Ewald summation in practice

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1 Problem statement

The Coulomb energy of N charges $q_1, \ldots q_N$ at positions $\mathbf{r}_1, \ldots \mathbf{r}_N$ is

$$E = \frac{1}{4\pi\epsilon_0} \frac{1}{2} {\sum_{i,j}}' \frac{q_i q_j}{|\mathbf{r}_{ij}|}, \tag{1}$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and ϵ_0 is the vacuum permittivity. The factor of $1/2$ counteracts double counting over ion pairs, i and j. The prime notation in ${\sum}'$ indicates that infinite self interactions, where $i = j$, are to be excluded from the sum.

Now consider a finite size system with periodic boundary conditions. The system volume can be any parallelpiped, but for simplicity let us here assume a cubic system with linear size L. Equation (1) generalizes to a sum over all pairs of atoms, *including* all periodic images of the system ($\mathbf{n} \in \mathbb{Z}^3$). The energy of one system image is formally written,

$$E = \frac{1}{4\pi\epsilon_0} \sum_{\mathbf{n}} \frac{1}{2} {\sum_{i,j}}' \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|} \quad \text{(p.b.c.)}. \tag{2}$$

It is necessary to enforce charge neutrality,

$$Q = \sum_i q_i = 0, \tag{3}$$

to avoid a strong divergence in the sum over images $\mathbf{n}$. If the net dipole moment,

$$\mathbf{P} = \sum_i \mathbf{r}_i q_i, \tag{4}$$

is nonzero, then the sum in Eq. (2) is still only conditionally convergent. To understand this intuitively, consider that two system images, separated by a large distance $r = |\mathbf{n}L|$, effectively interact via their net dipoles. Dipole-dipole interactions decay like r^{-3}. At large distances r, the sum over $\mathbf{n} \in \mathbb{Z}^3$ can effectively be approximated as an integral, $\sum_{\mathbf{n}} (\cdot) \to \int_{\mathbb{R}^3} (\cdot) r^2 d\mathbf{r}$. If we naïvely insert cubic decay for dipole-dipole interactions, $(\cdot) \to r^{-3}$, it appears that there is

logarithmic divergence. A more careful analysis should include also the angular dependence of dipole-dipole interactions; in this case, Eq. (2) can converge, but the result depends on the order of summation over $\mathbf{n}$. Any real material sample will have finite volume, and the conditional convergence highlights the importance of surface boundary effects, e.g., the geometry of the finite sample.

Ewald summation is a way to regularize the infinite sum of Eq. (2) and give it a particular meaning. Its derivation involves a series of formal manipulations.

2 Preliminaries

To set the stage, first consider the case of a single point charge q at the origin. In continuum language, this is a Dirac-δ charge distribution,

$$\rho(\mathbf{r}) = q\delta(\mathbf{r}). \tag{5}$$

The Ewald method will effectively decompose this distribution as,

$$\begin{aligned} \rho(\mathbf{r}) &= \rho^L(\mathbf{r}) + \rho^S(\mathbf{r}) \\ &= qG(\mathbf{r}) + [\rho(\mathbf{r}) - qG(\mathbf{r})]. \end{aligned}$$

The first term $\rho^L(\mathbf{r})$ is a Gaussian smoothing of the original point-charge, where

$$G(\mathbf{r}) = \frac{1}{\sigma^3(2\pi)^{3/2}} \exp\left[-r^2/2\sigma^2\right], \tag{6}$$

and $r = |\mathbf{r}|$. The length scale σ is a tuneable parameter, and will eventually be adjusted to optimize numerical efficiency.

The smoothed charge distribution $\rho^L(\mathbf{r})$ is useful because it produces an accurate electrostatic potential at *long* ranges. In general, the potential $\varphi(\mathbf{r})$ associated with an arbitrary charge density $\rho(\mathbf{r})$ is defined to satisfy,

$$\epsilon_0 \nabla^2 \varphi(\mathbf{r}) = -\rho(\mathbf{r}), \tag{7}$$

or equivalently,

$$\varphi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'. \tag{8}$$

For a point charge, $\rho(\mathbf{r}) \to q\delta(\mathbf{r})$, the solution is

$$\varphi(\mathbf{r}) = \frac{q}{4\pi\epsilon_0 r}. \tag{9}$$

For the Gaussian cloud, $\rho(\mathbf{r}) \to qG(\mathbf{r})$, the solution is instead,

$$\varphi^L(\mathbf{r}) = \frac{q}{4\pi\epsilon_0 r} \text{erf}\left(\frac{r}{\sqrt{2}\,\sigma}\right). \tag{10}$$

The error function erf(x) converges to 1 very rapidly when $x \gg 1$; this confirms that $\varphi^L(\mathbf{r})$ rapidly converges to $\varphi(\mathbf{r})$ at long range. The deviations are only significant at *short* range,

$$\varphi^S(\mathbf{r}) = \frac{q}{4\pi\epsilon_0 r} \mathrm{erfc}\left(\frac{r}{\sqrt{2}\,\sigma}\right), \tag{11}$$

where $\mathrm{erfc(x)} = 1 - \mathrm{erf(x)}$. By construction,

$$\varphi(\mathbf{r}) = \varphi^L(\mathbf{r}) + \varphi^S(\mathbf{r}), \tag{12}$$

exactly.

Note that the potential for a Gaussian charge cloud is smooth everywhere, including the origin. Using

$$\lim_{x \to 0} \mathrm{erf}(x) = 2x/\sqrt{\pi}, \tag{13}$$

one finds,

$$\lim_{|\mathbf{r}| \to 0} \varphi^L(\mathbf{r}) = \frac{q}{4\pi\epsilon_0} \sqrt{\frac{2}{\pi}} \frac{1}{\sigma}. \tag{14}$$

3 Energy decomposition

Now we return to the full periodic Coulomb energy of Eq. (2). Upon rearranging terms, it can be written

$$E = \frac{1}{2} \sum_i q_i \phi_i', \tag{15}$$

where

$$\phi_i' = \frac{1}{4\pi\epsilon_0} {\sum_{j,\mathbf{n}}}' \frac{q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|}, \tag{16}$$

is a formal sum (only conditionally convergent) giving the electrostatic potential at $\mathbf{r}_i$, as generated by all ions j and their $\mathbf{n}$th periodic images. As before, the prime in $\sum'$ indicates that we are excluding the infinite self-potential when $j = i$ and $\mathbf{n} = (0,0,0)$.

In analogy with Eq. (12), one may decompose ϕ_i' into long and short range parts. For convenience, we will also add and subtract the electrostatic potential for the center of the ith Gaussian charge cloud, Eq. (14). The final decomposition to be used by Ewald is,

$$\phi_i' = \phi_i^L + \phi_i'^S - \frac{q_i}{4\pi\epsilon_0} \sqrt{\frac{2}{\pi}} \frac{1}{\sigma}, \tag{17}$$

where

$$\phi_i^L = \frac{1}{4\pi\epsilon_0} \sum_{j,\mathbf{n}} \frac{q_j}{r_{ij\mathbf{n}}} \mathrm{erf}\left(\frac{r_{ij\mathbf{n}}}{\sqrt{2}\,\sigma}\right) \tag{18}$$

$$\phi_i'^S = \frac{1}{4\pi\epsilon_0} {\sum_{j,\mathbf{n}}}' \frac{q_j}{r_{ij\mathbf{n}}} \mathrm{erfc}\left(\frac{r_{ij\mathbf{n}}}{\sqrt{2}\,\sigma}\right), \tag{19}$$

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and for convenience,
$$r_{ij\mathbf{n}} = |\mathbf{r}_j + \mathbf{n}L - \mathbf{r}_i|. \tag{20}$$
The prime in $\phi_i'^S$ is a reminder that the divergent term involving $r_{ij\mathbf{n}} = 0$ is excluded from the sum. Note, however, that the definition of ϕ_i^L involves an unrestricted sum, *including* the case where $r_{ij\mathbf{n}} = 0$. This self-contribution to ϕ_i^L is canceled by the final term in Eq. (17).

Substituting Eq. (17) into Eq. (2) yields the desired decomposition of energy,
$$E = E_L + E_S - E_{\text{self}}, \tag{21}$$

with

$$E_L = \frac{1}{2} \sum_{i,\mathbf{n}} q_i \phi_i^L \tag{22}$$

$$E_S = \frac{1}{4\pi\epsilon_0} \frac{1}{2} {\sum_{i,j,\mathbf{n}}}' \frac{q_i q_j}{r_{ij\mathbf{n}}} \text{erfc}\left(\frac{r_{ij\mathbf{n}}}{\sqrt{2}\,\sigma}\right) \tag{23}$$

$$E_{\text{self}} = \frac{1}{4\pi\epsilon_0} \frac{1}{\sqrt{2\pi}\,\sigma} \sum_i q_i^2. \tag{24}$$

The term E_S involves real-space sum over pair-interactions that decay rapidly with distance $r_{ij\mathbf{n}}$. The term E_L captures the long-range part of Coulomb interactions, to be discussed in the next section.

3.1 Fourier space treatment of long-range interactions

The steps so far have involved only rearrangements of the energy contributions. It remains now to give precise meaning to the long-range Coulomb interactions E_L.

The electrostatic potential $\phi_i^L = \phi^L(\mathbf{r}_i)$ involves a sum over periodic images, Eq. (18), which is only conditionally convergent. The solution Eq. (10) to (7) suggests an alternative starting point: we can *define* the long-range potential $\phi^L(\mathbf{r})$ as a solution to the Poisson equation,
$$\epsilon_0 \nabla^2 \phi^L(\mathbf{r}) = -\sum_{j,\mathbf{n}} q_j G(\mathbf{r}_j + \mathbf{n}L - \mathbf{r}), \tag{25}$$

subject to periodic boundary conditions. The right-hand side is a convolution,
$$\epsilon_0 \nabla^2 \phi^L(\mathbf{r}) = -\rho(\mathbf{r}) * G(\mathbf{r}), \tag{26}$$

involving the charge density field for all ion images,
$$\rho(\mathbf{r}) = \sum_{j,\mathbf{n}} q_j \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{n}L), \tag{27}$$

and the Gaussian kernel defined in Eq. (6). Taking the Fourier transform of both sides of Eq. (25) and using the convolution theorem, one finds
$$\hat{\phi}^L(\mathbf{k}) = \frac{1}{\epsilon_0 k^2} \hat{\rho}(\mathbf{k}) \hat{G}(\mathbf{k}). \tag{28}$$

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The Fourier transform of charge density is

$$\hat{\rho}(\mathbf{k}) = \int e^{-i\mathbf{k}\cdot\mathbf{r}}\rho(\mathbf{r})d\mathbf{r} = \sum_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}q_j. \tag{29}$$

The Fourier transform of the Gaussian kernel is another Gaussian,

$$\hat{G}(\mathbf{k}) = e^{-\sigma^2 k^2/2}. \tag{30}$$

Parseval's theorem states that the long-range energy can be expressed as a integral over either real space or Fourier space,

$$E_L = \frac{1}{2}\int \rho(\mathbf{r})\phi^L(\mathbf{r})d\mathbf{r} = \frac{1}{2V}\sum_{\mathbf{k}\neq\mathbf{0}}\hat{\rho}(-\mathbf{k})\hat{\phi}^L(\mathbf{k}), \tag{31}$$

where $V = L^3$ is the system volume. The sum on the right is over all wave vectors with appropriate periodicity, i.e. $k_\alpha = 2\pi n_\alpha/L$ for integer n_α. Charge neutrality implies $\hat{\rho}(\mathbf{0}) = \sum_j q_i = 0$, and it is reasonable to also impose $\hat{\phi}^L(\mathbf{0}) = \sum_i \phi(\mathbf{r}_i) = 0$ on the solution of Eq. (25). This choice justifies excluding $\mathbf{k} = \mathbf{0}$ from the Fourier space sums.

Collecting results,

$$E_L = \frac{1}{2V\epsilon_0}\sum_{\mathbf{k}\neq\mathbf{0}}\frac{e^{-\sigma^2 k^2/2}}{k^2}\left|\hat{\rho}(\mathbf{k})\right|^2. \tag{32}$$

Note that $\hat{\rho}(-\mathbf{k}) = \hat{\rho}(\mathbf{k})^*$ because the charge density $\rho(\mathbf{r})$ is real.

4   A numerical method

The total Ewald energy of Eq. (21) may be calculated as a sum of real space contributions,

$$E_S = \frac{1}{4\pi\epsilon_0}\frac{1}{2}{\sum_{i,j,\mathbf{n}}}'\frac{q_i q_j}{r_{ij\mathbf{n}}}\mathrm{erfc}\left(\frac{r_{ij\mathbf{n}}}{\sqrt{2}\,\sigma}\right), \tag{33}$$

and Fourier space contributions,

$$E_L = \frac{1}{2V\epsilon_0}\sum_{\mathbf{k}\neq\mathbf{0}}\frac{e^{-\sigma^2 k^2/2}}{k^2}\left|\hat{\rho}(\mathbf{k})\right|^2, \tag{34}$$

involving the Fourier transform of charge density,

$$\hat{\rho}(\mathbf{k}) = \sum_i q_i e^{-i\mathbf{k}\cdot\mathbf{r}_i}. \tag{35}$$

Finally, one must subtract the self-energy,

$$E_{\mathrm{self}} = \frac{1}{4\pi\epsilon_0}\frac{1}{\sqrt{2\pi}\,\sigma}\sum_i q_i^2. \tag{36}$$

Below, we will discuss how to impose cutoffs on these sums, and how to select an optimal length scale σ.

Although these formulas have been derived in the context of a cubic volume, they continue to hold for a parallelpiped volume spanned by arbitrary lattice vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. In this generalized context, pairwise displacements are

$$\mathbf{r}_{ij\mathbf{n}} = \mathbf{r}_j - \mathbf{r}_i + \sum_\alpha n_\alpha \mathbf{a}_\alpha. \tag{37}$$

The system volume is $V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$. The associated reciprocal lattice vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are defined to satisfy

$$\mathbf{a}_\alpha \cdot \mathbf{b}_\beta = 2\pi \delta_{\alpha\beta}. \tag{38}$$

In real space, the charge density is periodic $\rho(\mathbf{r}_{ij\mathbf{n}}) = \rho(\mathbf{r}_{ij\mathbf{0}})$ for arbitrary cell indices n_1, n_2, n_3. Consequently, the $\mathbf{k}$ vectors contributing to $\hat{\rho}(\mathbf{k})$ must be integer multiples of $\mathbf{b}_\alpha$,

$$\mathbf{k}_\mathbf{m} = \sum_\beta m_\beta \mathbf{b}_\beta. \tag{39}$$

In a numerical implementation, we will truncate the sums of E^S and E^L by imposing upper bounds to the summation

$$r_{ij\mathbf{n}}/\sqrt{2}\sigma \le c_0 \tag{40}$$
$$\sigma k_\mathbf{m}/\sqrt{2} \le c_0. \tag{41}$$

Convergence of the sums will be exponentially fast in the cutoff squared, c_0^2.

It remains to select the parameter σ that optimizes numerical efficiency. Let N denote the number of ions in a system with fixed ion density $\rho_{\mathrm{ion}} = N/V$. Calculating E_S requires iterating over all N ions; each ion interacts with order $\rho_{\mathrm{ion}} r_{\mathrm{cut}}^3$ neighbors, where $r_{\mathrm{cut}} \sim c_0 \sigma$. At large N, the total cost of this real space summation is

$$\mathcal{C}_S \cong \chi_S N \sigma^3, \tag{42}$$

with some prefactor $\chi_S \propto \rho_{\mathrm{ion}} c_0^3$.

Calculating E_L requires summing over a discrete set of Fourier modes, Eq. (39), up to a maximum of $k_{\mathrm{cut}} \sim m_{\mathrm{cut}}/L \sim c_0/\sigma$. The maximum cutoff index scales as $m_{\mathrm{cut}} \sim cL/\sigma$, and the total number of modes scales as $m_{\mathrm{cut}}^3 \sim c_0^3 V/\sigma$. For each mode $\mathbf{k}$, one must calculate $\hat{\rho}(\mathbf{k})$ in Eq. (35) by summing over all N ions. The asymptotic cost of this Fourier space summation is

$$\mathcal{C}_L \cong \chi_L N^2/\sigma^3, \tag{43}$$

with some prefactor $\chi_L \propto \rho_{\mathrm{ion}}^{-1} c_0^3$.

The length σ that minimizes the total cost $\mathcal{C}_S + \mathcal{C}_L$ satisfies

$$\sigma^3 = \sqrt{N\frac{\chi_L}{\chi_S}}, \tag{44}$$

With this choice, the cost is equally weighted between real and Fourier space, $\mathcal{C}_S = \mathcal{C}_L = N^{3/2}\sqrt{\chi_L \chi_S}$, and we observe the scaling,

$$\mathcal{C}_S + \mathcal{C}_L \propto N^{3/2}. \tag{45}$$

Reinserting the dependence ion density, ($\chi_S \propto \rho_{\text{ion}}$ and $\chi_L \propto \rho_{\text{ion}}^{-1}$), one finds

$$\sigma = \frac{L}{c_1 N^{1/6}}, \tag{46}$$

where $L \propto V^{1/3}$. The constant c_1 should be selected according to implementation details, specifically the relative costs of real and Fourier space summation.

To summarize, the Ewald method is controlled by two dimensionless parameters:

1. $c_0 \approx 4$ (maybe), which controls accuracy. The error decays exponentially in c_0^2.

2. $c_1 \approx 2$ (maybe); larger values make σ smaller, and shift more work to the Fourier space sum. *To select c_1 optimally, one must equally balance real and Fourier space costs.*

5 Inclusion of dipoles

5.1 Review: from charges to dipoles

To understand dipole interactions, one can start with the electrostatic potential of two charges q_i and q_j,

$$E_{\text{cc}} = \frac{q_i q_j}{4\pi\epsilon_0} \frac{1}{r_{ij}}, \tag{47}$$

where $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$. A point dipole $\mathbf{p}_j$ can be modeled as two competing charges $q_j = \pm 1/\varepsilon$, displaced by $\pm\varepsilon\mathbf{p}_j$, for $\varepsilon \to 0$. The charge-dipole interaction energy is therefore

$$E_{\text{cd}} = \frac{q_i}{4\pi\epsilon_0} \lim_{\varepsilon\to 0} \frac{1}{\varepsilon} \left(\frac{1}{|(\mathbf{r}_j + \epsilon\mathbf{p}_j) - \mathbf{r}_i|} - \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} \right). \tag{48}$$

This is a directional derivative,

$$E_{\text{cd}} = \frac{q_i(-\mathbf{p}_j \cdot \nabla_j)}{4\pi\epsilon_0} \frac{1}{r_{ij}} = \frac{q_i}{4\pi\epsilon_0} \frac{\mathbf{p}_j \cdot \hat{\mathbf{r}}_{ij}}{r_{ij}^2}, \tag{49}$$

where ∇_j denotes the gradient with respect to $\mathbf{r}_j$. Now consider a system of two dipoles, $\mathbf{p}_i$ and $\mathbf{p}_j$. Iterating the same perturbation procedure on the charge $q_i = \pm 1/\epsilon$, the resulting energy is,

$$E_{\text{dd}} = \frac{(-\mathbf{p}_i \cdot \nabla_i)(-\mathbf{p}_j \cdot \nabla_j)}{4\pi\epsilon_0} \frac{1}{r_{ij}}$$

$$= \frac{1}{4\pi\epsilon_0} \left[\frac{\mathbf{p}_i \cdot \mathbf{p}_j - 3(\mathbf{p}_j \cdot \hat{\mathbf{r}}_{ij})(\mathbf{p}_i \cdot \hat{\mathbf{r}}_{ij})}{r_{ij}^3} \right] + \cancel{\delta(\mathbf{r}_{ij})} \frac{\mathbf{p}_i \cdot \mathbf{p}_j}{3\epsilon_0}. \tag{50}$$

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The first term is recognized as the usual dipole-dipole energy. The second term disappears when $\mathbf{r}_i \neq \mathbf{r}_j$, as we will assume.

The general procedure to introduce a point dipole $\mathbf{p}_i$ along with every charge q_i is to substitute

$$q_i \to q_i - \mathbf{p}_i \cdot \nabla_i, \tag{51}$$

into the energy formula, e.g. Eq. (2). This procedure continues to work for the Ewald energy of Eqs. (33)–(35).

5.2   Short range part

Following this substitution procedure, the local interactions of Eq. (33) become

$$
\begin{aligned}
E_S &= \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sideset{}{'}\sum_{i,j,\mathbf{n}} (q_i + \mathbf{p}_i \cdot \nabla_j)(q_j - \mathbf{p}_j \cdot \nabla_j)\frac{\mathrm{erfc}\left(\frac{r_{ij\mathbf{n}}}{\sqrt{2}\,\sigma}\right)}{r_{ij\mathbf{n}}} \\
&= \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sideset{}{'}\sum_{i,j,\mathbf{n}} \Bigg[q_i q_j \mathcal{E}_{\mathrm{cc}}(\mathbf{r}_{ij\mathbf{n}}) \\
&\qquad + (q_i \mathbf{p}_j - \mathbf{p}_i q_j) \cdot \overrightarrow{\mathcal{E}}_{\mathrm{cd}}(\mathbf{r}_{ij\mathbf{n}}) \\
&\qquad + (\mathbf{p}_i \otimes \mathbf{p}_j) : \overleftrightarrow{\mathcal{E}}_{\mathrm{dd}}(\mathbf{r}_{ij\mathbf{n}}) \Bigg].
\end{aligned}
\tag{52}
$$

We have used $\nabla_i = -\nabla_j$, which follows from the definition in Eq. (35).

Charge-charge interaction scalar is as before,

$$\mathcal{E}_{\mathrm{cc}}(\mathbf{r}) = \frac{\mathrm{erfc}\left(\frac{r}{\sqrt{2}\,\sigma}\right)}{r}. \tag{53}$$

Charge-dipole interaction vector is

$$
\begin{aligned}
\overrightarrow{\mathcal{E}}_{\mathrm{cd}}(\mathbf{r}) &= -\nabla \frac{\mathrm{erfc}\left(\frac{r}{\sqrt{2}\,\sigma}\right)}{r} \\
&= \frac{\hat{\mathbf{r}}}{r^2} \left[\mathrm{erfc}\left(\frac{r}{\sqrt{2}\,\sigma}\right) + \sqrt{\frac{2}{\pi}} \frac{r}{\sigma} e^{-r^2/2\sigma^2} \right]
\end{aligned}
\tag{54}
$$

Finally, dipole-dipole interaction tensor is

$$
\begin{aligned}
\overleftrightarrow{\mathcal{E}}_{\mathrm{dd}}(\mathbf{r}) &= -\nabla \otimes \nabla \frac{\mathrm{erfc}\left(\frac{r}{\sqrt{2}\,\sigma}\right)}{r}. \\
&= \frac{I}{r^3} \left(\mathrm{erfc}\left(\frac{r}{\sqrt{2}\,\sigma}\right) + \sqrt{\frac{2}{\pi}} \frac{r}{\sigma} e^{-r^2/2\sigma^2} \right) \\
&\quad - \frac{3\hat{\mathbf{r}} \otimes \hat{\mathbf{r}}}{r^3} \left[\mathrm{erfc}\left(\frac{r}{\sqrt{2}\,\sigma}\right) + \left(1 + \frac{r^2}{3\sigma^2}\right) \sqrt{\frac{2}{\pi}} \frac{r}{\sigma} e^{-r^2/2\sigma^2} \right],
\end{aligned}
\tag{55}
$$

where I is the identity tensor.

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5.3 Long range part

The long range interactions of Eqs. (34) involve the Fourier transform of the Dirac charge distribution, Eq. (35). Upon applying the substitution of Eq. (51), one gets

$$\hat{\rho}(\mathbf{k}) \to \hat{\rho}_{\text{eff}}(\mathbf{k}) = \sum_j (q_j - \mathbf{p}_j \cdot \nabla_j) e^{-i\mathbf{k}\cdot\mathbf{r}_j}. \tag{56}$$

The long-range energy remains a sum in Fourier space,

$$E_L = \frac{1}{2V\epsilon_0} \sum_{\mathbf{k}\neq\mathbf{0}} \frac{e^{-\sigma^2 k^2/2}}{k^2} |\hat{\rho}'(\mathbf{k})|^2, \tag{57}$$

but now involving both charges and dipoles,

$$\hat{\rho}_{\text{eff}}(\mathbf{k}) = \sum_j (q_j + i\mathbf{p}_j \cdot \mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}_j}. \tag{58}$$

5.4 Self-energy

The above procedure introduces an unphysical dipole self-interaction in Fourier space. To correct for this, the self-energy must include an additional term,

$$E_{\text{self}} = \frac{1}{4\pi\epsilon_0} \left(\frac{1}{\sqrt{2\pi}\,\sigma} \sum_i q_i^2 + \frac{1}{3} \frac{1}{\sqrt{2\pi}\,\sigma^3} \sum_i d_i^2 \right). \tag{59}$$

TODO: DERIVE THIS. A modern reference is https://doi.org/10.1063/1.481216. Rappaport book also includes this term, and its references goes back to de Leeuw ~1980, e.g. Proc. Roy. Soc. Lond. A 373, 57-66 (1980).

6 Effective pair interactions

In the context of simulating model lattice systems, Ewald can be used to precompute the effective interaction between two sites, accounting for all periodic images. The long-range energy expands to

$$E_L = \frac{1}{2V\epsilon_0} \sum_{\mathbf{k}\neq\mathbf{0}} \frac{e^{-\sigma^2 k^2/2}}{k^2} \sum_{ij} (q_i - i\mathbf{p}_i \cdot \mathbf{k})(q_j + i\mathbf{p}_j \cdot \mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}_{ij}}. \tag{60}$$

The short-range part E_S is given in Eq. (52).

Consider, for simplicity, an ordered pair of dipoles $\mathbf{p}_i$ and $\mathbf{p}_j$. The energy for this periodic, pairwise interaction is

$$E_{ij} = \frac{1}{4\pi\epsilon_0} \mathbf{p}_i \cdot \left[\frac{4\pi}{2V} \sum_{\mathbf{k}\neq\mathbf{0}} \frac{e^{-\sigma^2 k^2/2}}{k^2} (\mathbf{k} \otimes \mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}_{ij}} + \sum_{\mathbf{n}} \overset{\leftrightarrow}{\mathcal{E}}_{\text{dd}}(\mathbf{r}_{ij\mathbf{n}}) \right] \cdot \mathbf{p}_j, \tag{61}$$

where $\overleftrightarrow{\mathcal{E}}_{\mathrm{dd}}$ was defined in Eq. (55). A factor of two is required to account for contributions from both E_{ij} and E_{ji}. Similar formulas hold for charge-charge and charge-dipole interactions.