Evaluation of Coulomb potential in a triclinic cell with periodic boundary conditions

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Abstract

Lekner [J. Lekner, Mol. Simul. 20 (1998)] and Sperb’s [R. Sperb, Mol. Simul. 13, (1994)] work on the evaluation of Coulomb energy and forces under periodic boundary conditions is generalized that makes it possible to use a triclinic unit cell in simulations in 3D rather than just an orthorhombic cell. The expressions obtained are in a similar form as previously obtained by Lekner and Sperb for the especial case of orthorhombic cell.

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I. INTRODUCTION

Molecular dynamics and Monte Carlo simulations of electrically charged point particles are indispensable in condensed matter physics. Generally, in simulations, periodic boundary conditions (pbc) are imposed to avoid unwanted effects of boundaries. In presence of pbc, it becomes necessary to include the effect of image charges while calculating interaction energy and forces. The treatment of image charges is rather trivial for short range forces; one simply subdivides the simulation cell into several smaller cells, such that each of these cells is bigger than the range of interaction. The simulation time obviously scales as $N$ for such short range potentials. However, if the interaction is long range, such as the Coulomb interaction, it becomes impossible to take into account all of image charges without taking recourse to some analytical technique. One of the techniques applied extensively in treating long range Coulomb interaction is the Ewald method. Usually, when working with several thousand charges, the $N^2$ cost of computing energy of a system carrying $N$ charges overwhelms even supercomputers. To deal with such cases, one usually works with a variant of the Ewald method known as PPPM. Another popular method is Fast Multipole method. Recently another method known as the MMM method was shown to be faster and more accurate than the PPPM when a high accuracy is required, but has yet to attract the attention of researchers. Our aim in this paper is not to consider achieving linear scaling but rather to give a genuine alternative to the Ewald method for smaller systems.

There are two main alternatives to the Ewald method. The first one is the so called Lekner method, and the second one is due to Sperb. These methods are limited in their application in that they were derived only for an orthorhombic simulation cell. In this regard, these methods are not as versatile as the Ewald method that can be applied even for a triclinic cell. However, only recently, a method was proposed that extends Sperb’s method and makes it possible to employ it even for a triclinic cell. In this paper, our aim is to directly generalize Lekner’s work on orthorhombic simulation cells to a triclinic cell. Simple expressions will be derived to this end. However, our way of approaching this problem will be different from that of Lekner. The end results will of course contain Lekner’s work as a special case.
II. GENERALIZATION OF LEKNER METHOD

We consider $N$ charges $q_i$ contained in a triclinic simulation cell in 3-dimensional space. The index $i$ runs over $i = 1$ to $N$. We assume that the system is periodic in all dimensions. These charges interact via the Coulomb potential. The electrostatic energy of $N$ charges can be expressed as

$$E_{\text{total}} = \frac{1}{2} \sum_{i,j: i \neq j} q_i q_j G(r_i - r_j) + \frac{1}{2} \sum_i q_i^2 G_{\text{self}} + \frac{2\pi}{3} \left( \sum_i q_i r_i \right)^2,$$

(2.1)

where the position of charges in the simulation cell is denoted by $r_i$. We will obtain expressions for $G(r)$ and $G_{\text{self}}$ in 3D in this section.

The interaction between a pair of charges, a separation $r$ apart, goes as $|r|^{-1}$. Such pairwise interactions when added under pbc lead to a diverging series, if the simulation cell is not overall charge neutral. However, if one has a charge neutral system, then the sum leads to a conditionally convergent series. To give a well defined meaning to the series, one has to specify how the terms in series are to be grouped together. Usually, one assumes that the particles interact with a screened potential that goes as $\exp \left( -\beta |r| / |r| \right)$; finally the limit $\beta \to 0$ is taken. This is equivalent to introducing artificial background charges, and also to taking sums over expanding cubes. However, this technique only leads to the intrinsic part of the energy. A dipole term has to be added if one wants the energy in the limit of expanding spherical shells\textsuperscript{10}. The last term in Eq. (2.1) represents this dipole term.

We introduce a slightly different way of including the $\beta$ factor. Instead of working with the exponential functions, we will work with the modified Bessel function of the second kind. Of course there is not much difference between these two different ways as for the large arguments, the modified Bessel functions of the second kind decay exponentially as well. We start with the fact that the limit of $K_{1/2}(\beta r)$ as $\beta$ tends to zero is given by

$$\lim_{\beta \to 0} K_{1/2}(\beta r) \sim \sqrt{\frac{\pi}{2}} \frac{1}{(\beta r)^{1/2}},$$

(2.2)

that makes it possible to write

$$\frac{1}{r} = \sqrt{\frac{2}{\pi}} \lim_{\beta \to 0} \beta^{1/2} K_{1/2}(\beta r) r^{1/2}.$$  

(2.3)

In a triclinic cell, the position of a charge can be specified by $x_1$, $x_2$, and $x_3$, where $0 \leq x_i < l_i$ for $i = 1, 2, 3$. Here $l_i$ denote the lengths of the sides of the triclinic basic cell. To obtain
the interaction between a pair of charges one may assume that one of the charges is located at the origin and the other one at \((x_1, x_2, x_3)\). Due to the pbc, one has to also consider the interaction of the second charge with all of the periodic images of the charge at the origin. These periodic images are located at \((l_1 m, l_2 n, l_3 p)\), where \(m, n\) and \(p\) are integers ranging over \(-\infty\) to \(+\infty\). The distance between the first charge and a periodic image at \((l_1 m, l_2 n, l_3 p)\) is given by

\[
 r_{m,n,p}^2 = (x_1 + l_1 m)^2 + (x_2 + l_2 n)^2 + (x_3 + l_3 p)^2 \\
 + 2(x_1 + l_1 m) (x_2 + l_2 n) \cos \alpha \\
 + 2 (x_2 + l_2 n) (x_3 + l_3 p) \cos \beta \\
 + 2 (x_3 + l_3 p) (x_1 + l_1 m) \cos \gamma. \tag{2.4}
\]

The function \(G\) can be expressed now as

\[
 G(r) = \lim_{\beta \to 0} G(r; \beta) = \lim_{\beta \to 0} \sqrt{\frac{2}{\pi}} \beta^{1/2} \sum_{m,n,p} \frac{K_{1/2} (\beta r_{m,n,p})}{r_{m,n,p}^{1/2}}. \tag{2.5}
\]

Now, we switch over to the cylindrical coordinates by defining

\[
 r_{m,n,p}^2 = (x_{n,p} + l_1 m)^2 + \rho_{n,p}^2, \tag{2.6}
\]

where

\[
 x_{n,p} = x_1 + (x_2 + l_2 n) \cos \alpha + (x_3 + l_3 p) \cos \gamma, \tag{2.7}
\]

and

\[
 \rho_{n,p}^2 = (x_2 + l_2 n)^2 \sin^2 \alpha + (x_3 + l_3 p)^2 \sin^2 \gamma \\
 + 2 (x_2 + l_2 n) (x_3 + l_3 p) (\cos \beta - \cos \alpha \cos \gamma). \tag{2.8}
\]

For later convenience we also define

\[
 x_{n,p}^0 = l_2 n \cos \alpha + l_3 p \cos \gamma, \\
 \rho_{n,p}^0 = \sqrt{(l_2 n)^2 \sin^2 \alpha + (l_3 p)^2 \sin^2 \gamma + 2 (l_2 n) (l_3 p) (\cos \beta - \cos \alpha \cos \gamma)}. \tag{2.9}
\]
and
\[\rho_{0,0} = \left[ x_2^2 \sin^2 \alpha + x_3^2 \sin^2 \gamma + 2x_2x_3 (\cos \beta - \cos \alpha \cos \gamma) \right]^{1/2} \]
\[x_{0,0} = x_1 + x_2 \cos \alpha + x_3 \cos \gamma. \quad (2.10)\]

Now, as shown in the appendix, \( G \) can be written as
\[ G (r) = \frac{2}{l_1} \lim_{\beta \to 0} \sum_m \sum_{n,p} \exp \left( i2\pi m \frac{x_{n,p}}{l_1} \right) K_0 \left( \sqrt{m^2 + \beta^2 \rho_{n,p}} \right) \]
\[= U (r) + Q (r), \quad (2.11)\]

where
\[ U (r) = \frac{2}{l_1} \left( \lim_{\beta \to 0} \sum_{n,p=-\infty}^{\infty} K_0 (\beta \rho_{n,p}) \right), \quad (2.12)\]
and
\[ Q (r) = \frac{4}{l_1} \sum_{n,p} \sum_{m=1}^{\infty} K_0 \left( 2\pi m \frac{\rho_{n,p}}{l_1} \right) \cos \left( 2\pi m \frac{x_{n,p}}{l_1} \right). \quad (2.13)\]

We note that \( Q \) has excellent convergence for \( \varepsilon = \rho_{0,0}/l_1 > 0.1 \). However, for smaller \( \varepsilon \) we will modify \( Q \). But before doing that we would like to obtain an expression for \( U \). This can be done following Sperb. For this we first express \( \rho_{n,p} \) as follows
\[\rho_{n,p}^2 = \sin^2 \alpha \left[ x_2 + l_2n + (x_3 + l_3p) \left( \frac{\cos \beta - \cos \alpha \cos \gamma}{\sin^2 \alpha} \right) \right]^2 \]
\[+ (x_3 + l_3p)^2 \left[ \sin^2 \gamma - \left( \frac{\cos \beta - \cos \alpha \cos \gamma}{\sin \alpha} \right)^2 \right] \]
\[= \sin^2 \alpha \left[ (y_p + l_2n)^2 + (x_3 + l_3p)^2 \Omega^2 \right], \quad (2.14)\]

where
\[ y_p = x_2 + (x_3 + l_3p) \zeta, \quad (2.15)\]
\[ \zeta = \left( \frac{\cos \beta - \cos \alpha \cos \gamma}{\sin^2 \alpha} \right), \quad (2.16)\]
and
\[ \Omega = \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma \over \sin^2 \alpha}. \quad (2.17)\]

We note that \( \zeta \) and \( \Omega \) are purely geometrical factors. Also, note the relation
\[ \Omega^2 + \zeta^2 = {\sin^2 \gamma \over \sin^2 \alpha}, \quad (2.18)\]
which will be useful later. In order to further recast the expression for $U$ we use the identity

$$
\sum_{n=\infty}^{\infty} K_0 \left[ \beta \sqrt{(y + nl)^2 + x^2} \right] = \frac{\pi \exp \left( -\beta |x| \right)}{l},
$$

which implies

$$
\lim_{\beta \to 0} \sum_{n=\infty}^{\infty} K_0 \left[ \beta \sqrt{(y + nl)^2 + x^2} \right] = \lim_{\beta \to 0} \frac{\pi \exp \left( -\beta |x| \right)}{l} - \frac{1}{2} L \left[ x/y, l \right],
$$

where we have defined

$$
L[x, y] = \ln \left[ 1 - 2 \exp \left( -2\pi |x| \right) \cos (2\pi y) + \exp \left( -4\pi |x| \right) \right].
$$

Thus, we obtain from Eq. (2.13) and (2.19)

$$
U(r) = \frac{2\pi}{l_1 l_2} \lim_{\beta \to 0} M(x_3, \beta) - \frac{1}{l_1} \sum_{p=\infty}^{\infty} L \left[ x_3 + l_3 p, x_3 l_2 \Omega, l_2 \right].
$$

The $M$ in Eq. (2.22) stands for

$$
M(x_3, \beta) = \sum_{p=-\infty}^{\infty} \frac{\exp \left(-\beta \Omega \sin \alpha |x_3 + l_3 p| \right)}{\beta}
$$

$$
= \frac{\Omega l_3 \sin \alpha}{2} \frac{\cosh \left[ \xi \left( 1 - 2 \frac{|x_3|}{l_3} \right) \right]}{\xi \sinh \xi},
$$

where $\xi = (\beta \Omega l_3/2) \sin \alpha$ and a simple geometric sum has been carried out. The limit $\beta \to 0$ can now be carried out

$$
\lim_{\beta \to 0} M(x_3, \beta) \approx \frac{\Omega l_3 \sin \alpha}{2} \left[ \frac{1}{3} - 2 \frac{|x_3|}{l_3} + 2 \left( \frac{x_3}{l_3} \right)^2 + \frac{1}{\chi^2} \right]
$$

$$
= \frac{\Omega l_3 \sin \alpha}{6} \left[ 1 - \frac{6|x_3|}{l_3} + \left( \frac{x_3}{l_3} \right)^2 \right] + \frac{2}{\beta^2 \Omega l_3 \sin \alpha}.
$$

Using Eq. (2.11), (2.22), (2.23) and (2.24) we obtain the following expression for the energy

$$
G(r) = \frac{4}{l_1} \sum_{n,p}^{\infty} K_0 \left( 2\pi m \frac{\rho_{n,p}}{l_1} \right) \cos \left( 2\pi m \frac{x_{n,p}}{l_1} \right) - \frac{1}{l_1} \sum_{p=\infty}^{\infty} L \left[ x_3 + l_3 p, x_3 l_2 \Omega, l_2 \right]
$$

$$
+ \frac{\Omega l_3 \sin \alpha \pi}{l_1 l_2} \left[ 1 - 6 \frac{|x_3|}{l_3} + \left( \frac{x_3}{l_3} \right)^2 \right],
$$

(2.25)
where we have dropped the constant factor $4\pi/(V\beta^2)$, and $V = l_1l_2l_3 \Omega \sin \alpha$ denotes the volume of the basic simulation cell. This dropping of the constant factor is justified on account of charge neutrality: The overall contribution to the energy from this term would be $E_\beta$

$$E_\beta = \frac{4\pi}{V} \left[ \sum_{i=1}^{N-1} \sum_{j=i+1}^N q_i q_j \left( \frac{1}{\beta^2} \right) + \frac{1}{2} \sum_{i=1}^N q_i^2 \left( \frac{1}{\beta^2} \right) \right]$$

$$= 0 \quad (2.26)$$

The result in Eq. (2.25) is the main result of this paper. The form of $G$ as written in Eq. (2.25) has excellent convergence for the most part of the simulation cell. However, the convergence is bad for the case when $\varepsilon = \rho_{0,0}/l_1 \ll 1$. The problem lies with the series corresponding to $n = 0$ and $p = 0$ in Eq. (2.13) for $Q$. For this case the argument of the function $K_0$ becomes very small and it takes a lot of summation terms over $m$ to achieve convergence. However, now there is now a well defined way to fix this problem; we isolate the series corresponding to $n = 0$ and $p = 0$, and rewrite it in terms of Polygamma and Zeta functions\textsuperscript{11}. For this we first define

$$f(x, \rho, l) = \frac{1}{\sqrt{\rho^2 + x^2}} + \sum_{n=1}^{\infty} \left( \frac{1}{\sqrt{\rho^2 + (nl + x)^2}} + \frac{1}{\sqrt{\rho^2 + (nl - x)^2}} - \frac{2}{nl} \right)$$

$$= \frac{4}{l} \sum_{m=1}^{\infty} K_0 \left( \frac{2\pi m \rho_0}{l} \right) \cos \left( \frac{2\pi m x}{l} \right) - \frac{2}{l} \left\{ \gamma + \ln \left( \frac{\rho_0}{2} \right) \right\} \quad (2.27)$$

Using Eq. (2.26) and (2.27), we can write

$$G(r) = \frac{4}{l_1} \sum_{n,p} \sum_{m=1}^{\infty} K_0 \left( 2\pi m \frac{\rho_{n,p}}{l_1} \right) \cos \left( 2\pi m \frac{x_{n,p}}{l_1} \right)$$

$$- \frac{1}{l_1} \sum_p L \left[ \frac{x_3 + l_3 \rho_0 \Omega y_p}{l_2} \right] + 2\pi \left( \frac{x_3^2}{l_1 l_2 l_3} - \frac{|x_3|}{l_1} \right) + \frac{2\gamma}{l_1}$$

$$+ f(x_{0,0}, \rho_{0,0}, l_1) + \frac{1}{l_1} \left\{ 2 \ln \left( \frac{\rho_{0,0}}{2} \right) - L \left[ \frac{x_3}{l_2} \Omega, \frac{y_0}{l_2} \right] \right\} \quad (2.28)$$

where a prime over the summation sign indicates that the term corresponding to $n = 0$ and $p = 0$ is not to be included in the summation. As written in Eq. (2.28), the series has two convergence problems when $\rho_{0,0}$ tends to zero. Firstly, when $\rho_{0,0} = 0$ the last term is not defined. And secondly, as mentioned earlier, the function $f(x, \rho, l)$ does not converge fast for small $\rho$. Both of these problem may be fixed by taking the limit $\rho_{0,0} \to 0$ and combining
the appropriate terms as follows. Using Eq. (2.14) we note that \( \rho_{0,0} \to 0 \) means \( y_0 \to 0 \) and \( x_3 \to 0 \). Also,

\[
\rho_{n,p}^2 = \sin^2 \alpha \left[ (y_p + l_2n)^2 + (x_3 + l_3p)^2 \Omega^2 \right]
\]

implies

\[
\rho_{0,0}^2 = \sin^2 \alpha \left[ y_0^2 + x_3^2 \Omega^2 \right].
\]

So, the last term in Eq. (2.28) may be written as

\[
S = \frac{1}{l_1} \left\{ 2 \ln \left( \frac{\rho_{0,0}}{2} \right) - L \left[ \frac{x_3 \Omega, y_0}{l_2} \right] \right\}
= \frac{1}{l_1} \left\{ \ln \left( \frac{\sin^2 \alpha \left[ y_0^2 + x_3^2 \Omega^2 \right]}{4l_2^2} \right) - L \left[ \frac{x_3 \Omega, y_0}{l_2} \right] \right\}
= \frac{1}{l_1} \left\{ \ln \left( \frac{\left[ y_0^2 + x_3^2 \Omega^2 \right]}{l_2^2} \right) - L \left[ \frac{x_3 \Omega, y_0}{l_2} \right] - 2 \ln \left( \frac{2}{l_2 \sin \alpha} \right) \right\}.
\]

Now, through a simple Taylor expansion it could be shown that for small \( y \) and \( z \) we have

\[
\ln \left( y^2 + z^2 \right) - L \left[ y, z \right] = L a \left[ y, z \right] - 2 \ln \left( 2\pi \right),
\]

where

\[
L a[y, z] = 2\pi z + \frac{\pi^2}{3} \left( y^2 - z^2 \right) + \frac{\pi^4}{90} \left( y^4 - 6y^2z^2 + z^4 \right) + \frac{2\pi^6}{2835} \left( y^6 - 15y^4z^2 + 15y^2z^4 - z^6 \right) + \text{higher order terms}.
\]

With the help of identity in Eq. (2.32) we can write \( S \) for small \( \rho_{0,0} \) as follows:

\[
S = \frac{1}{l_1} L a \left[ \frac{x_3 \Omega, y_0}{l_2} \right] - \frac{2}{l_1} \ln \left( \frac{4\pi}{l_2 \sin \alpha} \right).
\]

This fixes the first problem. To fix the second problem in order to achieve a better convergence for small \( \rho \), we re-express \( f \left( x, \rho, l \right) \) using the results of Ref.11 as follows:

\[
f \left( x, \rho, l \right) = \frac{1}{(r_1^2 + r_2^2 + r_3^2 + 2r_1r_2 \cos \alpha + 2r_2r_3 \cos \beta + 2r_3r_1 \cos \gamma)^{1/2}}
+ \frac{1}{l} \sum_{n=1}^{N-1} \left( \frac{1}{\sqrt{\rho^2 + (n + x)^2}} + \frac{1}{\sqrt{\rho^2 + (n - x)^2}} \right)
- \frac{2\gamma}{l} \frac{\psi(N + x) + \psi(N - x)}{l}
+ \frac{1}{l} \sum_{m=1}^{\infty} \left( -1/2 \right)^m \rho^{2m} \left[ \zeta \left( 2m + 1, N + x \right) + \zeta \left( 2m + 1, N - x \right) \right].
\]
where \( \psi \) and \( \zeta \) stand for digamma and Hurwitz Zeta functions respectively, and \( N \geq 1 \) is chosen such that \( N > (\rho + x) \). However, for better convergence it is desirable that \( N > (\rho + 1) \). Thus, using this alternate form for function \( f \) from Eq. (2.33) we obtain a different representation of \( G \) which gives very fast convergence as \( \rho \) tends to zero. The important fact here is that the Coulomb singularity toward small \( |r| \) has been isolated.

Also, it is now a simple matter to obtain the self-energy using the fact that

\[
\lim_{\rho, x \to 0} S = \lim_{y_0 \to 0, x_3 \to 0} \left( \frac{1}{l_1} L a \left[ \frac{x_3}{l_2} \Omega, \frac{y_0}{l_2} \right] - \frac{2}{l_1} \ln \left( \frac{4\pi}{l_2 \sin \alpha} \right) \right) = -\frac{2}{l_1} \ln \left( \frac{4\pi}{l_2 \sin \alpha} \right).
\]

It then follows

\[
G_{\text{self}} = \lim_{\rho, x \to 0} \left( G(r) - \frac{1}{\sqrt{\rho^2 + x^2}} \right)
\]

\[
= \frac{4}{l_1} \sum_{n,p} \sum_{m=1}^{\infty} K_0 \left( 2\pi m \rho_{n,p}^0 l_1 \right) \times \cos \left( 2\pi m x_{n,p}^0 l_1 \right) + \frac{2\gamma}{l_1} - \frac{1}{l_1} \sum_p L \left[ \frac{l_3 p}{l_2} \Omega, \frac{\zeta l_3 p}{l_2} \right] - 2 \ln \left( \frac{4\pi}{l_2 \sin \alpha} \right),
\]

where

\[
\rho_{n,p}^0 = \sqrt{\sin^2 \alpha \left[ (l_3 p \zeta + l_2 n)^2 + (l_3 p)^2 \Omega^2 \right]}.
\]

Expressions in Eq. (2.25) and (2.34) are the generalization of Sperb’s and Lekner’s work from an orthorhombic cell to a a triclinic cell. In the special case when an orthorhombic cell is considered, Eq. (2.25) reduces to

\[
G_{\text{ortho}} = \frac{4}{l_1} \sum_{n,p} \sum_{m=1}^{\infty} K_0 \left( 2\pi m \sqrt{\frac{(x_2 + l_2 n)^2 + (x_3 + l_3 p)^2}{l_1}} \right) \cos \left( 2\pi m x_1 l_1 \right)
\]

\[
- \frac{1}{l_1} \sum_p \ln \left[ 1 - 2 \exp \left( -\frac{2\pi}{l_2} |x_3 + l_3 p| \right) \times \cos \left( 2\pi x_2 l_2 \right) + \exp \left( -\frac{4\pi}{l_2} |x_3 + l_3 p| \right) \right] + \frac{2}{l_1} \ln \left( \sqrt{x_2^2 + x_3^2} \right) + f \left( x_1, \sqrt{x_2^2 + x_3^2} l_1, l_1 l_2 l_3 \right) - 2\pi \frac{|x_3|}{l_1 l_2} + 2\pi \frac{x_2^2}{l_1 l_2 l_3}.
\]
This result is in agreement with the ones derived by Sperb and Lekner. Finally, to summarize our results, the total energy of \( N \) charges is given by Eq. (2.1). The function \( G \) in Eq. (2.1) may be obtained by using

\[
G(r) = 4\frac{l_1}{l_1'} \sum_{n,p} \sum_{m=1}^{\infty} K_0 \left( 2\pi m \frac{\rho_{n,p}}{l_1} \right) \cos \left( 2\pi m \frac{x_{n,p}}{l_1} \right) - \frac{1}{l_1} \sum_{p=-\infty}^{\infty} L \left[ \frac{x_3 + l_3 p}{l_2} \Omega, \frac{y_p}{l_2} \right] \\
+ \frac{\Omega l_3 \sin \alpha \pi}{l_1 l_2} \left[ 1 - 6 \frac{|x_3|}{l_3} + \left( \frac{x_3}{l_3} \right)^2 \right],
\]

(2.36)

where \( \rho_{n,p}, x_{n,p}, y_p \) are defined in Eqs. (2.8), (2.7), and (2.15). The \( \Omega \) is defined by Eq. (2.17) and the function \( L \) is defined in Eq. (2.21). For the case when \( \varepsilon = \rho_{0,0}/l_1 \ll 1 \), one should use the following expression

\[
G(r) = 4\frac{l_1}{l_1'} \sum_{n,p} \sum_{m=1}^{\infty} K_0 \left( 2\pi m \frac{\rho_{n,p}}{l_1} \right) \cos \left( 2\pi m \frac{x_{n,p}}{l_1} \right) \\
- \frac{1}{l_1} \sum_{p} L \left[ \frac{x_3 + l_3 p}{l_2} \Omega, \frac{y_p}{l_2} \right] + 2\pi \left( \frac{x_3^2}{l_1 l_2} - \frac{|x_3|}{l_1 l_2} \right) \\
+ \frac{3}{l_1} \sum_{p} L \left[ \frac{l_3 p}{l_2} \Omega, \frac{\zeta l_3 p}{l_2} \right] - \frac{2}{l_1} \ln \left( \frac{4\pi}{l_2 \sin \alpha} \right),
\]

(2.37)

where and \( f \) is is defined in Eq. (2.33) and \( La \) is defined in Eq. (2.32). The expression for force may be obtained by using \( F(r) = -\nabla G(r) \). Finally, the self-energy required in Eq. (2.1) is obtained by using

\[
G_{\text{self}} = 4\frac{l_1}{l_1'} \sum_{n,p} \sum_{m=1}^{\infty} K_0 \left( 2\pi m \frac{\rho_{n,p}}{l_1} \right) \times \cos \left( 2\pi m \frac{x_{n,p}}{l_1} \right) \\
- \frac{1}{l_1} \sum_{p} L \left[ \frac{l_3 p}{l_2} \Omega, \frac{\zeta l_3 p}{l_2} \right] - \frac{2}{l_1} \ln \left( \frac{4\pi}{l_2 |\sin \alpha|} \right).
\]

(2.38)

### III. RESULTS AND CONCLUSIONS

We have obtained complete expressions for the Coulomb potential in 3D, including self-energies. The results were derived for the most general case of a triclinic cell in 3D. The formulas derived here are in the same form as derived earlier by Lekner\(^6\) and Sperb\(^7\) for the case of an orthorhombic cell. With our results, it should now be possible to extend any written code for Lekner or Sperb summation to a triclinic cell with minimal effort. The results obtained in this paper reduces to the results of a recent paper\(^11\) when all angles
pertaining to the unit cell are set to $\pi/2$. The results also agree with the special cases considered by Lekner and Sperb.

**APPENDIX A: REPRESENTATION FOR $G(r; \beta)$**

The solution of
\[
(\nabla^2 - \beta^2) S_d(r; \beta) = -C_d \delta_d(r)
\]
(A1)
in $d$-dimensional space is given by
\[
S_d(r; \beta) = \frac{C_d}{(2\pi)^{\nu+1/2}} \left[ \beta^\nu K_\nu (\beta r) \right],
\]
(A2)
where $C_d$ is defined as
\[
C_d = \begin{cases} 
2 & d = 1 \\
2\pi & d = 2, \\
4\pi^{\nu+1}/\Gamma(\nu) & d > 2.
\end{cases}
\]

Here, $\Gamma(\nu)$ stands for the Gamma function, and $\nu = (d - 2)/2$. For $d = 3$ we can write the solution in the Fourier space using Eq. (A1):
\[
S_3(r; \beta) = \frac{C_3}{(2\pi)^2} \int dk_1 dk_\rho e^{i2\pi(x_{n,p} + k_\rho l_1) + k_\rho \cdot \rho_{n,p}} e^{i2\pi \left[k_1^2 + k_\rho^2 + \frac{\beta^2}{4\pi^2}\right]},
\]
(A3)
where we have written the vector $r$ in cylindrical coordinates as $(x, \rho)$. Now, using Eq. (2.5) we can write
\[
G(r; \beta) = \frac{C_3}{(2\pi)^2} \sum_{n,p} \sum_m \int dk_1 dk_\rho \frac{e^{i2\pi k_{1}m} K_{1/2}(\beta r_{m,n,p})}{k_1^2 + k_\rho^2 + \frac{\beta^2}{4\pi^2}}.
\]
(A4)

Now, using the fact that
\[
\sum_m e^{i2\pi k_1 m} = \frac{1}{l_1} \sum_m \delta(k_1 - m),
\]
(A5)
we can replace the integral over $k_1$ with a summation:
\[
G(r; \beta) = \frac{C_3}{(2\pi)^2} \frac{1}{l_1} \sum_{n,p} \sum_m \int dk_\rho \frac{e^{i2\pi (m x_{n,p} + k_\rho \rho_{n,p})}}{m^2 + k_\rho^2 + \frac{\beta^2}{4\pi^2}}
\]
\[
= \frac{C_3}{C_2 l_1} \sum_{n,p} \sum_m \exp \left(i2\pi m \frac{x_{np}}{l_1}\right) K_0 \left(\sqrt{m^2 + \beta^2 \rho_{n,p}}\right),
\]
(A6)
where

\[ \rho_{n,p} = |\rho_{n,p}| \]

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