{103}$$

We see, that the function is non-zero only in the Fourier points $\mathbf{h} = -(\mathbf{m} \div \mathbf{L})$, and also up to the δ factor is equal to the function F_2, defined previously (67).

5.4 Special choice of ϕ

5.4.1 Definition

In [4] and later in [2] it is proposed to use the following ϕ function:

$$\phi(r) = \frac{\Gamma(w/2, K^2 \pi r^2)}{\Gamma(w/2)} \tag{104}$$

where

$$\Gamma(w/2, a) \equiv \int_a^\infty t^{w/2-1} e^{-t} dt \tag{105}$$

$\Gamma(w/2) \equiv \Gamma(w/2, 0)$ is a Gamma function, and K is some constant. To be consistent with our previous definitions, we require that the following equality holds:

$$\alpha^2 = \pi K^2 \tag{106}$$

where α is a constant used in Ewald procedure. Thus, we can re-write the definition of ϕ:

$$\phi(r) = \frac{1}{\Gamma(w/2)} \int\limits_{\alpha^2 r^2}^{\infty} t^{w/2-1} e^{-t} dt \tag{107}$$

For $w = 1$ we have:

$$\Gamma(1/2, \alpha^2 r^2) = \int\limits_{\alpha^2 r^2}^{\infty} t^{-1/2} e^{-t} dt = 2 \int\limits_{\substack{t=\alpha^2 r^2 \\ \sqrt{t}=\alpha r}}^{\infty} e^{-(\sqrt{t})^2} \frac{dt}{2\sqrt{t}} = 2 \frac{\sqrt{\pi}}{2} \mathrm{erfc}(\alpha r) \tag{108}$$

From the same expression we find $\Gamma(1/2) = \sqrt{\pi}$ which gives

$$\phi(r) = \mathrm{erfc}(\alpha r) \tag{109}$$

5.4.2 Fourier part

Now we can use this function in our derivations. In Ref. [4], Appendix 3, the Fourier transformation of $(1-\phi(r))/r^w$ is given, and after that generalized for $K \neq 1$ in Ref. [2]:

$$FT_3\left[\frac{1-\phi(r)}{r^w}\right] = \frac{\pi^{w-3/2}h^{w-3}}{\Gamma(1/2)}\Gamma(-w/2+3/2, \frac{\pi h^2}{K^2}) \tag{110}$$

In our notation

$$\pi K^2 = \alpha^2 \Rightarrow K^2 = \frac{\alpha^2}{\pi} \Rightarrow \frac{\pi h^2}{K^2} = \frac{\pi h^2}{\alpha^2/\pi} = \frac{\pi^2 h^2}{\alpha^2} \tag{111}$$

Inserting (103) and (110) into (99) we have

$$I_{21} = \frac{1}{2V}\int_{\mathbb{R}^3}\sum_{js} A_{js}\sum_{\mathbf{m}}\delta((\mathbf{m}\div\mathbf{L})+\mathbf{h})\exp(2\pi i(\mathbf{m}\div\mathbf{L})\cdot(\mathbf{r}_s-\mathbf{r}_j))\frac{\pi^{w-3/2}h^{w-3}}{\Gamma(w/2)}\Gamma(-w/2+3/2, \frac{\pi^2 h^2}{\alpha^2})d\mathbf{h} \tag{112}$$

Using the properties of δ function this integral can be rewritten as a sum, with $\mathbf{h} = -\mathbf{m}\div\mathbf{L}$:

$$I_{21} = \frac{1}{2V}\frac{\pi^{w-3/2}}{\Gamma(w/2)}\sum_{\mathbf{m}} F_2(2\pi\mathbf{h}_\mathbf{m})|\mathbf{h}_\mathbf{m}|^{w-3}\Gamma(-w/2+3/2, \frac{\pi^2|\mathbf{h}_\mathbf{m}|^2}{\alpha^2}) \tag{113}$$

where $\mathbf{h}_\mathbf{m} \equiv \mathbf{m}\div\mathbf{L}$, $F_2(2\pi\mathbf{h}_\mathbf{m}) = \sum_{js} A_{js}\exp(2\pi i\mathbf{h}_\mathbf{m}\cdot(\mathbf{r}_s-\mathbf{r}_j))$ There is the special case $\mathbf{m}=0$. If $w \leq 3$, than the sum diverges in general case, and the condition $\sum_{sj} A_{sj} = 0$ required. For $w > 3$ in Ref. [2] the following expression is given (without the proofs or explanations):

$$\lim_{h\to 0} F_2(\mathbf{h})h^{w-3}\Gamma(-w/2+3/2, \frac{\pi h^2}{K^2}) = F_2(0)\pi^{3/2-w/2}K^{w-3}\frac{2}{w-3} \tag{114}$$

To prove this relation, we can use the following property of $\Gamma(z;b^2)$:

$$\Gamma(z+1;b^2) = \int_{b^2}^{\infty} t^z e^{-t}dt = t^z e^{-t^2}\Big|_{b^2}^{\infty} - z\int(-e^{-t})t^{z-1}dt = b^{2z}e^{-b^2} + z\Gamma(z;b^2) \tag{115}$$

Which gives the reccurent formula:

$$\Gamma(z;b^2) = \frac{1}{z}\Gamma(z+1;b^2) - \frac{1}{z}b^{2z}e^{-b^2} \tag{116}$$

$$= \frac{1}{z(z+1)}\Gamma(z+2;b^2) - \frac{1}{z(z+1)}b^{2(z+1)}e^{-b^2} - \frac{1}{z}b^{2z}e^{-b^2} \tag{117}$$

$$= \frac{1}{z(z+1)(z+2)}\Gamma(z+3;b^2) - \frac{1}{z(z+1)(z+2)}b^{2(z+2)}e^{-b^2} - \frac{1}{z(z+1)}b^{2(z+1)}e^{-b^2} - \frac{1}{z}b^{2z}e^{-b^2} \tag{118}$$

$$= ... \tag{119}$$

Applying this procedure M times we get the following representation

$$\Gamma(z;b^2) = \frac{\Gamma(z+M;b^2)}{z(z+1)...(z+M-1)} - e^{-b^2}\sum_{p=0}^{M-1}\frac{b^{2(z+p)}}{z(z+1)...(z+p)} \tag{120}$$

For $z = 3/2 - w/2$, $b^2 = \pi h^2/K^2$,$M > w/2$, we have

$$h^{w-3}\Gamma(z;b^2) = \frac{h^{w-3}\Gamma(\frac{3}{2} - \frac{w}{2} + M; b^2)}{z(z+1)...(z+M-1)} - e^{-b^2}\sum_{p=0}^{M-1}\frac{h^{w-3}\pi^{z+p}h^{2(z+p)}K^{-2(z+p)}}{z(z+1)...(z+p)} \tag{121}$$

Using that $2(z+p) = 3 - w + 2p$ we have

$$h^{w-3}\Gamma(z;b^2) = \frac{h^{w-3}\Gamma(\frac{3}{2} - \frac{w}{2} + M; b^2)}{z(z+1)...(z+M-1)} - e^{-b^2}\sum_{p=0}^{M-1}\frac{\pi^{3/2-w/2+p}K^{w-3-2p}}{z(z+1)...(z+p)}h^{2p} \tag{122}$$

Taking a limit $h \to 0$, $b \to 0$, we have

$$\Gamma(3/2 - w/2 + M; b^2) = \Gamma(3/2 - w/2 + M) < \infty \tag{123}$$

(because $3/2 - w/2 + M > 1$ and Γ behaves like factorial in this region), $h^{w-3} \to 0$, $h^{2p} \to 0$ when $p > 0$

The only non-zero term is a summand at $p = 0$:

$$h^{w-3}\Gamma(\frac{3}{2} - \frac{w}{2}; b^2) \to -\frac{e^0\pi^{3/2-w/2}K^{w-3}}{3/2 - w/2} = \frac{2}{w-3}\pi^{3/2-w/2}K^{w-3} \tag{124}$$

In that case, considering that $F_2(0) = \sum_{sj} A_{sj}$ and $K^{w-3} = (\alpha^2/\pi)^{0.5(w-3)}$ we have

$$F_2(0)\pi^{3/2-w/2}K^{w-3}\frac{2}{w-3} = \left(\sum_{sj} A_{sj}\right)\pi^{3/2-w/2}\frac{\alpha^{w-3}}{\pi^{w/2-3/2}}\frac{2}{w-3} \tag{125}$$

$$= \left(\sum_{sj} A_{sj}\right)\pi^{3-w}\alpha^{w-3}\frac{2}{w-3} \tag{126}$$

Then we can write I_{21} in a following way:

$$I_{21} = \frac{\pi^{w-3/2}}{2V\Gamma(w/2)}\left(\sum_{\mathbf{m}\neq 0} F_2(2\pi\mathbf{h_m})|\mathbf{h_m}|^{w-3}\Gamma(-w/2+3/2, \frac{\pi^2|\mathbf{h_m}|^2}{\alpha^2}) + \pi^{3-w}\alpha^{w-3}\frac{2}{w-3}\left(\sum_{sj} A_{sj}\right)\right) \tag{127}$$

$$= \frac{1}{2V\Gamma(w/2)}\left(\pi^{w-3/2}\sum_{\mathbf{m}\neq 0} F_2(2\pi\mathbf{h_m})|\mathbf{h_m}|^{w-3}\Gamma(-w/2+3/2, \frac{\pi^2|\mathbf{h_m}|^2}{\alpha^2}) + \pi^{3/2}\alpha^{w-3}\frac{2}{w-3}\left(\sum_{sj} A_{sj}\right)\right) \tag{128}$$

(Again, for $w < 3$ we have $\sum A_{sj} = 0$, and there are no second summand)

5.4.3 Real part

We can also calculate the real integral I_{22}, using the formula (92) and definition of ϕ given by (104). In this definitions we have

$$1 - \phi(r) = 1 - \frac{\Gamma(w/2, \alpha^2 r^2)}{\Gamma(w/2)} = \frac{1}{\Gamma(w/2)}\left(\Gamma(w/2) - \Gamma(w/2, \alpha^2 r^2)\right) \tag{129}$$

Using the definition of $\Gamma(w/2, a)$ we have

$$\Gamma(w/2) - \Gamma(w/2, \alpha^2 r^2) = \int_0^\infty t^{w/2-1} e^{-t} dt - \int_{\alpha^2 r^2}^\infty t^{w/2-1} e^{-t} dt = \int_0^{\alpha^2 r^2} t^{w/2-1} e^{-t} dt \tag{130}$$

Using this representation we have for I_{22} the following expression:

$$I_{22} = \frac{1}{2} \sum_j A_{jj} \lim_{r \to 0} \frac{1 - \phi(r)}{r^w} = \frac{1}{2\Gamma(w/2)} \left(\sum_j A_{jj} \right) \lim_{r \to 0} \frac{1}{r^w} \int_0^{\alpha^2 r^2} t^{w/2-1} e^{-t} dt \tag{131}$$

To find limiting value for the integral we can expand e^{-t} into the Taylor series, i.e.

$$\int_0^{\alpha^2 r^2} t^{w/2-1} e^{-t} dt = \int_0^{\alpha^2 r^2} t^{w/2-1} (1 - t + \ldots) dt = \int_0^{\alpha^2 r^2} t^{w/2-1} dt - \int_0^{\alpha^2 r^2} t^{w/2} dt + \ldots \tag{132}$$

$$= \frac{1}{w/2} t^{w/2} \Big|_0^{\alpha^2 r^2} - \frac{1}{w/2+1} t^{w/2+1} \Big|_0^{\alpha^2 r^2} + \ldots = \frac{2}{w} \alpha^w r^w - \frac{1}{w/2} \alpha^{w+2} r^{w+2} + \ldots \tag{133}$$

This representation gives

$$\frac{1}{r^w} \int_0^{\alpha^2 r^2} t^{w/2-1} e^{-t} dt = \frac{2}{w} \alpha^w + O(r^2) \tag{134}$$

Inserting this into (131) gives

$$I_{22} = \frac{1}{2\Gamma(w/2)} \left(\sum_j A_{jj} \right) \frac{2\alpha^w}{w} \tag{135}$$

5.4.4 Final expression

Using the ϕ function definition (104) we can also write the real-space sum S_1:

$$S_1 = \frac{1}{2\Gamma(w/2)} \sum_{\mathbf{n}} \sum_{\substack{sj \\ \mathbf{r}_{sj;\mathbf{n}} \neq 0}} A_{sj} \frac{\Gamma(w/2, \alpha^2 |\mathbf{r}_{sj;\mathbf{n}}|^2)}{|\mathbf{r}_{sj;\mathbf{n}}|^w} \tag{136}$$

where $\mathbf{r}_{sj;\mathbf{n}} \equiv \mathbf{r}_s - \mathbf{r}_j + \mathbf{n} \circ \mathbf{L}$.

Combining now all the summands we can write the final expression for the latice sum:

$$S = S_1 + I_{21} - I_{22} = \tag{137}$$

$$\frac{1}{2\Gamma(w/2)} \left(\sum_{\mathbf{n}} \sum_{\substack{sj \\ \mathbf{r}_{sj;\mathbf{n}} \neq 0}} A_{sj} \frac{\Gamma(w/2, \alpha^2 |\mathbf{r}_{sj;\mathbf{n}}|^2)}{|\mathbf{r}_{sj;\mathbf{n}}|^w} \right. \tag{138}$$

$$+ \frac{\pi^{w-3/2}}{V} \sum_{\mathbf{m} \neq 0} F_2(2\pi \mathbf{h}_{\mathbf{m}}) |\mathbf{h}_{\mathbf{m}}|^{w-3} \Gamma(-w/2 + 3/2, \frac{\pi^2 |\mathbf{h}_{\mathbf{m}}|^2}{\alpha^2}) \tag{139}$$

$$\left. + \frac{\pi^{3/2} \alpha^{w-3}}{V} \frac{2}{w-3} \left(\sum_{sj} A_{sj} \right) - \left(\sum_j A_{jj} \right) \frac{2\alpha^w}{w} \right) \tag{140}$$

For $\alpha^2 = \pi K^2$, $A_{sj} = q_s q_j$ this sum is the same as the result in Ref. [2]

6 Particular cases

6.1 w=1: electrostatic interaction

For $w = 1$ we have

$$\phi(r) = \frac{\Gamma(1/2; \alpha^2 r^2)}{\Gamma(1/2)} = \mathrm{erfc}(\alpha r) \tag{141}$$

$$\Gamma(1/2) = \sqrt{\pi} \tag{142}$$

(see (108), (109) for the derivation).

$$\Gamma(-w/2 + 3/2; b^2) = \Gamma(1; b^2) = \int_{b^2}^{\infty} e^{-t} dt = e^{-b^2} \tag{143}$$

Also, in case of electrostatic interaction we have

$$A_{sj} = q_s q_j \tag{144}$$

$$\sum_{sj} A_{sj} = \left(\sum_j q_j \right)^2 = 0 \tag{145}$$

$$\sum_j A_{jj} = \sum_j q_j^2 \tag{146}$$

$$F_2(2\pi \mathbf{h_m}) = \sum_{sj} q_s q_j e^{2\pi i \mathbf{h_m}(\mathbf{r}_s - \mathbf{r}_j)} = \left(\sum_j q_j e^{-2\pi i \mathbf{h_m} \mathbf{r}_j} \right) \left(\sum_s q_s e^{2\pi i \mathbf{h_m} \mathbf{r}_s} \right) = F(\mathbf{k_m}) F(-\mathbf{k_m}) = |F(\mathbf{k_m})|^2 \tag{147}$$

where

$$F(\mathbf{k_m}) \equiv F(2\pi \mathbf{h_m}) = \sum_j q_j e^{-2\pi i \mathbf{h_m} \mathbf{r}_j} \tag{148}$$

Inserting this into the general expression for S (137) we have

$$S = \frac{1}{2\sqrt{\pi}} \left(\sum_{\mathbf{n}} \sum_{\substack{sj \\ \mathbf{r}_{sj;\mathbf{n}} \neq 0}} q_s q_j \frac{\sqrt{\pi} \mathrm{erfc}(\alpha |\mathbf{r}_{sj;\mathbf{n}}|)}{|\mathbf{r}_{sj;\mathbf{n}}|} \right. \tag{149}$$

$$+ \frac{\pi^{-1/2}}{V} \sum_{\mathbf{m} \neq 0} |F(\mathbf{k_m})|^2 |\mathbf{h_m}|^{-2} e^{\frac{-\pi^2 |\mathbf{h_m}|^2}{\alpha^2}} \tag{150}$$

$$\left. -2\alpha \left(\sum_j q_j^2 \right) \right) \tag{151}$$

Using the definitions $\mathbf{k_m} \equiv 2\pi \mathbf{h_m}$, $F(\mathbf{k_m}) \equiv \hat{\rho}(\mathbf{k_m})$, we have

$$|\mathbf{h_m}|^{-2} = \frac{1}{|\mathbf{k_m}|^2 / 4\pi^2} = \frac{4\pi^2}{|\mathbf{k_m}|^2} \tag{152}$$

$$\frac{\pi^2 |\mathbf{h_m}|^2}{\alpha^2} = \frac{\pi^2 |\mathbf{k_m}|^2 / 4\pi^2}{\alpha^2} = \frac{|\mathbf{k_m}|^2}{4\alpha^2} \tag{153}$$

So, we have

$$S = \frac{1}{2}\sum_{\mathbf{n}}\sum_{\substack{sj\\ \mathbf{r}_{sj;\mathbf{n}}\neq 0}} q_s q_j \frac{\mathrm{erfc}(\alpha|\mathbf{r}_{sj;\mathbf{n}}|)}{|\mathbf{r}_{sj;\mathbf{n}}|} \quad + \quad \frac{1}{2V}\sum_{\mathbf{m}\neq 0}|\hat{\rho}(\mathbf{k_m})|^2\frac{4\pi}{|\mathbf{k_m}|^2}e^{\frac{-|\mathbf{k_m}|^2}{4\alpha^2}} \quad - \quad \sqrt{\frac{\alpha^2}{\pi}}\sum_j q_j^2 \tag{154}$$

which is the same as the usual Ewald sum (61) with the Fourier component computed as (216).

6.2 Lennard-Jones interaction

6.2.1 General case: w=2k+2

The Lennard-Jones potential between the particles s and j in a general case can be defined as

$$U_{sj}(r) = 4\epsilon_{sj}\left(\left(\frac{\sigma_{sj}}{r}\right)^{12} - \left(\frac{\sigma_{sj}}{r}\right)^{6}\right) = \frac{4\epsilon_{sj}\sigma_{sj}^{12}}{r^{12}} - \frac{4\epsilon_{sj}\sigma_{sj}^{6}}{r^{6}} = \frac{A_{sj}}{r^{12}} - \frac{B_{sj}}{r^6} \tag{155}$$

To calculate Ewald sums for the potentials $1/r^6$ and $1/r^{12}$ we can start from the more general case $w = 2k+2$ where $k \in \mathbb{Z}_+$. To compute the sum (137) we need to know the values of two functions:

$$\Phi_w(a) = \frac{\Gamma(\frac{w}{2}; a^2)}{\Gamma(\frac{w}{2})} = \frac{\Gamma(k+1; a^2)}{\Gamma(k+1)} \tag{156}$$

$$\Psi_w(b) = \frac{\Gamma(-\frac{w}{2}+\frac{3}{2}; b^2)}{\Gamma(\frac{w}{2})} = \frac{\Gamma(-k+\frac{1}{2}; b^2)}{\Gamma(k+1)} \tag{157}$$

For the Γ function there is a known relation which allows to calculate its values:

$$\Gamma(x+1) = x\Gamma(x) \tag{158}$$

In particular, $\Gamma(k+1) = k!$. We can find the same relation for the function $\Gamma(z; a^2)$. To do it, we use integration by parts:

$$\Gamma(z+1; a^2) = \int_{a^2}^{\infty} t^z e^{-t}dt = -t^z e^{-t}\Big|_{a^2}^{\infty} - z\int_{a^2}^{\infty} -e^{-t}t^{z-1}dt = a^{2z}e^{-a^2} + z\Gamma(z; a^2) \tag{159}$$

Using this relation, we can calulate some particular values of $\Gamma(z, a^2)$. For example:

k=z=0, w=2: $\Gamma(1; a^2) = \int_{a^2}^{\infty} e^{-t}dt = e^{-a^2}$

k=z=1, w=4: $\Gamma(2; a^2) = a^2e^{-a^2} + e^{-a^2} = e^{-a^2}(1+a^2)$

k=z=2, w=6: $\Gamma(3; a^2) = a^4e^{-a^2} + 2e^{-a^2}(1+a^2) = e^{-a^2}(2+2a^2+a^4)$

In the general case

$$\Gamma(\frac{w}{2}, a^2) = \Gamma(k+1; a^2) = a^{2k}e^{-a^2} + k\Gamma(k; a^2) \tag{160}$$

$$= a^{2k}e^{-a^2} + k\cdot\Big(a^{2k-2}e^{-a^2} + (k-1)\Gamma(k-1; a^2)\Big) = ... \tag{161}$$

$$= a^{2k}e^{-a^2} + ka^{2k-2}e^{-a^2} + k(k-1)a^{2k-4}e^{-a^2} + ... + k!e^{-a^2} \tag{162}$$

This gives the following expression for $\phi(k+1;a^2)$:

$$\Phi_w(a) = \frac{\Gamma(k+1;a^2)}{\Gamma(k+1)} = e^{-a^2}\left(\frac{a^{2k}}{k!} + \frac{a^{2(k-1)}}{(k-1)!} + ... + \frac{a^2}{1!} + 1\right) = e^{-a^2}\sum_{p=0}^{k}\frac{a^{2p}}{p!} \tag{163}$$

We can also rewrite (159) from right to left, i.e.:

$$\Gamma(z;b^2) = \frac{1}{z}\left(\Gamma(z+1;b^2) - b^{2z}e^{-b^2}\right) \tag{164}$$

Changing $z \to z-1$ we have

$$\Gamma(z-1;b^2) = \frac{1}{z-1}\left(\Gamma(z;b^2) - b^{2z-2}e^{-b^2}\right) \tag{165}$$

This relation allows us to calculate the values of $\Gamma(-\frac{w}{2}+\frac{3}{2};b^2) = \Gamma(-k-1+3/2;b^2)$ For a given k argument is $3/2-k-1 = z-1$ which gives $z = 3/2-k$ Thus, we have

$$\Gamma(3/2-k-1;b^2) = \Gamma(1/2-k;b^2) = \frac{1}{1/2-k}(\Gamma(3/2-k;b^2) - b^{1-2k}e^{-b^2}) \tag{166}$$

$$\begin{array}{ll}
k=0,\ z=3/2,\ w=2: & \Gamma(1/2-k;b^2) = \Gamma(1/2;b^2) = \sqrt{\pi}\mathrm{erfc}(b) \\
k=1,\ z=1/2,\ w=4: & \begin{array}{l}\Gamma(1/2-1;b^2) = \frac{1}{-1/2}(\sqrt{\pi}\mathrm{erfc}(b) - b^{-1}e^{-b^2}) \\ = -2\sqrt{\pi}\mathrm{erfc}(b) + 2b^{-1}e^{-b^2}\end{array} \\
k=2,\ z=-1/2,\ w=6: & \begin{array}{l}\Gamma(1/2-2;b^2) = \frac{1}{-3/2}(-2\sqrt{\pi}\mathrm{erfc}(b) + 2b^{-1}e^{-b^2} - b^{-3}e^{-b^2}) \\ = \frac{4}{3}\sqrt{\pi}\mathrm{erfc}(b) - \frac{4}{3}b^{-1}e^{-b^2} + \frac{2}{3}b^{-3}e^{-b^2}\end{array}
\end{array}$$

We can also derive a general formula. We can do it step-by-step.

$$\Gamma(3/2-w/2;b^2) = \Gamma(3/2-k-1;b^2) = \Gamma(1/2-k;b^2) \tag{167}$$

$$= \frac{1}{1/2-k}\left(\Gamma(1/2-k+1;b^2) - b^{1-2k}e^{-b^2}\right) \tag{168}$$

$$= \frac{2}{1-2k}\Gamma(1/2-k+1;b^2) - \frac{2}{1-2k}b^{1-2k}e^{-b^2} \tag{169}$$

Recoursively changing $\Gamma(1/2-k+1;b^2)$ to its representation we have:

$$\Gamma(3/2-w/2;b^2) = \tag{170}$$

$$= \frac{2}{(1-2k)}\frac{1}{(3/2-k)}\Gamma(1/2-k+2;b^2) - \frac{2}{(1-2k)}\frac{1}{3/2-k}b^{3-2k}e^{-b^2} - \frac{2}{1-2k}b^{1-2k}e^{-b^2} \tag{171}$$

$$= \frac{2}{(1-2k)}\frac{2}{(3-2k)}\Gamma(1/2-k+2;b^2) - \frac{2}{(1-2k)}\frac{2}{(3-2k)}b^{3-2k}e^{-b^2} - \frac{2}{1-2k}b^{1-2k}e^{-b^2} \tag{172}$$

Doing this k times we come to $\Gamma(1/2-k+k;b^2) = \Gamma(1/2;b^2) = \sqrt{\pi}\mathrm{erfc}(b)$. So, we have the following formula:

$$\Gamma(3/2-w/2;b^2) = \tag{173}$$

$$= \frac{2}{(1-2k)} \frac{2}{(3-2k)} \cdots \frac{2}{(2k-1-2k)} \sqrt{\pi}\mathrm{erfc}(b) \tag{174}$$

$$- \frac{2}{(1-2k)} \frac{2}{(3-2k)} \cdots \frac{2}{(2k-1-2k)} b^{-1} e^{-b^2} \tag{175}$$

$$- \frac{2}{(1-2k)} \frac{2}{(3-2k)} \cdots \frac{2}{(2k-3-2k)} b^{-3} e^{-b^2} \tag{176}$$

$$- \frac{2}{(1-2k)} \frac{2}{(3-2k)} \cdots \frac{2}{(2k-5-2k)} b^{-5} e^{-b^2} \tag{177}$$

$$-... \tag{178}$$

$$- \frac{2}{(1-2k)} \frac{2}{(3-2k)} b^{3-2k} e^{-b^2} \tag{179}$$

$$- \frac{2}{(1-2k)} b^{1-2k} e^{-b^2} \tag{180}$$

Above equations can be rewritten using the following notation:

$$\Gamma(3/2 - w/2; b^2) = \tag{181}$$

$$= (-2)^k \frac{1}{(2k-1)!!} \left(\sqrt{\pi}\mathrm{erfc}(b) - b^{-1} e^{-b^2} \right) \tag{182}$$

$$-(-2)^{k-1} \frac{1!!}{(2k-1)!!} b^{-3} e^{-b^2} \tag{183}$$

$$-(-2)^{k-2} \frac{3!!}{(2k-1)!!} b^{-5} e^{-b^2} \tag{184}$$

$$-... \tag{185}$$

$$-(-2)^2 \frac{(2k-5)!!}{(2k-1)!!} b^{3-2k} e^{-b^2} \tag{186}$$

$$-(-2) \frac{(2k-3)!!}{(2k-1)!!} b^{1-2k} e^{-b^2} \tag{187}$$

where $(2m-1)!! \equiv 1 \cdot 3 \cdot 5 \cdot \cdots \cdot (2m-1)$. This gives the following final formula (for $w \geq 4$, $k \geq 1$):

$$\Gamma(\frac{3}{2} - \frac{w}{2}; b^2) = \frac{1}{(2k-1)!!} \left((-2)^k \left(\sqrt{\pi}\mathrm{erfc}(b) - b^{-1} e^{-b^2} \right) - e^{-b^2} \sum_{p=1}^{k-1} (-2)^{k-p} (2p-1)!! b^{-2p-1} \right) \tag{188}$$

6.2.2 Case $w = 6$

Using the general formulae (163) and (188) for the case $w = 6$ we have:

$$\Gamma(\frac{w}{2}; a^2) = e^{-a^2}\left(2 + 2a^2 + a^4\right) \tag{189}$$

$$\Gamma(\frac{3}{2} - \frac{w}{2}; b^2) = \frac{4}{3}\sqrt{\pi}\mathrm{erfc}(b) + \left(-\frac{4}{3}b^{-1} + \frac{2}{3}b^{-3}\right) e^{-b^2} \tag{190}$$

$$\Gamma(\frac{w}{2}) = \Gamma(3) = 2! = 2 \tag{191}$$

Inserting these values to the (137) we have

$$S = \frac{1}{4}\left(\sum_{\mathbf{n}} \sum_{\substack{sj \\ \mathbf{r}_{sj;\mathbf{n}} \neq 0}} A_{sj} \frac{\exp(-a^2)}{|\mathbf{r}_{sj;\mathbf{n}}|^6}\left(2 + 2a^2 + a^4\right)\right. \tag{192}$$

$$+\frac{\pi^{9/2}}{V}\sum_{\mathbf{m}\neq 0} F_2(2\pi\mathbf{h_m})|\mathbf{h_m}|^3\left(\frac{4}{3}\sqrt{\pi}\mathrm{erfc}(b) + \left(-\frac{4}{3}b^{-1} + \frac{2}{3}b^{-3}\right) e^{-b^2}\right) \tag{193}$$

$$\left.+\frac{\pi^{3/2}\alpha^3}{V}\frac{2}{3}\left(\sum_{sj} A_{sj}\right) - \left(\sum_{j} A_{jj}\right)\frac{2\alpha^6}{6}\right) \tag{194}$$

where $a^2 \equiv \alpha^2 r^2_{sj;\mathbf{n}}$, $b^2 \equiv \pi^2 |\mathbf{h_m}|^2/\alpha^2$.

After opening the brackets:

$$S = \frac{1}{2}\sum_{\substack{\mathbf{n}sj \\ \mathbf{r}_{sj;\mathbf{n}} \neq 0}} A_{sj}\frac{\exp(-a^2)}{|\mathbf{r}_{sj;\mathbf{n}}|^6}\left(1 + a^2 + \frac{1}{2}a^4\right) \tag{195}$$

$$+\frac{\pi^{9/2}}{3V}\sum_{\mathbf{m}\neq 0} F_2(2\pi\mathbf{h_m})|\mathbf{h_m}|^3\left(\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b}\right) e^{-b^2}\right) \tag{196}$$

$$+\frac{1}{6}\frac{\pi^{3/2}\alpha^3}{V}\left(\sum_{sj} A_{sj}\right) - \frac{\alpha^6}{12}\left(\sum_{j} A_{jj}\right) \tag{197}$$

This expression is the same as the result in [2], up to subtitution $\alpha^2 \to \pi K^2$, $A_{sj} \to q_s q_j$.

If we use the definition of $a^2 = \alpha^2 r^2_{sj;\mathbf{n}}$, we have $r^6_{sj;\mathbf{n}} = a^6/\alpha^6$. Also, we can use that $\mathbf{h_m} = \mathbf{k_m}/2\pi$, and $h^3_m = k^3_m/8\pi^3$. In that case the sum can be written as follows

$$S = \frac{\alpha^6}{2}\sum_{\substack{\mathbf{n}sj \\ \mathbf{r}_{sj;\mathbf{n}} \neq 0}} A_{sj}\left(a^{-6} + a^{-4} + \frac{1}{2}a^{-2}\right) e^{-a^2} \tag{198}$$

$$+\frac{\pi^{3/2}}{24V}\sum_{\mathbf{m}\neq 0} F_2(\mathbf{k_m})|\mathbf{k_m}|^3\left(\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b}\right) e^{-b^2}\right) \tag{199}$$

$$+\frac{1}{6}\frac{\pi^{3/2}\alpha^3}{V}\left(\sum_{sj} A_{sj}\right) - \frac{\alpha^6}{12}\left(\sum_{j} A_{jj}\right) \tag{200}$$

In this representation the sum is the same that eq. (24) in Ref. [3], up to subtitution $\alpha \to 1/\eta$, $A_{sj} \to B_{sj}$, $V \to \Omega$, $\mathbf{k_m} \to \mathbf{h}$.

6.2.3 Case $w = 12$

Using the general formulae (163) and (188) for the case $w = 12$ we have:

$$\Gamma(\frac{w}{2}; a^2) = \left(a^{10} + 5a^8 + 20a^6 + 60a^4 + 120a^2 + 120\right) e^{-a^2} \tag{201}$$

$$\Gamma(\frac{3}{2} - \frac{w}{2}; b^2) = -\frac{32}{945}\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{32}{945}b^{-1} - \frac{16}{945}b^{-3} + \frac{8}{315}b^{-5} - \frac{4}{63}b^{-7} + \frac{2}{9}b^{-9}\right) e^{-b^2} \tag{202}$$

$$= \frac{2}{945}\left(-16\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{16}{b} - \frac{8}{b^3} + \frac{12}{b^5} - \frac{30}{b^7} + \frac{105}{b^9}\right) e^{-b^2}\right) \tag{203}$$

$$\Gamma(\frac{w}{2}) = \Gamma(6) = 5! = 120 \tag{204}$$

Inserting these values into (137) we get

$$S = \frac{1}{240}\left(\sum_{\substack{\mathbf{n}sj \\ \mathbf{r}_{sj;\mathbf{n}}\neq 0}} A_{sj}\frac{e^{-a^2}}{r^{12}_{sj;\mathbf{n}}}\left(a^{10} + 5a^8 + 20a^6 + 60a^4 + 120a^2 + 120\right)\right. \tag{205}$$

$$+\frac{2}{945}\frac{\pi^{10.5}}{V}\sum_{\mathbf{m}\neq 0} F_2(2\pi\mathbf{h_m})|\mathbf{h_m}|^9\left(-16\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{16}{b} - \frac{8}{b^3} + \frac{12}{b^5} - \frac{30}{b^7} + \frac{105}{b^9}\right) e^{-b^2}\right) \tag{206}$$

$$\left.+\frac{\pi^{3/2}\alpha^9}{V}\frac{2}{9}\left(\sum_{sj} A_{sj}\right) - \left(\sum_{j} A_{jj}\right)\frac{2\alpha^{12}}{12}\right) \tag{207}$$

Opening the brackets

$$S = \frac{1}{2}\sum_{\substack{\mathbf{n}sj \\ \mathbf{r}_{sj;\mathbf{n}}\neq 0}} A_{sj}\frac{e^{-a^2}}{r^{12}_{sj;\mathbf{n}}}\left(\frac{a^{10}}{120} + \frac{a^8}{24} + \frac{a^6}{6} + \frac{a^4}{2} + a^2 + 1\right) \tag{208}$$

$$+\frac{1}{945\cdot 120}\frac{\pi^{10.5}}{V}\sum_{\mathbf{m}\neq 0} F_2(2\pi\mathbf{h_m})|\mathbf{h_m}|^9\left(-16\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{16}{b} - \frac{8}{b^3} + \frac{12}{b^5} - \frac{30}{b^7} + \frac{105}{b^9}\right) e^{-b^2}\right) \tag{209}$$

$$+\frac{\pi^{3/2}\alpha^9}{1080V}\left(\sum_{sj} A_{sj}\right) - \frac{\alpha^{12}}{1440}\left(\sum_{j} A_{jj}\right) \tag{210}$$

Using that $r^{12}_{sj;\mathbf{n}} = a^{12}/\alpha^{12}$ and $h^9_m = k^9_m/512\pi^9$ we can rewrite the expression above as follows:

$$S = \frac{\alpha^{12}}{2}\sum_{\substack{\mathbf{n}sj \\ \mathbf{r}_{sj;\mathbf{n}}\neq 0}} A_{sj}\left(\frac{a^{-2}}{120} + \frac{a^{-4}}{24} + \frac{a^{-6}}{6} + \frac{a^{-8}}{2} + a^{-10} + 1\right) e^{-a^2} \tag{211}$$

$$+\frac{1}{945\cdot 120\cdot 512}\frac{\pi^{3/2}}{V}\sum_{\mathbf{m}\neq 0} F_2(\mathbf{k_m})|\mathbf{k_m}|^9\left(-16\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{16}{b} - \frac{8}{b^3} + \frac{12}{b^5} - \frac{30}{b^7} + \frac{105}{b^9}\right) e^{-b^2}\right) \tag{212}$$

$$+\frac{\pi^{3/2}\alpha^9}{1080V}\left(\sum_{sj} A_{sj}\right) - \frac{\alpha^{12}}{1440}\left(\sum_{j} A_{jj}\right) \tag{213}$$

7 Numerical aspects

7.1 Representation of the Fourier-space sum

7.1.1 w=1

To compute the fourier-space sum

$$U_{fourier} = \frac{1}{2V} \sum_{\mathbf{k_m} \neq 0} \frac{4\pi}{|\mathbf{k_m}|^2} \sum_{js} q_j q_s e^{i\mathbf{k_m}\cdot(\mathbf{r}_j - \mathbf{r}_i)} e^{\frac{-|\mathbf{k_m}|^2}{4\alpha^2}} \tag{214}$$

we use that for point charges $\rho(\mathbf{r}) = \sum_j q_j \delta(\mathbf{r}_j)$ and $\hat{\rho}(\mathbf{k_m}) = \sum_j q_j e^{i\mathbf{k_m}\mathbf{r}_j}$
Then

$$|\hat{\rho}(\mathbf{k_m})|^2 \equiv \hat{\rho}(\mathbf{k_m})\hat{\rho}(-\mathbf{k_m}) = \sum_{js} q_j q_s e^{i\mathbf{k_m}(\mathbf{r}_j - \mathbf{r}_s)} \tag{215}$$

and one can rewrite the k-space sum in the following form:

$$U_{fourier} = \frac{1}{2V} \sum_{\mathbf{m} \neq 0} \frac{4\pi}{|\mathbf{k_m}|^2} |\hat{\rho}(\mathbf{k_m})|^2 e^{-\frac{|\mathbf{k_m}|^2}{4\alpha^2}} \tag{216}$$

This is consistent with Ref. [5].

Let now use the following units:

$$L = L_x = L_y = L_z = 1 \tag{217}$$

$$\mathbf{k_m} = \frac{2\pi}{L}\mathbf{m} \tag{218}$$

Then

$$e^{-\frac{|\mathbf{k_m}|^2}{4\alpha^2}} = \exp(-\frac{4\pi^2}{L^2} m^2 \frac{1}{4\alpha^2}) = \exp(-\frac{\pi^2 m^2}{\alpha^2}) \tag{219}$$

And the Fourier sum can be rewritten in a following form:

$$U_{fourier} = \sum_{\mathbf{m} \neq 0} \beta(\mathbf{k_m}) \rho(\mathbf{k_m}) \rho(-\mathbf{k_m}) \tag{220}$$

where

$$\beta(\mathbf{k_m}) = \frac{1}{2V} \frac{4\pi L^2}{4\pi^2 m^2} \exp(-\frac{\pi^2 m^2}{\alpha^2}) = [V = 1, L = 1] = \frac{1}{2\pi m^2} \exp(-\frac{\pi^2 m^2}{\alpha^2}) \tag{221}$$

7.1.2 w=6

Similar representation can be also written for the case $w = 6$ and $w = 12$.

For $w = 6$ we have

$$U_{fourier} = \frac{\pi^{9/2}}{3V} \sum_{\mathbf{m} \neq 0} F_2(\mathbf{k_m}) |\mathbf{h_m}|^3 \left(\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right) \tag{222}$$

where $b^2 = \pi^2 |\mathbf{h_m}|^2 / \alpha^2$ Thus $|\mathbf{h_m}| = \alpha b / \pi$, and

$$U_{fourier} = \frac{\pi^{9/2}}{3V} \sum_{\mathbf{m} \neq 0} F_2(\mathbf{k_m}) \frac{\alpha^3 b^3}{\pi^3} \left(\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right) \tag{223}$$

$$= \sum_{\mathbf{m}\neq 0} F_2(\mathbf{k_m})\beta_6(\mathbf{k_m}) \tag{224}$$

where

$$\beta_6(\mathbf{k_m}) = \frac{\alpha^3}{V} B_6(b = \pi h_m/\alpha) \tag{225}$$

$$B_6(b) = \frac{\pi^{3/2}}{3}\left(b^3\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{1}{2} - b^2\right)e^{-b^2}\right) \tag{226}$$

7.1.3 w=12

For $w = 12$ we have

$$U_{fourier} = \tag{227}$$

$$\frac{1}{945\cdot 120}\frac{\pi^{10.5}}{V}\sum_{\mathbf{m}\neq 0} F_2(\mathbf{k_m})|\mathbf{h_m}|^9\left(-16\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{16}{b} - \frac{8}{b^3} + \frac{12}{b^5} - \frac{30}{b^7} + \frac{105}{b^9}\right)e^{-b^2}\right) \tag{228}$$

Changing $h_m \to \alpha b/\pi$

$$U_{fourier} = \tag{229}$$

$$\frac{1}{945\cdot 120}\frac{\pi^{10.5}}{V}\sum_{\mathbf{m}\neq 0} F_2(\mathbf{k_m})\frac{\alpha^9 b^9}{\pi^9}\left(-16\sqrt{\pi}\mathrm{erfc}(b) + \left(\frac{16}{b} - \frac{8}{b^3} + \frac{12}{b^5} - \frac{30}{b^7} + \frac{105}{b^9}\right)e^{-b^2}\right) \tag{230}$$

$$= \sum_{\mathbf{m}\neq 0} F_2(\mathbf{k_m})\beta_{12}(\mathbf{k_m}) \tag{231}$$

where

$$\beta_{12}(\mathbf{k_m}) = \frac{\alpha^9}{V} B_{12}(b) \tag{232}$$

$$B_{12}(b) = \frac{\pi^{3/2}}{945\cdot 120}\left(-16b^9\sqrt{\pi}\mathrm{erfc}(b) + \left(16b^8 - 8b^6 + 12b^4 - 30b^2 + 105\right)e^{-b^2}\right) \tag{233}$$

We note, that functions B_6, B_{12} depend only on one argument and do not depend on the parameters of the system. So, they can be tabulated before the calculations start.

7.2 Calculation of $|\hat{\rho}(k)|^2$

For $w = 1$ we need to calculate $|\hat{\rho}(k)|^2$

$$\hat{\rho}(\mathbf{k})\hat{\rho}(-\mathbf{k}) = (\sum_j q_j\cos(\mathbf{k}\cdot\mathbf{r}_j) + i\sum_j q_j\sin(\mathbf{k}\cdot\mathbf{r}_j))(\sum_j q_j\cos(\mathbf{k}\cdot\mathbf{r}_j) - i\sum_j q_j\sin(\mathbf{k}\cdot\mathbf{r}_j)) \tag{234}$$

$$= \left(\sum_j q_j\cos(\mathbf{k}\cdot\mathbf{r}_j)\right)^2 - i^2\left(\sum_j q_j\sin(\mathbf{k}\cdot\mathbf{r}_j)\right)^2 \tag{235}$$

$$= \left(\sum_j q_j\cos(\mathbf{k}\cdot\mathbf{r}_j)\right)^2 + \left(\sum_j q_j\sin(\mathbf{k}\cdot\mathbf{r}_j)\right)^2 \tag{236}$$

Now, using the symmetry in k-space we can reduce the sum to the sum over $k_x, k_y, k_z \geq 0$ Indeed, $\beta(\mathbf{k}) = \beta(|\mathbf{k}|)$. For $\hat{\rho}(\mathbf{k})$ we can introduce the following definitions:

$$|\hat{\rho}_{s_x,s_y,s_z}(\mathbf{k})|^2 \equiv C^2_{s_x s_y s_z}(\mathbf{k}) + S^2_{s_x s_y s_z}(\mathbf{k}) \tag{237}$$

where

$$C^2_{s_x s_y s_z}(\mathbf{k}) = \left(\sum_j q_j \cos(s_x k_x x_j + s_y k_y y_j + s_z k_z z_j)\right)^2 \tag{238}$$

$$S^2_{s_x s_y s_z}(\mathbf{k}) = \left(\sum_j q_j \sin(s_x k_x x_j + s_y k_y y_j + s_z k_z z_j)\right)^2 \tag{239}$$

where

$$s_x, s_y, s_z \in \{+1, -1\} \equiv \{+, -\} \tag{240}$$

for example

$$|\hat{\rho}_{+-+}(\mathbf{k})|^2 \equiv |\hat{\rho}_{+1,-1,+1}(\mathbf{k})|^2 \equiv C^2_{+-+}(\mathbf{k}) + S^2_{+-+}(\mathbf{k}) \tag{241}$$

$$\equiv \left(\sum_j q_j \cos(k_x x_j - k_y y_j + k_z z_j)\right)^2 + \left(\sum_j q_j \sin(k_x x_j - k_y y_j + k_z z_j)\right)^2 \tag{242}$$

In general, for $k_x, k_y, k_z \geq 0$ there exist 8 combinations of s_x, s_y, s_z. Due to the symmetry, we have

$$|\hat{\rho}_{s_x,s_y,s_z}(\mathbf{k})|^2 = |\hat{\rho}_{-s_x,-s_y,-s_z}(\mathbf{k})|^2 \tag{243}$$

which means that only 4 of 8 combinations are independent.

Then, the sum can be rewritten in a following form:

$$U_{fourier} = \sum_{\mathbf{m}\neq 0} \beta(\mathbf{k_m})\rho(\mathbf{k_m})\rho(-\mathbf{k_m}) = \tag{244}$$

$$= 2 \sum_{m_x,m_y,m_z>0} \beta(|\mathbf{k_m}|) \left(|\hat{\rho}_{+++}(\mathbf{k_m})|^2 + |\hat{\rho}_{++-}(\mathbf{k_m})|^2 + |\hat{\rho}_{+-+}(\mathbf{k_m})|^2 + |\hat{\rho}_{+--}(\mathbf{k_m})|^2\right) \tag{245}$$

$$+2 \sum_{m_x,m_y>0,m_z=0} \beta(|\mathbf{k_m}|) \left(|\hat{\rho}_{+++}(\mathbf{k_m})|^2 + |\hat{\rho}_{+-+}(\mathbf{k_m})|^2\right) \tag{246}$$

$$+2 \sum_{m_x=0,m_z>0,m_y=0} \beta(|\mathbf{k_m}|) \left(|\hat{\rho}_{+++}(\mathbf{k_m})|^2 + |\hat{\rho}_{++-}(\mathbf{k_m})|^2\right) \tag{247}$$

$$+2 \sum_{m_x>0,m_y,m_z=0} \beta(|\mathbf{k_m}|) \left(|\hat{\rho}_{+++}(\mathbf{k_m})|^2\right) \tag{248}$$

$$+ \sum_{m_x=0,m_y,m_z>0} \beta(|\mathbf{k_m}|) \left(|\hat{\rho}_{+++}(\mathbf{k_m})|^2 + |\hat{\rho}_{++-}(\mathbf{k_m})|^2 + |\hat{\rho}_{+-+}(\mathbf{k_m})|^2 + |\hat{\rho}_{+--}(\mathbf{k_m})|^2\right) \tag{249}$$

$$+ \sum_{m_x,m_z=0,m_y>0} \beta(|\mathbf{k_m}|) \left(|\hat{\rho}_{+++}(\mathbf{k_m})|^2 + |\hat{\rho}_{+-+}(\mathbf{k_m})|^2\right) \tag{250}$$

$$+ \sum_{m_x,m_y=0,m_z>0} \beta(|\mathbf{k_m}|) \left(|\hat{\rho}_{+++}(\mathbf{k_m})|^2 + |\hat{\rho}_{++-}(\mathbf{k_m})|^2\right) \tag{251}$$

So cumbersome representation appears because we need to account for all cases when one of coordinates is zero. In that case we need to avoid double summation. E.g., if $k_z = 0$, then $\cos(xk_x + yk_y + zk_z)$ and $\cos(xk_x + yk_y - zk_z)$ represent the same summand, thus $\hat{\rho}(++-)$ should be excluded from summation. The same is with all other coordinates. The sum can be rewritten in a more compact manner with the use of sign function:

$$\mathrm{sgn}(x) = \begin{cases} -1, & x < 0 \\ 0, & x = 0 \\ 1, & x > 0 \end{cases} \tag{252}$$

The sum can be written in a following form

$$\begin{aligned} U_{fourier} = \sum_{\substack{m_x,m_y,m_z \geq 0 \\ \mathbf{m}\neq 0}} (\mathrm{sgn}(m_x)+1)\beta(|\mathbf{k_m}|)\Big(|\hat{\rho}_{+++}(\mathbf{k_m})|^2 + & \ \mathrm{sgn}(m_y)|\hat{\rho}_{+-+}(\mathbf{k_m})|^2 \\ + & \ \mathrm{sgn}(m_z)|\hat{\rho}_{++-}(\mathbf{k_m})|^2 \\ + & \ \mathrm{sgn}(m_y m_z)|\hat{\rho}_{+--}(\mathbf{k_m})|^2\Big) \end{aligned} \tag{253}$$

The values of $|\hat{\rho}_{s_x s_y s_z}(\mathbf{k_m})|^2 = C^2_{s_x s_y s_z}(\mathbf{k}) + S^2_{s_x s_y s_z}(\mathbf{k})$ should be pre-computed for the combinations $+++$, $++-$, $+-+$, $+--$ and for all $k_x, k_y, k_z \geq 0$.

The values of $C^2_{s_x s_y s_z}(\mathbf{k})$, $S^2_{s_x s_y s_z}(\mathbf{k})$ can be calculated recurrently, atom-by-atom and k-by-k, using the formulae for sin/cos of sums and differences of angles. For example, for the atom at coordinates (x, y, z) we have

$$\cos(xk_x + yk_y + z(k_z + dk_z)) = \cos(xk_x + yk_y + zk_z)\cos(dk_z) - \sin(xk_x + yk_y + zk_z)\sin(dk_z) \tag{254}$$

which allows us to calculate the values of cos k-by-km and avoid multiple calls of the cos procedure.

7.3 Calculation of $F_2(k)$

In ewald summation we rewrite the fourier part sum in a form

$$U_{fourier} = \sum_{\mathbf{m}} \beta(\mathbf{k_m}) F_2(\mathbf{k_m}) \tag{255}$$

where beta(k) differs for $1/r$, $1/r^6$, $1/r^12$ potentials and

$$F_2(\mathbf{k_m}) = \sum_{sj} A_{sj} \exp(i\mathbf{k_m} \cdot (\mathbf{r}_s - \mathbf{r}_j)) \tag{256}$$

If $A_{sj} = q_s q_j$ then $F_2(k_m)$ can be represented as

$$F_2(\mathbf{k_m}) = \hat{\rho}(\mathbf{k_m})\hat{\rho}(-\mathbf{k_m}) = |\hat{\rho}(\mathbf{k_m})|^2 \tag{257}$$

where

$$\hat{\rho}(\mathbf{k_m}) = \sum_j q_j \exp(i\mathbf{k_m} \cdot \mathbf{r}_j) \tag{258}$$

This calculation requires only N operations, while calculation of double sum using the original notation requires N^2 operations, where N is the number of particles.

For other potentials we cannot do such reduction, because in general case $A_{sj} \neq A_s A_j$. However, if there are not very much atoms with different A_{sj} values (which is usually the case, for example for Lennard Jones potential), we can rewrite summation in a following way:

$$F_2(\mathbf{k_m}) = \sum_{t_1=1}^{M} \sum_{t_2=1}^{M} A_{t_1 t_2} \sum_{s=1}^{N(t_1)} \sum_{j=1}^{N(t_2)} \exp(i\mathbf{k_m} \cdot (\mathbf{r}_s^{t_1} - \mathbf{r}_j^{t_2}) = \sum_{t_1,t_2} A_{t_1 t_2} F^{t_1}(\mathbf{k_m}) F^{t_2}(\mathbf{k_m}) \tag{259}$$

where M is the number of different atomtypes in the system, $N(t)$ is the number of atoms of type t, $\mathbf{r}_s^t$ are the coordinates of s-th particle of type t, and

$$F^t(\mathbf{k_m}) = \sum_{s=1}^{N(t)} \exp(i\mathbf{k_m} \cdot \mathbf{r}_s^t) \tag{260}$$

In this notation the total number of operations is $N + M^2$, so if $M << N$ it is almost the same as in Coulomb potential case.

To avoid operations with the complex numbers in the calculations we can rewrite the definition above in a following way:

$$F^t(\mathbf{k_m}) = C_{\mathbf{m}}^t + iS_{\mathbf{m}}^t \tag{261}$$

where

$$C_{\mathbf{m}}^t = \sum_{s=1}^{N(t)} \cos(i\mathbf{k_m}\mathbf{r}_s) \tag{262}$$

$$S_{\mathbf{m}}^t = \sum_{s=1}^{N(t)} \sin(i\mathbf{k_m}\mathbf{r}_s) \tag{263}$$

Then

$$F^1(\mathbf{k_m})F^2(-\mathbf{k_m}) = (C_{\mathbf{m}}^1 + iS_{\mathbf{m}}^1)(C_{\mathbf{m}}^2 - iS_{\mathbf{m}}^2) = C_{\mathbf{m}}^1C_{\mathbf{m}}^2 + S_{\mathbf{m}}^1S_{\mathbf{m}}^2 - iC_{\mathbf{m}}^1S_{\mathbf{m}}^2 + iS_{\mathbf{m}}^1C_{\mathbf{m}}^2 \tag{264}$$

Normally most of potentials are symmetric, i.e $A_{sj} = A_{js}$. In that case we can rewrite $F_2(\mathbf{k_m})$ in a following way:

$$F_2(\mathbf{k_m}) = \sum_t A_{tt}F^t(\mathbf{k_m})F^t(-\mathbf{k_m}) + \sum_{t_1}\sum_{t_2>t_1} A_{t_1t_2}\left(F^{t_1}(\mathbf{k_m})F^{t_2}(-\mathbf{k_m}) + F^{t_2}(\mathbf{k_m})F^{t_1}(-\mathbf{k_m})\right) \tag{265}$$

We have:

$$F^t(\mathbf{k_m})F^t(-\mathbf{k_m}) = (C_{\mathbf{m}}^t)^2 + (S_{\mathbf{m}}^t)^2 \tag{266}$$

And

$$F^1(\mathbf{k_m})F^2(-\mathbf{k_m}) + F^2(\mathbf{k_m})F^1(-\mathbf{k_m}) = \tag{267}$$

$$= C_{\mathbf{m}}^1C_{\mathbf{m}}^2 + S_{\mathbf{m}}^1S_{\mathbf{m}}^2 - iC_{\mathbf{m}}^1S_{\mathbf{m}}^2 + iS_{\mathbf{m}}^1C_{\mathbf{m}}^2 + \tag{268}$$

$$C_{\mathbf{m}}^1C_{\mathbf{m}}^2 + S_{\mathbf{m}}^1S_{\mathbf{m}}^2 + iC_{\mathbf{m}}^1S_{\mathbf{m}}^2 - iS_{\mathbf{m}}^1C_{\mathbf{m}}^2 \tag{269}$$

$$= 2(C_{\mathbf{m}}^1C_{\mathbf{m}}^2 + S_{\mathbf{m}}^1S_{\mathbf{m}}^2) \tag{270}$$

This gives the following formula for F_2:

$$F_2(\mathbf{k_m}) = \sum_{t_1t_2} A_{t_1t_2}\left(C_{\mathbf{m}}^{t_1}C_{\mathbf{m}}^{t_2} + S_{\mathbf{m}}^{t_1}S_{\mathbf{m}}^{t_2}\right) \tag{271}$$

We can see, that the sum is again symmetric:

$$F_2(-\mathbf{k_m}) = F_2(\mathbf{k_{-m}}) = \sum_{t_1t_2}\left(C_{-\mathbf{m}}^{t_1}C_{-\mathbf{m}}^{t_2} + S_{-\mathbf{m}}^{t_1}S_{-\mathbf{m}}^{t_2}\right) \tag{272}$$

Due to the properties of sin and cos we have

$$C_{-\mathbf{m}}^t = C_{\mathbf{m}}^t, \qquad S_{-\mathbf{m}}^t = -S_{\mathbf{m}}^t \tag{273}$$

which gives

$$F_2(-\mathbf{k_m}) = \sum_{t_1 t_2} \left(C^{t_1}_{\mathbf{m}} C^{t_2}_{\mathbf{m}} + (-S^{t_1}_{\mathbf{m}})(-S^{t_2}_{\mathbf{m}}) \right) = F_2(\mathbf{k_m}) \tag{274}$$

As well as in case of Coulomb potential we can use the symmetry of $\beta(\mathbf{k_m})$ and F_2 to reduce the whole sum to the sum over $k_x, k_y, k_z > 0$.

we can also use symmetry of beta again:

$$\begin{aligned} U_{fourier} = \sum_{\substack{m_x, m_y, m_z \geq 0 \\ \mathbf{m} \neq 0}} (\mathrm{sgn}(m_x) + 1)\beta(\mathbf{k_m}) \Big(F_2^{+++}(\mathbf{k_m}) + & \ \mathrm{sgn}(m_y) F_2^{+-+}(\mathbf{k_m}) \\ + & \ \mathrm{sgn}(m_z) F_2^{++-}(\mathbf{k_m}) \\ + & \ \mathrm{sgn}(m_y m_z) F_2^{+--}(\mathbf{k_m}) \Big) \end{aligned} \tag{275}$$

where

$$F_2^{s_x s_y s_z}(\mathbf{k_m}) = \sum_{t_1 t_2} \left(C^{t_1}_{\mathbf{m}}(s_x, s_y, s_z) C^{t_2}_{\mathbf{m}}(s_x, s_y, s_z) + S^{t_1}_{\mathbf{m}}(s_x, s_y, s_z) S^{t_2}_{\mathbf{m}}(s_x, s_y, s_z) \right) \tag{276}$$

$$C^{t}_{\mathbf{m}}(s_x, s_y, s_z) = \sum_{j=1}^{N(t)} \cos(s_x x^t_j k^x_{\mathbf{m}} + s_y y^t_j k^y_{\mathbf{m}} + s_z z^t_j k^z_{\mathbf{m}}) \tag{277}$$

$$S^{t}_{\mathbf{m}}(s_x, s_y, s_z) = \sum_{j=1}^{N(t)} \sin(s_x x^t_j k^x_{\mathbf{m}} + s_y y^t_j k^y_{\mathbf{m}} + s_z z^t_j k^z_{\mathbf{m}}) \tag{278}$$

$(x^t_j, y^t_j, z^t_j) = \mathbf{r}^t_j$ are the coordinates of the j-th particle of type t.

7.4 Lennard Jones Potential

For calculation of the Lennard-Jones potential we can use the general formulae for $1/r^6$ and $1/r^{12}$ potentials. However, to calculate F_2^{LJ6} and F_2^{LJ12} is not practical in that case, because the sums are almost the same up to the $A_{t_1 t_2}$ coefficients. Indeed, the Lennard-Jones energy can be written as difference of $LJ12$ and $LJ6$ terms:

$$U^{LJ}_{fourier} = U^{LJ12}_{fourier} - U^{LJ6}_{fourier} \tag{279}$$

where

$$U^{LJ12}_{fourier} = \sum_{\mathbf{m} \geq 0} (1 + \mathrm{sgn}(m_x)) \beta_{12}(\mathbf{k_m}) F_2^{LJ12}(\mathbf{k_m}) \tag{280}$$

$$U^{LJ6}_{fourier} = \sum_{\mathbf{m} \geq 0} (1 + \mathrm{sgn}(m_x)) \beta_{6}(\mathbf{k_m}) F_2^{LJ6}(\mathbf{k_m}) \tag{281}$$

$$\begin{aligned} F_2^{LJ6,12}(\mathbf{k_m}) = \textstyle\sum_{t_1 t_2} A^{LJ6,12}_{t_1 t_2} \Big[& \ C^{t_1(+++)}_{\mathbf{m}} C^{t_2(+++)}_{\mathbf{m}} + S^{t_1(+++)}_{\mathbf{m}} S^{t_2(+++)}_{\mathbf{m}} \\ + \mathrm{sgn}(k_y) \cdot & \left(C^{t_1(+-+)}_{\mathbf{m}} C^{t_2(+-+)}_{\mathbf{m}} + S^{t_1(+-+)}_{\mathbf{m}} S^{t_2(+-+)}_{\mathbf{m}} \right) \\ + \mathrm{sgn}(k_z) \cdot & \left(C^{t_1(++-)}_{\mathbf{m}} C^{t_2(++-)}_{\mathbf{m}} + S^{t_1(++-)}_{\mathbf{m}} S^{t_2(++-)}_{\mathbf{m}} \right) \\ + \mathrm{sgn}(k_y k_z) \cdot & \left(C^{t_1(+--)}_{\mathbf{m}} C^{t_2(+--)}_{\mathbf{m}} + S^{t_1(+--)}_{\mathbf{m}} S^{t_2(+--)}_{\mathbf{m}} \right) \Big] \end{aligned} \tag{282}$$

Expanding all the definitions, for $U^{LJ}_{fourier}$ we get

$$\begin{aligned}U^{LJ}_{fourier} = \sum_{\mathbf{m}\geq 0}\sum_{t_1 t_2}\beta^{t_1 t_2}_{LJ}(\mathbf{k_m})\Big[\quad & C^{t_1(+++)}_{\mathbf{m}} C^{t_2(+++)}_{\mathbf{m}} + S^{t_1(+++)}_{\mathbf{m}} S^{t_2(+++)}_{\mathbf{m}} \\ +\mathrm{sgn}(k_y)\cdot \quad & \left(C^{t_1(+-+)}_{\mathbf{m}} C^{t_2(+-+)}_{\mathbf{m}} + S^{t_1(+-+)}_{\mathbf{m}} S^{t_2(+-+)}_{\mathbf{m}}\right) \\ +\mathrm{sgn}(k_z)\cdot \quad & \left(C^{t_1(++-)}_{\mathbf{m}} C^{t_2(++-)}_{\mathbf{m}} + S^{t_1(++-)}_{\mathbf{m}} S^{t_2(++-)}_{\mathbf{m}}\right) \\ +\mathrm{sgn}(k_y k_z)\cdot \quad & \left(C^{t_1(+--)}_{\mathbf{m}} C^{t_2(+--)}_{\mathbf{m}} + S^{t_1(+--)}_{\mathbf{m}} S^{t_2(+--)}_{\mathbf{m}}\right)\Big]\end{aligned} \tag{283}$$

where

$$\beta^{t_1 t_2}_{LJ}(\mathbf{k_m}) \equiv (1+\mathrm{sgn}(m_x))\left(A^{LJ12}_{t_1 t_1}\beta_{12}(\mathbf{k_m}) + A^{LJ6}_{t_1 t_2}\beta_6(\mathbf{k_m})\right) \tag{284}$$

we note, that $\beta^{t_1 t_2}_{LJ}$ do not depend on the particle coordinates, which means that they can be computed ones at startup and then used. We note, that the calculations using the formula (283) are faster than the direct calculations of two sums (280), (281). Indeed, let we have N_t different types of molecules and N_k grid points in the positive part of k-space ($m_x, m_y, m_z \geq 0$). Then calculation of (282) for each k-space gri point requires $8N_k N_t^2$ multiplications for each of F_2^{LJ6} and F_2^{LJ12}, thus in total $16 N_k N_t^2$ multiplications [3] . Eqch of calculations using formulae (280),(281) require N_k multiplications, thus in total using the irect scheme we get $(2+16N_t^2)N_k$ multiplications. The same calculations using the formula (283) require only $9N_t^2 N_k$ multiplications. We note also, that for LJ potential coefficients are symmetric, i.e. $A_{t_1 t_2} = A_{t_2 t_1}$ which implies $\beta^{t_1 t_2}_{LJ} = \beta^{t_2 t_1}_{LJ}$. This allows one to count only half of summands, i.e.:

$$\begin{aligned}U^{LJ}_{fourier} = \sum_{\mathbf{m}\geq 0}\sum_{t_1}\sum_{t_2\geq t_1}(2-\delta_{t_1 t_2})\beta^{t_1 t_2}_{LJ}(\mathbf{k_m})\Big[\quad & C^{t_1(+++)}_{\mathbf{m}} C^{t_2(+++)}_{\mathbf{m}} + S^{t_1(+++)}_{\mathbf{m}} S^{t_2(+++)}_{\mathbf{m}} \\ +\mathrm{sgn}(k_y)\cdot \quad & \left(C^{t_1(+-+)}_{\mathbf{m}} C^{t_2(+-+)}_{\mathbf{m}} + S^{t_1(+-+)}_{\mathbf{m}} S^{t_2(+-+)}_{\mathbf{m}}\right) \\ +\mathrm{sgn}(k_z)\cdot \quad & \left(C^{t_1(++-)}_{\mathbf{m}} C^{t_2(++-)}_{\mathbf{m}} + S^{t_1(++-)}_{\mathbf{m}} S^{t_2(++-)}_{\mathbf{m}}\right) \\ +\mathrm{sgn}(k_y k_z)\cdot \quad & \left(C^{t_1(+--)}_{\mathbf{m}} C^{t_2(+--)}_{\mathbf{m}} + S^{t_1(+--)}_{\mathbf{m}} S^{t_2(+--)}_{\mathbf{m}}\right)\Big]\end{aligned} \tag{285}$$

This summation requires only $9/2N_k(N_t^2 + N_t)$ multiplications [4] .

8 Forces

8.1 Real space

To calculate forces which act on the particles we need to take the derivatives of the potential. The force component over the x axis acting on particle s is

$$F^x_p = -\frac{\partial U}{\partial x_p} \tag{286}$$

In our case, all potential components (Coulomb, LJ6, LJ12) can be written in a following form:

$$U = \frac{1}{2}\sum_{sj,\mathbf{n}} u_{sj}(r_{sj;\mathbf{n}}) = \frac{1}{2}\sum_{sj;\mathbf{n}} A_{sj}\psi(r_{sj;\mathbf{n}}) \tag{287}$$

[3] we do not count multiplication by sgn functions, because they are usually implemented with logical statements.

[4] Again, multiplication by $2-\delta_{t_1 t_2}$ can be implemented with logical operations and summation: if t1=t2 then Sum := Sum + Sum

where $r_{sj;\mathbf{n}} = |\mathbf{r}_{sj;\mathbf{n}}| = |\mathbf{r}_s - \mathbf{r}_j + \mathbf{n} \circ \mathbf{L}|$

From the general expressions for the Ewald sum for different potentials (154), (198), (211) and remembering that $a \equiv \alpha r_{sj;\mathbf{n}}$, we have the following expressions for ψ in Coulomb and LJ potentials

$$\psi^C(r) = \frac{\mathrm{erfc}(\alpha r)}{r} \tag{288}$$

For Lennard-Jones interactions

$$\psi^{LJ6}(r) = e^{-\alpha^2 r^2} \left(\frac{1}{r^6} + \frac{\alpha^2}{r^4} + \frac{\alpha^4}{2r^2} \right) \tag{289}$$

$$\psi^{LJ12}(r) = e^{-\alpha^2 r^2} \left(1 + \frac{\alpha^2}{r^{10}} + \frac{\alpha^4}{2r^8} + \frac{\alpha^6}{6r^6} + \frac{\alpha^8}{24r^4} + \frac{\alpha^{10}}{120r^2} \right) \tag{290}$$

Using the general expression (137) for particular case of $w = 2k + 2$ ((163)) we have

$$\psi^w(r) = \frac{1}{r^w} \frac{\Gamma(w/2; \alpha^2 r/^2)}{\Gamma(w/2)} = r^{-w} \Phi_w(\alpha r) = e^{-\alpha^2 r^2} \sum_{l=0}^{w/2-1} \frac{1}{l!} \frac{\alpha^{2l}}{r^{w-2l}} \tag{291}$$

Now we can take the derivative of (287) we have

$$\frac{\partial U}{\partial x_p} = \frac{1}{2} \sum_{sj;\mathbf{n}} A_{sj} \frac{\partial \psi(r_{sj;\mathbf{n}})}{\partial r_{sj;\mathbf{n}}} \frac{\partial r_{sj;\mathbf{n}}}{\partial x_p} \tag{292}$$

Using the definition of $r_{sj;\mathbf{n}}$ we get

$$\frac{\partial r_{sj;\mathbf{n}}}{x_p} = \frac{\partial}{x_p} \sqrt{(x_s - x_j + n_x L_x)^2 + (y_s - y_j + n_y L_y)^2 + (z_s - z_j + n_z L_z)^2} \tag{293}$$

$$= \frac{\delta_{sp}}{2r_{pj;\mathbf{n}}} 2(x_p - x_j + n_x L_x) + \frac{\delta_{jp}}{2r_{sp;\mathbf{n}}} 2(x_s - x_p + n_x L_x)(-1) \tag{294}$$

$$= \frac{\delta_{sp}}{r_{pj;\mathbf{n}}} (x_p - x_j + n_x L_x) + \frac{\delta_{sp}}{r_{pj;\mathbf{n}}} (x_p - x_s - n_x L_x) \tag{295}$$

Inserting this into (292) we get

$$\frac{\partial U}{\partial x_p} = \frac{1}{2} \sum_{s=p,j;\mathbf{n}} A_{pj} \frac{\partial \psi(r_{pj;\mathbf{n}})}{\partial r_{pj;\mathbf{n}}} \frac{1}{r_{pj;\mathbf{n}}} (x_p - x_j + n_x L_x) \tag{296}$$

$$+ \frac{1}{2} \sum_{s,j=p;\mathbf{n}} A_{sp} \frac{\partial \psi(r_{sp;\mathbf{n}})}{\partial r_{sp;\mathbf{n}}} \frac{1}{r_{sp;\mathbf{n}}} (x_p - x_s - n_x L_x) \tag{297}$$

Renaming in the second sum $s \to j$, $\mathbf{n} \to -\mathbf{n}$ (sum is anyway over all space) we get

$$\frac{\partial U}{\partial x_p} = \frac{1}{2} \sum_{j;\mathbf{n}} A_{pj} \frac{\partial \psi(r_{pj;\mathbf{n}})}{\partial r_{pj;\mathbf{n}}} \frac{1}{r_{pj;\mathbf{n}}} (x_p - x_j + n_x L_x) \tag{298}$$

$$+ \frac{1}{2} \sum_{j;-\mathbf{n}} A_{jp} \frac{\partial \psi(r_{jp;-\mathbf{n}})}{\partial r_{jp;-\mathbf{n}}} \frac{1}{r_{jp;-\mathbf{n}}} (x_p - x_j + n_x L_x) \tag{299}$$

Now, we see that

$$r_{jp;-\mathbf{n}} = |\mathbf{r}_j - \mathbf{r}_p - \mathbf{n}\circ\mathbf{L}| = |-(\mathbf{r}_p - \mathbf{r}_j + \mathbf{n}\circ\mathbf{L})| = r_{pj;\mathbf{n}} \tag{300}$$

Then, using that $A_{pj} = A_{jp}$ the two sums can be combined in one:

$$\frac{\partial U}{\partial x_p} = \sum_{j;\mathbf{n}} A_{pj} \frac{\partial \psi(r_{pj;\mathbf{n}})}{\partial r_{pj;\mathbf{n}}} \frac{1}{r_{pj;\mathbf{n}}} (x_p - x_j + n_x L_x) \tag{301}$$

Because the similar expressions can be written also for the derivatives over y_p,z_p, we can write

$$\mathbf{F}_p = -\sum_{j;\mathbf{n}} A_{pj} \frac{\partial \psi(r_{pj;\mathbf{n}})}{\partial r_{pj;\mathbf{n}}} \frac{1}{r_{pj;\mathbf{n}}} (\mathbf{r}_p - \mathbf{r}_j + \mathbf{n}\circ\mathbf{L}) = \sum_{j;\mathbf{n}} A_{pj} F_R(r_{pj;\mathbf{n}}) \circ \mathbf{r}_{pj;\mathbf{n}} \tag{302}$$

where $\circ$ means point-wise multiplication and

$$F_R(r) = -\frac{1}{r}\frac{\partial \psi(r)}{\partial r} \tag{303}$$

Having the exact expressions (288),(289), (290), (291), we can calculate the force components.

8.1.1 Coulomb potential

For Coulomb potential:

$$\frac{\partial \psi^C(r)}{\partial r} = -\frac{1}{r^2}\mathrm{erfc}(\alpha r) + \frac{1}{r}\frac{\partial}{\partial r}\mathrm{erfc}(\alpha r) \tag{304}$$

Considering the definition of erfc:

$$\mathrm{erfc}(\alpha r) = 1 - \mathrm{erf}(\alpha r) = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\alpha r} e^{-t^2} dt \tag{305}$$

which gives

$$\frac{\partial}{\partial r}\mathrm{erfc}(\alpha r) = \alpha \frac{\partial}{\partial \alpha r}\mathrm{erfc}(\alpha r) = -\frac{2\alpha}{\sqrt{\pi}} e^{-\alpha^2 r^2} \tag{306}$$

and

$$\frac{\partial \psi^C(r)}{\partial r} = -\frac{1}{r^2}\mathrm{erfc}(\alpha r) - \frac{2}{r\sqrt{\pi}} e^{-\alpha^2 r^2} \tag{307}$$

Which gives

$$F_R^C(r) = \frac{1}{r^2}\left(\frac{\mathrm{erfc}(\alpha r)}{r} + \frac{2}{\sqrt{\pi}} e^{-\alpha^2 r^2}\right) \tag{308}$$

8.1.2 Lennard-Jones

In case of Lennard-Jones potential we may start from the general expression (291) for $w = 2k+2$, namely:

$$\frac{\partial}{\partial r}\psi^w(r) = \frac{\partial}{\partial r}\left(e^{-\alpha^2 r^2} \sum_{l=0}^{w/2-1} \frac{1}{l!}\frac{\alpha^{2l}}{r^{w-2l}}\right) \tag{309}$$

$$= -2\alpha^2 r e^{-\alpha^2 r^2} \sum_{l=0}^{w/2-1} \frac{1}{l!} \frac{\alpha^{2l}}{r^{w-2l}} + e^{-\alpha^2 r^2} \sum_{l=0}^{w/2-1} \frac{1}{l!} \frac{\alpha^{2l}(2l-w)}{r^{w-2l+1}} \tag{310}$$

$$= -e^{-\alpha^2 r^2} \left(\sum_{l=0}^{w/2-1} \frac{2}{l!} \frac{\alpha^{2l+2}}{r^{w-2l-1}} - \sum_{l=0}^{w/2-1} \frac{1}{l!} \frac{\alpha^{2l}(w-2l)}{r^{w-2l+1}} \right) \tag{311}$$

Changing in the first sum $l \to l'$, where $l' = l+1$ and using that $l! = (l'-1)! = l'!/l'$ we have:

$$\frac{\partial}{\partial r} \psi^w(r) = -e^{-\alpha^2 r^2} \left(\sum_{l=0,l'=1}^{l=w/2-1,l'=w/2} \frac{2l'}{l'!} \frac{\alpha^{2l'}}{r^{w-2l'+1}} - \sum_{l=0}^{w/2-1} \frac{1}{l!} \frac{\alpha^{2l}(w-2l)}{r^{w-2l+1}} \right) \tag{312}$$

Considering that at $l' = 0$ the first summand is zero and at that $l = w/2$ causes $w - 2l - 0$ which nullify the second summand, we can rewrite the sum in a following form:

$$\frac{\partial}{\partial r} \psi^w(r) = -e^{-\alpha^2 r^2} \sum_{l=0}^{w/2} \frac{(2l + w - 2l)}{l!} \frac{\alpha^{2l}}{r^{w-2l+1}} = -we^{-\alpha^2 r^2} \sum_{l=0}^{w/2} \frac{1}{l!} \frac{\alpha^{2l}}{r^{w-2l+1}} \tag{313}$$

This gives

$$F_R^w(r) = -\frac{1}{r} \frac{\partial \psi^w}{\partial r} = we^{-\alpha^2 r^2} \sum_{l=0}^{w/2} \frac{1}{l!} \frac{\alpha^{2l}}{r^{w-2l+2}} \tag{314}$$

Comparing this to the expression (291) we can see, that expressions have similarities. Actually, the force component F_R^w can be written in a following way:

$$F_R^w(r) = \frac{w}{r^2} \left(\psi^w(r) + e^{-\alpha^2 r^2} \frac{\alpha^w}{(w/2)!} \right) \tag{315}$$

where $\psi^w(r) = r^{-w} \Phi_w(\alpha r)$. From the numerical point of view, it is also reasonable to define the function $C_w(r)$:

$$C_w(r) = \sum_{l=0}^{w/2-1} \frac{1}{l!} (\alpha r)^{2l} \tag{316}$$

Then

$$\psi^w(r) = \frac{e^{-\alpha^2 r^2}}{r^w} C_w(r) \tag{317}$$

$$F_R(r) = w \frac{e^{-\alpha^2 r^2}}{r^2} \left(\frac{C_w(r)}{r^w} + \frac{\alpha^w}{(w/2)!} \right) \tag{318}$$

For the LJ potential components:

$$F_R^6(r) = \frac{6}{r^2} e^{-\alpha^2 r^2} \left(\frac{C_6(r)}{r^6} + \frac{\alpha^6}{6} \right) \tag{319}$$

$$F_R^{12}(r) = \frac{12}{r^2} e^{-\alpha^2 r^2} \left(\frac{C_{12}(r)}{r^{12}} + \frac{\alpha^{12}}{720} \right) \tag{320}$$

Inserting them into the sum and considering that we get:

$$\mathbf{F}_p^{LJ} = \mathbf{F}_p^{LJ12} - \mathbf{F}_p^{LJ6} = \tag{321}$$

$$\sum_{j\mathbf{n}}(A_{pj}^{LJ12}F_R^{12}(r_{pj;\mathbf{n}}) - A_{pj}^{LJ6}F_R^{6}(r_{pj;\mathbf{n}}))\mathbf{r}_{pj;\mathbf{n}} = \sum_{j\mathbf{n}} F_R^{LJ(p,j)}(r_{pj;\mathbf{n}})\mathbf{r}_{pj;\mathbf{n}} \tag{322}$$

where

$$F_R^{LJ(p,j)}(r) = A_{pj}^{LJ12}F_R^{12}(r) - A_{pj}^{LJ6}F_R^{6}(r) \tag{323}$$

Considering that $A_{pj}^{LJ6} = 4\epsilon_{pj}\sigma_{pj}^6$, $A_{pj}^{LJ12} = 4\epsilon_{pj}\sigma_{pj}^{12}$ we have

$$F_R^{LJ(p,j)}(r) = 4\epsilon_{pj}\left(\sigma_{pj}^{12}F_R^{12}(r) - \sigma_{pj}^{6}F_R^{6}(r)\right) \tag{324}$$

Considering the definition of F_R^{12}, F_R^{6} we have

$$F_R^{LJ(p,j)}(r) = \frac{4\epsilon_{pj}e^{-\alpha^2r^2}}{r^2}\left(12\left(\frac{\sigma_{pj}}{r}\right)^{12}C_{12}(r) + 12\frac{\sigma_{pj}^{12}\alpha^{12}}{720} - 6\left(\frac{\sigma_{pj}}{r}\right)^{6}C_6(r) - 6\frac{\sigma_{pj}^{6}\alpha^{6}}{6}\right) \tag{325}$$

To reduce the number of operations, the values of $(\sigma/r)^6$ and $(\alpha r)^6$ can be pre-computed. Then we rewrite the last expression in a following way:

$$F_R^{LJ(p,j)}(r) = \frac{4\epsilon_{pj}e^{-\alpha^2r^2}}{r^2}\left(12\left(\frac{\sigma_{pj}}{r}\right)^{12}C_{12}(r) + 12\left(\frac{\sigma_{pj}}{r}\right)^{12}\frac{(\alpha r)^{12}}{720} - 6\left(\frac{\sigma_{pj}}{r}\right)^{6}C_6(r) - 6\left(\frac{\sigma_{pj}}{r}\right)^{6}\frac{(\alpha r)^{6}}{6}\right) \tag{326}$$

$$= \frac{4\epsilon_{pj}e^{-\alpha^2r^2}}{r^2}\left\{6\left(\frac{\sigma_{pj}}{r}\right)^{6}\left[2\left(\frac{\sigma_{pj}}{r}\right)^{6}\left(C_{12}(r) + \frac{(\alpha r)^{12}}{720}\right) - C_6(r) - \frac{(\alpha r)^6}{6}\right]\right\} \tag{327}$$

To see, how the number of operations reduces, we can use the definitions

$$S \equiv \left(\frac{\sigma_{pj}}{r}\right)^6 \qquad A = (\alpha r)^6 \tag{328}$$

Then the above expression can be written more compactely:

$$F_R^{LJ(p,j)}(r) = \frac{4\epsilon_{pj}e^{-\alpha^2r^2}}{r^2}\left\{6S\left[2S\left(C_{12}(r) + \frac{A^2}{720}\right) - C_6(r) - \frac{A}{6}\right]\right\} \tag{329}$$

8.2 Fourier space

8.2.1 Coulomb potential

The Fourier space sum can be written as a sum of Coulomb and Lennard-Jones sums:

$$U_{fourier} = U_{fourier}^{C} + U_{fourier}^{LJ} \tag{330}$$

where $U_{fourier}^{C}$ and $U_{fourier}^{LJ}$ are defined by eqs. (373), (285) respectively. For the Coulomb potential we have

$$\begin{aligned}\frac{\partial U^C}{\partial x_p} = \sum_{\mathbf{m}\geq 0}(1+\mathrm{sgn}(m_x))\beta(\mathbf{k_m})\Big[& \frac{\partial}{\partial x_p}\left(C_{+++}^2(\mathbf{k_m}) + S_{+++}^2(\mathbf{k_m})\right)\\ +\mathrm{sgn}(m_y) \cdot & \frac{\partial}{\partial x_p}\left(C_{+-+}^2(\mathbf{k_m}) + S_{+-+}^2(\mathbf{k_m})\right)\\ +\mathrm{sgn}(m_z) \cdot & \frac{\partial}{\partial x_p}\left(C_{++-}^2(\mathbf{k_m}) + S_{++-}^2(\mathbf{k_m})\right)\\ +\mathrm{sgn}(m_y m_z) \cdot & \frac{\partial}{\partial x_p}\left(C_{+--}^2(\mathbf{k_m}) + S_{+--}^2(\mathbf{k_m})\right)\Big]\end{aligned} \tag{331}$$

Now we calculate the derivative of separate sumands. For the cosine sum:

$$\frac{\partial}{\partial x_p} C^2_{s_x s_y s_z}(\mathbf{k_m}) = 2C_{s_x s_y s_z} \sum_j q_j \frac{\partial}{\partial x_p} \cos(s_x x_j k^x_m + s_y y_j k^y_m + s_z z_j k^z_m) \tag{332}$$

$$= 2C_{s_x s_y s_z} \sum_j q_j \delta_{pj} (-\sin(\mathbf{r}_p^{(s_x s_y s_z)} \cdot \mathbf{k_m})) s_x k^x_m = (-s_x) 2C_{s_x s_y s_z} q_p \sin(\mathbf{r}_p^{s_x s_y s_z} \cdot \mathbf{k_m}) k^x_m \tag{333}$$

where $\mathbf{r}_p^{s_x s_y s_z} \equiv (s_x x_p, s_y y_p, s_z z_p)$ By analogy for the sine sum:

$$\frac{\partial}{\partial x_p} S^2_{s_x s_y s_z}(\mathbf{k_m}) = 2S_{s_x s_y s_z} \sum_j q_j \frac{\partial}{\partial x_p} \sin(s_x x_j k^x_m + s_y y_j k^y_m + s_z z_j k^z_m) \tag{334}$$

$$= (+s_x) 2S_{s_x s_y s_z} q_p \cos(\mathbf{r}_p^{s_x s_y s_z} \cdot \mathbf{k_m}) k^x_m \tag{335}$$

Combining both togather:

$$\frac{\partial}{\partial x_p} \Big(C^2_{s_x s_y s_z}(\mathbf{k_m}) + S^2_{s_x s_y s_z}(\mathbf{k_m}) \Big) = (s_x) 2 q_p k^x_m \left(S_{s_x s_y s_z} \cos(\mathbf{r}_p^{s_x s_y s_z} \mathbf{k_m}) - C_{s_x s_y s_z} \sin(\mathbf{r}_p^{s_x s_y s_z} \mathbf{k_m}) \right) \tag{336}$$

and the total $\partial U^C_{fourier}/\partial x_p$ is

$$\begin{aligned} \frac{\partial U^C_{fourier}}{\partial x_p} = 2 q_p k^x_m \sum_{\mathbf{m} \geq 0} (1 + \mathrm{sgn}(m_x)) \beta(\mathbf{k_m}) \quad & \Big[\quad S_{+++} \cos(\mathbf{r}_p^{+++} \mathbf{k_m}) - C_{+++} \sin(\mathbf{r}_p^{+++} \mathbf{k_m}) \\ + \mathrm{sgn}(m_y) \quad & \cdot \quad \big(S_{+-+} \cos(\mathbf{r}_p^{+-+} \mathbf{k_m}) - C_{+-+} \sin(\mathbf{r}_p^{+-+} \mathbf{k_m}) \big) \\ + \mathrm{sgn}(m_z) \quad & \cdot \quad \big(S_{++-} \cos(\mathbf{r}_p^{++-} \mathbf{k_m}) - C_{++-} \sin(\mathbf{r}_p^{++-} \mathbf{k_m}) \big) \\ + \mathrm{sgn}(m_y m_z) \quad & \cdot \quad \big(S_{+--} \cos(\mathbf{r}_p^{+--} \mathbf{k_m}) - C_{+--} \sin(\mathbf{r}_p^{+--} \mathbf{k_m}) \big) \Big] \end{aligned} \tag{337}$$

By analogy, $\partial U^C/\partial y_p$, $\partial U^C/\partial z_p$ are:

$$\begin{aligned} \frac{\partial U^C_{fourier}}{\partial y_p} = 2 q_p k^y_m \sum_{\mathbf{m} \geq 0} (1 + \mathrm{sgn}(m_x)) \beta(\mathbf{k_m}) \quad & \Big[\quad S_{+++} \cos(\mathbf{r}_p^{+++} \mathbf{k_m}) - C_{+++} \sin(\mathbf{r}_p^{+++} \mathbf{k_m}) \\ - \mathrm{sgn}(m_y) \quad & \cdot \quad \big(S_{+-+} \cos(\mathbf{r}_p^{+-+} \mathbf{k_m}) - C_{+-+} \sin(\mathbf{r}_p^{+-+} \mathbf{k_m}) \big) \\ + \mathrm{sgn}(m_z) \quad & \cdot \quad \big(S_{++-} \cos(\mathbf{r}_p^{++-} \mathbf{k_m}) - C_{++-} \sin(\mathbf{r}_p^{++-} \mathbf{k_m}) \big) \\ - \mathrm{sgn}(m_y m_z) \quad & \cdot \quad \big(S_{+--} \cos(\mathbf{r}_p^{+--} \mathbf{k_m}) - C_{+--} \sin(\mathbf{r}_p^{+--} \mathbf{k_m}) \big) \Big] \end{aligned} \tag{338}$$

$$\begin{aligned} \frac{\partial U^C_{fourier}}{\partial z_p} = 2 q_p k^z_m \sum_{\mathbf{m} \geq 0} (1 + \mathrm{sgn}(m_x)) \beta(\mathbf{k_m}) \quad & \Big[\quad S_{+++} \cos(\mathbf{r}_p^{+++} \mathbf{k_m}) - C_{+++} \sin(\mathbf{r}_p^{+++} \mathbf{k_m}) \\ + \mathrm{sgn}(m_y) \quad & \cdot \quad \big(S_{+-+} \cos(\mathbf{r}_p^{+-+} \mathbf{k_m}) - C_{+-+} \sin(\mathbf{r}_p^{+-+} \mathbf{k_m}) \big) \\ - \mathrm{sgn}(m_z) \quad & \cdot \quad \big(S_{++-} \cos(\mathbf{r}_p^{++-} \mathbf{k_m}) - C_{++-} \sin(\mathbf{r}_p^{++-} \mathbf{k_m}) \big) \\ - \mathrm{sgn}(m_y m_z) \quad & \cdot \quad \big(S_{+--} \cos(\mathbf{r}_p^{+--} \mathbf{k_m}) - C_{+--} \sin(\mathbf{r}_p^{+--} \mathbf{k_m}) \big) \Big] \end{aligned} \tag{339}$$

Then the force $\mathbf{F}_p^C = -\partial U_C/\partial \mathbf{r}_p$ can be written in a following way:

$$\mathbf{F}_p^C = -\frac{\partial U^C_{fourier}}{\partial \mathbf{r}_p} =$$
$$\begin{array}{rcl} = 2q_p \sum_{\mathbf{m}\geq 0}(1+\mathrm{sgn}(m_x))\beta(\mathbf{k_m}) & \Big[& \mathbf{k}_\mathbf{m}^{+++} \circ \left(C_{+++}\sin(\mathbf{r}_p\mathbf{k}_\mathbf{m}^{+++}) - S_{+++}\cos(\mathbf{r}_p\mathbf{k}_\mathbf{m}^{+++})\right) \\ + \cdot\, \mathrm{sgn}(m_y) & \cdot & \mathbf{k}_\mathbf{m}^{+-+} \circ \left(C_{+-+}\sin(\mathbf{r}_p\mathbf{k}_\mathbf{m}^{+-+}) - S_{+-+}\cos(\mathbf{r}_p\mathbf{k}_\mathbf{m}^{+-+})\right) \\ +\mathrm{sgn}(m_z) & \cdot & \mathbf{k}_\mathbf{m}^{++-} \circ \left(C_{++-}\sin(\mathbf{r}_p\mathbf{k}_\mathbf{m}^{++-}) - S_{++-}\cos(\mathbf{r}_p\mathbf{k}_\mathbf{m}^{++-})\right) \\ +\mathrm{sgn}(m_y m_z) & \cdot & \mathbf{k}_\mathbf{m}^{+--} \circ \left(C_{+--}\sin(\mathbf{r}_p\mathbf{k}_\mathbf{m}^{+--}) - S_{+--}\cos(\mathbf{r}_p\mathbf{k}_\mathbf{m}^{+--})\right) \Big] \end{array} \tag{340}$$

where $\mathbf{k}_\mathbf{m}^{\mathbf{s_x s_y s_z}} \equiv (s_x, s_y, s_z) \circ \mathbf{k_m} = (s_x k_m^x, s_y k_m^y, s_z k_m^z)$, $\circ$ is a point-wise multiplication.

8.2.2 LJ forces

To calculate the forces induced by the LJ interaction we need to take the derivative of the fourier LJ representation (285):

$$\begin{array}{rl} \dfrac{\partial U^{LJ}_{fourier}}{\partial x_p^\tau} = \displaystyle\sum_{\mathbf{m}\geq 0}\sum_{t_1 t_2} \beta_{LJ}^{t_1 t_2}(\mathbf{k_m})\Big[& \frac{\partial}{\partial x_p^\tau}\left(C_\mathbf{m}^{t_1(+++)}C_\mathbf{m}^{t_2(+++)} + S_\mathbf{m}^{t_1(+++)}S_\mathbf{m}^{t_2(+++)}\right) \\ +\mathrm{sgn}(k_y)\cdot & \frac{\partial}{\partial x_p^\tau}\left(C_\mathbf{m}^{t_1(+-+)}C_\mathbf{m}^{t_2(+-+)} + S_\mathbf{m}^{t_1(+-+)}S_\mathbf{m}^{t_2(+-+)}\right) \\ +\mathrm{sgn}(k_z)\cdot & \frac{\partial}{\partial x_p^\tau}\left(C_\mathbf{m}^{t_1(++-)}C_\mathbf{m}^{t_2(++-)} + S_\mathbf{m}^{t_1(++-)}S_\mathbf{m}^{t_2(++-)}\right) \\ +\mathrm{sgn}(k_y k_z)\cdot & \frac{\partial}{\partial x_p^\tau}\left(C_\mathbf{m}^{t_1(+--)}C_\mathbf{m}^{t_2(+--)} + S_\mathbf{m}^{t_1(+--)}S_\mathbf{m}^{t_2(+--)}\right)\Big] \end{array} \tag{341}$$

Now we can calculate the derivatives separately for each of sumands:

$$\frac{\partial}{\partial x_p^\tau}\left(C_\mathbf{m}^{t_1(s_x s_y s_z)}C_\mathbf{m}^{t_2(s_x s_y s_z)}\right) = \left(\frac{\partial}{\partial x_p^\tau}C_\mathbf{m}^{t_1(s_x s_y s_z)}\right)C_\mathbf{m}^{t_2(s_x s_y s_z)} + C_\mathbf{m}^{t_1(s_x s_y s_z)}\left(\frac{\partial}{\partial x_p^\tau}C_\mathbf{m}^{t_2(s_x s_y s_z)}\right) \tag{342}$$

$$\frac{\partial}{\partial x_p^\tau}C_\mathbf{m}^{t(s_x s_y s_z)} = \sum_{j=1}^{N(t)}\frac{\partial}{\partial x_p^\tau}\cos(s_x x_j^t k_m^x + s_y y_j^t k_m^y s_z z_j^t k_m^z) \tag{343}$$

$$= \sum_{j=1}^{N(t)} \delta_{\tau t}\delta_{pj}(-\sin(\mathbf{k}_\mathbf{m}^{s_x s_y s_z}\mathbf{r}_p^\tau))s_x k_m^x = (-s_x)k_m^x \delta_{\tau t}\sin(\mathbf{k}_\mathbf{m}^{s_x s_y s_z}\mathbf{r}_p^\tau) \tag{344}$$

Then

$$\sum_{\mathbf{m}\geq 0}\sum_{t_1 t_2}\beta_{LJ}^{t_1 t_2}(\mathbf{k_m})\frac{\partial}{\partial x_p^\tau}\left(C_\mathbf{m}^{t_1(s_x s_y s_z)}C_\mathbf{m}^{t_2(s_x s_y s_z)}\right) \tag{345}$$

$$= (-s_x)k_m^x \sum_{\mathbf{m}\geq 0}\sum_{t_1 t_2}\beta_{LJ}^{t_1 t_2}(\mathbf{k_m})\delta_{t_1\tau}\sin(\mathbf{k}_\mathbf{m}^{s_x s_y s_z}\mathbf{r}_p^\tau)C_\mathbf{m}^{t_2(s_x s_y s_z)} \tag{346}$$

$$+(-s_x)k_m^x \sum_{\mathbf{m}\geq 0}\sum_{t_1 t_2}\beta_{LJ}^{t_1 t_2}(\mathbf{k_m})C_\mathbf{m}^{t_1(s_x s_y s_z)}\delta_{\tau t_2}\sin(\mathbf{k}_\mathbf{m}^{s_x s_y s_z}\mathbf{r}_p^\tau) \tag{347}$$

$$= (-s_x)k_m^x \sum_{\mathbf{m}\geq 0}\left(\sum_{t_2}\beta_{LJ}^{\tau t_2}(\mathbf{k_m})\sin(\mathbf{k}_\mathbf{m}^{s_x s_y s_z}\mathbf{r}_p^\tau)C_\mathbf{m}^{t_2(s_x s_y s_z)}\right. \tag{348}$$

$$+\sum_{t_1}\beta_{LJ}^{t_1\tau}(\mathbf{k_m})\sin(\mathbf{k_m}^{s_xs_ys_z}\mathbf{r}_p^\tau)C_{\mathbf{m}}^{t_1(s_xs_ys_z)}\Big) \tag{349}$$

Considering, that $\beta_{LJ}^{\tau t}=\beta_{LJ}^{t\tau}$ the sums are the same up to renaming $t_1\leftrightarrow t_2$. Thus, we have

$$\sum_{\mathbf{m}\geq 0}\sum_{t_1t_2}\beta_{LJ}^{t_1t_2}(\mathbf{k_m})\frac{\partial}{\partial x_p^\tau}\left(C_{\mathbf{m}}^{t_1(s_xs_ys_z)}C_{\mathbf{m}}^{t_2(s_xs_ys_z)}\right) \tag{350}$$

$$=(-s_x)2k_m^x\sum_{\mathbf{m}\geq 0}\sum_{t}\beta_{LJ}^{\tau t}(\mathbf{k_m})C_{\mathbf{m}}^{t(s_xs_ys_z)}\sin(\mathbf{k_m}^{s_xs_ys_z}\mathbf{r}_p^\tau) \tag{351}$$

The same for sum of sines:

$$\frac{\partial}{\partial x_p^\tau}S_{\mathbf{m}}^{t(s_xs_ys_z)}=\sum_{j=1}^{N(t)}\frac{\partial}{\partial x_p^\tau}\sin(s_xx_j^tk_m^x+s_yy_j^tk_m^ys_zz_j^tk_m^z)=s_xk_m^x\delta_{\tau t}\cos(\mathbf{k_m}^{s_xs_ys_z}\mathbf{r}_p^\tau) \tag{352}$$

which implies

$$\sum_{\mathbf{m}\geq 0}\sum_{t_1t_2}\beta_{LJ}^{t_1t_2}(\mathbf{k_m})\frac{\partial}{\partial x_p^\tau}\left(S_{\mathbf{m}}^{t_1(s_xs_ys_z)}S_{\mathbf{m}}^{t_2(s_xs_ys_z)}\right) \tag{353}$$

$$=(+s_x)2k_m^x\sum_{\mathbf{m}\geq 0}\sum_{t}\beta_{LJ}^{\tau t}(\mathbf{k_m})S_{\mathbf{m}}^{t(s_xs_ys_z)}\cos(\mathbf{k_m}^{s_xs_ys_z}\mathbf{r}_p^\tau) \tag{354}$$

This gives the following expression for the $\partial U_{LJ}/\partial x_p^\tau$:

$$\begin{aligned}\frac{\partial U_{fourier}^{LJ}}{\partial x_p^\tau}=2k_m^x\sum_{\mathbf{m}\geq 0}\sum_{t}\beta_{LJ}^{\tau t}(\mathbf{k_m})\Big[&\Big(S_{\mathbf{m}}^{t(+++)}\cos(\mathbf{k}_{\mathbf{m}}^{+++}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+++)}\sin(\mathbf{k}_{\mathbf{m}}^{+++}\mathbf{r}_p^\tau)\Big)\\ +\mathrm{sgn}(k_y)\cdot&\Big(S_{\mathbf{m}}^{t(+-+)}\cos(\mathbf{k}_{\mathbf{m}}^{+-+}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+-+)}\sin(\mathbf{k}_{\mathbf{m}}^{+-+}\mathbf{r}_p^\tau)\Big)\\ +\mathrm{sgn}(k_z)\cdot&\Big(S_{\mathbf{m}}^{t(++-)}\cos(\mathbf{k}_{\mathbf{m}}^{++-}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(++-)}\sin(\mathbf{k}_{\mathbf{m}}^{++-}\mathbf{r}_p^\tau)\Big)\\ +\mathrm{sgn}(k_yk_z)\cdot&\Big(S_{\mathbf{m}}^{t(+--)}\cos(\mathbf{k}_{\mathbf{m}}^{+--}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+--)}\sin(\mathbf{k}_{\mathbf{m}}^{+--}\mathbf{r}_p^\tau)\Big)\Big]\end{aligned} \tag{355}$$

Considering the signs of s_y and s_z we can also write $\partial U_{LJ}/\partial y_p^\tau$ and $\partial U_{LJ}/\partial z_p^\tau$:

$$\begin{aligned}\frac{\partial U_{fourier}^{LJ}}{\partial y_p^\tau}=2k_m^y\sum_{\mathbf{m}\geq 0}\sum_{t}\beta_{LJ}^{\tau t}(\mathbf{k_m})\Big[&\Big(S_{\mathbf{m}}^{t(+++)}\cos(\mathbf{k}_{\mathbf{m}}^{+++}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+++)}\sin(\mathbf{k}_{\mathbf{m}}^{+++}\mathbf{r}_p^\tau)\Big)\\ -\mathrm{sgn}(k_y)\cdot&\Big(S_{\mathbf{m}}^{t(+-+)}\cos(\mathbf{k}_{\mathbf{m}}^{+-+}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+-+)}\sin(\mathbf{k}_{\mathbf{m}}^{+-+}\mathbf{r}_p^\tau)\Big)\\ +\mathrm{sgn}(k_z)\cdot&\Big(S_{\mathbf{m}}^{t(++-)}\cos(\mathbf{k}_{\mathbf{m}}^{++-}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(++-)}\sin(\mathbf{k}_{\mathbf{m}}^{++-}\mathbf{r}_p^\tau)\Big)\\ -\mathrm{sgn}(k_yk_z)\cdot&\Big(S_{\mathbf{m}}^{t(+--)}\cos(\mathbf{k}_{\mathbf{m}}^{+--}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+--)}\sin(\mathbf{k}_{\mathbf{m}}^{+--}\mathbf{r}_p^\tau)\Big)\Big]\end{aligned} \tag{356}$$

$$\begin{aligned}\frac{\partial U_{fourier}^{LJ}}{\partial z_p^\tau}=2k_m^z\sum_{\mathbf{m}\geq 0}\sum_{t}\beta_{LJ}^{\tau t}(\mathbf{k_m})\Big[&\Big(S_{\mathbf{m}}^{t(+++)}\cos(\mathbf{k}_{\mathbf{m}}^{+++}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+++)}\sin(\mathbf{k}_{\mathbf{m}}^{+++}\mathbf{r}_p^\tau)\Big)\\ +\mathrm{sgn}(k_y)\cdot&\Big(S_{\mathbf{m}}^{t(+-+)}\cos(\mathbf{k}_{\mathbf{m}}^{+-+}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+-+)}\sin(\mathbf{k}_{\mathbf{m}}^{+-+}\mathbf{r}_p^\tau)\Big)\\ -\mathrm{sgn}(k_z)\cdot&\Big(S_{\mathbf{m}}^{t(++-)}\cos(\mathbf{k}_{\mathbf{m}}^{++-}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(++-)}\sin(\mathbf{k}_{\mathbf{m}}^{++-}\mathbf{r}_p^\tau)\Big)\\ -\mathrm{sgn}(k_yk_z)\cdot&\Big(S_{\mathbf{m}}^{t(+--)}\cos(\mathbf{k}_{\mathbf{m}}^{+--}\mathbf{r}_p^\tau)-C_{\mathbf{m}}^{t(+--)}\sin(\mathbf{k}_{\mathbf{m}}^{+--}\mathbf{r}_p^\tau)\Big)\Big]\end{aligned} \tag{357}$$

This gives the following representation for the force:

$$
\begin{aligned}
&\mathbf{F}^{LJ}_{p_\tau} = -\frac{\partial U^{LJ}_{fourier}}{\partial \mathbf{r}^\tau_p} = \\
= 2\sum_{\mathbf{m}\geq 0}\sum_t \beta^{\tau t}_{LJ}(\mathbf{k_m})\Big[\quad &\mathbf{k}^{+++}_{\mathbf{m}} \circ \Big(C^{t(+++)}_{\mathbf{m}} \sin(\mathbf{k}^{+++}_{\mathbf{m}} \mathbf{r}^\tau_p) - S^{t(+++)}_{\mathbf{m}} \cos(\mathbf{k}^{+++}_{\mathbf{m}} \mathbf{r}^\tau_p) \Big) \\
+\mathrm{sgn}(k_y)\cdot \quad &\mathbf{k}^{+-+}_{\mathbf{m}} \circ \Big(C^{t(+-+)}_{\mathbf{m}} \sin(\mathbf{k}^{+-+}_{\mathbf{m}} \mathbf{r}^\tau_p) - S^{t(+-+)}_{\mathbf{m}} \cos(\mathbf{k}^{+-+}_{\mathbf{m}} \mathbf{r}^\tau_p) \Big) \\
+\mathrm{sgn}(k_z)\cdot \quad &\mathbf{k}^{++-}_{\mathbf{m}} \circ \Big(C^{t(++-)}_{\mathbf{m}} \sin(\mathbf{k}^{++-}_{\mathbf{m}} \mathbf{r}^\tau_p) - S^{t(++-)}_{\mathbf{m}} \cos(\mathbf{k}^{++-}_{\mathbf{m}} \mathbf{r}^\tau_p) \Big) \\
+\mathrm{sgn}(k_y k_z)\cdot \quad &\mathbf{k}^{+--}_{\mathbf{m}} \circ \Big(C^{t(+--)}_{\mathbf{m}} \sin(\mathbf{k}^{+--}_{\mathbf{m}} \mathbf{r}^\tau_p) - S^{t(+--)}_{\mathbf{m}} \cos(\mathbf{k}^{+--}_{\mathbf{m}} \mathbf{r}^\tau_p) \Big) \Big]
\end{aligned}
\tag{358}
$$

where $\mathbf{k}^{\mathbf{s_x s_y s_z}}_{\mathbf{m}} \equiv (s_x, s_y, s_z) \circ \mathbf{k_m} = (s_x k^x_m, s_y k^y_m, s_z k^z_m)$, $\circ$ is a point-wise multiplication.

9 Monte Carlo Move

9.1 Energy difference

9.1.1 Real space

For the Monte Carlo move one need:

1. randomly select a molecule.
2. change the coordinates of the molecule(either randomly or using the force-bias, as we do)
3. count the energy difference between the new and initial position and either accept or decline the move

Let M be the indexes of the atoms of the selected molecule. We can calculate the real-space forces using the expressions (302), (308), (321), (329) and k-space forces using the expressions (340), (358). Using these forces we can calculate the new position of the molecule. Let $\{\mathbf{r}^{new}_j; j \in M\}$ be the new positions of the atoms of the molecule. The energy difference in the real-space we can calculate using the real-part sums in expressions (154), (198), (211). Considering that for $s, j \notin M$ the sums are equal, and ignoring the intermolecular interactions (which are anyway constant for the rigid molecules) we can write the difference in a following way:

$$
\Delta U_{real} = [U_{real}]^{new}_M - [U_{real}]^{old}_M \tag{359}
$$

where

$$
[U_{real}]^{old,new}_M = \sum_{\mathbf{n}}\sum_{s\in M}\sum_{j\notin M}\Bigg[q_s q_j \frac{\mathrm{erfc}(\alpha|\mathbf{r}^{old,new}_{sj;\mathbf{n}}|)}{|\mathbf{r}^{old,new}_{sj;\mathbf{n}}|} \tag{360}
$$

$$
+\exp(-\alpha^2|\mathbf{r}^{old,new}_{sj;\mathbf{n}}|^2)\Bigg(\frac{A^{LJ12}_{sj}}{|\mathbf{r}^{old,new}_{sj;\mathbf{n}}|^{12}} C_{12}(|\mathbf{r}^{old,new}_{sj;\mathbf{n}}|) - \frac{A^{LJ6}_{sj}}{|\mathbf{r}^{old,new}_{sj;\mathbf{n}}|^{6}} C_{6}(|\mathbf{r}^{old,new}_{sj;\mathbf{n}}|) \Bigg) \Bigg] \tag{361}
$$

where $\mathbf{r}^{old}_{sj;\mathbf{n}} = \mathbf{r}_s - \mathbf{r}_j + \mathbf{n}\circ\mathbf{L}$, $\mathbf{r}^{new}_{sj;\mathbf{n}} = \mathbf{r}^{new}_s - \mathbf{r}_j + \mathbf{n}\circ\mathbf{L}$,

$$
C_w(r) = \sum_{l=0}^{w/2-1} \frac{(\alpha r)^{2l}}{l!} \tag{362}
$$

9.1.2 K-space coulomb

For the k-space sum we can write the difference as a sum of coulomb and LJ parts:

$$\Delta U_{fourier} = \Delta U^{C}_{fourier} + \Delta U^{LJ}_{fourier} \tag{363}$$

where

$$\Delta U^{C}_{fourier} = [U^{C}_{fourier}]^{new} - U^{C}_{fourier} \tag{364}$$

$$\Delta U^{C}_{fourier} = [U^{LJ}_{fourier}]^{new} - U^{LJ}_{fourier} \tag{365}$$

and Coulomb and Lennard-Jones energies are calculated with formulae (373) and (285) with new and old atom positions respectively. For the $[U^{C}_{fourier}]^{new}_{M}$ we have

$$\begin{aligned} &[U^{C}_{fourier}]^{new} = \\ \sum_{\substack{m_x,m_y,m_z\geq 0\\ \mathbf{m}\neq 0}} &(\mathrm{sgn}(m_x)+1)\beta(|\mathbf{k_m}|)\Big[\quad \left(([C^{+++}_{\mathbf{m}}]^{new})^2 + ([S^{+++}_{\mathbf{m}}]^{new})^2\right) \\ &+\mathrm{sgn}(m_y)\cdot \quad \left(([C^{+-+}_{\mathbf{m}}]^{new})^2 + ([S^{+-+}_{\mathbf{m}}]^{new})^2\right) \\ &+\mathrm{sgn}(m_z)\cdot \quad \left(([C^{++-}_{\mathbf{m}}]^{new})^2 + ([S^{++-}_{\mathbf{m}}]^{new})^2\right) \\ &+\mathrm{sgn}(m_y m_z)\cdot \quad \left(([C^{+--}_{\mathbf{m}}]^{new})^2 + ([S^{+--}_{\mathbf{m}}]^{new})^2\right)\Big] \end{aligned} \tag{366}$$

where

$$[C^{s_x s_y s_z}_{\mathbf{m}}]^{new} = \sum_{j\notin M} q_j \cos(\mathbf{k_m r}_j) + \sum_{j\in M} q_j \cos(\mathbf{k_m r}^{new}_j) = C^{s_x s_y s_z}_{\mathbf{m}} + \Delta C^{s_x s_y s_z}_{\mathbf{m}} \tag{367}$$

$$[S^{s_x s_y s_z}_{\mathbf{m}}]^{new} = \sum_{j\notin M} q_j \sin(\mathbf{k_m r}_j) + \sum_{j\in M} q_j \sin(\mathbf{k_m r}^{new}_j) = S^{s_x s_y s_z}_{\mathbf{m}} + \Delta S^{s_x s_y s_z}_{\mathbf{m}} \tag{368}$$

The increments $\Delta C^{s_x s_y s_z}_{\mathbf{m}}$, $\Delta S^{s_x s_y s_z}_{\mathbf{m}}$ are the sums other the atoms of the molecule. We will indicate such sums with the subscript $_M$, i.e.:

$$\Delta C^{s_x s_y s_z}_{\mathbf{m}} = [C^{s_x s_y s_z}_{\mathbf{m}}]^{new}_{M} - [C^{s_x s_y s_z}_{\mathbf{m}}]_{M} \tag{369}$$

$$\Delta S^{s_x s_y s_z}_{\mathbf{m}} = [S^{s_x s_y s_z}_{\mathbf{m}}]^{new}_{M} - [S^{s_x s_y s_z}_{\mathbf{m}}]_{M} \tag{370}$$

where

$$[C^{s_x s_y s_z}_{\mathbf{m}}]^{new}_{M} = \sum_{j\in M} q_j \cos(\mathbf{k_m r}^{new}_j); \qquad [C^{s_x s_y s_z}_{\mathbf{m}}]_{M} = \sum_{j\in M} q_j \cos(\mathbf{k_m r}_j) \tag{371}$$

$$[S^{s_x s_y s_z}_{\mathbf{m}}]^{new}_{M} = \sum_{j\in M} q_j \sin(\mathbf{k_m r}^{new}_j); \qquad [S^{s_x s_y s_z}_{\mathbf{m}}]_{M} = \sum_{j\in M} q_j \sin(\mathbf{k_m r}_j) \tag{372}$$

Using the representations (367),(368) we can calculate the difference

$$\begin{aligned} &([C^{s_x s_y s_z}_{\mathbf{m}}]^{new})^2 - (C^{s_x s_y s_z}_{\mathbf{m}})^2 \\ &= (C^{s_x s_y s_z}_{\mathbf{m}})^2 + 2C^{s_x s_y s_z}_{\mathbf{m}}\Delta C^{s_x s_y s_z}_{\mathbf{m}} + (\Delta C^{s_x s_y s_z}_{\mathbf{m}})^2 - (C^{s_x s_y s_z}_{\mathbf{m}})^2 \\ &= (2C^{s_x s_y s_z}_{\mathbf{m}} + \Delta C^{s_x s_y s_z}_{\mathbf{m}})\,\Delta C^{s_x s_y s_z}_{\mathbf{m}} \end{aligned}$$

and

$$([S_{\mathbf{m}}^{s_x s_y s_z}]^{new})^2 - (S_{\mathbf{m}}^{s_x s_y s_z})^2 = (2S_{\mathbf{m}}^{s_x s_y s_z} + \Delta S_{\mathbf{m}}^{s_x s_y s_z})\,\Delta S_{\mathbf{m}}^{s_x s_y s_z}$$

This gives the following representation for $\Delta U^c_{fourier}$:

$$\begin{aligned}
&\Delta U^C_{fourier} = \\
\sum_{\substack{m_x,m_y,m_z\geq 0\\ \mathbf{m}\neq 0}} (\mathrm{sgn}(m_x)+1)\beta(|\mathbf{k_m}|)\Big[&\Big((2C_{\mathbf{m}}^{+++} + \Delta C_{\mathbf{m}}^{+++})\,\Delta C_{\mathbf{m}}^{+++} + (2S_{\mathbf{m}}^{+++} + \Delta S_{\mathbf{m}}^{+++})\,\Delta S_{\mathbf{m}}^{+++}\Big) \\
+\mathrm{sgn}(m_y)\cdot &\Big(\big(2C_{\mathbf{m}}^{+-+} + \Delta C_{\mathbf{m}}^{+-+}\big)\,\Delta C_{\mathbf{m}}^{+-+} + \big(2S_{\mathbf{m}}^{+-+} + \Delta S_{\mathbf{m}}^{+-+}\big)\,\Delta S_{\mathbf{m}}^{+-+}\Big) \\
+\mathrm{sgn}(m_z)\cdot &\Big(\big(2C_{\mathbf{m}}^{++-} + \Delta C_{\mathbf{m}}^{++-}\big)\,\Delta C_{\mathbf{m}}^{++-} + \big(2S_{\mathbf{m}}^{++-} + \Delta S_{\mathbf{m}}^{++-}\big)\,\Delta S_{\mathbf{m}}^{++-}\Big) \\
+\mathrm{sgn}(m_y m_z)\cdot &\Big(\big(2C_{\mathbf{m}}^{+--} + \Delta C_{\mathbf{m}}^{+--}\big)\,\Delta C_{\mathbf{m}}^{+--} + \big(2S_{\mathbf{m}}^{+--} + \Delta S_{\mathbf{m}}^{+--}\big)\,\Delta S_{\mathbf{m}}^{+--}\Big)\Big]
\end{aligned} \tag{373}$$

9.1.3 K-space LJ

For calculation of the LJ sum we can use expression (285), which in non-expanded form can be written as follows:

$$U^{LJ}_{fourier} = \sum_{\mathbf{m}\in\mathbb{Z}^3} \sum_{t_1} \sum_{t_2} \beta^{t_1 t_2}_{LJ}(\mathbf{k_m})\Big(C^{t_1}_{\mathbf{m}} C^{t_2}_{\mathbf{m}} + S^{t_1}_{\mathbf{m}} S^{t_2}_{\mathbf{m}}\Big) \tag{374}$$

Here we return back to the summation over all $\mathbf{m} \in \mathbb{Z}^3$ (rather than over only positive), and to the full summation over t_1 and t_2 (instead of the $t_2 \geq t_1$). This is done to make derivations simpler. Then we can write the same expansion for $[U^{LJ}_{fourier}]^{new}$:

$$[U^{LJ}_{fourier}]^{new} = \sum_{\mathbf{m}\in\mathbb{Z}^3} \sum_{t_1 t_2} \beta^{t_1 t_2}_{LJ}(\mathbf{k_m})\Big([C^{t_1}_{\mathbf{m}}]^{new}[C^{t_2}_{\mathbf{m}}]^{new} + [S^{t_1}_{\mathbf{m}}]^{new}[S^{t_2}_{\mathbf{m}}]^{new}\Big) \tag{375}$$

where

$$[C^t_{\mathbf{m}}]^{new} = \sum_{j\notin M_t} \cos(\mathbf{k_m r}_j) + \sum_{j\in M_t} \cos(\mathbf{k_m r}^{new}_j) = C^t_{\mathbf{m}} + \Delta C^t_{\mathbf{m}}$$

$$[S^t_{\mathbf{m}}]^{new} = \sum_{j\notin M_t} \sin(\mathbf{k_m r}_j) + \sum_{j\in M_t} \sin(\mathbf{k_m r}^{new}_j) = S^t_{\mathbf{m}} + \Delta S^t_{\mathbf{m}}$$

$$M_t = \{j \in M : T(j) = t\}$$

and $T(j)$ is the type of the atom with index j.

In this notation

$$[U^{LJ}_{fourier}]^{new} = \sum_{\mathbf{m}\in\mathbb{Z}^3} \sum_{t_1 t_2} \beta^{t_1 t_2}_{LJ}(\mathbf{k_m})\Big((C^{t_1}_{\mathbf{m}} + \Delta C^{t_1}_{\mathbf{m}})(C^{t_2}_{\mathbf{m}} + \Delta C^{t_2}_{\mathbf{m}}) + (S^{t_1}_{\mathbf{m}} + \Delta S^{t_1}_{\mathbf{m}})(S^{t_2}_{\mathbf{m}} + \Delta S^{t_2}_{\mathbf{m}})\Big) \tag{376}$$

Considering that

$$(C^1 + \Delta C^1)(C^2 + \Delta C^2) - C^1 C^2 = C^1 \Delta C^2 + C^2 \Delta C^1 + \Delta C^1 \Delta C^2$$

we have for the energy difference the following:

$$\Delta U^{LJ}_{fourier} = [U^{LJ}_{fourier}]^{new} - U^{LJ}_{fourier}$$

$$= \sum_{\mathbf{m}} \left[\sum_{t_1 t_2} \beta_{LJ}^{t_1 t_2} C_{\mathbf{m}}^{t_1} \Delta C_{\mathbf{m}}^{t_2} + \sum_{t_1 t_2} \beta_{LJ}^{t_1 t_2} C_{\mathbf{m}}^{t_2} \Delta C_{\mathbf{m}}^{t_1} + \sum_{t_1 t_2} \beta_{LJ}^{t_1 t_2} \Delta C_{\mathbf{m}}^{t_1} \Delta C_{\mathbf{m}}^{t_2} \right.$$

$$\left. + \sum_{t_1 t_2} \beta_{LJ}^{t_1 t_2} S_{\mathbf{m}}^{t_1} \Delta S_{\mathbf{m}}^{t_2} + \sum_{t_1 t_2} \beta_{LJ}^{t_1 t_2} S_{\mathbf{m}}^{t_2} \Delta S_{\mathbf{m}}^{t_1} + \sum_{t_1 t_2} \beta_{LJ}^{t_1 t_2} \Delta S_{\mathbf{m}}^{t_1} \Delta S_{\mathbf{m}}^{t_2} \right]$$

Considering that $\beta_{LJ}^{t_1 t_2} = \beta_{LJ}^{t_2 t_1}$, the first and the second summands are actually the same. Then we can rewrite:

$$\Delta U_{fourier}^{LJ} = \sum_{\mathbf{m}} \sum_{t_1 t_2} \beta_{LJ}^{t_1 t_2}(\mathbf{k_m}) \left[\left(2C_{\mathbf{m}}^{t_1} + \Delta C_{\mathbf{m}}^{t_1} \right) \Delta C_{\mathbf{m}}^{t_2} + \left(2S_{\mathbf{m}}^{t_1} + \Delta S_{\mathbf{m}}^{t_1} \right) \Delta S_{\mathbf{m}}^{t_2} \right]$$

To reduce the total number of operations, we can use that for types which are not present in the selected molecule the increments $\Delta C_{\mathbf{m}}^{t}$, $\Delta S_{\mathbf{m}}^{t}$ are zero:

$$\Delta C_{\mathbf{m}}^{t} = [C_{\mathbf{m}}^{t}]_M^{new} - [C_{\mathbf{m}}^{t}]_M$$

$$\Delta S_{\mathbf{m}}^{t} = [S_{\mathbf{m}}^{t}]_M^{new} - [S_{\mathbf{m}}^{t}]_M$$

where

$$[C, S_{\mathbf{m}}^{t}]_M = \sum_{j \in M_t} \cos, \sin(\mathbf{k_m} \mathbf{r}_j)$$

$$[C, S_{\mathbf{m}}^{t}]_M^{new} = \sum_{j \in M_t} \cos, \sin(\mathbf{k_m} \mathbf{r}_j^{new})$$

For t not in types of the molecule M_t is empty:

$$t \notin T(M) \Leftrightarrow M_t = \varnothing$$

where

$$T(M) = \bigcup_{j \in M} T(j)$$

Then we can rewrite the sum as follows:

$$\Delta U_{fourier}^{LJ} = \sum_{\mathbf{m}} \sum_{t_1} \sum_{t_2 \in M_t} \beta_{LJ}^{t_1 t_2}(\mathbf{k_m}) \left[\left(2C_{\mathbf{m}}^{t_1} + \Delta C_{\mathbf{m}}^{t_1} \right) \Delta C_{\mathbf{m}}^{t_2} + \left(2S_{\mathbf{m}}^{t_1} + \Delta S_{\mathbf{m}}^{t_1} \right) \Delta S_{\mathbf{m}}^{t_2} \right]$$

Again, this sum can be rewritten as a sum for $\mathbf{m} \geq 0$:

$$\begin{aligned} & \Delta U_{fourier}^{LJ} = \\ \sum_{\mathbf{m}} \sum_{t_1} \sum_{t_2 \in M_t} \beta_{LJ}^{t_1 t_2}(\mathbf{k_m}) \Bigg\{ \quad & \left[\left(2C_{\mathbf{m}}^{t_1(+++)} + \Delta C_{\mathbf{m}}^{t_1(+++)} \right) \Delta C_{\mathbf{m}}^{t_2(+++)} + \left(2S_{\mathbf{m}}^{t_1(+++)} + \Delta S_{\mathbf{m}}^{t_1(+++)} \right) \Delta S_{\mathbf{m}}^{t_2(+++)} \right] \\ \mathrm{sgn}(m_y) \cdot \quad & \left[\left(2C_{\mathbf{m}}^{t_1(+-+)} + \Delta C_{\mathbf{m}}^{t_1(+-+)} \right) \Delta C_{\mathbf{m}}^{t_2(+-+)} + \left(2S_{\mathbf{m}}^{t_1(+-+)} + \Delta S_{\mathbf{m}}^{t_1(+-+)} \right) \Delta S_{\mathbf{m}}^{t_2(+-+)} \right] \\ \mathrm{sgn}(m_z) \cdot \quad & \left[\left(2C_{\mathbf{m}}^{t_1(++-)} + \Delta C_{\mathbf{m}}^{t_1(++-)} \right) \Delta C_{\mathbf{m}}^{t_2(++-)} + \left(2S_{\mathbf{m}}^{t_1(++-)} + \Delta S_{\mathbf{m}}^{t_1(++-)} \right) \Delta S_{\mathbf{m}}^{t_2(++-)} \right] \\ \mathrm{sgn}(m_y m_z) \cdot \quad & \left[\left(2C_{\mathbf{m}}^{t_1(+--)} + \Delta C_{\mathbf{m}}^{t_1(+--)} \right) \Delta C_{\mathbf{m}}^{t_2(+--)} + \left(2S_{\mathbf{m}}^{t_1(+--)} + \Delta S_{\mathbf{m}}^{t_1(+--)} \right) \Delta S_{\mathbf{m}}^{t_2(+--)} \right] \Bigg\} \end{aligned} \tag{377}$$

10 The Algorithm

Using the derivations done in the previous section, we can write the following Mote Carlo Move algorithm:

1. Select the molecule M.
2. Calculate $[U_{real}]_M^{old}$.
3. Calculate $[S_{\mathbf{m}}]_M$, $[C_{\mathbf{m}}]_M$ and $[S_{\mathbf{m}}^t]_M$, $[C_{\mathbf{m}}^t]_M$ for $t \in T(M)$
4. Calculate the forces
5. Select the new position of the molecule
6. Calculate $[U_{real}]_M^{new}$
7. $\Delta U_{real} = [U_{real}]_M^{new} - [U_{real}]_M^{old}$
8. Calculate $[S_{\mathbf{m}}]_M^{new}$, $[C_{\mathbf{m}}]_M^{new}$ and $[S_{\mathbf{m}}^t]_M^{new}$, $[C_{\mathbf{m}}^t]_M^{new}$ for $t \in T(M)$
9. $\Delta C, S_{\mathbf{m}} = [C, S_{\mathbf{m}}]_M^{new} - [C, S_{\mathbf{m}}]_M$
   $$\Delta C, S_{\mathbf{m}}^t = \begin{cases} [C, S_{\mathbf{m}}^t]_M^{new} - [C, S_{\mathbf{m}}^t]_M, & t \in T(M) \\ 0, & t \notin T(M) \end{cases}$$
10. Calculate $\Delta U_{fourier}^C$, $\Delta U_{fourier}^{LJ}$
11. $\Delta U_{fourier} = \Delta U_{fourier}^C + \Delta U_{fourier}^{LJ}$
12. Calculate new forces (needed to decide about acception/decination the move)
13. Accept or decline the move
14. **if** accepted **then** update the sums:
    $$[C, S_{\mathbf{m}}]^{new} = C, S_{\mathbf{m}} + \Delta C, S_{\mathbf{m}}$$
    $$[C, S_{\mathbf{m}}^t]^{new} = \begin{cases} C, S_{\mathbf{m}}^t + \Delta C, S_{\mathbf{m}}^t & t \in T(M) \\ C, S_{\mathbf{m}}^t & t \notin T(M) \end{cases}$$

However, the algorithm can be accelerated a little-bit. Indeed, we can save the time needed for computation of the forces and the energies in the real space. The real-space sum can be defined in a following way:

$$U_{real} = \frac{1}{2} \sum_{sj\mathbf{n}} u_{sj}(|\mathbf{r}_{sj;\mathbf{n}}|)$$

where

$$u_{sj}(r) = q_s q_j \psi^C(r) + 4\epsilon_{sj}(\sigma_{sj}^{12}\psi^{12}(r) + \sigma_{sj}^6\psi^6(r))$$

$$\psi^C(r) = \frac{\operatorname{erfc}(\alpha r)}{r}$$

$$\psi^w(r) = \frac{e^{-\alpha^2 r^2}}{r^w} C_w(r)$$

$$C_w(r) = \sum_{l=0}^{w/2-1} \frac{(\alpha r)^{2l}}{l!}$$

We can re-write the sum in a following form:

$$U_{real} = \frac{1}{2} \sum_j u_j$$

where

$$u_j = \sum_{s;\mathbf{n}} u_{sj}(|\mathbf{r}_{sj;\mathbf{n}}|)$$

Then if the molecule M moves, we need to update the sums:

$$U_{real}^{new} = U_{real} + \Delta U_{real}$$

where

$$\Delta U_{real} = [U_{real}]_M^{new} - [U_{real}]_M$$

$$[U_{real}]_M^{new} = \sum_{j \in M} \sum_{s;\mathbf{n}} u_{sj}(|\mathbf{r}_{sj;\mathbf{n}}^{new}|) = \sum_{j \in M} u_j^{new}$$

$$[U_{real}]_M = \sum_{j \in M} u_j$$

So, if u_j are stored, then to calculate the potential energy difference in a real space we only need to re-calculate u_j^{new} for $j \in M$ which is NN_M operations where N_M is number of atoms in the molecule. Note, that in calculation of u_j we can avoid summation of the inter-molecular contributions, because the molecules are rigid and thus the total inter-molecular contributions are constant (do not change after the move). Let $M(j)$ be the molecule which contains the atom j. Then we define

$$u_j \equiv \sum_{s \notin M(j);\mathbf{n}} u(r_{sj;\mathbf{n}}) \qquad u_j^{new} \equiv \sum_{s \notin M(j);\mathbf{n}} u(r_{sj;\mathbf{n}}^{new})$$

However, if the move is accepted, we need then to update the u_j. To do this, let's look at u_j where $j \notin M$:

$$u_j^{new} = \sum_{s \notin M;\mathbf{n}} u(|\mathbf{r}_{sj;\mathbf{n}}|) + \sum_{s \in M;\mathbf{n}} u(|\mathbf{r}_{sj;\mathbf{n}}^{new}|) = u_j + [u_j]_M^{new} - [u_j]_M$$

where

$$[u_j]_M = \sum_{s \in M;\mathbf{n}} u(|\mathbf{r}_{sj;\mathbf{n}}|)$$

$$[u_j]_M^{new} = \sum_{s \in M;\mathbf{n}} u(|\mathbf{r}_{sj;\mathbf{n}}^{new}|)$$

The same with forces. The real-space force acting at atom p can be written as

$$\mathbf{F}_p = \sum_{j;\mathbf{n}} f_{pj}(\mathbf{r}_{pj;\mathbf{n}}) \qquad (378)$$

where

$$f_{pj}(\mathbf{r}) = \Big(q_p q_j F_R^C(|\mathbf{r}|) + F_R^{LJ(p,j)}(|\mathbf{r}|)\Big) \circ \mathbf{r}$$

where F_R^C, $F_R^{LJ(p,j)}$ are defined by (308) and (329) and $\circ$ means a point-wise multiplication. Then, if the molecule M moves, the new forces can be written as follows:

$$\mathbf{F}_p^{new} = \begin{cases} \sum\limits_{j\notin M,\mathbf{n}} f_{pj}(\mathbf{r}_{pj;\mathbf{n}}^{new}) & p \in M \\ \sum\limits_{j\notin M,\mathbf{n}} f_{pj}(\mathbf{r}_{pj;\mathbf{n}}) + \sum\limits_{j\in M,\mathbf{n}} f_{pj}(\mathbf{r}_p - \mathbf{r}_j^{new} + \mathbf{n}\circ\mathbf{L}) & p \notin M \end{cases}$$

For $p \in M$ we do take sum over $j \notin M$, because we assume that the molecule is rigid, thus the inter-molecular forces should compensate itself. Considering that the sum is over all $\mathbf{n} \in \mathbb{Z}^3$ we can change $\mathbf{n} \to -\mathbf{n}$ and re-write the second sum in case $p \notin M$ as follows:

$$[\mathbf{F}_p]_M^{new} \equiv \sum_{j\in M,\mathbf{n}} f_{pj}(\mathbf{r}_p - \mathbf{r}_j^{new} + \mathbf{n}\circ\mathbf{L}) = \sum_{j\in M,\mathbf{n}} f_{pj}(\mathbf{r}_p - \mathbf{r}_j^{new} - \mathbf{n}\circ\mathbf{L}) = \sum_{j\in M;\mathbf{n}} f_{pj}(-\mathbf{r}_{jp;\mathbf{n}}^{new})$$

where $\mathbf{r}_{jp;\mathbf{n}}^{new} = \mathbf{r}_j^{new} - \mathbf{r}_p + \mathbf{n}\circ\mathbf{L}$. We also can represent the sum over $j \notin M$ as a difference of a full sum (378) and the sum over $j \in M$ (again sum over $\mathbf{n}$ is equivalent to sum over $-\mathbf{n}$:

$$\sum_{j\notin M,\mathbf{n}} f_{pj}(\mathbf{r}_{pj;\mathbf{n}}) = \mathbf{F}_p - \sum_{j\in M,\mathbf{n}} f_{pj}(\mathbf{r}_p - \mathbf{r}_j - \mathbf{n}\circ\mathbf{L})$$

$$= \mathbf{F}_p - \sum_{j\in M,\mathbf{n}} f_{pj}(-(\mathbf{r}_j - \mathbf{r}_p + \mathbf{n}\circ\mathbf{L})) = \mathbf{F}_p - [\mathbf{F}_p]_M$$

where

$$[\mathbf{F}_p]_M \equiv \sum_{j\in M,\mathbf{n}} f_{pj}(-(\mathbf{r}_j - \mathbf{r}_p + \mathbf{n}\circ\mathbf{L})) = \sum_{j\in M,\mathbf{n}} f_{pj}(-\mathbf{r}_{jp;\mathbf{n}})$$

Then for $p \notin M$ we can write

$$\mathbf{F}_p^{new} = \mathbf{F}_p + [\mathbf{F}_p]_M^{new} - [\mathbf{F}_p]_M$$

We note, also, that some actions better do in connection. For example, calculation of forces is better do with the calculation of the energy, because the formulae for their calculation has many common parts (and thus calculations can be accelerated by their re-useage). With these additions, the algorithm can be re-written as follows:

Input:

- $\mathbf{r}_j$ for $j = 1 \ldots N$
- u_j, $\mathbf{F}_j$, for all $j = 1 \ldots N$
- $C_\mathbf{m}$ $S_\mathbf{m}$ $C_\mathbf{m}^t$ $S_\mathbf{m}^t$ for all $\mathbf{m} \in \mathbb{Z}^3$ for all $t = 1 \ldots N_t$ where $2\pi|\mathbf{m}|/L < K_{max}$

Output:
If accepted:

- Selected molecule M
- $\mathbf{r}_j^{new}$ for $j \in M$
- u_j^{new}, $\mathbf{F}_j^{new}$, for all $j = 1 \ldots N$

- $[C_{\mathbf{m}}]^{new}$ $[S_{\mathbf{m}}]^{new}$ $[C^t_{\mathbf{m}}]^{new}$ $[S^t_{\mathbf{m}}]^{new}$ for all $\mathbf{m} \in \mathbb{Z}^3$ for all $t = 1 \dots N_t$

Algorithm:

1. Select the molecule M.
2. $[U_{real}]^{old}_M = \sum_{j \in M} u_j$.
3. Calculate $[S_{\mathbf{m}}]_M$, $[C_{\mathbf{m}}]_M$ and $[S^t_{\mathbf{m}}]_M$, $[C^t_{\mathbf{m}}]_M$ for $t \in T(M)$
4. Calculate total force and total torque of the molecule M:
$$\mathbf{F}^M = \sum_{j \in M} \mathbf{F}_j \qquad \boldsymbol{\tau}^M = \sum_{j \in M} \mathbf{d}_j \times \mathbf{F}_j$$
where $\mathbf{d}_j = \mathbf{r}_j - \mathbf{R}^M_C$, $\mathbf{R}^M_C$ is the center of mass of the molecule.
5. Select the new position of the molecule
6. For $p \in M$, $j \notin M$ calculate
   - $u^{new}_p = \sum_{j \notin M; \mathbf{n}} u_{pj}(r^{new}_{pj;\mathbf{n}})$
   - $[u_j]^{new}_M = \sum_{p \in M} u_{pj}(r_{pj;\mathbf{n}})$
   - $[U_{real}]^{new}_M = \sum_{p \in M} u^{new}_p$
   - $\mathbf{F}^{new}_p = \sum_{j \notin M} f_{pj}(\mathbf{r}^{new}_{pj;\mathbf{n}})$
   - $[\mathbf{F}_j]^{new}_M = \sum_{p \in M} f_{pj}(-\mathbf{r}^{new}_{jp;\mathbf{n}})$
7. $\Delta U_{real} = [U_{real}]^{new}_M - [U_{real}]^{old}_M$
8. Calculate $[S_{\mathbf{m}}]^{new}_M$, $[C_{\mathbf{m}}]^{new}_M$ and $[S^t_{\mathbf{m}}]^{new}_M$, $[C^t_{\mathbf{m}}]^{new}_M$ for $t \in T(M)$
9. $\Delta C, S_{\mathbf{m}} = [C, S_{\mathbf{m}}]^{new}_M - [C, S_{\mathbf{m}}]_M$
$$\Delta C, S^t_{\mathbf{m}} = \begin{cases} [C, S^t_{\mathbf{m}}]^{new}_M - [C, S^t_{\mathbf{m}}]_M, & t \in T(M) \\ 0, & t \notin T(M) \end{cases}$$
10. Calculate $\Delta U^C_{fourier}$, $\Delta U^{LJ}_{fourier}$
11. $\Delta U_{fourier} = \Delta U^C_{fourier} + \Delta U^{LJ}_{fourier}$
12. Calculate new forces and torques for molecule M:
$$\mathbf{F}^M_{new} = \sum_{j \in M} \mathbf{F}^{new}_j \qquad \boldsymbol{\tau}^M_{new} = \sum_{j \in M} \mathbf{d}_j \times \mathbf{F}^{new}_j$$
13. Accept or decline the move

14. **if** accepted **then**:

   (a) Update k-space sums: $[C,S_{\mathbf{m}}]^{new} = C,S_{\mathbf{m}} + \Delta C,S_{\mathbf{m}}$
   $$[C,S^t_{\mathbf{m}}]^{new} = \begin{cases} C,S^t_{\mathbf{m}} + \Delta C,S^t_{\mathbf{m}} & t \in T(M) \\ C,S^t_{\mathbf{m}} & t \notin T(M) \end{cases}$$

   (b) For $j \notin M$ calculate

   - $[u_j]_M = \sum_{p\in M;\mathbf{n}} u(\mathbf{r}_{pj;\mathbf{n}})$
   - $[\mathbf{F}_j]_M = \sum_{p\in M;\mathbf{n}} f_{pj}(-\mathbf{r}_{jp;\mathbf{n}})$

   (c) For $j \notin M$ update u_j,$\mathbf{F}_j$:
   $u_j^{new} = u_j + [u_j]_M^{new} - [u_j]_M \qquad \mathbf{F}_j^{new} = \mathbf{F}_j + [\mathbf{F}_j]_M^{new} - [\mathbf{F}_j]_M$

References

[1] M. P. Allen and D. J. Tildesley. *Computer Simulation of Liquids*. Oxford University Press, 1991.

[2] Donald E. Williams. Accelerated convergence of crystal-lattice potential sums. *Acta Crystallographica Section A*, 27:452–455, 1971.

[3] Naoki Karasawa and William A. Goddard III. Acceleration of convergence for lattice sums. *J. Phys. Chem.*, 93:7320–7327, 1989.

[4] B. R. A. Nijboer and F. W. de Wette. On the calculation of lattice sums. *Physica*, 23:309–321, 1957.

[5] Daan Frenkel and Berend Smit. *Understanding Molecular Simulations*. Academic Press, 2002.