

Communication: On the origin of the surface term in the Ewald formula

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A transparent derivation of the Ewald formula for the electrostatic energy of a periodic three-dimensional system of point charges is presented. The problem of the conditional convergence of the lattice sum is dealt with by separating off, in a physically natural and mathematically simple way, long-range non-absolutely integrable contributions in the series. The general expression, for any summation order, of the surface (or dipole) term emerges very directly from those long-range contributions. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4872019>]

Molecular simulations are commonly performed under periodic boundary conditions and by using a lattice-sum method to solve the Poisson equation with the imposed periodicity, thereby avoiding any truncation of long-range Coulomb interactions.^{1–5} The electrostatic energy, per cell, of the simulated periodic system is then given by the Ewald formula which expresses that energy E as a sum of short-range interactions (computed in real-space) and of smooth long-range interactions (computed in Fourier space). The Ewald formula, or numerically optimized mesh-based variants of it,⁶ are used to perform simulations of charged systems containing from a few to millions of interacting particles. Other methods than Ewald's exist also to compute lattice-sums.⁶

The energy E of a simulation cell containing N particles j , with position \mathbf{r}_j and point charge q_j , is defined by the coulombic lattice sum

$$E = \frac{1}{2} \sum_{\mathbf{m}} \sum_{i,j=1}^N \star \frac{q_i q_j}{|\mathbf{r}_i - (\mathbf{r}_j + \mathbf{m})|}, \quad (1)$$

where vector \mathbf{m} represents the center of a periodic copy of the simulation cell (assumed to be electrically neutral) and where the asterisk indicates that $i = j$ terms are omitted when $\mathbf{m} = 0$. The cell is triclinic, with a volume $V_{\text{cell}} = |(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3|$ spanned by the three basis lattice vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 . The sum (1) is conditionally convergent due to dipolar $1/r^3$ interactions (between the simulation cell and a distant periodic replica), which are at the limit of integrability in three-dimensional space. A summation order must hence be specified in (1): the sum is performed first over all cells inside a volume V (one adds the condition $\mathbf{m} \in V$ in (1) thereby defining an energy E_V), and $E = \lim_{V \rightarrow \infty} E_V$ is defined as the energy when the assembly of unit cells grows infinitely large with fixed shape S specified by V .

Several derivations of the Ewald formula that treat properly the conditionally convergent character of the lattice-sum (1) are available, but they are quite long and mathematically involved, leading to a loss of physical insight on how the surface contributions to the energy, and to the electrostatic potential, arise from the conditional convergence. Those surface contributions, absent in the original Ewald formula,⁷ have first been derived by Redlack and Grindlay.⁸ Mathematically well

controlled proofs of the Ewald formula, including surface terms, were given later by de Leeuw, Perram, and Smith,^{9,10} who also generalized the formula for the surface term to the case where the macroscopic (pseudo)crystal is surrounded by a dielectric medium of dielectric constant ϵ . The proof in Ref. 9 uses a convergence factor $\exp(-s|\mathbf{m}|^2)$ ($s \rightarrow 0$) to enforce a summation order over concentric spherical shells, while another more general technique based on integral transforms is used in Ref. 10. The resulting general expression for the surface contributions, valid for any even crystal shape, was later rewritten in a much more compact and transparent form using a depolarization tensor.^{11,12} Another derivation of the Ewald formula which uses a non trivial generalization of the Poisson-Jacobi summation formula to a finite number of lattice points is given in Ref. 12. Finally, an elegant proof, due to Piller, can be found in a paper by Hansen.¹³ The works^{14,15} do not contain complete proofs of the Ewald formula, but offer insights on the dipolar and quadrupolar surface contributions to the electrostatic potential.

As the Ewald formula is widely used in simulations (often with a vanishing surface term associated to metallic boundary conditions), having a simple derivation of that formula that is physically intuitive while mathematically sound would certainly be useful to many researchers. It should also be helpful for deriving generalizations of the Ewald formula to other long-range interactions. The surface term in the Ewald formula takes a special importance when computing absolute positions of crystalline energy bands,¹⁶ when simulating dielectric fluids^{17–19} and when using the Ewald method to simulate interfacial properties of three-dimensional systems.²⁰

The main trick in the present proof of the Ewald formula is to isolate the conditionally convergent contributions in the lattice sum (1) by merely adding and subtracting a well chosen conditionally convergent series according to

$$E = \sum_{n=1}^{\infty} a_n = \sum_{n=1}^{\infty} (a_n - b_n) + \sum_{n=1}^{\infty} b_n. \quad (2)$$

The terms b_n are chosen such that the series $S_1 = \sum_n (a_n - b_n)$ is absolutely convergent and such that the series $S_2 = \sum_n b_n$ can be computed without difficulty. The adequate choice

for b_n turns out to be the long-range dipole-dipole interaction between the simulation cell and a distant cell *uniformly* polarized by the same dipole moment. The absolutely convergent sum S_1 provides the intrinsic (shape-independent) Ewald energy, while the sum S_2 contains all conditionally convergent contributions and provides the surface term. Since the content of each cell is replaced in S_2 by a continuous distribution of dipolar moment, one recovers (and proves) that the surface term can be computed using only macroscopic electrostatics.¹⁵ The surface term is of course independent of the particular method used to compute the (Ewald) energy defined by the sum S_1 .

Besides the conditional convergence problem, the Coulomb potential poses another difficulty, namely, its strong variations near the origin. In the Ewald method, these two difficulties are treated separately by splitting the potential into a short-range part that contains the strong variations at short distances and a smooth long-range part that can be represented by a quickly converging Fourier series.

The proof starts by splitting the Coulomb potential according to the trivial identity

$$\frac{1}{|\mathbf{r}|} = \frac{1}{|\mathbf{r}|} - \phi(\mathbf{r}) + \phi(\mathbf{r}), \quad (3)$$

where $\phi(\mathbf{r})$ captures the long-range part of the potential so that $\psi(\mathbf{r}) = 1/|\mathbf{r}| - \phi(\mathbf{r})$ is short-ranged (i.e., decays faster than $1/r^3$). The energy (1) splits into

$$E = E_{\text{SR}} + E_{\text{LR}}, \quad (4)$$

where

$$E_{\text{SR}} = \frac{1}{2} \sum_{\mathbf{m} \in \mathbb{R}^3} \sum_{i,j}^* q_i q_j \psi(\mathbf{r}_i - \mathbf{r}_j - \mathbf{m}), \quad (5)$$

$$E_{\text{LR}} = \frac{1}{2} \sum_{\mathbf{m} \in V} \sum_{i,j}^* q_i q_j \phi(\mathbf{r}_i - \mathbf{r}_j - \mathbf{m}). \quad (6)$$

Since $\psi(\mathbf{r})$ is short-ranged, the calculation of the fast converging sum E_{SR} poses no difficulty. E_{LR} is implicitly understood to be computed in the limit $V \rightarrow \infty$. The restriction on the sum implied by the asterisk can be lifted by adding the “missing” $i = j$ terms when $\mathbf{m} = 0$ and subtracting them:

$$E_{\text{LR}} = E'_{\text{LR}} - E_{\text{self}}, \quad (7)$$

where

$$E'_{\text{LR}} = \frac{1}{2} \sum_{\mathbf{m} \in V} \sum_{i,j} q_i q_j \phi(\mathbf{r}_i - \mathbf{r}_j - \mathbf{m}), \quad (8)$$

and $E_{\text{self}} = \frac{1}{2} \sum_i q_i^2 \phi(\mathbf{0})$ corrects for the $\phi(\mathbf{r} = 0)$ interaction of each particle with itself that are included in E'_{LR} . Notice that $E'_{\text{LR}} = \frac{1}{2} \sum_i q_i \Phi(\mathbf{r}_i)$ where

$$\Phi(\mathbf{r}) = \sum_{\mathbf{m} \in V} \sum_j q_j \phi(\mathbf{r} - \mathbf{r}_j - \mathbf{m}) \quad (9)$$

is the far contribution to the electrostatic potential at \mathbf{r} . Since $\phi(\mathbf{r})$ reduces at large distances to the Coulomb interaction, the sum (8) contains the same conditionally convergent contributions caused by dipolar interactions between the primary cell

and its periodic copies, as in the original lattice-sum (1). From the Taylor expansion

$$\frac{1}{|\mathbf{r} - \mathbf{r}_j|} \sim \frac{1}{|\mathbf{r}|} - (\mathbf{r}_j \cdot \nabla) \frac{1}{|\mathbf{r}|} + \frac{1}{2} (\mathbf{r}_j \cdot \nabla)^2 \frac{1}{|\mathbf{r}|} + \dots, \quad (10)$$

valid for large $|\mathbf{r}|$, and using $\sum_i q_i = 0$, one finds that

$$\sum_j q_j \phi(\mathbf{r} - \mathbf{r}_j - \mathbf{m}) \sim -(\mathbf{M} \cdot \nabla) \frac{1}{|\mathbf{r} - \mathbf{m}|} + \dots, \quad (11)$$

when $|\mathbf{r} - \mathbf{m}|$ is large. In (11), $\mathbf{M} = \sum_{j=1}^N q_j \mathbf{r}_j$ is the total dipole moment of the simulation box. The leading term in (11) corresponds to the interaction energy between a test charge at \mathbf{r} in the primary cell and a point dipole \mathbf{M} located at the center \mathbf{m} of a distant copy of the primary cell. Imagine that we replace the point dipole \mathbf{M} at \mathbf{m} by a uniform distribution of dipolar moment (of volume density $\mathbf{M}/V_{\text{cell}}$) within the cell of center \mathbf{m} . When $|\mathbf{m}| \rightarrow \infty$, the interaction between the test charge at \mathbf{r} and this distant uniformly polarized cell,

$$-\frac{1}{V_{\text{cell}}} (\mathbf{M} \cdot \nabla) \int_{V_{\text{cell}}} d\mathbf{x} \frac{1}{|\mathbf{r} - \mathbf{m} - \mathbf{x}|}, \quad (12)$$

behaves as (11) at leading order because deviations appear only at the next (quadrupolar) order. We now apply the simple trick (2), i.e., subtract and add the problematic conditionally converging contributions in (8), using form (12) rather than (11):

$$E'_{\text{LR}} = E''_{\text{LR}} + E_{\text{surf}}, \quad (13)$$

where

$$E''_{\text{LR}} = \frac{1}{2} \sum_{\mathbf{m} \in V} \sum_i q_i \left(\sum_j q_j \phi(\mathbf{r}_i - \mathbf{r}_j - \mathbf{m}) + \frac{1}{V_{\text{cell}}} (\mathbf{M} \cdot \nabla_i) \int_{V_{\text{cell}}} d\mathbf{x} \frac{1}{|\mathbf{r}_i - \mathbf{m} - \mathbf{x}|} \right), \quad (14)$$

$$E_{\text{surf}} = -\frac{1}{2V_{\text{cell}}} \sum_{\mathbf{m} \in V} \sum_i q_i (\mathbf{M} \cdot \nabla_i) \int_{V_{\text{cell}}} d\mathbf{x} \frac{1}{|\mathbf{r}_i - \mathbf{m} - \mathbf{x}|}. \quad (15)$$

By construction, the sum over \mathbf{m} in (14) is absolutely convergent (as long as $\sum_i q_i = 0$). One can therefore replace $\sum_{\mathbf{m} \in V}$ by $\sum_{\mathbf{m} \in \mathbb{R}^3}$ and use the Poisson-Jacobi formula

$$\sum_{\mathbf{m}} f(\mathbf{r} + \mathbf{m}) = \frac{1}{V_{\text{cell}}} \sum_{\mathbf{k}} \hat{f}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (16)$$

where $\hat{f}(\mathbf{k}) = \int_{V_{\text{cell}}} f(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}$ is the Fourier transform of the fast-decaying function $f(\mathbf{r})$ and \mathbf{k} is a vector on the reciprocal lattice. Notice that the rhs of (16) is merely the Fourier series of the periodic function of the lhs. Using the Fourier transform $4\pi/k^2$ of the Coulomb potential and Eq. (16), one finds

$$E''_{\text{LR}} = \frac{1}{2V_{\text{cell}}} \sum_i q_i \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}_i} \left(\sum_j q_j e^{-i\mathbf{k} \cdot \mathbf{r}_j} \hat{\phi}(\mathbf{k}) + (\mathbf{M} \cdot i\mathbf{k}) \frac{4\pi}{k^2} \frac{1}{V_{\text{cell}}} \int_{V_{\text{cell}}} d\mathbf{x} e^{-i\mathbf{k} \cdot \mathbf{x}} \right). \quad (17)$$

The integral over V_{cell} in (17) vanishes for all wave vectors except for $\mathbf{k} = 0$ where it gives V_{cell} . The regularization introduced in (14) to make the sum absolutely convergent affects therefore only the zero Fourier mode.

Since $\phi(\mathbf{r})$ reduces to the Coulomb potential at large distances, its Fourier transform $\hat{\phi}(\mathbf{k})$ behaves as $4\pi/k^2$ when $k \rightarrow 0$ [see later Eq. (23)]. By expanding the parenthesis in (17) at small k and by using $\sum_i q_i = 0$, it is easy to verify that the $\mathbf{k} = 0$ term vanishes thanks to the regularization.²¹ One finds therefore²²

$$E''_{\text{LR}} = \frac{1}{2V_{\text{cell}}} \sum_{\mathbf{k} \neq 0} |\hat{\rho}(\mathbf{k})|^2 \hat{\phi}(\mathbf{k}), \quad (18)$$

where $\hat{\rho}(\mathbf{k}) = \sum_{i=1}^N q_i \exp(-i\mathbf{k} \cdot \mathbf{r}_i)$ is the Fourier transform of the charge density $\rho(\mathbf{r}) = \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i)$.

It remains to calculate, in the limit $V \rightarrow \infty$, the surface term E_{surf} [Eq. (15)], which captures all conditionally convergent contributions in the original lattice-sum. The integral over \mathbf{x} in V_{cell} together with the sum over $\mathbf{m} \in V$ can be replaced by an integral over the volume V of the macroscopic sample:²³

$$E_{\text{surf}} = -\frac{1}{2V_{\text{cell}}} \sum_i q_i (\mathbf{M} \cdot \nabla_i) \int_V d\mathbf{x} \frac{1}{|\mathbf{r}_i - \mathbf{x}|}. \quad (19)$$

Remembering the expression of the charge-dipole interaction [see rhs of Eq. (11)], Eq. (19) shows that the energy E_{surf} is merely the sum of the energies of the N point charges q_i in an electrostatic potential created by a continuous body of volume $V \rightarrow \infty$ that is uniformly polarized by a volume dipolar density $\mathbf{P} = \mathbf{M}/V_{\text{cell}}$. The electric field $\mathbf{E}_{\text{dep}}(\mathbf{r})$ that derives from that potential is called the depolarization field. By moving the operator $(\mathbf{M} \cdot \nabla_i)$ inside the integral and by applying the gradient theorem, one sees that

$$E_{\text{surf}} = -\frac{1}{2} \sum_i q_i \int_S \frac{1}{|\mathbf{r}_i - \mathbf{x}|} \mathbf{P} \cdot d\mathbf{S} \quad (20)$$

is entirely determined by surface contributions (surface charge density $\sigma_b = \mathbf{P} \cdot d\mathbf{S}$), a well-known result of macroscopic electrostatics. In the limit $V \rightarrow \infty$, $\mathbf{E}_{\text{dep}}(\mathbf{r}) = \mathbf{E}_{\text{dep}}$ is uniform across the primary unit cell, for any sample shape, because the surface charges that produce it are located infinitely far away.

The integral in (19) gives the potential at \mathbf{r}_i in a body carrying a uniform unit charge density. In the case of a sphere of radius R , $\int_V \frac{1}{|\mathbf{r}-\mathbf{x}|} d\mathbf{x} = 2\pi(R^2 - r^2/3)$ and hence

$$E_{\text{surf}} = \frac{2\pi}{3} \mathbf{M}^2 \quad (\text{spherical sample}). \quad (21)$$

In the general case, one can expand, as in (10), the Coulomb potential in (20) since $|\mathbf{r}_i| \ll |\mathbf{x}|$. The first term in that expansion drops by charge neutrality, while all other terms, apart from the second one, vanish in the limit $V \rightarrow \infty$. Therefore, $E_{\text{surf}} = -\frac{1}{2} \mathbf{M} \cdot \mathbf{E}_{\text{dep}}$, where $\mathbf{E}_{\text{dep}} = -\int_S (\nabla \frac{1}{|\mathbf{x}|}) \mathbf{P} \cdot d\mathbf{S}$. The energy E_{surf} can be interpreted as the work performed against the uniform depolarizing field when charging up the simulation cell. The depolarizing field is often written as $\mathbf{E}_{\text{dep}} = -\mathbf{J} \cdot \mathbf{P}$, where $\mathbf{J} = \int_V d\mathbf{x} \nabla \nabla \frac{1}{|\mathbf{x}|}$ is the depolarization tensor which depends only on the shape S of V . The tensor \mathbf{J} is known for var-

ious shapes.²⁴ E_{surf} is sometimes called the dipole term since it depends on particle coordinates solely via the total dipole moment \mathbf{M} .

Gathering results, one has proved the Ewald formula

$$\begin{aligned} E &= E_{\text{SR}} + E''_{\text{LR}} - E_{\text{self}} + E_{\text{surf}} \\ &= \frac{1}{2} \sum_{\mathbf{m} \in \mathbb{R}^3} \sum_{i,j}^* q_i q_j \psi(\mathbf{r}_i - \mathbf{r}_j - \mathbf{m}) + \frac{1}{2V_{\text{cell}}} \sum_{\mathbf{k} \neq 0} |\hat{\rho}(\mathbf{k})|^2 \hat{\phi}(\mathbf{k}) \\ &\quad - \frac{1}{2} \sum_i q_i^2 \phi(\mathbf{0}) + \frac{1}{2V_{\text{cell}}} \mathbf{M} \cdot \mathbf{J} \cdot \mathbf{M}, \end{aligned} \quad (22)$$

in the general case of an arbitrarily shaped crystal. The splitting $1/|\mathbf{r}| = \psi(\mathbf{r}) + \phi(\mathbf{r})$ is often done by defining $\phi(\mathbf{r})$ as the potential created by a Gaussian charge distribution $s(\mathbf{r}) = \exp(-\alpha^2 r^2) \alpha^3 / \pi^{3/2}$ of width controlled by parameter α , though other choices are possible.²⁵ The sums E_{SR} and E''_{LR} converge then exponentially fast. Indeed, the convolution $\phi(\mathbf{r}) = \int s(\mathbf{r}') \cdot 1/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}'$ that gives the long-range part of the interaction becomes the fast-decaying function

$$\hat{\phi}(\mathbf{k}) = \frac{4\pi}{k^2} \hat{s}(\mathbf{k}) = \frac{4\pi}{k^2} e^{-k^2/(4\alpha^2)}, \quad (23)$$

in Fourier space, while $\psi(\mathbf{r}) = \frac{1 - \text{erf}(\alpha r)}{r} = \frac{\text{erfc}(\alpha r)}{r}$ is also short-ranged. The truncations used in practice for computing the sums E_{SR} and E''_{LR} introduce numerical errors that are very sensitive (exponential dependence) to the chosen cutoffs and chosen α . The error estimate of Ref. 26 can be used to determine the α that provides the best accuracy at given cutoffs. The Ewald formula for the force $\mathbf{F}_i = -q_i \nabla_i E$ on a particle i follows by taking the gradient of the Ewald energy (22).

Equation (22) holds for any summation order specified by a crystal shape V . We recall that, for a spherical sample surrounded by a medium of dielectric constant ϵ , the generalization of Eq. (21) reads $E_{\text{surf}} = 2\pi \mathbf{M}^2 / (2\epsilon + 1)$.²⁷ Besides the spherical order, the cylindrical order (radius $R \rightarrow \infty$ and height $H \rightarrow \infty$) is of particular interest. In slab-shaped systems, one performs first the sum over images m_x and m_y up to some radius R , let $R \rightarrow \infty$, and then sums over $m_z \in [-H/2, H/2]$ with $H \rightarrow \infty$. In cylindrical rod-like systems, the one-dimensional infinite ($H \rightarrow \infty$) summation on m_z is performed first, followed by $R \rightarrow \infty$. The expressions for the surface term in those two cases can be derived by taking the corresponding limits in the formula for the depolarization tensor \mathbf{J} of an ellipsoid surrounded by a dielectric medium ϵ .²⁴ For a slab-shaped system (with z -axis normal to the slab), $E_{\text{surf}} = 2\pi M_z^2 / V_{\text{cell}}$, independently of ϵ , a result which is useful for simulating planar interfaces using three-dimensional Ewald sums with a gap introduced in the z direction.²⁰ For a rod-like system, with z -axis parallel to the rod, one finds $E_{\text{surf}} = 2\pi (M_x^2 + M_y^2) / ((\epsilon + 1)V_{\text{cell}})$. That result is useful for simulating rod-like systems using three-dimensional Ewald sums with gaps in the x and y directions and vacuum boundary conditions ($\epsilon = 1$). The surface energy gives rise in general to a force $\mathbf{F}_i^{\text{surf}} = -q_i \nabla_i E_{\text{surf}}$ on a particle i . That force vanishes, in spherical and rod-like systems, only if metallic boundary conditions ($\epsilon = \infty$) are applied. The treatment of long-range interactions in the case where periodic boundary

conditions are applied in two dimensions only (no summation over m_z) is discussed in Refs. 5 and 28.

We have presented a proof of the Ewald formula in which the effects due to the long-range character of the coulomb interaction (absence of the ill-defined $\mathbf{k} = 0$ term in the sum over Fourier modes, emergence of a surface contribution to the energy) are treated in a very simple and physically transparent manner. The surface term is seen to arise directly from the conditionally convergent long-range dipole-dipole (or equivalently a sum of charge-dipole) interactions between the simulation cell and its periodic copies when one isolates an intrinsic (shape-independent, absolutely convergent) Ewald contribution in the total energy. Thanks to its simplicity, the present approach should be quite useful for deriving generalizations of the Ewald formula to other long-range interactions in three or less dimension(s).

Our approach can be applied as well to the lattice-sum for the potential, where quadrupolar surface contributions arise, and also when the macroscopic sample is surrounded by a dielectric medium. As will be shown in a future work,²⁹ the discrepancy between different published formulas^{2,15} for the surface contributions to the potential in a periodic system with a net charge can in particular be resolved.

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²¹No non-analytic $\hat{\mathbf{k}} = \mathbf{k}/k$ can survive in (17) because the summand in (16) is absolutely convergent.

²²The electric neutrality of the simulation cell is often invoked as the reason for the exclusion of the $\mathbf{k} = 0$ term in (18), but neutrality alone is not sufficient because that $\mathbf{k} = 0$ term would still be plagued by an indeterminacy of the form $0 \times \infty$. That indeterminacy is intimately linked to how the long-range contributions in the lattice sum (1) are handled and it is resolved only by an adequate treatment of those contributions, performed here via the splitting (2).

²³One can show indeed that no term arises in (19), in the limit $V \rightarrow \infty$, from the difference between the volume V and the crenelated volume made up of an integer number of cells.

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