EXISTENCE OF A "WELL DEFINED" SPECIFIC ENERGY FOR AN IONIC CRYSTAL; JUSTIFICATION OF EWALD'S FORMULAE AND OF THEIR USE TO DEDUCE EQUATIONS FOR MULTIPOLE LATTICES*

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Abstract — The EWALD[1] calculation of the potential defined by an ionic lattice is shown to be justified under simple general conditions which are given for the existence of a "well-defined" specific energy for an ionic crystal. The significance of the Ewald calculation and of these conditions is clarified by a prior discussion of the connection between the specific energy for finite and infinite lattices. It is shown that the original argument given[2] to justify the deduction of formulae for multipole lattices from Ewald's equations contains a logical error which led to misleading statements about the potential defined by a lattice of dipoles. Conditions for the validity of these formulae are given and proved. Advantages of these formulae are discussed.

1. EXISTENCE OF A "WELL-DEFINED" SPECIFIC ENERGY FOR AN IONIC LATTICE

To discuss the validity of the EWALD[1] calculation, it will be necessary to consider briefly the problems which arise because the potential of each lattice site varies as r^{-1}. The infinite series are at most conditionally (i.e. simply) convergent.† Any series which fails to converge absolutely possesses the well known property that it can be made to diverge or to converge to any arbitrary value by an appropriate choice of order of summation. This property has a different implication in one dimension than it has in two or more dimensions. A one dimensional series,

$$\sum a_n \tag{1}$$

has a "natural" order of summation, the order of increasing n. This order for the infinite series corresponds to computing the limit for finite lattices of increasing size.

For a P dimensional series, $P \geq 2$, the analogue of a sum for all $n \leq N$ would be a sum over all $\langle n_1, \ldots, n_P \rangle$ such that

$$0 \leq f(\langle n_1, \ldots, n_P \rangle) \leq \text{constant} \tag{2}$$

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† EMERSLEBEN gives a simple proof that the series for NaCl converges only conditionally.

where $f(\langle n_1, \ldots, n_P \rangle)$ is an arbitrary monotone increasing function of each n_i. This order for the infinite series corresponds to computing the limit for finite lattices of increasing size and the fixed shape defined by the function $f(\langle n_1, \ldots, n_P \rangle)$. Thus it is only in one dimension that the model for increasing the size of a finite lattice imposes a unique order of summation. Conversely, in two or more dimensions, it is necessary to specify the function $f(\langle n_1, \ldots, n_P \rangle)$. In other words, the concepts of potential and of specific energy are defined for an infinite lattice *only* if the order of summation is specified.* In physical terms, this order can be specified by *defining* the specific energy to be the limit (if it exists) obtained by increasing the size of finite lattices of a fixed shape.

Thus the absence of absolute convergence gives rise to two practically important questions:†

(1) Consider a particular crystal structure and finite electrically neutral specimens of fixed shape. If the specimen size is increased without changing the shape does the specific energy approach a limiting value and, if so, what is the limit? If the limit exists, macroscopic specimens of this shape will have a specific energy which will be constant within experimental error and can, therefore, be said to be "well-defined".

(2) If the series converges, does it converge to the minimum specific energy, i.e. is the shape in the class of one or more most stable crystal forms? Finally, do actual specimens attain one of these most stable forms under the conditions in which they are grown? In this case the observed macroscopic specimens can be said to have a "well defined" specific energy. Therefore, to investigate the validity of Ewald's calculation, it is necessary to consider the order of summation which Ewald's calculation implicitly assumes and to determine whether this order defines a convergent series. If it does, then the limit will be the specific energy obtained by increasing the size of finite crystals of the shape corresponding to the assumed order of summation. Simple general conditions will be given which ensure the conditional convergence of the lattice sums. First one, and then two and three dimensional lattices will be considered. Then it will be shown that whenever these conditions are satisfied, the series converge for the Ewald order of summation. The practical need for careful attention to the question of summation order is illustrated by the fact that even in the case of the simple NaCl lattice, divergent orders have been assumed to be convergent.‡

The standard theorem on alternating series states: A (real) alternating series of which the absolute values of the terms form a monotonic null sequence is invariably convergent . . .

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* Frequently the Madelung constant is supposed to be defined as the limiting value of the work per ion required to remove it from the lattice. This definition suffers from the defect that the work depends upon the shape assumed for the crystals for which the limit is to be computed. Both mathematically and physically, the term "infinite lattice" can only mean a suitably defined limiting process on finite lattices.

† EMERSLEBEN[3b] has pointed out that the problem of convergence for the infinite series is directly related to the effects of boundary regions of finite crystals. He did not develop this observation as it is done here. BOUMAN[4a] (in his discussion of Ewald's and Kornfeld's formulae) observes that the absolute convergence "signifie que cette force dans un cristal infini ne depend pas de la forme sous laquelle on fait croitre le crystal a l'infini". However, he did not develop this observation to show what shape their work implicitly assumes. Instead, he chose to discuss their work in terms of charge distributions which would have the same potential.

‡ EMERSLEBEN[3c] gives an example from the recent literature.

Its value lies between any two successive partial sums.[5] It follows at once that the series for the potential of any simple one-dimensional lattice of alternating equal plus and minus charges converges conditionally.

Whereas this model is too restrictive, the theorem has a simple generalization of wider applicability.

Theorem I. Generalized alternating series theorem

1. Let $I = \sum_p a_p$ where the a_p are real and $|a_p|$ form a monotone non-increasing null sequence.

2. Suppose there is a positive integer n such that for each j, a_j and a_{n+j} have opposite signs.

Then, the series I converges conditionally and for each positive integer k, its limit lies between the successive partial sums,

$$\sum_{p=1}^{kn} a_p, \quad \sum_{p=1}^{(k+1)n} a_p, \tag{3}$$

This theorem generalizes the requirement of an alternation of sign for successive terms to a requirement that if the terms are divided into a sequence of ordered n-tuples,

$$X_1 = \langle a_1, \ldots, a_n \rangle, \qquad X_2 = \langle a_{n+1}, \ldots, a_{2n} \rangle, \ldots, \tag{4}$$

then the i-th element of X_i and X_{i+1} have opposite signs. The proof, which parallels that for the standard theorem, is a consequence of the generalized alternation in sign and non-increasing conditions. It follows that the series converges if it is summed in the order of increasing n. Since this is the order specified by increasing the size of a finite specimen, it follows that any one-dimensional lattice which satisfies this generalized sign alternation has a "well-defined" specific energy.

To generalize the result to two dimensions it is only necessary to suppose that two axes (x, y) can be found for which generalized alternating sign conditions hold. To describe these conditions, let:

$\langle L_1, L_2 \rangle$: the set of pairs of integers which order the lattice sites in the (x, y) coordinate system; (5)

$\mathcal{L}_j$: the array of lattice points parallel to the y axis for which $x = x_j$ (i.e. the set of lattice points designated by the set of ordered pairs, $\{\langle j, L_2 \rangle\}$). (6)

The conditions are:

Condition A. The alternating sign condition for an array parallel to the y axis

Suppose that for each $\mathcal{L}_j$, the set of lattice points of $\mathcal{L}_j$ give a series which satisfies the generalized alternating sign condition of Theorem I. Then the series necessarily converges conditionally to a value which will be denoted by U_j.

Condition B. The alternating sign condition for an array parallel to the x axis

If arrays parallel to the x axis also follow the generalized alternating sign condition, then there will be a positive integer m such that for each j and each L_2, the charges at the lattice site $\langle j, L_2 \rangle$ and $\langle j + m, L_2 \rangle$ are of opposite sign.

It can be seen that in this case the series of the U_j obeys a generalized alternating sign condition and that, therefore, the series for the potential of the two-dimensional array converges conditionally. Finally, consider the order of summation defined by including all points contained within an increasing sequence of parallelopipeds whose edges are parallel to the axes. The argument given above can be completed to show that this order defines a convergent series. The extension to three dimensions is obvious.

2. JUSTIFICATION OF EWALD'S FORMULAE FOR IONIC LATTICES

EWALD[1] conceived of an elegant approach to the problem of calculating the potential of a general ionic crystal. By an ingenious device, he was able to construct two absolutely convergent series which in some cases converge far more rapidly and whose limit is just the desired limit of the one more slowly conditionally convergent series. However, only heuristic arguments were given to establish the basis for his approach.[1a] Recognizing this, KORNFELD[2] later remarked that his work (based upon Ewald's equations) had at least the justification of Ewald's. The argument of Section 1 has shown that whenever a generalized sign alternation holds for each of three independent axes (x_1, x_2, x_3), then the series converge when they are summed for points contained within an increasing sequence of parallelopipeds whose edges are parallel to the axes. Equivalently, finite specimens of such a shape can be said to possess a "well-defined" specific energy. The proof of Ewald's formula as given below will show that they yield the limiting specific energy for crystals of this shape.

Let $\mathbf{r}$: vector from some lattice point which is taken as the origin to some point, P, at which the potential is to be computed, where P is not a lattice point;

$U(\mathbf{r})$: the potential at P defined by an electrically neutral crystal; ρ: a vector from the origin to an arbitrary lattice point;

$\mathbf{R} \equiv \mathbf{r} - \rho$: a vector of magnitude, R. $\hfill (7)$

The potential of a point charge at the endpoint of ρ is replaced by an approximating function, $\varphi(R, k_0)$, which satisfies the following conditions:

Condition 1: k_0 is an imaginary number,

$$k_0 = u + iw \cdot * \hfill (8a)$$

$\varphi(R, k_0)$ is continuous at the origin and has the limit:

$$\lim_{k_0 \to 0} \varphi(R, k_0) = 1/R \hfill (8b)$$

Condition 2: Consider an electrically neutral ionic lattice and a summation order which gives a series converging to $U(\mathbf{r})$ [cf. equation (7)]. Form a corresponding series by multiplying $\varphi(R, k_0)$ by the charge of the lattice site. Suppose $\varphi(R, k_0)$ is chosen so that:

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* For the purpose of this argument, u can be taken to be zero. However, k_0 is used as a complex number to maintain agreement with Ewald's notation.

(a) The series converges absolutely to $U(\mathbf{r}, k_0)$ whenever $w > 0$ (This will permit interchange of order of algebraic operations.)

(b) For each u, the series converges uniformly for $w \geq 0$. Then it follows from the continuity of $\varphi(R, k_0)$ that

$$U(\mathbf{r}) = \lim_{k_0 \to 0, w \geq 0} U(\mathbf{r}, k_0). \tag{9}$$

Thus if $\varphi(R, k_0)$ can be chosen to give a convenient equation for $U(\mathbf{r}, k_0)$, the desired potential can be computed as $U(\mathbf{r}, 0)$. Ewald derived a convenient equation in the study of optical potentials of the form:*

$$\sum_{p'} \{P(p') \exp[ik_0 R_{pp'} + i(\xi \cdot \mathbf{R}_{(p')})]\}/R_{pp'} \tag{10}$$

$R_{pp'}$: the distance between p and p'.

To examine the validity of his equations for the electrostatic potential, we can replace $P(p')$ by the charge at p', set $\xi = \mathbf{0}$, choose k_0 to be a pure imaginary, $k_0 = iw, w > 0$, so that the approximating potential for a unit charge is:

$$\varphi(\mathbf{R}, k_0) = [\exp(-wR)]/R \tag{11}$$

Clearly, this choice satisfies condition (1). To see that it satisfies the uniformity requirement of condition (2), it is sufficient to use the simple alternating sign condition of Section I. (The argument for the general condition is essentially the same and merely has more complicated notation.)

Along any of the three axes for which the alternating sign condition holds, select two successive sites, R_1 and R_2. Then $(1/R_1) > (1/R_2)$ and the convergence will be uniform if

$$(1/R_1) - (1/R_2) > [\exp(-wR_1)]/R_1 - [\exp(-wR_2)]/R_2 \tag{12}$$

To establish the inequality, define

$$f(R_1, R_2) \equiv (R_2/R_2) - [1 - \exp(-wR_1)]/[1 - \exp(-wR_2)]. \tag{13a}$$

Then rearrangement of (12) shows that the inequality will hold if

$$(R_2 > R_1) \to (f(R_1, R_2) > 0) \tag{13b}$$

Now $f(R_1, R_2)$ vanishes when $R_2 = R_1$. The partial derivative satisfies the inequality:

$$\partial f/\partial R_2 = [1 - \exp(-wR_1) - wR_1 \exp(-wR_2)]/[R_1\{1 - \exp(-wR_1)\}] \geq [1 - (1 + wR_1)\exp(-wR_1)]/[R_1\{1 - \exp(-wR_1)\}]. \tag{14}$$

Since $(1 + wR_1)\exp(-wR_1) < 1$ for $wR_1 > 0$, both numerator and denominator are positive. This proves (13b) and, therefore, establishes that the convergence is uniform when the series

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* See EWALD[l], equation (6), p. 256.

is summed over lattice sites contained in an increasing sequence of parallelopipeds whose edges are parallel to the axes.† It follows that whenever the alternating sign conditions hold, the Ewald equation for $U(\mathbf{r}, 0)$ gives the limiting value for the potential of an increasing sequence of parallelopipeds whose edges are parallel to the three axes.‡

3. RELATION OF CONDITIONS TO SOME PREVIOUS STUDIES OF CRYSTAL SHAPE

EMERSLEBEN[6a] treated rigorously the onedimensional ionic crystal which satisfies the more restrictive simple alternating sign condition of Section 1. He showed that for a finite crystal the total energy, E, could be written as the sum:

$$E = e_1 n + e_0 + Z(n) \tag{15a}$$

e_1, e_0: constants, independent of n

n: number of ion pairs

$Z(n)$: a remainder term such that $\lim_{n \to \infty} Z(n) = 0$.

The value of this subdivision lay in the following facts: (1) he was able to develop an interpretation of $e_0/2$ as the energy per end of the finite chain; (2) e_1 is just the limit of the specific energy defined uniquely by the order of summation corresponding to a one-dimensional crystal of increasing size.[7a] Therefore, he viewed $e_1 n$ as a "bulk" energy and $Z(n)$ as a correction term.

Since he was not able to extend his treatment rigorously to any two or three dimensional lattices, he made many numerical studies. Upon the basis of these results he postulated that the total coulombic energy for finite parallelopipeds could be written as a sum analogous to (15a):

$$E = e_3 n^3 + e_2 n^2 + e_1 n + e_0 + Z(n) \tag{15b}$$

e_3, e_2, e_1, e_0: constants independent of n

n: number of ion-pairs along a crystal edge

$Z(n)$: a remainder term such that $\lim_{n \to \infty} Z(n) = 0$

The total number of pairs in the parallelopiped is proportional to n^3, where the proportionality factor depends upon the crystal structure. Therefore, dividing by n^3 and passing to the limit as $n \to \infty$ shows that e_3 is proportional to the limiting specific energy/ion pair. At first he did not realize that the criterion that a finite crystal be electrically neutral is not sufficient to define a unique limiting value for the specific energy as $n \to \infty$. Subsequently,

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† BOUMAN[4b] gives the analogue of equation (9) [cf. equation (23), p. 4]. However, he does not establish the uniform convergence, nor does he note that the uniformity is relative to the presumed order of summation,. Neglect of this would lead to the immediate contradiction of the valid equation (9): $\lim_{k_0 \to 0} U(\mathbf{r}, k_0)$ is unique,. but the value of $U(\mathbf{r})$ depends upon the order of summation.

‡ This same conclusion can also be reached independently by the argument developed for multiple formulae in the next section.

he studied different parallelopipeds for two and three dimensional electrically neutral crystals which could be divided into two groups:

Class I. All boundaries electrically neutral;

Class II. Some boundaries electrically charged.

The different classes gave different values for e_3 for the same crystal structure. It is interesting that the stable shapes of Class I are those for which the axes satisfy the alternating sign conditions of Section 1.*

Such studies of specific shapes represent a step towards the answer to question (2) of Section 1. Whereas Emersleben deals only with the point charge contribution, it is necessary to consider other terms as well. Some of the more general problems are discussed briefly by EWALD and JURETSCHKE.[9] They also offer an alternative attempt to calculate the surface energy for a perfect bounded lattice.†

4. DEDUCTION OF EQUATIONS FOR MULTIPOLE LATTICES FROM EWALD'S EQUATIONS

The potential at a point P_β produced by a multipole of the n-th order of moment $p^{(n)}$, and characteristic directions $\mathbf{s}_1, \ldots, \mathbf{s}_n$ is defined as

$$\frac{(-1)^n p^{(n)}}{n!}(\mathbf{s}_n \cdot \nabla_\beta) \ldots (\mathbf{s}_1 \cdot \nabla_\beta)(1/r\langle A, \beta\rangle);$$

$$\mathbf{s}_1, \ldots \mathbf{s}_n : \text{unit vectors}$$

$$r\langle A, \beta\rangle = \left\{ \sum_{i=1}^{3}(X_\beta^i - X_A^i)^2 \right\}^{1/2};$$

$$\nabla_\beta = \langle \partial/\partial X_\beta^1, \partial/\partial X_\beta^2, \partial/\partial X_\beta^3\rangle.$$

(16)

Similarly the energy of interaction between multipoles of order m and q is a scalar multipole of an $(m+q)$-th order directional derivative.‡ This led KORNFELD[2] to suggest that the formulae for multipole lattices could be deduced by taking directional derivatives of Ewald's equations for an ionic lattice. Kornfeld's discussion of the justification for his work does not establish the validity of interchanging the order of the limiting processes involved in Ewald's transformation and of differentiation. Furthermore, it contains a logical error which led to misleading statements.

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* It seems that EMERSLEBEN thought of a surface contribution to the energy in two distinct senses. In the first sense, the specific surface energy was proportional to e_2 of equation (15b).[7] In the second sense, the surface contribution was a change in e_3 (i.e. in the "bulk" energy, $e_3 n^3$)[8] as the order of summation (i.e. the shape of the finite specimen) was changed. It would be desirable to use different terms for these two distinct interpretations.

† As the authors carefully note, their formulae depend upon the validity of interchanging the order of certain limiting operations. This interchange must still be investigated.

‡ For further discussion of the use of multipoles, see CAMPBELL.[10]

To understand the problem, it will be necessary to consider some details of Ewald's derivation. The exact formulae will be given here to connect the argument to a subsequent extension of KORNFELD'S work.[10]

The entire crystal lattice is decomposed into sublattices, each of which is a simple translation lattice in the sense that the entire sub-lattice can be reproduced from a single point by a combination of unit translations along three independent axes. Let:

e_T: charge at each site of the simple translation lattice, T;

$(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$: vectors which define a unit cell for the crystal;

$L = \langle L_1, L_2, L_3 \rangle$, an arbitrary ordered triple of integers;

$$\mathbf{r}_L = \sum_{i=1}^{3} L_i \mathbf{a_i}; \qquad (17)$$

$\mathbf{b}_i$: the vector reciprocal to $\mathbf{a}_i, i = 1, 2, 3$, [i.e. $\mathbf{b}_i = (\mathbf{a}_j \times \mathbf{a}_k)/(\mathbf{a}_i \cdot \mathbf{a}_j \times \mathbf{a}_k)$, where $\langle i, j, k \rangle$ may undergo any cyclic permutation];

$$\mathbf{q}_L = 2\pi \sum_{i=1}^{3} L_i \mathbf{b_i};$$

a vector of magnitude g_L. By applying a transformation on a theta function of three variables, Ewald was able to deduce an alternative representation for $U(\mathbf{r}, k_0)$, the potential at the endpoint of $\mathbf{r} = \langle r^1, r^2, r^3 \rangle$, defined by a crystal of singularities, $\varphi(R, k_0)$. This representation is a sum over the set of translation lattices:

$$U_T(\mathbf{r}, k_0) = \sum_{T} e_T U_T(\mathbf{r}, k_0). \qquad (18a)$$

e_T: the charge at each site of the simple translation lattice T.

For each translation lattice, $U_T(\mathbf{r}, k_0)$ is itself a sum of two functions:*

$$U_T(\mathbf{r}, k_0) = U_{T,1}(\mathbf{r}, k_0, \epsilon) + U_{T,2}(\mathbf{r}, k_0, \epsilon). \qquad (18b)$$

Subsequently, it will be seen to be convenient to decompose the first term, $U_{T,1}(\mathbf{r}, k_0, \epsilon)$, into two terms, one of which is independent of $\mathbf{r}$ and of L:

$$U_{T,1}(\mathbf{r}, k_0) = U'_{T,1}(\mathbf{r}, k_0, \epsilon) + U''_{T,1}(k_0, \epsilon); \qquad (19a)$$

$$U'_{T,1}(\mathbf{r}, k_0, \epsilon) = \frac{4\pi}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)} {\sum}' \{(q_L)^2 + k_0^2\}^{-1} \times \exp\left\{ \frac{-[(q_L)^2 - k_0^2]}{4\epsilon^2} + i(\mathbf{q}_L \cdot \mathbf{r} - \mathbf{r}_T) \right\}; \qquad (19b)$$

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* These are essentially EWALD'S equations (33,4), p. 273,[1] specialized for an ionic lattice. In terms of the symbols of equation (10), this means that $\xi = \mathbf{0}$ and $P(p')$ is replaced by the charge at p'. Note that there is a misprint in EWALD'S equation (33). The magnitude χ_L should read χ_L^2. [Compare with his equation (30), p. 272.] In agreement with KORNFELD's notation[2] χ_L has been replaced by $\mathbf{q}_L$ and E by ϵ.

$$\sum{}' \quad \text{Summation over all } L \text{ such that } q_L \neq 0; \tag{19c}$$

$$U''_{T,1}(k_0, \epsilon) = \frac{4\pi}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)} k_0^{-2} \exp(k_0^2/4\epsilon^2); \tag{19d}$$

$$U_{T,2}(\mathbf{r}, k_0, \epsilon) = \sum_{\{L\}} \{ \frac{\cos(k_0 R_{L,T})}{R_{L,T}} - 1/2 R_{L,T} [\exp(ik_0 R_{L,T}) \phi(\epsilon R_{L,T} + ik_0/2\epsilon) +$$
$$\exp(-ik_0 R_{L,T}) \phi(\epsilon R_{L,T} - ik_0/2\epsilon)] \}; \tag{19e}$$

$$\mathbf{R}_{L,T} = \mathbf{r} - (\mathbf{r}_L + \mathbf{r}_T); \tag{19f}$$

$$\mathbf{R}_{L,T} = \left\{ \sum_{i=1}^{3} [r^i - r_L^i - r_T^i]^2 \right\}^{1/2}; \tag{19g}$$

$$\phi(X) = \frac{2}{\sqrt{(\pi)}} \int_0^X \exp(-\alpha^2) d\alpha; \tag{19h}$$

$$\epsilon : \text{an arbitrary parameter (vide infra)}. \tag{19i}$$

Whenever the lattice is neutral so that,

$$\sum_{\{T\}} e_T = 0 \tag{20}$$

then, [since $U''_{T,1}(k_0, \epsilon)$ is the same for lattice T],

$$\sum_{\{T\}} e_T U''_{T,1}(k_0, \epsilon) = 0 \tag{21}$$

In this case, equation (18) can be written in the form:

$$U(\mathbf{r}, k_0) = \sum_{\{T\}} e_T U'_T(\mathbf{r}, k_0); \tag{22a}$$

$$U'_T(\mathbf{r}, k_0) = U'_{T,1}(\mathbf{r}, k_0, \epsilon) + U_{T,2}(\mathbf{r}, k_0, \epsilon) \tag{22b}$$

Ewald's transformation which gives equation (18) is valid only for $w > 0$. However, for neutral lattices, this equation can be replaced by (22) which converges uniformly for $w \geq 0$ and is continuous at $k_0 = 0$. Thus the original conditionally convergent series for an ionic

lattice has been replaced by a sum of absolutely convergent series, two for each translation lattice. Obviously, the finite sum,

$$U'_T(\mathbf{r}, 0) = U'_{T,1}(\mathbf{r}, 0, \epsilon) + U_{T,2}(\mathbf{r}, 0, \epsilon)$$

is *not* the infinite potential defined by a simple translation lattice [the infinite potential is, of course, $\lim_{k_0 \to 0} U_T(\mathbf{r}, k_o)$];

$$U'_T(\mathbf{r}, 0)$$

is merely the contribution of a simple translation lattice to the sum (22a) for the potential of a neutral ionic lattice. KORNFELD[2] made the logical error of equating the potential of a simple translation lattice of dipoles to the contribution the simple lattice makes to a sum for the potential. This can be seen by citing the steps he used to deduce equations for the potential of a simple translation lattice of dipoles:

Step I: Take the directional derivative of Ewald's equation for a neutral ionic lattice composed of two simple translation lattices and multiply by minus one [cf. equation (16)].

Step II: Determine the contribution of each simple translation lattice to the directional derivative.

Step III: Infer that the contribution of each simple translation lattice to the directional derivative of the equation for a neutral lattice is the negative of the potential defined by a simple lattice of unit dipoles.

Unfortunately, it is well known that the series for the potential of a simple lattice of dipoles fails to converge absolutely. Thus, just as in the case of the ionic lattice, two conclusions follow immediately: (1) The convergence of the series must be established for the particular order of summation which is assumed; (2) The question of whether the summation order prescribed by crystal growth for this shape will give a "well-defined" specific energy is equivalent to the question of whether the summation order prescribed by crystal growth for this shape gives a convergent series. As previously seen, the Ewald formulae are for summation along the axes of the translation lattice and it is shown in Appendix B* that the series for this order of summation does not converge. It is, therefore, inappropriate to speak of the potential of a simple translation lattice of dipoles as computed by the Kornfeld formulae.†

Conditions under which the equations derived from Ewald's formulae will be valid can be established by the following steps.

Step I: Convergence of lattice sums for multipoles for the Ewald order of summation

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* Conversely, as is well-known, it is a simple consequence of the symmetry of the dipole potential that leading terms in any sum over a spherically symmetric set of lattice sites must vanish [cf. equation (C.6) of Appendix C]. For this order, the series does converge.

† BOUMAN[4] also discusses the Kornfeld formulae. As noted under the discussion of ionic lattices, he does not include a proof of the uniform convergence which he asserts. Furthermore, since he discusses the calculation in terms of equivalent distributions, it is worthwhile to present a simple justification of the Kornfeld formulae which shows clearly their relation to the order of summation.

In Appendix C it is shown that (at least in the case of the general orthogonal crystal), the necessary and sufficient condition under which the potential for a dipole crystal converges for the Ewald order of summation is that the crystal has a zero net dipole moment [cf. equation (C.11):

$$\sum_{\{T\}} p_T \mathbf{s}_T = \mathbf{0}].^*$$

Furthermore, the argument of Appendix D shows that the interaction energy between a dipole and a simple translation lattice of dipoles always converges for this order of summation (at least in the case of the general orthogonal crystal). The series for all higher order interactions decrease as $1/r^n$, $n \geq 4$ and necessarily converge.

Step II: Use of the Ewald equations; Inversion of order of limiting operations

Consider an n-th order directional derivative of $\varphi(R, k_o)$. For each $w \geq 0$, it can be shown that the lattice sum for $\varphi(R, k_o)$ and the lattice sum for such a directional derivative converge uniformly over the exterior of any sphere containing the endpoint of $\mathbf{r}$. Since the derivatives of ϕ are continuous, it follows that the series for the lattice sum of $\varphi(R, k_o)$ can be differentiated termwise to obtain

$$\sum_{\{L\}} \prod_{j=1}^{n} (\mathbf{s}_{j,T} \cdot \nabla) \varphi(R_{L,T}, k_0) = \prod_{j=1}^{n} (\mathbf{s}_{j,T} \cdot \nabla) U_T(R_{L,T}, k_0);$$

$$\nabla = (\partial/\partial^1, \partial/\partial^2, \partial/\partial^3) \tag{23}$$

It should be possible to assume suitable conditions (e.g. those of Appendix C) under which equation (23) could be shown to converge uniformly for the Ewald summation order for $w \geq 0$. Then it would be justified to pass to the limit $k_o = 0$. Since a careful and general argument would involve complicated notation, it is better to proceed by the following steps

Step IIA: Termwise differentiation of $U'_{T,1}$ and $U_{T,2}$; Formation of the lattice sum

Consider the series,

$$U'_T(\mathbf{r}, 0) = U'_{T,1}(\mathbf{r}, 0, \epsilon) + U_{T,2}(\mathbf{r}, 0, \epsilon); \tag{24}$$

$$U'_{T,1}(\mathbf{r}, 0, \epsilon) = \frac{4\pi}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)} {\sum}'(q_L)^{-2} \times \exp[-(q_L)^2/4\epsilon^2 + i(\mathbf{q}_L \cdot \mathbf{r} - \mathbf{r}_T)]; \tag{25a}$$

$$U_{T,2}(\mathbf{r}, 0, \epsilon) = \sum_{\{L\}} G(\epsilon R_{L,T})/R_{L,T}; \quad G(x) = 1 - \phi(x) \tag{25b}$$

Since for each $\epsilon > 0$ the derived series for $U'_{T,1}$ and $U_{T,2}$ converge uniformly over the exterior domain of any sphere centered at $\mathbf{r}$, and since the derivatives of the terms of the

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* This condition is often used. Since, as has been observed, the series does converge conditionally (e.g. when summed over spherically symmetric arrays of lattice sites) it is desirable to include a careful proof for the Ewald summation order.

series are continuous, they can be differentiated termwise. Multiplication by the magnitude of the multipole of the T-th translation lattice and summation over $\{T\}$ gives:

$$\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)U'(\mathbf{r},0) = \sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)U'_{T,1}(\mathbf{r},0,\epsilon)+$$
$$\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)U_{T,2}(\mathbf{r},0,\epsilon). \tag{26}$$

Step IIB: Reordering of the derived series for $U_{T,2}$ and introduction of the multipole series

Since the derived series for $U_{T,2}$ converges absolutely, it can be reordered to give [cf.(25b)],

$$\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)U_{T,2}(\mathbf{r},0,\epsilon) = \sum_{\{L\}}\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)[G(\epsilon R_{L,T})/R_{L,T}]. \tag{27}$$

According to equation (25b), $G(x) = 1 - \phi(x)$. If the multipole lattice sum,

$$U(\mathbf{r}, \{\mathbf{s}_j\}) = \sum_{\{L\}}\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)(1/R_{L,T}), \tag{28}$$

converges for the Ewald order of summation (cf. Step I), then the right side of equation (27) must (24) be the sum of two convergent series:

$$\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)U_{T,2}(\mathbf{r},0,\epsilon) = U(\mathbf{r}, \{\mathbf{s}_j\}) + U_2(\mathbf{r}, \{\mathbf{s}_j\}, \epsilon);$$
$$U_2(\mathbf{r}, \{\mathbf{s}_j\}, \epsilon) = \sum_{\{L\}}\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla) \times [\phi(\epsilon R_{L,T})/R_{L,T}]. \tag{29}$$

Substitution of (29) into (26) gives the absolutely convergent series on the left of (26) as a sum of 3 convergent series, one of which is the multipole summation:

$$\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)U'_T(\mathbf{r},0) = \sum_{\{T\}} p_T(\mathbf{s}_{j,T}\cdot\nabla)U'_{T,1}(\mathbf{r},0,\epsilon) + U(\mathbf{r}, \{\mathbf{s}_j\}) + U_2(\mathbf{r}, \{\mathbf{s}_j\}, \epsilon) \tag{30}$$

The sum of the second and third terms on the right side of (30) can be shown to vanish by the following argument. Since Ewald's work implies that $U'_T(r,0)$ is independent of ϵ, therefore, the right side of (30) must be independent of ϵ so that:

$$\sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T}\cdot\nabla)U'_{T,1}(\mathbf{r},0,\epsilon) + U_2(\mathbf{r},0,\epsilon) = C; \tag{31}$$

C: a constant

Now examination of (25a) shows that,

$$\lim_{\epsilon \to 0} \prod_{j=1}^{n} (\mathbf{s}_{j,T} \cdot \nabla) U'_{T,1}(\mathbf{r}, 0, \epsilon) = 0. \tag{32}$$

Therefore, $\lim_{\epsilon \to 0} U_2(\mathbf{r}, \{\mathbf{s}_j\}, \epsilon) = C$. But since the form of $\phi(x)$, [cf.(19h)] shows that $\lim_{\epsilon \to 0}$ of any partial sum for U_2 vanishes, $C = 0$. Thus, whenever $U(\mathbf{r}, \{\mathbf{s}_j\})$ converges for the Ewald order of summation, its limit (for this order) can be computed as the sum of absolutely convergent series:

$$U(\mathbf{r}, \{\mathbf{s}_j\}) = \sum_{\{T\}} p_T \prod_{j=1}^{n} (\mathbf{s}_{j,T} \cdot \nabla) U'_{T,1}(\mathbf{r}, 0, \epsilon) + \prod_{j=1}^{n} (\mathbf{s}_{j,T} \cdot \nabla) U_{T,2}(\mathbf{r}, 0, \epsilon). \tag{33}$$

The general equations for the right side of equation (33) have been obtained in a form convenient for calculation on an electronic computer.[10] These equations have two marked advantages over the direct use of equation (28):

(1) *Convenient check for error.* The functions $U'_{T,1}$ and $U_{T,2}$ (and their derivatives) depend upon the arbitrary parameter ϵ, but their sum, U'_T (and its derivatives) do not. This provides a simple independent check of the calculation by performing the computation for two different values of ϵ. It is imperative to note that approximate agreement is meaningless. Two values for a given $U_T(\mathbf{r}, 0)$ which agreed to a few per cent were found to be in error by one hundred per cent.

(2) *Rapidity of convergence.* In general, the series given by (33) should converge more rapidly than those given by (28). Since a decrease [increase] in ϵ will cause $U'_{T,1}(\mathbf{r}, 0, \epsilon)$ $[U_{T,2}(\mathbf{r}, 0, \epsilon)]$ to converge more rapidly, values should be chosen in a range to minimize the total work.

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APPENDIX A

Generalized integral tests for the convergence of multiple series

The first theorem is a simple extension of the ordinary theorem for series in one index whose terms are all either positive or negative.*

Theorem 1. Suppose:

(1) $f(\{x_i\})$ is a non-negative function defined over the set of $\{x_i\}$, $1 \le x_i$, $i = 1, \ldots, n$.

(2) For any fixed choice of $(n-1)$ variables, $f(\{x_i\})$ is a monotone non-increasing function of the n-th variable.

(3) For each ordered n-tuple of positive integers, $\langle p_1, \ldots, p_n \rangle$, define

$$F(\langle p_1, \ldots, p_n \rangle) = f(\{p_i\}).$$

Then,

$$\int_2^{q_n+1} \ldots \int_2^{q_1+1} f(\{p_i\}) \prod_{i=1}^{n} \mathrm{d}x_i \le \sum_{p_n=2}^{q_n} \ldots \sum_{p_1=2}^{q_1} F(\langle p_1, \ldots, p_n \rangle) \le \int_2^{q_n} \ldots \int_2^{q_1} f(\{p_i\}) \prod_{i=1}^{n} \mathrm{d}x_i \, .$$

The proof parallels that for the standard theorem.*

A second theorem is a test for the convergence of the difference of two series, each of which satisfies the condition of Theorem 1.

Theorem 2. Suppose

(1) $f(\{x_i\}) = g(\{x_i\}) - h(\{x_i\})$ where g and h satisfy the conditions of Theorem 1.

(2) For each ordered n-tuple of positive integers $\langle p_1, \ldots, p_n \rangle$, define

$$F(\langle p_1, \ldots, p_n \rangle) = f(\{p_i\}); \ \ G(\langle p_1, \ldots, p_n \rangle) = g(\{p_i\}); \ \ H(\langle p_1, \ldots, p_n \rangle) = h(\{p_i\}).$$

Then:

$$-\int_2^{q_n} \ldots \int_2^{q_1} h(\{x_i\}) \prod_{i=1}^{n} \mathrm{d}x_i + \int_2^{q_n+1} \ldots \int_2^{q_1+1} g(\{x_i\}) \prod_{i=1}^{n} \mathrm{d}x_i \le \sum_{p_n=2}^{q_n} \sum_{p_1=2}^{q_1} F(\langle p_1, \ldots, p_n \rangle)$$

$$\le \int_2^{q_n} \ldots \int_2^{q_1} g(\{x_i\}) \prod_{i=1}^{n} \mathrm{d}x_i - \int_2^{q_n+1} \ldots \int_2^{q_1+1} h(\{x_i\}) \prod_{i=1}^{n} \mathrm{d}x_i \, .$$

This follows immediately from the inequalities of Theorem 1 for g and h.

APPENDIX B

Potential of a simple translation lattice of dipoles

Since the equations of the next Appendix could be used to establish the well-known result that the series for the potential would converge when summed over a spherically symmetric set of lattice points, a careful proof has been included to show that they do not converge for the Ewald summation order. In other words, a sequence of finite specimens in the shape of parallelopipeds whose edges are parallel to the axes of the translation lattice will not give a "well-defined" potential in the sense of Section 1.

For simplicity, consider a simple cubic lattice whose unit cell has unit length along each axis. Suppose that the potential is to be computed at a point, P, which is not a lattice point. Place the origin at the

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* See KNOPP,[5] p. 64.

nearest lattice site and let $\rho = \langle \rho^1, \rho^2, \rho^3 \rangle$ be the vector from the origin to P. Then each $|\rho^i| < 1$. The potential at P defined by a lattice of unit dipoles of characteristic direction, $\mathbf{s} = \langle s^1, s^2, s^3 \rangle$, is

$$U(P) = -\sum_{\{L^3\}}\sum_{\{L^2\}}\sum_{\{L^1\}} \frac{\mathbf{s}\cdot\rho - \mathbf{r}_L}{\|\mathbf{r}_L - \rho\|^3}; \tag{B.1}$$

$\mathbf{r}_L = \langle L^1, L^2, L^3 \rangle$, each L^i an integer.

Consider the coefficient of s^1 in the equation for $U(P)$. The terms in the coefficient for a fixed L^1 satisfy the conditions of Theorem 1 of Appendix A so that for $L^1 > |\rho^1|$:

$$I \equiv (x^1 - \rho^1)\int_2^\infty\int_2^\infty \left[\mathrm{d}x^2\mathrm{d}x^3 / \left\{ \sum_{i=1}^3 (L^i - \rho^i)^2 \right\}^{3/2} \right] \le (L^1 - \rho^1)\sum_2^\infty\sum_2^\infty \left\{ \sum_{i=1}^3 (L^i - \rho^i)^2 \right\}^{3/2} \tag{B.2}$$

$$x^1 = L^1$$

To obtain a simple bound for I first translate the origin and then transform to plane polar coordinates to obtain:

$$I = (x^1 - \rho^1)\int_{2-\rho^2}^\infty\int_{2-\rho^3}^\infty \frac{\mathrm{d}y^2\mathrm{d}y^3}{\{(x^1-\rho^1)^2 + (y^2)^2 + (y^3)^2\}^{3/2}} \ge$$
$$2\pi(x^1 - \rho^1)\int_3^\infty \frac{r\mathrm{d}r}{\{(x^1-\rho^1)+r^2\}^{3/2}} = \frac{2\pi(x^1-\rho^1)}{\{9+(x^1-\rho^1)\}^{3/2}} \tag{B.3}$$

Thus, for each $\epsilon > 0$, for sufficiently large $x^1 = L^1$ $I \ge 2\pi - \epsilon$. That is, although the contribution to the coefficient of s^1 in the potential by lattice sites in the plane $\langle L^1, x^2, x^3 \rangle$ approaches asymptotically minus one times the contribution by sites in the plane $\langle -L^1, x^2, x^3 \rangle$ it approaches a finite non-zero value as $L^1 \to \infty$. Physically, this would mean that in a finite crystal of this shape, the potential would depend upon the number of planes to either side of the point at which the potential is to be computed.

APPENDIX C

Sufficient conditions for the existence of a "well-defined potential" of a finite lattice of dipoles for the shape corresponding to the Ewald summation order

This Appendix derives sufficient conditions to ensure that a dipolar crystal of this shape will possess a "well-defined" potential. Let:

$\mathbf{r}_T$: a vector from the origin to a site of the simple translation lattice T of dipoles;

p_T, $\mathbf{s}_T$: the moment and characteristic direction of the dipoles of translation lattice T;

$\mathbf{r}$: a vector whose end point does not lie at any lattice site;

$\mathbf{r}_L$: a vector defining sites of a simple translation lattice [see equation (17)].

Then the potential defined at the endpoint of $\mathbf{r}$ by the entire lattice is given by the following sum over the sets $\{L\}$ and $\{T\}$:

$$U = -\sum_{\{L\}}\sum_{\{T\}} p_T \frac{(\mathbf{s}_T\cdot\mathbf{r} - [\mathbf{r}_L + \mathbf{r}_T])}{\|\mathbf{r} - [\mathbf{r}_L + \mathbf{r}_T]\|^3}. \tag{C.2}$$

In order to derive conditions for the convergence of U, we shall expand each term for which $\mathbf{r}_L \ne \langle 0,0,0 \rangle$ in a Taylor Series about $\mathbf{r} - \mathbf{r}_T = 0$. This gives:

$$U = -\sum_{\{T\}} \frac{p_T(\mathbf{s}\cdot\mathbf{r} - \mathbf{r}_T)}{\|\mathbf{r} - \mathbf{r}_T\|^3} + \sideset{}{'}\sum_{\{T\}} p_T \frac{(\mathbf{s}_T\cdot\mathbf{r}_L)}{\|\mathbf{r}_L\|^3}$$
$$- \left[\frac{(\mathbf{s}_T\cdot\mathbf{r})}{\|\mathbf{r}_L\|^3} - 3\frac{(\mathbf{s}_T\cdot\mathbf{r}_L)(\mathbf{r}_T\cdot\mathbf{r}_L)}{\|\mathbf{r}_L\|^5} \right] + \left[\frac{(\mathbf{s}_T\cdot\mathbf{r}_T)}{\|\mathbf{r}_L\|^3} - 3\frac{(\mathbf{s}_T\cdot\mathbf{r}_L)(\mathbf{r}_T\cdot\mathbf{r}_L)}{\|\mathbf{r}_L\|^5} \right] + O(1/\|\mathbf{r}_L\|^4); \tag{C.3}$$

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$\sum'$: a summation over all $\mathbf{r}_L \neq \langle 0, 0, 0 \rangle$

Since any term of the order of $1/\|\mathbf{r}_L\|^4$ will surely give a convergent series, the Taylor Series Expansion will be valid whenever the three [ ] under $\sum'$ give convergent series. The argument of Appendix B shows that the series from the first term of the double sum does not converge in general for this summation order. Since it will be shown below that the second and third terms give convergent series,* it follows that U will converge if and only if a condition is imposed which will ensure the convergence of the series from the first term.   This will occur if and only if

$$\sum_{\{T\}} p_T \mathbf{s}_T = \mathbf{0} \tag{C.4}$$

i.e. the crystal has no net dipole moment.

The convergence of the series from the third term will now be established rigorously for the case when the simple translation lattice is orthogonal with arbitrary unit lengths $\langle a^3, a^2, a^3 \rangle$ along the three axes. Thus $\mathbf{r}_L$ is of the form,

$$\mathbf{r}_L = \langle L^1 a^1, L^2 a^2, L^3 a^3 \rangle; \; L^1, L^2, L^3 \text{ integers}. \tag{C.5}$$

Since $(\mathbf{s}_T \cdot \mathbf{r}_L)(\mathbf{r}_T \cdot \mathbf{r}_L)/\|\mathbf{r}_L\|^5$ varies as $1/\|\mathbf{r}_L\|^3$, the symmetry of the summation ensures that the series for terms which are odd functions of the components, r_L^i must converge to zero. Therefore:

$$\sum' \frac{(\mathbf{s}_T \cdot \mathbf{r}_L)}{\|\mathbf{r}_L\|^3} - 3 \frac{(\mathbf{s}_T \cdot \mathbf{r}_L)(\mathbf{r}_T \cdot \mathbf{r}_L)}{\|\mathbf{r}_L\|^5} = \sum' \left\{ \sum_{i=1}^{3} s_T^i r_T^i \left[\frac{1}{\|\mathbf{r}_L\|^3} - \frac{3(r_L^i)^2}{\|\mathbf{r}_L\|^5} \right] \right\}. \tag{C.6}$$

Since the coefficients of $s_T^i r_T^i$ are of the same form for each i, it is necessary to consider only the case $i = 1$. This series satisfies the conditions of Theorem 2 of Appendix A so that the integral test can be applied. Since the argument is similar for the integrals of both sides of the inequality, we shall consider only the integrals of the right side. These integrals can be rewritten as a sum:

$$\int_1^{q_3} \int_1^{q_2} \int_1^{q_1} \frac{\mathrm{d}x^1 \mathrm{d}x^2 \mathrm{d}x^3}{\|\mathbf{r}_L\|^3} - \int_2^{q_3+1} \int_2^{q_2+1} \int_2^{q_1+1} \frac{3(a^1 x^1)^2}{\|\mathbf{r}_L\|^5} \mathrm{d}x^1 \mathrm{d}x^2 \mathrm{d}x^3 \equiv I + S; \tag{C.7a}$$

$$I = \int_1^{q_3} \int_1^{q_2} \int_1^{q_1} \left\{ \frac{1}{\|\mathbf{r}_L\|^3} - \frac{3(a^1 x^1)^2}{\|\mathbf{r}_L\|^5} \right\} \mathrm{d}x^1 \mathrm{d}x^2 \mathrm{d}x^3 \tag{C.7b}$$

S:a sum of triple integrals (*vide infra*).

For each triple integral of the sum S, the range of integration for at least one coordinate x^i, remains finite as $q_i \to \infty$. Since the integrand varies as $1/\|\mathbf{r}_L\|^3$ each triple integral of S converges. It remains to show that I converges. To cast the integral in a standard form, let $y^i = a^i x^i$, to obtain

$$|I| = \frac{1}{a^1 a^2 a^3} \left| \int_{2a^3}^{q_3 a^3} \int_{2a^2}^{q_2 a^2} \int_{2a^1}^{q_1 a^1} \left\{ \frac{1}{Y \sqrt{Y}} - \frac{3(y^1)^2}{Y^2 \sqrt{Y}} \right\} \mathrm{d}y^1 \mathrm{d}y^2 \mathrm{d}y^3 \right|; \tag{C.8a}$$

$$Y = \sum_{i=1}^{3} (y^i)^2. \tag{C.8b}$$

Integration over y^1 gives†

$$|I| = \frac{1}{a^1 a^2 a^3} \left| \int_{2a^3}^{q_3 a^3} \int_{2a^2}^{q_2 a^2} \left\{ \frac{q^1 a_1}{[(y2)^2 + (y^3)^+ (q^1 a^1)^2]^{3/2}} - \frac{2a_1}{[(y2)^2 + (y^3)^+ (2a^1)^2]^{3/2}} \right\} \mathrm{d}y^2 \mathrm{d}y^3 \right|. \tag{C.9}$$

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  * The proof is given only for the case in which each simple translation lattice is orthogonal.
  † cf. equation (174), p. 25 OF PIERCE.[11]

Since the absolute value of the integral is less than or equal to the integral of the absolute values, and since $a^2 + b^2 \geq 2|a||b|$ (or $(a^2 + b^2)^{-2/3} \leq [2|a||b|]^{-3/2}$) it follows that

$$|I| \leq \frac{1}{2^{3/2}a^1 a^2 a^3} \int_{2a^3}^{q_3 a^3} \int_{2a^2}^{q_2 a^2} \left\{ \frac{1}{(2a^1)^2} + \frac{1}{(q_1 a^1)^2} \right\} \left\{ \frac{1}{(y^2)^2 + (y^3)^2} \right\}^{3/2} \mathrm{d}y^2 \mathrm{d}y^3. \qquad (C.10)$$

Since the last two dimensional integral clearly converges, the series converges by the integral test. The convergence of the series from the second [ ] can be established by the same argument.†

Thus for the general orthogonal crystal, the series for the dipole potential converges if it is summed for points contained within an increasing sequence of parallelopipeds whose edges are parallel to the axes if and only if the crystal has zero net dipole moment:

$$\sum_{\{T\}} p_T \mathbf{s}_T = \mathbf{0} \qquad (C.11)$$

Equivalently, finite specimens of such a shape will give a "well-defined" potential in the sense of Section 1.

APPENDIX D

Energy of interaction between a dipole and a simple translation lattice of dipoles

Consider a dipole of moment p and characteristic direction $\mathbf{s}$. If the dipole is located at the endpoint of $\mathbf{r}$, then using the notation of equations (C.1,2) the interaction energy with a simple translation lattice of dipoles is:

$$E = -p\, p_T \sum_{\{L\}} \left\{ \frac{(\mathbf{s} \cdot \mathbf{s}_T)}{\|\mathbf{r} - [\mathbf{r}_L + \mathbf{r}_T]\|} - 3\frac{(\mathbf{s} \cdot \mathbf{r} - [\mathbf{r}_L + \mathbf{r}_T])(\mathbf{s}_T \cdot \mathbf{r} - [\mathbf{r}_L + \mathbf{r}_T])}{\|\mathbf{r} - [\mathbf{r}_L + \mathbf{r}_T]\|^5} \right\}. \qquad (D.1)$$

In a Taylor Series Expansion [cf. Appendix C, especially equation (C.3)] the only terms of order ≤ 3 in reciprocal distance are:

$$-p\, p_T \sum_{\{L\}}' \left\{ \frac{(\mathbf{s} \cdot \mathbf{s}_T)}{\|\mathbf{r}_L\|} - 3\frac{(\mathbf{s} \cdot \mathbf{r}_L)(\mathbf{s}_T \cdot \mathbf{r}_L)}{\|\mathbf{r}_L\|^5} \right\}. \qquad (D.2)$$

The argument of Appendix C shows that this series converges when summed for points contained within an increasing sequence of parallelopipeds whose edges are parallel to the axes. Equivalently, finite specimens of such a shape always give "well-defined" specific interaction energies.

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† Whenever (C.11) holds, after summation over $\{T\}$ each term in the $\sum'$ vanishes identically. It is not convenient to use this argument since the same series occurs in Appendix D where (C.11) is not assumed, and Appendix D relies upon the arguments of Appendix C.