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Coulomb potential inside a large finite crystal

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Abstract. We review long-range Coulomb interactions in systems consisting of periodically repeated replicas of identical unit cells containing a net dipole moment. Cases of both infinite and large finite samples of arbitrary shape are considered. The general result due to Smith (1981 *Proc. Roy. Soc. Lond. A* **375** 475) for a large finite sample is considerably simplified. This allowed us to reveal further its physical meaning. We show that extra shape-dependent terms both in the electrostatic potential and energy have a pure macroscopic origin. We also suggest an alternative derivation for the Coulomb potential of a large finite sample of arbitrary shape which is believed to be simpler than the original one due to Smith.

1. Introduction

Long-range Coulomb interaction plays a dominant role in almost every condensed matter system and has been substantially discussed in the literature (see, e.g. [1–12]; of course, this list is by no means complete). Periodic boundary conditions (PBC) have become a powerful tool in simulating extended systems when a big but finite portion of the system (a simulation cell) is periodically repeated in three-dimensional (3D) space. PBC have been extensively used in solid-state physics, in particular for electronic band structure calculations and for molecular dynamics simulations [13–15], as well as for quantum Monte Carlo simulations of crystals [11].

The fundamental difficulty with long-range Coulomb interactions for *infinite* systems arises due to their *conditional* convergence, i.e. the result of the summation in the corresponding infinite series depends on the order of terms in the summation. Therefore, when using various methods for summing up the series one can obtain different answers. Of course, for *finite* samples the order of summation does not matter. Note also that the potential is defined up to an arbitrary constant so that only its variation across the cell is important.

Starting from Ewald [1], most authors (see, e.g. [2, 16]) have been preoccupied with speeding up the convergence of the series in numerical calculations and therefore have not paid sufficient attention to the fact of conditional convergence. It is likely that the difference between the *infinite* and *finite* samples was not understood at this time. Redlack and Grindlay [3] were the first authors to notice the importance of looking carefully at the Coulomb series from a mathematical point of view. They recognized that for *infinite* samples (true PBC) the conditional convergence may result only in an arbitrary choice of the physically insignificant constant term in the periodic potential, the latter being chosen in, for example, Ewald form [1] (note that two periodical solutions of the *same* Poisson equation may differ only by a constant which is the only periodical solution of the Laplace equation). However, they showed that if the

sample is *finite* and consists of identical replicas of the same unit cell, then the total potential consists of intrinsic and extrinsic contributions. The *intrinsic* part is periodic and is the same as for the infinite sample (e.g. the Ewald potential). However, the *extrinsic* part depends explicitly on the sample *shape* and *dipole moment* in the unit cell. Redlack and Grindlay also gave the detailed solution for a sample of the ellipsoidal shape. The conditional convergence of the Madelung series was also studied in [4] for a special case of the zero cell dipole moment; the authors arrived at conclusions similar to those of Redlack and Grindlay. In addition, they derived an explicit expression for the extrinsic part of the potential for an *arbitrary shape* of a finite sample, which in this particular case of zero dipole moment is a constant. A spherical sample with a net dipole moment in the cell was then studied in [5] (see also the recent work in [10, 11, 17]). It was found that in this case the extrinsic contribution is *linear* with \mathbf{r} and is given by the well known Lorenz term, $\phi_{ext}(\mathbf{r}) = (4\pi/3)\mathbf{p} \cdot \mathbf{r}$, where \mathbf{p} is the dipole moment per unit volume. As one can see, the periodic symmetry is broken by this term. This is not surprising, however, due to the fact that this term has a simple macroscopic meaning as an electrostatic field inside a uniformly polarized insulating sphere (see e.g., [11, 18]).

The general case of a finite sample of arbitrary shape and non-zero dipole moment in the unit cell was considered for the first time in [6, 7]. It was shown that the extrinsic contribution to the total electrostatic energy of the system is proportional to the square of the dipole moment and is given as a six-dimensional integral containing integration over the sample volume. This last integration brings about the implicit dependence on the sample shape. The whole contribution, however, does not depend on the sample volume. It was also clearly stated in [7] that the surface relaxation effects would be likely to completely suppress the extrinsic part of the potential leading to substantial gain in the Coulomb energy of the system. Although the importance of this general work seems to be obvious, these papers have remained largely unnoticed (see, e.g., recent studies in [10–12]). This is probably due to a quite cumbersome and sophisticated method used in [6, 7] to consider the Coulomb series. Another reason is that the general result derived in the cited papers looks very complicated and not transparent enough to make the comparison with simple macroscopic electrostatics feasible. As a result, these papers are not properly understood and remain underestimated by the scientific community. Instead, a less fundamental paper by the same authors [5] is more frequently cited in the general context of arbitrary sample shape although in this paper only one particular case of a spherical shape is considered.

Another confusion which has become commonplace in the literature (see, e.g., [10, 11]) is concerned with the fact that the results (usually those of [5]) derived for a large finite sample are sometimes used to calculate the Coulomb series in true PBC, although the latter corresponds to the *infinite* sample. This results in unjustified attempts to apply the extrinsic part of the electrostatic potential alongside the Ewald part in the PBC calculations. As has already been mentioned above, both the electrostatic potential and the energy differ in the cases of finite and infinite samples if there is a net dipole moment in the cell (see [3, 6, 7]): there are additional shape-dependent terms in the case of a large finite sample although the *periodic* Ewald's expression for the potential is *valid* in the case of PBC.

This controversy in the literature inspired us to consider the summation of conditionally convergent Coulomb series once again. We review in section 2 the main results of [6, 7] and show that, after some additional algebra, the extra term expressed there as a six-dimensional integral can be rearranged into a much more simple form given by a 3D integral. This transformation makes it possible to perform a direct comparison with macroscopic electrostatics. It allows us to demonstrate in the general case of *arbitrary* shape that this extra term in the potential and energy has a pure macroscopic origin. Although this *physical* fact should be clear from the previous studies of [3, 5, 7] (see also [11]), it has been demonstrated

explicitly only for the spherical shape. In addition, in section 3 we suggest another derivation for the electrostatic potential of a large finite sample well inside it, which results directly in the simplified form of the extra terms. We believe that our derivation is simpler than that suggested in [6, 7] and therefore it is worth reproducing here for completeness. Finally, conclusions are drawn in section 4.

2. Analysis of electrostatic potential and energy of a large finite sample

Let us consider a large finite sample P of arbitrary shape consisting of identical replicas of a unit cell with distributed point charges q_s . We also assume that there is a non-zero dipole moment \mathbf{P} in every cell, associated with these charges. To calculate the electrostatic potential at an arbitrary point \mathbf{r} inside the body of the sample, we first consider a potential due to a periodic lattice of unit point charges confined in a finite sample P . It was rigorously shown in [6, 7] that the potential is given as (up to a constant)

$$\phi^{(N)}(\mathbf{r}) = \sum_{l \in P} \frac{1}{|\mathbf{r} + \mathbf{R}_l|} = \phi_{Ew}(\mathbf{r}) - \frac{\pi}{v_c} r_\alpha J_{\alpha\beta} r_\beta \quad (1)$$

$$J_{\alpha\beta} = \frac{2}{\pi^3} \int_{(all)} \frac{d\mathbf{w}}{w^2} w_\alpha w_\beta \left(\int_P e^{2i\mathbf{w} \cdot \mathbf{x}} d\mathbf{x} \right) \quad (2)$$

where the summation is performed with respect to all such direct lattice vectors \mathbf{R}_l which are inside the volume of P ,

$$\phi_{Ew}(\mathbf{r}) = \sum_l \frac{\text{erfc}(G|\mathbf{r} - \mathbf{R}_l|)}{|\mathbf{r} - \mathbf{R}_l|} + \frac{4\pi}{v_c} \sum_{g \neq 0} \frac{1}{R_g^2} e^{-R_g^2/4G^2} e^{-i\mathbf{R}_g \cdot \mathbf{r}} \quad (3)$$

is the Ewald potential (note that the $l = 0$ term in the direct lattice summation in equation (3) is to be replaced by $-2G\sqrt{\pi}$ if $\mathbf{r} = 0$), \mathbf{R}_g is a reciprocal lattice vector, v_c is the unit cell volume and N is the number of unit cells in the sample P . The first integral in equation (2) (over \mathbf{w}) is taken over the whole space while the second integral (over \mathbf{x}) is taken over the volume of the sample. This result is correct up to terms $O(1/N)$ and therefore represents an asymptotic expansion of the total potential for large N . Note that hereafter the summation convention for the Cartesian components α, β of vectors and tensors is implied. In equation (1) the Ewald part represents the intrinsic part of the potential while the correction term, $-(\pi/v_c)r_\alpha J_{\alpha\beta} r_\beta$, gives the shape-dependent extrinsic part with shape dependence coming explicitly from the second (over \mathbf{x}) integral. Note also that the integral $J_{\alpha\beta}$ does *not* depend on the sample *size* (this is easily checked by making a substitution $\mathbf{x} \rightarrow \lambda\mathbf{x}$ in the second integral in equation (2)). The electrostatic potential due to all charges q_s in the unit cell positioned at vectors \mathbf{X}_s in every cell is then given as [7]

$$\phi_{tot}^{(N)}(\mathbf{r}) = \sum_s q_s \phi^{(N)}(\mathbf{X}_s - \mathbf{r}) = \sum_s q_s \phi_{Ew}(\mathbf{X}_s - \mathbf{r}) - \frac{\pi}{3v_c} J_{\alpha\beta} (Q_{\alpha\beta} + \delta_{\alpha\beta} Q_0 - 6r_\alpha P_\beta) \quad (4)$$

where $Q_0 = \sum_s q_s X_s^2$ is the cell *spheropole* (see [8, 9]), while $P_\alpha = \sum_s q_s X_{s\alpha}$ and $Q_{\alpha\beta} = \sum_s q_s (3X_{s\alpha} X_{s\beta} - \delta_{\alpha\beta} X_s^2)$ are the unit cell *dipole* and *quadrupole* moments, respectively. Note that the quadratic in \mathbf{r} terms disappeared from the total potential due to electro-neutrality of the cell, $\sum_s q_s = 0$. Several particular cases of the sample shape have been considered in [6, 7]. For instance, in the case of spherical and cube shapes, $J_{\alpha\beta} = \frac{2}{3}\delta_{\alpha\beta}$. Finally, the electrostatic energy (per unit cell) of the sample is given as [6, 7]

$$E^{(N)} = \frac{1}{2} \sum_{ss'} q_s q_{s'} \phi_{tot}^{(N)}(\mathbf{X}_s - \mathbf{X}_{s'}) = E_{Ew}^{(N)} + P_\alpha J_{\alpha\beta} P_\beta \quad (5)$$

where $E_{Ew}^{(N)}$ is the usual Ewald energy of point charges. This result is also correct up to $O(1/N)$.

The results contained in equations (4) and (5) are very general. They show clearly that the potential due to a large finite sample contains (apart from the shape-dependent constant terms) a term linear with r corresponding to a constant macroscopic electrostatic field across the whole sample. As a result, the total energy also gains an additional shape-dependent term which vanishes only if there is no net dipole moment in the cell.

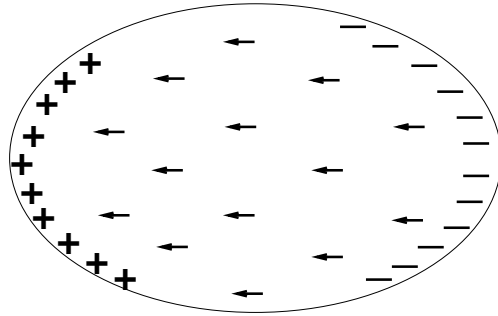


Figure 1. A finite crystalline sample with a non-zero dipole moment periodically repeated in every unit cell (see text).

In order to gain a deeper insight into the results above, we first have to simplify the correction term. Both in the potential, equation (4), and in the energy, equation (5), it is represented via a complicated six-dimensional integral, $J_{\alpha\beta}$, equation (2). We will show now that in fact it can be transformed into a 3D integral which would allow us to give a transparent physical meaning to the correction term. To this end, let us consider equation (2). We first split the integral over x into two integrals: over a sphere around the origin, P_1 , and over the remainder of the volume, P_2 . The spherical volume P_1 contributes $\frac{2}{3}\delta_{\alpha\beta}$ to $J_{\alpha\beta}$ (see above). To calculate the contribution from the volume P_2 we note that $x \neq 0$ there by the construction. This allows us to interchange the two integrals in equation (2). Using also the identity

$$\int_{(all)} \frac{dw}{w^2} w_\alpha w_\beta e^{2iw \cdot x} = -\frac{\partial^2}{4\partial x_\alpha \partial x_\beta} \int_{(all)} \frac{dw}{w^2} e^{2iw \cdot x} = -\frac{\partial^2}{4\partial x_\alpha \partial x_\beta} \frac{\pi^2}{|\mathbf{x}|}$$

we finally obtain the following simple result

$$J_{\alpha\beta} = \frac{2}{3}\delta_{\alpha\beta} + \frac{1}{2\pi}\bar{T}_{\alpha\beta} \quad (6)$$

where

$$\bar{T}_{\alpha\beta} = \int_P T_{\alpha\beta}(\mathbf{x}) d\mathbf{x} \quad (7)$$

is a *form factor* introduced in [4] with $T_{\alpha\beta}(\mathbf{x}) = (\delta_{\alpha\beta}/x^3) - (3x_\alpha x_\beta/x^5)$ being the dipole tensor. Note that the form factor does not depend on the volume of the sample P and therefore depends only on its shape, as is expected. Also, the integral is equal to zero for spherical volumes due to symmetry (the dipole tensor is proportional to the real spherical polynomials $Y_{2m}(\hat{\mathbf{x}})$). For the same reason, there is no singularity around the origin as one can always cut out a sphere around $x = 0$ which gives a zero contribution. For other shapes of P the central spherical part gives a zero contribution and therefore only the part close to the sample surface may contribute to the integral in equation (7). Therefore, only that part of the sample which is

near or at the surface contributes to the form factor thereby representing pure *surface* effects. Some properties of the form factor are considered in the appendix.

Our new expression for the correction term is much simpler than the original one, equation (2), since it is expressed only as a simple 3D integral. Another advantage of the transformed expression (6) is that it allows for a very simple physical interpretation of the total electrostatic potential. Indeed, we first use equation (6) in (4), and obtain

$$\phi_{tot}^{(N)}(\mathbf{r}) = \sum_s q_s \phi_{Ew}(\mathbf{X}_s - \mathbf{r}) - \frac{1}{6v_c} Q_{\alpha\beta} \bar{T}_{\alpha\beta} - \frac{2\pi}{3v_c} Q_0 + \frac{4\pi}{3v_c} \mathbf{P} \cdot \mathbf{r} + \frac{1}{v_c} r_\alpha P_\beta \bar{T}_{\alpha\beta}. \quad (8)$$

Note that the first two constant correction terms above (after the Ewald contribution) were derived for the first time in [4].

Let us now consider a large macroscopic sample of arbitrary shape with a uniformly distributed dipole moment $\mathbf{p} = \mathbf{P}/v_c$ per unit volume as depicted in figure 1. We notice that both the Ewald potential (the first term in equation (8)) and $\phi_{tot}^{(N)}(\mathbf{r})$ satisfy the same Poisson equation since the correction linear with \mathbf{r} obviously satisfies the Laplace equation. To choose the right solution, one has to consider carefully the corresponding boundary conditions for the Laplace equation. If we have a finite (although may be very large) sample of the crystalline material with identical dipole moments in each unit cell, then one can imagine that a charge of one sign is accumulated on one side of the sample (towards one end of the dipoles) and that a charge of opposite sign is accumulated on the other side (at the other end of the dipoles) as shown in figure 1. This system behaves as a *capacitor* and the appearance of the constant electric field (or the linear contribution to the Ewald potential) which depends on the capacitor *geometry* (the shape of the sample) is physically reasonable. One can therefore expect that the linear shape-dependent part of the electrostatic potential can be derived independently using a classical consideration. To this end, let us calculate the macroscopic electrostatic potential well inside the sample as

$$\phi_{macro}(\mathbf{r}) = \int_P \frac{\mathbf{p} \cdot (\mathbf{r} - \mathbf{x})}{|\mathbf{r} - \mathbf{x}|^3} d\mathbf{x} = \int_P p_\alpha e_\alpha(\mathbf{r} - \mathbf{x}) d\mathbf{x}.$$

This integral is calculated in the following way. First of all, we cut out a sphere of the largest possible radius R inside our sample and consider the potential at an arbitrary point \mathbf{r} well inside the sphere. The integral is split into two contributions: from the sphere P_1 and from the remainder P_2 of P . The contribution from the sphere is well known from undergraduate electrostatics and can be easily calculated by transforming the volume integral into a surface integral with respect to the function $\mathbf{p}/|\mathbf{r} - \mathbf{x}|$ and expanding $1/|\mathbf{r} - \mathbf{x}|$ in spherical functions $Y_{lm}(\hat{\mathbf{x}})$. The result is the Lorenz potential $(4\pi/3)\mathbf{p} \cdot \mathbf{r}$. To calculate the integral over the rest of the volume, we make use of the fact that the point \mathbf{r} (which is well inside the sphere) is far away from any integration point $\mathbf{x} \in P_2$ (which is outside), i.e. $|\mathbf{r}| \ll |\mathbf{x}|$. Therefore, we expand the function $e_\alpha(\mathbf{r} - \mathbf{x})$ in a Taylor series with respect to \mathbf{r}

$$e_\alpha(\mathbf{r} - \mathbf{x}) = -e_\alpha(\mathbf{x}) + T_{\alpha\beta}(\mathbf{x})r_\beta + O(r^2)$$

and then integrate it with respect to $\mathbf{x} \in P_2$. Since the functions $e_\alpha(\mathbf{x})$ and $T_{\alpha\beta}(\mathbf{x})$ are proportional to the corresponding spherical functions, the integration can be extended to include the spherical volume as well since the contribution from it is zero anyway. Finally, one has

$$\phi_{macro}(\mathbf{r}) = -p_\alpha \int_P e_\alpha(\mathbf{x}) d\mathbf{x} + \frac{4\pi}{3} \mathbf{p} \cdot \mathbf{r} + p_\alpha r_\beta \int_P T_{\alpha\beta}(\mathbf{x}) d\mathbf{x} + O(r^2). \quad (9)$$

One can immediately recognize that, apart from physically insignificant constant terms, the macroscopic potential $\phi_{macro}(\mathbf{r})$ is in fact identical to the shape-dependent correction potential in equation (8). This means therefore that the correction terms have a pure macroscopic origin

and correspond to the macroscopic potential due to a uniformly distributed dipole moment in the large finite sample. Note that the Ewald potential averages to a constant (which does not depend on the charge distribution) when integrated over any unit cell (see, e.g., [17]) so that the *macroscopic* electrostatic field originates exclusively from the extrinsic potential as given by equation (9), i.e.

$$(\varepsilon_{macro})_{\beta} = -\frac{\partial}{\partial r_{\beta}} \phi_{macro}(\mathbf{r}) = -\frac{4\pi}{3} p_{\beta} - p_{\alpha} \bar{T}_{\alpha\beta} + O(\mathbf{r}). \quad (10)$$

If we use equation (6) in the energy expression, (5), we will get the following expression for the total electrostatic energy per cell

$$E^{(N)} = E_{Ew}^{(N)} + \frac{2\pi}{3v_c} \mathbf{P}^2 + \frac{1}{2v_c} P_{\alpha} \bar{T}_{\alpha\beta} P_{\beta} \quad (11)$$

which contains the Ewald part and two correction terms which vanish if $\mathbf{P} = 0$. Note that the first correction term is present for *any* shape of the finite sample whereas the second one originates from the non-symmetric part of the sample P near its surface and therefore represents a pure *surface* effect. Finally, we note that it is straightforward to generalize the expressions given above for an arbitrary charge distribution $\rho(\mathbf{r})$. We do not give them here to save space.

A completely independent derivation for the potential of equation (8) well inside a large finite sample of arbitrary shape is given in the next section for completeness. We believe that this derivation is simpler than the original one suggested in [6, 7] and therefore is worth reproducing here.

3. Alternative derivation of the potential well inside the body of a large finite sample

The derivation which is given here is based essentially on the ideas of [4]. Consider a *finite* sample of a crystal consisting of N unit cells. The electrostatic potential at an arbitrary point \mathbf{r} well inside the sample is given by

$$\phi^{(N)}(\mathbf{r}) = \sum_s q_s \sum_{l \in P} \frac{\text{erfc}(G|\mathbf{r} - \mathbf{R}_{ls}|)}{|\mathbf{r} - \mathbf{R}_{ls}|} + \sum_s q_s \frac{2}{\sqrt{\pi}} \int_{\epsilon}^G \left(\sum_{l \in P} e^{-t^2|\mathbf{r} - \mathbf{R}_{ls}|^2} \right) dt + \phi_{ext}^{(N)}(\mathbf{r}) \quad (12)$$

where we have used the identity

$$\frac{1}{x} = \frac{\text{erfc}(Gx) + \text{erf}(Gx)}{x} = \frac{\text{erfc}(Gx)}{x} + \frac{2}{\sqrt{\pi}} \int_0^{\epsilon} e^{-t^2x^2} dt + \frac{2}{\sqrt{\pi}} \int_{\epsilon}^G e^{-t^2x^2} dt$$

and

$$\phi_{ext}^{(N)}(\mathbf{r}) = \frac{2}{\sqrt{\pi}} \sum_{l \in P} \sum_s q_s \int_0^{\epsilon} e^{-t^2|\mathbf{r} - \mathbf{R}_{ls}|^2} dt. \quad (13)$$

Here G is an arbitrary positive constant (Ewald's parameter) and $\epsilon > 0$ is some small positive constant which will tend to zero at the end of the calculation. The first two terms in equation (12) are absolutely converging series so that the summation can be extended over the infinite lattice ($N \rightarrow \infty$). As the integrand in the second term is a periodic function with respect to the lattice translations, \mathbf{R}_l , it can be expanded into a Fourier series, so that one has

$$\phi^{(N)}(\mathbf{r}) = \sum_s q_s \phi_{Ew}(\mathbf{X}_s - \mathbf{r}) + \phi_{ext}^{(N)}(\mathbf{r}) \quad (14)$$

where $\phi_{ext}^{(N)}(\mathbf{r})$ appears as the correction term (*extrinsic potential*) to be calculated in the limit of $\epsilon \rightarrow +0$ for large N . Making the substitution $\lambda = t|\mathbf{r} - \mathbf{R}_l|$, the integral is transformed into

$$\phi_{ext}^{(N)}(\mathbf{r}) = \frac{2}{\sqrt{\pi}} \sum_{l \in P} \sum_s \frac{q_s}{|\mathbf{r} - \mathbf{R}_l|} \int_0^{\epsilon|\mathbf{r} - \mathbf{R}_l|} e^{-\lambda^2} e^{-\sigma_{ls}\lambda^2} d\lambda \quad (15)$$

with $\sigma_{ls} = (X_s^2 + 2\mathbf{X}_s \cdot (\mathbf{R}_l - \mathbf{r}))|\mathbf{r} - \mathbf{R}_l|^{-2}$. Let us now expand the exponential term, $e^{-\sigma_{ls}\lambda^2}$, in power series with respect to $\sigma_{ls}\lambda^2$. Due to electro-neutrality of the cell, the very first term will vanish. Other terms in the expansion contain various inverse powers of $|\mathbf{r} - \mathbf{R}_l|$. However, it can be recognized that only a few terms will contribute in equation (15). For example, the lattice summation $\sum_l |\mathbf{r} - \mathbf{R}_l|^{-n} \int_0^{\epsilon|\mathbf{r} - \mathbf{R}_l|} e^{-\lambda^2} \lambda^m d\lambda$ for any $n \geq 4$ and any positive integer m can be bounded from above by the series $(\int_0^\infty e^{-\lambda^2} \lambda^m d\lambda) \sum_l |\mathbf{r} - \mathbf{R}_l|^{-n}$, which converges absolutely and uniformly for any $\epsilon > 0$. This means that the $\epsilon \rightarrow +0$ limit can be applied to every term in the summation and we see that all such terms will vanish. Similar consideration is applied to other types of terms. Finally, only three terms will survive in the Taylor expansion of equation (15) and one obtains

$$\phi_{ext}^{(N)}(\mathbf{r}) = \frac{2}{\sqrt{\pi}} \sum_{l=1}^N \{-Q_0 \xi(|\mathbf{r} - \mathbf{R}_l|) - 2P_\alpha \zeta_\alpha(\mathbf{r} - \mathbf{R}_l) + 2\tilde{Q}_{\alpha\beta} \chi_{\alpha\beta}(\mathbf{r} - \mathbf{R}_l)\} \quad (16)$$

where $\tilde{Q}_{\alpha\beta} = \frac{1}{3}(Q_{\alpha\beta} + \delta_{\alpha\beta}Q_0)$. It is implied that the point \mathbf{r} in equation (16) lies in the zero cell. The following functions have been introduced: $\xi(x) = x^{-3} \int_0^{\epsilon x} e^{-\lambda^2} \lambda^2 d\lambda$ and $\zeta_\alpha(\mathbf{x}) = x_\alpha \xi(x)$; in addition, $\chi_{\alpha\beta}(\mathbf{x}) = (x_\alpha x_\beta / 2x^2)(3\xi(x) - \epsilon^3 e^{-\epsilon^2 x^2})$. Noting that these functions are well defined around $x = 0$ (this is easily checked by the substitution $\lambda \rightarrow \lambda/x$), let us expand them around some point \mathbf{x} in the zero cell and then sum over $l \in P$. For example,

$$\sum_{l \in P} \xi(|\mathbf{r} - \mathbf{R}_l|) = \sum_{l \in P} \xi(|\mathbf{R}_l + \mathbf{x}|) - (\mathbf{r} + \mathbf{x})_\alpha \sum_{l \in P} \xi'_\alpha(|\mathbf{R}_l + \mathbf{x}|) + \dots \quad (17)$$

The first derivative $\xi'_\alpha(|\mathbf{R}_l + \mathbf{x}|)$ contains terms which are either exponential ($\propto e^{-\epsilon^2 |\mathbf{R}_l + \mathbf{x}|^2}$) or contain $|\mathbf{R}_l + \mathbf{x}|^{-n}$ with $n \geq 4$ which, as has been explained above, ensure absolute and uniform convergence of the corresponding series; these terms tend to zero in the $\epsilon \rightarrow +0$ limit. And so are the other terms (not shown explicitly in equation (17)) in the last expansion which contain higher derivatives of the function ξ . Thus, integrating both sides of equation (17) with respect to \mathbf{x} , we have in the $\epsilon \rightarrow +0$ limit

$$\sum_{l \in P} \xi(|\mathbf{r} - \mathbf{R}_l|) \rightarrow \frac{1}{v_c} \sum_{l \in P} \int_{cell} \xi(|\mathbf{R}_l + \mathbf{x}|) d\mathbf{x} = \frac{1}{v_c} \int_P \xi(\mathbf{x}) d\mathbf{x} \quad (18)$$

Similar analysis shows that in the $\epsilon \rightarrow +0$ limit

$$\sum_{l \in P} \chi_{\alpha\beta}(\mathbf{r} - \mathbf{R}_l) \rightarrow \frac{1}{v_c} \int_P \chi_{\alpha\beta}(\mathbf{x}) d\mathbf{x} \quad (19)$$

Therefore, the first and the third lattice summations on the right-hand side of equation (16) given by (18) and (19), respectively, are constants represented as volume integrals (cf. [4]). In the Taylor expansion of $\zeta_\alpha(\mathbf{r} - \mathbf{R}_l)$ around \mathbf{x} , however, one also has to keep the first derivative term

$$\sum_{l \in P} \zeta_\alpha(\mathbf{r} - \mathbf{R}_l) \rightarrow \frac{1}{v_c} \int_P \zeta_\alpha(\mathbf{x}) d\mathbf{x} - \frac{1}{v_c} \sum_{l \in P} \int_{cell} (r_\beta + x_\beta) \zeta'_{\alpha\beta}(\mathbf{R}_l + \mathbf{x}) d\mathbf{x} \quad (20)$$

where

$$\zeta'_{\alpha\beta}(\mathbf{x}) = \frac{\partial}{\partial x_\beta} \zeta_\alpha(\mathbf{x}) = T_{\alpha\beta}(\mathbf{x}) \xi(x) x^3 + \epsilon^3 \frac{x_\alpha x_\beta}{x^2} e^{-\epsilon^2 x^2}.$$

The last term in equation (20) consists of two terms. The first one, containing r_β , is transformed into an integral with respect to the volume P as we did above in other cases. The second (*constant*) term containing x_β can always be ensured to be zero by choosing the unit cell in the form of a parallelepiped or Wigner–Seitz cell (both contain the centre of inversion) and assuming that there is always translation $-\mathbf{R}_l$ for every vector \mathbf{R}_l . Hence, the expression in equation (20) takes the form

$$\sum_{l \in P} \zeta_\alpha(\mathbf{r} - \mathbf{R}_l) \rightarrow \frac{1}{v_c} \int_P \zeta_\alpha(\mathbf{x}) \, d\mathbf{x} - \frac{r_\beta}{v_c} \int_P \zeta'_{\alpha\beta}(\mathbf{x}) \, d\mathbf{x}. \quad (21)$$

Collecting all terms together in equation (16), we have

$$\begin{aligned} \phi_{ext}^{(N)}(\mathbf{r}) = \frac{2}{\sqrt{\pi} v_c} \int_P \left[-\frac{x^3}{3} Q_{\alpha\beta} T_{\alpha\beta}(\mathbf{x}) \xi(\mathbf{x}) - \epsilon^3 \frac{x_\alpha x_\beta}{x^2} e^{-\epsilon^2 x^2} \tilde{Q}_{\alpha\beta} \right. \\ \left. - 2P_\alpha \zeta_\alpha(\mathbf{x}) + 2P_\alpha r_\beta \zeta'_{\alpha\beta}(\mathbf{x}) \right] d\mathbf{x}. \end{aligned} \quad (22)$$

Now we have to deal with all of the four terms above. Consider the first term containing the function $x^3 \xi(\mathbf{x}) = (\sqrt{\pi}/4) - f(\epsilon x)$ where $f(y) = \int_y^\infty e^{-\lambda^2} \lambda^2 \, d\lambda$ is a rapidly decaying function of y . Therefore, the volume integral with this part, $\int_P T_{\alpha\beta}(\mathbf{x}) f(\epsilon x) \, d\mathbf{x}$, in equation (22) can be replaced (in the $N \rightarrow \infty$ limit) by the volume integral with respect to the whole space and it appears to be equal to zero by symmetry due to angular integration. Thus, the first term in equation (22) results in $-(1/6v_c) Q_{\alpha\beta} \bar{T}_{\alpha\beta}$.

The second term in equation (22) contains the exponential which cuts off the effect of the boundary of the volume P . Therefore, as above, we can extend the integration over the whole volume, make the substitution $\epsilon \mathbf{x} \rightarrow \mathbf{x}$ and finally use the symmetry. As a result, one has the following contribution:

$$-\tilde{Q}_{\alpha\beta} \frac{2}{\sqrt{\pi} v_c} \int_{(all)} \frac{x_\alpha x_\beta}{x^2} e^{-x^2} \, d\mathbf{x} = -\delta_{\alpha\beta} \tilde{Q}_{\alpha\beta} \frac{2}{3\sqrt{\pi} v_c} \int e^{-x^2} \, d\mathbf{x} = -\frac{2\pi}{3v_c} Q_0. \quad (23)$$

The third term in equation (22) is transformed similarly,

$$-\frac{4P_\alpha}{\sqrt{\pi} v_c} \int_P \zeta_\alpha(\mathbf{x}) \, d\mathbf{x} \rightarrow -\frac{4P_\alpha}{\sqrt{\pi} v_c} \int_P \frac{x_\alpha \sqrt{\pi}}{x^3} \, d\mathbf{x} \rightarrow -\frac{P_\alpha}{v_c} \int_P e_\alpha(\mathbf{x}) \, d\mathbf{x} = -\frac{P_\alpha}{v_c} \bar{e}_\alpha \quad (24)$$

where $e_\alpha(\mathbf{x}) = x_\alpha/x^3$ is the electrostatic field of a point charge. Apart from high-symmetry cases in which the integral $\bar{e}_\alpha = 0$, it depends on the sample *volume* V as $V^{1/3}$. However, this is a constant term which we have every right to ignore here.

A similar derivation for the fourth term in equation (22) gives

$$\frac{4P_\alpha r_\beta}{\sqrt{\pi} v_c} \int_P \zeta'_{\alpha\beta}(\mathbf{x}) \, d\mathbf{x} \rightarrow \frac{4\pi}{3v_c} \mathbf{P} \cdot \mathbf{r} + \frac{1}{v_c} P_\alpha \bar{T}_{\alpha\beta} r_\beta. \quad (25)$$

Collecting all contributions together in equation (22) one recovers the correction term of equation (8) of the previous section.

4. Conclusions

In this paper we have considered long-range interactions in crystalline systems consisting of an arbitrary neutral charge distribution periodically repeated in 3D space. Both the electrostatic potential and the electrostatic energy are discussed in the context of *infinite* and *finite* samples, and we have emphasized once again the importance of distinguishing between these two cases. The previous work by Smith and Perram [6, 7] is re-examined and a new expression for the

correction term to the potential (the extrinsic contribution) of a finite sample of arbitrary shape has been derived which is much simpler than the original one suggested in [6, 7]. This modification has allowed us to shed more light on the physical meaning of the extrinsic potential. We have shown that in the general case of *arbitrary* sample shape the extrinsic potential has a pure macroscopic origin and represents a classical electrostatic potential due to a uniformly polarized sample well inside it. This result can be easily understood as the uniformly polarized sample manifests itself as a capacitor of a certain geometry. Also, we have suggested an alternative derivation for the electrostatic energy and potential of a finite sample of arbitrary shape which, we believe, is less cumbersome than the original derivation suggested in [6, 7].

In a real experiment any sample has a certain finite size and shape. One can therefore ask the question ‘Which model is closer to physical reality, the model of a finite or of an infinite sample?’ This is important for the understanding of whether results of PBC calculations can be directly compared with experimental results and whether one has to use the correction terms in the energy in PBC calculations. In order to answer this question, it is relevant to mention that both models are just specific approximations to the physical reality which is lying somewhere in between. Indeed, if there is a dipole moment in the cell which is periodically repeated inside some large finite volume, then the arising macroscopic field ε_{macro} would substantially increase the internal Coulomb energy of the system by $(1/8\pi) \int_P \varepsilon_{macro}^2 dV = (\varepsilon_{macro}^2/8\pi)V$, where V is the sample volume. Therefore, it is energetically favourable for the surface atoms to relax in order to compensate for this large positive energy. There will also be substantial electronic redistribution at the surface in order to create an electrostatic field in the direction opposite to that of ε_{macro} . This effect has indeed been observed in a number of theoretical studies of polar surfaces [19, 20]. Some mechanisms of stabilization of polar surfaces are considered in [21]. This effect was also mentioned in [7]. Therefore, as the surface provides some ‘compensating’ mechanism to suppress the effect of the macroscopic field, the model of periodically repeated *identical* cells confined in a finite (although may be very large) volume will never be correct so that the correction terms have to be either removed altogether (which would correspond to true PBC) or substantially damped (partial surface effects). The extent to which the surface effects are suppressed may also depend on the experimental conditions (e.g. the sample preparation) so that care is needed when making a comparison of theory and experiment. We believe that in the correct calculation of the system in which there is a net dipole moment in the cell the surface relaxation effects should be accounted for using direct minimization of the total energy of the *entire* sample, which is a formidable task. This is especially true for the case of nanoclusters. It is probable that complete compensation and therefore PBC are the closest approximations to reality. Note also that artificial ‘compensating’ mechanisms designed to eliminate the effect of the macroscopic field in PBC calculations have also been suggested: for example, in [11, 17] a sample was surrounded by a metal which screens out any macroscopic electrostatic field. A similar idea was suggested in [22] where the dipole moment in the slab calculations was compensated by an artificial electrostatic field of the opposite direction by placing a planar dipole layer in the middle of the vacuum region. Finally, in a number of studies (see, e.g., [23]) simulations are discussed in which a finite sample is surrounded by a continuum with some dielectric constant treated as a parameter (for a general discussion of simulations with the shape-dependent term see [24, 25]).

Appendix

To calculate the integral $\bar{T}_{\alpha\beta} = \int_P T_{\alpha\beta}(\mathbf{x}) d\mathbf{x}$ for a *finite* sample with a specific shape of interest, use can be made of the fact that $T_{\alpha\beta}(\mathbf{x}) = -e^{(\alpha)} \nabla(e^{(\beta)} \nabla(1/|\mathbf{x}|))$, $e^{(\alpha)}$ being a unit vector along the axis α , so that the volume integral is transformed into an integral over the

surface of the sample as follows

$$\bar{T}_{\alpha\beta} = - \int \int_S n_\beta \left(e^{(\alpha)} \nabla \frac{1}{|\mathbf{x}|} \right) dS$$

where $\mathbf{n} = (n_x, n_y, n_z)$ is the unit vector of the surface normal. In doing so, one has to eliminate the singularity around $\mathbf{x} = 0$ by cutting off a sphere of some radius R around the origin. The result will not depend on R and the surface integration above is performed over the inner spherical surface as well. We also note that $\bar{T}_{\alpha\alpha} = 0$ due to the familiar ‘sum-rule’ property of the dipole tensor itself, $T_{\alpha\alpha}(\mathbf{r}) = 0$. For a spherical volume the integral is equal to zero by symmetry as mentioned in the text. In the case of a cube, $\bar{T}_{\alpha\beta} = \delta_{\alpha\beta} \bar{T}$, and again the integral is equal to zero due to the sum rule above. The same result can be recovered for any high-symmetry shape (such as diamond). In cases of lower symmetry the integral is not equal to zero.

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