Methods for efficient computer simulations of charged systems

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August 2010

1 1. Introduction

1.1 Electrostatics

We assume N charges $q_i e$ at positions r_i. This corresponds to a charge density

$$\rho e = \sum_{i=1}^{N} q_i e \delta(r - r_i). \tag{1.1}$$

If the charges move slowly, then we can ignore magnetic forces, and the force on each particle is

$$F_i = q_i e E(r_i) \tag{1.2}$$

and the total electrostatic energy

$$U_E = \int \rho(r) e E(r) dr, \tag{1.3}$$

where E is the electrostatic field with the properties

$$\nabla \cdot E = \rho e/\epsilon \tag{1.4}$$

$$\nabla \times E = 0. \tag{1.5}$$

The latter implies that E is the gradient of an up to a constant unique scalar electrostatic potential Φ such that $E = -\nabla\Phi$. Inserting into (1.4) gives

$$-\nabla^2 \Phi = \rho e/\epsilon, \tag{1.6}$$

which is a defining differential equation for Φ. For a single charge, it has the solution:

$$-\nabla^2 \frac{q_i e}{4\pi\epsilon} \frac{1}{r - r_i} = q_i e \delta(r - r_i)/\epsilon \tag{1.7}$$

It is convenient to define the *Bjerrum length*

$$l_\mathrm{B} = \frac{e^2}{4\pi\epsilon k_\mathrm{B} T}, \tag{1.8}$$

which is the distance at which two unit charges feel an electrostatic interaction equal to $1 k_\mathrm{B} T$; this means for example that by spontaneous thermal fluctuations, two oppositely charged unit charges can be separated by a distance up to l_B. The Bjerrum length in water at room temperature is 0.7nm due to its large relative permittivity of $\epsilon/\epsilon_0 \approx 80$.

Then the electrostatic forces and potential are

$$F_i = k_\mathrm{B} T \, l_\mathrm{B} \sum_{j \neq i} \frac{q_i q_j}{|r_i - r_j|^3} (r_i - r_j) \quad \text{and} \quad U_E = \frac{1}{2} k_\mathrm{B} T \, l_\mathrm{B} \sum_{i=1}^{N} \sum_{j \neq i} \frac{q_i q_j}{r_i - r_j}, \tag{1.9}$$

where the (infinite) self interactions of point charges are omitted. The differential equation for Φ is

$$-\nabla^2 \Phi = 4\pi \frac{l_\mathrm{B} k_\mathrm{B} T}{e} \rho. \tag{1.10}$$

In the following, the Bjerrum length and $k_\mathrm{B} T$will be omitted.

1.2 Boundary conditions and conditional convergence

To avoid finite size effects, computer simulations are typically performed with periodic boundary conditions. This means, we consider an infinite set of charges $q_i e$ at positions $r_i + n$, where

$$n = (kl_x, ll_y, ml_z) \quad \forall\, k, l, m \in \mathbb{Z} \tag{1.11}$$

and l_x, l_y, l_z are the periodic cell sizes in the three spatial dimensions. In the following, we use the short notation $n \in l\mathbb{Z}^3$, and $V = l_x \cdot l_y \cdot l_x$ denotes the volume of the periodic cell. We assume *charge neutrality*, that is

$$\sum_{i=1}^{N} q_i = 0. \tag{1.12}$$

We consider the electrostatic energy of the N primary charges with all others, that is

$$U_E = \frac{1}{2} \sum_{i=1}^{N} \sum_{n \in l\mathbb{Z}^3} \sum_{j=1}^{N}{}' \frac{q_i q_j}{r_i - r_j - n}, \tag{1.13}$$

where $'$ denotes that for $n = 0$, the $j = i$-term is omitted. While being the obvious extension of Eqn. (1.9) to a periodic system, this is in fact not a well defined equation. The reason is that the sum is not absolutely convergent; the value of U_E depends on the order of summation over k, l, m. Since we assume that our N particles are representative for the bulk of a large, macroscopic sample that is approximated by the periodic sum, a reasonable choice is a summation in radially ascending shells:

$$U_E = \frac{1}{2} \sum_{i=1}^{N} \sum_{S=0}^{\infty} \sum_{n^2=S} \sum_{j=1}^{N}{}' \frac{q_i q_j}{r_i - r_j - n}. \tag{1.14}$$

Different summation orders are possible, which result in different values for U_E. In addition, U_E can be defined via different routes. For example, one can solve the differential Eqn. (1.10) under periodic boundary conditions, then

$$U_E = \frac{1}{2} \sum_{i=1}^{N} q_i \Phi(r_i). \tag{1.15}$$

This definition of the electrostatic potential is called *intrinsic*. Finally, one can use *convergence factors* to define U_E:

$$U_E := \lim_{\beta \to 0} \frac{1}{2} \sum_{i=1}^{N} \sum_{S=0}^{\infty} f(S, \beta) \sum_{n^2=S} \sum_{j}{}' \frac{q_i q_j}{r_i - r_j - n}, \tag{1.16}$$

where the convergence factor $f(S, \beta)$ has the following properties:

1. $f(S, \beta)$ is a continuous function for $\beta \geq 0$
2. $f(S, 0) = 1$
3. $f(S + 1, \beta) \leq f(S, \beta)$ for all S, β
4. $0 \leq f(S, \beta) \leq 1$ for all S, β.

That is, *formally* we recover the original series for $\beta = 0$. However, if at fixed $\beta > 0$, $f(S, \beta)$ decays fast enough (for example exponentially), then

$$\sum_{S=0}^{\infty} f(S, \beta) \sum_{n^2=S} \sum_{j=1}^{N}{}' \frac{q_i q_j}{r_i - r_j - n}, \tag{1.17}$$

is absolutely convergent and well defined, so that also the limit (1.16) is well defined.

The convergence factor approach is the most general one, since it allows to obtain the same results as the other approaches; we will use this approach to prove some of the methods for evaluating the Coulomb sum. For example, the convergence factor $e^{-\beta S^2}$ corresponds to summation in ascending spherical shells. The convergence factor $e^{-\beta|r+S|^2}$ leads to the intrinsic potential.

However, the difference between summation orders is not as big as expected. Smith has shown that for example

$$U_{\text{spherical}} = U_{\text{intrinsic}} + \frac{2\pi}{3V} M^2 \tag{1.18}$$

$$U_{\text{slabwise}} = U_{\text{intrinsic}} + \frac{2\pi}{V} M_z^2, \tag{1.19}$$

where $U_{\text{spherical}}$ denotes the summation result for summation in ascending shells, U_{slabwise} diskwise summation in two dimensions, and after that symmetric summation in the remaining dimension, and $U_{\text{intrinsic}}$ the intrinsic solution.

Note that the *dipole term* $\frac{2\pi}{3V} M^2$ has in fact a physical interpretation, if written as

$$\frac{2\pi}{(2\epsilon_r' + 1)V} M^2, \tag{1.20}$$

where ϵ_r' is the dielectric permittivity of a medium that is supposed to surround the crystal (remember that we interpret the crystal as growing in ascending shells). For vacuum, $\epsilon_r' = 1$, so that we recover the term as in Eqn. (1.18). Another important value are metallic boundary conditions, for which the term vanishes. In case the system contains free ions, this is the only reasonable boundary condition, since otherwise this term imposes a harmonic potential that drives the particles back to an imaginary central cell.

Note also that for this term the unfolded positions r_i matter. For calculating the energy (1.13), it seems that the position r_i only matter up to multiples of l_x, l_y and l_z. After all, we are investigating a large, periodic crystal, and shifting r_i for example by l_x in the x-direction, the internal structure of the crystal will not change. However, the dipole term will change; moreover, it will be discontinuous, even if particle coordinates are modified only by multiples of l_*. Therefore, it is important to use unfolded, that is continuous coordinates for its calculation.

Instead of three dimensional periodicity, one can also consider two- or onedimensionally periodic systems; this is used for studying inter-/surfaces or wires and nanotubes. One can also generalize the periodicity to non-orthorombic simulation boxes. Another problem arises when for example calculating solvation free energies. In this case, a single charge is added to the system, which consequently becomes non-neutral. As one can easily, the energy of a non-neutral system is necessarily infinite. However, one can assume a homogeneous neutralizing background, which being homogeneous does not generate forces on the particles. Therefore, the dynamics of the system is unbiased by the background. But to calculate the energy, this background is necessary, since otherwise the result depends on the applied method, and even on non-physical tuning parameters.

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2 Ewald method

The Ewald method is *the* classical method for calculating electrostatic interactions in computer simulations with periodic boundary conditions. It dates back to 1921 and was original invented by Ewald to calculate crystal energies, especially the Madelung constant (by hand, not by computer, of course!). By carefully tuning the method parameters, the method nevertheless has a computational scaling of $N^{3/2}$ and is therefore significantly faster than a plain all-with-all N^2-force calculation. Nowadays, there are several other methods scaling like $N \log N$ or even N, but all are much less elegant than the Ewald methods, and have rather large overheads, so that for small systems, Ewald's method is still a good choice. Moreover, unlike its mesh-extensions, the Ewald method converges exponentially, that is to double the amount of valid digits in the result, one just needs to double the computational effort.

The main trick of the Ewald method is to split the two main problems of the Coulomb potential sum - the singularities at the positions of the charges, and the slow decay of the potential, which makes it conditionally convergent. To this aim, the delta distributions that represent the charge densities of the charges are replaced by Gaussian charge clouds of width α^{-1}:

$$q_i \delta(r - r_i) = q_i \left[\delta(r - r_i) - \rho_{\text{Gauss}}(r - r_i)\right] + q_i \, \rho_{\text{Gauss}}(r - r_i) \tag{2.1}$$

where the Gaussian cloud is defined as

$$\rho_{\text{Gauss}}(r) = \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 e^{-\alpha^2 r^2}. \tag{2.2}$$

To make use of this splitting, we calculate the electrostatic energy via the electrostatic potential, that is as

$$U_E = \frac{1}{2} \sum_{j=1}^{N} q_j \Phi(r_j), \tag{2.3}$$

where

$$\Phi(r) = \sum_{j=1}^{N} \sum_{n \in l\mathbb{Z}^3}{}' \frac{q_j}{|r - r_j - n|}. \tag{2.4}$$

The $'$ on the sum denotes that the (infinite) terms with $r = r_j$ are omitted.

Fourier space sum

Although the sum over the Gaussians still leads to an only conditionally convergent sum, we can however solve the differential equation for the electrostatic potential, since unlike the original charge distribution, the Gaussians are smooth, and (1.10) can be solved for a periodic and smooth solution. Such a function can be conventiently represented as Fourier series:

$$f(r) = \frac{1}{l^3} \sum_{k \in \frac{2\pi}{l}\mathbb{Z}^3} \hat{f}(k) e^{ikr}, \tag{2.5}$$

where

$$\hat{f}(k) = \int_V dr \, f(r) e^{-ikr} \tag{2.6}$$

is the Fourier transform of f. Note that for simplicity we assume a cubic periodic cell V of size $l \times l \times l$. Since for any smooth periodic function

$$\nabla_r f(r) = \frac{1}{l^3} \sum_{k \in \frac{2\pi}{l}\mathbb{Z}^3} \hat{f}(k) \nabla_r e^{ikr} = \frac{1}{l^3} \sum_{k \in \frac{2\pi}{l}\mathbb{Z}^3} ik\hat{f}(k) e^{ikr}, \tag{2.7}$$

Poisson's equation for the Fourier series of the electrostatic potential Φ transforms into

$$k^2 \hat{\Phi}(k) = 4\pi \hat{\rho}(k). \tag{2.8}$$

We now consider the charge density given by the sum of all Gaussians, which has the Fourier series

$$\hat{\rho}_G(k) = \int_V dr\, e^{-ikr} \sum_{j=1}^{N} q_j \sum_{n \in l\mathbb{Z}^3} \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 e^{-\alpha^2 (r - r_j - n)^2} = \sum_{j=1}^{N} q_j e^{-ikr_j} e^{-k^2/4\alpha^2} \tag{2.9}$$

Note that

$$\hat{\rho}_G(0) = \int_V dr \sum_{j=1}^{N} q_j \sum_{n \in l\mathbb{Z}^3} \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 e^{-\alpha^2 (r - r_j - n)^2} = \sum_{j=1}^{N} q_j = 0 \tag{2.10}$$

due to charge neutrality; therefore, Eqn. (2.8) trivially holds, but does not allow to determine $\Phi(0)$. However, normalization requires that this constant term is 0. By insertion of Eqn. (2.9) into (2.8), we obtain the electrostatic potential due to the Gaussians Φ_G, and from this the interaction of the charges with these Gaussians:

$$U_F = \frac{1}{2} \sum_{j=1}^{N} q_j \Phi_G(r_j) = \frac{1}{2} \sum_{j=1}^{N} q_j \sum_{k \neq 0} e^{-ikr_j} \frac{4\pi}{k^2} \hat{\rho}_G(k) = \frac{1}{2V} \sum_{k \neq 0} \left| \sum_{i=1}^{N} q_i e^{ikr_j} \right|^2 \frac{4\pi}{k^2} e^{-k^2/4\alpha^2}. \tag{2.11}$$

Real space sum

What remains is to calculate the contribution due to the interaction between the charges and the real, discrete charges and the charge-inverted Gaussians. The potential of the inverted Gaussians rapidly screens the potential of the point-like charges, so that the sum of both over the lattice is absolutely and quickly convergent; therefore, we can perform it efficiently in real space.

For this, we need is the potential also due to a single Gaussian. Again, we use Poisson's equation, but this time in real space:

$$-\frac{1}{r} \frac{\partial^2 r \Phi_{\text{Gauss}}(r)}{\partial r^2} = 4\pi \rho_{\text{Gauss}}. \tag{2.12}$$

Integration on both sides gives

$$-\frac{\partial r \Phi_{\text{Gauss}}(r)}{\partial r} = -\int_r^\infty dr 4\pi r \rho_{\text{Gauss}} = -\left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \int_r^\infty dr 4\pi r e^{-\alpha^2 r^2} = -2\frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 r^2}. \tag{2.13}$$

And a second integration gives

$$\Phi_{\text{Gauss}}(r) = \frac{2\alpha}{\sqrt{\pi} r} \int_0^r dr e^{-\alpha^2 r^2} = \frac{\text{erf}(\alpha r)}{r}, \tag{2.14}$$

where erf denotes the error function.

We now compute the real space energy

$$\begin{aligned} U_R =& \frac{1}{2} \sum_{i \neq j} q_j q_i \left[\frac{1}{|r_i - r_j|} - \Phi_{\text{Gauss}}(|r_i - r_j|) \right] + \frac{1}{2} \sum_i q_i^2 \Phi_{\text{Gauss}}(0) \\ &+ \frac{1}{2} \sum_{i,j} q_j q_i \sum_{n \neq 0} \left[\frac{1}{|r_i - r_j - n|} - \Phi_{\text{Gauss}}(|r_i - r_j - n|) \right] \end{aligned} \tag{2.15}$$

where the first line are the contributions due to the primary image $n = 0$, in which we have to omit the singular self-energy of the point charges. We need therefore to evaluate two terms:

$$\Phi_{\text{Gauss}}(0) = \lim_{r\to 0} \Phi_{\text{Gauss}}(r) = \frac{\alpha}{\sqrt{\pi}} \tag{2.16}$$

and

$$\frac{1}{r} - \Phi_{\text{Gauss}}(r) = \frac{\operatorname{erfc}(\alpha r)}{r} \tag{2.17}$$

The complementary error function erfc decays exponentially fast. By choosing α sufficiently large, one can obtain U_R easily by a summation only over nearest images of each pair of charges.

The total (intrinsic) Coulomb energy is then approximately given by

$$\begin{aligned} U_E = U_{\text{intrinsic}} \approx \quad & \frac{1}{2V} \sum_{0<|k|^2<K^2} \left| \sum_{i=1}^{N} q_i e^{ikr_j} \right|^2 \frac{4\pi}{k^2} e^{-k^2/4\alpha^2} \\ & + \frac{1}{2} \sum_{\substack{i\neq j \\ |r_i - r_j|_{\text{m.i.}} < r_c}} q_i q_j \frac{\operatorname{erfc}(\alpha |r_i - r_j|_{\text{m.i.}})}{|r_i - r_j|_{\text{m.i.}}} \\ & - \frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2, \end{aligned} \tag{2.18}$$

where we have introduced the computationally necessary truncations in k-space by cutoff K and in real space by cutoff r_c. The force on particle i can be easily obtained by taking the derivative with respect to r_i, since all sums are absolutely and fast converging.

2.1 Error estimates

What are now optimal values for K, R and α? Or given values, what is the numerical error we make? From Eqn. (2.18), it is easy to see that the real space cutoff should be inversely proportional to α, while the k-space cutoff should be proportional. This allows us to estimate the computational effort of the Ewald summation: Using a cell list-like approach and assuming homogeneously distributed particles at a fixed density, the computation time for the evaluation of the real space sum is Nr_c^3. At constant density, the volume is proportional to the number of particles. Therefore, the number of k-vectors we need to sum over in Eqn. (2.18) grows proportional to NK^3, and the computation time of the Fourier space sum is N^2K^3. Inserting the expected scalings with α, we get a total computation time $N\alpha^{-3} + N^2\alpha^3$, which is minimal for $\alpha = N^{-1/6}$. Therefore, the optimal scaling of the Ewald sum is $N^{3/2}$. Note that with increasing system size, the optimal Ewald cutoff grows. For reasonably large systems, the time spent for the Ewald real space sum will always dominate the calculation of the short-ranged forces.

This alone does not yet allow to reliably choose the parameters; for that, we need quantitative error estimates. However, there is no unique or optimal measure of accuracy. In molecular dynamics simulations, the main interest lies in force errors, which we will consider here, while in Monte Carlo simulations, one is concerned with the errors in the energy. One can be interested in either absolute or relative errors; we will consider the first. The reason is again practical — most applications, particulary in soft matter research, include a considerable level of thermal noise on the forces. As long as the absolute error in the electrostatic force is significantly below this noise level, the errors should not influence the system.

In the following, we discuss the force error estimates by Kolafa and Perram for the Ewald sum. Giving a general expression for the expected error is difficult; there are always pathological cases, in which the errors of the used methods are unusually high. However, this are only a few special configurations, which we will rarely encounter in a thermal simulation. Therefore, we assume the

most common case, namely that the charges are homogeneously and randomly distributed within the periodic cell V. Then, our goal is to calculate the root mean square (RMS) error

$$\Delta F = \sqrt{\langle (F^{\text{exact}} - F^{\text{Ewald}})^2 \rangle} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \Delta F_i^2}, \tag{2.19}$$

where $\Delta F_i = F_i^{\text{exact}} - F_i^{\text{Ewald}}$ denotes the error in the force on particle number i.

It is reasonable to assume that the error in the force on particle i can be written as

$$\Delta F_i = q_i \sum_{j \neq i} q_j \chi_{ij}, \tag{2.20}$$

that is, we assume that the error on F_i is a sum of errors stemming from the $N-1$ interactions with the other charges. χ_{ij} is a pairwise error, which is algorithm dependent; we assume that

$$\langle \chi_{ij} \cdot \chi_{ik} \rangle = \delta_{jk} \left\langle \chi_{ij}^2 \right\rangle = \delta_{jk} \, \chi^2, \tag{2.21}$$

i. e. that the contributions from different particles are uncorrelated and that the magnitude is independent of the particle properties, except for the charge prefactor. The first assumption is justified only for random systems, as we have assumed. Inserting into Eqn. (2.20) gives

$$\left\langle \Delta F_i^2 \right\rangle = q_i^2 \sum_{j \neq i} \sum_{k \neq i} q_j q_k \langle \chi_{ij} \cdot \chi_{ik} \rangle = q_i^2 \, \chi^2 \sum_{j=1}^{N} q_j^2, \tag{2.22}$$

which shows that the RMS force error has the form

$$\Delta F \approx \frac{\sum q_i^2}{\sqrt{N}} \chi, \tag{2.23}$$

where the factor χ is the only constant that is algorithm-dependent. We further simplify the problem by assuming that the real and Fourier space errors are uncorrelated; this is sensible, since the parts are calculated by very different types of algorithms. In this case, we can calculate their contributions separately:

$$\Delta F^2 = \Delta F_{\text{real}}^2 + \Delta F_{\text{Fourier}}^2 \approx \frac{\sum q_i^2}{\sqrt{N}} \left(\chi_{\text{real}} + \chi_{\text{Fourier}} \right). \tag{2.24}$$

By replacing the sums over n and k by an integral, both errors χ_{real} and χ_{Fourier} can be estimated. The resulting errors are:

$$\Delta F_{\text{real}} \approx \frac{\sum q_i^2}{\sqrt{N}} \frac{2}{\sqrt{r_c V}} e^{-\alpha^2 r_c^2} \qquad \text{and} \tag{2.25}$$

$$\Delta F_{\text{Fourier}} \approx \frac{\sum q_i^2}{\sqrt{N}} \frac{2\alpha}{\sqrt{\pi K V}} e^{-K^2/4\alpha^2}. \tag{2.26}$$

This error estimates do not only allow to estimate the error at given K, r_c and α, but can also be used to tune the Ewald sum optimally for given error goal ΔF. To this aim, one loops over Fourier-cutoffs K and determines the minimal α numerically from Eqn. (2.26), such that the RMS error is below $\Delta F/\sqrt{2}$. Then, Eqn. (2.25) allows to determine the minimal cutoff r_c, so that the real space error is also below $\Delta F/\sqrt{2}$. Now, one just needs to try through a couple of Fourier space cutoffs to see which combination of K and r_c is optimal for the given implementation and hardware.

2.2 Neutralization

As mentioned before, it is possible to consider systems with a net charge by assuming a homogeneous background that fills the entire simulation and neutralizes the system. This background does not exert a force due to symmetry, but it contributes to the energy; the contribution in the case of the Ewald summation is

$$U_N = -\frac{\pi}{2\alpha^2 V}\left(\sum_{i=1}^{N} q_i\right)^2, \tag{2.27}$$

which can for example be easily calculated by integrating the implicit pair interaction

$$U_{ij} = \frac{1}{V}\sum_{0<|k|^2<K^2} q_i q_j e^{ik(r_i-r_j)}\frac{4\pi}{k^2}e^{-k^2/4\alpha^2} + q_i q_j \sum_{n\in l\mathbb{Z}^3}\frac{\operatorname{erfc}(\alpha|r_i-r_j-n|}{|r_i-r_j-n|} \tag{2.28}$$

in r_i over the whole periodic cell V. Only the second sum contributes, and gives the above term. Note that this contribution depends on α, therefore it must not be neglected when calculating the energy of nonneutral systems, otherwise U_E will depend on the tuning parameter α; in the worst case, that is, if the algorithm is tuned for the underlying hardware, the result can be even hardware dependent.

Literature

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3 Mesh-accelerated Ewald methods (P^{3}M)

The Fourier transformations involved in Eqn. (2.18) are the most time consuming part of the Ewald sum. The mesh-accelerated Ewald methods are based on the idea to modify the problem in such a way that it permits application of the Fast Fourier Transformation (FFT). This reduces the complexity of the reciprocal part of the Ewald sum to $\mathcal{O}(N \log N)$ and allows for a constant cutoff in the real space, so that the real space computation time scales like $\mathcal{O}(N)$.

Performing the Fourier transformations in the reciprocal space part of the Ewald sum by FFT routines is by no means straightforward, and consists of four main steps:

1. The point charges with continuous coordinates have to be replaced by a grid based charge density, since the FFT is a discrete and finite transformation.

2. The potential has to be calculated in the discrete Fourier space by solving Poisson's equation; that is, by multiplication of the Fourier transformed charge density with the Green's function. It is neither obvious nor true that the best grid approximation to the continuum solution of the Poisson equation is achieved by using the continuum Green's function $4\pi/k^2$.

3. The electric field has to be calculated by differentiation from the electric potential. There are at least three possibilities for implementing this differentiation, which differ in accuracy and speed.

4. Finally, the forces on the particle have to calculated from the electric field that is known only on the discrete grid points. This can – under certain circumstances – lead to unwanted violations of Newton's third law. They can be anything between harmless and disastrous.

There exist three major mesh-based Ewald summation methods – similar in spirit but different in detail, namely in how the four steps above are performed. The oldest is the original particle-particle–particle-mesh (P^{3}M) method of Hockney and Eastwood, and then there are two variants, namely the Particle Mesh Ewald (PME) method of Darden *et al.* and an extension of the latter by Essmann *et al.*, which is usually referred to as Smooth Particle Mesh Ewald (SPME). Deserno *et al.* have shown how the three methods differ in detail, and it was demonstrated that the oldest method, namely the original P^{3}M algorithm is actually the most accurate one. Since in addition error estimates exist, this mesh method should be the preferred method of choice, and will be introduced here.

3.1 P^{3}M in a Nutshell

The P^{3}M method maps the system onto a mesh, such that the necessary Fourier transformations can be accomplished by Fast Fourier routines. At the same time the simple Coulomb Green function $4\pi/k^2$ is adjusted to make the result of the mesh calculation most closely resemble the continuum solution.

The first step, i.e., generating the mesh based charge density $\rho_{\mathbb{M}}$ (defined at the mesh points $r_p \in \mathbb{M}$), is carried out with the help of a charge assignment function W:

$$\rho_{\mathbb{M}}(r_p) = \frac{1}{h^3} \sum_{i=1}^{N} q_i W(r_p - r_i). \tag{3.1}$$

Here h is the mesh spacing, and the number of mesh points $N_{\mathbb{M}} = L/h$ along each direction should preferably be a power of two, since in this case the FFT is most efficient. The charge assignment

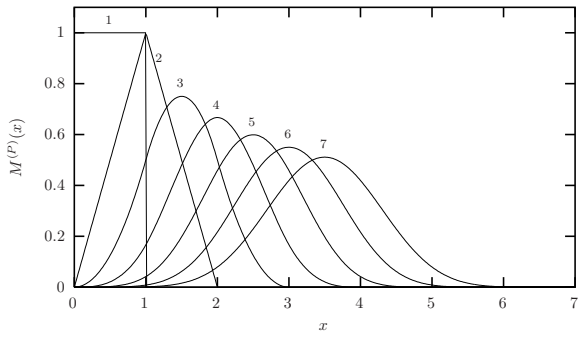


Figure 3.1: Sketch of the first 7 cardinal-B-splines $M^{(P)}(x)$, parameterized by P. Note that the charge assignment functions $W^{(P)}(x)$ for the P^{3}M algorithm are just the "centered" B-splines.

function is classified according to its order P, i.e. between how many grid points – per coordinate direction – each charge is distributed. For W a cardinal B-spline is chosen, which is a piecewise polynomial function of weight one. The order P gives the number of sections in the function. The first 7 cardinal-B-splines are sketched in Fig. 3.1. Their Fourier transforms are

$$\tilde{W}(k) = h^3 \left(\frac{\sin(\frac{1}{2}k_x h)}{\frac{1}{2}k_x h} \frac{\sin(\frac{1}{2}k_y h)}{\frac{1}{2}k_y h} \frac{\sin(\frac{1}{2}k_z h)}{\frac{1}{2}k_z h} \right)^P \tag{3.2}$$

The second and third step, i. e. solving Poisson's equation and deriving the mesh-based electric field $E(r_p)$ from it, happen simultaneously. There exist several alternatives for implementing the differentiation on a lattice; here we will restrict ourselves to the case of ik-*differentiation*, that is, multiplying the Fourier transformed potential with ik. In this case $E(r_p)$ can be written as

$$E(r_p) \;=\; \overleftarrow{\mathrm{FFT}} \left[-ik \;\times\; \hat{G}_{\mathrm{opt}} \;\times\; \overrightarrow{\mathrm{FFT}} \left[\rho_{\mathbb{M}}\right] \right] (r_p). \tag{3.3}$$

In words, $E(r_p)$ is the *backward* finite Fourier transform of the product of $-ik$, the *forward* finite Fourier transform of the mesh based charge density $\rho_{\mathbb{M}}$ and the so-called optimal influence function $\hat{G}_{\mathrm{opt}}$, given by

$$\hat{G}_{\mathrm{opt}}(k) = \frac{\mathrm{i}k \cdot \sum_{m\in\mathbb{Z}^3} \tilde{U}^2(k + \frac{2\pi}{h}m)\tilde{R}(k + \frac{2\pi}{h}m)}{|k|^2 \left[\sum_{m\in\mathbb{Z}^3} \tilde{U}^2(k + \frac{2\pi}{h}m)\right]^2}, \tag{3.4}$$

where the true, analytic reference force is derived from (2.18) as

$$\tilde{R}(k) := \; -\mathrm{i}k\frac{4\pi}{k^2}e^{-k^2/4\alpha^2} \tag{3.5}$$

and the dimensionless Fourier transform of the B-spline is

$$\tilde{U}(k) := \tilde{W}(k)/h^3. \tag{3.6}$$

The last step of P^{3}M, the back-interpolation of the forces onto the particles, is performed done again using the B-splines. The force on particle i is determined as

$$F_i = q_i \sum_{r_p\in\mathbb{M}} E(r_p)W(r_i - r_p). \tag{3.7}$$

The sum extends over the complete mesh $\mathbb{M}$; however, since the B-splines have compact carrier, the sum in fact only extends over a small vicinity of r_i.

Although the presented formulas (3.1–3.7) look somewhat complicated, they are rather easy to implement step by step. If the real space cutoff r_c is chosen small enough, so that the real space contribution (the second sum in Eqn. (2.18)) can be calculated in order $\mathcal{O}(N)$, the complete algorithm is of order $\mathcal{O}(N \log N)$.

3.1.1 The error measure of Hockney and Eastwood

While the real space error estimate of Kolafa and Perram of course also applies to the P^3M real space sum, the four steps involved in any particle mesh calculation introduce completely different errors than the simple k-space truncation of the standard Ewald sum. In fact, being a discrete Fourier transform, the P^3M k-space sum is *not* truncated at all. However, there are new sources of errors, originating, e. g., from discretization, interpolation or aliasing[1] problems. Since these contributions are not independent of each other (reducing one might enhance another), the only reasonable demand is the minimization of the *total* error at given computational effort.

The most interesting ingredient of the P^3M method is the optimal influence function from Eqn. (3.4). It is constructed such that the result of the mesh calculation is as close as possible to the solution of the original continuum problem. More precisely, the P^3M method is derived from the requirement that the resulting Fourier space contribution to the force minimizes the the following error measure Q:

$$Q := \frac{1}{h^3} \int_{h^3} dr_1 \int_V dr \big[F(r; r_1) - R(r)\big]^2 \tag{3.8}$$

$F(r; r_1)$ is the Fourier space contribution of the force between two unit charges at positions r_1 and $r_1 + r$ as calculated by the P^3M method (note that due to broken rotational and translational symmetry this does in fact depend on the coordinates of *both* particles), and $R(r)$ is the corresponding exact reference force (whose Fourier transform is just Eqn. (3.5)). The inner integral over r scans all particle separations, whereas the outer integral over r_1 averages over all possible locations of the first particle within a mesh cell. Obviously, up to a factor L^{-3} this expression is just the mean square error in the force for two unit charges, in other words, the quantity χ^2 from Eqn. (2.22). Inserting into Eqn. (2.23), the RMS force error of an N particle system is given by

$$\Delta F \approx \sum q_i^2 \sqrt{\frac{Q}{NV}}. \tag{3.9}$$

It is important to realize that Hockney and Eastwood not only provide a closed expression for the optimal influence function $\hat{G}_{\text{opt}}$, but also a closed expression for the corresponding "optimal error" $Q_{\text{opt}} = Q[\hat{G}_{\text{opt}}]$:

$$Q_{\text{opt}} = \frac{1}{L^3} \sum_{k \in \hat{\mathbb{M}}} \Bigg\{ \sum_{m \in \mathbb{Z}^3} \Big| \tilde{R}(k + \frac{2\pi}{h} m) \Big|^2 \tag{3.10}$$

$$- \frac{\Big| \mathrm{i} k \cdot \sum_{m \in \mathbb{Z}^3} \tilde{U}^2(k + \frac{2\pi}{h} m) \tilde{R}^*(k + \frac{2\pi}{h} m) \Big|^2}{|k|^2 \Big[\sum_{m \in \mathbb{Z}^3} \tilde{U}^2(k + \frac{2\pi}{h} m) \Big]^2} \Bigg\}. \tag{3.11}$$

Here, the asterisk denotes the complex conjugate.

Admittedly, Eqn. (3.11) looks rather complicated. Still, in combination with Eqn. (3.9) it gives the RMS force error of the Fourier contribution of the P^3M method. After all, the computation of Q_{opt} and that of $\hat{G}_{\text{opt}}$ are quite similar. It should be emphasized that the formula (3.11) for the optimal Q-value and the optimal influence function (3.4) are of a very general nature, and can be applied to for different charge assignment functions, reference forces or other differentiation schemes [1].

[1] A finite grid cannot represent arbitrarily large k-vectors. Instead, they are folded back into the first "Brillouin zone" and distort there the true spectrum. This effect is usually referred to as "aliasing".

With the real space error estimate by Kolafa and Perram and the k-space error estimate by Hockney and Eastwood at hand, it is easy to determine the optimal value of the splitting parameter α *a priori* just from the system parameters N, $\sum q_i^2$ and L and the tuning parameters of the algorithm r_c, $N_{\mathbb{M}}$, P. Just like for the standard Ewald method, a good approximation to the optimal α can be obtained by requiring the real and k-space RMS force errors to be equal, and a similar tuning routine can be applied, although now the two parameters $N_{\mathbb{M}}$ and P both need to be tried out.

3.2 Parallelization

Being an order $\mathcal{O}(N \log N)$-method, P^{3}M and other mesh-based Ewald methods are well suited to study even large systems with many thousands of particles. This quickly raises the question of parallelization, i. e. employing N_P processors to compute the electrostatic energy simultaneously. Just as with the charge interpolation and differentation, there are several ways of parallelization; we briefly present here one that we found to scale rather well even on large computers with hundreds of processors.

The real space part of the Ewald sum is a short-ranged potential, for which several good parallelization strategies exist. In fact, every parallel Molecular Dynamics code has such a strategy built in, or rather, is built around such a strategy. And to be able to scale up to hundreds of processors, almost all codes use a domain decomposition and cell lists, often combined with Verlet lists. These methods reach the ideal N/N_P scaling with modern fast networks, at least in weak scaling, i. e. constant number of particles per processor. Moreover, communication only occurs between neighboring processors in a 3D toroidal structure, which is efficiently handled by most hardware.

The domain decomposition strategy also allows to conveniently split up the work load of charge assignment and force interpolation, by using the same domain decomposition also for the k-space mesh. What remains, is computing the 3D Fourier transform. The Fourier transforms are typically performed by highly efficient libraries, e. g. the excellent FFTW. However, this library at present does not scale very well when it comes to parallel 3D Fourier transforms. And it is the parallelization of the 3D Fourier transform, which is in fact the major bottle neck. To understand this, one has to see that a 3D Fourier transform of a mesh of $N_{\mathbb{M}}^3$ total points consists of three times performing $N_{\mathbb{M}}^2$ 1D Fourier transforms of length $N_{\mathbb{M}}$. To perform the latter, all data should be available on one processor. This means, that to perform the 1D Fourier transforms along the different axes, one has to completely exchange the data between all the processors, requiring rather inefficient global communication.

To our knowledge the most efficient way to implement the 3D Fourier transform is as follows:

1. redistribute the 3D domain-decomposed mesh such that the processors form a 2D mesh in the x, y-plane, and each processor obtains all data of its domain, in particulary always has one or more *full* columns along the z-axis. Calculate the Fourier transforms along the z-axis.

2. redistribute such that the processors form a 2D mesh in the x, z-plane and have full columns along the y-axis. Calculate the Fourier transforms along the y-axis.

3. redistribute such that the processors form a 2D mesh in the y, z-plane and have full columns along the y-axis. Calculate the Fourier transforms along the x-axis.

After applying the optimal influence function and the difference operator,

4 distribute the data back into the original, 3D domain-decomposed mesh.

Literature

[1] M. Deserno and C. Holm. How to mesh up Ewald sums. I. A theoretical and numerical comparison of various particle mesh routines. *J. Chem. Phys.*, 109:7678, 1998.

[2] M. Deserno and C. Holm. How to mesh up Ewald sums. II. An accurate error estimate for the Particle-Particle-Particle-Mesh algorithm. *J. Chem. Phys.*, 109:7694, 1998.

[3] R. W. Hockney and J. W. Eastwood. *Computer Simulation Using Particles.* IOP, London, 1988.

[4] FFTW website, `http://www.fftw.org`.

4 MMM, MMM2D, MMM1D

The algorithm MMM[1] by R. Strebel and R. Sperb will be the first non-Ewald type method that we will consider, although it is still based on a Fourier transform. However, MMM uses the convergence factor $e^{-\beta|r_{ij}+n|}$, which as discussed in the introduction, gives the intrinsic energy

$$U_E = U_{\text{intrinsic}} = \frac{1}{2}\lim_{\beta\to 0}\sum_{n\in l\mathbb{Z}^3}\sum_{i,j=1}^{N}{}' \frac{q_i q_j e^{-\beta|r_{ij}+n|}}{|r_{ij}+n|} =: \frac{1}{2}\lim_{\beta\to 0}\sum_{i,j=1}^{N} q_i q_j \phi_\beta(r_{ij}), \tag{4.1}$$

where the screened pairwise potential is defined as

$$\phi_\beta(r) = \sum_{n\in l\mathbb{Z}^3}{}' \frac{e^{-\beta|r+n|}}{|r+n|}. \tag{4.2}$$

This potential is called screened, since from the physical point of view the Coulomb interaction is replaced by a screened Coulomb interaction with screening length $1/\beta$. $U_E N$ is the energy in the limit of infinite screening length. This also explains why this solution recovers the intrinsic solution without polarization contribution — even if we assume a very large screening length, any polarization at infinite distance is still screened by it.

For particles sufficiently separated in the z–axis we can use the the *Poisson formula*

$$\sum_{n\in l\mathbb{Z}} f(x+n) = \frac{1}{l}\sum_{k\in\frac{2\pi}{l}\mathbb{Z}} \widehat{f}\,(k)\, e^{\mathrm{i}kx} \tag{4.3}$$

using the transforms

$$\begin{aligned} \widehat{\left(\frac{e^{-\beta\sqrt{c^2+x^2}}}{\sqrt{c^2+x^2}}\right)} &= 2\,\mathrm{K}_0\left(c\sqrt{\beta^2+k^2}\right) \quad \text{and} \\ \widehat{\left(\mathrm{K}_0\left(\beta\sqrt{c^2+x^2}\right)\right)} &= \pi\frac{e^{-c\sqrt{\beta^2+k^2}}}{\sqrt{\beta^2+k^2}}, \end{aligned} \tag{4.4}$$

where K_0 is the so-called modified Bessel function of order 0. This allows us to Fourier transform the potential along both x and y, while the summation in z can be performed directly by a geometric series. We obtain the *far formula* as

$$\begin{aligned} \phi_\beta(r) &= \frac{2}{l_x}\sum_{p\in\frac{2\pi}{l_x}\mathbb{Z}}\left(\sum_{l,m\in l\mathbb{Z}}\mathrm{K}_0\left(\sqrt{\beta^2+p^2}\sqrt{(y+l)^2+(z+m)^2}\right)\right)e^{\mathrm{i}px} \\ &= \frac{2\pi}{l_x l_y}\sum_{p,q\in\frac{2\pi}{l}\mathbb{Z}}\sum_{m\in l_z\mathbb{Z}}\frac{e^{-\sqrt{\beta^2+p^2+q^2}|z+m|}}{\sqrt{\beta^2+p^2+q^2}}e^{\mathrm{i}px}e^{\mathrm{i}qy} \\ &= \frac{2\pi}{l_x l_y}\sum_{\substack{p,q\in\frac{2\pi}{l}\mathbb{Z}\\ p^2+q^2>0}}\frac{e^{\sqrt{p^2+q^2}z}+e^{\sqrt{p^2+q^2}(l_z-z)}}{\sqrt{p^2+q^2}\left(e^{\sqrt{p^2+q^2}l_z}-1\right)}e^{\mathrm{i}px}e^{\mathrm{i}qy} \\ &\quad + \frac{2\pi}{l_x l_y}\left(\frac{1}{l_z}z^2 - z + \frac{l_z}{6}\right) + \frac{2\pi}{V}\beta^{-1} + \mathcal{O}_{\beta\to 0}(\beta). \end{aligned} \tag{4.5}$$

[1] Even the authors of the method have no idea what this acronym stands for.

Note the singularity in β; this singularity prohibits us from exchanging the limit and the sum in Eqn. (4.1). However, this singularity is independent of the particle coordinates; therefore, when summing it up over a charge neutral set of particles, this singularity exactly cancels out.

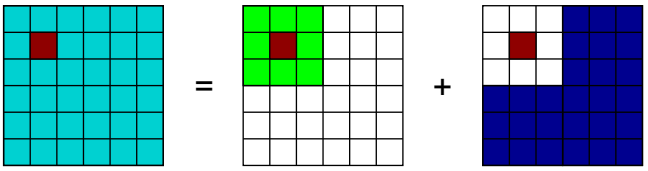
The advantage of this far formula is that it allows for a product decomposition into components of the particles, just as in the Ewald sum. Therefore one just has to calculate the sum over all these exponentials on the left side and on the right side and multiply them together, which can be done in $\mathcal{O}(N)$ computation time. As can be seen easily, the convergence of the series is excellent as long as z is sufficiently large. By symmetry one can choose the coordinate with the largest distance as z to optimise the convergence. However, if particles are spatially really close, we need a different formula.

For sufficiently small distance we obtain after some lengthy maths the *near formula* as

$$\begin{aligned}
\phi(r) = & \frac{4\pi}{l_x l_y} \sum_{\substack{p,q\in\frac{2\pi}{l}\mathbb{Z}\\ p,q>0}} \frac{\cosh(\sqrt{p^2 2+q^2}|z|)}{\sqrt{p^2 2+q^2}\left(e^{\sqrt{p^2+q^2}l_z}-1\right)} e^{\mathrm{i}px} e^{\mathrm{i}qy} \\
& + \frac{4}{l_x} \sum_{p\in\frac{2\pi}{l_x}\mathbb{Z}} \sum_{l\in l_y\mathbb{Z}} \left(\mathrm{K}_0(p\sqrt{(y+l)^2+z^2}) + \mathrm{K}_0(p\sqrt{(y+l)^2+z^2})\right) cos(px) \\
& - \frac{2}{l_x} \sum_{n\geq 1} \frac{b_{2n}(2\pi)^{2n}}{2n(2n)!} \Re\left[\left(\frac{z+\mathrm{i}y}{l_y}\right)^{2n}\right] \\
& + \frac{1}{l_x} \sum_{n\geq 0} \binom{-\frac{1}{2}}{n} \frac{\left(\psi^{(2n)}(1+x/l_x)+\psi^{(2n)}(1-x/l_x)\right)}{(2n)!} \left(\frac{y^2+z^2}{l_x^2}\right)^n \\
& - 2\log(4\pi) +' \frac{1}{|r|} + \frac{2\pi}{V}\beta^{-1} + \mathcal{O}_{\beta\to 0}(\beta),
\end{aligned} \tag{4.6}$$

where b_n denotes the Bernoulli numbers, and $\psi^{(m)}(x)$ the polygamma function of m-th order. Note that the self contribution $1/r$ is added explicitely, so that it can be easily omitted for the calculation of the self interaction term. Eqn. (4.6) is derived using the same convergence factor approach as used for Eqn. (4.5), and consequently the same singularity in β is obtained. This is important since otherwise the charge neutrality argument does not hold and the limit $\beta \to 0$ could not be performed.

The near formula does not split as nicely as the far formula, therefore one cannot straightforwardly exploit the far formula, as we need to consider particle pairs according to their spatial positions differently. Nevertheless, we will explain now how to obtain a computational order of $\mathcal{O}(N \log N)$, that is, the same as the $\mathrm{P^3M}$ method. A simple implementation segments the simulation box in $B = S^3$ smaller boxes or cells. For all particles the interactions within the cell itself and the 26 neighbouring cells are treated using the near formula, while for the rest the far formula is used. In two dimensions this looks like this:



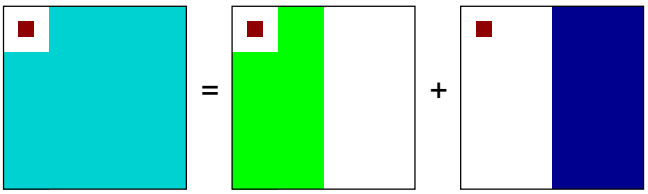
The interactions of the red cell with the light green cells is done via the near formula, while all the dark blue cells are treated using the far formula. One first determines the product decomposition components for each cell and then adds them up over all pairs of cells which are not neighbours.

For this simple approach, we can again estimate the computation time. Here, the cutoff of the far formula summation has to be chosen inversely proportional to the particle distance, as can be easily seen from Eqn. (4.5). Using the algorithm described above, the minimal distance of two particles calculated with the far formula is l_z/S. Therefore for a constant pairwise error the Fourier space cutoff

R has to be chosen proportional to S. This leads to a calculation time for the far formula of $\mathcal{O}(NS^2)$. The near formula has to be used for $\mathcal{O}(N^2S^{-3})$ particle pairs. Since the calculation time for the near formula is practically parameter independent, this is also the scaling of the calculation time. The total computation time has a minimum for $S \sim N^{1/5}$, resulting in an overall computation time scaling of $\mathcal{O}(N^{\frac{7}{5}})$. Upper error bounds can be found easily by approximating the sums by integrals, similar to the MMM2D/1D methods described below.

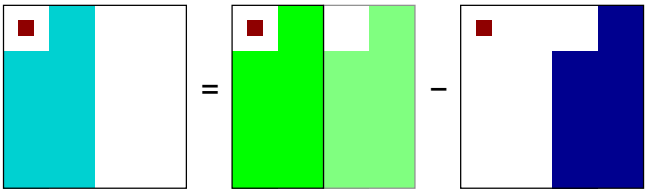
To decrease the computational effort of MMM down to $\mathcal{O}(N \log(N))$ as promised, we use the periodicity in all spatial dimensions to maximize the minimal distance at which the far formula has to be applied. This is an important point, since it explains, why for partially periodic dimensions MMM does not achieve the same favorable scaling, although the approach itself can be transferred, as we will see.

In the following we assume that the number of cells per side is a power of 2, i. e. $S = 2^L$. The main idea is to increase l_z/S not by decreasing S, but rather by increasing l_z. This is possible due to the periodic boundary conditions. The idea will be presented graphically in two dimensions, and as before, we calculate the interactions with the small red cell. First the primary simulation cell will be divided into small cells along the x–coordinate:



The particles in the right part are far away and can be calculated using the far formula with a reasonably small cutoff.

The other half will now be calculated using a cell length of $l_x/2$. This introduces artificial particles in the right part, which are just copies of the particles in the left side. Their contribution can be subtracted easily together with the contribution of the real particles in the right half.



Now we are left with a cell containing roughly $N/2$ particles (provided the simulation cell is filled homogeneously) and cell dimensions $l_x/2 \times l_y \times l_z$. For this system we apply the same trick again to one of the other axes, e. g. y, then to z and again to x and so on, until the calculation using the near formula is more efficient than another subdivision. The subdivision occurs in the coordinate which occurs in the exponential. Therefore the shift of the particle coordinates is actually only a multiplication.

In pseudo code the algorithm for a subdivision step looks like this

```
for each (p, q)
        for each cell c
                calculate the coefficients σ_c of the product decomposition of cell c
        end
        for each row r
                calculate the sum Σ_r of all coefficients from the σ_c in row r
        end
        for each row r
                calculate the sum Φ_r of the Σ_r of the rows more far away than l_z/2
                        for row r
                add to Φ_r the Σ_r of the rows closer than l_z/2 but not adjacent
                        for row r multiplied by the shift factor
        end
        for each cell c
                use the Φ_r and the σ_c of the adjacent rows of all cells c'
                        not adjacent to cell c multiplied by the shift factor
                        to calculate the contribution to the energy
                        from the far particles and the artificial images
        end
end
```

This algorithm can be further optimised with respect to computation time, but even in the present form one can see that it its implementation is more demanding than the Ewald or multipole methods. The implementation is even more complex as the presented code should work with all three coordinates symmetrically for reuse in the subdivision steps. The calculation time for each of the subdivision steps is proportional to half of the number of particles left, i. e. $N/2, N/4, N/8, \ldots$. To maintain a constant calculation time of the near formula, one has to ensure that $2^L \sim N$ or $L \sim \log N$. Therefore the overall computation time is $\mathcal{O}(NL) = \mathcal{O}(N \log N)$.

4.1 MMM2D

MMM can also be applied to systems with only two periodic dimensions and one non-periodic one, which we assume to be z without loss of generality. This method we call MMM2D, since although the formulas are very similar to MMM, the algorithmic implementation is different.

The *far formula* of MMM2D is

$$\phi(r) = \frac{2\pi}{l_x l_y} \sum_{\substack{p,q \in \frac{2\pi}{l}\mathbb{Z} \\ p^2+q^2>0}} \frac{e^{-\sqrt{p^2+q^2}|z|}}{\sqrt{p^2+q^2}} e^{\mathrm{i}px} e^{\mathrm{i}qy} \; - \; \frac{2\pi}{l_x l_y}|z|, \tag{4.7}$$

omitting again a constant singularity in β. As before the far formula is well convergent for $|z| \gg 0$,

but does not converge for small $|z|$. In this case, we use the *near formula*

$$\begin{aligned}\phi(r) = &\frac{4}{l_x}\sum_{l\in l_y\mathbb{Z}}\sum_{p\in\frac{2\pi}{l_x}\mathbb{N}}\left(\mathrm{K}_0(p\sqrt{(y+l)^2+z^2})+\mathrm{K}_0(p\sqrt{(y-l)^2+z^2}\right)\cos(px)\\ &-\frac{2}{l_x}\sum_{n\geq 1}\frac{b_{2n}(2\pi)^{2n}}{2n(2n)!}\Re\left[\left(\frac{z+\mathrm{i}y}{l_y}\right)^{2n}\right]\\ &-\frac{1}{l_x}\sum_{n\geq 0}\binom{-\frac{1}{2}}{n}\frac{\psi^{(2n)}(2+\frac{l_x}{x})+\psi^{(2n)}(2-\frac{l_x}{x})}{(2n)!}\left(\frac{y^2+z^2}{l_x^2}\right)^n\\ &+\frac{1}{\sqrt{(x+l_x)^2+y^2+z^2}}+\frac{1}{\sqrt{(x-l_x)^2+y^2+z^2}}+'\frac{1}{|r|}-\frac{2}{l_x}\log\left(4\pi\frac{l_x}{l_y}\right).\end{aligned} \tag{4.8}$$

We cannot apply the same algorithmic tricks as used in MMM for 3D periodic boundary conditions, since these tricks require the periodicity of all coordinates. However, the far formula still allows for a product decomposition and can be evaluated in linear time with respect to the number of particles with constant cutoffs.

To draw advantage from this linear computation time scaling, one splits the system into B equally sized layers along the nonperiodic z–coordinate. Now for all particle in one slice, the interactions with the neighboring slices are calculated using the near formula, while for the further distant slices the far formula is used. This ensures that the far formula is used only for particle pairs more distant than h/B, where h is the total system height. The far formula is evaluated in a similar fashion as will be presented below for the ELC method, although some more involved book keeping is necessary. This is due to the fact that the far contribution is only needed for particles from certain slices, whereas the ELC term has to be calculated for all particles.

First, we again determine the scaling of the computation time of MMM2D. Assuming that N/B particles are located in every slice, one can show that the far formula scales like $\mathcal{O}(B^2N)+\mathcal{O}(B^3)$. The time for the calculation of the near formula for a single particle pair is nearly constant, leading to a scaling of $\mathcal{O}(N(2N/B))$. Minimizing the total time with respect to the number of slices B leads to $B\propto N^{1/3}$, yielding an asymptotic optimal computational time of $\mathcal{O}(N^{\frac{5}{3}})$.

As for all the other methods, we are interested in error estimates for MMM2D. It is rather tedious to calculate the parameter χ^2 of formula (2.22), but one can relatively easily determine an upper bound for it. The derivation of the error estimates is straight forward, and we present only the results here. For the maximal pairwise force error of the far formula, one obtains the upper bound

$$\tau_F^{\mathrm{far}} = \frac{e^{-2\pi R|z|}}{|z|}\left(2\pi R+2(\frac{1}{l_x}+\frac{1}{l_y})+\frac{1}{|z|}\right), \tag{4.9}$$

where R is the (p,q) cutoff radius of the far formula. A similar expression can also be found for the energy error. For the near formula, one has separate error estimates for the sum of Bessel terms, the complex sum and the polygamma sum, which one can use to determine the individual cutoffs and by that limit the overall χ. For the Bessel sum, the maximal force error is

$$\tau_F^{\mathrm{Bessel}} = \frac{16\pi}{l_x^2}\,\mathrm{K}_1(l_yL)\left(l_x\frac{e^{\pi l_y/l_x}}{\pi l_y}\left(l_x\frac{L+\frac{1}{l_y}}{\pi}-1\right)+\sum_{p=1}^{\lceil\frac{l_xL}{\pi}\rceil-1}pe^{-\pi l_yp/l_x}\right) \tag{4.10}$$

where the summation takes place over $0<p<\frac{L}{\pi u_x}$ and $0<l<\frac{l_xL}{2\pi p}+1$. For the summation of the complex sum up to order N, one obtains the maximal error bound

$$\tau_F^{\mathrm{Bernoulli}} = \frac{16}{l_xl_y}\left(\frac{y^2+z^2}{l_y^2}\right)^{N-1}\leq\frac{16\sqrt{2}}{l_xl_y}2^{-N}. \tag{4.11}$$

The polygamma sum finally is a sum of alternating coefficients with monotonously decreasing value, and therefore by Leibniz' criterion, the absolute value of last term taken into account is an upper error bound.

Note that the error distribution of MMM2D is non-uniform in z; particles near the system boundaries in z will have smaller errors than particles in the center; therefore it is vital to tune MMM2D for rather small errors, especially since increasing MMM2D's performance is rather inexpensive.

4.2 MMM1D

For completeness, we also give the MMM equivalent algorithm for one dimensionally periodic systems, which can for example model nanotubes or wires. In this case, we have only a single coordinate for Fourier transformation, so that we are left with the Bessel function in the far formula. Therefore, neither near nor far formula can be split up, and the overall computational effort is still $\mathcal{O}(N^2)$ for a plain all-by-all summation. Nevertheless, we need both formulas, since none of them is convergent for all distances.

In the following, the periodic dimension is z without loss of generality. Then, the *far formula* is

$$\phi(r) = \frac{4}{l_z} \sum_{p \in \frac{2\pi}{l_z}\mathbb{N}} \mathrm{K}_0(p\sqrt{x^2+y^2}) \cos(pz) - \frac{2}{l_z} \log\left(\frac{\sqrt{x^2+y^2}}{2l_z}\right) - \frac{2\gamma}{l_z} + \mathcal{O}(\beta), \tag{4.12}$$

where we as usual omitted a singular term of $\mathcal{O}(\log \beta)$. The *near formula* is given by

$$\begin{aligned}\phi(r) = &- \frac{1}{l_z} \sum_{n \geq 0} \binom{-\frac{1}{2}}{n} \frac{\left(\psi^{(2n)}(2+z/l_z) + \psi^{(2n)}(2-z/l_z)\right)}{(2n)!} \left(\frac{x^2+y^2}{l_z^2}\right)^n \\ &- \frac{2\gamma}{l_z} + \frac{1}{\sqrt{x^2+y^2+(z+l_z)^2}} + \frac{1}{\sqrt{x^2+y^2+(z-l_z)^2}} +' \frac{1}{|r|}.\end{aligned} \tag{4.13}$$

The evaluation is very simple, since one simply has to loop over all pairs of charges, and use the far or near formula, depending on the distance of the particles. Clearly, the resulting computational scaling of $\mathcal{O}(N^2)$ prohibits to employ the methods for systems larger than a couple of hundred particles. However, the numerical prefactor is rather small, so that for small systems, the method is rather competitive. Finally note, that of course there are error estimates for MMM1D, just like for MMM or MMM2D.

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5 Electrostatic Layer Correction (ELC)

6 Tree codes and fast multipole methods

7 Maggs' method (MEMD)