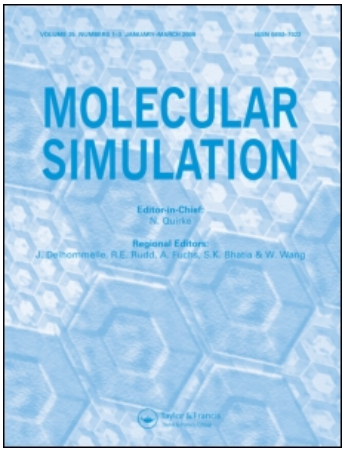

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An Alternative to Ewald Sums, Part 2: The Coulomb Potential in a Periodic System

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AN ALTERNATIVE TO EWALD SUMS, PART 2: THE COULOMB POTENTIAL IN A PERIODIC SYSTEM

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The formulae for the Coulomb potential derived in this paper apply to the situation most commonly encountered in applications: a basic cell containing N charges and their periodic images. The Coulomb energy or the Coulomb forces can then be calculated using *e.g.*, Ewald sums. The formulae given here have several advantages over the Ewald technique, in particular when N is large.

Keywords: Coulomb potential; Ewald sums

1. INTRODUCTION

Consider a basic cell C (a cube of side 1) containing N charges q_i with total charge zero. A standard situation is to consider all replicas of C filling the whole three dimensional space or else a two-dimensional layer of finite thickness. In both situations one is interested in the Coulomb energy, more precisely, in the expression

$$E = \frac{1}{2} \sum_{\vec{n} \in \mathbb{Z}^3}{}' \sum_{i,j=1}^{N} q_i q_j \frac{1}{|\vec{r}_i - \vec{r}_j + \vec{n}|}. \tag{1.1}$$

For a two-dimensional layer one has $\vec{n} \in \mathbb{Z}^2$ in the place of $\mathbb{Z}^3$.

Here the prime indicates that the singular term that would arise for $i = j$ is to be excluded. $\vec{n}$ is a lattice vector and $\vec{r}_i$ is the position vector of a charge q_i.

Since the infinite sum is only conditionally convergent one has to specify in (1.1) how the summation has to be executed. Standard practice is to take spherical means, *i.e.*,

$$E = \frac{1}{2} \lim_{R \to \infty} \left(\sum_{|\vec{n}| \leq R}{}' \sum_{i,j=1}^{N} q_i q_j \frac{1}{|\vec{r}_i - \vec{r}_j + \vec{n}|} \right). \tag{1.2}$$

The first paper giving an expression for the Coulomb potential, *i.e.*,

$$U(\vec{r}) = \sum_{\vec{n} \in \mathbb{Z}^3} \sum_{i=1}^{N} q_i \frac{1}{|\vec{r} - \vec{r}_i + \vec{n}|} \tag{1.3}$$

was by Madelung [6]. His expression is only valid for $\vec{r} \neq \vec{r}_i$ and is not correct for spherical means. His method of derivation only works for the Coulomb potential. Ewald [2] then derived his now well-known formula for the Coulomb energy. A variant of Madelung's formula applicable to (1.1) was derived by Lekner [4] and by different methods in [9]. The formula of Lekner converges faster than Ewald's but it is not simple to apply to the case in which N gets large.

In this paper a new formula for the Coulomb energy (and also Coulomb forces) is derived which converges at about the same rate as Lekner's, but which has an advantage in the application to dense systems, *i.e.*, when N is large.

2. THE COULOMB POTENTIAL

Our starting point is the formula (3.30) of [8] which can be put into the following form:

$$\begin{aligned} E = \frac{1}{2} \sum_{i \neq j=1}^{N} q_i q_j \{ V(x_i - x_j, y_i - y_j, z_i - z_j) + 2\pi(|z_i - z_j|^2 - |z_i - z_j|) \} \\ + Q_0 \cdot \sum_{i=1}^{N} q_i^2 + \frac{2\pi}{3} \left(\sum_{i=1}^{N} q_i \vec{r}_i \right)^2 . \end{aligned} \tag{2.1}$$

The last term (dipole moment) was missing there, but it has to be included if in (1.1) one wants a limit of spherical means (see DeLeeuw–Perram–Smith [1]). Without the dipole term E corresponds to a limit of two dimensional infinite plates. For the explicit form of $V(x, y, z)$ in (2.1) we introduce the

following abbreviations which will be used later on also:

$$Be[\rho, x] := 4\sum_{p=1}^{\infty} K_0(2\pi p \cdot \rho)\cos(2\pi p x), K_0 = \text{Besselfunction} \tag{2.2}$$

and

$$L[y, z] = \log(1 - 2\cos(2\pi y)\exp(-2\pi|z|) + \exp(-4\pi|z|)). \tag{2.3}$$

With this notation one has

$$V(x, y, z) = \sum_{k,\ell=-\infty}^{\infty} Be\left[\sqrt{(y+k^2+(z+\ell)^2}, x\right] - \sum_{m=-\infty}^{\infty} L[y, z+m] \tag{2.4}$$

and the constant is

$$Q_0 = \frac{1}{2}\sum_{k,\ell=-\infty}^{\infty}{}' Be\left[\sqrt{k^2+\ell^2}, 0\right] - \frac{1}{2}\sum_{m=1}^{\infty} L[0, m] + \gamma - \log(4\pi) \cong -1.942248 \tag{2.5}$$

where $\gamma = 0.577216$ is Euler's constant.

For the case of a layer of some finite thickness $0 \leq z \leq h$ extending to infinity only in x and y-direction one has

$$E = \sum_{i\neq j=1}^{N} q_i q_j\{\tilde{V}(x_i - x_j, y_i - y_j, z_i - z_j) - 2\pi|z_i - z_j|\} + \tilde{Q}_0 \cdot \sum_{i=1}^{N} q_i^2, \tag{2.6}$$

where now

$$\tilde{V}(x, y, z) = \sum_{k=-\infty}^{\infty} Be\left[\sqrt{(y+k)^2+z^2}, x\right] - L[y, z] \tag{2.7}$$

and

$$\tilde{Q}_0 = \sum_{k=1}^{\infty} Be[k, 0] + \gamma - \log(4\pi) = -1.95013246. \tag{2.8}$$

We now derive alternative formulae for the Coulomb potential. The advantages of these new formulae will become clear later on.

In order to transform the functions $V(x, y, z)$ and $\tilde{V}(x, y, z)$ we apply a simple Lemma which was introduced in [7] and used extensively again in [9]. For the sake of completeness we reproduce it here.

LAMMA *Let the infinite sum S be given as*

$$S(x,r) = \sum_{k=-\infty}^{\infty} p(|x+k|, r). \tag{2.9}$$

where $r > 0$ *and* $p(,)$ *is such that the series converges for* $x \in [0,1]$ *and any* $r > 0$. *Then*

$$S(x,r) = \int_0^\infty p(s,r)ds + 4\sum_{\ell=1}^{\infty}\int_0^\infty p(s,r)\cos(2\pi\ell s)ds \cdot \cos(2\pi\ell x). \tag{2.10}$$

The formula (2.10) is just the Fourier series of $S(x,r)$. For more details see *e.g.* [9].

We now apply formula (2.10) to the case

$$p(s,r) = K_0(2\pi p\sqrt{s^2+r^2}). \tag{2.11}$$

The integrals in (2.10) can be looked up in any standard collection of Fourier-transforms or else Besseltransforms. One is then led to the identity (see [9], Eq. (3.5))

$$\sum_{k=-\infty}^{\infty} K_0\left(2\pi p\sqrt{(y+k)^2+r^2}\right) = \frac{1}{2p}e^{-2\pi rp} + \sum_{\ell=1}^{\infty}\frac{1}{\sqrt{p^2+\ell^2}}e^{-2\pi r\sqrt{p^2+\ell^2}}\cdot\cos(2\pi\ell y). \tag{2.12}$$

We first apply (2.12) in the expression (2.7) for $\tilde{V}(x,y,z)$. Then it remains first to calculate

$$\begin{aligned} 2\sum_{p=1}^{\infty}\frac{1}{p}e^{-2\pi|z|p}\cdot\cos(2\pi py) &= 2\mathrm{Re}\int_\zeta^\infty \sum_{p=1}^{\infty} e^{-p\cdot w}dw \\ &= 2\mathrm{Re}\int_\zeta^\infty \frac{e^{-w}}{1-e^{-w}}dw = -2\mathrm{Re}(\log(1-e^{-\zeta})) \end{aligned} \tag{2.13}$$

with $\zeta = 2\pi(|z| - i\cdot y)$. Calculation of the real part gives

$$2\sum_{p=1}^{\infty}\frac{1}{p}e^{-2\pi|z|p}\cdot\cos(2\pi py) = -L[y,z], \tag{2.14}$$

which is the second term on the right of (2.7).

After some rearrangement of Eq. (3.4) and use of Eqs. (2.12) and (2.14) one finds

$$\tilde{V}(x,y,z) = \sum_{\vec{n}>0} \frac{1}{|\vec{n}|} \exp[-2\pi|\vec{n}||z|] \cos(2\pi\vec{n}\cdot\vec{\rho}), \tag{2.15}$$

with $\vec{n} \in \mathbb{Z}^2$ and $\vec{\rho} = (x,y)$.

In the case of $V(x,y,z)$ we have to replace r in (2.12) by $|z+m|$ and sum over m from $-\infty$ to ∞. The first term on the right of (2.12) then leads to the second term on the right of (2.4). The summation over m in

$$\sum_{\ell=1}^{\infty} \sum_{m=-\infty}^{\infty} \frac{1}{\sqrt{p^2+\ell^2}} \exp[-2\pi|z+m|\sqrt{p^2+\ell^2}] \cdot \cos(2\pi\ell y)$$

consists of two geometric series. Some routine steps and rearrangement show that one has

$$V(x,y,z) = \sum_{|\vec{n}|>0} \frac{1}{|\vec{n}|} \frac{\mathrm{Cosh}(\pi\cdot|\vec{n}|(1-2|z|))}{\mathrm{Sinh}(\pi\cdot|\vec{n}|)} \cos(2\pi\vec{n}\cdot\vec{\rho}). \tag{2.16}$$

Note that also here $\vec{n} \in \mathbb{Z}^2$. The functions $V(x,y,z)$ and $\tilde{V}(x,y,z)$ are obviously symmetric in x and y. An important point is that

$$U(x,y,z) := V(x,y,z) + 2\pi(z^2 - |z|) \tag{2.17}$$

is symmetric in x,y,z! This is not obvious from the form of $V(x,y,z)$, but it has to be true if one goes back to the original meaning. One can however check numerically that $U(x,y,z)$ is indeed symmetric in x,y,z.

We summarize our results in the form of

THEOREM 1 *The Coulomb energy as defined by* (1.2) *can be written as*

$$E = \frac{1}{2} \sum_{i\neq j=1}^{N} q_i q_j U(x_i - x_j, y_i - y_j, z_i - z_j) + \frac{2\pi}{3} \left(\sum_{i=1}^{N} q_i \vec{r}_i \right)^2 + Q_0 \cdot \sum_{i=1}^{N} q_i^2 \tag{2.18}$$

where $U(x,y,z)$ *defined by* (2.16), (2.17) *is symmetric in* x,y,z *and* $Q_0 \cong -1.942248$.

Remarks

(a) If $z_i = z_j$ we can take advantage of the symmetry and interchange in (2.16) the variables x,y,z.

(b) The fact that the function $V(x,y,z)$ involves only a double sum in contrast to the Ewald sum or the form (2.4) is a considerable improvement.

For the case of a layer the analogue of Theorem 1 is

THEOREM 2 *The Coulomb energy defined by* (1.2) *with* $\vec{n} \in \mathbb{Z}^2$ *is given by*

$$E = \frac{1}{2}\sum_{i\neq j=1}^{N} q_i q_j \tilde{U}(x_i - x_j, y_i - y_j, z_i - z_j) + \tilde{Q}_0 \cdot \sum_{i=1}^{N} q_i^2 \tag{2.19}$$

with

$$\tilde{U}(x,y,z) = \sum_{|\vec{n}|>0} \frac{1}{|\vec{n}|} \exp[-2\pi|\vec{n}||z|] \cos(2\pi\vec{\rho}\cdot\vec{n}) - 2\pi|z| \tag{2.20}$$

where $\vec{n} \in \mathbb{Z}^2$, $\vec{\rho} = (x,y)$, $\tilde{Q}_0 = -1.95013246$.

Remarks

(a) If $z_i = z_j$ one has to use (2.4) instead of (2.19), (2.20).
(b) If the basic cell is not a cube but still orthorhombic with sides a, b, c the formulae (2.3)–(2.6) are just slightly changed (see Lekner [5]).
(c) If the distance between two charges q_i, q_j is very small then the series in (2.4), (2.7), (2.16) or (2.20), converge slowly. One can then use identities derived in [9]. It was shown (Eqs. (3.40)–(3.42) there) that if $\rho = \sqrt{y^2+z^2}$ is small (say < 0.5) one has

$$Be[\rho,x] - L[y,z] = c_0 + H[y,z] + G[\rho,x] + \frac{1}{\sqrt{x^2+\rho^2}} \tag{2.21}$$

where

$$c_0 = 4\gamma - \log(16\pi^2) = -5.0620485, \tag{2.22}$$

$$\begin{aligned} H[y,z] &= -L[y,z] + \log\rho^2 + \log(4\pi^2) \\ &= 2\pi|z| + \frac{\pi^2}{3}(y^2 - z^2) + \frac{\pi^4}{90}(y^4 - 6y^2z^2 + z^4) + \text{higher order terms} \end{aligned} \tag{2.23}$$

and

$$G[\rho,x] = \sum_{\ell=1}^{\infty} \binom{-1/2}{\ell} \rho^{2\ell}\{\zeta(2\ell+1,1+x) + \zeta(2\ell+1,1-x)\} - \psi(1+x) - \psi(1-x). \tag{2.24}$$

Here

$$\zeta(m,s)=\sum_{k=0}^{\infty}\frac{1}{(k+s)^m} \tag{2.25}$$

is the Hurwitz Zetafunction (a multiple of the polygamma function) and ψ is the Digammafunction. The function $G[\rho,x]$ is an even function of x and symmetric with respect to $x=\pm(1/2)$. One can therefore restrict x to the interval $[0,(1/2)]$.

Equation (2.21) gives a decomposition of $V(x,y,z)$ into a regular and singular part which will be used in the next section.

(d) The Coulomb forces follow from the gradient of the corresponding potential for which we have different versions. For example the x-component of the force on charge q_i can be written as

$$F_x^i=-2\pi q_i\sum_{j\neq i}q_j\sum_{|\vec{n}|>0}\frac{n_x\mathrm{Cosh}(\pi\vec{n}|(1-|z_j-z_i|))}{|\vec{n}|\cdot\mathrm{Sinh}(\pi|\vec{n}|)}\sin(2\pi\vec{n}\cdot(\vec{\rho}_j-\vec{\rho}_i))$$
$$+\frac{4\pi}{3}q_i\sum_{j\neq i}q_j(x_j-x_i) \tag{2.26}$$

if the form (2.16), (2.17) of the potential is used.

A different version follows for the same force from (2.4). One now obtains

$$F_x^i=-8\pi q_i\sum_{j\neq i}\sum_{p=1}^{\infty}\sum_{k,\ell=-\infty}^{\infty}pK_0\left(2\pi p\sqrt{(y_j-y_i+\ell)^2+(z_j-z_i+\ell)^2}\right)$$
$$\cdot\sin(2\pi p(x_j-x_j))+\frac{4\pi}{3}q_i\sum_{j\neq i}q_j(x_j-x_i). \tag{2.27}$$

Note that

$$q_i\sum_{j\neq i}q_j(x_j-x_i)=q_i\sum_{j=1}^{N}q_jx_j=:q_i\cdot D_x$$

because of the charge neutrality. Two more versions are possible if in (2.16), (2.17) x, y, z are interchanged.

DENSE SYSTEMS

In this paper only the main ideas are presented. The detailed analysis and numerical results will be given in a separate work.

If the number N of charges q_i in the basic cell gets large (10^4 or more) it would be very time consuming to calculate the energy E or all the forces pairwise. The procedure for such dense systems is to use a product decomposition in the following sense.

Assume that we have to calculate

$$S = \sum_{i,j=1}^{N} f(x_i, x_j) \tag{3.1}$$

for some f. Suppose now that we have a decomposition

$$f(x_i, x_j) = \sum_{\ell=1}^{\infty} g_\ell(x_i) h_\ell(x_j). \tag{3.2}$$

Then we can approximate

$$S \cong \sum_{\ell=1}^{L} \sum_{i=1}^{N} g_\ell(x_i) \sum_{j=1}^{N} h_\ell(x_j), \tag{3.3}$$

so that we have $2 \cdot L \cdot N$ terms instead of N^2 terms to sum. In the case of the Coulomb energy (or forces) there are several possible decompositions of the form (3.2).

The main problem in applying any decomposition formula (3.2) in the case of Coulomb forces is that the limit L in (3.3) gets large as the distance of two charges gets small.

To account for this we split up the basic cell into M^3 sub-cells ("boxes")

$$B_{\alpha\beta\gamma} = \left\{ (x,y,z) \middle| \frac{\alpha-1}{M} \le x < \frac{\alpha}{M}, \frac{\beta-1}{M} \le y < \frac{\beta}{M}, \frac{\gamma-1}{M} \le z < \frac{\gamma}{M} \right\}, \quad \alpha, \beta, \gamma = 1, \ldots, M. \tag{3.4}$$

The number of boxes will be chosen much smaller than the number of charges in the basic cell.

For the Coulomb energy E one needs all $(1/2)N(N-1)$ pair interactions which we replace by box interactions.

A. Distant Boxes

Applying the addition theorems for cosines and exponential functions one is led to the approximation

$$V(\vec{\rho}_i - \vec{\rho}_j, z_i - z_j) \cong \sum_{0<|\vec{n}|\leq\nu} \overbrace{\frac{1}{|\vec{n}|(1-\exp(-2\pi|\vec{n}|))}}^{c(|\vec{n}|)} \exp(-2\pi|\vec{n}|z_j|)\exp(2\pi|\vec{n}|z_i) \cdot \cos(2\pi\vec{n}\cdot\vec{\rho}_i)\cos(2\pi\vec{n}\cdot\vec{\rho}_j|) + \text{similar terms} \tag{3.5}$$

where $\vec{\rho} = (x, y)$ and $z_i \geq z_j$ is assumed.

The limit ν depends on the accuracy required. We restrict our attention to a typical term as given by the right side of (3.5) since the remaining terms are of the same structure.

One can then first define sum over "layers":

$$L_\gamma^{\pm}(|\vec{n}|) = \sum_{\alpha,\beta=1}^{M} \sum_{B_{\alpha\beta\gamma}} q_i \exp(\pm 2\pi|\vec{n}|z_i)\cos(2\pi\vec{n}\cdot\vec{\rho}_i), \tag{3.6}$$

from which the energy contribution due to the interaction of two such layers follows as

$$E(\gamma,\tilde{\gamma}) = \sum_{0<|\vec{n}|<\nu(\delta)} c(|\vec{n}|)L_\gamma^{+}(|\vec{n}|)\cdot L_{\tilde{\gamma}}^{-}(|\vec{n}|), \tag{3.7}$$

where $\delta = \tilde{\gamma} - \gamma \geq 2$. The value $\nu(\delta)$ is not hard to determine but we omit the explicit dependence on δ here. Finally one has to form

$$E_L = \sum_{\gamma=1}^{M-2} \sum_{\tilde{\gamma}\geq\gamma+2} E(\gamma,\tilde{\gamma}) \tag{3.8}$$

to get the total energy contribution from these layer interactions.

We still have to calculate the interaction of all the charges within a layer $Z_\gamma = \{(x, y, z) \mid (\gamma - 1/M) \leq z < (\gamma/M)\}$. At this point the (x, y, z)-symmetry of the potential $U(x, y, z)$ defined by (2.16), (2.17) can be exploited. One forms sums over "stripes"

$$S_{\beta\gamma}^{\pm}(|\vec{n}|) = \sum_{\alpha=1}^{M} \sum_{B_{\alpha\beta\gamma}\in Z_\gamma} q_i \cdot \exp(\pm 2\pi|\vec{n}|y_i)\cos(2\pi\vec{n}\cdot\vec{\rho}_i), \tag{3.9}$$

where now $\vec{\rho} = (x, z)$. The energy contribution due to such stripe interactions is then

$$E_\gamma(\beta,\tilde{\beta}) = \sum_{0<|\vec{n}|\leq\nu(\delta)} c(|\vec{n}|)\cdot S_{\beta\gamma}^{+}(|\vec{n}|)\cdot S_{\tilde{\beta}\gamma}^{-}(|\vec{n}|), \tag{3.10}$$

with $\delta = \tilde{\beta} - \beta \geq 2$. It remains to form

$$E_S = \sum_{\gamma=1}^{M} \sum_{\beta=1}^{M-2} \sum_{\tilde{\beta} \geq \beta+2} E_\gamma(\beta, \tilde{\beta}). \tag{3.11}$$

The last pieces to consider are boxes within a stripe, that is

$$B^{\pm}_{\alpha\beta\gamma}(|\vec{n}|) = \sum_{B_{\alpha\beta\gamma}} q_i \cdot \exp(\pm 2\pi |\vec{n}| x_i) \cos(2\pi \vec{n} \cdot \vec{\rho}_i), \quad \vec{\rho} = (y, z), \tag{3.12}$$

which leads to

$$E_{\beta\gamma}(\alpha, \tilde{\alpha}) = \sum_{0<|\vec{n}| \leq \nu(\delta)} c(|\vec{n}|) B^{+}_{\alpha\beta\gamma}(|\vec{n}|) B^{-}_{\tilde{\alpha}\beta\gamma}(|\vec{n}|), \tag{3.13}$$

$\delta = \tilde{\alpha} - \alpha \geq 2$, and finally

$$E_B = \sum_{\gamma=1}^{M} \sum_{\beta=1}^{M} \sum_{\alpha=1}^{M-2} \sum_{\tilde{\alpha} \geq \alpha+2} E_{\beta\gamma}(\alpha, \tilde{\alpha}). \tag{3.14}$$

The contribution to the Coulomb energy is $E_L + E_S + E_B$.

B. Neighboring Boxes

In this section the interaction of a box $B_{\alpha\beta\gamma}$ with itself and all nearest neighbors is discussed. The basic formula is now (2.4) and the decomposition (2.21). If $q_i \in B_{\alpha\beta\gamma}$ and $q_j \in B_{\tilde{\alpha}\tilde{\beta}\tilde{\gamma}}$ where $|\tilde{\alpha} - \alpha|, |\tilde{\beta} - \beta|, |\tilde{\gamma} - \gamma| \leq 1$ then we can assume *e.g.*, that $((x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2)^{1/2} \leq 0.2$. We decompose $V(x, y, z)$ given by (2.4) as follows:

$$V(x, y, z) = \sum_{(k,\ell) \neq (0,0)} Be\left[\sqrt{(y+k)^2 + (z+\ell)^2}, x\right] - \sum_{m \neq 0} L[y, z+m] + Be[\rho, x] - L[y, z] \tag{3.15}$$

with $\rho = \sqrt{y^2 + z^2}$ and applying (2.21)

$$V(x,y,z) = \sum_{(k,\ell)\neq(0,0)} Be\left[\sqrt{(y+k)^2+(z+\ell)^2}, x\right] - \sum_{m\neq 0} L[y, z+m]$$
$$+ H[y,z] + G[\rho,x] + c_0 + \frac{1}{\sqrt{x^2+y^2+z^2}} \tag{3.16}$$
$$= W(x,y,z) + \frac{1}{\sqrt{x^2+y^2+z^2}}.$$

The important point is that $W(x,y,z)$ has no singularities for $0 \leq x^2 + y^2 + z^2 < 1$. In addition the function

$$W(x,y,z) + 2\pi(z^2 - |z|) = \phi(x,y,z) \tag{3.17}$$

is symmetric in x, y, z and an even function of its arguments. In the range of variables under consideration all series occurring converge very quickly. We first deal with the regular part $\phi(x,y,z)$ of the potential.

The boxes $B_{\alpha\beta\gamma}$ have sides of length $(1/M)$. We approximate $\phi(x, y, z)$ in a cube of side $s = (3/M)$ as

$$\phi(x,y,z) \cong \sum_{k,\ell,m=1}^{P} \varphi_{k\ell m}\mathrm{Cosh}(kx)\,\mathrm{Cosh}(\ell z)\,\mathrm{Cosh}(mz). \tag{3.18}$$

The coefficients $\varphi_{k\ell m}$ depend on P. Numerical tests show that for $s = 0.3$ and an error $\leq 10^{-6}$ $P = 3$ will suffice. Moreover, the $\varphi_{k\ell m}$ have to be calculated only once.

Let $N_{\alpha\beta\gamma}$ be the neighboring boxes of $N_{\alpha\beta\gamma}$ (in the basic cell). Then the contribution to E stemming from $\phi(x, y, z)$ is

$$E_r = \frac{1}{2} \sum_{q_i \in B_{\alpha\beta\gamma}} \sum_{q_j \in B_{\alpha\beta\gamma} \cup N_{\alpha\beta\gamma}} q_i q_j \phi(x_i - x_j, y_i - y_j, z_i - z_j). \tag{3.19}$$

The addition theorem for the hyperbolic cosine and (3.18) allow us to decompose $\phi(x_i - x_j,\ y_i - y_j,\ z_i - z_j)$ into eight products of the form

$$C^i_{k\ell m} C^j_{k\ell m} = \mathrm{Cosh}(kx_i)\,\mathrm{Cosh}(\ell y_i)\,\mathrm{Cosh}(mz_i)\,\mathrm{Cosh}(kx_j)\,\mathrm{Cosh}(\ell y_j)\,\mathrm{Cosh}(mz_j), \tag{3.20}$$

so that E_r can be split up into expressions like

$$E_r^{(1)} = \sum_{k,\ell,m=1}^{P} \varphi_{k\ell m}\left\{\left(\sum_{B_{\alpha\beta\gamma}} q_i C^i_{k\ell m}\right)^2 + \sum_{B_{\alpha\beta\gamma}} q_i C^i_{k\ell m} \sum_{N_{\alpha\beta\gamma}} q_j C^j_{k\ell m}\right\}. \tag{3.21}$$

The last item and the real "pièce de résistance" is the singular term $(x^2 + y^2 + z^2)^{-1/2}$. We need the interactions

$$E_S(\alpha, \beta, \gamma) = \frac{1}{2} \sum_{q_i \in B_{\alpha\beta\gamma}} \sum_{q_j \in B_{\alpha\beta\gamma} \cup N_{\alpha\beta\gamma}} q_i q_j \frac{1}{|\vec{r}_i - \vec{r}_j|}, \quad i \neq j. \tag{3.22}$$

In order to calculate $E_S(\alpha, \beta, \gamma)$ we subdivide the box $B_{\alpha\beta\gamma}$ into two more subregions

$$B^{(1)}_{\alpha\beta\gamma} \subset B^{(2)}_{\alpha\beta\gamma} \subset B_{\alpha\beta\gamma}$$

and similarly the whole neighborhood $B_{\alpha\beta\gamma} \cup N_{\alpha\beta\gamma}$ into subregions

$$B_{\alpha\beta\gamma} \subset N^{(1)}_{\alpha\beta\gamma} \subset N^{(2)}_{\alpha\beta\gamma} \cdots \subset N^{(s)}_{\alpha\beta\gamma} = B_{\alpha\beta\gamma} \cup N_{\alpha\beta\gamma}.$$

The size and number of these subregions depends on N. For the interaction

$$B^{(1)}_{\alpha\beta\gamma} \times \{B^{(1)}_{\alpha\beta\gamma} \cup B^{(2)}_{\alpha\beta\gamma}\}$$

we calculate the energy pairwise according to (3.22). For the interactions

$$B^{(1)}_{\alpha\beta\gamma} \times N^{(\ell)}, \quad \ell = 1, \ldots, s$$

we use the same approach as for the regular part since now $(1/|\vec{r}_i - \vec{r}_j|)$ is bounded by a fixed constant which depends on the size of the subregions. The limit P in (3.18) depends sensitively on s.

As an illustration for the sensitive dependence a few values are listed for the function $(x^2 + a^2)^{-1/2}$, approximated in the interval $I = (-0.13, 0.13)$ by a set of functions

$$b_p(x) = \sum_{\ell=1}^{p} \alpha^p_\ell \cdot Ch(\ell \cdot x) \tag{3.23}$$

which are orthonormal on the slightly larger interval $(-0.15, 0.15)$. Setting $\varepsilon = \max_I |(x^2 + a^2)^{-1/2} - f_P(x)|$ with

$$f_P(x) = \sum_{p=1}^{P} c_p \cdot b_p(x) \tag{3.24}$$

one finds values listed in the following table:

$a = 0.2$:	P	ε
	2	$3 \cdot 10^{-2}$
	3	$3 \cdot 10^{-3}$
	4	$3 \cdot 10^{-4}$
$a = 0.25$:	2	$1 \cdot 10^{-2}$
	3	$8 \cdot 10^{-4}$
	4	$6 \cdot 10^{-5}$
$a = 0.3$:	2	$6 \cdot 10^{-3}$
	3	$3 \cdot 10^{-4}$
	4	$15 \cdot 10^{-6}$

Remark A different approach to calculate (3.22) is that of Greengard and Rokhlin [3]. Numerical tests indicate however that it is considerably slower.

CONCLUDING REMARKS

(a) Calculation of Forces

It is quite obvious that for large N the forces can be calculated with a similar scheme as used for the energy. The expression on the right of (2.31) can be decomposed into products the same way as in (3.5). Furthermore, one will encounter the same terms already calculated for the energy, just in new combinations now.

(b) Modifications for the Two-dimensional Case

The potential $\tilde{U}(x, y, z)$ defined in (2.20) has only (x, y)-symmetry. For all charges q_i, q_j in the same layer $|z_i - z_j| \leq \delta$, δ small, one has to use the form (2.7) and then apply (2.21).

(c) Product Decomposition Involving Bessel Functions

It is possible to decompose into products the expression $Be\left[\sqrt{(y+\ell)^2 + (z+\ell)^2}, x\right]$ occurring *e.g.*, in (3.15). One has to write the square-root term in polar coordinates and then apply the Gegenbauer addition theorem which states that for $R > r > 0$

$$K_0\left(\sqrt{R^2 + r^2 - 2Rr\cos\varphi}\right) = K_0(R)I_0(r) + 2\sum_{\nu=1}^{\infty} K_\nu(R)I_\nu(r)\cos(\nu\varphi).$$

The analysis becomes however rather complicated (see [8]) and tests showed that the procedure described in this paper is faster.

(d) Numerical Tests

Tests show that when $N > 100$ (with error $\leq 10^{-6}$), the product decomposition described in Section 3 becomes faster than the pairwise calculation using (2.1).

For $N = 10^4$ the calculation of E and all forces with relative error less than 10^{-6} on an Alpha EV5.6 processor at 500 MHz required 4.5 seconds.

References

[1] De Leuuw S. W. Perram, J. W. and J. M. Smith, E. R. (1980). "Simulation of electrostatic systems in periodic boundary conditions. I. Lattice sums and dielectric constants", *Proc. R. Soc. A*, **373**, 27–56.
[2] Ewald, P. P. (1921). "Die Berechnung optischer und elektrostatischer Gitterpotentiale", *Ann. Phys.*, **64**, 253–287.
[3] Greengard, J. and Rokhlin, M. (1987). "A fast Algorithm for Particle Simulations", *J. of Comp. Ph.*, **73**, 325–348.
[4] Lekner, J. (1991). "Summation of Coulomb fields in computer simulated disordered systems", *Physica A*, **176**, 485–498.
[5] Lekner, J. (1998). "Coulomb forces and potentials in systems with an orthorhombic unit cell", *Mol. Simulation*, **20**, 356–368.
[6] Madelung, E. (1918). "Das elektrische Feld in Systemen von regelmässig angeordneten Punktladungen", *Phys. Zeitschrift*, **19**, 524–532.
[7] Sperb, R. (1994). "Extension and simple proof of Lekner's summation formula for Coulomb forces", *Mol. Simulation*, **13**, 189–193.
[8] Sperb, R. "The Coulomb energy for a dense periodic system", Research Report No. 98-03, Seminar für Angewandte Mathematik, ETH Zürich.
[9] Sperb, R. (1998). "An alternative to Ewald sums. Part I: Identities for sums". *Mol. Simulation*, **20**, 179–200.